Supporting Information

Enhanced Heck reaction on flower-like Co(Mg or Ni)Al layered double hydroxides supported ultrafine PdCo alloy nanoclusters catalysts: the promotional effect of Co

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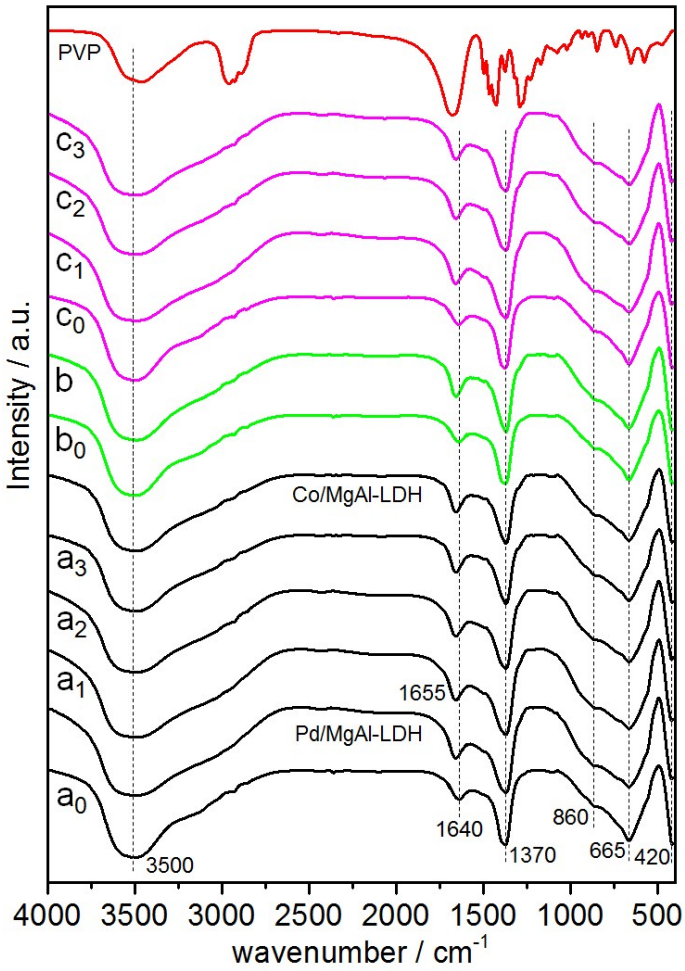


Fig. S1 FT-IR spectra of 0.81-$PdCo_{0.10}$/MgAl-LDH (a_1), 0.86-$PdCo_{0.28}$/MgAl-LDH (a_2), 0.79-$PdCo_{0.54}$/MgAl-LDH (a_3), 0.64-$PdCo_{0.28}$/NiAl-LDH (b), and x-$PdCo_{0.28}$/CoAl-LDH (x = 0.67 (c_1), 0.10 (c_2), 0.01 (c_3)) compared with Pd/MgAl-LDH, Co/MgAl-LDH, corresponding supports (a_0-c_0) and PVP.

