

## Supporting information

# Easily available nickel complexes as catalysts for the intermolecular hydroamination of alkenes and alkynes

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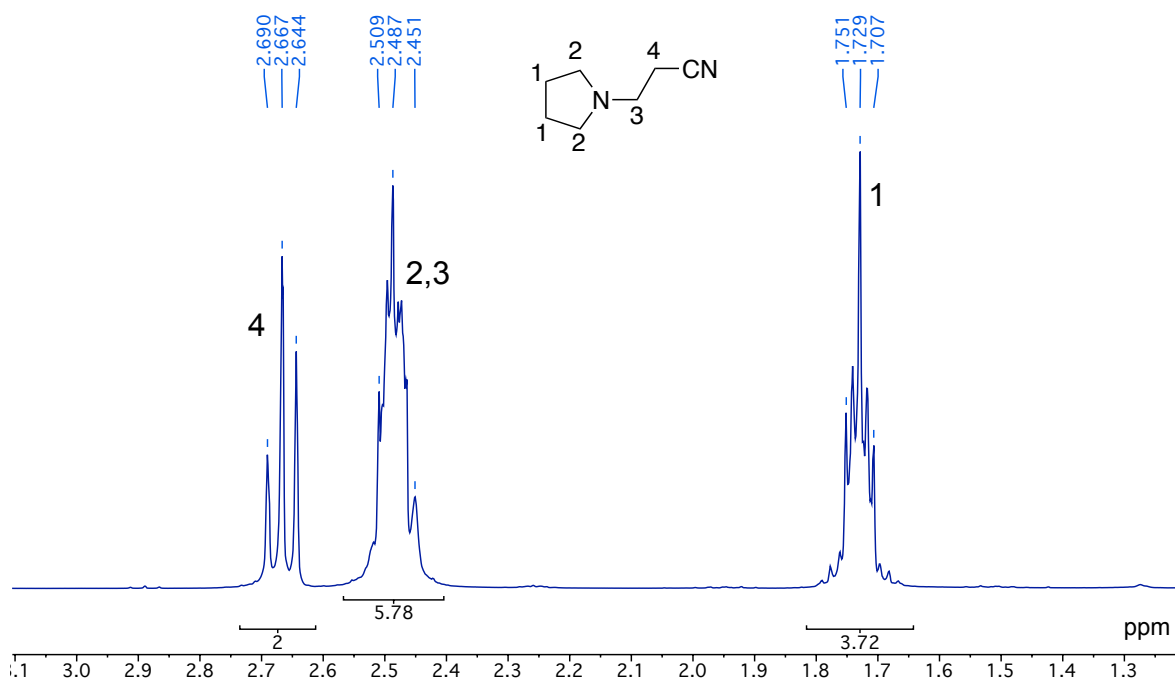
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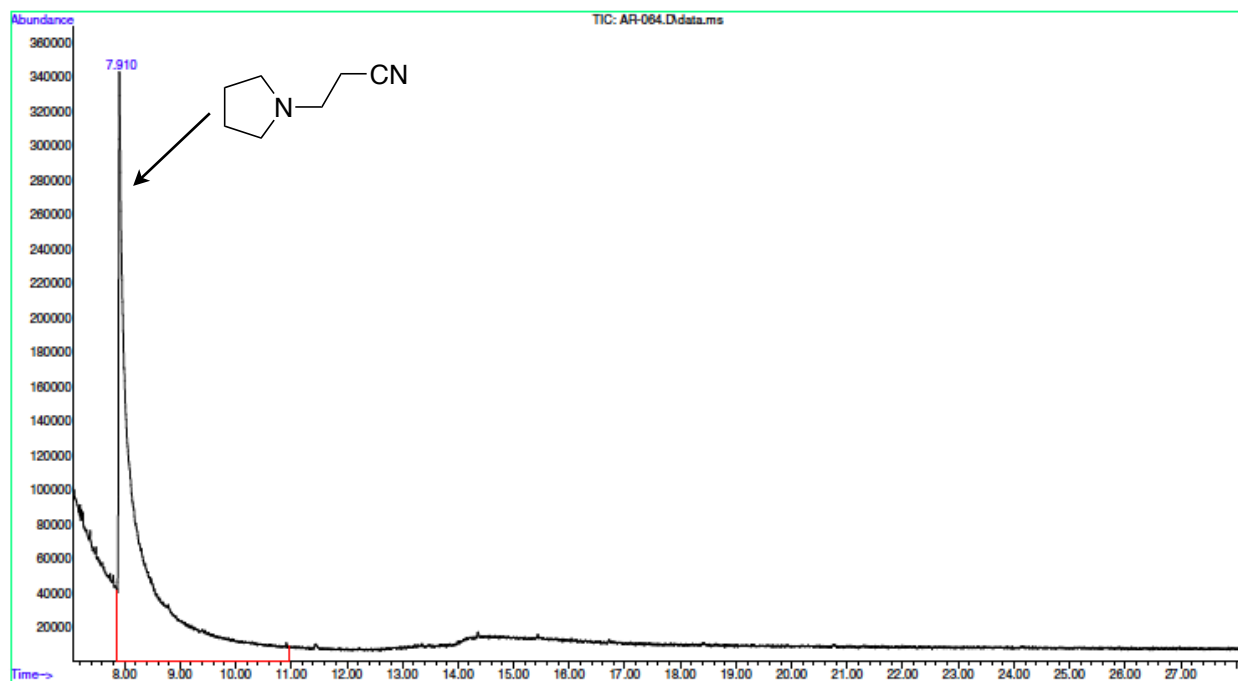
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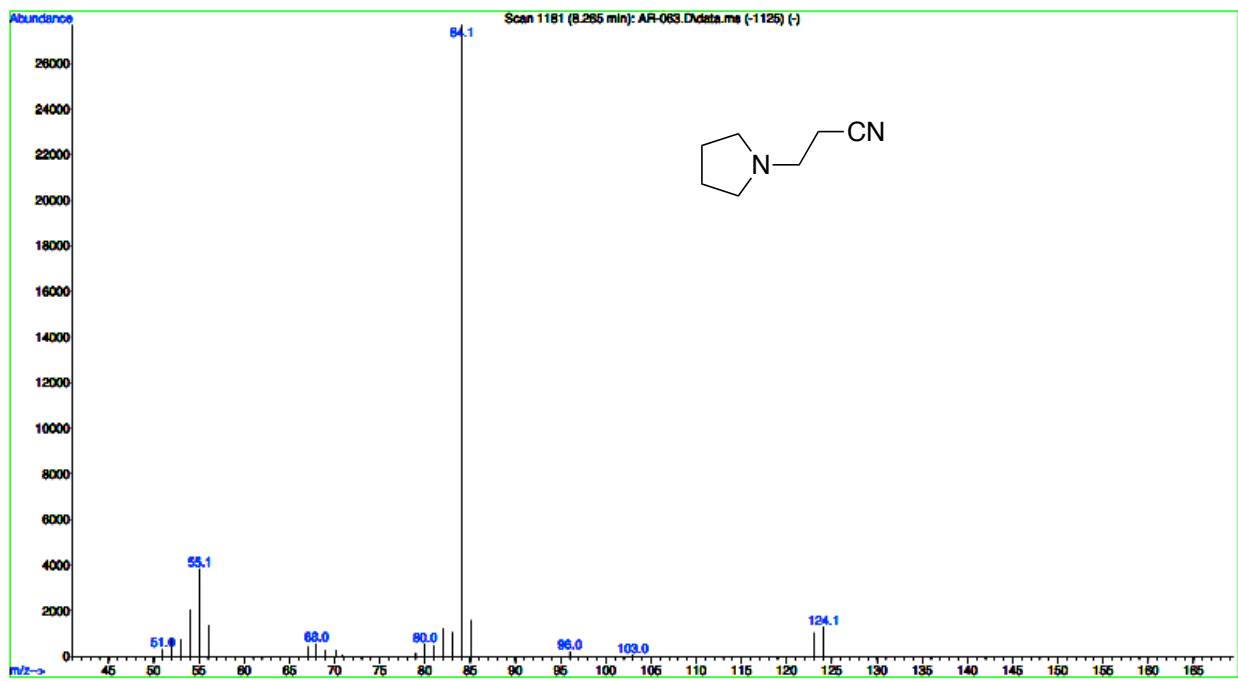
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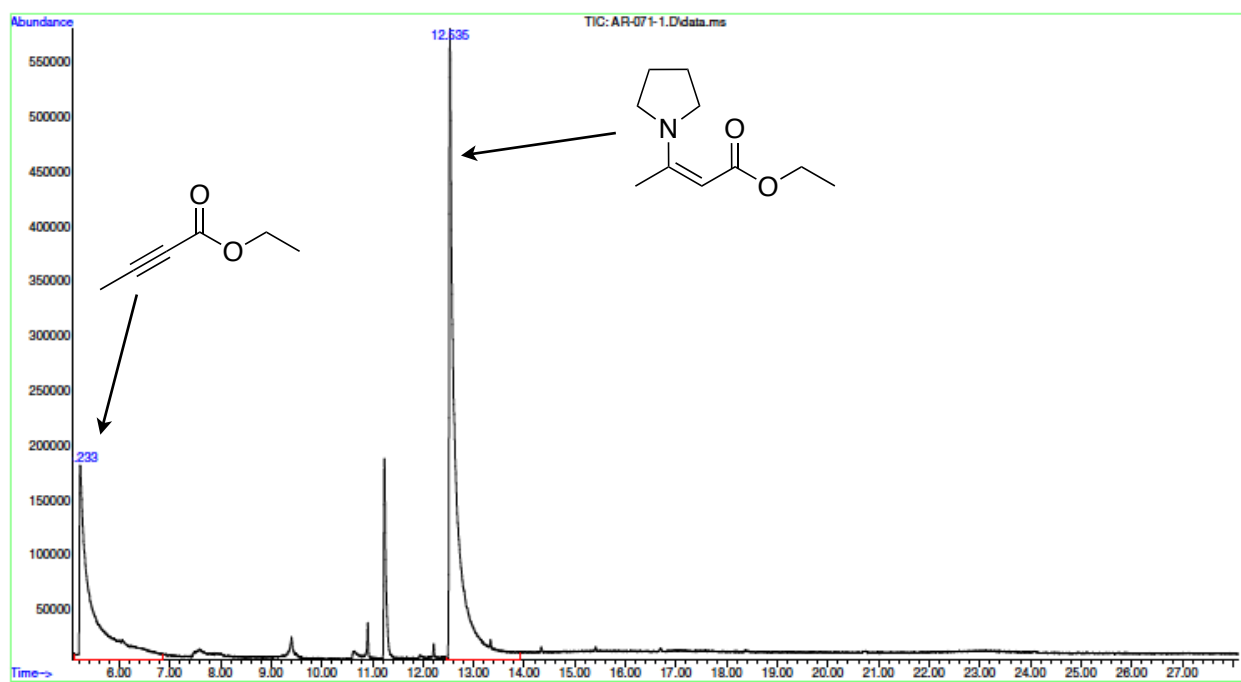
Scheme S1.  $^1\text{H}$  NMR spectrum of the hydroamination product of acrylonitrile with pyrrolidine mediated by dicathionic Ni(II) in  $\text{CD}_2\text{Cl}_2$



