# Supporting Information

# Synthesis of Isoxazoline-*N*-oxides via [Hydroxy(tosyloxy)iodo]benzene (HTIB) Mediated Oxidative *N*-*O* Coupling

*Mustafa J. Raihan, Veerababurao Kavala, Pateliya Mujjamil Habib, Qiao-Zhi Guan, Chun-Wei Kuo and Ching-Fa Yao**

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei, Taiwan 116 R.O.C.

cheyaocf@ntnu.edu.tw

# Table of Contents

# 1. General Information

Reagents and solvents were purchased from various commercial sources and were used directly without any further purification unless otherwise stated. Column chromatography was performed with 63-200 mesh silicagel. $^{1}H$ and $^{13}C$ NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million ($\delta$) using TMS as an internal standard and coupling constants are expressed in hertz. IR spectra were recorded on an FT-IR spectrometer and are reported in $cm^{-1}$. Melting points were recorded using an electro thermal capillary melting point apparatus and are uncorrected. Sonication was conducted at 42 kHz with a power of 100W. The β-hydroxyketones were synthesized by following literature reports.[r1, r2, r3] **26a** and **28a** are known compounds.[3b,d,e]

# 2. Experimental Procedures

## 2.1. Representative procedure for preparation of oximes

Pyridine (4.5 mmol) was added to a stirred solution of β-hydroxyketone (3 mmol) and hydroxylamine hydrochloride (6 mmol) in 5 ml methanol at room temperature and the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated in a vacuum. 5 ml of a 10% HCl solution was added and the white salt was dissolved in water. The organic compound was extracted with ethyl acetate (25 ml × 3). The combined organic layer was washed with water and brine; dried over $MgSO_4$, filtered and concentrated in a vacuum. The resulting residue was further purified by flash column chromatography.

## 2.2. Preparation of (6-(hydroxyimino)cyclohex-1-enyl)(2-nitrophenyl)methyl acetate (30)

To a stirred solution of 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone (5 mmol) and acetic anhydride (20 mmol) in DCM (5 ml) was added 4,4-dimethylaminopyridine (10 mol%) and the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was added to ice cold water (50 ml) and the organic component was extracted with ethyl acetate (50 ml × 3). The combined organic layer was washed with brine, dried over magnesium sulfate and concentrated in a vacuum. The

resulting residue was further purified by flash column chromatography to give pure (2-nitrophenyl)(6-oxocyclohex-1-enyl)methyl acetate. It was then treated with hydroxylamine hydrochloride in the presence of pyridine (See representative procedure for the preparation of oxime (section **2.1**)).

**2.3. General procedure for the oxidative N-O coupling**.

Method A

To a 50 ml beaker containing the oxime derivative (0.5 mmol) in 5 ml of methanol was added [hydroxy(tosyloxy)iodo]benzene (0.55 mmol) in small portions with continuous stirring over a period of 25 min and the stirring was continued for an additional 5 min. An equal amount of water was then added. If the solid product precipitated out at the bottom of the beaker, the precipitate was filtered and washed with 60% methanol in water to give the pure product. In cases where the product did not precipitate, an additional 10 ml of water was added to the reaction mixture and the organic compound was isolated by extraction with ethyl acetate (15 ml × 3). The combined organic layer was dried over magnesium sulfate and concentrated in a vacuum. The resulting residue was further purified by flash column chromatography.

Method B

To a 50 ml beaker containing the oxime derivative (0.5 mmol) in 5 ml of water was added [hydroxy(tosyloxy)iodo]benzene (0.55 mmol) in small portions with continuous stirring over a period of 45 min. After completion of the addition, the stirring was continued for an additional 5 min. The crude precipitated product was then isolated by filtration and washed with water. In the case of an oily product, the reaction mixture was extracted with ethyl acetate (2 × 10 mL). The organic layer was separated, dried over magnesium sulfate and concentrated in a vacuum. The resulting residue was further purified by flash column chromatography.

**2.4. Preparation of (2Z)-3-(methylimino)-2-(2-nitrobenzylidene)butanal (33)**

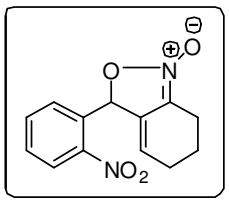
To a stirred solution of 3-methyl-4-(2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (2 mmol) in 1.6 ml of DMSO was added triethylamine (4.4 mmol) and the reaction was monitored by TLC. After 0.5 h, the reaction mixture was transferred into 50 ml of water in a beaker and extracted with ethyl acetate (50ml × 3). The combined organic layer was washed with a brine solution (50 ml × 2), dried over magnesium sulfate and concentrated in a vacuum. The resulting residue was further purified by flash column chromatography. (15% EA in hexane).

**2.5. Preparation of 3-(hydroxyimino)-2-(2-nitrobenzylidene)butylidene)-5,5-dimethylcyclohexane-1,3-dione (34)**

To a 20 ml vial containing (2Z)-3-(methylimino)-2-(2-nitrobenzylidene)butanal (0.5 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (0.6 mmol) was added 5ml of water, followed by stirring for 5 min. It was then sonicated for 18 h. The solid was isolated on a filter and the resulting residue was further purified by flash column chromatography.

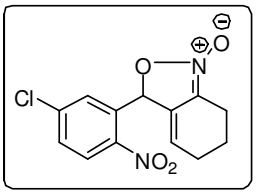
# 3. Spectral Data

**3-(2-nitrophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (1a).**



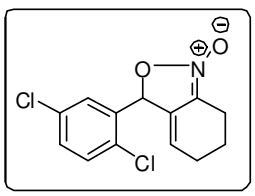
A pale yellow solid; mp 156-158 $^{o}$C; IR [KBr, cm$^{-1}$]: 3079, 2928, 2835, 1652, 1628, 1524, 1435, 1353, 1269, 1246, 1188, 1165; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.08 (d, $J$ = 8.0 Hz, 1H), 7.75-7.69 (m, 2H), 7.57-7.51 (m, 1H), 6.80-6.79 (m, 1H), 5.87 (dd, $J$ = 6.8, 4.4 Hz, 1H), 2.71-2.56 (m, 2H), 2.31-2.23 (m, 1H), 2.18-2.11 (m, 1H), 1.89-1.73 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 147.3, 136.2, 134.8, 134.5, 129.4, 128.2, 125.2, 123.2, 115.2, 75.3, 25.1, 21.2, 20.4; MS m/z (relative intensity): 261 ($M^+$+1, 12), 260 ($M^+$, 100), 231 (16), 214 (48), 197 (61), 182 (14), 168 (20), 158 (22); HRMS calcd for $C_{13}H_{12}N_2O_4$ ($M^+$): 260.0792, found 260.0807; Anal. Calcd for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.96; H, 4.63; N, 10.72.

**3-(2-nitro-5-chlorophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (2a).**



A yellow solid; mp 172-174$^{o}$C; IR [KBr, cm$^{-1}$]: 3099, 2947, 2864, 1656, 1628, 1527, 1343, 1270, 1256, 1183, 1110; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.09 (d, $J$ = 8.8 Hz, 1H), 7.72 (d, $J$ = 2.2 Hz, 1H), 7.48 (dd, $J$ = 8.8, 2.3 Hz, 1H), 6.83 (dd, $J$ = 5.6, 2.8 Hz, 1H), 5.88-5.85 (m, 1H), 2.71-2.58 (m, 2H), 2.31-2.18 (m, 1H), 2.18-2.11 (m, 1H), 1.87-1.76 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 145.4, 141.6, 136.9, 135.8, 129.7, 128.3, 126.9, 123.7, 114.9, 74.8, 25.2, 21.3, 20.4; MS m/z (relative intensity): 296 ($M^+$+2, 23), 294 ($M^+$, 83), 248 (100), 231 (73), 192 (26), 167 (18), 126 (8), 95 (4); HRMS calcd for $C_{13}H_{11}ClN_2O_4$ ($M^+$): 294.0402, found 294.0416 and calcd for $C_{13}H_{11}{}^{37}ClN_2O_4$ ($M^+$): 296.0372, found 296.0389.

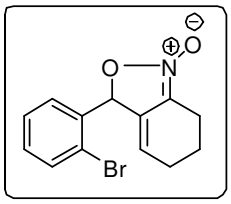
**3-(2,4-dichlorophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (3a).**



A brown solid; mp 63-65 $^{o}$C; IR [KBr, cm$^{-1}$] 3070, 2945, 2834, 1657, 1624, 1587, 1561, 1472, 1451, 1381, 1355, 1263; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44 (d, $J$ = 1.8 Hz, 1H), 7.40 (d, $J$ = 8.4 Hz, 1H), 7.30 (dd, $J$ = 8.4, 1.8 Hz, 1H), 6.44 (d, $J$ = 2.6 Hz, 1H), 5.80 (d, $J$ = 2.4, 1H), 2.65-2.61 (m, 2H), 2.29-2.19 (m, 2H), 1.86-1.79 (m, 2H); $^{13}$C

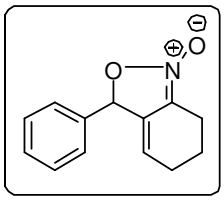
NMR (100 MHz, $CDCl_3$): $\delta$ 136.4, 135.3, 135.0, 133.2, 129.9, 129.0, 128.0, 121.9, 115.6, 76.5, 24.9, 21.2, 20.5; MS m/z (relative intensity): 283 ($M^+$, 100), 248 (17), 218 (5), 173 (13), 159 (2); HRMS calcd for $C_{13}H_{11}{}^{35}Cl_2NO_2$ ($M^+$): 283.0161, found 283.0164 and calcd for $C_{13}H_{11}Cl_1{}^{37}ClNO_2$ ($M^+$): 285.0132, found 285.0136.

**3-(2-bromophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (4a).**



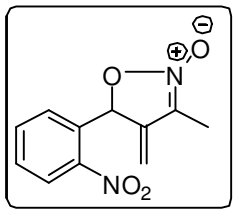
A colorless solid; mp 93-95 $^oC$; IR [KBr, $cm^{-1}$]: 3063, 2930, 2834, 1657, 1628, 1469, 1439, 1355, 1266; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.59 (d, $J$ = 8.0 Hz, 1H), 7.44 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.36 (t, $J$ = 7.7 Hz, 1H), 7.24-7.20 (m, 1H), 6.49 (dd, $J$ = 5.8, 2.9 Hz, 1H), 5.84 (dd, $J$ = 7.2, 4.4 Hz, 1H), 2.70-2.57 (m, 2H), 2.30-2.12 (m, 2H), 1.87-1.77 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 138.0, 136.7, 133.4, 130.4, 128.3, 128.2, 122.1, 121.8, 115.8, 79.1, 25.0, 21.2, 20.6; MS m/z (relative intensity): 296 ($M^+$+3, 13), 293 ($M^+$, 100), 215 (4), 214 (20), 183 (26), 156 (17); HRMS calcd for $C_{13}H_{12}{}^{79}BrNO_2$ ($M^+$): 293.0046, found 293.0028; calcd for $C_{13}H_{12}{}^{81}BrNO_2$ ($M^+$): 295.0025, found 295.0004.

**3-phenyl-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (5a).**



A yellow gummy solid; IR [KBr, $cm^{-1}$]: 3063, 3033, 2945, 1653, 1631, 1451, 1355, 1266; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.43-7.35 (m, 5H), 6.02 (m, 1H), 5.60 (dd, $J$ = 6.9, 4.3 Hz, 1H), 2.64 (t, $J$ = 6.6 Hz, 2H), 2.31-2.14 (m, 2H), 1.91-1.80 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 138.3, 137.5, 129.1, 129.0, 126.9, 121.2, 116.2, 80.6, 24.9, 21.1, 20.7; MS m/z (relative intensity): 216 ($M^+$+1, 45), 215 ($M^+$, 100), 198 (9), 185 (5), 169 (22), 157 (14), 141 (22), 129 (10), 105 (33); HRMS calcd for $C_{13}H_{13}NO_2$ ($M^+$): 215.0941, found 215.0948.

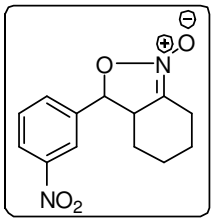
**3-methyl-4-methylene-5-(2-nitrophenyl)-4,5-dihydroisoxazole-2-oxide (7a).**



A yellow solid; mp 115-117$^oC$; IR [KBr, $cm^{-1}$]: 3077, 2863, 1646, 1606, 1528, 1351, 1263; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 (d, $J$ = 8.2 Hz, 1H), 7.72 (t, $J$ = 7.4

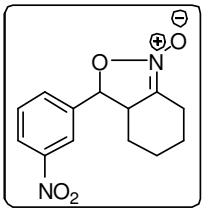
Hz, 1H), 7.65 (d, $J$ = 7.8 Hz, 1H), 7.54 (t, $J$ = 7.6 Hz, 1H), 6.83 (t, $J$ = 2.5 Hz, 1H), 5.13 (m, 2H), 2.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 147.9, 144.7, 134.4, 133.8, 129.9, 128.7, 125.2, 115.6, 106.8, 75.7, 8.9; MS m/z (relative intensity): 235 ($M^+$+1, 11), 234 ($M^+$, 100), 203 (5), 187 (17), 171 (5), 158 (38), 130 (33), 103 (45), 93 (14), 79 (36), 76 (23); HRMS calcd for $C_{11}H_{10}N_2O_4$ ($M^+$): 234.0635, found 234.0639.

**3-(3-nitrophenyl)-3,3a,4,5,6,7-hexahydrobenzo[c]isoxazole-1-oxide (anti) (8a).**



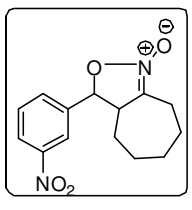
A colorless solid; mp 152-154$^o$C; IR [KBr, cm$^{-1}$]: 3080, 2930, 2855, 1655, 1532, 1345, 1270, 1236; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.24 (s, 1H), 8.18 (d, $J$ = 8.1 Hz, 1H), 7.74 (d, $J$ = 7.6 Hz, 1H), 7.59 (t, $J$ = 7.9 Hz, 1H), 5.20 (d, $J$ = 9.4 Hz, 1H), 3.19-3.13 (m, 1H), 2.81 (dd, $J$ = 15.7, 4.3 Hz, 1H), 2.22-2.14 (m, 2H), 1.99-1.90 (m, 2H), 1.56-1.41 (m, 2H), 1.40-1.27 (m 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.6, 140.2, 132.1, 130.2, 123.8, 121.1, 116.7, 82.4, 51.6, 30.9, 24.0, 23.9, 23.6; MS m/z (relative intensity): 262 ($M^+$, 52), 245 (45), 170 (1), 150 (15), 111 (28), 81 (100); HRMS calcd for $C_{13}H_{14}N_2O_4$ ($M^+$): 262.0948, found 262.0960.

**3-(3-nitrophenyl)-3,3a,4,5,6,7-hexahydrobenzo[c]isoxazole-1-oxide (syn) (9a).**



A colorless gummy solid; IR [KBr, cm$^{-1}$]: 2934, 2860, 1703, 1661, 1530, 1448, 1350, 1282, 1231; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.18 (d, $J$ = 8.2 Hz, 1H), 8.14 (s, 1H), 7.69 (d, $J$ = 7.7 Hz, 1H), 7.60 (t, $J$ = 7.9 Hz, 1H), 5.82 (d, $J$ = 10.2 Hz, 1H), 3.70-3.62 (m, 1H), 2.88-2.83 (m, 1H), 2.25-2.18 (m, 1H), 1.92-1.88 (m, 1H), 1.80-1.73 (m, 1H), 1.55-1.50 (m, 1H), 1.32-1.19 (m, 2H), 0.76-0.66 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.6, 138.9, 131.9, 130.1, 123.5, 121.1, 115.4, 77.2, 47.9, 28.4, 24.4, 24.1, 24.0.

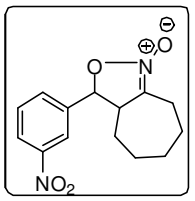
**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (anti) (10a).**



A pale yellow solid; mp 101-103$^o$C; IR [KBr, cm$^{-1}$]: 3077, 2930, 2856, 1639, 1532, 1451, 1347, 1274, 1241, 1211; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.27 (s, 1H), 8.25 (d, $J$ =

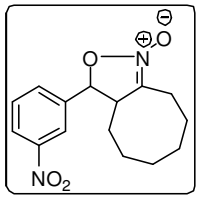
8.2 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 5.16 (d, *J* = 8.1 Hz, 1H), 3.35-3.30 (m, 1H), 2.70-2.65 (m, 1H), 2.57-2.49 (m, 1H), 2.04-1.92 (m, 4H), 1.79-1.68 (m, 1H), 1.52-1.34 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.7, 140.6, 132.2, 130.3, 123.9, 121.3, 120.3, 81.6, 55.5, 32.9, 30.2, 28.9, 27.7, 25.3; MS m/z (relative intensity): 276 ($M^+$, 37), 259 (25), 176 (2), 150 (11), 125 (13), 95 (100); HRMS calcd for $C_{14}H_{16}N_2O_4$ ($M^+$): 276.1105, found 276.1114.

**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (*syn*) (11a).**



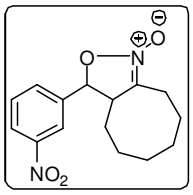
A pale yellow solid; mp 105-107°C; IR [KBr, $cm^{-1}$]: 2930, 2856, 1639, 1532, 1451, 1351, 1277, 1218, 1203; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.21 (d, *J* = 8.2 Hz, 1H), 8.18 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 5.77 (d, *J* = 9.0 Hz, 1H), 3.64-3.59 (m, 1H), 2.74-2.69 (m, 1H), 2.58-2.49 (m, 1H), 2.05-1.94 (m, 2H), 1.82-1.79 (m, 1H), 1.50-1.47 (m, 1H), 1.30-1.26 (m, 1H), 1.22-1.13 (m, 2H), 1.12-1.05 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5, 137.6, 132.5, 130.0, 123.6, 121.6, 120.8, 79.0, 50.4, 30.2, 29.6, 29.1, 27.5, 25.3; MS m/z (relative intensity): 276 ($M^+$, 39), 259 (20), 231 (4), 176 (3), 150 (9), 125 (14), 95 (100), 67 (17); HRMS calcd for $C_{14}H_{16}N_2O_4$ ($M^+$) 276.1105, found 276.1112.

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9-octahydrocycloocta[c]isoxazole-1-oxide (anti) (12a).**



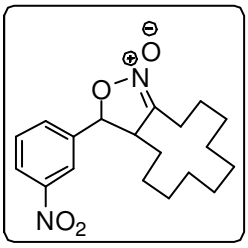
A colorless solid; mp 98-100 °C; IR [KBr, $cm^{-1}$]: 3085, 2922, 2863, 1635, 1532, 1462, 1347, 1292; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.24-8.22 (m, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 8.6 Hz, 1H), 5.29 (d, *J* = 6.8 Hz, 1H), 3.30 (dd, *J* = 11.5, 7.2 Hz, 1H), 2.76-2.69 (m, 1H), 2.34-2.27 (m, 1H), 2.09-2.05 (m, 1H), 1.92-1.84 (m, 4H), 1.71-1.66 (m, 2H), 1.63-1.57 (m, 1H), 1.55-1.42 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.8, 141.3, 131.7, 130.3, 123.8, 120.8, 119.2, 79.9, 53.9, 29.2, 26.3, 25.6, 25.5, 24.0, 23.6; MS m/z (relative intensity): 290 ($M^+$, 44), 273 (14), 244 (5), 162 (3), 150 (9), 109 (100), 67 (57); HRMS calcd for $C_{15}H_{18}N_2O_4$ ($M^+$): 290.1261, found 290.1269.

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9-octahydrocycloocta[c]isoxazole-1-oxide (syn) (13a).**



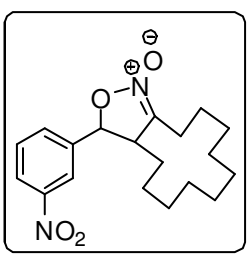
A pale yellow solid; mp 130-132°C; IR [KBr, $cm^{-1}$]: 3092, 2929, 2858, 1630, 1529, 1463, 1443, 1349; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.22 (d, $J$ = 7.3 Hz, 1H), 8.20 (s, 1H), 7.73 (d, $J$ = 7.7 Hz, 1H), 7.62-7.58 (m, 1H), 5.82 (d, $J$ = 7.9 Hz, 1H), 3.45-3.39 (m, 1H), 2.68-2.58 (m, 2H), 2.04-1.99 (m, 1H), 1.72-1.61 (m, 2H), 1.58-1.46 (m, 3H), 1.32-1.26 (m, 3H), 1.18-1.11 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5, 136.9, 132.3, 129.9, 123.5, 121.9, 121.4, 80.3, 48.9, 28.7, 27.5, 26.1, 25.9, 23.9, 22.7; MS m/z (relative intensity): 290 ($M^+$, 39), 273 (48), 150 (100), 109 (65); HRMS calcd for $C_{15}H_{18}N_2O_4$ ($M^+$): 290.1267, found 290.1262.

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9,10,11,12,13-dodecahydrocyclododeca[c]isoxazole-1-oxide (anti) (14a).**



A colorless solid; mp 113-115 °C; IR [KBr, $cm^{-1}$]: 2932, 2863, 1637, 1531, 1469, 1444, 1351; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.22-8.20 (m, 2H), 7.76 (d, $J$ = 7.7 Hz, 1H), 7.63-7.58 (m, 1H), 5.29 (d, $J$ = 5.6 Hz, 1H), 3.32 (dd, $J$ = 10.0, 4.8 Hz, 1H), 2.53-2.46 (m, 1H), 2.43-2.36 (m, 1H), 1.94-1.75 (m, 3H), 1.61-1.46 (m, 5H), 1.46-1.25 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.8, 142.2, 131.5, 130.4, 123.8, 120.6, 117.2, 79.3, 54.6, 29.7, 25.7, 25.1, 24.3, 24.2, 23.6, 23.3, 23.2, 22.3; MS m/z (relative intensity): 346 ($M^+$, 100), 329 (53), 299 (34), 230 (5), 216 (9), 202 (14), 163 (23), 150 (15), 95 (30), 83 (55); HRMS calcd for $C_{19}H_{26}N_2O_4$ ($M^+$): 346.1893, found 346.1885.

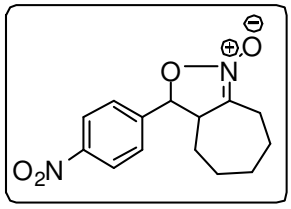
**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9,10,11,12,13-dodecahydrocyclododeca[c]isoxazole-1-oxide (syn) (15a).**



A colorless solid; mp 118-120 °C; IR [KBr, $cm^{-1}$]: 3091, 2934, 2864, 1651, 1634, 1538, 1531, 1469, 1445, 1348; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23-8.20 (m, 2H), 7.72 (d, $J$ = 7.7 Hz, 1H), 7.61 (t, $J$ = 7.8 Hz, 1H), 5.79 (d, $J$ = 8.6 Hz,

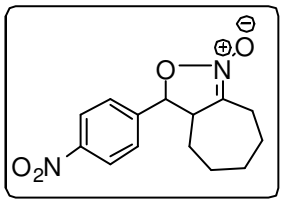
1H), 3.59 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.63-2.55 (m, 1H), 2.47-2.40 (m, 1H), 1.76-1.70 (m, 1H), 1.68-1.62 (m, 1H), 1.53-1.47 (m, 2H), 1.43-1.35 (m, 7H), 1.29-1.20 (m, 4H), 1.18-1.11 (m, 2H), 1.01-0.97 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5, 137.2, 132.4, 129.9, 123.6, 121.6, 120.4, 79.1, 48.2, 25.9, 25.8, 24.5, 24.2, 23.7, 23.6, 23.4, 22.9, 22.8; MS m/z (relative intensity): 346 ($M^+$, 100), 329 (77), 298 (11), 228 (3), 222 (8), 178 (11), 163 (20), 95 (30), 83 (61); HRMS calcd for $C_{19}H_{26}N_2O_4$ ($M^+$): 346.1893, found 346.1885.

**3-(4-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (anti) (16a).**



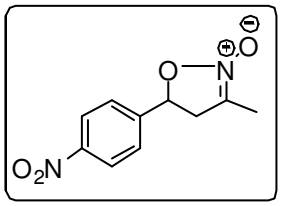
A colorless solid; mp 135-137 $^o$C; IR [KBr, $cm^{-1}$]: 3079, 2928, 2855, 1640, 1607, 1521, 1451, 1349, 1275; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.28-8.25 (m, 2H), 7.62-7.59 (m, 2H), 5.16 (d, *J* = 7.8 Hz, 1H), 3.30-3.25 (m, 1H), 2.67-2.62 (m, 1H), 2.57-2.49 (m, 1H), 1.99-1.91 (m, 4H), 1.79-1.70 (m, 1H), 1.47-1.40 (m, 1H), 1.36-1.32 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.4, 145.7, 126.9, 124.4, 120.1, 81.5, 55.6, 33.2, 30.1, 28.9, 27.7, 25.3; MS m/z (relative intensity): 276 ($M^+$, 39), 259 (6), 230 (2), 176 (2), 125 (14), 95 (100), 67 (10); HRMS calcd for $C_{14}H_{16}N_2O_4$ ($M^+$): 276.1105, found 276.1111.

**3-(4-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (syn) (17a).**



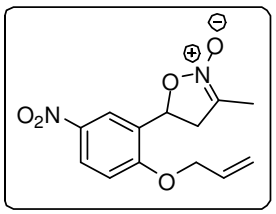
A colorless solid; mp 95-97 $^o$C; IR [KBr, $cm^{-1}$]: 3079, 2929, 2855, 1640, 1606, 1519, 1451, 1382, 1348, 1278; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.25 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 5.75 (d, *J* = 9.0 Hz, 1H), 3.65-3.59 (m, 1H), 2.73-2.68 (m, 1H), 2.57-2.48 (m, 1H), 2.03-1.94 (m, 2H), 1.81-1.78 (m, 1H), 1.53-1.44 (m, 1H), 1.29-1.21 (m, 1H), 1.16 (dd, *J* = 22.6, 11.4 Hz, 2H), 1.10-0.99 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.2, 142.7, 127.5, 124.0, 120.7, 79.0, 50.5, 30.1, 29.6, 29.2, 27.5, 25.3; MS m/z (relative intensity): 276 ($M^+$, 46), 259 (16), 184 (5), 150 (8), 125 (14), 95 (100), 67 (13); HRMS calcd for $C_{14}H_{16}N_2O_4$ ($M^+$): 276.1105, found 276.1102.

**3-methyl-5-(4-nitrophenyl)-4,5-dihydroisoxazole-2-oxide (18a).**



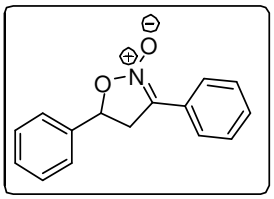
A colorless solid; mp 123-125 $^{o}$C; IR [KBr, cm$^{-1}$]: 3107, 2922, 2849, 1653, 1598, 1513, 1351; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.28 (d, $J$ = 8.5 Hz, 2H), 7.58 (d, $J$ = 8.5 Hz, 2H), 5.69 (dd, $J$ = 9.4, 7.1 Hz, 1H), 3.63 (dd, $J$ = 17.0, 9.8 Hz, 1H), 3.03 (dd, $J$ = 17.0, 6.6 Hz, 1H), 2.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.3, 146.6, 126.4, 124.5, 111.1, 73.9, 42.5, 11.9; MS m/z (relative intensity): 223 ($M^+$+1, 23), 222 ($M^+$, 100), 205 (7), 175 (18), 150 (44), 146 (7), 84 (4), 71 (39), 55 (7); HRMS calcd for $C_{10}H_{10}N_2O_4$ ($M^+$): 222.0635, found 222.0644.

**5-(2-(allyloxy)-5-nitrophenyl)-3-methyl-4,5-dihydroisoxazole-2-oxide (19a).**



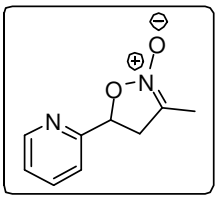
A yellow solid; mp 85-87 $^{o}$C; IR [KBr, cm$^{-1}$]: 3086, 2923, 1659, 1652, 1613, 1593, 1520, 1488, 1338, 1271; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.43 (d, $J$ = 2.7 Hz, 1H), 8.22 (dd, $J$ = 9.0, 2.8 Hz, 1H), 6.98 (d, $J$ = 9.1 Hz, 1H), 6.09-5.99 (m, 1H), 5.81 (dd, $J$ = 10.0, 2.8 Hz, 1H), 5.45-5.37 (m, 2H), 4.74-4.65 (m, 2H), 3.65-3.57 (m, 1H), 3.00-2.94 (m, 1H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.9, 141.7, 131.6, 129.4, 125.8, 122.1, 119.3, 111.9, 111.7, 70.6, 70.0, 41.3, 11.9; MS m/z (relative intensity): 278 ($M^+$, 5), 261 (8), 221 (7), 209 (11), 206 (100), 191 (39), 166 (20), 96 (10), 73 (8); HRMS calcd for $C_{13}H_{14}N_2O_5$ ($M^+$): 278.0897, found 278.0887.

**3,5-diphenyl-4,5-dihydroisoxazole-2-oxide (20a).**



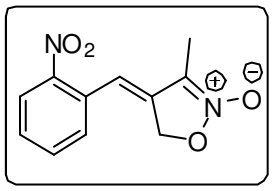
A colorless solid; mp 76-78 $^{o}$C; IR [KBr, cm$^{-1}$]: 3048, 2937, 1613, 1591, 1498, 1447, 1384, 1226; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.93 (d, $J$ = 7.7 Hz, 2H), 7.46-7.35 (m, 8H), 5.73 (t, $J$ = 8.5 Hz, 1H), 3.92 (dd, $J$ = 16.2, 9.5 Hz, 1H), 3.55 (dd, $J$ = 16.2, 7.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 138.9, 129.7, 129.2, 129.1, 128.9, 126.9, 126.4, 125.9, 114.1, 75.9, 40.5; MS m/z (relative intensity): 239 ($M^+$, 100), 192 (10), 117 (4), 105 (12), 103 (18); HRMS calcd for $C_{15}H_{13}N_1O_2$ ($M^+$): 239.0941, found 239.0944.

**3-methyl-5-(pyridin-2-yl)-4,5-dihydroisoxazole-2-oxide (21a).**



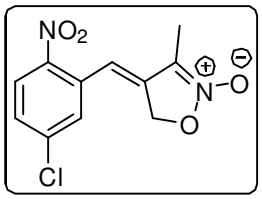
A brown oil; IR [KBr, $cm^{-1}$]: 3057, 3012, 2922, 1713, 1652, 1593, 1573, 1475, 1438, 1395, 1352, 1259; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.59 (d, $J$ = 4.2 Hz, 1H), 7.76 (t, $J$ = 7.6 Hz, 1H), 7.61 (d, $J$ = 7.8 Hz, 1H), 7.29-7.26 (m, 1H), 5.64 (dd, $J$ = 9.9, 5.4 Hz, 1H), 3.63-3.56 (m, 1H), 3.39 (dd, $J$ = 17.4, 4.0 Hz, 1H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 158.4, 149.8, 137.4, 123.6, 120.6, 112.4, 74.9, 40.3, 11.9.

