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Supporting Information

Post-synthetic modified MOF for A^3-coupling reaction of aldehyde, amine, and alkyne

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1. Ligand synthesis

1.1 Synthesis of N,N′-Bis(4-carboxyphenyl)ethylenediimine (L_A) [1-2]

The compound N,N′-Bis(4-carboxyphenyl)ethylenediimine (L_A) was synthesized according to the previous report [1-2] with slight modification.

In a 100 mL round bottom flask containing a magnetic bar, 4-aminobenzoic acid (10 g, 72.92 mmol) was dissolved in 30 mL dry methanol and the mixture was stirred until all the chemicals dissolved. Subsequently, 4 drops of formic acid were added to the mixture solution, followed by dropwise addition of 40% W/W aqueous solution of glyoxal (4.18 mL, 36.46 mmol). The reaction mixture was stirred at ambient temperature for 24 h until white solid products formed. The product was collected by filtration, washed with cold methanol and dried in air. Yield:

60.47%. Mp: >300 °C. **^{1}H-NMR (500 MHz, DMSOd6, TMS):** δ 8.35 (d, 2H), δ 8.07 (d, 2H), δ 7.83 (d, 2H).

1.2 Synthesis of 1,3-Bis(4-carboxyphenyl)imidazolium Chloride ($H_2L^+Cl^-$) [1-2]

L_A (5g, 16.89 mmol) was dissolved in anhydrous THF (30 mL) under argon atmosphere. Afterwards a solution of paraformaldehyde (635 mg, 21.16 mmol) in 12 M HCl (2.1 mL, 25.33 mmol) was added to 4 ml dioxane at 0 °C. The reaction mixture was stirred for 4 h at room temperature. The product formed was collected by filtration, washed with Et_2O and dried in Vacuum. Yield: 71.81%. Mp: >300 °C. **^{1}H-NMR (500 MHz, DMSOd6, TMS):** δ 10.66 (s, 1H), δ 8.75 (d, 2H), δ 8.24 (d, 2H), δ 8.09 (d, 2H). **^{13}C-NMR:** δ 166.64, δ 138.17, δ 135.95, δ 132.57, δ 131.61, δ 122.61, δ 122.42.

2. ***1*** *synthesis*

1 was synthesized following the procedure reported in the literature [1-3]. To 594.98 mg (2.0 mmol) of $Zn(NO_3)_2.6H_2O$ in 3 mL pre-dried DMF was added 172.38 mg (0.5 mmol) of $H_2L^+Cl^-$ in a Teflon-lined autoclave. The reaction mixture was heated under autogeneous pressure to 120 °C for 48 h followed by cooling to room temperature at the rate of 10 °C/h. The product was collected by filtration and washed with the pre-dried DMF. The product was dried in vacuo at 80°C overnight. Yield: 56.33%.

3. *EDS Mapping and Spectrum of* ***1-Ag(1)***

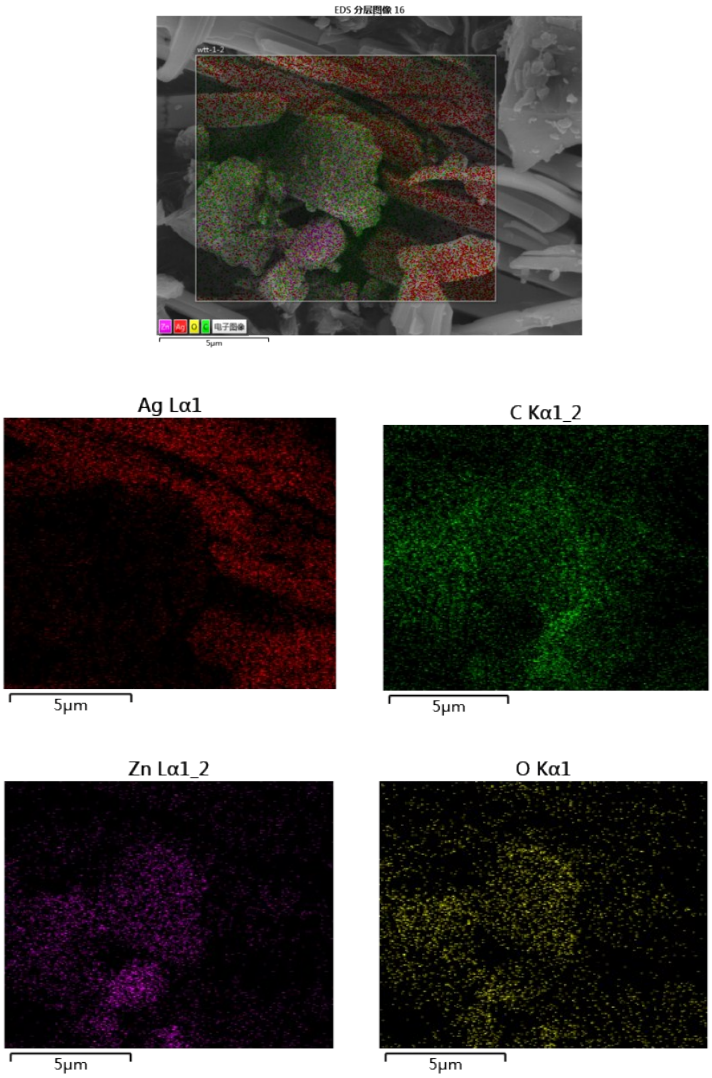


Figure S1. EDS mapping of **1-Ag(1)** indicating the presence of Zn, O, C and Ag

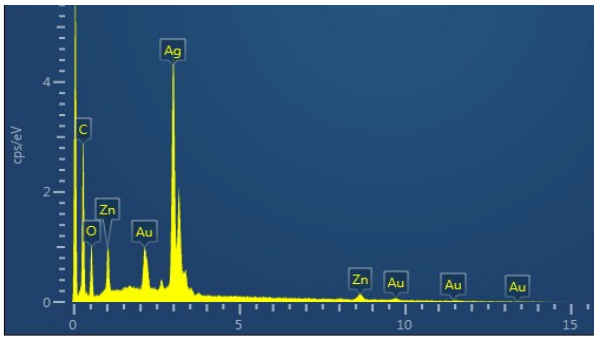


Figure S2. EDS spectrum of **1-Ag(1)**

*4. ICP-MS of the **1-Ag***

According to the ICP-MS analyses the silver content of **1-Ag (1)**, **1-Ag (0.8)**, **1-Ag(0.5)**, **1-Ag(0.3)** amounts to 15.62 wt%, 14.20 wt%, 11.41 wt%, and 6.23 wt% respectively. On the other hand, as shown in the Table S1, the percentage of Zn did not change remarkably confirming that the main structure of the framework remained unaffected.

Table S1. ICP-MS of the **1-Ag**

Entry	Compound	Ag	Zn
1	**1-Ag(1)**	15.62	23.91
2	**1-Ag(0.8)**	14.20	23.47
3	**1-Ag(0.5)**	11.41	22.54
4	**1-Ag(0.3)**	6.23	27.39

In order to show that the silver presence enhances the catalytical activity of the MOF, the molar ratio substrate:silver and substrate:zinc were calculated based on the ICP-MS analysis (Table S1, Entry 3) and using limiting reagent (aldehyde, 1.0 mmol). According to the calculations, the ratios of 190:1 for substrate:Ag, and 60:1 for substrate:Zn were observed. From this, it is evident that the ratio of substrate:Ag is 3 times higher than the ratio of substrate:Zn, and reaction time is 24 times faster, which evidences the efficiency of the presence of silver metal inside the framework and shows its direct relation to higher activity of the silver containing catalyst.

