

Synthesis, characterization and catalytic properties of cationic N-heterocyclic carbene silver complexes

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Abstract: Three new dibenzimidazolium salts bridged by 2-methylenepropane-1,3-diyl group were synthesized. Their dinuclear N-heterocyclic carbene Ag(I) complexes were prepared by the reactions of these salts with Ag₂O. The structures of the synthesized compounds were defined by nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FT-IR), elemental analysis, and LC-MSMS (for complexes) techniques. Stability of the silver complexes was confirmed by ¹H NMR spectroscopy. Catalytic activities of Ag(I) compounds were tested for three-component coupling reaction of some aldehydes, amines, and phenylacetylene.

Key words: N-heterocyclic carbene, silver, dinuclear complex, coupling, propargylamine

1. Introduction

N-heterocyclic carbenes (NHCs) and their transition metal complexes have been very popular in organometallic chemistry for many years. NHC metal complexes with powerful metal-carbon bonds have been typically employed as efficient catalysts in various transformations. NHC-Ag(I) complexes are of capital importance among these complexes. Using of these complexes as carbene transfer reagents for the synthesis of transition metal complexes is one of the most used methods [1–7]. There have been numerous reports related to biological and medicinal applications [8–13]. Also, NHC silver complexes may have luminescence properties [14–17], and these are of significance in material science. NHC-Ag(I) complexes exhibit catalytic efficiencies in cycloaddition of CO₂ to terminal epoxides [18–20], three component coupling reaction of aldehydes, amines and alkynes (A³-coupling reaction) [15,21–32], L-lactide polymerization [33,34], hydration of nitriles [35] and hydroboration of alkynes [36].

Dibenzimidazolium salts are featured compounds since NHC procured from these salts can generate easily numerous NHC metal complexes with structural variety. There are many studies related bidentate bis(NHC) ligands in which a linking group acts as a bridge between two NHC units. Silver complexes of these type ligands with particularly antibacterial and antitumor activities are prepared by the reaction of the salts with silver oxide in general [37–39]. Silver complexes containing bis(NHC) and halide ligands (terminal or bridging) form monomeric, oligomeric and polymeric neutral complexes in the solid state [40–42]. Cationic silver bis(NHC) complexes have dinuclear [Ag₂(NHC)₂]X₂ (X = PF₆ or BF₄) formulation [43,44].

Multicomponent reactions (MCRs) allow the attainment of complex molecules starting from more than two simple building blocks in one step. So, they have importance in various aspects in organic synthesis. A³-coupling reaction is one of the best examples of MCRs. This method is a beneficial approachment to propargylamines, recurring parts in biologically active compounds and intermediates giving more complex N-heterocycles. As A³-coupling has high selectivity for the demanding product and the only by-product is water, it is an encouraging way. Transition metal compounds containing copper, silver, gold, iron, cobalt, and zinc have been frequently used to catalyze this reaction [45–49].

In this study, synthesis of three novel 2-methylenepropane-1,3-diyl group bridged dibenzimidazolium salts and dinuclear NHC-Ag(I) complexes are reported. As far as is known, the studies about alkenyl bridged bis(NHC) are relatively less than those of alkyl bridged groups. To synthesize stable metal complexes containing chelating carbene ligands, we have prepared these dinuclear silver complexes. We hope that the metal NHC complexes formed by transmetalation by using these silver NHC complexes can be employed as effective catalysts. Besides, findings regarding catalytic tests of the complexes in A³-coupling reactions are presented.

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2. Experimental

2.1. General remarks

All experimental operations were performed in air. The chemicals commercially available were used without any purification. For recording ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra, a Varian VNMRJ spectrometer was employed. Elemental and mass analyses were executed by a LECO-932 CHNS device and a SHIMADZU LC-MSMS-8040 mass spectrometer, respectively. Thermogravimetric analysis was accomplished using EXSTAR TG-DTA 7300 instrument. IR spectra were obtained with Perkin-Elmer FT-IR spectrophotometer in the range of 400–4000 cm^{-1} using KBr.

2.2. Synthesis of dibenzimidazolium salts

2.2.1. Synthesis of $\text{L}_1 \cdot 2\text{HBr}$ (2a)

The mixture of **1** (1 mmol) and 3,5-dimethylbenzyl bromide (2 mmol) was stirred in DMF (3 mL) at 80 °C for 24 h. After cooling to the room temperature and addition of Et_2O (15 mL), the suspension was filtered. The solid was washed by EtOH (2x5 mL) and Et_2O (2x5 mL) and dried in air. Yield: 91%. IR $\nu_{(\text{NCN})}$: 1558 cm^{-1} . ^1H NMR (CD_3OD): δ = 9.78 (s, 2H, NCHN), 7.93–7.85 (m, 4H, Ar-H), 7.71–7.63 (m, 4H, Ar-H), 7.13 (s, 4H, Ar-H), 7.05 (s, 2H, Ar-H), 5.65 (s, 4H, NCH_2), 5.45 (s, 4H, NCH_2), 5.31 (s, 2H, $=\text{CH}_2$), 2.29 (s, 12H, Me) ppm. ^{13}C NMR (CD_3OD): δ = 139.07, 135.75, 132.61, 131.62, 131.47, 130.49, 127.22, 127.16, 125.90, 118.65, 113.81, 113.35, 50.83, 49.00, 19.83 ppm. LC-MSMS: $[\text{M}-\text{Br}]^+$ at m/z 607.20. Anal. Calc. for $\text{C}_{36}\text{H}_{38}\text{N}_4\text{Br}_2$: C, 62.97; H, 5.59; N, 8.16. Found: C, 63.07; H, 5.42; N, 7.77%.

2.2.2. Synthesis of $\text{L}_2 \cdot 2\text{HBr}$ (2b)

Compound **2b** was obtained by the reaction of **1** with 3,5-dimethoxybenzyl bromide with the same procedure for **2a** except that drying in vacuum. Yield: 77%. IR: $\nu_{(\text{NCN})}$: 1554 cm^{-1} . ^1H NMR ($\text{dmsO}-d_6$): δ = 10.11 (s, 2H, NCHN), 8.03–7.95 (m, 4H, Ar-H), 7.67–7.59 (m, 4H, Ar-H), 6.73 (d, 4H, J = 1.4 Hz, Ar-H), 6.47 (s, 2H, Ar-H), 5.68 (s, 4H, NCH_2), 5.42 (s, 4H, NCH_2), 5.27 (s, 2H, $=\text{CH}_2$), 3.70 (s, 12H, OMe) ppm. ^{13}C NMR ($\text{dmsO}-d_6$): δ = 161.29, 143.49, 136.50, 136.27, 131.66, 131.48, 127.29, 127.19, 119.26, 114.48, 114.43, 107.22, 100.42, 55.84, 50.47, 49.22 ppm. LC-MSMS: $[\text{M}-\text{Br}-\text{H}]^+$ at m/z 669.20. Anal. Calc. for $\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_4\text{Br}_2$: C, 57.60; H, 5.11; N 7.47. Found: C, 56.85; H, 4.74; N, 7.38%.

2.2.3. Synthesis of $\text{L}_3 \cdot 2\text{HBr}$ (2c)

Compound **2c** was obtained by the reaction of **1** with 3,5-di-tert-butylbenzyl bromide with the same procedure for **2a** except that washing process. The solid was washed by Et_2O (4x5 mL) and dried in air. Yield: 97%. IR $\nu_{(\text{NCN})}$: 1562 cm^{-1} . ^1H NMR ($\text{dmsO}-d_6$): δ = 10.17 (s, 2H, NCHN), 8.11 (dd, 2H, J_1 = 8.6 Hz, J_2 = 4.5 Hz, Ar-H), 7.99–7.91 (m, 2H, Ar-H), 7.71–7.56 (m, 4H, Ar-H), 7.41 (s, 4H, Ar-H), 7.35 (s, 2H, Ar-H), 5.75 (s, 4H, NCH_2), 5.45 (s, 4H, NCH_2), 5.09 (s, 2H, $=\text{CH}_2$), 1.22 (s, 36H, Bu^t) ppm. ^{13}C NMR ($\text{dmsO}-d_6$): δ = 151.56, 143.30, 137.14, 133.55, 131.56, 131.51, 127.27, 127.22, 123.29, 122.64, 114.54, 114.38, 51.01, 49.08, 35.06, 31.58 ppm. LC-MSMS: $[\text{M}-\text{Br}]^+$ at m/z 775.40. Anal. Calc. for $\text{C}_{48}\text{H}_{62}\text{N}_4\text{Br}_2 \cdot 1.5\text{H}_2\text{O}$: C, 65.36; H, 7.44; N, 6.35. Found: C, 65.63; H, 7.43; N, 7.32%.

2.3. General procedure for synthesis of NHC-Ag(I) complexes

The mixture of the salt (1 mmol) and Ag_2O (2 mmol) was stirred in MeOH (20 mL) at room temperature for 24 h in dark. After filtration through celite, NH_4PF_6 (2.5 mmol) in MeOH (10 mL) was added to the filtrate and it was stirred at 25 °C for 2 h in dark. Filtration, washing with MeOH (2 x 5 mL) and Et_2O (2 x 5 mL), and finally recrystallization from MeCN/ Et_2O (1/3) gave the pure product.

2.3.1 $[\text{Ag}_2(\text{L}_1)_2](\text{PF}_6)_2$ (3a)

Yield: 77%. IR $\nu_{(\text{NCN})}$: 1400 cm^{-1} . ^1H NMR ($\text{dmsO}-d_6$): δ = 7.62 (t, 8H, J = 9.1 Hz, Ar-H), 7.34 (s, 8H, Ar-H), 6.76 (s, 12H, Ar-H), 5.55 (s, 8H, NCH_2), 5.36 (s, 8H, NCH_2), 4.96 (s, 4H, $=\text{CH}_2$), 2.00 (s, 24H, Me) ppm. ^{13}C NMR ($\text{dmsO}-d_6$): δ = 140.40, 138.31, 136.30, 133.79, 133.68, 129.88, 125.14, 124.90, 124.71, 112.92, 52.23, 52.02, 21.12 ppm. LC-MSMS: $[\text{M}-\text{PF}_6]^+$ at m/z 1409.35. Anal. Calc. for $\text{C}_{72}\text{H}_{72}\text{N}_8\text{Ag}_2\text{P}_2\text{F}_{12}$: C, 55.60; H, 4.68; N 7.21. Found: C, 56.53; H, 4.67; N, 7.24%.

2.3.2 $[\text{Ag}_2(\text{L}_2)_2](\text{PF}_6)_2$ (3b)

Yield: 76%. IR $\nu_{(\text{NCN})}$: 1400 cm^{-1} . ^1H NMR ($\text{dmsO}-d_6$): δ = 7.68–7.59 (m, 8H, Ar-H), 7.35 (q, 8H, J = 7.5 Hz, Ar-H), 6.27 (d, J = 8.1 Hz, 12H, Ar-H), 5.56 (s, 8H, NCH_2), 5.38 (s, 8H, NCH_2), 4.91 (s, 4H, $=\text{CH}_2$), 3.52 (s, 24H, OMe) ppm. ^{13}C NMR ($\text{dmsO}-d_6$): δ = 162.16, 140.46, 138.53, 133.78, 133.71, 124.90, 124.76, 112.85, 105.65, 99.16, 55.42, 52.15, 51.97 ppm. LC-MSMS: $[\text{M}-\text{PF}_6]^+$ at m/z 1537.40. Anal. Calc. for $\text{C}_{72}\text{H}_{72}\text{N}_8\text{O}_8\text{Ag}_2\text{P}_2\text{F}_{12}$: C, 51.37; H, 4.32; N, 6.66. Found: C, 52.14; H, 4.16; N, 6.71%.

2.3.3 $[\text{Ag}_2(\text{L}_3)_2](\text{PF}_6)_2$ (3c)

Yield: 70%. IR $\nu_{(\text{NCN})}$: 1400 cm^{-1} . ^1H NMR ($\text{dmsO}-d_6$): δ = 7.86 (d, 4H, J = 8.2 Hz, Ar-H), 7.50–7.40 (m, 8H, Ar-H), 7.36 (t, 4H, J = 7.6 Hz, Ar-H), 7.22 (s, 4H, Ar-H), 7.16 (s, 8H, Ar-H), 5.69 (s, 8H, NCH_2), 5.34 (s, 8H, NCH_2), 4.74 (s, 4H, $=\text{CH}_2$), 1.01 (s, 72H, Bu^t) ppm. ^{13}C NMR ($\text{dmsO}-d_6$): δ = 151.19, 135.72, 133.95, 133.50, 125.06, 124.93, 122.19, 121.92, 113.28,

112.72, 52.75, 34.78, 31.36 ppm. LC-MSMS: $[M-PF_6]^+$ at m/z 1746.60. Anal. Calc. for $C_{96}H_{120}N_8Ag_2P_2F_{12}$: C, 60.94; H, 6.41; N, 5.92. Found: C, 61.30; H, 6.41; N, 5.69%.

2.4. General procedure for A³-coupling reaction

NHC silver complex (3 mol%), aldehyde (1 mmol), amine (1.2 mmol) and phenylacetylene (168 μ L, 1.5 mmol) were placed in a test tube with screw cap. The mixture was stirred at 80 °C for 18 h in dark medium. After cooling to room temperature, Et₂O and MgSO₄ were added to the mixture. Filtration was done and Et₂O was removed from the filtrate. Related propargylamine was obtained in pure form by column chromatography.

3. Results and discussion

Synthesis methods of dibenzimidazolium salts and dinuclear NHC-Ag(I) complexes are in Figure 1. Dibenzimidazole compound **1** was prepared by the reaction of two equivalents of benzimidazole and one equivalent of 1,1-bis(chloromethyl) ethylene by using NaH base in THF [15]. Quaternization of **1** with two equivalents of substituted benzyl bromides afforded the dibenzimidazolium dibromide salts **2a-2c**. Transition metal complexes of N-benzylic benzimidazol-2-ylidene are of importance in organometallic chemistry, and there have been various studies on these compounds [50,51]. Dinuclear cationic NHC silver hexafluorophosphate complexes **3a-3c** were procured by the reactions of **2a-2c** with two equivalents of Ag₂O and then salt metathesis reactions of bromide complexes with NH₄PF₆ in methanol medium.

The results of elemental analysis confirm the expected formulations. While the signals of the acidic C2 protons of **2a-2c** appear at 9.78-10.17 ppm in the ¹H NMR spectra, these signals resonating in a low field do not exist in those of the Ag(I) complexes. This observation points out formation of a NHC metal complex as previously reported [52]. The absence of carbene carbon signals in the ¹³C NMR spectra of the silver complexes may be attributed to the fluxional behaviour of the NHC silver complexes [15,53]. IR peaks concerning the stretching vibrations of -C=N- groups for the salts are present at 1554–1562 cm⁻¹. Whereas, these values decrease to 1400 cm⁻¹ for the metal complexes. These data are compatible with the literature [54]. The stretching frequencies related to P-F bond for the complexes appear in the range of 834–840 cm⁻¹. The sharp band observed in 3390 cm⁻¹ for **2c** is assigned to the $\nu(O-H)$ of hydrated water. TGA/DTA analysis supports that this compound is a hydrate molecule. Unfortunately, single crystals required for XRD analysis were not obtained despite all efforts. The molecular weights of **2a-2c** and **3a-3c** were proved by LC-MSMS spectroscopic analysis. $[M-Br]^+$ and $[M-2Br]^+$ peaks are observed for **2a-2c**. There are $[M-PF_6]^+$ signals at 1409.35, 1537.40, and 1746.60, respectively in the mass spectra of **3a-3c**. Mass data affirm dinuclear $[Ag_2(L)_2](PF_6)_2$ formulation. It is believed that the cationic silver complexes **3a-3c** isolated as hexafluorophosphate salts do not form polymers.

Stabilities of the silver complexes in solution were studied by ¹H NMR spectroscopy for a period of ten days. ¹H NMR spectra were recorded on the day their dms_o-d₆ solutions were prepared and after one, four, seven, and ten days. The spectra for stability testing are shown in Figures S7-S9 in supporting information. The results evidently point out that the complexes are stable in solution even after ten days.

