Supporting Information

Sequential Glaser reaction - diastereoselective cyclocarboxylation of propargylamines with CO_2: A green catalytic access to bis-oxazolidinonedienes and their topochemical polymerization

Francesco Mele, Ana Maria Constantin, Filippo Sacchelli, Debora Schiroli, Paolo Pio Mazzeo, Giovanni Maestri, Elena Motti, Raimondo Maggi, Raffaella Mancuso, Bartolo Gabriele, Francesco Pancrazzi and Nicola Della Ca'

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1. General Information

All reagents were used as received from commercial sources without further purification. All solvents were dried over activated 4 Å molecular sieves for 24 h. All reactions were analysed by TLC and by GC using a 30 m SE-30 capillary column. Flash column chromatography was performed on silica gel 60 (70–230 mesh). Melting points were measured with an Electrothermal apparatus and are uncorrected. Electron impact mass spectra [m/z, relative intensity (%)] were determined with a GC-MS apparatus at 70 eV ionization energy.

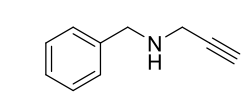
HRMS spectra were obtained with LTQ Orbitrap XL Thermo. Unless otherwise indicated NMR spectra were recorded on Bruker AVANCE 400 and JEOL 600MHz ECZ600R spectrometers in deuterated chloroform, using the solvent residual signals as internal reference (7.26 and 77.00 ppm, respectively for ^{1}H and ^{13}C), or deuterated dimethyl sulfoxide (2.50 and 39.52 ppm, respectively for ^{1}H and ^{13}C). Chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively.

Single Crystal X-ray Diffraction. SCXRD analyses were performed on single crystal samples of **3b** and **3i**, on a Bruker D8 Venture diffractometer equipped with a kappa goniometer. Data collection was performed using microfocused MoKα radiation (λ = 0.71073 Å) and CuKα radiation (λ = 1.54178 Å) under nitrogen flux with Oxford Cryosteam. Lorentz polarization and absorption correction were applied. Data were reprocessed using APEX v4 software. Structures were solved by direct methods using SHELXT[1] and refined by full-matrix least-squares on all F2 using SHELXL[2] implemented in Olex2.21[3]. For all samples anisotropic displacement parameters were refined except for hydrogen atoms.

Powder X-ray diffraction. Monomer-to-polymer conversion in batch was checked by PXRD. The data were collected on a Rigaku Smartlab XE diffractometer in θ−θ Bragg−Brentano geometry with Cu Kα radiation. The samples were placed on glass supports and exposed to radiation (5° ≤ 2θ ≤ 50°) at a scan rate of 5 °/min. The diffracted beam was collected on a two-dimensional (2D) Hypix 3000 solid-state detector; 5° radiant Soller slits were used as a compromise for high flux and moderate peak asymmetry at low angles. A beam stopper and antiscatterer air component were used to mitigate the scattering at a low angle. All of the experimental data were refined with a Pawley fit performed with TOPAS v6[4] against the cell parameters extracted from SCXRD analyses opportunely refined to compensate for the difference in the data collection temperature.

2. Experimental Procedures

Propargylic amines tested in this study.



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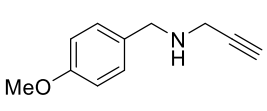

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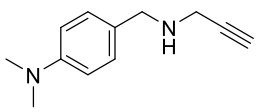

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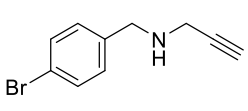

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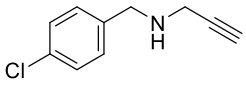

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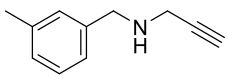

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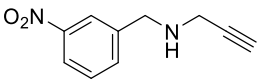

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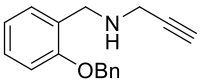

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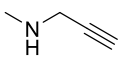

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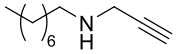

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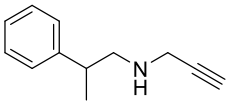

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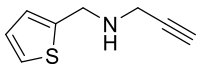

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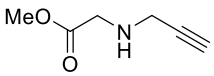

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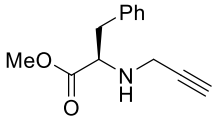

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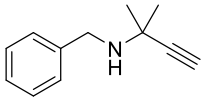

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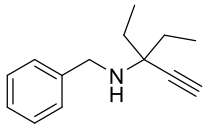
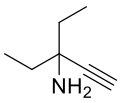


1p

Unsuccessful substrates



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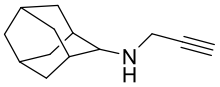

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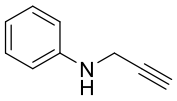

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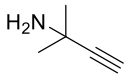


1t

Figure S1. Propargylic amines used in this work.

General procedures for the synthesis of propargyl amines 1

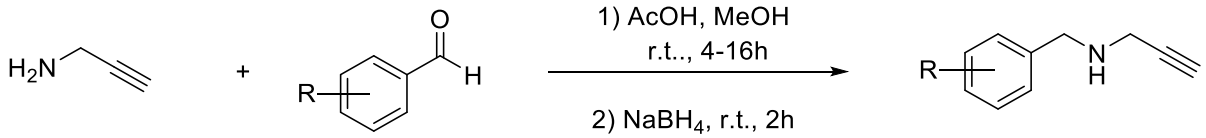
The propargyl amines were synthesized using two different methods.

Procedure A: synthesis from propargyl bromide (**1a**, **1j**, **1m**, **1n**, **1s**)

Following the literature procedure[5], the propargyl bromide (1 equiv.) was added dropwise to the corresponding neat amine (6 equiv.) at 0 °C, under nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred overnight. Then, a mixture of a solution 1 M of NaOH (4 mL/mmol) and Et_2O (4 mL/mmol) was added and stirred for 15 min. The mixture was transferred to a separating funnel, and it was extracted with Et_2O (3x). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was then purified by flash column chromatography (eluent Hexane:EtOAc).

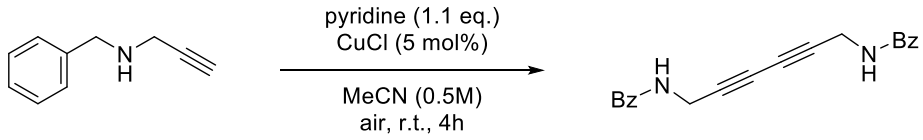
For amines **1m** and **1n** some modifications were adopted. In a Schlenk tube under nitrogen atmosphere, K_2CO_3 (10 mmol) was added to a stirred suspension of the corresponding amino acid methyl ester hydrochloride (16 mmol) in ACN dry. Then, the mixture was cooled in an ice bath and after 10 min propargyl bromide (4 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After 16 h, the mixture was diluted with diethyl ether and concentrated under vacuum. Then, the mixture was transferred to a separating funnel, and it was extracted with DCM (3x). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was then purified by flash column chromatography (eluent Hexane/EtOAc).

Procedure B: reductive amination (**1b**-**1h**, **1k**, **1l**, **1o**, **1p** and **1r**)



According to the literature procedure[6], one drop of AcOH was added to a solution of propargyl amine (1 equiv.) and aryl aldehyde (1.1 eq.) in MeOH (0.6 M). The resulting mixture was then stirred at room temperature and was monitored with TLC until propargyl imine was formed. $NaBH_4$ (1.5 equiv.) was added in three different portions at 0 °C and the solution was then stirred for 1 h prior to the evaporation of the solvent. The mixture was diluted with water, extracted with DCM (2 times), and the combined organic layers were then washed with a 1 M HCl solution. Aqueous layers were neutralized, extracted with DCM (2 times), and the resulting organic phase was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and finally purified by flash column chromatography (eluent Hexane/EtOAc gradient).

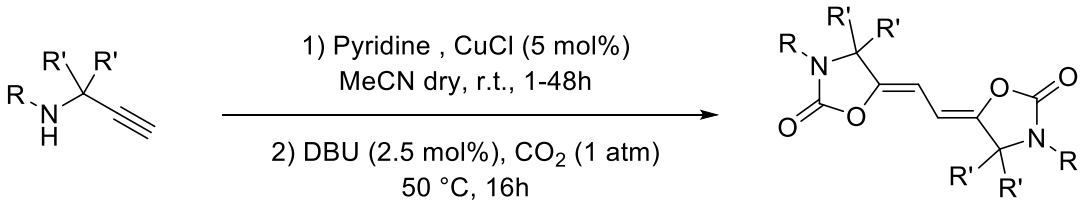
Synthesis of Glaser product 2a



1a **2a**

In a 10 mL Schlenk tube open to air, propargyl amine (1 eq.), pyridine (1.1 eq.) and CuCl (0.05 mmol) were dissolved in MeCN (0.5 M) and kept under stirring. The reaction proceeded at room temperature for 4h. The crude was then recovered with DCM and directly purified by flash silica gel column chromatography. Product **2a** was isolated in 67% yield.

General procedure for the synthesis of 3



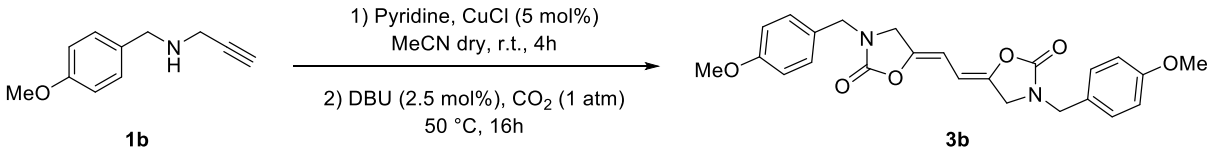
1 **3**

R' = H, -CH_3 or -CH_2CH_3

In a 10 mL Schlenk tube open to air, propargyl amine (1.0 mmol), pyridine (1.1 mmol) and CuCl (0.05 mmol) were dissolved in MeCN dry (2 mL) under stirring. The Glaser reaction (*step 1*) was monitored by TLC until complete conversion of **1**. The solvent was degassed through a freeze-pump-thaw procedure and, then, the tube was filled with CO_2 (balloon) and DBU (2.5 mol%) was added to the mixture (*step 2*). The reaction was kept at 50 °C under stirring for 16 h. The suspension was filtered on a Büchner funnel and washed with a 1:1 ethyl acetate/hexane mixture (2-3 mL) and a saturated NH_4OH solution (2 mL). Finally, the solid product was dried up under reduced pressure, quantified and directly characterized.

Figure S2. Synthesis of compounds **3**.

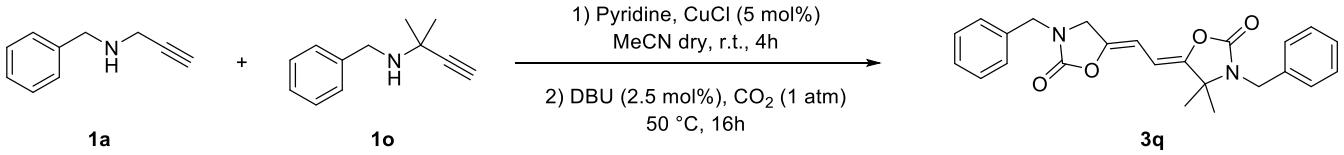
Procedure for Gram Scale synthesis of 3b



1b **3b**

In a 25 mL Schlenk tube open to air, propargyl amine (4.3 mmol), pyridine (4.8 mmol) and CuCl (0.215 mmol) were dissolved in MeCN dry (4 mL) under stirring. The Glaser reaction (*step 1*) was monitored by TLC until complete conversion of **1b**. The solvent was degassed through a freeze-pump-thaw procedure and, then, the tube was filled with CO_2 (balloon) and DBU (2.5 mol%) was added to the mixture (*step 2*). The reaction was kept at 50 °C under stirring for 16 h. The suspension was filtered on a Büchner funnel and washed with a 1:1 ethyl acetate/hexane mixture (5 mL) and a saturated NH_4OH solution (5 mL). Finally, the solid was dried up under reduced pressure to give product **3b** (0.82 g, 89% yield).

Procedure for the synthesis of 3q

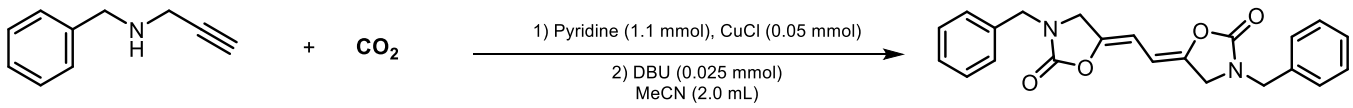


1a **1o** **3q**

In a 10 mL Schlenk tube open to air, propargyl amine **1a** (0.5 mmol), propargyl amine **1o** (0.5 mmol), pyridine (1.1 mmol) and CuCl (0.05 mmol) were dissolved in MeCN dry (2 mL) under stirring. The reaction (step 1) was monitored by TLC until complete conversion of the starting materials. The solvent was degassed through a freeze-pump-thaw procedure and, then, the tube was filled with CO_2 (balloon) and DBU (2.5 mol%) was added to the mixture (step 2). The reaction was kept at 50 °C under stirring for 16 h. After that, the crude mixture was recovered with DCM and directly purified by flash column chromatography (Eluents DCM:Hexane:EtOAc 10:8:1) to yield product **3q** (49% yield).

3. Green chemistry metrics calculations

Green chemistry parameters were evaluated as described in literature. [7,8]



1a

$C_{10}H_{11}N$
MW : 145.1
145.0 mg, 1.0 mmol

Carbon Dioxide
MW: 44.0
44.0 mg, 1.0 mmol

Pyridine
MW: 79.1
87.0 mg, 1.1 mmol

DBU
MW:152.1
3.8 mg, 0.025 mmol

CuCl
MW: 99.0
5.0 mg, 0.05 mmol

MeCN
MW: 41.0
1,572 g, 38.3 mmol

3a

$C_{22}H_{20}N_2O_4$
MW: 376.1
188.1 mg, 0.5 mmol

Scheme S1. Calculation of green metrics for the synthesis of **3a**.

$$Atom\ Economy\ (\%)\ (\boldsymbol{AE}) = \frac{MW\ (Product)}{\sum MW\ (Reagents)} x100 = 99.5\%$$

$$Reaction\ mass\ efficiency\ (\%)\ (\boldsymbol{RME}) = \frac{m_{product}}{m_{reactans} + m_{reagents}} x100 = 68.1\%$$

$$\boldsymbol{E-Factor} = \frac{m_{reagents} + m_{reactans} + m_{catalyst} + m_{solvent} - m_{product}}{m_{product}} = 8.8$$

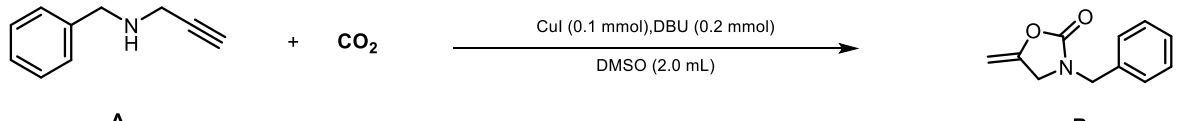
$$Process\ Mass\ Intensity\ (\boldsymbol{PMI}) = \frac{m_{reactans} + m_{reagents} + m_{catalyst} + m_{solvent}}{m_{product}} = 9.9$$

$$Process\ Mass\ Intensity\ (\boldsymbol{PMI})\ \text{considering purification} = \frac{m_{reactans} + m_{reagents} + m_{catalyst} + m_{solvent}}{m_{product}}$$

$$= \frac{(0.087\ \text{g})_{reactans} + (0.145\ \text{g} + 0.044\ \text{g})_{reagents} + (0.004\ \text{g} + 0.005\ \text{g})_{catalysts} + (1.572\ \text{g} + 1.353\ \text{g} + 0.991\ \text{g} + 1.820\ \text{g})_{solvent}}{(0.188\ g)_{product}}$$

$$= 32.0$$

PMI was calculated for a typical synthesis of 2-oxazolidinones described in literature[9]. In this work, a column chromatography (EtOAc: Petroleum ether 1:20) was necessary to obtain the product with an acceptable purity. We estimated a minimal consumption of eluent of 300 mL (Petroleum ether 285.7 mL, 183 g; EtOAc, 14.3 mL, 12.9 g) and of silica gel (30 g).



A

$C_{10}H_{11}N$
MW : 145.1
145.0 mg, 1.0 mmol

Carbon Dioxide
MW: 44.0
44.0 mg, 1.0 mmol

DBU
MW: 152.1
30.4 mg, 0.2 mmol

CuI
MW: 190.4
19.0 mg, 0.1 mmol

DMSO
MW: 78.1
2,2 g, 28.2 mmol

B

$C_{11}H_{11}NO_2$
MW: 189.1
189.1 mg, 1.0 mmol

$$Process\ Mass\ Intensity\ (\boldsymbol{PMI}) = \frac{m_{reactans} + m_{reagents} + m_{catalyst} + m_{solvent}}{m_{product}} = 13.0$$

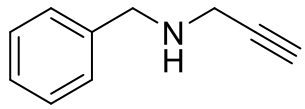
$$Process\ Mass\ Intensity\ (\boldsymbol{PMI})\ \text{considering purification} = \frac{m_{reactans} + m_{reagents} + m_{catalyst} + m_{solvent} + m_{silica-gel}}{m_{product}}$$

$$= \frac{(0.145\ \text{g} + 0.044\ \text{g})_{reagents} + (0.019\ \text{g} + 0.030\ \text{g})_{catalysts} + (2.202\ \text{g} + 182.854\ \text{g} + 12.881\ \text{g})_{solvent} + (30.000\ \text{g})_{silica-gel}}{(0.189\ g)_{product}}$$

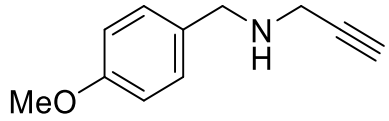
$$= 1207.3$$

4. Characterization Data

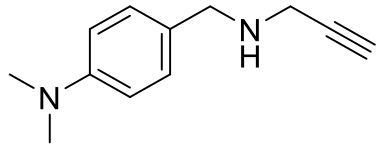
Characterization of Substrates 1



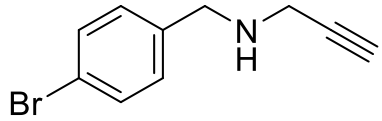
N-benzylprop-2-yn-1-amine (1a). Yellow oil (522 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.29 (ddd, J = 6.1, 4.7, 2.4 Hz, 1H), 3.91 (s, 2H), 3.46 (d, J = 2.4 Hz, 2H), 2.29 (t, J = 2.4 Hz, 1H), 1.62 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.4, 128.5, 128.4, 127.2, 82.1, 71.6, 52.3, 37.3. The NMR data closely match the ones previously reported in the literature.[10]



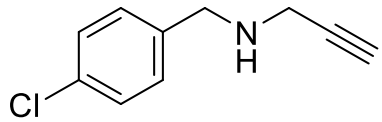
N-(4-methoxybenzyl)prop-2-yn-1-amine (1b). Yellow oil (399 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 6.93 – 6.84 (m, 2H), 3.83 (s, 2H), 3.81 (s, 3H), 3.42 (d, J = 2.4 Hz, 2H), 2.28 (t, J = 2.4 Hz, 1H), 1.59 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 131.5, 129.6, 113.8, 82.2, 71.5, 55.3, 51.6, 37.2. The NMR data closely match the ones previously reported in the literature.[10]



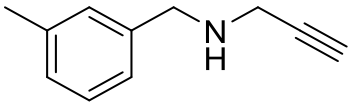
N,N-dimethyl-4-((prop-2-yn-1-ylamino)methyl)aniline (1c). Red oil (376 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 6.79 – 6.70 (m, 2H), 3.81 (s, 2H), 3.44 (d, J = 2.4 Hz, 2H), 2.96 (s, 6H), 2.27 (t, J = 2.4 Hz, 1H), 1.54 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 129.4, 127.3, 112.7, 82.3, 71.3, 51.8, 40.8, 37.2. The NMR data closely match the ones previously reported in the literature.[6]



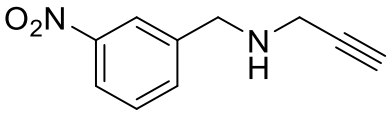
N-(4-bromobenzyl)prop-2-yn-1-amine (1d). Yellow oil (624 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 2H), 7.29 – 7.20 (m, 2H), 3.42 (dt, J = 2.2, 0.9 Hz, 2H), 2.28 (t, J = 2.4 Hz, 1H), 1.61 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 131.5, 130.1, 121.0., 81.8, 71.8, 51.5, 37.2. The NMR data closely match the ones previously reported in the literature.[10]



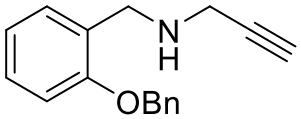
N-(4-chlorobenzyl)prop-2-yn-1-amine (1e). Yellow Oil (644 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 3.83 (s, 2H), 3.39 (d, J = 2.4 Hz, 2H), 2.28 (t, J = 2.4 Hz, 1H), 1.55 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9, 132.8, 129.8, 128.5, 81.9, 71.8, 51.4, 37.2. The NMR data closely match the ones previously reported in the literature.[10]



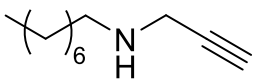
N-(3-methylbenzyl)prop-2-yn-1-amine (1f). Yellow Oil (369 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 1H), 7.20 (s, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 3.88 (s, 2H), 3.46 (d, J = 2.4 Hz, 2H), 2.38 (s, 3H), 2.29 (t, J = 2.4 Hz, 1H), 1.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 138.1, 129.2, 128.4, 128.0, 125.5, 82.0, 71.7, 52.3, 37.4, 21.4.



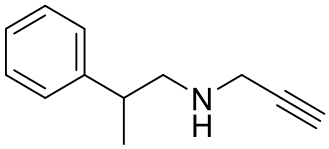
N-(3-nitrobenzyl)prop-2-yn-1-amine (1g). Yellow oil (418 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 4.00 (s, 2H), 3.45 (d, J = 2.4 Hz, 2H), 2.30 (t, J = 2.4 Hz, 1H), 2.17 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 141.6, 134.5, 129.3, 123.2, 122.3, 81.4, 72.2, 51.2, 37.3.



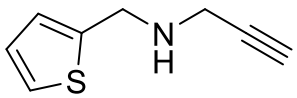
N-(2-(benzyloxy)benzyl)prop-2-yn-1-amine (1h). Yellow oil (773 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.21 (m, 2H), 7.03 – 6.92 (m, 2H), 5.14 (s, 2H), 3.97 (s, 2H), 3.44 (d, J = 2.5 Hz, 2H), 2.22 (t, J = 2.4 Hz, 1H), 1.84 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.8, 137.1, 130.2, 128.6, 128.5, 127.9, 127.2 (2C), 120.8, 111.8, 82.1, 71.4, 69.9, 48.1, 37.5.



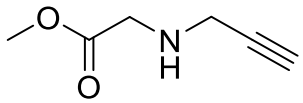
N-(prop-2-yn-1-yl)octan-1-amine (1j). Yellow oil (548 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.44 (s, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.22 – 2.21 (t, 1H), 1.60 – 1.39 (m, 4H), 1.30 (d, J = 11.2 Hz, 10H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 82.3, 71.2, 48.7, 38.2, 31.8, 29.8, 29.5, 29.3, 27.3, 22.7, 14.1.



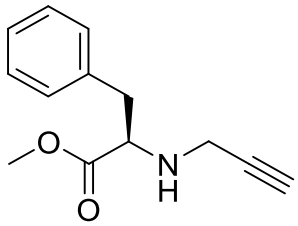
N-(2-phenylpropyl)prop-2-yn-1-amine (1k). Yellow Oil (187 mg, 27% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.26 (d, J = 7.5 Hz, 3H), 3.41 (t, J = 2.3 Hz, 2H), 3.00 – 2.92 (m, 2H), 2.89 – 2.81 (m, 1H), 2.22 (t, J = 2.4 Hz, 1H), 1.38 (s, 1H), 1.31 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0, 128.6, 127.2, 126.5, 82.1, 71.3, 55.7, 40.1, 38.3, 20.2.



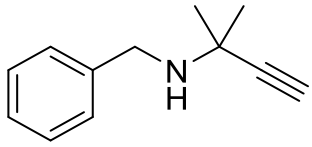
N-(thiophen-2-ylmethyl)prop-2-yn-1-amine (1l). Yellow oil (574 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 4.8, 1.5 Hz, 1H), 7.03 – 6.94 (m, 2H), 4.11 (s, 2H), 3.47 (d, J = 2.4 Hz, 2H), 2.29 (t, J = 2.4 Hz, 1H), 1.75 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 126.7, 125.5, 124.8, 81.7, 71.9, 46.7, 37.0. The NMR data closely match the ones previously reported in the literature.[10]



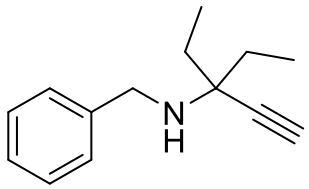
Methyl prop-2-yn-1-ylglycinate (1m). Colourless oil (290 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.53 (s, 2H), 3.49 (d, *J* = 2.1 Hz, 2H), 2.24 (t, *J* = 2.4 Hz, 1H), 1.86 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 81.1, 72.1, 51.9, 49.0, 37.6.



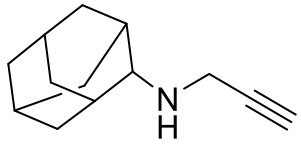
Methyl prop-2-yn-1-yl-D-phenylalaninate (1n). Yellow oil (617 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 3.78 (dd, *J* = 7.2, 6.3 Hz, 1H), 3.70 (s, 3H), 3.46 (dd, *J* = 17.0, 2.5 Hz, 1H), 3.39 (dd, *J* = 17.0, 2.5 Hz, 1H), 3.05 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.98 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.21 (t, *J* = 2.5 Hz, 1H), 1.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 136.8, 129.2, 128.5, 126.9, 81.1, 71.8, 61.1, 51.8, 39.4, 36.8.



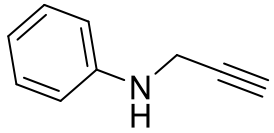
N-benzyl-2-methylbut-3-yn-2-amine (1o). Yellow oil (672 mg, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.25 (m, 5H), 3.92 (s, 2H), 2.41 (d, *J* = 1.0 Hz, 1H), 1.47 (s, 6H), 1.39 (bs, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 128.5, 127.0, 89.1, 69.9, 50.1, 49.0, 29.6.



N-benzyl-3-ethylpent-1-yn-3-amine (1p). Yellow Oil (716 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 3.85 (s, 2H), 2.40 (s, 1H), 1.81 – 1.62 (m, 4H), 1.23 (s, 1H), 1.03 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 128.5, 128.4, 126.9, 87.8, 71.5, 57.4, 48.1, 30.5, 8.1.

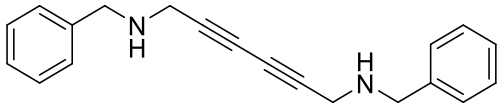


N-(prop-2-yn-1-yl)adamantan-2-amine (1r). White solid (605 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.45 (d, J = 2.4 Hz, 2H), 2.93 (d, J = 2.6 Hz, 1H), 2.20 (t, J = 2.4 Hz, 1H), 2.02 (dd, J = 12.6, 3.1 Hz, 2H), 1.91 – 1.70 (m, 10H), 1.54 – 1.46 (m, 2H), 1.29 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 77.4, 77.0, 76.7, 70.7, 60.5, 37.9, 37.4, 35.5, 31.9, 31.3, 27.8, 27.7.



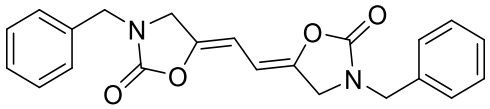
***N*-(prop-2-yn-1-yl)aniline (1s).** Red oil (472 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (td, J = 7.3, 2.1 Hz, 2H), 6.87 (t, J = 7.4 Hz, 1H), 6.76 (dd, J = 8.7, 1.1 Hz, 2H), 3.98 (d, J = 2.5 Hz, 2H), 2.29 (t, J = 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 129.3, 118.7, 113.6, 81.2, 71.4, 33.7. The NMR data closely match the ones previously reported in the literature.[10]

Characterization of 2a

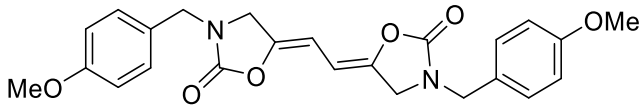


***N*^{1},*N*^{6}-dibenzylhexa-2,4-diyne-1,6-diamine (2a).** Red Brown oil (289 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 8H), 7.32 – 7.29 (m, 2H), 3.92 (s, 4H), 3.54 (s, 4H), 1.66 (bs, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 128.5, 128.4 (2C), 127.3, 68.2, 52.3, 38.0.

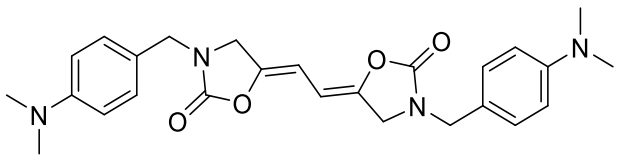
Characterization of Products 3



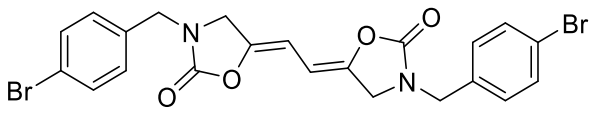
***(5Z,5'Z)*-5,5'-(ethane-1,2-diylidene)bis(3-benzyloxazolidin-2-one) (3a).** White solid (175.1 mg, 96% yield); dec. 276 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.43 – 7.25 (m, 10H), 5.53 (s, 2H), 4.44 (s, 4H), 4.20 (s, 4H). **^{13}C NMR** (101 MHz, DMSO) δ 155.2, 142.3, 136.2, 129.2, 128.24, 128.22, 95.5, 47.9, 47.6. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{20}N_2NaO_4$ $[M+Na]^+$: 399.1315, found: 399.1312.



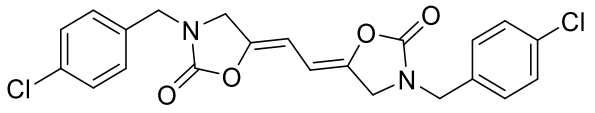
***(5Z,5'Z)*-5,5'-(ethane-1,2-diylidene)bis(3-(4-methoxybenzyl)oxazolidin-2-one) (3b).** White solid (216.5 mg, 90% yield); dec. 230 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.4 Hz, 4H), 5.52 (s, 2H), 4.42 (s, 4H), 4.06 (s, 4H), 3.83 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 155.2, 141.2, 129.6, 126.8, 114.4, 95.9, 55.3, 47.4, 47.3. **HRMS (ESI)** *m/z* calculated for $C_{24}H_{24}N_2NaO_6$ $[M+Na]^+$: 459.1526, found: 459.1525.



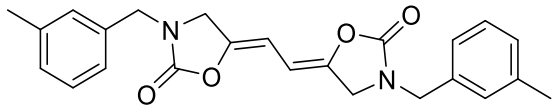
***(5Z,5'Z)*-5,5'-(ethane-1,2-diylidene)bis(3-(4-(dimethylamino)benzyl)oxazolidin-2-one) (3c).** White Solid (212.4 mg, 91% yield); dec. 241 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 4H), 6.75 (d, J = 8.0 Hz, 4H), 5.51 (t, J = 0.8 Hz, 2H), 4.39 (s, 4H), 4.07 – 4.02 (m, 4H), 2.98 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 150.4, 141.3, 129.4, 122.5, 112.8, 95.8, 47.5, 47.2, 40.5. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{30}N_4NaO_4$ $[M+Na]^+$: 485.2159, found: 485.2156.



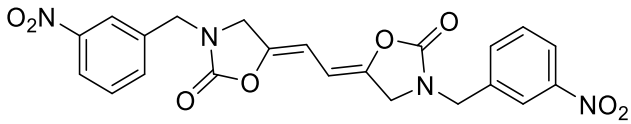
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(4-bromobenzyl)oxazolidin-2-one) (3d). White Solid (256 mg, 93% yield); dec. 320 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.61 – 7.53 (m, 4H), 7.31 – 7.23 (m, 4H), 5.52 (s, 2H), 4.41 (s, 4H), 4.20 (s, 4H). **^{13}C NMR** (101 MHz, DMSO) δ 155.2, 142.3, 135.7, 132.1, 130.5, 121.4, 95.5, 48.0, 47.0. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{18}Br_2N_2NaO_4$ $[M+Na]^+$: 554.9525, found: 554.9523.



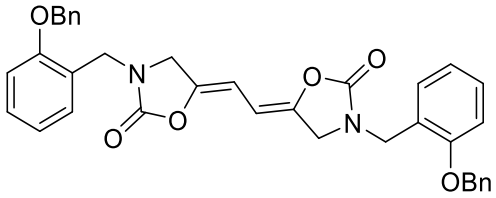
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(4-chlorobenzyl)oxazolidin-2-one) (3e). White Solid (216.7 mg, 97% yield); dec. 310 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.45 – 7.40 (m, 4H), 7.35 – 7.30 (m, 4H), 5.52 (s, 2H), 4.43 (s, 4H), 4.21 (s, 4H). **^{13}C NMR** (101 MHz, DMSO) δ 155.2, 142.3, 135.3, 133.0, 130.2, 129.2, 95.5, 48.0, 46.9. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{18}Cl_2N_2NaO_4$ $[M+Na]^+$: 467.0536, found: 467.0532.



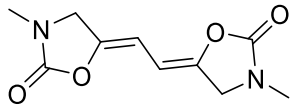
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(3-methylbenzyl)oxazolidin-2-one) (3f). White solid (158 mg, 91% yield); dec. 260 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, J = 7.5 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 7.10 (s, 2H), 7.08 (d, J = 8.5 Hz, 2H), 5.54 (s, 2H), 4.45 (s, 4H), 4.08 (s, 4H), 2.37 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 141.2, 138.9, 134.7, 129.1, 128.9 (2C), 125.2, 96.0, 47.9, 47.4, 21.4. **HRMS (ESI)** *m/z* calculated for $C_{24}H_{24}N_2NaO_4$ $[M+Na]^+$: 427.1628, found: 427.1626.



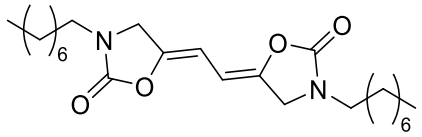
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(3-nitrobenzyl)oxazolidin-2-one) (3g). Pale yellow solid (206.8 mg, 89% yield); dec. 225 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.18 (d, J = 8.1 Hz, 2H), 8.15 (s, 2H), 7.78 (d, J = 7.7 Hz, 2H), 7.69 (t, J = 7.8 Hz, 2H), 5.55 (s, 2H), 4.59 (s, 4H), 4.27 (s, 4H). **^{13}C NMR** (101 MHz, DMSO) δ 160.1, 153.3, 147.1, 143.4, 139.7, 135.5, 127.9, 127.8, 100.3, 52.9, 51.5. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{18}N_4NaO_8$ $[M+Na]^+$: 489.1017, found: 489.1016.



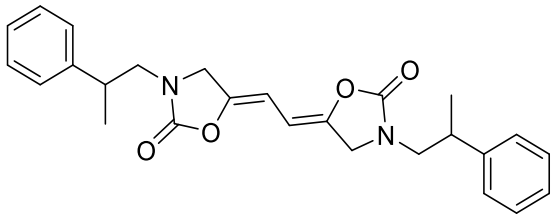
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(2-(benzyloxy)benzyl)oxazolidin-2-one) (3h). Orange solid (279.25 mg, 94% yield); dec. 185 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 10H), 7.32 (t, *J* = 7.5 Hz, 4H), 6.99 (t, *J* = 7.8 Hz, 4H), 5.46 (s, 2H), 5.12 (s, 4H), 4.56 (s, 4H), 4.05 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 155.3, 141.4, 136.5, 130.5, 129.7, 128.7, 128.3, 127.5, 123.5, 121.2, 111.9, 95.7, 70.3, 48.1, 42.8. **HRMS (ESI)** *m/z* calculated for $C_{36}H_{32}N_2NaO_6$ $[M+Na]^+$: 611.2152, found: 611.2151.



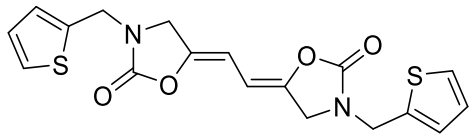
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-methyloxazolidin-2-one) (3i). White solid (122 mg, 89%); dec. 264 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.60 (s, 2H), 4.24 (s, 4H), 2.97 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.4, 141.0, 95.8, 50.1, 30.6. **HRMS (ESI)** *m/z* calculated for $C_{10}H_{12}N_2NaO_4$ $[M+Na]^+$: 247.0689, found: 247.0685.



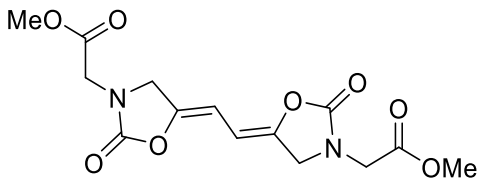
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-octyloxazolidin-2-one) (3j). White Solid (192.15 mg, 91% yield); m.p. 186-188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.59 (s, 2H), 4.22 (s, 4H), 3.32 (t, *J* = 7.3 Hz, 4H), 1.62 – 1.52 (m, 4H), 1.37 – 1.25 (m, 20H), 0.89 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 141.2, 95.8, 48.0, 43.9, 31.7, 29.1 (2C), 27.2, 26.6, 22.6, 14.1. **HRMS (ESI)** *m/z* calculated for $C_{24}H_{40}N_2NaO_4$ $[M+Na]^+$: 443.2880, found: 443.2878.



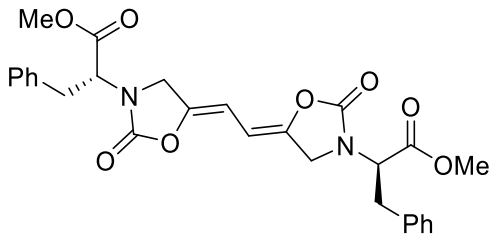
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(2-phenylpropyl)oxazolidin-2-one) (3k). White solid (198.6 mg, 96% yield); m.p. 215-217 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.3 Hz, 4H), 7.28 – 7.18 (m, 6H), 5.40 (s, 2H), 3.95 (d, J = 13.9 Hz, 2H), 3.76 (d, J = 13.8 Hz, 2H), 3.60 (dd, J = 14.0, 6.8 Hz, 2H), 3.34 (dd, J = 14.0, 8.7 Hz, 2H), 3.09 (h, J = 7.0 Hz, 2H), 1.31 (d, J = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.4, 143.3, 141.1, 128.9, 127.1, 127.0, 95.6, 51.0, 48.7, 38.6, 19.2. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{28}N_2NaO_4$ $[M+Na]^+$: 455.1941, found: 455.1940.



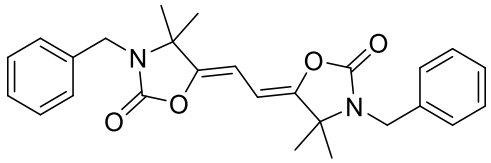
(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-(thiophen-2-ylmethyl)oxazolidin-2-one) (3l). White solid (178 mg, 92% yield); dec. 283°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 5.0, 1.3 Hz, 2H), 7.06 – 7.03 (m, 2H), 7.01 (dd, J = 5.0, 3.5 Hz, 2H), 5.56 (t, J = 0.8 Hz, 2H), 4.68 (d, J = 0.7 Hz, 4H), 4.19 – 4.15 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.7, 141.1, 136.9, 127.5, 127.2, 126.3, 96.1, 47.3, 42.4. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{16}N_2NaO_4S_2$ $[M+Na]^+$: 411.0443, found: 411.0441.



