Supplementary Information

External-Oxidant-Free Amino-Benzoyloxylation of Unactivated Alkenes of Unsaturated Ketoximes with O-Benzoylhydroxylamines

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(A) General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

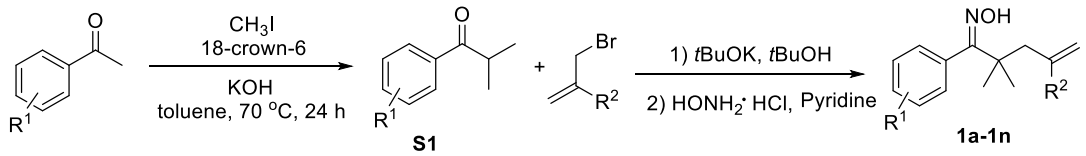
NMR spectrum: All ^{1}H, ^{13}C and ^{19}F spectra are recorded on the Bruker AVANCE spectrometer, operating at 400/500 MHz for ^{1}H NMR and 100/125 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from $CDCl_3$ (δ: 7.26 ppm) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), m (multiple), dd (doublet of doublet). Coupling constants are reported in Hertz (Hz).

Mass spectroscopy: High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry.

Chromatography: Column chromatography was performed with silica gel (300-400 mesh ASTM).

Melting point: Melting point was recorded on Hanon MP100 Apparatus.

(a) General Procedure for the preparation of Oximes (1):[1,2]



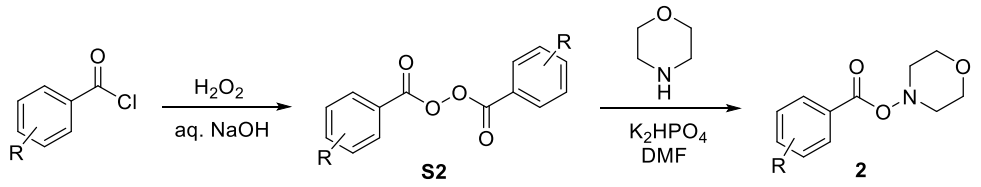
Substrates **S1** are prepared according to literature procedure:[1] To a stirred suspension of KOH (5.6 g, 0.1 mol) in toluene (10 mL) containing of Acetophenone (1.2 g, 0.01 mol) and 18-crown-6 (60 mg) was added CH_3I (5.0 mL) dropwise. The mixture was stirred at 70 °C for 24 h. After cooling to room temperature, separation of the solid phase by filtration and evaporation of the toluene, used for next step without further purification.

A mixture of isobutyl ketone (10 mmol), 3-bromopropene (12 mmol) and *t*-BuOK (20 mmol) in *t*-BuOH (0.5 M) was heated at reflux under a nitrogen atmosphere. When the starting materials were consumed completely as monitored by TLC, *t*-BuOH was removed by distillation and the crude mixture was extracted into ether

and a usual aqueous work-up was performed. The combined organic layers were concentrated in vacuo. Purification of the residue by silica gel column chromatography to give product as a yellow oil.[2]

To a solution of γ,δ-unsaturated ketone (10 mmol) in methol was added pyridine (40 mmol) and hydroxylamine hydrochloride (15 mmol) at room temperature. The mixture was heated to reflux for 1h and concentrated in vacuo. Then, the mixture was extracted with ethyl acetate and the combined organic layers were washed with water and brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the γ,δ-unsaturated oxime.[2]

(b) General Procedure for the Preparation of *O*-Benzoyl Hydroxylamines Oximes (2):[3,4]



Substrates **S2** are prepared according to literature procedure[3]: Hydrogen peroxide (1.67 g, 35 wt. % in H_2O, 17.2 mmol) was added dropwise over10 min to a cold (ice bath) solution of acid chloride (30mmol) in diethyl ether (7 mL). This was followed by the dropwise addition of an aqueous solution of NaOH (1.52g, 37.9mmol, 10 mL) over 20 min. The resulting white precipitate was collected by filtration. After washing with water (3×5 mL) and diethyl ether (3×5 mL), the solid was crystallized from a cold acetone / water mixture (1 : 3 v/v).[3]

O-Benzoyl-hydroxylamines were prepared by literature procedure[4]: A 50-mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar was charged with benzoyl peroxide (2.42 g, 10 mmol), K_2HPO_4 (2.61 g, 15 mmol), and N, N-dimethyl formamide (25 mL). The suspension was stirred and the amine (12 mmol) was added via syringe in one portion. The suspension was stirred at ambient temperature for the indicated reaction time. Deionized water (25 mL) was added and

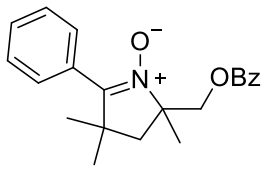
the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was transferred to a 100 mL separatory funnel and extracted with 25 mL of ethyl acetate. The organic phase was collected and washed with two 25 mL portions of saturated aq $NaHCO_3$ solution. All of the aqueous fractions were combined and extracted with three 25 mL portions of ethyl acetate. All of the organic fractions were combined and washed with three 100 mL portions of deionized water, 25 mL of brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The resulting crude product mixture was purified by flash column chromatography, eluting with the indicated solvent system, to afford desired product **2**.[4]

(c) General Procedure for Copper-Catalyzed Amino-Acyloxylation of Unactivated Alkenes of Unsaturated Ketoximes (1) with *O*-Acylhydroxylamines (2):

To a 10 mL Schlenk tube were added oxime **1** (0.2 mmol), *O*-benzoyl-hydroxylamine **2** (0.1 mmol), CuCl (0.01 mmol), phosphoric acid **L1** (0.02 mmol) and 1,2-dichloroethane (2.0 mL). Then the tube is evacuated briefly under high vacuum and charged with nitrogen through using standard Schlenk techniques and this process is repeated three times. The reaction mixture was stirred at room temperature for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3**.

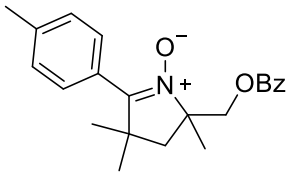
(B) Analytical Data

2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole -1-oxide (3aa):



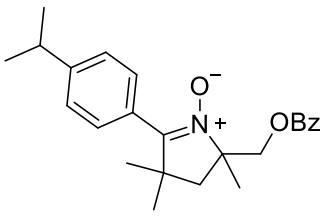
Yield = 76%, 25.5 mg, Yellow solid, mp 84.3-85.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 6.8 Hz, 2H), 7.88 (d, *J* = 6.4Hz, 2H), 7.55-7.53 (m, 1H), 7.46-7.39 (m, 5H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 2.34 (d, *J* = 13.2 Hz, 1H), 2.04 (d, *J* = 11.2 Hz, 1H), 1.64 (s, 1H), 1.51 (s, 1H), 1.30 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 148.1, 133.2, 129.7, 129.6, 129.5, 129.2, 128.4, 128.3, 74.4, 66.9, 43.8, 41.9, 30.0, 29.0, 23.2. HRMS (ESI): Calcd for $C_{21}H_{24}NO_3$ [M+H$^+$] 338.1751, found 338.1749.

2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(p-tolyl)-3,4-dihydro-2*H*-pyrrole-1-oxid e (3ba):



Yield = 47%, 16.5 mg, White foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.78(d, *J* = 7.2 Hz, 2H), 7.50-7.45 (m, 1H), 7.35-7.31 (m, 2H), 7.20-7.19 (m, 2H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 2.32(s, 3H), 2.25 (d, *J* = 12.8 Hz, 1H), 1.95 (d, *J* = 13.6Hz, 1H), 1.44 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 166.1, 139.8, 133.2, 129.7, 129.6, 129.1, 128.4, 128.3, 126.3, 74.2, 67.0, 43.9, 41.9, 30.0, 29.2, 23.2, 21.5.HRMS (ESI): Calcd for $C_{22}H_{26}NO_3$ [M+H$^+$] 352.1907, found 352.1908.

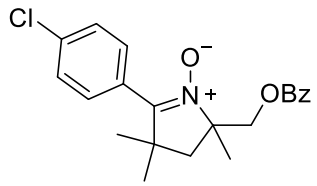
2-((benzoyloxy)methyl)-5-(4-isopropylphenyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-py rrole-1-oxide (3ca):



Yield = 41%, 15.5 mg, Yellow solid. mp 132.1-133.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.57-7.52 (m, 1H), 7.43-7.38 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.72 (d, *J* = 11.2 Hz, 1H), 4.47 (d, *J* = 11.2 Hz, 1H), 2.97-2.89 (m, 1H), 2.32 (d, *J* = 13.6 Hz, 1H), 2.02 (d, *J* =

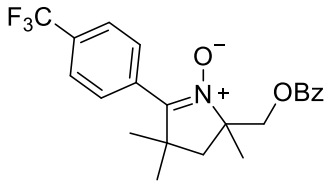
13.2Hz, 1H), 1.63 (s, 3H), 1.51 (s, 3H), 1.32(s, 3H), 1.26 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 150.5, 148.0, 133.2, 129.7, 129.6, 128.4, 128.4, 126.6, 126.5, 74.2, 67.0, 43.9, 41.9, 34.1, 30.0, 29.3, 29.2, 23.7, 23.2. HRMS (ESI) Calcd for $C_{24}H_{30}NO_3$ [M+H$^+$] 380.2220, found 380.2225.

2-((benzoyloxy)methyl)-5-(4-chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrro le- 1-oxide (3da):



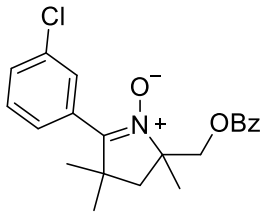
Yield = 73%, 27.1 mg, Slight yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.57-7.52 (m, 1H), 7.43-7.38 (m, 4H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 2.33 (d, *J* = 13.2 Hz, 1H), 2.04 (d, *J* = 13.6 Hz, 1H), 1.63 (s, 3H), 1.51 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 146.6, 135.4, 133.2, 129.7, 129.5, 128.7, 128.4, 127.6, 74.6, 66.9, 43.9, 41.8, 30.1, 29.1, 23.1. HRMS (ESI) Calcd for $C_{21}H_{23}ClNO_3$ [M+H$^+$] 372.1361, found 372.1372.

2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydr o-2*H*-pyrrole-1-oxide (3ea):



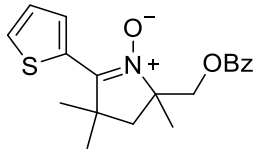
Yield = 78%, 31.6 mg, White foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.58-7.53 (m, 2H), 7.43-7.39 (m, 2H), 4.73 (d, *J* = 11.2 Hz 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 2.37 (d, *J* = 13.2 Hz, 1H), 2.07 (d, *J* = 13.2 Hz, 1H), 1.65 (s, 3H), 1.53 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 146.4, 133.3, 132.8, 131.8, 129.6, 129.5, 128.7, 128.5, 125.4 (q, J_{C-F} = 3.6 Hz), 75.0, 66.8, 43.9, 41.9, 30.0, 29.1, 23.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0. HRMS (ESI) Calcd for $C_{22}H_{23}F_3NO_3$[M+H$^+$] 406.1625, found 406.1627.

2-((benzoyloxy)methyl)-5-(3-chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3fa):



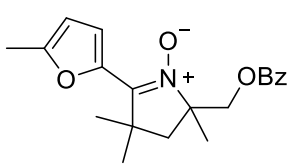
Yield = 66%, 24.5 mg, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.96 (m, 3H), 7.76-7.75 (m, 1H), 7.58-7.54 (m, 1H), 7.44-7.35 (m, 4H), 4.70 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 2.34 (d, *J* = 13.6 Hz, 1H), 2.05 (d, *J* = 13.2 Hz, 1H), 1.64 (s, 3H), 1.50 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 146.4, 134.5, 133.3, 130.9, 129.7, 129.7, 129.6, 128.5, 128.3, 126.4, 74.8, 66.8, 43.9, 41.9, 41.8, 30.0, 29.1, 23.2. HRMS (ESI) Calcd for $C_{21}H_{23}ClNO_3$ [M+H$^+$] 372.1361, found 372.1375.

2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole-1-oxide (3ga):



Yield = 56%, 19.2 mg, White solid. mp 134.7-135.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.71-7.70 (m, 1H), 7.54-7.48 (m, 2H), 7.37-7.33 (m, 2H), 7.21-7.19 (m, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 2.36 (d, *J* = 13.6 Hz, 1H), 2.06 (d, *J* = 14.0Hz, 1H), 1.62 (s, 6H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 144.1, 133.2, 129.8, 129.6, 129.5, 128.5, 128.4, 127.1, 126.1, 73.3, 66.9, 44.7, 41.4, 29.7, 29.6, 29.4, 23.6. HRMS (ESI): Calcd for $C_{19}H_{22}NO_3S$ [M+H$^+$] 344.1315, found 344.1322.

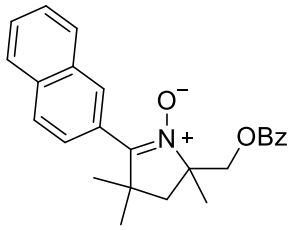
2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(5-methylfuran-2-yl)-3,4-dihydro-2*H*-pyrrole-1-oxide (3ha):



Yield = 60%, 20.4 mg, Yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.92 (m, 3H), 7.55-7.50 (m, 1H), 7.40-7.36 (m, 2H), 6.21 (s, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 2.39 (s, 3H), 2.30 (d, *J* = 13.2 Hz, 1H), 1.99 (d, *J* = 13.2 Hz, 1H), 1.59 (s, 3H), 1.55 (s, 3H), 1.50 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 153.6, 144.1, 140.4, 133.1, 129.6, 128.4, 117.6, 108.5, 126.3, 74.3, 66.8, 44.0, 40.7, 29.3, 28.9, 23.6,

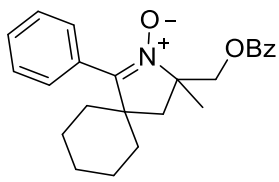
13.9. HRMS (ESI): Calcd for $C_{20}H_{24}NO_4$ [M+H$^+$] 342.1700, found 342.1705.

2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyrrole-1-oxide (3ia):



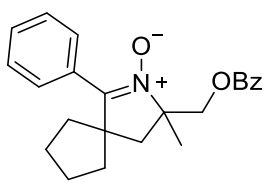
Yield = 60%, 23.2 mg, White foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.93-7.83 (m, 4H), 7.54-7.50 (m, 3H), 7.42-7.38 (m, 2H), 2.39 (d, *J* = 13.6 Hz, 1H), 2.09 (d, *J* = 13.6 Hz, 1H), 1.69 (s, 3H), 1.60 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 147.8, 133.5, 133.2, 133.0, 129.6, 128.7, 128.6, 128.4, 127.9, 127.5, 127.1, 126.7, 126.3, 125.1, 74.5, 67.0, 44.0, 42.1, 30.2, 29.2, 23.2. HRMS (ESI) Calcd for $C_{25}H_{26}NO_3$ [M+H$^+$] 388.1907, found 388.1928.

3-((benzoyloxy)methyl)-3-methyl-1-phenyl-2-azaspiro[4.5]dec-1-ene-2-oxide (3ja):



Yield = 53%, 20.0 mg, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.58-7.56 (m, 3H), 7.46-7.44 (m, 5H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 2.28 (d, *J* = 13.6 Hz, 1H), 2.17 (d, *J* = 13.6 Hz, 1H), 2.05-2.00 (m, 1H), 1.78-1.69 (m, 6H), 1.65 (s, 3H), 1.64-1.56 (m, 2H), 1.49-1.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 149.3, 133.2, 129.7, 129.6, 129.3, 128.8, 128.4, 74.5, 67.0, 46.3, 38.1, 36.0, 35.8, 24.9, 23.9, 22.1, 21.8. HRMS (ESI): Calcd for $C_{24}H_{28}NO_3$ [M+H$^+$] 378.2064, found 378.2061.

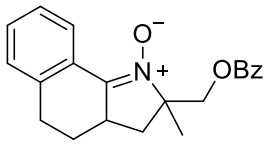
3-((benzoyloxy)methyl)-3-methyl-1-phenyl-2-azaspiro[4.4]non-1-ene-2-oxide (3ka):



Yield = 58%, 21.1 mg, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.81 (m, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.40 (m, 5H), 4.73 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 2.29 (d, *J* = 12.8 Hz, 1H),

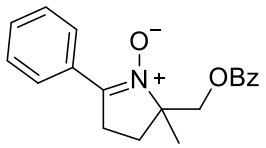
2.16-2.11 (m, 1H), 2.07 (d, *J* = 13.2 Hz, 1H), 2.04-1.98 (m, 1H), 1.83-1.73 (m, 3H), 1.70-1.66 (m, 2H), 1.60 (s, 3H), 1.61-1.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 146.8, 133.2, 129.7, 129.6, 129.5, 129.3, 128.5, 128.4, 74.8, 67.0, 52.3, 44.4, 39.6, 39.2, 24.4, 24.2, 23.1. HRMS (ESI): Calcd for $C_{23}H_{26}NO_3$ [M+H$^+$] 364.1907, found 364.1921.

2-((benzoyloxy)methyl)-2-methyl-3,3a,4,5-tetrahydro-2*H*-benzo[g]indole- 1-oxide (3la):



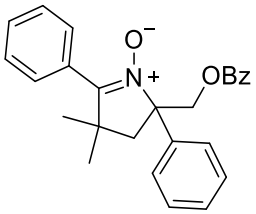
Yield = 77%, 25.8 mg, dr = 3:1, slight yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39-9.35 (m, 1H), 7.95-7.92 (m, 2H), 7.54-7.49 (m, 1H), 7.38-7.35 (m, 4H), 7.26-7.23 (m, 1H), 4.82 (d, *J* = 11.2 Hz, 0.75H), 4.66 (d, *J* = 11.2 Hz, 0.25H), 4.58-4.56 (m, 1H), 3.22-3.18 (m, 1H), 3.02-2.95 (m, 2H), 2.30-2.20 (m, 2H), 2.07-2.01 (m, 1H), 1.62 (s, 0.77H), 1.56 (s, 2.23H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 139.8, 138.8, 138.7, 133.2, 133.1, 130.5, 130.4, 129.6, 129.6, 129.5, 128.5, 128.4, 127.0, 126.7, 125.8, 77.2, 76.3, 67.4, 65.9, 39.0, 37.8, 36.1, 33.8, 30.3, 30.2, 30.0, 29.5, 22.8, 20.3. HRMS (ESI): Calcd for $C_{21}H_{22}NO_3$ [M+H$^+$] 336.1594, found 336.1610.

2-((benzoyloxy)methyl)-2-methyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3ma):



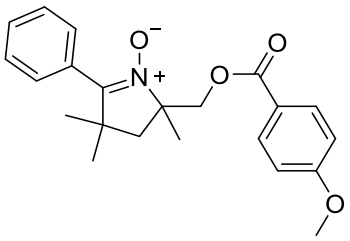
Yield = 62%, 19.1 mg, Colorless solid. 114.6-116.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 6.8 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.51-7.46 (m, 4H), 7.37-7.32 (m, 2H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 3.14-3.08 (m, 2H), 2.49-2.41 (m, 1H), 2.16-2.08 (m, 1H), 1.6 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 139.6, 133.2, 130.4, 129.6, 129.5, 129.4, 128.5, 128.4, 127.3, 77.5, 67.3, 27.5, 26.8, 21.8. HRMS (ESI): Calcd for $C_{19}H_{20}NO_3$ [M+H$^+$] 310.1438, found 310.1436.

2-((benzoyloxy)methyl)-4,4-dimethyl-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3na):



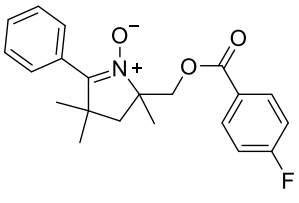
Yield = 54%, 21.5 mg, Yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.6 Hz, 4H), 7.59-7.54 (m, 3H), 7.52-7.48 (m, 3H), 7.46-7.44 (m, 2H), 7.43-7.38 (m, 4H), 7.35-7.31 (m, 1H), 5.00 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 2.64 (d, *J* = 12.8 Hz, 1H), 2.45 (d, *J* = 12.8 Hz, 1H), 1.31 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 149.4, 139.6, 133.2, 129.7, 129.6, 129.2, 128.8, 128.5, 128.4, 128.3, 128.1, 126.1, 81.0, 65.9, 45.5, 42.1, 29.1, 27.9. HRMS (ESI): Calcd for $C_{26}H_{26}NO_3$ [M+H$^+$] 400.1907, found 400.1933.

2-(((4-methoxybenzoyl)oxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (3ab):



Yield = 62%, 22.7 mg, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.47-7.40 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.47 (d, *J* = 11.2 Hz, 1H), 3.83 (s, 3H), 2.32 (d, *J* = 12.4 Hz, 1H), 2.02 (d, *J* = 13.6 Hz, 1H), 1.63 (s, 3H), 1.49 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 163.5, 148.0, 131.6, 129.5, 128.4, 128.3, 122.0, 113.7, 74.5, 66.5, 55.4, 43.8, 41.9, 30.0, 29.0, 23.1. HRMS (ESI) Calcd for $C_{22}H_{26}NO_4$ [M+H$^+$] 368.1856, found 368.1874.

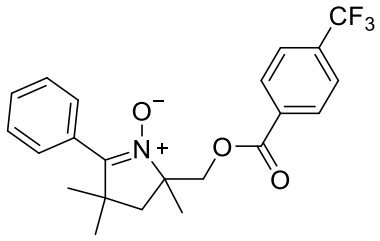
2-(((4-fluorobenzoyl)oxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3ac):



Yield = 60%, 21.3 mg, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (t, *J* = 6.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.47-7.39 (m, 3H), 7.08 (t, *J* = 8.0 Hz, 2H), 4.71 (d, *J* =11.6 Hz, 1H), 4.47 (d, *J* =11.6 Hz, 1H), 2.31 (d, *J* =13.2 Hz, 1H), 2.04 (d, *J* =13.2 Hz, 1H), 1.64 (s, 3H), 1.50 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 165.0, 148.2, 132.1 (d, $J_{C\text{-}F}$ = 9.4 Hz), 129.6, 129.1, 128.4 (d, $J_{C\text{-}F}$ = 13.3 Hz), 126.0 (d, $J_{C\text{-}F}$

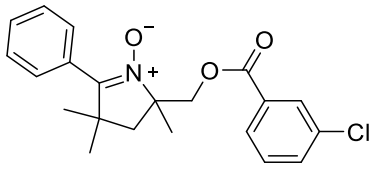
= 2.9 Hz), 74.4, 67.0, 43.8, 42.0, 29.9, 29.1, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.0. HRMS (ESI) Calcd for $C_{21}H_{23}FNO_3$ [M+H$^+$] 356.1656, found 356.1655.

2,4,4-trimethyl-5-phenyl-2-(((4-(trifluoromethyl)benzoyl)oxy)methyl)-3,4-dihydro-2*H*-pyrrole-1-oxide (3ad):



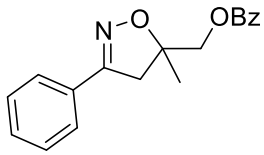
Yield = 47%, 19.0 mg, Slight yellow solid. mp 101.2-103.1°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.49-7.40 (m, 3H), 4.77 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 2.31 (d, *J* = 13.2 Hz, 1H), 2.06 (d, *J* = 14.0 Hz, 1H), 1.65 (s, 3H), 1.52 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 147.8, 132.9, 130.0, 129.7, 129.1, 128.5, 128.3, 125.5 (q, J_{C-F} = 3.6 Hz), 74.3, 67.4, 43.9, 42.0, 30.0, 29.2, 23.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2. HRMS (ESI) Calcd for $C_{22}H_{23}F_3NO_3$ [M+H$^+$] 406.1625, found 406.1626.

2-(((3-chlorobenzoyl)oxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3ae):



Yield = 61%,22.6 mg, White solid. mp 115.8-117.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.90-7.81 (m, 3H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48-7.39 (m, 3H), 7.38-7.33 (m, 1H), 4.73 (d, *J* = 11.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 2.31 (d, *J* = 13.6 Hz, 1H), 2.05 (d, *J* = 13.6 Hz, 1H), 1.64 (s, 3H), 1.49 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 148.1, 134.4, 133.2, 131.4, 129.8, 129.7, 129.6, 129.1, 128.5, 128.3, 127.7, 74.3, 67.3, 43.8, 41.9, 29.9, 29.0, 23.1. HRMS (ESI) Calcd for $C_{21}H_{23}ClNO_3$ [M+H$^+$] 372.1361, found 372.1371.

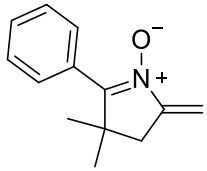
(5-methyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl benzoate (5oa):



Yield = 53%, 15.6 mg, White solid. mp 84.0-85.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.68-7.66 (m, 1H), 7.54 (dd, *J* = 7.2 Hz, *J* = 7.6 Hz, 1H), 7.42-7.36 (m, 5H),

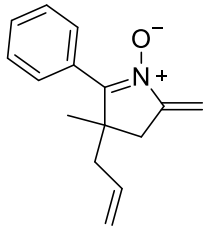
4.45 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 3.44 (d, *J* = 16.8 Hz, 1H), 3.18 (d, *J* = 16.4 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ166.2, 156.2, 133.2, 130.1, 129.7, 129.6 129.5, 128.7, 128.4, 126.5, 85.2, 68.6, 43.2, 23.1. HRMS (ESI): Calcd for $C_{18}H_{18}NO_3$ [M+H$^+$] 296.1281, found 296.1279.

