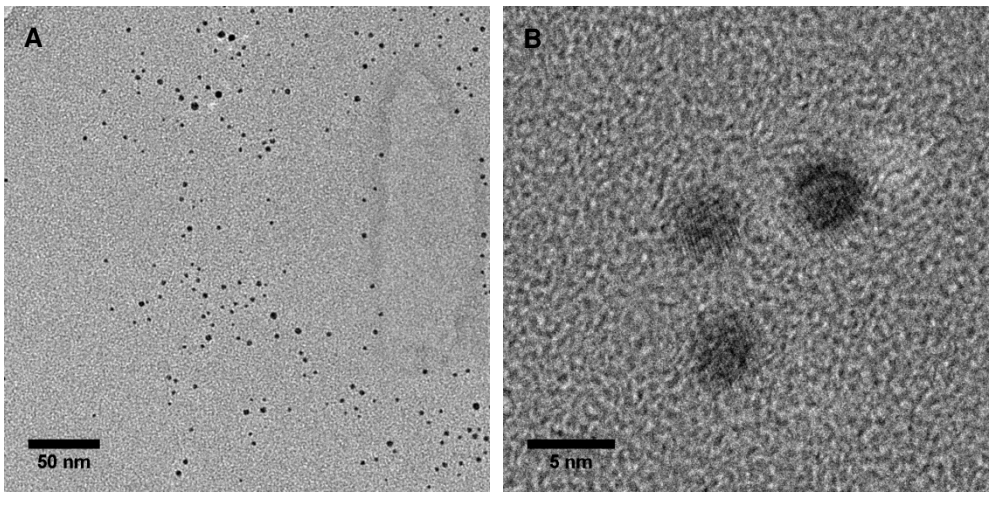
ELECTRONIC SUPPORTING INFORMATION (ESI)

FOR NEW JOURNAL OF CHEMISTRY

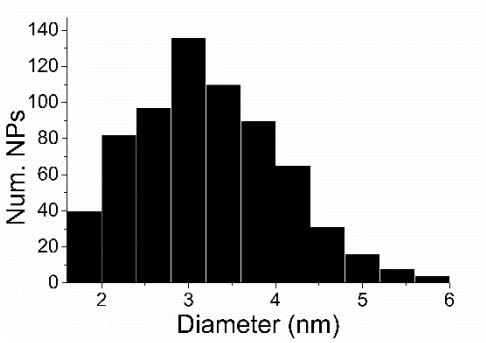
Gold nanoparticles stabilized by PEG-tagged imidazolium salts as recyclable catalysts for the synthesis of propargylamines and the cycloisomerization of γ-alkynoic acids

Guillem Fernández,[a] Laura Bernardo,[a] Ana Villanueva,[a] and Roser Pleixats*[a

Figure S1. TEM images and size distribution histogram of **M2'**



C



(A) TEM image of **M2'**; (B) HRTEM image of **M2'**; (C) Size distribution histogram of **M2'**.

Figure S2. XPS spectra (Au) of **M1A**, **M1B**, **M2'** and **M2 recycled**

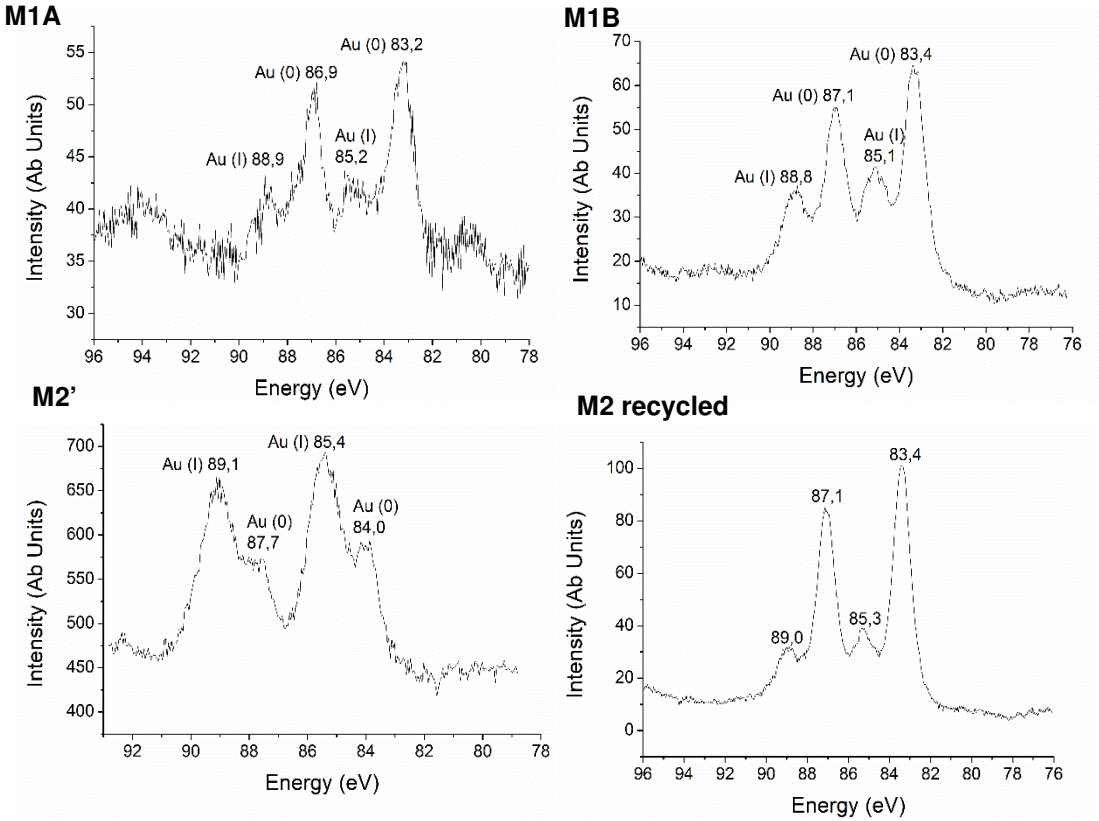


Figure S3. XPS spectra (Cl) of **M2** and **M2'**

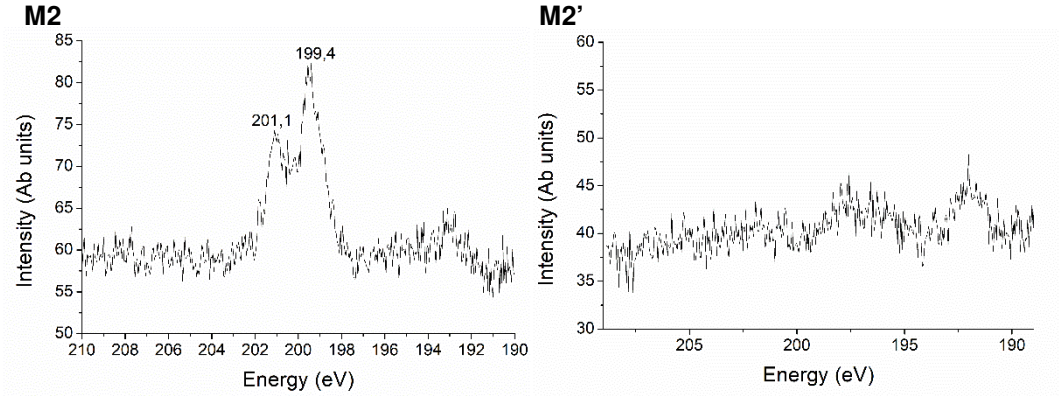
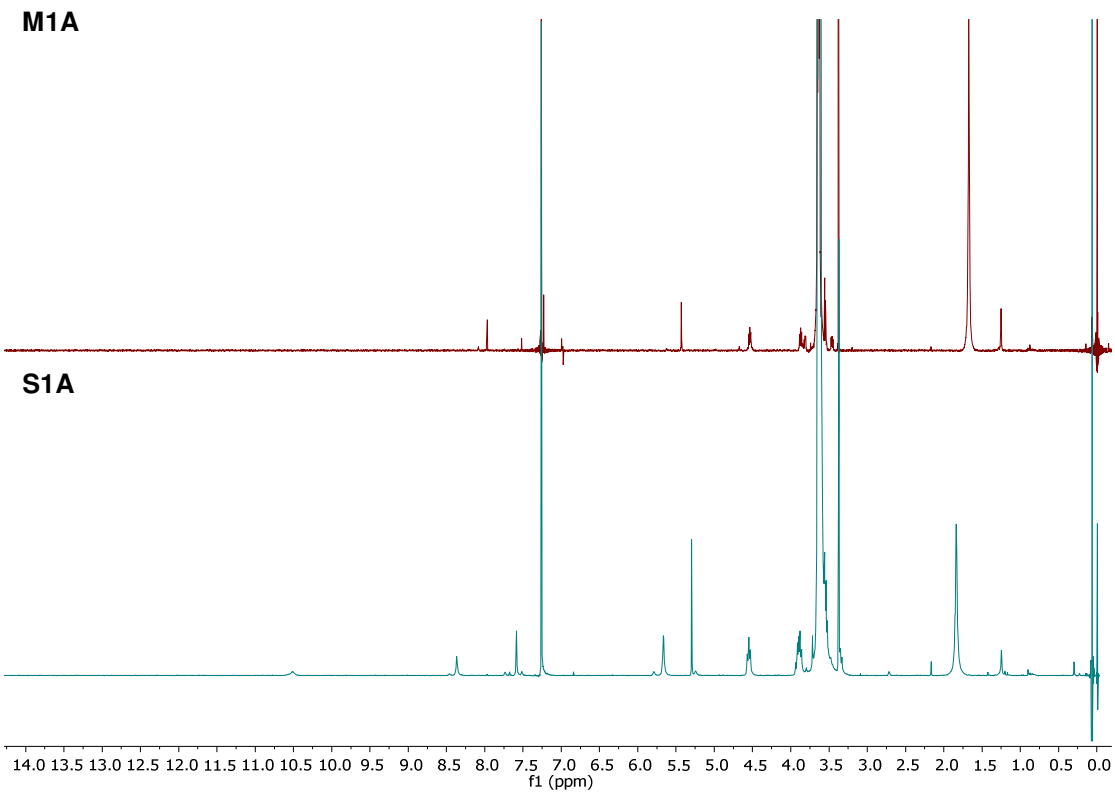
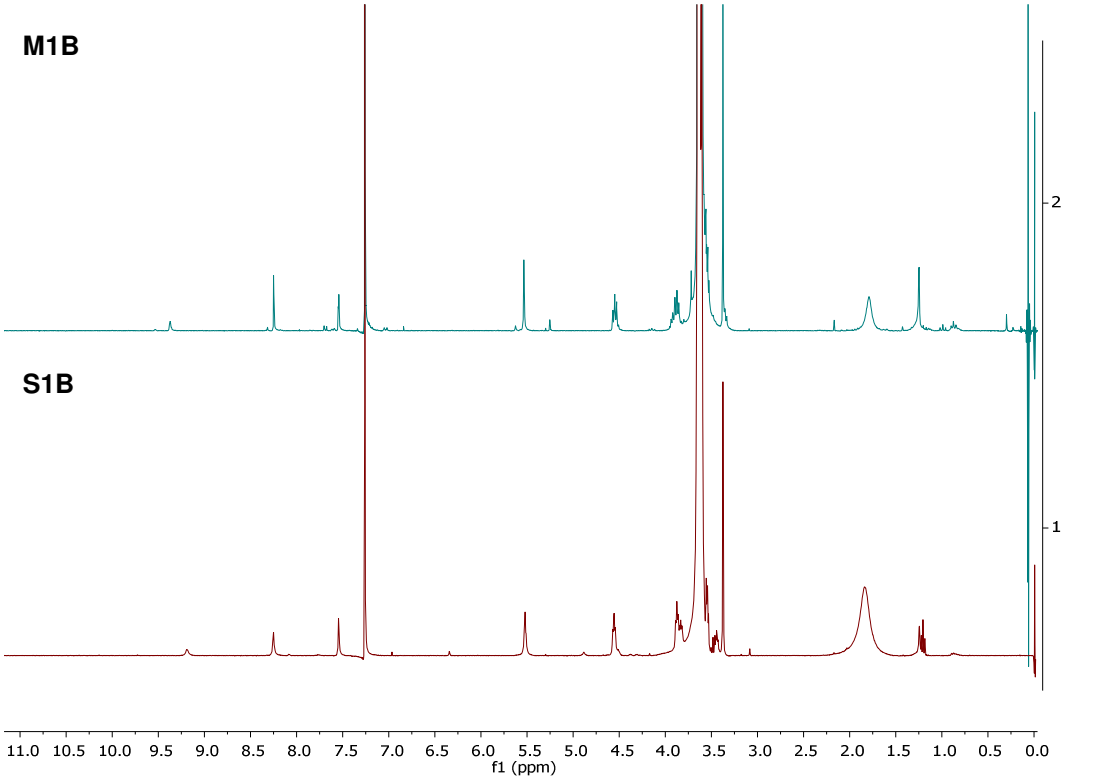
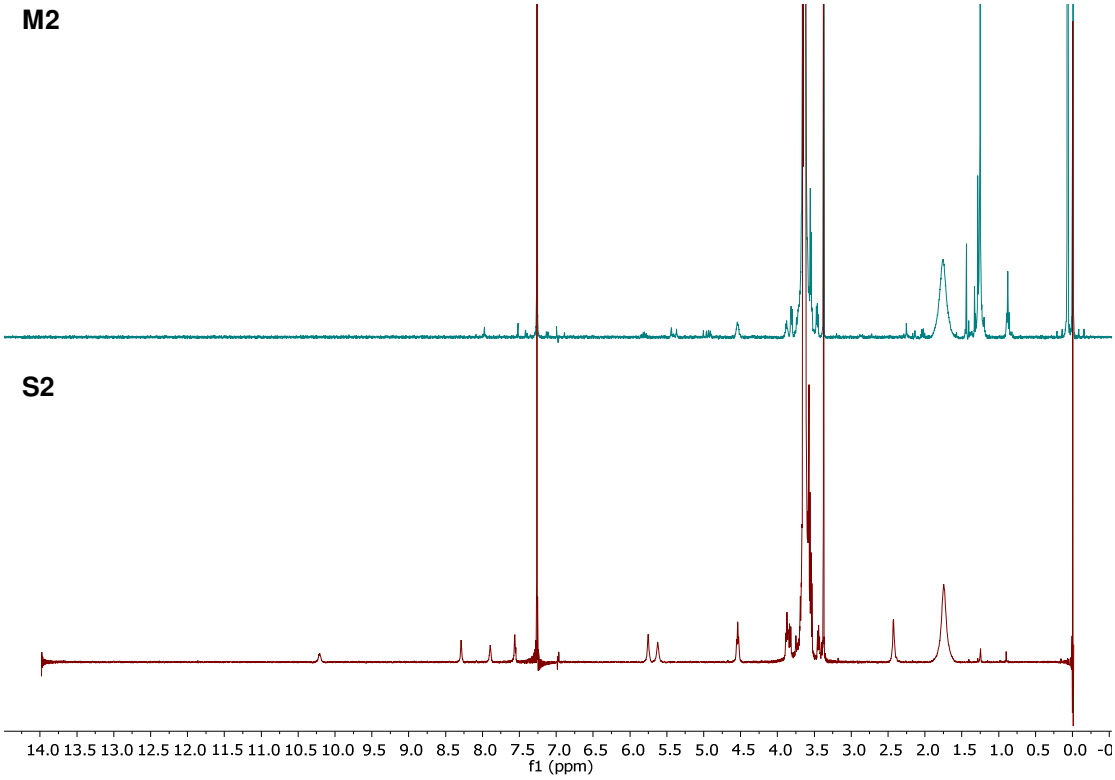


