Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Diacetyliminoxyl as a selective radical reagent for organic synthesis: dehydrogenation and dehydrogenative C–O coupling reactions

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General

In all experiments RT stands for 22-25 °C. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE II 300 and Bruker Fourier 300HD (300.13 for ^{1}H and 75.47 MHz for ^{13}C, respectively) spectrometers in $CDCl_3$ and DMSO-D_6. Chemical shifts were reported in parts per million(ppm), and the residual solvent peak was used as an internal reference: ^{1}H ($CDCl_3$ δ = 7.26 ppm), ^{13}C ($CDCl_3$ δ = 77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). FT-IR spectra were recorded on Bruker Alpha instrument. High resolution mass spectra (HR-MS) were measured on a Bruker maXis instrument using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). A syringe injection was used for all acetonitrile solutions (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

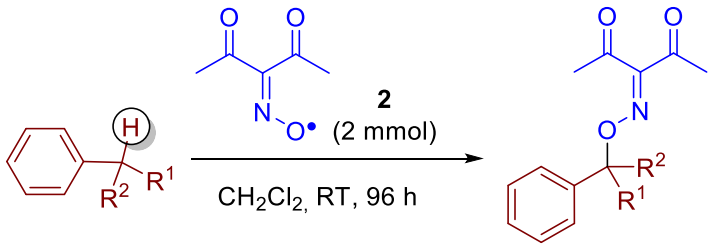
In all experiments RT stands for 22-25 °C. Iron(III) perchlorate hydrate reagent grade ($Fe(ClO_4)_3$•nH_2O, Alfa Aesar, anhydrous basis purity ca. 65%), 2,2,6,6-tetramethylpiperidinooxy (TEMPO) 98%, 2,6-di-tert-butyl-4-methylphenol (BHT) 99.8%, 2,4,6-di-tert-butylphenol 97%, 2,4-dimethyl-6-tert-butylphenol 97%, 4-hydroxy-3,5-dimethylbenzonitrile 98%, 3,5-ditert-butyl-4-hydroxybenzaldehyde 97%, 2,4,6-trimethylphenol 99%, 2,2′-methylenebis(6-tert-butyl-4-methylphenol) 99%, hydroquinone 99%, 1-naphthol 99%, 2'-hydroxyacetophenone 99%, thiophenol 99%, ethanethiol 99+% were used as is from commercial sources. Preparation of diacetyliminoxyl radical is described earlier.[1] To a stirred solution of diacetyl oxime (258 mg, 2 mmol) in 4 mL of CH_2Cl_2 was added $Pb(OAc)_4$ (469 mg, 1.0 mmol) was added with vigorous stirring. Stirring was continued for 10 min, then the reaction mixture was chromatographed on silica gel using CH_2Cl_2 as eluent. The fraction corresponding to the dark-red spot was collected, so that the volume of the fraction was 50 mL. Isoxazolin-5-ones were prepared by according procedures.[2,3]

Quantum chemical calculations were carried out in the Gaussian 16 package[4] and visualized in GaussView6 program. All calculations were performed for temperature of 218.15K and pressure of 1 atm. BDE values for compounds **1a**–**1c**, **6a** (BHT), **6j**, **16** and **18** were calculated by CBS-QB3 composite method[5,6] without any solvation model according to the formulae BDE(R–H) = H(R) + H(H) – H(R-H), where H is the calculated enthalpy value.

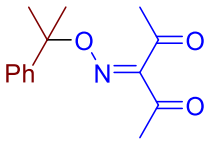
The geometries of the reactants, transition states, intermediates and products (Scheme 7, Scheme 8) were fully optimized at the level of ωB97X-D/6-311++G(d, p) using long-range corrected hybrid density functional ωB97X-D[7] that incorporates empirical London-dispersion correction with a version of Grimme's D2 dispersion model.[8] The chosen contracted basis set was composed of 6-311G core[9,10] with addition of diffuse functions[11] for long-range interactions and single polarization functions on both non-hydrogen and hydrogen atoms.[12] Open shell systems

were modeled with unrestricted SCF calculations for Kohn-Sham orbitals. Solvent effects were described using the polarizable continuum model (PCM)[13] for dichloroethane. The synchronous transit-guided quasi-Newton (STQN) method,[14] optimization of structures as saddle points and scanning of potential energy surface by one and two coordinates along supposed transition vectors were employed for obtaining the transition states. In order to provide an estimate of the zero-point vibrational energies, as well as their corresponding thermochemical parameters, frequency calculations were performed for all of the stationary points and transition states at a temperature of 218.15K and pressure of 1 atm. All these optimized geometries were respectively characterized by the frequency analysis to verify the feature of transition state with only one unique imaginary frequency and the stationary points without imaginary frequency.[15–17] Following the transition state, the intrinsic reaction coordinate (IRC) path was performed to confirm the energy profile connecting each transition state with the two associated minima of the proposed mechanism.[18,19] Finally, the reactant or product complexes were obtained by applying unconstrained optimization on the structure taken from following IRC as far as possible in the reactant or product direction, respectively. For C–O coupling products and intermediates the basis set superposition error (BSSE) energies were estimated by the counterpoise method.[20] Gibbs free energies of C–O bond formation between pyrazolone- or isoxazolone-derived C-centered radicals (A, B, see Scheme 4) and N-oxyl radicals (diacetyliminoxyl and TEMPO) were calculated analogously by ωB97X-D/6-311++G(d, p)/PCM(CH_2Cl_2) method following by BSSE correction by counterpoise method.

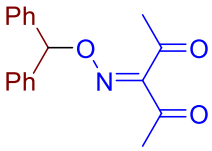
Reactions of diacetyliminoxyl radical 2 with alkylarenes 1 (experimental details for Scheme 2)



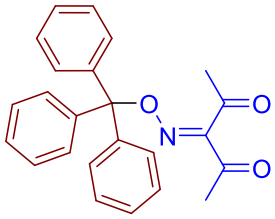
General procedure: to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) at RT was added alkylarene **1** (1 mmol, 120-244 mg). Reaction mixture was stirred for 96 h and then analyzed by ^{1}H NMR (see spectra in SI). At the end of the allotted time the reaction mixture was diluted with 0.05M solution (20 mL) of $Na_2S_2O_4$ and shaken. The organic layer was separated and washed with brine (20 mL), dried over $MgSO_4$, and rotary evaporated under water-jet vacuum.



3-(((2-Phenylpropan-2-yl)oxy)imino)pentane-2,4-dione 3a was synthesized as pale yellow oil (8%, purified by column chromatography with DCM as eluent). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 5H), 2.36 (s, 3H), 2.26 (s, 3H), 1.72 (s, 6H).**^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 199.2, 194.7, 155.8, 145.1, 128.4, 127.5, 125.3, 85.8, 30.7, 27.8, 25.6. **FT-IR** (thin layer): ν_{max} = 1724, 1689, 1365, 1303, 977, 702. **HR-MS (ESI):** *m/z* = 248.1288, calcd. for $C_{14}H_{17}NO_3$+H^+: 248.1281.

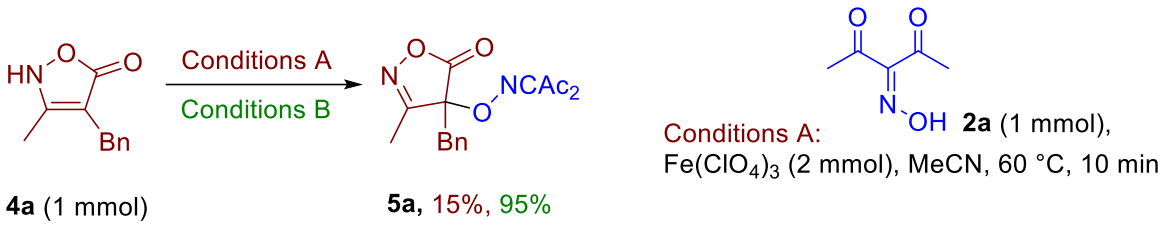


3-((Benzhydryloxy)imino)pentane-2,4-dione 3b was synthesized as pale yellow oil (12%, purified by column chromatography with DCM/PE = 1/1 as eluent). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 10H), 6.38 (s, 1H), 2.35 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.5, 194.5, 156.5, 139.7, 128.7, 128.3, 127.4, 89.7, 30.7, 25.7. **FT-IR** (thin layer): ν_{max} = 1726, 1688, 1453, 1363, 1301, 993, 961, 750, 700. **HR-MS (ESI):** *m/z* = 318.1102, calcd. for $C_{18}H_{17}NO_3$+Na^+: 318.1101.

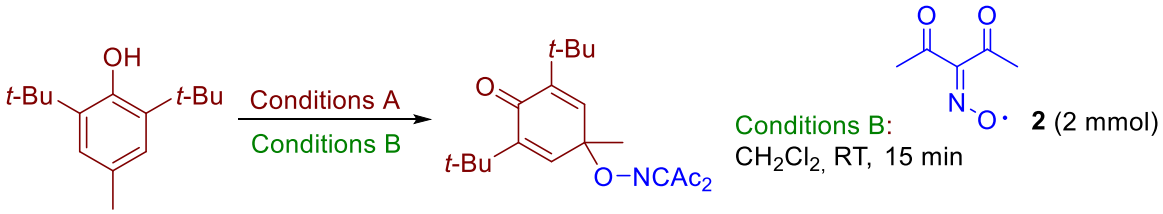


3-((Trityloxy)imino)pentane-2,4-dione, 3c was synthesized as white crystals (97%, purified by column chromatography with DCM as eluent). Reaction time was 4 days. Mp = 108–109 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.37–7.24 (m, 15H), 2.38 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.9, 194.5, 156.1, 143.0, 129.1, 128.0, 127.9, 94.5, 30.5, 25.8; **FT-IR** (thin layer): ν_{max} = 1717, 1695, 1491, 1447, 1363, 1301, 954, 900, 758, 742, 701, 634. **HR-MS (ESI):** *m/z* = 394.1406, calcd. for $C_{24}H_{21}NO_3$+Na^+: 394.1414. Single crystal X-Ray analysis is available (see Fig. S1, page S25).

Reactions of diacetyliminoxyl radical 2 with isoxazolin-5-one 4a and BHT 6a (experimental details for Scheme 3)



4a (1 mmol) **5a,** 15%, 95%

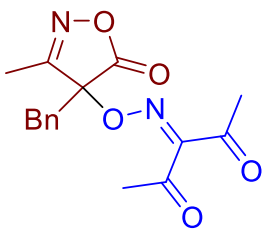


6a (1 mmol) **7a**, 14%, 75%

General procedure (conditions A): to a mixture of diacetyl oxime **2a** (1 mmol, 129 mg) and isoxazolin-5-one **4a** (1 mmol, 189 mg) or BHT **6a** (1 mmol, 220 mg) in MeCN (5 mL) at 60 °C $Fe(ClO_4)_3 \bullet nH_2O$ (2 mmol, 1089 mg) was added for 5–20 seconds; stirring was continued at 60 °C for 10 min.

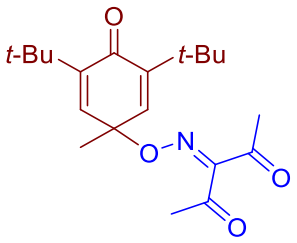
The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and water (20 mL) and shaken. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and all organic extracts were combined. In the case of an intensive color of extract indicative of the presence of metal complexes, it was additionally washed with 0.05M solution (20 mL) of $Na_2S_2O_4$. Organic extract was washed with water (2 × 20 mL), dried over $MgSO_4$, and rotary evaporated under a water-jet vacuum. C–O coupling products **5a** and **7a** were isolated by column chromatography on silica gel.

General procedure (conditions B): to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) was added isoxazolin-5-one **4a** (1 mmol, 189 mg) or BHT **6a** (1 mmol, 220 mg). Reaction mixture was stirred for 15 minutes until the dark red color disappeared, after that reaction mixture was rotary evaporated under a water-jet vacuum. C-O coupling products **5a** and **7a** were isolated by column chromatography on silica gel.



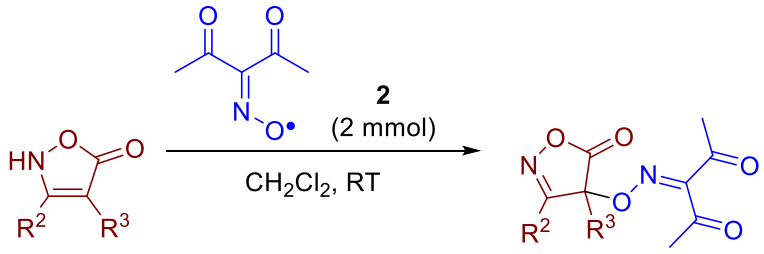
3-(((4-Benzyl-3-methyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, **5a** was synthesized as slight yellow powder (95%, purified by column chromatography with PE/DCM

= 1/3 as eluent). Reaction time was 15 min. Mp = 82–83 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 3H), 7.19–7.07 (m, 2H), 3.35 (d, *J* = 13.7 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 196.3, 193.2, 173.6, 164.9, 158.7, 129.9, 129.8, 129.2, 128.7, 87.4, 38.4, 30.6, 26.1, 12.1; **FT-IR** (thin layer): ν_{max} = 1806, 1729, 1698, 1425, 1364, 1290, 1194, 1118, 1084, 1022, 931, 891, 720, 702, 552. **elemental analysis calcd**. (%) for $C_{16}H_{16}N_2O_5$: C, 60.76; H, 5.10; N, 8.86. found: C, 60.71; H, 4.99; N, 8.83.

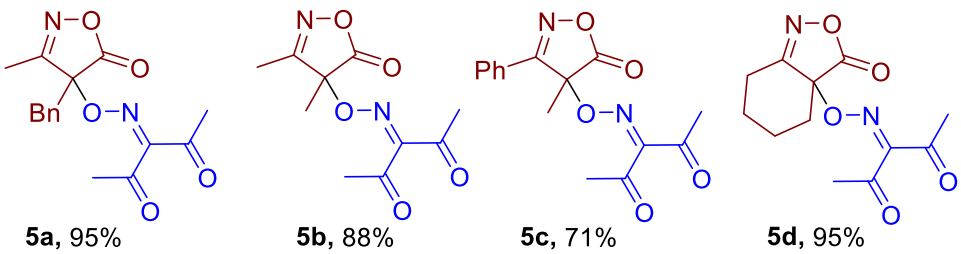


3-(((3,5-Di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione 7a, was synthesized as slightly yellow crystals (75%, 261 mg, purified by column chromatography with PE/EtOAc = 10/1 eluent). Reaction time was 15 min. Mp = 79 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.47 (s, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.51 (s, 3H), 1.22 (s, 18H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.2, 194.3, 186.5, 156.0, 148.6, 139.5, 79.5, 35.0, 30.8, 29.6, 25.5, 24.8; **FT-IR** (thin layer): ν_{max} = 2958, 1723, 1698, 1647, 1363, 1295, 1062, 955. **elemental analysis** calcd. (%) for $C_{20}H_{29}NO_4$: C, 69.14; H, 8.41; N, 4.03. found: C, 69.13; H, 8.41; N, 4.06.

Reactions of diacetyliminoxyl radical 2 with isoxazolin-5-ones 4a–d (experimental details for Scheme 4)



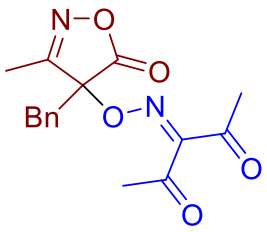
4a-d (1 mmol) **5a-d**, 71-95%



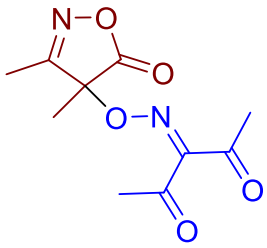
5a, 95% **5b,** 88% **5c,** 71% **5d,** 95%

General procedure: to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) were added isoxazolin-5-ones **4a-d** (1 mmol, 113-189 mg). Reaction mixture was stirred for 0.25-24 h until the dark red color disappeared, after that reaction mixture was rotary evaporated under

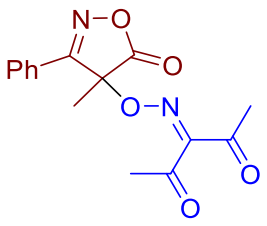
a water-jet vacuum. C-O coupling products **5a-d** were isolated by column chromatography on silica gel.



3-(((4-Benzyl-3-methyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, **5a** was synthesized as slight yellow powder (95%, purified by column chromatography with PE/DCM = 1/3 as eluent). Reaction time was 15 min. Mp = 82–83 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 3H), 7.19–7.07 (m, 2H), 3.35 (d, *J* = 13.7 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 196.3, 193.2, 173.6, 164.9, 158.7, 129.9, 129.8, 129.2, 128.7, 87.4, 38.4, 30.6, 26.1, 12.1; **FT-IR** (thin layer): ν_{max} = 1806, 1729, 1698, 1425, 1364, 1290, 1194, 1118, 1084, 1022, 931, 891, 720, 702, 552. **elemental analysis calcd**. (%) for $C_{16}H_{16}N_2O_5$: C, 60.76; H, 5.10; N, 8.86. found: C, 60.71; H, 4.99; N, 8.83.

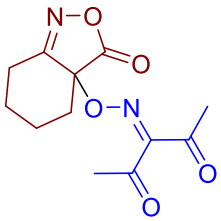


3-(((3,4-Dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, **5b** was synthesized as slightly yellow crystals (88%, purified by column chromatography with DCM/EtOAc = 90/1 as eluent). Reaction time was 2 h. Mp = 63 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H), 1.63 (s, 3H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ =196.2, 193.2, 174.0, 166.0, 158.5, 83.5, 30.6, 26.0, 18.0, 11.2; **FT-IR** (thin layer): ν_{max} = 1809, 1729, 1701, 1259, 1143, 1096, 1065, 974, 851, 559, 544. **elemental analysis calcd**. (%) for $C_{10}H_{12}N_2O_5$: C, 50.00; H, 5.04; N, 11.66. found: C, 49.69; H, 4.90; N, 11.50.



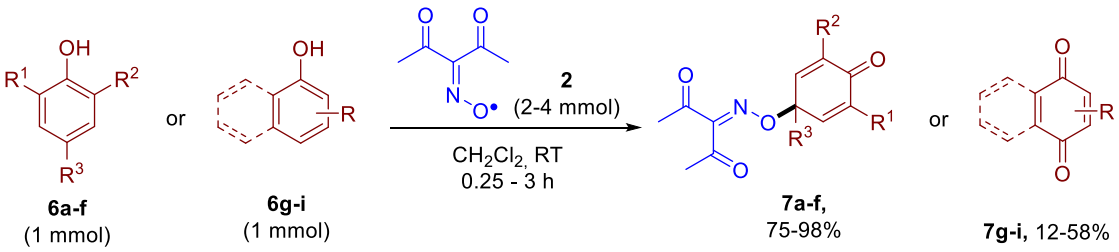
3-(((4-Methyl-5-oxo-3-phenyl-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, **5c** was synthesized as brownish powder (71%, purified by column chromatography with PE/EtOAc

= 2/1 as eluent). Reaction time was 20 min. Mp = 96–97 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.88–7.71 (m, 2H), 7.63–7.44 (m, 3H), 2.41 (s, 3H), 2.25(s, 3H), 1.82 (s, 3H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 196.3, 193.3, 174.5, 164.3, 158.4, 132.7, 129.6, 126.9, 125.8, 84.0, 30.7, 26.0, 20.1. **FT-IR** (thin layer): ν_{max} = 1813, 1728, 1699, 1448, 1419, 1363, 1293, 1253, 1170, 1120, 1066, 967, 926, 879, 842, 765, 721, 694, 680, 633, 552. **elemental analysis calcd**. for $C_{15}H_{14}N_2O_5$: C, 59.60; H, 4.67; N, 9.27. found: C, 59.60; H, 4.68; N, 9.28.

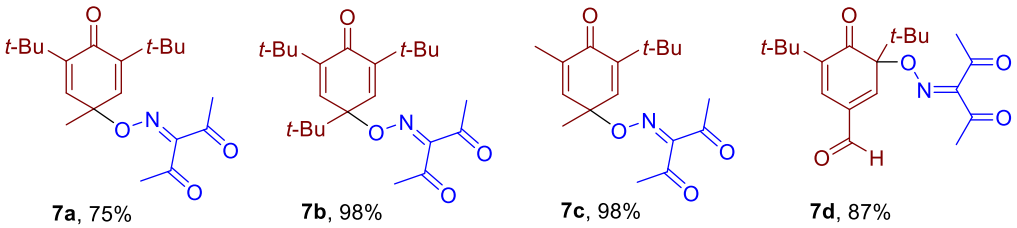


3-(((3-Oxo-4,5,6,7-tetrahydrobenzo[c]isoxazol-3a(3H)-yl)oxy)imino)pentane-2,4-dione, **5d** was synthesized as yellow powder. Reaction time was 24 h Mp = 86–87 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 2.87–2.69 (m, 1H), 2.53–2.25 (m, 8H), 2.23–2.11 (m, 1H), 1.87–1.45 (m, 4H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 196.3, 193.3, 173.9, 167.9, 158.8, 82.7, 33.3, 30.7, 27.2, 26.0, 25.2, 20.0. **FT-IR** (thin layer): ν_{max} = 1802, 1732, 1698, 1362, 1292, 1158, 1013, 926, 839, 558. **HR-MS (ESI)**: *m/z* = 289.0793, calcd. for $C_{12}H_{14}N_2O_5$+Na^+: 289.0795.

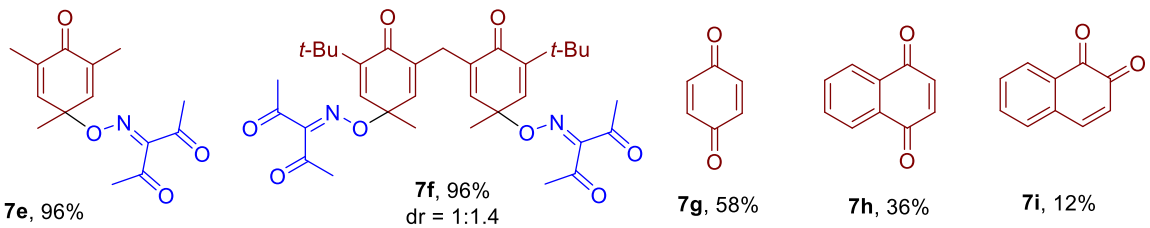
Reactions of diacetyliminoxyl radical 2 with phenols (experimental details for Scheme 5 and Table 1)



6a-f (1 mmol) | **6g-i** (1 mmol) | **7a-f,** 75-98% | **7g-i,** 12-58%

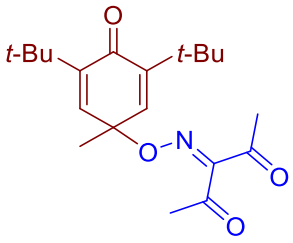


7a, 75% | **7b**, 98% | **7c**, 98% | **7d**, 87%

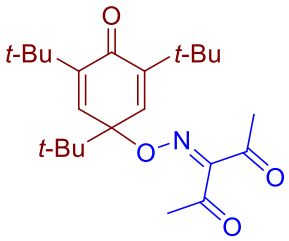


7e, 96% | **7f**, 96% dr = 1:1.4 | **7g**, 58% | **7h**, 36% | **7i**, 12%

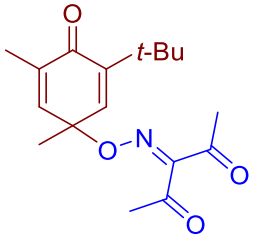
General procedure: to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) were added phenols **6a-j** (1 mmol, 110-262 mg). Reaction mixture was stirred for 15 min (for **6d** and **6j** the reaction time was 3 and 24 h respectively) until the dark red color disappeared, after that reaction mixture was rotary evaporated under a water-jet vacuum. C-O coupling products **7a-i** were isolated by column chromatography on silica gel.



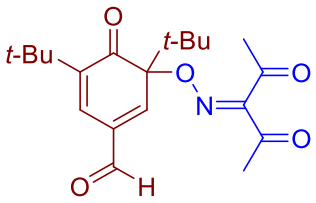
3-(((3,5-Di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione 7a, was synthesized as slightly yellow crystals (75%, 261 mg, purified by column chromatography with PE/EtOAc = 10/1 eluent). Mp = 79 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.47 (s, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.51 (s, 3H), 1.22 (s, 18H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.2, 194.3, 186.5, 156.0, 148.6, 139.5, 79.5, 35.0, 30.8, 29.6, 25.5, 24.8; **FT-IR** (thin layer): ν_{max} = 2958, 1723, 1698, 1647, 1363, 1295, 1062, 955. **elemental analysis** calcd. (%) for $C_{20}H_{29}NO_4$: C, 69.14; H, 8.41; N, 4.03. found: C, 69.13; H, 8.41; N, 4.06.



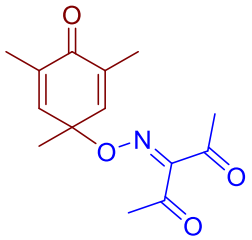
3-(((1,3,5-Tri-tert-butyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione 7b, was synthesized as yellow powder (98%, 381 mg, purified by column chromatography with PE/EtOAc = 10/1 eluent). Mp = 74–75 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.59 (s, 2H), 2.38 (s, 3H), 2.20 (s, 3H), 1.24 (s, 18H), 0.98 (s, 9H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.1, 194.3, 186.7, 156.6, 149.6, 138.5, 86.9, 39.6, 35.3, 30.8, 29.7, 26.0, 25.4; **FT-IR** (thin layer): ν_{max} = 2964, 1726, 1690, 1686, 1648, 1463, 1364, 1301, 959, 886; **HR-MS** (ESI): *m/z* = 412.2448, calcd. for $C_{23}H_{35}NO_4$+Na^+: 412.2458.



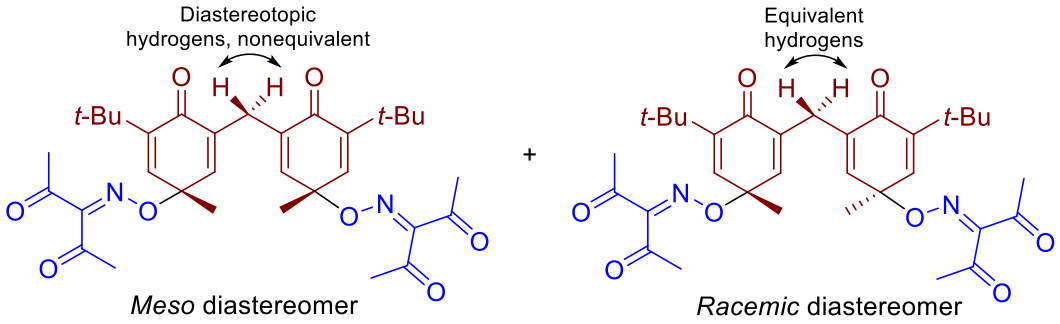
3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione 7c, was synthesized as pale yellow oil (98%, 302 mg, purified by column chromatography with DCM/EtOAc = 20/1 as eluent). Mp = 59 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.52 (d, *J* = 3.1 Hz, 1H), 6.49 (dq, *J* = 3.2, 1.4 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H), 1.83 (d, *J* = 1.4 Hz, 3H), 1.46 (s, 3H), 1.17 (s, 9H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.0, 194.2, 186.0, 156.1, 146.9, 141.7, 141.6, 137.4, 79.3, 34.6, 30.6, 29.3, 25.5, 24.4, 16.1; **FT-IR** (thin layer): ν_{max} = 2959, 2926, 1727, 1692, 1650, 1365, 1297, 1197, 1061, 958, 900. **HR-MS** (ESI): *m/z* = 328.1524, calcd. for $C_{17}H_{23}NO_4$+Na^+: 328.1519.



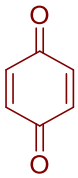
3,5-Di-tert-butyl-3-(((2,4-dioxopentan-3-ylidene)amino)oxy)-4-oxocyclohexa-1,5-diene-1-carbaldehyde, 7d, was synthesized as yellow powder (87%, 314 mg). Mp = 119 °C dec. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 7.20 (s, 1H), 7.16 (s, 1H), 2.47 (s, 3H), 2.16 (s, 3H), 1.24 (s, 9H), 0.99 (s, 9H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 199.8, 198.1, 193.8, 189.3, 157.3, 154.1, 148.1, 137.7, 128.0, 93.3, 41.6, 35.3, 30.4, 29.4, 25.7, 25.1; FT-IR (thin layer): ν_{max} = 1729, 1691, 1674, 1362, 1295, 1180, 982, 947, 935, 891. **HR-MS** (ESI): *m/z* = 384.1772, calcd. for $C_{20}H_{27}NO_5$+Na^+: 384.1781. Single crystal X-Ray analysis is available (See Fig. S2, page S27)



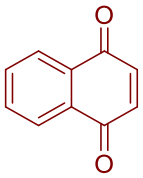
3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione 7e, was synthesized as pale yellow oil (96%, 252 mg, purified by column chromatography with DCM/EtOAc = 20/1 as eluent). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.56 (s, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 1.85 (s, 6H), 1.47 (s, 3H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 198.0, 194.2, 186.5, 156.3, 143.4, 136.0, 79.1, 30.6, 25.6, 24.2, 15.8; **FT-IR** (thin layer): ν_{max} = 1727, 1690, 1646, 1432, 1365, 1298, 1061, 1046, 1019, 959, 917, 732. **HR-MS** (ESI): *m/z* = 286.1046, calcd. for $C_{14}H_{17}NO_4$+Na^+: 286.1050.



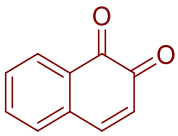
3,3'-(((Methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3) 7f, was synthesized as yellow gum (96%, 571 mg, purified by column chromatography with DCM/EtOAc = 40/1 as eluent). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.55 (s, 4H), 3.47 (d, *J* = 15.3 Hz, 0.6H), 3.33 (s, 0.9H), 3.19 (d, *J* = 15.3 Hz, 0.6H), 2.29 (s, 6H), 2.23 (s, 6H), 1.48 (s, 3H), 1.46 (s, 3H), 1.19 (s, 18H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 197.9, 197.8, 194.2, 194.1, 184.8, 156.4, 156.3, 147.21, 147.16, 143.5, 143.2, 141.8, 141.7, 138.5, 138.3, 79.31, 79.26, 77.4, 34.9, 30.7, 29.5, 29.3, 25.7, 24.5, 24.4; **FT-IR** (thin layer): ν_{max} = 2960, 2871, 1727, 1693, 1648, 1601, 1420, 1365, 1297, 1195, 1061, 958, 758, 722. **HR-MS (ESI)**: *m/z* = 617.2830, calcd. for $C_{33}H_{42}N_2O_8$+Na^+: 617.2833.



Cyclohexa-2,5-diene-1,4-dione (1,4-benzoquinone) 7g, was synthesized as yellow crystals (58%, 63 mg, purified by column chromatography with DCM/EtOAc = 40/1 as eluent). Mp = 113–114 °C (Lit.[21] mp = 112–114 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 6.78 (s, 4H); **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 187.3, 136.7.

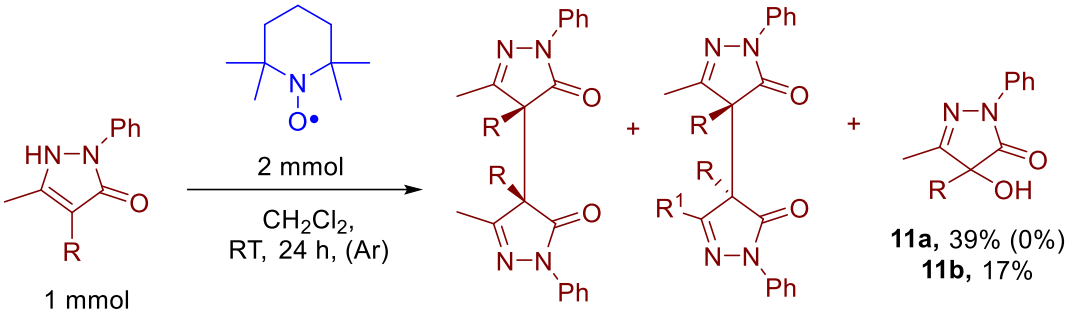


Naphthalene-1,4-dione (1,4-naphthoquinone) 7h, was synthesized as yellow crystals (36%, 57 mg, purified by column chromatography with PE/EtOAc = 6/1 as eluent). Mp = 125–127 °C (Lit.[22] mp = 124–128 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.72 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.95 (s, 2H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 185.1, 138.7, 134.0, 132.0, 126.5.



Naphthalene-1,2-dione (1,2-naphthoquinone) 7i, was synthesized as yellow crystals (12%, 19 mg, purified by column chromatography with DCM as eluent). Mp = 144–145 °C dec (Lit.[23] mp = 145–146 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 8.18–7.99 (m, 1H), 7.73–7.57 (m, 1H), 7.55–7.39 (m, 2H), 7.40–7.31 (m, 1H), 6.41 (d, *J* = 10.1 Hz, 1H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 180.9, 178.9, 145.5, 136.0, 134.8, 131.6, 130.9, 130.1, 130.0, 127.9.

Reactions of diacetyliminoxyl radical 2 with pyrazoline-5-ones in comparison with TEMPO (experimental details for Scheme 6)

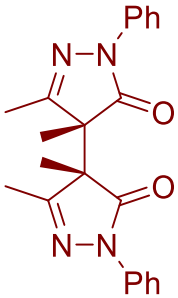


1 mmol
8a: R = Me
8b: R = Bn

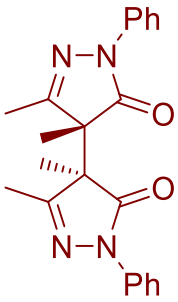
10-meso
a, 35% (50%)
b, 54%

10-racemic
a, 11% (21%)
b, 18%

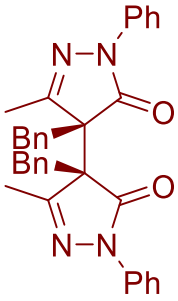
General procedure for reactions of pyrazoline-5-ones with TEMPO: to a stirred solution of pyrazolin-5-ones **8a,b** (0.5 mmol, 94-132 mg) in DCM (25 mL) was added TEMPO (1 mmol, 156 mg). The resulting orange-red solution was left for 24 hours at room temperature, then concentrated on a rotary evaporator to a volume of about 1 ml and dimerization products **10-meso-a,b**, **10-racemic-a,b** and hydroxylation products **11a,b** were isolated by column chromatography on silica gel with CH_2Cl_2/EtOAc = 20/1 as eluent. In an additional experiment in an argon atmosphere, a solution of pyrazoline-5-one **8a** in DCM was bubbled with argon before addition of TEMPO.



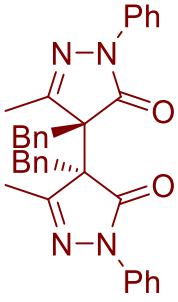
Meso-3,3',4,4'-tetramethyl-1,1'-diphenyl-[4,4'-bipyrazol]-5,5'-dione, 10-meso-a: white powder. Mp = 161–162 °C (Lit.[24] mp = 163–164 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.2 Hz, 4H), 7.49-7.34 (m, 4H), 7.22 (t, *J* = 7.3 Hz, 2H), 1.93 (s, 6H), 1.73 (s, 6H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 173.1, 161.9, 137.6, 129.2, 125.7, 119.1, 54.5, 14.7, 14.6.



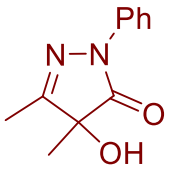
Racemic-3,3',4,4'-tetramethyl-1,1'-diphenyl-[4,4'-bipyrazol]-5,5'-dione, 10-racemic-a: slightly yellow powder. Mp = 141–142 °C (Lit.[24] mp = 140–141 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.9 Hz, 4H), 7.45-7.31 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 2.19 (s, 6H), 1.60 (s, 6H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 173.1, 159.8, 137.7, 129.0, 125.4, 119.3, 55.7, 16.0, 15.4.



Meso-4,4'-dibenzyl-5,5'-dimethyl-2,2'-diphenyl-[4,4'-bipyrazole]-5,5'-dione, 10-meso-b, was synthesized as slightly yellow powder (54%, 70 mg).[24,25] Mp = 146–148 °C (Lit.[24] mp = 147–148 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.3 Hz, 4H), 7.46–7.33 (m, 1H), 7.27–7.13 (m, 12H), 4.42 (d, *J* = 13.2 Hz, 2H), 3.59 (d, *J* = 13.2 Hz, 2H), 1.99 (s, 6H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 172.4, 159.6, 137.0, 133.7, 129.8, 129.0, 128.5, 127.7, 126.0, 119.8, 60.7, 33.9, 15.6. **FT-IR** (thin layer): ν_{max} = 1703, 1597, 1500, 1455, 1394, 1368, 1321, 1284, 1265, 1123, 909, 758, 727, 692. **HR-MS** (ESI): *m/z* = 549.2258, calcd. for $C_{34}H_{30}N_4O_2$+Na^+: 549.2261.

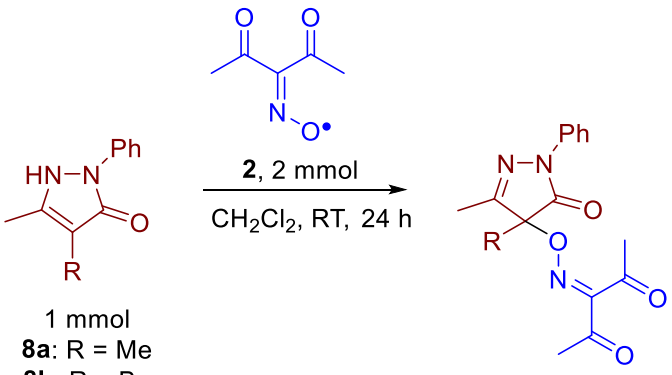


Racemic-4,4'-dibenzyl-5,5'-dimethyl-2,2'-diphenyl-[4,4'-bipyrazole]-5,5'-dione, 10-racemic-b, was synthesized as slightly yellow powder (18%, 23 mg).[24] Mp = 166–167 °C (Lit.[24] mp = 165–166 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.0 Hz, 4H), 7.35–7.26 (m, 4H), 7.24–7.10 (m, 12H), 4.15 (d, J = 13.1 Hz, 2H), 3.32 (d, *J* = 13.1 Hz, 2H), 2.35 (s, 6H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 171.9, 157.1, 137.1, 133.4, 129.8, 128.81, 128.50, 127.8, 125.8, 120.3, 62.2, 34.7, 17.4. **FT-IR** (thin layer): ν_{max} = 1703, 1597, 1498, 1367, 1272, 1123, 1079, 756, 725, 695. **HR-MS** (ESI): *m/z* = 549.2254, calcd. for $C_{34}H_{30}N_4O_2$+Na^+: 549.2261.

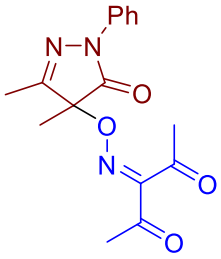


4-Hydroxy-3,4-dimethyl-1-phenyl-pyrazolin-5-one, 11a, was synthesized as slightly yellow solid (39%, 40 mg).[25] Mp = 103–105 °C (Lit.[26] mp = 105 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.93-7.80 (m, 2H), 7.46-7.32 (m, 2H), 7.24-7.13 (m, 1H), 3.53 (s, 1H), 2.19 (s, 3H), 1.54 (s, 3H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 174.73, 163.40, 137.70, 128.96, 125.45, 118.97, 77.40, 22.27, 12.71.

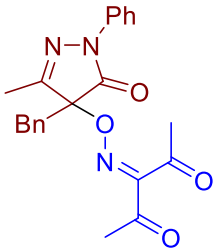
4-Benzyl-4-hydroxy-3-methyl-1-phenyl-pyrazolin-5-one 11b, was synthesized as slightly yellow solid (17%, 24 mg).[25] Mp = 144–145 °C (Lit.[26] mp = 145 °C).. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.27 (m, 2H), 7.23 – 7.11 (m, 6H), 4.38 (s, 1H), 3.29 (d, *J* = 13.0 Hz, 1H), 3.17 (d, *J* = 13.2 Hz, 1H), 2.20 (s, 3H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 173.9, 161.7, 137.2, 132.4, 129.7, 128.87, 128.59, 127.8, 125.7, 119.5, 81.2, 43.0, 13.7.



General procedure for reactions of pyrazoline-5-ones 8a,b with diacetyliminoxyl 2: to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) were added pyrazolin-5-ones **8a,b** (1 mmol, 188-264 mg). Reaction mixture was stirred for 24 h and rotary evaporated under a water-jet vacuum. C-O coupling products **9a,b** were isolated by column chromatography on silica gel using mixture CH_2Cl_2/EtOAc = 40/1 as eluent.

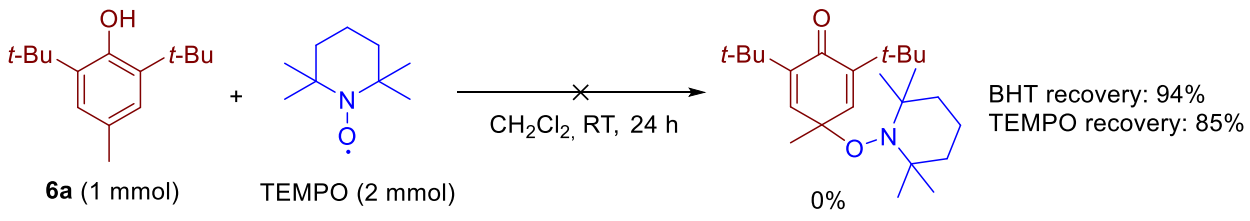


3-(((3,4-Dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, was synthesized as slightly yellow gum (71%, 223 mg).[1] **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ = 7.96–7.80 (m, 2H), 7.49–7.36 (m, 2H), 7.30–7.16 (m, 1H), 2.40 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (75.47 MHz, $CDCl_3$) δ: 197.0, 193.5, 170.2, 159.8, 158.1, 137.7, 129.1, 125.6, 118.8, 86.0, 30.6, 25.9, 17.8, 13.0.

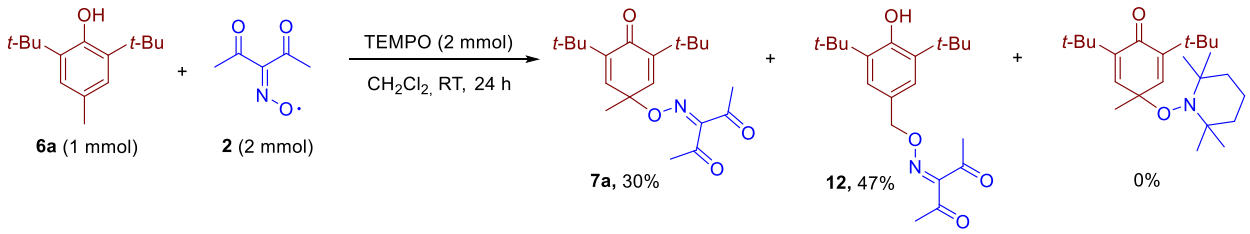


3-(((4-Benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9b, was synthesized as slightly yellow gum. Mp = 162 °C. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ = 7.76–7.60 (m, 2H), 7.46–7.32 (m, 2H), 7.31–7.12 (m, 6H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.26 (d, *J* = 13.4 Hz, 1H), 2.46 (s, 3H), 2.23 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (75.47 MHz, $CDCl_3$) δ = 196.9, 193.4, 169.6, 158.38, 158.23, 137.3, 130.9, 129.8, 128.94, 128.7, 128.1, 125.7, 119.1, 89.5, 38.3, 30.6, 25.8, 13.9. **FT-IR** (thin layer): ν_{max} = 1728, 1686, 1493, 1366, 1295, 1098, 1057, 954, 885, 760, 723, 696. **elemental analysis** calcd. for $C_{22}H_{21}N_3O_4$: C, 67.51; H, 5.41; N, 10.74. found: C, 67.51; H, 5.46; N, 10.69.

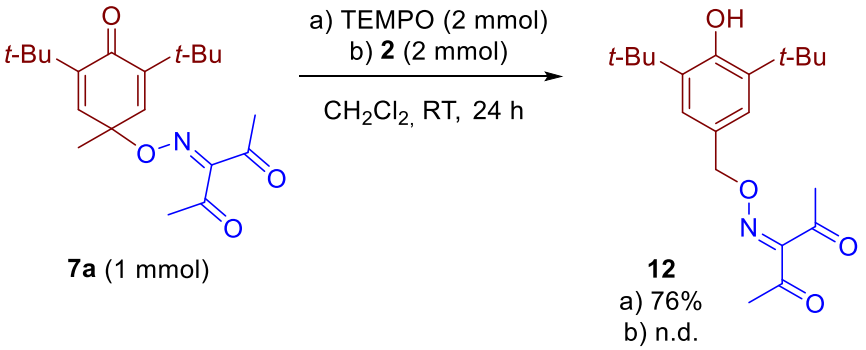
Experimental details for Scheme 8



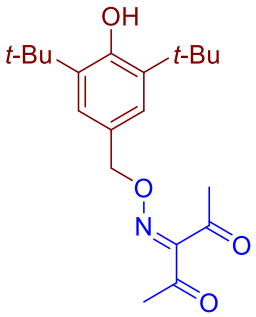
General procedure: to a stirred solution of TEMPO (2 mmol, 312 mg) in DCM (50 mL) was added BHT **6a** (1 mmol, 220 mg). Reaction mixture was stirred for 24 h at room temperature and then was rotary evaporated under a water-jet vacuum. Column chromatography on silica gel using PE/DCM = 1/1 as eluent afforded BHT (207 mg, 94% recovery), TEMPO (266 mg, 85% recovery).



General procedure: to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) were added TEMPO (2 mmol, 312 mg) and BHT **6a** (1 mmol, 220 mg). Reaction mixture was stirred for 24 h at room temperature and then was rotary evaporated under water-jet vacuum. Column chromatography on silica gel using PE/EtOAc = 10/1 as eluent afforded **7a** (105 mg, 30%), 3-(((3,5-di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione **12** (47%, 163 mg) and TEMPO (204 mg, 65% recovery).



General procedure a: to a stirred solution of **7a** (1 mmol, 347 mg) in DCM (5 mL) was added TEMPO (2 mmol, 312 mg). Reaction mixture was stirred for 24 h at room temperature and then was rotary evaporated under water-jet vacuum. Column chromatography on silica gel using PE/EtOAc = 10/1 as eluent afforded 3-(((3,5-di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione **12** (76%, 263 mg).

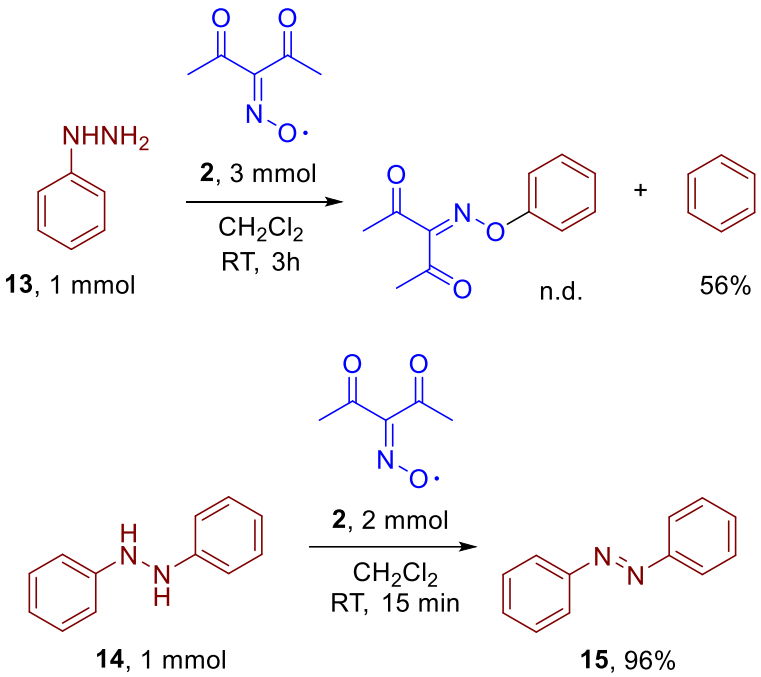


3-(((3,5-Di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione 12, was synthesized as pale yellow oil (47%, 163 mg, purified by column chromatography with PE/EtOAc = 10/1 as

eluent). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.16 (s, 2H), 5.30 (s, 1H), 5.17 (s, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 1.45 (s, 18 H).**^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 197.1, 193.0, 154.4, 152.8, 134.6, 124.9, 124.4, 78.2, 32.9, 29.2, 28.9, 24.2. **FT-IR** (thin layer): ν_{max} = 3627, 2959, 2928, 2872, 1726, 1682, 1361, 1144, 993**.** HR-MS (ESI): *m/z* = 370.1978, calcd. for $C_{20}H_{29}NO_4$+Na^+: 370.1989.

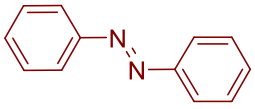
General procedure b: to a stirred solution of diacetyliminoxyl **2** (2 mmol) in DCM (50 mL) was added **7a** (1 mmol, 347 mg). Reaction mixture was stirred for 24 h at room temperature and then was rotary evaporated under water-jet vacuum. Column chromatography on silica gel using PE/EtOAc = 10/1 as eluent afforded **7a** (95% recovery, 330 mg).

Reactions of diacetyliminoxyl radical as dehydrogenating agent with hydrazines and thiols (experimental details for Scheme 9)

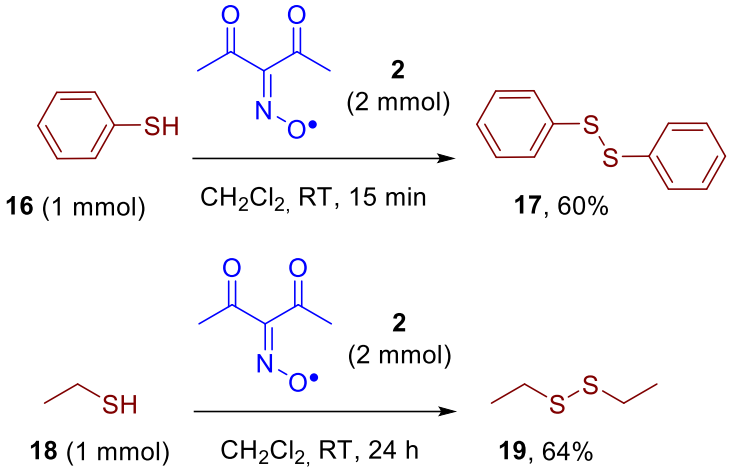


General procedure for phenylhydrazine 13: to a stirred solution of diacetyliminoxyl radical **2** (3 mmol) in DCM (50 mL) was added phenylhydrazine **13** (1 mmol, 108 mg). Reaction mixture was stirred for 3 h at room temperature and then was analyzed using ^{1}H-monitoring and GC-analysis with 1,1,2,2-tetrachloroethane as an internal standard.

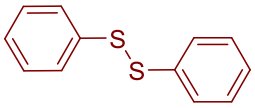
General procedure for 1,2-diphenylhydrazine 14: to a stirred solution of diacetyliminoxyl radical **2** (2-3 mmol) in DCM (50 mL) was added 1,2-diphenylhydrazine **14** (1 mmol, 184 mg). Reaction mixture was stirred for 15 min at room temperature and then was rotary evaporated under a water-jet vacuum. Column chromatography on silica gel using PE/DCM = 3/1 as eluent afforded azobenzene **15** (175 mg, 96%).



Azobenzene 15, was synthesized as orange powder (96%, 175 mg, purified by column chromatography with PE/DCM = 3/1 as eluent). Mp = 69–70 °C (Lit.[27] mp = 68–69 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 8.06 – 7.84 (m, 4H), 7.66 – 7.40 (m, 6H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 152.8, 131.1, 129.2, 123.0.



General procedure for thiophenol 16: to a stirred solution of diacetyliminoxyl radical **2** (2 mmol) in DCM (50 mL) was added thiophenol **16** (1 mmol, 110 mg). Reaction mixture was stirred for 0.5 h at room temperature and then was rotary evaporated under a water-jet vacuum. Column chromatography on silica gel using PE/DCM = 10/1 as eluent afforded diphenyl disulfide **17** (130 mg, 60%).



Diphenyl disulfide 17, was synthesized as yellow powder (60%, 130 mg, purified by column chromatography with PE/DCM = 10/1 as eluent). Mp = 62–63 °C (Lit.[28] mp = 61–63 °C). **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 7.61 – 7.47 (m, 4H), 7.39 – 7.20 (m, 6H). **^{13}C NMR** (75.47 MHz, $CDCl_3$): δ = 137.2, 129.2, 127.7, 127.3.

General procedure for ethanethiol 18: to a stirred solution of diacetyliminoxyl radical **2** (2-3 mmol) in DCM (50 mL) was added ethanethiol **18** (1 mmol, 62 mg). Reaction mixture was stirred for 24 h at room temperature and then was analyzed using ^{1}H-monitoring with 1,1,2,2-tetrachloroethane as an internal standard.

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X-ray single-crystal diffraction: Structure determination of compounds 3c and 7d

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_α-radiation (0.71073 Å). The intensity data were integrated by the SAINT program[1] and corrected for absorption and decay using SADABS.[2] The structure was solved by direct methods using SHELXT[3] and refined on F^2 using SHELXL-2018.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite[1] was used for molecular graphics. Crystal data and structure refinement for 3c are summarized in Table S1. Compound **3c** crystallizes in monoclinic space group $P2_1/c$ (Figure S1).

Table S1. Crystal data and structure refinement for **3c.**

Empirical formula	$C_{24}H_{21}NO_3$	
Formula weight	371.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.4081(3) Å	α = 90°
	b = 29.0616(9) Å	β = 115.5260(9)°
	c = 8.9737(3) Å	γ = 90°
Volume	1978.71(12) $Å^3$	
Z	4	
Density (calculated)	1.247 g/cm^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	784	
Crystal size	0.59 x 0.57 x 0.48 mm^3	
Theta range for data collection	2.611 to 37.790°	
Index ranges	-14<=h<=14, -47<=k<=50, -15<=l<=15	
Reflections collected	82890	
Independent reflections	10629 [R(int) = 0.0332]	
Observed reflections	8851	

Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8026 and 0.7773	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10629 / 0 / 256	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1183	
R indices (all data)	R1 = 0.0577, wR2 = 0.1283	
Largest diff. peak and hole	0.485 and -0.317 e.$Å^{-3}$	

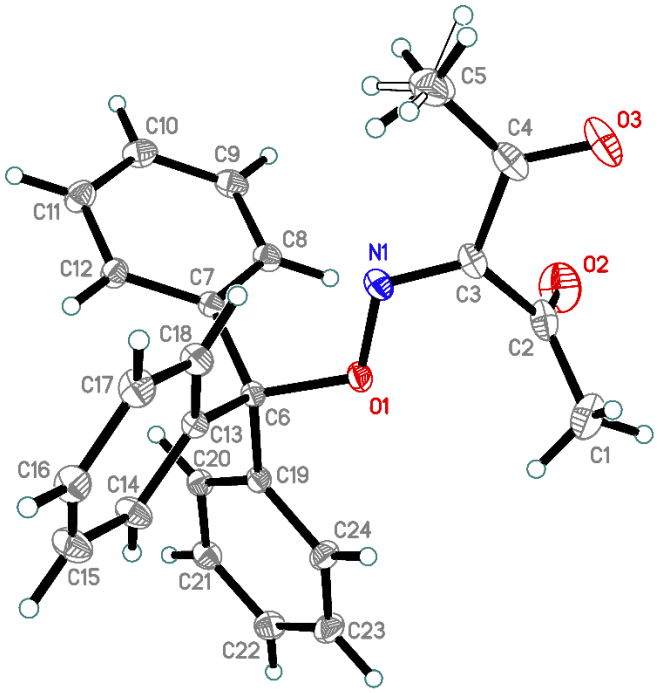

Figure S1. Crystal structure of compound **3c**, showing the atomic numbering and 50% probability displacement ellipsoids

Crystal data and structure refinement for **7d** are summarized in Table S2. Compound **7d** crystallizes in racemic form in orthorombic space group Pbca (Figure S2).

Table S2. Crystal data and structure refinement for **7d**.

Empirical formula	$C_{20}H_{27}NO_5$	
Formula weight	361.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	

Space group	Pbca	
Unit cell dimensions	a = 13.0105(3) Å	α = 90°.
	b = 15.4617(4) Å	β = 90°.
	c = 19.8646(5) Å	γ = 90°.
Volume	3996.05(17) $Å^3$	
Z	8	
Density (calculated)	1.202 g/cm^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	1552	
Crystal size	0.48 x 0.23 x 0.19 mm^3	
Theta range for data collection	2.288 to 30.515°	
Index ranges	-18<=h<=18, -22<=k<=22, -28<=l<=28	
Reflections collected	83405	
Independent reflections	6103 [R(int) = 0.0588]	
Observed reflections	4766	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8750 and 0.8062	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6103 / 0 / 243	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1094	
R indices (all data)	R1 = 0.0671, wR2 = 0.1235	
Largest diff. peak and hole	0.383 and -0.221 $e.Å^{-3}$	

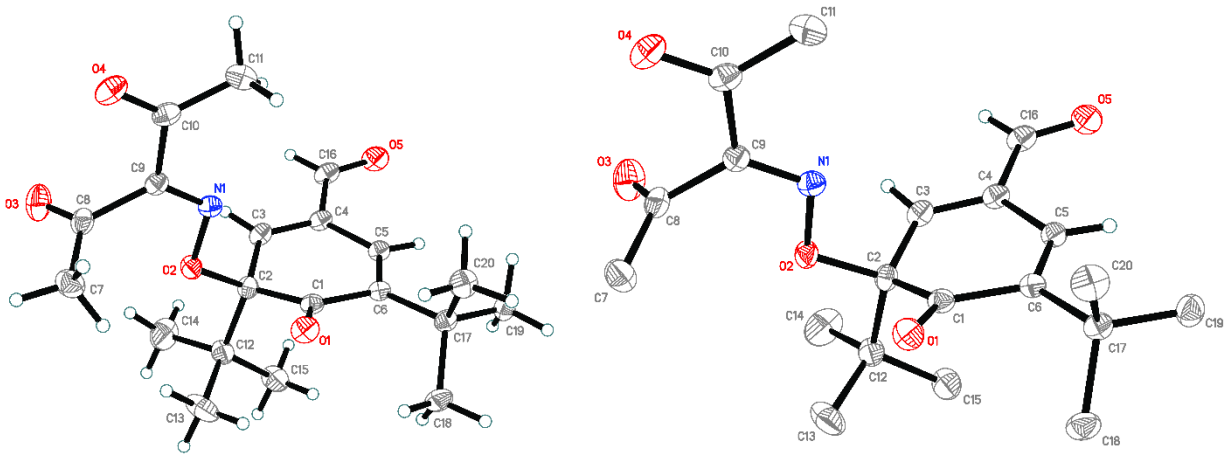

Figure S2. Crystal structure of compound **7d**, showing two independent molecules, atomic numbering and 50% probability displacement ellipsoids.

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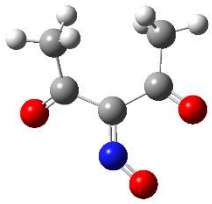
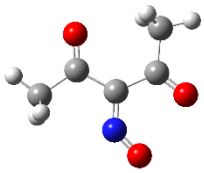
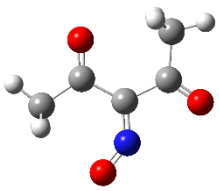
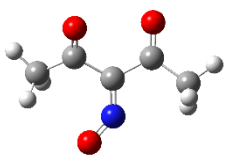
Quantum chemical calculations

Thermodynamic calculations of C–O coupling reactions with diacetyliminoxyl radical

Conformation analysis of diacetyliminoxyl radical and diacetyl oxime

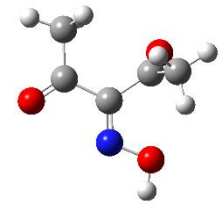
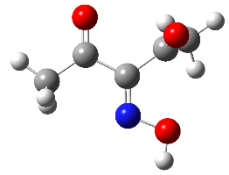
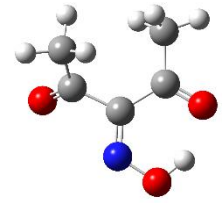
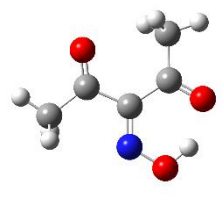
Diacetyliminoxyl free radical has two acetyl groups, rotation of which around C–C axis gave four distinct conformers **2(1)**, **2(2)**, **2(3)** and **2(4)** (Table S3). The geometries of the conformers were fully optimized, their corresponding free energies, enthalpies and electronic energies with corrections to zero-point energies (ZPE), measured from the most stable conformer **2(2)** are reported in Table S3. The free energy of the second stable conformer **2(4)** is greater than one of **2(2)** by 3.79 kcal/mol, which means that its equilibrium concentration will be approximately 600 times less than one of the most stable conformer.

Table S3. Free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) (in kcal/mol) of diacetyliminoxyl free radical conformers, as compared with the most stable conformer **2(2)**.

Conformer		ΔG rel. to **2(2)**	ΔH rel. to **2(2)**	Δ(E+ZPE) rel. to **2(2)**
2(1)		4.08	4.19	4.26
2(2)		0	0	0
2(3)		5.13	3.16	3.87
2(4)		3.79	3.8	3.77

In contrast to diacetyliminoxyl radical **2** for 3-(hydroxyimino)-2,4-pentanedione **2a** two stable conformers **2a(1)** and **2a(2)** were found (Table S4) in which one of the acetyl groups is out of plane of C=N-O fragment (almost perpendicular to that plane). The potential energy scan of the acetyl group rotation in the oxime **2a(2)** (Figure S3) has confirmed that the flat configurations do not correspond to the stationary points as it was in case of the diacetyliminoxyl free radical. Two more conformers were found by rotation of the hydrogen of the hydroxyimino group. Only two positions of the hydrogen were local minima: with the dihedral angle θ(CNOH) 180 and 0 degrees. In the latter case the C4 acetyl group was orienting itself with O6 oxygen atom towards the hydrogen of the hydroxyl group, giving a hydrogen bond with length of 1.61Å. It has fixed the rotation of the C4 acetyl group, forming flat configuration similar to **2(2)** geometry. Rotation of C5 acetyl group produced conformers **2a(3)** and **2a(4)**. The energies with ZPE correction, free energies and enthalpies of all four resulting conformers of the oxime are provided in Table S4. With the free energy as low as 1.37 kcal/mol for the conformation with hydrogen bond **2a(4)** in comparison with **2a(2)** the equilibrium concentration of **2a(4)** should be 10 times less than one of **2a(2)**. It was decided to discard the **2a(4)** structure for reaction modeling due to steric hindrance.

Table S4. Free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) (in kcal/mol) of diacetyl oxime conformers, as compared with the most stable conformer **2a(2)**.

Conformer		ΔG rel. to **2a(2)**	ΔH rel. to **2a(2)**	Δ(E+ZPE) rel. to **2a(2)**
2a(1)		3.59	3.17	3.32
2a(2)		0	0	0
2a(3)		6.61	4.72	5.36
2a(4)		1.37	0.16	0.73

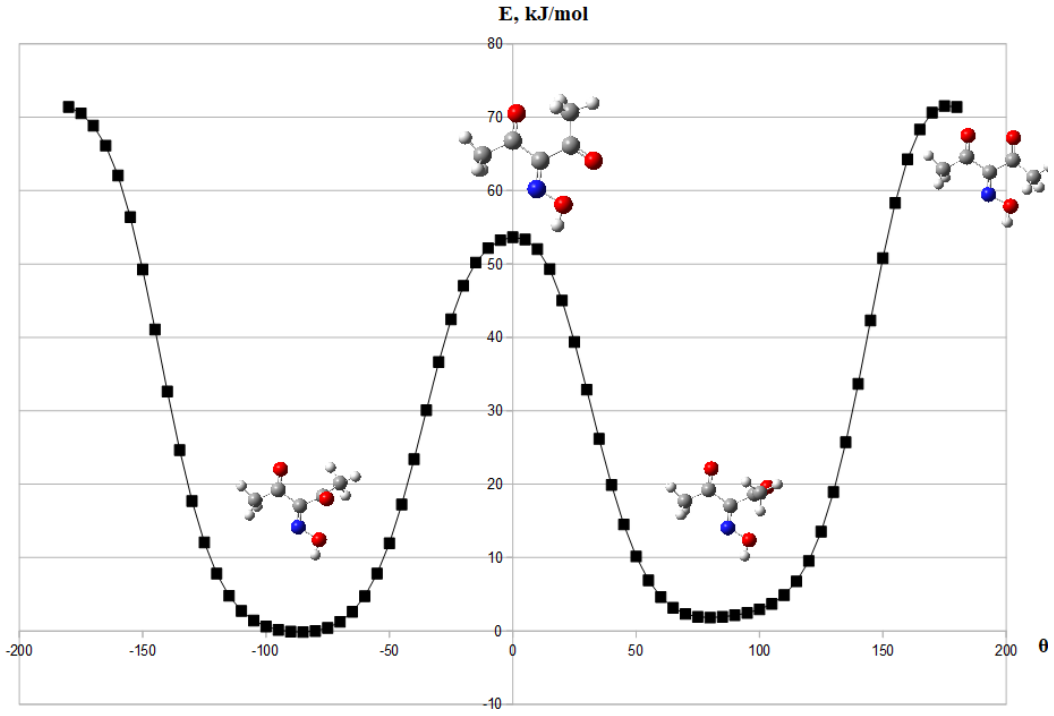
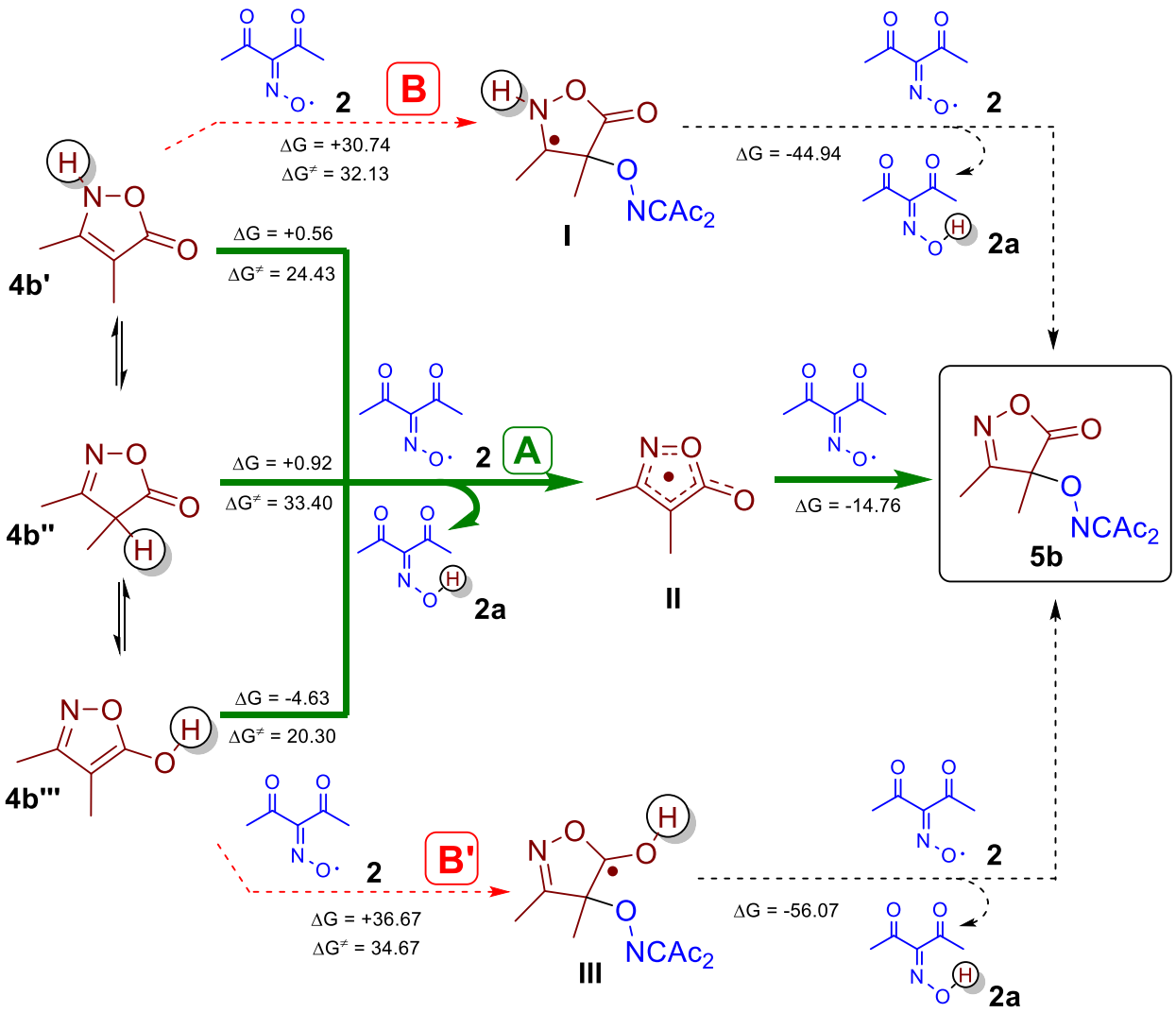


Figure S3. Potential energy scan along dihedral angle θ(NCCO) rotation of diacetyl oxime **2a**.

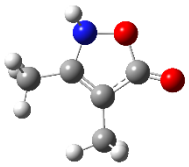
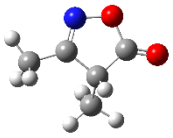
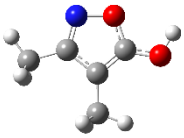
Oxidative C–O coupling of diacetyliminoxyl with isoxazolone 4b

Five reaction paths were modeled for C–O coupling reaction between 3,4-dimethyl-2H-1,2-oxazol-5-one (**4b**) and diacetyliminoxyl free radical **2** (Scheme S1). Three tautomers of the substrate **4b** (**4b'**, **4b''** and **4b'''**) were considered with two distinct conformations **4b'''(1)** and **4b'''(2)** for tautomer **4b'''**. Their thermodynamic stability is provided in Table S5. Three rotational conformers were found for product **5b** and intermediates **I** and **III** with dihedral angles θ(CCON) = -70º (**I(1)**, **III(1)** and **5b(1)**), 180º (**I(2)**, **III(2)** and **5b(2)**) and 60º (**I(3)**, **III(3)** and **5b(3)**). Three more conformers were added for each respectful C4 acetyl group rotation of diacetyliminoxyl fragment, giving structures **I(4-6)**, **III(4-6)** and **5b(4-6)**. The orientation of the hydrogen of NH group of **I** gave 6 more conformers: **I(7-12)**. Conformers **4b'''(1)** and **4b'''(2)** gave 2 distinct sets of intermediates **III**: **III(1-6)** for **4b'''(1)** and **III(7-12)** for **4b'''(2)**. Enantiomers of **4b''**, **I**, **III** and **5b** by C-4 position of isoxazole ring were not considered.



Scheme S1. Modeled mechanisms of oxidative C–O coupling of isoxazolone **4b** with diacetyliminoxyl **2**. Free energy (ΔG) and activation energy values (ΔG≠) are given in kcal/mol.

Table S5. Free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) (in kcal/mol) of 3,4-dimethyl-2H-1,2-oxazol-5-one tautomers, relative to isoxazolone **4b'**.

Structure		ΔG rel. to **4b''**	ΔH rel. to **4b''**	Δ(E+ZPE) rel. to **4b''**
4b'		0.36	0.87	0.71
4b''		0	0	0
4b'''(1)		7.41	7.6	7.45
4b'''(2)		5.55	6.95	6.51

Relative Gibbs free energies ΔG and enthalpies ΔH (Table S6) were calculated with the following formulae:

$$\Delta E(\mathbf{4b'}) = E(\mathbf{4b'}) + 2E(\mathbf{2(2)}) - E_0;$$

$$\Delta E(\mathbf{4b'''}) = E(\mathbf{4b'''}) + 2E(\mathbf{2(2)}) - E_0;$$

$$\Delta E(\mathbf{I}) = E(\mathbf{I}) + E_{BSSE}(\mathbf{I}) + E(\mathbf{2(2)}) - E_0;$$

$$\Delta E(\mathbf{II}) = E(\mathbf{II}) + E(\mathbf{2}) + E(\mathbf{2a(2)}) - E_0;$$

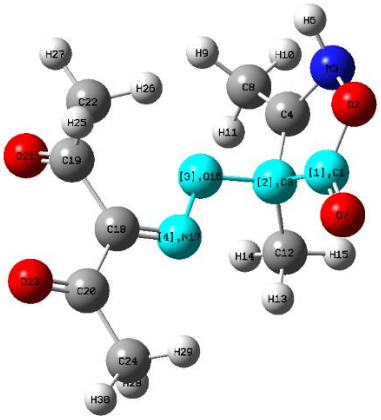
$$\Delta E(\mathbf{III}) = E(\mathbf{III}) + E_{BSSE}(\mathbf{III}) + E(\mathbf{2(2)}) - E_0;$$

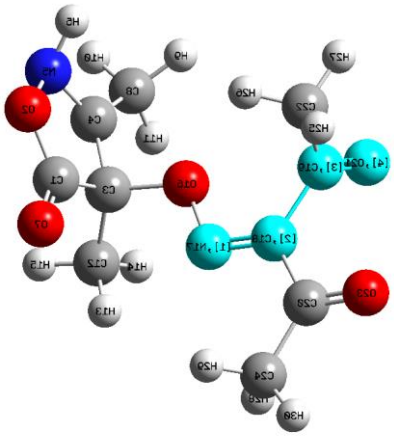
$$\Delta E(\mathbf{5b}) = E(\mathbf{5b}) + E_{BSSE}(\mathbf{5b}) + E(\mathbf{2a(2)}) - E_0,$$

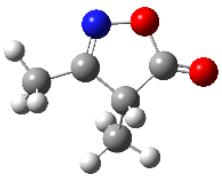
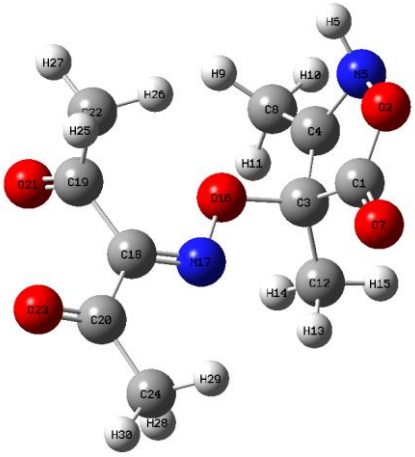
where E_0 was taken as the sum of energies of the most thermodynamically stable isoxazolone tautomer and two molecules of diacetyliminoxyl radical: $E_0 = E(\mathbf{4b''}) + 2E(\mathbf{2(2)})$ (ΔE(4b'') = 0).

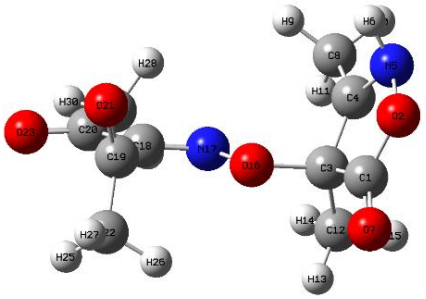
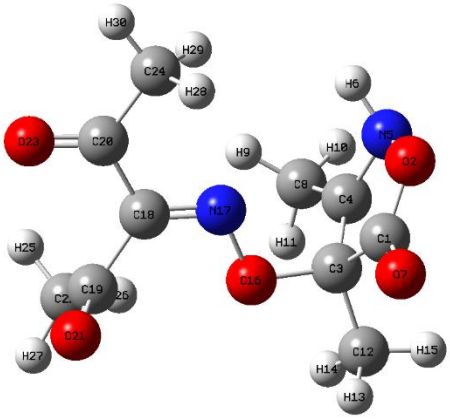
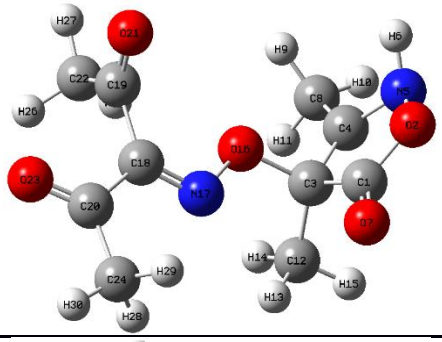
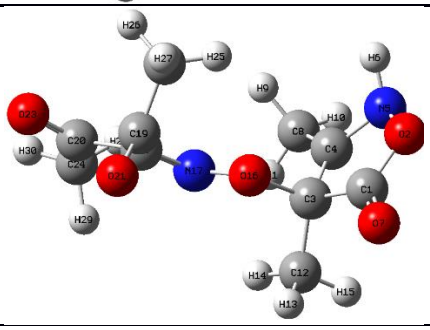
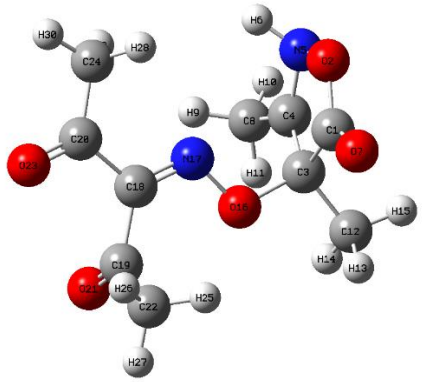
Table S6. Geometric properties (dihedral angles for diacetyliminoxyl fragment rotation θ(CCON) and acetyl rotation θ(NCCO)in degrees) and free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) and basis set superposition error energies (in kcal/mol) of reagents, intermediates and products for the reaction of isoxazolone **4b** with $ONCAc_2$ radical, relative to the most stable reagent tautomer **4b"**.