5. *BET surface area of **1** and **1-Ag (0.5)***

Table S2. BET surface area of **1** and **1-Ag (0.5)**

Entry	MOFs	BET Surface Area (m/g^2)	Langmuir Surface Area (m/g^2)	Single Point Total Pore Volume at P/P_0=0.139937895: (cm^2/g)	DFT Total Pore Volume (cm^2/g)	Pore size, nm
1	**1**	103.01	108.87	0.044	0.056	2.20
2	**1-Ag(0.5) Fresh**	92.35	110.52	0.039	0.057	1.30
3	**1-Ag(o.5) Reused**	15.48	17.06	0.0064	0.0051	1.75

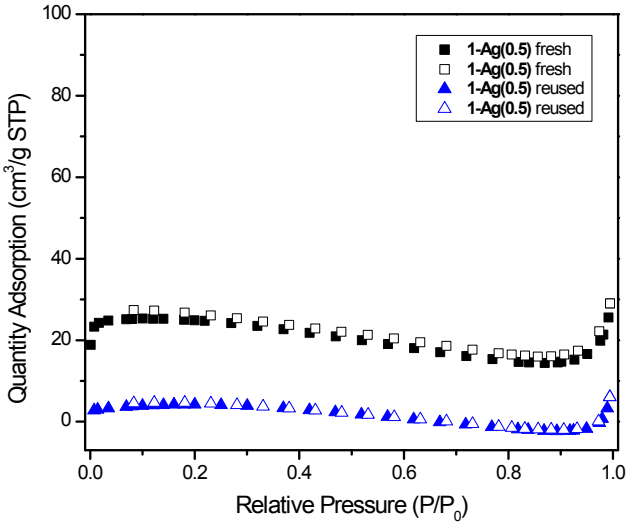


Figure S3. Isotherm plots of fresh **1-Ag(0.5)** and reused **1-Ag(0.5)**

The Figure S3 represents the isotherm plots of fresh **1-Ag(0.5)** and reused **1-Ag(0.5)**. According to the BET data (Table S2, Entry 2 and 3) the reused **1-Ag(0.5)** catalyst has a lower porosity compared to the fresh **1-Ag(0.5).** A possible explanation is that during the catalytical reaction substrates are trapped in the pores of the catalyst, which lead to the decrease of the surface area of reused catalyst, as confirmed by BET analysis (Table S2, Entry 3).

6. *TGA analysis of **1** and **1-Ag (0.5)***

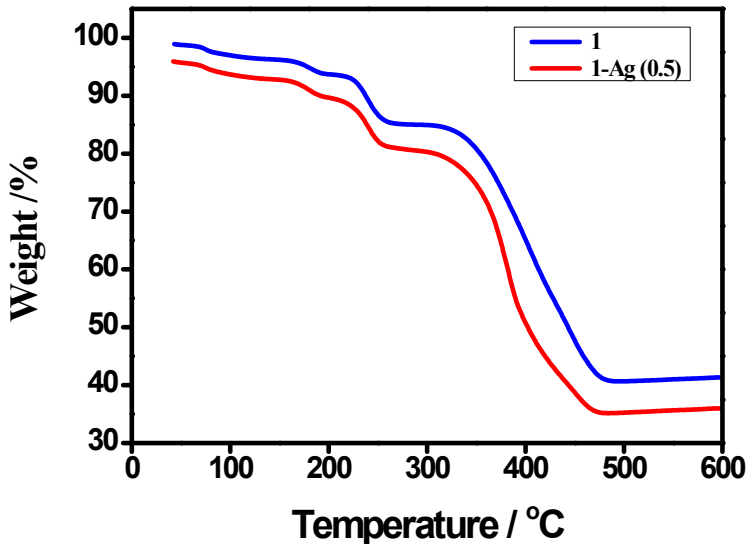


Figure S4. TGA analysis of **1** and **1-Ag (0.5)**

7. *FE-SEM of **1-Ag(0.5)** (a) before and (b) after catalytic activity*

The structural integrity of the metal organic framework of both catalysts was not affected significantly after the recycling test. FE-SEM images confirm that the morphology is not affected by the reaction (Figure S2).

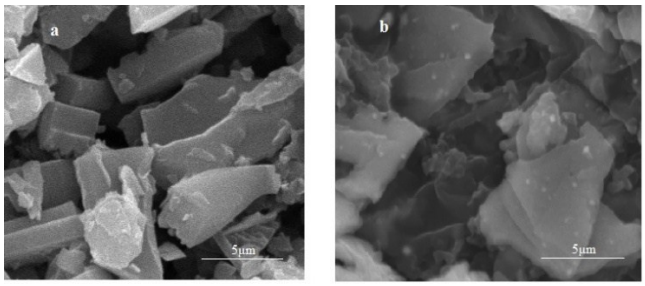
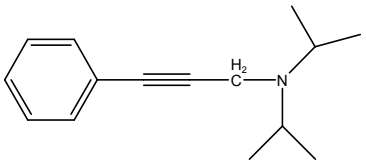


Figure S5. FE-SEM images of **1-Ag (0.5)** (a) before and (b) after catalytical activity

8. Characterization of the obtained products of Table 5

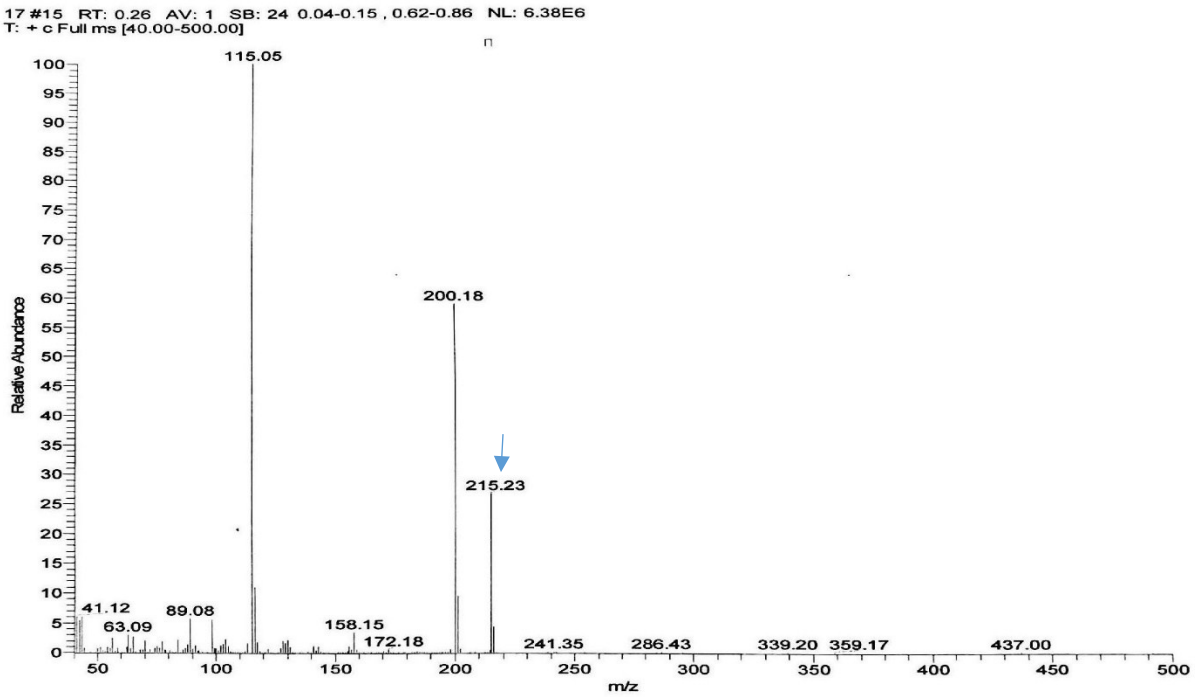
Entry 1



$C_{15}H_{21}N$

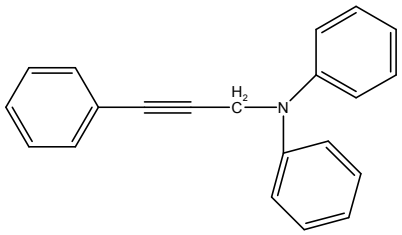
Diisopropyl-(1-isopropyl-3-phenyl-2-propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.43 (m, 3H), *δ* 7.31 (m, 2H), *δ* 3.68 (s, 1H), *δ* 3.30 (m, 2H), *δ* 1.19 (d, 12H). **^{13}C-NMR:** *δ* 131.62, *δ* 128.19, *δ* 123.89, *δ* 88.97, *δ* 83.39, *δ* 48.53, *δ* 34.81, *δ* 20.68. **EI-MS:** exact mass 215.17, found 215.23.



