SUPPORTING INFORMATION

Tuning the catalytic performance of Cu supported silica modified γ-Al_2O_3 nanocatalyst via cobalt-doping for A^3-coupling

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S1. Experimental

Materials and physical measurements

All the chemicals used were purchased from Aldrich Chemical Company. Belsorb Mini-X analyzer was used to determine N_2 adsorption-desorption isotherms and the BET specific surface area. The thermal stability of the synthesized catalysts was determined by recording TGA on Perkin Elmer, Diamond TG/DTA with heating rate of 10 °C min^{-1}. XRD was recorded in 2 theta range of 10-80˚ on a Bruker D8-Advance X-ray diffractometer using 2.2 kW Cu anode. SU8010 SERIES Field Emission Scanning Electron Microscope was used to record SEM, EDX and SEM-EDX mapping while HR-TEM images were recorded using FEI, Tecnai G2, F30 Transmission Electron Microscope. The amount of metal loading was determined by ICP-AES analysis using ARCOS, Simultaneous ICP spectrometer. XPS spectra of the catalysts were recorded on PHI 5000 Versa Probe II, FEI Inc. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of the products were recorded using $CDCl_3$ as solvent on Bruker Avance III spectrometer using TMS as an internal standard.

Catalyst preparation

Synthesis of silica-modified γ-alumina supports

Silica-modified γ-aluminas were prepared using a simple one-pot solvent deficient method in which firstly, aluminum isopropoxide (AIP, 5g) and water (2.21 mL) were mixed in a 1:5 molar ratio and then tetraethyl orthosilicate (TEOS) in a quantity sufficient to give 5 wt% of silica in the final support material, was added with water (1:2 molar ratio). Next step involves the mixing of precursor for 30 min. in a mortar pestle followed by calcination at 600 °C for 2 h at the heating rate of 2.5 °C/min. to form 5 wt% silica modified γ-alumina [SA(5)-600]. Samples

containing 0, 7.5 and 10 wt% of silica were prepared following the same procedure [SA(0)-600, SA(7.5)-600 and SA(10)-600].

Changing the calcination temperature from 600 to 700 °C, four more support materials containing varying proportions of silica in γ-aluminas were prepared- SA(0)-700, SA(5)-700, SA(7.5)-700 and SA(10)-700.

Synthesis of Cu@SA(7.5)-600

In order to immobilize copper(0) nanoparticles onto SA(7.5)-600, $Cu(acac)_2$ (0.262 g, 1 mmol), and SA(7.5)-600 support (1 g) were dispersed in ethanol (50 mL) in a two neck round bottom flask and the mixture was stirred at 80 °C (refluxing conditions) for 3 h under N_2 atmosphere, followed by the dropwise addition of aq. $NaBH_4$ (2 mmol, 10 mL) under continuous stirring. The reaction mixture was then cooled, and stirred for 24 h at room temperature. Cu@SA(7.5)-600, thus obtained was filtered and washed successively with water (3×20 mL) and ethanol (3×20 mL), and then dried under vacuum at room temperature.

Synthesis of Co^{2+}-Cu@SA(7.5)-600

To a dispersed solution of Cu@SA(7.5)-600 (1g) in ethanol (30 mL), solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 0.058 g) in ethanol (10 mL) was added dropwise with stirring, which was further continued for 24 h at room temperature. The resultant Co^{2+}-doped Cu nano-catalyst was filtered using scintered glass crucible followed by repeated washing with deionized water (3×20 mL) and ethanol (3×20 mL) and then drying under vacuum at room temperature.

General procedure for the Co^{2+}-Cu@SA(7.5)-600 catalyzed A^3-coupling reaction

To a mixture of aldehyde (1 mmol), amine (1.2 mmol), alkyne (1.5 mmol) and Co^{2+}-Cu@SA(7.5)-600 (0.05 g) in a round bottom flask (25 mL), toluene (4 mL) was added and the reaction mixture was stirred at 110 °C for a specific time period. After the completion of reaction (monitored by TLC), solid catalyst was removed from the reaction mixture by filtration through a sintered glass crucible and the solvent was removed under low pressure in a rotavapor. The recovered catalyst was washed with deionized water (3×10 mL) and ethyl acetate (3×5 mL), dried in a vacuum desiccator and used for another consecutive reaction run. The crude product thus obtained, was then directly purified by passing through column of silica gel using n-hexane and ethyl acetate as eluents. The structure of the products were confirmed by ^{1}H and ^{13}C NMR and mass spectral data.

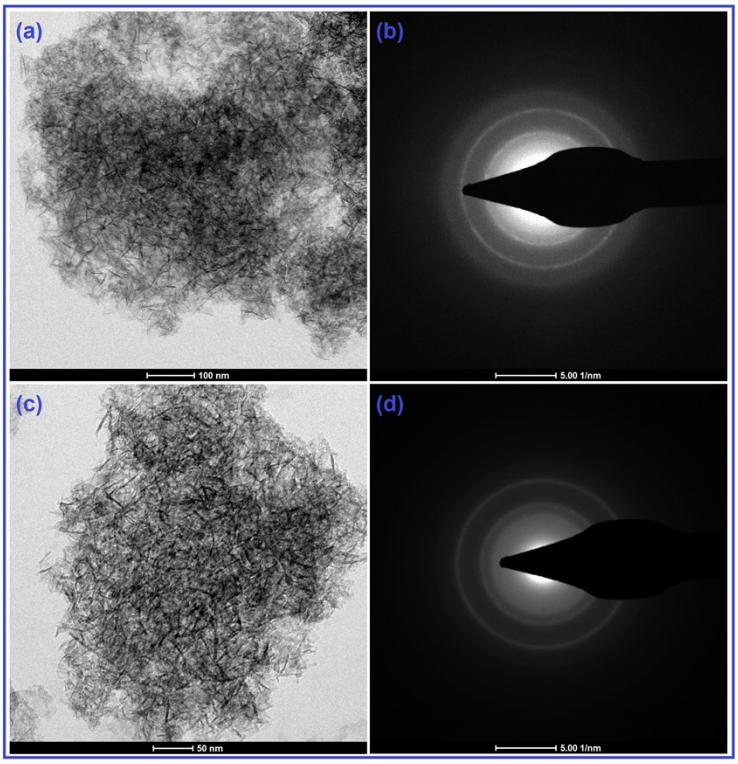


Fig. S1 HRTEM image and SAED pattern of Cu@SA(7.5)-600 **(a,b)** and Co^{2+}-Cu@SA(7.5)-600 **(c,d)**.

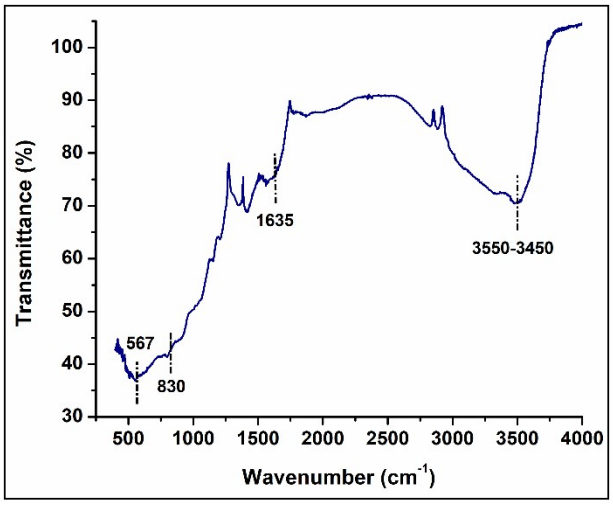


Fig. S2 FTIR spectrum of reused Co^{2+}-Cu@SA(7.5)-600 in case of A^3-coupling (**entry 2**, **Table 4**) after five catalytic runs.

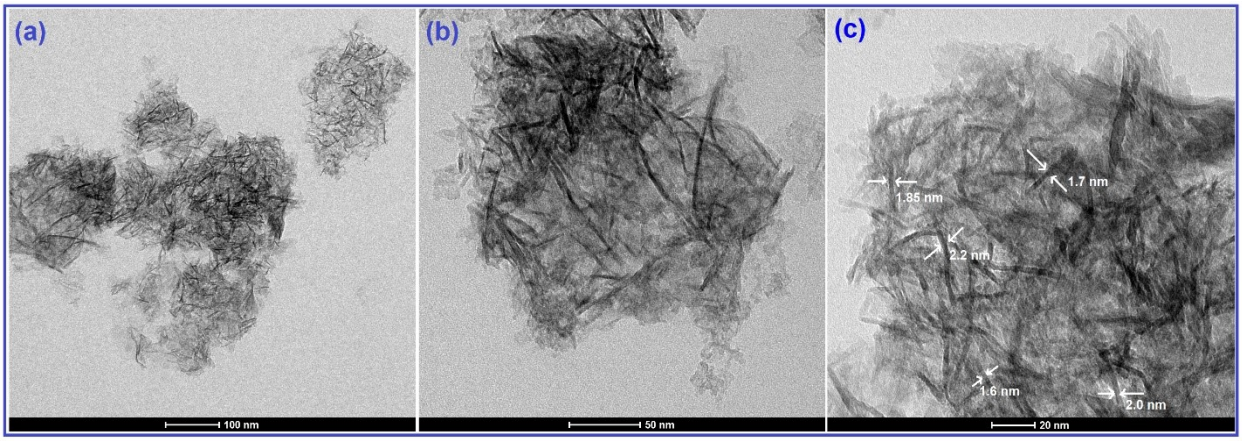
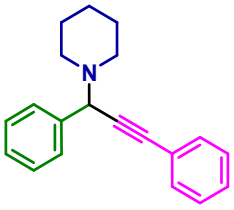


Fig. S3 HRTEM images of reused Co^{2+}-Cu@SA(7.5)-600 in case of A^3-coupling (**entry 2**, **Table 4**) after five catalytic runs.