4,4-dimethyl-2-methylene-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6p)



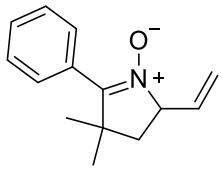
Yield = 55%, 11.1 mg, Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.48-7.42 (m, 3H), 6.00 (s, 1H), 5.04 (s, 1H), 2.75-2.74 (m, 2H), 1.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 130.1, 128.7, 128.6, 128.4, 128.3, 101.2, 48.0, 41.5, 40.5, 27.5. HRMS (ESI): Calcd for $C_{13}H_{16}NO$ [M+H$^+$] 202.1226, found 202.1230.

4-allyl-4-methyl-2-methylene-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6q)



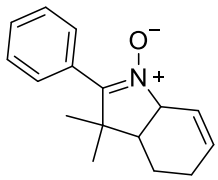
Yield = 43%, 9.8 mg, Slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.49-7.41 (m, 3H), 5.99 (s, 1H), 5.67-5.57 (m, 1H), 5.09-5.01 (m, 3H), 2.95 (d, *J* = 16.8 Hz, 1H), 2.62-2,52 (m, 2H), 2.39-2.33 (m, 1H), 1.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.1, 132.5, 130.2, 128.9, 128.5, 128.4, 119.7, 101.1, 44.8, 44.1, 36.6, 26.4. HRMS (ESI) Calcd for $C_{15}H_{18}NO$ [M+H$^+$] 228.1383, found 228.1381.

4,4-dimethyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6r):



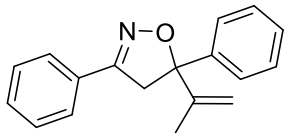
Yield = 67%, 14.4 mg, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.45-7.36 (m, 3H), 6.18-6.09 (m, 1H), 5.45-5.40 (m, 2H), 4.74-4.68 (m, 1H), 2.31-2.26 (m, 1H), 2.04-1.93 (m, 1H), 1.42 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 135.0, 129.5, 128.8, 128.3, 128.2, 119.9, 73.5, 43.6, 42.1, 28.1, 26.9. HRMS (ESI): Calcd for $C_{14}H_{18}NO$ [M+H$^+$] 216.1383, found 216.1381.

3,3-dimethyl-2-phenyl-3a,4,5,7a-tetrahydro-3*H*-indole-1-oxide (6s):



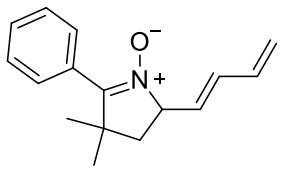
Yield = 79%, 19.0 mg, Yellow solid. mp 101.4-102.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2H), 6.31-6.28 (m, 1H), 6.23-6.18 (m, 1H), 4.66 (s, 1H), 2.21-2.14 (m, 2H), 2.04-1.95 (m, 1H), 1.81-1.77 (m, 1H), 1.48 (s, 3H), 1.44-1.32 (m, 2H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 133.6, 129.3, 129.0, 128.2, 121.8, 45.8, 44.0, 26.3, 24.0, 21.8, 21.1. HRMS (ESI): Calcd for $C_{16}H_{20}NO$ [M+H$^+$] 242.1539, found 242.1543.

3,5-diphenyl-5-(prop-1-en-2-yl)-4,5-dihydroisoxazole (6t):



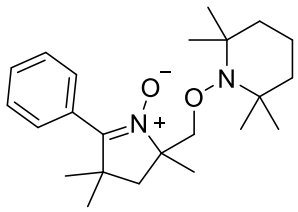
Yield = 48%, 12.6 mg, White foam; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.66 (m, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.38-7.33 (m, 5H), 7.29-7.25 (m, 1H), 5.15 (s, 1H), 5.04 (s, 1H), 3.81 (d, *J* = 16.4 Hz, 1H), 3.55 (d, *J* = 16.4 Hz, 1H), 1.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 145.8, 142.6, 130.0, 129.6, 128.6, 128.3, 127.5, 126.5, 125.6, 112.5, 93.1, 44.7, 19.0. HRMS (ESI): Calcd for $C_{18}H_{18}NO$ [M+H$^+$] 264.1381, found 264.1380.

(*E*)-2-(buta-1,3-dien-1-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6u):



Yield = 66%, 15.9 mg, Yellow solid. mp 85.5-87.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.45-7.37 (m, 3H), 6.43- 6.33 (m, 2H), 5.97 (dd, *J* = 14.4 Hz, *J* = 7.6 Hz, 1H), 5.28 (d, *J* = 16.0 Hz, 1H), 4.76 (q, *J* = 8.0 Hz, 1H), 2.30 (dd, *J* = 12.8Hz, *J* = 8.0 Hz, 1H), 2.04-1.93 (m, 1H), 1.42 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 135.9, 135.5, 130.0, 129.6, 128.8, 128.3, 128.2, 118.8, 72.8, 43.6, 42.5, 28.1, 26.8. HRMS (ESI) Calcd for $C_{16}H_{20}NO$ [M+H$^+$] 242.1539, found 242.1541.

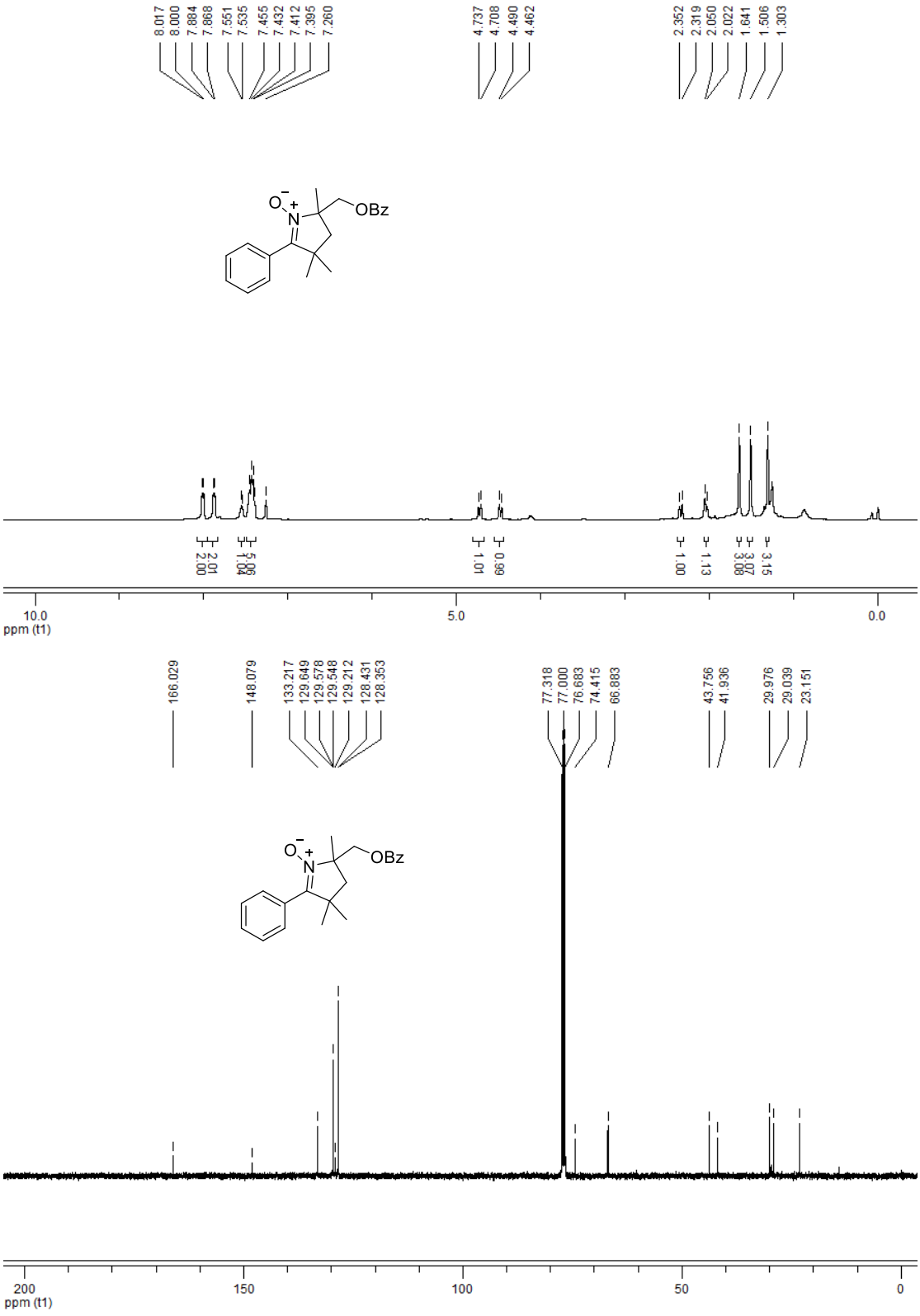
2,4,4-trimethyl-5-phenyl-2-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3,4-dihydro-2*H*-pyrrole-1-oxide (7):



Yield = 68%, 25.2 mg, White solid. mp 146.2-148.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.44-7.40 (m, 2H), 7.38-7.34 (m, 1H), 4.35 (d, *J* = 8.8 Hz, 1H), 3.58 (d, *J* = 9.2 Hz, 1H), 2.62 (d, *J* = 12.8 Hz, 1H), 1.88 (d, *J* = 12.8 Hz, 1H), 1.45 (s, 9H), 1.36 (s, 3H), 1.30-1.25 (m, 6H), 1.19 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 129.9, 129.0, 128.5, 128.3, 77.6, 60.1, 43.5, 41.8, 39.9, 39.8, 33.2, 32.8, 30.4, 29.7, 28.6, 23.9, 20.8, 20.3, 17.0. HRMS (ESI) Calcd for $C_{23}H_{37}N_2O_2$ [M+H$^+$] 373.2850, found 373.2852.

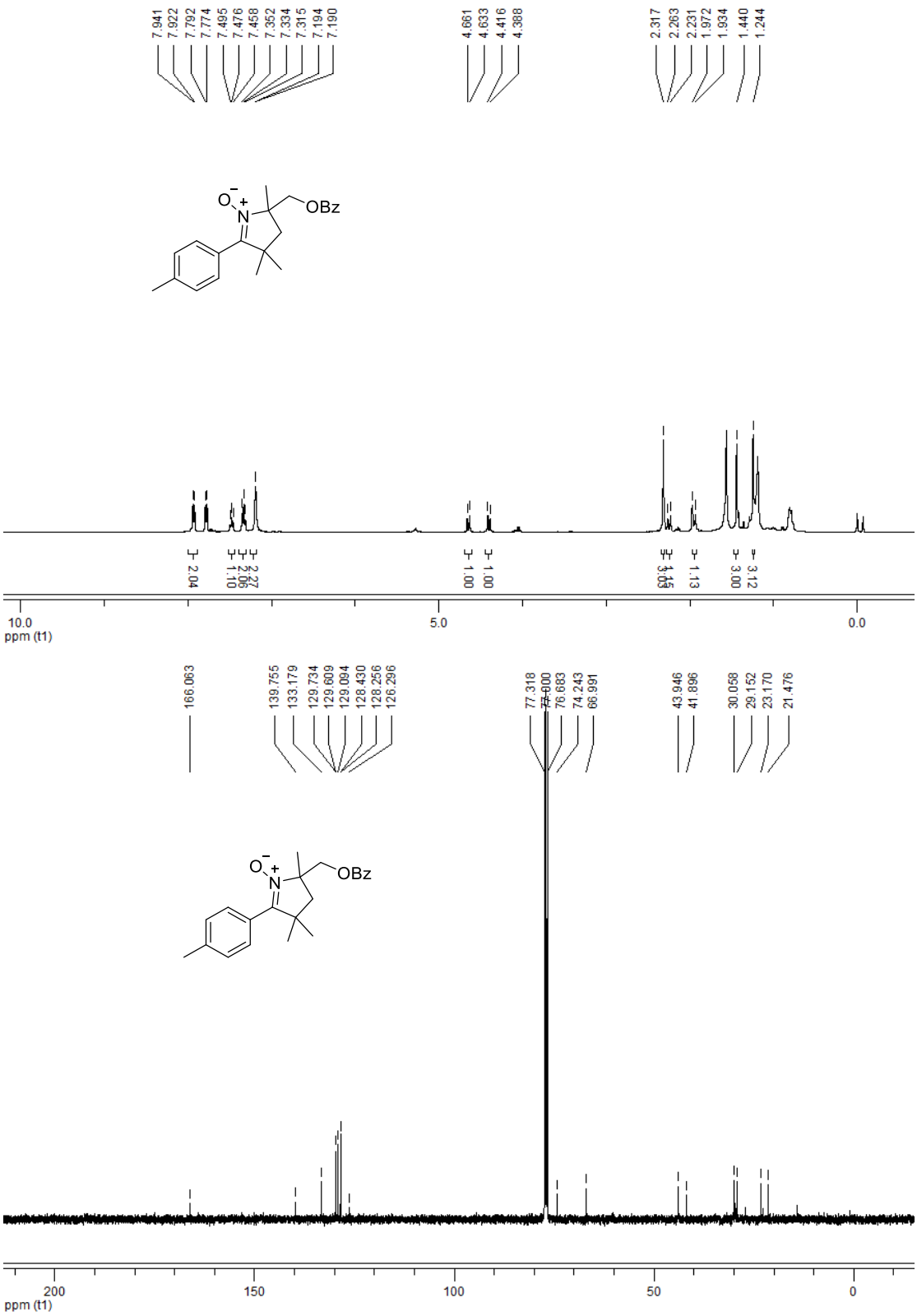
(B) NMR Spectra

2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole -1-oxide (3aa)：



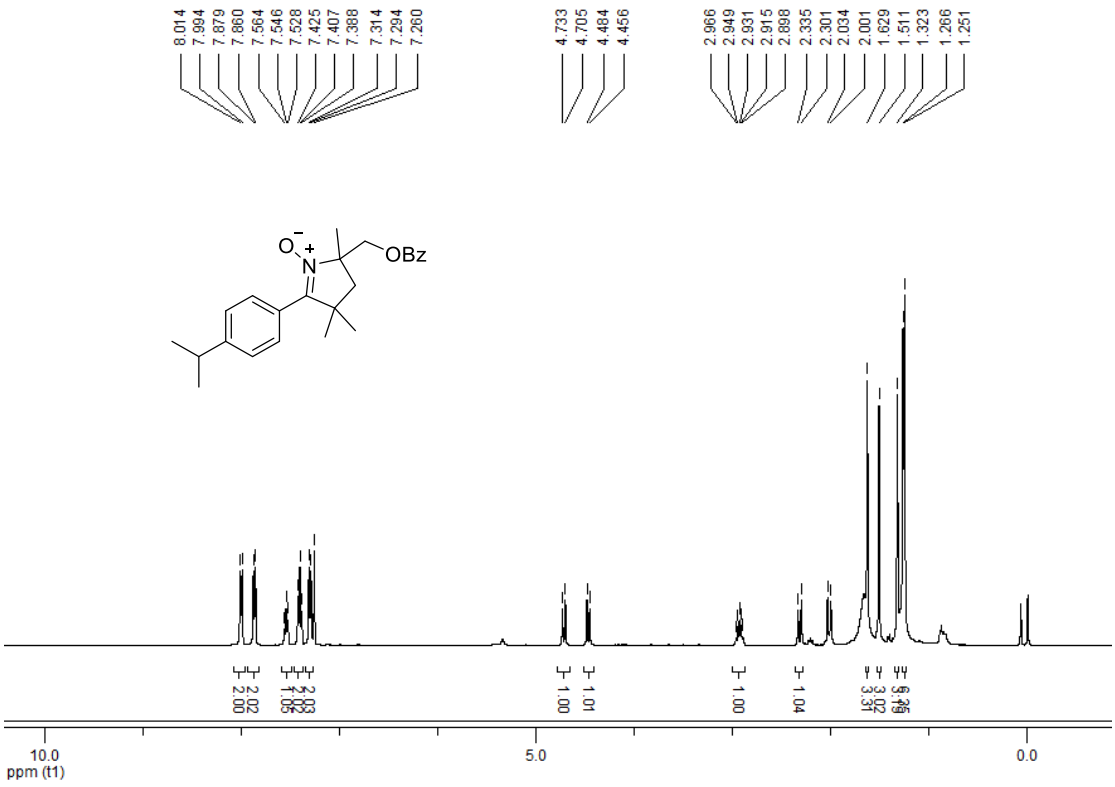
2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(p-tolyl)-3,4-dihydro-2*H*-pyrrole-1-oxid

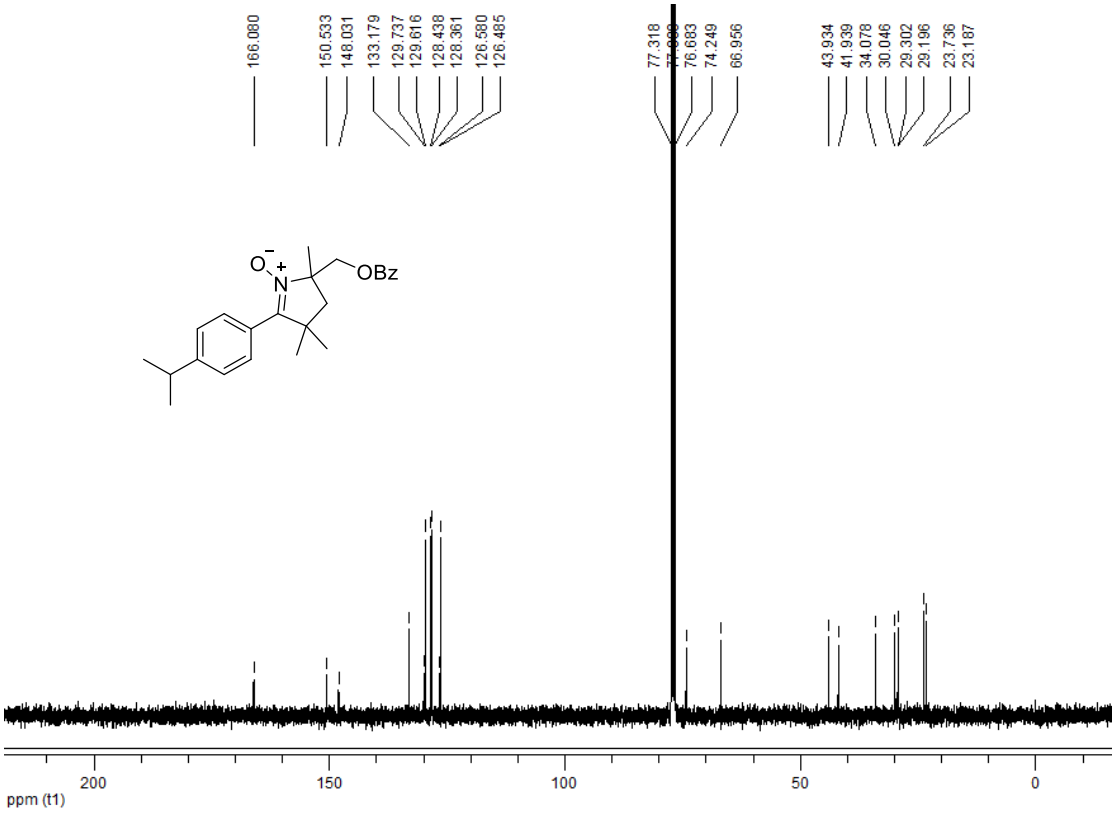
e (3ba):



2-((benzoyloxy)methyl)-5-(4-isopropylphenyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-py

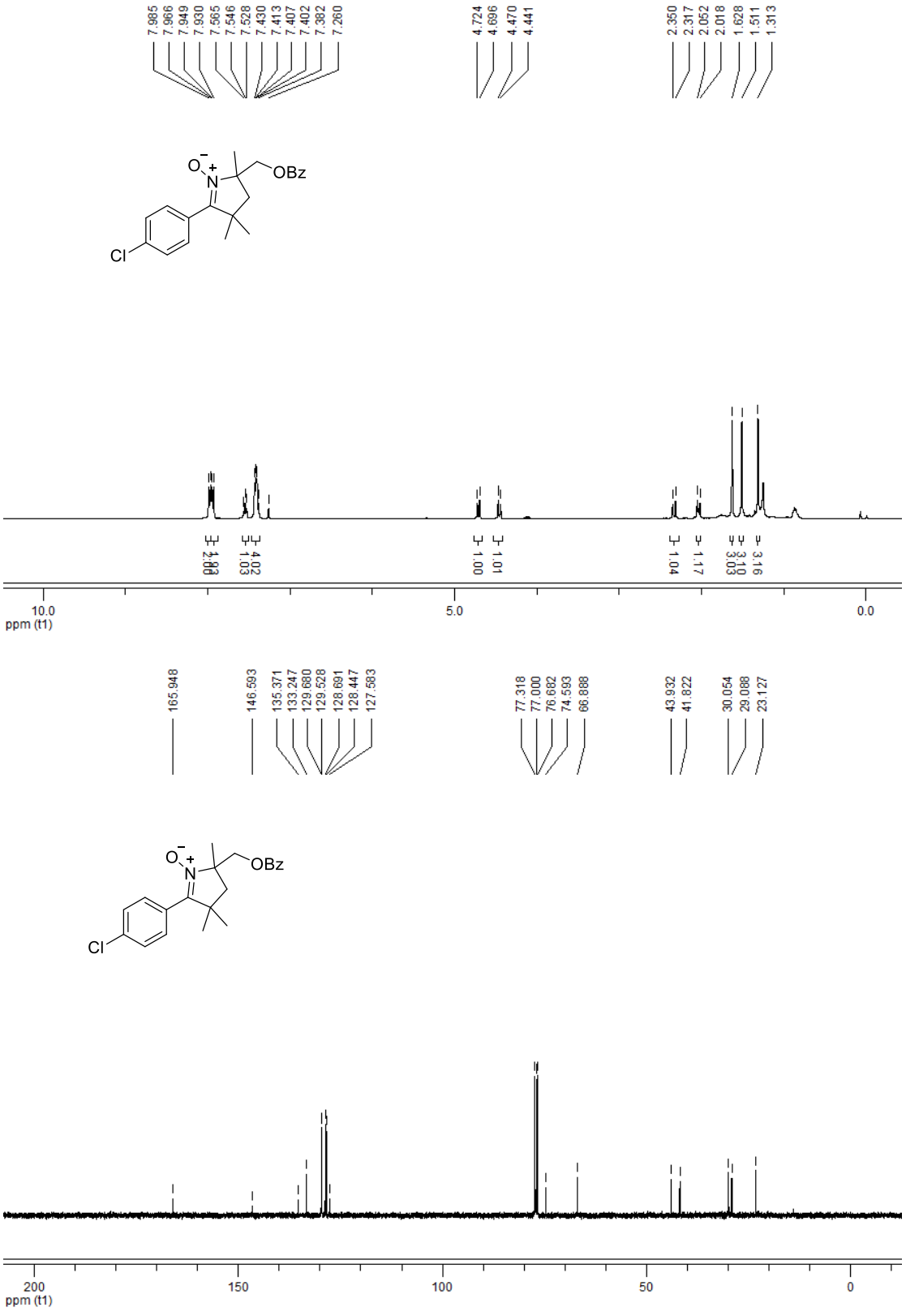
rrole-1-oxide (3ca):





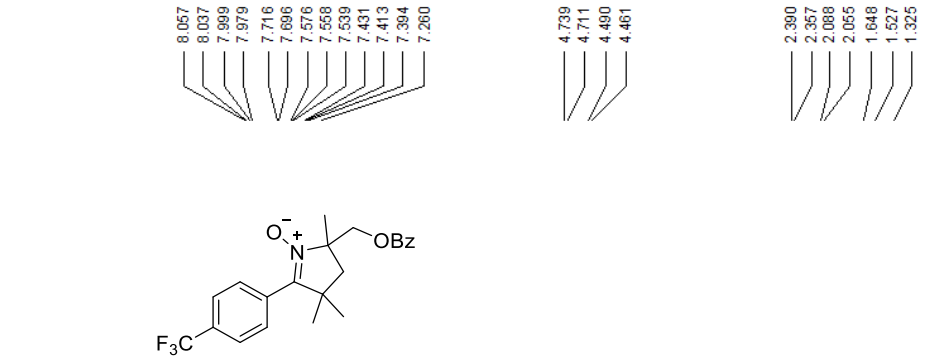
2-((benzoyloxy)methyl)-5-(4-chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrro

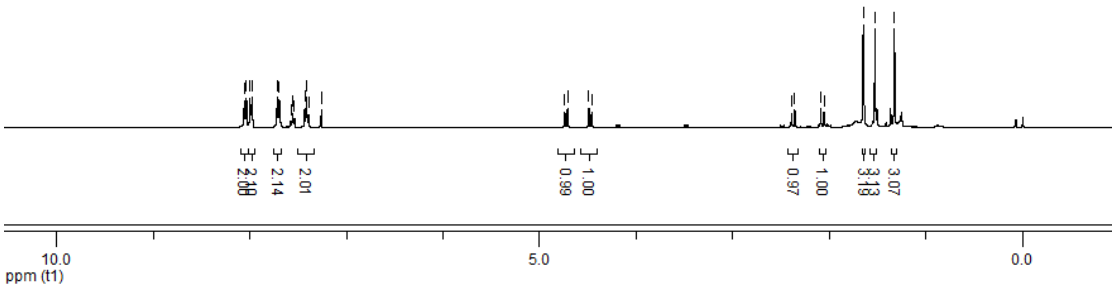
le- 1-oxide (3da):

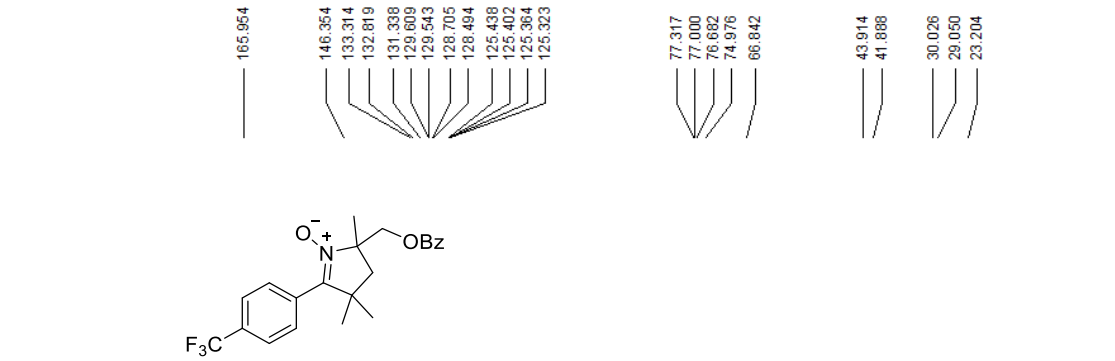


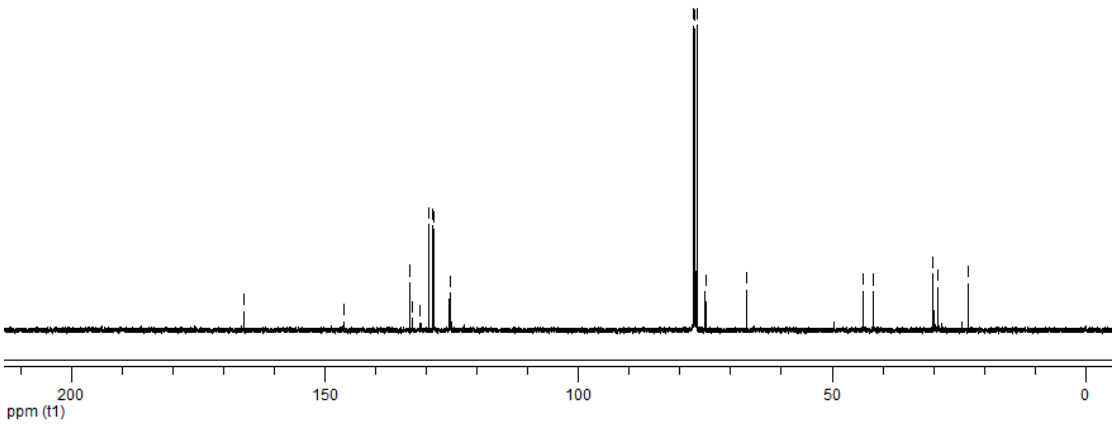
2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydr

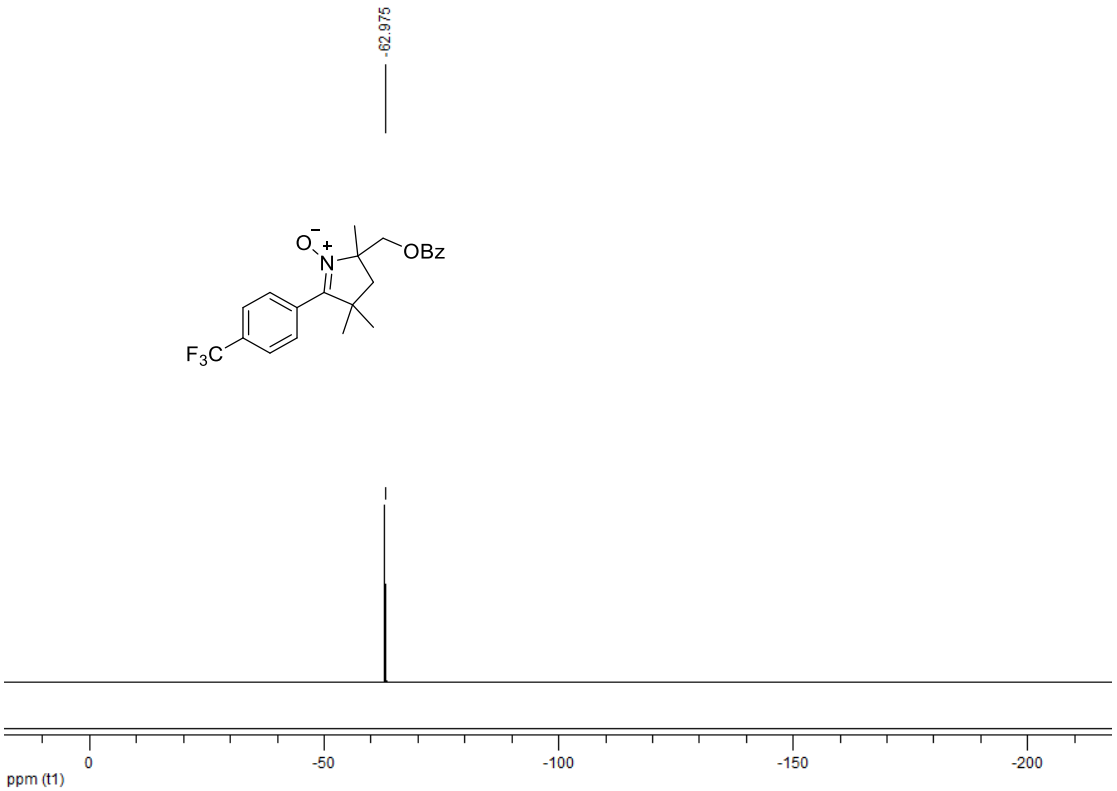
o-2*H*-pyrrole-1-oxide (3ea):



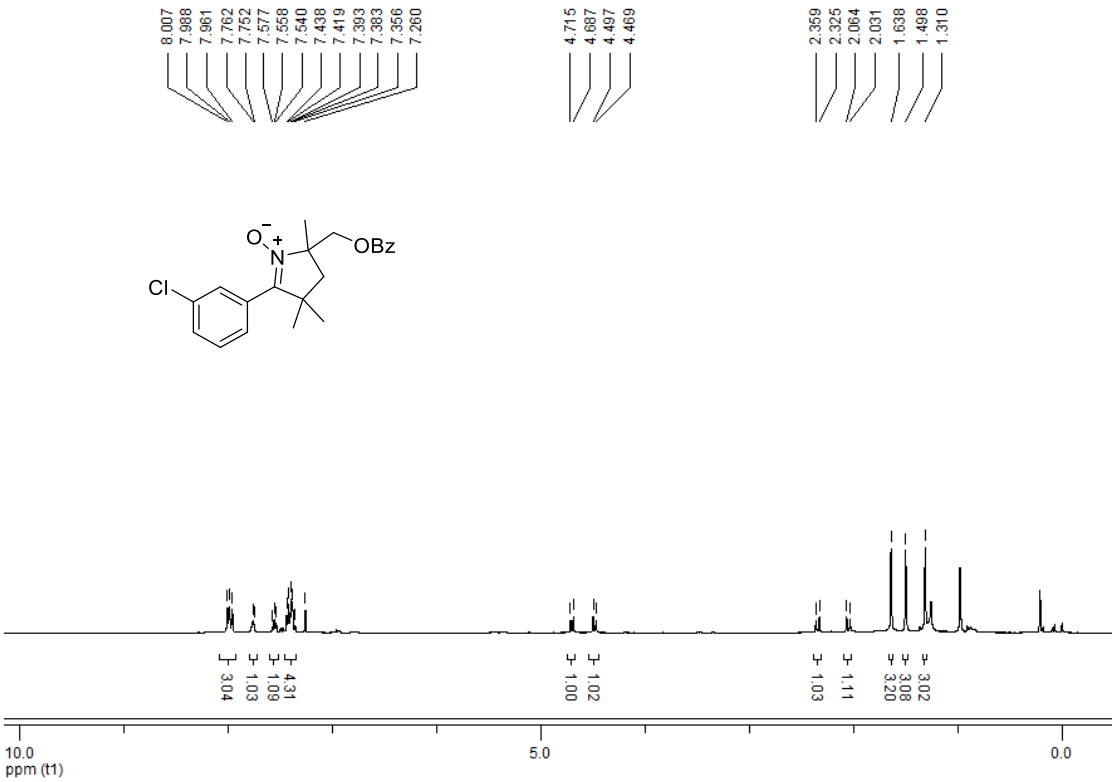


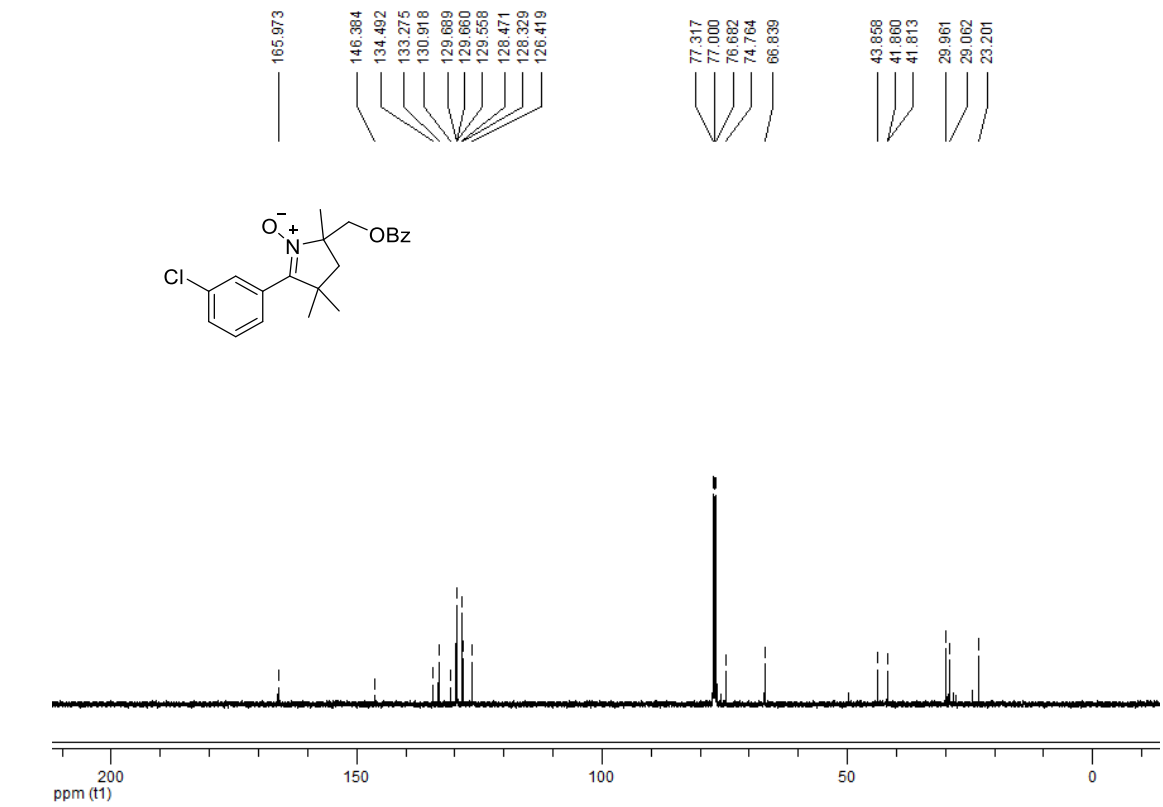




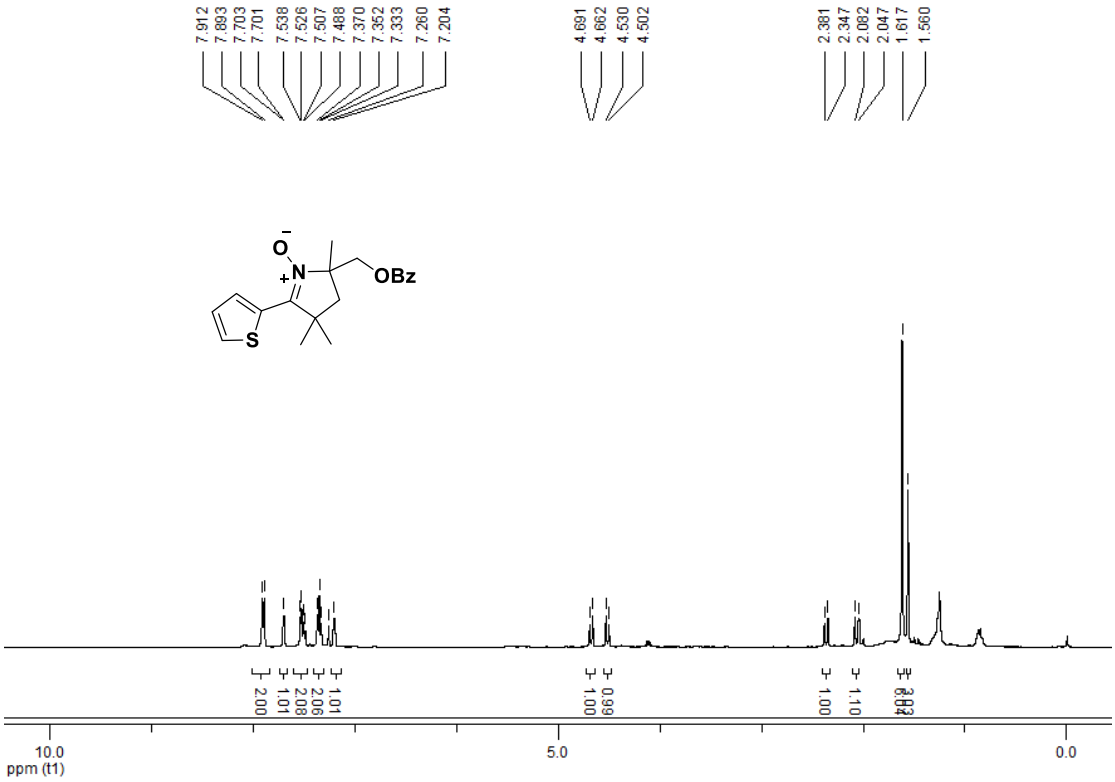

-62.975
O
N
OBz
F3C
0
-50
-100
-150
-200
ppm (t1)

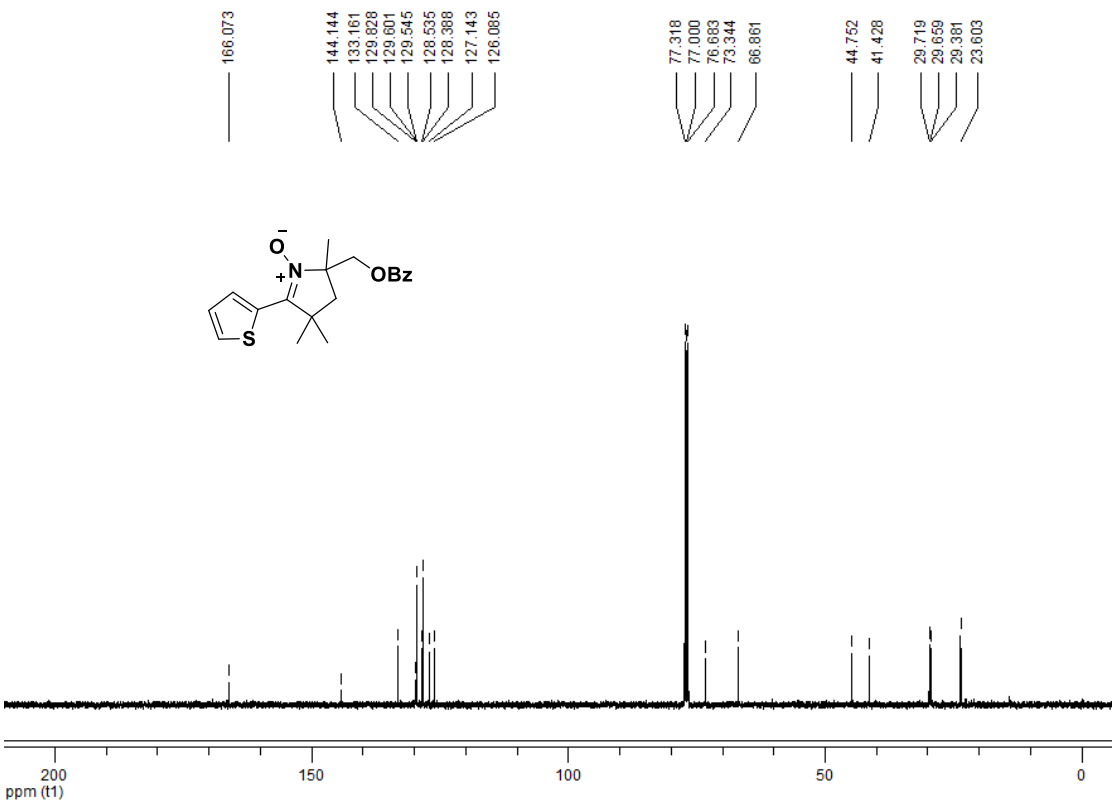
2-((benzoyloxy)methyl)-5-(3-chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrro le-1-oxide (3fa):



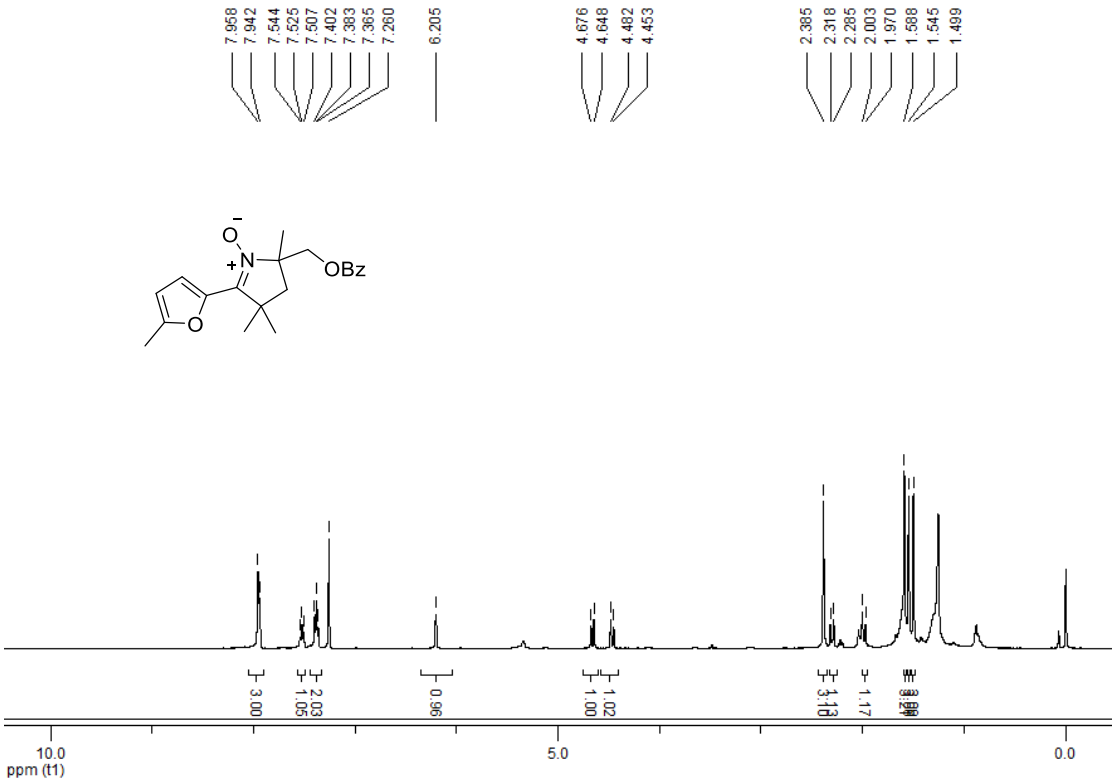


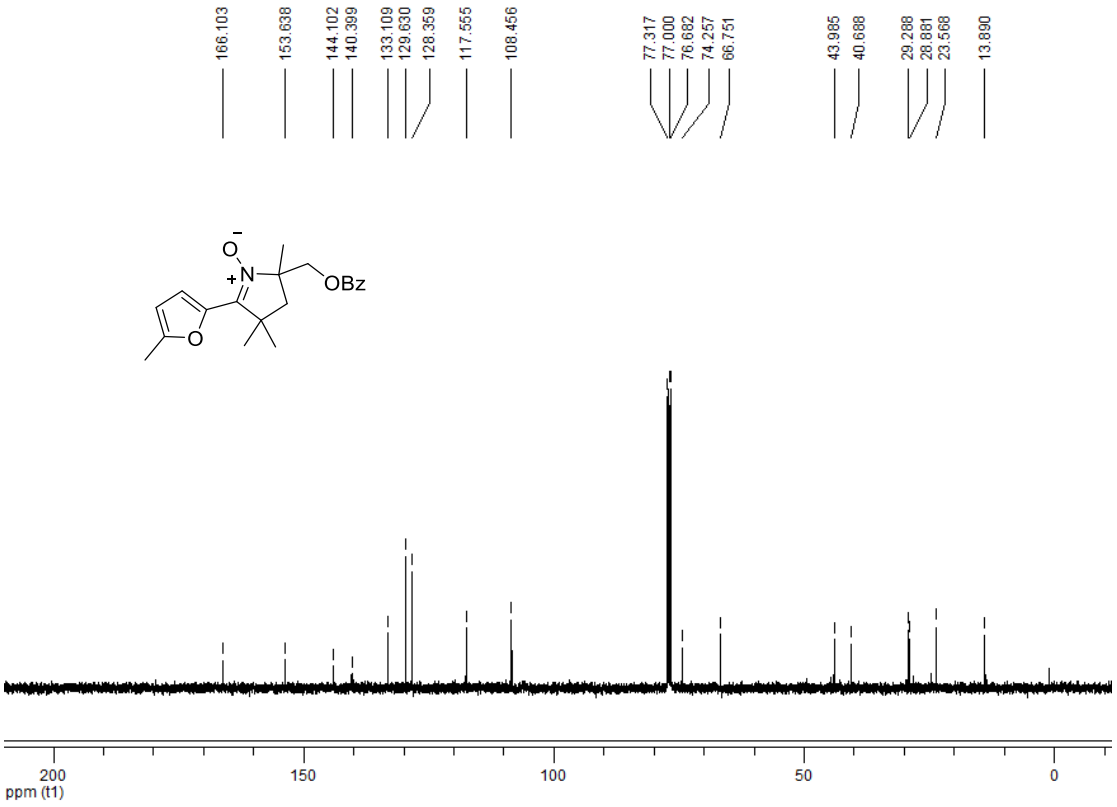
2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole -1-oxide (3ga):



