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Catalyzed formation of α,β-unsaturated ketones or aldehydes from propargylic acetates by a recoverable and recyclable nanocluster catalyst

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General information

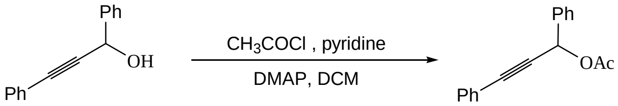
All the chemicals and reagents (including the ~23 nm gold nanoparticles) were commercially available except for anion and neutral $Au_{25}(SCH_2CH_2Ph)_{18}$, $Au_{38}(SCH_2CH_2Ph)_{24}$, $Au_{144}(SCH_2CH_2Ph)_{60}$, $Au_{25}(SG)_{18}$, ~3 nm gold nanoparticles and propargylic acetates. UV/Vis/NIR measurements were conducted with Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were recorded on a Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon). ^1H NMR was recorded on a Bruker AC-400 FT spectrometer (400 MHz) using tetramethylsilane as an internal reference. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The high resolution mass spectra were recorded on a LC-TOF spectrometer (Micromass). Electrospray ionization mass spectrometry (ESI-MS) data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MOLDI-TOF-MS) was done on an Bruker Autoflex Speed MALDI-TOF/TOF instrument operating in linear positive ion mode using DCTB (*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix (the mole ratio of $DCTB/Au_{25}(SR)_{18}^-$ is 500/1). $Au_{38}(SCH_2CH_2Ph)_{24}$[1], $Au_{144}(SCH_2CH_2Ph)_{60}$[2], ~3 nm gold nanoparticles without protecting by ligands[3], ~3 nm gold nanoparticles protected by phenylethanethiolate[4], neutral $Au_{25}(SCH_2CH_2Ph)_{18}$[4] and $Au_{25}(SG)_{18}$[5] were synthesized following previous methods.

Synthesis of $Au_{25}(SCH_2CH_2Ph)_{18}^-$

$Au_{25}(SCH_2CH_2Ph)_{18}^-$ was prepared according to the literature procedure.[2] Briefly, $HAuCl_4\cdot 4H_2O$ (206 mg, 0.5 mmol) and Tetra-n-octylammonium bromide (TOABr, 273 mg, 0.5 mmol) were dissolved in 20 mL THF in a three-necked flask at 0 °C under nitrogen. After the mixture was stirred over a period of 0.5 h, $PhCH_2CH_2SH$ (414 mg, 0.41 mL, 3.0 mmol) was added. The solution was stirred for 3 h until it turned clear, after which $NaBH_4$ (189 mg, 5.0 mmol) dissolved in 3.0 mL ice water was rapidly added to the reaction mixture at once under vigorous stirring. The synthesis proceeded overnight. After removal of the water layer, a large amount of cold water was added. The precipitates were collected and washed with excessive MeOH three times, then recrystallized to obtain needlelike $Au_{25}(SCH_2CH_2Ph)_{18}^-$ (40 mg, 25% yield, the counter ion is TOA^+).

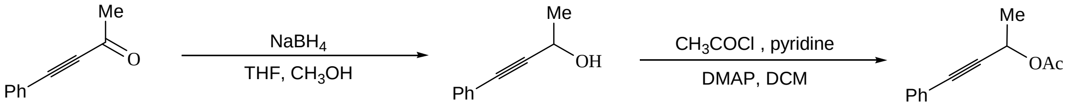
Synthesis of propargylic acetates

(1) 1,3-Diphenylprop-2-ynyl acetate



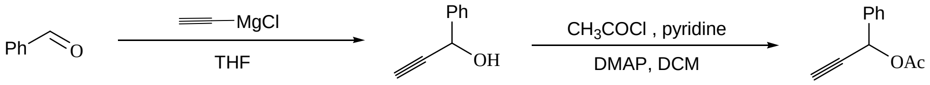
Acetyl chloride (156 mg, 0.15 mL, 2.0 mmol) was added slowly to a solution of 1,3-diphenylprop-2-yn-1-ol (208 mg, 1.0 mmol), DMAP (12.2 mg, 10 mol %), and pyridine (790 mg, 0.83 mL, 10.0 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C. The mixture was stirred for 0.5 h, and then diluted with hexane (15 mL). The obtained precipitate was filtered and washed with hexane (20 mL). The combined filtrates were dried over anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/20) to give 1,3-diphenylprop-2-ynyl acetate (229 mg, 92%) as a colorless oil.

(2) 4-Phenylbut-3-yn-2-yl acetate



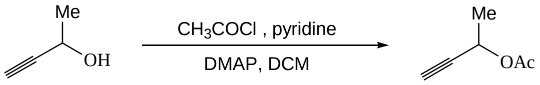
To a solution of 4-phenylbut-3-yn-2-one (144 mg, 1.0 mmol) in methanol (3.0 mL) and THF (3.0 mL) was added sodium borohydride (57.0 mg, 1.2 mmol). The mixture was stirred at room temperature for 2 h, added water (5.0 mL), and extracted with ethyl acetate (2 x 10 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5) to get 4-phenylbut-3-yn-2-ol (139 mg, 95%). It was then esterified to 4-phenylbut-3-yn-2-yl acetate (161 mg, 90%) by the method of (1).

(3) 1-Phenylprop-2-ynyl acetate



Benzaldehyde (106 mg, 1.0 mmol) was dissolved in 5.0 mL THF, and then ethynyl magnesium chloride (1.2 mL, 1.2 mmol, 1.0 M in THF) was added dropwise to the solution under nitrogen at 0 °C. After that the mixture was warmed to room temperature and stirred for 1 h. Ice water (5.0 mL) was added, and the mixture was extracted with ethyl acetate (2 x 20 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by preparative TLC, developing with ethyl acetate/petroleum ether = 1/5, to afford the 1-phenylprop-2-yn-1-ol (199 mg, 90%). It was then esterified to 1-phenylprop-2-ynyl acetate (141 mg, 90%) by the method of (1).

(4) But-3-yn-2-yl acetate



but-3-yn-2-yl acetate (108 mg, 96%) was obtained according to the method of (1).

General procedure for the formation of *α,β*-unsaturated ketones or aldehydes from propargylic acetates catalyzed by $Au_{25}(SR)_{18}^-$

A mixture of a propargylic acetate (0.20 mmol), $Au_{25}(SR)_{18}^-$ (3.0 mg), K_2CO_3 (27.6 mg, 0.2 mmol), and H_2O (0.2 mL) in DMSO (2.0 mL) was stirred at the preset tempearture for 2 h. The mixture was washed with water (10 mL), and extracted with ethyl acetate (2×20 mL). The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated. The residue was purified by preparative thin layer chromatography, developing with ethyl acetate/petroleum ether = 1/10 to afford an *α,β*-unsaturated ketone or an aldehyde.