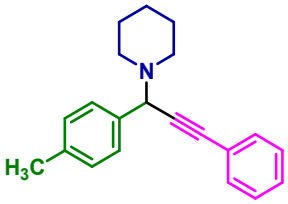
S2. Spectral details of the compounds listed in Table 4

1-(1,3-Diphenylprop-2-ynyl)piperidine (entry 1)



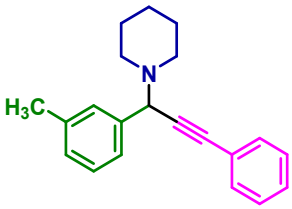
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.5 Hz, 2H, ArH), 7.56-7.53 (m, 2H, ArH), 7.40-7.30 (m, 6H, ArH), 4.84 (s, 1H, CH), 2.60 (br, 4H, $2CH_2$), 1.68-1.57 (m, 4H, $2CH_2$), 1.48-1.45 (m, 2H, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.40, 131.82, 128.62, 128.29, 128.08, 127.52, 123.30, 87.85, 86.00, 62.35, 50.61, 26.10, 24.40.

1-(3-Phenyl-1-p-tolylprop-2-ynyl)piperidine (entry 2)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (m, 4H, ArH), 7.35-7.34 (m, 3H, ArH), 7.19 (d, *J* = 7.9 Hz, 2H, ArH), 4.80 (s, 1H, CH), 2.59 (t, *J* = 4.6 Hz, 4H, $2CH_2$), 2.38 (s, 3H, CH_3), 1.65-1.58 (m, 4H, $2CH_2$), 1.49-1.45 (m, 2H, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.18, 135.36, 131.80, 128.77, 128.55, 128.26, 128.02, 123.37, 87.63, 86.28, 62.10, 50.67, 26.09, 24.41, 21.13; **MS (ESI)**: 290 $[M+1]^+$.

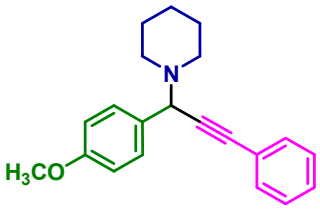
1-(3-Phenyl-1-m-tolylprop-2-ynyl)piperidine (entry 3)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.45 (br, 2H), 7.38-7.34 (m, 3H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.77 (s, 1H), 2.60-2.58 (m, 4H), 2.40 (s, 3H), 1.67-1.56 (m, 4H), 1.47 (dt, *J* = 8.8, 4.6 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.29, 137.70, 131.82,

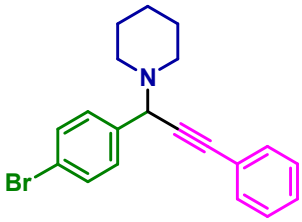
129.29, 128.45, 128.27, 128.05, 127.95, 125.74, 123.36, 87.73, 86.21, 62.41, 50.78, 26.09, 24.40, 21.54.

1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)piperidine (entry 4)



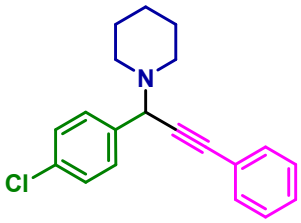
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.56 (m, 4H, ArH), 7.39-7.35 (m, 3H, ArH), 6.94 (d, *J* = 8.6 Hz, 2H, ArH), 4.79 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 2.60 (br, 4H, $2CH_2$), 1.69-1.58 (m, 4H, $2CH_2$), 1.50-1.47 (m, 2H, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.02, 131.83, 130.73, 129.69, 128.31, 128.05, 123.43, 113.42, 87.67, 86.47, 61.82, 55.27, 50.64, 26.23, 24.54.

1-(1-(4-Bromophenyl)-3-phenylprop-2-ynyl)piperidine (entry 5)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.50 (m, 6H, ArH), 7.37-7.36 (m, 3H, ArH), 4.78 (s, 1H, CH), 2.57 (br, 4H, $2CH_2$), 1.68-1.56 (m, 4H, $2CH_2$), 1.49-1.48 (m, 2H, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.81, 131.83, 131.18, 130.23, 128.35, 128.25, 123.07, 121.41, 88.29, 85.28, 61.78, 50.71, 26.15, 24.38.

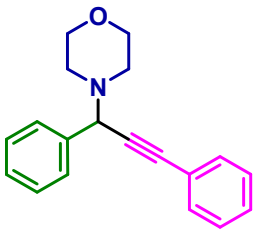
1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)piperidine (entry 6)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H, ArH), 7.55-7.53 (m, 2H, ArH), 7.37-7.34 (m, 5H, ArH), 4.79 (s, 1H, CH), 2.56 (t, *J* = 4.7 Hz, 4H, $2CH_2$), 1.65-1.58 (m, 4H, $2CH_2$),

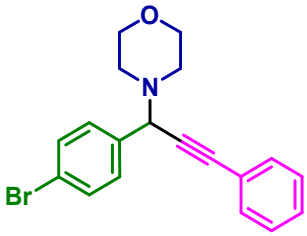
1.48-1.45 (m, 2H, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.32, 133.19, 131.82, 130.93, 129.83, 128.33, 128.20, 123.10, 88.24, 85.39, 61.73, 50.73, 26.16, 24.39.

4-(1,3-Diphenylprop-2-ynyl)morpholine (entry 7)



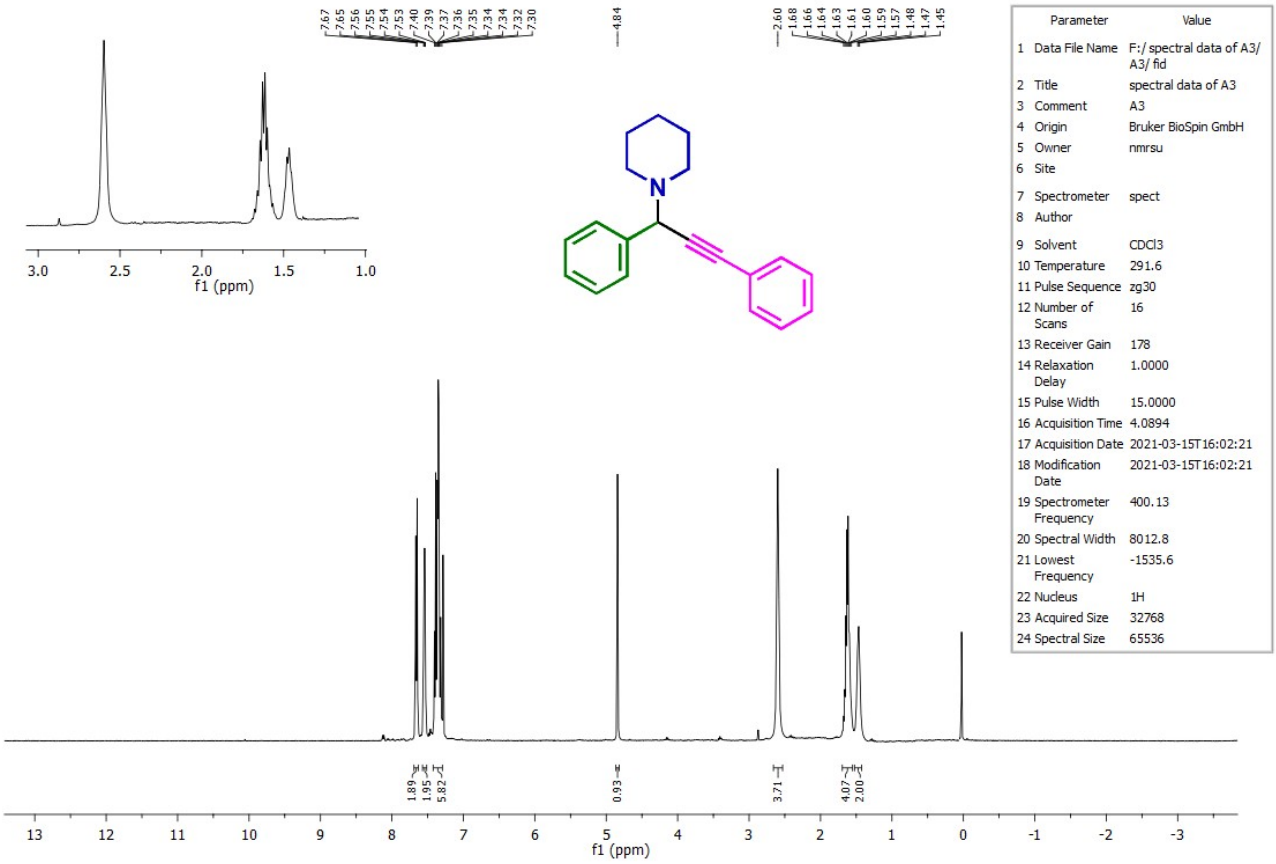
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.3 Hz, 2H, ArH), 7.58-7.55 (m, 2H, ArH), 7.43-7.33 (m, 6H, ArH), 4.84 (s, 1H, CH), 3.82-3.73 (m, 4H, $2CH_2$), 2.68 (br, 4H, $2CH_2$); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.84, 131.85, 128.63, 128.36, 128.30, 128.27, 127.82, 123.01, 88.53, 85.08, 67.20, 62.07, 49.91.