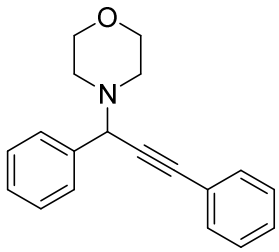
Figure S4. Comparison of ^{1}NMR spectra of **M1A**, **M1B** and **M2** with that of **S1A, S1B** and **S2**




M1B
S1B
2
1
11.0 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)

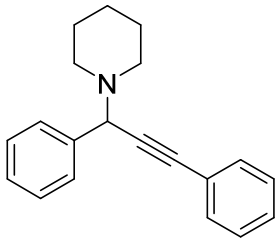

M2
S2
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

Spectral data of propargylamines **8** and **10**



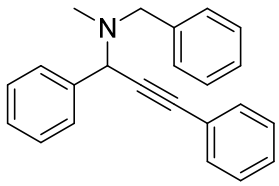
4-(1,3-Diphenylprop-2-yn-1-yl)morpholine ***8aaa***[1]

Brown oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.64-7.70 (m, 2H), 7.52-7.57 (m, 2H), 7.32-7.40 (m, 6H), 4.81 (s, 1H), 3.70-3.80 (m, 4H), 2.62-2.69 (m, 4H).



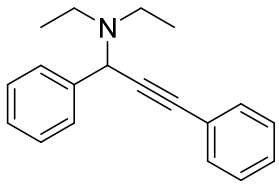
1-(1,3-Diphenylprop-2-yn-1-yl)piperidine ***8aba***[1]

Brown oil (56 %). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.63-7.70 (m, 2H), 7.52-7.57 (m, 2H), 7.39-7.27 (m, 6H), 4.82 (s, 1H), 2.58 (t, *J* = 5.4 Hz, 4 H), 1.54-1.68 (m, 4H), 1.42-1.53 (m, 2H).



N-Benzyl-N-methyl-1,3-diphenylprop-2-yn-1-amine ***8aca***[1]

Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.69-7.76 (m, 2H), 7.58-7.65 (m, 2H), 7.26-7.49 (m, 11H), 4.97 (s, 1H), 3.73 (AB system, *J* = 13.2 Hz, 2H), 2.29 (s, 3H).



N,N-Diethyl-1,3-diphenylprop-2-yn-1-amine ***8ada***[2]

Brown oil (46 %) ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.69-7.73 (m, 2H), 7.50-7.55 (m, 2H), 7.30-7.40 (m, 6H), 5.08 (s, 1H), 2.54-2.69 (m, 4H), 1.10 (t, *J* = 7.2 Hz, 6H).

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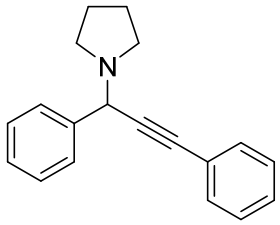
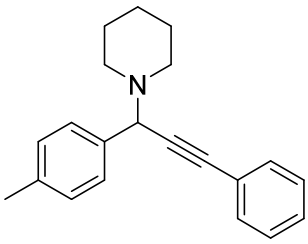
[1] Albadalejo, M. J.; Alonso, F.; Moglie, Y.; Yus, M.; *Eur. J. Org. Chem.* 2012, 3093-3104

[2] Lin, Z.; Yu, D.; Zhang, Y. *Tetrahedron Lett.* 2011, ***52***, 4967-4970.



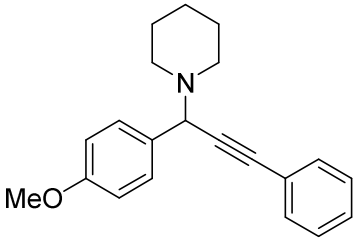
1-(1,3-Diphenylprop-2-ynyl)pyrrolidine ***8aea***[3]

Brown oil. ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.59-7.64 (m, 2H), 7.46-7.51 (m, 2H), 7.28-7.38 (m, 6H), 4.93 (s, 1H), 2.69-2.77 (m, 4H), 1.70-1.86 (m, 4H).



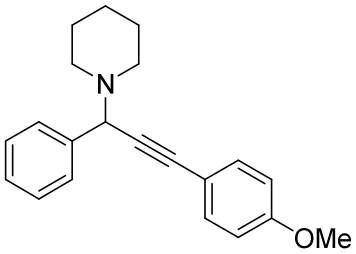
1-(3-Phenyl-1-(p-tolyl)prop-2-yn-1-yl)piperidine ***8bba***[4]

Brown oil. ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.54-7.51 (m, 4H), 7.34-7.31 (m, 3H), 7.20-7.16 (m, 2H), 4.77 (s, 1H), 2.60-2.52 (m, 4H), 2.37 (s, 3H), 1.64-1.54 (m, 4H), 1.48-1.40 (m, 2H).



1-[1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl]piperidine ***8cba***[1]

Brown oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.56-7.48 (m, 4H), 7.34-7.30 (m, 3H), 6.91-6.86 (m, 2H), 4.75 (s, 1H), 3.82 (s, 3H), 2.59-2.52 (m, 4H), 1.64-1.54 (m, 4H), 1.48-1.40 (m, 2H).

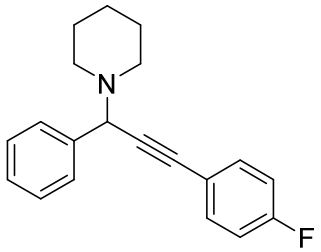


1-[3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-yl]piperidine ***8abc***[1]

[3] Kar-Yan Lo, V.; Ka-Yan Kung, K.; Wong, M.-K.; Che, C.-M. *J. Organomet. Chem.* 2009, **694**, 583-591.

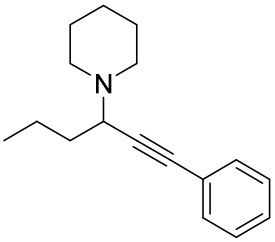
[4] Samai, S.; Nandi, G. C.; Singh, M. S. *Tetrahedron Lett.*, 2010, **51,** 5555-5558.

Pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.69-7.65 (m, 2H), 7.51-7.45 (m, 2H), 7.42-7.27 (m, 3H), 6.86-6.90 (m, 2H), 4.80 (s, 1H), 3.83 (s, 3H), 2.59 (t, *J* = 5.3 Hz, 4H), 1.67-1.57 (m, 4H), 1.51-1.42 (m, 2H).



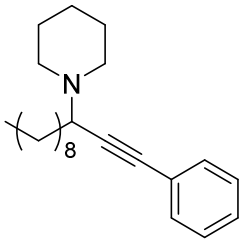
1-[3-(4-Fluorophenyl)-1-phenylprop-2-yn-1-yl]piperidine ***8abd***[5]

Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.65-7.61 (m, 2H), 7.53-7.47 (m, 2H), 7.40-7.30 (m, 3H), 7.06-6.99 (m, 2H), 4.78 (s, 1H), 2.56 (t, *J* = 5.1 Hz, 4H), 1.64-1.56 (m, 4H), 1.47-1.43 (m, 2H).



N-[4-(3-Phenyl-1-propyl-2-propynyl)]piperidine ***8dba***[6]

Pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.44-7.42 (m, 2H), 7.30-7.27 (m, 3H), 3.53-3.47 (m, 1H), 2.72-2.64 (m, 2H), 2.53-2.46 (m, 2H), 1.77-1.43 (m, 10H), 0.97 (t, *J* = 7.2 Hz, 3H).



1-(1-Phenyldodec-1-yn-3-yl)piperidine ***8eba***[1]

Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.46-7.41 (m, 2H), 7.32-7.26 (m, 3H), 3.50-3.44 (m, 1H), 2.73-2.64 (m, 2H), 2.53-2.44 (m, 2H), 1.75-1.25 (m, 22H), 0.88 (t, *J* = 6.6 Hz, 3H).

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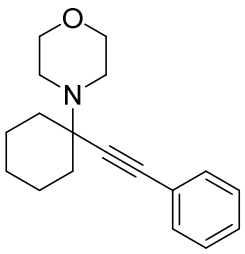
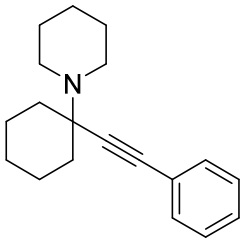
[5] Chng, L. L., Yang, J., Wei, Y., Ying, J. Y. *Adv. Synth. Catal.* 2009, **351**, 2887-2896

[6] Wang, M., Li, P., Wang, L. *Eur. J. Org. Chem.* 2008, 2255-2261



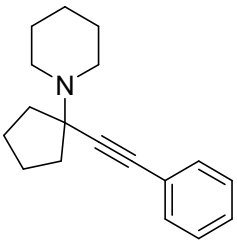
1-[1-(Phenylethynyl)cyclohexyl]morpholine ***10aaa***[1]

Pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.50-7.20 (m, 5H), 3.85-7.69 (m, 4H), 2.77-2.65 (m, 4H), 2.08-1.98 (m, 2H), 1.75-1.43 (m, 7H), 1.31-1.22 (m, 1H).



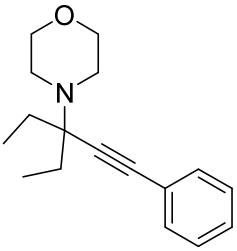
1-(1-(Phenylethynyl)cyclohexyl)piperidine ***10aba***[7]

Pale yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.48-7.42 (m, 2H), 7.31-7.27 (m, 3H), 2.73-2.64 (m, 4H), 2.17-2.03 (m, 2H), 1.86-1.44 (m, 13H), 1.28-1.21 (m, 1H).



1-(1-(Phenylethynyl)cyclopentyl)piperidine ***10bba***[8]

Pale yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.47-7.42 (m, 2H), 7.33-7.27 (m, 3H), 2.70-2.64 (m, 4H), 2.15-2.06 (m, 2H), 1.74-1.57 (m, 10H), 1.50-1.42 (m, 2H).



4-(1,1-diethyl-3-phenyl-2-propyn-1-yl)morpholine ***10caa***[9]

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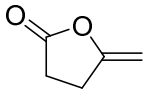
[7] Cheng, M.; Zhang, Q.; Hu, X.-Y.; Li, B.-G.; Ji, J.-X.; Chan, A.S.C. *Adv. Synth. Catal.* 2011, **353**, 1274-1278

[8] Hosseini-Sarvari, M.; Moeini, F. *New J. Chem.*, 2014, **38**, 624

[9] Katritzky, A. R., Yang, H., Singh, K. S. *J. Org. Chem.* 2005, **70**, 286-290

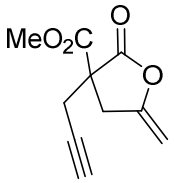
Colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.44-7.40 (m, 2H), 7.30-7.26 (m, 3H), 3.76-3.72 (m, 4H), 2.70-2.66 (m, 4H), 1.77-1.68 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 6H).

Spectral data of enol lactones **12**



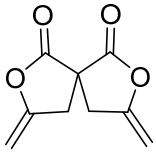
5-Methylenedihydrofuran-2(3H)-one ***12a***[10]

^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 4.82 (m, 1H), 4.39 (m, 1H), 2.98-2.93 (m, 2H), 2.78-2.73 (m, 2H).



Methyl 5-methylene-2-oxo-3-(prop-2-yn-1-yl)tetrahydrofuran-3-carboxylate ***12b***[10]

^{1}H NMR (360 MHz, CDCl3, ppm): δ 4.84 (m, 1H), 4.42 (m, 1H), 3.80 (s, 3H), 3.29-3.24 (m, 2H), 2.89 (d, *J* = 2.6 Hz, 2H), 2.08 (t, *J* = 2.6 Hz, 1H).



