Supporting Information for

Combining Visible Light Catalysis and Transfer Hydrogenation for *in situ* Efficient and Selective Semihydrogenation of Alkynes under Ambient Condition

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Experimental details

a) General information

Unless stated otherwise, all reactions were carried out under Argon. ¹H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). ¹³C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. ¹⁹F NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer (CFCl₃ as an external reference (0 ppm)). High resolution mass spectra were recorded using a Trio-2000 GC-MS spectrometer. Hydrogen content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). Commercially available reagents and solvents were used without further purification unless indicated otherwise. Irradiation with green light was performed using green LEDs (3W, $\lambda = 525 \pm 10$ nm, 145 lm @700mA).

b) Method for the synthesis of colloidal Pd nanoparticle aqueous solution.

A solution of 5.0×10^{-4} M K₂PdCl₄ was prepared in 100 mL water, to which we added 2.0 mL 1.0 $\times 10^{-2}$ M sodium polyacrylate (MW = 3000). Ar gas was bubbled through the solution for 20 min. Then a high flow rate of H₂ (150 mL/min) was bubbling through the solution for 5 min. The reaction vessel was then sealed, and the solution was left for about 5~6 h until the solution turned lightly dark. The lightly dark solution could be used for the reaction and it would be stable for about two months.

c) General procedure for the semihydrogenation of alkynes by visible light catalysis.

The corresponding alkynes **1** in 1.5 mL CH₃CN (0.1 mmol, 1 equiv.), TEOA (0.3 mmol, 3 equiv.), eosin Y (0.003 mmol, 3 mol %), colloidal Pd nanoparticle aqueous solution (4.0 mL, 5.0×10^{-4} M), were dissolved in a 15 mL reaction tube equipped with magnetic stirring bar, the reaction tube was sealed and the resulting mixed solution was strictly degassed with argon for 15 minutes, then reaction tube was irradiated by green LEDs for 2 h. After reaction, the organic layer was extracted with diethyl ether (3 × 5 mL). The combined organic phases were washed with brine and dried over sodium sulphate. The solvent was removed by rotary evaporation and purified by column chromatography on

silica gel using hexane/ethyl acetate (100:1) as eluent.

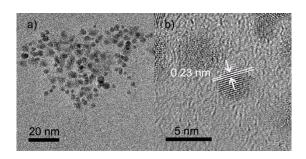


Figure S1. TEM images of colloidal Pd nanoparticle.

entry	TEOA	eosin Y	solvent	solvent	con.	yield (%)		
	y (eq.)	(%)		[%]	alkene	E/Z	alkane	
1		3%	H ₂ O/CH ₃ CN					
2	3.0 eq.		H ₂ O/CH ₃ CN					
3 ^b	3.0 eq.	3%	H ₂ O/CH ₃ CN					
4 ^c	3.0 eq.	3%	H ₂ O/CH ₃ CN					

Table S1. Optimization of reaction conditions.^a

^a Reaction conditions: 0.1 mmol 1,2-diphenylacetylene **1a** in1.5 mL CH₃CN, 4 mL colloidal Pd nanoparticle aqueous solution (5.0×10^{-4} M), degassed by bubbling Ar gas, 2 h irradiation under 525 nm green LEDs; ^b no light; ^c no colloidal Pd nanoparticle.

Scheme S1. Gram-scale reaction (Reaction conditions: 7.5 mmol alkynes 1a in 60 mL CH₃CN, 3.0 eq. TEOA, 2 % eosin Y, 160 mL colloidal Pd nanoparticle aqueous solution $(5.0 \times 10^{-4} \text{ M})$, 525 nm green LEDs, 18 h irradiation at room temperature and pressure).

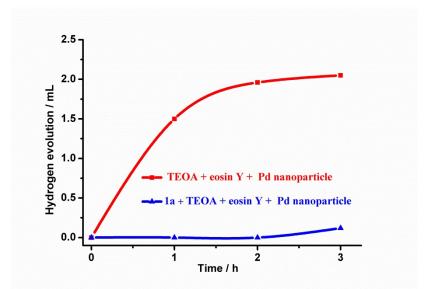


Figure S2. Hydrogen evolution performance in the system with (blue) and without (red) 1a.