While A³-coupling reactions have been catalyzed by many transition metal ions, the number of studies on using NHC silver complexes is limited. In this work, catalytic activities of Ag(I) compounds were studied for three-component coupling reaction of some aldehydes, amines and phenylacetylene. The reaction of p-formaldehyde, diethylamine, and phenylacetylene was carried out using different solvents and different amount of catalyst **3a** (Table 1, entries 1-8). The

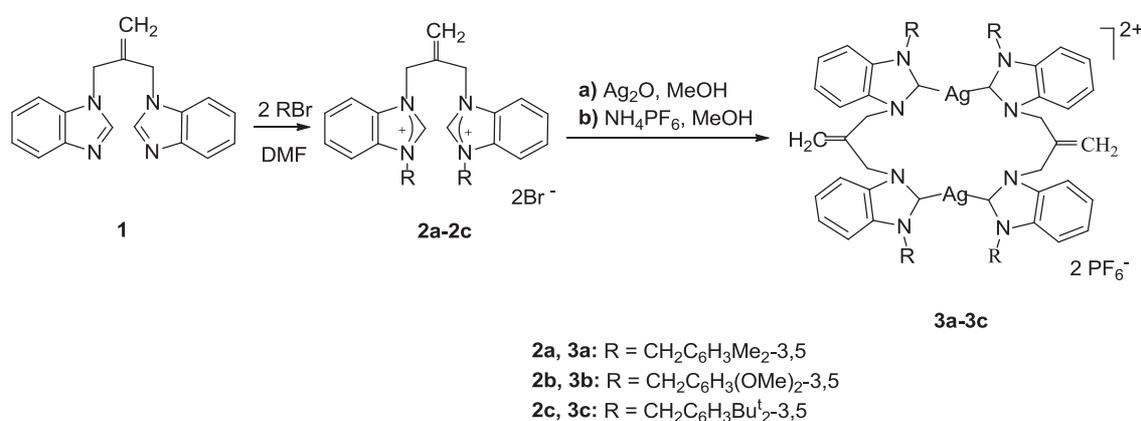
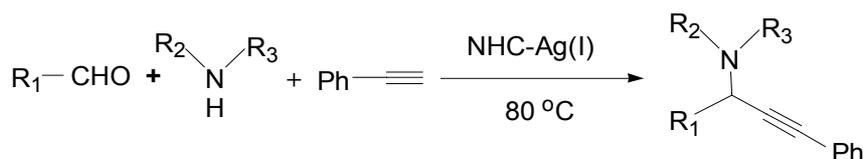


Figure 1. Synthesis of **2a-2c** and **3a-3c**.

**Table 1.** NHC silver catalyzed A³-coupling reaction ^a

Entry	Catalyst (% mol)	Solvent	Aldehyde	Amine	Yield (%) ^{b,c}
1	3a (1)	-	HCHO	NHEt ₂	42
2	3a (2)	-	HCHO	NHEt ₂	64
3	3a (3)	-	HCHO	NHEt ₂	78
4	3a (3)	water	HCHO	NHEt ₂	15
5	3a (3)	toluene	HCHO	NHEt ₂	18
6	3a (3)	DMF	HCHO	NHEt ₂	24
7	3a (3)	acetone	HCHO	NHEt ₂	45
8	3a (3)	MeCN	HCHO	NHEt ₂	62
9	3b (3)	-	HCHO	NHEt ₂	80
10	3c (3)	-	HCHO	NHEt ₂	80
11	3a (3)	-	HCHO	piperidine	51
12	3b (3)	-	HCHO	piperidine	51
13	3c (3)	-	HCHO	piperidine	52
14	3a (3)	-	CH ₃ (CH ₂) ₄ CHO	NHEt ₂	44
15	3a (3)	-	C ₆ H ₁₁ CHO	piperidine	68
16	3a (3)	-	HCHO	morpholine	14
17	3a (3)	-	CH ₃ (CH ₂) ₄ CHO	morpholine	26
18	3a (3)	-	PhCHO	morpholine	10

^a Reaction conditions: Aldehyde (1.0 mmol), amine (1.2 mmol), phenylacetylene (1.5 mmol), catalyst, 18 h, 80 °C, in air.

^b Isolated yields.

^c Average of two runs.

results showed that solvent free medium and increased amount of catalyst raised the activity. N,N-diethyl-3-phenylprop-2-yn-1-amine was obtained in 78% yield with 3 mol% catalyst (Table 1, entry 3). When the same reaction was performed by using piperidine instead of diethylamine, 51%–52% yields were obtained (Table 1, entries 11-13). These data are comparable with the literature [25,30]. It was understood that each of the three complexes exhibited similar activities in both reactions examined. In our previous work, 59% yield was obtained for this reaction with a similar complex containing 3-methoxybenzyl group on NHC ligand [15]. The presence of a larger number of alkyl groups on the benzyl substituent causes a decrease in the catalytic activity. 3,5-dimethylbenzyl, 3,5-dimethoxybenzyl and 3,5-di-tert-butylbenzyl substituents on NHC ligands did not affect the catalytic behaviours of the catalysts. This consequence is consistent with the literature [23,55]. In the case of using aliphatic aldehydes and the amines, such as diethylamine and piperidine, the propargylamine compounds were gained in moderate yields (Table 1, entries 14,15). Using morpholine caused low yields (Table 1, entries 16–18). When the results are compared, it is seen that the prepared complexes show less activity than monomeric NHC silver complexes possibly because of steric hindrance. This result is consistent with the literature [31].

Based on the literature [56–58], a mechanism can be proposed (Figure 2). Firstly, C-H activation of phenylacetylene forms a silver-acetylide complex and acidic proton. The formation of this complex may proceed through a π -complex. Then, in situ formed silver acetylide reacts with iminium cation to give propargylamine and the catalyst.

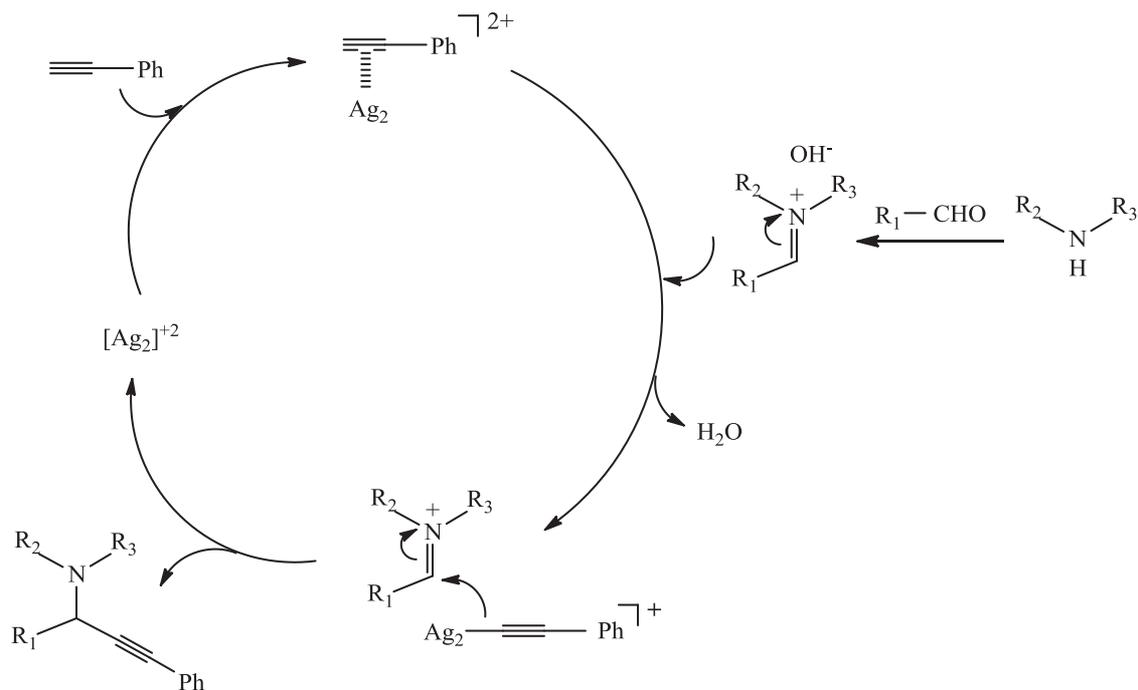


Figure 2. Proposed mechanism of propargylamine formation.

4. Conclusion

A new series of dibenzimidazolium salts bridged by 2-methylenepropane-1,3-diyl group and their dinuclear NHC-Ag(I) complexes were synthesized and characterized. Preliminary catalytic tests for A^3 -coupling reactions of some aldehydes, amines and phenylacetylene were performed. The results deduced that **3a-3c** exhibited similar activities, and the substituents on NHC ligands in the catalysts did not change the yields. Preparation of different transition metal complexes obtained from these compounds and their catalytic experiments have proceeded.

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Supporting Information

Synthesis, characterization and catalytic properties of cationic
N-heterocyclic carbene silver complexes

Deniz DEMİR ATLI

Table of Contents

• ^1H NMR and ^{13}C NMR spectra of the synthesized compounds	S2
• ^1H NMR spectra of the silver complexes for the stability tests	S8
• FT-IR spectra of the synthesized compounds	S11
• LC-MSMS spectra of the synthesized compounds	S14
• TGA/DTA graph of 2c	S17
• Characterization data for the catalytic products	S18
• ^1H NMR and ^{13}C NMR spectra of the catalytic products	S22

- ^1H NMR and ^{13}C NMR spectra of the synthesized compounds.

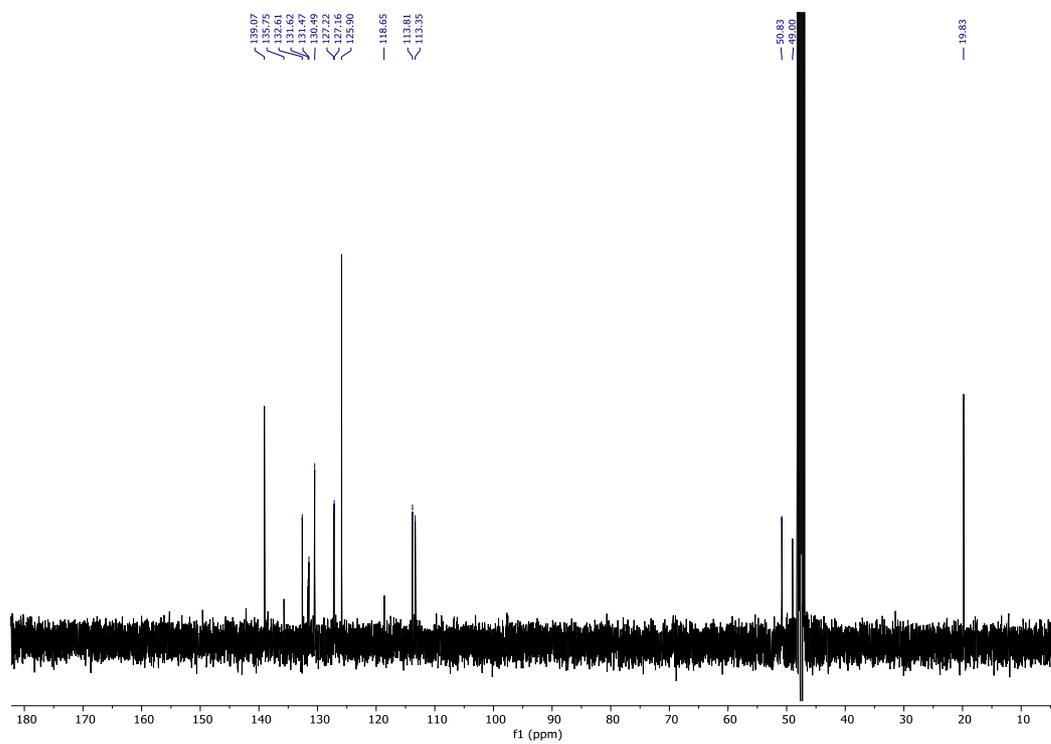
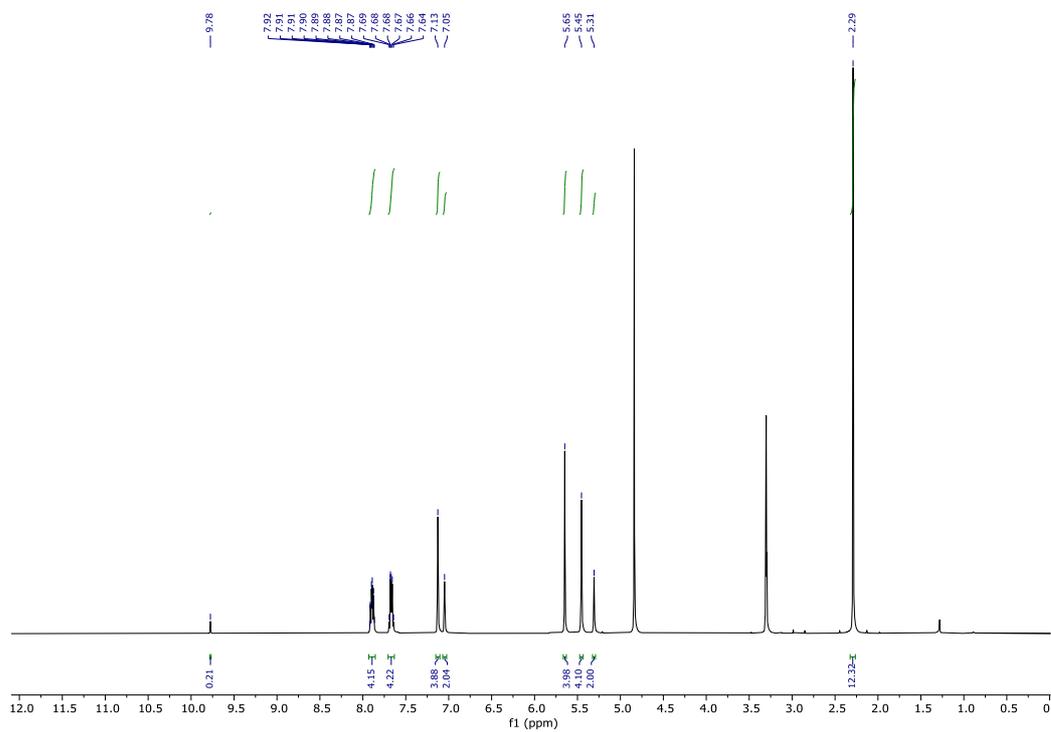


Figure S1. ^1H and ^{13}C NMR spectra of 2a.

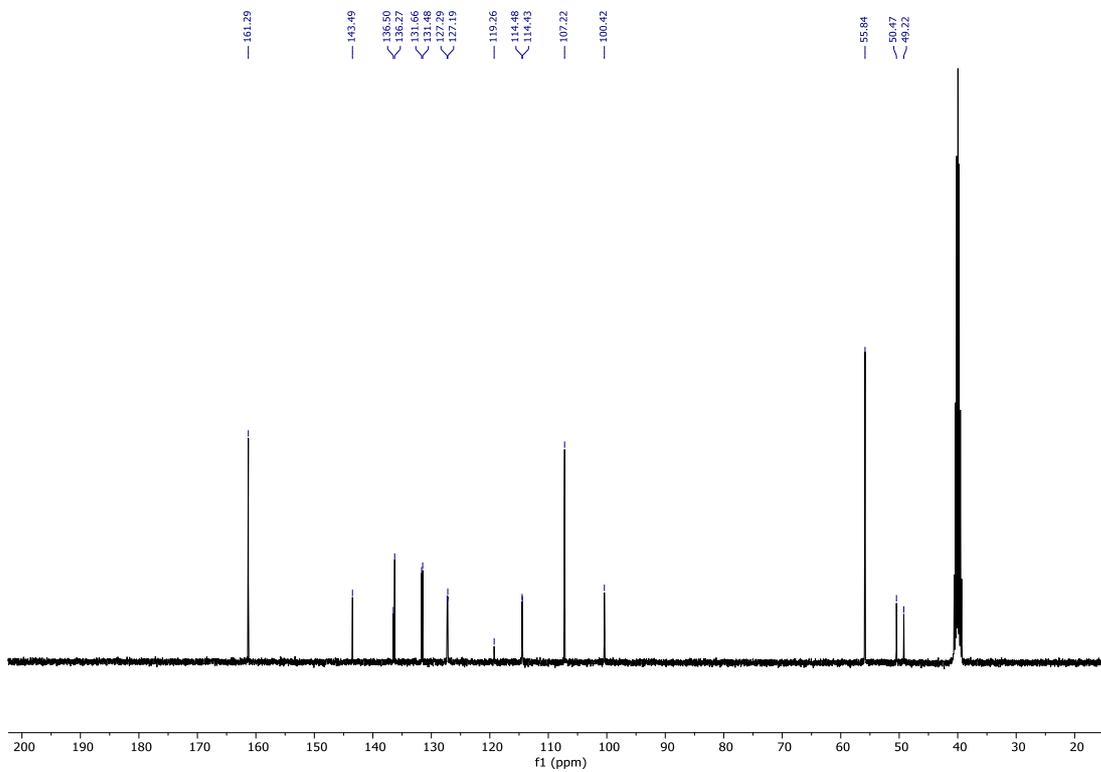
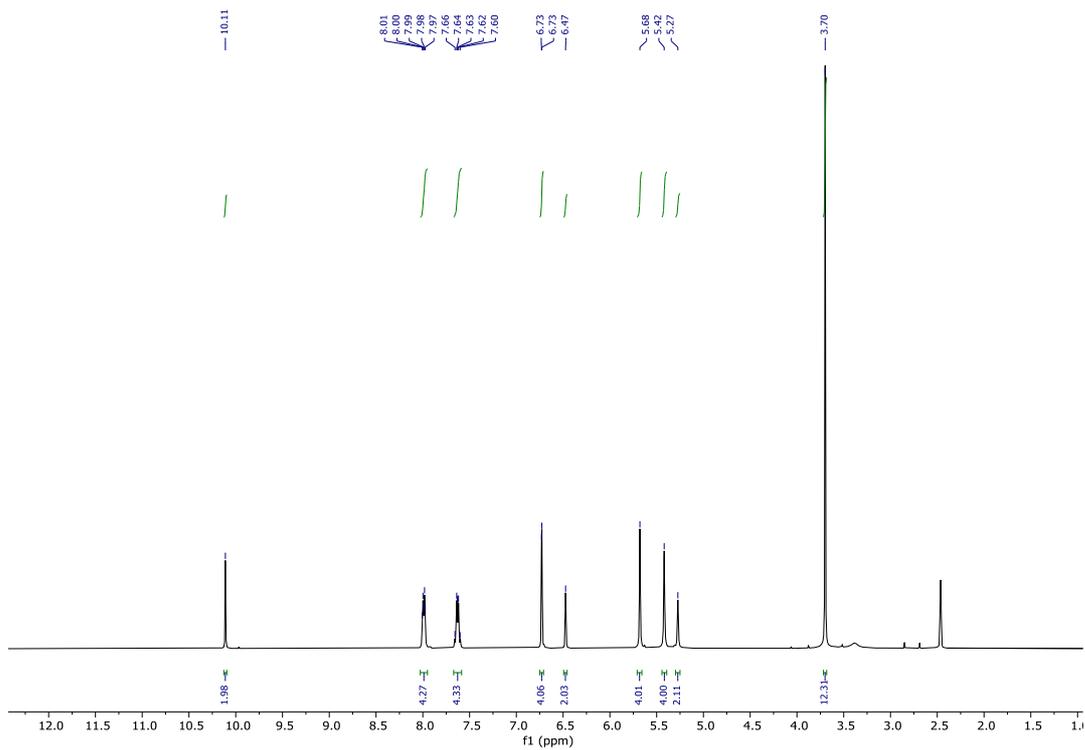


Figure S2. ^1H and ^{13}C NMR spectra of **2b**.