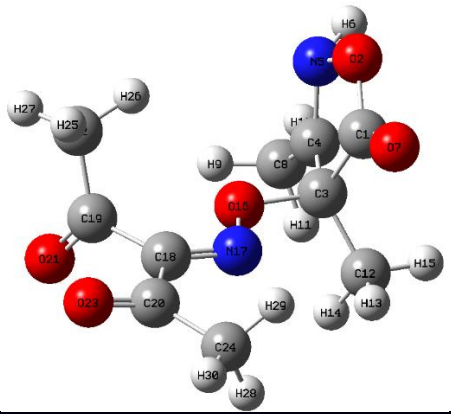
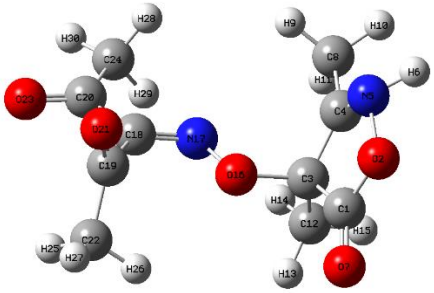
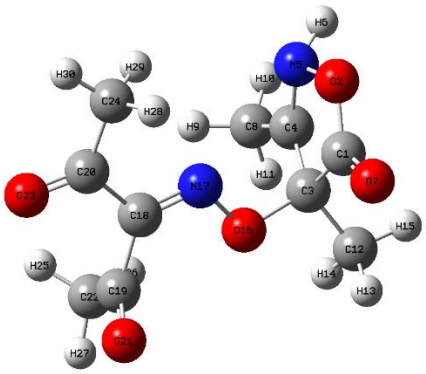
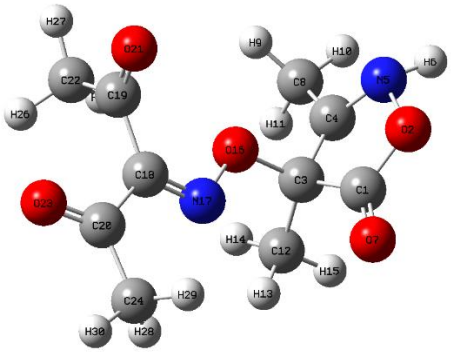
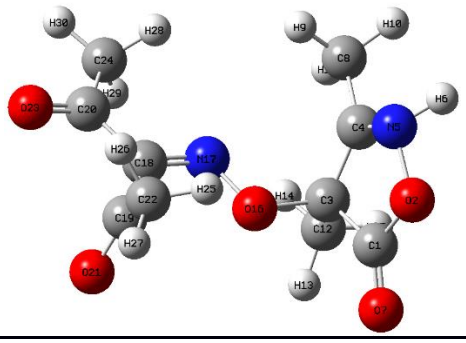
Given dihedral angles (columns 3,4) description on example of structure I(1):

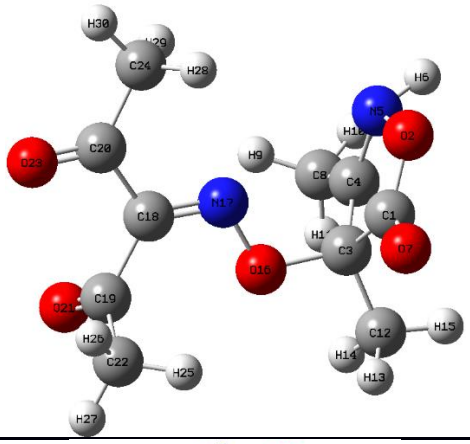
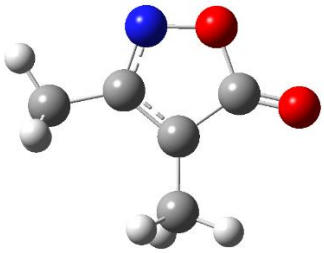
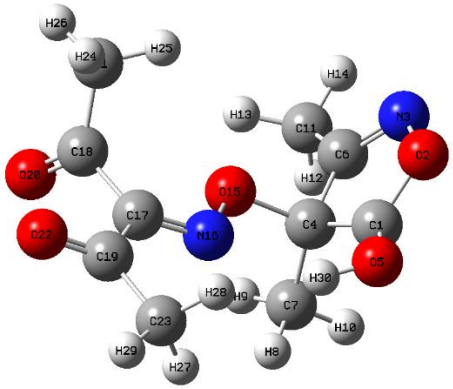
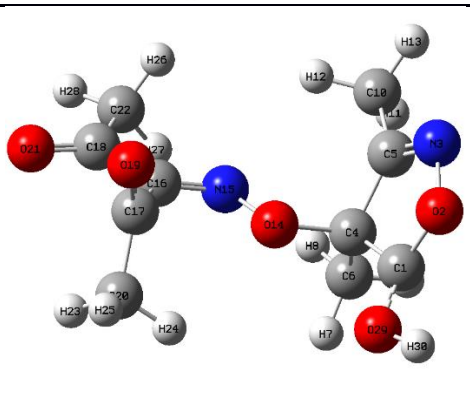
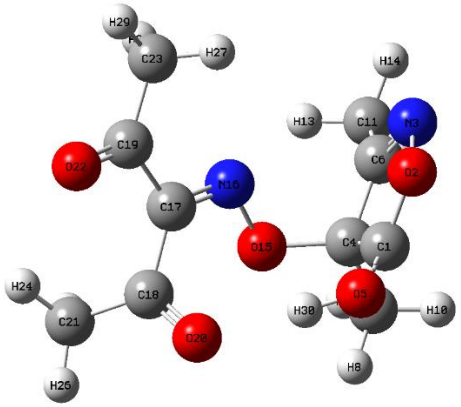
θ(CCON) = 

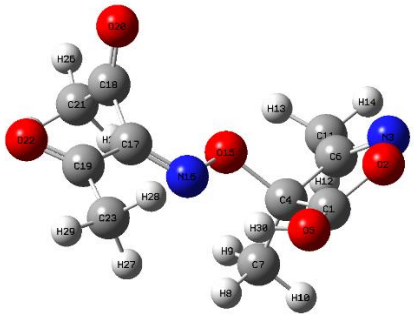
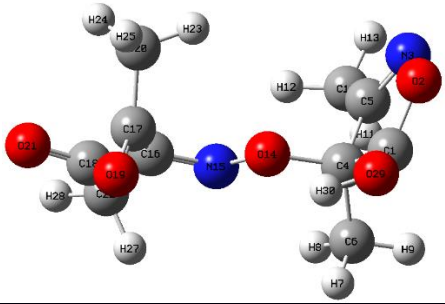
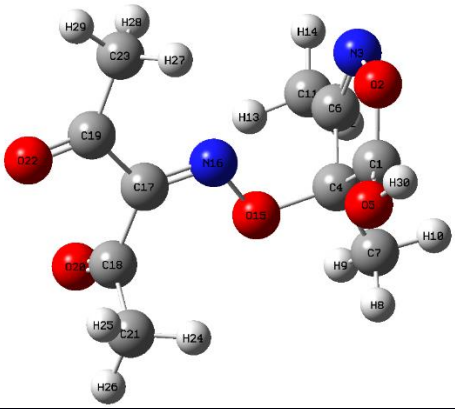
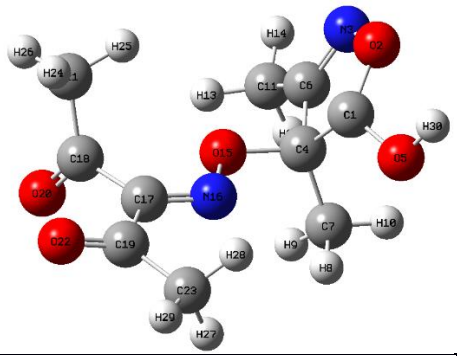
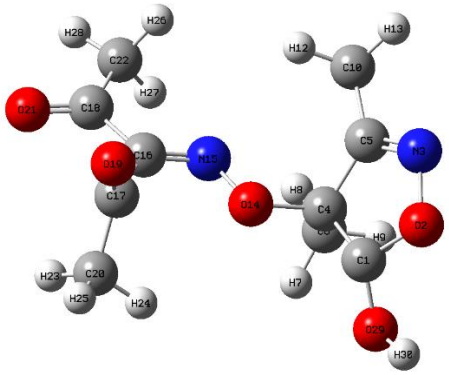
θ(NCCO) = 

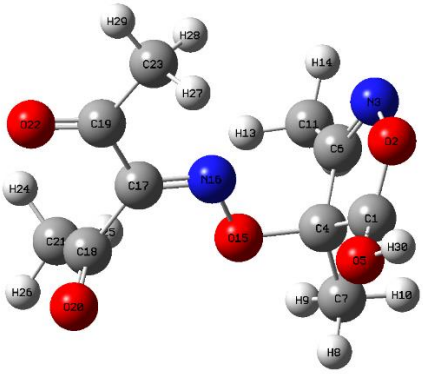
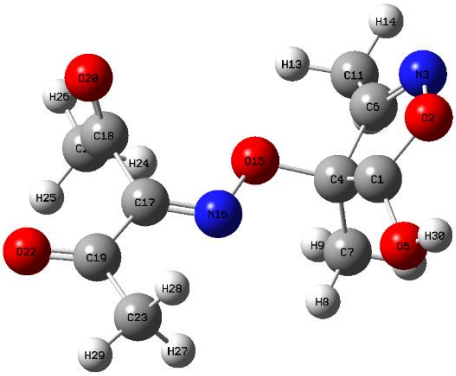
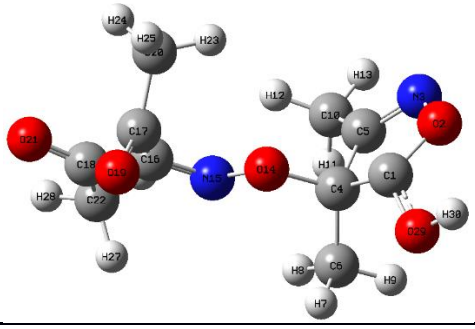
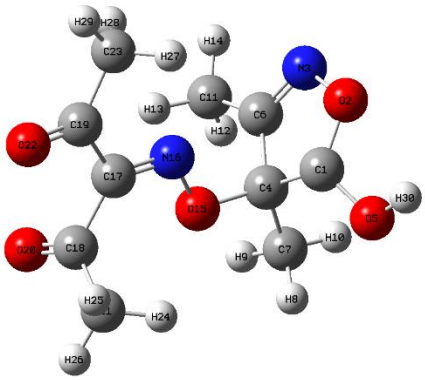
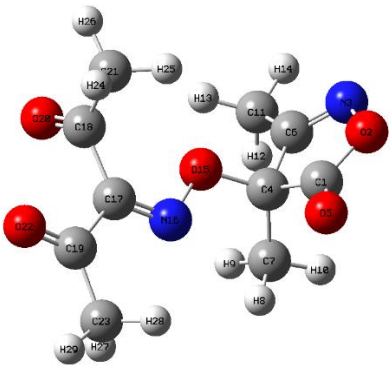
Structure		θ(CCON)	θ(NCCO)	ΔG	ΔH	Δ (E+ZPE)
4b"		-	-	0	0	0
I(1)		-75.38272	95.03099	33.5	22.28	21.92

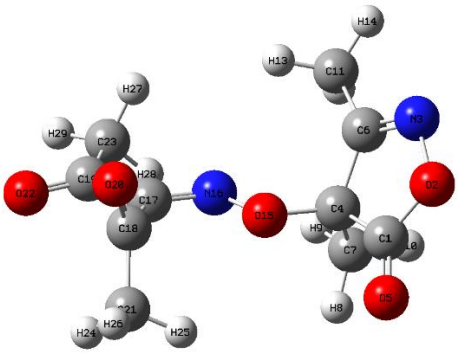
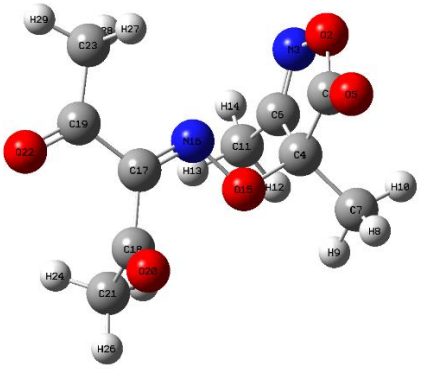
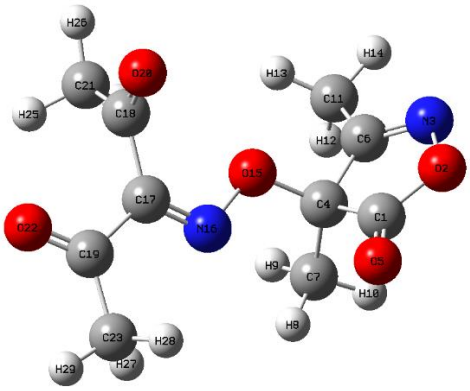
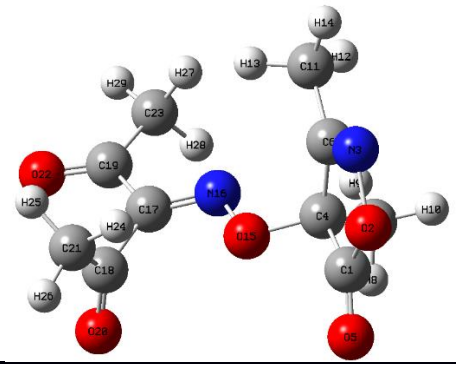
I(2)		173.32299	97.2112	33.45	21.77	21.47
I(3)		55.52578	99.66814	32.56	20.01	19.84
I(4)		-73.18093	-97.176	33.14	22.39	21.96
I(5)		171.37191	-98.1281	33.92	22.14	21.84
I(6)		58.2743	-96.2077	31.1	19.56	19.25

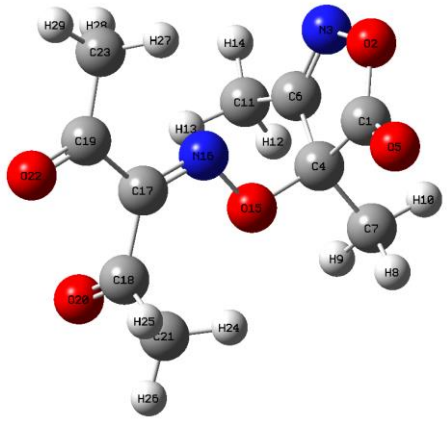
I(7)		-71.61408	96.92723	33.33	21.32	21.1
I(8)		170.11373	98.52094	32.83	21.02	20.77
I(9)		51.38043	99.21079	32.06	19.92	19.73
I(10)		-70.99017	-98.3817	33.42	21.72	21.47
I(11)		165.60897	-98.9664	32.89	21.01	20.8

I(12)		54.41451	-96.1304	31.48	19.6	19.36
II		-	-	0.92	1.85	1.43
III(1)		-55.19168	94.13073	44.31	31.81	31.59
III(2)		177.20903	99.74925	45.03	33.27	32.94
III(3)		61.07758	64.08972	45.47	33.71	33.38

III(4)		-56.49031	-99.3492	44.65	31.05	31.1
III(5)		-179.3218	-94.7411	45.61	33.74	33.36
III(6)		52.78969	-95.9972	42.4	30.74	30.37
III(7)		-61.32607	96.68368	43.49	32.03	31.63
III(8)		179.84421	98.47596	44.35	32.53	32.2

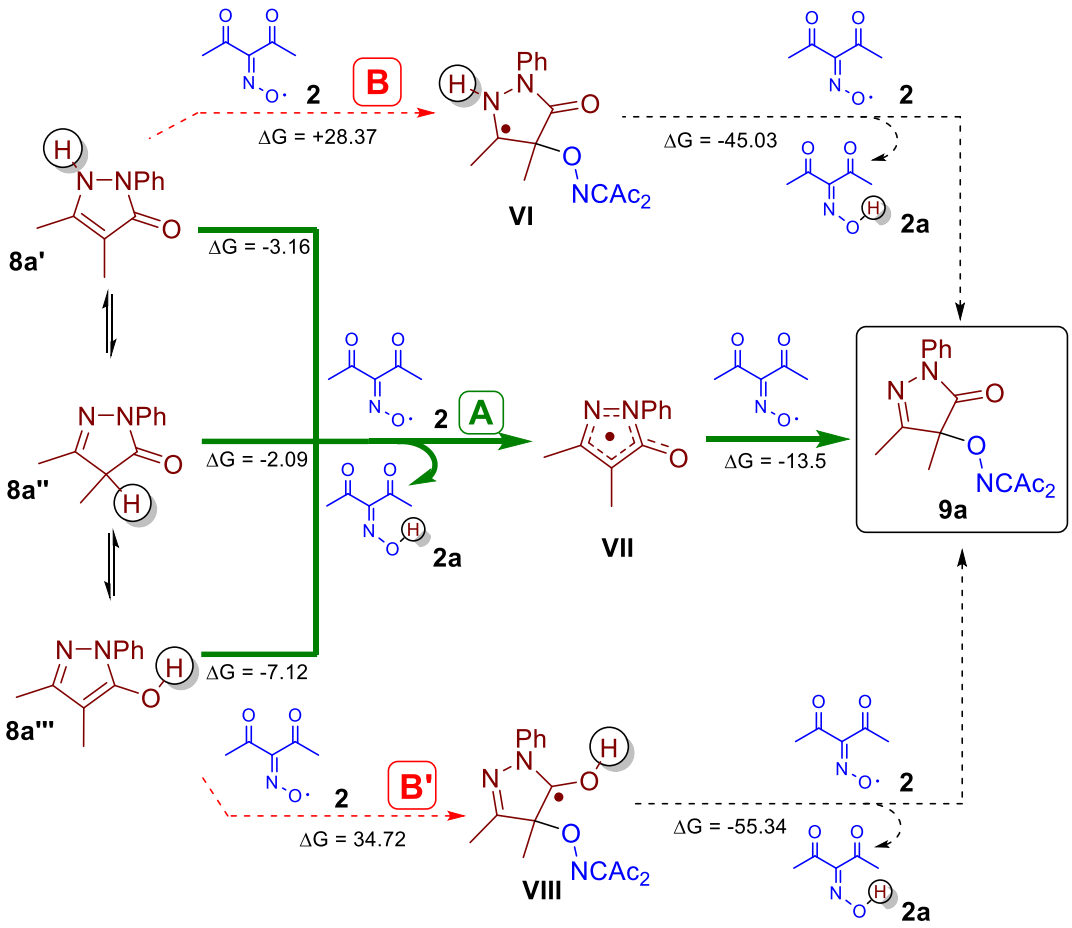
III(9)		52.24277	97.44508	43.2	30.96	30.63
III(10)		-60.80684	-98.535	44.51	32.38	32.08
III(11)		179.34997	-97.9259	44.2	32.48	32.13
III(12)		55.08777	-96.8725	42.23	30.59	30.19
5b(1)		-77.35382	94.34532	-11.52	-24.17	-24.41

5b(2)		-177.6352	97.6828	-11	-24.11	-24.31
5b(3)		53.97879	96.39042	-12.46	-26.19	-26.27
5b(4)		-76.22496	-94.9813	-10.77	-23.7	-23.92
5b(5)		-178.0827	-97.9009	-10.91	-23.92	-24.13

5b(6)		54.26897	-94.5691	-13.84	-26.7	-26.94

Oxidative C–O coupling of diacetyliminoxyl with pyrazolone 8a

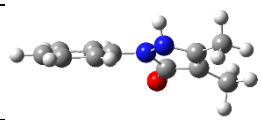
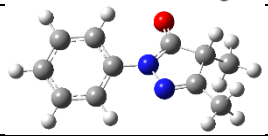
The summary of modeled plausible reaction pathways of the oxidative C–O coupling of diacetyliminoxyl **2** with pyrazolone **8a** are shown in Scheme S2. There are three possible tautomers of **8a** (**8a**', **8a''** and **8a'''**). For each tautomer hydrogen atom abstraction by radical **2** is possible (pathway A) followed by addition of the second radical molecule **2** to the resultant intermediate **VII**. For tautomers **8a'** and **8a'''** containing C=C bond the addition of radical **2** followed by hydrogen atom abstraction is possible (pathway B).

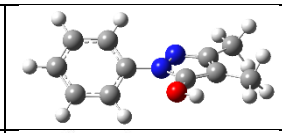
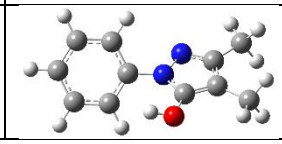


Scheme S2. Oxidative C–O coupling of diacetyliminoxyl **2** with pyrazolone **8a.** Free energies ΔG are given in kcal/mol.

The molecular geometries of three tautomers **8a'**, **8a''** and **8a'''** of the pyrazolone **8a** were optimized. Two conformations of the tautomer **8a'''** were found: **8a'''(1)** with the hydrogen of OH group oriented outwards phenyl and **8a'''(2)** with OH group oriented towards phenyl. Their relative energies are listed in the Table S7.

Table S7. Free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) (in kcal/mol) of 4,5-dimethyl-2-phenyl-4H-pyrazol-3-one tautomers and conformers, relative to tautomer **8a'**.

Conformer		ΔG	ΔH	Δ(E+ZPE)
8a'		1.07	1.48	1.28
8a''		0	0	0

8a'''(1) θ(HOCN) ~ -174°		5.03	5.79	5.4
8a'''(2) θ(HOCN) ~ -18°		5.72	6.4	6.01

The optimized geometries and corresponding thermodynamic values for conformers of intermediates **VI**, **VII**, **VIII** and final product **9a** are summarized in Table S8. The thermodynamic energies were calculated with the following formulae:

$$\Delta E(\mathbf{8a'}) = E(\mathbf{8a'}) + 2E(\mathbf{2}) - E_0;$$

$$\Delta E(\mathbf{8a'''}) = E(\mathbf{8a'''}) + 2E(\mathbf{2}) - E_0;$$

$$\Delta E(\mathbf{VI}) = E(\mathbf{VI}) + E_{BSSE}(\mathbf{VI}) + E(\mathbf{2}) - E_0;$$

$$\Delta E(\mathbf{VII}) = E(\mathbf{VII}) + E(\mathbf{2}) + E(\mathbf{2a}) - E_0;$$

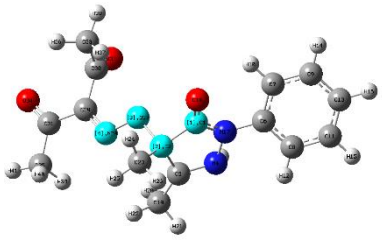
$$\Delta E(\mathbf{VIII}) = E(\mathbf{VIII}) + E_{BSSE}(\mathbf{VIII}) + E(\mathbf{2}) - E_0;$$

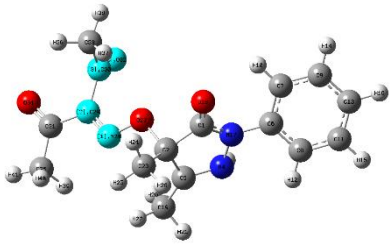
$$\Delta E(\mathbf{9a}) = E(\mathbf{9a}) + E_{BSSE}(\mathbf{9a}) + E(\mathbf{2a}) - E_0,$$

where E_{BSSE} is a basis set superposition error energy, calculated for structures assembled from two fragments, and E_0 was taken as the sum of energies of the most thermodynamically stable pyrazolone tautomer and two molecules of diacetyliminoxyl radical: $E_0 = E(\mathbf{8a''}) + 2E(\mathbf{2})$.

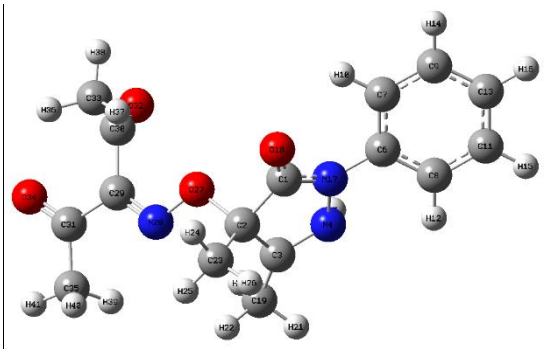
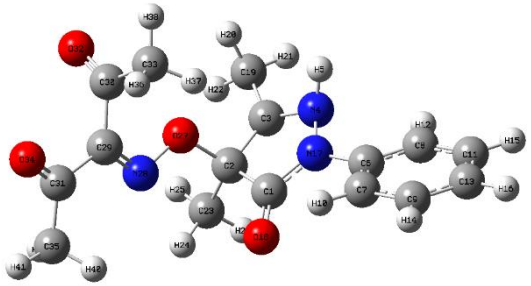
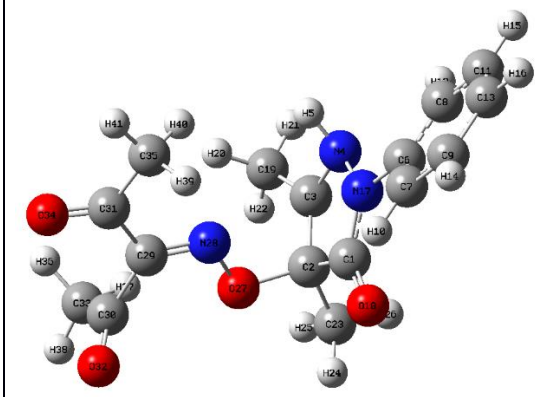
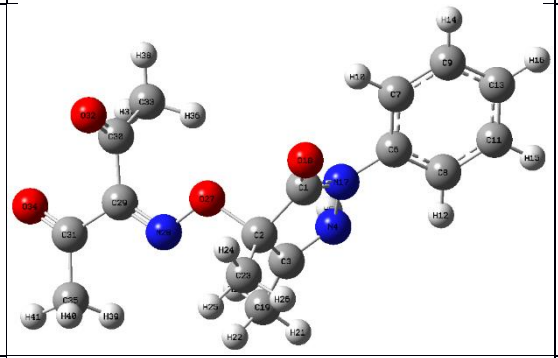
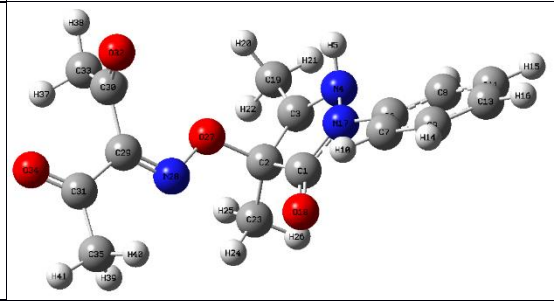
Table S8. Geometric properties (dihedral angles for diacetyliminoxyl fragment rotation θ(CCON) and acetyl rotation θ(NCCO)in degrees) and free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) (in kcal/mol) of intermediates and products for Scheme 1, relative to the most stable reagent tautomer **8a''**.

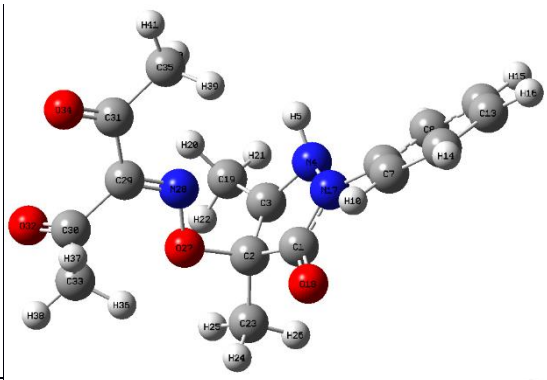
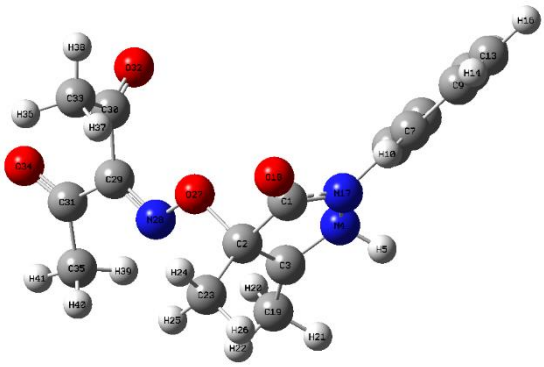
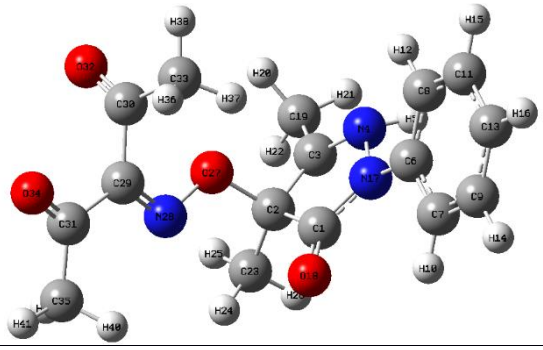
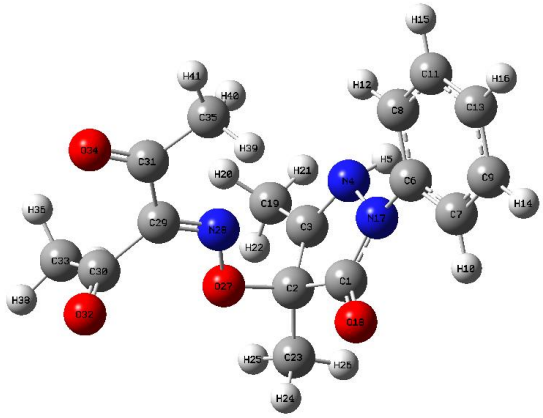
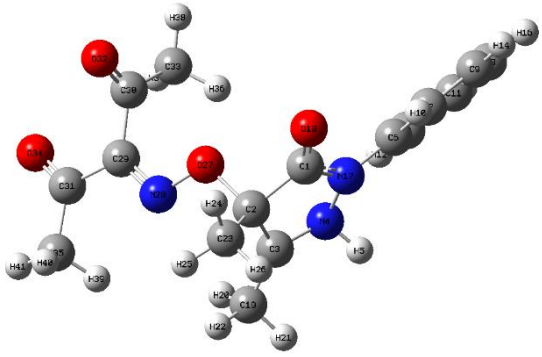
Given dihedral angles (columns 3,4) description on example of structure VI(1):

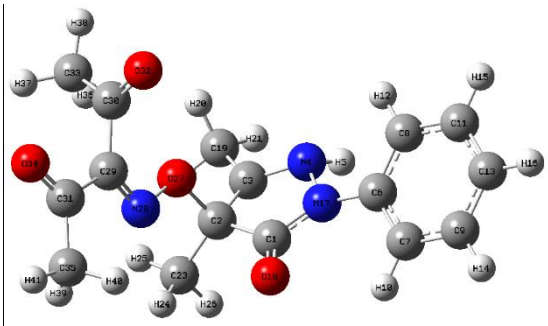
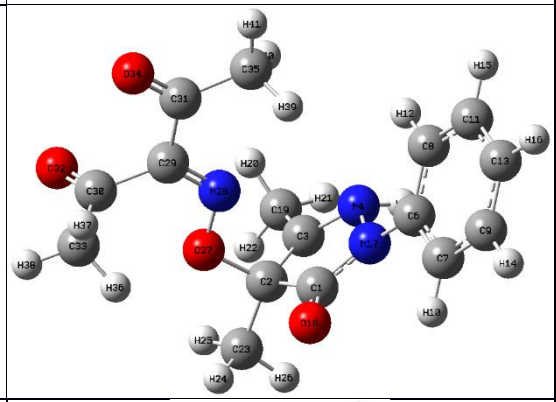
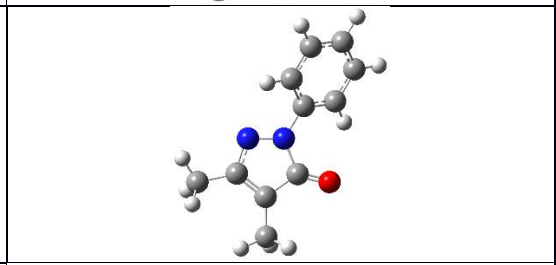
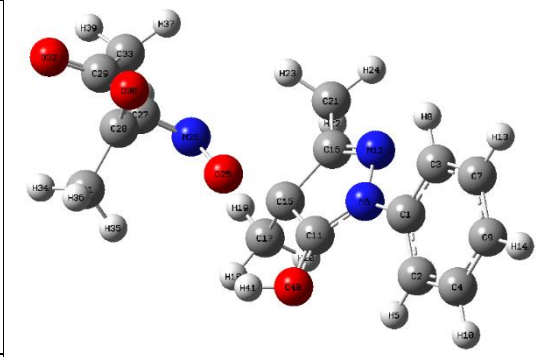
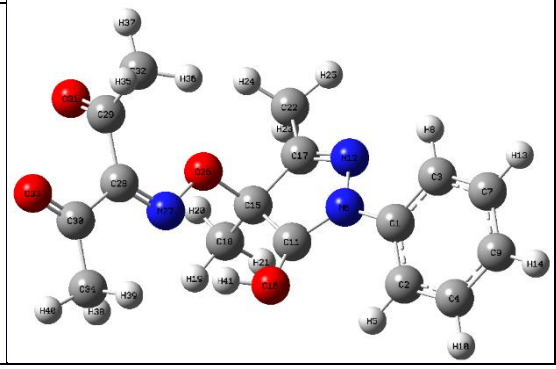
θ(CCON) = 

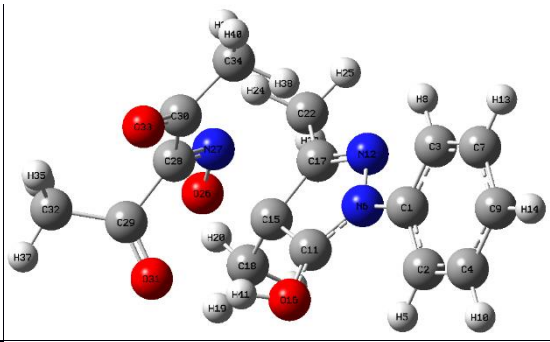
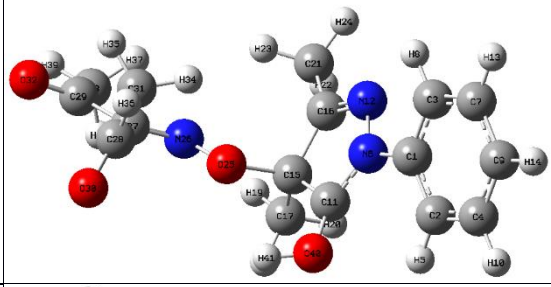
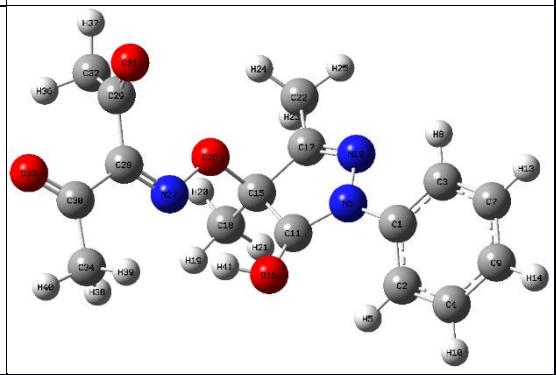
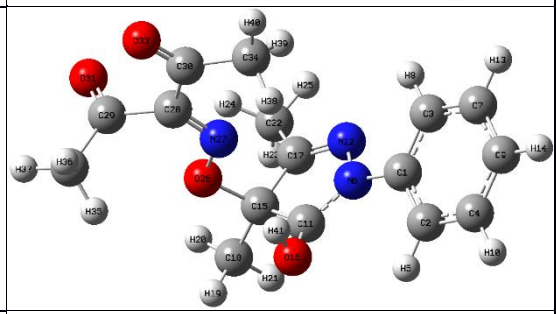
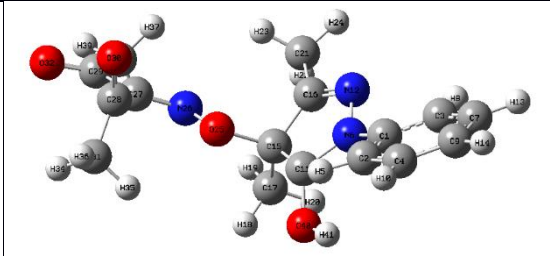
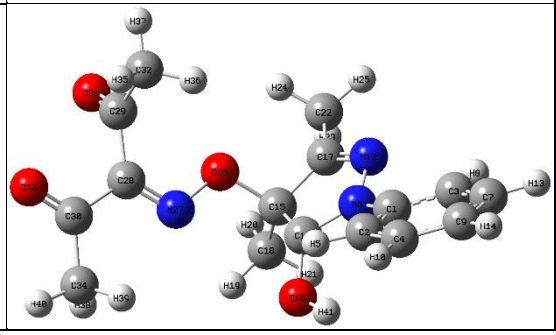
θ(NCCO) = 

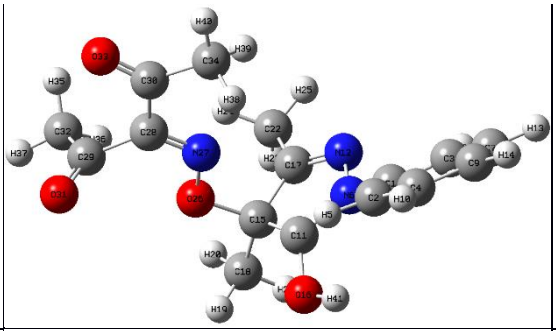
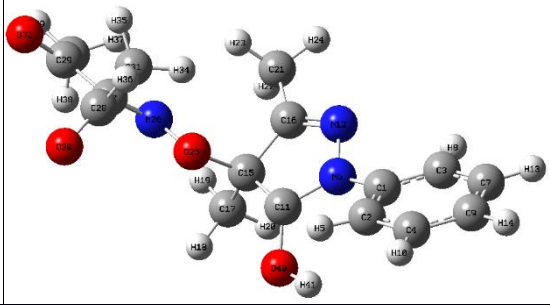
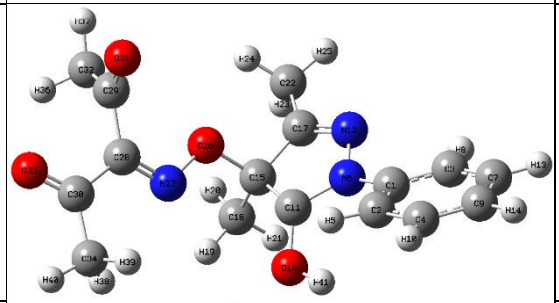
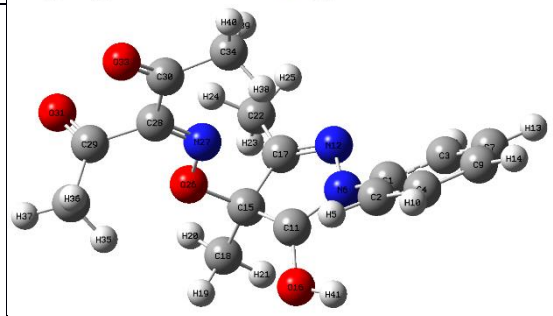
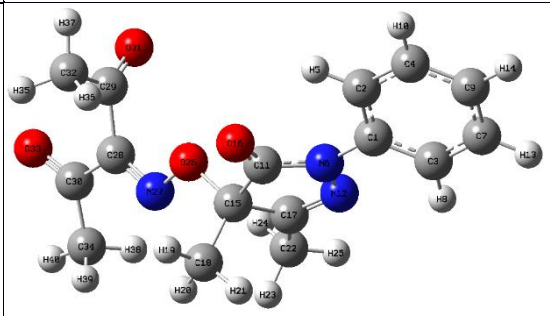
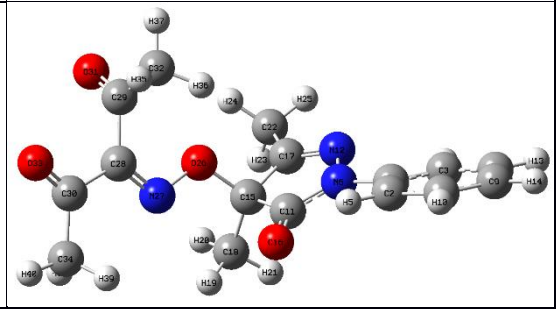
Structure	θ(CCON)	θ(NCCO)	Δ G	Δ H	Δ (E+ZPE)

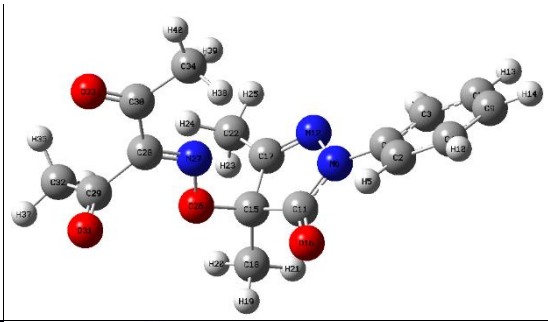
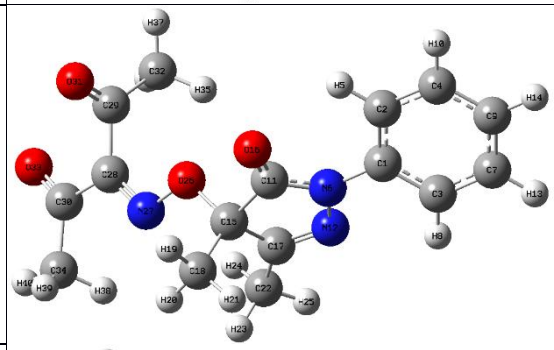
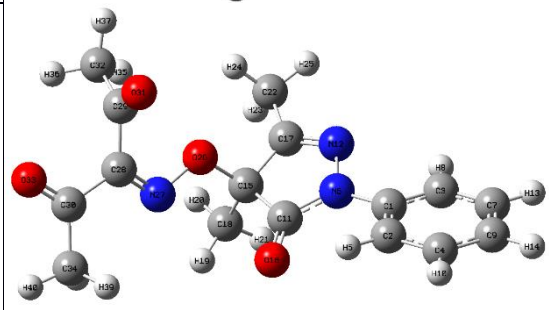
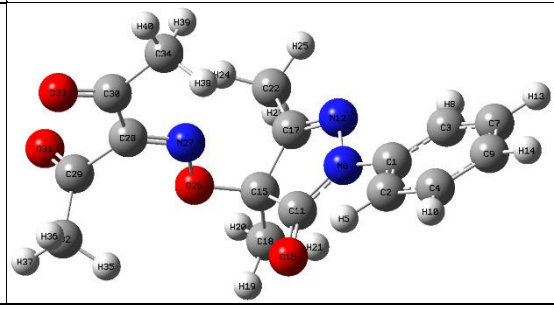
VI(1)		176.963	97.797	31.65	19.57	19.26
VI(2)		-74.672	98.114	32.00	20.06	19.74
VI(3)		56.116	100.018	30.57	17.69	17.50
VI(4)		173.307	-100.232	32.46	19.92	19.70
VI(5)		-72.930	-98.527	32.43	20.27	19.97

VI(6)		58.428	-97.420	29.70	17.28	17.03
VI(7)		170.158	99.611	31.87	19.69	19.40
VI(8)		-75.509	100.509	32.22	20.07	19.78
VI(9)		52.097	100.192	29.72	17.82	17.52
VI(10)		166.334	-101.428	32.20	19.74	19.52

VI(11)		-76.273	-98.975	32.63	20.68	20.37
VI(12)		53.614	-97.693	29.44	17.29	16.97
VII		-	-	-2.09	-0.48	-1.05
VIII(1)		175.906	98.827	42.38	30.88	30.18
VIII(2)		-57.544	94.235	42.73	29.80	29.60

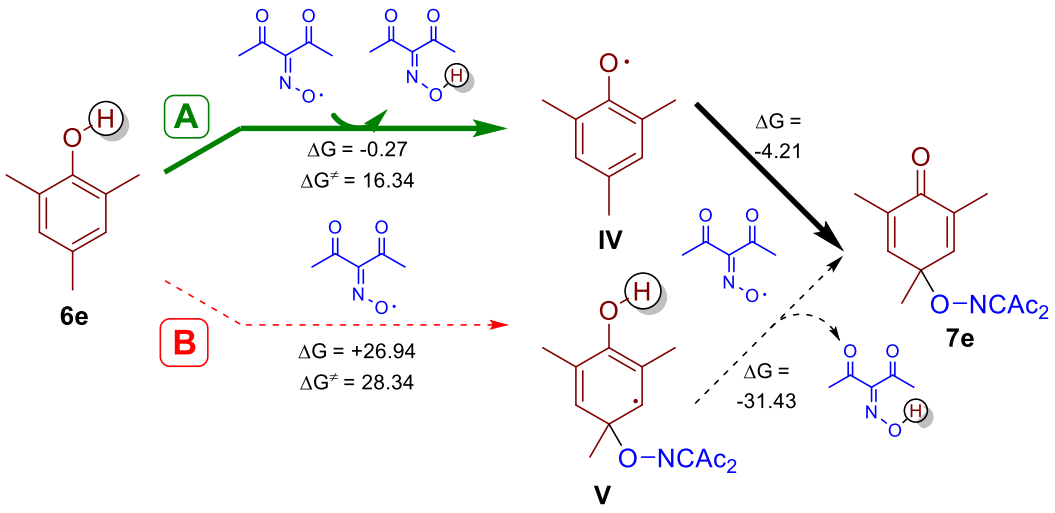
VIII(3)		55.485	67.034	41.69	27.98	27.85
VIII(4)		179.705	-96.139	42.21	30.52	29.97
VIII(5)		-59.672	-101.072	42.80	29.88	29.68
VIII(6)		42.245	-95.185	39.90	28.59	28.04
VIII(7)		-179.300	99.158	42.95	30.79	30.33
VIII(8)		-59.748	97.936	41.55	30.17	29.57

VIII(9)		51.904	97.954	40.10	28.43	27.88
VIII(10)		179.991	-98.562	42.41	30.66	30.18
VIII(11)		-61.303	-98.894	42.19	30.48	29.97
VIII(12)		50.988	-98.445	39.75	28.36	27.80
9a(1)		-175.453	97.515	-12.78	-25.91	-26.11
9a(2)		-77.351	96.771	-12.92	-25.98	-26.24

9a(3)		54.382	97.089	-14.92	-28.21	-28.45
9a(4)		-178.354	-98.020	-12.77	-25.83	-26.11
9a(5)		-76.314	-96.047	-12.26	-25.49	-25.73
9a(6)		56.313	-96.030	-15.59	-28.63	-28.87

Oxidative C–O coupling of diacetyliminoxyl with phenol 6e

Two reaction paths for the oxidative coupling of oxime radical **2** with 2,4,6-trimethilphenol **(6e)** were considered: (A) hydrogen atom abstraction by diacetyliminoxyl **2** from phenol **6e** followed by coupling of second molecule of **2** with the resultant phenoxyl radical **IV**, and (B) addition of **2** to **6e** followed by hydrogen atom abstraction from adduct **V** (Scheme S3). The results of calculations are summarized in the scheme. The reaction pathway “A” appears to be favorable, similarly to reactions of diacetyliminoxyl **2** with izoxazolone **4b** and pyrazolone **8a**.



Scheme S3. The favored (**A**) and the unfavoured (**B**) routes of the C–O coupling of phenol **6e** with diacetyliminoxyl **2**. Free energies ΔG and activation energies ΔG≠ are given in kcal/mol.

Conformations of the C–O coupling product **7e** and adduct intermediate **V** with different values of dihedral angles θ(CCON) and θ(NCCO) were found (Table S9). Among the conformers of the product **7e** and intermediate **V** the most stable were **7e(3)** and **V(3).** Thermodynamic energies for the C–O coupling were calculated by the following formula:

$$\Delta E(\mathbf{6e}) = E(\mathbf{6e}) + 2E(\mathbf{2}) - E_0;$$

$$\Delta E(\mathbf{IV}) = E(\mathbf{IV}) + E(\mathbf{2}) + E(\mathbf{2a}) - E_0;$$

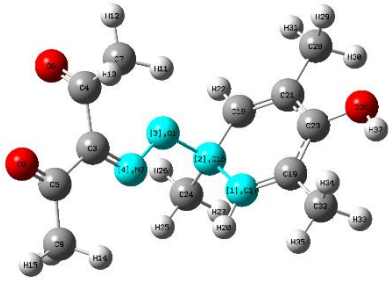
$$\Delta E(\mathbf{V}) = E(\mathbf{V}) + E_{BSSE}(\mathbf{V}) + E(\mathbf{2}) - E_0;$$

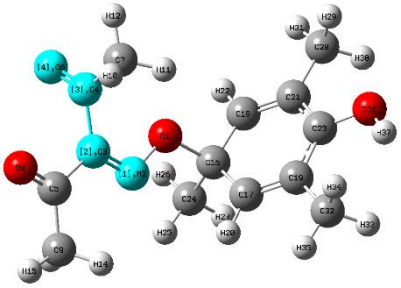
$$\Delta E(\mathbf{7e}) = E(\mathbf{7e}) + E_{BSSE}(\mathbf{7e}) + E(\mathbf{2a}) - E_0,$$

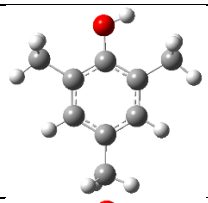
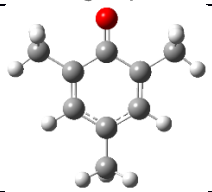
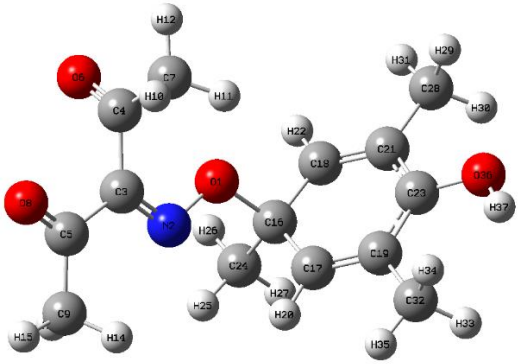
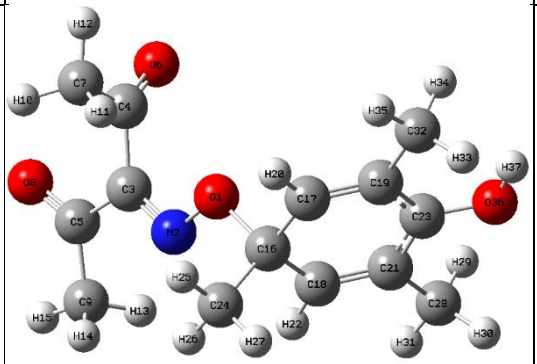
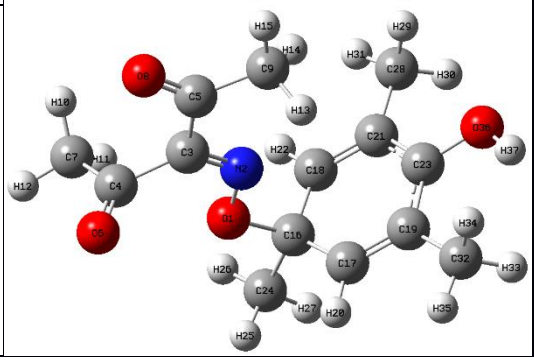
(where E_0 was taken as energy of reagents E(**6e**) + 2E(**2**)) and are listed in the Table S9.

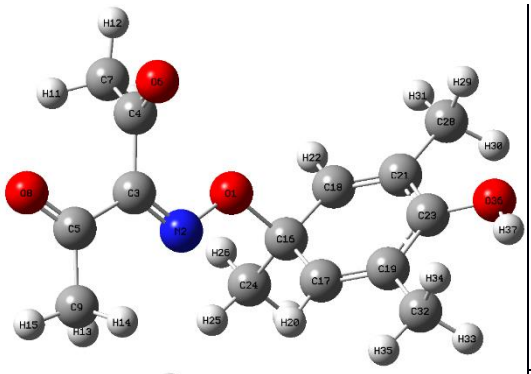
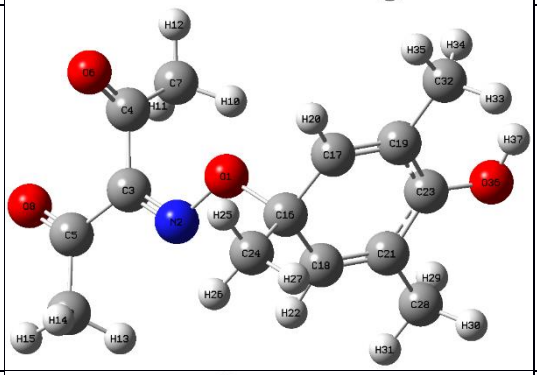
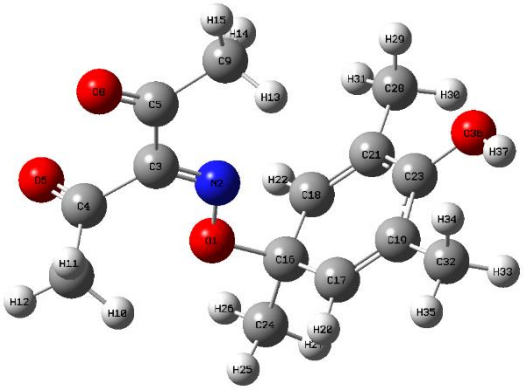
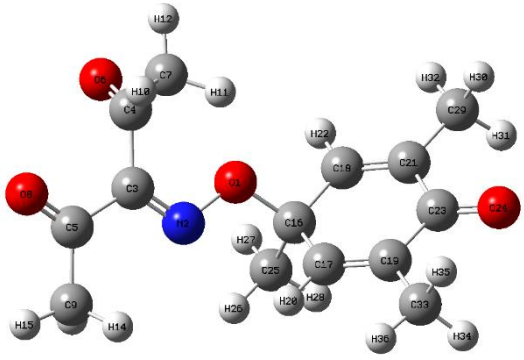
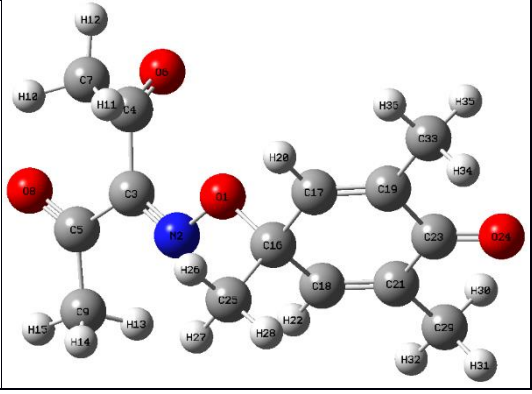
Table S9. Geometric properties (dihedral angles for diacetyliminoxyl fragment rotation θ(CCON) and acetyl rotation θ(NCCO)in degrees) and free energies ΔG, enthalpies ΔH and energies with ZPE correction Δ(E+ZPE) and basis set superposition error energies (in kcal/mol) of reagents, intermediates and products for C-O coupling reaction with phenol, relative to the reagent **6e**.

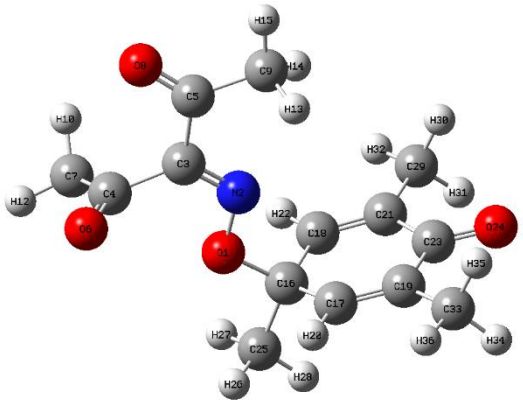
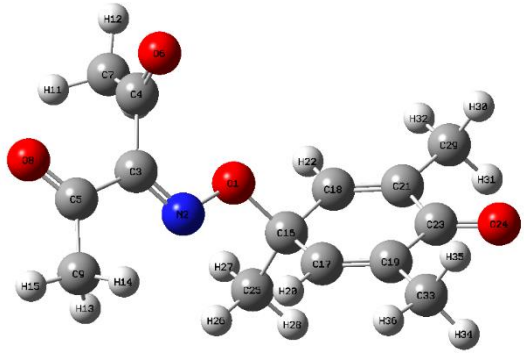
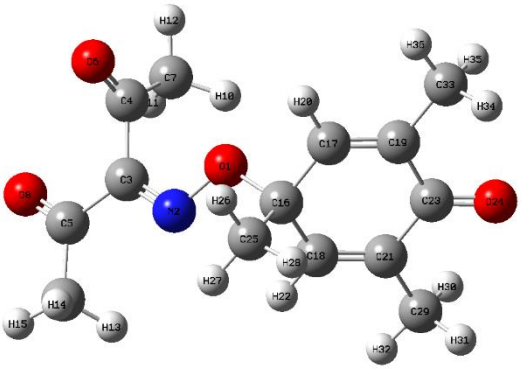
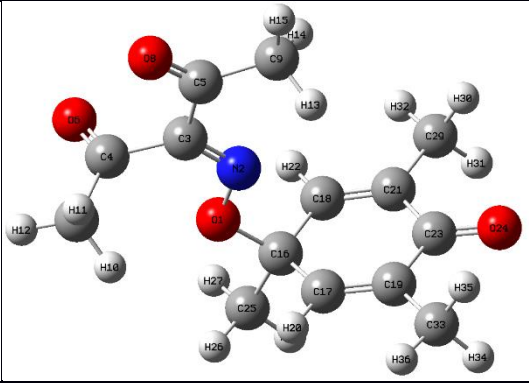
Given dihedral angles (columns 3,4) description on example of structure VI(1):

θ(CCON) = 

θ(NCCO) = 

Structure		θ(CCON)	θ(NCCO)	Δ G	Δ H	Δ (E+ZPE)
6e		-	-	0.00	0.00	0.00
IV				-0.27	2.13	1.31
V(1)		-59.49982	99.61425	28.54	17.15	16.68
V(2)		-179.12254	98.2266	28.79	17.37	16.90
V(3)		61.89346	98.00732	26.94	15.71	15.19

V(4)		-61.66826	-98.31928	28.83	17.34	16.87
V(5)		179.37862	-99.12728	28.74	17.14	16.71
V(6)		61.16159	-97.98305	27.16	15.80	15.32
7e(1)		-62.09355	96.59962	-3.57	-15.59	-16.13
7e(2)		-176.59265	96.70929	-2.89	-15.35	-15.81

7e(3)		62.36712	96.50213	-4.49	-16.86	-17.32
7e(4)		-61.92123	-96.70841	-2.89	-15.35	-15.81
7e(5)		-176.50595	-96.59759	-3.57	-15.59	-16.13
7e(6)		62.73922	-96.50324	-4.49	-16.86	-17.32

Transition states of the C–O coupling between isoxazolone 4b, phenol 6e and diacetyliminoxyl radical 2

For isoxazolone **4b** and phenol **6e** energies of transition states of the limiting stages of reactions with diacetyliminoxyl **2** were calculated. The studies of transition states for pyrazolone **8a** were omitted due to its resemblance to isoxazolone **4b**. Only the most stable conformers of the reagents, products and intermediates obtained previously were used for the transition state

search. The transition states for the following the first step reactions were found and characterized (Figure S4). The corresponding pre- and post-reaction complexes were found. The activation energies for the listed reactions are provided in Table S10. ΔG_a Gibbs free energy values were calculated as G value of the corresponding TS minus G value of the corresponding pre-reaction complex. Values ΔG_a^{-1} were calculated as G value of the corresponding TS minus G value of the corresponding post-reaction complex (or monomolecular intermediate product). ΔH_a and ΔH_a^{-1} were calculated analogously using enthalpy values of TS, pre- and post-reaction complexes (or monomolecular intermediate products). $\mathbf{\Delta G^{\neq}}$ Gibbs free activation energy values were calculated as G value of the corresponding TS minus G values of the individual reagents in the most stable conformations.

Table S10. Activation free energies ΔG_a and enthalpies ΔH_a of pre-reaction complexes of forward and reverse (ΔG_a^{-1} and ΔH_a^{-1}) critical steps of reactions 1-7 and summary energy barrier $\Delta G^{\neq}$ of forward reactions in kcal/mol.

Reaction	ΔG_a	ΔH_a	ΔG_a^{-1}	ΔH_a^{-1}	$\Delta G^{\neq}$
(1) **[4b'** + **2]** to **I** *via* **TS1**	21.81	19.47	4.07	3.39	32.13
(2) **[4b'** + **2]** to **[II** + **2a]** *via* **TS2**	12.45	14.84	21.45	20	24.43
(3) **[4b''** + **2]** to **[II**+**2a]** *via* **TS3**	27.98	26.49	26.32	23.92	33.4
(4) **[4b'''** + **2]** to **[II**+**2a]** *via* **TS4**	12.2	11.41	19.87	17.76	20.3
(5) **[4b'''** + **2]** to **III** *via* **TS5**	27.91	27.62	0.52	0.24	34.67
(6) **[6e** + **2]** to **[IV+2a]** *via* **TS6**	9.47	8.49	14.33	12.39	16.34
(7) **[6e** + **2]** to **V** *via* **TS7**	20.15	18.98	3.63	2.55	28.34

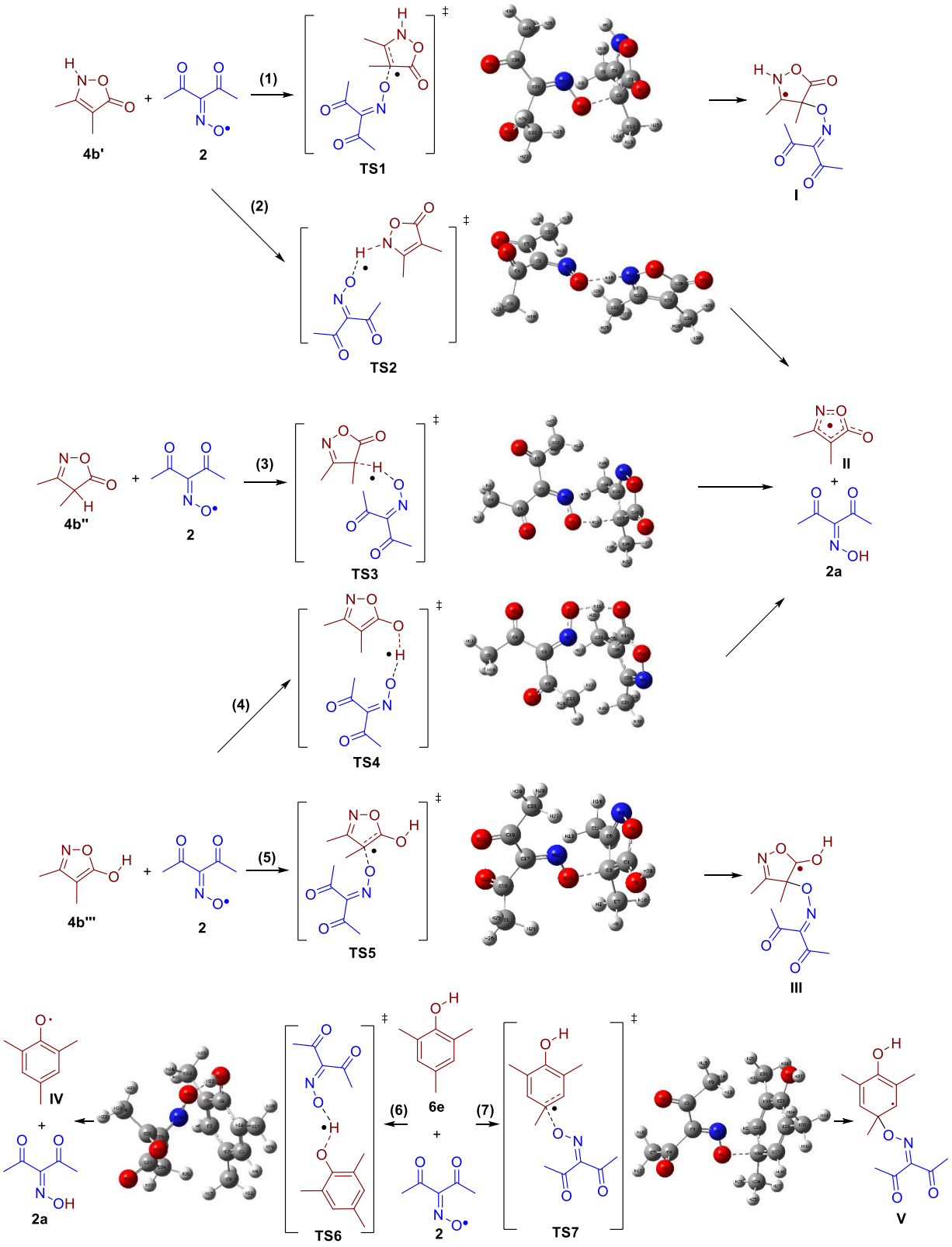


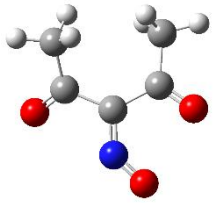
Figure S4. Optimized geometries of the activated complexes for first step reactions of isoxazolone **4b** (TS1-TS5) and phenol **6e** (TS6,TS7) with diacetyliminoxyl **2**

Cartesian coordinates and energies for calculated structures

All energy values are given for 298.15 K and 1 atm. in atomic units (hartree), unless otherwise stated. Two numbers given before lists of atomic coordinates for each structure correspond to the charge and multiplicity, respectively.

Conformation analysis of diacetyliminoxyl radical and diacetyl oxime

Diacetyliminoxyl radical, conformer 2(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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 Sum of electronic and thermal Enthalpies= -474.333125
 Sum of electronic and thermal Free Energies= -474.380963
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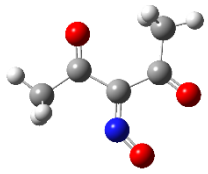
N	0.61147700	-1.48299100	0.05182300
C	0.05754800	-0.30970700	-0.00062300
C	0.98630100	0.87444800	-0.02770300
C	-1.44679400	-0.35856600	-0.04247400
O	2.17031800	0.69163900	0.14401900
O	-1.99153900	-1.35878500	-0.45393400
C	-2.23628600	0.80820900	0.48308800
H	-1.79210300	1.21751200	1.39224700
H	-2.27625800	1.60408900	-0.26447500
H	-3.25269700	0.47305300	0.68265800
C	0.43213300	2.24011000	-0.32904100
H	-0.22973400	2.21347400	-1.19669600
H	-0.13841400	2.61480100	0.52328100
H	1.26521100	2.91358300	-0.52061600

Diacetyliminoxyl radical, conformer 2(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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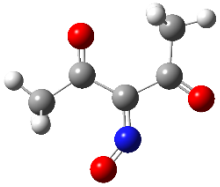
C	-0.04224400	0.21852500	0.00004000
C	1.29524100	-0.48032200	0.00009800
C	-1.39305900	-0.41716800	0.00002000
O	2.29794800	0.19762800	-0.00008200
O	-1.50527800	-1.62399300	0.00001400
C	1.33648000	-1.97988100	-0.00001300
H	0.81420300	-2.37052700	0.87506900
H	0.81410700	-2.37040600	-0.87509300
H	2.37769400	-2.29782900	-0.00009300
C	-2.58829900	0.49987300	-0.00004700
H	-2.57457500	1.14562600	0.88118100
H	-2.57450500	1.14557900	-0.88130700
H	-3.49327200	-0.10466900	-0.00006700

Diacetyliminoxyl radical, conformer 2(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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N	-0.50156700	-1.44496600	-0.00013500
C	0.00795400	-0.25332100	-0.00015800
C	-0.87628100	0.96729600	-0.00045900
C	1.51979500	-0.26440200	0.00019300
O	-0.36871200	2.06578600	-0.00112500
O	2.08872600	-1.33460100	-0.00015600
C	2.27071300	1.03199400	0.00066000
H	2.00253500	1.62707000	-0.87444900
H	2.00127000	1.62726200	0.87524800
H	3.33735400	0.81300900	0.00142400
C	-2.36688400	0.77399300	0.00096800
H	-2.68643600	0.21050900	-0.87951600
H	-2.68480400	0.21043000	0.88199400
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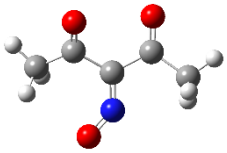
Diacetyliminoxyl radical, conformer 2(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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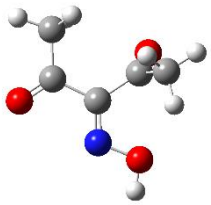
N	-0.07774300	1.44502800	-0.03735800
C	0.06021100	0.16476500	-0.01086700
C	-1.14198700	-0.75268900	-0.12163700
C	1.46277000	-0.35364400	0.13031500
O	-1.00701600	-1.82558400	-0.65374200
O	1.65012500	-1.49887800	0.46704700
C	-2.45164900	-0.25693800	0.42249700
H	-2.32213700	0.23001900	1.39136600
H	-2.87844500	0.48088300	-0.26333000
H	-3.13744500	-1.09813700	0.50739500
C	2.58229300	0.61223100	-0.14835300
H	2.55188500	0.91882800	-1.19736000
H	2.47753500	1.51395400	0.45951400
H	3.53307100	0.12872800	0.06761400

Diacetyl oxime, conformer 2a(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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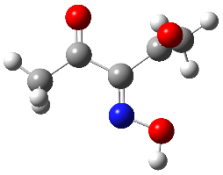
C	-0.86775700	-0.84008400	-0.14541500
C	1.54503900	0.20969100	0.08642900
O	-0.86278400	-1.47938700	-1.17087800
O	2.25750100	1.17369500	0.23135000
O	-1.75114400	1.63515700	-0.21031400

H	-1.94738500	2.57659900	-0.23181100
C	2.07405400	-1.19397100	0.02023600
H	1.59922200	-1.81810100	0.78352700
H	1.83436000	-1.63592400	-0.95042000
H	3.15155700	-1.18535500	0.17114500
C	-1.69159200	-1.18217200	1.05708400
H	-1.02323700	-1.44240800	1.88460900
H	-2.27014200	-0.31010600	1.36950300
H	-2.35030300	-2.02102000	0.83669300

Diacetyl oxime, conformer 2a(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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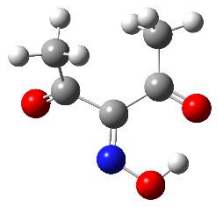
C	-1.13379800	-0.61132300	0.20471900
C	1.43552200	-0.42018300	-0.03527100
O	-1.45727100	-0.96508400	1.31176500
O	1.45245800	-1.63194200	-0.08076600
O	-1.19849800	2.03082100	0.01671900
H	-1.09020400	2.98355400	-0.06047700
C	-1.85548300	-0.97711800	-1.05324200
H	-2.74271200	-1.56650700	-0.82616200
H	-2.12912800	-0.06648100	-1.59336500
H	-1.17878400	-1.54859200	-1.69594600
C	2.67379800	0.42560600	-0.05468400
H	2.63944600	1.12808900	-0.88998200
H	2.73256800	1.01730600	0.86190500
H	3.54681100	-0.21898800	-0.14005100

Diacetyl oxime, conformer 2a(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

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 Sum of electronic and thermal Free Energies=         -474.998745
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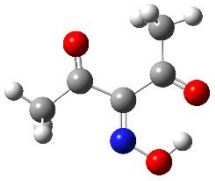
 N                  0.63914000   -1.51103400    0.11100300
 C                  0.08749100   -0.34873400   -0.00782300
 C                  0.83722100    0.93861600   -0.08544800
 C                 -1.42599400   -0.43030100   -0.08905400
 O                  2.05552400    0.92604300    0.04199700
 O                 -1.94357500   -1.19626300   -0.86585600
 O                  1.96416800   -1.60415100    0.22819900
 H                  2.34840200   -0.69432200    0.20233500
 C                 -2.23737500    0.42221400    0.85282000
 H                 -1.67121700    0.72649800    1.73400800
 H                 -2.57843300    1.31949600    0.32890700
 H                 -3.12072900   -0.14142200    1.15354900
 C                  0.10233900    2.21252100   -0.36460000
 H                 -0.64668000    2.07560700   -1.14740700
 H                 -0.41370700    2.54240300    0.54143700
 H                  0.81735500    2.97804100   -0.65994000
```

Diacetyl oxime, conformer 2a(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

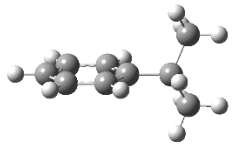


```
Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=              -474.962122
 Sum of electronic and thermal Enthalpies=            -474.961178
 Sum of electronic and thermal Free Energies=         -475.007086
0 1
 N                 -0.02013400   -1.54540500   -0.01658500
 C                  0.04099000   -0.24979500   -0.01354100
 C                 -1.16835900    0.63391700    0.01930900
 C                  1.44984900    0.27997000   -0.05371200
 O                 -2.27195600    0.10090300   -0.05664600
 O                  1.65499100    1.45275400   -0.28199500
 O                 -1.19313200   -2.16064200   -0.03744900
 H                 -1.90552600   -1.46970200   -0.06683000
 C                 -1.05584000    2.11455500    0.17768000
 H                 -0.60289300    2.54741300   -0.71625700
 H                 -2.05364700    2.52212500    0.33245900
 H                 -0.39943600    2.36655200    1.01209600
 C                  2.57395500   -0.69253400    0.17959200
 H                  2.45478800   -1.19255800    1.14286400
 H                  2.56919200   -1.46961300   -0.58704900
```

H	3.51567300	-0.14718000	0.15155400

Calculations for Scheme 2. Calculation of BDE values for hydrocarbons – CH-substrates for oxidative C-O coupling with diacetyliminoxyl

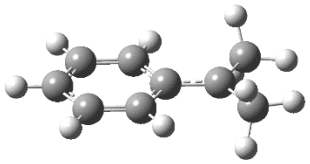
Cumene **1a** (CBS-QB3, gas phase)



Number of imaginary frequencies = 0
CBS-QB3 Energy= -349.465476
CBS-QB3 Enthalpy= -349.464532
CBS-QB3 Free Energy= -349.507965
0 1

C	0.13679800	-0.19453000	0.00003000
C	-2.65027100	0.21466000	0.00001300
C	-0.75045700	-1.27486300	0.00000800
C	-0.40189300	1.09886600	-0.00001400
C	-1.77882100	1.30304300	-0.00002500
C	-2.13058600	-1.07658300	0.00001300
H	-0.35496500	-2.28596600	-0.00001000
H	0.25976200	1.95876300	-0.00003700
H	-2.17311900	2.31350000	-0.00004800
H	-2.79769500	-1.93176900	0.00003000
H	-3.72282800	0.37325700	-0.00000100
C	1.64142100	-0.42726500	0.00000600
H	1.79399600	-1.51276700	0.00003300
C	2.30901300	0.13141700	-1.26946100
H	2.20874600	1.21947500	-1.32539800
H	1.85851800	-0.29130500	-2.17090500
H	3.37738800	-0.10443900	-1.27912500
C	2.30903700	0.13147100	1.26944600
H	2.20940400	1.21961500	1.32500400
H	3.37727200	-0.10499600	1.27942400
H	1.85808000	-0.29066500	2.17093200

Cumene radical (CBS-QB3, gas phase)

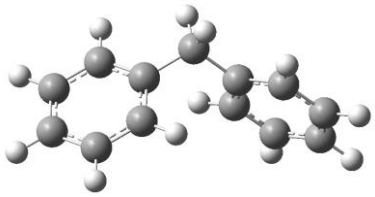


Number of imaginary frequencies = 0
CBS-QB3 Energy= -348.827891
CBS-QB3 Enthalpy= -348.826947
CBS-QB3 Free Energy= -348.871686

0 2

C	0.00000000	0.00000000	-0.18638500
C	0.00000000	0.00000000	2.65653400
C	-0.00020400	1.21054500	0.56301800
C	0.00020400	-1.21054500	0.56301800
C	0.00000000	-1.20462400	1.94824500
C	0.00000000	1.20462400	1.94824500
H	0.00055500	2.16059100	0.04387700
H	-0.00055500	-2.16059100	0.04387700
H	-0.00032300	-2.14681800	2.48589300
H	0.00032300	2.14681800	2.48589300
H	0.00000000	0.00000000	3.74030300
C	0.00000000	0.00000000	-1.61382000
C	0.00947900	-1.29282500	-2.38035400
H	-0.87650200	-1.90516800	-2.16610100
H	0.88018800	-1.91313700	-2.13181400
H	0.03072700	-1.11480700	-3.45644800
C	-0.00947900	1.29282500	-2.38035400
H	-0.88018800	1.91313700	-2.13181400
H	-0.03072700	1.11480700	-3.45644800
H	0.87650200	1.90516800	-2.16610100

Diphenylmethane **1b** (CBS-QB3, gas phase)

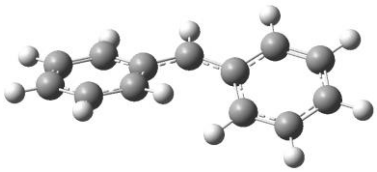


Number of imaginary frequencies = 0
CBS-QB3 Energy= -501.626667
CBS-QB3 Enthalpy= -501.625723
CBS-QB3 Free Energy= -501.675803
0 1

H	0.73057500	1.84871800	-0.42990400
C	1.49516800	1.09147300	-0.29088100
C	3.45278300	-0.85559200	0.03737600
C	1.27791900	0.05440400	0.62451100
C	2.67288200	1.15682600	-1.02809300
C	3.65765200	0.18204000	-0.86668700
C	2.27114200	-0.91609000	0.77621500
H	2.82361400	1.96874600	-1.73116200
H	4.57488600	0.23225900	-1.44256100
H	2.12058300	-1.72686300	1.48216300
H	4.21074700	-1.61983600	0.17004000
C	0.00000000	0.00000000	1.44457100
H	-0.04252800	0.87407400	2.10307300
H	0.04252800	-0.87407500	2.10307300
C	-1.27792000	-0.05440400	0.62451100
C	-3.65765200	-0.18204000	-0.86668800

C	-2.27114200	0.91609000	0.77621400
C	-1.49516900	-1.09147400	-0.29088100
C	-2.67288200	-1.15682600	-1.02809300
C	-3.45278300	0.85559200	0.03737500
H	-2.12058300	1.72686400	1.48216200
H	-0.73057500	-1.84871900	-0.42990300
H	-2.82361400	-1.96874600	-1.73116200
H	-4.21074600	1.61983700	0.17003800
H	-4.57488600	-0.23225900	-1.44256200

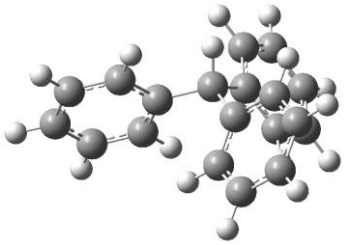
Diphenylmethane radical (CBS-QB3, gas phase)



Number of imaginary frequencies = 0
CBS-QB3 Energy= -500.993336
CBS-QB3 Enthalpy= -500.992392
CBS-QB3 Free Energy= -501.040062
0 2

H	-0.70219700	0.76715300	-1.54401800
C	-0.36387800	1.57297200	-0.90726100
C	0.35271800	3.70570300	0.74194200
C	0.00000000	1.30203000	0.43656700
C	-0.35214700	2.86781800	-1.40527100
C	0.01538700	3.94250200	-0.59325500
C	0.33642600	2.41686500	1.24838200
H	-0.64566100	3.04494800	-2.43426800
H	0.02478700	4.95088400	-0.99035900
H	0.59976300	2.24360900	2.28660400
H	0.62605100	4.53333400	1.38720600
C	0.00000000	0.00000000	1.03566000
H	0.00000000	0.00000000	2.12246100
C	0.00000000	-1.30203000	0.43656700
C	-0.01538700	-3.94250200	-0.59325500
C	-0.33642600	-2.41686500	1.24838200
C	0.36387800	-1.57297200	-0.90726100
C	0.35214700	-2.86781800	-1.40527100
C	-0.35271800	-3.70570300	0.74194200
H	-0.59976300	-2.24360900	2.28660400
H	0.70219700	-0.76715300	-1.54401800
H	0.64566100	-3.04494800	-2.43426800
H	-0.62605100	-4.53333400	1.38720600
H	-0.02478700	-4.95088400	-0.99035900

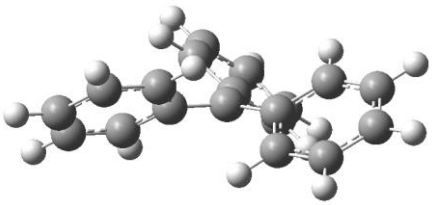
Triphenylmethane 1c (CBS-QB3, gas phase)



Number of imaginary frequencies = 0
CBS-QB3 Energy= -732.242500
CBS-QB3 Enthalpy= -732.241556
CBS-QB3 Free Energy= -732.301441
0 1

C	0.00000000	1.47337600	0.32496200
C	-0.10052200	4.18998700	-0.39686400
C	-0.73652700	2.39232900	1.08233500
C	0.68955200	1.94042500	-0.79711400
C	0.63725400	3.28711000	-1.15688000
C	-0.78785100	3.73684800	0.72831700
H	-1.27893000	2.04675800	1.95689600
H	1.28059400	1.25161400	-1.38887400
H	1.18087700	3.62944400	-2.03068700
H	-1.36137100	4.43151000	1.33222300
H	-0.13629400	5.23756600	-0.67398900
C	0.00000000	0.00000000	0.74169300
H	0.00000000	0.00000000	1.83753400
C	1.27598100	-0.73668800	0.32496200
C	3.67889600	-2.00793900	-0.39686400
C	1.33568100	-1.56738200	-0.79711400
C	2.44008100	-0.55831400	1.08233500
C	3.63013100	-1.18612500	0.72831700
C	2.52809400	-2.19543300	-1.15688000
H	0.44363200	-1.73483400	-1.38887400
H	2.41201000	0.08420600	1.95689600
H	4.51848600	-1.03677300	1.33222300
H	2.55275200	-2.83739200	-2.03068700
H	4.60401200	-2.50074900	-0.67398900
C	-1.27598100	-0.73668800	0.32496200
C	-3.57837400	-2.18204800	-0.39686400
C	-1.70355500	-1.83401600	1.08233500
C	-2.02523400	-0.37304300	-0.79711400
C	-3.16534800	-1.09167700	-1.15688000
C	-2.84228000	-2.55072300	0.72831700
H	-1.13308000	-2.13096500	1.95689600
H	-1.72422700	0.48322000	-1.38887400
H	-3.73363000	-0.79205200	-2.03068700
H	-3.15711500	-3.39473700	1.33222300
H	-4.46771900	-2.73681700	-0.67398900

Triphenylmethane radical (CBS-QB3, gas phase)

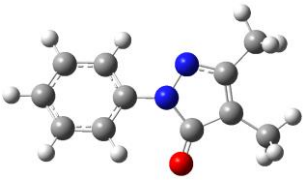


Number of imaginary frequencies = 0
CBS-QB3 Energy= -731.614137
CBS-QB3 Enthalpy= -731.613193
CBS-QB3 Free Energy= -731.670967
0 2

C	0.00000000	1.46306700	0.00000000
C	0.00000000	4.29267400	0.00000000
C	0.99185700	2.19901700	-0.68685900
C	-0.99185700	2.19901700	0.68685900
C	-0.98710100	3.58759100	0.68918700
C	0.98710100	3.58759100	-0.68918700
H	1.75526800	1.66606000	-1.24012300
H	-1.75526800	1.66606000	1.24012300
H	-1.75330600	4.12396100	1.23830200
H	1.75330600	4.12396100	-1.23830200
H	0.00000000	5.37669300	0.00000000
C	0.00000000	0.00000000	0.00000000
C	-1.26705300	-0.73153300	0.00000000
C	-3.71756500	-2.14633700	0.00000000
C	-1.40847600	-1.95848200	0.68685900
C	-2.40033300	-0.24053500	-0.68685900
C	-3.60049500	-0.93894100	-0.68918700
C	-2.61339500	-2.64865000	0.68918700
H	-0.56521600	-2.35313700	1.24012300
H	-2.32048400	0.68707700	-1.24012300
H	-4.44810800	-0.54357300	-1.23830200
H	-2.69480200	-3.58038800	1.23830200
H	-4.65635300	-2.68834600	0.00000000
C	1.26705300	-0.73153300	0.00000000
C	3.71756500	-2.14633700	0.00000000
C	1.40847600	-1.95848200	-0.68685900
C	2.40033300	-0.24053500	0.68685900
C	3.60049500	-0.93894100	0.68918700
C	2.61339500	-2.64865000	-0.68918700
H	0.56521600	-2.35313700	-1.24012300
H	2.32048400	0.68707700	1.24012300
H	4.44810800	-0.54357300	1.23830200
H	2.69480200	-3.58038800	-1.23830200
H	4.65635300	-2.68834600	0.00000000

Calculations for Scheme 7. Calculation of free energy values of C-O bond formation of C-O coupling products 9a, 5a, C, D

4,5-Dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one radical **A** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

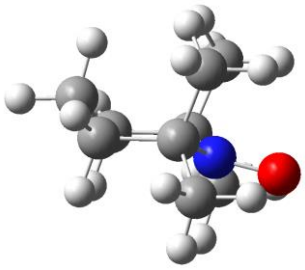


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -610.234559
Sum of electronic and thermal Enthalpies= -610.233615
Sum of electronic and thermal Free Energies= -610.289091

0 2

C	-1.23450200	0.09107600	0.05175400
C	-1.95650900	-0.98609600	0.55867700
C	-1.88934000	1.19379600	-0.49103000
C	-3.34492200	-0.95662400	0.50817200
H	-1.43914600	-1.83370700	0.98710400
N	0.18286900	0.07762800	0.09424700
C	-3.27719000	1.21717900	-0.52003100
H	-1.31010000	2.02058100	-0.88226500
C	-4.00917300	0.14180800	-0.02643100
H	-3.90827500	-1.79539900	0.90038000
C	1.04027000	-1.01890900	-0.15765600
N	0.87039300	1.20515700	0.25974200
H	-3.78710500	2.07670200	-0.93956300
H	-5.09234700	0.16063900	-0.05741700
C	2.37572700	-0.44411700	-0.09411200
O	0.67734800	-2.16039500	-0.39063000
C	2.19204300	0.89558400	0.15799500
C	3.62785500	-1.22244800	-0.26435800
H	3.86422300	-1.77969300	0.64815400
H	3.52266700	-1.95174800	-1.07087100
H	4.47152600	-0.56745800	-0.48664200
C	3.21630900	1.96466900	0.34045200
H	3.71382100	1.86539500	1.30888300
H	3.98302500	1.90525800	-0.43511400
H	2.74668700	2.94758600	0.29388300

(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, TEMPO (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

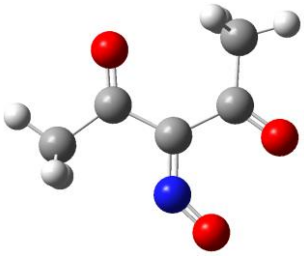


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -483.444430
Sum of electronic and thermal Enthalpies= -483.443486
Sum of electronic and thermal Free Energies= -483.492645

0 2

O	0.00017100	-2.02038700	-0.09069100
N	0.00002700	-0.75199500	-0.20522000
C	1.31936400	-0.07529700	-0.02323600
C	-1.31937500	-0.07538200	-0.02321900
C	-1.23795700	1.37961900	-0.50538300
C	-0.00007200	2.11504800	-0.01280900
H	-2.15303300	1.88688500	-0.18650100
H	-1.23588600	1.38595200	-1.60160500
C	1.23785800	1.37971300	-0.50538400
H	-0.00007100	2.19406200	1.07905100
H	-0.00009300	3.13848300	-0.39653400
H	2.15290600	1.88702500	-0.18647800
H	1.23577900	1.38609600	-1.60160000
C	1.72513300	-0.15114500	1.45687500
H	2.75740600	0.19065700	1.56790500
H	1.66158600	-1.18291800	1.80842000
H	1.09406400	0.47209900	2.09221900
C	2.34803100	-0.82657600	-0.87096500
H	2.50076900	-1.84084900	-0.50282000
H	3.30011600	-0.29119600	-0.82945900
H	2.02487300	-0.87737100	-1.91367000
C	-2.34800400	-0.82666300	-0.87098700
H	-3.30017700	-0.29146100	-0.82922200
H	-2.50053400	-1.84105700	-0.50309200
H	-2.02497600	-0.87713000	-1.91375200
C	-1.72516900	-0.15125900	1.45688300
H	-2.75741700	0.19060600	1.56793700
H	-1.09404600	0.47187900	2.09226700
H	-1.66167900	-1.18306000	1.80835900

Diacetyliminoxyl radical (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

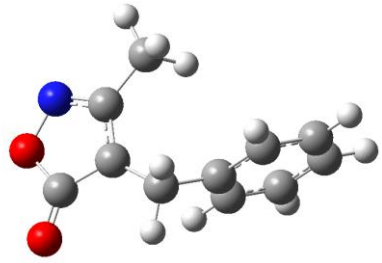


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -474.340745
Sum of electronic and thermal Enthalpies= -474.339801
Sum of electronic and thermal Free Energies= -474.387457

0 2

O	0.85427600	2.32544700	0.00001900
N	-0.02684800	1.51620200	0.00001500
C	-0.04224400	0.21852500	0.00004000
C	1.29524100	-0.48032200	0.00009800
C	-1.39305900	-0.41716800	0.00002000
O	2.29794800	0.19762800	-0.00008200
O	-1.50527800	-1.62399300	0.00001400
C	1.33648000	-1.97988100	-0.00001300
H	0.81420300	-2.37052700	0.87506900
H	0.81410700	-2.37040600	-0.87509300
H	2.37769400	-2.29782900	-0.00009300
C	-2.58829900	0.49987300	-0.00004700
H	-2.57457500	1.14562600	0.88118100
H	-2.57450500	1.14557900	-0.88130700
H	-3.49327200	-0.10466900	-0.00006700

4-benzyl-3-methylisoxazol-5(4H)-one radical **B** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



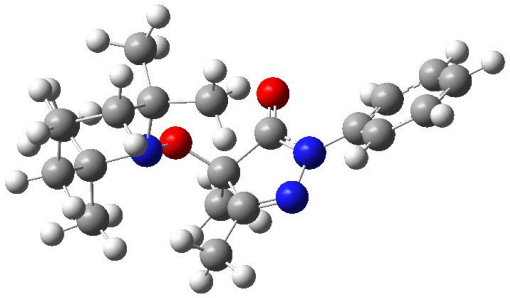
Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -630.088282
Sum of electronic and thermal Enthalpies= -630.087338
Sum of electronic and thermal Free Energies= -630.141038

0 2

N	-2.58185600	1.30393600	-0.68251700
O	-3.24407600	0.09865700	-0.62627200
C	-2.46599500	-0.81721100	0.05248500
C	-1.25462500	-0.12120400	0.43777500

C	-1.41370800	1.17275800	-0.06119000
C	-0.48014900	2.32969100	0.02670700
H	-0.21964000	2.52769200	1.06868600
H	-0.94199900	3.21926700	-0.40121200
H	0.44463300	2.10951800	-0.51136800
C	-0.12766700	-0.72015800	1.19980700
H	-0.32063300	-1.78945400	1.32370000
H	-0.11091600	-0.28490400	2.20527800
C	1.21264800	-0.49532300	0.52736400
C	3.66677200	-0.06626100	-0.74278100
C	1.42791400	-0.95705300	-0.77197600
C	2.23798800	0.18130800	1.18256700
C	3.46037000	0.39406300	0.55232500
C	2.64639600	-0.74415600	-1.40401400
H	0.63589300	-1.48625300	-1.29310800
H	2.08023700	0.55021000	2.19097200
H	4.24997000	0.92278500	1.07434700
H	2.80044700	-1.10865000	-2.41341500
H	4.61777700	0.10086800	-1.23558600
O	-2.83372900	-1.95207700	0.22313400

4,5-dimethyl-2-phenyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,4-dihydro-3H-pyrazol-3-one C (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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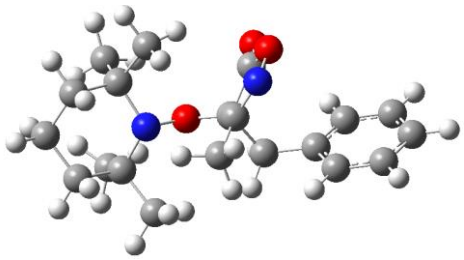
Sum of electronic and thermal Energies= -1093.703595
Sum of electronic and thermal Enthalpies= -1093.702651
Sum of electronic and thermal Free Energies= -1093.780102

0 1

N	1.47034600	-0.80332900	1.43234200
C	0.25161300	-1.16016400	1.27578100
C	-0.08386900	-1.40086400	-0.18373300
C	1.21458500	-0.91070100	-0.84983100
N	2.07716800	-0.65478200	0.18357400
C	-0.61044800	-1.42772200	2.45622200
H	-0.02075500	-1.33440300	3.36841200
H	-1.03241200	-2.43484900	2.40583800
H	-1.43827100	-0.71709500	2.47038100
C	-0.20266500	-2.90396800	-0.45175900
H	0.71836600	-3.42207000	-0.17265700

H	-0.38119800	-3.05370600	-1.51832100
H	-1.02904800	-3.32895600	0.11767900
C	3.36014900	-0.06377600	0.11295800
C	3.77887600	0.79065200	1.13169600
C	5.03803000	1.37233300	1.06378600
C	4.19652200	-0.33376800	-0.96915600
C	5.44889200	0.26538000	-1.02890000
C	5.87649200	1.11708300	-0.01637300
O	1.42597300	-0.79665500	-2.03650900
O	-1.18352900	-0.73357000	-0.78817700
N	-1.98597200	0.09208600	0.05522300
C	-3.39285200	-0.38336500	-0.11030200
C	-1.69404900	1.52663700	-0.24727800
C	-2.63795400	2.36887700	0.62865200
C	-4.10531500	1.99663900	0.48155900
H	-2.47328400	3.42165600	0.38020900
H	-2.34198000	2.23595300	1.67604700
C	-4.27824500	0.51281000	0.76983700
H	-4.46692100	2.23940900	-0.52251100
H	-4.71022700	2.58556900	1.17653300
H	-5.31806000	0.20351300	0.62698500
H	-4.02656700	0.32142700	1.81987300
C	-3.90271200	-0.41081500	-1.56408700
H	-4.80242200	-1.03007300	-1.61157300
H	-3.15292700	-0.85144500	-2.22301200
H	-4.16543300	0.57338400	-1.94743800
C	-3.48591100	-1.81404300	0.42900000
H	-2.98411200	-2.51874600	-0.23457900
H	-4.53753100	-2.10617100	0.48857700
H	-3.05625100	-1.89211500	1.42775900
C	-0.26324300	1.83793900	0.20536400
H	-0.11214100	2.92029100	0.18863000
H	0.48022700	1.40638000	-0.46699500
H	-0.08345900	1.48504800	1.22210600
C	-1.80605400	1.91616100	-1.73182200
H	-1.28605700	2.86447900	-1.89096800
H	-2.83404800	2.04880600	-2.06508800
H	-1.33009500	1.16051900	-2.35896000
H	3.12129600	0.98926100	1.96784900
H	6.85660500	1.57688400	-0.06736700
H	6.09629600	0.05535100	-1.87266300
H	5.36096600	2.03423000	1.85932300
H	3.86805200	-1.00051700	-1.75422500

4-benzyl-3-methyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)isoxazol-5(4H)-one D (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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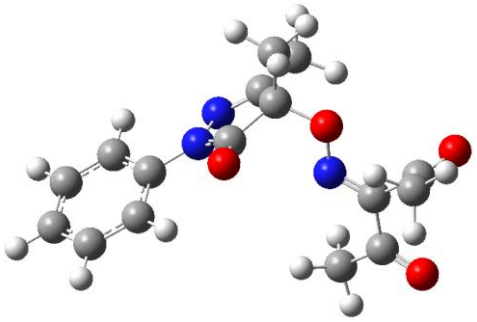
Sum of electronic and thermal Enthalpies= -1113.559717
Sum of electronic and thermal Free Energies= -1113.635831

0 1

N	1.28266800	1.11723000	1.80763200
O	1.58938000	2.02252200	0.75295500
C	1.10562800	1.55010800	-0.41591400
C	0.52689500	0.15545900	-0.16155000
C	0.63809400	0.11765100	1.34419900
C	0.20944600	-0.96350100	2.26905400
H	0.61507400	-0.77945100	3.26384300
H	0.55993700	-1.93467200	1.91261600
H	-0.88033200	-0.99264800	2.30388400
C	1.46143100	-0.89629300	-0.81667900
H	1.27973500	-0.81463200	-1.89109400
H	1.11967500	-1.88059100	-0.49439600
C	2.93093000	-0.72716500	-0.51430600
C	5.64689700	-0.37503000	0.06808900
C	3.74516900	0.03437200	-1.35367100
C	3.49899200	-1.31725500	0.61539800
C	4.84642600	-1.14263700	0.90727300
C	5.09339600	0.21114900	-1.06488100
H	3.31921600	0.49346500	-2.23962000
H	2.88555800	-1.92601600	1.27173700
H	5.27142900	-1.60899900	1.78888400
H	5.71190600	0.80582900	-1.72756400
H	6.69834900	-0.23805200	0.29395300
O	1.16847500	2.16483700	-1.43820300
O	-0.73854700	0.06632400	-0.79126700
N	-1.87353900	-0.16348500	0.04787900
C	-3.91725000	0.78440600	0.97897600
C	-3.80322500	-1.61692200	0.37305000
C	-4.71515500	-0.40291500	0.46344700
C	-2.55676900	-1.37790100	-0.49422700
C	-2.66616100	1.10142800	0.14109100
H	-3.59750200	0.57709000	2.00707500
H	-3.47382300	-1.89231300	1.38209400
H	-5.15757700	-0.17803900	-0.51192800

H	-4.53321200	1.68794500	1.01128400
H	-4.33642200	-2.47952200	-0.03749400
H	-5.54943100	-0.61179500	1.13857600
C	-3.03774100	1.73707200	-1.20977300
H	-2.17865200	1.73000100	-1.88280000
H	-3.32895100	2.77752400	-1.04429900
H	-3.87124300	1.24057400	-1.70356000
C	-1.84776500	2.12942600	0.92871200
H	-1.46475800	1.70516700	1.85811600
H	-2.49034700	2.97596300	1.18313800
H	-1.02066200	2.53233600	0.34157900
C	-2.92601900	-1.30510500	-1.98796300
H	-2.09158200	-0.91274200	-2.57125600
H	-3.80457500	-0.69412400	-2.18600200
H	-3.14420500	-2.31467200	-2.34593700
C	-1.62403000	-2.57936500	-0.31493100
H	-1.23509700	-2.63302400	0.70214200
H	-0.79332000	-2.54433900	-1.02012900
H	-2.18268300	-3.49784600	-0.51166200

3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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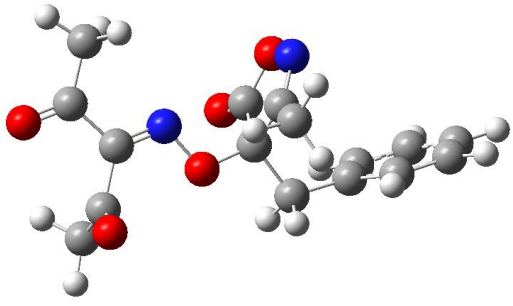
Sum of electronic and thermal Enthalpies= -1084.622294
Sum of electronic and thermal Free Energies= -1084.702087

0 1

C	-2.94873500	-0.14096200	0.07764300
C	-3.10461800	-1.17098100	1.00532700
C	-3.99263200	0.19243900	-0.78530800
C	-4.31337800	-1.85426300	1.06753700
H	-2.29409500	-1.43126500	1.67054100
N	-1.73156000	0.57604500	-0.00265700
C	-5.18987900	-0.50677700	-0.71581400
H	-3.85929600	0.98862700	-1.50525600
C	-5.35893300	-1.52982100	0.21136100
H	-4.43049900	-2.65302600	1.79101100

C	-0.77534800	0.74158400	0.95952100
N	-1.40606100	1.21673900	-1.20814500
H	-5.99678900	-0.24406800	-1.39037200
H	-6.29678600	-2.07025400	0.26423300
C	0.27614600	1.66574800	0.32083600
O	-0.75059400	0.29716700	2.08556100
C	-0.27862100	1.80015700	-1.07789000
C	0.37235200	2.98436400	1.06496600
H	0.64733100	2.79197000	2.10331500
H	1.12695300	3.61997100	0.59909800
H	-0.58945900	3.49980700	1.04243600
C	0.38771300	2.54256100	-2.17624100
H	0.50029500	3.59714000	-1.90976400
H	1.38977700	2.13916100	-2.34515100
H	-0.19319600	2.46447000	-3.09448500
O	1.57372200	1.08210800	0.35907000
N	1.55087000	-0.14546600	-0.25758800
C	2.67363700	-0.73853000	-0.19433300
C	3.90970600	-0.14603400	0.46839100
C	2.77638100	-2.10748600	-0.80629100
O	4.72065200	0.42412100	-0.21831800
C	4.01593200	-0.33701800	1.94704000
O	3.80790200	-2.72244200	-0.64770800
C	1.59894700	-2.63363900	-1.57022100
H	3.11805600	0.05905000	2.42973500
H	4.05753300	-1.40909700	2.16306800
H	4.90681400	0.15732800	2.33154500
H	0.70476600	-2.62292500	-0.94345600
H	1.39738400	-1.98765300	-2.42833400
H	1.81299700	-3.64616300	-1.90740600

3-(((4-benzyl-3-methyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione 5a (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1104.478610
Sum of electronic and thermal Enthalpies= -1104.477666
Sum of electronic and thermal Free Energies= -1104.557489

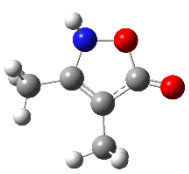
0 1

N	1.06438300	2.09742800	0.49725600

O	1.08566700	1.91371100	-0.92216400
C	0.62789200	0.68899200	-1.24459700
C	0.41442400	-0.08442300	0.06089200
C	0.66631100	1.02210100	1.05151000
C	0.46323600	0.91654700	2.51715200
H	0.76680800	1.83811400	3.01176500
H	1.03154500	0.07890400	2.92618100
H	-0.59367300	0.72634800	2.72215100
C	1.38101700	-1.27206000	0.17566400
H	1.11106400	-1.96613900	-0.62414400
H	1.17811600	-1.76680200	1.12834000
C	2.83634300	-0.87896300	0.07160700
C	5.51482000	-0.09583200	-0.12936100
C	3.45580100	-0.78305700	-1.17506200
C	3.57905900	-0.58943900	1.21600000
C	4.90924300	-0.19878600	1.11811600
C	4.78578500	-0.39189700	-1.27581400
H	2.89486100	-1.01845300	-2.07350100
H	3.12060100	-0.67985000	2.19513100
H	5.47321800	0.02091000	2.01742600
H	5.25301300	-0.32242000	-2.25148600
H	6.55241900	0.20816200	-0.20724100
O	0.46173700	0.32173500	-2.36812400
O	-0.88729600	-0.63450900	0.14536100
N	-1.82998300	0.35825700	-0.02549000
C	-3.01531900	-0.09555700	0.03072900
C	-4.14863200	0.87478200	-0.17081200
C	-3.35352300	-1.55747300	0.29449300
O	-5.27161600	0.42494200	-0.21554800
O	-3.57608800	-1.90272900	1.42780700
C	-3.38687400	-2.45046000	-0.90296400
H	-4.15626700	-2.09034000	-1.59276900
H	-3.59986400	-3.47631800	-0.60620100
H	-2.42746500	-2.39326700	-1.42499000
C	-3.82166500	2.33003800	-0.31027100
H	-3.31320600	2.68467000	0.58945100
H	-4.74111200	2.89092200	-0.46702400
H	-3.13760500	2.48348800	-1.14779800

Thermochemical calculations for Scheme 10 (Scheme S1)

3,4-Dimethyl-2H-1,2-oxazol-5-one tautomer 4b’ (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

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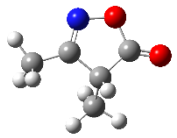
 Sum of electronic and thermal Energies=              -399.771864
 Sum of electronic and thermal Enthalpies=            -399.770920
 Sum of electronic and thermal Free Energies=         -399.812563
0 1
 C                 -1.23026800   -0.16762100    0.01070900
 O                 -0.80927000   -1.48112500    0.00039400
 C                 -0.05030000    0.66824700    0.00272400
 C                  1.01132400   -0.16887700   -0.00617800
 N                  0.58161200   -1.48103600   -0.11451600
 H                  0.95905200   -2.15356800    0.54496100
 O                 -2.41204800    0.08952600    0.01300300
 C                  2.47412800    0.09732500    0.01309600
 H                  2.97232500   -0.53574600    0.75117900
 H                  2.90976800   -0.11816900   -0.96526500
 H                  2.66920900    1.13954200    0.26029000
 C                 -0.10842400    2.15806500   -0.00145600
 H                 -0.66617400    2.52671700    0.86301300
 H                  0.89096400    2.59406000    0.02557800
 H                 -0.61463200    2.52437700   -0.89868700
```

