Supporting Information

Selective cross-dehydrogenative C-O coupling of N-hydroxy compounds with pyrazolones. Introduction of diacetyliminoxyl radical into practice of organic synthesis

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General

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE II 300 (300.1 and 75.5 MHz, respectively) spectrometers in $CDCl_3$ and DMSO-d_6.

The EPR spectra were recorded on a Bruker ER-200D spectrometer in a X-band range (ν~9300 MHz). The magnetic field strength was measured with an accuracy of ± 0.02 G using an ER 035M magnetometer built in the EPR spectrometer. The microwave frequency in the cavity was determined using a ChZ-46 frequency meter with an accuracy ± 0.1 MHz. The magnetic field modulation frequency was 100 kHz with 0.1 G modulation amplitude. 100-μL glass micropipettes equipped with a stopper at the bottom were used as ESR tubes (inner diameter 1.2 mm).

ICP-MS measurement of trace lead content in diacetyliminoxyl radical **21** solution was done on "Analytik Jena Plasma Quant MS Elite" instrument using Fluka Multielement standard solution 4 for ICP (ISO/IEC 17025 certified).

FT-IR spectra were recorded on Nicolet Magna-IR-750 and Bruker Alpha instruments with resolution 2 cm^{-1}. For the study of diacetyliminoxyl free radical **21** a liquid transmission cell was used (KBr windows, path length 0.13 cm).

X-ray structural study was fulfilled using a STOE STADI VARI PILATUS-100K diffractometer.

CH_2Cl_2 and $C_2H_4Cl_2$ were distilled prior to use. MeCN and EtOAc were distilled over P_2O_5. Glacial acetic acid was used as is from commercial sources.

Column chromatography was performed using silica gel (0.060-0.200 mm, 60 A, Acros).

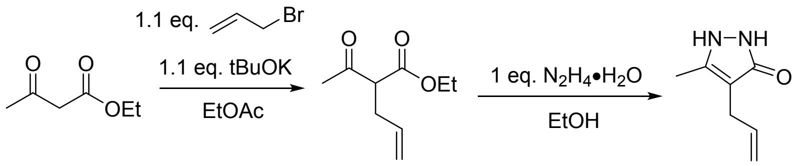
Iron(III) perchlorate hydrate reagent grade (Alfa Aesar, anhydrous basis purity ca. 65%), $Fe(NO_3)_3 \cdot 9H_2O$ 99+%, $FeCl_3$ 98% anhydrous, $(NH_4)_2Ce(NO_3)_6$ 99%, $Pb(OAc)_4$ 95%, $PhI(OAc)_2$ 98%, $Cu(ClO_4)_2 \cdot 6H_2O$ 98%, $Mn(OAc)_3 \cdot 2H_2O$ 95%, $KMnO_4$ 99%, $Co(OAc)_2 \cdot 4H_2O$ 98%, $Co(NO_3)_2 \cdot 6H_2O$ 99%, Bu_4NI 98%, *t*-BuOOH (70% aqueous solution), H_2O_2 (34% aqueous solution), N-hydroxyphthalimide 98%, N-hydroxybenzotriazole hydrate 98% (11–26% H_2O), 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) 98%, benzaldehyde 98+%, $N_2H_4 \cdot H_2O$ (64% hydrazine), 4-Butyl-1,2-diphenyl-3,5-pyrazolidinedione (Phenylbutazone) 99+% (Acros), $NH_2OH \cdot HCl$ 99%, $NaHCO_3$ 99%, Molecular sieves 4Å 8-12 Mesh Grade 514 (Fisher Scientific) were used as is from commercial sources.

The synthesis of starting materials

Pyrazoline-5-ones **1a**, **1c–g** were synthesized by condensation of β-keto esters with $N_2H_4 \cdot H_2O$ (1.5 equiv.) in ethanol at 18–23 °C for 24–48 h under air atmosphere. Pyrazoline-5-ones **1b**, **1h** and **1i** were synthesized as described below.

4-Allyl-5-methyl-1,2-dihydro-3H-pyrazol-3-one 1b

Scheme S1.

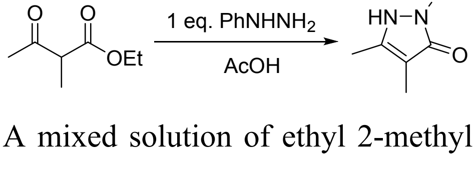


A mixed solution of ethyl 3-oxobutanoate (10.0 g, 76.9 mmol) and allylbromide (10.2 g, 84.6 mmol) in EtOAc (100 mL, distilled over P_2O_5) was cooled by ice-NaCl bath to -5 °C under argon atmosphere. Then t-BuOK (9.49 g, 84.6 mmol) was added so that the temperature did not exceed 20-25 °C; the mixture was mixed for 4 h at room temperature, then it was left for 24 h. The mixture was concentrated in a water jet vacuum, petroleum ether (50 mL) and water (50 mL) were added. The organic layer was separated, washed with water (50 mL), and dried over Na_2SO_4, evaporation in a water jet vacuum gave ethyl 2-acetylpent-4-enoate as a slightly orange oil (9.73 g, 57.2 mmol). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.81-5.59 (m, 1H, HC=), 5.16-4.95 (m, 2H, H_2C=), 4.17 (q, *J* = 7.1 Hz, 2H, OCH2), 3.49 (t, *J* = 7.4 Hz, 1H, CH), 2.65-2.49 (m, 2H, CH_2), 2.21 (s, 3H, CH_3), 1.25 (t, J = 7.1 Hz, 3H, CH_3). The obtained product was used in the second step of the synthesis without purification.

To a mixed solution of ethyl 2-acetylpent-4-enoate (9 g, 52.9 mmol) in ethanol (20 mL) cooled by ice-NaCl bath to 0 °C under argon atmosphere a solution of $N_2H_4 \bullet H_2O$ (2.65 g, 52.9 mmol) in ethanol (10 mL) was added for 5 min, the mixture was allowed to gradually warm to room temperature and was left overnight. A white precipitate of 4-allyl-5-methyl-1,2-dihydro-3H-pyrazol-3-one was filtered and dried in air (4.10 g, 29.7 mmol, yield 42% for 2 steps). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 10.28 (bs, 2H, NH), 5.91-5.70 (m, 1H, HC=), 5.02-4.83 (m, 2H, =CH_2), 2.96 (d, J = 5.5, 2H, CH_2), 2.01 (s, 3H, CH_3).

4,5-Dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one 1h

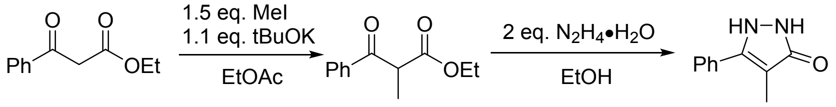
Scheme S2.



A mixed solution of ethyl 2-methyl-3-oxobutanoate (3.00 g, 20.8 mmol) in AcOH (10 mL) was cooled by ice bath until the beginning of AcOH crystallization. $PhNHNH_2$ (2.25 g, 20.8 mmol) was added dropwise for 2 min, mixing was continued for 1 h, the mixture was allowed to gradually warm to room temperature and was left overnight. The mixture was rotary evaporated under water-jet vacuum at 50-60 °C. Toluene (5 mL) was added followed by rotary evaporation at 50-60 °C three times. 4,5-Dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (3.92 g, 20.8 mmol, 100%) was obtained as slightly yellow crystals. Mp = 118-119 °C. ^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 10.5 (bs, 1H, NH), 7.78-7.68 (m, 2H, ArH), 7.48-7.36 (m, 2H, ArH), 7.24-7.12 (m, 1H, ArH), 2.09 (s, 3H, CH$_3$), 1.77 (s, 3H, CH$_3$).

4-Metyl-5-phenyl-1,2-dihydro-3H-pyrazol-3-one 1i

Scheme S3.



A mixed solution of ethyl benzoylacetate (Acros 90% tech., 5.00 g, 24.2 mmol) and MeI (5.16 g, 36.4 mmol) in EtOAc (40 mL, distilled over P_2O_5) was cooled by ice-NaCl bath to -5 °C under argon atmosphere. Then t-BuOK (2.99 g, 26.6 mmol) was added so that the temperature did not exceed 20-25 °C; the mixture was stirred for 4 h at room temperature, then it was left for 72 h. Petroleum ether (50 mL) and water (50 mL) were added, organic layer was separated, washed with water (30 mL), and dried over Na_2SO_4, evaporation in a water jet vacuum gave ethyl 2-methyl-3-oxo-3-phenylpropanoate (5.19 g) as a slightly yellow oil, ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.03-7.93 (m, 2H, ArH), 7.64-7.53 (m, 1H, ArH), 7.53-7.41 (m, 2H, ArH), 4.37 (q, J = 7.1 Hz, 1H, CHMe), 4.14 (q, J = 7.1 Hz, 2H, OCH$_2$Me), 1.49 (d, J = 7.1 Hz, 3H, CH$_3$), 1.16 (t, J = 7.1 Hz, 3H, CH$_3$). The obtained product was used in the second step of the synthesis without purification.

To a mixed solution of ethyl 2-methyl-3-oxo-3-phenylpropanoate (5 g, 24.2 mmol) in ethanol (25 mL) cooled by ice-NaCl bath to 0 °C $N_2H_4 \bullet H_2O$ (2.43 g, 48.5 mmol) was added for 1 min, the solution was allowed to gradually warm to room temperature and was left overnight. The mixture was rotary evaporated under water-jet vacuum giving yellow sticky solid. Et_2O (20 mL) was added, solid was grinded, the mixture was treated in an ultrasonic bath, the precipitate was filtered, washed with Et_2O (10 mL) and air dried. 4-Methyl-5-phenyl-1,2-dihydro-3H-pyrazol-3-one (3.12 g, 17.9 mmol, yield 77% for two steps) was obtained as yellow powder. ^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 9.63 (bs, 2H, NH), 7.57-7.50 (m, 2H, ArH), 7.49-7.40 (m, 2H, ArH), 7.38-7.29 (m, 1H, ArH), 1.99 (s, 3H, CH$_3$).

Oximes **2b**,[1] **2c**,[1] **2d**,[2] **2e**,[3] **2f**,[4] **2g**[5] were synthesized according to the reported procedures.

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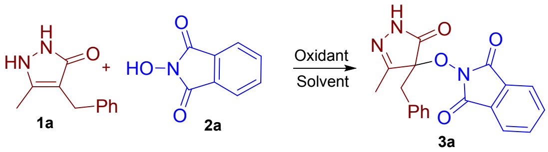
Optimization of oxidative C-O coupling of pyrazolin-5-one 1a and NHPI 2a (Full table 1 and experimental details)

Table S1.



Run	Oxidant (mole per mole of **1a**)	Solvent	t, °C	Time, min	Yield **3a**, %
1	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	60	5	90
2	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	60	10	90
3	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	rt	20	72
4	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	80	10	80
5	$Fe(NO_3)_3$•$9H_2O$ (2)	MeCN	60	20	<5
6	$FeCl_3$ (2)	$C_2H_4Cl_2$	60	20	<5
7	$FeCl_3$ (2)	MeCN	60	20	15
8	$(NH_4)_2Ce(NO_3)_6$ (2)	MeCN	60	10	87
9	$(NH_4)_2Ce(NO_3)_6$ (2)	MeCN	rt	20	87
10	$Pb(OAc)_4$ (1)	MeCN	60	20	84
11	$PhI(OAc)_2$ (1)	MeCN	60	20	69
12	$PhI(OAc)_2$ (1)	AcOH	60	20	38

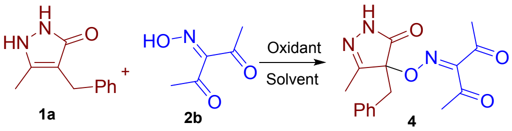
13	$Cu(ClO_4)_2•6H_2O$ (2)	MeCN	60	20	24
14	$Mn(OAc)_3•2H_2O$ (2)	AcOH	60	20	9
15	$KMnO_4$ (0.4)	AcOH	60	20	35
16	$Mn(OAc)_3•2H_2O$ (2)	MeCN	60	20	6
17	$Fe(ClO_4)_3•nH_2O$ (0.1); O_2	MeCN	60	10	5
18	$Co(OAc)_2•4H_2O$ (0.05); H_2O_2 34% aq. (1)	AcOH	60	20	9
19	$Co(NO_3)_2•6H_2O$ (0.05); O_2	MeCN	60	20	<5
20	Bu_4NI (0.2); *t*-BuOOH 70% aq. (1)	MeCN	60	20	<5

General reaction conditions: To a stirred at given temperature mixture of 4-benzyl-3-methylpyrazolin-5-one **1a** (150 mg, 0.797 mmol), N-hydroxyphthalimide **2a** (130 mg, 0.797 mmol) and solvent (5 mL) an oxidant (9.9–874 mg, 0.05-2 mole per mole of **1a**) was added for 5-20 seconds; stirring was continued at the same temperature for the given time. In the runs 18 and 20, $Co(OAc)_2•4H_2O$ (9.9 mg, 0.0399 mmol) or Bu_4NI (58.9 mg, 0.159 mmol) was added first, after 30 seconds 34%aq. H_2O_2 (79.7 mg, 0.797 mmol) or 70%aq. *t*-BuOOH (103 mg, 0.797 mmol) was added for 30 seconds; stirring was continued at the same temperature for 20 min. In the runs 17 and 19 after addition of $Fe(ClO_4)_3•nH_2O$ (43.4 mg, 0.0797 mmol) or $Co(NO_3)_2•6H_2O$ (11.6 mg, 0.0399 mmol) oxygen gas was bubbled through the mixture (0.3 mL/sec.) until the end of the synthesis.

Reaction mixture was cooled to the room temperature, diluted with CH_2Cl_2 (10 mL) and water (20 mL) and shaken. Organic layer was separated and aqueous was extracted with CH_2Cl_2 (2×10 mL), all organic extracts were combined. In case of intensive color of extract indicative of presence of metal complexes, it was additionally washed with aqueous solution of $Na_2S_2O_4$ (200 mg in 20 mL of water). Organic extract was washed with water (2×20 mL), dried over Na_2SO_4, rotary evaporated under water-jet vacuum. C-O coupling product **3a** was isolated by column chromatography on silica gel using $EtOAc/CH_2Cl_2$ eluent; volume part of EtOAc was gradually increased from 0 to 20%.

Optimization of oxidative C-O coupling of pyrazolin-5-one 1a and diacetyl oxime 2b (experimental details for the scheme 4)

Table S2.



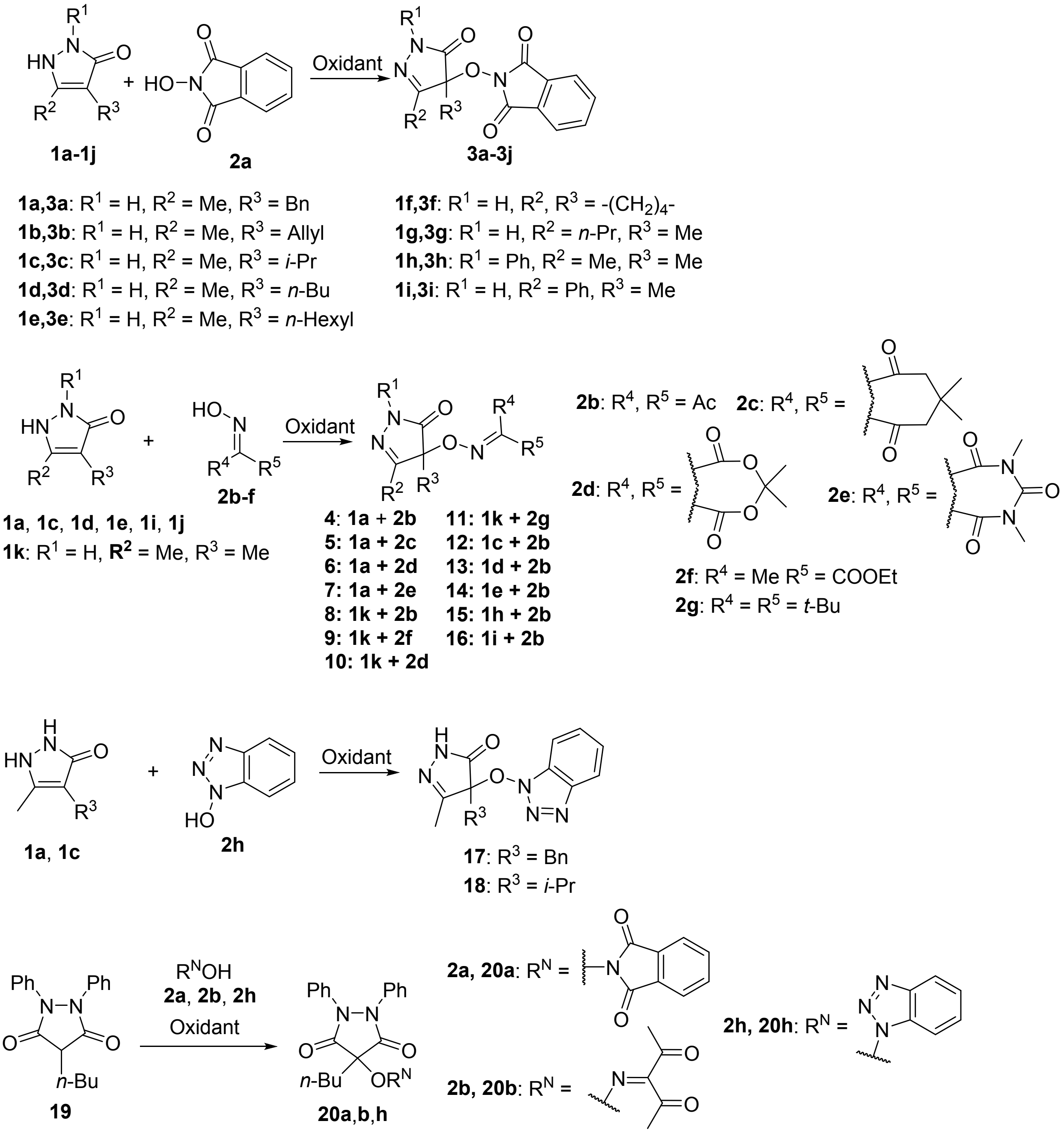
Run	Oxidant (mole per mole of **1a**)	Solvent	t, °C	Time, min.	Yield **4**, %
1	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	60	10	91
2	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	60	60	90
3	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	rt	20	90
4	$Fe(ClO_4)_3$•nH_2O (2)	MeCN	rt	5	69
5	$Fe(ClO_4)_3$•nH_2O (2)	5 mL MeCN 0.25 mL H_2O	60	10	81
6	$KMnO_4$ (0.4)	AcOH	60	10	85
7	$KMnO_4$ (0.4)	AcOH	rt	5	69
8	$Mn(OAc)_3$•$2H_2O$ (2)	AcOH	60	10	52
9	$Mn(OAc)_3$•$2H_2O$ (2)	MeCN	60	60	20
10	$Cu(ClO_4)_2$•$6H_2O$ (2)	MeCN	60	10	36
11	$(NH_4)_2Ce(NO_3)_6$ (2)	MeCN	60	10	24
12	$Pb(OAc)_4$ (1)	MeCN	60	10	43
13	$PhI(OAc)_2$ (1)	MeCN	60	10	30
14	$Cu(ClO_4)_2$•$6H_2O$ (0.05) *t*-BuOOH 70% aq. (1)	MeCN	60	10	<5

General reaction conditions: To a stirred at given temperature mixture of 4-benzyl-3-methylpyrazolin-5-one **1a** (150 mg, 0.797 mmol), 3-(hydroxyimino)-2,4-pentanedione **2b** (103 mg, 0.797 mmol) and solvent (5 mL) an oxidant (14.8–874 mg, 0.05–2 mole / mole **1a**) was added for 5-20 seconds; stirring was continued at the same temperature for the given time. In the run 12, $Cu(ClO_4)_2$•$6H_2O$ (14.8 mg, 0.0399 mmol) was added first, after 30 seconds 70% aq. *t*-BuOOH (103 mg, 0.797 mmol) was added for 30 seconds, stirring was continued at the same temperature for 10 min.

The coupling product **4** was isolated as described above for **3a**.

Oxidative C-O coupling of pyrazolin-5-ones 1a-1i and pyrazolidin-3,5-dione 19 with N-hydroxycompounds 2a-2h (experimental details for the table 2 and scheme 5)

Scheme S4.



1a-1j **2a** **3a-3j**

1a,3a: R^1 = H, R^2 = Me, R^3 = Bn
1b,3b: R^1 = H, R^2 = Me, R^3 = Allyl
1c,3c: R^1 = H, R^2 = Me, R^3 = *i*-Pr
1d,3d: R^1 = H, R^2 = Me, R^3 = *n*-Bu
1e,3e: R^1 = H, R^2 = Me, R^3 = *n*-Hexyl
1f,3f: R^1 = H, R^2, R^3 = $-(CH_2)_4-$
1g,3g: R^1 = H, R^2 = *n*-Pr, R^3 = Me
1h,3h: R^1 = Ph, R^2 = Me, R^3 = Me
1i,3i: R^1 = H, R^2 = Ph, R^3 = Me

1a, **1c**, **1d**, **1e**, **1i**, **1j**
1k: R^1 = H, $\mathbf{R^2}$ = Me, R^3 = Me

2b-f

4: **1a** + **2b**
5: 1a + 2c
6: 1a + 2d
7: 1a + 2e
8: 1k + 2b
9: 1k + 2f
10: 1k + 2d
11: 1k + 2g
12: 1c + 2b
13: 1d + 2b
14: 1e + 2b
15: 1h + 2b
16: 1i + 2b

2b: R^4, R^5 = Ac **2c**: R^4, R^5 =
2d: R^4, R^5 =
2e: R^4, R^5 =
2f: R^4 = Me R^5 = COOEt
2g: R^4 = R^5 = *t*-Bu

1a, **1c** **2h**

17: R^3 = Bn
18: R^3 = *i*-Pr

19 **20a**,**b**,**h**

2a, 20a: R^N =
2b, 20b: R^N =
2h, 20h: R^N =

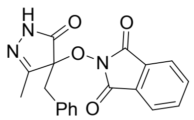
General procedure *a* (all experiments on the scheme 5 and experiments in table 2 with note[a]): to a stirred at 60 °C mixture of pyrazolone (1.5 mmol), N-hydroxycompound (1.5 mmol) and MeCN (5 mL) $Fe(ClO_4)_4 \cdot nH_2O$ (3 mmol) was added; stirring was continued for 10 min at 60 °C.

General procedure *b* (experiments in table 2 with note[b]): to a stirred at room temperature mixture of pyrazolone (1.5 mmol), N-hydroxycompound (1.5 mmol) and MeCN (5 mL) $(NH_4)_2Ce(NO_3)_6$ (3 mmol) was added; stirring was continued for 20 min at room temperature.

General procedure *c* (experiments in table 2 with note[c]): to a stirred at room temperature mixture of N-hydroxyphthalimide (1.5 mmol) and MeCN (5 mL) $(NH_4)_2Ce(NO_3)_6$ (3 mmol) was added for 5-10 seconds, stirring was continued for 4 min, then pyrazolone (1.5 mmol) was added portion wise for 7-10 min; after the complete addition of pyrazolone, stirring was continued for 5 min at room temperature.

General procedure *d* (experiments in table 2 with note[d]): to a stirred at 60 °C mixture of N-hydroxyphthalimide (1.5 mmol) and MeCN (5 mL) $Fe(ClO_4)_4 \cdot nH_2O$ (3 mmol) was added for 5-10 seconds, then pyrazolone (1.5 mmol) was added portion wise for 1 min; stirring was continued for 5 min at 60 °C.

The products **3a-i**, **4-18**, **20a,b,h** were isolated as described for **3a** in experiment for table 1.



4-Benzyl-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3a

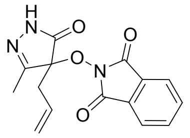
White powder. Mp = 176-177 °C dec.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 8.18 (bs, 1H), 7.93-7.82 (m, 2H), 7.82-7.72 (m, 2H), 7.32-7.15 (m, 5H), 3.55 (d, J = 13.1 Hz, 1H), 3.43 (d, J = 13.1 Hz, 1H), 2.27 (s, 3H)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 171.0, 163.8, 157.5, 135.0, 131.2, 130.0, 128.9, 128.8, 127.9, 124.1, 87.8, 38.3, 14.7.

IR (KBr): ν_{max} = 3200, 3108, 1802, 1751, 1370, 1359, 1342, 1309, 1187, 1070, 1015, 1002, 952, 872, 745, 700, 566, 558, 520 cm^{-1}

elemental analysis calcd. (%) for $C_{19}H_{15}N_3O_4$: C, 65.32; H, 4.33; N, 12.03. found: C, 65.14; H, 4.31; N, 11.94.



4-Allyl-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3b

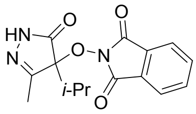
White powder. Mp = 154-155 °C dec.

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.29 (bs, 1H), 7.89 (m, 4H), 5.56-5.33 (m, 1H), 5.25 (d, *J* = 16.7 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 2.87 (dd, J_1 = 7.0 Hz, J_2 = 12.9 Hz, 1H), 2.74 (dd, J_1 = 7.0 Hz, J_2 = 12.9 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 170.4, 163.3, 155.9, 135.2, 128.3, 123.6, 121.4, 86.1, 35.6, 13.8.

IR (KBr): ν_{max} = 3374, 1795, 1750, 1732, 1367, 1350, 1308, 875, 711, 700 cm^{-1}

HR-MS (ESI): *m*/*z* = 322.0786, calcd. for $C_{15}H_{13}N_3O_4$+Na$^+$: 322.0798



4-(Isopropyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3c

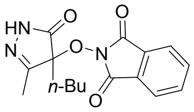
White powder. Mp = 188-188.5 °C dec.

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.15 (bs, 1H), 7.87 (m, 4H), 2.43-2.22 (m, 1H), 2.13 (s, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 170.4, 163.0, 156.7, 135.2, 128.1, 123.5, 90.3, 31.1, 15.9, 14.62, 14.57

IR (KBr): ν_{max} = 3297, 1796, 1748, 1731, 1467, 1375, 1349, 1188, 1055, 992, 874, 708 cm^{-1}

elemental analysis calcd. (%) for $C_{15}H_{15}N_3O_4$: C, 59.80; H, 5.02; N, 13.95. found: C, 59.51; H, 5.09; N, 14.07.



4-(Butyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3d

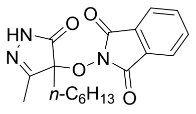
White powder. Mp = 168-168.5 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.48 (bs, 1H), 7.88-7.78 (m, 2H), 7.78-7.70 (m, 2H), 2.25-2.11 (m, 1H), 2.22 (s, 3H), 2.03 (td, J_t = 12.5, J_d = 4.9, 1H), 1.45-1.26 (m, 2H), 1.26-0.98 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 171.4, 163.8, 158.3, 134.9, 129.0, 124.0, 87.8, 31.4, 24.4, 22.7, 14.0, 13.8

IR (KBr): ν_{max} = 3303, 1794, 1752, 1467, 1377, 1351, 1314, 1188, 1017, 1001, 944, 876, 707, 650, 630, 606, 562, 520 cm^{-1}

elemental analysis calcd. (%) for $C_{16}H_{17}N_3O_4$: C, 60.94; H, 5.43; N, 13.33. found: C, 60.93; H, 5.40; N, 13.18.



4-(Hexyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3e

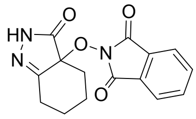
White powder. Mp = 121-122 °C

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.27 (bs, 1H), 7.88 (m, 4H), 2.10 (s, 3H), 2.04-1.91 (m, 2H), 1.38-1.13 (m, 6H), 1.13-0.91 (m, 2H), 0.84 (t, J = 6.4 Hz, 3H)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 170.9, 163.3, 156.5, 135.1, 128.3, 123.5, 87.2, 30.9, 30.8, 28.4, 21.8, 21.7, 13.8, 13.5

IR (KBr): ν_{max} = 3219, 2961, 2929, 1799, 1740, 1468, 1456, 1439, 1363, 1346, 1303, 1188, 1075, 1016, 994, 939, 874, 753, 707, 563, 521 cm^{-1}

HR-MS (ESI): *m*/*z* = 366.1417, calcd. for $C_{18}H_{21}N_3O_4$+Na$^+$: 366.1424



2-((3-Oxo-2,3,4,5,6,7-hexahydro-3aH-indazol-3a-yl)oxy)isoindoline-1,3-dione 3f

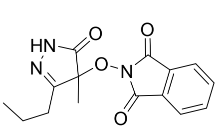
White powder. Mp = 180-182 °C dec.

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.25 (bs, 1H), 7.87 (m, 4H), 2.73-2.40 (m, 2H), 2.40-2.20 (m, 1H), 2.17-1.90 (m, 2H), 1.81-1.62 (m, 1H), 1.62-1.25 (m, 2H)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 171.6, 163.3, 159.0, 135.2, 128.3, 123.6, 82.8, 32.5, 27.3, 27.0, 19.7

IR (KBr): ν_{max} = 3187, 1796, 1739, 1713, 1363, 1347, 1308, 1187, 1104, 1015, 1000, 956, 875, 791, 748, 705. 676, 606, 563, 521 cm^{-1}

HR-MS (ESI): *m*/*z* = 300.0988, calcd. for $C_{15}H_{13}N_3O_4$+H$^+$: 300.0979



2-((4-methyl-5-oxo-3-propyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)isoindoline-1,3-dione 3g

White powder.

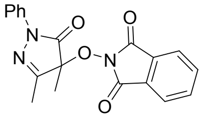
Mp = 156.5-157.5 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.61 (bs, 1H), 7.94-7.64 (m, 4H), 2.77-2.61 (m, 1H), 2.51-2.35 (m, 1H), 1.85-1.68 (m, 2H), 1.65 (s, 3H), 1.03 (t, J = 7.4 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 172.2, 163.9, 161.6, 134.9, 129.0, 124.0, 84.3, 29.7, 18.6, 18.1, 14.0

IR (KBr): ν_{max} = 3270, 1795, 1742, 1709, 1468, 1368, 1355, 1311, 1187, 1162, 1109, 1076, 975, 874, 752, 702, 671, 650, 607, 588, 565, 520 cm^{-1}

elemental analysis calcd. (%) for $C_{15}H_{15}N_3O_4$: C, 59.80; H, 5.02; N, 13.95. found: C, 59.83; H, 4.93; N, 13.90.



3,4-dimethyl-1-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3h

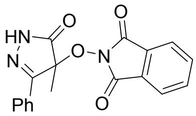
White powder. Mp = 133-136 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 7.91-7.78 (m, 4H), 7.78-7.68 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 2.37 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 168.0, 163.9, 158.5, 137.6, 134.9, 129.0, 125.5, 124.1, 118.9, 86.6, 18.4, 13.7

IR (KBr): ν_{max} = 1792, 1747, 1720, 1595, 1499, 1465, 1399, 1364, 1311, 1186, 1146, 1121, 1080, 1065, 962, 876, 763, 751, 704, 690, 573, 519 cm^{-1}

HR-MS (ESI): *m*/*z* = 372.0942, calcd. for $C_{19}H_{15}N_3O_4+Na^+$: 372.0955



4-Methyl-3-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3i

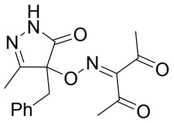
White powder. Mp = 206-208 °C dec.

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.91 (bs, 1H), 8.09-7.94 (m, 2H), 7.94-7.79 (m, 4H), 7.62-7.39 (m, 3H), 1.75 (s, 3H, CH$_3$)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 171.8, 163.4, 154.7, 135.1, 130.3, 129.5, 128.8, 128.4, 126.1, 123.5, 83.7, 19.3

IR (KBr): ν_{max} = 3281, 1743, 1733, 1720, 1372, 1362, 1349, 1188, 1083, 970, 876, 771, 696, 649, 520 cm^{-1}

HR-MS (ESI): *m*/*z* = 358.0794, calcd. for $C_{18}H_{13}N_3O_4+Na^+$: 358.0798



3-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 4

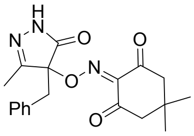
White powder. Mp = 139-140 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.26 (bs, 1H), 7.35-7.22 (m, 3H), 7.22-7.09 (m, 2H), 3.26 (d, J = 13.4 Hz, 1H), 3.17 (d, J = 13.4 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 2.00 (s, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 197.0, 193.5, 173.4, 158.7, 158.3, 131.0, 130.0, 128.8, 128.1, 87.3, 38.0, 30.7, 25.9, 14.1

IR (KBr): ν_{max} = 3178, 3114, 1734, 1692, 1366, 1298, 1049, 1017, 1009, 942, 755, 700 cm^{-1}

elemental analysis calcd. (%) for $C_{16}H_{17}N_3O_4$: C, 60.94; H, 5.43; N, 13.33. found: C, 60.91; H, 5.39; N, 13.41.



2-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-5,5-dimethylcyclohexane-1,3-dione 5

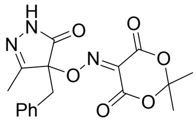
Slightly yellow powder. Mp = 145-147 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.22 (s, 1H), 7.29 (m, 5H), 3.44-3.09 (m, 2H), 2.92-2.43 (m, 4H), 1.95 (s, 3H), 1.18 (s, 3H), 1.06 (s, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 192.4, 190.3, 173.8, 158.9, 151.2, 131.6, 130.2, 128.7, 127.9, 88.3, 55.2, 54.3, 38.2, 30.5, 29.6, 27.7, 14.3

IR (KBr): ν_{max} = 3356, 3321, 1735, 1693, 1620, 1570, 1255, 1213, 1030, 1006, 989, 957, 758, 730, 699, 632, 598, 578, 571, 555 cm^{-1}

elemental analysis calcd. (%) for $C_{19}H_{21}N_3O_4$: C, 64.21; H, 5.96; N, 11.82. found: C, 63.98; H, 5.78; N, 11.72.



5-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-2,2-dimethyl-1,3-dioxane-4,6-dione 6

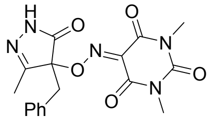
Slightly yellow powder. Mp = 150-152 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.27 (bs, 1H), 7.40-7.15 (m, 5H), 3.49-3.28 (m, 2H), 1.98 (s, 3H), 1.83 (s, 3H), 1.80 (s, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 172.9, 157.9, 155.8, 150.7, 136.7, 131.0, 130.2, 128.8, 128.2, 116.7, 106.5, 89.5, 38.0, 28.8, 27.7, 14.3

IR (KBr): ν_{max} = 3231, 1782, 1756, 1730, 1577, 1395, 1385, 1301, 1268, 1240, 1227, 1201, 1085, 1044, 1020, 976, 932, 891, 758, 729, 702 cm^{-1}

elemental analysis calcd. (%) for $C_{17}H_{17}N_3O_6$: C, 56.82; H, 4.77; N, 11.69. found: C, 56.71; H, 4.70; N, 11.59.



5-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione 7

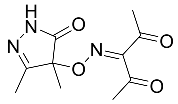
White powder. Mp = 164-166 °C

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.10 (s, 1H), 7.52-7.10 (m, 5H), 3.49-3.05 (m, 2H), 3.17 (s, 3H), 3.15 (s, 3H), 1.88 (s, 3H)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 173.0, 157.2, 156.7, 152.7, 150.4, 137.2, 132.0, 130.1, 128.2, 127.4, 88.6, 36.9, 28.4, 27.9, 13.7

IR (KBr): ν_{max} = 3308, 1740, 1692, 1676, 1450, 1419, 1378, 1292, 1051, 1011, 927, 749 cm^{-1}

elemental analysis calcd. (%) for $C_{17}H_{17}N_5O_5$: C, 54.98; H, 4.61; N, 18.86. found: C, 54.90; H, 4.63; N, 18.83.



3-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 8

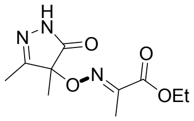
White powder. Mp = 106-107 °C

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.25 (bs, 1H), 2.33 (s, 3H), 2.21 (s, 3H), 1.96 (s, 3H), 1.41 (s, 3H)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 197.6, 193.1, 173.8, 158.5, 157.3, 83.6, 30.1, 25.4, 16.9, 12.6

IR (KBr): ν_{max} = 3322, 1742, 1716, 1687, 1364, 1298, 1204, 1190, 1125, 1067, 964, 929, 681, 619, 583, 564 cm^{-1}

elemental analysis calcd. (%) for $C_{10}H_{13}N_3O_4$: C, 50.21; H, 5.48; N, 17.57. found: C, 50.08; H, 5.20; N, 17.48.



Ethyl 2-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)propanoate 9

Mixture of E and Z isomers, E/Z = 8/1; configuration was determined by NOESY, NMR signal assignment was made based on HMBC NMR experiment, see pages S79-S82)

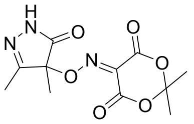
White powder. Mp = 82-85 °C

^{1}H NMR (300.13 MHz, DMSO-d$_6$): *major E isomer:* δ = 11.07 (bs, 1H, NH), 4.24-4.13 (m, 2H, OCH$_2$), 2.04 (s, 3H, $\underline{CH_3}$-C=N-O), 1.89 (s, 3H, $\underline{CH_3}$-C=N-NH), 1.40 (s, 3H, $\underline{CH_3}$-C-O-N), 1.21 (t, J = 7.1 Hz, 3H, $\underline{CH_3}$-CH$_2$); *minor Z isomer:* δ = 11.02 (bs, 1H, NH), 4.37-4.24 (m, 2H, OCH$_2$), 1.95 (s, 3H, $\underline{CH_3}$-C=N-O), 1.88 (s, 3H, $\underline{CH_3}$-C=N-NH), 1.27 (t, J = 7.1 Hz, 3H, $\underline{CH_3}$-CH$_2$), 1.26 (s, 3H, $\underline{CH_3}$-C-O-N).

^{13}C NMR (75.47 MHz, DMSO-d$_6$): *major E isomer:* δ = 174.6 (HN-$\underline{C}$=O), 162.4 (O-$\underline{C}$=O), 159.2 ($\underline{C}$=N-NH), 152.0 ($\underline{C}$=N-O), 82.6 ($\underline{C}$-O-N), 61.5 (O$\underline{C}$H$_2$), 17.4, 13.9, 12.5, 11.6 (CH$_3$); *minor Z isomer:* δ = 17.1, 16.2, 12.4.

IR (KBr): ν_{max} = 3222, 1717, 1432, 1374, 1329, 1308, 1204, 1178, 1151, 1124, 1006, 932, 863, 754, 673, 570 cm^{-1}

elemental analysis calcd. (%) for $C_{10}H_{15}N_3O_4$: C, 49.79; H, 6.27; N, 17.42. found: C, 49.71; H, 6.25; N, 17.40.



5-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-2,2-dimethyl-1,3-dioxane-4,6-dione 10

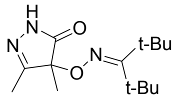
White powder. Mp = 143-146 °C dec.

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 11.31 (bs, 1H), 1.95 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H), 1.52 (s, 3H)

^{13}C NMR (75.47 MHz, DMSO-d$_6$): δ = 173.5, 158.2, 156.0, 150.5, 137.1, 105.9, 85.4, 27.6, 27.4, 16.9, 12.6

IR (KBr): ν_{max} = 3330, 1778, 1738, 1570, 1399, 1387, 1373, 1314, 1296, 1271, 1244, 1197, 1157, 1110, 1057, 1036, 984, 952, 911, 894, 794, 638, 629, 568 cm^{-1}

elemental analysis calcd. (%) for $C_{11}H_{13}N_3O_6$: C, 46.65; H, 4.63; N, 14.84. found: C, 46.40; H, 4.43; N, 14.80.



4,5-dimethyl-4-(((2,2,4,4-tetramethylpentan-3-ylidene)amino)oxy)-2,4-dihydro-3H-pyrazol-3-one 11

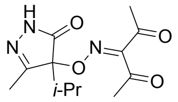
White powder. Mp = 143-144 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.22 (bs, 1H), 1.96 (s, 3H), 1.44 (s, 9H), 1.39 (s, 3H), 1.12 (s, 9H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 176.7, 171.2, 162.3, 82.1, 40.7, 38.8, 29.9, 29.8, 17.6, 13.1

IR (KBr): ν_{max} = 3215, 3104, 3010, 2991, 2975, 2956, 2931, 2872, 1710, 1625, 1482, 1448, 1433, 1392, 1381, 1369, 1311, 1195, 1122, 1075, 1024, 970, 892, 868, 746, 673, 574 cm^{-1}

elemental analysis calcd. (%) for $C_{14}H_{25}N_3O_2$: C, 62.89; H, 9.43; N, 15.72. found: C, 62.83; H, 9.56; N, 15.55.



3-(((4-isopropyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 12

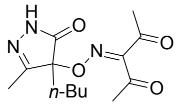
Slightly yellow viscous gum.

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.64 (bs, 1H), 2.38 (s, 3H), 2.33–2.15 (m, 1H), 2.27 (s, 3H), 1.98 (s, 3H), 1.08 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 197.0, 193.6, 173.7, 159.2, 158.1, 89.4, 31.0, 30.5, 25.8, 16.0, 14.6, 14.1

IR (Thin layer): ν_{max} = 3280, 2975, 2940, 2923, 1727, 1696, 1609, 1469, 1421, 1392, 1364, 1295, 1192, 1089, 1051, 1004, 944, 756, 718, 690, 678, 629, 615, 569, 548 cm^{-1}

elemental analysis calcd. (%) for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.41; N, 15.72. found: C, 53.80; H, 6.48; N, 15.68.



3-(((4-butyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 13

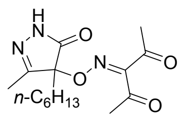
White powder. Mp = 42-43 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.30 (bs, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 2.04-1.89 (m, 1H), 2.00 (s, 3H), 1.87-1.72 (m, 1H), 1.44-1.10 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 197.0, 193.6, 174.0, 159.5, 158.1, 87.2, 31.1, 30.6, 25.9, 23.8, 22.7, 13.8, 13.4

IR (KBr): ν_{max} = 3267, 2961, 2934, 2874, 1729, 1697, 1421, 1364, 1293, 1185, 1082, 1047, 1008, 982, 936, 697, 620, 586, 567 cm^{-1}

elemental analysis calcd. (%) for $C_{13}H_{19}N_3O_4$: C, 55.51; H, 6.81; N, 14.94. found: C, 55.25; H, 6.97; N, 14.70.



3-(((4-hexyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 14

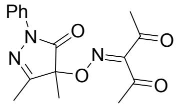
White powder. Mp = 62-63 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.44 (bs, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 2.05-1.89 (m, 1H), 2.00 (s, 4H), 1.86-1.71 (m, 1H), 1.39-1.12 (m, 8H), 0.86 (t, *J* = 6.6 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 197.0, 193.6, 174.0, 159.5, 158.1, 87.2, 31.43, 31.37, 30.6, 29.2, 25.9, 22.5, 21.7, 14.1, 13.4

IR (KBr): ν_{max} = 3204, 3120, 2955, 2932, 2860, 1729, 1696, 1459, 1427, 1385, 1363, 1293, 1183, 1082, 1062, 1050, 1021, 1003, 935, 767, 717, 620, 591, 563, 542 cm^{-1}

elemental analysis calcd. (%) for $C_{15}H_{23}N_3O_4$: C, 58.24; H, 7.49; N, 13.58. found: C, 58.10; H, 7.55; N, 13.49.



3-(((3,4-dimethyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 15

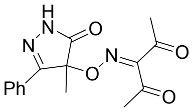
Slightly yellow gum.

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 7.92-7.84 (m, 2H), 7.48-7.37 (m, 2H), 7.25-7.17 (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

IR (Thin layer): ν_{max} = 1728, 1697, 1596, 1502, 1398, 1367, 1312, 1293, 1239, 1194, 1151, 1119, 1090, 1066, 1023, 968, 929, 907, 759, 692 cm^{-1}

HR-MS (ESI): *m/z* = 338.1112, calcd. for $C_{16}H_{17}N_3O_4+Na^+$: 338.1111



3-(((4-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 16

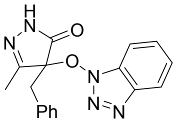
White powder, Mp = 112-113 °C

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.93 (bs, 1H), 7.84-7.70 (m, 2H), 7.52-7.34 (m, 3H), 2.43 (s, 3H), 2.20 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 197.0, 193.7, 174.5, 158.0, 157.8, 131.0, 129.2, 129.1, 126.2, 84.4, 30.8, 25.9, 19.7

IR (KBr): ν_{max} = 3200, 3120, 1736, 1708, 1691, 1630, 1359, 1297, 1216, 1118, 982, 754, 723, 695, 635, 618, 552, 516 cm^{-1}

HR-MS (ESI): *m/z* = 324.0952, calcd. for $C_{15}H_{15}N_3O_4+Na^+$: 324.0955



4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-benzyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 17

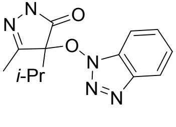
Slightly yellow powder. Mp = 158-161 dec. °C

^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 11.09 (s, 1H), 8.08-8.01 (m, 1H), 7.91-7.83 (m, 1H), 7.71-7.61 (m, 1H), 7.52-7.43 (m, 1H), 7.39-7.24 (m, 5H), 3.65 (d, *J* = 12.9 Hz, 1H), 3.50 (d, *J* = 12.9 Hz, 1H), 2.36 (s, 3H)

^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 170.6, 156.0, 142.1, 131.0, 130.0, 128.8, 128.5, 127.8, 127.7, 125.4, 119.5, 110.3, 90.8, 36.8, 14.4

IR (KBr): ν_{max} = 3294, 1743, 1711, 1081, 993, 769, 754, 744, 731, 697, 672, 637, 569 cm^{-1}

elemental analysis calcd. (%) for. $C_{17}H_{15}N_5O_2$: C, 63.54; H, 4.71; N, 21.79. found: C, 63.16; H, 4.38; N, 21.50.



4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-isopropyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 18

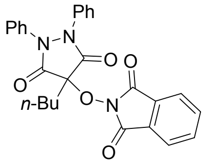
White powder. Mp = 110-111 °C dec.

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 8.28 (bs, 1H), 7.95-7.86 (m, 1H), 7.84-7.75 (m, 1H), 7.54-7.43 (m, 1H), 7.40-7.29 (m, 1H), 2.66-2.46 (m, 1H), 2.42 (s, 3H), 1.30 (d, J = 6.8 Hz, 3H), 1.08 (d, J = 7.0 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 171.1, 158.5, 143.0, 128.6, 125.1, 119.9, 110.5, 92.7, 31.9, 16.1, 15.1, 14.5

IR (KBr): ν_{max} = 3309, 3124, 2973, 1734, 1726, 1704, 1467, 1445, 1379, 1281, 1240, 1196, 1157, 1100, 1073, 1042, 996, 784, 766, 745, 687, 638, 622, 573, 545, 431 cm^{-1}

elemental analysis calcd. (%) for $C_{13}H_{15}N_5O_2$: C, 57.13; H, 5.53; N, 25.63. found: C, 57.03; H, 5.48; N, 25.58.



2-((4-butyl-3,5-dioxo-1,2-diphenylpyrazolidin-4-yl)oxy)isoindoline-1,3-dione 20a

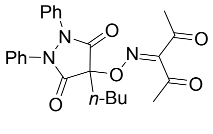
Sligthly yellow powder. Mp = 156-158 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 7.89-7.80 (m, 2H), 7.80-7.72 (m, 2H), 7.43-7.14 (m, 10H), 2.52-2.34 (m, 2H), 1.54-1.33 (m, 4H), 0.93 (t, *J* = 6.6 Hz, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 165.3, 163.4, 135.0, 134.8, 129.2, 128.9, 127.7, 124.0, 123.6, 83.7, 33.0, 24.9, 22.8, 13.8

IR (KBr): ν_{max} = 1794, 1762, 1741, 1726, 1594, 1493, 1372, 1353, 1319, 1295, 1265, 1188, 1175, 1125, 980, 877, 755, 744, 708, 691, 523 cm^{-1}

elemental analysis calcd. (%) for. $C_{27}H_{23}N_3O_5$: C, 69.07; H, 4.94; N, 8.95. found: C, 68.69; H, 5.01; N, 8.91.



4-Butyl-4-(((2,4-dioxopentan-3-ylidene)amino)oxy)-1,2-diphenylpyrazolidine-3,5-dione 20b

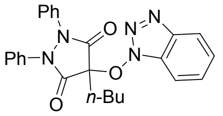
Slightly yellow powder. Mp = 47-49 °C

^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 7.45-7.31 (m, 8H), 7.30-7.20 (m 2H), 2.41 (s, 3H), 2.25 (s, 3H), 2.22-2.12 (m, 2H), 1.54-1.30 (m, 4H), 0.91 (t, *J* = 6.7 H, 3H)

^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 196.0, 193.0, 168.0, 157.9, 135.4, 129.3, 127.5, 122.5, 83.8, 32.8, 30.6, 26.0, 24.3, 22.7, 13.7

IR (KBr): ν_{max} = 2960, 2932, 1768, 1732, 1696, 1596, 1488, 1460, 1420, 1360, 1292, 1176, 1104, 1084, 1048, 1024, 1004, 928, 760, 740, 716, 692, 636, 624, 556, 500 cm^{-1}

HR-MS (ESI): *m/z* = 458.1676, calcd. for $C_{24}H_{25}N_3O_5$+Na^+: 458.1686



4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-butyl-1,2-diphenylpyrazolidine-3,5-dione 20h

Slightly yellow powder. Mp = 130-131 °C

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.01-7.91 (m, 1H), 7.78-7.70 (m, 1H), 7.57-7.45 (m, 1H), 7.42-7.10 (m, 11H), 2.57-2.43 (m, 2H), 1.73-1.41 (m, 4H), 0.99 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 165.6, 143.3, 134.5, 129.2, 128.8, 127.9, 125.2, 123.7, 120.0, 110.0, 86.3, 33.6, 24.4, 22.8, 13.8

IR (KBr): ν_{max} = 2960, 2928, 2872, 2860, 1760, 1728, 1596, 1488, 1460, 1440, 1380, 1348, 1312, 1280, 1236, 1172, 1156, 1080, 1052, 780, 760, 744, 692 cm^{-1}

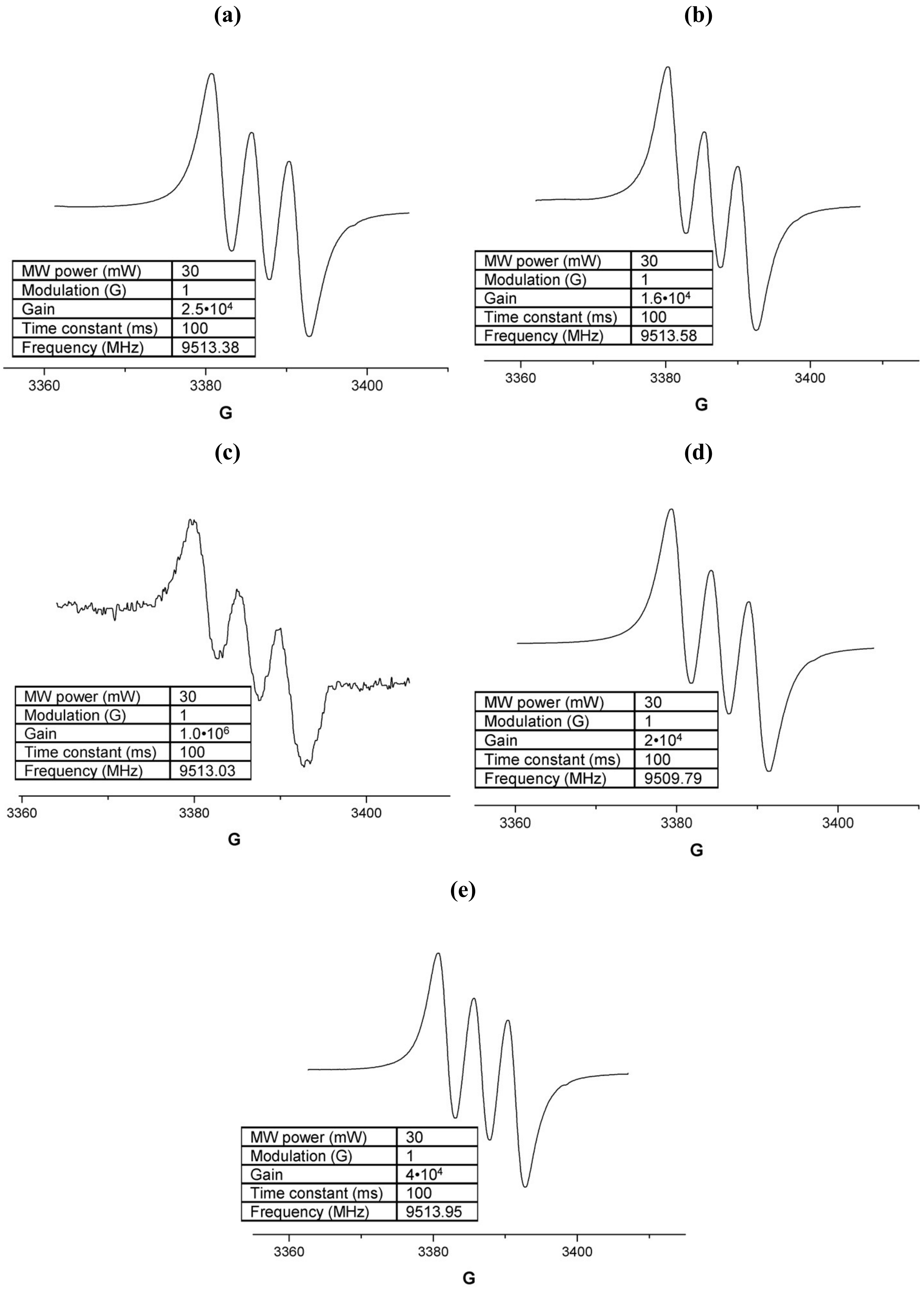
HR-MS (ESI): *m/z* = 464.1685, calcd. for $C_{25}H_{23}N_5O_3$+Na^+: 464.1693

Generation of phthalimide-N-oxyl radical from N-hydroxyphthalimide (experimental details for the scheme 7)

Oxidant (quantities are given below) was added to a 0.002 M solution of N-hydroxyphthalimide in MeCN (20 mL) at room temperature (18–23 °C), the mixture was shaken until the complete dissolution of oxidant; EPR spectrum of the solution was registered 5-15 min after mixing. Following oxidants were used: $(NH_4)_2Ce(NO_3)_6$ (21.9 mg, 0.04 mmol), $Fe(ClO_4)_3$•nH_2O (ca. 35% H_2O, 21.8 mg, 0.04 mmol), $Cu(ClO_4)_2$•$6H_2O$ (14.8 mg, 0.04 mmol), $Pb(OAc)_4$ (8.9 mg, 0.02 mmol), $PhI(OAc)_2$ (6.4 mg, 0.02 mmol). Triplet EPR spectrum characteristic for phthalimide-N-oxyl radical was observed in all cases (Table S3, figure S1).