4-(1-(4-Bromophenyl)-3-phenylprop-2-ynyl)morpholine (entry 8)

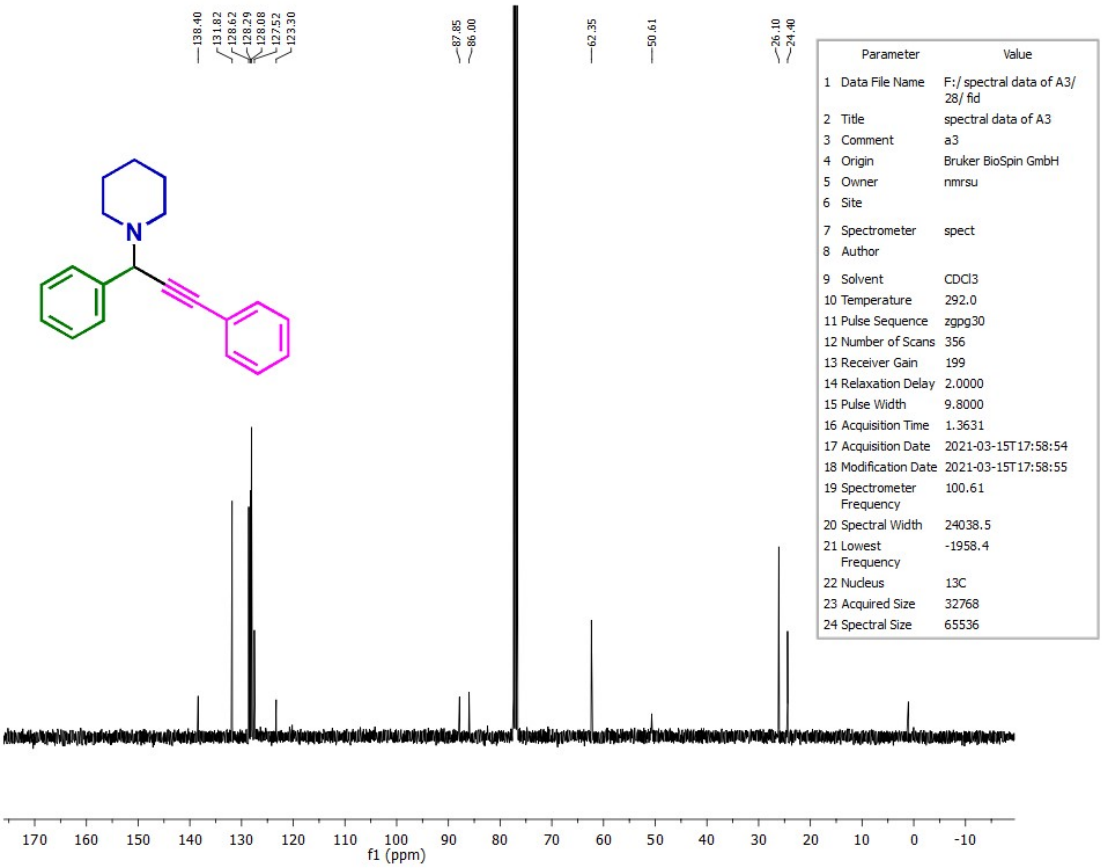


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.50 (m, 6H), 7.38-7.35 (m, 3H), 4.77 (s, 1H), 3.79-3.72 (m, 4H), 2.64 (t, *J* = 4.4 Hz, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.96, 131.81, 131.35, 130.26, 128.44, 128.37, 122.67, 121.75, 88.93, 84.23, 67.11, 61.42, 49.77.

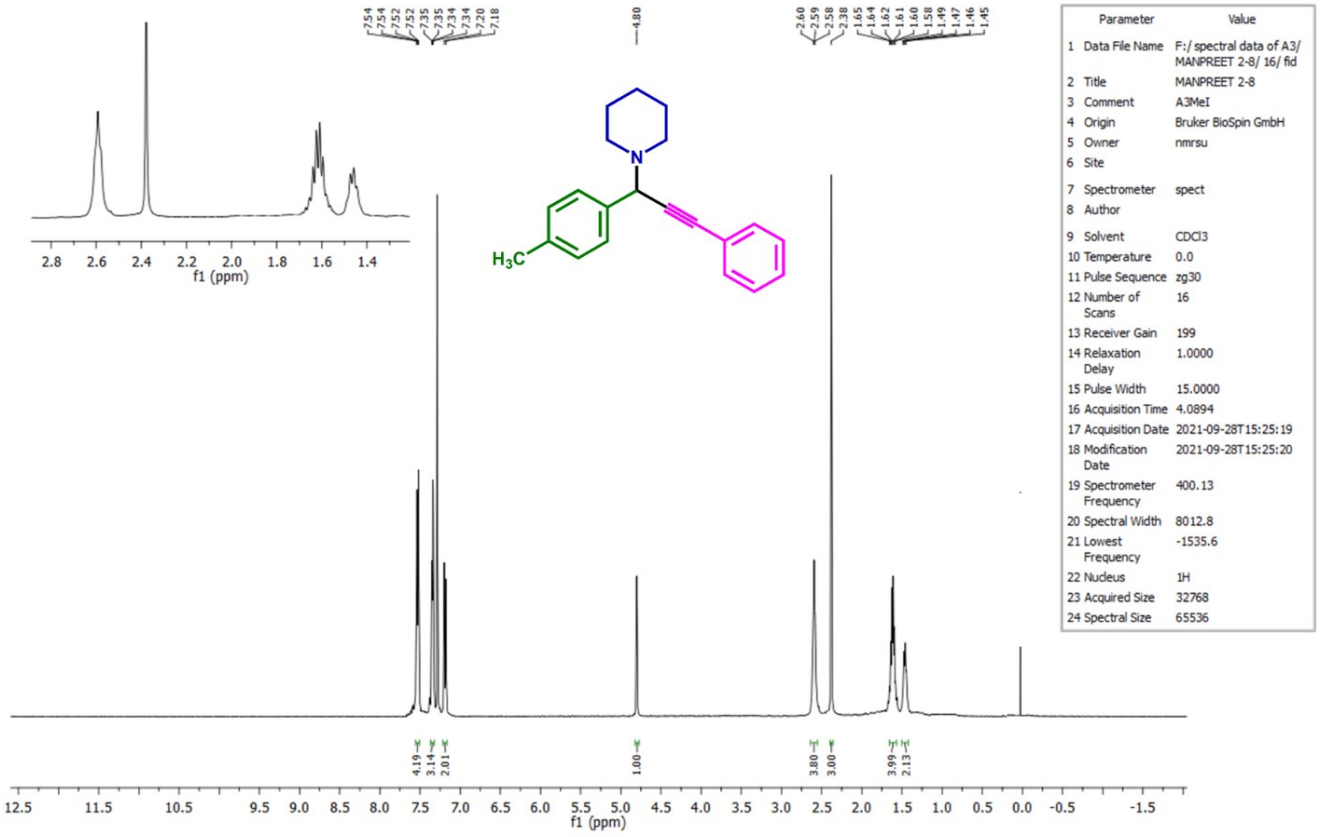
S3. ^{1}H and ^{13}C NMR spectra of compounds listed in Table 4