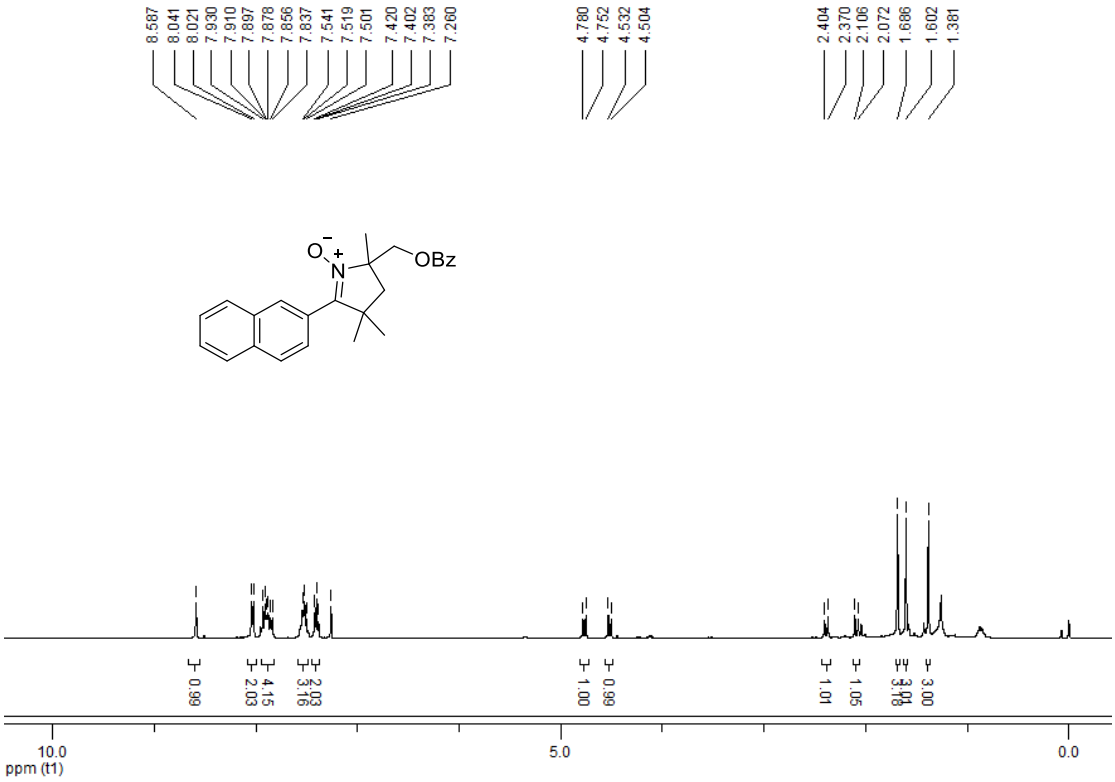


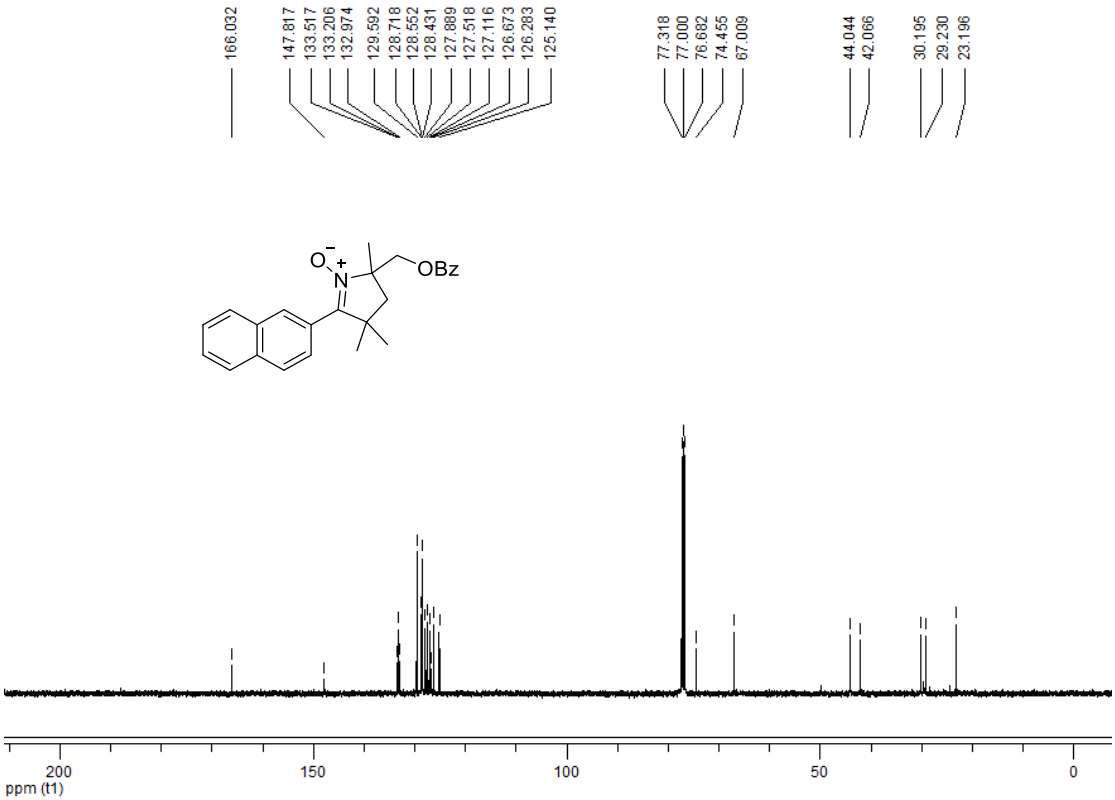
2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(5-methylfuran-2-yl)-3,4-dihydro-2*H*-pyrrole-1-oxide (3ha):



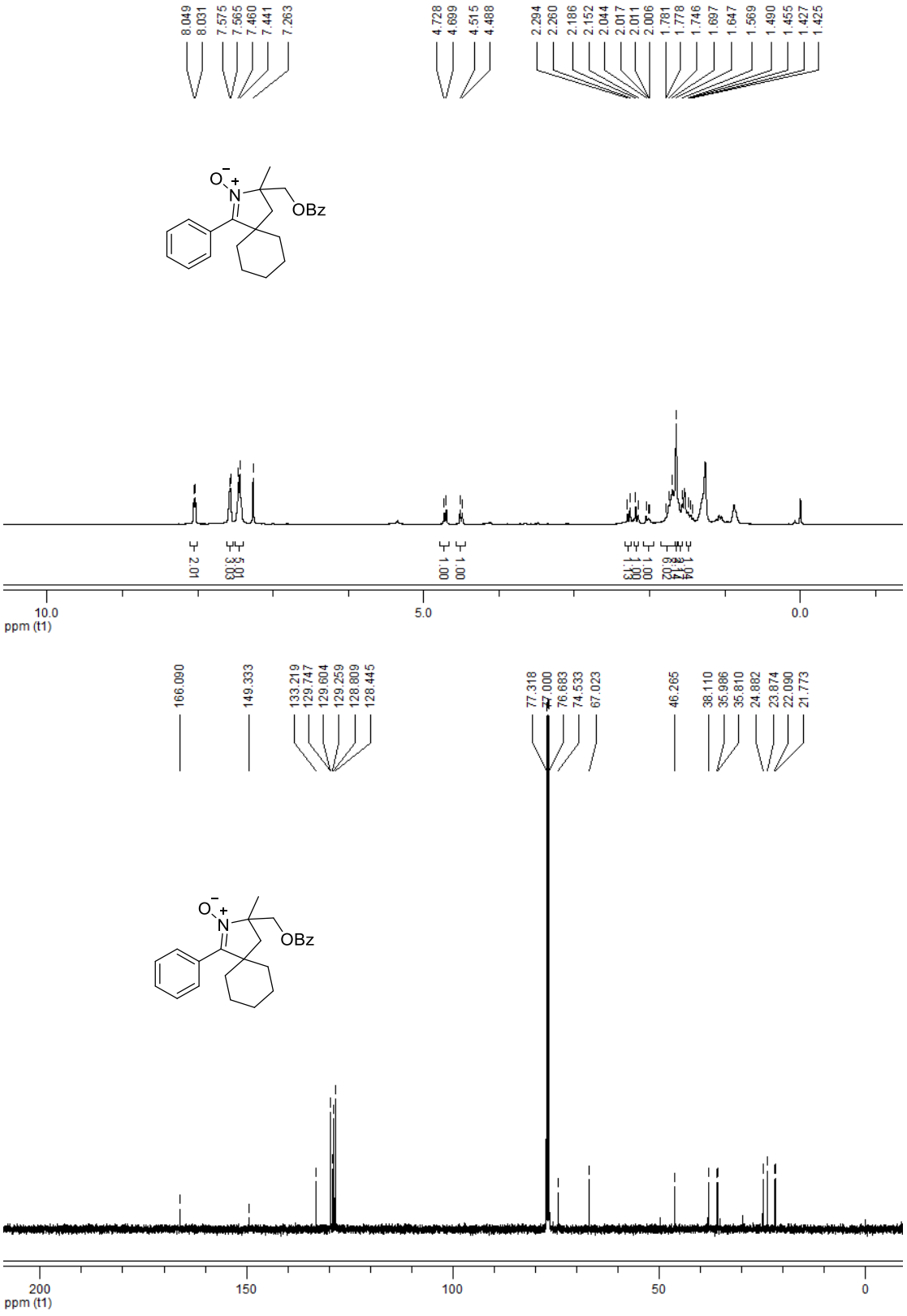


2-((benzoyloxy)methyl)-2,4,4-trimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyrrole-1-oxide (3ia):

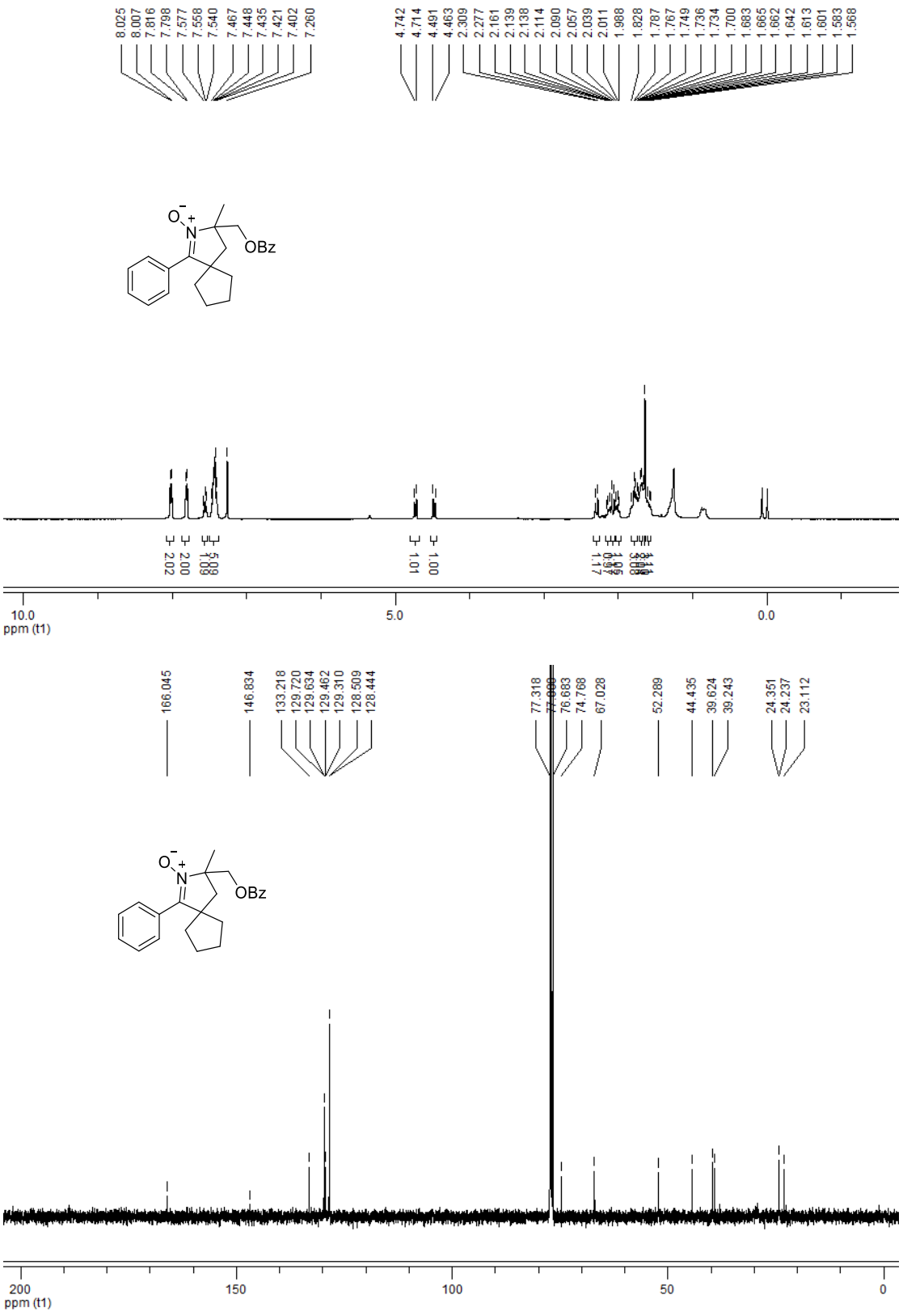




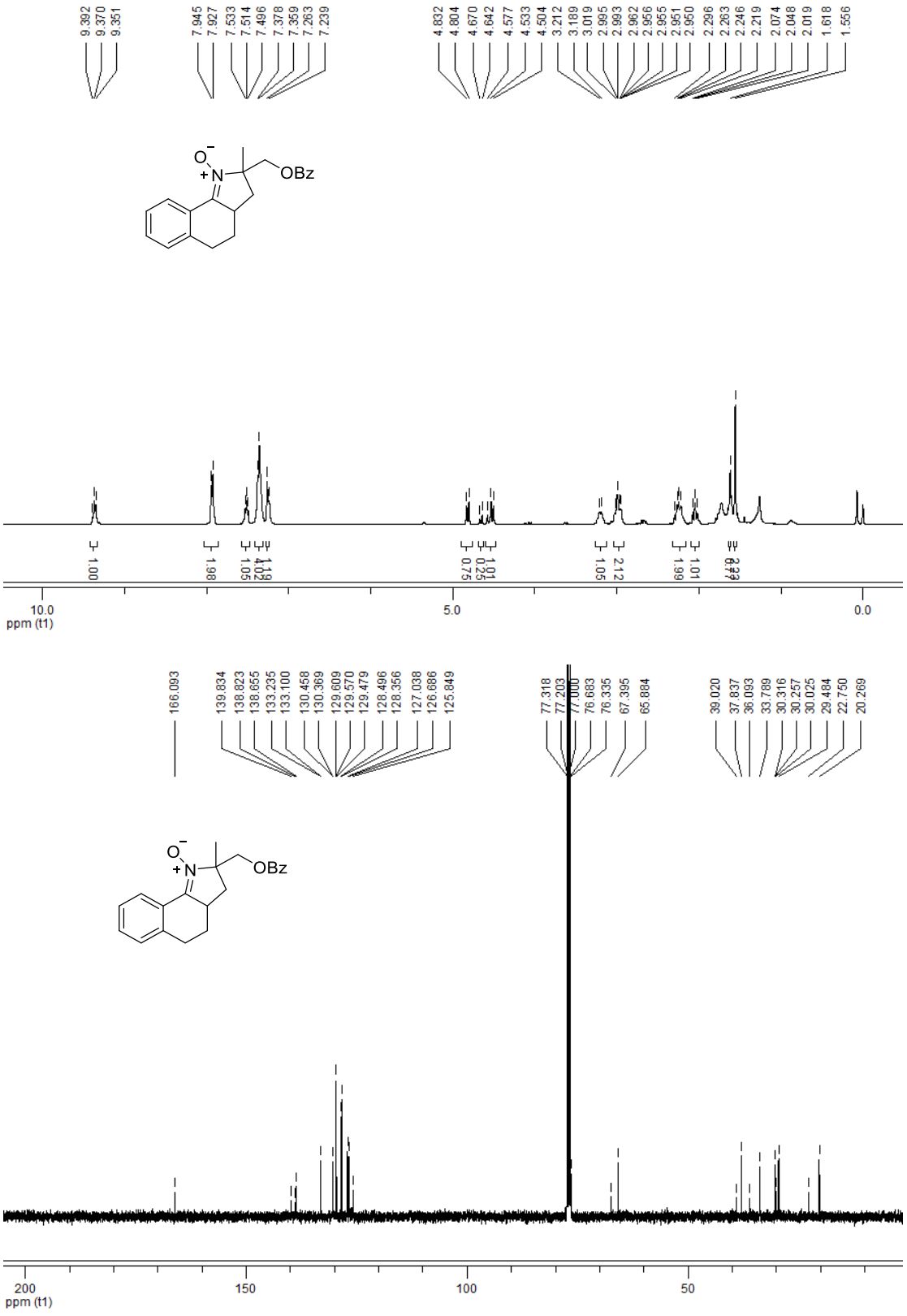
3-((benzoyloxy)methyl)-3-methyl-1-phenyl-2-azaspiro[4.5]dec-1-ene-2-oxide (3ja):



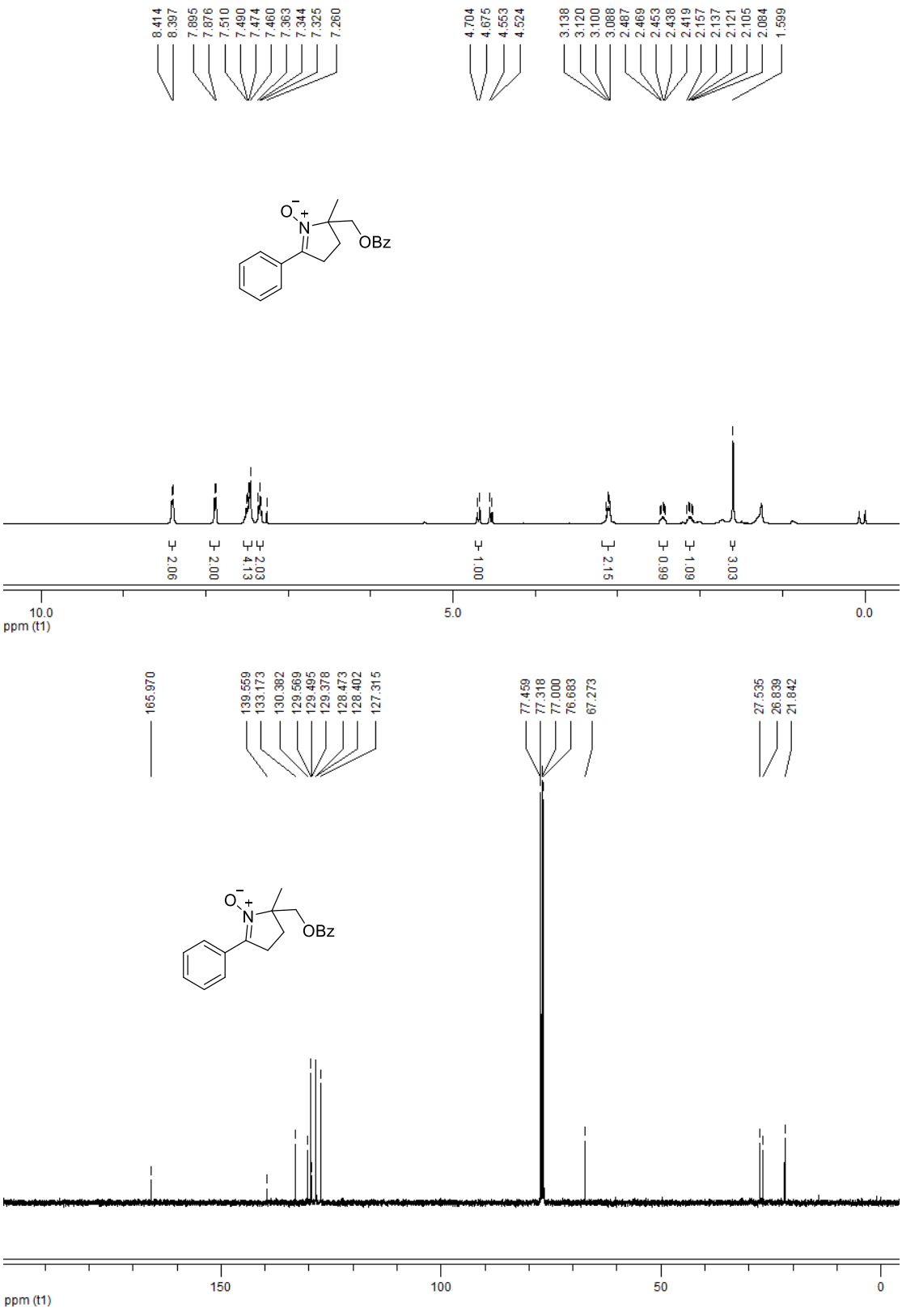
3-((benzoyloxy)methyl)-3-methyl-1-phenyl-2-azaspiro[4.4]non-1-ene-2-oxide (3ka):



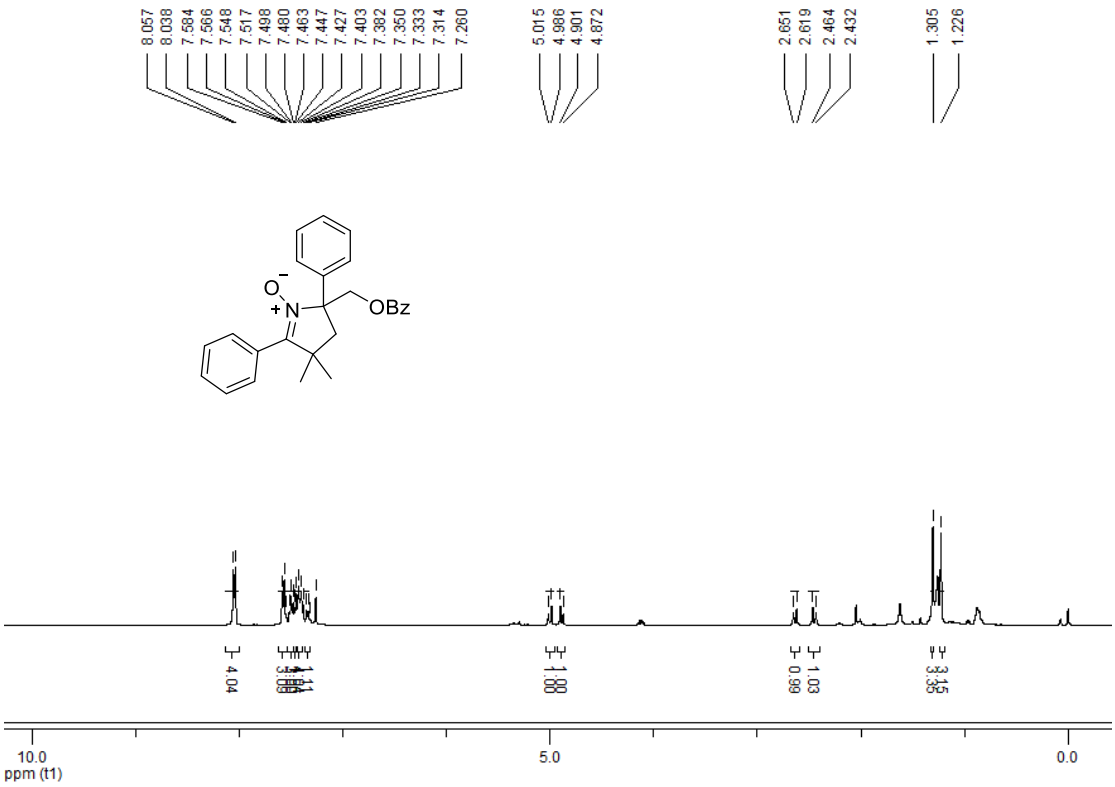
2-((benzoyloxy)methyl)-2-methyl-3,3a,4,5-tetrahydro-2*H*-benzo[g]indole-1-oxide (3la):

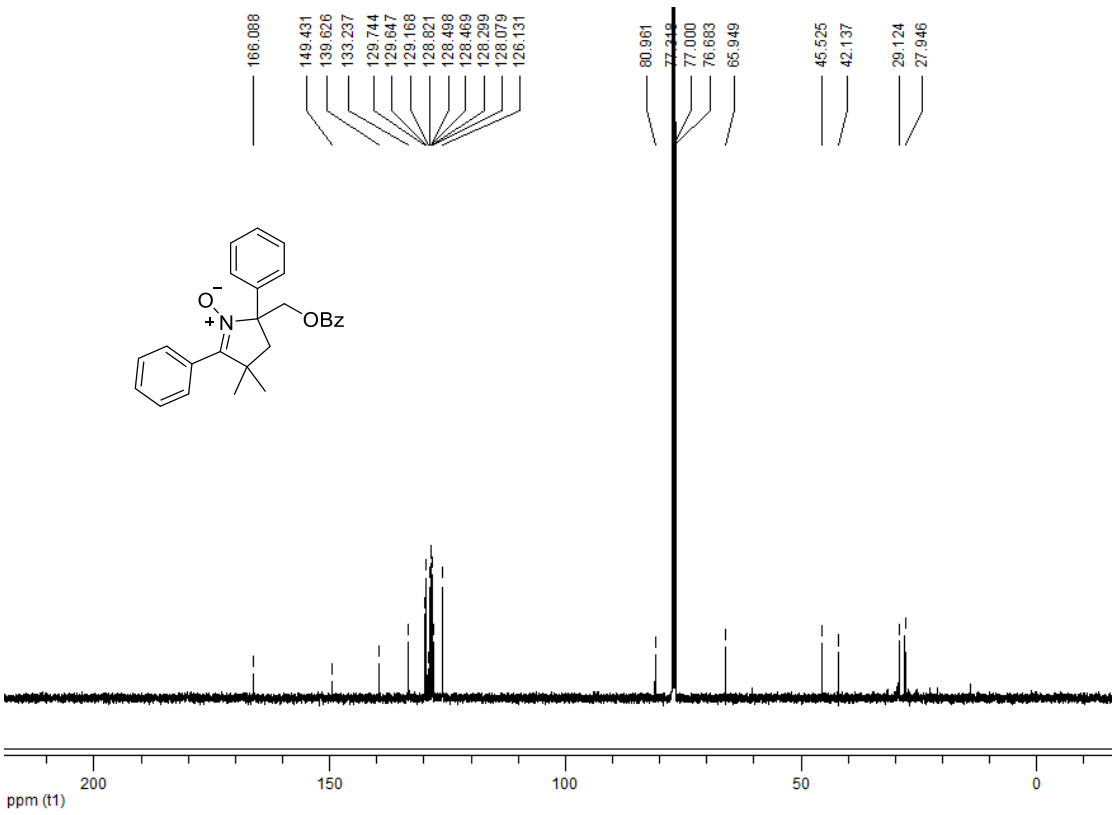


2-((benzoyloxy)methyl)-2-methyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3ma):