**3-methyl-4-(2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (22a).**



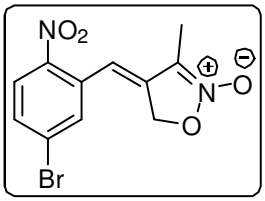
A yellow solid; mp 128-130 $^o$C; IR [KBr, $cm^{-1}$]: 1641, 1595, 1509, 1361, 1269; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.04 (dd, $J$ = 8.2, 1.1 Hz, 1H), 7.66-7.62 (m, 1H), 7.47-7.43 (m, 1H), 7.27 (d, $J$ = 7.6, 1H), 6.78 (t, $J$ = 3.1 Hz, 1H), 5.29 (d, $J$ = 3.1 Hz, 2H), 2.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.2, 138.5, 133.5, 130.4, 128.8, 128.5, 125.6, 117.5, 113.6, 68.3, 9.1; MS m/z (relative intensity): 235 ($M^+$+1, 12), 234 ($M^+$, 100), 158 (15), 146 (11), 130 (11), 119 (22), 104 (6), 92 (36); HRMS calcd for $C_{11}H_{10}N_2O_4$ ($M^+$): 234.0635, found 234.0640.

**3-methyl-4-(5-chloro-2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (23a).**



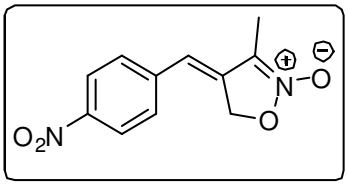
A yellow solid; mp 129-131 $^o$C; IR [KBr, $cm^{-1}$]: 3109, 3070, 2923, 1644, 1600, 1578, 1517, 1334, 1279; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.03 (d, $J$ = 8.8 Hz, 1H), 7.41 (dd, $J$ = 8.8, 2.0 Hz, 1H), 7.22 (d, $J$ = 1.7 Hz, 1H), 6.74 (t, $J$ = 3.0 Hz, 1H), 5.31 (d, $J$ = 3.0 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 146.3, 139.9, 139.8, 132.4, 128.6, 128.4, 127.2, 117.4, 112.4, 68.1, 9.2; MS m/z (relative intensity): 270 ($M^+$+2, 25), 268 ($M^+$, 100), 208 (6), 192 (20), 153 (38), 125 (46), 90 (6), 55 (6); HRMS calcd for $C_{11}H_9ClN_2O_4$ ($M^+$): 268.0245, found 268.0257 and calcd for $C_{11}H_9{}^{37}ClN_2O_4$ ($M^+$): 270.0216, found 270.0225.

**3-methyl-4-(5-bromo-2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (24a).**



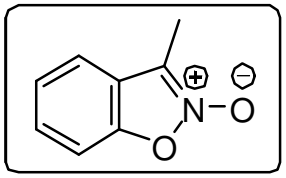
A yellow solid; mp 125-127 $^{o}$C; IR [KBr, cm$^{-1}$]: 3092, 3070, 1642, 1580, 1517, 1336, 1274; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.92 (d, $J$ = 8.8 Hz, 1H), 7.56 (dd, $J$ = 8.7, 1.9 Hz, 1H), 7.39 (d, $J$ = 1.7 Hz, 1H), 6.73 (t, $J$ = 3.1 Hz, 1H), 5.30 (d, $J$ = 3.1 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 146.8, 139.8, 132.4, 131.6, 131.4, 128.4, 127.2, 117.4, 112.3, 68.1, 9.2; MS m/z (relative intensity): 314 ($M^+$+2, 81), 312 ($M^+$, 100), 297 (3), 266 (8), 210 (36), 199 (52), 171 (72), 145 (13), 130 (7), 90 (18), 55 (13); HRMS calcd for $C_{11}H_9BrN_2O_4$ ($M^+$): 311.9740, found 311.9745 and calcd for $C_{11}H_9{}^{81}BrN_2O_4$ ($M^+$): 313.9720, found 313.9728.

**3-methyl-4-(4-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (25a).**



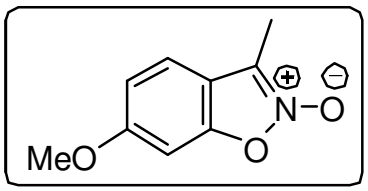
A yellow solid; mp 184-186 $^{o}$C; IR [KBr, cm$^{-1}$]: 1635, 1603, 1570, 1508, 1340, 1273; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.27 (d, $J$ = 8.8 Hz, 2H), 7.27 (d, $J$ = 8.8 Hz, 2H), 6.38 (t, $J$ = 3.1 Hz, 1H), 5.44 (d, $J$ = 3.0 Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 146.3, 142.1, 139.1, 128.8, 124.6, 117.6, 116.5, 69.0, 9.2; MS m/z (relative intensity): 235 ($M^+$+1, 11), 234 ($M^+$, 100), 205 (5), 176 (8), 150 (5), 130 (4), 84 (5); HRMS calcd for $C_{11}H_{10}N_2O_4$ ($M^+$): 234.0635, found 234.0643.

**3-methylbenzo[d]isoxazole-2-oxide (26a).**



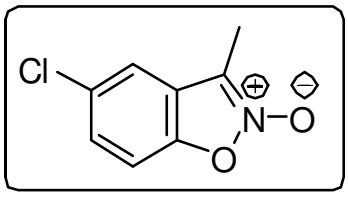
A colorless solid; mp 81-83$^{o}$C; IR [KBr, cm$^{-1}$]: 1599, 1588, 1457, 1406, 1297, 1217; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.51-7.45 (m, 1H), 7.44 (d, $J$ = 7.7 Hz, 1H), 7.31-7.26 (m, 1H), 7.18 (d, $J$ = 8.2 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 150.3, 128.8, 124.1, 121.4, 119.3, 116.4, 107.2, 9.5; MS m/z (relative intensity): 149 ($M^+$, 100), 134 (1), 121 (4), 119 (16), 105 (2), 92 (2), 91 (70); HRMS calcd for $C_8H_7NO_2$ ($M^+$): 149.0471, found 149.0477.

**6-methoxy-3-methylbenzo[d]isoxazole-2-oxide (27a).**



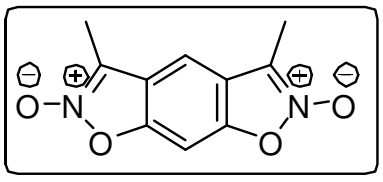
A colorless solid; mp 113-115 $^{o}$C; IR [KBr, cm$^{-1}$]: 2974, 2834, 1599, 1504, 1427; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.29 (d, $J$ = 8.5 Hz, 1H), 6.88 (dd, $J$ = 8.6, 2.2 Hz, 1H), 6.72 (d, $J$ = 2.1 Hz, 1H), 3.86 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 161.7, 151.6, 119.9, 116.3, 113.8, 112.9, 92.2, 55.9, 9.5; MS m/z (relative intensity): 179 ($M^+$, 100), 150 (4), 149 (54), 121 (52), 91 (5), 77 (4); HRMS calcd for $C_9H_9NO_3$ ($M^+$): 179.0577, found 179.0587.

**5-chloro-3-methylbenzo[d]isoxazole-2-oxide (28a).**



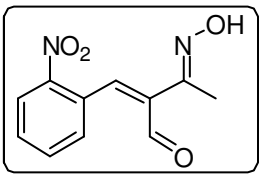
A colorless solid; mp 105-107 $^{o}$C; IR [KBr, cm$^{-1}$]: 1599, 1582, 1456, 1271, 1211; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44 (d, $J$ = 8.7 Hz, 1H), 7.39 (s, 1H), 7.12 (d, $J$ = 8.6 Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5, 129.8, 128.8, 122.8, 118.9, 115.6, 108.3, 9.5; MS m/z (relative intensity): 183 ($M^+$, 100), 157 (2), 155 (7), 142 (1), 127 (21), 125 (74), 118 (7), 99 (3), 89 (6); HRMS calcd for $C_8H_6NO_2Cl$ ($M^+$): 183.0082, found 183.0089.

**Bisisoxazoline-*N*-oxide derivative (29a).**



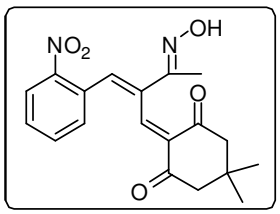
A colorless solid; mp 176-178 °C; IR [KBr, cm$^{-1}$]: 1599, 1582, 1456, 1271, 1211; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.37 (s, 1H), 7.03 (d, $J$ = 0.4 Hz, 1H), 2.48 (s, 6H); $^{13}$C NMR (100 MHz, DMSO): $\delta$ 150.2, 117.9, 115.2, 111.5, 86.9, 9.1; MS m/z (relative intensity): 220 ($M^+$, 100), 190 (9), 148 (13), 131 (16), 122(13); HRMS calcd for $C_{10}H_8N_2O_4$ ($M^+$): 220.0484, found 220.0483.

**(2Z)-3-(methylimino)-2-(2-nitrobenzylidene)butanal (33).**



The product, a yellow solid, was obtained as a non-separable mixture of *syn* and *anti* oximes in a ratio 2:1; mp 130-132 °C; IR [KBr, $cm^{-1}$]: 3276, 2922, 2849, 1686, 1522, 1342; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ (for major peaks) 9.76 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.87 (s, 1H), 7.69 (dd, *J* = 16.2, 7.36 Hz, 1H), 7.65-7.56 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 1.89 (s, 3H) and δ (for minor peaks) 9.76 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.99 (s, 1H), 7.98 (s, 1H), 7.69 (dd, *J* = 16.2, 7.36 Hz, 1H), 7.65-7.56 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 2.18 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): *δ* (for major peaks) 191.8, 151.6, 147.5, 147.4, 139.5, 134.1, 133.3, 130.6, 129.9, 125.2, 13.1 and δ (for minor peaks) 190.5, 154.7, 147.4, 143.3, 137.5, 133.8, 133.3, 130.9, 129.9, 125.6, 15.1; MS m/z (relative intensity): 233 ($M^+$-1, 14), 205 (44), 170 (55), 130 (100), 103 (92); HRMS calcd for $C_{11}H_9N_2O_4$ ($M^+$-1): 233.0562, found 233.0563.

**3-(hydroxyimino)-2-(2-nitrobenzylidene)butylidene)-5,5-dimethylcyclohexane-1,3-dione (34).**

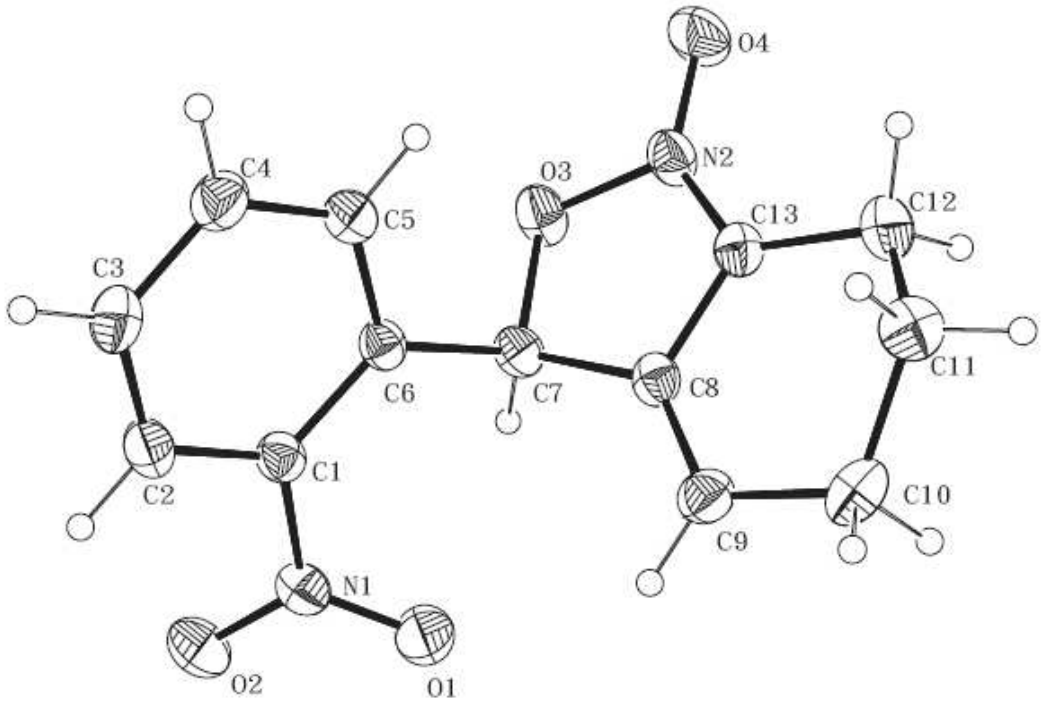


A yellow solid; mp 212-214 °C; IR [KBr, $cm^{-1}$]: 3284, 2959, 2871, 1630, 1590, 1531, 1399, 1359, 1264; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.51-7.43 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.16 (s, 2H), 2.35-2.17 (m, 4H), 2.09 (s, 3H), 1.03 (s, 3H), 0.97 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): *δ* 194.9, 171.5, 153.8, 149.3, 132.9, 129.8, 129.1, 124.6, 122.9, 118.9, 110.9, 72.4, 50.5, 42.1, 32.6, 29.3, 27.6, 9.5; MS m/z (relative intensity): 358 ($M^+$+2, 2), 356 (M+, 56), 339 (66), 293 (64), 292 (45), 280 (16), 235 (5), 222 (30), 188 (35), 169 (100), 158 (43), 83 (16); HRMS calcd for $C_{19}H_{20}N_2O_5$ ($M^+$): 356.1372, found 356.1376.

# 4. X-ray crystallographic structures

### 5.1. X-ray crystallographic structure of 1a

CCDC number of the crystal 792924



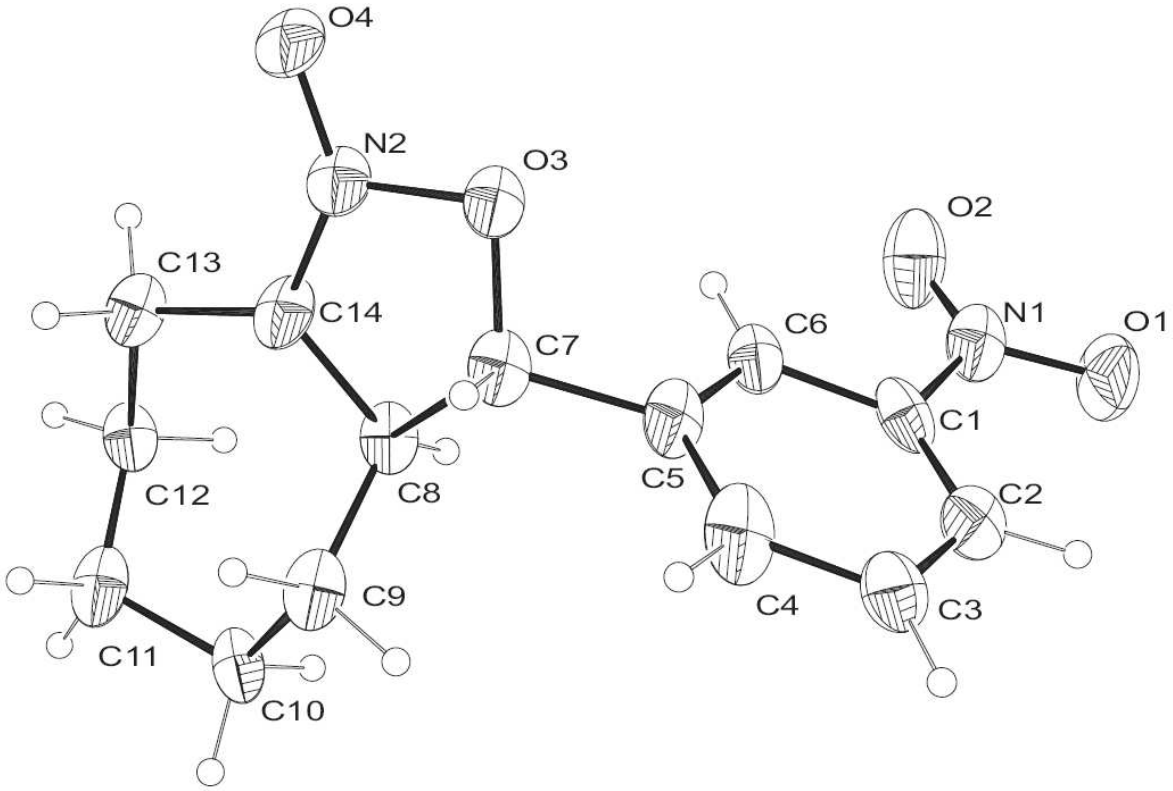

**Crystal data and structure refinement for 1a**

| | | |
|---|---|---|
| Identification code | a9342 | |
| Empirical formula | C13 H12 N2 O4 | |
| Formula weight | 260.25 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 8.7484(2) Å | α= 90°. |
| | b = 14.5938(4) Å | β= 108.899(2)°. |
| | c = 9.8507(2) Å | γ = 90°. |
| Volume | 1189.86(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.453 $Mg/m^3$ | |
| Absorption coefficient | 0.110 $mm^{-1}$ | |
| F(000) | 544 | |
| Crystal size | 0.60 x 0.55 x 0.28 $mm^3$ | |
| Theta range for data collection | 2.59 to 25.02°. | |
| Index ranges | -10<=h<=10, -17<=k<=17, -10<=l<=11 | |
| Reflections collected | 8598 | |
| Independent reflections | 2071 [R(int) = 0.0260] | |
| Completeness to theta = 25.02° | 98.3 % | |
| Absorption correction | multi-scan | |
| Max. and min. transmission | 0.9699 and 0.9371 | |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2071 / 0 / 172 |
| Goodness-of-fit on $F^2$ | 1.135 |
| Final R indices [I>2sigma(I)] | R1 = 0.0469, wR2 = 0.1391 |
| R indices (all data) | R1 = 0.0606, wR2 = 0.1574 |
| Largest diff. peak and hole | 0.499 and -0.468 e.Å$^{-3}$ |

## 5.2. X-ray crystallographic structure of 10a

CCDC number of the crystal 792922



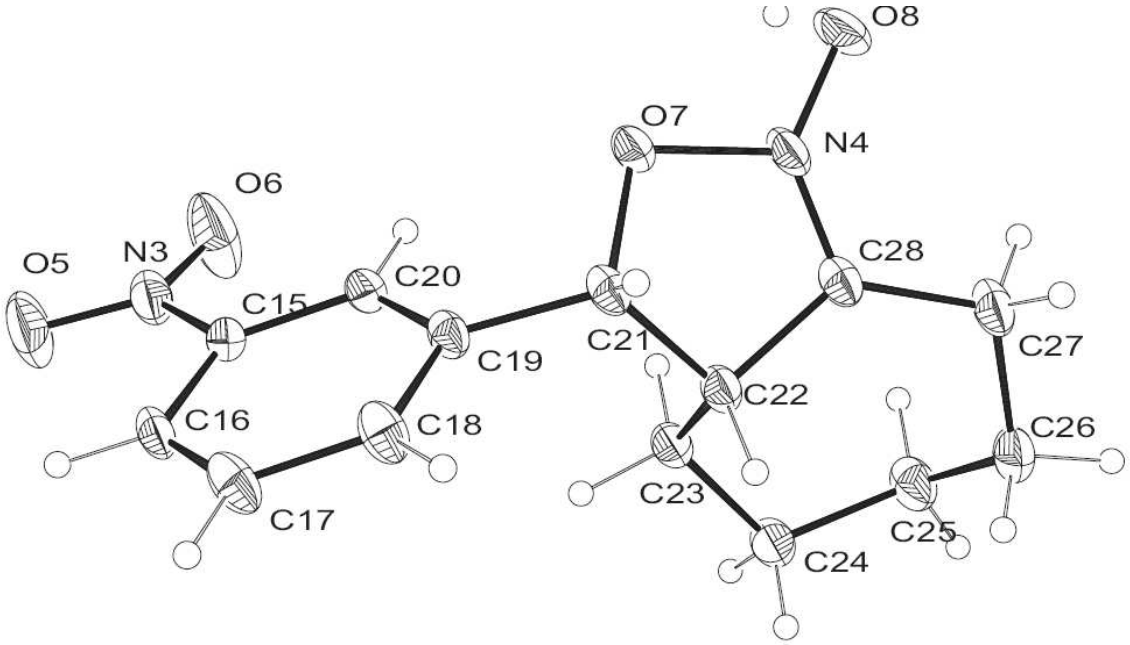

**Crystal data and structure refinement for 10a.**

| | | |
|---|---|---|
| Identification code | a10697 | |
| Empirical formula | C14 H16 N2 O4 | |
| Formula weight | 276.29 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/c | |
| Unit cell dimensions | a = 6.74(2) Å | α= 90°. |
| | b = 12.46(4) Å | β= 91.77(7)°. |
| | c = 15.25(5) Å | γ = 90°. |

| | |
|---|---|
| Volume | 1281(7) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.433 $Mg/m^3$ |
| Absorption coefficient | 0.106 $mm^{-1}$ |
| F(000) | 584 |
| Crystal size | 0.55 x 0.08 x 0.02 $mm^3$ |
| Theta range for data collection | 2.67 to 24.26°. |
| Index ranges | -7<=h<=5, -14<=k<=13, -5<=l<=17 |
| Reflections collected | 4392 |
| Independent reflections | 1714 [R(int) = 0.2833] |
| Completeness to theta = 24.26° | 82.6 % |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9979 and 0.9439 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1714 / 0 / 181 |
| Goodness-of-fit on $F^2$ | 1.116 |
| Final R indices [I>2sigma(I)] | R1 = 0.1771, wR2 = 0.3848 |
| R indices (all data) | R1 = 0.2822, wR2 = 0.4406 |
| Largest diff. peak and hole | 0.791 and -0.639 $e.Å^{-3}$ |

### 5.3 X-ray crystallographic structure of 11a

CCDC number of the crystal 792920



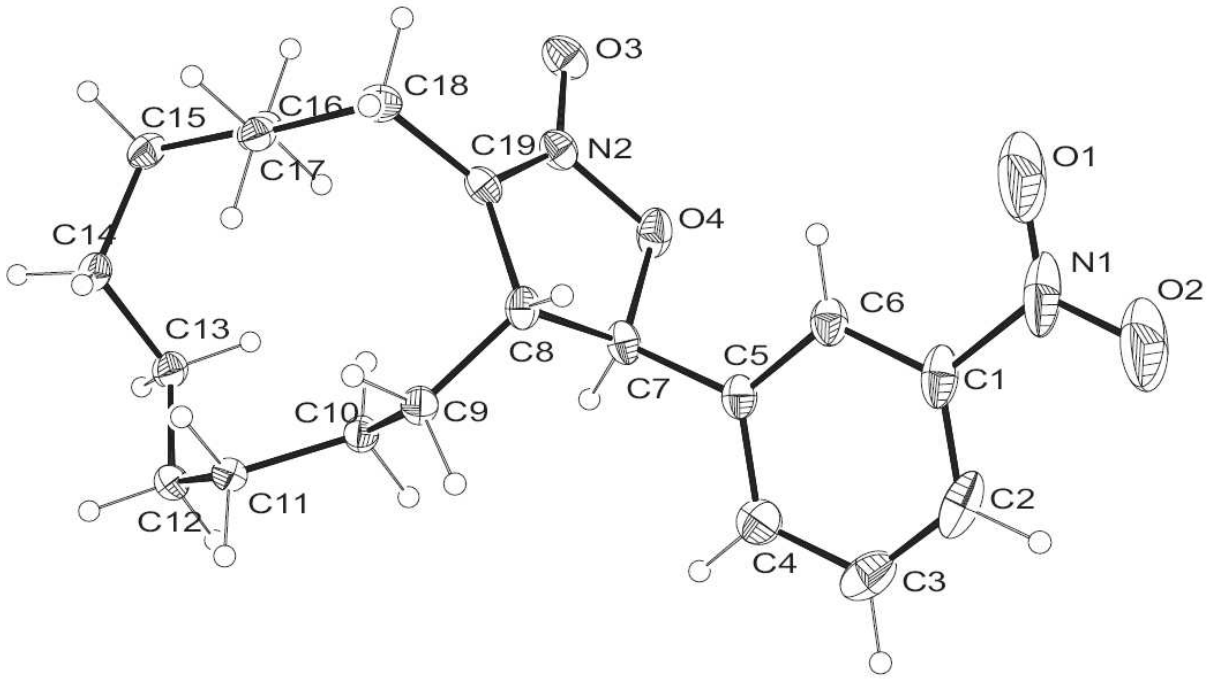

**Crystal data and structure refinement for 11a**.

| | | |
|---|---|---|
| Identification code | 10908 | |
| Empirical formula | C14 H16 N2 O4 | |
| Formula weight | 276.29 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 6.3130(2) Å | α= 90.0380(10)°. |
| | b = 10.4530(3) Å | β= 90.0260(10)°. |
| | c = 20.3210(7) Å | γ = 90.037(2)°. |
| Volume | 1340.98(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.369 $Mg/m^3$ | |
| Absorption coefficient | 0.101 $mm^{-1}$ | |
| F(000) | 584 | |
| Crystal size | 0.4 x 0.35 x 0.3 $mm^3$ | |
| Theta range for data collection | 2.19 to 25.06°. | |
| Index ranges | -7<=h<=7, -10<=k<=12, -23<=l<=24 | |
| Reflections collected | 9089 | |
| Independent reflections | 4521 [R(int) = 0.0389] | |
| Completeness to theta = 25.06° | 95.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9957 and 0.9336 | |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4521 / 0 / 361 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final R indices [I>2sigma(I)] | R1 = 0.0431, wR2 = 0.1232 |
| R indices (all data) | R1 = 0.0632, wR2 = 0.1461 |
| Largest diff. peak and hole | 0.323 and -0.431 e.Å$^{-3}$ |

## 5.4. X-ray crystallographic structure of 14a

CCDC number of the crystal 792923



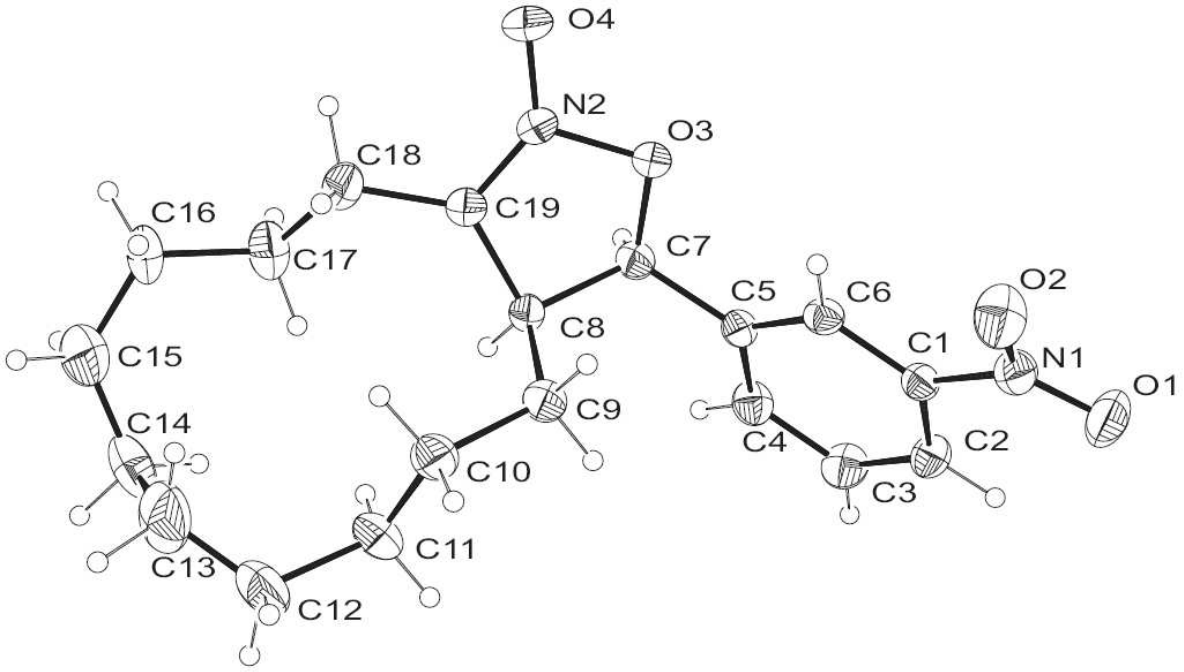

**Crystal data and structure refinement for 14a.**

| | | |
|---|---|---|
| Identification code | a11044 | |
| Empirical formula | C19 H26 N2 O4 | |
| Formula weight | 346.42 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 7.5626(3) Å | α= 108.6670(10)°. |
| | b = 10.9151(3) Å | β= 98.9220(10)°. |
| | c = 11.7483(3) Å | γ = 100.8220(10)°. |

| | |
|---|---|
| Volume | 877.97(5) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.310 $Mg/m^3$ |
| Absorption coefficient | 0.092 $mm^{-1}$ |
| F(000) | 372 |
| Crystal size | 0.68 x 0.48 x 0.20 $mm^3$ |
| Theta range for data collection | 1.88 to 25.03°. |
| Index ranges | -8<=h<=4, -12<=k<=12, -13<=l<=13 |
| Reflections collected | 6336 |
| Independent reflections | 3000 [R(int) = 0.0241] |
| Completeness to theta = 25.03° | 97.4 % |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9818 and 0.9401 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3000 / 0 / 221 |
| Goodness-of-fit on $F^2$ | 1.599 |
| Final R indices [I>2sigma(I)] | R1 = 0.0571, wR2 = 0.1653 |
| R indices (all data) | R1 = 0.0671, wR2 = 0.1785 |
| Largest diff. peak and hole | 0.667 and -0.559 $e.Å^{-3}$ |