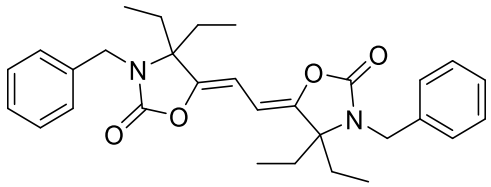
Dimethyl 2,2'-((5Z,5'Z)-ethane-1,2-diylidenebis(2-oxooxazolidin-3-yl-5-ylidene))diacetate (3m). White Solid (112.3 mg, 65% yield); dec. 200 °C. **^{1}H NMR** (400 MHz, DMSO) δ 5.62 (s, 2H), 4.35 (s, 4H), 4.14 (s, 4H), 3.70 (s, 6H). **^{13}C NMR** (101 MHz, DMSO) δ 169.3, 155.3, 142.3, 95.6, 52.7, 48.8, 45.0. **HRMS (ESI)** *m/z* calculated for $C_{14}H_{16}N_2NaO_8$ $[M+Na]^+$: 363.0799, found: 363.0798.



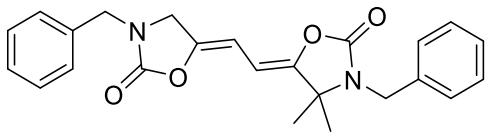
Dimethyl 2,2'-((5Z,5'Z)-ethane-1,2-diylidenebis(2-oxooxazolidin-3-yl-5-ylidene))(2R,2'R)-bis(3-phenylpropanoate) (3n). White Solid (232.4 mg, 74% yield); m.p. 175-178 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 6H), 7.21 (dt, J = 7.9, 1.5 Hz, 4H), 5.49 (s, 2H), 4.88 (dd, J = 10.9, 5.3 Hz, 2H), 4.36 (dd, J = 13.3, 3.5 Hz, 2H), 4.13 (dd, J = 13.2, 4.3 Hz, 2H), 3.78 (d, J = 1.5 Hz, 6H), 3.40 (dd, J = 14.8, 5.3 Hz, 2H), 3.01 (ddd, J = 14.8, 10.9, 1.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 155.2, 141.2, 135.5, 129.0, 128.4, 127.4, 96.0, 56.4, 52.7, 45.5, 35.1. **HRMS (ESI)** *m/z* calculated for $C_{28}H_{28}N_2NaO_8$ $[M+Na]^+$: 543.1738, found: 543.1735.



(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-benzyl-4,4-dimethyloxazolidin-2-one) (3o). White solid (201.1 mg, 92% yield); m.p. 225-228 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 10H), 5.58 (s, 2H), 4.48 (s, 4H), 1.33 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6, 152.7, 137.4, 128.7, 127.8, 127.7, 93.8, 61.9, 44.1, 27.5. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{28}N_2NaO_4$ $[M+Na]^+$: 455.1941, found: 455.1938.

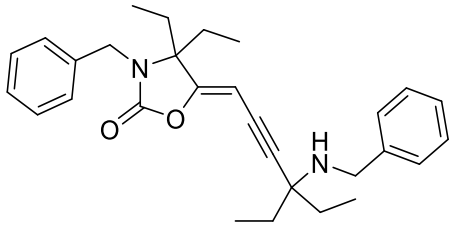


(5Z,5'Z)-5,5'-(ethane-1,2-diylidene)bis(3-benzyl-4,4-diethyloxazolidin-2-one) (3p). White Solid (129.4 mg, 53%) dec. 238 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.40 – 7.26 (m, 6H), 5.49 (s, 2H), 4.35 (s, 4H), 1.75 (dq, J = 14.5, 7.2 Hz, 4H), 1.51 (dq, J = 14.6, 7.3 Hz, 4H), 0.61 (t, J = 7.2 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 148.8, 137.1, 128.9, 128.6, 128.0, 94.3, 70.3, 44.3, 31.6, 7.5. **HRMS (ESI)** *m/z* calculated for $C_{30}H_{36}N_2NaO_4$ $[M+Na]^+$: 511.2567, found: 511.2565.



(Z)-3-benzyl-5-((Z)-2-(3-benzyl-2-oxooxazolidin-5-ylidene)ethylidene)-4,4-dimethyloxazolidin-2-one (3q). Pale yellow oil (99.0 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 10H), 5.57 (s, 2H), 4.50 (s, 2H), 4.47 (s, 2H), 4.10 (s, 2H), 1.32 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 154.5, 152.7, 141.1, 137.4, 134.8, 129.0, 128.7, 128.4, 128.2, 127.8, 127.8, 96.3, 93.5, 61.8, 48.0, 47.4, 44.1, 27.5. **HRMS (ESI)** *m/z* calculated for $C_{24}H_{24}N_2NaO_4$ $[M+Na]^+$: 427.1628, found: 427.1622.

Characterization of 4p

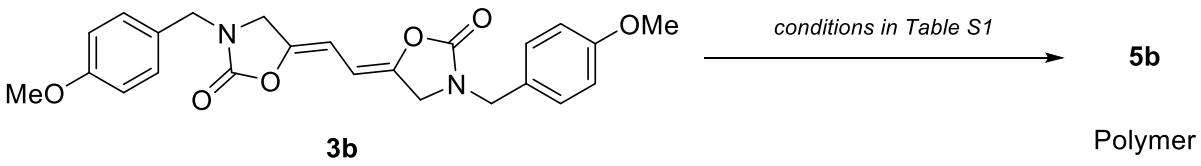


(Z)-3-benzyl-5-(4-(benzylamino)-4-ethylhex-2-yn-1-ylidene)-4,4-diethyloxazolidin-2-one (4p). Pale yellow oil (81.6 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 4H), 7.37 – 7.32 (m, 4H), 7.26 (t, J = 7.3 Hz, 2H), 4.71 (s, 1H), 4.37 (s, 2H), 3.86 (s, 2H), 1.74 (dtq, J = 28.5, 14.3, 7.3 Hz, 6H), 1.48 (dd, J = 14.7, 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 6H), 0.67 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 155.6, 141.1, 137.0, 128.9, 128.6, 128.6, 128.4, 128.1, 126.8, 99.2, 81.9, 76.1, 70.5, 58.4, 48.3, 44.3, 31.9, 30.6, 8.3, 7.5. **HRMS (ESI)** *m/z* calculated for $C_{29}H_{36}N_2NaO_2$ $[M+Na]^+$: 467.2669, found: 467.2666.

5. Crystallographic Data

Powder X-Ray Diffraction Data

Reaction conditions tested to promote the polymerization of 3b to 5b. The ball mill grinding experiments were performed by means of a Fritsch Pulverisette 23 shaker mill with a vertical movement. This mill has a fixed amplitude of 9 mm and adjustable frequency from 15 to 50 Hz with an adjustable timer.



3b

Entry	Metodology	Solvent	Oxidant	Milling Frequency (Hz)	Temperature (°C)	Time (h)
1[a]	Batch	MeCN	O_2 (1 atm)	-	80	72
2[a]	Batch	MeCN	O_2 (1 atm)	-	100	72
3[b]	Ball Milling	neat	Air (1 atm)	50 Hz	r.t.	1.5

Table S1. Reaction conditions: [a] **3b** (0.1 mmol) was dissolved in MeCN (1.5 mL) and was kept at 80-100 °C under O_2 atmosphere for 72h. [b] **3b** (0.1 mmol) was milled at the frequency of 50 Hz in a 15 mL stainless-steel jar under atmosphere conditions for 1.5h.

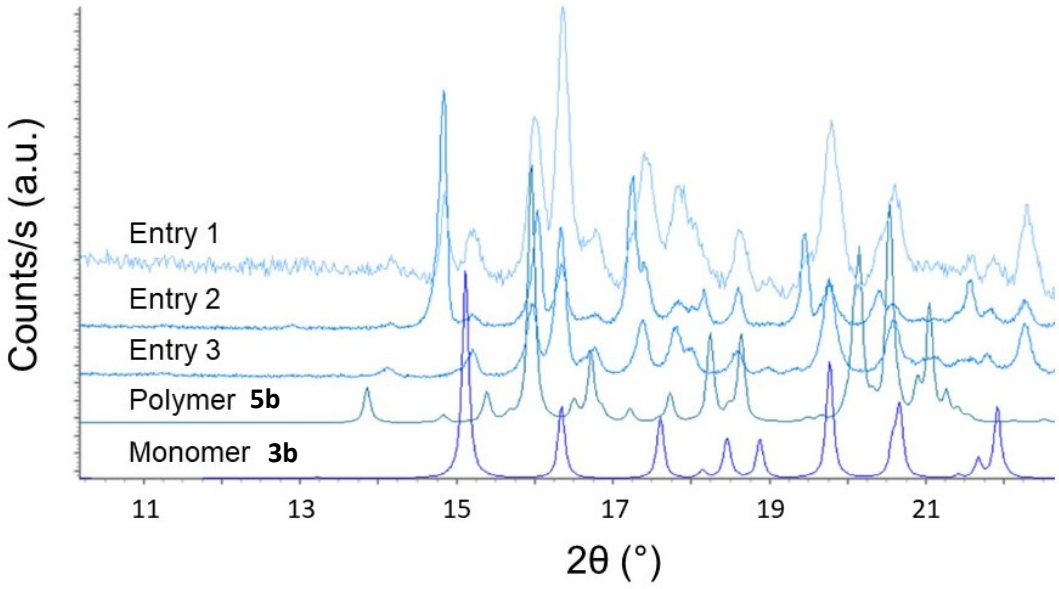


Figure S3. Cascade visualization of PXRD pattern of polymer formation from **3b**. Experimental conditions refer to those in TableS1. From lower to upper powder pattern: calculated powder pattern of **3b**; calculated powder pattern of **5b**; experimental data after treating **3b** under conditions of Entry 3; experimental data after treating **3b** under conditions of Entry 2; experimental data after treating **3b** under conditions of Entry 1.

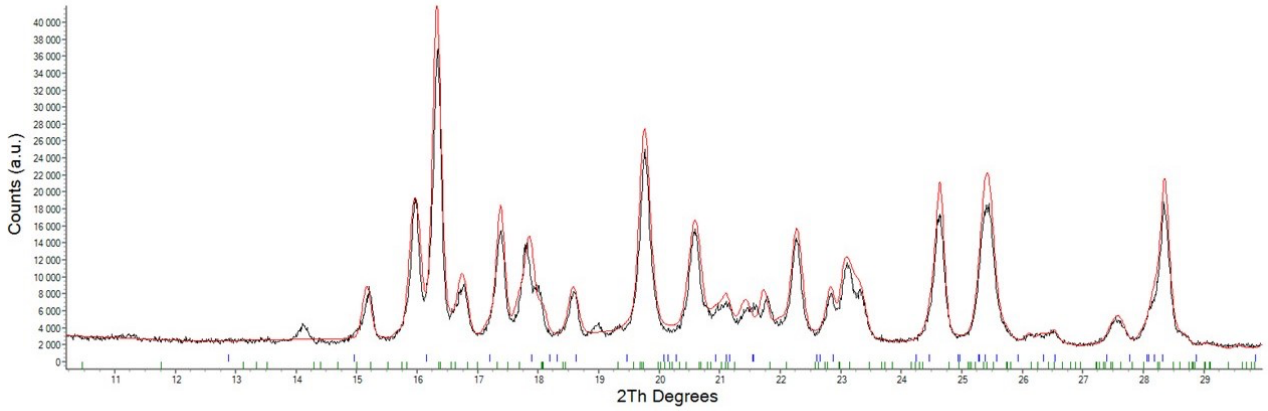


Figure S4. Pawley refinement of **3b** after the mechanochemical treatment as reported in the experimental section. Multi-phase model (red line) against experimental data (black line) shows the co-presence of both **3b** and **5b**. Green and Blue ticks reported at the below the powder pattern refers to the modelled peaks positions of **5b** and **3b** respectively.

Single Crystal X-Ray Diffraction Data

Identification code	**3b**	**3i**	**5b**
Empirical formula	$C_{24}H_{24}N_2O_6$	$C_{10}H_{12}N_2O_4$	$C_{36}H_{36}N_3O_9$
Formula weight	436.45	224.22	654.68
Temperature/K	200.00	200.00	293.00(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	$P2_1/n$	P-1
a/Å	40.9802(7)	6.6549(3)	6.0202(3)
b/Å	5.98560(10)	12.8056(5)	13.4077(7)
c/Å	8.7293(2)	6.6575(3)	19.4725(12)
α/°	90	90	97.433(5)
β/°	97.2560(10)	116.973(2)	91.503(4)
γ/°	90	90	92.772(4)
Volume/Å^3	2124.07(7)	505.64(4)	1555.89(15)
Z	4	2	2
ρ_{calc}g/cm^3	1.365	1.473	1.397
μ/mm^{-1}	0.818	0.115	0.837
F(000)	920.0	236.0	690.0
Crystal size/mm^3	0.3 × 0.05 × 0.05	0.8 × 0.7 × 0.7	0.2 × 0.03 × 0.03
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.348 to 140.084	6.364 to 52.804	6.658 to 133.2
Index ranges	-49 ≤ h ≤ 49 -7 ≤ k ≤ 7 -9 ≤ l ≤ 10	-8 ≤ h ≤ 8, -15 ≤ k ≤ 13 -8 ≤ l ≤ 8	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	13280	4910	27348
Independent reflections	2013 R_{int} = 0.0367 R_{sigma} = 0.0205	1022 R_{int} = 0.0480 R_{sigma} = 0.0353	5448 R_{int} = 0.1104, R_{sigma} = 0.0604
Data/restraints/parameters	2013/0/193	1022/0/75	5448/2/455
Goodness-of-fit on F^2	1.046	1.103	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0343 wR_2 = 0.0886	R_1 = 0.0334 wR_2 = 0.0860	R_1 = 0.0952, wR_2 = 0.2692
Final R indexes [all data]	R_1 = 0.0366 wR_2 = 0.0910	R_1 = 0.0347 wR_2 = 0.0868	R_1 = 0.1274, wR_2 = 0.3203
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19	0.19/-0.15	0.63/-0.41

Table S2. Crystal data and structure refinement for **3b**, **3i** and **5b**.

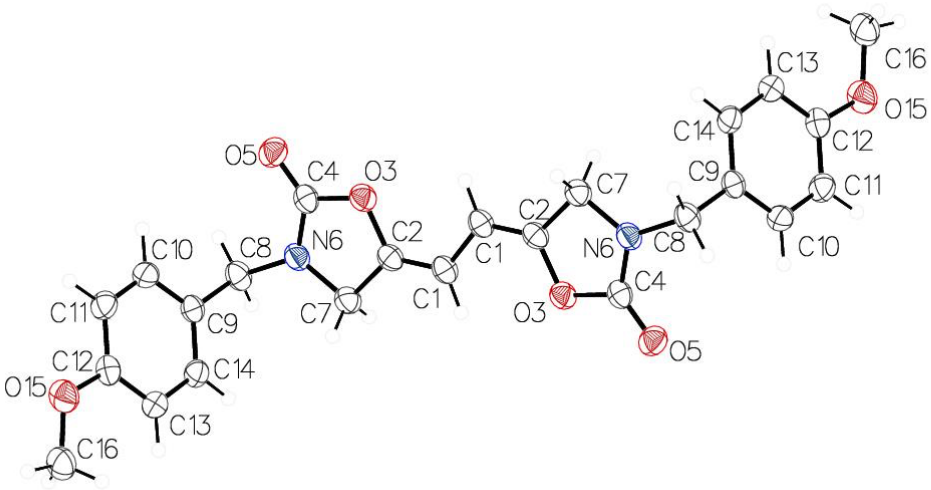


Figure S5 – ORTEP drawing of **3b**. All non-hydrogen atoms shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Colour code: O=red, N=blue, C=white. Symmetry related atoms are marked with the same label.

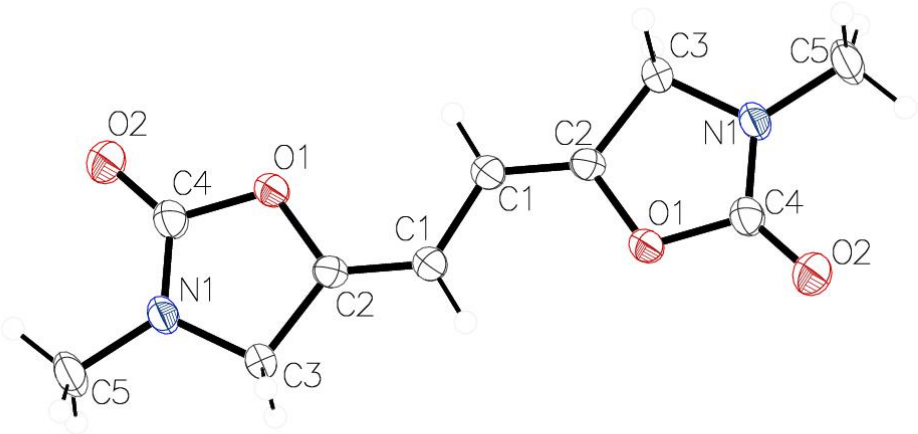


Figure S6 – ORTEP drawing of **3i**. All non-hydrogen atoms shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Colour code: O=red, N=blue, C=white. Symmetry related atoms are marked with the same label.

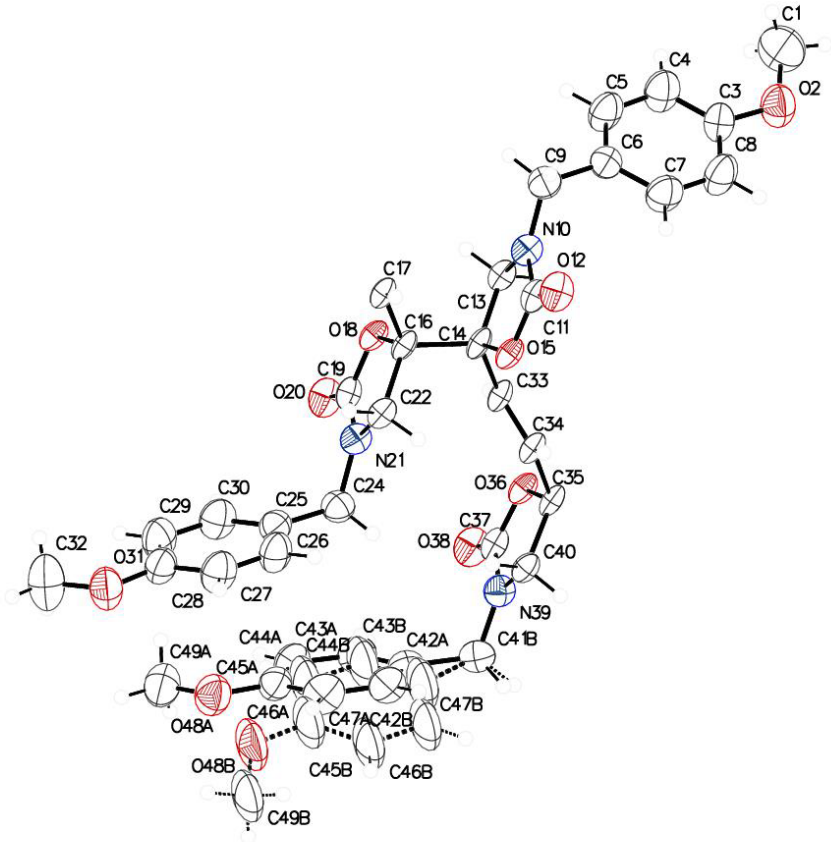


Figure S7 – ORTEP drawing of asymmetric unit of **5b**. All non-hydrogen atoms shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Colour code: O=red, N=blue, C=white. Disordered atoms are split in two parts labelled with *a* and *b* suffixes respectively.

6. References

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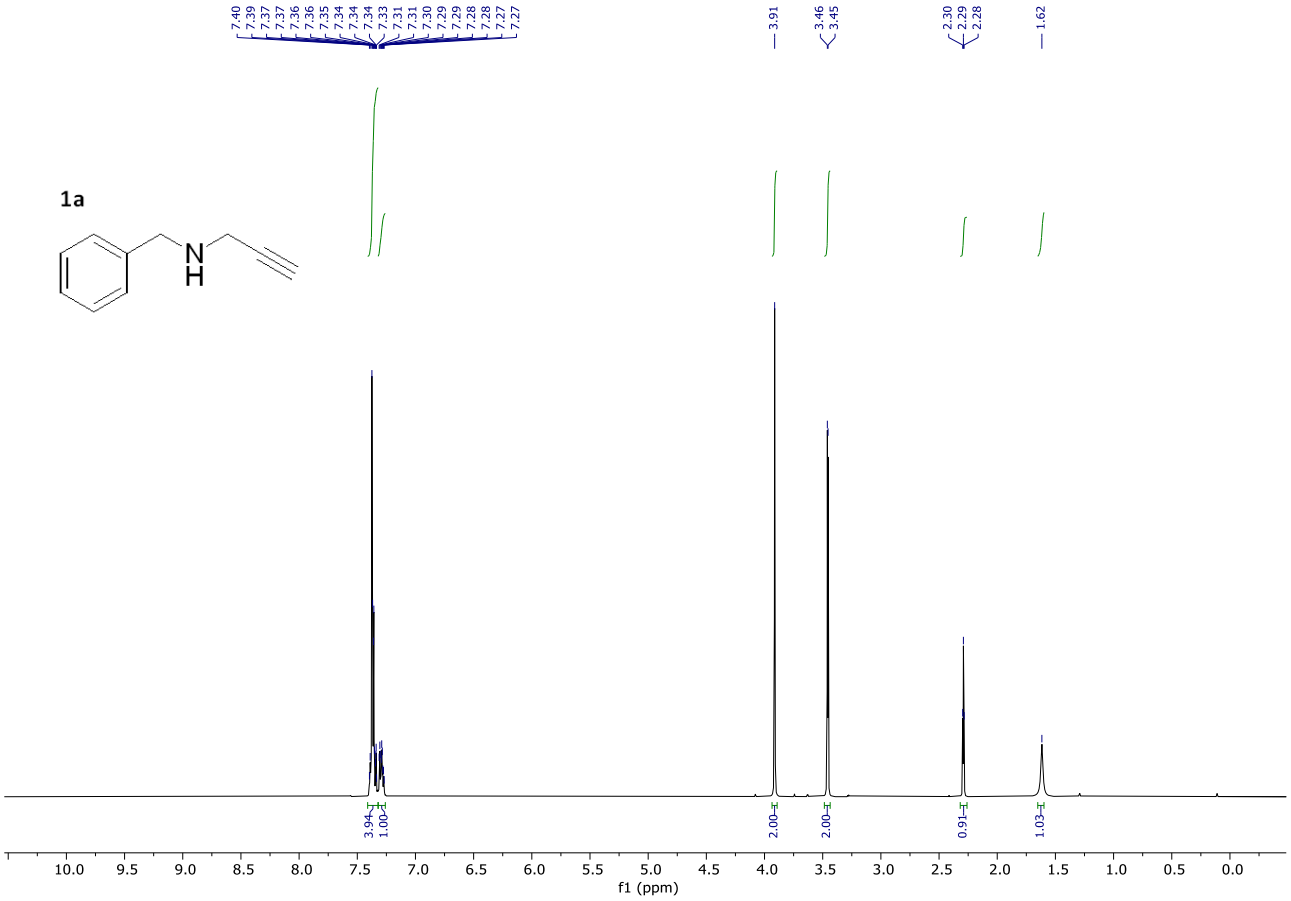
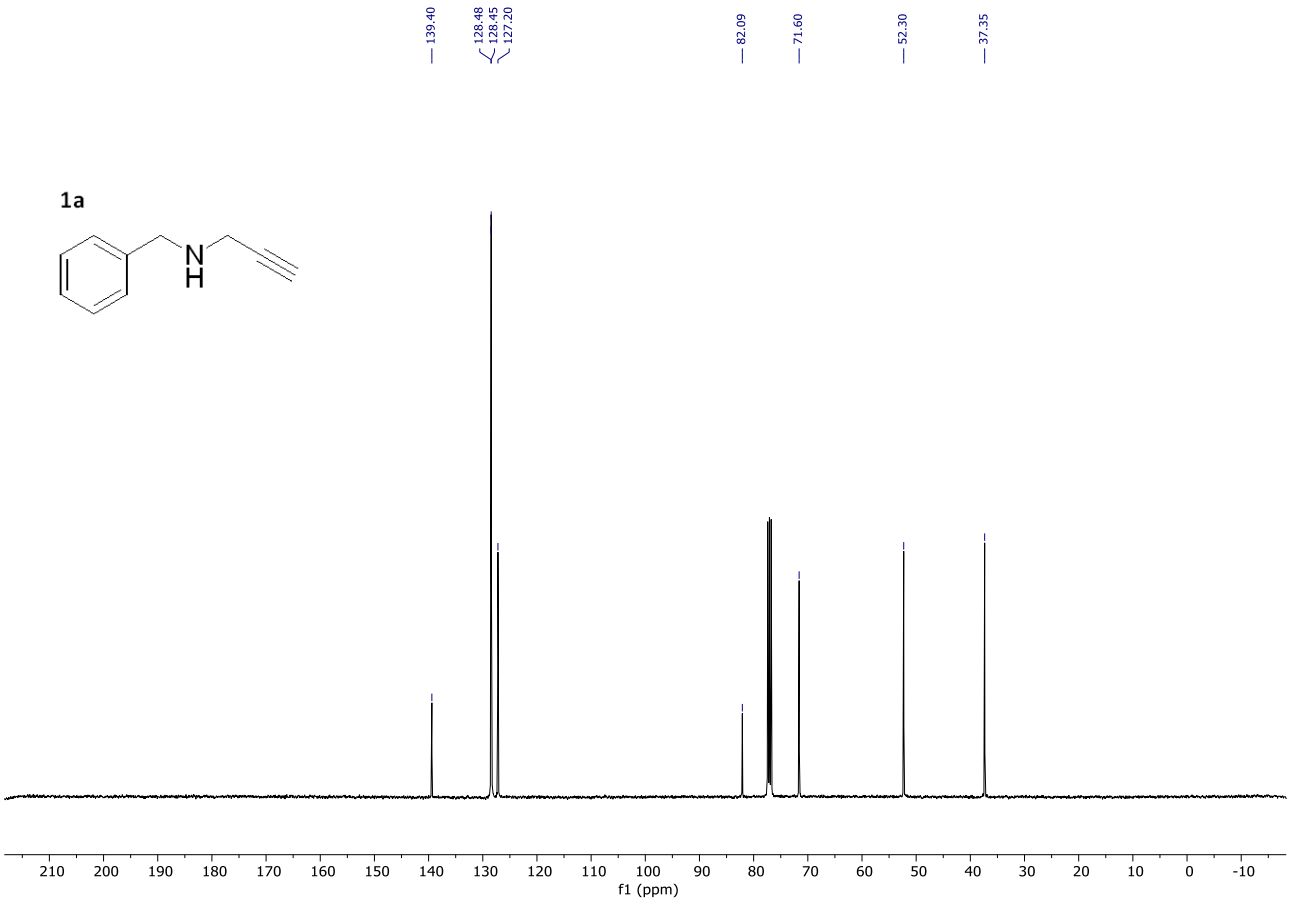
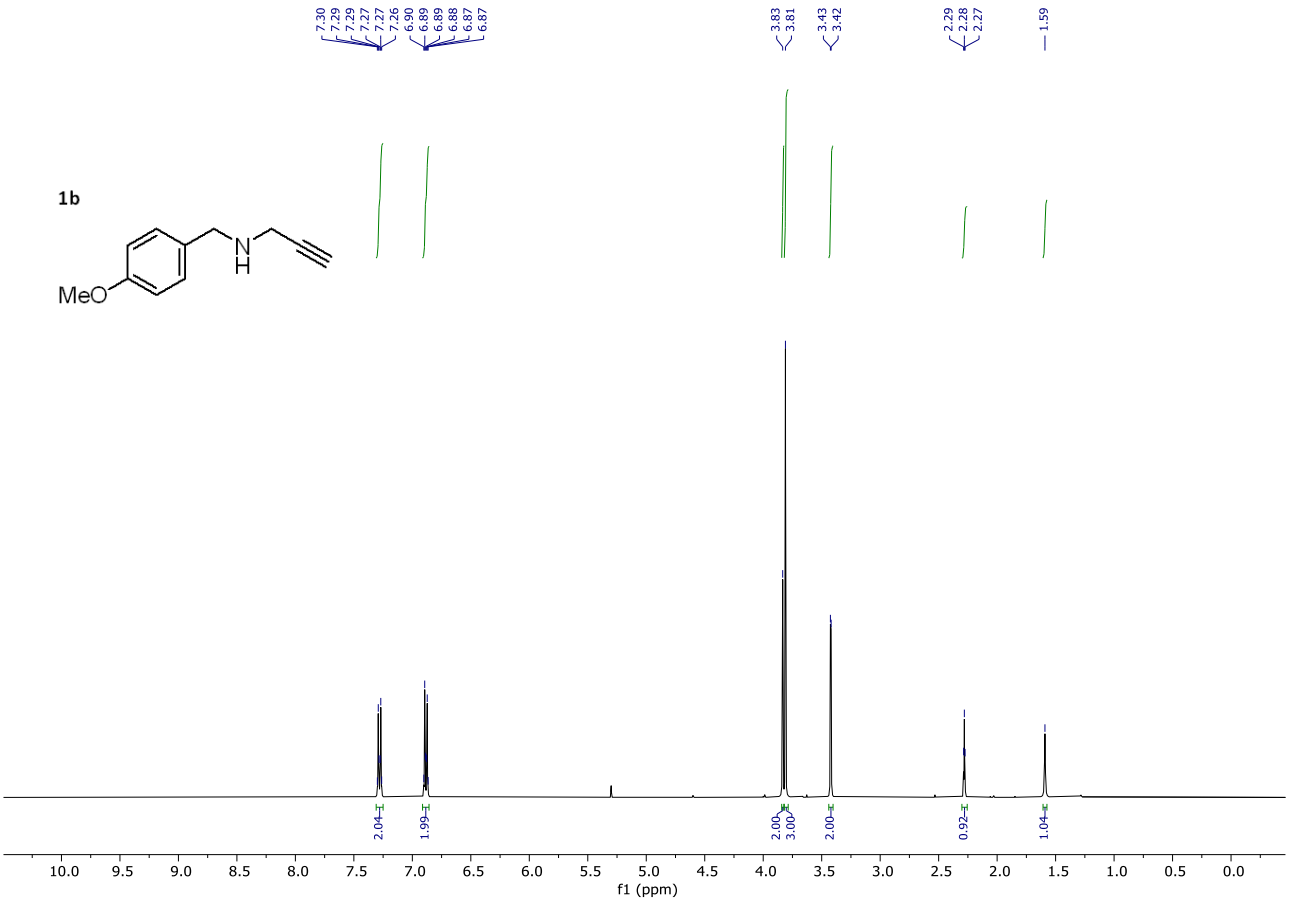
7. Copy of NMR Spectra