Dihydro-5-methylenefuran-2(3H)-one-3-spiro-dihydro-5'-methylenefuran-2'(3H)-one ***12c***[11]

^{1}H NMR (360 MHz, CDCl3, ppm): δ 4.94-4.91 (m, 1H), 4.51-4.49 (m, 1H), 3.47 (d, *J* = 16.2 Hz, 1H), 2.95 (d, *J* = 16.2 Hz, 1H)

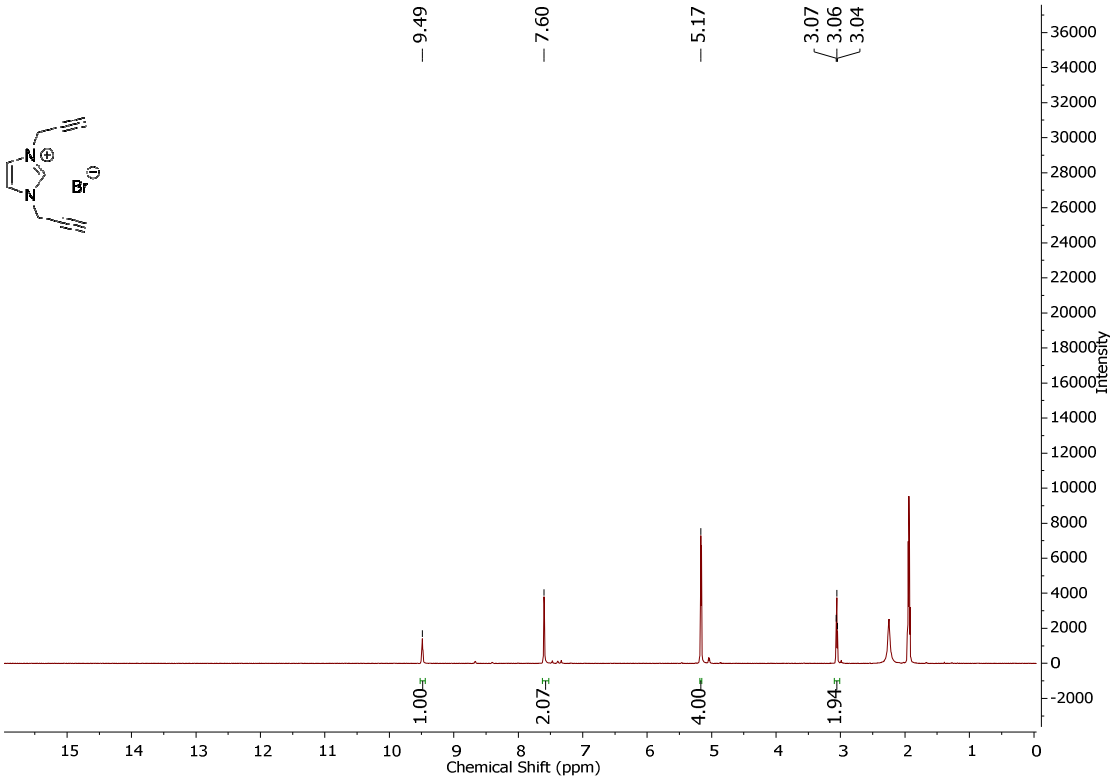
[10] Ferré, M.; Cattoën, X.; Wong Chi Man, M.; Pleixats, R. *ChemCatChem,* 2016, **8**, 2824-2831

[11] Alemán, J.; Solar, V.; Navarro-Ranninger, C. *Chem. Commun.,* 2010, **46**, 454-456

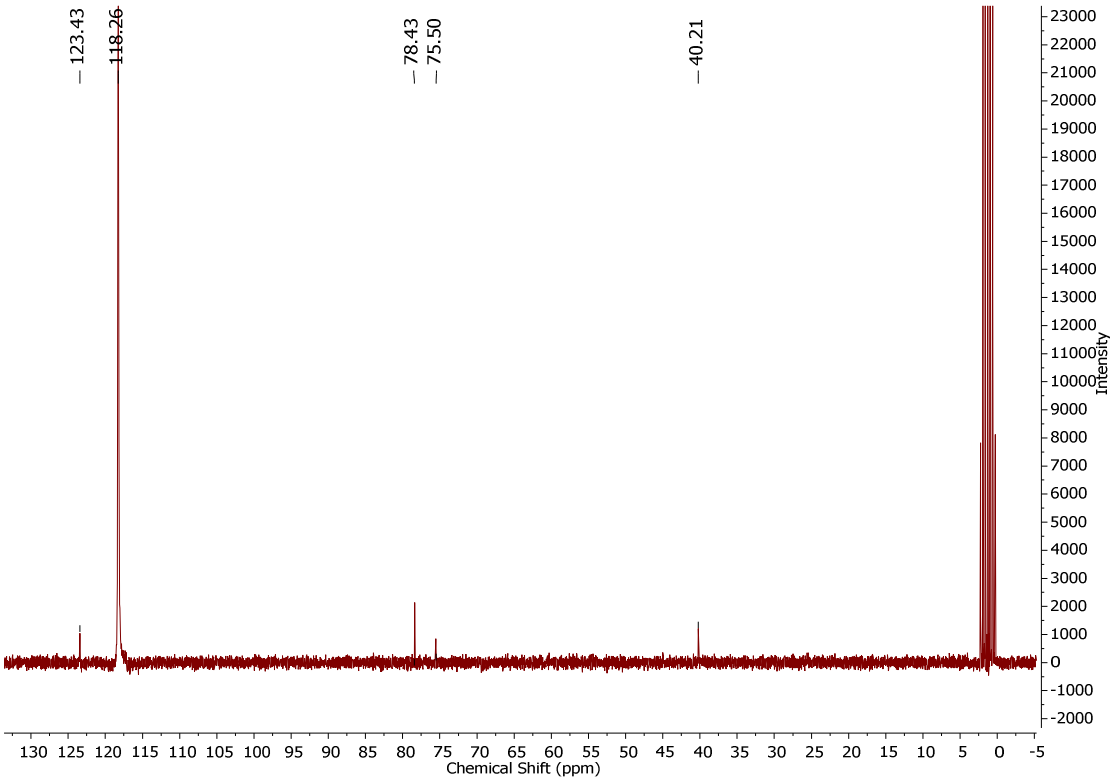
Spectra of compounds **1a**, **1b**, **S1A**, **S1B**, **4**, **S2**, **8**, **10**, **12**

1,3-Di(2-propyn-1-yl)imidazolium bromide ***1a***

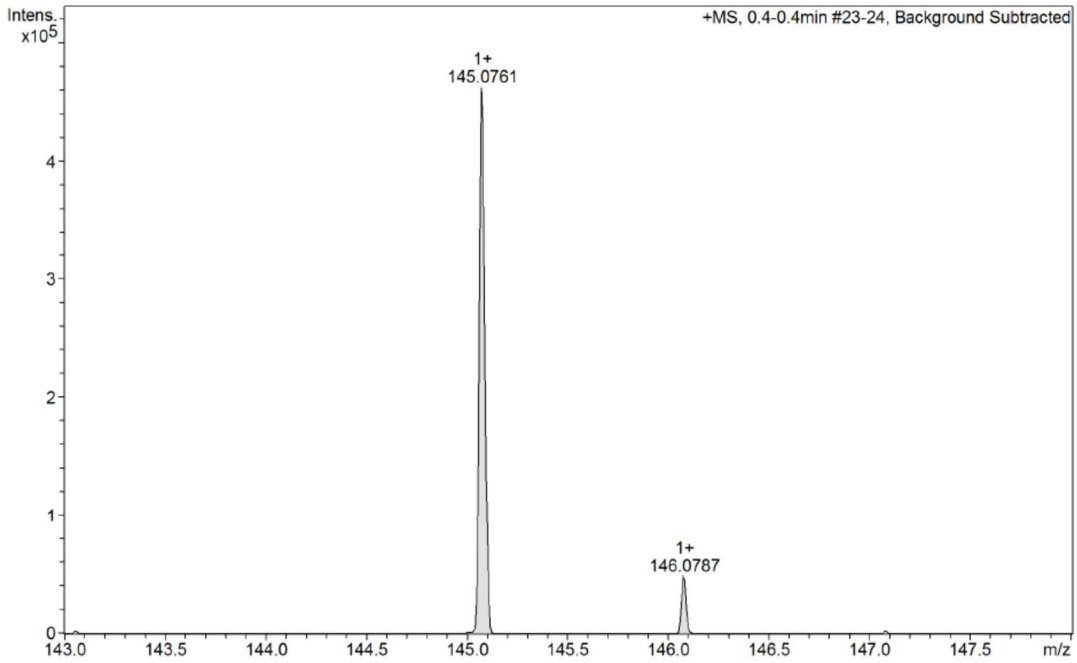
^{1}H NMR (250 MHz, CD_3CN)



^{13}C NMR (62.5 MHz, CD_3CN)



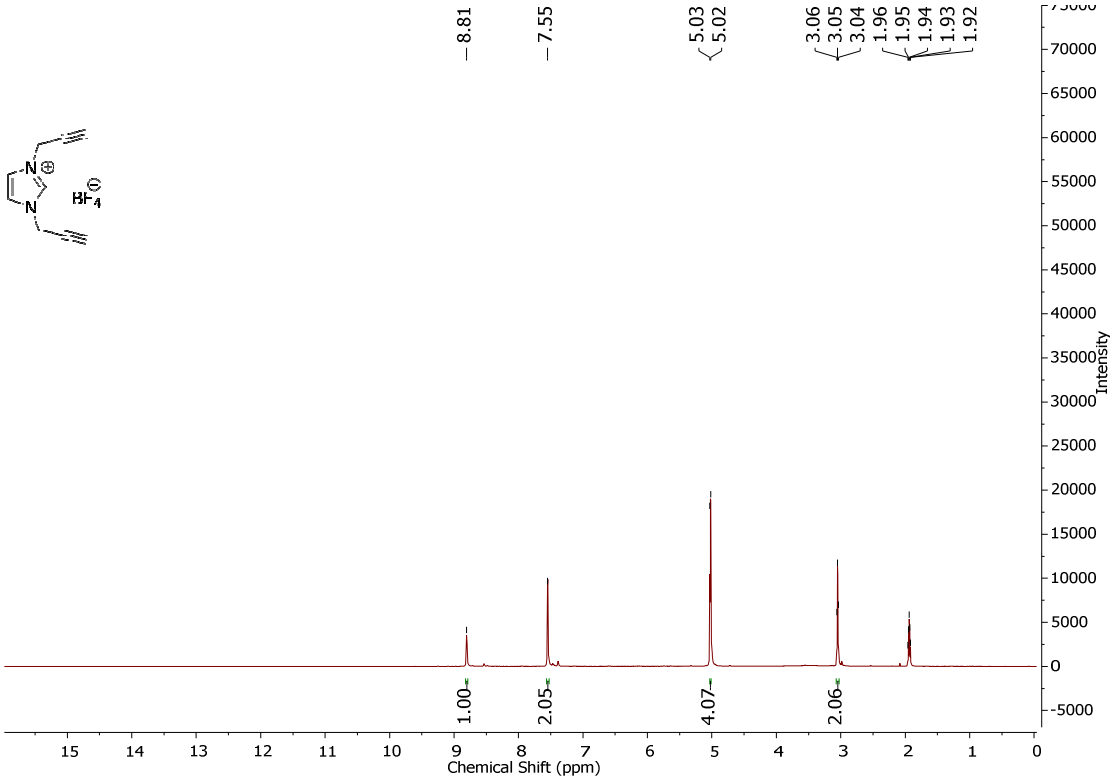
HRMS-ESI:



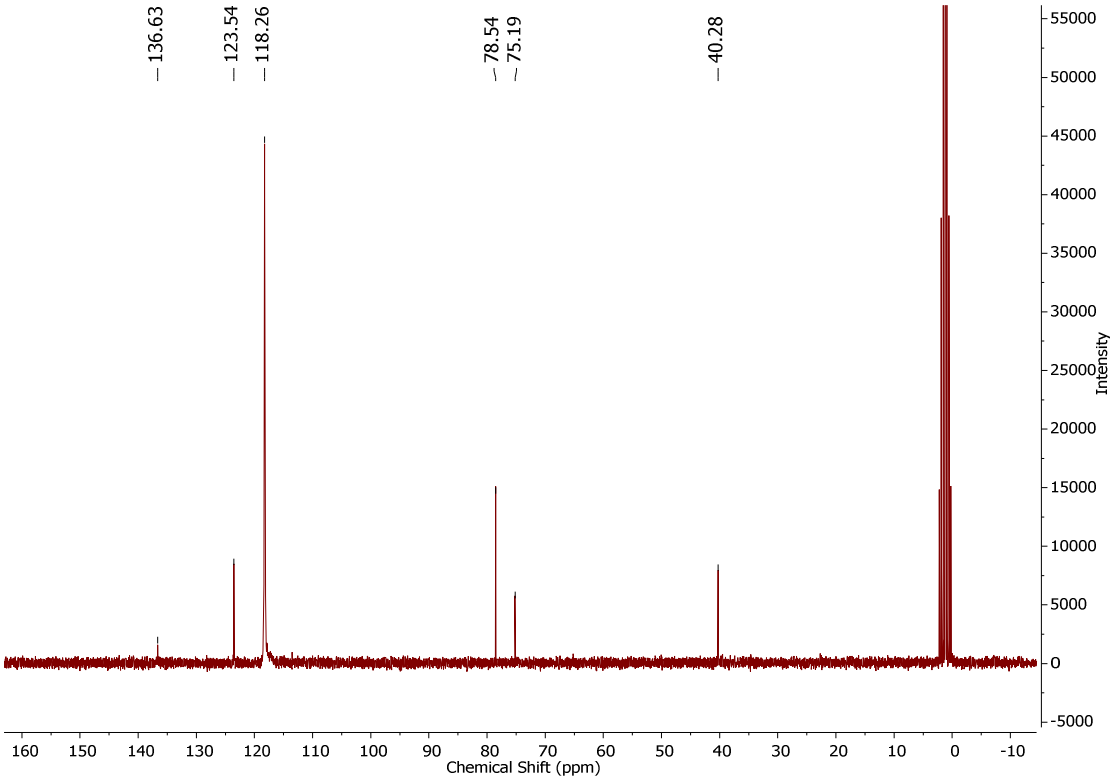
#	m/z	I	I %
1	145.0761	462219	100.0
2	146.0787	48338	10.5

1,3-Di(2-propyn-1-yl)imidazolium tetrafluoroborate ***1b***

^{1}H NMR (250 MHz, CD_3CN)

