

## Supporting Information

### Unlocking the potential of water-soluble gold(I)–NHC complexes: Unveiling the role of carboxylic acid in cycloisomerization of alkynyl amino acid derivatives.

Liddier O. Pérez,<sup>a</sup> Tomás A. Dómina,<sup>a</sup> Gabriela A. Fernández,<sup>b</sup> Gustavo F. Silbestri<sup>b,\*</sup> and Sebastián A. Testero<sup>a,\*</sup>

<sup>a</sup>Instituto de Química Rosario - IQUIR (CONICET), Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, Rosario, S2002LRK, Argentina. E-mail: testero@iquir-conicet.gov.ar

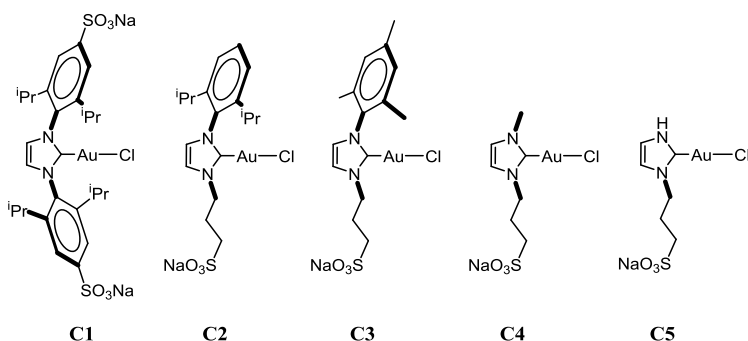
<sup>b</sup>INQUISUR, Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET, B8000CPB Bahía Blanca, Argentina. E-mail: gsilbestri@uns.edu.ar

#### Table of Contents

1.	REFERENCES FOR KNOWN SUBSTRATES AND CATALYSTS .....	3
1.1.	Synthesis of 2-(( <i>tert</i> -butoxycarbonyl)amino)hex-4-ynoic acid (1b): .....	5
1.1.1.	Diethyl 2- <i>tert</i> -butoxycarbonylamino malonate (13).....	5
1.1.2.	Diethyl 2-(but-2-yn-1-yl)-2-(( <i>tert</i> -butoxycarbonyl)amino)malonate (14).....	6
1.1.3.	2-(( <i>tert</i> -butoxycarbonyl)amino)hex-4-ynoic acid (1b).....	6
1.2.	Synthesis of <i>p</i> -trifluoromethylphenyl derivate 1d and <i>p</i> -methoxyphenyl derivate 1e.....	6
1.2.1.	Methyl 2-(( <i>tert</i> -butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoate (15a).....	6
1.2.2.	2-(( <i>tert</i> -Butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoic acid (1d).....	7
1.2.3.	Methyl 2-(( <i>tert</i> -butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate (15b) ..	7
1.2.4.	2-(( <i>tert</i> -Butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoic acid (1e).....	7
1.3.	Time-course of the conversion of 1a into 2a monitored by GC-FID. ....	8
2.	COPIES OF <sup>1</sup> H AND <sup>13</sup> C NMR SPECTRA .....	9
2.1.	1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene gold(I) Chloro (C1).....	9
2.2.	1-(2,6-Diisopropylphenyl)-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C2).....	11
2.3.	1-Mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C3).....	12
2.4.	1-Methyl-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C4).....	14
2.5.	(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C5).....	15
2.6.	Diethyl 2- <i>tert</i> -Butoxycarbonylamino malonate (13).....	16
2.7.	Diethyl 2-(but-2-yn-1-yl)-2-(( <i>tert</i> -butoxycarbonyl)amino)malonate (14).....	17
2.8.	2-(( <i>tert</i> -butoxycarbonyl)amino)hex-4-ynoic acid (1b).....	18
2.9.	<i>tert</i> -Butyl (5-methylene-2-oxotetrahydrofuran-3-yl)carbamate (2a).....	19
2.10.	<i>tert</i> -Butyl ( <i>Z</i> )-(5-ethylidene-2-oxotetrahydrofuran-3-yl)carbamate (2b).....	20

2.11.	<i>tert</i> -Butyl (6-methyl-2-oxo-3,4-dihydro-2H-pyran-3-yl)carbamate (2b <i>endo</i> ). .....	20
2.12.	<i>tert</i> -Butyl ( <i>Z</i> )-(5-benzylidene-2-oxotetrahydrofuran-3-yl)carbamate (2c).....	21
2.13.	Methyl 2-(( <i>tert</i> -butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoate (15a).....	22
2.14.	2-(( <i>tert</i> -Butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoic acid (1d).....	23
2.15.	<i>tert</i> -butyl ( <i>Z</i> )-(5-(4-methoxybenzylidene)-2-oxotetrahydrofuran-3-yl)carbamate (2d). .....	24
2.16.	2-(( <i>tert</i> -butoxycarbonyl)amino)-5-(4-methoxyphenyl)-4-oxopentanoic acid (2d-Hydration). .....	24
2.17.	Methyl 2-(( <i>tert</i> -butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate (15b).....	26
2.18.	2-(( <i>tert</i> -Butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoic acid (1e).....	27
2.19.	<i>tert</i> -Butyl ( <i>Z</i> )-(2-oxo-5-(4-(trifluoromethyl)benzylidene)tetrahydrofuran-3-yl) carbamate (2e):... 28	
2.20.	Methyl 2-acetamido-4-oxopentanoate (4).....	29
3.	REUSE PROCESS OF CATALYSTS C1 – C5. ....	30
4.	KINETIC STUDY ON THE FORMATION OF ENOL-LACTONE 2a MONITORED BY GC-FID. . 60	
4.1.	Kinetic 1:.....	60
4.1.1.	Comparison of chromatograms of samples taken from kinetics 1 for the product in the GC-FID. 60	
	Figure S9. Time-resolved GC-FID chromatograms of the formation of product 2a (kinetic 1). .....	60
4.2.	Kinetic 2:.....	61
4.2.1.	Comparison of chromatograms of samples taken from kinetics 2 for the product in the GC-FID. 61	
	Figure S11. Time-resolved GC-FID chromatograms of the formation of product 2a (kinetic 2). .....	61
4.3.	Kinetic 3:.....	62
4.3.1.	Comparison of chromatograms of samples taken from kinetics 3 for the product in the GC-FID. 62	
	Figure S13. Time-resolved GC-FID chromatograms of the formation of product 2a (kinetic 3). .....	62
4.4.	Comparison of the three kinetics.....	63
4.4.1.	Graph of calculated average and error in the gold-catalyzed conversion of 1a into 2a. ....	63
5.	REFERENCES .....	64

## 1. REFERENCES FOR KNOWN SUBSTRATES AND CATALYSTS.



**Figure S1.** Catalysts **C1-5** were synthesized according to reference 1.

**1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene gold(I) Chloro (C1).** White solid (0.465 g, 0.57 mmol, 95%); mp > 300 °C. The complex is soluble in water, methanol, tert-butanol, isopropanol and DMSO, and insoluble in tetrahydrofuran, diethyl ether and acetone; Water solubility at 25 °C: 111 g/L; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 7.76 (s, 4H, Ar), 7.67 (s, 2H, Imz), 2.57 (h, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, 4H, CHMe<sub>2</sub>), 1.28 (d, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, 12H, CHMe<sub>2</sub>), 1.20 (d, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, 12H, CHMe<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 8.00 (s, 2H, Imz), 7.58 (s, 4H, Ar), 2.17 (h, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 4H, CHMe<sub>2</sub>), 1.22 (t, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 24H, CHMe<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ 171.6 (s, Imz C2), 147.4 (s, Ar C3), 144.7 (s, Ar C4), 136.1 (s, Ar C2), 124.3 (s, Ar C1), 121.4 (s, Imz C4,5), 28.8 (s, CHMe<sub>2</sub>), 23.5 (s, CHMe<sub>2</sub>), 22.9 (s, CHMe<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ 173.0 (s, Imz C2), 149.8 (s, Ar C4), 144.8 (s, Ar C2), 134.0 (s, Ar C1), 124.6 (s, Ar C3), 121.1 (s, Imz C4,5), 28.4 (s, CHMe<sub>2</sub>), 23.9 (s, CHMe<sub>2</sub>), 23.5 (s, CHMe<sub>2</sub>).

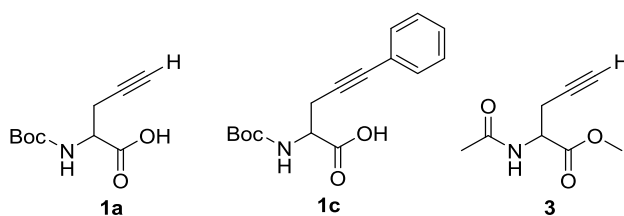
**1-(2,6-Diisopropylphenyl)-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C2).** Brown solid (0.332 g, 0.55 mmol, 92%); mp 240-243 °C. Complex **C2** is soluble in water, methanol, tert-butanol and DMSO, partially soluble in isopropanol, and insoluble in tetrahydrofuran, diethyl ether and acetone. Water solubility at 25 °C: 80 g/L; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 7.79 (s, 1H, Imz), 7.68 (s, 1H, Imz), 7.51 (m, 1H, Ar H4), 7.40 (m, 2H, Ar H3), 4.39 (t, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 2H, NCH<sub>2</sub>), 2.90 (t, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 2H, CH<sub>2</sub>S), 2.21 (h, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 2H, CHMe<sub>2</sub>), 1.92 (q, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.09 (t, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 12H, CHMe<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 6.95 (s, 1H, Imz), 6.75 (s, 1H, Imz), 6.63 (t, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 1H, Ar H4), 6.46 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, Ar H3), 3.41 (t, <sup>3</sup>J<sub>H-H</sub> = 6.2 Hz, 2H, NCH<sub>2</sub>), 1.61 (t, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 2H, CH<sub>2</sub>S), 1.39 (h, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 2H, CHMe<sub>2</sub>), 1.29 (q, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.31 (d, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 6H, CHMe<sub>2</sub>), 0.21 (d, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 6H, CHMe<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ 170.7 (s, Imz C2), 144.4 (s, Ar C1), 134.9 (s, Ar C2), 130.2 (s, Ar C4), 125.5 (s, Ar C3), 124.4 (s, Imz C4), 120.6 (s, Imz C5), 52.2 (s, NCH<sub>2</sub>), 49.3 (s, SCH<sub>2</sub>), 30.1 (s, CHMe<sub>2</sub>), 26.5 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.3 (s, CHMe<sub>2</sub>), 22.0 (s, CHMe<sub>2</sub>).

**1-Mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C3).** White solid (0.302 g, 0.54 mmol, 90%); mp 197-199 °C. Complex **C3** is soluble in water, methanol, tert-butanol and DMSO, partially soluble in isopropanol, and insoluble in tetrahydrofuran, diethyl ether and acetone.

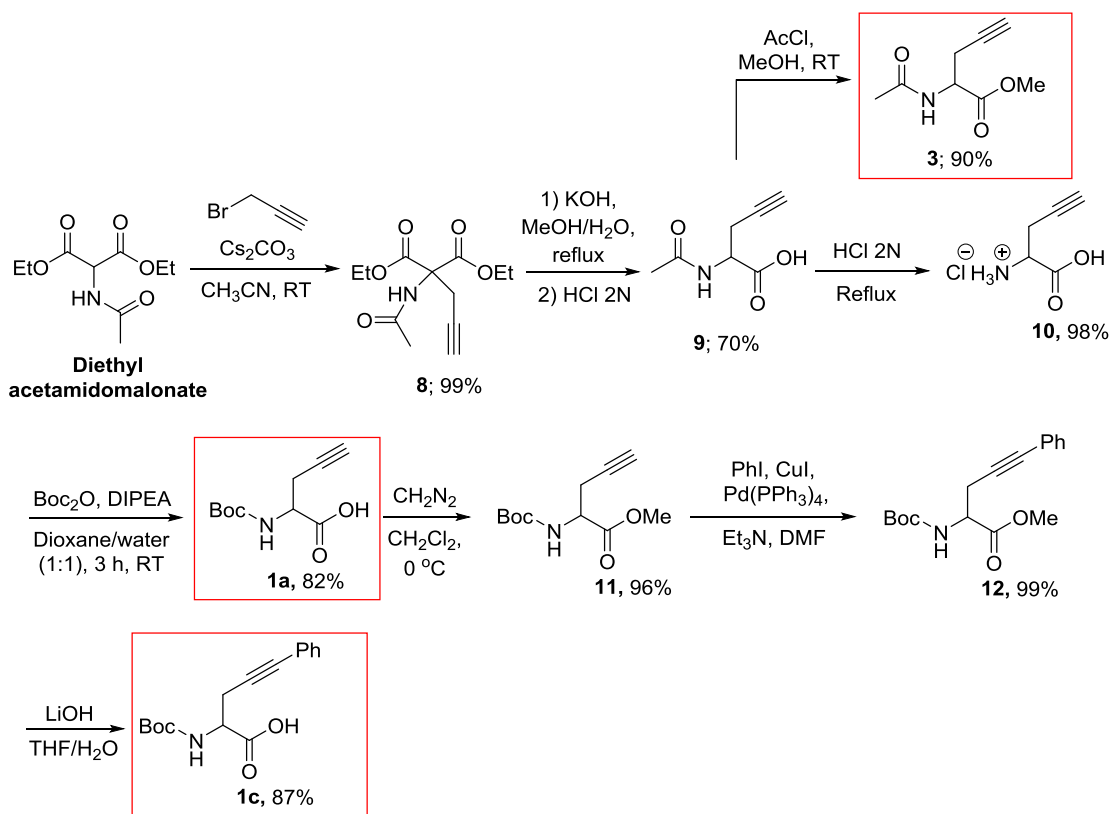
Water solubility at 25 °C: 180 g/L;  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.57 (d,  $^3J_{\text{H-H}} = 2.0$  Hz, 1H, Imz), 7.06 (s, 2H, Ar), 7.03 (d,  $^3J_{\text{H-H}} = 2.0$  Hz, 1H, Imz), 4.40 (t,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{NCH}_2$ ), 2.91 (t,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{CH}_2\text{S}$ ), 2.26 (s, 3H, *p*-MeAr), 2.08 (q, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.98 (s, 6H, *o*-MeAr);  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  7.81 (s, 1H, Imz), 7.47 (s, 1H, Imz), 7.07 (s, 2H, Ar), 4.29 (t,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{NCH}_2$ ), 2.41 (t,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{CH}_2\text{S}$ ), 2.31 (s, 3H, Ar *p*-Me), 2.15 (q, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.95 (s, 6H, Ar *o*-Me);  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  169.7 (s, Imz C2), 138.5 (s, Ar C1), 134.2 (s, Ar C2), 134.1 (s, Ar C4), 128.7 (s, Ar C3), 122.5 (s, Imz C4), 122.0 (s, Imz C5), 49.4 (s,  $\text{NCH}_2$ ), 47.8 (s,  $\text{SCH}_2$ ), 27.1 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 20.3 (s, *p*-MeAr), 16.9 (s, *o*-MeAr).

**1-Methyl-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C4).** White solid (0.106 g, 0.22 mmol, 89%); mp 143-145 °C. The complex is soluble in water, methanol, tert-butanol and DMSO, partially soluble in isopropanol, and insoluble in tetrahydrofuran, diethyl ether and acetone. Water solubility at 25 °C: 645 g/L (lit: 680 g/l);  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.15 (d,  $^3J_{\text{H-H}} = 1.4$ , 1H, Imz), 7.09 (d,  $^3J_{\text{H-H}} = 1.4$ , 1H, Imz), 4.16 (t,  $^3J_{\text{H-H}} = 7.0$ , 2H,  $\text{NCH}_2$ ), 3.67 (s, 3H,  $\text{NCH}_3$ ), 2.82 (t,  $^3J_{\text{H-H}} = 7.5$ , 2H,  $\text{CH}_2\text{S}$ ), 2.17 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  167.7 (s, Imz C2), 122.8 (s, Imz C5), 121.2 (s, Imz C4), 49.3 (s,  $\text{NCH}_2$ ), 47.9 (s,  $\text{SCH}_2$ ), 37.8 (s,  $\text{NCH}_3$ ), 26.1 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ).

**(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C5).** White solid (0.119 g, 0.24 mmol, 80%); mp 153-155 °C. The complex is soluble in methanol, tert-butanol and DMSO, partially soluble in isopropanol, and insoluble in tetrahydrofuran, diethyl ether and acetone.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  7.82 (s, 1H, NH), 7.25 (d,  $^3J_{\text{H-H}} = 1.4$ , 1H, Imz), 6.99 (d,  $^3J_{\text{H-H}} = 1.4$ , 1H, Imz), 4.10 (t,  $^3J_{\text{H-H}} = 7.0$ , 2H,  $\text{NCH}_2$ ), 2.36 (t,  $^3J_{\text{H-H}} = 7.5$ , 2H,  $\text{CH}_2\text{S}$ ), 1.99 (q, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  164.2 (s, Imz C2), 123.0 (s, Imz C5), 121.7 (s, Imz C4), 48.4 (s,  $\text{NCH}_2$ ), 45.9 (s,  $\text{SCH}_2$ ), 27.6 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ).

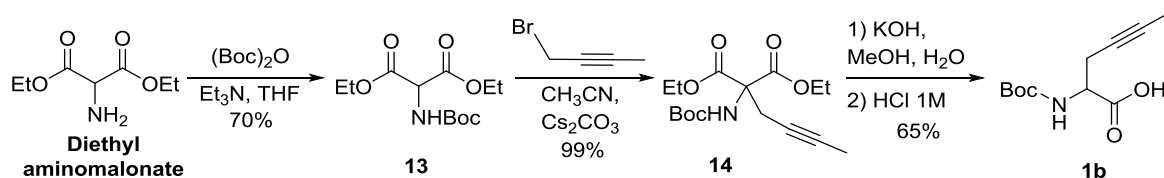


**Figure S2.** *N*-Boc-Propargylglycine (**1a**), 2-((*tert*-butoxycarbonyl)amino)-5-phenylpent-4-ynoic acid (**1c**) and methyl 2-acetyl-amino-4-pentynoate (**3**) were synthesized in 4, 7 and 3 steps respectively from diethyl acetamidomalonate according to reference <sup>2</sup> (Scheme S1).



**Scheme S1.** Synthetic sequence for preparation of **1a**, **1c** and **3**.

### 1.1. Synthesis of 2-((*tert*-butoxycarbonyl)amino)hex-4-ynoic acid (**1b**):



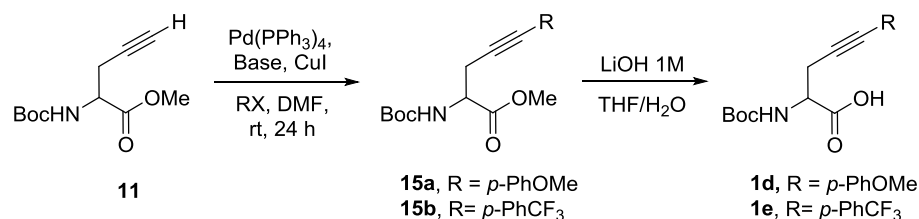
**Scheme S2.** Synthetic sequence for preparation of **1b**.

**1.1.1. Diethyl 2-*tert*-butoxycarbonylamino**malonate (**13**).<sup>3</sup> To a suspension of diethyl aminomalonate (1.25 g, 5.92 mmol) and Et<sub>3</sub>N (4 mL, 29.5 mmol) in THF (10 mL) was added a solution of (Boc)<sub>2</sub>O (1.93 g, 8.86 mmol) in THF (5 mL), and the solution was stirred overnight at room temperature. After evaporation of the solvent, the residue was taken up in AcOEt and the organic phase was washed with water and brine and dried over Na<sub>2</sub>SO<sub>4</sub>. filtered and concentrated under reduced pressure. The product was purified by chromatography obtaining 1.13 g (4.2 mmol, 70 %) of **13** as a colorless oil. R<sub>f</sub> = 0.64 (hexanes:ethyl acetate = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.30 (t, *J* = 7.0 Hz, 6H), 1.45 (s, 9H), 4.27 (m, 4H), 4.94 (d, *J* = 7.6 Hz, 1H), 5.56 (d, *J* = 6.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 14.0, 28.2, 57.5, 62.4, 80.6, 154.8, 166.7.

**1.1.2. Diethyl 2-(but-2-yn-1-yl)-2-((*tert*-butoxycarbonyl)amino)malonate (**14**).** 1-bromobut-2-yne (0.2 mL, 2.66 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.6 g, 1.77 mmol) were added to a solution of diethyl 2-*tert*-butoxycarbonylaminomalonate (**13**) (0.5 g, 1.77 mmol) in CH<sub>3</sub>CN (10 mL). The resulting heterogeneous mixture was stirred at room temp. for 24 h. Then, the reaction mixture was filtered, concentrated, and the residue was dissolved in AcOEt. The organic solution was washed with water, brine and dried with Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave the crude product as a yellowish white solid, which was purified by column chromatography (AcOEt/hexane) to give 0.58 g of **14** as a colorless oil (1.76 mmol, 99.4 %). R<sub>f</sub> = 0.46 (hexanes:ethyl acetate = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.26 (t, *J* = 7.1 Hz, 6H), 1.44 (s, 9H), 1.75 (s, 3H), 3.16 (s, 2H), 4.26 (m, 4H), 6.07 (s, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 3.5, 13.9, 24.7, 28.2, 62.6, 65.8, 72.9, 78.7, 80.4, 153.9, 167.2 ppm. HRMS (ESI): 350.1574 (calc. for C<sub>16</sub>H<sub>25</sub>NNaO<sub>6</sub>: 350.1574).

**1.1.3. 2-((*tert*-butoxycarbonyl)amino)hex-4-ynoic acid (**1b**).**<sup>4</sup> KOH (0.6 g, 4.5 mmol) was added portion wise to a well-stirred suspension of **14** (0.6 g, 1.8 mmol) in MeOH/H<sub>2</sub>O (5:1) (60 mL). The mixture was heated at reflux for 4 h. The solvents were evaporated to dryness, and the residue was dissolved with AcOEt and treated with 1 M HCl to pH = 1. The aqueous phase was extracted with AcOEt, the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvents evaporated to obtain the crude compound which was purified by chromatography obtaining 0.27 g (1.18 mmol, 65 % yield) of the desired *N*-Boc-protected alkynyl amino acid **1b** as a white solid. R<sub>f</sub> = 0.43 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.47 (s, 9H), 1.80 (s, 3H), 2.64 – 2.80 (m, 2H), 4.46 (t, *J* = 4.0 Hz, 1H), 5.31 (s, 1H), 10.75 (s, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 3.57, 22.7, 28.3, 52.0, 72.7, 79.6, 80.5, 155.5, 175.9 ppm.

## 1.2. Synthesis of *p*-trifluoromethylphenyl derivat **1d** and *p*-methoxyphenyl derivat **1e**.



**Scheme S3.** Synthetic sequence for preparation of **1d** and **1e**.

**1.2.1. Methyl 2-((*tert*-butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoate (**15a**).** To a solution of *N*-protected methyl propargyl glycinate **11** (0.036 g, 0.16 mmol) in dimethylformamide (DMF) (2 mL), 1-iodo-4-methoxybenzene (0.066 g, 0.28 mmol), triethylamine (0.045 mL, 0.32 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.023 g, 0.02 mmol) were added. The light brown solution quickly turned dark upon addition of copper(I) iodide (0.011 g, 0.06 mmol). The reaction mixture was stirred at room temperature under a nitrogen atmosphere overnight. The solvent was evaporated and the reaction crude was purified by column chromatography obtaining 0.045 g (0.13 mmol, 85 % yield) of **15a** as a yellow solid. R<sub>f</sub> = 0.56 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.45 (s, 9H), 2.86-2.99 (m, 2H), 3.792 (s, 3H), 3.798 (s, 3H), 4.54 (q, *J* = 4.4 Hz, 1H), 5.39 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 23.9, 28.3, 52.3, 52.6, 55.2, 80.1, 82.2, 83.4, 113.8, 115.0, 133.1, 135.2, 155.1, 159.4, 171.4 ppm. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>23</sub>NNaO<sub>5</sub> [M + Na]<sup>+</sup> 356.1460, found 356.1468.

**1.2.2. 2-((*tert*-Butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoic acid (1d).** The methyl ester derivative **15a** (0.064 g, 0.19 mmol) was dissolved in THF/H<sub>2</sub>O (6 mL, 2:1) and cooled to 0 °C. Then, a 1 M solution of LiOH (0.35 mL, 0.35 mmol) was added. The mixture was stirred at room temperature, and the reaction was monitored by TLC. After complete conversion, the reaction mixture was poured into a beaker with ice, and a solution of HCl (1 M) was added until the pH was acidic. The aqueous solution was extracted with EtOAc, and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and obtaining 0.061 g (0.19 mmol, 99.5 % yield) of the desired *N*-Boc-protected alkynyl amino acid **1d** as a yellow solid. The product was used in the next step without further purification.

**1.2.3. Methyl 2-((*tert*-butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate (15b).** To a solution of *N*-protected methyl propargyl glycinate **11** (0.098g, 0.43 mmol) in dimethylformamide (DMF) (5 mL), were added 1-bromo-4-(trifluoromethyl)benzene (0.150 g, 0.65 mmol), diisopropylamine (0.10 mL, 0.64 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.054 g, 0.047 mmol). The light brown solution quickly turned dark upon addition of copper(I) iodide (0.022 g, 0.12 mmol). The reaction mixture was stirred at room temperature under a nitrogen atmosphere overnight. The solvent was evaporated and the reaction crude was purified by column chromatography obtaining 0.1 g (0.26 mmol, 64 % yield) of **15b** as a yellow solid. R<sub>f</sub> = 0.50 (hexanes:ethyl acetate = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.46 (s, 9H), 2.97 (d, *J* = 4.8 Hz, 2H), 4.58 (m, *J* = 4.5 Hz, 1H), 5.38 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 24.0, 28.3, 52.1, 52.7, 80.3, 82.3, 86.7, 122.5, 126.8, 129.7, 130.0, 131.9, 155.0, 171.2 ppm. HRMS (ESI): 394.1252 (calc. for C<sub>18</sub>H<sub>20</sub>F<sub>3</sub>NNaO<sub>4</sub>: 394.1237).

**1.2.4. 2-((*tert*-Butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoic acid (1e).** The methyl ester derivative **15b** (0.11 g, 0.29 mmol) was dissolved in THF/H<sub>2</sub>O (6 mL, 2:1) and cooled to 0 °C. Then, a 1 M solution of LiOH (0.44 mL, 0.44 mmol) was added. The mixture was stirred at room temperature, and the reaction was monitored by TLC. After complete conversion, the reaction mixture was poured into a beaker with ice, and a solution of HCl (1 M) was added until the pH was acidic. The aqueous solution was extracted with EtOAc, and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo obtaining 0.10 g (0.29 mmol, 99 % yield) of the desired carboxylic acid **1e** as a yellow solid. The product was used in the next step without further purification.

**1.3. Time-course of the conversion of 1a into 2a monitored by GC-FID.** To determine the concentration of the enol-lactone **2a** in each vial, the mass of the standard (MSV) in each vial is calculated as follows:

$$M_{SV} = \left( \frac{\text{Initial standard mass}}{\text{Toluene volume} \times 1000} \right) \times V_{\text{Injected aliquot}}$$

As 1  $\mu\text{L}$  is injected into the equipment, the mass of the standard injected (MS) is equal to MSV/1000. The mass of the product present in each vial is determined using the following equation:

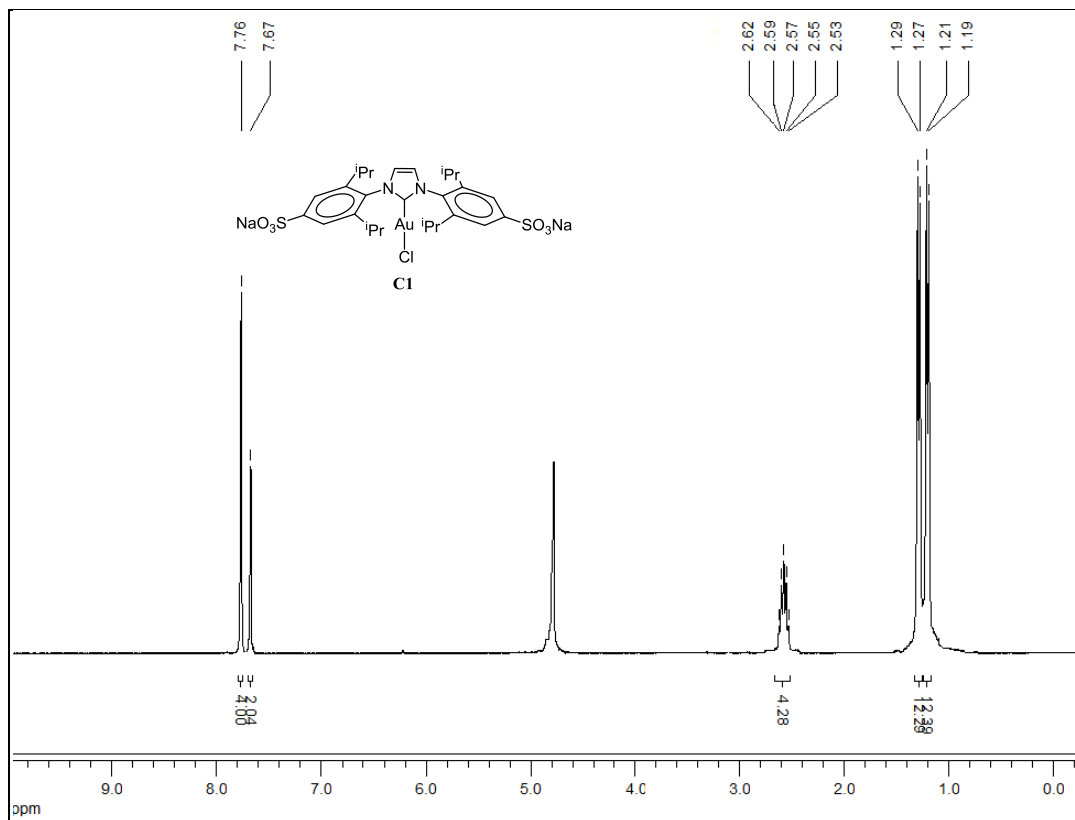
$$M_P = M_S \cdot \left( \frac{\text{Product area}}{\text{Standard area}} \right) \cdot \left( \frac{\text{Product molecular weight}}{\text{Standard molecular weight}} \right)$$



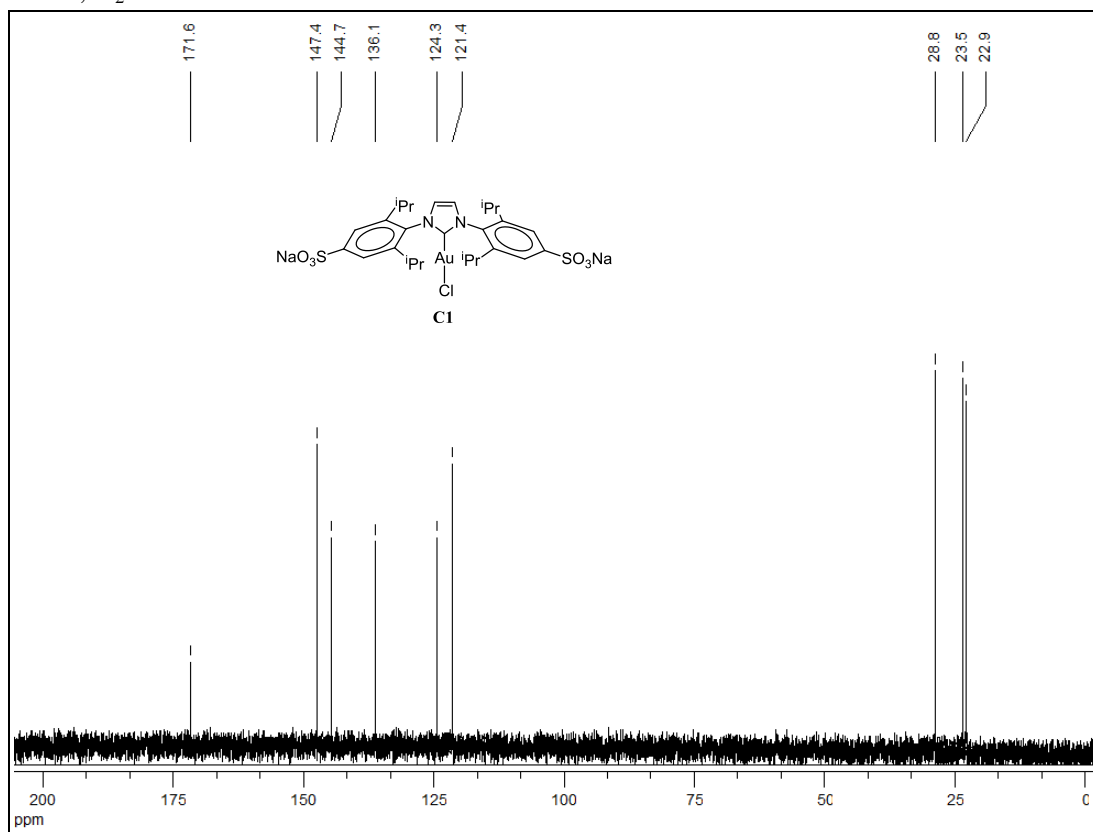
## 2. COPIES OF $^1\text{H}$ AND $^{13}\text{C}$ NMR SPECTRA