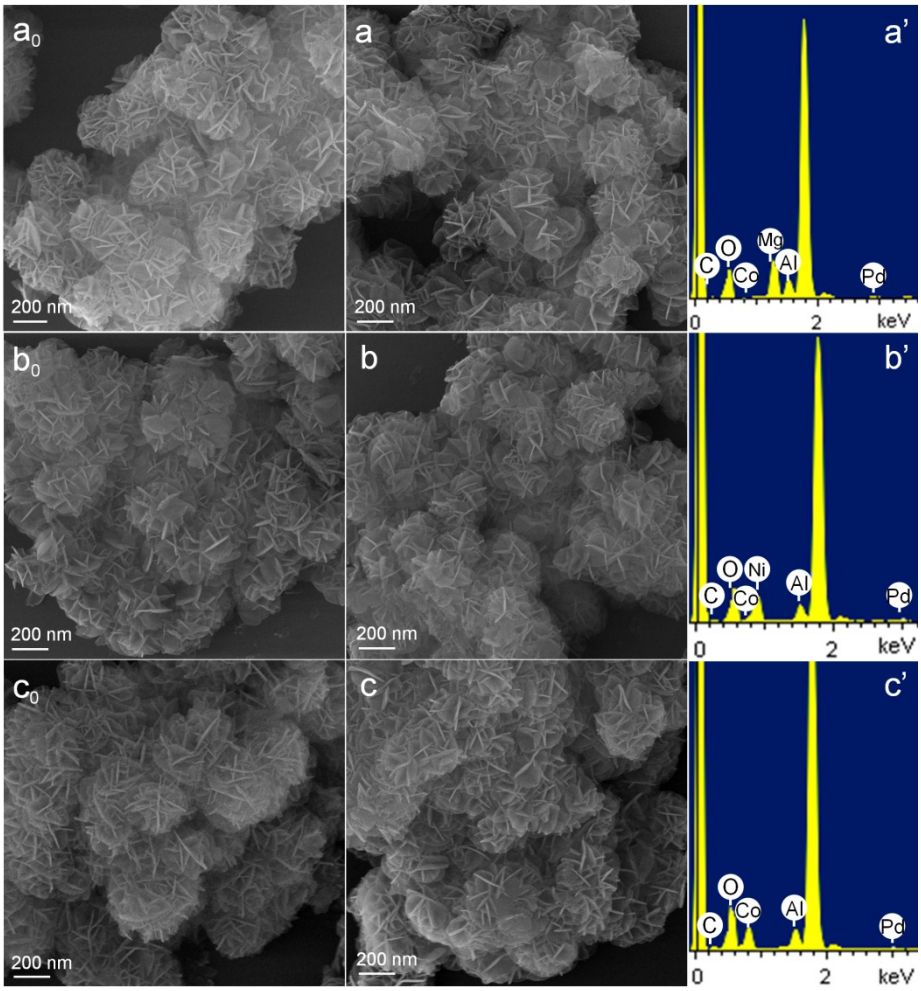


Fig. S2 SEM images and EDS spectra of 0.86-$PdCo_{0.28}$/MgAl-LDH (a, a'), 0.64-$PdCo_{0.28}$/NiAl-LDH (b, b') and 0.67-$PdCo_{0.28}$/CoAl-LDH (c, c') compared with corresponding supports (a_0-c_0).

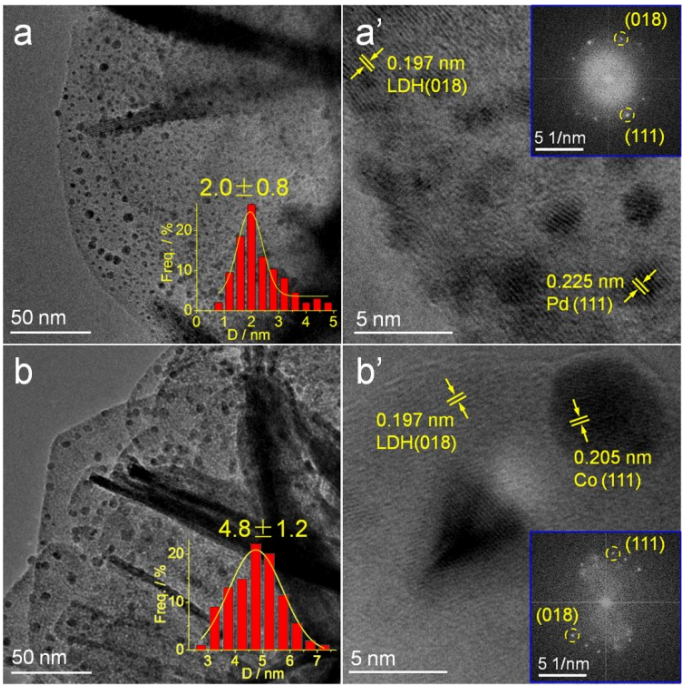


Fig. S3 HREM images of Pd/MgAl-LDH (a, a') and Co/MgAl-LDH (b, b') (insets: particle size distribution and FFT).