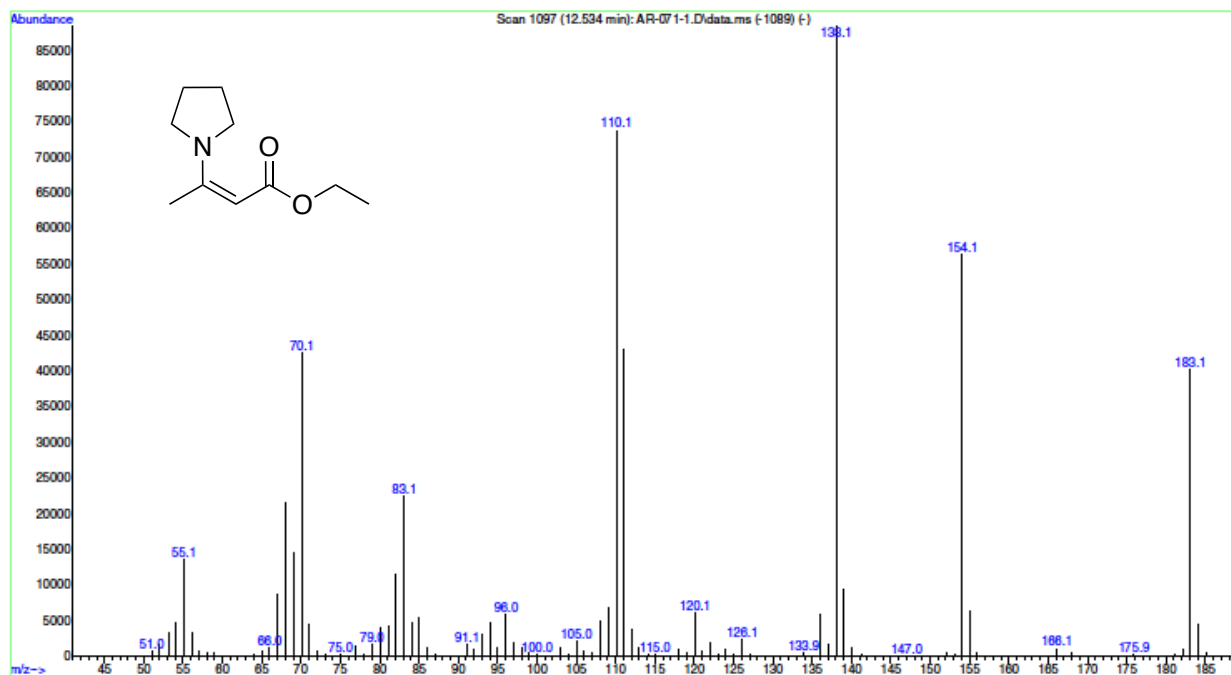
Scheme S2. Chromatogram of the catalytic hydroamination of acrylonitrile with dicathionic Ni(II) in benzonitrile



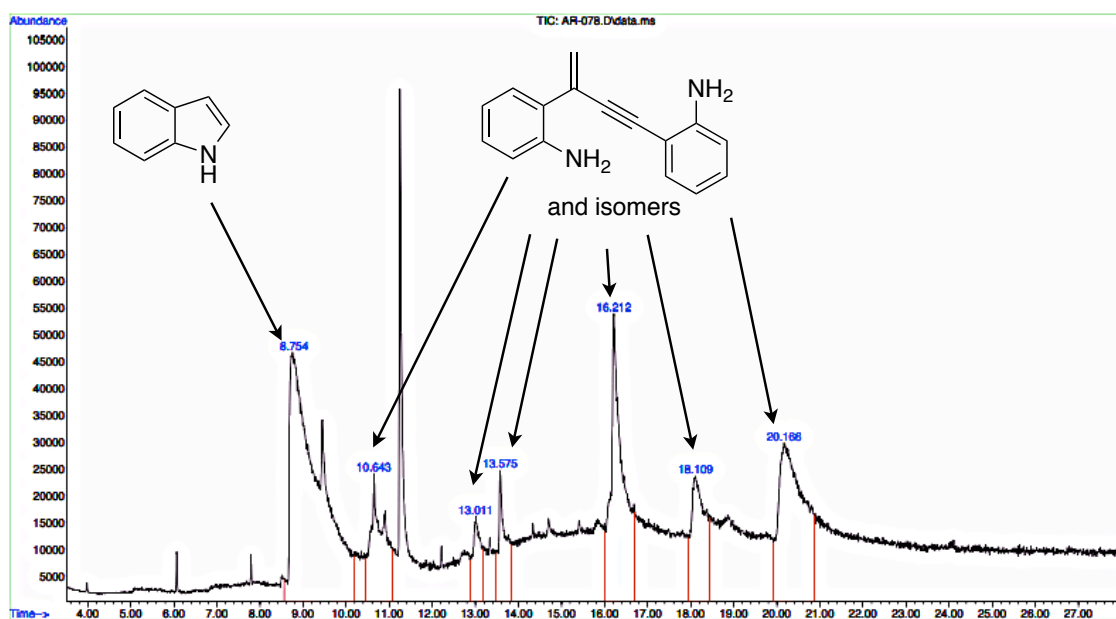
Scheme S3. Mass spectrum of the hydroamination product of acrylonitrile with pyrrolidine catalyzed by dicathionic Ni(II)