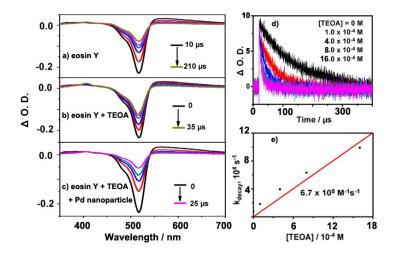


Figure S3. Transient absorption spectra observed after laser excitation ($\lambda_{ex} = 532$ nm) of system containing a) eosin Y (1.0×10^{-5} M), b) eosin Y (1.0×10^{-5} M), TEOA (1.0×10^{-3} M), c) eosin Y (1×10^{-5} M), TEOA (1.0×10^{-3} M), colloidal Pd nanoparticle aqueous solution (5.0×10^{-4} M). d) Transient absorbance time profiles at 560 nm due to ³[eosin Y]* in the absence and presence of TEOA after laser excitation ($\lambda_{ex} = 532$ nm). e) plot of k_{decay} versus [TEOA] for the reaction of ³[eosin Y]* with TEOA.

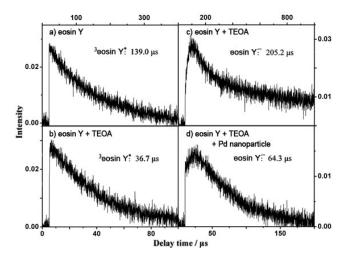


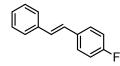
Figure S4. Decay profiles at a) 560 nm of eosin Y $(1.0 \times 10^{-5} \text{ M})$; b) 560 nm of eosin Y $(1.0 \times 10^{-5} \text{ M})$, TEOA $(1.0 \times 10^{-3} \text{ M})$; c) 410 nm of eosin Y $(1.0 \times 10^{-5} \text{ M})$, TEOA $(1.0 \times 10^{-3} \text{ M})$; d) 410 nm of eosin Y $(1.0 \times 10^{-5} \text{ M})$, TEOA $(1.0 \times 10^{-5} \text{ M})$,

Characterization data of the products

(*E*)-1,2-Diphenylethylene

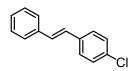
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.57 - 7.49$ (m, 4H), 7.37 (dd, J = 10.4, 4.8 Hz, 4H), 7.30 -7.24 (m, 2H), 7.12 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 138.3$, 129.6, 129.7, 128.5, 127.4. HRMS (EI⁺HR) calcd. for C₁₄H₁₂: 180.0939, found: 180.0939.

(E)-1-(4-fluorophenyl)-2-phenylethene



Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.55 - 7.45$ (m, 4H), 7.37 (t, J = 7.6 Hz, 2H), 7.30 - 7.24 (m, 1H), 7.13 - 6.98 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 163.6-161.1$ (d, J = 250 Hz), 137.2, 133.5, 128.7, 128.5, 127.9, 127.7, 127.5, 126.5, 115.7. ¹⁹F NMR (376 MHz, CDCl₃) $\delta = -114.3$. HRMS (EI⁺HR) calcd. for C₁₄H₁₁F: 198.0845, found: 198.0850.

(E)-1-(4-chloridephenyl)-2-phenylethene



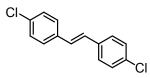
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.50$ (d, J = 7.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.33 (dt, J = 16.8, 7.8 Hz, 5H), 7.06 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 137.0, 135.9, 133.2, 129.3, 128.8,$ 128.7, 127.9, 127.7, 127.4, 126.6. HRMS (EI⁺HR) calcd. for C₁₄H₁₁Cl: 214.0549, found: 214.0546.

(E)-1-(4-bromidephenyl)-2-phenylethene

Br

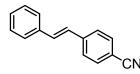
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.58 - 7.50$ (m, 4H), 7.40 - 7.27 (m, 4H), 7.33 - 7.29 (m, 1H), 7.09 (dd, J = 28.3, 16.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 136.9$, 136.3, 133.0, 131.8, 129.4, 128.7, 128.0, 127.6, 126.5, 121.3. HRMS (EI⁺HR) calcd. for C₁₄H₁₁Br: 258.0044, found: 258.0046.

(E)-1,2-Di-(4-chloridephenyl)ethylene



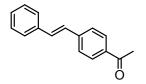
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.43$ (d, J = 8.5 Hz, 4H), 7.33 (d, J = 8.5 Hz, 4H), 7.03 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 136.4$, 134.4, 129.8, 128.9, 128.6. HRMS (EI⁺HR) calcd. for $C_{14}H_{10}Cl_2$: 248.0160, found: 248.0161.

(E)-1-(4-cyanidephenyl)-2-phenylethene



Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.65$ (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.34 (dd, J = 8.3, 6.3 Hz, 1H), 7.24 (d, J = 16.3 Hz, 1H), 7.11 (d, J = 16.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 142.8$, 137.2, 133.4, 133.4, 129.8, 129.6, 127.8, 127.8, 127.7, 119.9, 111.5. HRMS (EI⁺HR) calcd. for C₁₅H₁₁N: 205.0891, found: 205.0899.

