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Supporting Information

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Efficient Gold-Catalyzed Hydroamination of 1,3-Dienes

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Experimental Section

General Methods. Catalytic addition reactions were performed in sealed oven-dried Wheaton mini-vial under an atmosphere of dry nitrogen, in the dark at room temperature overnight. Flash column chromatography was performed with EM Science Geduran silica gel 60 (35-75μm). Thin layer chromatography was performed on EM Science silica gel 60 F254 plates (250 μm). NMR spectra were recorded on Varian XL 500 spectrometer for ^{1}H, ^{31}P, and ^{13}C NMR $CDCl_3$. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad), integration, coupling constant (Hz). Data for ^{13}C and ^{31}P NMR are reported in terms of chemical shift (δ, ppm). All chemicals were purchased from Aldrich and used as received. Dry 1,2-dichloroethane was obtained from Acros and used directly.

^{31}P NMR Studies (Figure S1)

The ^{31}P NMR of $Ph_3PAuOTf$ has already been reported.[1] Ph_3PAuCl (0.20 mmol, 0.10g) and AgOTf (0.20 mmol, 52mg) were dissolved in 0.50 mL of $CDCl_3$ and stirred for 5 min under N_2 in the dark. The mixture was filtered and the ^{31}P NMR spectrum recorded, (δ 28.10 ppm, s). A solution of $CbzNH_2$ (1.0 mmol, 0.15g) in 0.5 mL of $CDCl_3$ was then added and the ^{31}P NMR spectrum recorded. There was no difference between the spectra. A solution of 3-methyl-1,3-pentadiene (1.0 mmol, 0.11 mL) in 0.5 mL of $CDCl_3$ was added to the catalyst/carbamate solution and the ^{31}P NMR spectrum recorded. The ^{31}P NMR signal of the catalyst moved downfield to δ 29.88 ppm. A small peak at 41.79 ppm was also observed, which is the signal of $(Ph_3P)_2Au^+$.[2]