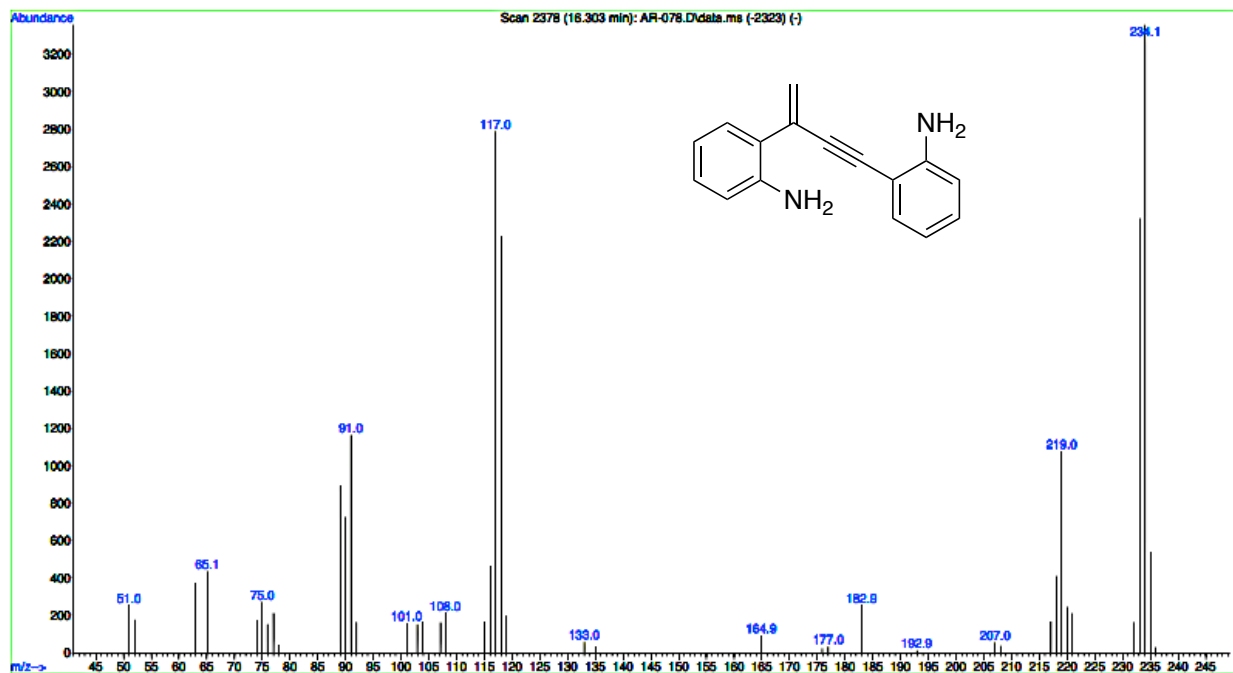
Scheme S4. Chromatogram of the catalytic hydroamination of alkyne 1e



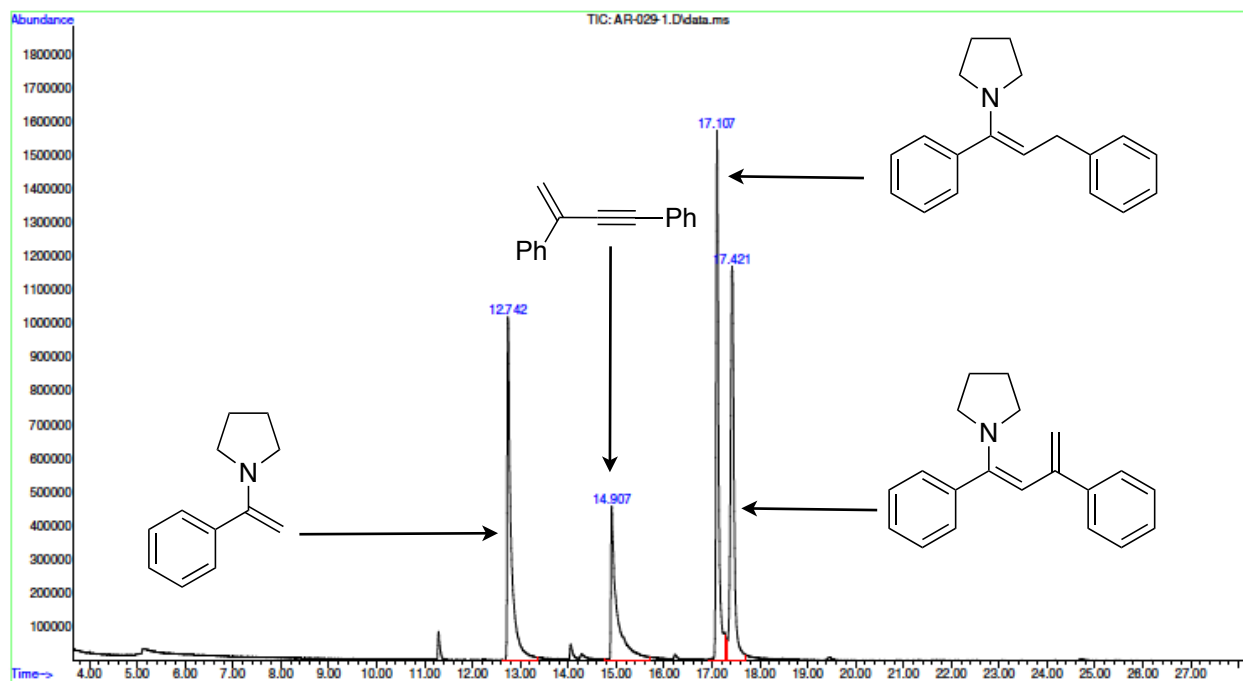
Scheme S5. Mass spectrum of the hydroamination product of alkyne 1c



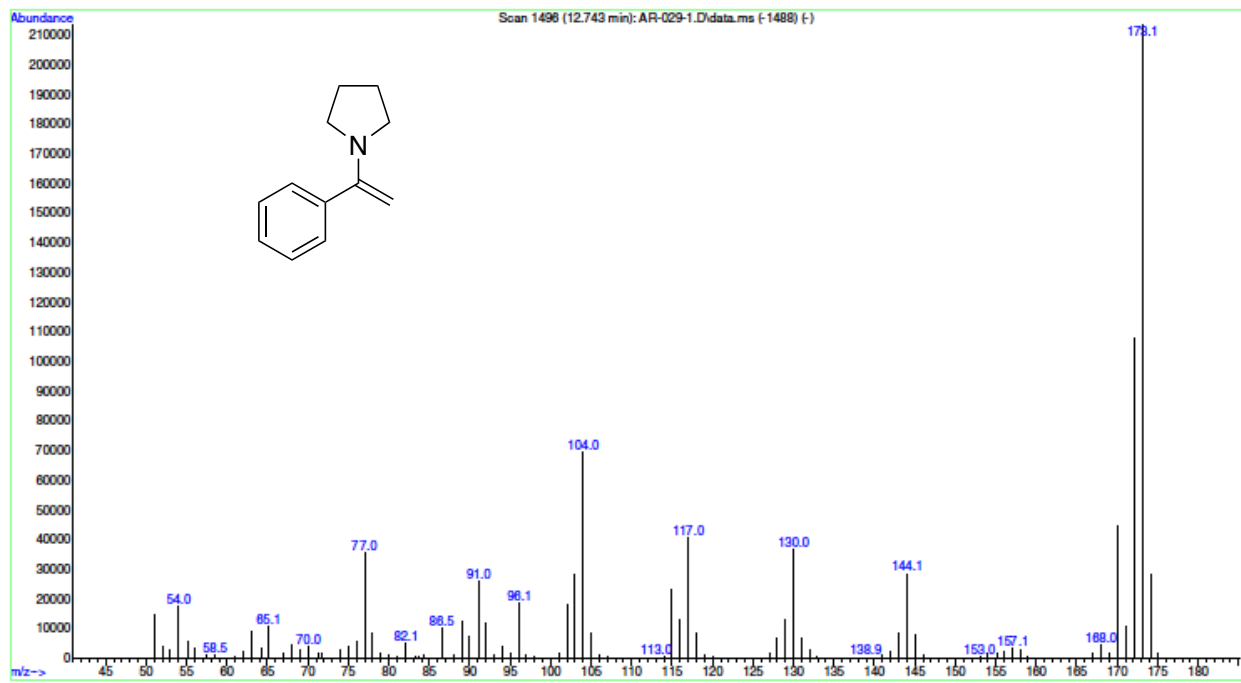
Scheme S6. Chromatogram of the intramolecular hydroamination of 2-ethynylaniline catalyzed by dicathionic Ni(II)