Procedure for the recovery of the catalyst

After the reaction was completed, $Au_{25}(SCH_2CH_2Ph)_{18}^-$ was isolated from the reaction mixture simply through silica gel flash column chromatography with dichloromethane as eluent succeeding the removal of product by ethyl acetate/petroleum ether (1:10, volume ratio), after evaporating dichloromethane in reduced pressure, the catalyst was recovered and could be reused in the subsequent catalysis without further treatment.

UV/Vis/NIR spectra of catalyst

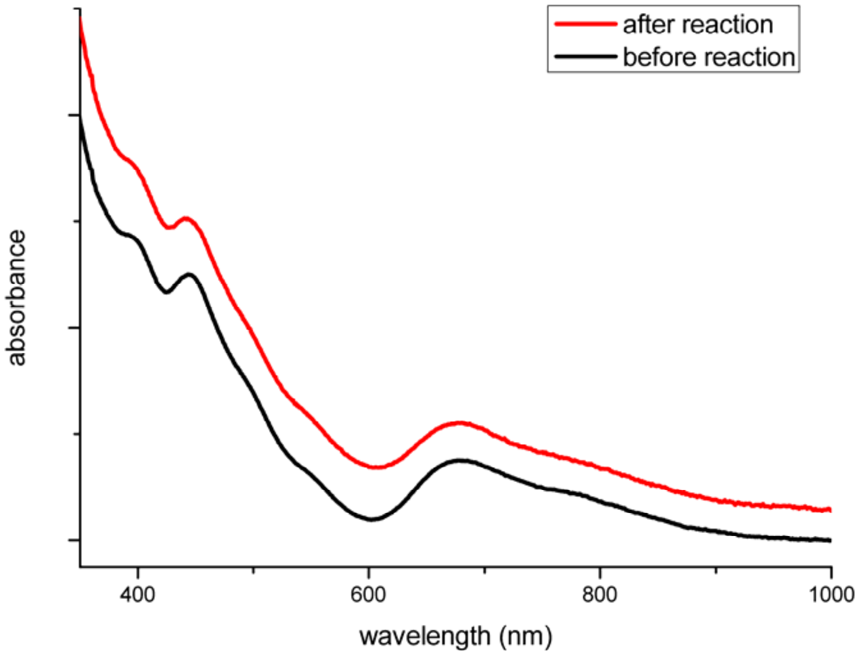


Figure S1 UV/Vis/NIR spectra of catalyst before and after reaction with DMF as solvent.

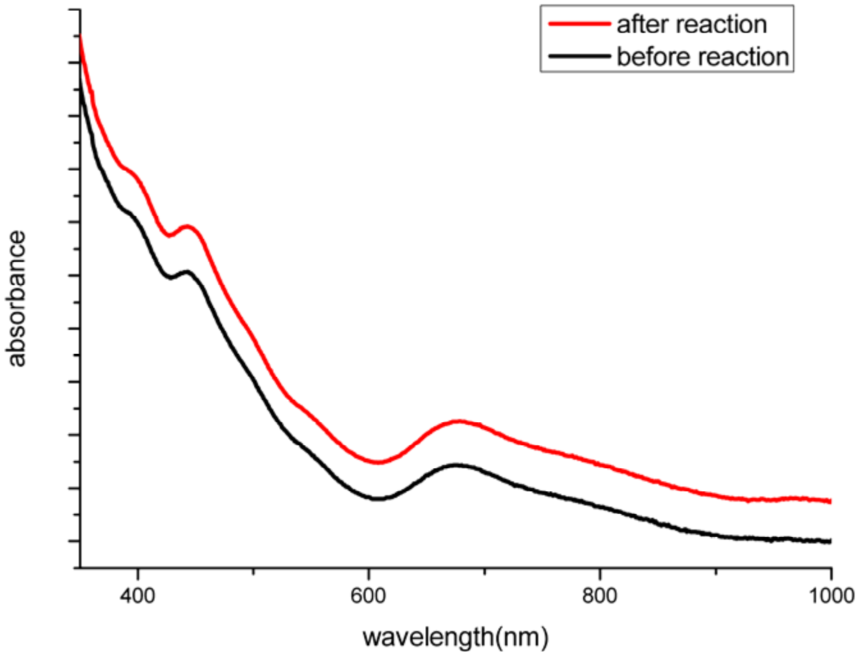


Figure S2 UV/Vis/NIR spectra of catalyst before and after reaction with DMSO as solvent.

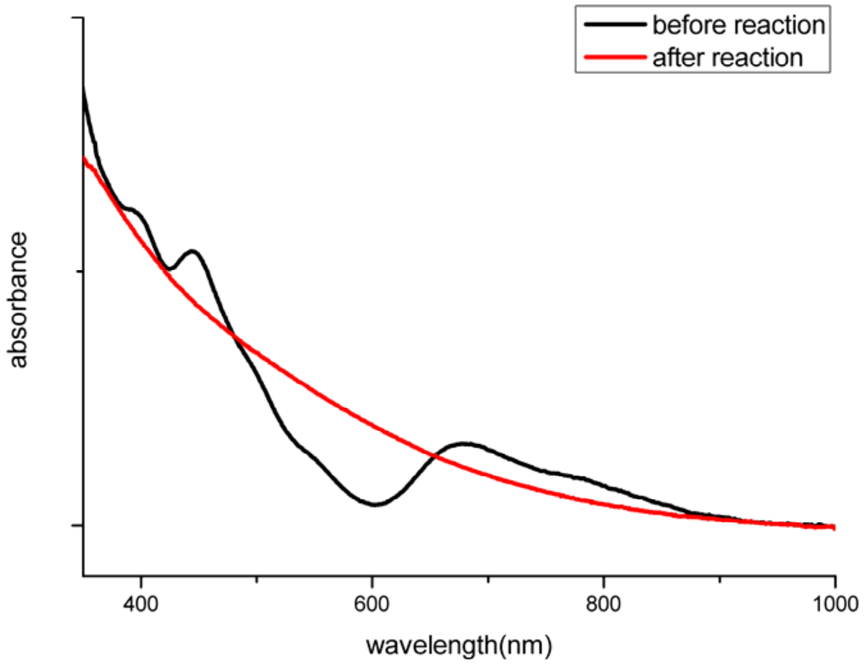


Figure S3 UV/Vis/NIR spectra of catalyst before and after reaction with toluene as solvent.