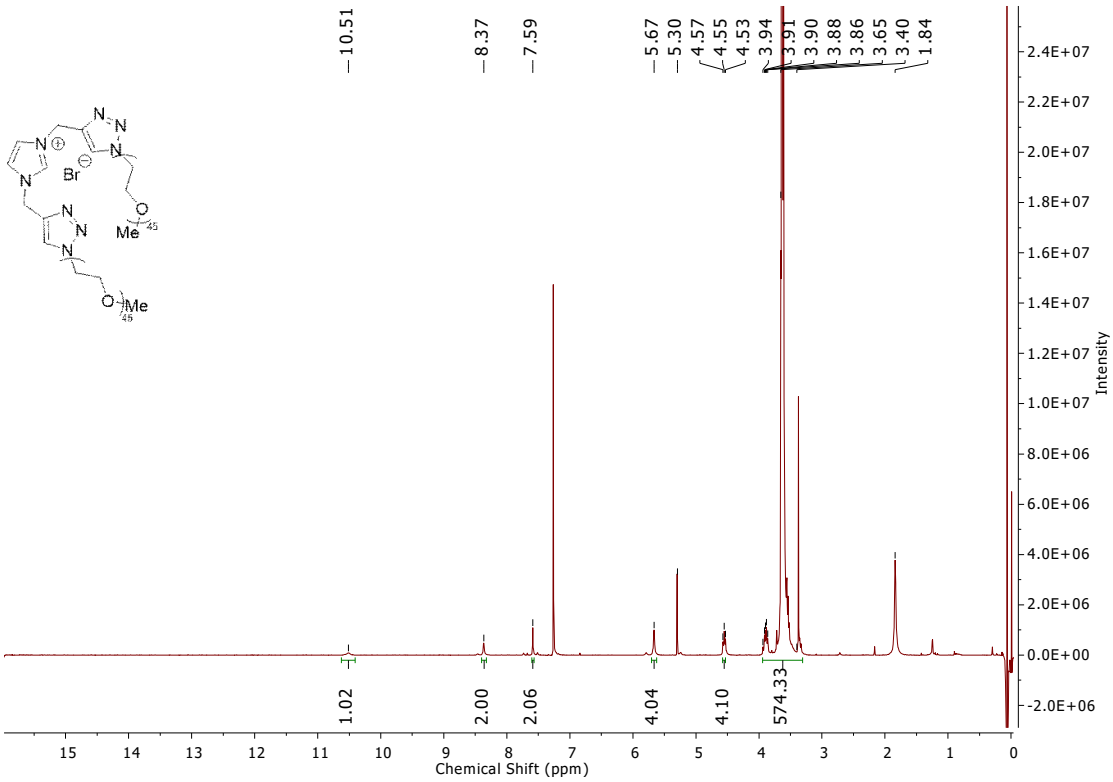


^{13}C NMR (62.5 MHz, CD_3CN)

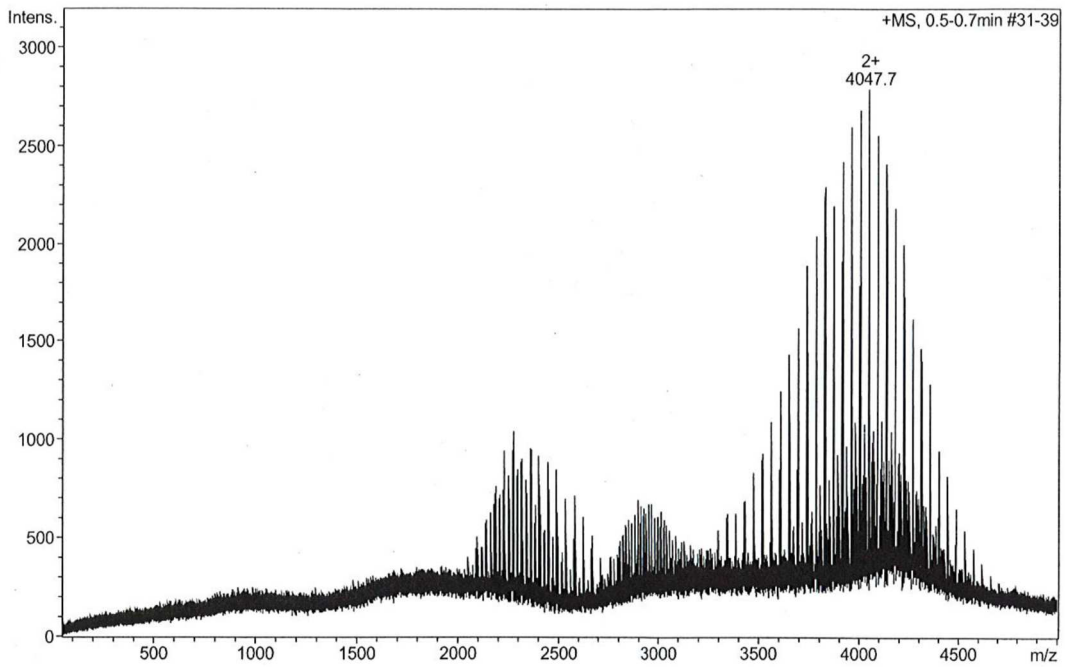


*PEG-tagged stabilizer **S1A***

^{1}H NMR (250 MHz, $CDCl_3$)

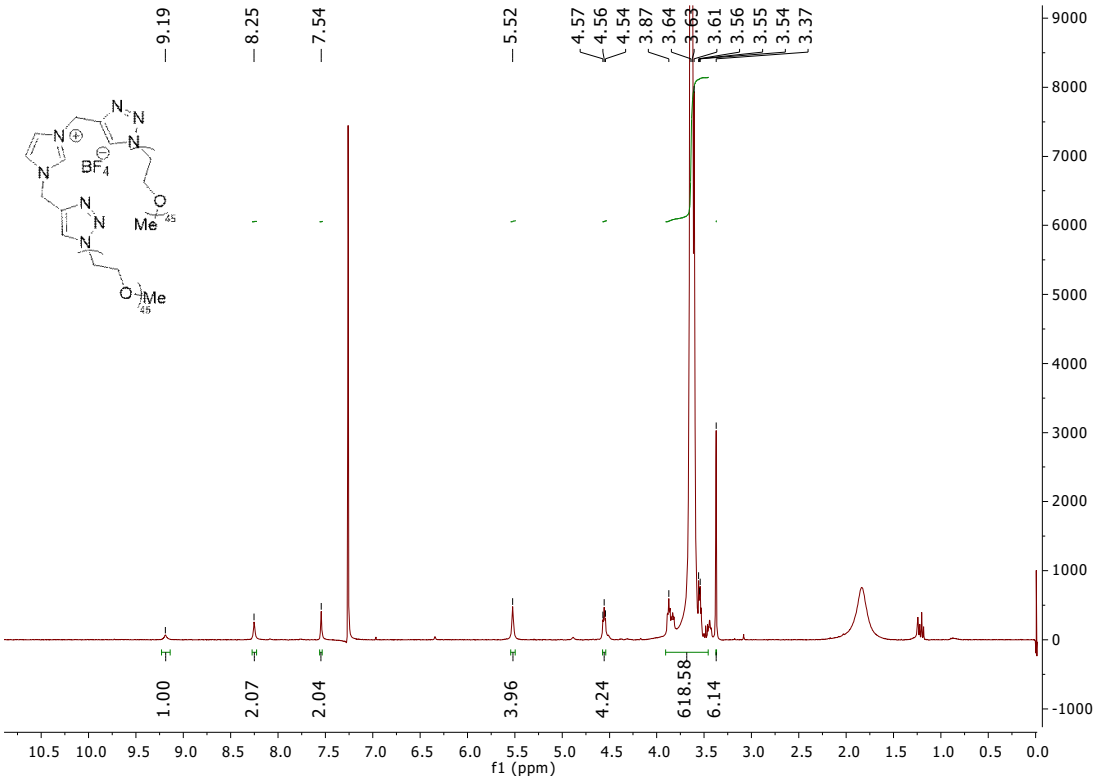


MS-ESI-TOF

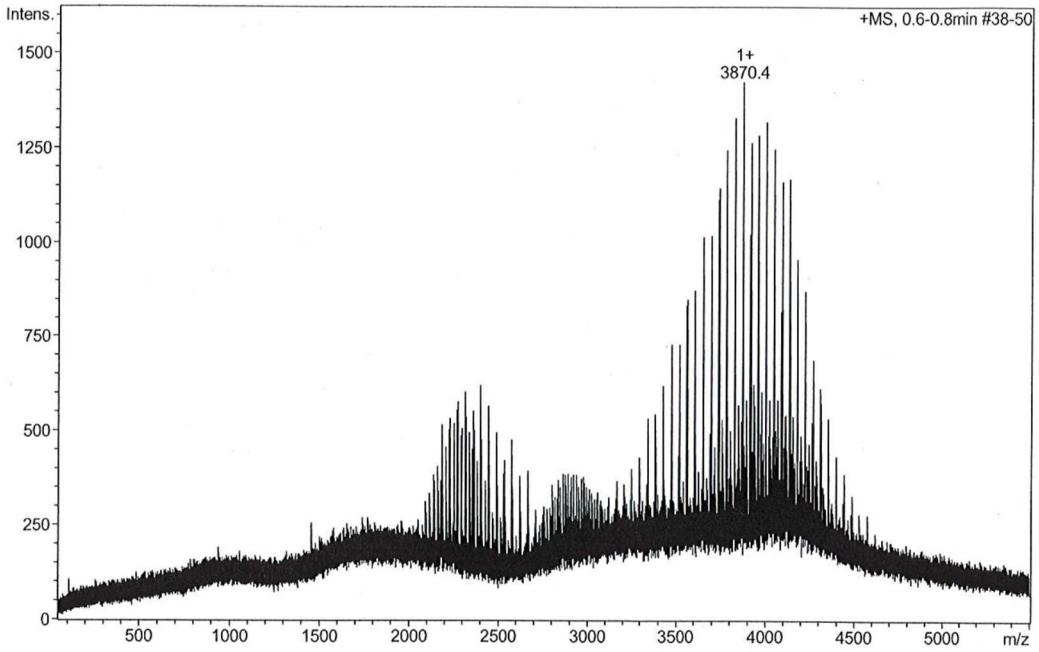


*PEG-tagged stabilizer **S1B***

^{1}H NMR (250 MHz, $CDCl_3$)

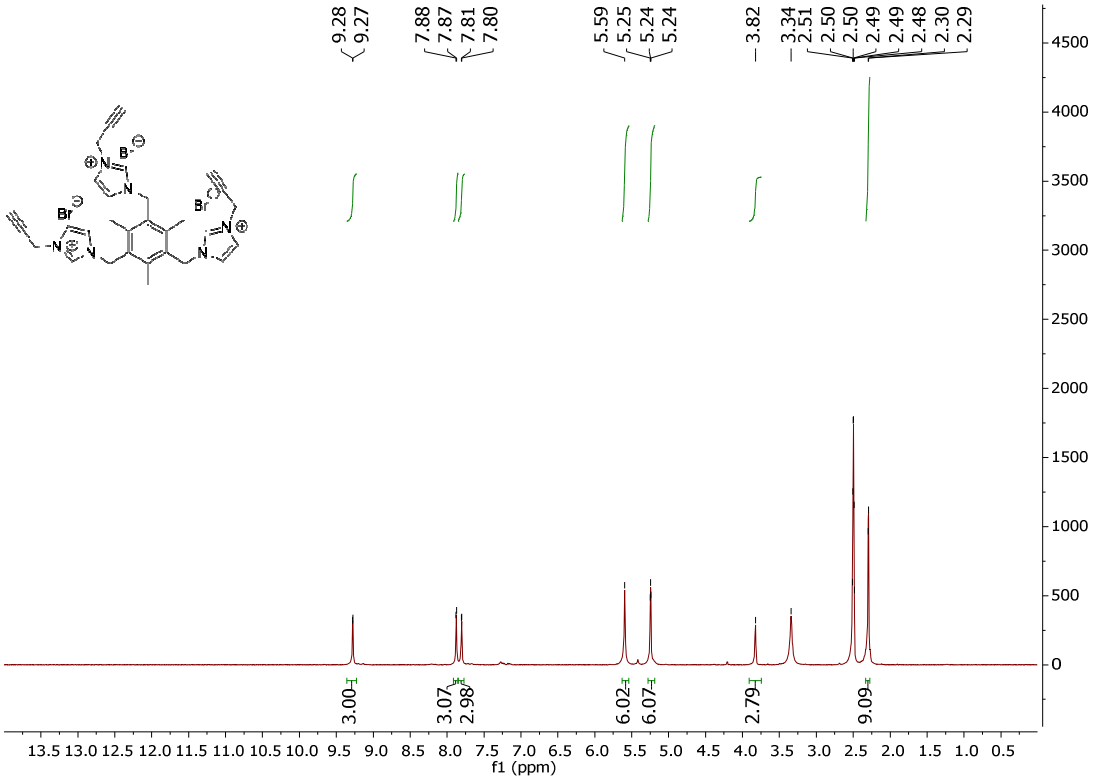


MS-ESI-TOF

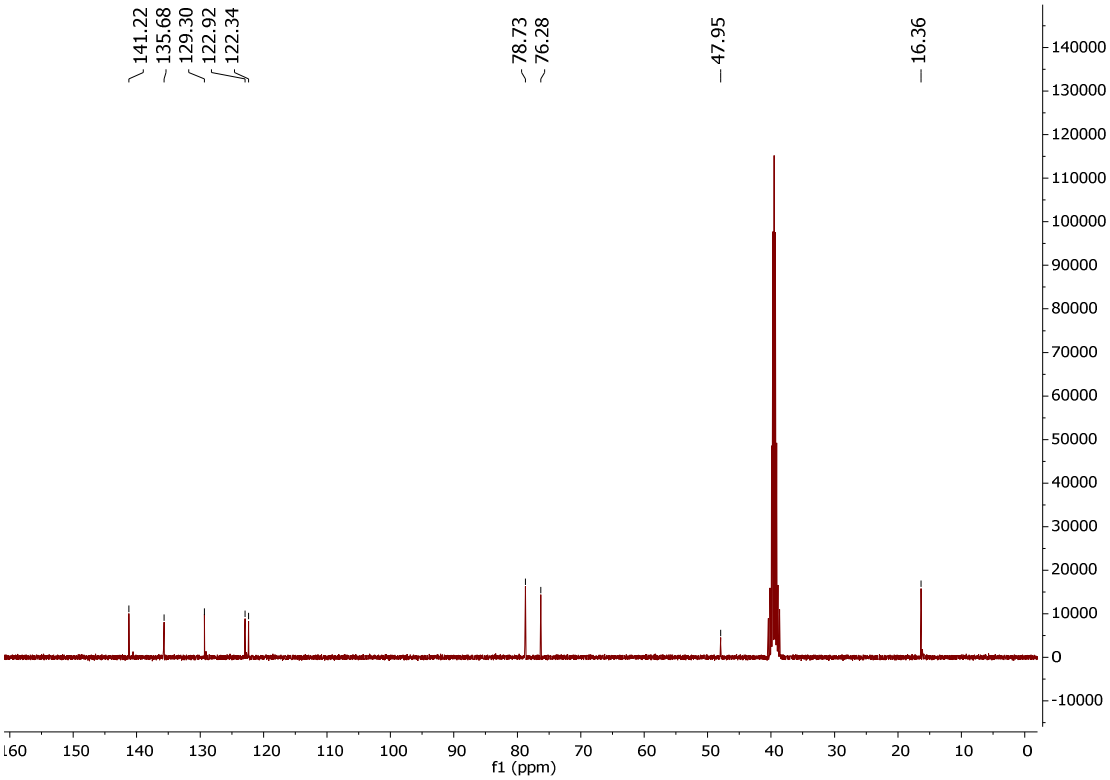


1,1',1"-[(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene)]tris(3-(2-propyn-1-yl)-1H-imidazol-3-ium) bromide ***4***