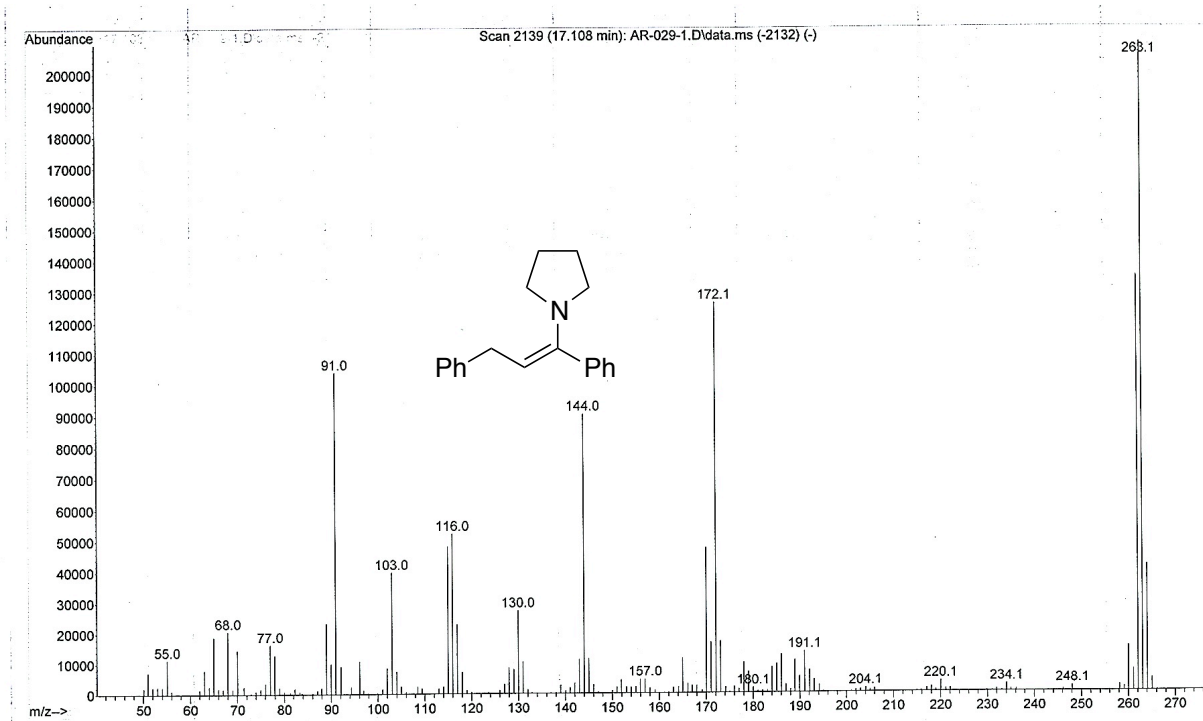
Scheme S7. Mass spectrum of one of the homocoupling products of 2-ethynylaniline



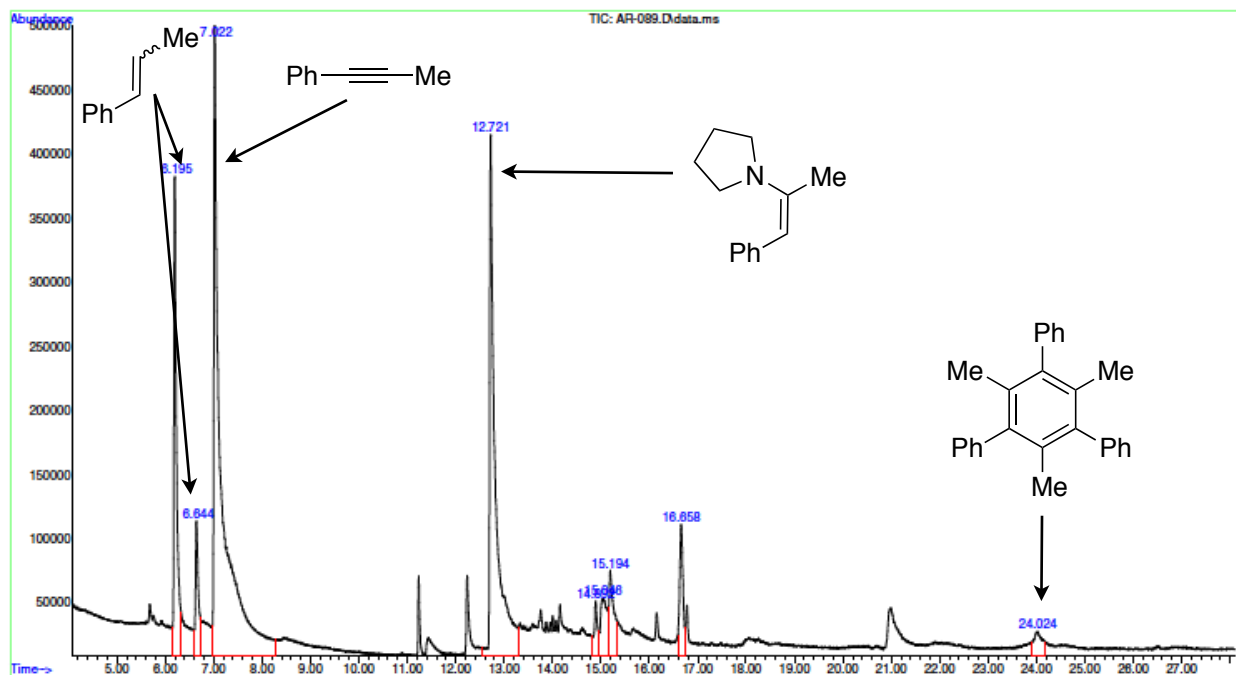
Scheme S8. Chromatogram of the hydroamination of phenylacetylene with neutral Ni(II) in pyrrolidine



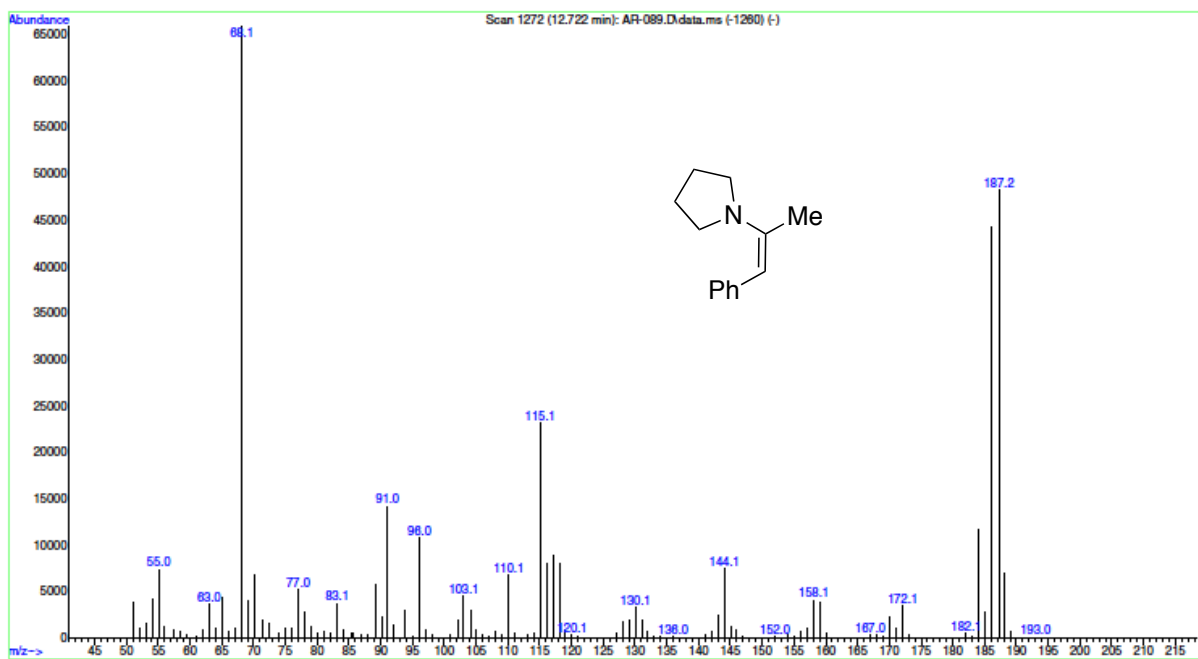
**Scheme S9. Mass spectrum of the hydroamination product of phenylacetylene with pyrrolidine**