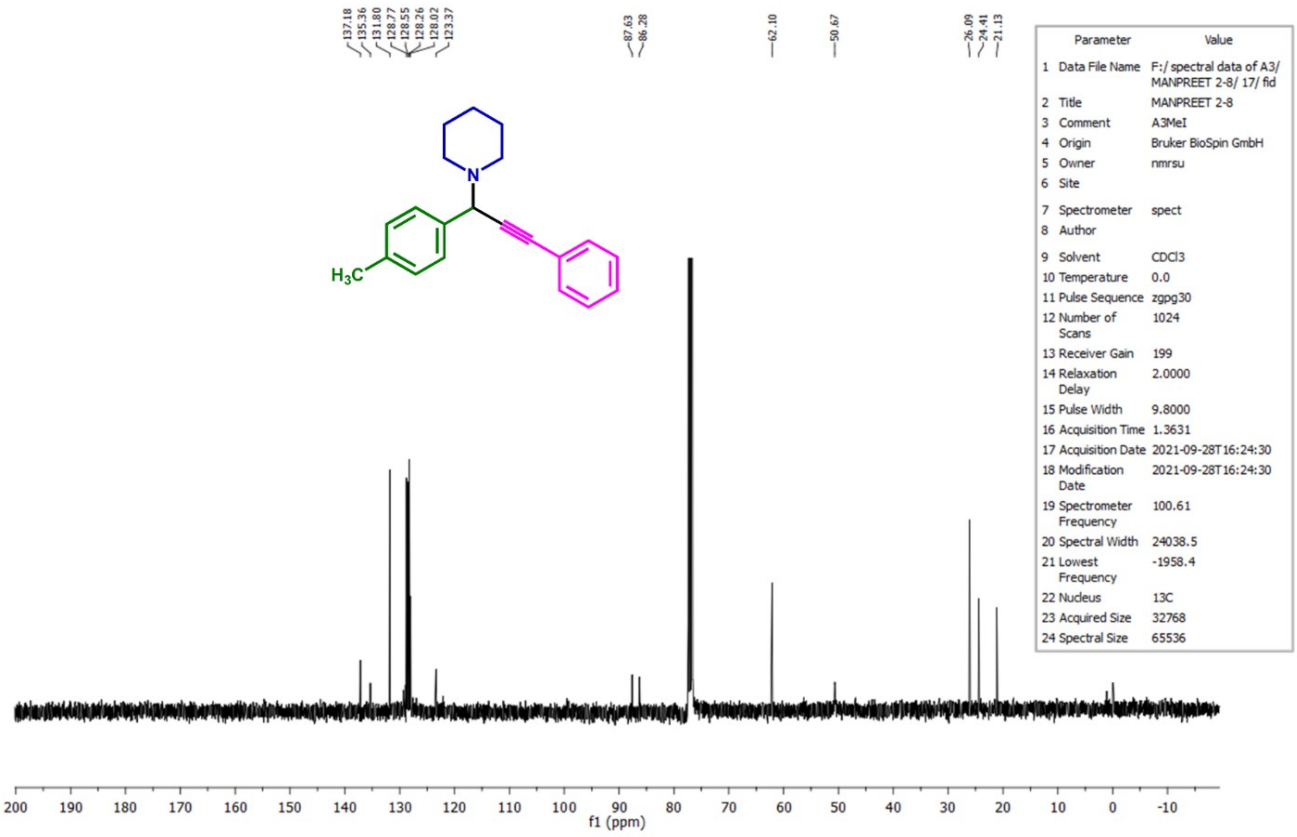
^{1}H NMR spectrum of **1-(1,3-Diphenylprop-2-ynyl)piperidine** (**entry 1**, **Table 4**)



^{13}C NMR spectrum of **1-(1,3-Diphenylprop-2-ynyl)piperidine** (**entry 1**, **Table 4**)



^{1}H NMR spectrum of **1-(3-Phenyl-1-p-tolylprop-2-ynyl)piperidine** (**entry 2**, **Table 4**)



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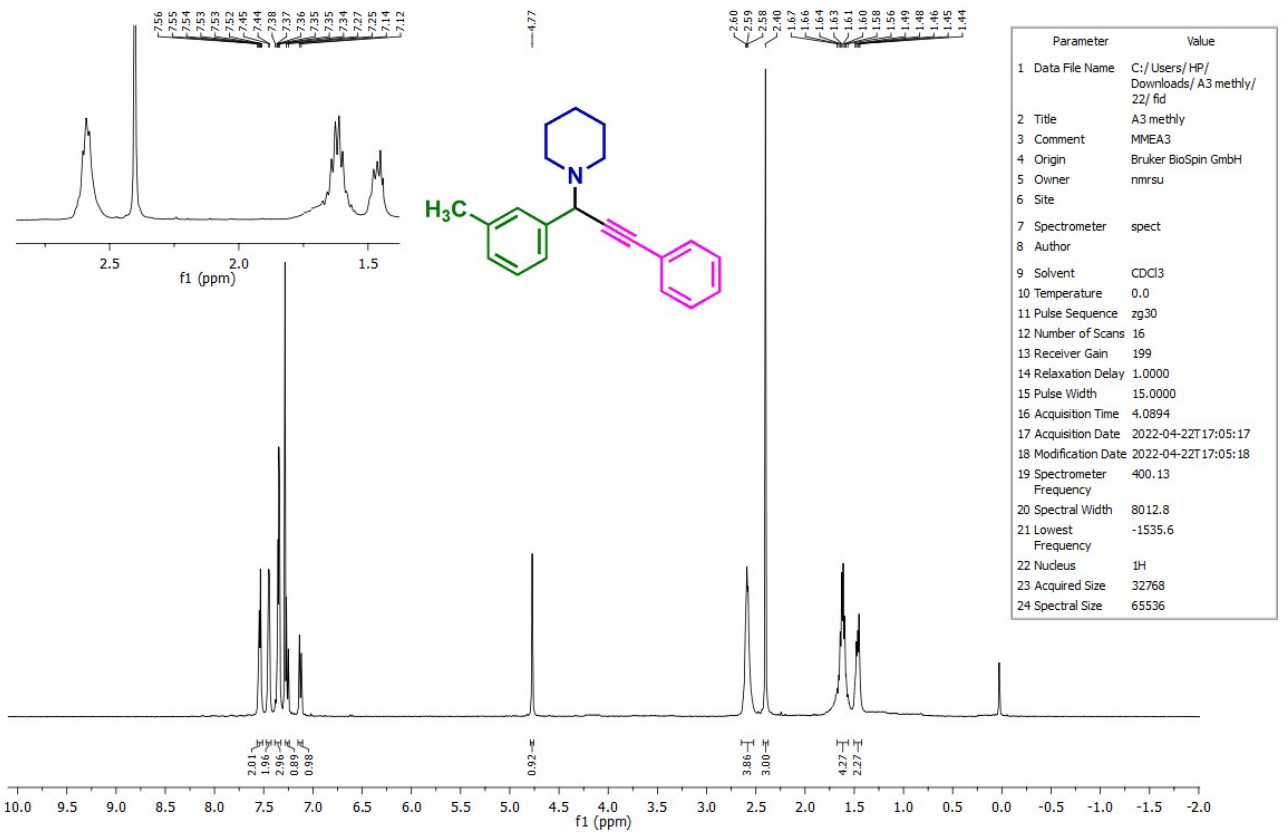
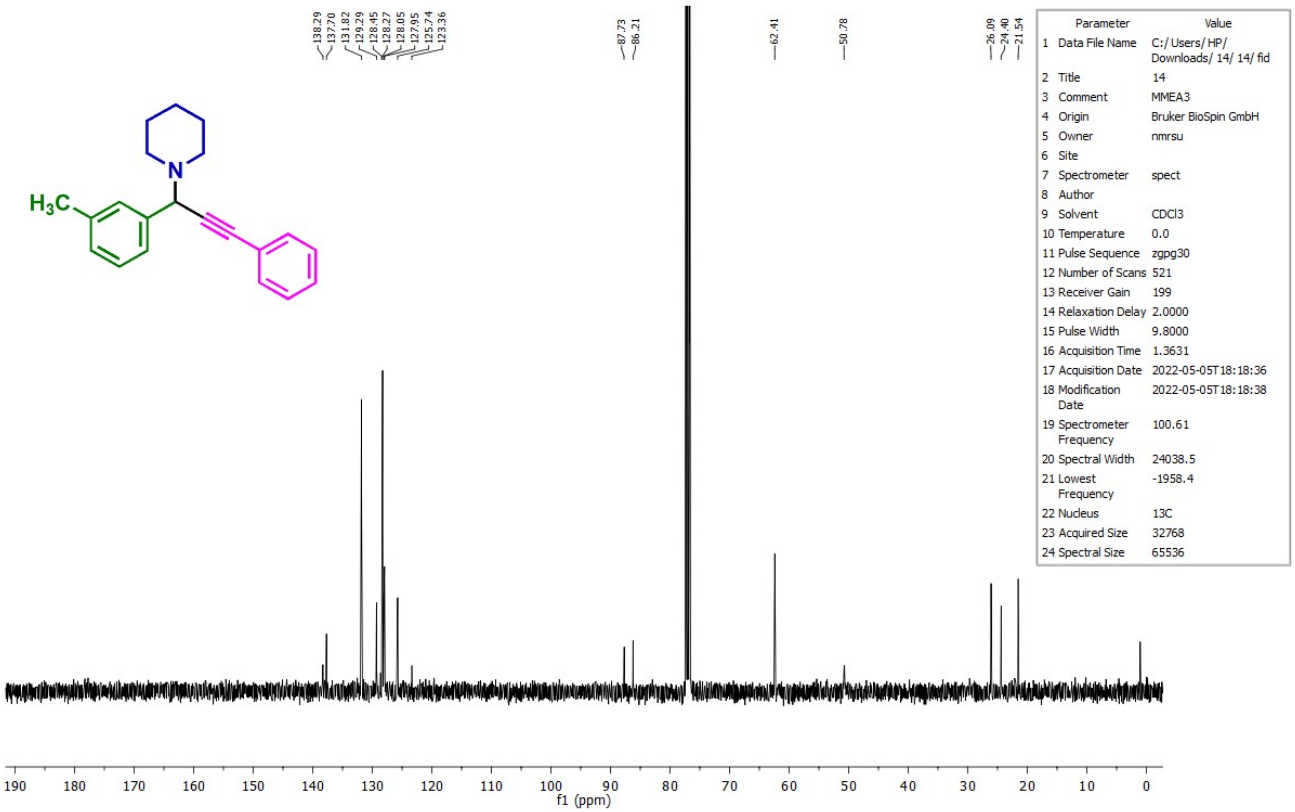
^{13}C NMR spectrum of **1-(3-Phenyl-1-p-tolylprop-2-ynyl)piperidine** (**entry 2**, **Table 4**)



