


Advanced 
**Synthesis &
Catalysis**

Supporting Information

Supporting Information:

Heterogeneous Gold-catalyzed Selective Semireduction of Alkynes Using Formic Acid as Hydrogen Source

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1. Materials and methods

1.1 General

Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), Palladium chloride (PdCl_2), Ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), were supplied by Aldrich and used without further purification. Inductively coupled plasma (ICP) measurements were performed on a Thermo Electron IRIS Intrepid II XSP spectrometer. BET specific surface areas were determined by adsorption-desorption of N_2 at 77 K, using a Micromeritics TriStar 3000 equipment. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX spectrometer. GC-FID was carried out on Agilent 7820A equipped with a HP-INNOWAX column (30 m \times 0.32 mm). HPLC was carried out on Agilent 1220 Infinity LC equipped with a Platisil ODS C18 column. X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu $K\alpha$ radiation source at 40 kV and 40 mA. X-ray photoelectron spectra (XPS) were recorded on a Perkin Elmer PHI 5000C spectrophotometer with Mg $K\alpha$ radiation (1253.6 eV). The binding energies scale was calibrated taking, as a reference, the adventitious C 1s peak at 284.6 eV. 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. Scanning electron microscope (SEM) observation was carried out using Nova NanoSem 450 instrument operated at an accelerating voltage of 5 kV.

1.2 Catalyst preparation

Preparation of rutile TiO_2 ($\text{TiO}_2\text{-R}$): Titanium tetrachloride (TiCl_4) was added dropwise into ethanol under stirring. A transparent yellowish sol was formed, and then slowly added to distilled water under stirring. The molar ratio of TiCl_4 , ethanol, and water was 2:20:280. After the addition was finished, the solution was further stirred for 30 min, and then was maintained in a closed system at 50 °C in an oven for 24 h. The white precipitate was harvested by centrifugation, and washed with distilled water and dried in an oven at 50 °C.

After that the sample was calcined at 400 °C for 3 h at a heating rate of 2 °C min⁻¹. The BET surface area of the resultant material was 65 m² g⁻¹.

Preparation of anatase TiO₂ (TiO₂-A): 10 mL of titanium bis(ammonium lactate) dihydroxide (TALH) aqueous solution (50 wt%) 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 m² g⁻¹.

Preparation of Au/TiO₂-P25, Au/TiO₂-R and Au/TiO₂-A catalysts: These Au/TiO₂-based catalysts were prepared by a modified deposition-precipitation (DP) method. Briefly, an appropriate amount of aqueous solutions of HAuCl₄ was heated to 80 °C under vigorous stirring. The pH was adjusted to 7 by dropwise addition of NaOH (0.2 M), and then 1.0 g TiO₂-P25 (Evonik, P25), TiO₂-R or TiO₂-A 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 25 °C for 12 h and then calcined in air at 300 °C for 2 h.

Preparation of Au/CeO₂: Au/CeO₂ catalyst was prepared by the routine DP procedure. Briefly, an appropriate amount of aqueous solutions of HAuCl₄ 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 CeO₂ (Evonik, Adnano 50) 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 25 °C for 12 h and then calcined in air at 300 °C for 2 h.

Preparation of ZrO₂: ZrO₂ powders were prepared by a conventional precipitation method. Briefly, 12.8 g ZrOCl₂·8H₂O was dissolved in 200 mL deionized water at room temperature, the pH was adjusted to 9.5 by dropwise addition of NH₄OH (2.5 M). The resultant hydrogel was washed with deionized water until free of Cl⁻ ions after stirring for 6 h at 25 °C. The precipitate was then dried at 100 °C overnight and calcined at 400 °C for 2 h in air. The BET surface area of the resultant material was 115 m² g⁻¹.

Preparation of Au/ZrO₂ and Au/SiO₂: Au/ZrO₂ and Au/SiO₂ catalysts were prepared by a modified DP method with NH₄OH. An appropriate amount of ZrO₂ or SiO₂ (Evonik, Aerosil 380) was added to the aqueous solution of HAuCl₄, the pH of which was adjusted to 9 with 0.25 M NH₄OH under stirring. The aqueous dispersion was stirred for 6 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 25 °C for 12 h, and reduced in 5 vol% H₂/Ar stream at 300 °C for 2 h.

Preparation of Au/Al₂O₃ catalyst: Au/Al₂O₃ catalyst was prepared by a modified DP method with urea. In a typical procedure, an appropriate amount of urea was dissolved in HAuCl₄ solution (urea/Au = 200, molar ratio) at 25 °C. 1 g of γ-Al₂O₃ was added to the solution and the aqueous dispersion was stirred for 6h at 80 °C, following by filtering and washing several times with distilled water. The sample was dried under vacuum at 25 °C for 12 h, and reduced in 5 vol% H₂/Ar at 300 °C for 2 h.

Preparation of Nanoporous gold catalyst: Nanoporous gold catalyst (AuNPore) was prepared by following the routine dealloying procedure as described in Ref. [S5] 40 μm thick Au/Ag alloy (30:70, at.%) was annealed at 850 °C for 18 h to release the rolling stress. The resulting foil was cut into small pieces followed by selective leaching of silver in 70 wt% nitric acid for 18 h at room temperature. The resulted nanoporous structure was washed successively with saturated aq. NaHCO_3 solution, distilled water and acetone, and dried under reduced pressure to give the AuNPore.

Preparation of Pd/TiO₂-R, Pt/TiO₂-R and Ru/TiO₂-R: Pd/TiO₂-R, Pt/TiO₂-R and Ru/TiO₂-R catalysts were prepared by incipient wetness technique. 1.0 g TiO₂-R was added to 10 mL of an aqueous solution containing appropriate amounts of PdCl₂, H₂PtCl₆, or RuCl₃. After a perfect mixing of the corresponding slurries, samples were dried at 100 °C for 5 h and then reduced in a 5 vol% H₂/Ar stream at 400 °C for 2 h.

2. Catalytic activity measurements

2.1 General Procedure for the Transfer Semireduction of Alkynes with FA: The mixture of alkyne (0.5 mmol), catalyst (metal: 0.5 mol%), formic acid (5 equiv.) as a FA/NEt₃ (3:2) mixture, acetone (2 mL) was added to a flask (10 mL) equipped with a reflux condenser. The resulting mixture was allowed to reflux with vigorous stirring (800 rpm) at 60 °C for given reaction time. After completion of the reaction, the reaction mixture was filtered and the filtrate was washed with water and extracted by ethyl acetate. The mixture was concentrated and dried under reduced pressure to give the crude product, which was purified by silica gel chromatography eluting with petroleum ether (60~90 °C)/ethyl acetate mixture. The products were confirmed by GC-MS and ¹H, ¹³C NMR. The conversion and selectivity were determined by GC-FID using *p*-xylene (PX) as an internal standard.

2.2 Hydrogenation of phenylacetylene using H₂: A mixture of phenylacetylene (0.5 mmol), acetone (2 mL), catalyst (Au: 0.5 mol %) was put into a three-necked round-bottomed flask (10 mL) fitted with a gas inlet tube for introducing H₂ by bubbling. The resulting mixture was stirred (600 rpm) at 60 °C for 0.5 h. The conversion and selectivity were determined by GC-FID using PX as an internal standard.

2.3 Hydrogenation of phenylacetylene using other hydrogen source: A mixture of phenylacetylene (0.5 mmol), acetone (2 mL), catalyst (Au: 0.5 mol %) and hydrogen source (5 equiv.) was put into a flask (10 mL) equipped with a reflux condenser. The resulting mixture was allowed to reflux with vigorous stirring (800 rpm) at 60 °C for 0.5 h. The conversion and selectivity were determined by GC-FID using PX as an internal standard.

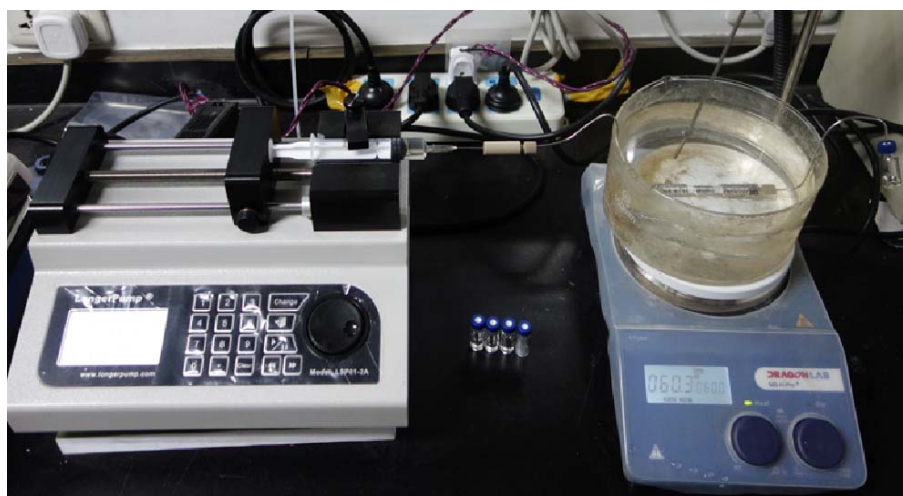
2.4 Recovery and reuse of 0.3% Au/TiO₂-R: The reused catalyst was recovered by filtering the solid 0.3% Au/TiO₂-R from liquid phase after the reaction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried under vacuum at room temperature for 12 h to obtain the reused catalyst. In the five cycles, the conversion of phenylacetylene within 0.5 h was 77 %, 77 %, 76%, 75% and 75 %, the selectivity of styrene kept >99% (GC yield). The filtrate was analyzed by ICP-AES to confirm that no leaching occurred during the reaction.

2.5 Gram-scale transfer semireduction of phenylacetylene using FA with 0.3% Au/TiO₂-R: The mixture of phenylacetylene (10 mmol), 0.3% Au/TiO₂-R (Au: 0.05 mol%), FA (5 equiv.) as a FA/NEt₃ (3:2) mixture, acetone (10 mL) was added to a flask (25 mL) equipped with a reflux condenser. The resulting mixture was allowed to reflux with vigorous stirring (800 rpm) at 60 °C for 20 h. The conversion and selectivity were determined by GC-FID using PX as an internal standard.

2.6 Sole decomposition of FA under otherwise identical conditions: FA (2.5 mmol) as a FA/NEt₃ (3:2) mixture, acetone (2 mL), catalyst (Au: 0.1 mol %) were placed into a three-necked round-bottomed flask (10 mL capacity). The resulting mixture was stirred (800 rpm) at 60 °C for given reaction time. Initial TOF calculations were based on H₂ generation. After the reaction, the concentration of residual FA was analyzed by a HPLC (HP 1100, Agilent) consisting of a Platisil ODS C18 column and a refractive index detector. H₂SO₄ (0.5 mM) was used as the mobile phase at a flow rate of 1 mL min⁻¹.

2.7 Decomposition of FA in the present of alkynes: Phenylacetylene (0.5 mmol), FA (2.5 mmol) as a FA/NEt₃ (3:2) mixture, acetone (2 mL), 0.3% Au/TiO₂-R (Au: 0.1 mol % based on FA) were placed into a three-necked round-bottomed flask (10 mL capacity). The resulting mixture was stirred (800 rpm) at 60 °C for given reaction time. After the reaction, the concentration of residual FA was analyzed by a HPLC (HP 1100, Agilent) consisting of a Platisil ODS C18 column and a refractive index detector. H₂SO₄ (0.5 mM) was used as the mobile phase at a flow rate of 1 mL min⁻¹.