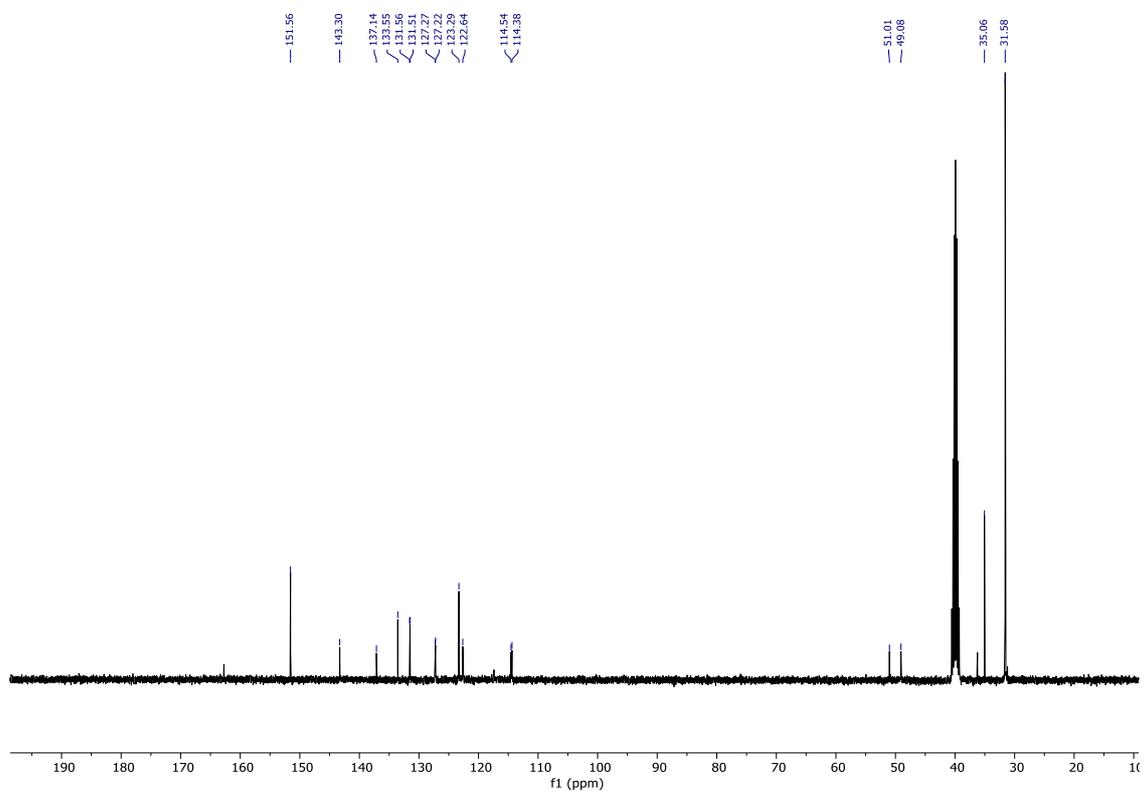
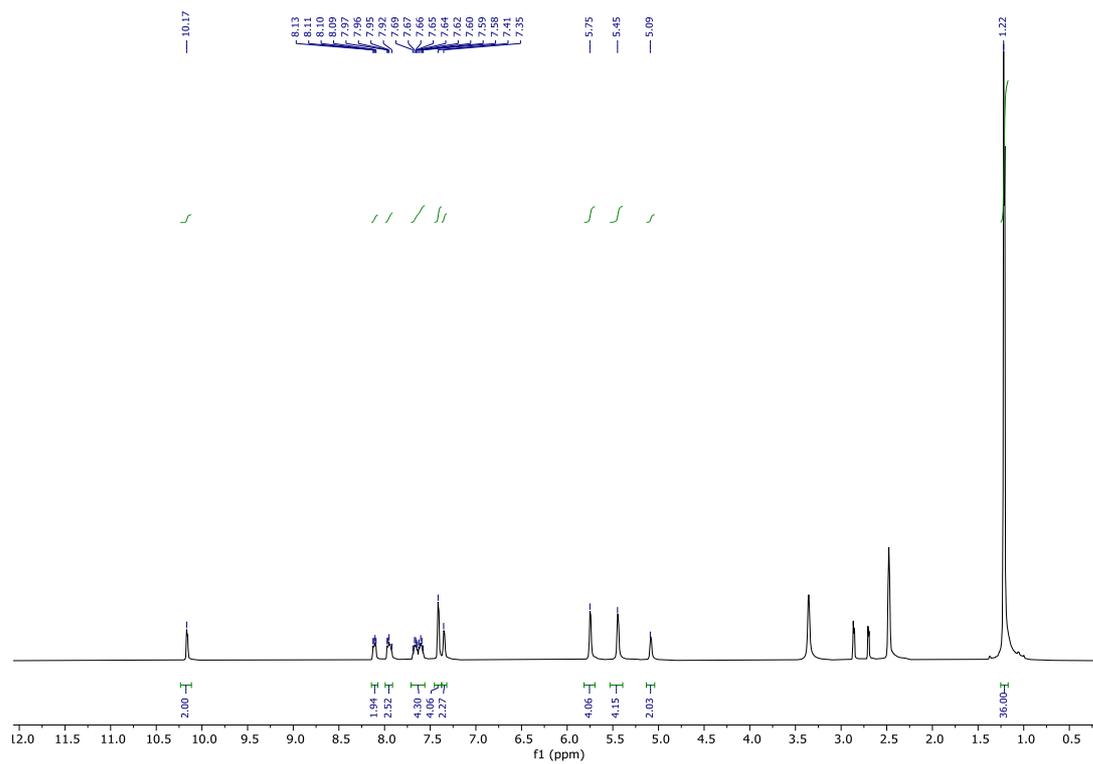


Figure S3. ^1H and ^{13}C NMR spectra of **2c**.

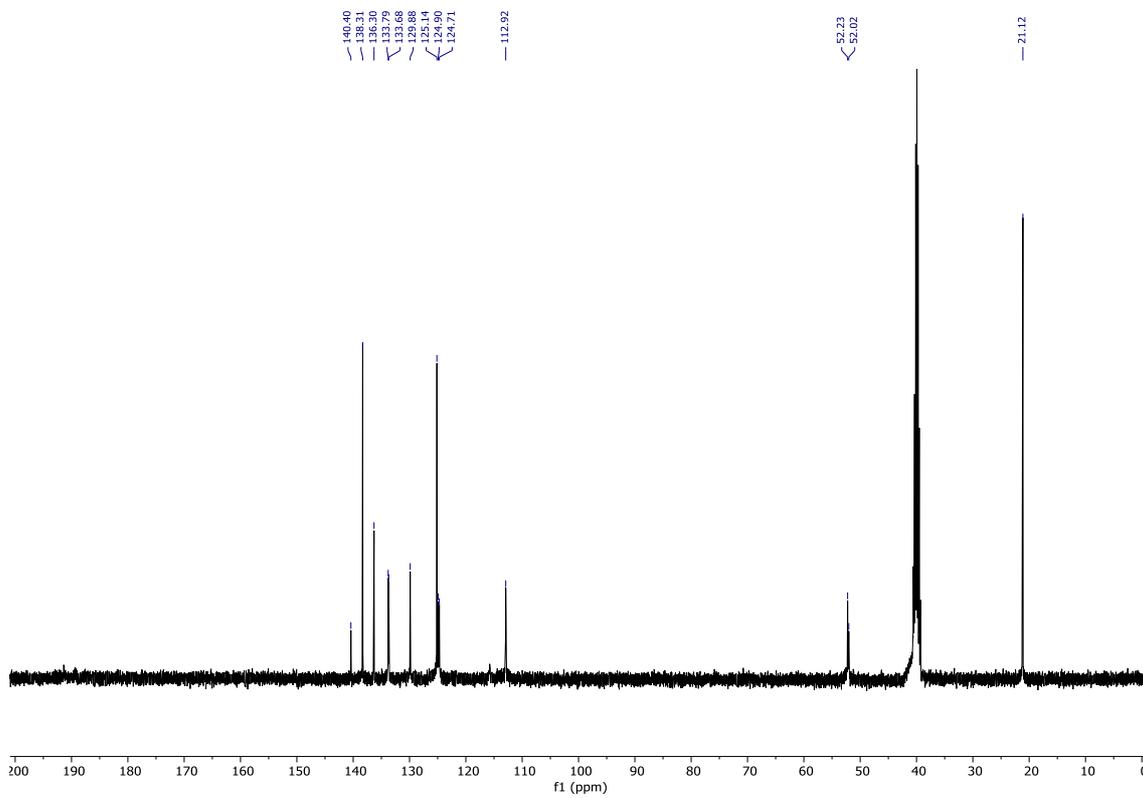
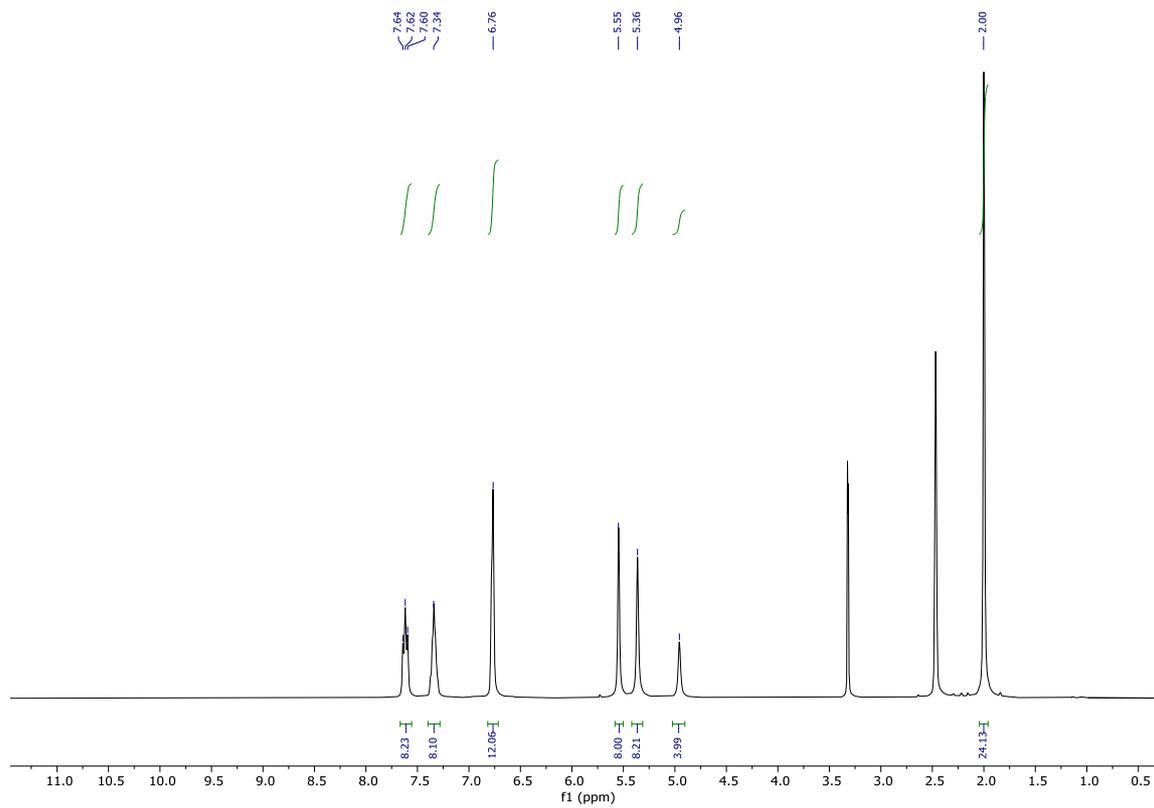


Figure S4. ¹H and ¹³C NMR spectra of **3a**.