### 5.5. X-ray crystallographic structure of 15a

CCDC number of the crystal 792921



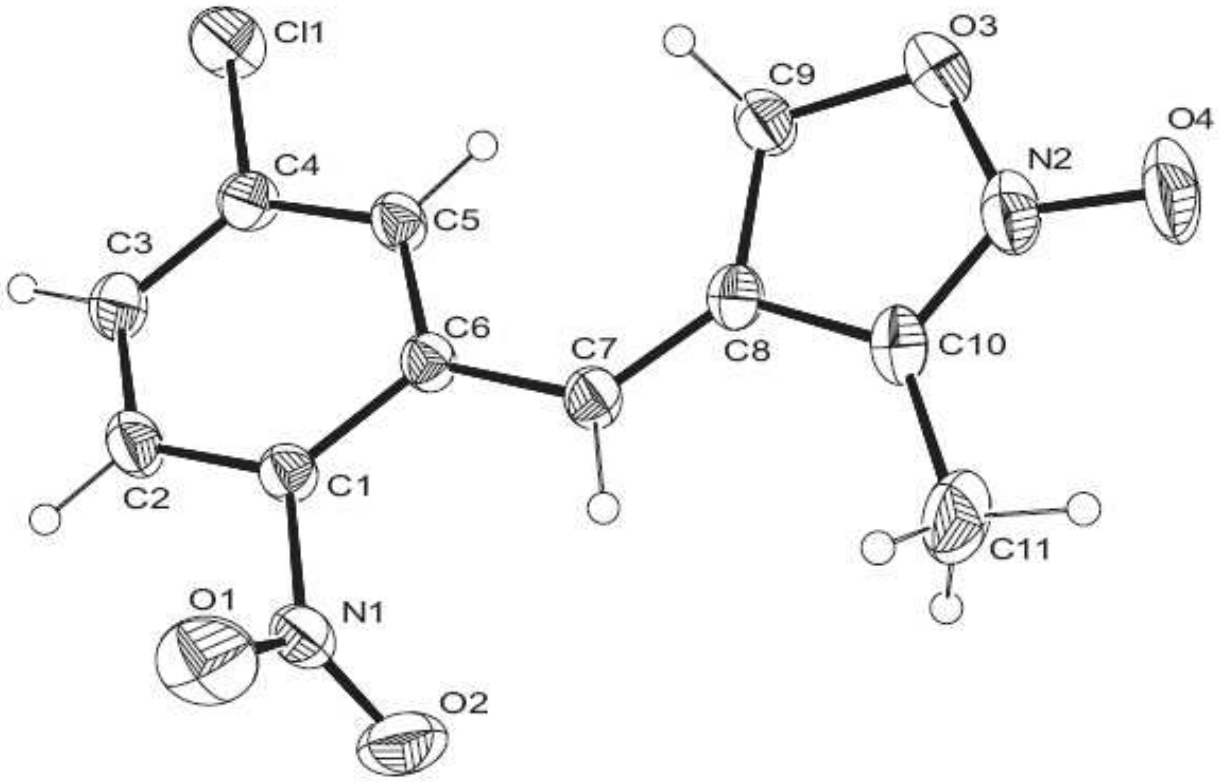

**Crystal data and structure refinement for 15a.**

| | | |
|---|---|---|
| Identification code | 11043 | |
| Empirical formula | C19 H26 N2 O4 | |
| Formula weight | 346.42 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 13.0697(3) Å | α= 90°. |
| | b = 7.7190(2) Å | β= 98.0780(10)°. |
| | c = 18.1460(5) Å | γ = 90°. |
| Volume | 1812.50(8) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.270 $Mg/m^3$ | |
| Absorption coefficient | 0.089 $mm^{-1}$ | |
| F(000) | 744 | |
| Crystal size | 0.66 x 0.58 x 0.4 $mm^3$ | |
| Theta range for data collection | 2.06 to 25.04°. | |
| Index ranges | -15<=h<=15, -9<=k<=8, -20<=l<=21 | |
| Reflections collected | 9668 | |
| Independent reflections | 3206 [R(int) = 0.0688] | |
| Completeness to theta = 25.04° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |

| | |
|---|---|
| Max. and min. transmission | 1.2356 and 0.8163 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3206 / 0 / 226 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final R indices [I>2sigma(I)] | R1 = 0.0816, wR2 = 0.2280 |
| R indices (all data) | R1 = 0.1106, wR2 = 0.2584 |
| Largest diff. peak and hole | 0.587 and -0.444 e.$Å^{-3}$ |

## 5.6. X-ray crystallographic structure of 23a

CCDC number of the crystal 792919



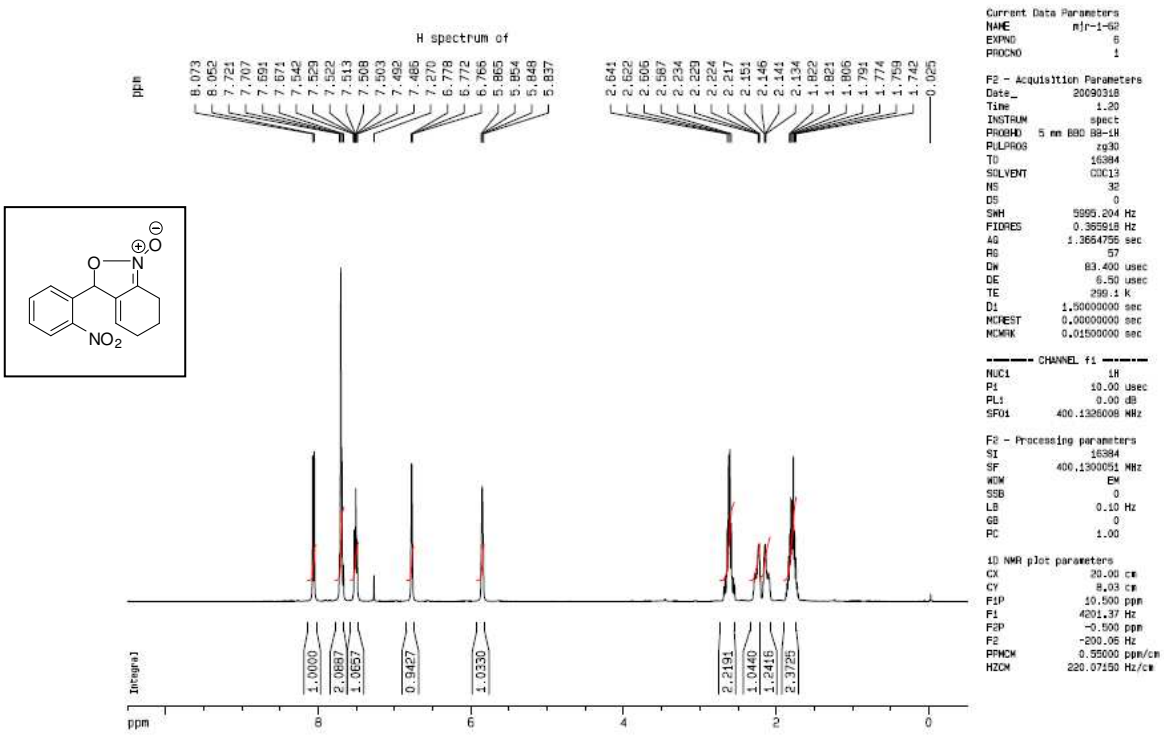

**Crystal data and structure refinement for 23a.**

| | |
|---|---|
| Identification code | 10377 |
| Empirical formula | C11 H9 Cl N2 O4 |
| Formula weight | 268.65 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |

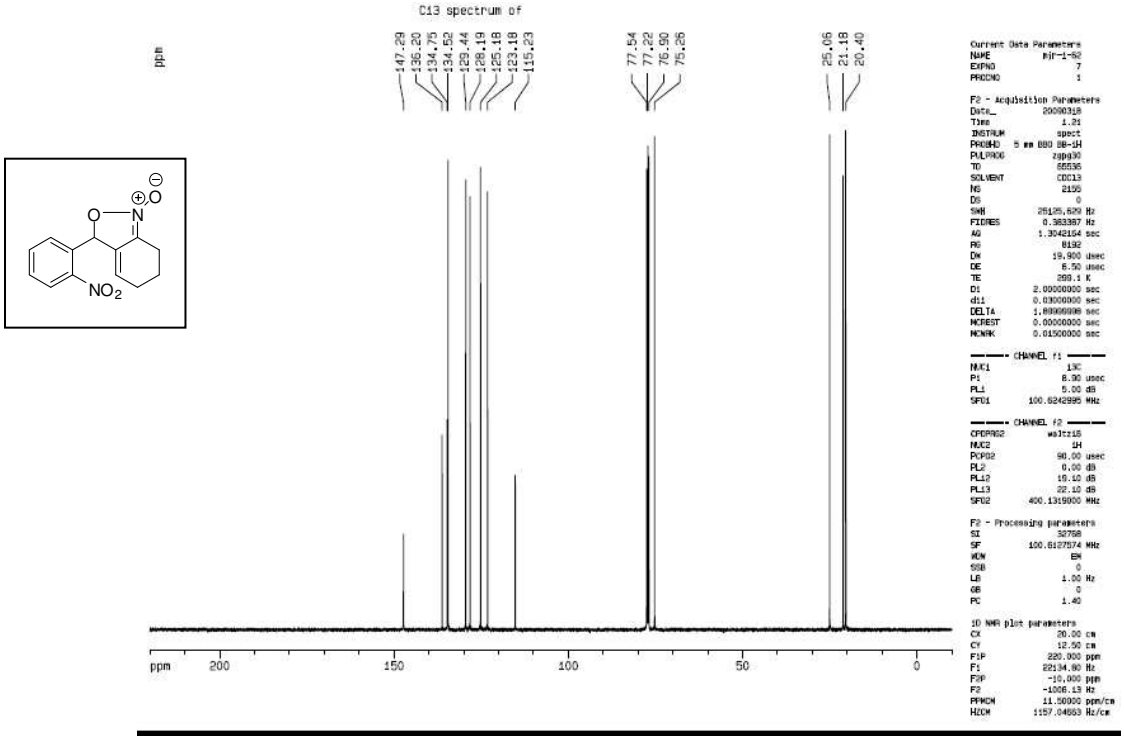
| | | |
|---|---|---|
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 7.6607(3) Å | α= 106.496(2)°. |
| | b = 7.7335(3) Å | β= 96.783(2)°. |
| | c = 10.9132(4) Å | γ = 106.600(2)°. |
| Volume | 579.96(4) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.538 $Mg/m^3$ | |
| Absorption coefficient | 0.338 $mm^{-1}$ | |
| F(000) | 276 | |
| Crystal size | 0.37 x 0.31 x 0.25 $mm^3$ | |
| Theta range for data collection | 2.84 to 25.05°. | |
| Index ranges | -9<=h<=9, -9<=k<=9, -12<=l<=12 | |
| Reflections collected | 4143 | |
| Independent reflections | 2028 [R(int) = 0.0363] | |
| Completeness to theta = 25.05° | 99.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9699 and 0.8014 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2028 / 0 / 163 | |
| Goodness-of-fit on $F^2$ | 1.005 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0443, wR2 = 0.1180 | |
| R indices (all data) | R1 = 0.0509, wR2 = 0.1239 | |
| Largest diff. peak and hole | 0.285 and -0.258 $e.Å^{-3}$ | |

# 5. $^{1}$H and $^{13}$C NMR spectra

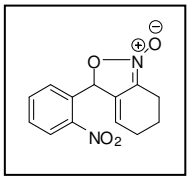
**3-(2-nitrophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (1a):** $^{1}$H NMR (400 MHz, $CDCl_3$)

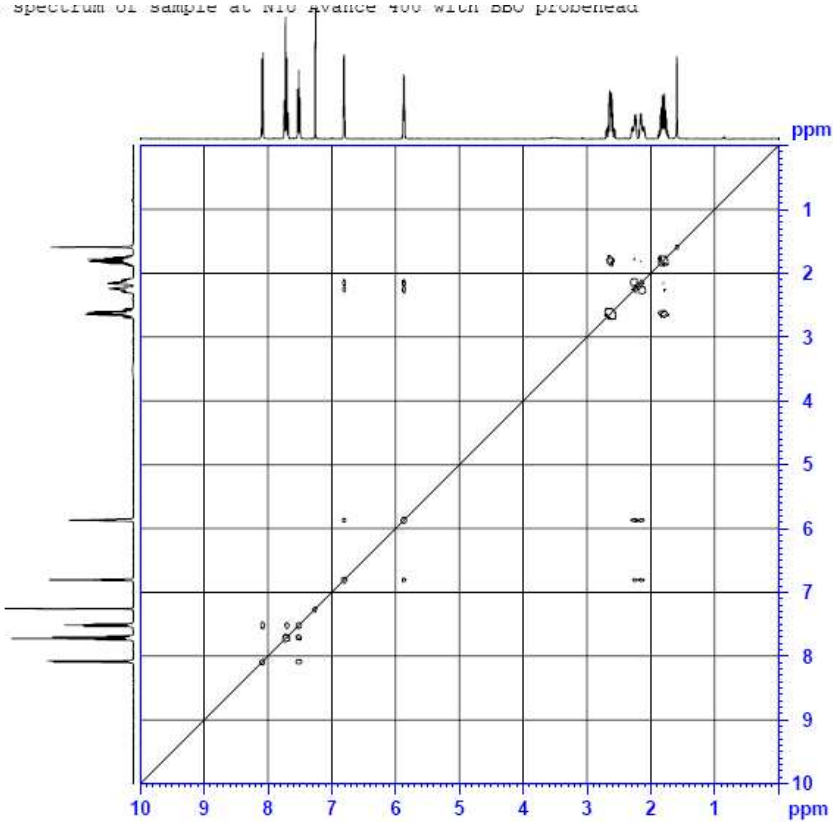



**3-(2-nitrophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (1a):** $^{13}$C NMR (100 MHz, $CDCl_3$)

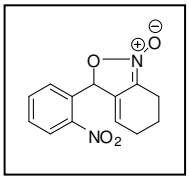


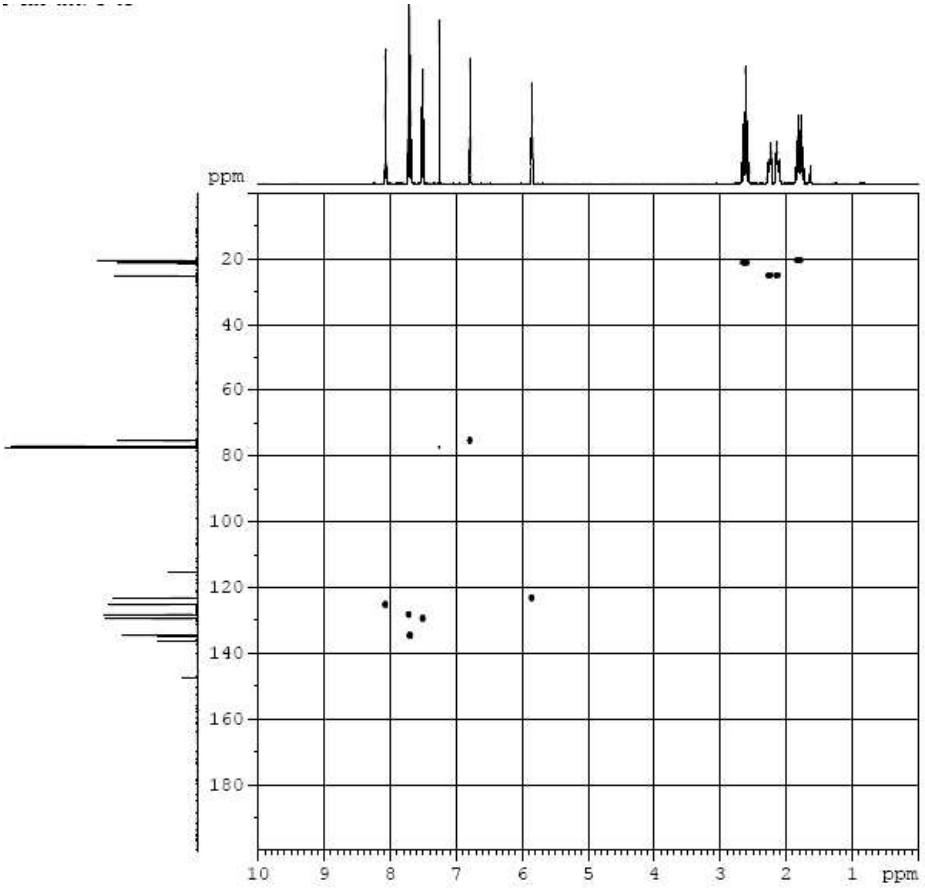
**3-(2-nitrophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (1a):** Cosy (400 MHz, $CDCl_3$)



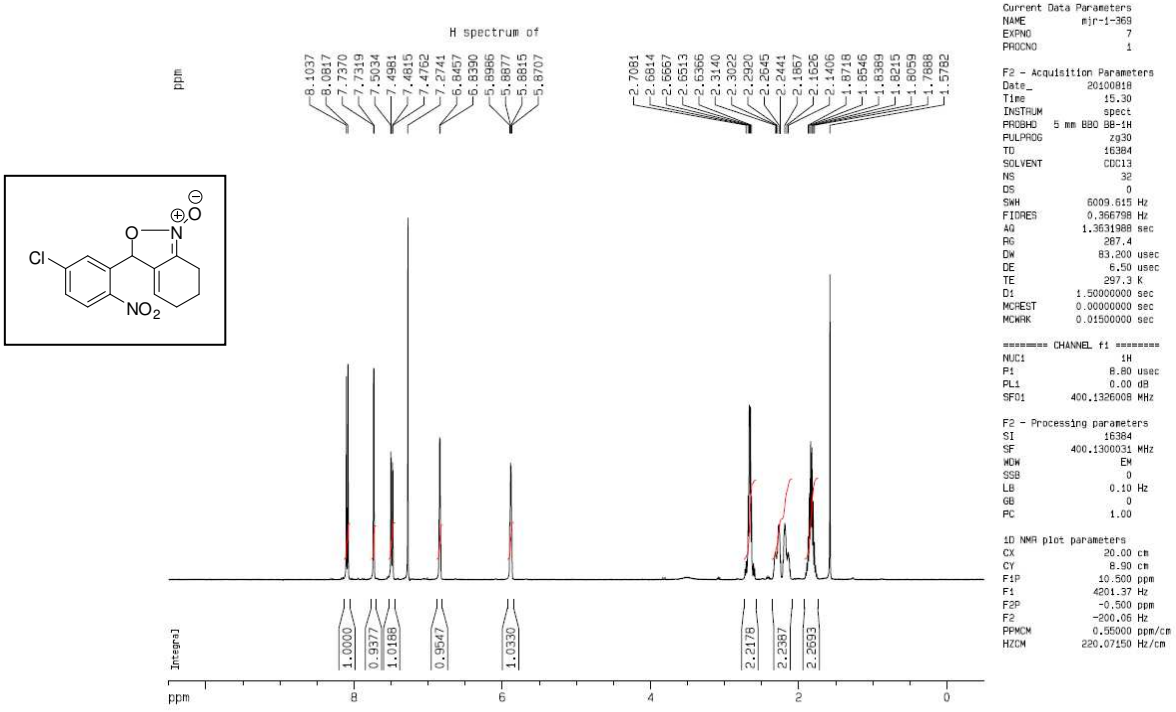



**3-(2-nitrophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (1a):** HMQC (500 MHz, $CDCl_3$)

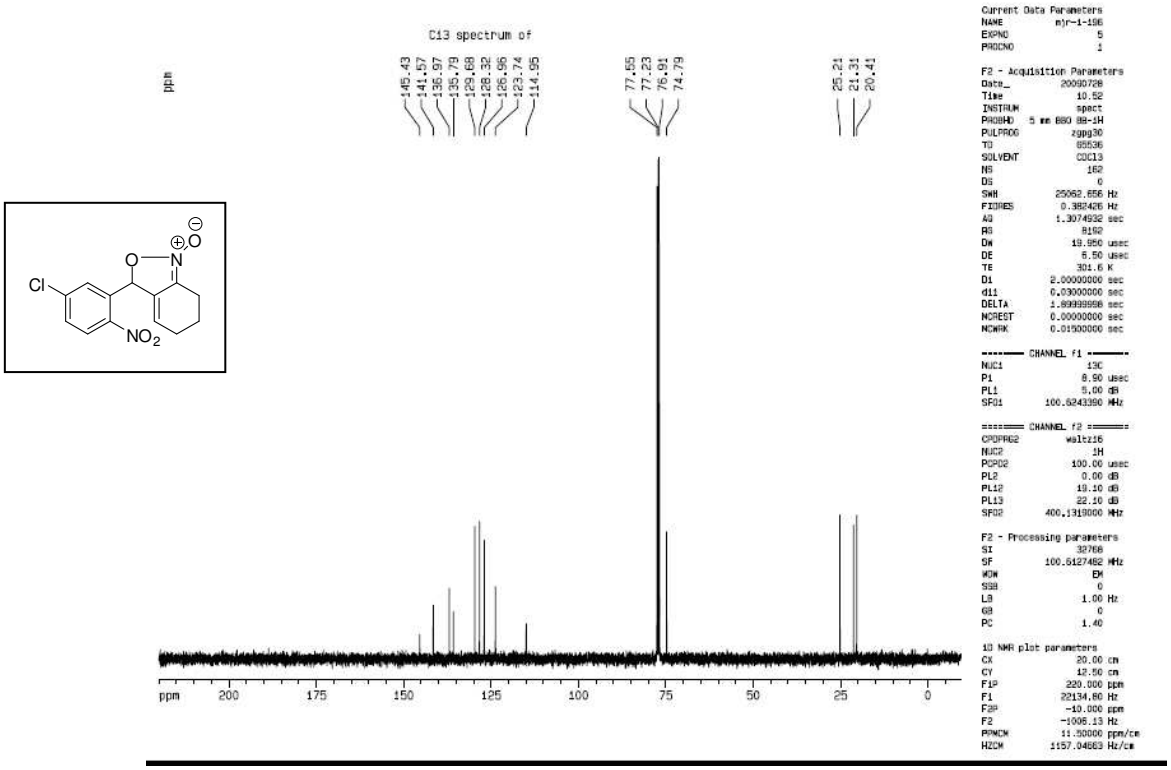




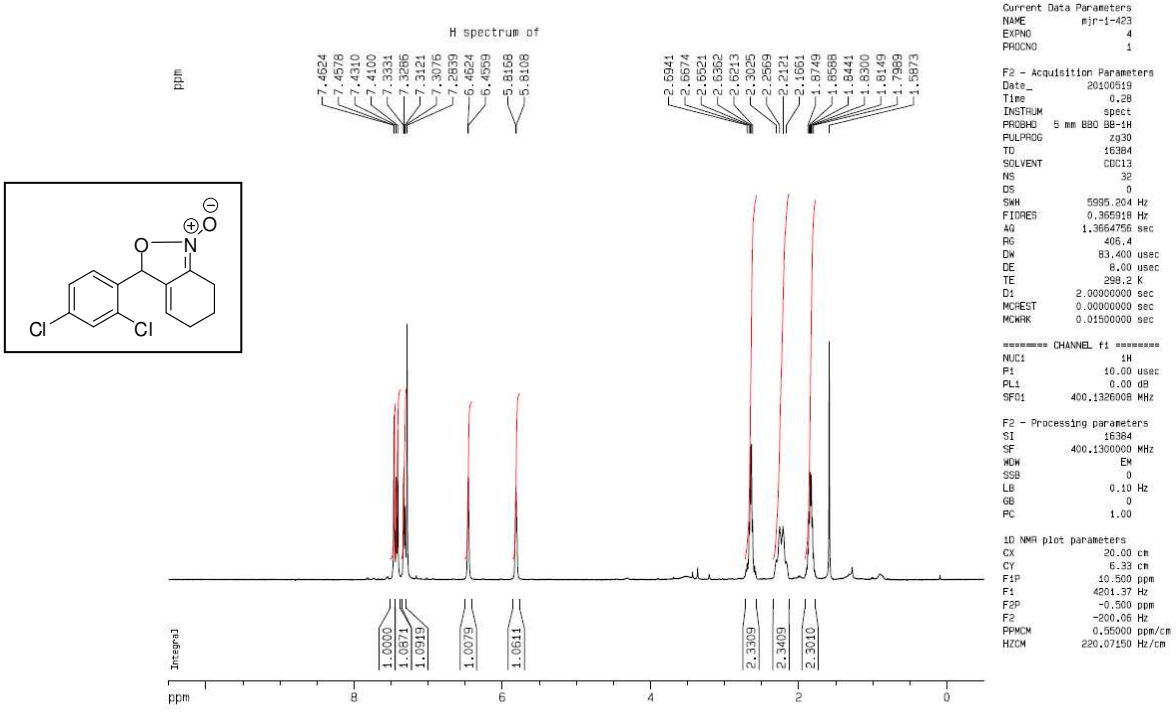
**3-(2-nitro-5-chlorophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (2a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



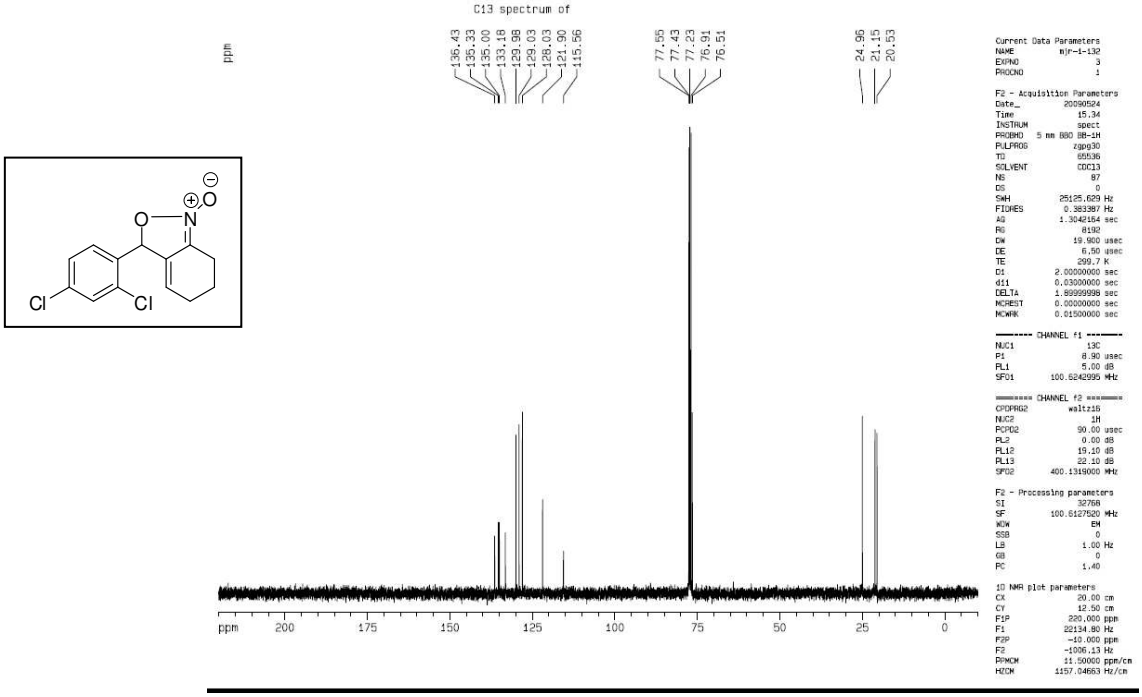

**3-(2-nitro-5-chlorophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (2a):** $^{13}$C NMR (100 MHz, $CDCl_3$)



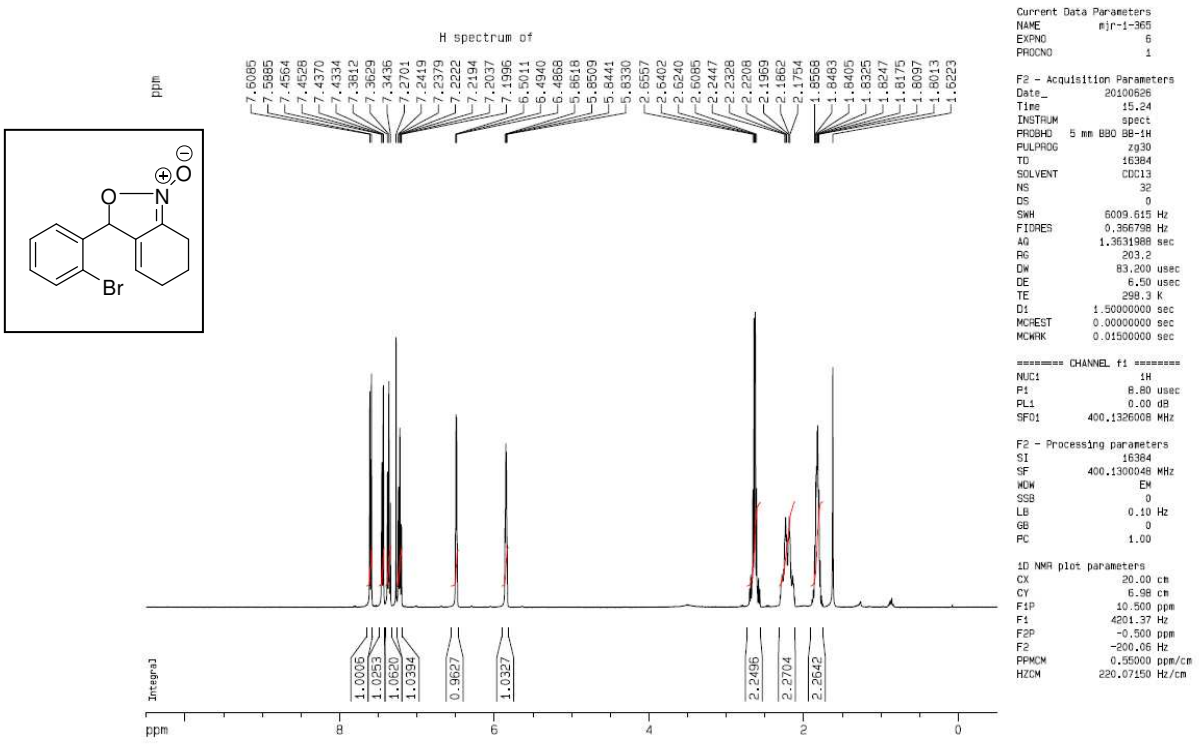
**3-(2,4-dichlorophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (3a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