Table S3. Measured values of g-factor and hyperfine coupling constant a_N of phthalimide-N-oxyl radical generated from NHPI and different oxidants.

Oxidant	g-factor	a_N
$(NH_4)_2Ce(NO_3)_6$	2.0072	4.79
$Fe(ClO_4)_3$•nH_2O	2.0072	4.79
$Cu(ClO_4)_2$•$6H_2O$	2.0072	4.90
$Pb(OAc)_4$	2.0071	4.90
$PhI(OAc)_2$	2.0072	4.79



(a)

MW power (mW)	30
Modulation (G)	1
Gain	$2.5{\bullet}10^4$
Time constant (ms)	100
Frequency (MHz)	9513.38

(b)

MW power (mW)	30
Modulation (G)	1
Gain	$1.6{\bullet}10^4$
Time constant (ms)	100
Frequency (MHz)	9513.58

(c)

MW power (mW)	30
Modulation (G)	1
Gain	$1.0{\bullet}10^6$
Time constant (ms)	100
Frequency (MHz)	9513.03

(d)

MW power (mW)	30
Modulation (G)	1
Gain	$2{\bullet}10^4$
Time constant (ms)	100
Frequency (MHz)	9509.79

(e)

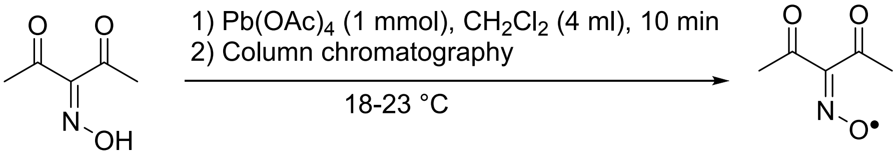
MW power (mW)	30
Modulation (G)	1
Gain	$4{\bullet}10^4$
Time constant (ms)	100
Frequency (MHz)	9513.95

Figure S1. EPR spectra of phthalimide-N-oxyl radical generated from N-hydroxyphthalimide under action of (a) $(NH_4)_2Ce(NO_3)_6$ (b) $Fe(ClO_4)_3{\bullet}nH_2O$ (c) $Cu(ClO_4)_2{\bullet}6H_2O$ (d) $Pb(OAc)_4$ (e) $PhI(OAc)_2$.

Generation and characterization of diacetyliminoxyl radical 21 (experimental details for the scheme 8, part 1)

All experiments with diacetyliminoxyl radical **21** (Scheme S5) were conducted at room temperature.

Scheme S5.



2b
(2 mmol)

21
solution in CH_2Cl_2

Diacetyl oxime **2b** (258 mg, 2 mmol) was dissolved in CH_2Cl_2 (4 mL) at 18–23 °C, then $Pb(OAc)_4$ (467 mg, 1 mmol) was added with vigorous stirring. The mixture immediately turned dark red, stirring was continued for 10 min, then the mixture was transferred to the chromatographic column, prepared by suspending the silica gel (12 g) in excess of CH_2Cl_2. CH_2Cl_2 was used as eluent, the fraction corresponding to the dark-red spot was collected, so that the volume of the fraction was 50 mL. Obtained solution of diacetyliminoxyl radical **21** in CH_2Cl_2 (50 mL, $C \approx 0.04$ mmol/mL according to quantitative EPR measurement, see below) was used for experiments described below. The photos of the preparation procedure of radical **21** are given on figure S2.

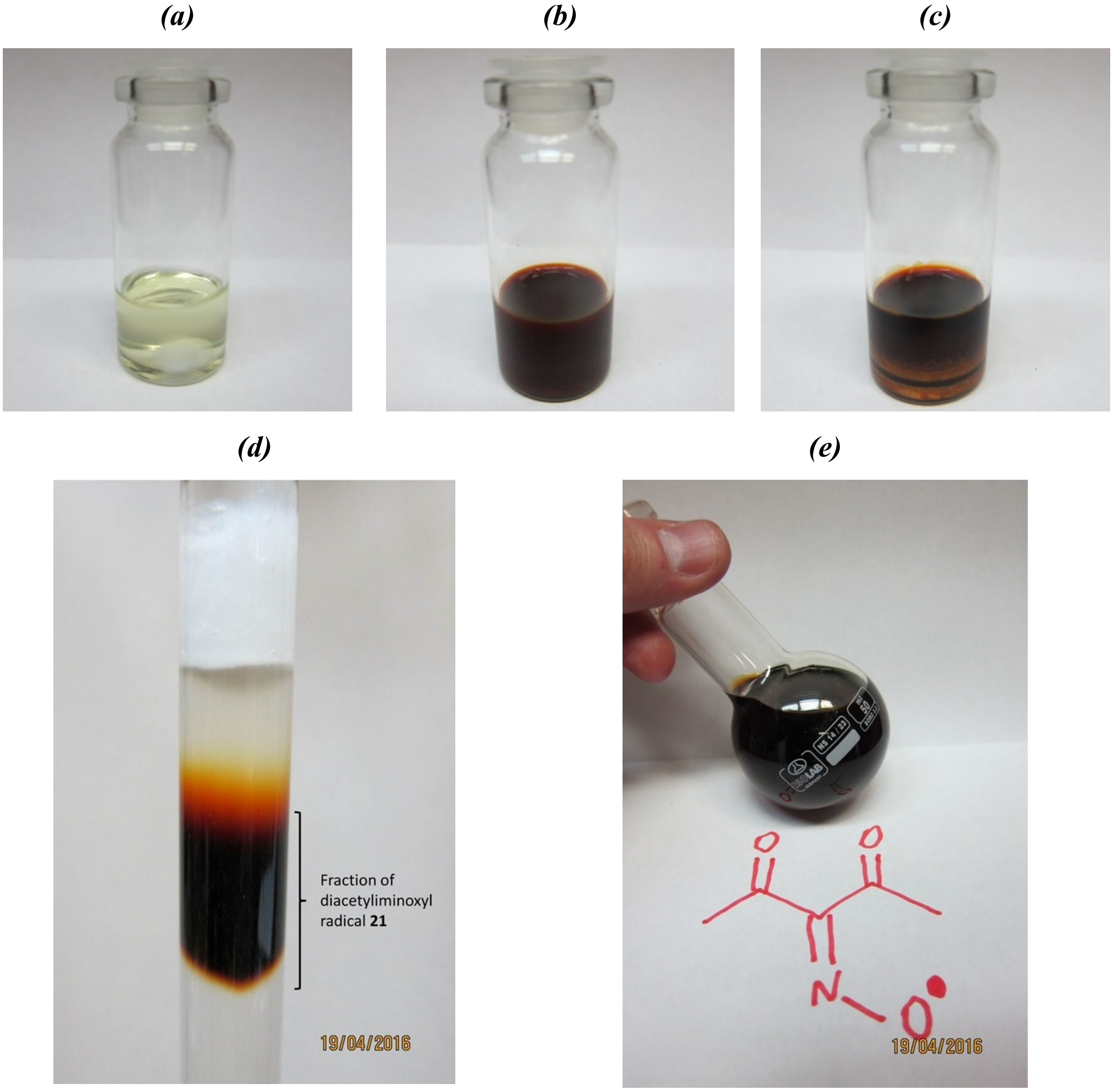


Figure S2. Preparation of the solution of diacetyliminoxyl radical **21**: ***(a)*** Solution of diacetyl oxime **2b** in CH_2Cl_2 ***(b)*** Reaction mixture right after addition of $Pb(OAc)_4$ ***(c)*** Reaction mixture 10 min after the addition of $Pb(OAc)_4$ ***(d)*** Isolation of diacetyliminoxyl radical **21** by column chromatography on silica gel ***(e)*** Resultant solution of diacetyliminoxyl radical **21**

Rotary evaporation of methylene chloride from the resultant solution of **21** under water jet vacuum at 18-23 °C gave dark-red volatile oil (215–239 mg, the weight decreased gradually under vacuum). Apparently radical **21** unstable if concentrated, as evidenced by the evolution of gas. Elemental analysis calculated for $C_5H_6NO_3$: C, 46.88; H, 4.72; N, 10.93. Found: C, 45.37; H, 4.46; N, 10.90.

Residual lead content in the solution of the oxime radical **21** was determined by ISP-MS. Solution of **21** (50 mL, prepared as described above) was rotary evaporated under water-jet vacuum at 18-23 °C. To the obtained dark-red oil (225 mg) solution of HNO_3 (prepared by dilution of 65-70% HNO_3 [2 mL] with water [4 mL]) was added. The resulting emulsion was heated to a light boiling, then immediately allowed to cool to room temperature. During the heating, brown gas evolution was observed and the disappearance of oily droplets with formation of a yellow-orange solution. The solution was diluted with water (44 mL) giving approximately 50 mL of solution that was analyzed by ICP-MS method. The lead content was 4.5 μg/L. The instrument parameters were set as follows:

atomization method – inductively coupled plasma
Plasma argon flow – 7.5 L/min
Auxiliary argon Flow – 1 L/min
Nebulizer argon Flow – 1 L/min
RF Power – 1.15 kW
Spray chamber cooling – +3 °C
Scan mode - Peak Hopping
Scans/Replicate – 10
Replicate/Sample – 10

EPR spectroscopy of diacetyliminoxyl radical 21 in CH_2Cl_2.

The yield of diacetyliminoxyl radical **21** in the oxidation of 2-(hydroxyimino)pentane-2,4-dione **2b** by $Pb(OAc)_4$ (see the procedure above) and it's stability in solution was estimated by EPR spectroscopy. A 0.04 M solution of TEMPO, prepared by dissolution of TEMPO (93.8 mg, 0.6 mmol) in CH_2Cl_2 (15 mL) was used as a concentration standard. EPR spectra of the analyzed solution of 21 and that of the concentration standard (figure S3) were recorded under the same conditions, then double integration of the spectra was performed to get EPR intensity (that is proportional to the concentration of the radical species).

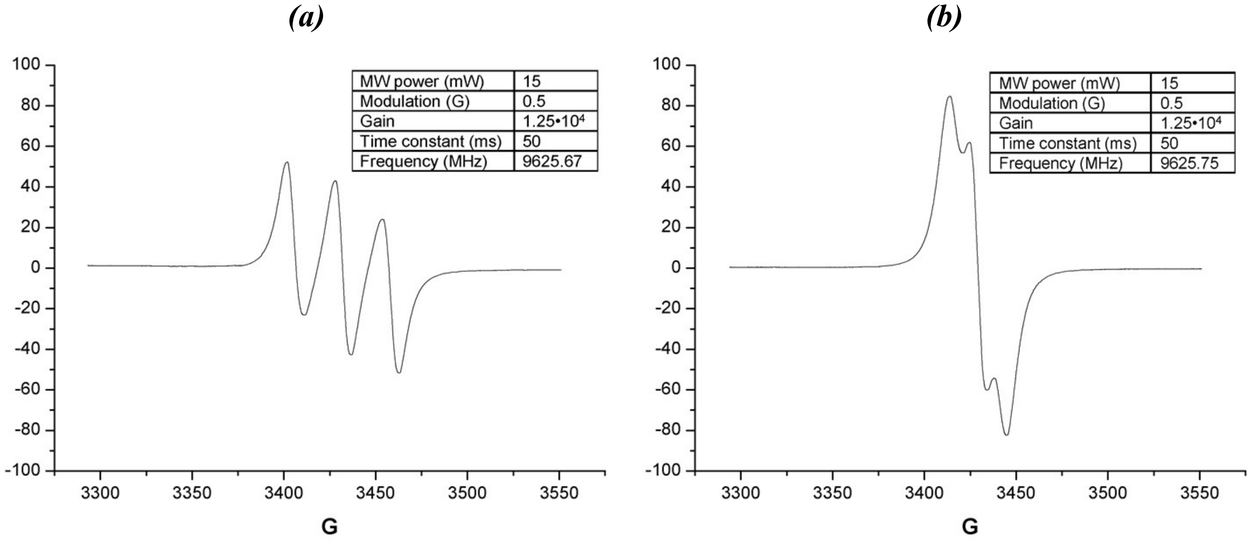


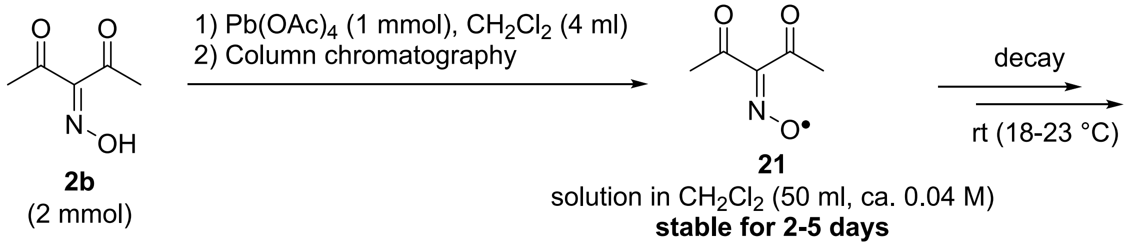
Figure S3. ***(a)*** EPR spectrum of the diacetyliminoxyl radical **21** solution in CH_2Cl_2 4 h after generation ***(b)*** EPR spectrum of the 0.04 M solution of TEMPO in CH_2Cl_2

The concentration of the diacetyliminoxyl radical **21** was calculated as follows:

$$\mathrm{C}(21) = \mathrm{C}(TEMPO) \cdot \frac{EPR\ Intensity(21)}{EPR\ Intensity\ (TEMPO)}$$

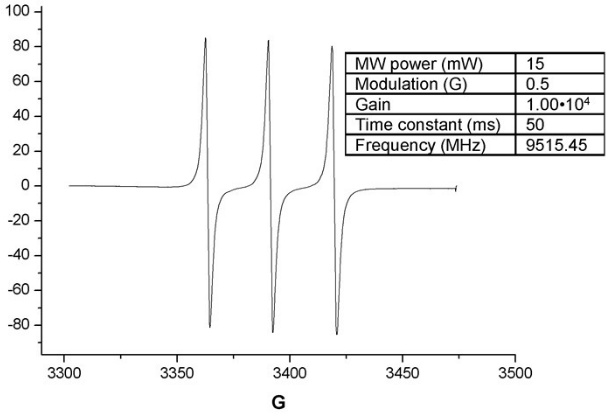
Table S4 shows that the yield of the radical **21** is nearly quantitative, that is why concentration of **21** in CH_2Cl_2 was assumed as 0.04 M for calculation of reagent quantities and yields of reactions of **21** with pyrazolones (losses of the yield during chromatography were neglected). The concentration of **21** decreased insignificantly during 2-5 days of storage at room temperature (Table S4), which makes diacetyliminoxyl radical convenient reagent for the laboratory use.

Table S4. Estimation of the yield and stability of diacetyliminoxyl radical **21** by EPR intensity measurement.



Time passed after generation of radical **21**	Radical **21** concentration, mol/L	Oxime to radical conversion, %
4 h	0.039	98
3 days	0.038	96
5 days	0.036	90
7 days	0.030	74
10 days	0.028	70
13 days	0.026	65
19 days	0.024	60

EPR spectrum of the diacetyliminoxyl radical **21** (g-factor = 2.0043, a_N = 28.0 G) with better resolution was recorded after dilution of the solution by a factor of 10 by CH$_2$Cl$_2$, see figure S4.



MW power (mW)	15
Modulation (G)	0.5
Gain	$1.00 \cdot 10^4$
Time constant (ms)	50
Frequency (MHz)	9515.45

Figure S4. EPR spectrum of the diluted solution (≈0.004 M) of diacetyliminoxyl radical **21** in CH$_2$Cl$_2$

FTIR spectroscopy of diacetyliminoxyl radical 21 in CH$_2$Cl$_2$.

The solution of diacetyliminoxyl radical **21** in CH$_2$Cl$_2$ (50 mL, ≈0.04 M, prepared as described above) was dried over molecular sieves (4Å 8-12 Mesh, 10 g) for 45 min. Part of the dried solution (25 mL) was concentrated on rotary evaporator at 18-23 °C to the volume of 10 mL (approximate concentration of the radical 0.1 mmol/mL), FT-IR spectrum was registered for the concentrated solution (Figure S5, a). During the storage of the solution of radical **21** for 2-5 days at room temperature no changes in it's FT-IR spectrum was observed. For comparison, the spectrum of the 0.1M solution of 3-(hydroxyimino)-2,4-pentanedione **2b** was recorded (Figure S5, b), obtained by dissolution of **2b** (129.1 mg, 1 mmol) in CH_2Cl_2 (10 mL, dried over 4Å molecular sieves analogously to the solution of radical **21**). Signals of the solvent (CH_2Cl_2) were subtracted, for the spectra without the subtraction of solvent signals, see page S130.

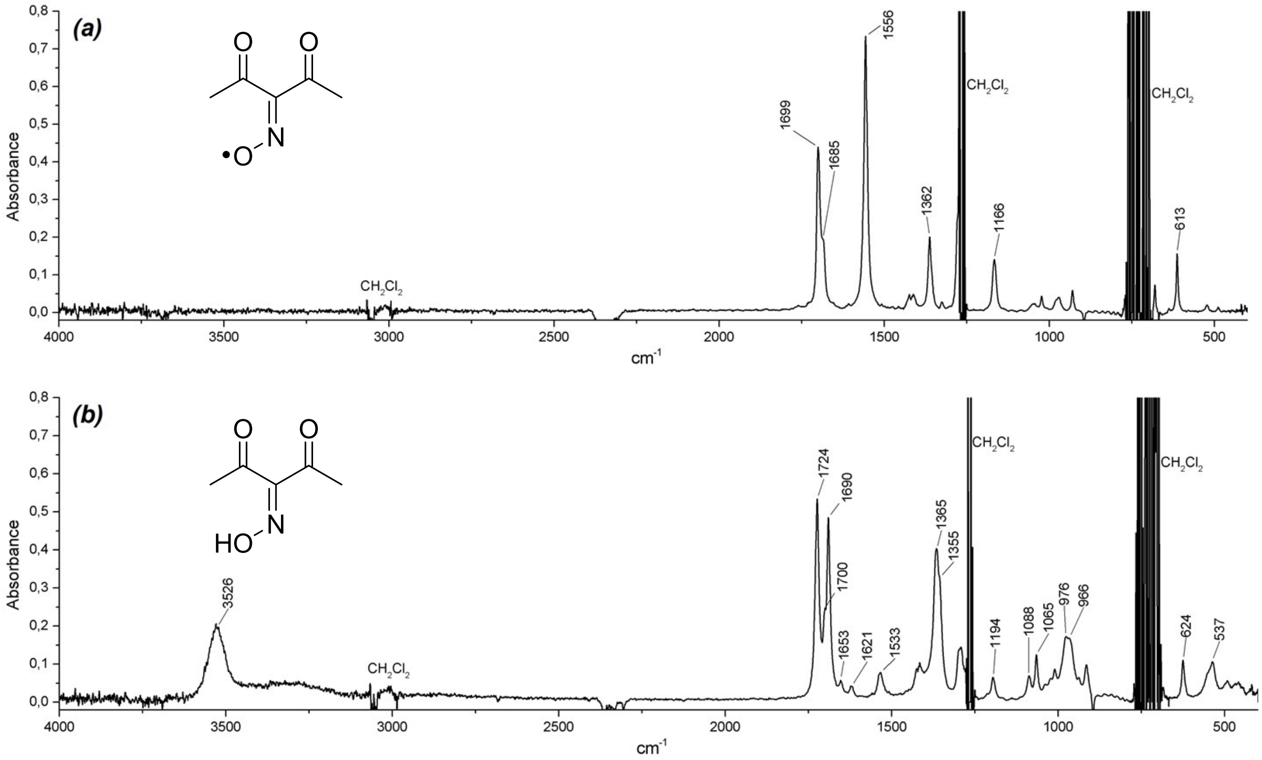
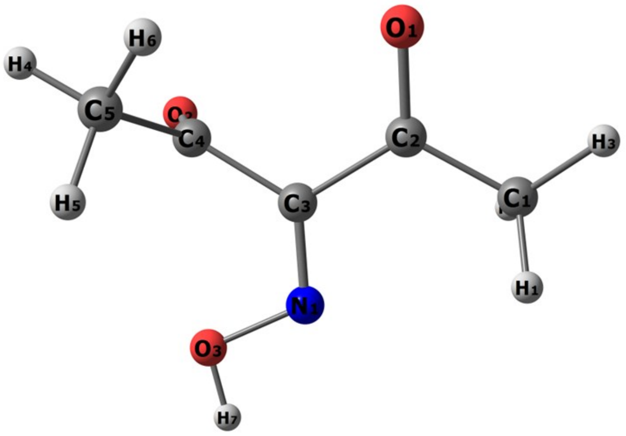
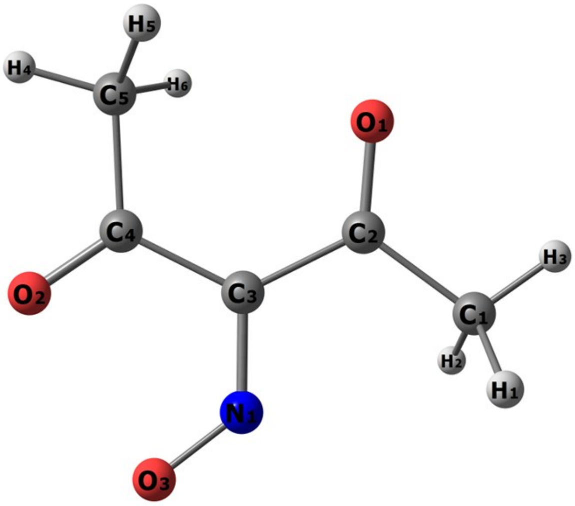


Figure S5. FTIR spectra with subtraction of CH_2Cl_2 absorbance: ***(a)*** diacetyliminoxyl radical **21** in CH_2Cl_2 (≈0.1 M); ***(b)*** 3-(hydroxyimino)-2,4-pentanedione **2b** (0.1 M).

Obviously, the signal of valent vibration of OH-group is present in the spectrum of parent oxime **2b** (ν_{OH} = 3526 cm^{-1}) and is absent in the spectrum of radical **21**. In order to interpret FTIR spectrum of diacetyliminoxyl radical **21** in characteristic range 1500–1800 cm^{-1} and determine it's plausible spatial structure, computational methods were used; the results were compared with those for diacetyl oxime **2b**. Geometry optimization, calculations of vibrational frequencies and their intensities were made in PRIRODA program package[1] on DFT PBE/sbk level of theory, complete input data for geometry optimization is given on pages S38-S47. Results of geometry optimization of oxime **2b** and radical **21** are summarized in table S5.

Table S5. Comparison of computed spatial structure of diacetyl oxime **2b** and diacetyliminoxyl radical **21**.

<table>
<tr><td colspan="2"> </td><td> </td></tr>
<tr><td colspan="2">2b</td><td>21</td></tr>
<tr><td colspan="3">Bond lengths, Å</td></tr>
<tr><td></td><td>Oxime 2b</td><td>Radical 21</td></tr>
<tr><td>N_1-O_3</td><td>1.40</td><td>1.22</td></tr>
<tr><td>C_3-N_1</td><td>1.29</td><td>1.32</td></tr>
<tr><td>C_3-C_4</td><td>1.53</td><td>1.51</td></tr>
<tr><td>C_3-C_2</td><td>1.50</td><td>1.49</td></tr>
<tr><td>C_2-O_1</td><td>1.23</td><td>1.23</td></tr>
<tr><td>C_4-O_2</td><td>1.22</td><td>1.23</td></tr>
<tr><td colspan="3">Angles, degrees</td></tr>
<tr><td>C_3-N_1-O_3</td><td>112</td><td>128</td></tr>
<tr><td>C_4-C_3-N_1</td><td>124</td><td>116</td></tr>
<tr><td>C_2-C_3-N_1</td><td>118</td><td>117</td></tr>
<tr><td>N_1-C_3-C_4-O_2</td><td>88</td><td>0</td></tr>
<tr><td>N_1-C_3-C_2-O_1</td><td>11</td><td>0</td></tr>
</table>

In comparison to oxime **2b**, radical **21** has substantially shorter N-O bond (1.22 Å vs 1.40 Å) and larger C=N-O angle (128° vs 112°) these calculated values are close to ones calculated for other oxime/iminoxyl radical pairs earlier.[2] In oxime **2b** one of the carbonyl groups is located out of plane of conjugated O-C=N-C=O system. In radical **21** both carbonyl groups are located in the same plane as C=N-O• moiety that is oriented towards one of the carbonyl groups. Similar preferential orientation of C=N-O• moiety towards carbonyl oxygen was reported recently for αoxo-Iminoxyls of isoxazolones, pyrazolones and 1,2,3-triazolone and was ascribed to a stabilizing interaction between a singly occupied orbital on the oxime oxygen and a lone pair orbital on the carbonyl oxygen.[3]

Characteristic vibrational frequencies calculated for structures **2b** and **21** are in good agreement with the experimental values (table S6). Assignment was made by visualization of vibrations in ChemCraft v. 1.8 program.

Table S6. Calculated and experimental vibrational frequencies of diacetyl oxime **2b** and diacetyliminoxyl radical **21**.[a]

Oxime **2b**		Radical **21**		Assignment
Calculated	Experimental	Calculated	Experimental	
1731 (154)	1724 vs	1661 (116)	1685 sh	ν $C_4=O_2$
1680 (143)	1690 vs	1685 (98)	1699 s	ν $C_2=O_1$
-	-	1533 (368)	1556 v.s	ν^{as} C=N-O•

[a] Values are given in cm^{-1}. Calculated relative intensities are given in brackets. Annotation: v – very, s – strong, sh – shoulder, ν - stretching.

To sum up, in comparison to the parent oxime **2b** FTIR spectrum of radical **21** is characterized by the absence of broad signal of stretching vibration of OH bond (3526 cm^{-1} for **2b**), significant shift of signal of $\nu(C_4=O_2)$ (1679 vs 1724 cm^{-1}), and by new and the most intensive signal of asymmetrical stretching vibration of C=N-O• moiety. FTIR spectral data confirm the individual state of radical **21** in solution and show no signs of presence of substantial amounts of organic impurities.

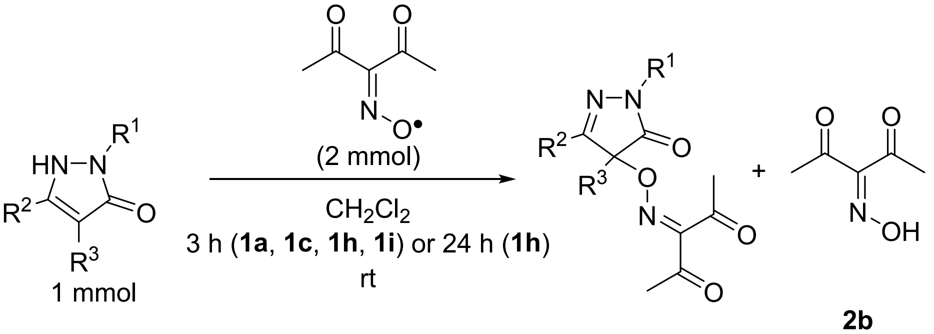
Based EPR, IP-MS and IR spectroscopy data the resultant solution contains radical **21** as the single major component (concentration ca. 0.04 mmol/mL).

References

1. (a) Laikov, D.N.; Ustynyuk, Y.A. *Russ. Chem. Bull.* **2005**, *54*, 820-826. DOI: 10.1007/s11172-005-0329-x (b) D.N.Laikov, PRIRODA, Electronic Structure Code, Version6, 2006
2. Pratt, D. A.; Blake, J. A.; Mulder, P.; Walton, J. C.; Korth, H.-G.; Ingold K. U. *J. Am. Chem. Soc.* **2004**, *126*, 10667–10675 DOI: 10.1021/ja047566y
3. Koch, R.; Wollweber, H.-J.; Müller-Starke, H.; Wentrup, C. *Eur. J. Org. Chem.* **2015**, 5143-5149. DOI: 10.1002/ejoc.201500728

Reactions of diacetyliminoxyl radical 21 with pyrazoline-5-ones 1a, 1c, 1h, 1i (experimental details for the scheme 8, part 2)

Scheme S6.



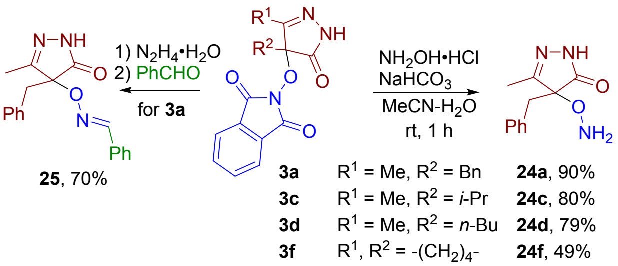
			2b
1a	R^1 = H, R^2 = Me, R^3 = Bn	**4**, 82%	50%
1c	R^1 = H, R^2 = Me, R^3 = iPr	**12**, 77%	53%
1h	R^1 = Ph, R^2 = Me, R^3 = Me	**15**, 71%	52%
1i	R^1 = H, R^2 = Ph, R^3 = Me	**16**, 68%	52%

General procedure: To a stirred solution of diacetyliminoxyl radical **21** in CH_2Cl_2 (50 mL, ca. 0.04 mol/L, ≈2 mmol, prepared as described above) pyrazolin-5-one (1 mmol; **1a**: 188.2 mg; **1c**: 140.2 mg; **1h**: 188.2 mg; **1i**: 174.2 mg) was added at room temperature. Stirring was continued for 3 h, gradual dissolution of pyrazolin-5-one and decrease of intensity of red color of the solution was observed. The mixture was rotary evaporated under water-jet vacuum, an aliquot (20 mg) of the residue was analyzed by ^1H and ^{13}C NMR, the rest was transferred to silica gel chromatographic column and eluted with EtOAc/CH_2Cl_2 (EtOAc content was increased gradually from 0 to 30%vol) to isolate reaction products. In the case of pyrazolin-5-one **1h** additional experiment was made with reaction time 24 h (instead of 3 h), the same products yields were observed.

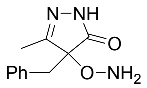
The ^1H and ^{13}C NMR spectra of the reaction mixtures of diacetyliminoxyl radical **21** with pyrazolones **1a,c,h,i** are given on pages S121-S129 Signals were assigned to the coupling products (**4**, **12**, **15** and **16**) and oxime **2b** by comparison of chemical shifts with the spectra of individual compounds. No significant impurity signals can be seen. Based on the observed composition of the products it can be concluded that one equivalent of the oxime radical **21** forms the coupling product (**4**, **12**, **15** or **16**) and the second equivalent plays the role hydrogen acceptor (oxidant) to form an oxime **2b**.

Synthesis of hydroxylamines 24a,c,d,f and oxime 25 from the products of oxidative C-O coupling 3a,c,d,f (experimental details for the scheme 9)

Scheme S7.



General procedure for the synthesis of hydroxylamines 24. The product of C-O coupling **3** (180–210 mg, 0.6 mmol), NH_2OH•HCl (83.4 mg, 1.2 mmol), MeCN (3 mL) and H_2O (0.5 mL) were placed in a 10 mL round-bottom flask. Then $NaHCO_3$ (101 mg, 1.2 mmol) was added with vigorous stirring at room temperature; stirring was continued for 1 h. The mixture was rotary evaporated to dryness, the residue was extracted with CH_2Cl_2 (3×7 mL). Combined extracts were washed with $NaHCO_3$ (2×3 mL), dried over $MgSO_4$, and rotary evaporated. Et_2O (1-2 mL) was added to the residue to cause crystallization, and then was rotary evaporated. Hydroxylamines **24a,c,d,f** were obtained as white powders.



4-(aminooxy)-4-benzyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24a

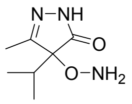
White powder. Mp = 55–57 °C

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.60 (bs, 1H), 7.36-7.19 (m, 3H), 7.19-7.04 (m, 2H), 5.63 (bs, 2H), 3.05 (d, J = 13.3 Hz, 1H), 2.96 (d, J = 13.3 Hz, 1H), 2.02 (s, 3H)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 175.6, 160.4, 132.3, 130.0, 128.5, 127.6, 88.0, 38.6, 14.2

IR (KBr): ν_{max} = 3313, 3247, 3174, 3107, 1717, 1455, 1435, 1147, 1072, 757, 737, 701, 640, 577, 562 cm^{-1}

HR-MS (ESI): m/z = 220.1082, calcd. for $C_{11}H_{13}N_3O_2+H^+$: 220.1081



4-(aminooxy)-4-isopropyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24c

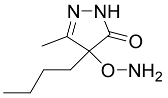
White powder. Mp = 100–102 °C

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 10.74 (s, 1H), 6.23 (s, 2H), 1.96-1.80 (m, 1H), 1.93 (s, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 7.1 Hz, 3H)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 175.5, 159.4, 88.7, 30.4, 16.1, 14.6, 13.9

HR-MS (ESI): *m*/*z* = 172.1074, calcd. for $C_7H_{13}N_3O_2$+H^+: 172.1081

IR (KBr): ν_{max} = 3296, 3226, 3150, 1730, 1591, 1293, 1282, 1161, 1083, 1069, 732, 667, 559 cm^{-1}



4-(aminooxy)-4-butyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24d

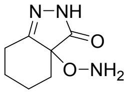
White powder. Mp = 89–90 °C

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.68 (bs, 1H), 5.49 (bs, 2H), 2.03 (s, 3H), 1.84-1.66 (m, 1H), 1.65-1.48 (m, 1H), 1.41-1.00 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 176.1, 161.3, 87.6, 31.7, 24.1, 22.8, 13.8, 13.5

IR (KBr): ν_{max} = 3299, 3233, 2961, 2926, 1731, 1595, 1248, 1166, 1080, 1072, 1059, 757, 748, 692, 643, 580, 562 cm^{-1}

HR-MS (ESI): *m*/*z* = 186.1239, calcd. for $C_8H_{15}N_3O_2$+H^+: 186.1237



3a-(aminooxy)-2,3a,4,5,6,7-hexahydro-3H-indazol-3-one 24f

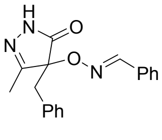
White powder. Mp = 111–112 °C

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 9.10 (bs, 1H), 5.53 (bs, 2H), 2.74-2.54 (m, 1H), 2.54-2.33 (m, 1H), 2.26-1.98 (m, 2H), 1.84-1.54 (m, 2H), 1.53-1.30 (m, 2H)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 176.5, 164.5, 83.4, 33.9, 28.9, 27.4, 20.3

IR (KBr): ν_{max} = 3288, 3175, 2943, 2925, 1719, 1677, 1619, 1225, 1171, 1146, 1111, 1024, 1008, 741, 683, 651, 595, 574 cm^{-1}

HR-MS (ESI): *m*/*z* = 192.0745, calcd. for $C_7H_{11}N_3O_2$+Na^+: 192.0743



(E)-benzaldehyde O-(4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl) oxime 25. N_2H_4•H_2O (32.2 mg, 0.644 mmol) and MeCN (3 mL) were placed in a 10 mL round-bottom flask, then 2-((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)isoindoline-1,3-dione **3a** (150 mg, 0.429 mmol) was added with intensive stirring, that was continued for 40 min at room temperature, precipitate formation was observed. Benzaldehyde (182 mg, 1.72 mmol) was added, the precipitate gradually dissolved. Stirring was continued for 2 h at room temperature, then the mixture was rotary evaporated to dryness. The product was isolated by column chromatography on silica gel using EtOAc/CH_2Cl_2 mixture as eluent with a gradual change in the ratio of solvents from 0 to 1/10. (E)-benzaldehyde O-(4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl) oxime **25** was obtained as a white powder (93 mg, 0.303 mmol, 70%). Signal assignment in ^1H and ^{13}C NMR spectra, as well as defining configuration of C=N bond was performed with aid of 2D NMR experiments HMBC and NOESY (see pages S117-S120).

Mp = 120–121 °C

^1H NMR (300.13 MHz, $CDCl_3$): δ = 10.88 (bs, 1H, NH), 8.46 (s, 1H, HC=N), 7.58-7.50 (m, 2H, ArH), 7.47-7.37 (m, 3H, ArH), 7.33-7.17 (m, 5H, ArH), 3.21 (d, J = 12.9 Hz, 1H, CH_2), 3.09 (d, J = 12.9 Hz, 1H, CH_2), 1.97 (s, 3H, CH_3)

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 174.2 (CONH), 158.1 (C=N-N), 151.8 (C=N-O), 132.3, 130.9, 130.7, 129.9, 128.9, 128.2, 127.2 (Ph), 86.0 (C-O-N), 37.2 (CH_2), 13.7 (CH_3)

IR (KBr): ν_{max} = 3417, 3221, 3065, 1732, 1702, 1455, 1377, 1161, 1076, 1016, 921, 758, 749, 697, 628, 570, 519, 510cm^{-1}

elemental analysis calcd. (%) for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. found: C, 70.31; H, 5.62; N, 13.59.

X-Ray single-crystal diffraction: Structure determination of 3,4-dimethyl-1-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3h

The molecular structure of **3h** was confirmed by X-ray structure determination. The single-crystal X-ray diffraction experiment was carried out at room temperature on a STOE STADI-VARI Pilatus 100K diffractometer using monochromated CuK$_\alpha$ radiation. The structure was solved with *SHELXS* [1] and refined with *SHELXL* [1]. All hydrogen atoms were located on a difference Fourier map, then placed in idealized positions (N-H 0.86 Å, C-H 0.93-0.97 Å), and refined as riding with U_{iso}(H)=1.2-1.5U_{eq}(C, N). The crystallographic data for **3g** are summarized in Table S7. Molecular structure of **3h** drawn with DIAMOND [2] is shown in Figure S6.

Table S7. Crystallographic data for **3h**.

	3h
Chemical formula	$C_{19}H_{15}N_3O_4$
M_r	349.34
Cell setting, space group	*Orthorhombic*, $Pca2_1$
a (Å)	16.2553(2)
b (Å)	8.31160(10)
c (Å)	24.8996(4)
V (Å^3)	3364.12(8)
Z	8
Radiation type	CuK$_\alpha$
θ_{max} (°)	66.4
No. of independent (observed) reflections	5873 (3832)
No. of parameters	473
Flack parameter	0.5(5)
Refinement on	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.148, 0.89

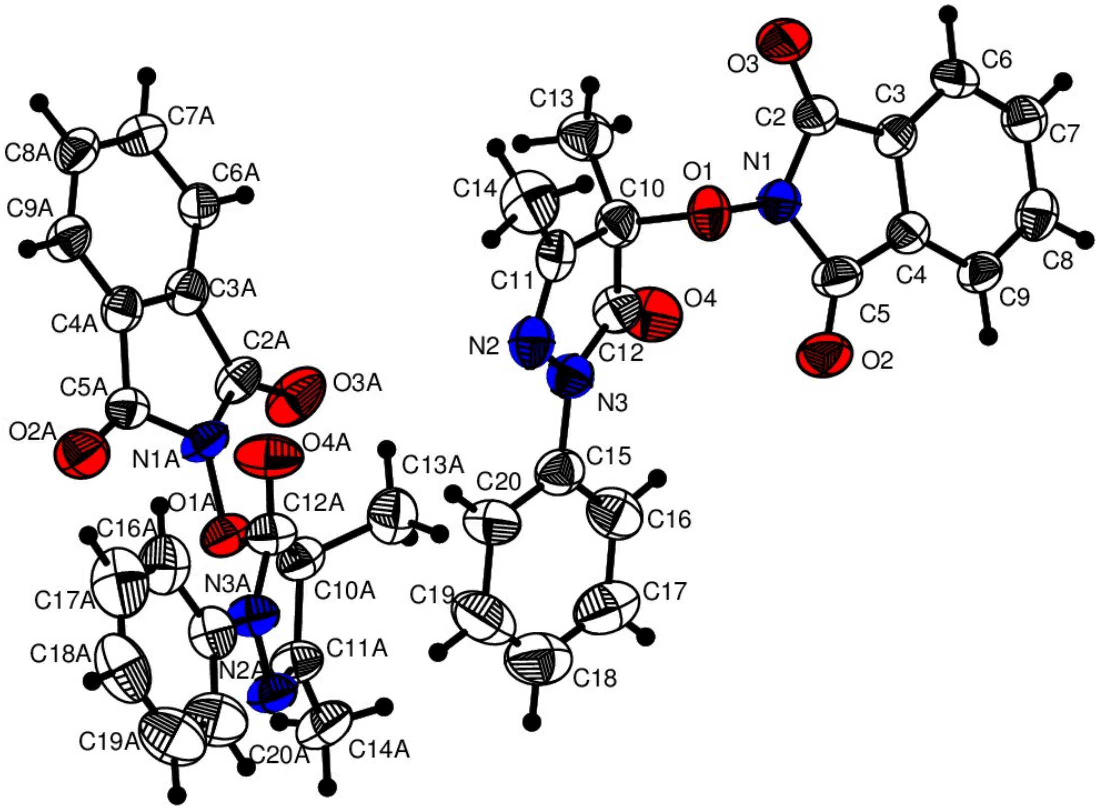


Figure S6. Two independent molecules of **3h**, showing the atomic numbering and 50% probability displacement ellipsoids.

Crystallographic data for **3h** have also been deposited - CCDC no. 1411623 - with the Cambridge Crystallographic Data Center, and they can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Structural discussion:

Compound **3h** crystallizes in orthorhombic non-centrosymmetric achiral space group *Pca2*$_1$. The asymmetric unit contains two independent molecules (Fig. 1) with almost identical conformations and normal values of bond lengths and angles. In the crystal, weak intermolecular C-H…O hydrogen bonds (Table S8) link the molecules related by translation in [010] into chains.

Table S8. Weak C-H…O interactions (Å, °) in **3h**.

D−H…A	*D−H*	*H…A*	*D…A*	**D−H…A**
C8−H8…O3^{i}	0.93	2.51	3.303(8)	143
C8A−H8A…O3A^{ii}	0.93	2.52	3.304(7)	142

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) *x*, *y*+1, *z*.

Acknowledgement.

X-ray structural study was fulfilled using a STOE STADI VARI PILATUS-100K diffractometer purchased by MSU Development Program.

References.

[1] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[2] Brandenburg, K.; Putz, H. **1999**, *DIAMOND.* Crystal Impact GbR, Bonn, Germany.

Input data for geometry optimization of oxime 2b

```
  molecule input:
     16 atoms,    68 electrons


   Atomic Coordinates:
     6     2.68961900   0.39824800   0.01542300
     6     1.42583600  -0.42818300  -0.02835700
     8     1.42949600  -1.64610400  -0.11161500
     6     0.10212700   0.27368700   0.02705800
     6    -1.14263300  -0.59023300   0.23424800
     8    -1.51754500  -0.81767400   1.36364400
     6    -1.80936300  -1.11456500  -1.01027200
     7     0.09379300   1.55066900  -0.09802600
     1     2.66240300   1.19367000  -0.73386900
     1     2.78097500   0.88538900   0.99218200
     1     3.54586300  -0.25635200  -0.14996400
     1    -2.70315900  -1.68046400  -0.74281500
     1    -2.07080800  -0.28186500  -1.67257500
     1    -1.10314100  -1.75973700  -1.54499100
     8    -1.19997600   2.06313700  -0.09034000
     1    -1.05800500   3.01607600  -0.18389900
   #
    formula: H7C5NO3
    internuclear distances:
    C1     |  C2    : 1.51065  H1    : 1.09310  H2    : 1.09531  H3    :
1.09042
    C2    |  C1    : 1.51065  O1    : 1.22077  C3    : 1.49930
    O1    |  C2    : 1.22077
    C3    |  C2    : 1.49930  C4    : 1.52929  N1    : 1.28312
    C4    |  C3    : 1.52929  O2    : 1.21154  C5    : 1.50608
    O2    |  C4    : 1.21154
    C5     |  C4    : 1.50608  H4    : 1.09117  H5    : 1.09562  H6    :
1.09587
    N1    |  C3    : 1.28312  O3    : 1.39159
```

```
H1    |  C1   : 1.09310
H2    |  C1   : 1.09531
H3    |  C1   : 1.09042
H4    |  C5   : 1.09117
H5    |  C5   : 1.09562
H6    |  C5   : 1.09587
O3    |  N1   : 1.39159  H7   : 0.96799
H7    |  O3   : 0.96799
   largest =    6.43660

atomic masses:
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   6  12.00000000
   8  15.99491000
   6  12.00000000
   6  12.00000000
   8  15.99491000
   6  12.00000000
   7  14.00307000
   1   1.00782500
   1   1.00782500
   1   1.00782500
   1   1.00782500
   1   1.00782500
   1   1.00782500
   8  15.99491000
   1   1.00782500
 Effective Core Potentials
 -------------------------

 atomic number  6: Ncore =  2, Lmax = 1

  L        c       n        a
  1     -0.893710  1      8.564680
```

```
  0      1.929260  0      2.814970
  0     14.881990  2      8.112960

 atomic number  8: Ncore =  2, Lmax = 1

  L        c       n        a
  1     -0.925500  1     16.117180
  0      1.960690  0      5.053480
  0     29.134420  2     15.953330

 atomic number  7: Ncore =  2, Lmax = 1

  L        c       n        a
  1     -0.912120  1     11.996860
  0      1.935650  0      3.838950
  0     21.733550  2     11.732470

 atomic number  1: no ECP


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   2   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
   3   8  O :  30/22  functions, {3,1,1/3,1,1/1,1}
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   7   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
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   9   1  H :   8/6   functions, {3,1,1/1}
  10   1  H :   8/6   functions, {3,1,1/1}
  11   1  H :   8/6   functions, {3,1,1/1}
  12   1  H :   8/6   functions, {3,1,1/1}
  13   1  H :   8/6   functions, {3,1,1/1}
```

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  14   1  H :   8/6   functions, {3,1,1/1}
  15   8  O :  30/22  functions, {3,1,1/3,1,1/1,1}
  16   1  H :   8/6   functions, {3,1,1/1}

Basis set input: 'sbk.bas'
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   3   8  O :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   4   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   5   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   6   8  O :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   7   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   8   7  N :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   9   1  H :   8/8   functions, {1,1,1,1,1/1}
  10   1  H :   8/8   functions, {1,1,1,1,1/1}
  11   1  H :   8/8   functions, {1,1,1,1,1/1}
  12   1  H :   8/8   functions, {1,1,1,1,1/1}
  13   1  H :   8/8   functions, {1,1,1,1,1/1}
  14   1  H :   8/8   functions, {1,1,1,1,1/1}
  15   8  O :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
  16   1  H :   8/8   functions, {1,1,1,1,1/1}

+---------------------------------------
| Number of atoms                     16
| Charge of molecule                   0
| Spin multiplicity                    1
| Number of alpha electrons           25
| Number of beta  electrons           25
| Number of core  electrons            9
| Theoretical Method                 DFT
| Approximation to E(xc)             PBE
| Dimension of wavefunction basis    240
| Dimension of   auxiliary  basis    389
+---------------------------------------
```

```
SCF Options:
convergence      = 1.0e-06 (1.0e-03)
number of iterations = 100     ( 16)
Cut-off for S,T,V integrals: 1.0e-10 (1.0e-06)

Grid options:
   30 radial shells for atomic number  1,
   40 radial shells for atomic number  6,
   40 radial shells for atomic number  7,
   40 radial shells for atomic number  8,
  570 radial shells total
Predefined accuracy of Exc:  1.0e-08 (1.0e-05) per radial shell
Cut-off for basis functions: 1.0e-09 (1.0e-06)

Geometry optimization options:
Coordinates: internal
Tolerance on gradient       = 0.00001000
Tolerance on displacement   = 0.00100000
Trust radius                = 0.75000000 (max), 0.04687500 (min)
Maximum number of steps     =        100
Updated hessian used
```

Input data for geometry optimization of diacetyliminoxyl radical 21

```
 molecule input:
    15 atoms,    67 electrons

  Atomic Coordinates:
    6     2.59469600  -0.58584300  -0.00014900
    6     1.41116500   0.36370100   0.00005600
    8     1.56266300   1.57594100   0.00035500
    6     0.04758600  -0.23232600  -0.00001000
    6    -1.26357400   0.51723300  -0.00000500
    8    -2.30007400  -0.12290100   0.00026500
    6    -1.25359900   2.02833900  -0.00038800
    7    -0.02984200  -1.54030100  -0.00007700
    1     2.57391900  -1.23552200   0.88053500
    1     2.57280200  -1.23654500  -0.88006900
    1     3.50995700   0.00632200  -0.00108800
    1    -2.28747900   2.37458200  -0.00184700
    1    -0.71743100   2.40823800   0.87289400
    1    -0.71446600   2.40830800  -0.87172300
    8    -1.00584600  -2.26427700  -0.00001900
  #
   formula: H6C5NO3
   internuclear distances:
   C1     |  C2    : 1.51736  H1    : 1.09459  H2    : 1.09460  H3    :
1.09012
   C2     |  C1    : 1.51736  O1    : 1.22167  C3    : 1.48815
   O1     |  C2    : 1.22167
   C3     |  C2    : 1.48815  C4    : 1.51029  N1    : 1.31026
   C4     |  C3    : 1.51029  O2    : 1.21824  C5    : 1.51114
   O2     |  C4    : 1.21824
   C5     |  C4    : 1.51114  H4    : 1.09032  H5    : 1.09290  H6    :
1.09282
   N1     |  C3    : 1.31026  O3    : 1.21521
   H1     |  C1    : 1.09459
```

```
 H2    |  C1   : 1.09460
 H3    |  C1   : 1.09012
 H4    |  C5   : 1.09032
 H5    |  C5   : 1.09290
 H6    |  C5   : 1.09282
 O3    |  N1   : 1.21521
    largest =    6.26250

atomic masses:
   6  12.00000000
   6  12.00000000
   8  15.99491000
   6  12.00000000
   6  12.00000000
   8  15.99491000
   6  12.00000000
   7  14.00307000
   1   1.00782500
   1   1.00782500
   1   1.00782500
   1   1.00782500
   1   1.00782500
   1   1.00782500
   8  15.99491000
 Effective Core Potentials
 -------------------------

 atomic number  6: Ncore =  2, Lmax = 1

  L        c       n        a
  1     -0.893710  1      8.564680
  0      1.929260  0      2.814970
  0     14.881990  2      8.112960
```

```
 atomic number  8: Ncore =  2, Lmax = 1

  L        c       n        a
  1     -0.925500  1     16.117180
  0      1.960690  0      5.053480
  0     29.134420  2     15.953330

 atomic number  7: Ncore =  2, Lmax = 1

  L        c       n        a
  1     -0.912120  1     11.996860
  0      1.935650  0      3.838950
  0     21.733550  2     11.732470

 atomic number  1: no ECP


Basis set input: 'sbk.bas'
   1   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
   2   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
   3   8  O :  30/22  functions, {3,1,1/3,1,1/1,1}
   4   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
   5   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
   6   8  O :  30/22  functions, {3,1,1/3,1,1/1,1}
   7   6  C :  30/22  functions, {3,1,1/3,1,1/1,1}
   8   7  N :  30/22  functions, {3,1,1/3,1,1/1,1}
   9   1  H :   8/6   functions, {3,1,1/1}
  10   1  H :   8/6   functions, {3,1,1/1}
  11   1  H :   8/6   functions, {3,1,1/1}
  12   1  H :   8/6   functions, {3,1,1/1}
  13   1  H :   8/6   functions, {3,1,1/1}
  14   1  H :   8/6   functions, {3,1,1/1}
  15   8  O :  30/22  functions, {3,1,1/3,1,1/1,1}
```

```
Basis set input: 'sbk.bas'
   1   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
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   3   8  O :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   4   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   5   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   6   8  O :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   7   6  C :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   8   7  N :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}
   9   1  H :   8/8   functions, {1,1,1,1,1/1}
  10   1  H :   8/8   functions, {1,1,1,1,1/1}
  11   1  H :   8/8   functions, {1,1,1,1,1/1}
  12   1  H :   8/8   functions, {1,1,1,1,1/1}
  13   1  H :   8/8   functions, {1,1,1,1,1/1}
  14   1  H :   8/8   functions, {1,1,1,1,1/1}
  15   8  O :  37/37  functions, {1,1,1,1,1,1/1,1,1/1,1,1/1}