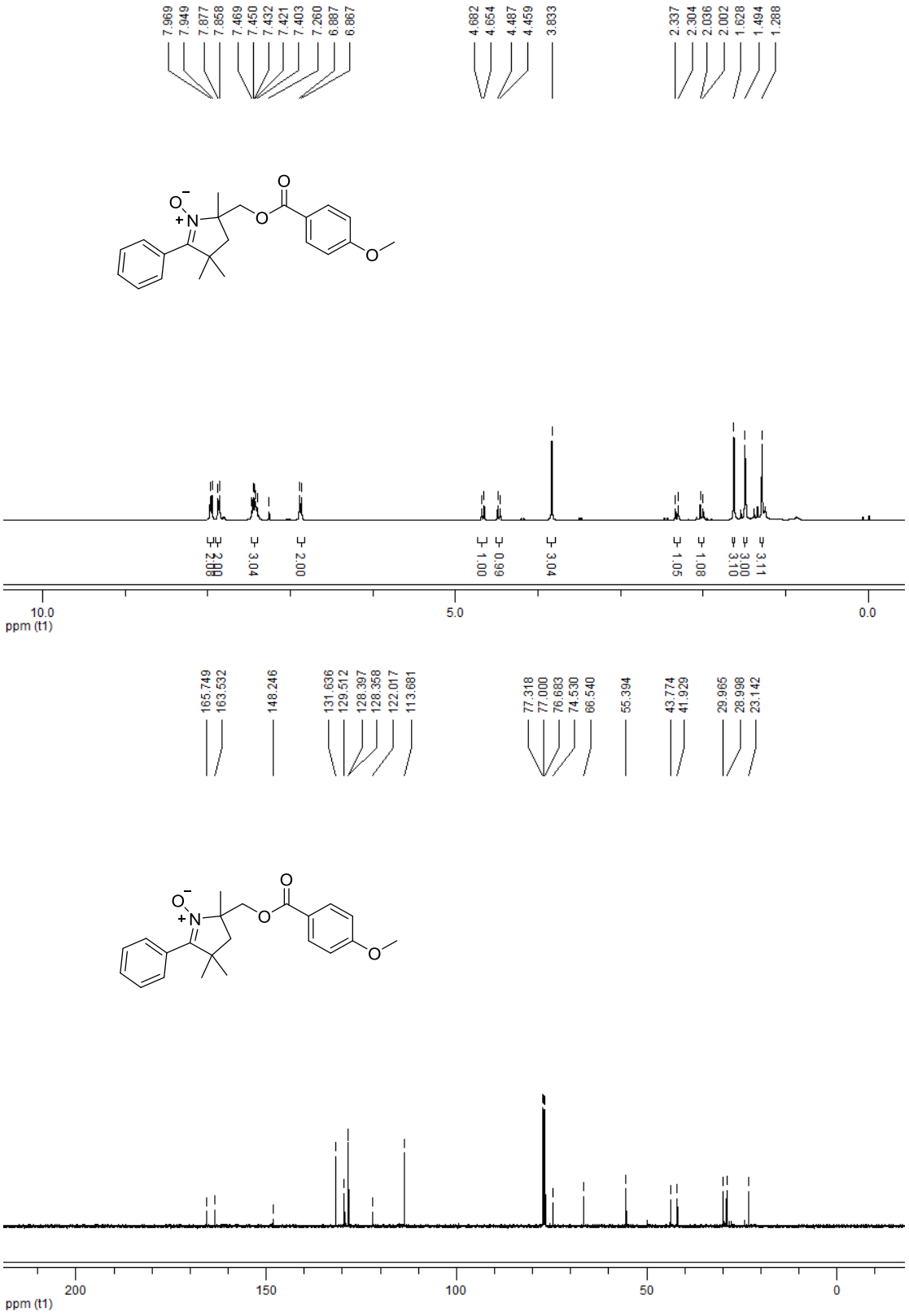


2-((benzoyloxy)methyl)-4,4-dimethyl-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (3na):

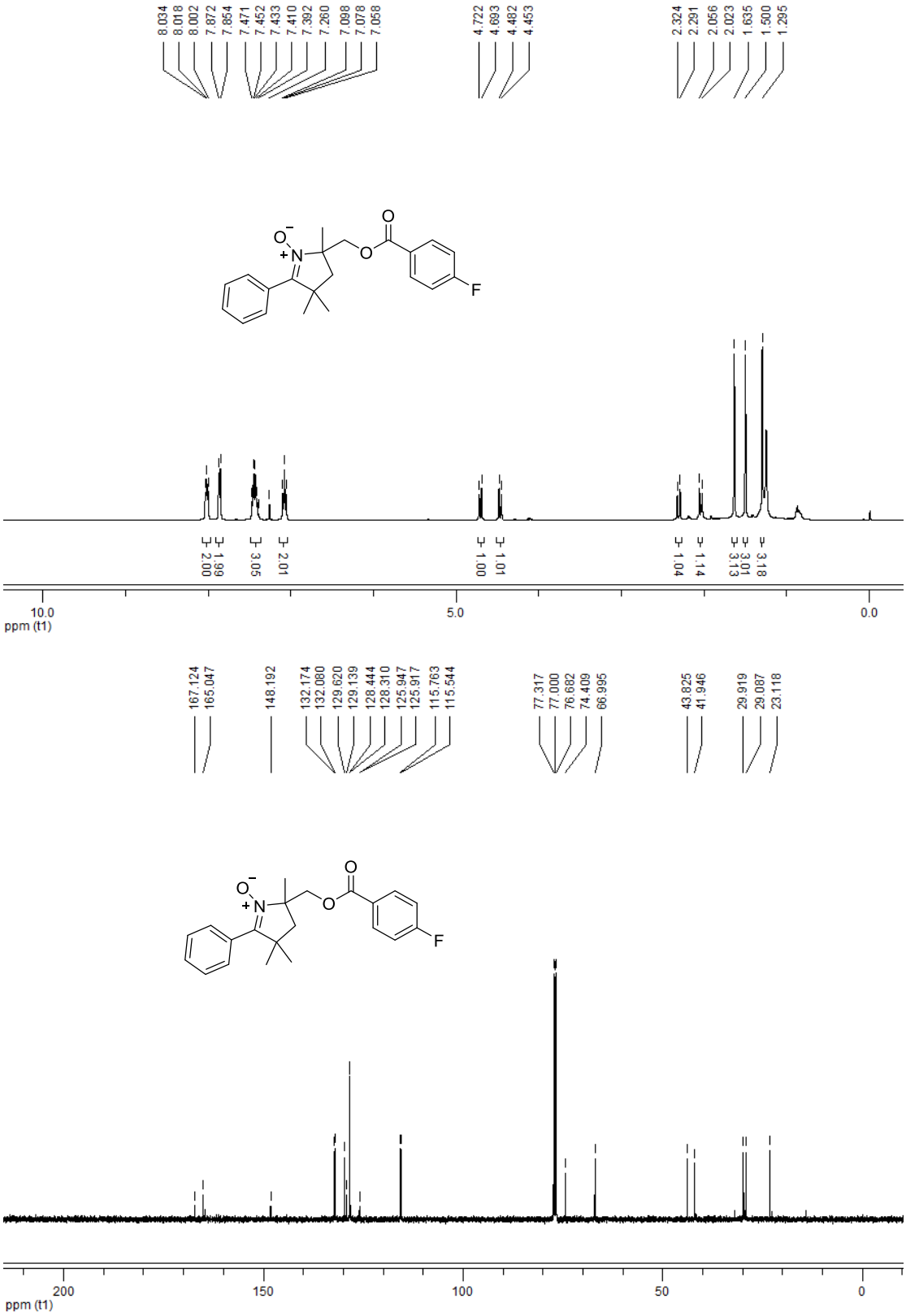


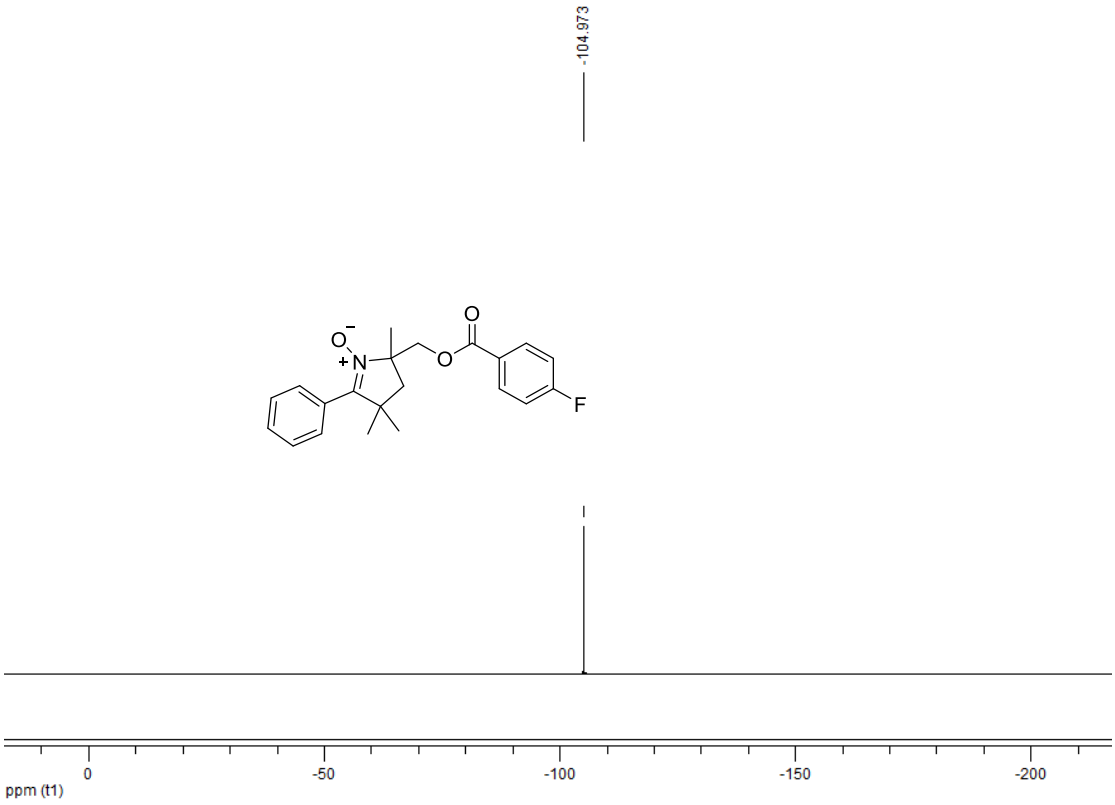


2-(((4-methoxybenzoyl)oxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (3ab):



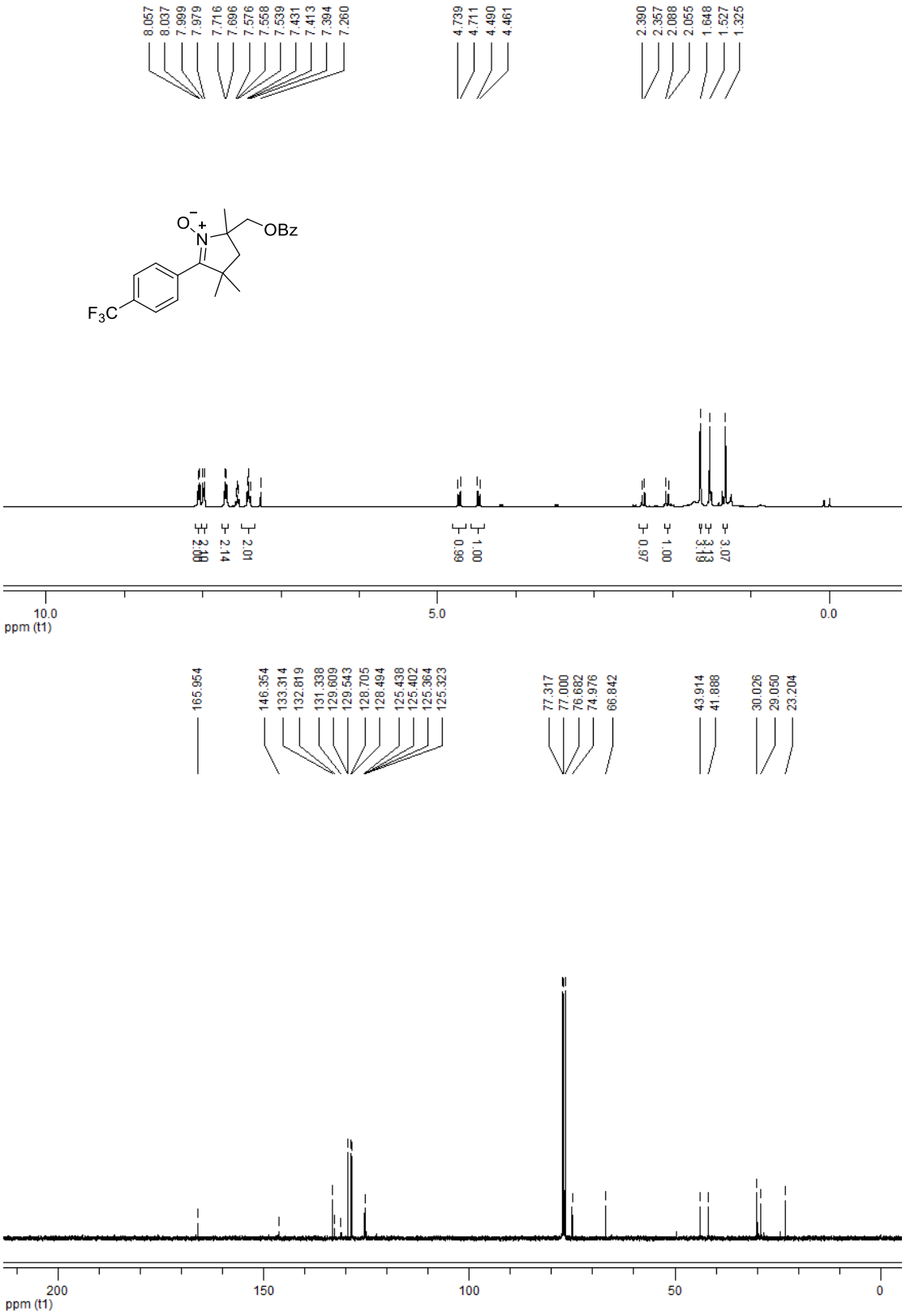
2-(((4-fluorobenzoyl)oxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrro le- 1-oxide (3ac):

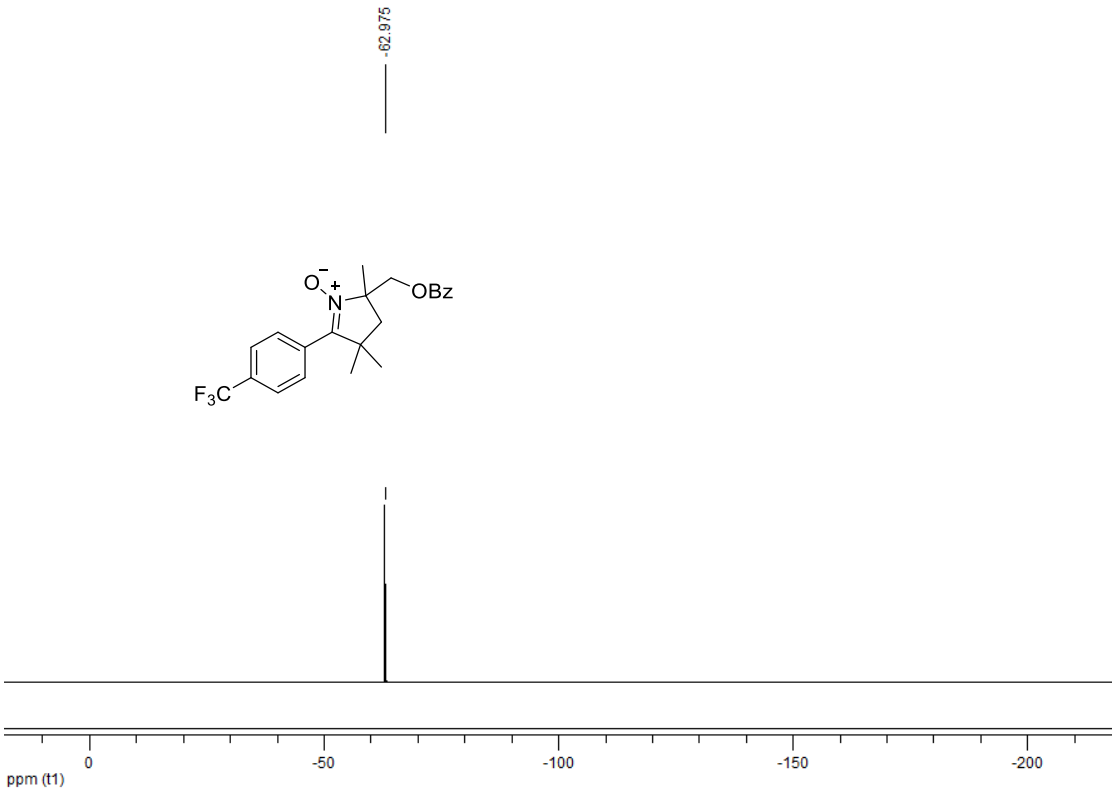



-104.973
O
O
N
O
F
0
-50
-100
-150
-200
ppm (t1)

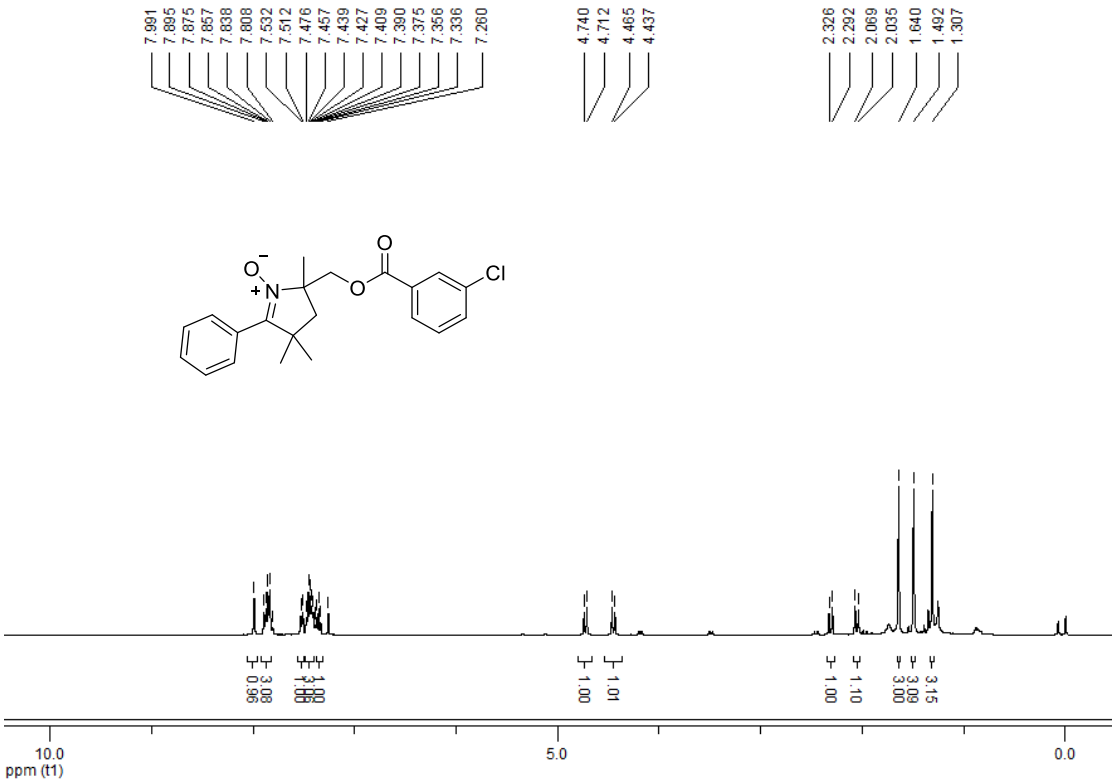
2,4,4-trimethyl-5-phenyl-2-(((4-(trifluoromethyl)benzoyl)oxy)methyl)-3,4-dihydr

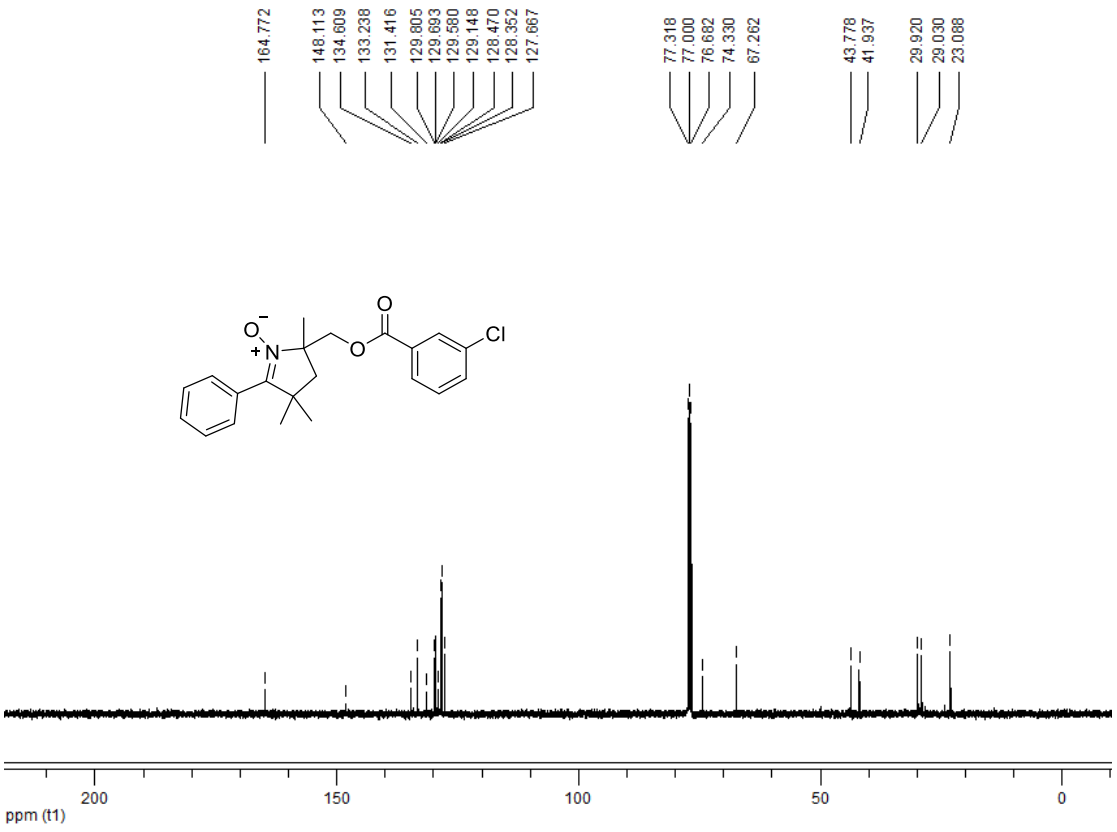
o-2*H*-pyrrole-1-oxide (3ad):



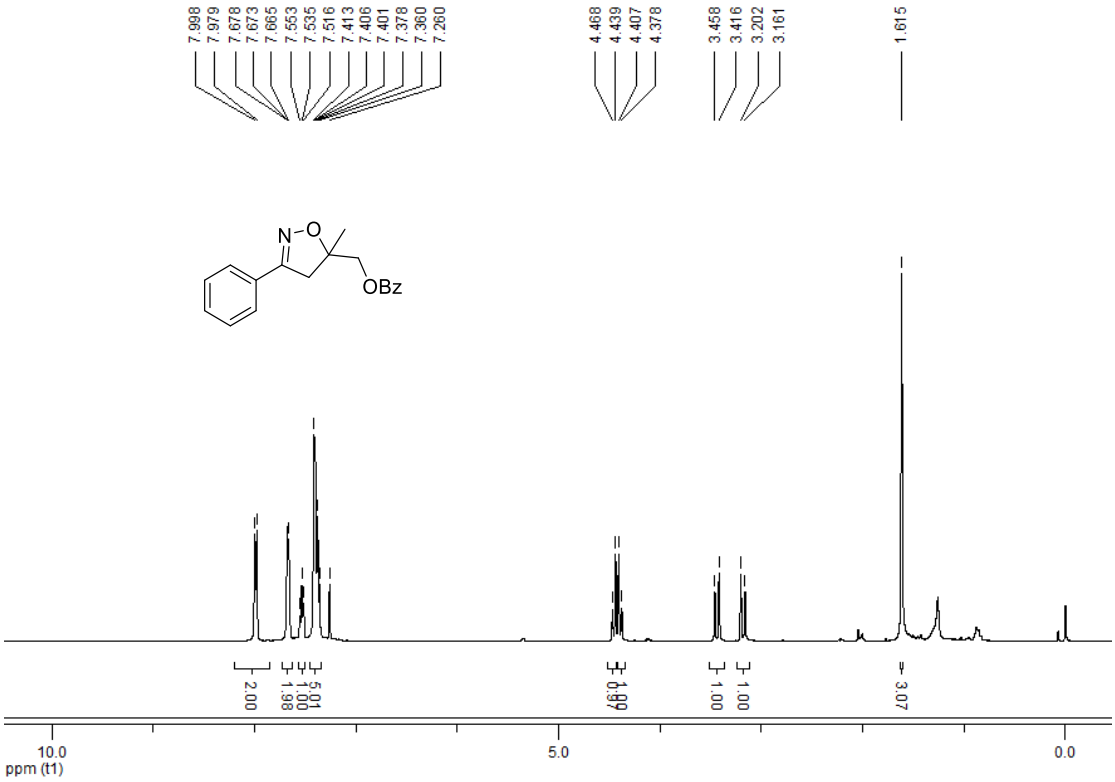

-62.975
O
N
OBz
F3C
0
-50
-100
-150
-200
ppm (t1)