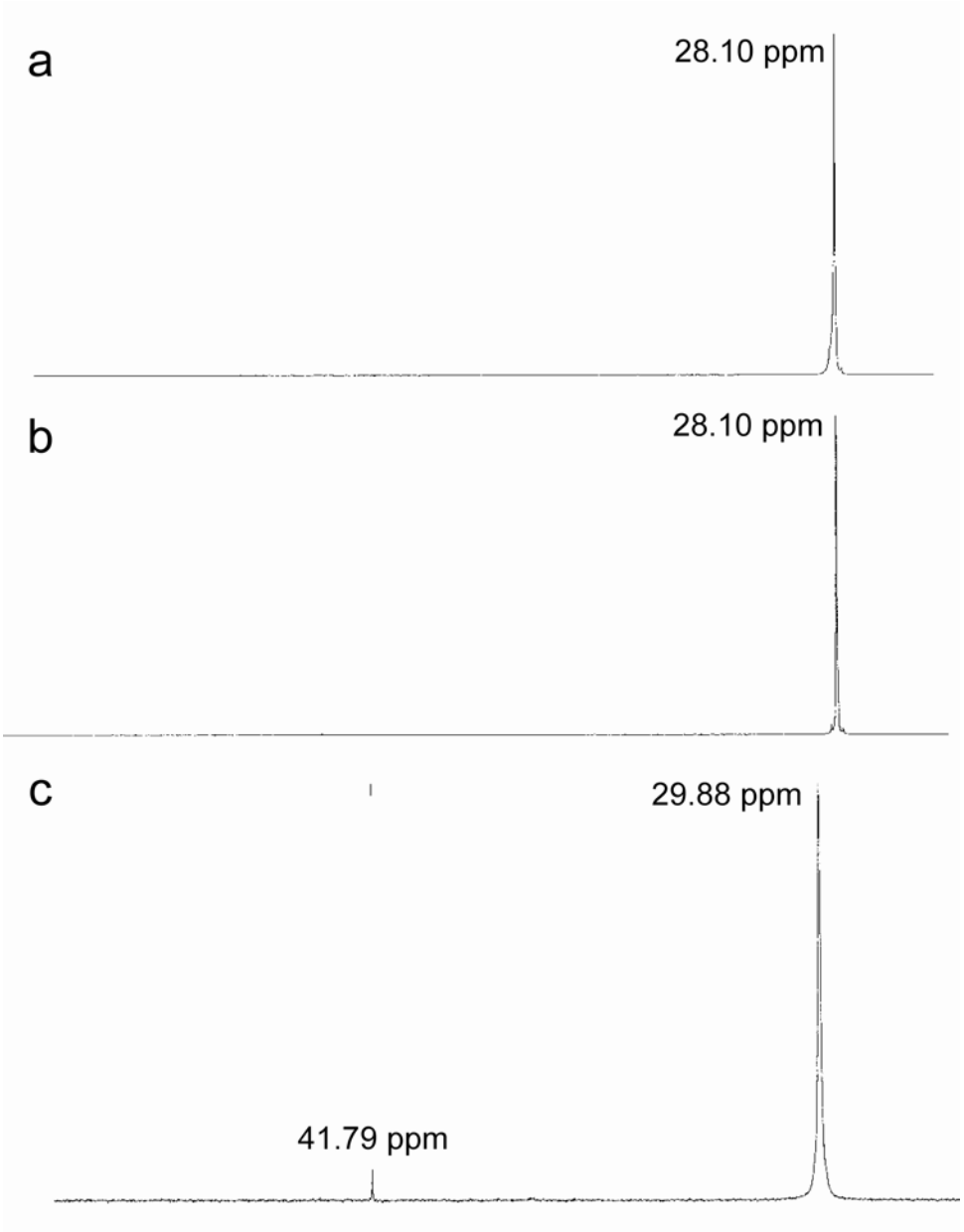


Figure S1: ^{31}P NMR spectra of a) $Ph_3PAuOTf$, b) $Ph_3PAuOTf$ and $CbzNH_2$, and c) $Ph_3PAuOTf$, $CbzNH_2$, and 3-methyl-1,3-pentadiene in CD_3Cl.

^{13}C NMR Studies (Figures S2, S3)

Benzyl carbamate (0.50 mmol, 75mg) and 3-methyl-1,3-pentadiene (0.60 mmol, 70μL) were dissolved in 0.50 mL of $CDCl_3$ under N_2 and the ^{13}C NMR spectrum was recorded (**S2**). Ph_3PAuCl (0.50 mmol, 0.25g) and AgOTf (0.50 mmol, 0.13g) were dissolved in 0.50 mL of $CDCl_3$ in the dark under N_2. After 5 min. of stirring, the mixture was filtered. This solution was added to the $CbzNH_2$/diene solution, and the ^{13}C NMR spectrum was recorded (**S3**). It can be seen that the signals attributed to the diene's internal carbon of the terminal olefin[3] at δ 110.03 (trans) and 112.99 (cis) are drastically reduced and are replaced with signals at δ 119.30 and

121.85 ppm. The signals of the terminal carbon of that olefin at δ 133.37 (cis) and 141.44 (trans) are also reduced.