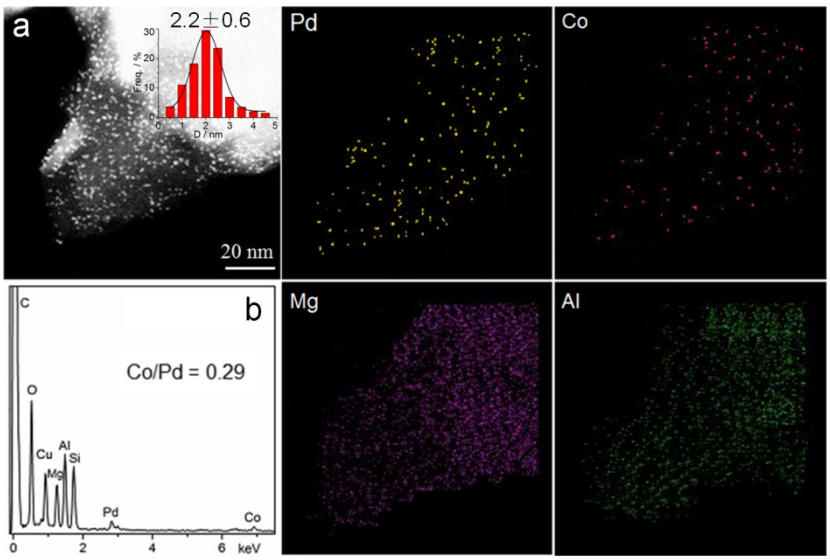


Fig. S4 HADDF-STEM (a), EDX (b) and element mapping images of 0.86-$PdCo_{0.28}$/MgAl-LDH (inset: histogram of size distribution).