^{1}H NMR spectrum of **1-(3-Phenyl-1-m-tolylprop-2-ynyl)piperidine** (**entry 3**, **Table 4**)



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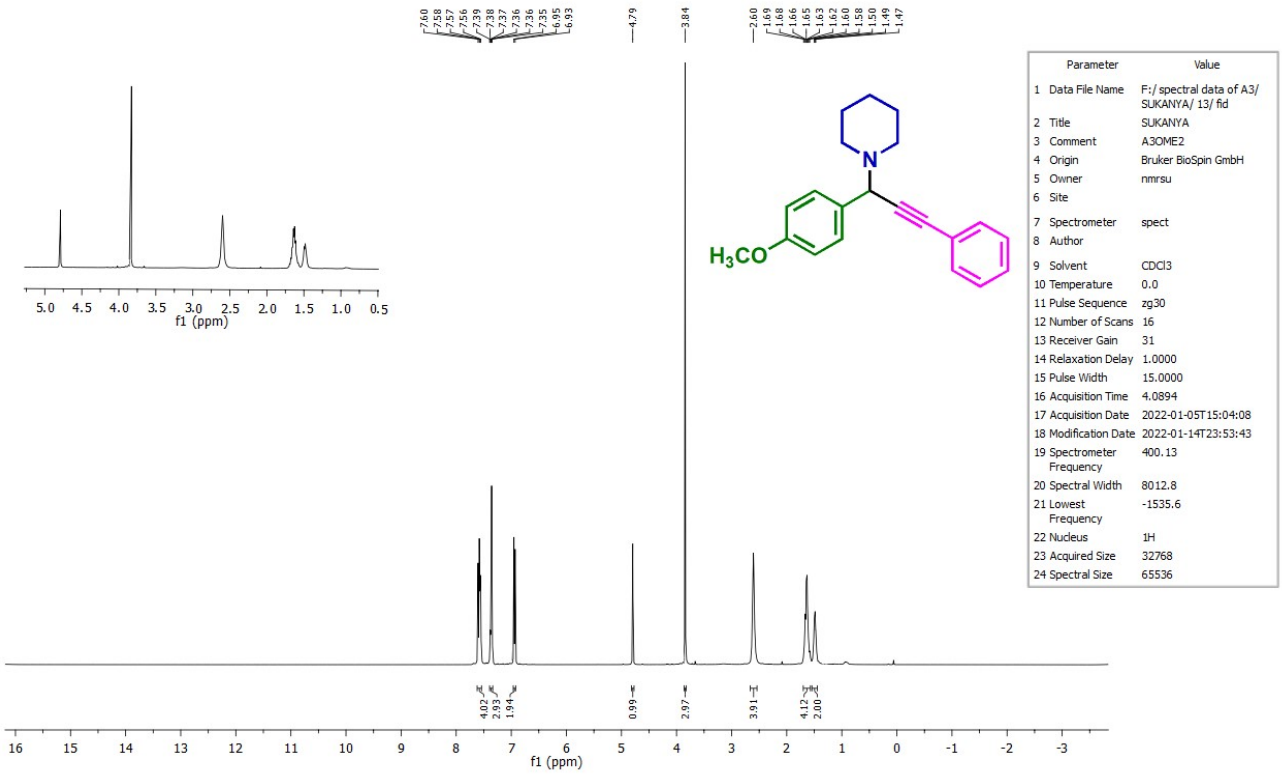
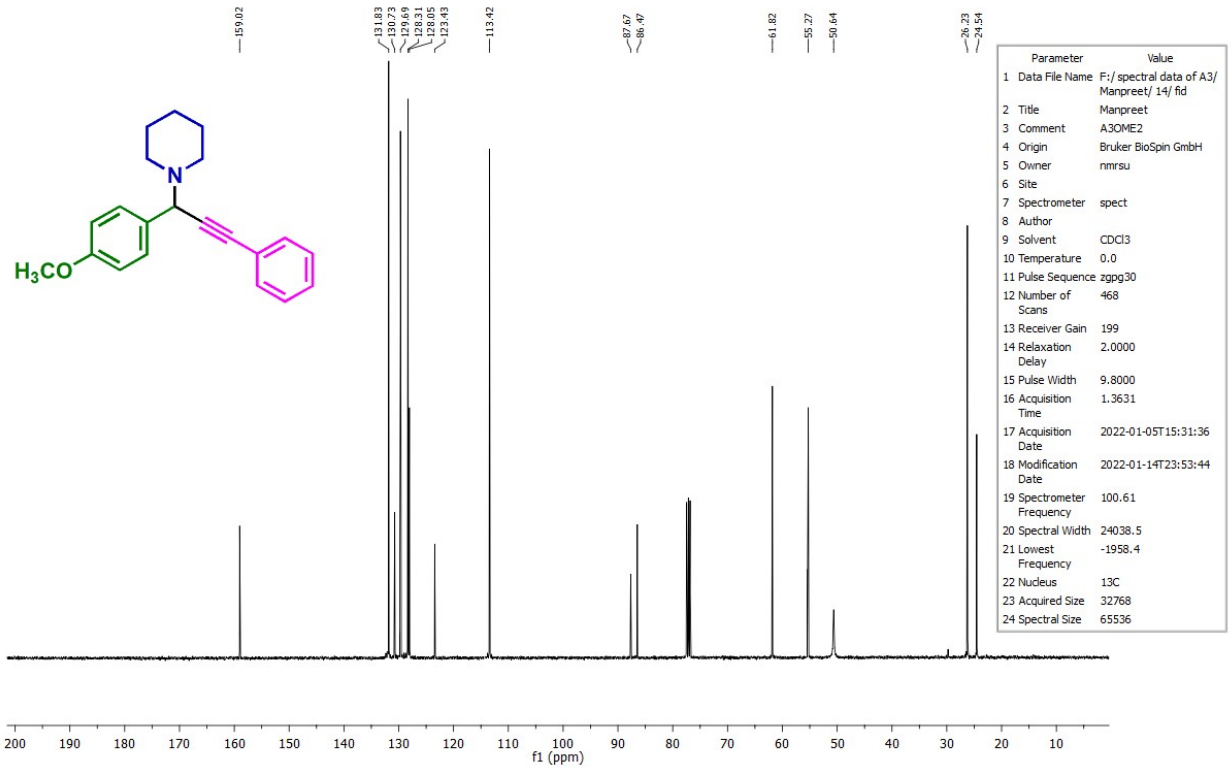
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.4
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

