Transition-metal-catalyzed synthesis of 1,3-diynes and ynamides from 2-bromo-1-iodoalkenes

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A. General method

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. $^1$H and $^{13}$C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer.

B. General procedure for the Pd-catalyzed synthesis of 1,3-diynes from 2-bromo-1-iodoalkenes

The mixture of 2-bromo-1-iodoalkene (0.5 mmol), triethylamine (1 mmol), and Pd(OAc)$_2$ (5 mol%) in DMF (1 mL) were stirred at 120 °C for 12 h in a 25 mL schlenk tube. Water (8 mL) was added after completion of the reaction, the aqueous solution was extracted with diethyl ether (3×5 mL) and the combined extract was dried with anhydrous MgSO$_4$. The solvent was removed and the crude product was separated by column chromatography to give the pure sample.

C. General procedure for the nano-Cu$_2$O-catalyzed synthesis of ynamides from 2-bromo-1-iodoalkenes

The mixture of 2-bromo-1-iodoalkene (0.25 mmol), carbamates (0.3 mmol), Cs$_2$CO$_3$ (2 equiv.), DMEDA (10 mol%), and nano-Cu$_2$O (5 mol%) in dioxane (1 mL) were stirred at 110 °C for 10 h in a 25 mL schlenk tube. Water (8 mL) was added after completion of the reaction, the aqueous solution was extracted with diethyl ether (3×5 mL) and the combined extract was dried with anhydrous MgSO$_4$. The solvent was removed and the crude product was separated by column chromatography to give the pure sample.
D. Characterization of Cu$_2$O particles

a) XRD Pattern of Cu$_2$O Particles.

b) SEM Images of nano-Cu$_2$O
E. NMR Spectra

$^1$H NMR and $^{13}$C NMR of 1,4-diphenylbuta-1,3-diyne (2a)
$^1$H NMR and $^{13}$C NMR of 1,4-dip-tolylbuta-1,3-diyne (2b)
$^1$H NMR and $^{13}$C NMR of 1,4-dim-tolylbuta-1,3-diyne (2c)
$^1$H NMR and $^{13}$C NMR of 1,4-dio-tolylbuta-1,3-diyne (2d)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(4-tert-butylphenyl)buta-1,3-diyn (2e)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne (2f)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(4-fluorophenyl)buta-1,3-diyne (2g)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(2-fluorophenyl)buta-1,3-diyne (2h)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(3-chlorophenyl)buta-1,3-diyne (2i)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(2-(trifluoromethyl)phenyl)buta-1,3-diyne (2j)
$^1$H NMR and $^{13}$C NMR of 1,4-bis(3,5-bis(trifluoromethyl)phenyl)buta-1,3-diyne (2k)
$^1$H NMR and $^{13}$C NMR of hexadeca-7,9-diyne (2l)
$^1$H NMR and $^{13}$C NMR of 1,6-dicyclohexylhexa-2,4-diyne (2m)
$^1$H NMR and $^{13}$C NMR of 3-(phenylethynyl)oxazolidin-2-one (3a)
$^1$H NMR and $^{13}$C NMR of 3-(p-tolylethynyl)oxazolidin-2-one (3b)
$^1$H NMR and $^{13}$C NMR of 3-((4-((tert-butyl)phenyl)ethynyl)oxazolidin-2-one (3c)
$^1$H NMR and $^{13}$C NMR of 3-((4-methoxyphenyl)ethynyl)oxazolidin-2-one (3d)
$^{1}$H NMR and $^{13}$C NMR of 3-((4-fluorophenyl)ethynyl)oxazolidin-2-one (3e)
$^1$H NMR and $^{13}$C NMR of 3-((4-chlorophenyl)ethyl)oxazolidin-2-one (3f)
$^1$H NMR and $^{13}$C NMR of (R)-4-benzyl-3-(phenylethynyl)oxazolidin-2-one (3g)
$^1$H NMR and $^{13}$C NMR of (R)-4-benzyl-3-((4-methoxyphenyl)ethynyl)oxazolidin-2-one (3h)
$^1$H NMR and $^{13}$C NMR of (R)-4-benzyl-3-((4-fluorophenyl)ethynyl)oxazolidin-2-one (3i)
$^1$H NMR and $^{13}$C NMR of ethyl phenyl(phenylethynyl)carbamate (3j)
$^1$H NMR and $^{13}$C NMR of ethyl phenyl(p-tolylethynyl)carbamate (3k)
$^1$H NMR and $^{13}$C NMR of ethyl ((4-chlorophenyl)ethynyl)(phenyl)carbamate (3l)