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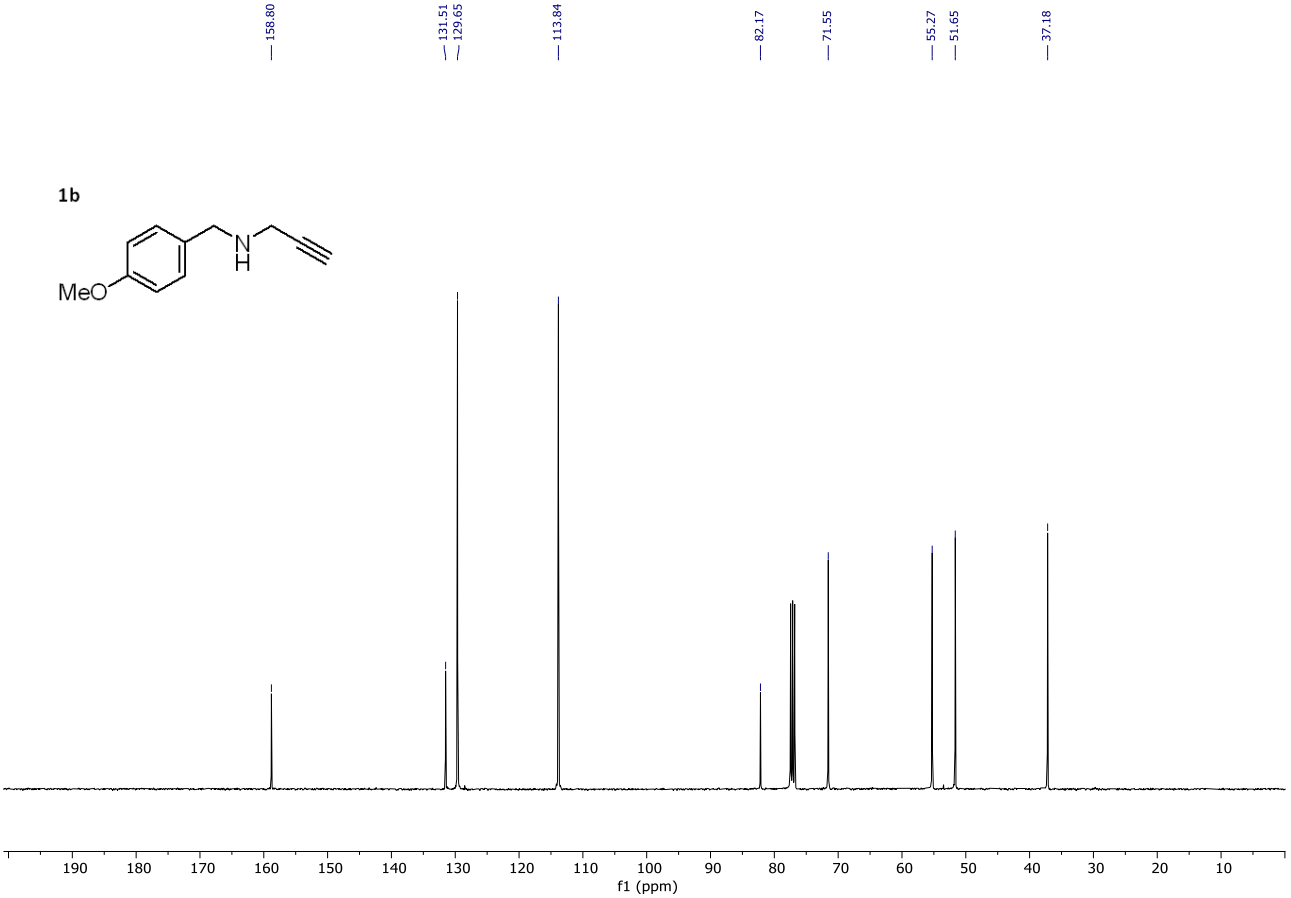
7.29
7.29
7.27
7.27
7.26
6.90
6.89
6.89
6.88
6.87
6.87
3.83
3.81
3.43
3.42
2.29
2.28
2.27
1.59
2.04
1.99
2.00
3.00
2.00
0.92
1.04
f1 (ppm)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55.27
51.65
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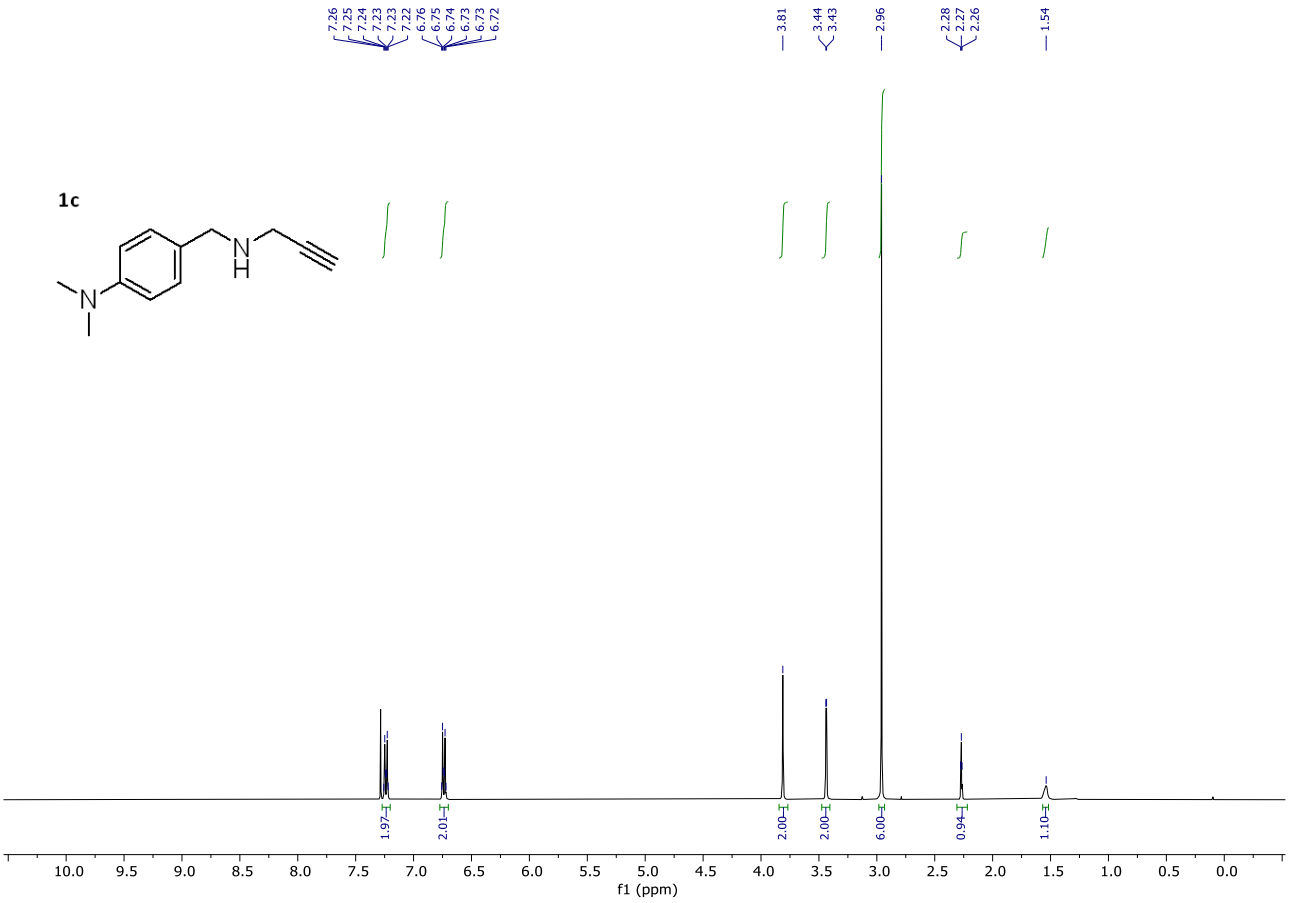
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7.23
7.22
6.76
6.75
6.74
6.73
6.73
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3.81
3.44
3.43
2.96
2.28
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1.54
1.97
2.01
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2.00
6.00
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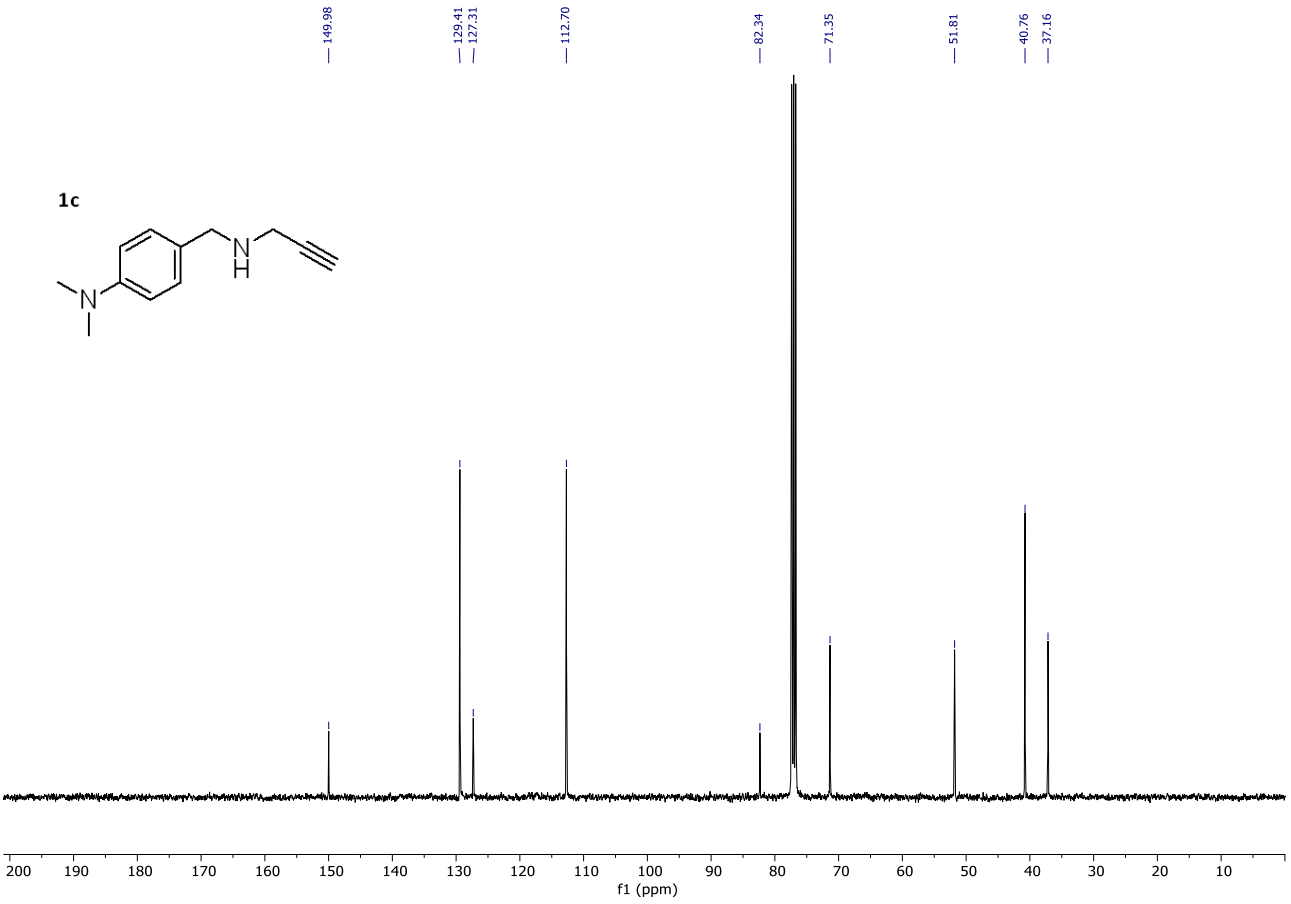
1.10
f1 (ppm)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71.35
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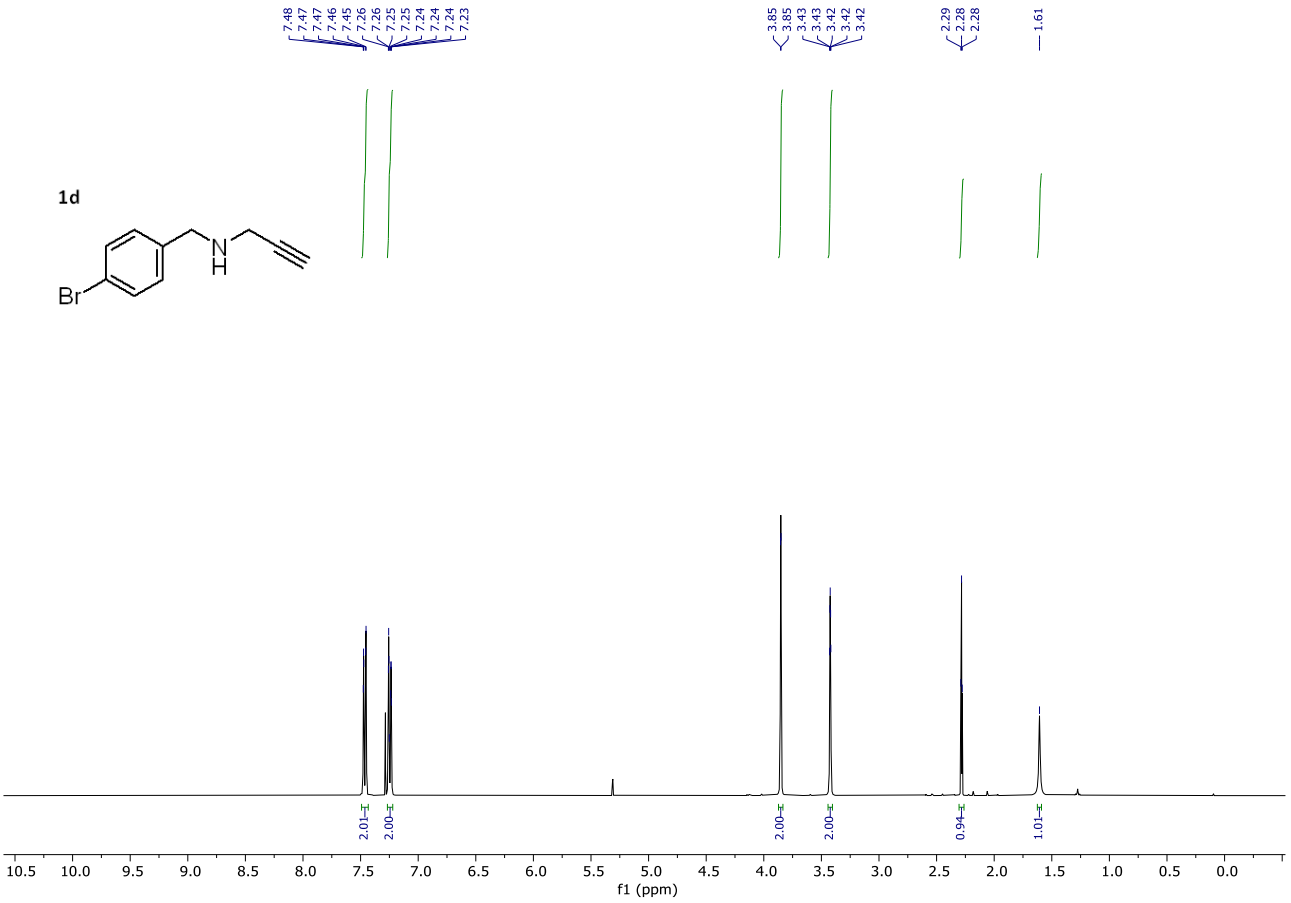
40.76
37.16
f1 (ppm)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7.47
7.46
7.45
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
3.85
3.85
3.43
3.43
3.42
3.42
3.42
2.29
2.28
2.28
1.61
1d
Br
N
H
2.01
2.00
2.00
2.00
0.94
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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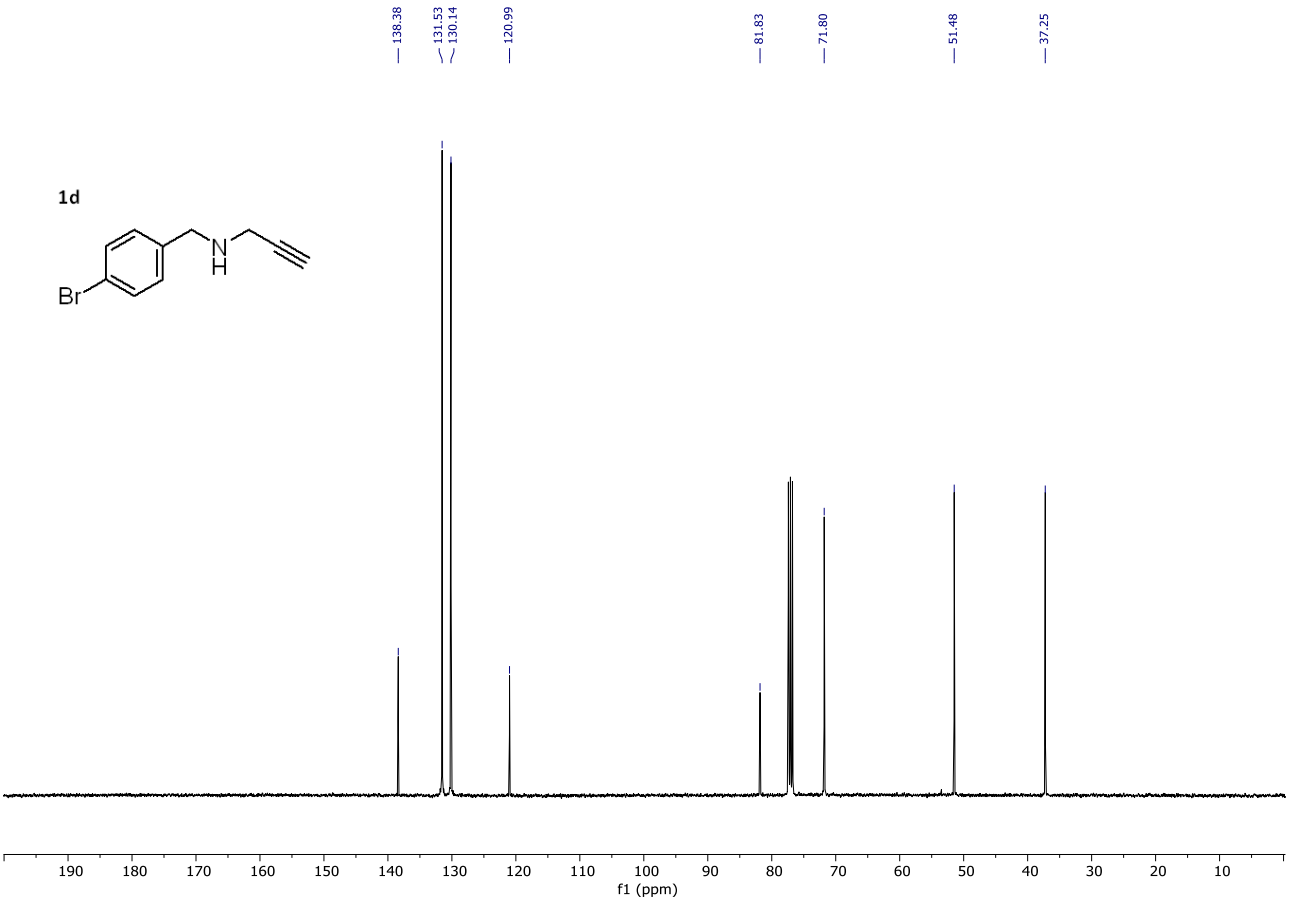
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H
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120
110
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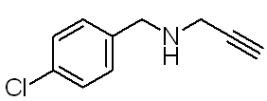
50
40
30
20
10
f1 (ppm)

1e



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3.40
3.39
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2.28
2.28
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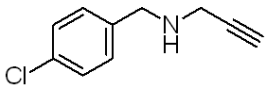
1.99
2.01
0.93
1.00
f1 (ppm)

1e



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71.83
51.41
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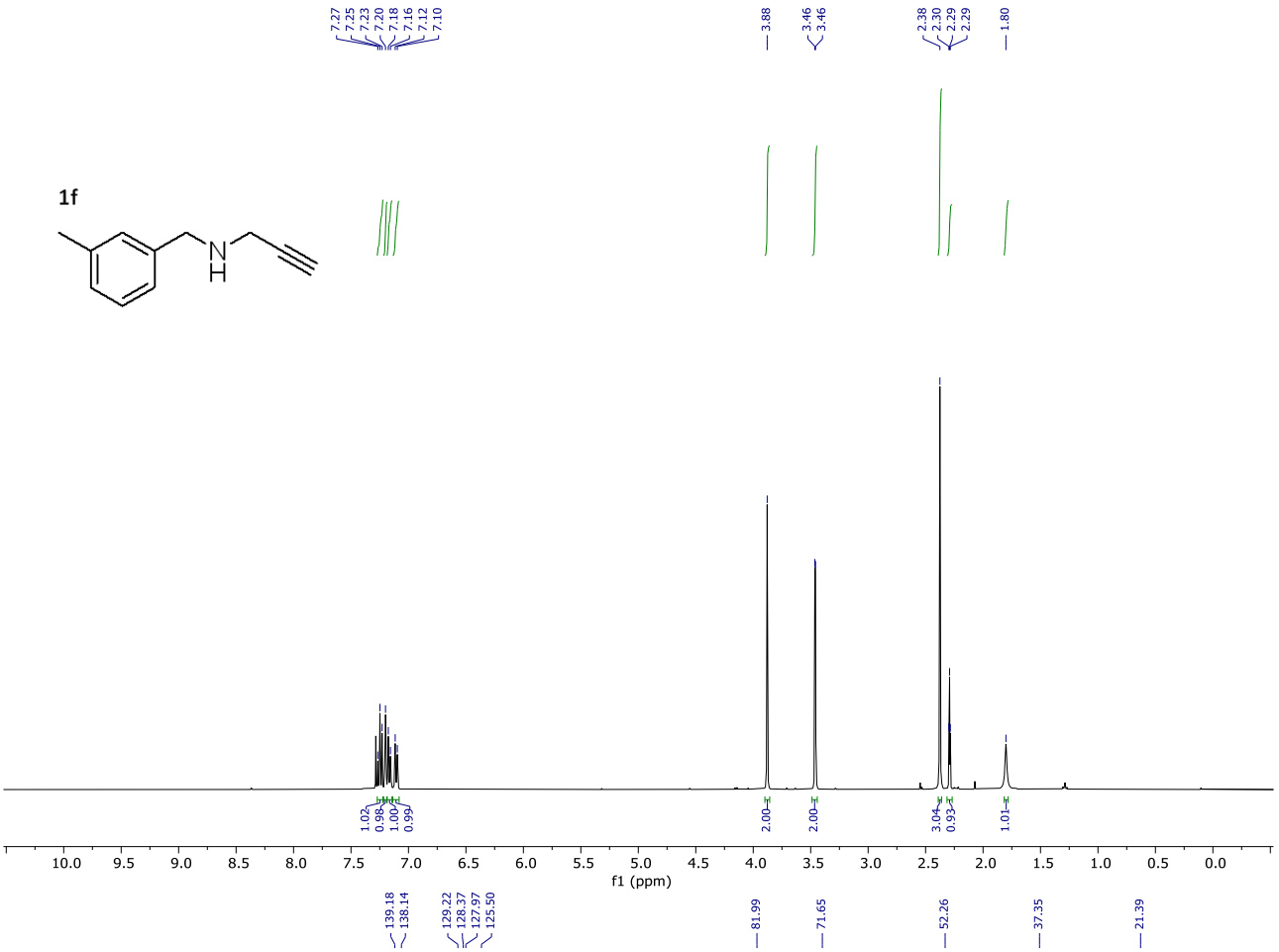
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2.30
2.29
2.29
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1.01
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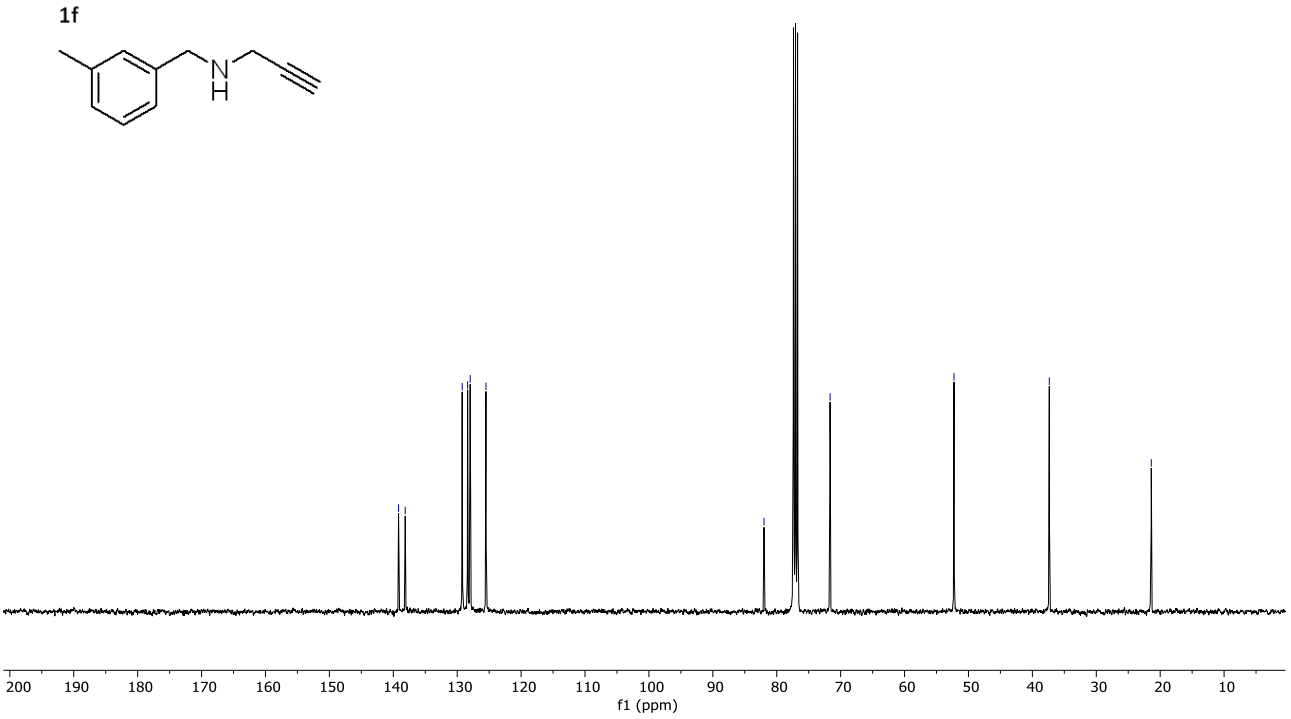
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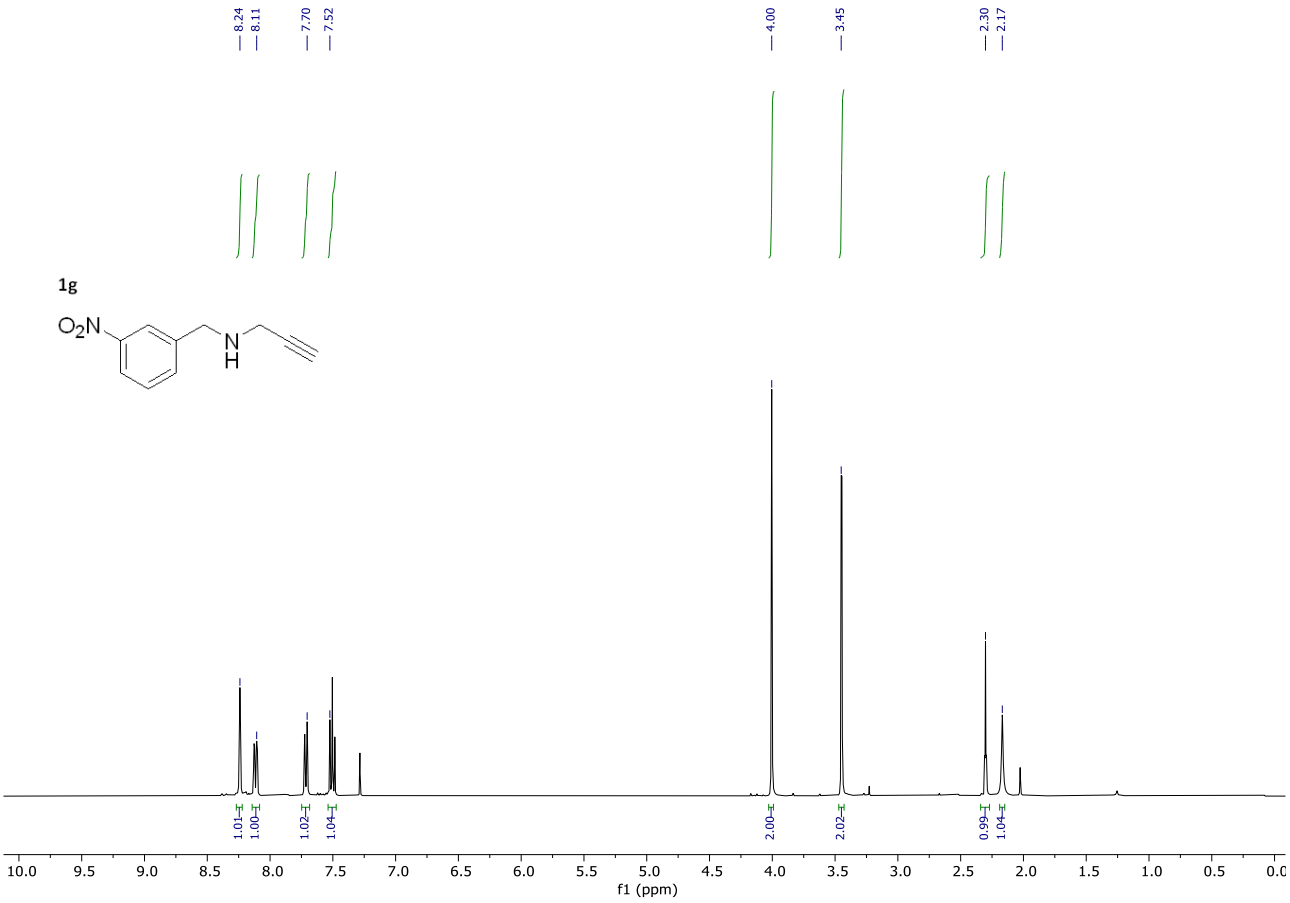
f1 (ppm)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H
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2.02
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1.04
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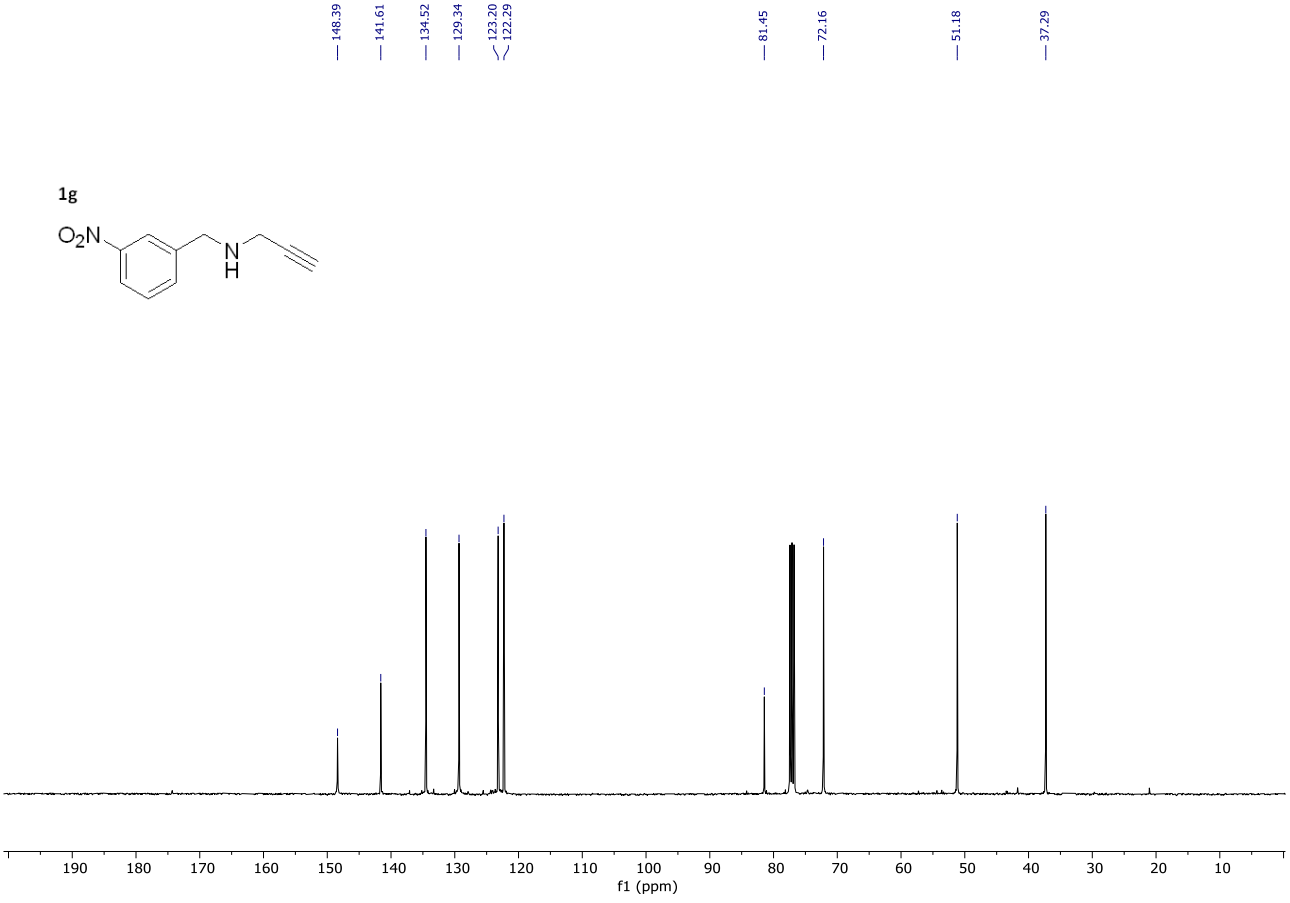
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N
H
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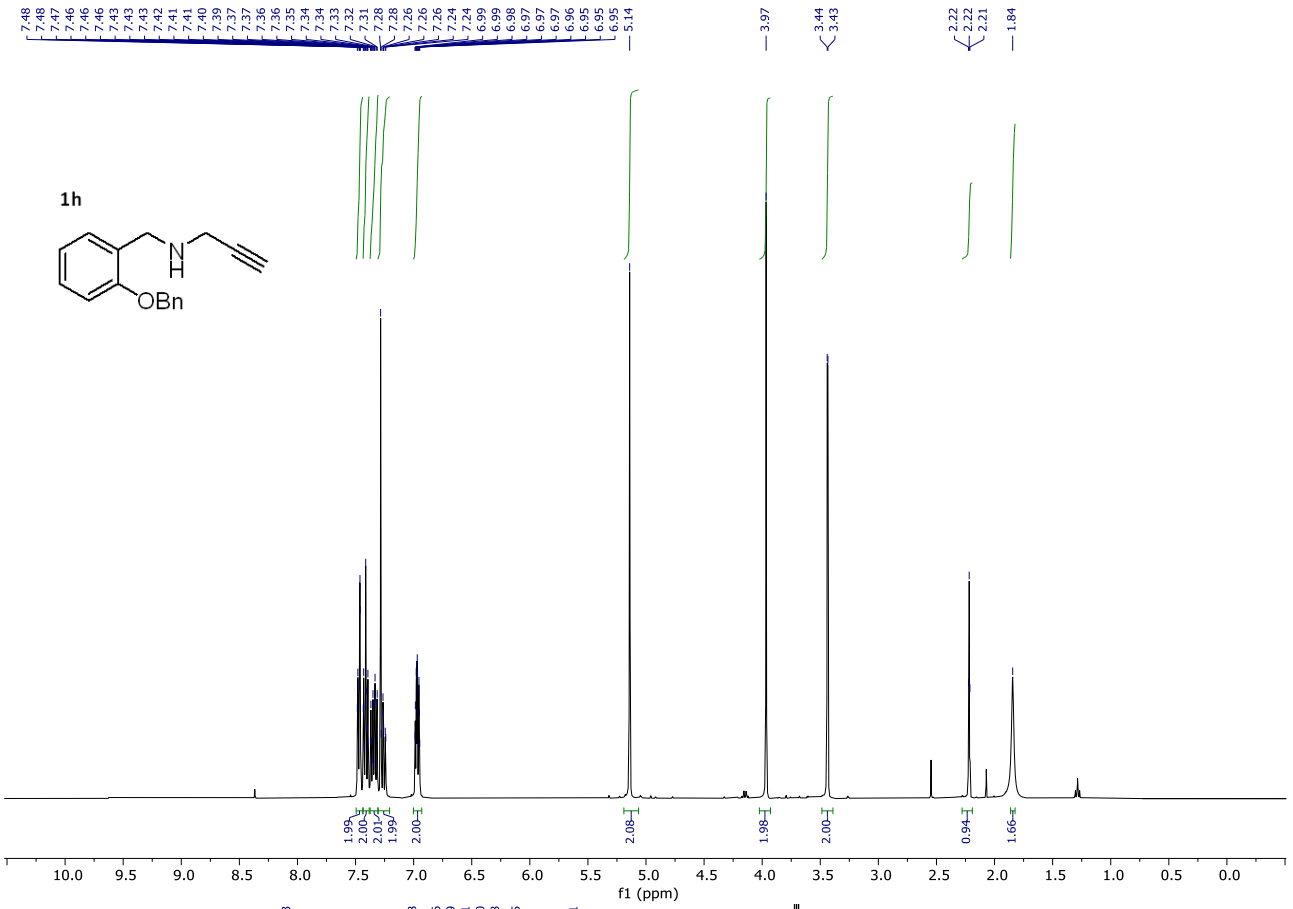
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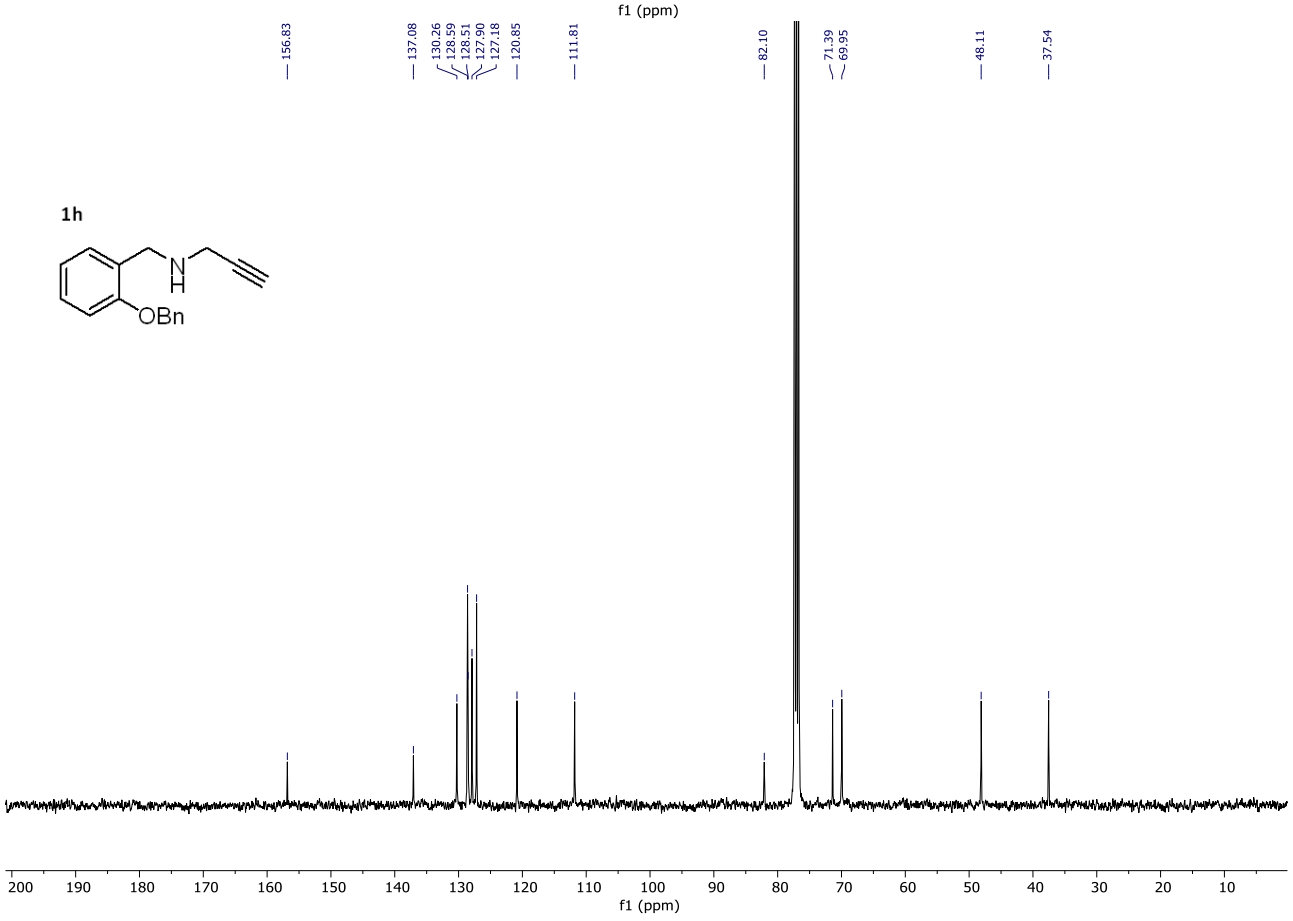
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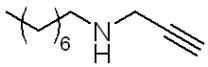

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1.50
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1.43
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1.31
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f1 (ppm)

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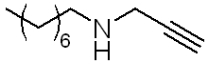