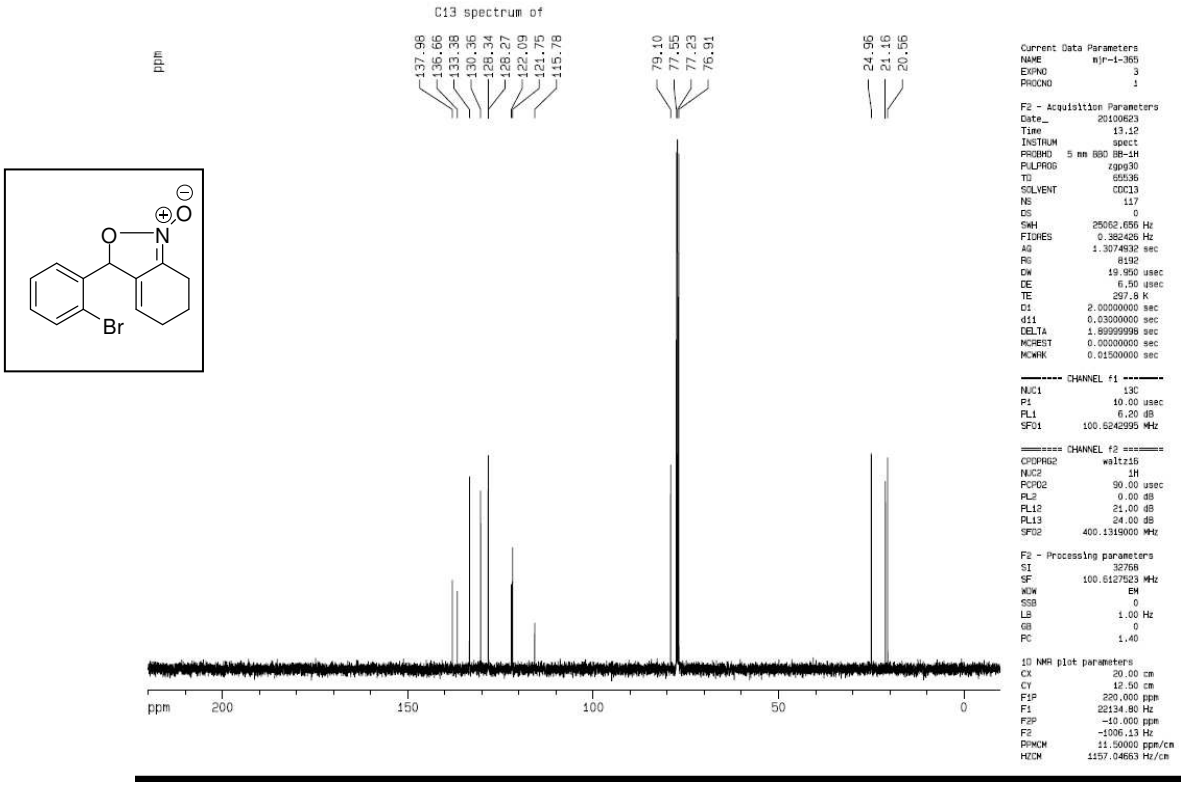

**3-(2,4-dichlorophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (3a):** $^{13}$C NMR (100 MHz, $CDCl_3$)



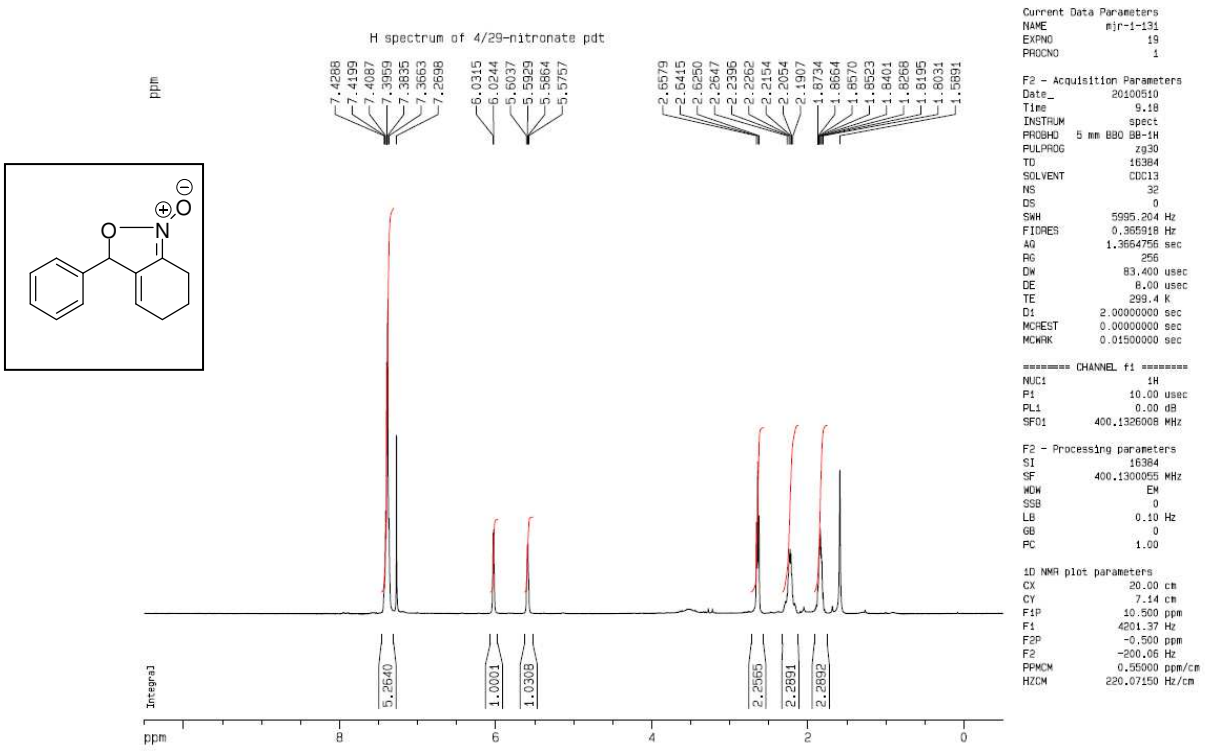

**3-(2-bromophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (4a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



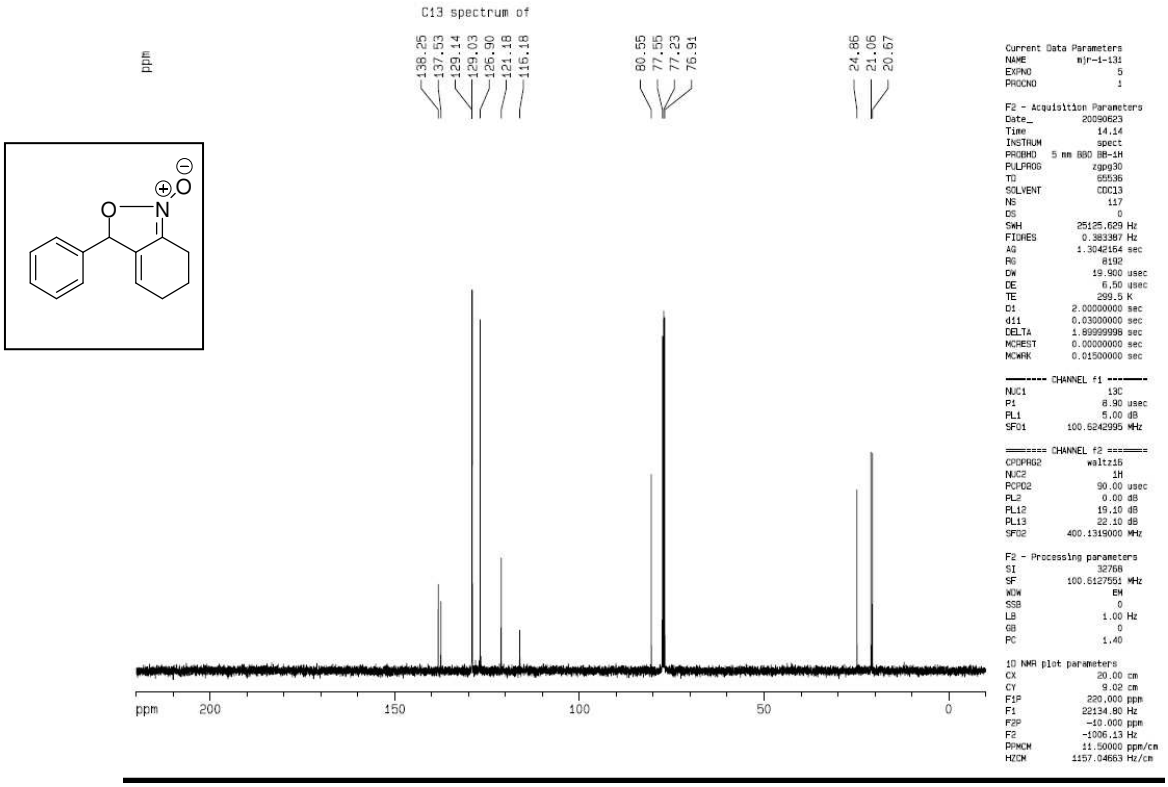

**3-(2-bromophenyl)-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (4a):** $^{13}$C NMR (100 MHz, $CDCl_3$)



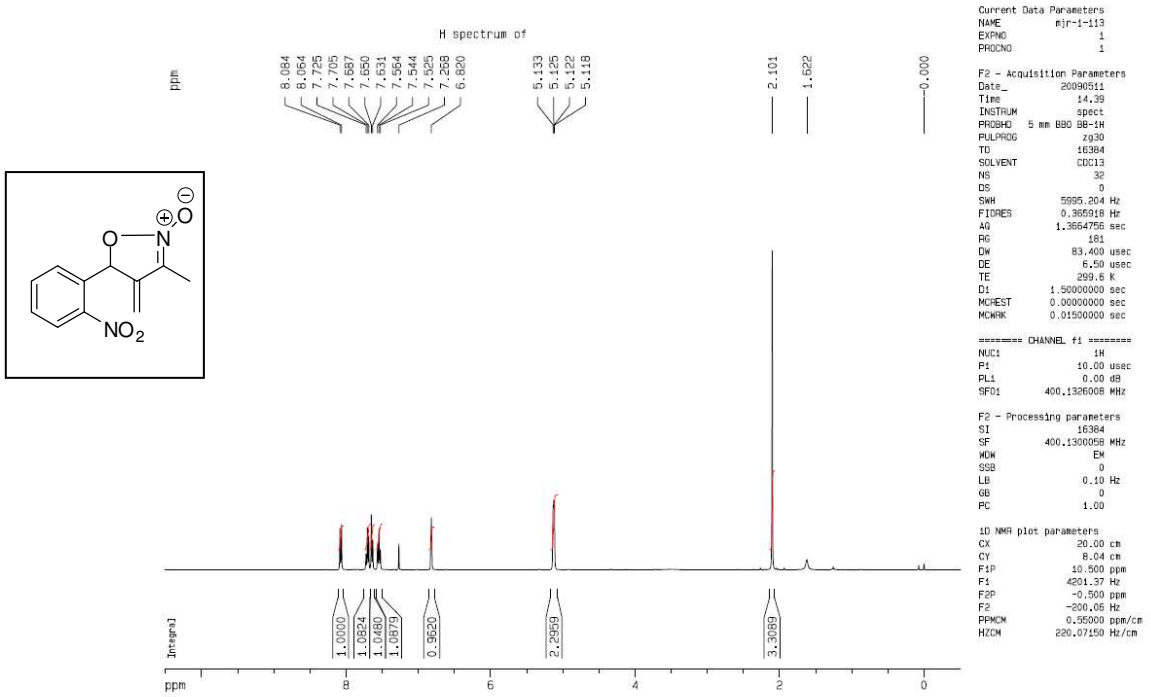

**3-phenyl-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (5a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



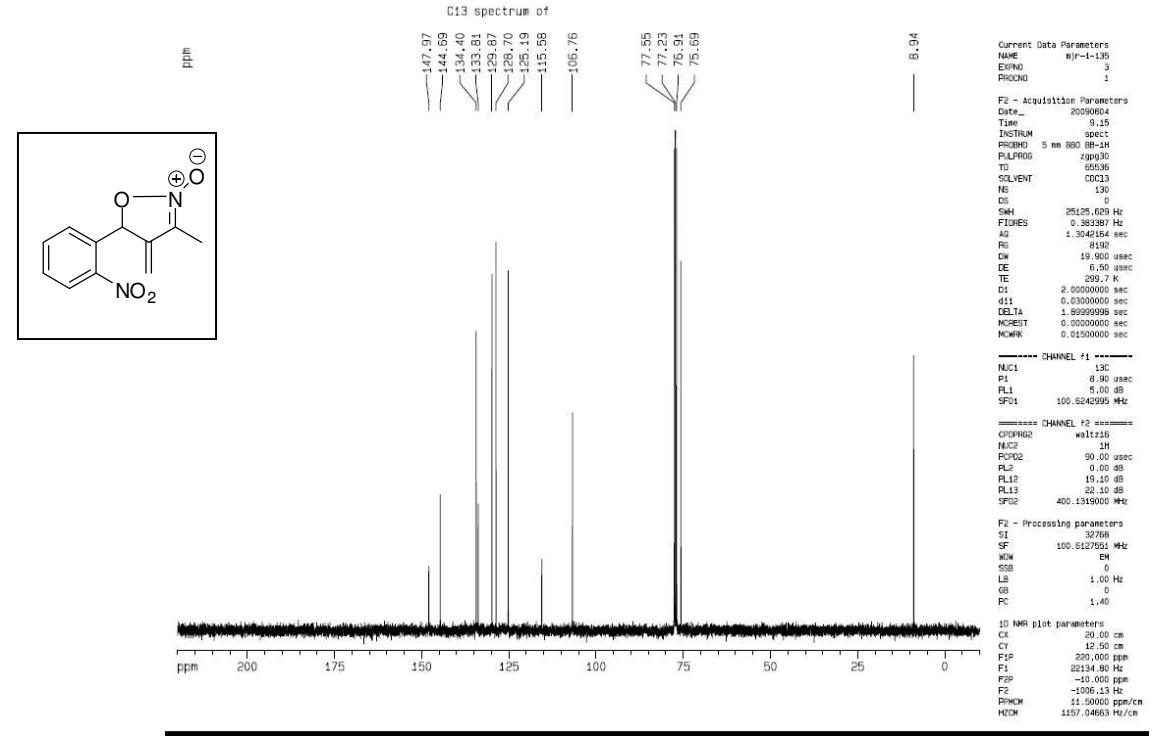

**3-phenyl-3,5,6,7-tetrahydrobenzo[c]isoxazole-1-oxide (5a):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



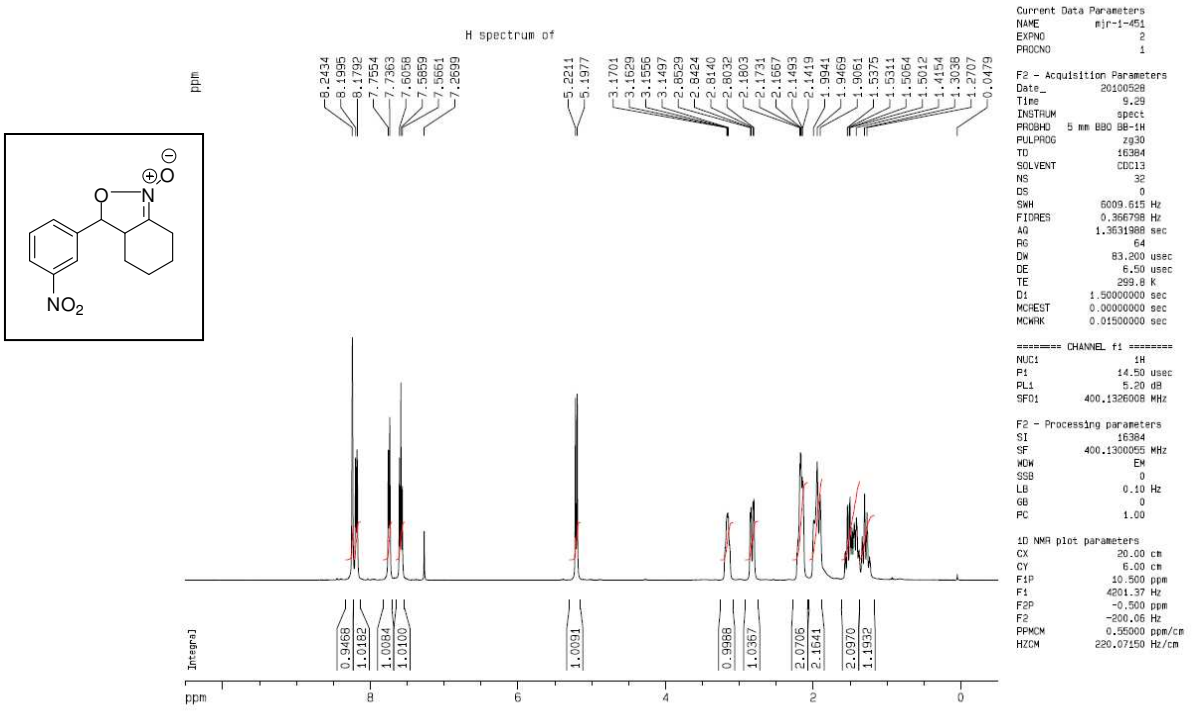

**3-methyl-4-methylene-5-(2-nitrophenyl)-4,5-dihydroisoxazole-2-oxide (7a):** $^{1}H$ NMR (400 MHz, $CDCl_3$)



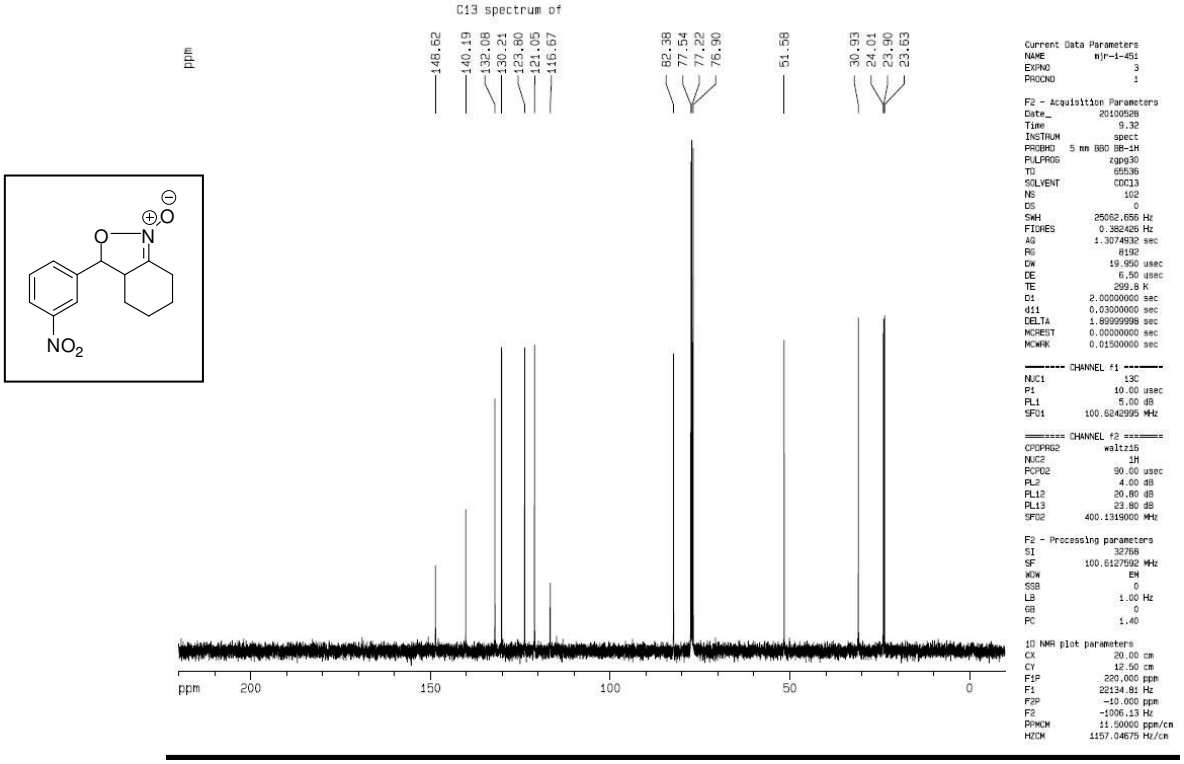

**3-methyl-4-methylene-5-(2-nitrophenyl)-4,5-dihydroisoxazole-2-oxide (7a):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



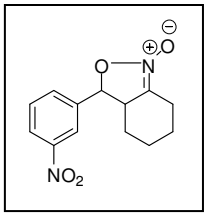

**3-(3-nitrophenyl)-3,3a,4,5,6,7-hexahydrobenzo[c]isoxazole-1-oxide (anti) (8a):** $^{1}H$ NMR (400 MHz, $CDCl_3$)

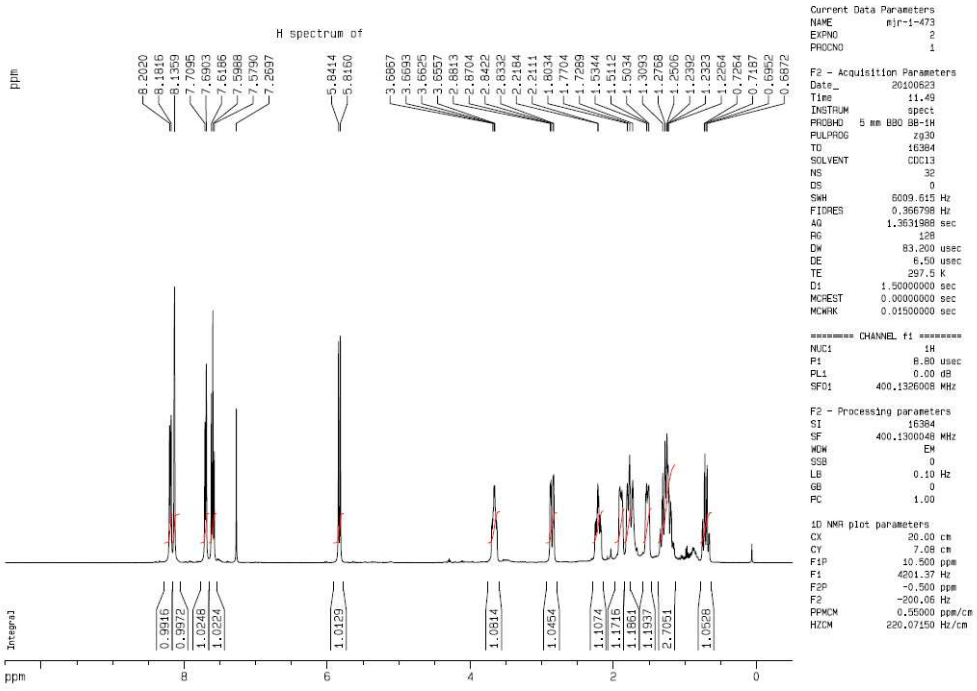


**3-(3-nitrophenyl)-3,3a,4,5,6,7-hexahydrobenzo[c]isoxazole-1-oxide (anti) (8a):** $^{13}C$ NMR (100 MHz, $CDCl_3$)

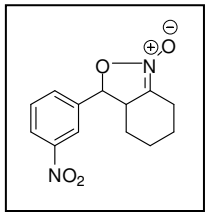


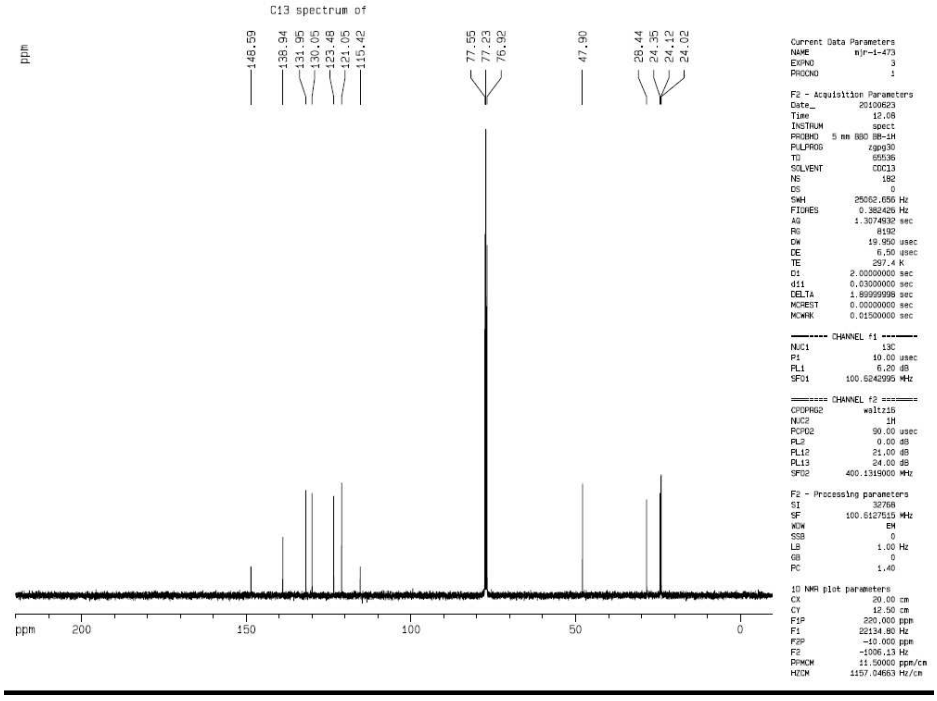
**3-(3-nitrophenyl)-3,3a,4,5,6,7-hexahydrobenzo[c]isoxazole-1-oxide (syn) (9a):** $^{1}H$ NMR (400 MHz, $CDCl_3$)