3,4-Dimethyl-2H-1,2-oxazol-5-one tautomer 4b'' (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



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Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=              -399.773253
 Sum of electronic and thermal Enthalpies=            -399.772308
 Sum of electronic and thermal Free Energies=         -399.813133
0 1
 C                 -1.25915300   -0.17805300    0.12543100
 O                 -0.82930800   -1.41192200   -0.24093500
 C                  1.04019700   -0.30915800    0.08332900
 N                  0.59479900   -1.45415600   -0.26429200
 O                 -2.42317800    0.09599700    0.18438900
 C                 -0.04181400    0.67272600    0.40143600
 H                 -0.02586100    0.90416000    1.47247300
 C                  2.49821500   -0.03282000    0.14781900
 H                  2.76946200    0.30211200    1.15213400
 H                  3.07002600   -0.92512100   -0.10459700
 H                  2.75623100    0.76850800   -0.54944600
 C                 -0.01647900    1.97424200   -0.40380100
 H                 -0.90734600    2.56114300   -0.17704800
 H                  0.86272400    2.56345200   -0.14032700
 H                  0.00525800    1.77061500   -1.47606100
```

3,4-Dimethyl-2H-1,2-oxazol-5-one tautomer 4b’’’(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -399.761137
 Sum of electronic and thermal Enthalpies=   -399.760192
 Sum of electronic and thermal Free Energies=   -399.801323
0 1

C	1.11304800	-0.17595100	-0.00064100
O	0.77637000	-1.46090500	-0.00015100
N	-0.61940600	-1.54888500	0.00018900
C	0.01924200	0.63204500	-0.00187800
O	2.42596700	0.03135700	-0.00155800
C	-1.04804400	-0.31230000	0.00053000
H	2.61022000	0.97467600	0.02423000
C	-2.50748300	-0.01210000	0.00089400
H	-3.08779900	-0.93476500	-0.00617400
H	-2.77531200	0.56868400	0.88694900
H	-2.77328400	0.58077000	-0.87781000
C	-0.07142600	2.12306000	-0.00008900
H	-0.48185800	2.49789000	0.94142200
H	0.90829300	2.58590000	-0.13987700
H	-0.71512800	2.47689400	-0.80928900

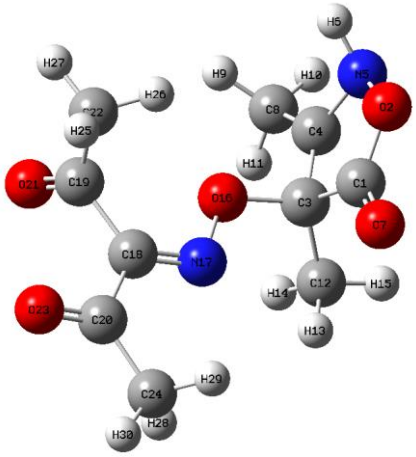
3,4-Dimethyl-2H-1,2-oxazol-5-one tautomer 4b’’’(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -399.762182
 Sum of electronic and thermal Enthalpies=   -399.761238
 Sum of electronic and thermal Free Energies=   -399.804282
0 1

C	-1.11320100	-0.11352900	0.00001100
O	-0.83031500	-1.41467800	0.00000300
N	0.56431700	-1.56140500	-0.00003600
C	0.01139700	0.64658400	-0.00000400
O	-2.39205100	0.24358000	-0.00007700
C	1.03886800	-0.34054400	-0.00002500
H	-2.95724800	-0.53614500	0.00063100
C	0.15006300	2.13308300	0.00000900
H	-0.83094000	2.61055100	-0.00159200

H	0.69200300	2.48079700	0.88370300
H	0.69471600	2.48043600	-0.88215100
C	2.50938300	-0.09973700	0.00002100
H	2.79898900	0.47771700	-0.88138500
H	2.79941300	0.47487000	0.88315200
H	3.05271400	-1.04475100	-0.00159100

Intermediate **I**, conformation **I(1)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -874.081637

Sum of electronic and thermal Enthalpies= -874.080693

Sum of electronic and thermal Free Energies= -874.151284

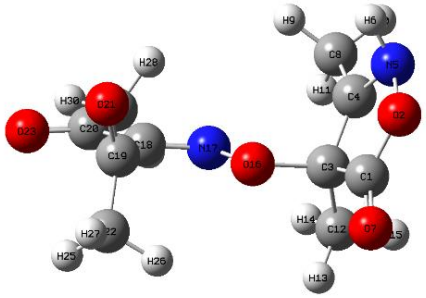
BSSE energy = 0.004086355053

0 2

C	1.88986700	-1.15790100	0.83643100
O	2.80877700	-0.46245100	1.54168000
C	1.60688800	-0.43808600	-0.48582300
C	2.65207400	0.59992400	-0.47170600
N	3.31955600	0.60118800	0.75567400
H	3.22249900	1.44332200	1.32240200
O	1.40727000	-2.16616300	1.26182500
C	2.85069300	1.71402900	-1.42528100
H	2.31277300	2.61892900	-1.11299400
H	3.91023500	1.96840700	-1.51336300
H	2.47994000	1.43471000	-2.41271700
C	1.56275600	-1.35707700	-1.69093000
H	0.80321800	-2.12628200	-1.55732900
H	1.33261200	-0.77629500	-2.58619000
H	2.53530700	-1.83469800	-1.81937200
O	0.32399100	0.27294300	-0.31375900
N	-0.75853100	-0.55866300	-0.35992200
C	-1.84462700	0.06019900	-0.11495000
C	-1.91926200	1.55084500	0.18041200
C	-3.11806700	-0.73003400	-0.10902800
O	-2.15849600	2.31815300	-0.71952000
C	-1.69197800	1.94938300	1.60441100

O	-4.13837300	-0.16468300	0.22306900
C	-3.06162300	-2.17528200	-0.50541700
H	-2.47023500	1.49693100	2.22672800
H	-0.73094200	1.55317100	1.94391300
H	-1.71573000	3.03350200	1.70592200
H	-2.70480200	-2.26348600	-1.53436000
H	-2.35267800	-2.71308600	0.12766000
H	-4.05505000	-2.61118000	-0.41562000

Intermediate **I**, conformation **I(2)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

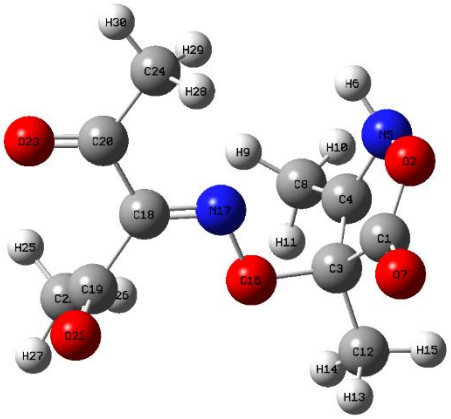
Sum of electronic and thermal Energies=	-874.082425
Sum of electronic and thermal Enthalpies=	-874.081481
Sum of electronic and thermal Free Energies=	-874.151355
BSSE energy =	0.004066063412

0 2

C	-2.59593700	-0.97404400	0.19961100
O	-3.26370400	-0.64771700	-0.92550800
C	-1.62913800	0.15371300	0.56575200
C	-2.04731800	1.20348500	-0.37766600
N	-2.95334900	0.68264400	-1.30624700
H	-2.63395300	0.63042800	-2.27344200
O	-2.78481800	-2.00744900	0.77004900
C	-1.48515500	2.55763800	-0.58081700
H	-0.66778900	2.55392200	-1.31398000
H	-2.25577500	3.24578800	-0.93790700
H	-1.07926200	2.94095300	0.35637300
C	-1.61500200	0.49174800	2.04208400
H	-1.35266600	-0.39557000	2.62063500
H	-0.88210800	1.27621100	2.23548500
H	-2.59904200	0.84416100	2.35521100
O	-0.32640500	-0.45535900	0.18877100
N	0.67580000	0.45636300	0.30245800
C	1.81139500	-0.02222800	-0.02143300
C	2.02068500	-1.44661600	-0.51384000
C	3.00325100	0.87918000	0.08555200
O	2.08401600	-1.64906600	-1.70176800
C	2.14275700	-2.49973800	0.54070000
O	4.10159300	0.40264800	-0.10662400

C	2.77469400	2.32192200	0.42881400
H	3.01238700	-2.27538700	1.16621200
H	1.25909000	-2.47165100	1.18428300
H	2.25155900	-3.48362500	0.08667300
H	2.14403300	2.78911100	-0.33134500
H	2.24568700	2.40433700	1.38061500
H	3.73382500	2.83345900	0.48582100

Intermediate **I**, conformation **I(3)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -874.085406

Sum of electronic and thermal Enthalpies= -874.084461

Sum of electronic and thermal Free Energies= -874.152947

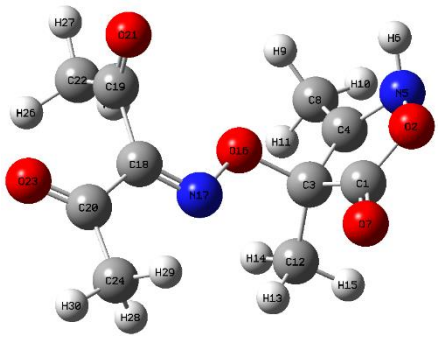
BSSE energy = 0.004247181062

0 2

C	-2.17001900	0.46633500	-1.10161700
O	-2.55681100	1.53123300	-0.36889800
C	-1.72957900	-0.66746000	-0.16889000
C	-2.05395600	-0.09481900	1.15084200
N	-2.48332000	1.22842600	1.01467100
H	-1.86754800	1.93419100	1.41947800
O	-2.20315700	0.47797500	-2.29684600
C	-1.63376900	-0.60260800	2.47625900
H	-0.64463900	-0.21729800	2.76160500
H	-2.34333600	-0.30925100	3.25389000
H	-1.57211700	-1.69223500	2.45949800
C	-2.34326900	-2.00753700	-0.52298600
H	-2.04964400	-2.29534900	-1.53358000
H	-2.00041200	-2.76729100	0.18148300
H	-3.43063100	-1.94349500	-0.47061000
O	-0.28708200	-0.87560600	-0.34694800
N	0.38654000	0.29353700	-0.13449800
C	1.64963300	0.13641400	-0.12753500
C	2.33311400	-1.20926000	-0.32340800
C	2.50680700	1.34665800	0.10377100
O	2.78082300	-1.48889600	-1.40740600
C	2.40606500	-2.08651900	0.88658600

O	3.69741100	1.18049300	0.25673300
C	1.84404300	2.69145500	0.13813400
H	3.02135400	-1.58962400	1.64345900
H	1.40513700	-2.21360700	1.30760600
H	2.83953000	-3.05242000	0.63119900
H	1.36766800	2.89331400	-0.82426400
H	1.05790600	2.70767400	0.89587500
H	2.59029200	3.45409700	0.35313800

Intermediate **I**, conformation **I(4)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

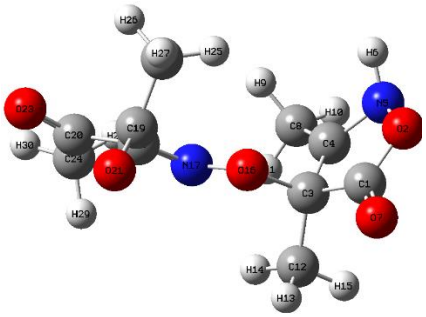
Sum of electronic and thermal Energies=	-874.081488
Sum of electronic and thermal Enthalpies=	-874.080544
Sum of electronic and thermal Free Energies=	-874.151890
BSSE energy =	0.004108555899

0 2

C	-1.96818900	-1.31040700	-0.58414300
O	-2.88537600	-0.75076700	-1.40364200
C	-1.60894100	-0.32171600	0.52993500
C	-2.62905900	0.72097000	0.32045700
N	-3.32556300	0.48546900	-0.86751800
H	-3.20067600	1.17541700	-1.60814300
O	-1.54741700	-2.41291700	-0.77647100
C	-2.74612700	2.03040400	1.00034400
H	-2.17125600	2.81076600	0.48380200
H	-3.78850900	2.35644700	1.04309300
H	-2.36564300	1.96017300	2.02080900
C	-1.52917000	-0.94803500	1.90748400
H	-0.78336600	-1.74223100	1.92110800
H	-1.25788500	-0.18652200	2.64128000
H	-2.49987400	-1.36741500	2.17609800
O	-0.32148300	0.29747900	0.15813000
N	0.74171100	-0.54776200	0.30266200
C	1.83862700	0.00854700	-0.02908100
C	1.93901500	1.43647800	-0.54563900
C	3.10098100	-0.78818400	0.10668200
O	1.98745200	1.62917700	-1.73561700
C	1.97856900	2.51077800	0.49502800
O	4.15609400	-0.22140000	-0.08384100

C	2.99187300	-2.23838500	0.47235700
H	1.10008900	2.42221500	1.14027300
H	2.86318300	2.36415700	1.12235400
H	2.01066300	3.49388500	0.02741100
H	2.43770600	-2.35343100	1.40614500
H	2.43241200	-2.77223700	-0.29965800
H	3.99048800	-2.66044800	0.57040600

Intermediate **I**, conformation **I(5)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -874.081848

Sum of electronic and thermal Enthalpies= -874.080904

Sum of electronic and thermal Free Energies= -874.150610

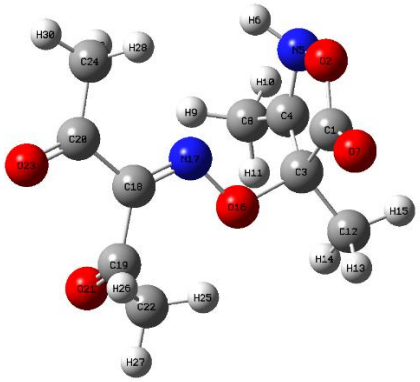
BSSE energy = 0.004073483938

0 2

C	-2.60569100	-0.92414600	0.30320400
O	-3.22305800	-0.72587200	-0.88008600
C	-1.63329800	0.22606500	0.57121200
C	-1.99712600	1.16220100	-0.50461900
N	-2.88221600	0.54989600	-1.39681000
H	-2.53746400	0.38690400	-2.34255400
O	-2.83537000	-1.88004200	0.98264700
C	-1.42987400	2.49042100	-0.82978000
H	-0.62101700	2.41991100	-1.56909900
H	-2.20036000	3.15050300	-1.23749800
H	-1.01223800	2.95015000	0.06672100
C	-1.66538200	0.73670200	1.99660200
H	-1.44881900	-0.08145600	2.68522000
H	-0.91761600	1.52055400	2.12508800
H	-2.64995200	1.14745200	2.22607500
O	-0.32783800	-0.44306400	0.32411100
N	0.68055500	0.46882600	0.32659500
C	1.81687400	-0.05720100	0.09031200
C	2.03186700	-1.54637300	-0.13623600
C	3.00726200	0.85119100	0.03209500
O	2.41161600	-2.22807100	0.78368700
C	1.76229400	-2.05138600	-1.51835200
O	4.06903600	0.38213800	-0.31859100
C	2.82154300	2.29194200	0.40723400
H	0.74715100	-1.77546700	-1.81600200

H	2.45371600	-1.56422800	-2.21305600
H	1.89079700	-3.13198900	-1.56064600
H	2.01612400	2.73876500	-0.17887700
H	2.53131900	2.36164000	1.45862800
H	3.75407300	2.82900200	0.24332200

Intermediate **I**, conformation **I(6)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

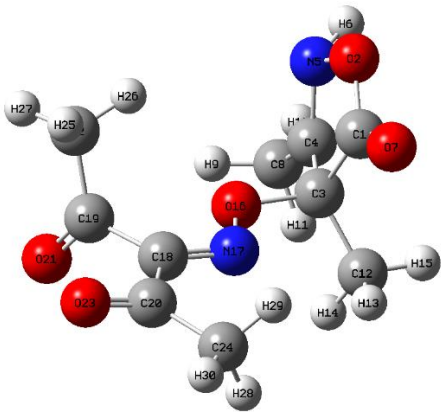
Sum of electronic and thermal Energies=	-874.086121
Sum of electronic and thermal Enthalpies=	-874.085177
Sum of electronic and thermal Free Energies=	-874.155265
BSSE energy =	0.004235414426

0 2

C	-2.04385800	-0.05358700	-1.26536400
O	-2.46815900	1.21351400	-1.08372300
C	-1.73067000	-0.69145800	0.09176500
C	-2.18176100	0.36531900	1.01496500
N	-2.55097200	1.50953000	0.30141800
H	-1.95212100	2.32371000	0.44355700
O	-1.94986100	-0.53759400	-2.35545300
C	-1.94294800	0.45299200	2.47289100
H	-0.99146200	0.95513600	2.69658800
H	-2.74092300	1.01121000	2.96894800
H	-1.89837300	-0.54688200	2.90761500
C	-2.32617600	-2.07472700	0.26015500
H	-1.93558700	-2.74394400	-0.50806800
H	-2.06855000	-2.46827300	1.24488400
H	-3.41195200	-2.02528400	0.17227600
O	-0.27867100	-0.91746200	0.15623800
N	0.38849900	0.26187700	-0.00597600
C	1.65271800	0.12259000	0.04116100
C	2.34750100	-1.20897700	0.28751000
C	2.49933700	1.34500900	-0.15757900
O	2.69655300	-1.48543300	1.40869600
C	2.55141100	-2.07658600	-0.91297900
O	3.70139800	1.20270100	-0.21656000
C	1.81266600	2.67312300	-0.28027600
H	1.58936500	-2.25128900	-1.40276100

H	3.19060600	-1.54767500	-1.62685000
H	3.01190800	-3.02115900	-0.62703000
H	1.11130300	2.65793900	-1.11740600
H	1.23392900	2.87832900	0.62350400
H	2.55976900	3.45034000	-0.43042400

Intermediate **I**, conformation **I(7)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -874.083180

Sum of electronic and thermal Enthalpies= -874.082236

Sum of electronic and thermal Free Energies= -874.151578

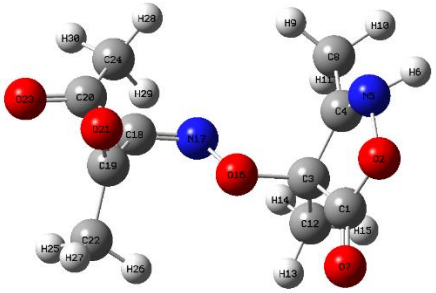
BSSE energy = 0.004102057493

0 2

C	1.85495600	-1.19557900	0.80824400
O	2.66034500	-0.46379000	1.61027900
C	1.61299400	-0.42830300	-0.49629600
C	2.67217800	0.58920300	-0.40793000
N	3.03252400	0.72953200	0.93371500
H	4.02584300	0.85655300	1.11246600
O	1.41482600	-2.25114600	1.15890400
C	3.01216300	1.64674200	-1.38702800
H	2.31789300	2.49420400	-1.32371900
H	4.02253400	2.02879500	-1.21927700
H	2.96220500	1.24882200	-2.40215900
C	1.59009200	-1.29351400	-1.73822600
H	0.82374600	-2.06243400	-1.64687700
H	1.37450400	-0.67569400	-2.61183500
H	2.56079700	-1.77323300	-1.87210400
O	0.32759100	0.28748800	-0.33325900
N	-0.74970400	-0.55036000	-0.35615800
C	-1.83868000	0.06755200	-0.12076600
C	-1.91980700	1.56500100	0.13702600
C	-3.10680800	-0.73047800	-0.08846300
O	-2.20248900	2.30306600	-0.77489200
C	-1.64252700	2.00721600	1.53892500
O	-4.12735100	-0.16759300	0.24693100
C	-3.04505400	-2.18094700	-0.46501000

H	-2.38479000	1.55793400	2.20591100
H	-0.65974900	1.63980700	1.84719000
H	-1.68331200	3.09315800	1.61131900
H	-2.71396900	-2.27907700	-1.50177200
H	-2.31443600	-2.70311800	0.15620000
H	-4.03143600	-2.62546400	-0.34479300

Intermediate **I**, conformation **I(8)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

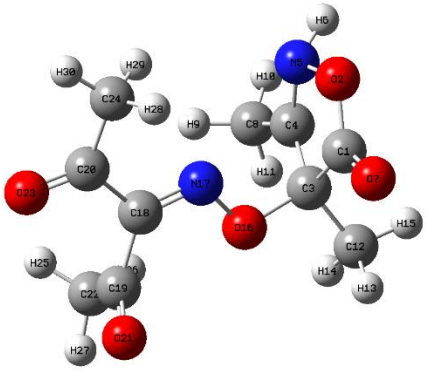
Sum of electronic and thermal Energies=	-874.083655
Sum of electronic and thermal Enthalpies=	-874.082710
Sum of electronic and thermal Free Energies=	-874.152360
BSSE energy =	0.004092832606

0 2

C	-2.59238000	-0.99588400	0.15099000
O	-3.18819800	-0.66136300	-1.01154400
C	-1.63092700	0.12055200	0.56588900
C	-2.05655400	1.19619700	-0.34061600
N	-2.71593500	0.61550600	-1.42460700
H	-3.53049000	1.11920300	-1.76693600
O	-2.81599200	-2.03371800	0.70156000
C	-1.60791600	2.60557200	-0.40882300
H	-0.71598900	2.71457500	-1.03797600
H	-2.39063800	3.25026500	-0.81951400
H	-1.35458000	2.96510700	0.58952700
C	-1.62530000	0.41446500	2.05051900
H	-1.38479100	-0.49547500	2.60254000
H	-0.87663600	1.17597900	2.27359900
H	-2.60386800	0.77685300	2.36908400
O	-0.32028000	-0.47476300	0.18411500
N	0.66480200	0.45707400	0.27382100
C	1.81048400	-0.01056800	-0.03090100
C	2.04830000	-1.44526300	-0.47869200
C	2.98700100	0.91228500	0.05802400
O	2.14470000	-1.67949300	-1.65837300
C	2.15869500	-2.46807500	0.60702300
O	4.09540700	0.44491000	-0.09571600
C	2.73295300	2.36526300	0.33355400
H	3.01542200	-2.21876400	1.24087800
H	1.26357500	-2.43053800	1.23379800

H	2.28448100	-3.46295300	0.18217500
H	2.15807200	2.79875000	-0.48869900
H	2.13714600	2.48379400	1.24055300
H	3.68500300	2.88330200	0.43432500

Intermediate **I**, conformation **I(9)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

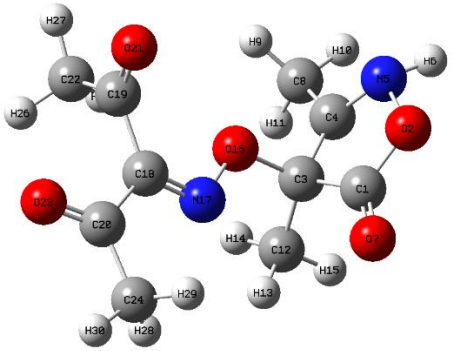
Sum of electronic and thermal Energies=	-874.085533
Sum of electronic and thermal Enthalpies=	-874.084589
Sum of electronic and thermal Free Energies=	-874.153722
BSSE energy =	0.004227937538

0 2

C	-2.11986200	0.64239300	-1.05344600
O	-2.49556300	1.60807500	-0.19067100
C	-1.71787400	-0.61580800	-0.27463700
C	-2.11034100	-0.23496500	1.09235300
N	-2.32070400	1.14546400	1.14058100
H	-3.14743100	1.44704600	1.65148400
O	-2.11791000	0.81948300	-2.23669100
C	-1.89718200	-0.99860800	2.34326000
H	-0.88577000	-0.84374600	2.74161700
H	-2.60768100	-0.70215100	3.11959800
H	-2.02337900	-2.06654300	2.15684200
C	-2.32698600	-1.88831500	-0.83215900
H	-2.01489600	-2.02282000	-1.86877700
H	-1.99359600	-2.74550100	-0.24465600
H	-3.41516500	-1.83250900	-0.78986600
O	-0.27008900	-0.82398000	-0.43636300
N	0.41367200	0.31703600	-0.13462800
C	1.67383900	0.14062900	-0.10119300
C	2.34501800	-1.20062400	-0.35714500
C	2.53670400	1.32184300	0.23232400
O	2.81383100	-1.42690800	-1.44501600
C	2.38011800	-2.14532100	0.80291900
O	3.71881900	1.12982400	0.42058000
C	1.88963400	2.67176000	0.31721300
H	2.98273600	-1.69852400	1.60005500
H	1.36828000	-2.28331400	1.19345500

H	2.80883800	-3.10070200	0.50355000
H	1.50761300	2.95456200	-0.66712000
H	1.03521000	2.64506900	0.99618400
H	2.62335000	3.40179100	0.65431000

Intermediate **I**, conformation **I(10)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

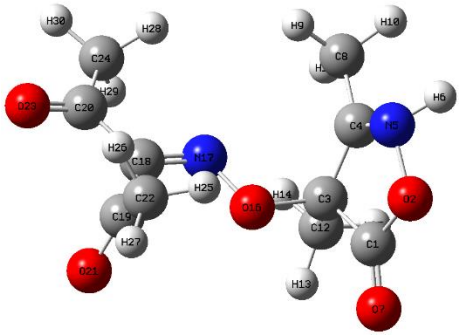


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -874.082519
Sum of electronic and thermal Enthalpies= -874.081575
Sum of electronic and thermal Free Energies= -874.151412
BSSE energy = 0.004084177197
0 2

C	-1.95005900	-1.33554400	-0.54936000
O	-2.78828000	-0.77806600	-1.45161100
C	-1.61182300	-0.29976600	0.52895900
C	-2.65128900	0.70829400	0.26667500
N	-3.08965100	0.55053800	-1.04897700
H	-4.08796100	0.67179000	-1.20059800
O	-1.56063800	-2.46004600	-0.66799100
C	-2.89634400	1.97806600	0.98839200
H	-2.18652300	2.75821700	0.68505600
H	-3.90526100	2.35263900	0.79689700
H	-2.78833200	1.82577400	2.06382200
C	-1.53598600	-0.86181300	1.93266100
H	-0.78885800	-1.65355700	1.98016600
H	-1.26299100	-0.06917500	2.63191100
H	-2.50508300	-1.27168200	2.22088600
O	-0.32261200	0.31795400	0.14540700
N	0.73469600	-0.53219600	0.29219900
C	1.83857400	0.01791100	-0.02706000
C	1.95708600	1.44839200	-0.53243400
C	3.09244900	-0.79127400	0.11386800
O	2.03935000	1.64687000	-1.71951700
C	1.97546600	2.51749000	0.51437200
O	4.15535600	-0.23089800	-0.05082000
C	2.96594800	-2.24681300	0.45221500
H	1.08398200	2.42756500	1.14099800

H	2.84705300	2.36617600	1.15872100
H	2.01904300	3.50269900	0.05215800
H	2.39122100	-2.37464400	1.37171800
H	2.41942500	-2.76268600	-0.34106000
H	3.95943100	-2.67767100	0.56329600

Intermediate **I**, conformation **I(11)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

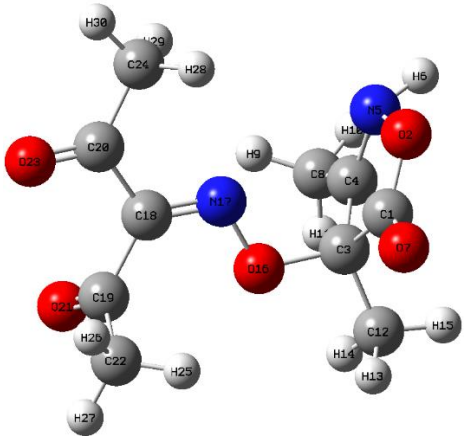
Sum of electronic and thermal Energies=	-874.083690
Sum of electronic and thermal Enthalpies=	-874.082746
Sum of electronic and thermal Free Energies=	-874.152298
BSSE energy =	0.004120420740

0 2

C	-2.60109500	-0.94340800	0.23013700
O	-3.08840600	-0.74247500	-1.01260800
C	-1.64363700	0.19665200	0.58595700
C	-1.97752000	1.16706000	-0.46531200
N	-2.55796400	0.47375500	-1.52776300
H	-3.33202300	0.94484400	-1.98982500
O	-2.89936800	-1.90252200	0.87847600
C	-1.53161600	2.56750800	-0.64176600
H	-0.62033900	2.62798400	-1.24924600
H	-2.30316500	3.16902700	-1.13204900
H	-1.31277700	3.01378700	0.32903000
C	-1.72454500	0.65964900	2.02356900
H	-1.55492500	-0.18713800	2.69003500
H	-0.96187500	1.41751700	2.20965200
H	-2.70660000	1.08754600	2.23101500
O	-0.32503900	-0.46430300	0.36855800
N	0.66519100	0.46532700	0.32500500
C	1.80873700	-0.04867400	0.09618200
C	2.04526200	-1.54098700	-0.08198700
C	2.98184300	0.87689000	-0.01070300
O	2.45829700	-2.18313700	0.85223400
C	1.75193000	-2.09862700	-1.43875500
O	4.04812300	0.41372900	-0.35583200
C	2.77483200	2.32831000	0.30859200
H	0.72469200	-1.85170500	-1.72019200
H	2.41621700	-1.62215500	-2.16662500

H	1.90084000	-3.17743800	-1.44744900
H	1.96389700	2.73925600	-0.29590500
H	2.48222300	2.43611500	1.35596000
H	3.69924500	2.87221700	0.12278600

Intermediate **I**, conformation **I(12)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

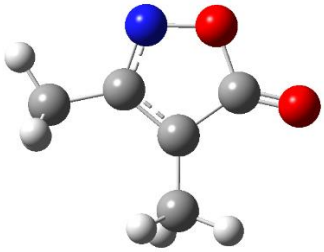
Sum of electronic and thermal Energies=	-874.086010
Sum of electronic and thermal Enthalpies=	-874.085066
Sum of electronic and thermal Free Energies=	-874.154623
BSSE energy =	0.004199543966

0 2

C	-2.00864000	0.14029200	-1.28366400
O	-2.46242100	1.35863700	-0.92818000
C	-1.71055300	-0.68613600	-0.02786400
C	-2.23491100	0.20162800	1.02165700
N	-2.44376300	1.47513200	0.48693300
H	-3.32298100	1.91942400	0.74229300
O	-1.86664700	-0.17034500	-2.43097200
C	-2.18028200	0.01379500	2.48925100
H	-1.21694400	0.34259600	2.90012000
H	-2.96742200	0.58154100	2.99276800
H	-2.30723800	-1.04099900	2.73886400
C	-2.27927300	-2.09186600	-0.08325900
H	-1.86681400	-2.62353900	-0.94210700
H	-2.01813700	-2.63042800	0.82918400
H	-3.36525400	-2.05397000	-0.17393200
O	-0.25651500	-0.90792800	0.04476000
N	0.41458400	0.27709400	-0.01025900
C	1.67666900	0.13084500	0.06778500
C	2.36230700	-1.21620600	0.24318200
C	2.53083200	1.36018900	-0.02177900
O	2.67451000	-1.57349500	1.35256100
C	2.60574700	-1.99775600	-1.00824500
O	3.73448300	1.21752200	-0.05175500
C	1.85094000	2.69580300	-0.07648600

H	1.65891400	-2.13946100	-1.53679500
H	3.26328200	-1.41904400	-1.66443300
H	3.06108400	-2.95924400	-0.77521000
H	1.16629700	2.73598000	-0.92633600
H	1.25181900	2.84500200	0.82485000
H	2.60333800	3.47789600	-0.16076400

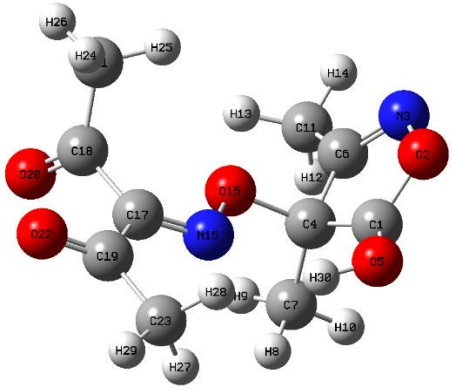
Intermediate **II** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -399.148673
Sum of electronic and thermal Enthalpies= -399.147728
Sum of electronic and thermal Free Energies= -399.189847
0 2

C	1.24198300	-0.13402700	-0.00114200
O	0.86065000	-1.46111200	0.00418700
N	-0.51432800	-1.53971700	0.00281100
C	0.01931300	0.64479800	-0.00482700
O	2.40403700	0.18578600	-0.00410300
C	-1.00376200	-0.30463700	-0.00106500
C	-0.06413400	2.12026500	0.00207200
H	-0.42269300	2.47562600	0.97417600
H	0.91324800	2.56424800	-0.18719300
H	-0.77331100	2.47137400	-0.75210500
C	-2.47494400	-0.07559600	-0.00268700
H	-2.77190800	0.48517300	0.88636400
H	-2.76661400	0.50613400	-0.88009500
H	-3.00665700	-1.02674900	-0.01560200

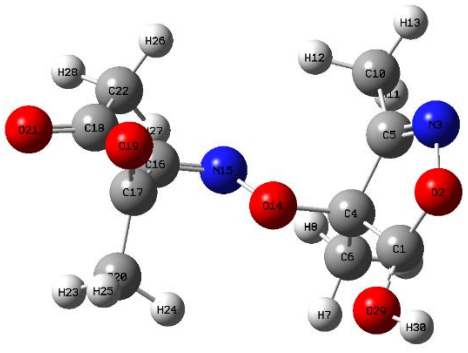
Intermediate **III**, conformation **III(1)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -874.066566

```
 Sum of electronic and thermal Enthalpies=            -874.065622
 Sum of electronic and thermal Free Energies=         -874.134188
 BSSE energy =       0.004207976723
0 2
 C                 -1.95315300   -1.37211600   -0.29809200
 O                 -2.73609000   -1.01743900   -1.35707000
 N                 -3.26068900    0.25021800   -1.09288700
 C                 -1.66889300   -0.20026300    0.54756500
 O                 -1.19603200   -2.45411600   -0.48100600
 C                 -2.70849400    0.71961600   -0.03450100
 C                 -1.68132100   -0.41220900    2.04955600
 H                 -0.92627100   -1.14884400    2.33145200
 H                 -1.46115200    0.52724400    2.55963700
 H                 -2.65921800   -0.77473000    2.36919700
 C                 -3.04572400    2.05998400    0.50915800
 H                 -3.45426400    1.96591300    1.51883700
 H                 -2.14449600    2.67526000    0.57186400
 H                 -3.77804900    2.55559700   -0.12714100
 O                 -0.35801600    0.45839000    0.19672200
 N                  0.65137300   -0.44972700    0.25383200
 C                  1.80116600    0.06811900    0.07010800
 C                  2.01795600    1.56333500   -0.12079400
 C                  2.99816100   -0.83405700    0.04991900
 O                  2.28950900    2.23829800    0.84097200
 C                  1.88005500    2.07558300   -1.51838300
 O                  4.08012600   -0.33594800   -0.17258900
 C                  2.79434800   -2.30275100    0.27867500
 H                  2.63712100    1.59721600   -2.14750400
 H                  0.90006000    1.79346600   -1.91350400
 H                  2.00407700    3.15724400   -1.54173200
 H                  2.19643500   -2.47932600    1.17450200
 H                  2.25670700   -2.73135900   -0.57198300
 H                  3.76436300   -2.78800700    0.36993000
 H                 -0.31069800   -2.25804700   -0.13566600
```

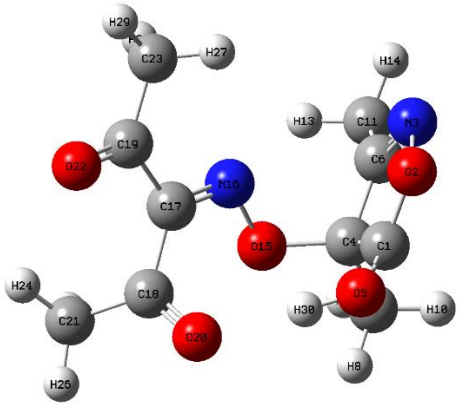
Intermediate **III**, conformation **III(2)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=              -874.064158
 Sum of electronic and thermal Enthalpies=            -874.063214
 Sum of electronic and thermal Free Energies=         -874.132948
 BSSE energy =       0.004116236110
0 2
 C                 -2.67086900   -0.81843400    0.30708800
 O                 -3.23998300   -0.62487400   -0.92499200
 N                 -2.93465300    0.68037900   -1.33765600
 C                 -1.63989900    0.21775400    0.55211000
 C                 -2.07943600    1.18527100   -0.52896100
 C                 -1.56984600    0.75302100    1.96974800
 H                 -1.35137700   -0.06528300    2.65873500
 H                 -0.78977000    1.50978800    2.05559700
 H                 -2.52760800    1.19816200    2.24280000
 C                 -1.57211400    2.57191400   -0.69905600
 H                 -1.78445000    3.16031100    0.19756600
 H                 -0.48897300    2.56210200   -0.83717800
 H                 -2.04605400    3.04520500   -1.55851900
 O                 -0.34294600   -0.37940800    0.16865500
 N                  0.68750000    0.50194800    0.29164200
 C                  1.80874100   -0.01501600   -0.02451500
 C                  1.97408800   -1.44807200   -0.50939600
 C                  3.03159600    0.84334000    0.09193600
 O                  2.08301400   -1.65350500   -1.69328900
 C                  2.00034000   -2.50648200    0.54711100
 O                  4.11532700    0.32074100   -0.05848000
 C                  2.85089900    2.30340500    0.38652900
 H                  2.84784800   -2.32096200    1.21428700
 H                  1.08840900   -2.44120800    1.14673600
 H                  2.08869100   -3.49337700    0.09505800
 H                  2.34170800    2.78287400   -0.45373000
 H                  2.22223900    2.44360300    1.26762900
 H                  3.82603000    2.76330800    0.53667200
 O                 -2.51493400   -2.08081800    0.71876100
 H                 -3.30144700   -2.59809500    0.51563500
```

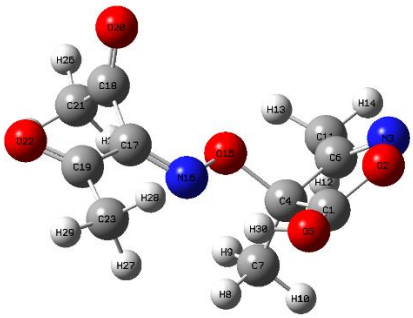
Intermediate **III**, conformation **III(3)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -874.067762
 Sum of electronic and thermal Enthalpies=   -874.066818
 Sum of electronic and thermal Free Energies=   -874.133629
 BSSE energy =   0.004820711681
0 2

C	1.65865900	-0.60082600	1.22715900
O	1.99136900	0.63919700	1.71192200
N	2.54133300	1.38773700	0.66610800
C	1.72958000	-0.59303000	-0.25824900
O	0.81264900	-1.30064400	1.98164300
C	2.41613800	0.73843700	-0.43048200
C	2.40640700	-1.79119500	-0.89874500
H	1.88487600	-2.70683600	-0.61410200
H	2.39069300	-1.69589200	-1.98602500
H	3.44061500	-1.85599600	-0.55950800
C	2.87008900	1.28629600	-1.73394000
H	3.63421200	0.64016200	-2.17403300
H	2.02815300	1.32738500	-2.43017100
H	3.27934000	2.28787000	-1.60578200
O	0.38267200	-0.60335200	-0.85966800
N	-0.33841200	0.50985700	-0.49247400
C	-1.55505000	0.22510100	-0.24642000
C	-2.07155300	-1.20657200	-0.18481200
C	-2.47971600	1.35082800	0.12970400
O	-1.63446600	-1.92793300	0.68665800
C	-3.07308300	-1.63367500	-1.20012000
O	-3.61284300	1.07037000	0.45441400
C	-1.94170300	2.74799200	0.09540300
H	-3.94480700	-0.97689400	-1.14740000
H	-2.63536600	-1.51503500	-2.19650800
H	-3.36286900	-2.67012500	-1.03656200
H	-1.02742300	2.81568400	0.68866100
H	-1.67864200	3.01621100	-0.93089800
H	-2.69665200	3.43263700	0.47748900
H	-0.00623100	-1.54356200	1.50267300

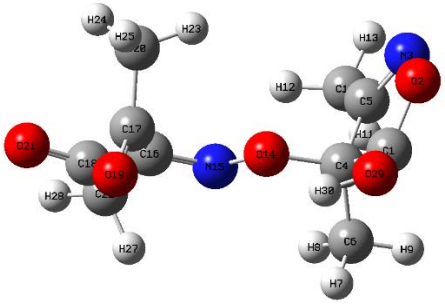
Intermediate **III**, conformation **III(4)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -874.066147
 Sum of electronic and thermal Enthalpies=   -874.065203
 Sum of electronic and thermal Free Energies=   -874.132871
 BSSE energy =   0.004187857708
0 2

C	-1.99998300	-1.39202800	-0.13725000
O	-2.84834800	-1.16121900	-1.18082500
N	-3.33781500	0.14043400	-1.05353200
C	-1.65050900	-0.12518000	0.53093900
O	-1.25740300	-2.49503800	-0.23464900
C	-2.71099900	0.73339200	-0.10474600
C	-1.58316700	-0.14041700	2.04711900
H	-0.82935000	-0.85504800	2.38383700
H	-1.31635900	0.85155600	2.41711100
H	-2.54878100	-0.43050200	2.46337300
C	-2.99333400	2.14138300	0.27464400
H	-3.33108500	2.19271400	1.31311200
H	-2.08309100	2.74069300	0.19008800
H	-3.76242900	2.56246000	-0.37185200
O	-0.35448400	0.45172600	0.02689200
N	0.64817300	-0.45581200	0.17570400
C	1.80087100	0.02847000	-0.06987000
C	2.02391900	1.47937500	-0.47372800
C	2.99629200	-0.86836100	0.06035500
O	2.17510100	1.74319300	-1.64033900
C	2.05350700	2.47475500	0.64245300
O	4.09463900	-0.36400000	-0.02214800
C	2.77109200	-2.33370400	0.28801500
H	1.14477200	2.37949300	1.24287800
H	2.90375600	2.24701300	1.29314700
H	2.14712200	3.48545900	0.24775800
H	2.12117000	-2.49434300	1.15083400
H	2.27799900	-2.76879900	-0.58556700
H	3.73003800	-2.82353600	0.44633600
H	-0.34843900	-2.26290800	0.01471300

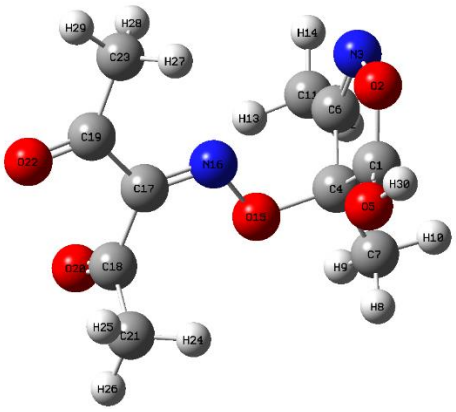
Intermediate **III**, conformation **III(5)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -874.063359

```
 Sum of electronic and thermal Enthalpies=            -874.062415
 Sum of electronic and thermal Free Energies=         -874.131976
 BSSE energy =       0.004068102905
0 2
 C                 -2.65032100   -0.77495900    0.47660300
 O                 -3.25398900   -0.77451700   -0.75400800
 N                 -2.94855500    0.43488100   -1.39014800
 C                 -1.65048700    0.32371300    0.54486700
 C                 -2.08268700    1.07295700   -0.69580900
 C                 -1.61918800    1.11330200    1.84050600
 H                 -1.39310300    0.44708400    2.67556900
 H                 -0.86106000    1.89523200    1.79583800
 H                 -2.59442000    1.57144800    2.01038300
 C                 -1.55851000    2.39776100   -1.11843200
 H                 -1.77489700    3.14873600   -0.35415500
 H                 -0.47327400    2.35222300   -1.23589600
 H                 -2.01409800    2.70338100   -2.05979200
 O                 -0.34954800   -0.33095800    0.30895100
 N                  0.70150900    0.53957700    0.35153000
 C                  1.80809400   -0.03533300    0.09261000
 C                  1.93562100   -1.52403400   -0.19827900
 C                  3.04985300    0.80532900    0.07130400
 O                  2.21280900   -2.27426200    0.70488700
 C                  1.70265400   -1.93876800   -1.61595500
 O                  4.08627800    0.27990100   -0.27347100
 C                  2.94134200    2.24710300    0.46959000
 H                  0.71537800   -1.59382100   -1.93621000
 H                  2.44427300   -1.45089500   -2.25591400
 H                  1.77766700   -3.02079400   -1.71382300
 H                  2.21484100    2.76011900   -0.16442600
 H                  2.58148600    2.32237300    1.49839200
 H                  3.91811900    2.71883500    0.37926500
 O                 -2.50606300   -1.98358800    1.03181600
 H                 -1.58570400   -2.13016400    1.28365600
```

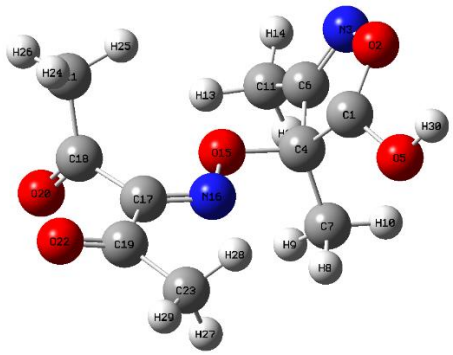
Intermediate **III**, conformation **III(6)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=              -874.068357
 Sum of electronic and thermal Enthalpies=            -874.067413
 Sum of electronic and thermal Free Energies=         -874.137323
 BSSE energy =       0.004295688105
0 2
 C                 -2.11932000    0.20520400   -1.22909200
 O                 -2.41624300    1.46613700   -0.78480600
 N                 -2.56388600    1.41359200    0.60967200
 C                 -1.74468900   -0.66280700   -0.08440700
 O                 -1.51752300    0.09969200   -2.41982000
 C                 -2.22042000    0.25143100    1.02153000
 C                 -2.32512900   -2.06481800   -0.09673200
 H                 -1.99492900   -2.59180700   -0.99365400
 H                 -1.99185000   -2.61796700    0.78329600
 H                 -3.41438800   -2.01560100   -0.09697600
 C                 -2.23485900   -0.11626800    2.46030700
 H                 -2.93085000   -0.94121000    2.63394300
 H                 -1.24030500   -0.45181400    2.76606500
 H                 -2.53096600    0.73605800    3.07077400
 O                 -0.29632600   -0.89330000    0.03624400
 N                  0.38868700    0.28468400    0.04945700
 C                  1.64907200    0.11489900    0.10968400
 C                  2.31481500   -1.25106900    0.18423300
 C                  2.52027800    1.33465700    0.10066700
 O                  2.62504100   -1.69407300    1.26293300
 C                  2.54299900   -1.94301400   -1.12189200
 O                  3.72153100    1.17814800    0.04435400
 C                  1.86001500    2.68014500    0.15512300
 H                  1.59478200   -2.02273200   -1.66074200
 H                  3.21600300   -1.33233100   -1.73173100
 H                  2.97577000   -2.92939200   -0.96097000
 H                  1.15424700    2.78882200   -0.67099100
 H                  1.28628800    2.77426700    1.08019700
 H                  2.62197300    3.45601100    0.10658500
 H                 -1.90778800    0.71677400   -3.04747500
```

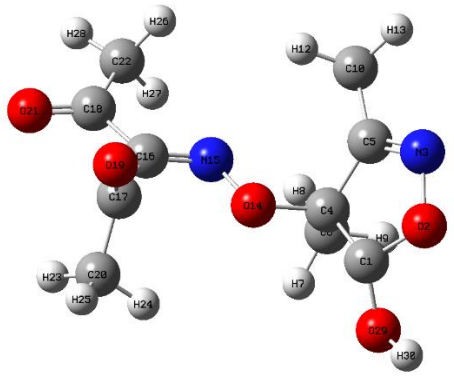
Intermediate **III**, conformation **III(7)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)




```
Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=              -874.065879
```

```
 Sum of electronic and thermal Enthalpies=            -874.064935
 Sum of electronic and thermal Free Energies=         -874.135148
 BSSE energy =       0.003868499091
0 2
 C                  1.90171700    1.15064500   -0.64781000
 O                  2.92584200    0.63908800   -1.40841800
 N                  3.27931700   -0.63197500   -0.91616200
 C                  1.57273300    0.19037100    0.44877600
 O                  1.96513300    2.47002200   -0.39139600
 C                  2.55680500   -0.90366000    0.10052700
 C                  1.68592400    0.73124300    1.86441400
 H                  0.97463200    1.54500200    2.00769800
 H                  1.46894400   -0.06262900    2.58114900
 H                  2.69330400    1.11180400    2.04250700
 C                  2.69523600   -2.17661000    0.85394800
 H                  2.99474600   -1.97140400    1.88502300
 H                  1.73548000   -2.69787300    0.88472500
 H                  3.44201000   -2.81749600    0.38679600
 O                  0.26370000   -0.42601500    0.25828100
 N                 -0.72084700    0.51515600    0.26170700
 C                 -1.87240900    0.00707300    0.06453100
 C                 -2.11350000   -1.48277800   -0.12910600
 C                 -3.05047400    0.93178900    0.01456600
 O                 -2.45342700   -2.14970500    0.81727300
 C                 -1.91225100   -2.00716800   -1.51542000
 O                 -4.12867300    0.46663300   -0.28848900
 C                 -2.83390200    2.38008000    0.33852800
 H                 -2.63298100   -1.52435700   -2.18279100
 H                 -0.91137000   -1.73917300   -1.86477600
 H                 -2.04857500   -3.08746400   -1.53807700
 H                 -2.49545800    2.47843400    1.37299100
 H                 -2.05111200    2.79937400   -0.29655200
 H                 -3.76725200    2.92263900    0.19918400
 H                  2.32846900    2.93480000   -1.15241500
```

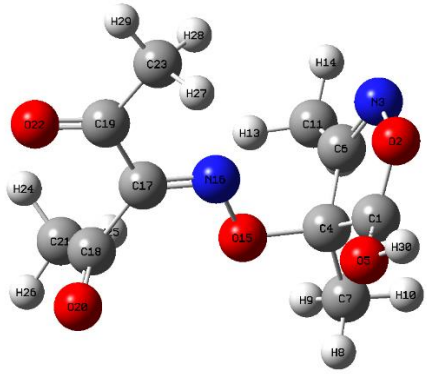
Intermediate **III**, conformation **III(8)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=              -874.064990
 Sum of electronic and thermal Enthalpies=            -874.064046
 Sum of electronic and thermal Free Energies=         -874.133692
 BSSE energy =       0.003784094780
0 2
 C                 -2.57499200   -0.94991800    0.08538900
 O                 -3.46801500   -0.47825300   -0.84211000
 N                 -3.06223300    0.80166600   -1.26097400
 C                 -1.58067800    0.11418000    0.41092500
 C                 -2.02950500    1.15483000   -0.59624500
 C                 -1.58206800    0.58310100    1.85833900
 H                 -1.31897800   -0.24803400    2.51422300
 H                 -0.86499100    1.39149900    1.99864000
 H                 -2.57827700    0.93954000    2.12687000
 C                 -1.39034500    2.48038600   -0.81119900
 H                 -1.33851600    3.03060800    0.13146100
 H                 -0.36802500    2.35363600   -1.17331900
 H                 -1.96188000    3.05995400   -1.53568100
 O                 -0.27853900   -0.43705800    0.04350900
 N                  0.73484500    0.44198200    0.28769700
 C                  1.87590600   -0.03903100   -0.01182500
 C                  2.08480700   -1.42716400   -0.59936900
 C                  3.08051900    0.81965900    0.23014200
 O                  2.23197900   -1.53898600   -1.79154100
 C                  2.10412600   -2.56197600    0.37451200
 O                  4.17660400    0.32247300    0.08402100
 C                  2.86568700    2.24715200    0.63871800
 H                  2.93835900   -2.41804600    1.06824000
 H                  1.18221300   -2.55195100    0.96229300
 H                  2.21246500   -3.51098700   -0.14862700
 H                  2.35874600    2.78529300   -0.16647600
 H                  2.22074800    2.30091400    1.51780800
 H                  3.82865800    2.71082800    0.84493100
 O                 -3.08573900   -1.71371000    1.06701500
 H                 -3.74986400   -2.31182700    0.70912100
```

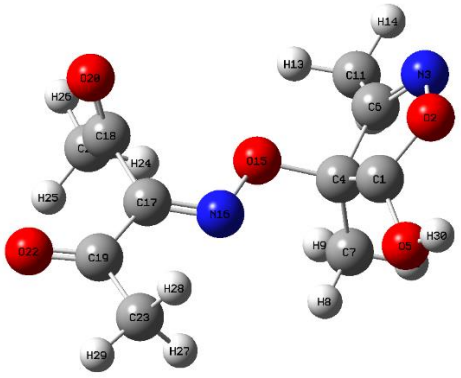
Intermediate **III**, conformation **III(9)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=              -874.067987
 Sum of electronic and thermal Enthalpies=            -874.067043
 Sum of electronic and thermal Free Energies=         -874.136017
 BSSE energy =       0.004275976811
0 2
 C                 -2.21214000    0.55098000   -1.05107500
 O                 -2.46815600    1.61361500   -0.22655700
 N                 -2.50165200    1.14229600    1.09350700
 C                 -1.74942700   -0.61260100   -0.25573600
 O                 -1.72366800    0.81929000   -2.26623900
 C                 -2.13223900   -0.08350800    1.10708300
 C                 -2.33099900   -1.95913300   -0.64507200
 H                 -2.06898500   -2.18788400   -1.67945400
 H                 -1.93423200   -2.74248200    0.00353000
 H                 -3.41707400   -1.93514400   -0.55206000
 C                 -2.03385700   -0.86742100    2.36467600
 H                 -2.71849600   -1.71913100    2.33510600
 H                 -1.02013300   -1.26110100    2.47769500
 H                 -2.27536400   -0.24423400    3.22497500
 O                 -0.29488100   -0.83848200   -0.32015900
 N                  0.39250800    0.29778100   -0.01456800
 C                  1.65391400    0.12547400   -0.03742600
 C                  2.32234500   -1.19528700   -0.38915900
 C                  2.52612500    1.29340500    0.31301700
 O                  2.72259000   -1.36932300   -1.51376600
 C                  2.44265200   -2.18837800    0.72349100
 O                  3.71786800    1.10133800    0.42945700
 C                  1.87841100    2.63245100    0.50344800
 H                  3.05437600   -1.75366600    1.52007400
 H                  1.45208200   -2.38763500    1.14143300
 H                  2.89661600   -3.11085700    0.36419500
 H                  1.41878600    2.95340300   -0.43474100
 H                  1.07964100    2.56816200    1.24486200
 H                  2.63077300    3.35446400    0.81585900
 H                 -2.15271300    1.59816400   -2.63542300
```

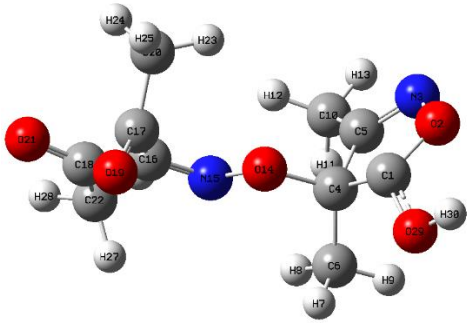
Intermediate **III**, conformation **III(10)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -874.065313
 Sum of electronic and thermal Enthalpies=   -874.064369
 Sum of electronic and thermal Free Energies=   -874.133520
 BSSE energy =   0.003864981517
0 2

C	1.97914100	1.22571100	-0.47438100
O	3.04690300	0.82516700	-1.24164900
N	3.34618600	-0.51964500	-0.95435200
C	1.56595300	0.10366600	0.42113100
O	2.04116300	2.48125200	0.00546800
C	2.55253300	-0.94157600	-0.04792800
C	1.60014200	0.39707900	1.91219100
H	0.89770800	1.19725100	2.14753400
H	1.32223400	-0.49829100	2.47134100
H	2.60102900	0.71210900	2.21227800
C	2.61956300	-2.32810300	0.48179200
H	2.85259600	-2.31154100	1.54976300
H	1.65186800	-2.82061500	0.35926800
H	3.38547000	-2.89967300	-0.04094700
O	0.26000800	-0.43692600	0.05797600
N	-0.70520100	0.51886500	0.15593200
C	-1.86894100	0.05466600	-0.07531500
C	-2.14257600	-1.39910700	-0.43187700
C	-3.03193500	0.99516100	0.02010900
O	-2.29088100	-1.70193700	-1.59010200
C	-2.21754400	-2.35526800	0.71673000
O	-4.14955700	0.53076800	-0.05653400
C	-2.75273300	2.45697300	0.20566400
H	-1.29920800	-2.28769400	1.30643000
H	-3.04787300	-2.06203400	1.36672600
H	-2.36627700	-3.37243300	0.35693600
H	-2.10934400	2.61629700	1.07307600
H	-2.21638900	2.83998800	-0.66618900
H	-3.69410100	2.98990500	0.32706800
H	2.45268200	3.06039200	-0.64431800

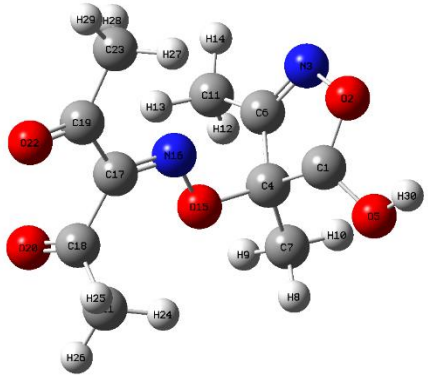
Intermediate **III**, conformation **III(11)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=              -874.065059
 Sum of electronic and thermal Enthalpies=            -874.064114
 Sum of electronic and thermal Free Energies=         -874.133919
 BSSE energy =       0.003766483884
0 2
 C                  2.59159400   -0.89621300   -0.25109300
 O                  3.42179500   -0.59122400    0.79730500
 N                  2.96913300    0.58917200    1.41335900
 C                  1.58602000    0.19177600   -0.42891700
 C                  1.96508900    1.04401200    0.76651300
 C                  1.63258400    0.90767000   -1.76999400
 H                  1.42102600    0.19879900   -2.57160300
 H                  0.89800100    1.71181200   -1.79968900
 H                  2.62793300    1.32762400   -1.92610900
 C                  1.29297300    2.30585000    1.17714000
 H                  1.27643900    3.01203600    0.34341000
 H                  0.25695800    2.11018400    1.46152100
 H                  1.81985300    2.75528800    2.01848200
 O                  0.28398700   -0.43955600   -0.22175100
 N                 -0.74088900    0.45164000   -0.34162800
 C                 -1.87535100   -0.08271900   -0.11649900
 C                 -2.06895200   -1.55507000    0.21598800
 C                 -3.08657200    0.79773200   -0.17961000
 O                 -2.38687800   -2.31548900   -0.66498600
 C                 -1.85765400   -1.94272600    1.64503500
 O                 -4.15185100    0.33053600    0.16239900
 C                 -2.91638600    2.20911200   -0.65908900
 H                 -0.86283800   -1.62208900    1.96599200
 H                 -2.58970800   -1.41587500    2.26509500
 H                 -1.96967200   -3.01896700    1.76845600
 H                 -2.15313400    2.72317600   -0.07153100
 H                 -2.57484100    2.20472100   -1.69727600
 H                 -3.86847900    2.73126200   -0.58333700
 O                  3.17247800   -1.45585400   -1.32597700
 H                  3.82443100   -2.10751000   -1.04829800
```

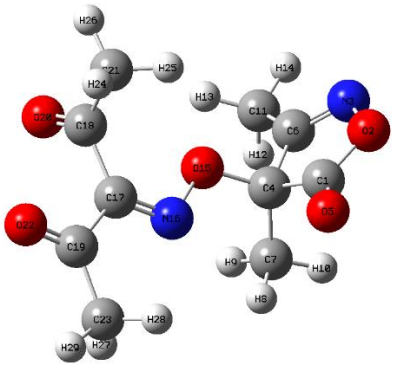
Intermediate **III**, conformation **III(12)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=              -874.068202
 Sum of electronic and thermal Enthalpies=            -874.067257
 Sum of electronic and thermal Free Energies=         -874.137187
 BSSE energy =       0.003889252163
0 2
 C                 -2.04997100    0.01780600   -1.17876500
 O                 -2.69050900    1.21206500   -0.96521900
 N                 -2.63720300    1.52389000    0.40756800
 C                 -1.65117400   -0.57498100    0.13041300
 O                 -2.55597300   -0.76415500   -2.14956400
 C                 -2.07125300    0.56429500    1.03128500
 C                 -2.27704300   -1.91775300    0.47130900
 H                 -1.98264700   -2.66220800   -0.26909800
 H                 -1.94430700   -2.24428900    1.45770700
 H                 -3.36467900   -1.83184600    0.46974800
 C                 -1.86192100    0.58792500    2.50167500
 H                 -2.40790100   -0.23350000    2.97311700
 H                 -0.80131400    0.45475100    2.72930700
 H                 -2.20581600    1.53234800    2.92169100
 O                 -0.21872100   -0.81473800    0.22559400
 N                  0.48797100    0.32535400   -0.02268700
 C                  1.74590800    0.12889800   -0.00397600
 C                  2.38648200   -1.22266100    0.27483500
 C                  2.64267600    1.29936200   -0.27733000
 O                  2.76640300   -1.47023200    1.39295600
 C                  2.50444200   -2.14960500   -0.89311000
 O                  3.83330900    1.09370200   -0.37918100
 C                  2.01958100    2.65639300   -0.41598300
 H                  1.51993300   -2.29023700   -1.34753000
 H                  3.15048100   -1.68713000   -1.64591500
 H                  2.92119700   -3.10594500   -0.58024200
 H                  1.26016600    2.64631000   -1.20056100
 H                  1.51526200    2.92879900    0.51426100
 H                  2.79424500    3.38485500   -0.64867100
 H                 -2.81242600   -0.22783000   -2.90679000
```

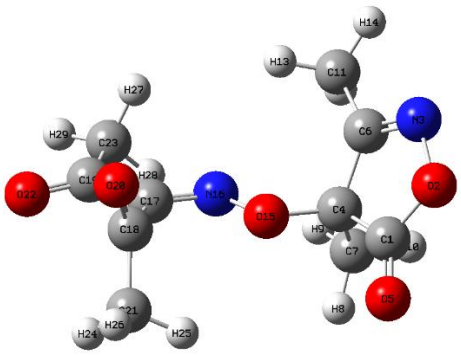
3-(((3,4-dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione
5b, conformation 5b(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -873.533896
 Sum of electronic and thermal Enthalpies=   -873.532952
 Sum of electronic and thermal Free Energies=   -873.601073
 BSSE energy =   0.003944798199
0 1

C	1.93401000	-1.11220400	0.88249300
O	3.04614100	-0.54301100	1.39802900
N	3.44937700	0.57247200	0.60461500
C	1.58255400	-0.36129200	-0.40743300
O	1.38147000	-2.03706000	1.39477800
C	2.64596100	0.70369400	-0.37525400
C	1.65890400	-1.25774900	-1.63220600
H	0.97634000	-2.09892000	-1.51947700
H	1.38783700	-0.68477300	-2.52061900
H	2.67556400	-1.63807900	-1.75032300
C	2.78512900	1.78966700	-1.37603300
H	2.95442300	1.36367100	-2.36818800
H	1.86113200	2.37126900	-1.41579800
H	3.61758200	2.44215600	-1.11662700
O	0.33419500	0.31537000	-0.26764300
N	-0.73453700	-0.54152900	-0.38049600
C	-1.83152200	0.04698000	-0.11921500
C	-1.93889900	1.51718800	0.26206700
C	-3.09470200	-0.76406600	-0.18445200
O	-2.16409100	2.32856700	-0.60112100
C	-1.76124100	1.83158300	1.71278600
O	-4.12574300	-0.23150800	0.16326100
C	-3.00758100	-2.18030900	-0.66667700
H	-2.54755400	1.32660100	2.28224300
H	-0.80232200	1.43420500	2.05717000
H	-1.81041600	2.90679700	1.87833200
H	-2.64179100	-2.19783300	-1.69628000
H	-2.29307500	-2.74220700	-0.06140800
H	-3.99306000	-2.63929700	-0.61274700

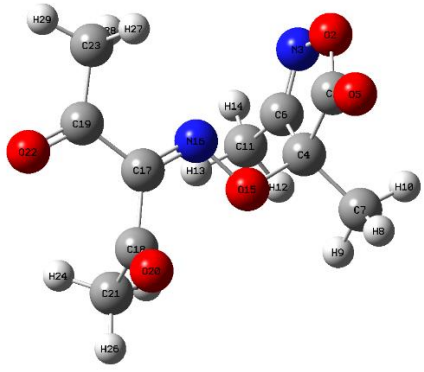
3-(((3,4-dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione
5b, conformation 5b(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -873.533755

```
 Sum of electronic and thermal Enthalpies=            -873.532811
 Sum of electronic and thermal Free Energies=         -873.600212
 BSSE energy =       0.003913614974
0 1
 C                 -2.59342400   -1.00924500    0.23967600
 O                 -3.51433800   -0.58570400   -0.64822600
 N                 -3.18711200    0.72136400   -1.12320600
 C                 -1.59506800    0.13024900    0.45683400
 O                 -2.61900700   -2.08660500    0.74980800
 C                 -2.12237500    1.12398400   -0.54945800
 C                 -1.63539700    0.62540600    1.89386100
 H                 -1.36892200   -0.19628200    2.56095300
 H                 -0.93177900    1.44690100    2.02598200
 H                 -2.63911100    0.97509800    2.14364700
 C                 -1.53422600    2.45354100   -0.85140000
 H                 -1.44378200    3.03930700    0.06642700
 H                 -0.53079600    2.33078600   -1.26428000
 H                 -2.15937600    2.98842800   -1.56545400
 O                 -0.32954700   -0.41764800    0.08996500
 N                  0.68528700    0.48686600    0.28488000
 C                  1.81894900   -0.00295300   -0.02045500
 C                  2.02300300   -1.40992300   -0.56796600
 C                  3.02847300    0.87021900    0.16700400
 O                  2.13403500   -1.55285800   -1.75991100
 C                  2.07985100   -2.51143100    0.44041900
 O                  4.11927100    0.36457300    0.02276800
 C                  2.81654800    2.31177600    0.51908800
 H                  2.91747800   -2.32831200    1.12046100
 H                  1.16350400   -2.50360600    1.03720200
 H                  2.20204200   -3.47338500   -0.05504000
 H                  2.28915500    2.81310500   -0.29668400
 H                  2.19144700    2.39941100    1.40985300
 H                  3.78159300    2.78712400    0.68436400
```

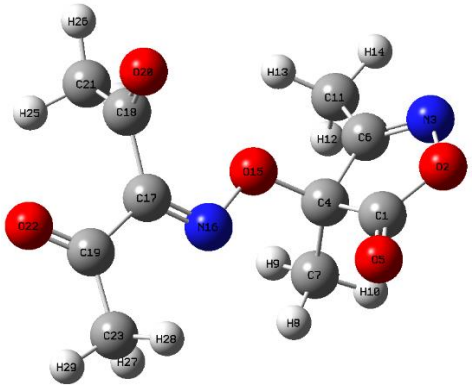
3-(((3,4-dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione
5b, conformation 5b(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)




```
Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=            -873.537265
 Sum of electronic and thermal Enthalpies=          -873.536321
```

```
 Sum of electronic and thermal Free Energies=         -873.602742
 BSSE energy =       0.004106309316
0 1
 C                 -2.10853600    0.58147700   -1.11436600
 O                 -2.75126500    1.47553500   -0.33488400
 N                 -2.71287000    1.06553100    1.03468700
 C                 -1.68013600   -0.58897600   -0.22166900
 O                 -1.96054200    0.72329400   -2.28948800
 C                 -2.10546800   -0.05065200    1.12014700
 C                 -2.37907600   -1.87790400   -0.61467600
 H                 -2.12538500   -2.12217400   -1.64710300
 H                 -2.05280800   -2.68631100    0.04121500
 H                 -3.46111100   -1.76523100   -0.52963500
 C                 -1.87691900   -0.73135300    2.41828300
 H                 -2.36972500   -1.70682600    2.42063200
 H                 -0.80655600   -0.89849300    2.56229900
 H                 -2.26331300   -0.12911200    3.23928300
 O                 -0.28559400   -0.83482800   -0.31213800
 N                  0.41179900    0.32427400   -0.04689600
 C                  1.66944300    0.14415300   -0.06521000
 C                  2.33801600   -1.18979700   -0.37396400
 C                  2.54970200    1.32714900    0.23932600
 O                  2.71748400   -1.39860300   -1.49842100
 C                  2.48042300   -2.13790700    0.77321900
 O                  3.73609300    1.12559900    0.37211100
 C                  1.90911200    2.67553600    0.36297800
 H                  3.09227700   -1.66736800    1.54885300
 H                  1.49590100   -2.33621300    1.20598100
 H                  2.94371100   -3.06624100    0.44245200
 H                  1.44213200    2.94826000   -0.58673500
 H                  1.11748400    2.65281800    1.11478100
 H                  2.66611500    3.40993300    0.63159800
```

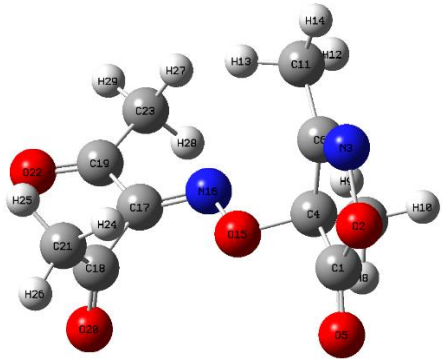
3-(((3,4-dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione
5b, conformation 5b(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)




```
Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=             -873.533150
 Sum of electronic and thermal Enthalpies=           -873.532206
 Sum of electronic and thermal Free Energies=        -873.599896
```