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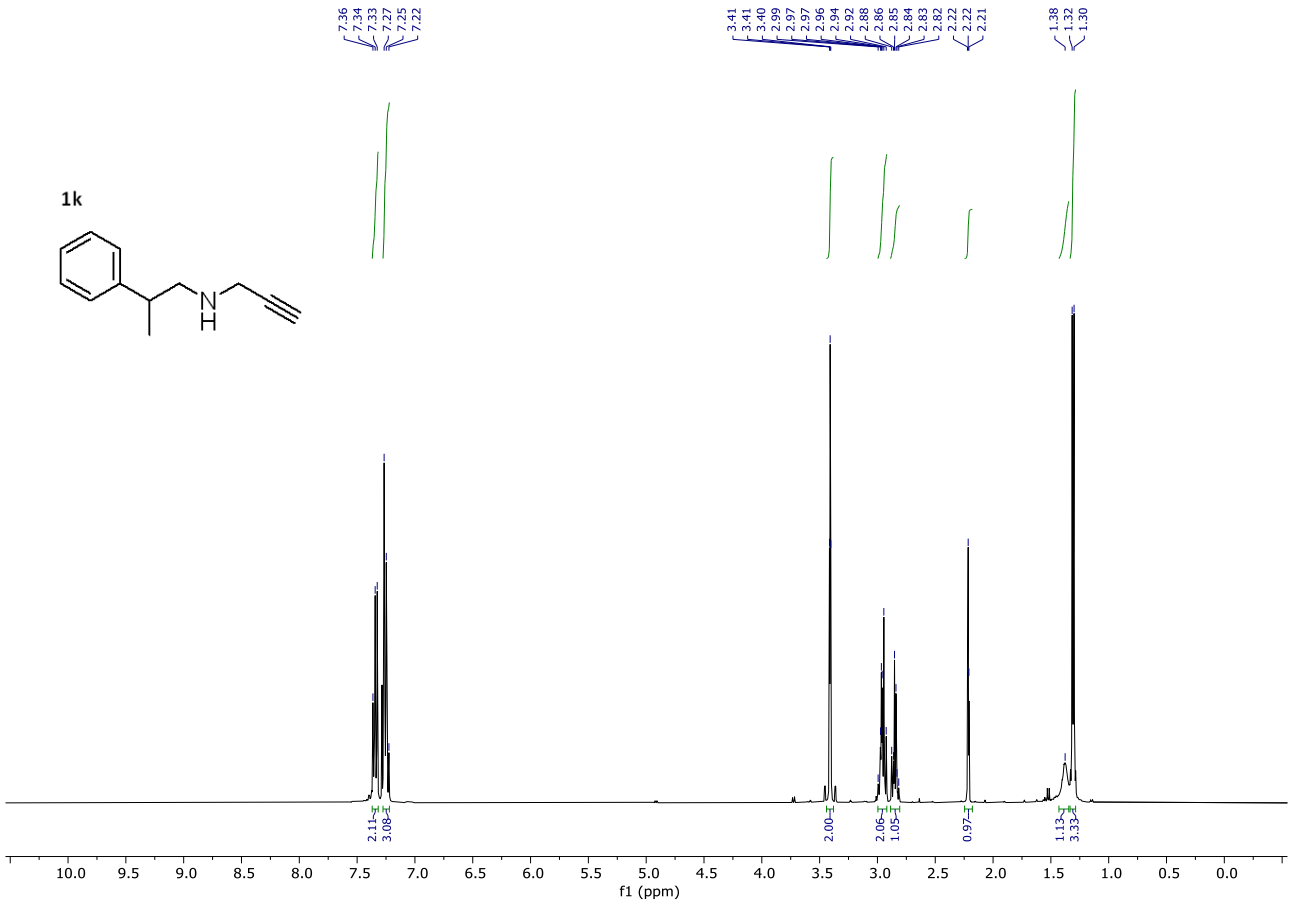
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2.22
2.22
2.21
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3.33
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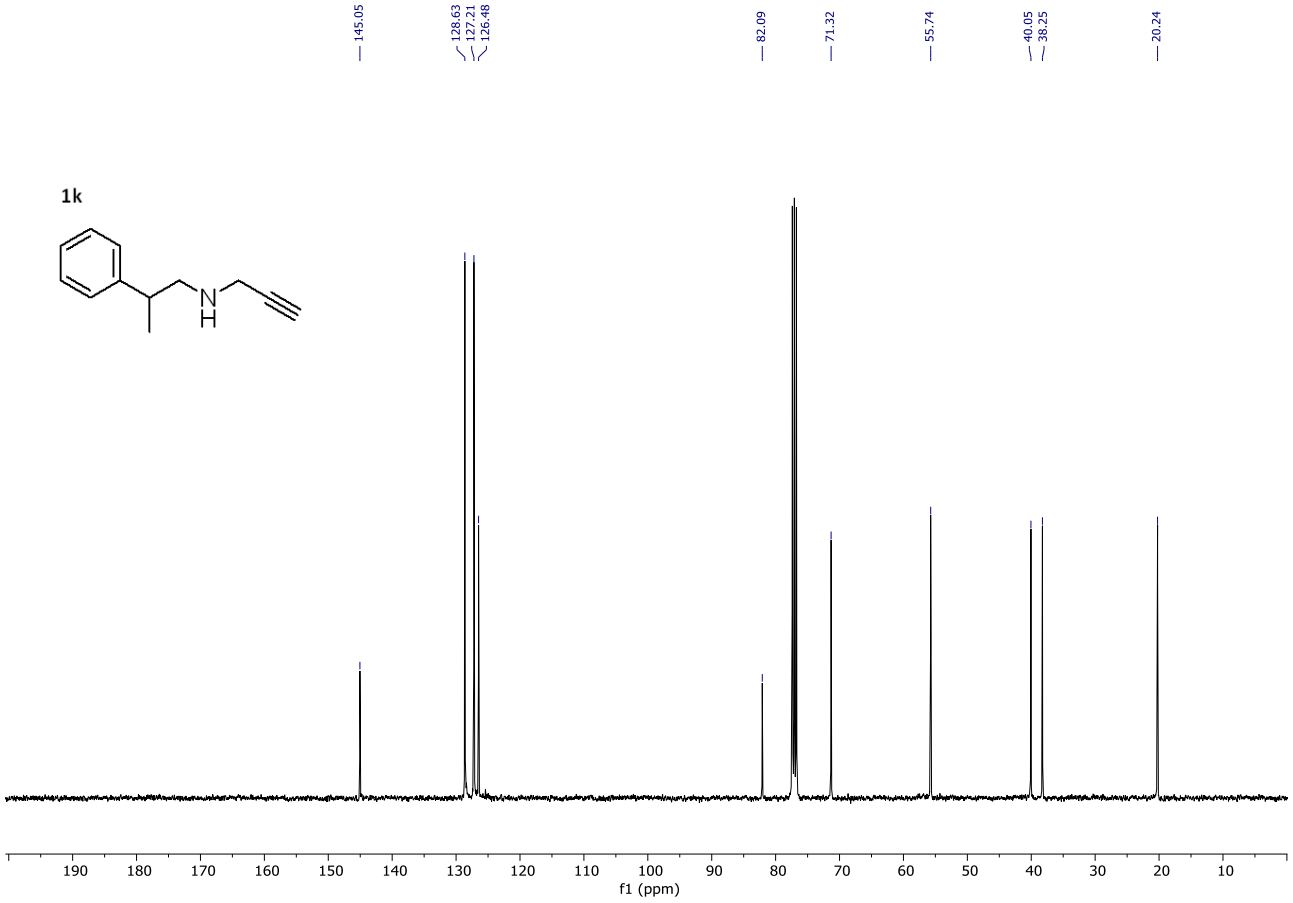
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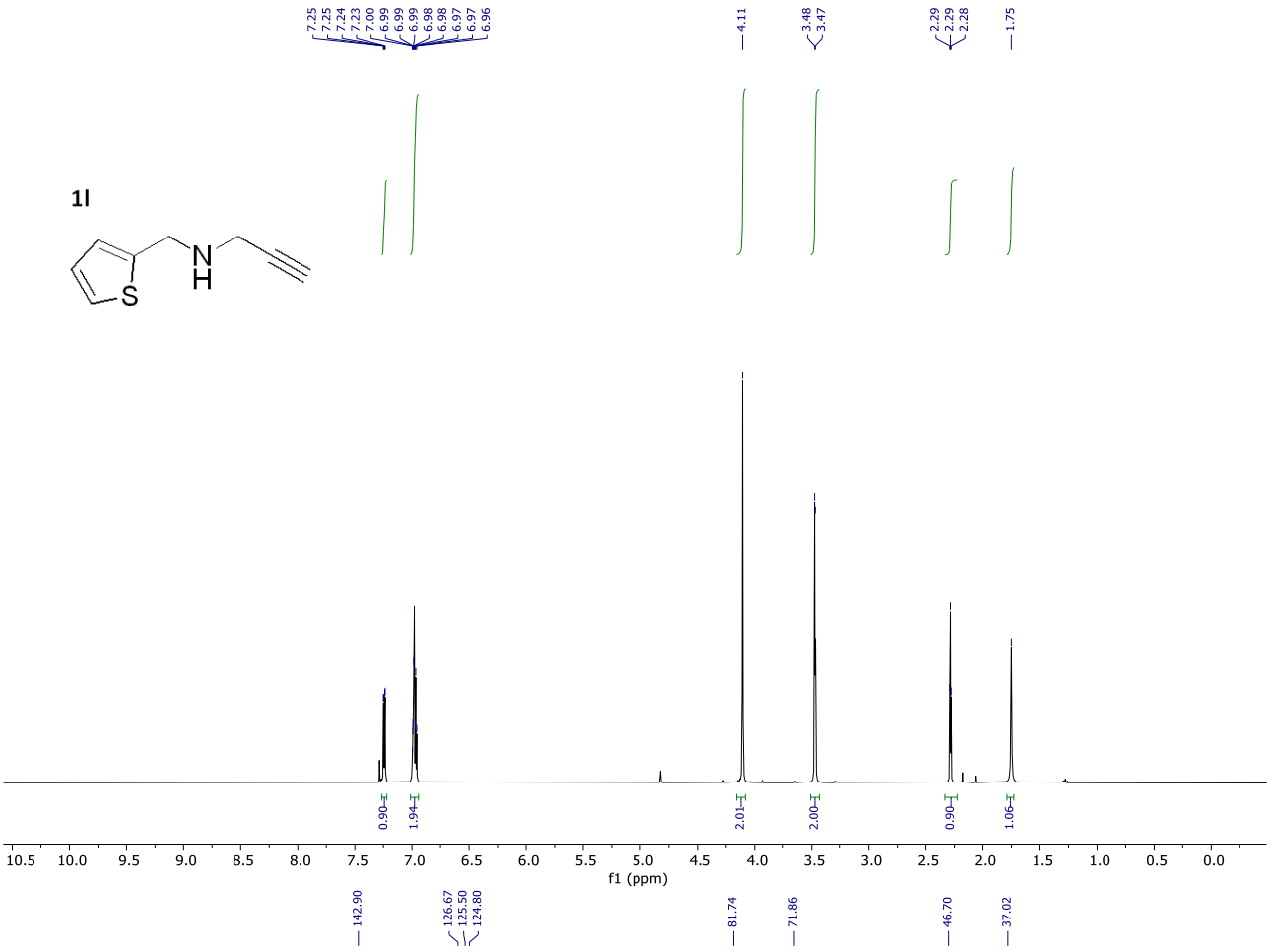
20.24
f1 (ppm)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6.99
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6.97
6.96
4.11
3.48
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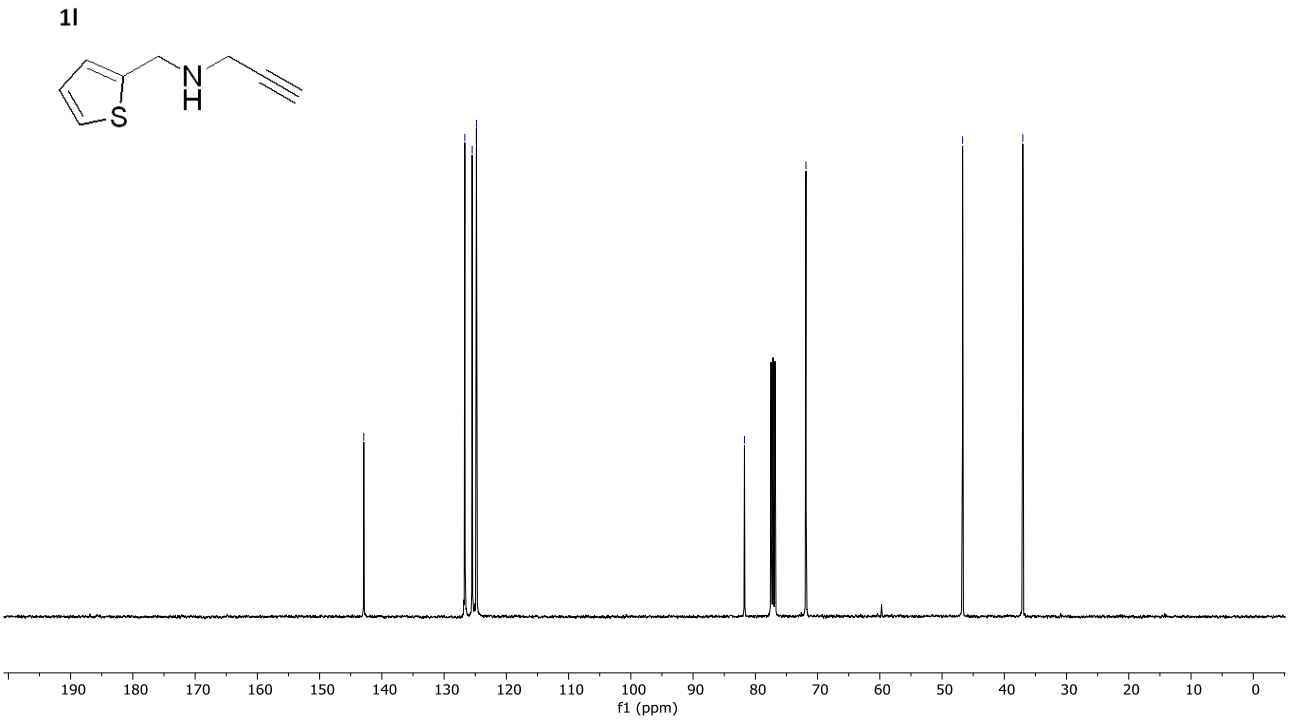
1.06
f1 (ppm)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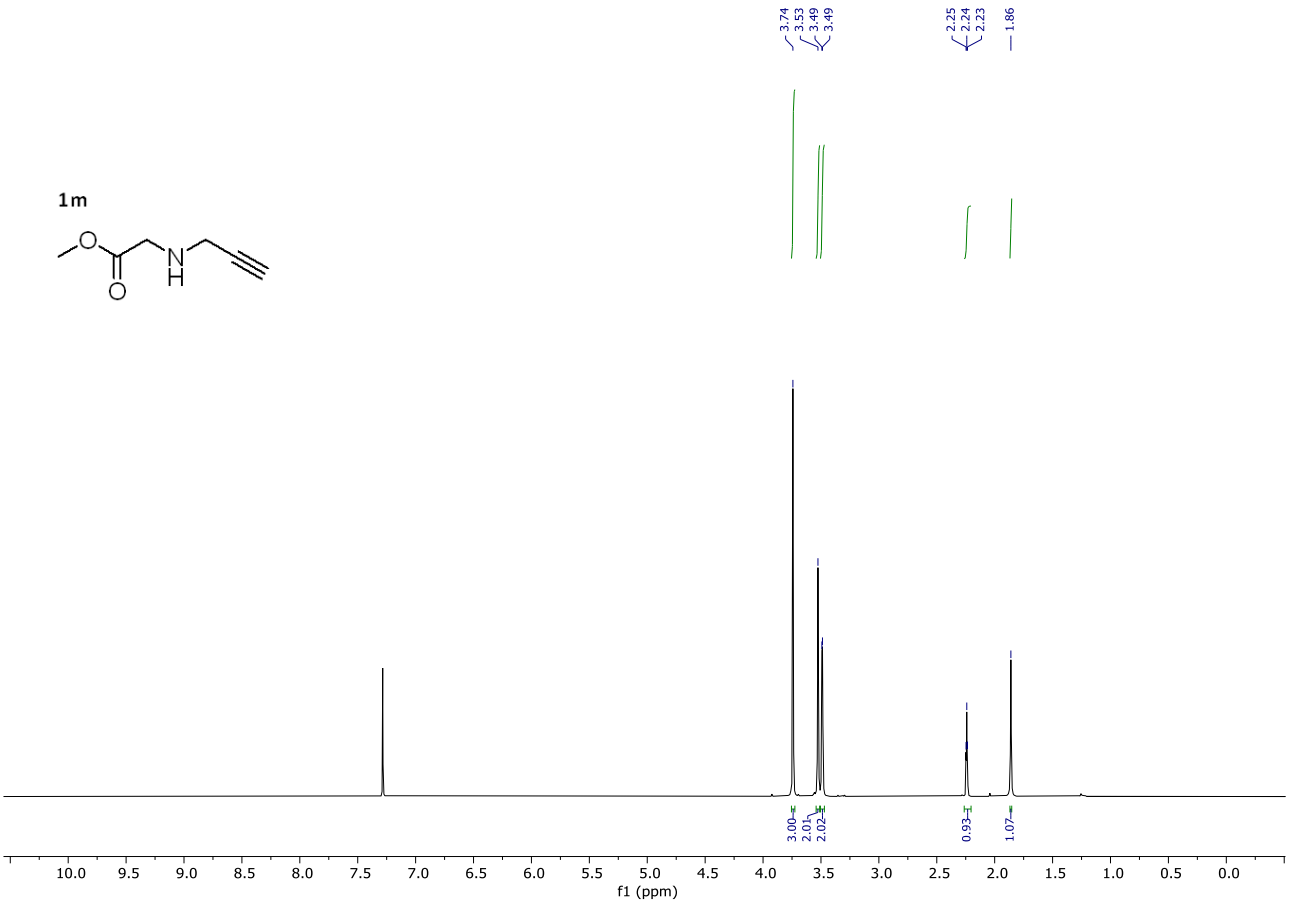
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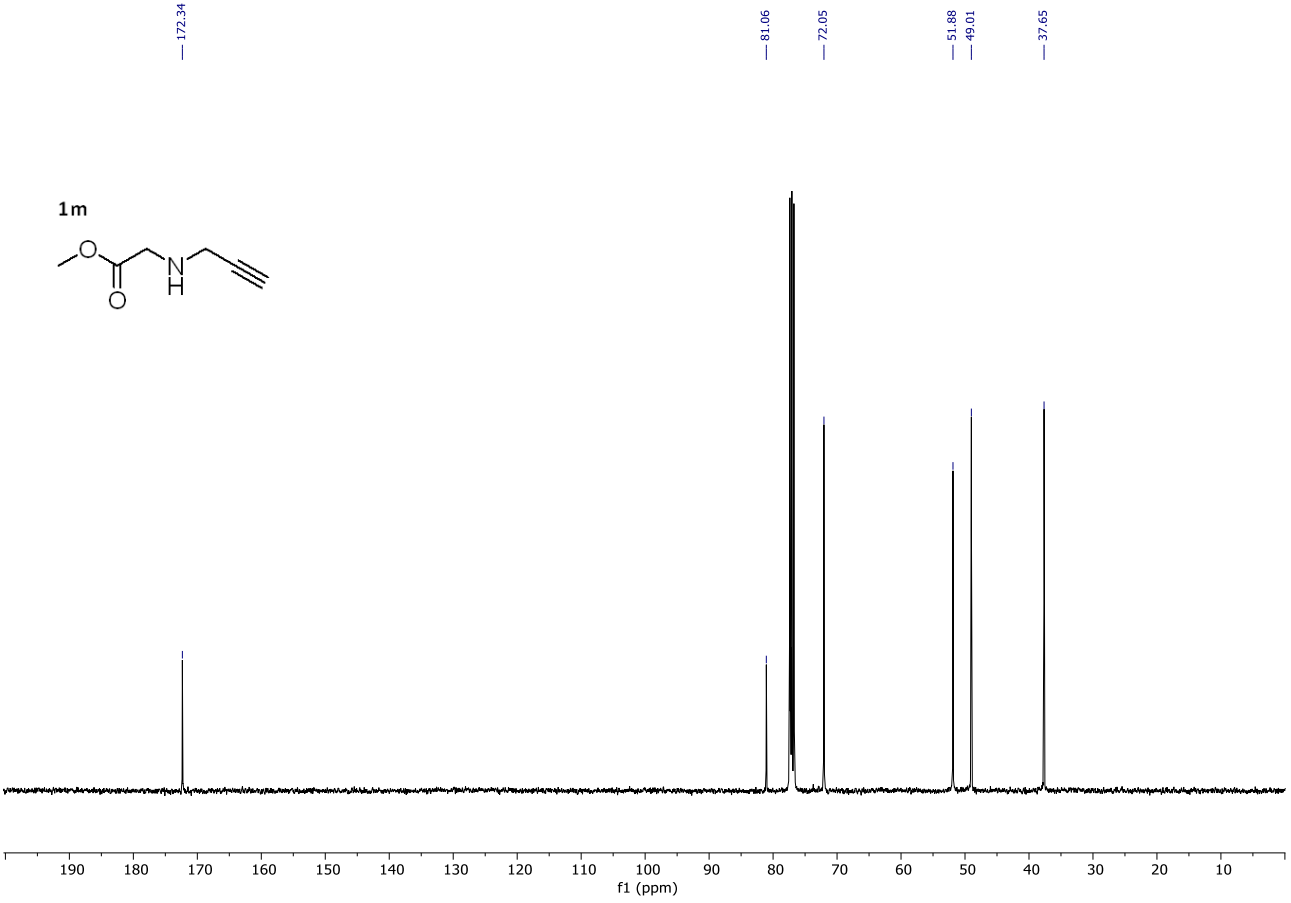
0.93
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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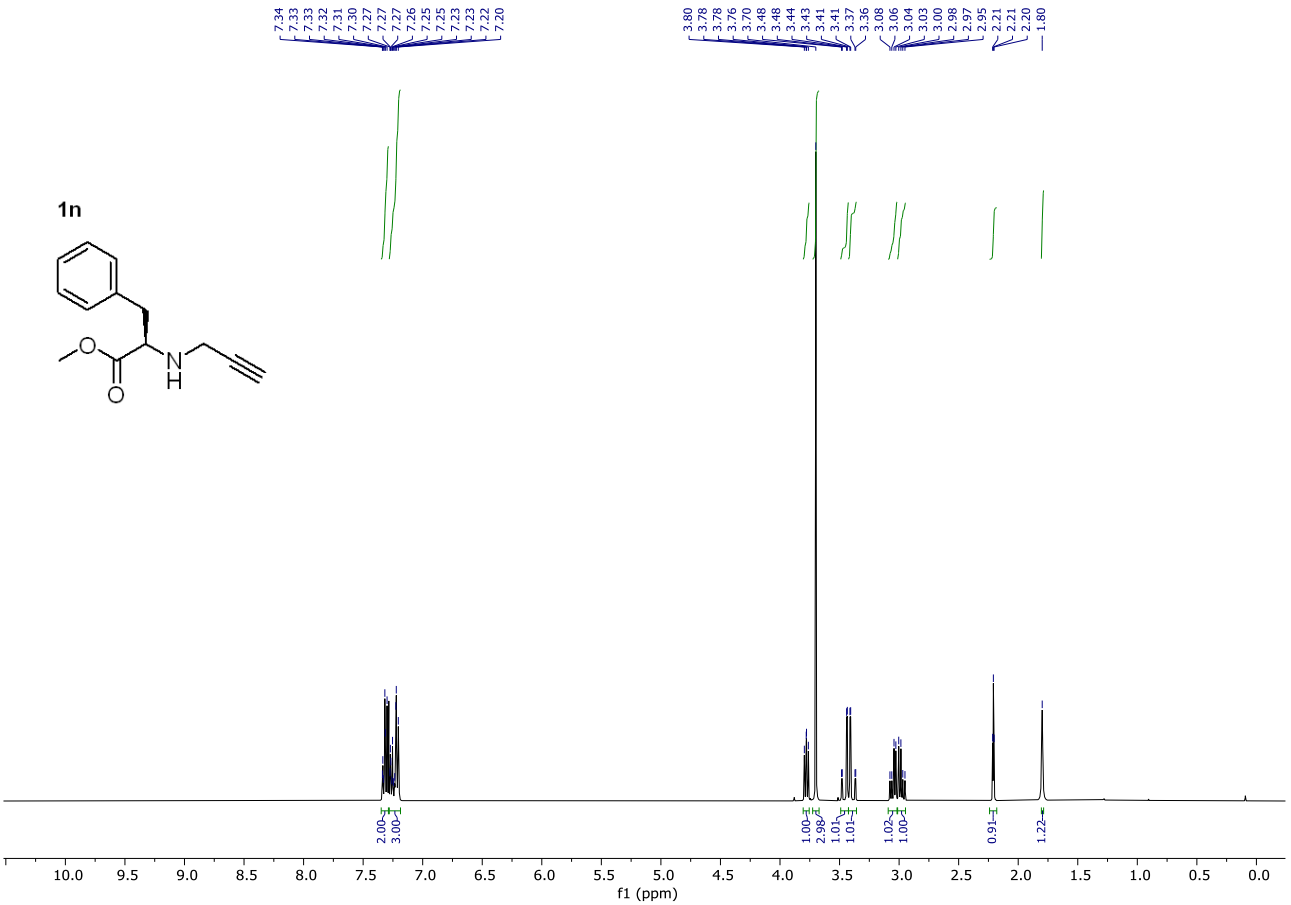
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7.23
7.23
7.22
7.20
3.80
3.78
3.78
3.76
3.70
3.48
3.48
3.44
3.43
3.41
3.41
3.37
3.36
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1.02
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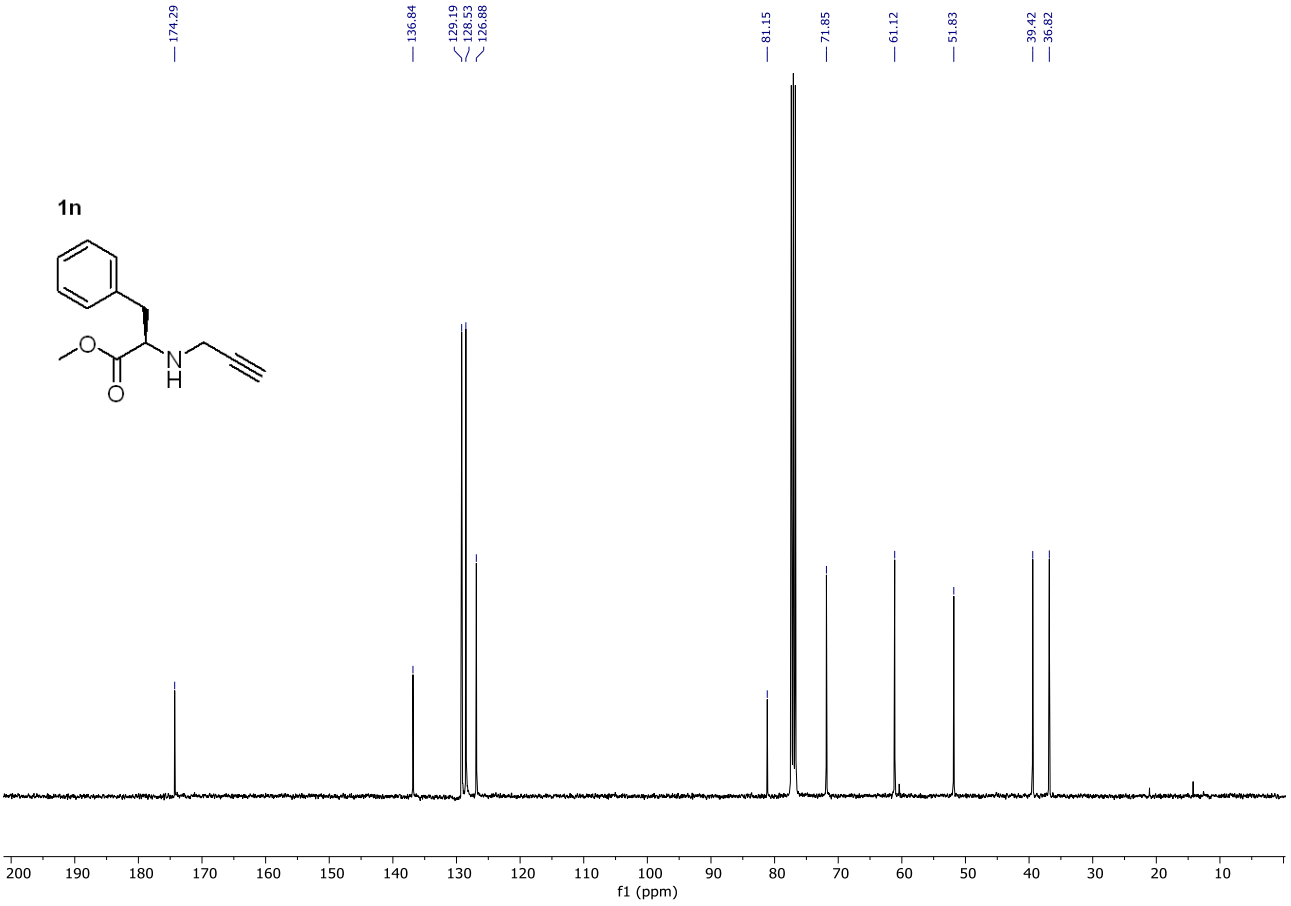
f1 (ppm)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200
190
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60
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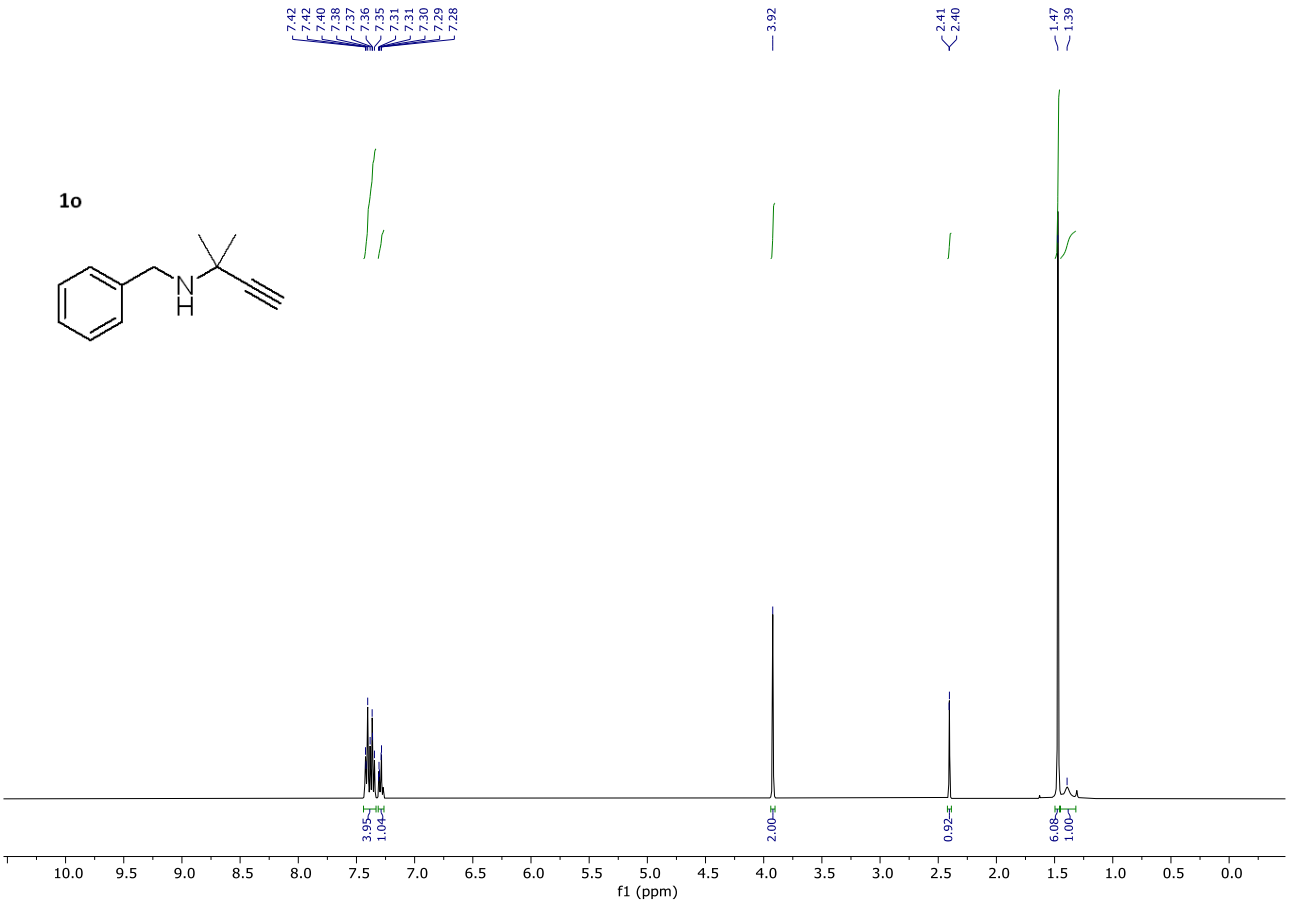
f1 (ppm)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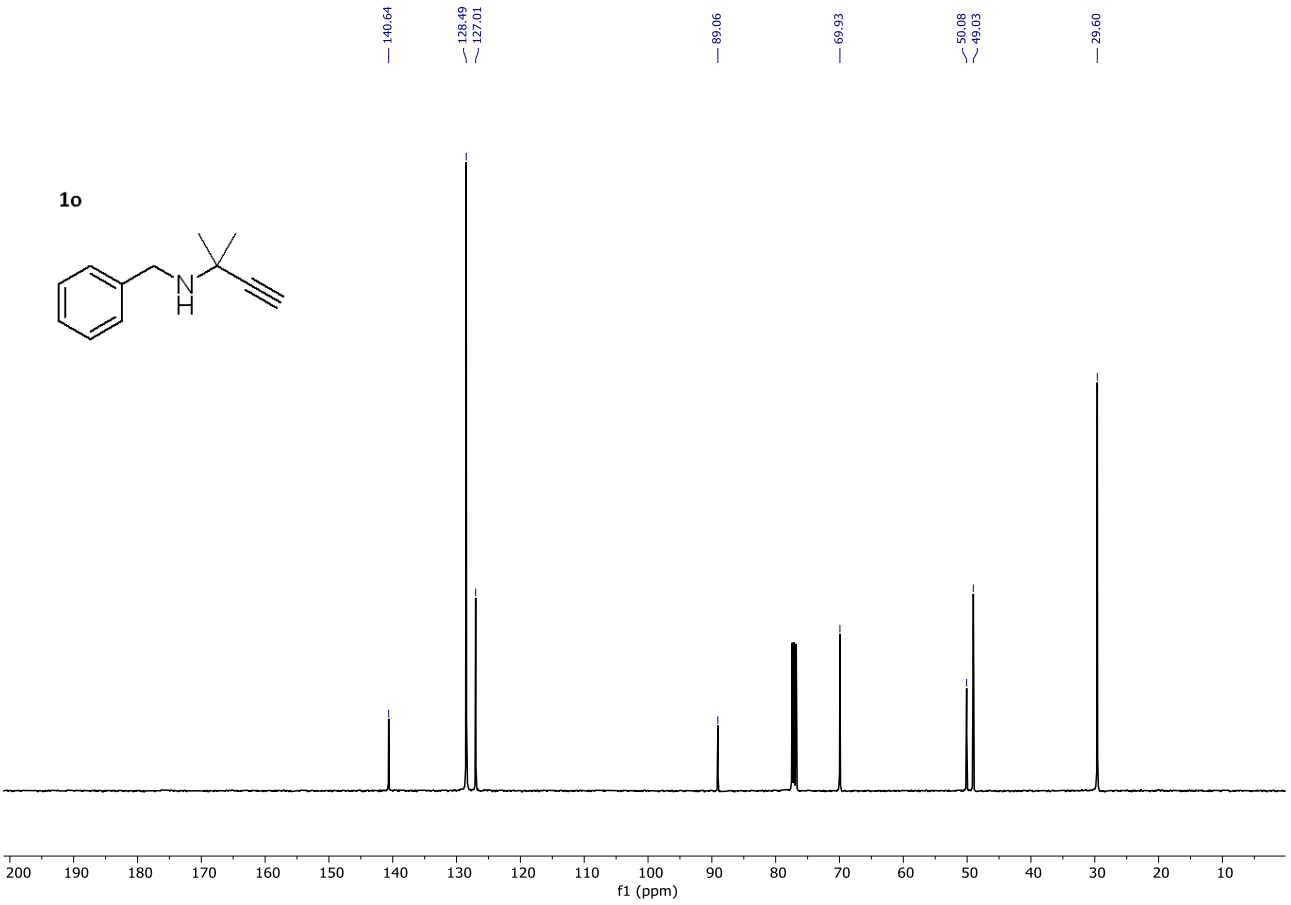
1.00
f1 (ppm)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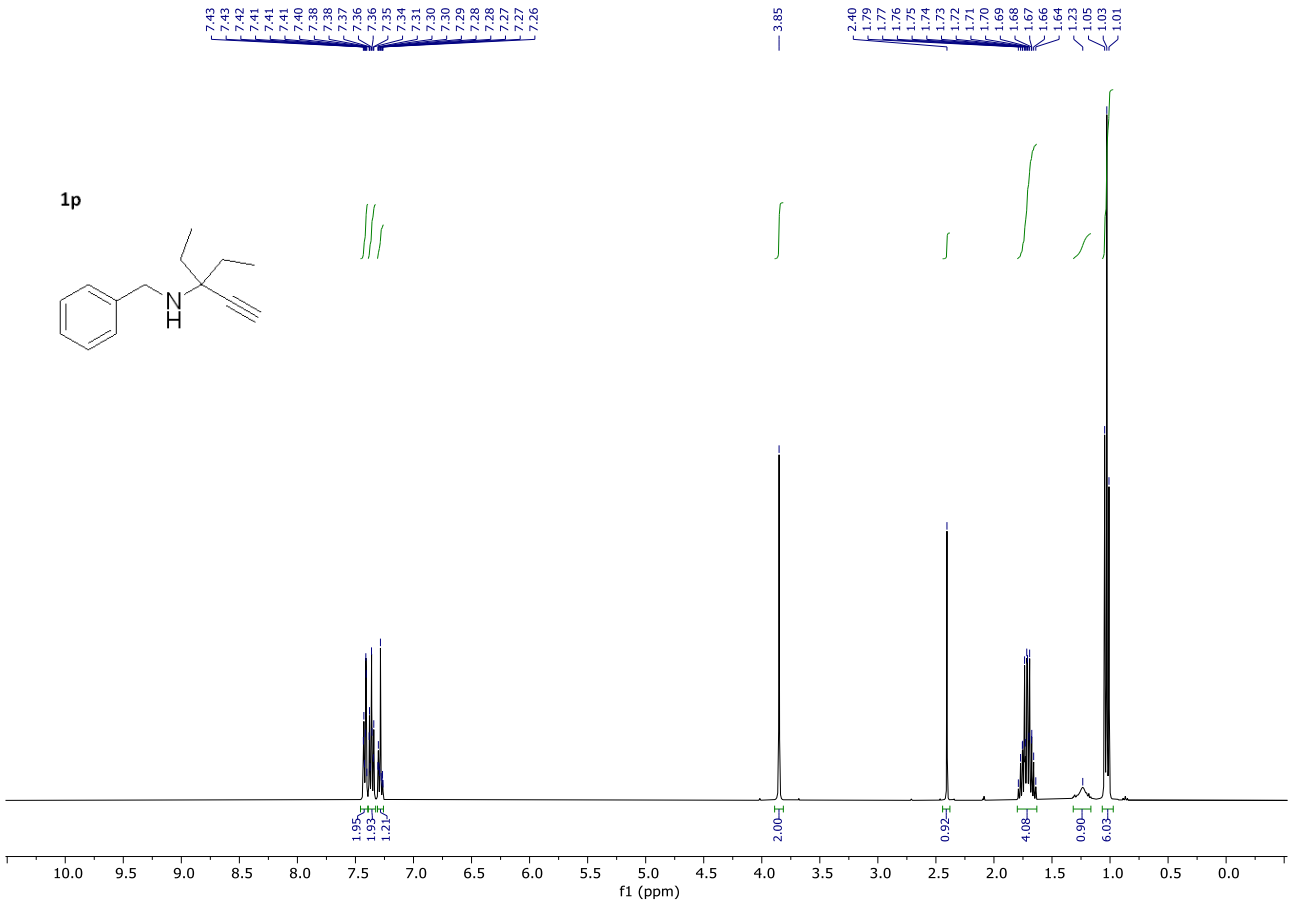
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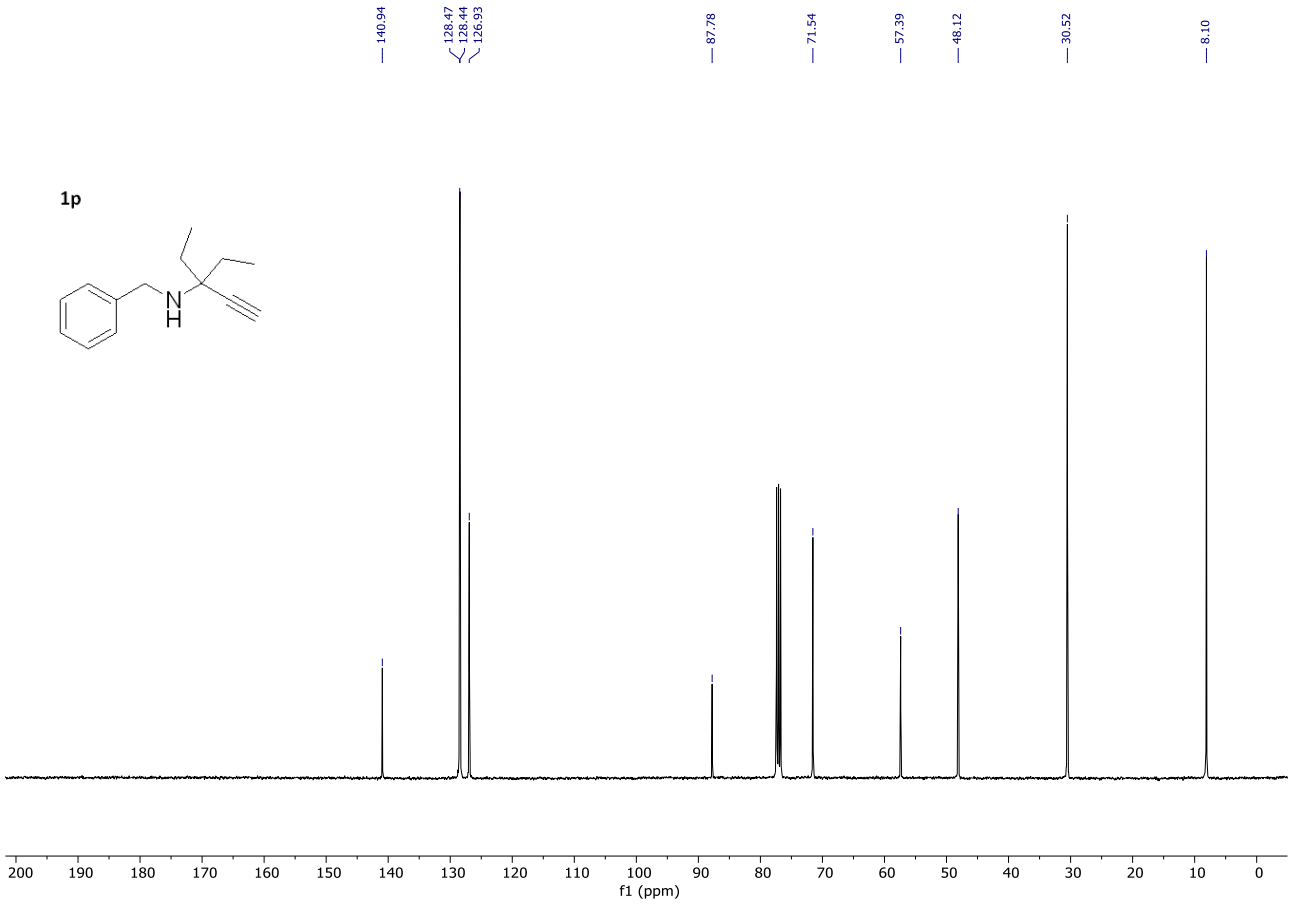
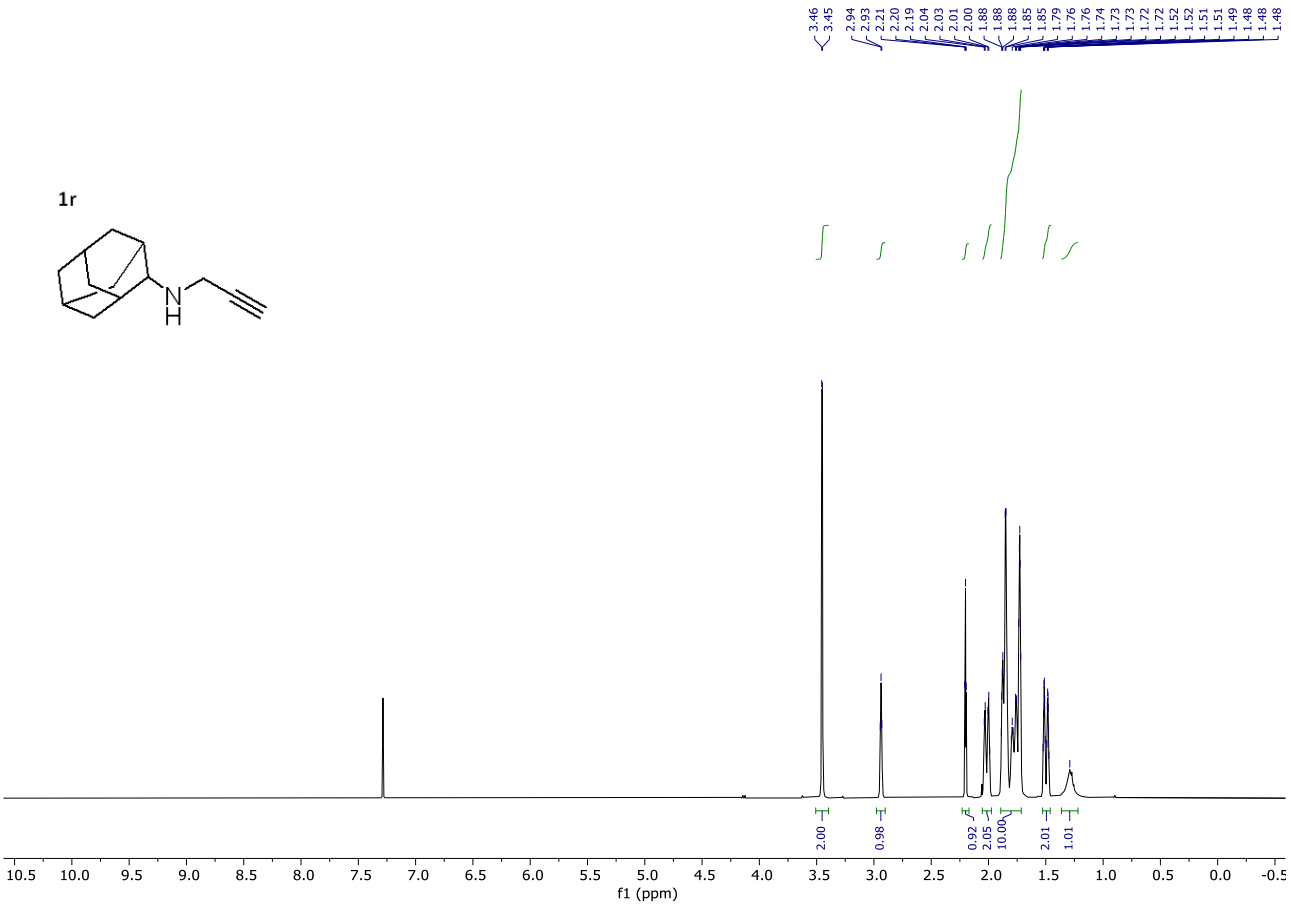
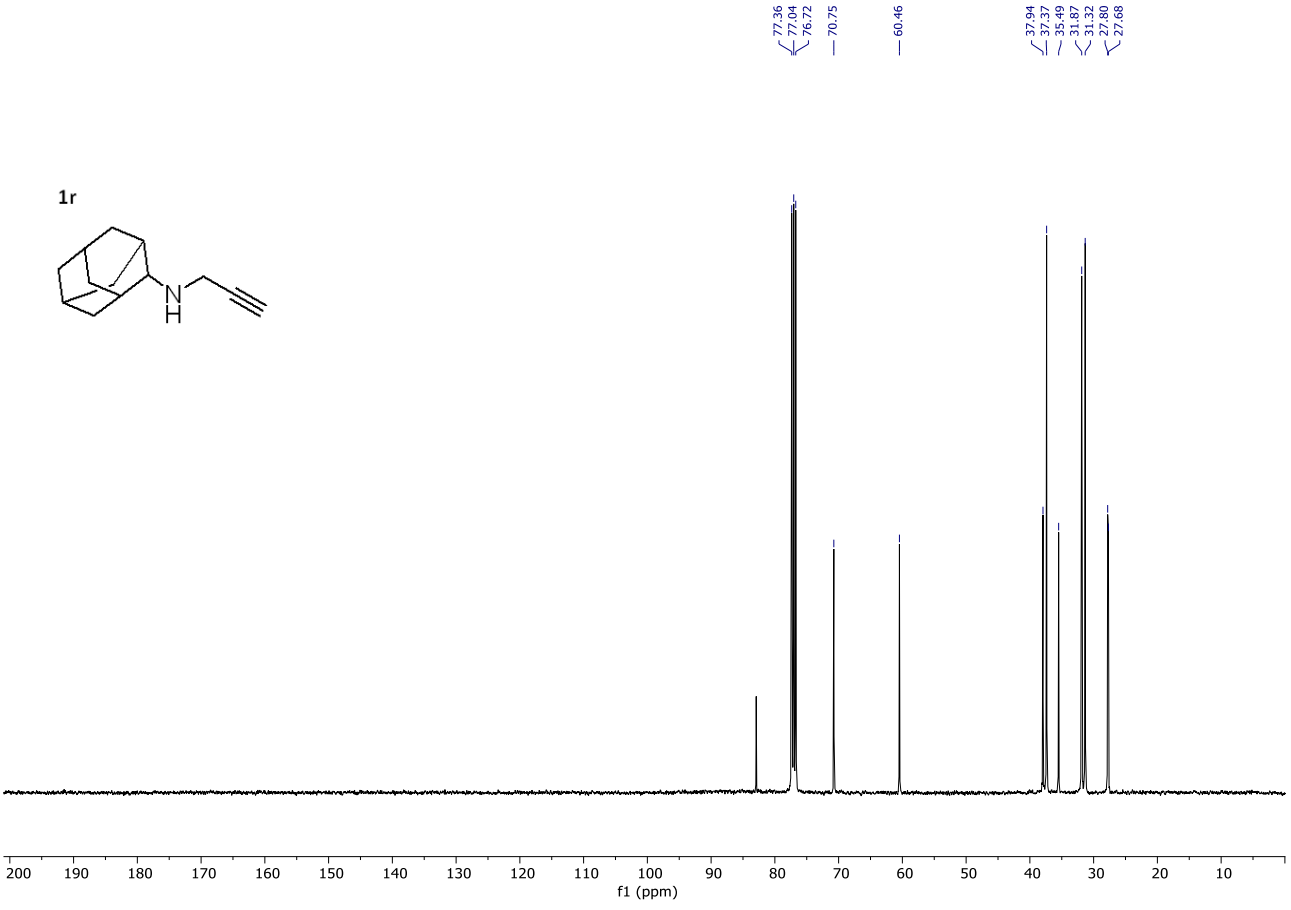
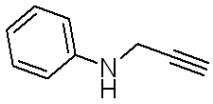
7.29
7.28
7.28
7.27
7.27
7.26
3.85
2.40
1.79
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.64
1.23
1.05
1.03
1.01
1.95
1.93
1.21
2.00
0.92
4.08
0.90
6.03
f1 (ppm)


