Supporting Information:

Efficient and exceptionally selective semireduction of alkynes using a supported gold catalyst under CO atmosphere

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Experimental Details

1. General

Gold catalysts including 1 wt% Au/TiO_2 (catalogue number 79-0165), 1 wt% Au/Al_2O_3 (catalogue number 79-0160) and 1 wt% Au/ZnO (catalogue number 79-0170) were supplied by Mintek. 5 wt% Pd/C (stock # 38300), 5 wt% Pt/C (stock # 38321), 5 wt% Ru/Al_2O_3 (stock #11749), Lindlar catalyst (5 wt% Pd on $CaCO_3$ poisoned with Pb, stock# 43172) were provided by Alfa Aesar. Inductively coupled plasma (ICP) measurements were performed on a Thermo Electron IRIS Intrepid II XSP spectrometer. BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of N_2 at liquid N_2 temperature, using a Micromeri- tics TriStar 3000 equipment. Powder X-ray diffraction (XRD) analysis of the catalysts was carried out on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA. Transmission electron microscopy (TEM) observations were carried out using a JEOL 2011 electron microscope operating at 200 kV. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX spectrometer. GC was carried out on a Shimadzu GC-17A equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and FID detector.

2. Catalyst preparation

Preparation of high surface area TiO_2 (HSA-TiO_2): HSA-TiO_2 was prepared through a previously reported method.[S1] 10 mL of titanium bis(ammonium lactate) dihydroxide (TALH) aqueous solution (50%) and a desired amount of 0.1 M urea were mixed followed by the addition of distilled water to reach a final volume of 100 mL. The resulting solution was transferred into a Teflon-lined autoclave, which was sealed and kept at 160

°C for 24 h. Then the autoclave was naturally cooled in air. The precipitates were separated by centrifugation, washed with distilled water until pH 7. The sample was oven dried overnight at 60 °C, and then calcined at 400 °C for 3 h. The BET surface area of the resultant material was 154 m^2/g.

Preparation of Au/HSA-TiO_2 and Au/TiO_2: Au/HSA-TiO_2 and Au/TiO_2 catalysts were prepared by a modified deposition-precipitation (DP) method according to our previous work.[S2] Briefly, an appropriate amount of aqueous solutions of chloroauric acid ($HAuCl_4$) was heated to 80 °C under vigorous stirring. The pH was adjusted to 8 by dropwise addition of NaOH (0.2 M), and then 1.0 g HSA-TiO_2 or TiO_2 (Degussa P25, 45 m^2/g) was dispersed in the solution. The mixture was stirred for 2 h at 80 °C, after which the suspension was cooled to RT. Extensive washing with deionized water was then followed until it was free of Cl^- ions. The samples were dried under vacuum at room temperature for 12 h and then calcined in air at 350 °C for 2 h.

Preparation of Au/CeO_2: Au/CeO_2 catalysts were prepared by a routine DP method. An appropriate amount of aqueous solutions of chloroauric acid ($HAuCl_4$) was heated to 80 °C under vigorous stirring. The pH was adjusted to 9 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO_2 (Degussa Adnano 50, 50 m^2/g) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to RT. Extensive washing with deionized water was then followed until it was free of Cl^- ions. The samples were dried under vacuum at RT for 12 h, then reduced in 5 vol% H_2/Ar stream at 300 °C for 2 h.

Preparation of Au/ZrO_2: The ZrO_2 support was prepared by a conventional precipitation method following the reported procedure.[S3] Au/ZrO_2 catalysts were prepared according to our previously reported procedure:[S4] An appropriate amount of ZrO_2 was added to the aqueous solution of $HAuCl_4$ (0.25 mM), the pH of which was adjusted to 9 with 0.25 M NH_4OH under stirring. The aqueous dispersion was stirred for 8 h at 25 °C while the pH was maintained constantly at 9.0, and then filtered. Extensive washing with deionized water was then followed until it was free of Cl^- ions. The sample was dried under vacuum at RT for 12 h, and reduced in 5 vol% H_2/Ar stream at 300 °C for 2 h.

Preparation of Ir/TiO_2: Ir/TiO_2 catalysts were prepared by a routine incipient wetness technique. 1.0 g TiO_2 (Degussa P25, 45 m^2/g) was added to 10 mL of an aqueous solution containing appropriate amounts of H_2IrCl_6. After a perfect mixing of the corresponding slurries, samples were dried at 100 °C for 5 h and then reduced in a 5vol% H_2/Ar stream at 300 °C for 2 h.

3. Catalytic activity measurements

General procedure for semireduction of alkynes by CO/H_2O: A mixture of substrate (0.5 mmol), supported metal catalysts (metal 1 mol%), solvent (4.5 mL), and water (0.5 mL) was put into a batch autoclave reactor (25 mL). After sealing the reactor, CO was fed to the reactor through a gas inlet tube to the arranged pressure. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 60 °C. The conversion and product selectivity were periodically determined by GC-FID using anisole as an internal standard.

Recovery and reuse of Au/HSA-TiO_2: The reused catalyst was recovered by filtering the solid Au/HSA-TiO_2 from liquid phase after the reaction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried under vacuum at room temperature for 12 h to obtain the reused catalyst. In the five successive cycles, the conversion of phenylacetyene was >99 %, 97 %, 98%, 97% and 96 %, the selectivity of styrene kept >99% (GC yield).

Procedure for 10-mmol scale semireduction of alkynes by CO/H_2O: A mixture of phenylacetyene (10 mmol), Au/HSA-TiO_2 (Au: 0.1 mol%), ethanol (18 mL) and water (2 mL) was put into a batch reactor (100 mL). After sealing the reactor, CO (20 atm) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 60 °C for 19 h. The conversion and product selectivity were periodically determined by GC-FID using anisole as an internal standard.

Procedure for semireduction of phenylacetyene by CO in the absence of water: A mixture of phenylacetyene (0.5 mmol), Au/HSA-TiO_2 (Au: 1 mol%), and anhydrous ethanol (5 mL) was put into a batch reactor (25 mL). After sealing the reactor, CO (10 atm) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 60 °C. Under these conditions, no conversion of styrene was observed up to 1 h of contact time.

Procedure for semireduction of phenylacetyene with H_2: A mixture of phenylacetyene (0.5 mmol), Au/HSA-TiO_2 (Au: 1 mol%) and anhydrous ethanol (5 mL) was put into a batch reactor (25 mL). After sealing the reactor, H_2 (10 atm) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 60 °C. The conversion and product selectivity were periodically determined by GC-FID using anisole as an internal standard.

Procedure for CO oxidation by supported gold catalysts: A mixture of catalyst, ethanol (4.5 mL), and water (0.5 mL) was put into a batch reactor (25 mL). After sealing the reactor, the reactor was filled with CO and O_2 to give a CO to O_2 ratio of 1:9 at a total pressure of 20 atm. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 25 °C. The initial rate of CO conversion was calculated by gas analysis after reaction.

Procedure for semireduction of various alkynes with CO/D_2O into 1,2-dideuterioalkenes: A mixture of substrate (0.5 mmol), Au/HSA-TiO_2 (Au: 1 mol%), acetonitrile (4.5 mL) and deuteroxide (D_2O, 0.5 mL) was put into a batch autoclave reactor (25 mL). After sealing the reactor, CO was fed to the reactor through a gas inlet tube to the arranged pressure. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at certain temperatures. The conversion, product selectivity and deuterium efficiency were determined by NMR and GC-FID using anisole as an internal standard. To avoid the H-D exchange between ethanol and deuteroxide which led to a low deuteration ratio, acetonitrile was used instead of ethanol as the solvent.