**Scheme S10. Mass spectrum of product 5j**

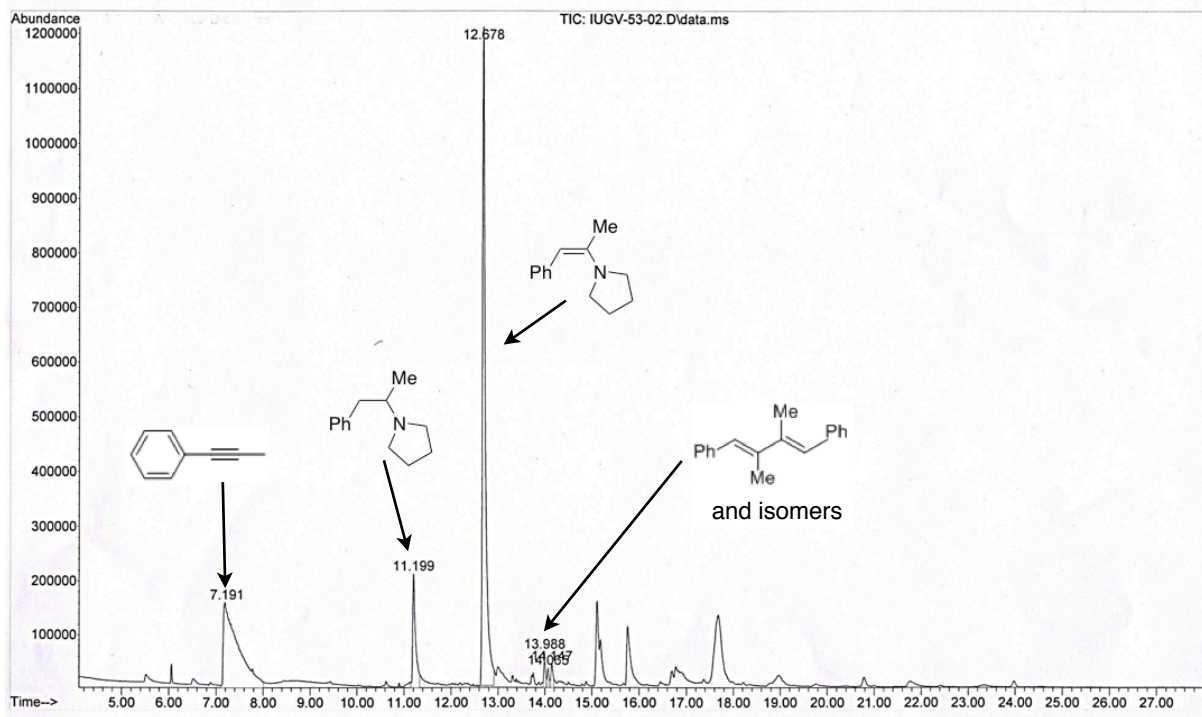


Scheme S11. Chromatogram of the hydroamination of 1-phenyl-1-propyne with neutral Ni(II)

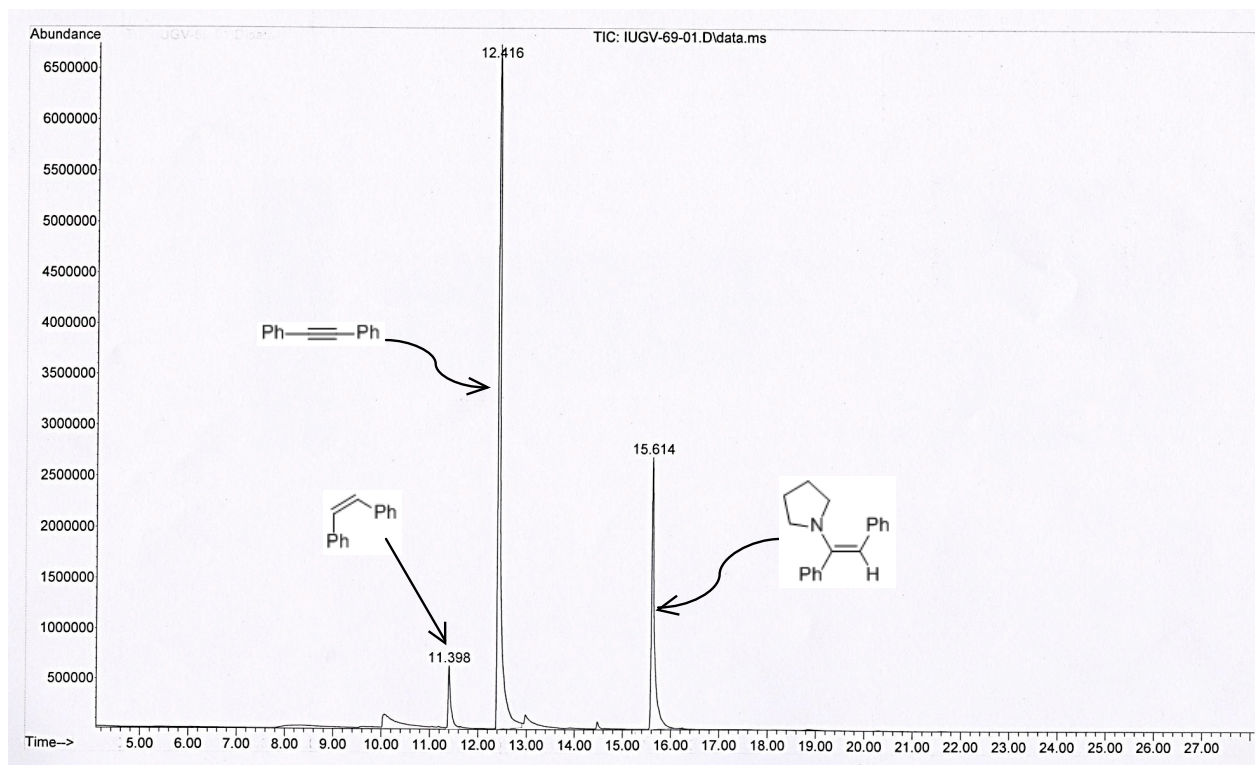


Scheme S12. Mass spectrum of the hydroamination product of 1-phenyl-1-propyne with neutral Ni(II)