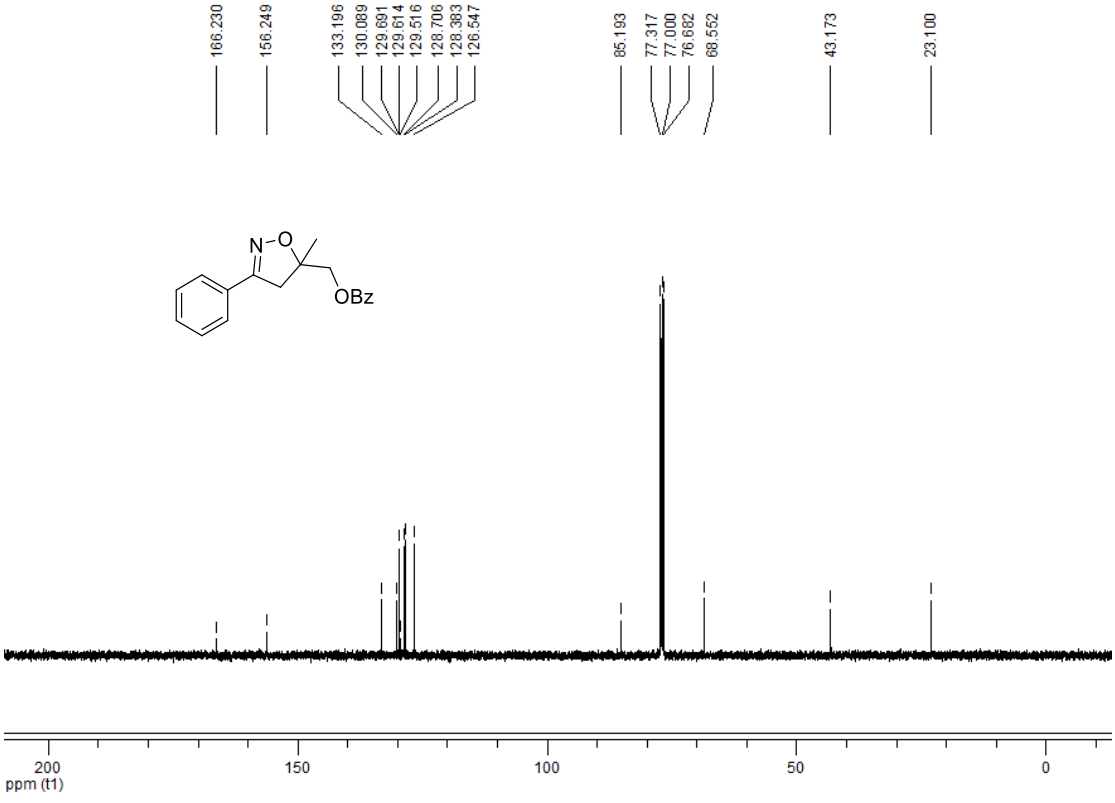
2-(((3-chlorobenzoyl)oxy)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrro le-1-oxide (3ae):



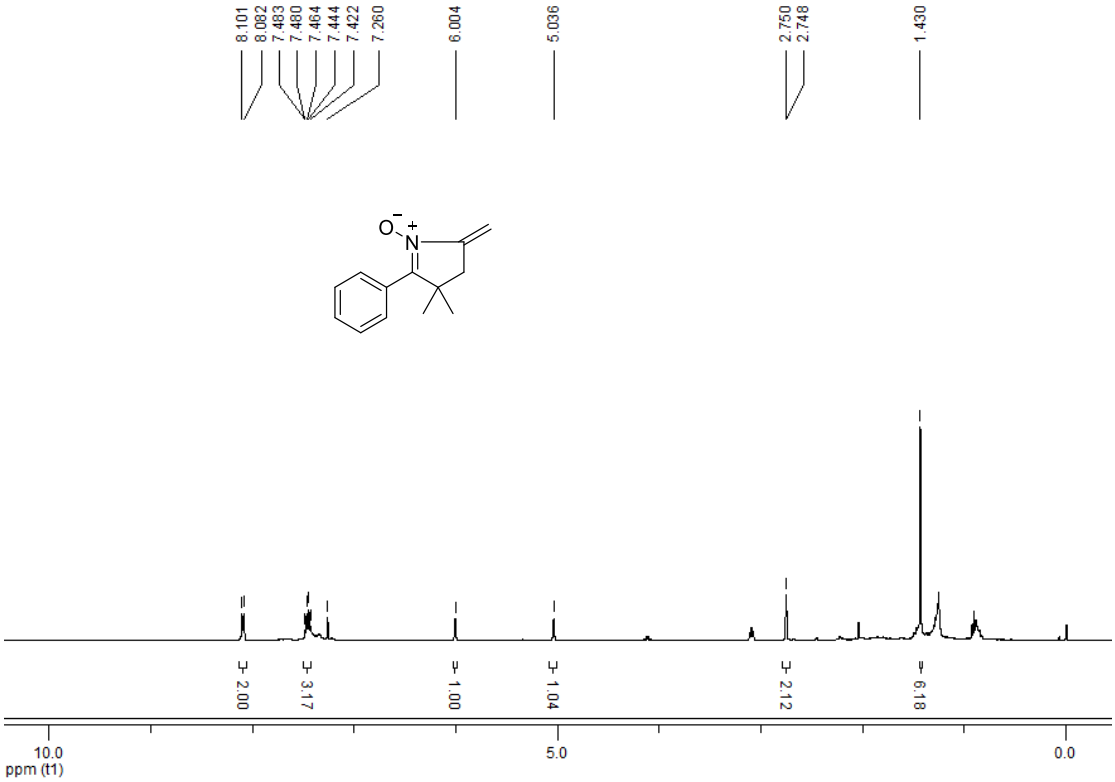


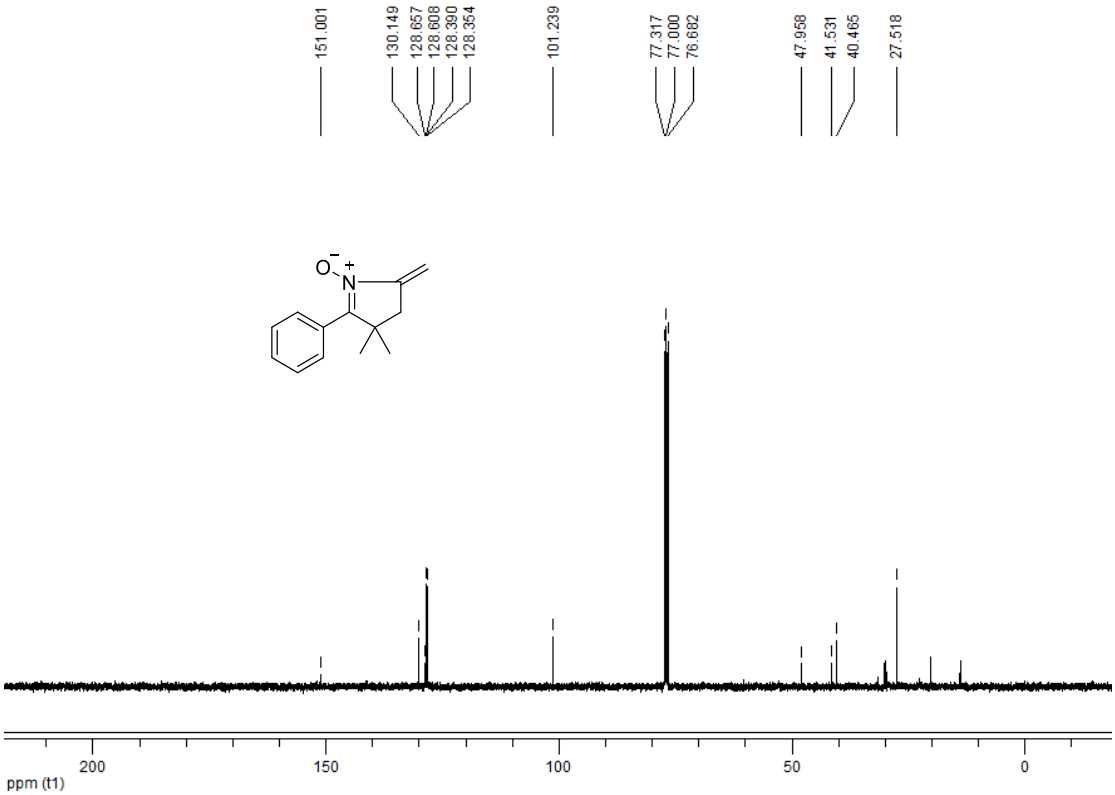
(5-methyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl benzoate (5oa):





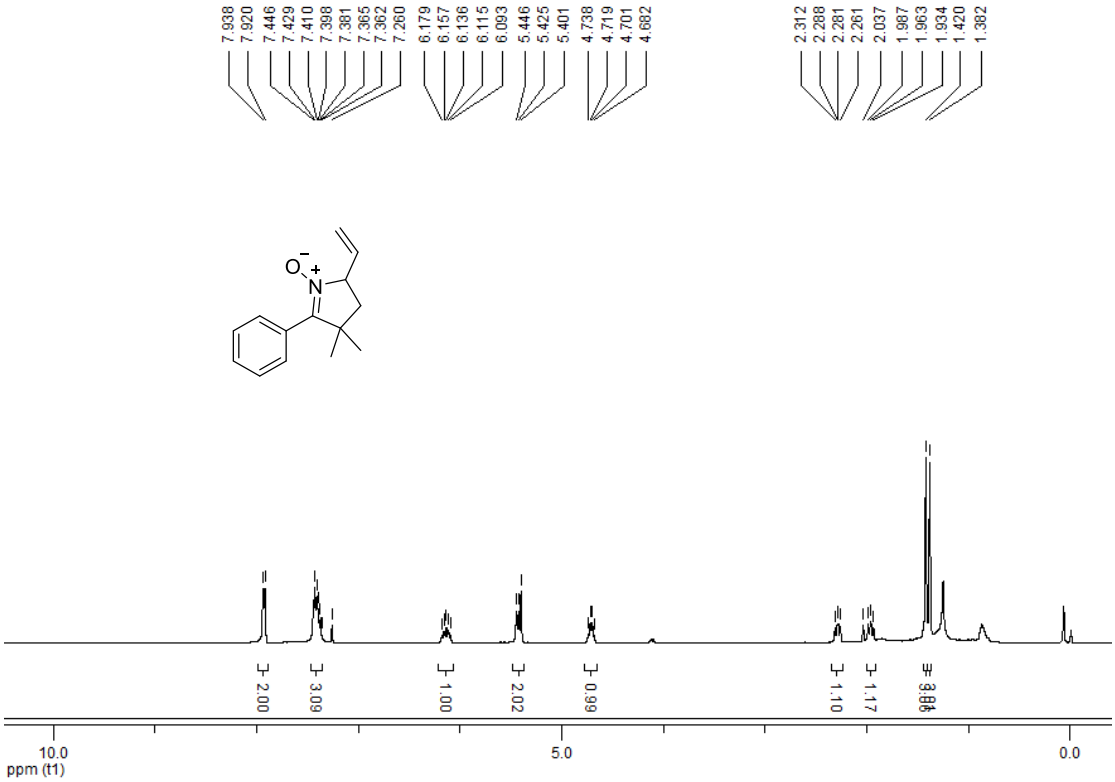
4,4-dimethyl-2-methylene-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6p)

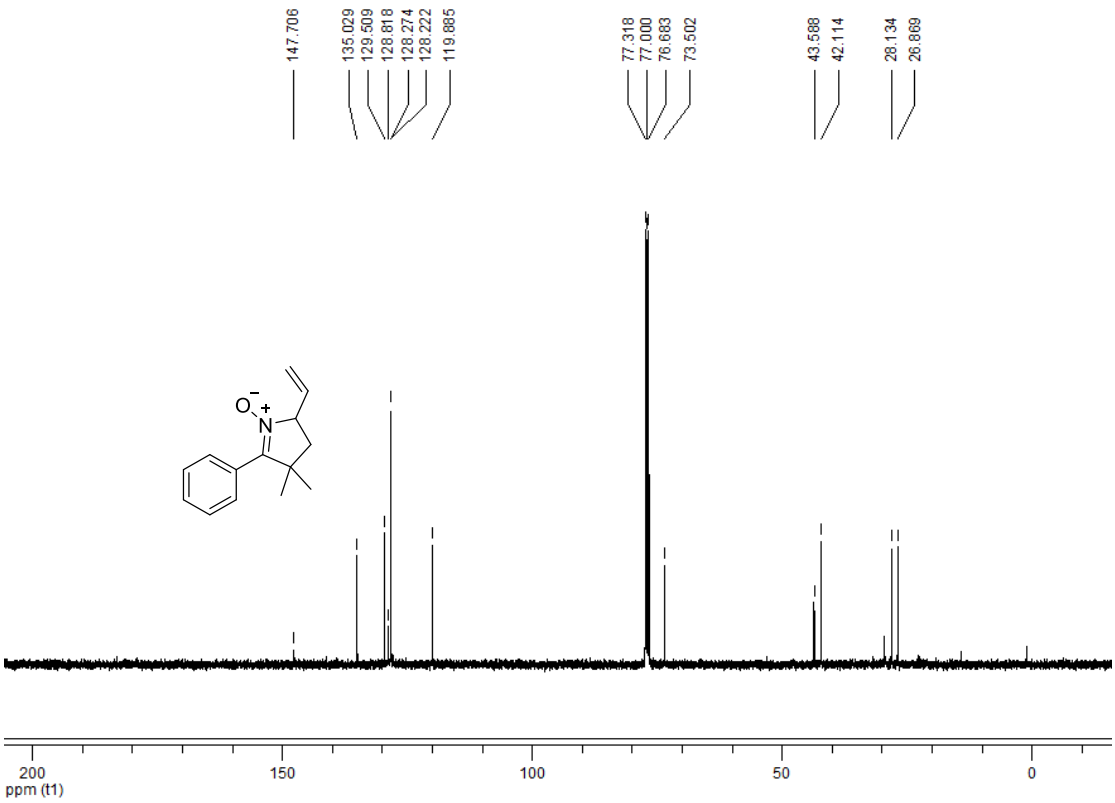




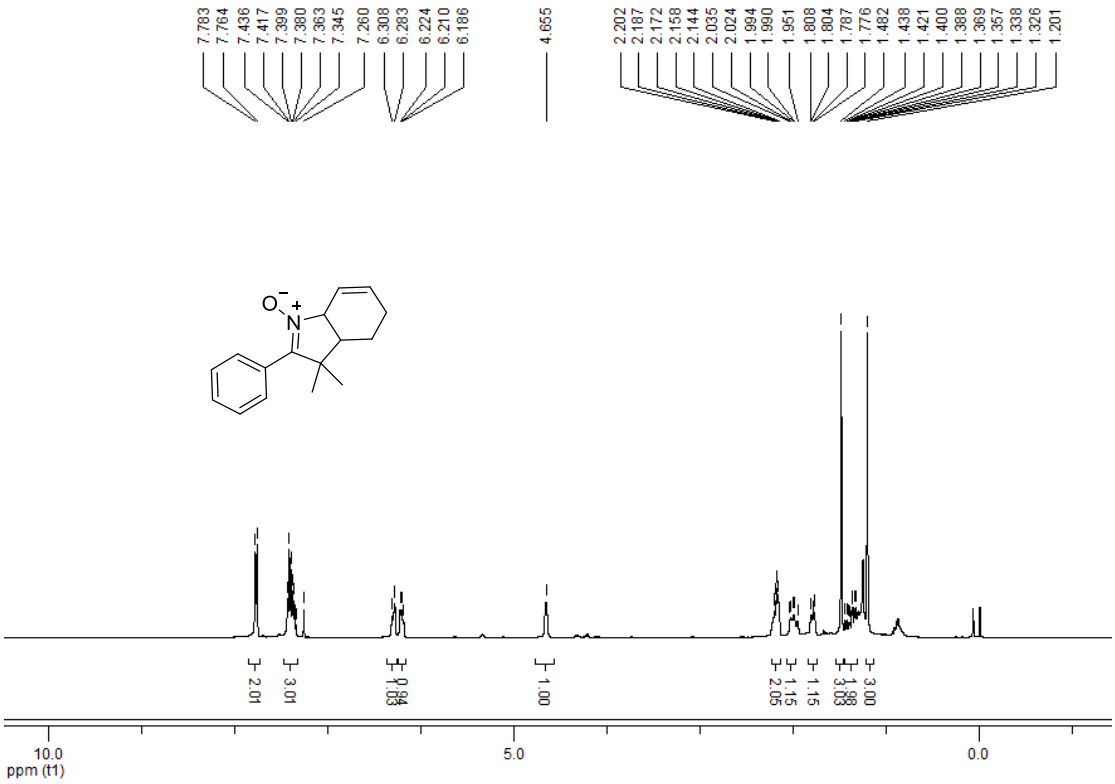
4-allyl-4-methyl-2-methylene-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6q)

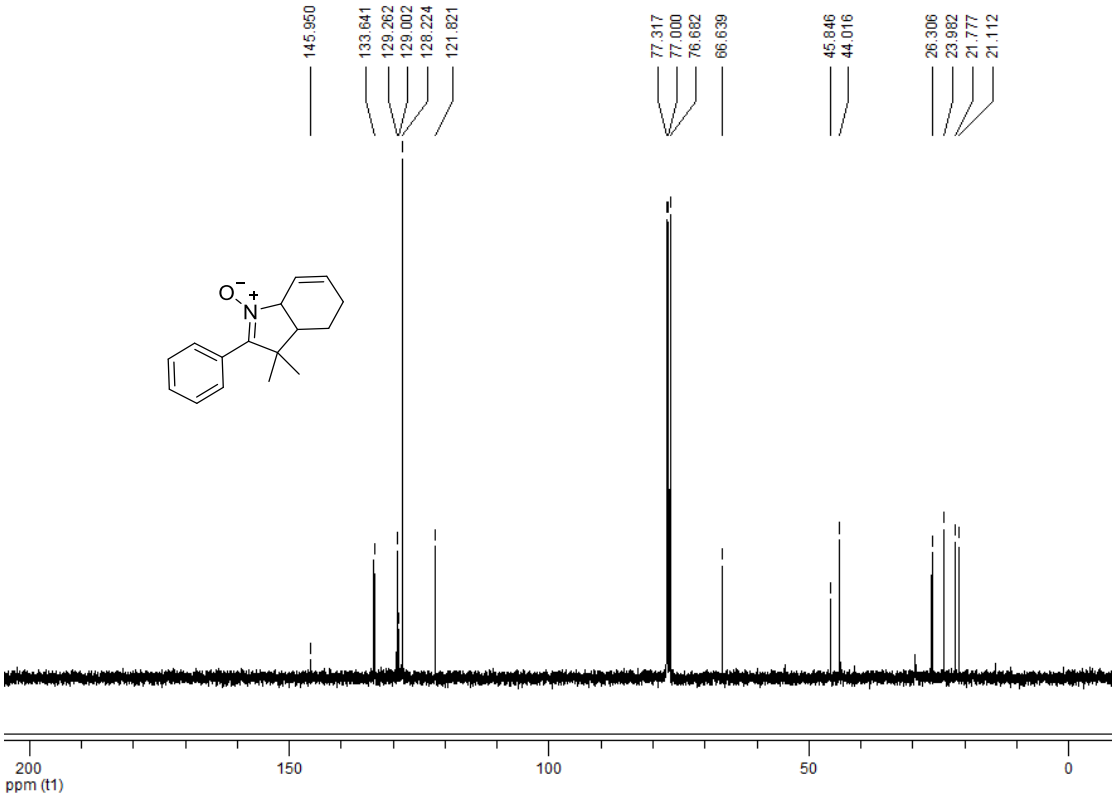
4,4-dimethyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6r):



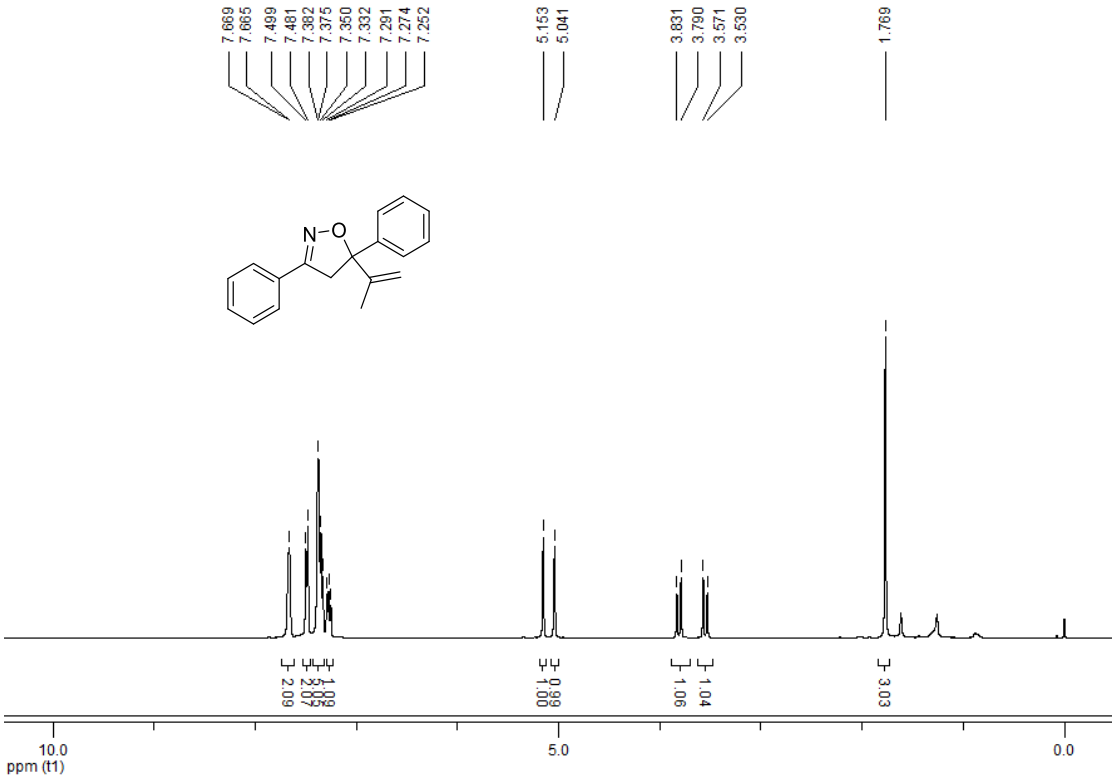


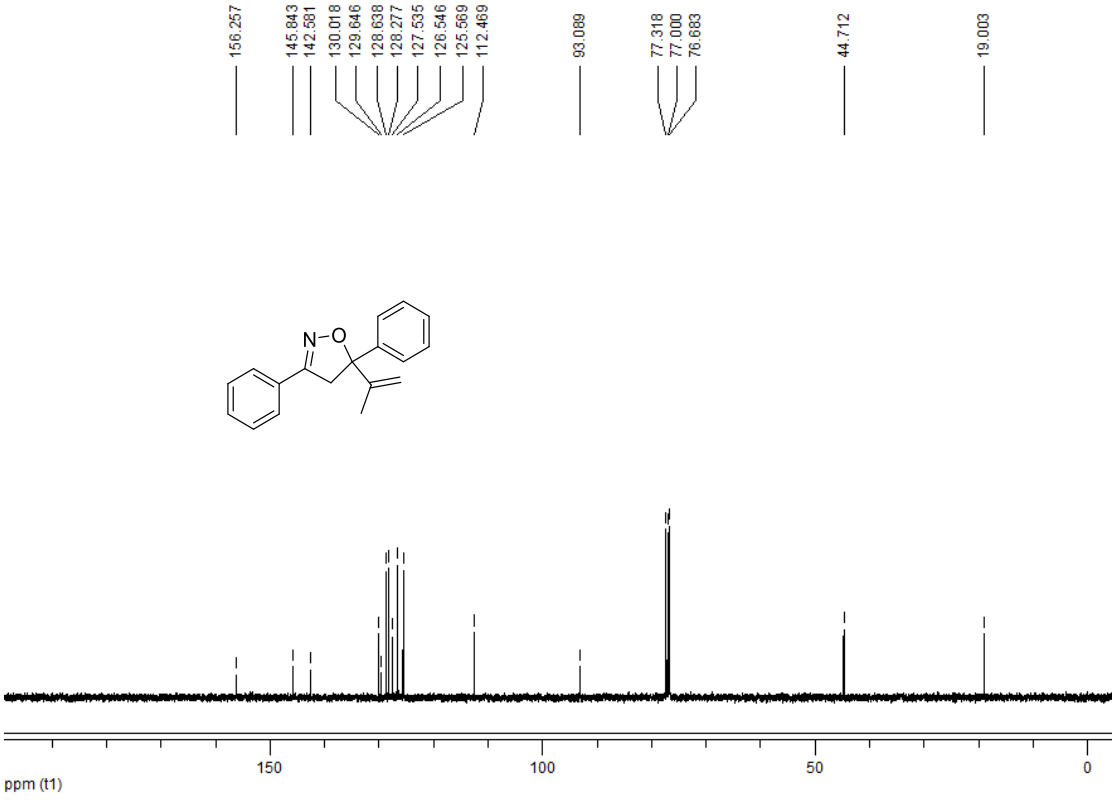
3,3-dimethyl-2-phenyl-3a,4,5,7a-tetrahydro-3*H*-indole-1-oxide (6s):