4. Results

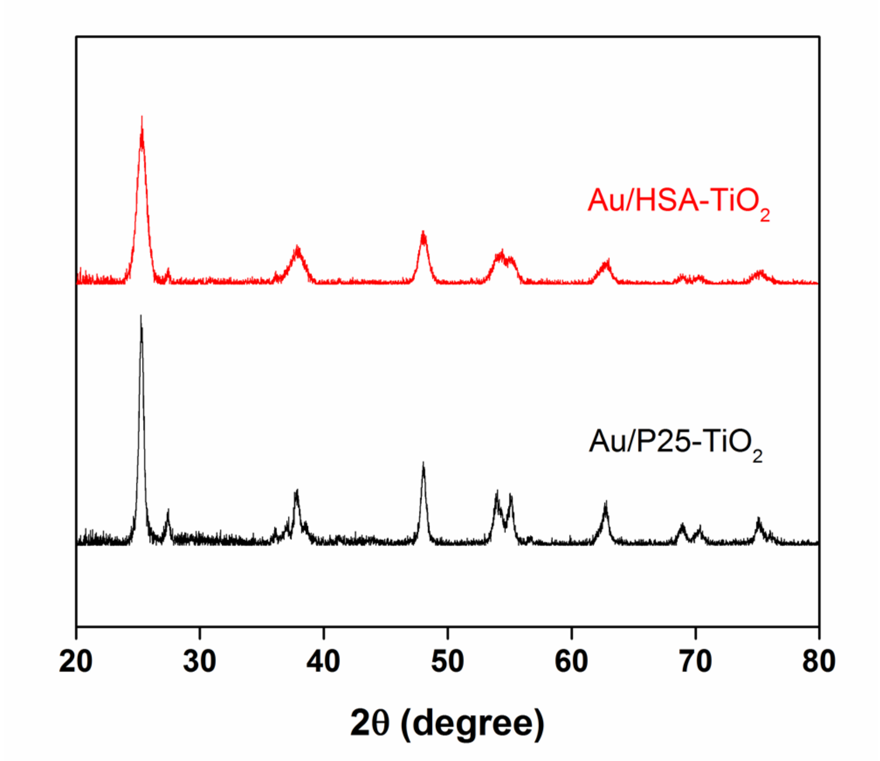
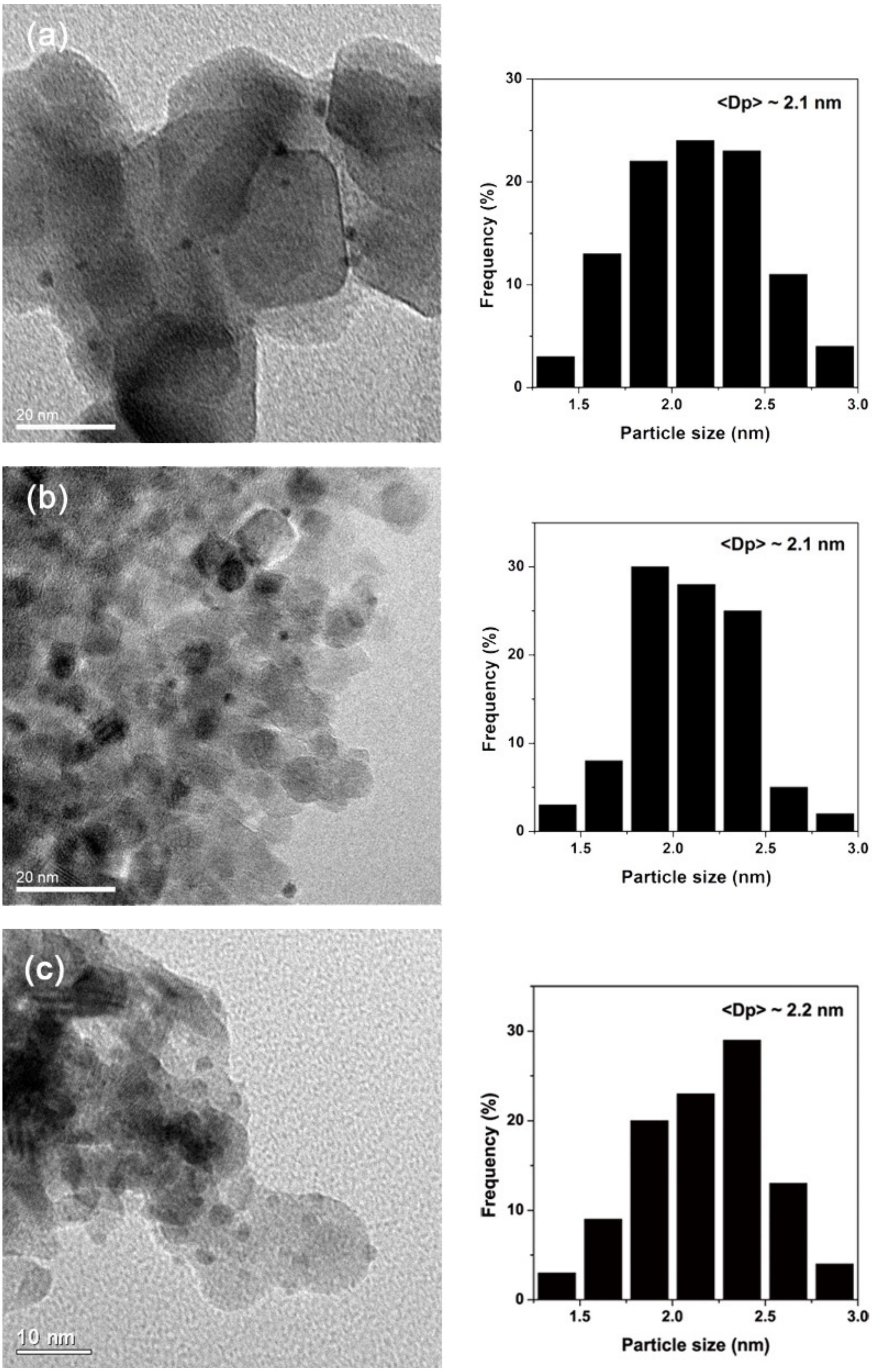


Fig. S1 X-ray diffraction (XRD) patterns for Au/HSA-TiO_2 and Au/P25-TiO_2.


(a)
20 nm
<Dp> ~ 2.1 nm
Frequency (%)
Particle size (nm)
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10
20
30
1.5
2.0
2.5
3.0
(b)
20 nm
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Frequency (%)
Particle size (nm)
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1.5
2.0
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3.0
(c)
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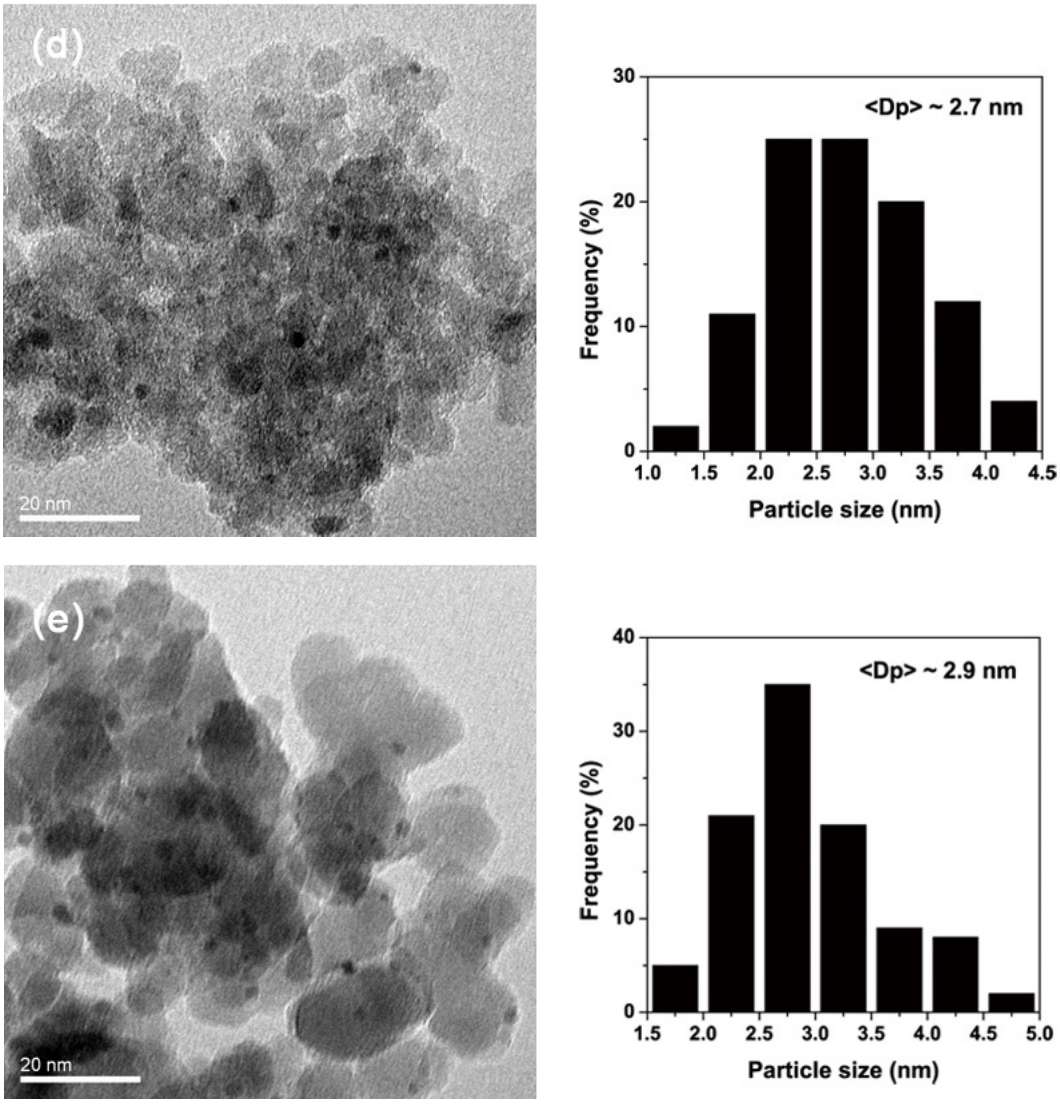


Fig. S2 TEM images and size distribution of (a) Au/P25-TiO_2, (b) Au/HSA-TiO_2, (c) Au/ZrO_2, (d) Au/Al_2O_3 and (e) Au/ZnO.

Table S1 Semireduction of phenylacetylene with CO/H_2O in various solvents.[a]

Entry	Solvent	Conversion[b] [%]	Selectivity[b] [%]
1	MeOH	61	>99
2	EtOH	>99	>99
3	n-PrOH	74	>99
4	i-PrOH	69	>99
5	Acetone	42	>99
6	MeCN	85	>99
7	THF	trace	/
8	DMF	41	89
9	Toluene	21	48
10	H_2O	38	>99

a Reaction conditions: Phenylancetyene (0.5 mmol), Au/HSA-TiO_2 (Au 1 mol%), CO (10 atm), H_2O (0.5 mL), Solvent (4.5 mL), 60^{o}C, 1h. [b] The conversion and selectivity were determined by means of GC.

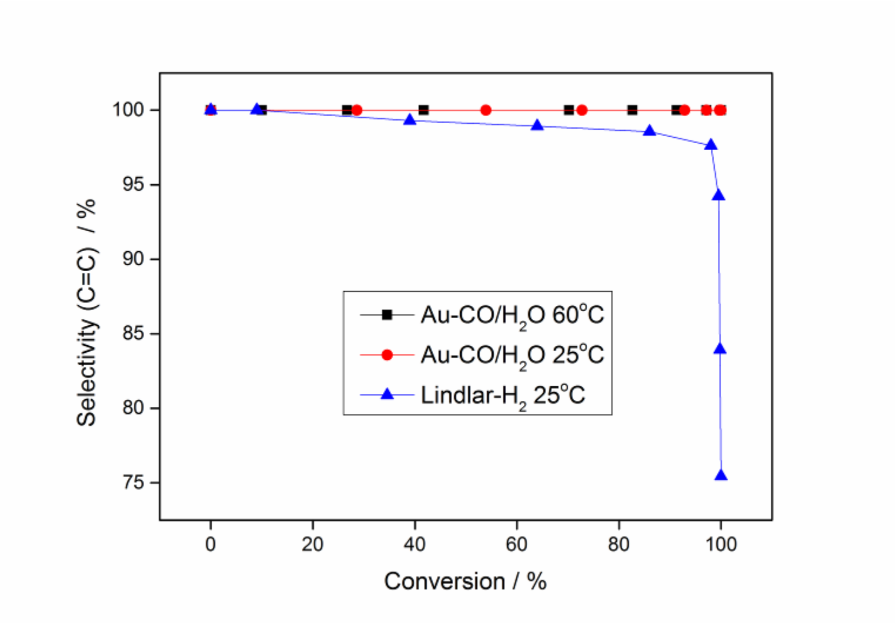


Fig. S3 Styrene selectivity depending on phenylacetyene conversion. Au-CO/H_2O system: phenylacetyene (0.5 mmol), Au/HSA-TiO_2 (Au 1 mol%), CO (10 atm), H_2O (0.5 mL), EtOH (4.5 mL); Lindlar-H_2 system: phenylacetyene (0.5 mmol), Lindlar catalyst (Pd 1 mol%), H_2 (1 atm), EtOH (5 mL).