### 2.1. 1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene gold(I) Chloro (C1).

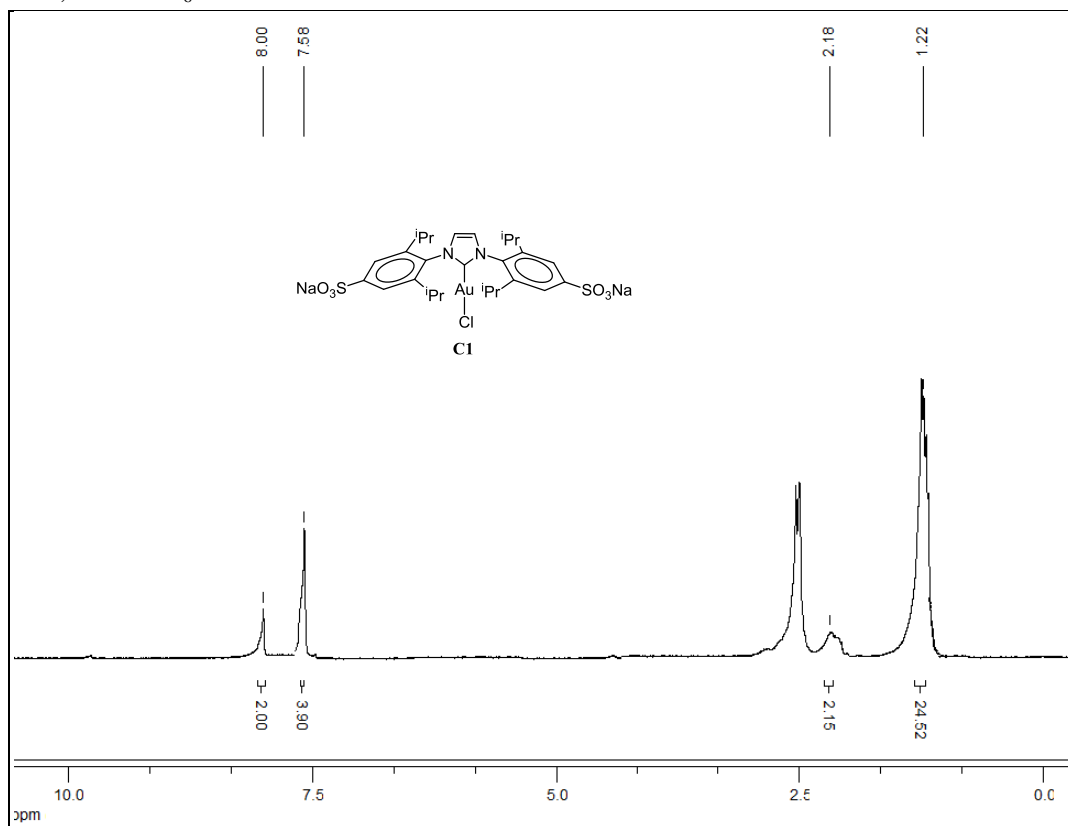
$^1\text{H}$  NMR,  $\text{D}_2\text{O}$



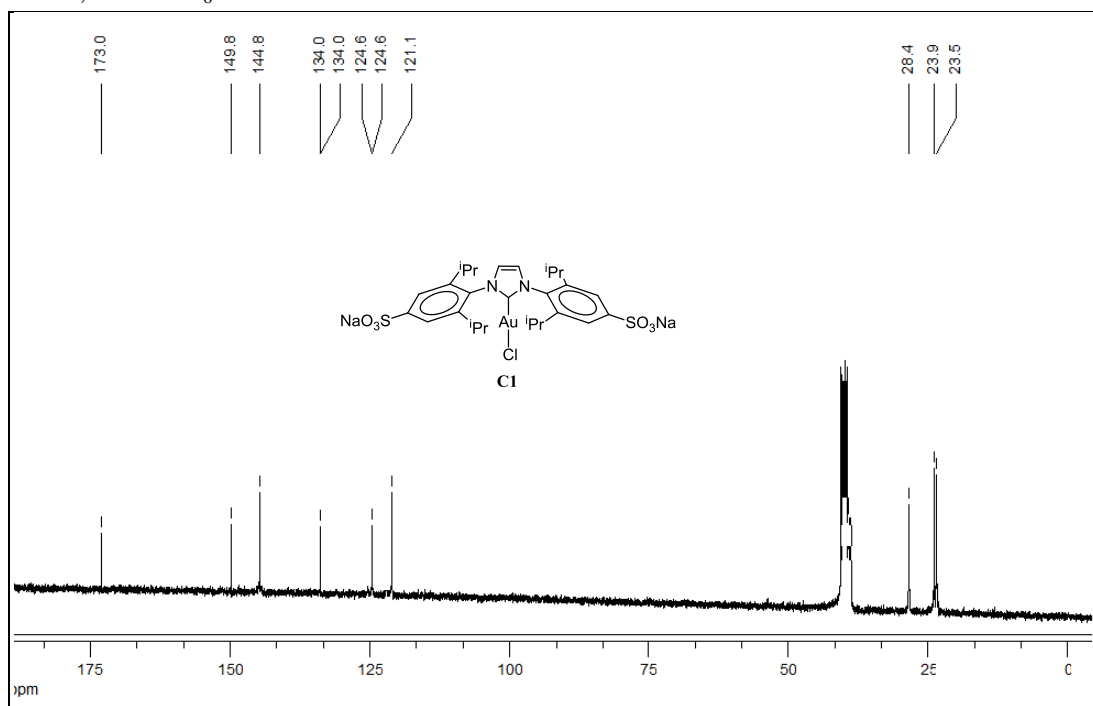
$^{13}\text{C}$  NMR,  $\text{D}_2\text{O}$



$^1\text{H}$  NMR,  $\text{DMSO-d}_6$

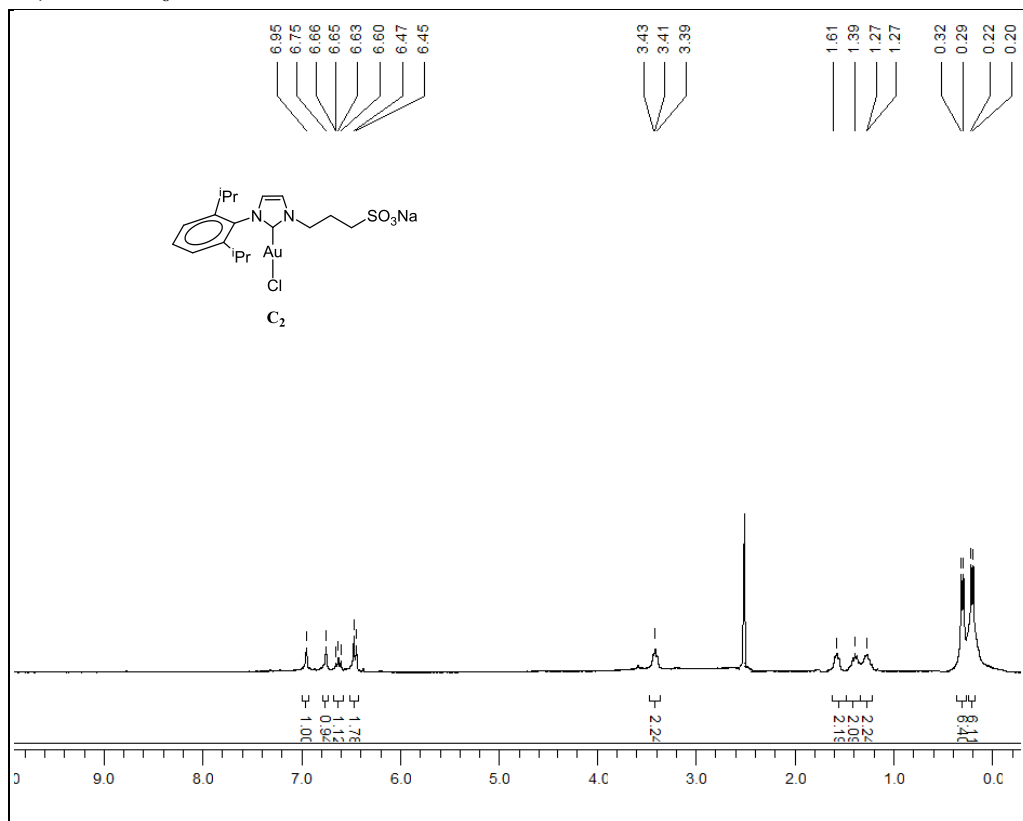


$^{13}\text{C}$  NMR, DMSO- $d_6$

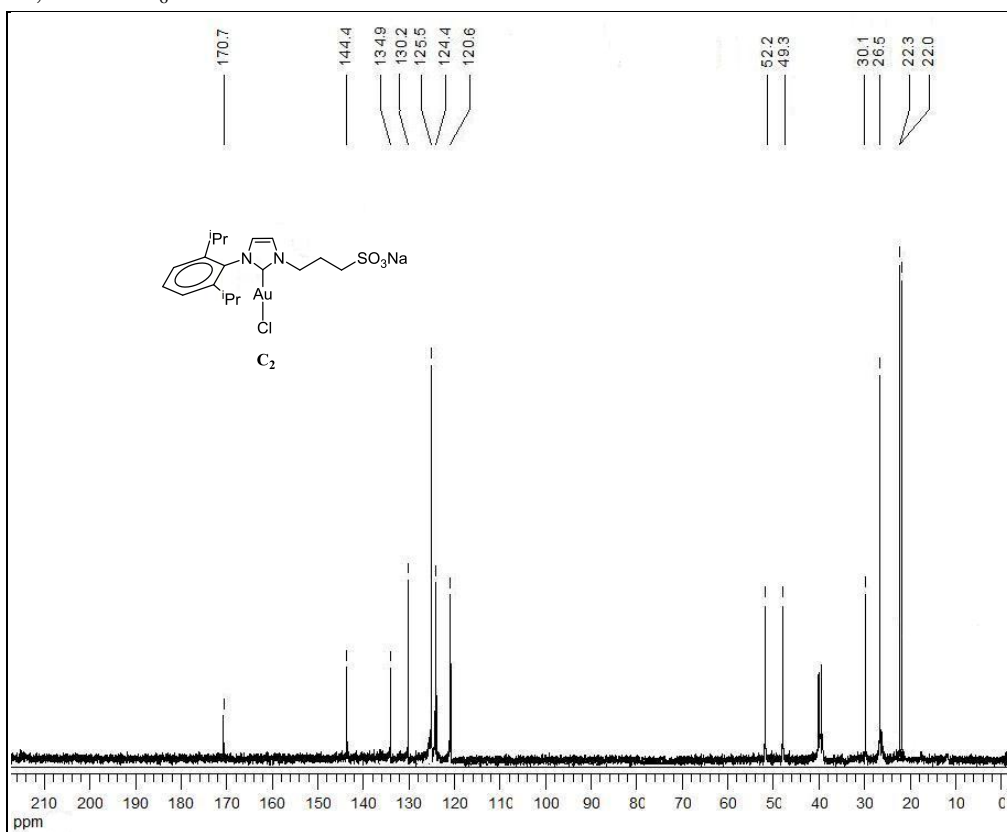


**2.2. 1-(2,6-Diisopropylphenyl)-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C2).**

$^1\text{H}$  RMN, DMSO- $d_6$

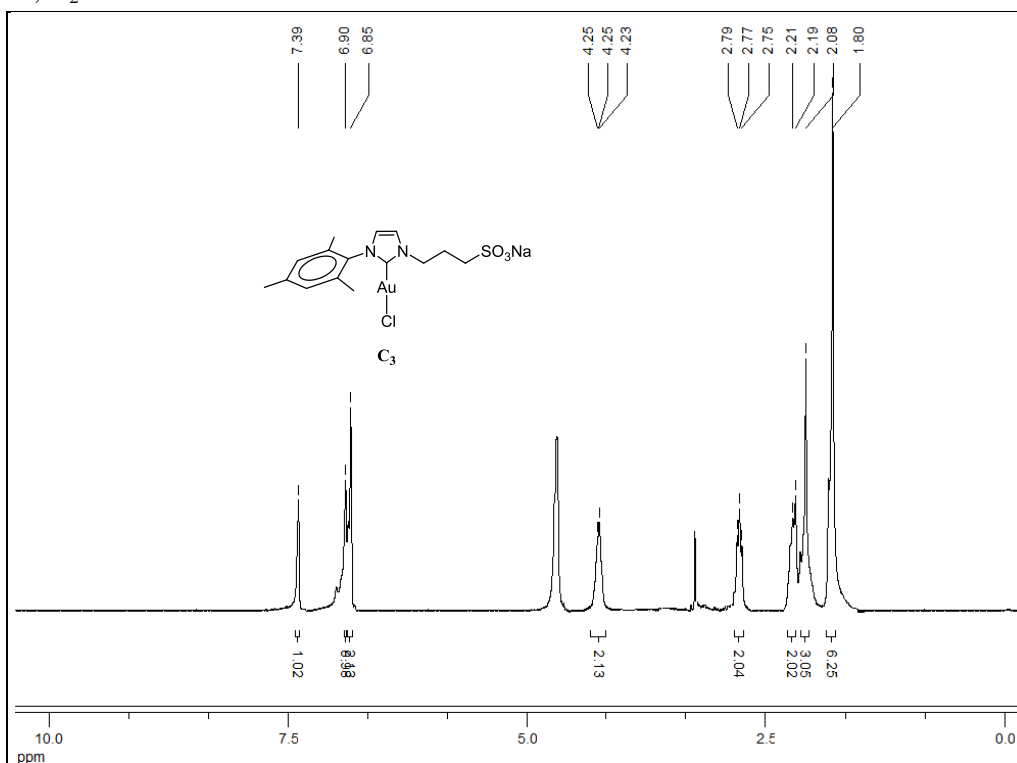


$^{13}\text{C}$  RMN, DMSO- $d_6$

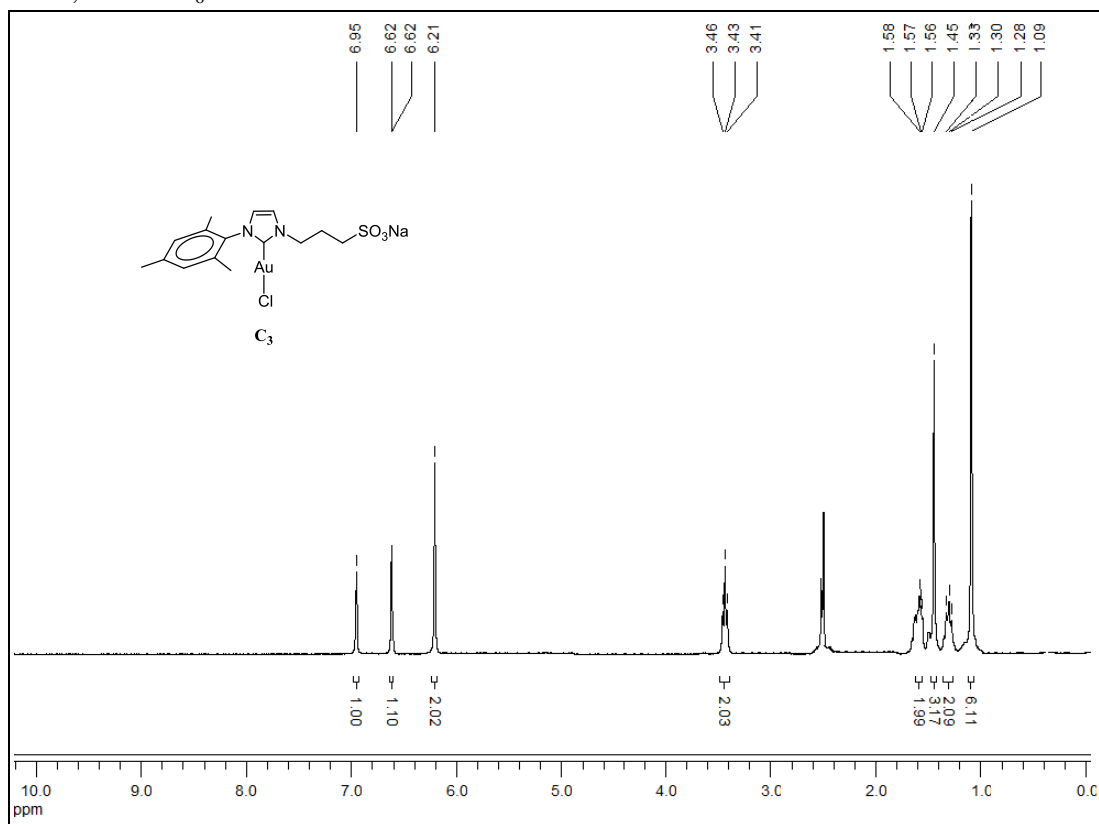


**2.3. 1-Mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C<sub>3</sub>).**

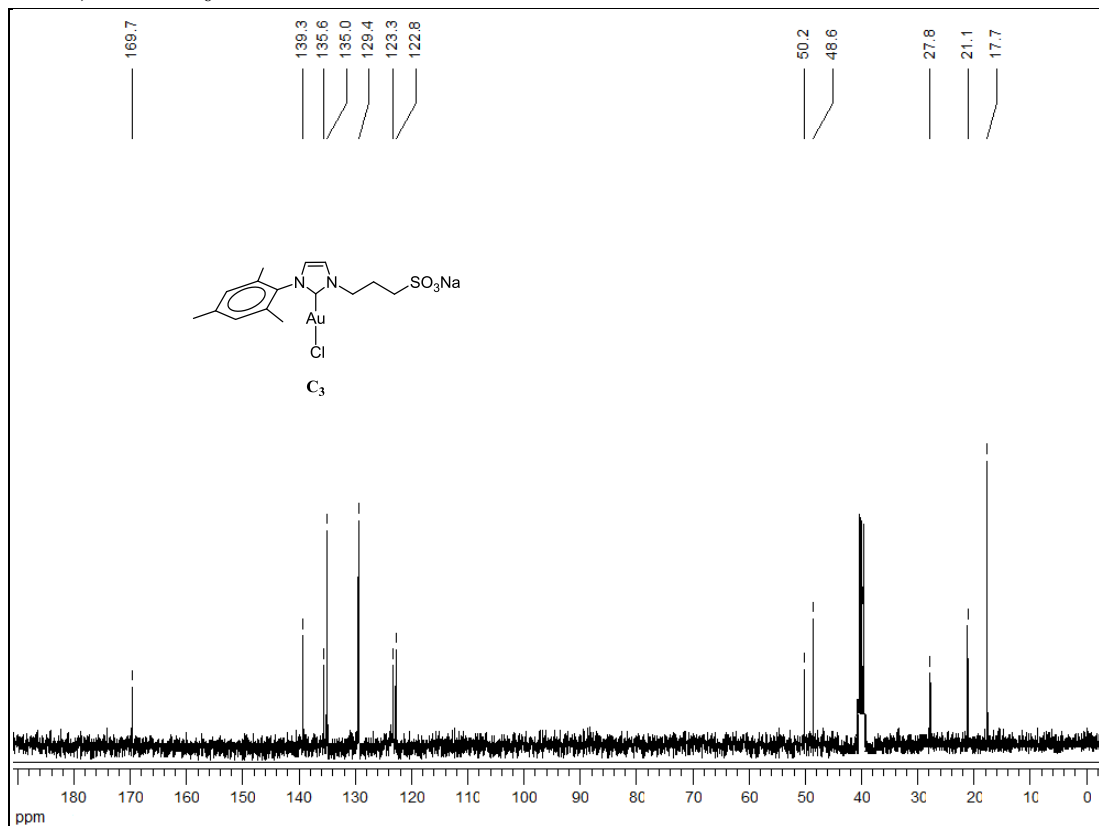
$^1\text{H}$  RMN,  $\text{D}_2\text{O}$



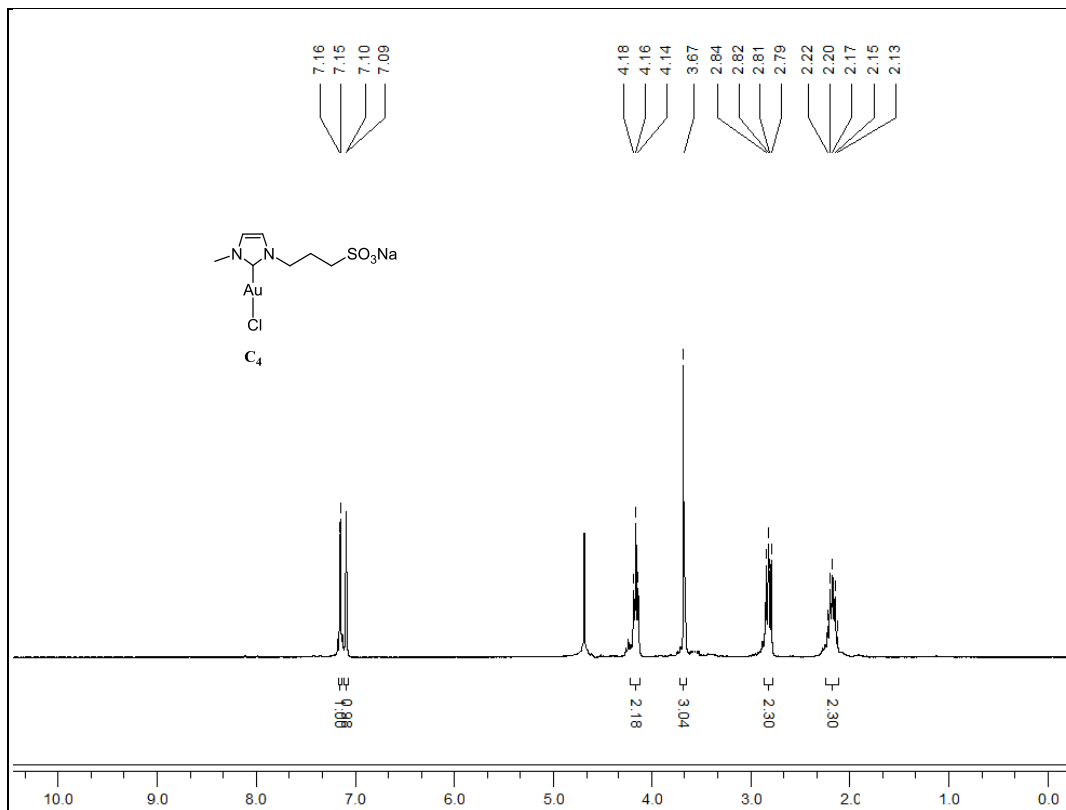
<sup>1</sup>H RMN, DMSO-d<sub>6</sub>



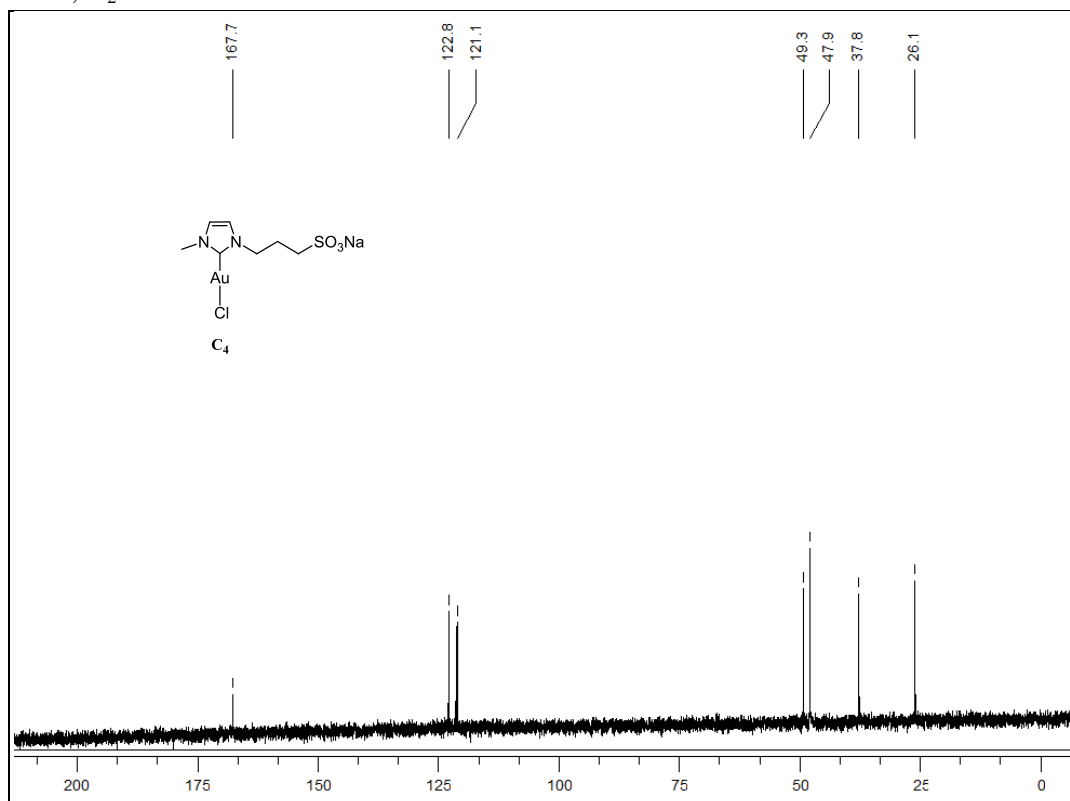
<sup>13</sup>C RMN, DMSO-d<sub>6</sub>



2.4. 1-Methyl-3-(3-sulfonatopropyl)imidazol-2-ylidene gold(I) Chloro (C4).  
<sup>1</sup>H RMN, D<sub>2</sub>O

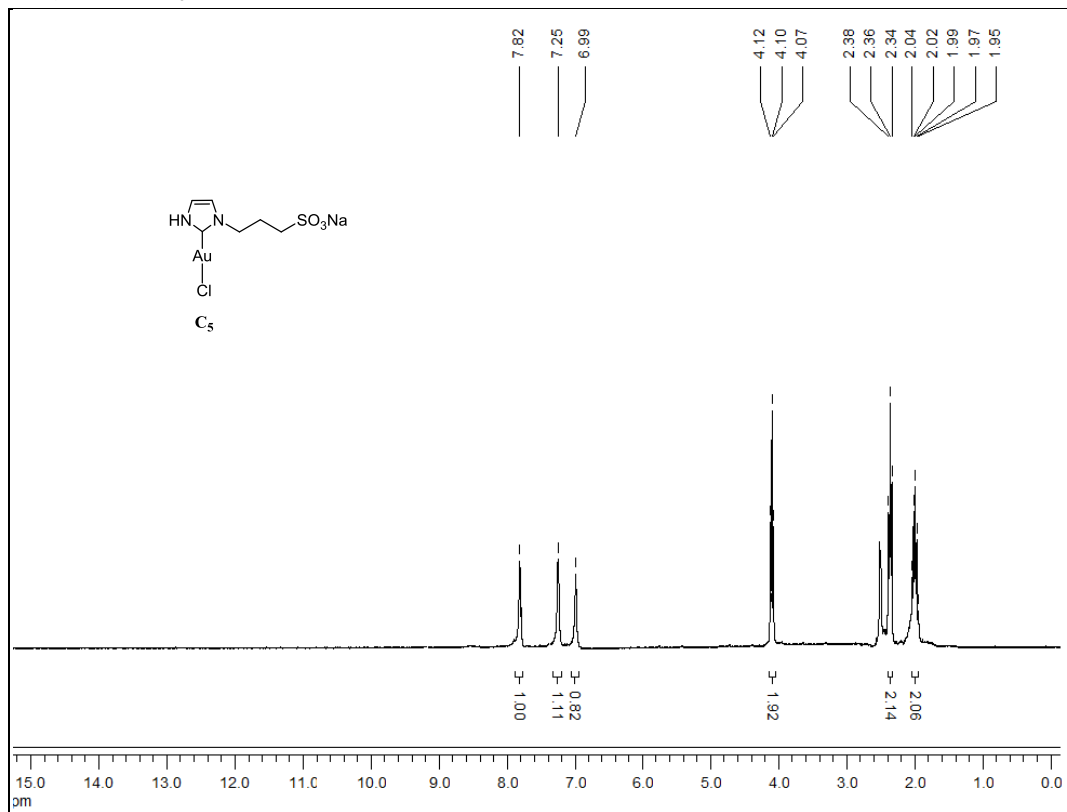


<sup>13</sup>C RMN, D<sub>2</sub>O

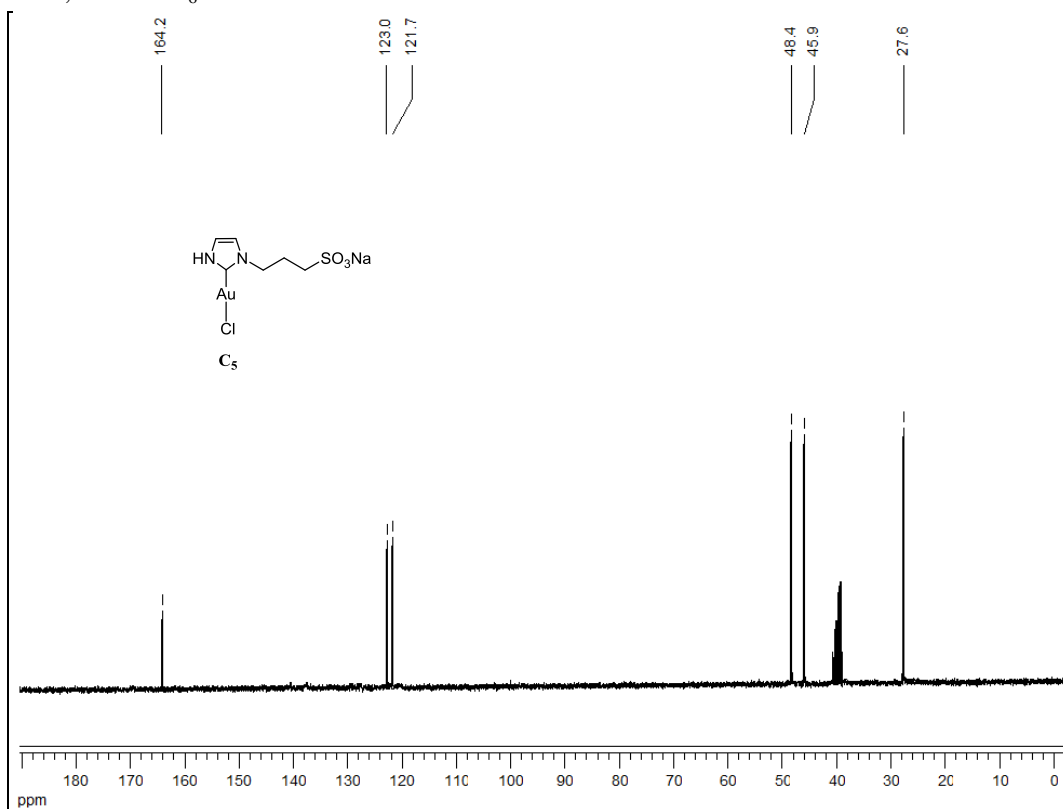


## 2.5. (3-sulfonatepropyl)imidazol-2-ylidene gold(I) Chloro (C5).

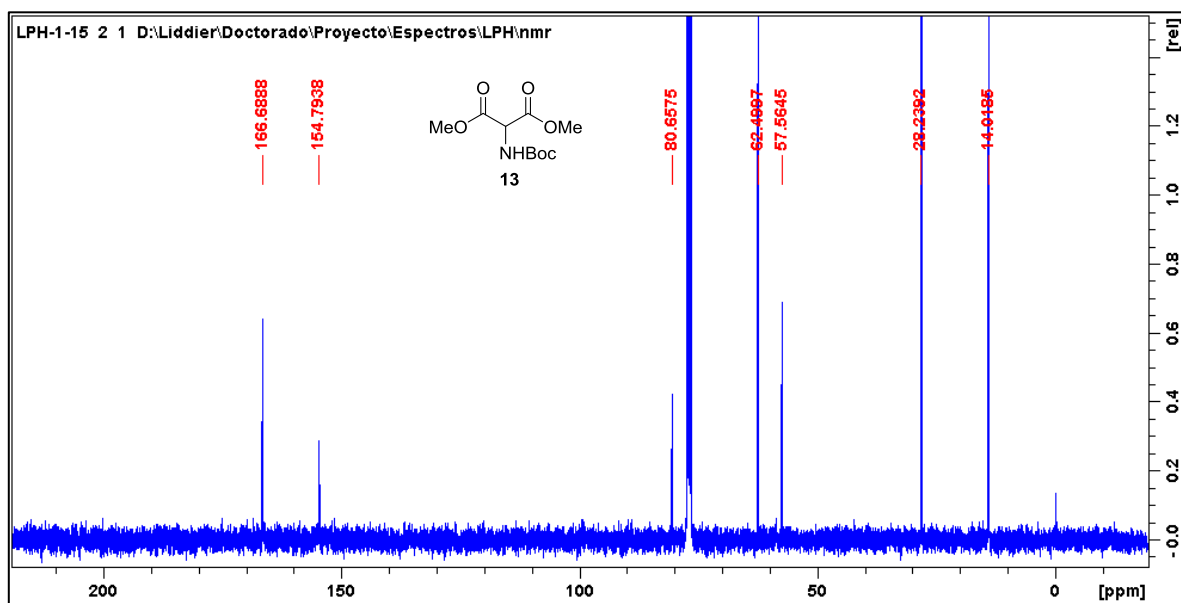
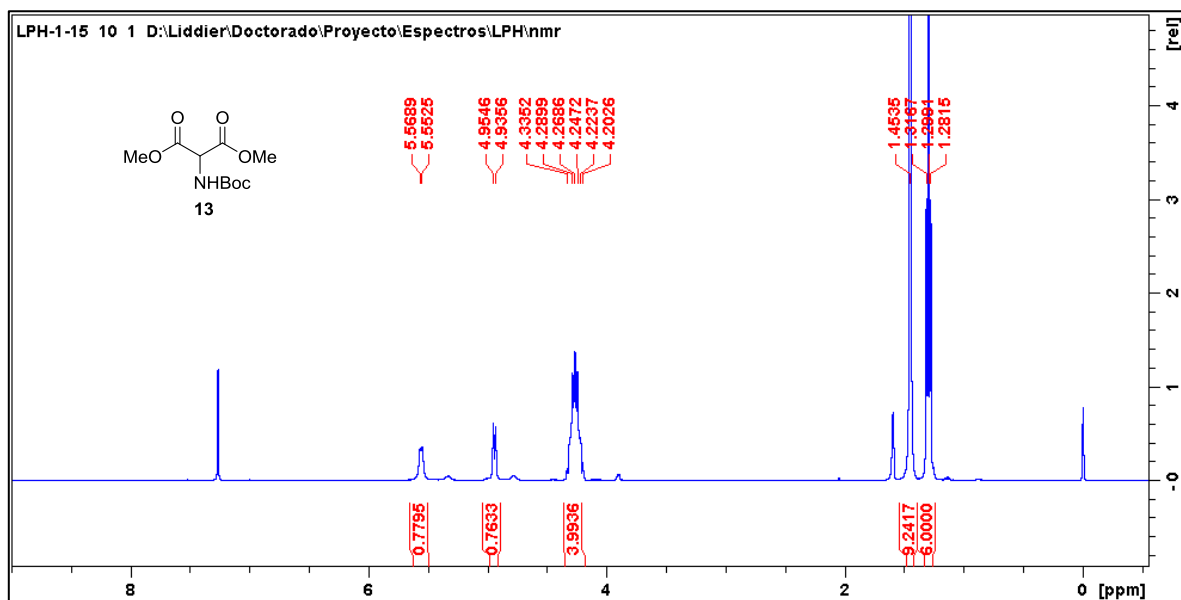
<sup>1</sup>H NMR, DMSO-d<sub>6</sub>