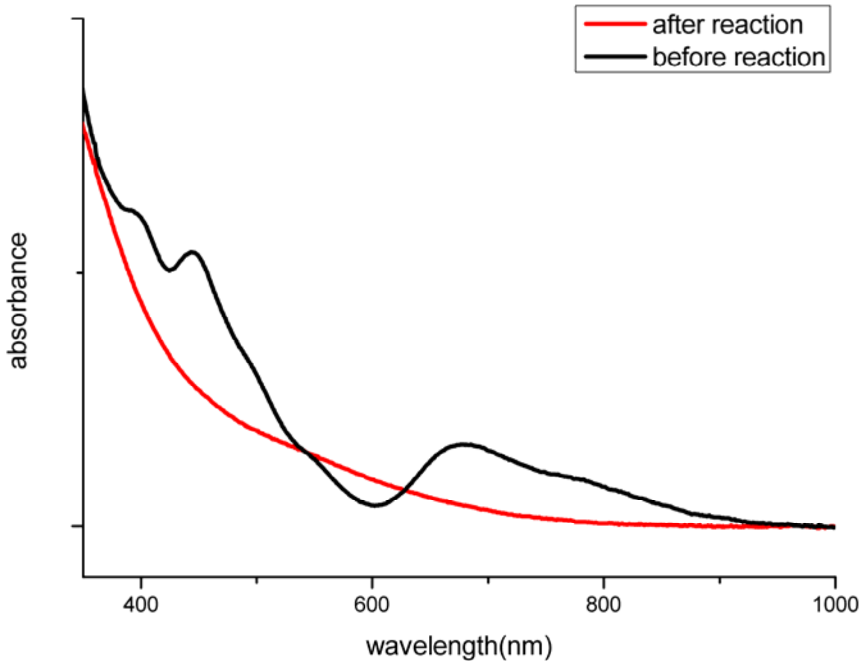


Figure S4 UV/Vis/NIR spectra of catalyst before and after reaction with THF as solvent.

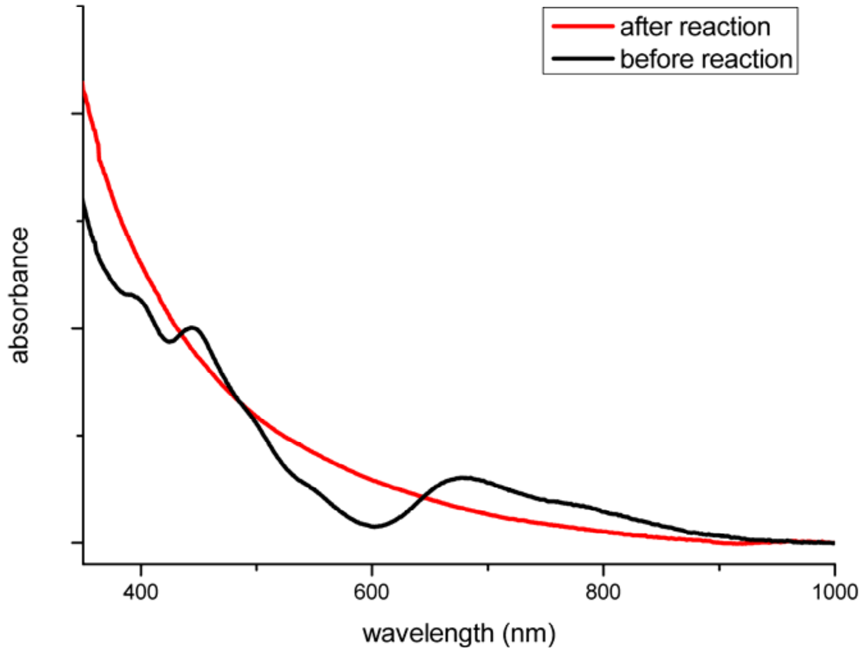


Figure S5 UV/Vis/NIR spectra of catalyst before and after reaction with 1,4-dioxane as solvent.

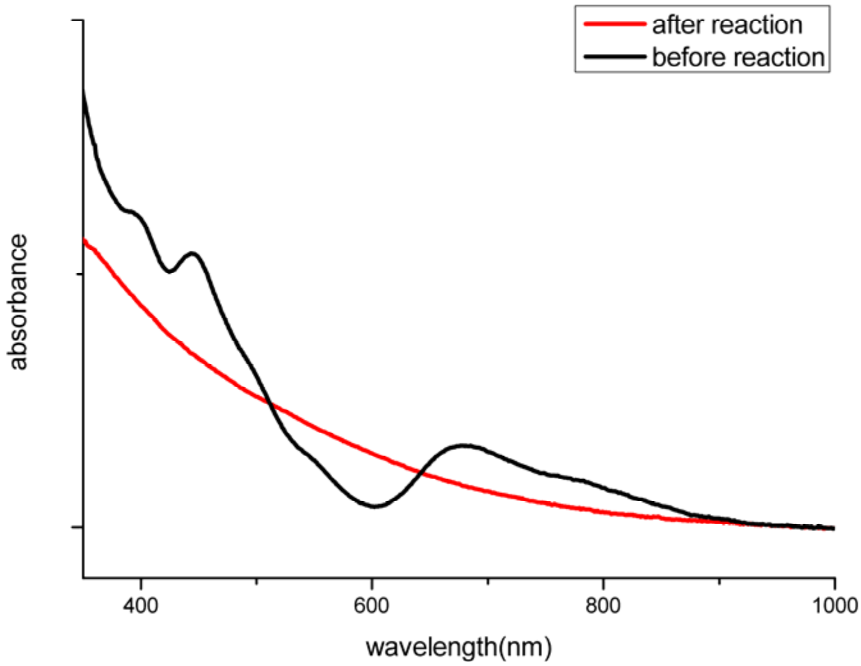


Figure S6 UV/Vis/NIR spectra of catalyst before and after reaction with 1,2-dichloroethane as solvent.

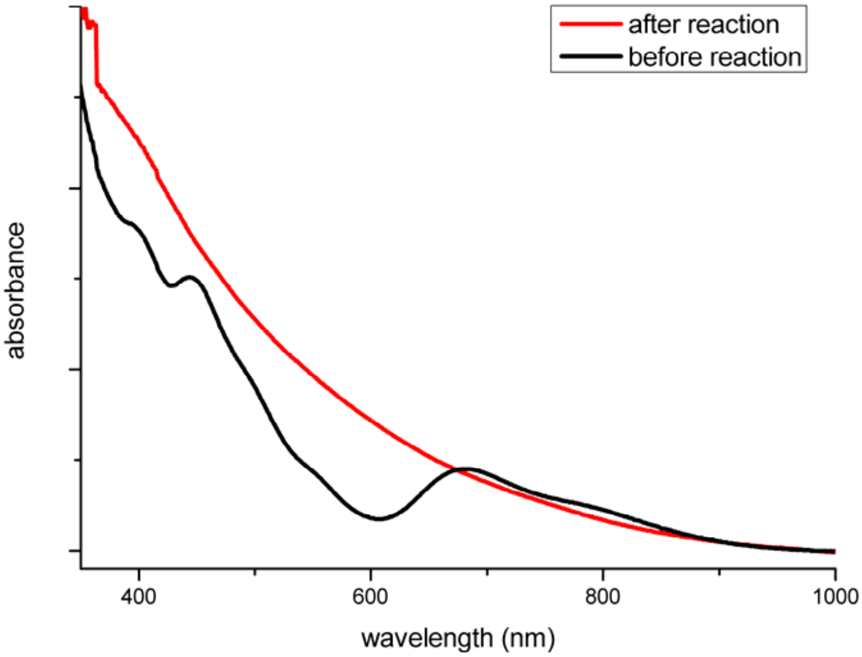


Figure S7 UV/Vis/NIR spectra of catalyst before and after reaction with acetone as solvent.