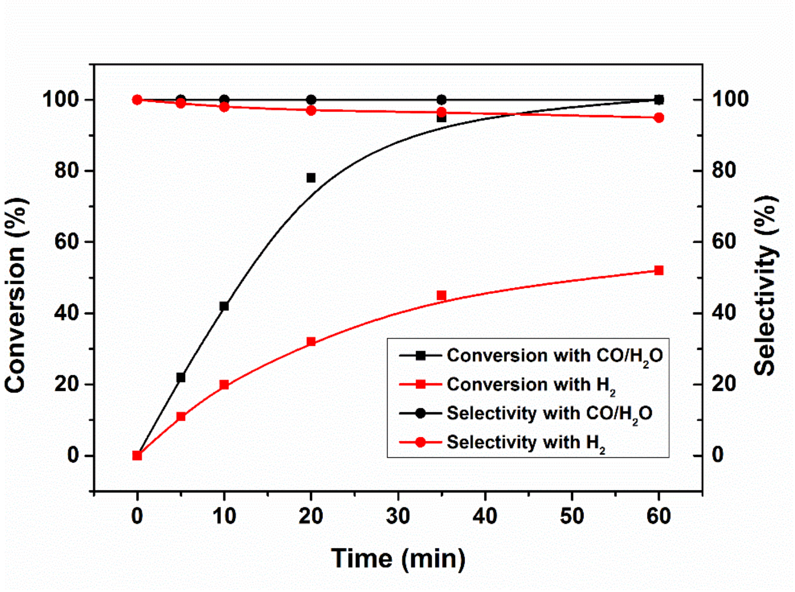


Fig. S4 Comparison of CO/H_2O system and H_2 system. Au-CO/H_2O: phenylacetyene (0.5 mmol), Au/HSA-TiO_2 (Au 1 mol%), CO (10 atm), H_2O (0.5 mL), EtOH (4.5 mL), 60 °C; Au-H_2: phenylacetyene (0.5 mmol), Au/HSA-TiO_2 (Au 1 mol%), H_2 (10 atm), EtOH (5 mL), 60 °C.

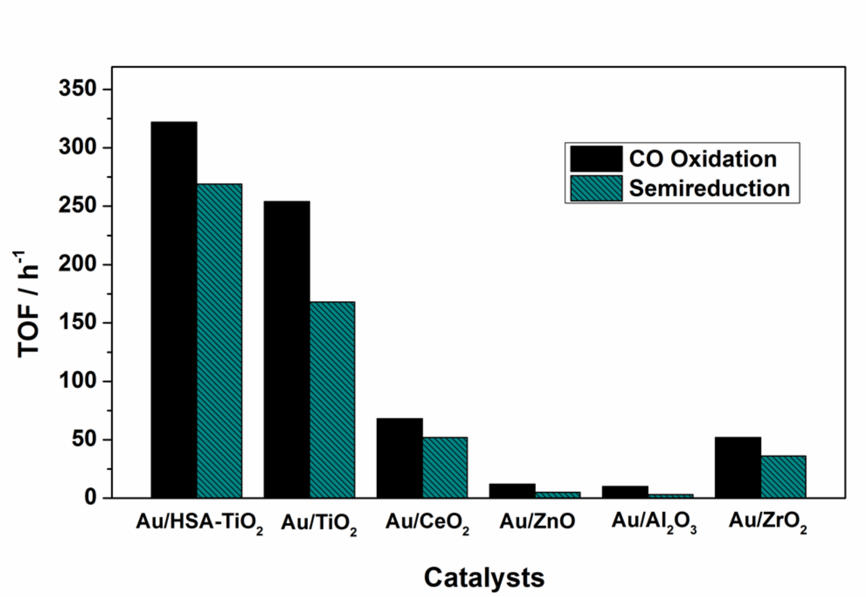


Fig. S5 Support effect of Au catalysts for semireduction of phenylancetyene and CO oxidation. Semireduction of phenylancetyene: 0.5 mmol substrate, Au 1 mol%, CO (10 atm), H_2O (0.5 mL), EtOH (4.5 mL), 60 °C; CO oxidation: Au 5×10^{-3} mmol, EtOH (4.5 mL), H_2O (0.5 mL), CO (2 atm), O_2 (18 atm), 25 °C. All TOF calculations were based on initial activities below 15 % conversion of the substrates or CO.

5. Reference

[S1] T. A. Kandiel, A. Feldhoff, L. Robben, R. Dillert and D. W. Bahnemann, *Chem. Mater.*, 2010, **22**, 2050-2060.

[S2] L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem. Int. Ed.*, 2009, **48**, 9538-9541.

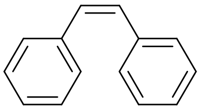
[S3] X. Zhang, H. Shi and B. Q. Xu, *Angew. Chem. Int. Ed.*, 2005, **44**, 7132-7135.

[S4] Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *J. Am. Chem. Soc.*, 2012, **134**, 8926-8933.

6. Product identification

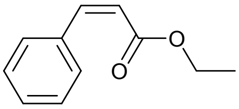
The products were characterized by GC, GC-MS, and NMR. Retention times (GC) and chemical shifts (^{1}H and ^{13}C NMR) of the products were in agreement with those of authentic samples.

2h:



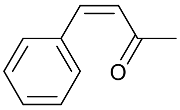
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25-7.16 (m, 10H), 6.60 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.3, 130.3, 128.9, 128.2, 127.1.

2i:



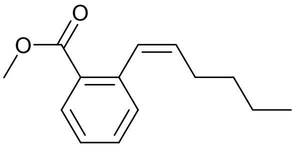
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, *J*=7.5 Hz, 2H), 7.37-7.32 (m, 3H), 6.95 (d, *J*=13.0 Hz, 1H), 5.95 (d, *J*=13.0 Hz, 1H), 4.17 (q, *J*=7.2, 2H), 1.24 (t, *J*=7.0, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.2, 142.9, 134.9, 129.7, 129.0, 128.0, 119.9, 60.3, 14.1.

2j:



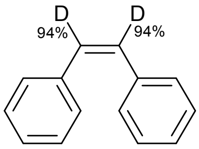
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56-7.50 (m, 3H), 7.41-7.39 (m, 3H), 6.74-6.70 (d, *J*=16.5 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.4, 143.4, 134.4, 130.5, 129.0, 128.2, 127.2, 27.5.

2k:



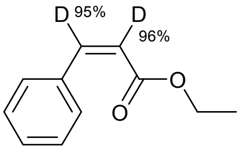
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, *J*=8.0 Hz, 1H), 7.44 (t, *J*=7.5 Hz, 1H), 7.27 (q, *J*=8.5 Hz, 2H), 6.83 (d, *J*=12.0 Hz, 1H), 5.73-5.67 (m, 1H), 3.85 (s, 3H), 2.09 (q, *J*=7.3 Hz, 2H), 1.39-1.33 (m, 2H), 1.30-1.23 (m, 2H), 0.82 (t, *J*=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.8, 139.2, 132.3, 131.4, 130.8, 130.3, 129.3, 128.5, 126.5, 51.9, 31.9, 28.0, 22.3, 13.9.

[D$_2$]-**2h**:



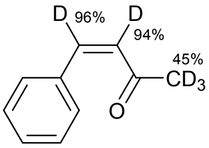
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.26-7.18 (m, 10H), 6.59 (s, 0.12H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 137.2, 130.3-129.6 (m), 128.9, 128.2, 127.1.

[D$_2$]-**2i**:



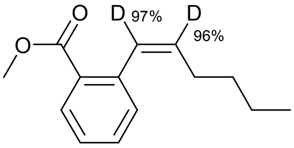
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.59 (d, *J*=7.0 Hz, 1.5 Hz, 2H), 7.37-7.32 (m, 3H), 6.94 (s, 0.05H), 5.95 (s, 0.04H), 4.17 (q, *J*=7.0 Hz, 2H), 1.24 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 166.2, 142.9-142.4(m), 134.8, 129.7, 129.0, 128.0, 119.9-119.4 (m), 60.3, 14.1.