2.8 Set up for the continuous-flow semireduction of alkynes with FA:



A short HPLC column (50 mm × 2.1 mm I.D. × 1/4 in. O.D.) was set as the reactor that packed with 200 mg of 0.3% Au/TiO₂-R (Particle size range from 60~80 mesh). Phenylacetylene (0.25 mol L⁻¹), FA (1.25 mol L⁻¹) as a FA/NEt₃ (3:2) mixture was dissolved in acetone and the solution was pumped by a syringe pump through the reactor at a flow rate of 4.5 mL h⁻¹. The reactor was heated by a water bath at 60 °C. The reaction mixture flow through was collected into glass vials and analysed by GC-FID. After 3 h on stream, the catalyst was washed by acetone (0.5 mL min⁻¹) for 30 min to regenerate for second cycle.

3. Supplementary data

Table S1. Optimization of the reaction with regard to the amine and the ratio of FA to amine.^[a]

Entry	FA/amine	T [°C]	t [h]	Conv. [%] ^[b]	Select. [%] ^[b]
1	FA	60	0.5	Trace	-
2	FA	60	5	Trace	-
3	FA	80	5	Trace	-
4	FA/DMF (3:2)	60	0.5	2	>99
5	FA/Triethanolamine (3:2)	60	0.5	15	>99
6	FA/Diethanolamine (3:2)	60	0.5	17	>99
7	FA/NEt ₃ (3:2)	60	0.5	56	>99
8	FA/NEt ₃ (10:1)	60	0.5	4	>99
9	FA/NEt ₃ (5:1)	60	0.5	18	>99
10	FA/NEt ₃ (5:2)	60	0.5	28	>99
11	FA/NEt ₃ (2:1)	60	0.5	36	>99
12	FA/NEt ₃ (1:1)	60	0.5	40	>99

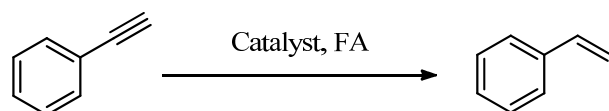
[a] Reaction conditions: Phenylacetylene (0.5 mmol), 0.5% Au/TiO₂-R (Au: 0.5 mol %), FA (5 equiv.) as a FA/amine mixture, acetone (2 mL). Ratio of FA/amine is based on molar ratio. [b] Determined by GC.

Table S2. The influence of solvents on the semireduction of phenylacetylene. ^[a]

Entry	Solvent	Conversion [%] ^[b]	Selectivity [%] ^[b]
1	Acetone	56	>99
2	Butanone	51	>99
3	Toluene	30	>99
4	Acetonitrile	Trace	-
5	THF	45	>99
6	EtOH	Trace	-

[a] Reaction conditions: Phenylacetylene (0.5 mmol), FA (5 equiv.) as a FA/NEt₃ (3:2) mixture, solvent (2 mL), 0.5% Au/TiO₂-R (Au: 0.5 mol %), 60 °C, 0.5 h. [b] Determined by GC.

Table S3. Catalytic performance of selected homogeneous and heterogeneous catalysts for the FA- mediated TSR of phenylacetylene on current work and literature data.



Entry	Catalyst	S/C ^[a]	Solvent/Temp.	TOF ^[b] [h ⁻¹]	TON	Yield [%]	Ref.
1	0.3% Au/TiO ₂ -R	200	Acetone/60 °C	286	-	>99	This work
2 ^[c]	0.3% Au/TiO ₂ -R	2000	Acetone/60 °C	300	1960	>99	This work
3 ^[d]	0.3% Au/TiO ₂ -R	-	Acetone/60 °C	374	3200	>99	This work
4	Pd(NHC)	100	THF/reflux	50	-	50	[S1]
5	Pd(NHC)	100	CH ₃ CN/reflux	3.5	-	>99	[S1]
6	Pd(Ph ₃ P ₄)	100	Dioxane/80 °C	33	-	90	[S2]
7	Fe(BF ₄) ₂ ·6H ₂ O/PP ₃	167	THF/40 °C	84	-	>99	[S3]
8	Ru-PC(<i>sp</i> ³)P	100	DME/90 °C	100	-	90	[S4]
9	AuNPore	20	DMF/70 °C	4.6	-	100	[S5]

[a] S/C: molar ratio of substrate and catalyst. [b] Average TOF based on conversion of substrate. [c] Gram-scale reaction condition (see Section 2.5 for detail). Initial TOF after 1 h. [d] Continuous-flow condition (see Section 2.8 for detail). TON after three cycles (9 h).

Table S4. Formic acid decomposition in the present of alkyne.

Entry	TON for 1h ^[c]
1 ^[a]	719
2 ^[b]	1064

[a] Sole decomposition of FA: FA (2.5 mmol) as a FA/NEt₃ (3:2) mixture, acetone (2 mL), 0.3% Au/TiO₂-R (Au: 0.1 mol % based on FA), 60 °C, 1 h. [b] Decomposition of FA in the presence of alkyne: FA (2.5 mmol) as a FA/NEt₃ (3:2) mixture, 0.5 mmol phenylacetylene, acetone (2 mL), 0.3% Au/TiO₂-R (Au: 0.1 mol % based on FA), 60 °C, 1 h. [c] Determined by HPLC.

Table S5. Semireduction of phenylacetylene with D-substituted FA over the 0.3% Au/TiO₂-R catalyst.^[a]

Entry	FA	Reaction rate ^[b] [mmol min ⁻¹ g _{Au} ⁻¹]	KIE ^[c]
1	HCOOH	40.5	-
2	HCOOD	38.9	1.04
3	DCOOH	9.8	4.13
4	DCOOD	9.6	4.22

[a] Reaction conditions: Phenylacetylene (0.5 mmol), FA (5 equiv.) as a FA/NEt₃ (3:2) mixture, acetone (2 mL), 0.3% Au/TiO₂-R (Au: 0.5 mol %), 60 °C. [b] Reaction rate based on low conversion levels (< 15%) determined by GC. [c] KIE(kinetic isotope effect) = rate(entry 1)/rate(entry n); n = 2–4.

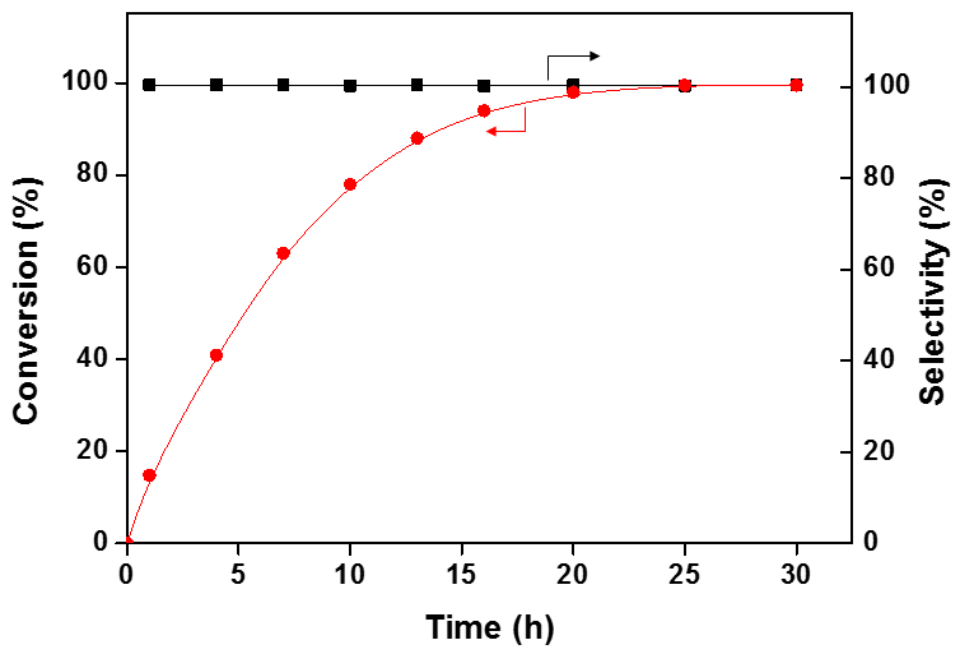
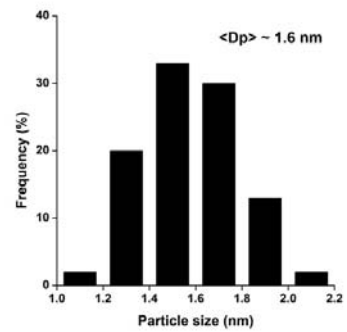
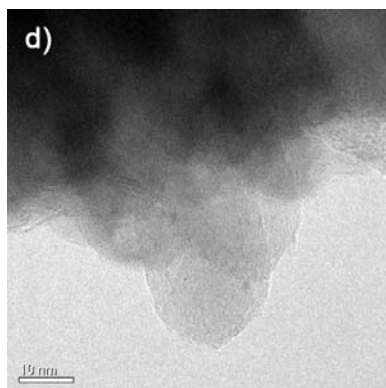
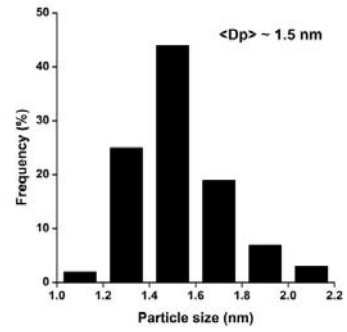
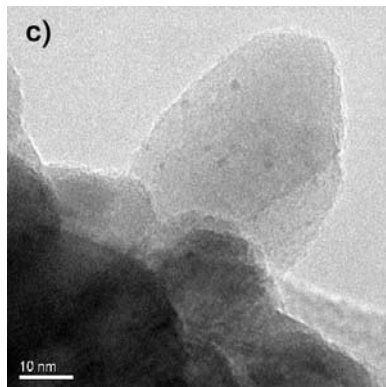
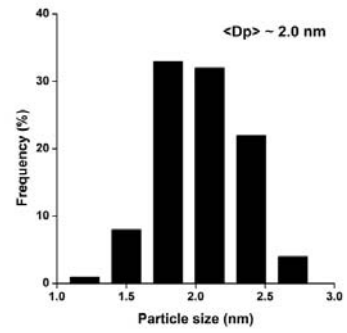
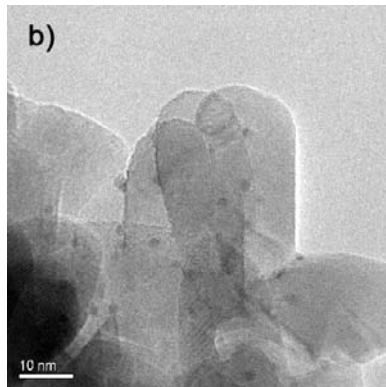
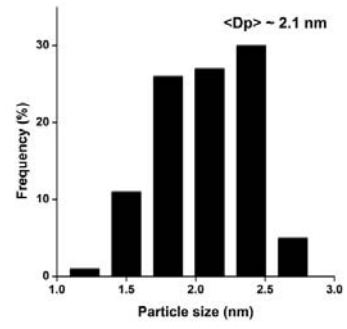
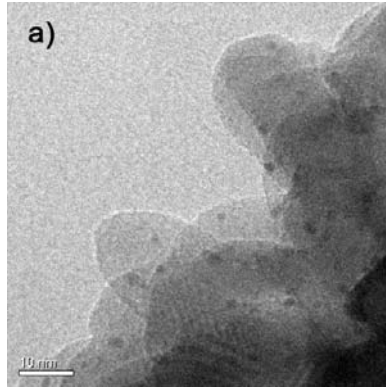


Figure S1. Time-course plot for the gram-scale TSR of phenylacetylene with FA using 0.3% Au/TiO₂-R. Reaction conditions: Phenylacetylene (10 mmol), acetone (10 mL), 0.3% Au/TiO₂-R (Au: 0.05 mol %), FA (5 equiv) as a 3:2 FA/NEt₃ mixture, 60 °C. The conversion and selectivity were determined by GC.