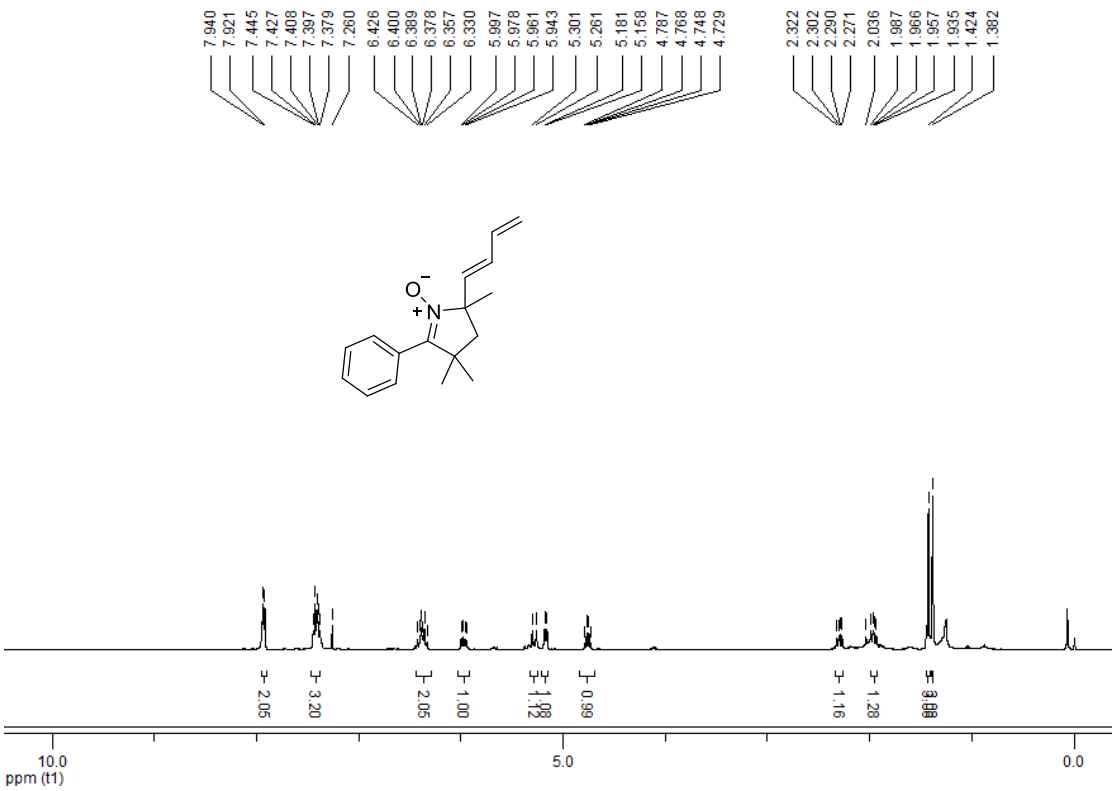


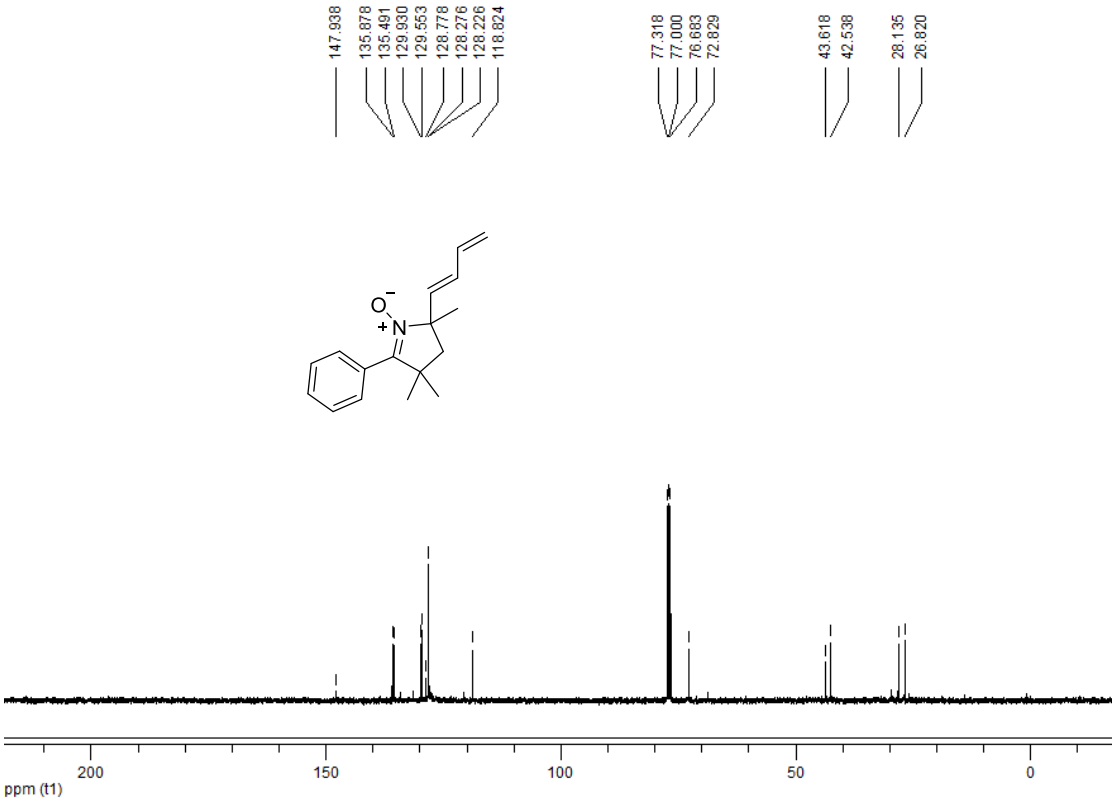
3,5-diphenyl-5-(prop-1-en-2-yl)-4,5-dihydroisoxazole (6t):



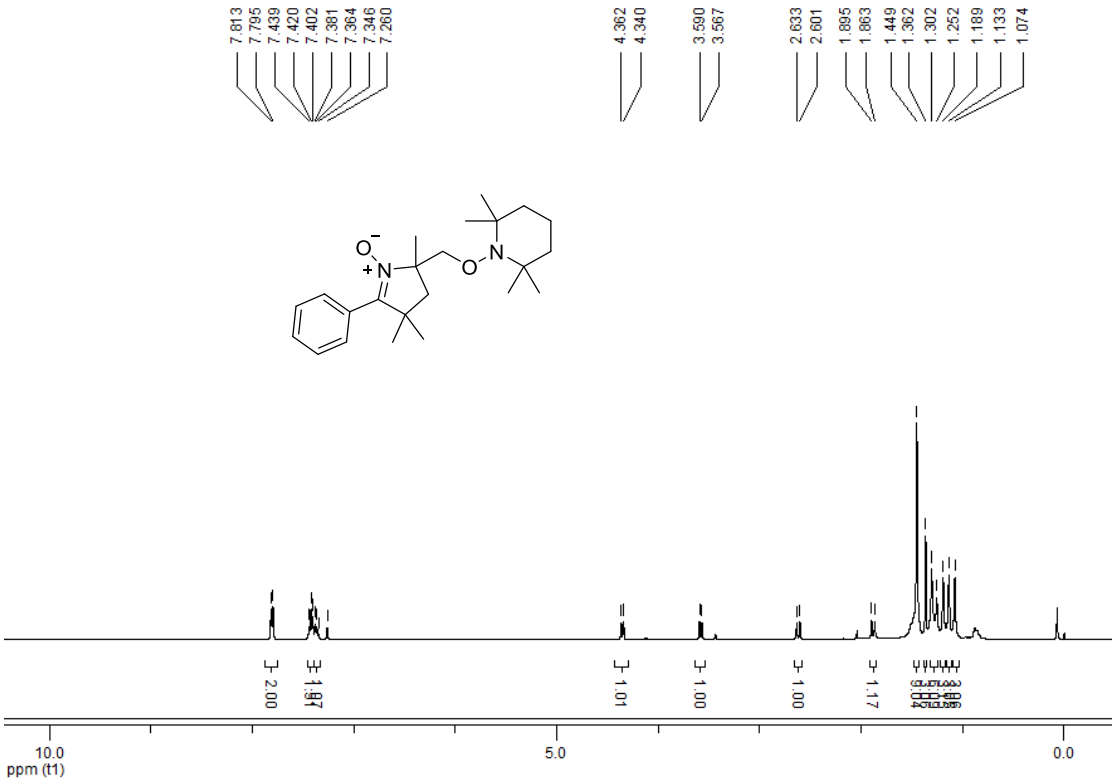


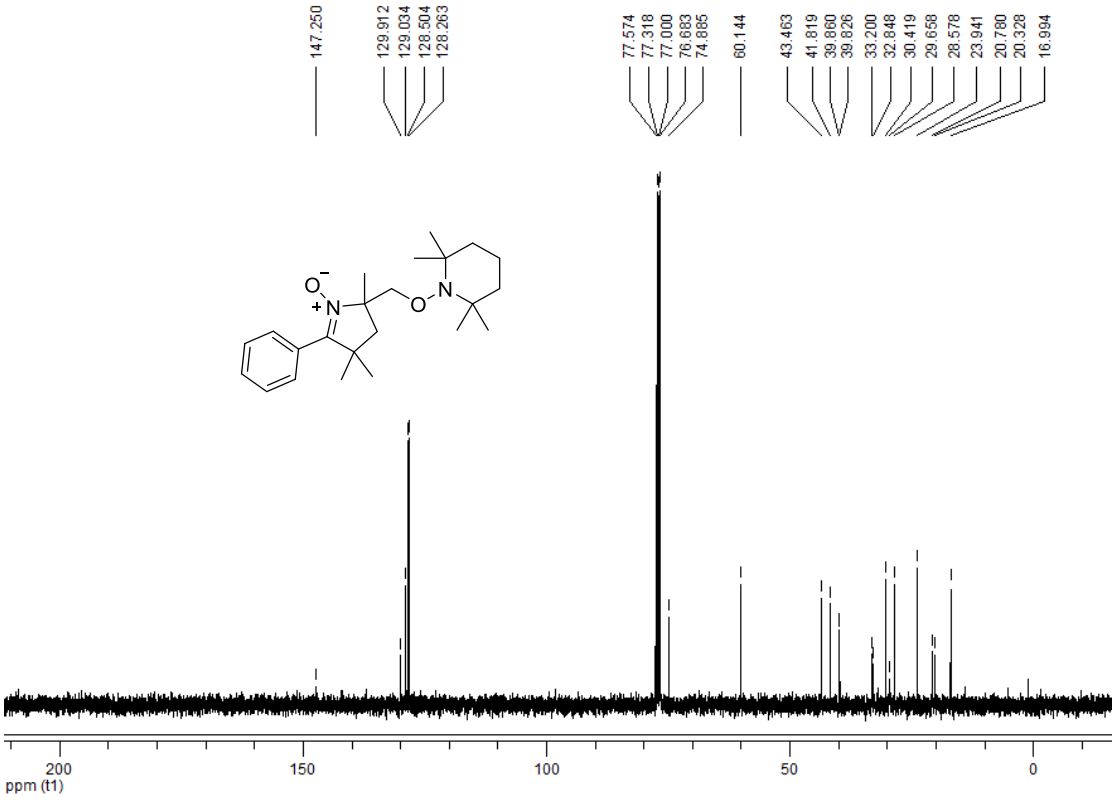
(*E*)-2-(buta-1,3-dien-1-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide (6aq):



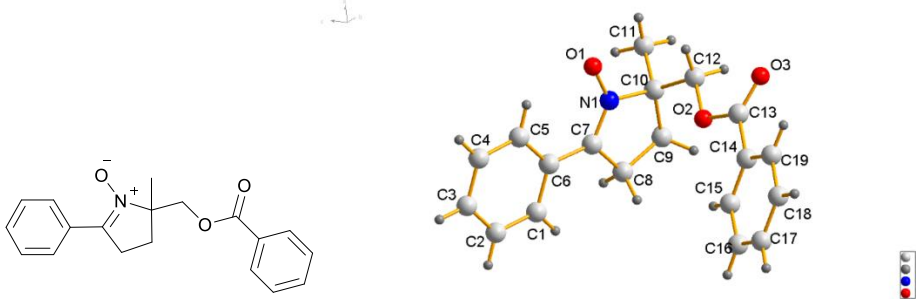


2,4,4-trimethyl-5-phenyl-2-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3,4-dihydro-2*H*-pyrrole-1-oxide (7):





(D) The X-ray Single-Crystal Diffraction Analysis



X-ray structure of compound **3ma** (CCDC: 2057134)

The thermal ellipsoid plot of 3ma with 30% displacement ellipsoids

Table S1. Crystal data and structure refinement for A.

Identification code	A	
Empirical formula	C19 H19 N O3	
Formula weight	309.35	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.5441(19) Å	α= 90°.
	b = 8.977(3) Å	β= 90°.
	c = 28.197(8) Å	γ = 90°.
Volume	1656.4(8) $Å^3$	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	656	
Crystal size	0.280 x 0.260 x 0.250 mm^3	
Theta range for data collection	2.381 to 25.489°.	
Index ranges	-7<=h<=7, -10<=k<=10, -34<=l<=32	
Reflections collected	12777	
Independent reflections	3076 [R(int) = 0.0274]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3076 / 0 / 209	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0787	

R indices (all data)	R1 = 0.0439, wR2 = 0.0839
Absolute structure parameter	0.2(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.142 and -0.097 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(5)	5120(4)	2724(2)	1978(1)	59(1)
C(4)	4650(4)	1397(3)	2196(1)	70(1)
C(1)	1577(4)	3312(3)	1954(1)	76(1)
C(3)	2681(5)	1007(3)	2294(1)	80(1)
C(2)	1146(5)	1964(3)	2171(1)	92(1)
C(6)	3573(3)	3714(2)	1852(1)	51(1)
N(1)	5715(3)	5653(2)	1491(1)	49(1)
C(7)	3939(3)	5150(2)	1624(1)	50(1)
O(1)	7468(2)	5016(2)	1528(1)	66(1)
C(9)	3377(4)	7565(3)	1294(1)	65(1)
C(10)	5648(4)	7175(2)	1267(1)	54(1)
C(11)	7009(4)	8211(3)	1553(1)	75(1)
C(8)	2317(4)	6240(3)	1507(1)	79(1)
C(12)	6471(4)	7047(2)	771(1)	62(1)
O(2)	5188(2)	6044(2)	509(1)	59(1)
O(3)	7226(3)	6352(2)	-115(1)	96(1)
C(15)	2333(4)	4537(2)	-22(1)	68(1)
C(13)	5718(4)	5807(3)	58(1)	64(1)
C(14)	4278(4)	4815(2)	-192(1)	62(1)
C(19)	4908(5)	4135(3)	-610(1)	82(1)
C(17)	1680(7)	2902(3)	-670(1)	98(1)
C(16)	1036(5)	3594(3)	-265(1)	83(1)
C(18)	3604(7)	3179(3)	-842(1)	101(1)

Table S3. Bond lengths [Å] and angles [°] for A.

C(5)-C(4)	1.375(3)
C(5)-C(6)	1.394(3)
C(5)-H(5)	0.9300
C(4)-C(3)	1.363(4)
C(4)-H(4)	0.9300
C(1)-C(2)	1.384(4)
C(1)-C(6)	1.386(3)
C(1)-H(1)	0.9300
C(3)-C(2)	1.367(4)
C(3)-H(3)	0.9300
C(2)-H(2)	0.9300
C(6)-C(7)	1.460(3)
N(1)-O(1)	1.286(2)
N(1)-C(7)	1.302(3)
N(1)-C(10)	1.505(3)
C(7)-C(8)	1.480(3)
C(9)-C(8)	1.503(3)
C(9)-C(10)	1.529(3)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(12)	1.503(3)
C(10)-C(11)	1.520(3)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(12)-O(2)	1.436(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
O(2)-C(13)	1.337(3)
O(3)-C(13)	1.204(3)
C(15)-C(16)	1.380(4)
C(15)-C(14)	1.383(4)
C(15)-H(15)	0.9300
C(13)-C(14)	1.476(3)

C(14)-C(19)	1.390(3)
C(19)-C(18)	1.374(4)
C(19)-H(19)	0.9300
C(17)-C(16)	1.367(4)
C(17)-C(18)	1.372(5)
C(17)-H(17)	0.9300
C(16)-H(16)	0.9300
C(18)-H(18)	0.9300

C(4)-C(5)-C(6)	120.3(2)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(3)-C(4)-C(5)	121.6(3)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(2)-C(1)-C(6)	120.8(3)
C(2)-C(1)-H(1)	119.6
C(6)-C(1)-H(1)	119.6
C(4)-C(3)-C(2)	118.8(2)
C(4)-C(3)-H(3)	120.6
C(2)-C(3)-H(3)	120.6
C(3)-C(2)-C(1)	120.8(3)
C(3)-C(2)-H(2)	119.6
C(1)-C(2)-H(2)	119.6
C(1)-C(6)-C(5)	117.7(2)
C(1)-C(6)-C(7)	118.4(2)
C(5)-C(6)-C(7)	123.8(2)
O(1)-N(1)-C(7)	128.20(16)
O(1)-N(1)-C(10)	117.64(18)
C(7)-N(1)-C(10)	114.16(17)
N(1)-C(7)-C(6)	125.40(18)
N(1)-C(7)-C(8)	110.31(19)
C(6)-C(7)-C(8)	124.29(19)
C(8)-C(9)-C(10)	106.69(19)
C(8)-C(9)-H(9A)	110.4
C(10)-C(9)-H(9A)	110.4
C(8)-C(9)-H(9B)	110.4
C(10)-C(9)-H(9B)	110.4

H(9A)-C(9)-H(9B)	108.6
C(12)-C(10)-N(1)	108.09(17)
C(12)-C(10)-C(11)	109.31(19)
N(1)-C(10)-C(11)	108.42(17)
C(12)-C(10)-C(9)	114.3(2)
N(1)-C(10)-C(9)	102.46(18)
C(11)-C(10)-C(9)	113.8(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(7)-C(8)-C(9)	106.31(19)
C(7)-C(8)-H(8A)	110.5
C(9)-C(8)-H(8A)	110.5
C(7)-C(8)-H(8B)	110.5
C(9)-C(8)-H(8B)	110.5
H(8A)-C(8)-H(8B)	108.7
O(2)-C(12)-C(10)	108.46(18)
O(2)-C(12)-H(12A)	110.0
C(10)-C(12)-H(12A)	110.0
O(2)-C(12)-H(12B)	110.0
C(10)-C(12)-H(12B)	110.0
H(12A)-C(12)-H(12B)	108.4
C(13)-O(2)-C(12)	115.97(18)
C(16)-C(15)-C(14)	120.3(3)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
O(3)-C(13)-O(2)	122.2(2)
O(3)-C(13)-C(14)	125.1(2)
O(2)-C(13)-C(14)	112.7(2)
C(15)-C(14)-C(19)	119.2(3)
C(15)-C(14)-C(13)	122.1(2)
C(19)-C(14)-C(13)	118.7(2)
C(18)-C(19)-C(14)	119.5(3)
C(18)-C(19)-H(19)	120.2
C(14)-C(19)-H(19)	120.2

C(16)-C(17)-C(18)	119.7(3)
C(16)-C(17)-H(17)	120.2
C(18)-C(17)-H(17)	120.2
C(17)-C(16)-C(15)	120.3(3)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(17)-C(18)-C(19)	121.1(3)
C(17)-C(18)-H(18)	119.5
C(19)-C(18)-H(18)	119.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(5)	67(2)	54(1)	56(1)	0(1)	3(1)	7(1)
C(4)	93(2)	54(1)	62(1)	7(1)	1(1)	12(1)
C(1)	64(2)	82(2)	81(2)	27(2)	-6(1)	-2(1)
C(3)	108(2)	64(2)	68(2)	18(1)	-2(2)	-12(2)
C(2)	78(2)	101(2)	96(2)	38(2)	-5(2)	-24(2)
C(6)	56(1)	54(1)	43(1)	1(1)	-2(1)	0(1)
N(1)	49(1)	47(1)	50(1)	0(1)	0(1)	7(1)
C(7)	50(1)	54(1)	46(1)	3(1)	-1(1)	6(1)
O(1)	49(1)	62(1)	88(1)	9(1)	3(1)	13(1)
C(9)	70(2)	58(1)	66(2)	10(1)	1(1)	16(1)
C(10)	61(1)	46(1)	55(1)	4(1)	-1(1)	3(1)
C(11)	87(2)	54(1)	83(2)	-3(1)	-8(2)	-3(1)
C(8)	56(1)	78(2)	103(2)	31(2)	1(1)	15(1)
C(12)	64(2)	62(1)	59(1)	6(1)	2(1)	-9(1)
O(2)	67(1)	61(1)	49(1)	4(1)	4(1)	-7(1)
O(3)	107(2)	112(2)	70(1)	-7(1)	32(1)	-34(1)
C(15)	90(2)	51(1)	61(2)	6(1)	-4(1)	1(1)
C(13)	80(2)	59(1)	52(1)	9(1)	8(1)	4(1)
C(14)	88(2)	50(1)	48(1)	10(1)	1(1)	4(1)
C(19)	117(2)	74(2)	56(2)	2(1)	5(2)	2(2)
C(17)	152(3)	70(2)	74(2)	3(2)	-25(2)	-21(2)
C(16)	103(2)	66(2)	81(2)	10(2)	-15(2)	-13(2)
C(18)	169(4)	80(2)	56(2)	-7(2)	-3(2)	-6(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(5)	6477	2961	1915	71
H(4)	5700	751	2280	83
H(1)	515	3956	1877	91
H(3)	2388	105	2441	96
H(2)	-204	1707	2233	110
H(9A)	3172	8440	1490	78
H(9B)	2843	7769	980	78
H(11A)	6594	8194	1880	112
H(11B)	6889	9207	1432	112
H(11C)	8403	7888	1529	112
H(8A)	1579	6527	1791	95
H(8B)	1356	5815	1283	95
H(12A)	6480	8018	620	74
H(12B)	7861	6673	779	74
H(15)	1896	4987	257	81
H(19)	6201	4325	-733	99
H(17)	817	2247	-829	118
H(16)	-280	3429	-153	100
H(18)	4034	2712	-1119	122

Table S6. Torsion angles [°] for A.