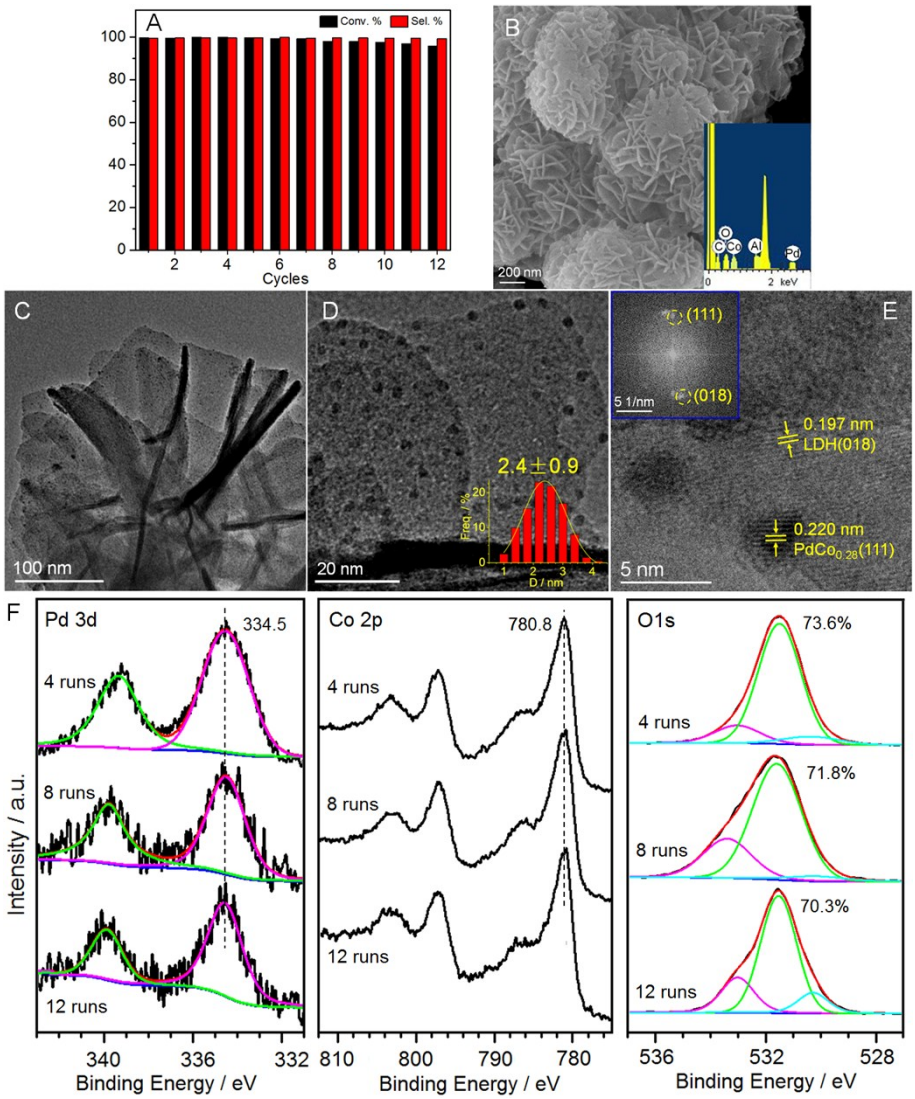


Fig. S5 (A) Recycling Heck reaction results of 0.67-$PdCo_{0.28}$/CoAl-LDH, (B–E) SEM, HRTEM images of the recycled catalyst after 12 runs (insets: EDX spectra, particle size distribution and FFT), and (F) Pd 3d, Co 2p and O 1s XPS spectra of the recovered catalysts after different runs compared with CoAl-LDH.

Clearly, the Pd 3d XPS of the recovered samples after 4, 8, and 12 runs show almost same Pd $3d_{5/2}$ BE values at ~334.50 eV as the fresh one, implying the well-kept active Pd^0 species after several runs. While the Co 2p spectra only show the Co^{2+} $2p_{3/2}$ originated from CoAl-LDH support, also almost same as the fresh one. The O 1s XPS after several runs show slightly decreased surface OH contents with an order of 75.5% (fresh) > 73.6% (4 runs) > 71.8% (8 runs) > 70.3% (12 runs), indicating the slightly weakened $PdCo_{0.28}$ NCs – CoAl-LDH interaction, in line with the slightly reduced Heck activity of the recovered sample after 12 runs.

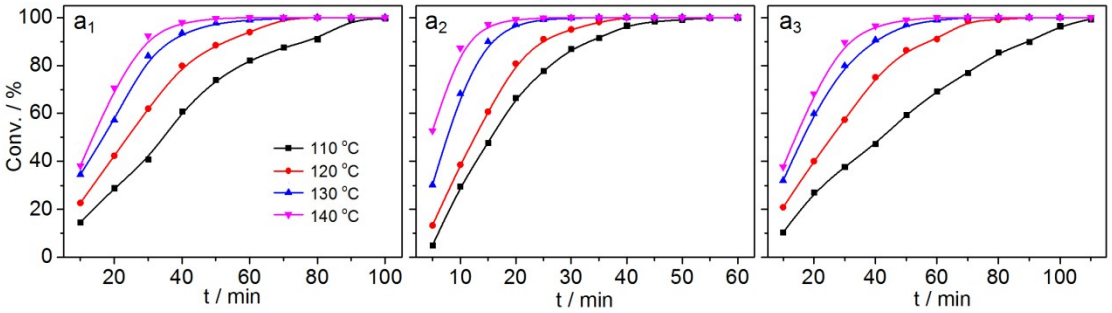


Fig. S6 Conv. – time (t) plots for the Heck reaction of PhI with styrene over the 0.81-$PdCo_{0.10}$/MgAl-LDH (a_1), 0.86-$PdCo_{0.28}$/MgAl-LDH (a_2) and 0.79-$PdCo_{0.54}$/ MgAl-LDH (a_3) at various reaction temperatures.