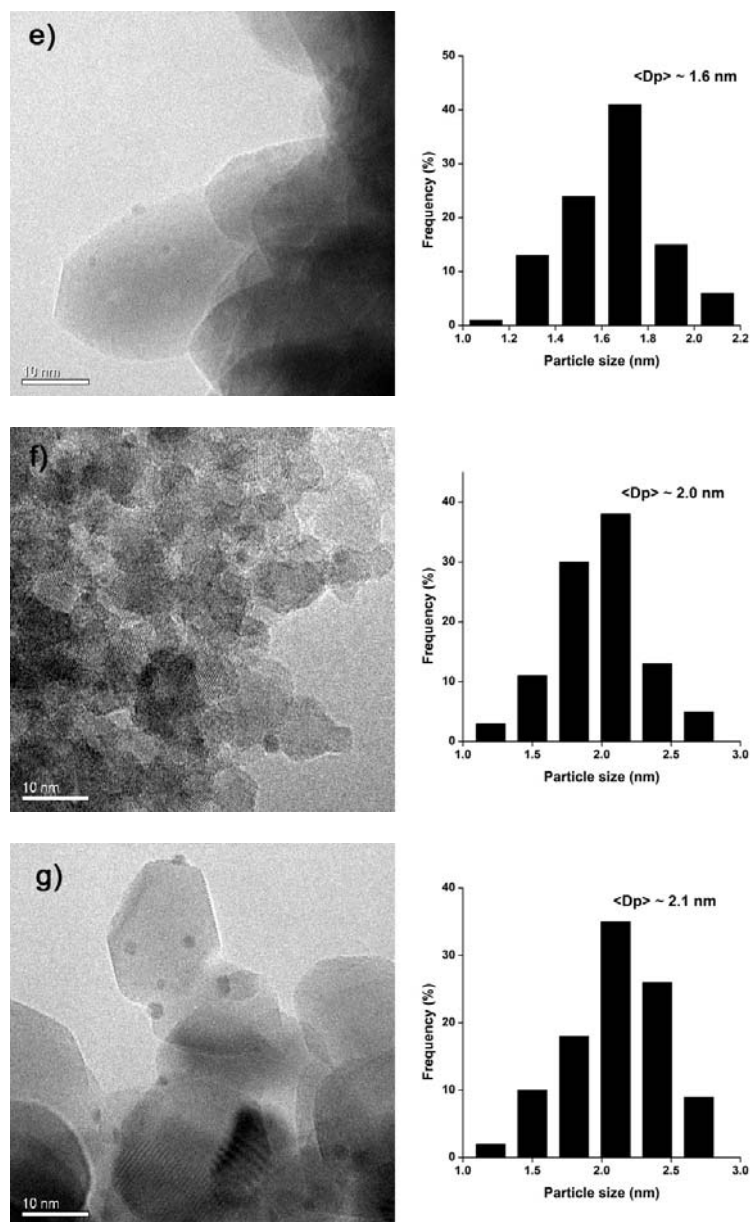


Figure S2. TEM image and size distribution of a) 0.8% Au/TiO₂-R; b) 0.5% Au/TiO₂-R; c) 0.3% Au/TiO₂-R; d) 0.3% Au/TiO₂-R after five runs; e) 0.1% Au/TiO₂-R; f) 0.5% Au/TiO₂-A; g) 0.5% Au/TiO₂-P25.

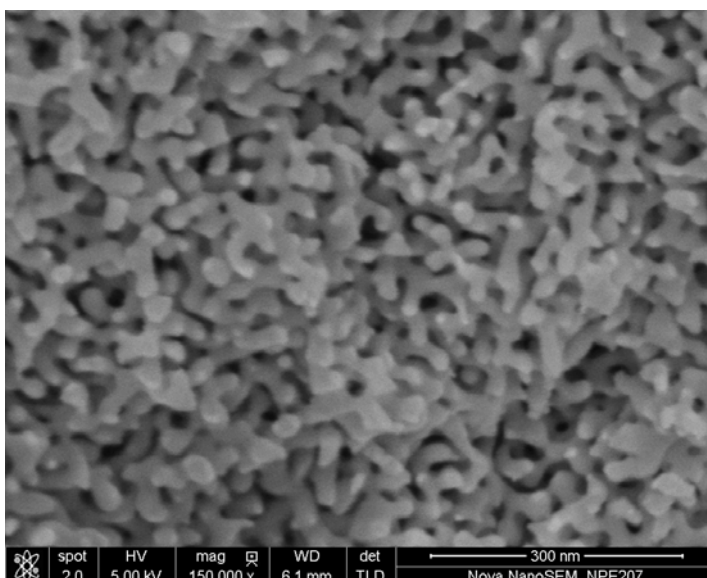


Figure S3. SEM image of AuNPore catalyst.

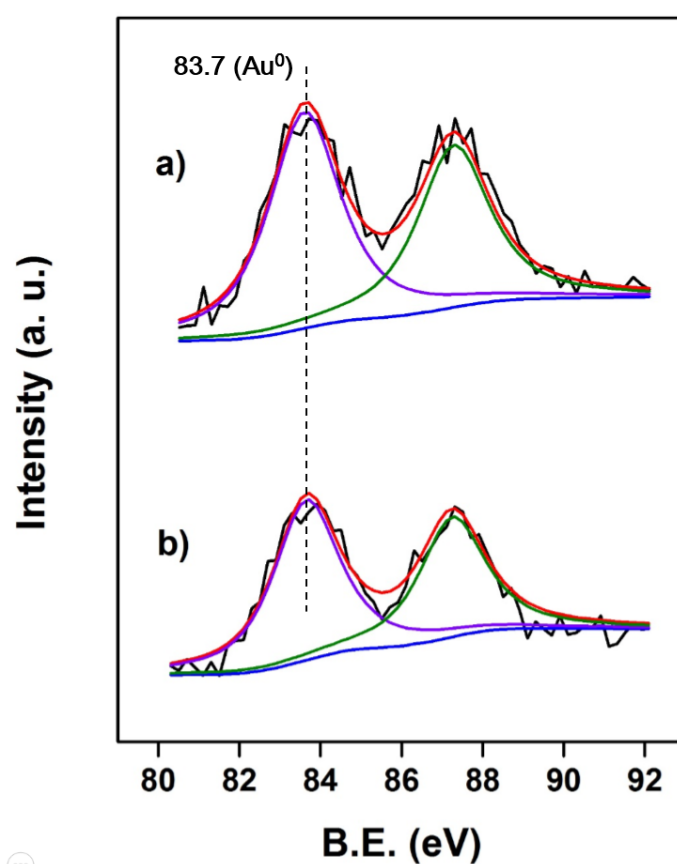


Figure S4. X-ray photoelectron spectroscopy (XPS) for 0.3% Au/TiO₂-R a) fresh; b) after five runs. Note that the metallic state of Au practically undergoes no change after the five successive runs.

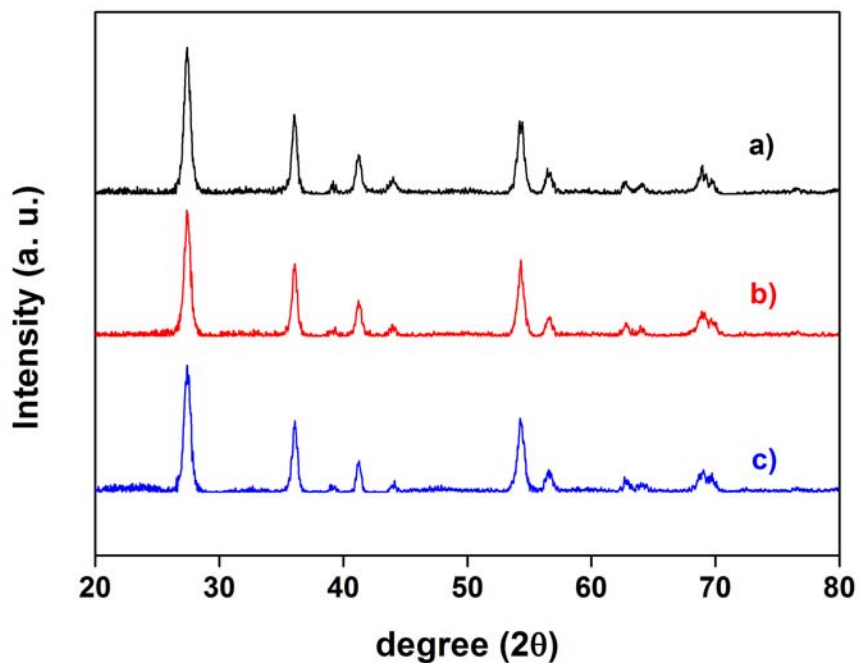


Figure S5. X-ray diffraction (XRD) patterns for a) TiO₂-R; b) fresh 0.3% Au/TiO₂-R; c) 0.3% Au/TiO₂-R after five runs. It is clear from this figure that XRD patterns for 0.3% Au/TiO₂-R show the characteristic diffraction peaks of rutile phase (JCPDS No. 21-1276) titania and no distinct Au reflections are visible, confirming the formation of very small gold particles on the rutile phase titania support.

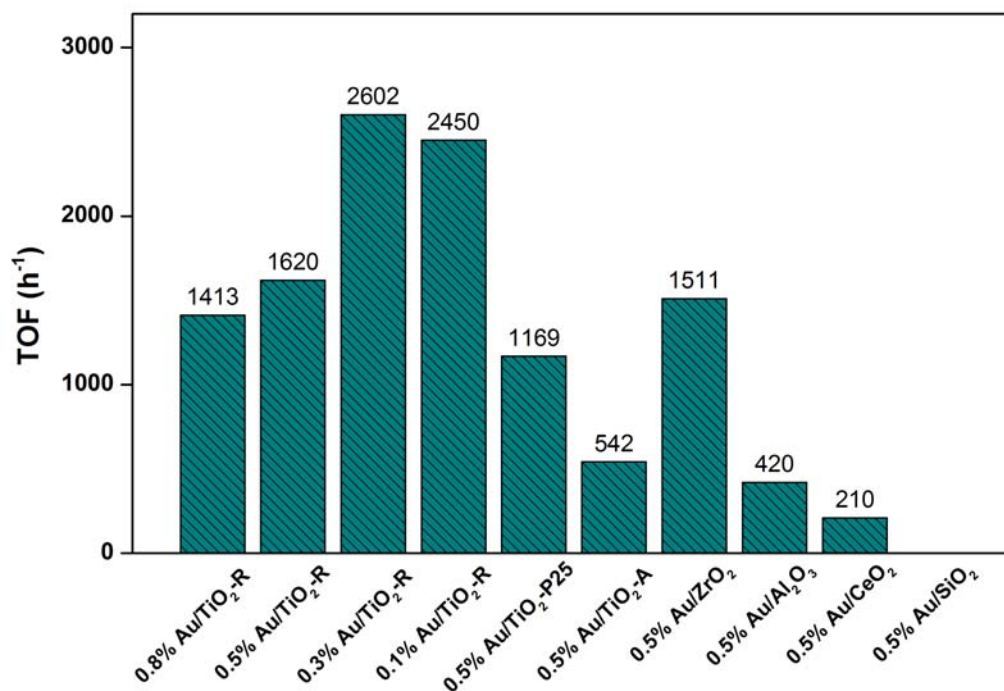


Figure S6. Decomposition of FA over various supported gold catalysts. Reaction conditions: FA (2.5 mmol) as a FA/NEt₃ (3:2) mixture, acetone (2 mL), catalyst (Au: 0.1 mol % based on FA), 60 °C. All TOF calculations were based on initial activities below 15 % conversion of FA.