+----------------------------------------
| Number of atoms                     15
| Charge of molecule                   0
| Spin multiplicity                    2
| Number of alpha electrons           25
| Number of beta  electrons           24
| Number of core  electrons            9
| Theoretical Method                 DFT
| Approximation to E(xc)             PBE
| Dimension of wavefunction basis    234
| Dimension of   auxiliary  basis    381
+----------------------------------------

SCF Options:
convergence      = 1.0e-06 (1.0e-03)
number of iterations = 100     ( 16)
Cut-off for S,T,V integrals: 1.0e-10 (1.0e-06)
```

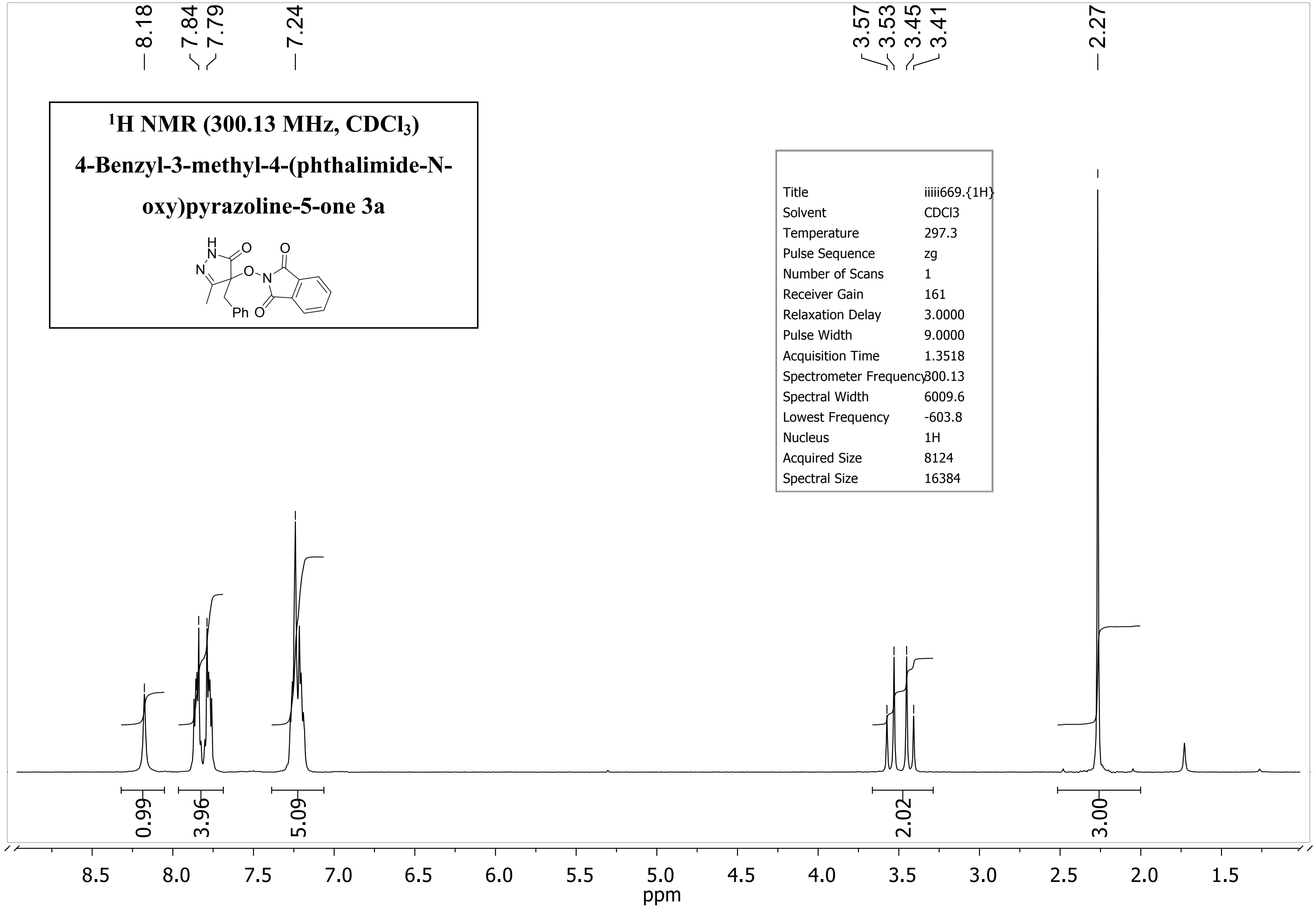
```
Grid options:
   30 radial shells for atomic number  1,
   40 radial shells for atomic number  6,
   40 radial shells for atomic number  7,
   40 radial shells for atomic number  8,
  540 radial shells total
Predefined accuracy of Exc:  1.0e-08 (1.0e-05) per radial shell
Cut-off for basis functions: 1.0e-09 (1.0e-06)