```
 BSSE energy =       0.003953539680
0 1
 C                 -2.00478700   -1.24472200   -0.68686700
 O                 -3.12364600   -0.74653500   -1.26005700
 N                 -3.47151300    0.50418900   -0.67104100
 C                 -1.58531500   -0.27869900    0.42868400
 O                 -1.49850100   -2.26697300   -1.03414200
 C                 -2.62782300    0.79032100    0.23937100
 C                 -1.62802800   -0.93419200    1.79886000
 H                 -0.96219100   -1.79609300    1.81680400
 H                 -1.31459800   -0.21494500    2.55764600
 H                 -2.64408900   -1.26606100    2.02130000
 C                 -2.70836900    2.04403500    1.02839200
 H                 -2.83417800    1.81116700    2.08873700
 H                 -1.77931300    2.60790400    0.91703300
 H                 -3.54601400    2.65258600    0.69074400
 O                 -0.33022600    0.32876900    0.12482200
 N                  0.72248200   -0.52956900    0.33319800
 C                  1.82853500   -0.00417800   -0.01113000
 C                  1.96187800    1.38468900   -0.62230000
 C                  3.07988700   -0.80970400    0.19833500
 O                  2.00054900    1.49004100   -1.82251300
 C                  2.05096300    2.52384000    0.34239000
 O                  4.14254800   -0.26668400   -0.01036300
 C                  2.94374000   -2.23082500    0.65403800
 H                  1.20160300    2.49037900    1.03004400
 H                  2.96070800    2.40751600    0.93968700
 H                  2.07443100    3.47295100   -0.19106400
 H                  2.39728000   -2.27302900    1.59875600
 H                  2.36550500   -2.80051700   -0.07728400
 H                  3.93418700   -2.66653500    0.77188600
```

3-(((3,4-dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione
5b, conformation 5b(5) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

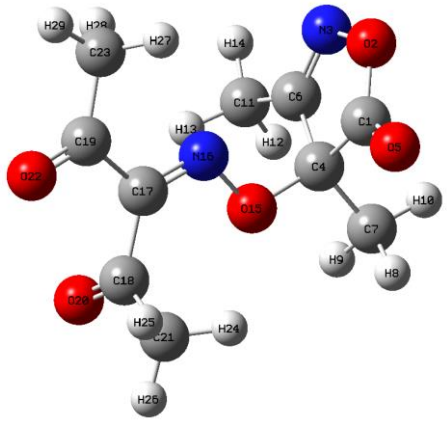



```
Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=             -873.533446
 Sum of electronic and thermal Enthalpies=           -873.532502
 Sum of electronic and thermal Free Energies=        -873.600052
 BSSE energy =       0.003895279262
```

0 1

C	-2.62131400	-0.92862400	0.39143300
O	-3.48823400	-0.63445700	-0.59880900
N	-3.10474000	0.57295800	-1.25700900
C	-1.60006700	0.20925800	0.47176400
O	-2.70291700	-1.90884800	1.06446400
C	-2.05763200	1.04202700	-0.70147500
C	-1.68010800	0.92450400	1.81061500
H	-1.46816300	0.21035100	2.60810600
H	-0.95444500	1.73657200	1.84497000
H	-2.68048600	1.33627400	1.95713600
C	-1.42345500	2.29618600	-1.18145800
H	-1.35557400	3.01784900	-0.36403300
H	-0.40749300	2.09169000	-1.52590700
H	-2.00530000	2.72363700	-1.99730100
O	-0.33627300	-0.41646100	0.24894200
N	0.69235300	0.48939000	0.33531900
C	1.81925800	-0.04929300	0.09407100
C	2.01379200	-1.52828500	-0.21477300
C	3.03401100	0.83665200	0.12080900
O	2.35534300	-2.26312900	0.67760300
C	1.77605400	-1.94640700	-1.63020500
O	4.08597300	0.36525700	-0.24988000
C	2.87462200	2.24807500	0.59993100
H	0.77202000	-1.64207000	-1.93794600
H	2.49020700	-1.42692800	-2.27677700
H	1.89510200	-3.02398700	-1.73238800
H	2.10295600	2.76162300	0.02276400
H	2.54980800	2.24655700	1.64349100
H	3.82597400	2.76854200	0.50689000

3-(((3,4-dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione
5b, conformation 5b(6) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

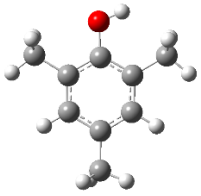
Sum of electronic and thermal Energies=	-873.538108
Sum of electronic and thermal Enthalpies=	-873.537164
Sum of electronic and thermal Free Energies=	-873.604957
BSSE energy =	0.004125055680

0 1

C	-2.02137200	0.21399700	-1.27986300
O	-2.71358000	1.29057900	-0.85693900
N	-2.77885900	1.31465300	0.57284400
C	-1.67529400	-0.62891400	-0.04781000
O	-1.77719200	-0.00037500	-2.42828400
C	-2.18908200	0.28471500	1.03500400
C	-2.36279900	-1.98203100	-0.08502900
H	-2.03390000	-2.52620800	-0.97150400
H	-2.10172000	-2.55029600	0.80881600
H	-3.44616900	-1.85803400	-0.12473800
C	-2.05860900	0.03007300	2.49032700
H	-2.57602100	-0.89541100	2.75519900
H	-1.00375800	-0.09381700	2.74764300
H	-2.47898300	0.85568200	3.06275100
O	-0.28216800	-0.88018800	0.04185200
N	0.41242500	0.30996800	0.00201100
C	1.66912000	0.13333500	0.06445700
C	2.33023400	-1.23207400	0.20403900
C	2.55269700	1.35015800	-0.00079800
O	2.61690900	-1.62483500	1.30713200
C	2.57785800	-1.97523900	-1.06846300
O	3.74980300	1.17400100	-0.04099300
C	1.90283900	2.69980800	-0.01968900
H	1.63483700	-2.09065700	-1.61033400
H	3.24774800	-1.38417100	-1.70046400
H	3.02015100	-2.94831000	-0.86031000
H	1.21578800	2.77483700	-0.86538800
H	1.31186900	2.84041300	0.88843900
H	2.67146700	3.46719500	-0.08929600

Thermochemical calculations for Scheme 11 (S3). C-O coupling of diacetyliminoxyl with phenol 6e

2,4,6-Trimethylphenol 6e (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -425.201483

Sum of electronic and thermal Enthalpies= -425.200539

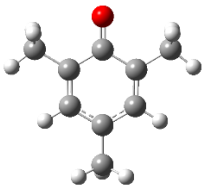
Sum of electronic and thermal Free Energies= -425.245753

0 1

C	0.97611700	-1.20900700	-0.00315500

C	1.02166000	1.17707100	-0.00323900
C	-0.41970100	-1.20584700	-0.00028200
H	1.49198700	-2.16518400	-0.00551500
C	-0.36714800	1.23219800	-0.00034100
H	1.57861200	2.11041400	-0.00575100
C	1.71758800	-0.03300400	-0.00365700
C	-1.07567100	0.02593000	0.00153300
C	3.22502200	-0.05310000	0.00431000
H	3.60759100	-1.07019900	-0.10258900
H	3.63326100	0.54841400	-0.81256600
H	3.62004700	0.35616700	0.93899800
C	-1.11043500	2.53947700	-0.00069100
H	-1.75711000	2.62516100	-0.87843400
H	-1.75536400	2.62655600	0.87817900
H	-0.41449800	3.37992500	-0.00202500
C	-1.20426600	-2.49195600	-0.00078100
H	-1.84345500	-2.57925700	0.88503500
H	-1.84551300	-2.57732800	-0.88529800
H	-0.53420500	-3.35220500	-0.00244300
O	-2.44073800	0.12020700	0.00332400
H	-2.83444300	-0.75468900	0.00362700

2,4,6-Trimethylphenoxyl radical IV (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -424.576470

Sum of electronic and thermal Enthalpies= -424.575525

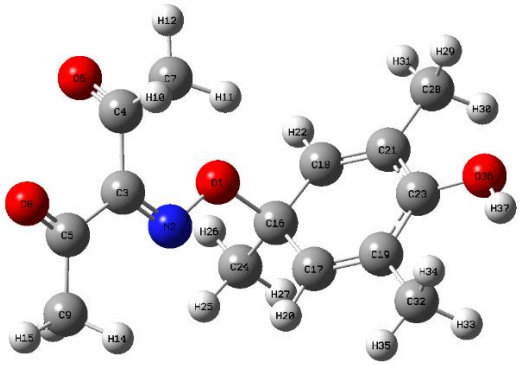
Sum of electronic and thermal Free Energies= -424.624373

0 2

C	-0.95162900	1.21576000	-0.01188400
C	-0.95126700	-1.21616100	-0.01186500
C	0.41968000	1.25442500	-0.00221900
H	-1.51111900	2.14666600	-0.01869200
C	0.42011800	-1.25433600	-0.00220700
H	-1.51039100	-2.14728200	-0.01865700
C	-1.66445800	-0.00035300	-0.01439300
C	1.17019100	0.00016200	0.00406100
C	-3.16252700	-0.00035300	0.01332400
H	-3.57031400	0.88591600	-0.47638300
H	-3.57036400	-0.89076000	-0.46869000
H	-3.51786700	0.00430300	1.04999600
C	1.18974400	-2.53657400	-0.00102600
H	1.84535500	-2.59394800	-0.87428700
H	1.83617000	-2.59761800	0.87878700

H	0.51898200	-3.39664000	-0.00625400
C	1.18889500	2.53691600	-0.00102100
H	1.83498200	2.59834700	0.87901500
H	1.84479400	2.59433500	-0.87405700
H	0.51785000	3.39676000	-0.00663600
O	2.41617900	0.00037600	0.01240500

Intermediate V, conformation V(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -899.517228

Sum of electronic and thermal Enthalpies= -899.516284

Sum of electronic and thermal Free Energies= -899.591004

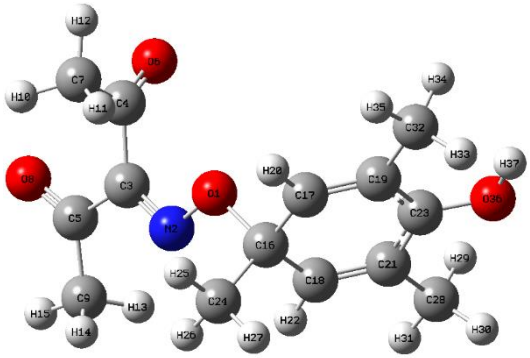
BSSE energy = 0.003272047788

0 2

O	-0.41114600	-0.43385700	0.61705200
N	-1.44303200	0.43171400	0.52089900
C	-2.47098800	-0.08670400	-0.03159600
C	-2.52182200	-1.52664300	-0.51598400
C	-3.67504200	0.77424100	-0.22568300
O	-3.05506300	-2.36508500	0.17017200
C	-1.89855900	-1.79369000	-1.85053600
O	-4.60791900	0.33061900	-0.86427800
C	-3.67239600	2.15085900	0.37446800
H	-2.44854200	-1.23315000	-2.61309600
H	-0.86871200	-1.42672800	-1.84987400
H	-1.92518400	-2.85833000	-2.07915100
H	-3.60510400	2.07802700	1.46277400
H	-2.80020200	2.71299400	0.03518300
H	-4.58866500	2.66687600	0.09259900
C	0.82284800	0.21089000	1.19127100
C	1.22381100	1.34492400	0.30770400
C	1.80702400	-0.91021800	1.18067200
C	2.29659900	1.29865700	-0.52808300
H	0.59873800	2.23108800	0.33731500
C	2.88076800	-0.95466600	0.35187600
H	1.61621600	-1.72916500	1.86713200
C	3.11991000	0.13859900	-0.53060400
C	0.48404100	0.66448700	2.60849800

H	-0.29101400	1.43310900	2.59255900
H	0.13432000	-0.18281900	3.20343000
H	1.37768600	1.07916200	3.07928700
C	3.83501900	-2.11669000	0.34741600
H	3.86868800	-2.58751300	-0.63849600
H	4.85159100	-1.79035800	0.58169500
H	3.53117900	-2.86560800	1.07968100
C	2.63782800	2.45499900	-1.43152200
H	3.63481100	2.85483700	-1.21789200
H	2.60941400	2.16310000	-2.48706000
H	1.92317100	3.26719600	-1.29947000
O	4.19767800	0.02712500	-1.34446600
H	4.28019200	0.80059400	-1.90814100

Intermediate V, conformation V(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -899.516821

Sum of electronic and thermal Enthalpies= -899.515877

Sum of electronic and thermal Free Energies= -899.590560

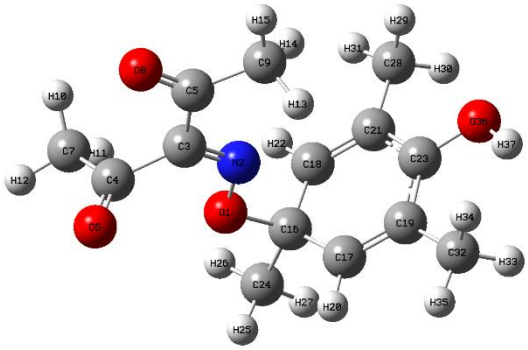
BSSE energy = 0.003223497986

0 2

O	0.40923200	-0.45492800	0.39245200
N	1.41991400	0.43971800	0.42386100
C	2.47832100	0.01194600	-0.14796000
C	2.58206400	-1.35176800	-0.81124600
C	3.68125000	0.89574500	-0.15370600
O	2.44618400	-1.44118800	-2.00757300
C	2.86780200	-2.50569100	0.09841200
O	4.72497000	0.44929200	-0.58554100
C	3.54416400	2.29292300	0.37898700
H	3.84340000	-2.34832300	0.56915600
H	2.11911800	-2.53345600	0.89471000
H	2.86852700	-3.44181300	-0.45845600
H	2.82812400	2.85073000	-0.22941700
H	3.15477200	2.27532700	1.39877700
H	4.51584100	2.78329100	0.35351800
C	-0.82164100	0.05382300	1.09334300
C	-1.77202800	-1.08659100	0.95143000

C	-1.29103100	1.29197800	0.40455300
C	-2.89938300	-1.03293500	0.19306300
H	-1.51831600	-1.99861000	1.48248500
C	-2.41433400	1.34473800	-0.35634600
H	-0.67495400	2.17716800	0.52286300
C	-3.22138700	0.17768400	-0.48228400
C	-0.44655100	0.30364000	2.55252200
H	-0.04676900	-0.60859500	3.00306800
H	0.30055500	1.09613600	2.62785900
H	-1.33593800	0.60838900	3.10762800
C	-2.83909600	2.60388900	-1.06018100
H	-2.88728300	2.44699200	-2.14093000
H	-3.83497900	2.91767100	-0.73683400
H	-2.13547400	3.41233100	-0.85789800
C	-3.81494100	-2.22190300	0.06532400
H	-4.82656600	-1.99308400	0.41679700
H	-3.88566000	-2.56245300	-0.97325700
H	-3.44258600	-3.05749300	0.65764100
O	-4.32690300	0.29311800	-1.25771900
H	-4.80833300	-0.53745600	-1.29315700

Intermediate V, conformation V(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -899.519800

Sum of electronic and thermal Enthalpies= -899.518856

Sum of electronic and thermal Free Energies= -899.593826

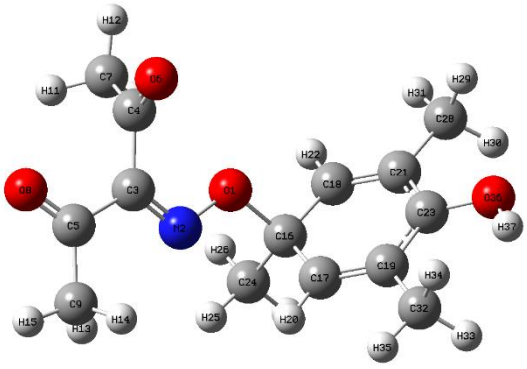
BSSE energy = 0.003551284607

0 2

O	0.65795500	-1.24616200	-0.13821200
N	0.86585700	0.08439700	-0.06683700
C	2.10254700	0.39950600	-0.07056600
C	3.23068900	-0.61376800	-0.16793500
C	2.45011700	1.84750100	0.03689200
O	3.74695400	-0.82559700	-1.23895000
C	3.63055300	-1.27984600	1.11161300
O	3.61890200	2.15740000	0.15155900
C	1.33342600	2.85132400	0.00220600
H	3.99934100	-0.51746200	1.80502000
H	2.75183500	-1.74213000	1.56937100

H	4.40394300	-2.02518100	0.93055500
H	0.82417400	2.80110800	-0.96339200
H	0.59013700	2.62137400	0.76794800
H	1.74254700	3.84849800	0.15599200
C	-0.81250600	-1.57526900	-0.10141300
C	-1.45903400	-0.95345400	-1.29072900
C	-1.37179100	-1.08558400	1.18982700
C	-2.36464100	0.05774900	-1.20584000
H	-1.14778500	-1.32477400	-2.26236300
C	-2.27657300	-0.07710000	1.27807800
H	-0.99604800	-1.55900600	2.09217400
C	-2.76259700	0.51945400	0.07965000
C	-0.77919800	-3.09749400	-0.18447300
H	-0.29345800	-3.41852400	-1.10885800
H	-0.23469100	-3.51359600	0.66652100
H	-1.79944700	-3.48439100	-0.17087700
C	-2.78440200	0.42414200	2.60163000
H	-2.54530800	1.48272100	2.73380500
H	-3.87145200	0.33057100	2.66713800
H	-2.33612500	-0.13777300	3.42199100
C	-2.95592500	0.68953100	-2.43866500
H	-4.04646200	0.59067500	-2.46149400
H	-2.71152300	1.75567600	-2.49941600
H	-2.56417700	0.21445600	-3.33789600
O	-3.64802700	1.53498800	0.23105300
H	-3.91677500	1.88179500	-0.62360900

Intermediate V, conformation V(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -899.516867

Sum of electronic and thermal Enthalpies= -899.515923

Sum of electronic and thermal Free Energies= -899.590484

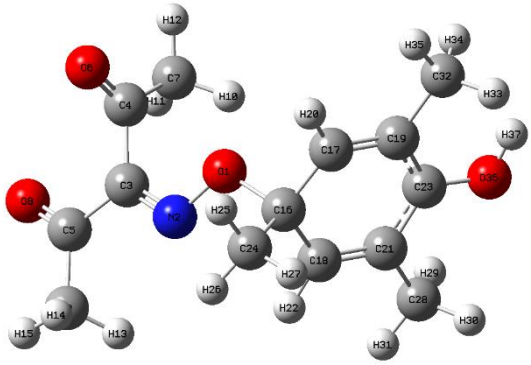
BSSE energy = 0.003222756258

0 2

O	-0.40714800	-0.45688700	0.40492100
N	-1.42179000	0.43303900	0.44054400
C	-2.47477700	0.00869500	-0.14372900
C	-2.56756800	-1.34398600	-0.83092500

C	-3.68162800	0.88723600	-0.14333400
O	-2.42704300	-1.41003600	-2.02827500
C	-2.84864900	-2.51641800	0.05598600
O	-4.71991100	0.44435800	-0.59155700
C	-3.55557000	2.27480400	0.41686900
H	-2.10222200	-2.55434100	0.85396900
H	-3.82669400	-2.37423300	0.52647600
H	-2.84154500	-3.44190900	-0.51833400
H	-3.18255700	2.23856900	1.44232900
H	-2.83128600	2.84555200	-0.16926300
H	-4.52792200	2.76351100	0.38573400
C	0.82327900	0.05588200	1.10455000
C	1.29105400	1.28754400	0.40370800
C	1.77458200	-1.08539300	0.97299900
C	2.41142200	1.33002300	-0.36690700
H	0.67645800	2.17451300	0.51537300
C	2.89677300	-1.04105100	0.21117500
H	1.52323900	-1.99057800	1.51702200
C	3.21506900	0.16199000	-0.48301100
C	0.44765300	0.31927700	2.56100700
H	-0.29817300	1.11339700	2.63025100
H	0.04663300	-0.58875600	3.01882600
H	1.33772700	0.62648000	3.11366600
C	3.82105800	-2.22052400	0.08770700
H	3.90281900	-2.54164300	-0.95391300
H	4.82909000	-1.96617500	0.42524600
H	3.45514100	-3.05874200	0.68185400
C	2.82187500	2.58828200	-1.08630300
H	3.81191000	2.93242600	-0.76842100
H	2.84727000	2.43902700	-2.17123600
H	2.11448200	3.39250000	-0.88477500
O	4.34124300	0.13973500	-1.23650500
H	4.47358200	0.98360700	-1.67602900

Intermediate V, conformation V(5) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



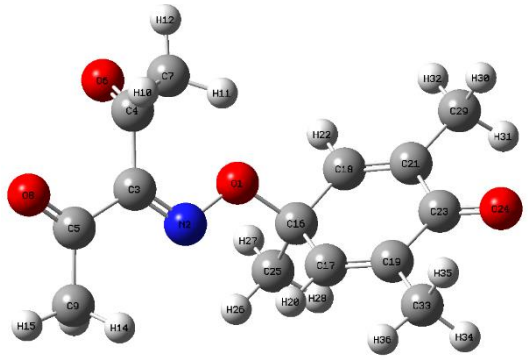
Number of imaginary frequencies = 0

Sum of electronic and thermal Energies=	-899.517245
Sum of electronic and thermal Enthalpies=	-899.516301

Sum of electronic and thermal Free Energies= -899.590688
BSSE energy = 0.003280968345
0 2

O	0.41011500	-0.42403600	0.62654700
N	1.44724400	0.43452800	0.52337900
C	2.47107700	-0.09386000	-0.02722900
C	2.50997500	-1.53619300	-0.50517000
C	3.68094600	0.75740500	-0.22732700
O	3.02872400	-2.37823700	0.18768600
C	1.89253000	-1.80089900	-1.84292200
O	4.61327600	0.30048400	-0.85736000
C	3.68432900	2.14128600	0.35585500
H	0.86649800	-1.42331000	-1.84975000
H	2.45250700	-1.24798400	-2.60375100
H	1.90982600	-2.86640600	-2.06840500
H	2.81793300	2.70485500	0.00422900
H	3.61020900	2.08293700	1.44455500
H	4.60558800	2.64760800	0.07264700
C	-0.82162300	0.23543800	1.18874400
C	-1.81101700	-0.88076500	1.19228100
C	-1.21539100	1.35855800	0.28770300
C	-2.88423400	-0.93153100	0.35879600
H	-1.62761800	-1.69027700	1.89160100
C	-2.28332400	1.30595700	-0.54944400
H	-0.58553400	2.24180100	0.30686900
C	-3.11363900	0.14870400	-0.53928600
C	-0.48430600	0.70651800	2.60063300
H	-0.13928100	-0.13370800	3.20825300
H	0.29382000	1.47173100	2.57563800
H	-1.37724800	1.13165300	3.06335400
C	-2.62641000	2.44144100	-1.47379200
H	-2.61197400	2.11237600	-2.51616700
H	-3.63103400	2.82187900	-1.27185700
H	-1.91392300	3.25907100	-1.35774000
C	-3.83980700	-2.09565000	0.37975700
H	-4.85970000	-1.77645400	0.61931900
H	-3.86436600	-2.61240300	-0.58578200
H	-3.53825000	-2.82515800	1.13111200
O	-4.15642900	0.15024400	-1.40482300
H	-4.65828500	-0.66600000	-1.33578300

Intermediate V, conformation V(6) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

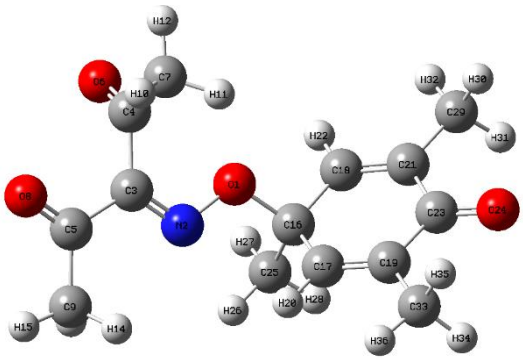


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -899.519636
 Sum of electronic and thermal Enthalpies= -899.518691
 Sum of electronic and thermal Free Energies= -899.593460
 BSSE energy = 0.003535817357
0 2

O	-0.65917300	-1.24412500	-0.12436200
N	-0.87008600	0.08647900	-0.06212400
C	-2.10760600	0.39830900	-0.06755500
C	-3.23328100	-0.61853400	-0.15722300
C	-2.45918300	1.84616500	0.02845100
O	-3.74929900	-0.83976500	-1.22638300
C	-3.63141600	-1.27571000	1.12755500
O	-3.62864900	2.15352300	0.14309100
C	-1.34558400	2.85289300	-0.01736300
H	-2.75172000	-1.73315800	1.58829400
H	-4.00126000	-0.50876800	1.81536900
H	-4.40357800	-2.02374200	0.95249600
H	-0.60477800	2.63620700	0.75466200
H	-0.83174800	2.79021800	-0.97973000
H	-1.75823100	3.85089100	0.12085500
C	0.81167200	-1.56988600	-0.09607600
C	1.37849100	-1.07034700	1.18776200
C	1.45047600	-0.95624800	-1.29419500
C	2.29062000	-0.06375500	1.26123100
H	1.00584900	-1.53312500	2.09672400
C	2.36054700	0.04858700	-1.22428400
H	1.12836200	-1.33222800	-2.26064400
C	2.77249900	0.51805200	0.05596400
C	0.78066600	-3.09298600	-0.16616700
H	0.24260700	-3.50364100	0.69158900
H	0.28943300	-3.42179700	-1.08488200
H	1.80175500	-3.47778000	-0.15680700
C	2.95042500	0.67647000	-2.45664100
H	2.72727300	1.74606500	-2.49176300
H	4.03878200	0.57552800	-2.46733400
H	2.54795500	0.20836200	-3.35581300
C	2.80097800	0.43904600	2.58605100
H	3.88771800	0.33179700	2.66890900

H	2.55284000	1.49536100	2.73661300
H	2.35259700	-0.12106100	3.40645900
O	3.66977000	1.53451200	0.06182900
H	3.88973700	1.79001800	0.96139500

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione
7e, conformation 7e(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -898.947782

Sum of electronic and thermal Enthalpies= -898.946838

Sum of electronic and thermal Free Energies= -899.020363

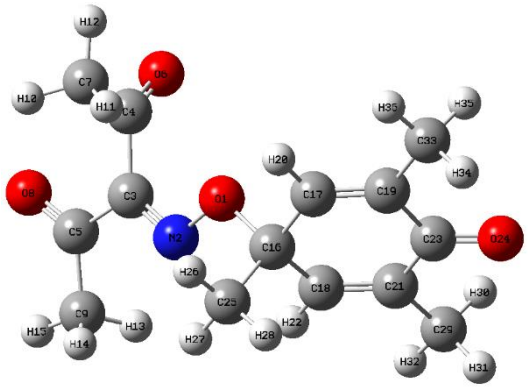
BSSE energy = 0.003280603983

0 1

O	-0.41723800	-0.47070600	0.43267300
N	-1.43622100	0.42920500	0.47042900
C	-2.51822100	-0.04678700	-0.00588800
C	-2.65485300	-1.46765400	-0.53266400
C	-3.71833800	0.84748300	-0.05467000
O	-3.10036900	-2.32252800	0.19298100
C	-2.22236000	-1.68783200	-1.94761900
O	-4.71589800	0.43564000	-0.60818900
C	-3.62318100	2.20575200	0.57557000
H	-2.84002400	-1.06984400	-2.60658300
H	-1.18621300	-1.35812500	-2.06422600
H	-2.32104300	-2.73813000	-2.21821500
H	-3.40921600	2.10598300	1.64231300
H	-2.80020200	2.77107300	0.13320600
H	-4.56357900	2.73459600	0.43091100
C	0.83285700	0.09157600	0.93822500
C	1.24986400	1.24170700	0.07165300
C	1.77309700	-1.07277600	0.88914500
C	2.42623200	1.31388600	-0.55336700
H	0.53775400	2.05965700	0.00588200
C	2.96288400	-1.04419300	0.28720900
H	1.44190500	-1.95991200	1.42244400
C	3.38584100	0.18068100	-0.44650000
O	4.48706400	0.24571600	-0.96647900
C	0.64566400	0.54973900	2.38770800
H	-0.07332100	1.36839600	2.43881000

H	0.28517700	-0.28157500	2.99741300
H	1.60227000	0.89338500	2.78544600
C	3.92273200	-2.19436600	0.30030900
H	4.15131800	-2.51658800	-0.71864500
H	4.86921500	-1.89948700	0.76033300
H	3.50920900	-3.03840600	0.85354100
C	2.85453200	2.49107700	-1.37540400
H	3.76797900	2.93215100	-0.96869600
H	3.07878100	2.18446400	-2.40017200
H	2.07454300	3.25319200	-1.39690200

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione
7e, conformation 7e(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

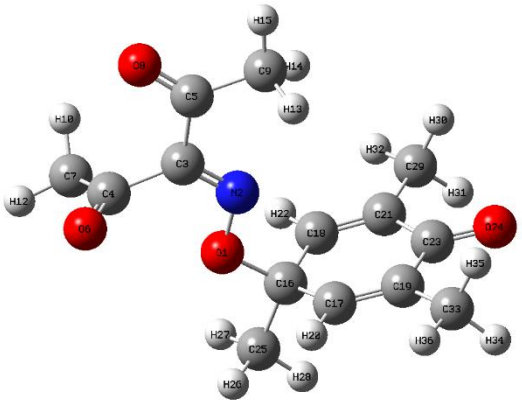


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -898.947380
Sum of electronic and thermal Enthalpies= -898.946436
Sum of electronic and thermal Free Energies= -899.019259
BSSE energy = 0.003265524424
0 1

O	0.41401900	-0.47065600	0.26420500
N	1.41109400	0.44664200	0.38142900
C	2.50918000	0.03505500	-0.11740000
C	2.67801500	-1.32006600	-0.78832300
C	3.70109600	0.93787200	-0.03149500
O	2.60199000	-1.39359700	-1.99008800
C	2.94472500	-2.47603600	0.12297300
O	4.77359700	0.50581000	-0.39769900
C	3.50824100	2.32491800	0.50680900
H	3.88699800	-2.29843100	0.65070500
H	2.15331300	-2.53510100	0.87524400
H	3.00272400	-3.40415200	-0.44390900
H	2.81681900	2.87715600	-0.13421800
H	3.06338900	2.28671300	1.50329700
H	4.47035300	2.83287600	0.54211900
C	-0.83340800	-0.00520600	0.86539100
C	-1.74948900	-1.17835100	0.70370100
C	-1.30198800	1.22929300	0.15552400
C	-2.96191000	-1.10530200	0.15315800
H	-1.38085000	-2.11592500	1.11138200

C	-2.50280500	1.34870800	-0.41310300
H	-0.60697000	2.06411700	0.16118000
C	-3.43691700	0.18988100	-0.40790800
O	-4.56000100	0.29232500	-0.87220000
C	-0.61447600	0.28142100	2.35443600
H	-0.21787100	-0.60727000	2.85078000
H	0.08669300	1.10689200	2.48451800
H	-1.56631400	0.55027500	2.81611900
C	-2.98301300	2.60466300	-1.07400300
H	-3.23914000	2.41531600	-2.11941500
H	-3.88891900	2.97367400	-0.58651300
H	-2.21837600	3.38136800	-1.03239400
C	-3.89735800	-2.27151800	0.05828000
H	-4.82759000	-2.06256700	0.59261100
H	-4.16549000	-2.46564100	-0.98314000
H	-3.44260300	-3.16884600	0.47964700

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione
7e, conformation 7e(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

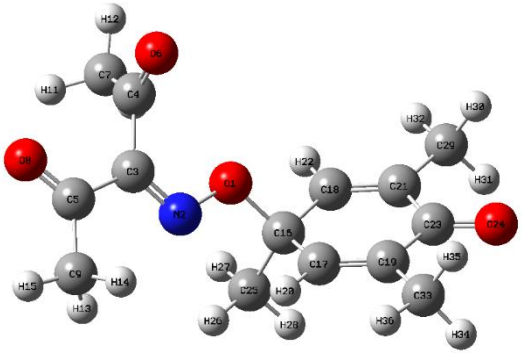


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -898.950038
Sum of electronic and thermal Enthalpies= -898.949094
Sum of electronic and thermal Free Energies= -899.022063
BSSE energy = 0.003518055077
0 1

O	0.61907300	-1.15333600	-0.16759500
N	0.94278600	0.16595100	-0.05907000
C	2.20170100	0.35882400	-0.05397400
C	3.23037900	-0.75487500	-0.18167000
C	2.69297100	1.76735200	0.08962100
O	3.70236700	-0.99546400	-1.26573300
C	3.58767200	-1.46995500	1.08272200
O	3.88564100	1.94664800	0.21738400
C	1.68519500	2.87820200	0.07057800
H	4.01881900	-0.75103900	1.78624900
H	2.67947400	-1.87213200	1.54018400
H	4.29919100	-2.26949700	0.88122100
H	1.17187400	2.89277700	-0.89400900

H	0.92403200	2.71448900	0.83598700
H	2.19302400	3.82650700	0.23711600
C	-0.82429200	-1.34021300	-0.14366000
C	-1.43141900	-0.64443000	-1.32293100
C	-1.35993300	-0.87529200	1.17550000
C	-2.47367300	0.18410200	-1.24249000
H	-0.98695400	-0.88608300	-2.28519500
C	-2.39948500	-0.05012100	1.30748600
H	-0.86356600	-1.28706500	2.05097000
C	-3.05141100	0.50794600	0.09064900
O	-4.02829300	1.23271000	0.18619500
C	-0.98855500	-2.85494300	-0.27959700
H	-0.54391000	-3.19708200	-1.21615100
H	-0.49830600	-3.36176600	0.55399000
H	-2.04938500	-3.10928000	-0.27543000
C	-2.96041800	0.36821400	2.63226500
H	-2.92141700	1.45504200	2.74091600
H	-4.01088400	0.07825800	2.71480100
H	-2.40333400	-0.08921700	3.45089600
C	-3.10884900	0.83197700	-2.43483400
H	-4.16206100	0.55006600	-2.51073400
H	-3.07712500	1.92067100	-2.34428800
H	-2.59855800	0.53850600	-3.35303200

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione
7e, conformation 7e(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies=	-898.947380
Sum of electronic and thermal Enthalpies=	-898.946436
Sum of electronic and thermal Free Energies=	-899.019259

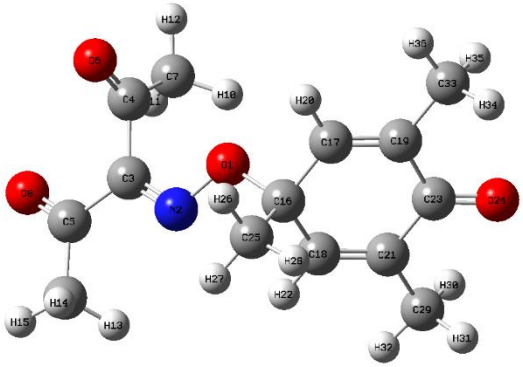
BSSE energy = 0.003265517932

0 1

O	-0.41401700	-0.47066000	0.26420200
N	-1.41109300	0.44663700	0.38142400
C	-2.50918500	0.03505300	-0.11739400
C	-2.67802600	-1.32006300	-0.78832400
C	-3.70109700	0.93787400	-0.03148500
O	-2.60200000	-1.39359000	-1.99008900
C	-2.94474000	-2.47603600	0.12296600
O	-4.77360100	0.50581800	-0.39768800

C	-3.50823600	2.32491900	0.50681800
H	-2.15334200	-2.53509700	0.87525200
H	-3.88702500	-2.29844200	0.65067900
H	-3.00272100	-3.40415100	-0.44392000
H	-3.06335900	2.28671700	1.50329400
H	-2.81683500	2.87716200	-0.13422700
H	-4.47035100	2.83287200	0.54215200
C	0.83341100	-0.00521000	0.86538400
C	1.30198700	1.22928800	0.15551300
C	1.74949300	-1.17835500	0.70369600
C	2.50280600	1.34870600	-0.41310800
H	0.60696600	2.06410900	0.16116600
C	2.96191600	-1.10530300	0.15315800
H	1.38085400	-2.11593000	1.11137600
C	3.43692100	0.18988100	-0.40790700
O	4.56001000	0.29233000	-0.87218400
C	0.61448000	0.28142100	2.35442800
H	-0.08669200	1.10688900	2.48451000
H	0.21787800	-0.60727100	2.85077500
H	1.56631800	0.55027900	2.81610900
C	3.89736800	-2.27151600	0.05828500
H	4.16550700	-2.46563600	-0.98313400
H	4.82759600	-2.06256300	0.59262200
H	3.44261300	-3.16884700	0.47964700
C	2.98301400	2.60466100	-1.07400600
H	3.88892200	2.97366900	-0.58652000
H	3.23913700	2.41531500	-2.11942000
H	2.21837800	3.38136800	-1.03239500

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione
7e, conformation 7e(5) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

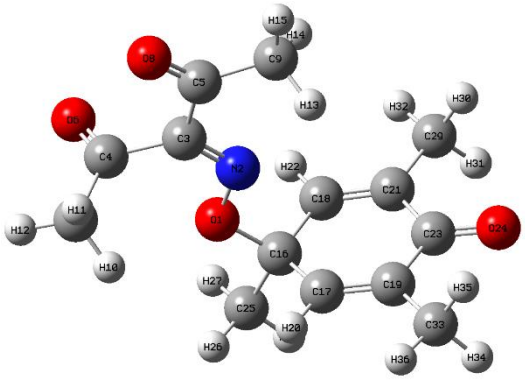


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -898.947782
Sum of electronic and thermal Enthalpies= -898.946838
Sum of electronic and thermal Free Energies= -899.020363
BSSE energy = 0.003280602665
0 1

O	0.41725000	-0.47073800	0.43262200
N	1.43621500	0.42918700	0.47042400

C	2.51823900	-0.04677700	-0.00586800
C	2.65492200	-1.46764000	-0.53264300
C	3.71832600	0.84753400	-0.05462500
O	3.10040900	-2.32251100	0.19302400
C	2.22250700	-1.68781700	-1.94762100
O	4.71594000	0.43569500	-0.60804900
C	3.62305100	2.20586800	0.57546000
H	1.18634400	-1.35816800	-2.06426400
H	2.84015700	-1.06978200	-2.60655300
H	2.32125900	-2.73810500	-2.21823100
H	2.80044700	2.77128100	0.13250300
H	3.40840400	2.10628700	1.64207900
H	4.56361900	2.73453900	0.43127700
C	-0.83285700	0.09149800	0.93818900
C	-1.77308700	-1.07285800	0.88903000
C	-1.24986900	1.24167800	0.07168300
C	-2.96288800	-1.04423100	0.28712300
H	-1.44187700	-1.96003500	1.42225000
C	-2.42625100	1.31390300	-0.55330500
H	-0.53775200	2.05962500	0.00594200
C	-3.38586800	0.18070200	-0.44647300
O	-4.48711900	0.24578900	-0.96638800
C	-0.64569000	0.54957800	2.38770300
H	-0.28520600	-0.28176800	2.99736400
H	0.07328900	1.36823800	2.43886300
H	-1.60230400	0.89319500	2.78544600
C	-2.85456300	2.49114400	-1.37526400
H	-3.07886000	2.18458900	-2.40003800
H	-3.76798300	2.93221600	-0.96849400
H	-2.07455800	3.25324600	-1.39675500
C	-3.92273500	-2.19440700	0.30015400
H	-4.86919500	-1.89957200	0.76025400
H	-4.15137100	-2.51652600	-0.71882100
H	-3.50918400	-3.03850200	0.85328200

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione
7e, conformation 7e(6) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -898.950038

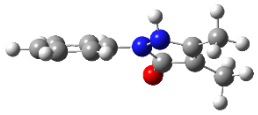
Sum of electronic and thermal Enthalpies= -898.949094
Sum of electronic and thermal Free Energies= -899.022062
BSSE energy = 0.003518061190

0 1

O	-0.61907200	-1.15333200	-0.16763800
N	-0.94278200	0.16595200	-0.05907900
C	-2.20169800	0.35882500	-0.05396700
C	-3.23037400	-0.75487400	-0.18167100
C	-2.69296900	1.76735000	0.08965600
O	-3.70238900	-0.99543500	-1.26572900
C	-3.58764100	-1.46998400	1.08271100
O	-3.88563700	1.94664100	0.21745300
C	-1.68520100	2.87820500	0.07056300
H	-2.67943000	-1.87209600	1.54020200
H	-4.01886000	-0.75109500	1.78622300
H	-4.29910300	-2.26957400	0.88119500
H	-0.92379600	2.71434900	0.83569800
H	-1.17218400	2.89296700	-0.89418600
H	-2.19298500	3.82647900	0.23741700
C	0.82429300	-1.34021200	-0.14369900
C	1.35992500	-0.87532500	1.17547700
C	1.43143000	-0.64440000	-1.32294700
C	2.39947400	-0.05015400	1.30749200
H	0.86355400	-1.28712300	2.05093300
C	2.47368200	0.18413100	-1.24247800
H	0.98697400	-0.88603100	-2.28522200
C	3.05140600	0.50794700	0.09067400
O	4.02828100	1.23271700	0.18624600
C	0.98855500	-2.85493900	-0.27967200
H	0.49830100	-3.36178200	0.55390000
H	0.54391300	-3.19705400	-1.21623700
H	2.04938400	-3.10927700	-0.27550600
C	3.10886600	0.83203600	-2.43480100
H	3.07712700	1.92072800	-2.34423600
H	4.16208300	0.55014000	-2.51069200
H	2.59859100	0.53857600	-3.35301200
C	2.96039600	0.36814900	2.63228500
H	4.01086500	0.07820400	2.71481700
H	2.92138100	1.45497400	2.74096600
H	2.40331400	-0.08931100	3.45090100

Thermochemical calculations for Scheme S2. C-O coupling of diacetyliminoxyl with pyrazolone 8a

4,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one 8a' (NH tautomer of pyrazolone 8a) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

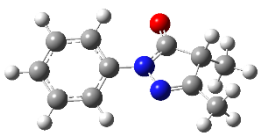


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -610.853051
 Sum of electronic and thermal Enthalpies= -610.852107
 Sum of electronic and thermal Free Energies= -610.905879

0 1

C	1.01157800	-1.03992100	0.04554200
C	2.34916000	-0.47055100	0.09953700
C	2.23113500	0.85983900	-0.12239800
N	0.89525800	1.21340100	-0.23975300
H	0.65479100	1.83039300	-1.00899100
C	-1.23625600	0.07427100	-0.10906800
C	-2.00741300	-1.01720800	-0.51179600
C	-1.85096000	1.21320400	0.41157400
C	-3.38811800	-0.96592000	-0.37341900
H	-1.52406700	-1.89325800	-0.92068700
C	-3.23512800	1.25497300	0.52786200
H	-1.24808600	2.05427000	0.73000300
C	-4.00976100	0.16715900	0.14199200
H	-3.98230700	-1.81840200	-0.68253900
H	-3.70634300	2.14339700	0.93278800
H	-5.08850200	0.20215900	0.23977500
N	0.16636400	0.02584800	-0.25717000
O	0.64485500	-2.19373200	0.24557800
C	3.26161100	1.92804900	-0.23640300
H	3.16771600	2.45786400	-1.18834500
H	3.14762400	2.65899300	0.56766100
H	4.26257500	1.50287500	-0.18052600
C	3.55882500	-1.29098000	0.39418400
H	3.68925100	-2.07568300	-0.35594700
H	4.46291300	-0.68059200	0.40916500
H	3.46619800	-1.78439700	1.36583100

4,5-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one 8a'' (CH tautomer of pyrazolone 8a) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



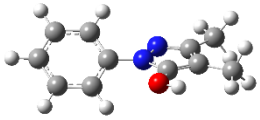
Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -610.855414
 Sum of electronic and thermal Enthalpies= -610.854470

Sum of electronic and thermal Free Energies= -610.907580

0 1

C	0.99161000	-1.10754900	-0.11992800
C	2.16307600	0.89951200	-0.27517100
N	0.91849200	1.19590000	-0.25635800
C	-1.22196800	0.07768700	-0.07094000
C	-2.01925600	-1.01187900	-0.42468900
C	-1.81211800	1.25500000	0.39084700
C	-3.40039900	-0.91704900	-0.30175000
H	-1.56342100	-1.92211600	-0.78626000
C	-3.19399100	1.33614600	0.49883000
H	-1.18772600	2.09753600	0.65562300
C	-3.99579200	0.25191500	0.15788800
H	-4.01352900	-1.76790800	-0.57660300
H	-3.64416200	2.25507000	0.85712800
H	-5.07380400	0.31868300	0.24739400
N	0.18523000	0.00508100	-0.18349000
O	0.63892400	-2.26362800	0.00065200
C	2.41127900	-0.57716300	-0.21492200
H	2.83328500	-0.91494700	-1.16899600
C	3.22522200	1.93574500	-0.35412200
H	3.86483000	1.75657500	-1.22269100
H	2.78546500	2.93005500	-0.42847100
H	3.86202700	1.89217300	0.53412000
C	3.30531200	-1.04825700	0.93306600
H	3.32778800	-2.13861700	0.95750800
H	4.32448900	-0.68266600	0.79759500
H	2.92946100	-0.68633200	1.89271600

3,4-dimethyl-1-phenyl-1H-pyrazol-5-ol 8a''' (OH tautomer of pyrazolone 8a), conformer 8a'''(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -610.846175

Sum of electronic and thermal Enthalpies= -610.845231

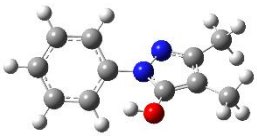
Sum of electronic and thermal Free Energies= -610.899562

0 1

C	-1.23015200	-0.10819800	0.04204900
C	-1.89336300	-1.19029200	-0.53205500
C	-1.95054000	0.94642300	0.59710700
C	-3.28163300	-1.21268100	-0.54977500
H	-1.31626300	-2.00305900	-0.95373300
N	0.18682200	-0.10873700	0.06999100
C	-3.33966100	0.92062000	0.55757900
H	-1.43070500	1.77646700	1.05669200
C	-4.01007700	-0.15630100	-0.01173100

H	-3.79523800	-2.05719400	-0.99494500
C	1.04519400	0.92304200	-0.13883000
N	0.87208200	-1.27338800	0.25692300
H	-3.89851500	1.74396600	0.98757500
H	-5.09356300	-0.17403900	-0.03343600
C	2.33062700	0.43870200	-0.07594600
O	0.55680800	2.15228400	-0.37678400
C	2.14941100	-0.94484900	0.17304500
H	1.28059100	2.74752600	-0.58783500
C	3.22410800	-1.96619800	0.34529200
H	2.78686200	-2.94817000	0.52960800
H	3.85269300	-2.02525900	-0.54778300
H	3.87433700	-1.71040200	1.18683200
C	3.61865200	1.17904700	-0.24817300
H	4.09454300	0.94915300	-1.20620700
H	3.47588200	2.26238400	-0.20512100
H	4.32719200	0.91934700	0.54284400

3,4-dimethyl-1-phenyl-1H-pyrazol-5-ol 8a’’’ (OH tautomer of pyrazolone 8a), conformer 8a’’’(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -610.845214

Sum of electronic and thermal Enthalpies= -610.844270

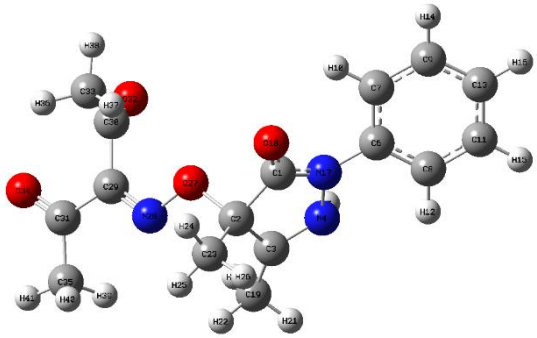
Sum of electronic and thermal Free Energies= -610.898464

0 1

C	-1.21773900	-0.13972400	0.06128200
C	-1.93180900	0.83445400	0.75526900
C	-1.88436000	-1.12781500	-0.65915300
C	-3.32189600	0.83286100	0.70195900
H	-1.40704700	1.57100700	1.35304400
N	0.19857600	-0.13032500	0.08778800
C	-3.27189800	-1.13416100	-0.68499000
H	-1.31002300	-1.87944700	-1.18588000
C	-3.99374600	-0.15015200	-0.01416700
H	-3.87723200	1.59246800	1.23954000
C	1.03284900	0.91487400	-0.16756700
N	0.90647500	-1.27649000	0.29740800
H	-3.79228200	-1.90547700	-1.24087200
H	-5.07699300	-0.15464500	-0.04566000
C	2.32588700	0.45872900	-0.09677400
O	0.61461800	2.16328200	-0.44026500
C	2.17701900	-0.91894400	0.20016700
H	-0.31222700	2.16656900	-0.70119300
C	3.58894700	1.23115700	-0.30022800
H	3.37457100	2.22886000	-0.68778700

H	4.14548400	1.34863800	0.63474600
H	4.24830400	0.72838900	-1.01338600
C	3.27499600	-1.91120800	0.39439700
H	3.91418900	-1.96310700	-0.49166700
H	3.90994400	-1.62983300	1.23927700
H	2.86151000	-2.90239400	0.58441900

Intermediate VI, conformer VI(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

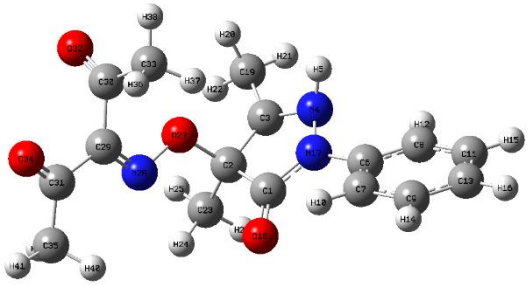


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.168026
Sum of electronic and thermal Enthalpies= -1085.167082
Sum of electronic and thermal Free Energies= -1085.248591
BSSE energy = 0.003991378945
0 2

C	1.14428800	-0.01460000	1.07361500
C	-0.12292800	-0.87252900	0.95887100
C	0.24843400	-1.83058500	-0.10288200
N	1.44355000	-1.43540800	-0.70971500
H	1.37944200	-1.21328500	-1.70340600
C	3.28099100	0.06879300	-0.19865300
C	3.67568100	1.36698600	0.12339400
C	4.19353800	-0.83174600	-0.74576500
C	4.99447300	1.74850400	-0.08602500
H	2.95961700	2.06382200	0.53578000
C	5.50633100	-0.43058100	-0.95942100
H	3.87529600	-1.83551300	-0.99614000
C	5.91408100	0.85641400	-0.62754200
H	5.29991000	2.75680700	0.16886000
H	6.21332400	-1.13389100	-1.38422900
H	6.93985900	1.16394600	-0.79373600
N	1.93763200	-0.32879500	0.00882100
O	1.39083300	0.77956900	1.95797000
C	-0.60730900	-2.84593100	-0.75951200
H	-1.17482800	-2.42314200	-1.60026700
H	-0.00139400	-3.67048700	-1.14507900
H	-1.33227100	-3.24706200	-0.04995200
C	-0.59154000	-1.43730600	2.28264300
H	-0.78141500	-0.62384100	2.98502600
H	-1.50690600	-2.01385600	2.14299900
H	0.17667200	-2.09190800	2.69778900

O	-1.11201600	0.13194300	0.47345000
N	-2.31717500	-0.44218000	0.23629700
C	-3.17429300	0.38576800	-0.21769500
C	-2.86687300	1.84912500	-0.49505400
C	-4.55400600	-0.12142800	-0.49557000
O	-2.60187600	2.18779200	-1.62297500
C	-2.92746200	2.77164300	0.68064200
O	-5.40652100	0.67723800	-0.82316000
C	-4.81389600	-1.59250700	-0.34752800
H	-3.94273000	2.75829900	1.08925600
H	-2.25449700	2.40598900	1.46117900
H	-2.65524800	3.78437900	0.38660900
H	-4.15709300	-2.15690800	-1.01348700
H	-4.58990500	-1.91313500	0.67226100
H	-5.85630700	-1.79800400	-0.58465700

Intermediate VI, conformer VI(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.167367

Sum of electronic and thermal Enthalpies= -1085.166423

Sum of electronic and thermal Free Energies= -1085.248165

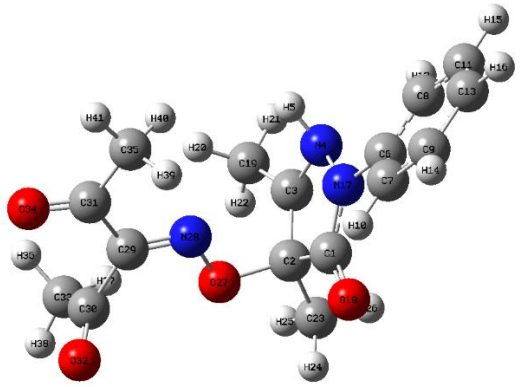
BSSE energy = 0.004123884129

0 2

C	0.80234200	0.19748700	-0.96392100
C	-0.15997000	1.38906900	-0.84531600
C	0.60939800	2.31901900	0.00917500
N	1.74004300	1.68086200	0.52428800
H	1.78210000	1.62146300	1.54183800
C	2.99735800	-0.34830200	0.07135200
C	2.96495700	-1.73681100	-0.05404400
C	4.19778500	0.30912800	0.33525600
C	4.14552200	-2.45856800	0.06402700
H	2.02863300	-2.24149600	-0.24684600
C	5.36801700	-0.42868300	0.46277000
H	4.21105600	1.38683200	0.43497700
C	5.34937200	-1.81184500	0.32349700
H	4.11869500	-3.53725300	-0.03905900
H	6.29985100	0.08594900	0.66722300
H	6.26546900	-2.38256800	0.42056400
N	1.79687800	0.39344200	-0.04720100
O	0.69683900	-0.74047900	-1.72756500

C	0.11716500	3.56892600	0.63251100
H	-0.37472000	3.37994300	1.59669400
H	0.93944200	4.26762500	0.80891800
H	-0.61252000	4.05482200	-0.01726500
C	-0.64484900	1.92228700	-2.17741400
H	-1.13653800	1.13593000	-2.74866700
H	-1.34715800	2.74257600	-2.01549300
H	0.20728300	2.29464800	-2.74841400
O	-1.29764900	0.93509200	-0.01228700
N	-2.15061600	0.10259400	-0.67270800
C	-2.98808700	-0.44286500	0.11894400
C	-3.00255400	-0.19800200	1.61960700
C	-3.98851600	-1.39463100	-0.45825800
O	-3.77382600	0.60570400	2.08400500
C	-2.03276300	-1.00969800	2.42079700
O	-4.70343300	-2.00794600	0.30673300
C	-4.05076300	-1.54496000	-1.94944400
H	-2.28574300	-2.06889700	2.31116300
H	-1.02450100	-0.87054900	2.02100600
H	-2.07103100	-0.72396800	3.47114000
H	-4.34674100	-0.59531700	-2.40222300
H	-3.06614800	-1.79766900	-2.34775300
H	-4.77350800	-2.31863000	-2.20277500

Intermediate VI, conformer VI(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

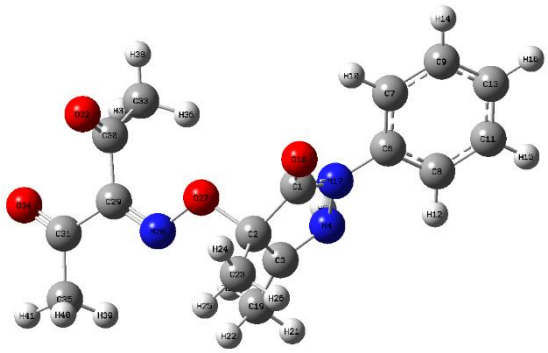


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.171252
Sum of electronic and thermal Enthalpies= -1085.170308
Sum of electronic and thermal Free Energies= -1085.250561
BSSE energy = 0.004233390235
0 2

C	-0.84079300	-0.98273800	-0.96139400
C	0.31678100	-1.77964500	-0.34168500
C	-0.07632300	-1.84624300	1.08313300
N	-1.20334000	-1.05369500	1.31294500
H	-1.06105900	-0.28648000	1.97105900
C	-2.88008000	0.09468800	-0.01575600
C	-3.12569100	1.01136900	-1.03810500

C	-3.85714300	-0.17268900	0.94237700
C	-4.36195200	1.64067300	-1.10473400
H	-2.36005700	1.22196500	-1.77131200
C	-5.08419500	0.47410000	0.86761100
H	-3.65492100	-0.88312500	1.73363300
C	-5.34449500	1.37838600	-0.15592400
H	-4.55181200	2.34944000	-1.90258600
H	-5.84152500	0.26275800	1.61379800
H	-6.30439100	1.87827300	-0.21171400
N	-1.62308800	-0.54784300	0.06703500
O	-1.02646800	-0.79893400	-2.14775200
C	0.79824600	-2.23346900	2.21424200
H	1.41683400	-1.39125600	2.55719000
H	0.20929800	-2.58286000	3.06610400
H	1.47470400	-3.03552200	1.91304300
C	0.58695600	-3.08983300	-1.05128900
H	0.83211600	-2.90144300	-2.09763000
H	1.42010800	-3.60856200	-0.57328100
H	-0.29814200	-3.72523800	-1.00272100
O	1.56604000	-1.01463500	-0.53070300
N	1.44269300	0.23147800	0.00177800
C	2.53230300	0.89073400	-0.02371200
C	3.83693300	0.34225200	-0.58098800
C	2.52111100	2.27686900	0.54530400
O	4.18204000	0.65569700	-1.69345800
C	4.61265300	-0.55259000	0.33420700
O	3.57945100	2.85600000	0.66748900
C	1.20032800	2.87381900	0.93386800
H	4.92632000	0.02865800	1.20724900
H	3.96785800	-1.36035700	0.69074000
H	5.48569200	-0.95648400	-0.17652500
H	0.56864400	2.97462200	0.04774900
H	0.67411700	2.21692900	1.62921000
H	1.36602700	3.84996700	1.38614900

Intermediate VI, conformer VI(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.167475

Sum of electronic and thermal Enthalpies= -1085.166531

Sum of electronic and thermal Free Energies= -1085.247303

```
 BSSE energy =       0.004000283296
0 2
 C                  1.14423200   -0.17793200    1.13517900
 C                 -0.13925400   -0.99640800    0.93885900
 C                  0.19129100   -1.80452400   -0.25247900
 N                  1.37216600   -1.33896500   -0.83618100
 H                  1.28604000   -0.99156100   -1.79138000
 C                  3.23555400    0.07787700   -0.18833900
 C                  3.64609300    1.32429000    0.28346500
 C                  4.12700600   -0.74800900   -0.87093000
 C                  4.96050900    1.72682900    0.08647500
 H                  2.94580000    1.96490000    0.80109300
 C                  5.43538900   -0.32533600   -1.06999700
 H                  3.79619100   -1.71163700   -1.23645500
 C                  5.85939300    0.90850100   -0.58977400
 H                  5.27889500    2.69387400    0.45843000
 H                  6.12644800   -0.97058400   -1.60013100
 H                  6.88186800    1.23241800   -0.74478900
 N                  1.89596900   -0.33858200    0.00639400
 O                  1.43318600    0.47598900    2.11542100
 C                 -0.67845900   -2.73998500   -1.00257600
 H                 -1.24898400   -2.22952400   -1.79112200
 H                 -0.08303300   -3.52564200   -1.47615400
 H                 -1.40107300   -3.20572600   -0.33135000
 C                 -0.59301200   -1.72867600    2.18255700
 H                 -0.74357900   -1.01658000    2.99539000
 H                 -1.52866000   -2.25476800    1.98736900
 H                  0.16374800   -2.45565600    2.48220700
 O                 -1.12321500    0.08151400    0.62351300
 N                 -2.32070500   -0.44348800    0.26574700
 C                 -3.16230400    0.44642200   -0.08946300
 C                 -2.86520900    1.93796400   -0.08997300
 C                 -4.51158900   -0.01397800   -0.54450100
 O                 -3.26369400    2.61715100    0.82426200
 C                 -2.09553000    2.45717300   -1.26402300
 O                 -5.27329800    0.80685400   -1.01130800
 C                 -4.84985300   -1.46978700   -0.40636400
 H                 -1.16640500    1.89079400   -1.36936800
 H                 -2.68598900    2.29515100   -2.17137300
 H                 -1.88350700    3.51846100   -1.14211000
 H                 -4.08643800   -2.08698300   -0.88408600
 H                 -4.86796500   -1.74229800    0.65193000
 H                 -5.82472900   -1.65598900   -0.85361700
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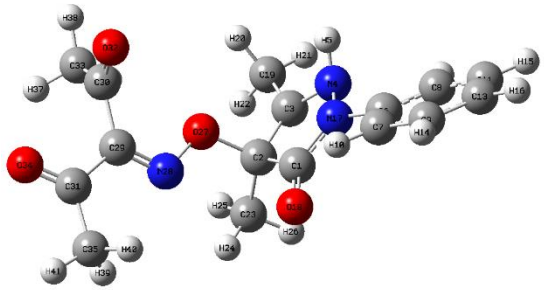
Intermediate VI, conformer VI(5) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

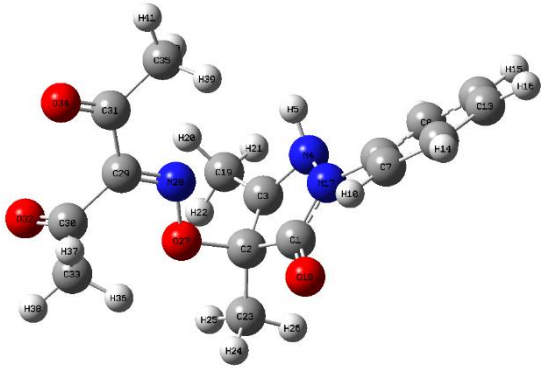


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -1085.166988
 Sum of electronic and thermal Enthalpies= -1085.166044
 Sum of electronic and thermal Free Energies= -1085.247429
 BSSE energy = 0.004080323390
0 2

C	-0.89683500	-0.04553000	0.93959600
C	0.12422600	1.09884900	1.03585300
C	-0.58923100	2.20356200	0.35807200
N	-1.73891900	1.72143800	-0.27124700
H	-1.76455100	1.83973300	-1.28404900
C	-3.10304900	-0.28585000	-0.18442100
C	-3.14154000	-1.67372200	-0.31347600
C	-4.26602800	0.46925300	-0.32623300
C	-4.35547400	-2.30065300	-0.56233000
H	-2.23314900	-2.25179000	-0.21729400
C	-5.47041600	-0.17211600	-0.58741800
H	-4.22331400	1.54653300	-0.22979600
C	-5.52253100	-1.55674700	-0.70162000
H	-4.38369700	-3.37996700	-0.65817900
H	-6.37296200	0.41813800	-0.69702200
H	-6.46489500	-2.05263900	-0.90282700
N	-1.86836700	0.35973000	0.06784500
O	-0.85376100	-1.10261700	1.53458300
C	-0.01401600	3.50609500	-0.05057500
H	0.49617400	3.44066000	-1.02176900
H	-0.79271100	4.26890600	-0.13353800
H	0.71951000	3.84404000	0.68360900
C	0.61732500	1.35961300	2.44358600
H	1.07850400	0.46307200	2.85670900
H	1.34747300	2.17165500	2.43730900
H	-0.22427300	1.64710700	3.07581800
O	1.25481600	0.76017100	0.14145800
N	2.04443400	-0.23808000	0.62386800
C	2.98152200	-0.53928500	-0.18664900
C	3.16458400	0.12331500	-1.54362200
C	3.95350100	-1.59999500	0.22594500
O	2.75104500	-0.43377800	-2.53119300
C	3.86719300	1.44467000	-1.54377000
O	4.91534600	-1.80499400	-0.48485300
C	3.69051200	-2.35006700	1.49826600

H	3.34533100	2.13119300	-0.87137300
H	4.88004400	1.30779800	-1.15238900
H	3.90863300	1.85521700	-2.55177900
H	3.62327700	-1.65616000	2.33883600
H	2.73007000	-2.86648800	1.43268000
H	4.49246800	-3.06721700	1.66460200

Intermediate VI, conformer VI(6) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.171883

Sum of electronic and thermal Enthalpies= -1085.170939

Sum of electronic and thermal Free Energies= -1085.251908

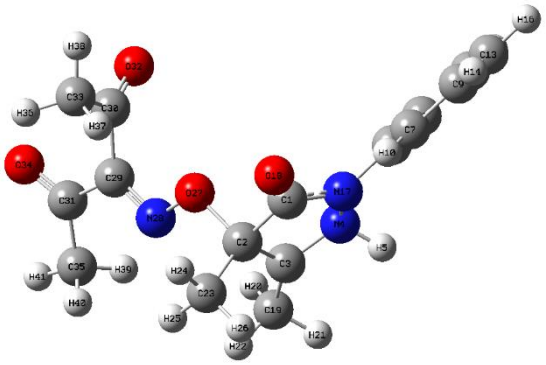
BSSE energy = 0.004201173575

0 2

C	0.76563800	0.99906400	-0.93940000
C	-0.32583800	1.84999100	-0.27468500
C	0.16381200	1.95408600	1.11649900
N	1.27058200	1.12251100	1.30468400
H	1.13031600	0.37951900	1.99095900
C	2.81332900	-0.13765700	-0.08343300
C	2.96412100	-1.08406900	-1.09719100
C	3.85089000	0.10380400	0.81625300
C	4.16625500	-1.76973500	-1.21420500
H	2.15266200	-1.27384000	-1.78537900
C	5.04269800	-0.59869400	0.69168600
H	3.72245100	0.83790500	1.60121000
C	5.20836400	-1.53370300	-0.32385700
H	4.28228900	-2.50160600	-2.00533000
H	5.84696700	-0.40698100	1.39265600
H	6.14101800	-2.07734200	-0.41860400
N	1.59196500	0.56218700	0.05257400
O	0.86886600	0.77242300	-2.12910600
C	-0.60436100	2.43341800	2.28828700
H	-1.21901800	1.63360900	2.72547700
H	0.06315600	2.80638600	3.06938800
H	-1.27766800	3.24119700	1.99635500
C	-0.61685900	3.13962300	-1.01165400
H	-0.93816700	2.92074600	-2.03118800
H	-1.40391700	3.69377600	-0.49696200

H	0.28266000	3.75525600	-1.04808500
O	-1.59966100	1.10119400	-0.36124600
N	-1.47643400	-0.10682100	0.25031000
C	-2.52984400	-0.81782800	0.16695500
C	-3.80659400	-0.35820900	-0.51970000
C	-2.49145200	-2.18575000	0.77595500
O	-4.69997900	0.10065400	0.14934800
C	-3.85105800	-0.52772200	-2.00501100
O	-3.45413000	-2.90830100	0.62940300
C	-1.25434000	-2.59557700	1.52116500
H	-2.98840800	-0.02719500	-2.45347700
H	-3.77076800	-1.59340700	-2.24125800
H	-4.77925900	-0.12465400	-2.40763800
H	-0.38728200	-2.55540700	0.85772000
H	-1.06359200	-1.90152000	2.34274300
H	-1.38556400	-3.60559800	1.90525700

Intermediate VI, conformer VI(7) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.167765

Sum of electronic and thermal Enthalpies= -1085.166821

Sum of electronic and thermal Free Energies= -1085.248171

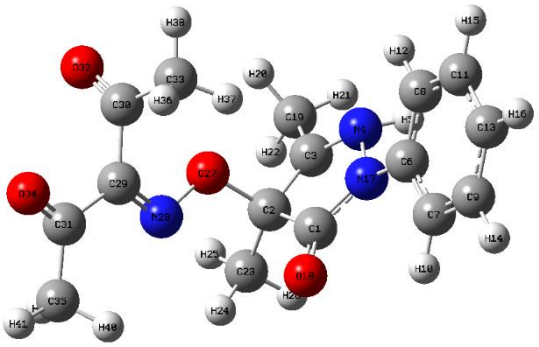
BSSE energy = 0.003927677512

0 2

C	-1.16710300	0.52663400	1.20240100
C	0.16450000	1.21991100	0.88325100
C	-0.16047800	1.96259700	-0.34270100
N	-1.33527800	1.45015500	-0.89462200
H	-1.96385300	2.15640000	-1.27206700
C	-3.17154900	0.01580600	-0.18803600
C	-4.06844200	-0.31592600	0.82708700
C	-3.44806800	-0.31998900	-1.51278400
C	-5.23324000	-1.00163700	0.50742100
H	-3.85245300	-0.04413700	1.85047000
C	-4.62394400	-0.99425400	-1.81639000
H	-2.74386900	-0.06444500	-2.29429700
C	-5.51854600	-1.34167000	-0.81057400
H	-5.92658300	-1.26260300	1.29870000
H	-4.83429400	-1.25489000	-2.84724900

H	-6.43258500	-1.87130000	-1.05213200
N	-1.98180800	0.71470900	0.12359100
O	-1.41725400	-0.11441000	2.20255400
C	0.66685800	2.92533900	-1.10489900
H	1.26753600	2.42346000	-1.87414400
H	0.04379900	3.67419500	-1.60432800
H	1.35621200	3.44356100	-0.43677100
C	0.76232200	1.99461900	2.03792500
H	0.86876800	1.33682500	2.90221100
H	1.74399700	2.38298500	1.76171900
H	0.11465300	2.83137400	2.30553400
O	1.03443700	0.03077000	0.61132100
N	2.22320400	0.42071700	0.09346000
C	2.99628300	-0.56072000	-0.16335300
C	2.61350600	-2.01616400	0.05621400
C	4.35277700	-0.25326200	-0.71381000
O	2.24417400	-2.67274500	-0.88688100
C	2.74017300	-2.53098100	1.45504200
O	5.14508600	-1.16366600	-0.83909400
C	4.66582400	1.16839100	-1.08102300
H	3.78731300	-2.45753600	1.76511900
H	2.15251300	-1.89999200	2.12731000
H	2.40424200	-3.56537600	1.51285100
H	3.99026400	1.50158500	-1.87271000
H	4.50651500	1.82665400	-0.22470600
H	5.69821700	1.23240600	-1.42034200

Intermediate VI, conformer VI(8) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.167412

Sum of electronic and thermal Enthalpies= -1085.166468

Sum of electronic and thermal Free Energies= -1085.247869

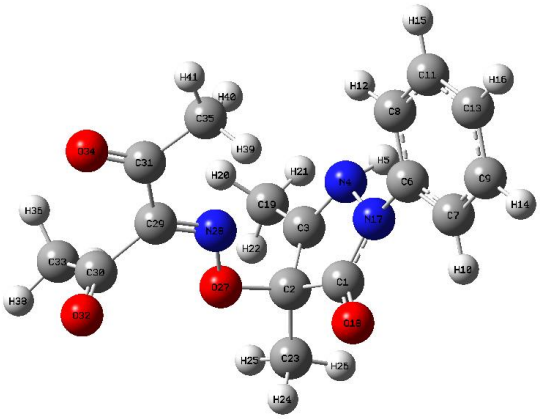
BSSE energy = 0.004183635840

0 2

C	0.72146700	0.81226000	-1.08284600
C	-0.27988500	1.80973200	-0.47884800
C	0.54203800	2.48595700	0.53784000
N	1.67014300	1.71005900	0.80914700
H	2.52707300	2.24346400	0.94337000
C	2.79979400	-0.20933000	-0.17083600

C	3.29235500	-0.80808100	-1.32973600
C	3.27393800	-0.59727900	1.08172800
C	4.24646000	-1.81196900	-1.22335000
H	2.92883100	-0.49273600	-2.29743500
C	4.23783400	-1.59364500	1.16941400
H	2.88474900	-0.12758200	1.97618000
C	4.72445700	-2.20823200	0.02111100
H	4.62466500	-2.27945800	-2.12522200
H	4.60345700	-1.89336500	2.14483200
H	5.47384800	-2.98752500	0.09508900
N	1.81912700	0.80694500	-0.26656200
O	0.53604300	0.10061300	-2.04874300
C	0.14391500	3.58147400	1.45091500
H	-0.40026300	3.20233700	2.32587700
H	1.01773000	4.12817400	1.81619300
H	-0.50831000	4.28884000	0.93531200
C	-0.99975200	2.68460000	-1.48236100
H	-1.49008700	2.07113500	-2.23716100
H	-1.75033300	3.29498100	-0.97635200
H	-0.27956100	3.34190600	-1.97249300
O	-1.24564400	0.96891200	0.27861400
N	-2.13330300	0.30889900	-0.51793800
C	-2.72647400	-0.62663600	0.11385200
C	-2.43318000	-0.96873200	1.56643000
C	-3.73562300	-1.44754800	-0.62631000
O	-3.17708600	-0.57559800	2.43189900
C	-1.21215300	-1.80164200	1.80728600
O	-4.20798300	-2.41688000	-0.06997700
C	-4.10379800	-1.03357900	-2.02048800
H	-1.34068100	-2.76912600	1.31208100
H	-0.34318000	-1.31529600	1.35579100
H	-1.05486800	-1.94729400	2.87519200
H	-4.58442600	-0.05232600	-1.99683200
H	-3.20818300	-0.93816400	-2.63753800
H	-4.78324000	-1.76977400	-2.44655500

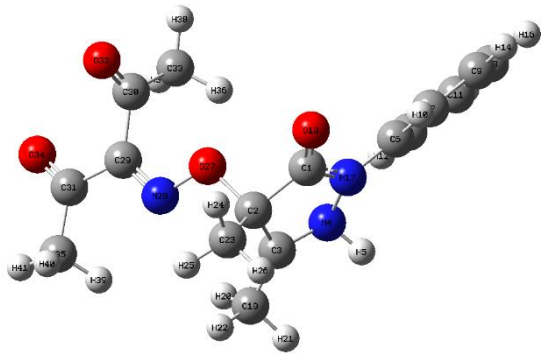
Intermediate VI, conformer VI(9) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

```
 Sum of electronic and thermal Energies=            -1085.171105
 Sum of electronic and thermal Enthalpies=          -1085.170161
 Sum of electronic and thermal Free Energies=       -1085.251960
 BSSE energy =       0.004288892593
0 2
 C                 -0.73077800   -1.42242700   -0.88473200
 C                  0.53094200   -1.99660500   -0.22178900
 C                  0.12589700   -2.08087000    1.18958800
 N                 -1.04645900   -1.35122200    1.38908800
 H                 -1.73017000   -1.80734000    1.98990600
 C                 -2.65938600   -0.15769600    0.02322500
 C                 -3.49808800   -0.16780300   -1.09047300
 C                 -2.85537900    0.76957400    1.04574800
 C                 -4.51702600    0.77174500   -1.18353100
 H                 -3.34946700   -0.89856900   -1.87275200
 C                 -3.88645600    1.69457100    0.94309700
 H                 -2.20077100    0.76793700    1.90756100
 C                 -4.71743600    1.70447100   -0.17154300
 H                 -5.16423000    0.76528100   -2.05303500
 H                 -4.03382900    2.41512700    1.73942900
 H                 -5.51837500    2.43035800   -0.24903000
 N                 -1.60548900   -1.09940500    0.11786800
 O                 -0.88912400   -1.23444800   -2.07254100
 C                  0.94160700   -2.52111400    2.34442300
 H                  1.56234200   -1.70319100    2.73504600
 H                  0.31136200   -2.87570300    3.16504200
 H                  1.60900300   -3.33432800    2.05311800
 C                  1.06086000   -3.25761300   -0.87188900
 H                  1.26603800   -3.06847800   -1.92667000
 H                  1.98246400   -3.57570000   -0.38097400
 H                  0.32318200   -4.05686900   -0.78956900
 O                  1.62188000   -1.01112900   -0.44350700
 N                  1.22297400    0.22276700   -0.04071200
 C                  2.13953900    1.10294700   -0.12296000
 C                  3.54885600    0.81441500   -0.61412600
 C                  1.79348500    2.49633000    0.30459400
 O                  3.85000400    1.09554600   -1.74800300
 C                  4.47686300    0.20049800    0.38728300
 O                  2.67805100    3.32536600    0.34157400
 C                  0.36914800    2.78690500    0.67958500
 H                  4.61601400    0.90377600    1.21457000
 H                  4.02227500   -0.70484400    0.79871400
 H                  5.43736700   -0.02845200   -0.07228200
 H                 -0.29912200    2.54442500   -0.14959000
 H                  0.07079900    2.15689100    1.52072000
 H                  0.27555900    3.83805300    0.94689000
```

Intermediate VI, conformer VI(10) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

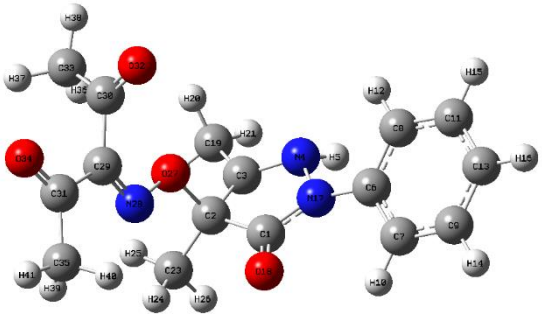


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies=   -1085.167757
 Sum of electronic and thermal Enthalpies=   -1085.166813
 Sum of electronic and thermal Free Energies=   -1085.247714
 BSSE energy =   0.003993385626
0 2

C	-1.15162300	0.91299000	1.10762800
C	0.20708100	1.48579400	0.68186800
C	-0.05214100	1.88953100	-0.70675400
N	-1.20102000	1.24410500	-1.16629700
H	-1.80276900	1.82467400	-1.74726600
C	-3.06896100	0.01310800	-0.20528100
C	-4.01801800	-0.06791400	0.81360100
C	-3.26553600	-0.66267700	-1.40917800
C	-5.15343800	-0.84509900	0.62392800
H	-3.86397000	0.46637400	1.74029400
C	-4.41300700	-1.42505100	-1.58666200
H	-2.52239500	-0.59707400	-2.19372500
C	-5.35866800	-1.52395300	-0.57242500
H	-5.88739200	-0.91040400	1.41890100
H	-4.56148600	-1.94931900	-2.52368700
H	-6.25062500	-2.12280500	-0.71419200
N	-1.90645000	0.79868700	-0.02560400
O	-1.46324300	0.56729900	2.22799600
C	0.80384500	2.65222300	-1.64340800
H	1.40710600	1.98796800	-2.27539300
H	0.20238600	3.28432400	-2.30503200
H	1.49127700	3.29297300	-1.08972800
C	0.78893600	2.51624700	1.62306500
H	0.82890300	2.10455100	2.63266700
H	1.79846400	2.78481500	1.30727100
H	0.16977000	3.41508200	1.62870500
O	1.05003500	0.24717800	0.75998000
N	2.23858400	0.44100900	0.13983700
C	2.93468000	-0.62566400	0.06972100
C	2.47663600	-1.96548100	0.62417400
C	4.26191200	-0.54995800	-0.61645900
O	2.91437200	-2.34706000	1.68205100
C	1.50425800	-2.72853300	-0.22033400

O	4.86885300	-1.58175600	-0.81431400
C	4.77307800	0.79960300	-1.02929300
H	0.64166300	-2.09575800	-0.44562500
H	1.98649500	-2.98080400	-1.17015500
H	1.18780500	-3.63735900	0.28964900
H	4.02440400	1.32883700	-1.62163900
H	4.96522200	1.40421500	-0.13915600
H	5.69300200	0.67682500	-1.59828500

Intermediate VI, conformer VI(11) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.166247

Sum of electronic and thermal Enthalpies= -1085.165303

Sum of electronic and thermal Free Energies= -1085.247030

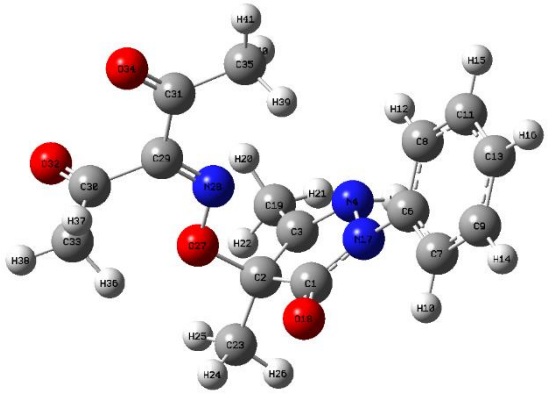
BSSE energy = 0.003986083741

0 2

C	0.88787100	0.31916300	-1.16088100
C	-0.18036600	1.39647800	-0.91117200
C	0.55439900	2.36892600	-0.08479900
N	1.70948300	1.77145900	0.42118500
H	2.53063500	2.37349000	0.42232000
C	3.02070200	-0.23503400	0.00564100
C	3.57992100	-1.08809600	-0.94560500
C	3.52268400	-0.20114700	1.30605400
C	4.63082900	-1.91892100	-0.57898800
H	3.19199800	-1.10188600	-1.95417400
C	4.58266100	-1.02950500	1.65220700
H	3.07947100	0.46003700	2.03984800
C	5.13833400	-1.89366600	0.71566400
H	5.06057400	-2.58484200	-1.31848800
H	4.96852200	-1.00146300	2.66473800
H	5.96250100	-2.54092500	0.99165800
N	1.94999300	0.61621200	-0.35426500
O	0.78102100	-0.64580900	-1.88988700
C	0.05757400	3.64440800	0.47987000
H	-0.47908500	3.48827300	1.42508700
H	0.88114300	4.33635900	0.67862700
H	-0.62978400	4.12724100	-0.21718700
C	-0.84150600	1.92640000	-2.16739500
H	-1.27419400	1.10747100	-2.74102900

H	-1.62953600	2.63571600	-1.90607000
H	-0.09727400	2.43500900	-2.78247800
O	-1.18976900	0.78098000	-0.01097100
N	-2.02363900	-0.08744600	-0.64294900
C	-2.83975500	-0.64243100	0.16466100
C	-2.84864100	-0.38551300	1.66391800
C	-3.84642900	-1.59407400	-0.40058000
O	-2.30789200	-1.17425000	2.40004100
C	-3.55662500	0.85270600	2.11805300
O	-4.70740900	-2.02618700	0.33761900
C	-3.74277200	-1.96075800	-1.85192600
H	-3.14108100	1.72002000	1.59788900
H	-4.61285400	0.77774700	1.84103200
H	-3.46164900	0.97260700	3.19648400
H	-3.78943600	-1.06354800	-2.47272100
H	-2.77785800	-2.43461000	-2.04671500
H	-4.55383600	-2.63976700	-2.10937600

Intermediate VI, conformer VI(12) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

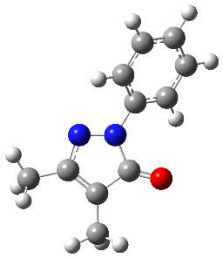


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.171953
Sum of electronic and thermal Enthalpies= -1085.171009
Sum of electronic and thermal Free Energies= -1085.252411
BSSE energy = 0.004286398753
0 2

C	0.65874100	1.38530500	-0.89004500
C	-0.53505600	2.02509500	-0.16585400
C	-0.02280800	2.16864400	1.20451200
N	1.14685900	1.42395400	1.35303200
H	1.88424500	1.89357400	1.87468900
C	2.62347300	0.12048200	-0.06582600
C	3.38355900	0.06466900	-1.23306100
C	2.86698200	-0.76904100	0.97970100
C	4.37364700	-0.90209600	-1.35427000
H	3.19574500	0.76599900	-2.03394400
C	3.86870800	-1.72225000	0.84721600
H	2.27037800	-0.71710200	1.88128900
C	4.62201100	-1.79710000	-0.31904700
H	4.96053100	-0.94705500	-2.26448900

H	4.05410000	-2.41357900	1.66129200
H	5.40043300	-2.54443100	-0.41890100
N	1.59938800	1.09104700	0.05887500
O	0.71841300	1.12518400	-2.07424400
C	-0.72068600	2.71424900	2.39077400
H	-1.30939900	1.94185200	2.90327700
H	-0.01110400	3.12286700	3.11631000
H	-1.40475800	3.51265000	2.09782400
C	-1.08606600	3.26474300	-0.83924600
H	-1.36838700	3.03031700	-1.86689000
H	-1.96473800	3.62573500	-0.30174800
H	-0.32957700	4.05051000	-0.84855000
O	-1.65900500	1.05441500	-0.26501000
N	-1.26705800	-0.16062500	0.19655400
C	-2.16728400	-1.05510400	0.09052300
C	-3.55693000	-0.79223500	-0.46689600
C	-1.81552000	-2.44242900	0.53116600
O	-4.47056700	-0.59591700	0.29718600
C	-3.67919600	-0.80774300	-1.95762300
O	-2.62580400	-3.32720400	0.35178000
C	-0.47134900	-2.66577100	1.16112100
H	-2.96232200	-0.10254100	-2.38719800
H	-3.41529400	-1.80520100	-2.32285100
H	-4.69434700	-0.55519200	-2.26072800
H	0.32368800	-2.33256500	0.49013800
H	-0.38686200	-2.07132600	2.07404600
H	-0.35431700	-3.72347200	1.39063800

Intermediate VII (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -610.234559

Sum of electronic and thermal Enthalpies= -610.233615

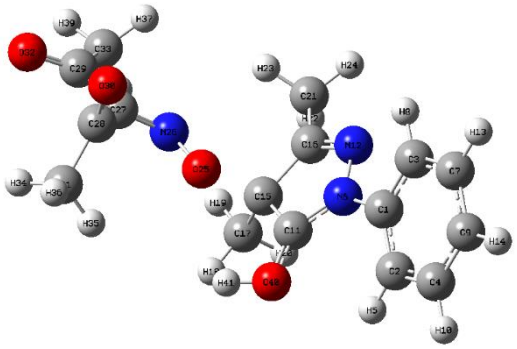
Sum of electronic and thermal Free Energies= -610.289091