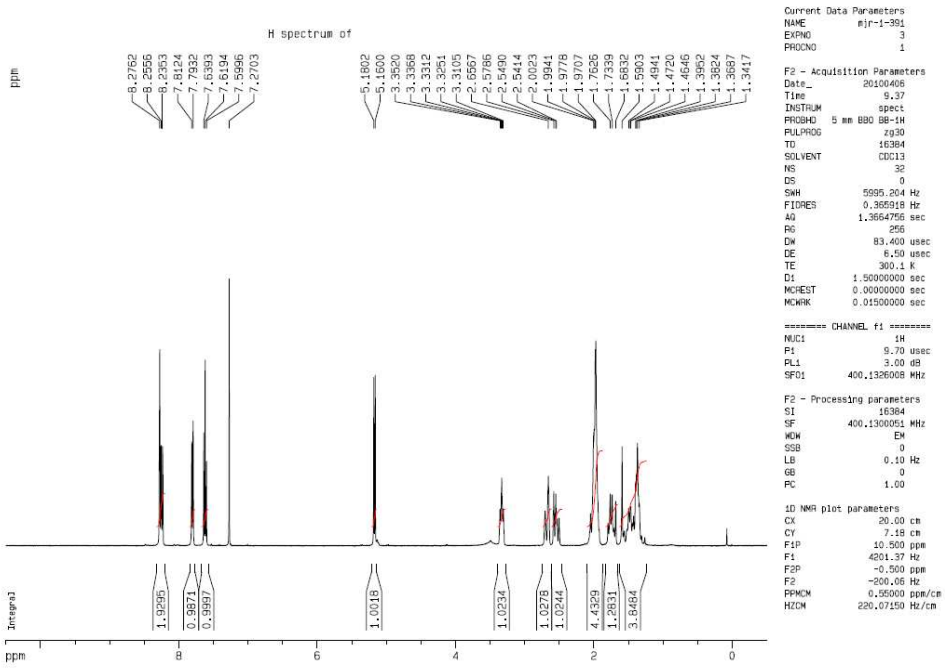



**3-(3-nitrophenyl)-3,3a,4,5,6,7-hexahydrobenzo[c]isoxazole-1-oxide (syn) (9a):** $^{13}$C NMR (100 MHz, $CDCl_3$)

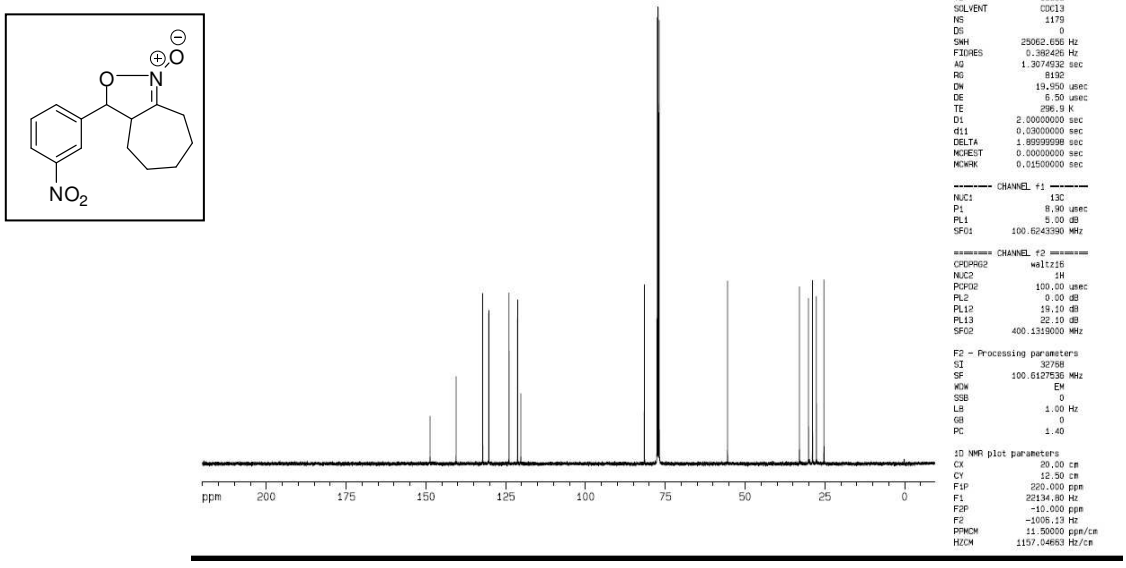




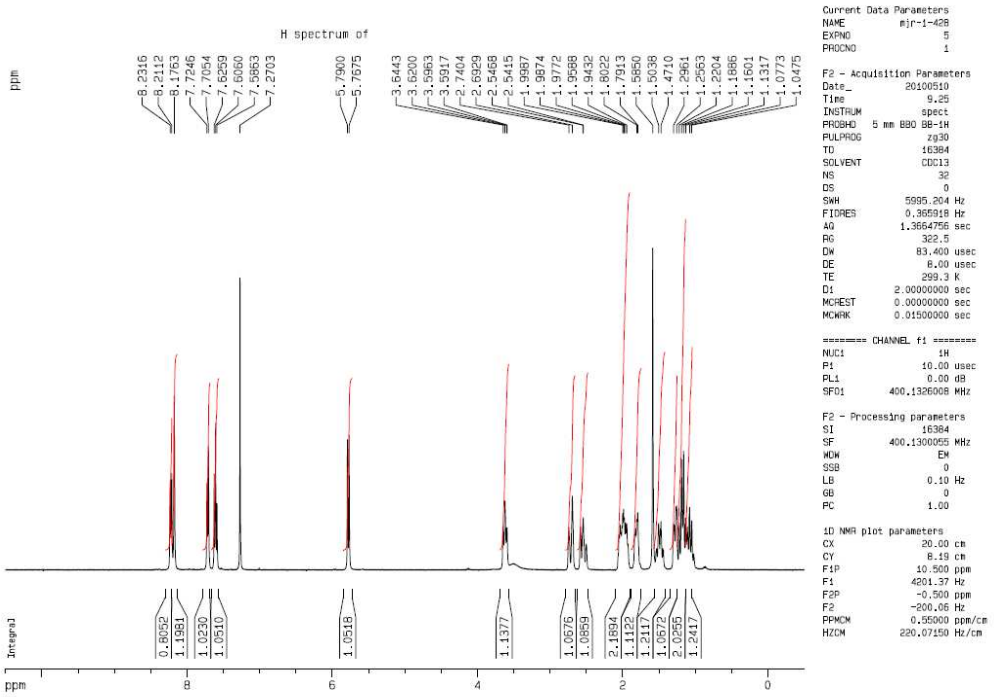

**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (anti) (10a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



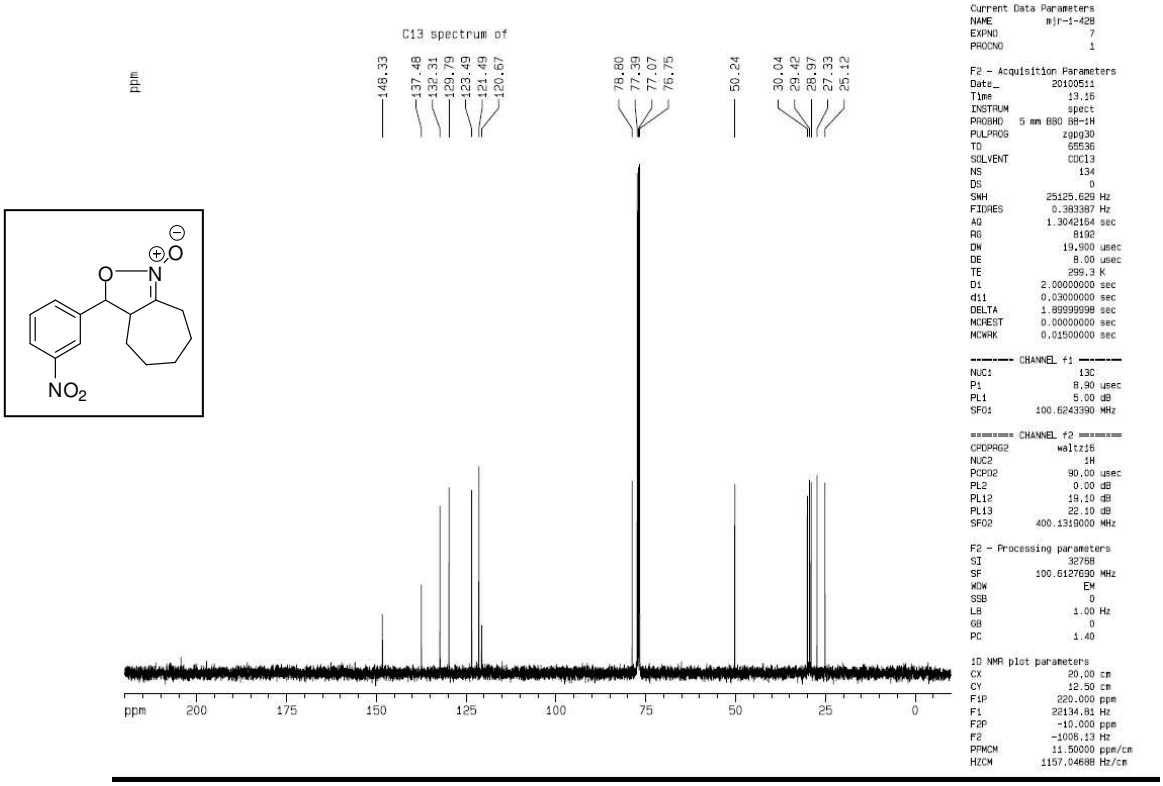

**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (anti) (10a):** $^{13}$C NMR (100 MHz, $CDCl_3$)



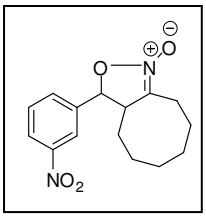

**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (syn) (11a)** $^{1}$H NMR (400 MHz, $CDCl_3$)

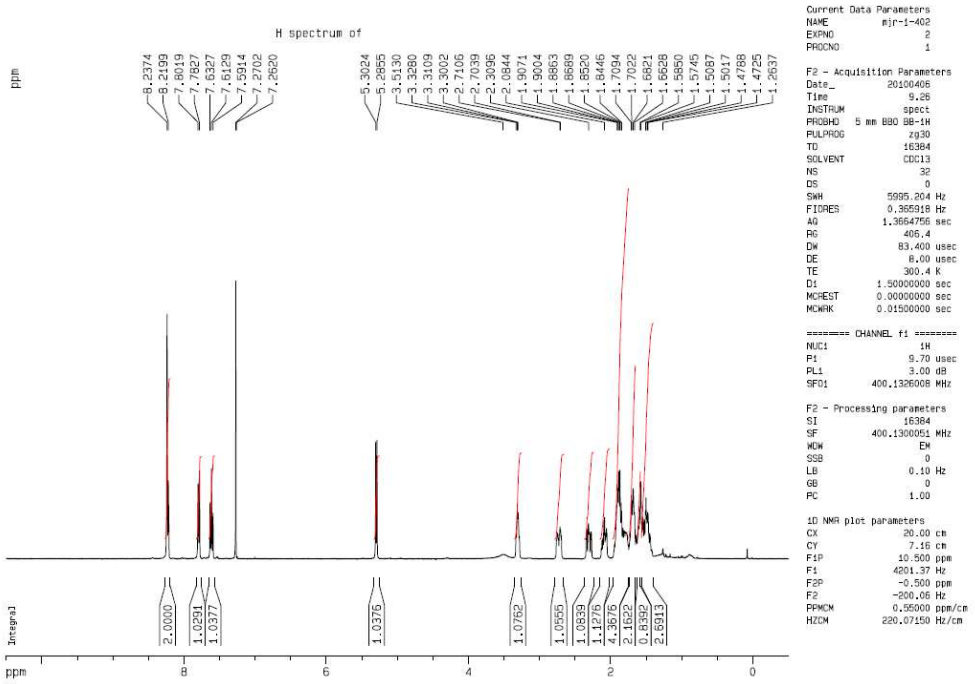



**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (syn) (11a)** $^{13}$C NMR (100 MHz, $CDCl_3$)

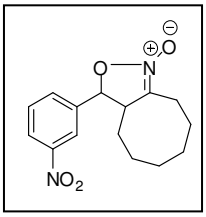


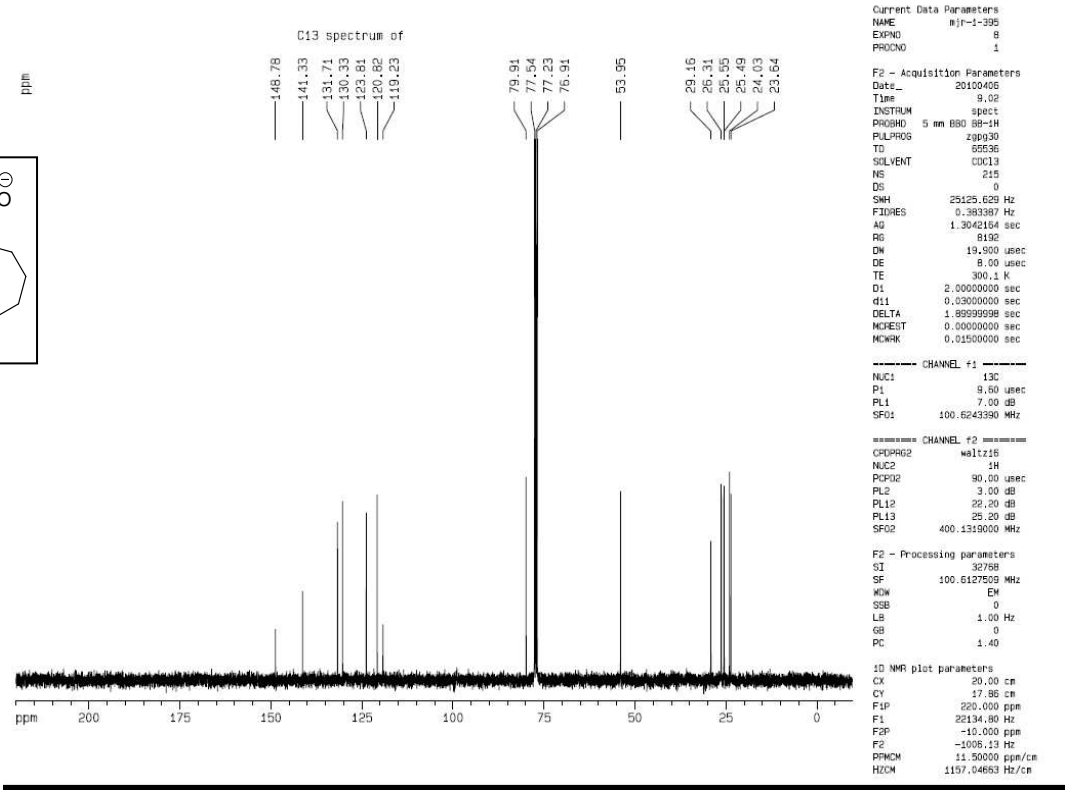

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9-octahydrocycloocta[c]isoxazole-1-oxide (anti) (12a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



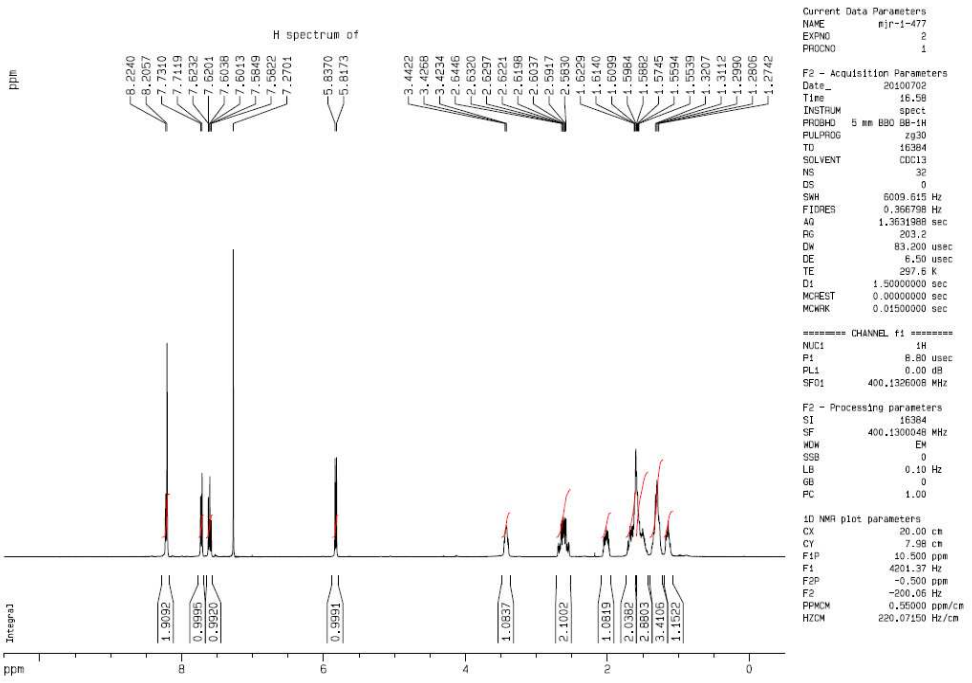



**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9-octahydrocycloocta[c]isoxazole-1-oxide (anti) (12a)** $^{13}C$ NMR (100 MHz, $CDCl_3$)

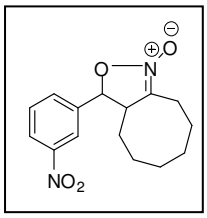


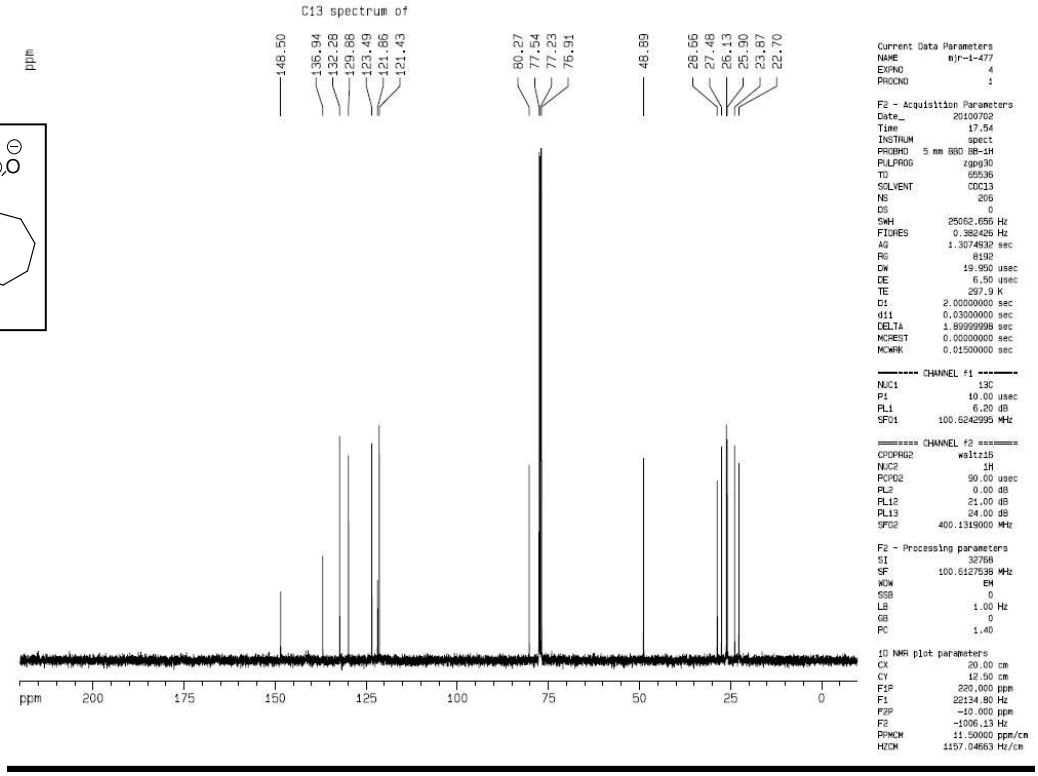



**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9-octahydrocycloocta[c]isoxazole-1-oxide (syn) (13a)** $^{1}H$ NMR (400 MHz, $CDCl_3$)

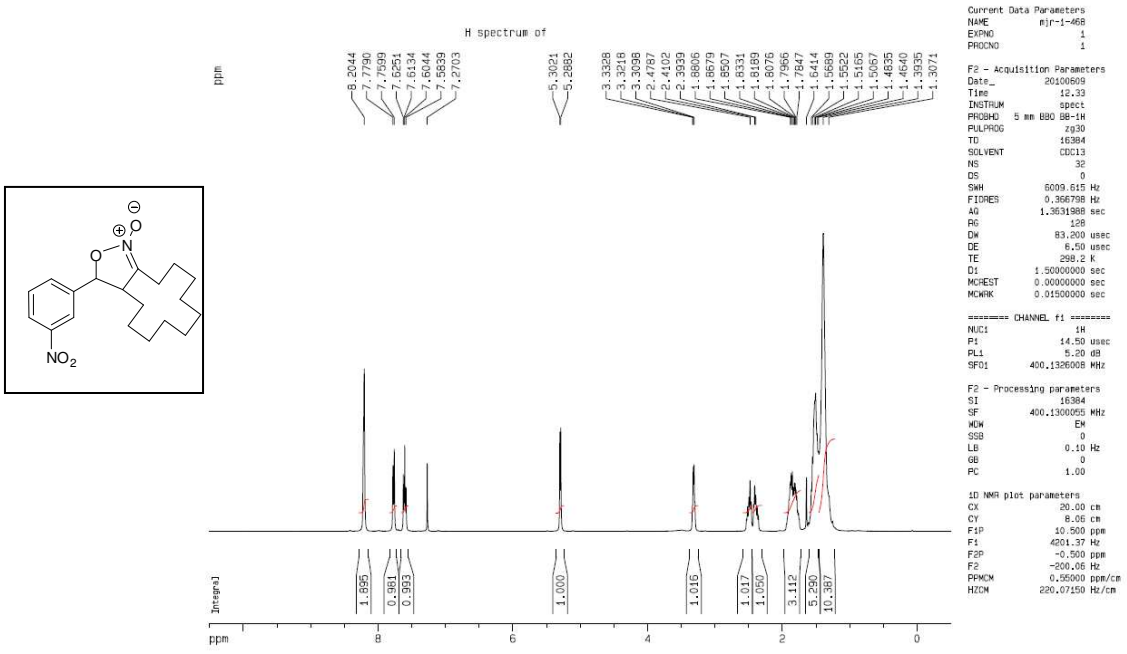



**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9-octahydrocycloocta[c]isoxazole-1-oxide (syn) (13a)** $^{13}$C NMR (100 MHz, $CDCl_3$)

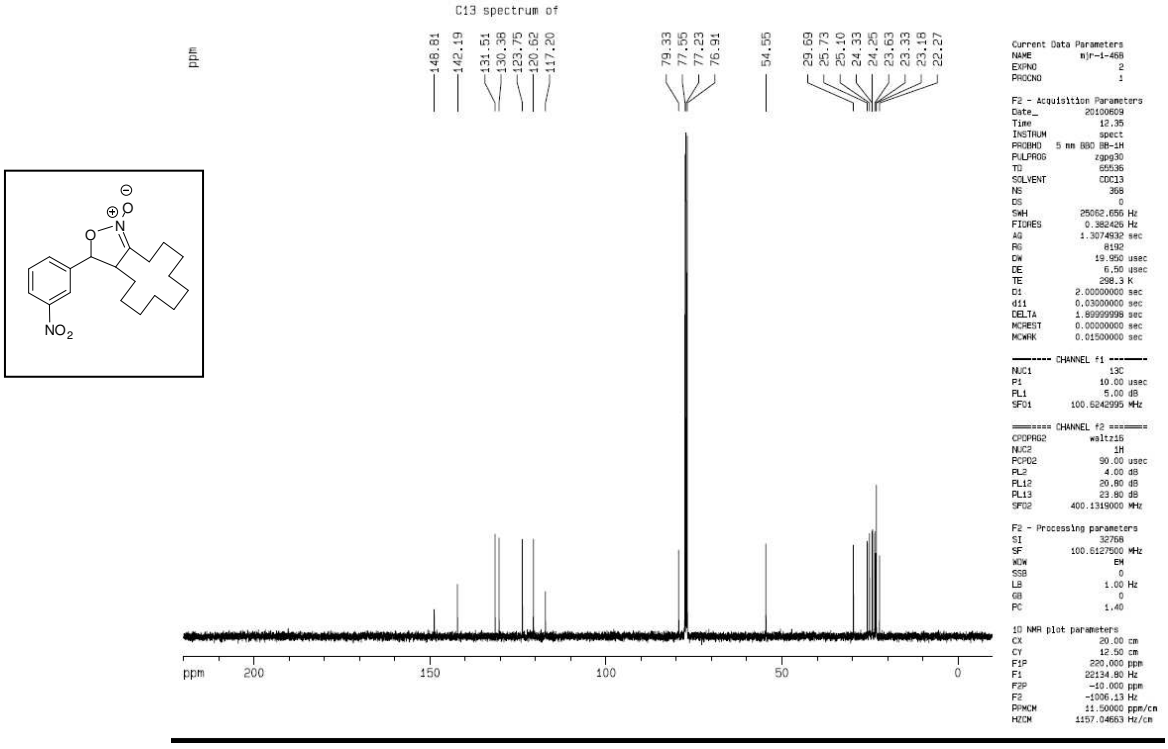


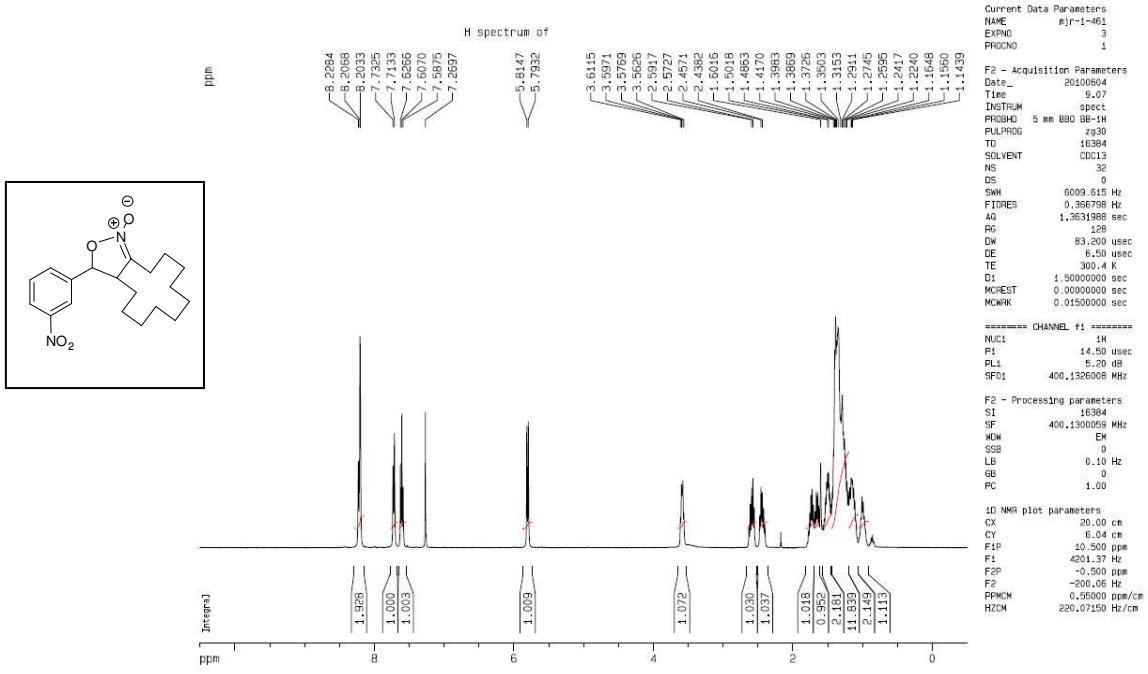

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9,10,11,12,13-dodecahydrocyclododeca[c]isoxazole-1-oxide (anti) (14a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



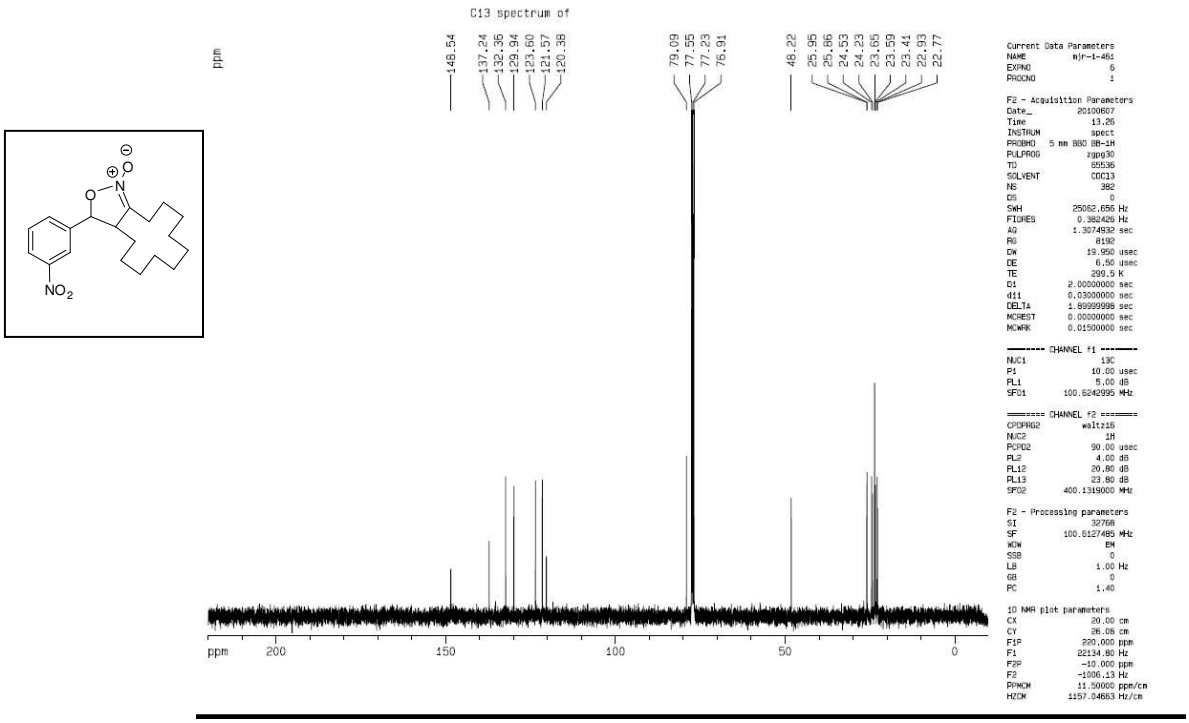

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9,10,11,12,13-dodecahydrocyclododeca[c]isoxazole-1-oxide (anti) (14a)** $^{13}C$ NMR (100 MHz, $CDCl_3$)



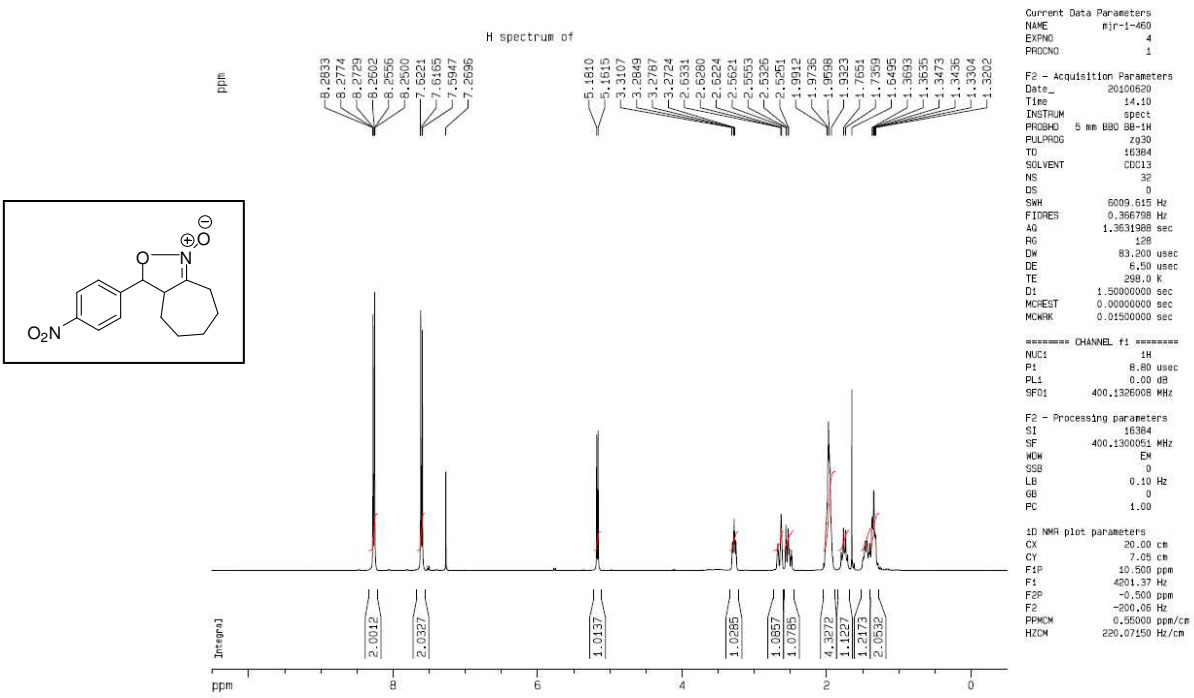

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9,10,11,12,13-dodecahydrocyclododeca[c]isoxazole-1-oxide (syn) (15a)** $^{1}H$ NMR (400 MHz, $CDCl_3$)



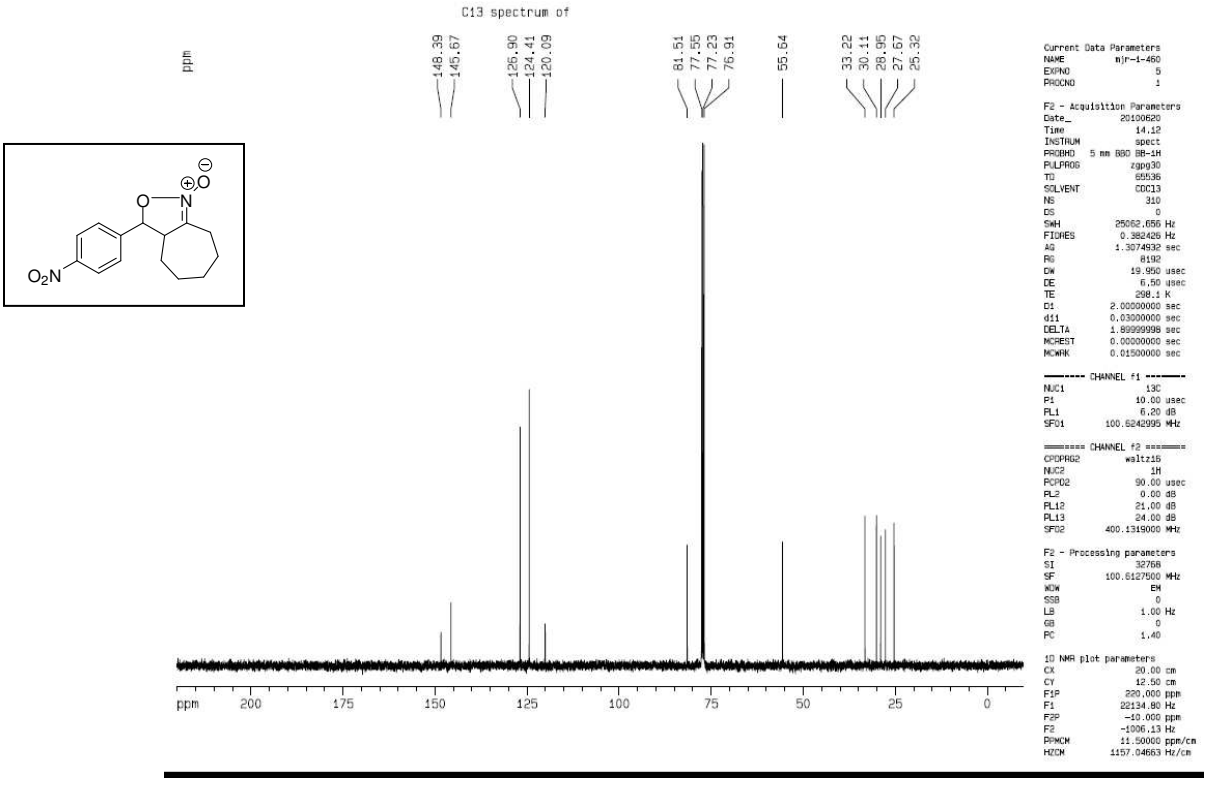

**3-(3-nitrophenyl)-3,3a,4,5,6,7,8,9,10,11,12,13-dodecahydrocyclododeca[c]isoxazole-1-oxide (syn) (15a)** $^{13}C$ NMR (100 MHz, $CDCl_3$)



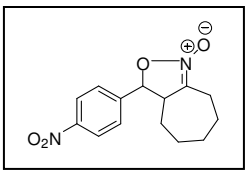

**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (anti) (16a)** $^{1}H$ NMR (400 MHz, $CDCl_3$)

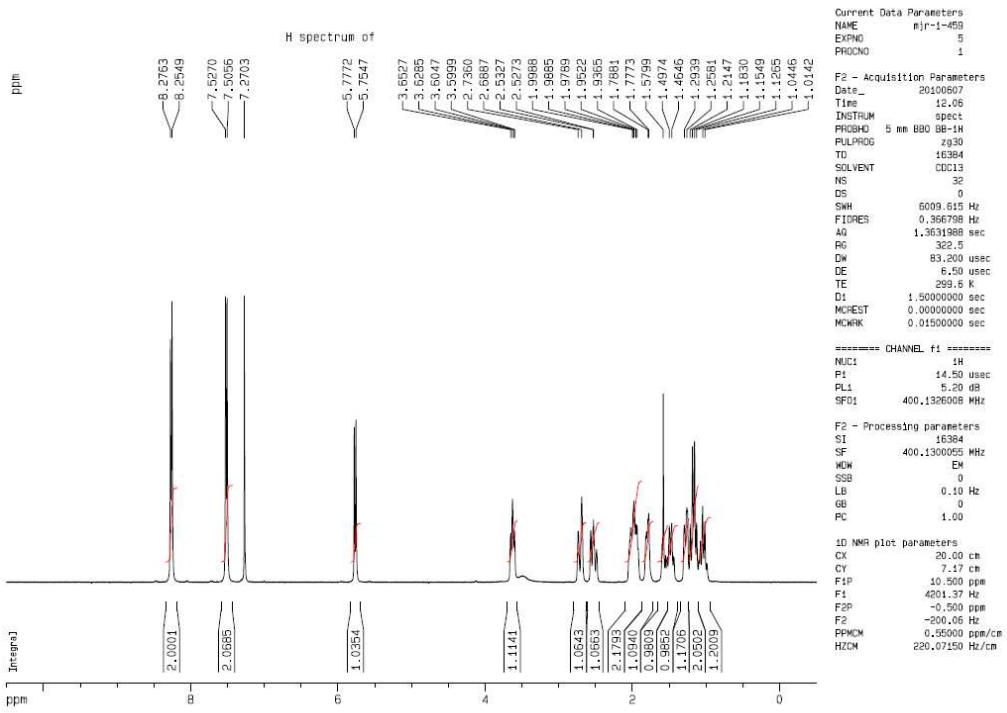


**3-(4-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (anti) (16a)** $^{13}$C NMR (100 MHz, $CDCl_3$)

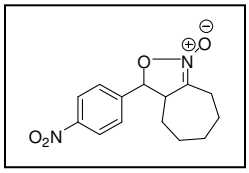


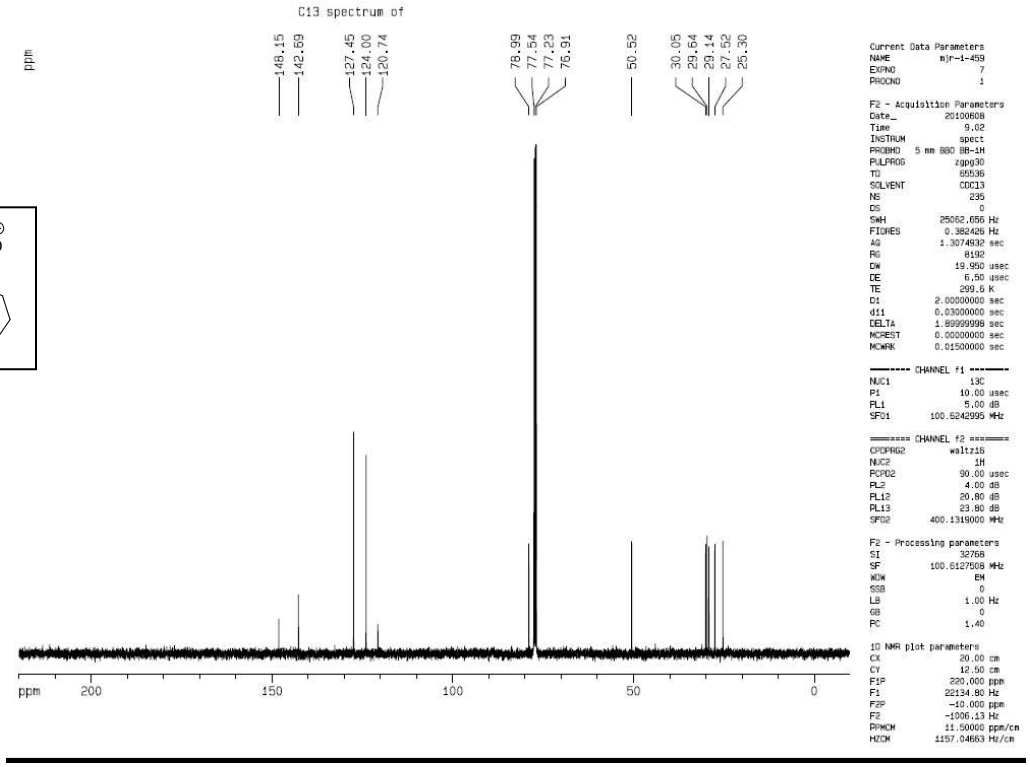
**3-(4-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (syn) (17a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