Geometry optimization options:
Coordinates: internal
Tolerance on gradient       = 0.00001000
Tolerance on displacement   = 0.00100000
Trust radius                = 0.75000000 (max), 0.04687500 (min)
Maximum number of steps     =        100
Updated hessian used
```

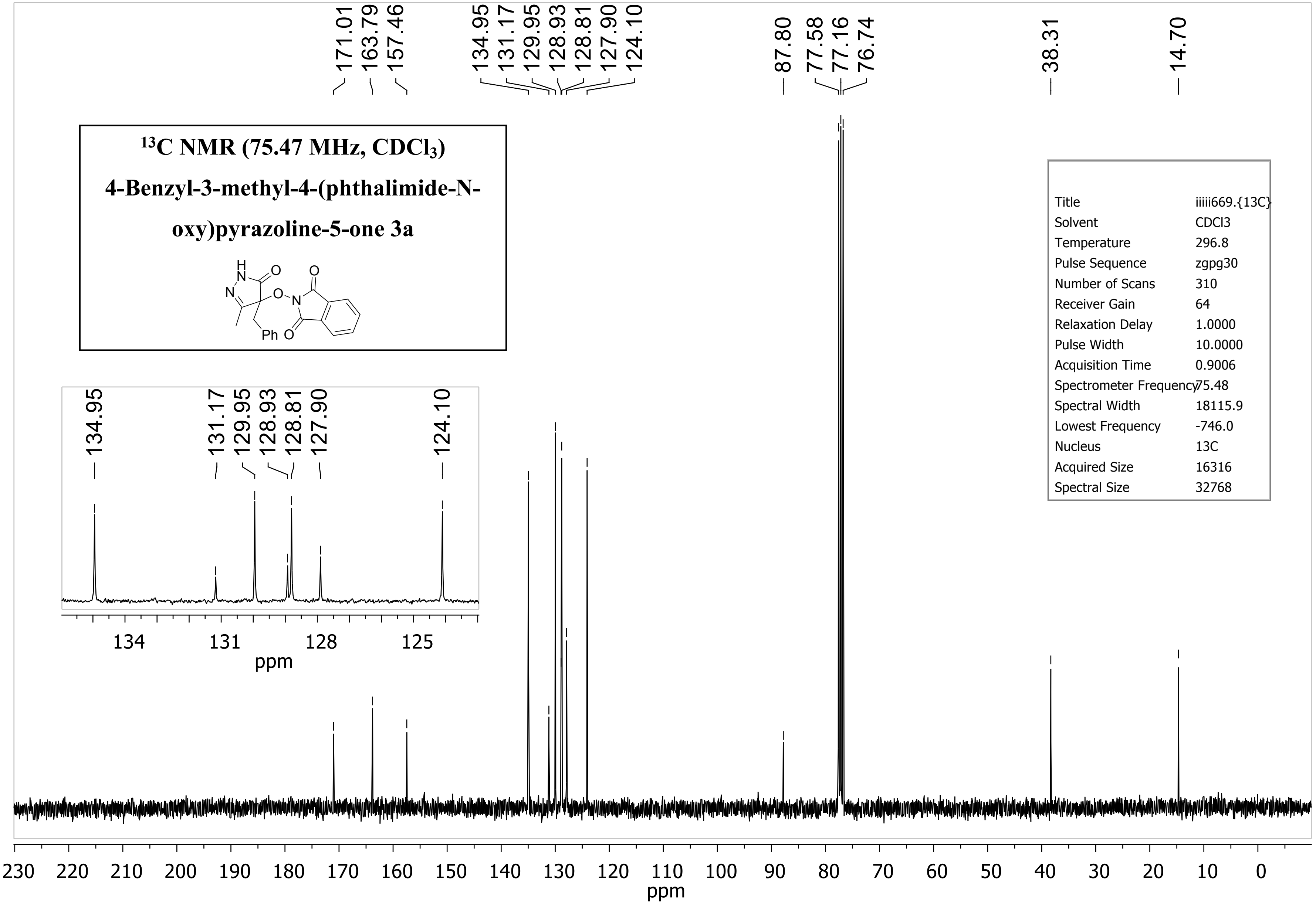
NMR Spectra of the synthesized products 3a-i, 4-18, 20a, 20b, 20h, 24a, 24c, 24d, 24f, and 25

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

4-Benzyl-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3a



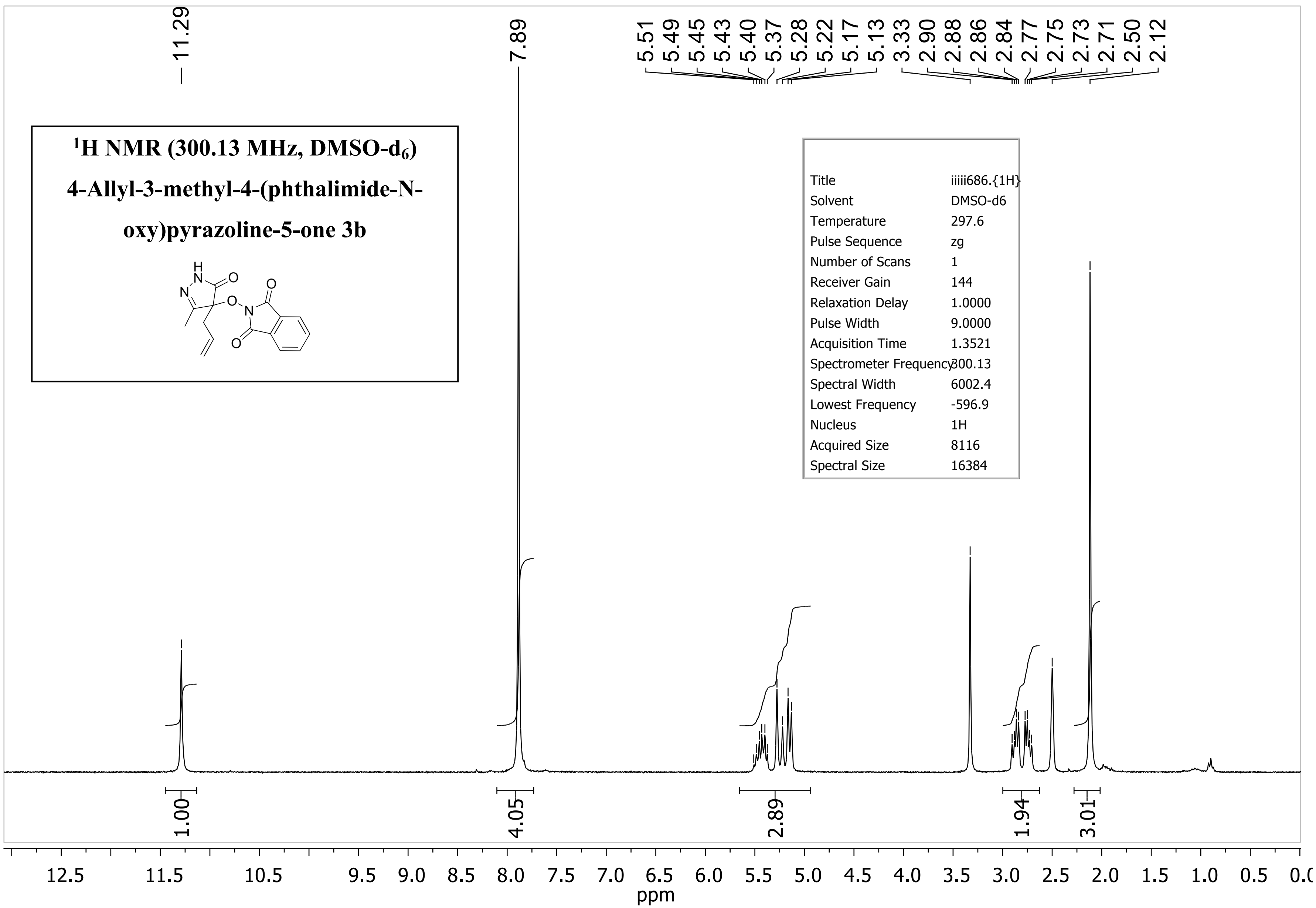
Title	iiiii669.{1H}
Solvent	CDCl3
Temperature	297.3
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	3.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-603.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



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

4-Benzyl-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3a

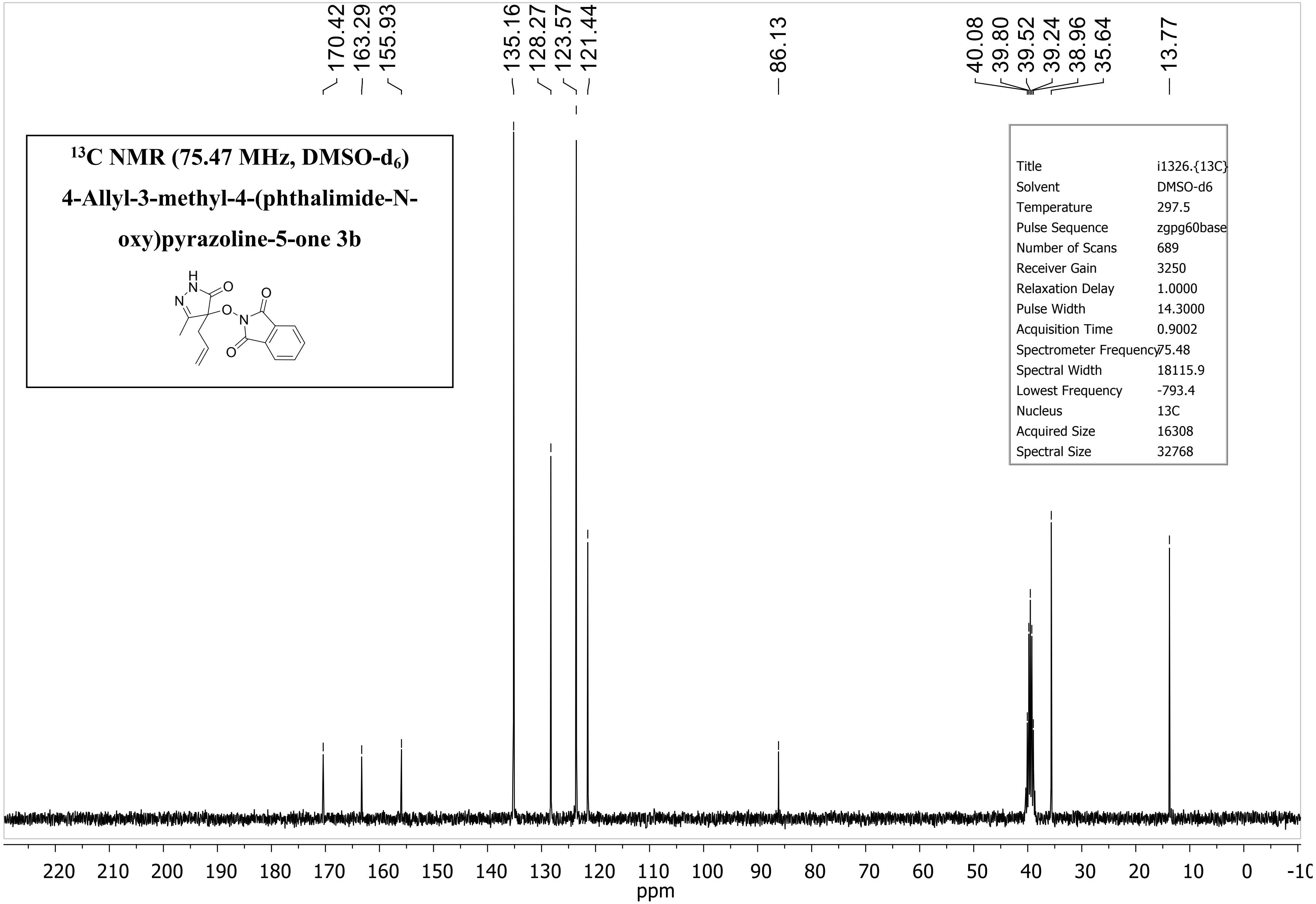
Title	iiiii669.{13C}
Solvent	CDCl3
Temperature	296.8
Pulse Sequence	zgpg30
Number of Scans	310
Receiver Gain	64
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-746.0
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



^{1}H NMR (300.13 MHz, DMSO-d$_6$)

4-Allyl-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3b

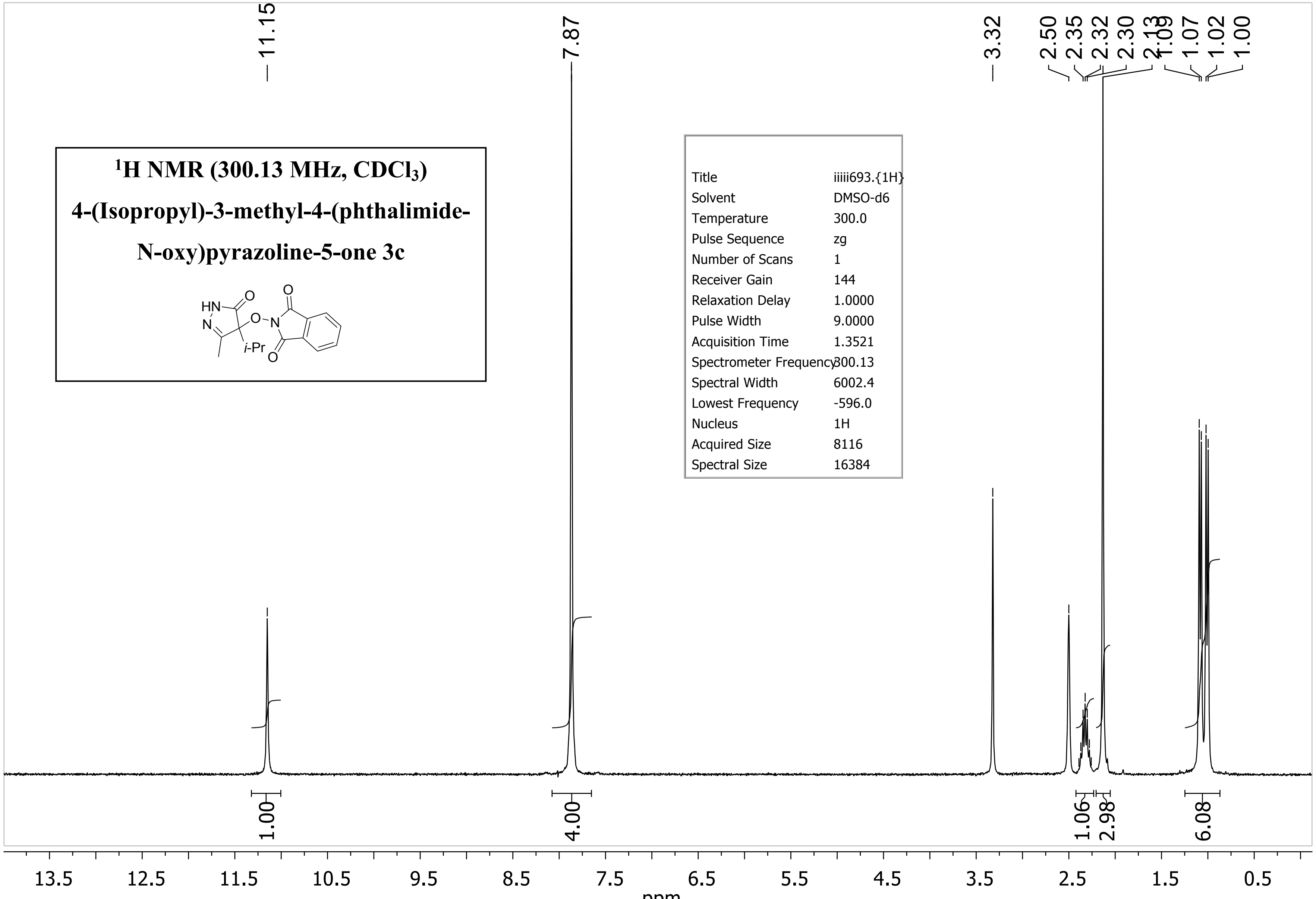
Title	iiiii686.{1H}
Solvent	DMSO-d6
Temperature	297.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-596.9
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d$_6$)

4-Allyl-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3b

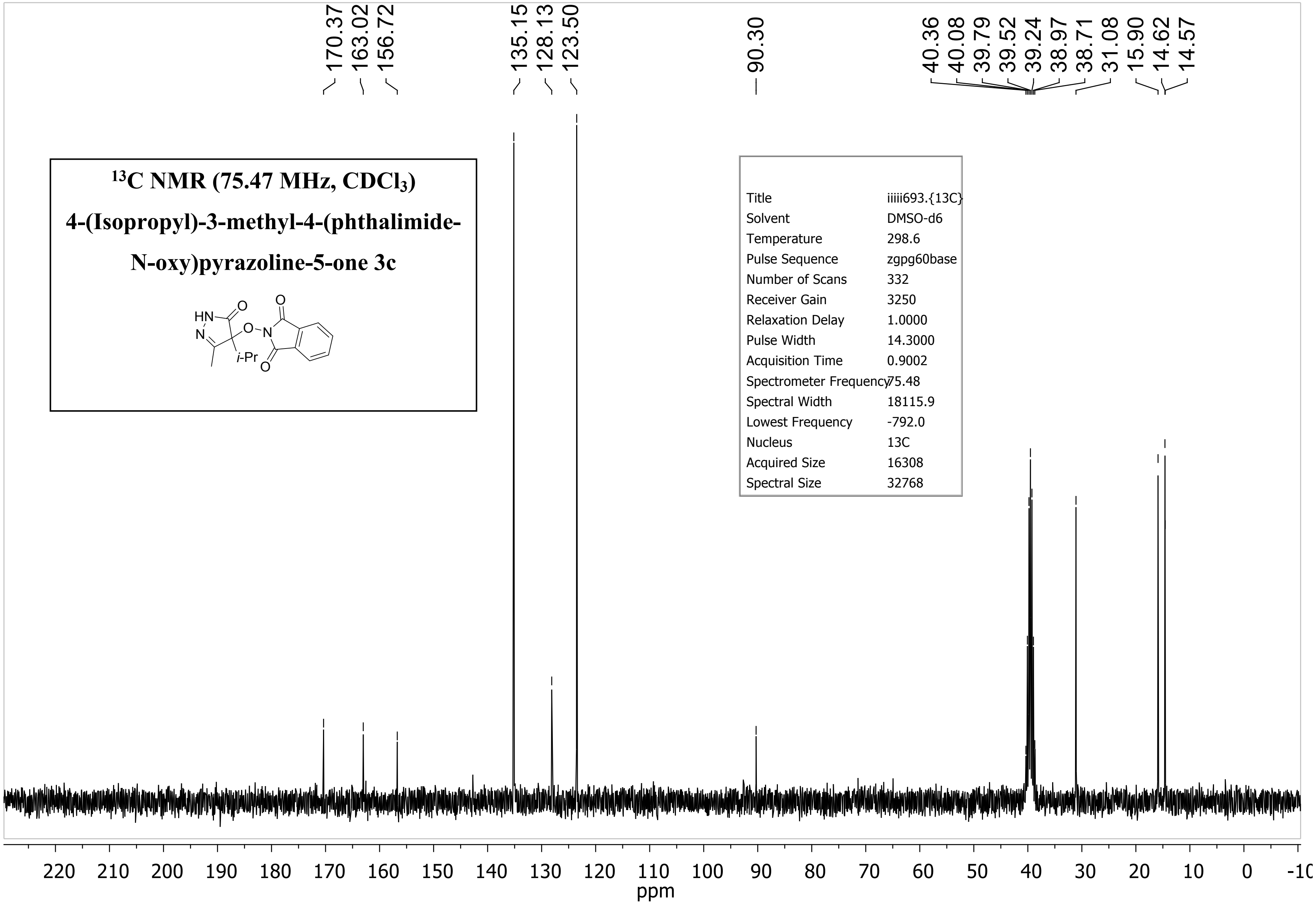
Title	i1326.{13C}
Solvent	DMSO-d6
Temperature	297.5
Pulse Sequence	zgpg60base
Number of Scans	689
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-793.4
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



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

4-(Isopropyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3c

Title	iiiii693.{1H}
Solvent	DMSO-d6
Temperature	300.0
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-596.0
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



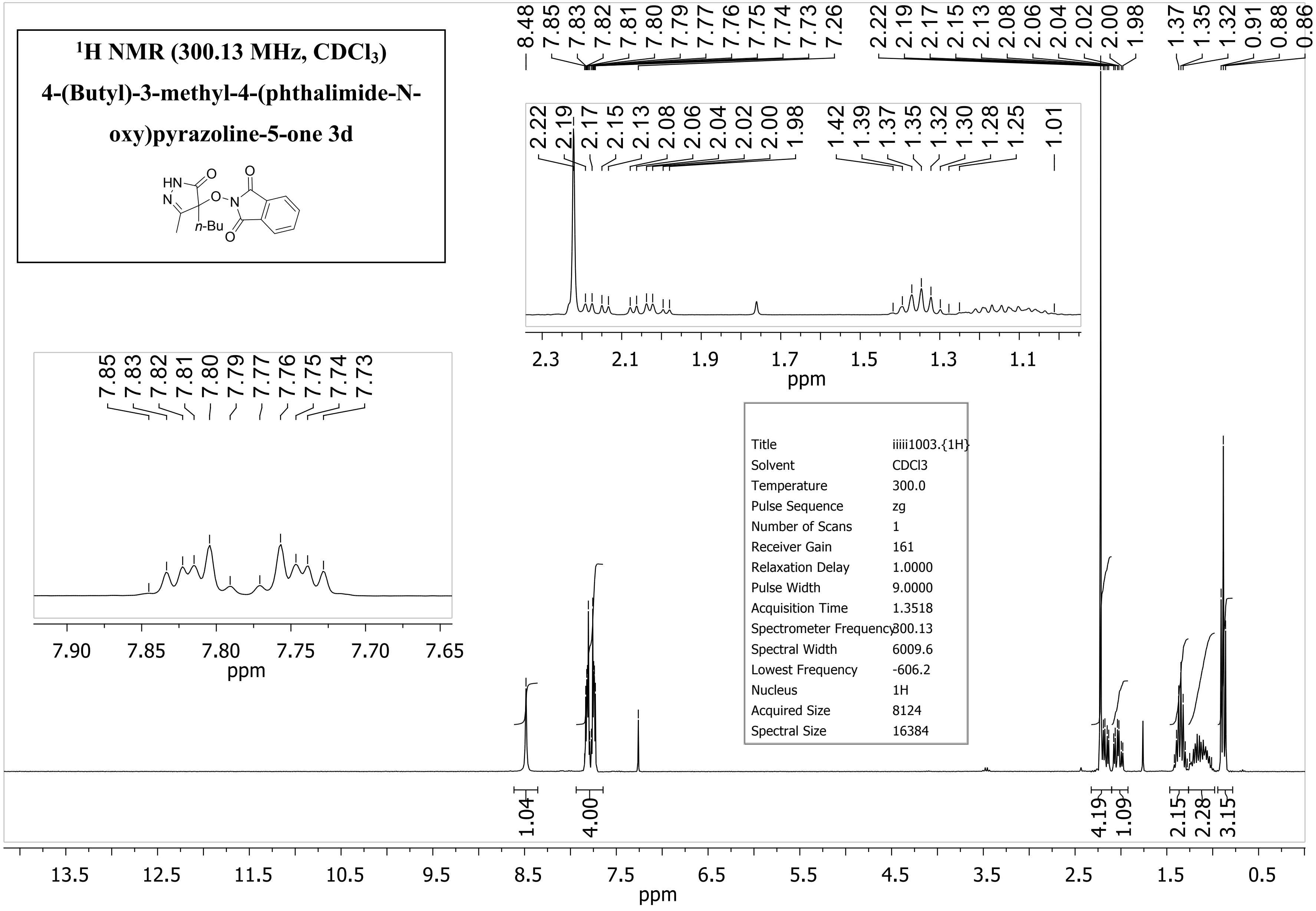
^{13}C NMR (75.47 MHz, $CDCl_3$)

4-(Isopropyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3c

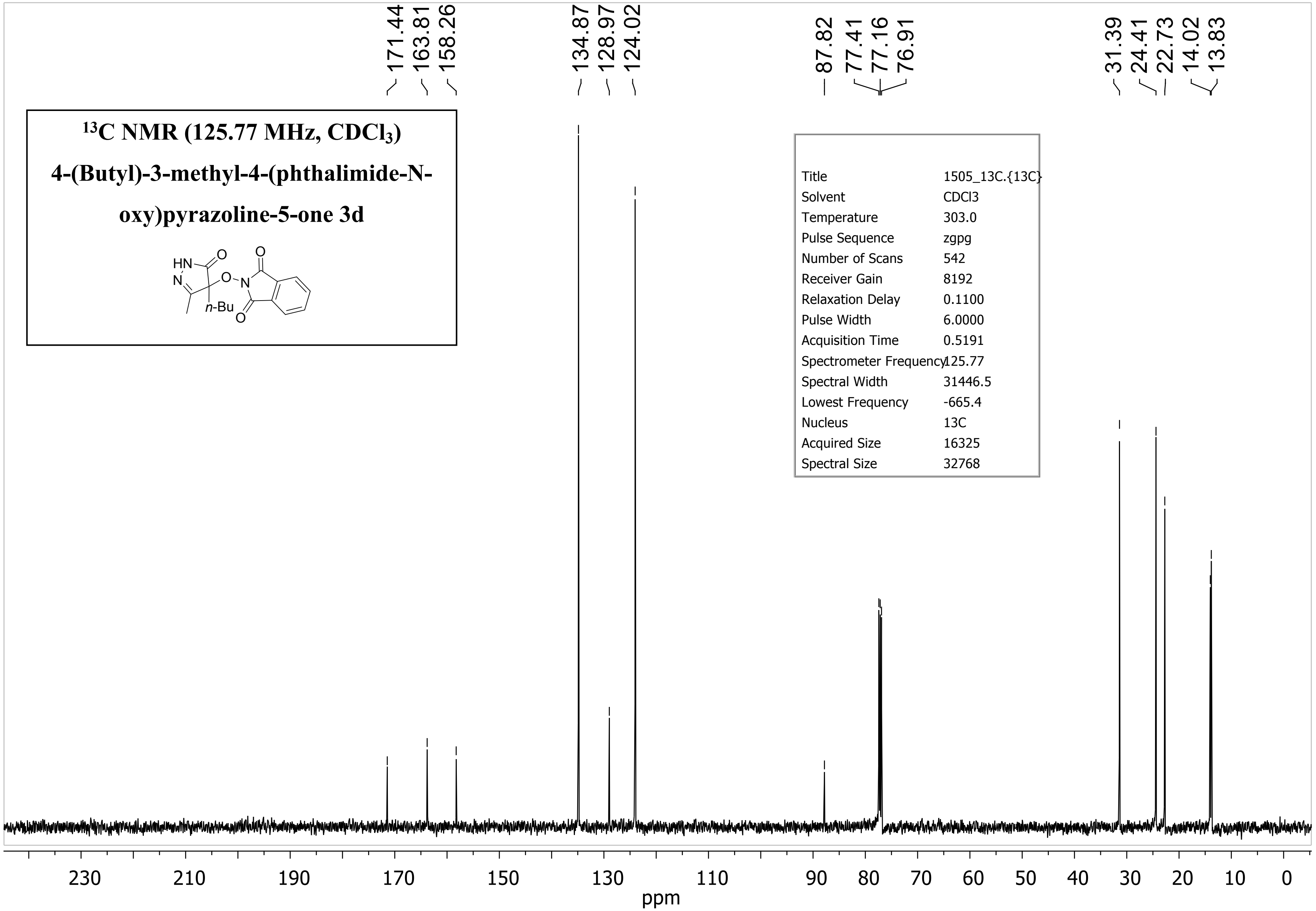
Title	iiiii693.{13C}
Solvent	DMSO-d6
Temperature	298.6
Pulse Sequence	zgpg60base
Number of Scans	332
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-792.0
Nucleus	13C
Acquired Size	16308
Spectral Size	32768

^{1}H NMR (300.13 MHz, CDCl$_3$)

4-(Butyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3d



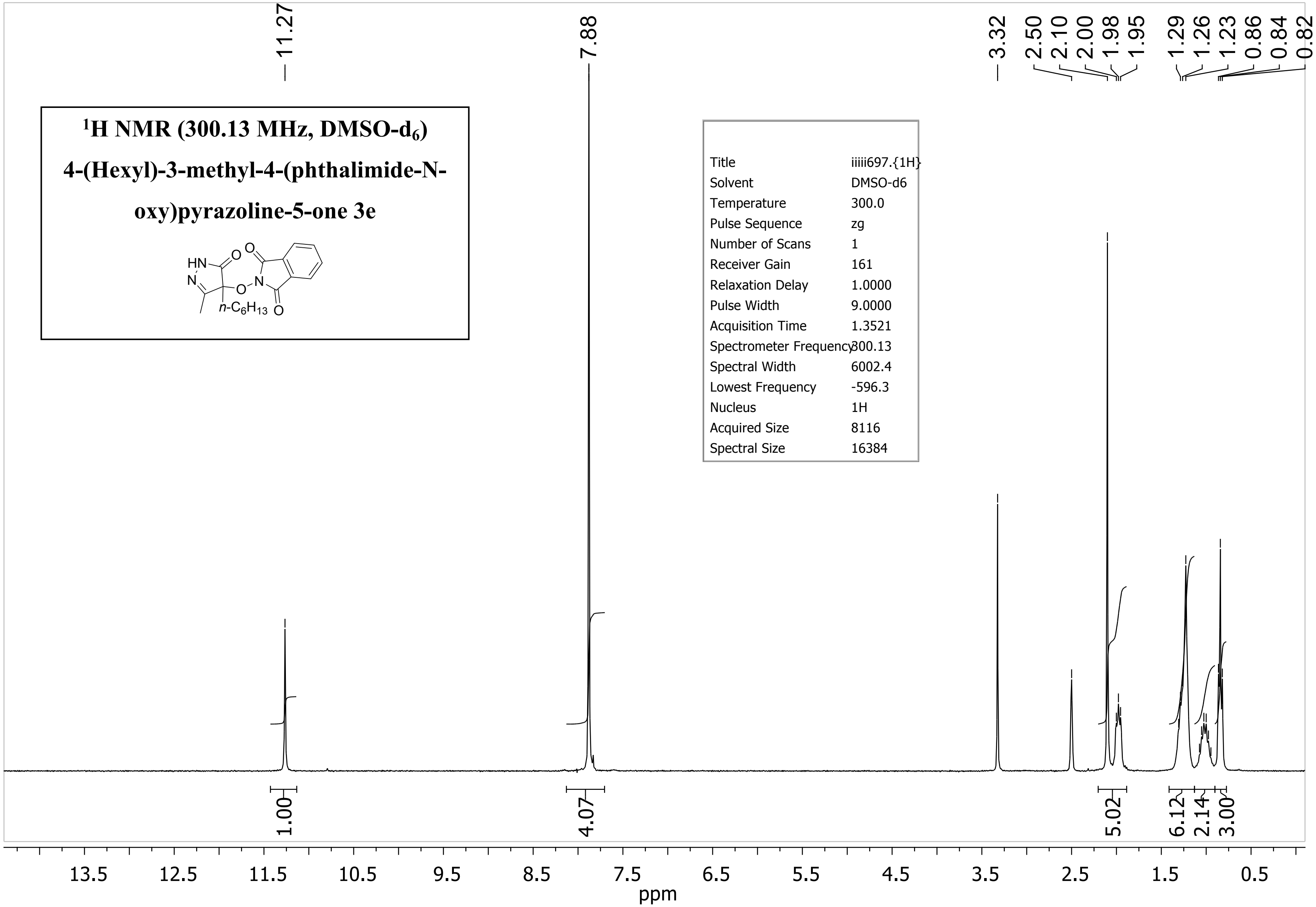
Title	iiiii1003.{1H}
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-606.2
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{13}C NMR (125.77 MHz, CDCl$_3$)

4-(Butyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3d

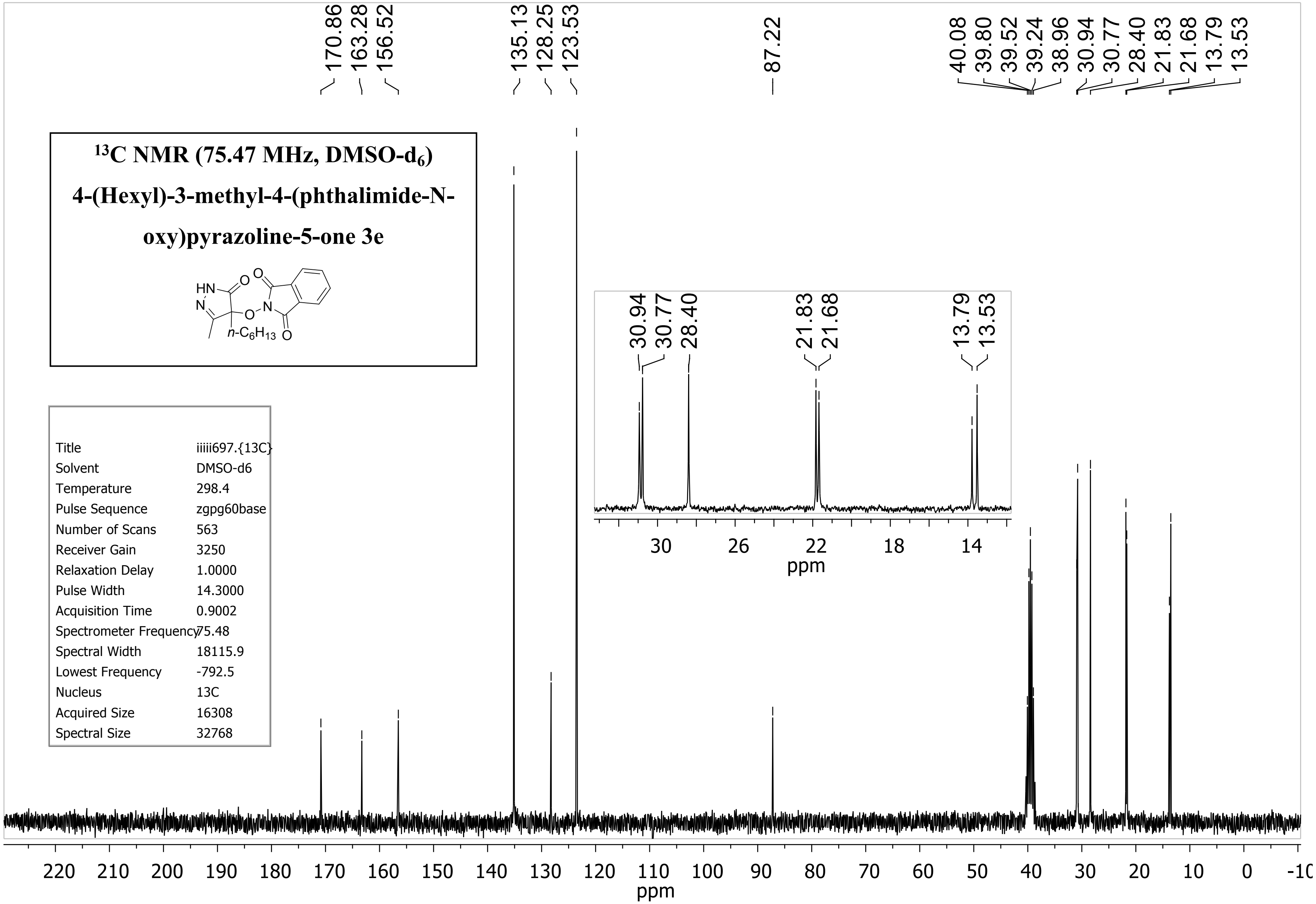
Title	1505_13C.{13C}
Solvent	CDCl3
Temperature	303.0
Pulse Sequence	zgpg
Number of Scans	542
Receiver Gain	8192
Relaxation Delay	0.1100
Pulse Width	6.0000
Acquisition Time	0.5191
Spectrometer Frequency	125.77
Spectral Width	31446.5
Lowest Frequency	-665.4
Nucleus	13C
Acquired Size	16325
Spectral Size	32768



^{1}H NMR (300.13 MHz, DMSO-d$_6$)

4-(Hexyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3e

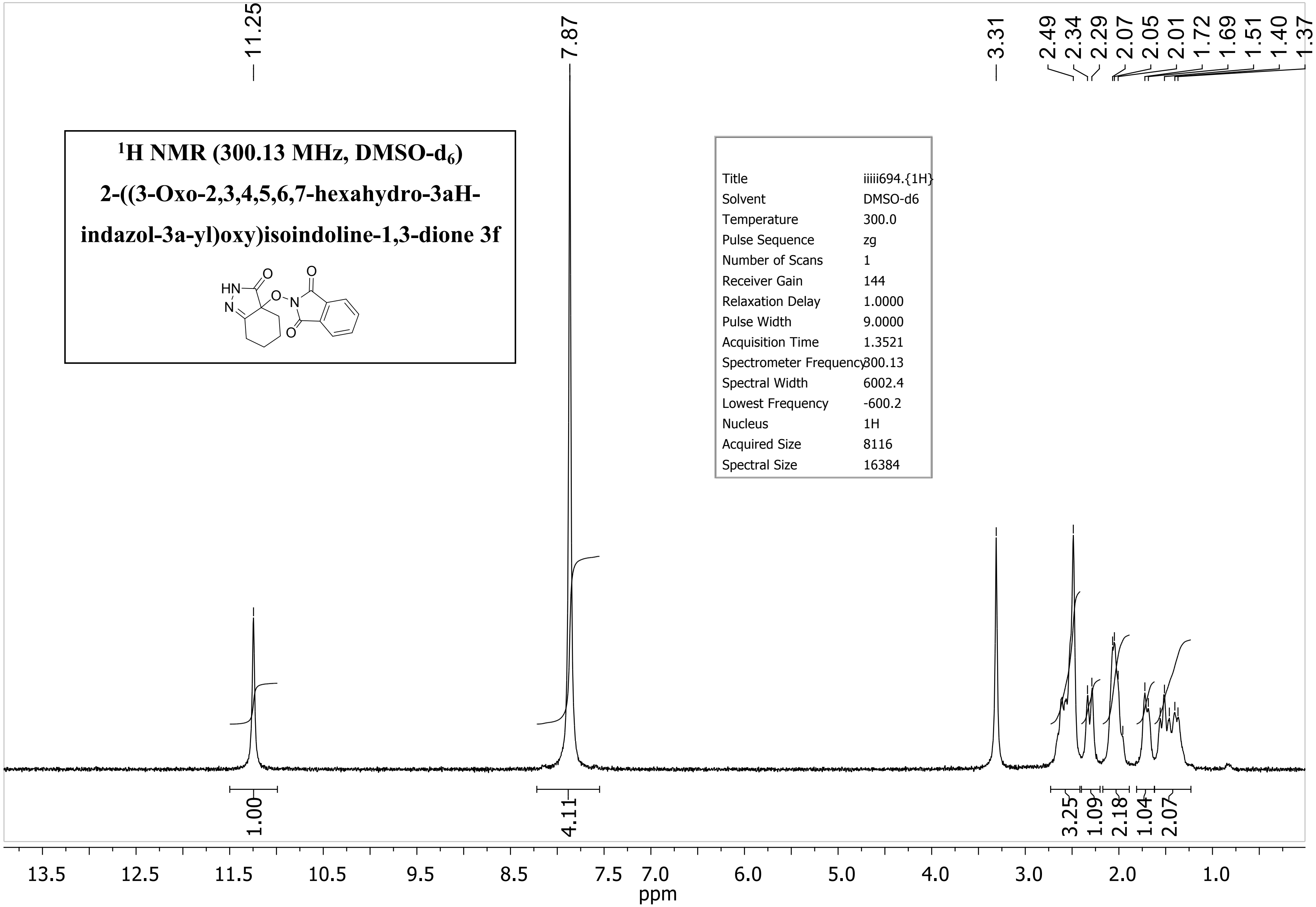
Title	iiiii697.{1H}
Solvent	DMSO-d6
Temperature	300.0
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-596.3
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d_6)

4-(Hexyl)-3-methyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3e

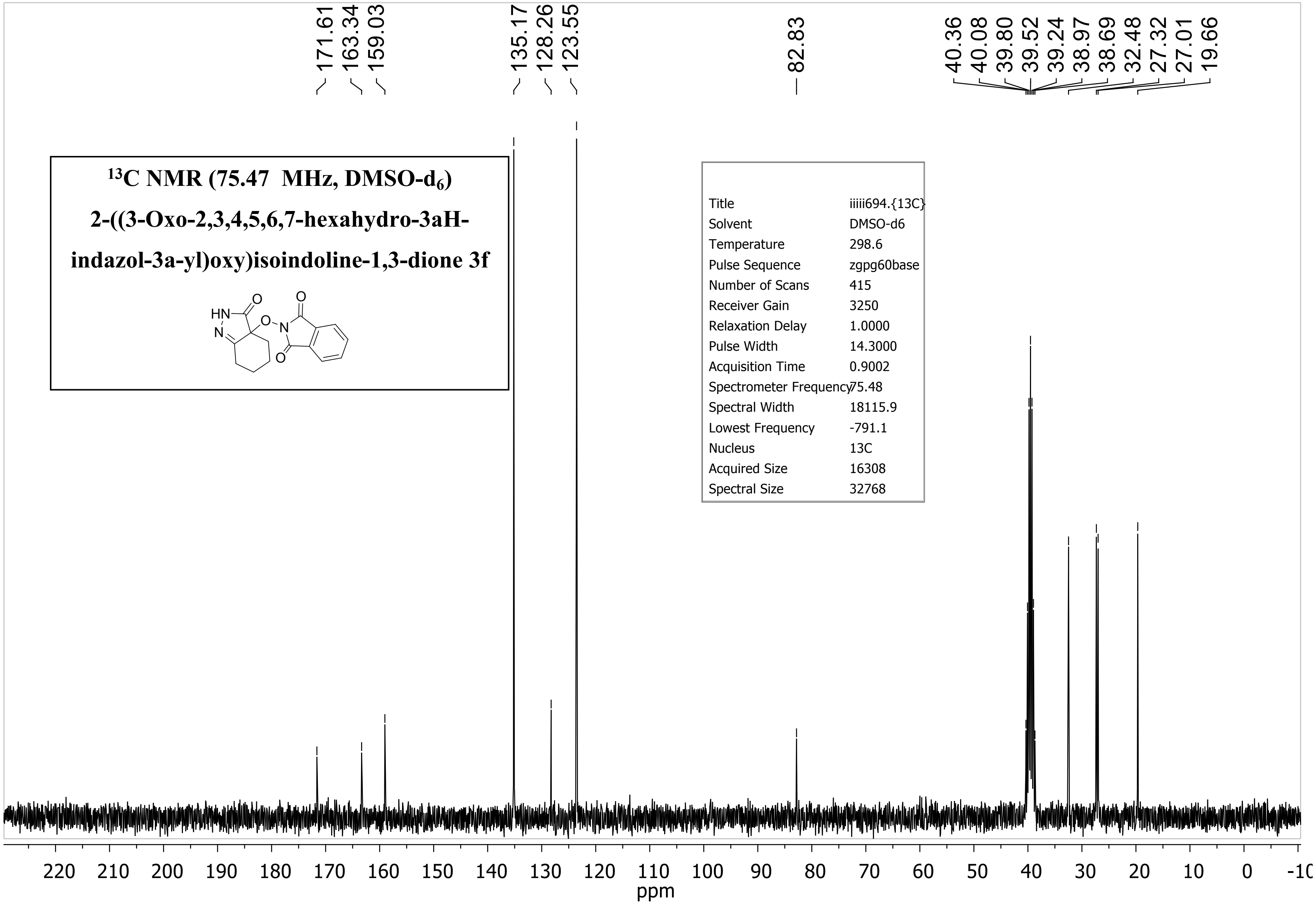
Title	iiiii697.{13C}
Solvent	DMSO-d6
Temperature	298.4
Pulse Sequence	zgpg60base
Number of Scans	563
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-792.5
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



^{1}H NMR (300.13 MHz, DMSO-d$_6$)

2-((3-Oxo-2,3,4,5,6,7-hexahydro-3aH-indazol-3a-yl)oxy)isoindoline-1,3-dione 3f

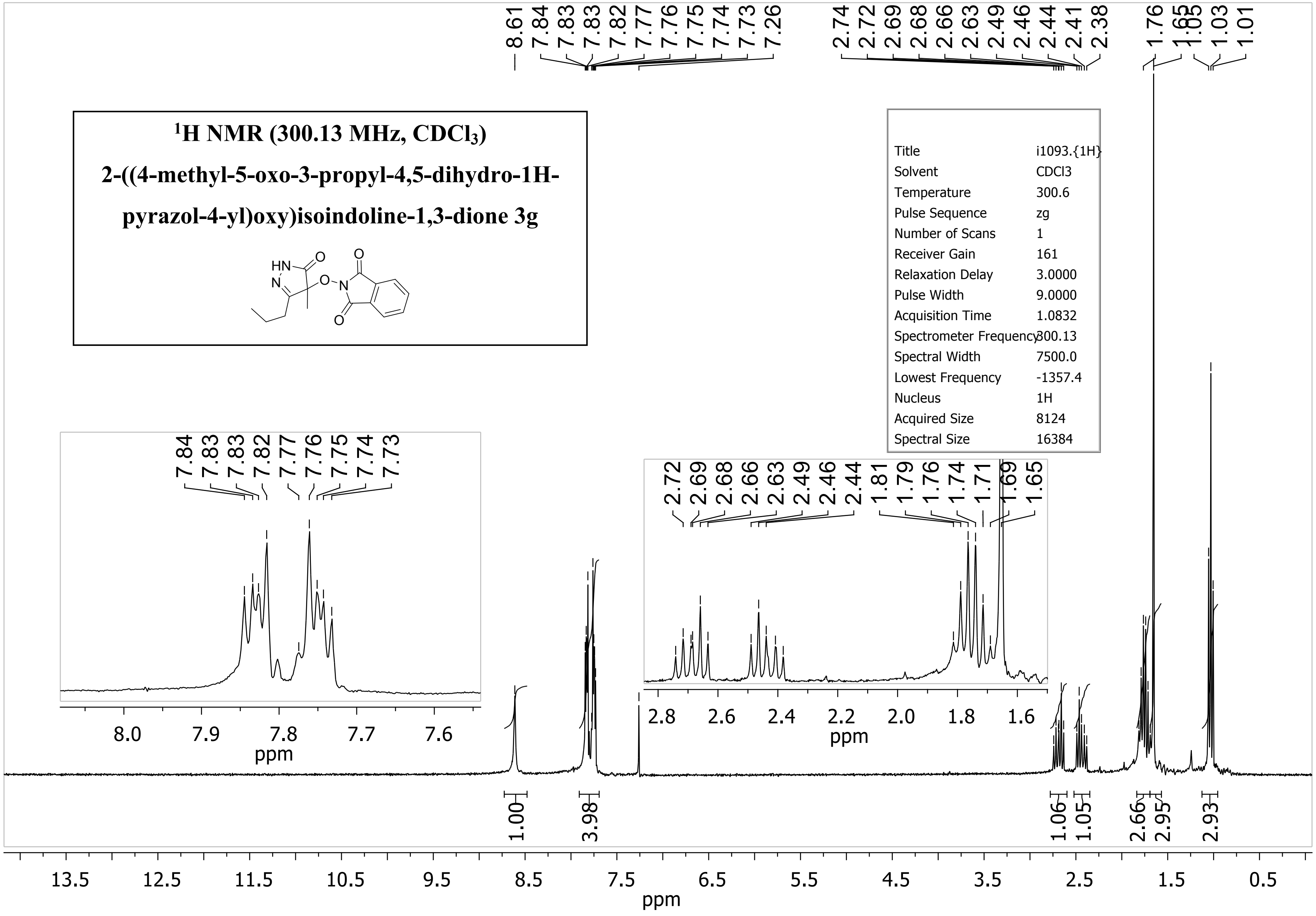
Title	iiiii694.{1H}
Solvent	DMSO-d6
Temperature	300.0
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-600.2
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d_6)

2-((3-Oxo-2,3,4,5,6,7-hexahydro-3aH-indazol-3a-yl)oxy)isoindoline-1,3-dione 3f

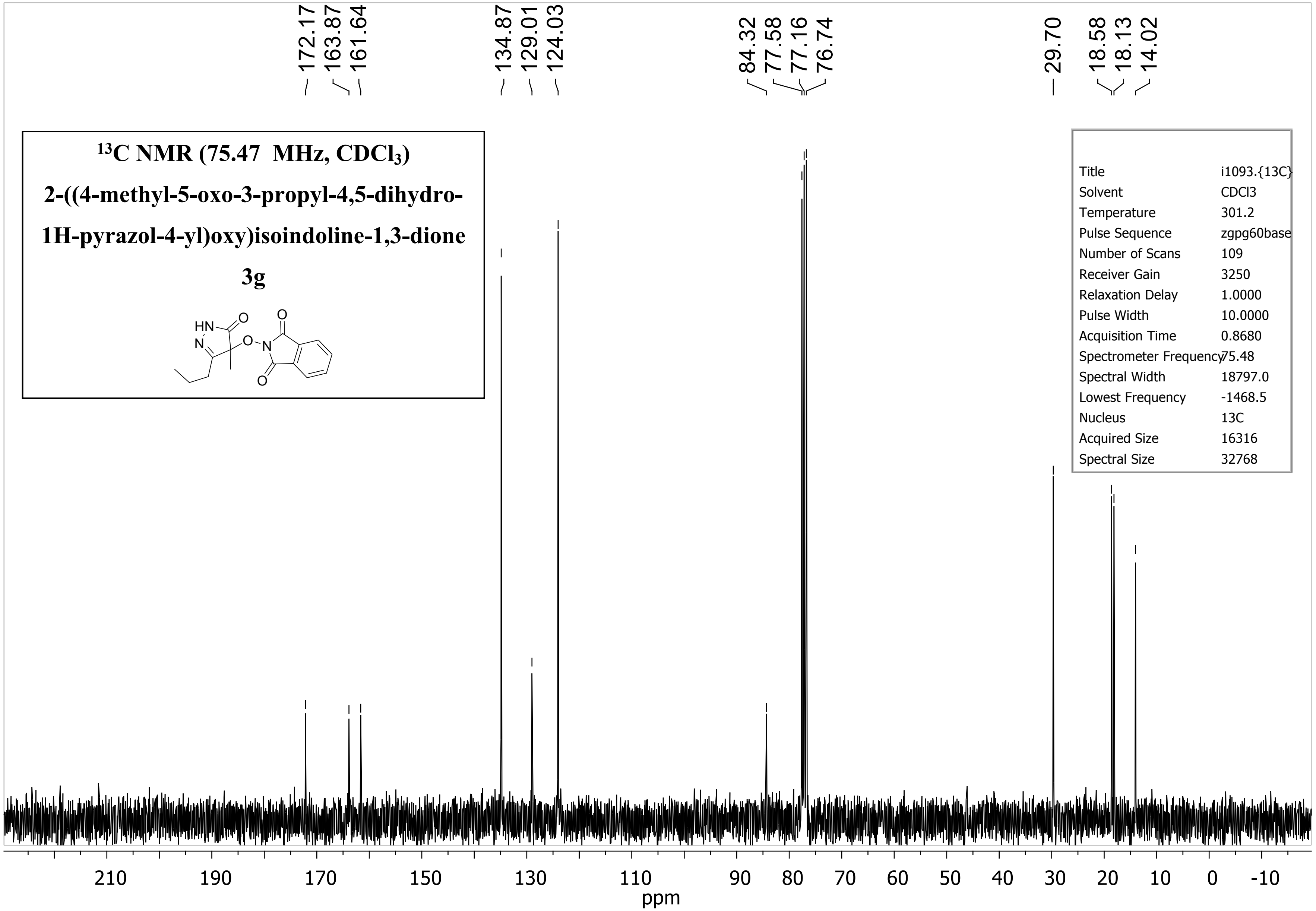
Title	iiiii694.{13C}
Solvent	DMSO-d6
Temperature	298.6
Pulse Sequence	zgpg60base
Number of Scans	415
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-791.1
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



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

2-((4-methyl-5-oxo-3-propyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)isoindoline-1,3-dione 3g

Title	i1093.{1H}
Solvent	CDCl3
Temperature	300.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	3.0000
Pulse Width	9.0000
Acquisition Time	1.0832
Spectrometer Frequency	300.13
Spectral Width	7500.0
Lowest Frequency	-1357.4
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{13}C NMR (75.47 MHz, CDCl$_3$)

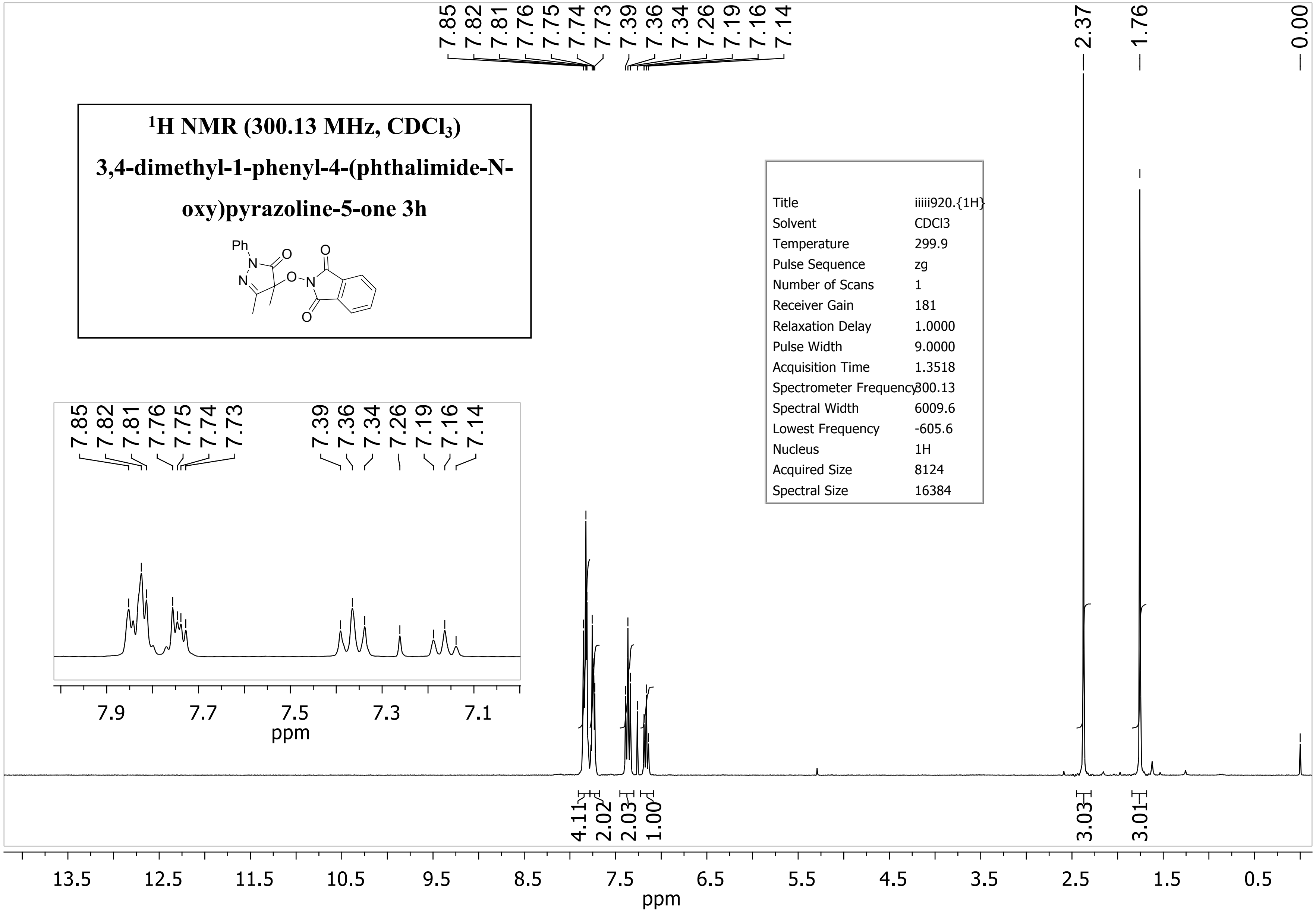
2-((4-methyl-5-oxo-3-propyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)isoindoline-1,3-dione

3g

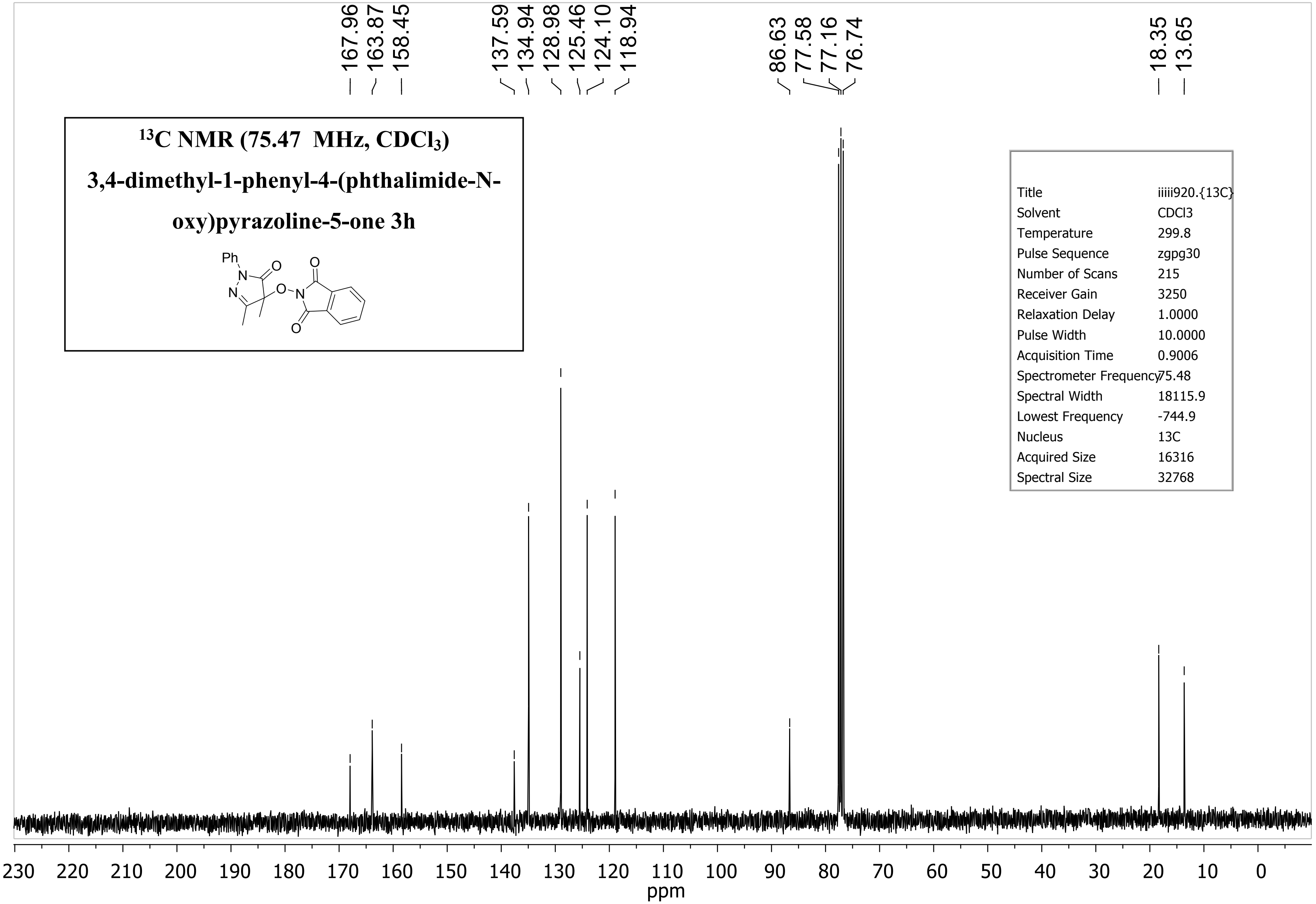
Title	i1093.{13C}
Solvent	CDCl3
Temperature	301.2
Pulse Sequence	zgpg60base
Number of Scans	109
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.8680
Spectrometer Frequency	75.48