Mass Spectrum of entry 1

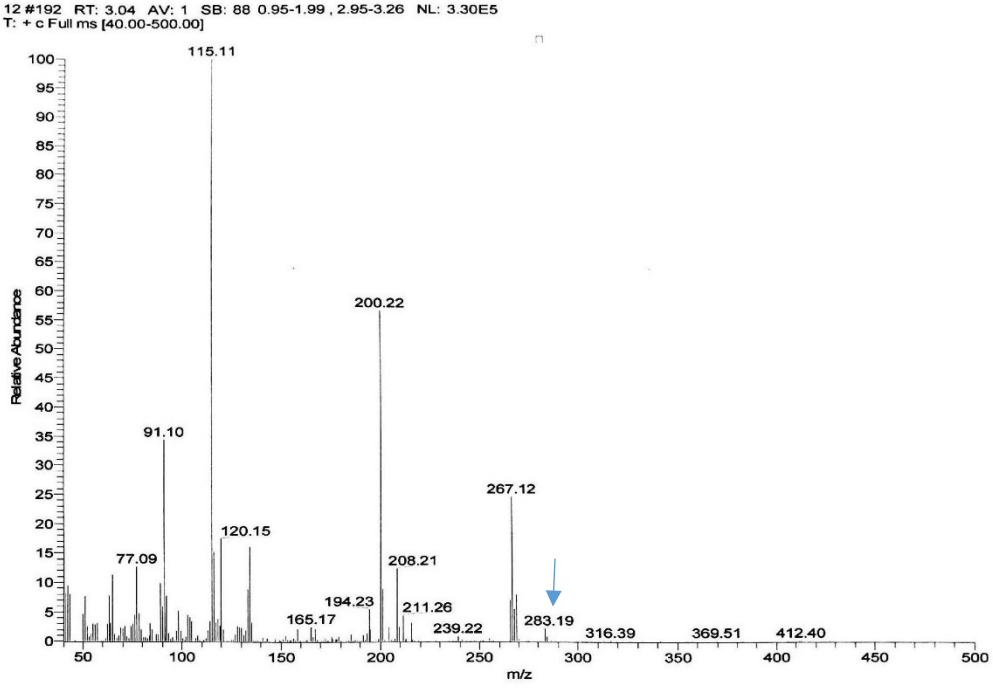
Entry 5



$C_{21}H_{17}N$

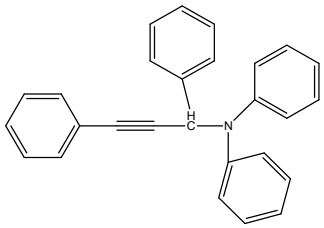
Diphenyl-(3-phenyl-2propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.59-7.57 (m, 2H), *δ* 7.42-7.25 (m, 3H), *δ* 7.15-7.14 (m, 2H), *δ* 7.03-7.00 (m, 4H), *δ* 6.92-6.90 (m, 4H), *δ* 3.56 (s, 2H). **^{13}C-NMR:** *δ* 143.22, *δ* 132.21, *δ* 129.63, *δ* 128.39, *δ* 122.08, *δ* 121.07, *δ* 118.07, *δ* 83.86, *δ* 77.23, *δ* 53.70. **EI-MS:** exact mass 283.14, found 283.19.



Mass Spectrum of entry 5

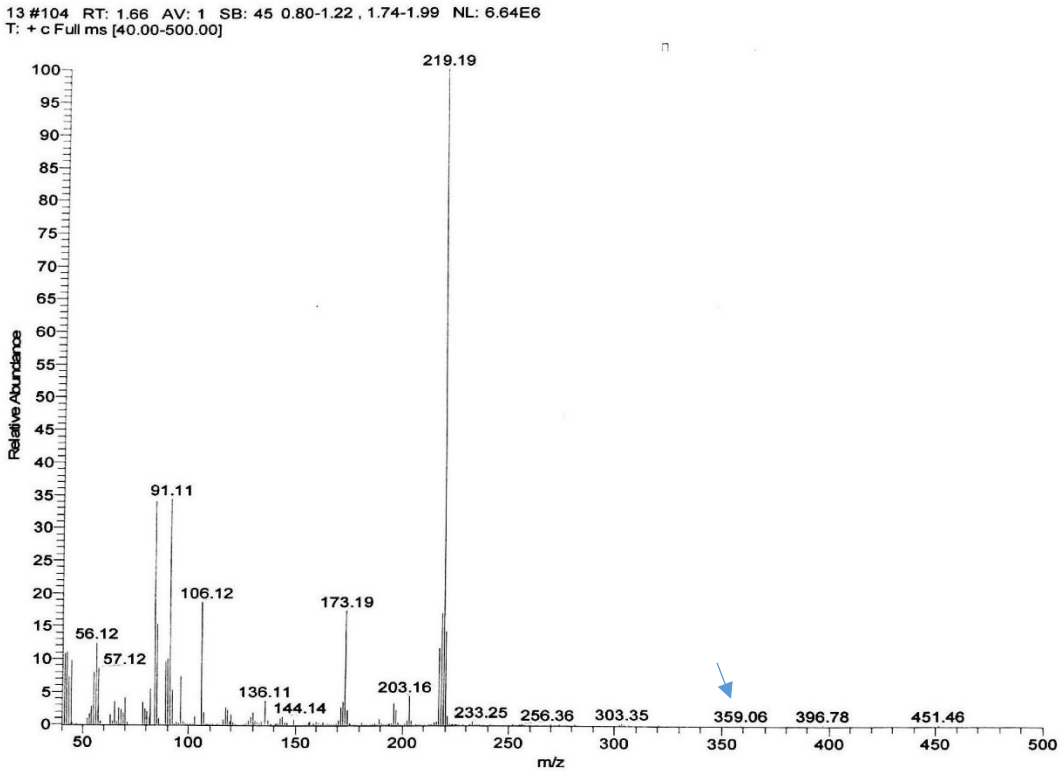
Entry 6



$C_{27}H_{21}N$

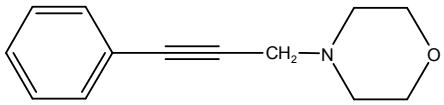
(1,3-Diphenyl-2-propynyl)diphenylamine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.71-7.68 (m, 4H), *δ* 7.61-7.56 (m, 6H), *δ* 7.41-7.28 (m, 4H), *δ* 7.15-7.13 (m, 2H), *δ* 7.01-6.98 (m, 4H), *δ* 3.57 (s, 1H). **^{13}C-NMR:** *δ* 143.22, *δ* 136.58, *δ* 134.56, *δ* 132.20, *δ* 129.82, *δ* 129.40, *δ* 129.06, *δ* 128.86, *δ* 128.38, *δ* 121.05, *δ* 117.89, *δ* 84.02, *δ* 77.14, *δ* 53.45. **EI-MS:** exact mass 359.17, found 359.06.



Mass Spectrum of entry 6

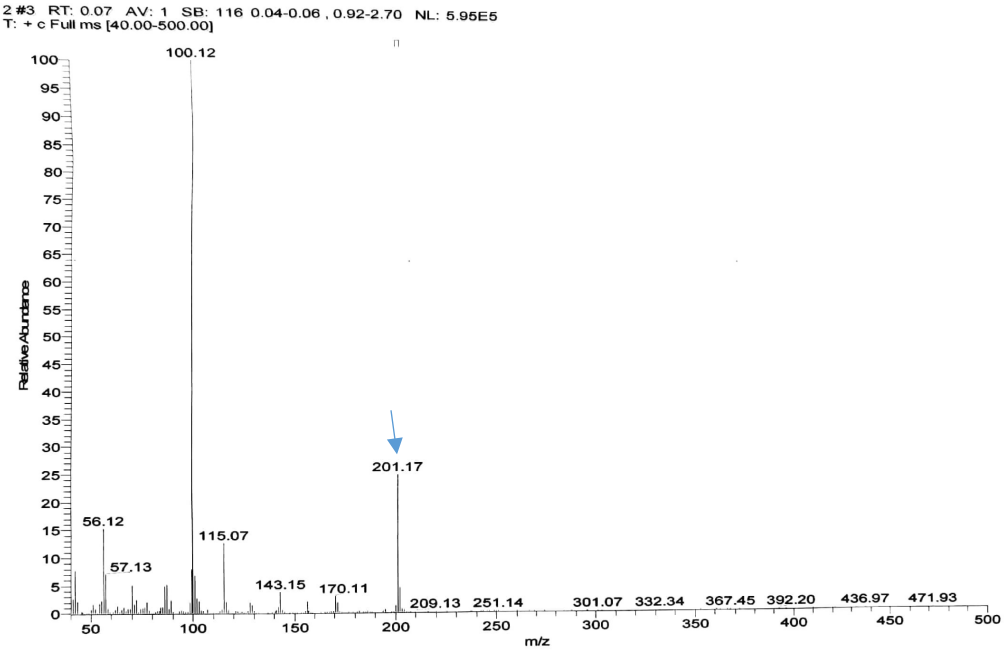
Entry 7



$C_{13}H_{15}NO$

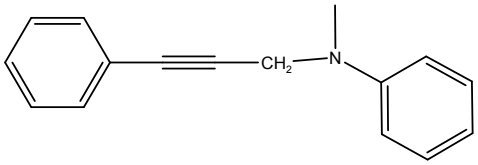
4-(3-Phenyl-2-propynyl)morpholine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.51-7.49 (m, 2H), *δ* 7.37-7.29 (m, 3H), *δ* 3.75-3.60 (m, 4H), *δ* 2.92 (s, 2H), *δ* 2.61-2.40 (m, 4H). **^{13}C-NMR:** *δ* 132.19, *δ* 128.77, *δ* 128.30, *δ* 122.31, *δ* 87.33, *δ* 81.67, *δ* 67.20, *δ* 52.02, *δ* 49.16. **EI-MS:** exact mass 201.12, found 201.17.