<sup>13</sup>C NMR, DMSO-d<sub>6</sub>

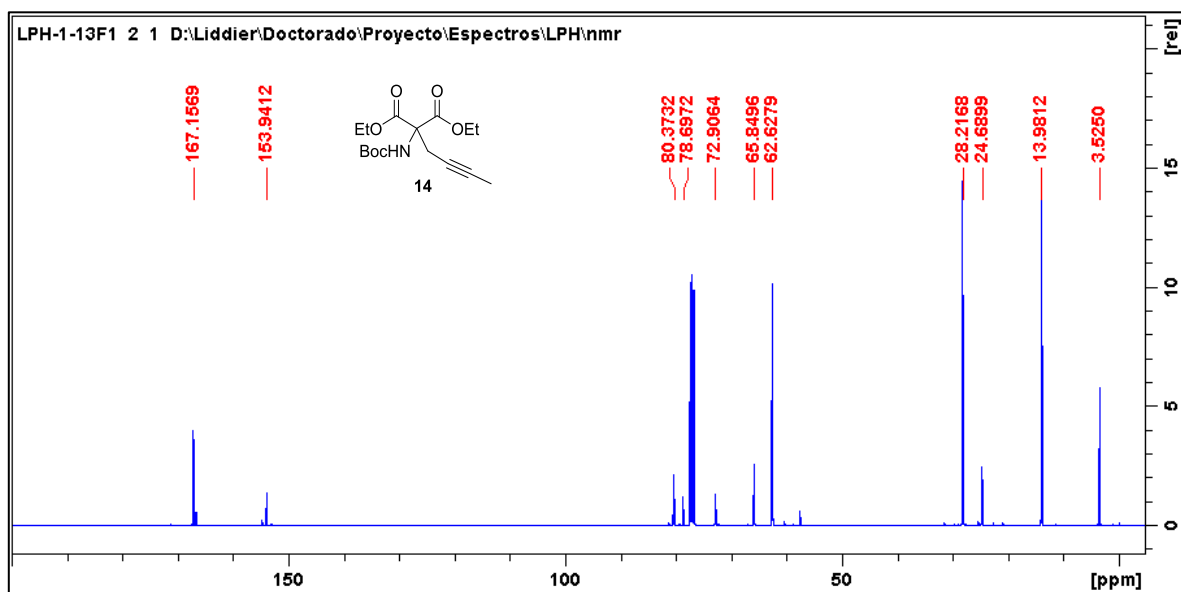
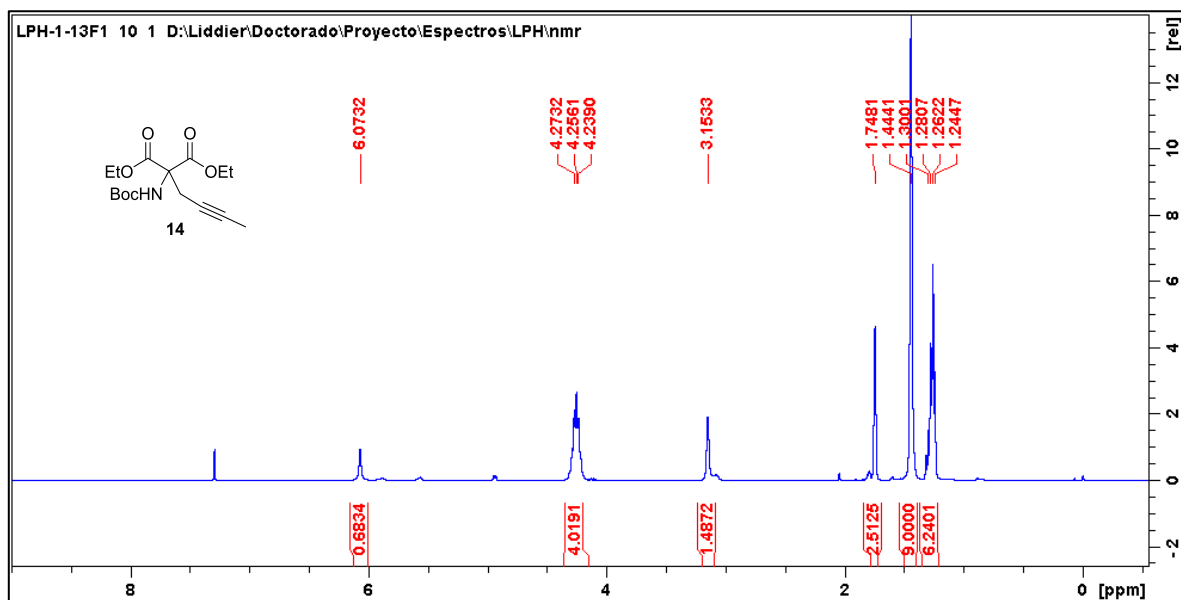


## 2.6. Diethyl 2-tert-Butoxycarbonylamino malonate (13).

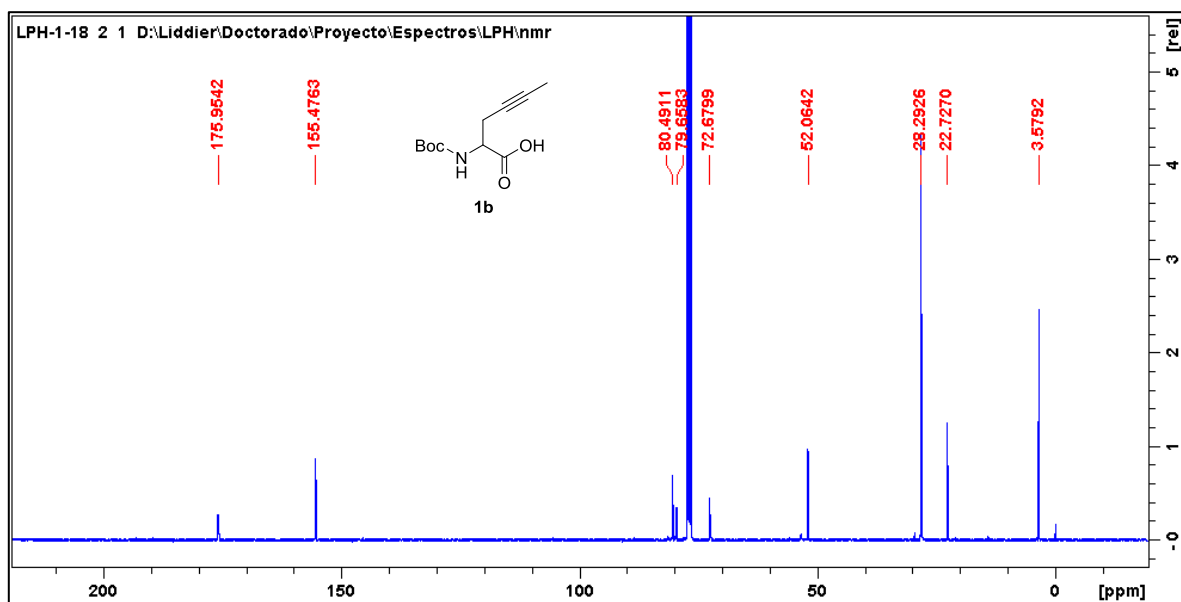
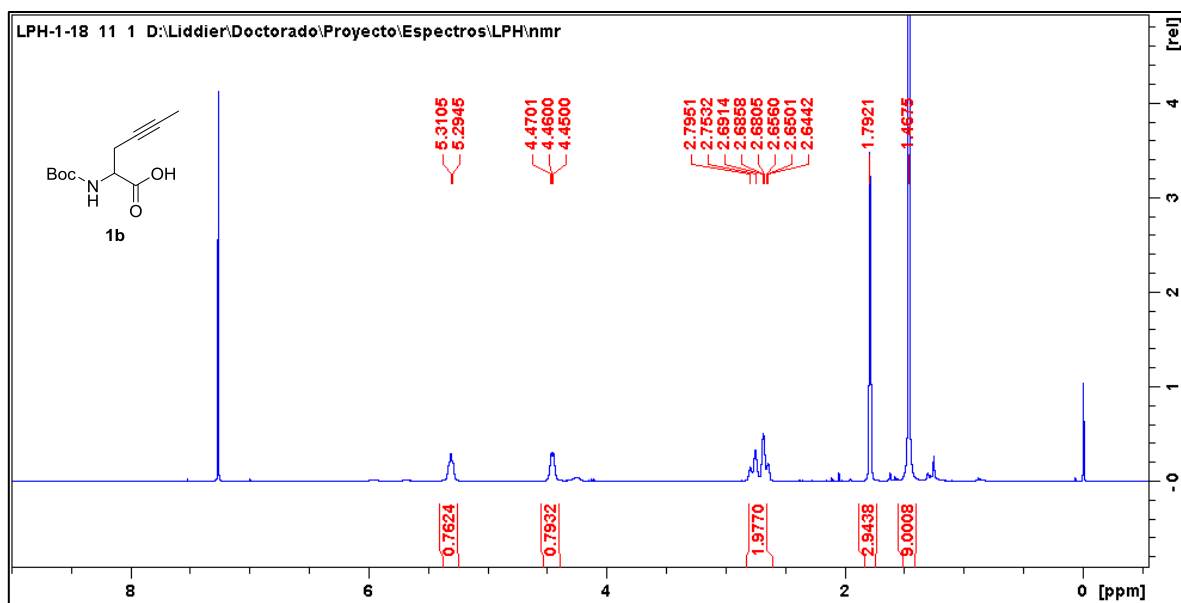




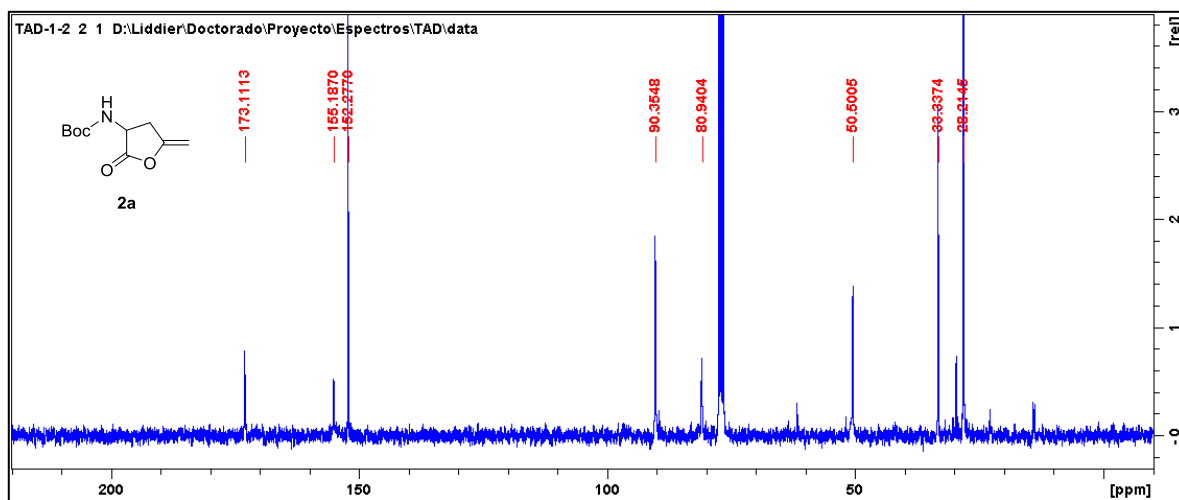
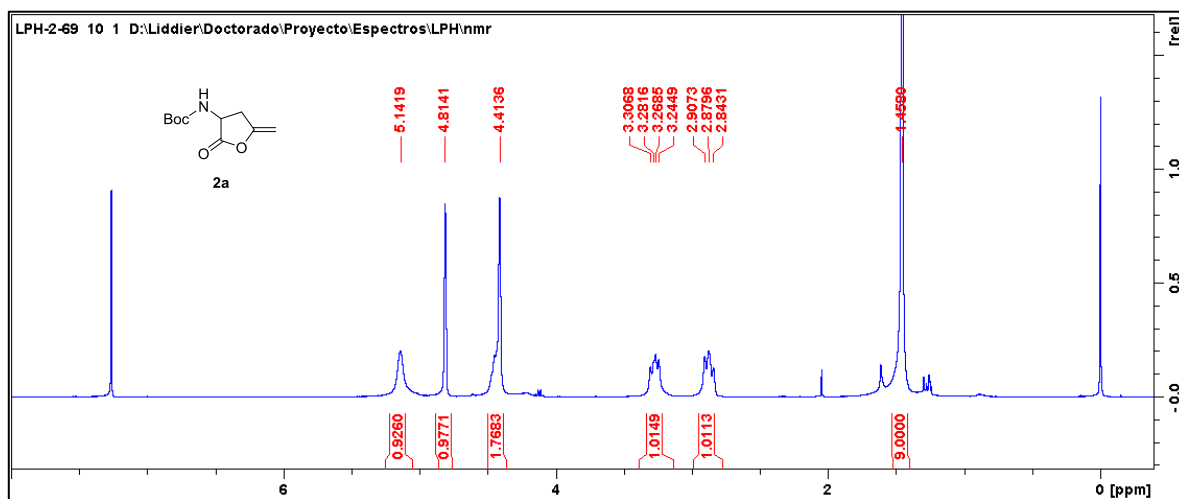
2.7. Diethyl 2-(but-2-yn-1-yl)-2-((tert-butoxycarbonyl)amino)malonate (14).



2.8. 2-((*tert*-butoxycarbonyl)amino)hex-4-ynoic acid (**1b**).

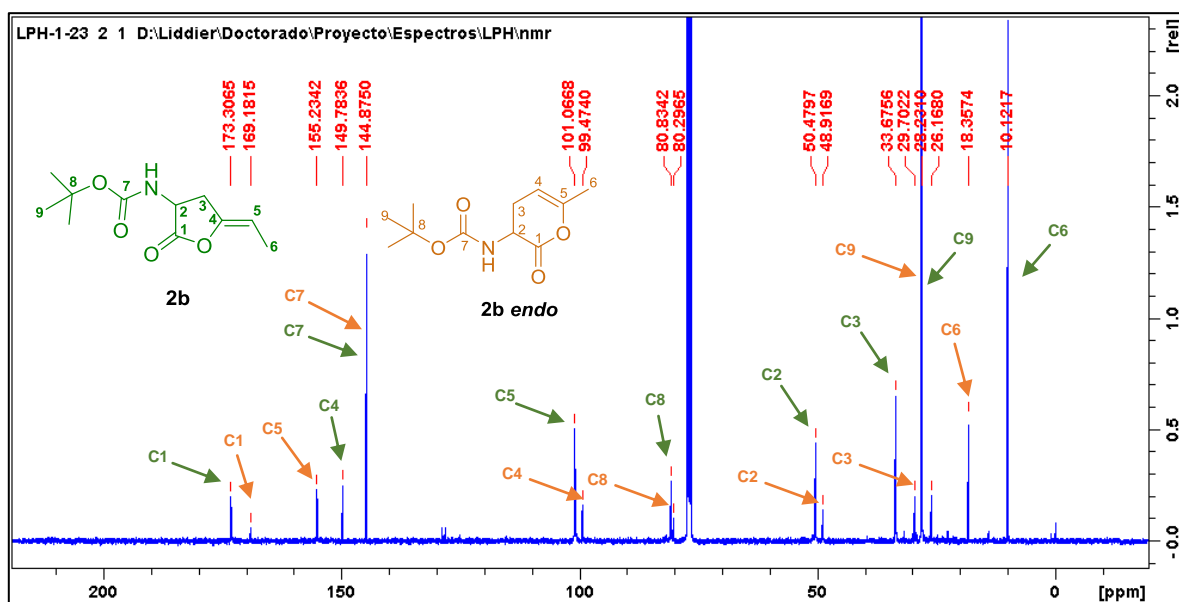
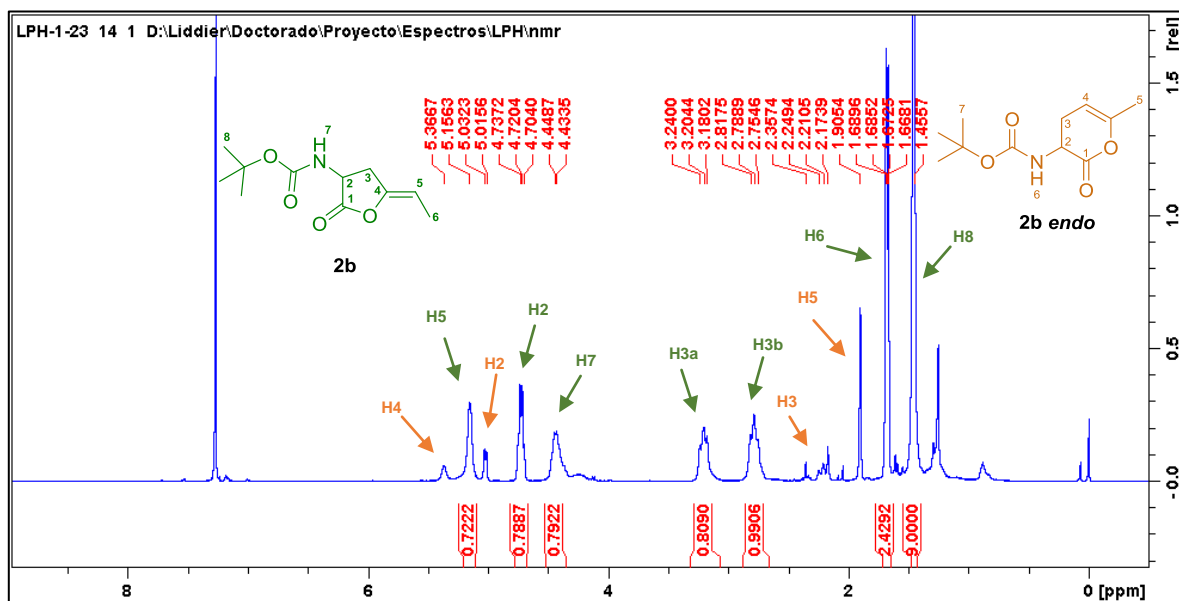


**2.9. *tert*-Butyl (5-methylene-2-oxotetrahydrofuran-3-yl)carbamate (2a).**<sup>2</sup> R<sub>f</sub> = 0.33 (hexanes:ethyl acetate = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.45 (s, 9H) 2.87 (t, *J* = 12.8 Hz, 1H), 3.27 (q, *J* = 8.25 Hz, 1H), 4.41 (br. s, 2H) 4.81 (br. s, 1H) 5.14 (s, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 28.2, 33.3, 50.5, 80.9, 90.3, 152.3, 155.2, 173.1 ppm. HRMS (ESI): 236.08967 (calc. for C<sub>11</sub>H<sub>17</sub>NO<sub>4</sub>Na: 236.08933).

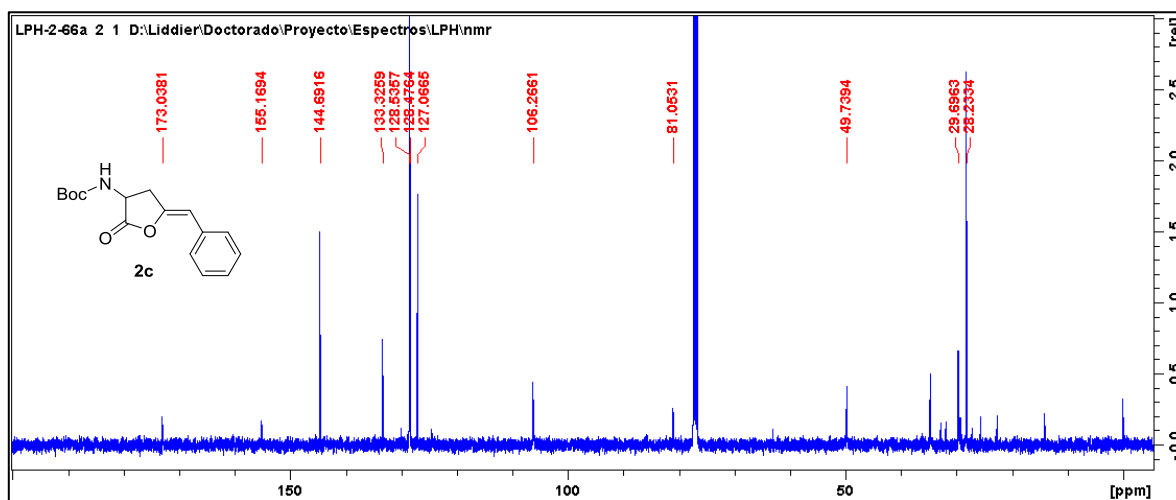
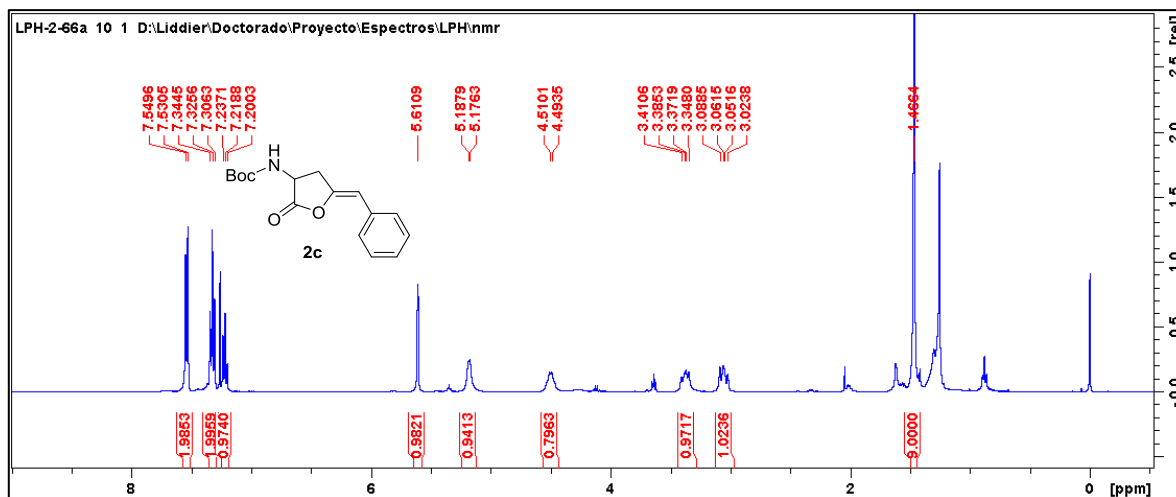


**2.10. *tert*-Butyl (*Z*)-(5-ethylidene-2-oxotetrahydrofuran-3-yl)carbamate (**2b**).<sup>4</sup> **2b** and **2b** *endo* form a non-separable mixture; R<sub>f</sub> = 0.53 (hexanes:ethyl acetate = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.45 (s, 9H) 1.67 (dd, *J* = 2.8 Hz, 3H) 2.78 (t, *J* = 12.5 Hz, 1H) 3.21 (t, *J* = 11.9 Hz, 1H) 4.72 (d, *J* = 6.7 Hz, 1H) 5.21 (s, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 10.1, 28.2, 33.6, 50.5, 80.8, 101.0, 144.8, 149.7, 173.3 ppm. HRMS (ESI): 250.1040 (calc. for C<sub>11</sub>H<sub>17</sub>NNaO<sub>4</sub>: 250.1050).**

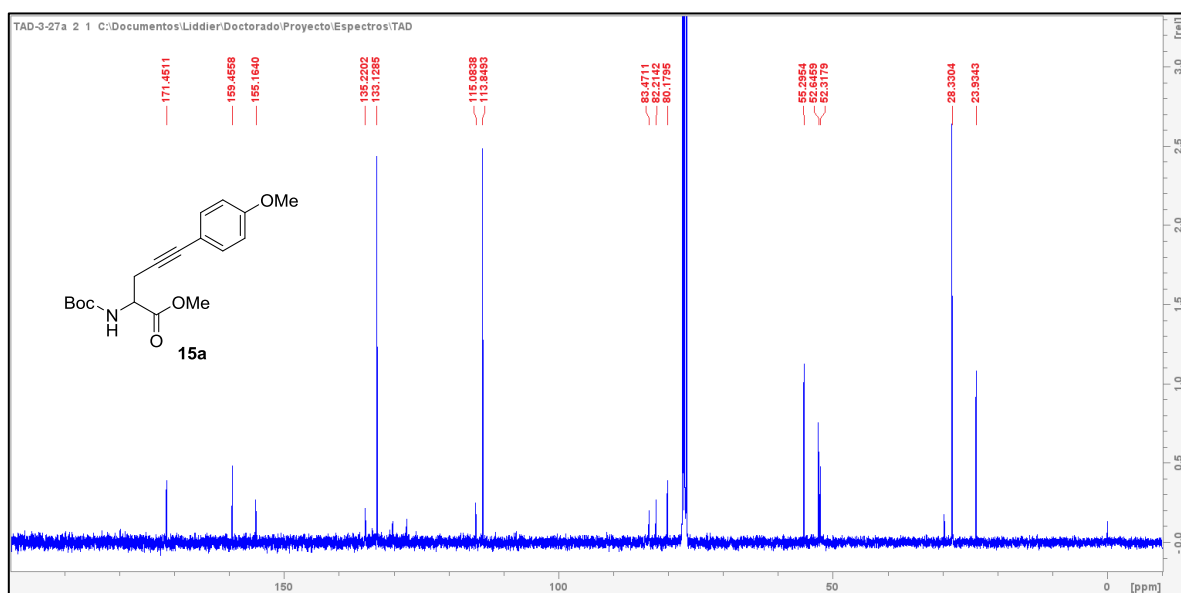
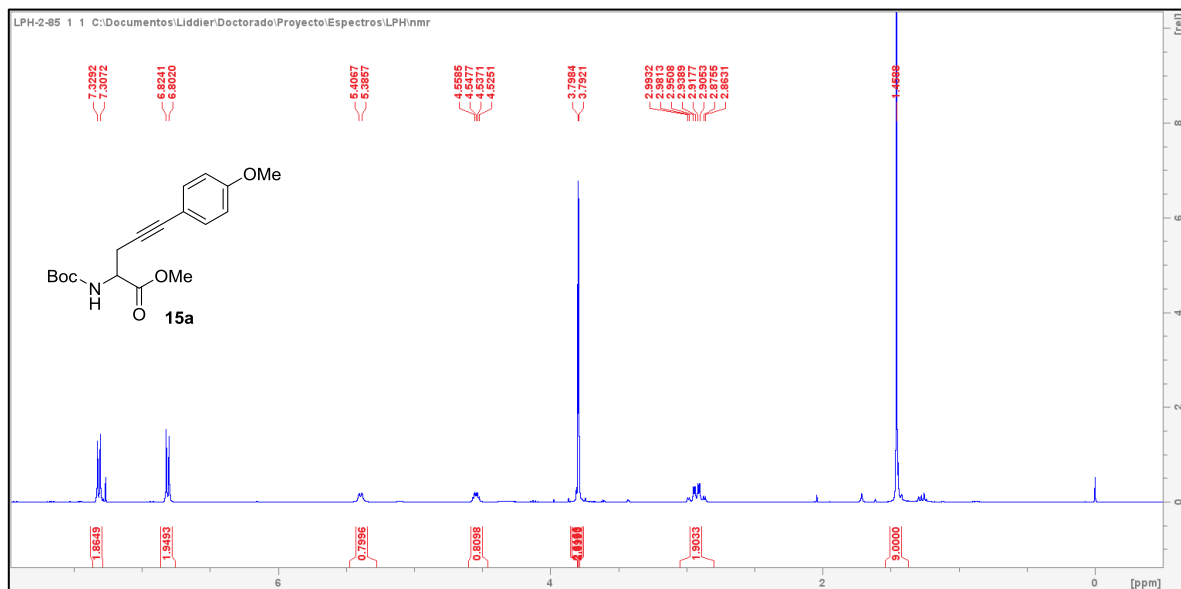
**2.11. *tert*-Butyl (6-methyl-2-oxo-3,4-dihydro-2H-pyran-3-yl)carbamate (**2b** *endo*). **2b** and **2b** *endo* form a non-separable mixture; R<sub>f</sub> = 0.51 (hexanes:ethyl acetate = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.45 (s, 9H) 1.90 (s, 3H) 2.26 (q, *J* = 24.4 Hz, 1H), 5.02 (d, *J* = 6.7 Hz, 1H), 5.36 (s, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 18.3, 28.2, 29.7, 48.9, 80.3, 99.5, 144.8, 149.7, 155.2, 169.2 ppm. HRMS (ESI): 250.1040 (calc. for C<sub>11</sub>H<sub>17</sub>NNaO<sub>4</sub>: 250.1050).**



**2.12. *tert*-Butyl (Z)-(5-benzylidene-2-oxotetrahydrofuran-3-yl)carbamate (2c).**<sup>2</sup> R<sub>f</sub> = 0.46 (hexanes:ethyl acetate = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.46 (s, 9H), 3.05 (t, *J* = 12.7 Hz, 1H), 3.38 (q, *J* = 8.38 Hz, 1H), 4.50 (d, *J* = 6.8 Hz, 1H), 5.20 (s, 1H), 5.61 (s, 1H), 7.20 – 7.54 (m, 5 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 1.5, 28.6, 33.9, 49.9, 80.2, 105, 127.4, 129.2, 129.3, 135.5, 147.6, 156.2, 174.0 ppm. HRMS (ESI): [M+Na]<sup>+</sup> 312.12063 (calc. for C<sub>16</sub>H<sub>17</sub>NNaO<sub>4</sub>, 312.12065).