Spectral Width	18797.0
Lowest Frequency	-1468.5
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

^{1}H NMR (300.13 MHz, CDCl$_3$)

3,4-dimethyl-1-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3h



Title	iiiii920.{1H}
Solvent	CDCl3
Temperature	299.9
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-605.6
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



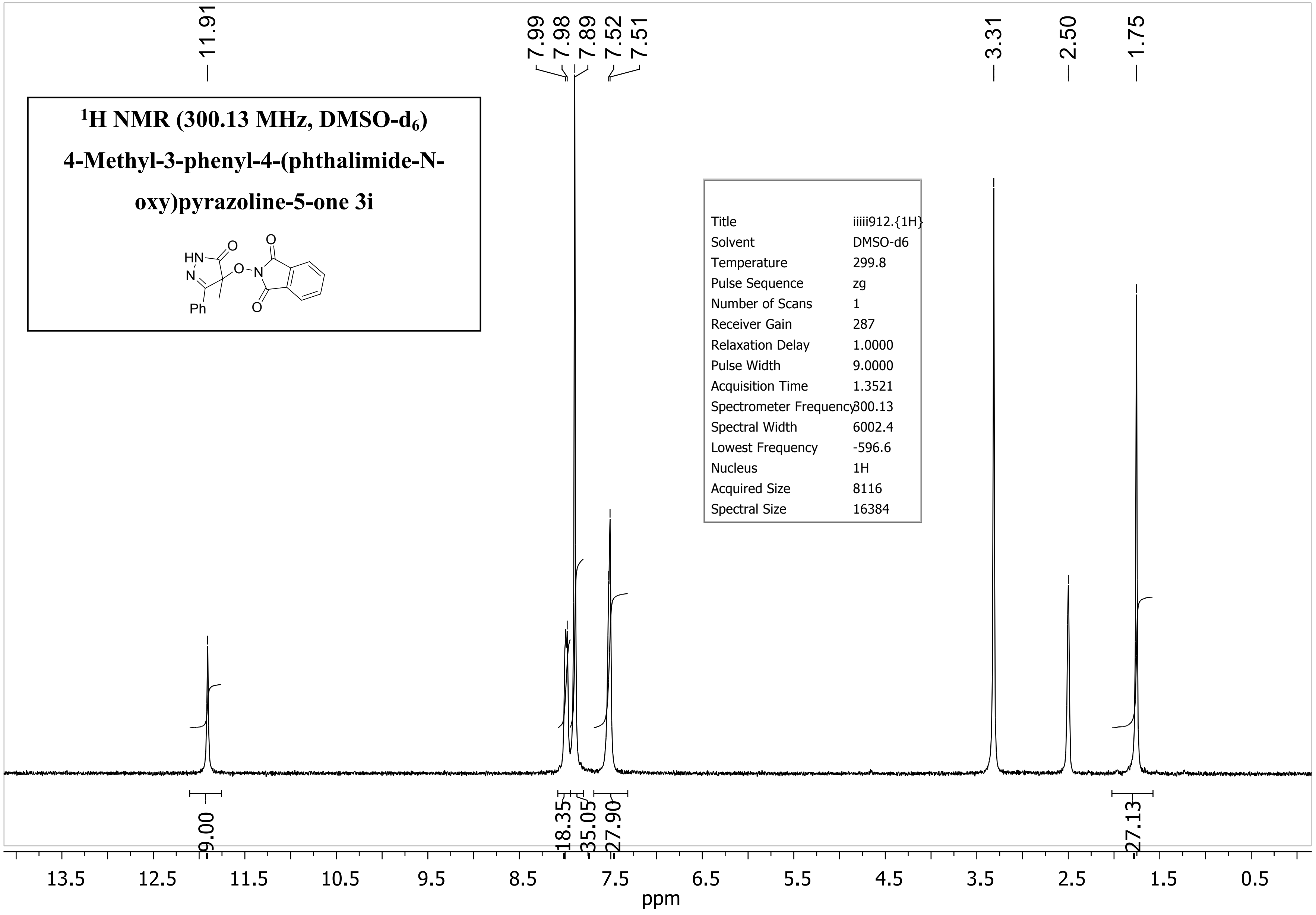
^{13}C NMR (75.47 MHz, CDCl$_3$)

3,4-dimethyl-1-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3h

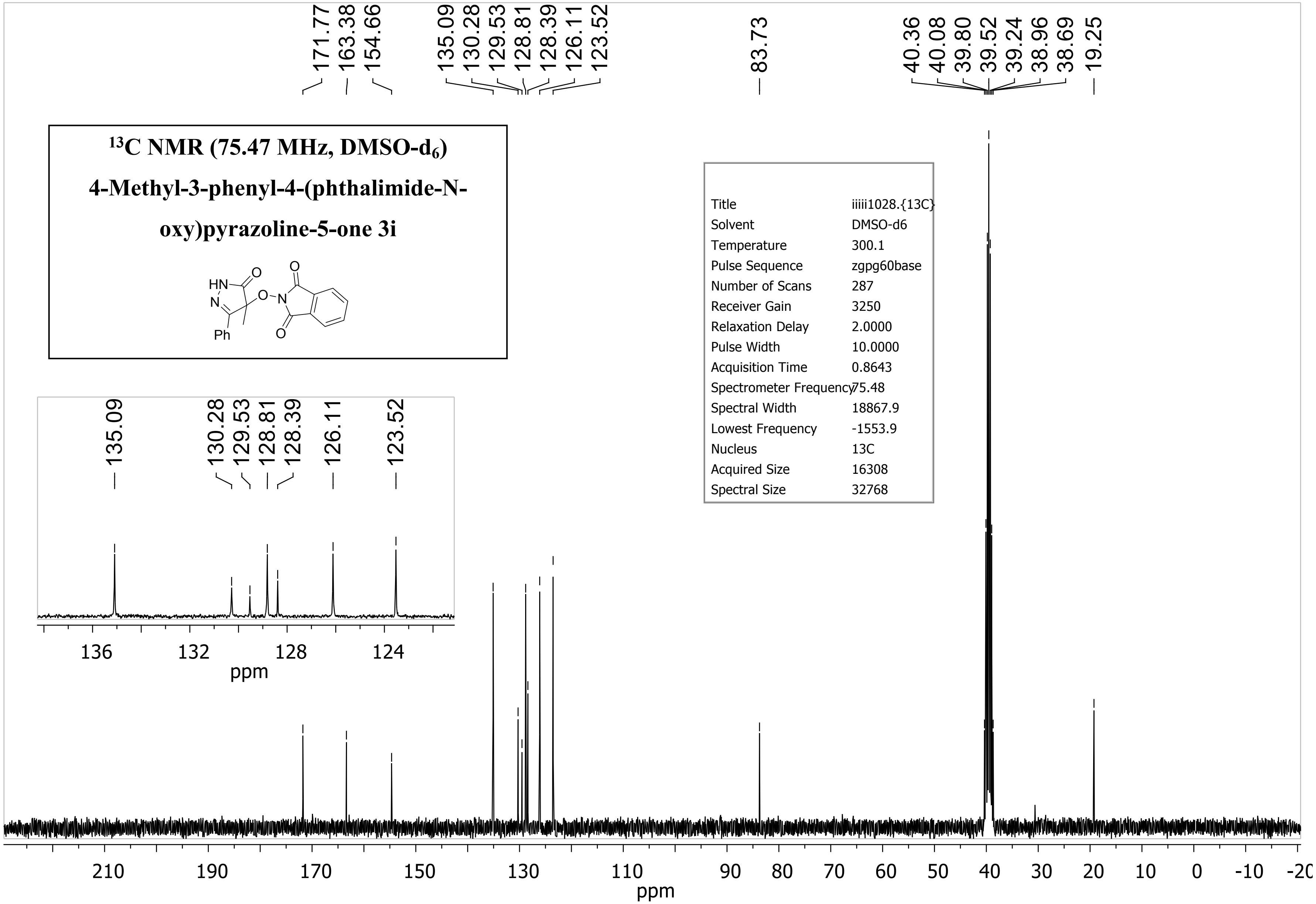
Title	iiiii920.{13C}
Solvent	CDCl3
Temperature	299.8
Pulse Sequence	zgpg30
Number of Scans	215
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-744.9
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

^{1}H NMR (300.13 MHz, DMSO-d_6)

4-Methyl-3-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3i



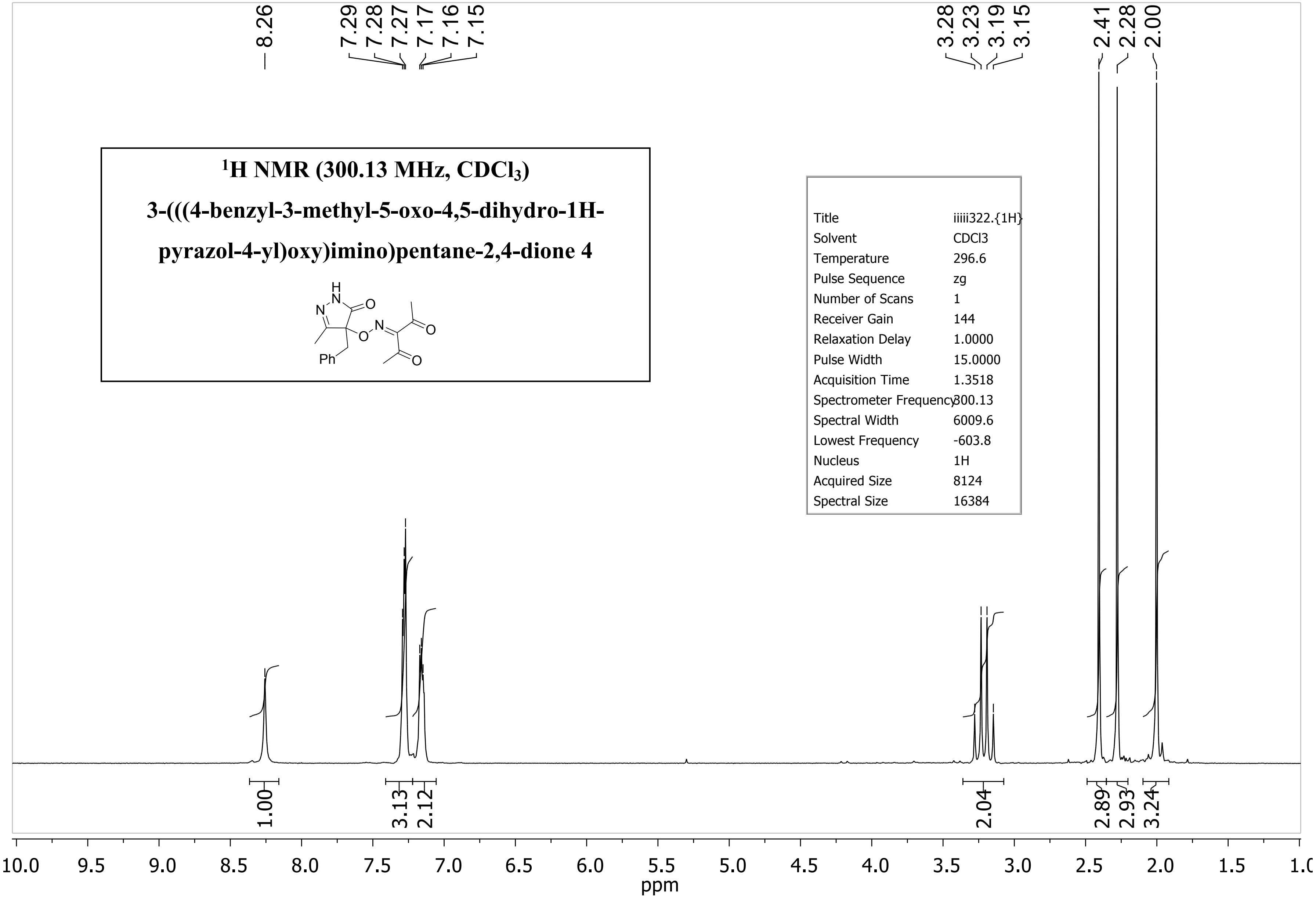
Title	iiiii912.{1H}
Solvent	DMSO-d6
Temperature	299.8
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-596.6
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d$_6$)

4-Methyl-3-phenyl-4-(phthalimide-N-oxy)pyrazoline-5-one 3i

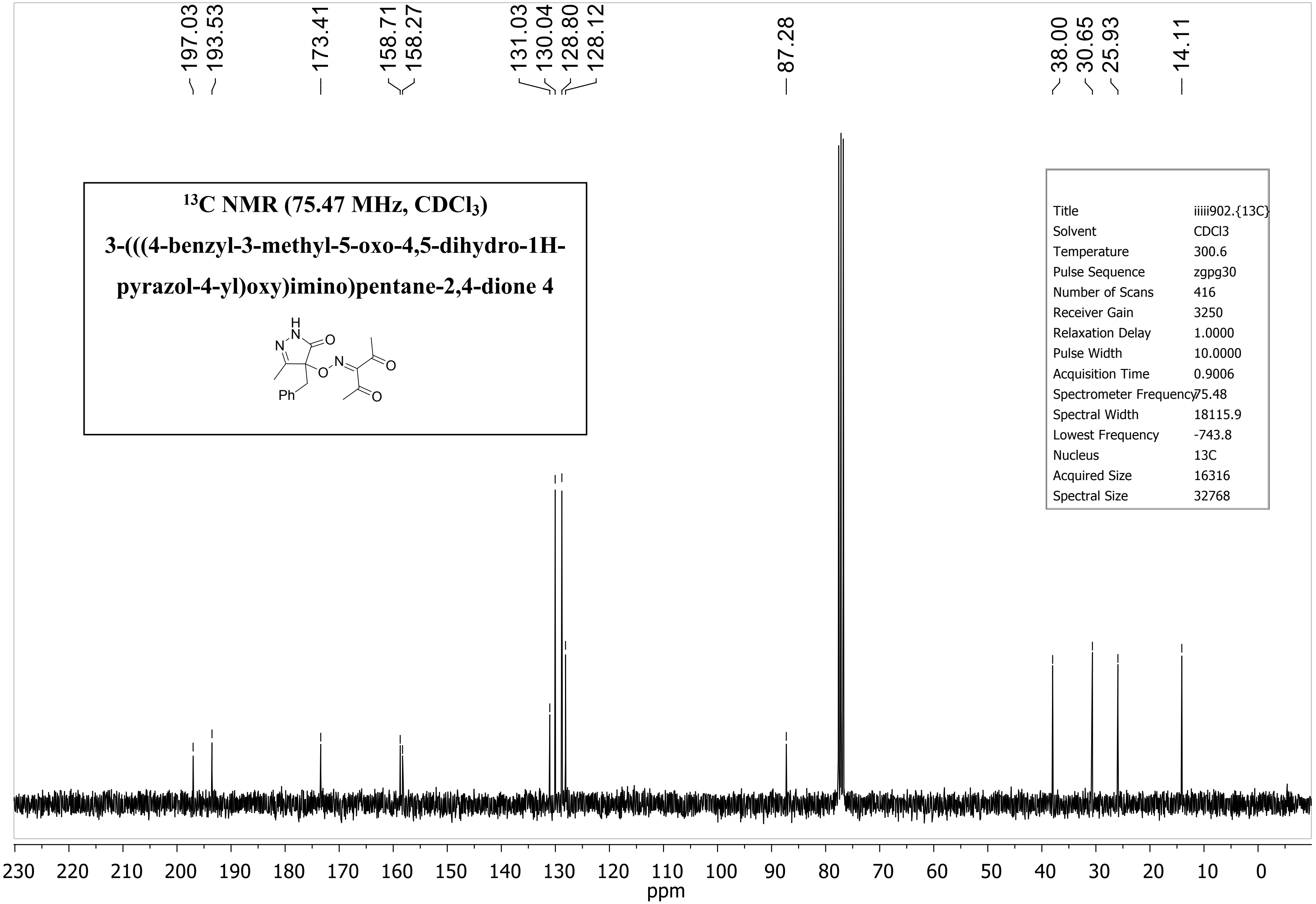
Title	iiiii1028.{13C}
Solvent	DMSO-d6
Temperature	300.1
Pulse Sequence	zgpg60base
Number of Scans	287
Receiver Gain	3250
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	0.8643
Spectrometer Frequency	75.48
Spectral Width	18867.9
Lowest Frequency	-1553.9
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



^{1}H NMR (300.13 MHz, CDCl$_3$)

3-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 4

Title	iiiii322.{1H}
Solvent	CDCl3
Temperature	296.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	15.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-603.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



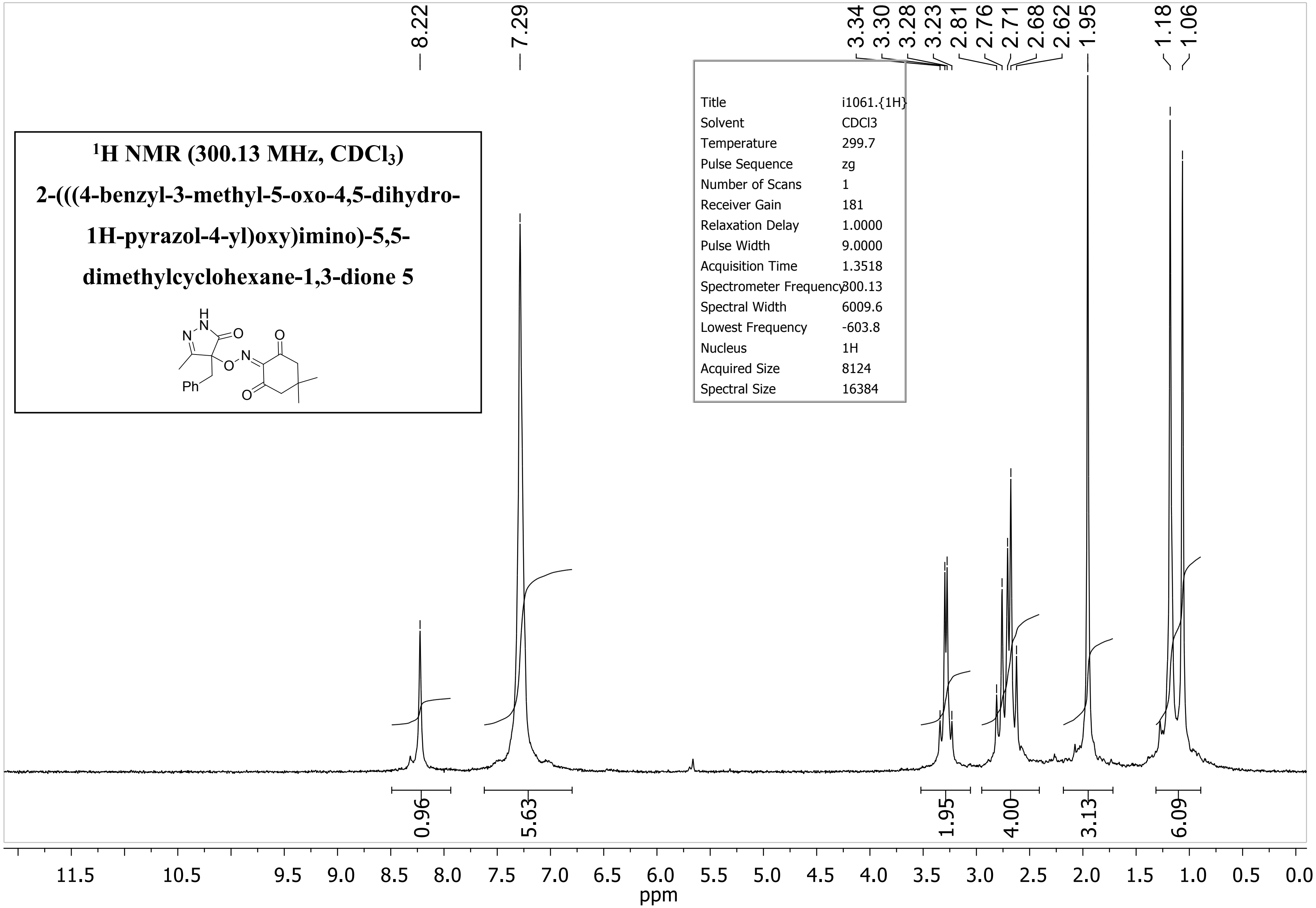
^{13}C NMR (75.47 MHz, $CDCl_3$)

3-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 4

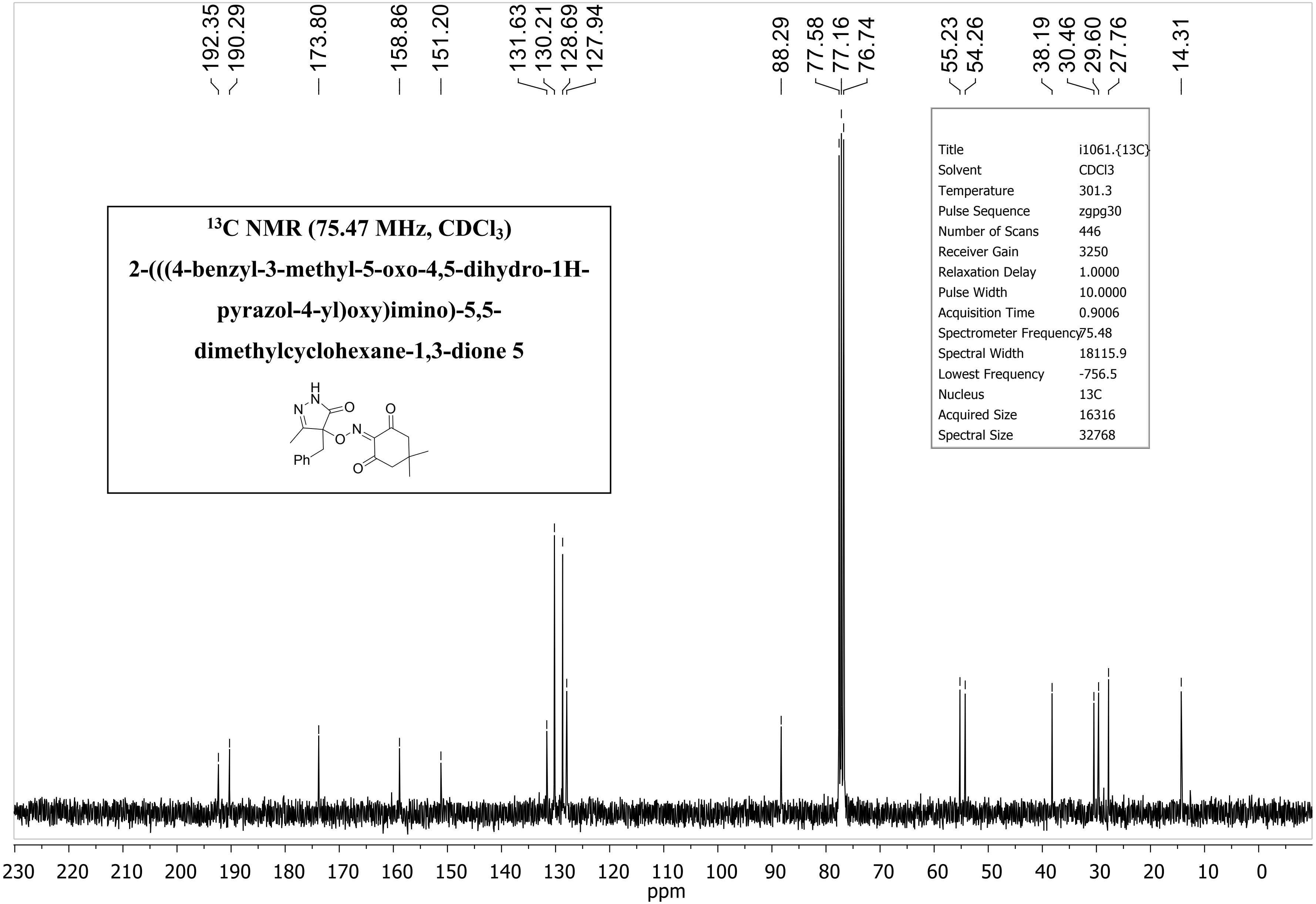
Title	iiiii902.{13C}
Solvent	CDCl3
Temperature	300.6
Pulse Sequence	zgpg30
Number of Scans	416
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-743.8
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

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

2-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-5,5-dimethylcyclohexane-1,3-dione 5



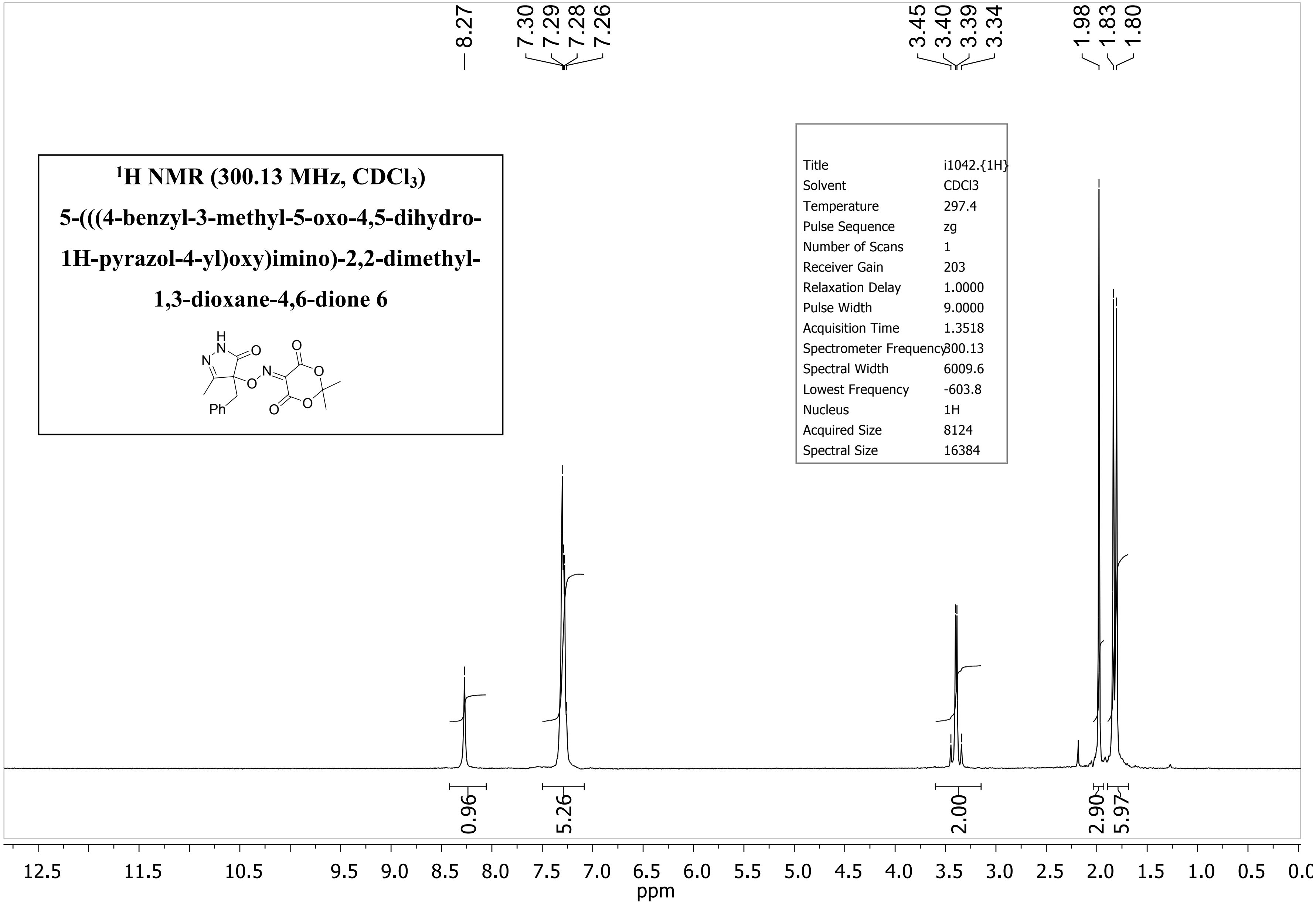
Title	i1061.{1H}
Solvent	CDCl3
Temperature	299.7
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-603.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



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

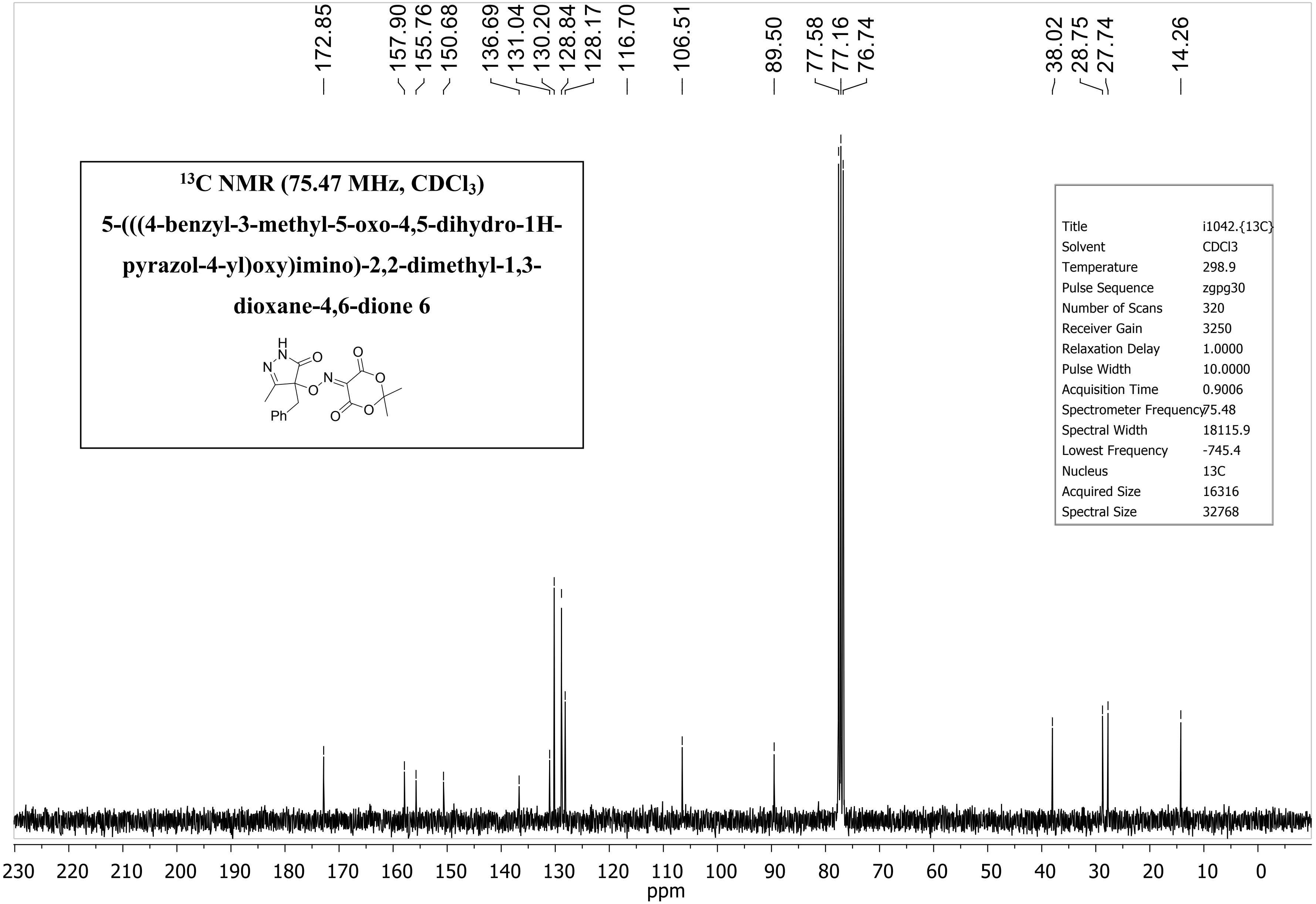
2-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-5,5-dimethylcyclohexane-1,3-dione 5

Title	i1061.{13C}
Solvent	CDCl3
Temperature	301.3
Pulse Sequence	zgpg30
Number of Scans	446
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	-756.5
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



^{1}H NMR (300.13 MHz, $CDCl_3$)
5-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-2,2-dimethyl-1,3-dioxane-4,6-dione 6

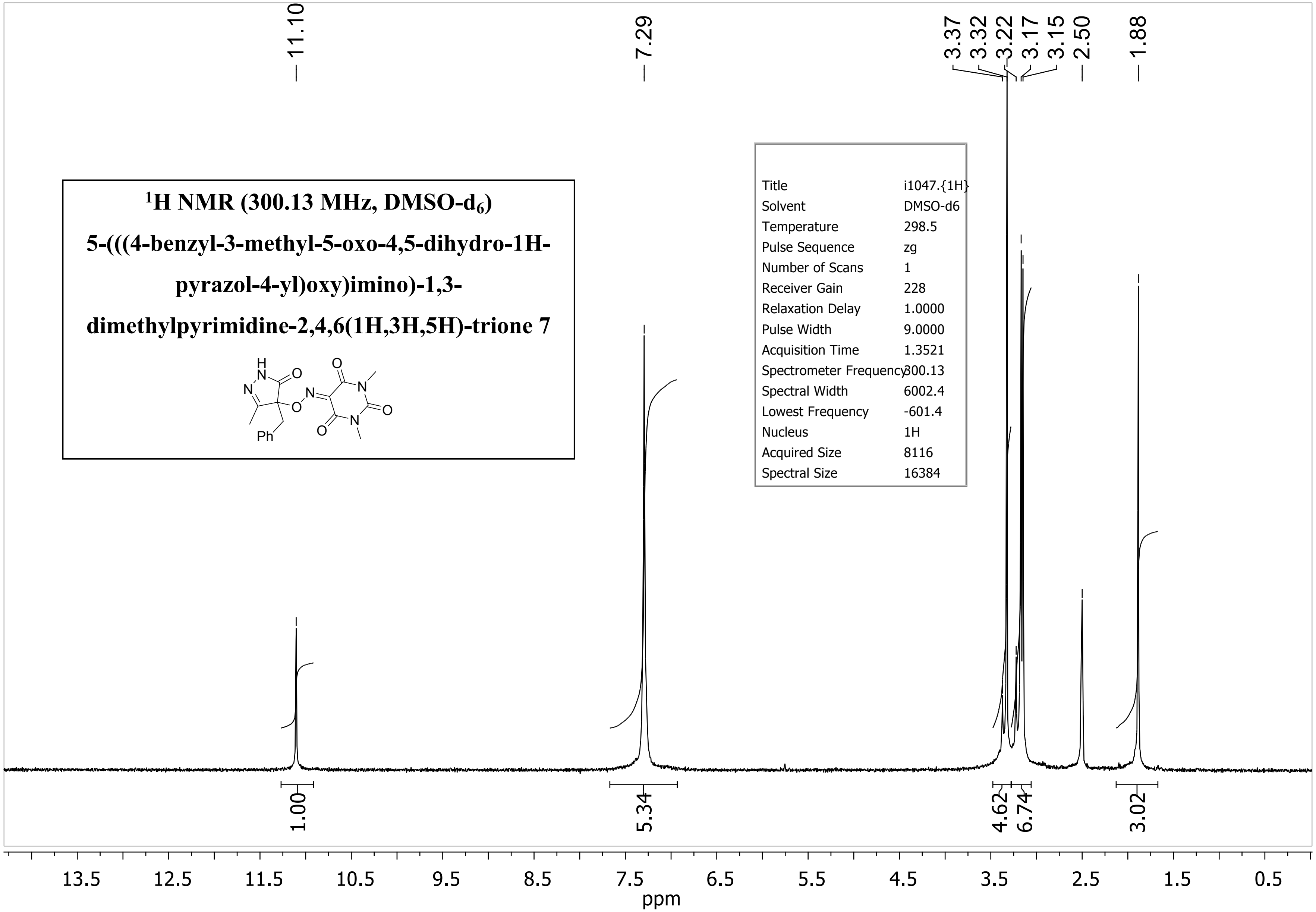
Title	i1042.{1H}
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-603.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{13}C NMR (75.47 MHz, CDCl$_3$)

5-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-2,2-dimethyl-1,3-dioxane-4,6-dione 6

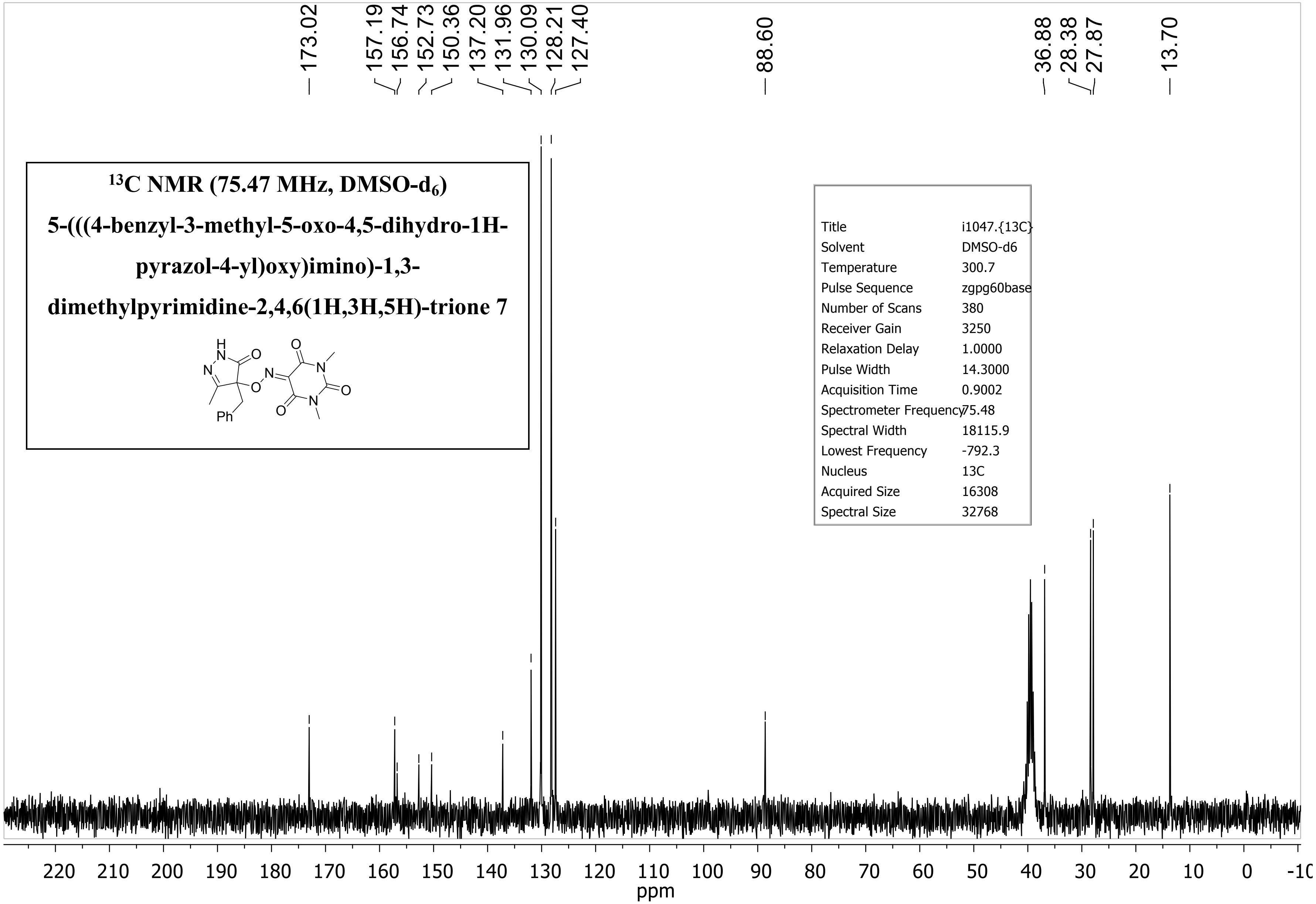
Title	i1042.{13C}
Solvent	CDCl3
Temperature	298.9
Pulse Sequence	zgpg30
Number of Scans	320
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-745.4
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



^{1}H NMR (300.13 MHz, DMSO-d_6)

5-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione 7

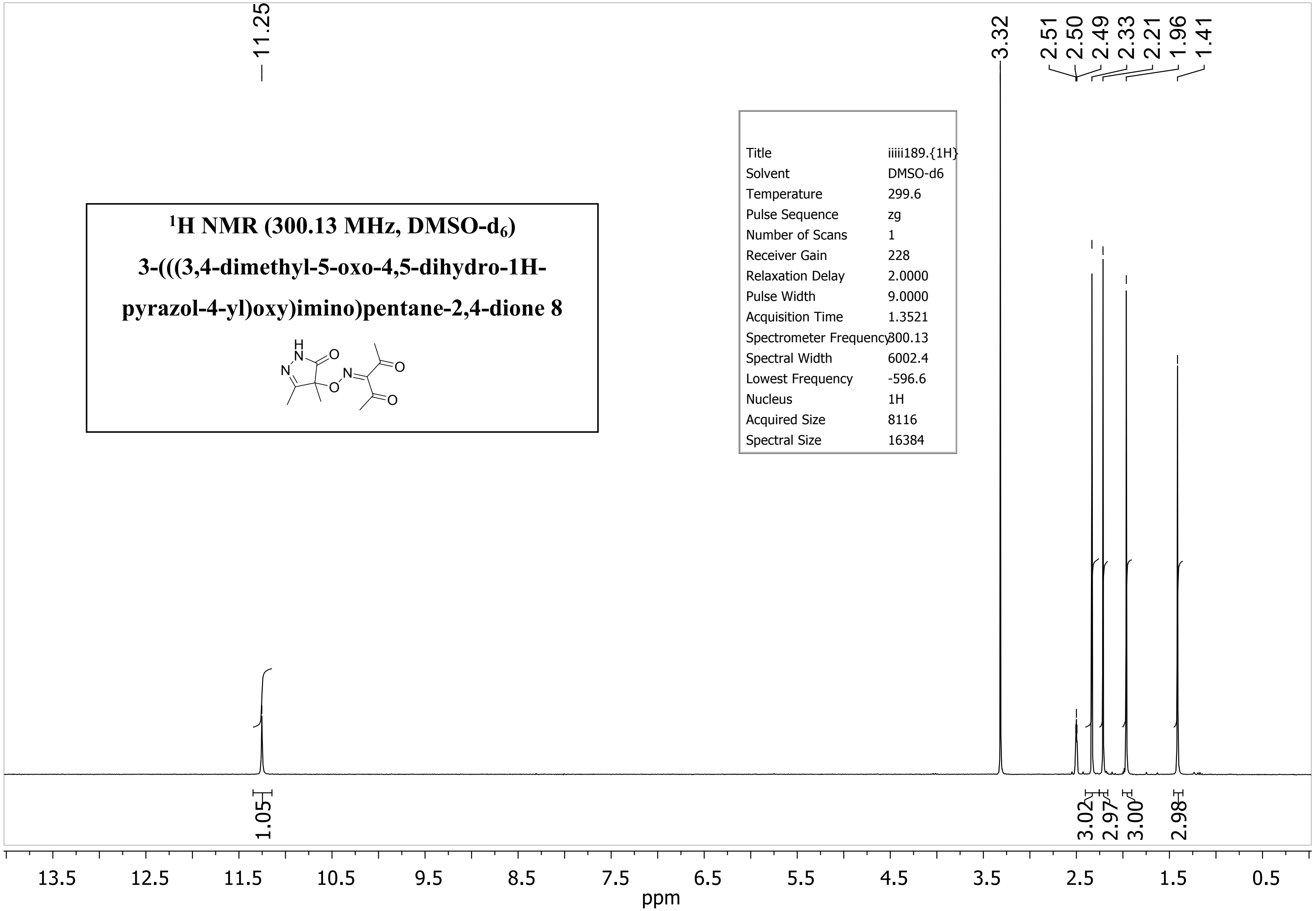
Title	i1047.{1H}
Solvent	DMSO-d6
Temperature	298.5
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-601.4
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d$_6$)

5-(((4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione 7

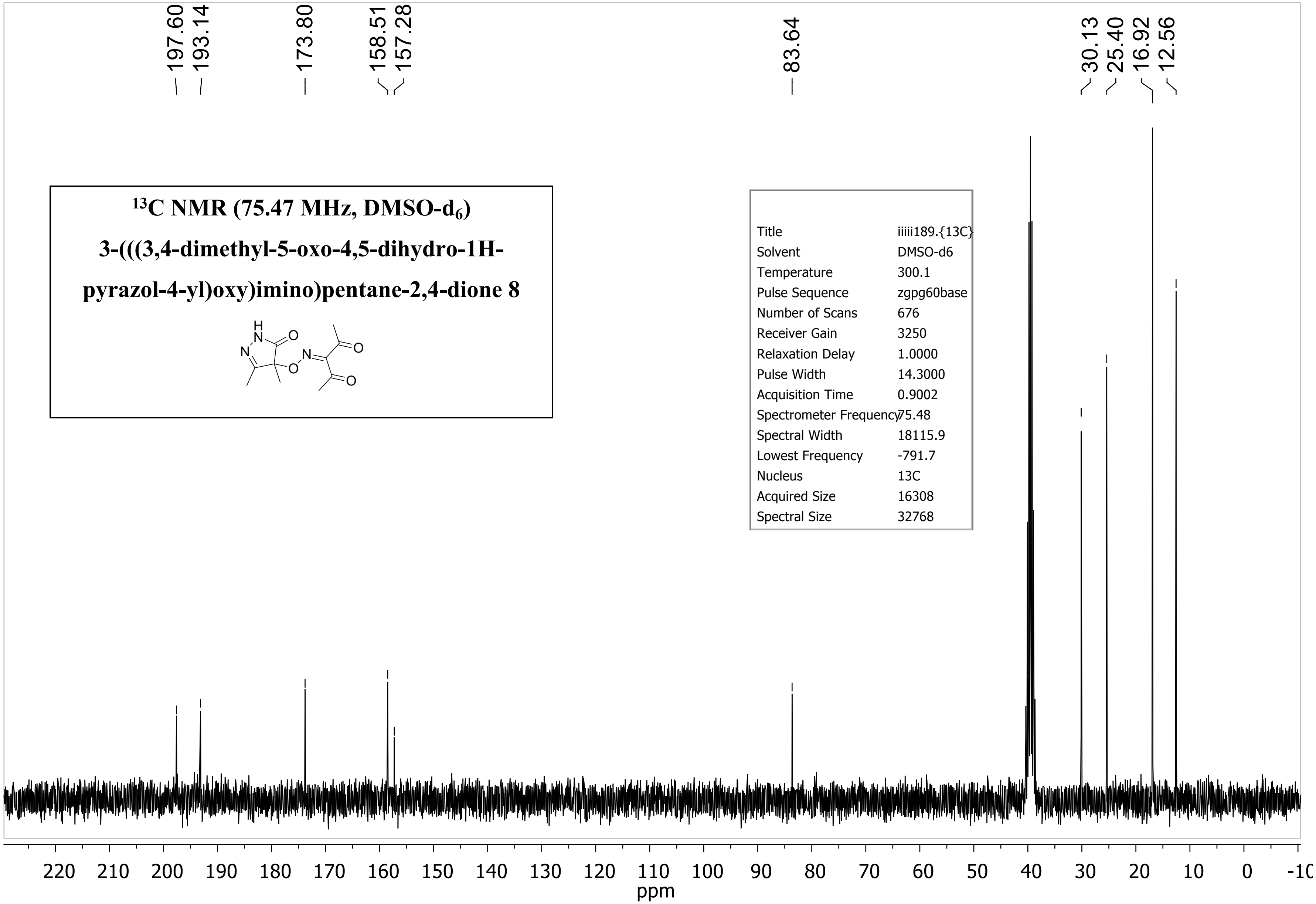
Title	i1047.{13C}
Solvent	DMSO-d6
Temperature	300.7
Pulse Sequence	zgpg60base
Number of Scans	380
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-792.3
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



^{1}H NMR (300.13 MHz, DMSO-d$_6$)

3-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 8

Title	iiiii189.{1H}
Solvent	DMSO-d6
Temperature	299.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	228
Relaxation Delay	2.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-596.6
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d_6)

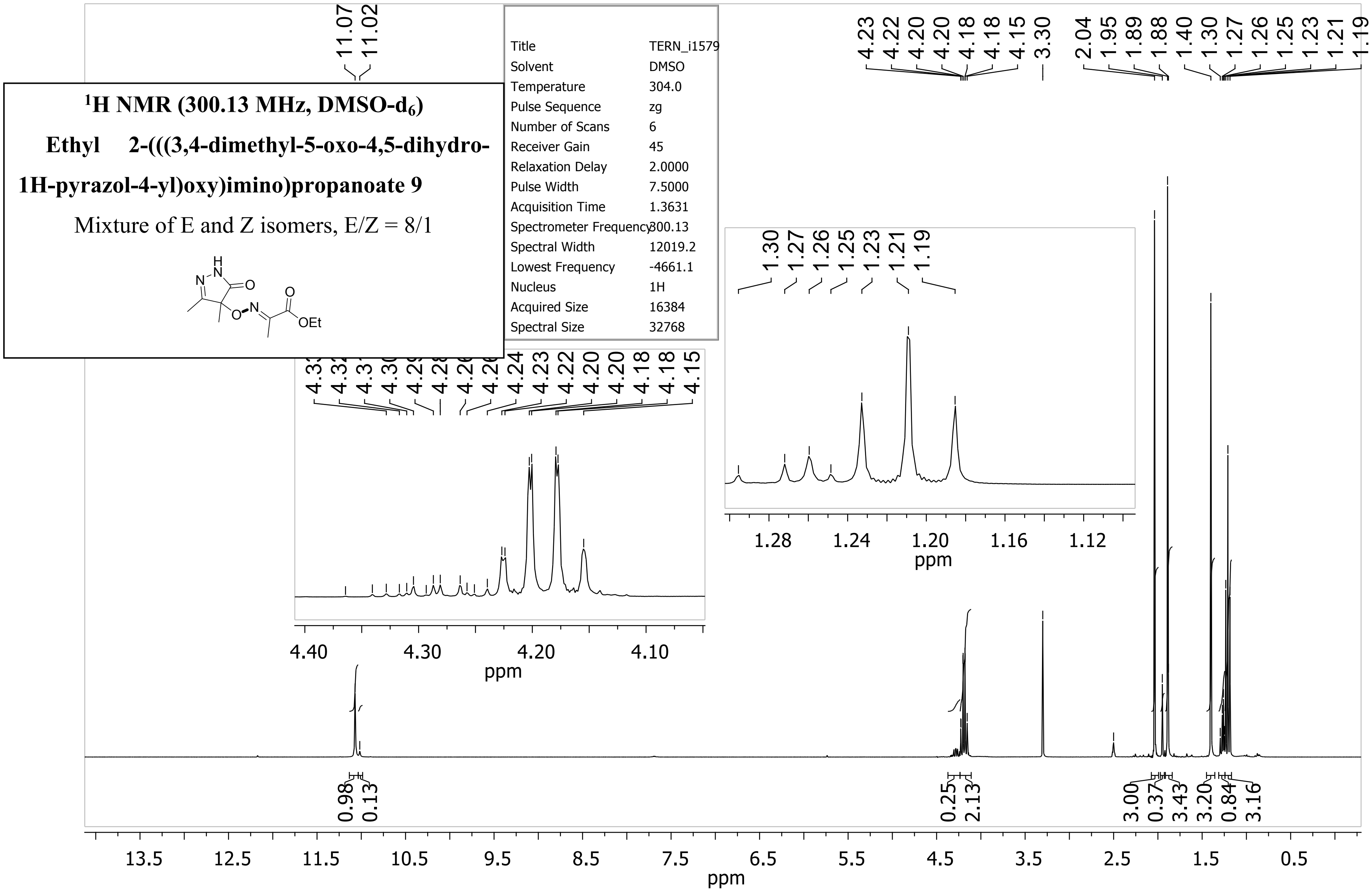
3-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 8

Title	iiiii189.{13C}
Solvent	DMSO-d6
Temperature	300.1
Pulse Sequence	zgpg60base
Number of Scans	676
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-791.7
Nucleus	13C
Acquired Size	16308
Spectral Size	32768

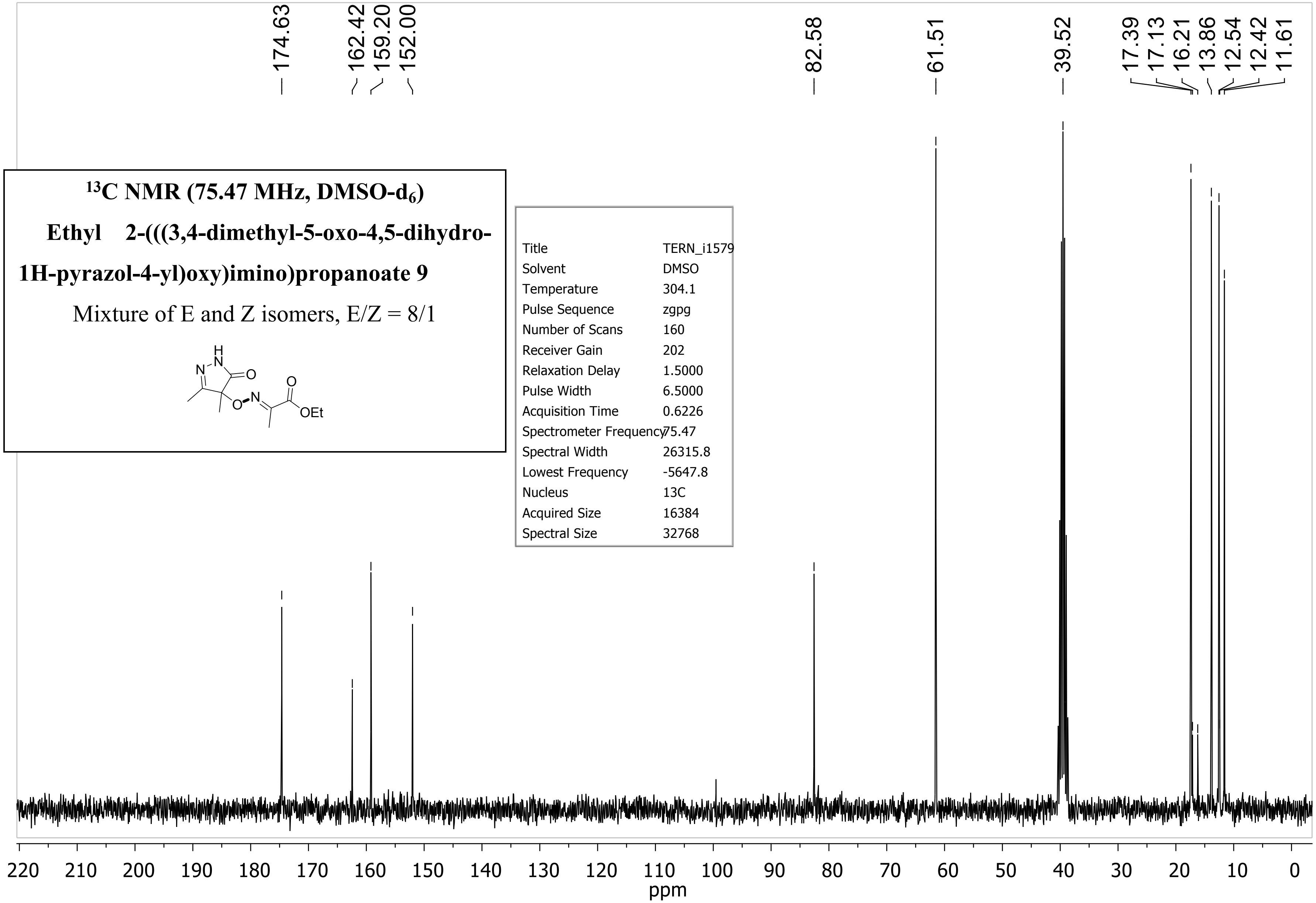
^{1}H NMR (300.13 MHz, DMSO-d$_6$)

Ethyl 2-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)propanoate 9

Mixture of E and Z isomers, E/Z = 8/1



Title	TERN_i1579
Solvent	DMSO
Temperature	304.0
Pulse Sequence	zg
Number of Scans	6
Receiver Gain	45
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.3631
Spectrometer Frequency	300.13
Spectral Width	12019.2
Lowest Frequency	-4661.1
Nucleus	1H
Acquired Size	16384