1p
140.94
128.47
128.44
126.93
87.78
71.54
57.39
48.12
30.52
8.10
f1 (ppm)


1r
3.46
3.45
2.94
2.93
2.21
2.20
2.19
2.04
2.03
2.01
2.00
1.88
1.88
1.88
1.85
1.85
1.79
1.76
1.76
1.74
1.73
1.73
1.72
1.72
1.52
1.52
1.51
1.51
1.49
1.48
1.48
1.48
2.00
0.98
0.92
2.05
10.00
2.01
1.01
f1 (ppm)


1r
77.36
77.04
76.72
70.75
60.46
37.94
37.37
35.49
31.87
31.32
27.80
27.68
f1 (ppm)

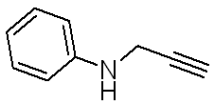
1s

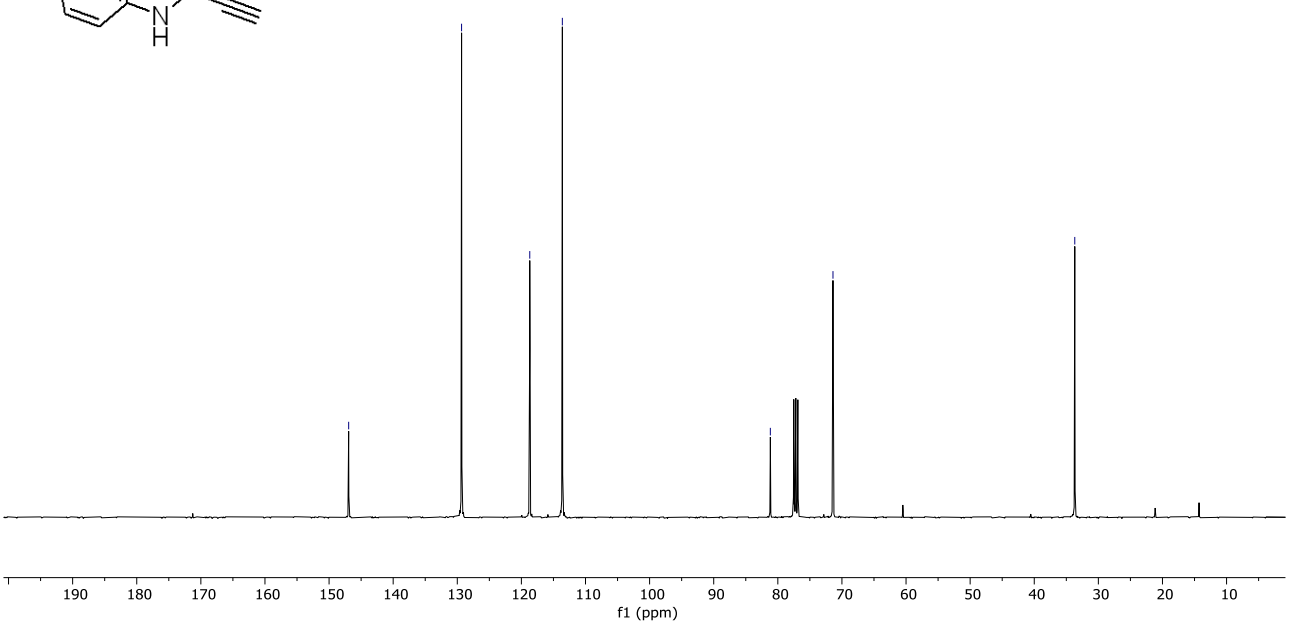


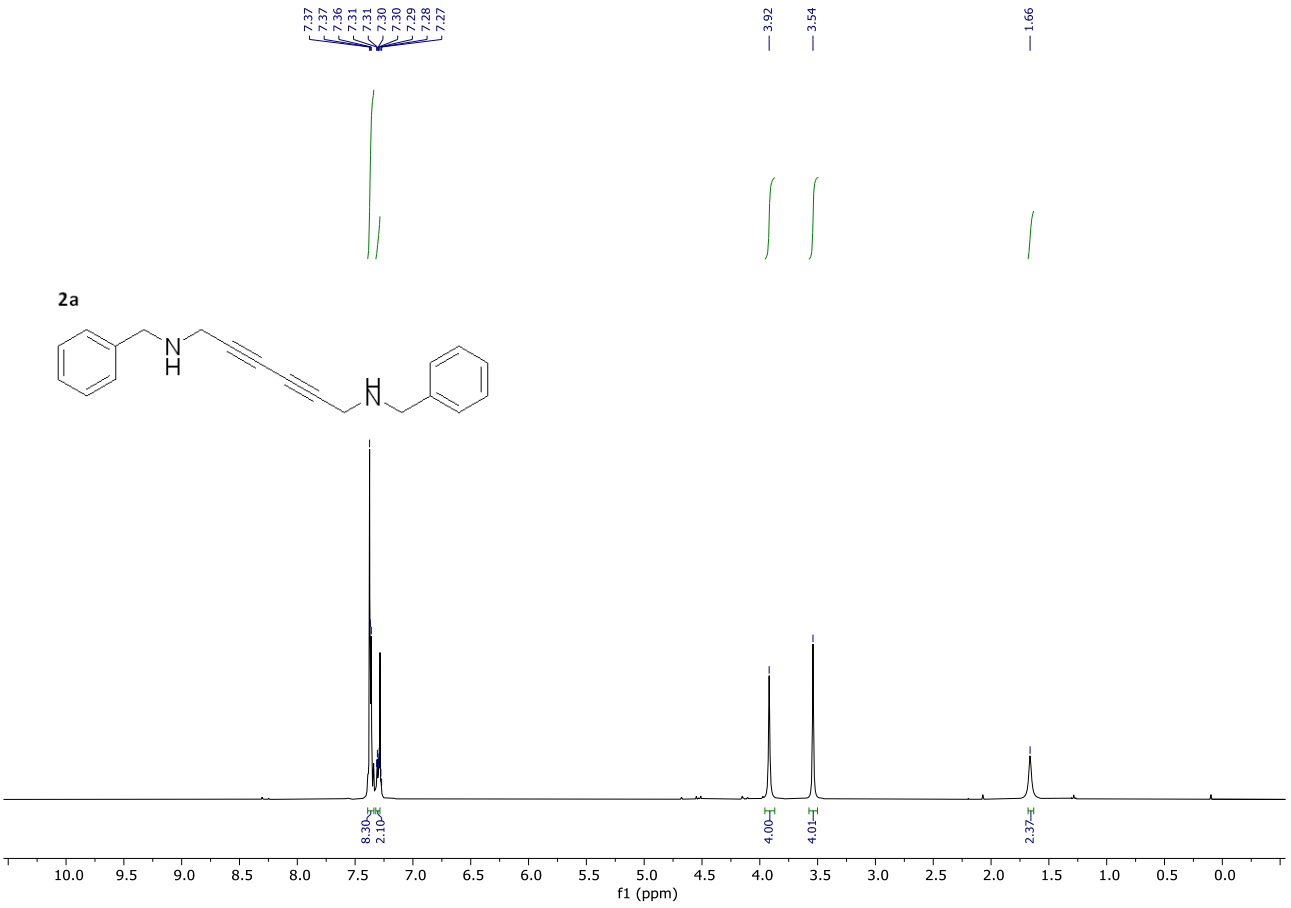
7.32
7.31
7.30
7.30
7.28
7.28
6.89
6.87
6.85
6.77
6.77
6.75
6.74
3.99
3.98
2.30
2.29
2.28
2.01
1.00
2.02
2.00
0.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

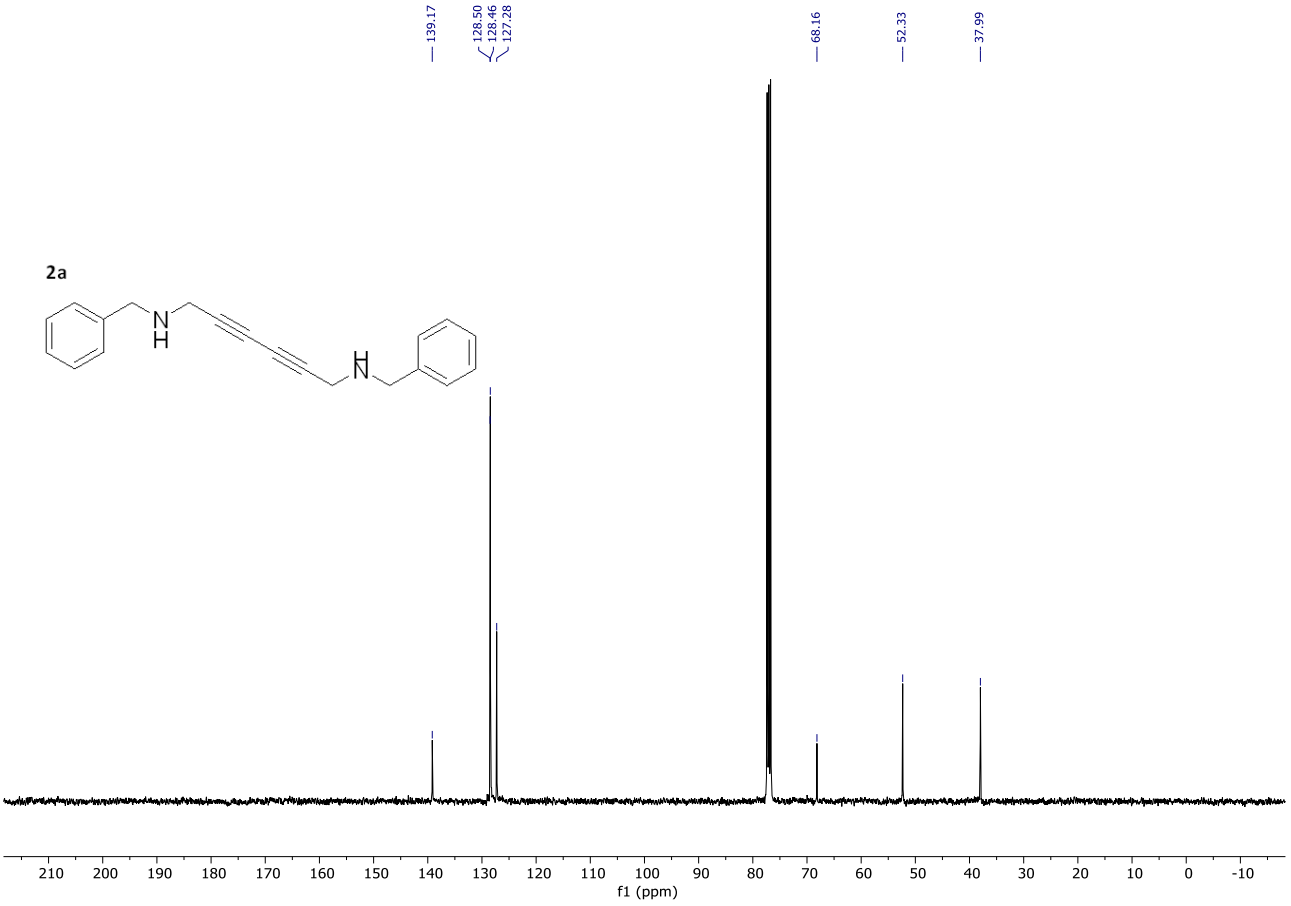

146.94
129.33
118.69
113.61
81.17
71.40
33.68

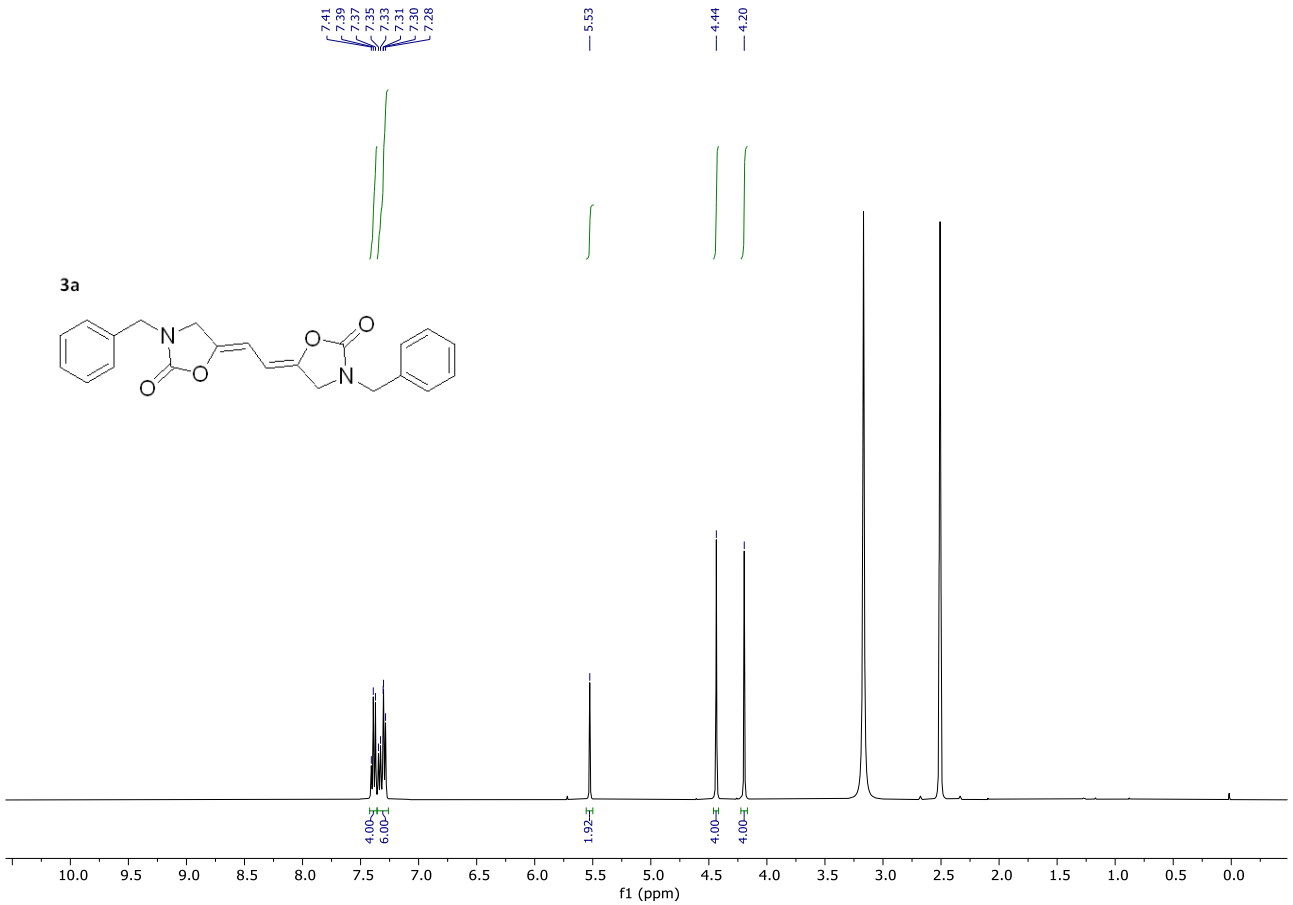
1s

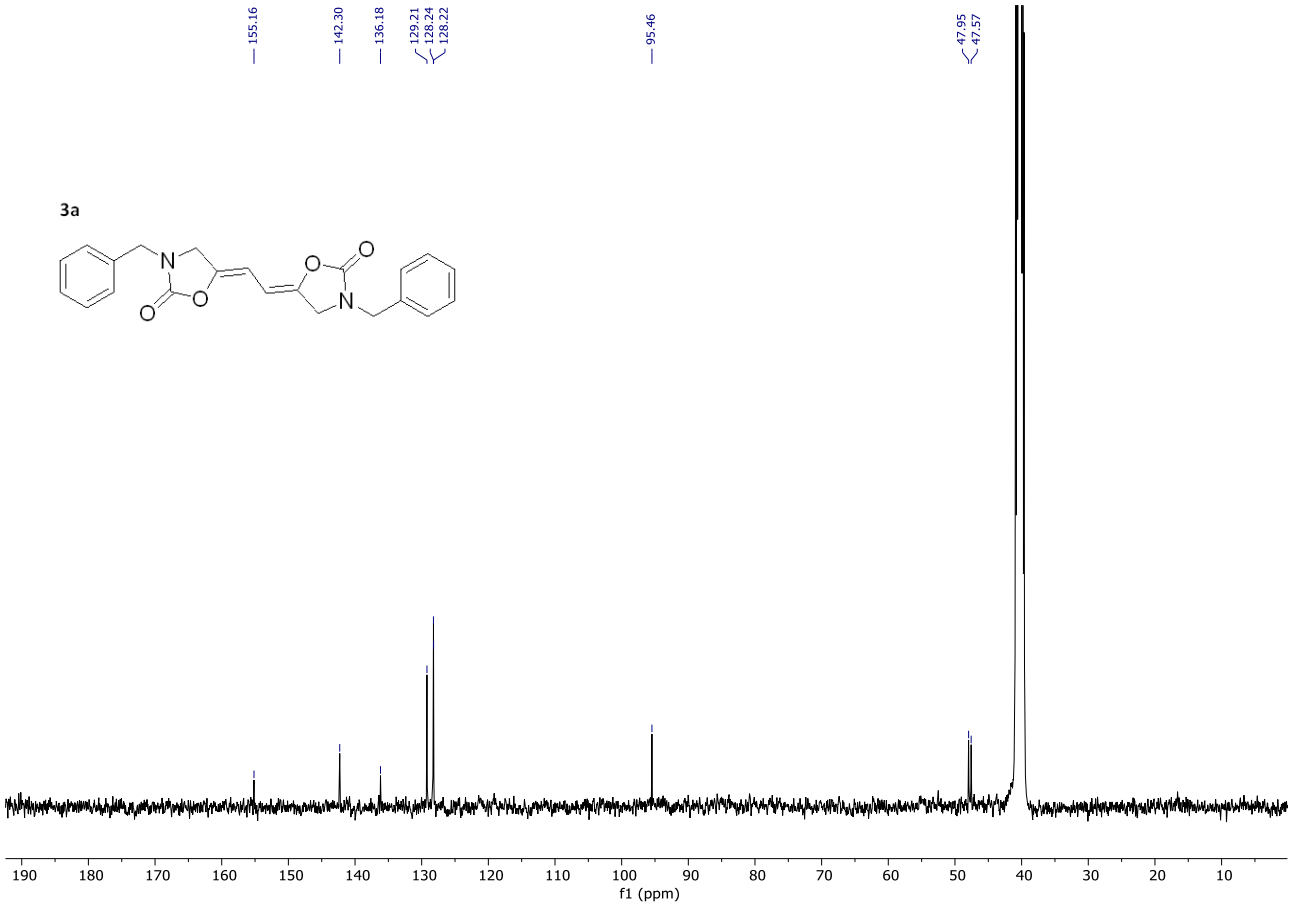


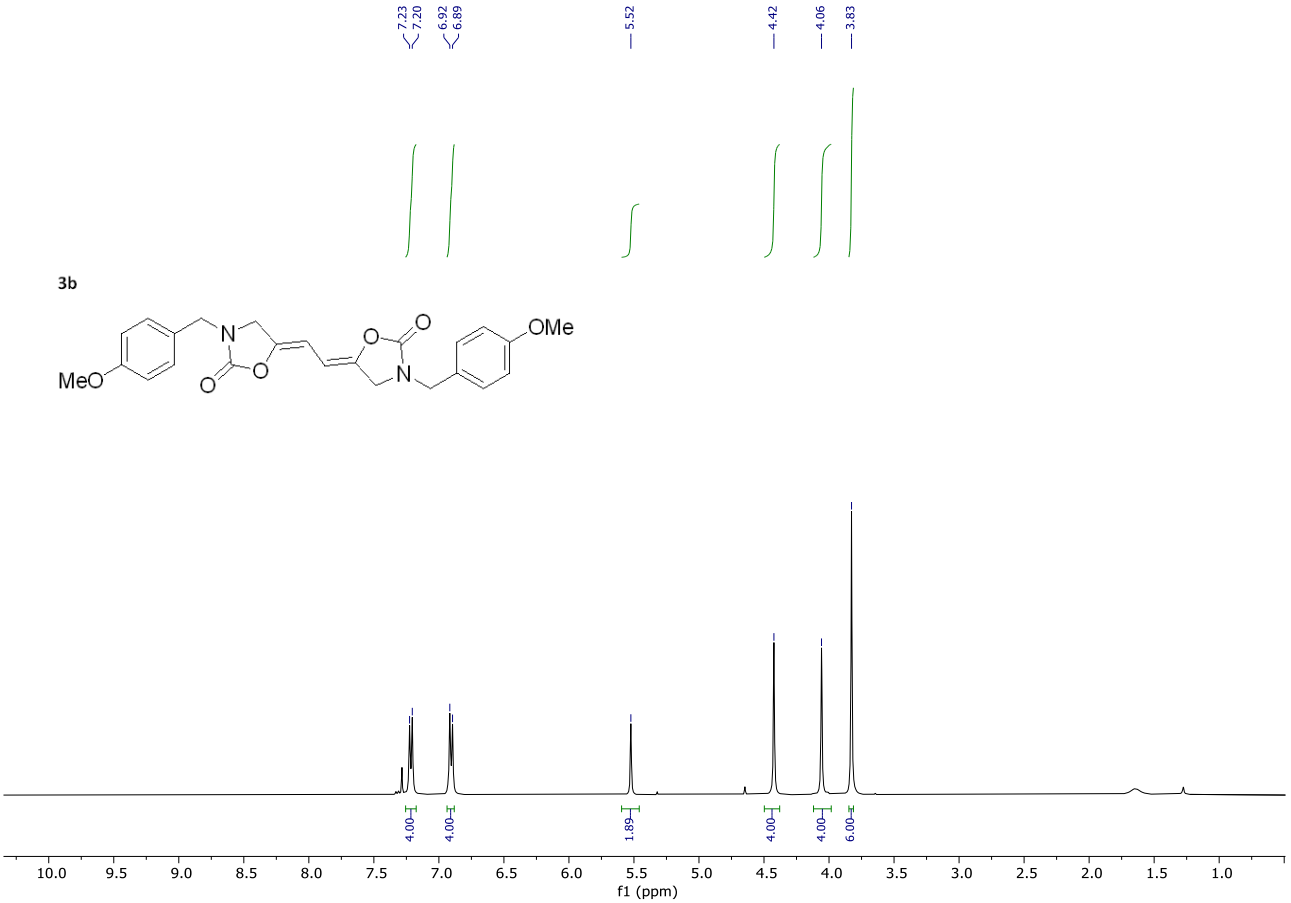

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

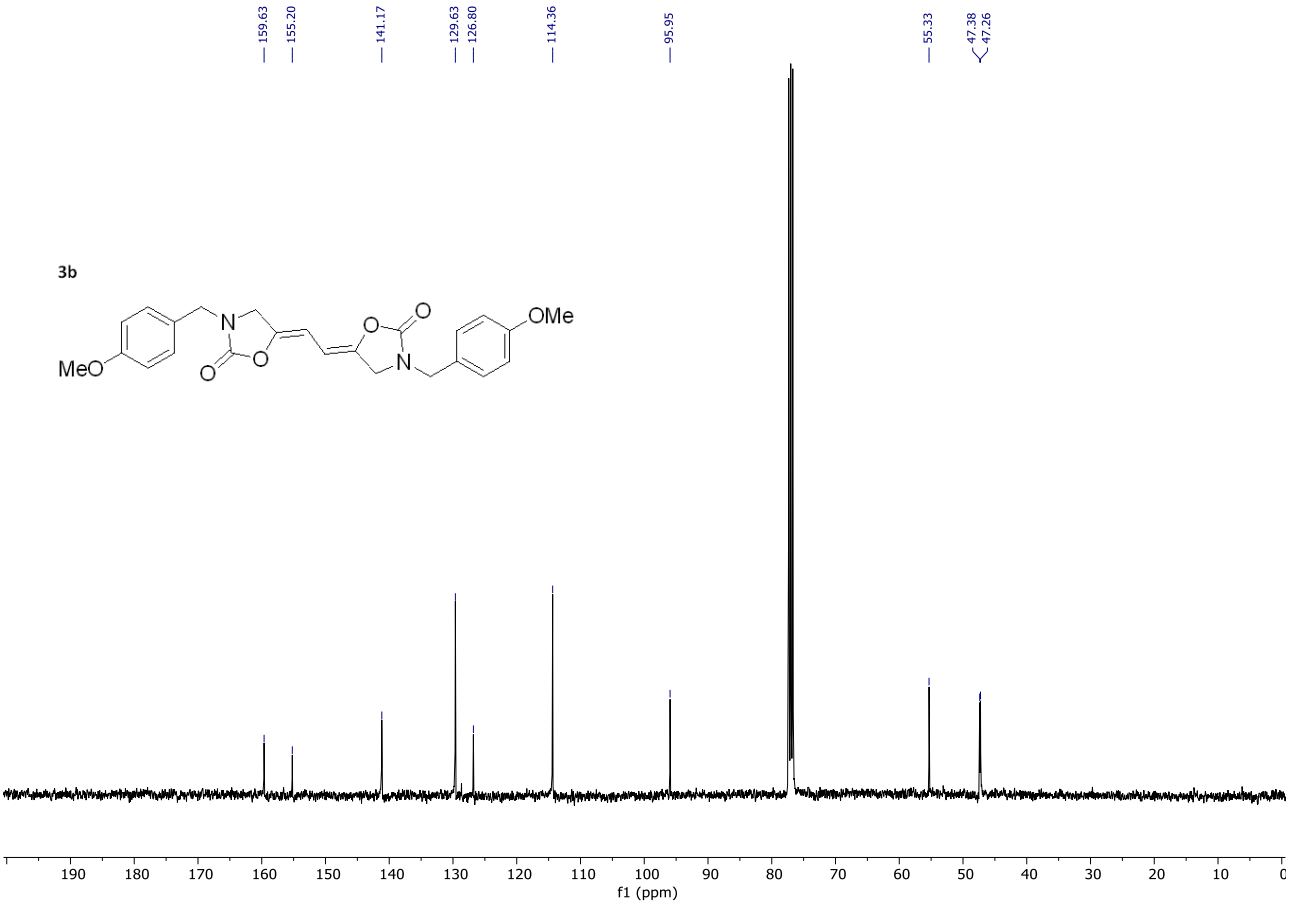

7.37
7.37
7.36
7.31
7.31
7.30
7.30
7.29
7.28
7.27
3.92
3.54
1.66
2a
8.30
2.10
4.00
4.01
2.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

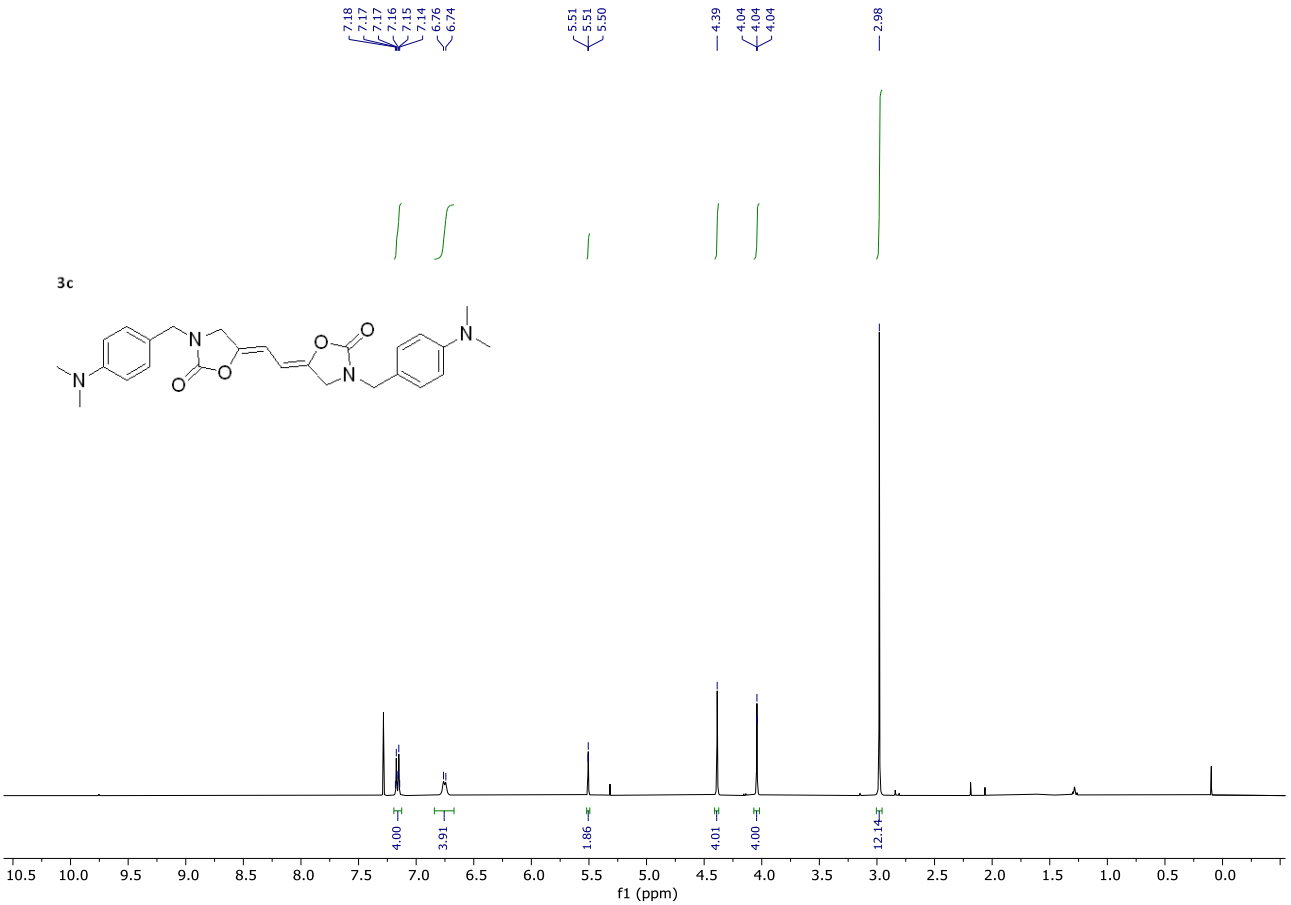

139.17
128.50
128.46
127.28
68.16
52.33
37.99
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

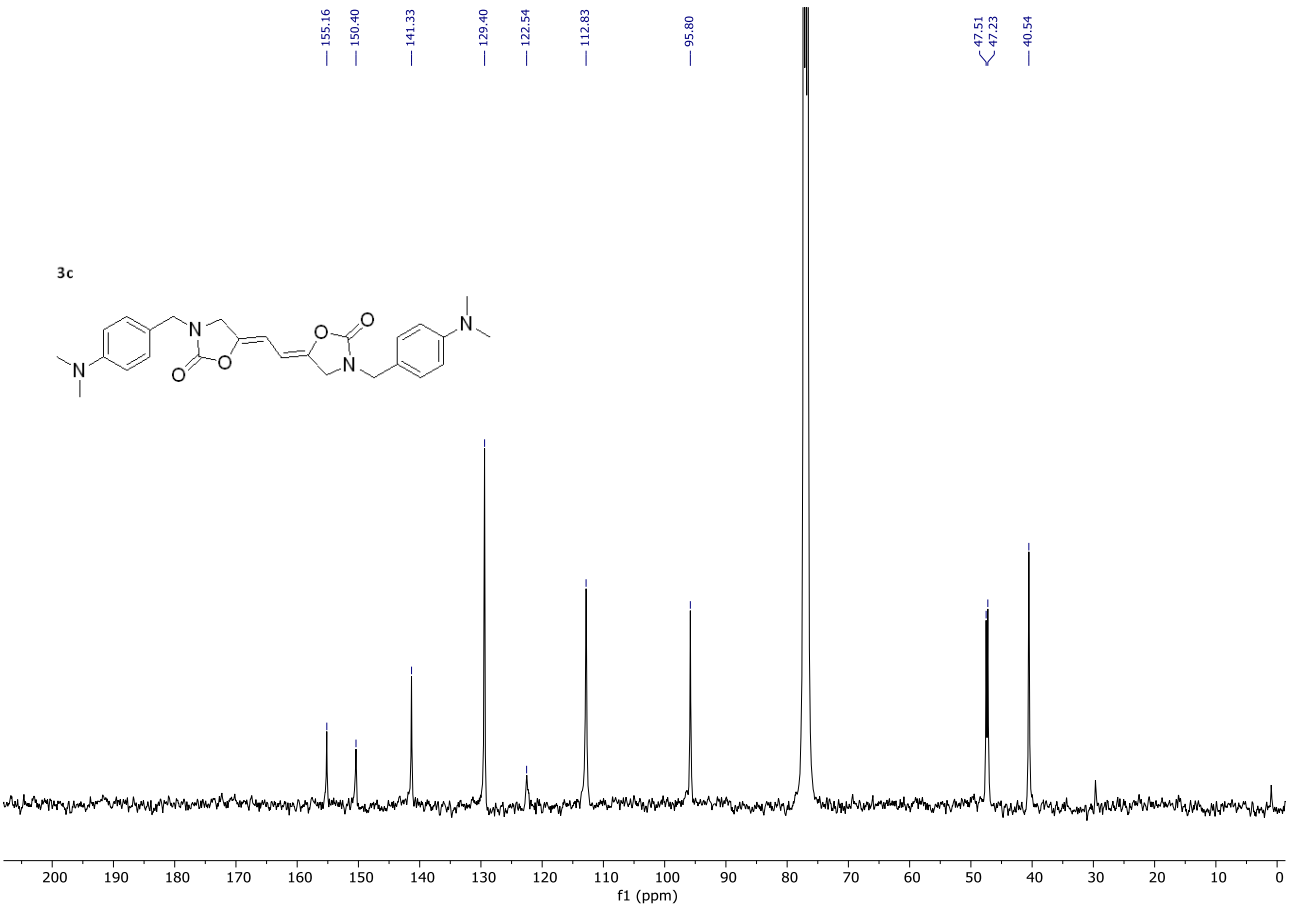

7.41
7.39
7.37
7.35
7.33
7.31
7.30
7.28
5.53
4.44
4.20
3a
4.00
6.00
1.92
4.00
4.00
f1 (ppm)