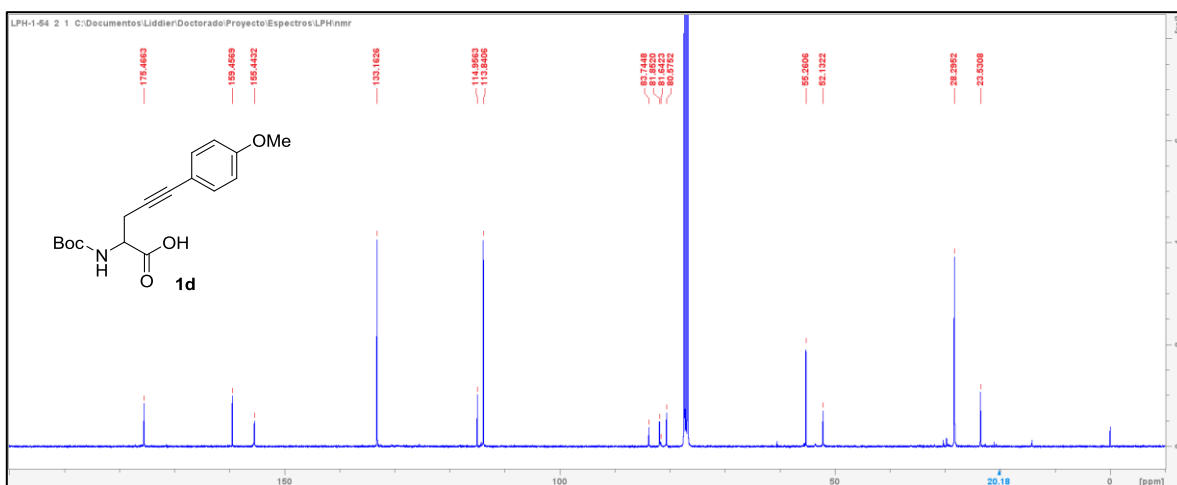
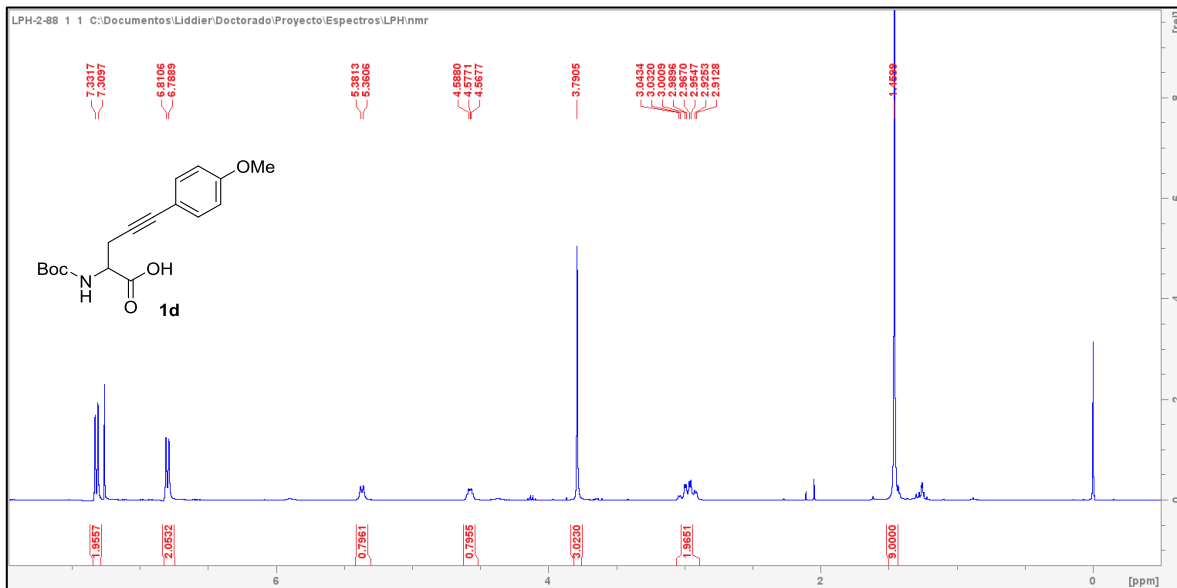


## 2.13. Methyl 2-((*tert*-butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoate (15a).



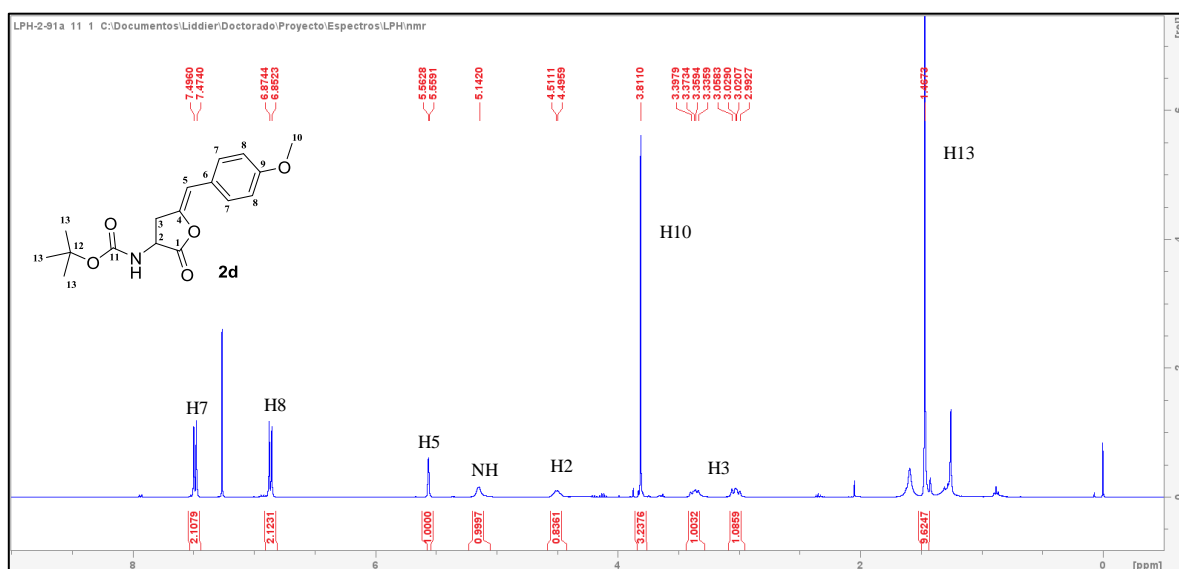
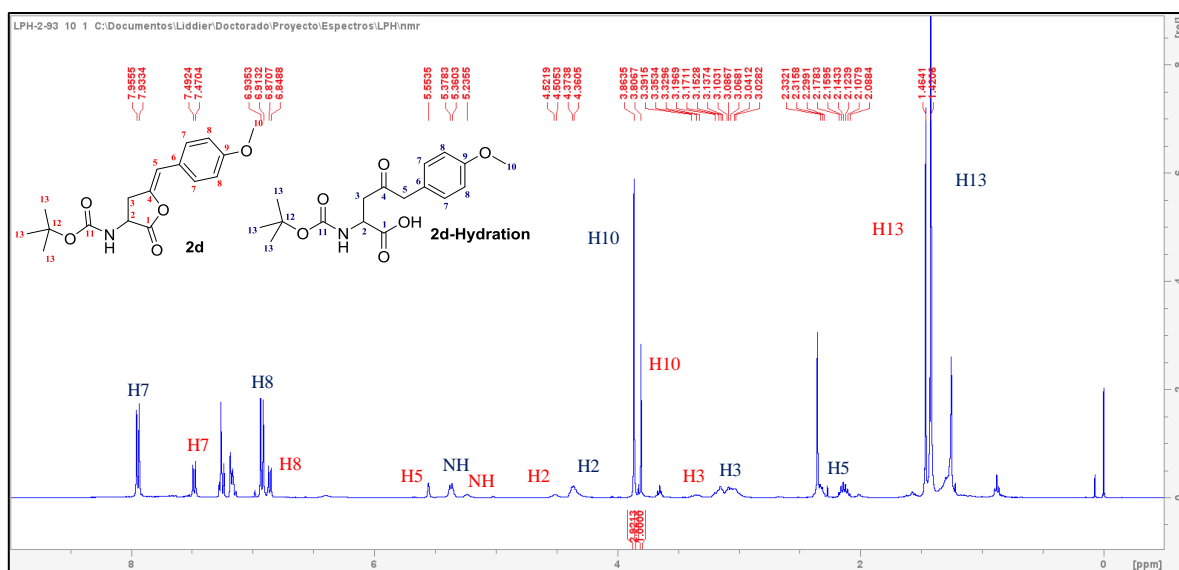
**2.14. 2-((*tert*-Butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-ynoic acid (1d).**

Rf = 0.14 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.45 (s, 9H), 2.91-3.04 (m, 2H), 3.79 (s, 3H), 4.57 (t, *J* = 4.0 Hz, 1H), 5.37 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 23.5, 28.2, 52.1, 52.2, 80.5, 81.8, 83.7, 113.8, 114.9, 133.1, 155.4, 159.4, 175.4 ppm.

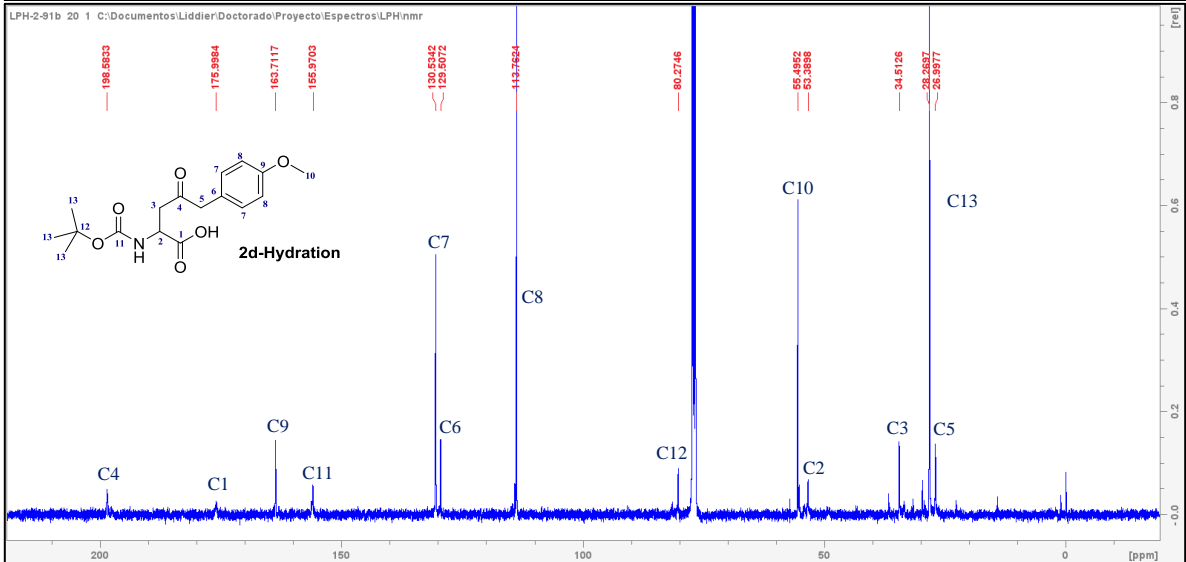
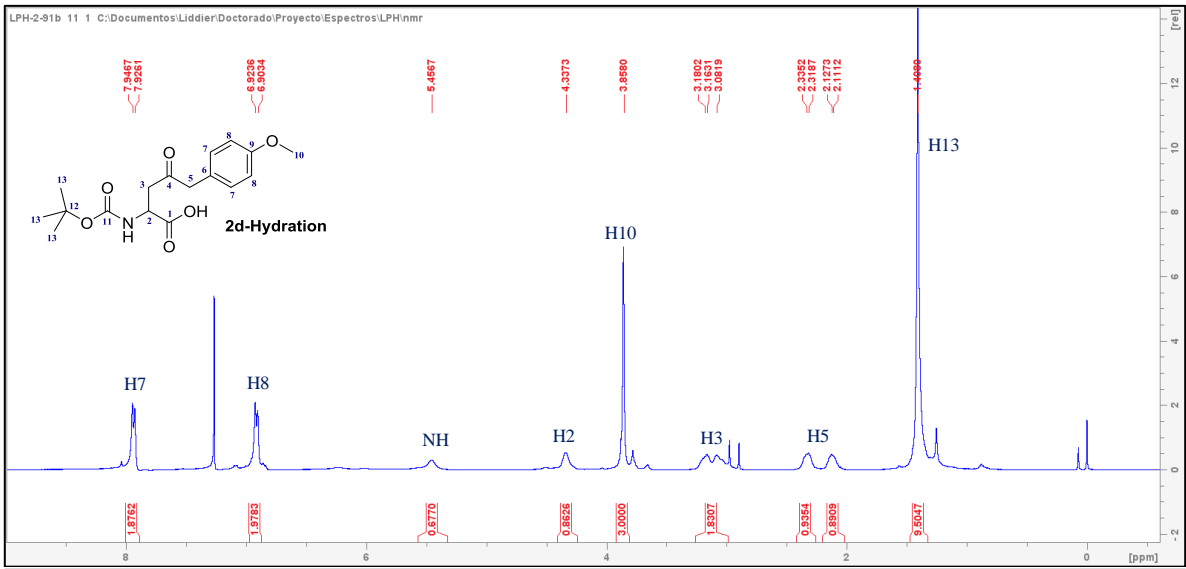
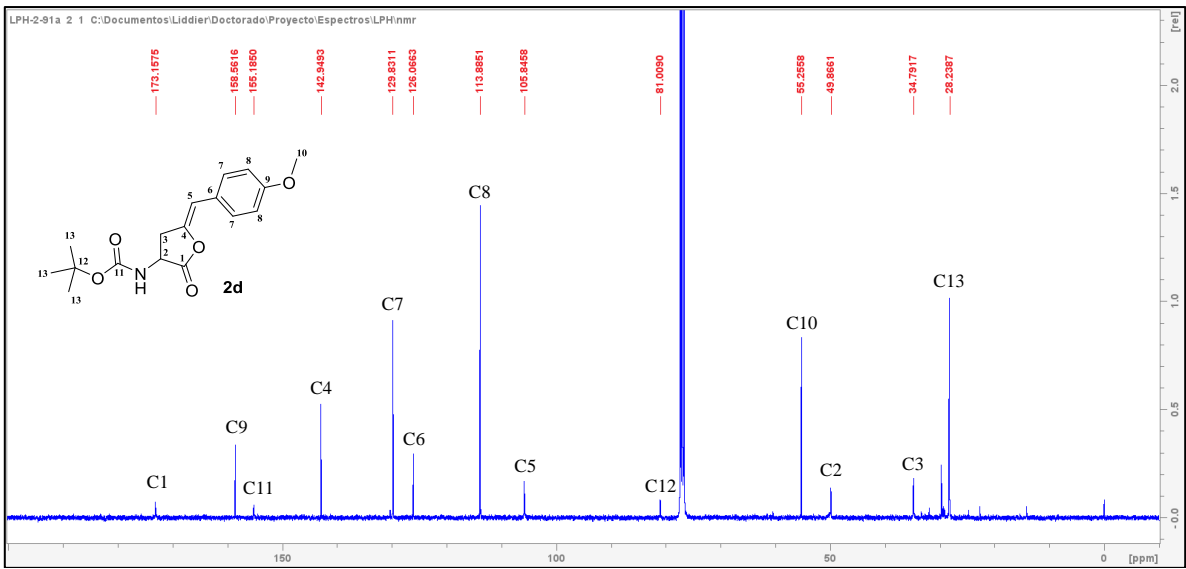


**2.15. *tert*-butyl (*Z*)-(5-(4-methoxybenzylidene)-2-oxotetrahydrofuran-3-yl)carbamate (2d).** Rf = 0.43 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.46 (s, 9H), 3.02 (q, *J* = 8.7 Hz, 1H), 3.36 (q, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 4.50 (d, *J* = 6.1 Hz, 1H), 5.23 (s, 1H), 5.55 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 28.2, 34.7, 49.8, 55.2, 81.0, 105.8, 113.8, 126.0, 129.8, 142.9, 155.1, 158.5, 173.1 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>21</sub>NNaO<sub>5</sub> [M + Na]<sup>+</sup> 342.1312, found 342.1315.

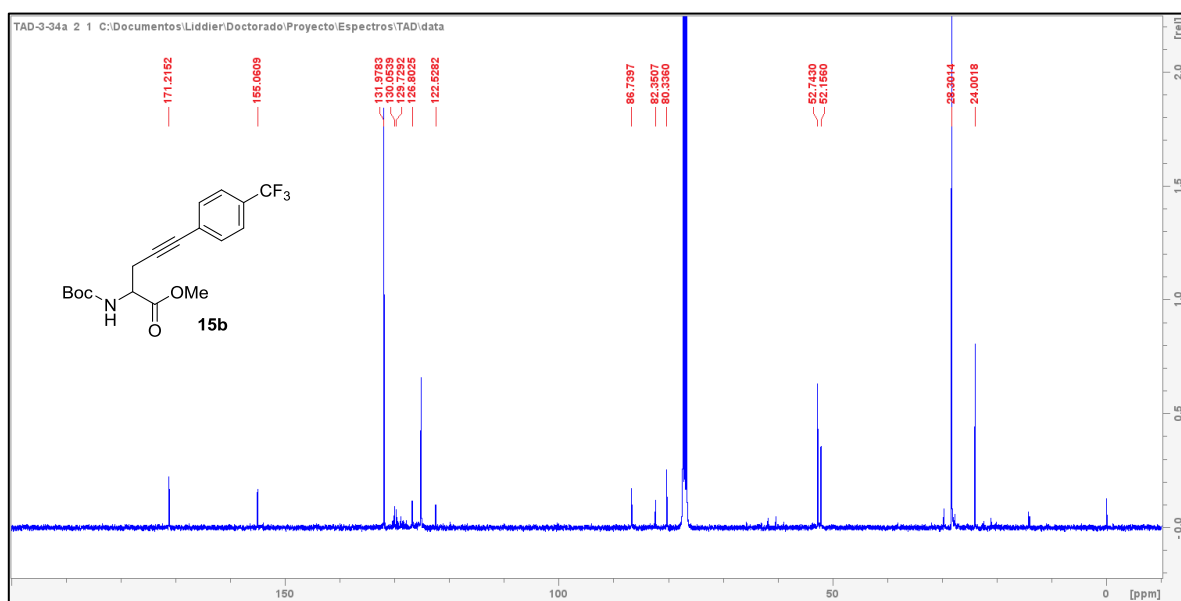
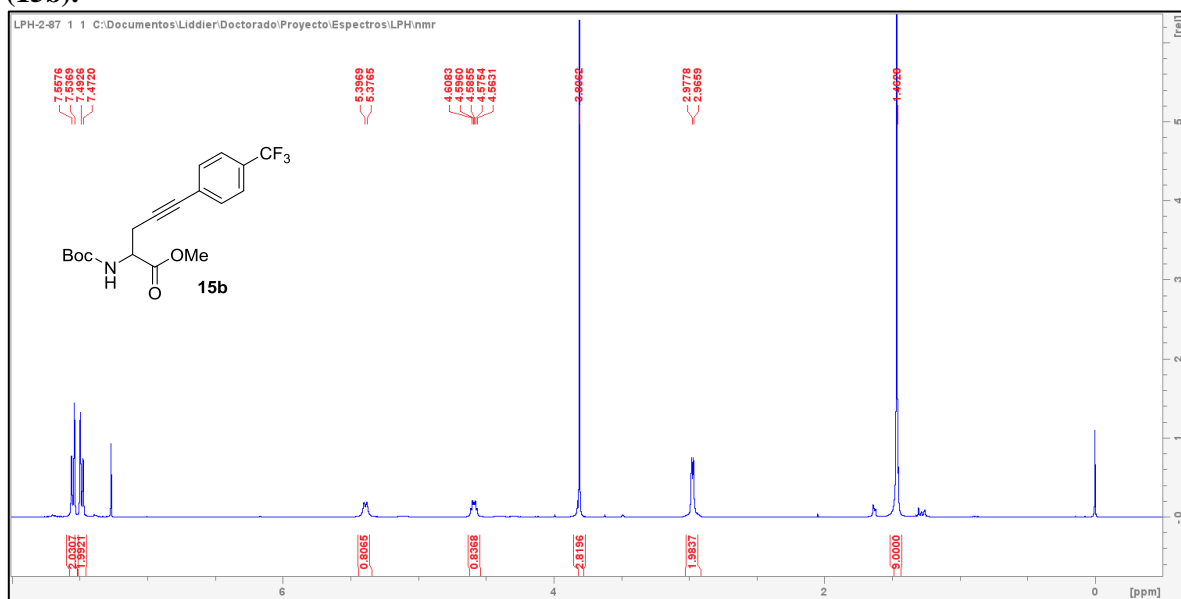
**2.16. 2-((*tert*-butoxycarbonyl)amino)-5-(4-methoxyphenyl)-4-oxopentanoic acid (2d-Hydration).** Rf = 0.11 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.40 (s, 9H), 2.11 (d, *J* = 6.4 Hz, 1H), 2.32 (d, *J* = 6.5 Hz, 1H), 3.13 (t, *J* = 19.6 Hz, 1H), 3.86 (s, 3H), 4.33 (s, 1H), 5.45 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 28.2, 55.4, 63.1, 80.2, 142.9, 158.5, 175.8, 198.3 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>23</sub>NNaO<sub>6</sub> [M + Na]<sup>+</sup> 360.1418, found 360.1422.



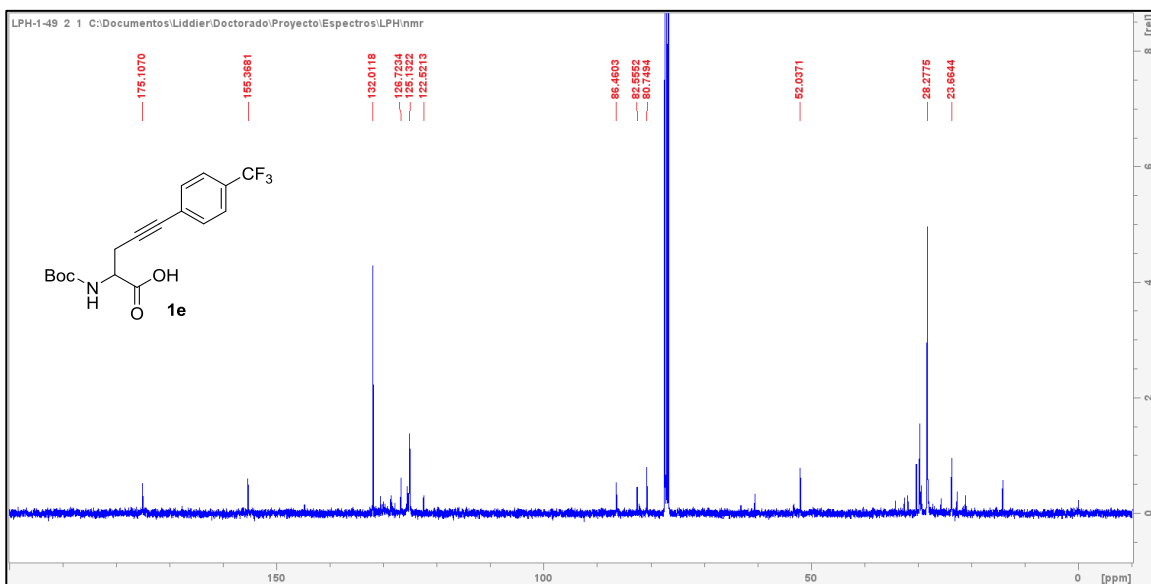
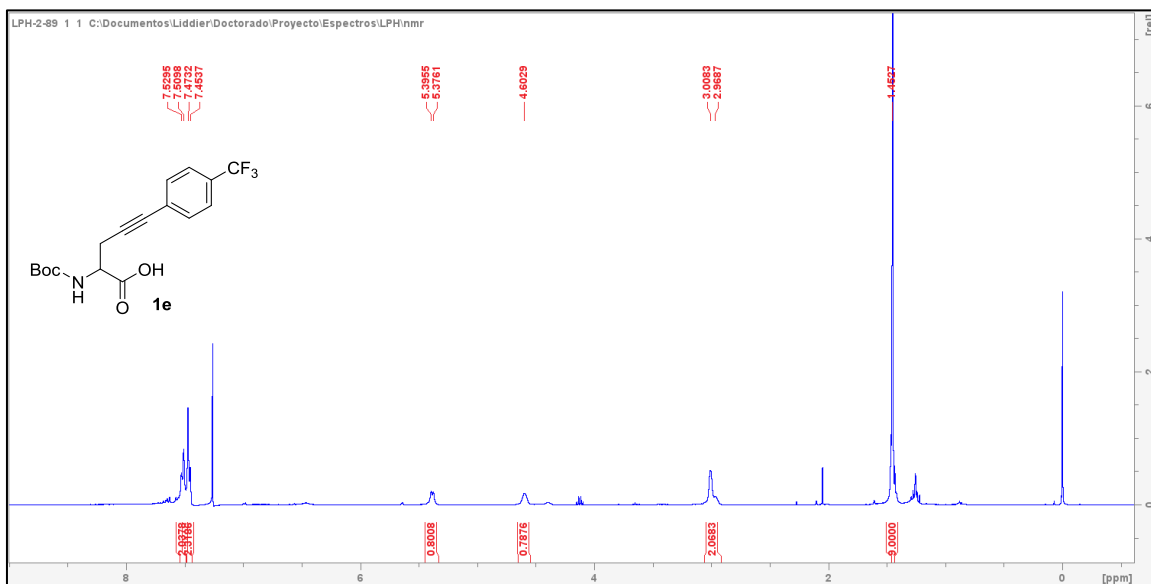




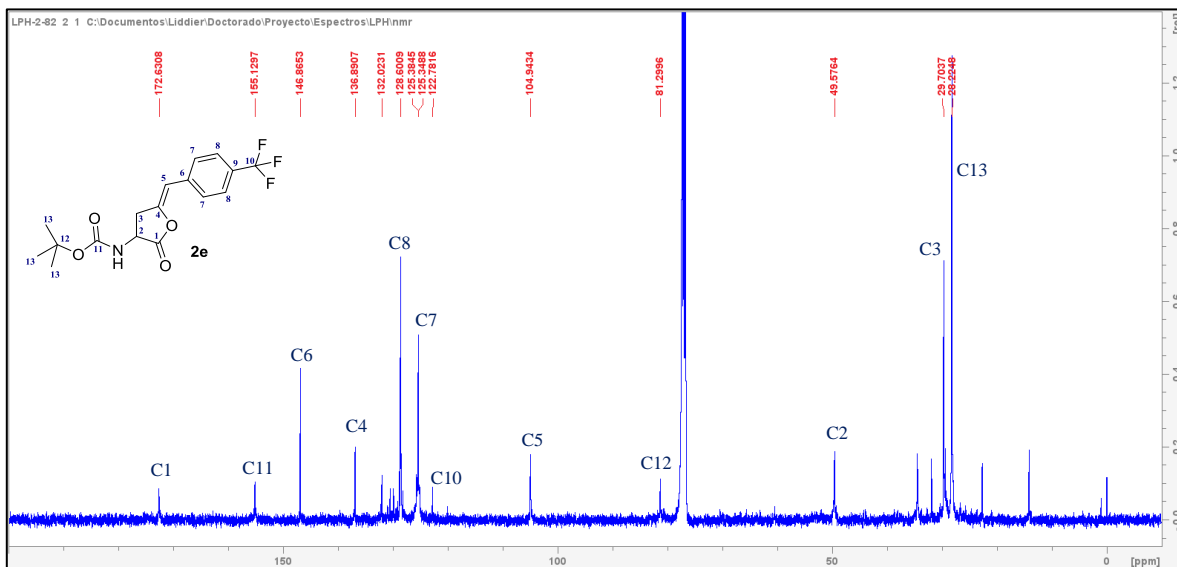
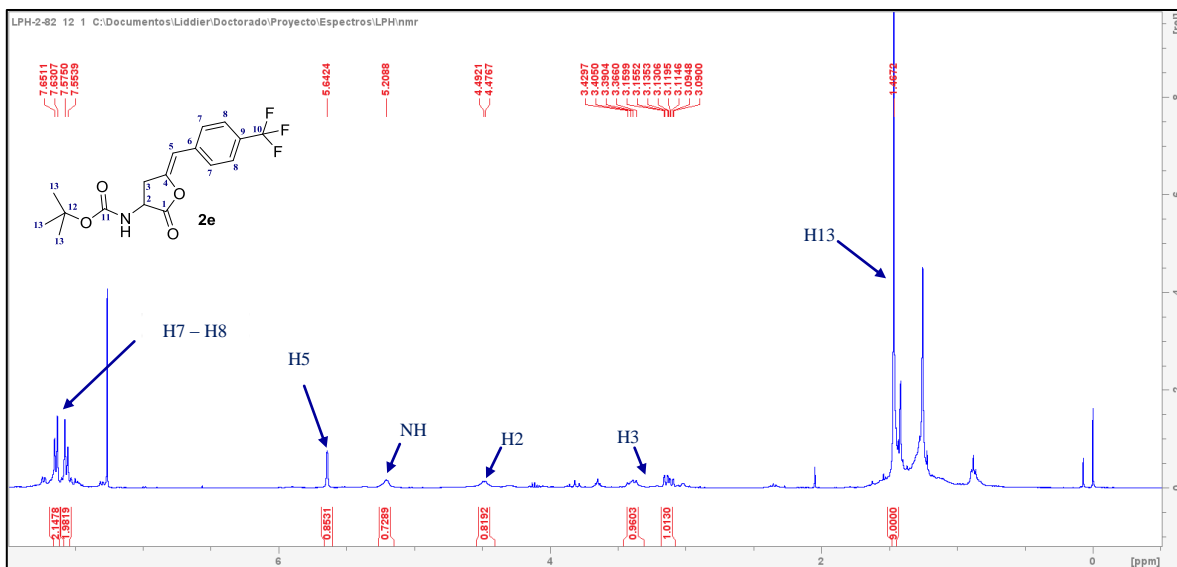
2.17. Methyl 2-((*tert*-butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate (15b).



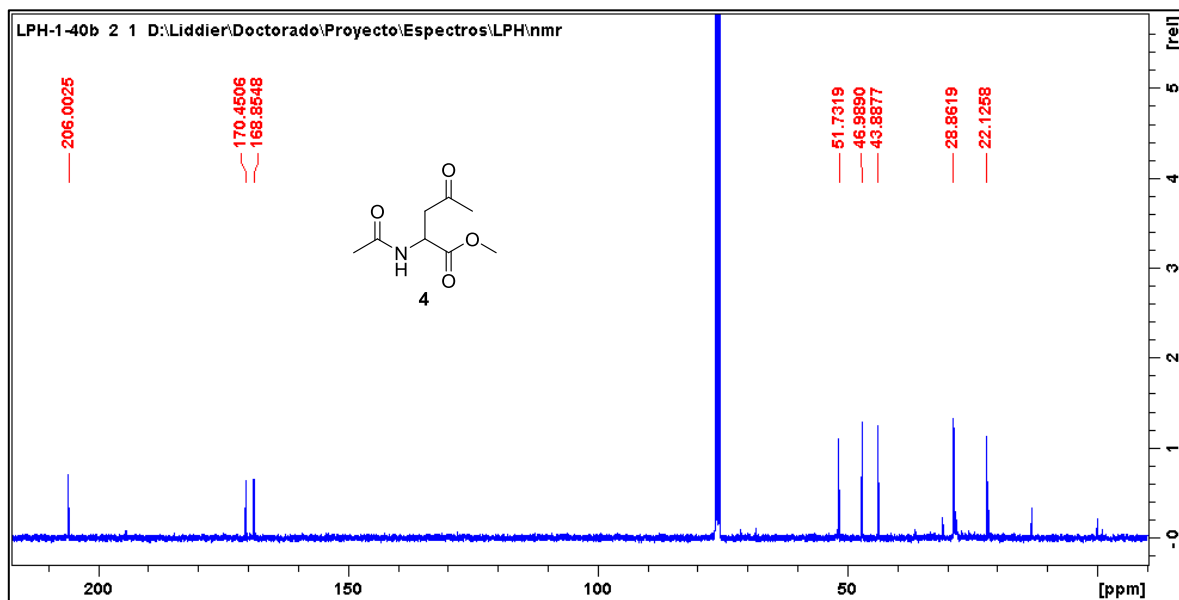
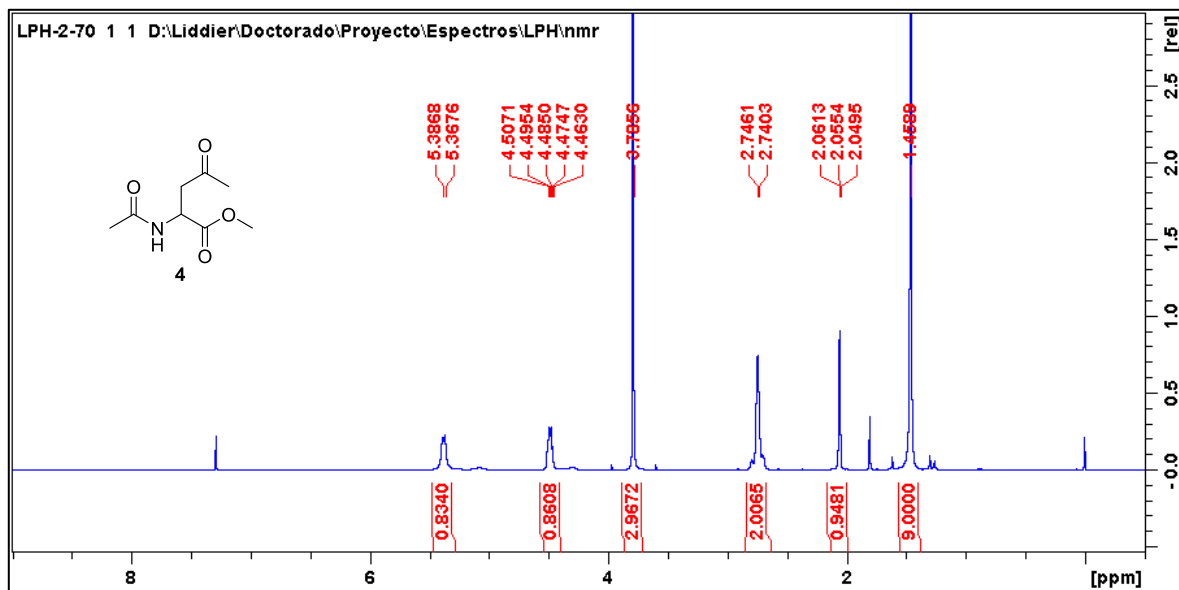
**2.18. 2-((*tert*-Butoxycarbonyl)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoic acid (1e).**  
 Rf = 0.13 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.45 (s, 9H), 2.98 (d, *J* = 15.8 Hz, 2H), 4.60 (s, 1H), 5.38 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 23.6, 28.2, 52.0, 80.7, 82.5, 86.4, 122.5, 125.1, 126.7, 132.0, 155.3, 175.1 ppm.