(E)-1-(4-Acetylphenyl)-2-phenylethene

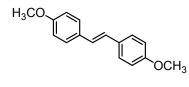


Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.8$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.97$ (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.22 (s, 1H), 7.14 (d, J = 16.3 Hz, 1H), 2.62 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 198.4, 142.9, 137.6, 136.9, 132.4, 129.8, 129.7, 129.2, 128.4, 127.7, 127.4, 27.5. HRMS (EI⁺HR) calcd. for C₁₆H₁₄O: 222.1045, found: 222.1044.

(E)-1-(4-methylphenyl)-2-phenylethene

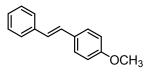
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.54 - 7.50$ (m, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 4.5 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 7.15 - 7.03 (dd, J = 16 Hz, m, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 138.5$, 135.5, 130.3, 129.6, 128.6, 128.3, 127.4, 127.3, 127.2, 22.2. HRMS (EI⁺HR) calcd. for C₁₅H₁₄: 194.1096, found: 194.1106.

(E)-1,2-Di-(4-methoxyphenyl)ethylene



Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.43$ (d, J = 8.7 Hz, 4H), 6.94 (s, 2H), 6.90 (d, J = 8.7 Hz, 4H), 3.84 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 159.9$, 131.4, 128.3, 127.1, 115.0, 56.2. HRMS (EI⁺HR) calcd. for C₁₆H₁₆O₂: 240.1150, found: 240.1153.

(E)-1-(4-methoxyphenyl)-2-phenylethene



Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 95:5. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.55 - 7.44$ (m, 5H), 7.34 (d, J = 7.9 Hz, 2H), 7.08 (d, J =16.3 Hz, 1H), 6.98 (d, J = 16.3 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 134.0$, 132.4, 129.6, 129.2, 128.9, 128.6, 128.1, 127.6, 127.2, 115.1, 56.3. HRMS (EI⁺HR) calcd. for C₁₅H₁₄O: 210.1045, found: 210.1044.

(Z)-3-phenylprop-2-en-1-ol

Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 50:1, $R_f = 0.7$), E/Z = 5:95. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.35$ (t, J = 7.4 Hz, 2H), 7.30 - 7.26 (m, 1H), 7.21 (d, J = 7.2 Hz, 2H), 6.58 (d, J = 11.7 Hz, 1H), 5.88 (dt, J = 11.9, 6.4 Hz, 1H), 4.45 (dd, J = 6.4, 1.6 Hz, 2H), 1.59 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 137.4$, 132.1, 132.0, 129.7, 129.2, 128.2, 60.6. HRMS (EI⁺HR) calcd. for C₉H₁₀O: 134.0732, found: 134.0733.

(Z)-methyl-3-phenylacrylate

CO₂CH₃

Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 80:1, $R_f = 0.8$), E/Z = 5:95. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.59$ (dd, J = 7.5, 1.6 Hz, 2H), 7.43 – 7.29 (m, 3H), 6.96 (d, J = 12.6 Hz, 1H), 5.96 (d, J = 12.6 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 167.5$, 144.3, 135.7, 130.6, 130.0, 129.0, 120.2, 52.3. HRMS (EI⁺HR) calcd. for C₁₀H₁₀O₂: 162.0681, found: 162.0681.

(Z)-ethyl-3-phenylacrylate

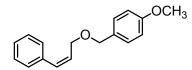
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 80:1, $R_f = 0.8$), E/Z = 5:95. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.61 - 7.55$ (m, 2H), 7.35 (d, J = 7.5 Hz, 3H), 6.95 (d, J = 12.6 Hz, 1H), 5.95 (d, J = 12.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 167.2$, 143.9, 135.8, 130.6, 129.9, 128.9, 120.8, 61.2, 15.0. HRMS (EI⁺HR) calcd. for C₁₁H₁₂O₂: 176.0837, found: 176.0835.

(Z)-hex-1-en-1-ylbenzene

C₄H₉

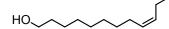
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.9$), E/Z = 5:95. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.36 - 7.30$ (m, 2H), 7.26 (dd, J = 13.7, 9.1 Hz, 3H), 6.40 (d, J = 11.6 Hz, 1H), 5.66 (dt, J = 11.6, 7.3 Hz, 1H), 2.38 - 2.27 (m, 2H), 1.46 - 1.41 (m, 2H), 1.35 (dd, J = 14.9, 7.3 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 137.9, 133.2, 128.8, 128.7, 128.5, 128.1, 126.4, 32.4, 28.4, 22.4, 14.0.$ HRMS (EI⁺HR) calcd. for C₁₂H₁₆: 160.1252, found: 160.1255.