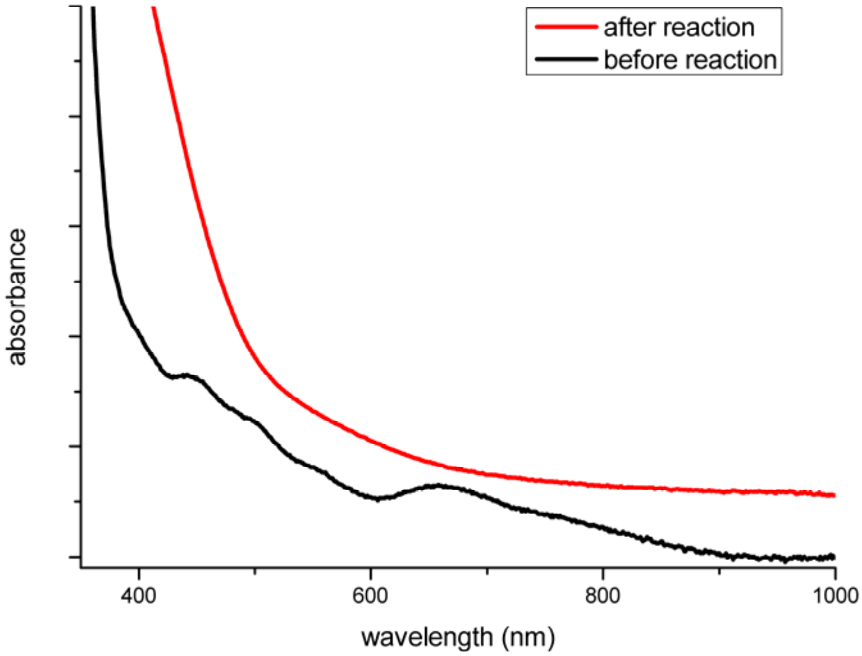


Figure S8 UV/Vis/NIR spectra of catalyst before and after reaction with H_2O as solvent.

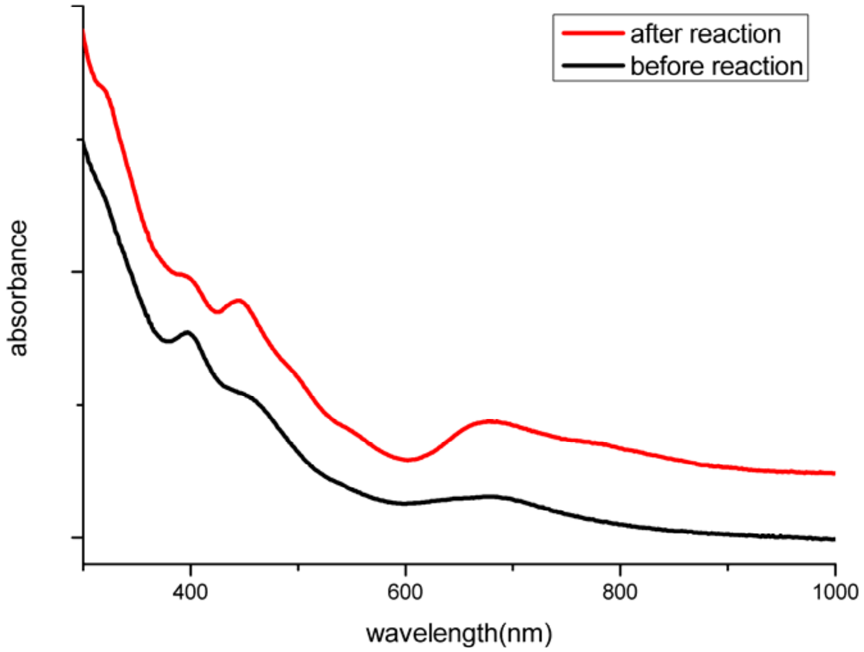


Figure S9 UV/Vis/NIR spectra of $Au_{25}(SR)_{18}^{0}$ before and after reaction in the solvent DMSO (the spectra in DMF before and after reaction are similar and not shown).

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Fluorescence spectra of catalyst

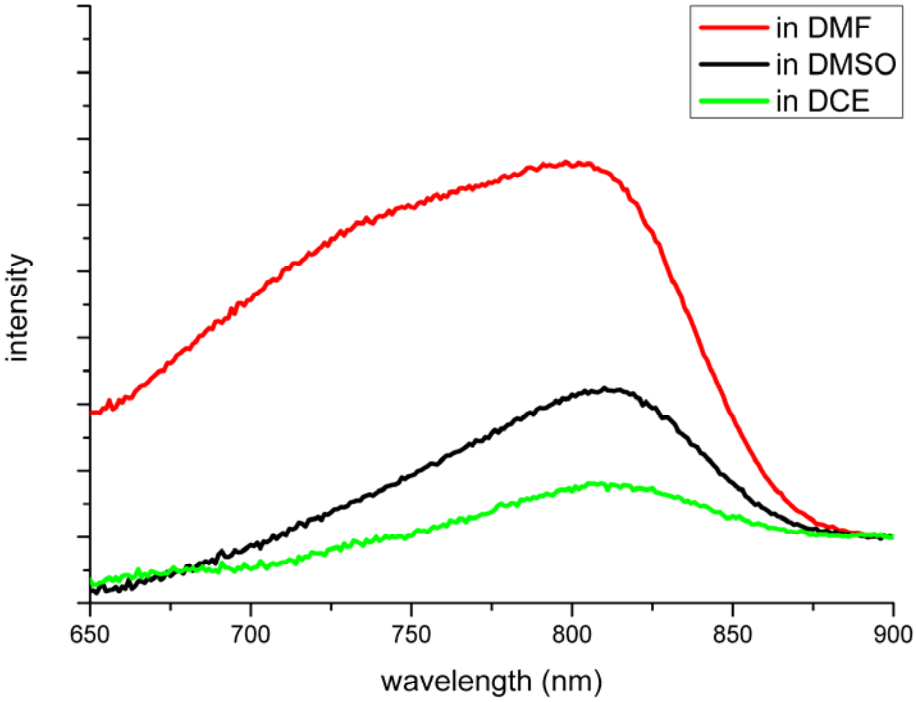
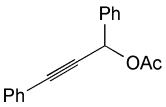
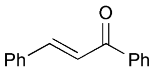


Figure S10 Fluorescence spectra of $Au_{25}(SR)_{18}^{-}$ cluster in different solvent (excited at 514nm).