**2.19. *tert*-Butyl (Z)-(2-oxo-5-(4-(trifluoromethyl)benzylidene)tetrahydrofuran-3-yl) carbamate (2e):** *R*<sub>f</sub> = 0.43 (hexanes:ethyl acetate = 3:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.46 (s, 9H), 3.12 (m, *J* = 4.0 Hz, 1H), 3.39 (q, *J* = 8.5 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 1H), 5.23 (s, 1H), 5.63 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 28.2, 29.7, 49.6, 81.3, 86.4, 104.9, 122.7, 125.34, 125.38, 128.6, 132.0, 136.8, 146.8, 155.1, 172.6 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>NNaO<sub>4</sub> [M + Na]<sup>+</sup> 380.1080, found 380.1084.



**2.20. Methyl 2-acetamido-4-oxopentanoate (4).**<sup>5</sup> R<sub>f</sub> = 0.55 (hexanes:ethyl acetate = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.94 (s, 3H), 2.09 (s, 3H), 2.93 (dd, *J* = 7.5 Hz, 1H), 3.15 (dd, *J* = 7.5 Hz, 1H), 3.66 (s, 3H), 4.68 – 4.72 (m, 1H), 6.45 (d, *J* = 6.6 Hz, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 22.1, 28.8, 43.8, 46.9, 51.7, 168.8, 170.4, 206.0 ppm. HRMS (ESI): 188.0924 (calc. for C<sub>8</sub>H<sub>14</sub>NO<sub>4</sub>: 188.0917).

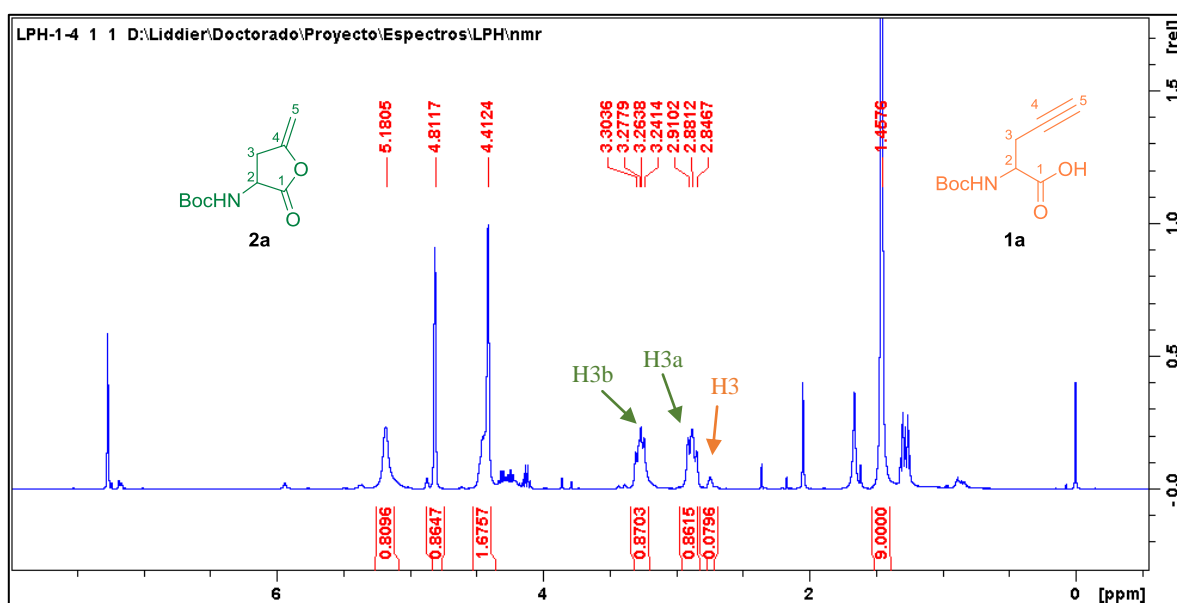


### 3. REUSE PROCESS OF CATALYSTS C1 – C5.

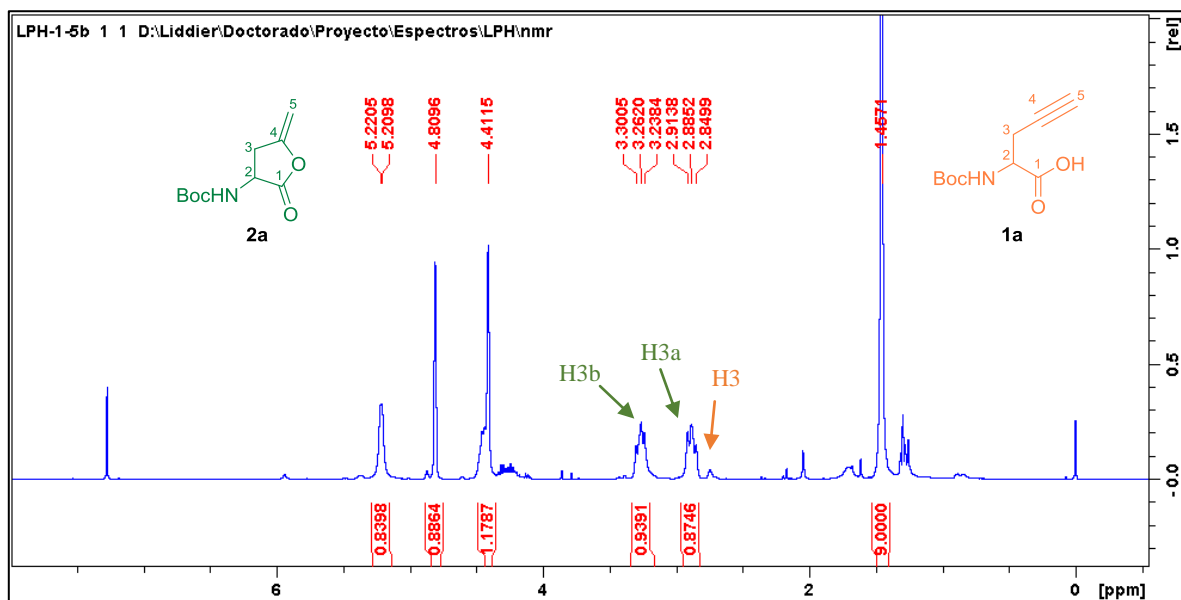
Table S1. C1 (1 mol%) catalyst reuse cycles

Cycle	Substrate (mg)	Product (mg)	Isolated Yield %	Ratio (Product/Substrate)	Conversion by <sup>1</sup> H NMR %
1	39.7	32.3	81.4	43 : 2	95.5
2	39.0	37.2	95.0	40 : 2	95.2
3	39.9	37.2	93.2	37 : 2	94.8
4	38.6	37.1	96.0	46 : 2	95.8
5	39.4	37.3	94.6	30 : 2	93.7
6	38.9	37.4	96.0	28 : 2	93.3
7	39.9	35.5	88.9	40 : 2	95.2
8	39.6	33.8	85.0	32 : 2	94.1
9	39.4	34.3	87.0	35 : 2	94.5
10	39.7	38.6	97.0	28 : 2	93.3
11	39.6	37.2	90.3	33 : 2	94.2
12	39.7	29.6	74.5	34 : 2	94.4
13	39.4	36.4	87.2	38 : 2	95.0
14	39.7	37.5	94.4	41 : 2	95.3
15	39.8	37.6	94.4	25.6 : 2	92.7