(Z)-1-methoxy-4-(((3-phenylallyl)oxy)methyl)benzene



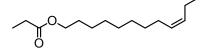
Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 60:1, $R_f = 0.7$), E/Z = 7:93. ¹H NMR (400 MHz, CDCl₃) $\delta = 7.34 - 7.31$ (m, 2H), 7.29 - 7.25 (m, 3H), 7.23 - 7.19 (m, 2H), 6.90 - 6.85 (m, 2H), 6.63 (d, J = 11.8 Hz, 1H), 5.97 - 5.85 (m, 1H), 4.47 (s, 2H), 4.29 (dd, J = 6.4, 1.6 Hz, 2H), 3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 160.2$, 137.6, 132.7, 131.2, 130.4, 130.0, 129.7, 129.1, 128.1, 114.7, 73.0, 67.5, 56.2. HRMS (EI⁺HR) calcd. for C₁₇H₁₈O₂: 254.1307, found: 254.1303.

(Z)-dodec-9-en-1-ol



Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 100:1, $R_f = 0.8$), E/Z = 8:92. ¹H NMR (400 MHz, CDCl₃) $\delta = 5.48 - 5.26$ (m, 2H), 3.63 (t, J = 6.6 Hz, 2H), 2.08 - 1.91 (m, 4H), 1.55 (dd, J = 14.0, 6.9 Hz, 2H), 1.47 (s, 1H), 1.32 (d, J = 19.1 Hz, 10H), 0.95 (td, J = 7.5, 2.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 132.5$, 130.2, 64.0, 33.7, 30.7, 30.4, 30.3, 30.1, 28.0, 26.7, 21.4, 15.3. HRMS (EI⁺HR) calcd. for C₁₂H₂₄O: 184.1827, found: 184.1832.

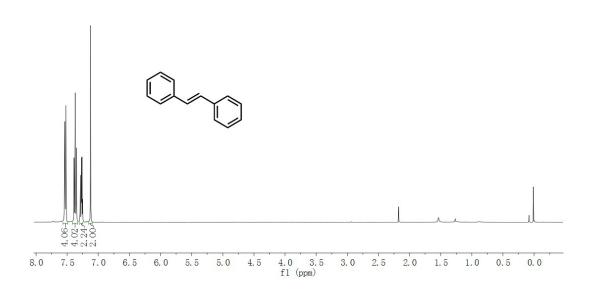
(Z)-dodec-9-en-1-yl propionate

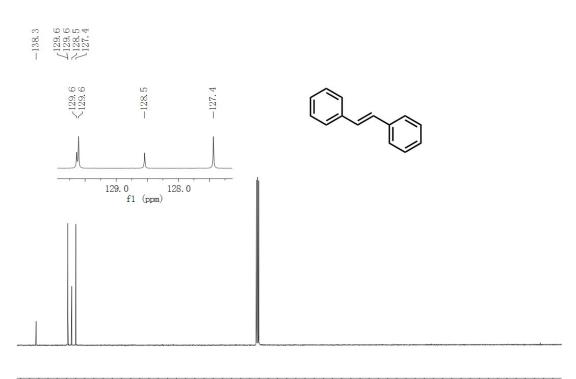


Purified by column chromatography on silica gel (eluting with hexane/ethyl acteate = 80:1, $R_f = 0.9$), E/Z = 6:94. ¹H NMR (400 MHz, CDCl₃) $\delta = 5.47 - 5.26$ (m, 2H), 4.06 (t, J = 6.7 Hz, 2H), 2.32 (q, J = 7.6 Hz, 2H), 2.09 - 1.93 (m, 4H), 1.61 (dd, J = 13.7, 6.8 Hz, 2H), 1.30 (s, 10H), 1.14 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 175.5, 132.5, 130.2, 65.4, 30.6, 30.3, 30.1, 30.1, 29.6, 28.6, 28.0, 26.8, 21.4, 15.3, 10.1.$ HRMS (EI⁺HR) calcd. for C₁₅H₂₈O₂: 240.2089, found:

¹H NMR and ¹³C NMR spectra

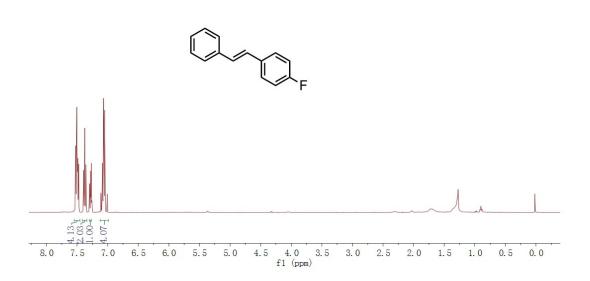




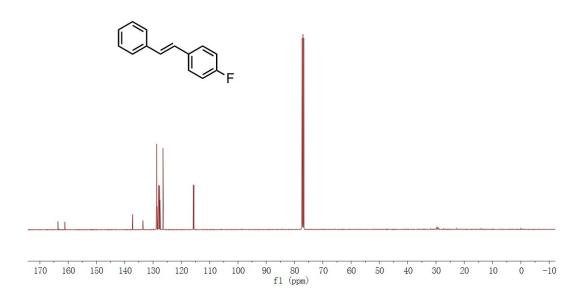


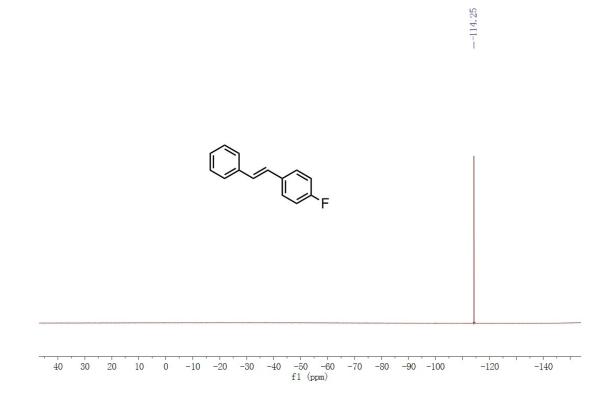
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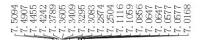
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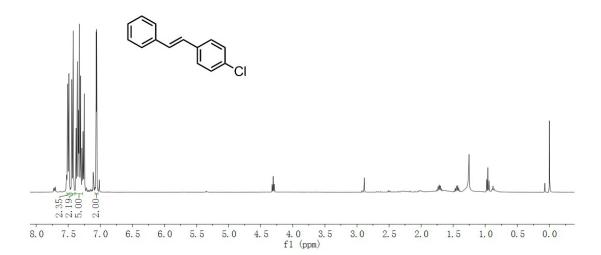




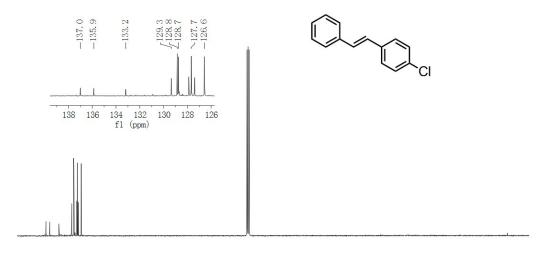






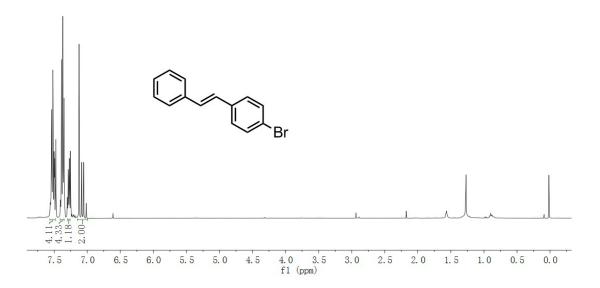




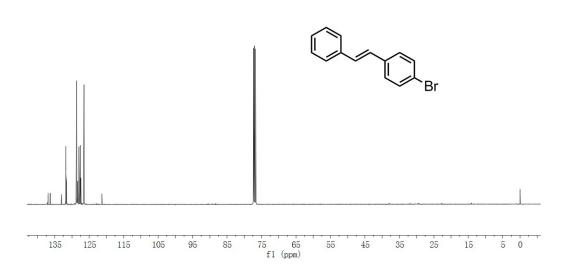


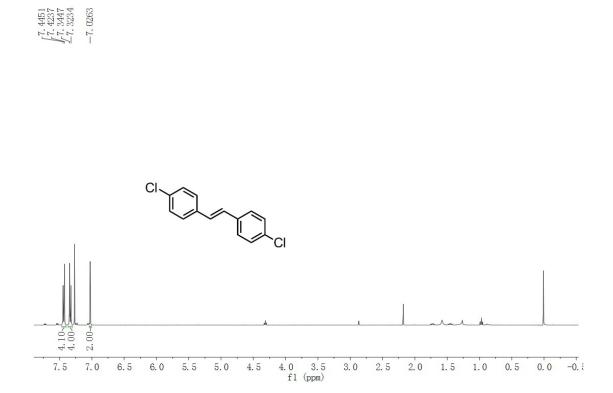
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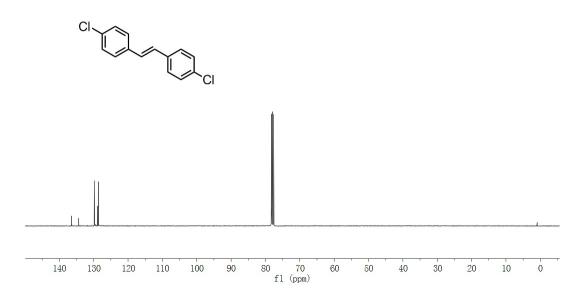