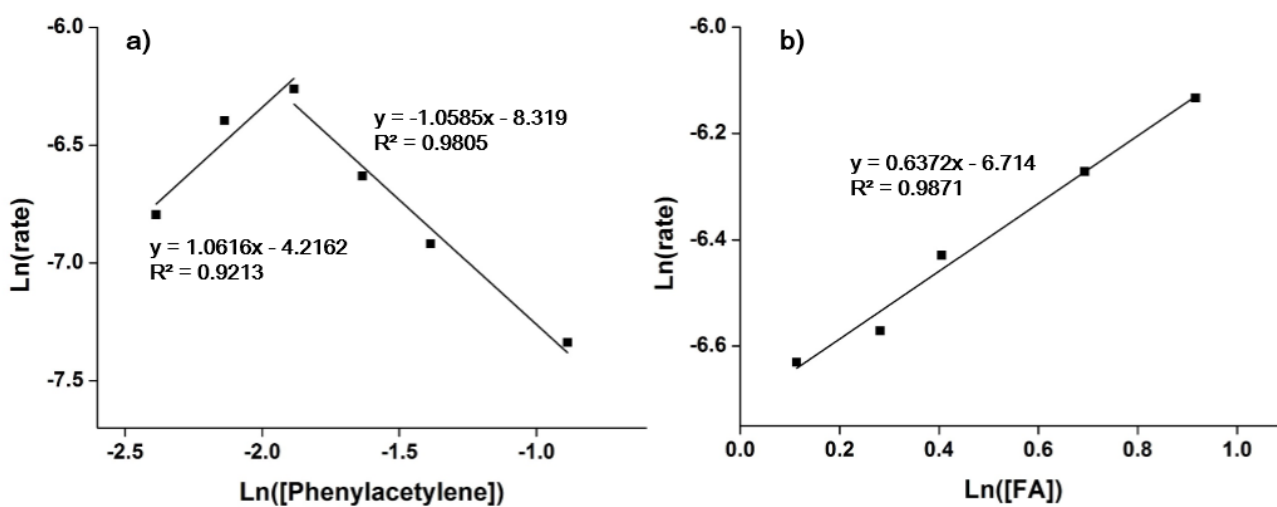
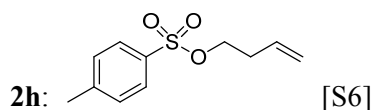
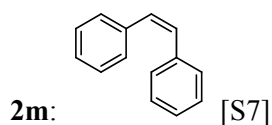


Figure S7. Results of mechanistic studies. Plot of ln(rate) versus a) ln([Phenylacetylene]); b) ln([FA]).

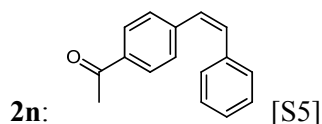
4. Product identification



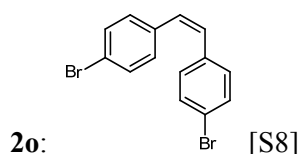
^1H NMR (CDCl_3 , 400 MHz) δ 7.79 (d, $J=8.0$ Hz, 2H), 7.35 (d, $J=8.0$ Hz, 2H), 5.72-5.62 (m, 1H), 5.10-5.05 (m, 2H), 4.06 (t, $J=6.4$ Hz, 2H), 2.45 (s, 3H), 2.42-2.37 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 144.7, 133.1, 132.4, 129.8, 127.9, 118.2, 69.4, 33.1, 21.6.



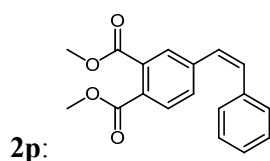
^1H NMR (CDCl_3 , 400 MHz) δ 7.20 (m, 10H), 6.59 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 137.3, 130.3, 128.9, 128.2, 127.1.



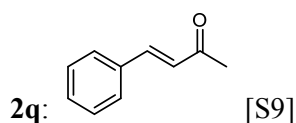
^1H NMR (CDCl_3 , 400 MHz) δ 7.83 (d, $J=8.4$ Hz, 2H), 7.35 (d, $J=8.4$ Hz, 2H), 7.24-7.26 (m, 5H), 6.75 (d, $J=12.4$ Hz, 1H), 6.63 (d, $J=12.4$ Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 197.6, 142.3, 136.6, 135.6, 132.4, 129.1, 129.0, 128.8, 128.3, 128.3, 127.5, 26.5.



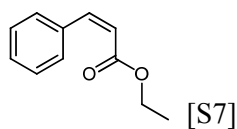
^1H NMR (CDCl_3 , 400 MHz) δ 7.34 (d, $J=8.4$ Hz, 4H), 7.07 (d, $J=8.0$ Hz, 4H), 6.52 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 135.7, 131.5, 130.4, 129.7, 121.2.



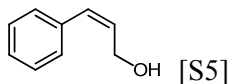
^1H NMR (CDCl_3 , 400 MHz) δ 7.61-7.58 (m, 2H), 7.38 (m, 1H), 7.25 (m, 5H), 6.77 (d, $J=12.4$ Hz, 1H), 6.59 (d, $J=12.4$ Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 168.1, 167.6, 140.7, 136.2, 133.0, 132.6, 131.0, 129.6, 129.2, 129.0, 128.7, 128.4, 128.0, 127.7, 52.6, 52.5; HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{16}\text{O}_4$ $[\text{M}+\text{Na}]^+$ 319.0941, observed 319.0941.



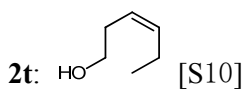
^1H NMR (CDCl_3 , 400 MHz) δ 7.56-7.50 (m, 3H), 7.41-7.39 (m, 3H), 6.72 (d, $J=16.4$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 198.3, 143.4, 134.4, 130.5, 128.9, 128.2, 127.1, 27.5.



¹H NMR (CDCl₃, 400 MHz) δ 7.57 (d, *J*=6.8 Hz, 2H), 7.36-7.31 (m, 3H), 6.94 (d, *J*=12.8 Hz, 1H), 5.94 (d, *J*=12.8 Hz, 1H), 4.17 (q, *J*=7.2 Hz, 2H), 1.24 (t, *J*=7.2 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 166.2, 142.9, 134.9, 129.6, 128.9, 127.9, 119.9, 60.2, 14.0.



¹H NMR (CDCl₃, 400 MHz) δ 7.36-7.19 (m, 5H), 6.57 (d, *J*=7.2 Hz, 1H), 5.90-5.84 (m, 1H), 4.45-4.43 (m, 2H), 1.69 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 136.5, 131.1, 131.0, 128.7, 128.2, 127.2, 59.7.

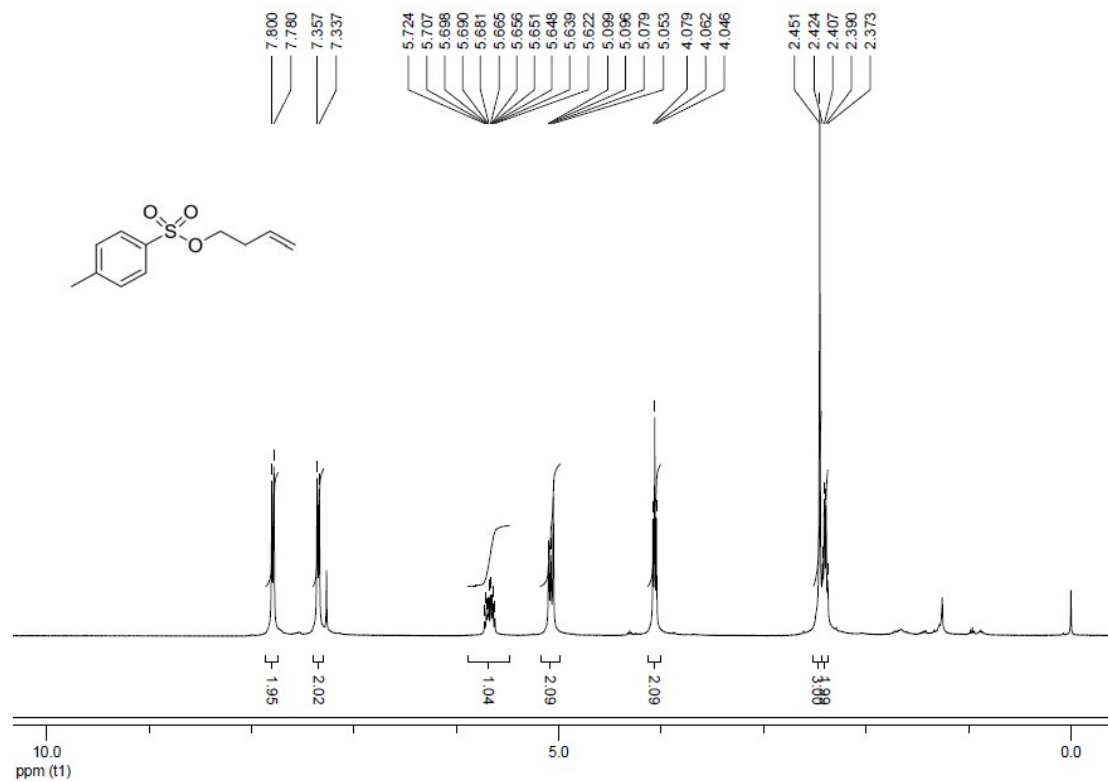


¹H NMR (CDCl₃, 400 MHz) δ 5.60-5.53 (m, 1H), 5.39-5.30 (m, 1H), 3.64 (t, *J*=6.4 Hz, 2H), 2.36-2.30 (m, 2H), 2.12-2.06 (m, 2H), 1.65 (s, 1H), 0.98 (t, *J*=7.6 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 135.0, 124.4, 62.2, 30.6, 20.6, 14.2.