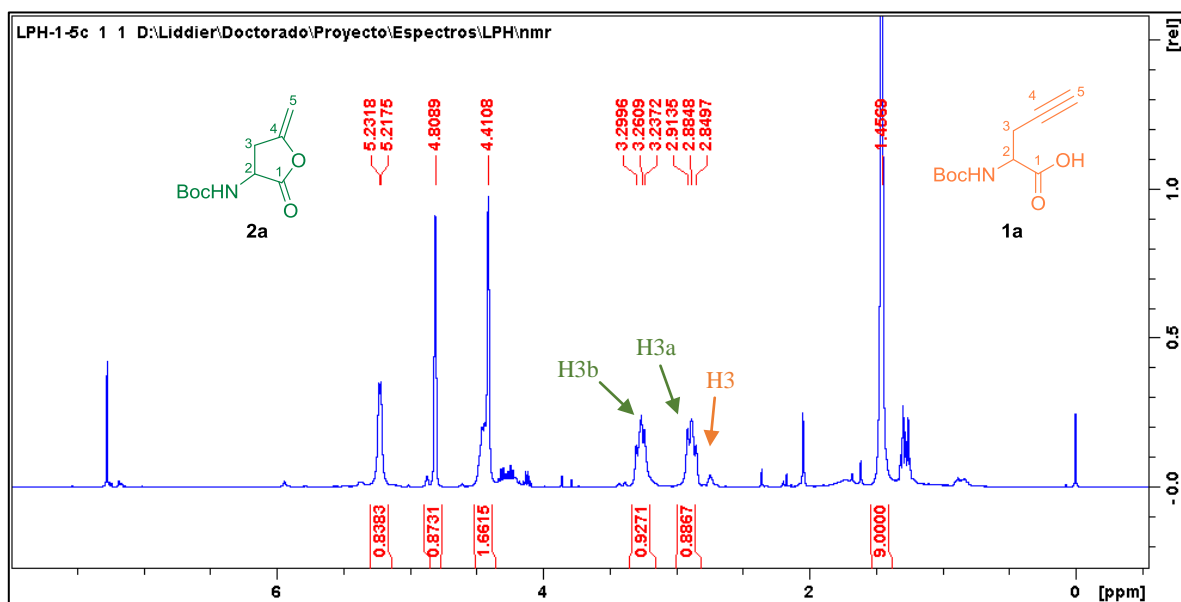
– Cycle 1



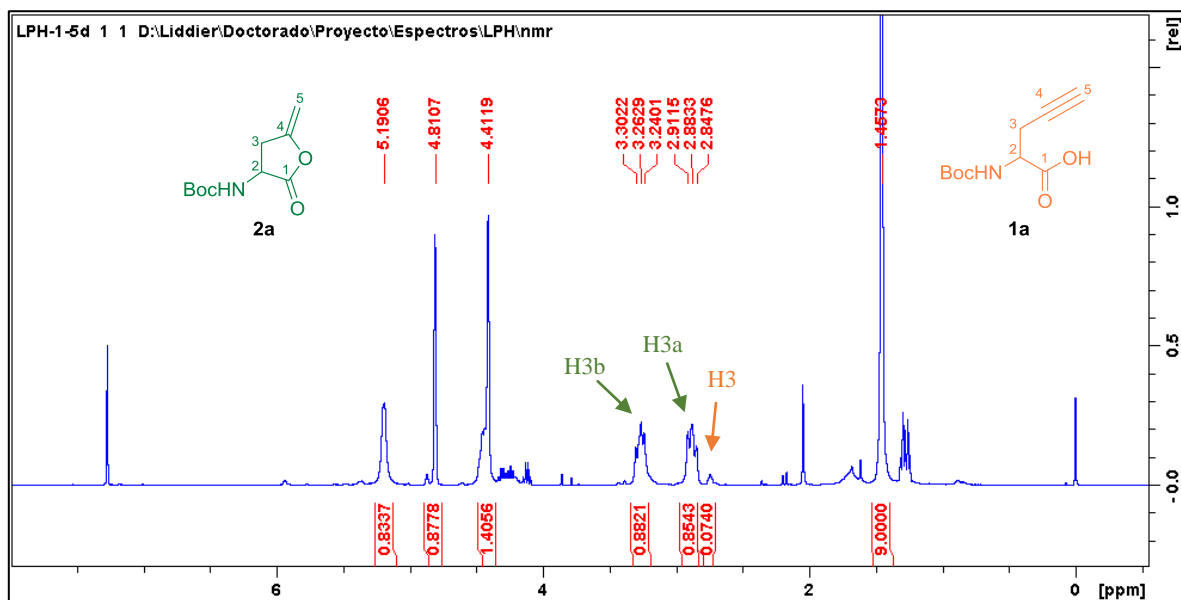
– Cycle 2



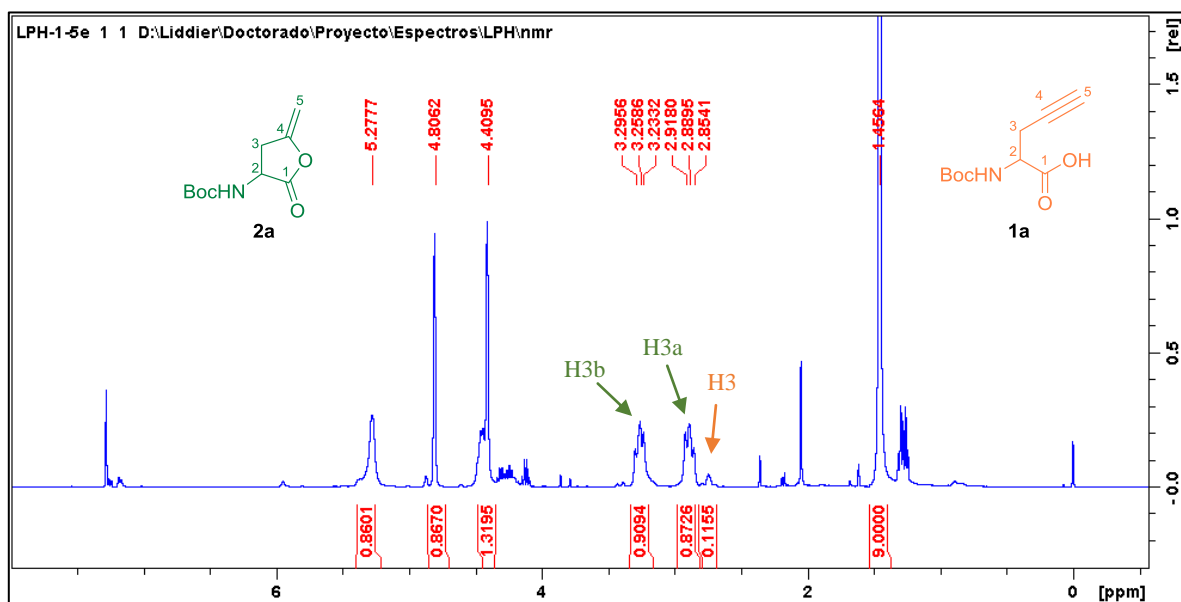
– Cycle 3



– Cycle 4

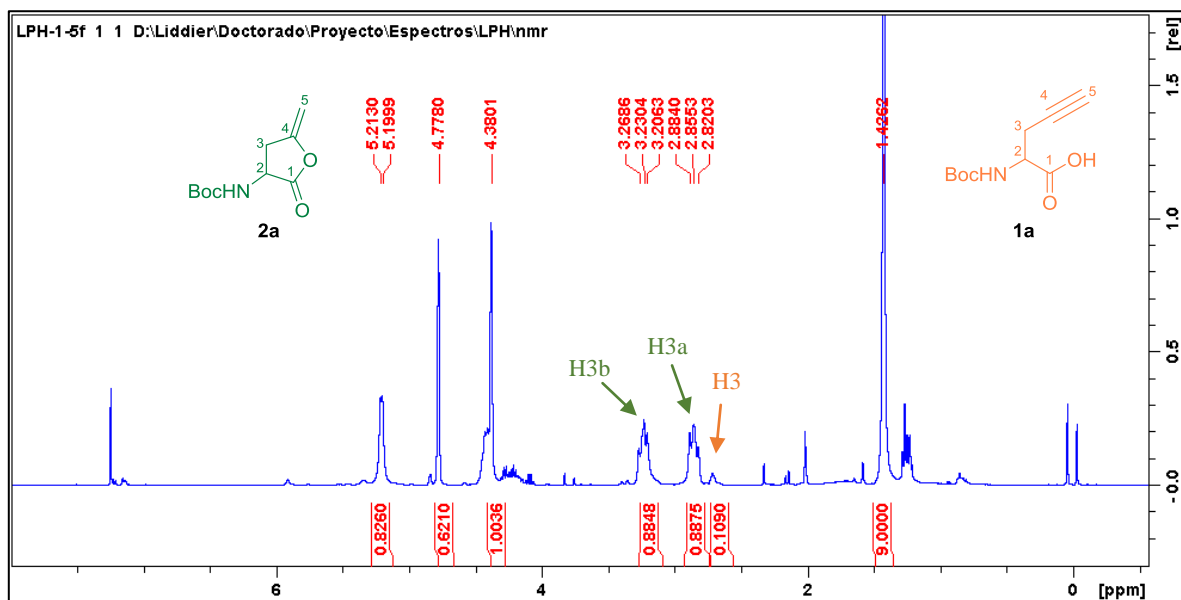


– Cycle 5

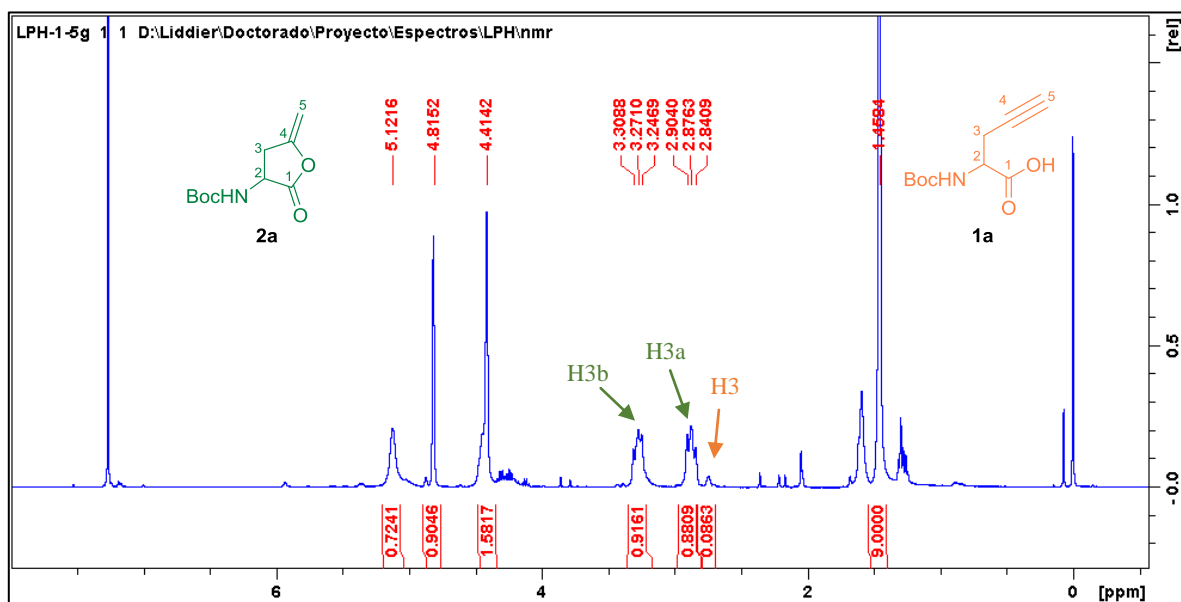




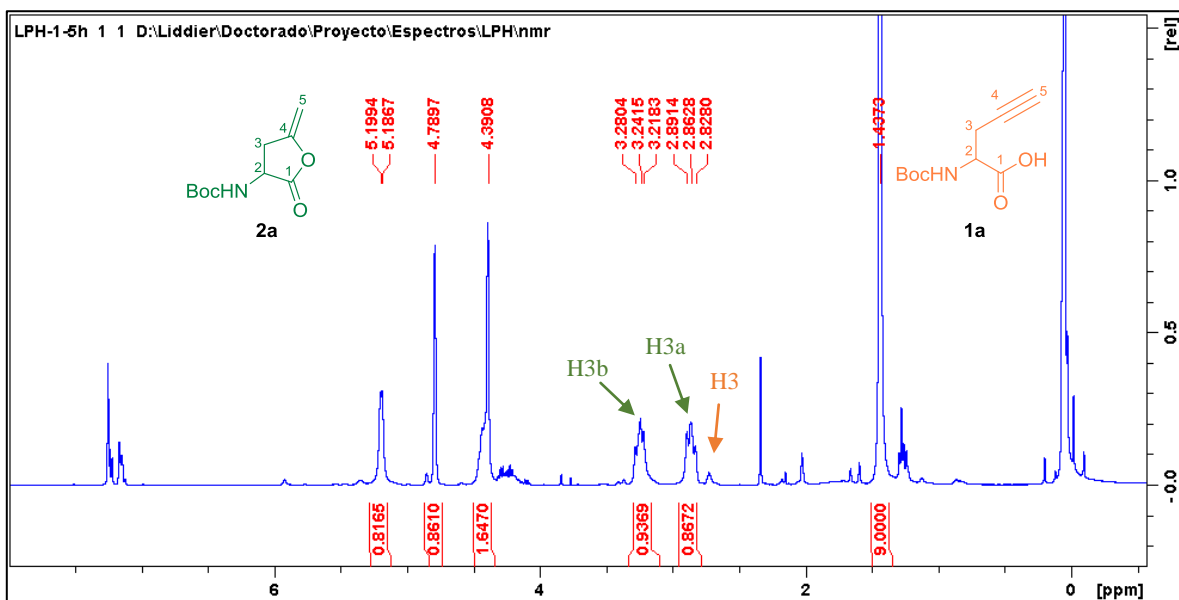
– Cycle 6



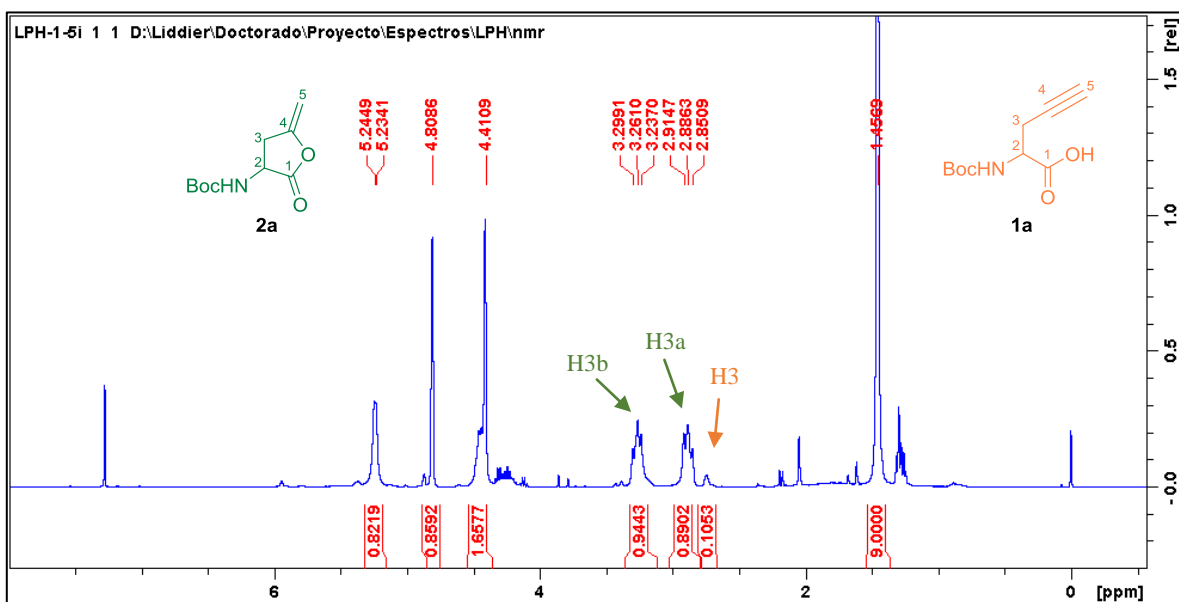
– Cycle 7



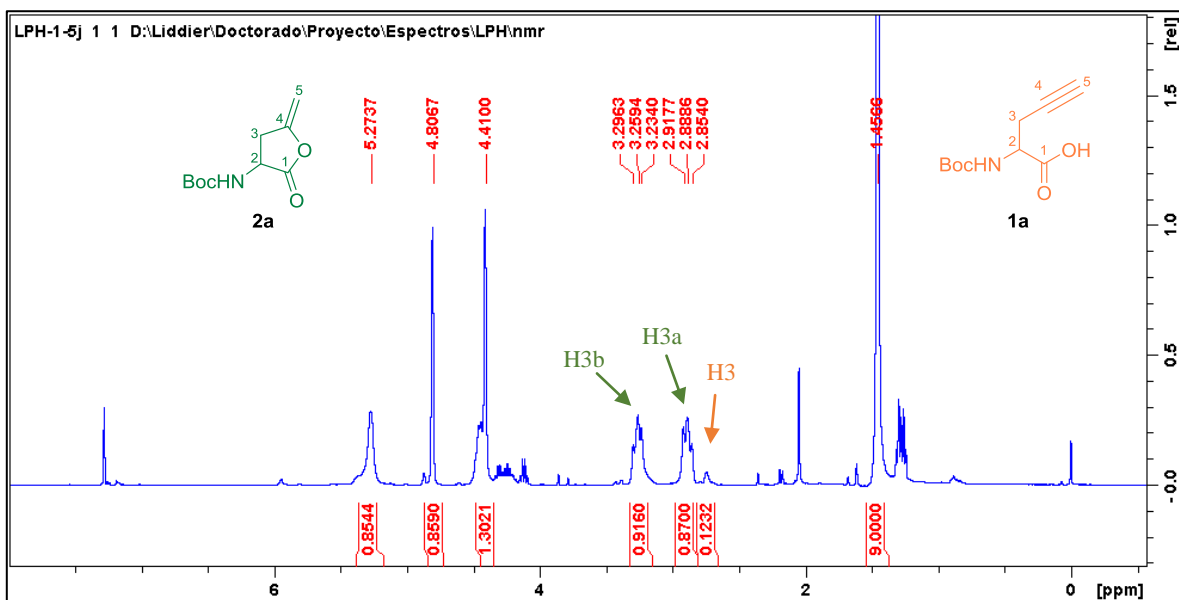
– Cycle 8



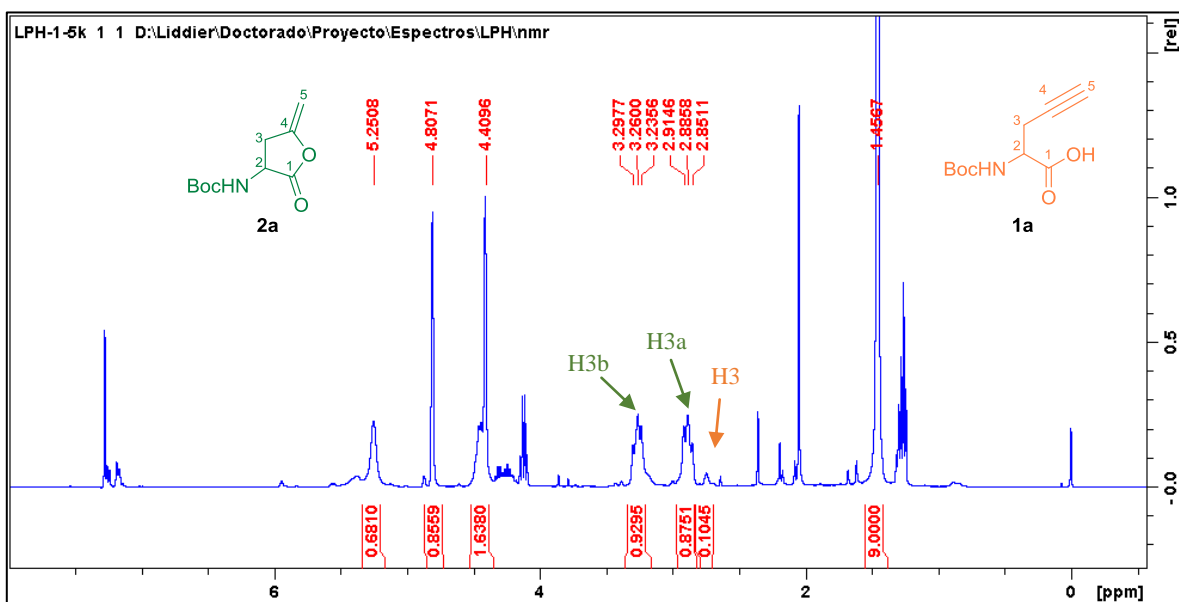
– Cycle 9



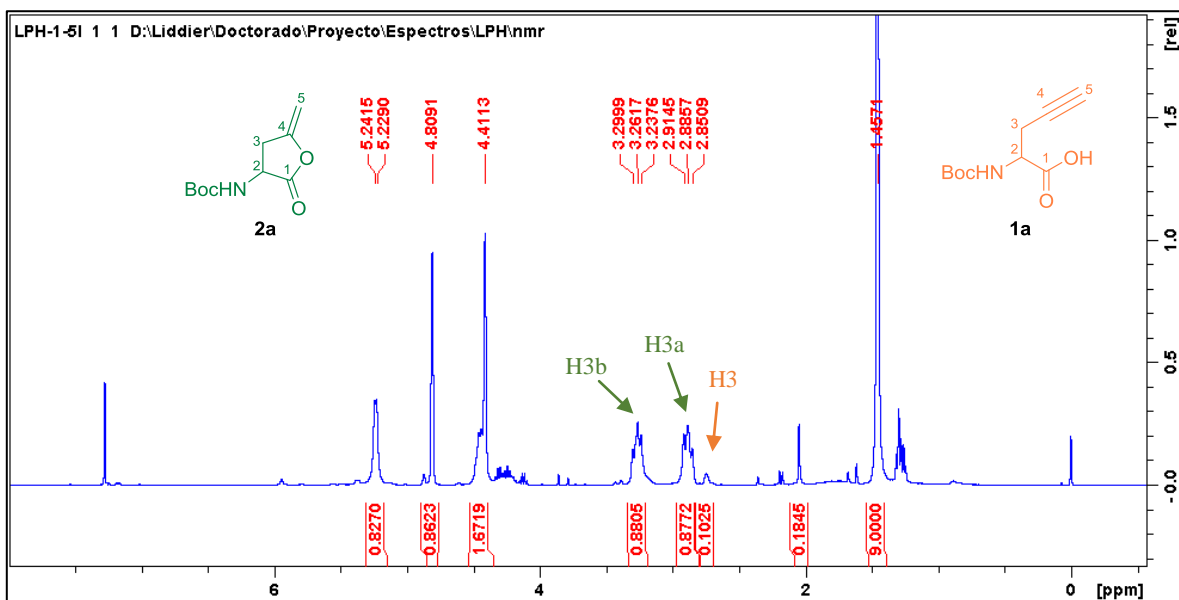
– Cycle 10



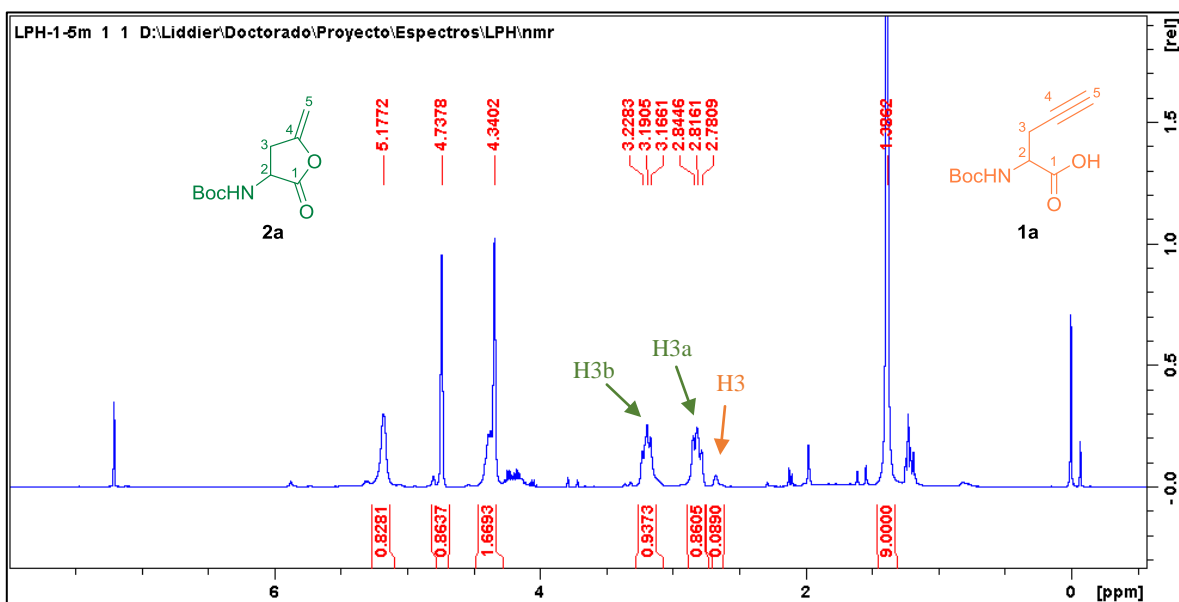
– Cycle 11



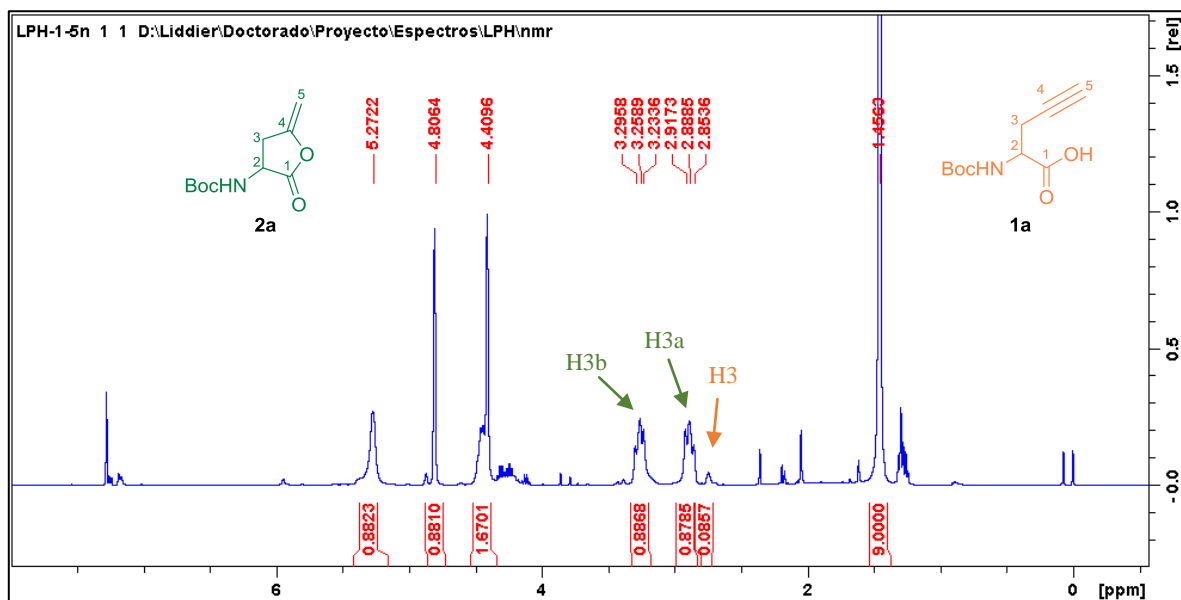
– Cycle 12



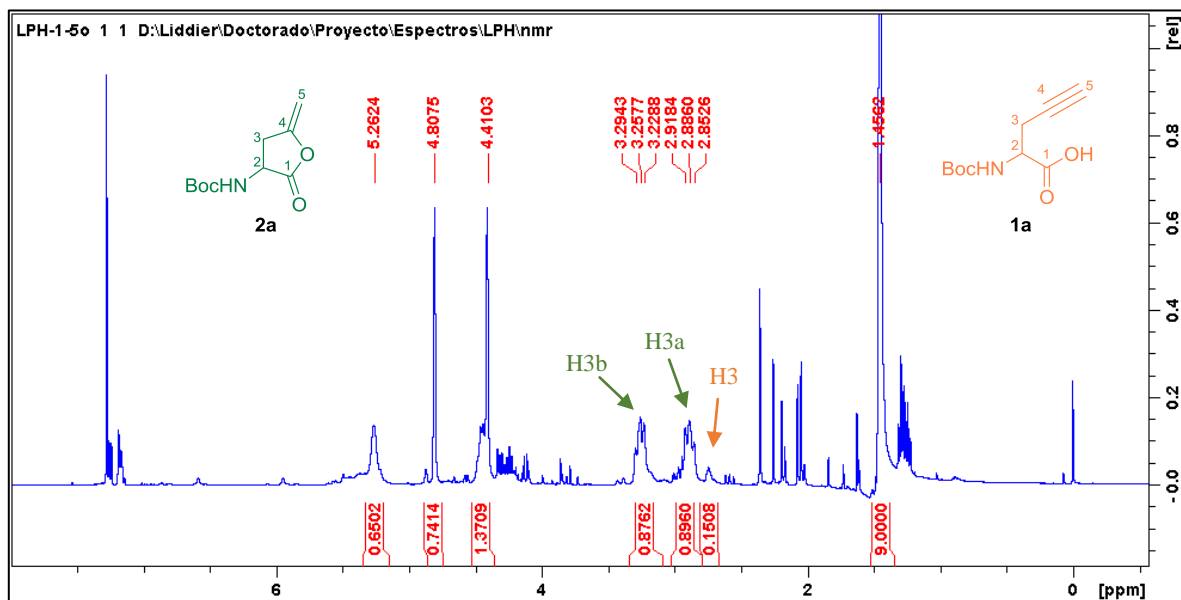
– Cycle 13



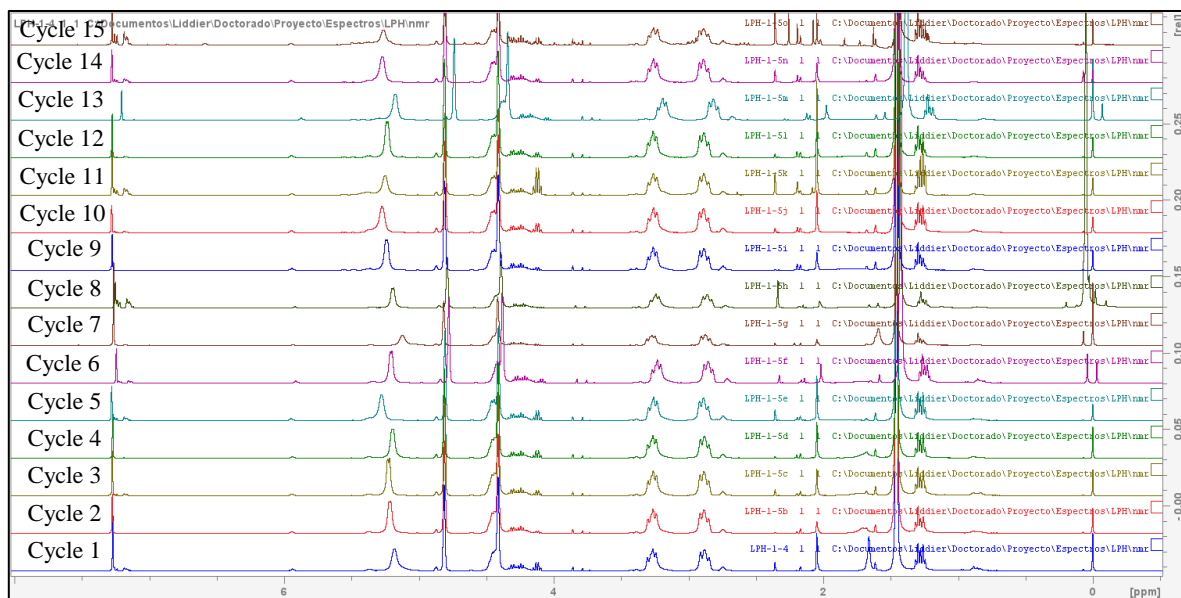
– Cycle 14



– Cycle 15



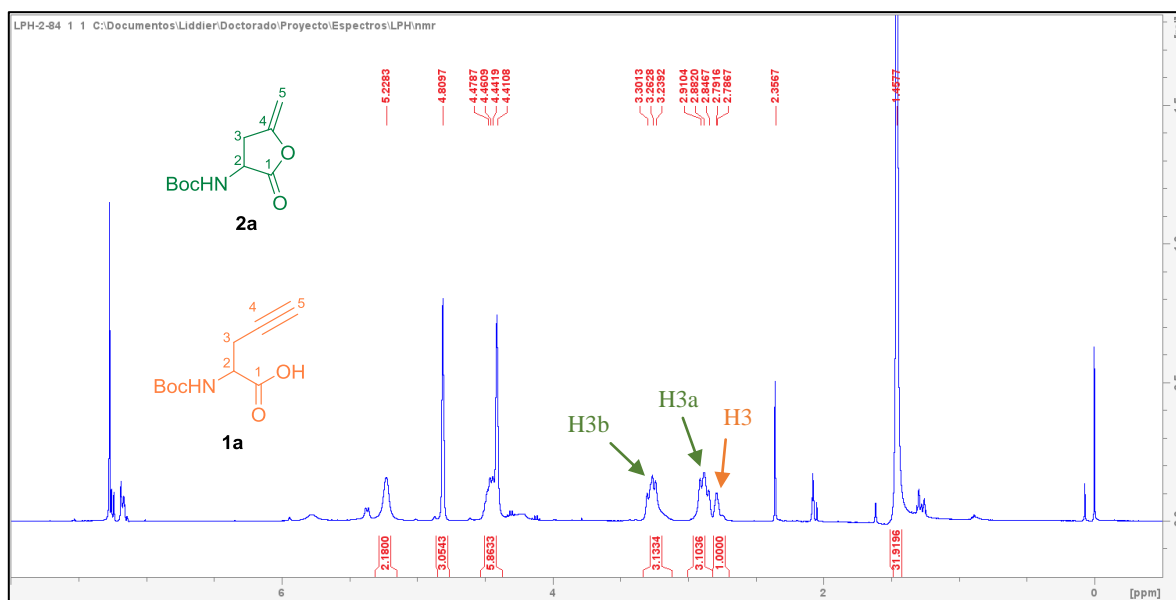
**Figure S3. Comparison of reuse cycles of C1, <sup>1</sup>H NMR spectra obtained after 1 h at room temperature.**



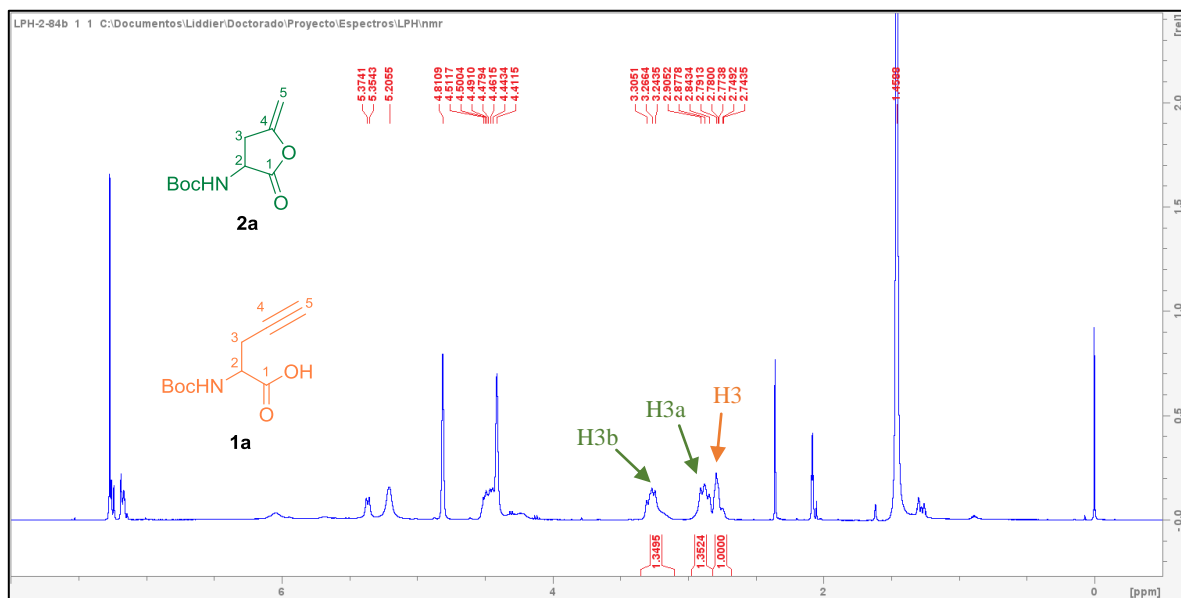
**Table S2. C2 (1 mol%) catalyst reuse cycles**

Cycle	Substrate (mg)	Product (mg)	Isolated Yield %	Ratio (Product/Substrate)	Conversion by <sup>1</sup> H NMR %
1	31.9	28.7	89.9	6.2:1	86.6
2	30.6	26.3	85.9	2.7:1	73.1
3	30.6	28.9	94.4	2.4:1	71.3
4	30.2	30.4	100.0	2.1:1	67.7
5	30.5	32.4	100.0	3.1:1	75.8
6	30.1	31.5	100.0	1.3:1	56.5

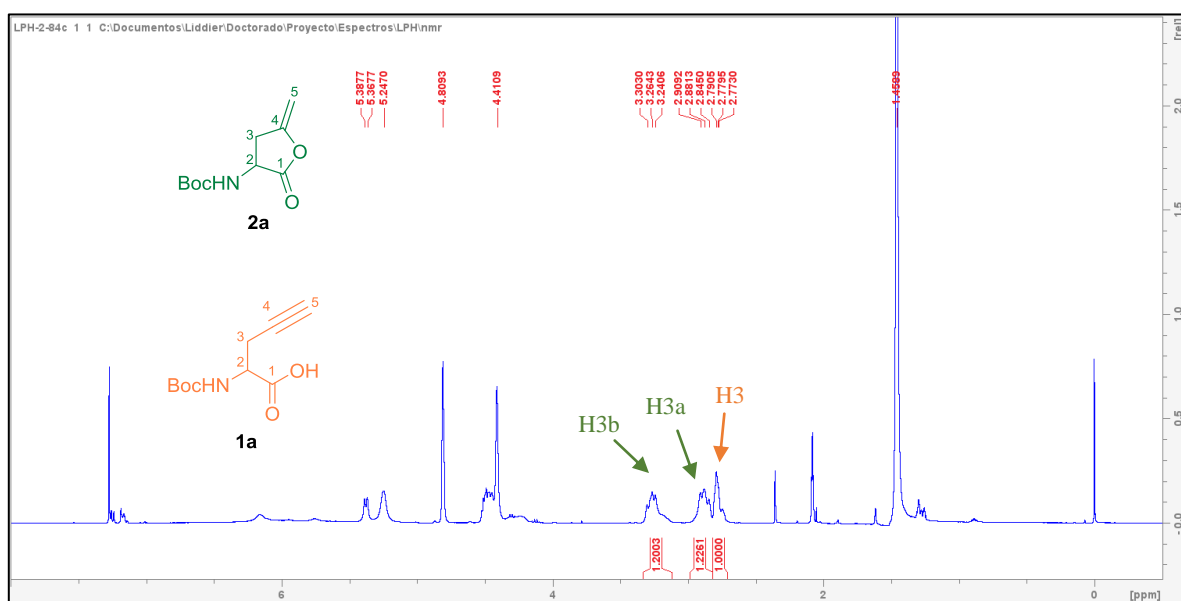
– Cycle 1



– Cycle 2

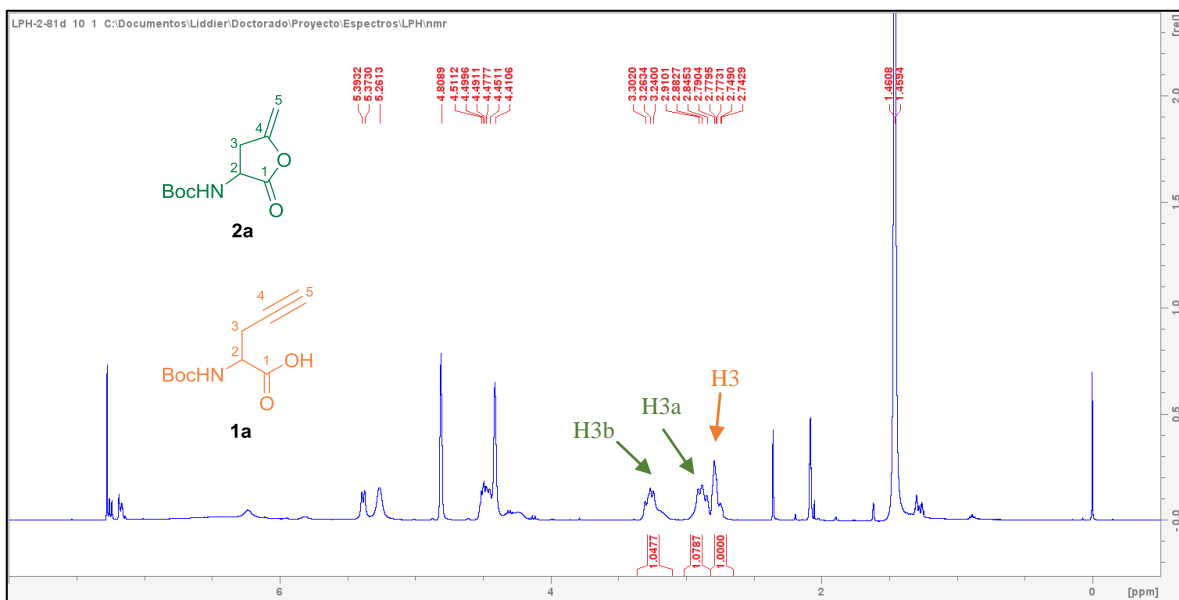


– Cycle 3

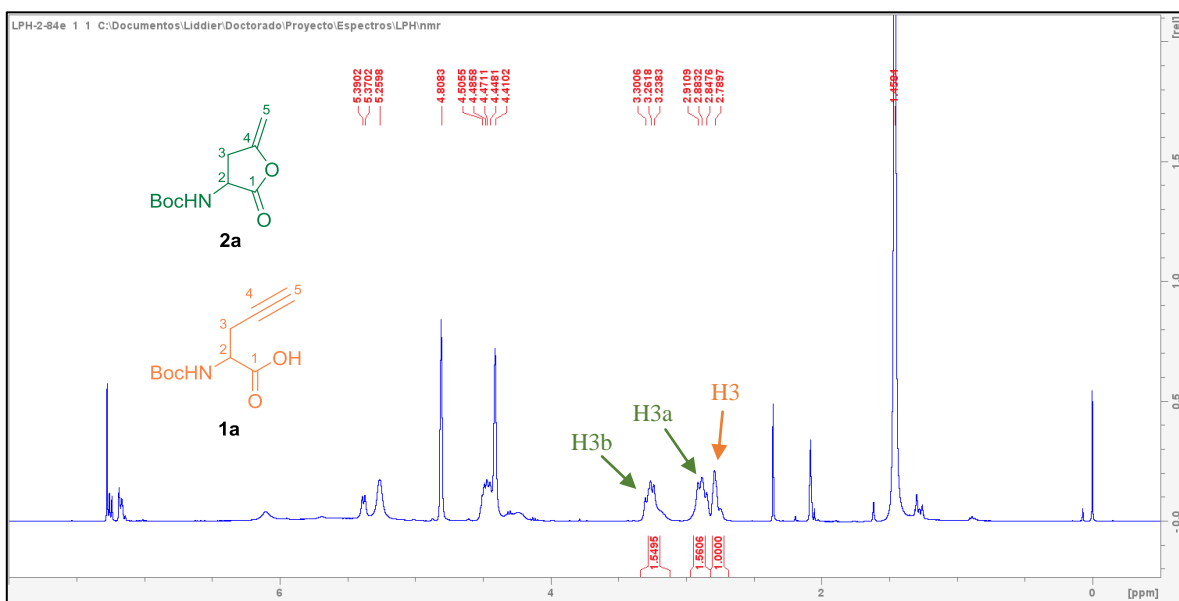




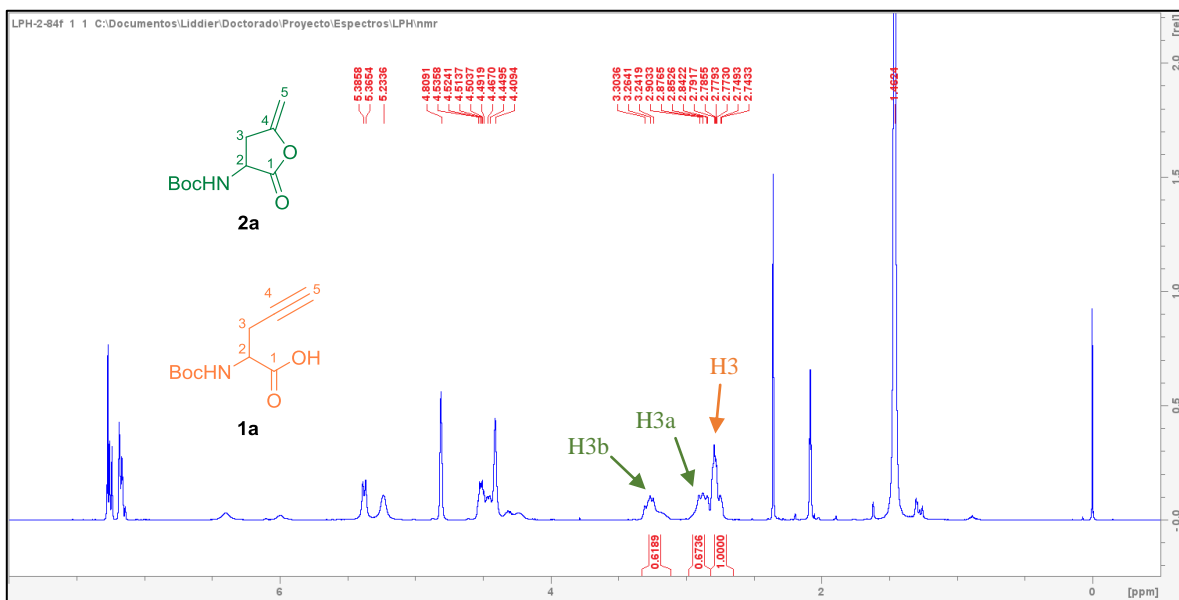
– Cycle 4



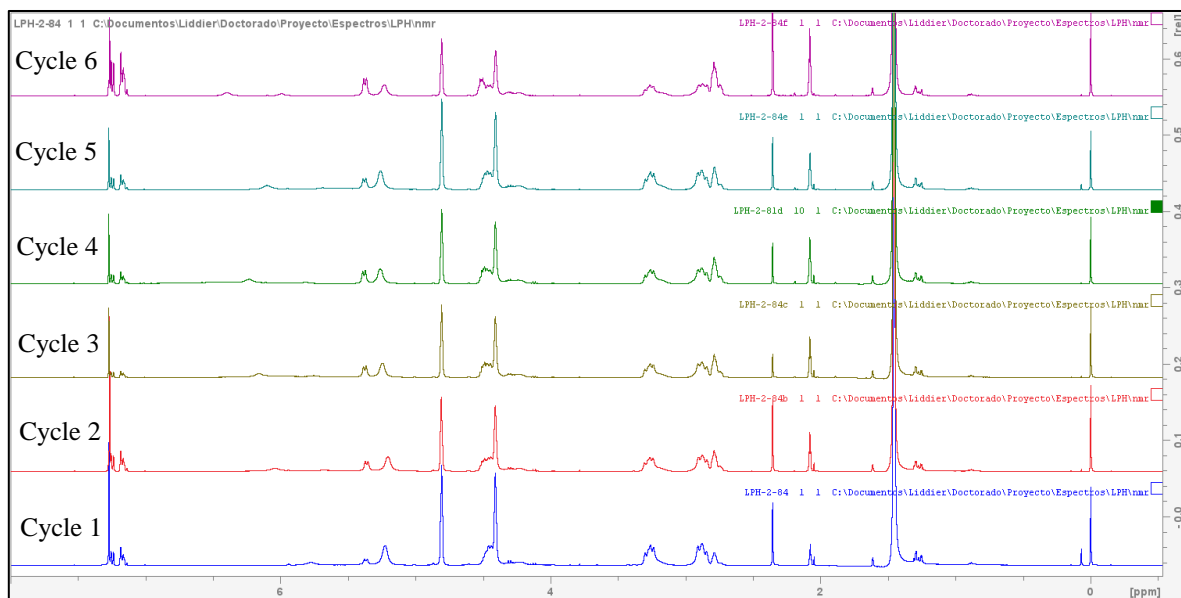
– Cycle 5



Cycle 6



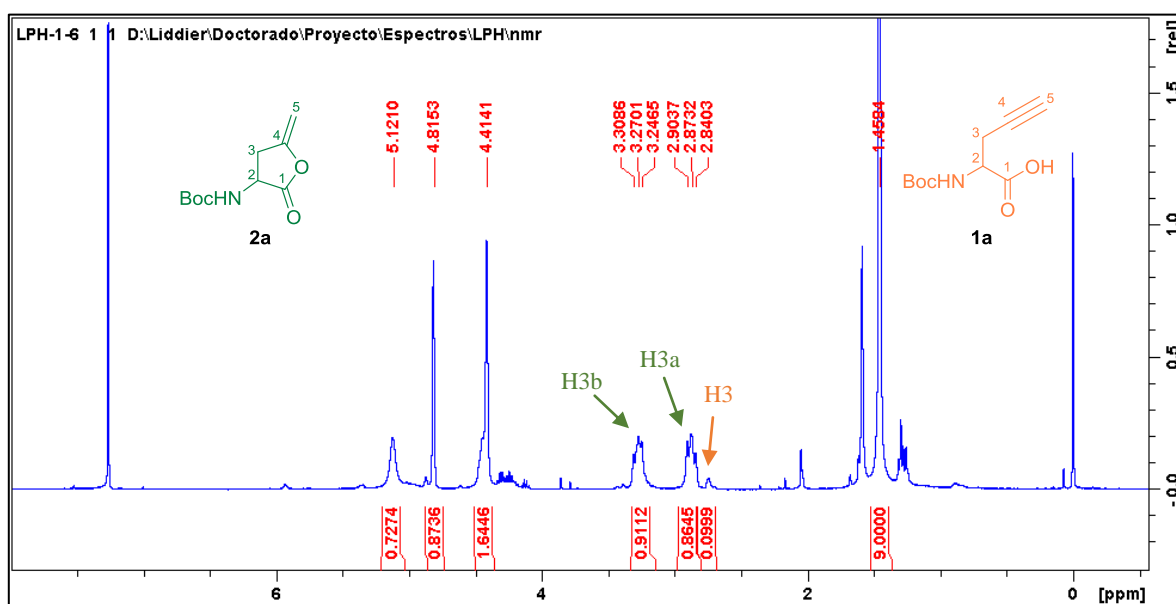
**Figure S4. Comparison of reuse cycles of C2,  $^1\text{H}$  NMR spectra obtained after 1 h at room temperature.**



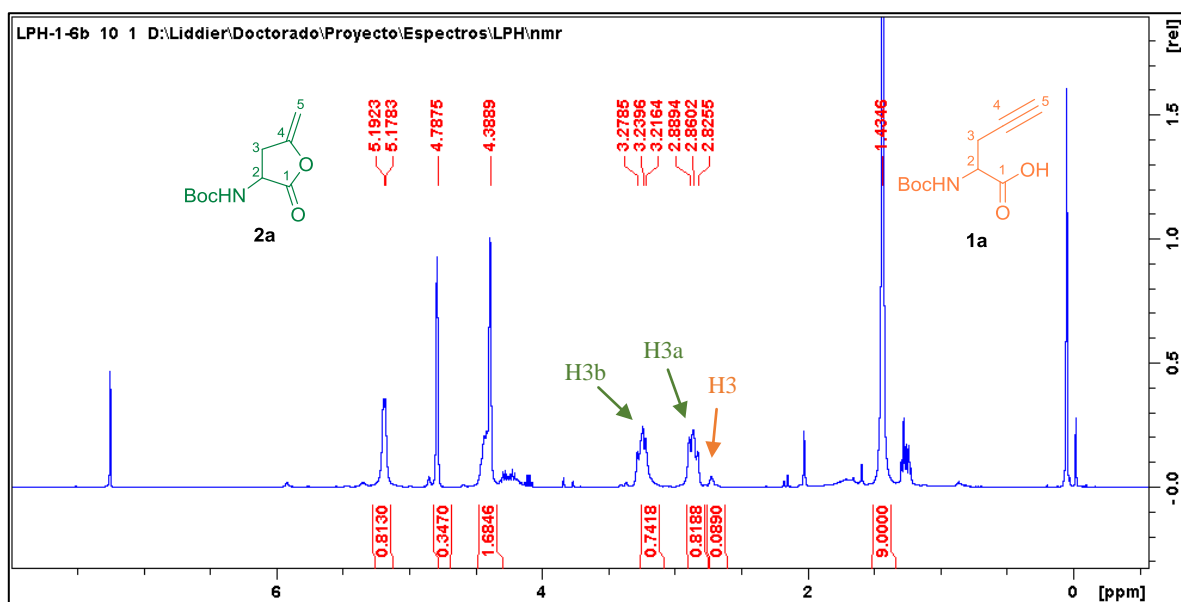
**Table S3. C3 (1 mol%) catalyst reuse cycles**

Cycle	Substrate (mg)	Product (mg)	Isolated Yield %	Ratio (Product/Substrate)	Conversion by <sup>1</sup> H NMR %
1	50.04	41.4	82.7	35 : 2	94.6
2	50.00	47.6	95.0	36 : 2	94.0
3	50.20	40.5	80.0	7 : 2	77.7
4	49.50	26.7	53.9	5 : 2	71.4
5	49.50	40.2	75.0	3.4 : 2	62.9
6	50.50	47.2	93.4	3 : 2	60.0