[D$_2$]-**2j**:



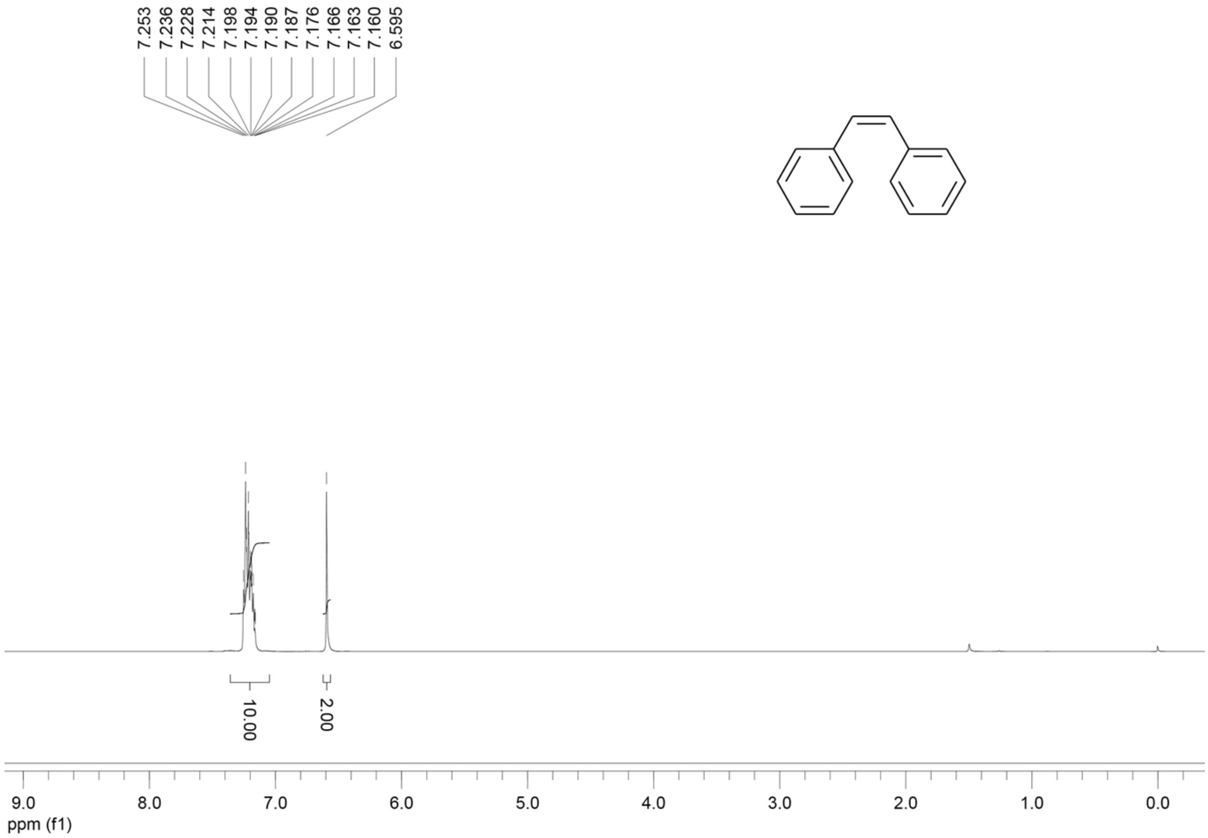
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.56-7.51 (m, 2.04H), 7.41-7.37 (m, 3H), 6.72-6.71 (t, *J*=2.0 Hz, 0.06H), 2.38-2.35 (m, 1.64H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 198.4, 143.3-143.0 (m), 134.4, 130.5, 129.0, 128.2, 127.1-126.6 (m), 27.5-27.1 (m).

[D$_2$]-**2k**:

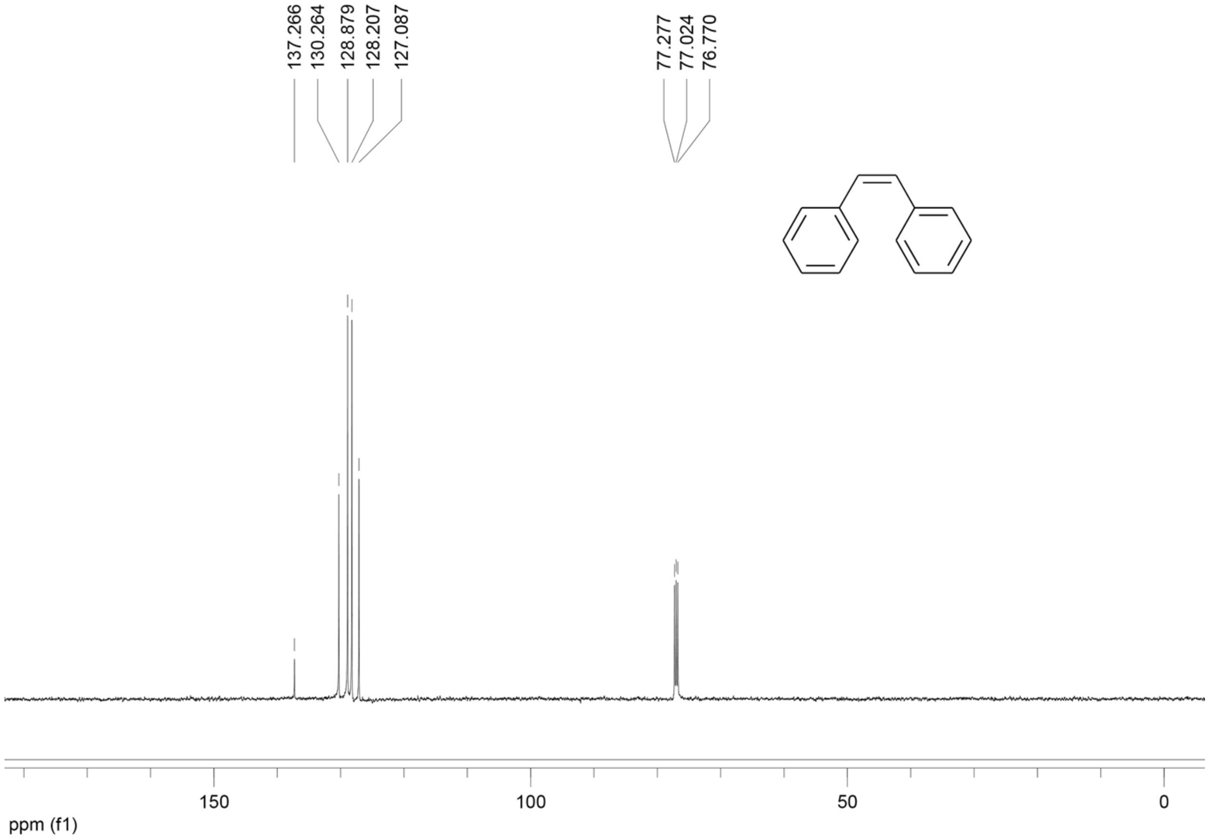


^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.88 (d, *J*=7.0 Hz, 1H), 7.42 (t, *J*=7.5 Hz, 1H), 7.25 (q, *J*=8.6 Hz, 2H), 6.80 (s, 0.03H), 5.67 (s, 0.04H), 3.83 (s, 3H), 2.07 (t, *J*=7.3 Hz, 2H), 1.36-1.30 (m, 2H), 1.28-1.21 (m, 2H), 0.79 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 167.8, 139.1, 132.3-132.0 (m), 131.4, 130.8, 130.3, 129.3, 128.5-128.3 (m), 126.5, 51.9, 31.9, 27.9, 22.3, 13.9.

^{1}H NMR of **2h**



^{13}C NMR of **2h**



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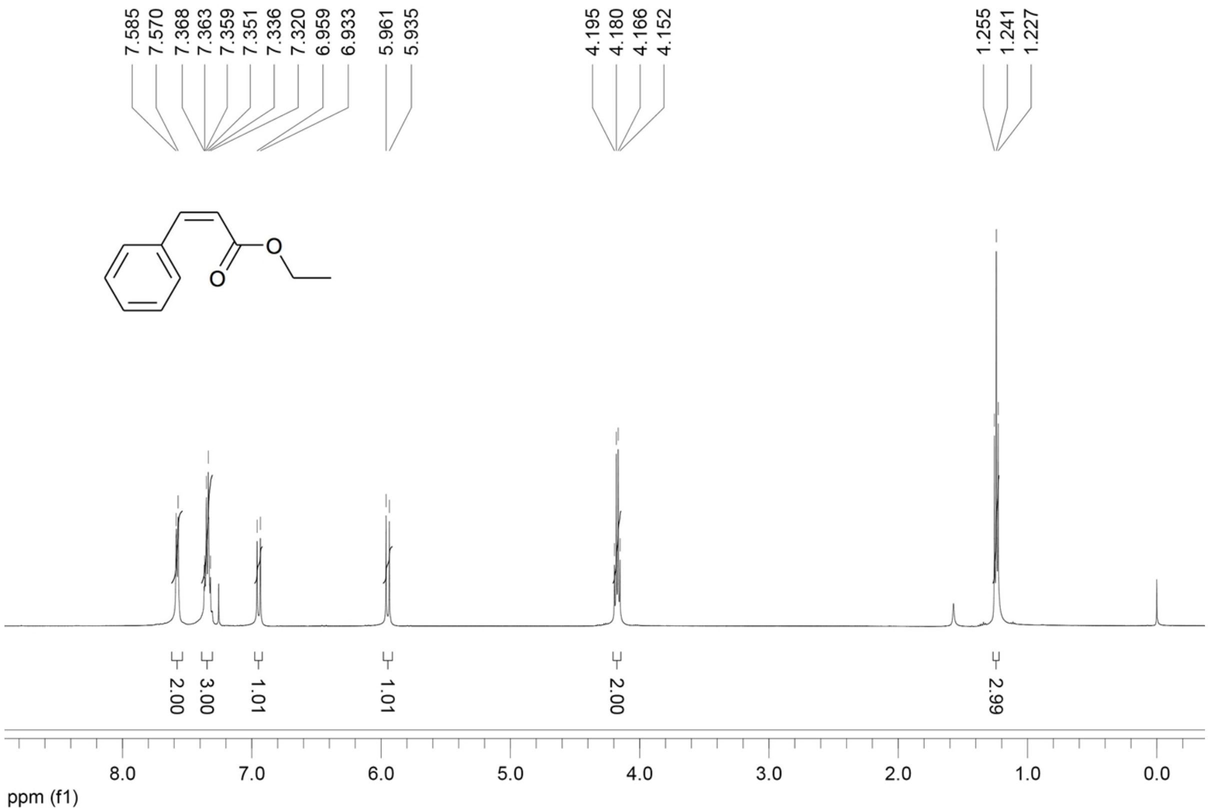