0 2

C	-1.23450200	0.09107600	0.05175400
C	-1.95650900	-0.98609600	0.55867700
C	-1.88934000	1.19379600	-0.49103000
C	-3.34492200	-0.95662400	0.50817200
H	-1.43914600	-1.83370700	0.98710400
N	0.18286900	0.07762800	0.09424700
C	-3.27719000	1.21717900	-0.52003100
H	-1.31010000	2.02058100	-0.88226500

C	-4.00917300	0.14180800	-0.02643100
H	-3.90827500	-1.79539900	0.90038000
C	1.04027000	-1.01890900	-0.15765600
N	0.87039300	1.20515700	0.25974200
H	-3.78710500	2.07670200	-0.93956300
H	-5.09234700	0.16063900	-0.05741700
C	2.37572700	-0.44411700	-0.09411200
O	0.67734800	-2.16039500	-0.39063000
C	2.19204300	0.89558400	0.15799500
C	3.62785500	-1.22244800	-0.26435800
H	3.86422300	-1.77969300	0.64815400
H	3.52266700	-1.95174800	-1.07087100
H	4.47152600	-0.56745800	-0.48664200
C	3.21630900	1.96466900	0.34045200
H	3.71382100	1.86539500	1.30888300
H	3.98302500	1.90525800	-0.43511400
H	2.74668700	2.94758600	0.29388300

Intermediate VIII, conformer VIII(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

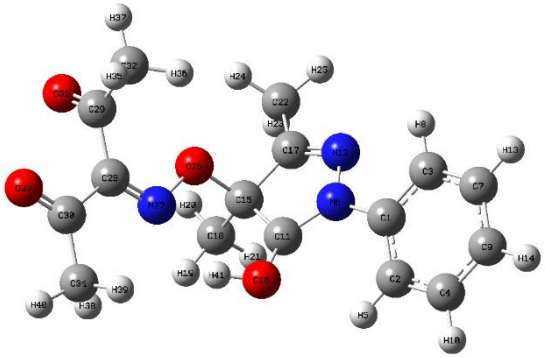


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.149673
Sum of electronic and thermal Enthalpies= -1085.148729
Sum of electronic and thermal Free Energies= -1085.231166
BSSE energy = 0.003666481081
0 2

C	-3.28667300	0.00691600	-0.19744700
C	-4.10175000	-0.47460000	0.82690100
C	-3.73414100	-0.01156900	-1.51923100
C	-5.35668100	-0.98572600	0.51777100
H	-3.76482800	-0.44668900	1.85384800
N	-2.00684700	0.53061300	0.08152400
C	-4.99582000	-0.51080500	-1.80908100
H	-3.09249200	0.36564700	-2.30450000
C	-5.81142300	-1.00541100	-0.79554200
H	-5.98594900	-1.35994100	1.31724500
C	-1.15975500	0.25458500	1.11304800
N	-1.49135200	1.52471500	-0.71031300
H	-5.33866300	-0.52090200	-2.83744300
H	-6.79356300	-1.40013900	-1.02793300
C	0.07897600	1.00350200	0.92928900

C	-0.32364500	1.84424500	-0.24077100
C	0.69711000	1.67874300	2.13833300
H	0.86393600	0.95293500	2.93737000
H	1.65221800	2.13357700	1.87371700
H	0.02587800	2.45659900	2.50658300
C	0.49820500	2.93186000	-0.83609400
H	0.73238800	3.69239600	-0.08510600
H	1.44822300	2.54082200	-1.20896100
H	-0.04411700	3.40261600	-1.65636400
O	1.10898600	-0.09034800	0.46050600
N	2.31149900	0.43510000	0.15163000
C	3.16040400	-0.44031100	-0.22879000
C	2.84343200	-1.92352500	-0.32478400
C	4.53583400	0.01945000	-0.58348200
O	2.56241700	-2.40349300	-1.39622900
C	2.92455600	-2.69715800	0.95474600
O	5.38537800	-0.81775800	-0.81175600
C	4.80053800	1.49631800	-0.64403900
H	3.96564100	-2.69933200	1.29360700
H	2.33049900	-2.19858600	1.72512500
H	2.58123400	-3.72018300	0.80647300
H	4.21850300	1.93707700	-1.45771900
H	4.48266800	1.98307800	0.27960700
H	5.86206900	1.66449800	-0.81762200
O	-1.41376900	-0.70970900	2.01016300
H	-0.59584800	-1.16510000	2.23574700

Intermediate VIII, conformer VIII(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

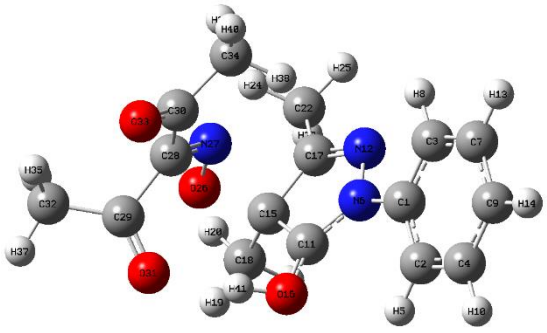


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.151855
Sum of electronic and thermal Enthalpies= -1085.150910
Sum of electronic and thermal Free Energies= -1085.231082
BSSE energy = 0.004134281086
0 2

C	3.06446200	-0.18632300	0.16085600
C	3.51859100	-1.27004800	-0.59413600
C	3.80024700	0.24920300	1.26670900
C	4.69514400	-1.91457600	-0.23059000
H	2.96118300	-1.60649000	-1.45739500

N	1.87210700	0.47690300	-0.17496000
C	4.97916700	-0.39751100	1.60727800
H	3.44433300	1.09120700	1.84551400
C	5.43285300	-1.48558600	0.86647200
H	5.03955800	-2.75530700	-0.82236800
C	0.86978500	0.07717400	-1.03895600
N	1.72270500	1.80228500	0.15055000
H	5.54400800	-0.05051100	2.46530300
H	6.35157800	-1.99064100	1.14073000
C	-0.16473900	1.14690400	-1.06807600
O	0.64927100	-1.22853600	-1.29705700
C	0.61253700	2.22671300	-0.35040800
C	-0.70974800	1.50774200	-2.44466000
H	-1.17686500	0.63638800	-2.90927100
H	-1.45873700	2.29753800	-2.35387600
H	0.09961400	1.85374700	-3.08881500
C	0.13223400	3.62376400	-0.18759600
H	0.03442200	4.11479600	-1.16048900
H	-0.85372200	3.63824600	0.28614600
H	0.83057900	4.19321700	0.42557400
O	-1.28696100	0.86269900	-0.19495100
N	-1.87832100	-0.32259800	-0.51065600
C	-2.91973100	-0.55874100	0.18433800
C	-3.47759300	0.42395600	1.20502900
C	-3.63380800	-1.86136300	-0.01665000
O	-4.34676900	1.18669600	0.86315200
C	-2.88938100	0.35033800	2.57743500
O	-4.59888500	-2.09228900	0.67886900
C	-3.10327800	-2.82113900	-1.04060300
H	-3.07905900	-0.64430700	2.99262000
H	-1.80497000	0.47741700	2.51298700
H	-3.32507400	1.11369800	3.22040600
H	-2.90427700	-2.31744400	-1.98787500
H	-2.15953300	-3.24336200	-0.68262400
H	-3.82249500	-3.62592800	-1.18185100
H	-0.30967900	-1.37000800	-1.27802000