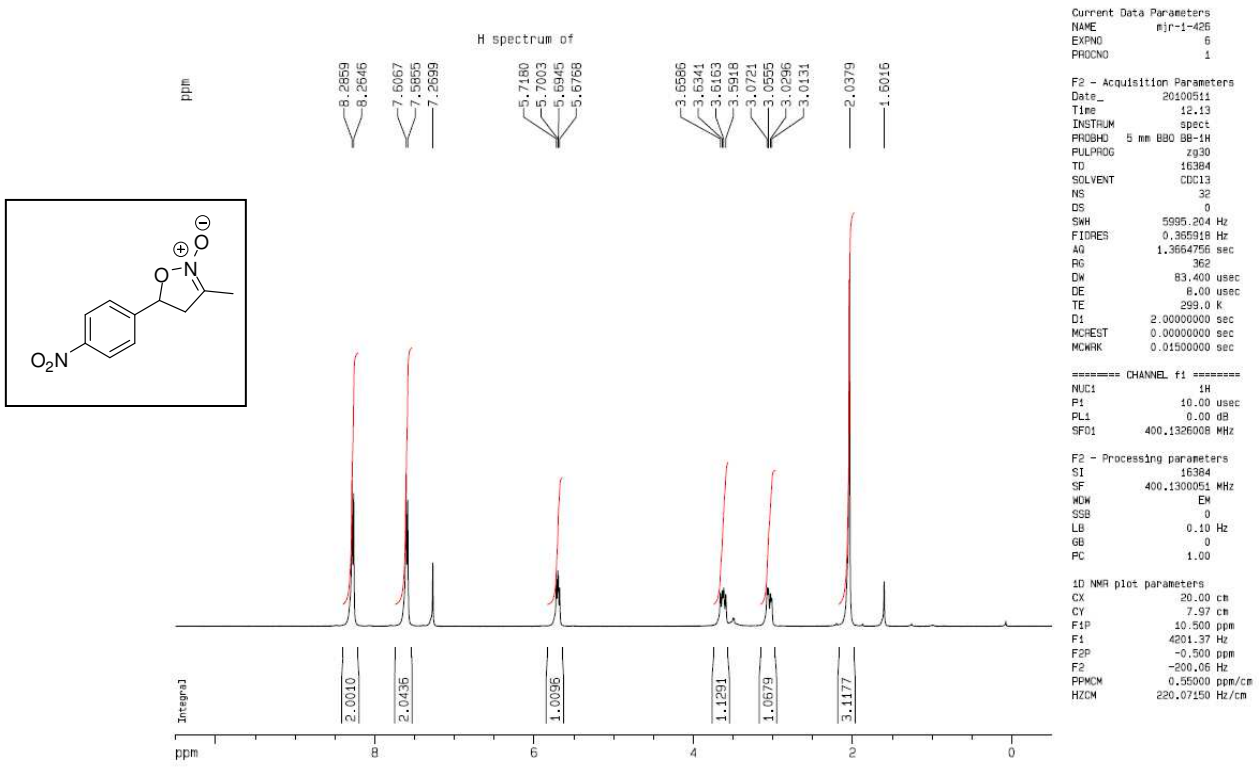



**3-(3-nitrophenyl)-3a,4,5,6,7,8-hexahydro-3H-cyclohepta[c]isoxazole-1-oxide (syn) (17a)** $^{13}$C NMR (100 MHz, $CDCl_3$)

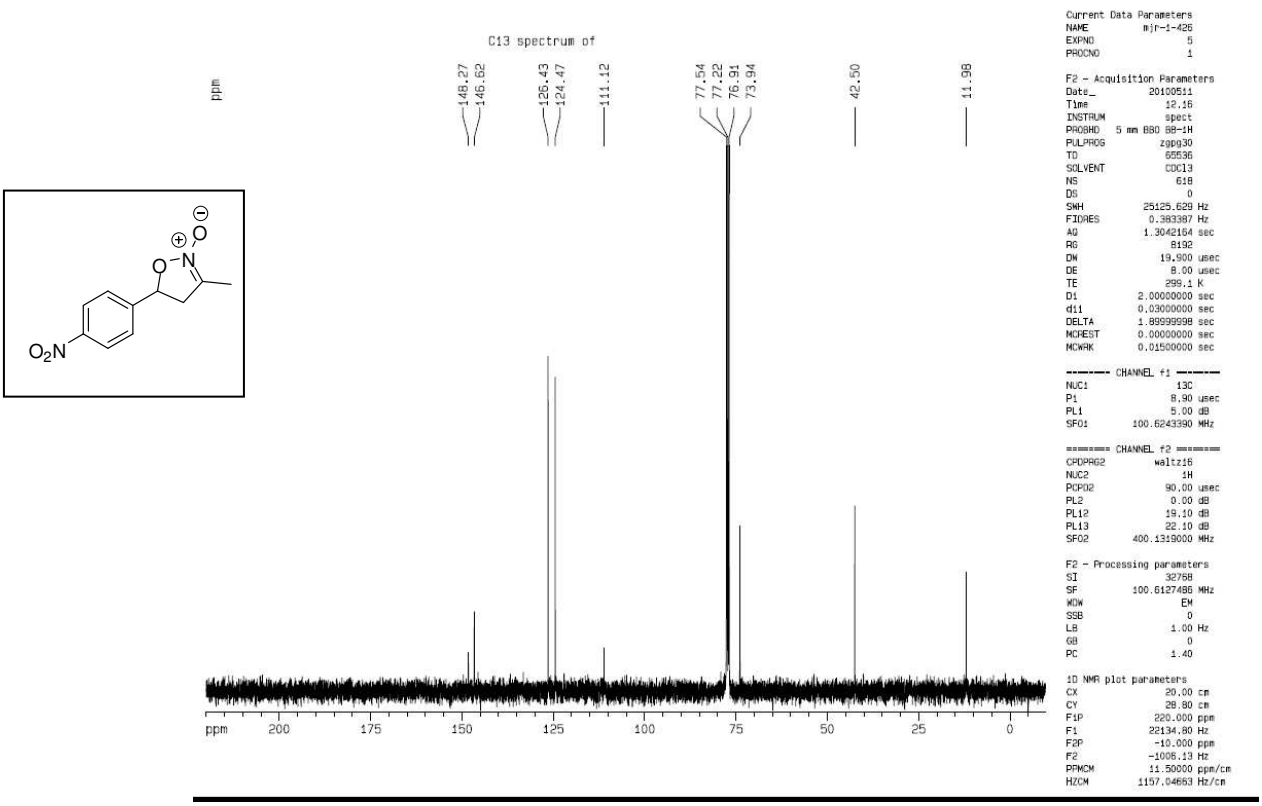




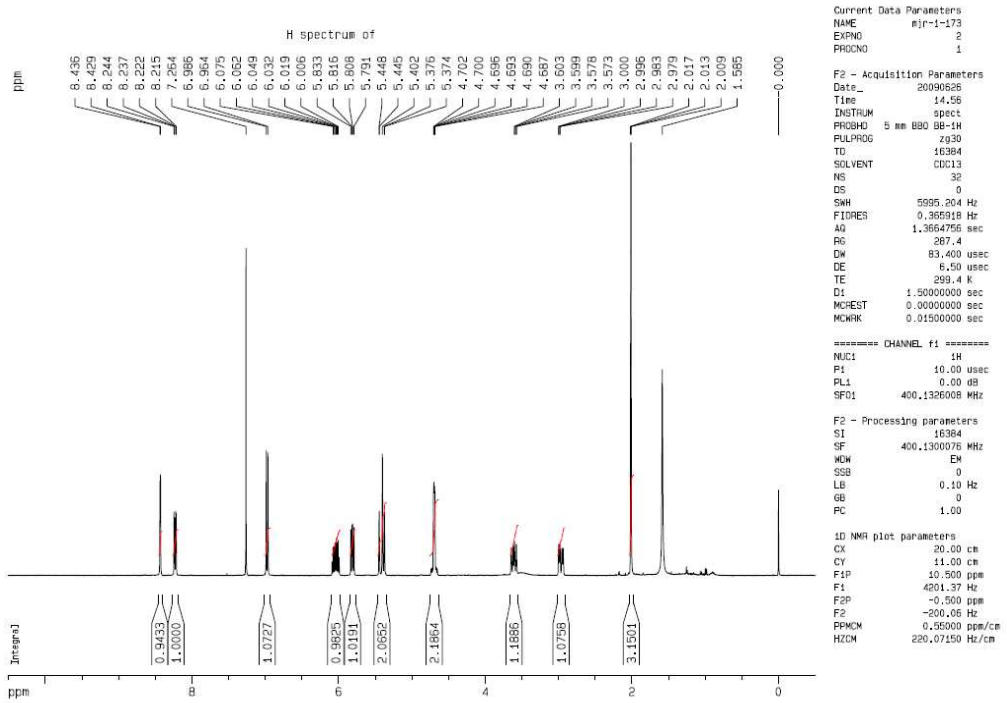

**3-methyl-5-(4-nitrophenyl)-4,5-dihydroisoxazole-2-oxide (18a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



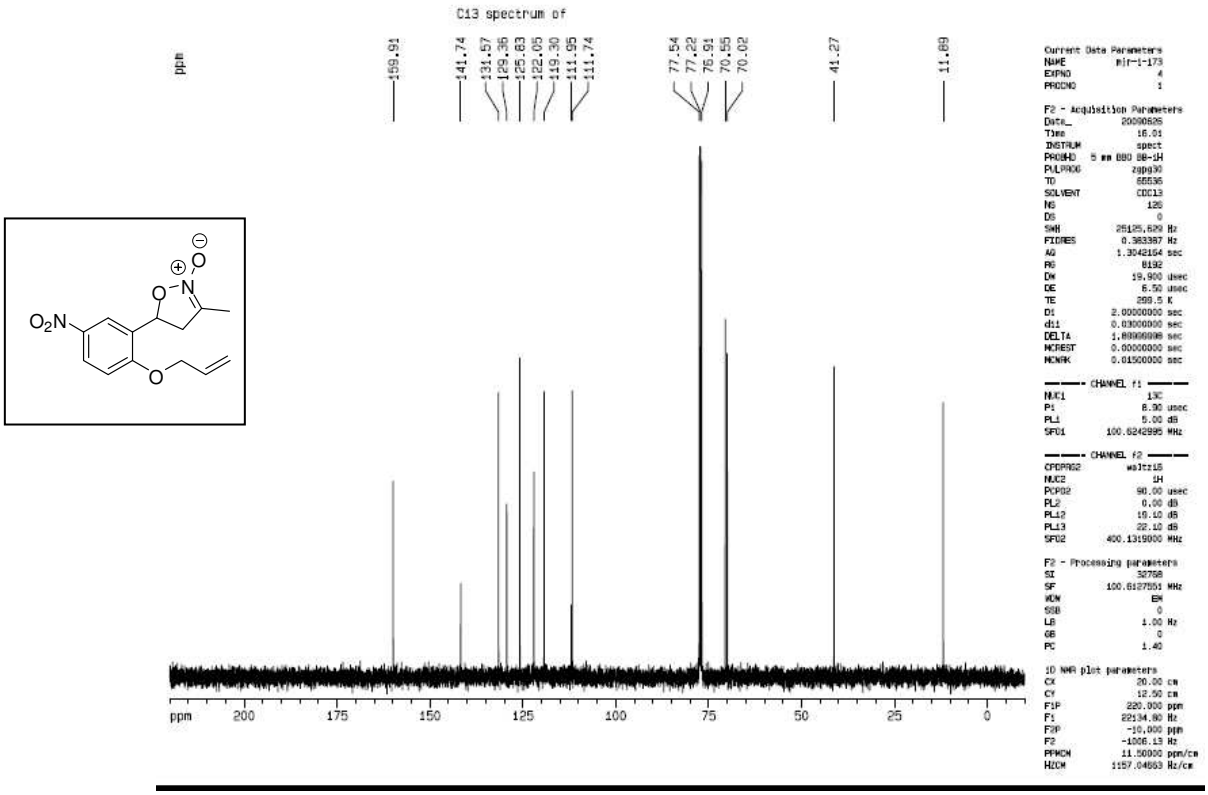

**3-methyl-5-(4-nitrophenyl)-4,5-dihydroisoxazole-2-oxide (18a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



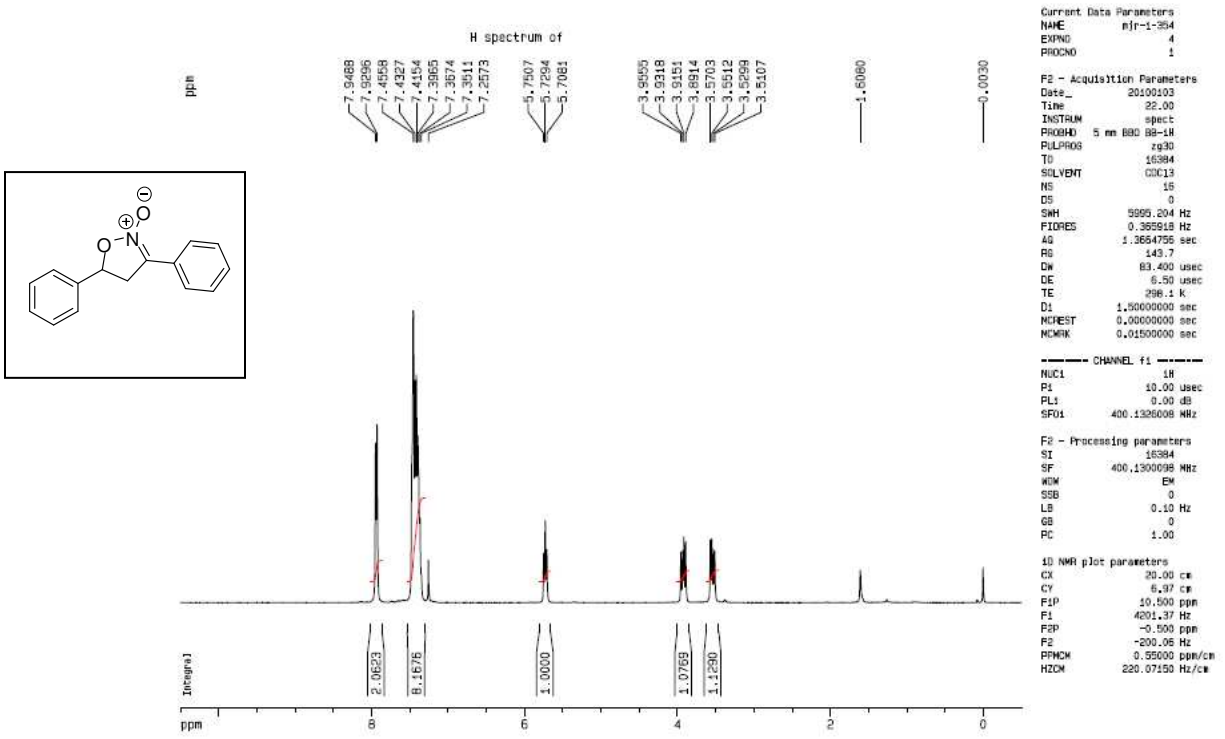

**5-(2-(allyloxy)-5-nitrophenyl)-3-methyl-4,5-dihydroisoxazole-2-oxide (19a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