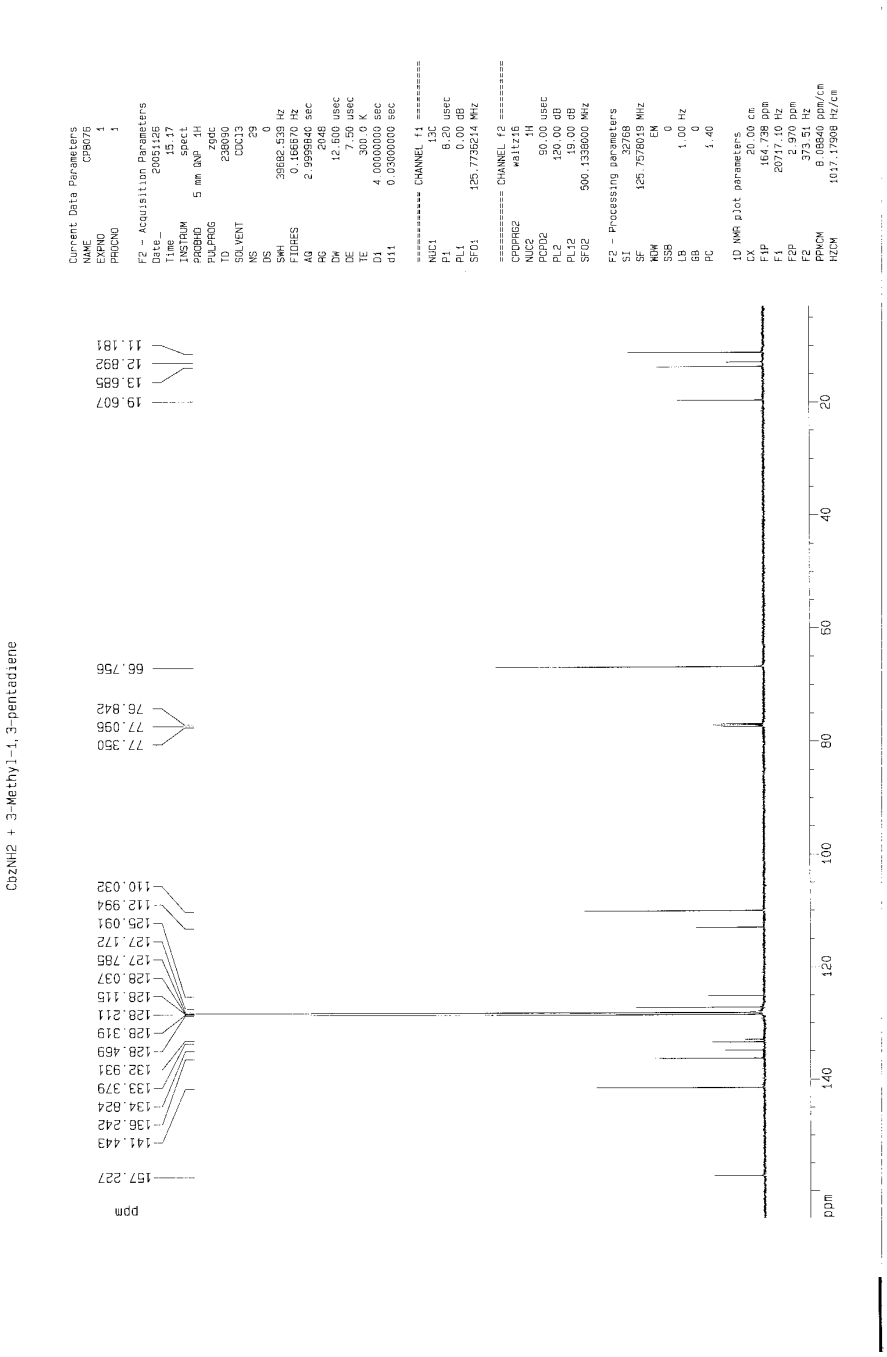


Figure S2: ^{13}C of $CbzNH_2$ and 3-methyl-1,3-pentadiene.