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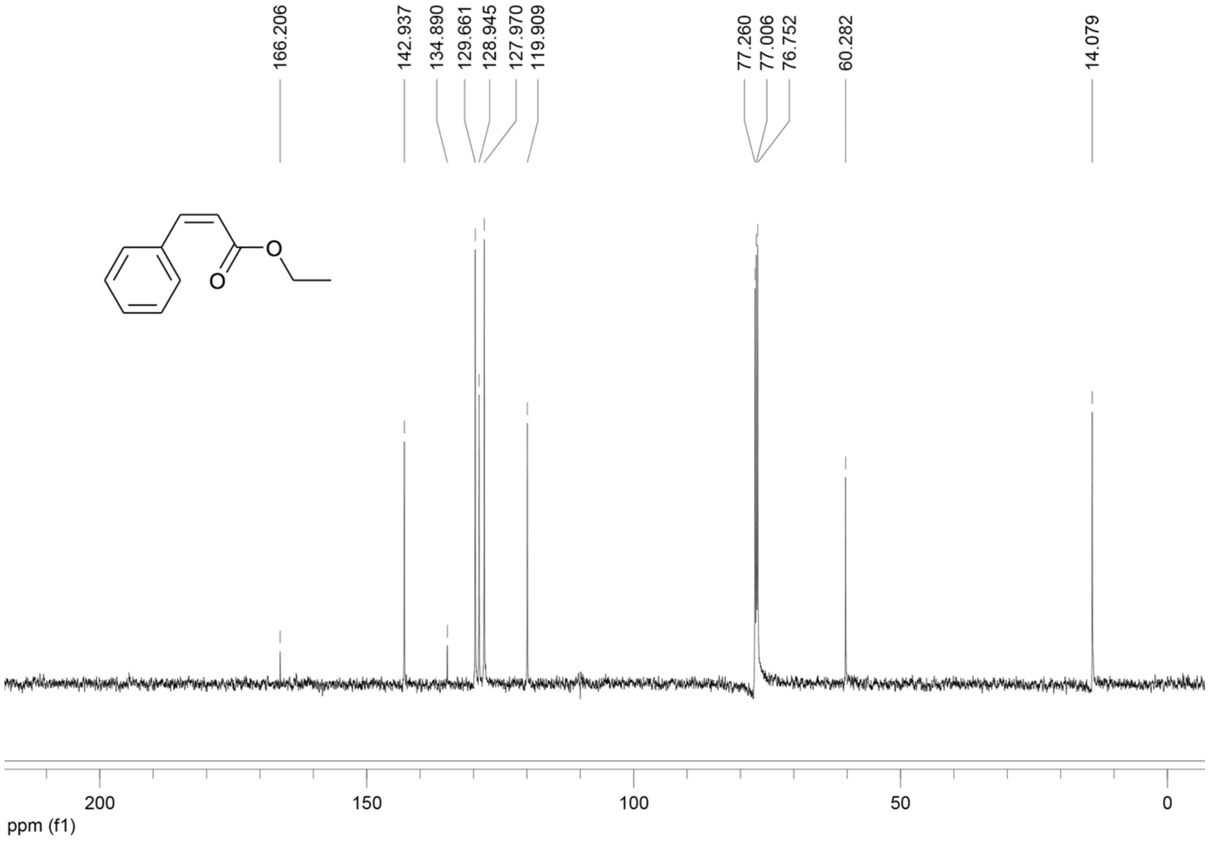

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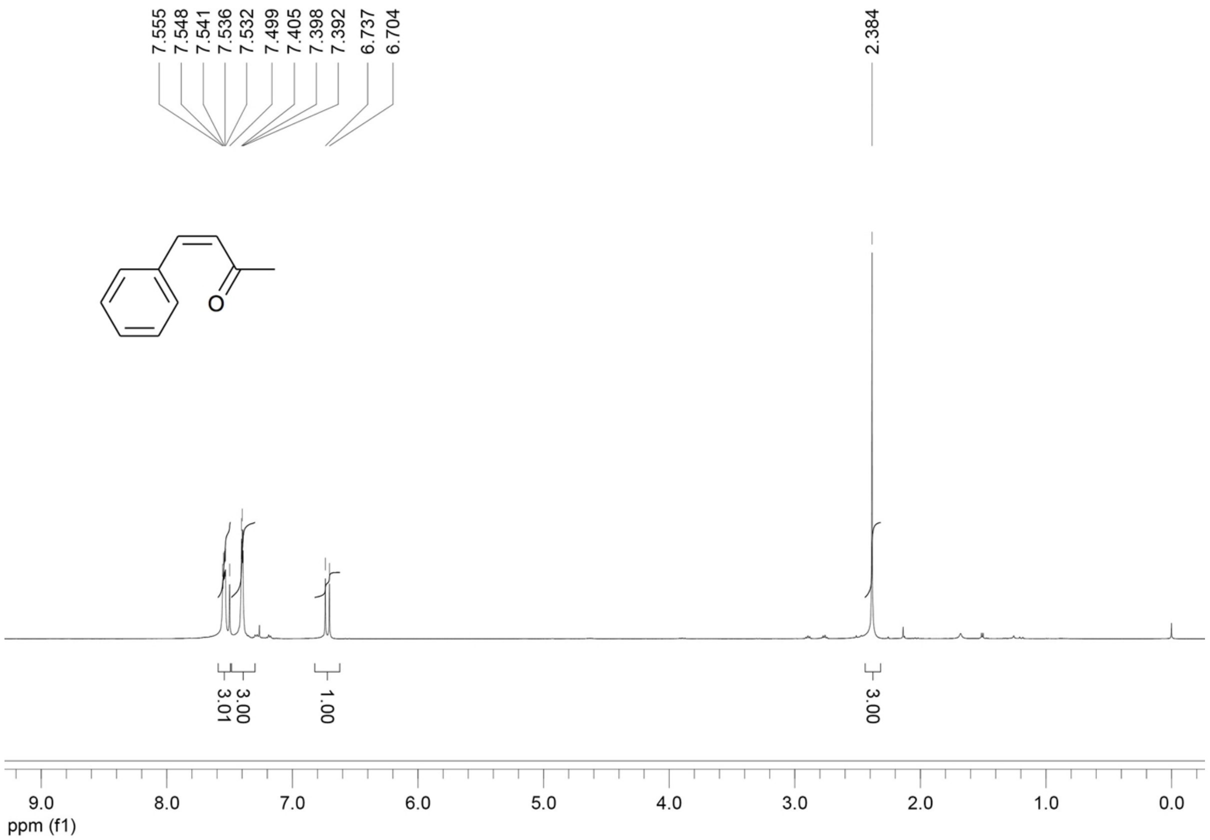

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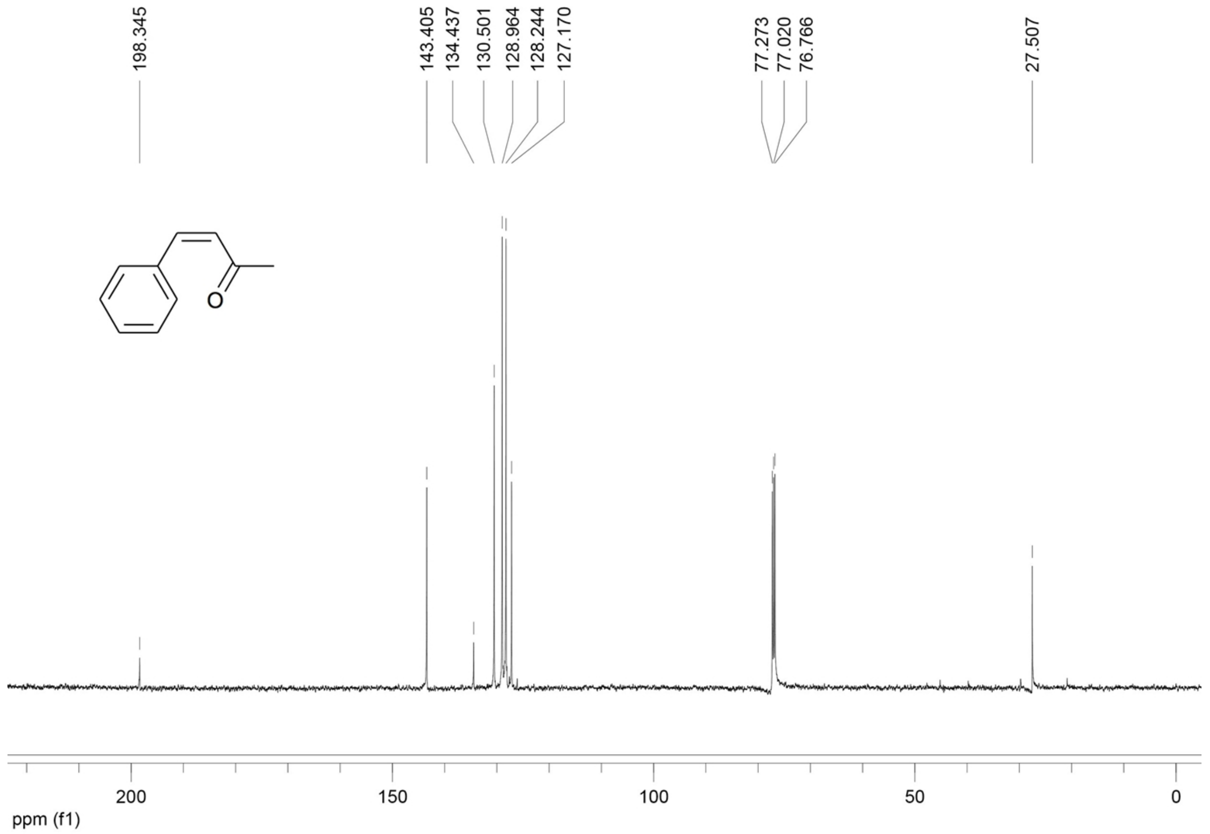