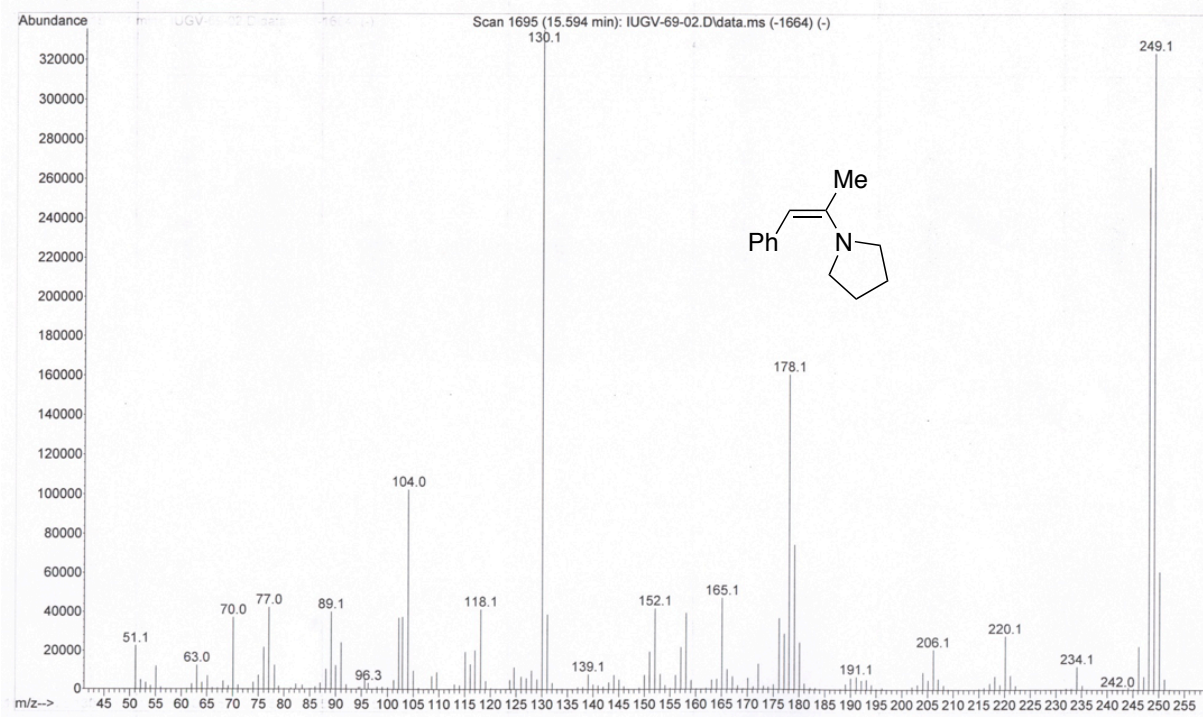




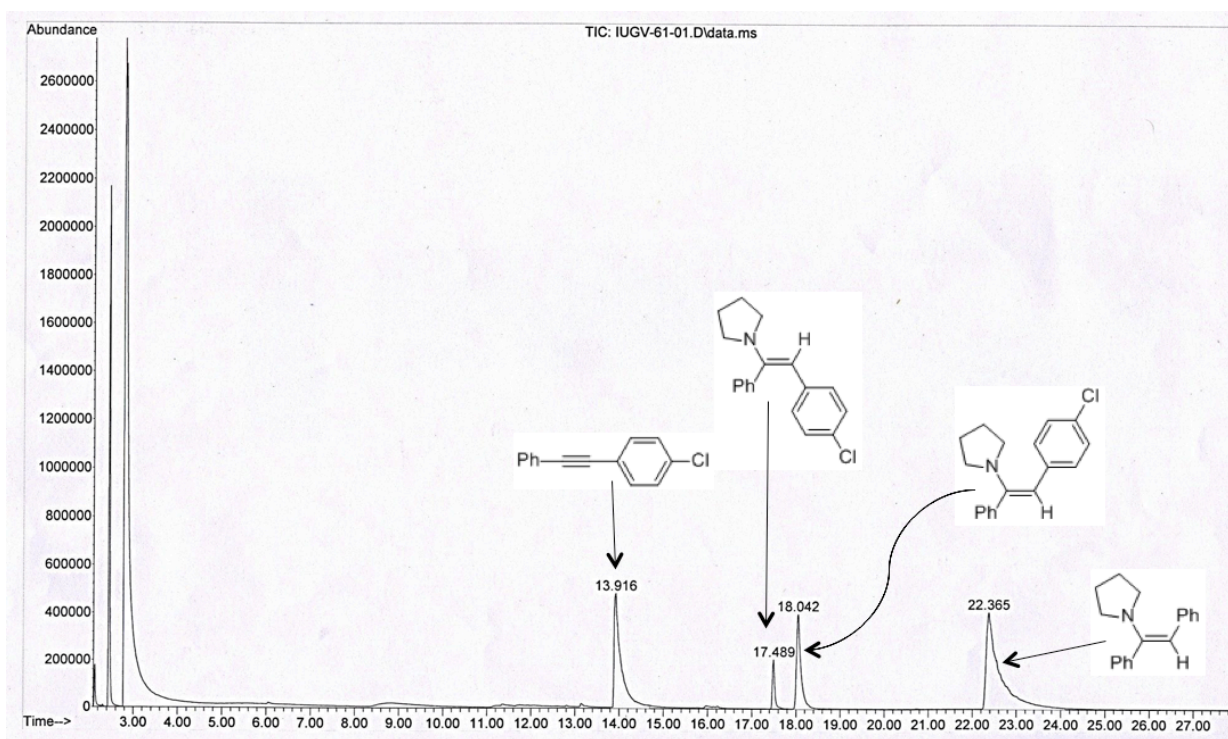
Scheme S13. Chromatogram of the hydroamination of 1-phenyl-1-propyne catalyzed by complex  $[(P(OPh)_3)_2Ni(cod)]$



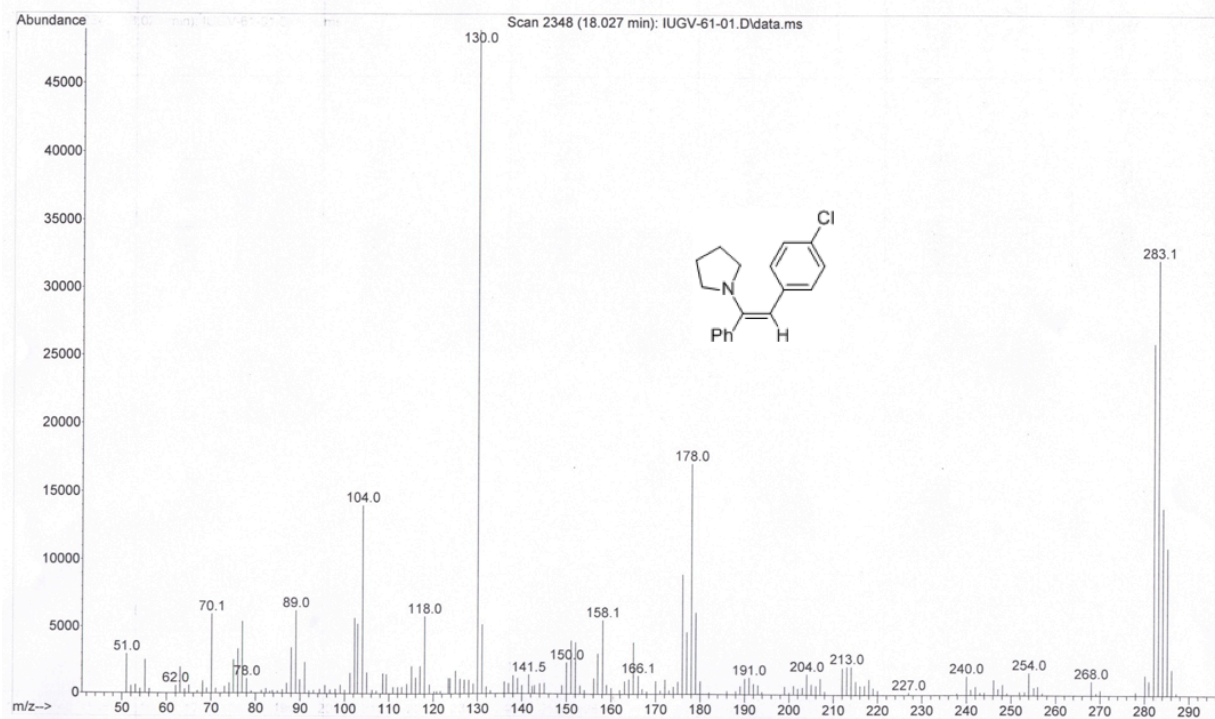
Scheme S14. Chromatogram for the hydroamination of diphenylacetylene (1n) catalyzed by  $[((PhO)_3P)_2NiCl_2]$



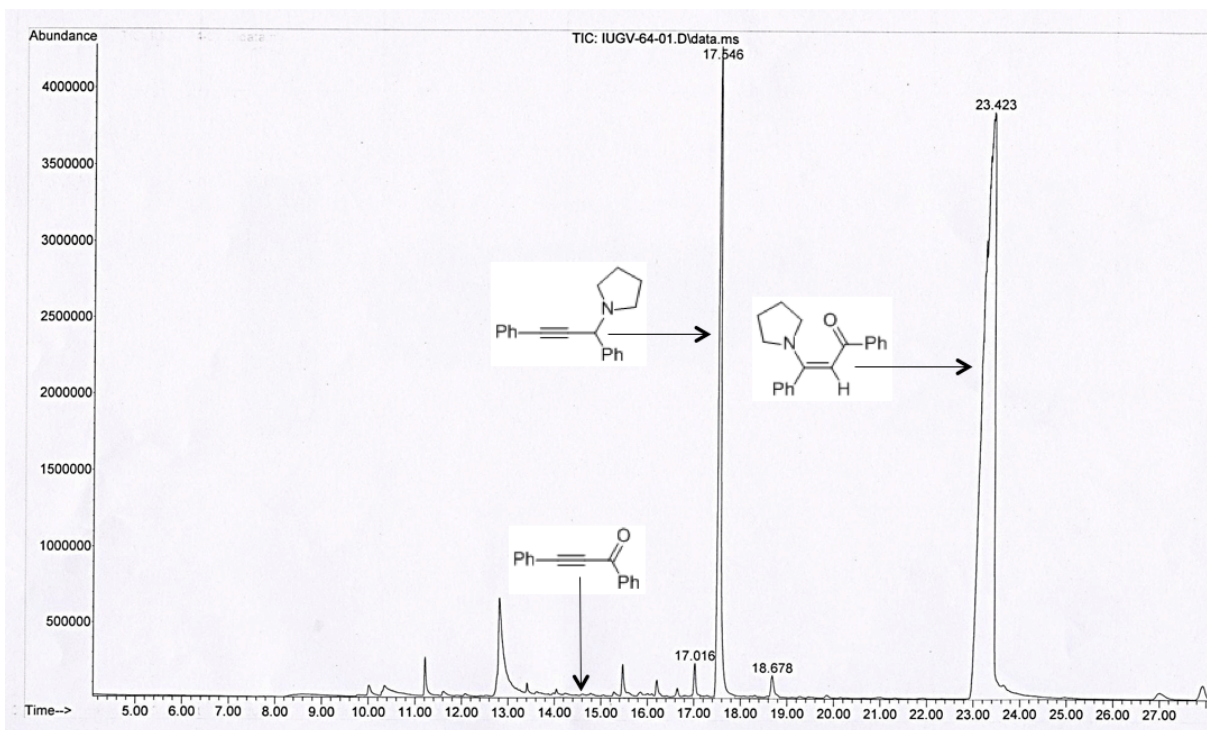
Scheme S15. Mass spectrum of the hydroamination product of 1-phenyl-1-propyne