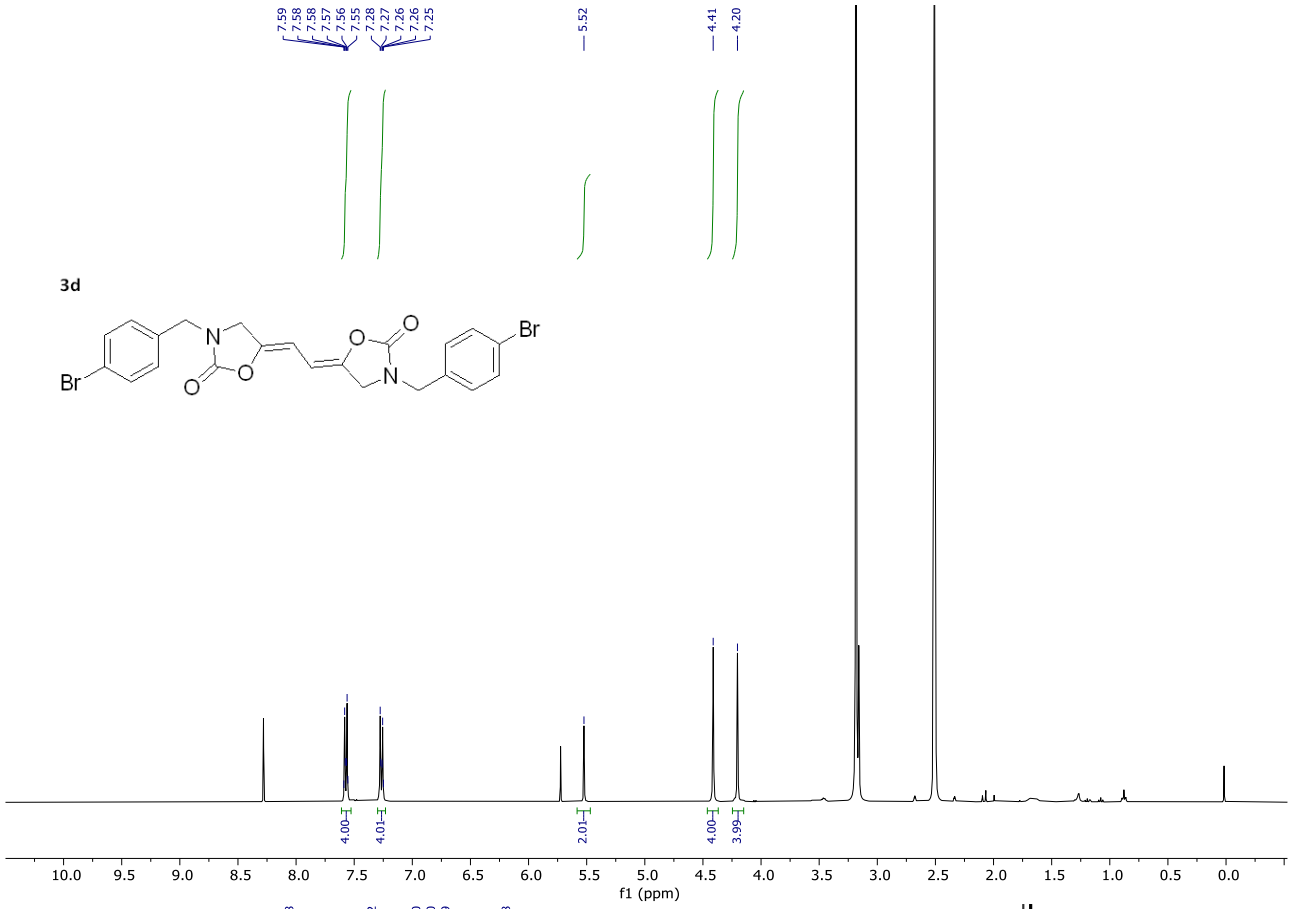

155.16
142.30
136.18
129.21
128.24
128.22
95.46
47.95
47.57
3a
f1 (ppm)

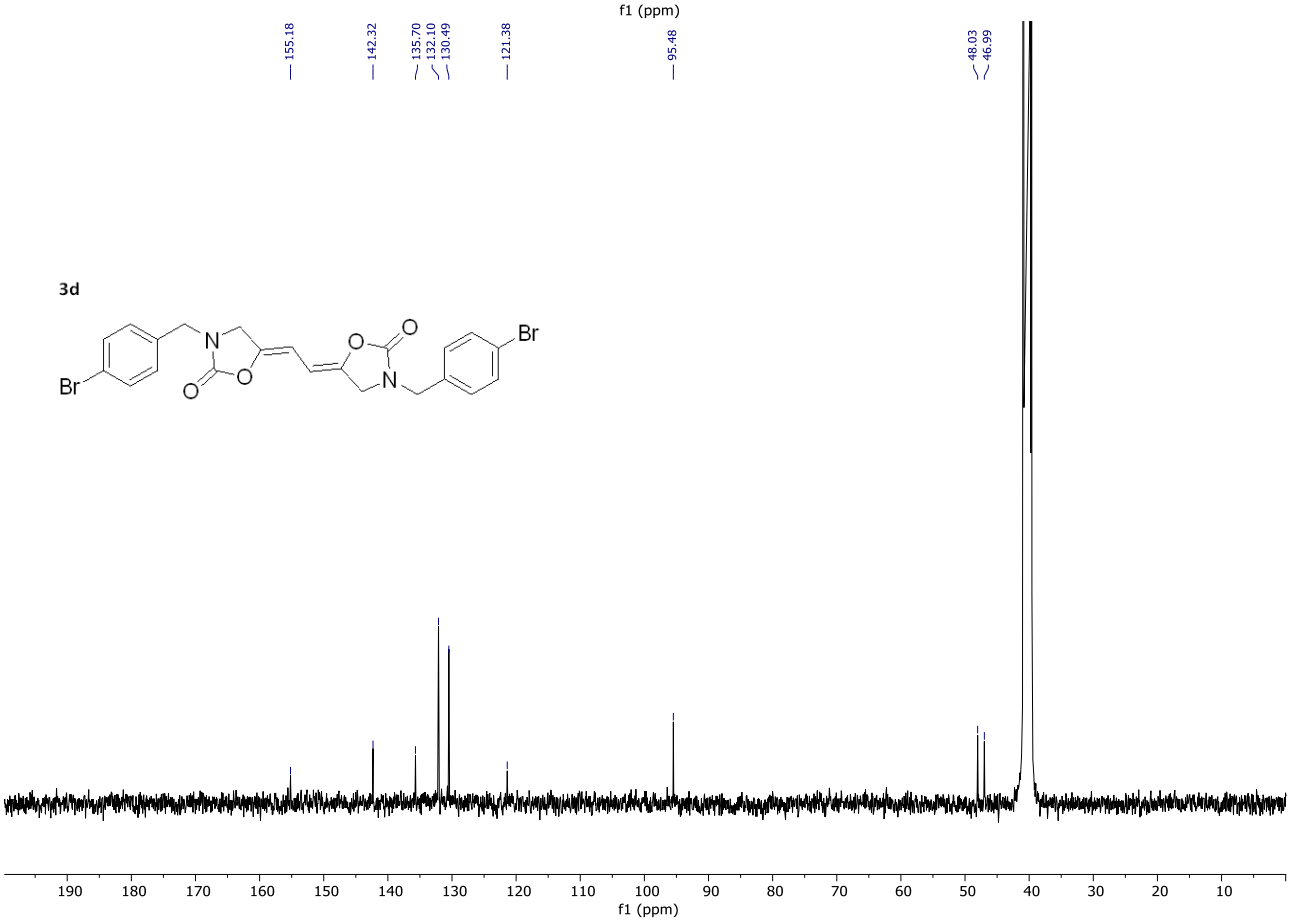

7.23
7.20
6.92
6.89
5.52
4.42
4.06
3.83
3b
MeO
OMe
4.00
4.00
1.89
4.00
4.00
6.00
f1 (ppm)

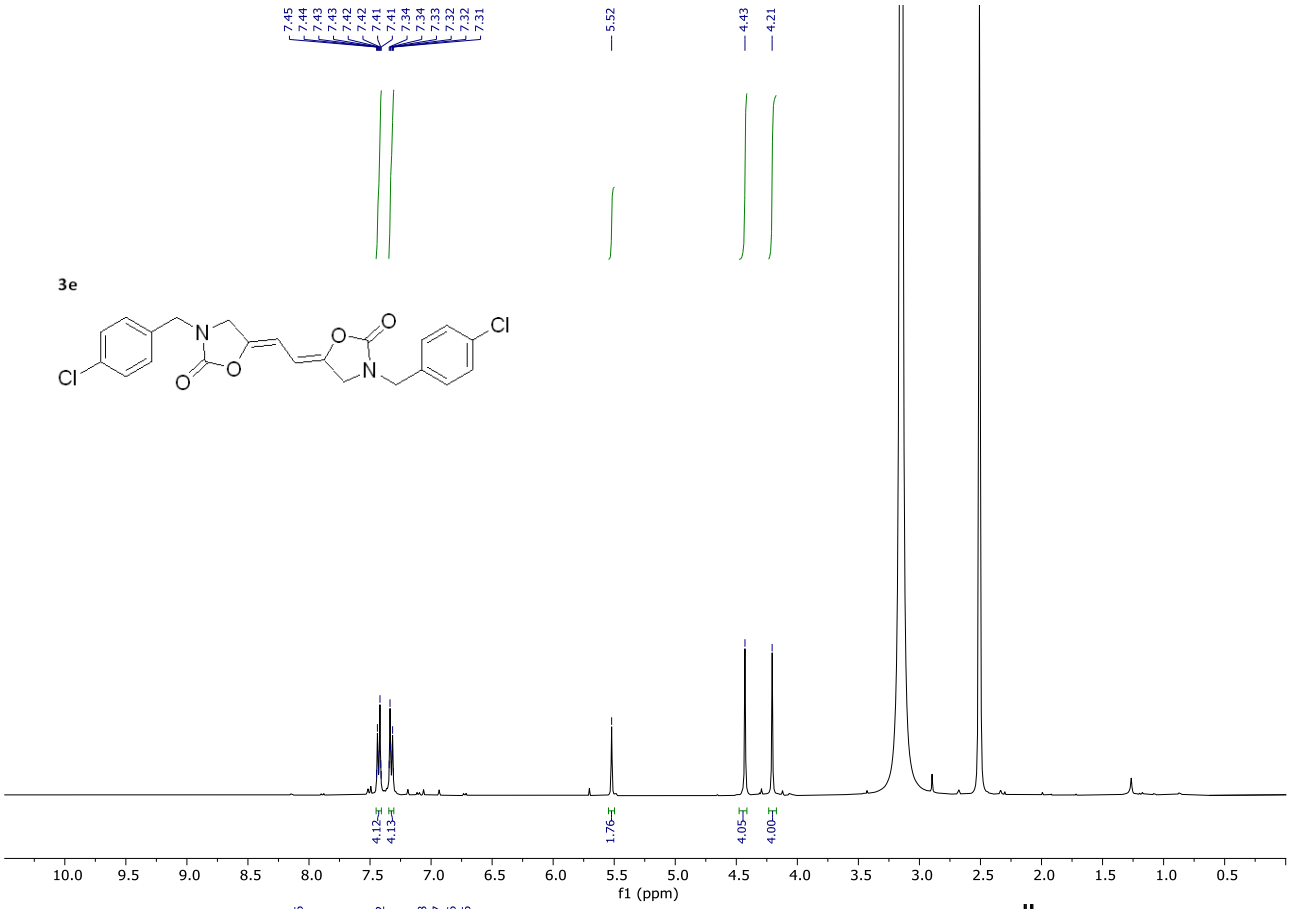

159.63
155.20
141.17
129.63
126.80
114.36
95.95
55.33
47.38
47.26
3b
MeO
OMe
f1 (ppm)

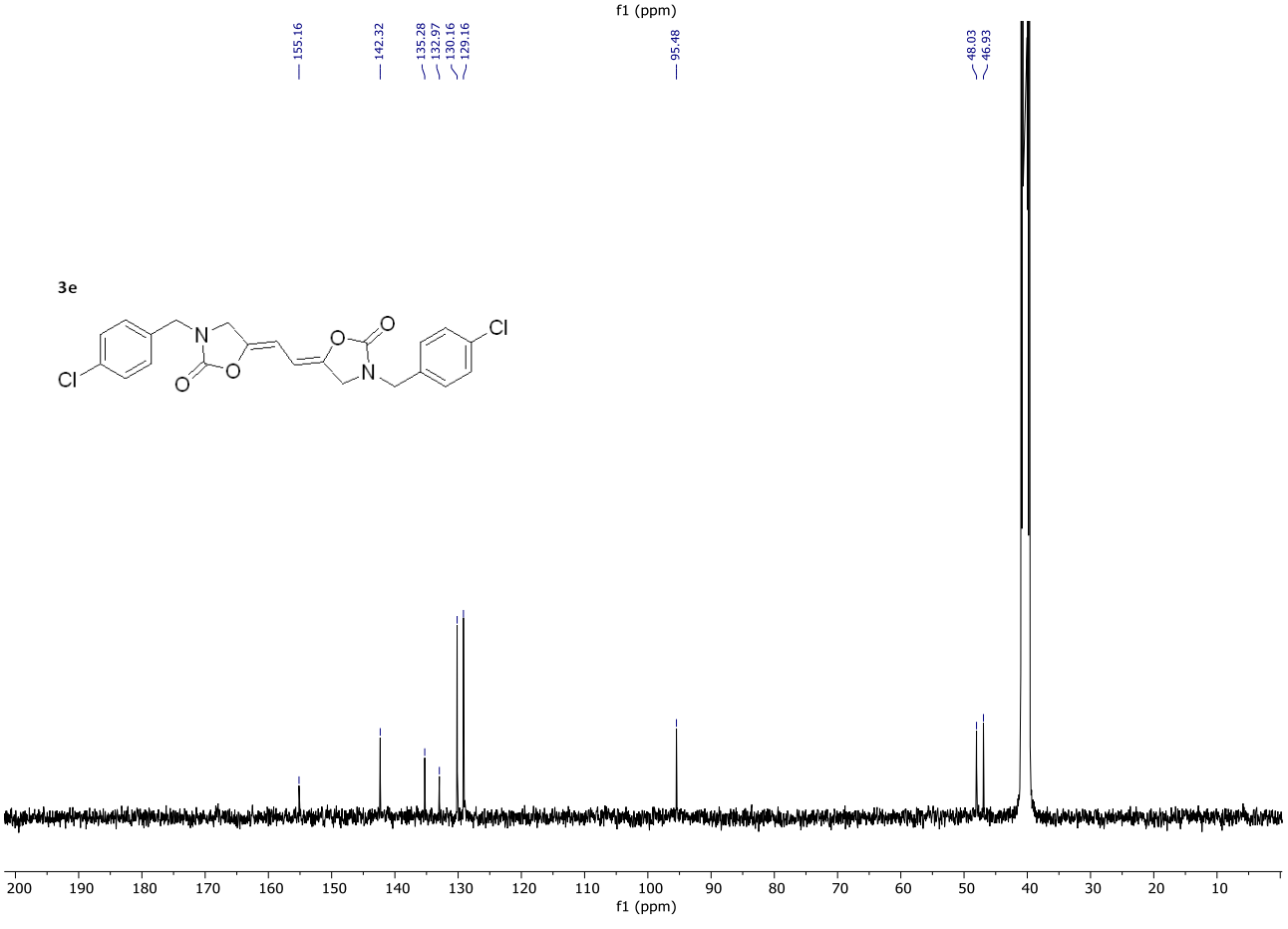

7.18
7.17
7.17
7.16
7.15
7.14
6.76
6.74
5.51
5.51
5.50
4.39
4.04
4.04
4.04
2.98
3c
4.00
3.91
1.86
4.01
4.00
12.14
f1 (ppm)

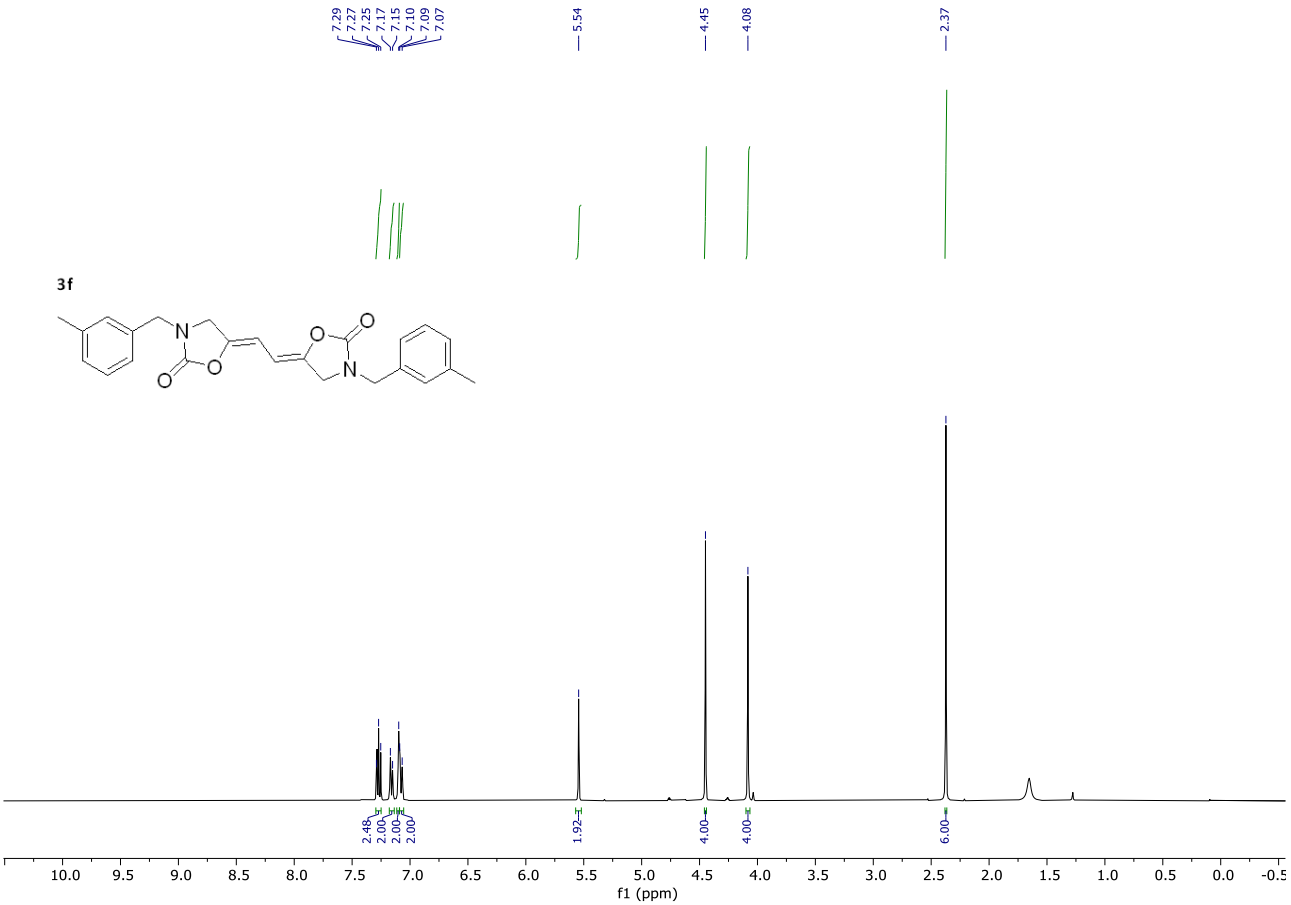

155.16
150.40
141.33
129.40
122.54
112.83
95.80
47.51
47.23
40.54
3c
f1 (ppm)

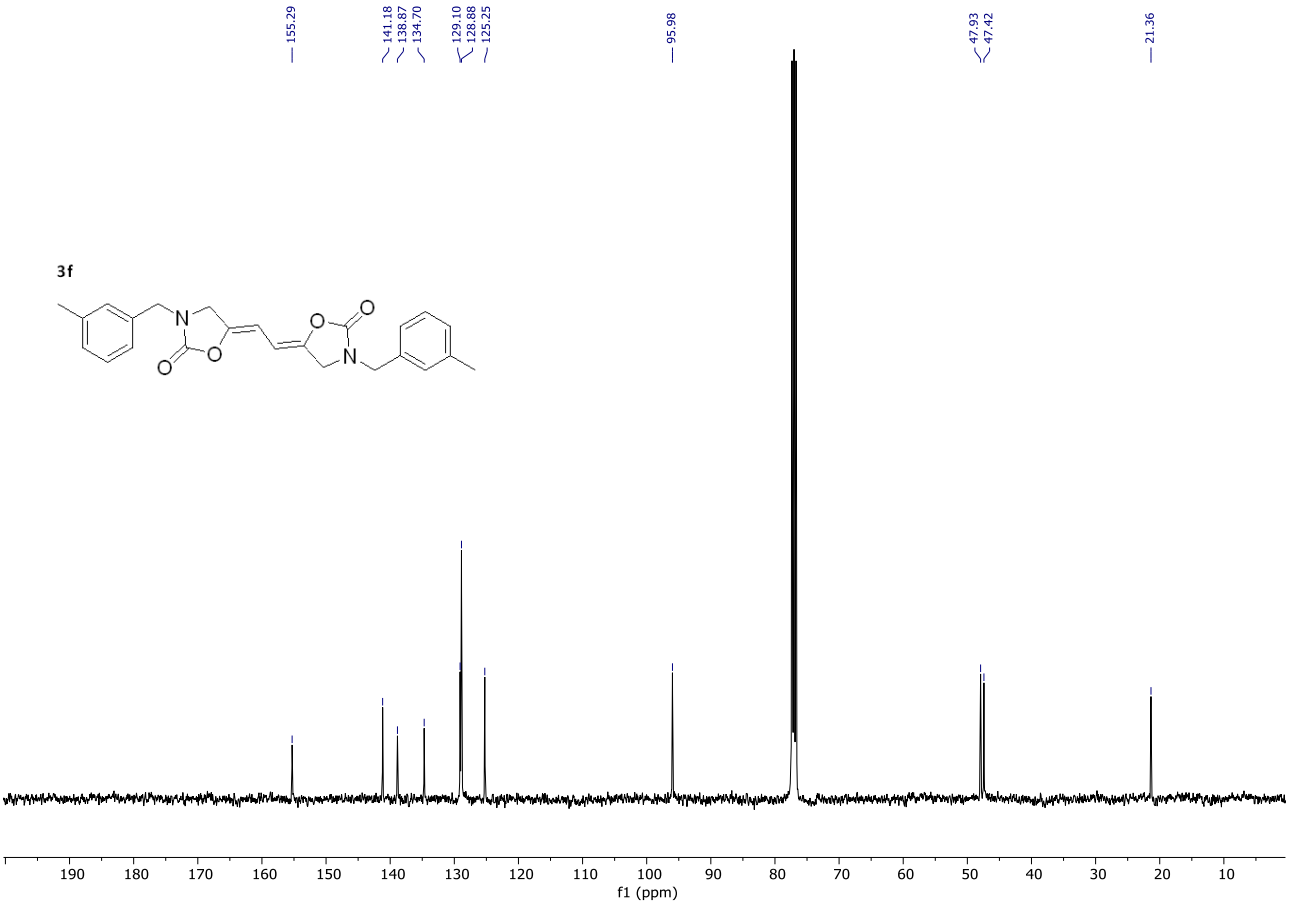

7.59
7.58
7.58
7.57
7.56
7.55
7.28
7.27
7.26
7.26
7.25
5.52
4.41
4.20
3d
Br
N
O
O
O
O
N
Br
4.00
4.01
2.01
4.00
3.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

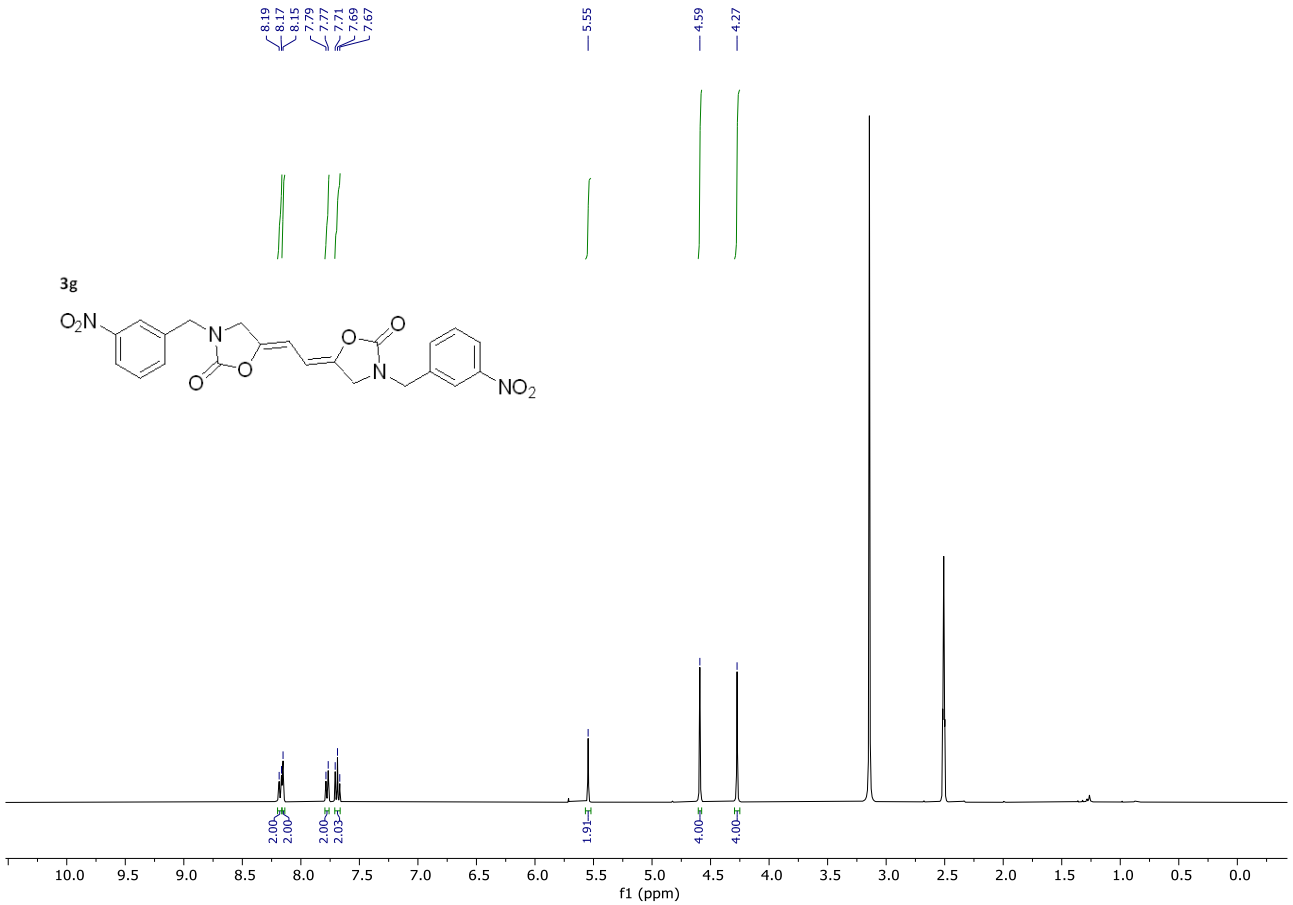

155.18
142.32
135.70
132.10
130.49
121.38
95.48
48.03
46.99
3d
Br
N
O
O
O
O
N
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

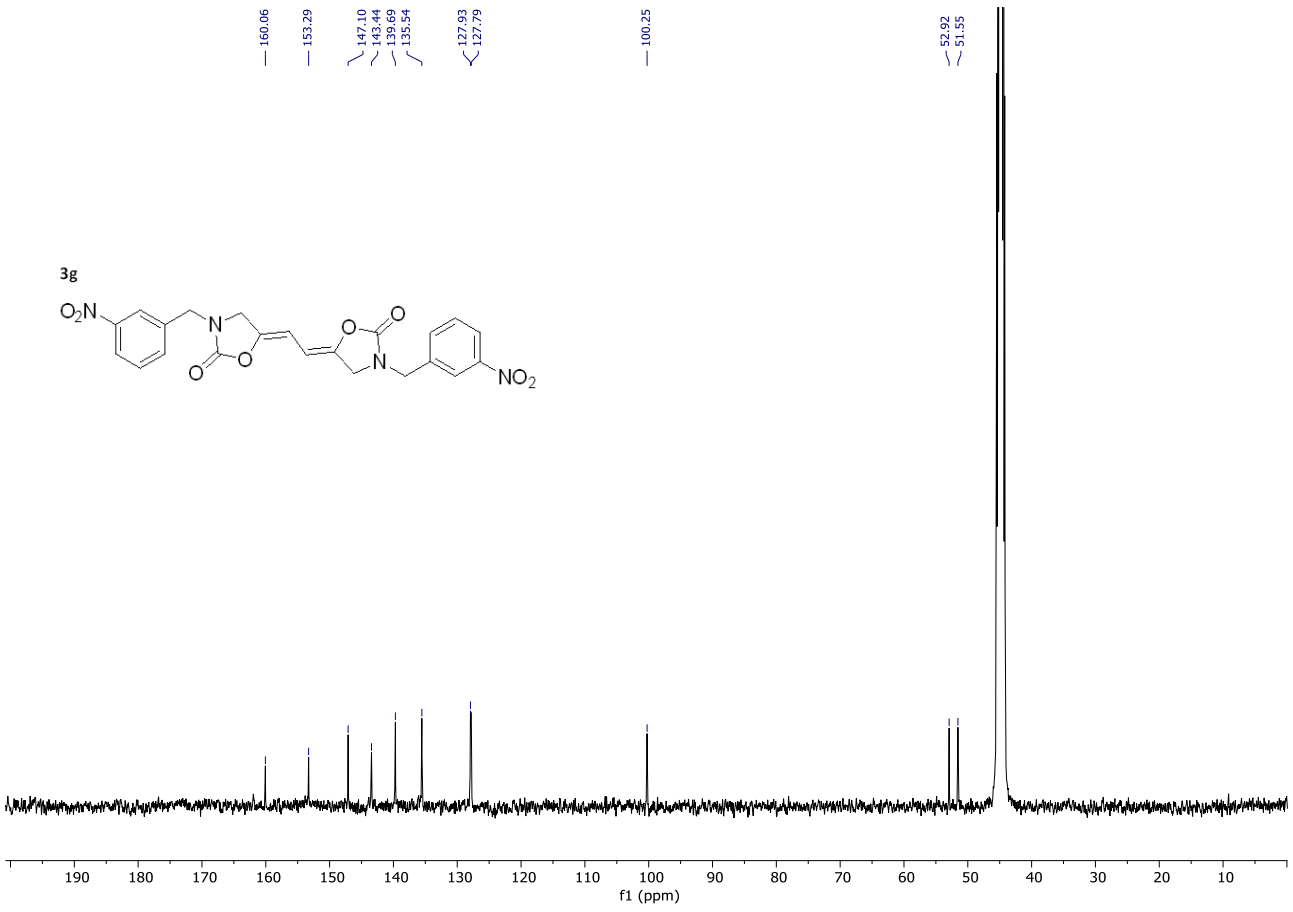

7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.34
7.34
7.33
7.32
7.32
7.31
5.52
4.43
4.21
3e
Cl
N
O
O
O
O
N
Cl
4.12
4.13
1.76
4.05
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

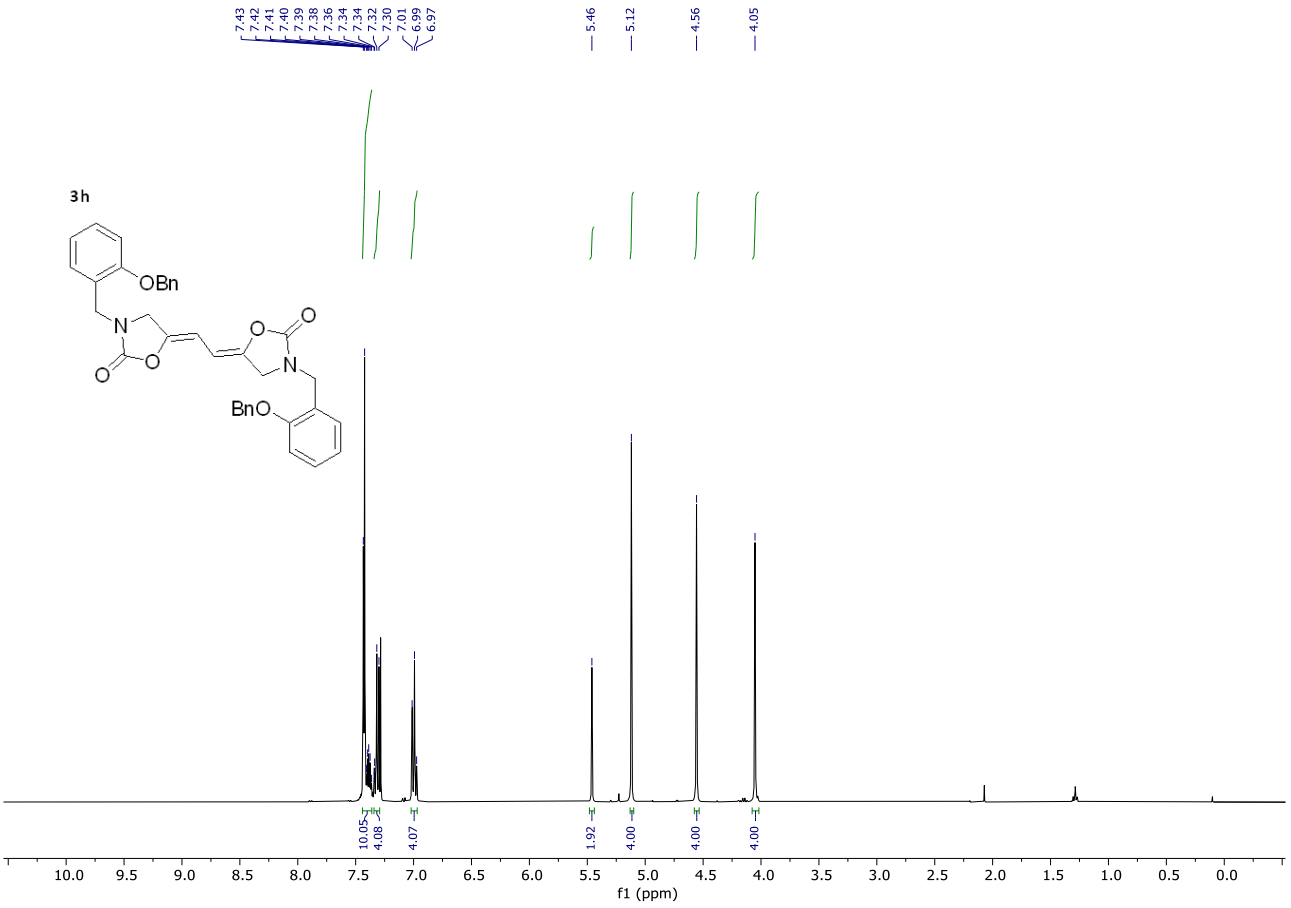

155.16
142.32
135.28
132.97
130.16
129.16
95.48
48.03
46.93
3e
Cl
N
O
O
O
O
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

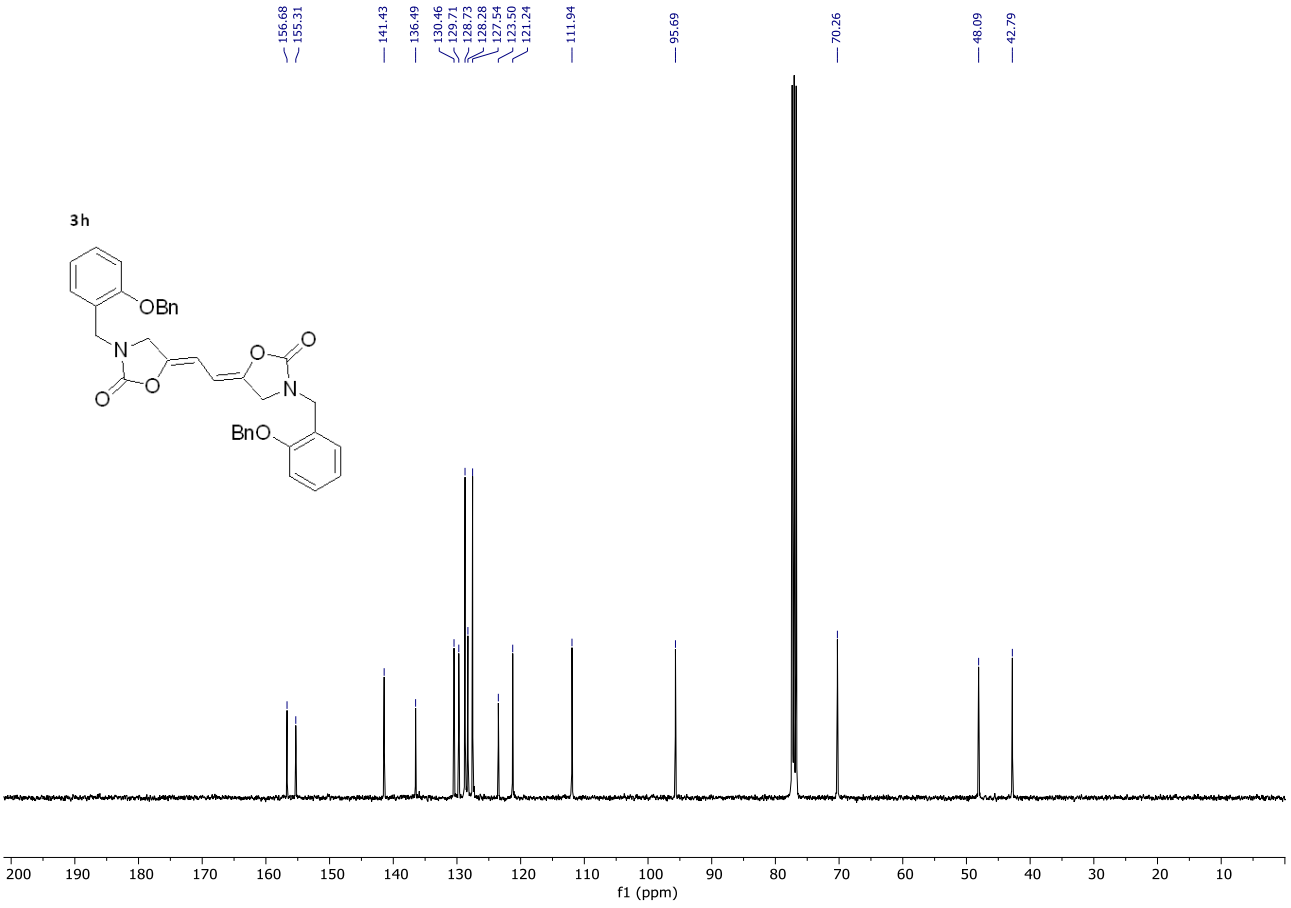

7.29
7.27
7.25
7.17
7.15
7.10
7.09
7.07
5.54
4.45
4.08
2.37
3f
2.48
2.05
2.00
2.00
1.92
4.00
4.00
6.00
f1 (ppm)