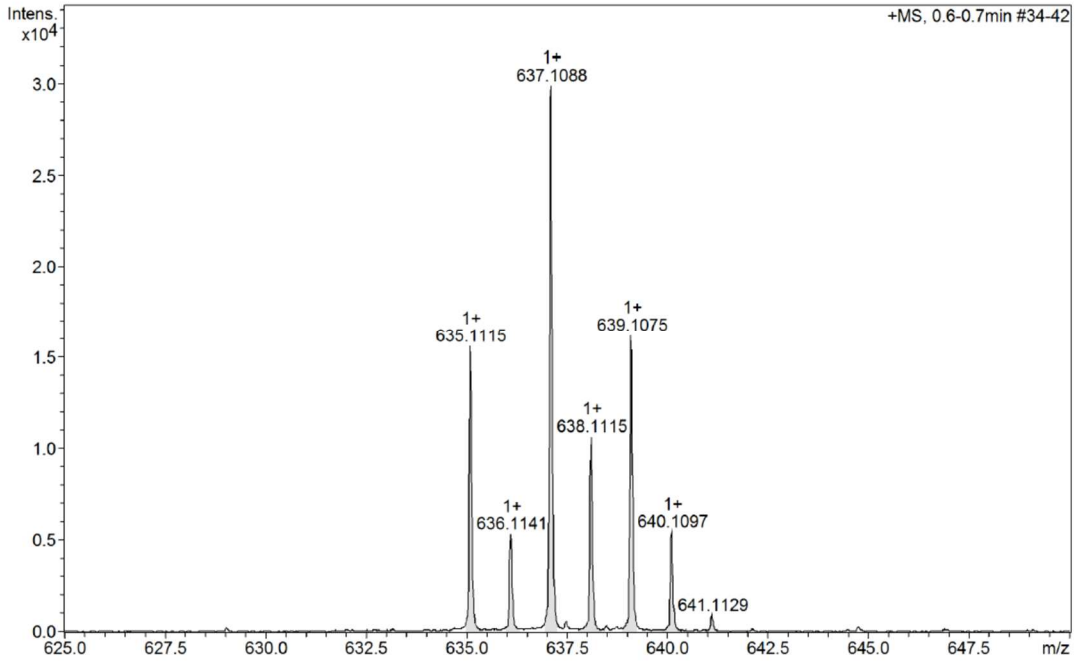
^{1}H NMR (360 MHz, $((CD_3)_2SO)$



^{13}C NMR (100.6 MHz, $((CD_3)_2SO)$

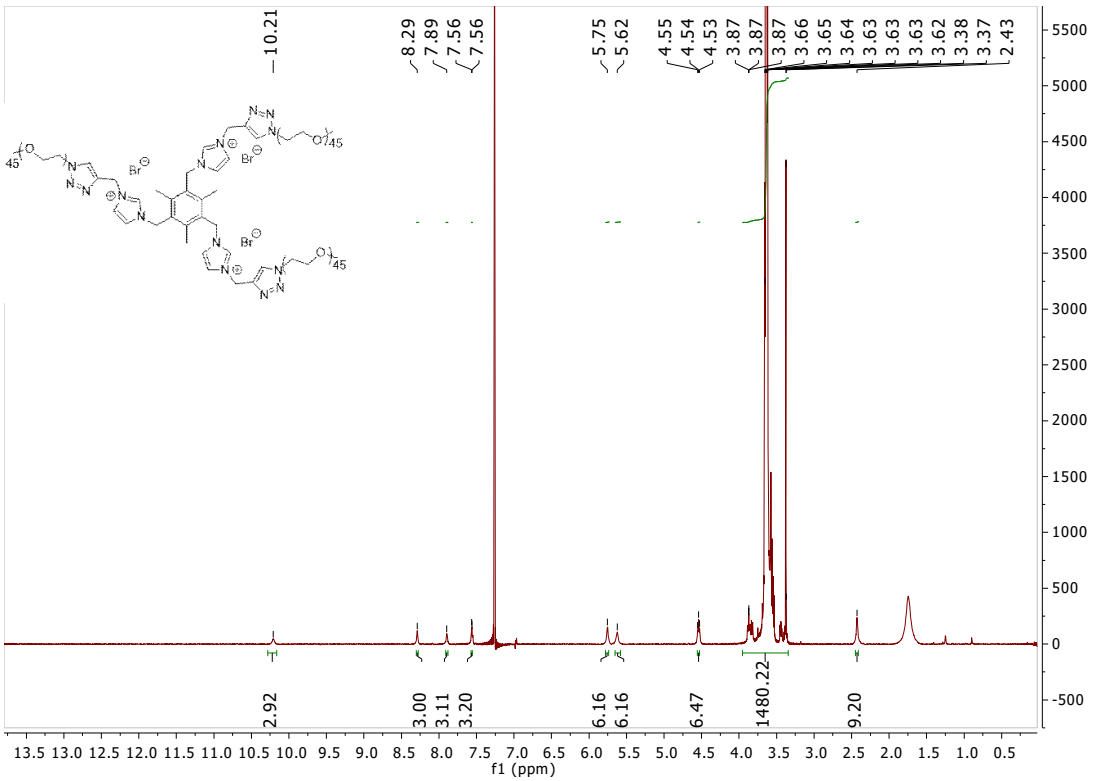


HRMS-ESI-TOF

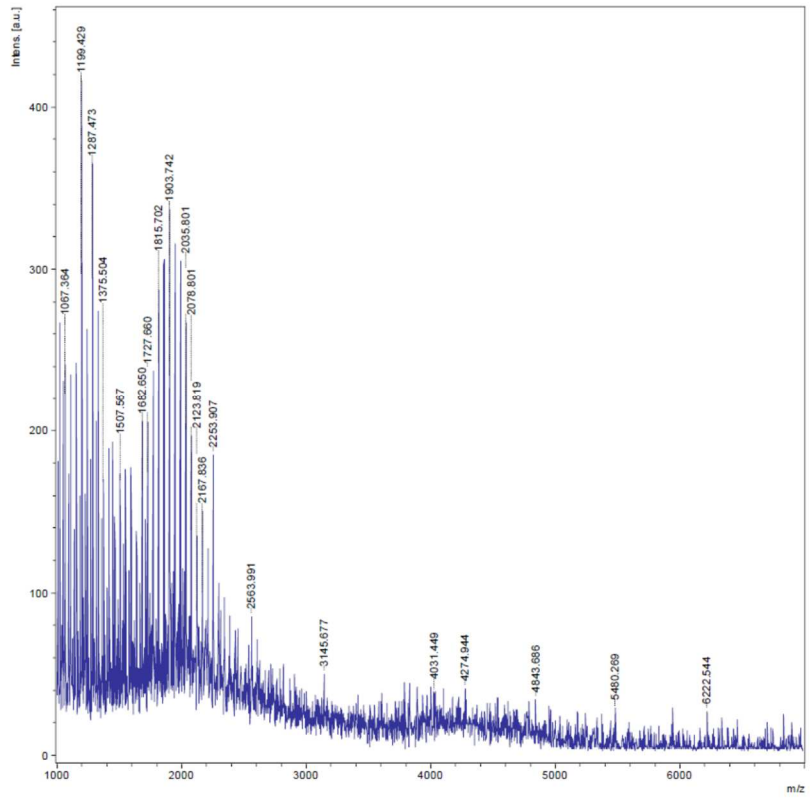


PEG-tagged stabilizer ***S2***

^{1}H NMR (360 MHz, ($CDCl_3$)

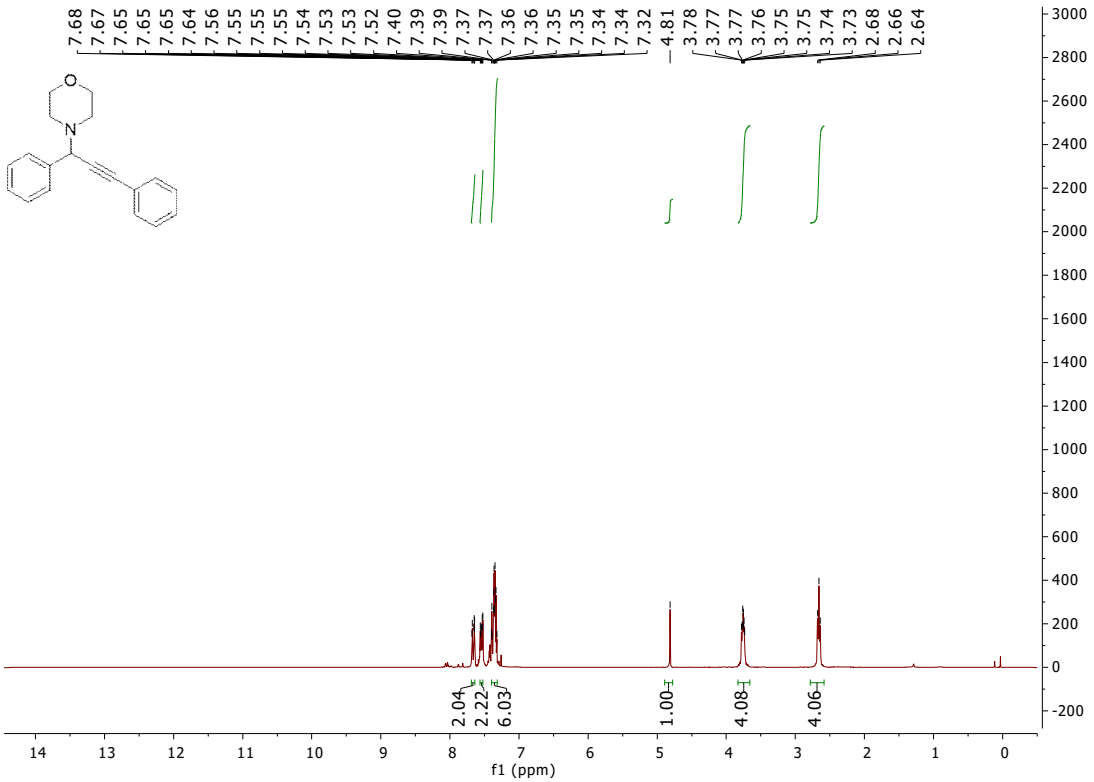


MS-MALDI-TOF



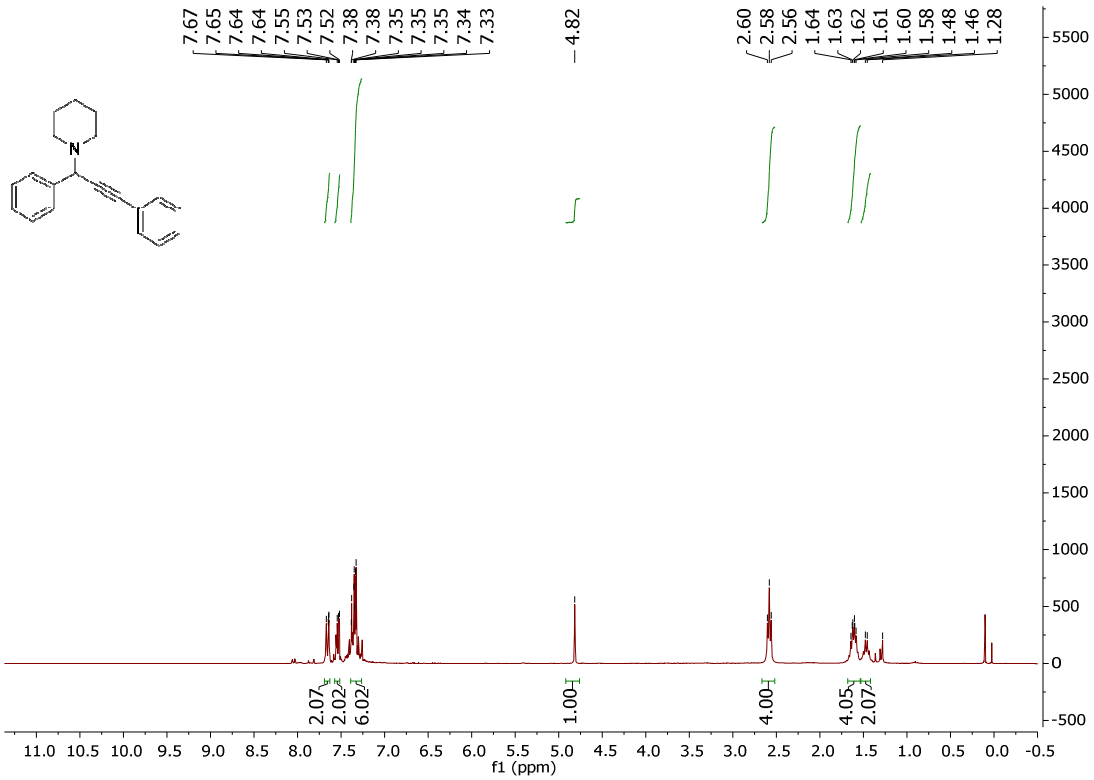
4-(1,3-Diphenylprop-2-yn-1-yl)morpholine ***8aaa***

^{1}H NMR (250 MHz, $CDCl_3$)