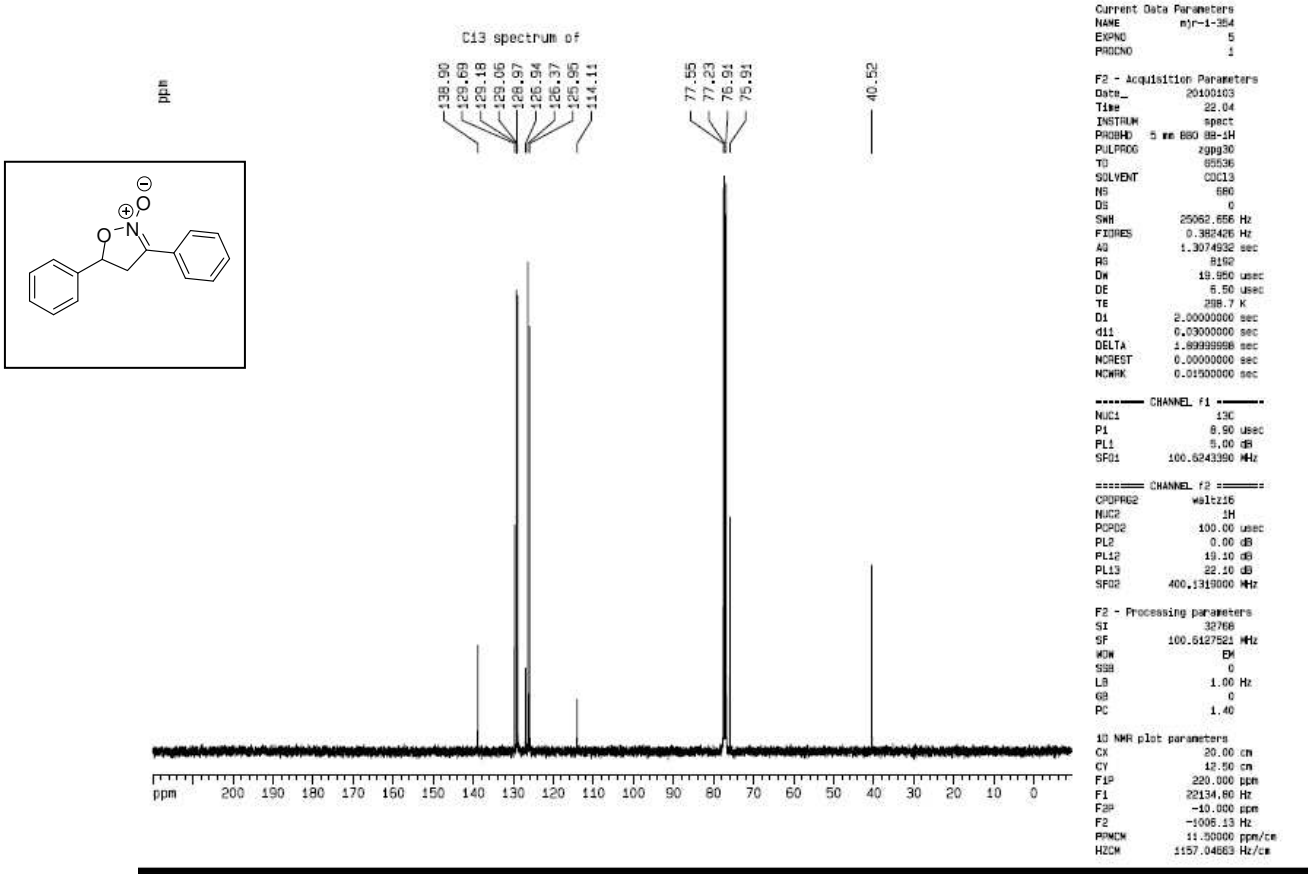

**5-(2-(allyloxy)-5-nitrophenyl)-3-methyl-4,5-dihydroisoxazole-2-oxide (19a)** $^{13}C$ NMR (100 MHz, $CDCl_3$)



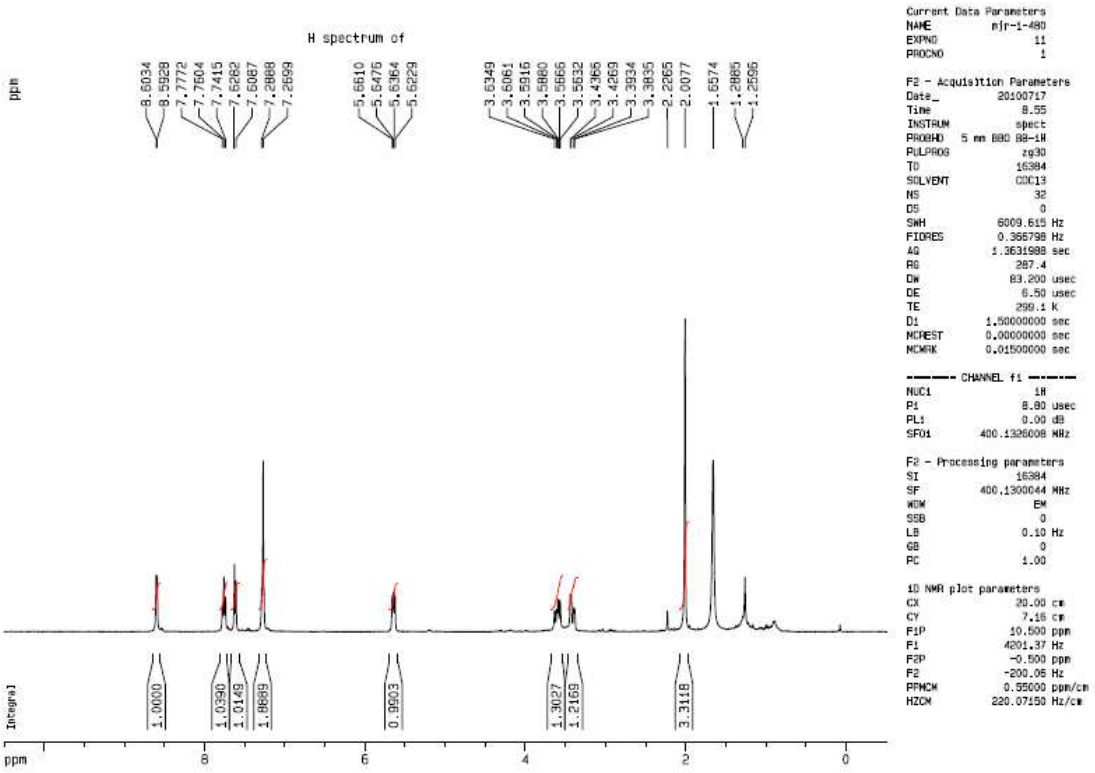

**3,5-diphenyl-4,5-dihydroisoxazole-2-oxide (20a)** $^{1}H$ NMR (400 MHz, $CDCl_3$)



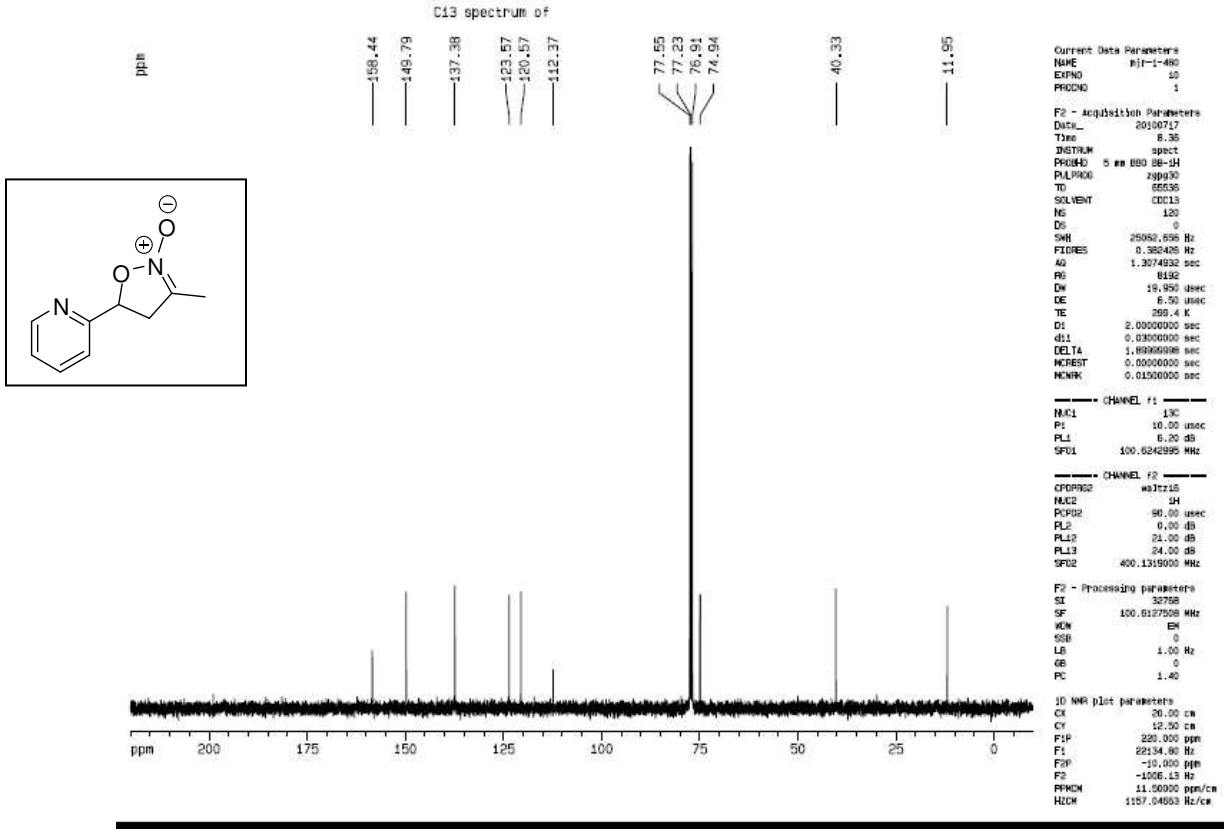

**3,5-diphenyl-4,5-dihydroisoxazole-2-oxide (20a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



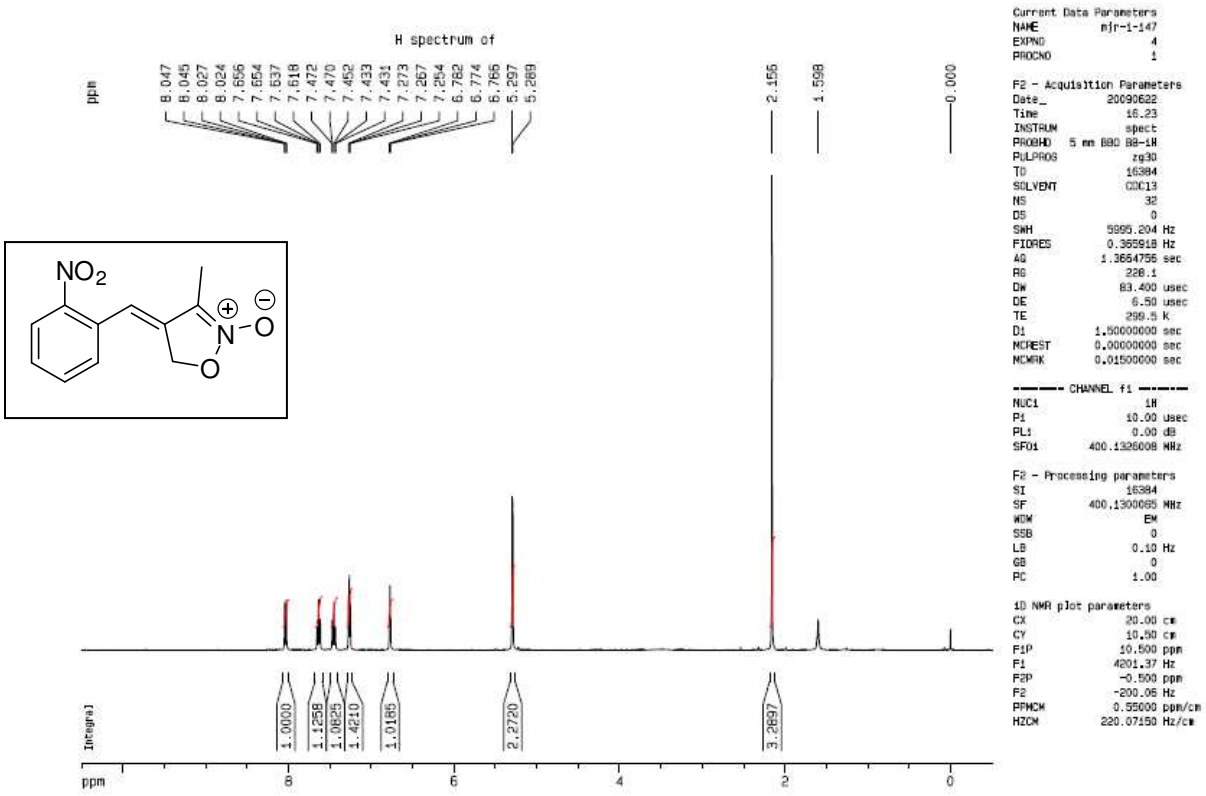

**3-methyl-5-(pyridine-2-yl)-4,5-dihydroisoxazole-2-oxide (21a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



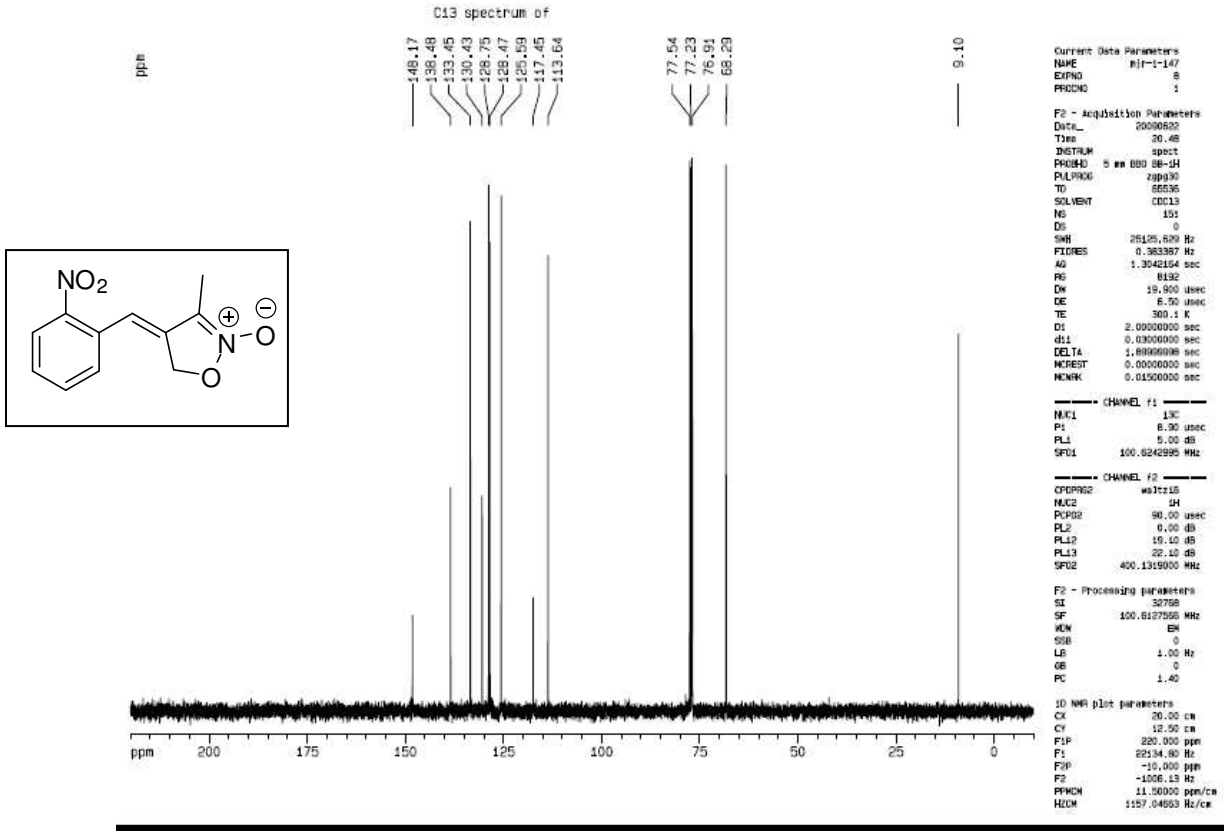

**3-methyl-5-(pyridine-2-yl)-4,5-dihydroisoxazole-2-oxide (21a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



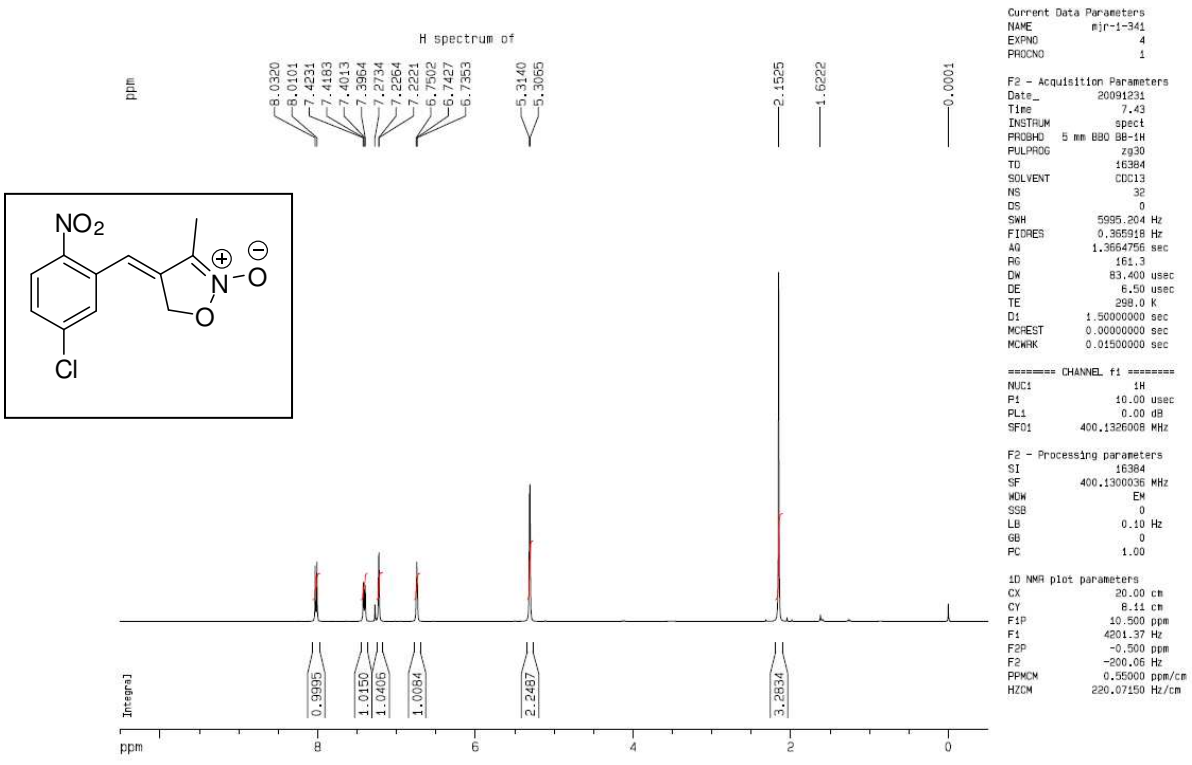

**3-methyl-4-(2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (22a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



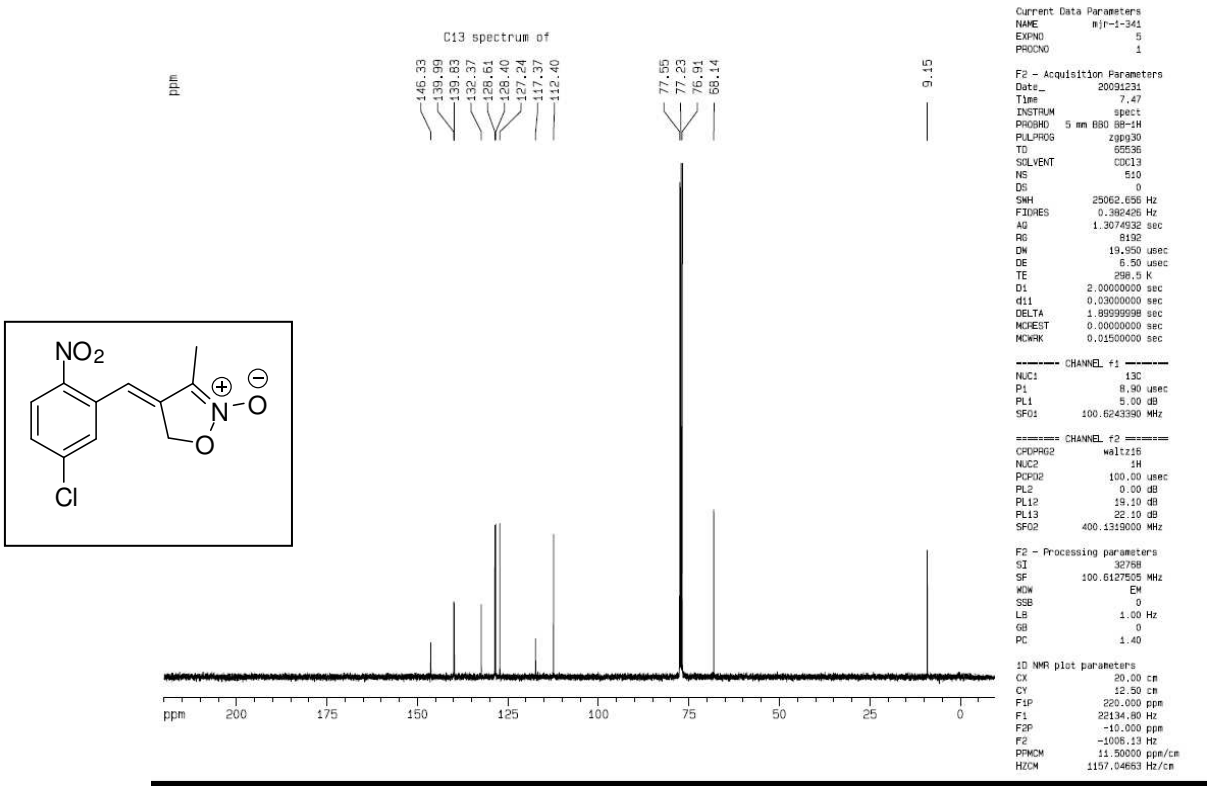

**3-methyl-4-(2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (22a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



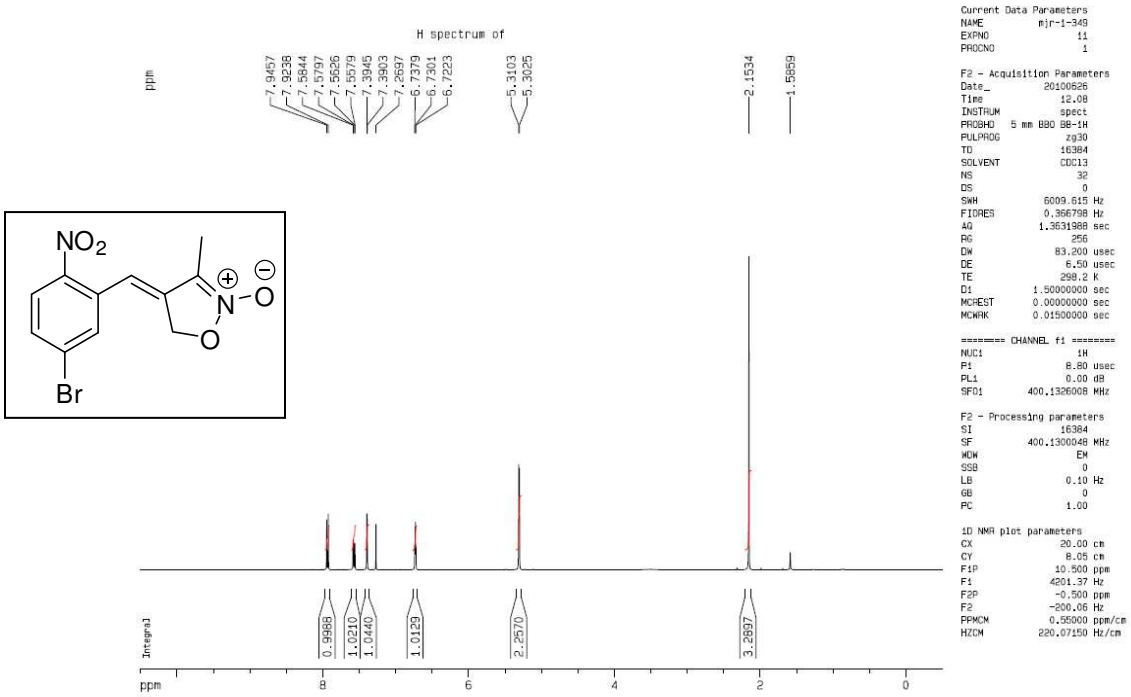

**3-methyl-4-(5-chloro-2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (23a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