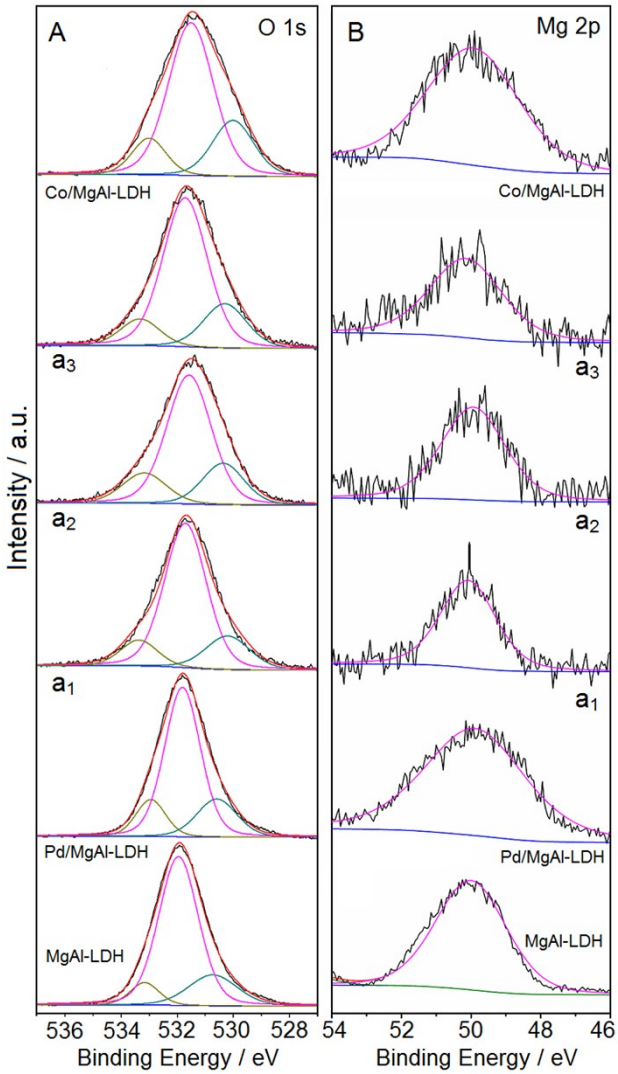


Fig. S7 O 1s (A) and Mg 2p (B) XPS spectra of 0.81-$PdCo_{0.10}$/MgAl-LDH (a_1), 0.86-$PdCo_{0.28}$/MgAl-LDH (a_2), 0.79-$PdCo_{0.54}$/MgAl-LDH (a_3) compared with Pd/MgAl-LDH, Co/MgAl-LDH and MgAl-LDH.

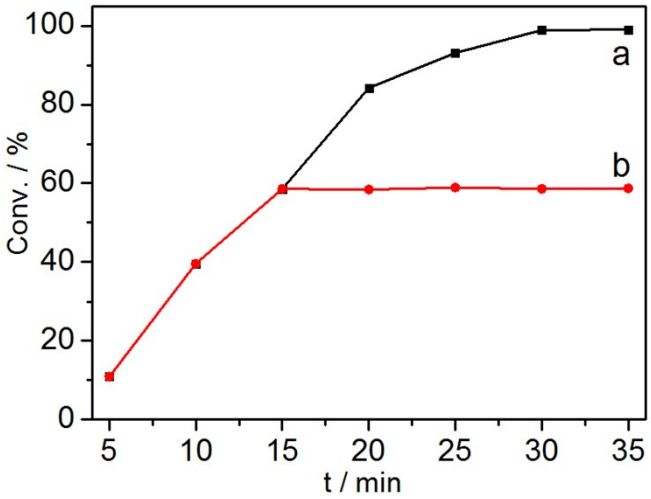


Fig. S8 Conv. – *t* plots for the Heck reaction of PhI with styrene over the 0.67-$PdCo_{0.28}$/CoAl-LDH (a) and with filtrate (b). Reaction conditions: PhI (1 mmol), styrene (1.5 mmol), catalyst (Pd: 0.3 mol%), v_{DMF}: v_{H2O} = 12 mL: 4 mL, K_2CO_3 (3 mmol), 120 °C.