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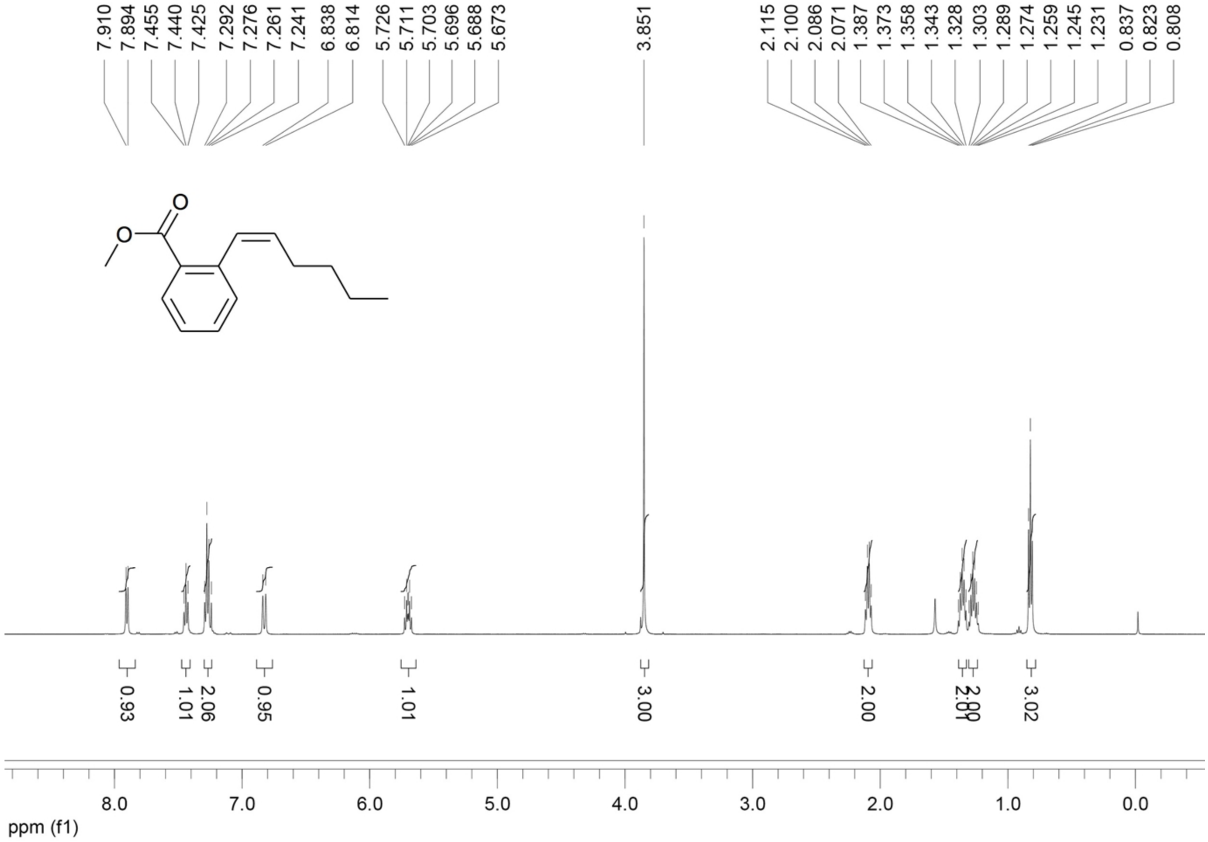

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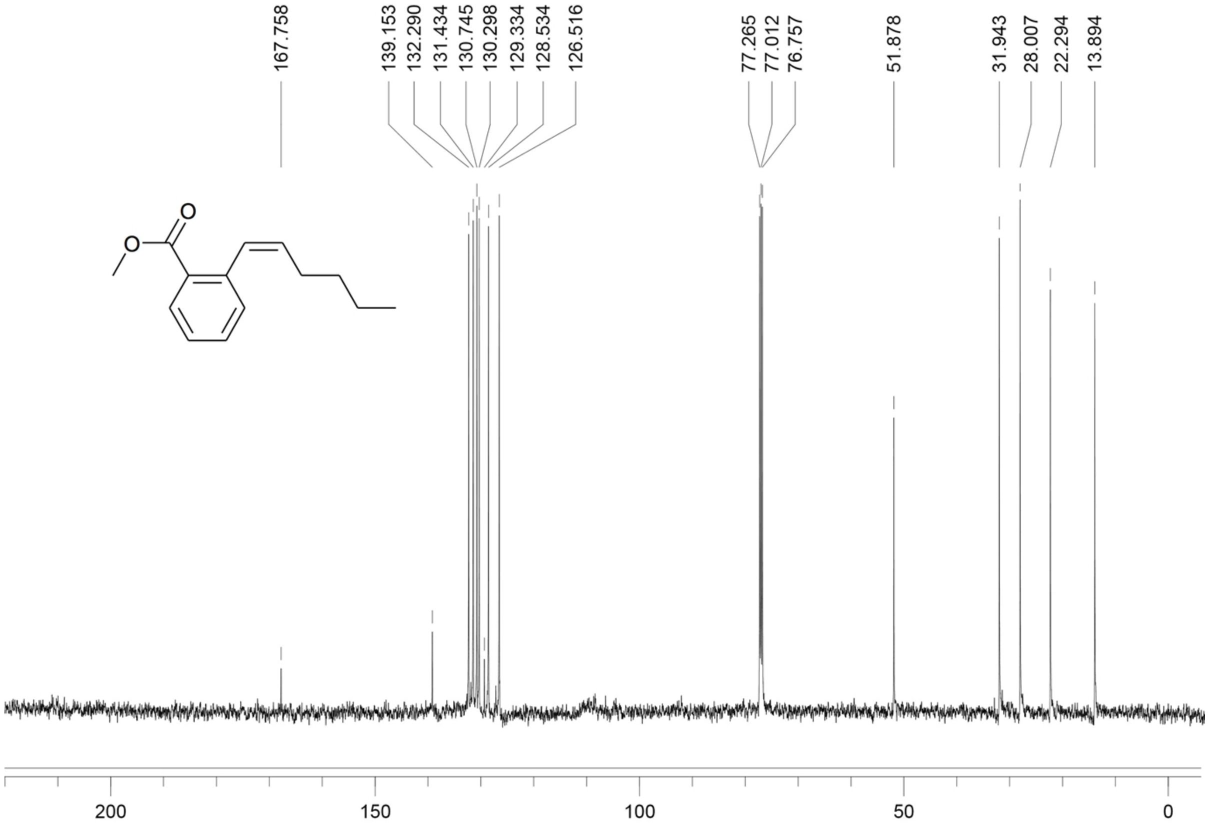

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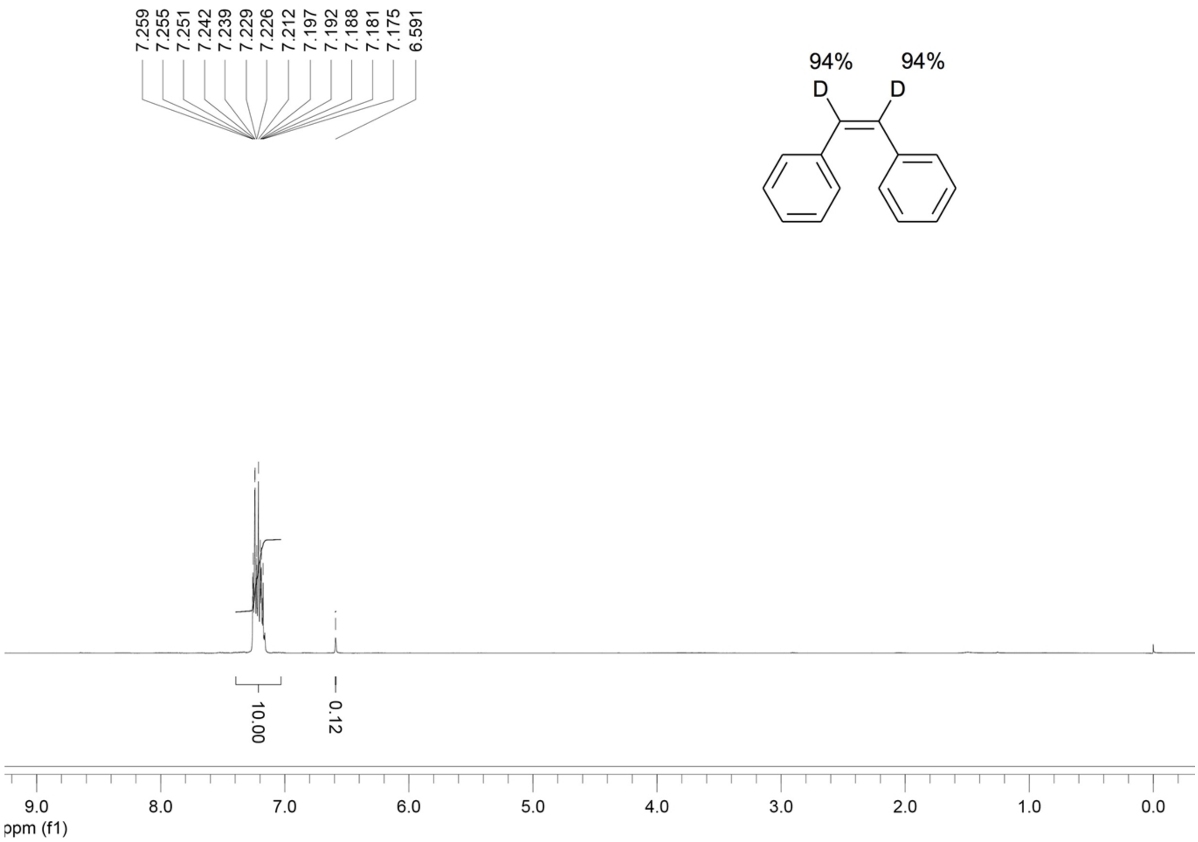