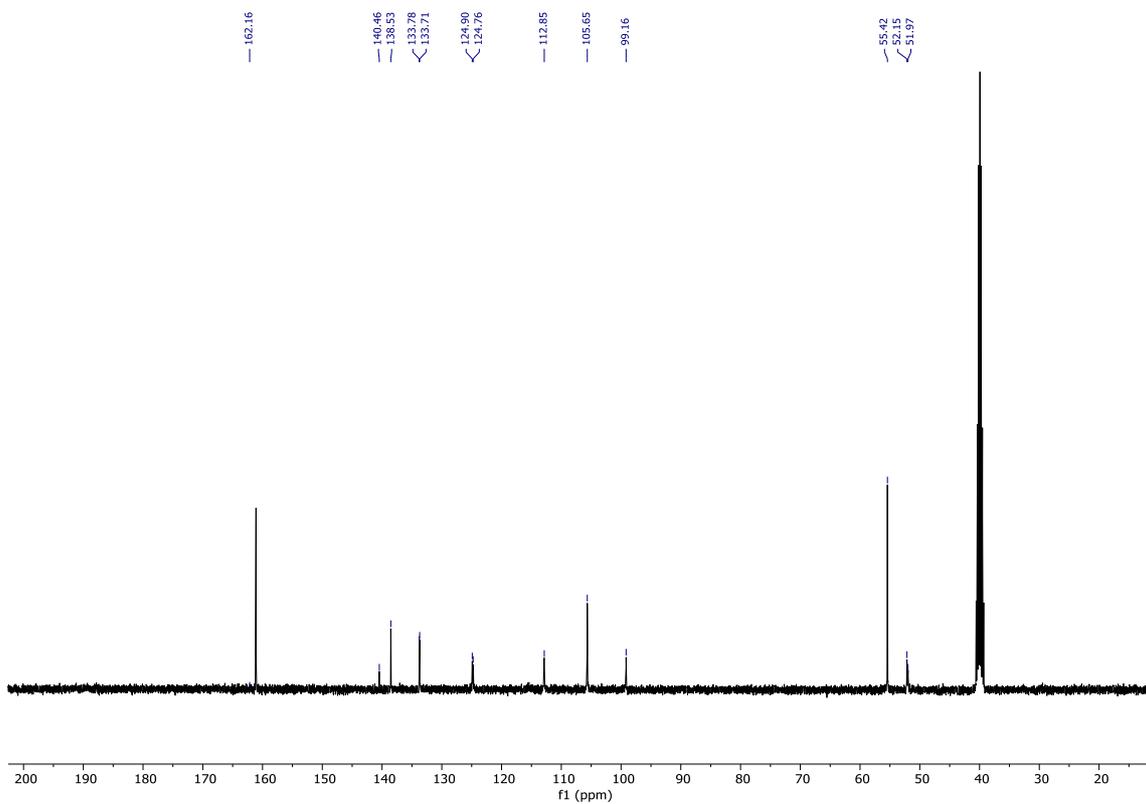
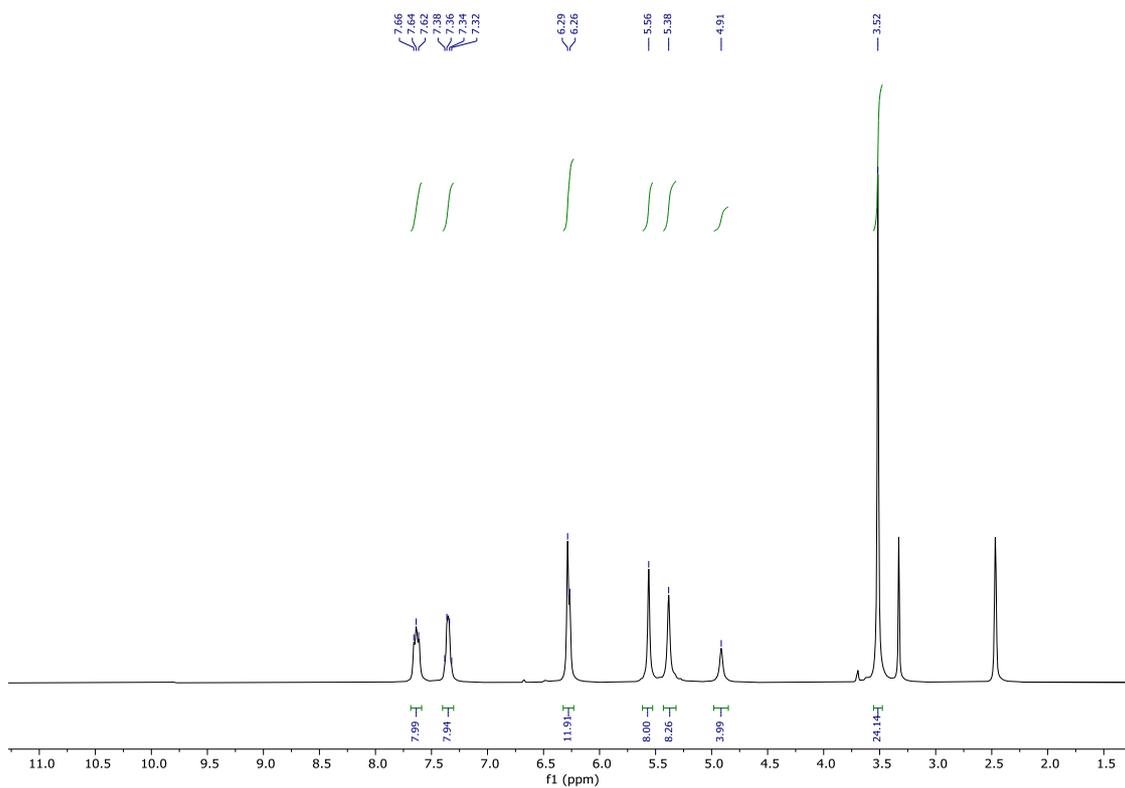


Figure S5. ^1H and ^{13}C NMR spectra of **3b**.

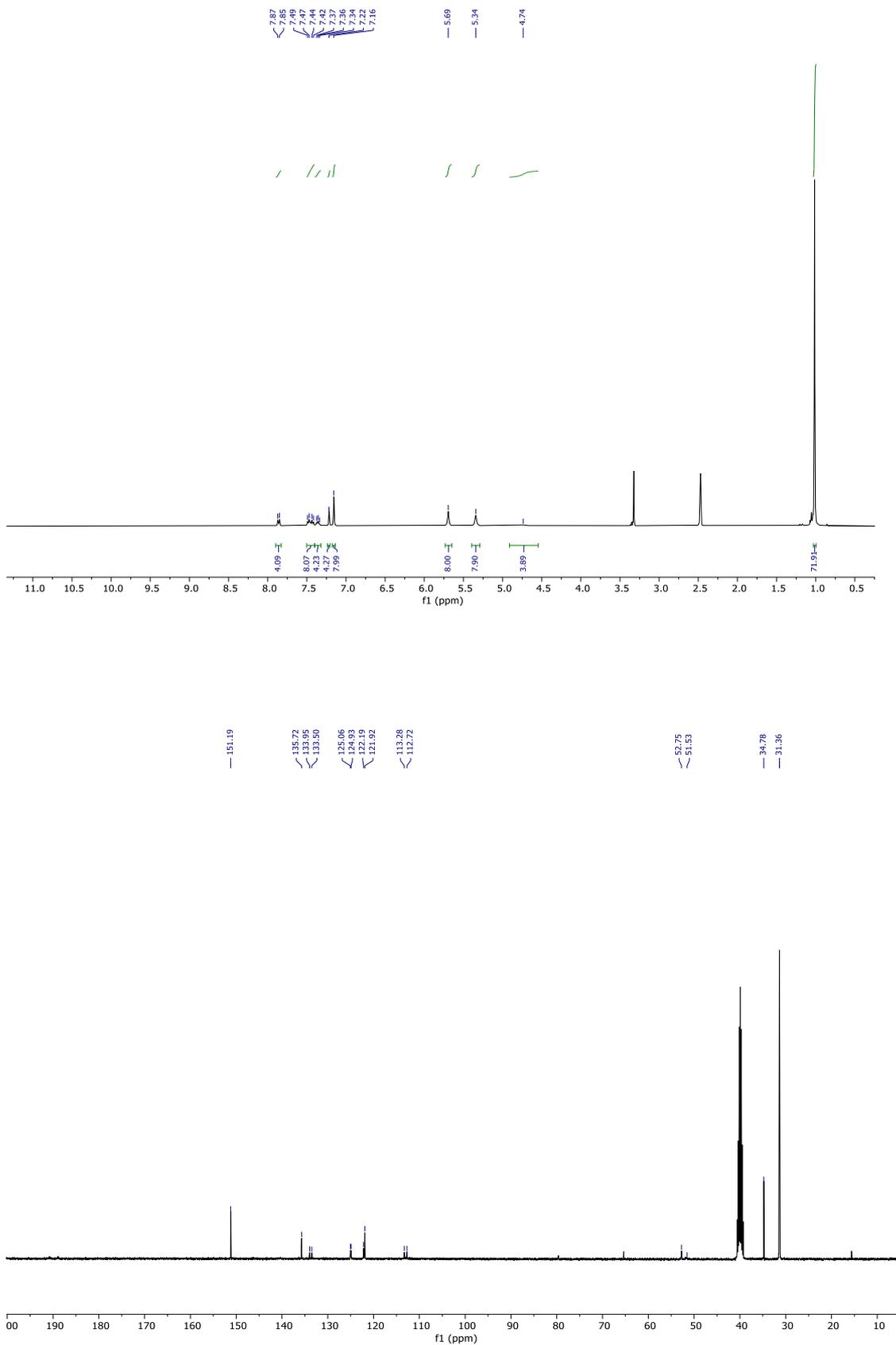


Figure S6. ¹H and ¹³C NMR spectra of **3c**.

- ^1H NMR spectra of the silver complexes for the stability tests

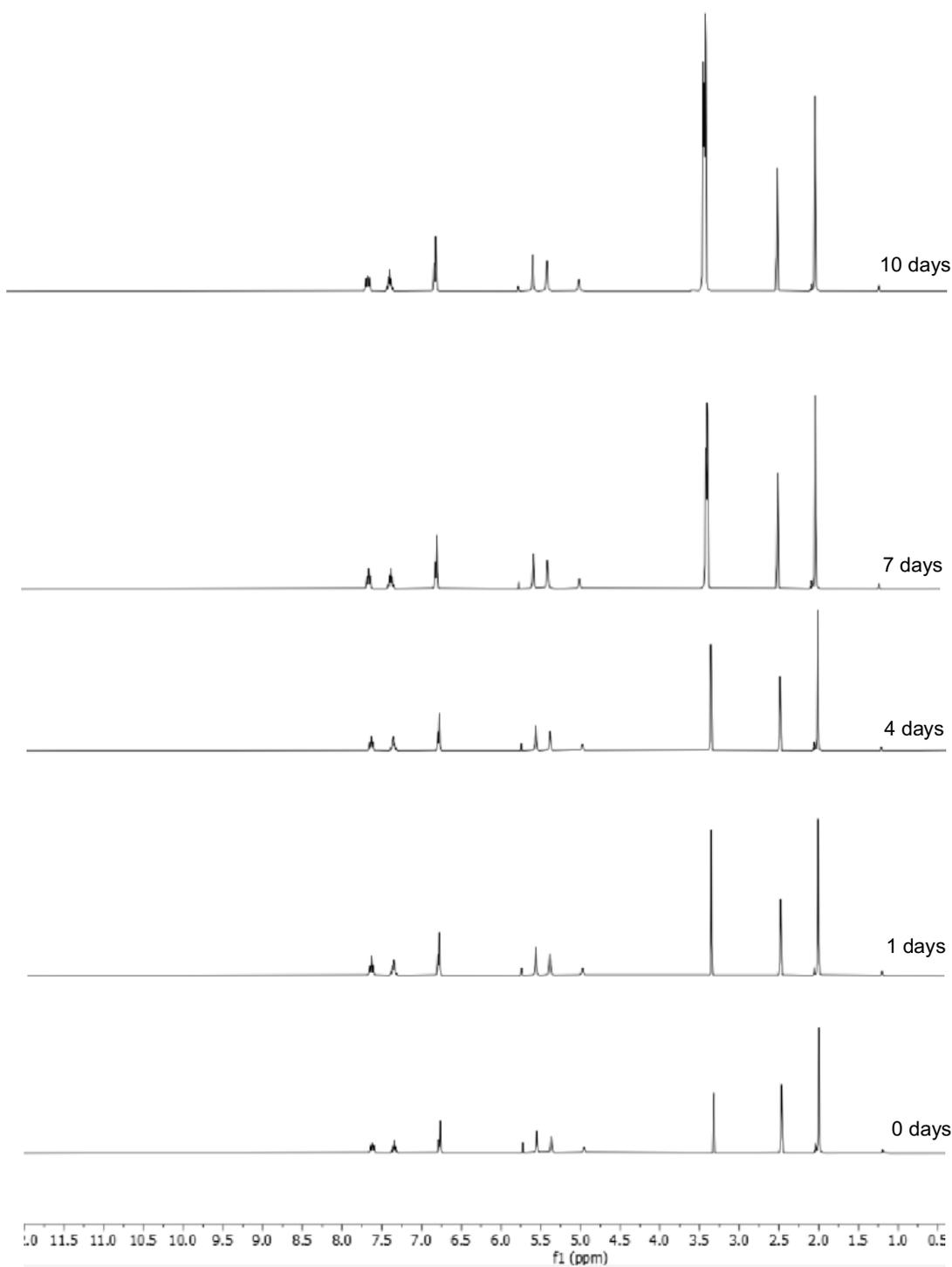


Figure S7. ^1H NMR spectra of **3a** measured at different times after preparation of the solution in $\text{dms}\text{-d}_6$.

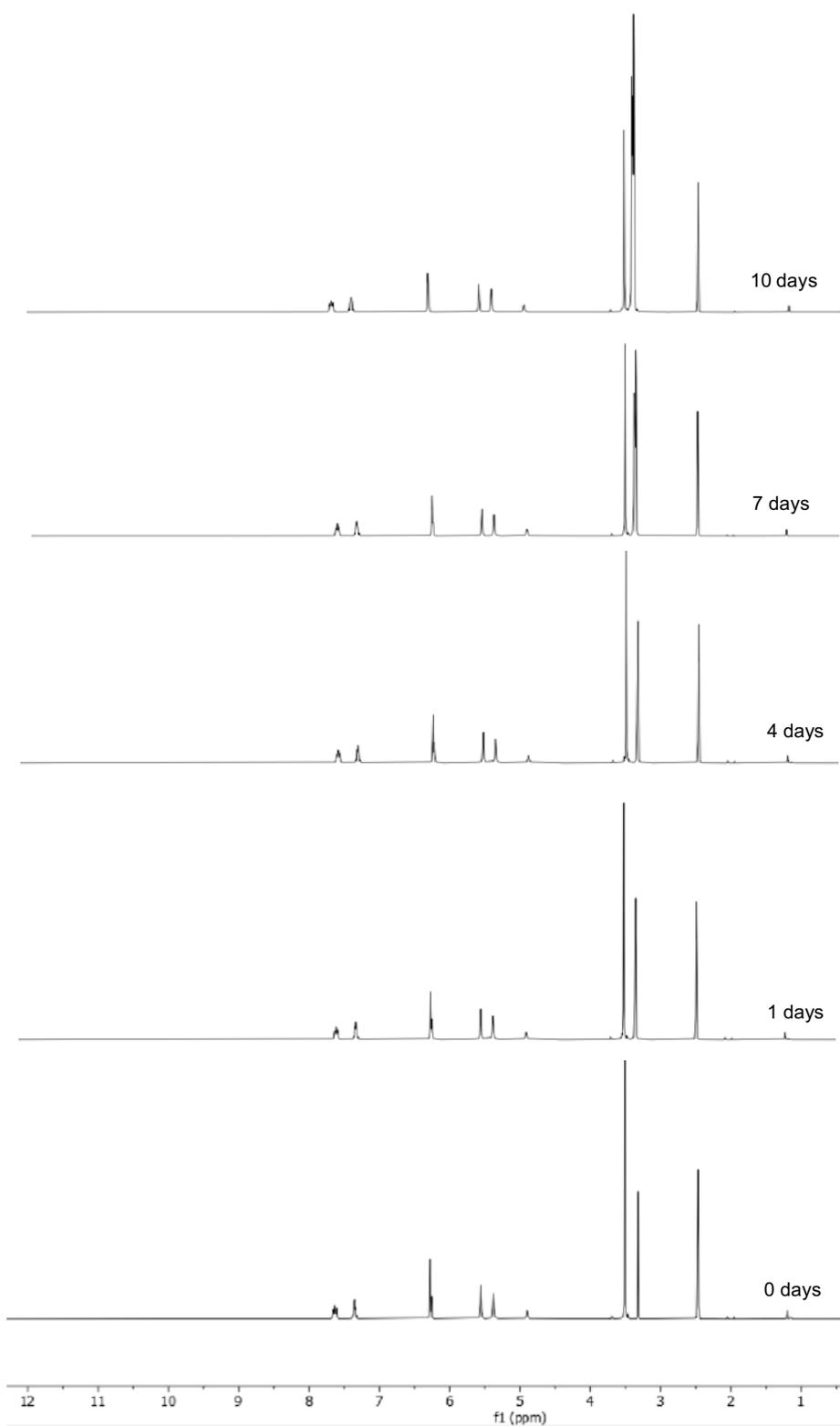


Figure S8. The ^1H NMR spectra of **3b** measured at different times after preparation of the solution in dms0-d_6 .

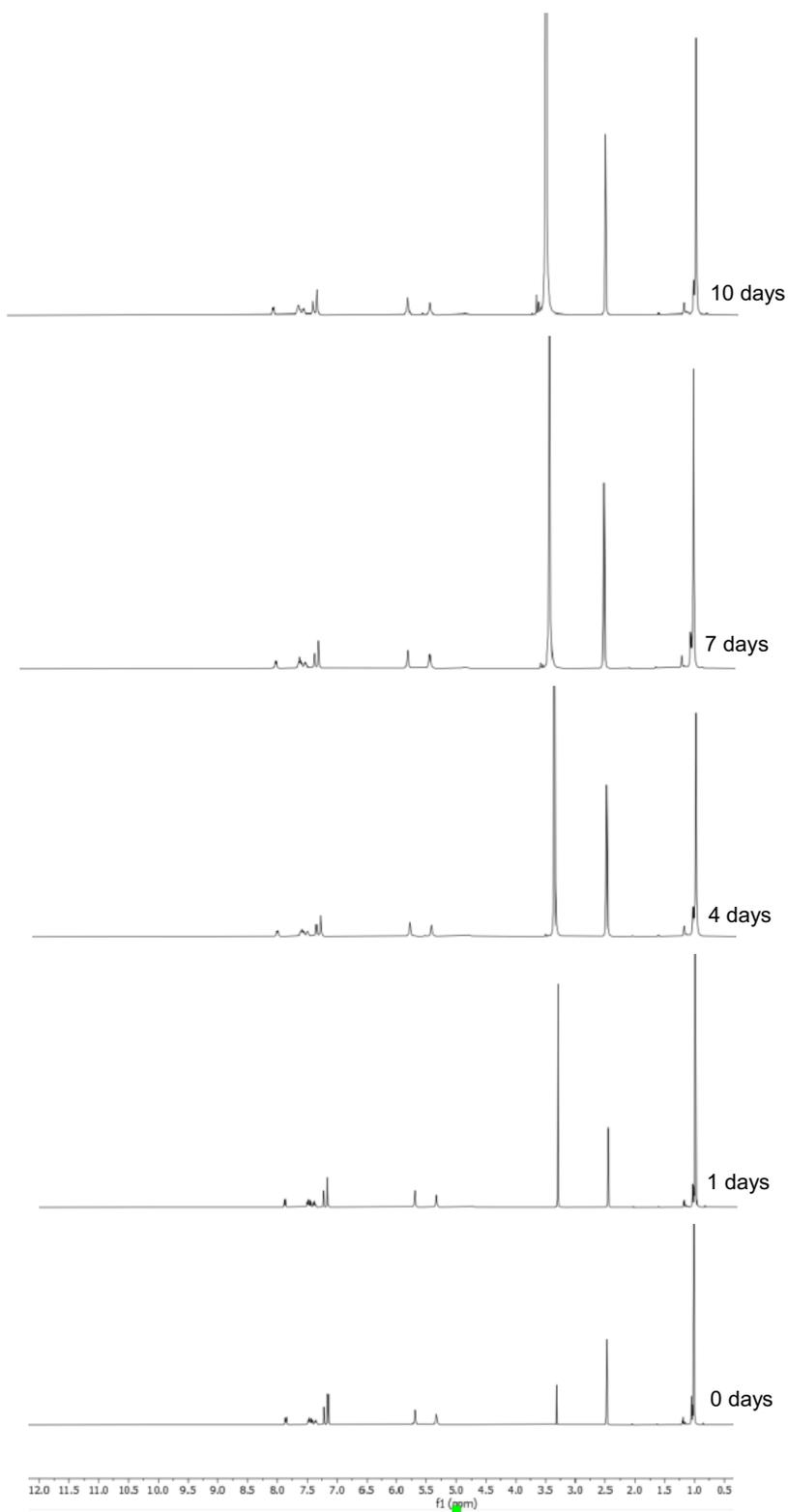


Figure S9. The ¹H NMR spectra of **3c** measured at different times after preparation of the solution in dms0-d₆.