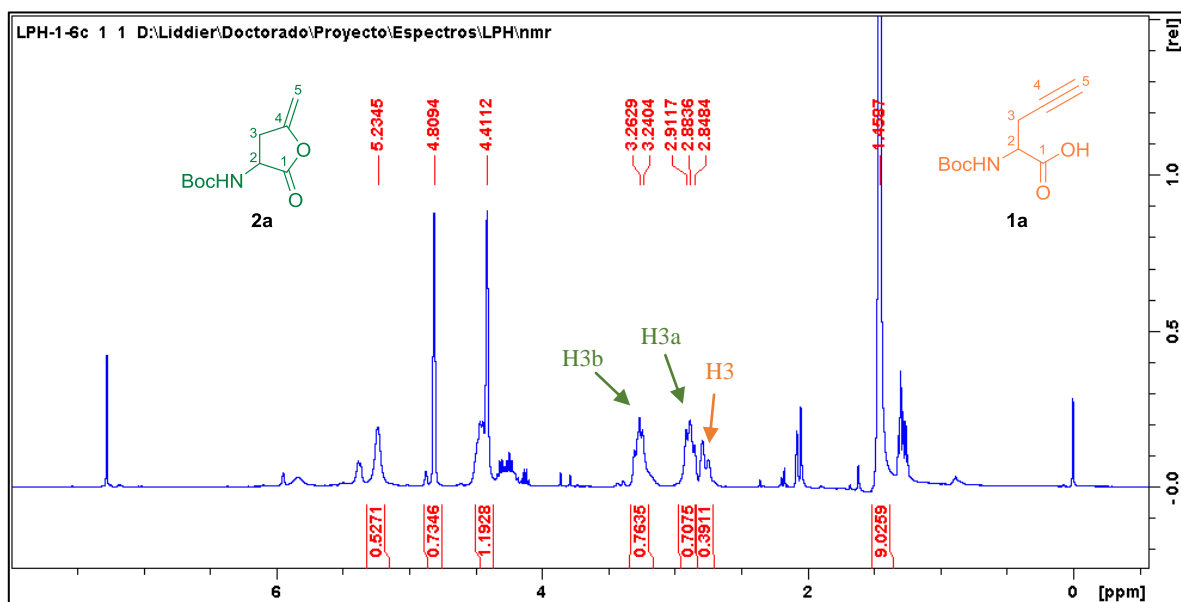
– Cycle 1



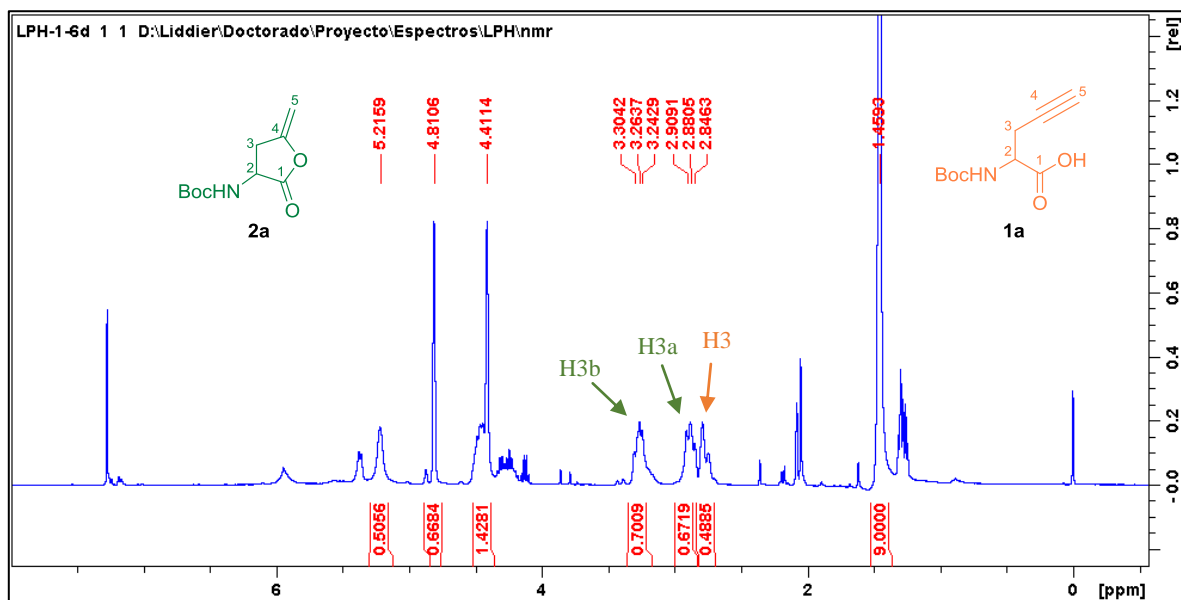
– Cycle 2



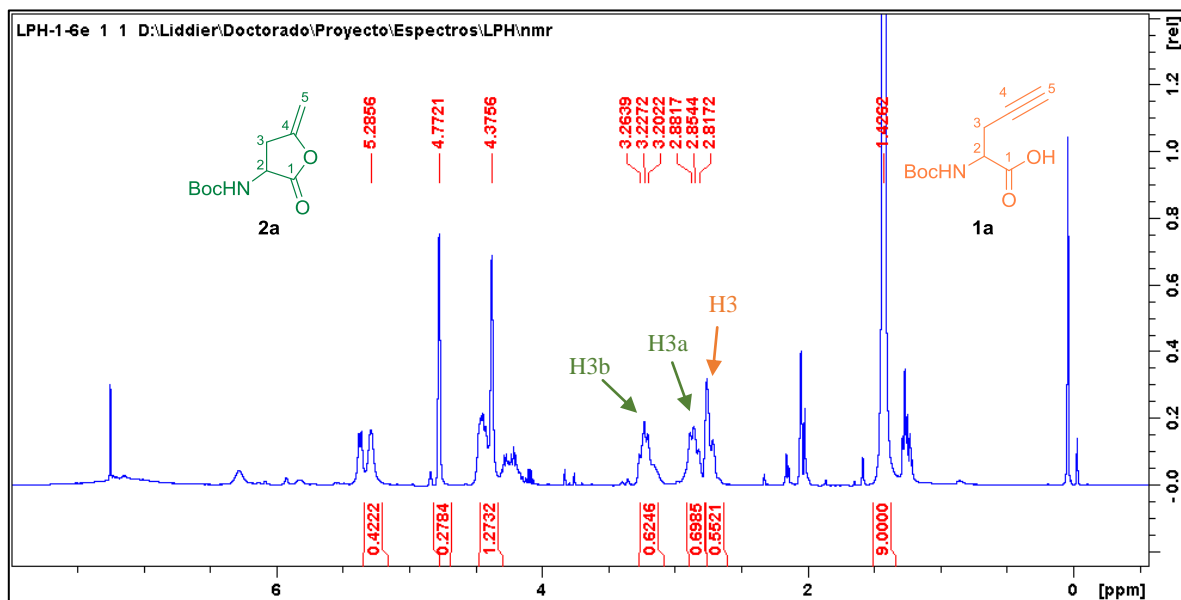
– Cycle 3



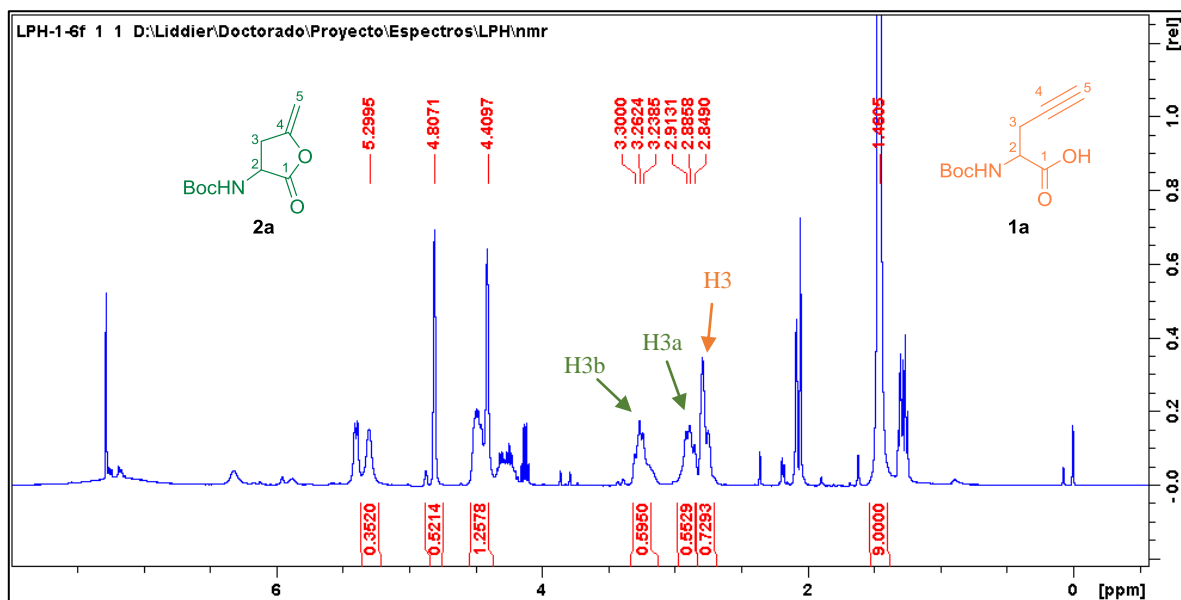
– Cycle 4



– Cycle 5



- Cycle 6



- Cycle 7

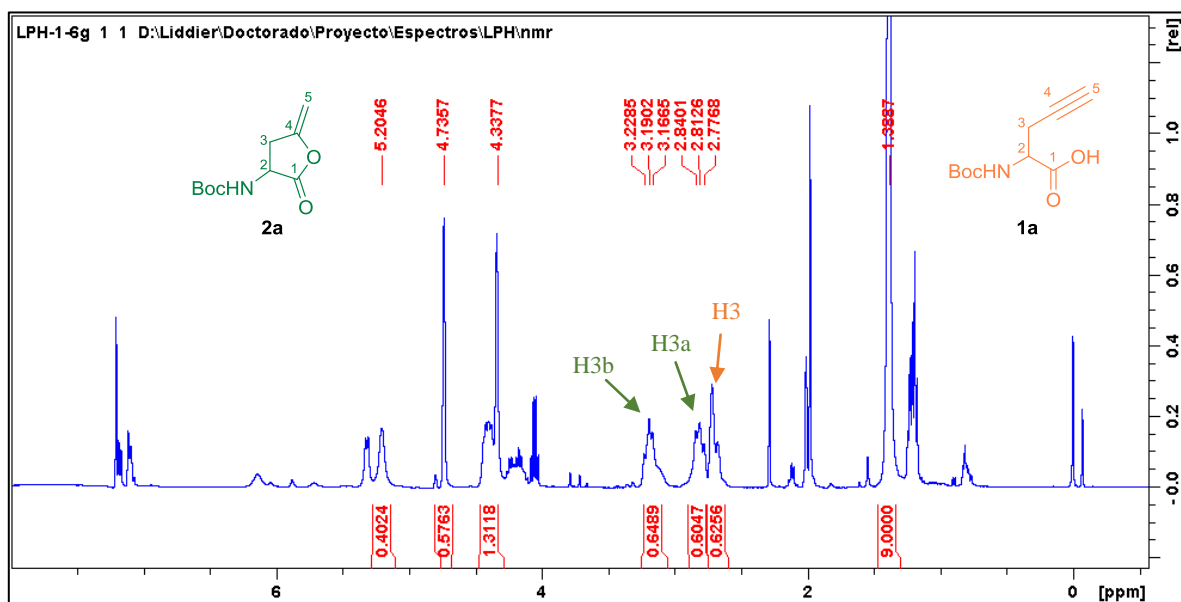
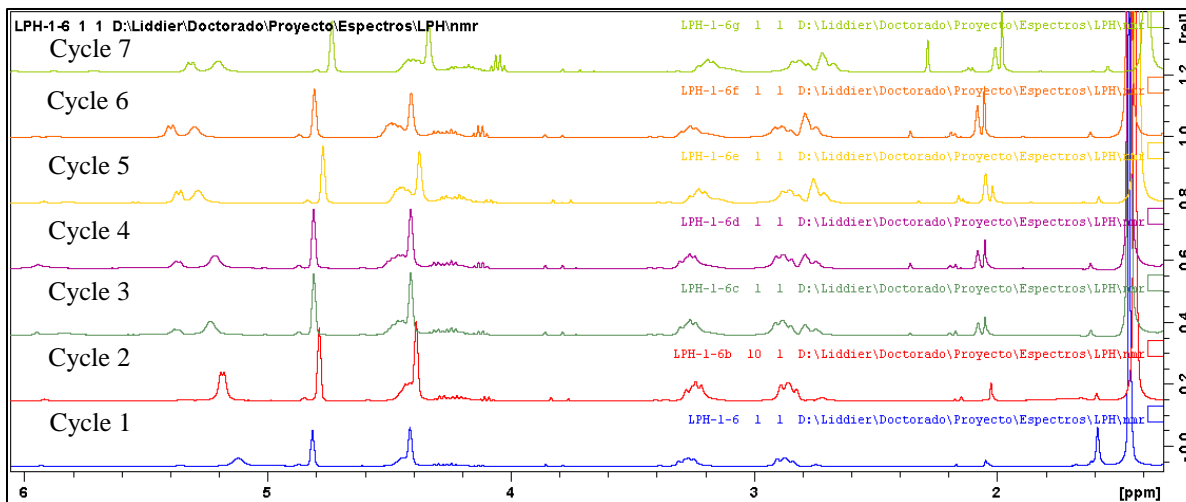


Figure S5. Comparison of reuse cycles of C3,  $^1\text{H}$  NMR spectra obtained after 1 h at room temperature.

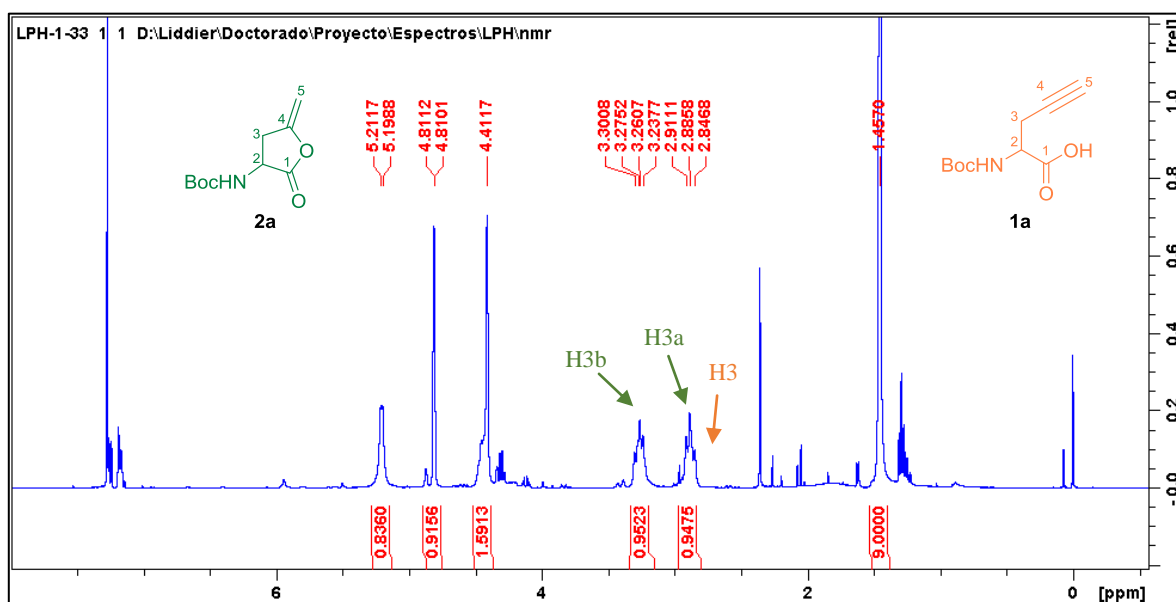




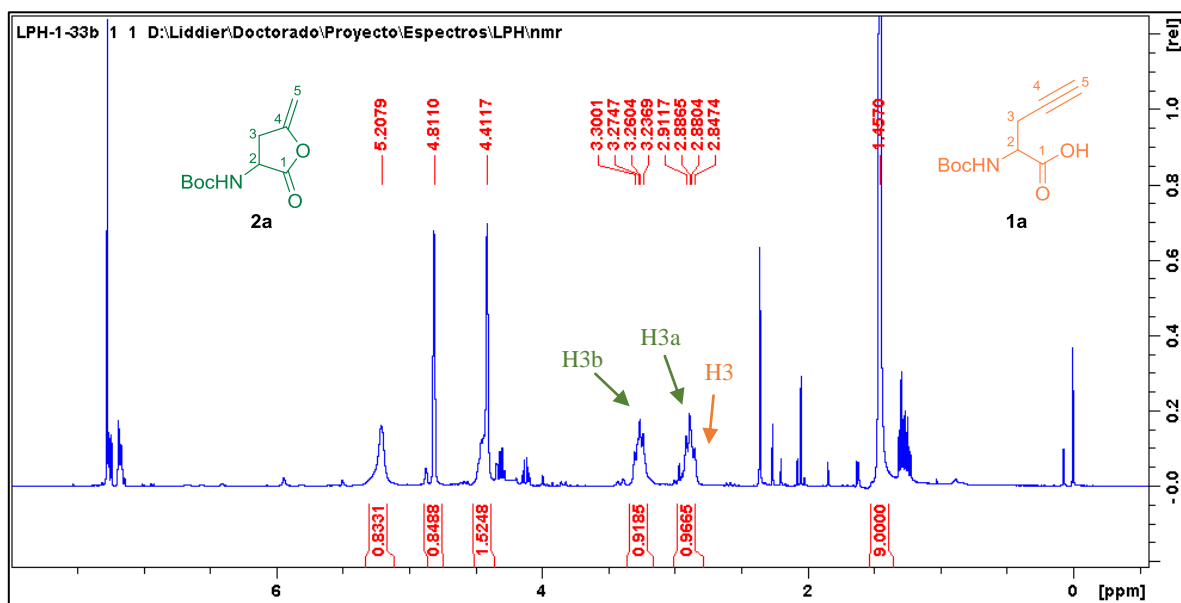
**Table S4. C4** (1 mol%) catalyst reuse cycles

Cycle	Substrate (mg)	Product (mg)	Isolated Yield %	Ratio (Product/Substrate)	Conversion by <sup>1</sup> H NMR %
1	29.8	29.3	98.3	1 : 0	99.0
2	29.7	29.0	97.6	1 : 0	99.0
3	29.6	29.0	97.9	18 : 2	90.0
4	30.2	27.5	91.0	4.3 : 2	68.2
5	29.8	27.8	93.2	6.9 : 2	77.8
6	29.8	27.6	92.6	11.6 : 2	85.6
7	30.5	26.3	86.2	3.5 : 2	63.6

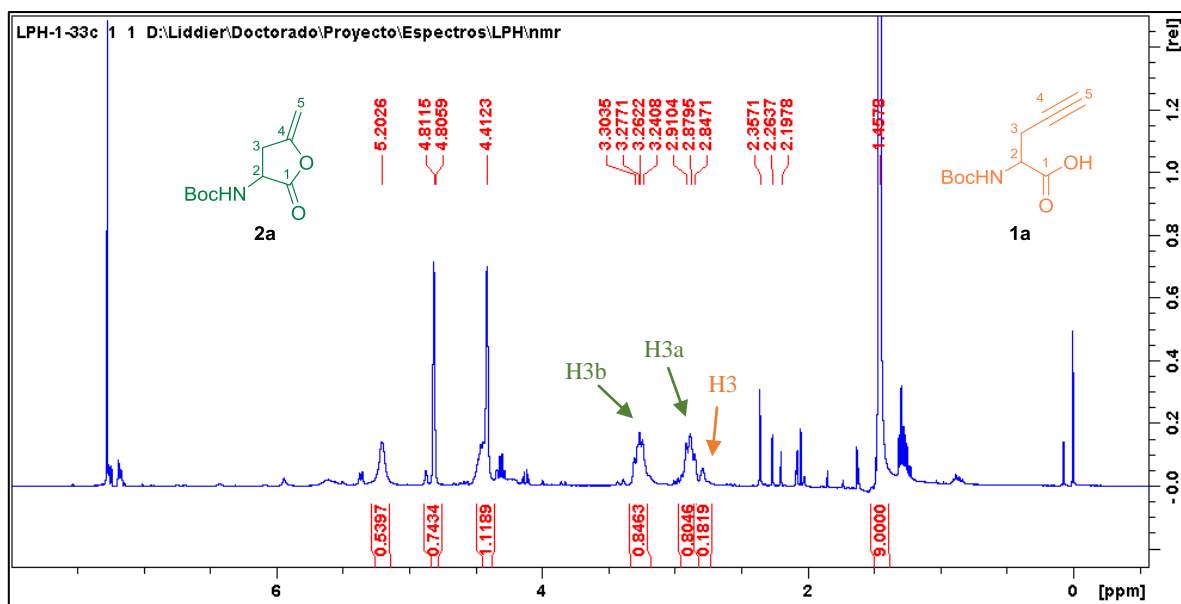
– Cycle 1



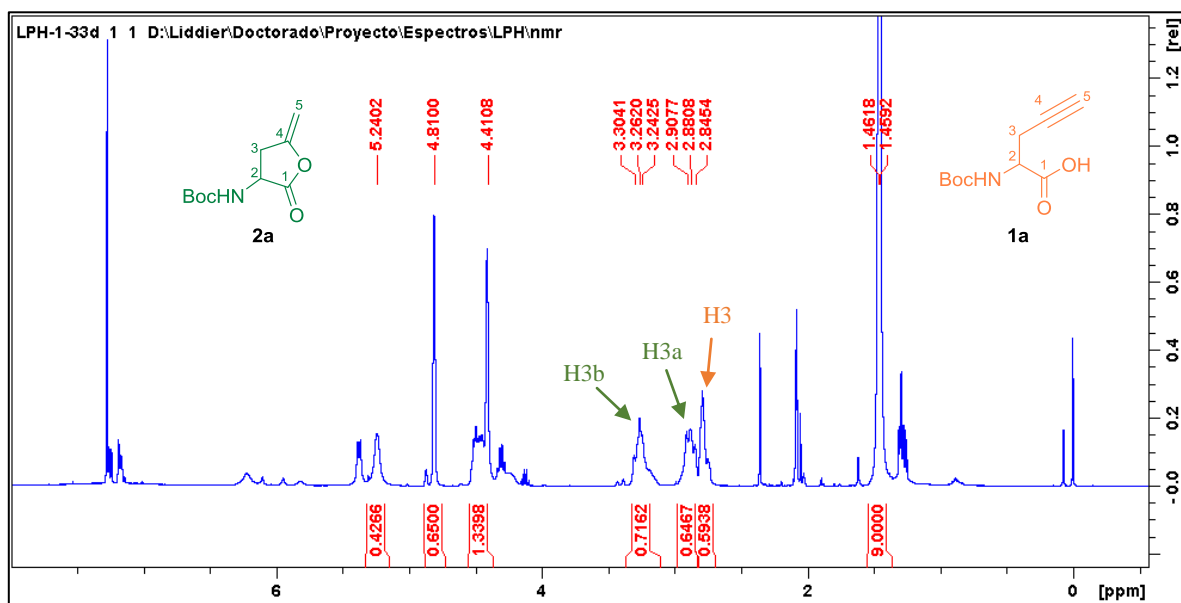
- Cycle 2



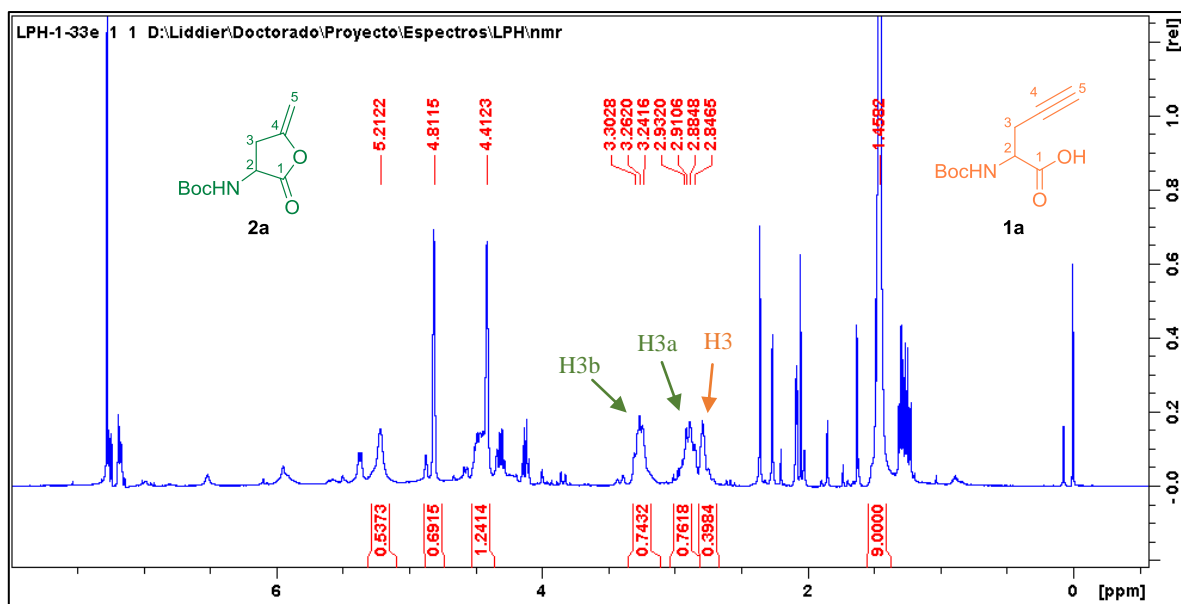
- Cycle 3



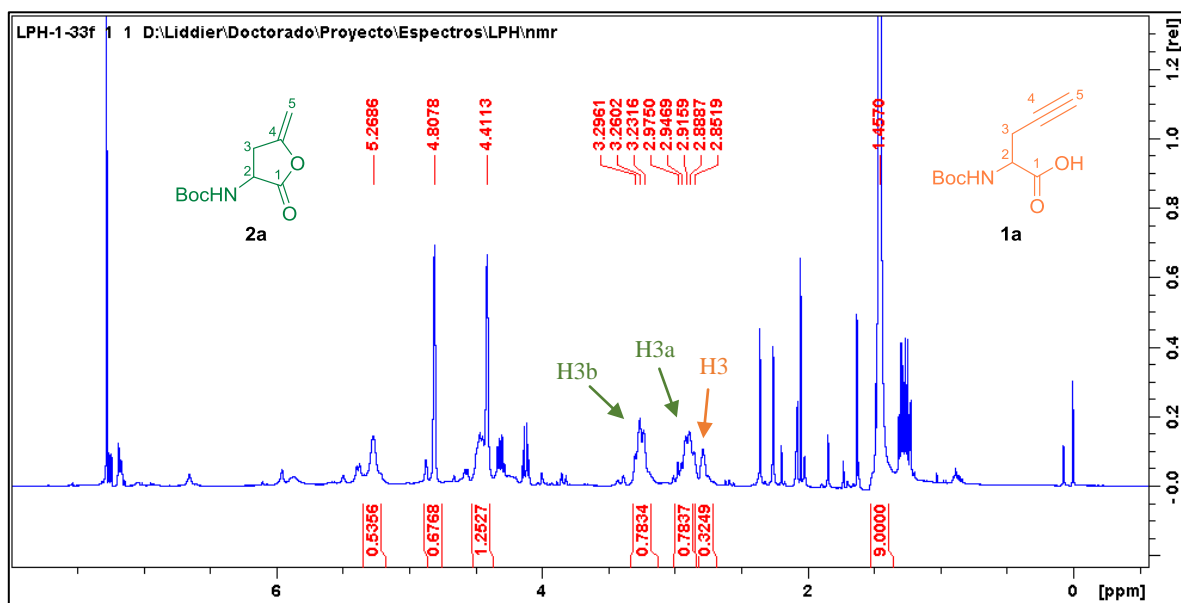
- Cycle 4



- Cycle 5



- Cycle 6



- Cycle 7

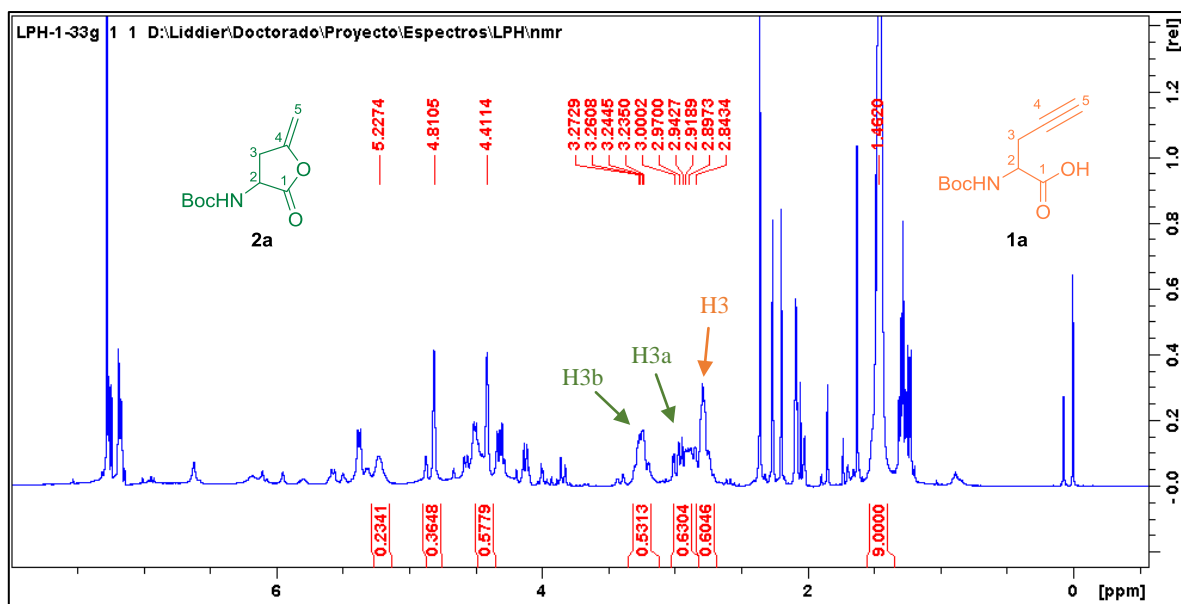
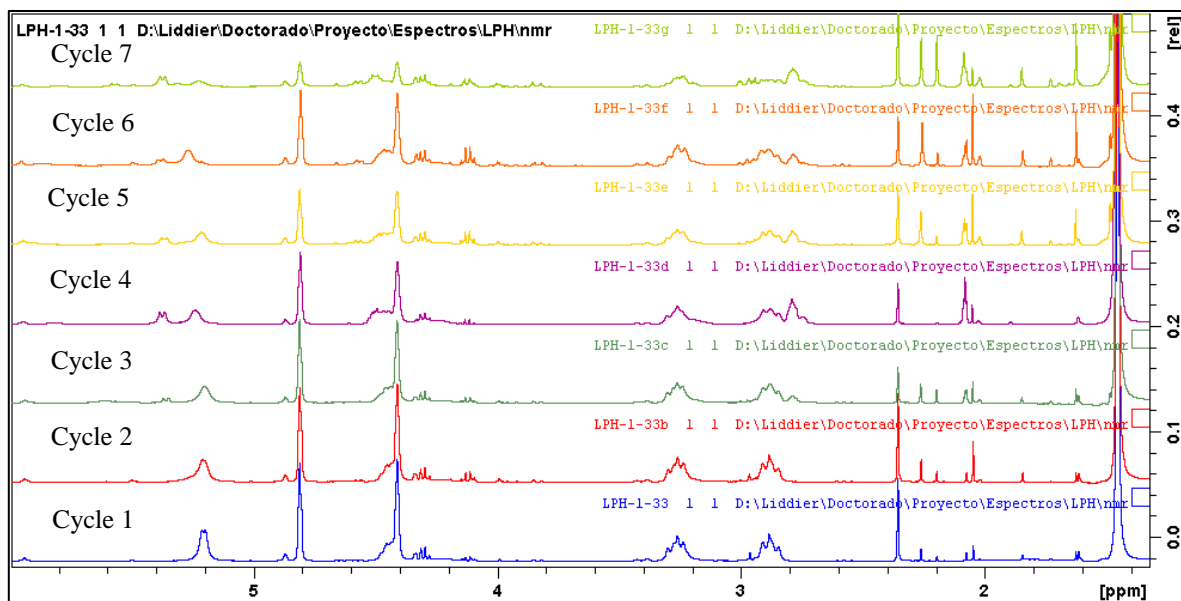


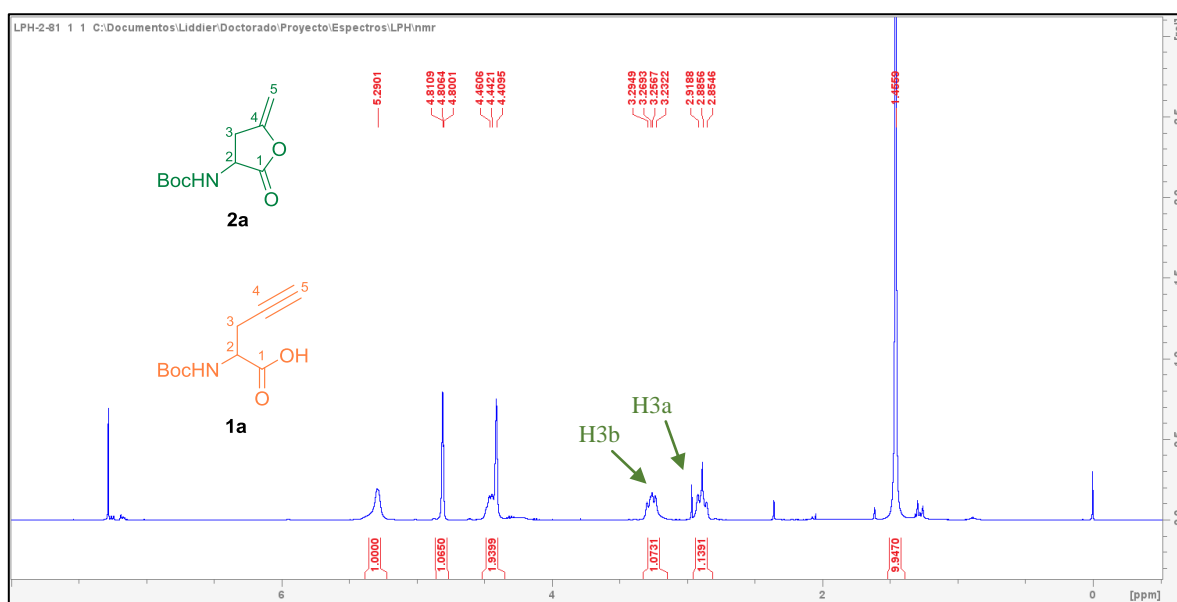
Figure S6. Comparison of reuse cycles of C4,  $^1\text{H}$  NMR spectra obtained after 1 h at room temperature.