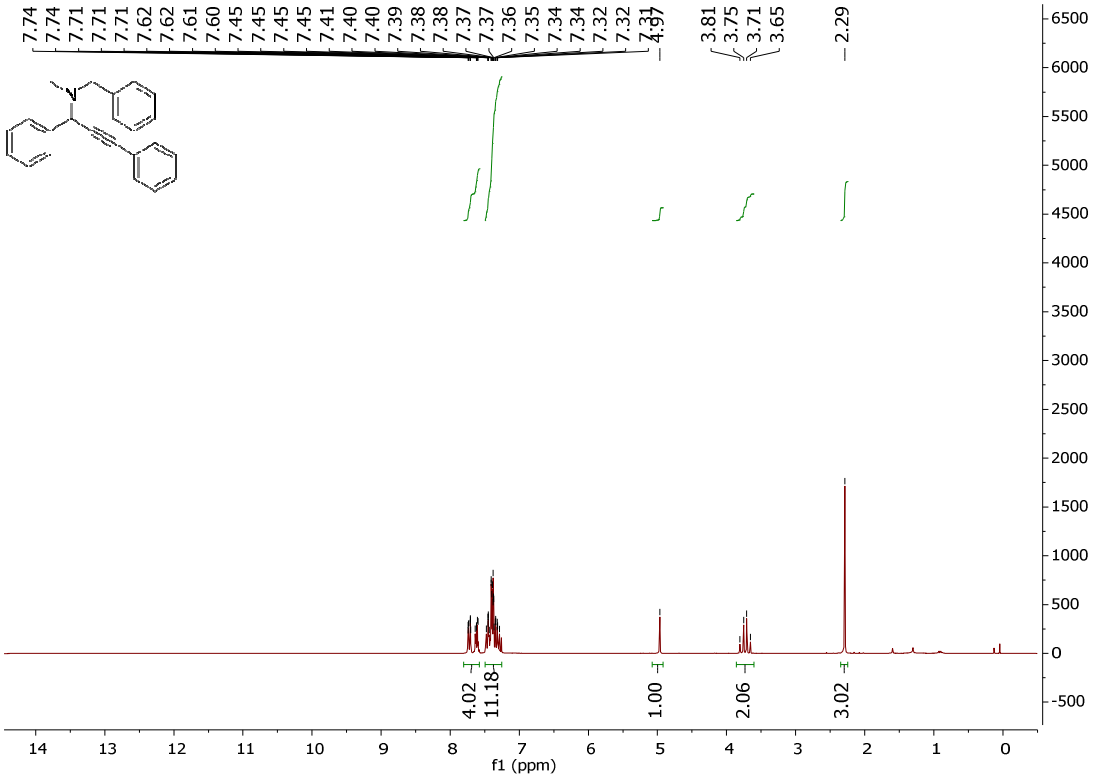
1-(1,3-Diphenylprop-2-yn-1-yl)piperidine ***8aba***

^{1}H NMR (250 MHz, $CDCl_3$)



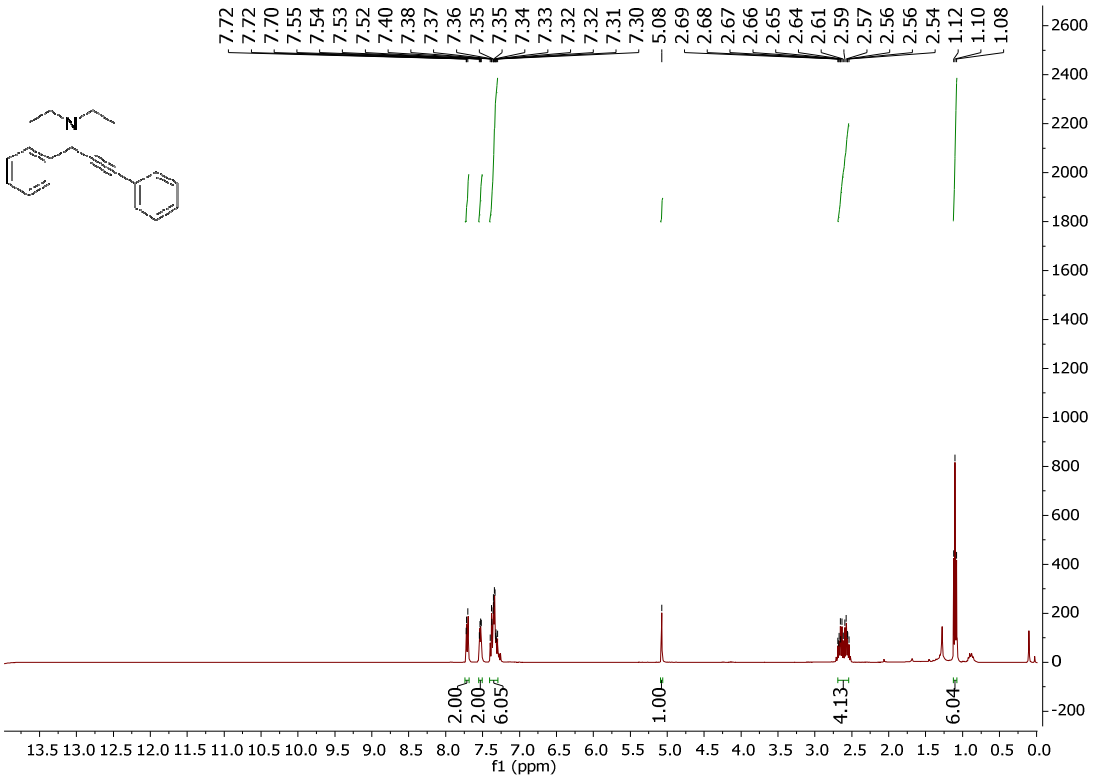
N-Benzyl-N-methyl-1,3-diphenylprop-2-yn-1-amine ***8aca***

^{1}H NMR (250 MHz, $CDCl_3$)



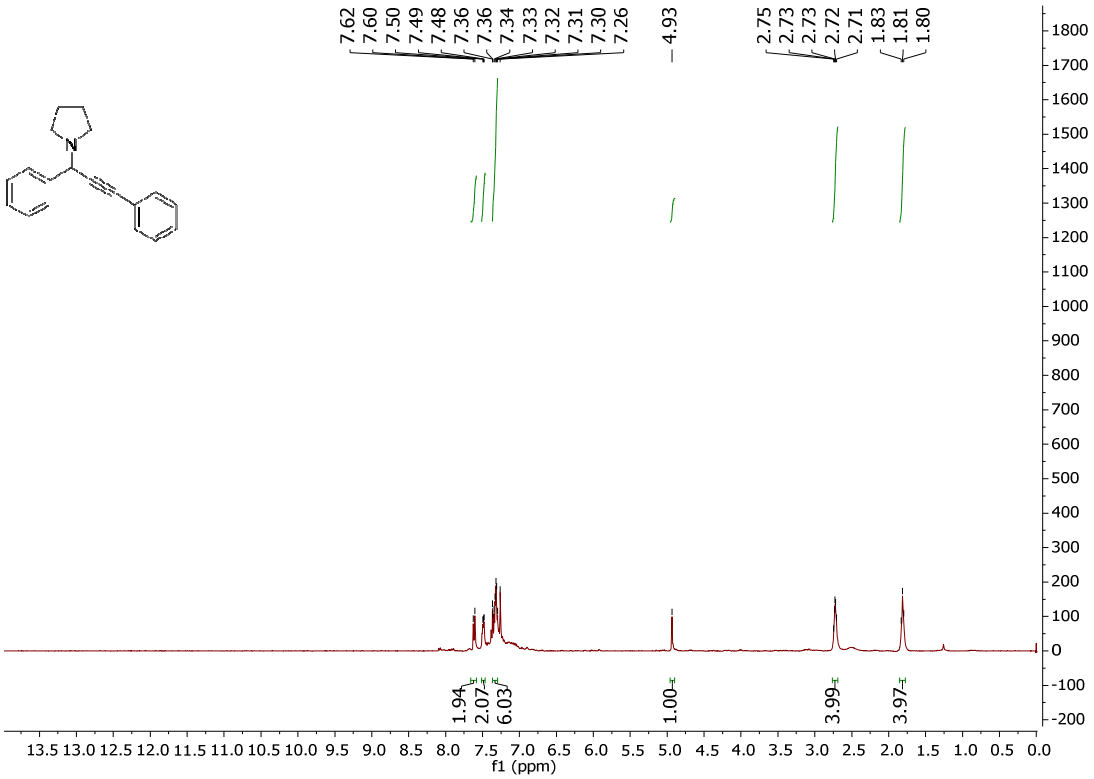
N,N-Diethyl-1,3-diphenylprop-2-yn-1-amine ***8ada***

^{1}H NMR (360 MHz, $CDCl_3$)



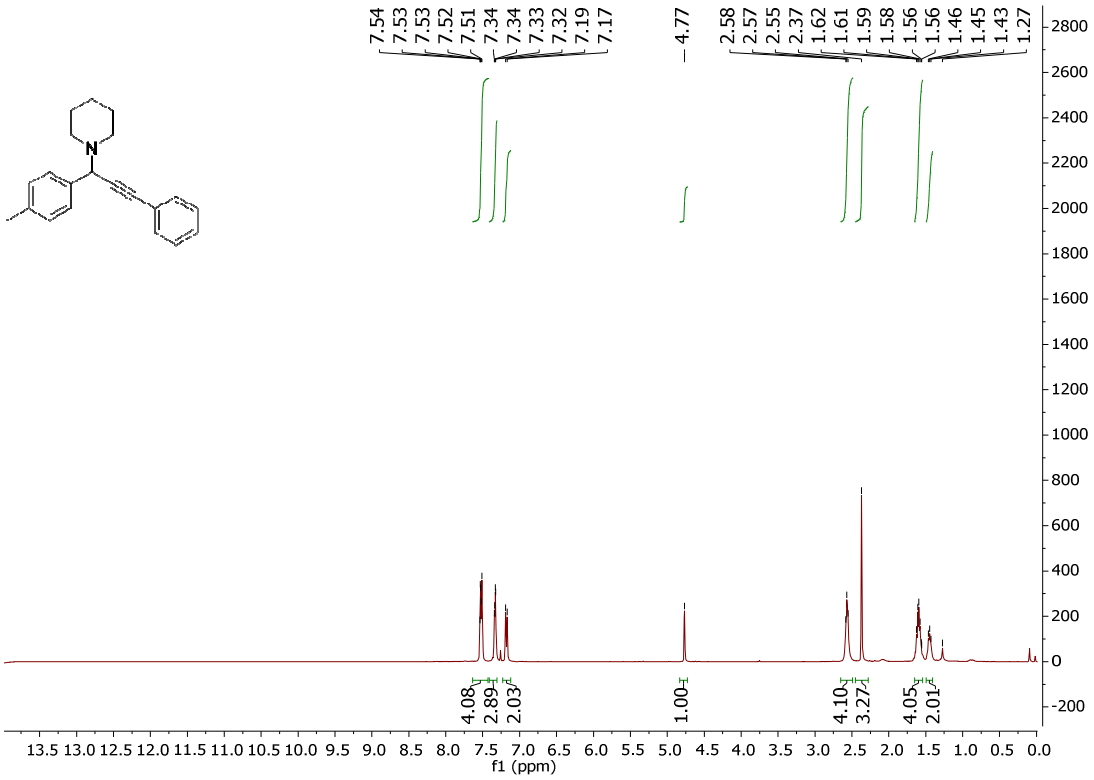
1-(1,3-Diphenylprop-2-ynyl)pyrrolidine ***8aea***

^{1}H NMR (360 MHz, $CDCl_3$)



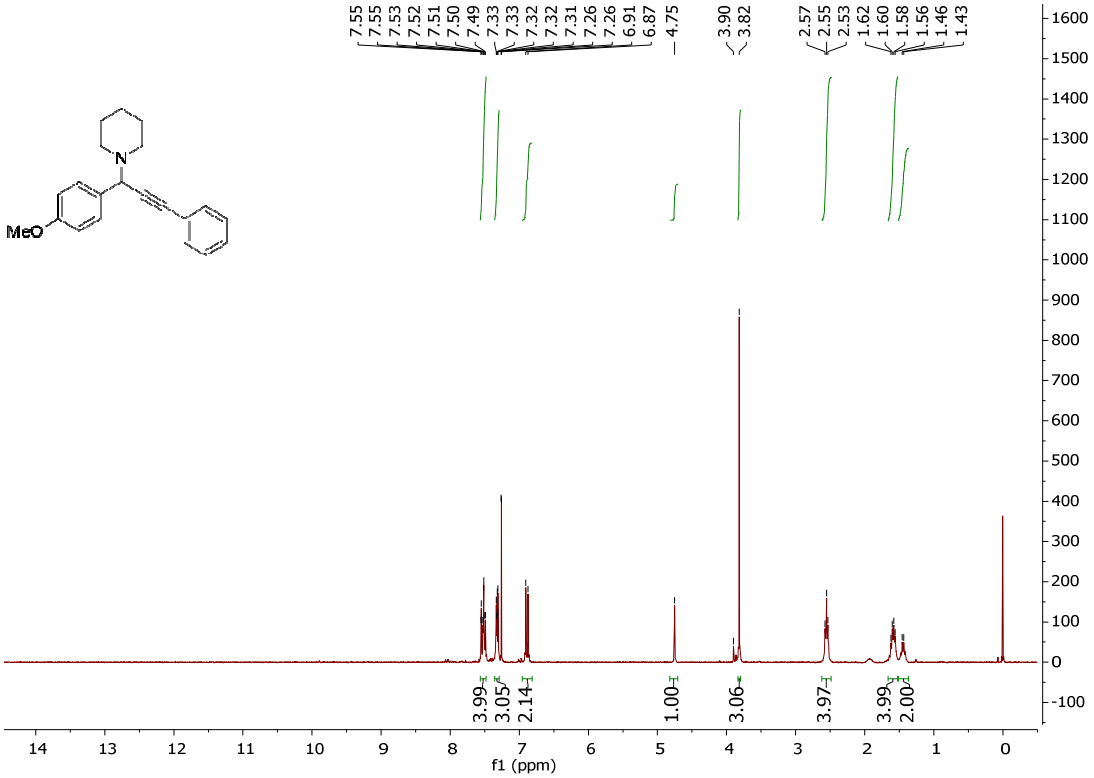
1-(3-Phenyl-1-(p-tolyl)prop-2-yn-1-yl)piperidine ***8bba***

^{1}H NMR (360 MHz, $CDCl_3$)