- FT-IR spectra of the synthesized compounds

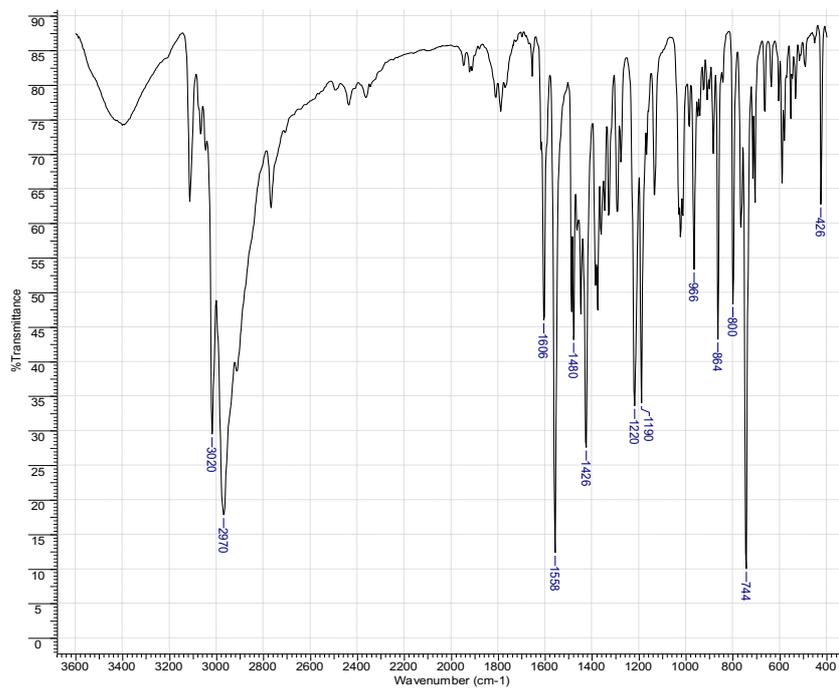


Figure S10. FT-IR spectrum of 2a.

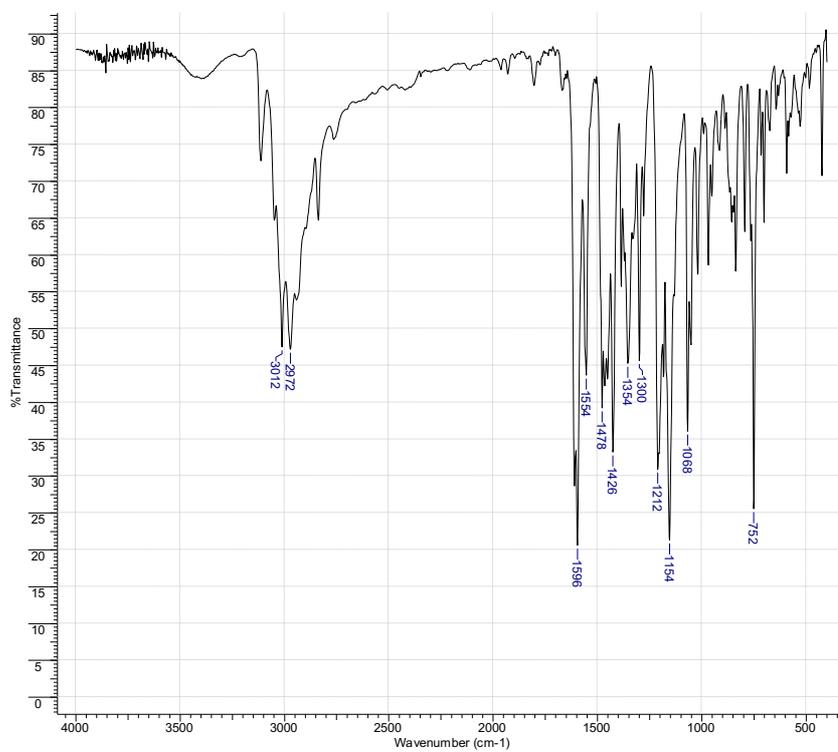


Figure S11. FT-IR spectrum of 2b.

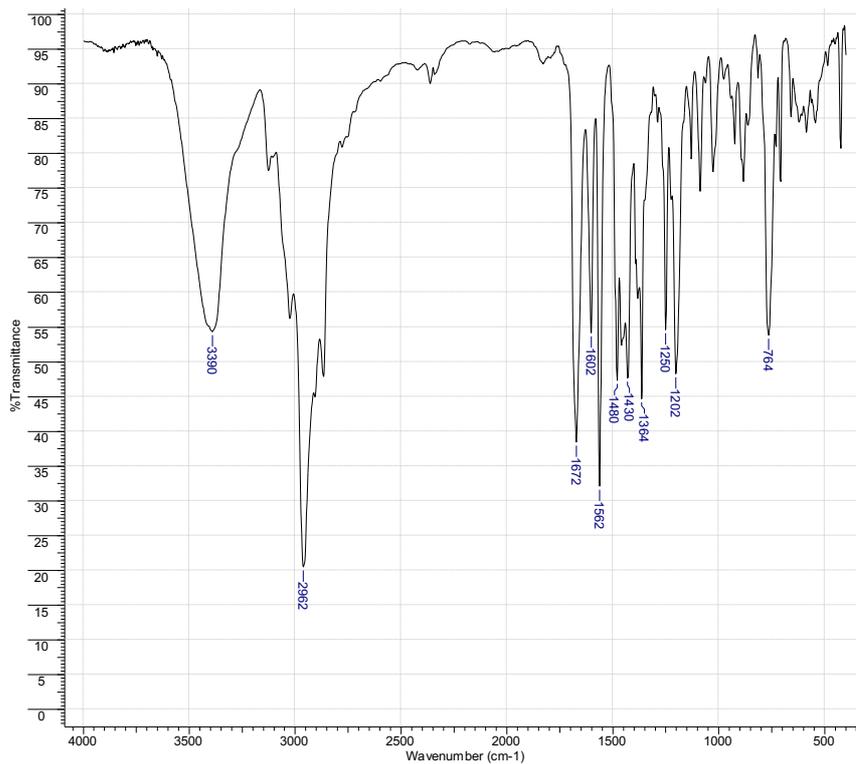


Figure S12. FT-IR spectrum of 2c.

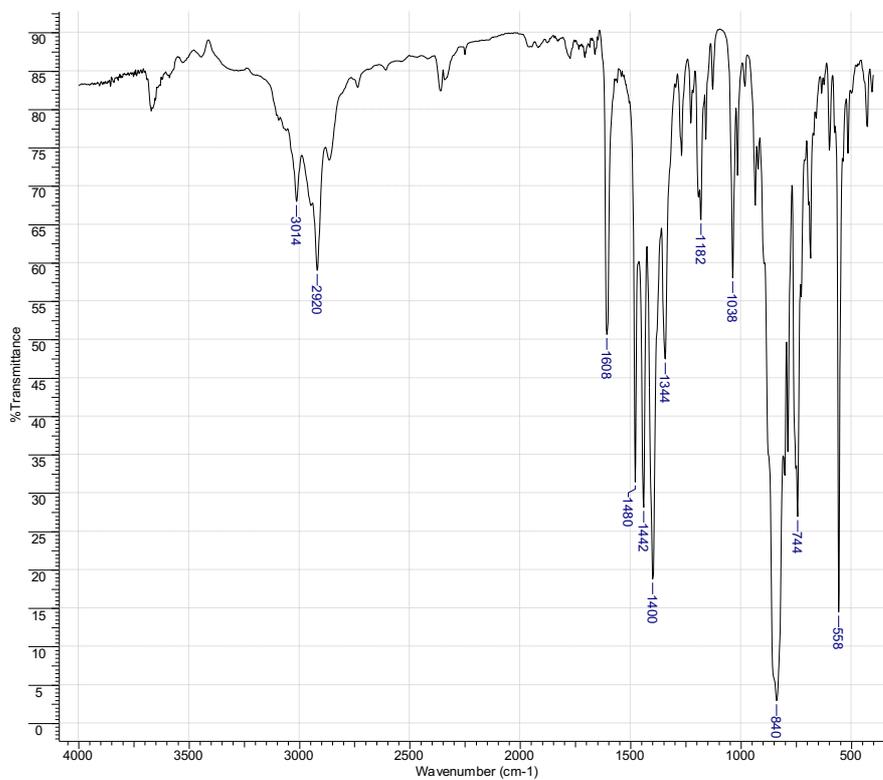


Figure S13. FT-IR spectrum of 3a.

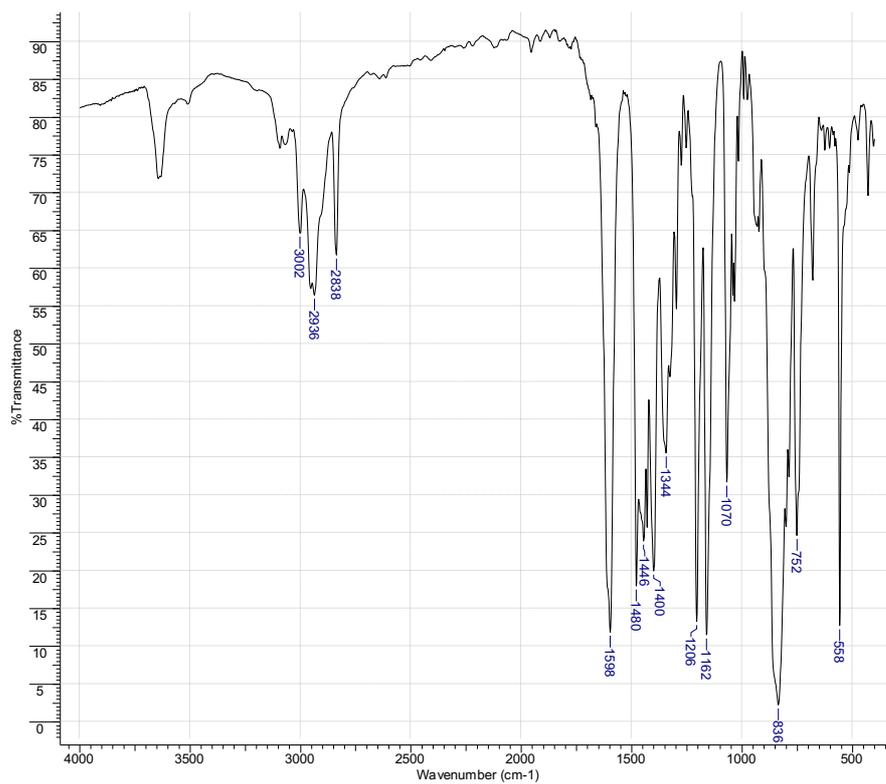


Figure S14. FT-IR spectrum of **3b**.

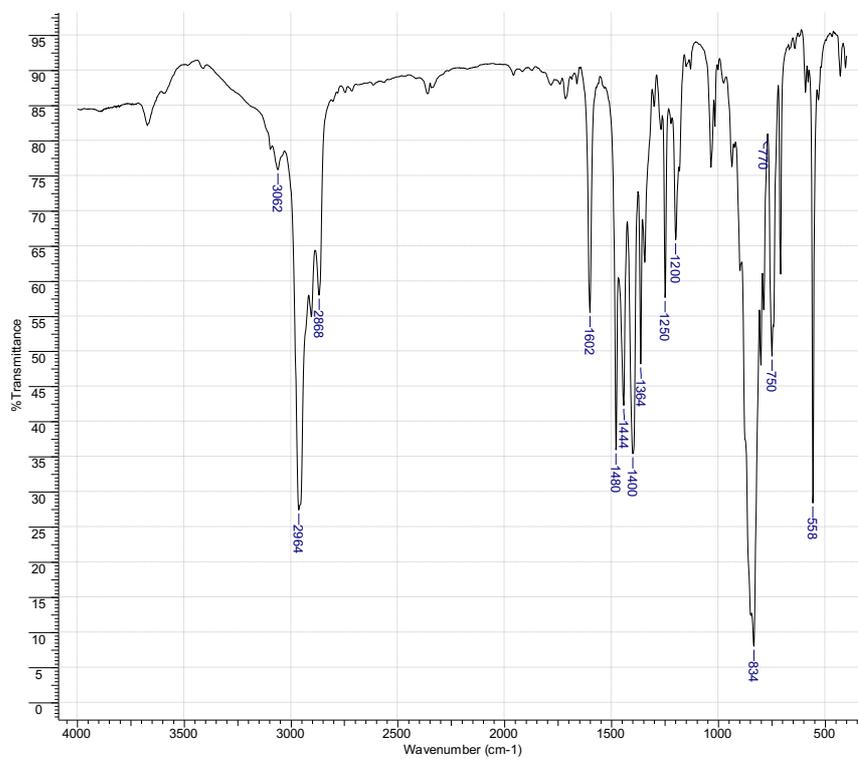


Figure S15. FT-IR spectrum of **3c**.

- LC-MSMS spectra of the synthesized compounds

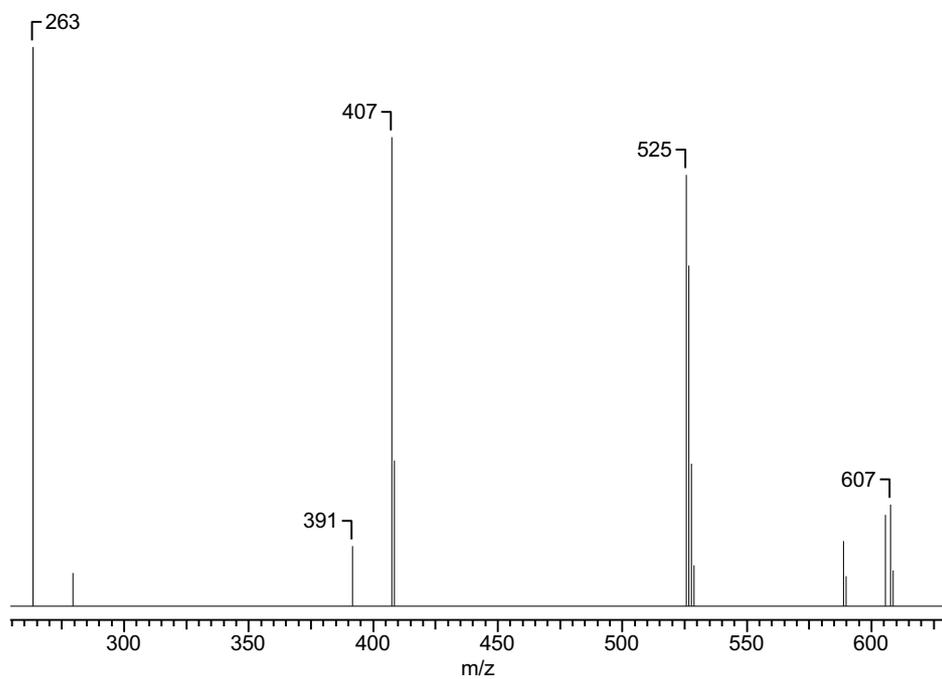


Figure S16. LC-MSMS spectrum of **2a**.