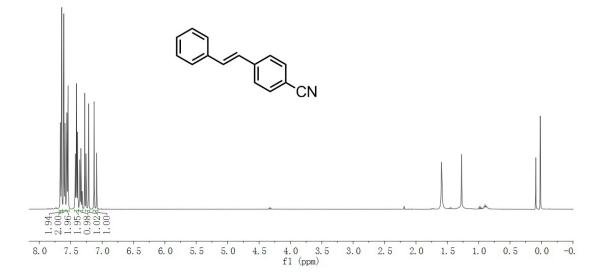




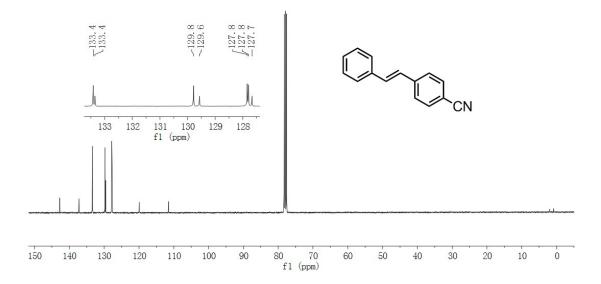


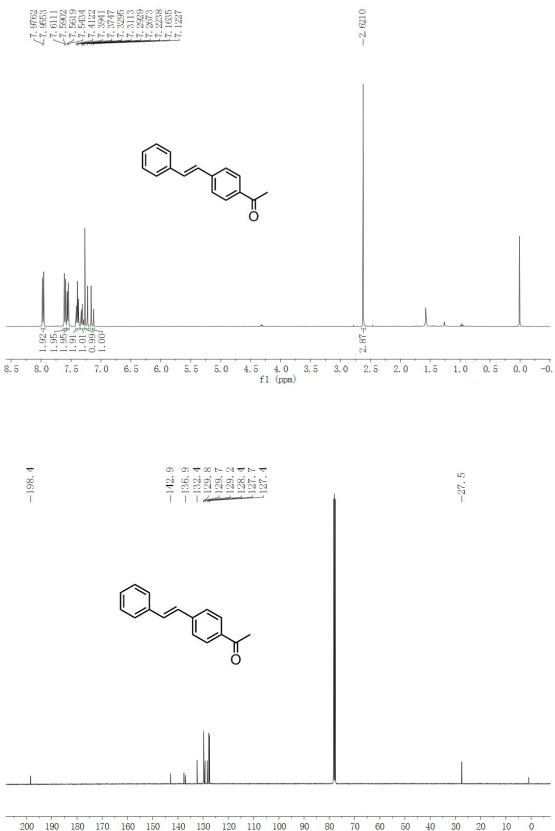
-136.4-134.4 -129.8 -128.9128.6



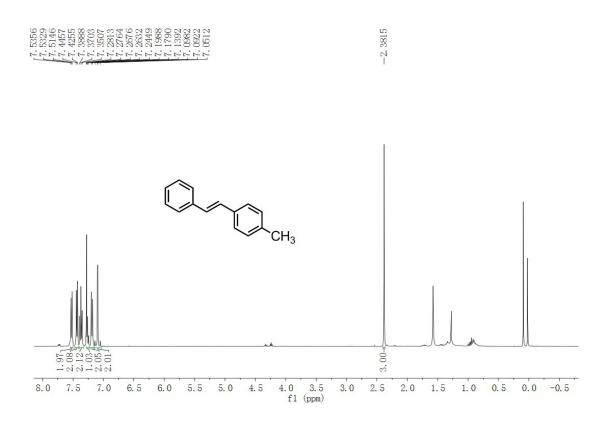


 $-142.8 \\ -137.2 \\ -133.4 \\ -133.4 \\ 127.8 \\ -119.9 \\ -111.5 \\ -1$



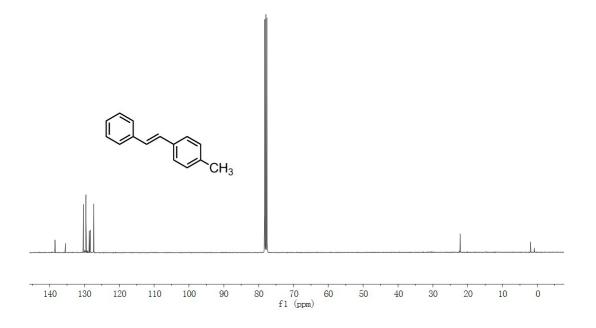