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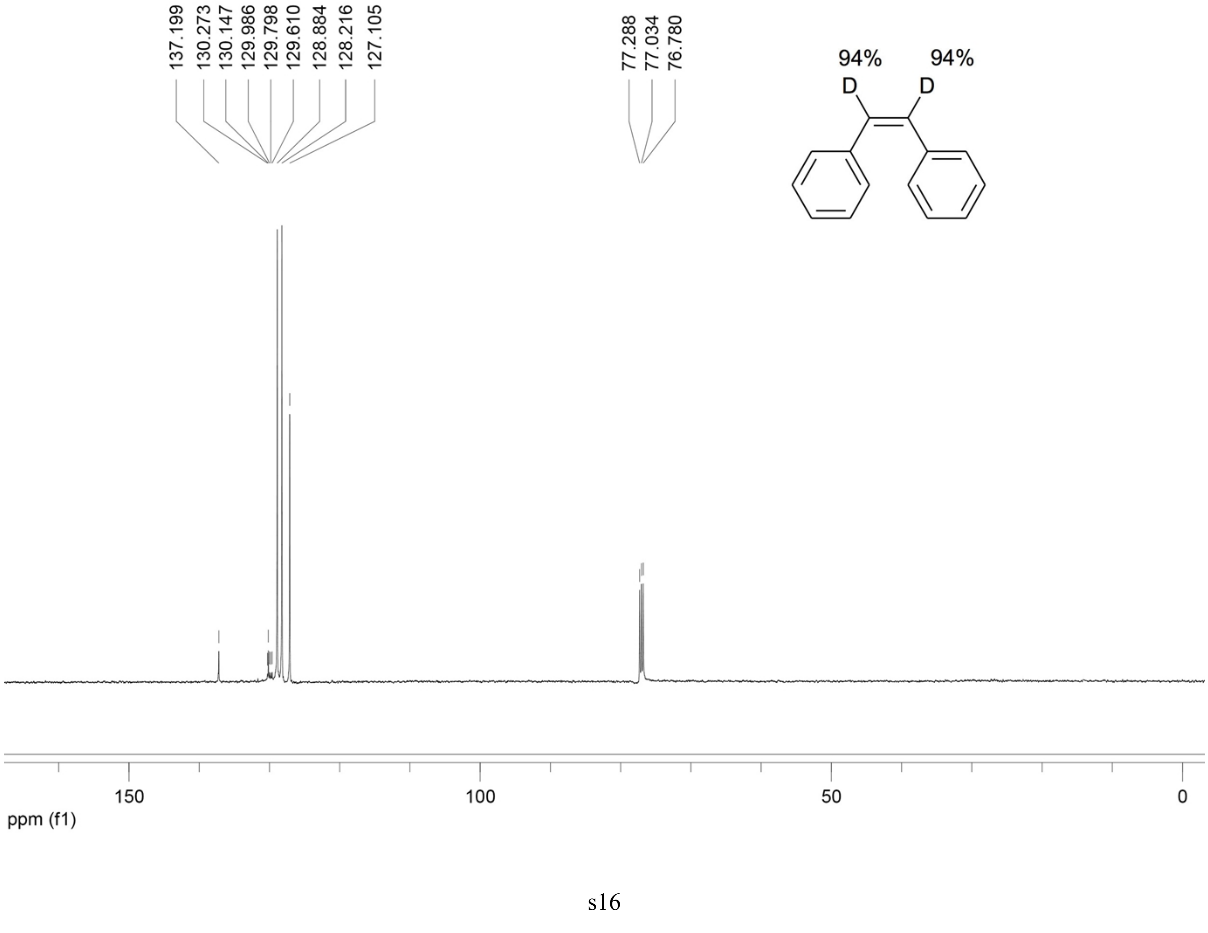

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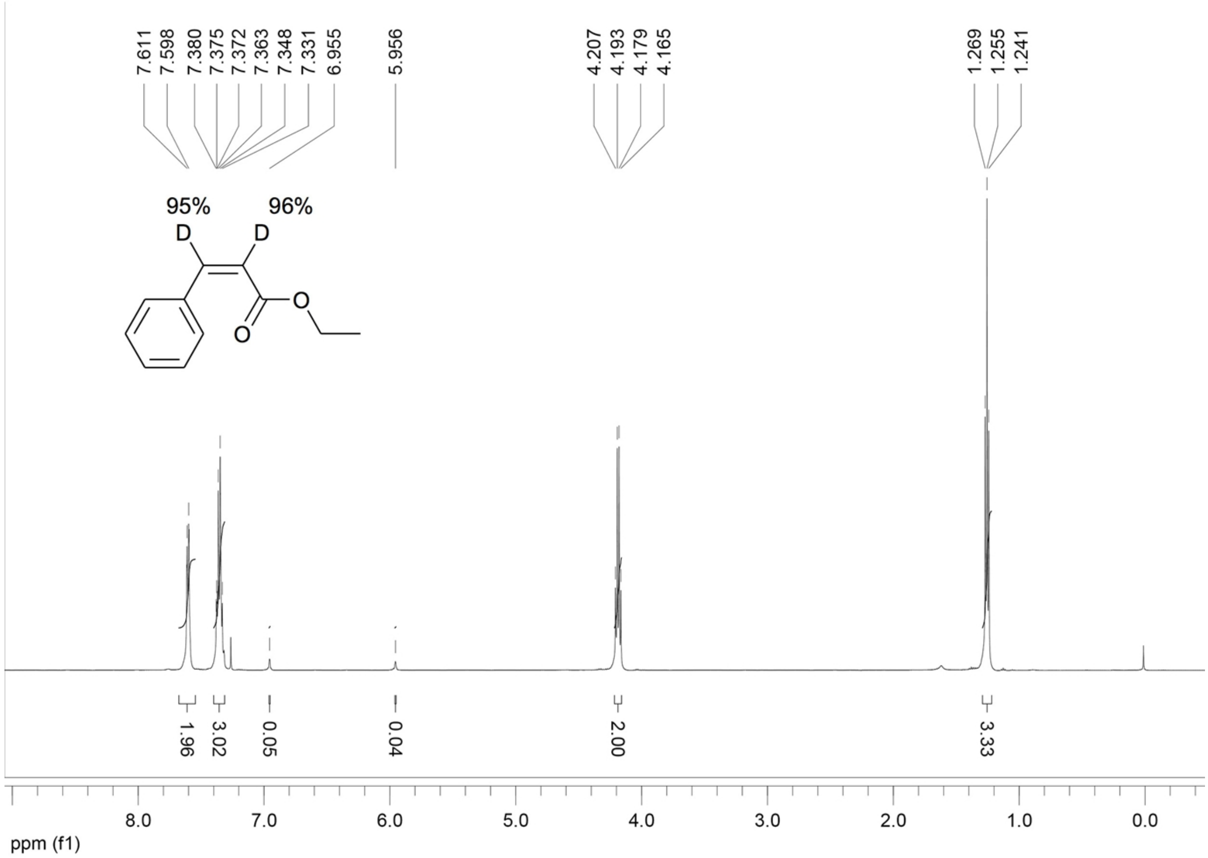

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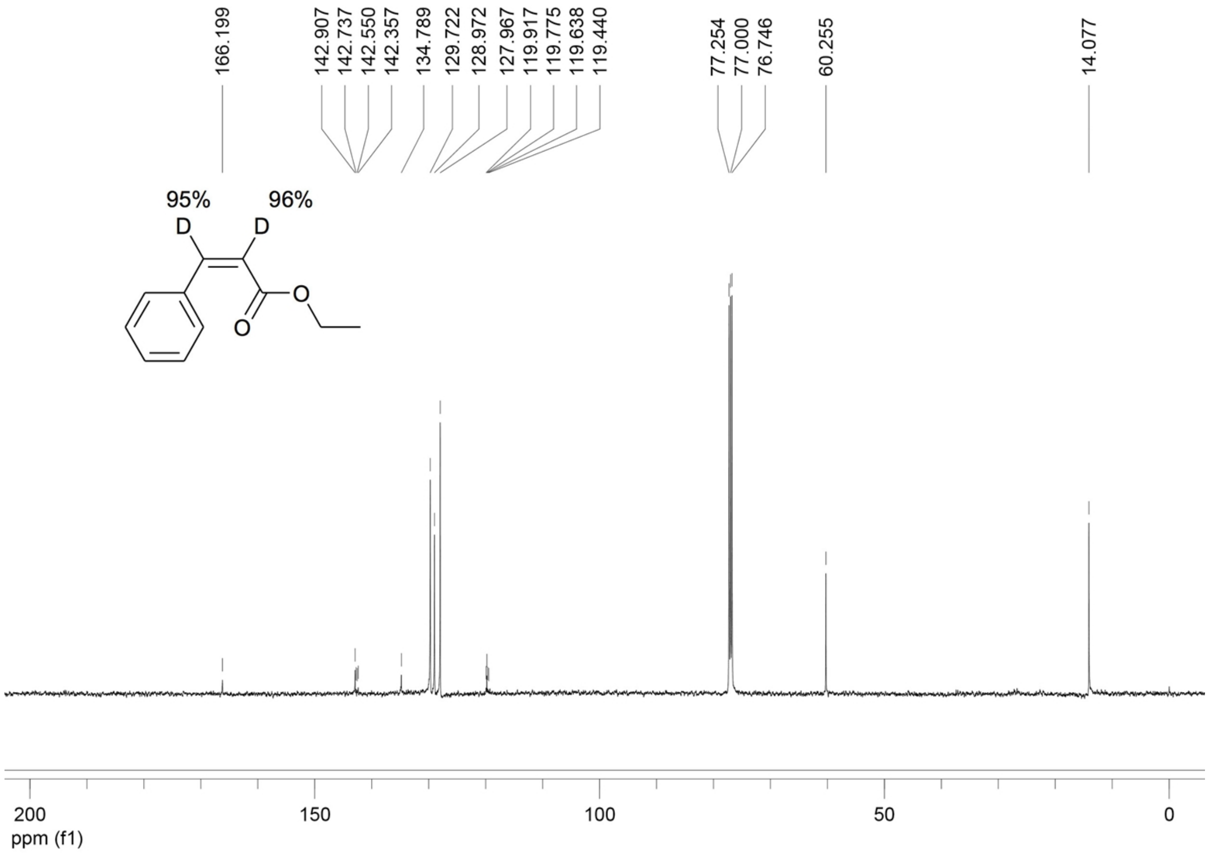