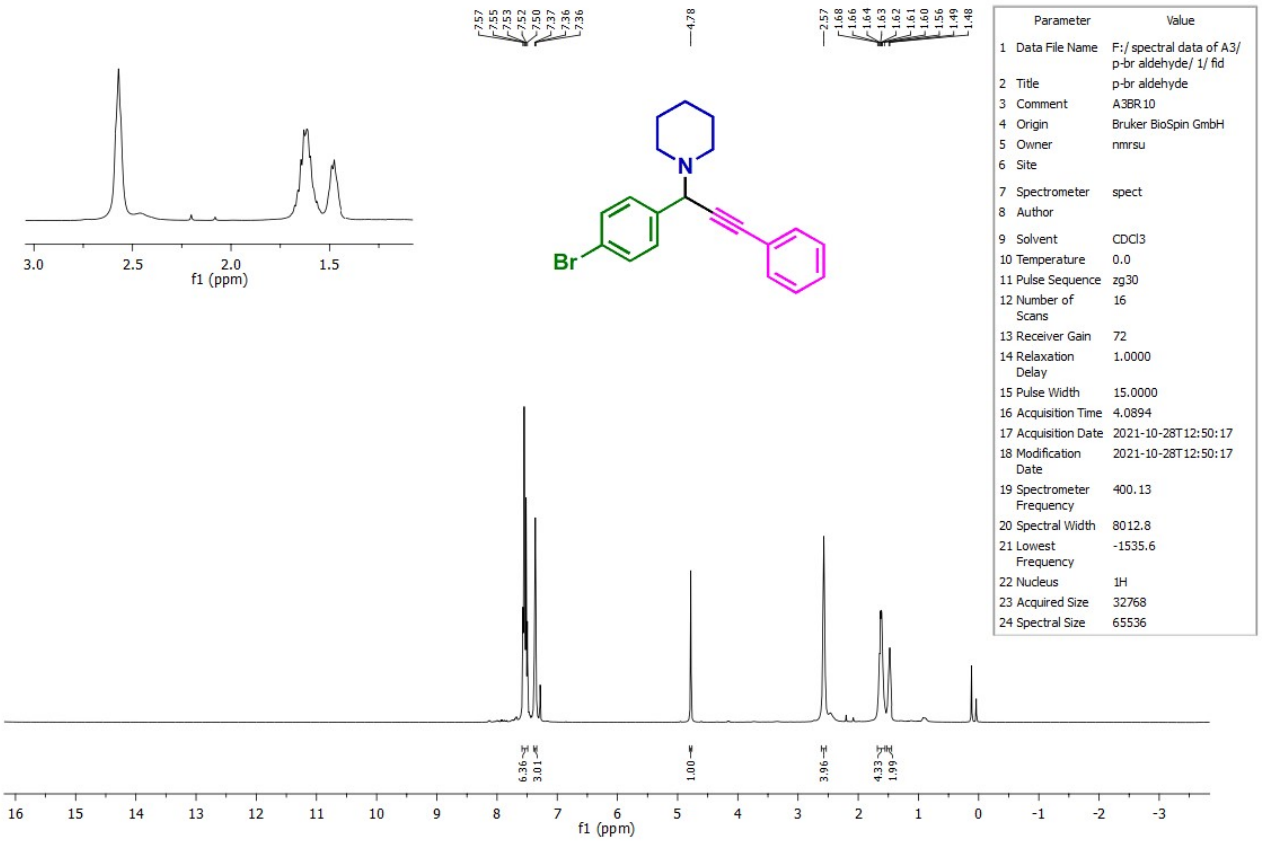
^{13}C NMR spectrum of **1-(3-Phenyl-1-m-tolylprop-2-ynyl)piperidine** (**entry 3**, **Table 4**)



^{1}H NMR spectrum of **1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)piperidine** (**entry 4**, **Table 4**)



^{13}C NMR spectrum of **1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)piperidine** (**entry 4**, **Table 4**)



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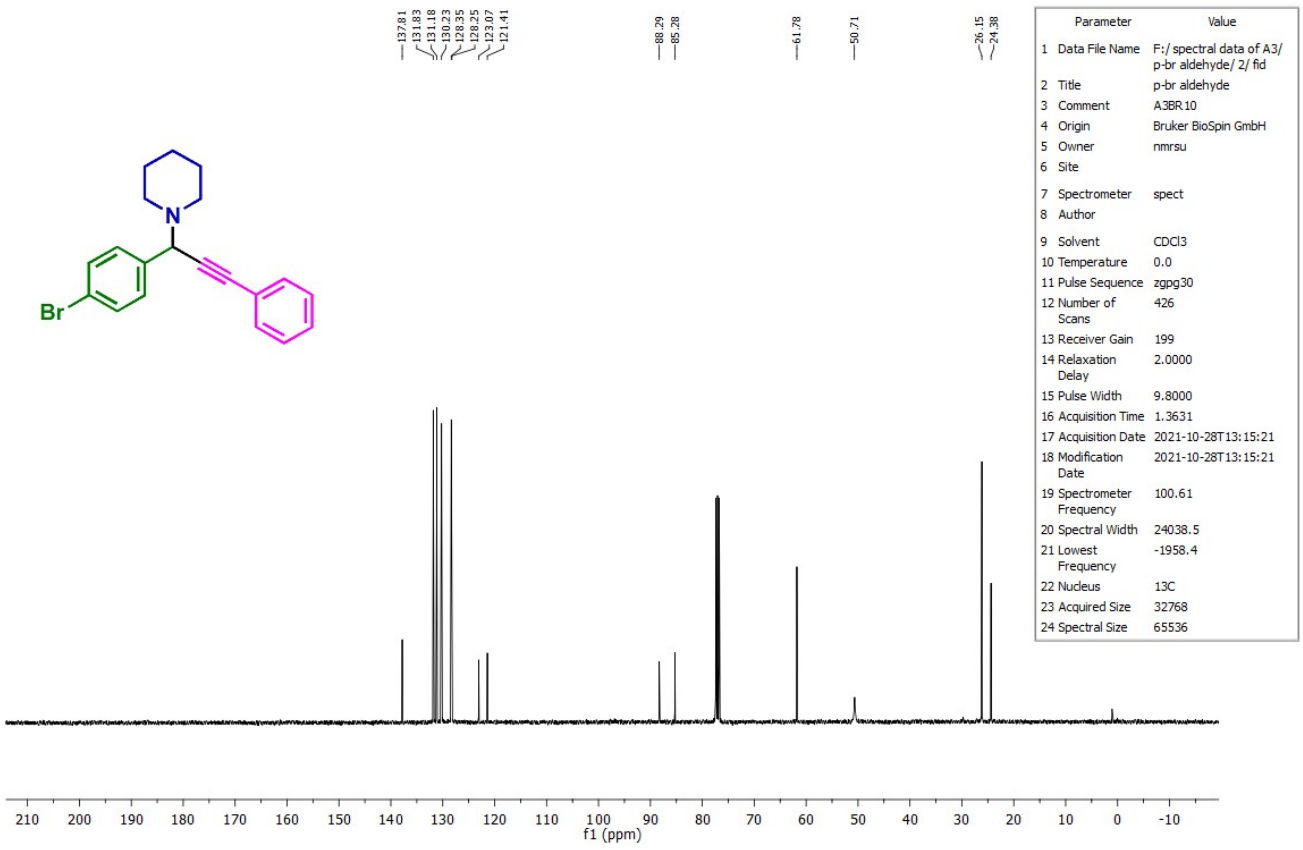
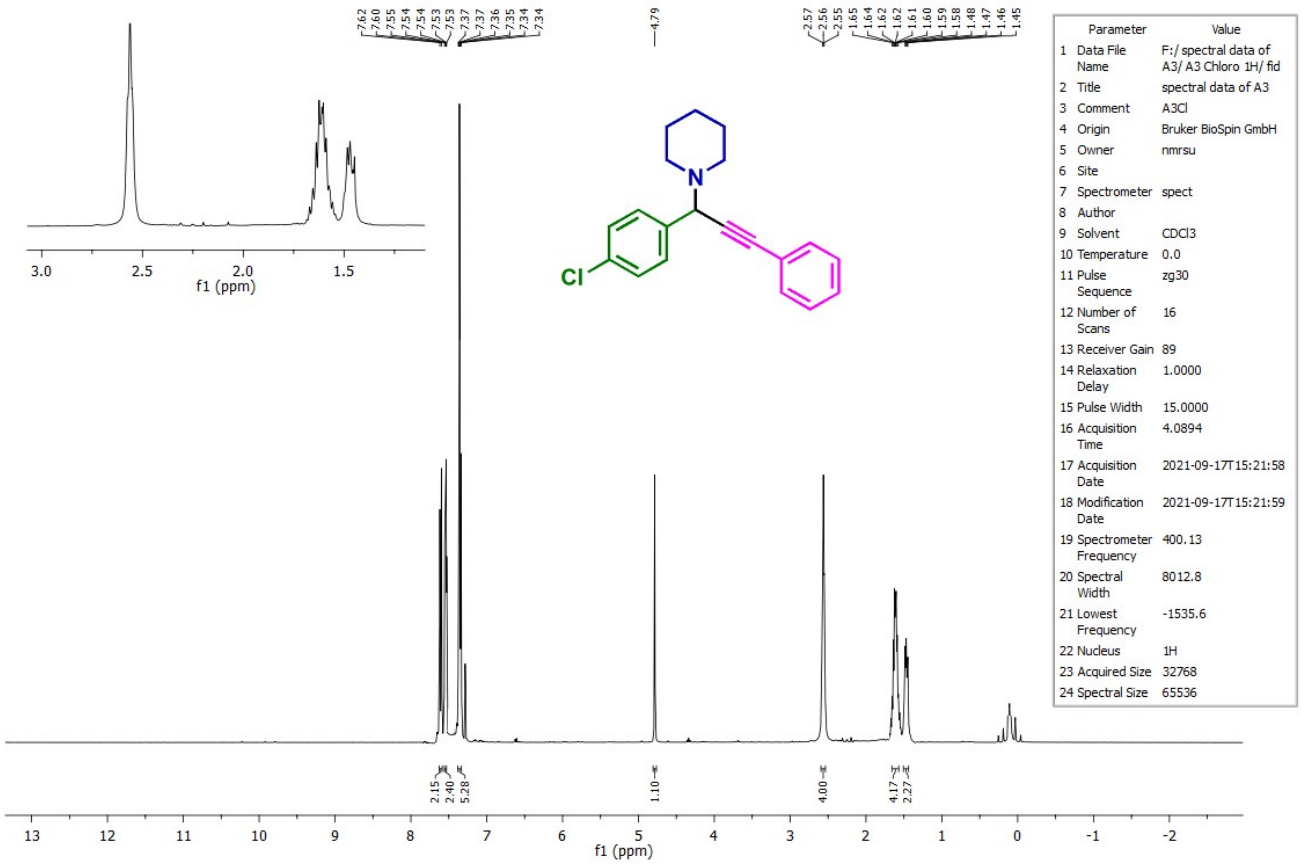
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H NMR spectrum of **1-(1-(4-Bromophenyl)-3-phenylprop-2-ynyl)piperidine** (**entry 5**, **Table 4**)