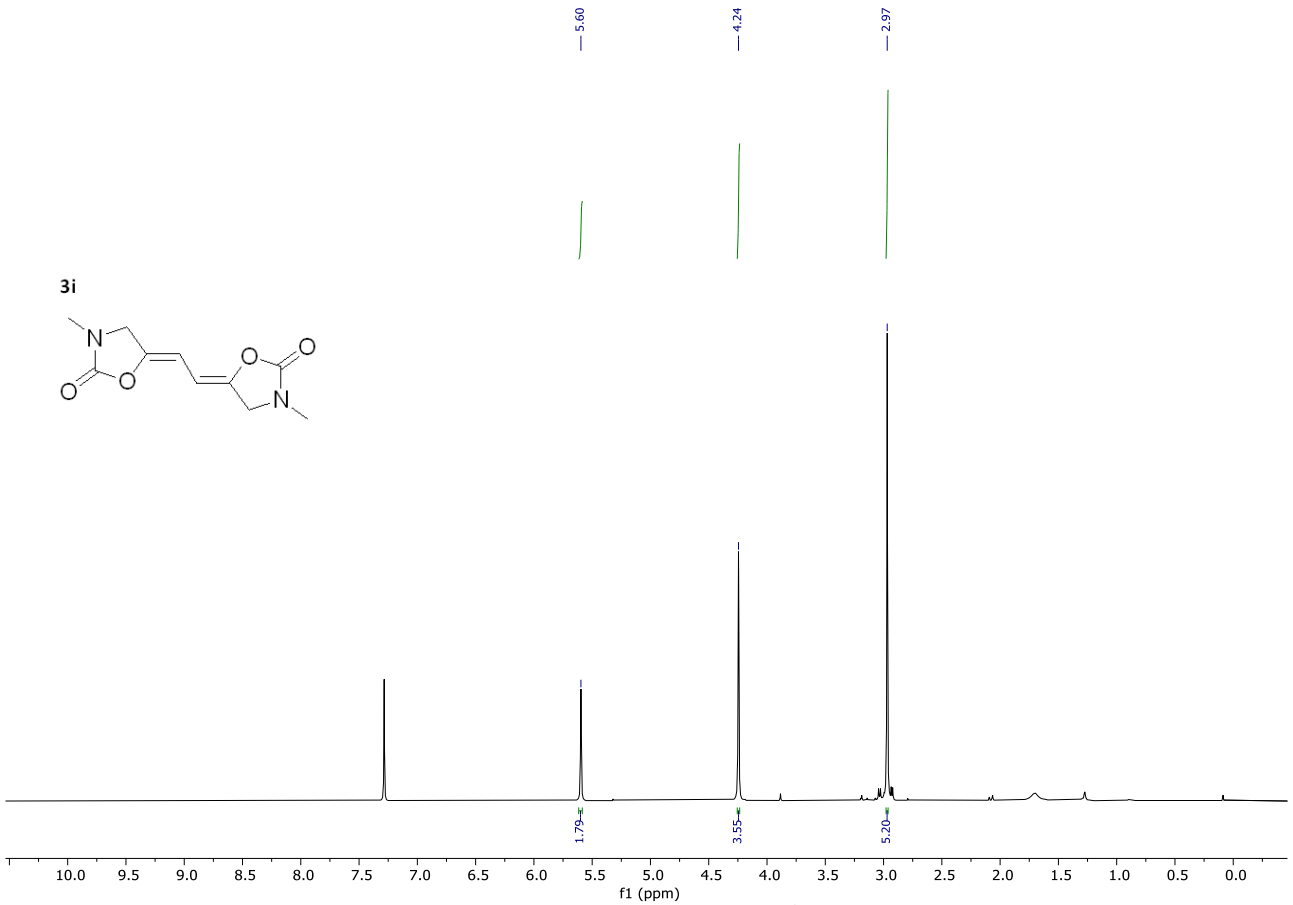

155.29
141.18
138.87
134.70
129.10
128.88
125.25
95.98
47.93
47.42
21.36
3f
f1 (ppm)

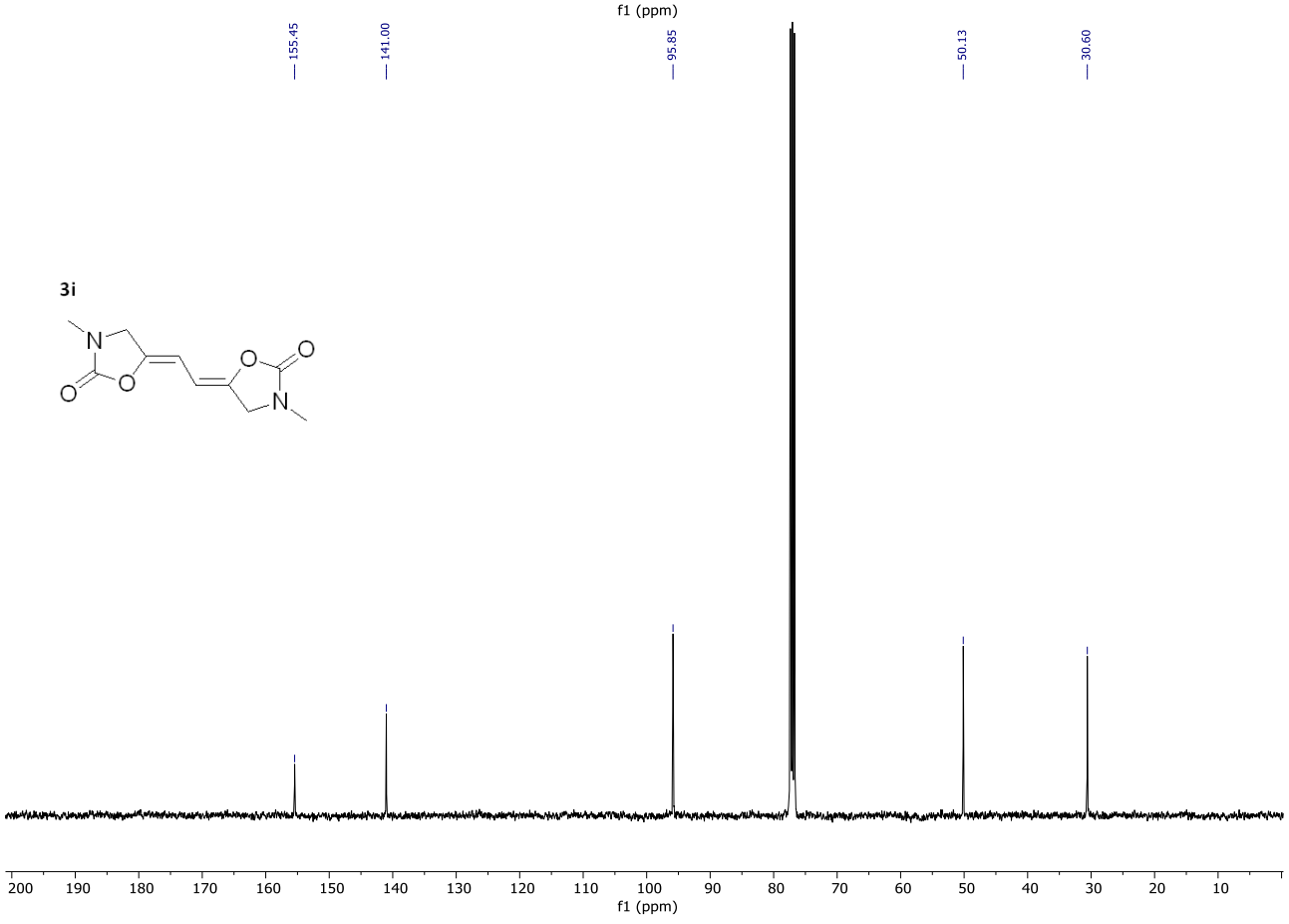

8.19
8.17
8.15
7.79
7.77
7.71
7.69
7.67
5.55
4.59
4.27
3g
O2N
NO2
2.00
2.00
2.00
2.03
1.91
4.00
4.00
f1 (ppm)

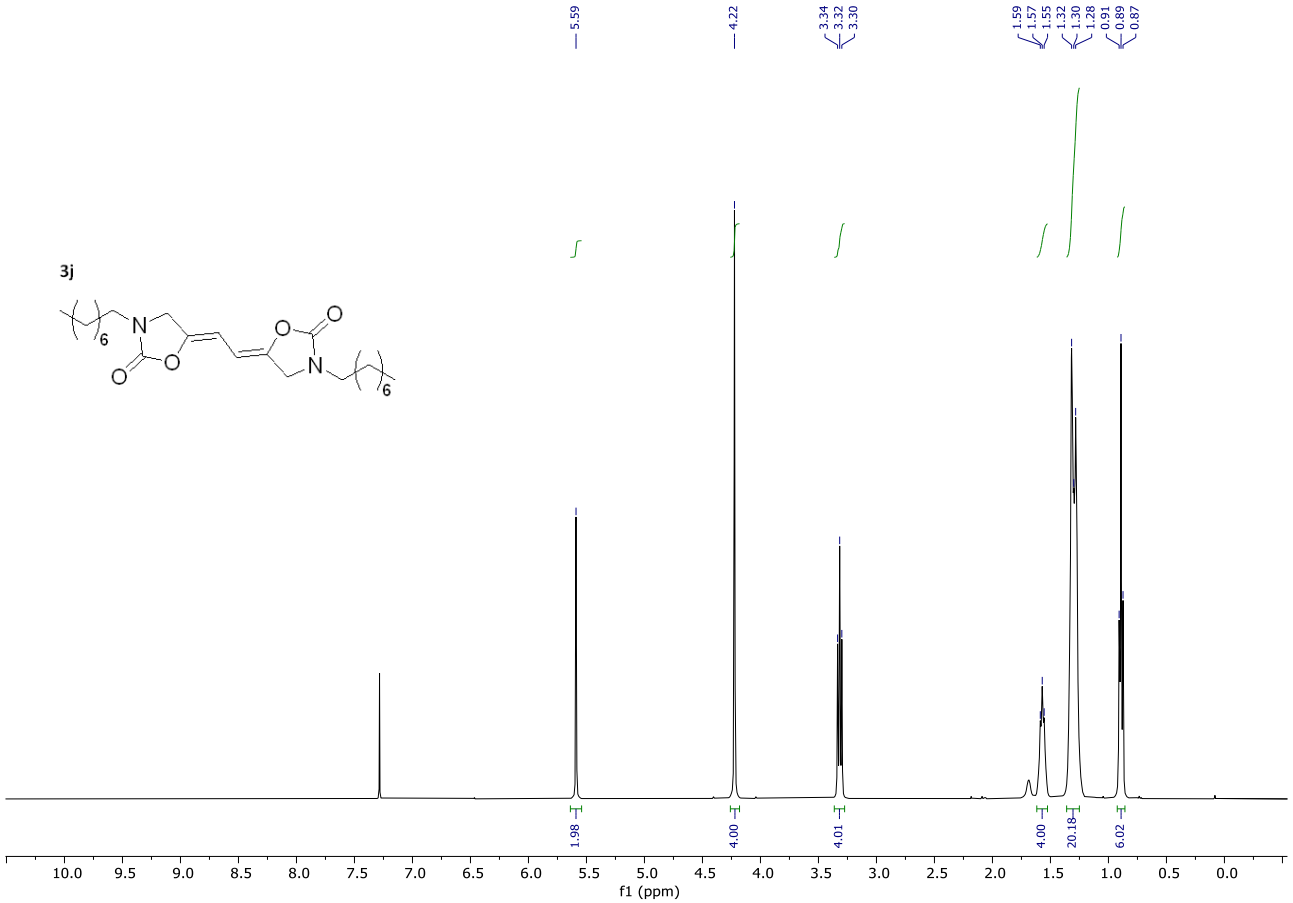

160.06
153.29
147.10
143.44
139.69
135.54
127.93
127.79
100.25
52.92
51.55
3g
O2N
NO2
f1 (ppm)

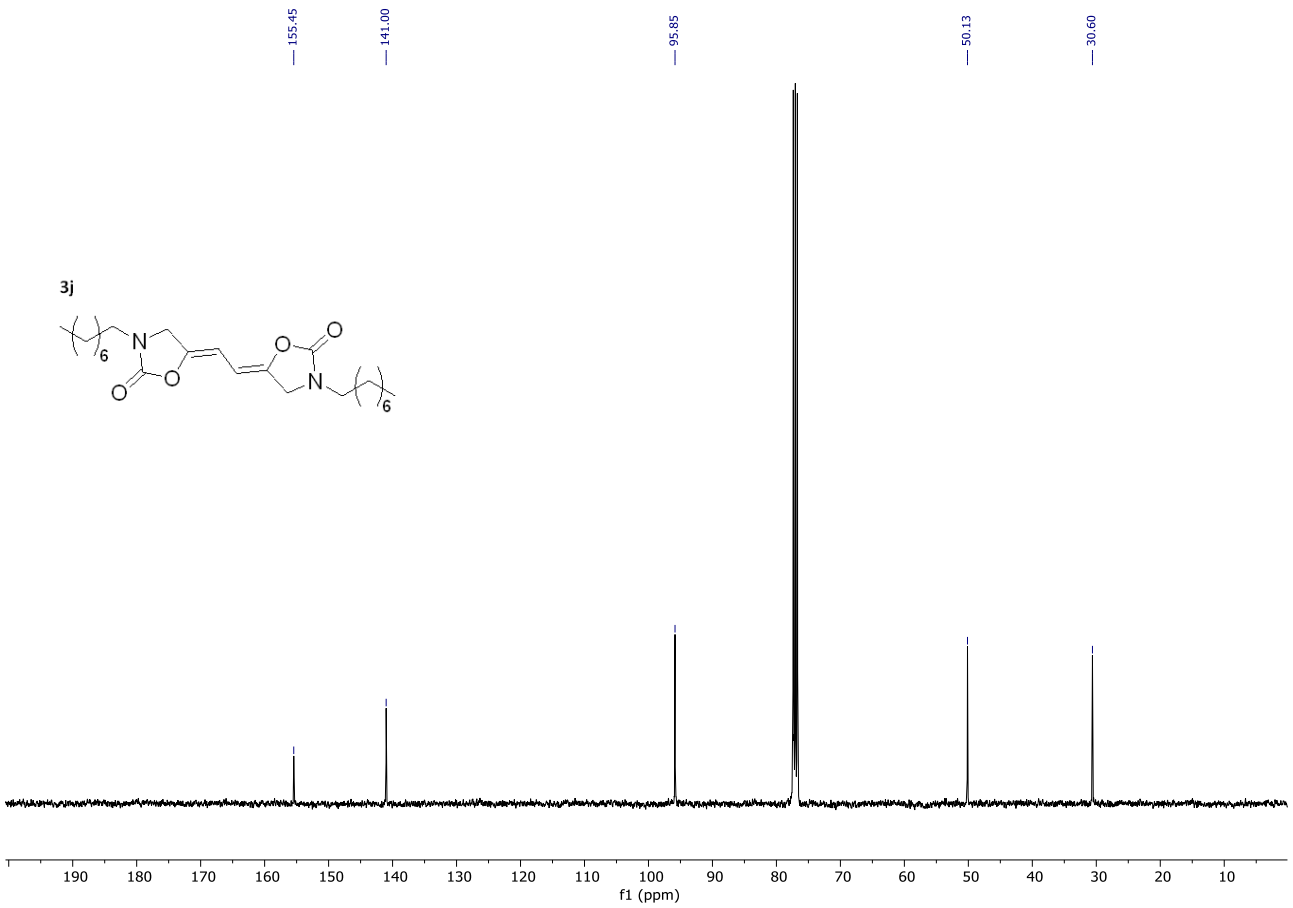

3h
OBn
BnO
7.43
7.42
7.41
7.40
7.39
7.38
7.36
7.34
7.34
7.32
7.30
7.01
6.99
6.97
5.46
5.12
4.56
4.05
10.05
4.08
4.07
1.92
4.00
4.00
4.00
f1 (ppm)

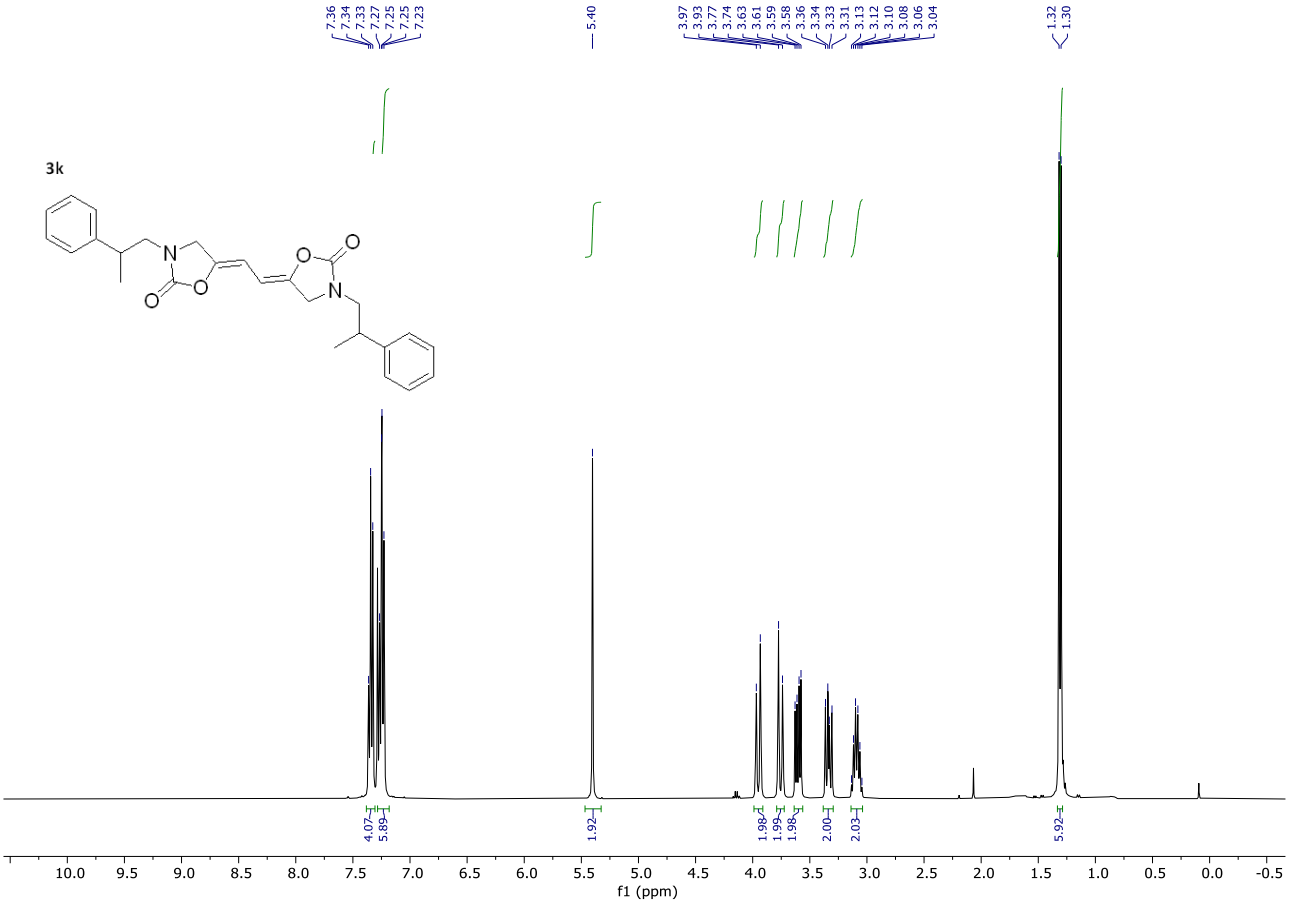

3h
OBn
BnO
156.68
155.31
141.43
136.49
130.46
129.71
128.73
128.28
127.54
123.50
121.24
111.94
95.69
70.26
48.09
42.79
f1 (ppm)

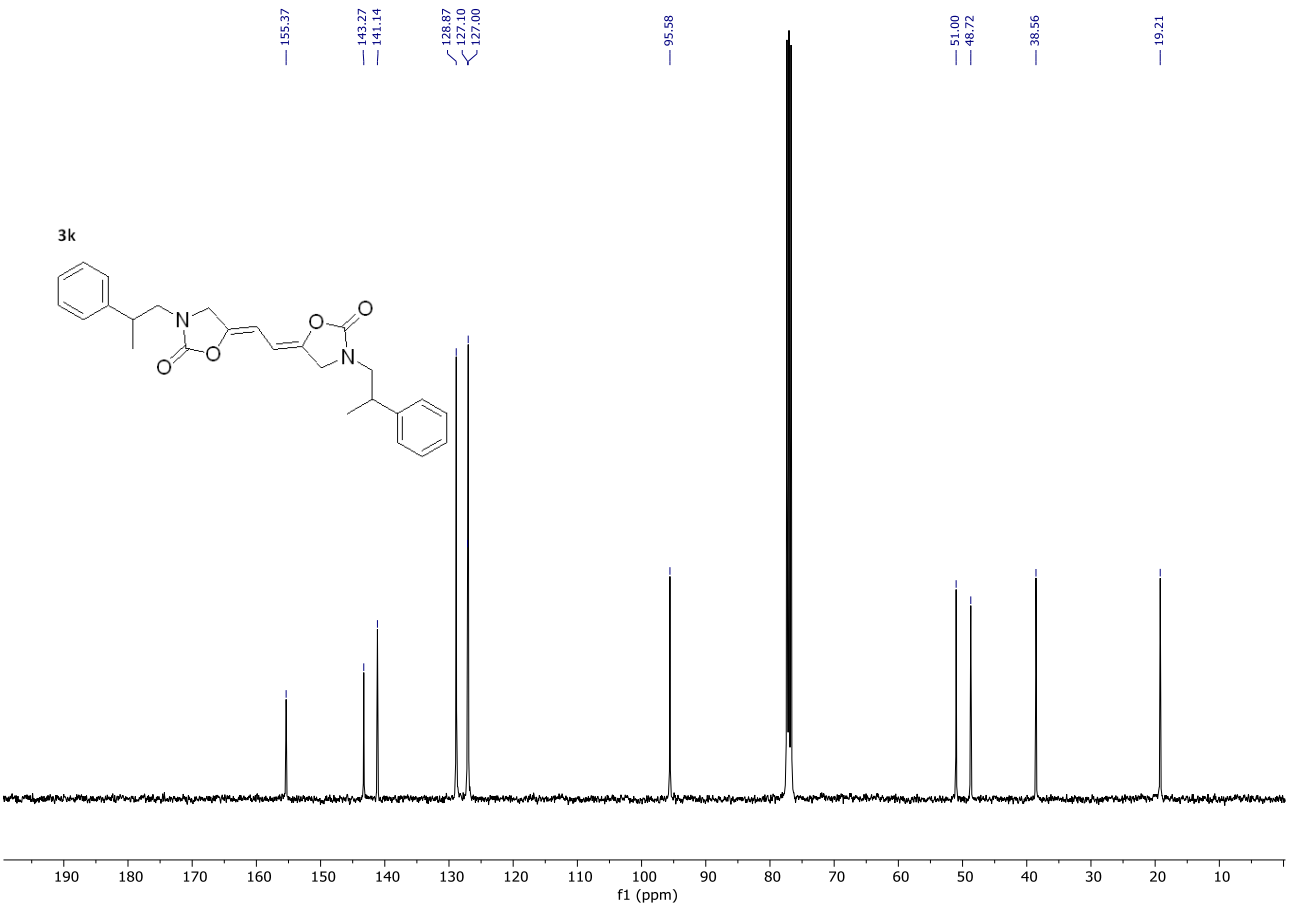

5.60
4.24
2.97
3i
1.79
3.55
5.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

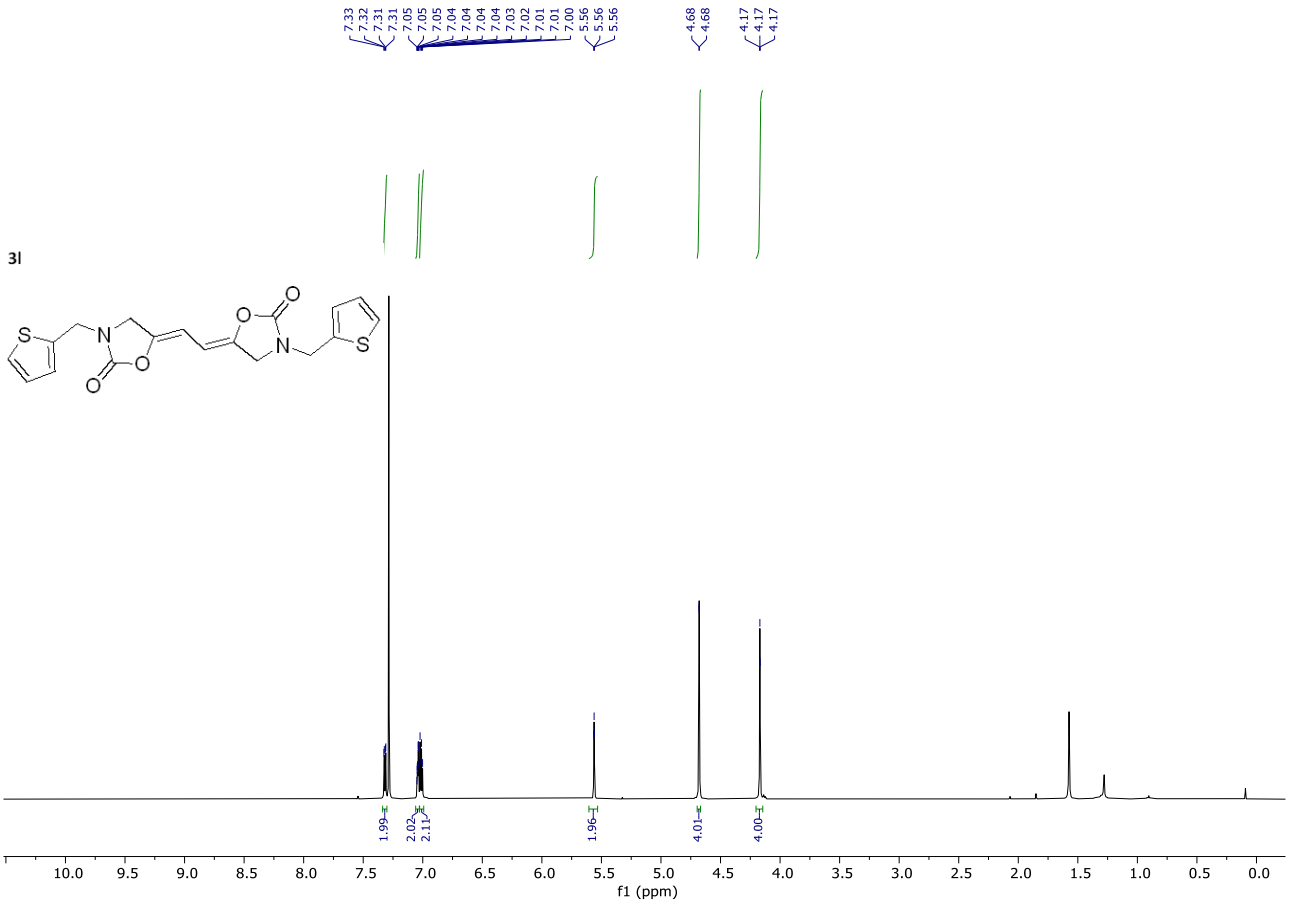

155.45
141.00
95.85
50.13
30.60
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

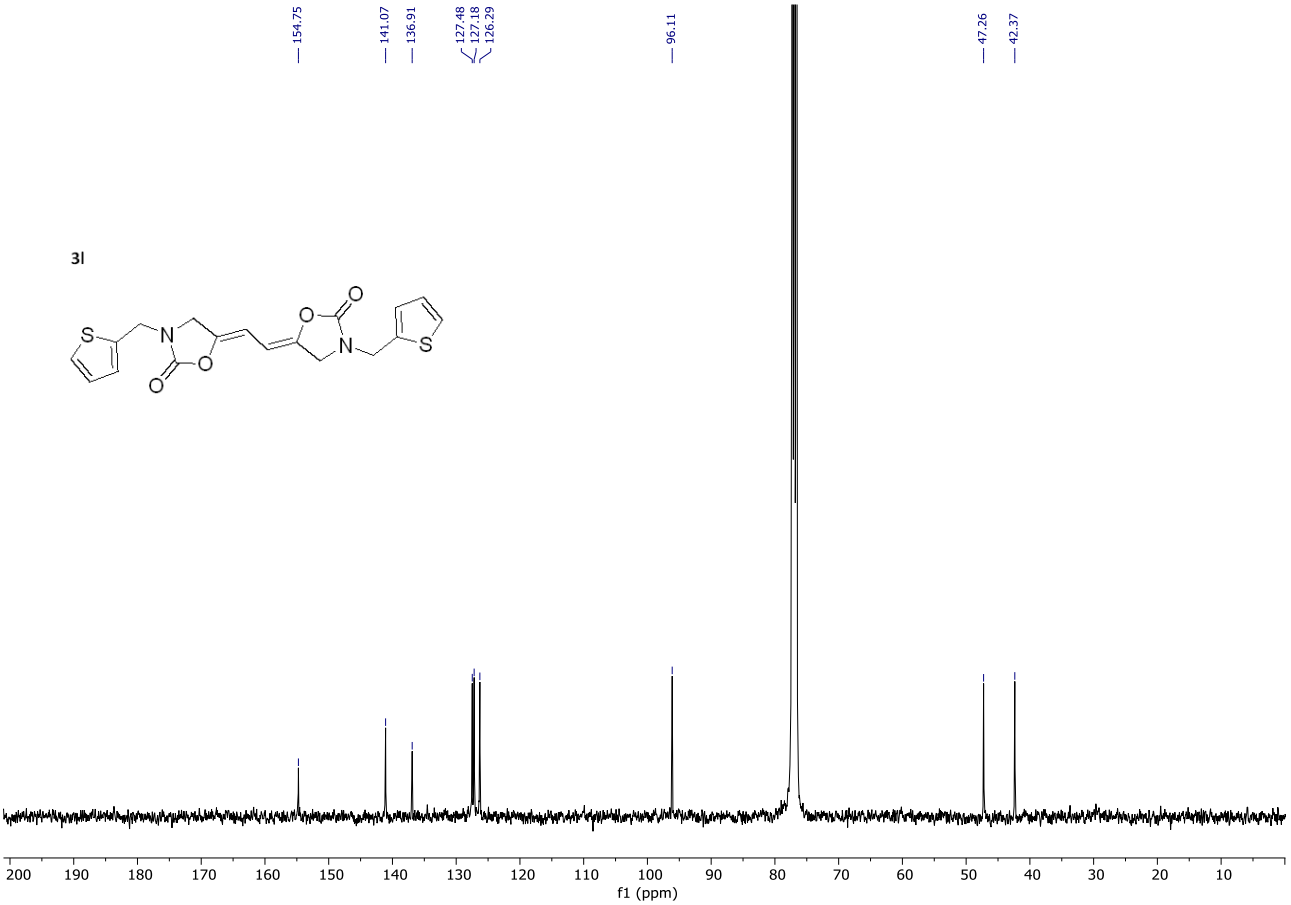

5.59
4.22
3.34
3.32
3.30
1.59
1.57
1.55
1.32
1.30
1.28
0.91
0.89
0.87
3j
1.98
4.00
4.01
4.00
20.18
6.02
f1 (ppm)

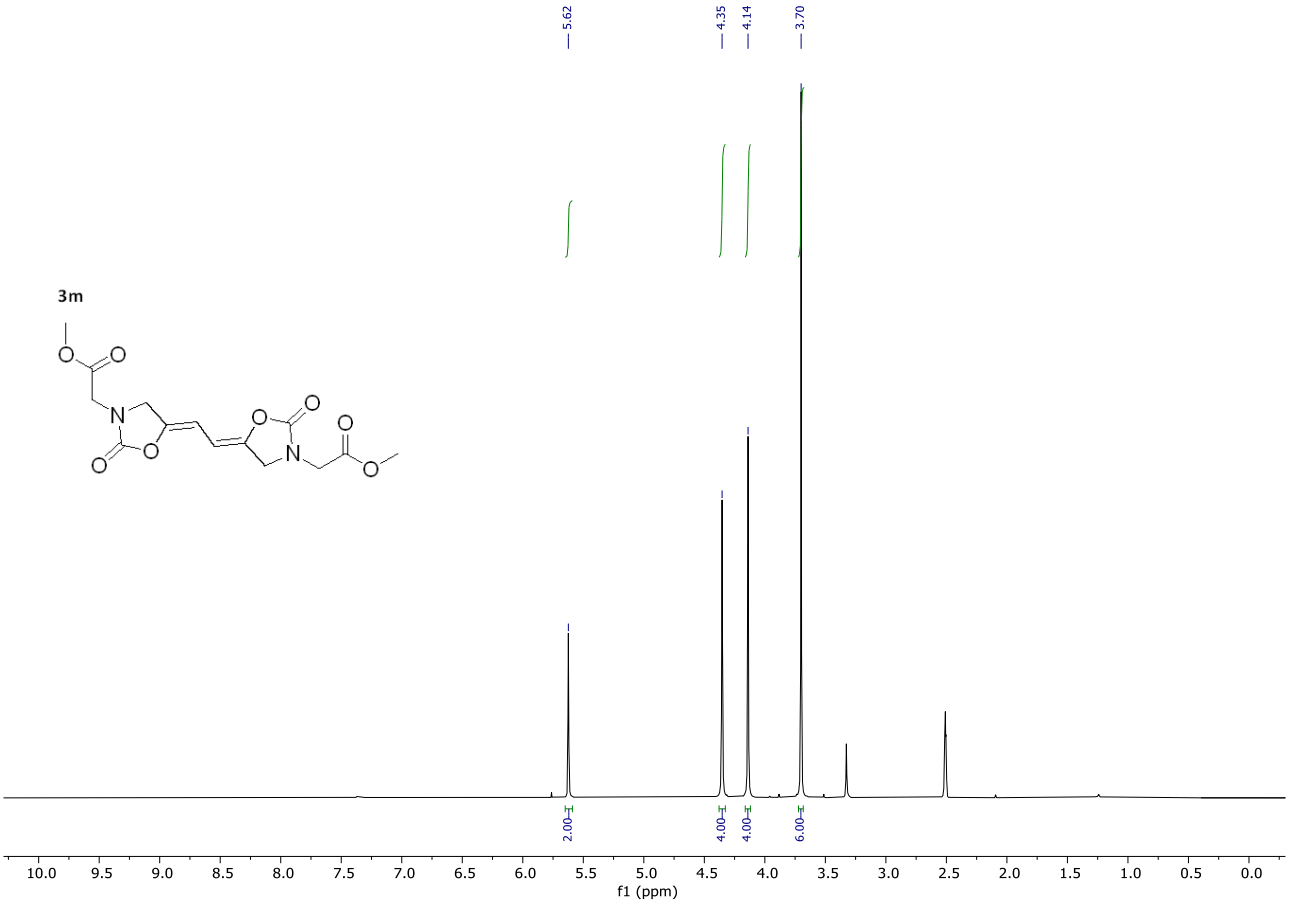

155.45
141.00
95.85
50.13
30.60
3j
f1 (ppm)

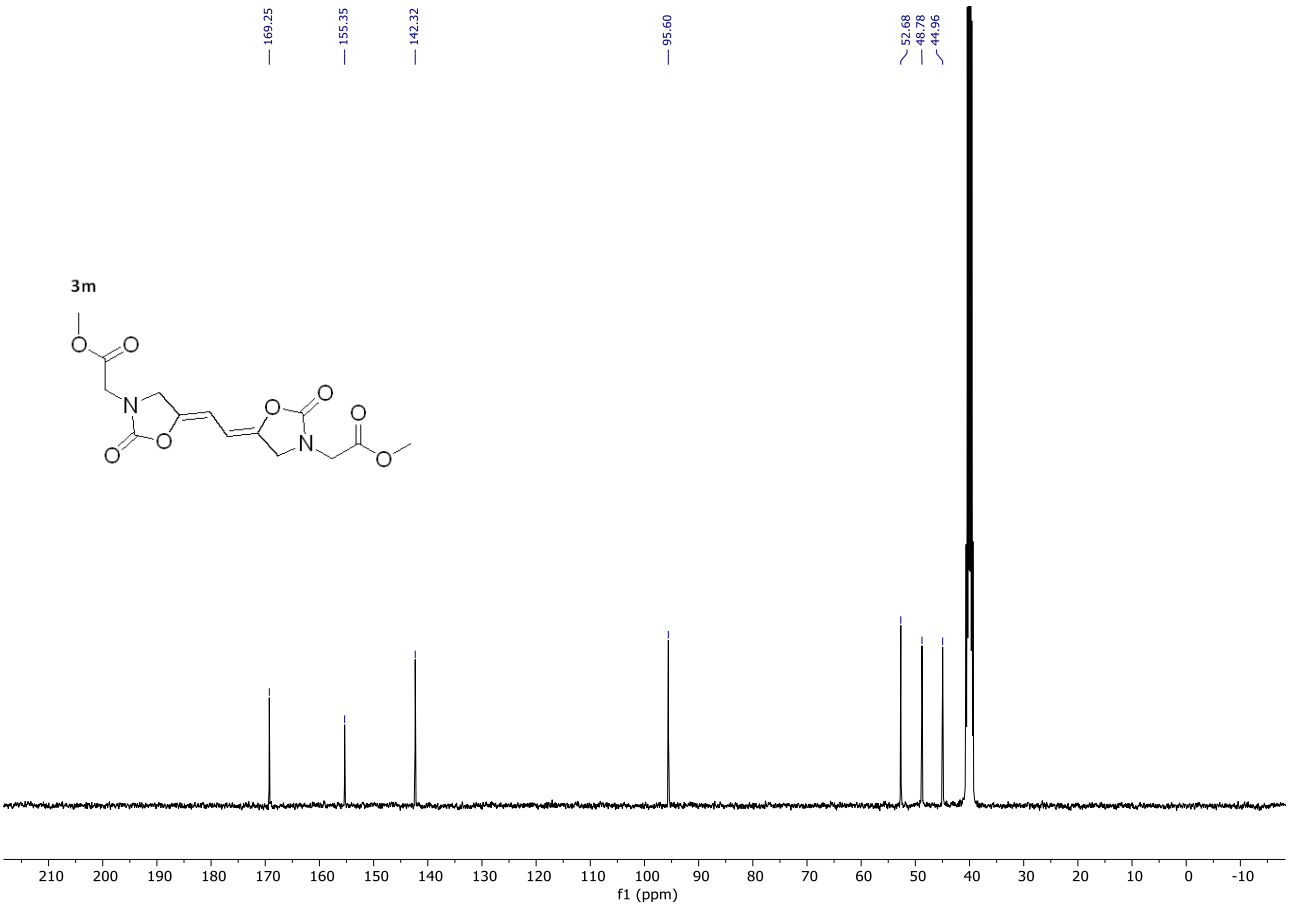

3k
7.36
7.34
7.33
7.27
7.25
7.25
7.23
5.40
3.97
3.93
3.77
3.74
3.63
3.61
3.59
3.58
3.36
3.34
3.33
3.31
3.13
3.12
3.10
3.08
3.06
3.04
1.32
1.30
4.07
5.89
1.92
1.98
1.99
1.98
2.00
2.03
5.92
f1 (ppm)