Spectral Size	32768



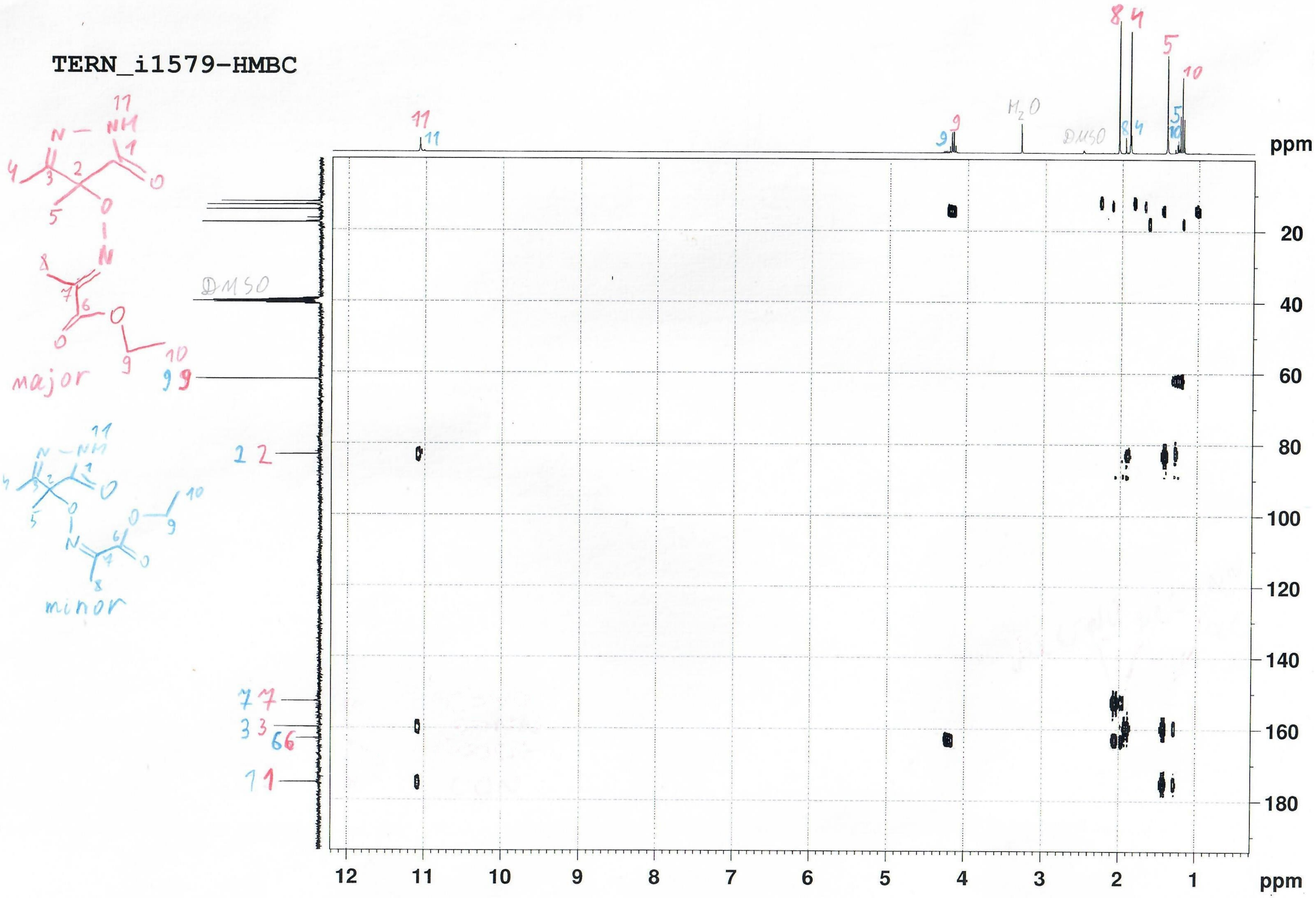
^{13}C NMR (75.47 MHz, DMSO-d$_6$)

Ethyl 2-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)propanoate 9

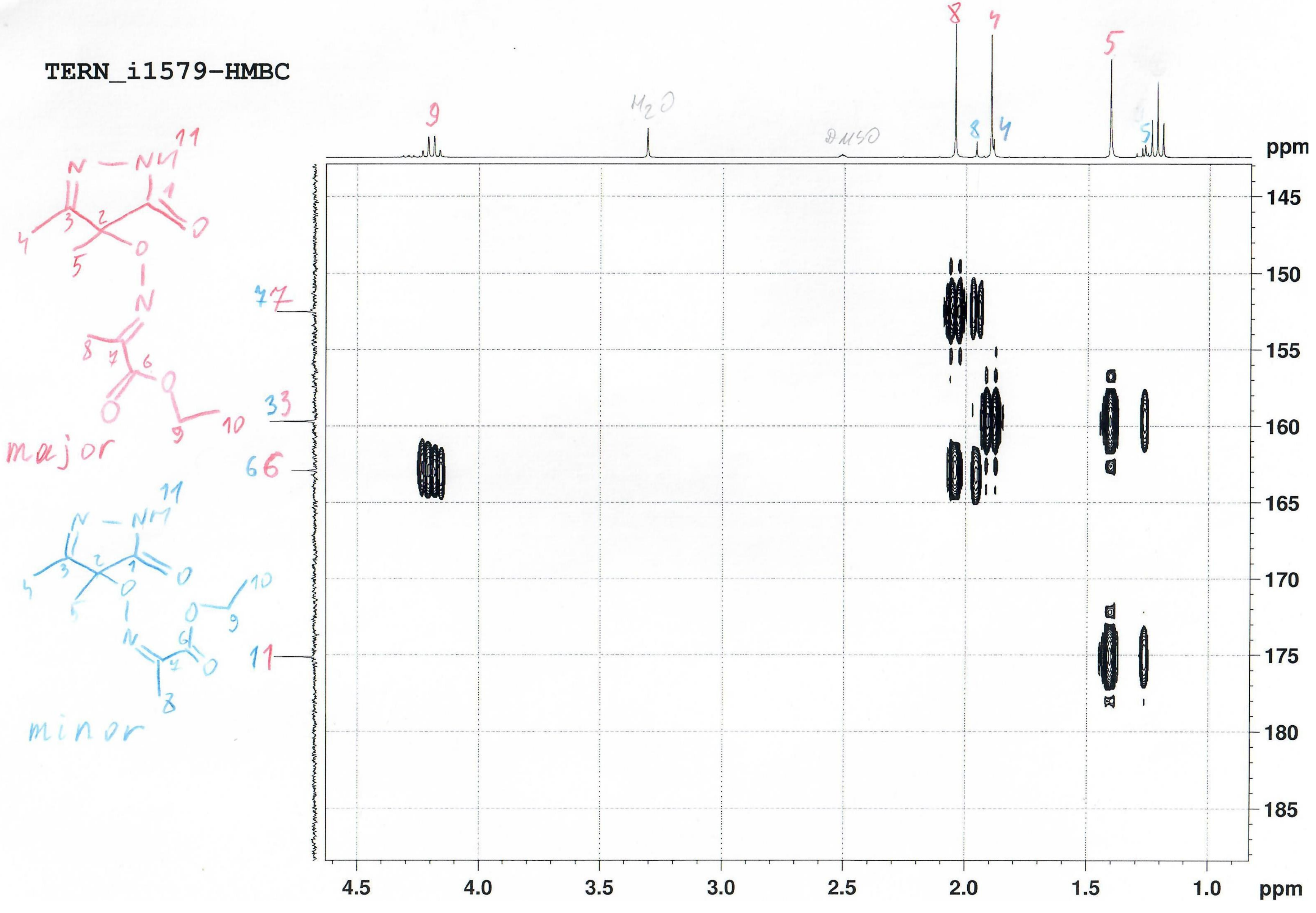
Mixture of E and Z isomers, E/Z = 8/1

Title	TERN_i1579
Solvent	DMSO
Temperature	304.1
Pulse Sequence	zgpg
Number of Scans	160
Receiver Gain	202
Relaxation Delay	1.5000
Pulse Width	6.5000
Acquisition Time	0.6226
Spectrometer Frequency	75.47
Spectral Width	26315.8
Lowest Frequency	-5647.8
Nucleus	13C
Acquired Size	16384
Spectral Size	32768

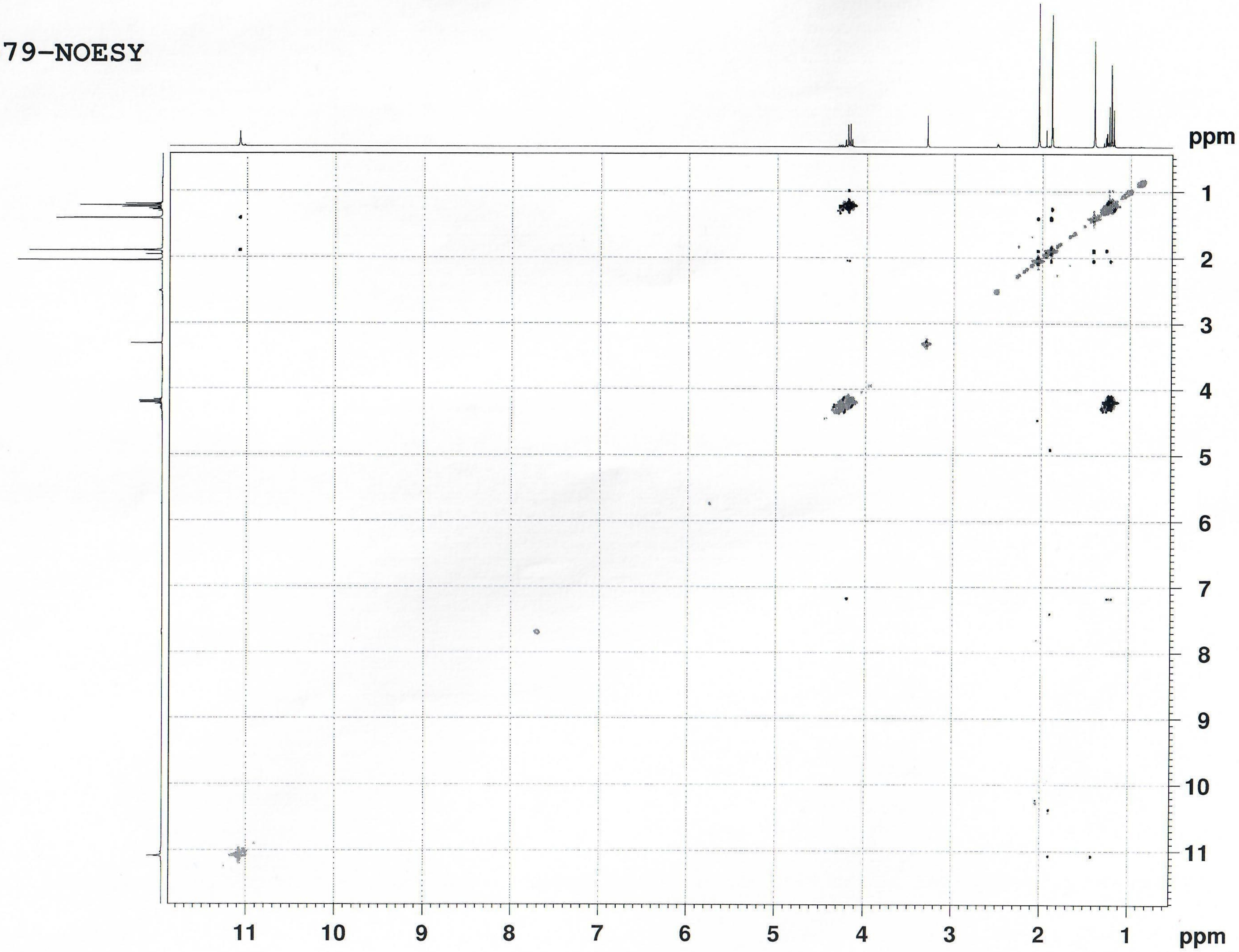
TERN_i1579-HMBC



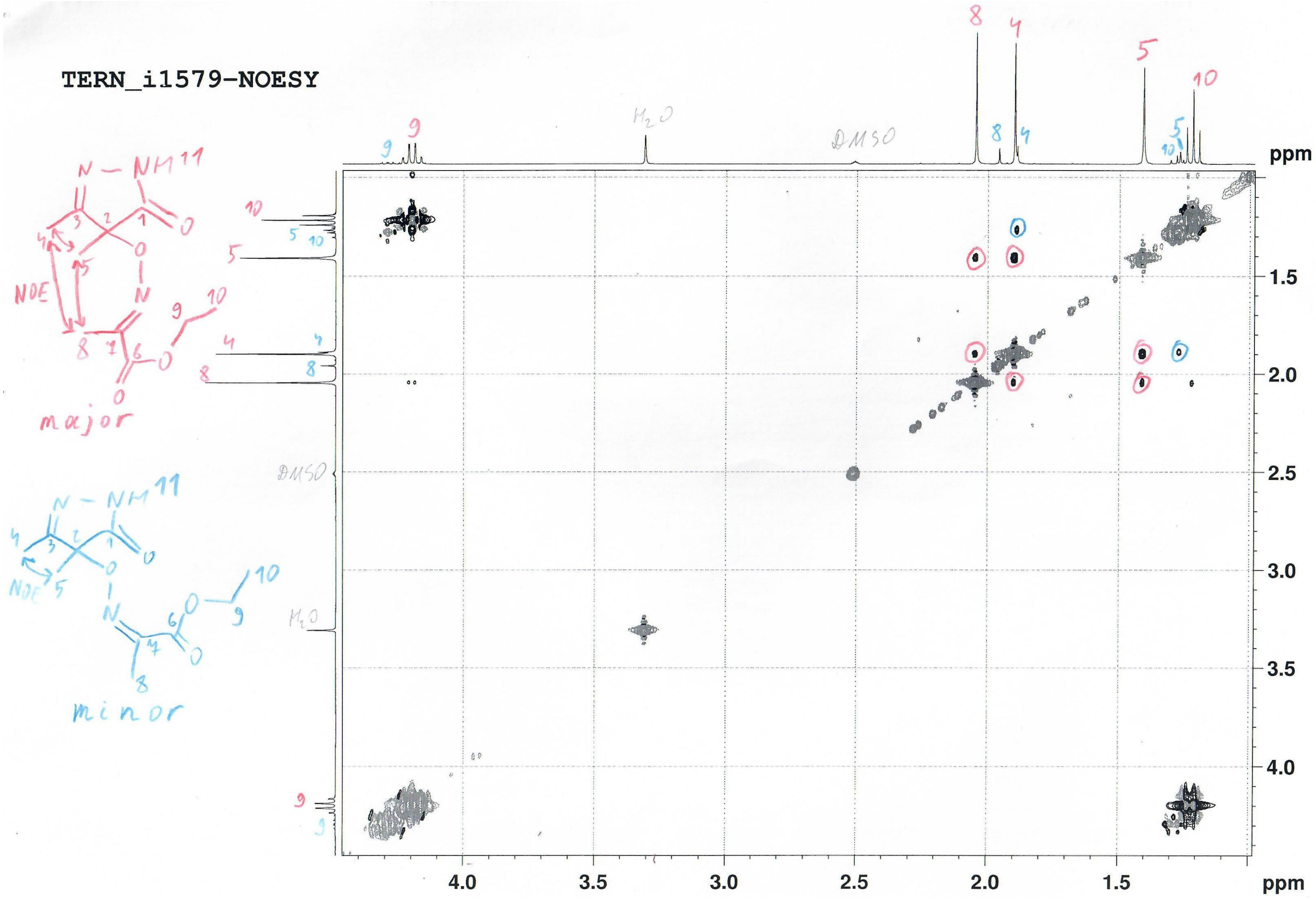
TERN_i1579-HMBC

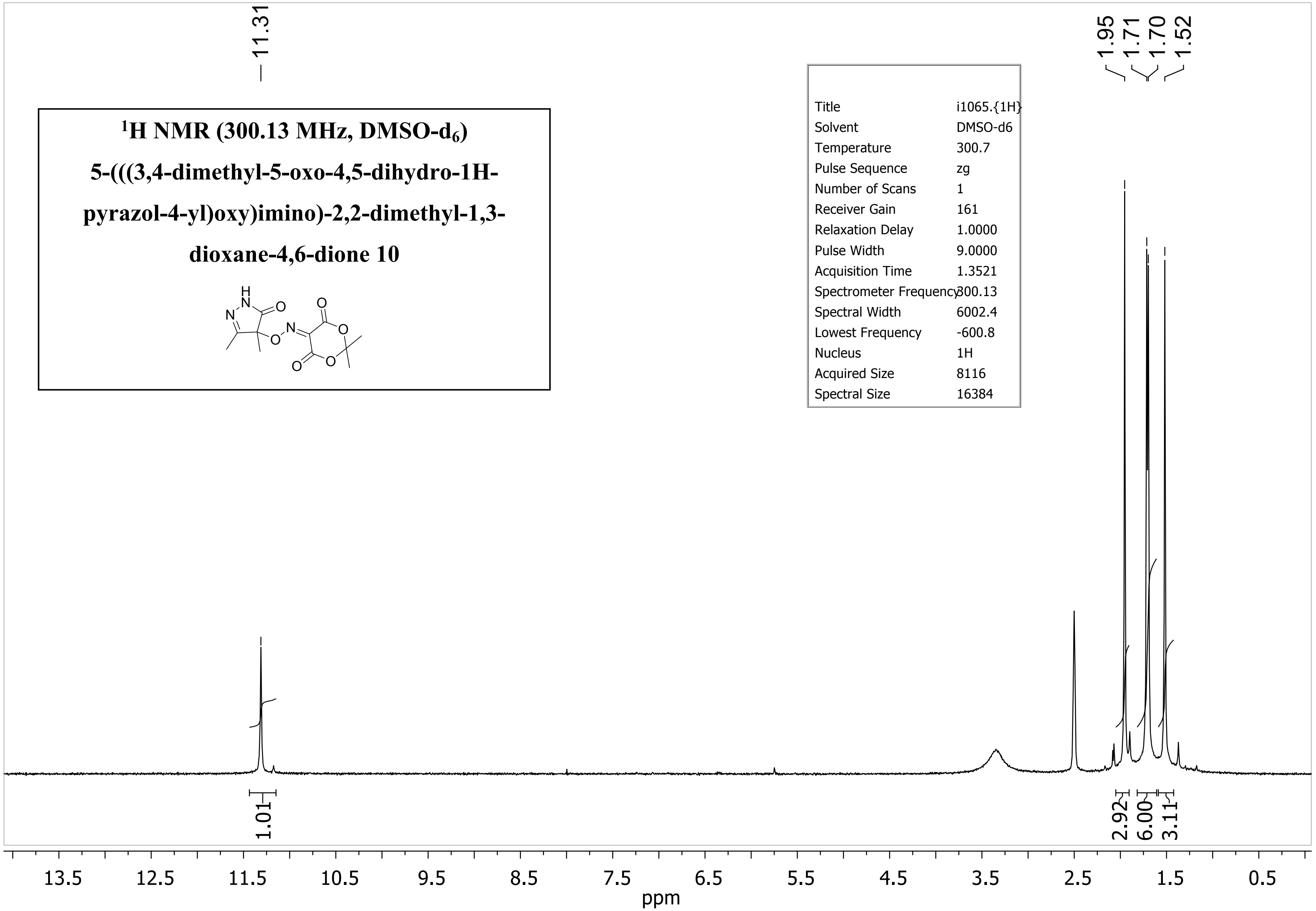


TERN_i1579-NOESY



TERN_i1579-NOESY

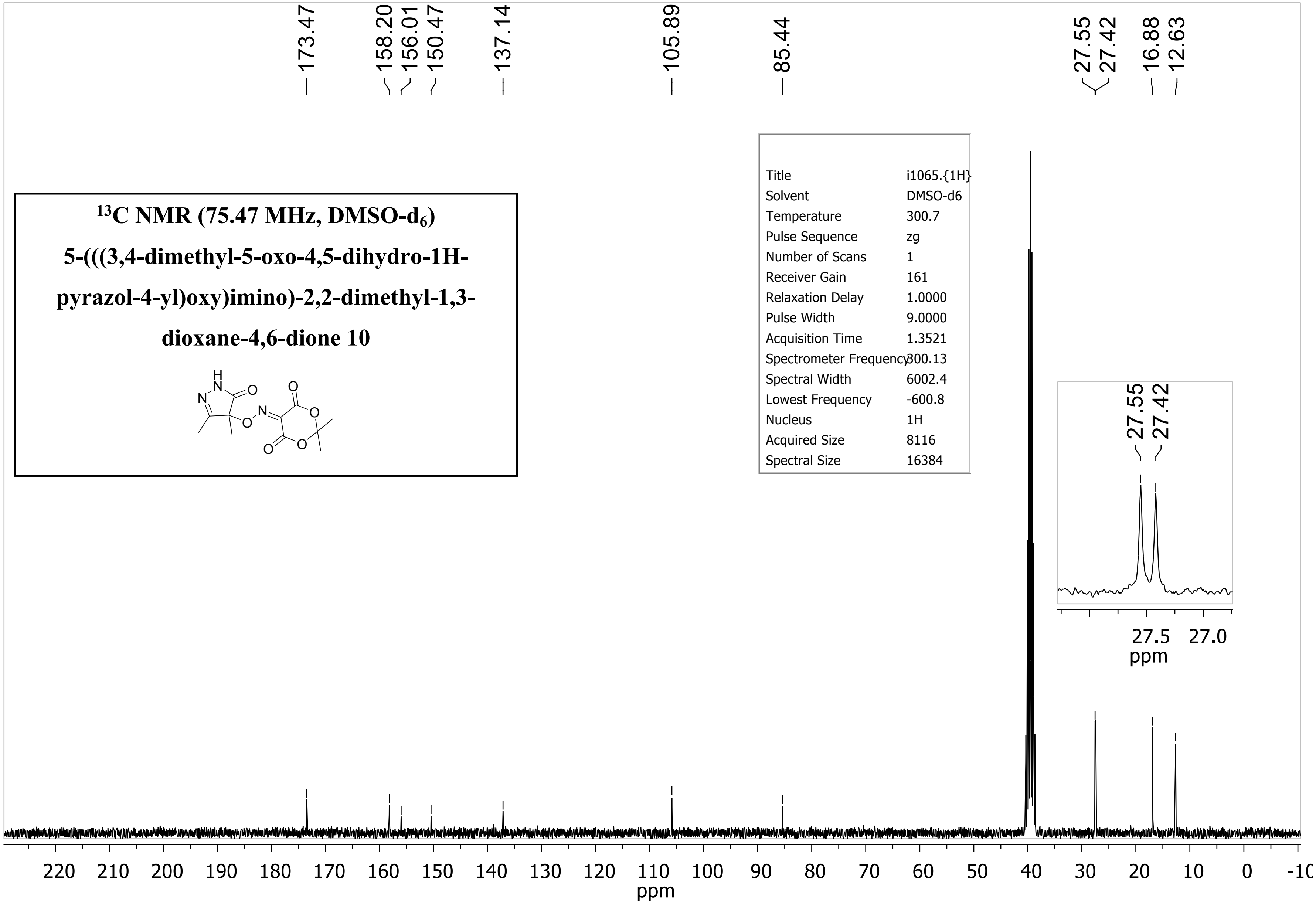




^{1}H NMR (300.13 MHz, DMSO-d$_6$)

5-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-2,2-dimethyl-1,3-dioxane-4,6-dione 10

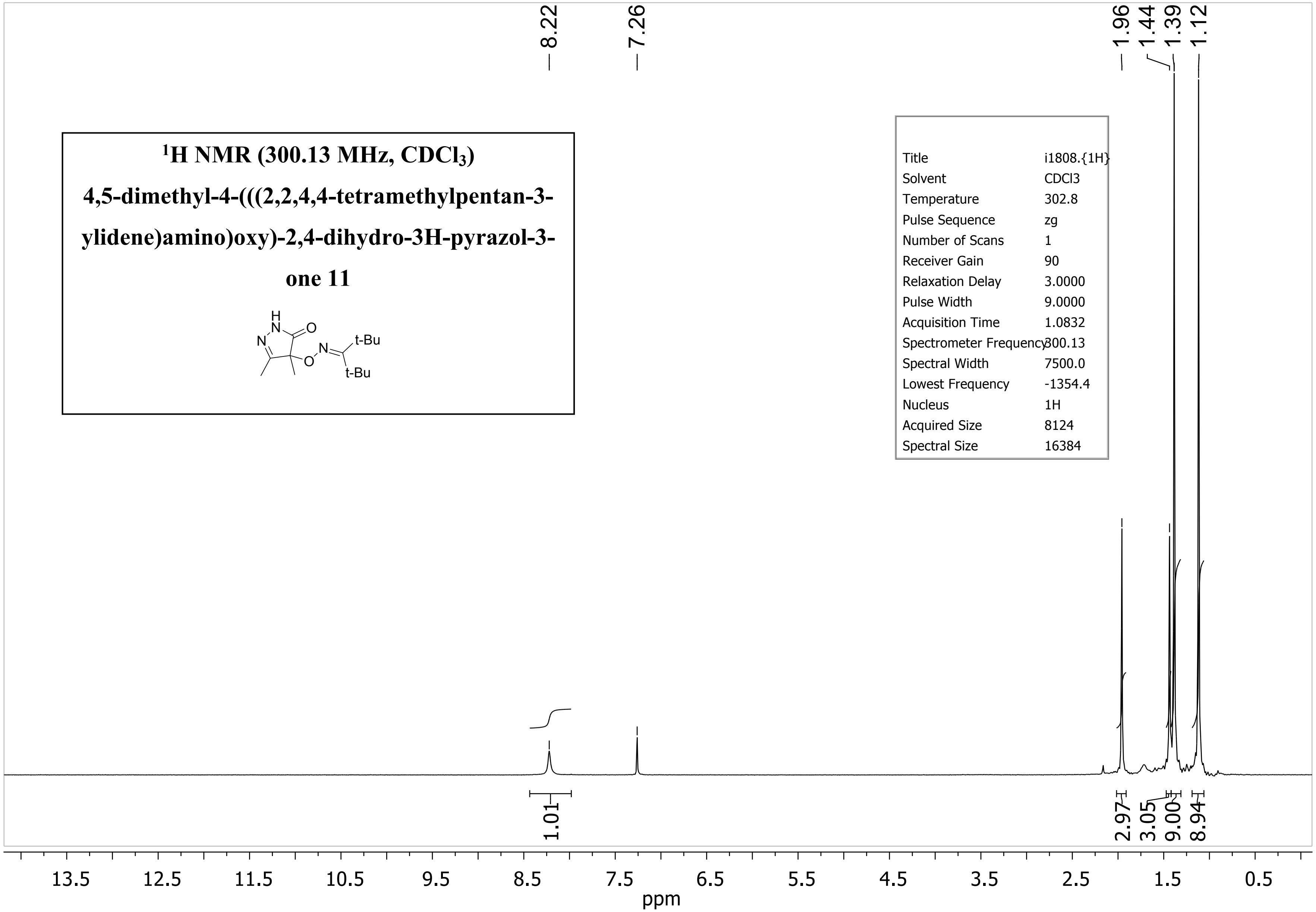
Title	i1065.{1H}
Solvent	DMSO-d6
Temperature	300.7
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-600.8
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d$_6$)

5-(((3,4-dimethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)-2,2-dimethyl-1,3-dioxane-4,6-dione 10

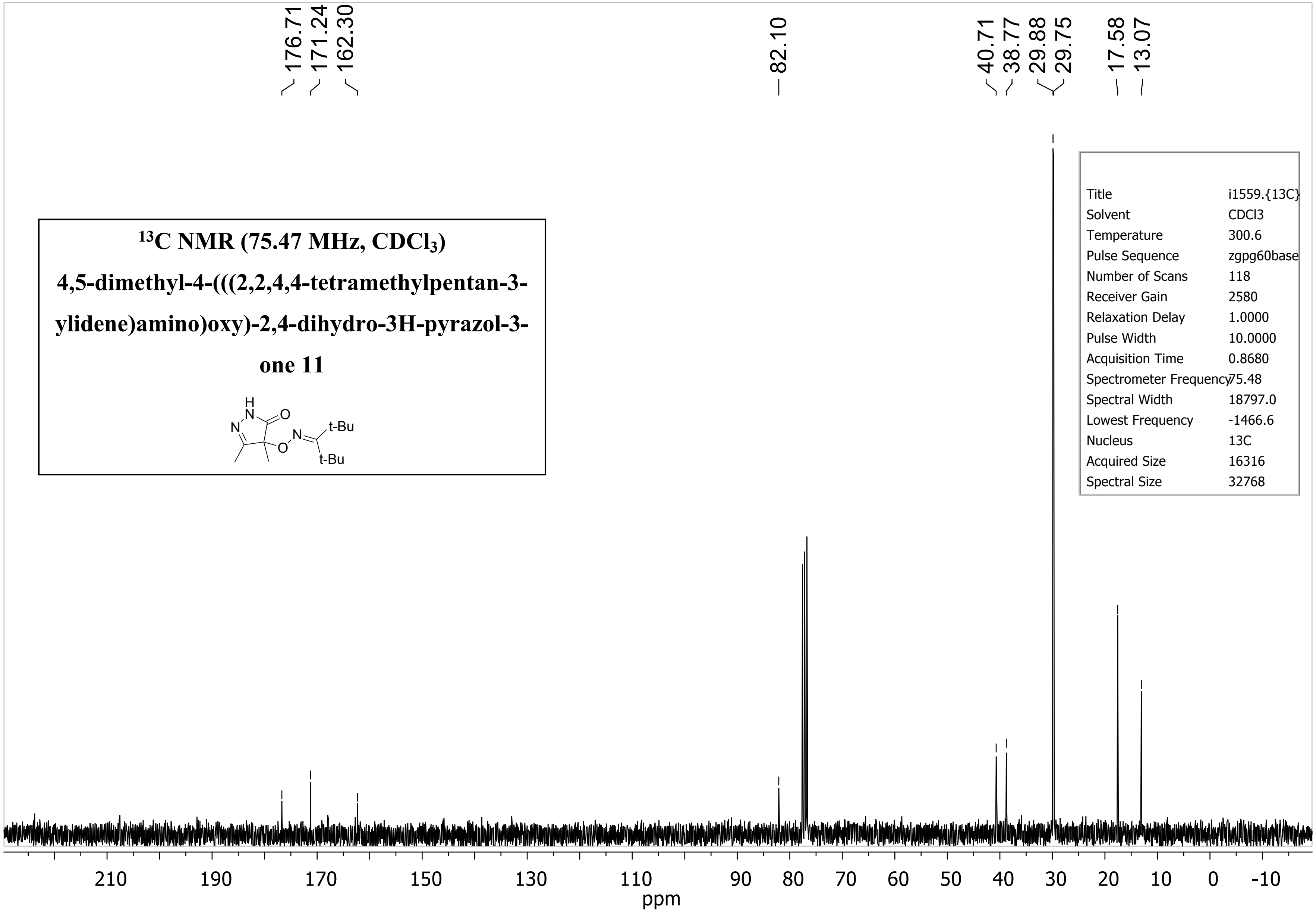
Title	i1065.{1H}
Solvent	DMSO-d6
Temperature	300.7
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-600.8
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



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

4,5-dimethyl-4-(((2,2,4,4-tetramethylpentan-3-ylidene)amino)oxy)-2,4-dihydro-3H-pyrazol-3-one 11

Title	i1808.{1H}
Solvent	CDCl3
Temperature	302.8
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	90
Relaxation Delay	3.0000
Pulse Width	9.0000
Acquisition Time	1.0832
Spectrometer Frequency	300.13
Spectral Width	7500.0
Lowest Frequency	-1354.4
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



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

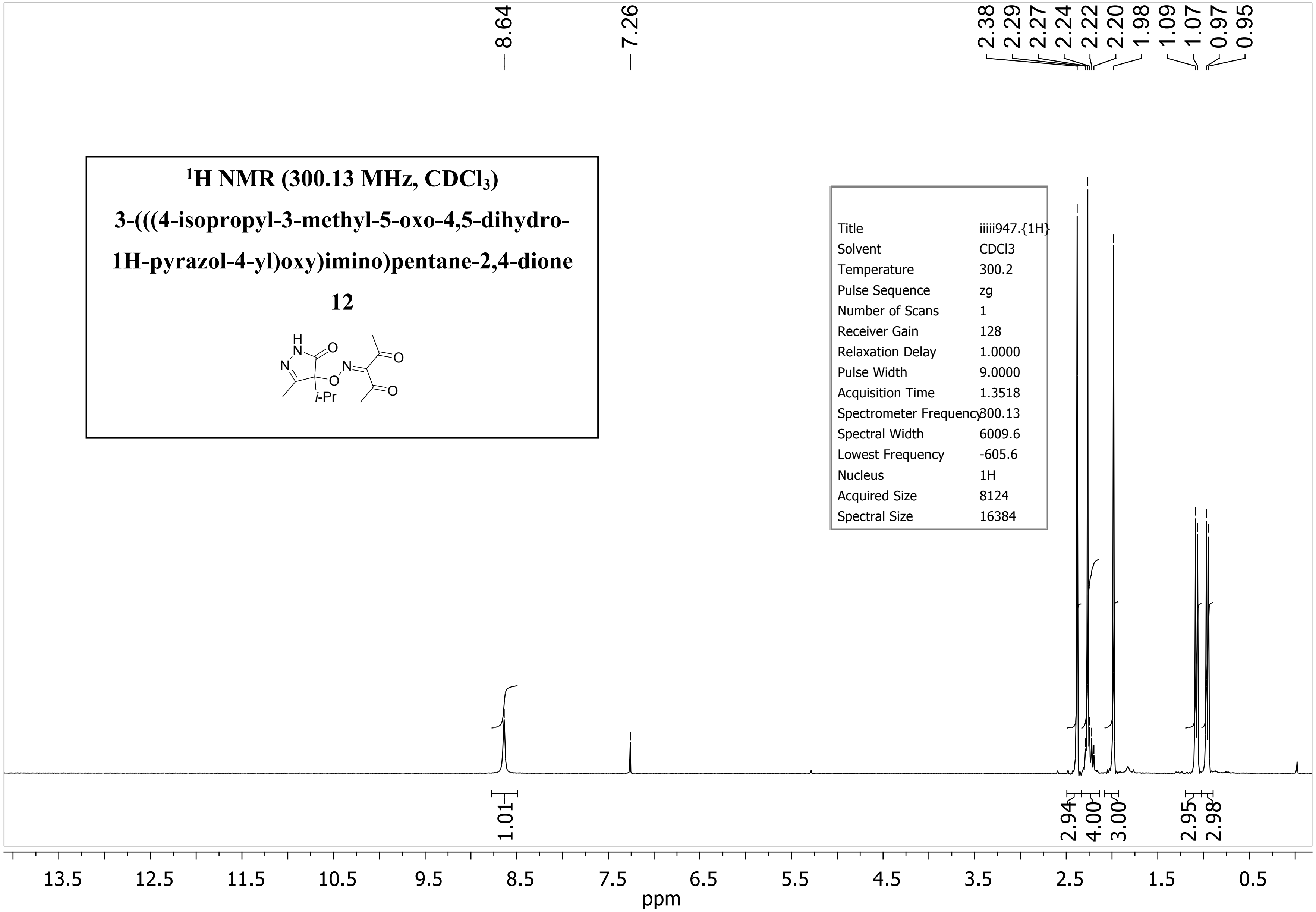
4,5-dimethyl-4-(((2,2,4,4-tetramethylpentan-3-ylidene)amino)oxy)-2,4-dihydro-3H-pyrazol-3-one 11

Title	i1559.{13C}
Solvent	CDCl3
Temperature	300.6
Pulse Sequence	zgpg60base
Number of Scans	118
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	-1466.6
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

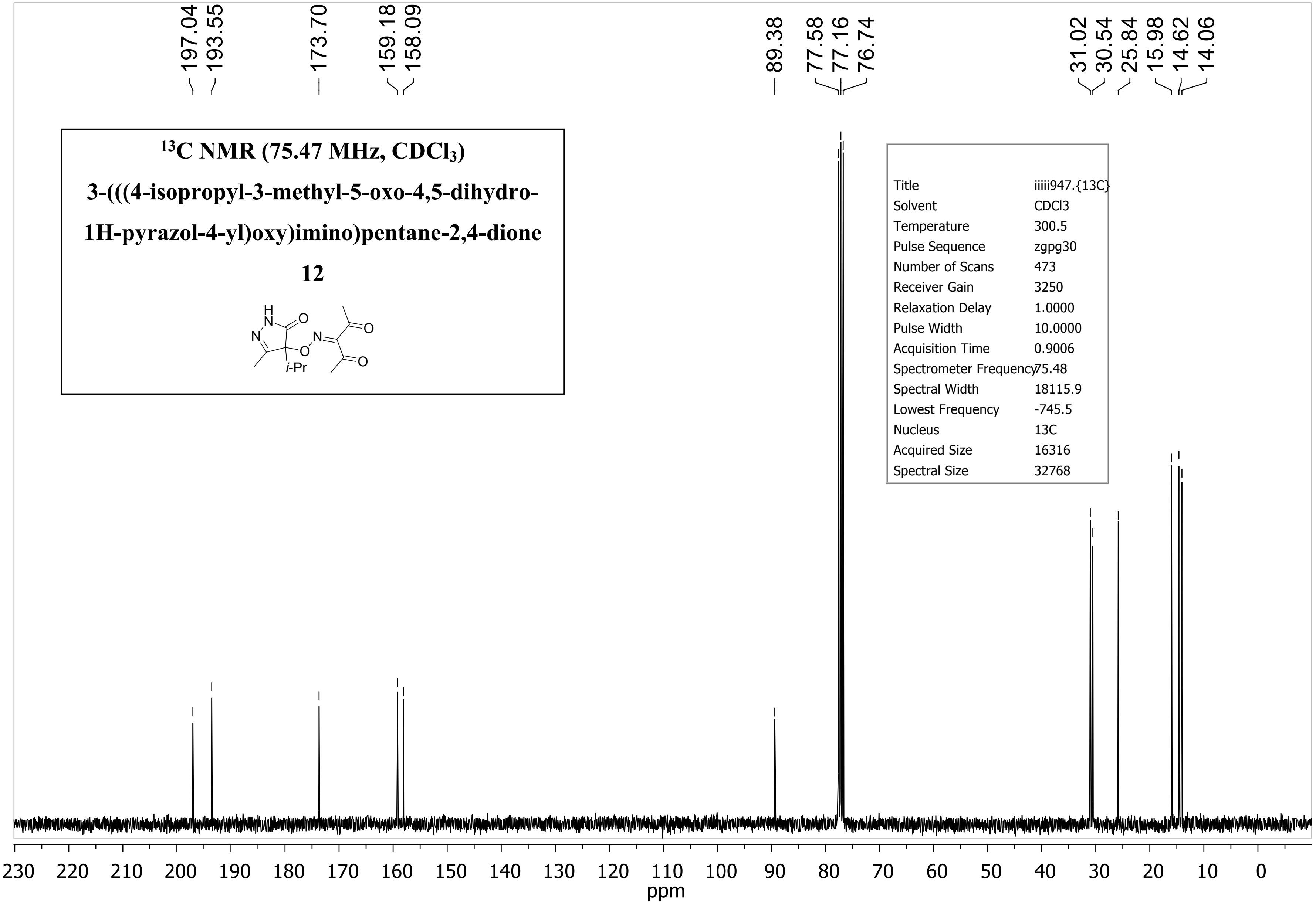
^{1}H NMR (300.13 MHz, $CDCl_3$)

3-(((4-isopropyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione

12



Title	iiiii947.{1H}
Solvent	CDCl3
Temperature	300.2
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-605.6
Nucleus	1H
Acquired Size	8124
Spectral Size	16384

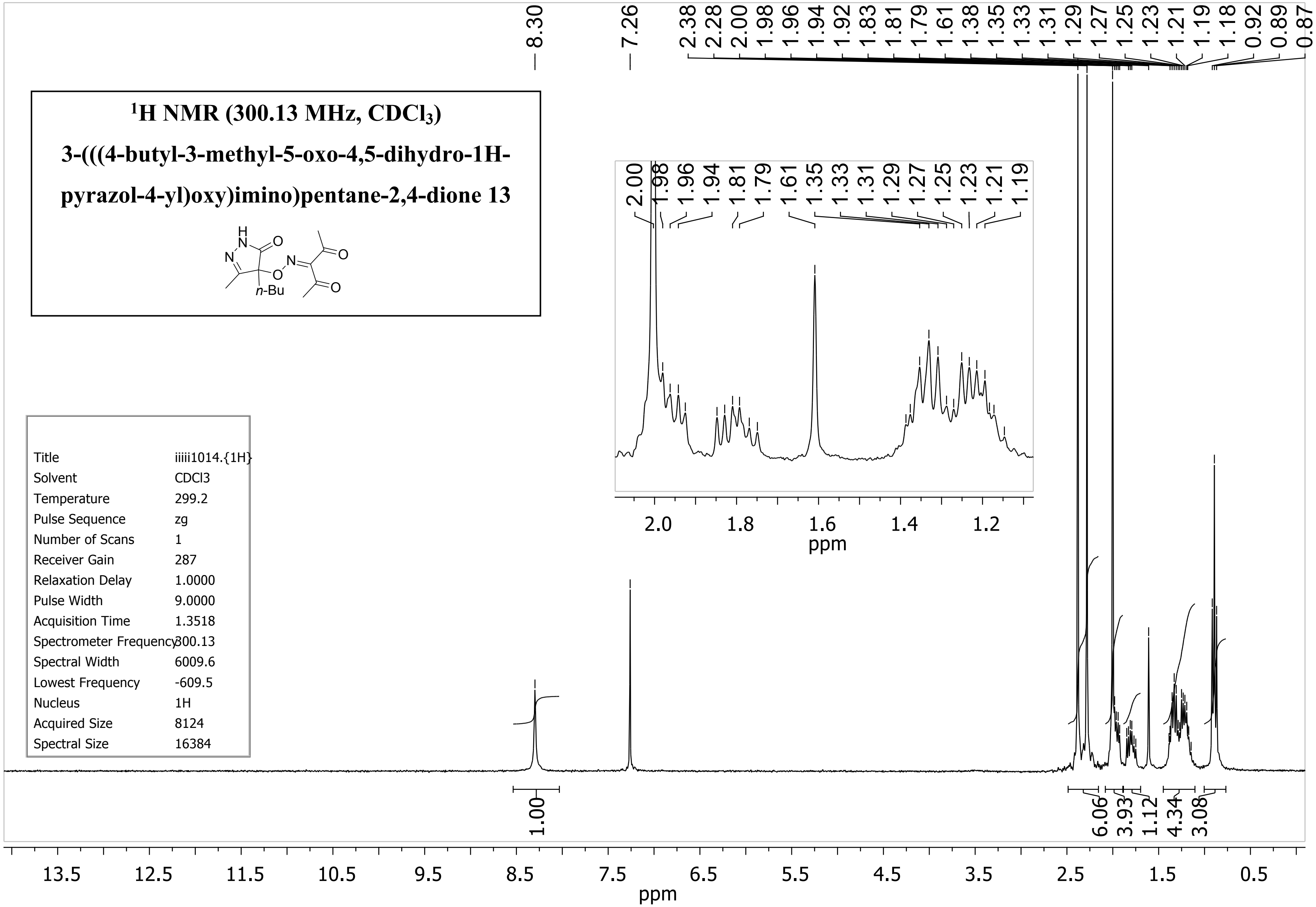


^{13}C NMR (75.47 MHz, CDCl$_3$)

3-(((4-isopropyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione

12

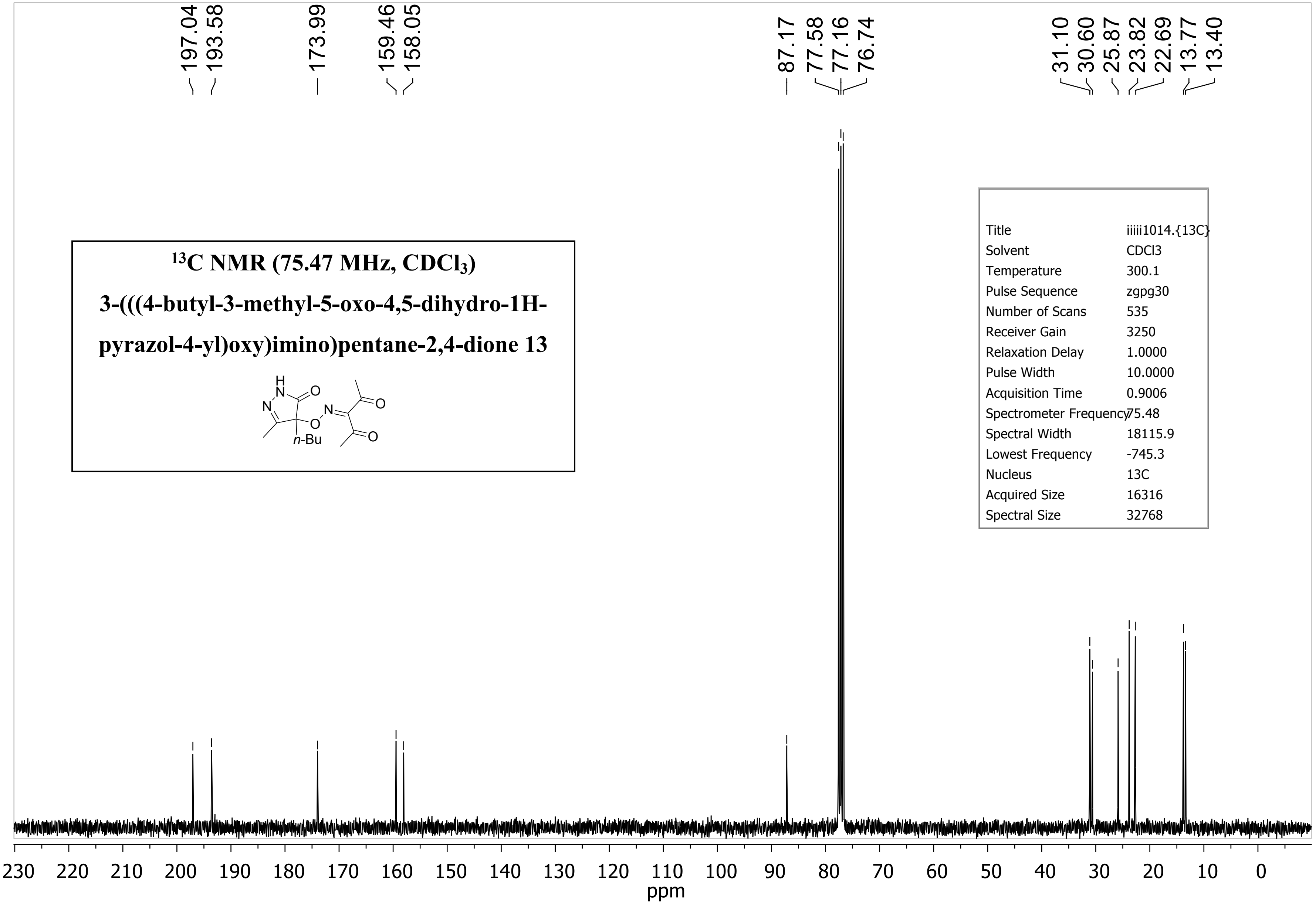
Title	iiiii947.{13C}
Solvent	CDCl3
Temperature	300.5
Pulse Sequence	zgpg30
Number of Scans	473
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-745.5
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



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

3-(((4-butyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 13

Title	iiiii1014.{1H}
Solvent	CDCl3
Temperature	299.2
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-609.5
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



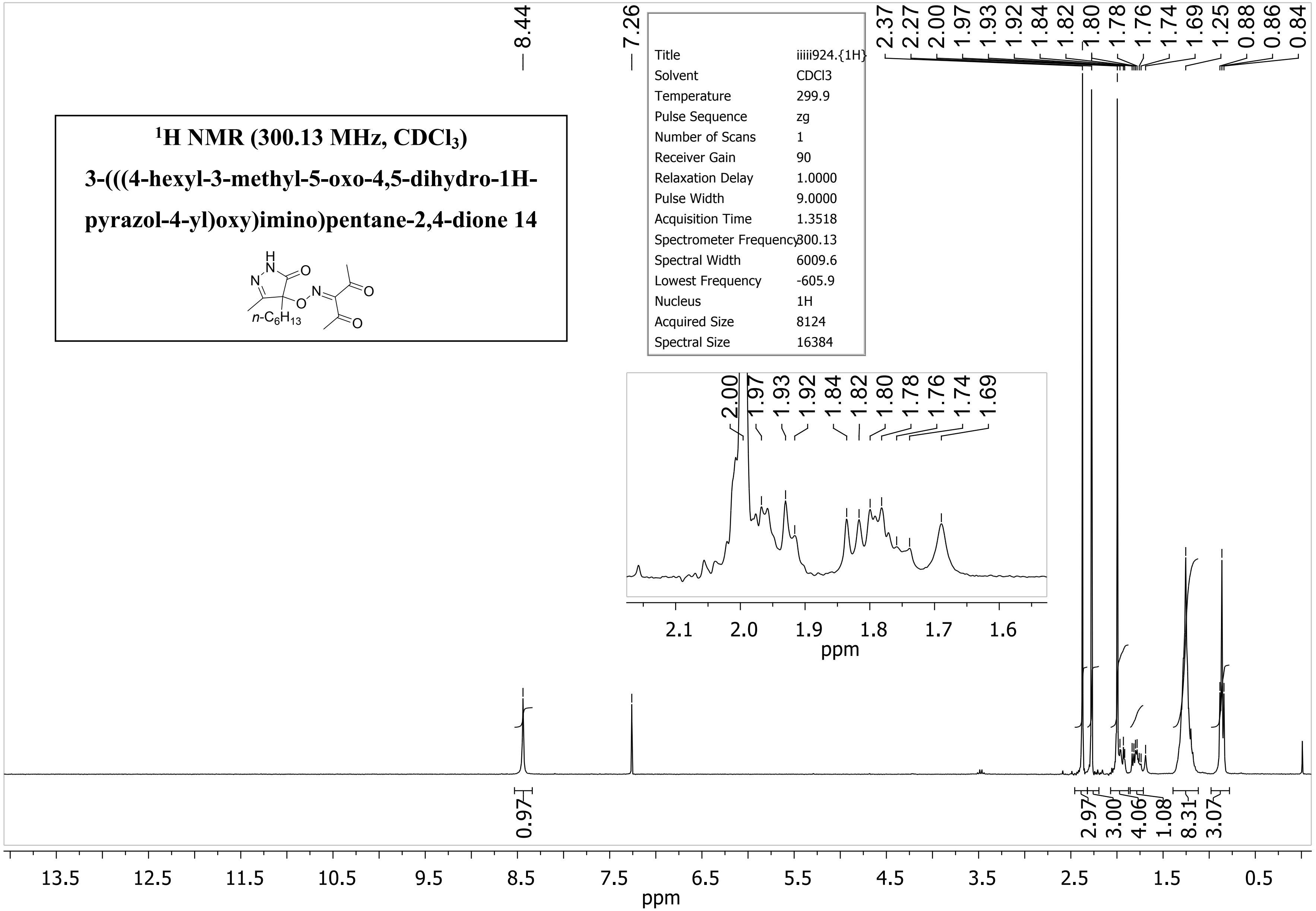
^{13}C NMR (75.47 MHz, CDCl$_3$)

3-(((4-butyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 13

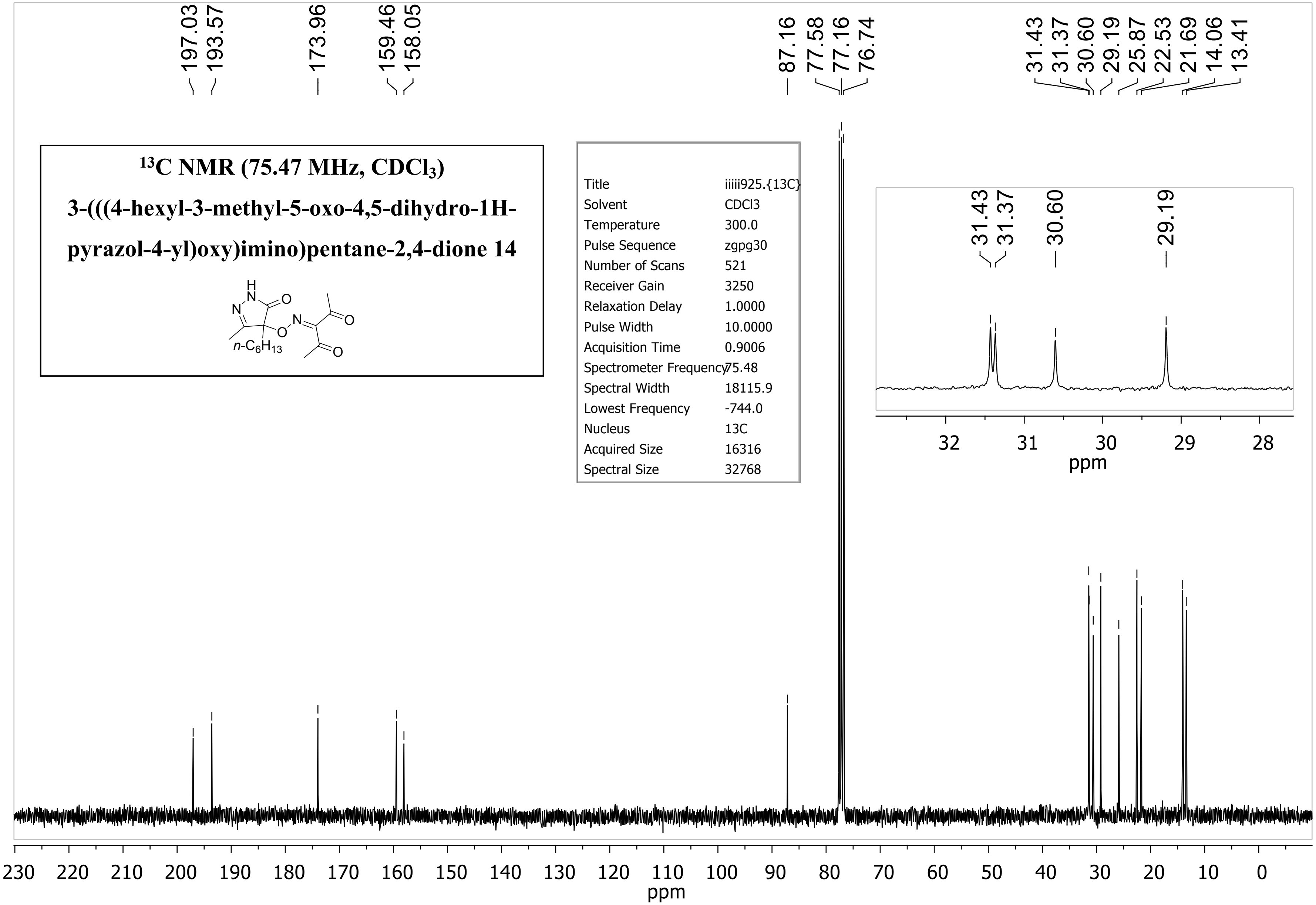
Title	iiiii1014.{13C}
Solvent	CDCl3
Temperature	300.1
Pulse Sequence	zgpg30
Number of Scans	535
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-745.3
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

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

3-(((4-hexyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 14



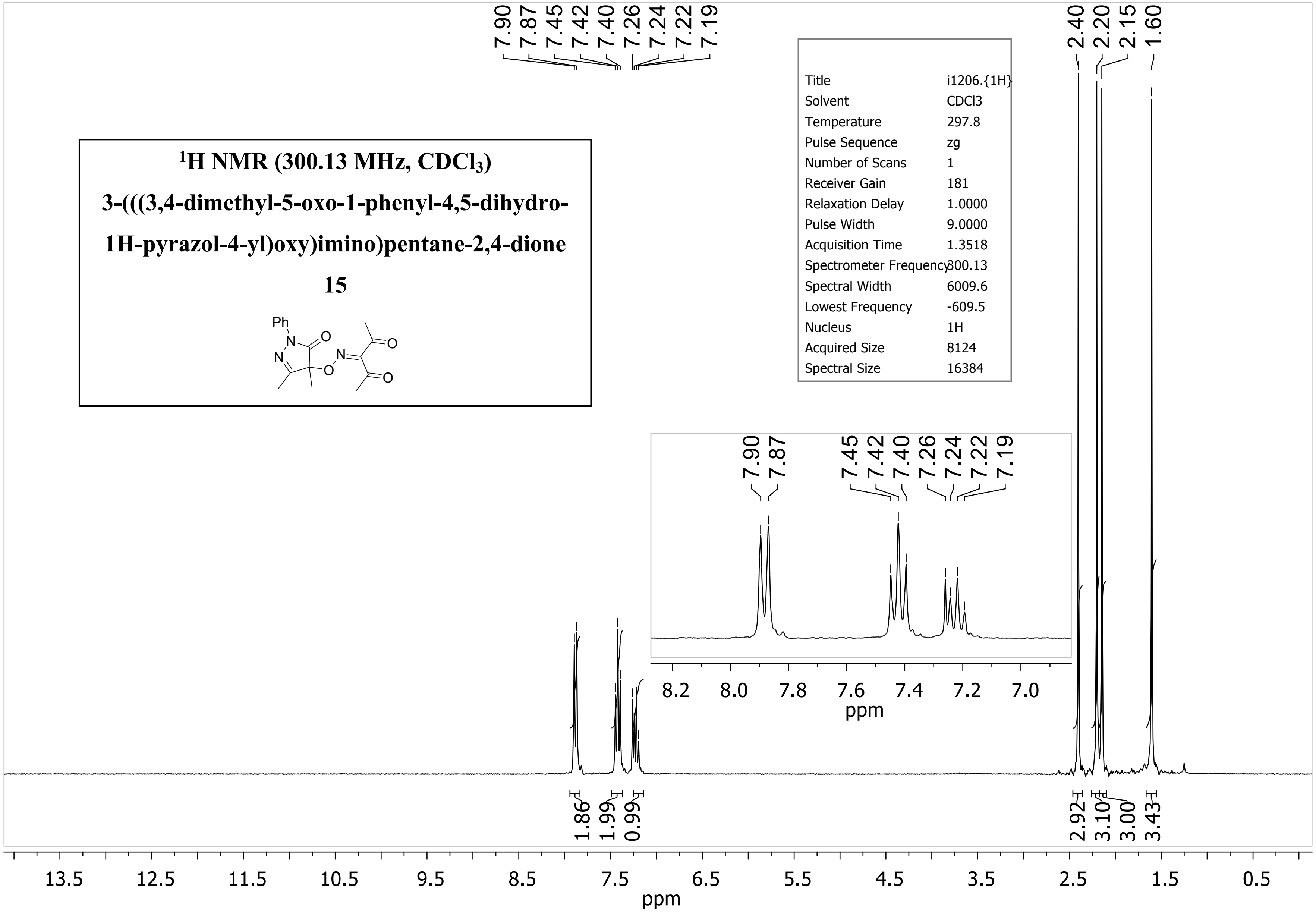
Title	iiiii924.{1H}
Solvent	CDCl3
Temperature	299.9
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	90
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-605.9
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



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

3-(((4-hexyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 14

Title	iiiii925.{13C}
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zgpg30
Number of Scans	521
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	-744.0
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

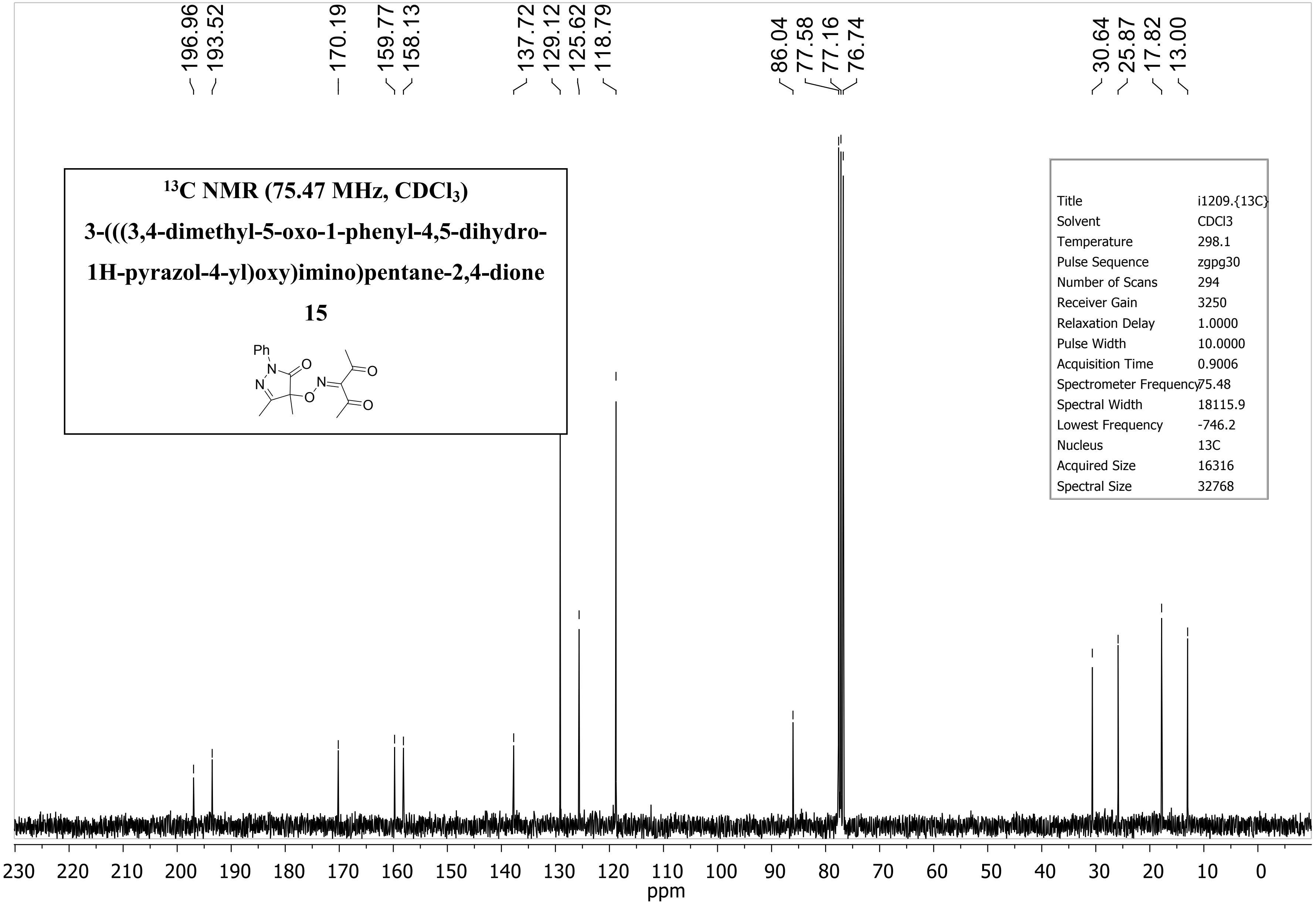


^{1}H NMR (300.13 MHz, CDCl$_3$)

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

15

Title	i1206.{1H}
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-609.5
Nucleus	1H
Acquired Size	8124
Spectral Size	16384

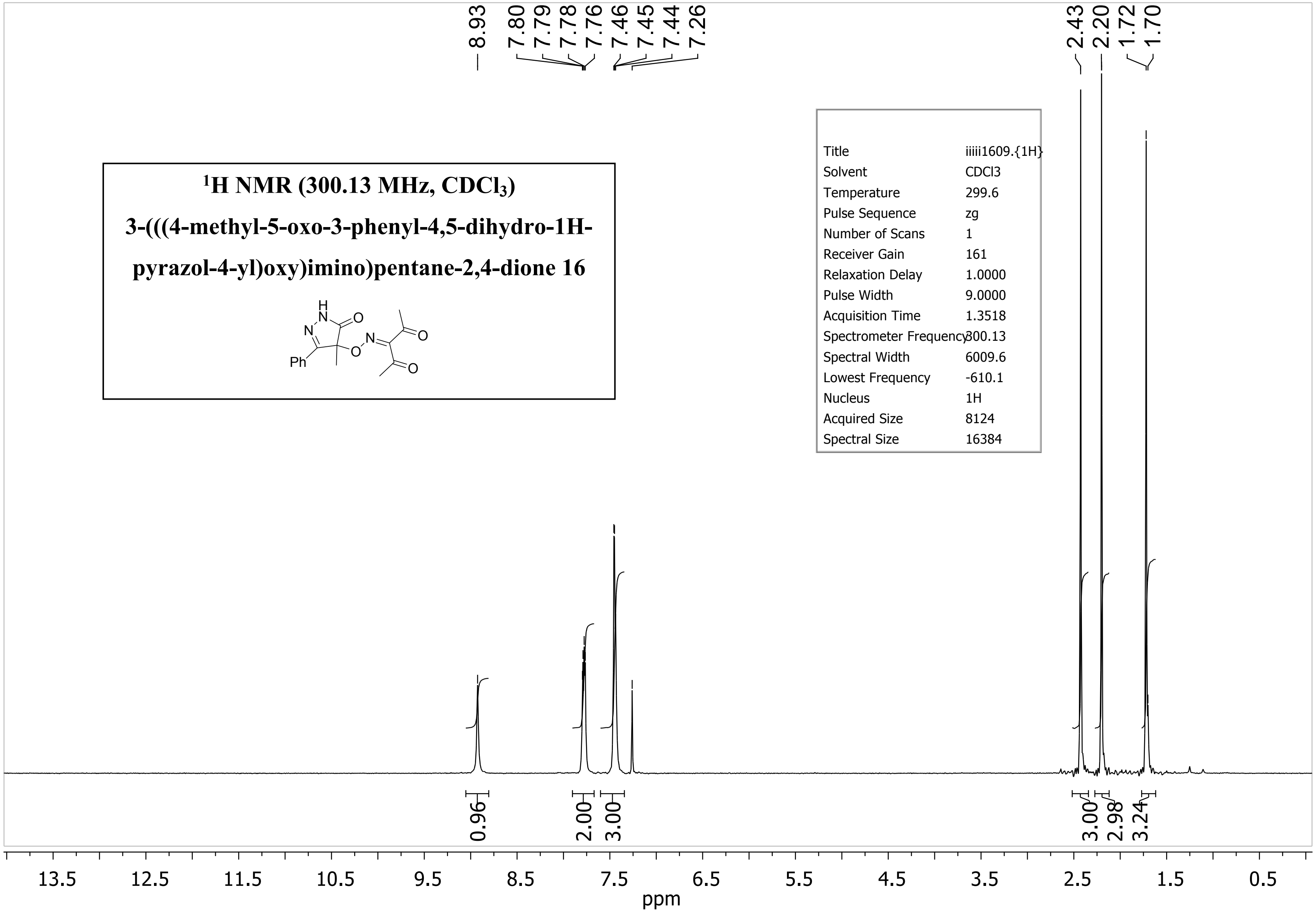


^{13}C NMR (75.47 MHz, CDCl$_3$)

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

15

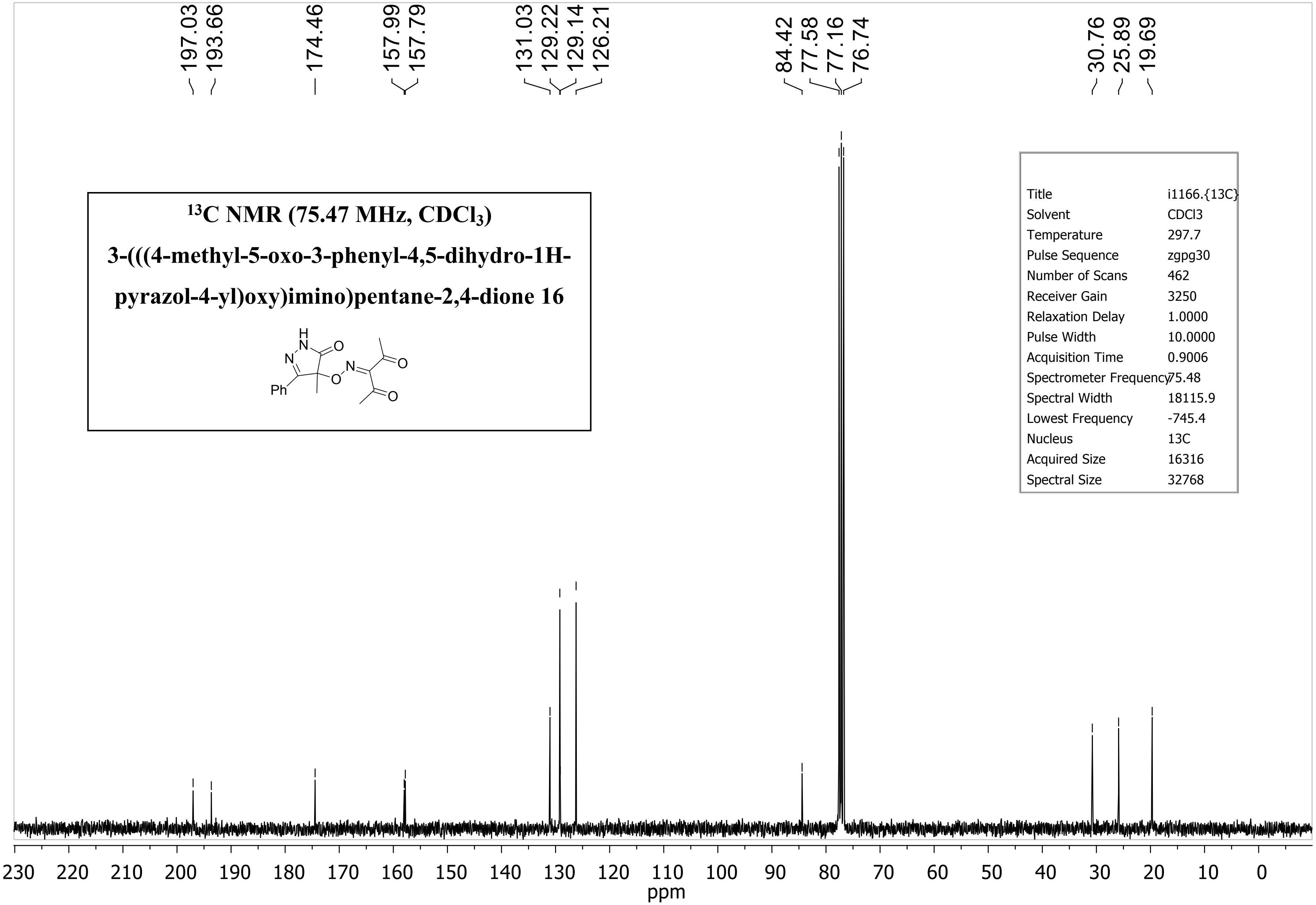
Title	i1209.{13C}
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Number of Scans	294
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-746.2
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



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

3-(((4-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 16

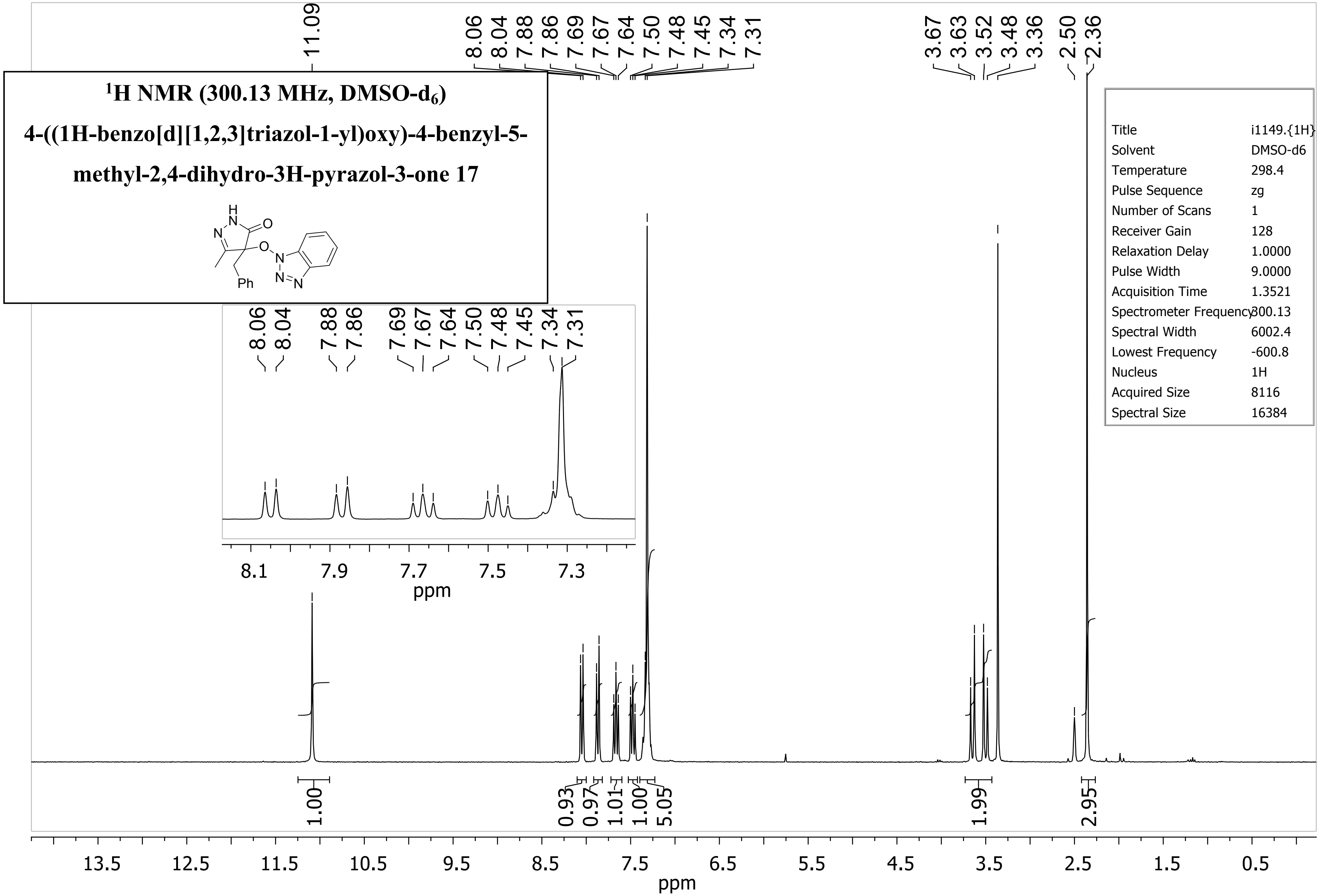
Title	iiiii1609.{1H}
Solvent	CDCl3
Temperature	299.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.1