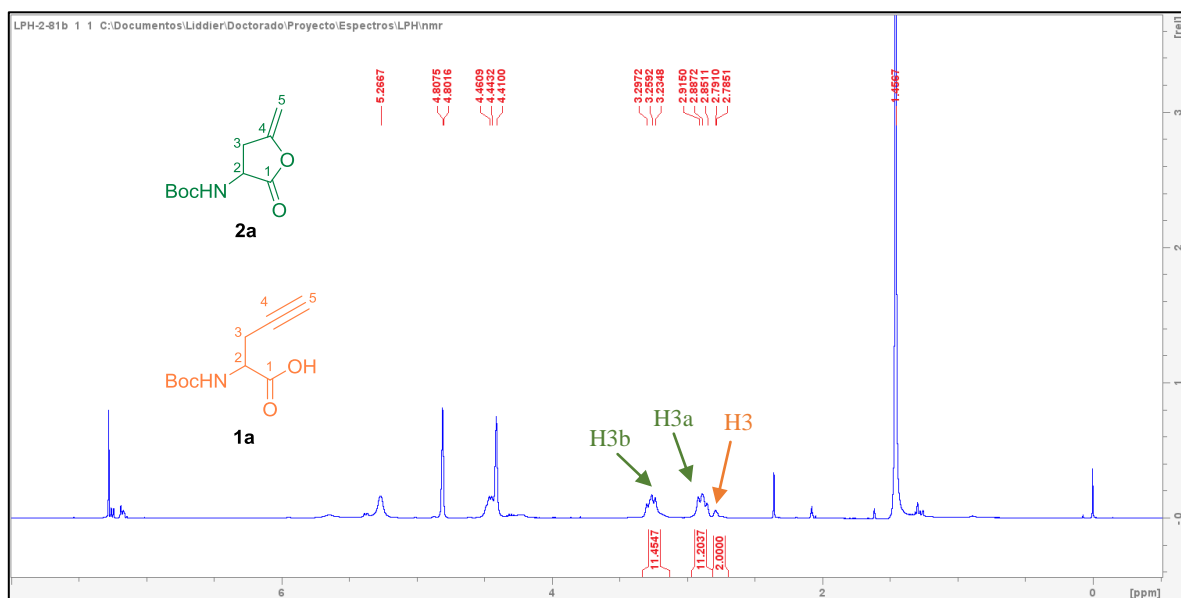
**Table S5. C5 (1 mol%) catalyst reuse cycles**

Cycle	Substrate (mg)	Product (mg)	Isolated Yield %	Ratio (Product/Substrate)	Conversion by <sup>1</sup> H NMR %
1	30.1	26.1	86.7	1:0	99.9
2	30.0	28.8	96.0	11.4:1	91.5
3	30.5	29.5	96.7	5.5:1	84.6
4	30.3	24.6	81.2	8.1:1	89.0
5	30.9	27.6	89.3	6:1	85.7
6	30.3	31.0	100	3.6:1	78.4
7	30.0	29.3	97.6	2.3:1	70.0
8	30.1	31.2	100	3.2:1	77.3
9	30.5	31.1	100	1.8:1	64.9

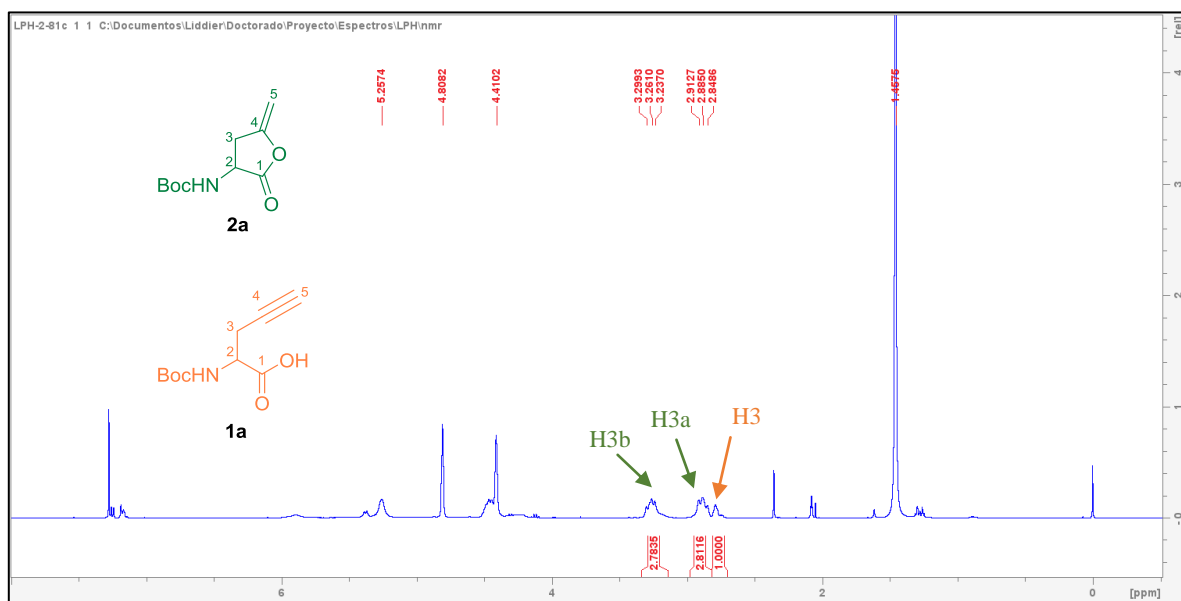
– Cycle 1



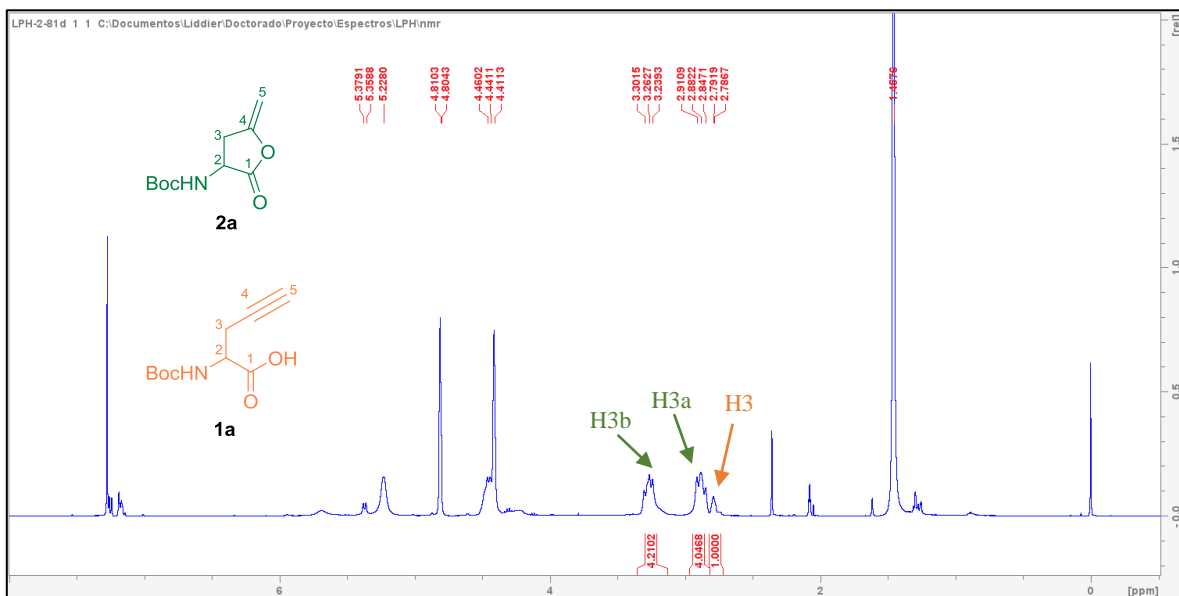
– Cycle 2



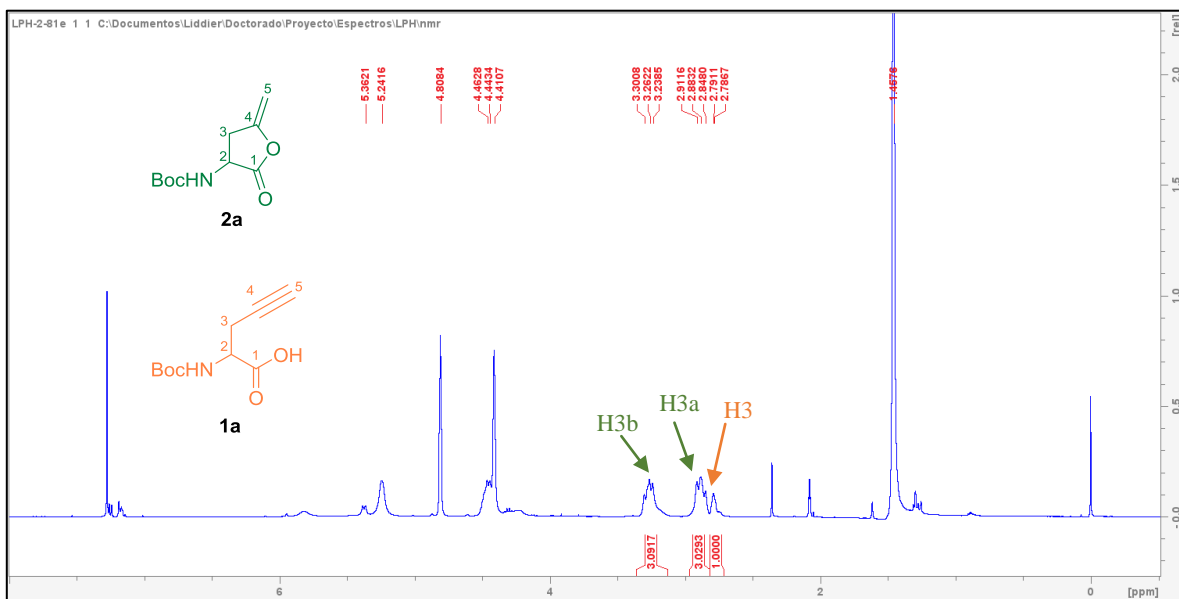
– Cycle 3



– Cycle 4

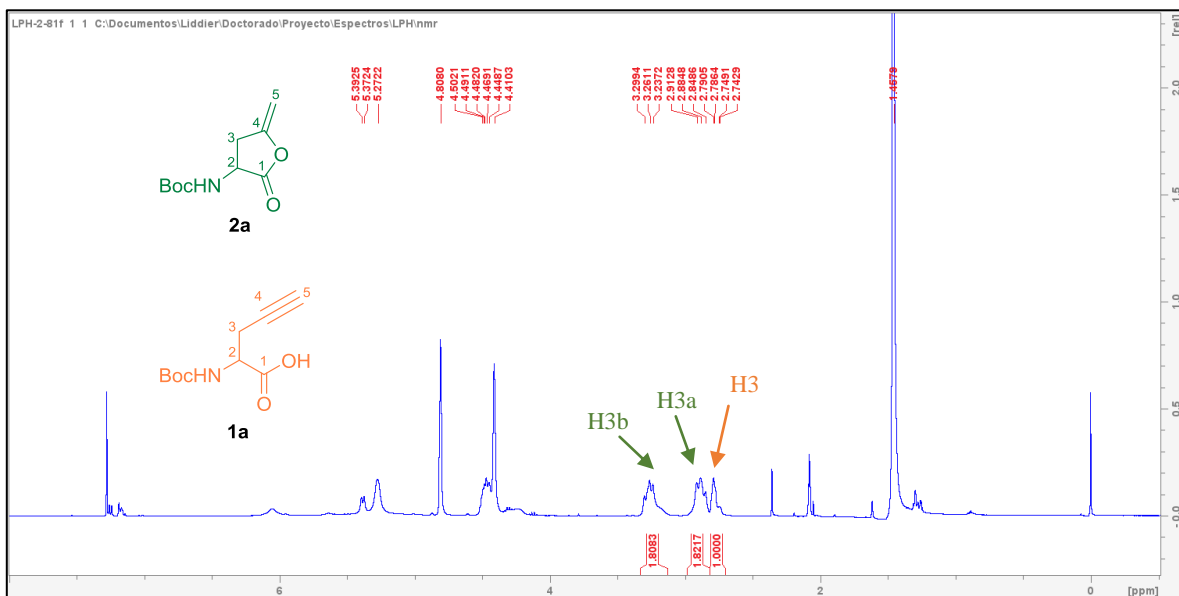


– Cycle 5

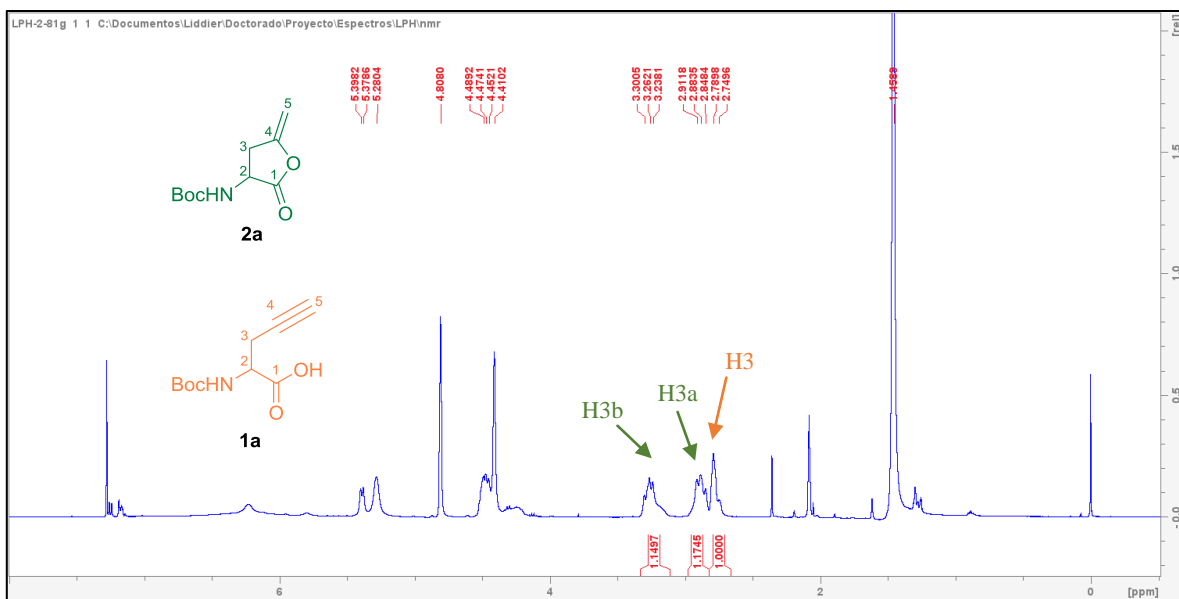




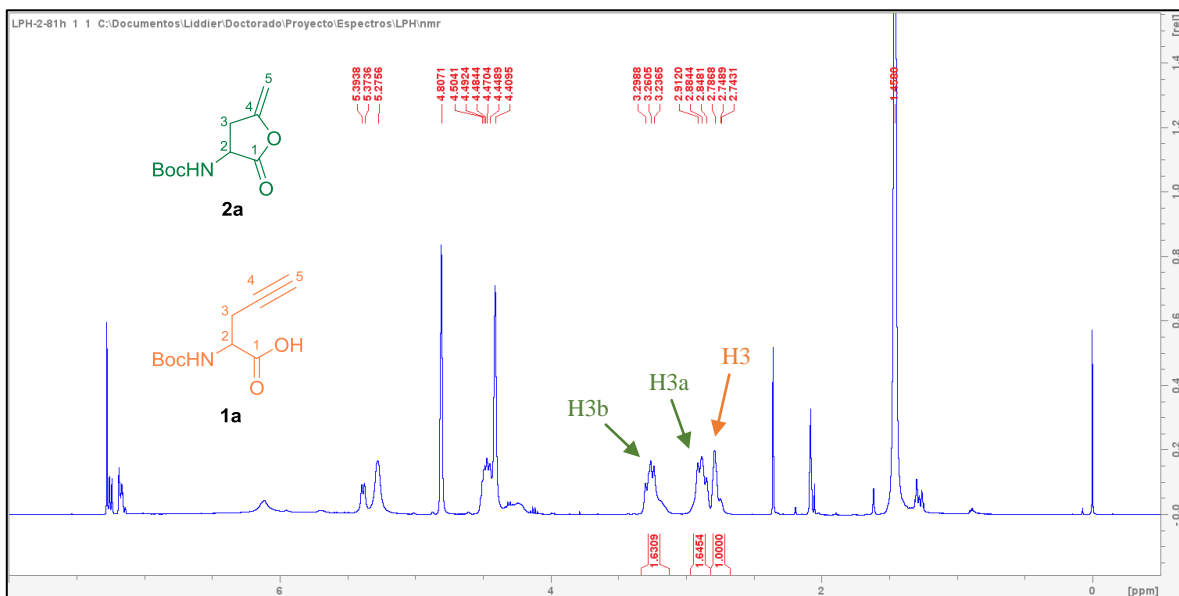
– Cycle 6



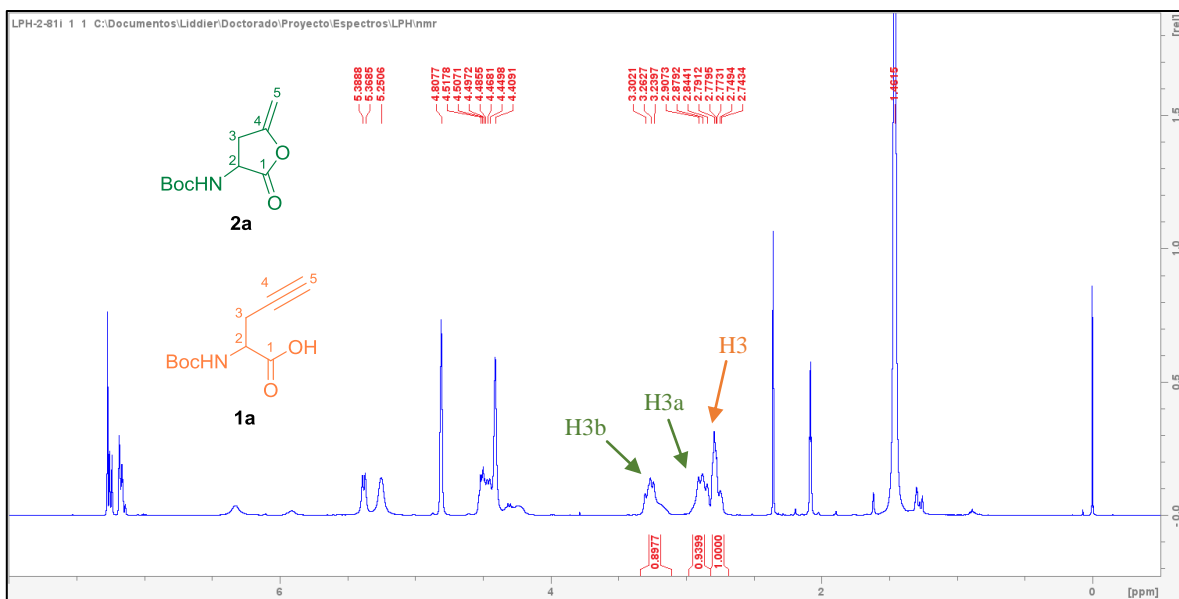
– Cycle 7



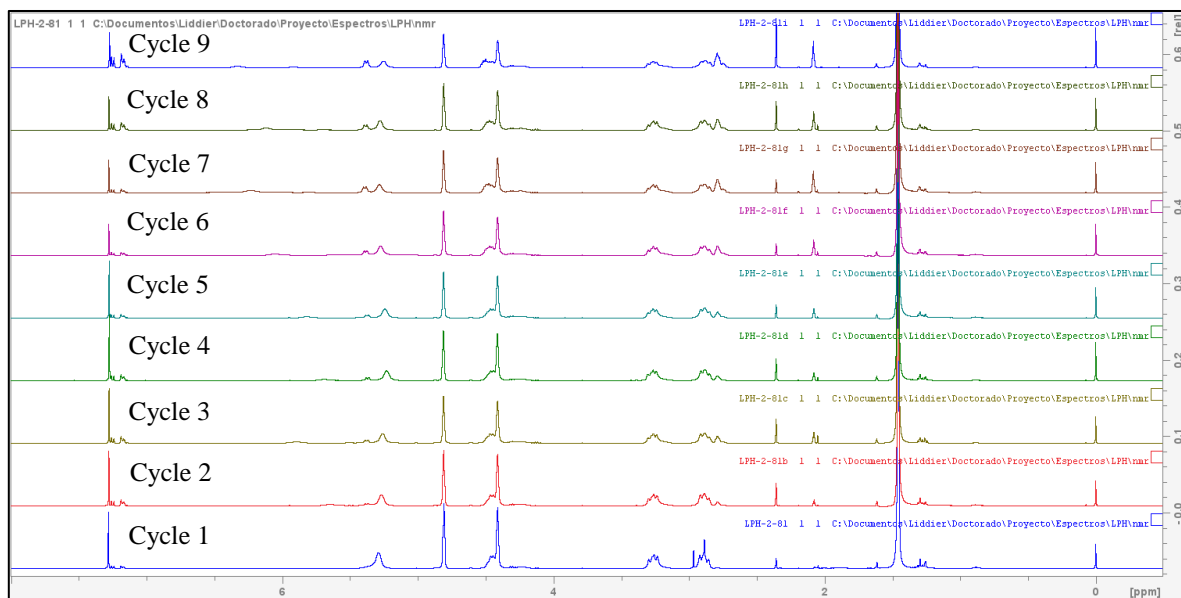
– Cycle 8



– Cycle 9



**Figure S7. Comparison of reuse cycles of C5,  $^1\text{H}$  NMR spectra obtained after 1 h at room temperature.**



#### 4. KINETIC STUDY ON THE FORMATION OF ENOL-LACTONE 2a MONITORED BY GC-FID.

##### 4.1. Kinetic 1:

Table S6. Peak area values of samples analyzed by GC-FID.

Vial	Time	Standard (mg)	Product concentration (mg P/ mL)	Product Area	Standard Area
1	1	10	1,242433718	16090	181445
2	2	10	1,811438046	48684	376552
3	3	10	1,999589561	22854	160134
4	4	10	2,516996986	28120	156529
5	5	10	3,189450807	30961	136007
6	10	10	5,668895147	68903	170295
7	20	10	6,186182507	81582	184771
8	30	10	6,109503101	81899	187817
9	45	10	6,204860531	75289	170005
10	50	10	6,17497284	106294	241177

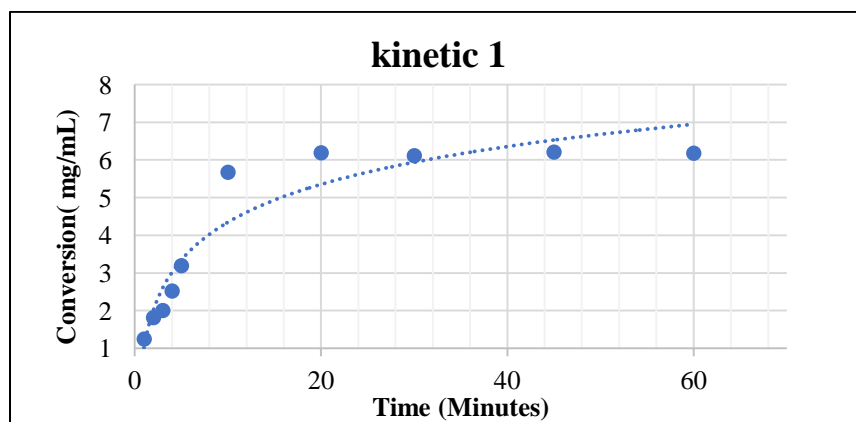


Figure S8. Time course of formation of enol-lactone 2a monitored by GC-FID (kinetic 1).

##### 4.1.1. Comparison of chromatograms of samples taken from kinetics 1 for the product in the GC-FID.

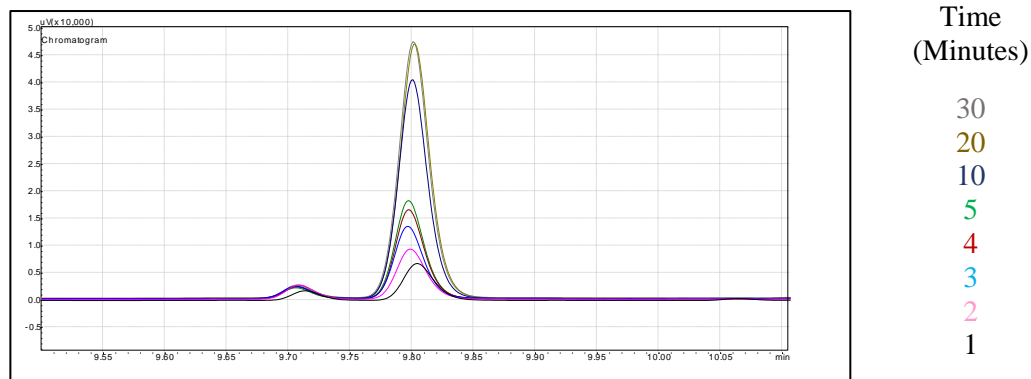


Figure S9. Time-resolved GC-FID chromatograms of the formation of product 2a (kinetic 1).

## 4.2. Kinetic 2:

Table S7. Peak area values of the samples analyzed by GC-FID for kinetic 2.

Vial	Time	Standard (mg)	Product concentration (mg P/ mL)	Product Area	Standard Area
1	1	10	0,25604795	3784	207058
2	2	10	1,031370424	14500	196977
3	3	10	1,882066273	21971	163560
4	4	10	2,725647266	39231	201661
5	5	10	3,527555948	56506	224431
6	10	10	5,679940517	94643	233457
7	20	10	5,363590237	93533	244327
8	30	10	5,640462358	95360	236872
9	45	10	5,913303147	82149	194641
10	50	10	5,458645227	88371	226823

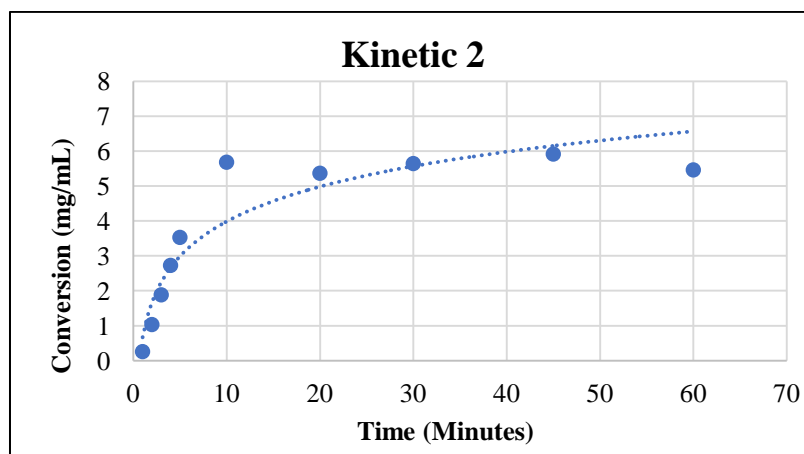


Figure S10. Time course of formation of enol-lactone **2a** monitored by GC-FID (kinetic 2).

### 4.2.1. Comparison of chromatograms of samples taken from kinetics 2 for the product in the GC-FID.

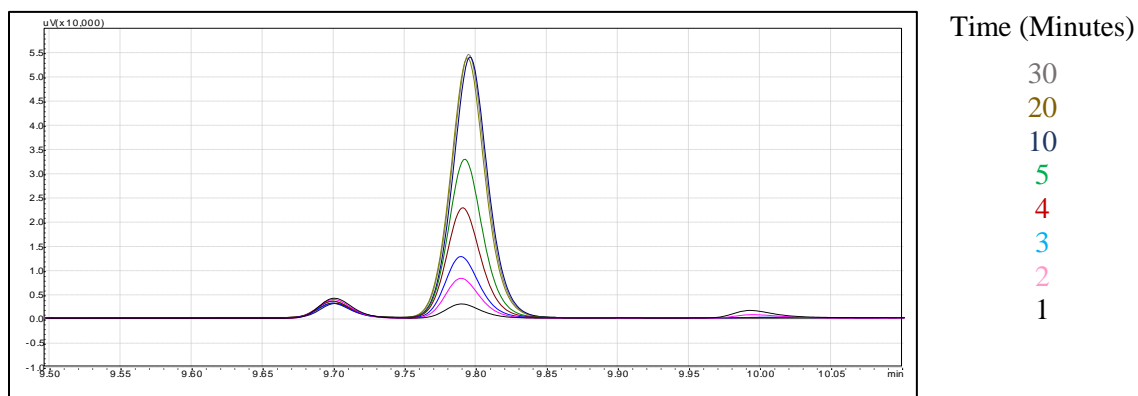
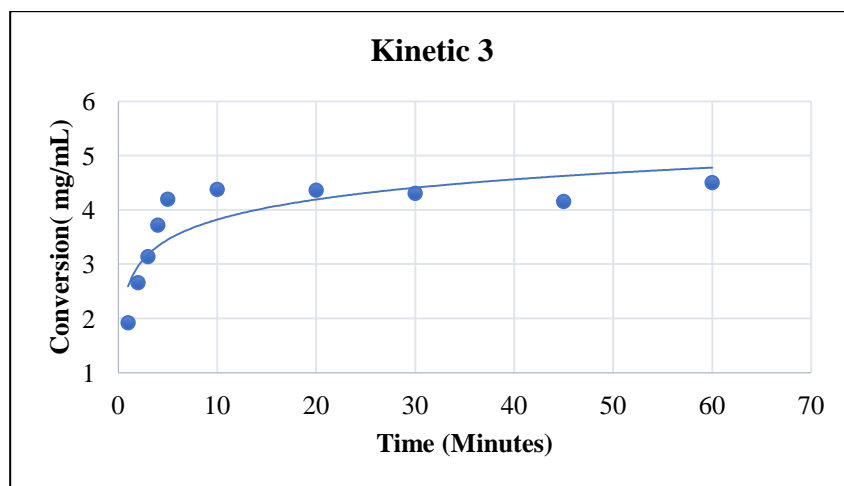


Figure S11. Time-resolved GC-FID chromatograms of the formation of product **2a** (kinetic 2).

### 4.3. Kinetic 3:

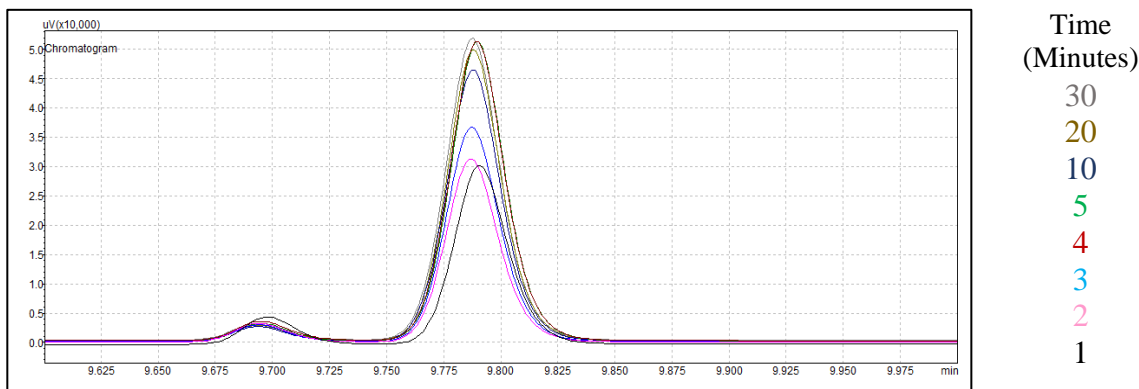
**Table S8.** Peak area values of the samples analyzed by GC-FID for kinetic 3.

Vial	Time	Standard (mg)	Product concentration (mg P/ mL)	Product Area	Standard Area
1	1	10	1,920340885	52861	385673
2	2	10	2,658957292	53581	282333
3	3	10	3,138531122	64003	285717
4	4	10	3,719363842	89478	337062
5	5	10	4,196990406	89488	298737
6	10	10	4,377943098	80590	257913
7	20	10	4,36298502	86065	276379
8	30	10	4,305315027	90052	293056
9	45	10	4,155594834	81301	274110
10	50	10	4,502624137	78529	244358



**Figure S12.** Time course of formation of enol-lactone **2a** monitored by GC-FID (kinetic 3).

#### 4.3.1. Comparison of chromatograms of samples taken from kinetics 3 for the product in the GC-FID.



**Figure S13.** Time-resolved GC-FID chromatograms of the formation of product **2a** (kinetic 3).

#### 4.4. Comparison of the three kinetics

Table S9. Average of kinetics 1, 2 and 3 and standard deviation.

Time	Standard (mg)	Conversion k1 (mg/mL)	Conversion k2 (mg/mL)	Conversion k3 (mg/mL)	Average (mg/mL)	Standard deviation	Error
1	10	1,242433718	0,25604795	1,920340885	1,139607518	0,836897643	0,483183079
2	10	1,811438046	1,031370424	2,658957292	1,833921921	0,814026349	0,469978332
3	10	1,999589561	1,882066273	3,138531122	2,340062319	0,693986494	0,400673289
4	10	2,516996986	2,725647266	3,719363842	2,987336031	0,642481339	0,370936774
5	10	3,189450807	3,527555948	4,196990406	3,637999053	0,512769218	0,296047446
10	10	5,668895147	5,679940517	4,377943098	5,242259587	0,748540410	0,432170007
20	10	6,186182507	5,363590237	4,36298502	5,304252588	0,913045994	0,527147350
30	10	6,109503101	5,640462358	4,305315027	5,351760162	0,936101154	0,540458253
45	10	6,204860531	5,913303147	4,155594834	5,424586171	1,108605289	0,640053562
60	10	6,17497284	5,458645227	4,502624137	5,378747401	0,839032355	0,484415556

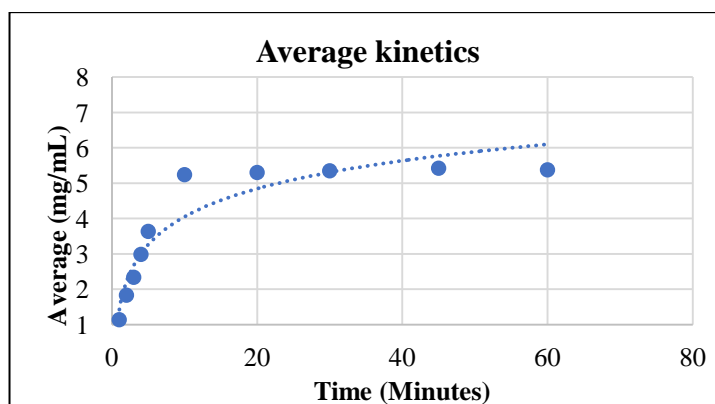


Figure S14. Average of kinetics.

#### 4.4.1. Graph of calculated average and error in the gold-catalyzed conversion of 1a into 2a.

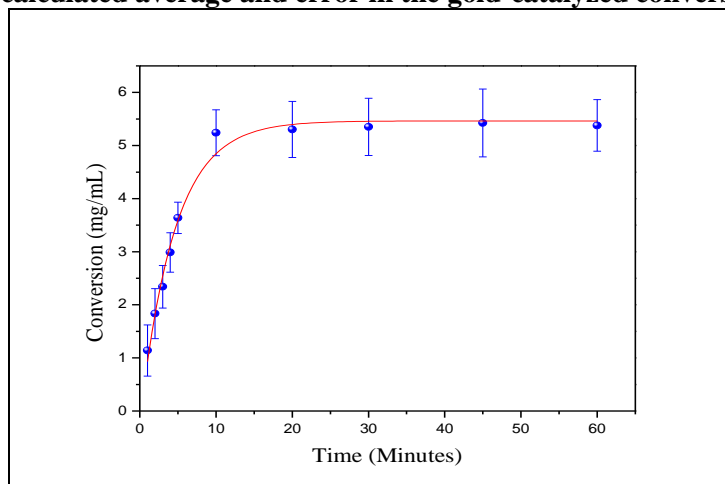


Figure S15. Progress of the conversion in relation to time of **1a** (0.14 mmol) into **2a** using toluene:water (2 mL:2 mL) as a medium at room temperature with 1 mol% of **C1**. Fit to equation  $f=a*(1-\exp(-b*x))$  (Exponential Rise to Maximum, Single, 2 Parameter; using program SigmaPlot 12)

## 5. REFERENCES

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