^{13}C NMR spectrum of **1-(1-(4-Bromophenyl)-3-phenylprop-2-ynyl)piperidine** (**entry 5**, **Table 4**)



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23	Acquired Size	32768
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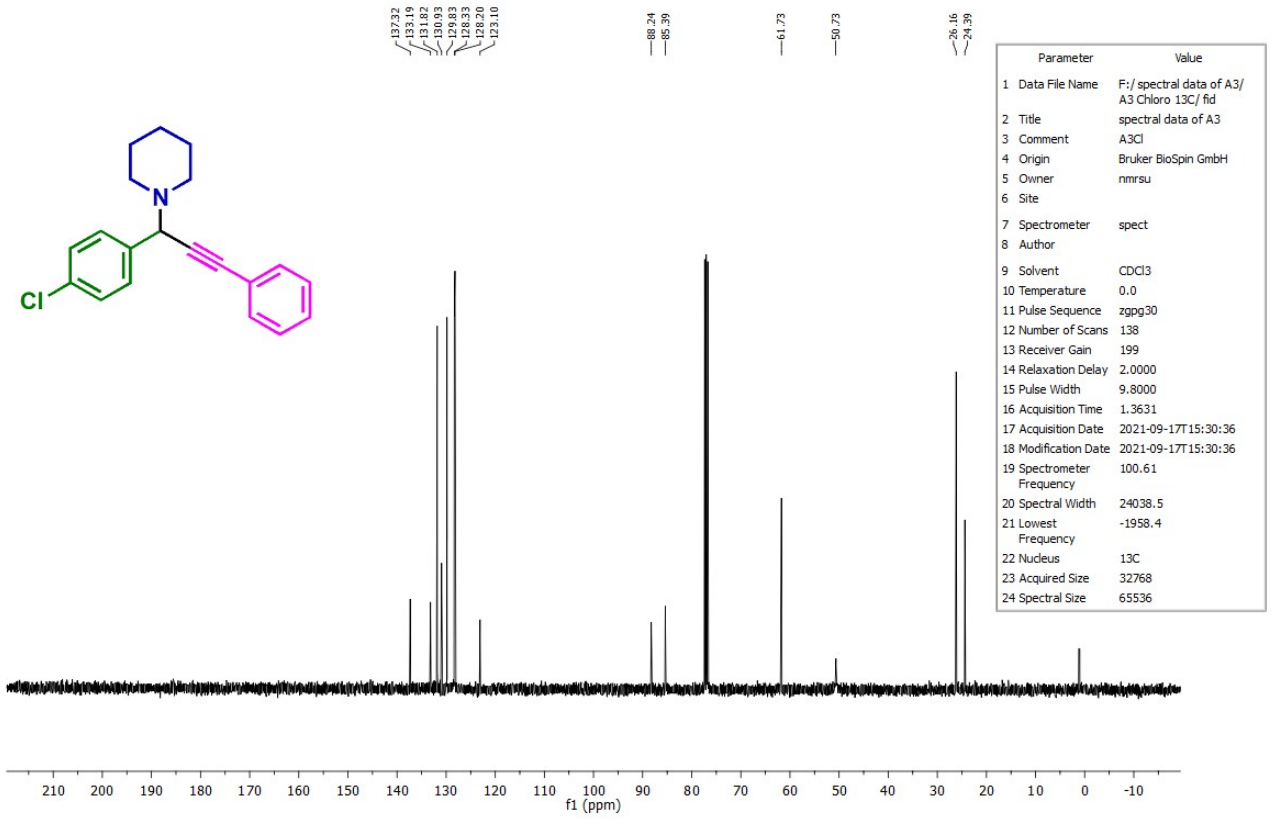
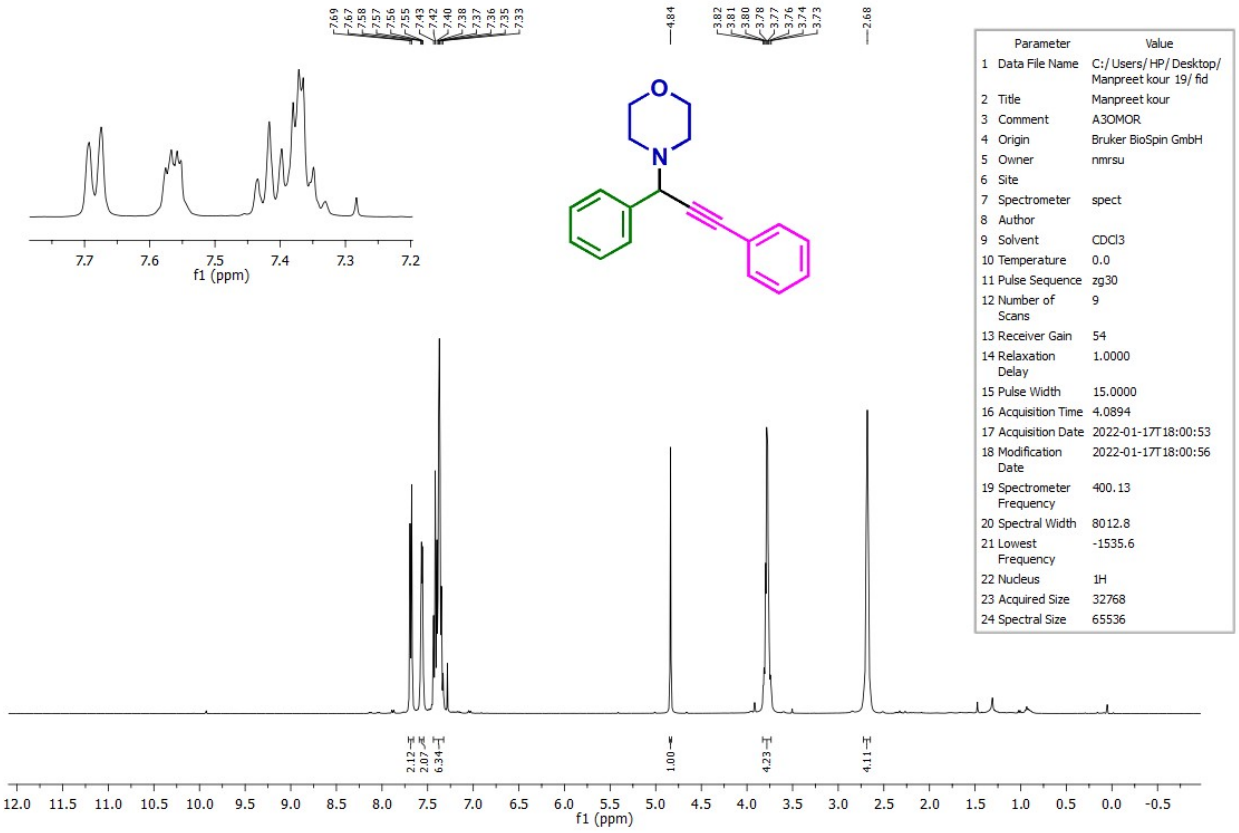
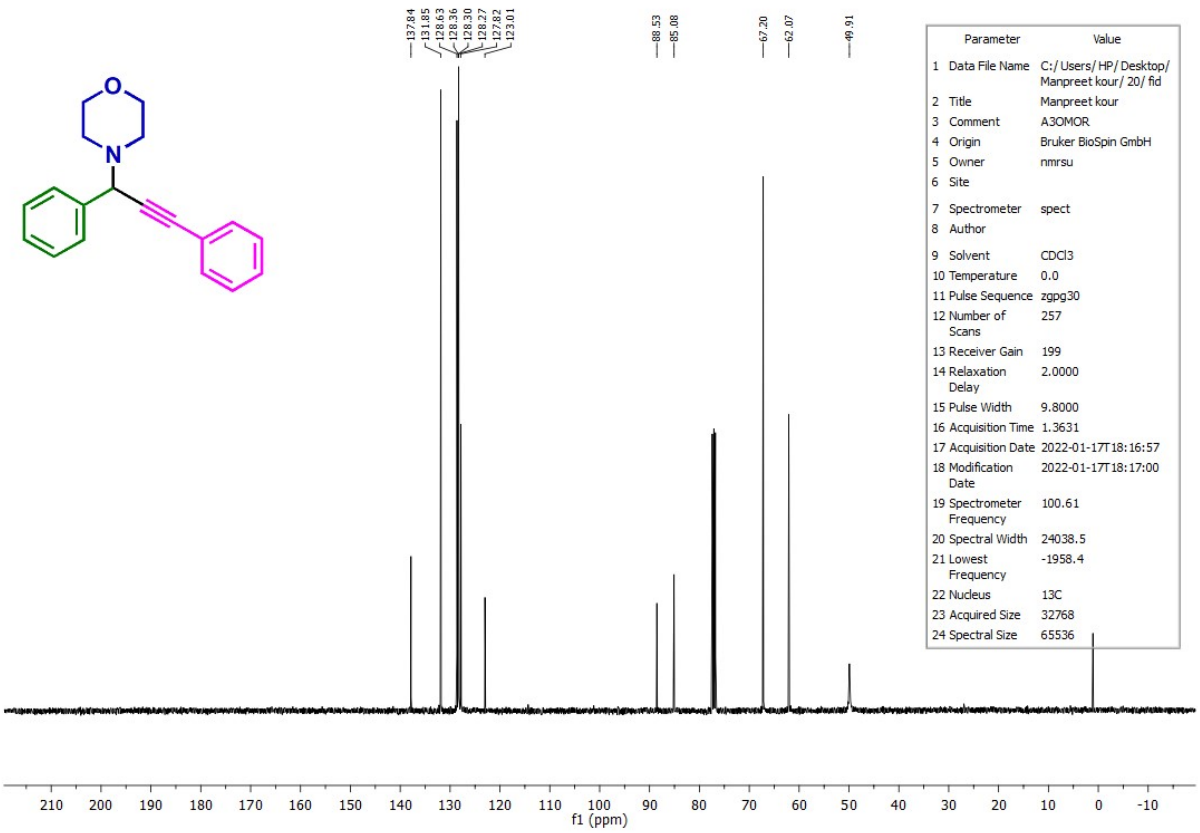
^{1}H NMR spectrum of **1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)piperidine** (**entry 6**, **Table 4**)