Intermediate VIII, conformer VIII(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.155441

```
 Sum of electronic and thermal Enthalpies=           -1085.154496
 Sum of electronic and thermal Free Energies=        -1085.233422
 BSSE energy =       0.004815470998
0 2
 C                  2.45211800    0.08012000   -0.17576400
 C                  2.94700700   -0.26690400   -1.43388700
 C                  3.03297800   -0.45391800    0.97656700
 C                  4.00964300   -1.15703500   -1.52918200
 H                  2.50758400    0.15489200   -2.32703000
 N                  1.36883800    0.96913400   -0.04861800
 C                  4.10335200   -1.33003700    0.86417900
 H                  2.64359500   -0.17614800    1.94714900
 C                  4.59448900   -1.69168300   -0.38668900
 H                  4.38809400   -1.42395400   -2.50946500
 C                  0.34131600    1.22036500   -0.92367900
 N                  1.22737600    1.71102900    1.09602300
 H                  4.55030500   -1.73889200    1.76338000
 H                  5.42642800   -2.38124600   -0.46951200
 C                 -0.65727600    2.04567300   -0.22844400
 O                  0.15387800    0.50410200   -2.04027000
 C                  0.10878200    2.35972700    1.01784100
 C                 -1.29969900    3.18672000   -0.99106600
 H                 -1.75531900    2.81591900   -1.91110500
 H                 -2.07070100    3.66146400   -0.38109700
 H                 -0.54321800    3.92961100   -1.24761100
 C                 -0.36965000    3.27234600    2.08829900
 H                 -0.47953200    4.29363200    1.71109200
 H                 -1.35024300    2.95029100    2.45149500
 H                  0.33287400    3.27922700    2.92182100
 O                 -1.88491100    1.16573200    0.08715900
 N                 -1.49919400    0.06502600    0.80029000
 C                 -2.04091600   -1.00596500    0.37058700
 C                 -2.88867500   -1.04674200   -0.89169500
 C                 -1.70811600   -2.29204100    1.06835400
 O                 -2.33928700   -0.84527700   -1.95510300
 C                 -4.34436800   -1.32628400   -0.74602600
 O                 -2.21197700   -3.31636100    0.65826800
 C                 -0.73968700   -2.24201800    2.21177300
 H                 -4.47694900   -2.28337500   -0.23516600
 H                 -4.78768500   -0.55360800   -0.10976000
 H                 -4.83137100   -1.33927200   -1.71963000
 H                  0.20262900   -1.79936700    1.87895900
 H                 -1.12885600   -1.60462700    3.00861500
 H                 -0.57235500   -3.25113400    2.58407800
 H                 -0.72383700    0.07076100   -2.03750600
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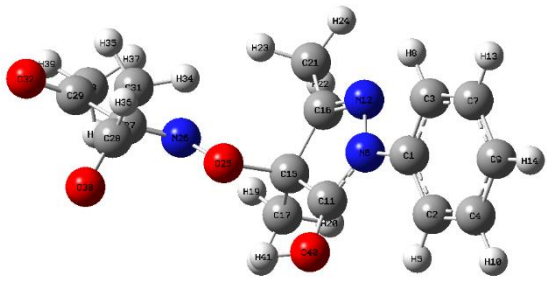
Intermediate VIII, conformer VIII(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

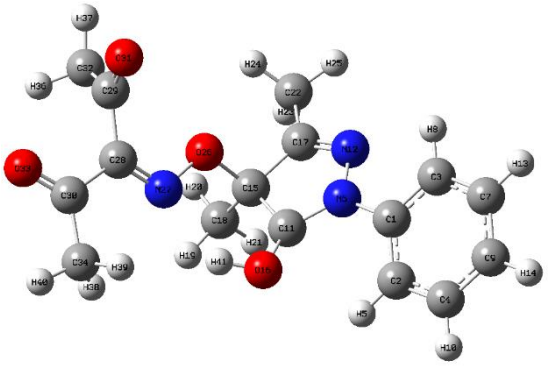


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -1085.150384
 Sum of electronic and thermal Enthalpies= -1085.149440
 Sum of electronic and thermal Free Energies= -1085.231587
 BSSE energy = 0.003812455583
0 2

C	-3.23080200	-0.01303200	-0.17261100
C	-4.02193300	-0.27855600	0.94645300
C	-3.72264300	-0.27265000	-1.45403200
C	-5.29334900	-0.81286500	0.77517100
H	-3.65221400	-0.06755000	1.94057100
N	-1.93610500	0.51651300	-0.02814400
C	-4.99949500	-0.79286100	-1.60758000
H	-3.10334300	-0.06258700	-2.31601600
C	-5.79086600	-1.07140700	-0.49672500
H	-5.90153300	-1.01724800	1.64910000
C	-1.13472800	0.55036600	1.09163300
N	-1.40968300	1.30474900	-1.02119000
H	-5.37479000	-0.98909300	-2.60563900
H	-6.78524800	-1.48342600	-0.62238400
C	0.13115200	1.21793100	0.72862100
C	-0.25975700	1.74460500	-0.62834000
C	0.70313800	2.20090000	1.73368100
H	0.85353800	1.70753500	2.69656000
H	1.65829000	2.59575200	1.38649500
H	0.00517400	3.02863200	1.86828800
C	0.57709300	2.64790400	-1.46186800
H	0.77613800	3.58465400	-0.93296500
H	1.54449300	2.18731900	-1.67963800
H	0.06726100	2.87263800	-2.39881600
O	1.10672800	0.07230900	0.56501900
N	2.35363600	0.47985800	0.21831300
C	3.13868000	-0.49934300	-0.00923500
C	2.71526100	-1.95477200	0.11662700
C	4.54088200	-0.19536300	-0.43247100
O	2.94748200	-2.55103600	1.14011100
C	2.02926600	-2.54294400	-1.07582500
O	5.25974100	-1.12134300	-0.74539300
C	4.98379900	1.23836000	-0.45461700
H	1.16539300	-1.92547300	-1.33745400
H	2.71792000	-2.52191100	-1.92617600

H	1.71864600	-3.56671700	-0.87185300
H	4.32898800	1.82703200	-1.10065800
H	4.91366500	1.66430300	0.54902100
H	6.01073700	1.29102700	-0.81184400
O	-1.28323700	-0.33348500	2.09773200
H	-0.43794000	-0.76190800	2.27750500

Intermediate VIII, conformer VIII(5) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

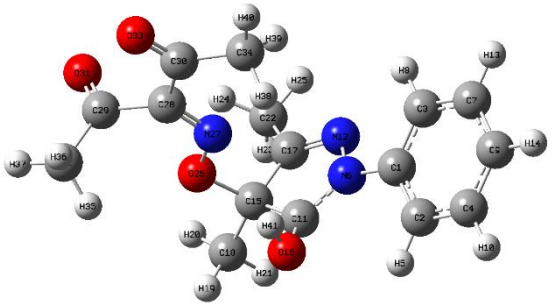


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.151688
Sum of electronic and thermal Enthalpies= -1085.150744
Sum of electronic and thermal Free Energies= -1085.230925
BSSE energy = 0.004096834824
0 2

C	3.13753500	-0.15067900	0.16682800
C	3.60124100	-1.24454200	-0.56707800
C	3.88886300	0.33801600	1.23924200
C	4.80413800	-1.84596600	-0.21626300
H	3.03047800	-1.62236900	-1.40421800
N	1.91941500	0.46948600	-0.15859600
C	5.09379600	-0.26597900	1.56711100
H	3.52379300	1.18598600	1.80346300
C	5.55804100	-1.36349300	0.84706600
H	5.15591400	-2.69534700	-0.79110800
C	0.90243300	0.00773700	-0.97307400
N	1.74378600	1.80165300	0.12004200
H	5.67051200	0.12165900	2.39943600
H	6.49709500	-1.83514900	1.11182800
C	-0.15790600	1.05177900	-1.01860700
O	0.70377100	-1.31371900	-1.15864900
C	0.60813400	2.17704400	-0.36224100
C	-0.74026700	1.34951100	-2.39564500
H	-1.18847300	0.44949500	-2.82246500
H	-1.51147500	2.11952900	-2.31600200
H	0.04514400	1.69886800	-3.06698300
C	0.09363200	3.56587600	-0.23742400
H	-0.04342700	4.01845400	-1.22417300
H	-0.87882800	3.57098100	0.26384100
H	0.79152000	4.17603700	0.33572900

O	-1.25341800	0.77228400	-0.11073300
N	-1.84988300	-0.41818200	-0.40298500
C	-2.91253700	-0.61897900	0.27065400
C	-3.45681400	0.38018200	1.28206200
C	-3.67000600	-1.89403500	0.04353600
O	-3.26069600	0.18557500	2.45567900
C	-4.22038800	1.53731400	0.72034300
O	-4.75640500	-2.01010800	0.56680100
C	-3.04828000	-2.95008000	-0.82147900
H	-3.61079400	2.04786600	-0.02989600
H	-5.11470800	1.15721000	0.21657200
H	-4.50514900	2.22554200	1.51487100
H	-2.77370900	-2.53680400	-1.79433300
H	-2.13413300	-3.32079100	-0.34985000
H	-3.75240300	-3.77031700	-0.94817300
H	-0.25029700	-1.47604200	-1.10273800

Intermediate VIII, conformer VIII(6) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.153779

Sum of electronic and thermal Enthalpies= -1085.152835

Sum of electronic and thermal Free Energies= -1085.235574

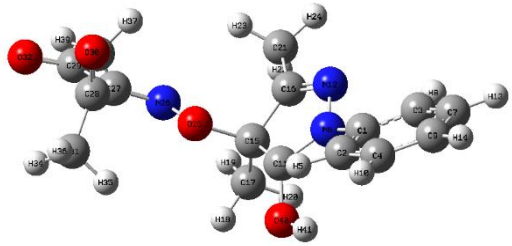
BSSE energy = 0.004121709622

0 2

C	2.73238900	-0.07819600	-0.03567600
C	3.49947400	-0.05235900	1.13094700
C	3.10247400	0.69955400	-1.13493400
C	4.62215500	0.76351300	1.19354800
H	3.22262700	-0.66717300	1.97675800
N	1.58419500	-0.88468800	-0.11683700
C	4.23584300	1.49684700	-1.06113500
H	2.50193800	0.67046800	-2.03463500
C	4.99816300	1.53954900	0.10255800
H	5.21359600	0.77965000	2.10202800
C	0.74672500	-1.30615800	0.89159300
N	1.16097000	-1.34796100	-1.33874700
H	4.51916400	2.09599600	-1.91914300
H	5.87878400	2.16881100	0.15668100
C	-0.43402800	-1.94455500	0.25762000
O	0.73938900	-0.73967500	2.11690300

C	0.05130700	-1.98450300	-1.16923100
C	-0.93125000	-3.24368100	0.85980700
H	-1.15228100	-3.10048800	1.91921100
H	-1.83726500	-3.57647900	0.34891300
H	-0.16554700	-4.01389000	0.75925700
C	-0.69120100	-2.62793600	-2.28319000
H	-0.75714300	-3.70948400	-2.13100500
H	-1.71367100	-2.24146800	-2.32892400
H	-0.19330600	-2.43505300	-3.23335500
O	-1.64191700	-1.05835000	0.33441900
N	-1.30131300	0.22553100	0.05959200
C	-2.30224000	1.01029100	-0.01600500
C	-3.74612100	0.55276800	0.12159600
C	-2.02693300	2.46090100	-0.26754000
O	-4.37935800	0.30546200	-0.87540900
C	-4.27616700	0.45192800	1.51656200
O	-2.96272400	3.23251000	-0.26289700
C	-0.60538800	2.88501300	-0.49956800
H	-3.63210700	-0.21122400	2.10093700
H	-4.23758400	1.44132300	1.98277500
H	-5.30004500	0.08077200	1.51068900
H	-0.00877700	2.69109900	0.39526900
H	-0.16136300	2.30563100	-1.31145700
H	-0.58322800	3.94782400	-0.73405100
H	0.40491700	0.16607400	2.06616100

Intermediate VIII, conformer VIII(7) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

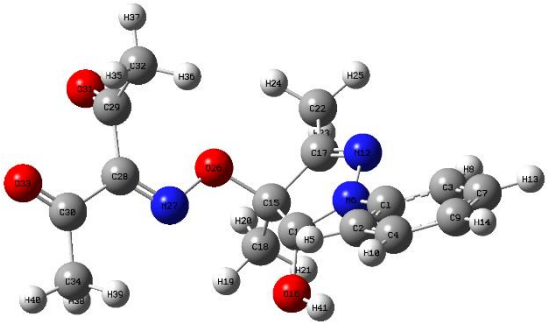


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.149847
Sum of electronic and thermal Enthalpies= -1085.148902
Sum of electronic and thermal Free Energies= -1085.230289
BSSE energy = 0.003701741477
0 2

C	3.34080600	-0.00817200	-0.18165200
C	3.58101000	1.35189800	0.02355700
C	4.35901500	-0.83272600	-0.66567600
C	4.84519000	1.87457000	-0.22713200
H	2.77487400	2.00755800	0.33570200
N	2.08296800	-0.55185300	0.11995100
C	5.60729600	-0.29204600	-0.93380100
H	4.16138900	-1.88465300	-0.82778900
C	5.86234700	1.05898600	-0.70634500

H	5.02361100	2.93146400	-0.06546900
C	1.13757600	-0.02858400	0.98655700
N	1.54668100	-1.53927900	-0.67754400
H	6.39301600	-0.93524600	-1.31367300
H	6.84376000	1.47111000	-0.90882100
C	-0.10983300	-0.82198400	0.81119600
C	0.32330500	-1.72788800	-0.32733700
C	-0.59266500	-1.54390300	2.06081300
H	-0.82826400	-0.82006300	2.84243700
H	-1.48089000	-2.13592400	1.84115100
H	0.19480300	-2.20731900	2.42421700
C	-0.53306600	-2.75826900	-0.97415200
H	-0.92839900	-3.45362800	-0.22827800
H	-1.38958100	-2.29563800	-1.47031800
H	0.04809100	-3.31668200	-1.70815200
O	-1.13473900	0.13957300	0.35593600
N	-2.34535400	-0.44746400	0.16661600
C	-3.23556100	0.38112500	-0.21692100
C	-2.96764400	1.85912700	-0.45620800
C	-4.62175300	-0.13666900	-0.44000700
O	-2.78701800	2.24737900	-1.58450500
C	-2.96434700	2.73449500	0.75710000
O	-5.50459400	0.66239900	-0.67240200
C	-4.84834100	-1.61833800	-0.36275400
H	-3.95516100	2.69786000	1.22084400
H	-2.24653300	2.34461300	1.48383600
H	-2.71570800	3.76003400	0.48749400
H	-4.27168600	-2.11993100	-1.14398400
H	-4.49827300	-2.00783800	0.59523200
H	-5.90898200	-1.82683700	-0.49164100
O	1.47043300	0.42305000	2.22208000
H	2.34120000	0.83237600	2.21174500

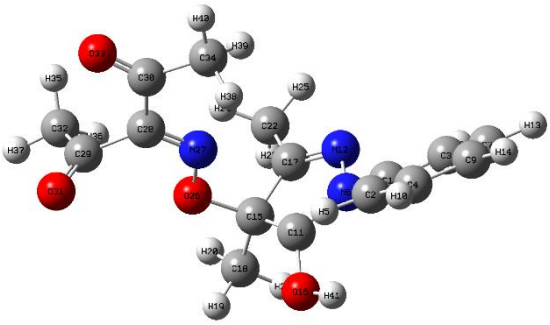
Intermediate VIII, conformer VIII(8) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.151072
Sum of electronic and thermal Enthalpies= -1085.150128
Sum of electronic and thermal Free Energies= -1085.232744
BSSE energy = 0.003928423950
0 2

C	-3.04015700	-0.25195400	-0.13432400
C	-2.90300100	-1.64209700	-0.15033900
C	-4.26449600	0.33280900	-0.46770300
C	-3.99597200	-2.43908300	-0.47266700
H	-1.94044800	-2.09818300	0.05480000
N	-1.95441500	0.55398500	0.23715600
C	-5.33834700	-0.47542900	-0.80854200
H	-4.35988100	1.41090800	-0.45873400
C	-5.21616800	-1.86349900	-0.80374400
H	-3.88096200	-3.51695000	-0.48208900
C	-0.83553300	0.16536000	0.96023300
N	-1.78279900	1.79510600	-0.33871300
H	-6.28462700	-0.01571200	-1.07057500
H	-6.06331300	-2.48769100	-1.06202700
C	0.14688100	1.28306200	0.87721800
O	-0.95067200	-0.55093900	2.10771300
C	-0.62876900	2.24564800	0.00189600
C	0.61940600	1.84697600	2.20658600
H	1.14267100	1.07781700	2.77547900
H	1.29679800	2.68500900	2.03320000
H	-0.23554600	2.19251200	2.79107700
C	-0.12148100	3.57663800	-0.42232500
H	0.03419300	4.22259600	0.44699400
H	0.84115000	3.47431000	-0.93026300
H	-0.83361000	4.05612000	-1.09363400
O	1.32432000	0.92345300	0.06317700
N	1.96840800	-0.15040200	0.58640400
C	2.95808300	-0.51871200	-0.12823300
C	3.37186100	0.18178100	-1.41308700
C	3.74227600	-1.71248400	0.31741200
O	4.26950100	0.98816700	-1.38247400
C	2.61633400	-0.20527100	-2.64528400
O	4.60410400	-2.14161800	-0.42126600
C	3.41969400	-2.31997000	1.65099000
H	2.78261000	-1.26928700	-2.84079900
H	1.54545500	-0.06654100	-2.47333700
H	2.94628100	0.38705800	-3.49767900
H	3.61226100	-1.59249400	2.44334600
H	2.36059400	-2.57950700	1.70453800
H	4.03540100	-3.20516400	1.80065400
H	-1.77905400	-1.04078300	2.11939800

Intermediate VIII, conformer VIII(9) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

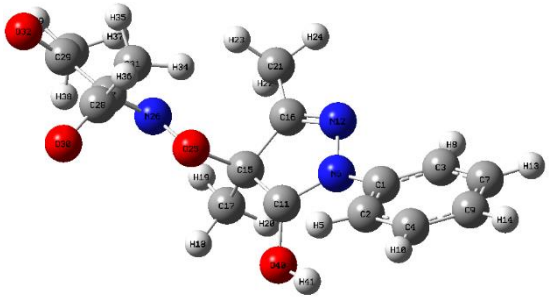


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -1085.153840
 Sum of electronic and thermal Enthalpies= -1085.152896
 Sum of electronic and thermal Free Energies= -1085.235067
 BSSE energy = 0.003928146121
0 2

C	-2.81018600	0.02009300	0.01331200
C	-2.79328200	1.05403100	-0.92409300
C	-3.89806400	-0.12499200	0.87648600
C	-3.87654200	1.92216900	-1.01186500
H	-1.92376800	1.20310000	-1.55559300
N	-1.74117600	-0.89082700	0.07565100
C	-4.96005500	0.76238900	0.79306300
H	-3.89825200	-0.92739500	1.60330600
C	-4.96174100	1.78298900	-0.15606600
H	-3.85707500	2.72271400	-1.74252800
C	-0.81309900	-1.13604900	-0.92070500
N	-1.27071200	-1.30322900	1.30585400
H	-5.80056200	0.64907400	1.46840400
H	-5.80033500	2.46605100	-0.22160900
C	0.34522300	-1.82078100	-0.30301400
O	-1.16779900	-1.39225700	-2.20151300
C	-0.11855400	-1.84957900	1.13507600
C	0.73504200	-3.16127500	-0.90025900
H	1.00682300	-3.04076500	-1.94954900
H	1.58519300	-3.57964300	-0.35865600
H	-0.10512400	-3.85434400	-0.83179100
C	0.67546500	-2.42887500	2.24993600
H	0.81692200	-3.50426000	2.10636600
H	1.66793800	-1.97061500	2.28869500
H	0.16935600	-2.26474500	3.20104500
O	1.59390300	-1.02187800	-0.41365700
N	1.39252200	0.23685200	0.04765200
C	2.44052900	0.96040500	0.00190000
C	3.77846200	0.47918500	-0.53621400
C	2.33659000	2.36248800	0.51545400
O	4.09013400	0.74829900	-1.67077400
C	4.62652000	-0.30345900	0.41669700
O	3.35027400	3.02527600	0.59111900
C	0.98233500	2.87413500	0.91224600

H	4.86826000	0.32892800	1.27659300
H	4.05652100	-1.15928100	0.78884000
H	5.54129300	-0.63781600	-0.07077200
H	0.32060600	2.87933600	0.04255700
H	0.52767200	2.21422500	1.65369200
H	1.08228800	3.88210200	1.31121500
H	-1.98614700	-0.93900300	-2.42743500

Intermediate VIII, conformer VIII(10) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

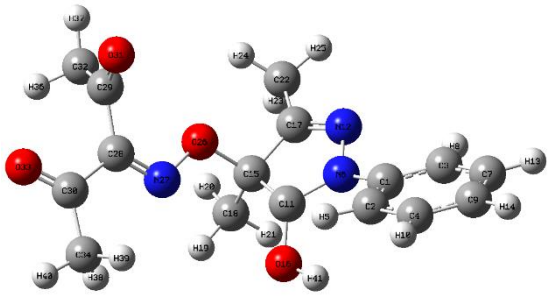


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1085.150023
Sum of electronic and thermal Enthalpies= -1085.149079
Sum of electronic and thermal Free Energies= -1085.231128
BSSE energy = 0.003672567900
0 2

C	3.29450300	0.00608400	-0.17506400
C	3.55710900	1.28993100	0.30748400
C	4.28360200	-0.69695200	-0.86671300
C	4.81565900	1.85199400	0.12242200
H	2.77197500	1.86395000	0.78846300
N	2.04371200	-0.58647600	0.05472300
C	5.52576200	-0.11333200	-1.06407400
H	4.06870600	-1.68924900	-1.24217600
C	5.80397300	1.15684300	-0.56278600
H	5.01192600	2.84867400	0.50068700
C	1.13820500	-0.25709500	1.04970000
N	1.47051600	-1.39065400	-0.90560900
H	6.28890200	-0.66133800	-1.60503900
H	6.78088600	1.60101900	-0.71225900
C	-0.12758000	-0.98224700	0.75506700
C	0.25921800	-1.64608500	-0.55458800
C	-0.59985000	-1.92740900	1.84908500
H	-0.80012900	-1.36801000	2.76394100
H	-1.50736500	-2.44594300	1.54099400
H	0.17897800	-2.66510000	2.05261400
C	-0.62711300	-2.52710400	-1.36223700
H	-1.00303100	-3.35526000	-0.75483100
H	-1.49642500	-1.97553100	-1.72862500
H	-0.07569400	-2.93135500	-2.21129800
O	-1.14224300	0.06820700	0.52224000
N	-2.36592200	-0.44913600	0.23758700

C	-3.22096500	0.45231600	-0.04988500
C	-2.90707400	1.94052300	-0.05489100
C	-4.60339200	0.01321500	-0.41662600
O	-3.20628600	2.60911500	0.90423900
C	-2.24609300	2.46843700	-1.28925100
O	-5.38811600	0.85081900	-0.81002300
C	-4.94632600	-1.44202800	-0.28487200
H	-1.33692100	1.89459200	-1.48822600
H	-2.92007400	2.32313800	-2.13938300
H	-2.01263900	3.52612600	-1.17494700
H	-4.23612600	-2.05351700	-0.84511500
H	-4.87362900	-1.74347000	0.76302400
H	-5.95867500	-1.60681000	-0.64966300
O	1.52220300	-0.08000700	2.33817100
H	2.39890900	0.31432400	2.38128200

Intermediate VIII, conformer VIII(11) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.150512

Sum of electronic and thermal Enthalpies= -1085.149568

Sum of electronic and thermal Free Energies= -1085.231671

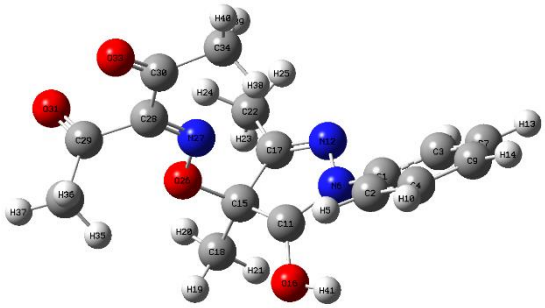
BSSE energy = 0.003871779448

0 2

C	-3.13399800	-0.19496800	-0.17415800
C	-3.05474500	-1.58163700	-0.32224000
C	-4.34374200	0.46438400	-0.40594900
C	-4.19022500	-2.30355200	-0.67321500
H	-2.10397700	-2.08964000	-0.20109400
N	-2.00406700	0.53096400	0.22894500
C	-5.46121000	-0.26751800	-0.77758900
H	-4.39450200	1.53989900	-0.29520300
C	-5.39631500	-1.65378200	-0.90322400
H	-4.11994000	-3.37936900	-0.78615900
C	-0.88797200	0.03837500	0.89063600
N	-1.79350500	1.80751800	-0.24508700
H	-6.39618000	0.24993200	-0.96068500
H	-6.27692500	-2.21881400	-1.18476600
C	0.13211800	1.12475500	0.88969900
O	-1.00926500	-0.77201800	1.97317900
C	-0.61655000	2.18335200	0.10759300
C	0.62977600	1.56347100	2.25750700

H	1.12858500	0.73408700	2.75990600
H	1.33472100	2.38971300	2.14703300
H	-0.20986900	1.89039700	2.87401800
C	-0.06297600	3.52377200	-0.21764800
H	0.14135400	4.08783200	0.69740800
H	0.88085500	3.42554200	-0.76072700
H	-0.77006100	4.08632300	-0.82689100
O	1.29334500	0.79675600	0.04044400
N	1.92662900	-0.31706500	0.48742100
C	2.96076800	-0.59944500	-0.20303400
C	3.41664900	0.21266300	-1.40547500
C	3.77077300	-1.79142300	0.19960100
O	3.13938100	-0.17218100	-2.51513800
C	4.20301800	1.45030400	-1.10600200
O	4.82510300	-1.98745900	-0.36828000
C	3.24025500	-2.68020100	1.28596900
H	3.63541500	2.08458500	-0.41975900
H	5.13004700	1.16448600	-0.59909400
H	4.43121300	1.98928800	-2.02454500
H	3.03305800	-2.09914900	2.18670200
H	2.29456900	-3.12552700	0.96741400
H	3.96789500	-3.46174800	1.49773000
H	-1.83190700	-1.26983900	1.93328300

Intermediate VIII, conformer VIII(12) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1085.153984

Sum of electronic and thermal Enthalpies= -1085.153040

Sum of electronic and thermal Free Energies= -1085.235650

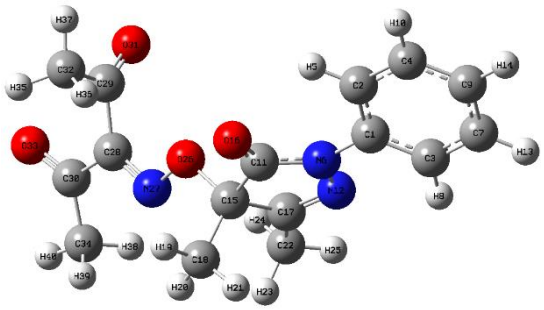
BSSE energy = 0.003964356428

0 2

C	-2.74833100	0.03073400	-0.05344700
C	-2.64317500	1.07384000	-0.97491700
C	-3.87356100	-0.06712200	0.76752200
C	-3.67471800	2.00015700	-1.08761200
H	-1.74798900	1.18099600	-1.57802800
N	-1.73012800	-0.93617400	0.03598800
C	-4.88343900	0.87666800	0.65921000
H	-3.94223900	-0.87655300	1.48316700
C	-4.79631000	1.90864300	-0.27344000
H	-3.58642900	2.80747500	-1.80567900

C	-0.74887000	-1.17654600	-0.90919800
N	-1.33551500	-1.38529200	1.28263400
H	-5.75261100	0.79964200	1.30264600
H	-5.59437400	2.63664000	-0.35837000
C	0.36784500	-1.88177300	-0.24078500
O	-1.03232100	-1.39614300	-2.21460100
C	-0.18264400	-1.94267100	1.16587300
C	0.79189200	-3.20776700	-0.84525900
H	1.12449900	-3.06369100	-1.87395000
H	1.60890600	-3.63919200	-0.26450300
H	-0.05063100	-3.90125200	-0.84254700
C	0.53564200	-2.56479200	2.30848500
H	0.66238100	-3.63928900	2.14532100
H	1.53358000	-2.12983400	2.41202100
H	-0.01967200	-2.41261100	3.23373700
O	1.62021400	-1.08044600	-0.25539800
N	1.38056000	0.17111600	0.20820300
C	2.40626300	0.92616100	0.16764900
C	3.76826100	0.47624600	-0.33493800
C	2.24136100	2.34006200	0.63081400
O	4.61112200	0.14469100	0.46319300
C	3.96048500	0.49182200	-1.81888400
O	3.17189600	3.10584700	0.48843700
C	0.92871500	2.73797000	1.24078600
H	3.17278300	-0.09959400	-2.29346600
H	3.85867000	1.52133700	-2.17641100
H	4.94268800	0.10110200	-2.08134400
H	0.10192500	2.48109700	0.57555800
H	0.77373000	2.18328200	2.16970000
H	0.93702700	3.80738400	1.44449500
H	-1.89043600	-1.02588700	-2.44431500

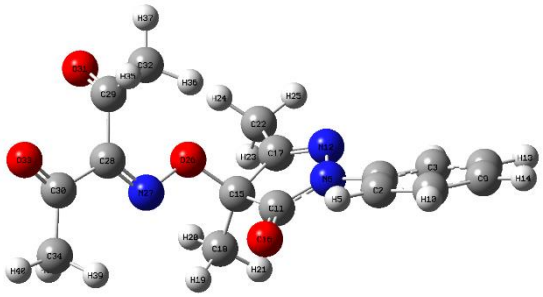
3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, conformer 9a(1) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1084.618672
Sum of electronic and thermal Enthalpies= -1084.617728
Sum of electronic and thermal Free Energies= -1084.697390
BSSE energy = 0.003799583428
0 1

C	3.40584300	0.03427300	-0.13144200
C	3.80145000	1.35491100	0.07819800
C	4.33323300	-0.92276900	-0.54198000
C	5.13254400	1.70522200	-0.11472100
H	3.07975000	2.09638500	0.38948500
N	2.05816800	-0.35082800	0.06698000
C	5.65675000	-0.55354600	-0.74007100
H	4.01340100	-1.94269100	-0.70854000
C	6.06441600	0.75868700	-0.52395800
H	5.43679700	2.73245900	0.05041700
C	1.12925000	0.21267200	0.89537000
N	1.56816000	-1.47284900	-0.61523200
H	6.37328900	-1.30079900	-1.06136300
H	7.09950300	1.04128700	-0.67623000
C	-0.11099300	-0.68772500	0.77701900
O	1.24215900	1.18549800	1.60533600
C	0.35408400	-1.67308800	-0.27325500
C	-0.43506600	-1.32563000	2.11775600
H	-0.63554400	-0.53929300	2.84802300
H	-1.30555600	-1.97524300	2.02993800
H	0.41554600	-1.91813400	2.46146900
C	-0.46475800	-2.77412500	-0.84179600
H	-0.85593500	-3.40991100	-0.04325300
H	-1.32290500	-2.36645400	-1.38187800
H	0.13780400	-3.37526200	-1.52220700
O	-1.14957100	0.17628800	0.30552200
N	-2.35641200	-0.46656000	0.24338000
C	-3.28049800	0.29811100	-0.18309200
C	-3.06091100	1.74325400	-0.60989400
C	-4.66801700	-0.26759400	-0.27232600
O	-2.92289700	1.98491000	-1.78339100
C	-3.04540600	2.76174600	0.48418000
O	-5.57309600	0.48779000	-0.55218000
C	-4.85778100	-1.73116100	-0.00631700
H	-4.00834500	2.73985600	1.00359800
H	-2.27278300	2.49862800	1.21204900
H	-2.86110400	3.75472800	0.07679800
H	-4.29500200	-2.31538700	-0.73855100
H	-4.46895600	-1.99036700	0.98062300
H	-5.91697700	-1.97345300	-0.07059200

3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, conformer 9a(2) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

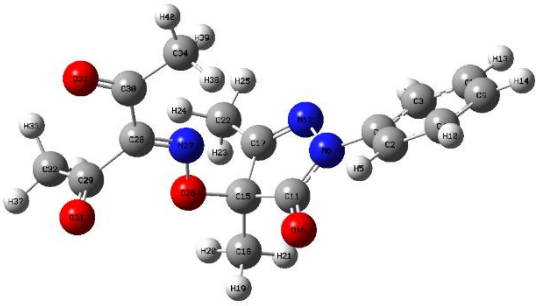


Number of imaginary frequencies = 0
 Sum of electronic and thermal Energies= -1084.618864
 Sum of electronic and thermal Enthalpies= -1084.617920
 Sum of electronic and thermal Free Energies= -1084.697672
 BSSE energy = 0.003866371981
0 1

C	3.15022300	-0.30108300	0.03850700
C	3.17500500	-1.69534400	0.01582700
C	4.32358500	0.42051900	0.25683900
C	4.38248500	-2.35802900	0.20205800
H	2.26438600	-2.25332300	-0.14798000
N	1.93490400	0.39827800	-0.15443200
C	5.51932700	-0.25755500	0.45084700
H	4.29174700	1.50155900	0.27966100
C	5.55692600	-1.64773500	0.42092800
H	4.39768700	-3.44175300	0.18236100
C	0.81679000	-0.00744300	-0.83139100
N	1.81538000	1.69634500	0.36016400
H	6.42778500	0.30850200	0.62224500
H	6.49344600	-2.17243500	0.56941100
C	-0.14824400	1.19106700	-0.76460300
O	0.61703700	-1.06751600	-1.38015100
C	0.66167800	2.15615300	0.06756000
C	-0.48932100	1.72208700	-2.14580200
H	-0.92475500	0.92943000	-2.75303600
H	-1.19818900	2.54791500	-2.06069600
H	0.41890400	2.08329200	-2.63307700
C	0.18761600	3.49798400	0.48704700
H	-0.02204600	4.11733800	-0.38948400
H	-0.74280500	3.40417200	1.05301900
H	0.93974000	3.99019100	1.10241500
O	-1.29700000	0.85727800	0.02006300
N	-2.19002900	0.07450700	-0.66459700
C	-3.09716400	-0.37852900	0.10511400
C	-3.16178000	-0.08904000	1.59780600
C	-4.15043000	-1.26161000	-0.49647700
O	-3.87367000	0.80093700	1.99295600
C	-2.32095600	-0.96553800	2.47089800
O	-4.94892700	-1.78360400	0.25123600
C	-4.15112900	-1.45715500	-1.98287300
H	-2.66901300	-1.99849600	2.37259200

H	-1.28322600	-0.93563900	2.12732200
H	-2.38886900	-0.64568400	3.50971600
H	-4.30845300	-0.49794800	-2.48202600
H	-3.18219100	-1.83699600	-2.31382200
H	-4.94312000	-2.15327600	-2.25311100

3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, conformer 9a(3) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

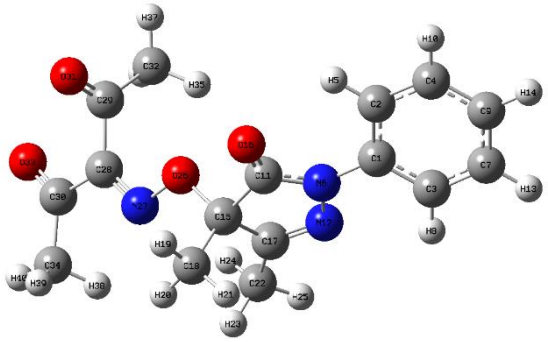


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1084.622561
Sum of electronic and thermal Enthalpies= -1084.621616
Sum of electronic and thermal Free Energies= -1084.701007
BSSE energy = 0.004014928112
0 1

C	2.96693200	0.09425300	0.02843100
C	3.17589000	1.12662900	0.94259900
C	3.97187100	-0.26605100	-0.86886600
C	4.39960700	1.78537500	0.95745900
H	2.39401200	1.40701600	1.63377700
N	1.73244600	-0.59646600	-0.00353000
C	5.18463900	0.40922700	-0.84721000
H	3.79689600	-1.06401700	-1.57803700
C	5.40697000	1.43418600	0.06652800
H	4.55870300	2.58618400	1.67056100
C	0.82215800	-0.75733200	1.00380900
N	1.33377800	-1.20903000	-1.20013000
H	5.96160500	0.12630700	-1.54822200
H	6.35676700	1.95583300	0.08226600
C	-0.28708900	-1.63865800	0.40039200
O	0.87172800	-0.34023600	2.13854800
C	0.20027200	-1.76823600	-1.02382600
C	-0.39694200	-2.96364100	1.13008800
H	-0.61979700	-2.77709300	2.18181000
H	-1.19268200	-3.56667100	0.68970700
H	0.54425000	-3.51146500	1.05804400
C	-0.53266500	-2.47916100	-2.10078800
H	-0.67376900	-3.53076100	-1.83633600
H	-1.52461100	-2.03866200	-2.23348400
H	0.01690300	-2.41584900	-3.03926800

O	-1.56259700	-1.01262100	0.49973400
N	-1.51171800	0.23776200	-0.06649900
C	-2.63818800	0.82686700	-0.04713300
C	-3.90384500	0.23223100	0.55547400
C	-2.71735300	2.19737500	-0.65974000
O	-4.21305500	0.54094100	1.67891500
C	-4.68091400	-0.69258400	-0.32593200
O	-3.81194000	2.70299900	-0.77617700
C	-1.44204000	2.85611500	-1.09122200
H	-5.00568500	-0.14353600	-1.21516600