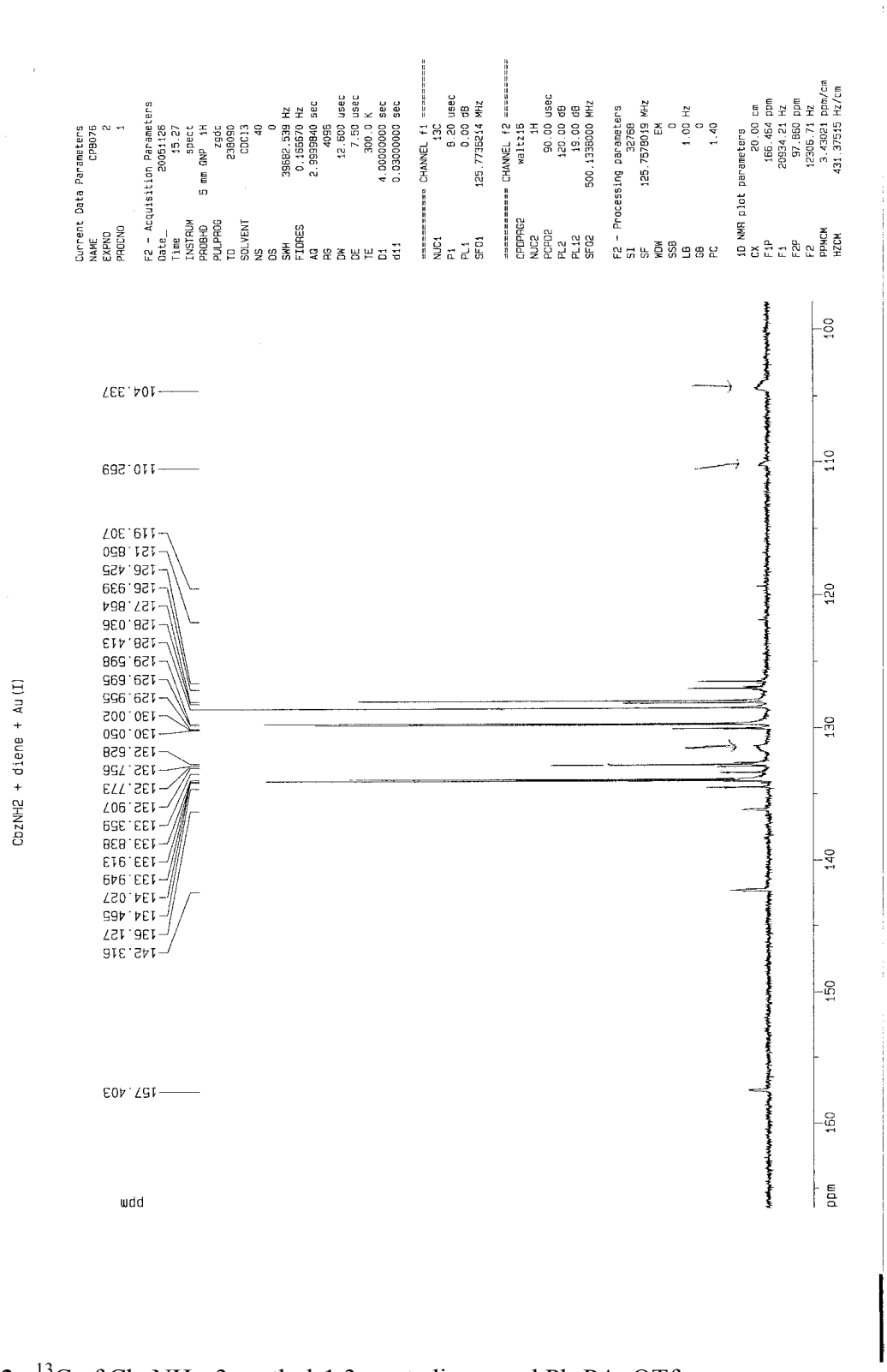
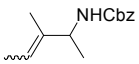


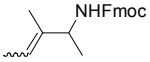
Figure S3: ^{13}C of $CbzNH_2$, 3-methyl-1,3-pentadiene, and $Ph_3PAuOTf$.

(1,2-Dimethyl-but-2-enyl)-carbamic acid benzyl ester



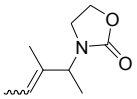
1c: A pale yellow oil. ^{1}H NMR δ 1.20 (d, 3H, *J*=7.00), 1.58 (d, 3H, *J*=6.00), 1.58 (s, 3H), 4.16 (bs, 1H), 4.72 (bs, 1H), 5.08 (q, 1H, *J*=13.5), 5.43 (bd, *J*=5.00), 7.30-7.35 (m, 5H). ^{13}C NMR δ 12.56, 13.10, 19.81, 29.64, 53.13, 66.42, 119.09, 127.99, 128.40, 136.30, 136.61, 155.54.

(1,2-Dimethyl-but-2-enyl)-carbamic acid 9H-fluoren-9-ylmethyl ester



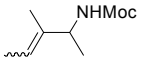
2c: Pale yellow flakes. ^{1}H NMR δ 1.23 (bd, 3H, *J*=6.00), 1.58 (d, 3H, *J*=21.5), 1.61 (s, 3H), 4.17 (bs, 1H), 4.22 (t, 1H, *J*=6.50), 4.41 (bd, 2H, *J*=6.50), 4.69 (bs, 1H), 5.44 (bs, 1H), 7.31 (t, 2H, *J*=7.50), 7.40 (t, 2H, *J*=7.50), 7.59 (dd, 2H, *J*=5.00, 6.50), 7.77 (d, 2H, *J*=7.50). ^{13}C NMR δ 12.73, 13.144, 19.87, 47.29, 53.08, 66.31, 119.10, 119.89, 124.98, 126.95, 127.57, 136.28, 141.26, 143.99, 155.56.