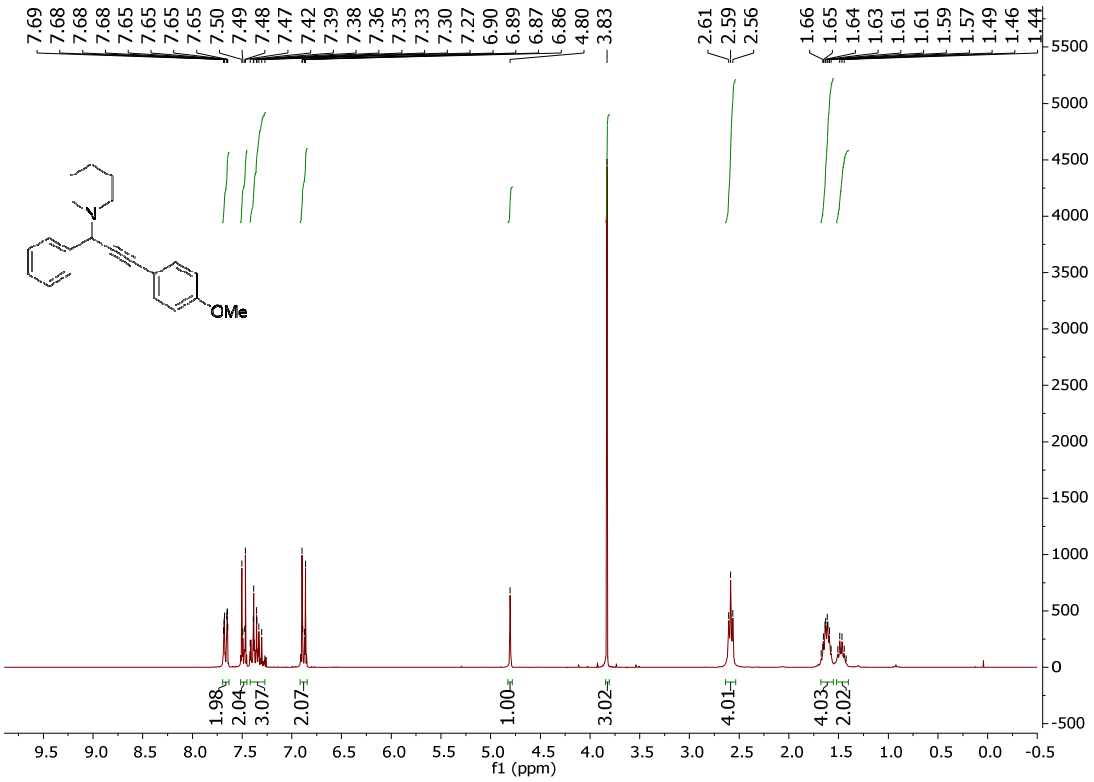
1-[1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl]piperidine ***8cba***

^{1}H NMR (250 MHz, $CDCl_3$)



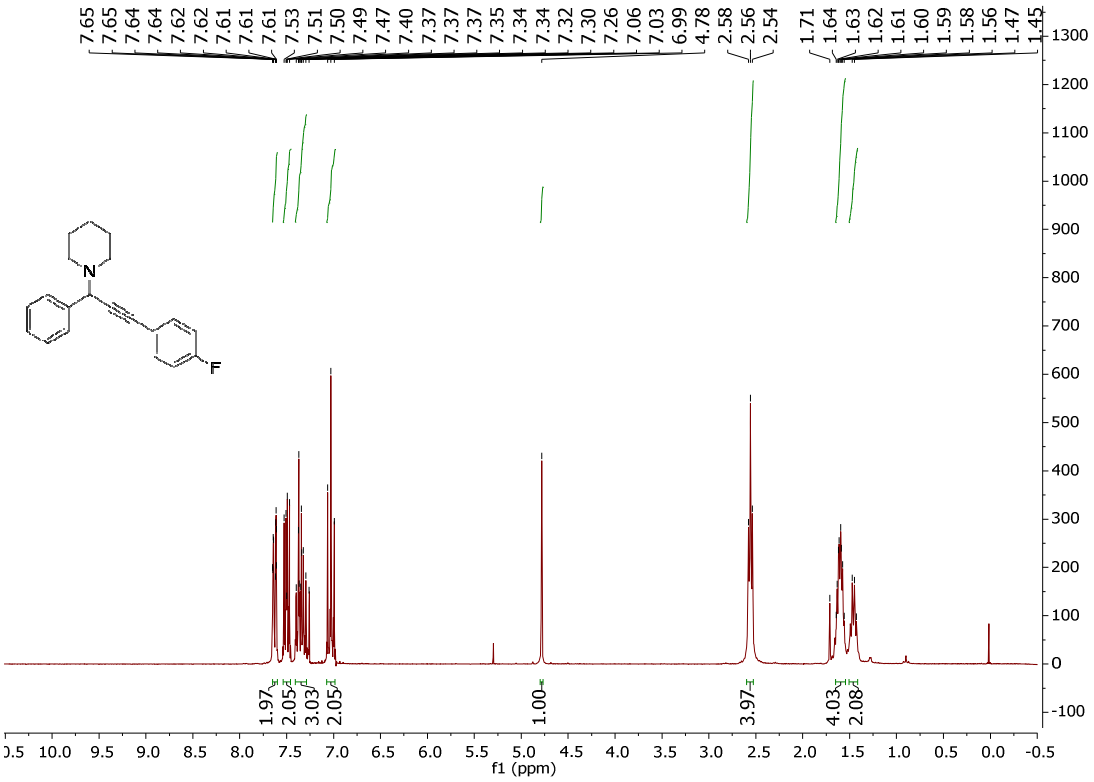
1-[3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-yl]piperidine ***8abc***

^{1}H NMR (250 MHz, $CDCl_3$)



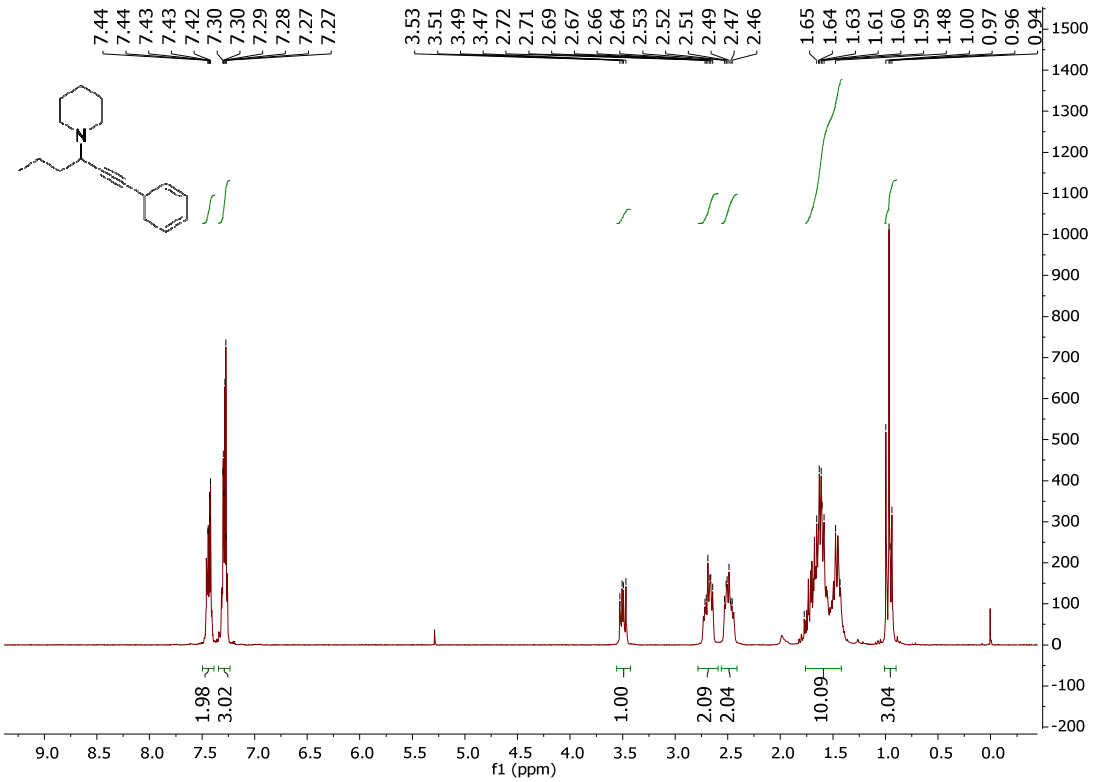
1-[3-(4-Fluorophenyl)-1-phenylprop-2-yn-1-yl]piperidine ***8abd***

^{1}H NMR (250 MHz, $CDCl_3$)



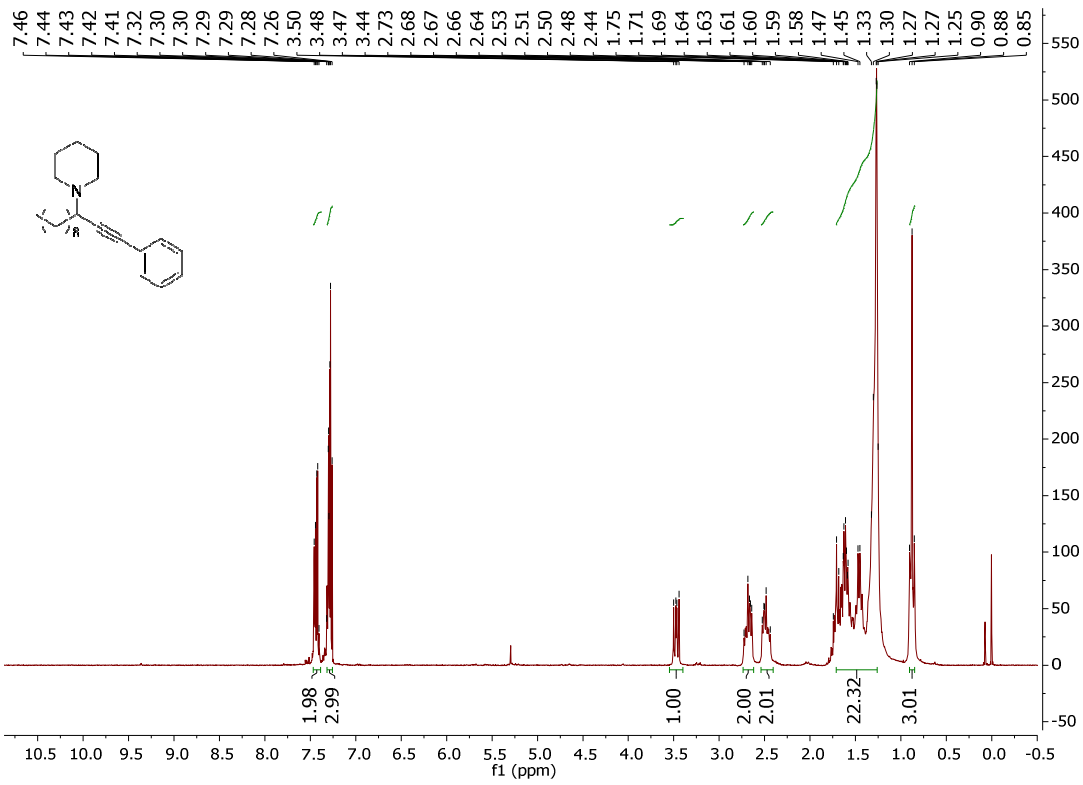
N-[4-(3-Phenyl-1-propyl-2-propynyl)]piperidine ***8dba***

^{1}H NMR (250 MHz, $CDCl_3$)



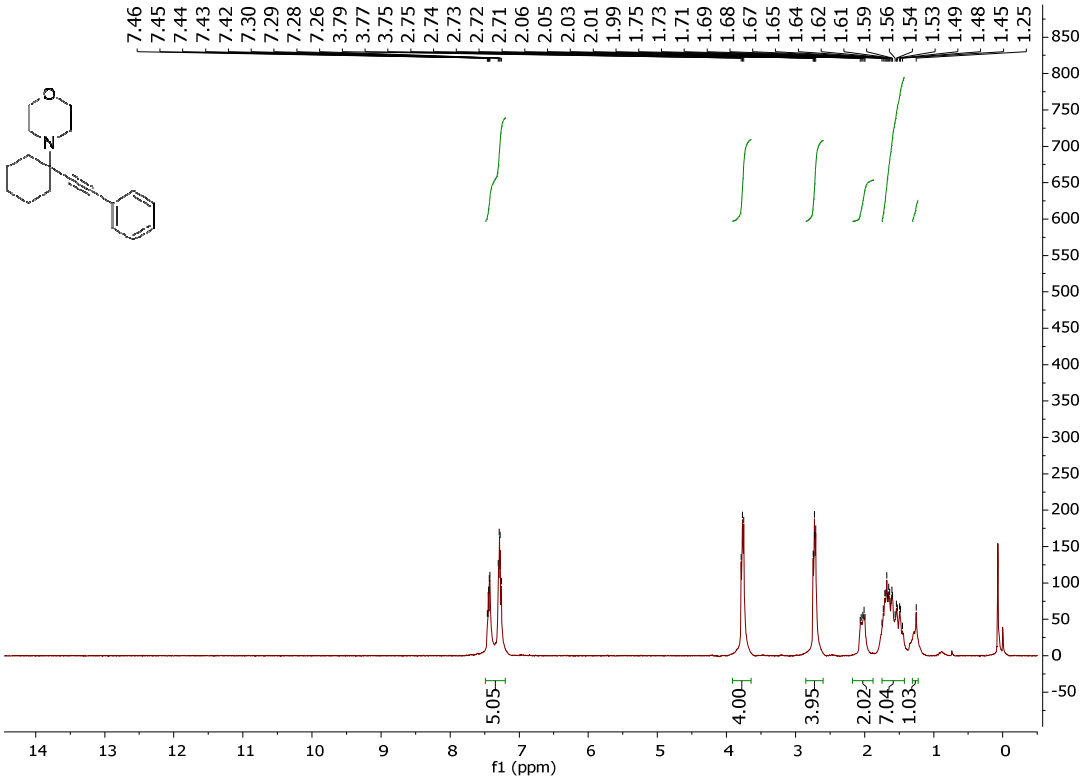
1-(1-Phenyldodec-1-yn-3-yl)piperidine ***8eba***

^{1}H NMR (250 MHz, $CDCl_3$)