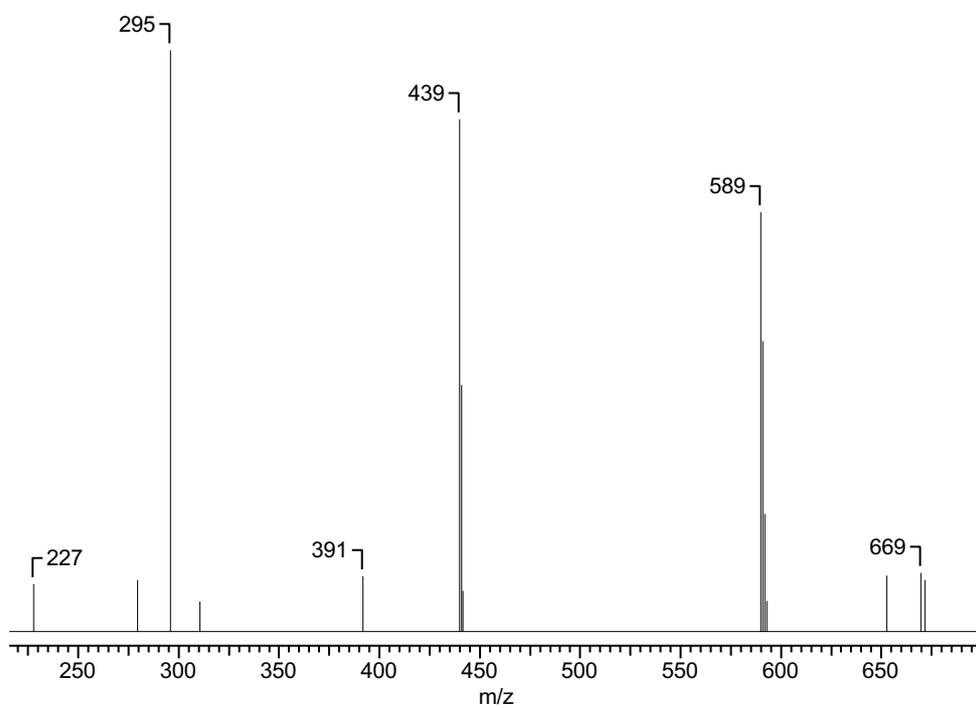


Figure S17. LC-MSMS spectrum of **2b**.

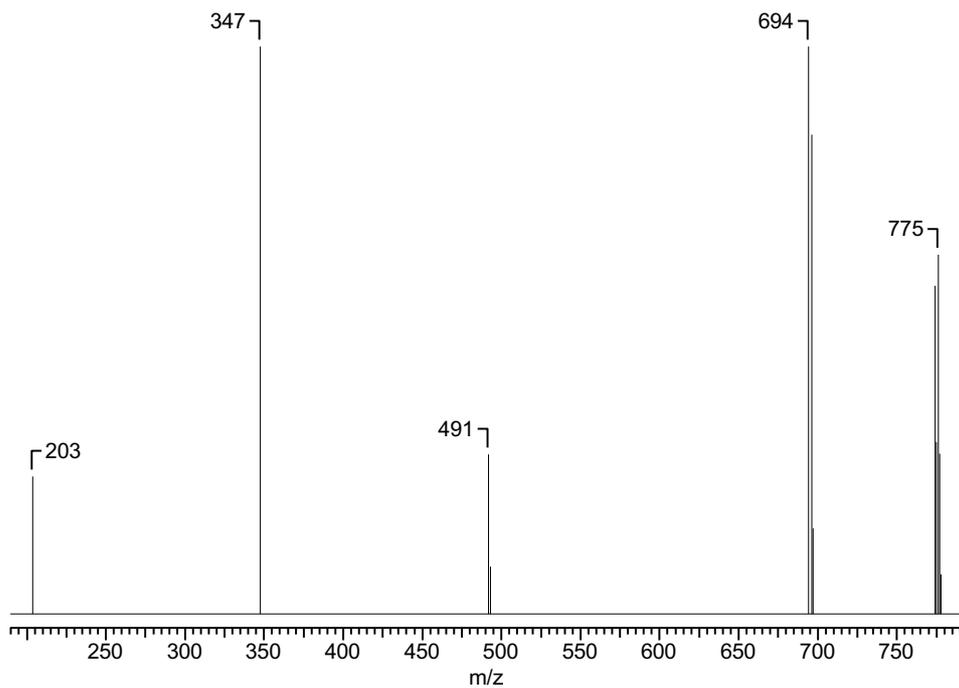


Figure S18. LC-MSMS spectrum of **2c**.

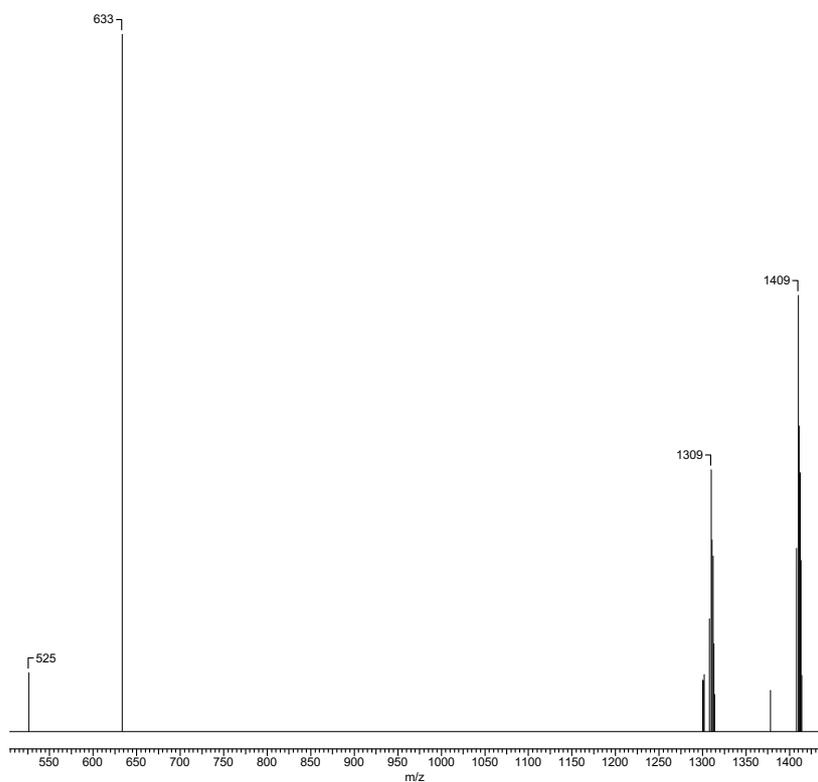


Figure S19. LC-MSMS spectrum of **3a**.

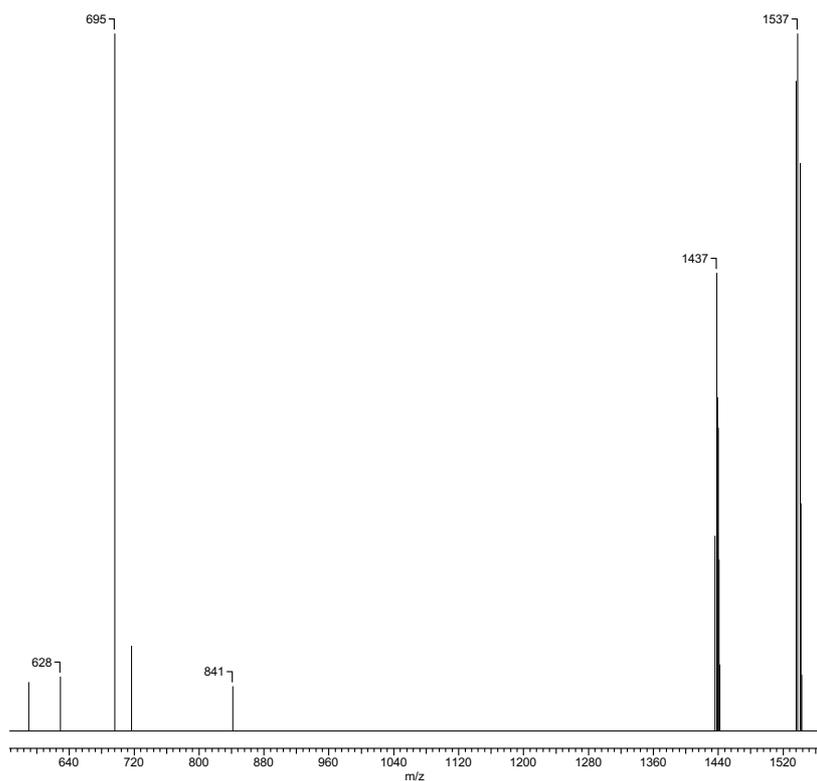


Figure S20. LC-MSMS spectrum of **3b**.

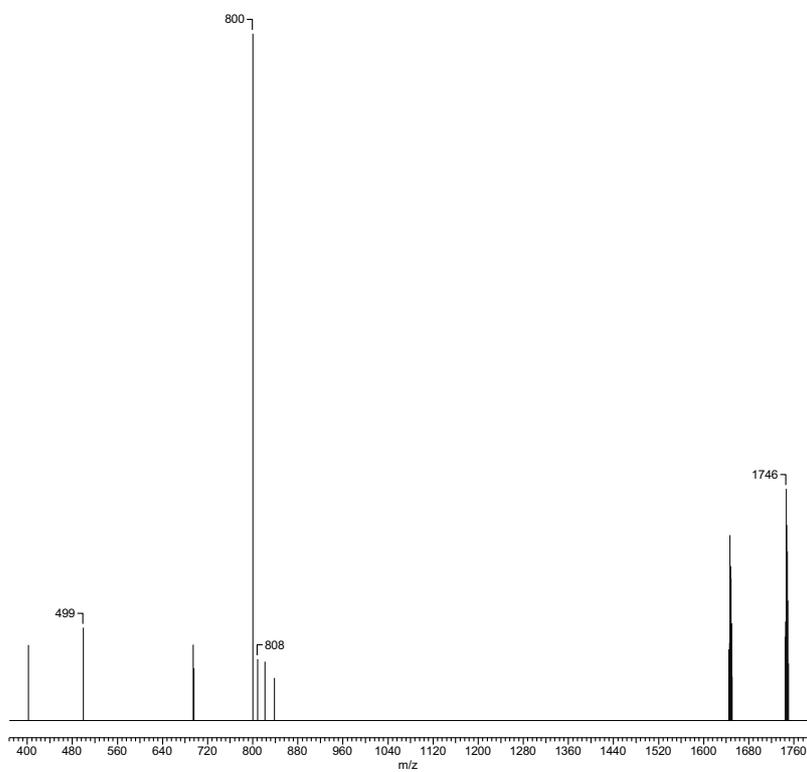


Figure S21. LC-MSMS spectrum of **3c**.

- TGA/DTA graph of 2c

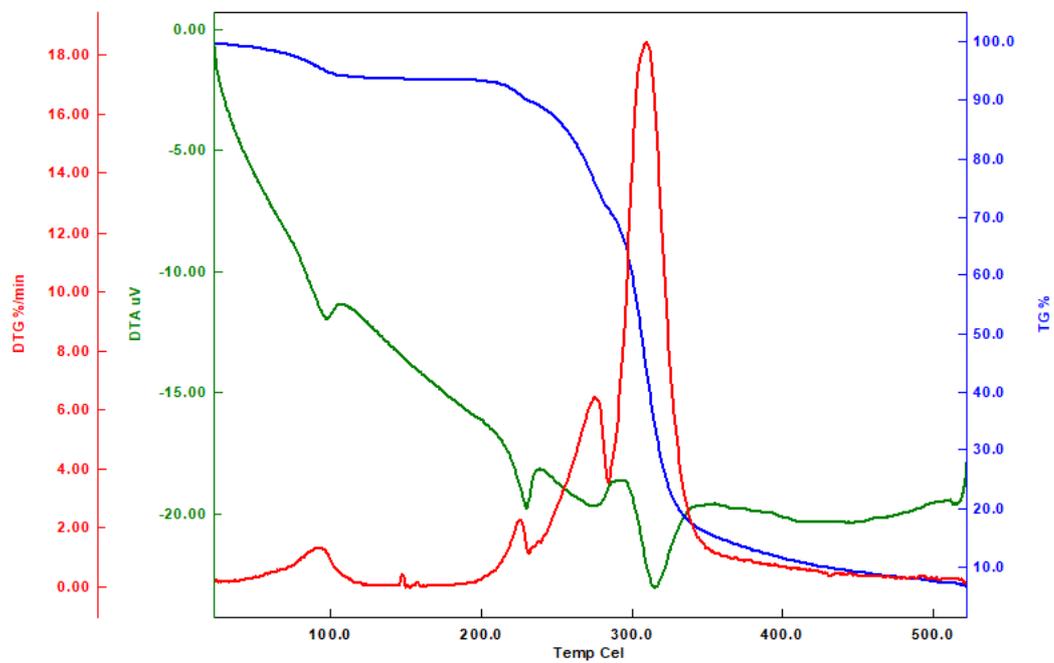
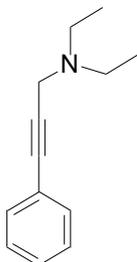


Figure S22. TGA/DTA graph of 2c.

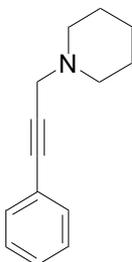
- Characterization data for the catalytic products

N,N-diethyl-3-phenylprop-2-yn-1-amine



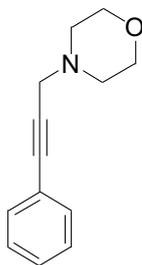
^1H NMR (CDCl_3): $\delta = 7.41$ (dd, $J_1 = 6.7$ Hz, $J_2 = 3.0$ Hz, 2H, Ar-H), 7.31–7.26 (m, 3H, Ar-H), 3.64 (s, 2H, CH_2), 2.62 (q, $J = 7.2$ Hz, 4H, CH_2), 1.11 (t, $J = 7.2$ Hz, 6H, CH_3) ppm. ^{13}C NMR (CDCl_3): $\delta = 131.81, 128.34, 128.03, 123.42, 85.07, 84.38, 47.40, 41.47, 12.73$ ppm.

1-(3-phenylprop-2-ynyl)piperidine



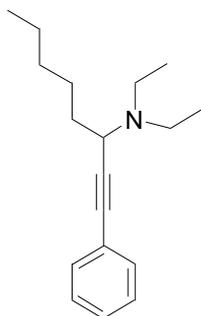
^1H NMR (CDCl_3): $\delta = 7.46$ –7.41 (m, 2H), 7.31–7.27 (m, 3H), 3.48 (s, 2H), 2.57 (s, 4H), 1.68–1.61 (m, 4H) ppm. ^{13}C NMR (CDCl_3): $\delta = 131.70, 128.21, 127.95, 123.29, 85.08, 54.90, 48.48, 25.96, 22.63$ ppm.

4-(3-phenylprop-2-ynyl)morpholine



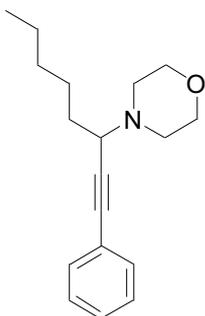
¹H NMR (CDCl₃): δ = 7.42 (dd, J₁ = 6.8 Hz, J₂ = 3.1 Hz, 2H, Ar-H), 7.30 (q, J = 3.7 Hz, 3H, Ar-H), 3.77 (t, J = 4.7 Hz, 4H), 3.50 (s, 2H, CH₂), 2.64 (t, J = 4.8 Hz, 4H, CH₂) ppm. ¹³C NMR (CDCl₃): δ = 131.81, 128.37, 128.30, 123.02, 85.68, 84.06, 66.98, 52.51, 48.15, 29.80 ppm.

N,N-diethyl-1-n-pentyl-3-phenylprop-2-yn-1-amine



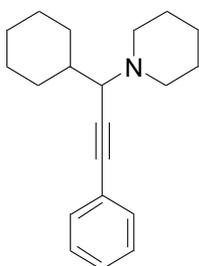
¹H NMR (CDCl₃): δ = 7.43-7.37 (m, 2H, Ar-H), 7.270 (dd, J₁ = 5.1 Hz, J₂ = 2.1 Hz, 3H, Ar-H), 3.67 (dd, J₁ = 8.6 Hz, J₂ = 6.2 Hz, 1H, CH), 2.76-2.66 (m, 2H, CH₂), 2.53-2.42 (m, 2H, CH₂), 1.75-1.61 (m, 2H, CH₂), 1.59-1.40 (m, 2H, CH₂), 1.32 (dq, J₁ = 7.4 Hz, J₂ = 3.8 Hz, 4H, CH₂), 1.04 (t, J = 7.2 Hz, 6H, CH₃), 0.92-0.87 (m, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 131.77, 128.30, 127.79, 123.75, 89.12, 84.68, 53.76, 44.98, 34.20, 31.73, 26.66, 22.71, 14.19, 13.83 ppm.