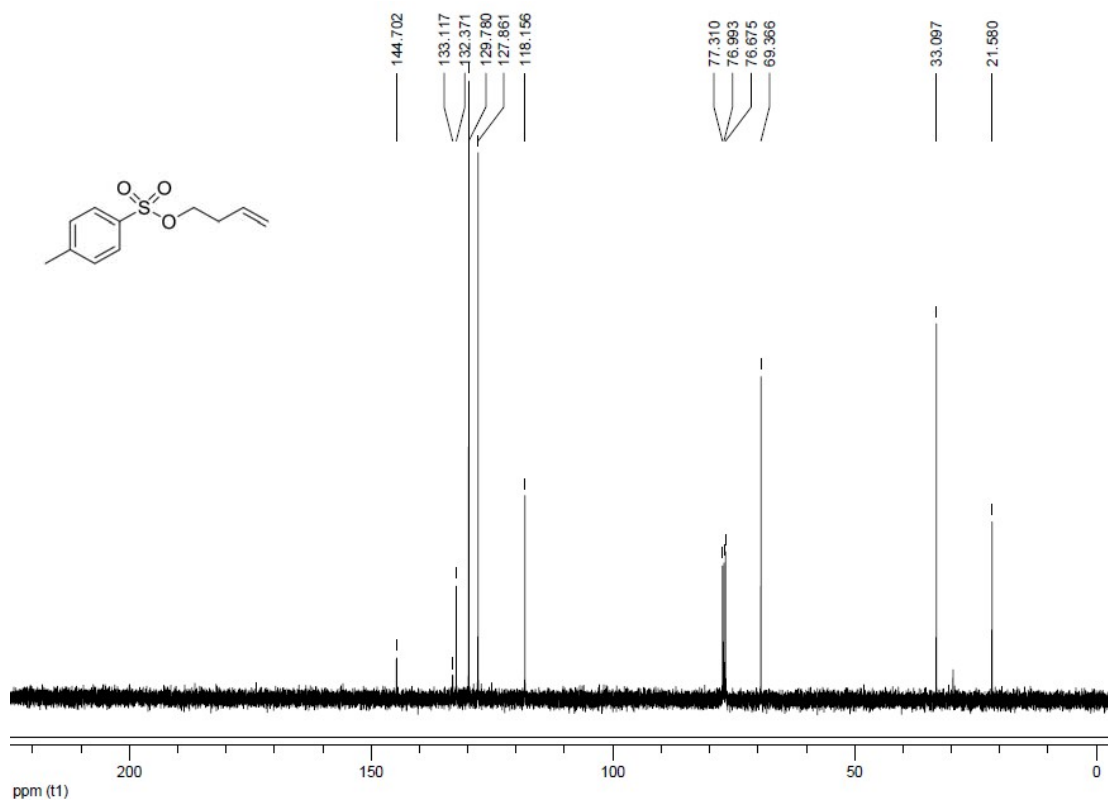
5. References

- [S1] P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani, C. J. Elsevier, *Angew. Chem. Int. Ed.* **2008**, *47*, 3223-3226.
- [S2] R. Shen, T. Chen, Y. Zhao, R. Qiu, Y. Zhou, S. Yin, W. Wang, M. Goto, L. B. Han, *J. Am. Chem. Soc.* **2011**, *133*, 17037-17044.
- [S3] G. Wienhöfer, F. A. Westerhaus, R. V. Jagadeesh, K. Junge, H. Junge, M. Beller, *Chem. Commun.* **2012**, *48*, 4827-4829.
- [S4] D. Gelmana, *Adv. Synth. Catal.* **2015**, *357*, 2351-2357.
- [S5] Y. S. Wagh, N. Asao, *J. Org. Chem.* **2015**, *80*, 847-851.
- [S6] N. A. Heaps, C. D. Poulter, *J. Org. Chem.* **2011**, *76*, 1838-1843.
- [S7] S. S. Li, X. Liu, Y. M. Liu, H. Y. He, K. N. Fan, Y. Cao, *Chem. Commun.* **2014**, *50*, 5626-5628.
- [S8] C. E. Janßen, N. Krause, *Eur. J. Org. Chem.* **2005**, *11*, 2322-2329.
- [S9] M. Bellassoued, J. Aatar, M. Bouzid, M. Damak, *Phosphorus, Sulfur, and Silicon* **2010**, *185*, 1886-1895.
- [S10] J. Zhou, G. Lu, X. Huang, S. Wu, *Synth. Commun.* **1991**, *3*, 435-441.