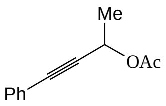
Spectroscopic characterization of propargylic acetates and α,β-unsaturated ketones and aldehydes



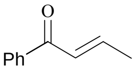
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.57 (m, 2H), 7.50–7.46 (m, 2H), 7.44–7.28 (m, 6H), 6.70 (s, 1H), 2.13 (s, 3H); HRMS (ESI) calcd for $C_{17}H_{14}O_2Na^+$ $(M+Na)^+$ 273.0886, found 273.0884.



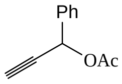
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 4.0 Hz, 2H), 7.82 (d, J = 16.0 Hz, 1H), 7.75–7.63 (m, 2H), 7.62–7.46 (m, 4H), 7.45–7.40 (m, 3H); HRMS (EI) calcd for $C_{15}H_{12}O$ $(M)^+$ 208.0888, found 208.0883.



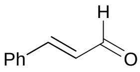
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.34–7.27 (m, 3H), 5.69 (q, J = 8.0 Hz, 1H), 2.10 (s, 3H), 1.58 (d, J = 8.0 Hz, 3H); HRMS (ESI) calcd for $C_{12}H_{12}O_2Na^+$ $(M+Na)^+$ 211.0730, found 211.0727.



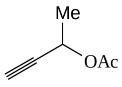
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 2H), 7.58–7.52 (m, 1H), 7.49–7.42 (m, 2H), 7.13–7.02 (m, 1H), 6.95–6.87 (m, 1H), 2.00 (dd, J = 8.0, 4.0 Hz, 3H); HRMS (ESI) calcd for $C_{10}H_{10}ONa^+$ $(M+Na)^+$ 169.0624, found 169.0620.



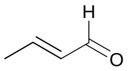
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 2H), 7.43–7.34 (m, 3H), 6.45 (d, J = 4.0 Hz, 1H), 2.66 (d, J = 4.0 Hz, 1H), 2.11 (s, 3H); HRMS (ESI) calcd for $C_{11}H_{10}O_2Na^+$ $(M+Na)^+$ 197.0573, found 197.0569.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 8.0 Hz, 1H), 7.59–7.53 (m, 2H), 7.48–7.39 (m, 4H), 6.73 (dd, J = 16.0, 8.0 Hz, 1H); HRMS (ESI) calcd for $C_9H_8ONa^+$ $(M+Na)^+$ 155.0467, found 155.0466.



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (dq, J = 8.0, 4.0 Hz, 1H), 2.46 (d, J = 4.0 Hz, 1H), 2.08 (s, 3H), 1.51 (d, *J* = 4.0 Hz, 3H); HRMS (ESI) calcd for $C_6H_8O_2Na^+$ $(M+Na)^+$ 135.0417, found 135.0412.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 8.0 Hz, 1H), 6.94–6.83 (m, 1H), 6.20–6.11 (m, 1H), 2.04 (dd, *J* = 8.0, 4.0 Hz, 3H); HRMS (ESI) calcd for $C_4H_7O^+$ $(M+H)^+$ 71.0491, found 71.0488.

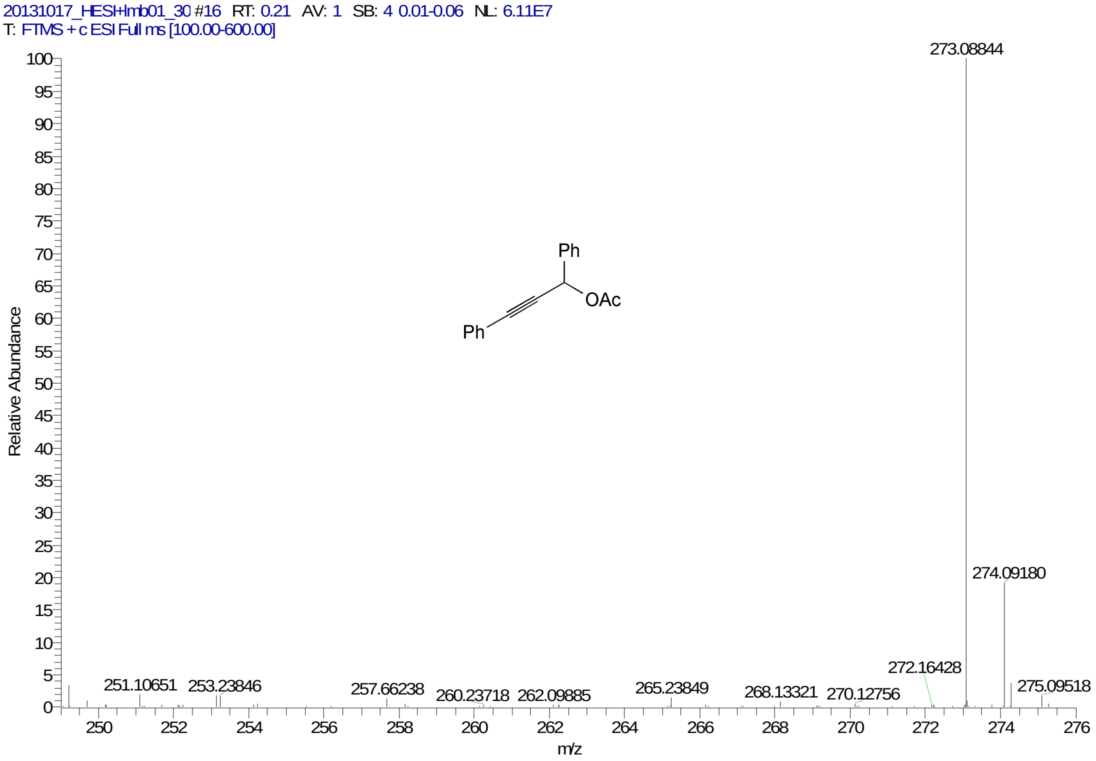


Figure S11 ESI mass spectra of 1,3-diphenylprop-2-ynyl acetate.