^{13}C NMR spectrum of **1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)piperidine** (**entry 6**, **Table 4**)



^{1}H NMR spectrum of **4-(1,3-Diphenylprop-2-ynyl)morpholine** (**entry 7**, **Table 4**)



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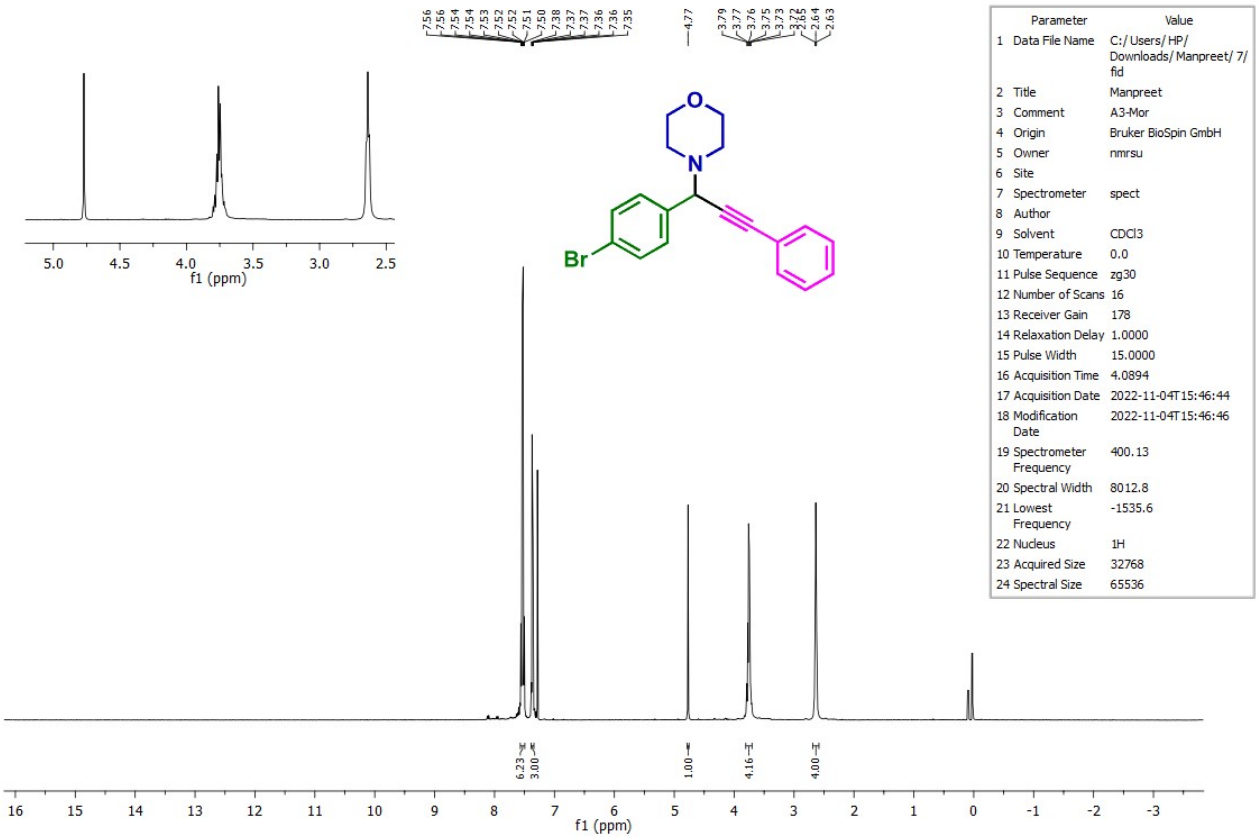
3	Comment	A3OMOR
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zgpg30
12	Number of Scans	257
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2022-01-17T18:16:57
18	Modification Date	2022-01-17T18:17:00
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.4
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C NMR spectrum of **4-(1,3-Diphenylprop-2-ynyl)morpholine** (**entry 7**, **Table 4**)



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4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
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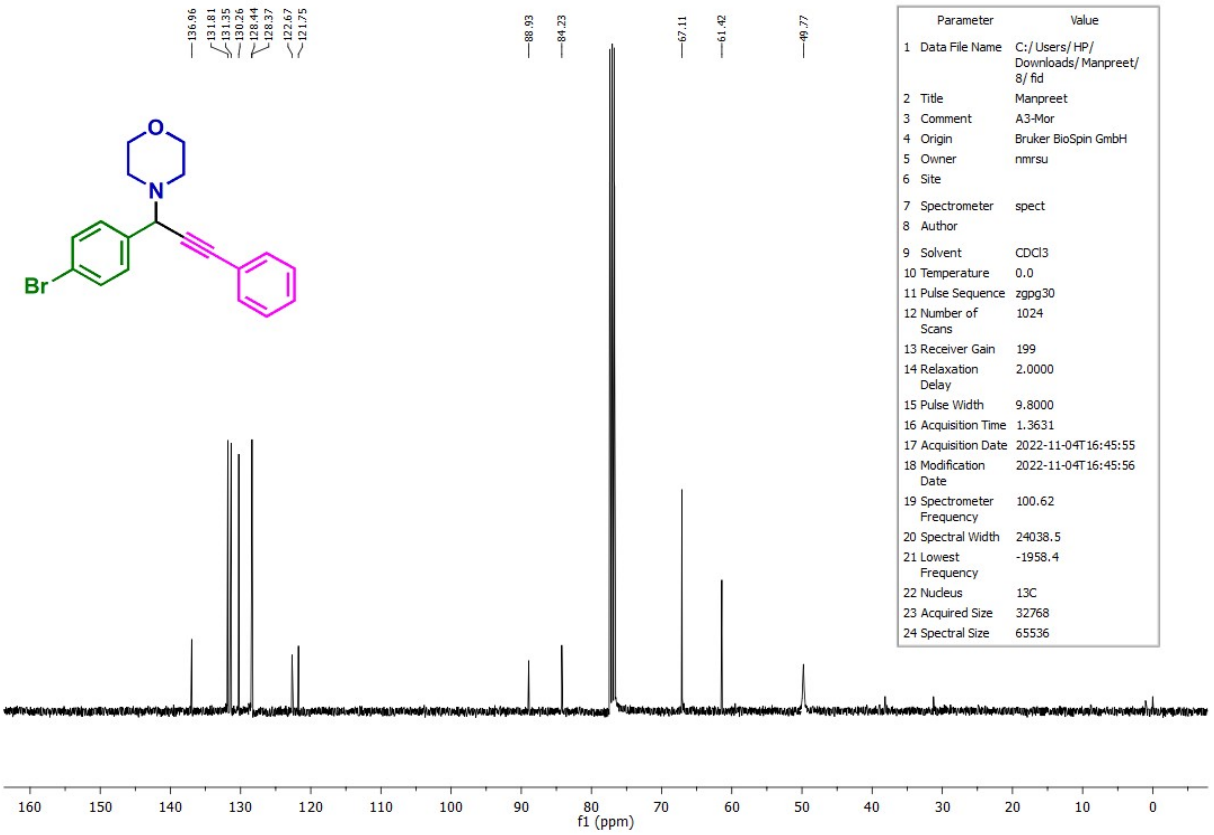
18	Modification Date	2022-11-04T15:46:46
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.6
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H NMR spectrum of **4-(1-(4-Bromophenyl)-3-phenylprop-2-ynyl)morpholine** (**entry 8**, **Table 4**)



^{13}C NMR spectrum of **4-(1-(4-Bromophenyl)-3-phenylprop-2-ynyl)morpholine** (**entry 8**, **Table 4**)