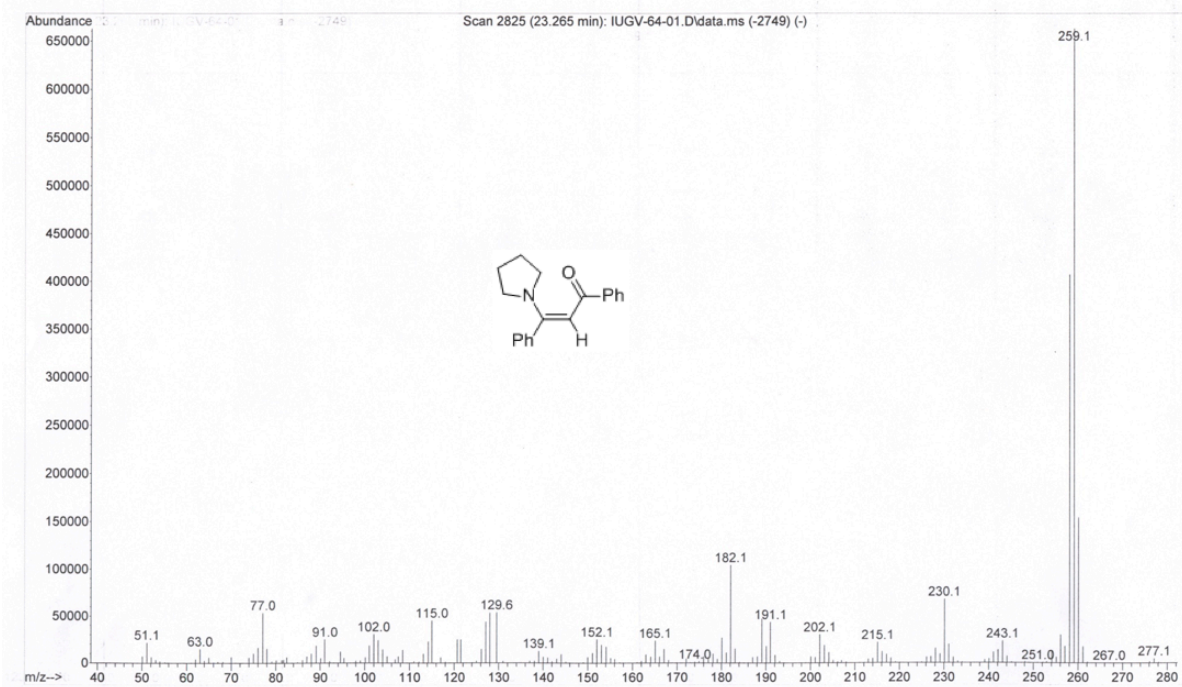
Scheme S16. Chromatogram for the hydroamination of alkyne 1g with  $[(\text{PhO})_3\text{P}]_2\text{NiCl}_2$



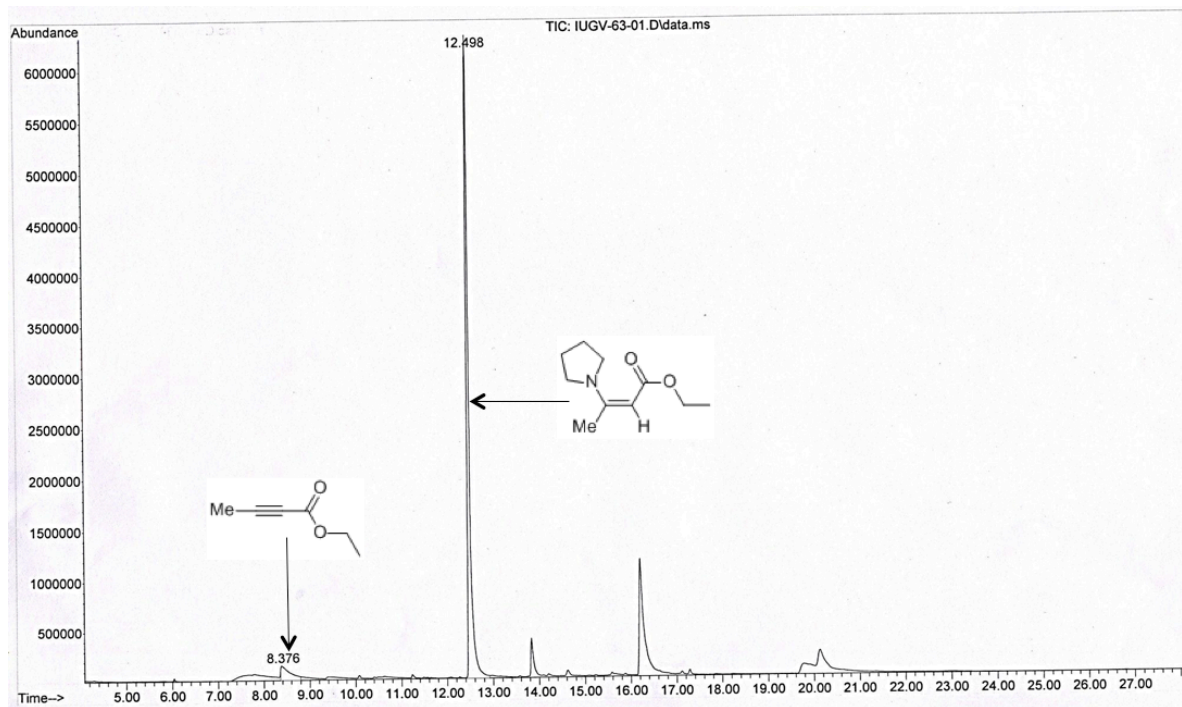
Scheme S17. Mass spectrum for the hydroamination product of alkyne **1g** catalyzed by complex  $[(\text{PhO})_3\text{P}]_2\text{NiCl}_2$



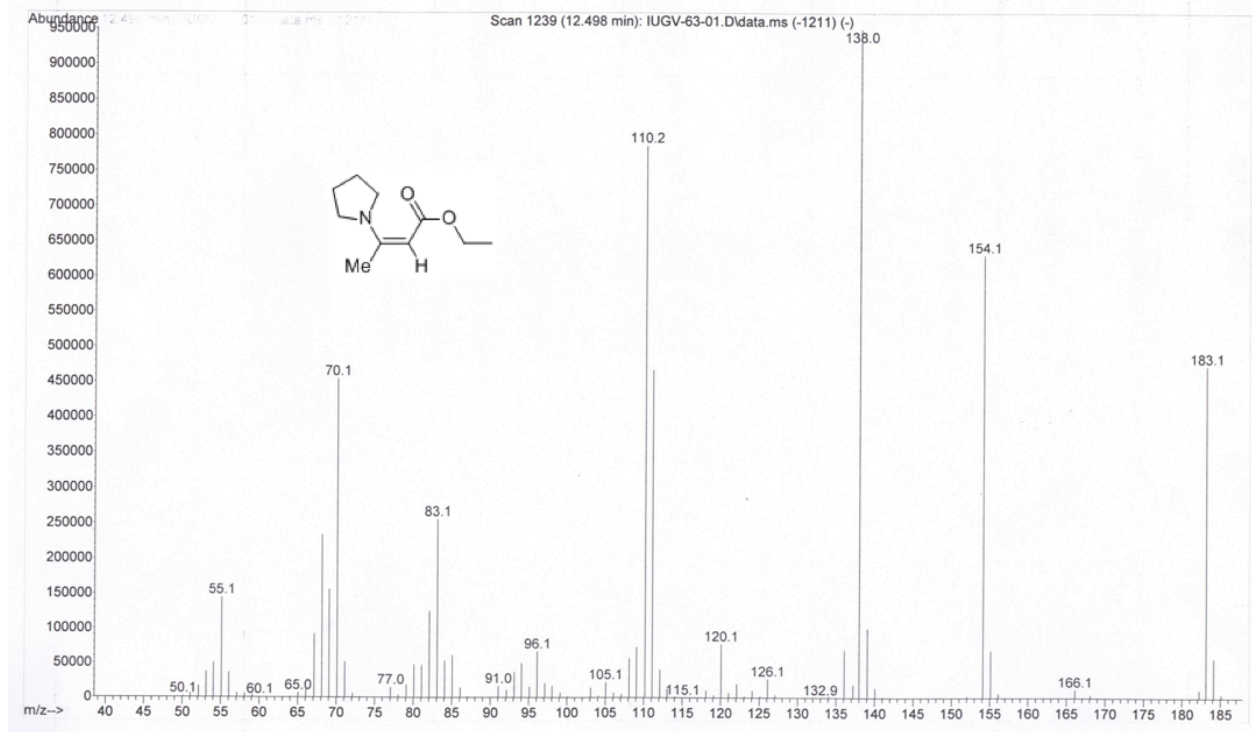
Scheme S18. Chromatogram for the hydroamination of alkyne **1p** catalyzed by complex  $[(\text{PhO})_3\text{P}]_2\text{NiCl}_2$