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 f1 (ppm) 10 0 20

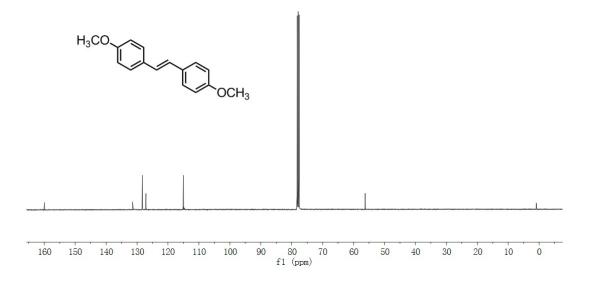


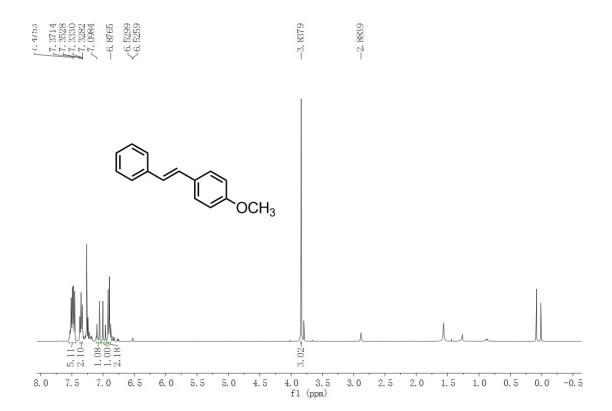




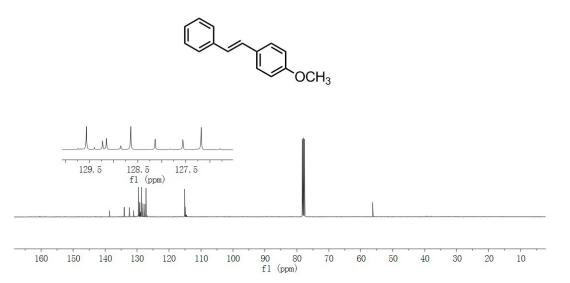






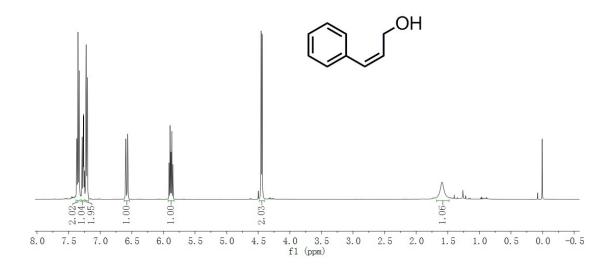






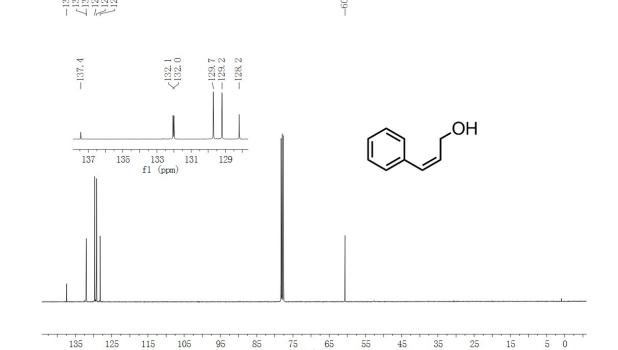