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



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

3-(((4-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)oxy)imino)pentane-2,4-dione 16

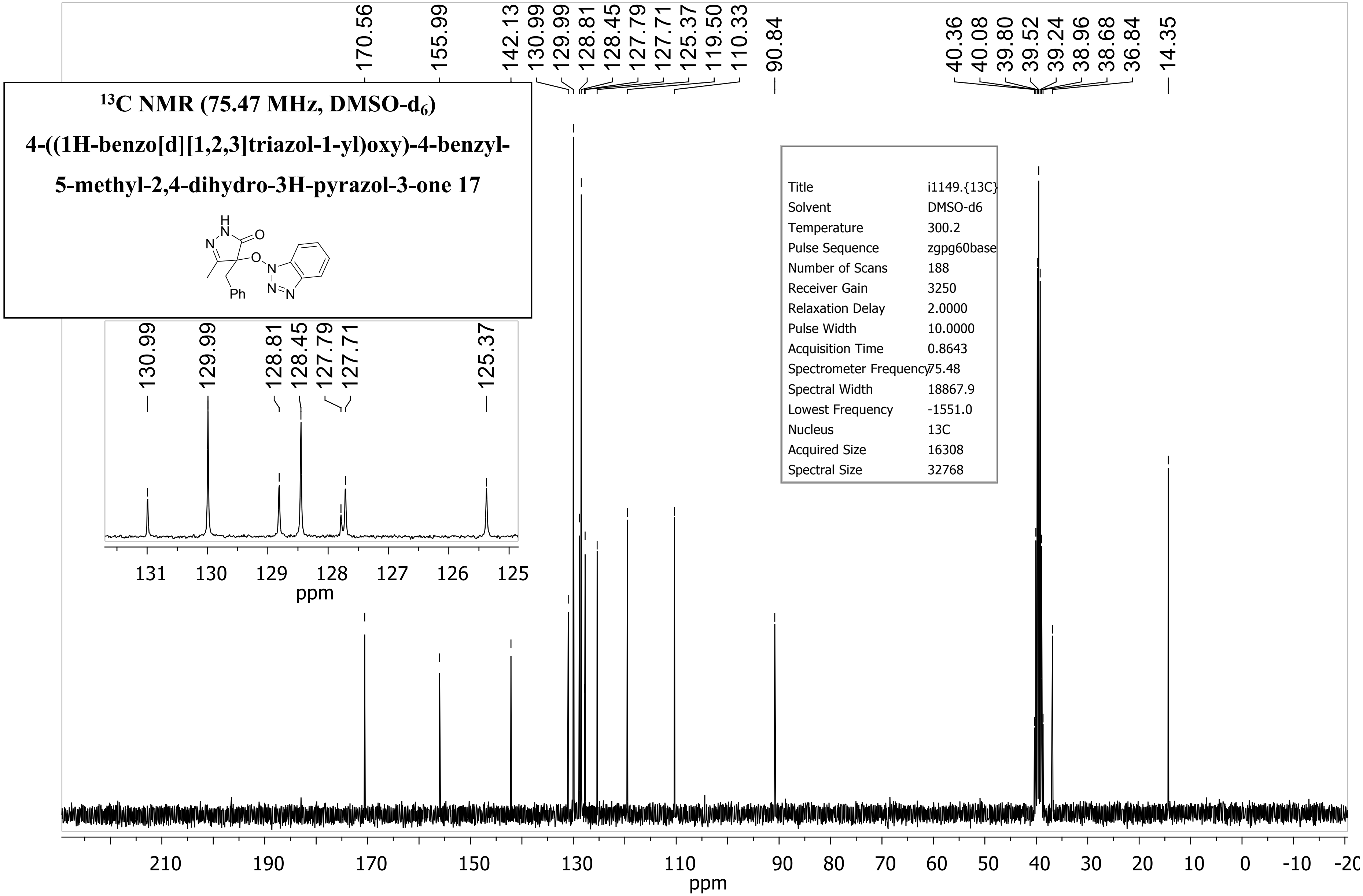
Title	i1166.{13C}
Solvent	CDCl3
Temperature	297.7
Pulse Sequence	zgpg30
Number of Scans	462
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-745.4
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



^{1}H NMR (300.13 MHz, DMSO-d_6)

4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-benzyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 17

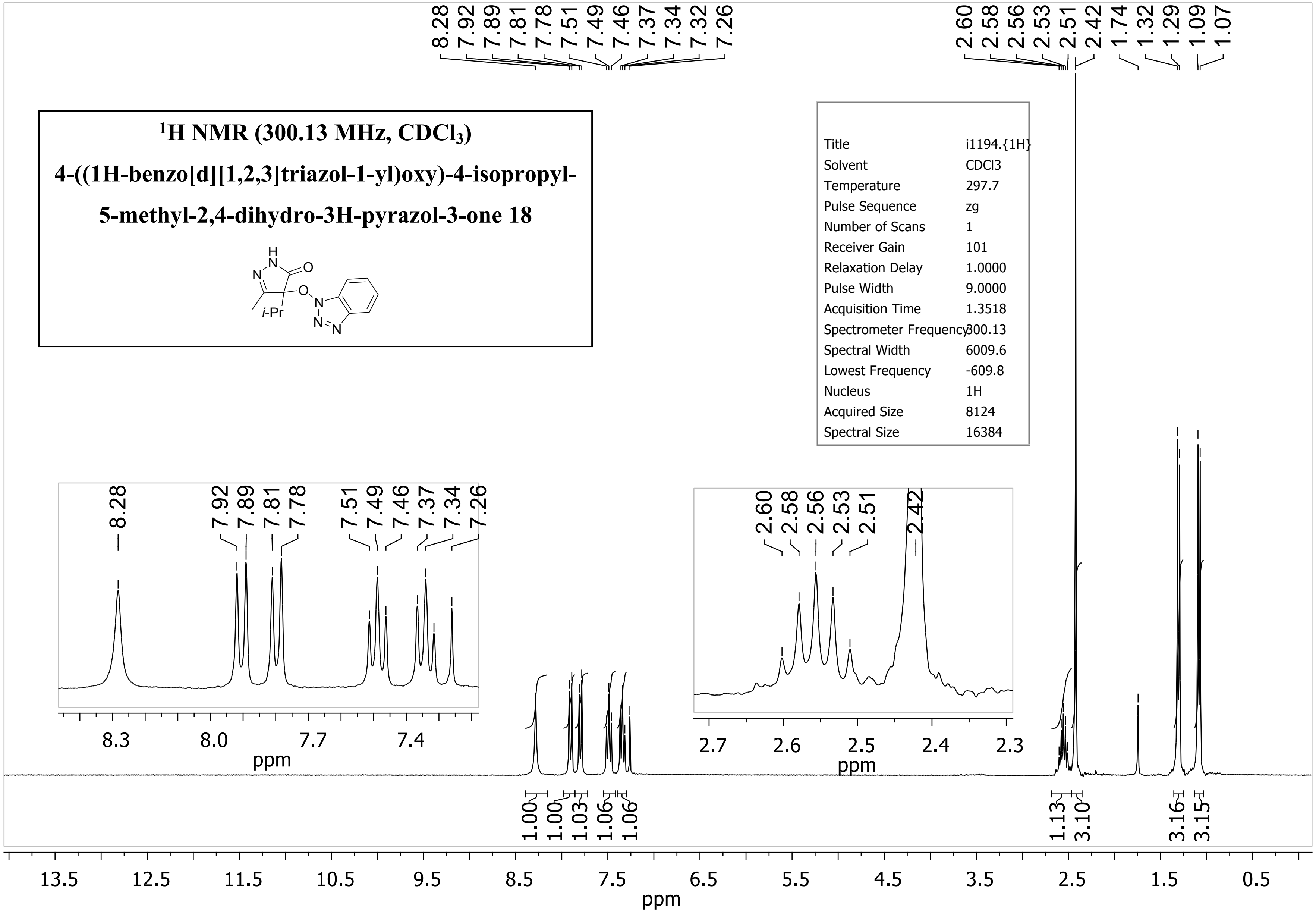
Title	i1149.{1H}
Solvent	DMSO-d6
Temperature	298.4
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3521
Spectrometer Frequency	300.13
Spectral Width	6002.4
Lowest Frequency	-600.8
Nucleus	1H
Acquired Size	8116
Spectral Size	16384



^{13}C NMR (75.47 MHz, DMSO-d$_6$)

4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-benzyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 17

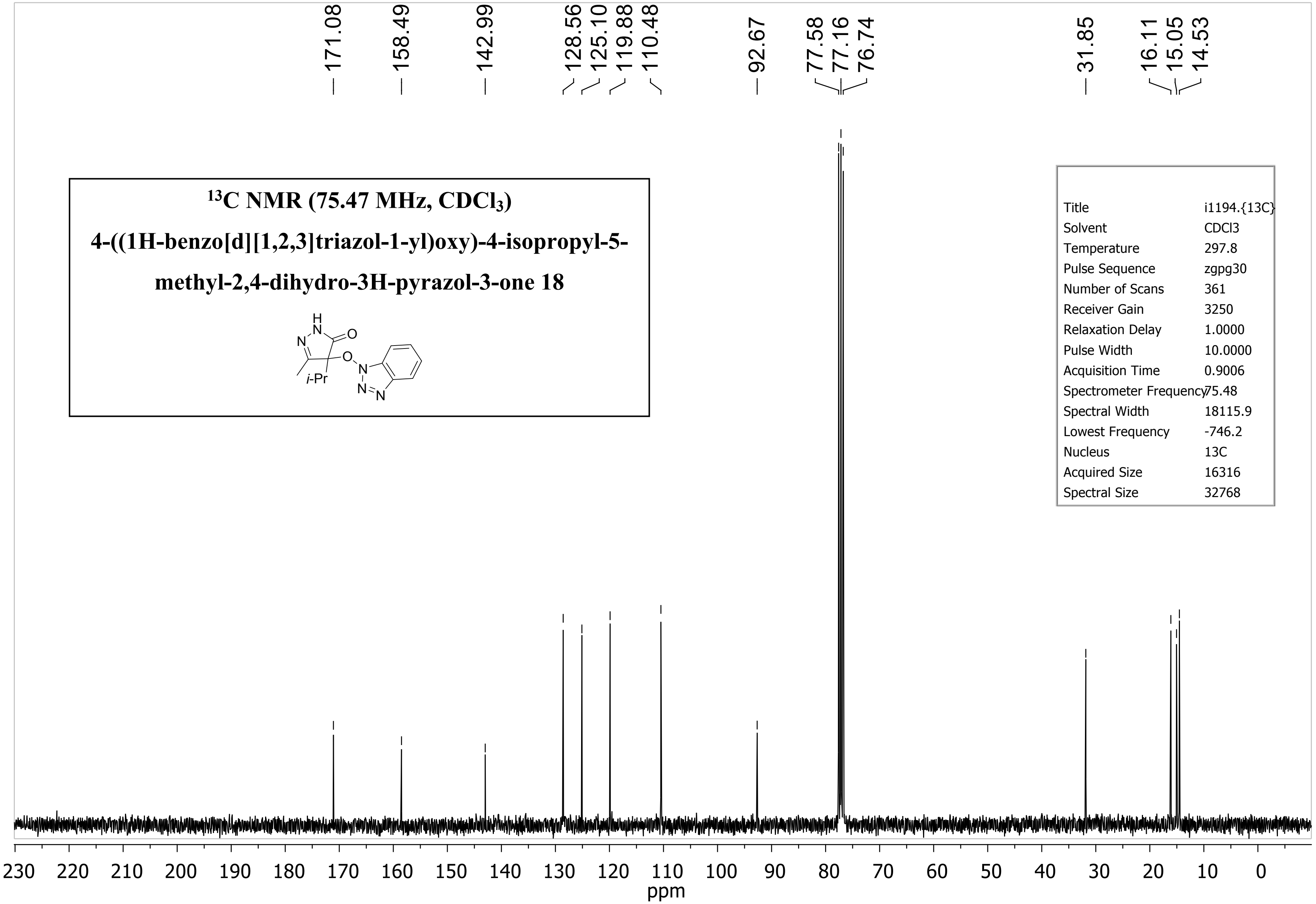
Title	i1149.{13C}
Solvent	DMSO-d6
Temperature	300.2
Pulse Sequence	zgpg60base
Number of Scans	188
Receiver Gain	3250
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	0.8643
Spectrometer Frequency	75.48
Spectral Width	18867.9
Lowest Frequency	-1551.0
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



^{1}H NMR (300.13 MHz, CDCl$_3$)

4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-isopropyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 18

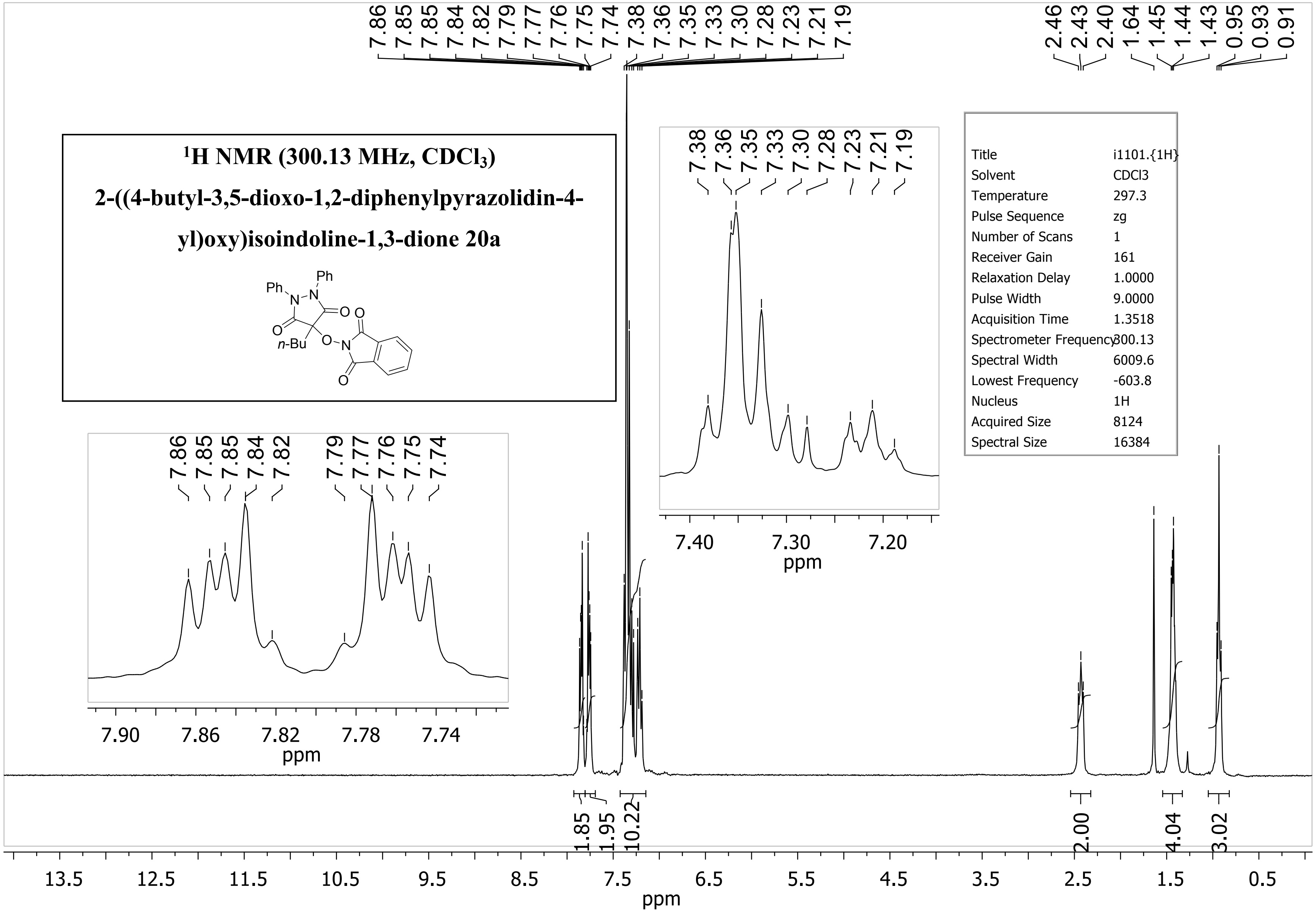
Title	i1194.{1H}
Solvent	CDCl3
Temperature	297.7
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	101
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-609.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{13}C NMR (75.47 MHz, CDCl$_3$)

4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-isopropyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 18

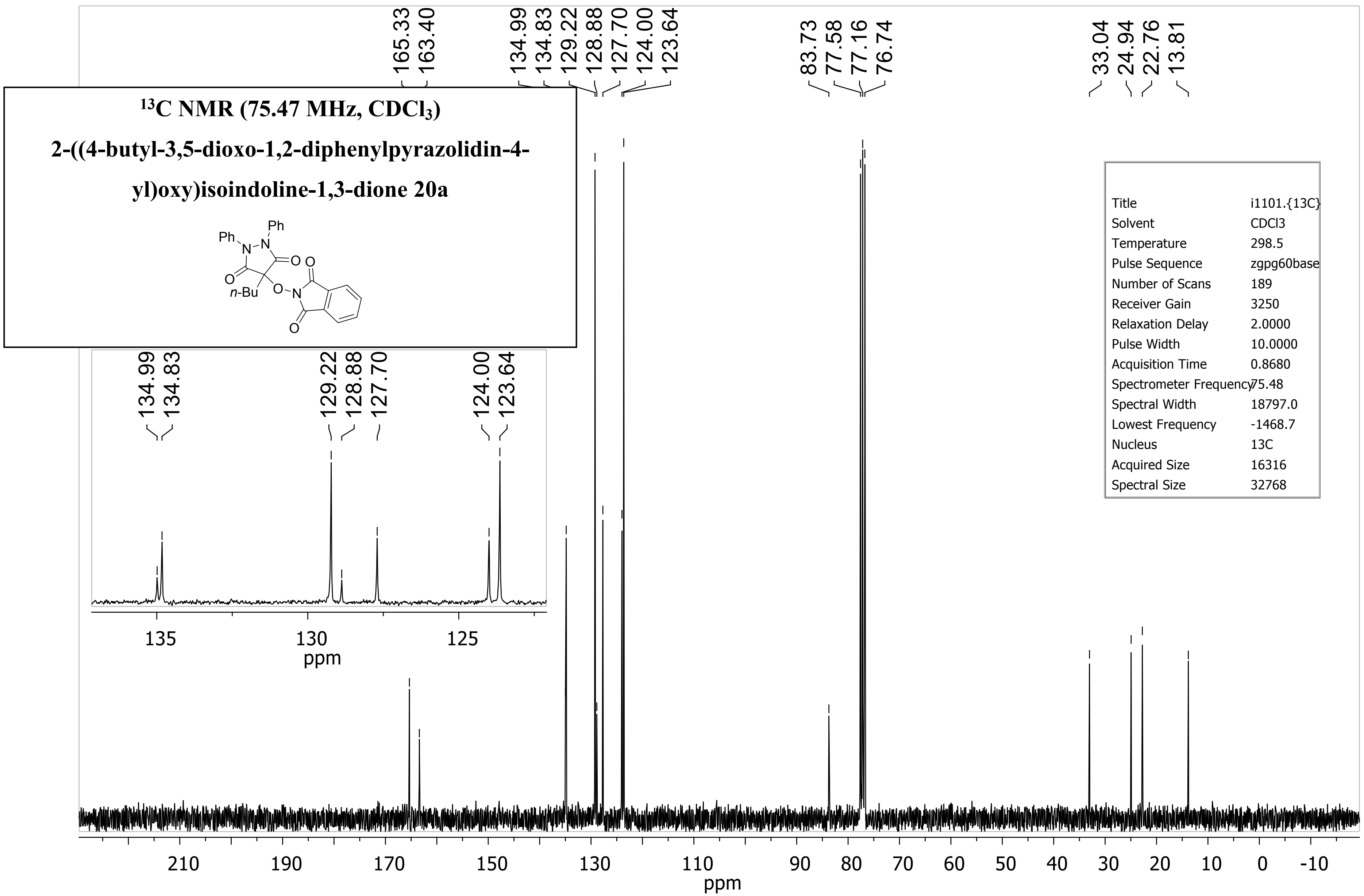
Title	i1194.{13C}
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Number of Scans	361
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-746.2
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



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

2-((4-butyl-3,5-dioxo-1,2-diphenylpyrazolidin-4-yl)oxy)isoindoline-1,3-dione 20a

Title	i1101.{1H}
Solvent	CDCl3
Temperature	297.3
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-603.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



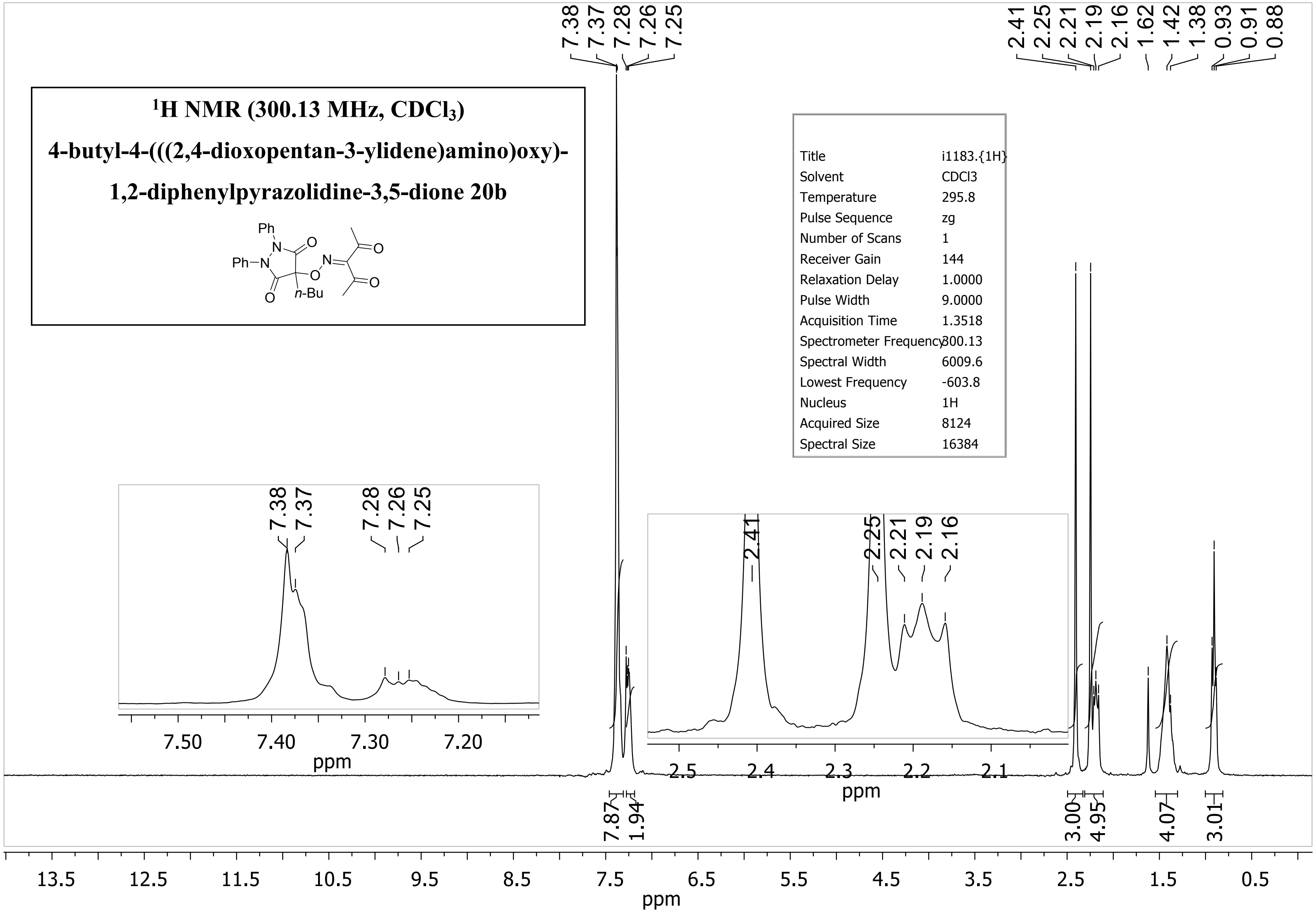
^{13}C NMR (75.47 MHz, $CDCl_3$)

2-((4-butyl-3,5-dioxo-1,2-diphenylpyrazolidin-4-yl)oxy)isoindoline-1,3-dione 20a

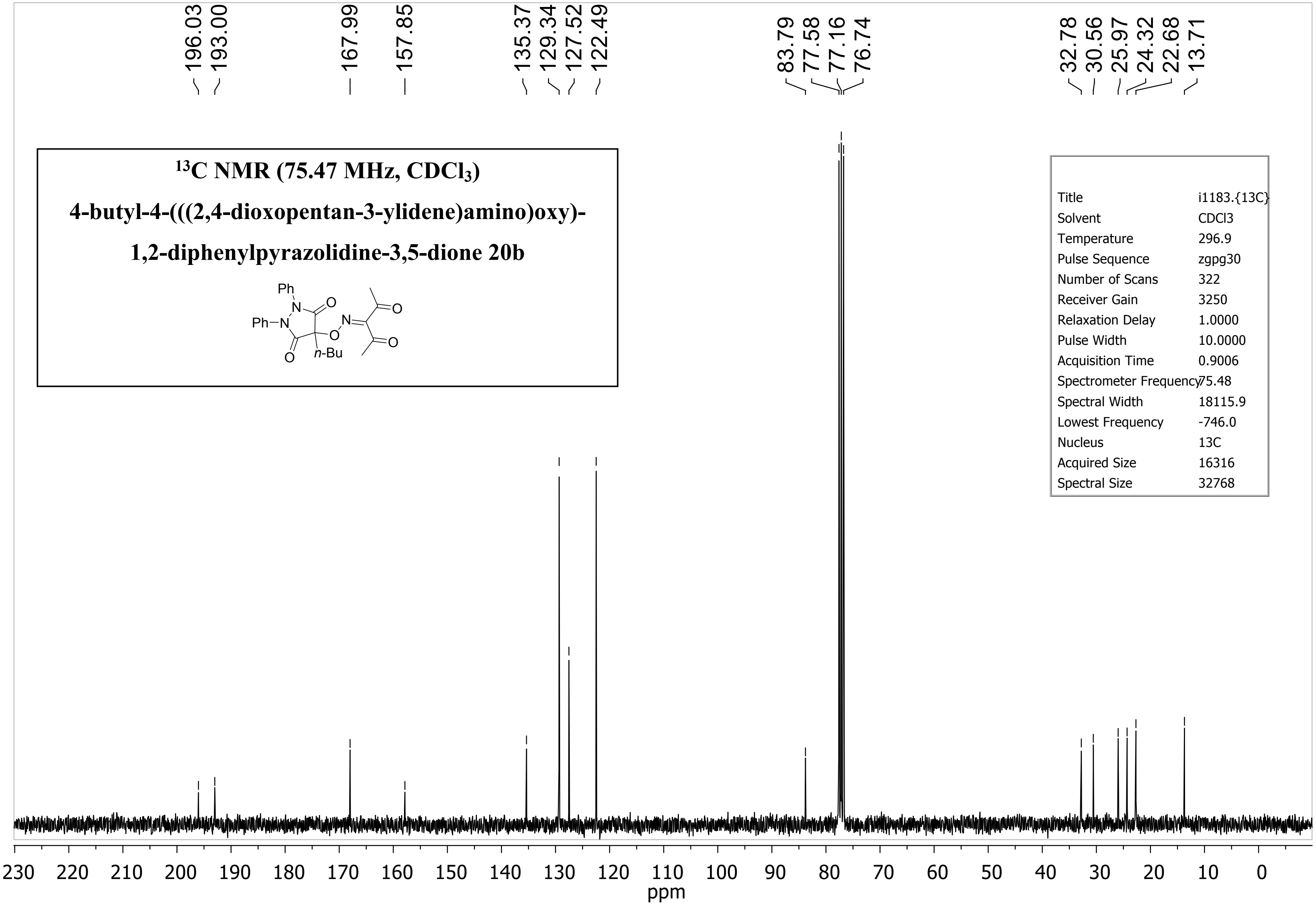
Title	i1101.{13C}
Solvent	CDCl3
Temperature	298.5
Pulse Sequence	zgpg60base
Number of Scans	189
Receiver Gain	3250
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	0.8680
Spectrometer Frequency	75.48
Spectral Width	18797.0
Lowest Frequency	-1468.7
Nucleus	13C
Acquired Size	16316
Spectral Size	32768

^{1}H NMR (300.13 MHz, CDCl$_3$)

4-butyl-4-(((2,4-dioxopentan-3-ylidene)amino)oxy)-1,2-diphenylpyrazolidine-3,5-dione 20b



Title	i1183.{1H}
Solvent	CDCl3
Temperature	295.8
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	-603.8
Nucleus	1H
Acquired Size	8124
Spectral Size	16384

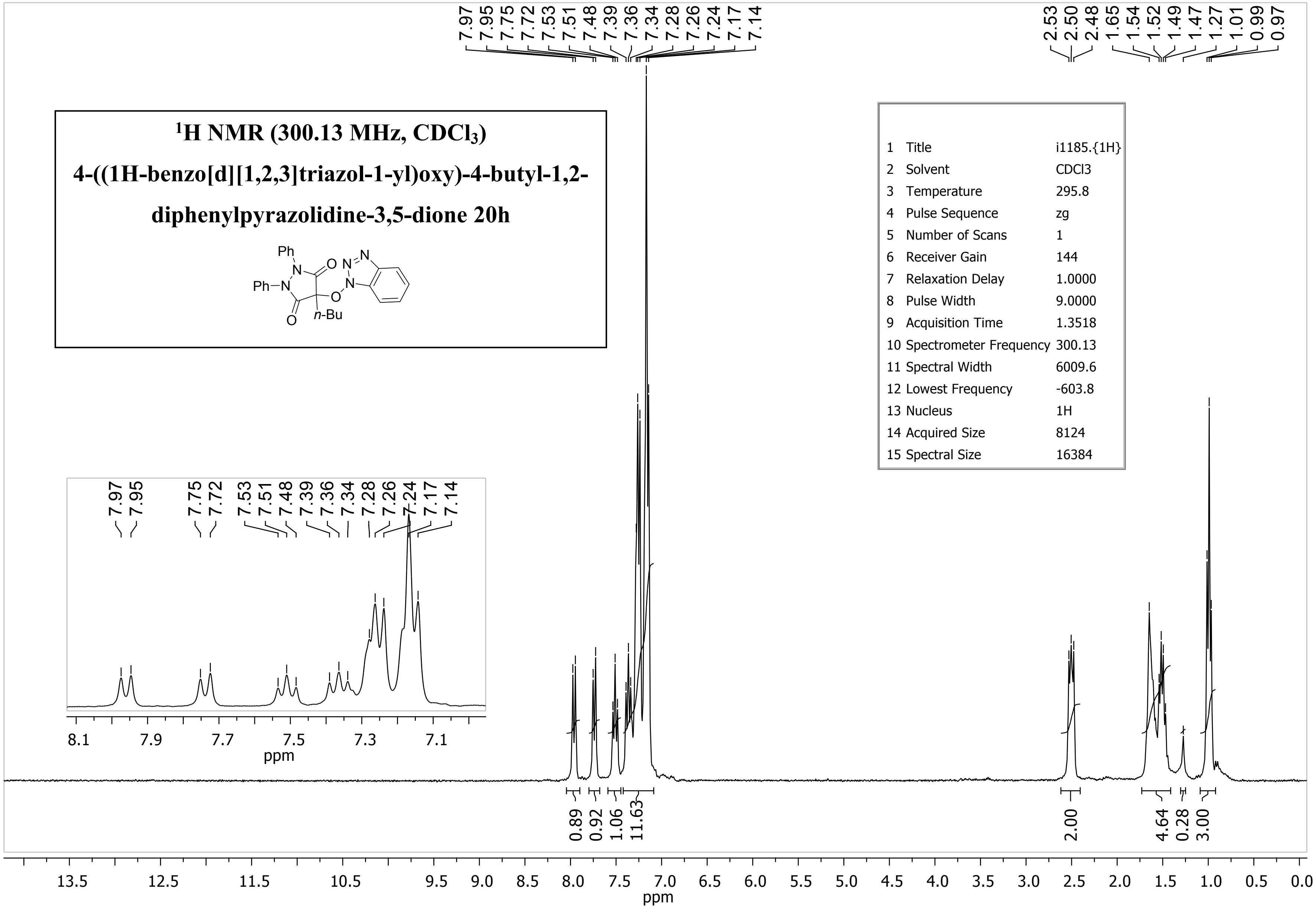


^{13}C NMR (75.47 MHz, CDCl$_3$)

4-butyl-4-(((2,4-dioxopentan-3-ylidene)amino)oxy)-

1,2-diphenylpyrazolidine-3,5-dione 20b

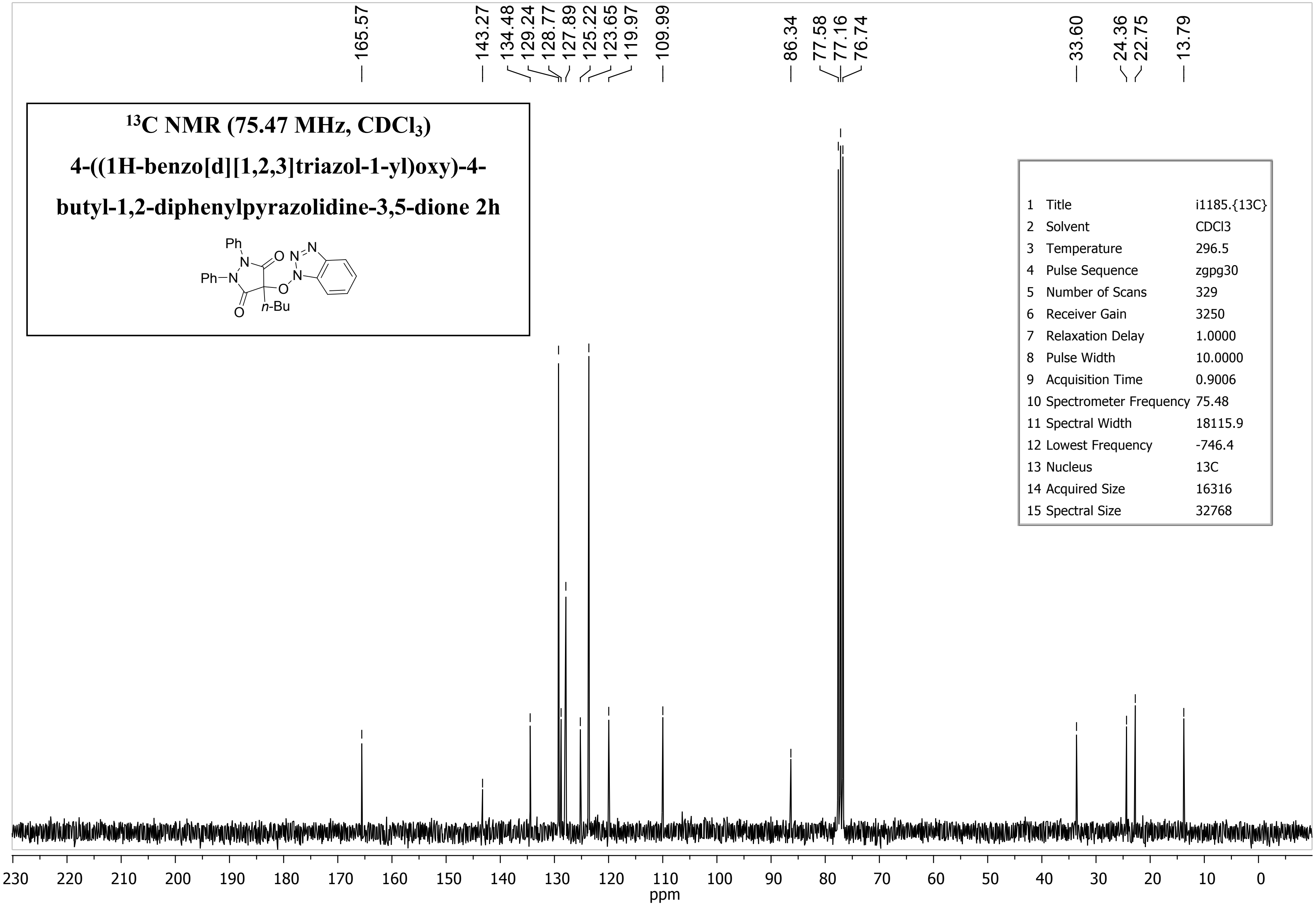
Title	i1183.{13C}
Solvent	CDCl3
Temperature	296.9
Pulse Sequence	zgpg30
Number of Scans	322
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.9006
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-746.0
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



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

4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-butyl-1,2-diphenylpyrazolidine-3,5-dione 20h

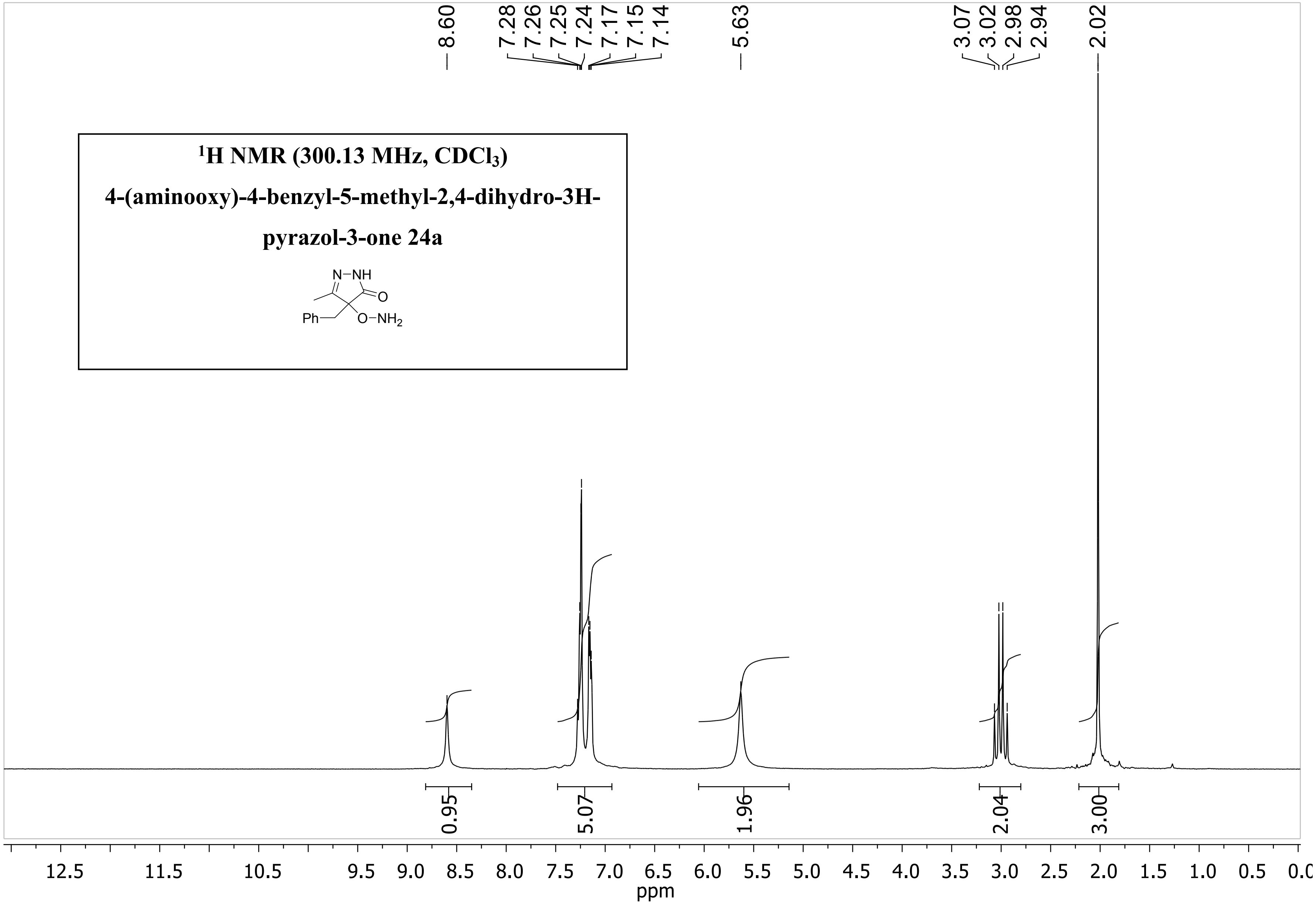
1	Title	i1185.{1H}
2	Solvent	CDCl3
3	Temperature	295.8
4	Pulse Sequence	zg
5	Number of Scans	1
6	Receiver Gain	144
7	Relaxation Delay	1.0000
8	Pulse Width	9.0000
9	Acquisition Time	1.3518
10	Spectrometer Frequency	300.13
11	Spectral Width	6009.6
12	Lowest Frequency	-603.8
13	Nucleus	1H
14	Acquired Size	8124
15	Spectral Size	16384

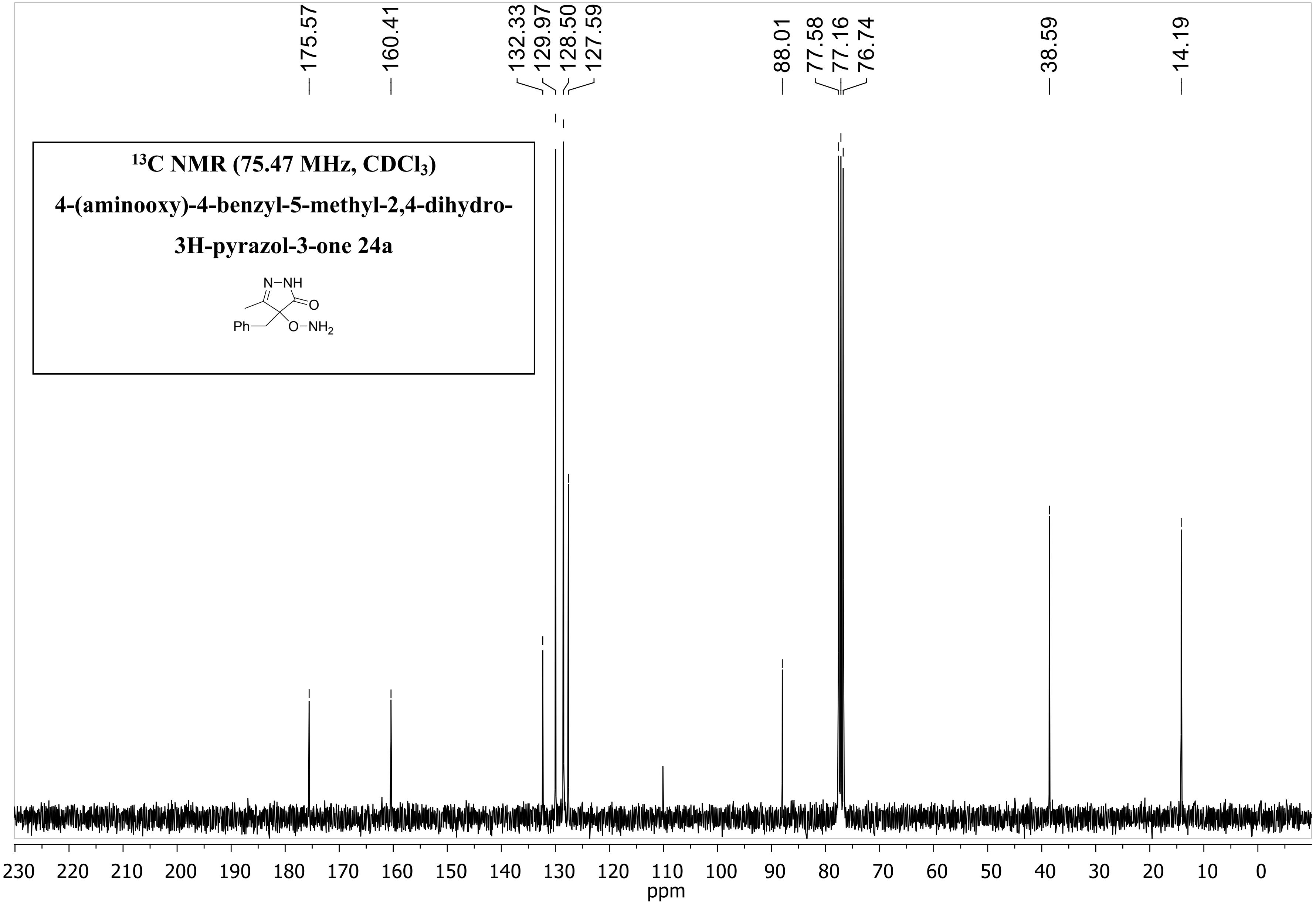


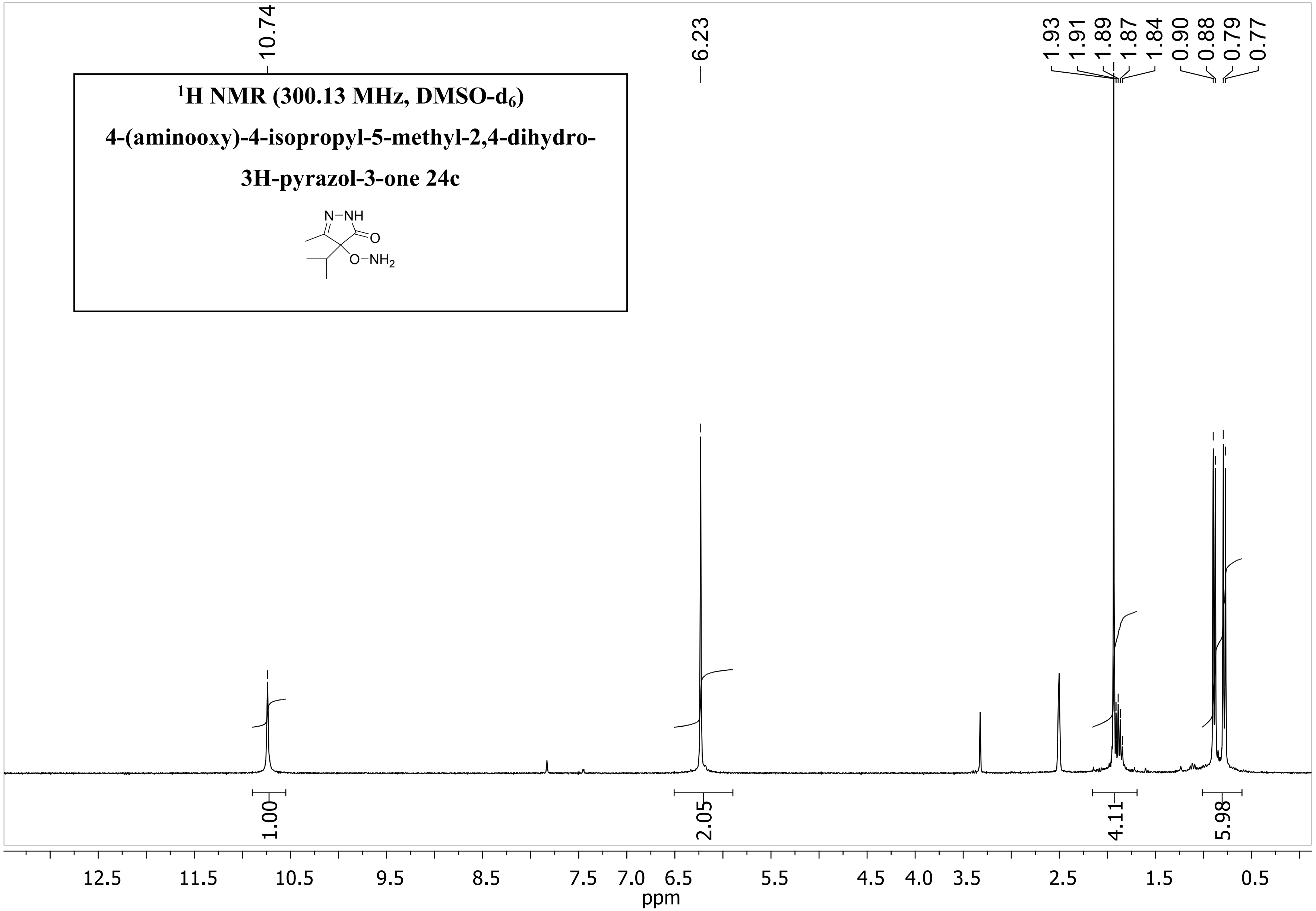
^{13}C NMR (75.47 MHz, $CDCl_3$)

4-((1H-benzo[d][1,2,3]triazol-1-yl)oxy)-4-butyl-1,2-diphenylpyrazolidine-3,5-dione 2h

1	Title	i1185.{13C}
2	Solvent	CDCl3
3	Temperature	296.5
4	Pulse Sequence	zgpg30
5	Number of Scans	329
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	-746.4
13	Nucleus	13C
14	Acquired Size	16316
15	Spectral Size	32768

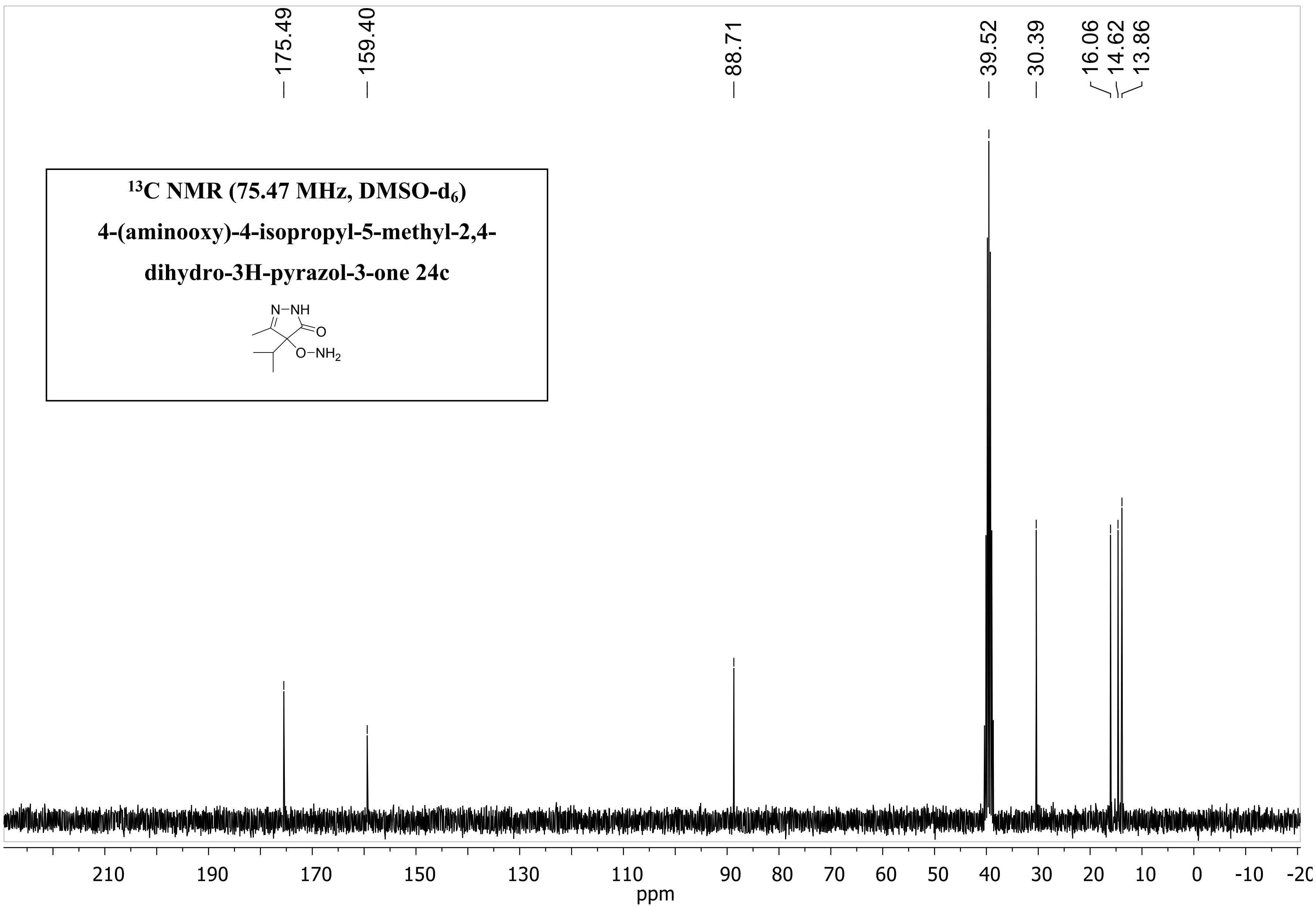

8.60
7.28
7.26
7.25
7.24
7.17
7.15
7.14
5.63
3.07
3.02
2.98
2.94
2.02
^{1}H NMR (300.13 MHz, CDCl$_3$)
4-(aminooxy)-4-benzyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24a
N–NH
O
Ph
O–NH$_2$
0.95
5.07
1.96
2.04
3.00
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


13C NMR (75.47 MHz, CDCl3)
4-(aminooxy)-4-benzyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24a
N–NH
O
Ph
O–NH2
175.57
160.41
132.33
129.97
128.50
127.59
88.01
77.58
77.16
76.74
38.59
14.19
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

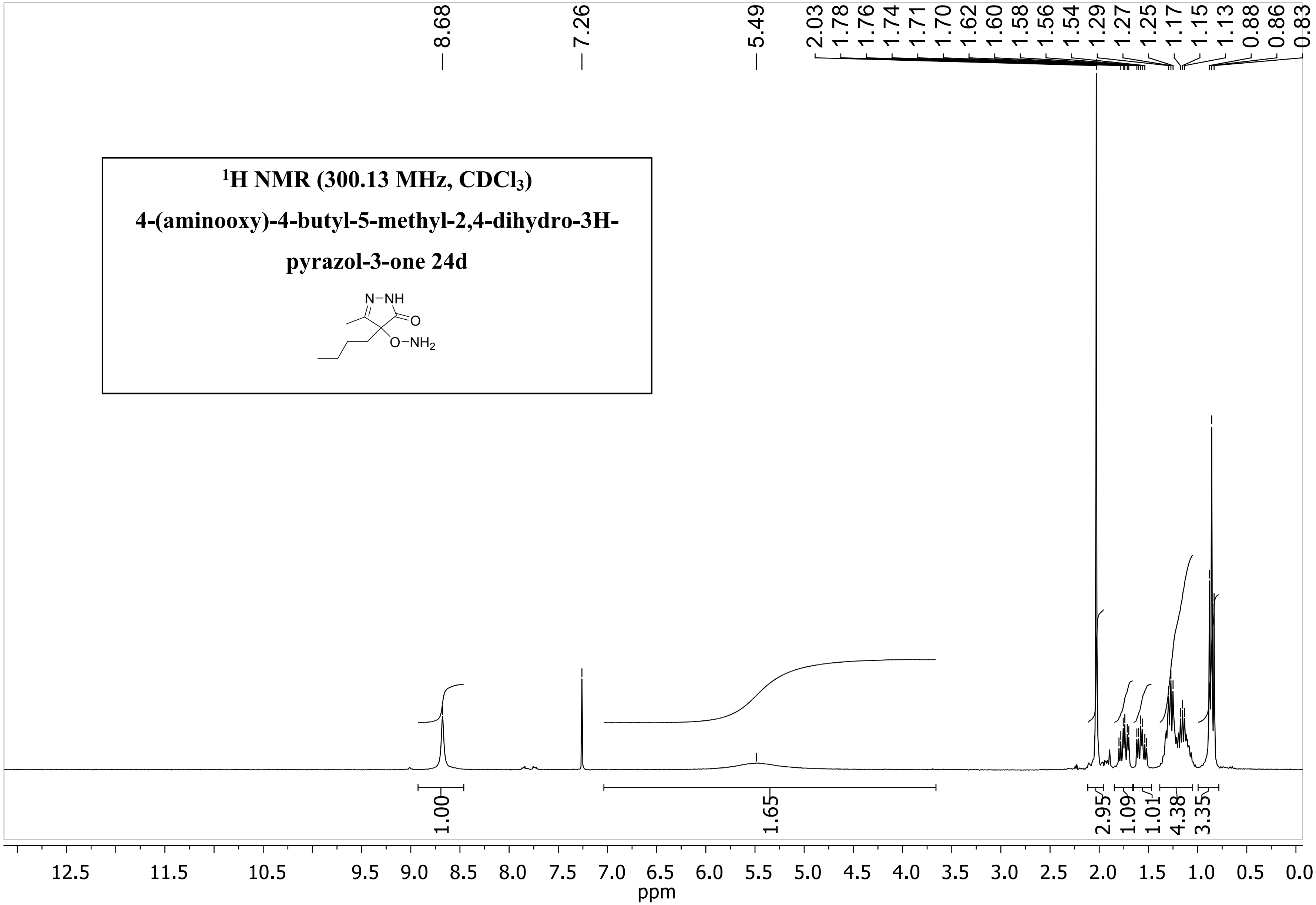


^{1}H NMR (300.13 MHz, DMSO-d_6)