Table S1 XRD parameters of a series of catalysts x-$PdCo_r$/Co(Mg or Ni)Al-LDH compared with corresponding supports.

Catalysts	d_{003} /nm	d_{110} /nm	a /nm [a]	c /nm [a]	D_{003} /nm [b]	D_{110} /nm [b]
Pd/MgAl-LDH	0.7570	0.1520	0.3040	2.271	14.7	58.6
0.81-$PdCo_{0.1}$/MgAl-LDH	0.7558	0.1522	0.3044	2.267	14.8	58.2
0.86-$PdCo_{0.28}$/MgAl-LDH	0.7518	0.1519	0.3038	2.255	14.3	58.0
0.79-$PdCo_{0.54}$/MgAl-LDH	0.7502	0.1520	0.3040	2.251	14.5	57.4
Co/MgAl-LDH	0.7581	0.1518	0.3036	2.274	14.8	56.9
MgAl-LDH	0.7570	0.1519	0.3038	2.271	14.9	57.1
0.64-$PdCo_{0.28}$/NiAl-LDH	0.7525	0.1508	0.3016	2.258	11.5	25.4
NiAl-LDH	0.7544	0.1507	0.3014	2.263	10.7	24.8
0.67-$PdCo_{0.28}$/CoAl-LDH	0.7657	0.1502	0.3004	2.297	14.6	49.8
0.10-$PdCo_{0.28}$/CoAl-LDH	0.7658	0.1502	0.3004	2.297	14.7	49.6
0.01-$PdCo_{0.28}$/CoAl-LDH	0.7657	0.1502	0.3004	2.297	14.6	49.9
CoAl-LDH	0.7659	0.1502	0.3004	2.298	14.8	49.7

[a] Based on hexagonal crystal system, a = $2d_{110}$， c = $3d_{003}$. [b] Estimated by Scherrer equation $D_{(hkl)} = 0.89\lambda/\beta\cos\theta$ (λ is X-ray wavelength (0.1542 nm), β is haft-height width in radian, θ is the Bragg angle in degree).

Table S2 Kinetic results of the Heck reaction over the present catalysts. [a]

Catalysts	T (K)	k (h^{-1}) [b]	R^2	E_a(kJ/mol) [c]	R^2
0.81-$PdCo_{0.10}$/MgAl-LDH	383.15	0.0340	0.9950	58.7	0.9996
	393.15	0.0551	0.9956		
	403.15	0.0862	0.9836		
	413.15	0.1292	0.9866		
0.86-$PdCo_{0.28}$/MgAl-LDH	383.15	0.0928	0.9982	48.9	0.9880
	393.15	0.1282	0.9972		
	403.15	0.2053	0.9782		
	413.15	0.2737	0.9678		
0.79-$PdCo_{0.54}$/MgAl-LDH	383.15	0.0248	0.9884	66.8	0.9938
	393.15	0.0465	0.9932		
	403.15	0.0736	0.9873		
	413.15	0.1154	0.9672		

[a] Reaction conditions: dosage of catalyst x-$PdCo_r$/MgAl-LDH (0.3 mol% Pd, based on PhI), PhI (1 mmol), styrene (1.5 mmol), mixed solvent: v_{DMF}:v_{H2O}=12 mL:4 mL, K_2CO_3 (3 mmol)，reaction temperature (T): 110 – 140 °C. [b] According to the equation: ln (C_t/C_0) = - kt, where C_t is the concentration of PhI at t time (mol/L), C_0 is the initial concentration of PhI (mol/L), k is the reaction rate constant (h^{-1}), t is the reaction time (h). [c] According to the Arrhenius equation: k = Aexp(-E_a/RT), E_a is the apparent activation energy (kJ/mol), A is the pre-exponential factor (h^{-1}), R is the molar gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), and T is the absolute temperature (K).