4-(1-n-pentyl-3-phenylprop-2-ynyl)morpholine



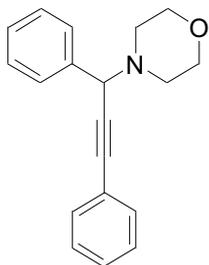
^1H NMR (CDCl_3): $\delta = 7.42$ (dd, $J = 6.6, 3.0$ Hz, 2H), 7.29 (q, $J = 2.9$ Hz, 3H), $3.81 - 3.69$ (m, 4H), 3.49 (dd, $J = 8.4, 6.5$ Hz, 1H), 2.75 (ddd, $J = 11.3, 6.0, 3.4$ Hz, 2H), 2.58 (ddd, $J = 11.5, 5.8, 3.3$ Hz, 2H), $1.76 - 1.63$ (m, 2H), $1.61 - 1.39$ (m, 2H), $1.38 - 1.27$ (m, 4H), $0.93 - 0.86$ (m, 3H) ppm. ^{13}C NMR (CDCl_3): $\delta = 131.82, 128.35, 128.08, 123.28, 87.17, 86.29, 67.19, 58.23, 50.44, 32.95, 31.66, 26.41, 22.67, 14.17$ ppm.

1-(1-cyclohexyl-3-phenylprop-2-ynyl)piperidine



^1H NMR (CDCl_3): $\delta = 7.46 - 7.41$ (m, 2H), $7.31 - 7.26$ (m, 3H), $3.13 - 3.06$ (m, 1H), 2.63 (ddd, $J = 10.9, 7.2, 3.7$ Hz, 2H), $2.45 - 2.35$ (m, 2H), $2.14 - 1.99$ (m, 2H), $1.81 - 1.70$ (m, 2H), $1.69 - 1.52$ (m, 6H), 1.43 (p, $J = 4.8, 3.6$ Hz, 2H), $1.33 - 1.13$ (m, 3H), 0.97 (dq, $J = 36.3, 12.2, 3.2$ Hz, 2H) ppm. ^{13}C NMR (CDCl_3): $\delta = 131.82, 128.29, 127.72, 123.89, 87.88, 86.21, 64.47, 50.83, 39.67, 31.44, 30.53, 26.90, 26.21, 24.82$ ppm.

4-(1,3-diphenylprop-2-ynyl)morpholine



^1H NMR (CDCl_3): $\delta = 7.62$ (d, $J = 7.3$ Hz, 2H, Ar-H), 7.54-7.48 (m, 2H, Ar-H), 7.39-7.27 (m, 6H, Ar-H), 4.78 (s, 1H, CH), 3.74 (dq, $J_1 = 9.3$ Hz, $J_2 = 4.4$ Hz, 4H, CH_2), 2.62 (s, 4H, CH_2) ppm. ^{13}C NMR (CDCl_3): $\delta = 137.87, 131.92, 128.71, 128.43, 128.38, 128.35, 127.90, 123.05, 88.58, 85.11, 67.27, 62.13, 49.96$ ppm.

- ^1H NMR and ^{13}C NMR spectra of the catalytic products

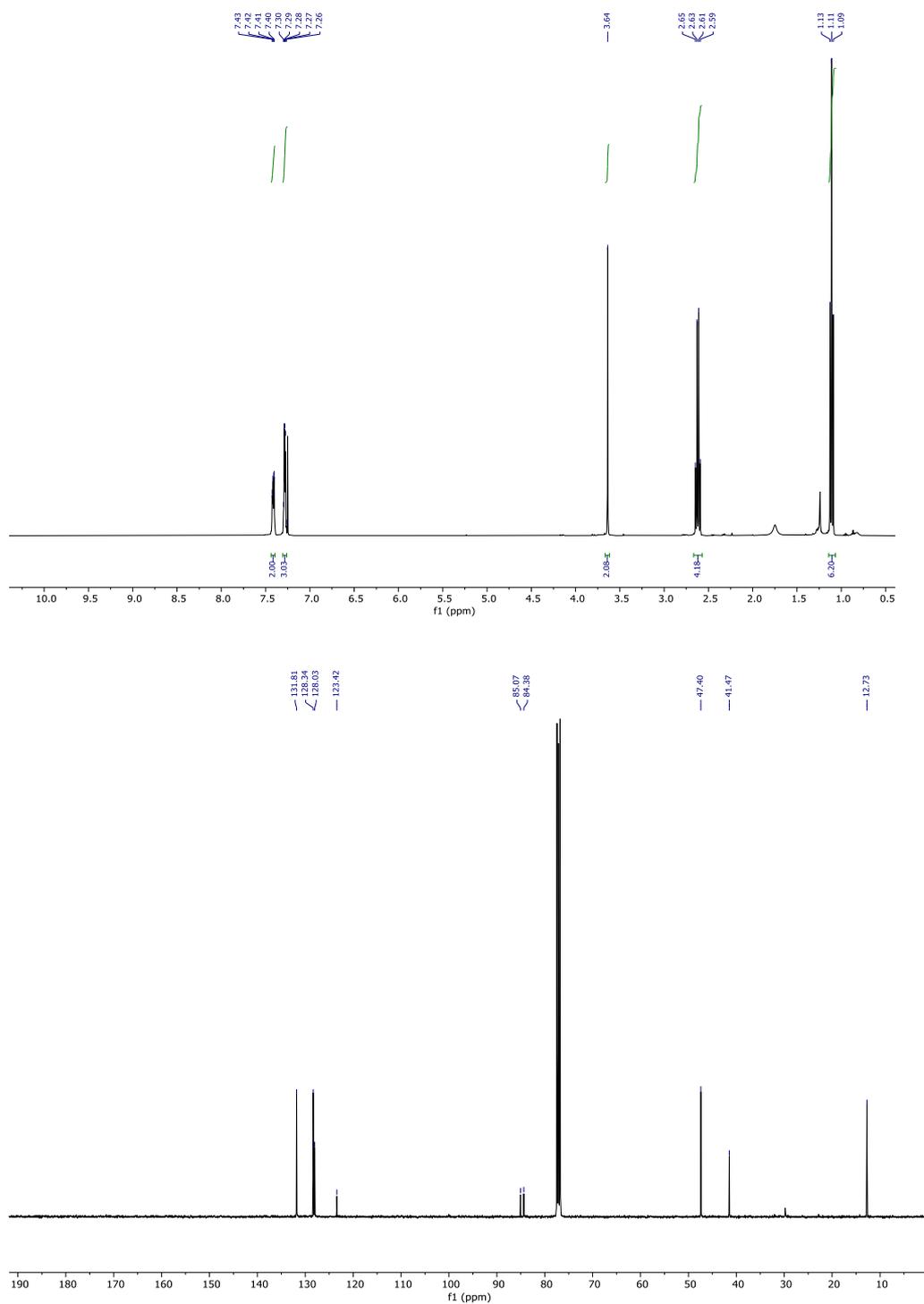


Figure S23. ^1H NMR and ^{13}C NMR spectra of N,N-diethyl-3-phenylprop-2-yn-1-amine.

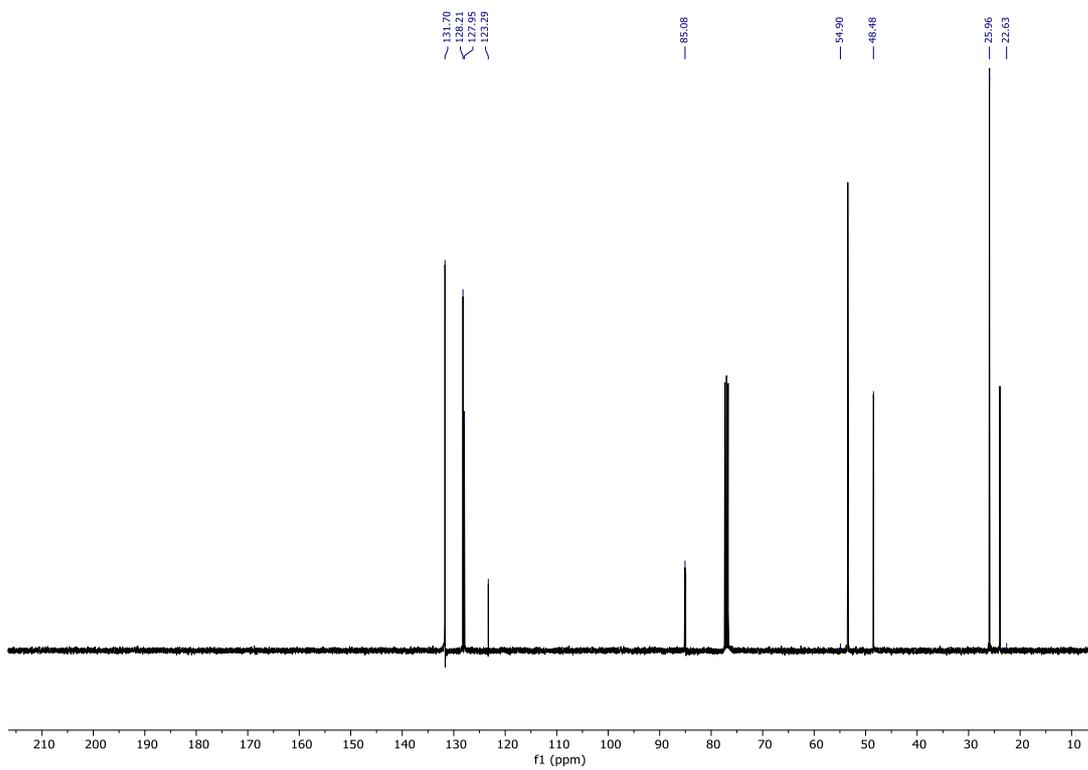
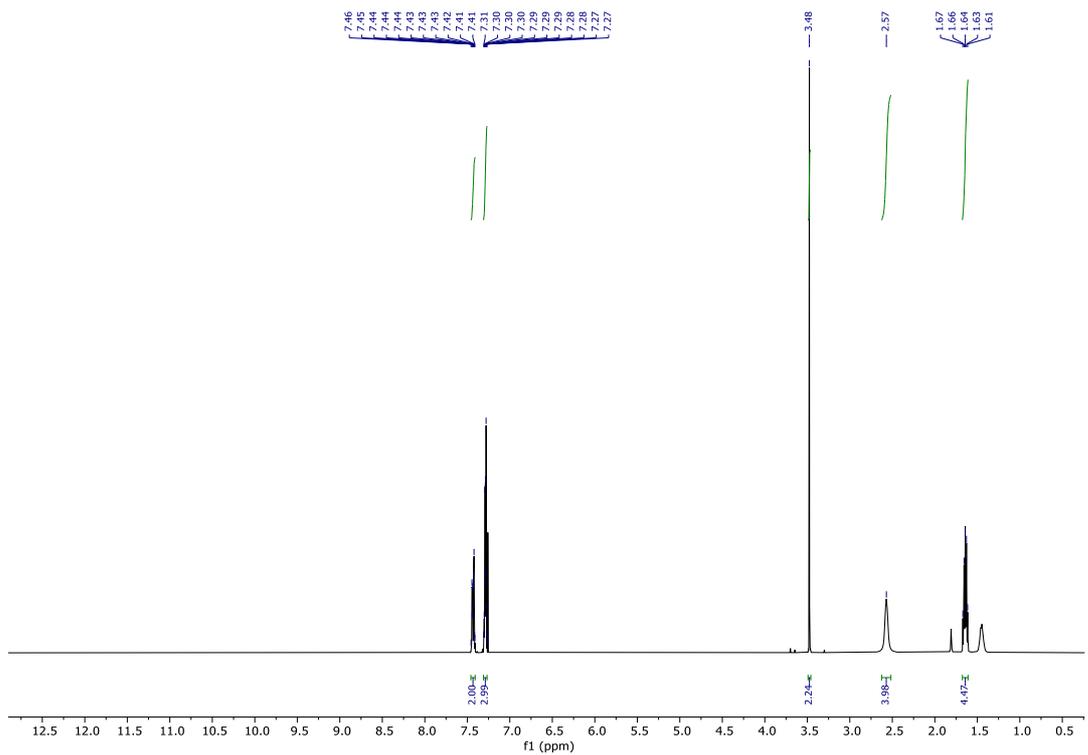


Figure S24. ^1H NMR and ^{13}C NMR spectra of 1-(3-phenylprop-2-ynyl)piperidine.

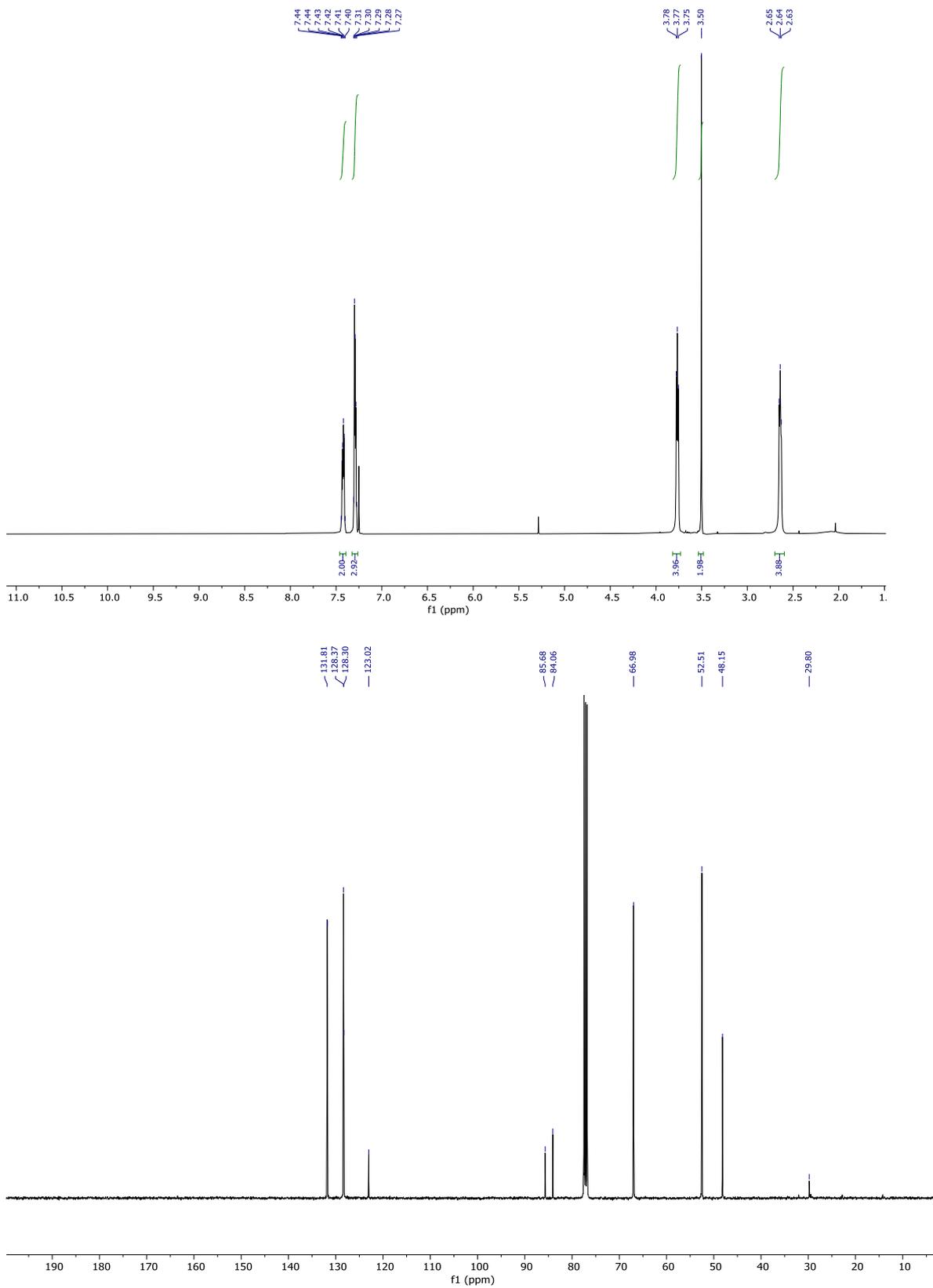


Figure S25. ¹H NMR and ¹³C NMR spectra of 4-(3-phenylprop-2-ynyl)morpholine.