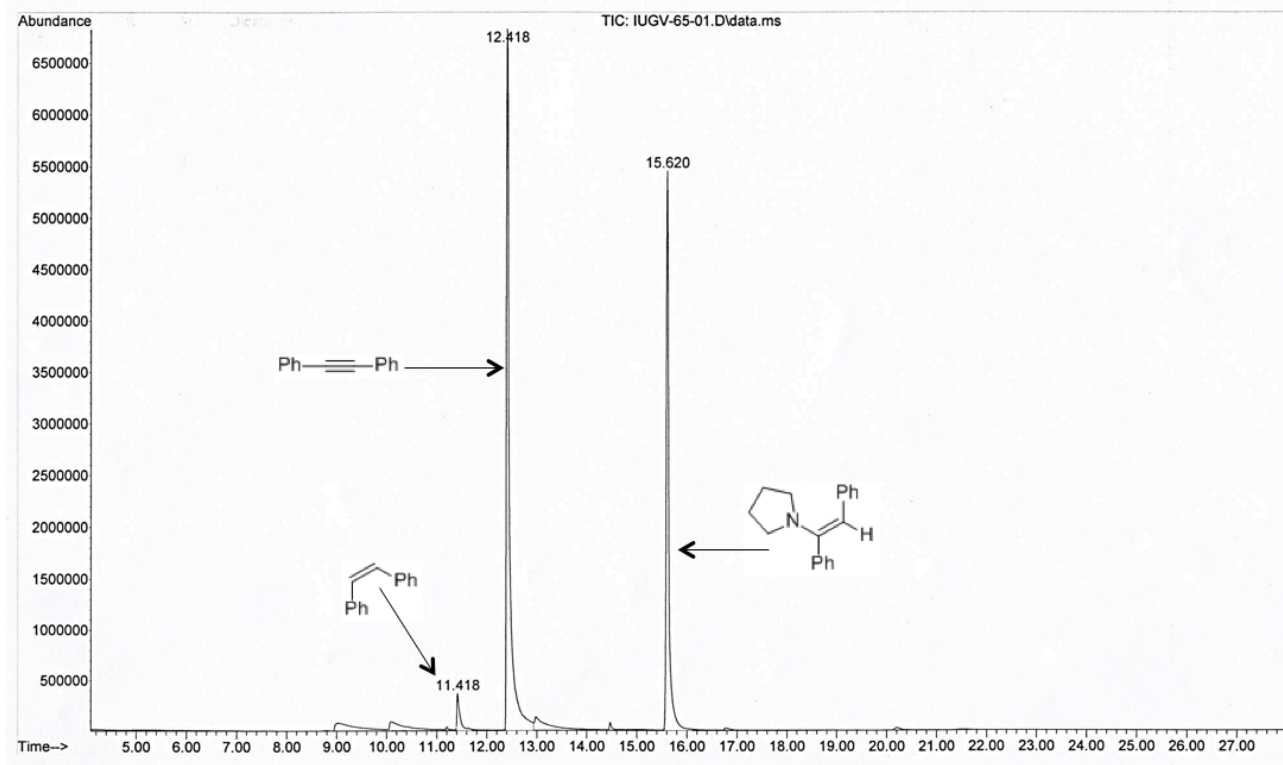
Scheme S19. Mass spectrum for the hydroamination product of alkyne 1p catalyzed by complex  $[(\text{PhO})_3\text{P}]_2\text{NiCl}_2$



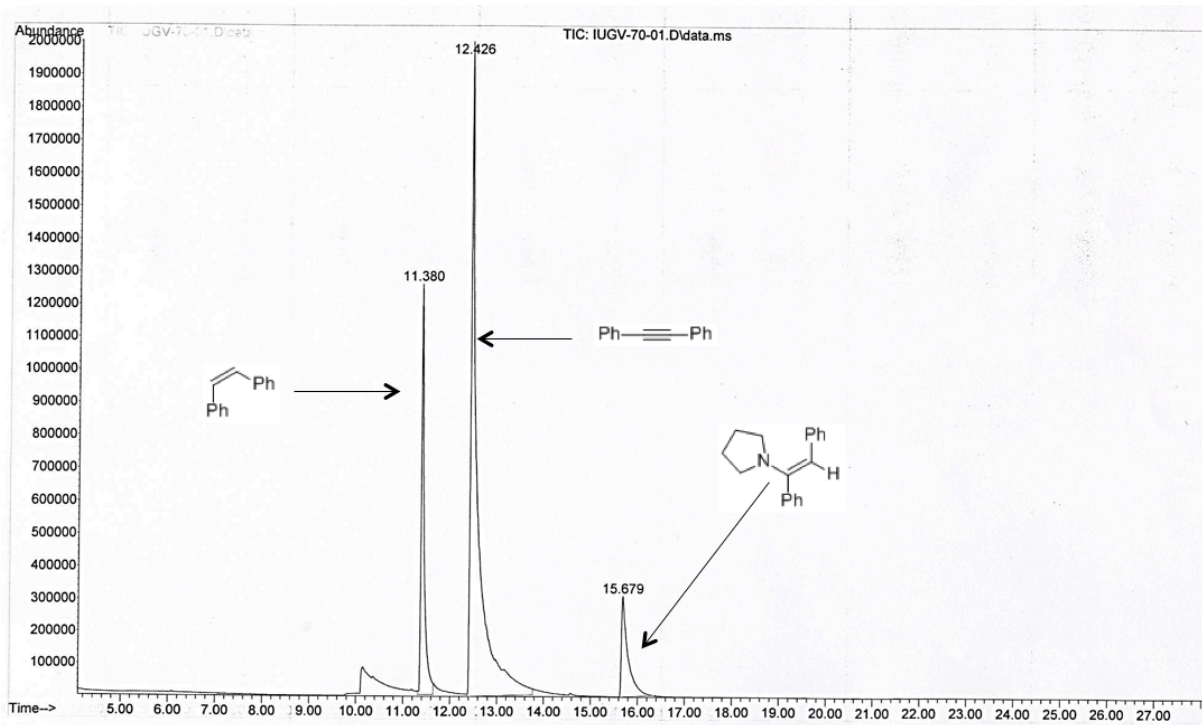
Scheme S20. Chromatogram for the hydroamination of alkyne 1e catalyzed by complex  $[(\text{PhO})_3\text{P}]_2\text{NiCl}_2$



Scheme S21. Mass spectrum for the hydroamination product of alkyne 1e catalyzed by complex  $[(\text{PhO})_3\text{P}]_2\text{NiCl}_2$



Scheme S22. Chromatogram for the hydroamination of alkyne 1n catalyzed by complex  $[(\text{EtO})_3\text{P}]_2\text{NiCl}_2$  at 140 °C



**Scheme S23. Chromatogram for the hydroamination of diphenylacetylene (1n) catalyzed by complex  $[(EtO)_3P)_2NiCl_2]$  at  $160\text{ }^\circ\text{C}$**