H	-4.03276400	-1.50699400	-0.66090300
H	-5.54487000	-1.08827800	0.20599500
H	-0.79516100	3.00690400	-0.22330700
H	-0.89907200	2.21414600	-1.78791100
H	-1.67117200	3.81284100	-1.55695600

3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, conformer 9a(4) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

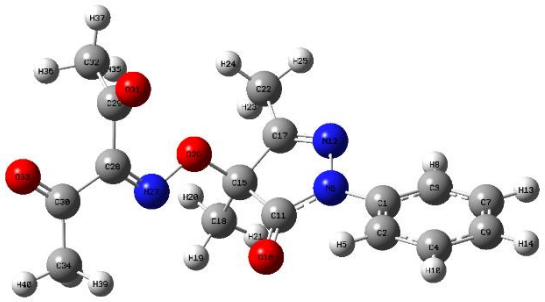


Number of imaginary frequencies = 0
Sum of electronic and thermal Energies= -1084.618525
Sum of electronic and thermal Enthalpies= -1084.617581
Sum of electronic and thermal Free Energies= -1084.697355
BSSE energy = 0.003777546050
0 1

C	-3.37342000	-0.03380200	-0.12522700
C	-3.79838400	-1.30567400	0.25810900
C	-4.26828400	0.86111900	-0.71123600
C	-5.12547400	-1.66819400	0.06016000
H	-3.10256100	-1.99961900	0.70720400
N	-2.02884600	0.36295800	0.07156500
C	-5.58798700	0.47898300	-0.91051800
H	-3.92673500	1.84283900	-1.01060600
C	-6.02474100	-0.78364700	-0.52350000
H	-5.45224900	-2.65703500	0.36096000
C	-1.13671700	-0.09369000	1.00148800
N	-1.50367800	1.38762300	-0.72603800
H	-6.27883200	1.17797800	-1.36791100
H	-7.05685900	-1.07590200	-0.67767500
C	0.12241300	0.76766200	0.80691700

O	-1.28896500	-0.96265900	1.82826000
C	-0.29974900	1.62169100	-0.36981900
C	0.43633500	1.55785000	2.06559800
H	0.59913900	0.86285700	2.89138100
H	1.32805000	2.16704800	1.91841200
H	-0.40270400	2.21164900	2.31332000
C	0.54164500	2.64654000	-1.04004500
H	0.92676600	3.36136500	-0.30840400
H	1.40419800	2.17664900	-1.51868600
H	-0.04362800	3.17606100	-1.79145700
O	1.15413100	-0.16708400	0.47033800
N	2.36104800	0.45532900	0.29959600
C	3.26886200	-0.35702700	-0.06972400
C	3.04808700	-1.85014600	-0.26956300
C	4.63801600	0.20145700	-0.32931600
O	3.35874400	-2.60730700	0.61581300
C	2.46658900	-2.26001400	-1.58505700
O	5.47424100	-0.53832300	-0.79989500
C	4.89213900	1.64273800	-0.00185300
H	1.52744200	-1.72553600	-1.75180700
H	3.15754000	-1.96815200	-2.38216300
H	2.30197700	-3.33623000	-1.60920700
H	4.17849300	2.28223400	-0.52581900
H	4.74866800	1.80910600	1.06852500
H	5.91043200	1.90122100	-0.28652800

3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, conformer 9a(5) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1084.618040

Sum of electronic and thermal Enthalpies= -1084.617096

Sum of electronic and thermal Free Energies= -1084.696597

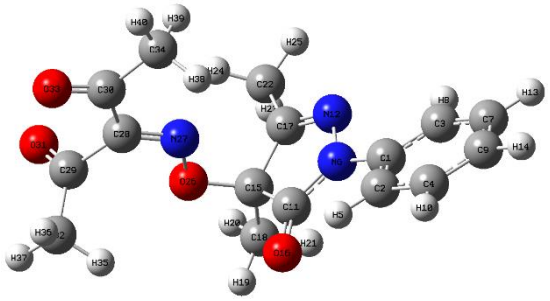
BSSE energy = 0.003835971878

0 1

C	-3.24432500	-0.24928700	-0.14027500
C	-3.33034900	-1.61521400	-0.40735600
C	-4.38860800	0.54739900	-0.16810900
C	-4.56996300	-2.17687200	-0.68976000
H	-2.44168200	-2.22971300	-0.39285300
N	-1.99552700	0.34540300	0.15978600

C	-5.61734600	-0.02773400	-0.46241000
H	-4.30958100	1.60730100	0.03374500
C	-5.71603100	-1.39107800	-0.72018800
H	-4.63299200	-3.23927400	-0.89563800
C	-0.89508300	-0.23303000	0.73362500
N	-1.81918500	1.71065100	-0.09704100
H	-6.50323700	0.59660100	-0.48484000
H	-6.67804800	-1.83628000	-0.94558400
C	0.11684400	0.91705900	0.90140900
O	-0.74604800	-1.38616800	1.06721100
C	-0.64694300	2.05586500	0.26975600
C	0.44970000	1.15717500	2.36440600
H	0.85049400	0.24625400	2.80800200
H	1.18454900	1.96002600	2.45066700
H	-0.45446900	1.44561100	2.90478000
C	-0.11505500	3.43144100	0.10569900
H	0.15084200	3.85618600	1.07754600
H	0.79184600	3.41017500	-0.50418800
H	-0.85722400	4.06859400	-0.37377300
O	1.27146500	0.70622600	0.08397700
N	2.11627300	-0.23739400	0.60586500
C	3.10058200	-0.46592100	-0.16833700
C	3.28968100	0.19885700	-1.52482600
C	4.13631700	-1.44986300	0.29082700
O	2.91819300	-0.37883500	-2.51602600
C	3.95153700	1.54027500	-1.51386800
O	5.14156800	-1.56948600	-0.37594100
C	3.87179800	-2.22807100	1.54446500
H	3.41687900	2.20783400	-0.83279200
H	4.96933500	1.42579900	-1.12783900
H	3.97896800	1.96015700	-2.51835100
H	3.69162900	-1.54920100	2.38057500
H	2.96866400	-2.83056500	1.42052000
H	4.72512000	-2.87003200	1.75563200

3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a, conformer 9a(6) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 0

Sum of electronic and thermal Energies= -1084.623238

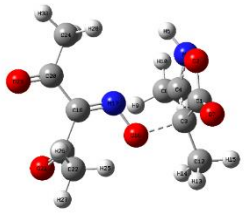
Sum of electronic and thermal Enthalpies= -1084.622294

Sum of electronic and thermal Free Energies= -1084.702087
BSSE energy = 0.004023197059
0 1

C	-2.94873500	-0.14096200	0.07764300
C	-3.10461800	-1.17098100	1.00532700
C	-3.99263200	0.19243900	-0.78530800
C	-4.31337800	-1.85426300	1.06753700
H	-2.29409500	-1.43126500	1.67054100
N	-1.73156000	0.57604500	-0.00265700
C	-5.18987900	-0.50677700	-0.71581400
H	-3.85929600	0.98862700	-1.50525600
C	-5.35893300	-1.52982100	0.21136100
H	-4.43049900	-2.65302600	1.79101100
C	-0.77534800	0.74158400	0.95952100
N	-1.40606100	1.21673900	-1.20814500
H	-5.99678900	-0.24406800	-1.39037200
H	-6.29678600	-2.07025400	0.26423300
C	0.27614600	1.66574800	0.32083600
O	-0.75059400	0.29716700	2.08556100
C	-0.27862100	1.80015700	-1.07789000
C	0.37235200	2.98436400	1.06496600
H	0.64733100	2.79197000	2.10331500
H	1.12695300	3.61997100	0.59909800
H	-0.58945900	3.49980700	1.04243600
C	0.38771300	2.54256100	-2.17624100
H	0.50029500	3.59714000	-1.90976400
H	1.38977700	2.13916100	-2.34515100
H	-0.19319600	2.46447000	-3.09448500
O	1.57372200	1.08210800	0.35907000
N	1.55087000	-0.14546600	-0.25758800
C	2.67363700	-0.73853000	-0.19433300
C	3.90970600	-0.14603400	0.46839100
C	2.77638100	-2.10748600	-0.80629100
O	4.72065200	0.42412100	-0.21831800
C	4.01593200	-0.33701800	1.94704000
O	3.80790200	-2.72244200	-0.64770800
C	1.59894700	-2.63363900	-1.57022100
H	3.11805600	0.05905000	2.42973500
H	4.05753300	-1.40909700	2.16306800
H	4.90681400	0.15732800	2.33154500
H	0.70476600	-2.62292500	-0.94345600
H	1.39738400	-1.98765300	-2.42833400
H	1.81299700	-3.64616300	-1.90740600

Calculations of activation energies for schemes 10 (S1) and 11 (S3)

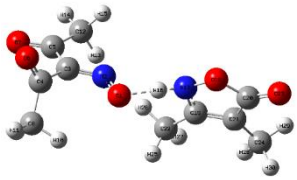
Transition state for [4b' + 2] to **I (TS1)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies= -874.080723
 Sum of electronic and thermal Enthalpies= -874.079779
 Sum of electronic and thermal Free Energies= -874.148819
0 2

C	-2.13304300	-0.34739400	-1.22712800
O	-2.22486200	1.00826900	-1.39074500
C	-1.96815800	-0.62487800	0.22912300
C	-2.19147200	0.63308700	0.83619900
N	-2.34633500	1.58273900	-0.12701500
H	-1.84369700	2.46377300	-0.09608800
O	-2.17191700	-1.09009100	-2.16567800
C	-2.17626000	0.98915600	2.27331200
H	-1.21626600	0.70799900	2.71557300
H	-2.33320000	2.05845100	2.41711400
H	-2.96158600	0.44900000	2.80869700
C	-2.42523900	-1.93146200	0.79688400
H	-2.00710600	-2.75415700	0.21644400
H	-2.10079100	-2.02586100	1.83377500
H	-3.51484500	-1.99415700	0.75863900
O	-0.21573900	-0.92424000	0.29512100
N	0.43791600	0.20397300	0.06616200
C	1.71523200	0.10130600	0.06983700
C	2.43865000	-1.20670400	0.33701500
C	2.51787500	1.32179300	-0.20928900
O	2.87340300	-1.43387900	1.44138700
C	2.56653400	-2.13854200	-0.82801600
O	3.72664600	1.22225000	-0.29328500
C	1.79402100	2.62792300	-0.38737600
H	1.57689000	-2.32711600	-1.25317400
H	3.16779900	-1.65168300	-1.60247300
H	3.03640200	-3.07293500	-0.52350200
H	1.07611300	2.55241200	-1.20682300
H	1.23070500	2.87069400	0.51654000
H	2.51943200	3.41242800	-0.59651800

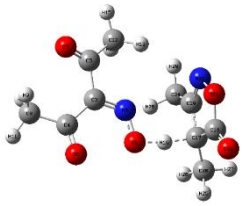
Transition state for [4b' + 2] to **[II + 2a] (TS2)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies= -874.089324
 Sum of electronic and thermal Enthalpies= -874.088379
 Sum of electronic and thermal Free Energies= -874.161093
0 2

O	0.62828100	-1.20069400	0.15115800
N	1.21972100	-0.12661900	-0.19259600
C	2.49785600	0.00646600	-0.15188100
C	3.41075500	-1.13011900	0.27929500
C	3.08680000	1.31299500	-0.54384900
O	4.09930000	-1.68354000	-0.54252100
O	4.28039800	1.48821200	-0.39829000
C	3.39313800	-1.47674500	1.73684800
H	3.79163400	-0.62577400	2.29884300
H	2.36452600	-1.63627700	2.06977100
H	3.99796400	-2.36249900	1.92625100
C	2.17068400	2.37511900	-1.08812400
H	1.44274100	2.66766600	-0.32757200
H	2.76377800	3.24110400	-1.37725800
H	1.61074200	1.99687400	-1.94551600
H	-0.68886100	-0.81055700	-0.26534200
N	-1.62818700	-0.28749100	-0.45895400
O	-2.55068100	-1.04792800	-1.12009900
C	-2.23688500	0.47820900	0.48271800
C	-3.80715100	-0.66505300	-0.66148300
C	-3.59395200	0.33314600	0.37421500
C	-1.41290100	1.29378400	1.41179000
O	-4.79939100	-1.14270600	-1.13780900
C	-4.69442700	0.99820600	1.11115300
H	-1.12666700	0.69166700	2.27777200
H	-0.50200400	1.63033800	0.91478800
H	-1.97533000	2.15788400	1.76302400
H	-4.32330200	1.81849300	1.72498100
H	-5.44096900	1.38541700	0.41344300
H	-5.20175000	0.28161400	1.76405000

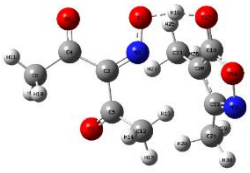
Transition state [4b" + 2] to **[II+2a] (TS3)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies=   -874.079233
 Sum of electronic and thermal Enthalpies=   -874.078289
 Sum of electronic and thermal Free Energies=   -874.147361
0 2

O	-0.00467800	-1.27289300	-0.29699400
N	-0.61903400	-0.17324100	-0.09531400
C	-1.89704100	-0.09238000	0.02658200
C	-2.78687600	-1.31111200	-0.11052500
C	-2.41178100	1.28892900	0.33094900
O	-2.28127800	-2.40905700	-0.06678000
O	-3.52136000	1.42222200	0.79909100
C	-4.25652000	-1.11682200	-0.34810200
H	-4.73361800	-0.78438800	0.57563000
H	-4.43422800	-0.34129400	-1.09568100
H	-4.68468100	-2.06486100	-0.66999800
C	-1.50996600	2.45577500	0.04384200
H	-0.55742400	2.34802200	0.56630200
H	-1.28651600	2.49427800	-1.02580100
H	-2.00943700	3.37262900	0.35139900
H	1.16712400	-0.95738800	-0.37092300
C	2.40950400	-0.44252100	-0.41303200
C	2.70827600	-0.52481300	1.03474900
C	2.04336000	0.94368500	-0.57915900
C	3.12929900	-1.28724000	-1.42398500
O	2.32420300	0.67265800	1.57863700
O	3.15401300	-1.41307400	1.70425900
N	1.94946500	1.56033900	0.56197200
C	1.72974900	1.63763100	-1.85473500
H	3.17225700	-2.32420800	-1.08879900
H	2.62497800	-1.24978200	-2.39074900
H	4.15372500	-0.92699900	-1.55564900
H	0.92483400	1.11601200	-2.37827200
H	1.42754100	2.66666700	-1.66329000
H	2.60721000	1.63601200	-2.50598700

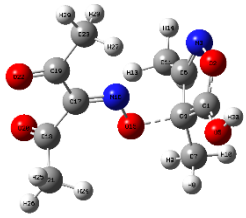
Transition state for [4b''' + 2] to **[II+2a] (TS4)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies= -874.092291
 Sum of electronic and thermal Enthalpies= -874.091347
 Sum of electronic and thermal Free Energies= -874.159396
0 2

O	-0.78546400	-2.07655800	-0.29051500
N	-0.70010600	-0.82335000	-0.42766100
C	-1.65443800	0.02259700	-0.24767900
C	-3.04291200	-0.40429200	0.17346300
C	-1.26811600	1.46540400	-0.40906200
O	-3.21899200	-1.50883700	0.63090800
O	-1.79168400	2.30303500	0.29402300
C	-4.16855900	0.57105200	-0.03381500
H	-4.11049500	1.35792500	0.72078800
H	-4.09634700	1.05260500	-1.01168000
H	-5.11436100	0.03963700	0.05826700
C	-0.26939000	1.81502600	-1.47478800
H	0.47524500	1.03452200	-1.62091700
H	-0.82200800	1.91371100	-2.41564800
H	0.20313900	2.76903600	-1.24503200
H	0.43935700	-2.44739500	-0.34279200
O	1.55143700	-2.43759300	-0.44078800
C	1.95866600	-1.24335300	-0.27275800
O	2.68906100	-0.67293300	-1.24107800
C	1.80199800	-0.33849000	0.78841800
N	3.04158100	0.61378200	-0.84043500
C	2.50888000	0.80823800	0.34118300
C	1.13333600	-0.56119200	2.09368700
C	2.67557300	2.10382700	1.05403000
H	0.69452400	-1.55767100	2.14700600
H	1.85287700	-0.45574400	2.91066400
H	0.34283300	0.17658800	2.25832400
H	1.69957200	2.55694600	1.24405000
H	3.16382900	1.94626100	2.01835100
H	3.27643300	2.79073700	0.45881900

Transition state for [4b''' + 2] to **III (TS5)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

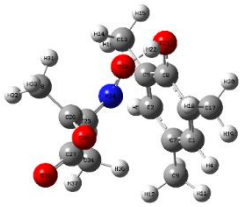


Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies= -874.067968
 Sum of electronic and thermal Enthalpies= -874.067024
 Sum of electronic and thermal Free Energies= -874.136484

0 2

C	-2.14630800	0.47928200	-1.03766500
O	-2.38465500	1.60415000	-0.35985700
N	-2.43812800	1.27724300	1.01017700
C	-1.87422800	-0.62682300	-0.18000400
O	-2.08774000	0.51225500	-2.35431400
C	-2.19411900	0.01443900	1.11534200
C	-2.34582500	-2.01867100	-0.51170200
H	-2.00976800	-2.30069400	-1.51011100
H	-1.94112400	-2.73001600	0.20948200
H	-3.43577100	-2.06258900	-0.47879500
C	-2.17346300	-0.67175000	2.43204800
H	-2.91789500	-1.47184600	2.45177500
H	-1.19226000	-1.12424500	2.59573700
H	-2.38564900	0.03305900	3.23518100
O	-0.21556500	-0.92348300	-0.13052100
N	0.44320000	0.23083900	-0.02563400
C	1.71380000	0.10607700	0.05589200
C	2.41710500	-1.24001200	0.05668000
C	2.53829600	1.34316300	0.14611000
O	2.74099800	-1.74356900	1.10606400
C	2.66919900	-1.85166400	-1.28656300
O	3.74926800	1.23872600	0.12453000
C	1.83303000	2.66570300	0.25097000
H	1.72750500	-1.91540000	-1.83866500
H	3.33695400	-1.19383400	-1.85186700
H	3.11844500	-2.83844600	-1.18175100
H	1.17967000	2.81450000	-0.61129500
H	1.19825400	2.68290400	1.13962200
H	2.57308600	3.46266300	0.30261700
H	-2.33033600	1.38428500	-2.68758700

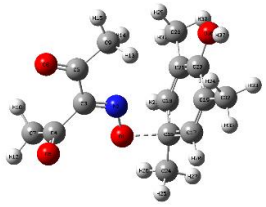
Transition state for [6e + 2] to **[IV+2a] (TS6)** (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)



Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies= -899.532784
 Sum of electronic and thermal Enthalpies= -899.531840
 Sum of electronic and thermal Free Energies= -899.607177
0 2

C	2.34614800	0.46442400	-1.38639500
C	2.87534900	0.40251400	0.97131600
C	1.61208600	-0.70249600	-1.28214800
H	2.43601900	0.94641400	-2.35472200
C	2.15219000	-0.75812400	1.13837300
H	3.36915400	0.84785400	1.82941500
C	2.98335300	1.03459400	-0.27918300
C	1.51376200	-1.32591900	-0.00160300
C	3.73649500	2.32432200	-0.40844100
H	4.61295200	2.33836500	0.24251500
H	4.05545700	2.50060300	-1.43670400
H	3.09457200	3.16081300	-0.11043800
C	2.01632600	-1.43663100	2.46683800
H	0.96240000	-1.55168200	2.73324600
H	2.44704800	-2.44077200	2.43672000
H	2.51743700	-0.86389600	3.24779000
C	0.96594200	-1.34304100	-2.47134300
H	-0.12105100	-1.38068600	-2.35878300
H	1.19889300	-0.79189400	-3.38234300
H	1.30923700	-2.37486000	-2.58468000
O	0.91214000	-2.49500800	0.13379900
H	-0.08994400	-2.40539400	-0.09816100
O	-1.40531700	-1.78972100	-0.12113600
N	-1.12865300	-0.56804500	0.08916200
C	-2.03565100	0.34565400	0.07931000
C	-3.48724600	0.00276700	-0.21682900
C	-1.67684600	1.75239300	0.37163700
O	-3.94328700	0.23816000	-1.30922300
O	-2.56980200	2.57463200	0.46327100
C	-4.26177100	-0.61425100	0.90669000
H	-3.72297500	-1.48496600	1.28970600
H	-4.33035500	0.11298300	1.72202100
H	-5.25962200	-0.89834000	0.57506600
C	-0.22826200	2.10288500	0.54148800
H	0.25225100	1.43660300	1.25990900
H	0.29018400	1.96704000	-0.41119700
H	-0.14220800	3.13907000	0.86456600

Transition state for [6e + 2] to V (TS7) (ωB97XD/6-311++G**, CH2Cl2, PCM solvation model)

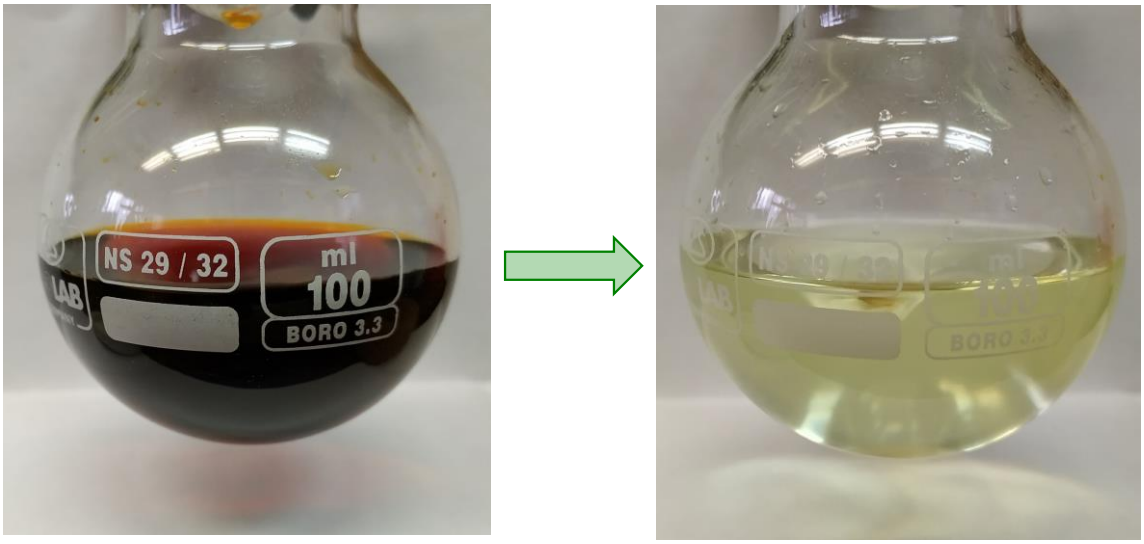


Number of imaginary frequencies = 1
 Sum of electronic and thermal Energies= -899.515744
 Sum of electronic and thermal Enthalpies= -899.514800
 Sum of electronic and thermal Free Energies= -899.588055
0 2

O	-0.63922400	1.39798400	-0.14012500
N	-0.77451300	0.10258300	-0.06466300
C	-1.97619300	-0.35460000	-0.06719400
C	-3.20029800	0.53364700	-0.16103400
C	-2.14772700	-1.82236000	0.03644200
O	-3.79944600	0.63091700	-1.20718500
C	-3.59910000	1.24468800	1.09692500
O	-3.26803200	-2.28994000	0.13697400
C	-0.91263900	-2.68435800	0.01376100
H	-3.89331800	0.49725600	1.84098500
H	-2.73886800	1.78603500	1.49916000
H	-4.42735900	1.92690600	0.90849200
H	-0.43620600	-2.61292200	-0.96744000
H	-0.18332400	-2.33729500	0.74738400
H	-1.19444400	-3.71732200	0.21228300
C	1.14028900	1.82585700	-0.10670500
C	1.62625400	1.13406700	-1.27800500
C	1.55502500	1.28210400	1.16632400
C	2.20786100	-0.10022900	-1.20284400
H	1.44957900	1.58873100	-2.24717400
C	2.13728200	0.05275100	1.27523500
H	1.32561200	1.85162600	2.06113600
C	2.43141300	-0.65840200	0.08211800
C	0.94071700	3.31487600	-0.20298100
H	0.41824900	3.57559400	-1.12489100
H	0.36405200	3.68185300	0.64784800
H	1.91280400	3.81470600	-0.20278900
C	2.47634500	-0.56266900	2.60262900
H	1.92537800	-1.49590900	2.74817800
H	3.54010200	-0.80514200	2.66580700
H	2.22374900	0.11803400	3.41633100
C	2.61240100	-0.86445800	-2.43391700
H	3.67995700	-1.10820500	-2.43010900
H	2.05067200	-1.80078400	-2.52548500
H	2.41255200	-0.27781400	-3.33023600
O	2.97014300	-1.88281200	0.23807200
H	3.13510000	-2.29809600	-0.61325500

Reaction monitoring by color disappearance of the reaction mixture

The progress of the reaction can be easily monitored by the color change of the reaction mixture - with complete conversion of the oxime radical, the characteristic dark red color disappears, and the solution becomes slightly orange or almost colorless (Figure S5).

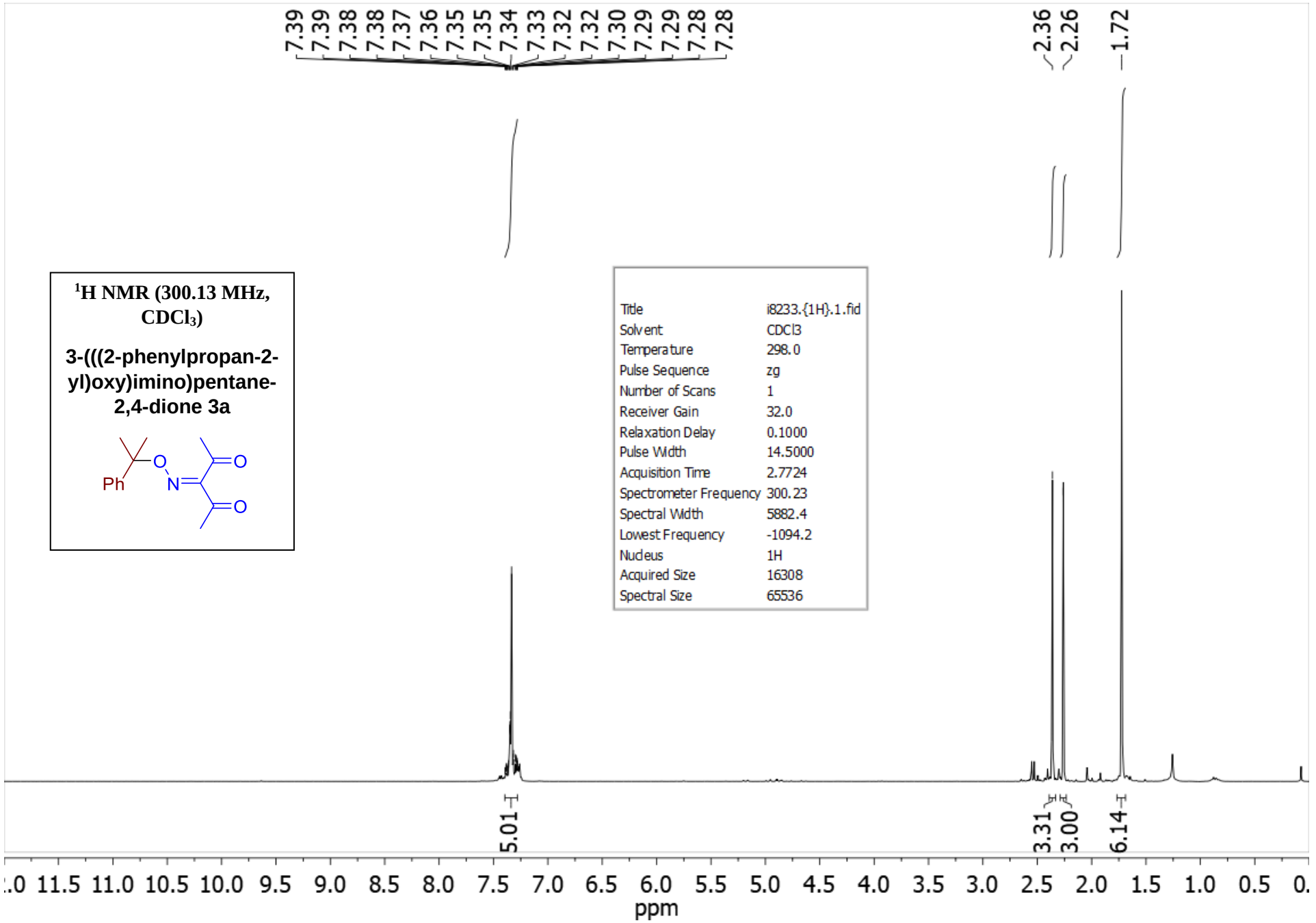


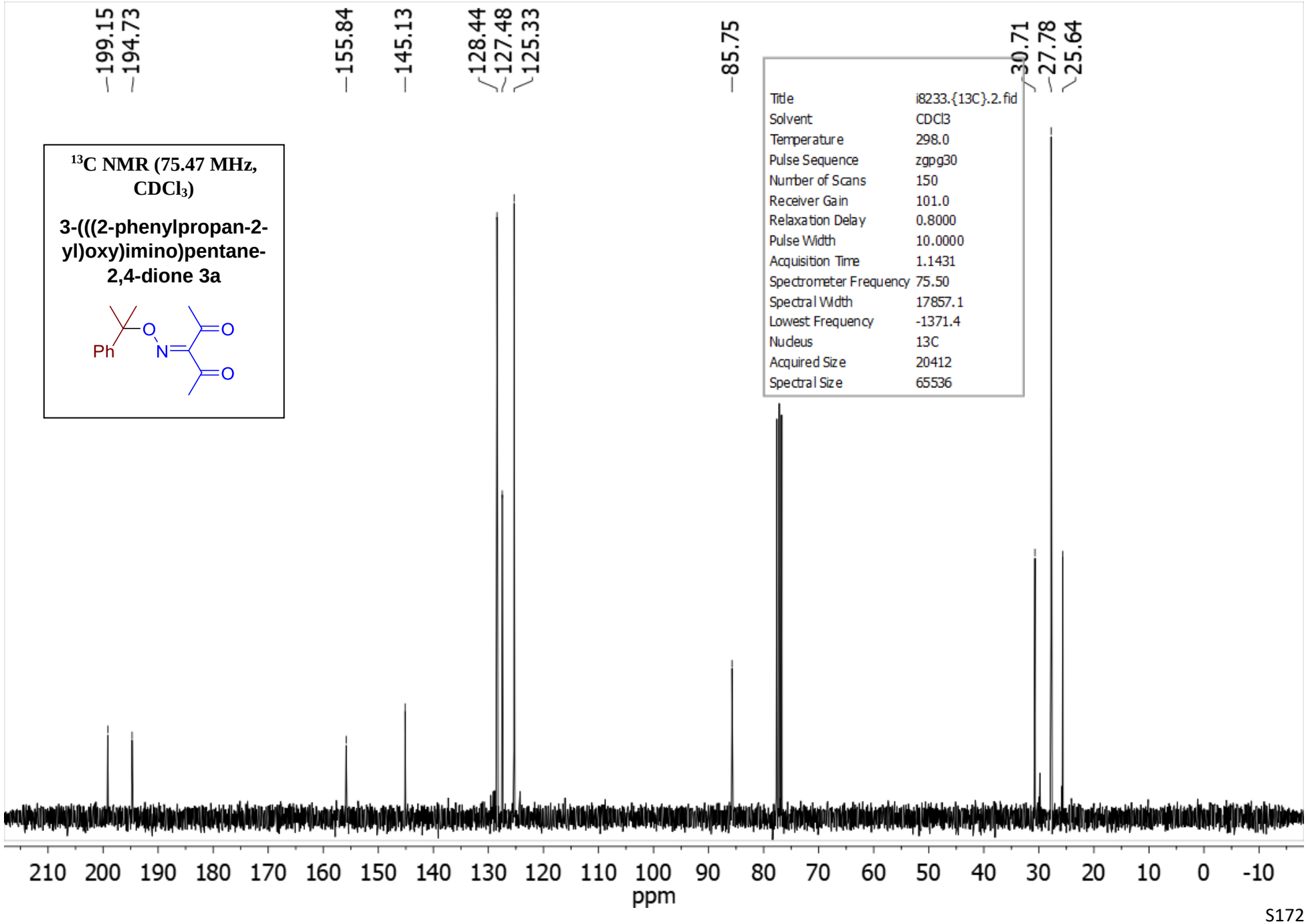
At the start of the reaction

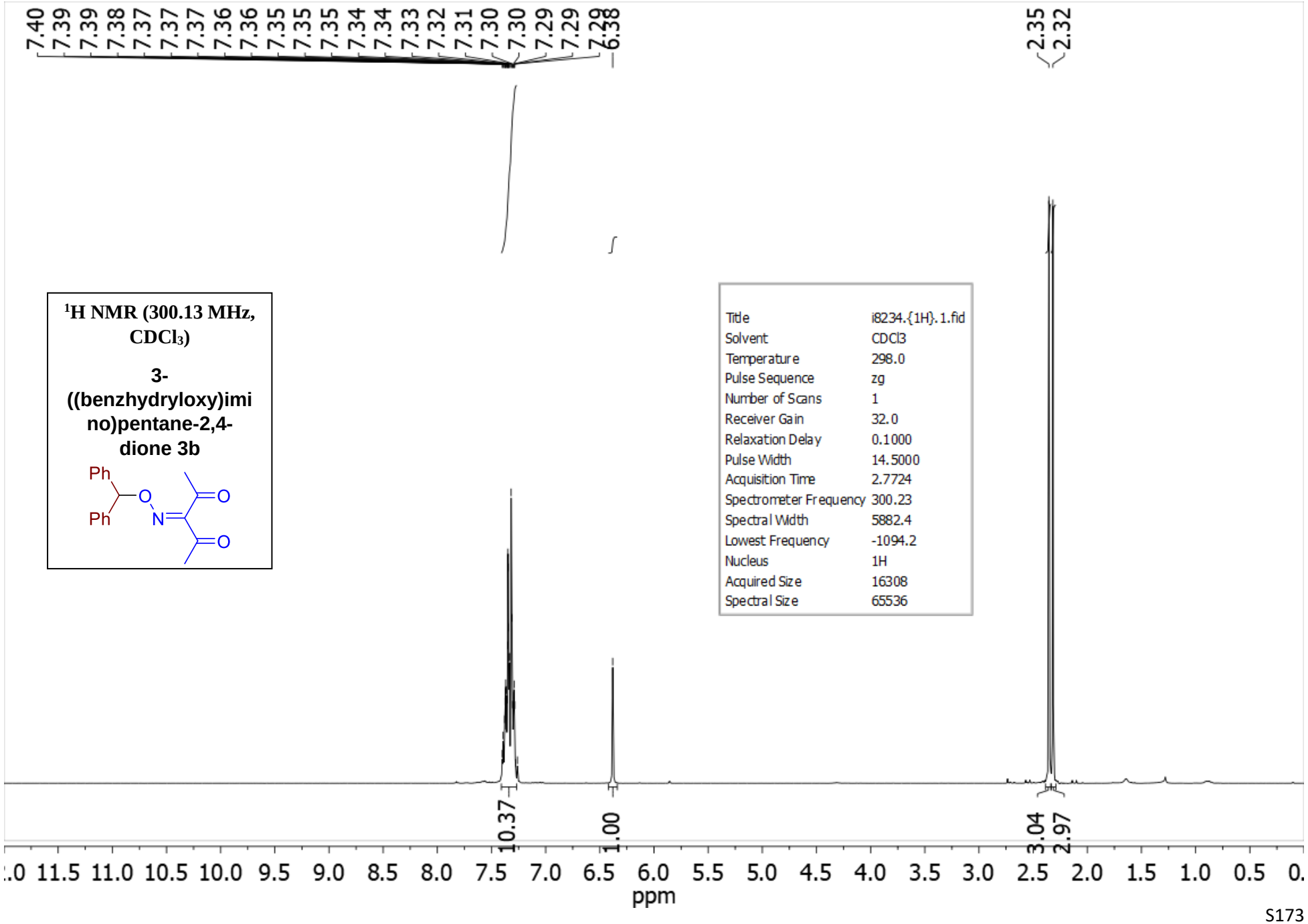
At the end of the reaction:
full conversion of diacetyliminoxyl

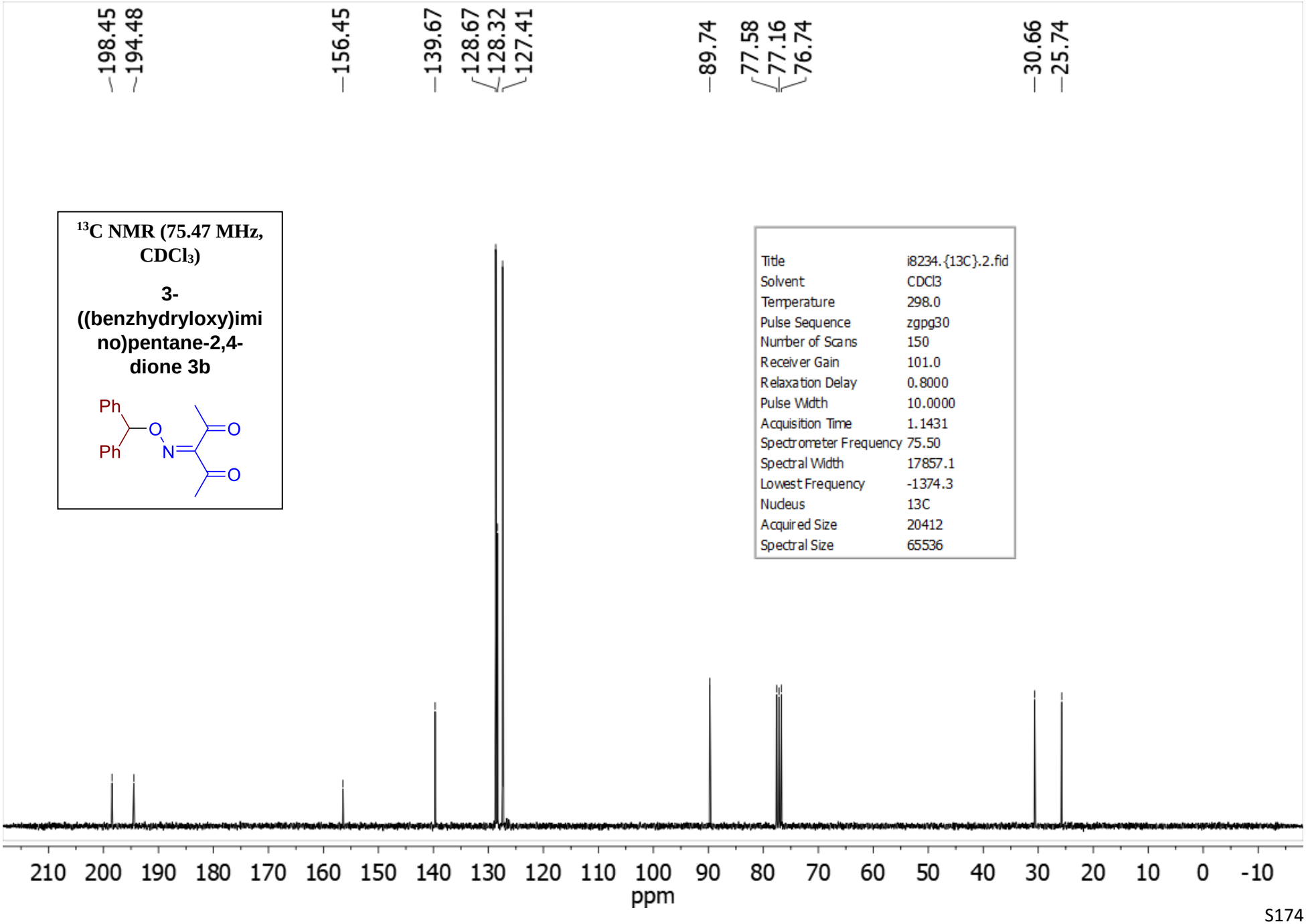
Figure S5. The reaction mixture at the 0% conversion (left) and at the 100% conversion (right) of diacetyliminoxyl.

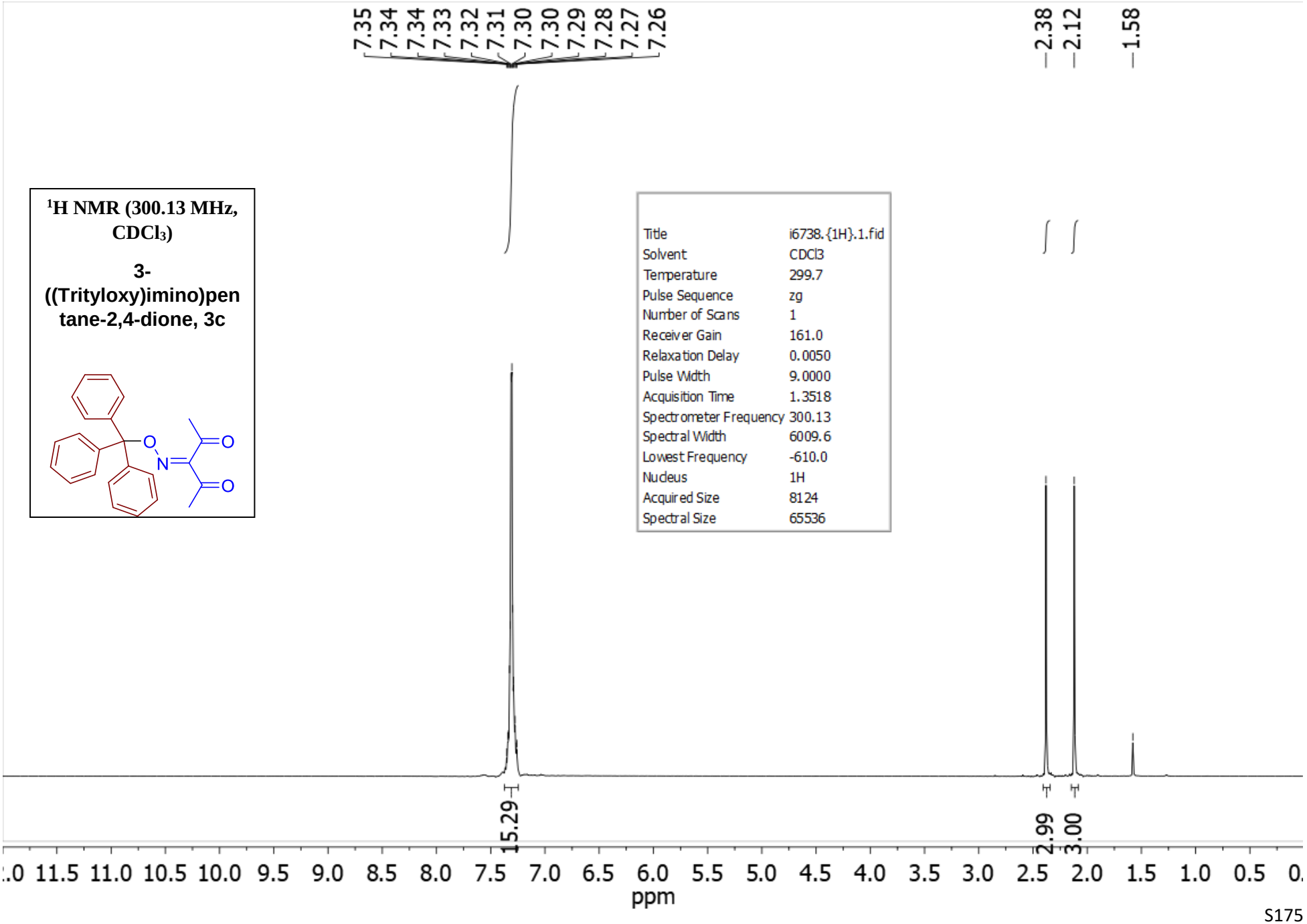
The ^{1}H and ^{13}C spectra of synthesized compounds


7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.30
7.29
7.29
7.28
7.28
2.36
2.26
1.72
^{1}H NMR (300.13 MHz, $CDCl_3$)
3-(((2-phenylpropan-2-yl)oxy)imino)pentane-2,4-dione 3a
Ph
O
N
O
O
Title i8233.{1H}.1.fid
Solvent CDCl3
Temperature 298.0
Pulse Sequence zg
Number of Scans 1
Receiver Gain 32.0
Relaxation Delay 0.1000
Pulse Width 14.5000
Acquisition Time 2.7724
Spectrometer Frequency 300.23
Spectral Width 5882.4
Lowest Frequency -1094.2
Nucleus 1H
Acquired Size 16308
Spectral Size 65536
5.01
3.31
3.00
6.14
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm


199.15
194.73
155.84
145.13
128.44
127.48
125.33
85.75
30.71
27.78
25.64
13C NMR (75.47 MHz, CDCl3)
3-(((2-phenylpropan-2-yl)oxy)imino)pentane-2,4-dione 3a
Ph
O
N
O
O
Title i8233.{13C}.2.fid
Solvent CDCl3
Temperature 298.0
Pulse Sequence zgpg30
Number of Scans 150
Receiver Gain 101.0
Relaxation Delay 0.8000
Pulse Width 10.0000
Acquisition Time 1.1431
Spectrometer Frequency 75.50
Spectral Width 17857.1
Lowest Frequency -1371.4
Nucleus 13C
Acquired Size 20412
Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


7.40 7.39 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.30 7.29 7.29 7.29 6.38
2.35 2.32
^{1}H NMR (300.13 MHz, CDCl$_3$)
3-((benzhydryloxy)imino)pentane-2,4-dione 3b
Ph
Ph
O
N
O
O
Title i8234.{1H}.1.fid
Solvent CDCl3
Temperature 298.0
Pulse Sequence zg
Number of Scans 1
Receiver Gain 32.0
Relaxation Delay 0.1000
Pulse Width 14.5000
Acquisition Time 2.7724
Spectrometer Frequency 300.23
Spectral Width 5882.4
Lowest Frequency -1094.2
Nucleus 1H
Acquired Size 16308
Spectral Size 65536
10.37
1.00
3.04
2.97
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm

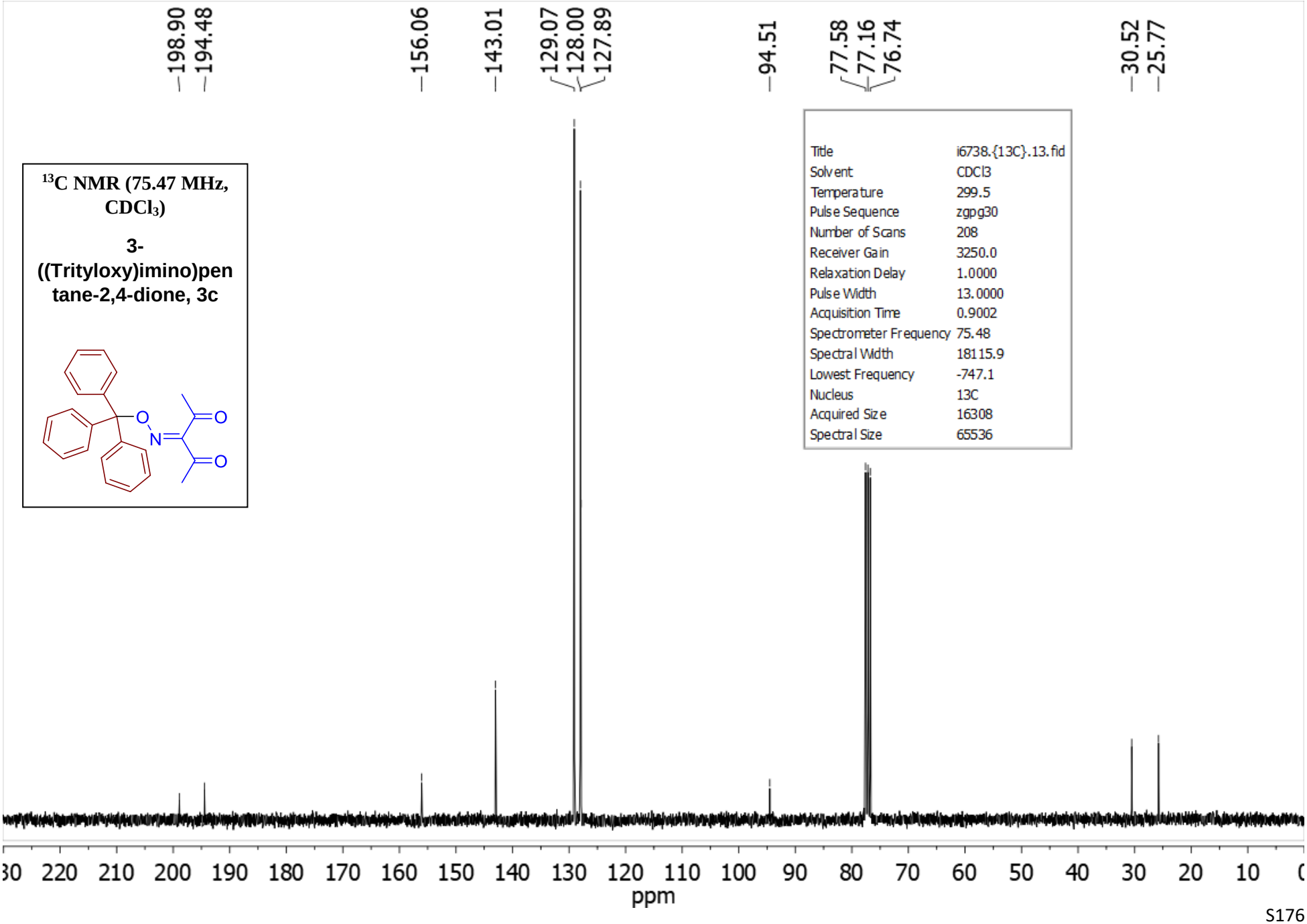

198.45
194.48
156.45
139.67
128.67
128.32
127.41
89.74
77.58
77.16
76.74
30.66
25.74
^{13}C NMR (75.47 MHz, CDCl$_3$)
3-((benzhydryloxy)imino)pentane-2,4-dione 3b
Ph
Ph
O
N
O
O
Title i8234.{13C}.2.fid
Solvent CDCl3
Temperature 298.0
Pulse Sequence zgpg30
Number of Scans 150
Receiver Gain 101.0
Relaxation Delay 0.8000
Pulse Width 10.0000
Acquisition Time 1.1431
Spectrometer Frequency 75.50
Spectral Width 17857.1
Lowest Frequency -1374.3
Nucleus 13C
Acquired Size 20412
Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



^{1}H NMR (300.13 MHz, $CDCl_3$)

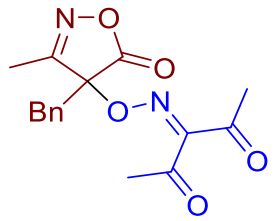
3-((Trityloxy)imino)pentane-2,4-dione, 3c

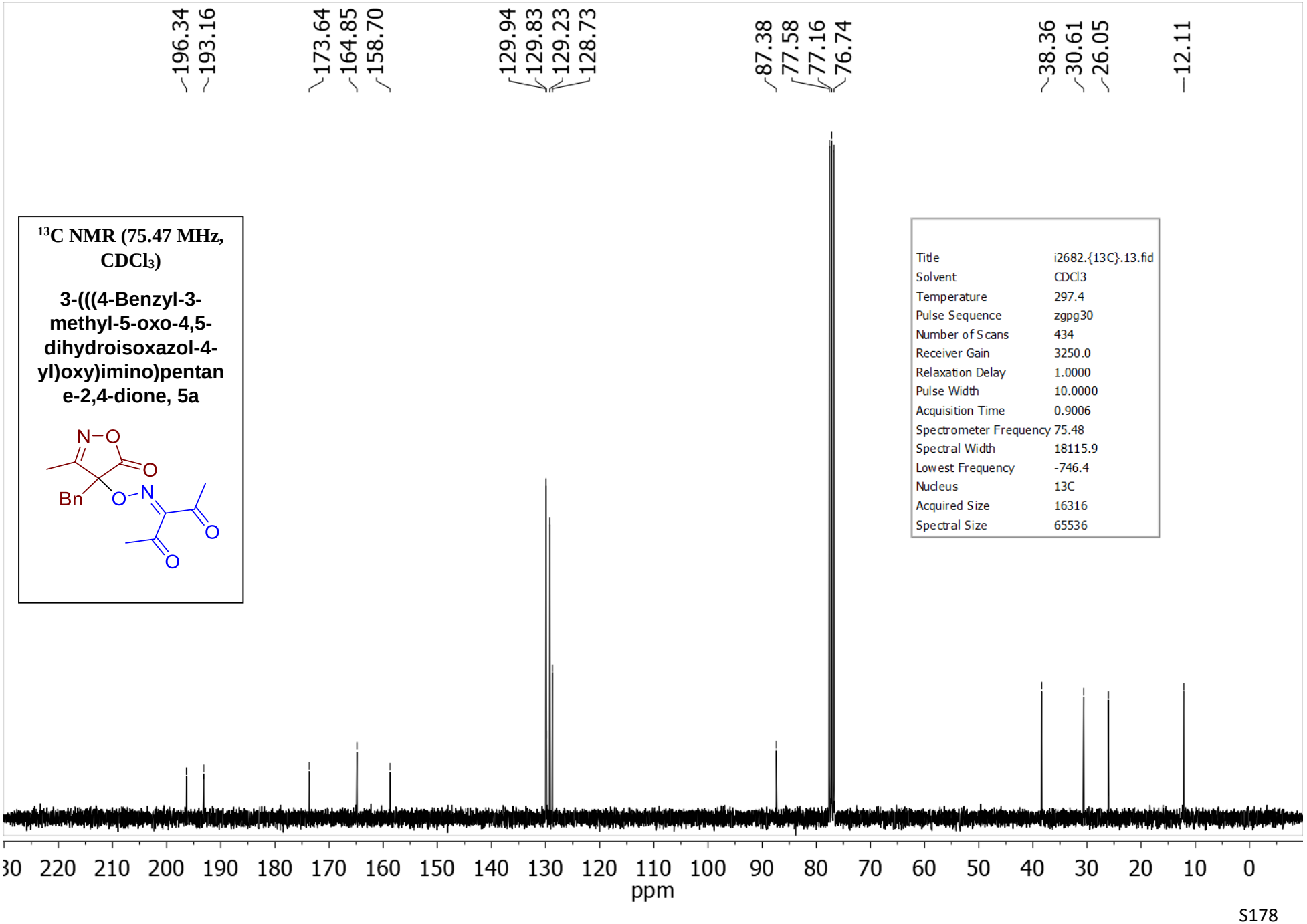
Title	i6738.{1H}.1.fid
Solvent	CDCl3
Temperature	299.7
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161.0
Relaxation Delay	0.0050
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.0
Nucleus	1H
Acquired Size	8124
Spectral Size	65536

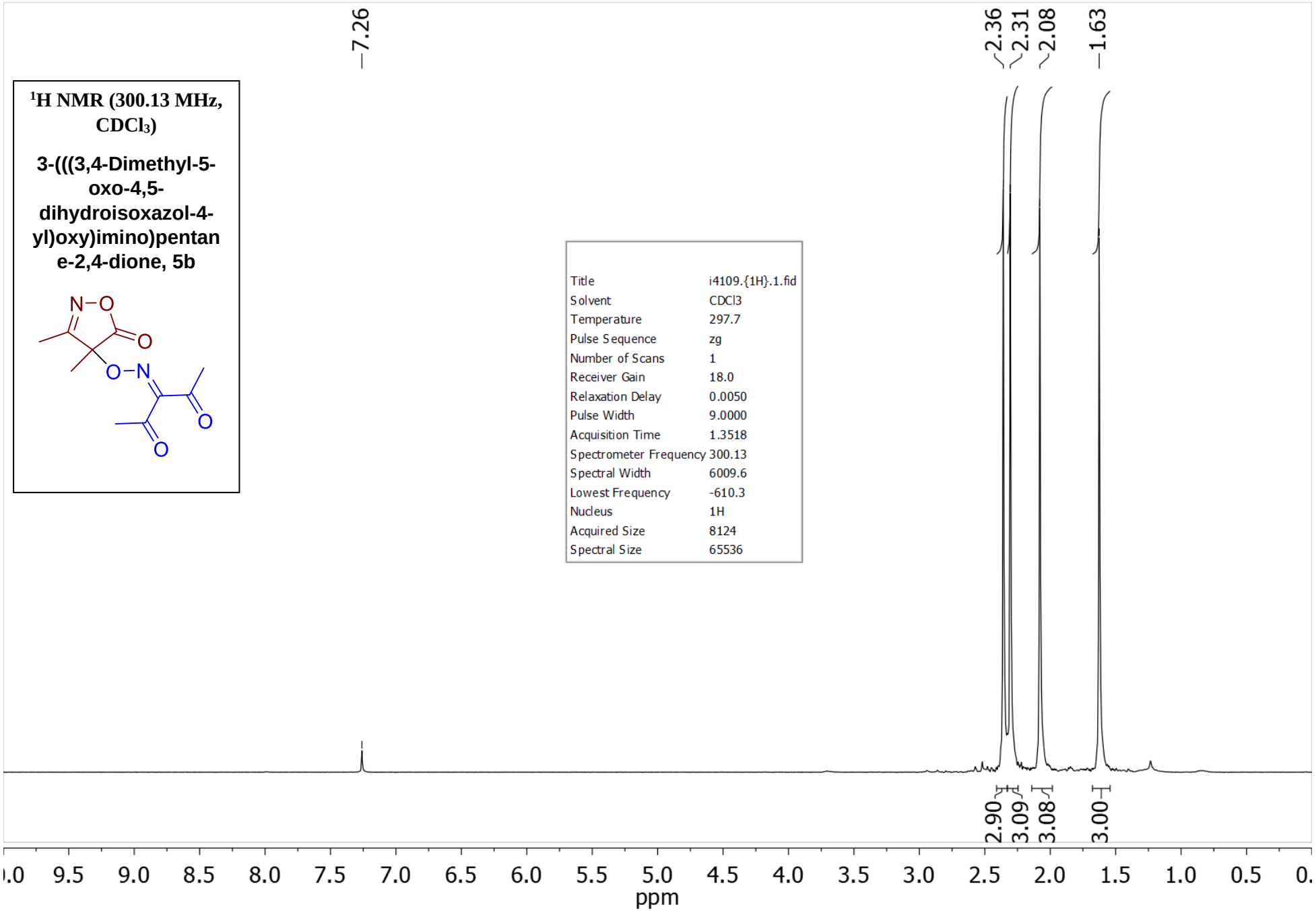

198.90
194.48
156.06
143.01
129.07
128.00
127.89
94.51
77.58
77.16
76.74
30.52
25.77
^{13}C NMR (75.47 MHz, $CDCl_3$)
3-((Trityloxy)imino)pentane-2,4-dione, 3c
Title i6738.{13C}.13.fid
Solvent CDCl3
Temperature 299.5
Pulse Sequence zgpg30
Number of Scans 208
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 13.0000
Acquisition Time 0.9002
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -747.1
Nucleus 13C
Acquired Size 16308
Spectral Size 65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

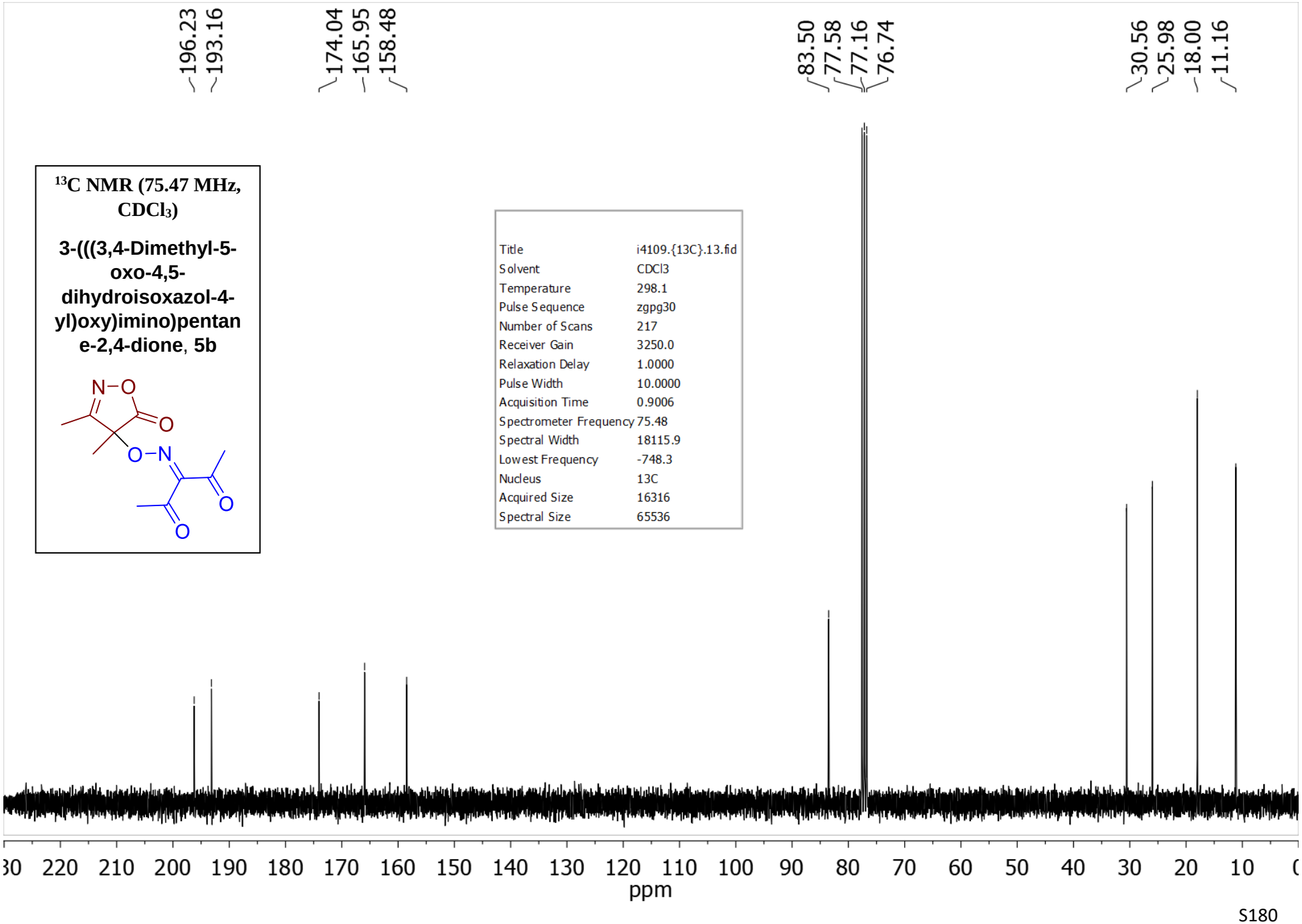
^{1}H NMR (300.13 MHz, $CDCl_3$)

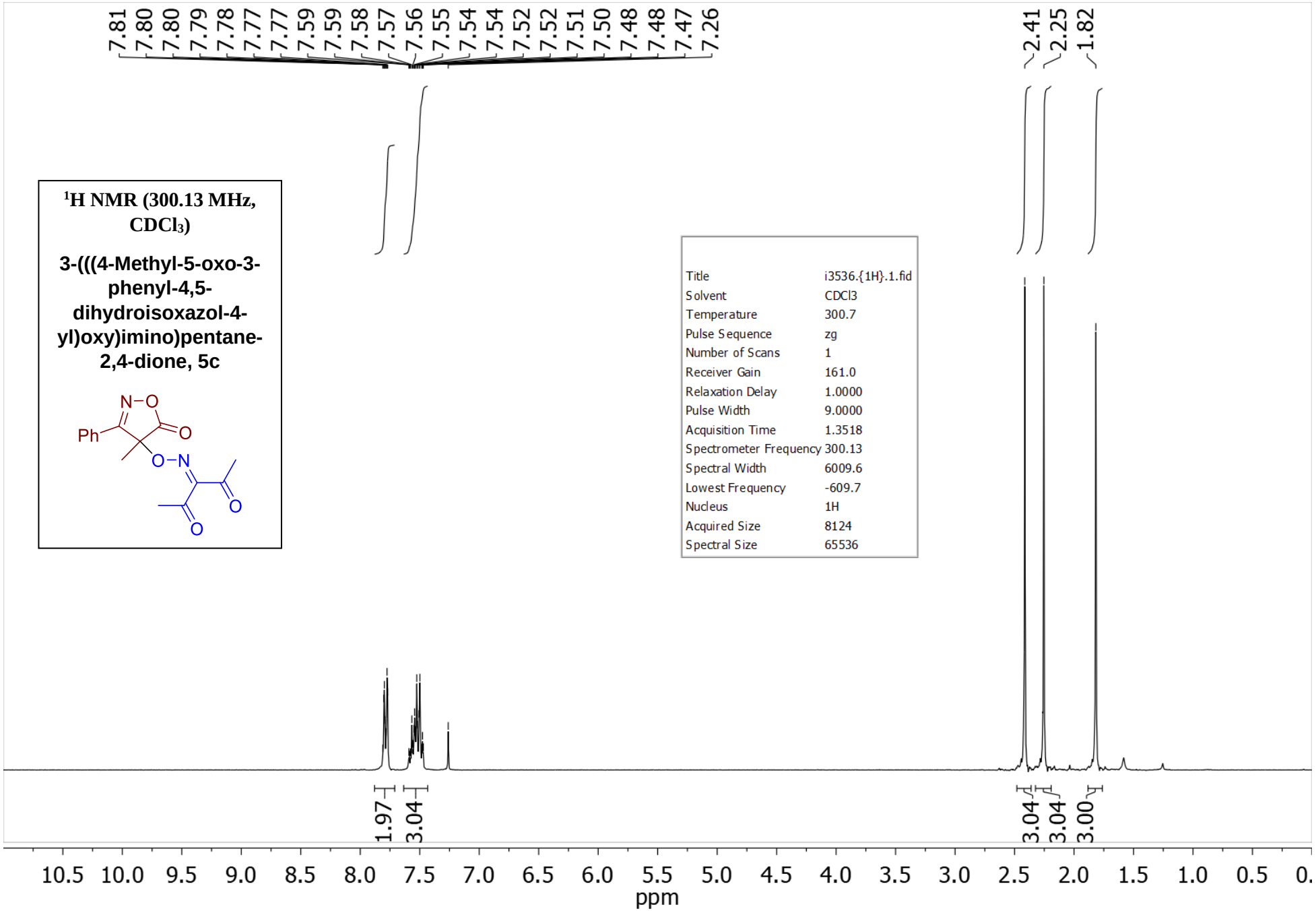
3-(((4-Benzyl-3-methyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, 5a

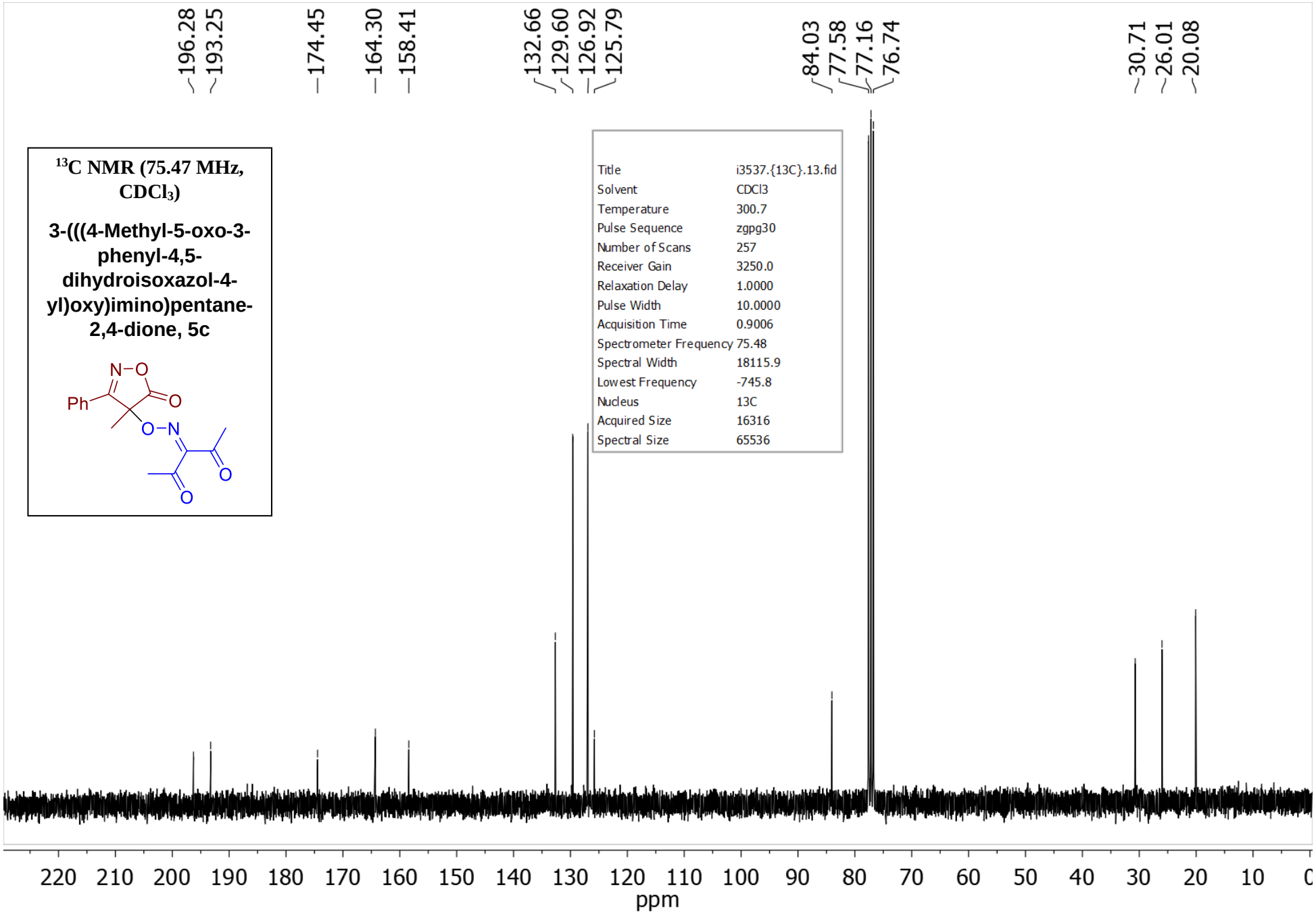


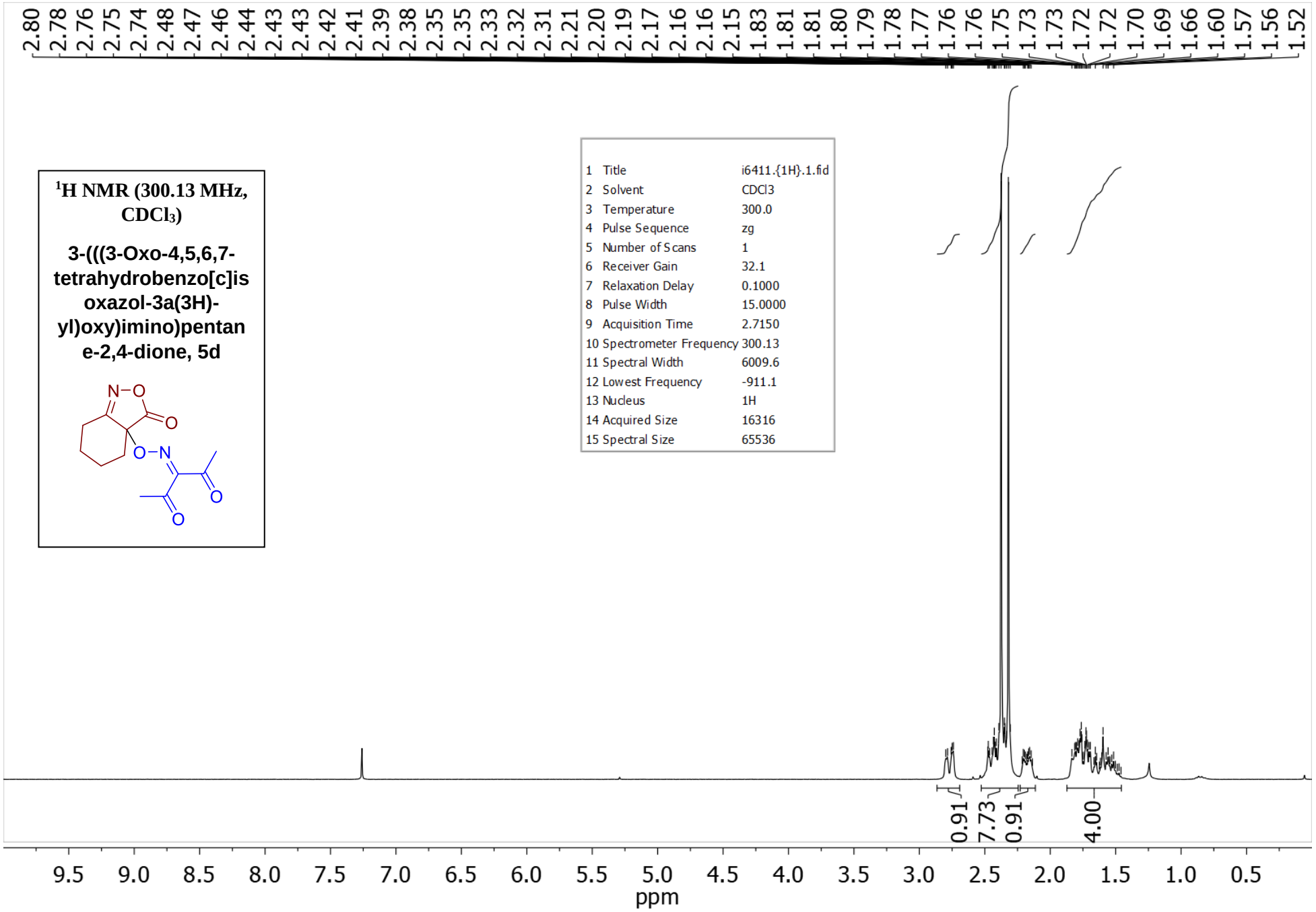

196.34
193.16
173.64
164.85
158.70
129.94
129.83
129.23
128.73
87.38
77.58
77.16
76.74
38.36
30.61
26.05
12.11
^{13}C NMR (75.47 MHz, CDCl$_3$)
3-(((4-Benzyl-3-methyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, 5a
Title i2682.{13C}.13.fid
Solvent CDCl3
Temperature 297.4
Pulse Sequence zgpg30
Number of Scans 434
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9006
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -746.4
Nucleus 13C
Acquired Size 16316
Spectral Size 65536
ppm

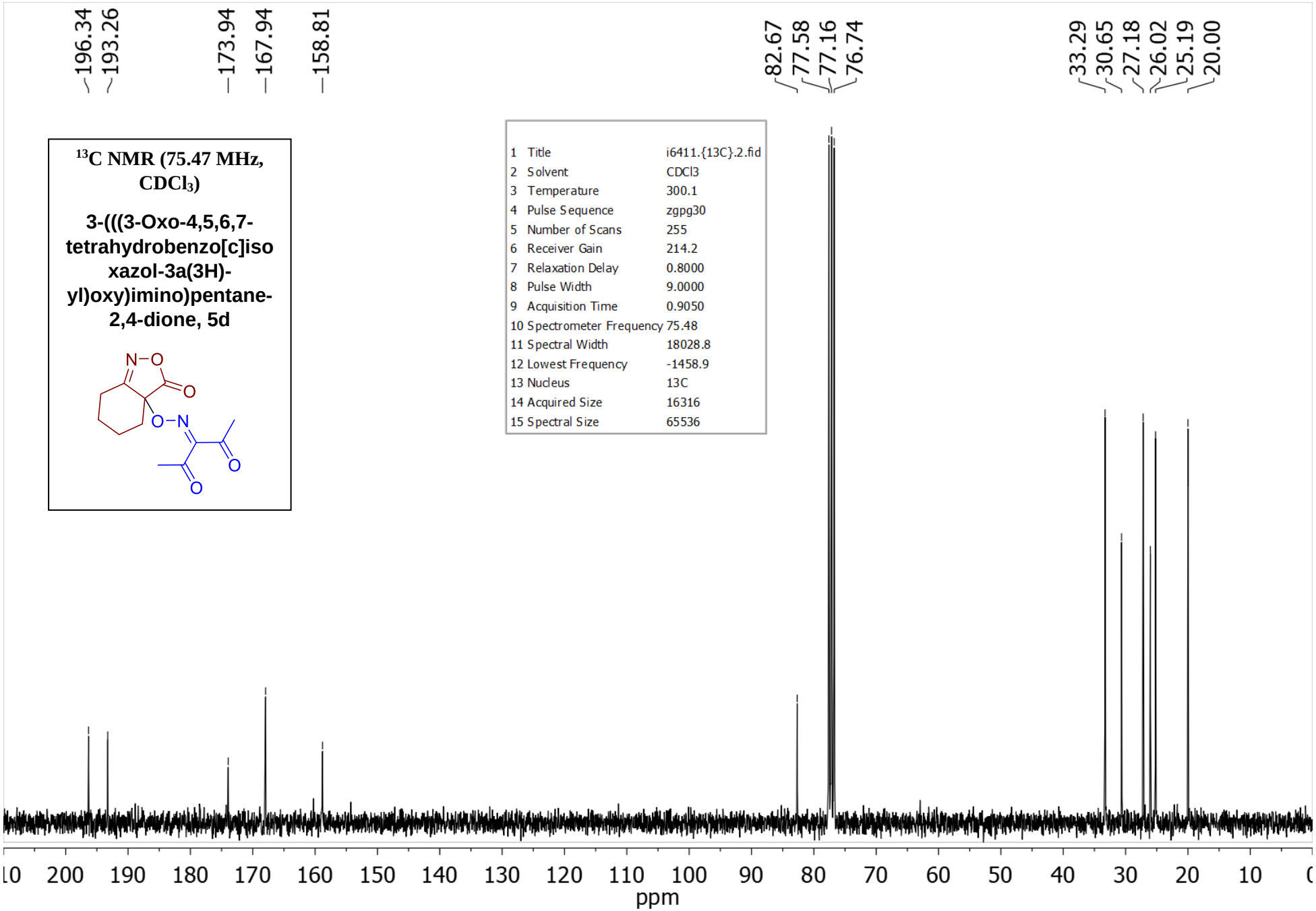

^{1}H NMR (300.13 MHz, $CDCl_3$)
3-(((3,4-Dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, 5b
7.26
2.36
2.31
2.08
1.63
Title i4109.{1H}.1.fid
Solvent CDCl3
Temperature 297.7
Pulse Sequence zg
Number of Scans 1
Receiver Gain 18.0
Relaxation Delay 0.0050
Pulse Width 9.0000
Acquisition Time 1.3518
Spectrometer Frequency 300.13
Spectral Width 6009.6
Lowest Frequency -610.3
Nucleus 1H
Acquired Size 8124
Spectral Size 65536
2.90
3.09
3.08
3.00
ppm


196.23
193.16
174.04
165.95
158.48
83.50
77.58
77.16
76.74
30.56
25.98
18.00
11.16
^{13}C NMR (75.47 MHz, $CDCl_3$)
3-(((3,4-Dimethyl-5-oxo-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, 5b
Title i4109.{13C}.13.fid
Solvent CDCl3
Temperature 298.1
Pulse Sequence zgpg30
Number of Scans 217
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9006
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -748.3
Nucleus 13C
Acquired Size 16316
Spectral Size 65536
ppm


7.81
7.80
7.80
7.79
7.78
7.77
7.77
7.59
7.59
7.58
7.57
7.56
7.55
7.54
7.54
7.52
7.52
7.51
7.50
7.48
7.48
7.47
7.26
2.41
2.25
1.82
1H NMR (300.13 MHz, CDCl3)
3-(((4-Methyl-5-oxo-3-phenyl-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, 5c
Ph
N–O
O
O–N
O
O
Title i3536.{1H}.1.fid
Solvent CDCl3
Temperature 300.7
Pulse Sequence zg
Number of Scans 1
Receiver Gain 161.0
Relaxation Delay 1.0000
Pulse Width 9.0000
Acquisition Time 1.3518
Spectrometer Frequency 300.13
Spectral Width 6009.6
Lowest Frequency -609.7
Nucleus 1H
Acquired Size 8124
Spectral Size 65536
1.97
3.04
3.04
3.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm

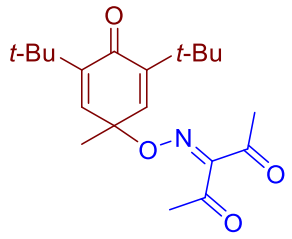

196.28
193.25
174.45
164.30
158.41
132.66
129.60
126.92
125.79
84.03
77.58
77.16
76.74
30.71
26.01
20.08
^{13}C NMR (75.47 MHz, CDCl$_3$)
3-(((4-Methyl-5-oxo-3-phenyl-4,5-dihydroisoxazol-4-yl)oxy)imino)pentane-2,4-dione, 5c
Title i3537.{13C}.13.fid
Solvent CDCl3
Temperature 300.7
Pulse Sequence zgpg30
Number of Scans 257
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9006
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -745.8
Nucleus 13C
Acquired Size 16316
Spectral Size 65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


2.80 2.78 2.76 2.75 2.74 2.48 2.47 2.46 2.44 2.43 2.43 2.42 2.41 2.39 2.38 2.35 2.35 2.33 2.32 2.31 2.21 2.20 2.19 2.17 2.16 2.16 2.15 1.83 1.81 1.81 1.80 1.79 1.78 1.77 1.76 1.76 1.75 1.73 1.73 1.72 1.72 1.70 1.69 1.66 1.60 1.57 1.56 1.52
1H NMR (300.13 MHz, CDCl3)
3-(((3-Oxo-4,5,6,7-tetrahydrobenzo[c]isoxazol-3a(3H)-yl)oxy)imino)pentane-2,4-dione, 5d
1 Title i6411.{1H}.1.fid
2 Solvent CDCl3
3 Temperature 300.0
4 Pulse Sequence zg
5 Number of Scans 1
6 Receiver Gain 32.1
7 Relaxation Delay 0.1000
8 Pulse Width 15.0000
9 Acquisition Time 2.7150
10 Spectrometer Frequency 300.13
11 Spectral Width 6009.6
12 Lowest Frequency -911.1
13 Nucleus 1H
14 Acquired Size 16316
15 Spectral Size 65536
0.91
7.73
0.91
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

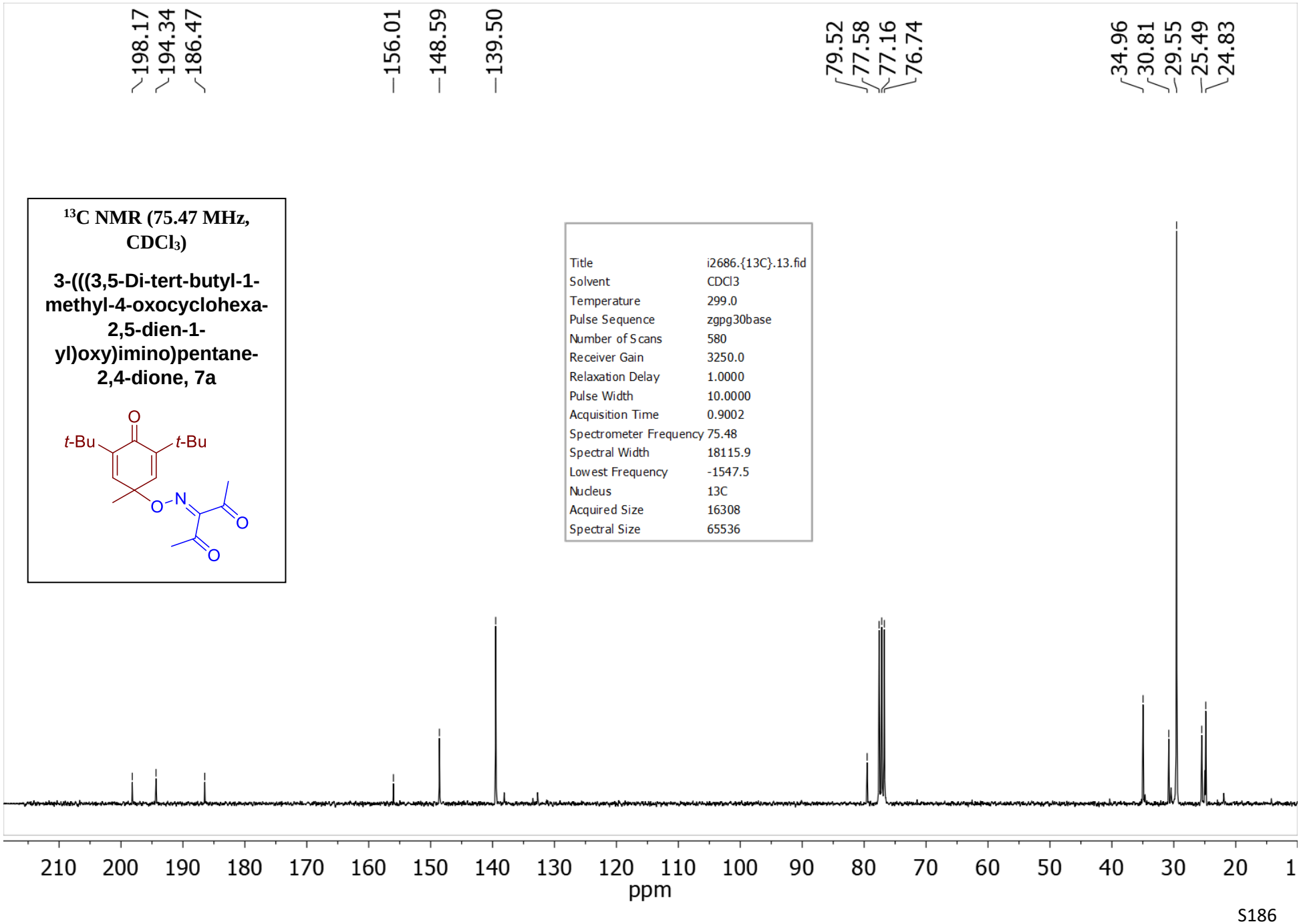

196.34
193.26
173.94
167.94
158.81
82.67
77.58
77.16
76.74
33.29
30.65
27.18
26.02
25.19
20.00
13C NMR (75.47 MHz, CDCl3)
3-(((3-Oxo-4,5,6,7-tetrahydrobenzo[c]isoxazol-3a(3H)-yl)oxy)imino)pentane-2,4-dione, 5d
1 Title i6411.{13C}.2.fid
2 Solvent CDCl3
3 Temperature 300.1
4 Pulse Sequence zgpg30
5 Number of Scans 255
6 Receiver Gain 214.2
7 Relaxation Delay 0.8000
8 Pulse Width 9.0000
9 Acquisition Time 0.9050
10 Spectrometer Frequency 75.48
11 Spectral Width 18028.8
12 Lowest Frequency -1458.9
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
ppm

^{1}H NMR (300.13 MHz, $CDCl_3$)

3-(((3,5-Di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7a