4-(aminooxy)-4-isopropyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24c

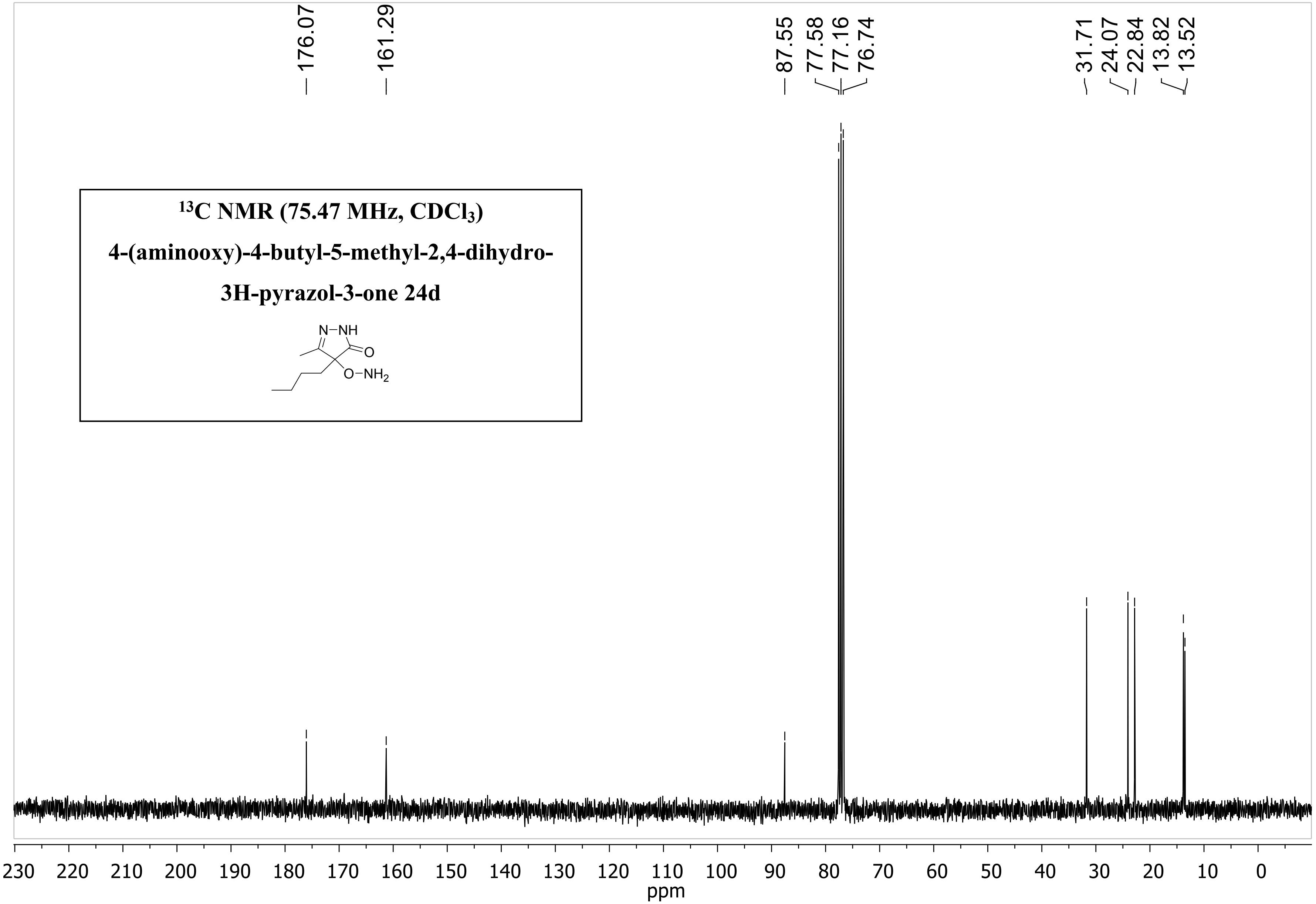


175.49
159.40
88.71
39.52
30.39
16.06
14.62
13.86
^{13}C NMR (75.47 MHz, DMSO-d$_6$)
4-(aminooxy)-4-isopropyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24c
N–NH
O
O–NH$_2$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
ppm



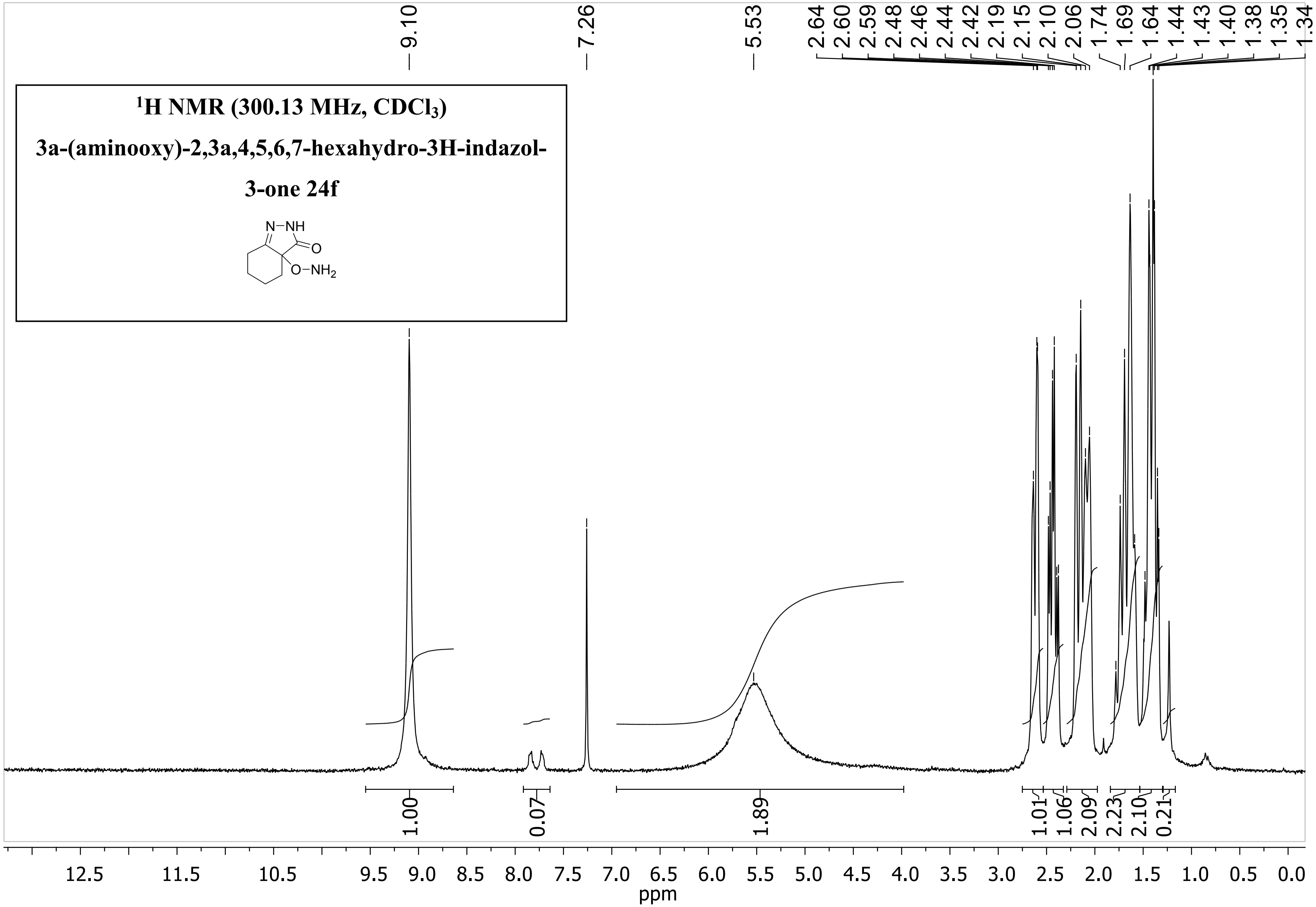
^{1}H NMR (300.13 MHz, $CDCl_3$)

4-(aminooxy)-4-butyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24d



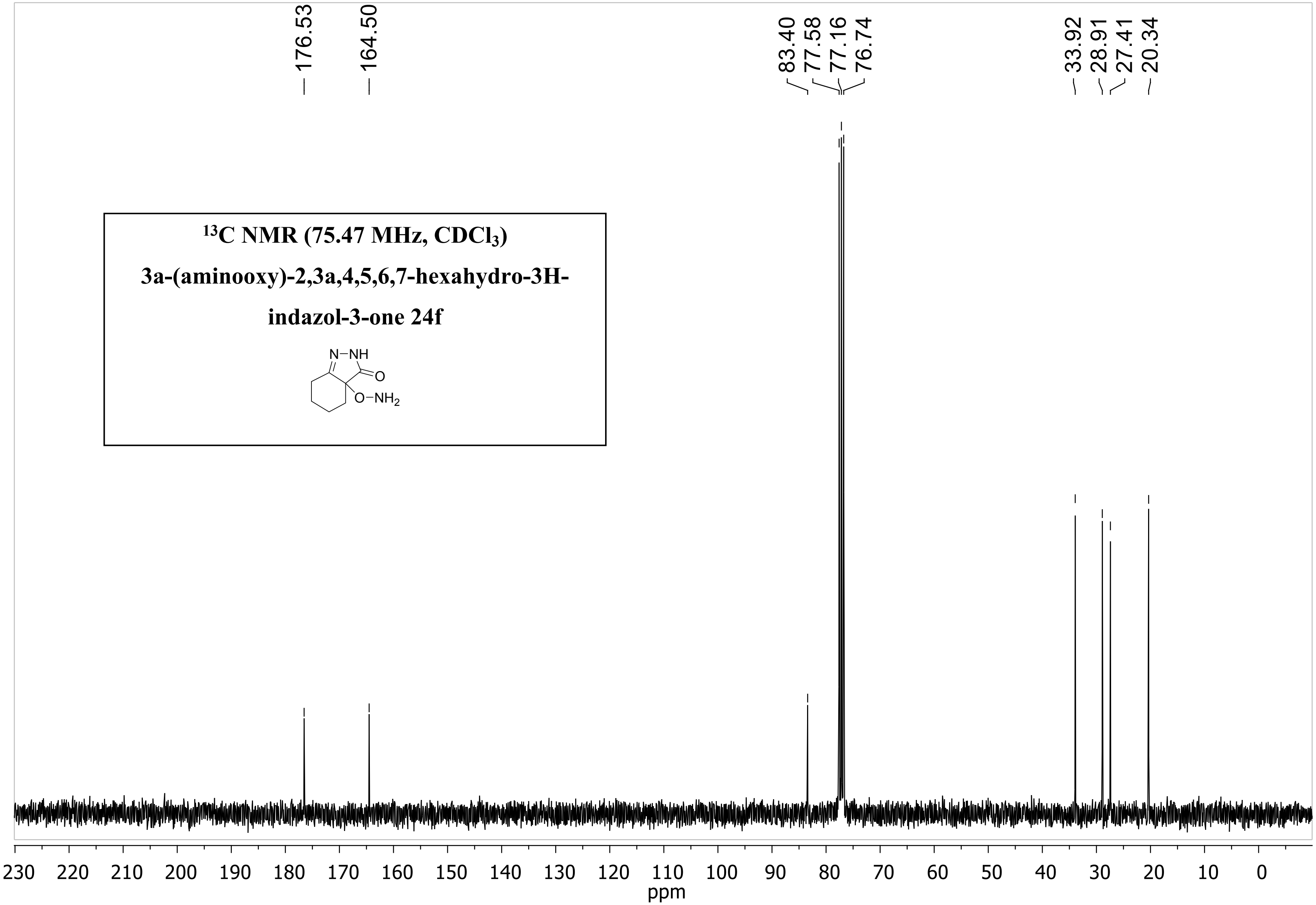
^{13}C NMR (75.47 MHz, $CDCl_3$)

4-(aminooxy)-4-butyl-5-methyl-2,4-dihydro-3H-pyrazol-3-one 24d



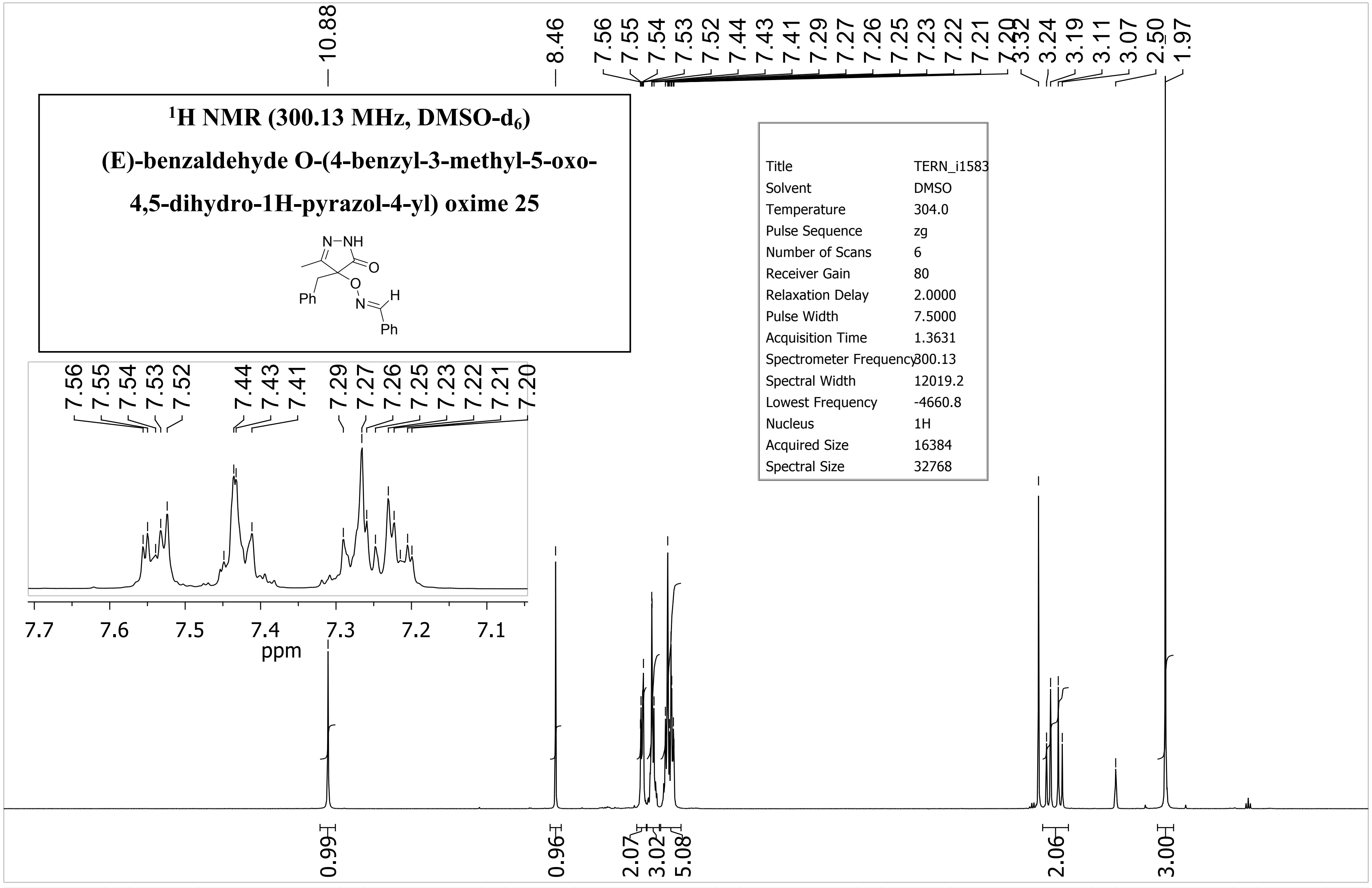
^{1}H NMR (300.13 MHz, CDCl$_3$)

3a-(aminooxy)-2,3a,4,5,6,7-hexahydro-3H-indazol-3-one 24f



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

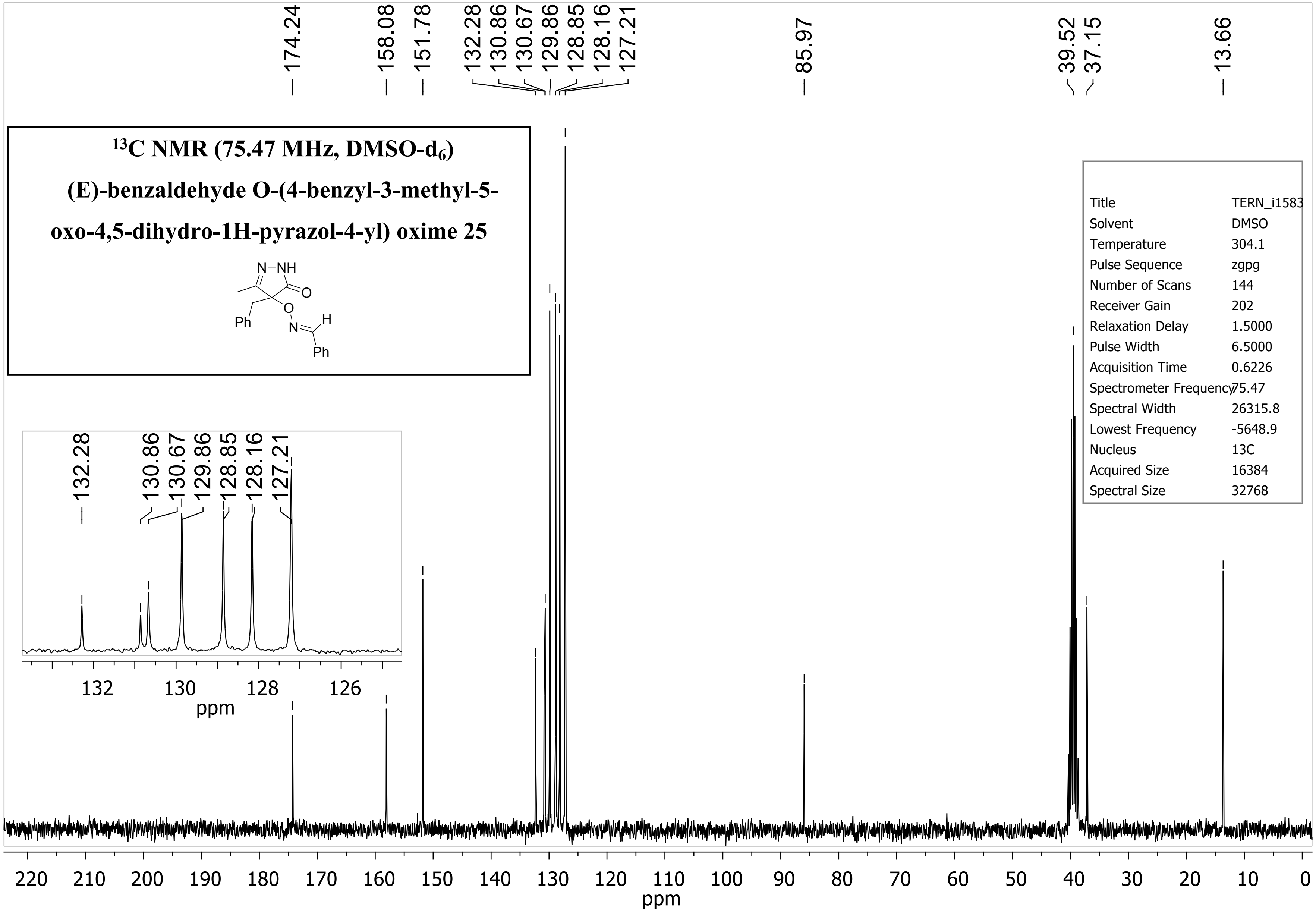
3a-(aminooxy)-2,3a,4,5,6,7-hexahydro-3H-indazol-3-one 24f



^{1}H NMR (300.13 MHz, DMSO-d$_6$)

(E)-benzaldehyde O-(4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl) oxime 25

Title	TERN_i1583
Solvent	DMSO
Temperature	304.0
Pulse Sequence	zg
Number of Scans	6
Receiver Gain	80
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.3631
Spectrometer Frequency	300.13
Spectral Width	12019.2
Lowest Frequency	-4660.8
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

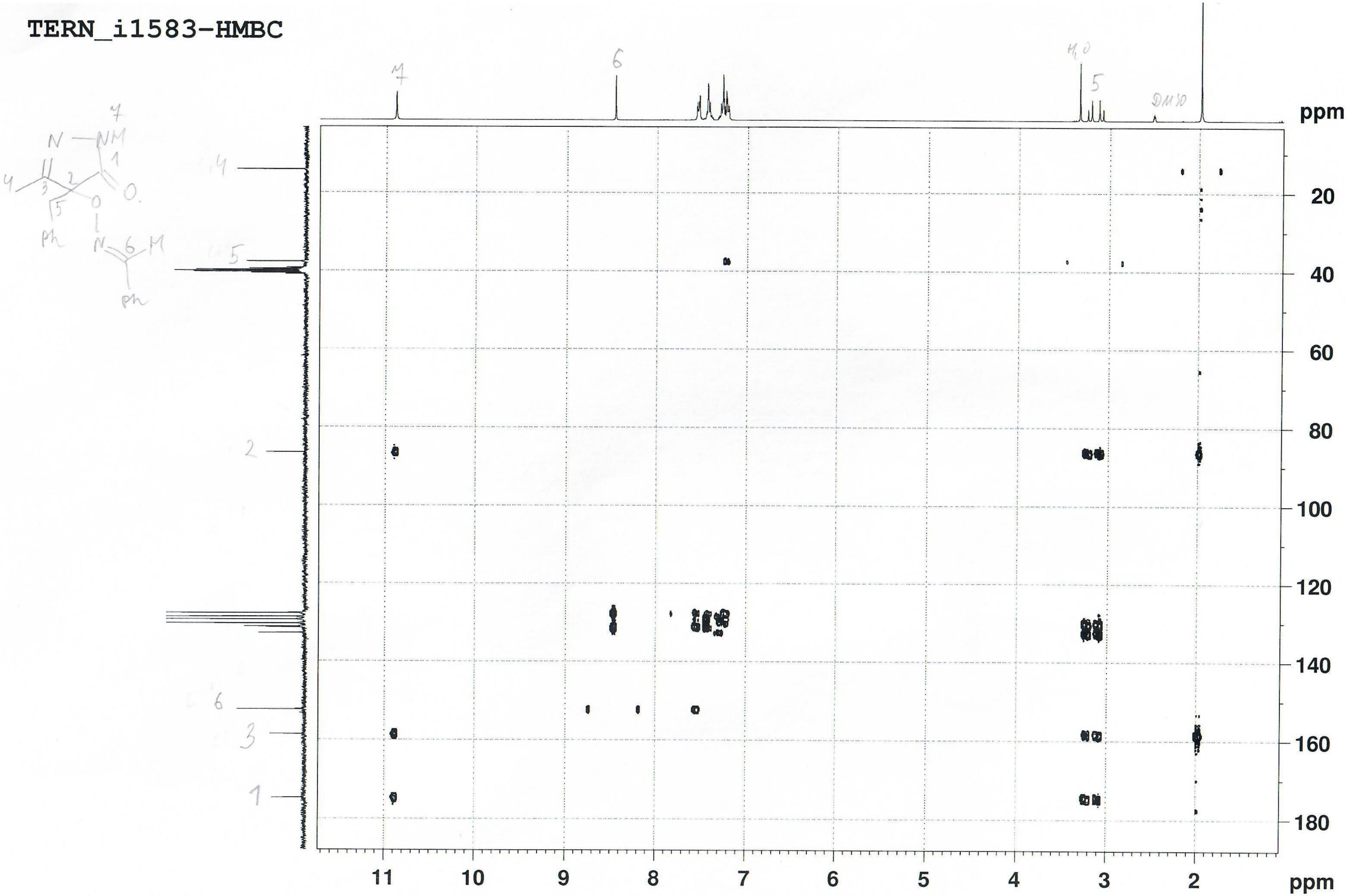


^{13}C NMR (75.47 MHz, DMSO-d$_6$)

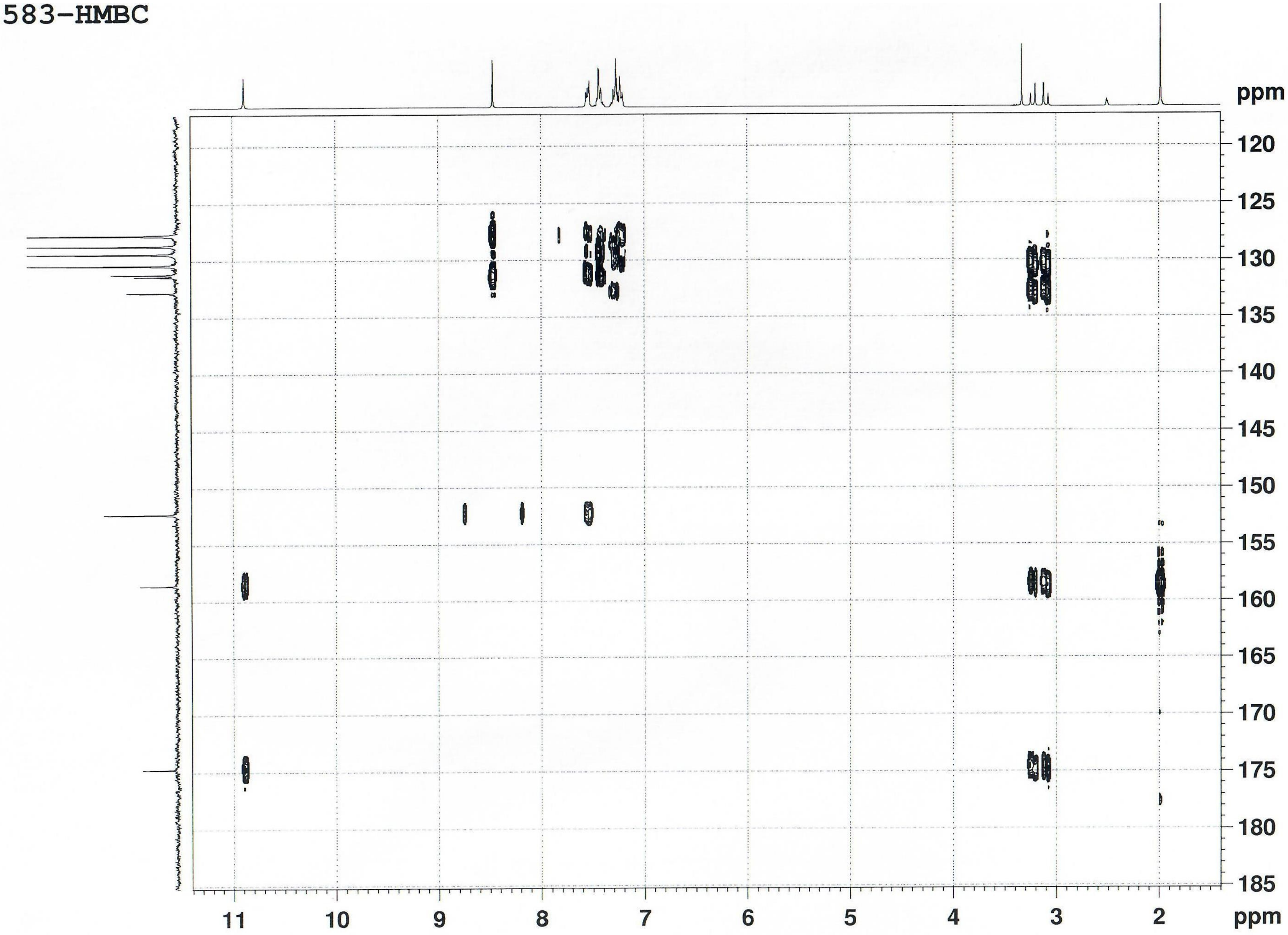
(E)-benzaldehyde O-(4-benzyl-3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl) oxime 25

Title	TERN_i1583
Solvent	DMSO
Temperature	304.1
Pulse Sequence	zgpg
Number of Scans	144
Receiver Gain	202
Relaxation Delay	1.5000
Pulse Width	6.5000
Acquisition Time	0.6226
Spectrometer Frequency	75.47
Spectral Width	26315.8
Lowest Frequency	-5648.9
Nucleus	13C
Acquired Size	16384
Spectral Size	32768

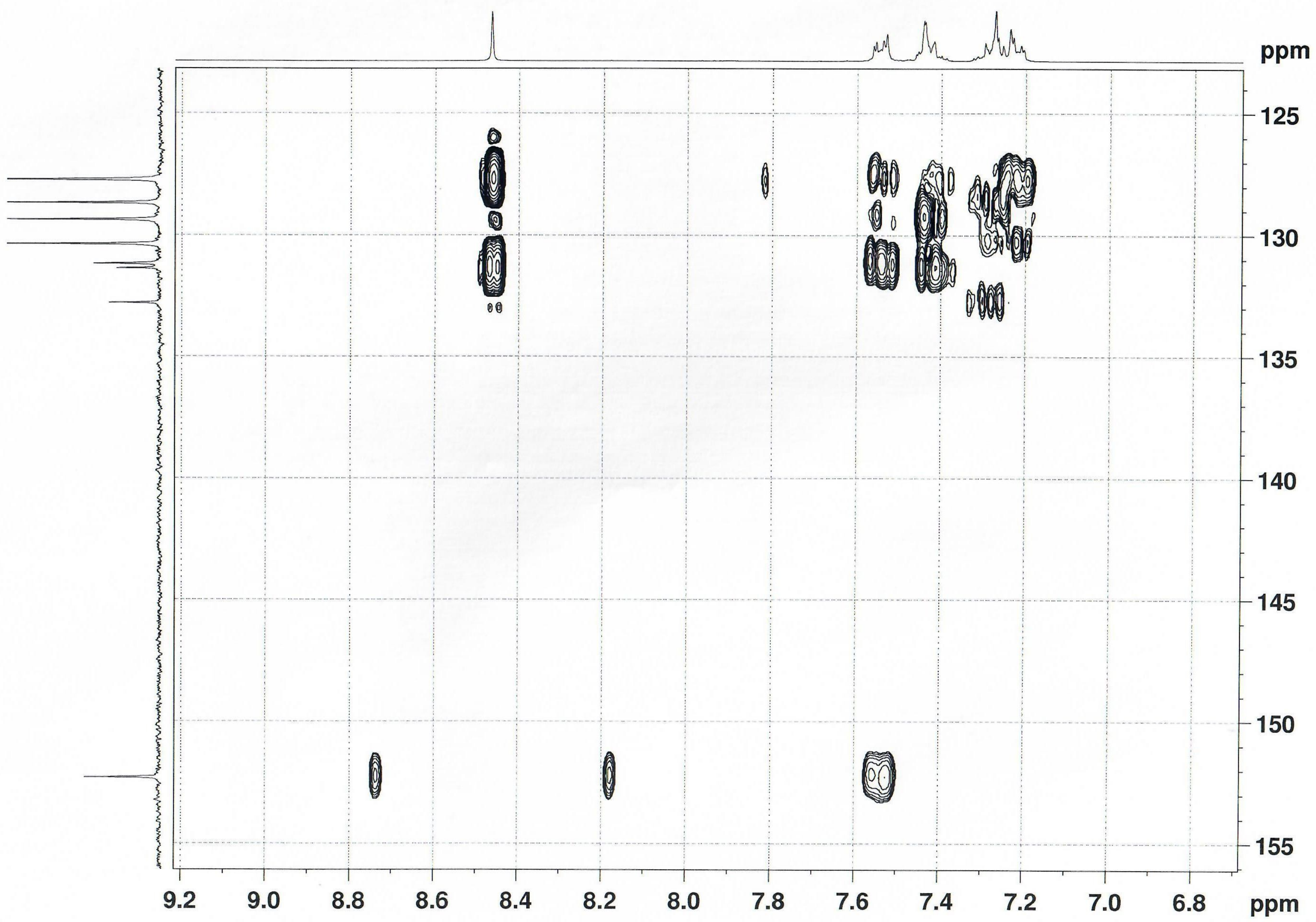
TERN_i1583-HMBC



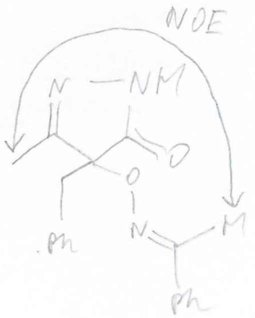
TERN_i1583-HMBC

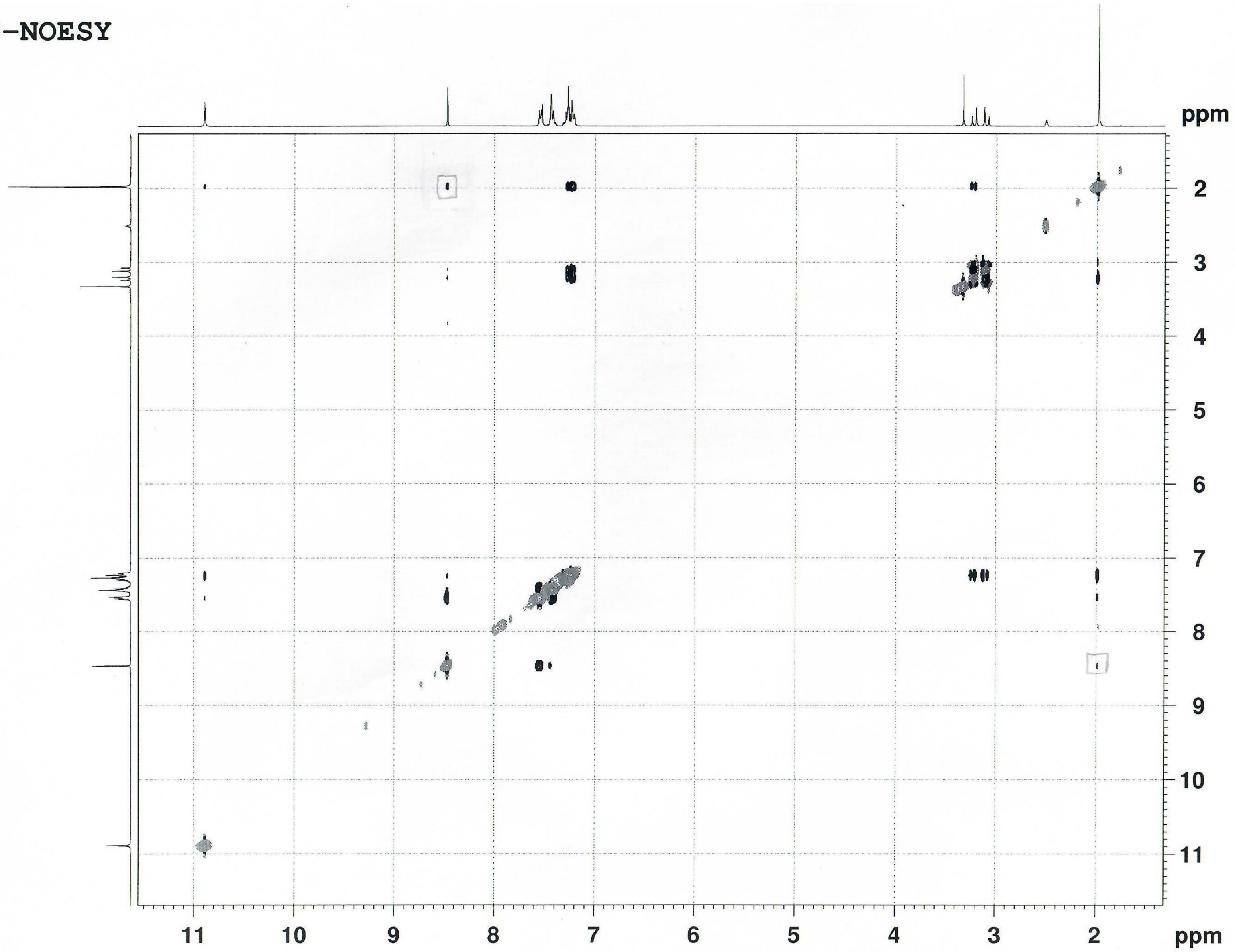


TERN_i1583-HMBC

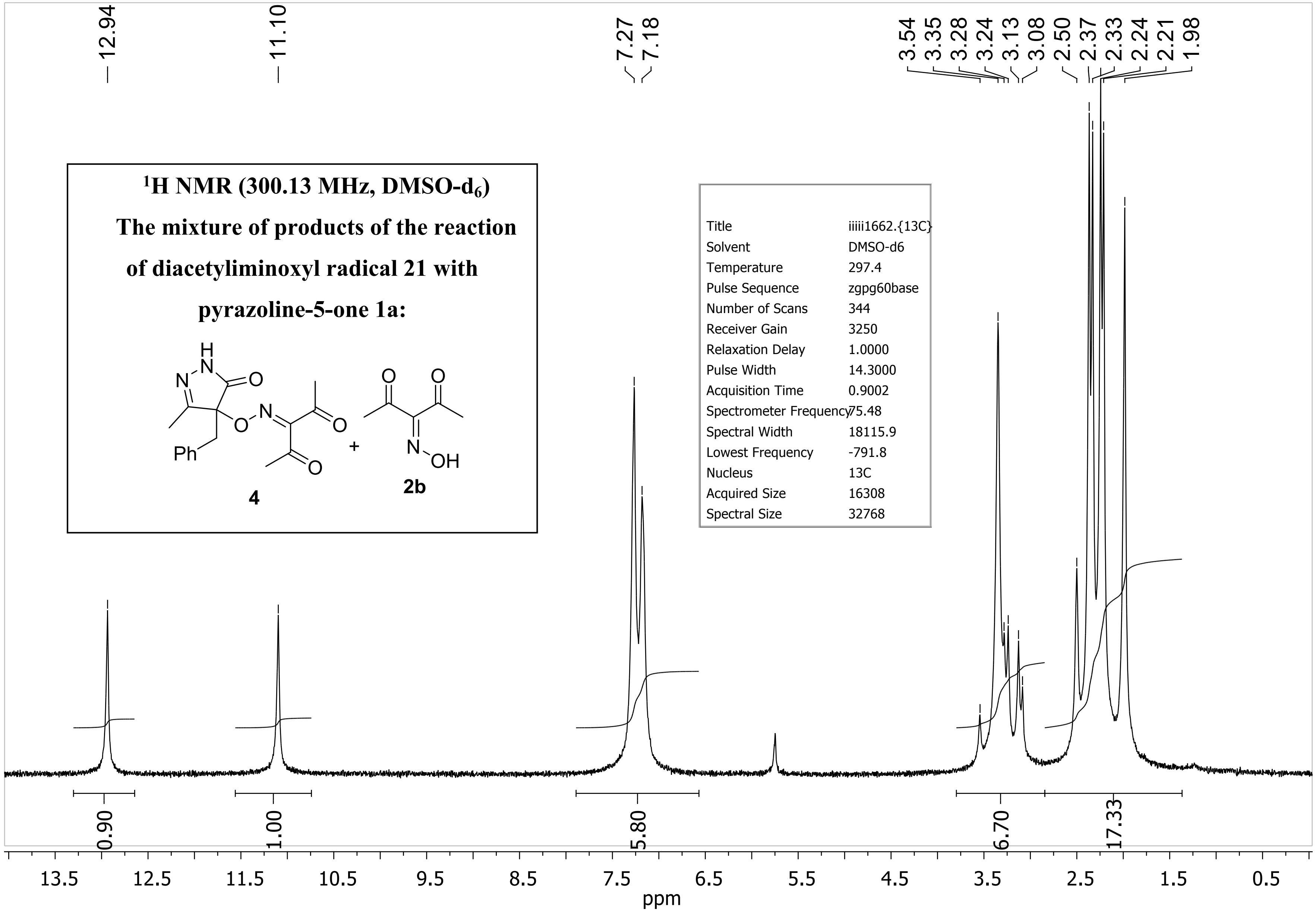


TERN_i1583-NOESY





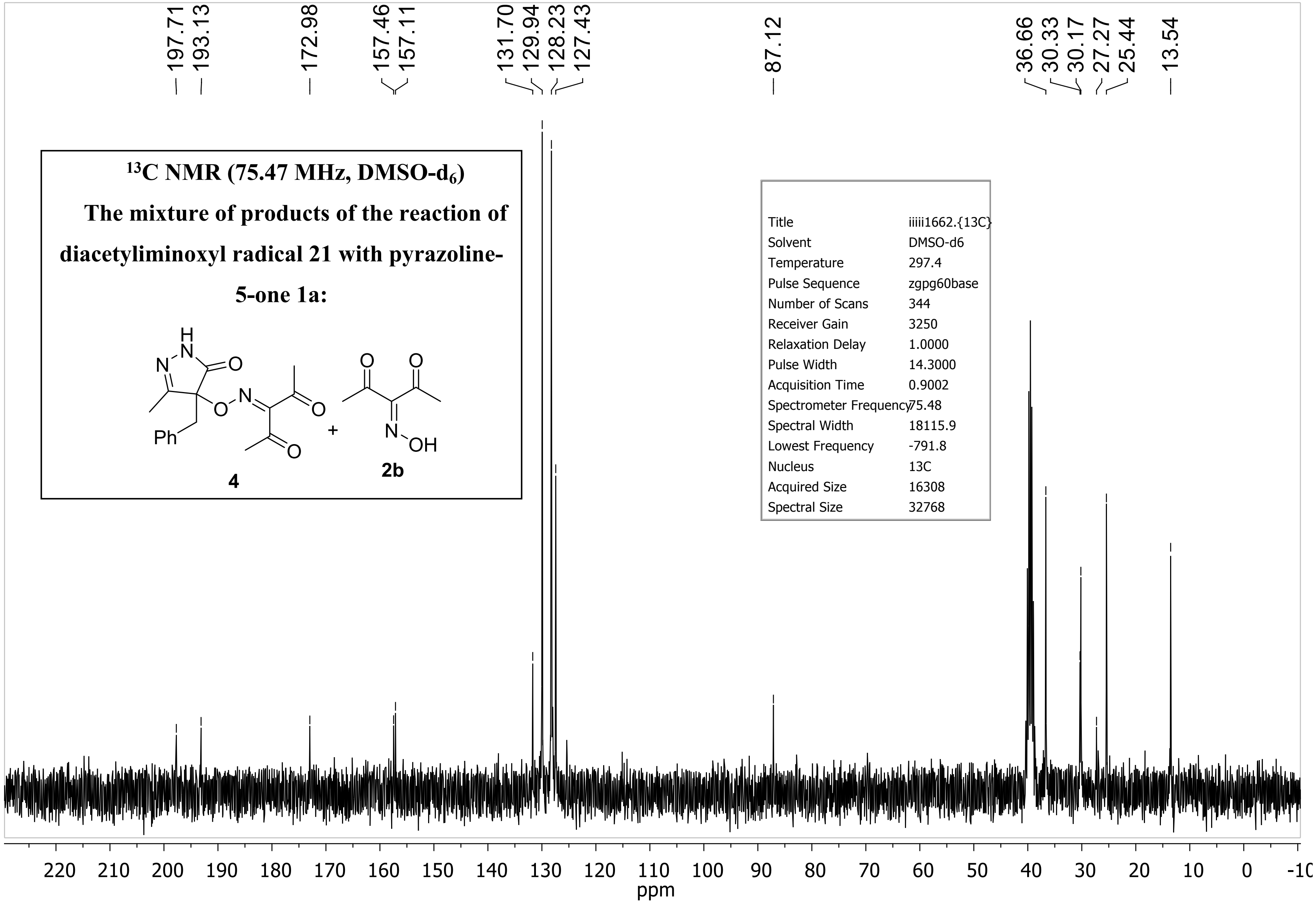
The spectra of the reaction mixtures of pyrazolin-5-ones (1a, 1c, 1h, 1i) with diacetyliminoxyl radical 21



^{1}H NMR (300.13 MHz, DMSO-d_6)

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1a:

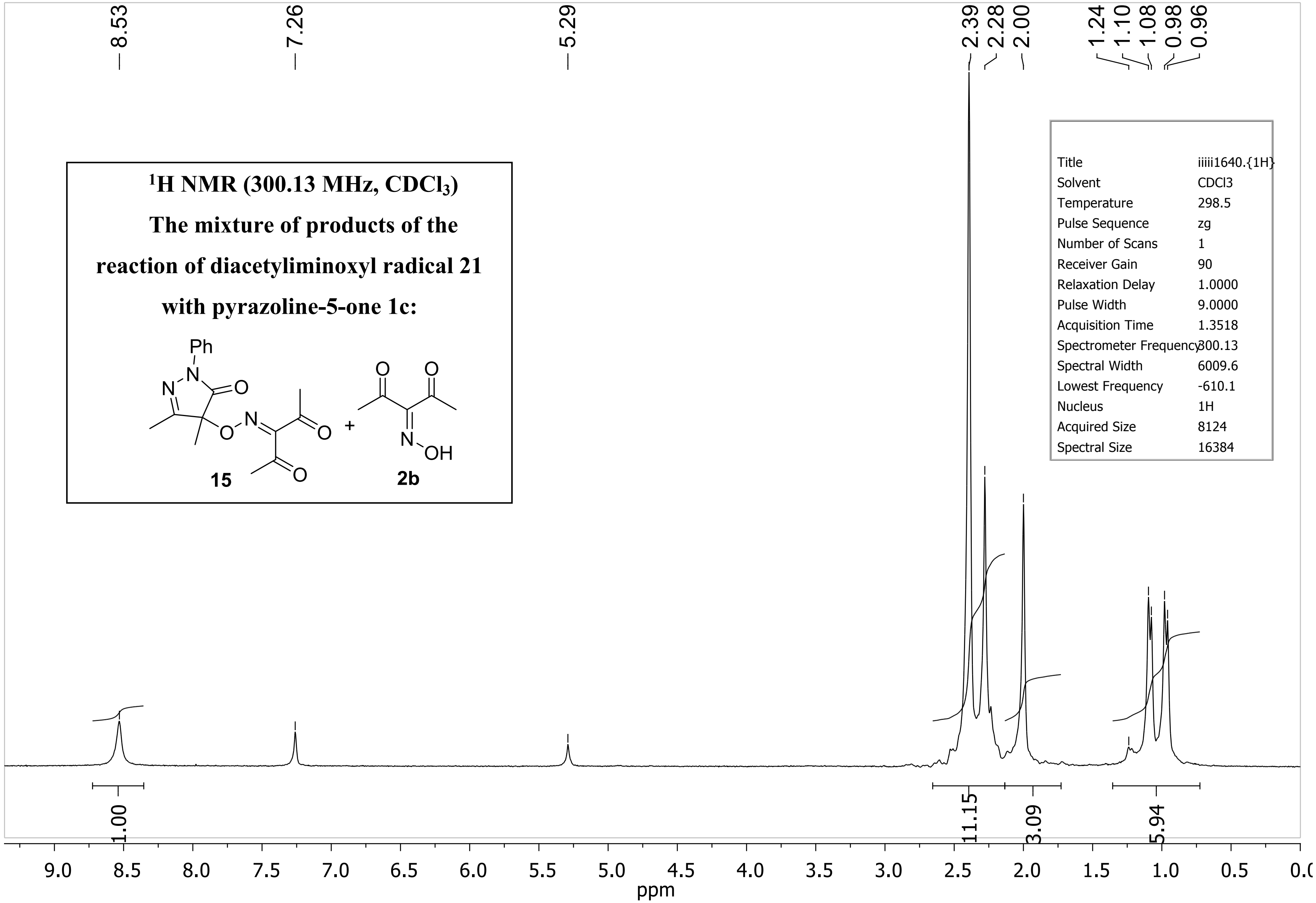
Title	iiiii1662.{13C}
Solvent	DMSO-d6
Temperature	297.4
Pulse Sequence	zgpg60base
Number of Scans	344
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-791.8
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



^{13}C NMR (75.47 MHz, DMSO-d_6)

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1a:

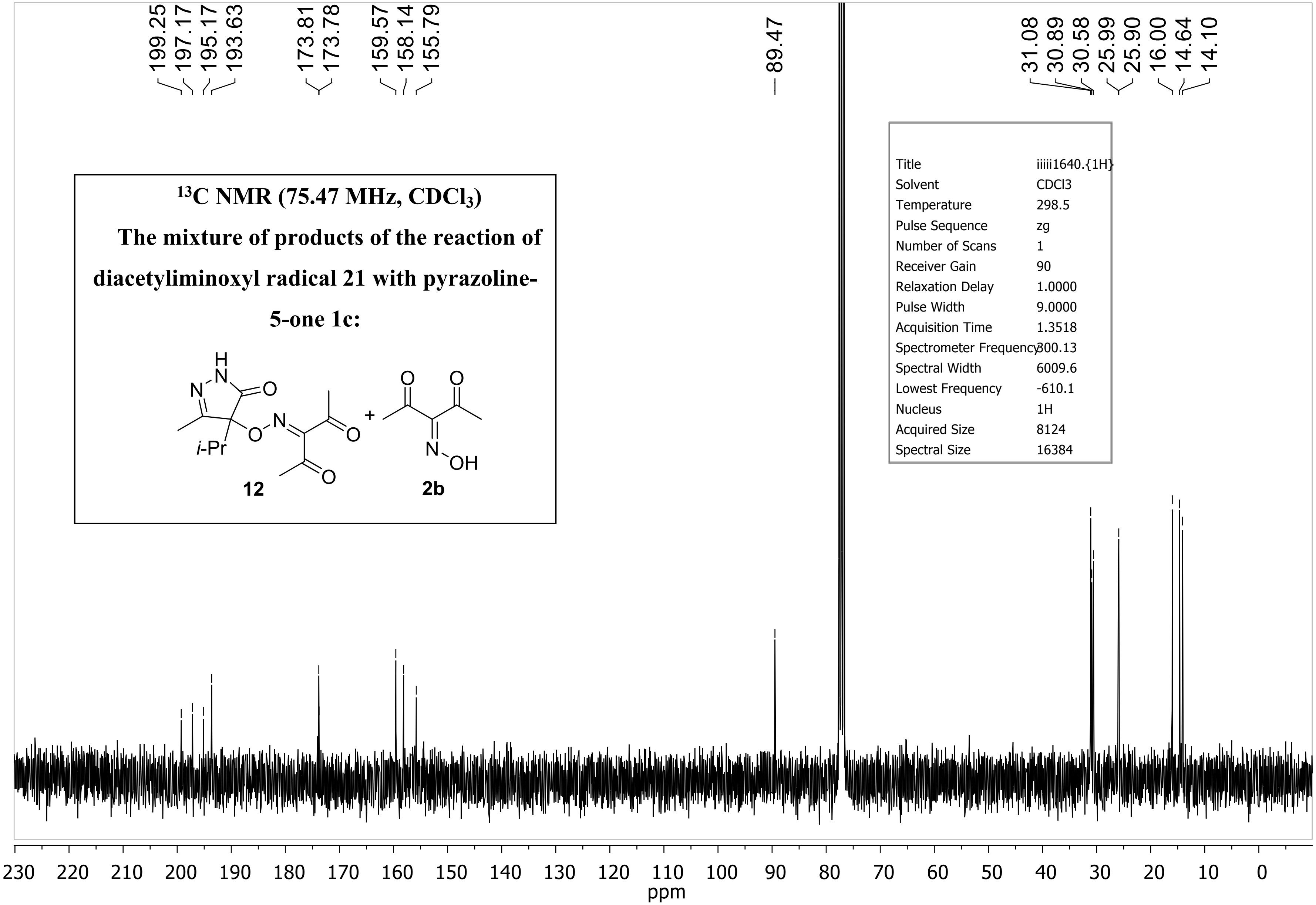
Title	iiiii1662.{13C}
Solvent	DMSO-d6
Temperature	297.4
Pulse Sequence	zgpg60base
Number of Scans	344
Receiver Gain	3250
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	0.9002
Spectrometer Frequency	75.48
Spectral Width	18115.9
Lowest Frequency	-791.8
Nucleus	13C
Acquired Size	16308
Spectral Size	32768



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

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1c:

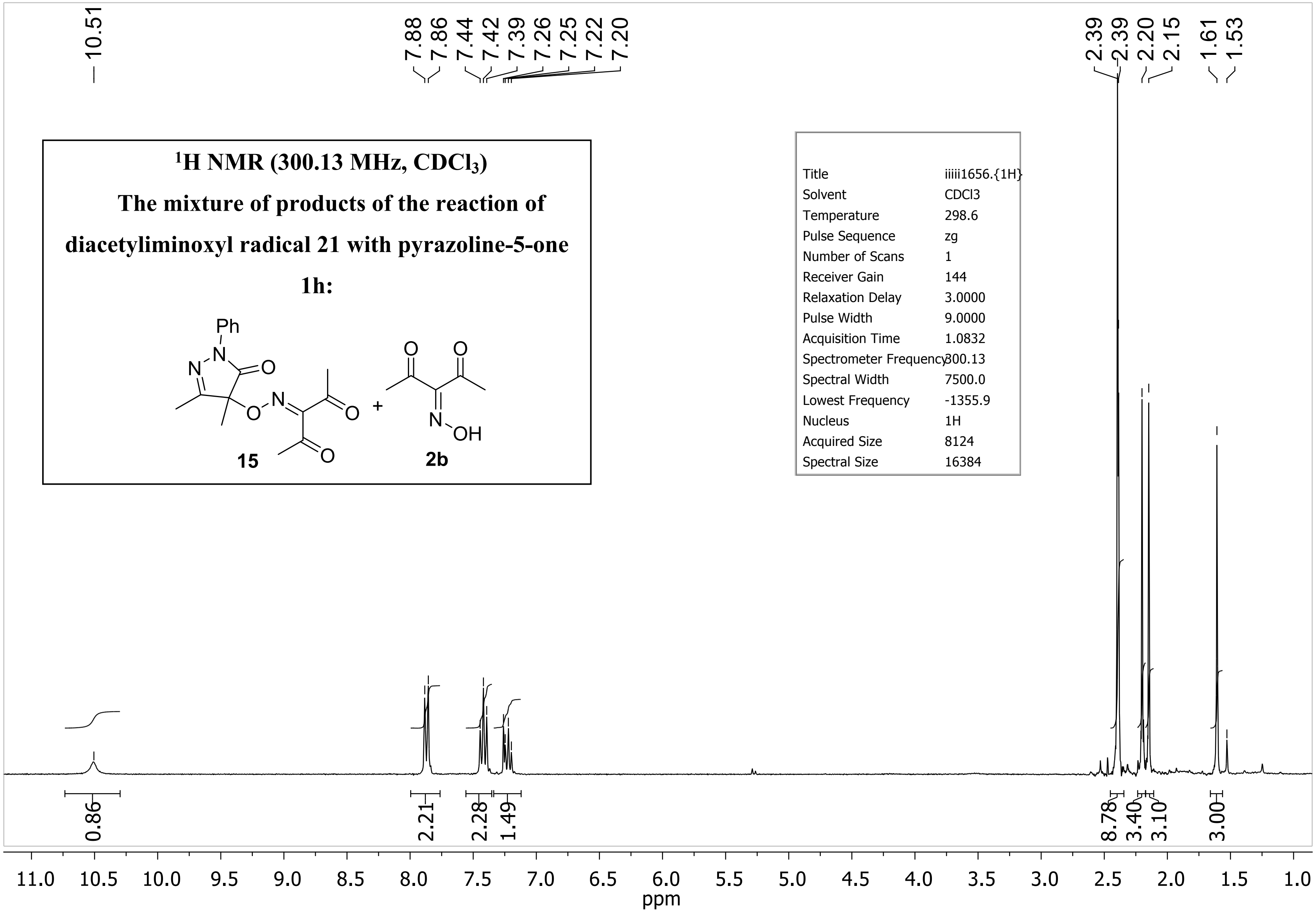
Title	iiiii1640.{1H}
Solvent	CDCl3
Temperature	298.5
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	90
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.1
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{13}C NMR (75.47 MHz, CDCl$_3$)

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1c:

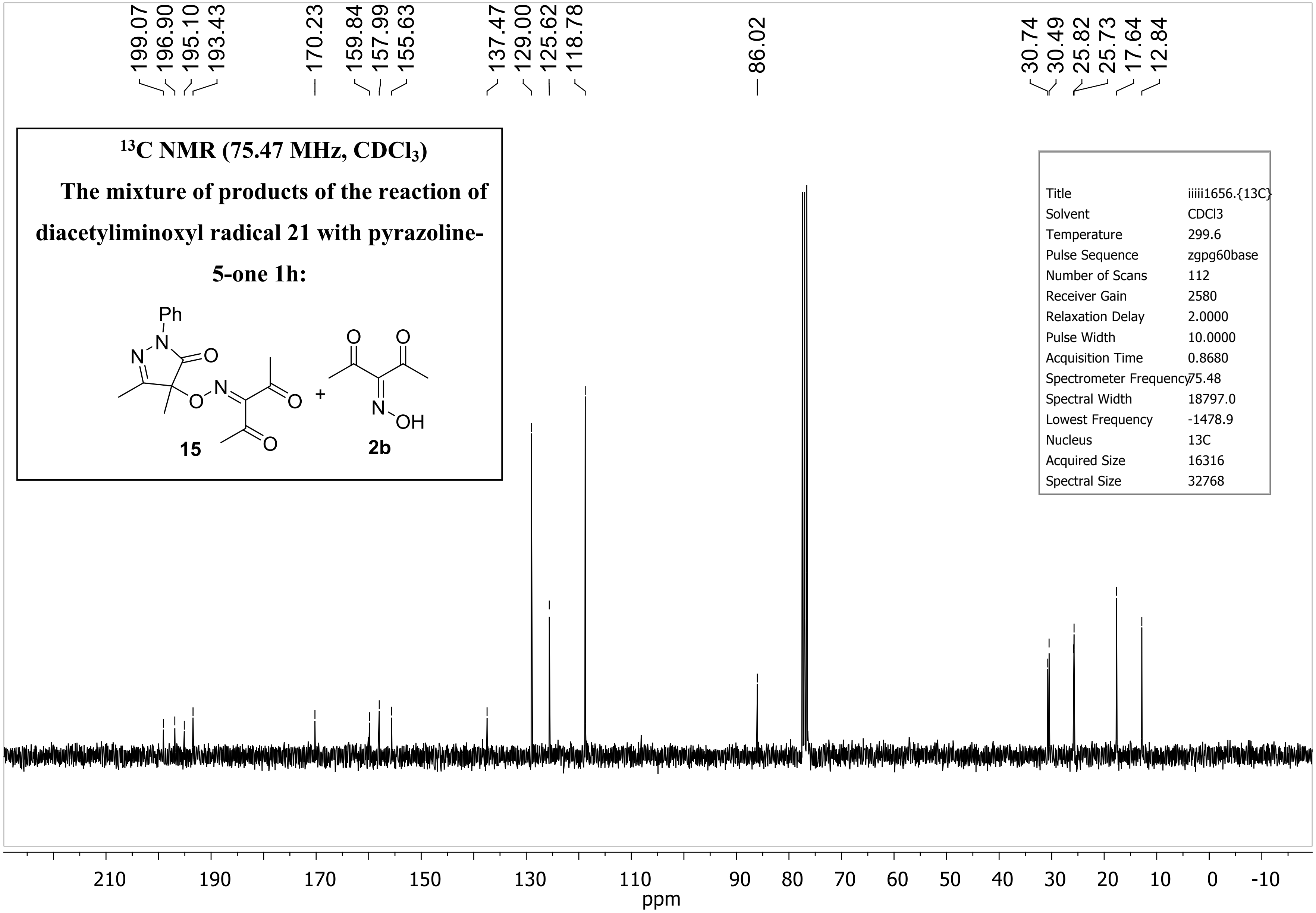
Title	iiiii1640.{1H}
Solvent	CDCl3
Temperature	298.5
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	90
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-610.1
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{1}H NMR (300.13 MHz, CDCl$_3$)

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1h:

Title	iiiii1656.{1H}
Solvent	CDCl3
Temperature	298.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	144
Relaxation Delay	3.0000
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

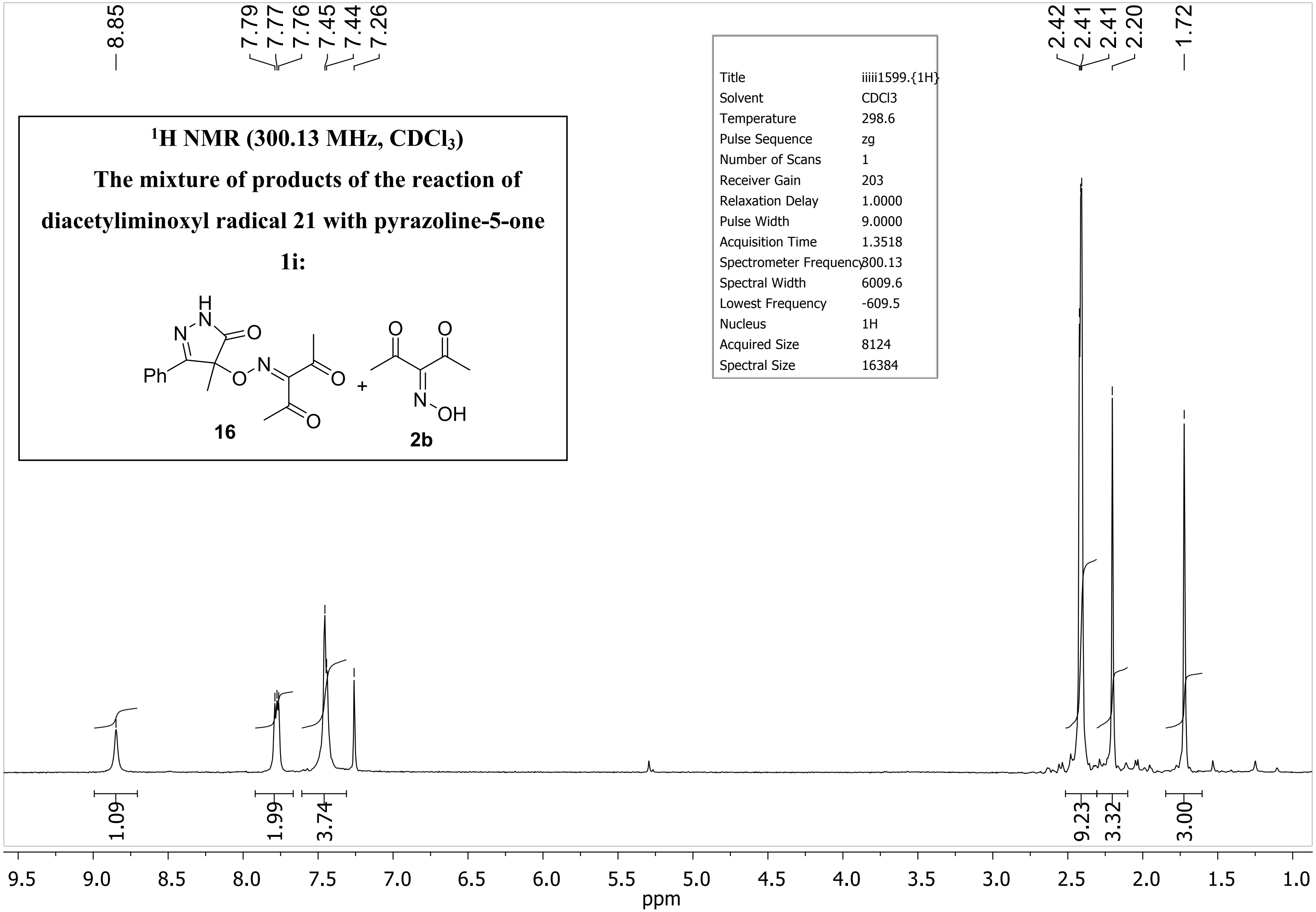


^{13}C NMR (75.47 MHz, CDCl$_3$)

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1h:

15 + **2b**

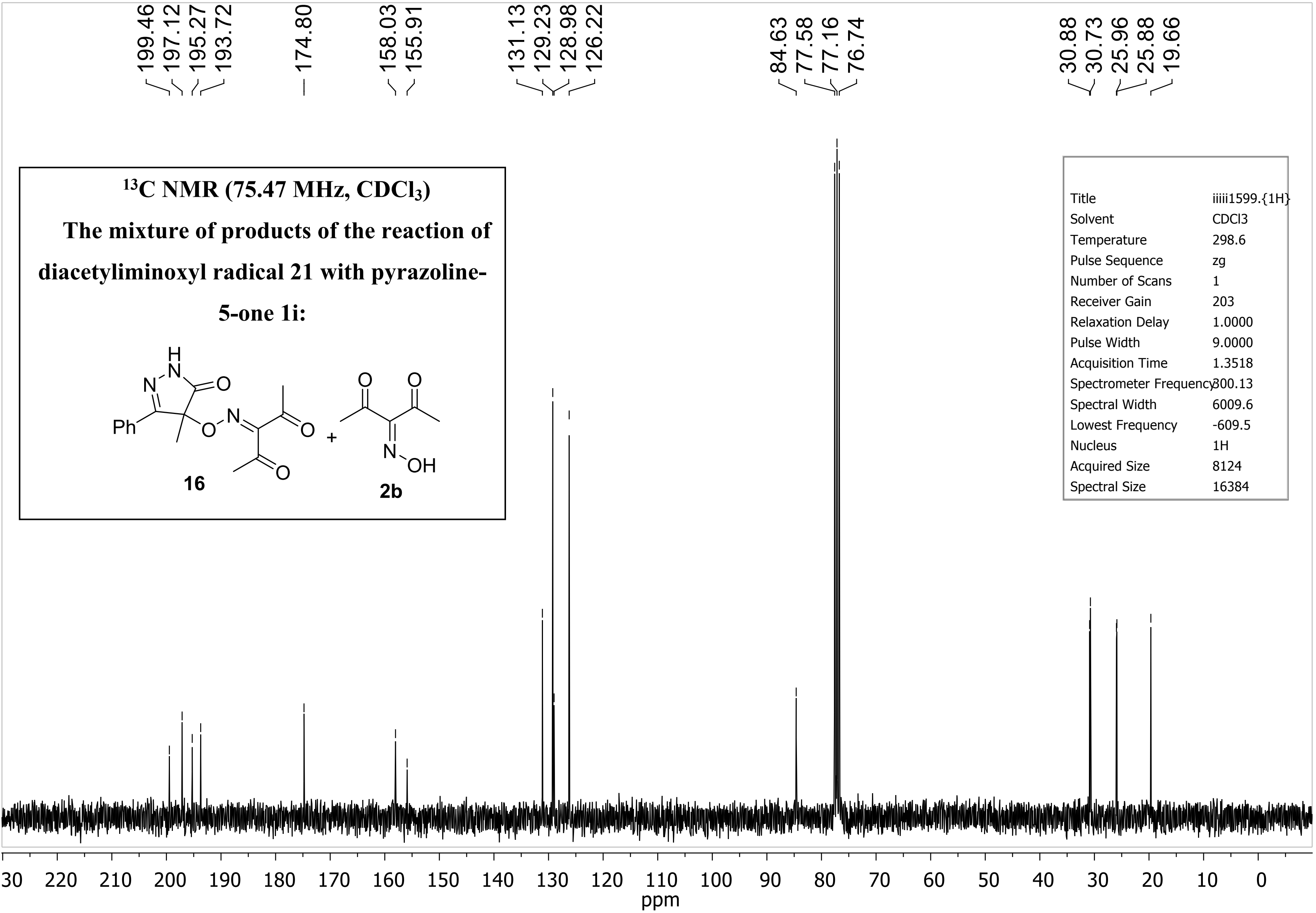
Title	iiiii1656.{13C}
Solvent	CDCl3
Temperature	299.6
Pulse Sequence	zgpg60base
Number of Scans	112
Receiver Gain	2580
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	0.8680
Spectrometer Frequency	75.48
Spectral Width	18797.0
Lowest Frequency	-1478.9
Nucleus	13C
Acquired Size	16316
Spectral Size	32768



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

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1i:

Title	iiiii1599.{1H}
Solvent	CDCl3
Temperature	298.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-609.5
Nucleus	1H
Acquired Size	8124
Spectral Size	16384



^{13}C NMR (75.47 MHz, CDCl$_3$)

The mixture of products of the reaction of diacetyliminoxyl radical 21 with pyrazoline-5-one 1i:

Title	iiiii1599.{1H}
Solvent	CDCl3
Temperature	298.6
Pulse Sequence	zg
Number of Scans	1
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	9.0000
Acquisition Time	1.3518
Spectrometer Frequency	300.13
Spectral Width	6009.6
Lowest Frequency	-609.5
Nucleus	1H
Acquired Size	8124
Spectral Size	16384

FTIR Spectra of diacetyliminoxyl radical 21 and 3-(hydroxyimino)-2,4-pentanedione 2b without subtraction of solvent signals