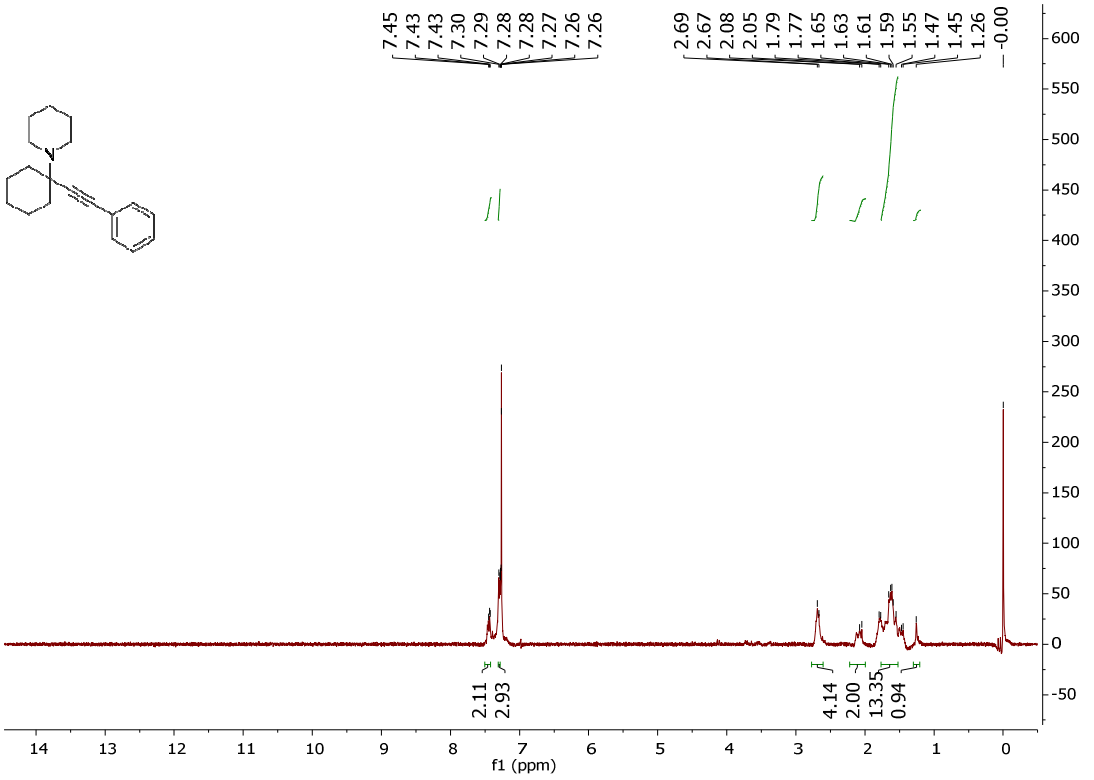
1-[1-(Phenylethynyl)cyclohexyl]morpholine ***10aaa***

^{1}H NMR (250 MHz, $CDCl_3$)



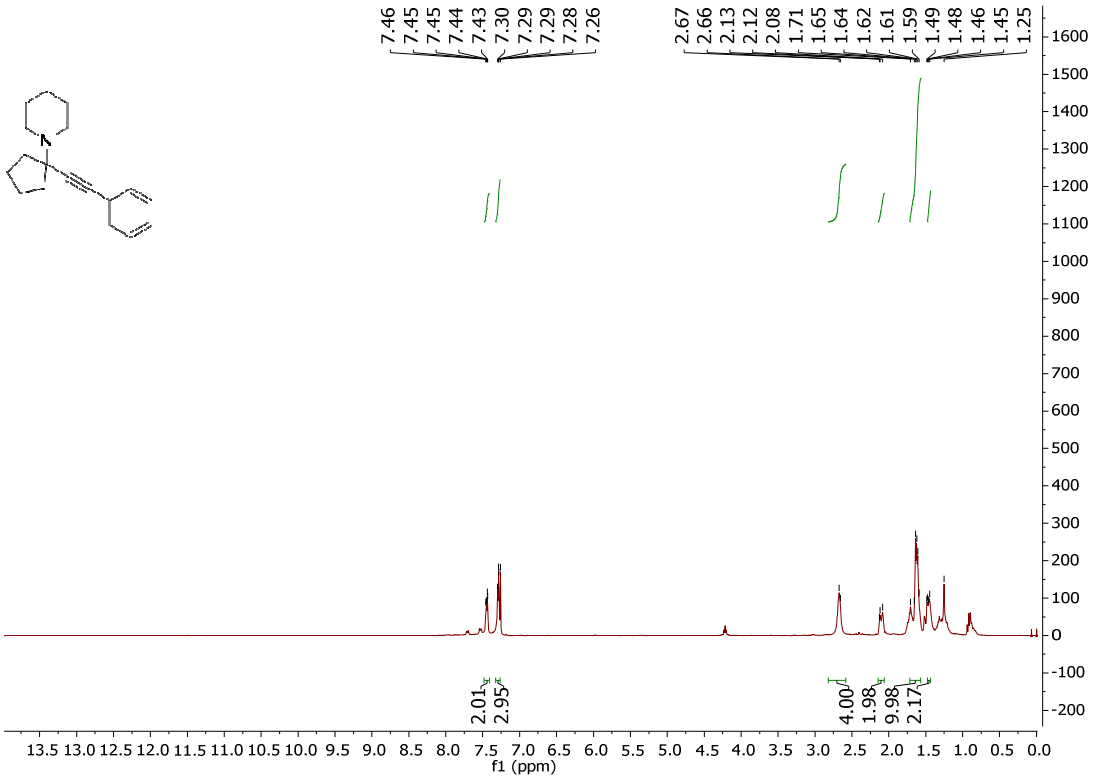
1-(1-(Phenylethynyl)cyclohexyl)piperidine ***10aba***

^{1}H NMR (250 MHz, $CDCl_3$)



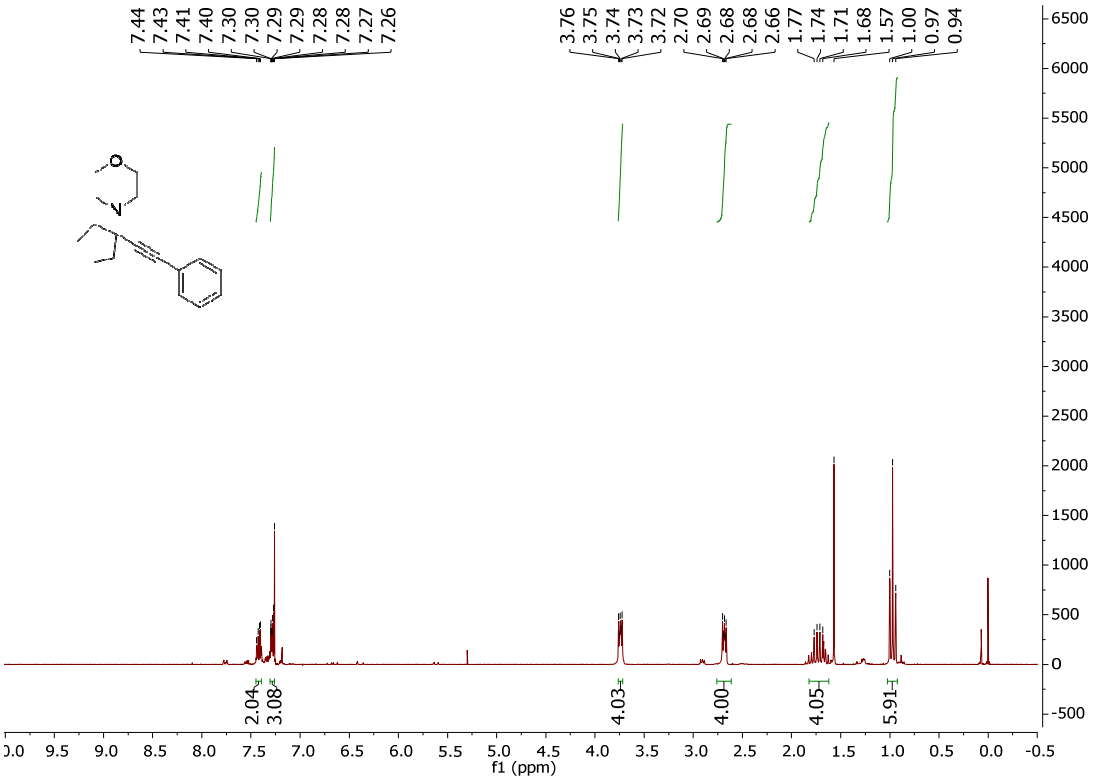
1-(1-(2-Phenylethynyl)cyclopentyl)piperidine ***10bba***

^{1}H NMR (360 MHz, $CDCl_3$)



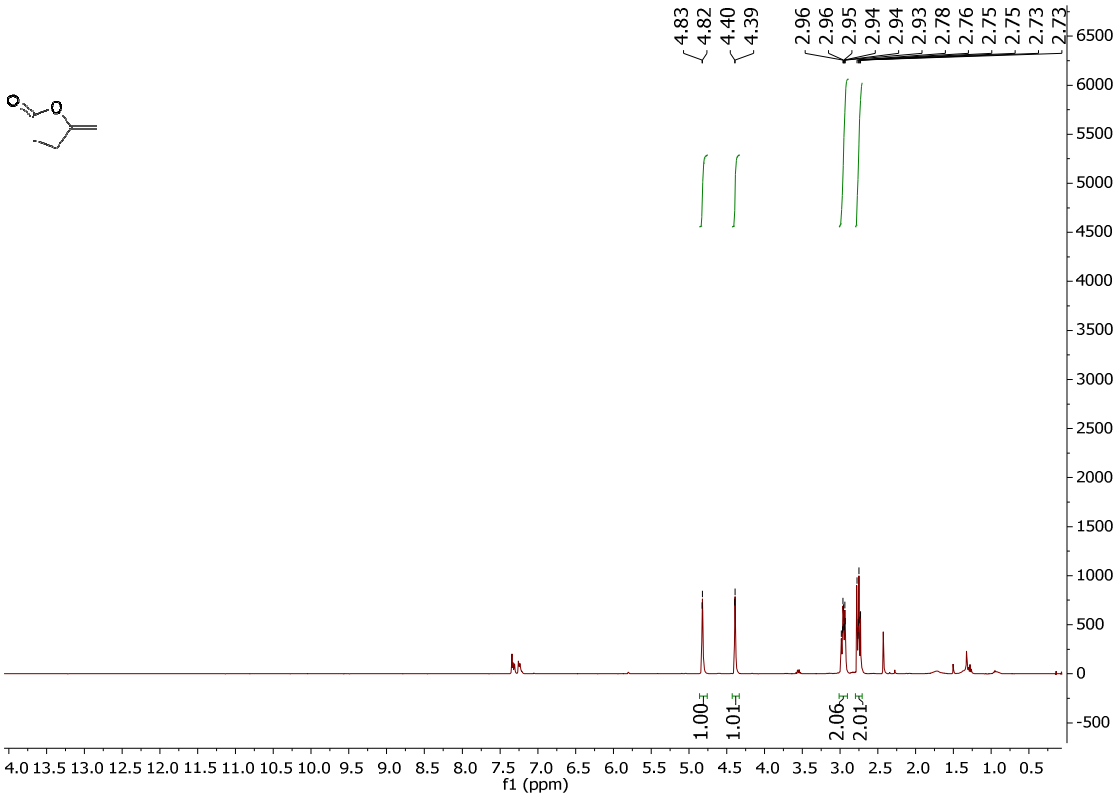
4-(1,1-diethyl-3-phenyl-2-propyn-1-yl)morpholine ***10caa***

^{1}H NMR (250 MHz, $CDCl_3$)



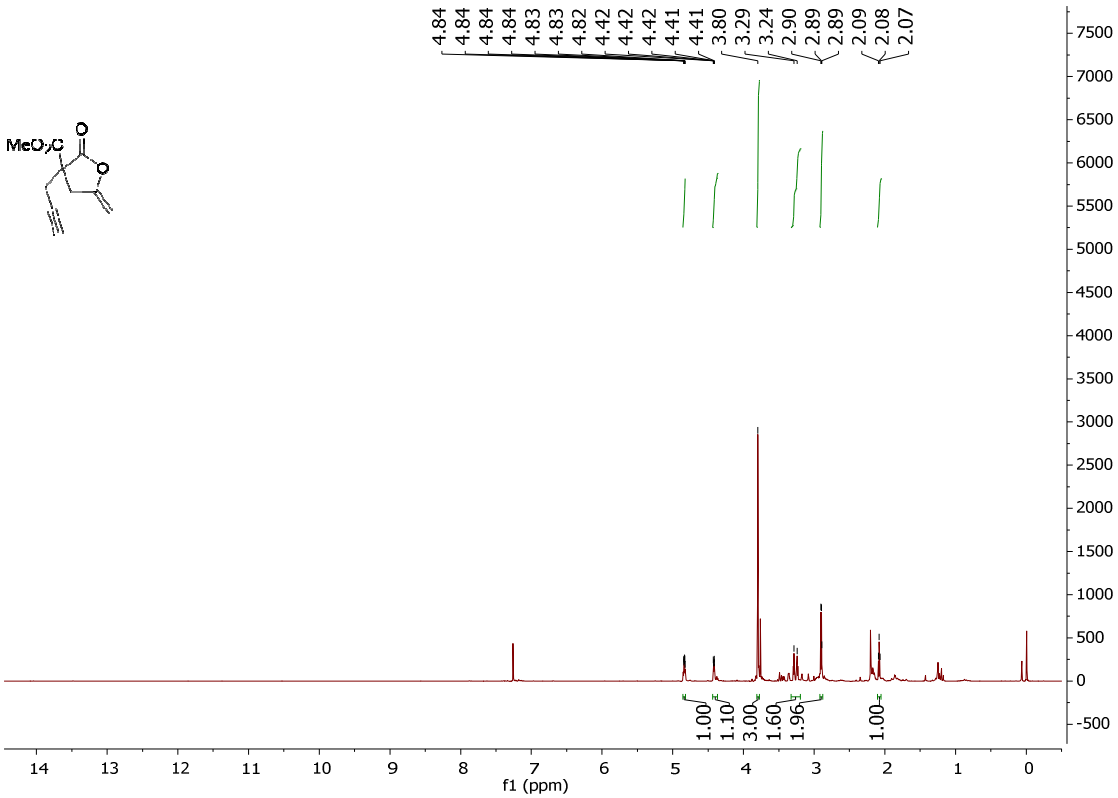
5-Methylenedihydrofuran-2(3H)-one ***12a***:

^{1}H NMR (360 MHz, $CDCl_3$)



Methyl 5-methylene-2-oxo-3-(prop-2-yn-1-yl)tetrahydrofuran-3-carboxylate ***12b****:*

^{1}H NMR (250 MHz, $CDCl_3$)



Dihydro-5-methylenefuran-2(3H)-one-3-spiro-dihydro-5'-methylenefuran-2'(3H)-one ***12c****:*

^{1}H NMR (250 MHz, $CDCl_3$)