-56.3



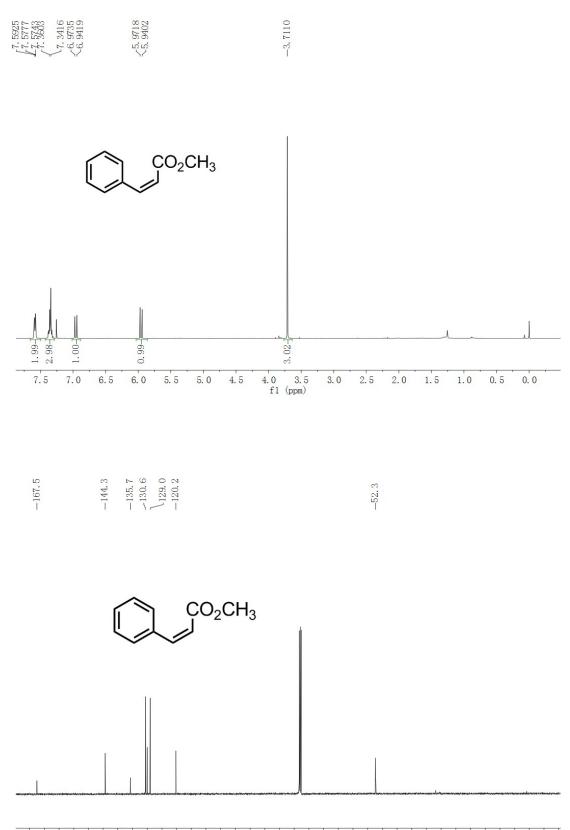




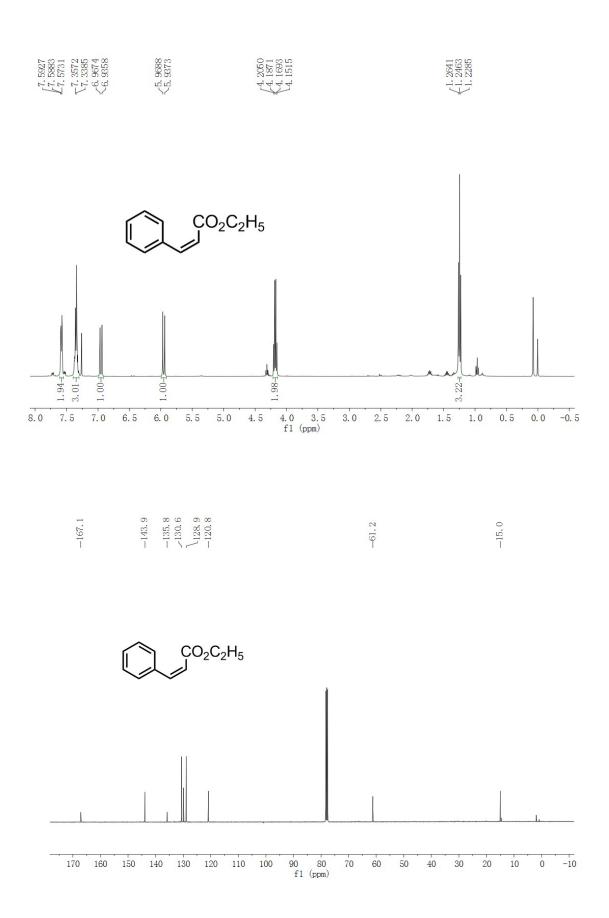




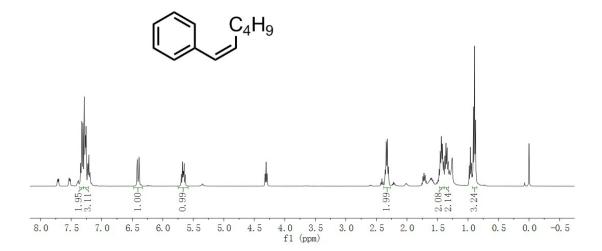




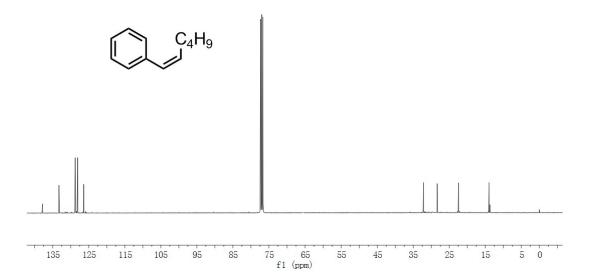
90 80 f1 (ppm) 0 -10

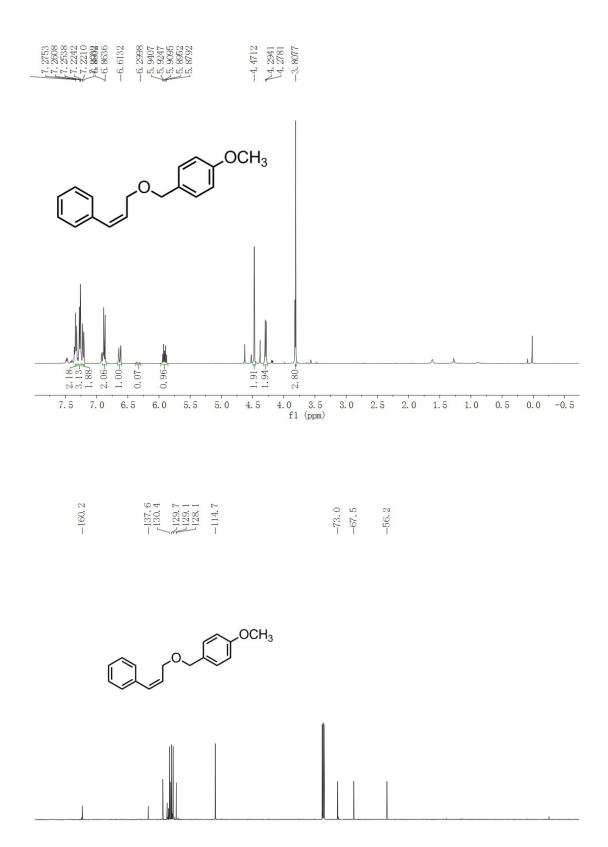












170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