C(6)-C(5)-C(4)-C(3)	0.2(4)
C(5)-C(4)-C(3)-C(2)	0.0(4)
C(4)-C(3)-C(2)-C(1)	-0.5(4)
C(6)-C(1)-C(2)-C(3)	0.9(5)
C(2)-C(1)-C(6)-C(5)	-0.7(4)
C(2)-C(1)-C(6)-C(7)	-179.9(2)
C(4)-C(5)-C(6)-C(1)	0.1(3)
C(4)-C(5)-C(6)-C(7)	179.3(2)
O(1)-N(1)-C(7)-C(6)	0.3(3)
C(10)-N(1)-C(7)-C(6)	-179.69(18)
O(1)-N(1)-C(7)-C(8)	-179.1(2)
C(10)-N(1)-C(7)-C(8)	0.8(3)
C(1)-C(6)-C(7)-N(1)	-177.3(2)
C(5)-C(6)-C(7)-N(1)	3.5(3)
C(1)-C(6)-C(7)-C(8)	2.1(3)
C(5)-C(6)-C(7)-C(8)	-177.1(2)
O(1)-N(1)-C(10)-C(12)	59.9(2)
C(7)-N(1)-C(10)-C(12)	-120.1(2)
O(1)-N(1)-C(10)-C(11)	-58.5(2)
C(7)-N(1)-C(10)-C(11)	121.6(2)
O(1)-N(1)-C(10)-C(9)	-179.02(18)
C(7)-N(1)-C(10)-C(9)	1.0(2)
C(8)-C(9)-C(10)-C(12)	114.3(2)
C(8)-C(9)-C(10)-N(1)	-2.3(3)
C(8)-C(9)-C(10)-C(11)	-119.1(2)
N(1)-C(7)-C(8)-C(9)	-2.4(3)
C(6)-C(7)-C(8)-C(9)	178.2(2)
C(10)-C(9)-C(8)-C(7)	2.9(3)
N(1)-C(10)-C(12)-O(2)	61.1(2)
C(11)-C(10)-C(12)-O(2)	178.96(17)
C(9)-C(10)-C(12)-O(2)	-52.2(2)
C(10)-C(12)-O(2)-C(13)	-179.98(18)
C(12)-O(2)-C(13)-O(3)	3.0(3)
C(12)-O(2)-C(13)-C(14)	-177.58(18)
C(16)-C(15)-C(14)-C(19)	0.0(3)
C(16)-C(15)-C(14)-C(13)	-179.6(2)

O(3)-C(13)-C(14)-C(15)	-162.9(2)
O(2)-C(13)-C(14)-C(15)	17.7(3)
O(3)-C(13)-C(14)-C(19)	17.5(4)
O(2)-C(13)-C(14)-C(19)	-161.9(2)
C(15)-C(14)-C(19)-C(18)	-1.2(4)
C(13)-C(14)-C(19)-C(18)	178.4(2)
C(18)-C(17)-C(16)-C(15)	-1.7(4)
C(14)-C(15)-C(16)-C(17)	1.4(4)
C(16)-C(17)-C(18)-C(19)	0.5(5)
C(14)-C(19)-C(18)-C(17)	1.0(4)

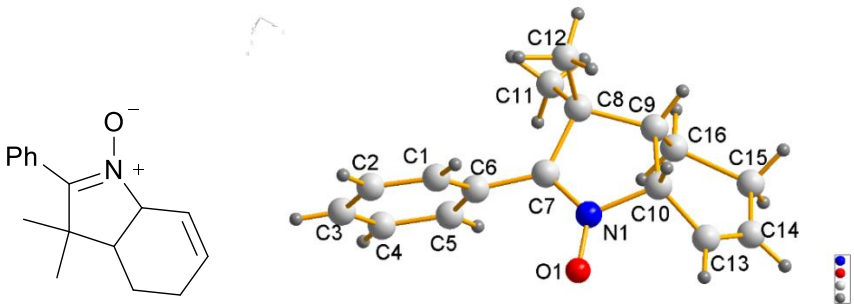
Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for A [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9B)...O(3)#1	0.97	2.59	3.545(3)	166.4

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,-z



X-ray structure of compound **6s** (CCDC: 2057127)

The thermal ellipsoid plot of 6s with 30% displacement ellipsoids

Table S8. Crystal data and structure refinement for A.

Identification code	a	
Empirical formula	C16 H19 N O	
Formula weight	241.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 7.059(8) Å	α= 90°.
	b = 19.92(2) Å	β= 91.125(12)°.
	c = 9.454(11) Å	γ = 90°.
Volume	1329(3) $Å^3$	
Z	4	
Density (calculated)	1.206 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	520	
Crystal size	0.25 x 0.24 x 0.22 mm^3	
Theta range for data collection	2.39 to 25.50°.	
Index ranges	-8<=h<=8, -22<=k<=24, -11<=l<=11	
Reflections collected	9430	
Independent reflections	4784 [R(int) = 0.0869]	
Completeness to theta = 25.50°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9838 and 0.9816	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4784 / 1 / 330	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.1241, wR2 = 0.3191	
R indices (all data)	R1 = 0.1885, wR2 = 0.3636	

Absolute structure parameter	-2(6)
Largest diff. peak and hole	0.379 and -0.468 e.Å^{-3}

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	9412(8)	1812(4)	1899(6)	43(2)
O(1)	11161(7)	1788(4)	2247(6)	55(2)
C(7)	8662(11)	1996(5)	701(8)	41(2)
C(6)	9789(11)	2248(6)	-441(8)	47(3)
C(10)	7994(11)	1508(5)	2892(8)	41(2)
C(1)	10656(12)	1794(7)	-1332(11)	64(3)
C(5)	10013(17)	2903(7)	-599(12)	69(3)
C(9)	6085(11)	1777(6)	2280(10)	55(3)
C(2)	11537(17)	2049(9)	-2457(11)	79(4)
C(8)	6553(11)	1852(5)	650(11)	57(3)
C(4)	10963(19)	3158(8)	-1749(14)	88(5)
C(12)	6213(15)	1194(7)	-158(12)	73(3)
C(3)	11770(20)	2702(10)	-2687(14)	98(5)
C(13)	8485(19)	1714(9)	4334(11)	93(5)
C(16)	5514(14)	2405(7)	2907(16)	91(5)
C(15)	5541(19)	2282(8)	4689(16)	100(5)
C(11)	5500(16)	2453(8)	-45(18)	99(5)
C(14)	7310(20)	2012(10)	5169(17)	128(7)
O(2)	11496(9)	4862(4)	7515(7)	63(2)
N(2)	9713(8)	4856(4)	7147(7)	39(2)
C(23)	8821(12)	4673(5)	6038(8)	45(2)
C(26)	8254(14)	5137(5)	8215(10)	51(2)
C(22)	9961(14)	4393(5)	4814(9)	46(2)
C(25)	6485(12)	4864(6)	7622(11)	59(3)
C(31)	7600(20)	4644(8)	10517(12)	87(4)
C(21)	10966(13)	4825(6)	3987(10)	59(3)
C(17)	9945(15)	3725(7)	4446(11)	64(3)
C(20)	11999(13)	4581(7)	2852(11)	67(3)
C(18)	10979(18)	3495(7)	3252(12)	73(3)
C(32)	8708(18)	4971(6)	9683(11)	68(3)
C(19)	11905(15)	3938(7)	2488(12)	65(3)
C(29)	5897(16)	4255(6)	8404(12)	65(3)
C(24)	6785(12)	4768(6)	6036(10)	56(3)

C(28)	6295(19)	5381(8)	5285(13)	89(4)
C(30)	5800(30)	4362(9)	9934(18)	126(7)
C(27)	5669(13)	4191(9)	5439(16)	113(7)

Table S10. Bond lengths [Å] and angles [°] for A.

N(1)-O(1)	1.272(8)
N(1)-C(7)	1.290(10)
N(1)-C(10)	1.512(10)
C(7)-C(6)	1.443(12)
C(7)-C(8)	1.519(11)
C(6)-C(5)	1.324(16)
C(6)-C(1)	1.388(15)
C(10)-C(13)	1.463(13)
C(10)-C(9)	1.546(12)
C(10)-H(10)	0.9800
C(1)-C(2)	1.341(16)
C(1)-H(1)	0.9300
C(5)-C(4)	1.384(15)
C(5)-H(5)	0.9300
C(9)-C(16)	1.446(17)
C(9)-C(8)	1.589(14)
C(9)-H(9)	0.9800
C(2)-C(3)	1.33(2)
C(2)-H(2)	0.9300
C(8)-C(11)	1.539(15)
C(8)-C(12)	1.541(16)
C(4)-C(3)	1.40(2)
C(4)-H(4)	0.9300
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(3)-H(3)	0.9300
C(13)-C(14)	1.301(19)
C(13)-H(13)	0.9300
C(16)-C(15)	1.70(2)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(15)-C(14)	1.42(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(11)-H(11A)	0.9600

C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(14)-H(14)	0.9300
O(2)-N(2)	1.299(9)
N(2)-C(23)	1.270(10)
N(2)-C(26)	1.560(12)
C(23)-C(24)	1.448(12)
C(23)-C(22)	1.529(12)
C(26)-C(32)	1.452(14)
C(26)-C(25)	1.469(14)
C(26)-H(26)	0.9800
C(22)-C(21)	1.369(14)
C(22)-C(17)	1.379(16)
C(25)-C(29)	1.482(16)
C(25)-C(24)	1.532(13)
C(25)-H(25)	0.9800
C(31)-C(32)	1.297(17)
C(31)-C(30)	1.49(2)
C(31)-H(31)	0.9300
C(21)-C(20)	1.397(14)
C(21)-H(21)	0.9300
C(17)-C(18)	1.432(15)
C(17)-H(17)	0.9300
C(20)-C(19)	1.331(17)
C(20)-H(20)	0.9300
C(18)-C(19)	1.320(17)
C(18)-H(18)	0.9300
C(32)-H(32)	0.9300
C(19)-H(19)	0.9300
C(29)-C(30)	1.467(19)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(24)-C(28)	1.442(18)
C(24)-C(27)	1.506(17)
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(30)-H(30A)	0.9700

C(30)-H(30B)	0.9700
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600

O(1)-N(1)-C(7)	127.9(7)
O(1)-N(1)-C(10)	118.6(6)
C(7)-N(1)-C(10)	112.9(6)
N(1)-C(7)-C(6)	122.0(7)
N(1)-C(7)-C(8)	111.0(7)
C(6)-C(7)-C(8)	126.8(7)
C(5)-C(6)-C(1)	121.4(10)
C(5)-C(6)-C(7)	119.6(10)
C(1)-C(6)-C(7)	119.0(10)
C(13)-C(10)-N(1)	108.4(8)
C(13)-C(10)-C(9)	116.1(9)
N(1)-C(10)-C(9)	102.5(6)
C(13)-C(10)-H(10)	109.9
N(1)-C(10)-H(10)	109.9
C(9)-C(10)-H(10)	109.9
C(2)-C(1)-C(6)	116.8(13)
C(2)-C(1)-H(1)	121.6
C(6)-C(1)-H(1)	121.6
C(6)-C(5)-C(4)	120.6(13)
C(6)-C(5)-H(5)	119.7
C(4)-C(5)-H(5)	119.7
C(16)-C(9)-C(10)	112.7(9)
C(16)-C(9)-C(8)	112.7(10)
C(10)-C(9)-C(8)	101.3(6)
C(16)-C(9)-H(9)	109.9
C(10)-C(9)-H(9)	109.9
C(8)-C(9)-H(9)	109.9
C(3)-C(2)-C(1)	124.0(14)
C(3)-C(2)-H(2)	118.0
C(1)-C(2)-H(2)	118.0
C(7)-C(8)-C(11)	109.1(8)
C(7)-C(8)-C(12)	109.2(9)
C(11)-C(8)-C(12)	112.3(9)

C(7)-C(8)-C(9)	102.1(7)
C(11)-C(8)-C(9)	111.9(11)
C(12)-C(8)-C(9)	111.8(9)
C(5)-C(4)-C(3)	118.0(14)
C(5)-C(4)-H(4)	121.0
C(3)-C(4)-H(4)	121.0
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(2)-C(3)-C(4)	118.7(13)
C(2)-C(3)-H(3)	120.7
C(4)-C(3)-H(3)	120.7
C(14)-C(13)-C(10)	123.7(14)
C(14)-C(13)-H(13)	118.1
C(10)-C(13)-H(13)	118.1
C(9)-C(16)-C(15)	106.9(10)
C(9)-C(16)-H(16A)	110.3
C(15)-C(16)-H(16A)	110.3
C(9)-C(16)-H(16B)	110.3
C(15)-C(16)-H(16B)	110.3
H(16A)-C(16)-H(16B)	108.6
C(14)-C(15)-C(16)	111.1(9)
C(14)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15A)	109.4
C(14)-C(15)-H(15B)	109.4
C(16)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(13)-C(14)-C(15)	122.8(15)
C(13)-C(14)-H(14)	118.6

C(15)-C(14)-H(14)	118.6
C(23)-N(2)-O(2)	133.6(7)
C(23)-N(2)-C(26)	108.6(7)
O(2)-N(2)-C(26)	117.9(7)
N(2)-C(23)-C(24)	116.1(8)
N(2)-C(23)-C(22)	118.3(7)
C(24)-C(23)-C(22)	125.5(7)
C(32)-C(26)-C(25)	116.8(10)
C(32)-C(26)-N(2)	113.8(8)
C(25)-C(26)-N(2)	100.6(7)
C(32)-C(26)-H(26)	108.4
C(25)-C(26)-H(26)	108.4
N(2)-C(26)-H(26)	108.4
C(21)-C(22)-C(17)	117.7(9)
C(21)-C(22)-C(23)	119.2(9)
C(17)-C(22)-C(23)	122.9(9)
C(26)-C(25)-C(29)	111.4(9)
C(26)-C(25)-C(24)	106.9(8)
C(29)-C(25)-C(24)	115.2(10)
C(26)-C(25)-H(25)	107.7
C(29)-C(25)-H(25)	107.7
C(24)-C(25)-H(25)	107.7
C(32)-C(31)-C(30)	119.3(11)
C(32)-C(31)-H(31)	120.3
C(30)-C(31)-H(31)	120.3
C(22)-C(21)-C(20)	120.2(11)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(22)-C(17)-C(18)	120.6(11)
C(22)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(19)-C(20)-C(21)	120.8(10)
C(19)-C(20)-H(20)	119.6
C(21)-C(20)-H(20)	119.6
C(19)-C(18)-C(17)	118.8(13)
C(19)-C(18)-H(18)	120.6
C(17)-C(18)-H(18)	120.6
C(31)-C(32)-C(26)	124.5(12)

C(31)-C(32)-H(32)	117.8
C(26)-C(32)-H(32)	117.8
C(18)-C(19)-C(20)	121.7(10)
C(18)-C(19)-H(19)	119.2
C(20)-C(19)-H(19)	119.2
C(30)-C(29)-C(25)	112.7(11)
C(30)-C(29)-H(29A)	109.0
C(25)-C(29)-H(29A)	109.0
C(30)-C(29)-H(29B)	109.0
C(25)-C(29)-H(29B)	109.0
H(29A)-C(29)-H(29B)	107.8
C(28)-C(24)-C(23)	109.4(10)
C(28)-C(24)-C(27)	110.1(10)
C(23)-C(24)-C(27)	114.7(9)
C(28)-C(24)-C(25)	109.6(10)
C(23)-C(24)-C(25)	99.8(7)
C(27)-C(24)-C(25)	112.8(10)
C(24)-C(28)-H(28A)	109.5
C(24)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(24)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(29)-C(30)-C(31)	111.4(12)
C(29)-C(30)-H(30A)	109.3
C(31)-C(30)-H(30A)	109.3
C(29)-C(30)-H(30B)	109.3
C(31)-C(30)-H(30B)	109.3
H(30A)-C(30)-H(30B)	108.0
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	20(3)	90(6)	19(3)	-3(4)	-1(2)	5(4)
O(1)	16(3)	94(6)	54(3)	12(4)	-4(2)	-2(3)
C(7)	26(4)	54(6)	42(4)	6(4)	3(3)	-3(4)
C(6)	22(4)	80(8)	40(4)	15(5)	-2(3)	-9(4)
C(10)	29(4)	67(6)	27(4)	11(4)	14(3)	-3(4)
C(1)	37(5)	88(9)	69(6)	0(6)	1(4)	6(6)
C(5)	65(7)	80(10)	61(7)	9(6)	25(5)	-2(6)
C(9)	26(4)	56(7)	83(7)	6(5)	27(4)	3(4)
C(2)	68(7)	129(13)	42(5)	-6(7)	0(5)	-17(8)
C(8)	23(4)	61(7)	86(7)	31(6)	-14(4)	-9(4)
C(4)	95(10)	76(10)	96(9)	37(7)	62(8)	-2(7)
C(12)	47(6)	103(10)	67(7)	-2(6)	-9(5)	-12(6)
C(3)	77(9)	158(17)	57(7)	35(9)	1(6)	2(10)
C(13)	89(9)	152(14)	38(5)	-3(7)	12(5)	-44(9)
C(16)	28(5)	88(11)	158(13)	17(9)	38(6)	1(5)
C(15)	75(9)	99(12)	131(12)	-64(9)	76(8)	-33(8)
C(11)	45(6)	97(11)	152(13)	45(9)	-18(7)	3(7)
C(14)	125(14)	156(16)	110(11)	-73(11)	104(11)	-58(12)
O(2)	38(3)	67(5)	85(5)	-5(4)	4(3)	-1(4)
N(2)	23(3)	37(4)	58(4)	-7(3)	10(3)	-4(3)
C(23)	35(4)	76(7)	25(4)	0(4)	0(3)	2(4)
C(26)	55(6)	46(6)	52(5)	-8(4)	6(4)	7(4)
C(22)	49(5)	49(7)	39(5)	1(4)	4(4)	7(4)
C(25)	34(5)	54(6)	90(7)	-11(6)	22(5)	6(5)
C(31)	140(13)	79(10)	43(6)	0(6)	14(7)	23(9)
C(21)	52(5)	68(7)	58(5)	-4(5)	24(4)	-6(5)
C(17)	57(6)	65(9)	70(7)	-1(5)	34(5)	5(5)
C(20)	29(5)	108(11)	65(6)	19(6)	25(4)	2(5)
C(18)	69(8)	81(10)	70(7)	-11(7)	7(6)	-3(7)
C(32)	91(8)	53(7)	60(6)	-3(5)	21(6)	0(6)
C(19)	55(6)	78(9)	64(7)	3(6)	31(5)	15(6)
C(29)	62(6)	58(7)	76(7)	7(5)	21(5)	-12(5)
C(24)	30(4)	82(8)	58(5)	-10(5)	10(4)	8(5)

C(28)	76(8)	130(12)	62(7)	-7(7)	18(6)	41(8)
C(30)	200(20)	78(11)	108(12)	16(9)	107(13)	31(12)
C(27)	19(5)	177(16)	145(12)	-96(12)	-20(6)	22(7)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(10)	8037	1018	2828	49
H(1)	10628	1334	-1157	77
H(5)	9527	3194	69	82
H(9)	5095	1441	2407	66
H(2)	12014	1752	-3116	95
H(4)	11063	3619	-1894	106
H(12A)	6887	1205	-1030	109
H(12B)	4882	1146	-357	109
H(12C)	6657	821	410	109
H(3)	12457	2853	-3455	117
H(13)	9708	1626	4673	111
H(16A)	4252	2533	2575	109
H(16B)	6385	2758	2655	109
H(15A)	5309	2706	5155	120
H(15B)	4535	1977	4939	120
H(11A)	6195	2857	134	148
H(11B)	4259	2493	346	148
H(11C)	5387	2384	-1046	148
H(14)	7638	2050	6122	154
H(26)	8208	5627	8115	61
H(25)	5492	5205	7728	71
H(31)	7925	4585	11469	105
H(21)	10962	5282	4181	71
H(17)	9257	3420	4977	76
H(20)	12761	4871	2344	80
H(18)	10999	3042	3019	88
H(32)	9872	5108	10049	81
H(19)	12507	3796	1675	78
H(29A)	4664	4116	8048	79
H(29B)	6791	3894	8228	79
H(28A)	7039	5743	5656	134
H(28B)	4974	5479	5402	134

H(28C)	6546	5328	4298	134
H(30A)	5541	3938	10403	152
H(30B)	4759	4668	10125	152
H(27A)	4353	4252	5645	170
H(27B)	6122	3778	5859	170
H(27C)	5822	4176	4433	170

Table S13. Torsion angles [°] for A.

O(1)-N(1)-C(7)-C(6)	-3.5(16)
C(10)-N(1)-C(7)-C(6)	-174.8(9)
O(1)-N(1)-C(7)-C(8)	171.4(9)
C(10)-N(1)-C(7)-C(8)	0.1(12)
N(1)-C(7)-C(6)-C(5)	-94.6(12)
C(8)-C(7)-C(6)-C(5)	91.2(13)
N(1)-C(7)-C(6)-C(1)	83.7(11)
C(8)-C(7)-C(6)-C(1)	-90.4(12)
O(1)-N(1)-C(10)-C(13)	44.4(13)
C(7)-N(1)-C(10)-C(13)	-143.4(10)
O(1)-N(1)-C(10)-C(9)	167.6(8)
C(7)-N(1)-C(10)-C(9)	-20.2(11)
C(5)-C(6)-C(1)-C(2)	-7.8(13)
C(7)-C(6)-C(1)-C(2)	173.8(8)
C(1)-C(6)-C(5)-C(4)	6.7(17)
C(7)-C(6)-C(5)-C(4)	-175.0(11)
C(13)-C(10)-C(9)-C(16)	26.8(13)
N(1)-C(10)-C(9)-C(16)	-91.1(9)
C(13)-C(10)-C(9)-C(8)	147.5(10)
N(1)-C(10)-C(9)-C(8)	29.6(10)
C(6)-C(1)-C(2)-C(3)	6.4(16)
N(1)-C(7)-C(8)-C(11)	137.9(11)
C(6)-C(7)-C(8)-C(11)	-47.5(15)
N(1)-C(7)-C(8)-C(12)	-99.1(10)
C(6)-C(7)-C(8)-C(12)	75.5(12)
N(1)-C(7)-C(8)-C(9)	19.4(11)
C(6)-C(7)-C(8)-C(9)	-166.0(10)
C(16)-C(9)-C(8)-C(7)	91.0(9)
C(10)-C(9)-C(8)-C(7)	-29.7(10)
C(16)-C(9)-C(8)-C(11)	-25.5(12)
C(10)-C(9)-C(8)-C(11)	-146.1(9)
C(16)-C(9)-C(8)-C(12)	-152.4(8)
C(10)-C(9)-C(8)-C(12)	86.9(9)
C(6)-C(5)-C(4)-C(3)	-4(2)
C(1)-C(2)-C(3)-C(4)	-4(2)
C(5)-C(4)-C(3)-C(2)	2(2)

N(1)-C(10)-C(13)-C(14)	125.4(15)
C(9)-C(10)-C(13)-C(14)	11(2)
C(10)-C(9)-C(16)-C(15)	-53.8(10)
C(8)-C(9)-C(16)-C(15)	-167.7(8)
C(9)-C(16)-C(15)-C(14)	52.5(14)
C(10)-C(13)-C(14)-C(15)	-12(3)
C(16)-C(15)-C(14)-C(13)	-19(2)
O(2)-N(2)-C(23)-C(24)	-178.3(10)
C(26)-N(2)-C(23)-C(24)	0.3(12)
O(2)-N(2)-C(23)-C(22)	0.0(16)
C(26)-N(2)-C(23)-C(22)	178.6(8)
C(23)-N(2)-C(26)-C(32)	142.9(9)
O(2)-N(2)-C(26)-C(32)	-38.3(12)
C(23)-N(2)-C(26)-C(25)	17.1(10)
O(2)-N(2)-C(26)-C(25)	-164.1(8)
N(2)-C(23)-C(22)-C(21)	-74.8(12)
C(24)-C(23)-C(22)-C(21)	103.3(12)
N(2)-C(23)-C(22)-C(17)	108.9(12)
C(24)-C(23)-C(22)-C(17)	-72.9(14)
C(32)-C(26)-C(25)-C(29)	-23.8(13)
N(2)-C(26)-C(25)-C(29)	99.9(9)
C(32)-C(26)-C(25)-C(24)	-150.5(10)
N(2)-C(26)-C(25)-C(24)	-26.8(11)
C(17)-C(22)-C(21)-C(20)	-2.8(14)
C(23)-C(22)-C(21)-C(20)	-179.2(8)
C(21)-C(22)-C(17)-C(18)	1.1(15)
C(23)-C(22)-C(17)-C(18)	177.4(9)
C(22)-C(21)-C(20)-C(19)	5.3(16)
C(22)-C(17)-C(18)-C(19)	-1.8(17)
C(30)-C(31)-C(32)-C(26)	5(2)
C(25)-C(26)-C(32)-C(31)	-5.2(17)
N(2)-C(26)-C(32)-C(31)	-121.9(12)
C(17)-C(18)-C(19)-C(20)	4.4(18)
C(21)-C(20)-C(19)-C(18)	-6.1(18)
C(26)-C(25)-C(29)-C(30)	52.9(15)
C(24)-C(25)-C(29)-C(30)	174.9(11)
N(2)-C(23)-C(24)-C(28)	98.2(11)
C(22)-C(23)-C(24)-C(28)	-80.0(13)

N(2)-C(23)-C(24)-C(27)	-137.6(12)
C(22)-C(23)-C(24)-C(27)	44.3(15)
N(2)-C(23)-C(24)-C(25)	-16.8(13)
C(22)-C(23)-C(24)-C(25)	165.0(10)
C(26)-C(25)-C(24)-C(28)	-87.8(11)
C(29)-C(25)-C(24)-C(28)	147.8(10)
C(26)-C(25)-C(24)-C(23)	27.1(12)
C(29)-C(25)-C(24)-C(23)	-97.4(11)
C(26)-C(25)-C(24)-C(27)	149.2(9)
C(29)-C(25)-C(24)-C(27)	24.8(13)
C(25)-C(29)-C(30)-C(31)	-52.9(17)
C(32)-C(31)-C(30)-C(29)	24(2)

Symmetry transformations used to generate equivalent atoms:

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