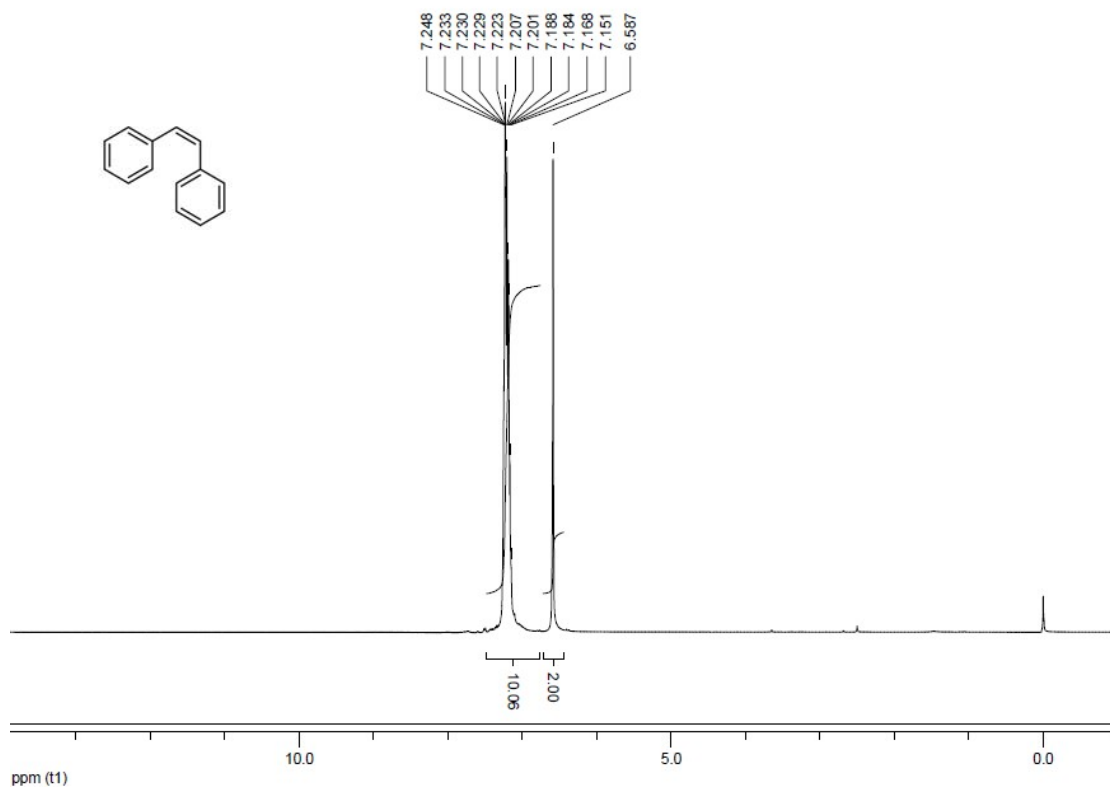
¹H-NMR of 2h



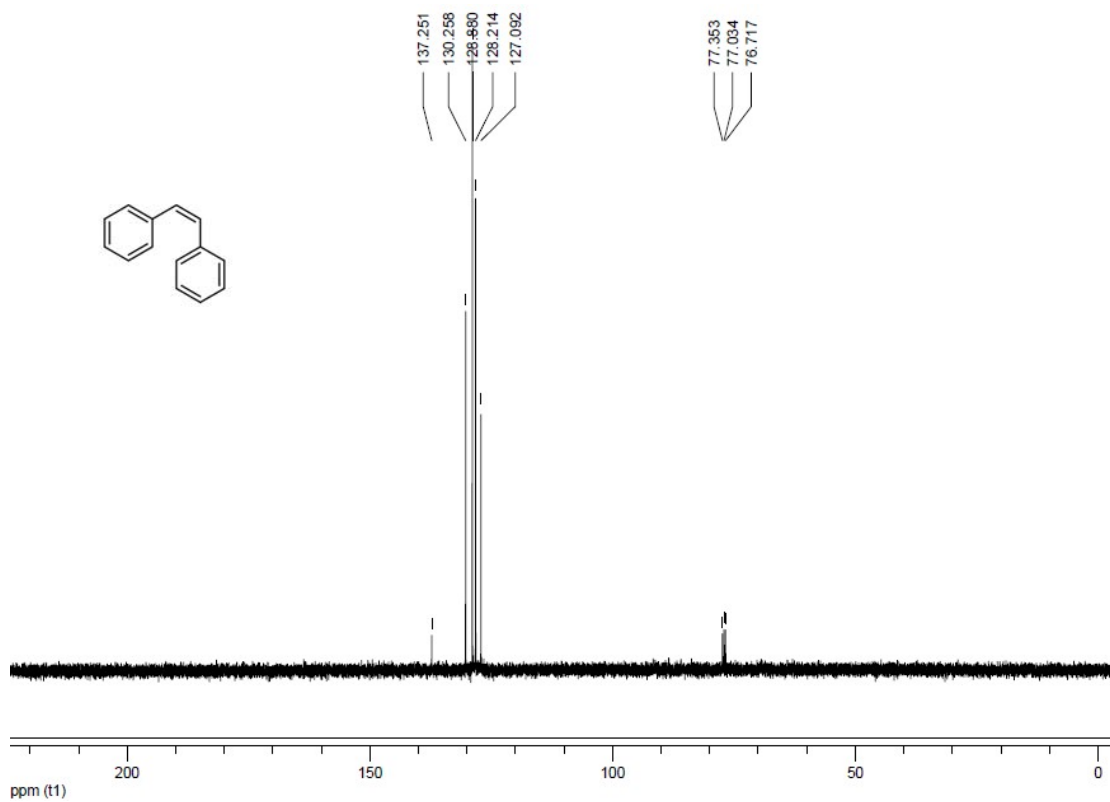
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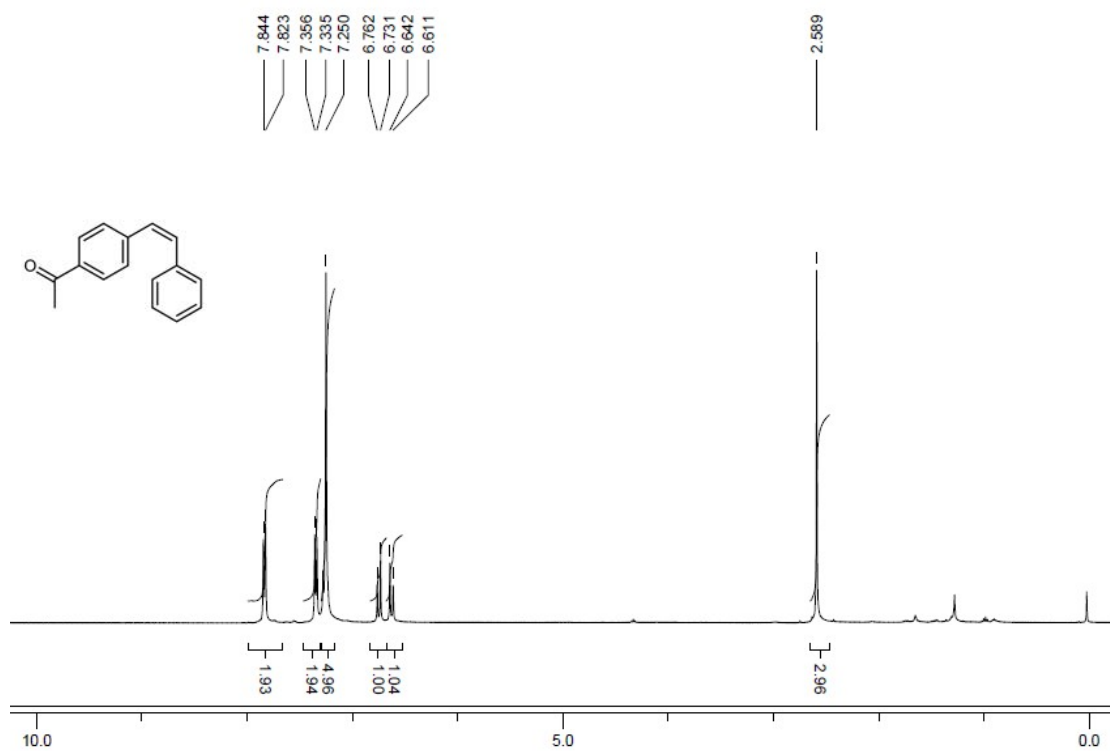
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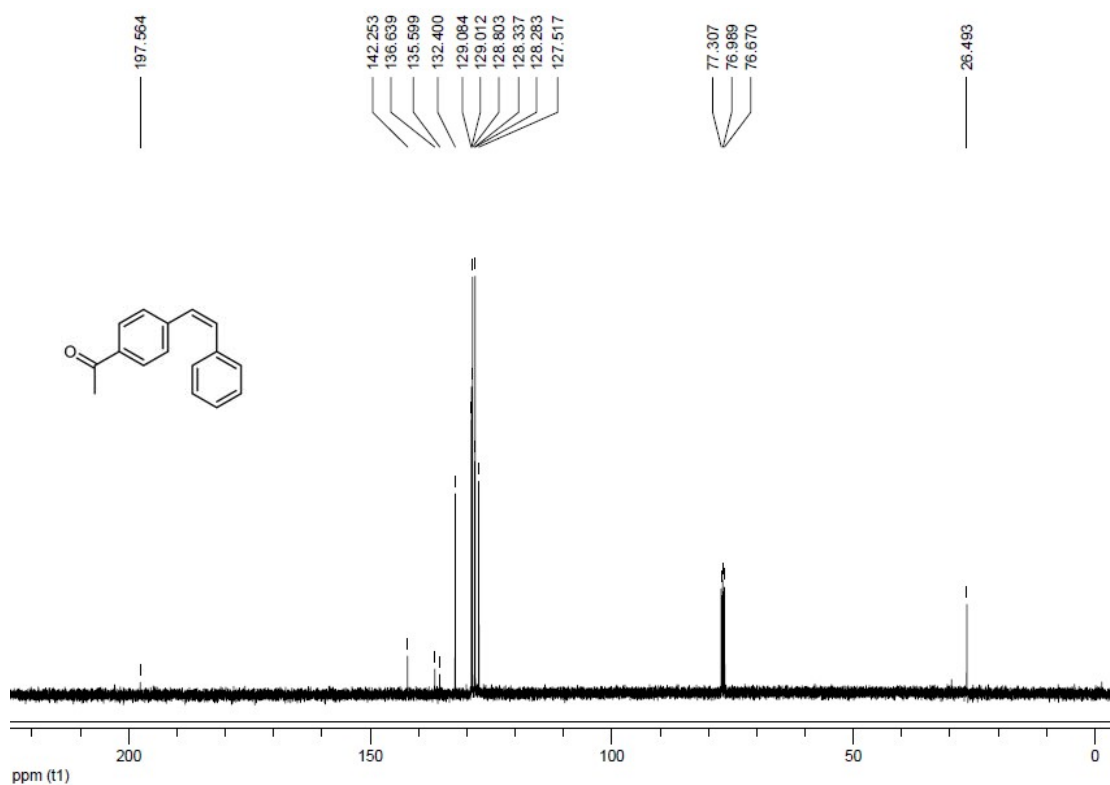
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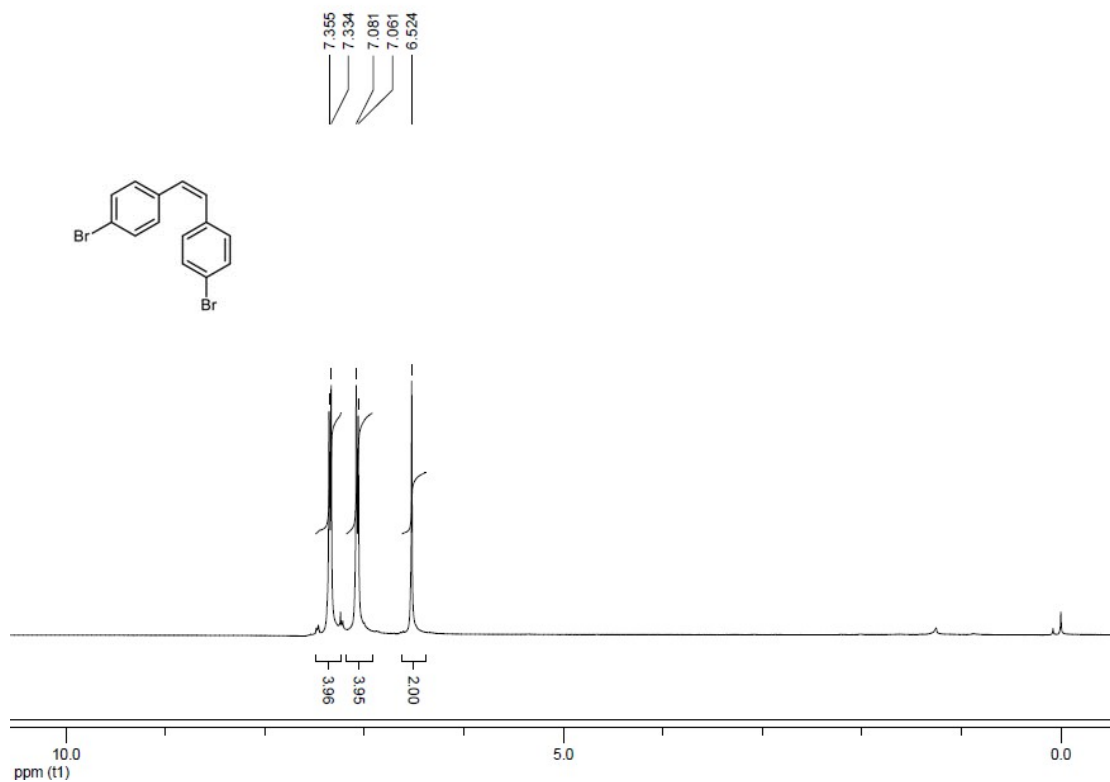