Mass Spectrum of entry 7

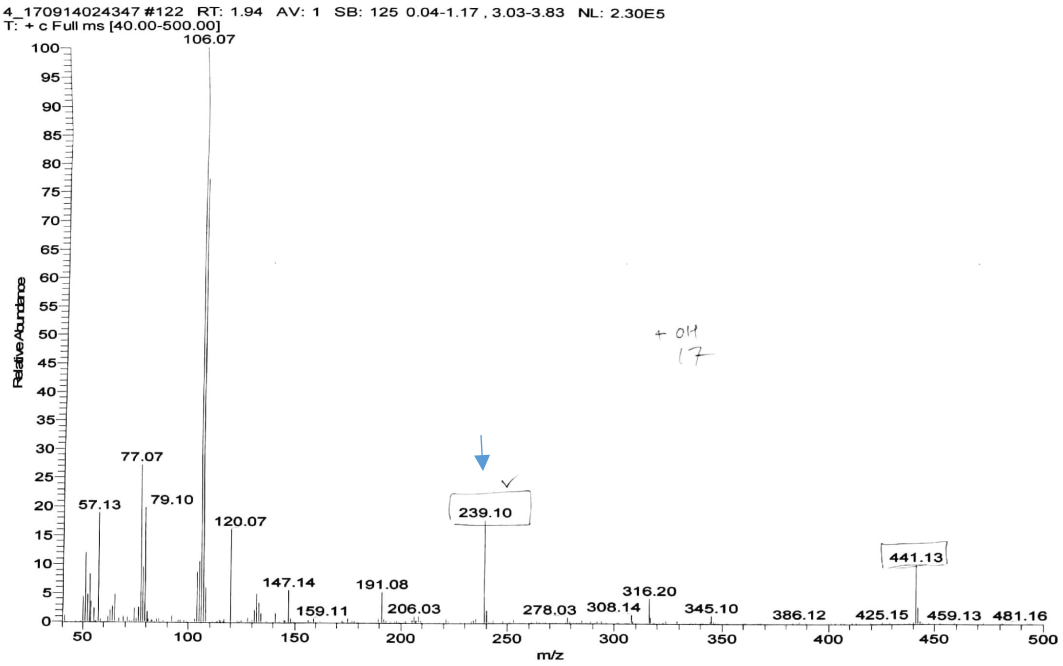
Entry 8



$C_{16}H_{15}N$

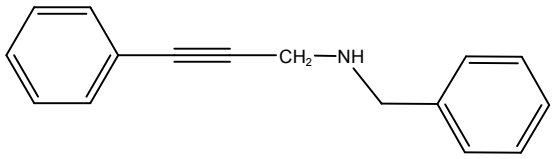
Methyl-phenyl-(3-phenyl-2-propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.56-7.54 (d, 1H), *δ* 7.40-7.23 (m, 4H), *δ* 6.91-6.89 (d, 1H), *δ* 6.85-6.83 (t, 2H), *δ* 6.78-6.75 (t, 1H), *δ* 6.67-6.66 (d, 1H), *δ* 4.82 (s, 2H), *δ* 2.93 (s, 3H). **^{13}C-NMR:** *δ* 149.56, *δ* 132.40, *δ* 129.42, *δ* 128.94, *δ* 128.35, *δ* 122.12, *δ* 117.48, *δ* 113.83, *δ* 77.07, *δ* 70.40, *δ* 36.21, *δ* 30.75. **EI-MS:** exact mass 221.12, found 239.10 (m/z +17).



Mass Spectrum of entry 8

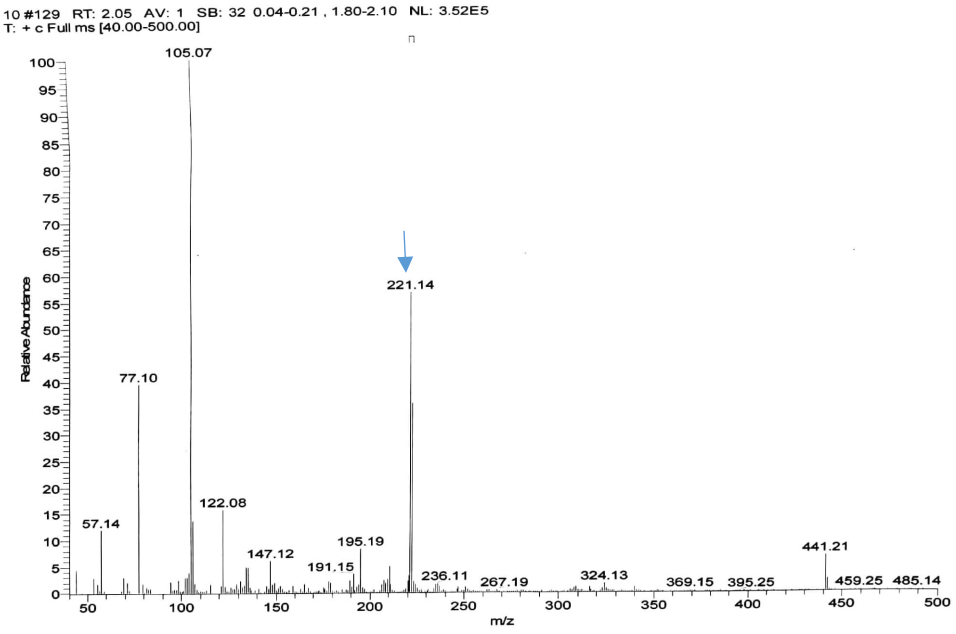
Entry 9



$C_{16}H_{15}N$

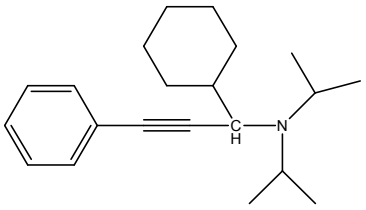
Benzyl-(3-phenyl-2-propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.57-7.55 (m, 2H), *δ* 7.40-7.37 (m, 3H), *δ* 7.34-7.31 (m, 3H), *δ* 7.29-7.26 (m, 2H), *δ* 3.73 (s, 2H), *δ* 3.13 (s, 2H), *δ* 1.28 (s, 1H). **^{13}C-NMR:** *δ* 138.39, *δ* 132.39, *δ* 128.93, *δ* 128.27, *δ* 127.05, *δ* 122.16, *δ* 76.86, *δ* 73.80, *δ* 57.35, *δ* 53.75, *δ* 15.19. **EI-MS:** exact mass 221.12, found 221.14.



Mass Spectrum of entry 9

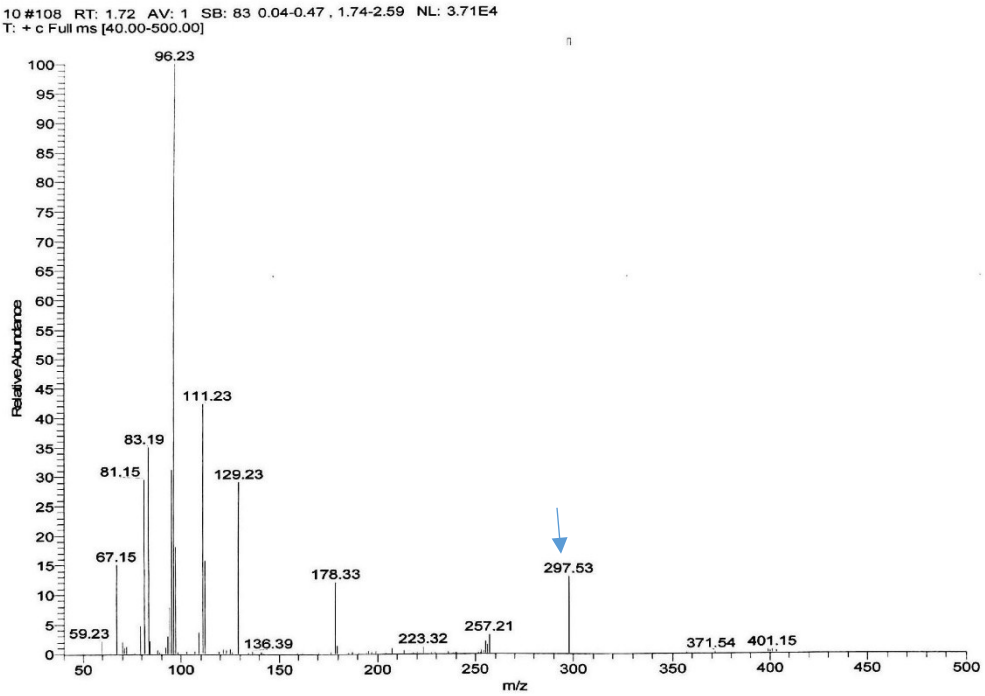
Entry 4



$C_{21}H_{31}N$

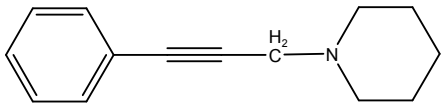
(1-Cyclohexyl-3-phenyl-2-proynyl)-diisopropylamine

^{1}H-NMR (500 MHz, CDCl3, TMS): δ 7.52-7.51 (d, 2H), δ 7.37-7.33 (m, 3H), δ 3.28-3.20 (s, 1H), δ 3.11-3.07 (m, 2H), δ 2.22-2.17 (m, 1H), δ 1.97-1.90 (m, 4H), δ 1.80-1.70 (m, 6H), δ 1.34-1.26 (m, 12H). **^{13}C-NMR:** δ 132.41, δ 128.78, δ 128.30, δ 122.13, δ 84.02, δ 76.77, δ 46.15, δ 45.06, δ 29.75, δ 26.06, δ 25.98, δ 25.01, δ 20.04. **EI-MS:** exact mass 297.25, found 297.53.



Mass Spectrum of entry 4

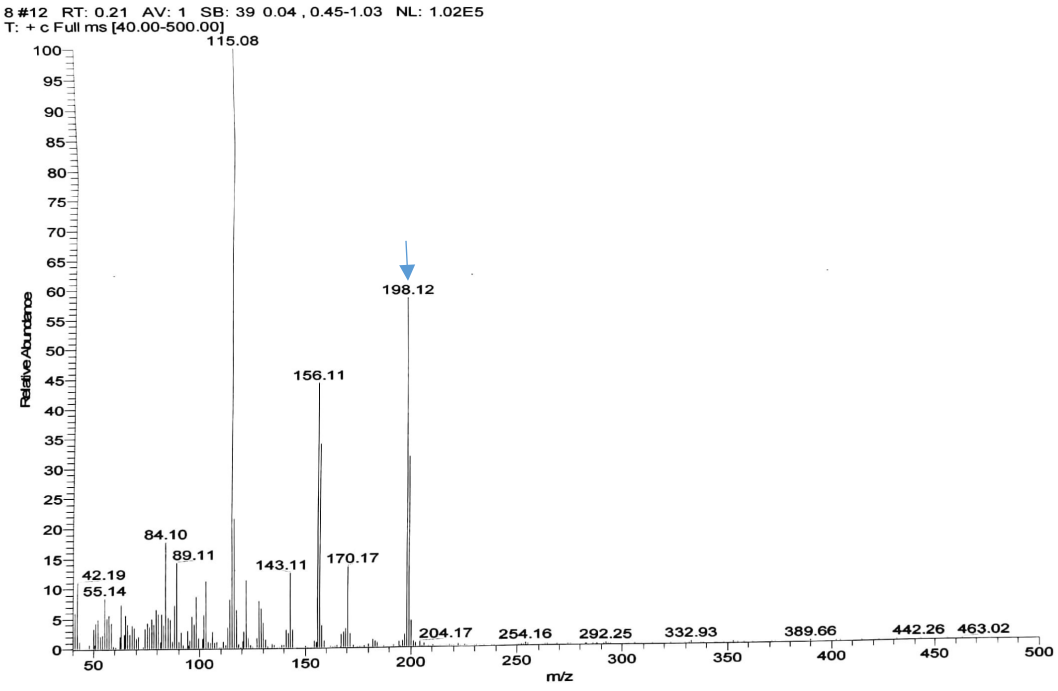
Entry 10



$C_{14}H_{17}N$

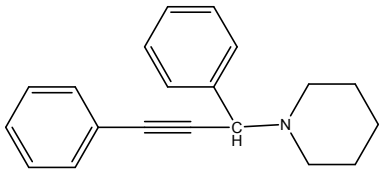
1-(3-Phenyl-2-propynyl)piperedine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.52-7.51 (m, 2H), *δ* 7.46-7.45 (m, 1H), *δ* 7.35-7.31 (m, 2H), *δ* 3.09 (s, 2H), *δ* 2.52-2.34 (m, 4H), *δ* 1.62-1.51 (m, 6H). **^{13}C-NMR:** *δ* 132.13, *δ* 131.72, *δ* 128.21, *δ* 123.35, *δ* 85.30, *δ* 82.77, *δ* 53.10, *δ* 48.75, *δ* 25.96, *δ* 24.98 **EI-MS:** exact mass 199.14, found 198.12 (m/z -1).



Mass Spectrum of entry 10

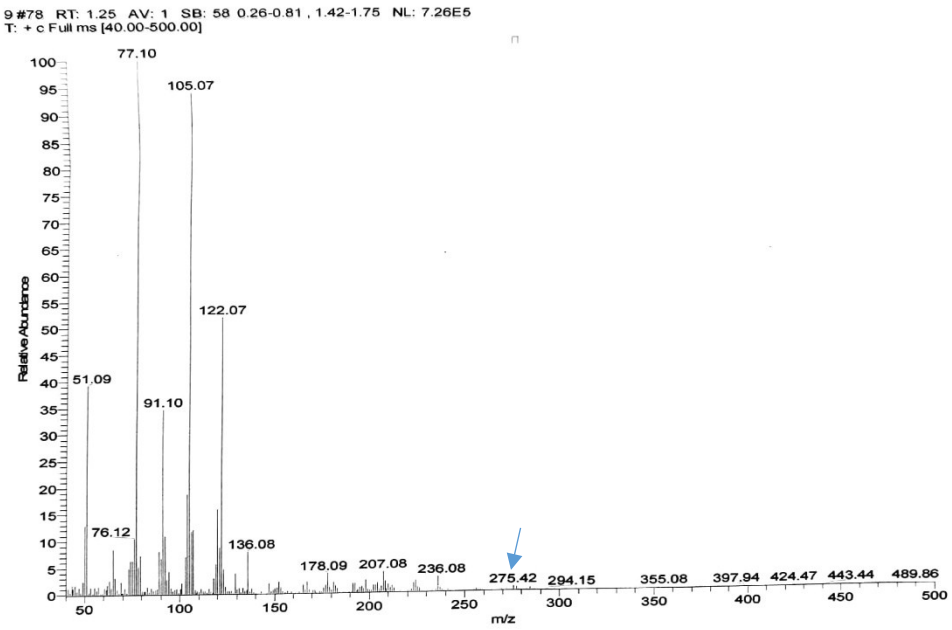
Entry 11



$C_{20}H_{21}N$

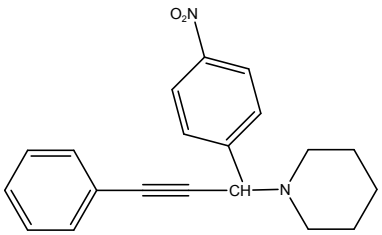
N-(1,3-Diphenyl-2-propynyl)piperidine

^{1}H-NMR (500 MHz, CDCl3, TMS): δ 7.91-7.89 (m, 2H), 7.56-7.53 (m, 2H), 7.41-7.20 (m, 6H), 4.09 (s, 1H), 2.95-2.79 (m, 4H), 1.72-1.53 (m, 4H), 1.53-1.37 (m, 2H). **^{13}C-NMR:** δ 138.65, δ 132.11, δ 128.99, δ 128.64, δ 128.29, δ 127.26, δ 123.37, δ 87.81, δ 86.09, δ 62.38, δ 53.09, δ 26.21, δ 24.52. **EI-MS:** exact mass 275.17, found 275.42.



Mass Spectrum of entry 11

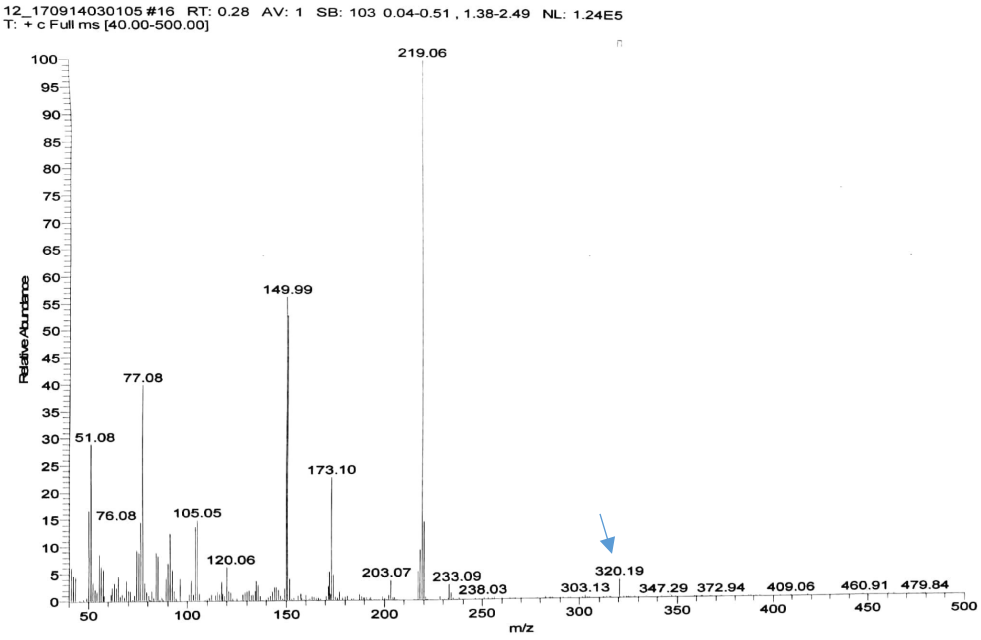
Entry 12



$C_{20}H_{20}N_2O_2$

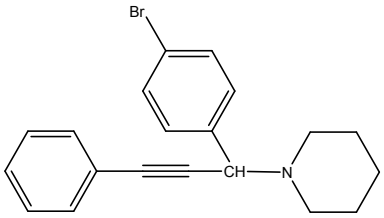
N-[1-(4-Nitrophenyl)-3-phenyl-2-propynyl]piperidine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 8.42-8.40 (m, 2H), *δ* 8.19-8.18 (m, 2H), *δ* 8.10-8.08 (m, 2H), *δ* 7.49-7.48 (m, 1H), *δ* 7.38-7.34 (m, 2H), *δ* 5.53 (s, 1H), *δ* 2.35-2.20 (m, 4H), *δ* 1.76-1.58 (m, 4H), *δ* 1.58-1.37 (m, 2H). **^{13}C-NMR:** *δ* 147.07, *δ* 143.98, *δ* 132.12, *δ* 130.47, *δ* 128.94, *δ* 128.30, *δ* 124.15, *δ* 122.84, *δ* 88.67, *δ* 77.05, *δ* 65.84, *δ* 50.05, *δ* 26.42, *δ* 25.34. **EI-MS:** exact mass 320.15, found 320.19.



Mass Spectrum of entry 12

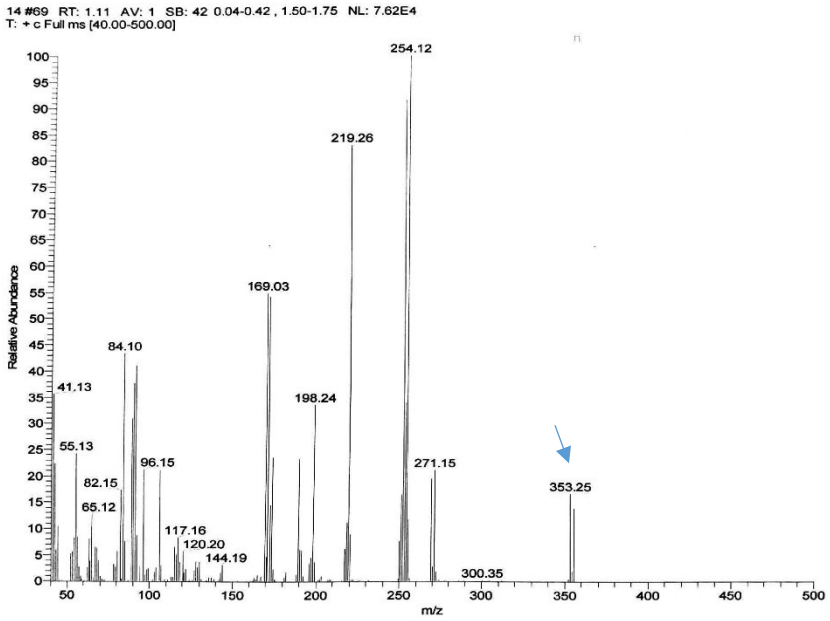
Entry 13



$C_{20}H_{20}N_2O_2$

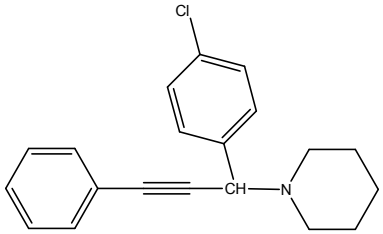
N-[1-(4-Bromophenyl)-3-phenyl-2-propynyl]piperidine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.77-7.76 (d, 2H), 7.71-7.70 (d, 2H), 7.52-7.50 (m, 2H), 7.37-7.32 (m, 2H), 7.10-7.09 (d, 1H), 5.31 (s, 1H), 2.30-2.30 (m, 4H), 1.62-1.52 (m, 4H), 1.52-1.39 (m, 2H). **^{13}C-NMR:** *δ* 135.12, *δ* 132.45, *δ* 130.97, *δ* 130.47, *δ* 128.78, *δ* 128.31, *δ* 122.42, *δ* 120.47, *δ* 89.10, *δ* 83.66, *δ* 65.88, *δ* 50.23, *δ* 47.52, *δ* 26.36, *δ* 25.31. **EI-MS:** exact mass 353.08, found 353.25.



Mass Spectrum of entry 13

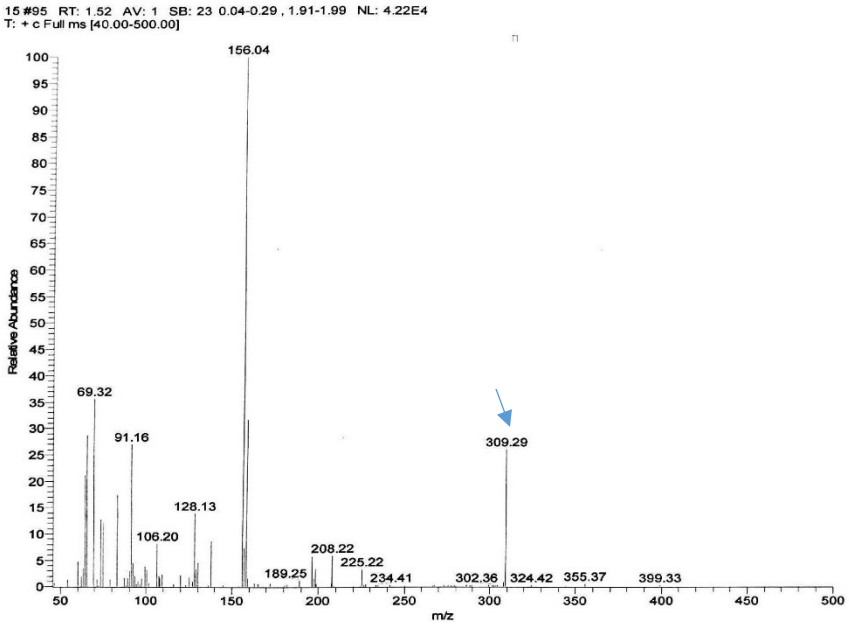
Entry 14



$C_{20}H_{20}ClN$

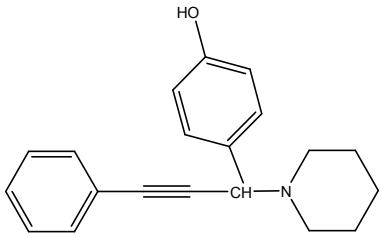
N-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]piperidine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.65-7.61 (m, 4H), *δ* 7.59-7.54 (m, 3H), *δ* 7.40-7.34 (m, 2H), *δ* 4.80 (s, 1H), *δ* 2.62-2.54 (m, 4H), *δ* 1.71-1.54 (m, 4H), *δ* 1.54-1.45 (m, 2H). **^{13}C-NMR:** *δ* *δ* 137.30, *δ* 134.34, *δ* 131.72, *δ* 131.01, *δ* 128.70, *δ* 128.30, *δ* 128.13, *δ* 122.10, *δ* 83.71, *δ* 76.82, *δ* 50.08, *δ* 44.77, *δ* 26.20, *δ* 23.32. **EI-MS:** exact mass 309.13, found 309.29.



Mass Spectrum of entry 14

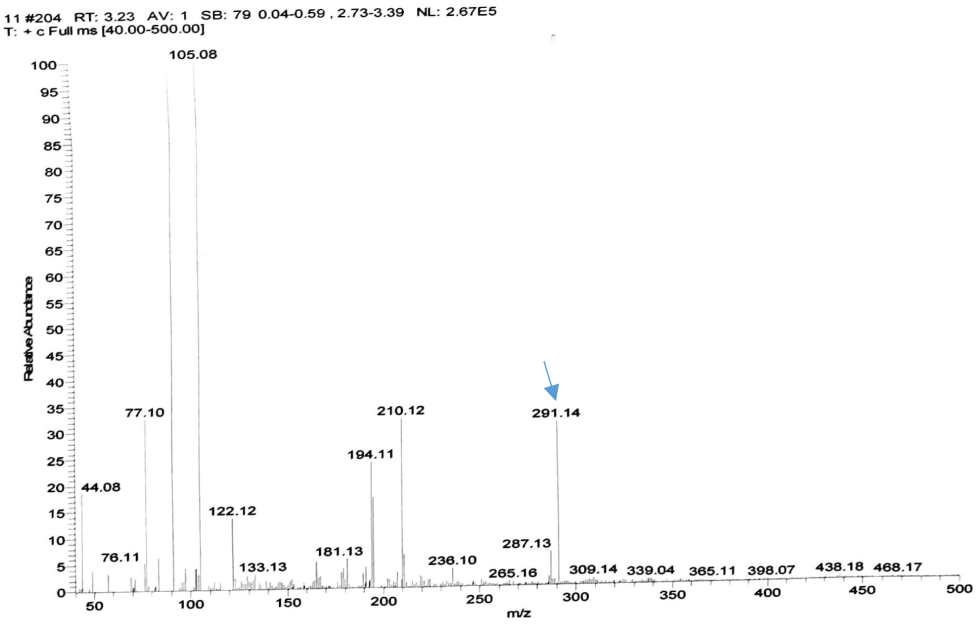
Entry 15



$C_{20}H_{21}NO$

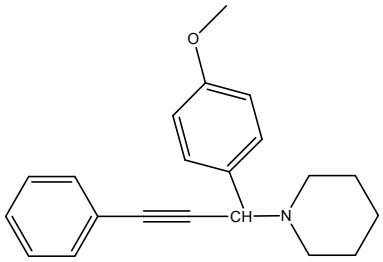
4-(3-Phenyl-1-piperidin-1-yl-prop-2-ynyl)-phenol

^{1}H-NMR (500 MHz, CDCl3, TMS): δ 7.45-7.43 (m, 2H), δ 7.39-7.36 (m, 2H), δ 7.29-7.26 (m, 2H), δ 7.00-6.99 (m, 1H), δ 6.84-6.79 (m, 2H), δ 5.10 (s, 1H), δ 3.86 (s, 1H), δ 3.05 (m, 4H), δ 1.53-1.29 (m, 6H). **^{13}C-NMR:** δ 156.23, δ 139.89, δ 136.85, δ 129.69, δ 128.76, δ 124.16, δ 119.30, δ 116.53, δ 83.81, δ 76.80, δ 58.20, δ 52.80, δ 50.37, δ 44.80. **EI-MS:** exact mass 291.16, found 291.14.



Mass Spectrum of entry 15

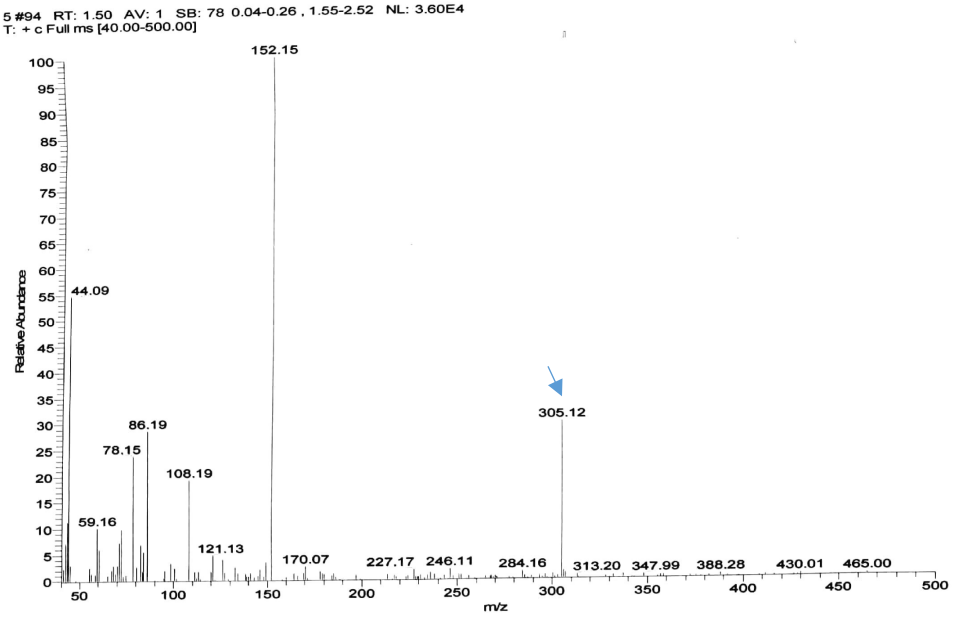
Entry 16



$C_{21}H_{23}NO$

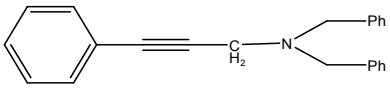
N-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]piperidine

^{1}H-NMR (500 MHz, CDCl3, TMS): δ 7.89-7.79 (m, 2H), δ 7.35-7.29 (m, 4H), δ 7.56-6.96 (m, 3H), δ 4.95 (s, 1H), δ 3.89 (s, 3H), δ 3.10-2.86 (m, 4H), δ 1.66-1.43 (m, 6H). **^{13}C-NMR:** δ 164.82, δ 132.10, δ 131.98, δ 129.95, δ 128.77, δ 128.29, δ 122.09, δ 114.80, δ 83.72, δ 82.63, δ 62.73, δ 55.58, δ 53.07, δ 26.01, δ 24.14. **EI-MS:** exact mass 305.18, found 305.12.



Mass Spectrum of entry 16

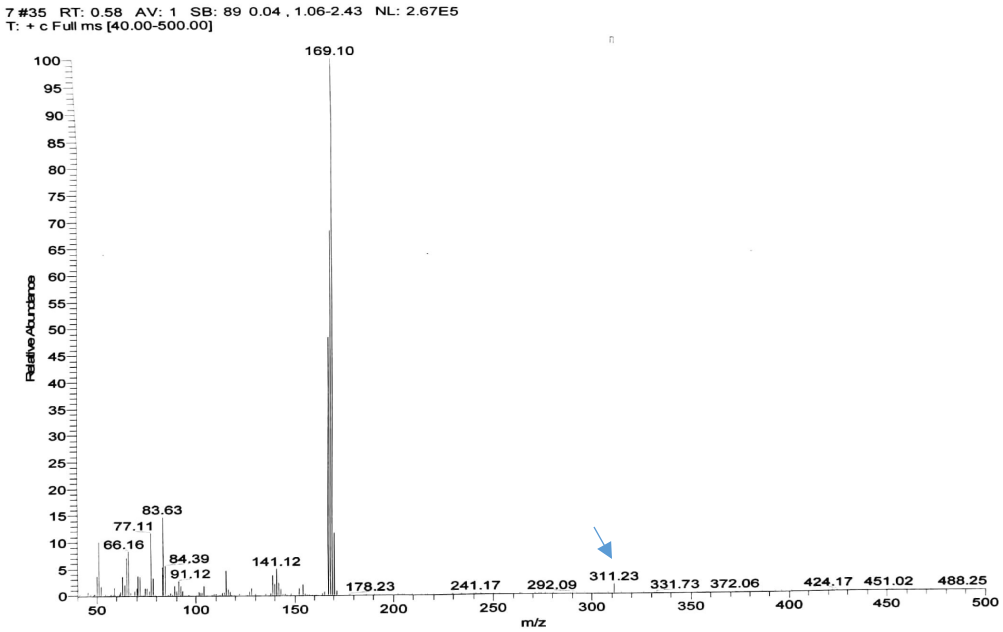
Entry 17



$C_{23}H_{21}N$

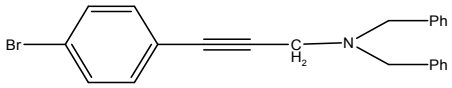
Dibenzyl-(3-phenyl-2-propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): δ 7.55-7.54 (m, 2H), 7.40-7.37 (m, 3H), 7.35-7.32 (m, 4H), 7.29-7.26 (m, 6H), 3.67 (s, 4H), 3.16 (s, 2H). **^{13}C-NMR:** δ 139.80, 132.17, 129.09, 128.44, 128.19, 127.00, 122.20, 83.89, 77.06, 56.17, 53.19. **EI-MS:** exact mass 311.17, found 311.23.



Mass Spectrum of entry 17

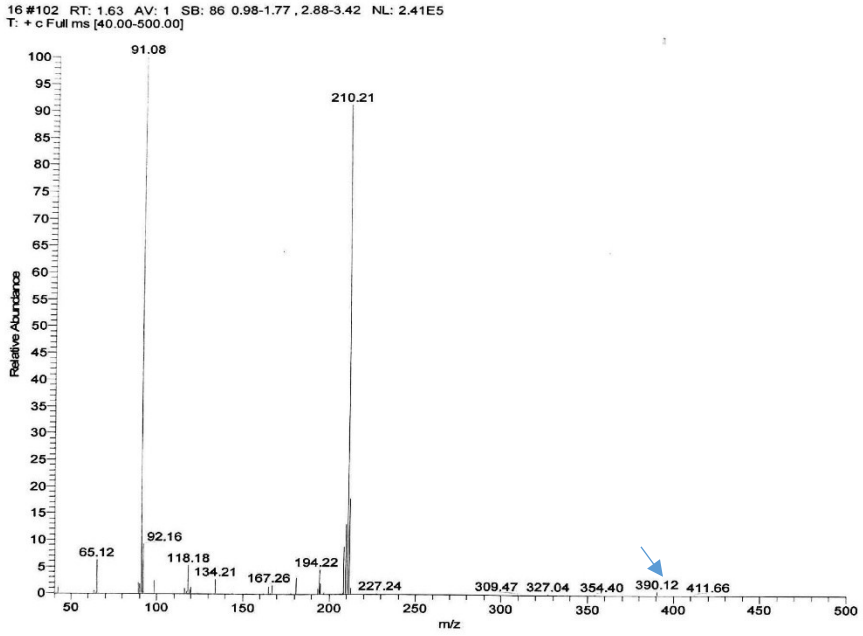
Entry 18



$C_{23}H_{20}BrN$

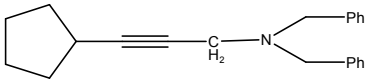
Dibenzyl-[3-(4-bromophenyl-2-propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): *δ* 7.51-7.49 (d, 2H), *δ* 7.38-7.36 (m, 2H), *δ* 7.35-7.33 (m, 4H), *δ* 7.29-7.26 (m, 6H), *δ* 3.63 (s, 4H), *δ* 3.16 (s, 2H). **^{13}C-NMR:** *δ* 139.91, *δ* 133.52, *δ* 131.76, *δ* 129.03, *δ* 128.21, *δ* 126.78, *δ* 123.18, *δ* 121,12, *δ* 82.61, *δ* 78.72, *δ* 65.88, *δ* 56.17. **EI-MS:** exact mass 389.09, found 390.12 (m/z +1).



Mass Spectrum of entry 18

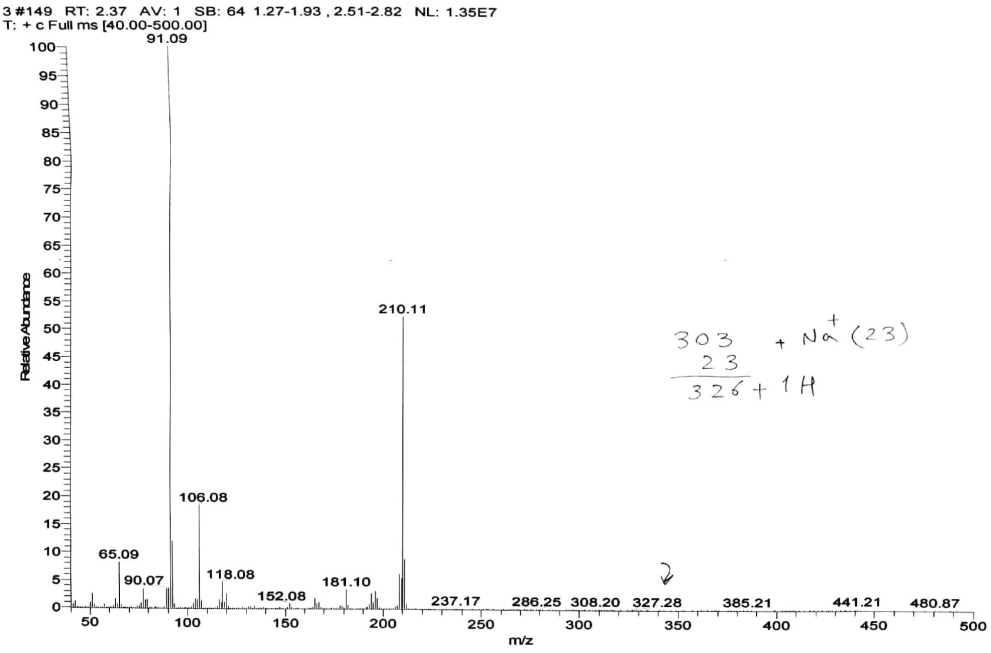
Entry 20



$C_{22}H_{25}NO$

Dibenzyl-(3-cyclopentyl-2-propynyl)amine

^{1}H-NMR (500 MHz, CDCl3, TMS): δ 7.42-7.39 (m, 4H), 7.36-7.33 (m, 2H), 7.29-7.26 (m, 4H), 3.67 (s, 4H), 3.16 (s, 2H), 2.69-2.65 (m, 1H), 1.74-1.68 (m, 4H), 1.27-1.25 (m, 4H). **^{13}C-NMR:** δ 140.03, 129.11, 128.07, 126.77, 77.05, 72.54, 65.83, 56.17, 34.13, 29.99, 25.30. **EI-MS:** exact mass 303.20, found 327.28.



Mass Spectrum of entry 20

9. References

[1] S. Sen, N.N. Nair, T. Yamada, H. Kitagawa, P.K. Bharadwaj, J. Am. Chem. Soc. 134 (47) (2012) 19432-19437.

[2] Su, H.Plenio, Chem. Comm. (43) (2005) 5417-5419.

[3] C.I. Ezugwu, B. Mousavi, M.A. Asraf, Z. Luo, F. Verpoort, J. Catal. 344 (Supplement C) (2016) 445-454.