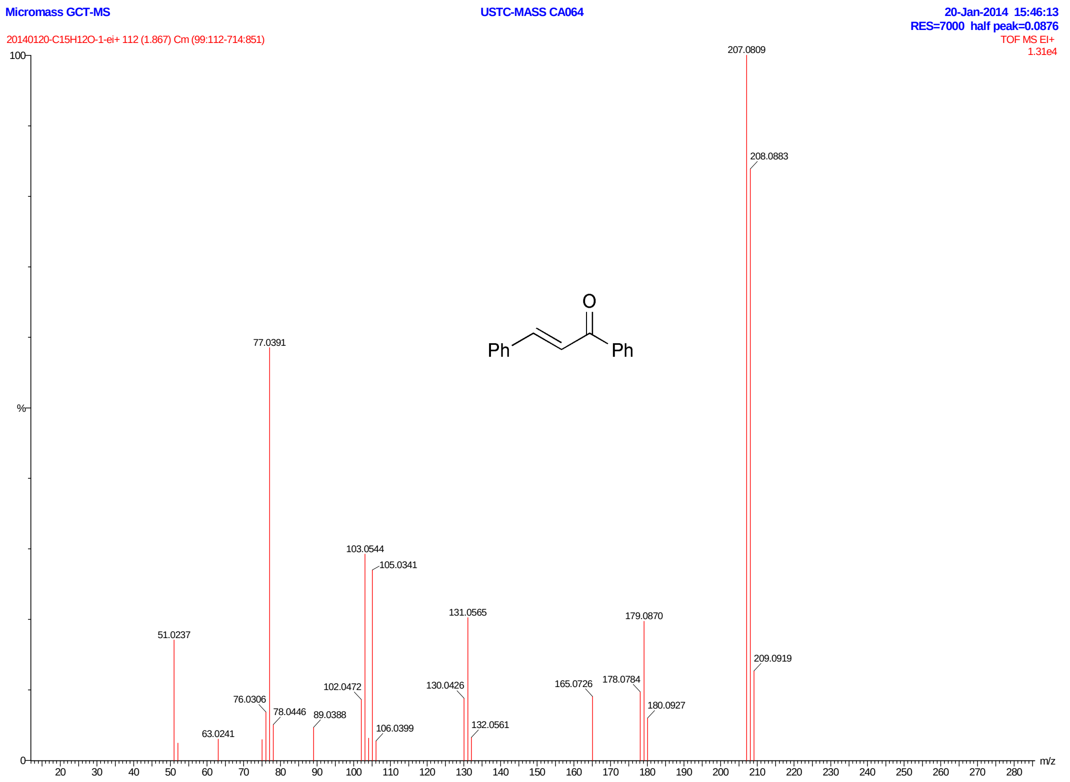


Figure S12 EI mass spectra of (*E*)-chalcone.

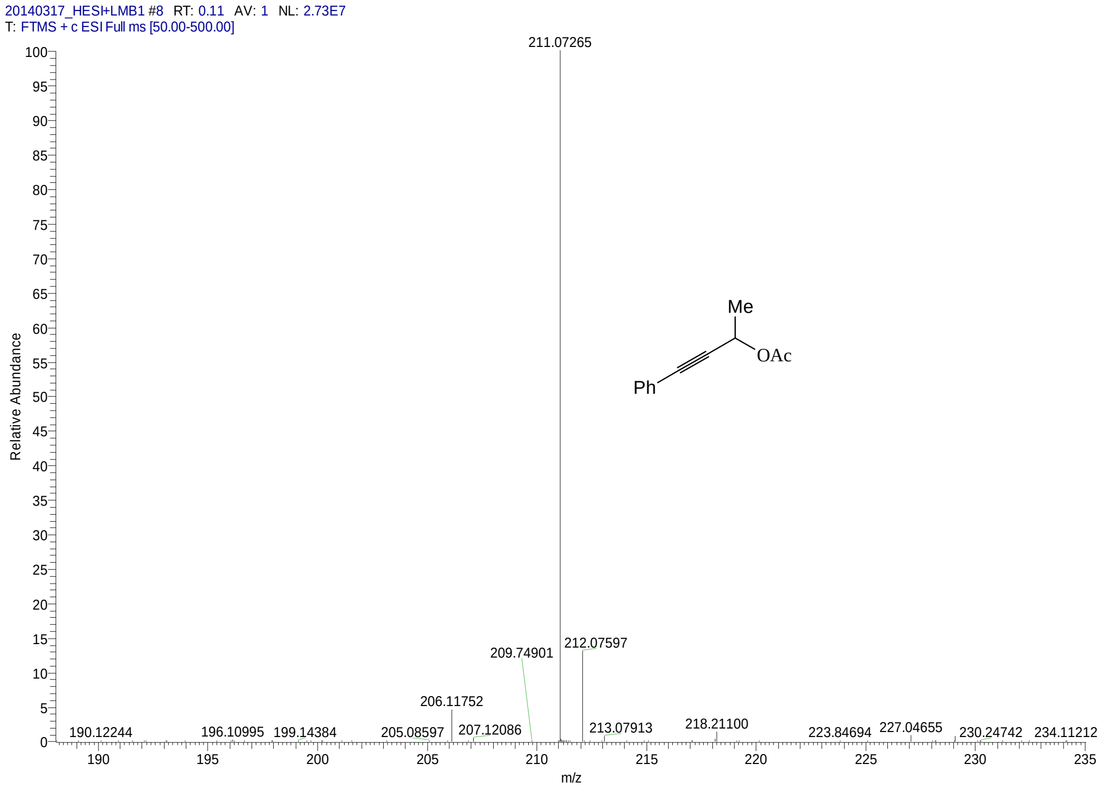


Figure S13 ESI mass spectra of 4-phenylbut-3-yn-2-yl acetate.