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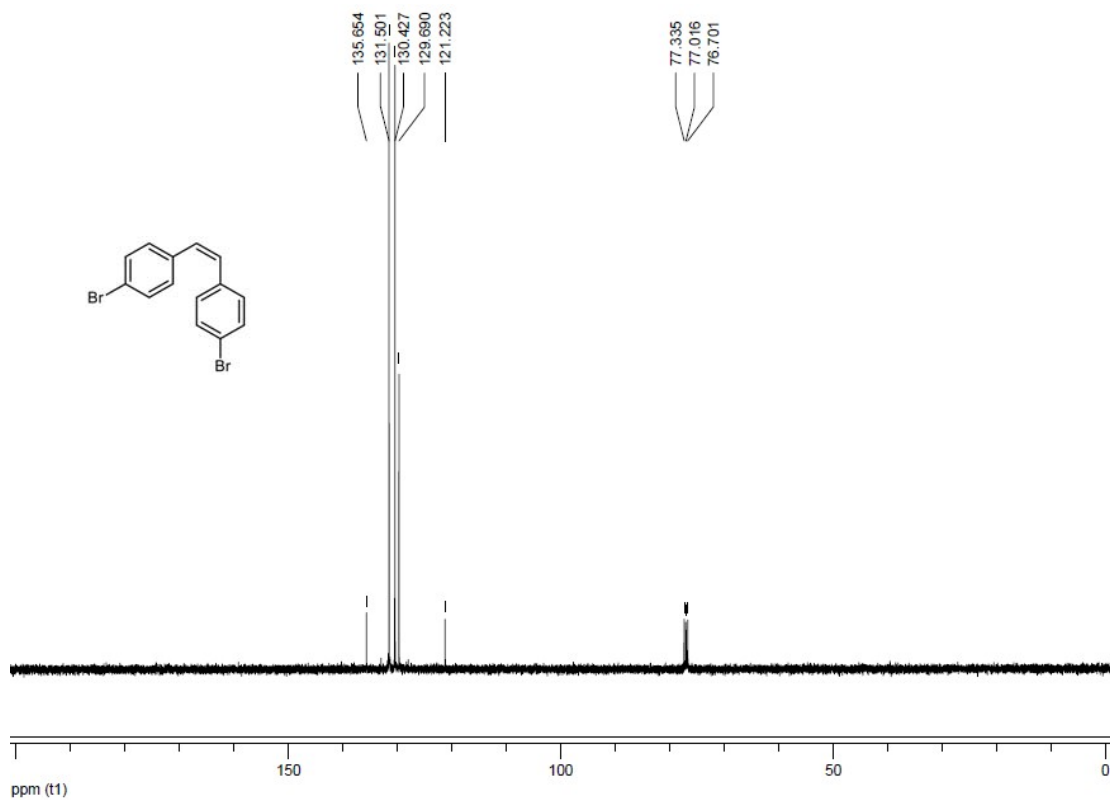
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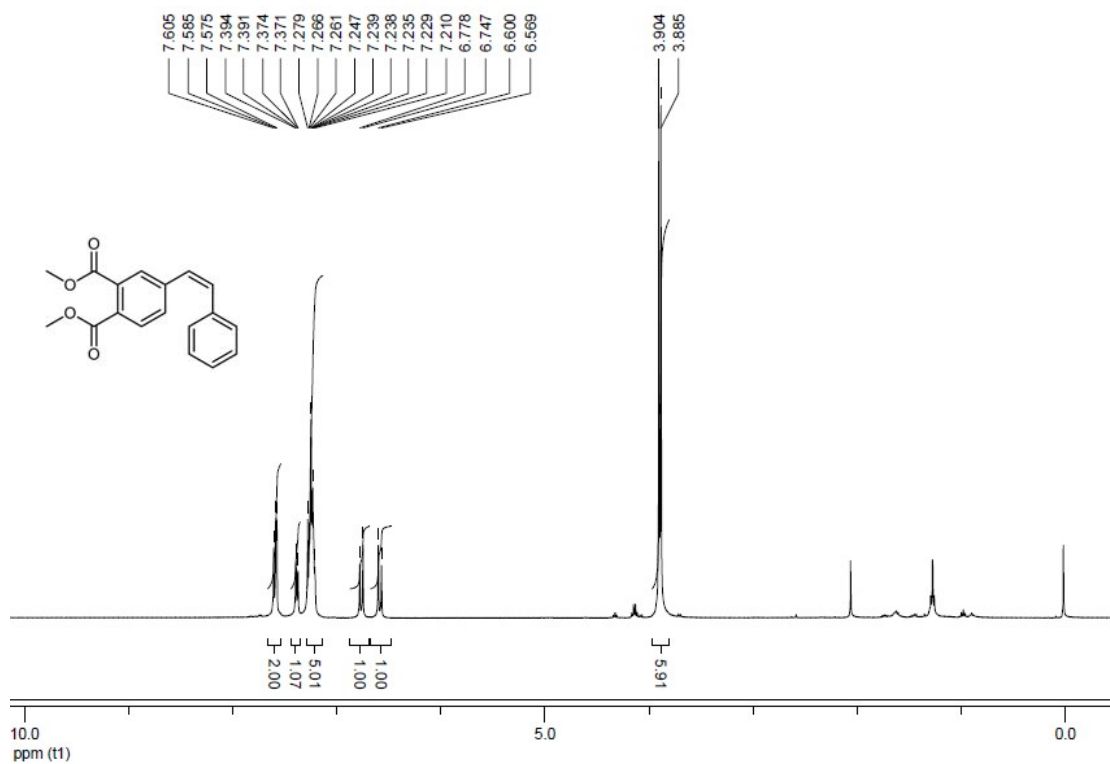
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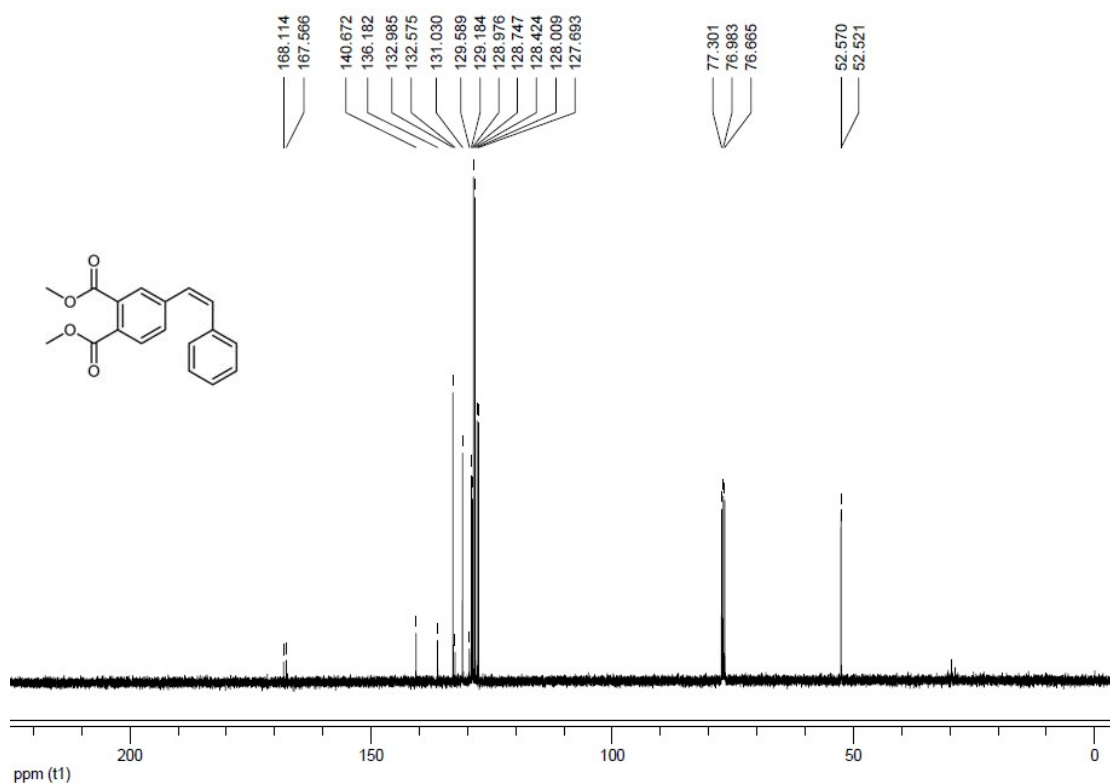
¹³C-NMR of 2o