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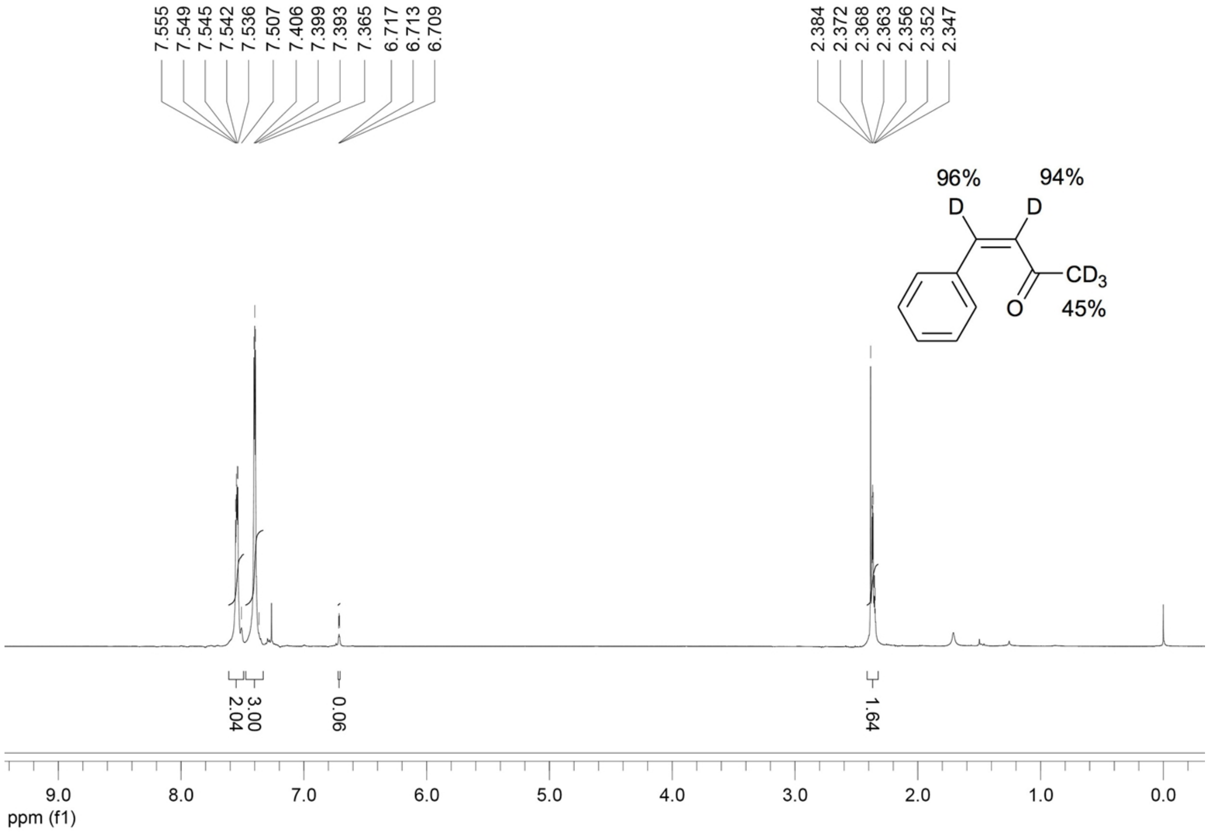

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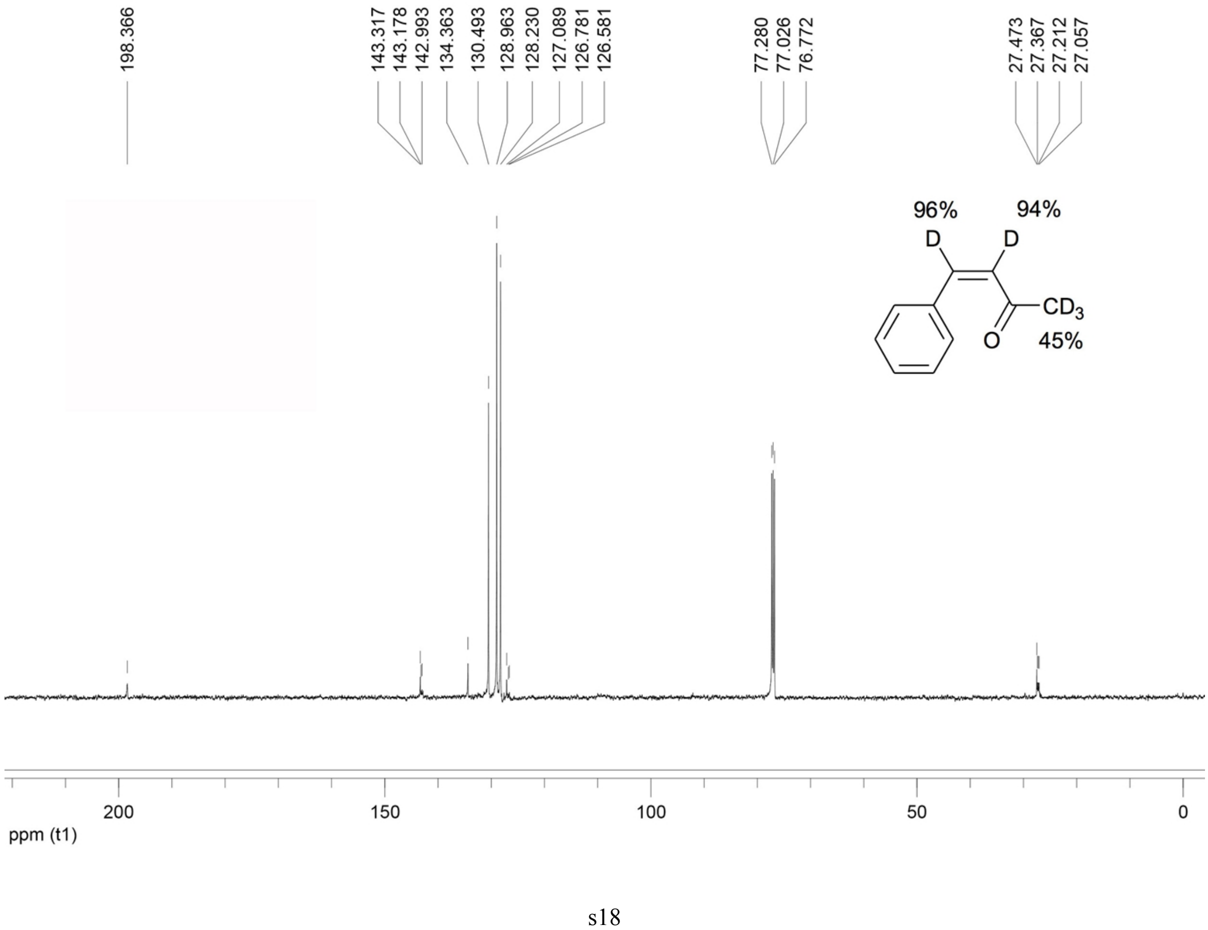

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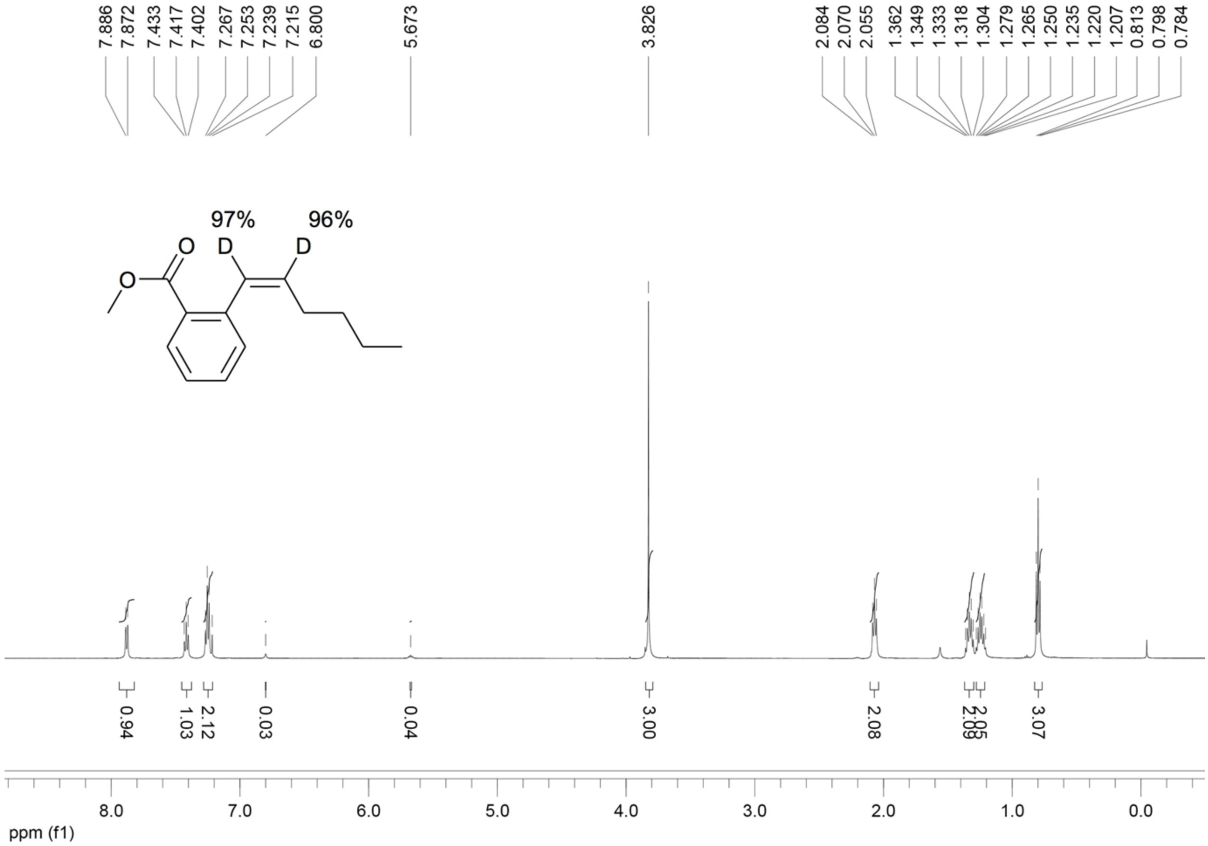

^{13}C NMR of [D$_2$]-**2k**