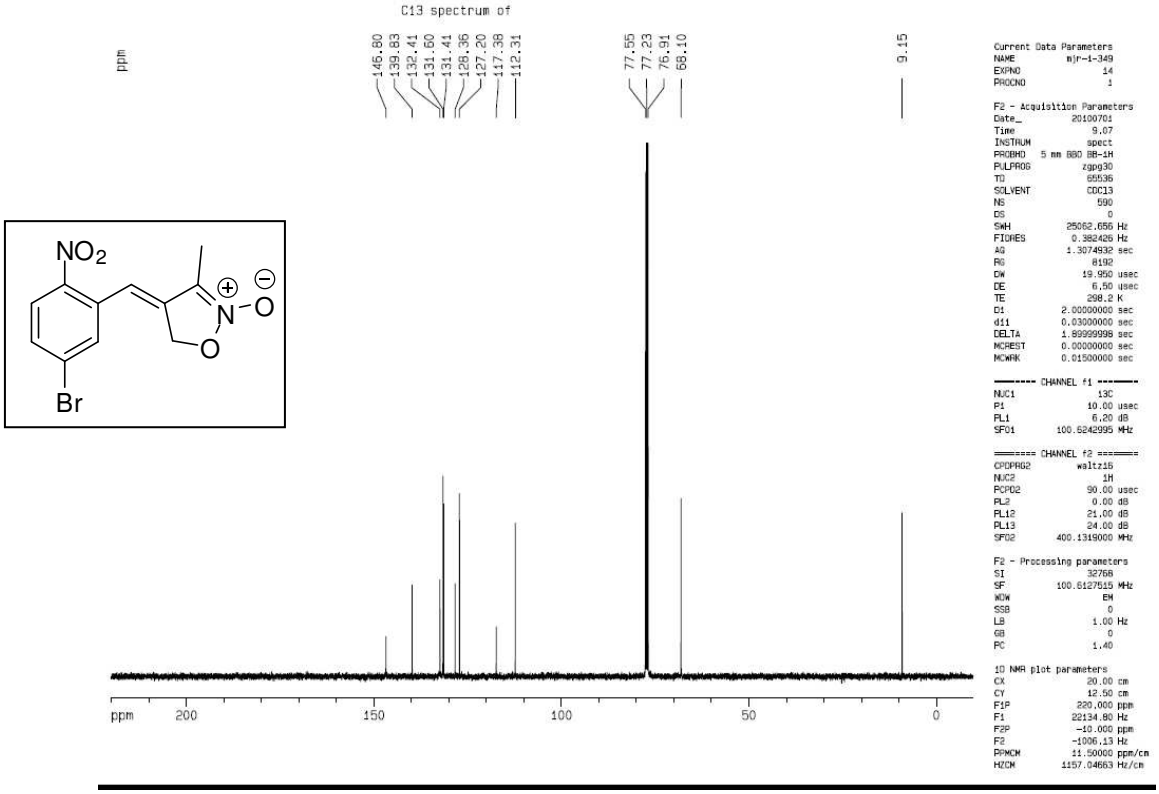

**3-methyl-4-(5-chloro-2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (23a)** $^{13}C$ NMR (100 MHz, $CDCl_3$)



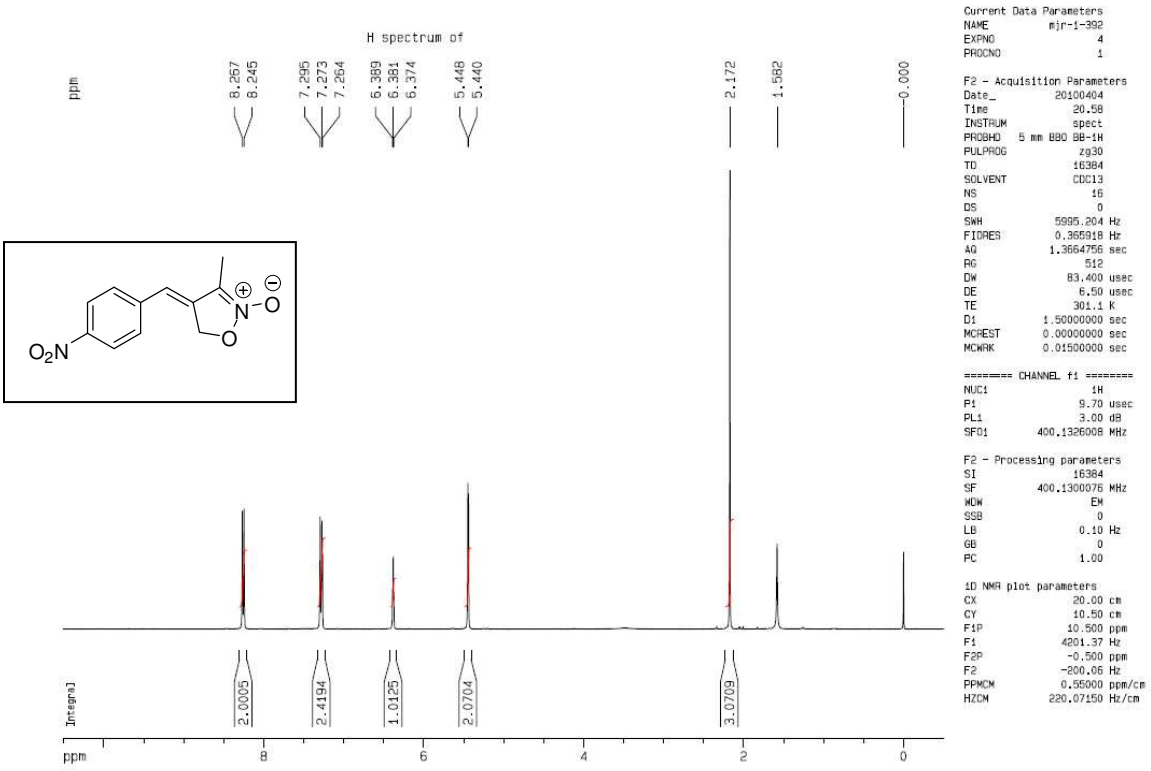

**3-methyl-4-(5-bromo-2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (24a)** $^{1}H$ NMR (400 MHz, $CDCl_3$)



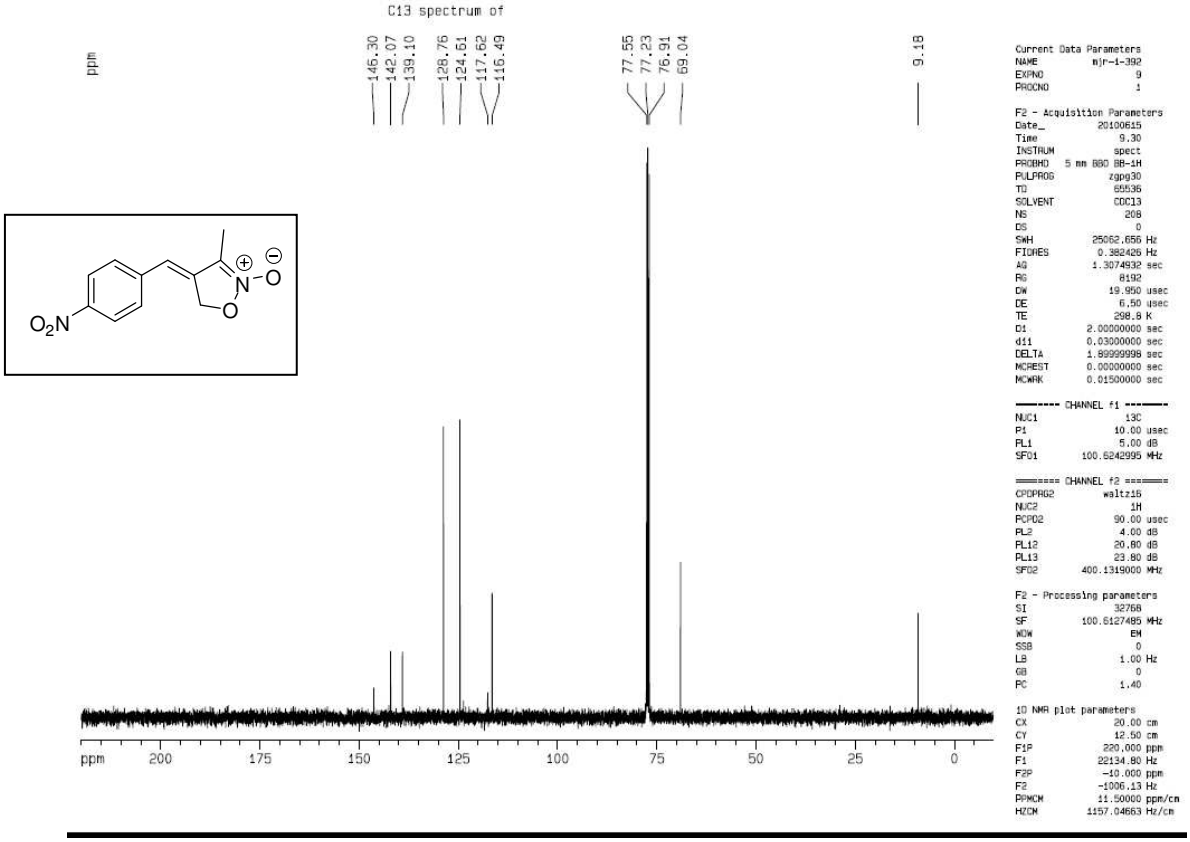

**3-methyl-4-(5-bromo-2-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (24a)** $^{13}C$ NMR (100 MHz, $CDCl_3$)



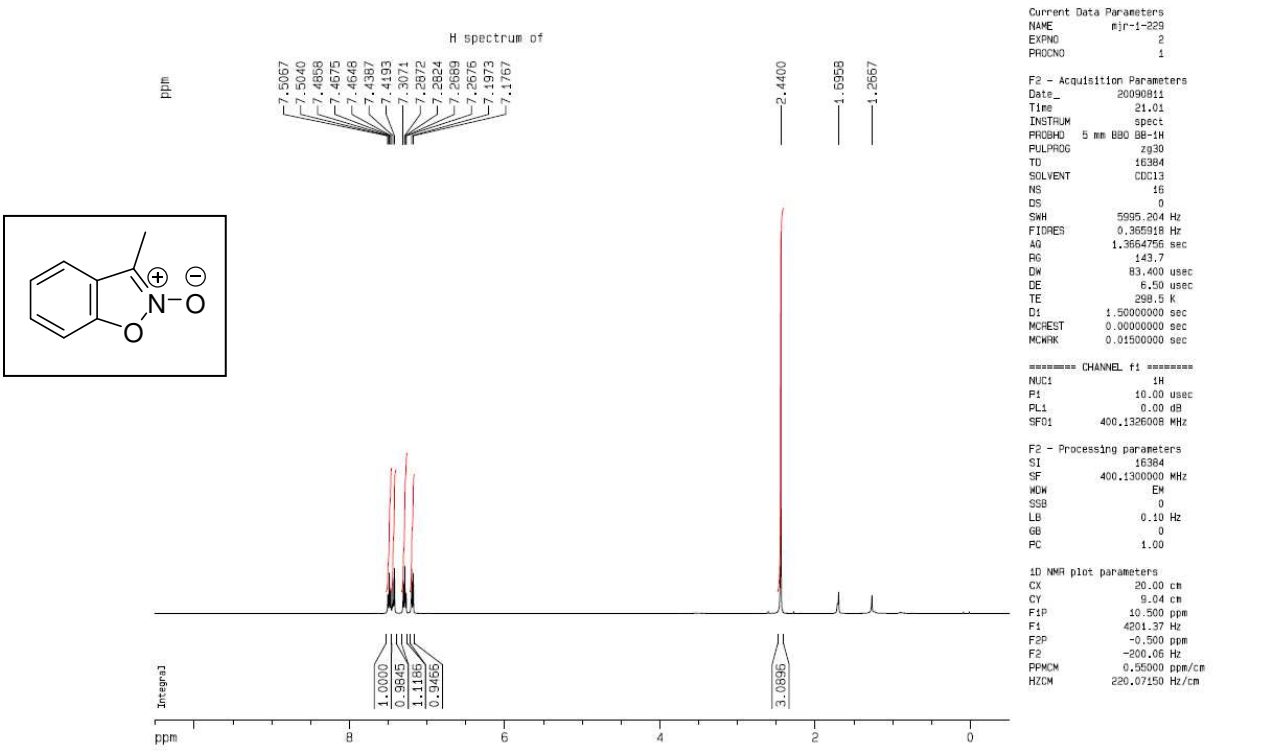

**3-methyl-4-(4-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (25a)** $^{1}H$ NMR (400 MHz, $CDCl_3$)



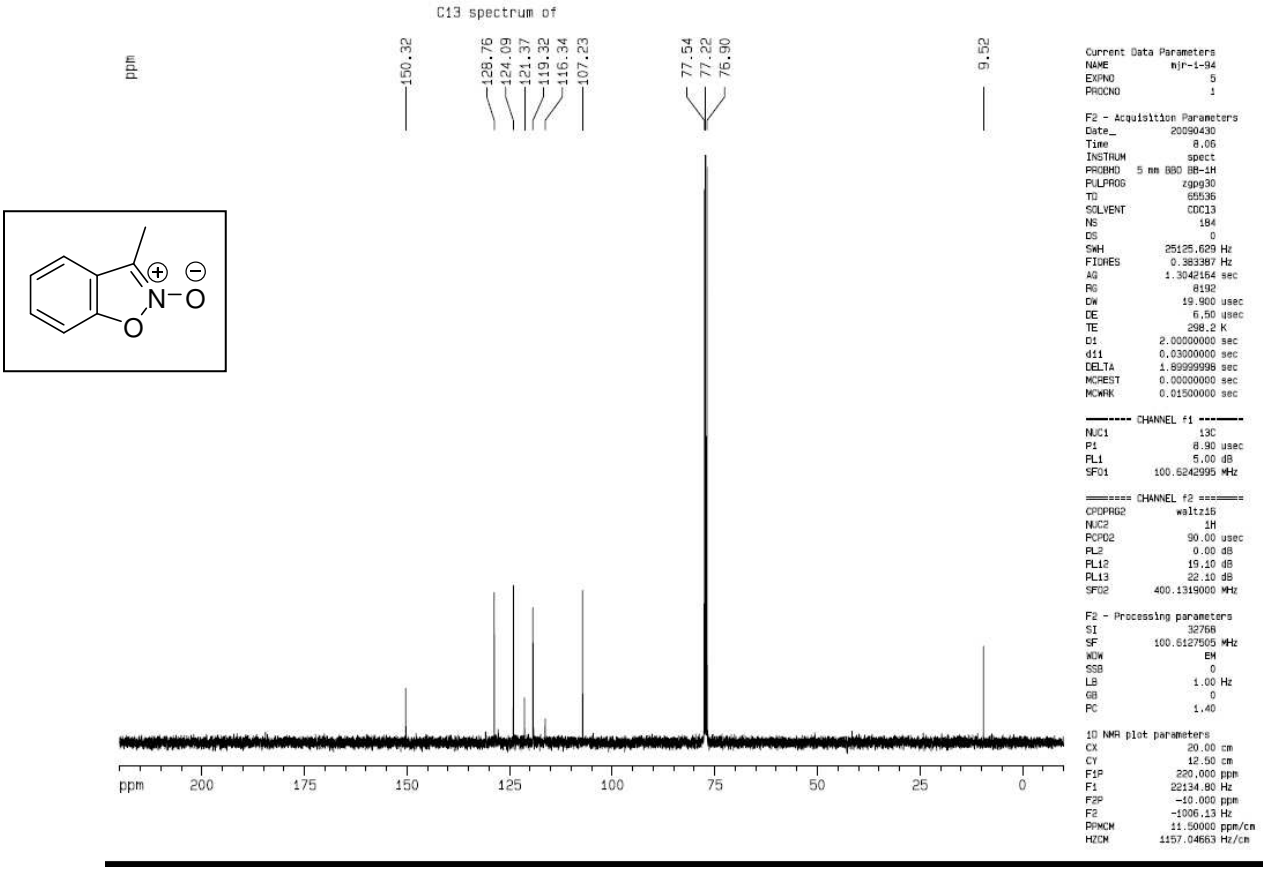

**3-methyl-4-(4-nitrobenzylidene)-4,5-dihydroisoxazole-2-oxide (25a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



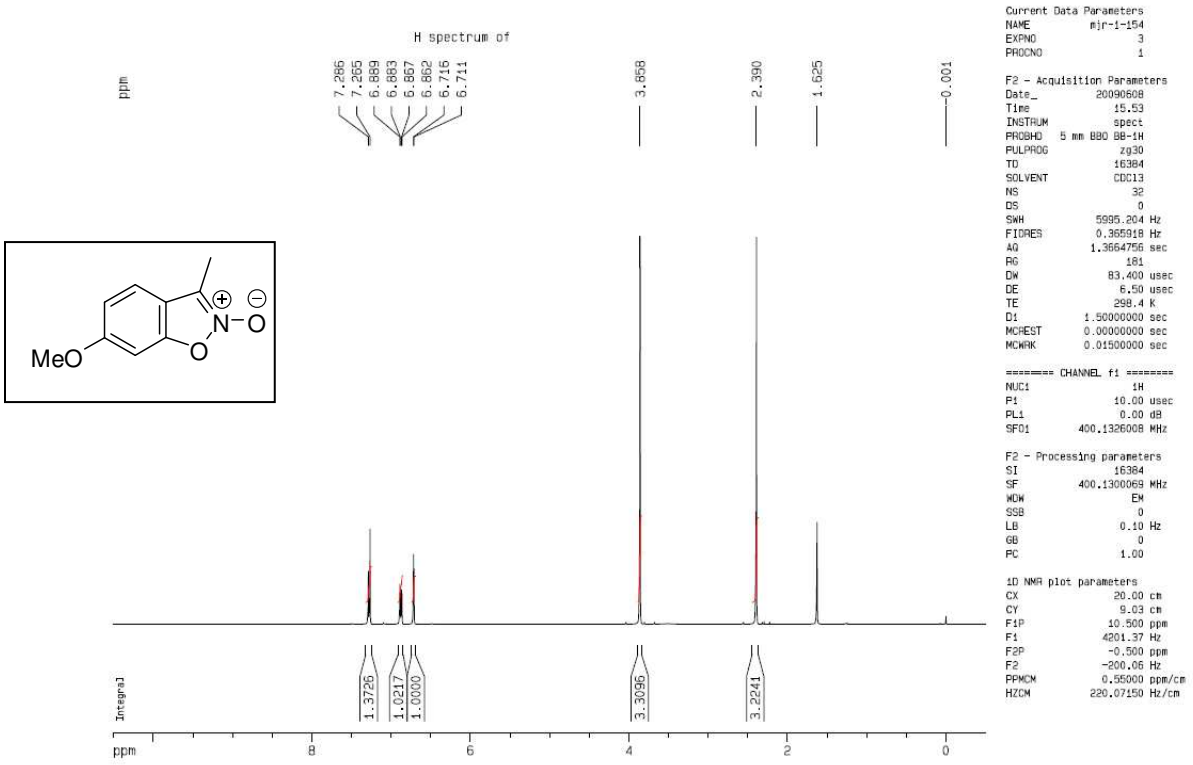

**3-methylbenzo[d]isoxazole-2-oxide (26a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



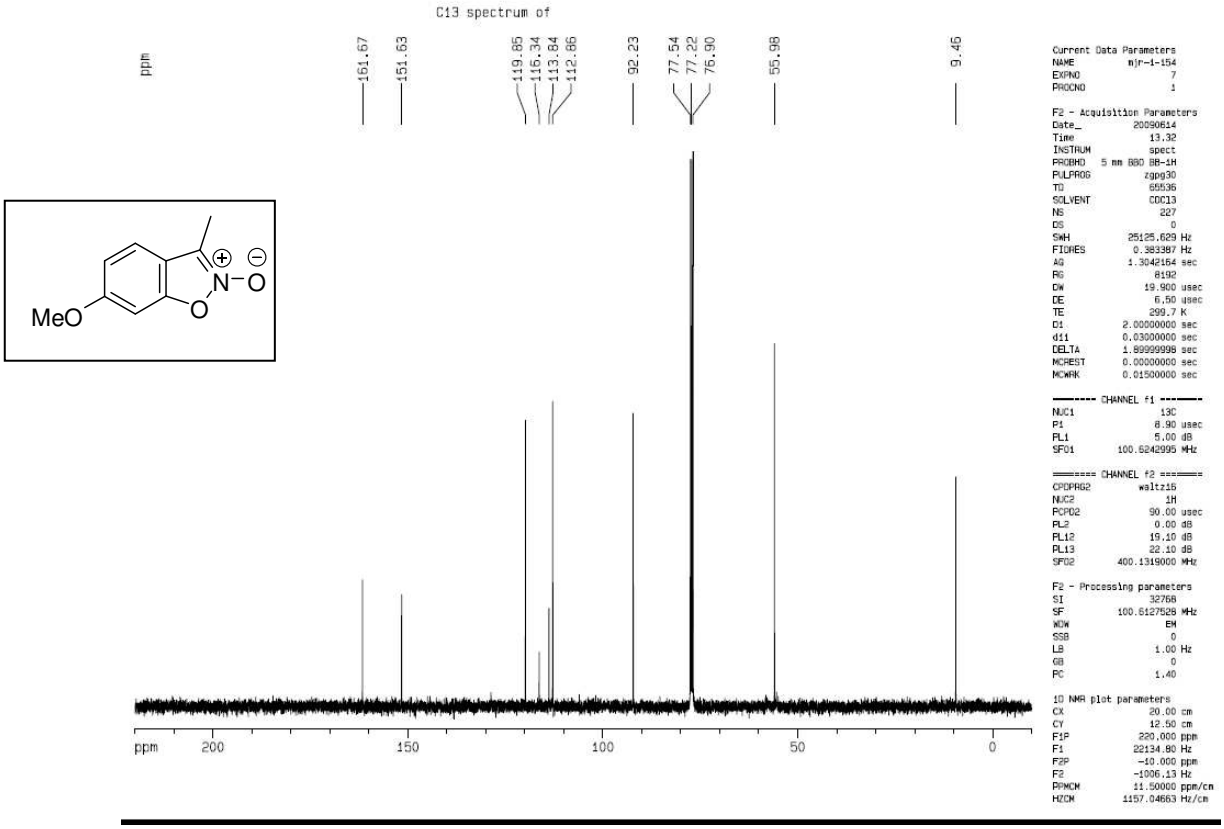

**3-methylbenzo[d]isoxazole-2-oxide (26a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



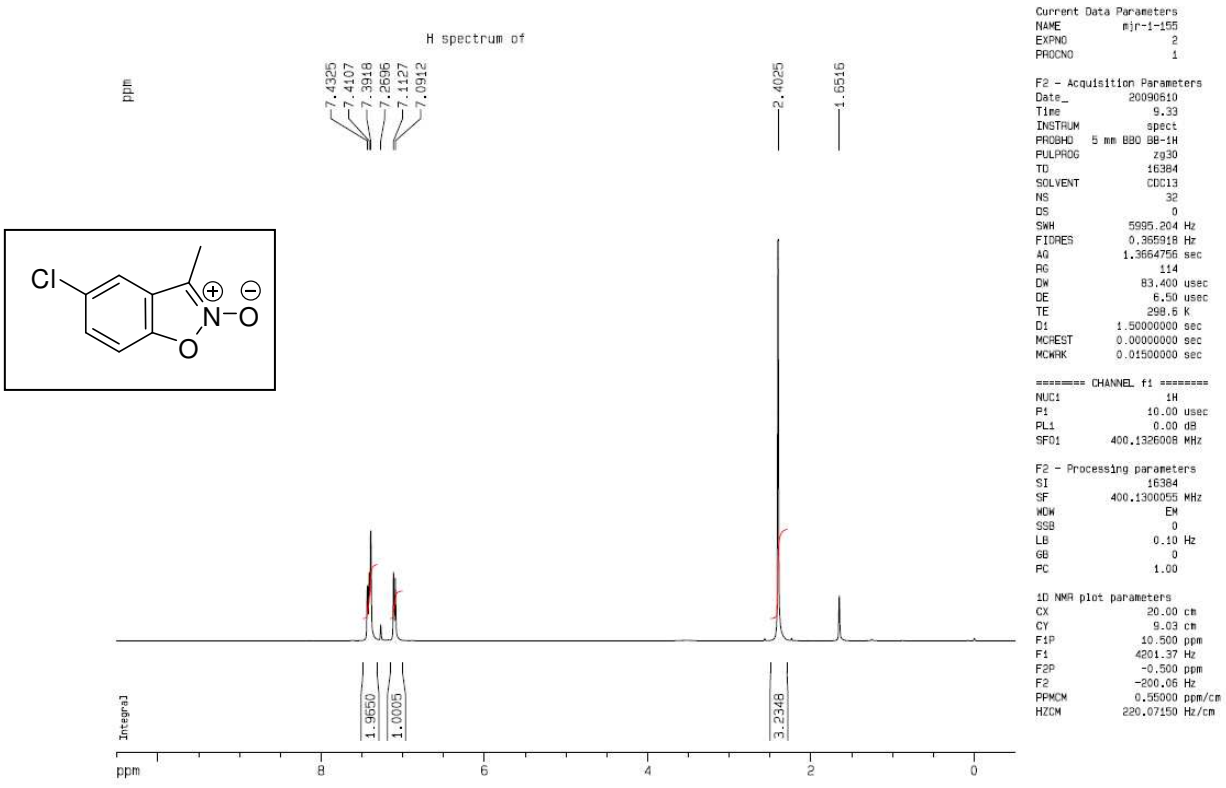

**6-methoxy-3-methylbenzo[d]isoxazole-2-oxide (27a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



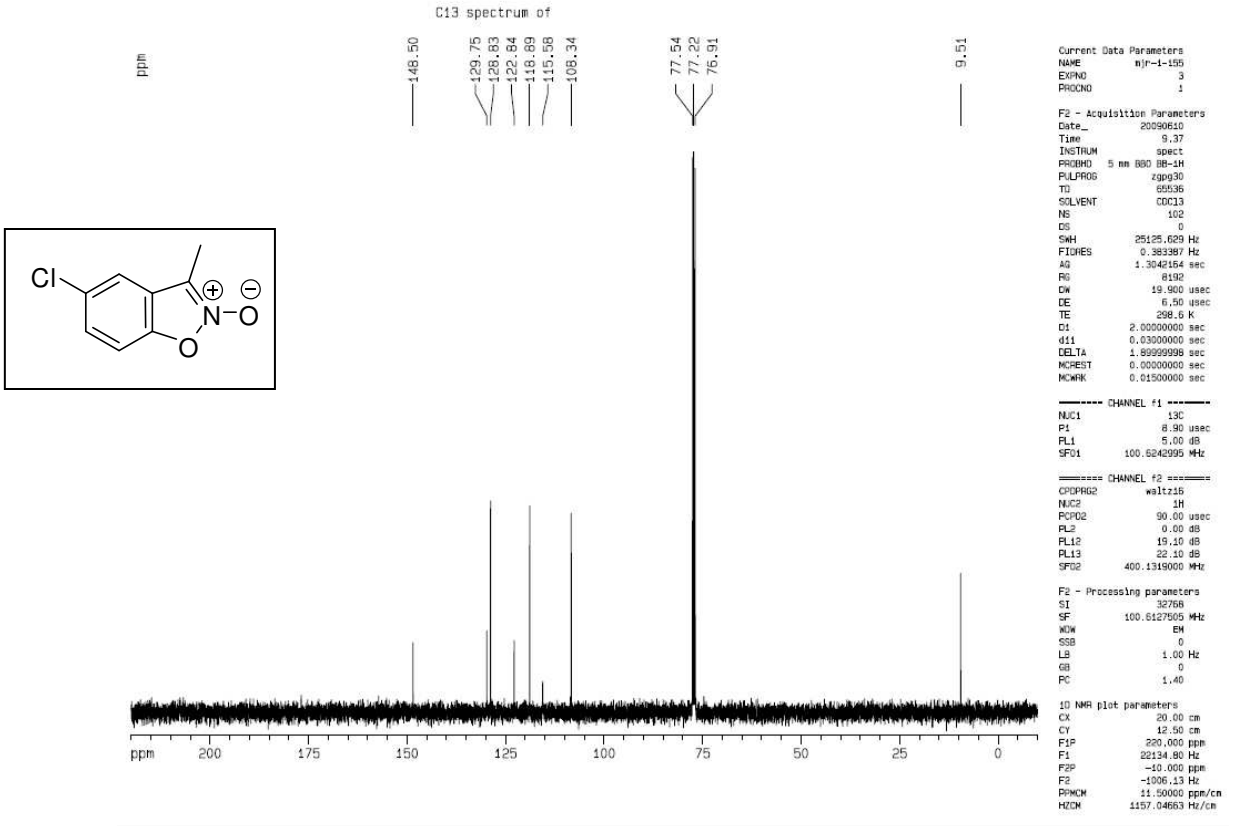

**6-methoxy-3-methylbenzo[d]isoxazole-2-oxide (27a)** $^{13}$C NMR (100 MHz, $CDCl_3$)



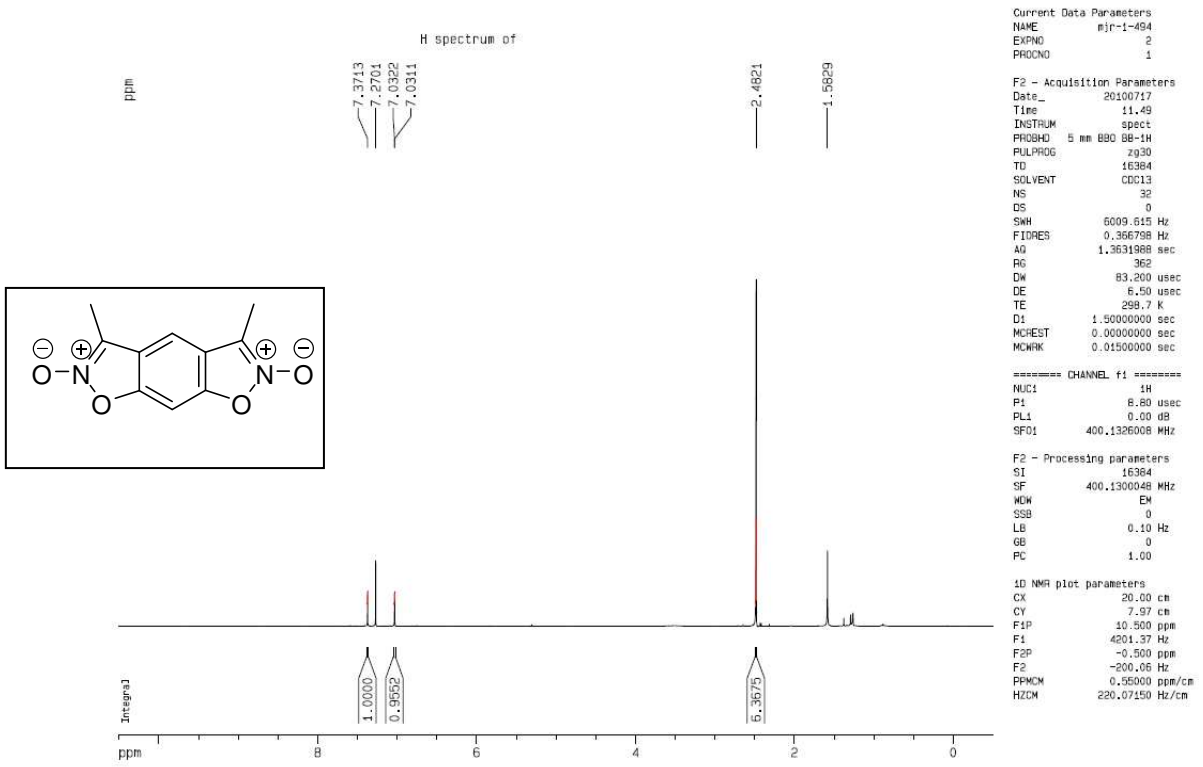

**5-chloro-3-methylbenzo[d]isoxazole-2-oxide (28a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



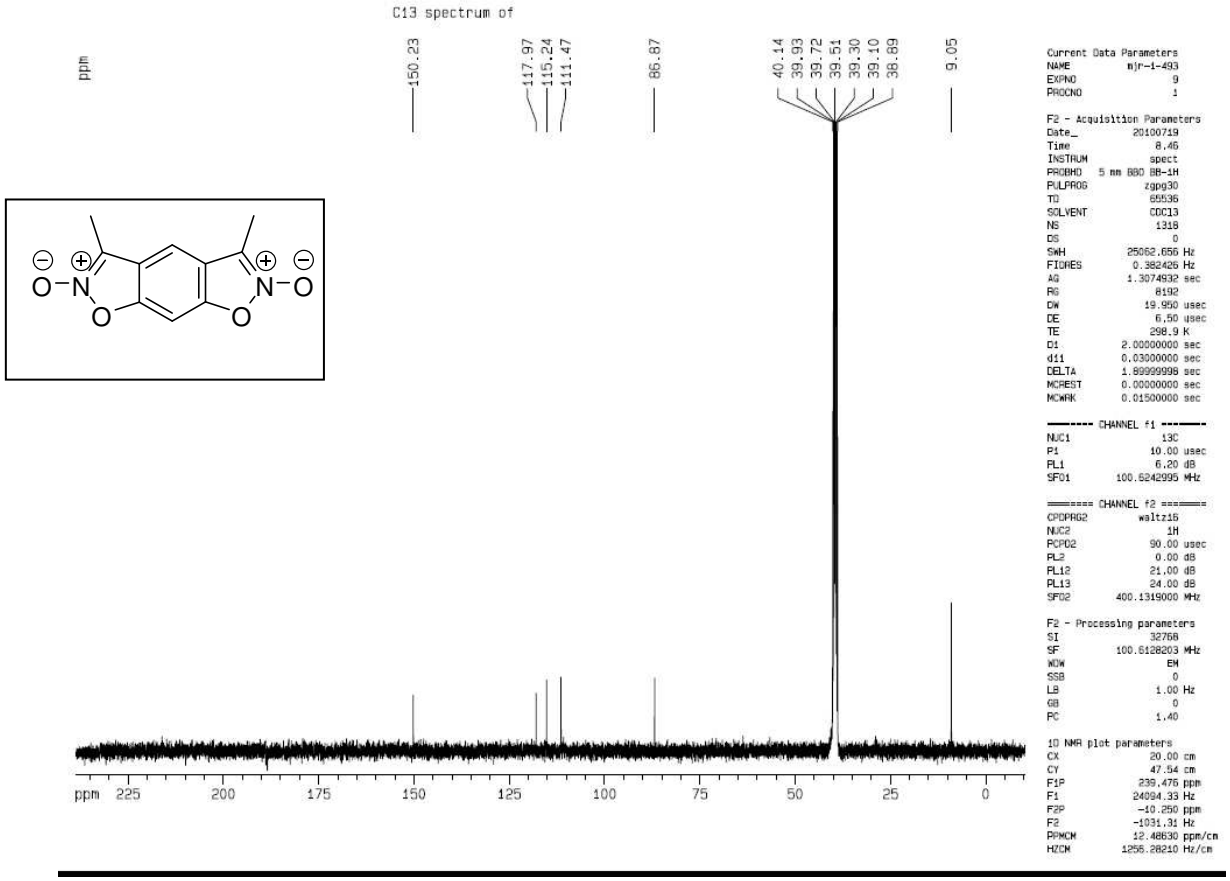

**5-chloro-3-methylbenzo[d]isoxazole-2-oxide (28a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



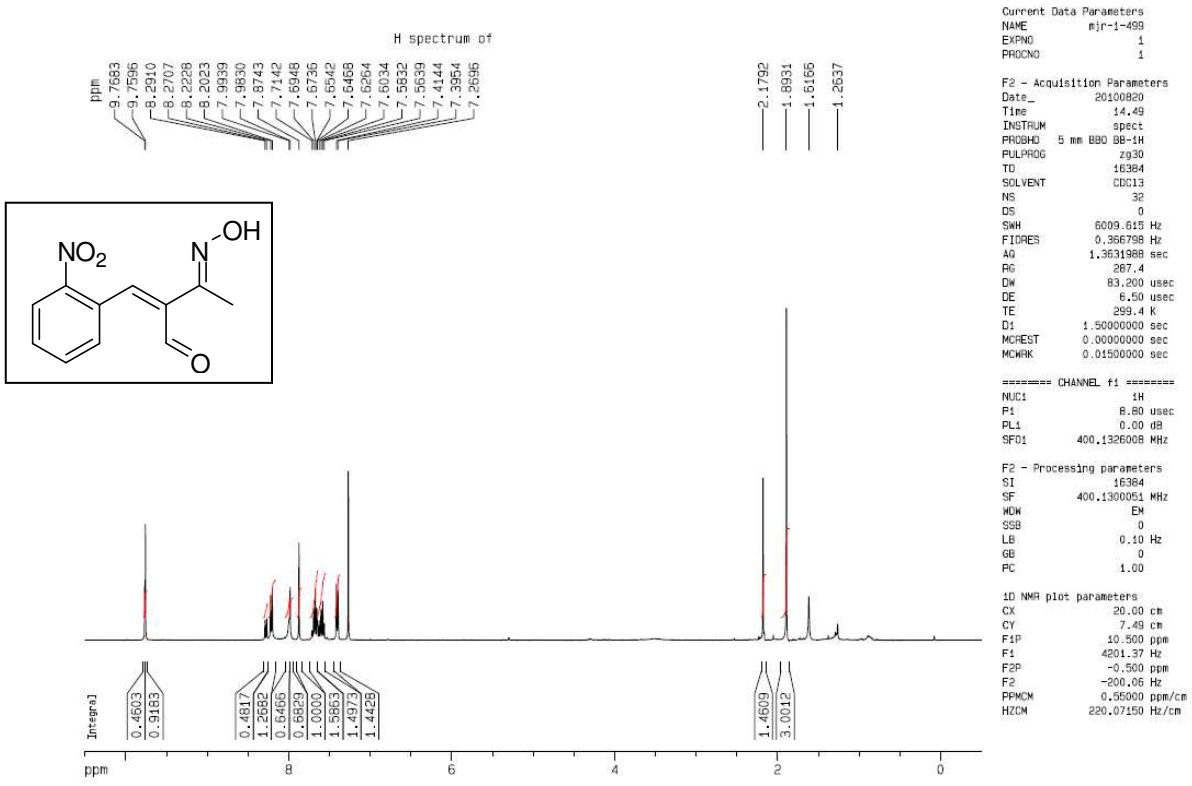

**Bisisoxazoline-*N*-oxide derivative (29a)** $^{1}$H NMR (400 MHz, $CDCl_3$)



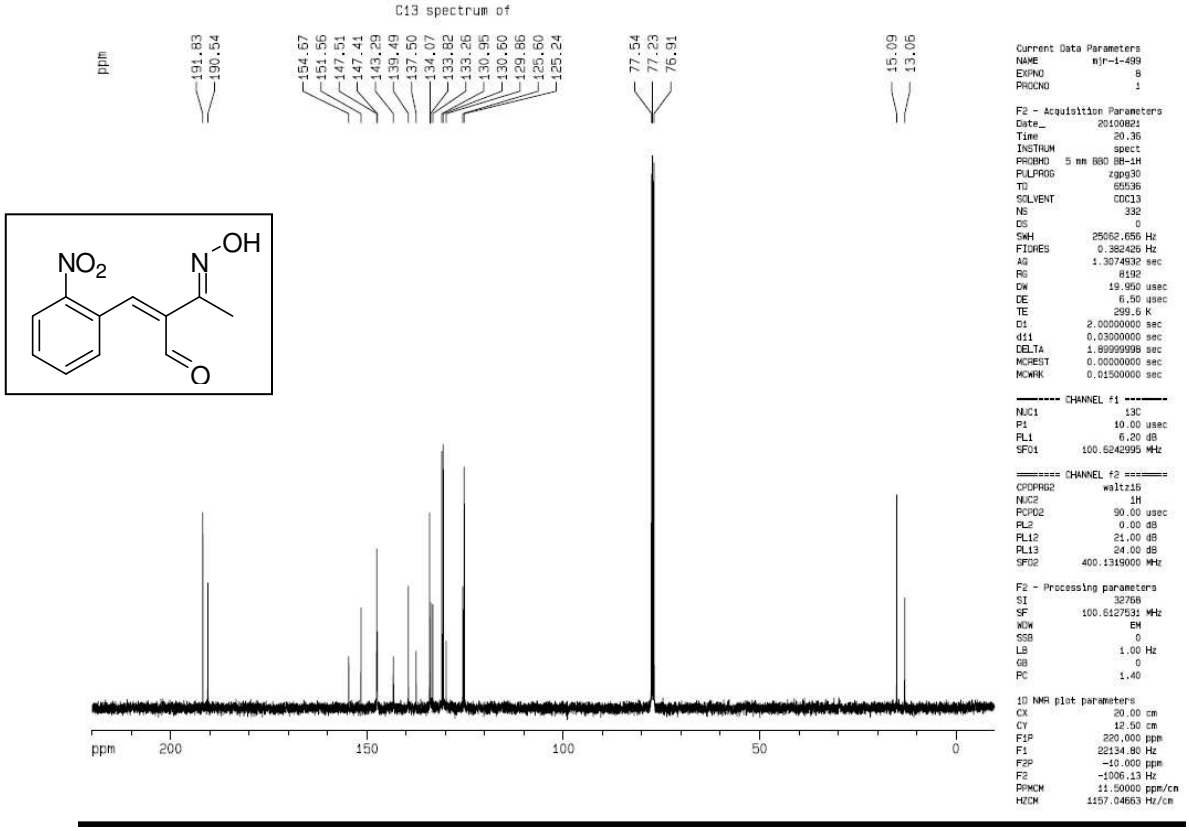

**Bisisoxazoline-*N*-oxide derivative (29a)** $^{13}$C NMR (100 MHz, DMSO)



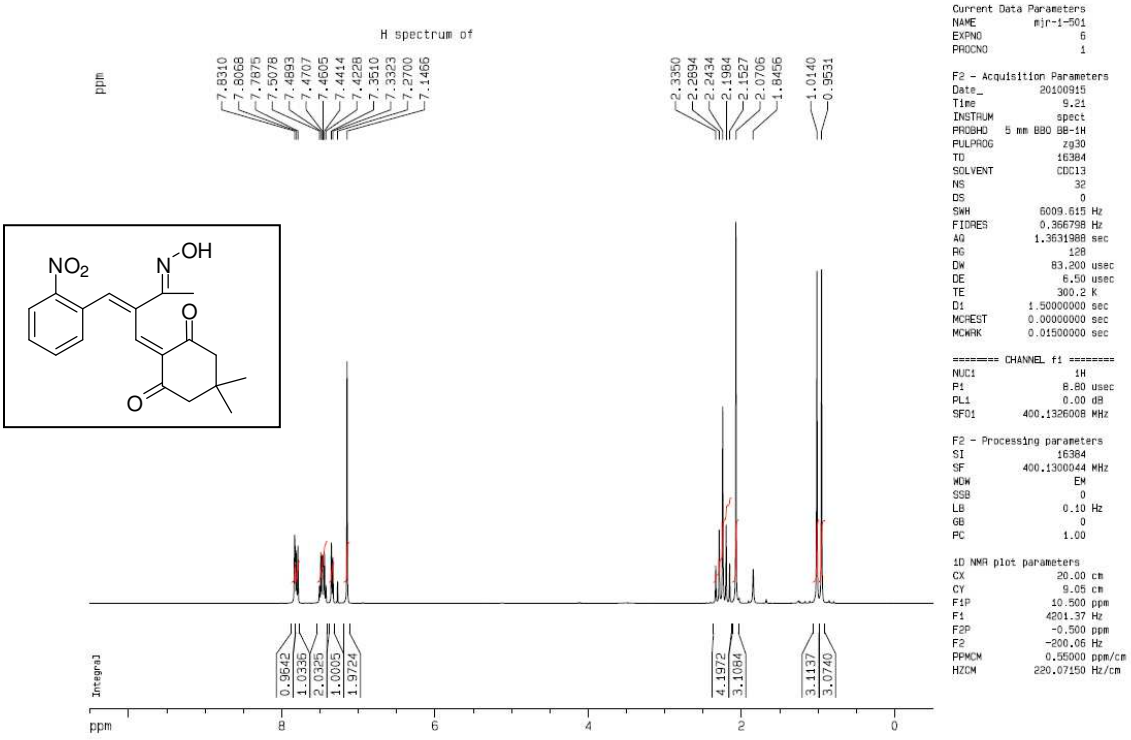

**(2Z)-3-(methylimino)-2-(2-nitrobenzylidene)butanal (33)** $^{1}$H NMR (400 MHz, $CDCl_3$)



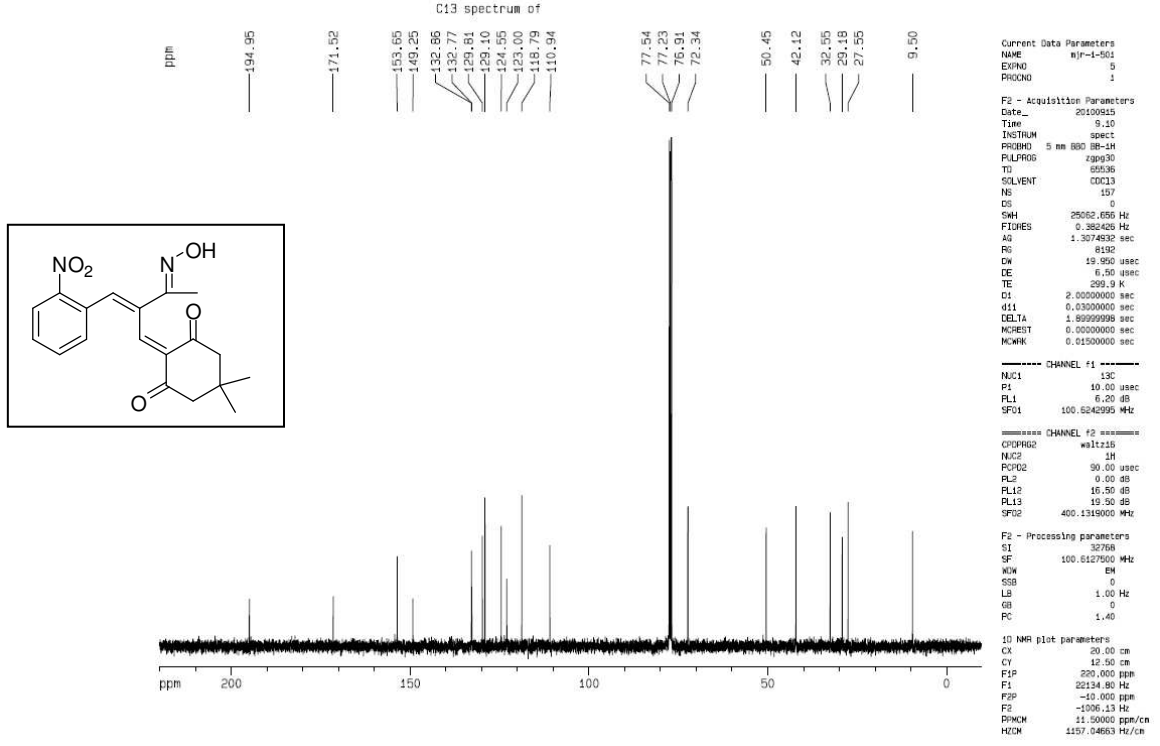

**(2Z)-3-(methylimino)-2-(2-nitrobenzylidene)butanal (33)** $^{13}$C NMR (100 MHz, $CDCl_3$)



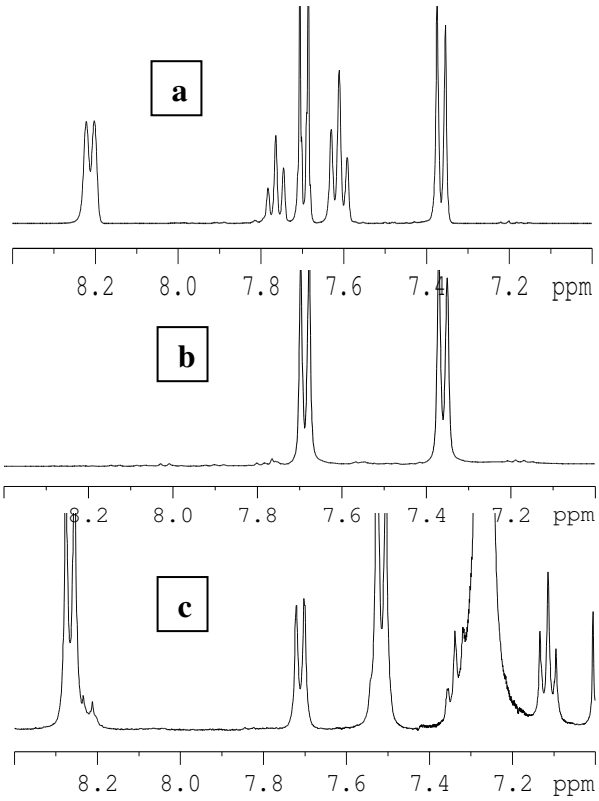
**3-(hydroxyimino)-2-(2-nitrobenzylidene)butylidene)-5,5-dimethylcyclohexane-1,3-dione (34)** $^{1}H$ NMR (400 MHz, $CDCl_3$)




**3-(hydroxyimino)-2-(2-nitrobenzylidene)butylidene)-5,5-dimethylcyclohexane-1,3-dione (34)** $^{13}C$ NMR (100 MHz, $CDCl_3$)



## 6. Spectra related to the $^1$H NMR experiment to support the proposed mechanism




**Spectra related to the $^1$H NMR experiment in $D_2O$**. (a) Immediately after the addition of reagent to the starting material and mild shaking. The doublet at 8.22 ppm, the triplet at 7.76 ppm and the triplet at 7.61 ppm are assigned to $PhI^+OH$. The deviation in chemical shift values, from our earlier report,[10a] is due to the difference in the environment around the in situ formed (hydroxyl)phenyliodinium ion. (b) Spectra, after a vigorous shaking with a mechanical shaker. The $PhI^+OH$ peaks have completely disappeared. (c) Spectra of the crude mixture after the $^1$H NMR experiment, in $CDCl_3$. The doublet at 7.72 ppm, triplet at 7.32 and 7.12 ppm are assigned to iodobenzene. The doublets at 7.52 and 7.51 ppm correspond to the product peak.

# References:

r1. For Baylis-Hillman adducts, please see. (a) Luo, S.; Wang, P. G.; Cheng, J.-P. *J. Org. Chem.* **2004**, *69*, 555. (b) Shi, M.; Jiang, J.-K.; Li, C.-Q. *Tetrahedon Lett.* **2002**, *43*, 127.

r2. (a) Chimni, S. S.; Mahajan, D. *Tetrahedron* **2005**, *61*, 5019. (b) Dimmock, J. R.;. Jha, A.; Kumar, P.; Zello, G. A.; Quail, J. W.; Oloo, E. O.; Oucharek, J. J.; Pasha, M. K.; Seitz, D.; Sharma, R. K.; Allen, T. M.; Santos, C. L.; Manavathu, E. K.; Clercq, E. D.; Balzarini, J.; Stables, J. P. *Eur. J. Med. Chem.* **2002**, *37*, 35.

r3. (a) Lee, K. Y.; Kim, J. M.; Kim, J. N. *Tetrahedron* **2003**, *59*, 385. (b) Kim, H. S.; Kim, T. Y.; Lee, K. Y.; Chung, Y. M.; Lee, H. J.; Kim, J. N. *Tetrahedron Lett.* **2000**, *41*, 2613. (c) Basavaiah, D.; Kumaragurubaran, N.; Padmaja, K. *Synlett.* **1999**, 1630. (d) Unpublished work; to be published.