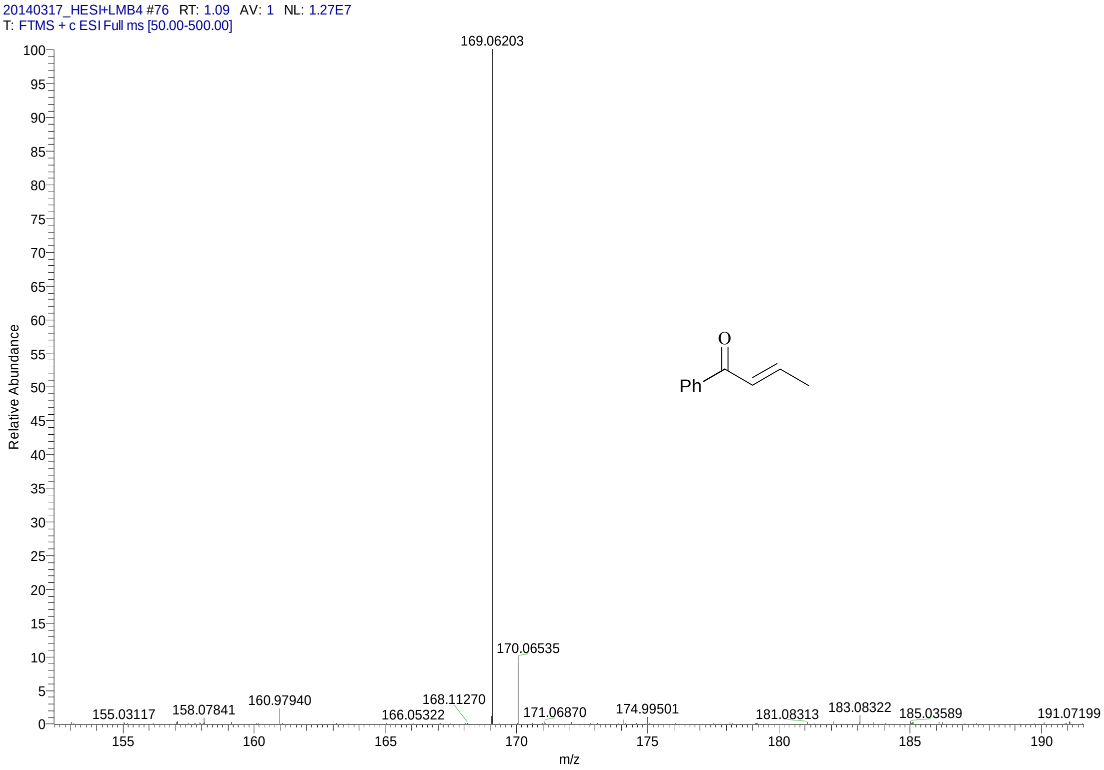


Figure S14 ESI mass spectra of (*E*)-1-phenylbut-2-en-1-one.

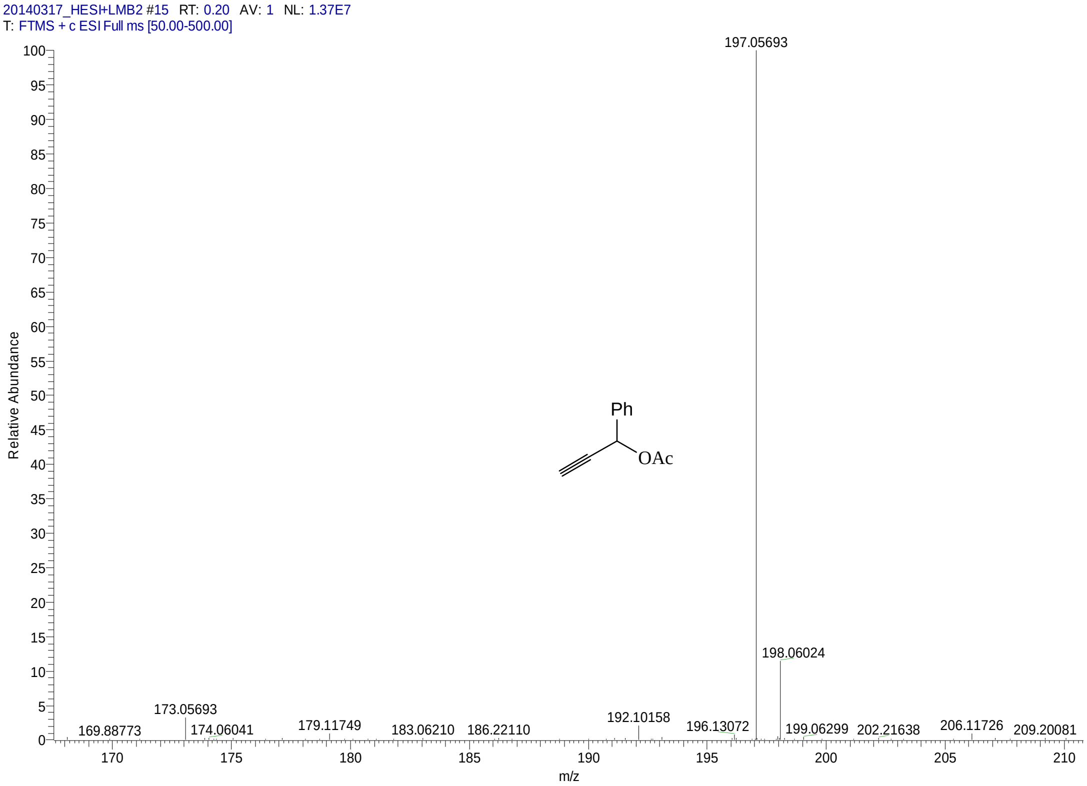


Figure S15 ESI mass spectra of 1-phenylprop-2-ynyl acetate.

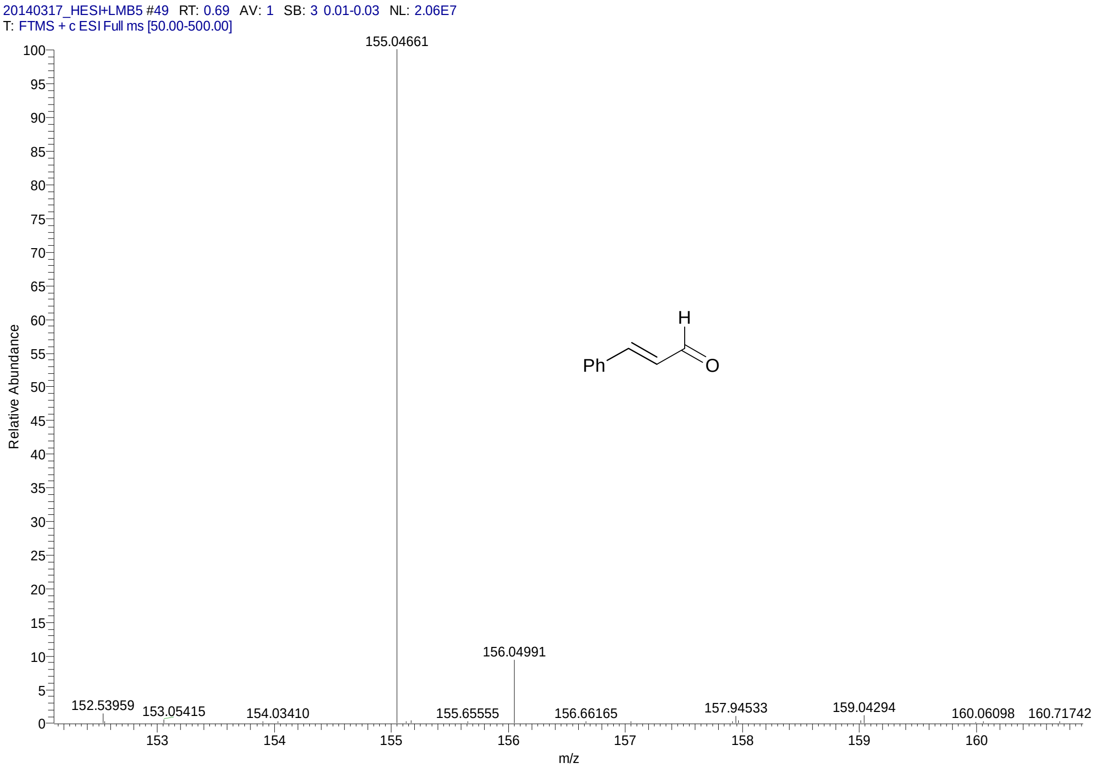


Figure S16 ESI mass spectra of cinnamaldehyde.