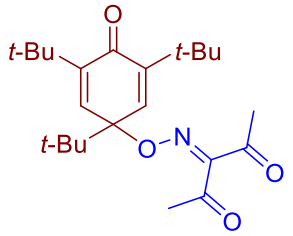


Title	i2686.{1H}.1.fid
Solvent	CDCl3
Temperature	298.3
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	57.0
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.3
Nucleus	1H
Acquired Size	8124
Spectral Size	65536

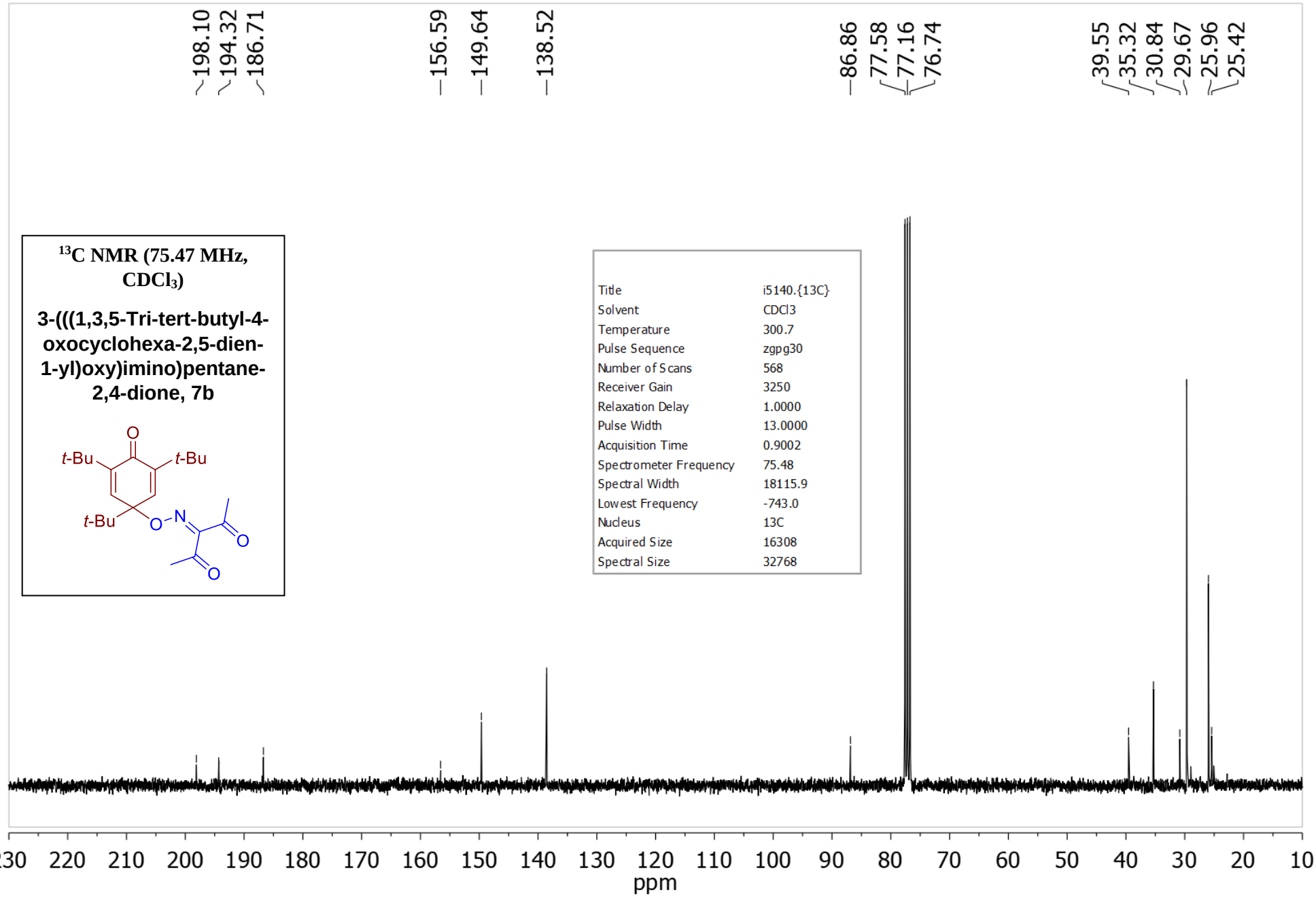

198.17
194.34
186.47
156.01
148.59
139.50
79.52
77.58
77.16
76.74
34.96
30.81
29.55
25.49
24.83
^{13}C NMR (75.47 MHz, $CDCl_3$)
3-(((3,5-Di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7a
t-Bu
t-Bu
O
N
O
O
O
Title i2686.{13C}.13.fid
Solvent CDCl3
Temperature 299.0
Pulse Sequence zgpg30base
Number of Scans 580
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9002
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -1547.5
Nucleus 13C
Acquired Size 16308
Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
ppm

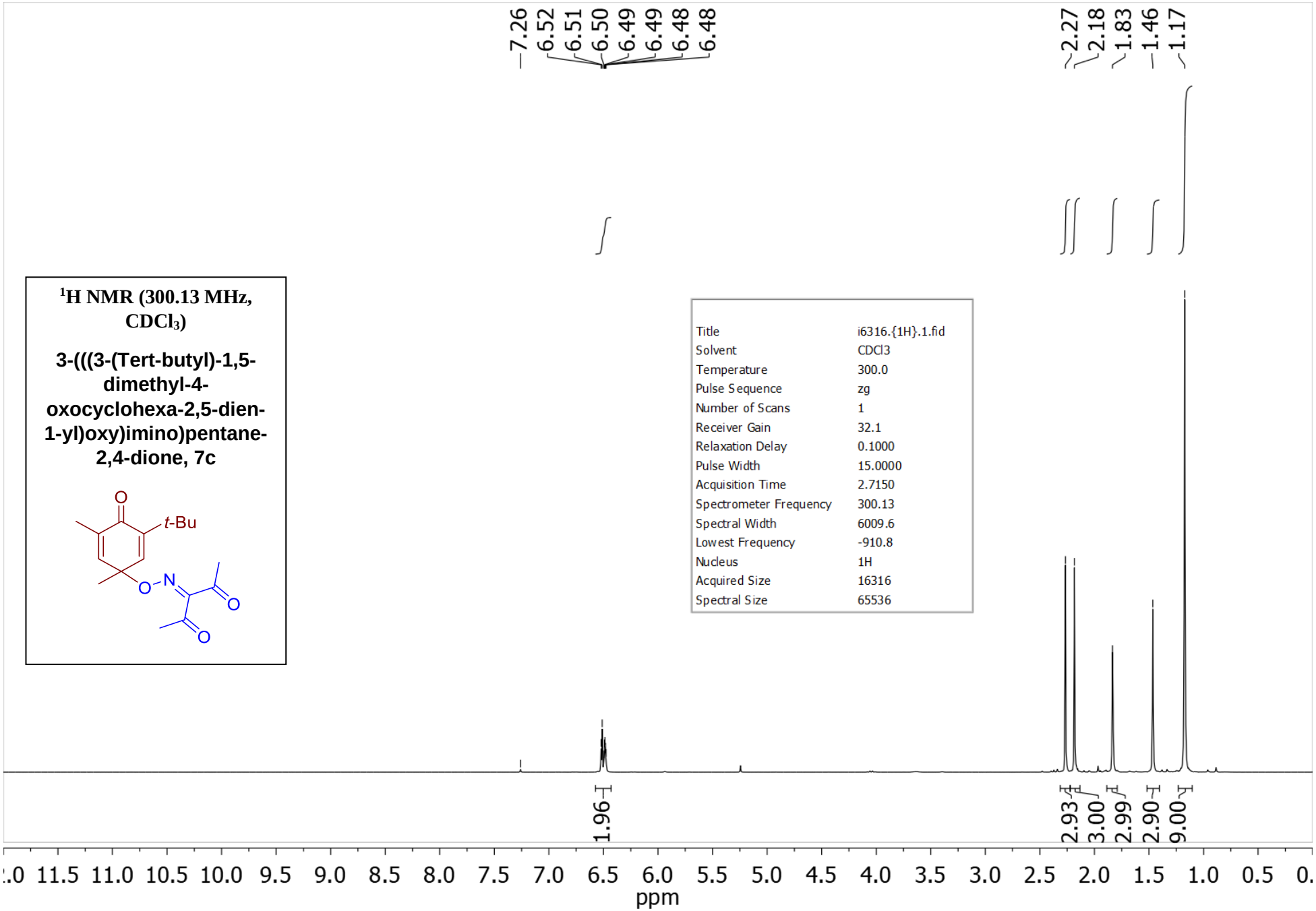
^{1}H NMR (300.13 MHz, $CDCl_3$)

3-(((1,3,5-Tri-tert-butyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7b



Title	i5140.{1H}
Solvent	CDCl3
Temperature	304.4
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	181
Relaxation Delay	0.0050
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.4
Nucleus	1H
Acquired Size	8124
Spectral Size	16384

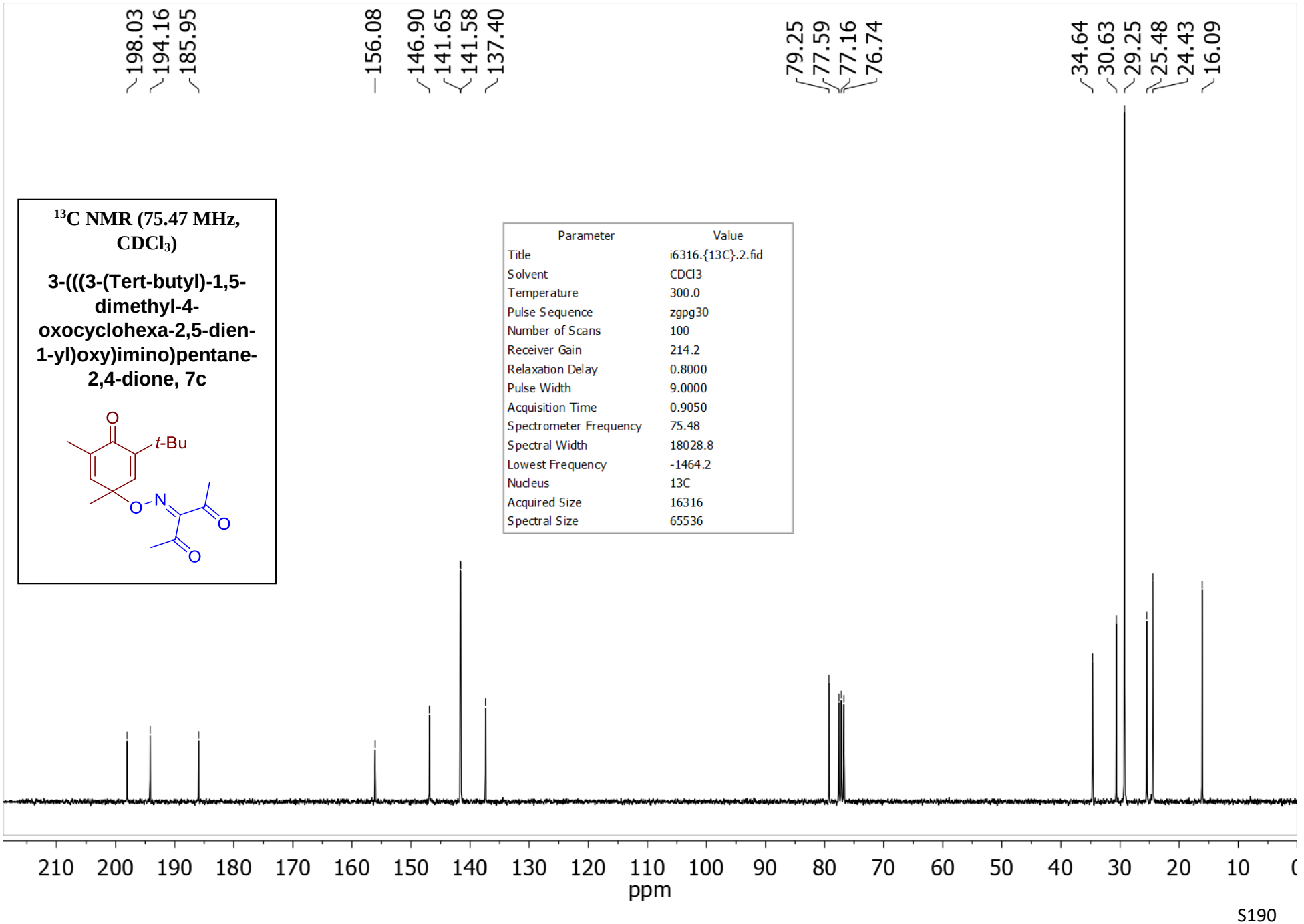

198.10
194.32
186.71
156.59
149.64
138.52
86.86
77.58
77.16
76.74
39.55
35.32
30.84
29.67
25.96
25.42
13C NMR (75.47 MHz, CDCl3)
3-(((1,3,5-Tri-tert-butyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7b
t-Bu
t-Bu
t-Bu
O
N
O
O
Title i5140.{13C}
Solvent CDCl3
Temperature 300.7
Pulse Sequence zgpg30
Number of Scans 568
Receiver Gain 3250
Relaxation Delay 1.0000
Pulse Width 13.0000
Acquisition Time 0.9002
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -743.0
Nucleus 13C
Acquired Size 16308
Spectral Size 32768
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm



^{1}H NMR (300.13 MHz, $CDCl_3$)

3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7c

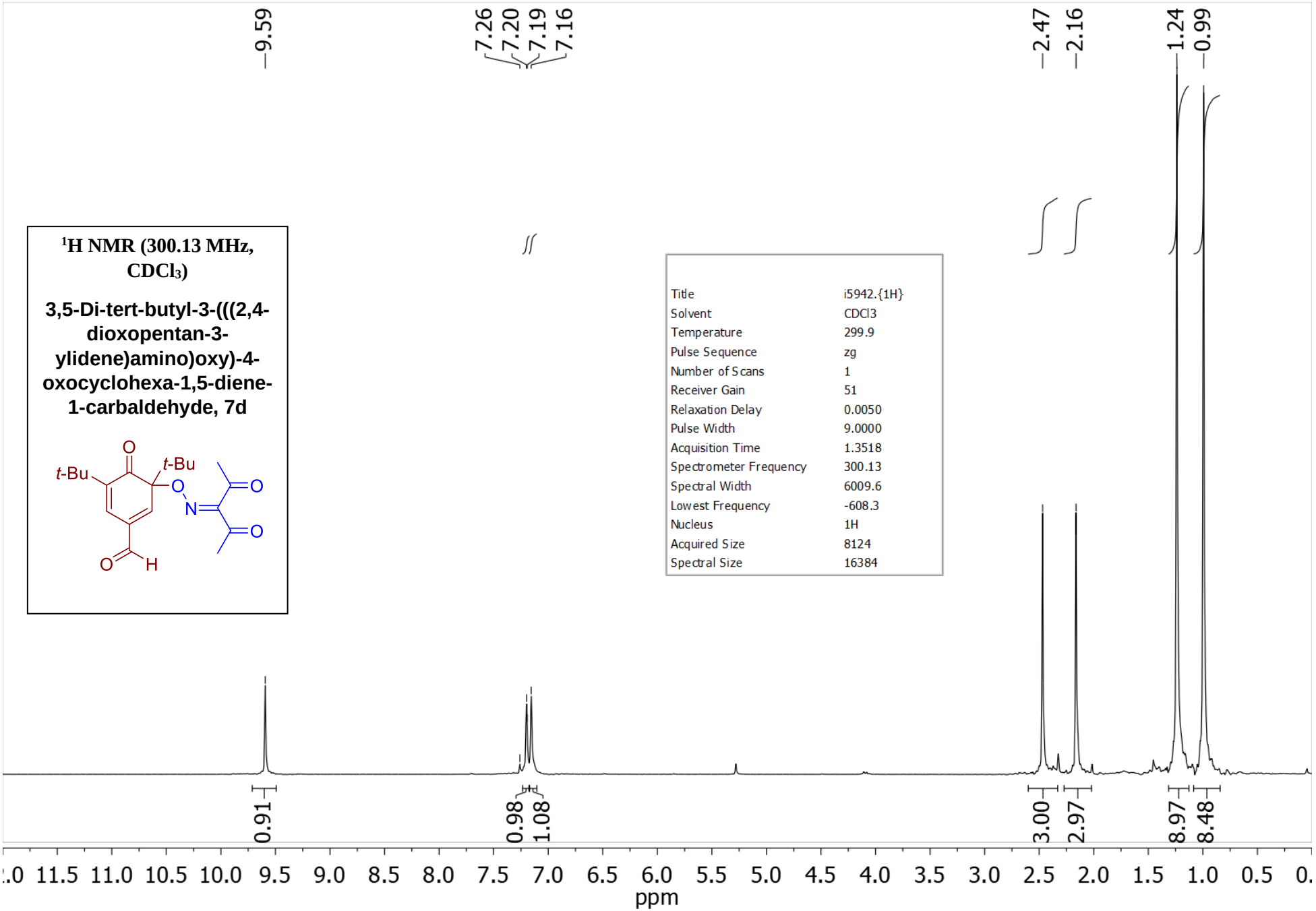
Title	i6316.{1H}.1.fid
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	32.1
Relaxation Delay	0.1000
Pulse Width	15.0000
Acquisition Time	2.7150
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-910.8
Nucleus	1H
Acquired Size	16316
Spectral Size	65536



^{13}C NMR (75.47 MHz, $CDCl_3$)

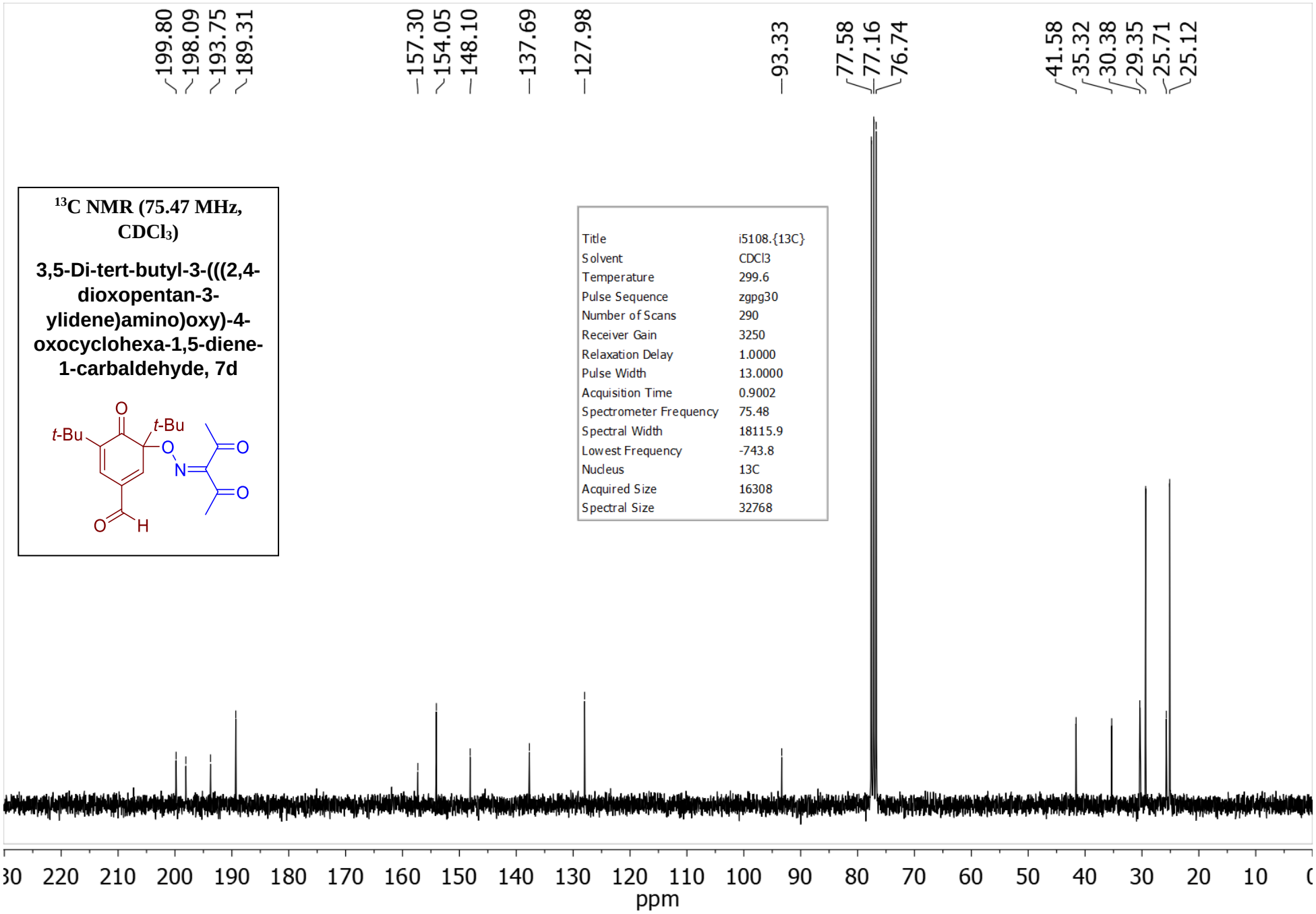
3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7c

Parameter	Value
Title	i6316.{13C}.2.fid
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zgpg30
Number of Scans	100
Receiver Gain	214.2
Relaxation Delay	0.8000
Pulse Width	9.0000
Acquisition Time	0.9050
Spectrometer Frequency	75.48
Spectral Width	18028.8
Lowest Frequency	-1464.2
Nucleus	13C
Acquired Size	16316
Spectral Size	65536



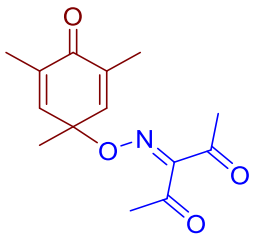
^{1}H NMR (300.13 MHz, $CDCl_3$)

3,5-Di-tert-butyl-3-(((2,4-dioxopentan-3-ylidene)amino)oxy)-4-oxocyclohexa-1,5-diene-1-carbaldehyde, 7d

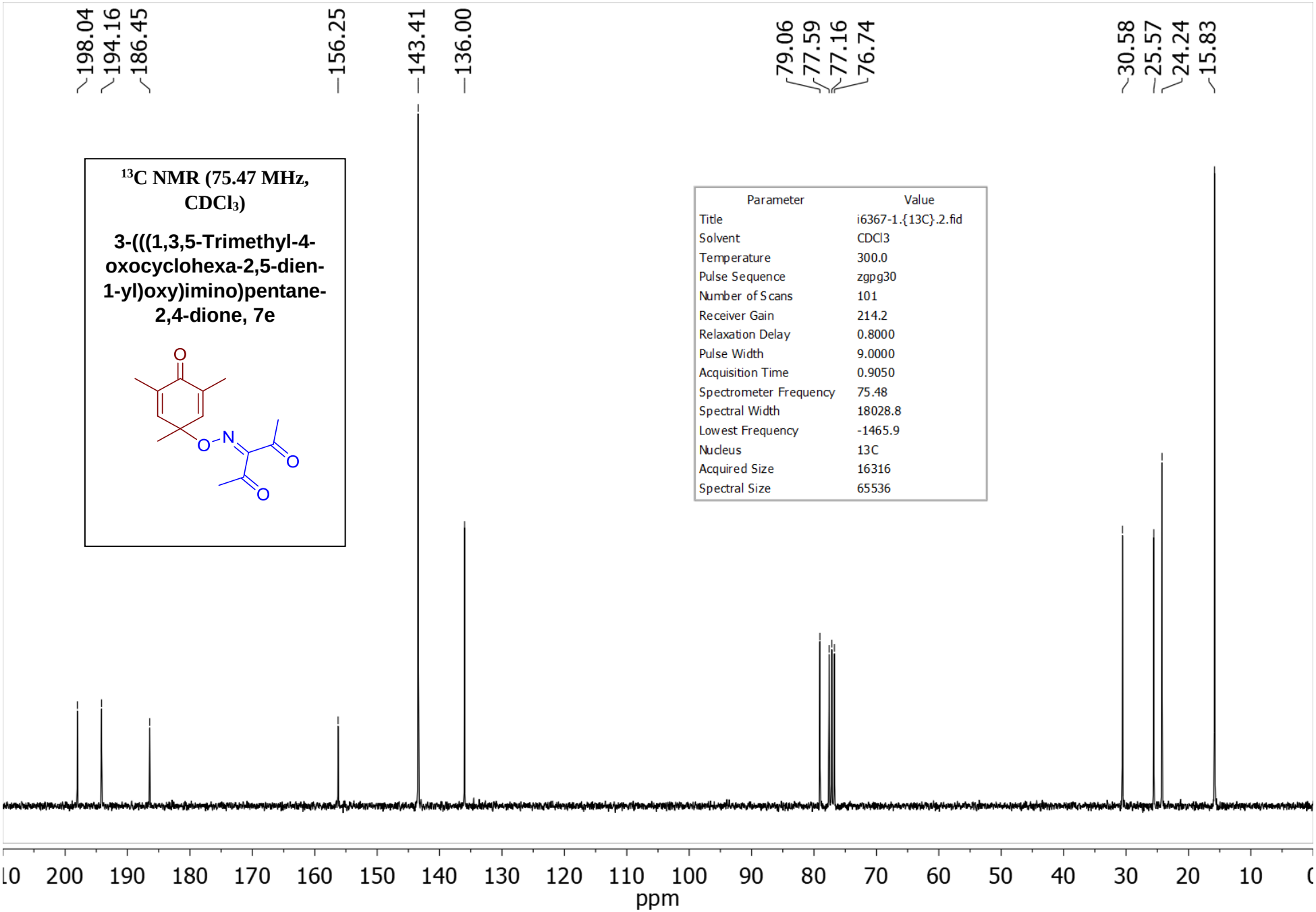

199.80
198.09
193.75
189.31
157.30
154.05
148.10
137.69
127.98
93.33
77.58
77.16
76.74
41.58
35.32
30.38
29.35
25.71
25.12
^{13}C NMR (75.47 MHz, CDCl$_3$)
3,5-Di-tert-butyl-3-(((2,4-dioxopentan-3-ylidene)amino)oxy)-4-oxocyclohexa-1,5-diene-1-carbaldehyde, 7d
t-Bu
t-Bu
O
O
N
O
O
H
Title i5108.{13C}
Solvent CDCl3
Temperature 299.6
Pulse Sequence zgpg30
Number of Scans 290
Receiver Gain 3250
Relaxation Delay 1.0000
Pulse Width 13.0000
Acquisition Time 0.9002
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -743.8
Nucleus 13C
Acquired Size 16308
Spectral Size 32768
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

^{1}H NMR (300.13 MHz, $CDCl_3$)

3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7e

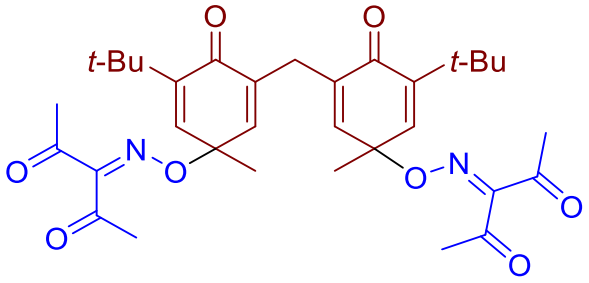


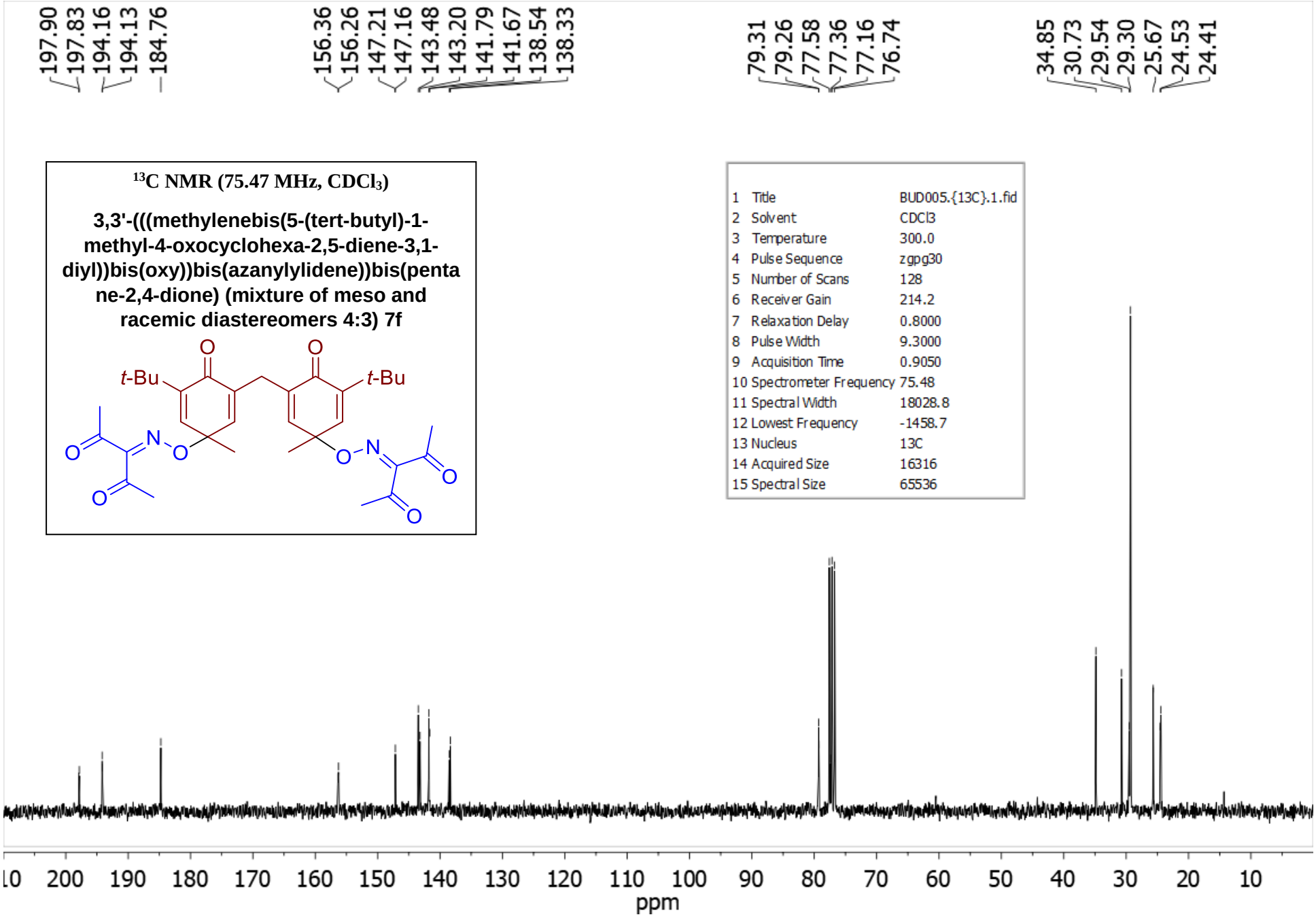
Parameter	Value
Title	i6367-1.{1H}.1.fid
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	32.1
Relaxation Delay	0.1000
Pulse Width	15.0000
Acquisition Time	2.7150
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-910.9
Nucleus	1H
Acquired Size	16316
Spectral Size	65536

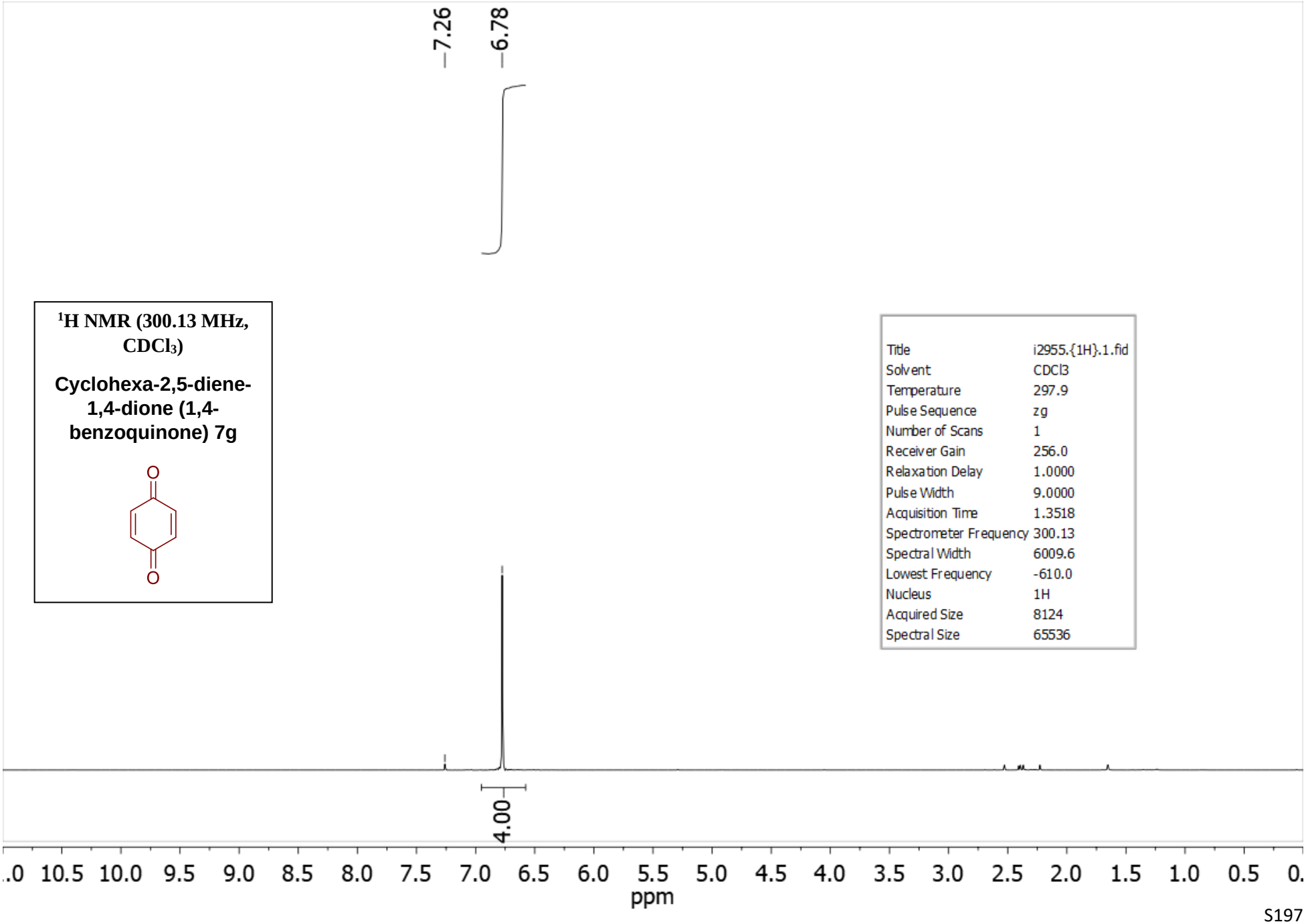

198.04
194.16
186.45
156.25
143.41
136.00
79.06
77.59
77.16
76.74
30.58
25.57
24.24
15.83
^{13}C NMR (75.47 MHz, CDCl$_3$)
3-(((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7e
Parameter Value
Title i6367-1.{13C}.2.fid
Solvent CDCl3
Temperature 300.0
Pulse Sequence zgpg30
Number of Scans 101
Receiver Gain 214.2
Relaxation Delay 0.8000
Pulse Width 9.0000
Acquisition Time 0.9050
Spectrometer Frequency 75.48
Spectral Width 18028.8
Lowest Frequency -1465.9
Nucleus 13C
Acquired Size 16316
Spectral Size 65536
ppm

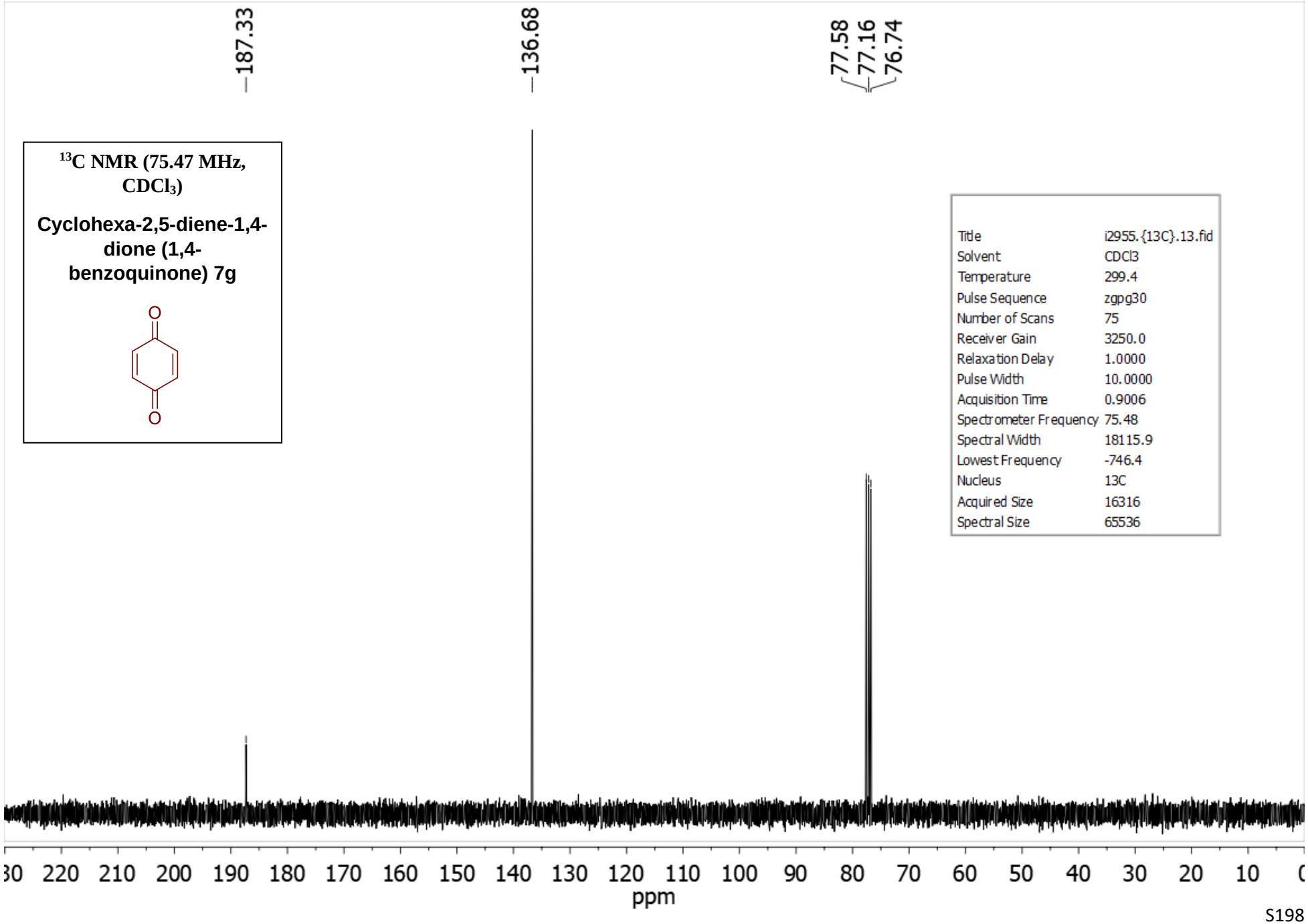
^{1}H NMR (300.13 MHz, $CDCl_3$)

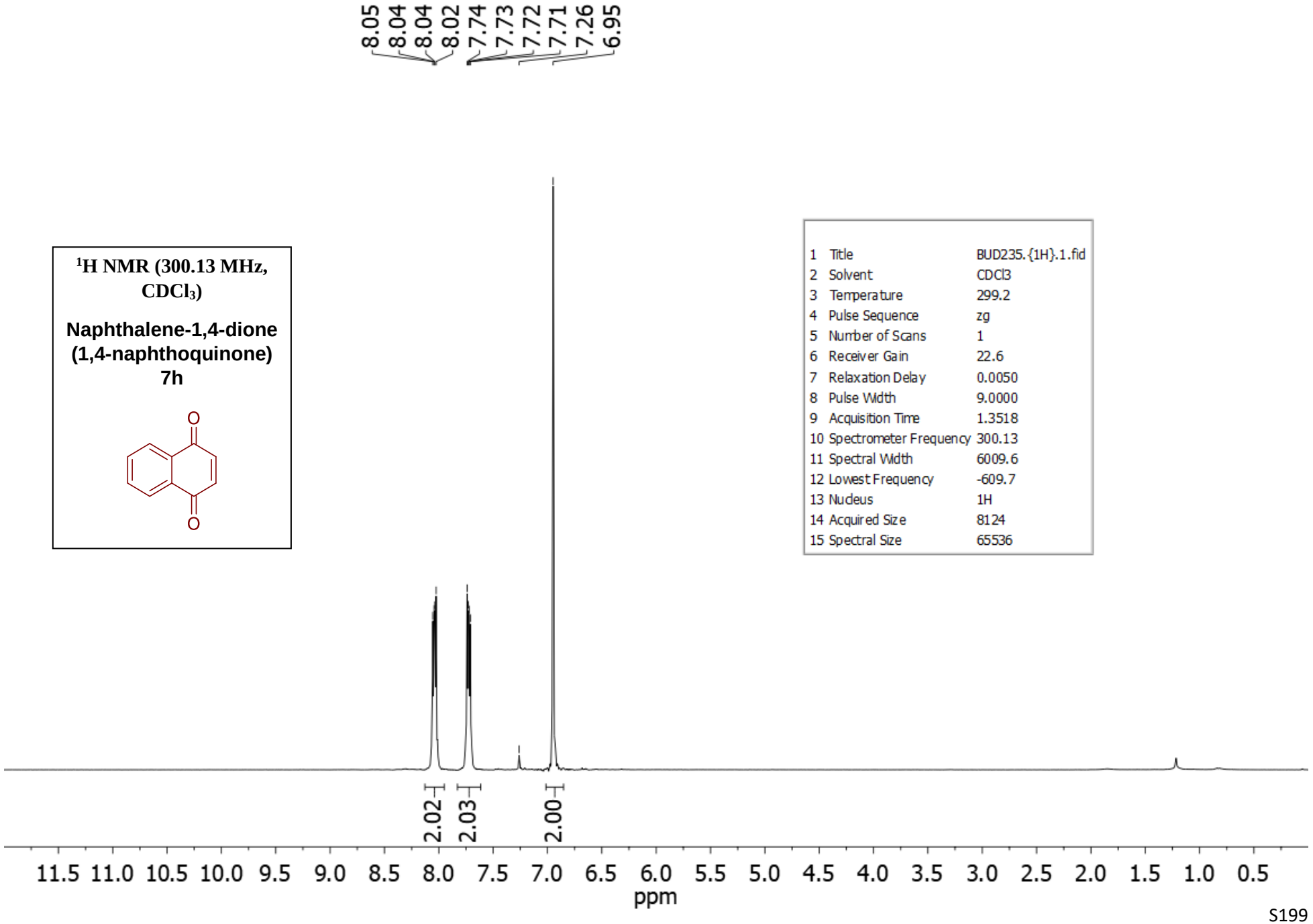
3,3'-(((methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3) 7f

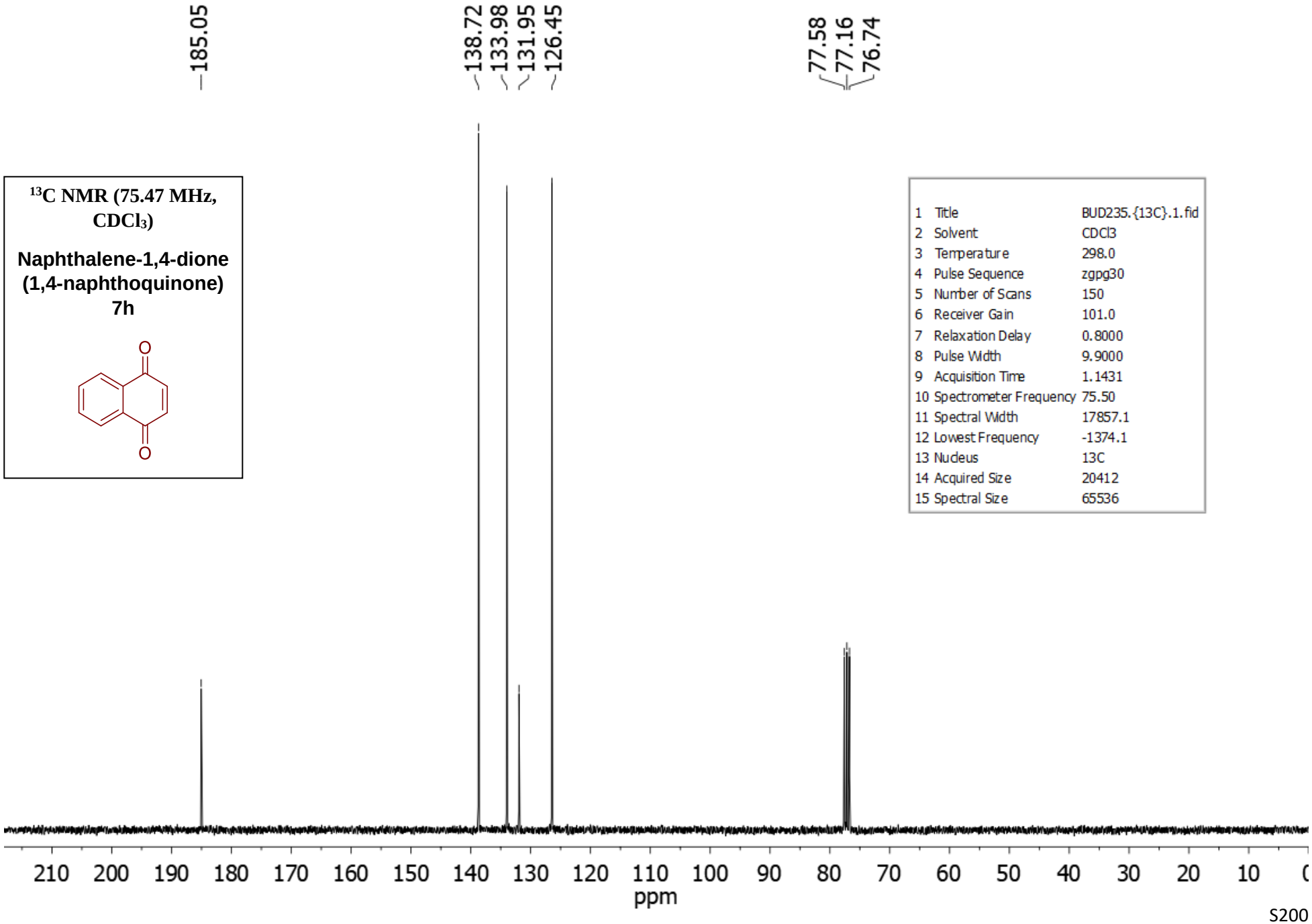


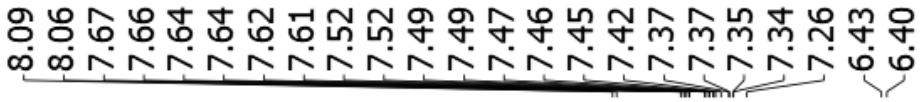

197.90
197.83
194.16
194.13
184.76
156.36
156.26
147.21
147.16
143.48
143.20
141.79
141.67
138.54
138.33
79.31
79.26
77.58
77.36
77.16
76.74
34.85
30.73
29.54
29.30
25.67
24.53
24.41
^{13}C NMR (75.47 MHz, $CDCl_3$)
3,3'-(((methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3) 7f
t-Bu
t-Bu
1 Title BUD005.{13C}.1.fid
2 Solvent CDCl3
3 Temperature 300.0
4 Pulse Sequence zgpg30
5 Number of Scans 128
6 Receiver Gain 214.2
7 Relaxation Delay 0.8000
8 Pulse Width 9.3000
9 Acquisition Time 0.9050
10 Spectrometer Frequency 75.48
11 Spectral Width 18028.8
12 Lowest Frequency -1458.7
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
ppm


7.26
6.78
^{1}H NMR (300.13 MHz, $CDCl_3$)
Cyclohexa-2,5-diene-1,4-dione (1,4-benzoquinone) 7g
O
O
Title i2955.{1H}.1.fid
Solvent CDCl3
Temperature 297.9
Pulse Sequence zg
Number of Scans 1
Receiver Gain 256.0
Relaxation Delay 1.0000
Pulse Width 9.0000
Acquisition Time 1.3518
Spectrometer Frequency 300.13
Spectral Width 6009.6
Lowest Frequency -610.0
Nucleus 1H
Acquired Size 8124
Spectral Size 65536
4.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm


187.33
136.68
77.58
77.16
76.74
13C NMR (75.47 MHz, CDCl3)
Cyclohexa-2,5-diene-1,4-dione (1,4-benzoquinone) 7g
O
O
Title i2955.{13C}.13.fid
Solvent CDCl3
Temperature 299.4
Pulse Sequence zgpg30
Number of Scans 75
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9006
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -746.4
Nucleus 13C
Acquired Size 16316
Spectral Size 65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

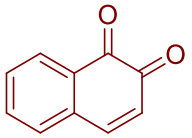

8.05
8.04
8.04
8.02
7.74
7.73
7.72
7.71
7.26
6.95
^{1}H NMR (300.13 MHz, $CDCl_3$)
Naphthalene-1,4-dione
(1,4-naphthoquinone)
7h
O
O
1 Title BUD235.{1H}.1.fid
2 Solvent CDCl3
3 Temperature 299.2
4 Pulse Sequence zg
5 Number of Scans 1
6 Receiver Gain 22.6
7 Relaxation Delay 0.0050
8 Pulse Width 9.0000
9 Acquisition Time 1.3518
10 Spectrometer Frequency 300.13
11 Spectral Width 6009.6
12 Lowest Frequency -609.7
13 Nucleus 1H
14 Acquired Size 8124
15 Spectral Size 65536
2.02
2.03
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


185.05
138.72
133.98
131.95
126.45
77.58
77.16
76.74
^{13}C NMR (75.47 MHz, $CDCl_3$)
Naphthalene-1,4-dione (1,4-naphthoquinone) 7h
1 Title BUD235.{13C}.1.fid
2 Solvent CDCl3
3 Temperature 298.0
4 Pulse Sequence zgpg30
5 Number of Scans 150
6 Receiver Gain 101.0
7 Relaxation Delay 0.8000
8 Pulse Width 9.9000
9 Acquisition Time 1.1431
10 Spectrometer Frequency 75.50
11 Spectral Width 17857.1
12 Lowest Frequency -1374.1
13 Nucleus 13C
14 Acquired Size 20412
15 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

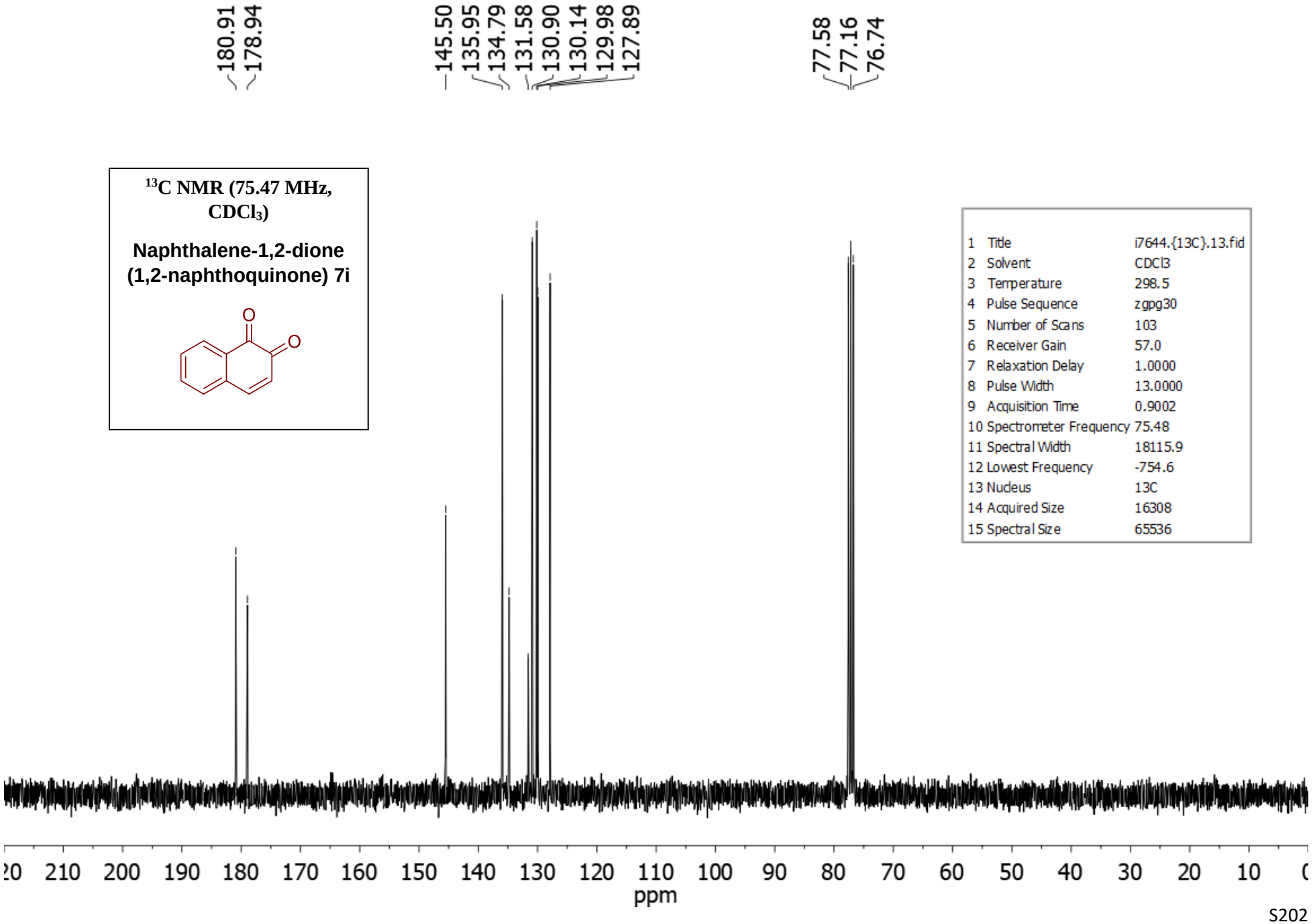


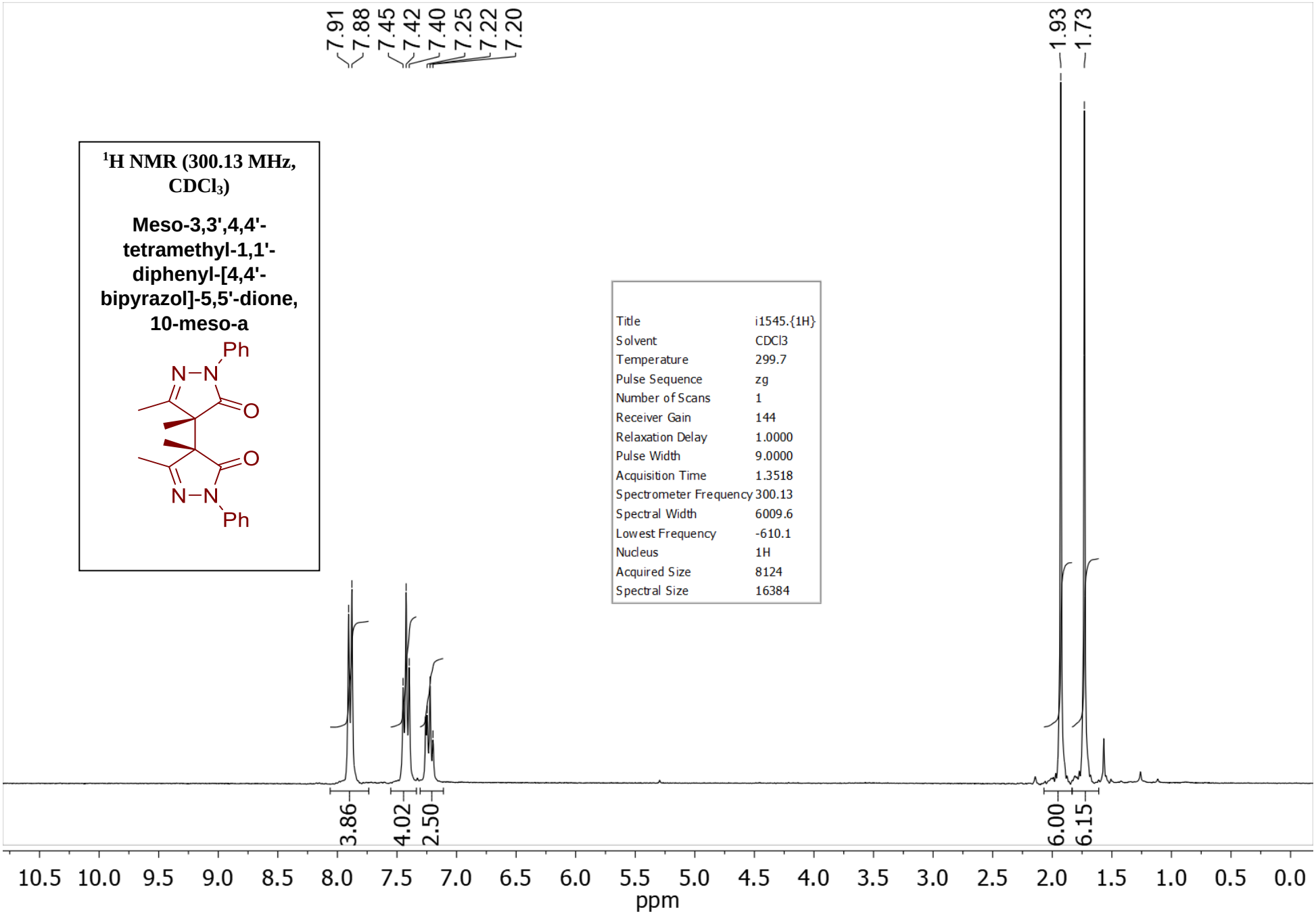
^{1}H NMR (300.13 MHz, $CDCl_3$)

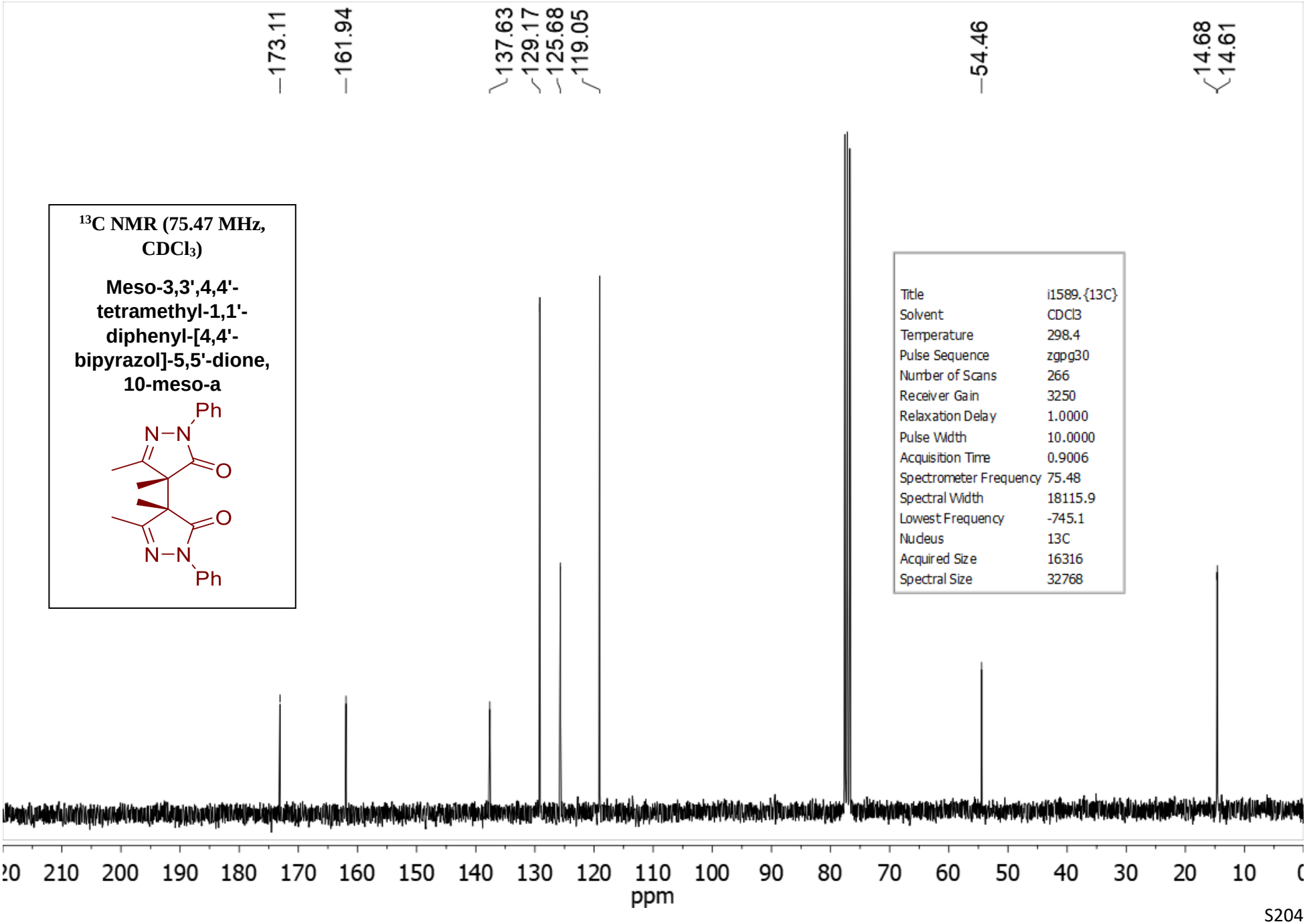
Naphthalene-1,2-dione (1,2-naphthoquinone) 7i

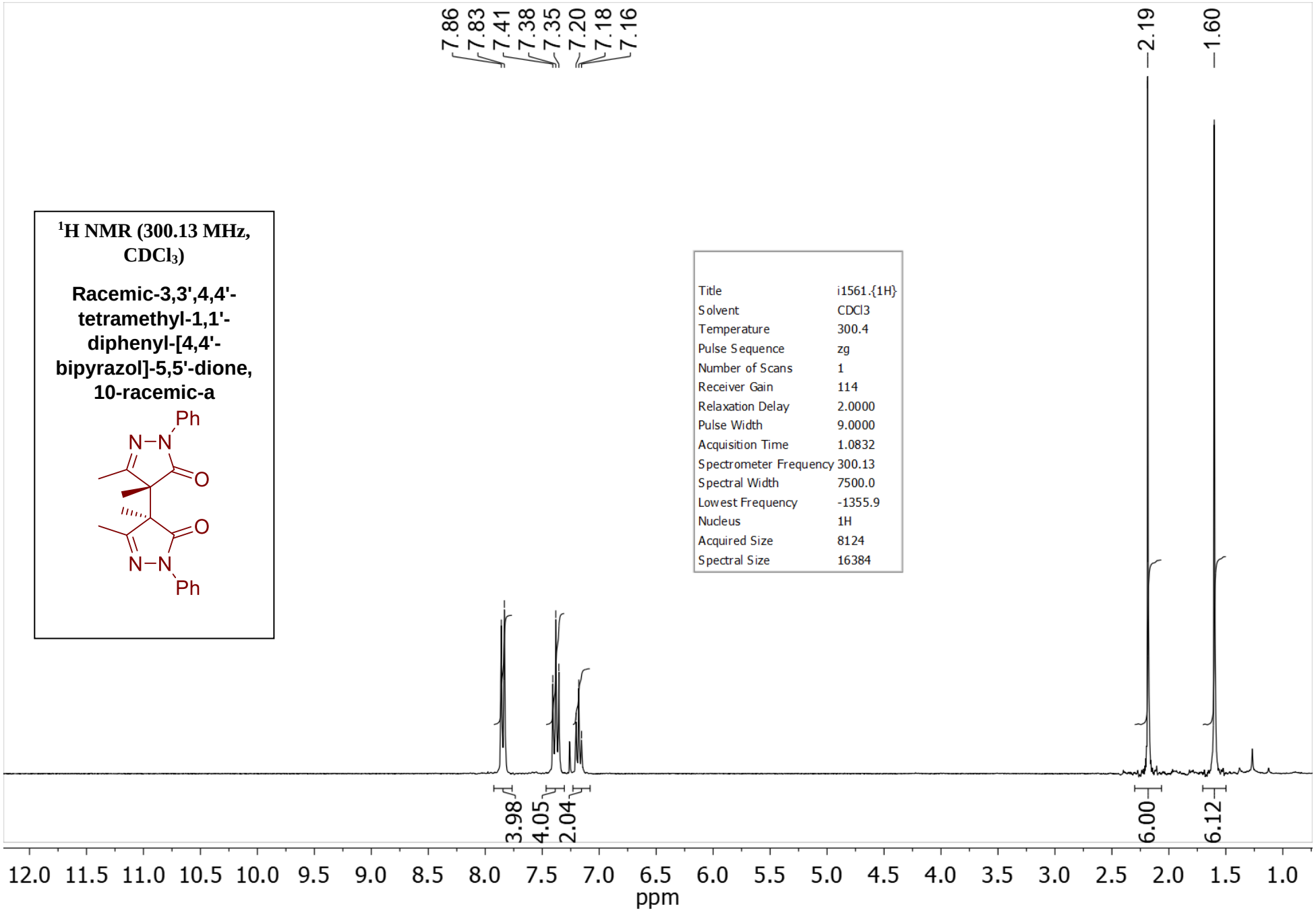


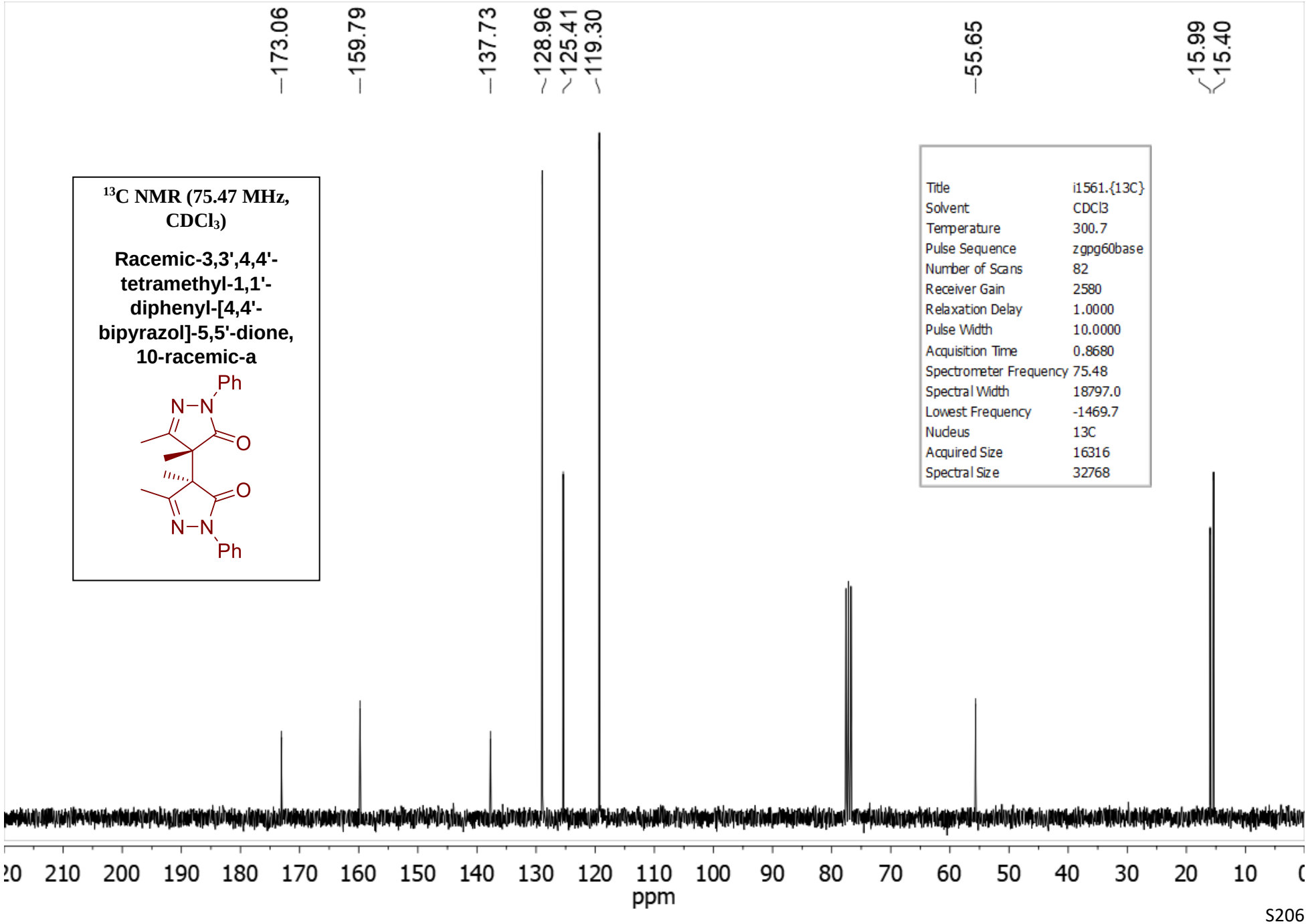
1	Title	i7644-1.{1H}.1.fid
2	Solvent	CDCl3
3	Temperature	300.0
4	Pulse Sequence	zg
5	Number of Scans	1
6	Receiver Gain	32.1
7	Relaxation Delay	0.1000
8	Pulse Width	15.0000
9	Acquisition Time	2.7150
10	Spectrometer Frequency	300.13
11	Spectral Width	6009.6
12	Lowest Frequency	-911.1
13	Nucleus	1H
14	Acquired Size	16316
15	Spectral Size	65536

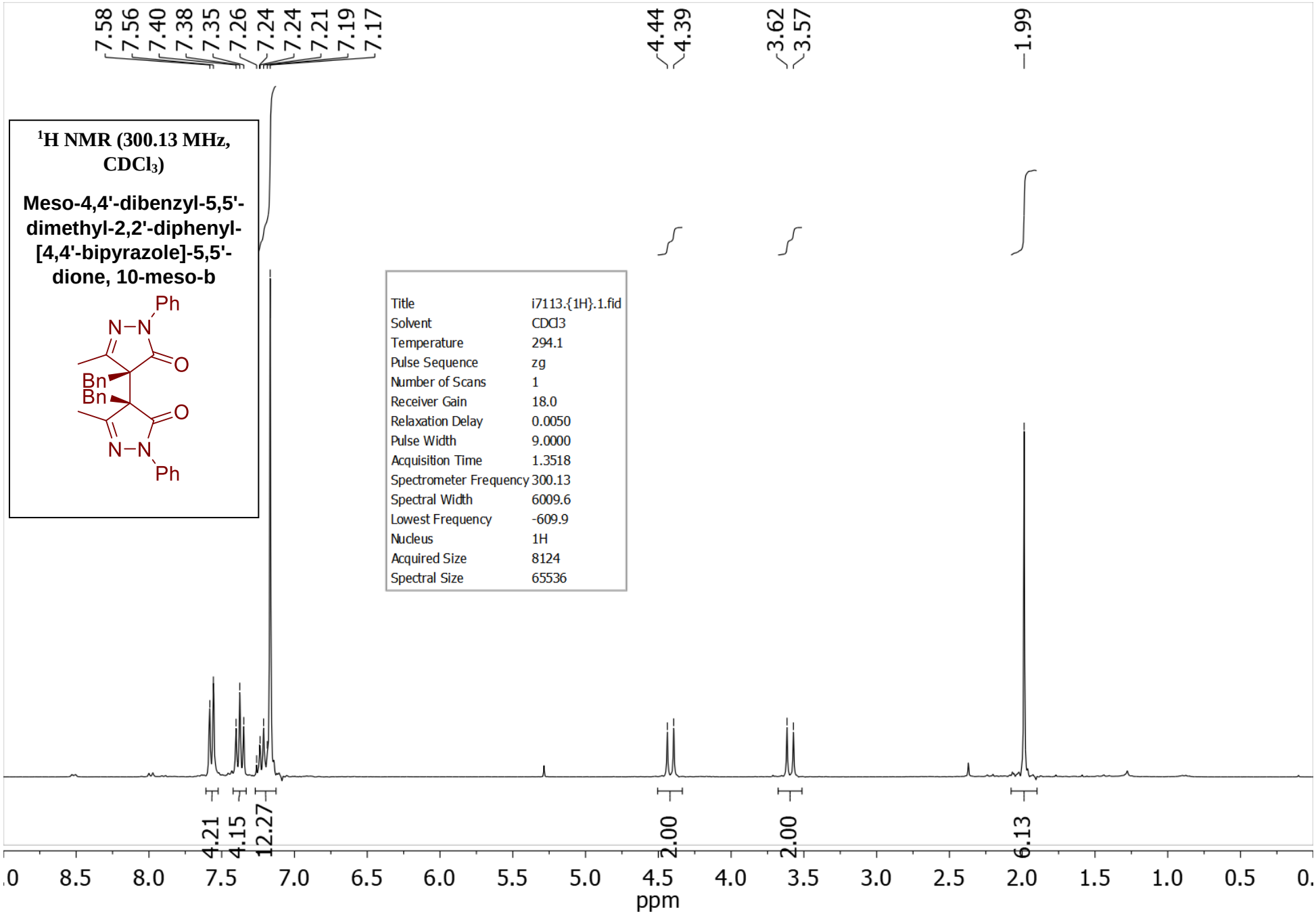

180.91
178.94
145.50
135.95
134.79
131.58
130.90
130.14
129.98
127.89
77.58
77.16
76.74
^{13}C NMR (75.47 MHz, $CDCl_3$)
Naphthalene-1,2-dione (1,2-naphthoquinone) 7i
O
O
1 Title i7644.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 298.5
4 Pulse Sequence zgpg30
5 Number of Scans 103
6 Receiver Gain 57.0
7 Relaxation Delay 1.0000
8 Pulse Width 13.0000
9 Acquisition Time 0.9002
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -754.6
13 Nucleus 13C
14 Acquired Size 16308
15 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

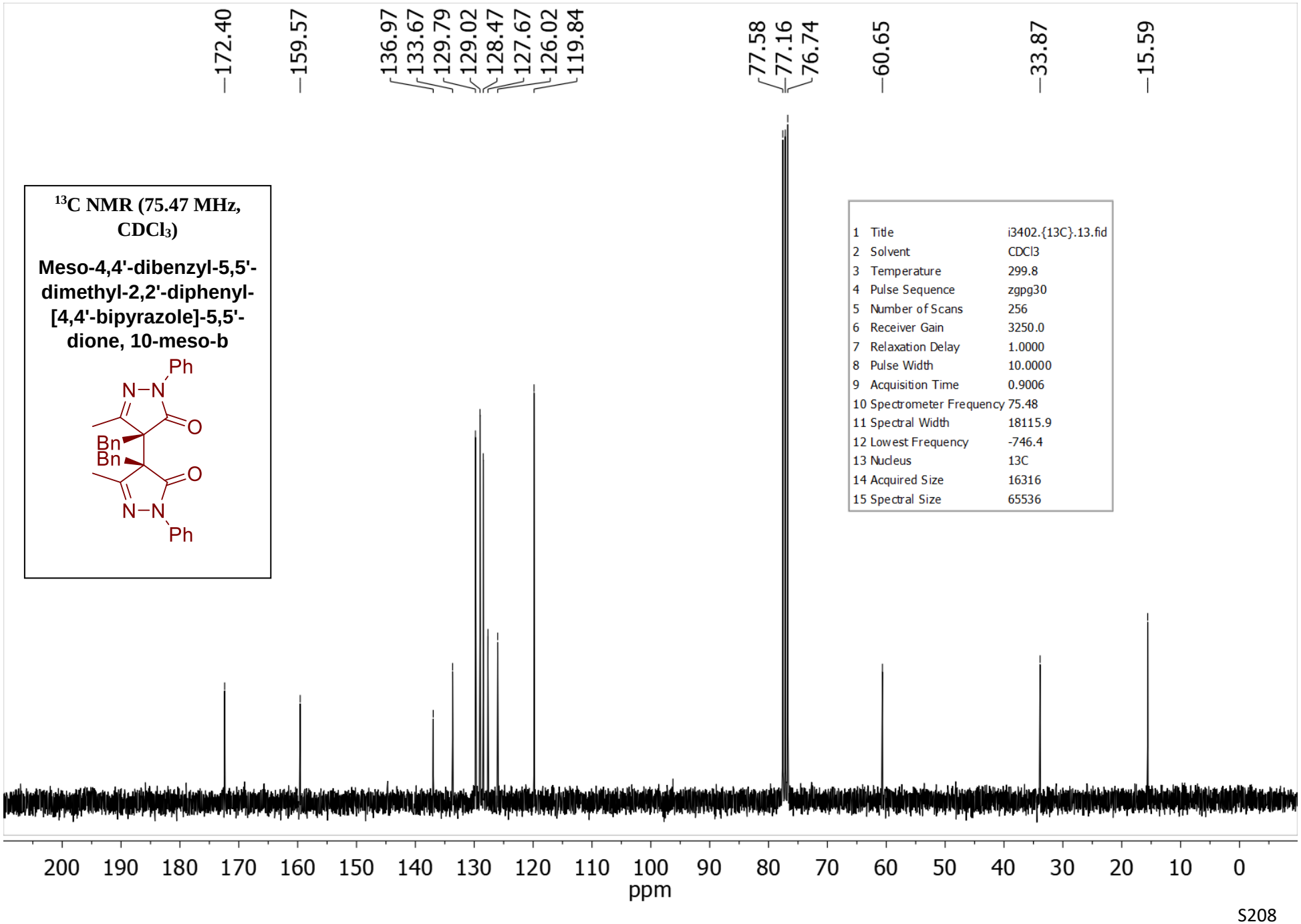

7.91
7.88
7.45
7.42
7.40
7.25
7.22
7.20
1.93
1.73
^{1}H NMR (300.13 MHz, $CDCl_3$)
Meso-3,3',4,4'-tetramethyl-1,1'-diphenyl-[4,4'-bipyrazol]-5,5'-dione, 10-meso-a
Ph
N–N
O
O
N–N
Ph
Title i1545.{1H}
Solvent CDCl3
Temperature 299.7
Pulse Sequence zg
Number of Scans 1
Receiver Gain 144
Relaxation Delay 1.0000
Pulse Width 9.0000
Acquisition Time 1.3518
Spectrometer Frequency 300.13
Spectral Width 6009.6
Lowest Frequency -610.1
Nucleus 1H
Acquired Size 8124
Spectral Size 16384
3.86
4.02
2.50
6.00
6.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

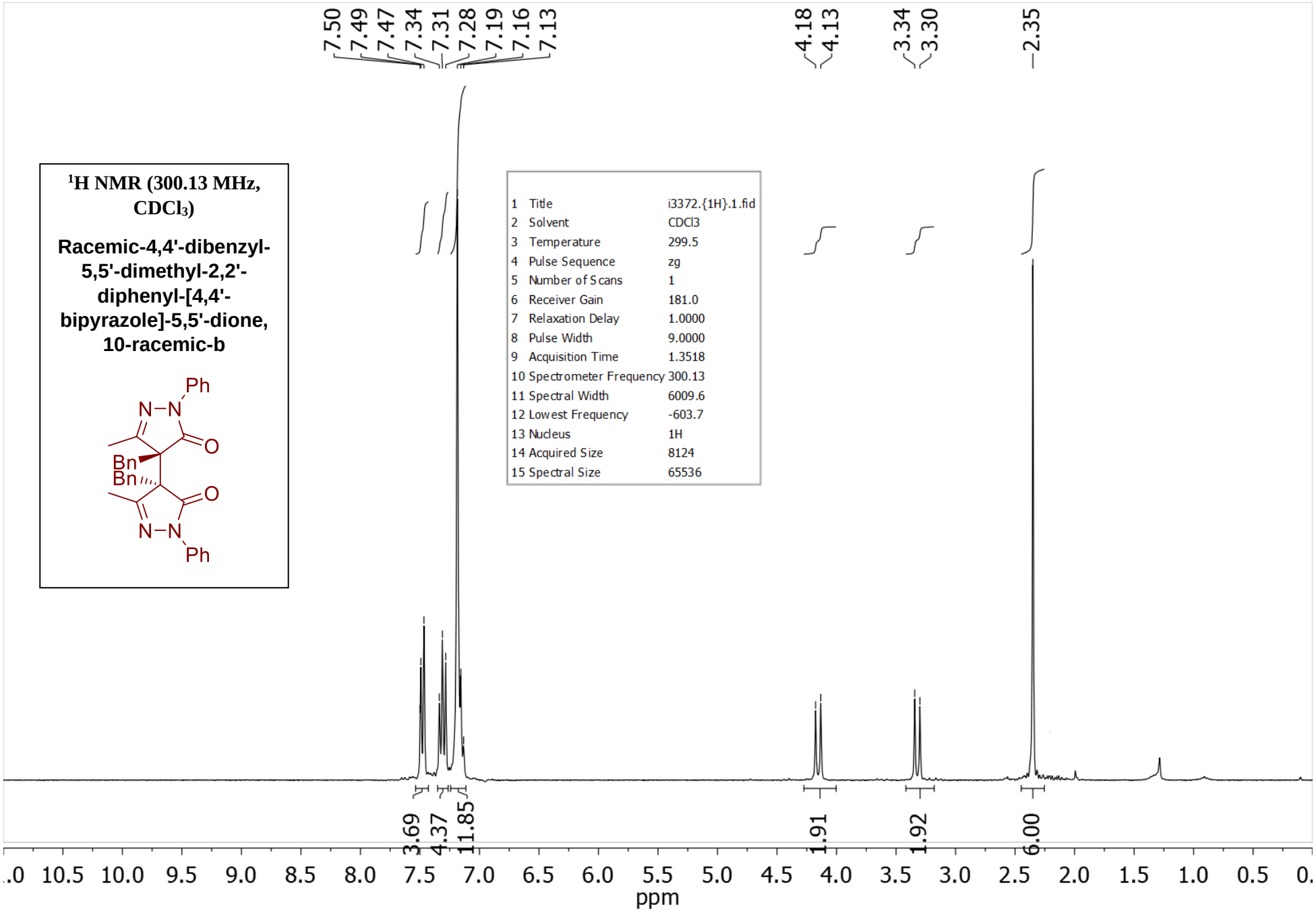

173.11
161.94
137.63
129.17
125.68
119.05
54.46
14.68
14.61
^{13}C NMR (75.47 MHz, $CDCl_3$)
Meso-3,3',4,4'-tetramethyl-1,1'-diphenyl-[4,4'-bipyrazol]-5,5'-dione, 10-meso-a
Ph
N–N
O
O
N–N
Ph
Title i1589.{13C}
Solvent CDCl3
Temperature 298.4
Pulse Sequence zgpg30
Number of Scans 266
Receiver Gain 3250
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9006
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -745.1
Nucleus 13C
Acquired Size 16316
Spectral Size 32768
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

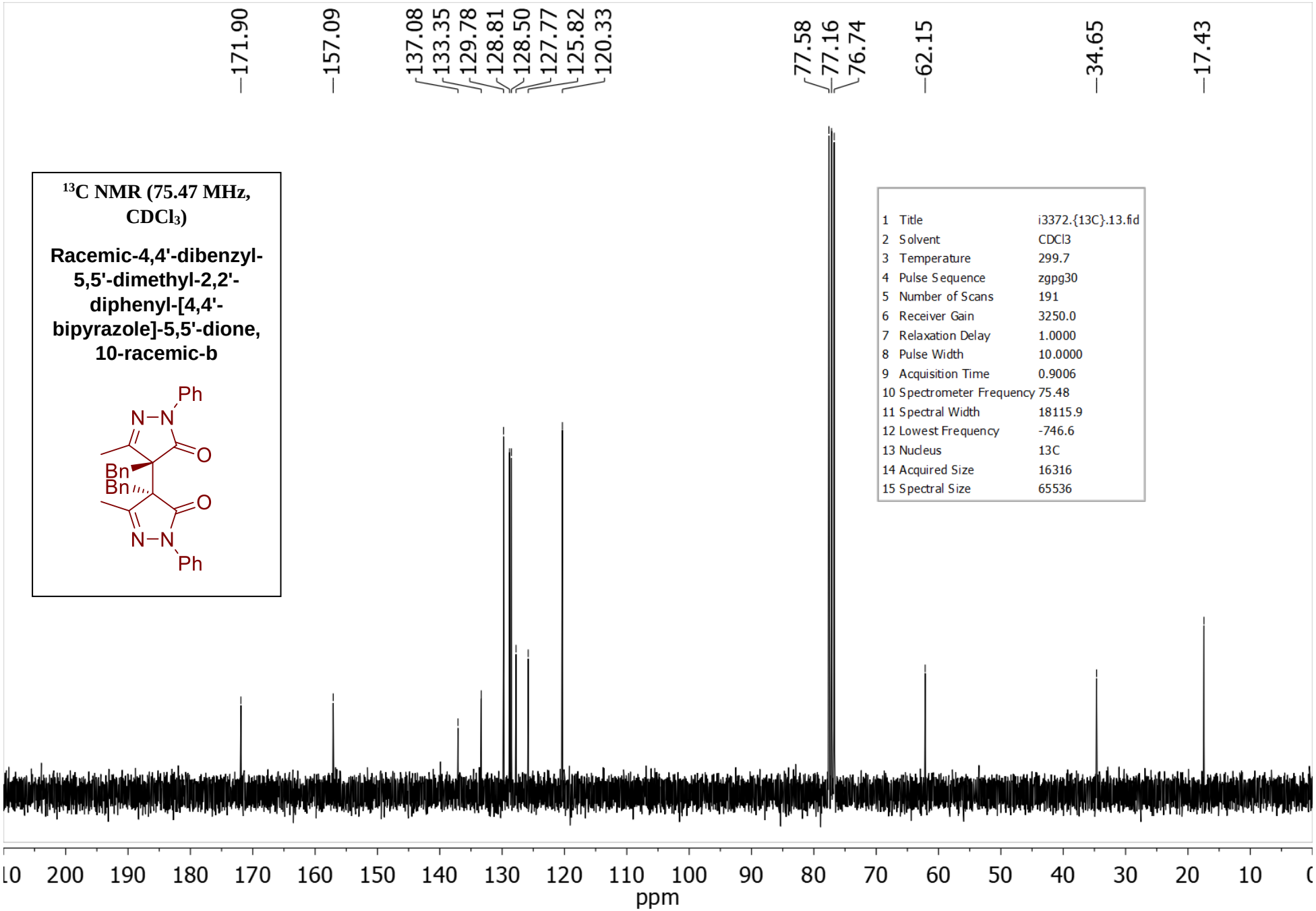

7.86
7.83
7.41
7.38
7.35
7.20
7.18
7.16
2.19
1.60
^{1}H NMR (300.13 MHz, $CDCl_3$)
Racemic-3,3',4,4'-tetramethyl-1,1'-diphenyl-[4,4'-bipyrazol]-5,5'-dione, 10-racemic-a
Ph
N–N
O
O
N–N
Ph
Title i1561.{1H}
Solvent CDCl3
Temperature 300.4
Pulse Sequence zg
Number of Scans 1
Receiver Gain 114
Relaxation Delay 2.0000
Pulse Width 9.0000
Acquisition Time 1.0832
Spectrometer Frequency 300.13
Spectral Width 7500.0
Lowest Frequency -1355.9
Nucleus 1H
Acquired Size 8124
Spectral Size 16384
3.98
4.05
2.04
6.00
6.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

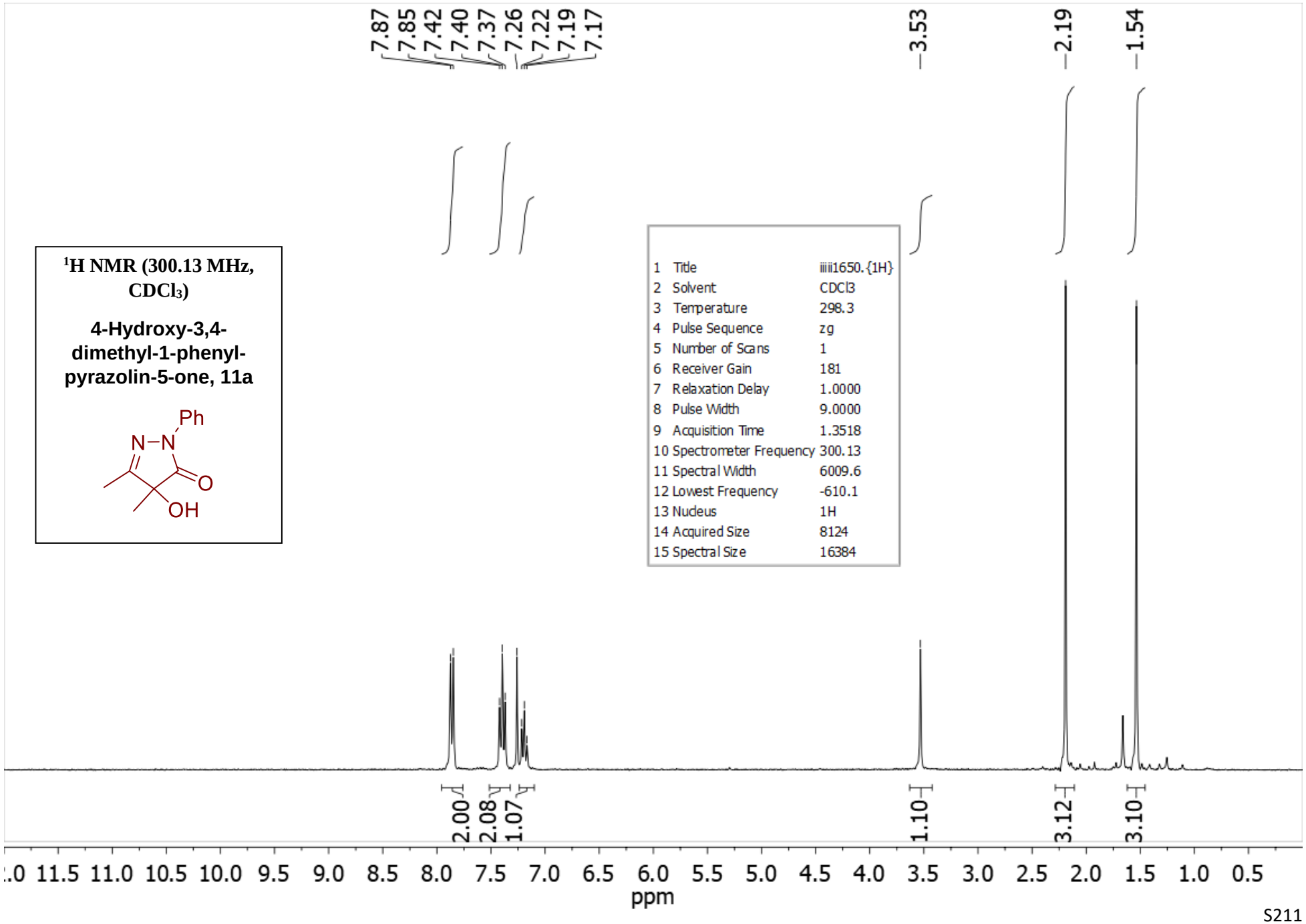

173.06
159.79
137.73
128.96
125.41
119.30
55.65
15.99
15.40
^{13}C NMR (75.47 MHz, $CDCl_3$)
Racemic-3,3',4,4'-tetramethyl-1,1'-diphenyl-[4,4'-bipyrazol]-5,5'-dione, 10-racemic-a
Ph
N–N
O
O
N–N
Ph
Title i1561.{13C}
Solvent CDCl3
Temperature 300.7
Pulse Sequence zgpg60base
Number of Scans 82
Receiver Gain 2580
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.8680
Spectrometer Frequency 75.48
Spectral Width 18797.0
Lowest Frequency -1469.7
Nucleus 13C
Acquired Size 16316
Spectral Size 32768
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


7.58
7.56
7.40
7.38
7.35
7.26
7.24
7.24
7.21
7.19
7.17
4.44
4.39
3.62
3.57
1.99
¹H NMR (300.13 MHz, CDCl₃)
Meso-4,4'-dibenzyl-5,5'-dimethyl-2,2'-diphenyl-[4,4'-bipyrazole]-5,5'-dione, 10-meso-b
Ph
N–N
O
Bn
Bn
O
N–N
Ph
Title i7113.{1H}.1.fid
Solvent CDCl3
Temperature 294.1
Pulse Sequence zg
Number of Scans 1
Receiver Gain 18.0
Relaxation Delay 0.0050
Pulse Width 9.0000
Acquisition Time 1.3518
Spectrometer Frequency 300.13
Spectral Width 6009.6
Lowest Frequency -609.9
Nucleus 1H
Acquired Size 8124
Spectral Size 65536
4.21
4.15
12.27
2.00
2.00
6.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


172.40
159.57
136.97
133.67
129.79
129.02
128.47
127.67
126.02
119.84
77.58
77.16
76.74
60.65
33.87
15.59
13C NMR (75.47 MHz, CDCl3)
Meso-4,4'-dibenzyl-5,5'-dimethyl-2,2'-diphenyl-[4,4'-bipyrazole]-5,5'-dione, 10-meso-b
Ph
N–N
O
Bn
Bn
O
N–N
Ph
1 Title i3402.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 299.8
4 Pulse Sequence zgpg30
5 Number of Scans 256
6 Receiver Gain 3250.0
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9006
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -746.4
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

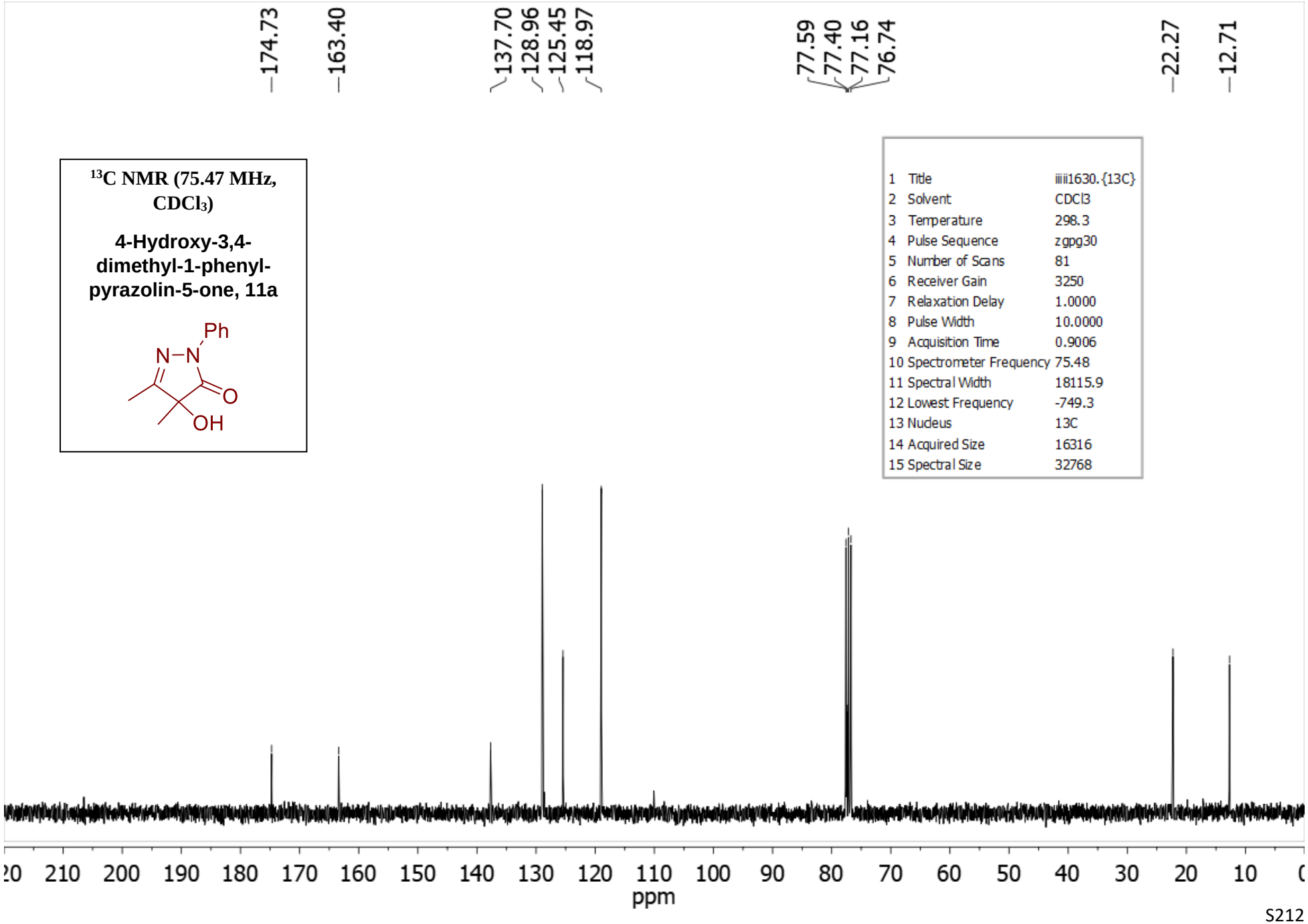

7.50
7.49
7.47
7.34
7.31
7.28
7.19
7.16
7.13
4.18
4.13
3.34
3.30
2.35
¹H NMR (300.13 MHz, CDCl₃)
Racemic-4,4'-dibenzyl-5,5'-dimethyl-2,2'-diphenyl-[4,4'-bipyrazole]-5,5'-dione, 10-racemic-b
Ph
N–N
O
Bn
Bn
O
N–N
Ph
1 Title i3372.{1H}.1.fid
2 Solvent CDCl3
3 Temperature 299.5
4 Pulse Sequence zg
5 Number of Scans 1
6 Receiver Gain 181.0
7 Relaxation Delay 1.0000
8 Pulse Width 9.0000
9 Acquisition Time 1.3518
10 Spectrometer Frequency 300.13
11 Spectral Width 6009.6
12 Lowest Frequency -603.7
13 Nucleus 1H
14 Acquired Size 8124
15 Spectral Size 65536
3.69
4.37
11.85
1.91
1.92
6.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm

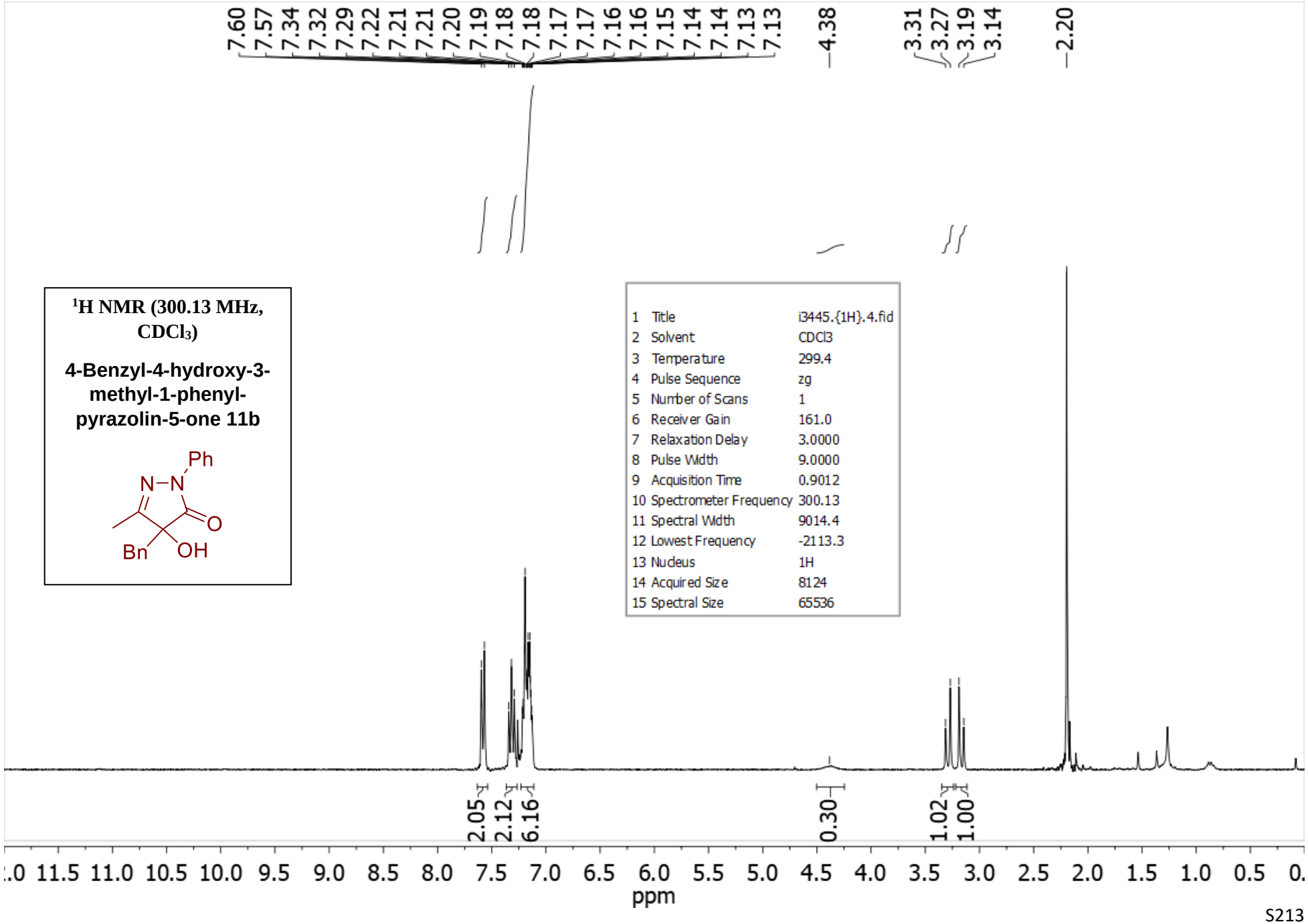

171.90
157.09
137.08
133.35
129.78
128.81
128.50
127.77
125.82
120.33
77.58
77.16
76.74
62.15
34.65
17.43
^{13}C NMR (75.47 MHz, $CDCl_3$)
Racemic-4,4'-dibenzyl-5,5'-dimethyl-2,2'-diphenyl-[4,4'-bipyrazole]-5,5'-dione, 10-racemic-b
Ph
N–N
O
Bn
Bn
O
N–N
Ph
1 Title i3372.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 299.7
4 Pulse Sequence zgpg30
5 Number of Scans 191
6 Receiver Gain 3250.0
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9006
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -746.6
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
ppm

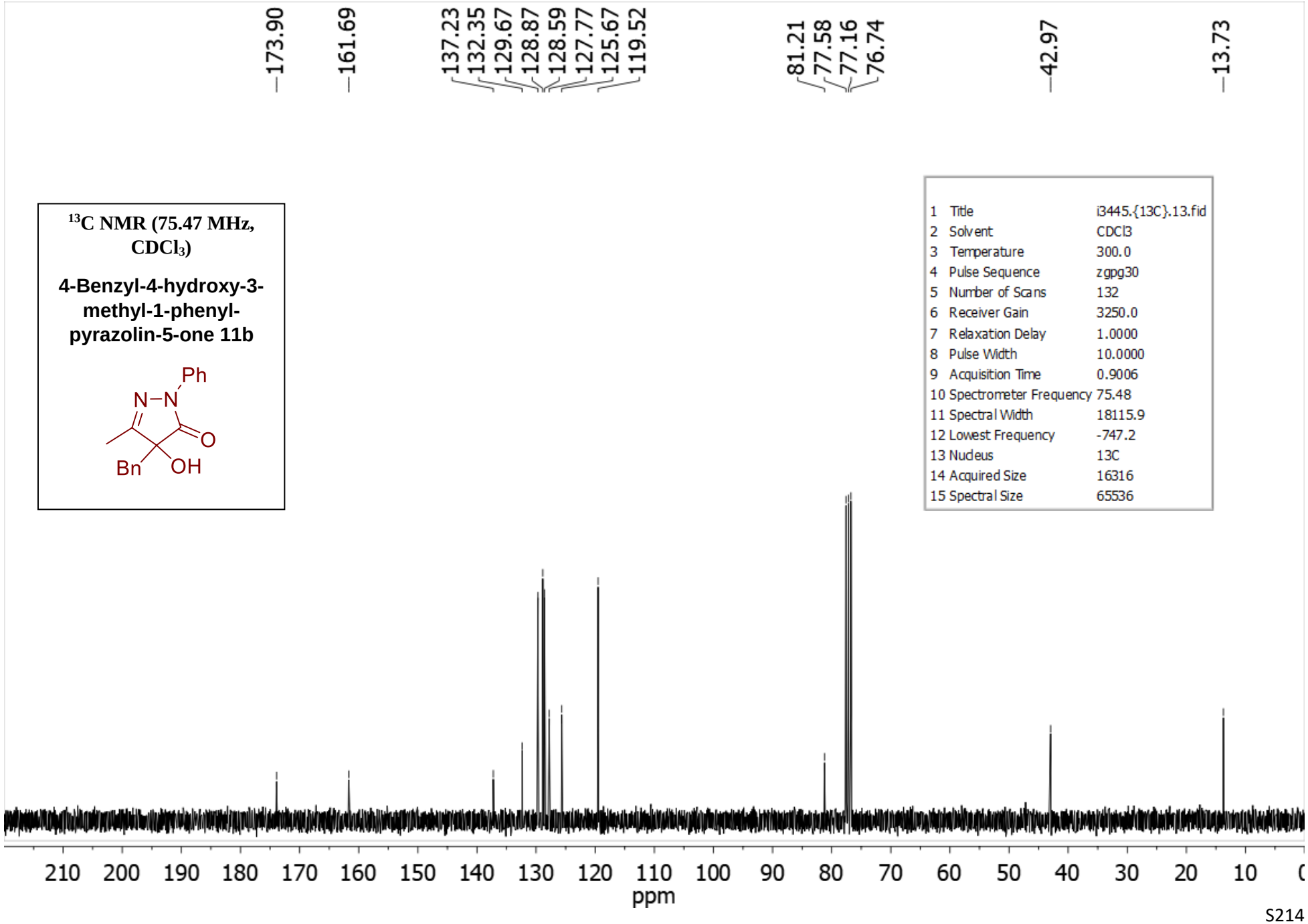


^{1}H NMR (300.13 MHz, $CDCl_3$)

4-Hydroxy-3,4-dimethyl-1-phenyl-pyrazolin-5-one, 11a

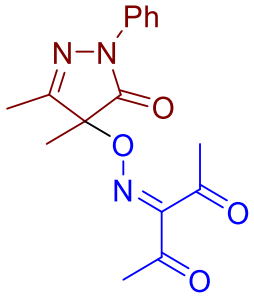

174.73
163.40
137.70
128.96
125.45
118.97
77.59
77.40
77.16
76.74
22.27
12.71
13C NMR (75.47 MHz, CDCl3)
4-Hydroxy-3,4-dimethyl-1-phenyl-pyrazolin-5-one, 11a
Ph
N–N
O
OH
1 Title iiii1630.{13C}
2 Solvent CDCl3
3 Temperature 298.3
4 Pulse Sequence zgpg30
5 Number of Scans 81
6 Receiver Gain 3250
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9006
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -749.3
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 32768
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

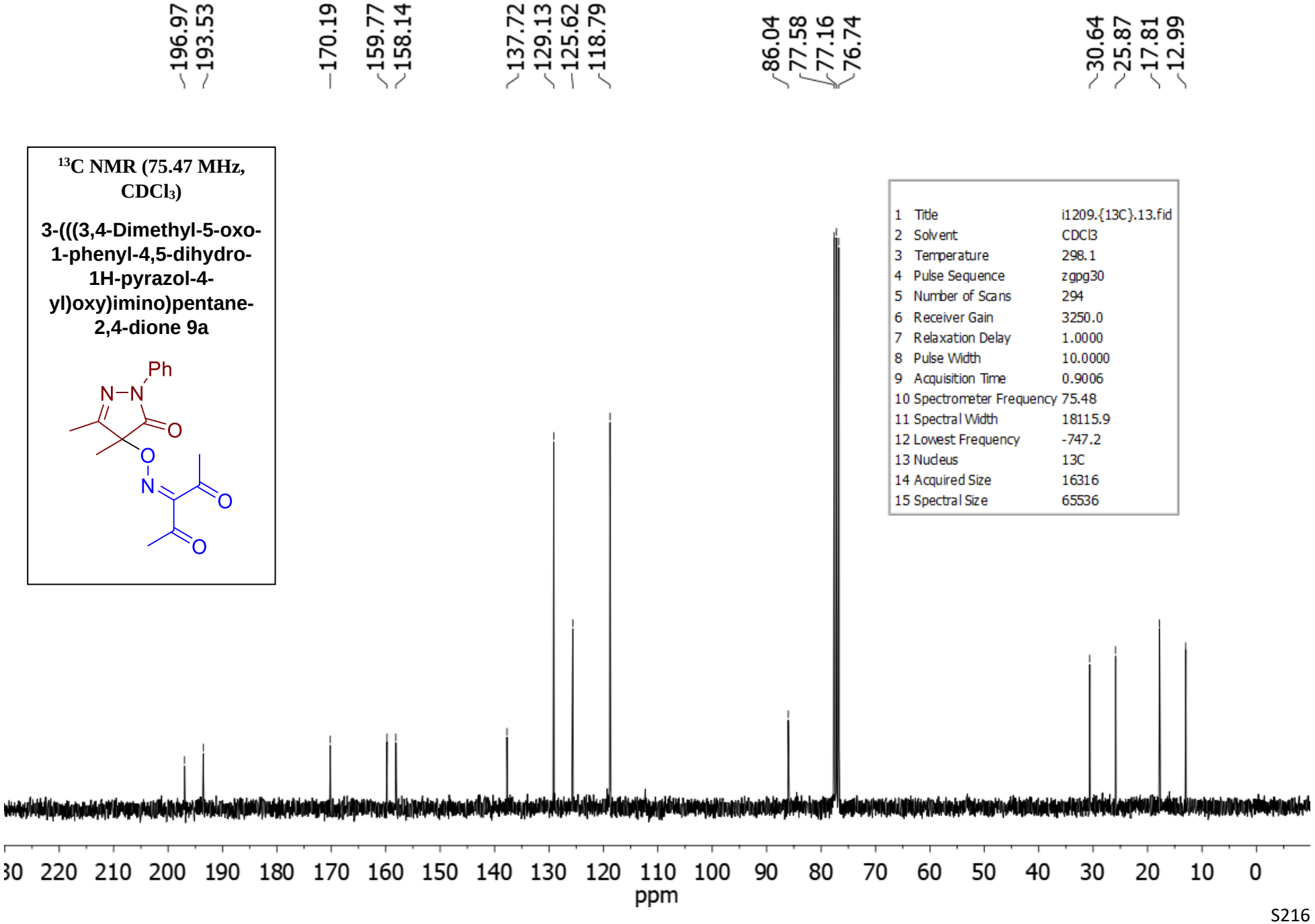

7.60
7.57
7.34
7.32
7.29
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.13
7.13
4.38
3.31
3.27
3.19
3.14
2.20
1H NMR (300.13 MHz, CDCl3)
4-Benzyl-4-hydroxy-3-methyl-1-phenyl-pyrazolin-5-one 11b
Ph
N–N
O
Bn
OH
1 Title i3445.{1H}.4.fid
2 Solvent CDCl3
3 Temperature 299.4
4 Pulse Sequence zg
5 Number of Scans 1
6 Receiver Gain 161.0
7 Relaxation Delay 3.0000
8 Pulse Width 9.0000
9 Acquisition Time 0.9012
10 Spectrometer Frequency 300.13
11 Spectral Width 9014.4
12 Lowest Frequency -2113.3
13 Nucleus 1H
14 Acquired Size 8124
15 Spectral Size 65536
2.05
2.12
6.16
0.30
1.02
1.00
ppm

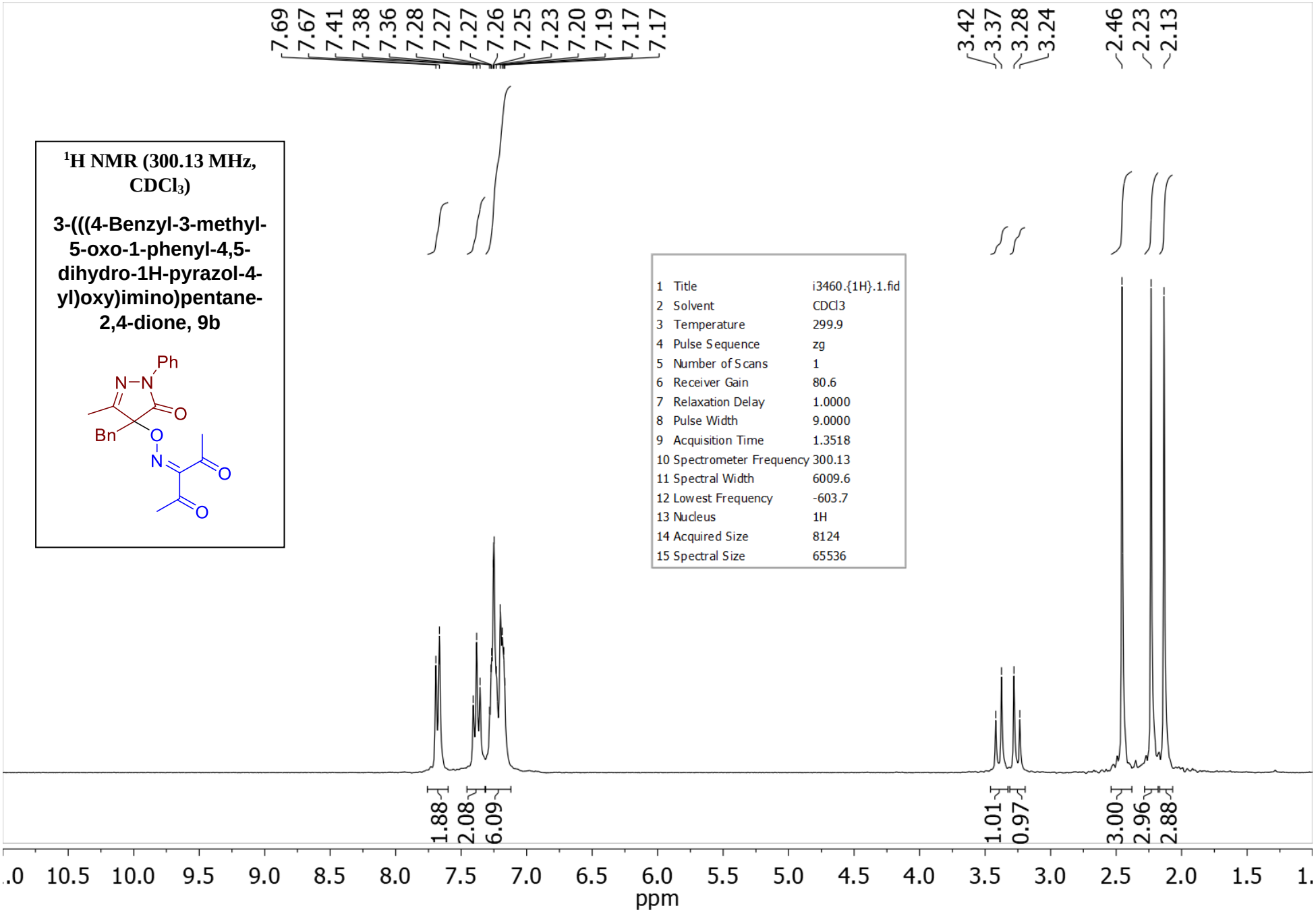

173.90
161.69
137.23
132.35
129.67
128.87
128.59
127.77
125.67
119.52
81.21
77.58
77.16
76.74
42.97
13.73
^{13}C NMR (75.47 MHz, $CDCl_3$)
4-Benzyl-4-hydroxy-3-methyl-1-phenyl-pyrazolin-5-one 11b
Ph
N–N
O
Bn
OH
1 Title i3445.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 300.0
4 Pulse Sequence zgpg30
5 Number of Scans 132
6 Receiver Gain 3250.0
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9006
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -747.2
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

^{1}H NMR (300.13 MHz, $CDCl_3$)

3-(((3,4-Dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a



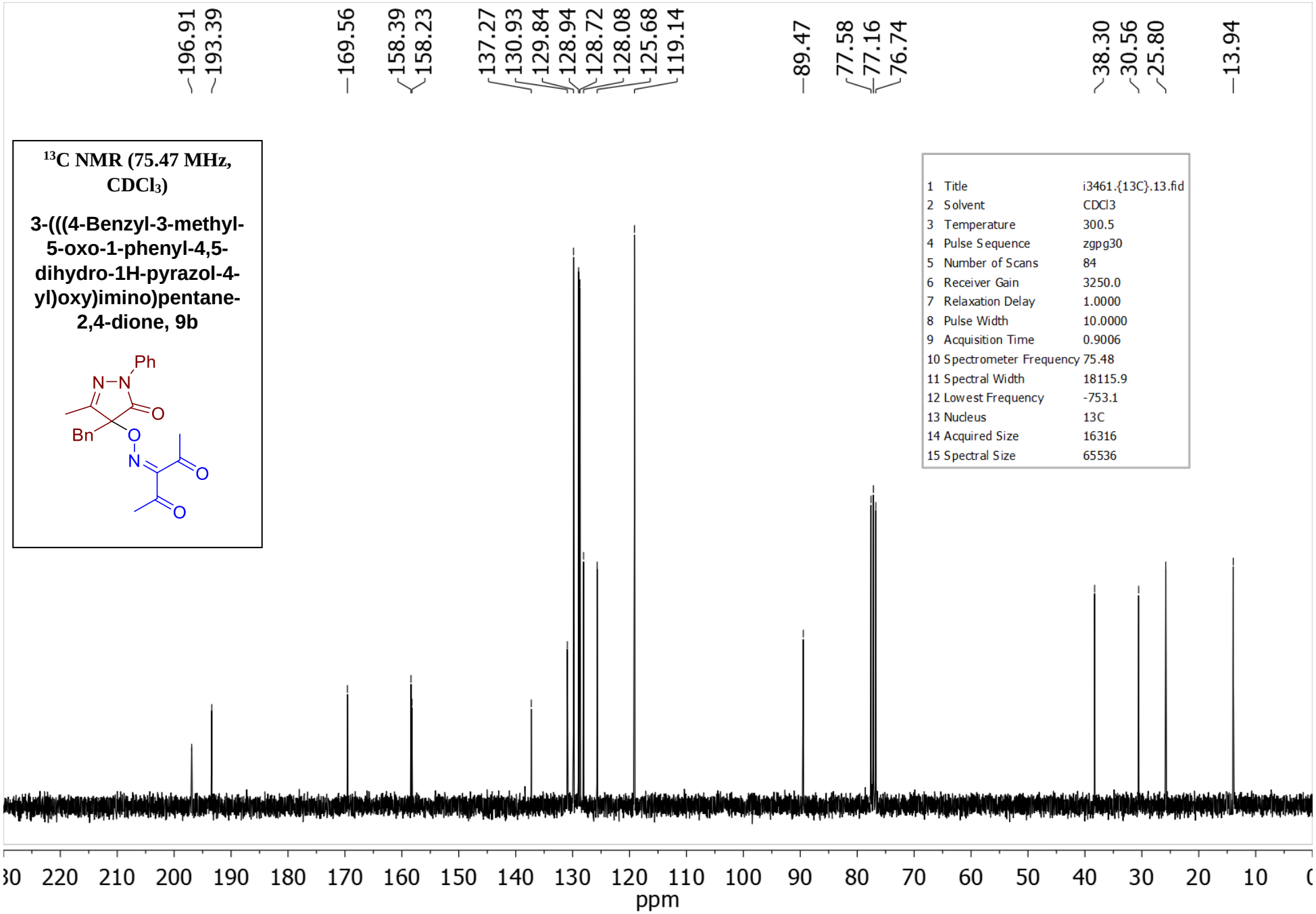

196.97
193.53
170.19
159.77
158.14
137.72
129.13
125.62
118.79
86.04
77.58
77.16
76.74
30.64
25.87
17.81
12.99
13C NMR (75.47 MHz, CDCl3)
3-(((3,4-Dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 9a
Ph
N–N
O
O
N
O
O
1 Title i1209.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 298.1
4 Pulse Sequence zgpg30
5 Number of Scans 294
6 Receiver Gain 3250.0
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9006
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -747.2
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



^{1}H NMR (300.13 MHz, $CDCl_3$)

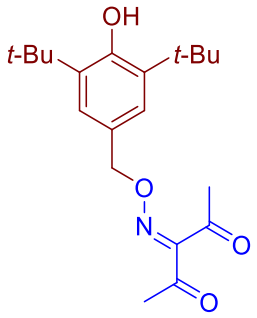
3-(((4-Benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione, 9b

1	Title	i3460.{1H}.1.fid
2	Solvent	CDCl3
3	Temperature	299.9
4	Pulse Sequence	zg
5	Number of Scans	1
6	Receiver Gain	80.6
7	Relaxation Delay	1.0000
8	Pulse Width	9.0000
9	Acquisition Time	1.3518
10	Spectrometer Frequency	300.13
11	Spectral Width	6009.6
12	Lowest Frequency	-603.7
13	Nucleus	1H
14	Acquired Size	8124
15	Spectral Size	65536

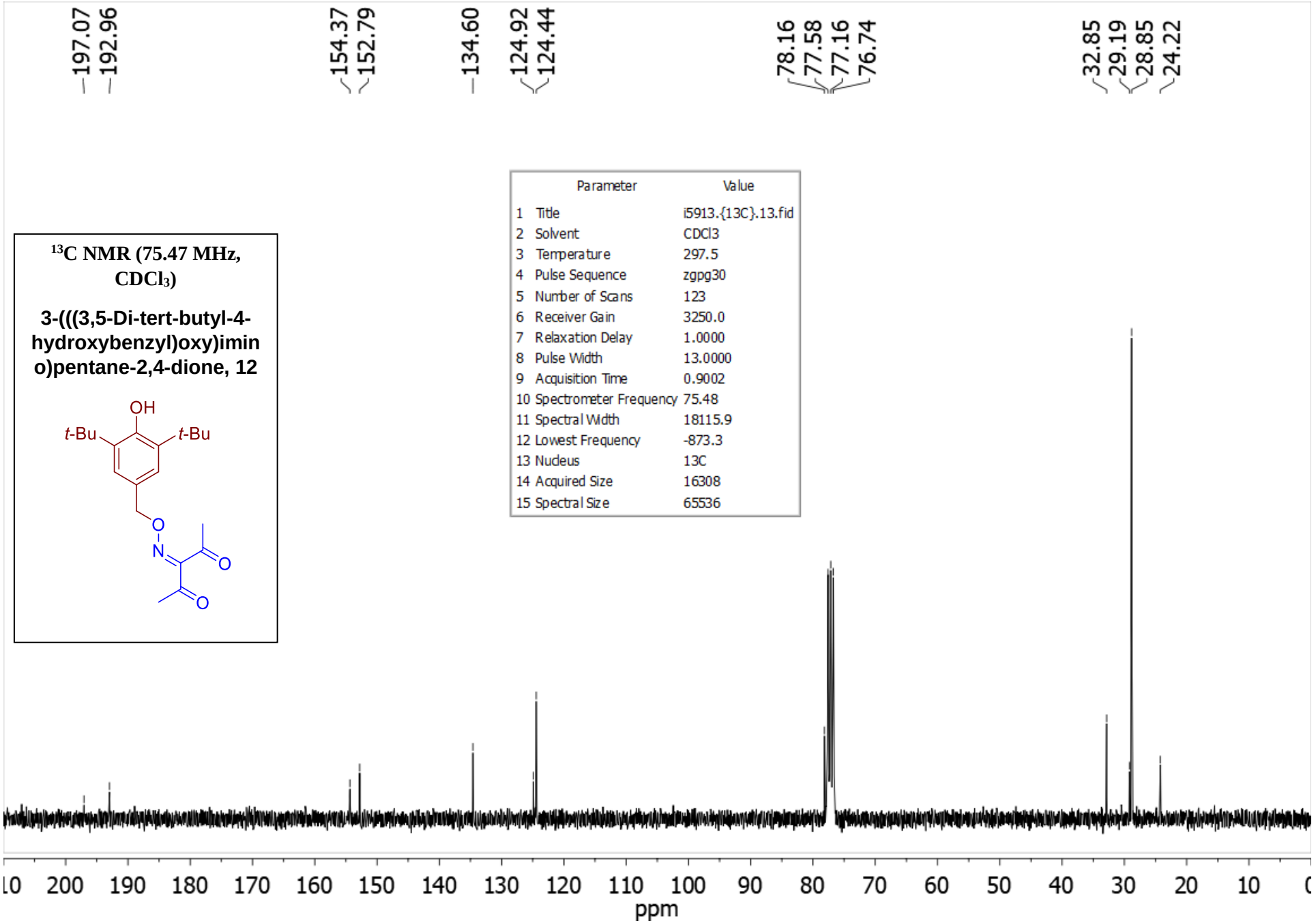

196.91
193.39
169.56
158.39
158.23
137.27
130.93
129.84
128.94
128.72
128.08
125.68
119.14
89.47
77.58
77.16
76.74
38.30
30.56
25.80
13.94
13C NMR (75.47 MHz, CDCl3)
3-(((4-Benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione, 9b
Ph
N–N
O
Bn
O
N
O
O
1 Title i3461.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 300.5
4 Pulse Sequence zgpg30
5 Number of Scans 84
6 Receiver Gain 3250.0
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9006
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -753.1
13 Nucleus 13C
14 Acquired Size 16316
15 Spectral Size 65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

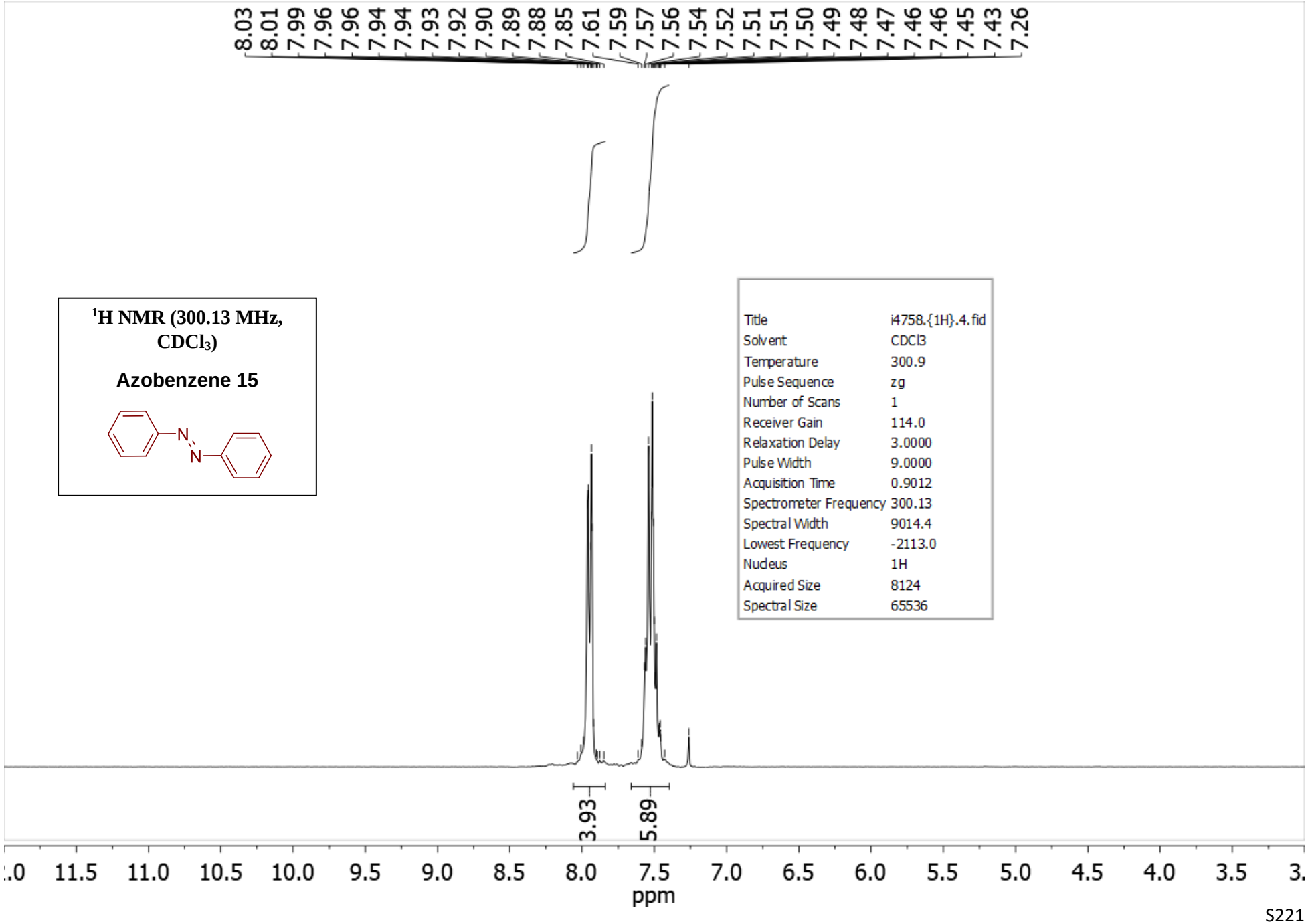
^{1}H NMR (300.13 MHz, $CDCl_3$)

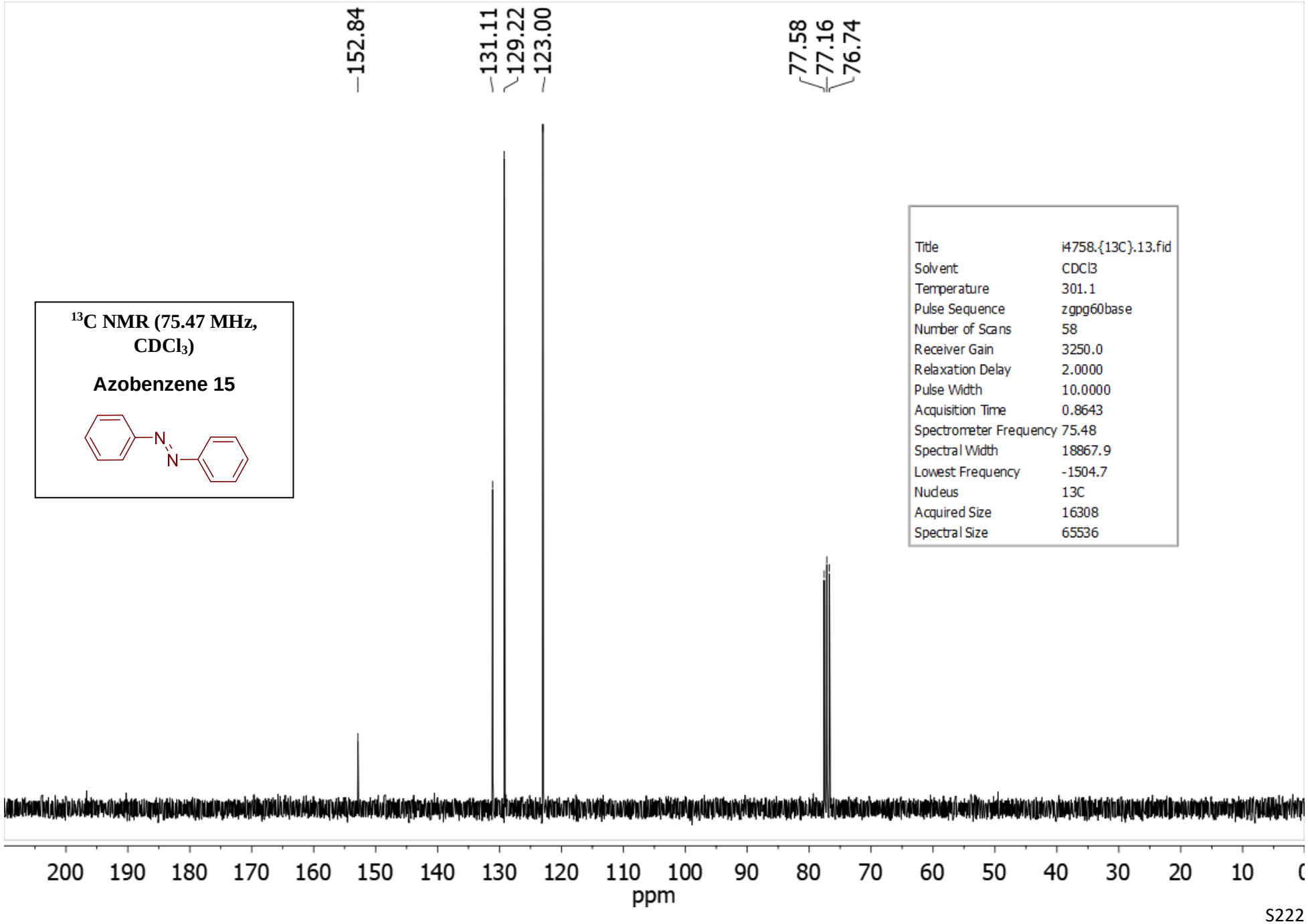
3-(((3,5-Di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione, 12

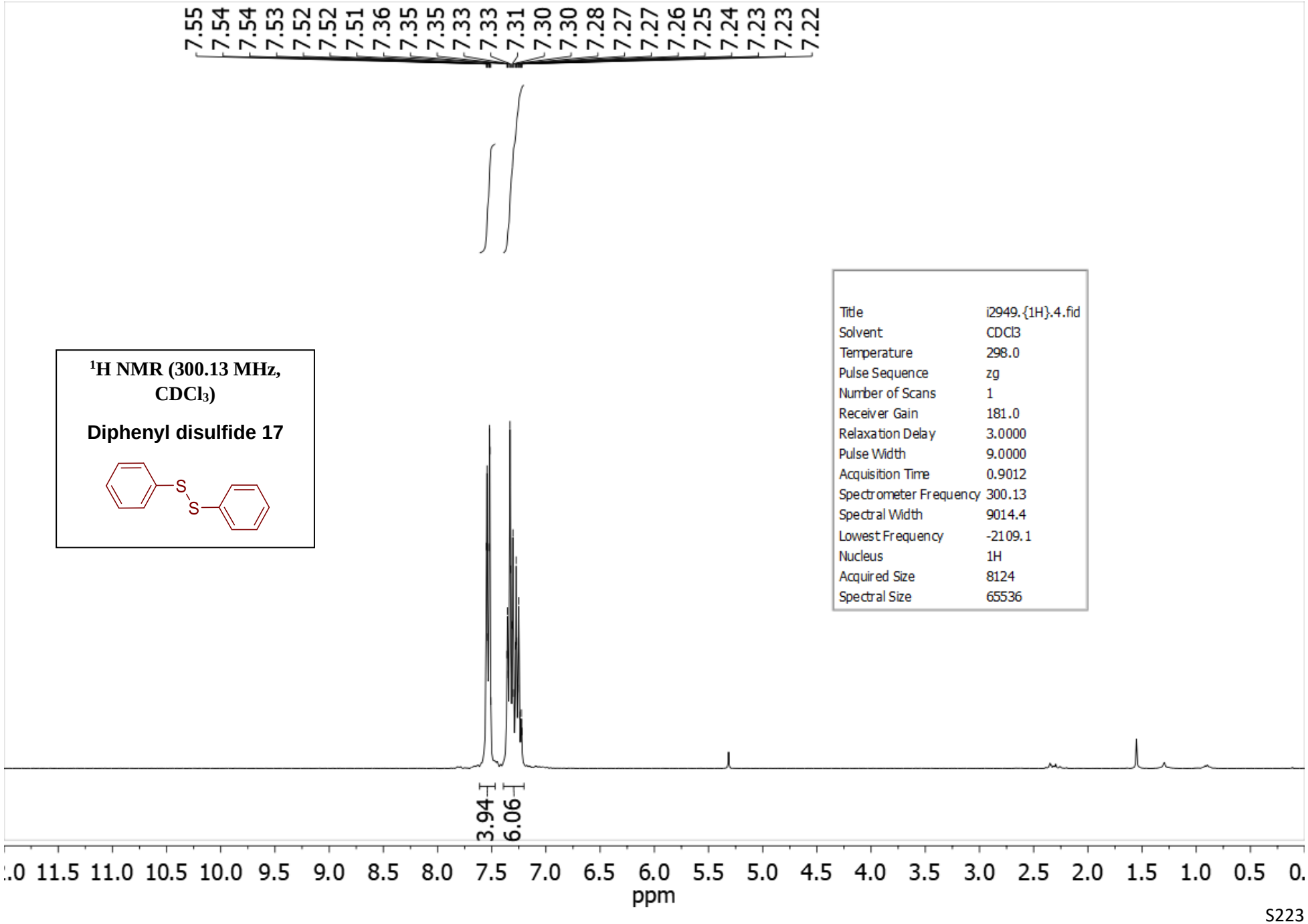


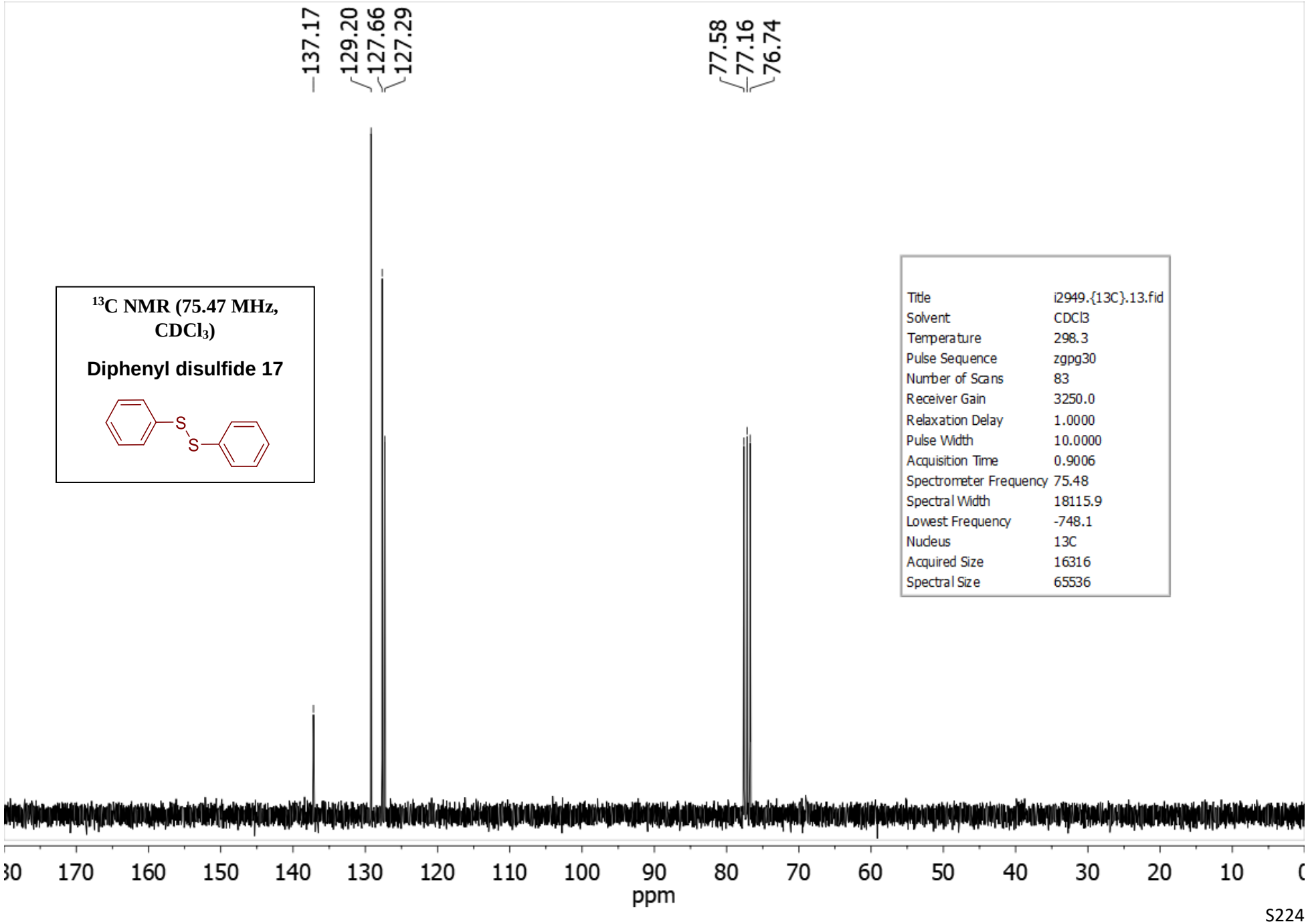
Title	i6438.{1H}.1.fid
Solvent	CDCl3
Temperature	299.5
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	128.0
Relaxation Delay	0.0050
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.9
Nucleus	1H
Acquired Size	8124
Spectral Size	65536


197.07
192.96
154.37
152.79
134.60
124.92
124.44
78.16
77.58
77.16
76.74
32.85
29.19
28.85
24.22
^{13}C NMR (75.47 MHz, CDCl$_3$)
3-(((3,5-Di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione, 12
OH
t-Bu
t-Bu
O
N
O
O
Parameter Value
1 Title i5913.{13C}.13.fid
2 Solvent CDCl3
3 Temperature 297.5
4 Pulse Sequence zgpg30
5 Number of Scans 123
6 Receiver Gain 3250.0
7 Relaxation Delay 1.0000
8 Pulse Width 13.0000
9 Acquisition Time 0.9002
10 Spectrometer Frequency 75.48
11 Spectral Width 18115.9
12 Lowest Frequency -873.3
13 Nucleus 13C
14 Acquired Size 16308
15 Spectral Size 65536
ppm


8.03
8.01
7.99
7.96
7.96
7.94
7.94
7.93
7.92
7.90
7.89
7.88
7.85
7.61
7.59
7.57
7.56
7.54
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.43
7.26
^{1}H NMR (300.13 MHz, $CDCl_3$)
Azobenzene 15
N
N
Title i4758.{1H}.4.fid
Solvent CDCl3
Temperature 300.9
Pulse Sequence zg
Number of Scans 1
Receiver Gain 114.0
Relaxation Delay 3.0000
Pulse Width 9.0000
Acquisition Time 0.9012
Spectrometer Frequency 300.13
Spectral Width 9014.4
Lowest Frequency -2113.0
Nucleus 1H
Acquired Size 8124
Spectral Size 65536
3.93
5.89
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


152.84
131.11
129.22
123.00
77.58
77.16
76.74
^{13}C NMR (75.47 MHz, $CDCl_3$)
Azobenzene 15
Title i4758.{13C}.13.fid
Solvent CDCl3
Temperature 301.1
Pulse Sequence zgpg60base
Number of Scans 58
Receiver Gain 3250.0
Relaxation Delay 2.0000
Pulse Width 10.0000
Acquisition Time 0.8643
Spectrometer Frequency 75.48
Spectral Width 18867.9
Lowest Frequency -1504.7
Nucleus 13C
Acquired Size 16308
Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

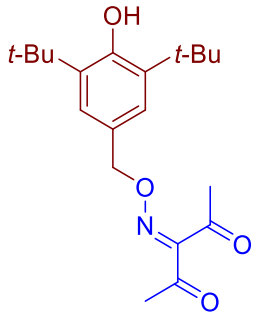

7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.36 7.35 7.35 7.33 7.33 7.31 7.30 7.30 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.23 7.22
^{1}H NMR (300.13 MHz, $CDCl_3$)
Diphenyl disulfide 17
S
S
Title i2949.{1H}.4.fid
Solvent CDCl3
Temperature 298.0
Pulse Sequence zg
Number of Scans 1
Receiver Gain 181.0
Relaxation Delay 3.0000
Pulse Width 9.0000
Acquisition Time 0.9012
Spectrometer Frequency 300.13
Spectral Width 9014.4
Lowest Frequency -2109.1
Nucleus 1H
Acquired Size 8124
Spectral Size 65536
3.94
6.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

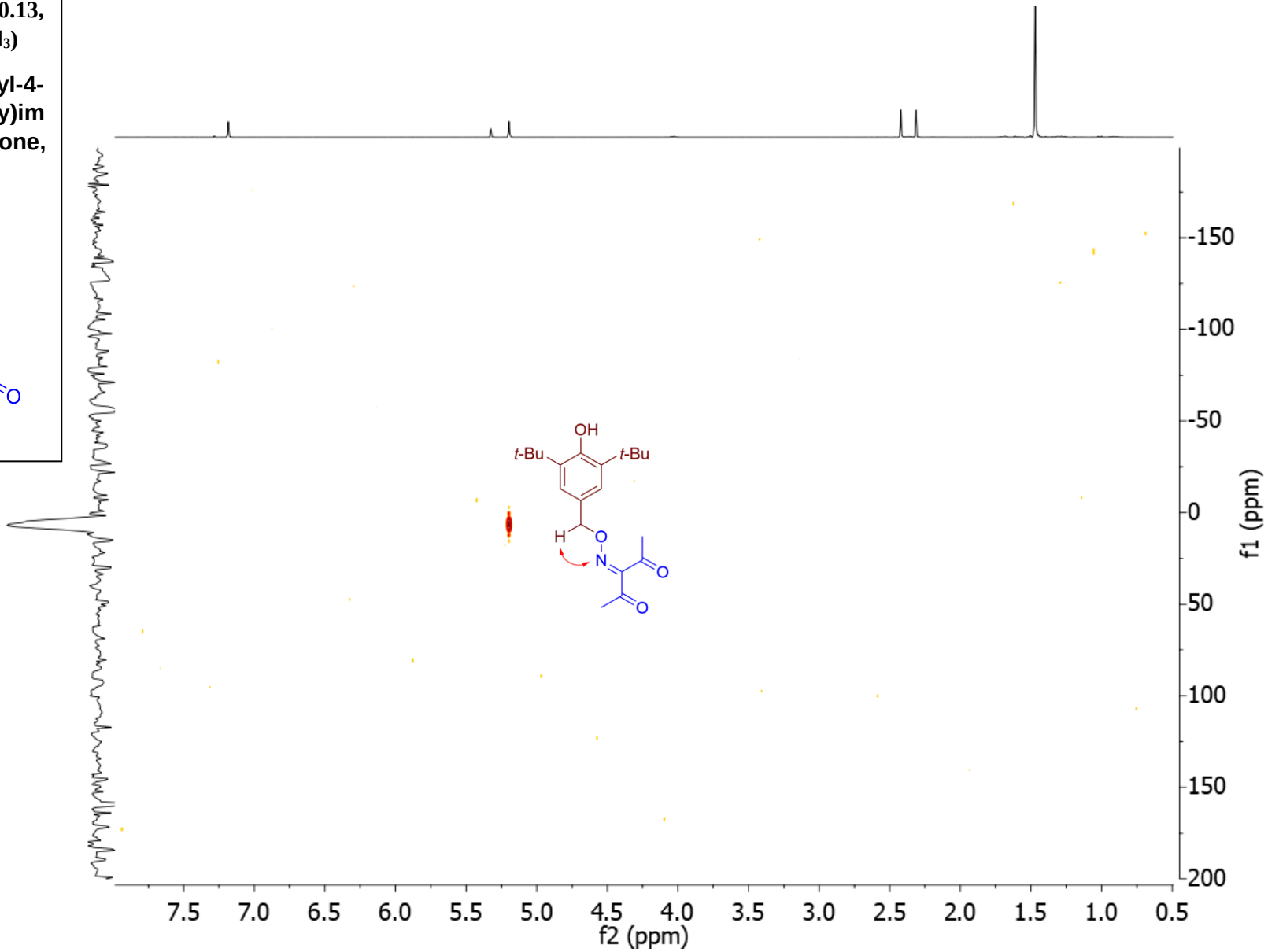

137.17
129.20
127.66
127.29
77.58
77.16
76.74
^{13}C NMR (75.47 MHz, $CDCl_3$)
Diphenyl disulfide 17
S
S
Title i2949.{13C}.13.fid
Solvent CDCl3
Temperature 298.3
Pulse Sequence zgpg30
Number of Scans 83
Receiver Gain 3250.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 0.9006
Spectrometer Frequency 75.48
Spectral Width 18115.9
Lowest Frequency -748.1
Nucleus 13C
Acquired Size 16316
Spectral Size 65536
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

{^{1}H-^{15}N} HMBC Spectrum of 3-(((3,5-di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione, 12

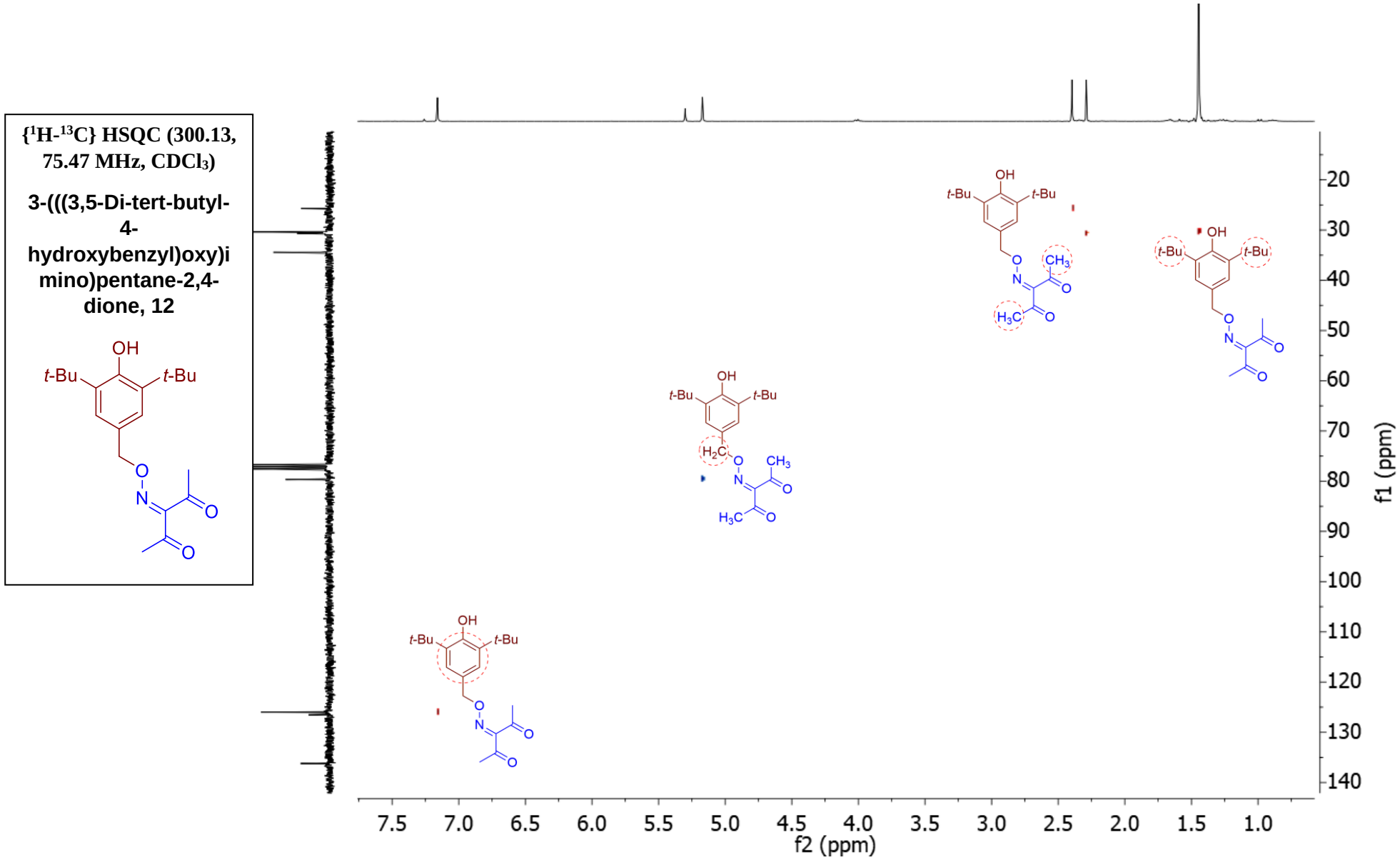
{^{1}H-^{15}N} HMBC (600.13, 60.81 MHz, $CDCl_3$)

3-(((3,5-Di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione, 12

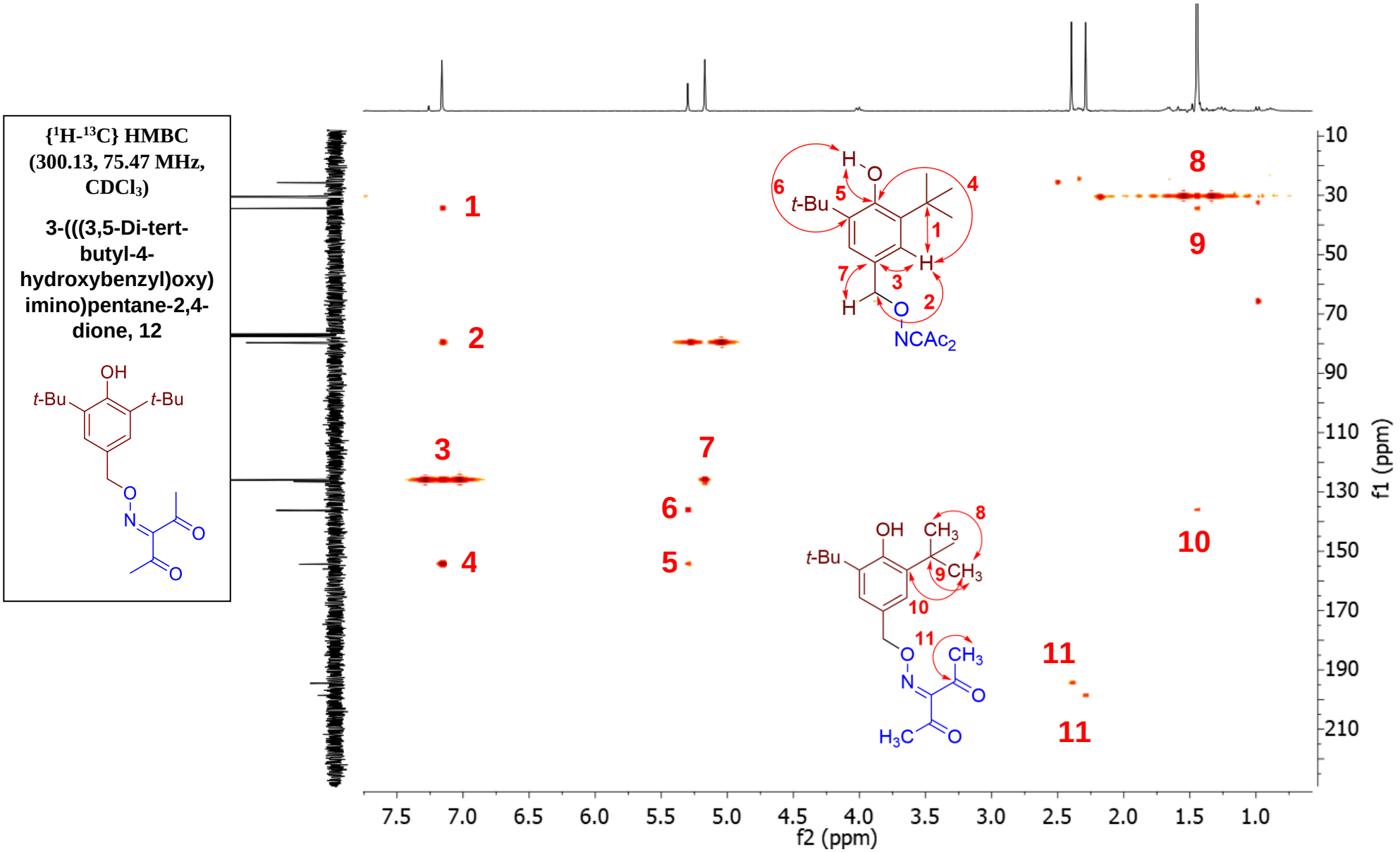




{^{1}H-^{13}C} HSQC Spectrum of 3-(((3,5-di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione, 12



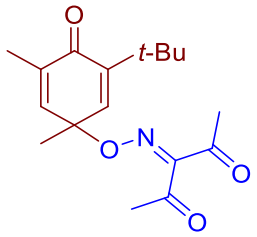
{^{1}H-^{13}C} HMBC Spectrum of 3-(((3,5-di-tert-butyl-4-hydroxybenzyl)oxy)imino)pentane-2,4-dione, 12

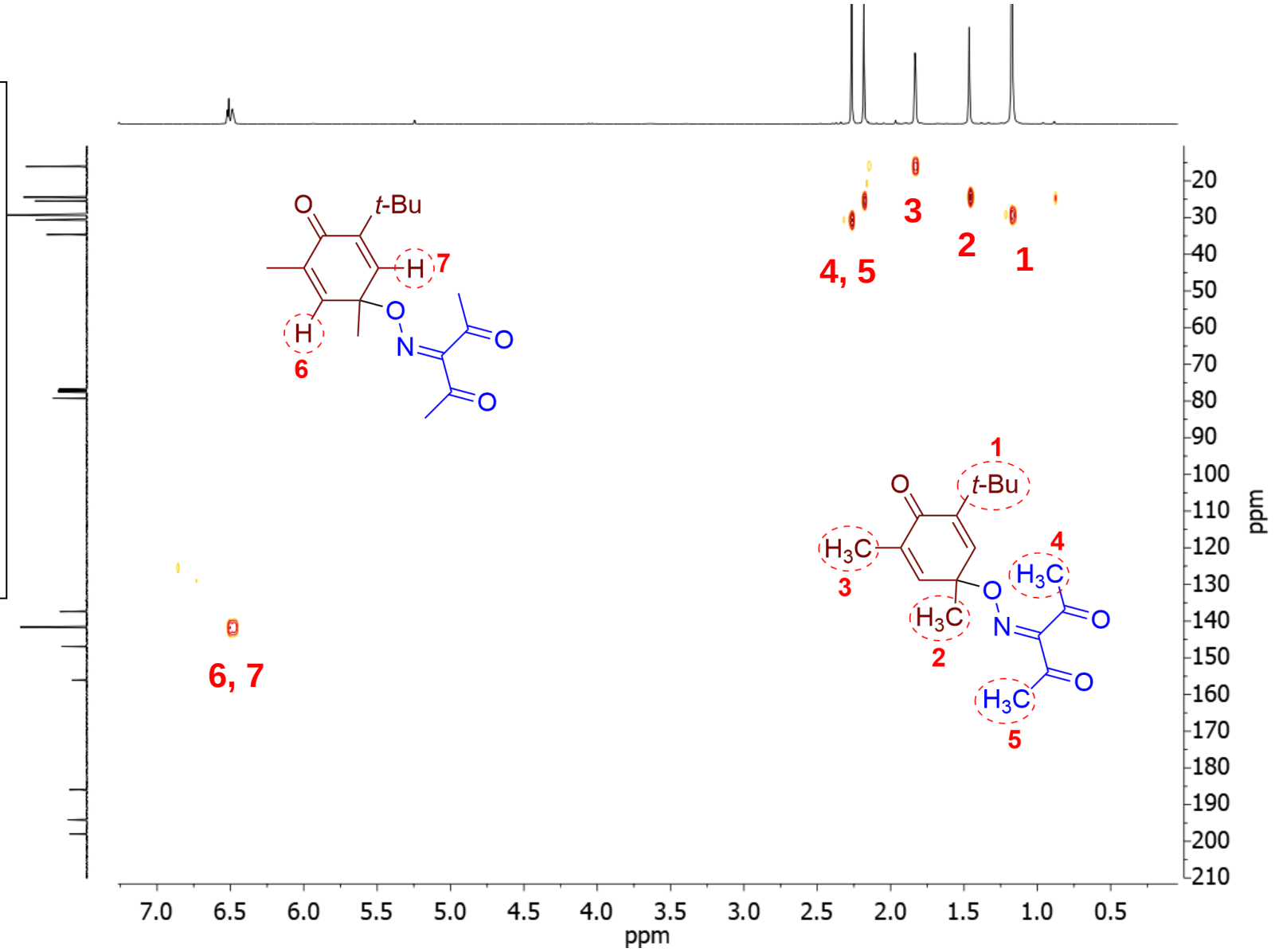


{^{1}H-^{13}C} HSQC Spectrum of 3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7c

{^{1}H-^{13}C} HSQC (300.13, 75.47 MHz, $CDCl_3$)

3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7c

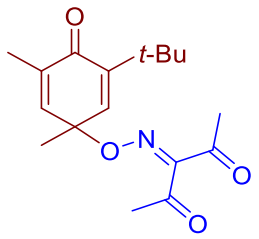


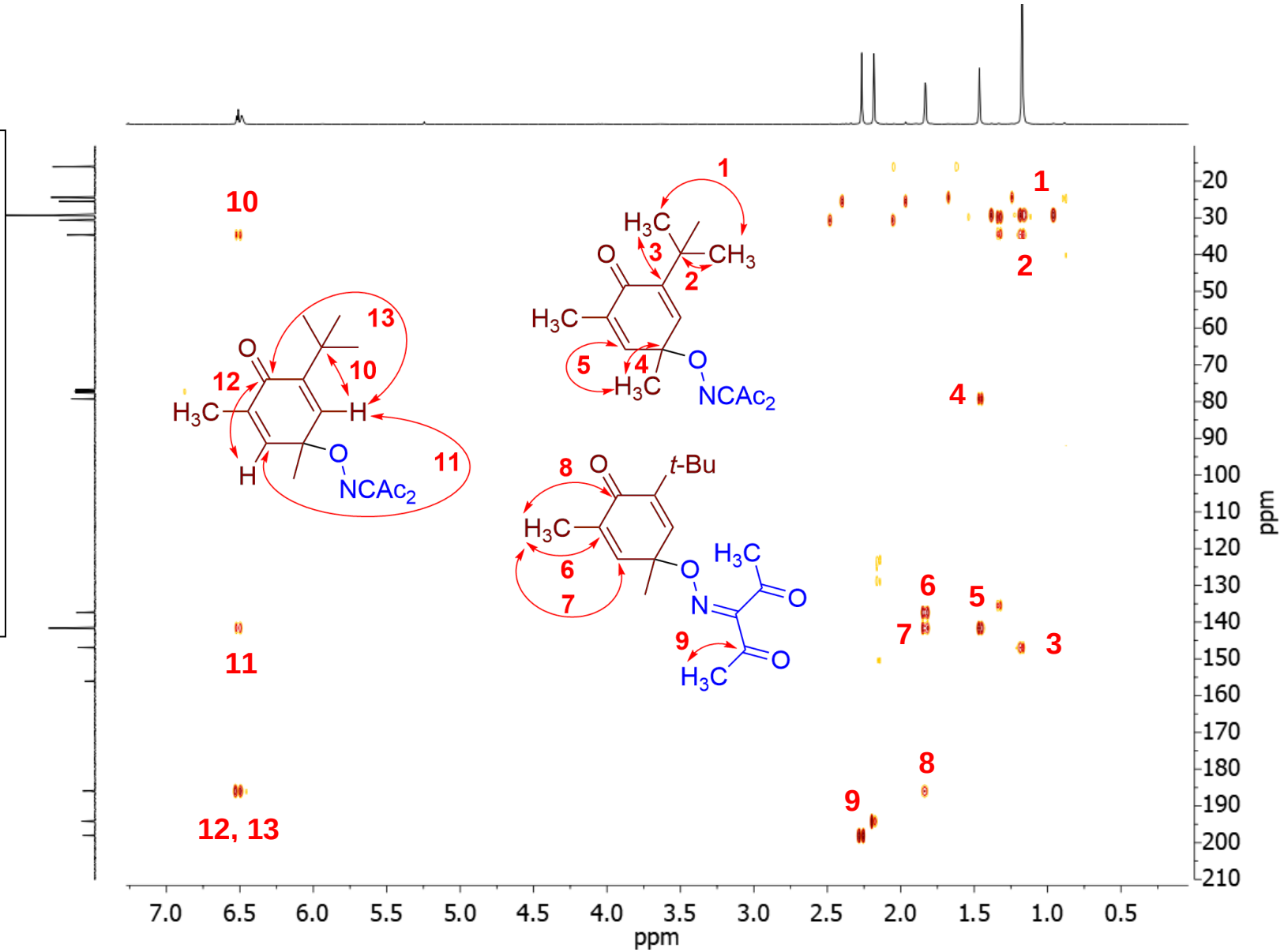


{^{1}H-^{13}C} HMBC Spectrum of 3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7c

{^{1}H-^{13}C} HMBC (300.13, 75.47 MHz, $CDCl_3$)

3-(((3-(Tert-butyl)-1,5-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)imino)pentane-2,4-dione, 7c

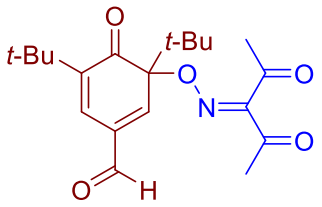


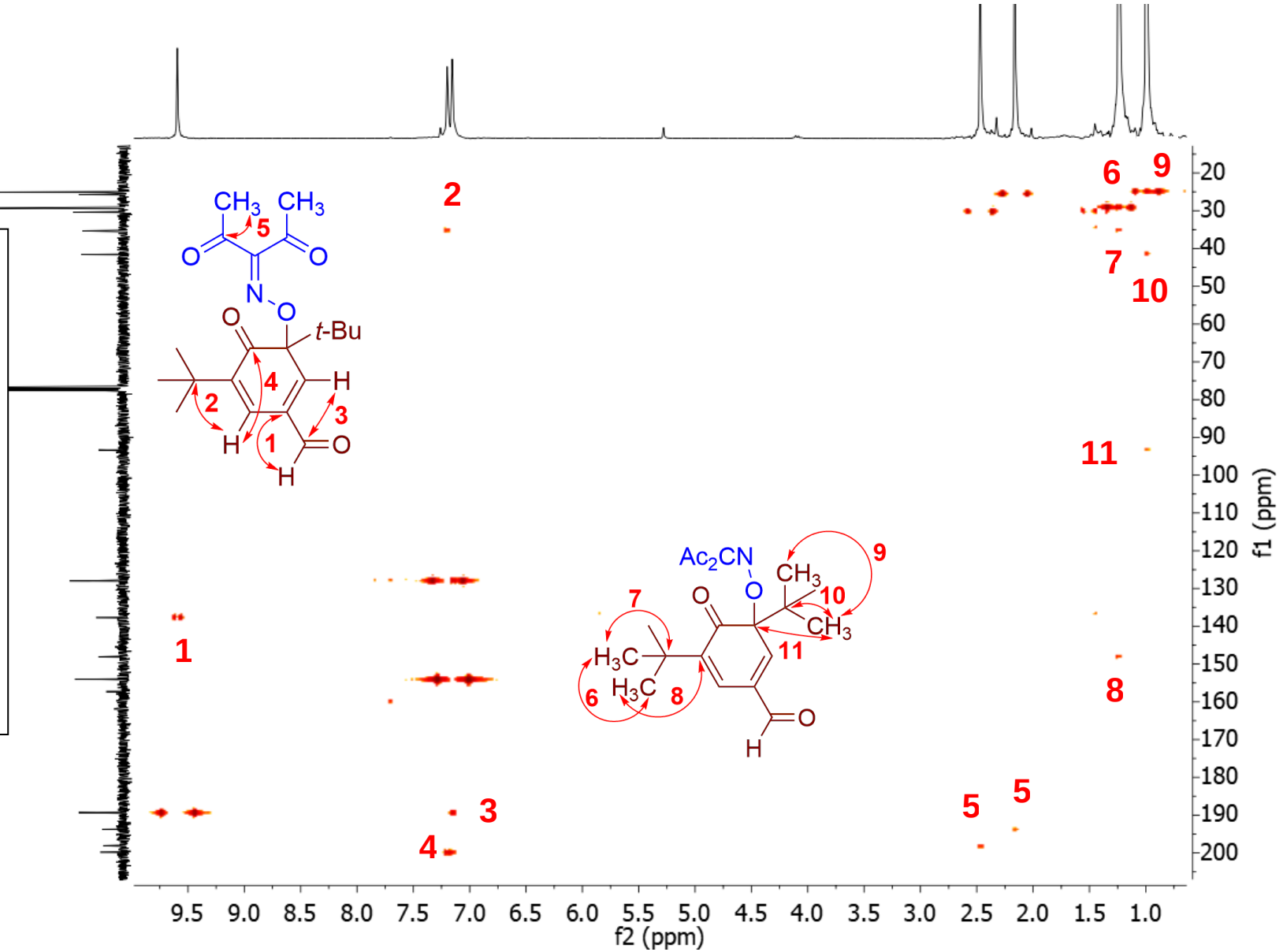


{^{1}H-^{13}C} HMBC Spectrum of 3,5-di-tert-butyl-3-(((2,4-dioxopentan-3-ylidene)amino)oxy)-4-oxocyclohexa-1,5-diene-1-carbaldehyde, 7d

{^{1}H-^{13}C} HMBC (300.13, 75.47 MHz, $CDCl_3$)

3,5-Di-tert-butyl-3-(((2,4-dioxopentan-3-ylidene)amino)oxy)-4-oxocyclohexa-1,5-diene-1-carbaldehyde, 7d

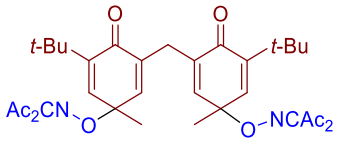


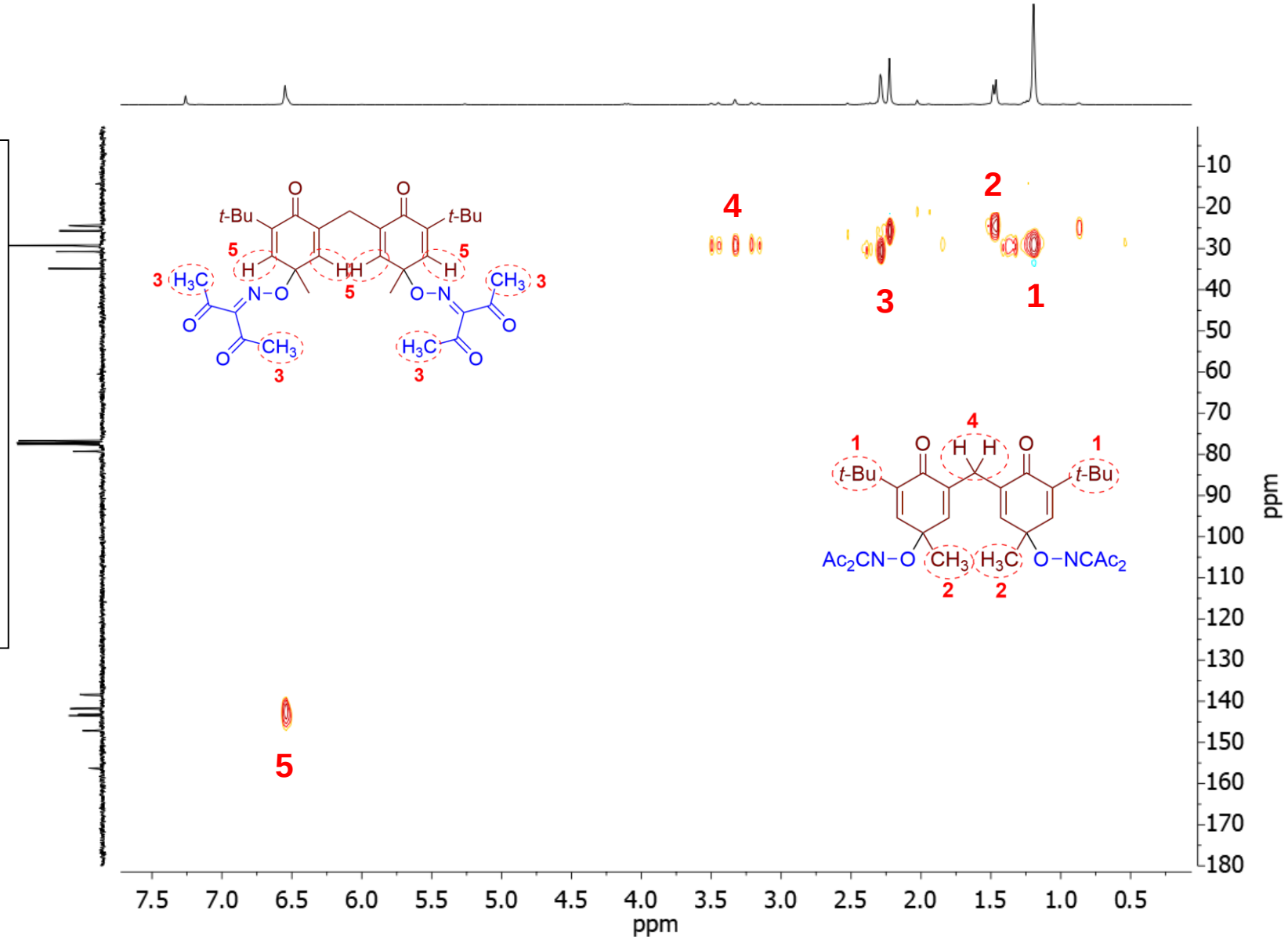


{^{1}H-^{13}C} HSQC Spectrum of 3,3'-(((methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3), 7f

{^{1}H-^{13}C} HSQC (300.13, 75.47 MHz, $CDCl_3$)

3,3'-(((methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3), 7f

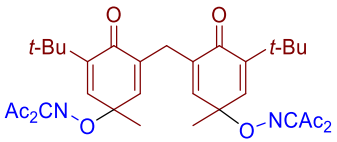


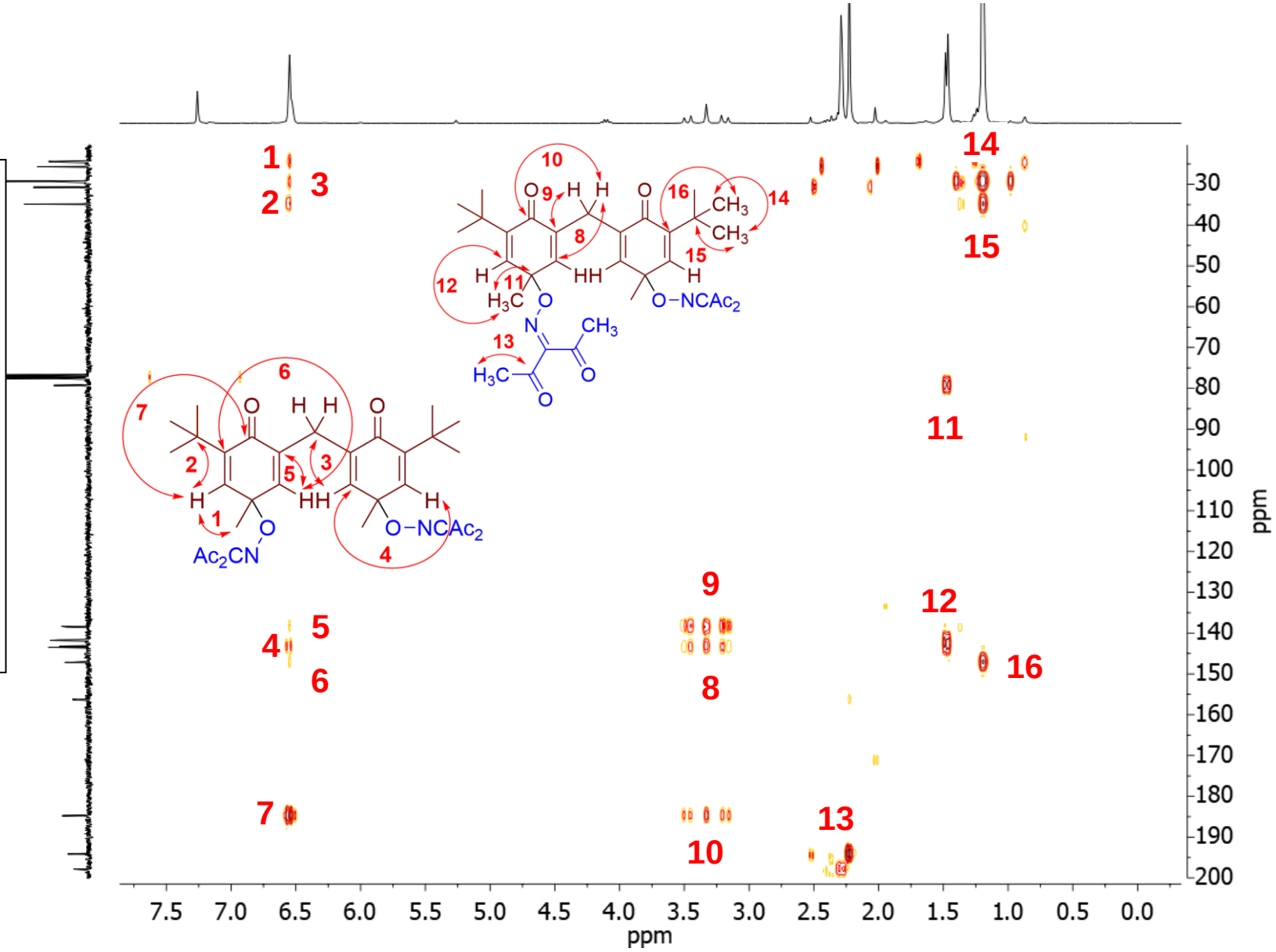


{^{1}H-^{13}C} HMBC Spectrum of 3,3'-(((methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3), 7f

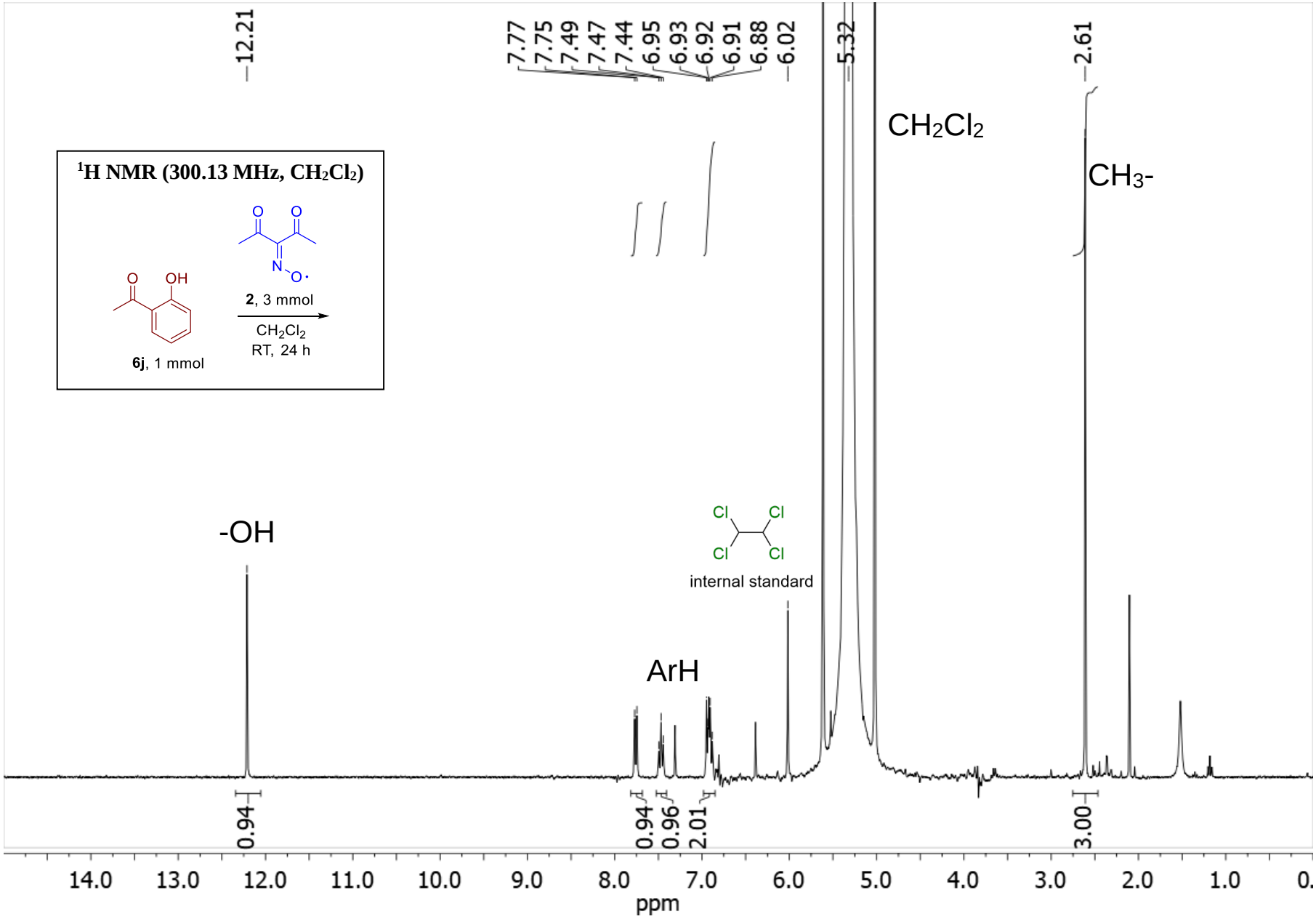
{^{1}H-^{13}C} HMBC (300.13, 75.47 MHz, $CDCl_3$)

3,3'-(((methylenebis(5-(tert-butyl)-1-methyl-4-oxocyclohexa-2,5-diene-3,1-diyl))bis(oxy))bis(azanylylidene))bis(pentane-2,4-dione) (mixture of meso and racemic diastereomers 4:3), 7f





^{1}H-NMR monitoring of reaction mixtures



^{1}H NMR (300.13 MHz, CH_2Cl_2)

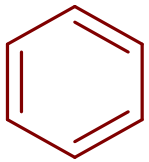
6j, 1 mmol

2, 3 mmol

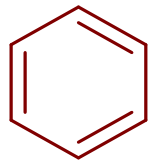
CH_2Cl_2

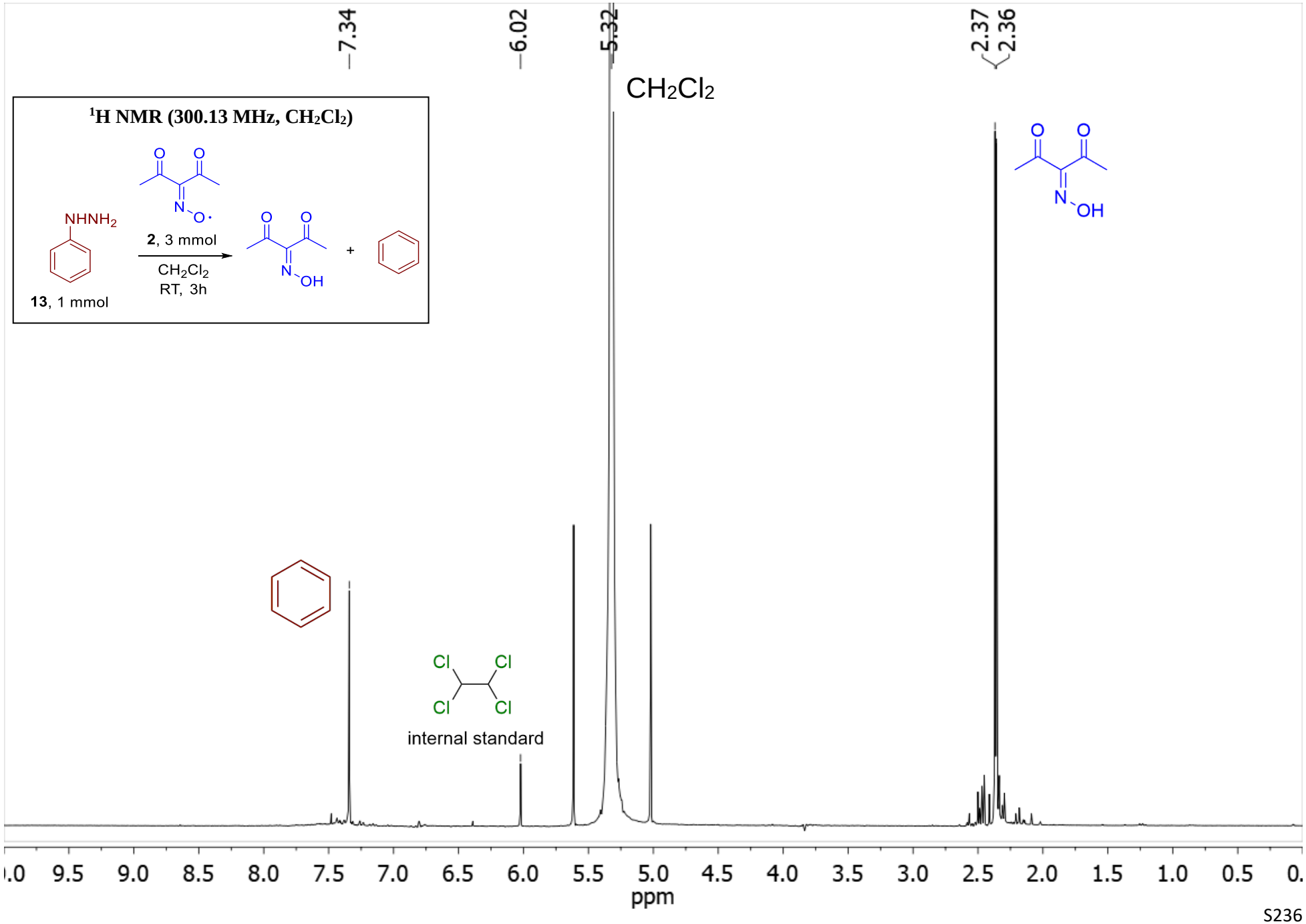
RT, 24 h

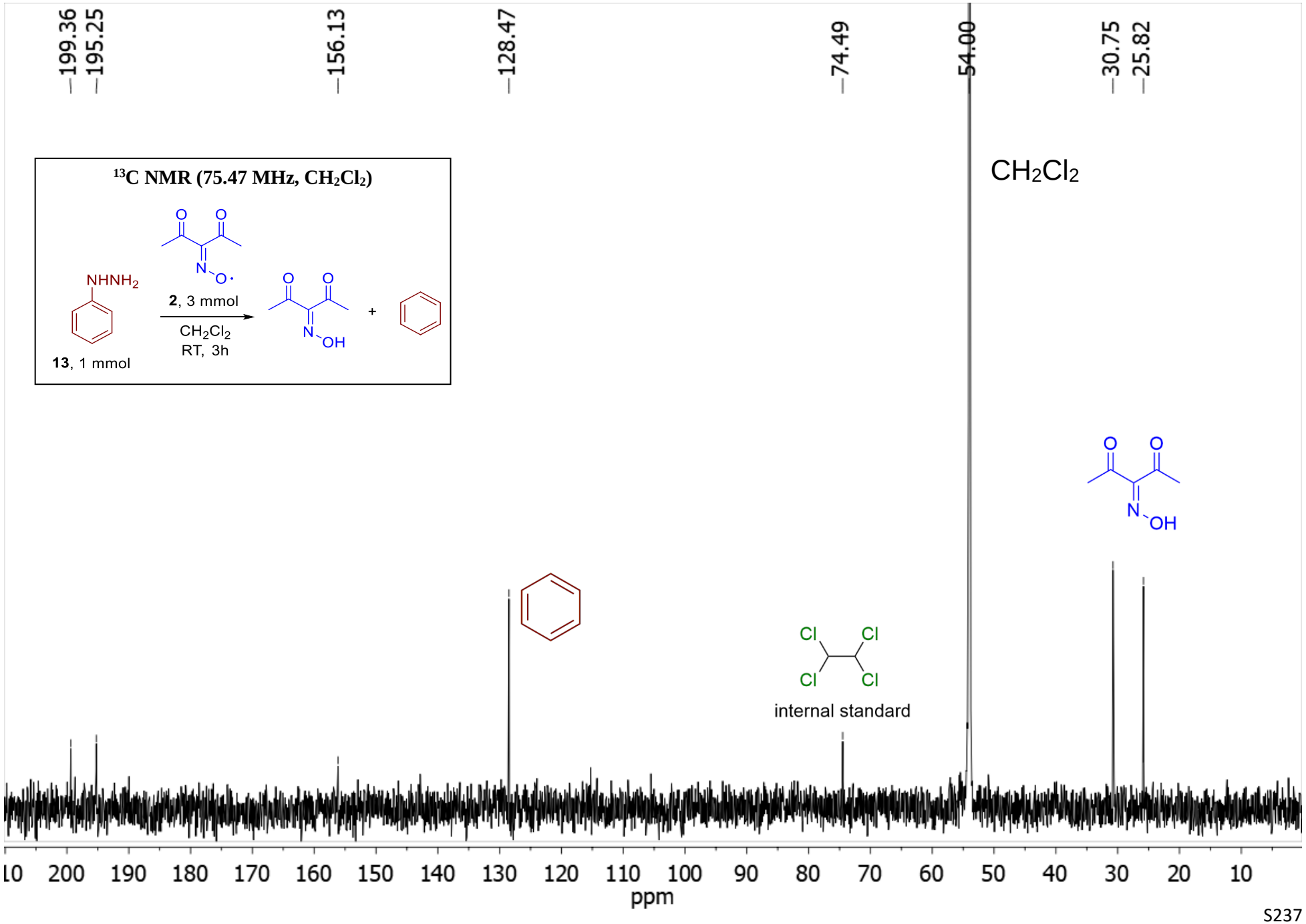
^{1}H NMR (300.13 MHz, CH_2Cl_2)



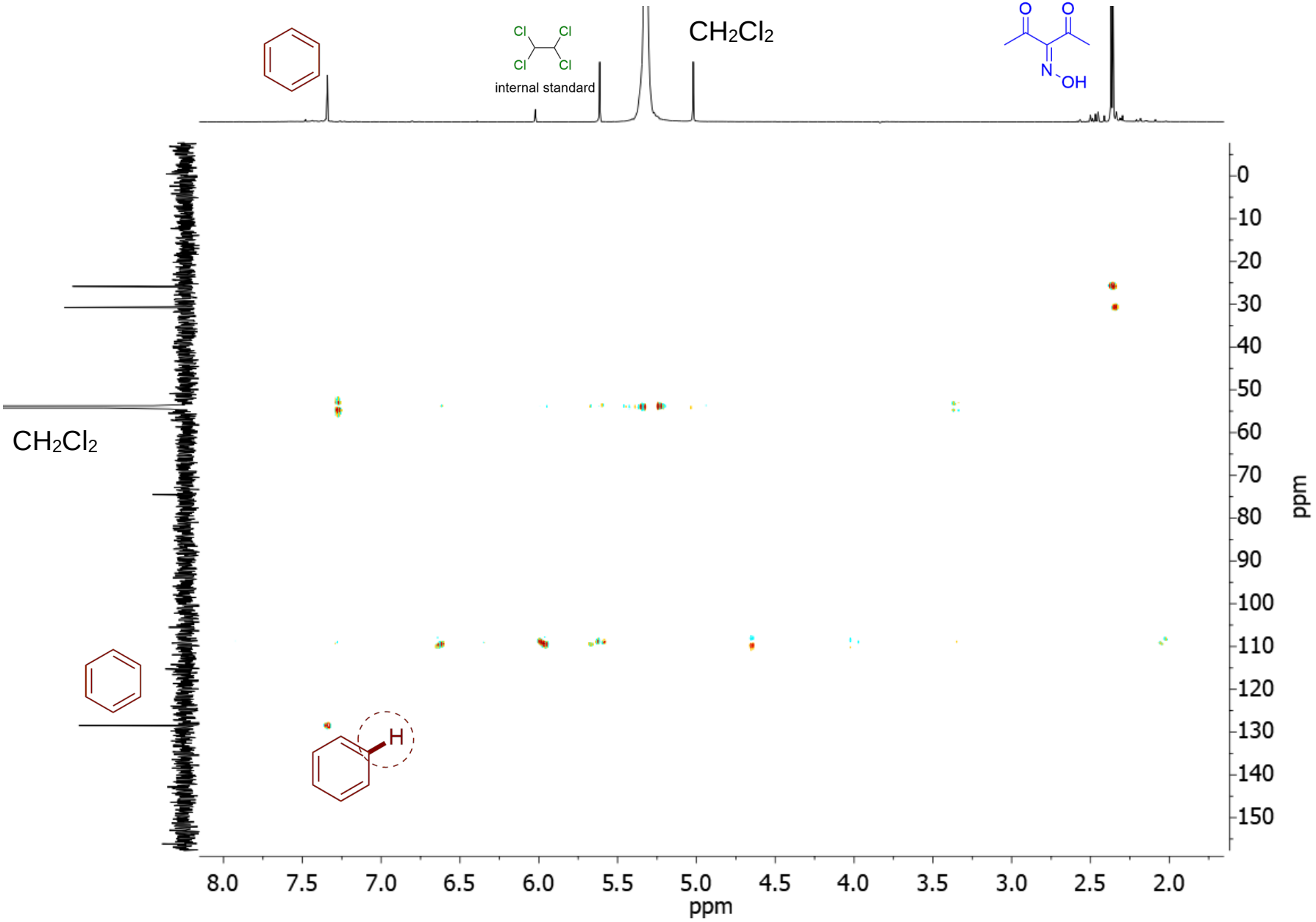
^{13}C NMR (75.47 MHz, CH_2Cl_2)

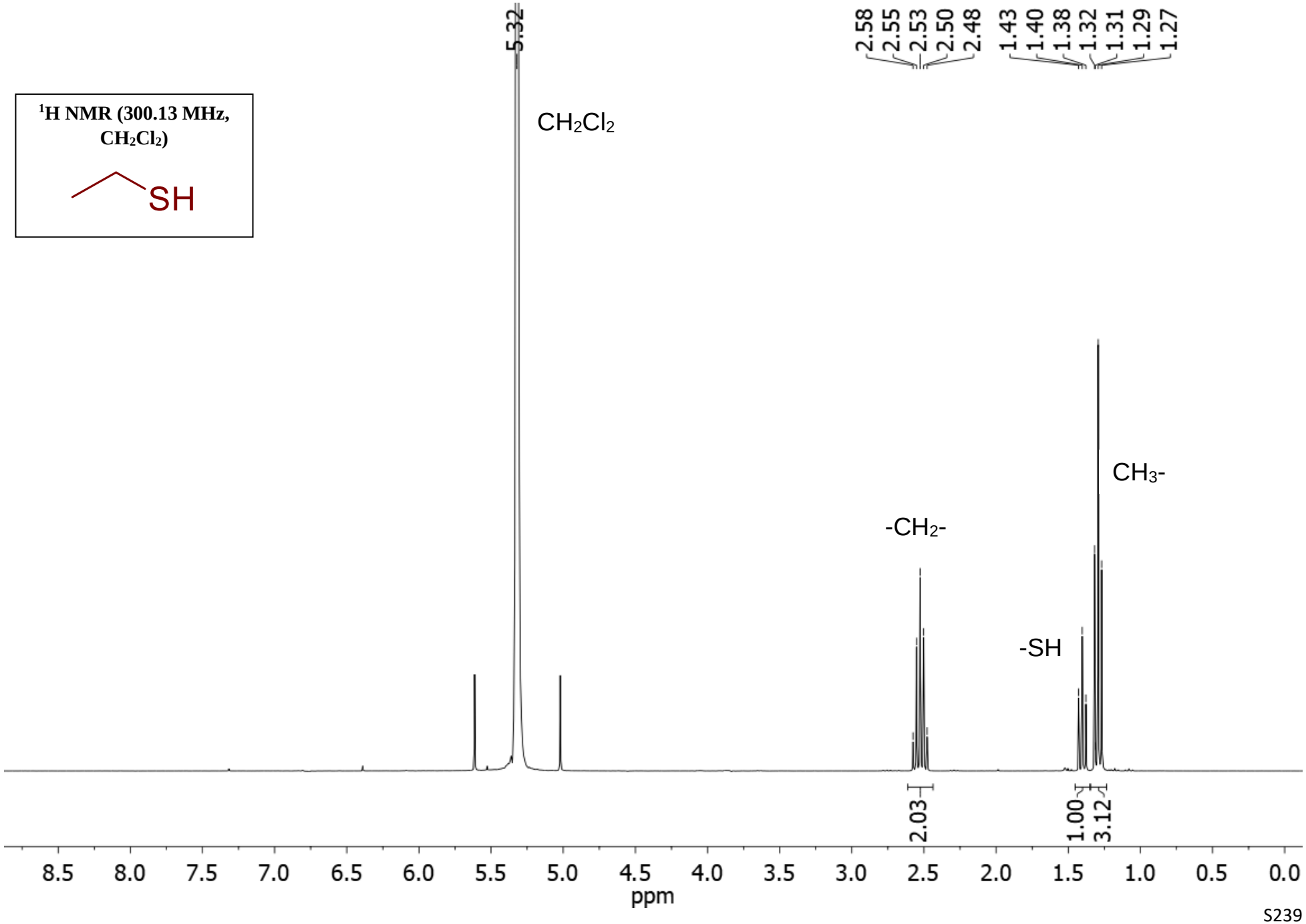


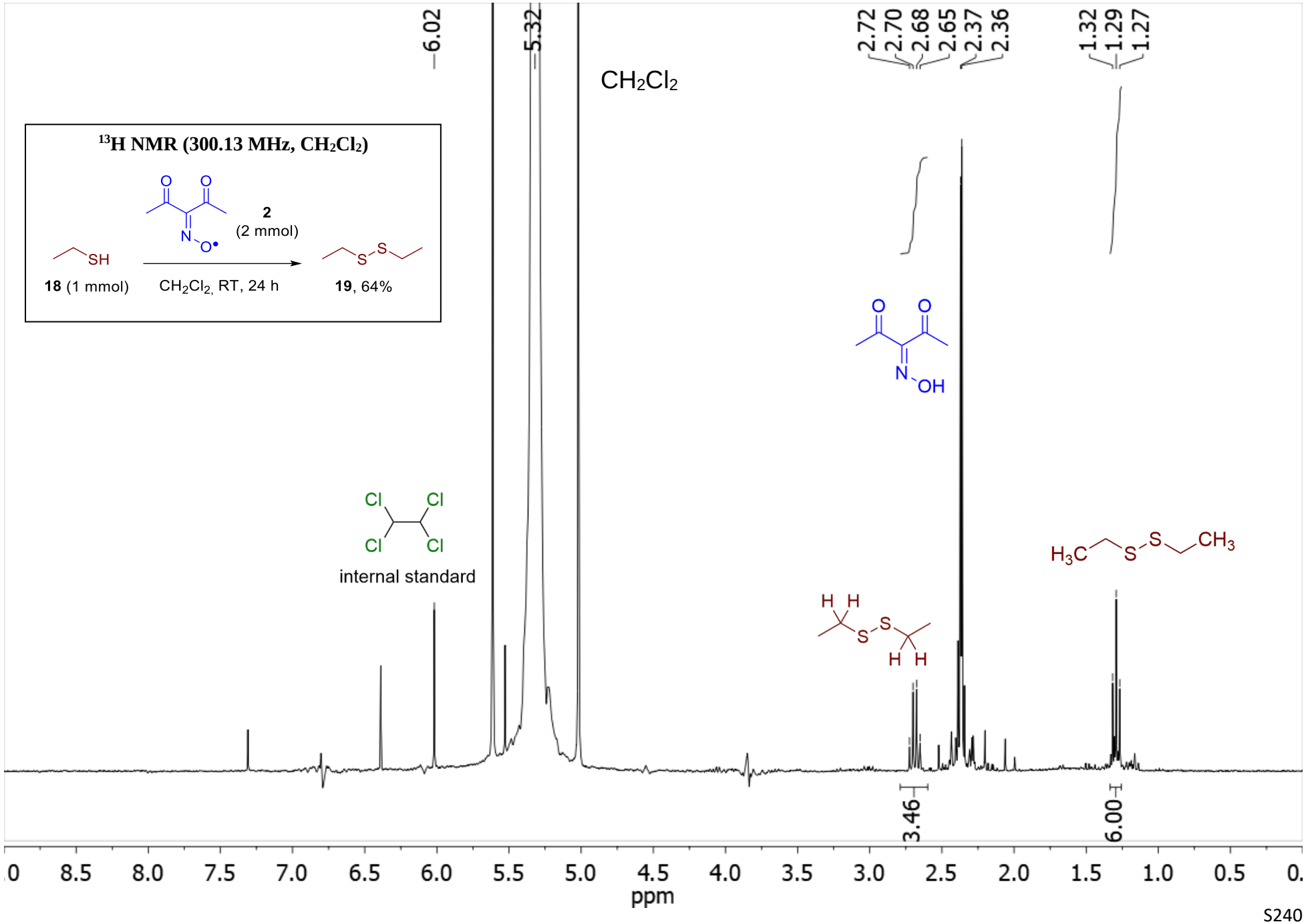

7.34
6.02
5.32
2.37
2.36
CH2Cl2
1H NMR (300.13 MHz, CH2Cl2)
NHNH2
13, 1 mmol
2, 3 mmol
CH2Cl2
RT, 3h
OH
internal standard
ppm

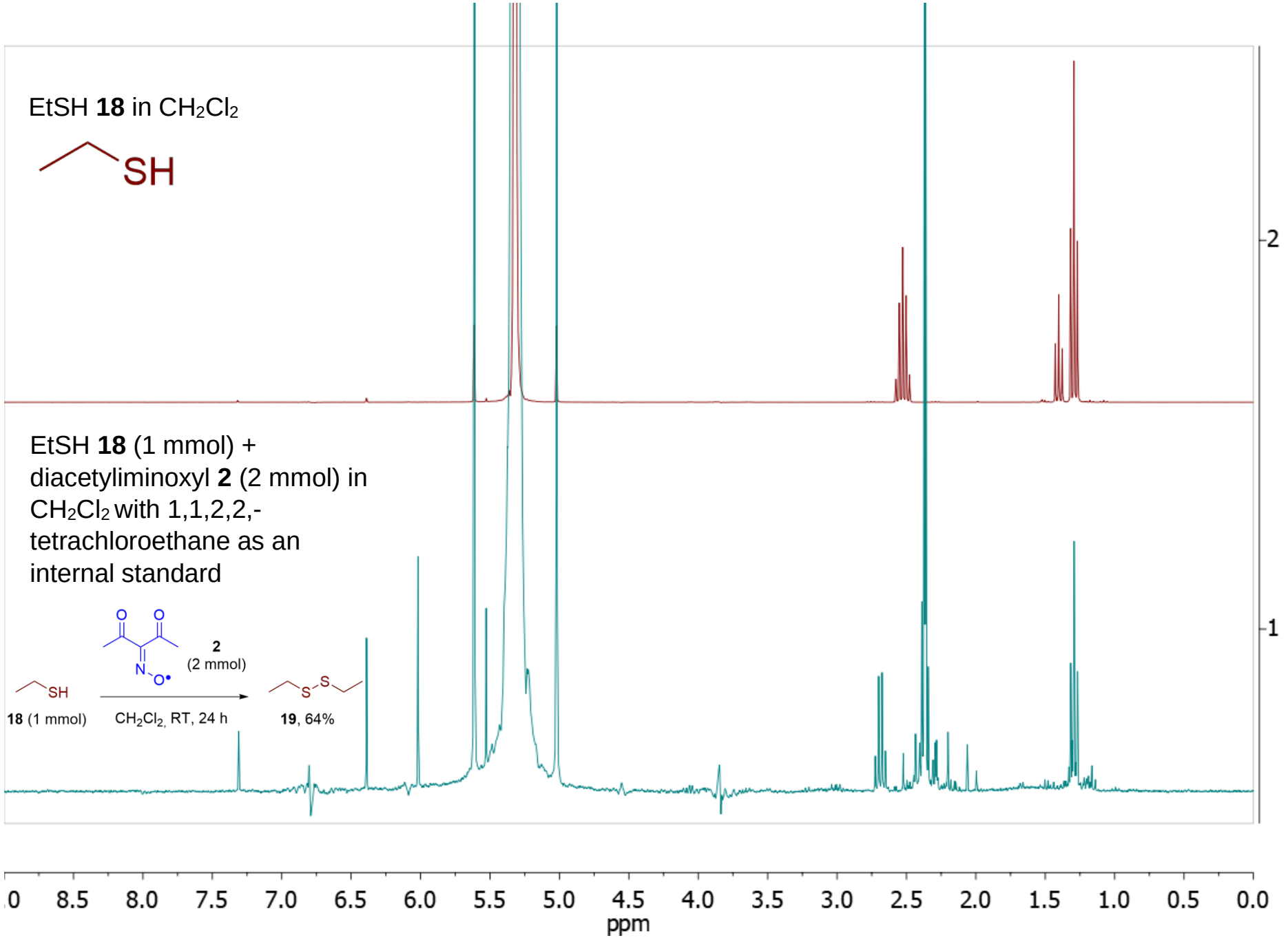

199.36
195.25
156.13
128.47
74.49
54.00
30.75
25.82
^{13}C NMR (75.47 MHz, CH_2Cl_2)
NHNH$_2$
13, 1 mmol
2, 3 mmol
CH_2Cl_2
RT, 3h
OH
+
CH_2Cl_2
internal standard
ppm

{^{1}H-^{13}C} HSQC Spectrum of crude reaction mixture of phenylhydrazine 13 with diacetyliminoxyl 2




^{1}H NMR (300.13 MHz, CH_2Cl_2)
SH
5.32
CH_2Cl_2
2.58
2.55
2.53
2.50
2.48
1.43
1.40
1.38
1.32
1.31
1.29
1.27
-CH_2-
-SH
CH_3-
2.03
1.00
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


13H NMR (300.13 MHz, CH2Cl2)
2
(2 mmol)
SH
18 (1 mmol)
CH2Cl2, RT, 24 h
19, 64%
6.02
5.32
CH2Cl2
2.72
2.70
2.68
2.65
2.37
2.36
1.32
1.29
1.27
OH
Cl
Cl
Cl
Cl
internal standard
H3C
S
S
CH3
H H
S
S
H H
3.46
6.00
ppm


EtSH **18** in CH_2Cl_2
SH
2
EtSH **18** (1 mmol) + diacetyliminoxyl **2** (2 mmol) in CH_2Cl_2 with 1,1,2,2,-tetrachloroethane as an internal standard
1
2 (2 mmol)
SH
18 (1 mmol)
CH_2Cl_2, RT, 24 h
19, 64%
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm