Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis and characterization of Cu(II) Schiff base complex immobilized on graphene oxide and its catalytic application in the green synthesis of propargylamines†

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Synthesis of Ligand (L):

The ligand (L) was synthesized by literature procedure.[1] initially 2-ethoxyaniline (1 mmol) was mixed with 2 mL $NaNO_2$ solution (1.2 mmol), then HCl (37%) was added until the pH reached 2. The mixture was stirred for 30 min. Salicylaldehyde (1 mmol) was dissolved in 5 mL of pH:12 buffer solution containing NaOH and Na_2CO_3 (1:2). The diazonium solution was added very slowly to the salicylaldehyde solution. While adding, the temperature was kept at 0–2^oC and the pH was kept at around 7–8. The dark orange product was filtered and dried under vacuum at 60^oC for 12 h.

Synthesis of Cu(II) Schiff base complex immobilized on graphene oxide (GO-Cu):

For the preparation of Cu(II) Schiff base complex immobilized on graphene oxide sheets, initially, we synthesized graphite oxide (GO) for a support material by using the modified Hummers method.[2] In first step, GO (1000 mg) was dispersed in 100 ml toluene by sonication for an hour and then it refluxed with 2.0 ml of APTMS under a nitrogen atmosphere for 24 hours. Black products of APTMS coated GO was filtered, washed with ethanol, and dried under vacuum at 50°C. In the next step, 100 mg of GO-APTMS dispersed in 100 ml of ethanol and was refluxed with 500 mg L under a nitrogen atmosphere for 6 h. In the final step, 100 mg of GO-APTMS-L was dispersed in 100 ml of ethanol and then mixed with 100 mg ethanolic solution of $Cu(OAc)_2.H_2O$ for 4 h. Then, the final product was washed with ethanol repetitively to remove the undigested content of $Cu(OAc)_2.H_2O$, dried in an vacuum oven at 50^oC for 12 h.

General procedure for synthesis of propargylamines:

The GO-Cu (20 mg) was added to a stirred solution of aldehydes (1 mmol), amines (1 mmol) and alkynes (1.2 mmol) in water (5 mL) under N_2 atmosphere. The reaction mixture was heated under reflux for specific time (8-12 h). After completion, the reaction mixture was cooled to room temperature and the GO-Cu catalyst removed by filtration. The filtrate was

treated with ethyl acetate (3x10 mL). The combined organic layers were treated with saturated brine solution and dried over anhydrous sodium sulphate. The removal of solvent yielded crude product, which after purification by column chromatography over silica gel (100-200 mesh), afforded the desired products.

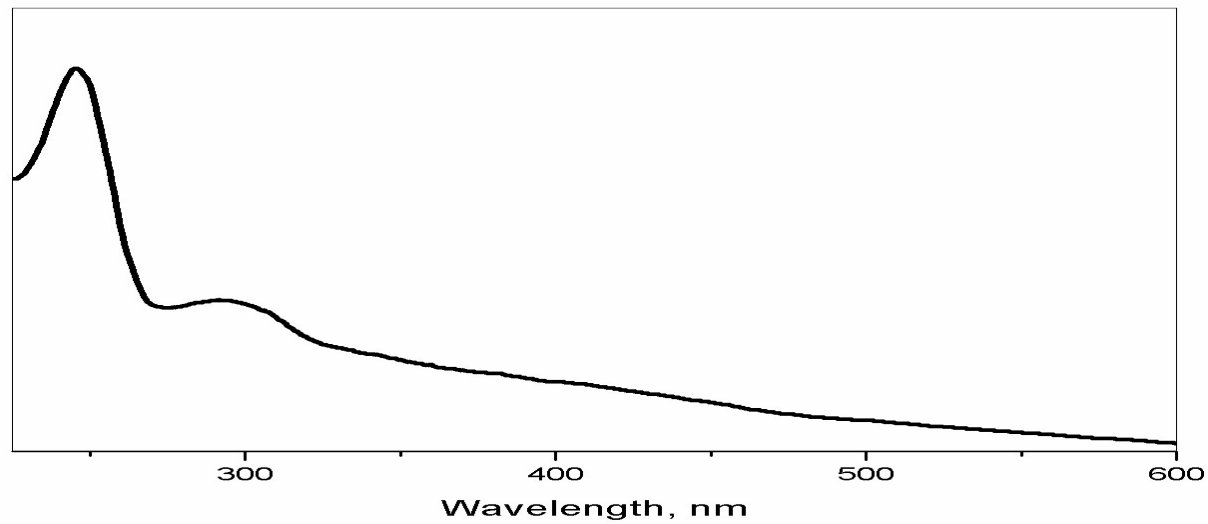


Figure S1. UV-visible spectrum of GO.

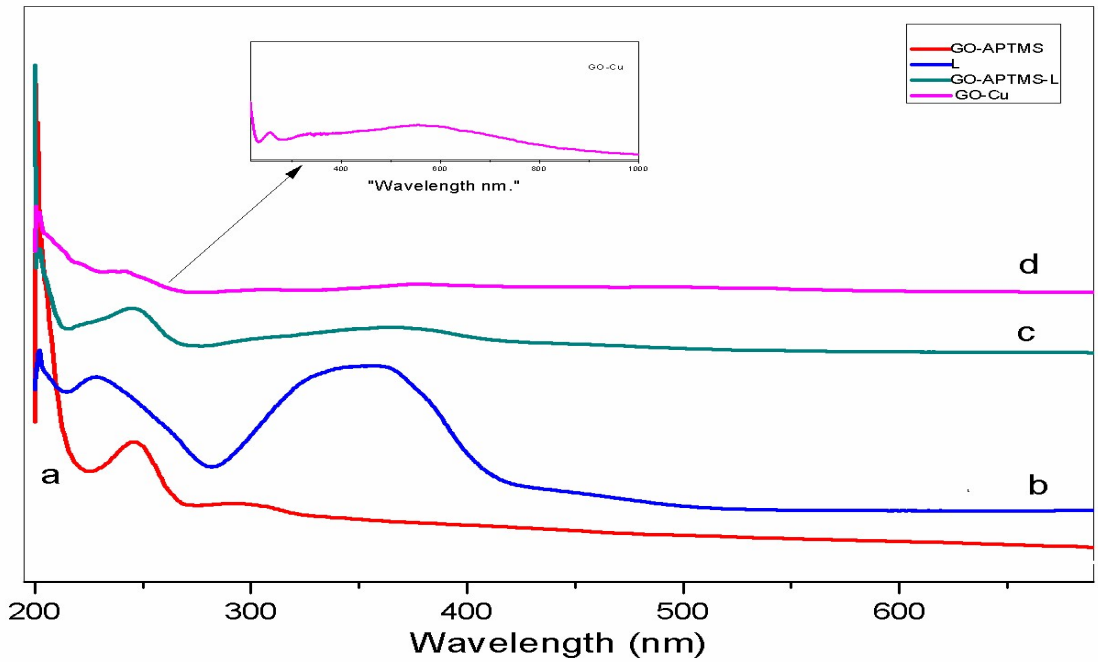


Figure S2. UV-visible spectra of GO- APTMS, L, GO-APTMS-L and GO-Cu.

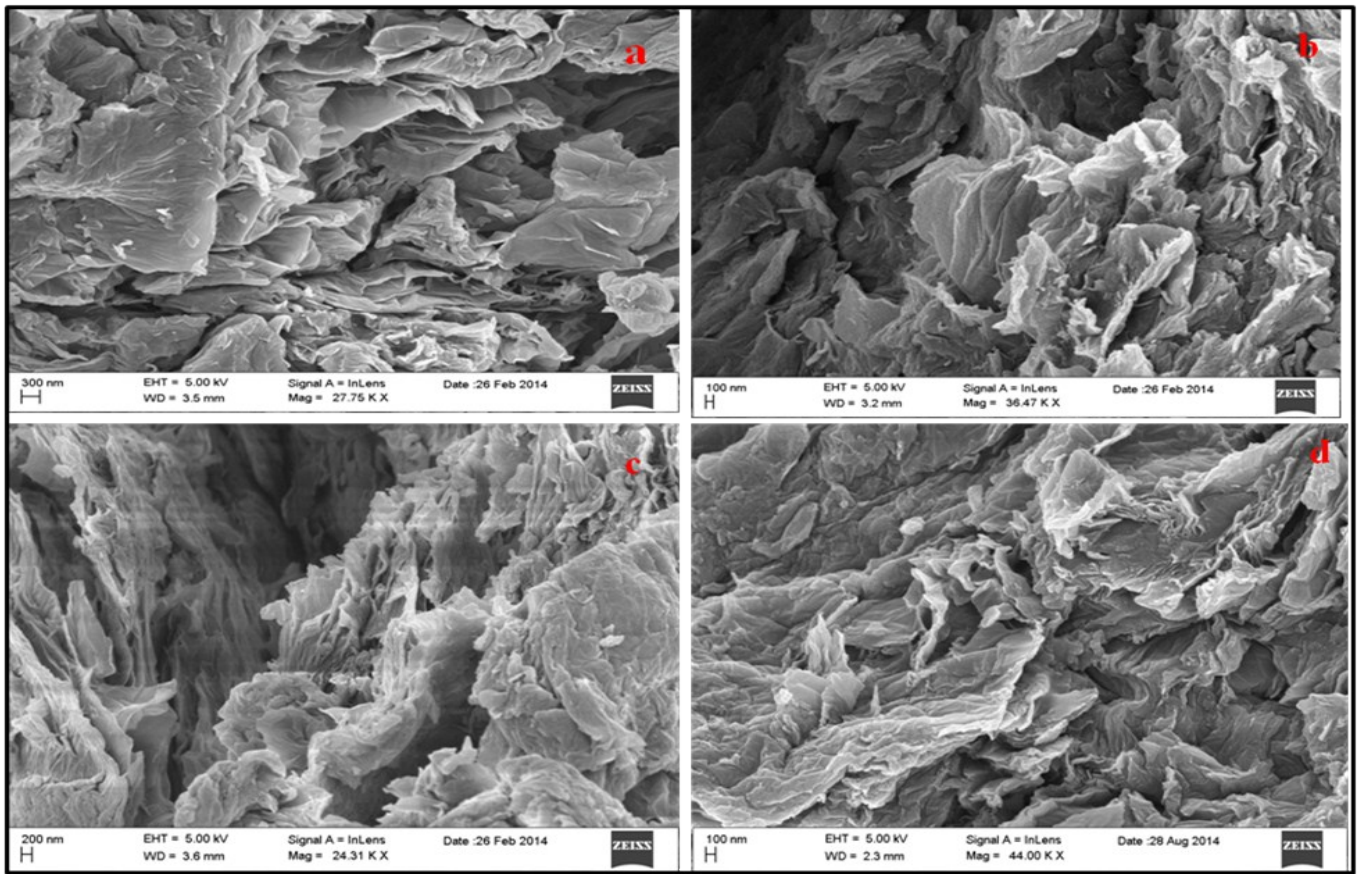


Figure S3. FEEM image of (a) GO (b) GO-APTMS (c) GO-APTMS-L and (d) GO-Cu.

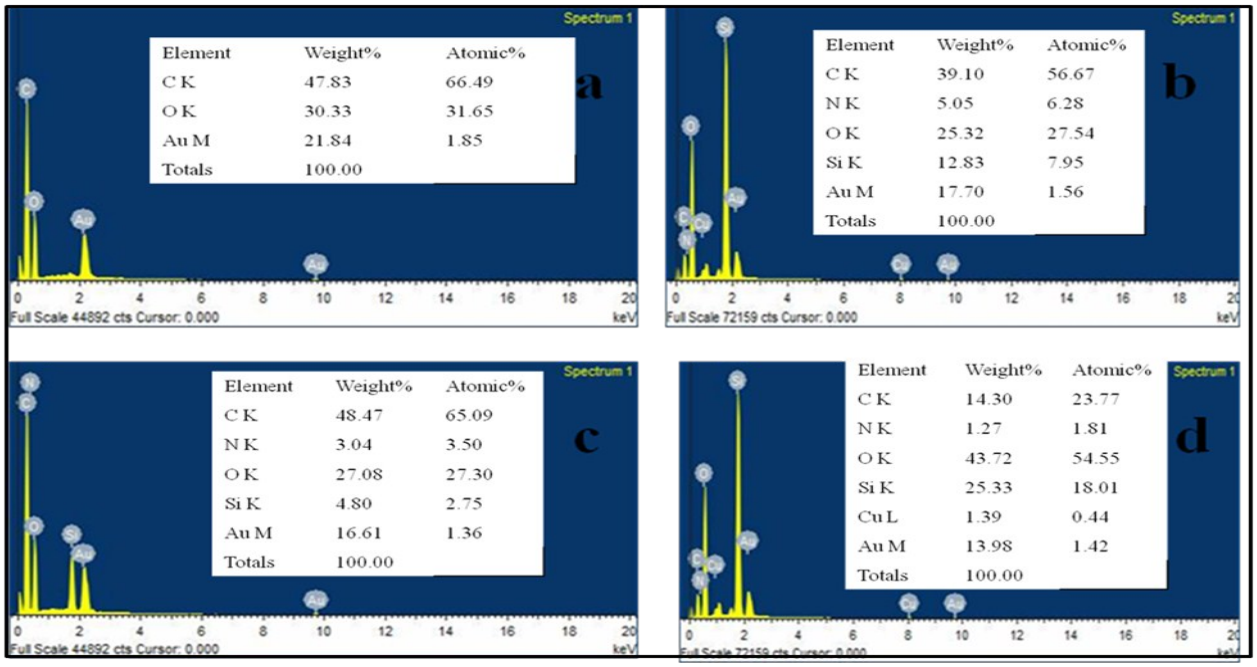


Figure S4. EDAX of (a) GO, (b) GO-APTMS, (c) GO-APTMS-L and (d) GO-Cu.

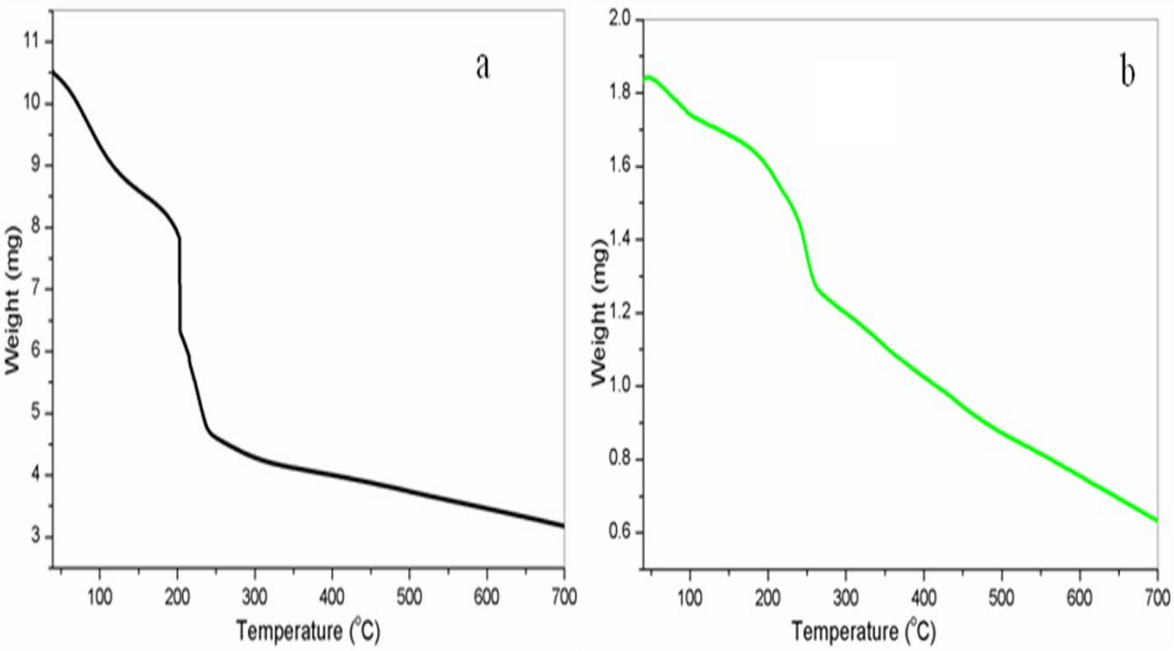


Figure S5. TGA thermograms of (a) GO and (b) GO-Cu.

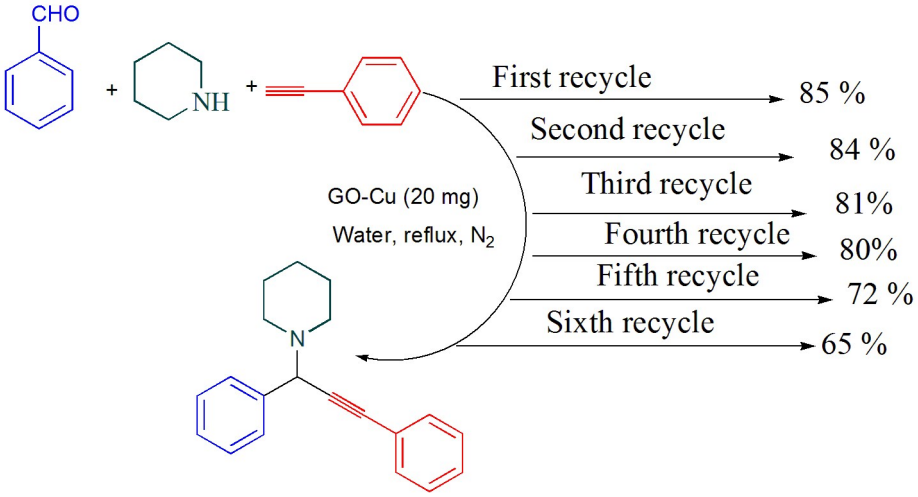
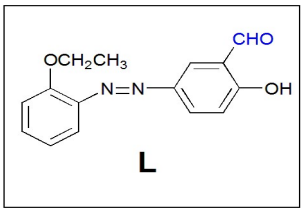
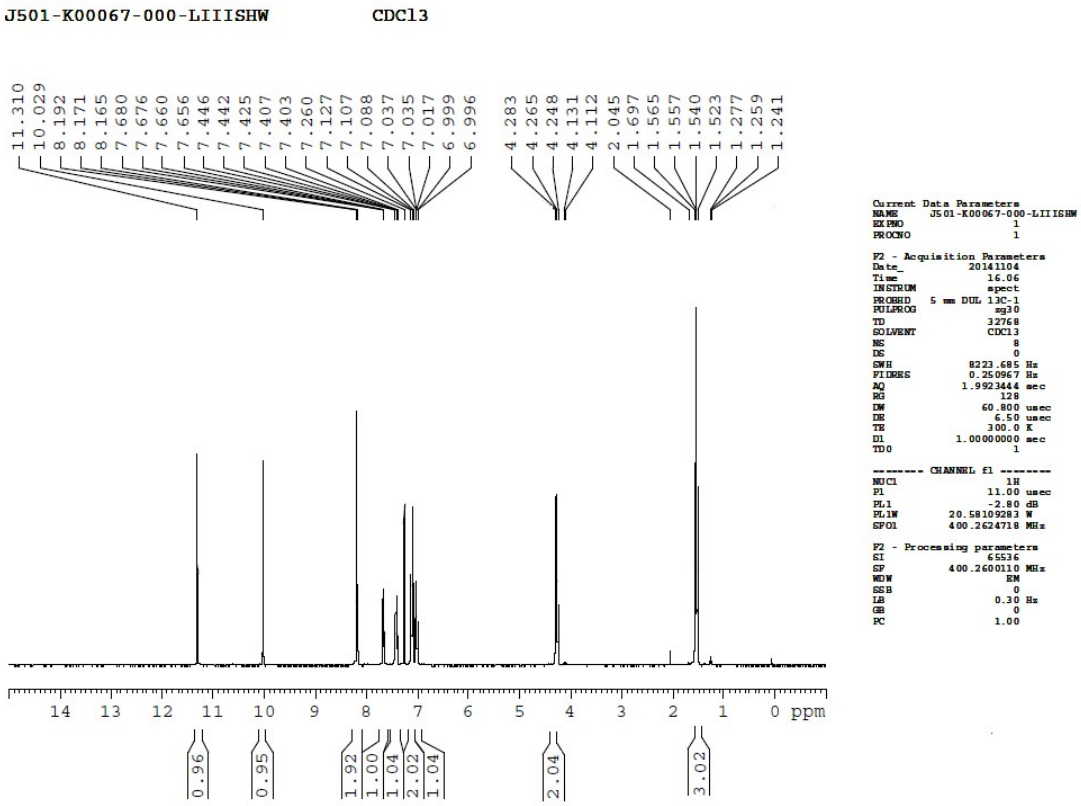


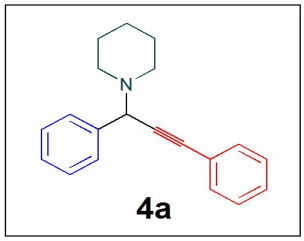
Figure S6. Recyclability of the catalyst.

Spectral data of synthesized Ligand and propargylamines:

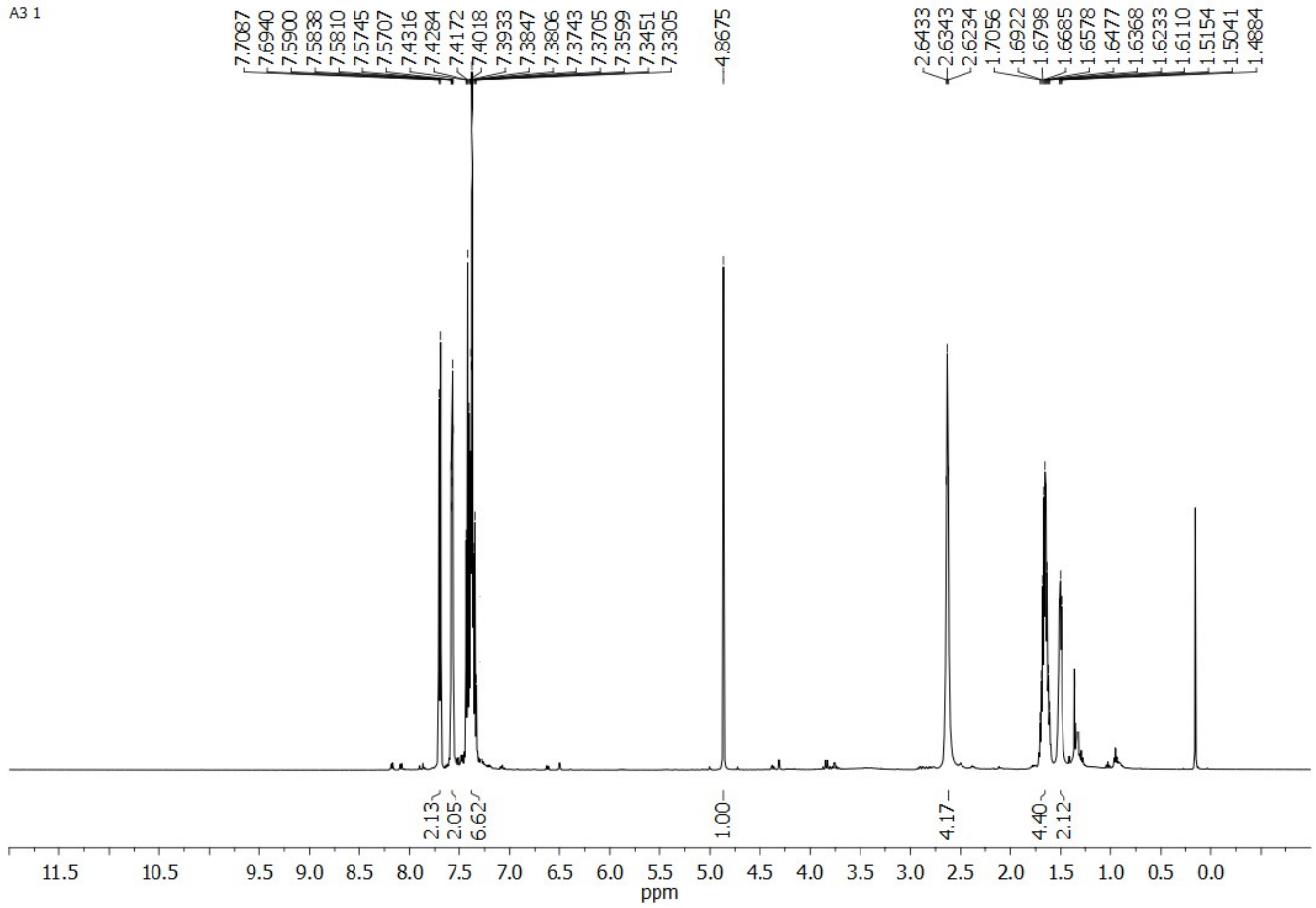


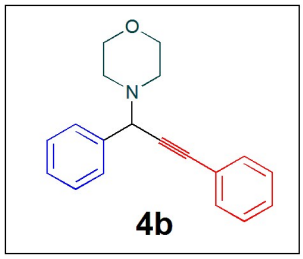
5-((2-ethoxyphenyl)diazenyl)-2-hydroxybenzaldehyde, Orange solid; FT-IR (m, cm^{-1}): 3538, 2969, 2942, 1650, 1485; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 11.31 (s, 1 H, -OH), δ 10.02 (s, 1 H, -CHO), δ 8.19-8.16 (d, 2H), δ 7.68-7.40 (d, 2H), δ 7.26-7.01 (t, 2H) δ 6.99 (s, 1H), δ 4.28-4.11 (m, 2H), δ 1.69-1.24 (m, 3H).



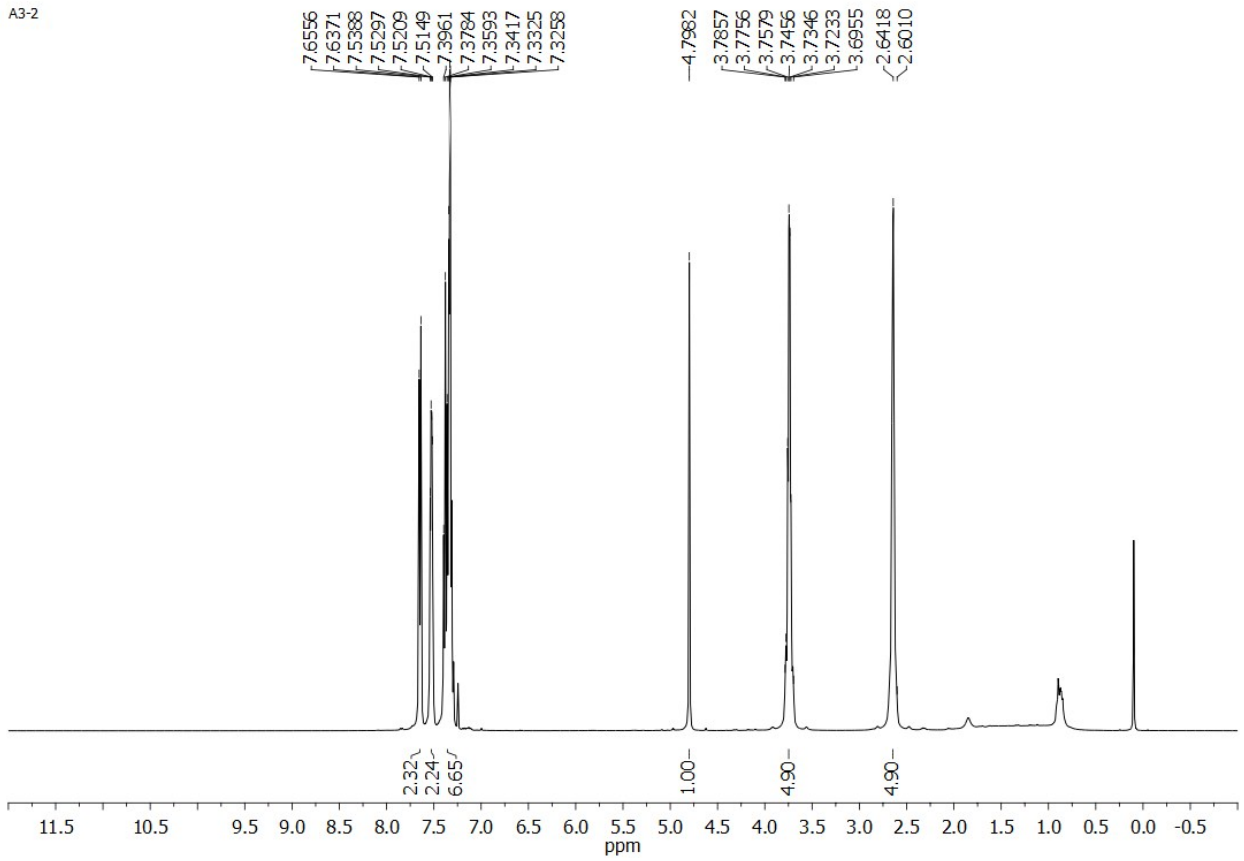


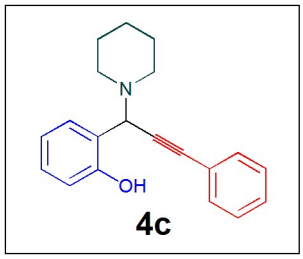
1-(1,3-diphenylprop-2-ynyl)piperidine, FT-IR (m, cm^{-1}): 3045, 2981, 1611, 1520, 1432, 1320, 1162; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.70-7.69 (m,-Ar 2H), δ 7.59-7.57 (m,-Ar 2H), δ 7.43-7.33 (m,-Ar 6H), δ 4.86 (s, -CH, 1H), δ 2.64-2.62 (t, 4H), δ 1.70-1.61 (m, 4H), δ 1.51-1.1.48 (m, 2H).



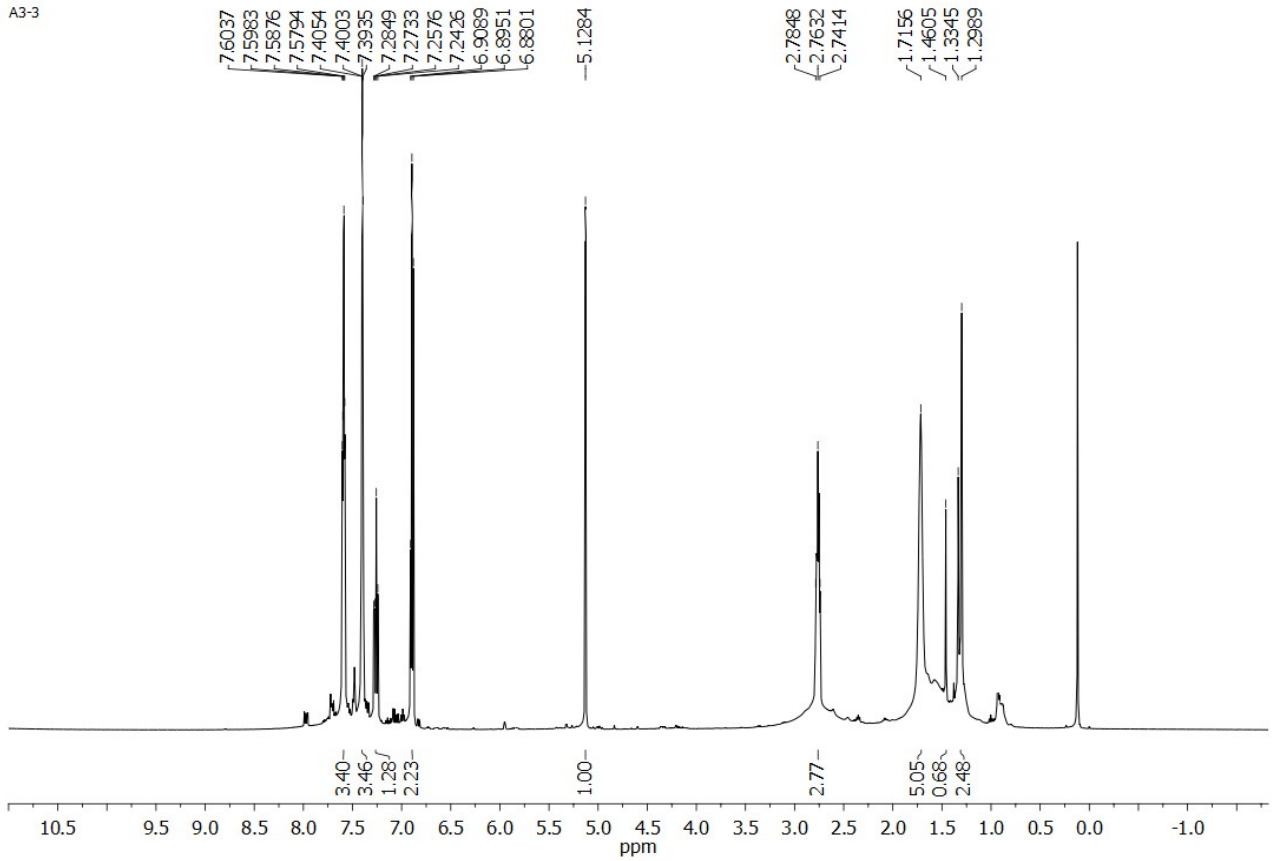


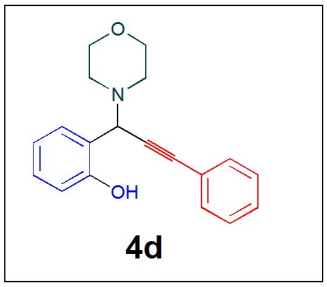
4-(1,3-diphenylprop-2-ynyl)morpholine, Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.70-7.69 (m, 2H), δ 7.59-7.57 (m, 2H), δ 7.43-7.33 (m, 6H), δ 4.86 (s, 1H), δ 3.72-3.75 (t, 4H), δ 2.62-2.65 (t, 4H).



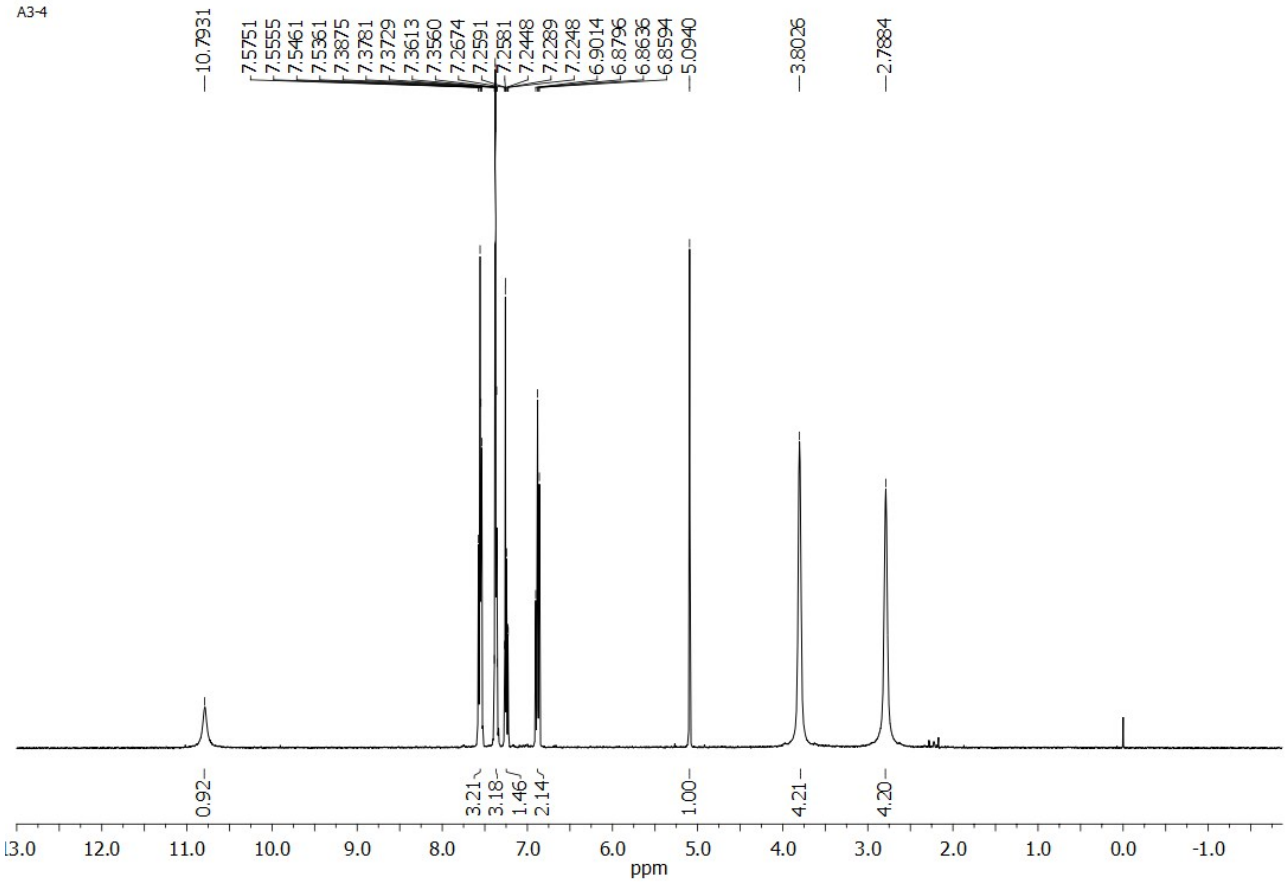


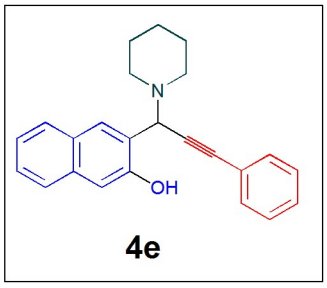
2-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenol.



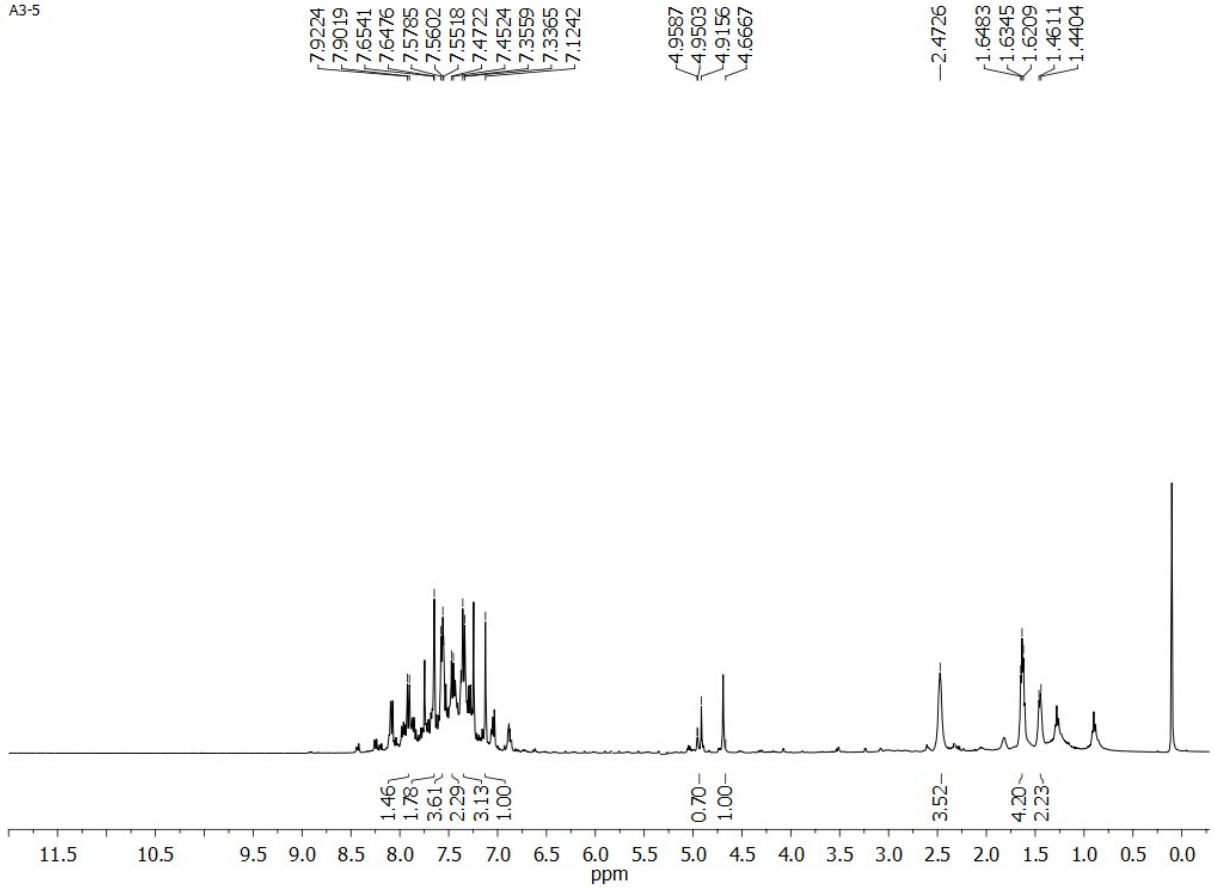


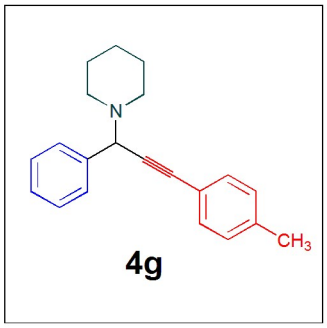
2-(1-morpholino-3-phenylprop-2-ynyl)phenol.



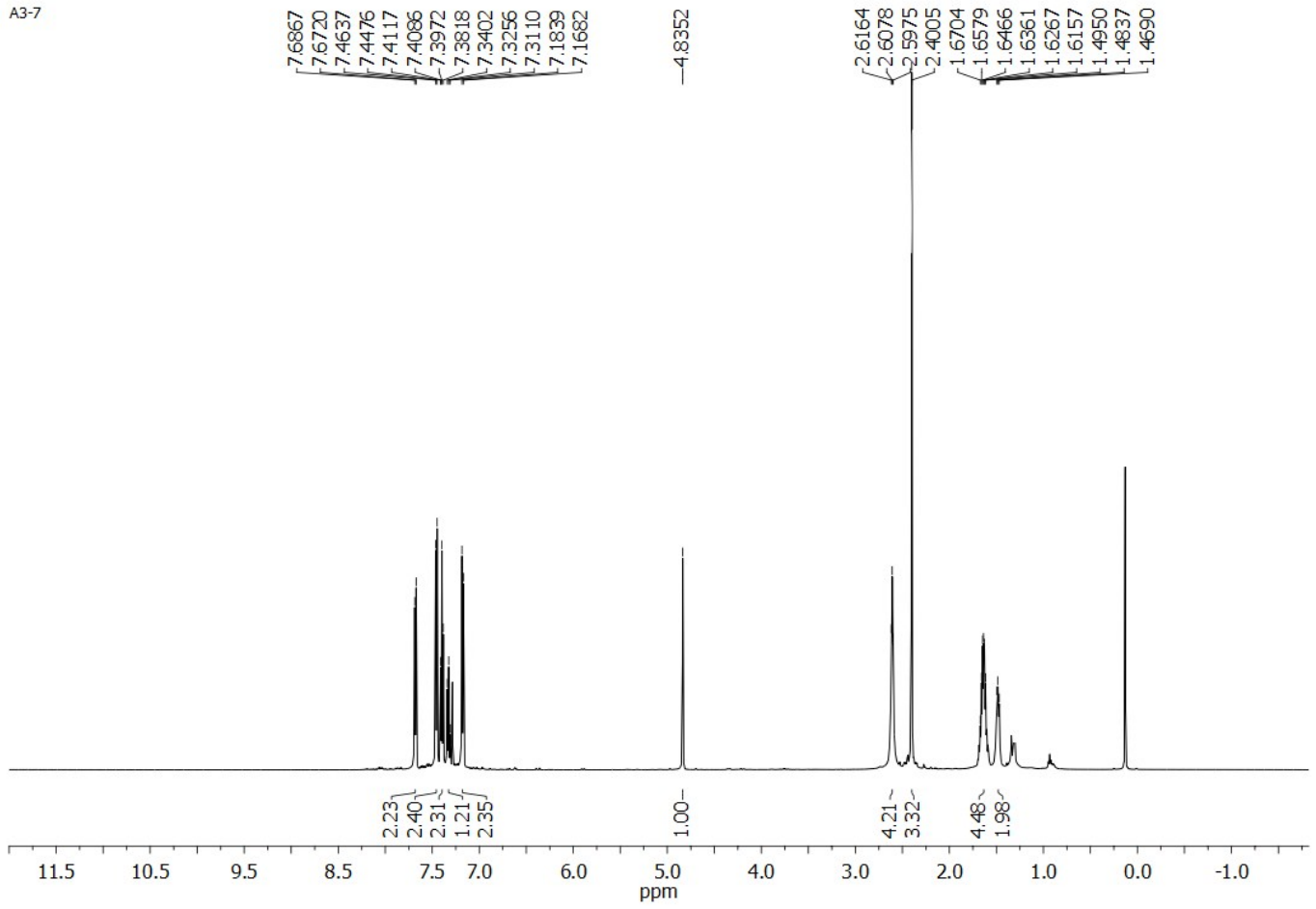


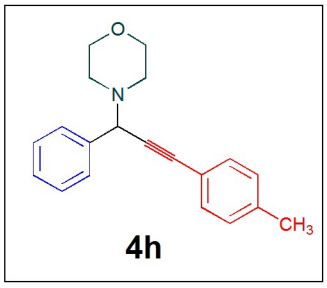
3-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)naphthalen-2-ol.



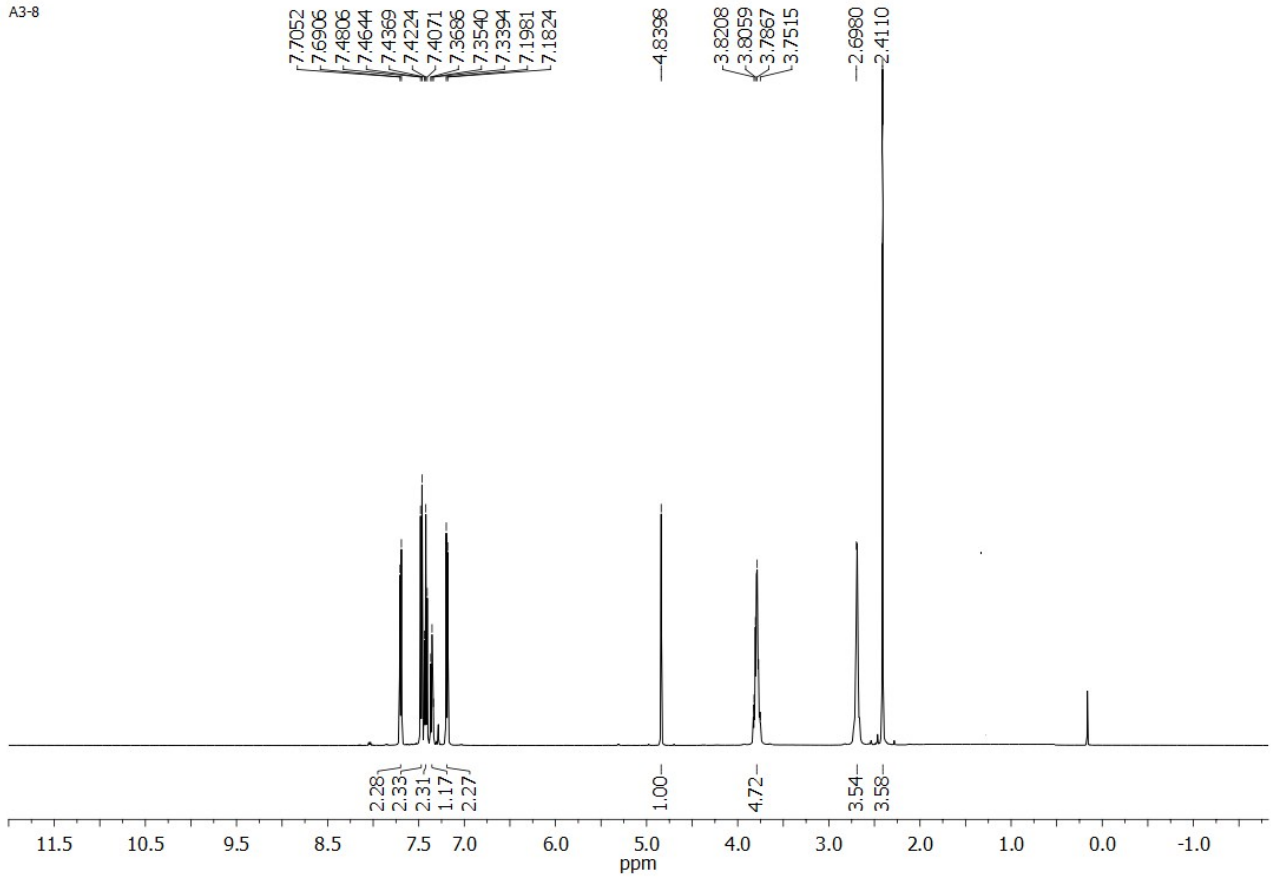


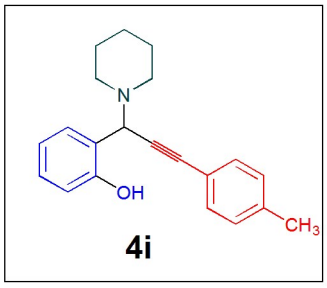
1-(1-phenyl-3-p-tolylprop-2-ynyl)piperidine.



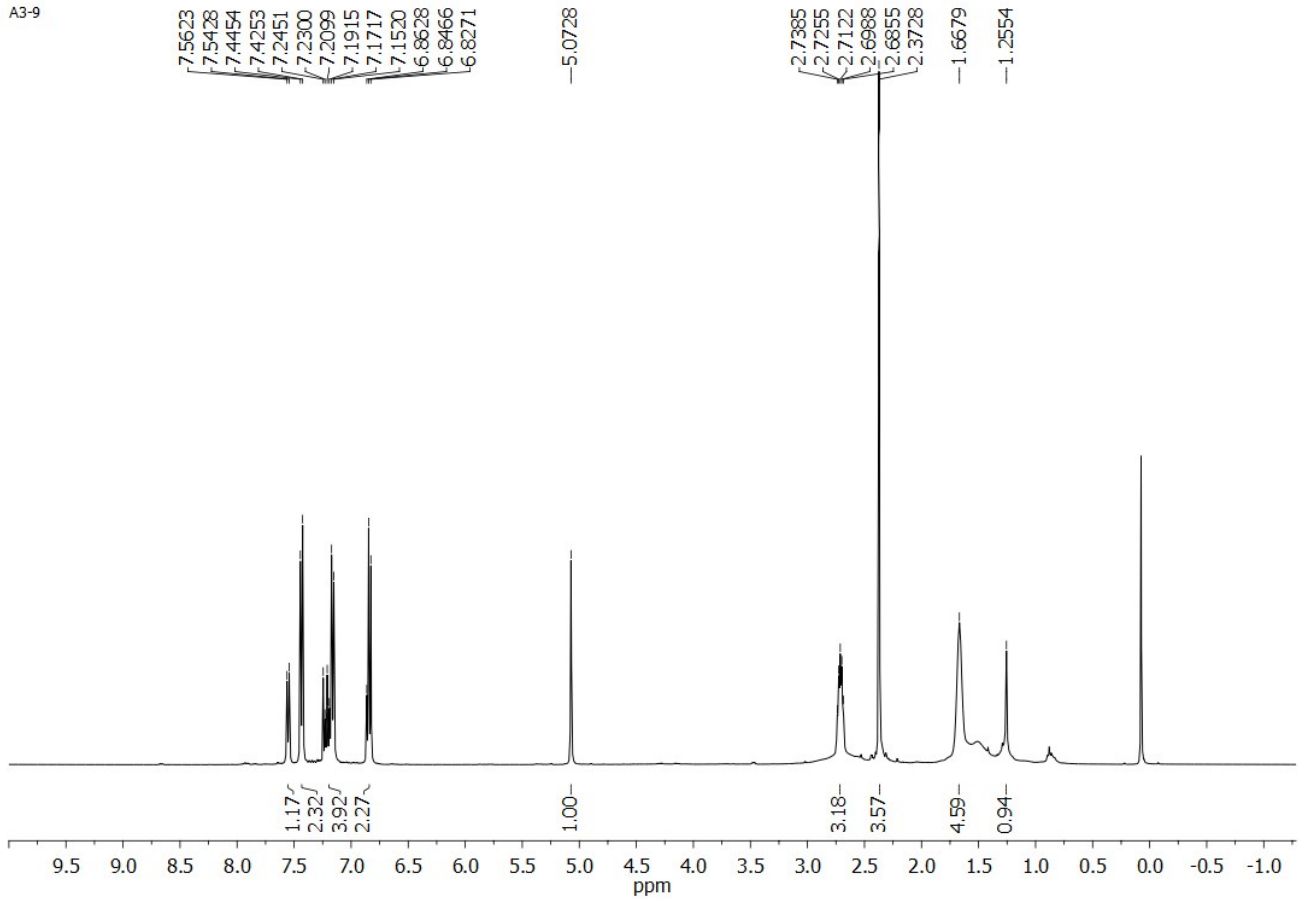


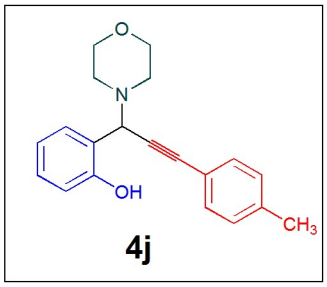
4-(1-phenyl-3-p-tolylprop-2-ynyl)morpholine.





2-(1-(piperidin-1-yl)-3-p-tolylprop-2-ynyl)phenol.





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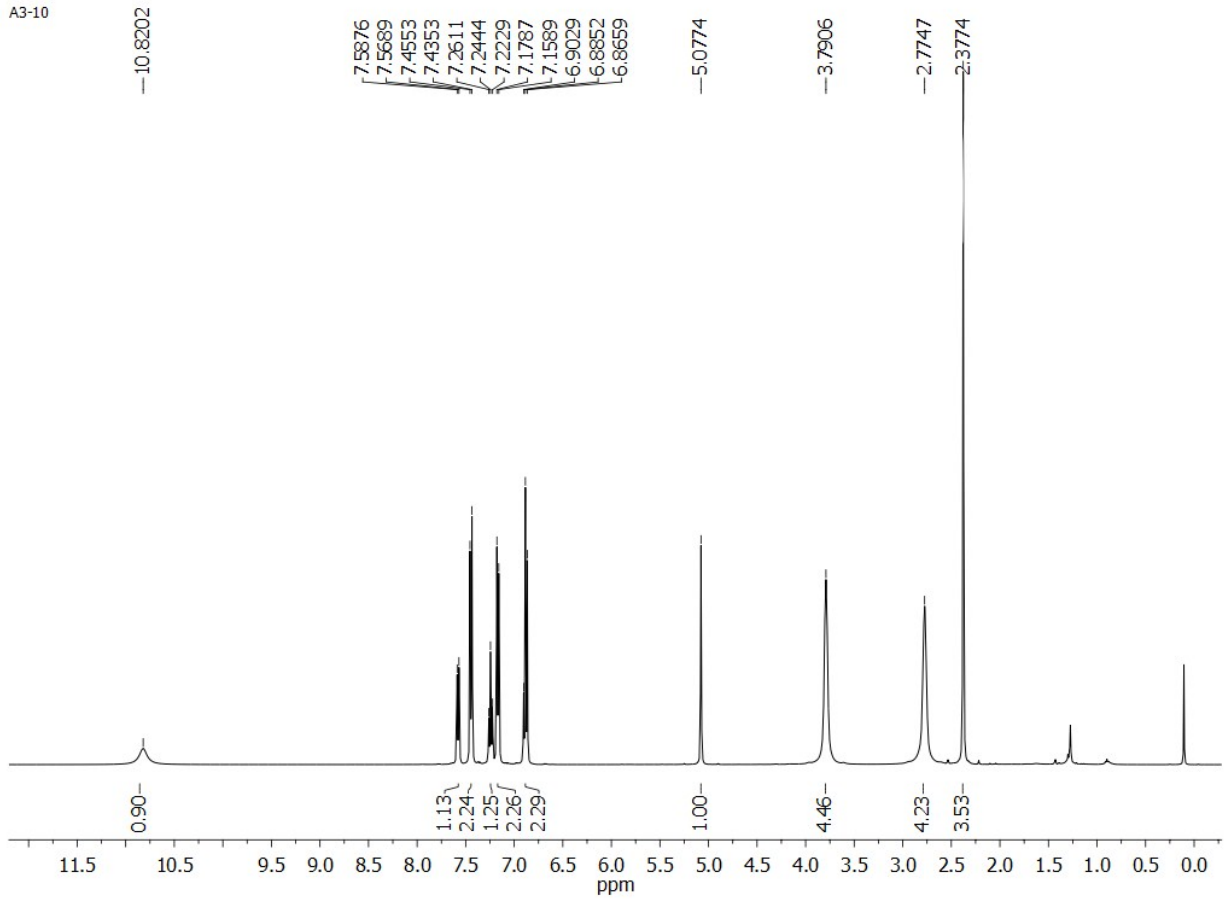
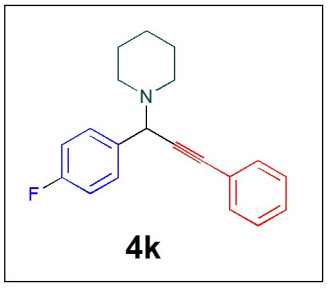
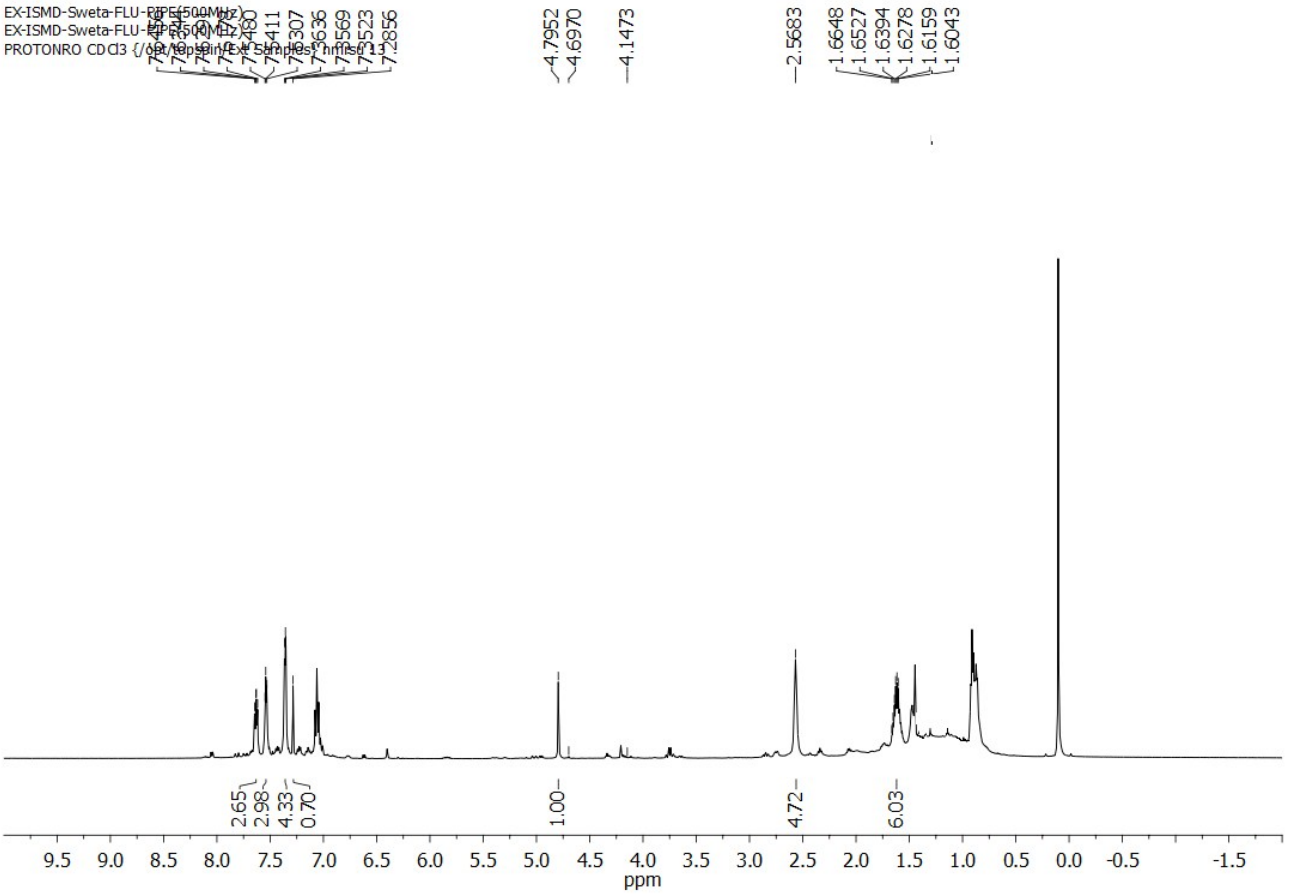
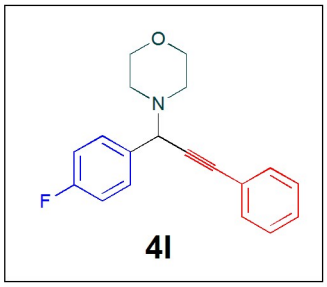
2-(1-morpholino-3-p-tolylprop-2-ynyl)phenol, Yellow oily liquid.



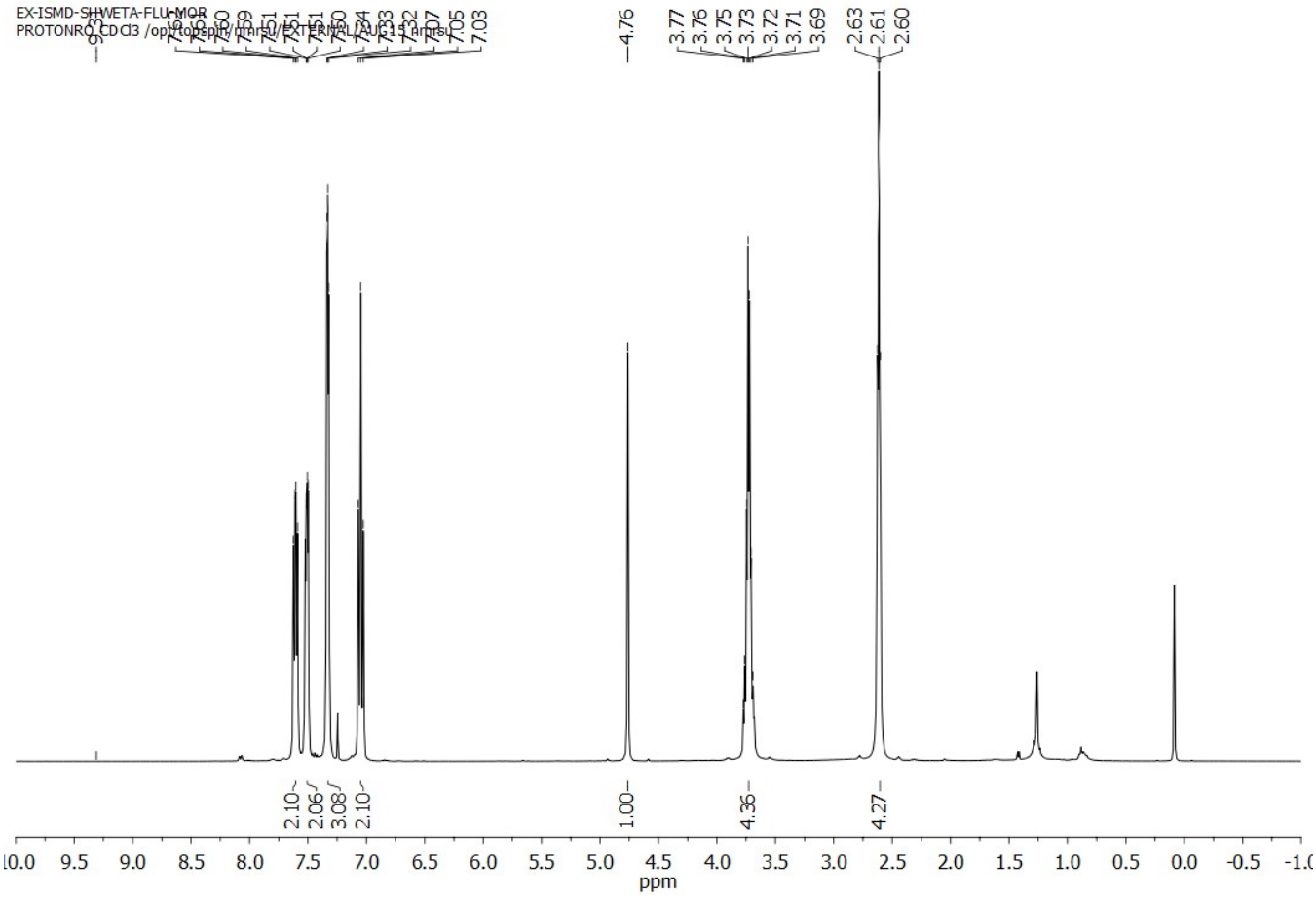


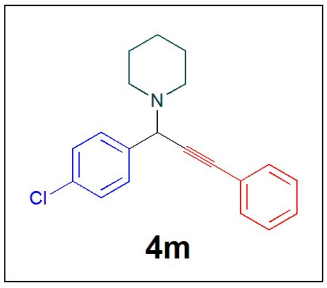
1-(1-(4-fluorophenyl)-3-phenylprop-2-ynyl)piperidine.





4-(1-(4-fluorophenyl)-3-phenylprop-2-ynyl)morpholine.





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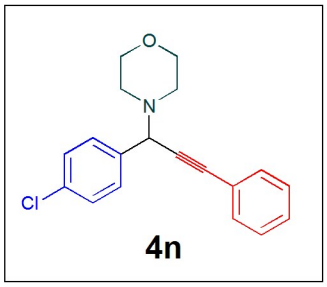

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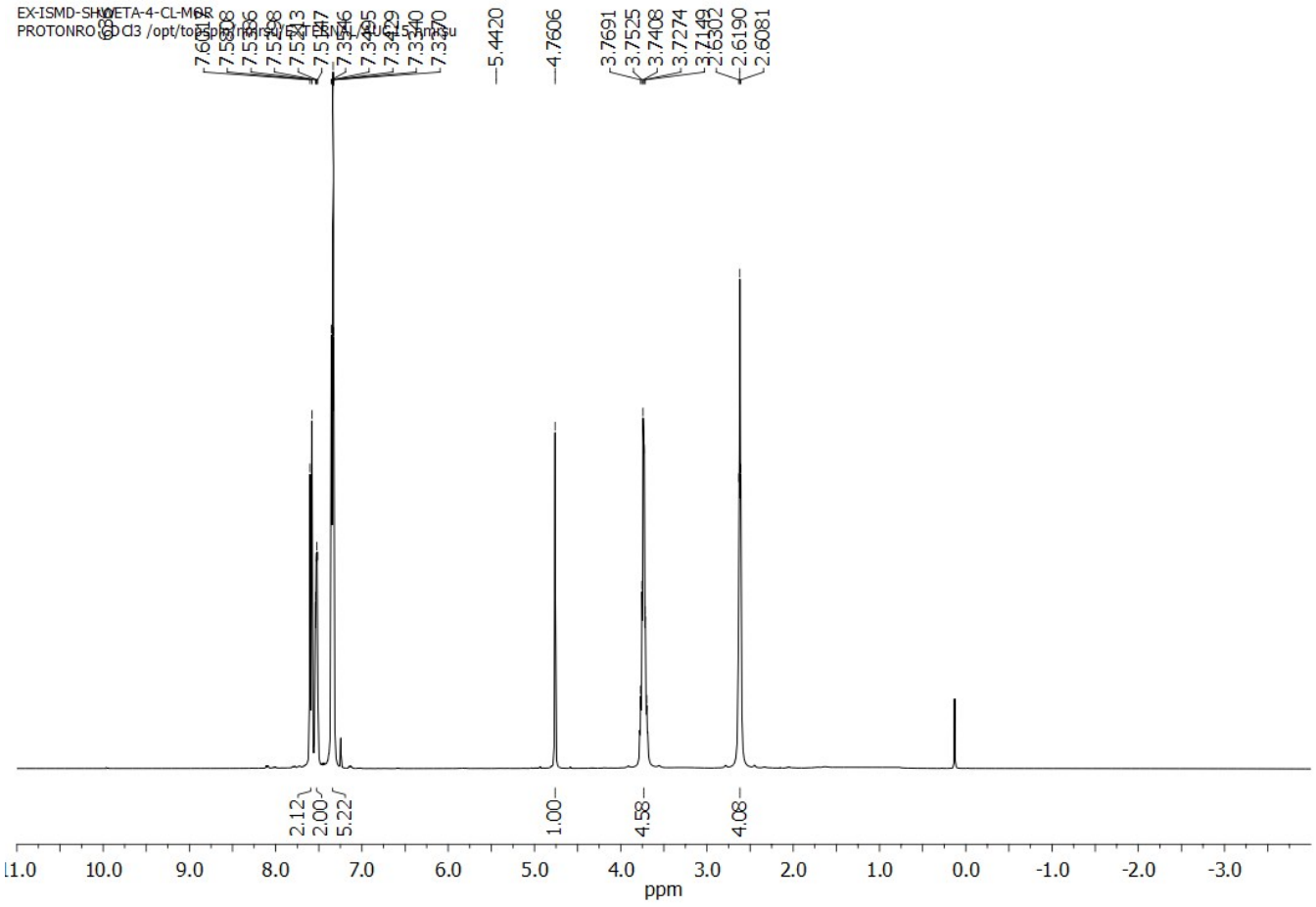
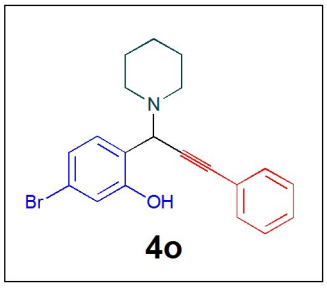
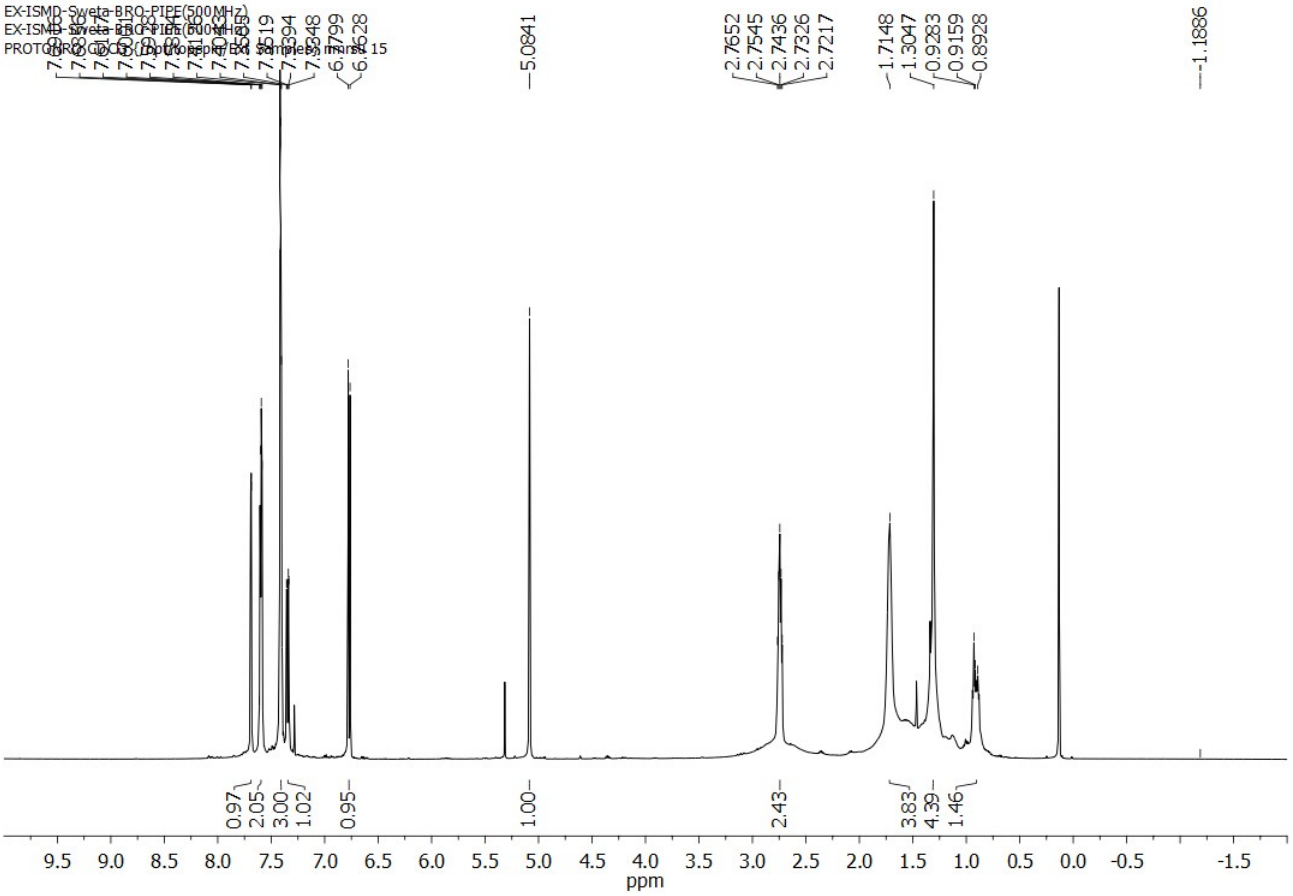
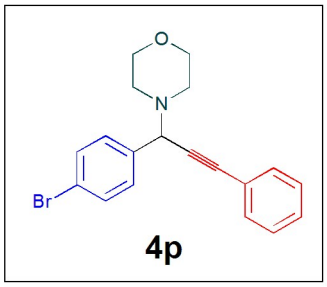




5-bromo-2-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenol.





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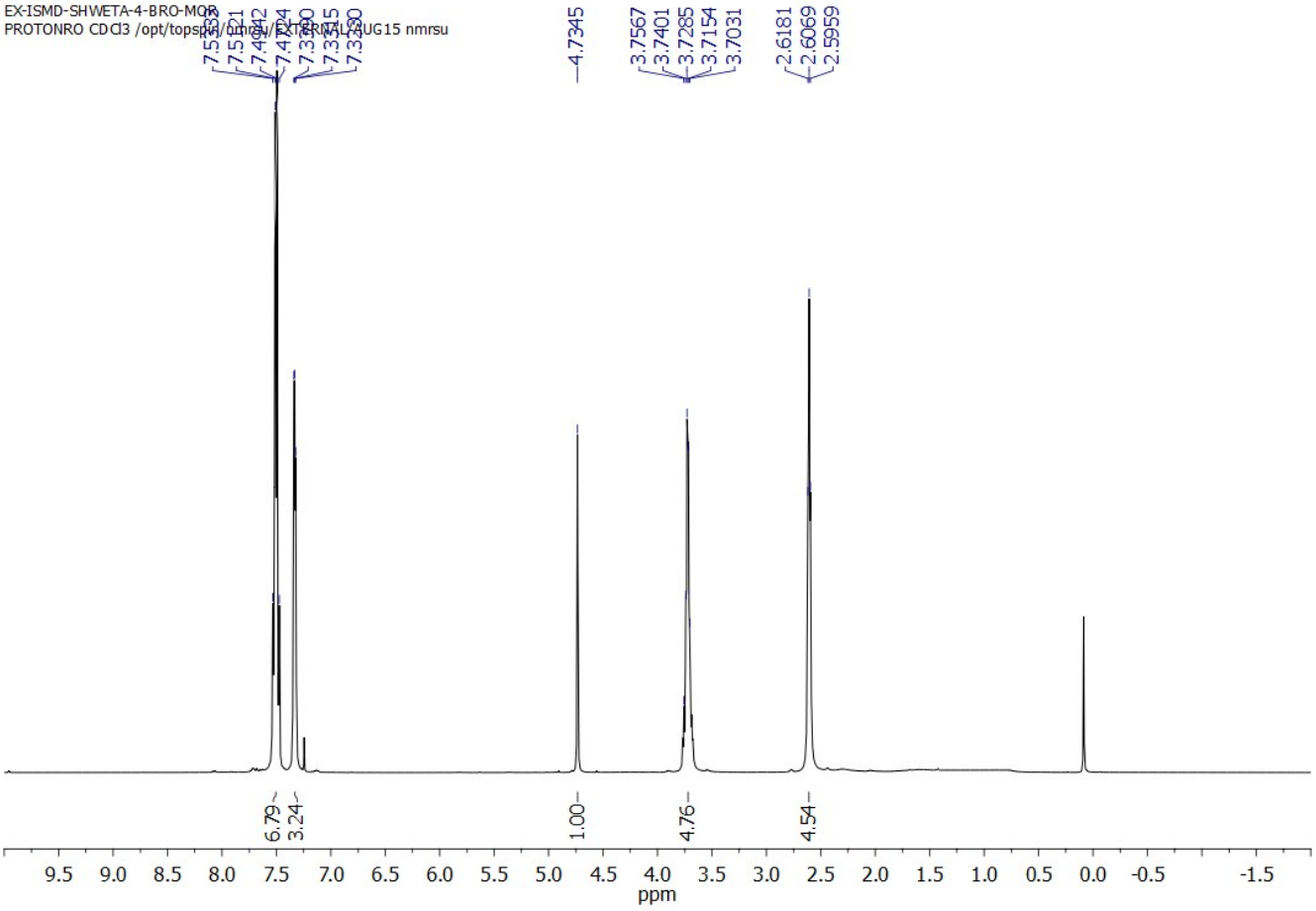
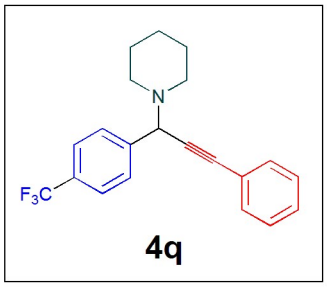
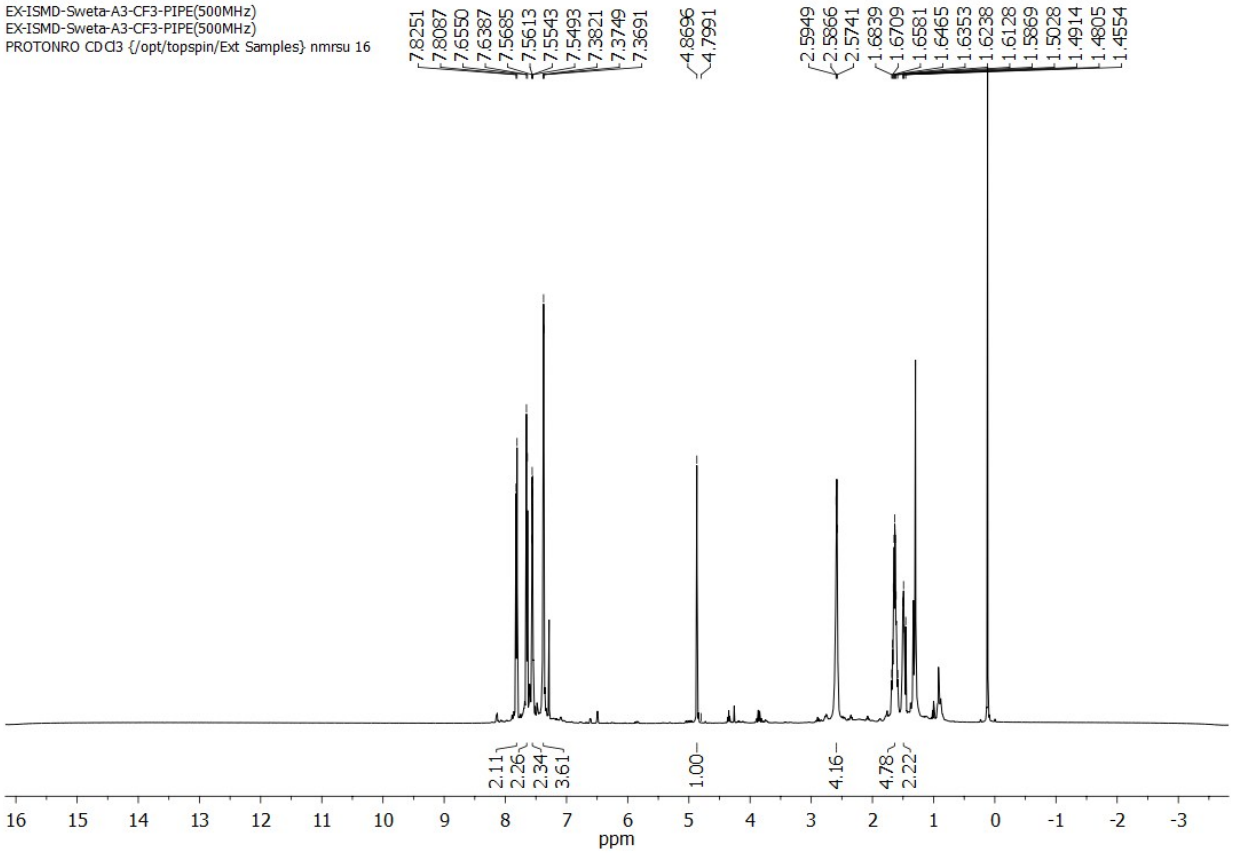
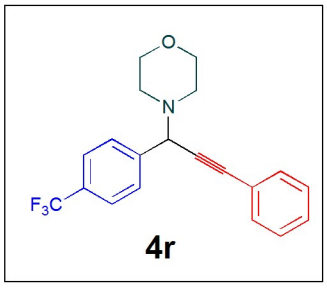


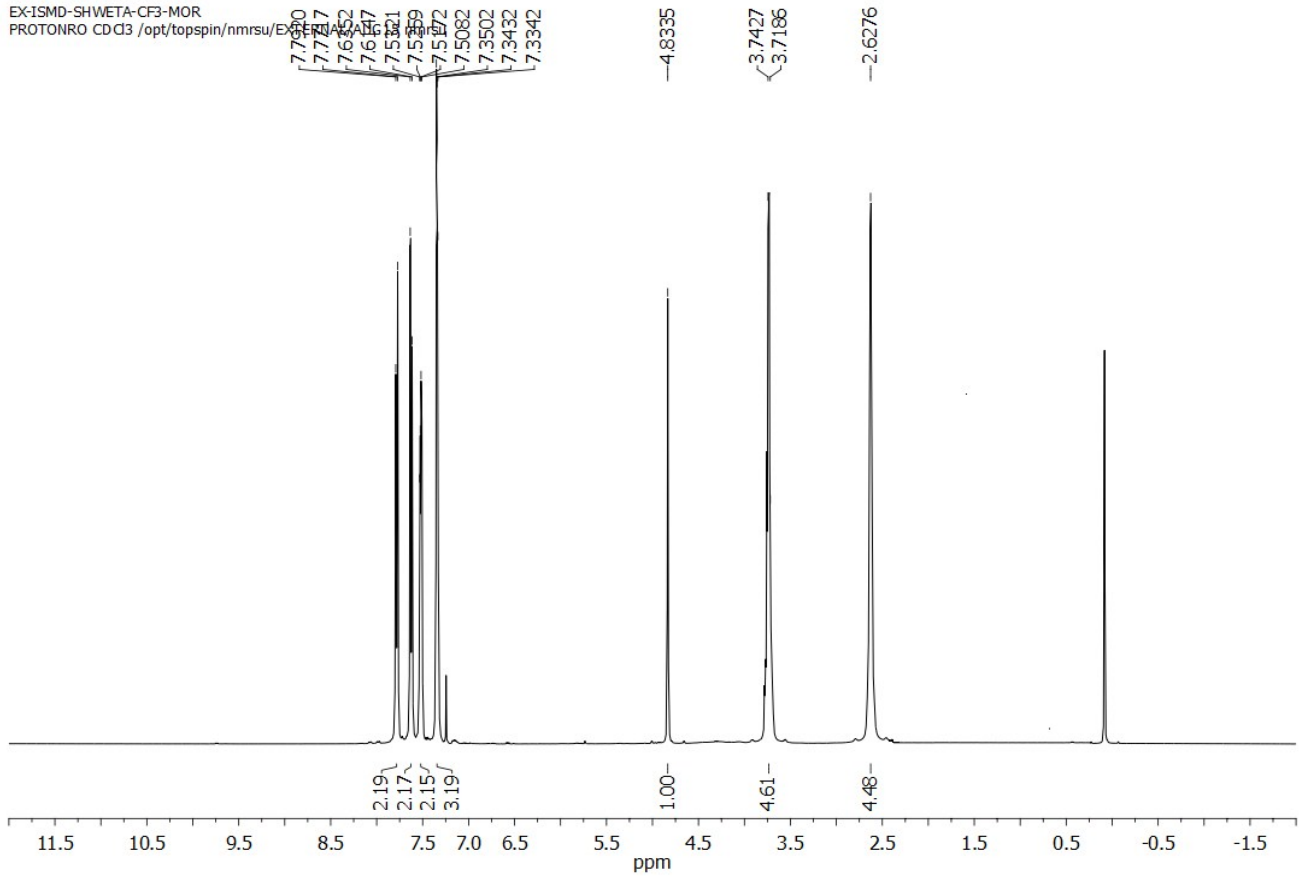


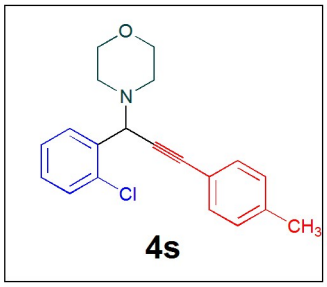
1-(3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-ynyl)piperidine.



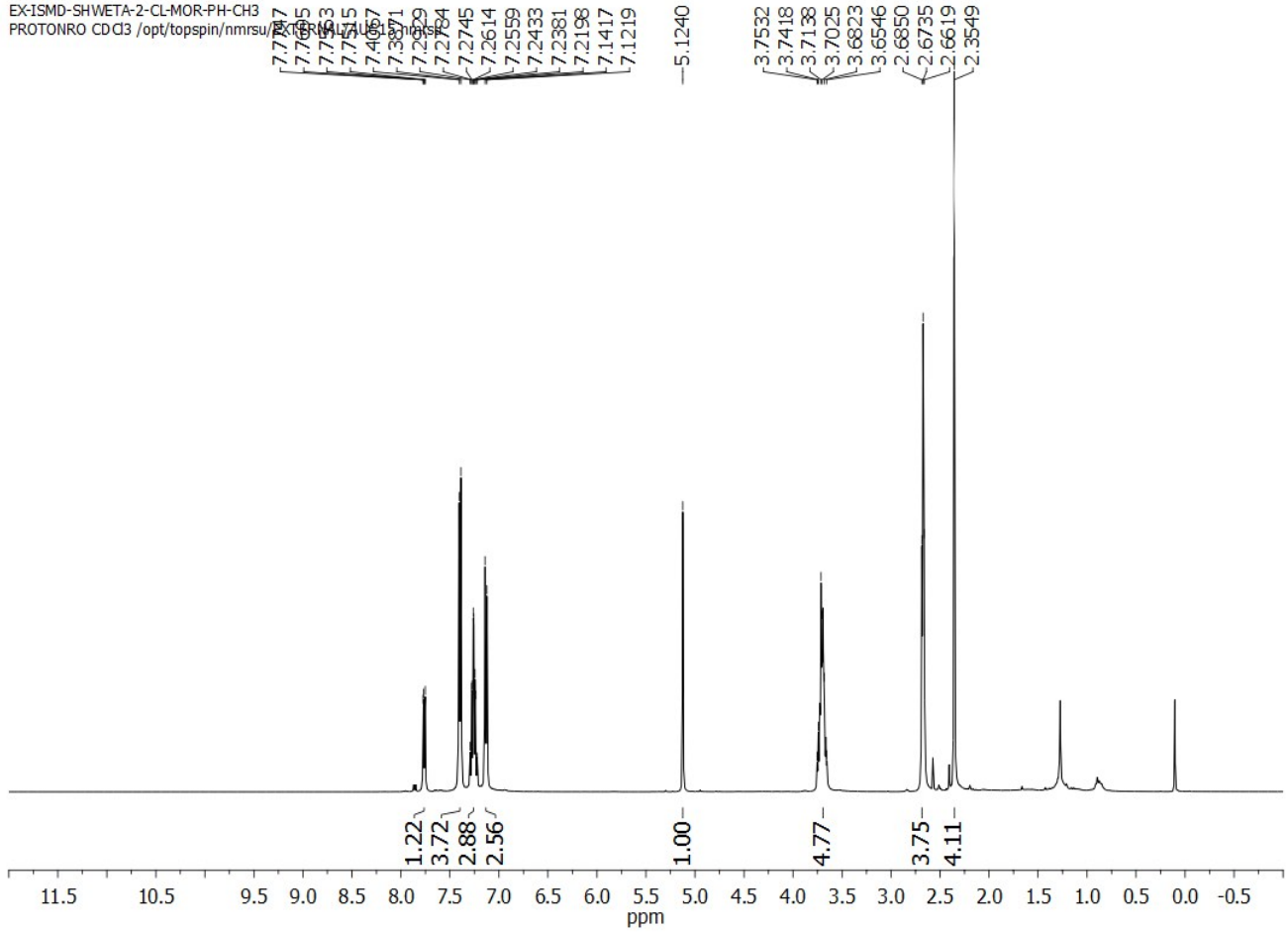


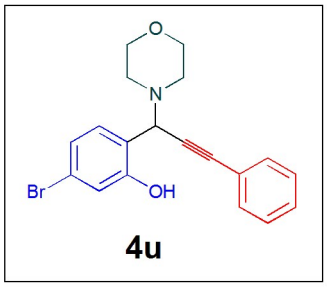
4-(3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-ynyl)morpholine.



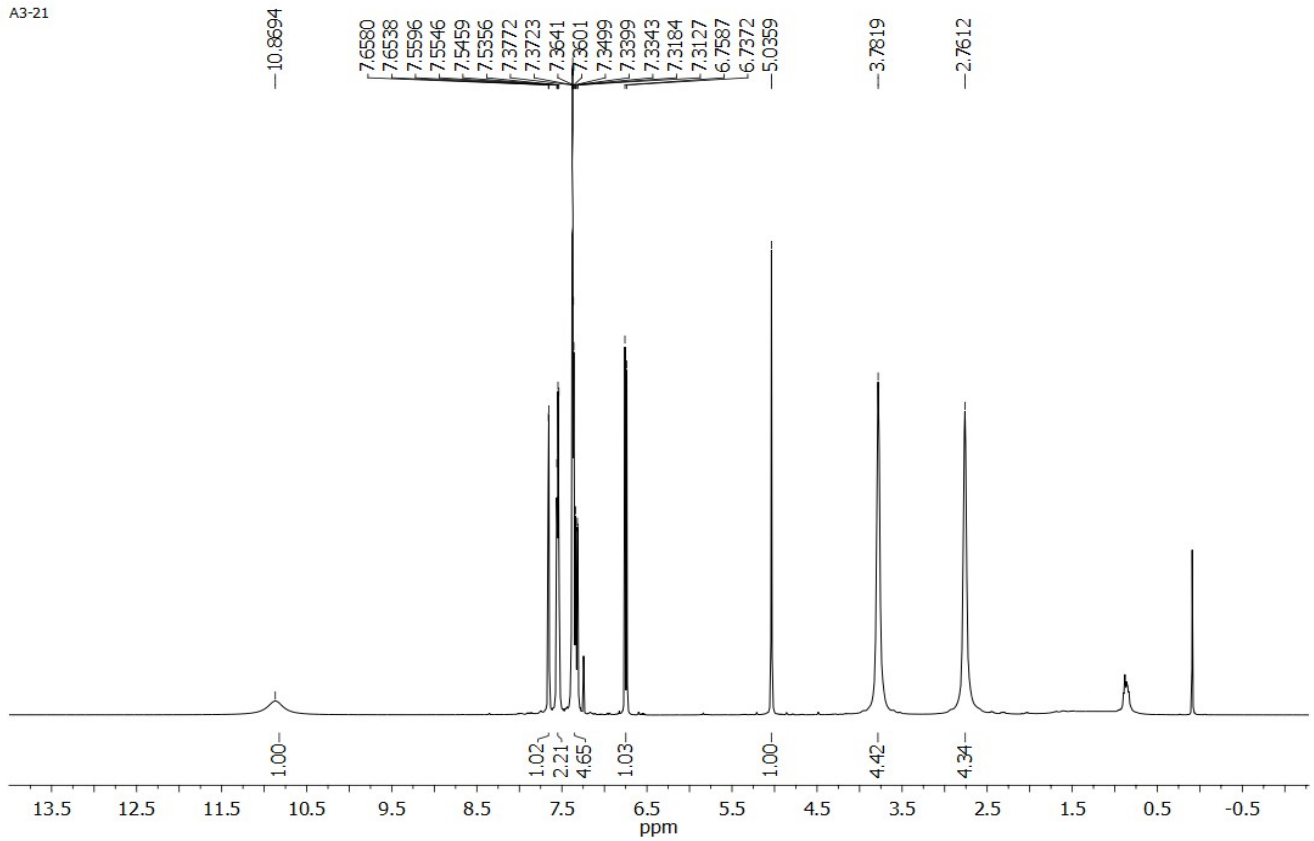


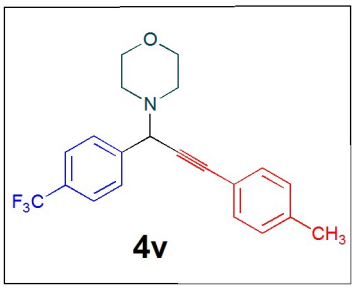
4-(1-(2-chlorophenyl)-3-p-tolylprop-2-ynyl)morpholine.



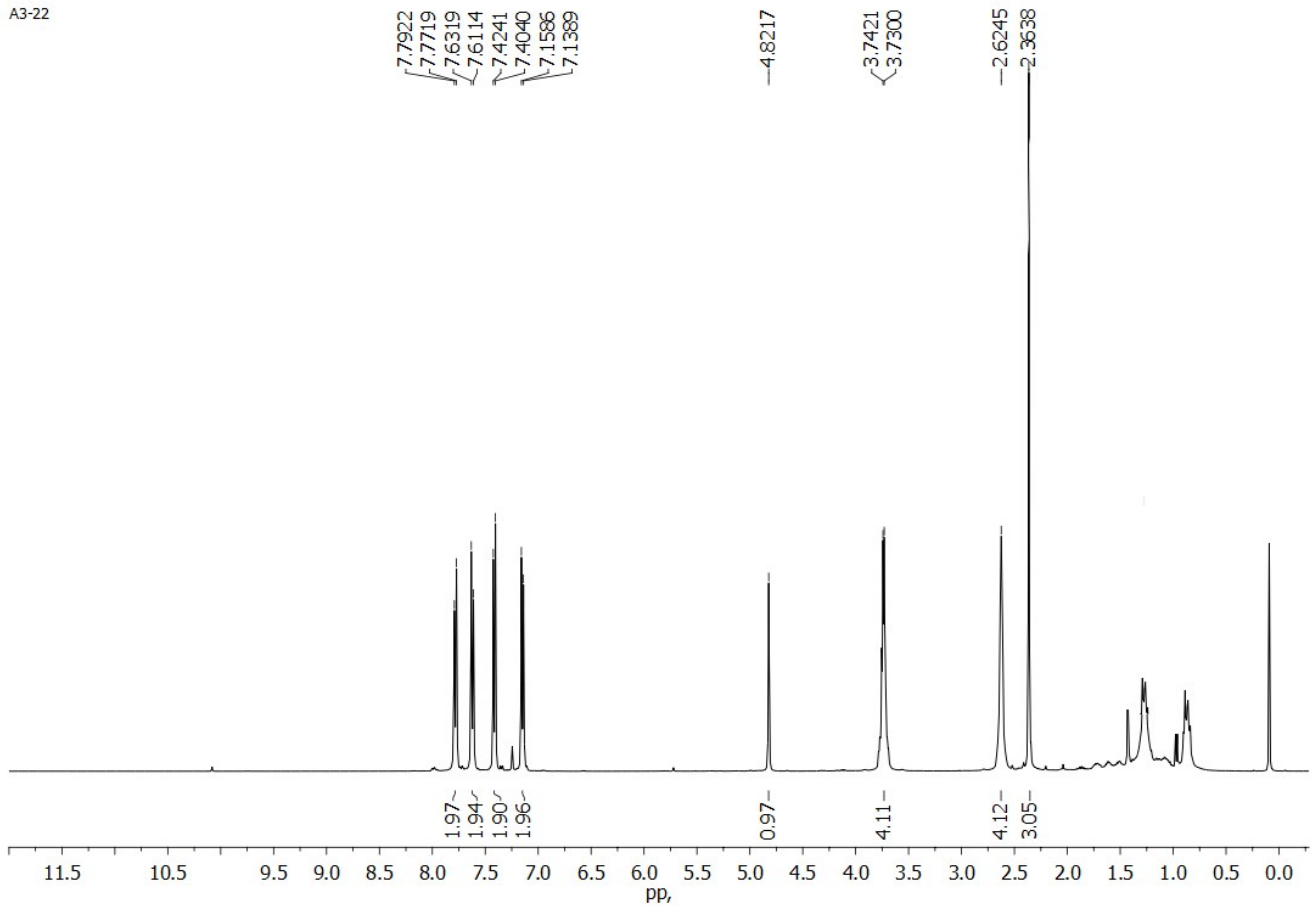


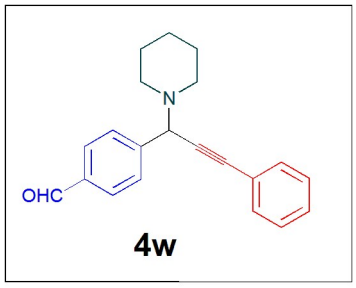
5-bromo-2-(1-morpholino-3-phenylprop-2-ynyl)phenol.



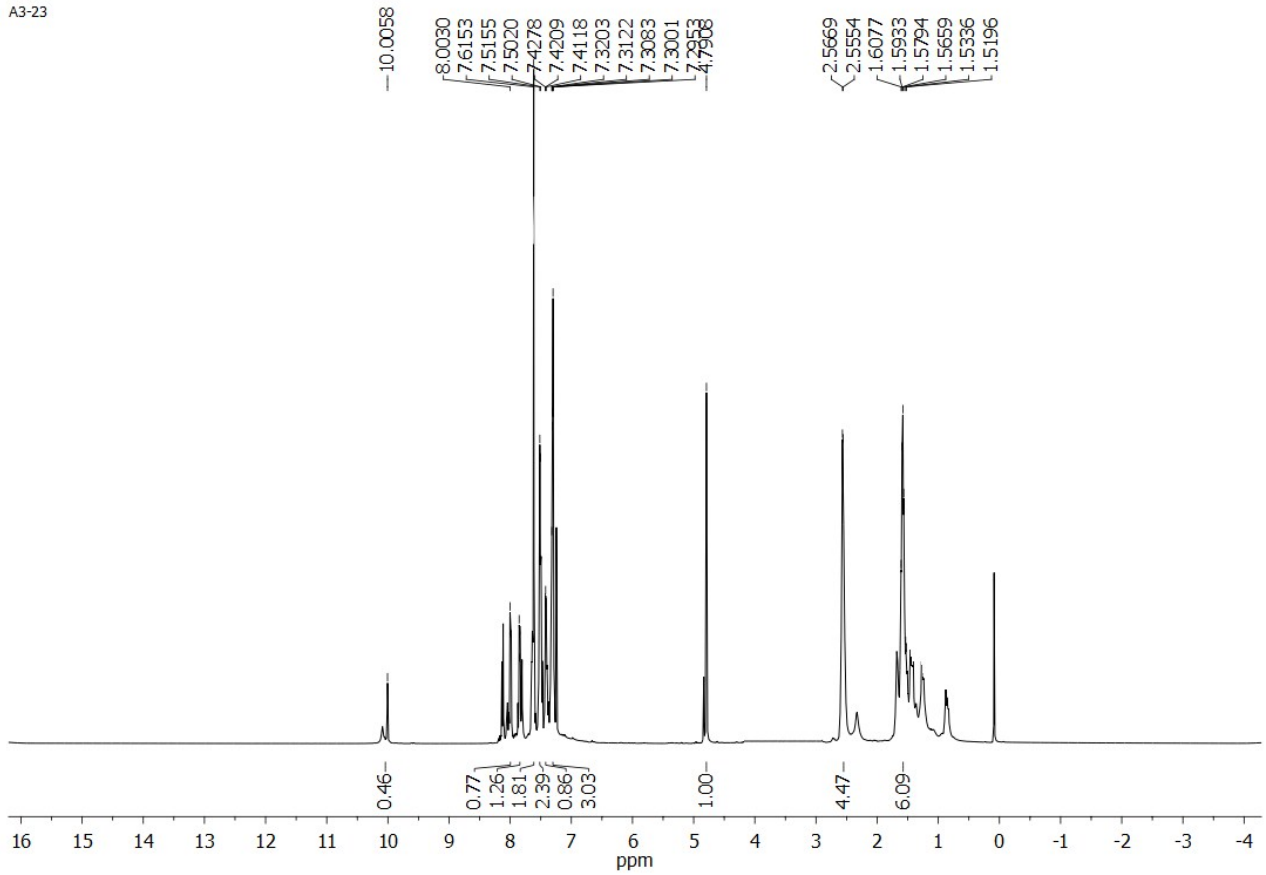


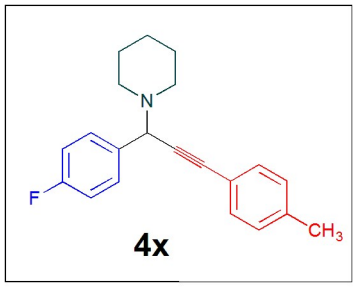
4-(3-p-tolyl-1-(4-(trifluoromethyl)phenyl)prop-2-ynyl)morpholine.



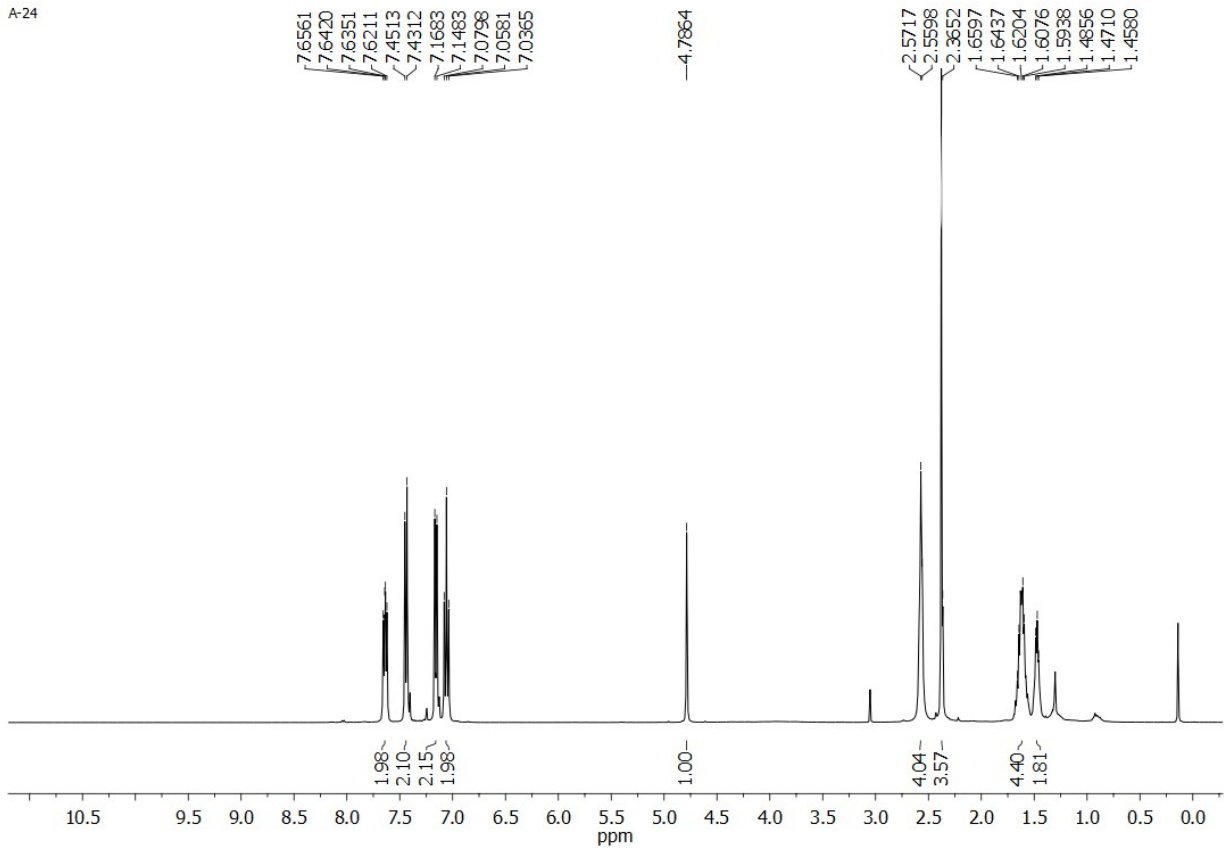


4-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)benzaldehyde.





1-(1-(4-fluorophenyl)-3-p-tolylprop-2-ynyl)piperidine.



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