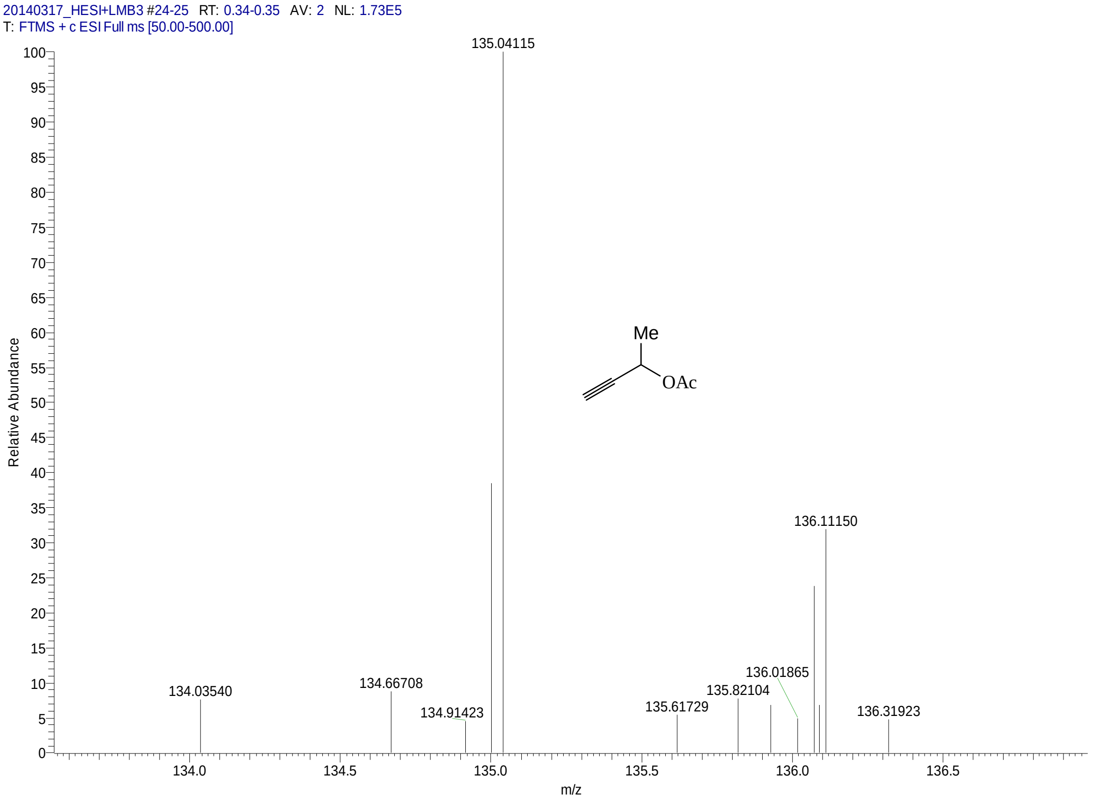


Figure S17 ESI mass spectra of but-3-yn-2-yl acetate.

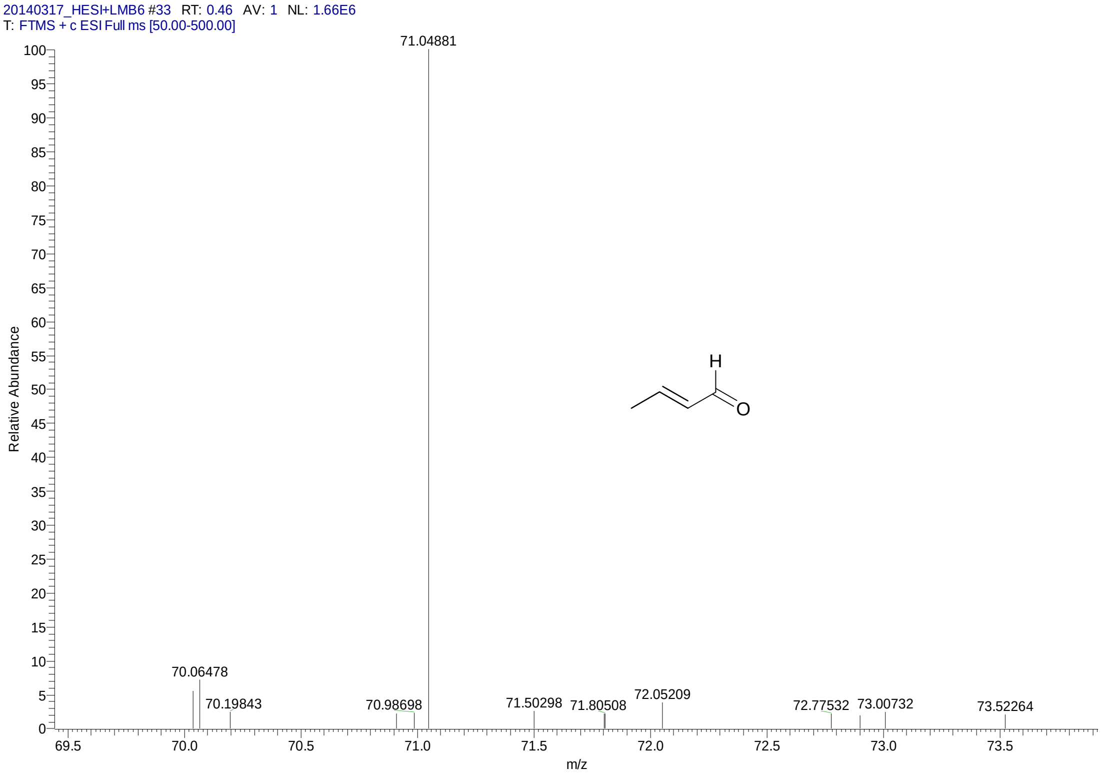


Figure S18 ESI mass spectra of (*E*)-but-2-enal.

References

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