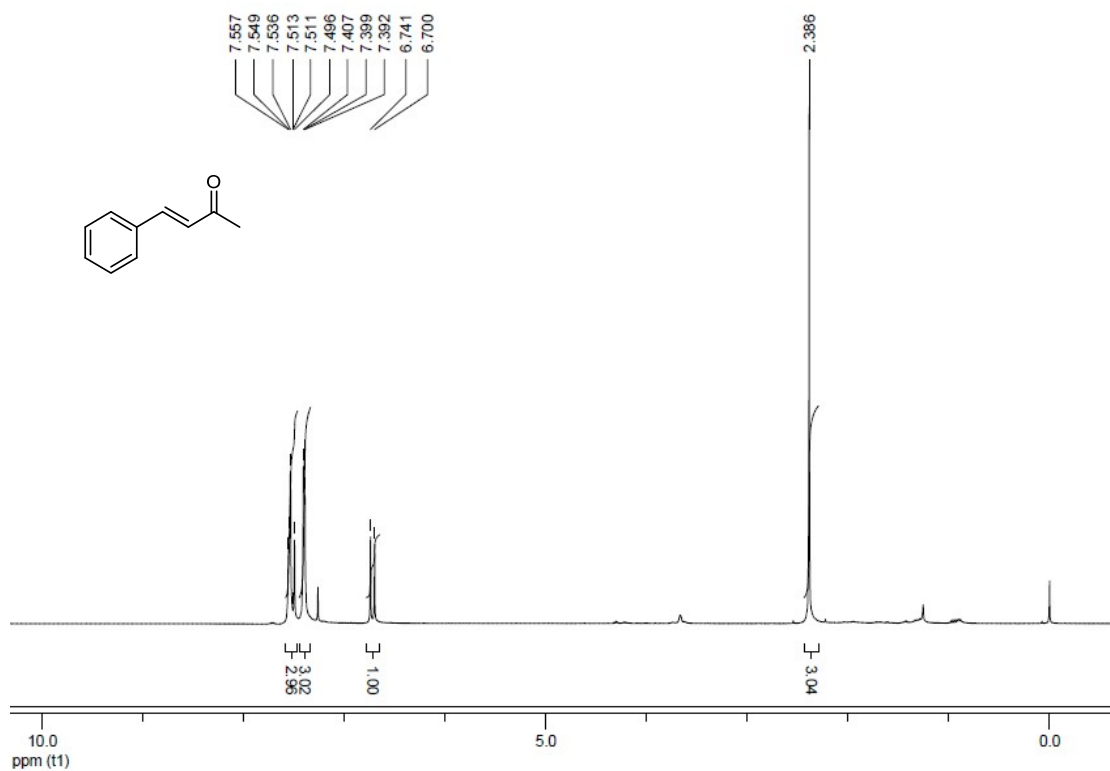
¹H-NMR of 2p



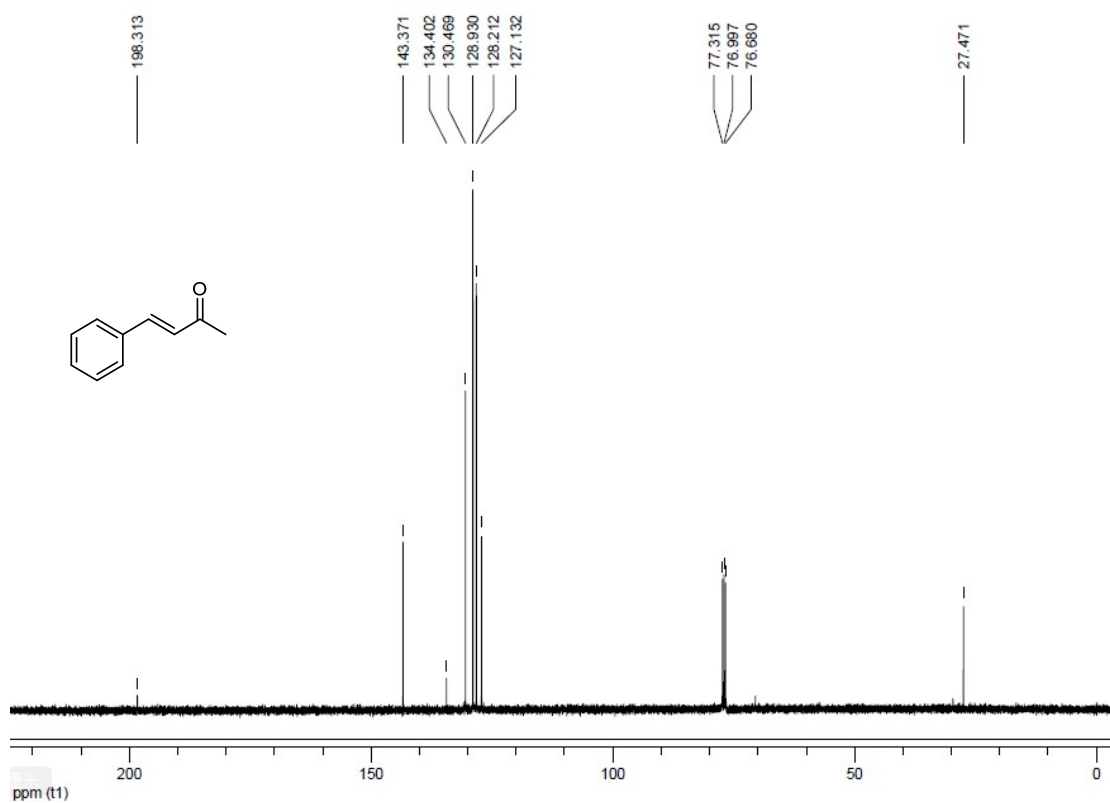
¹³C-NMR of 2p



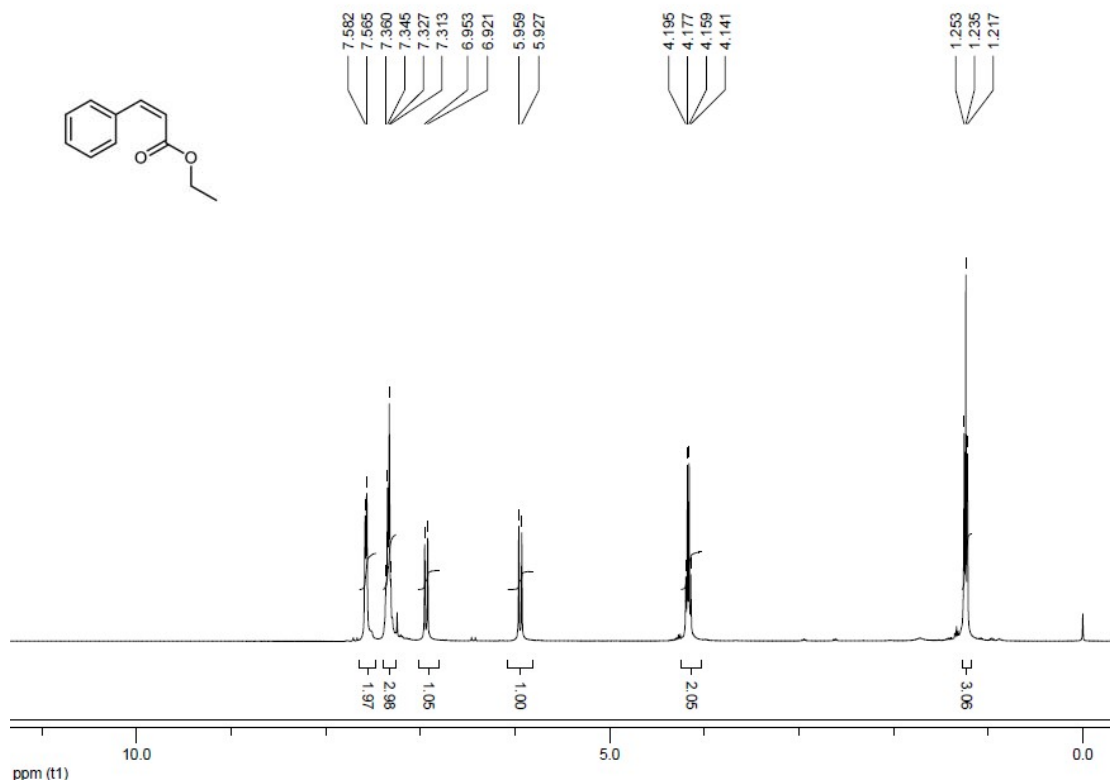
¹H-NMR of 2q



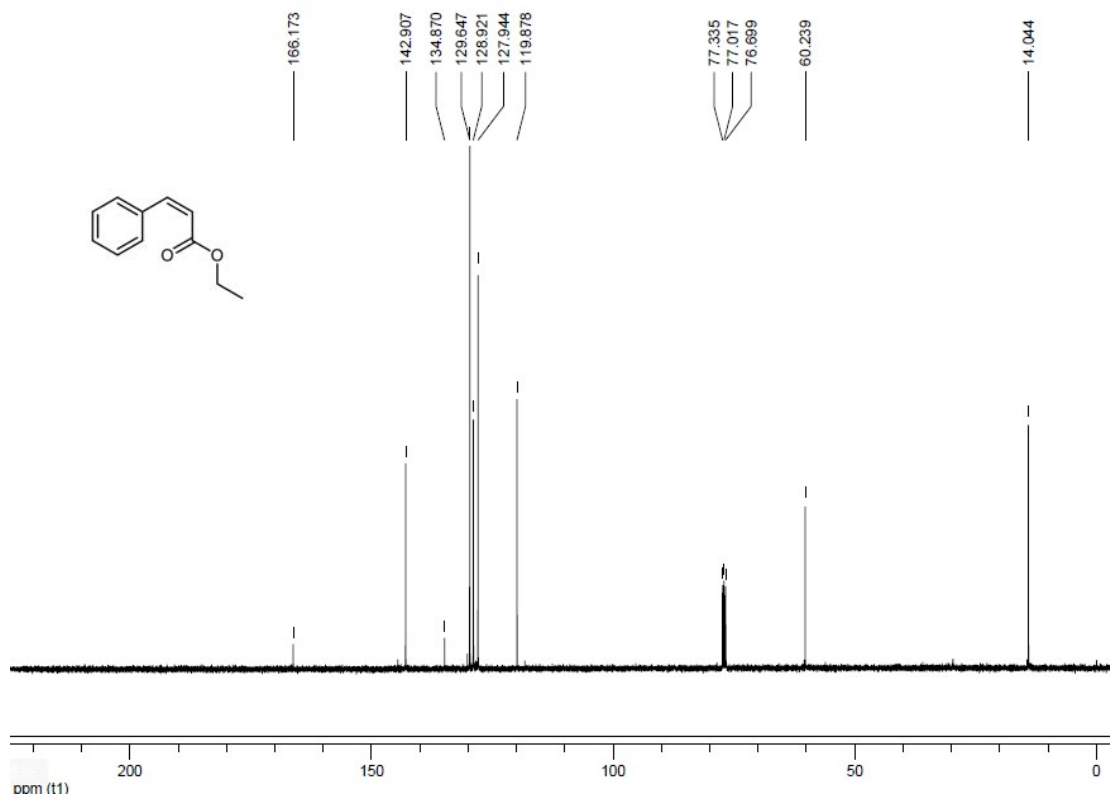
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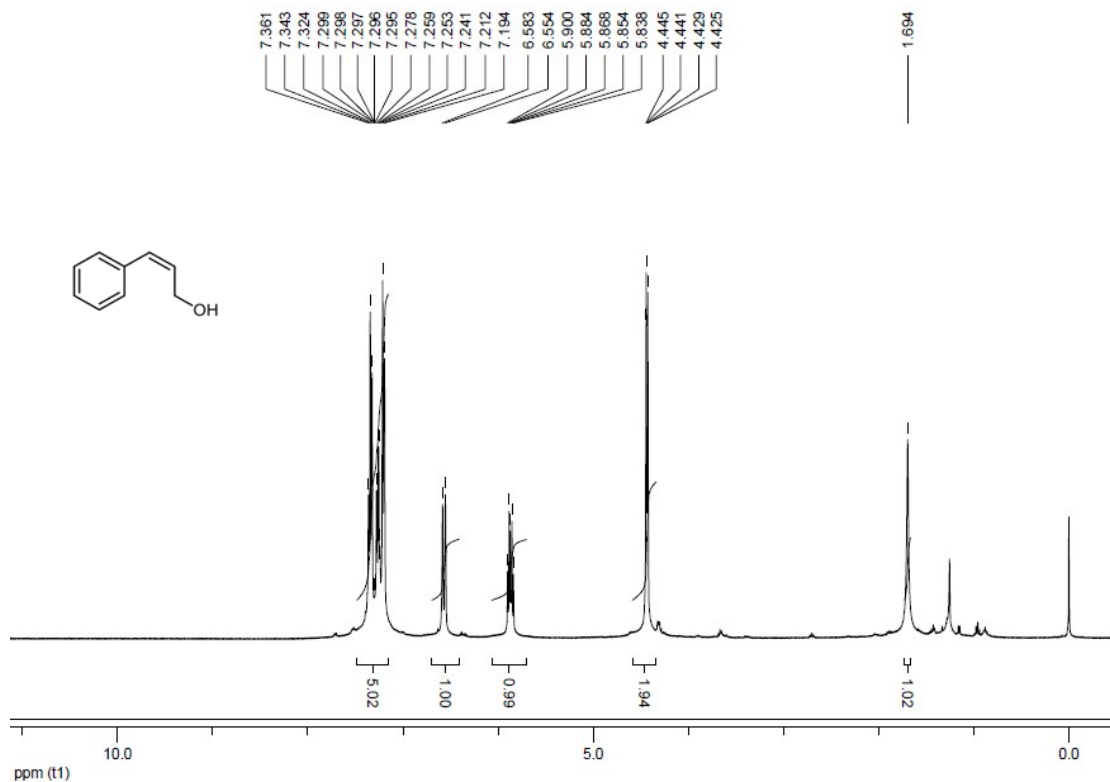
¹H-NMR of 2r



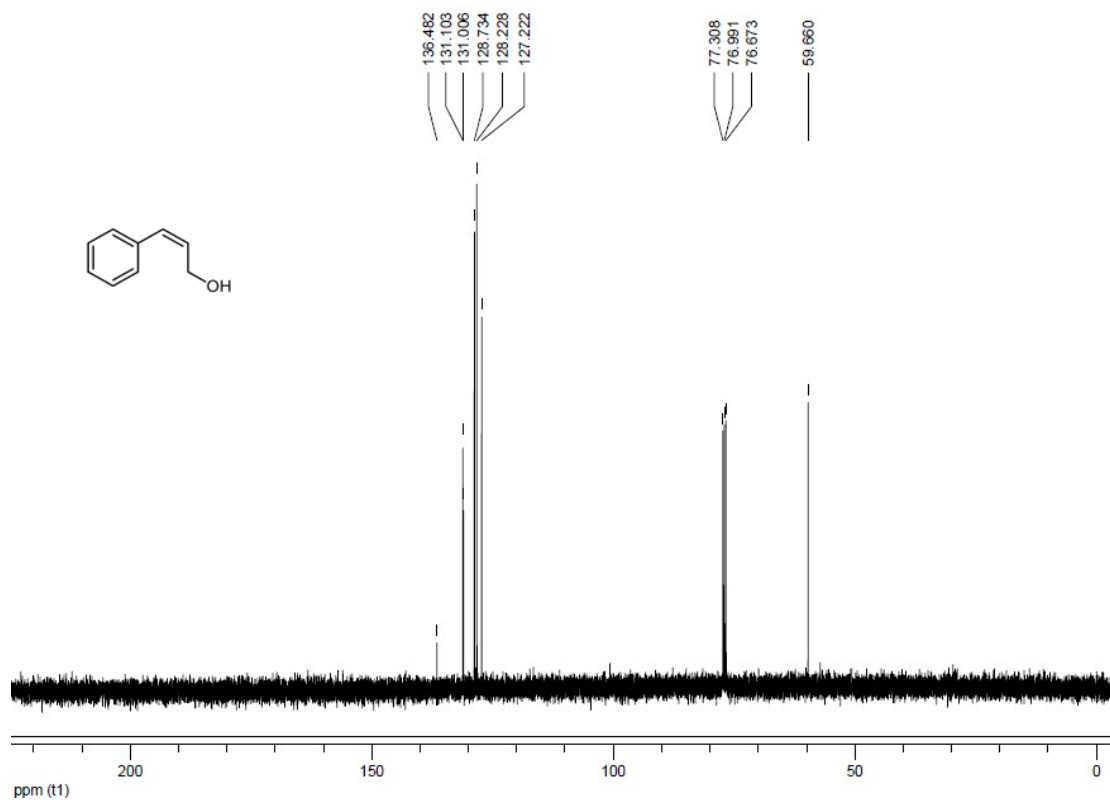
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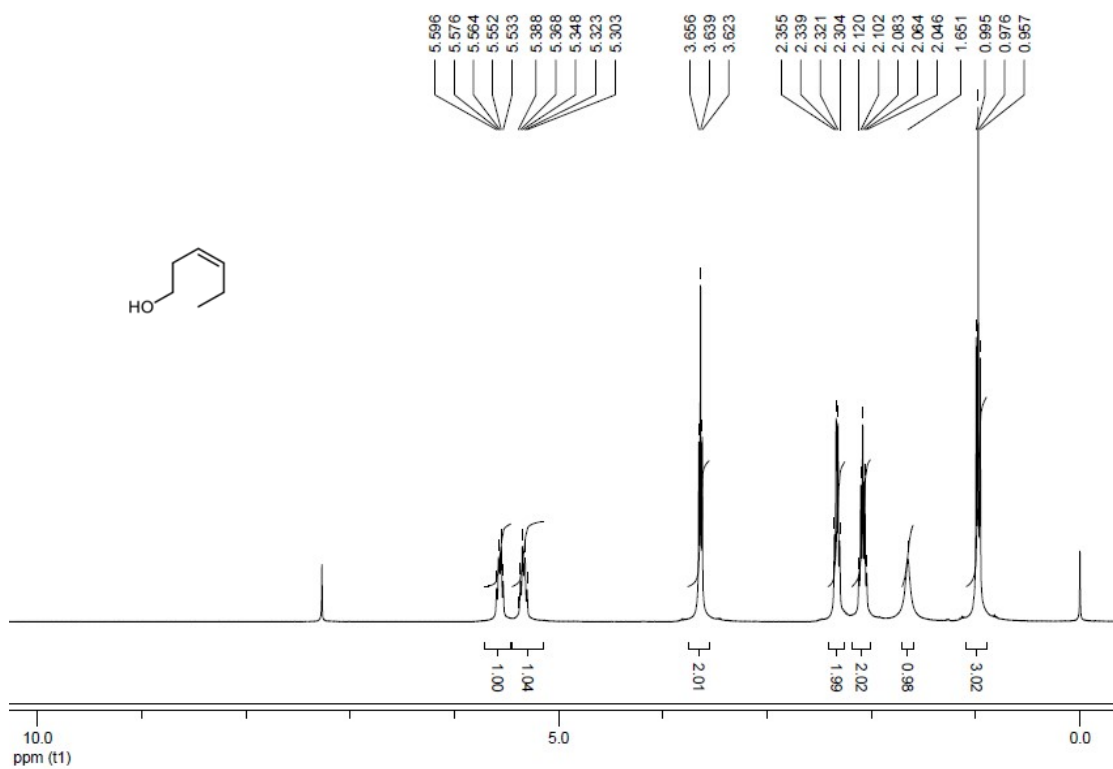
¹H-NMR of 2s



¹³C-NMR of 2s



¹H-NMR of 2t



¹³C-NMR of 2t