3-(1,2-Dimethyl-but-2-enyl)-oxazolidin-2-one



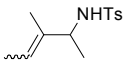
3c: An off-clear oil. ^{1}H NMR δ 1.28 (d, 3H, *J*=6.92), 1.618 (s, 3H), 1.64 (d, 3H, *J*=5.65), 3.25 (q, 1H, *J*=6.83), 3.43 (q, 1H, *J*=7.74), 4.26-4.33 (m, 2H), 4.38 (q, 1H, *J*=6.84), 5.46 (q, 1H, *J*=4.16). ^{13}C NMR δ 13.24, 14.53, 15.09, 40.09, 53.61, 61.87, 120.95, 133.89, 158.18.

(1,2-Dimethyl-but-2-enyl)-carbamic acid methyl ester



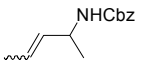
4c: A pale yellow oil. ^{1}H NMR δ 1.19 (d, 3H, *J*=11.3), 1.59 (d, 3H, *J*=6.57), 1.60 (s, 3H), 3.65 (s, 3H), 4.15 (bs, 1H), 4.72 (bs, 1H), 5.44 (bd, 1H, *J*=5.84). ^{13}C NMR δ 12.53, 13.00, 19.80, 29.56, 51.73, 52.99, 118.93, 136.32, 156.16.

N-(1,2-Dimethyl-but-2-enyl)-4-methyl-benzenesulfonamide



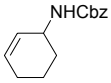
5c: A pale yellow wax. ^{1}H NMR δ 1.08 (d, 3H, *J*=4.50), 1.24 (s, 3H), 1.34 (d, 3H, *J*=6.50), 2.35 (s, 3H), 3.77 (m, 1H, *J*=7.00), 4.47 (d, 1H, *J*=7.00), 5.22 (q, 1H, *J*=6.50), 7.19 (d, 2H, *J*=5.50), 7.63 (d, 2H, *J*=6.50). ^{13}C NMR δ 10.95, 12.86, 20.34, 21.37, 56.73, 121.258, 127.22, 129.11, 134.98, 137.96, 142.77.

(1-Methyl-but-2-enyl)-carbamic acid phenyl ester



6c: A pale yellow oil. ^{1}H NMR δ 1.21 (d, 3H, *J*=6.50), 1.67 (d, 3H, *J*=6.50), 4.24 (bs, 1H), 4.69 (bs, 1H), 5.09 (bq, 1H, *J*=12.0), 5.42 (dd, 1H, *J*=10.0, 14.5), 5.59 (m, 1H), 7.31-7.36 (m, 5H). ^{13}C NMR δ 17.56, 21.06, 48.21, 66.45, 125.29, 127.96, 128.40, 132.62, 136.58, 155.47.

Cyclohex-2-enyl-carbamic acid phenyl ester [4]



7c: Pale yellow flakes. ^{1}H NMR δ 1.54-1.58 (m, 2H), 1.62-1.66 (m, 2H), 1.97 (m, 1H), 1.99-2.00 (m, 2H), 4.23 (bs, 1H), 4.73 (bd, 1H), 5.10 (s, 2H), 5.61 (d, *J*=10, 1H), 5.83 (d, *J*=4, 1H), 7.31-7.37 (m, 5H). ^{13}C NMR δ 19.53, 24.69, 29.64, 46.26, 66.48, 127.67, 128.01, 128.07, 128.44, 130.73, 136.54, 155.58.

[1] M. Preisenberger, A. Schier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1999**, 1645.
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[4] W. J. Brouillette, A. Saeed, A. Abuelyaman, T. L. Hutchison, P. E. Wolkowicz, J. B. McMillin, *J. Org. Chem.* **1994**, *59*, 4297.