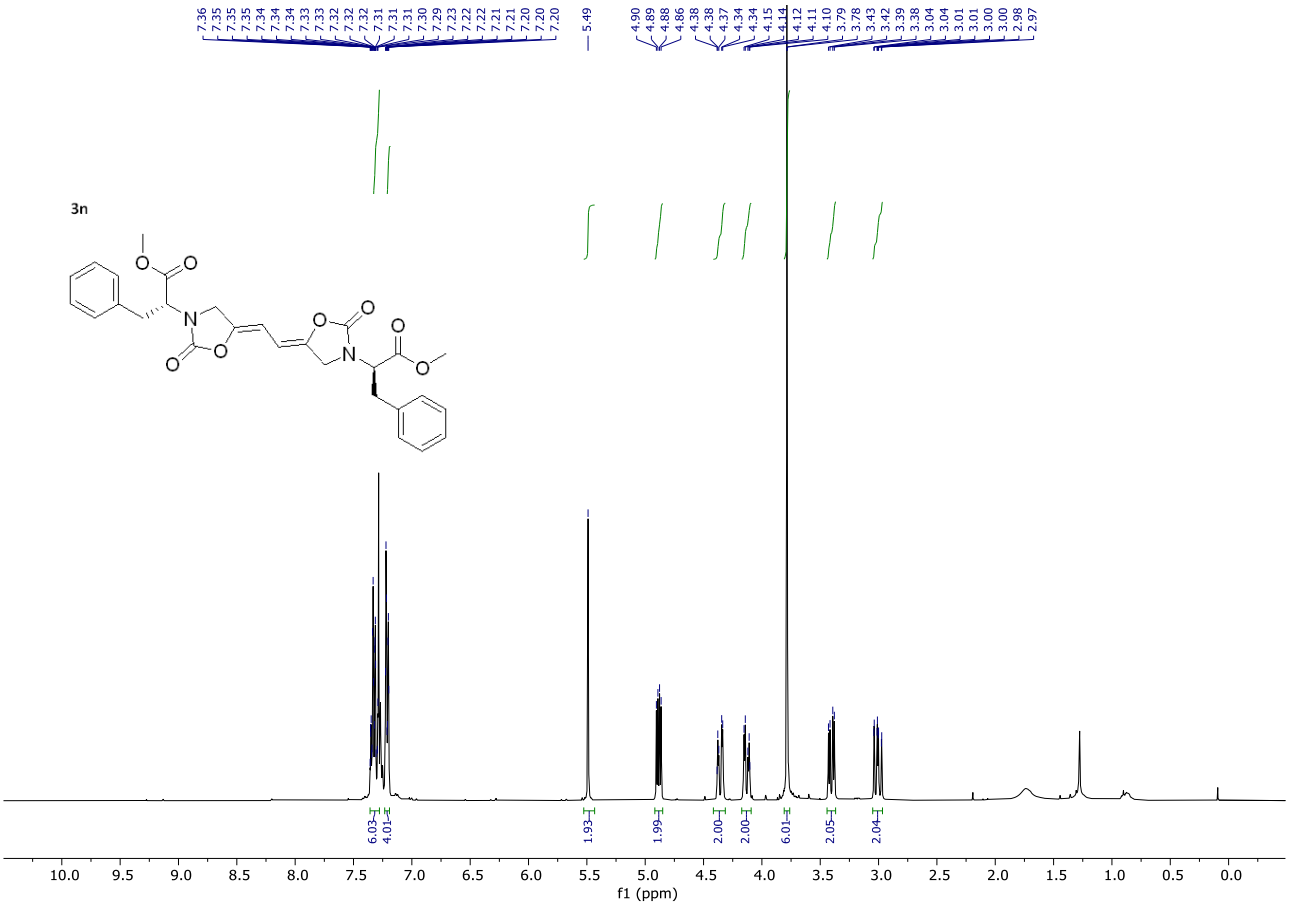

3k
155.37
143.27
141.14
128.87
127.10
127.00
95.58
51.00
48.72
38.56
19.21
f1 (ppm)

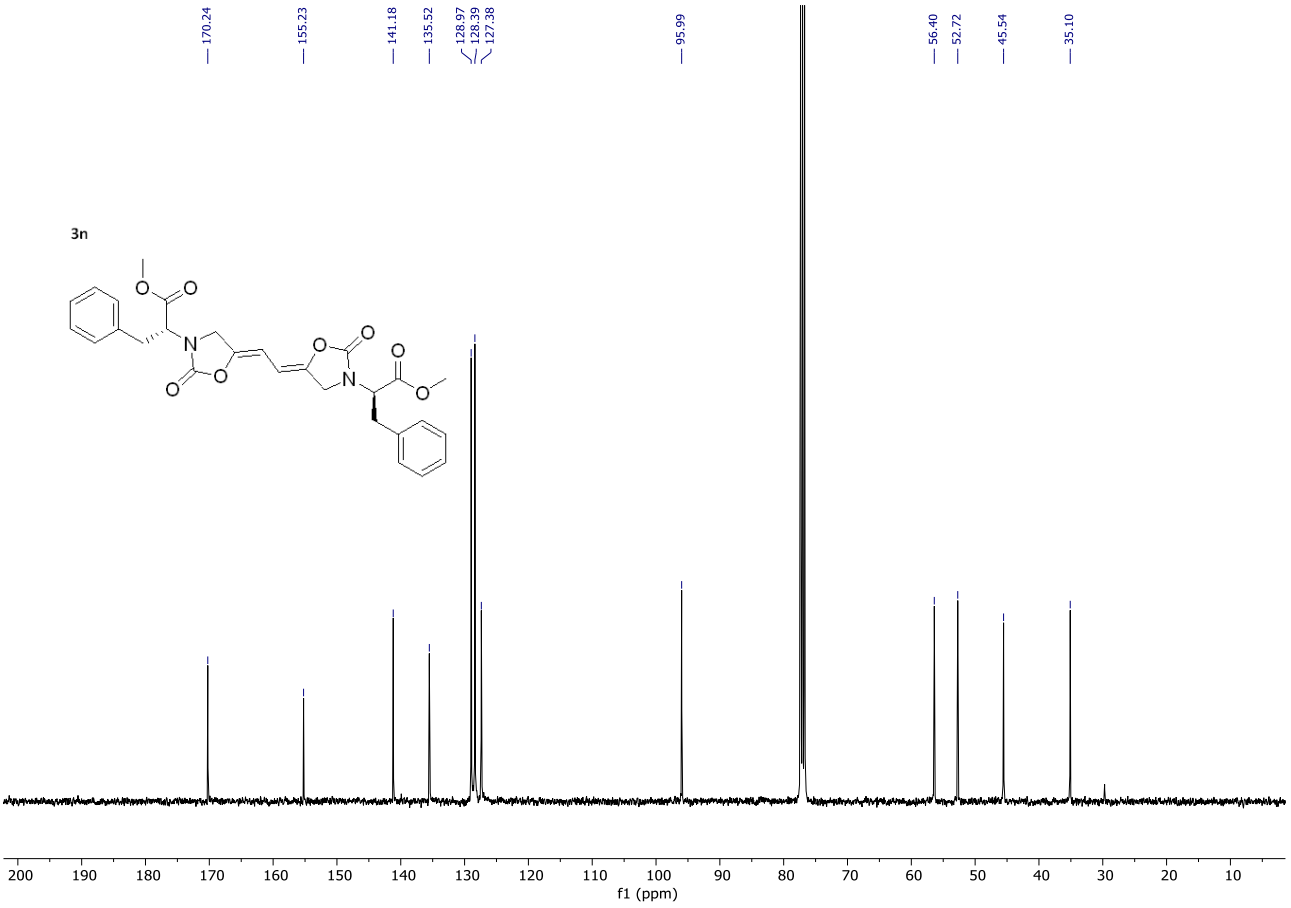

7.33
7.32
7.31
7.31
7.05
7.05
7.05
7.04
7.04
7.04
7.04
7.03
7.02
7.01
7.01
7.00
5.56
5.56
5.56
4.68
4.68
4.17
4.17
4.17
3l
1.99
2.02
2.11
1.96
4.01
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

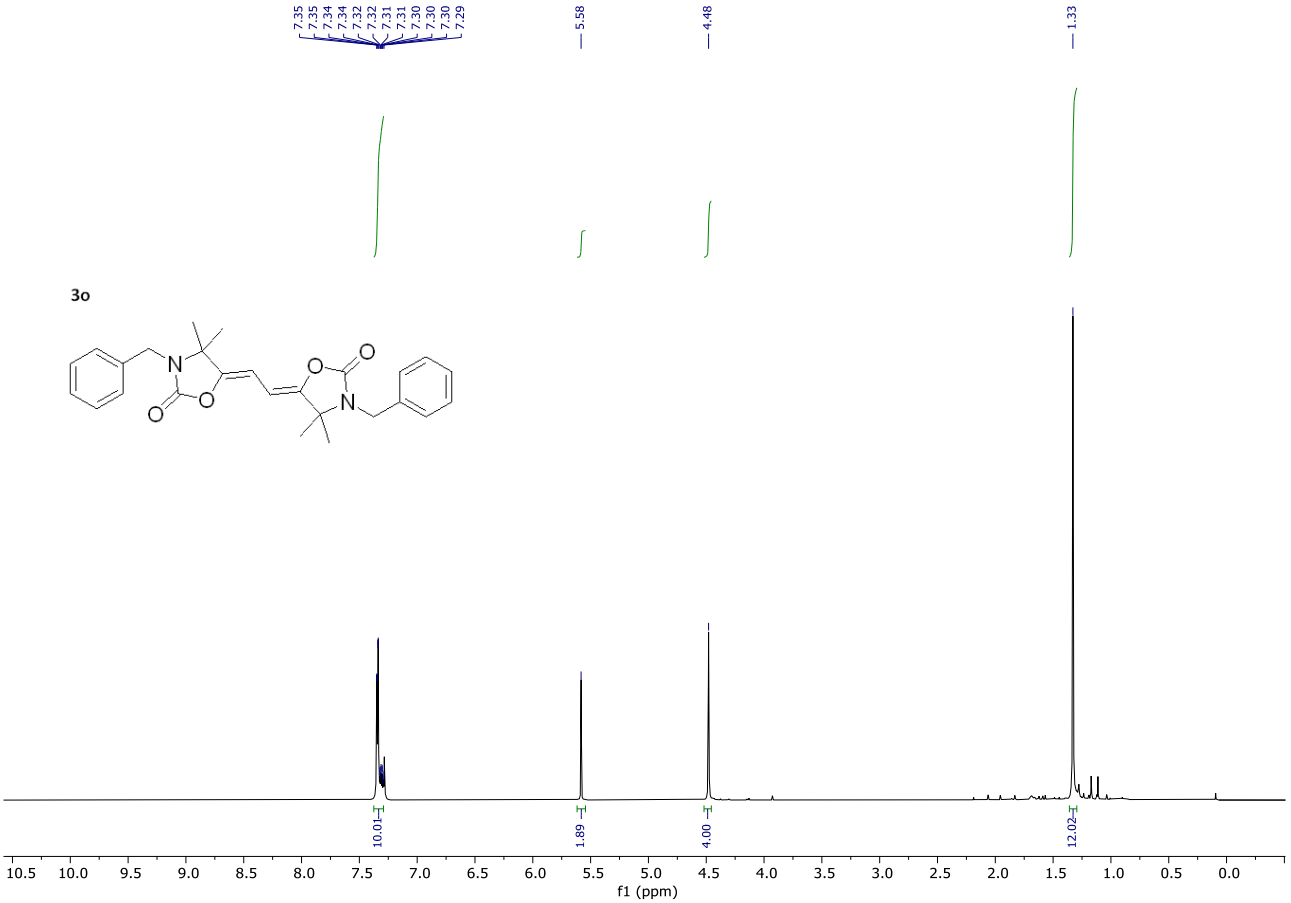

154.75
141.07
136.91
127.48
127.18
126.29
96.11
47.26
42.37
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

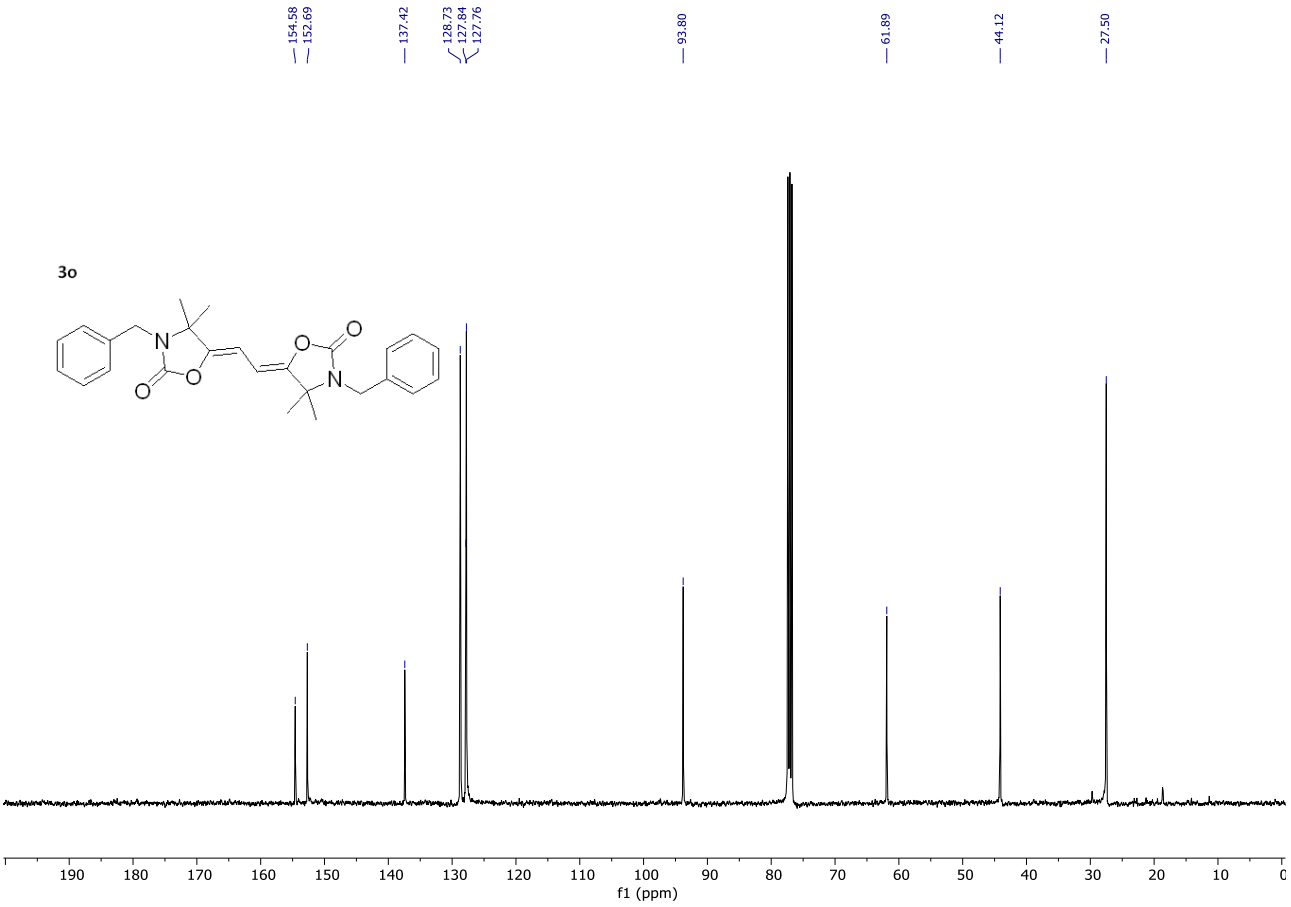

5.62
4.35
4.14
3.70
3m
2.00
4.00
4.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

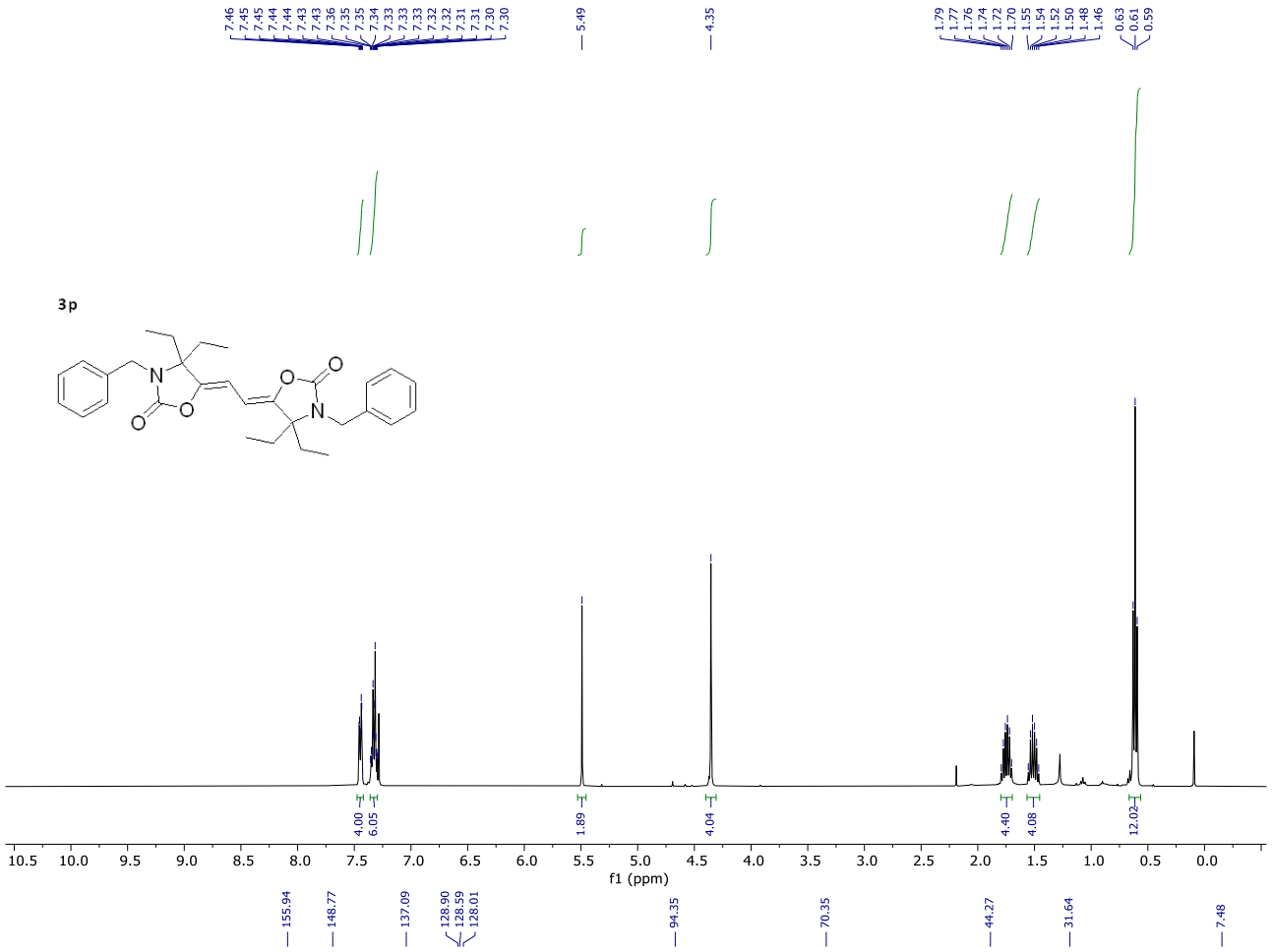

169.25
155.35
142.32
95.60
52.68
48.78
44.96
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

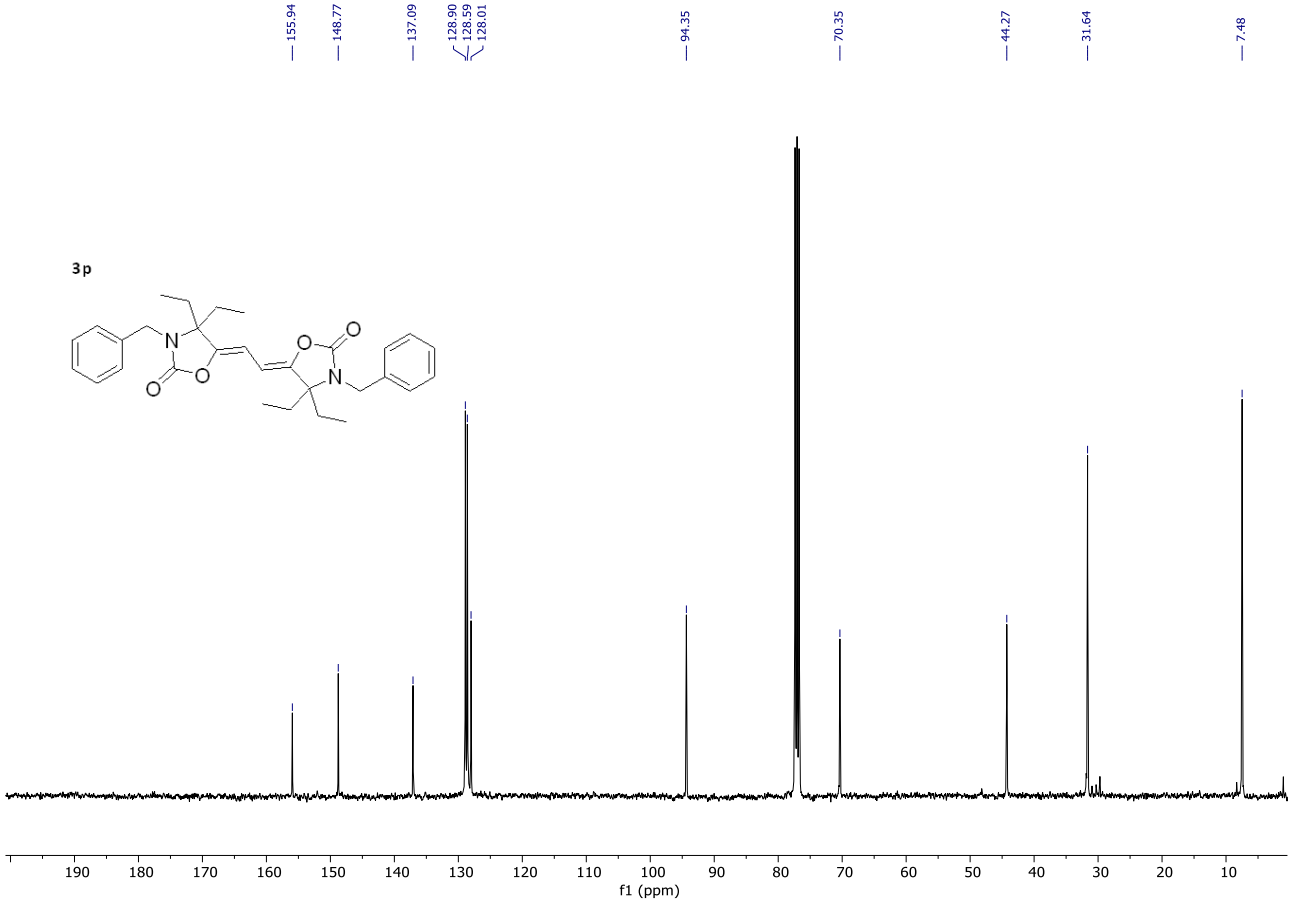

3n
7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.20
5.49
4.90 4.89 4.88 4.86 4.38 4.37 4.34 4.34 4.15 4.14 4.12 4.11 4.10 3.79 3.78 3.43 3.42 3.39 3.38 3.04 3.04 3.01 3.01 3.00 3.00 2.98 2.97
6.03 4.01 1.93 1.99 2.00 2.00 6.01 2.05 2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

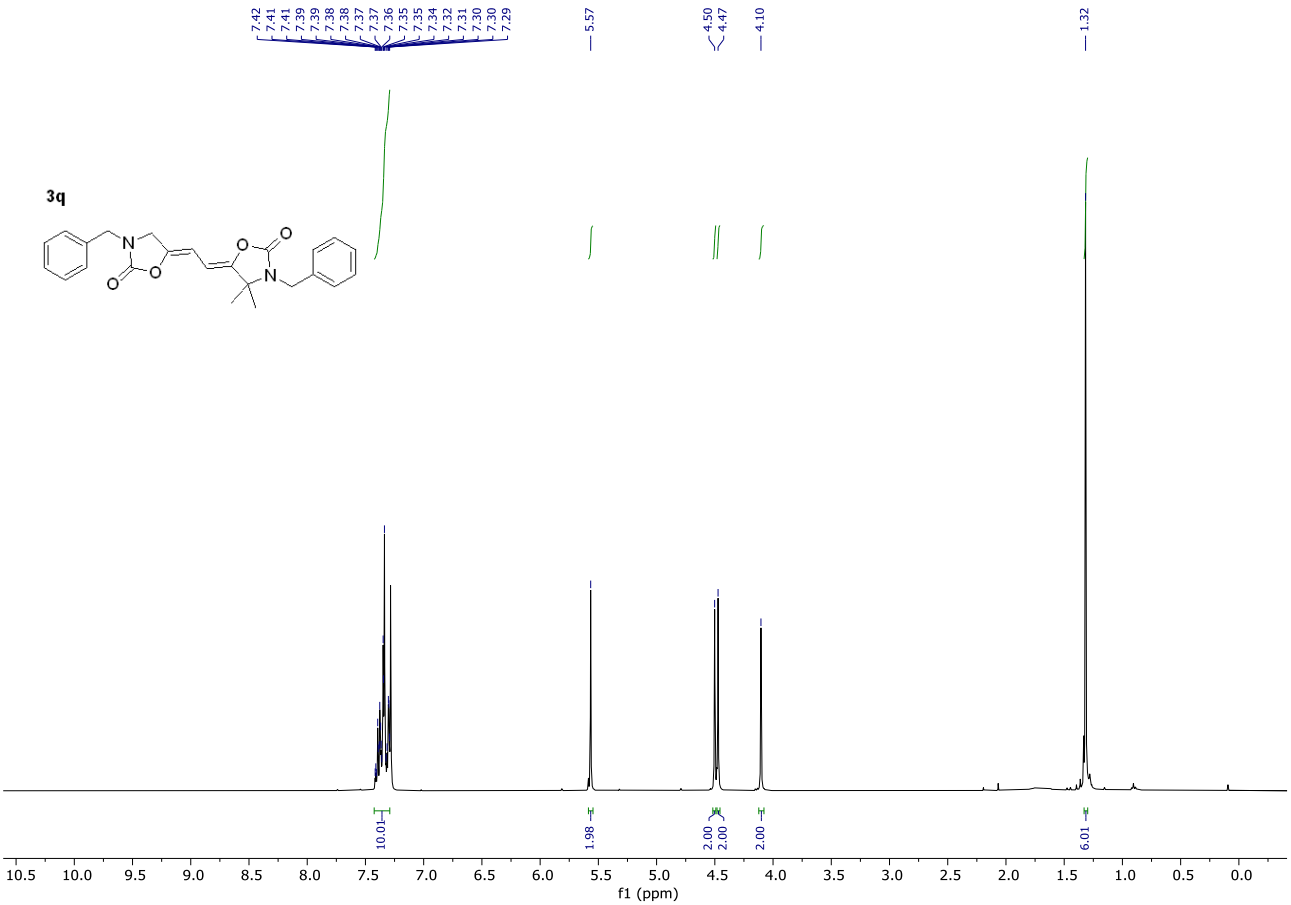

3n
170.24
155.23
141.18
135.52
128.97
128.39
127.38
95.99
56.40
52.72
45.54
35.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

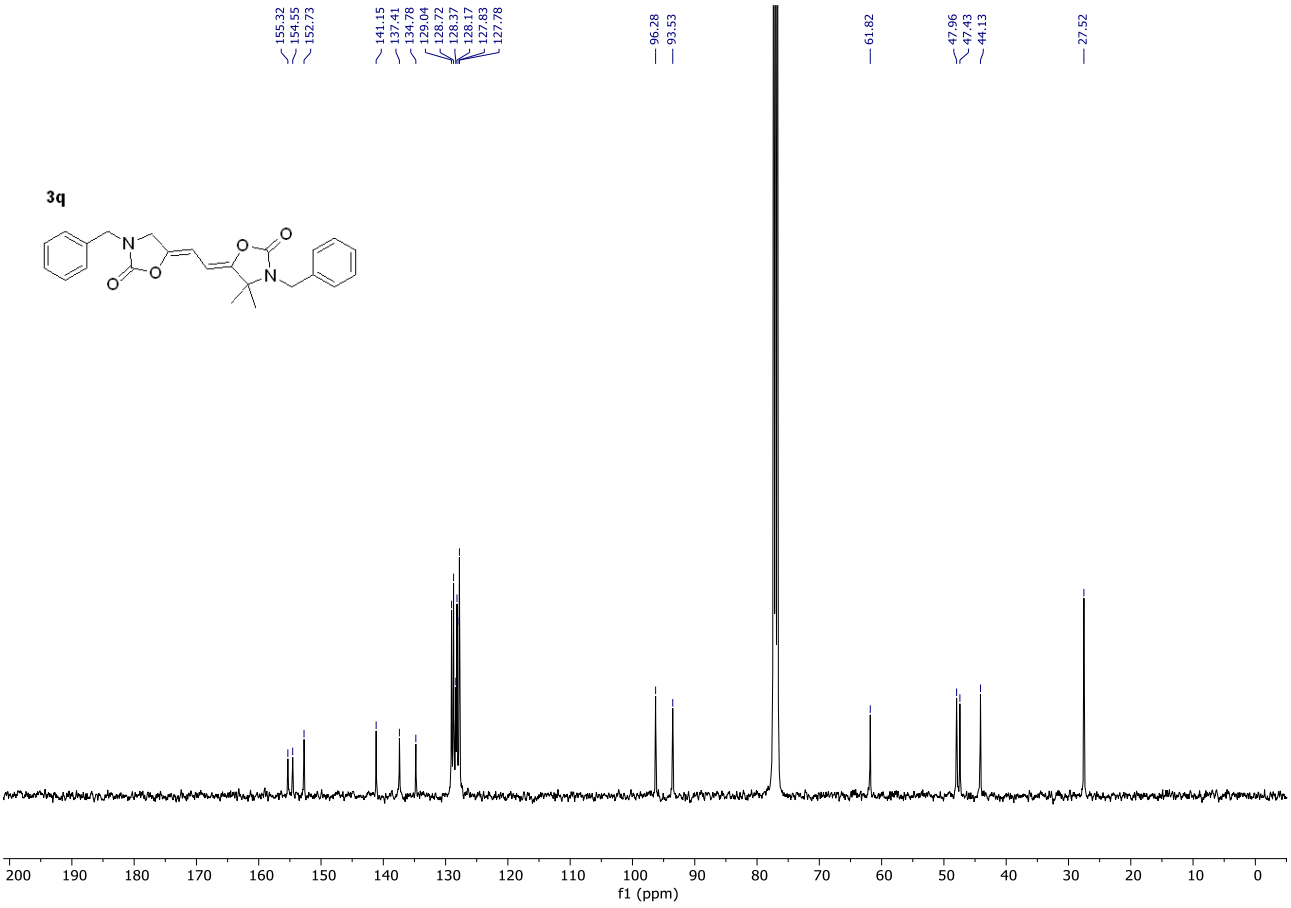

7.35
7.35
7.34
7.34
7.32
7.31
7.31
7.30
7.30
7.30
7.29
5.58
4.48
1.33
3o
10.01
1.89
4.00
12.02
f1 (ppm)

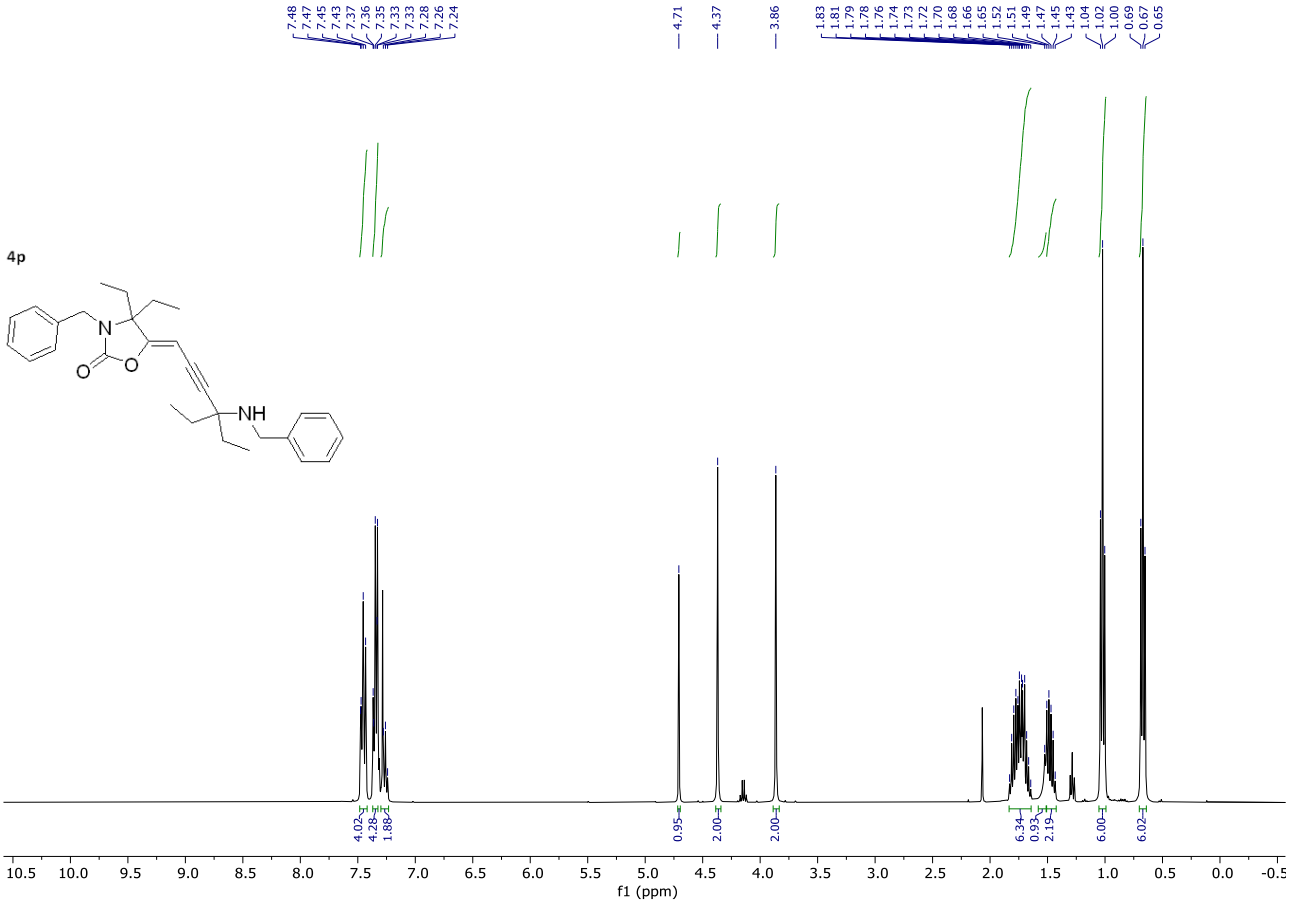

154.58
152.69
137.42
128.73
127.84
127.76
93.80
61.89
44.12
27.50
3o
f1 (ppm)

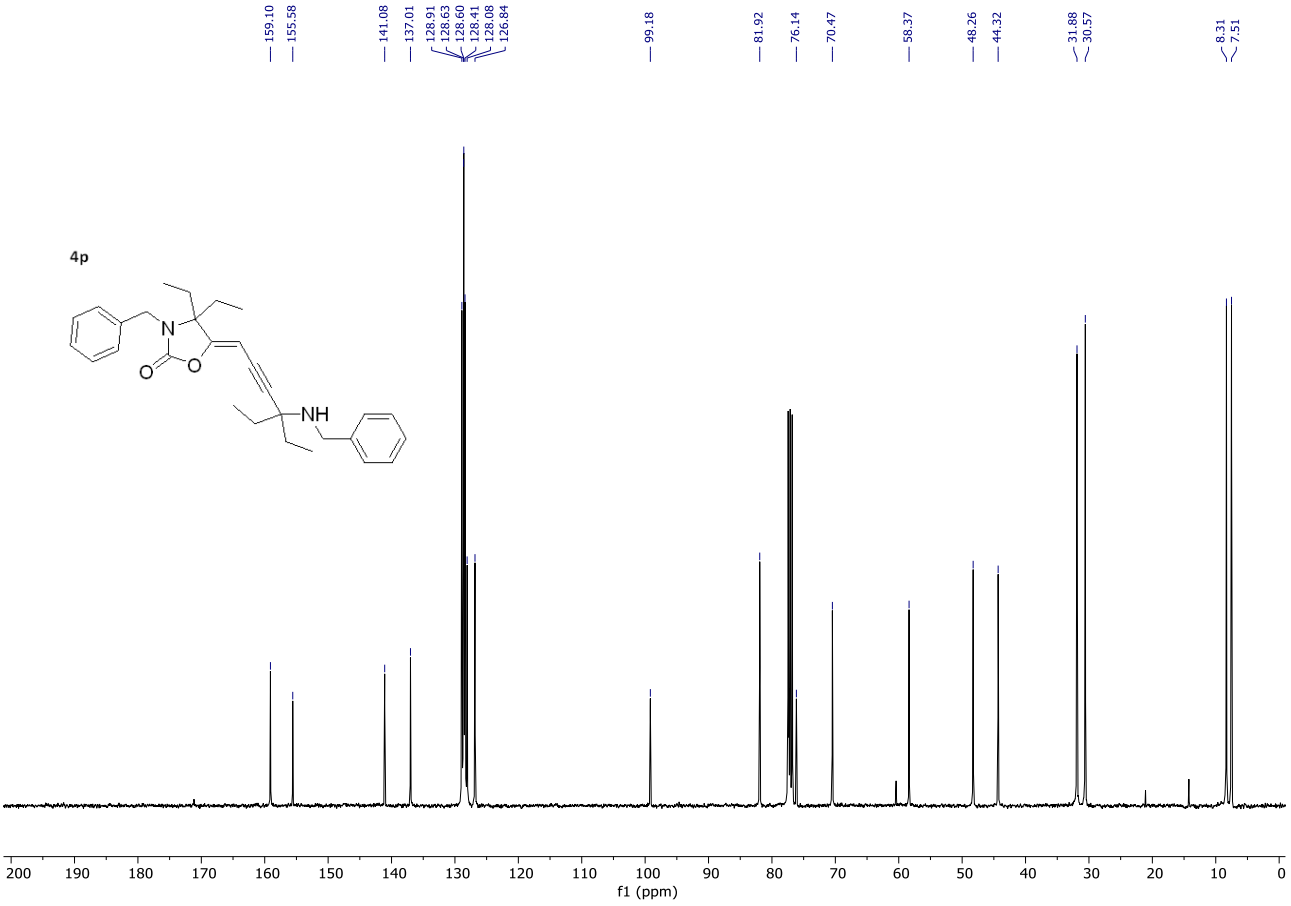

7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
5.49
4.35
1.79
1.77
1.76
1.74
1.72
1.70
1.55
1.54
1.52
1.50
1.48
1.46
0.63
0.61
0.59
3p
4.00
6.05
1.89
4.04
4.40
4.08
12.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.94
148.77
137.09
128.90
128.59
128.01
94.35
70.35
44.27
31.64
7.48
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.42
7.41
7.41
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.32
7.31
7.30
7.30
7.29
5.57
4.50
4.47
4.10
1.32
3q
10.01
1.98
2.00
2.00
2.00
6.01
f1 (ppm)


155.32
154.55
152.73
141.15
137.41
134.78
129.04
128.72
128.37
128.17
127.83
127.78
96.28
93.53
61.82
47.96
47.43
44.13
27.52
3q
f1 (ppm)


4p
7.48
7.47
7.45
7.43
7.37
7.36
7.35
7.33
7.33
7.28
7.26
7.24
4.71
4.37
3.86
1.83
1.81
1.79
1.78
1.76
1.74
1.73
1.72
1.70
1.68
1.66
1.65
1.52
1.51
1.49
1.47
1.45
1.43
1.04
1.02
1.00
0.69
0.67
0.65
4.02
4.28
1.88
0.95
2.00
2.00
6.34
0.93
2.19
6.00
6.02
f1 (ppm)


4p
159.10
155.58
141.08
137.01
128.91
128.63
128.60
128.41
128.08
126.84
99.18
81.92
76.14
70.47
58.37
48.26
44.32
31.88
30.57
8.31
7.51
f1 (ppm)