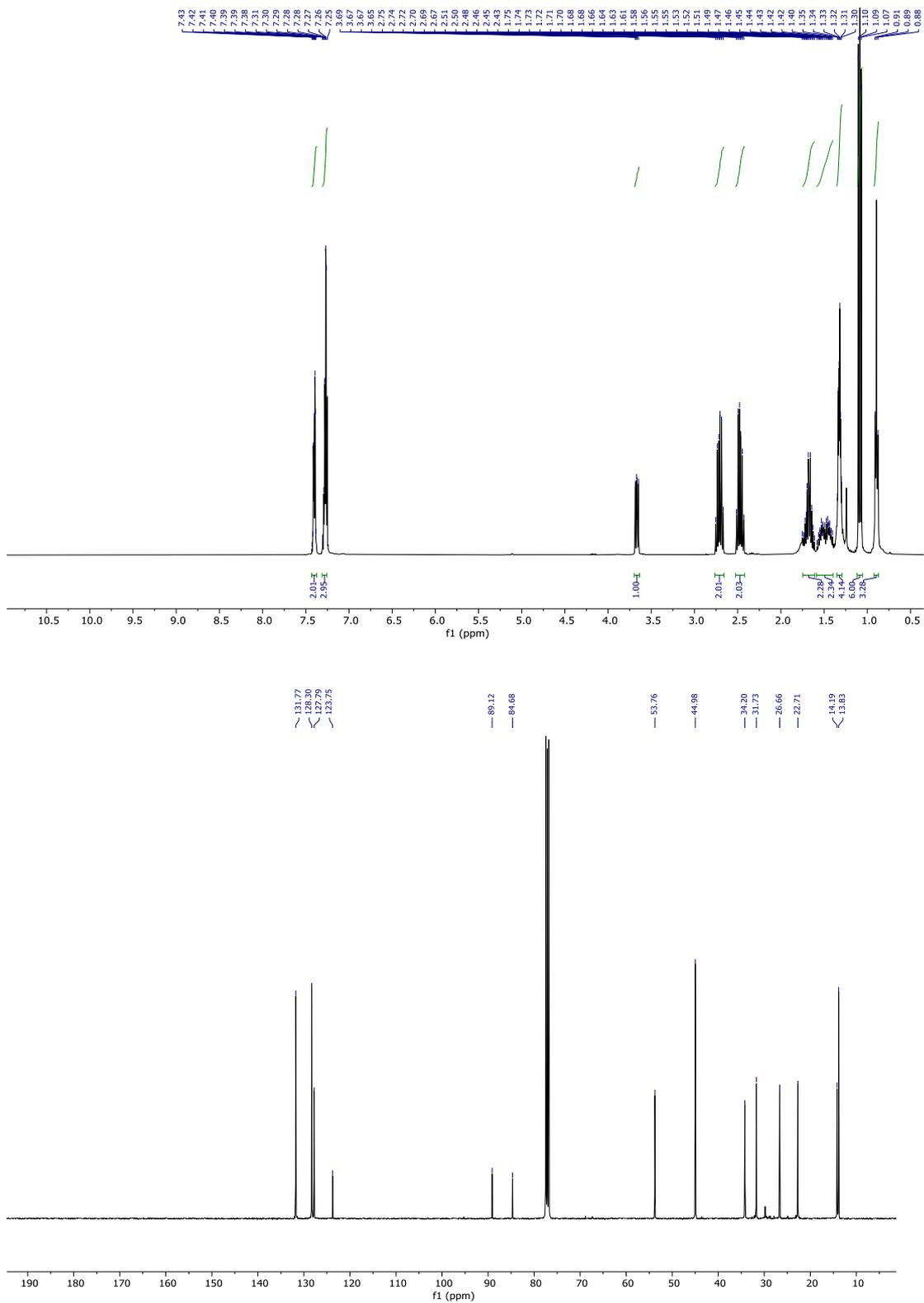
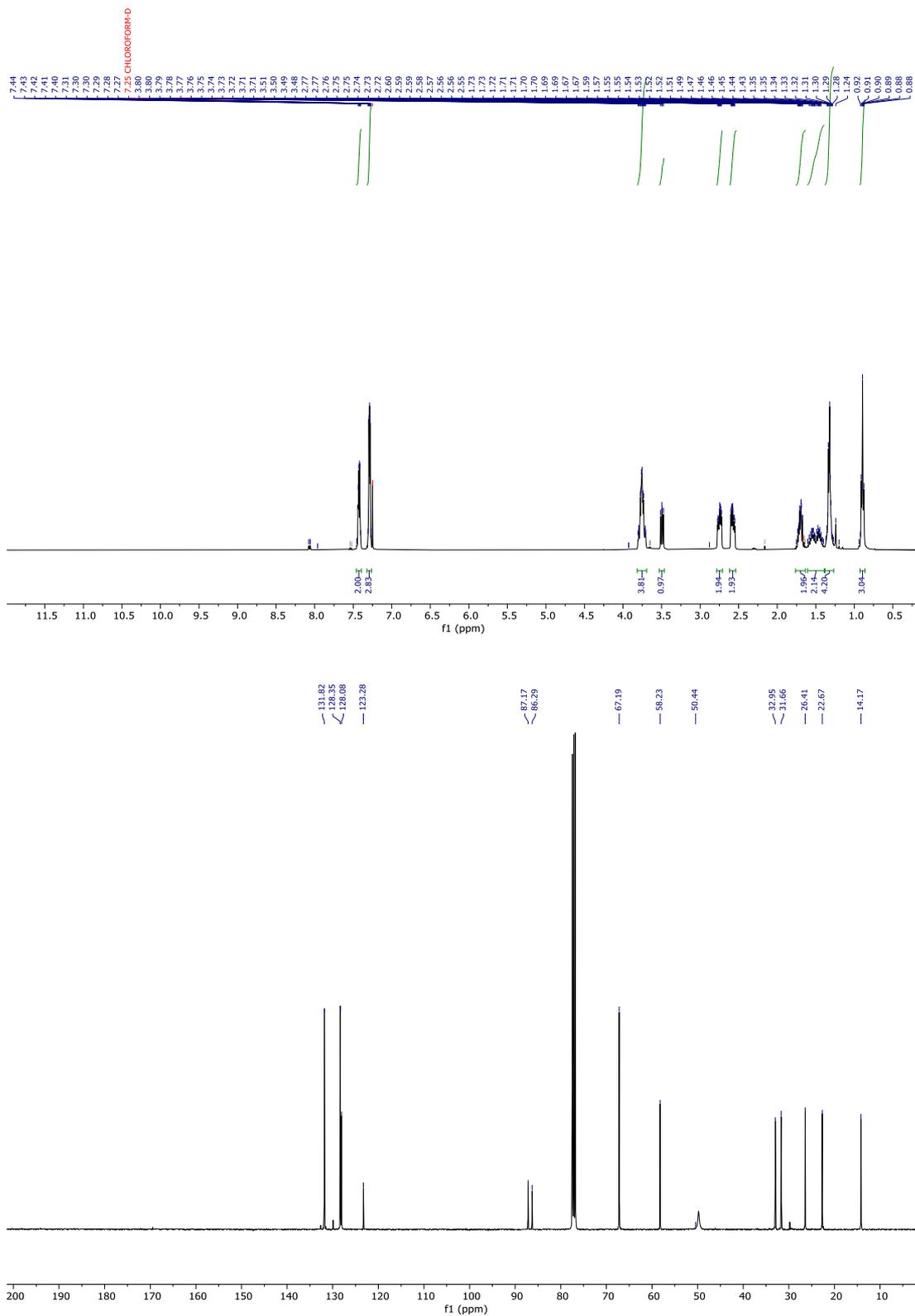


Figure S26. ¹H NMR and ¹³C NMR spectra of N,N-diethyl-1-n-pentyl-3-phenylprop-2-yn-1-amine.



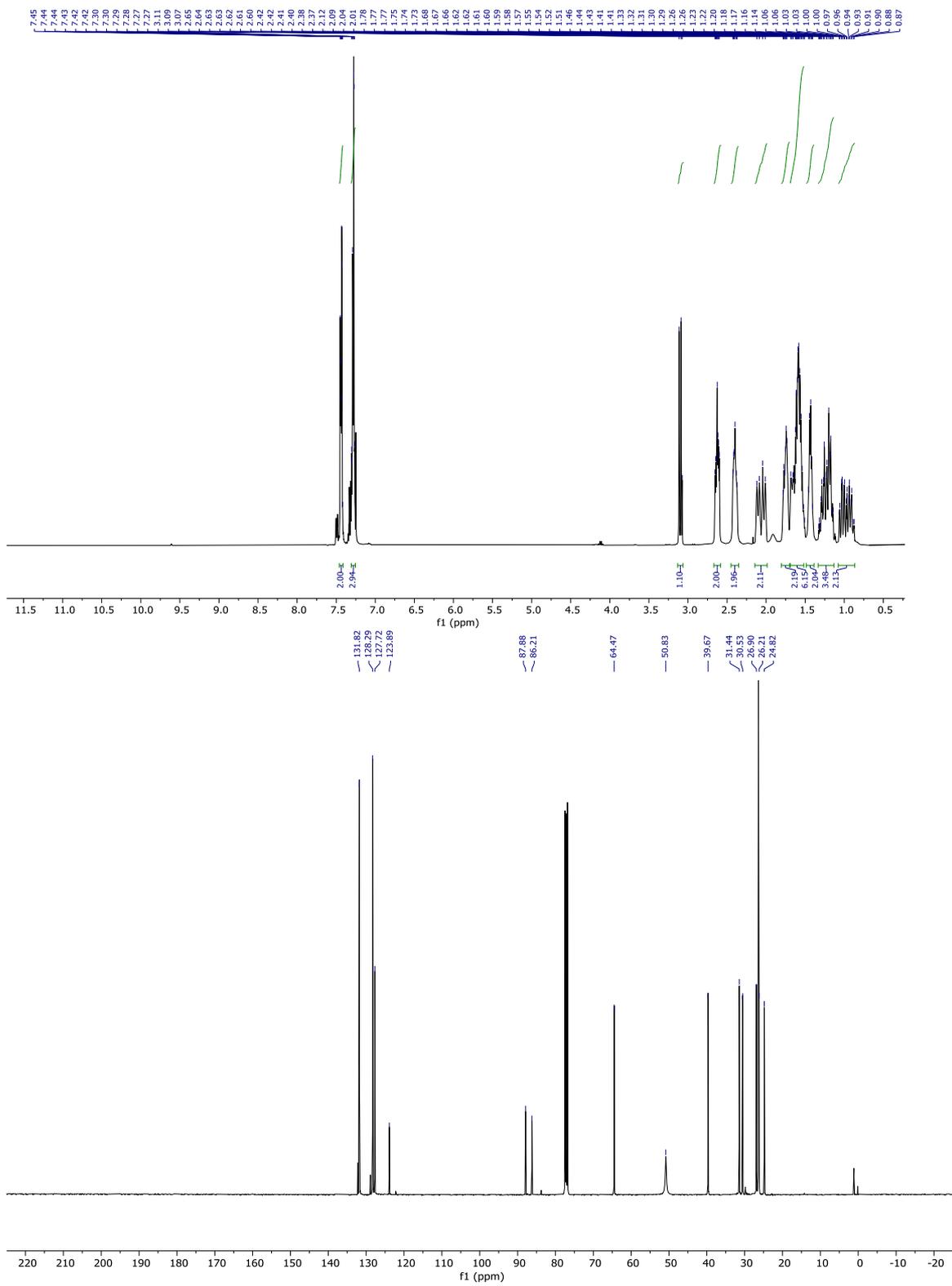


Figure S28. ¹H NMR and ¹³C NMR spectra of 1-(1-cyclohexyl-3-phenylprop-2-ynyl)piperidine.

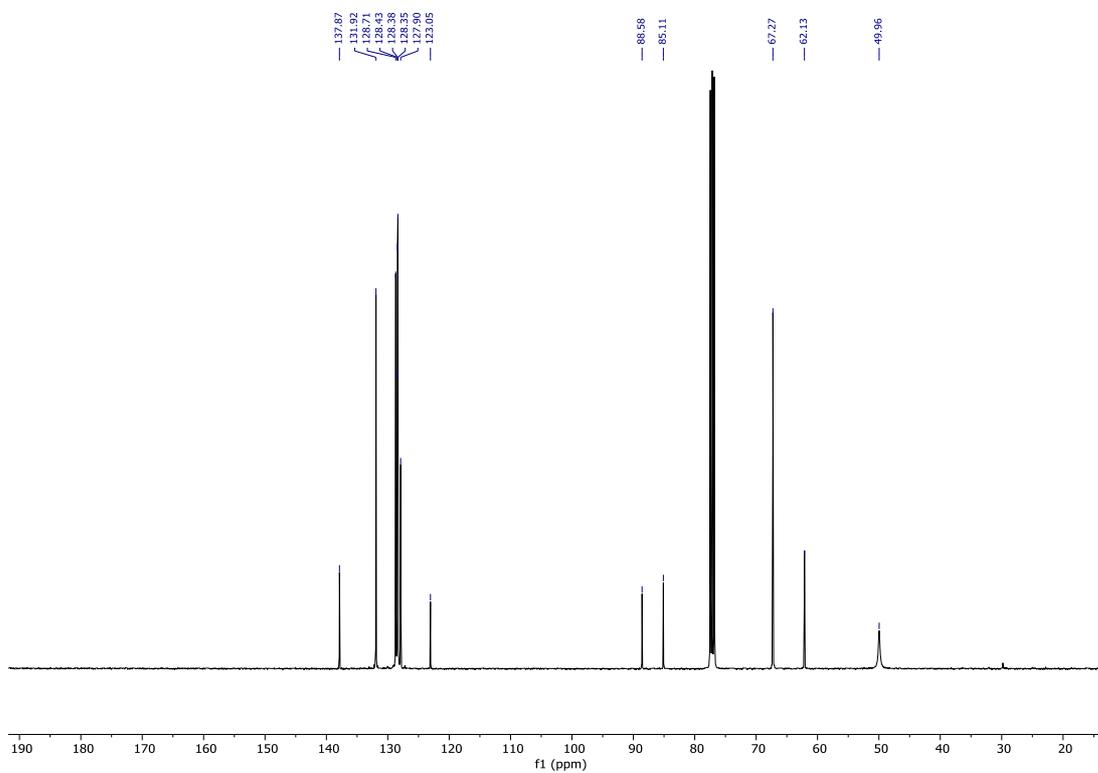
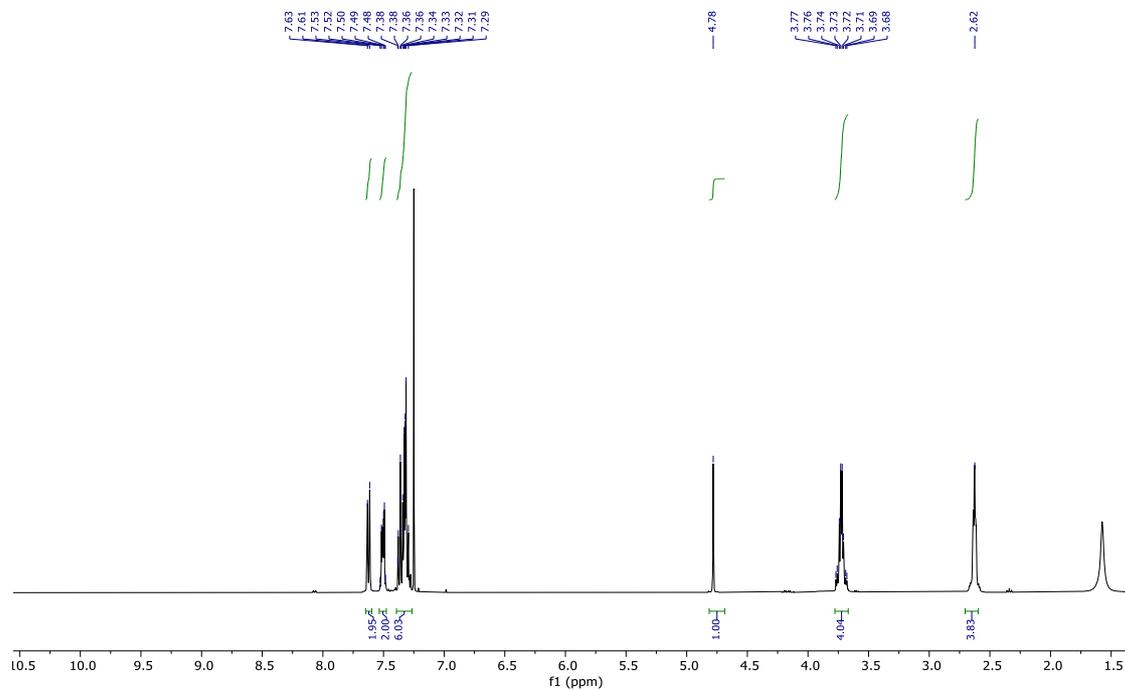


Figure S29. ¹H NMR and ¹³C NMR spectra of 4-(1,3-diphenylprop-2-ynyl)morpholine.