Table S3 XPS data of the catalysts compared with monometallic catalysts and support.

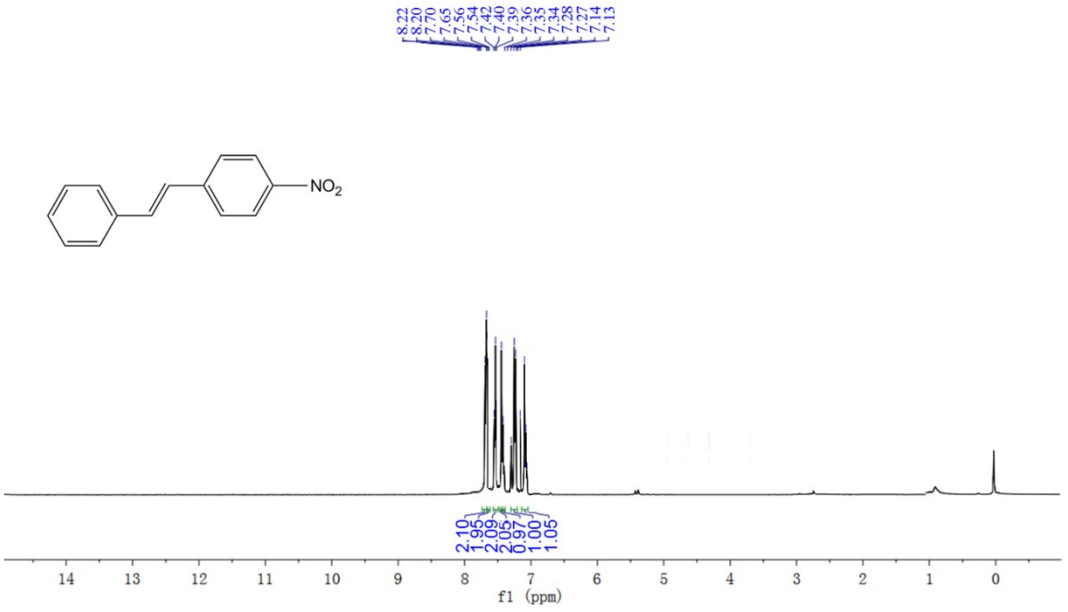
Samples	Pd^0 $3d_{5/2}$ (eV)	$Pd^0/(Pd^0+Pd^{II})$(%)	Co^0 $2p_{3/2}$ (eV)	O 1s (eV)			Mg 2s (eV)
				-OH	O^{2-}	H_2O	
Pd/MgAl-LDH	335.70	78.0	-	531.78 (68.2%)	530.61	532.96	50.05
0.81-$PdCo_{0.10}$/MgAl-LDH	335.25	90.9	778.25	531.69 (68.1%)	530.21	533.38	50.16
0.86-$PdCo_{0.28}$/MgAl-LDH	334.69	100	777.80	531.59 (69.2%)	530.37	533.16	50.19
0.79-$PdCo_{0.54}$/MgAl-LDH	334.92	86.0	778.15	531.73 (68.2%)	530.31	533.32	50.14
Co/MgAl-LDH	-	-	778.80	531.52 (68.6%)	530.02	533.02	50.09
MgAl-LDH	-	-	-	531.97 (73.3%)	530.71	533.15	50.01
0.67-$PdCo_{0.28}$/CoAl-LDH	334.50	100	n.d.	531.59 (75.5%)	530.61	532.99	780.80 [a]
0.01-$PdCo_{0.28}$/CoAl-LDH	n.d.	-	n.d.	531.54 (76.1%)	530.33	532.96	780.60
CoAl-LDH	-	-	n.d.	531.39 (78.3%)	530.35	532.95	781.40

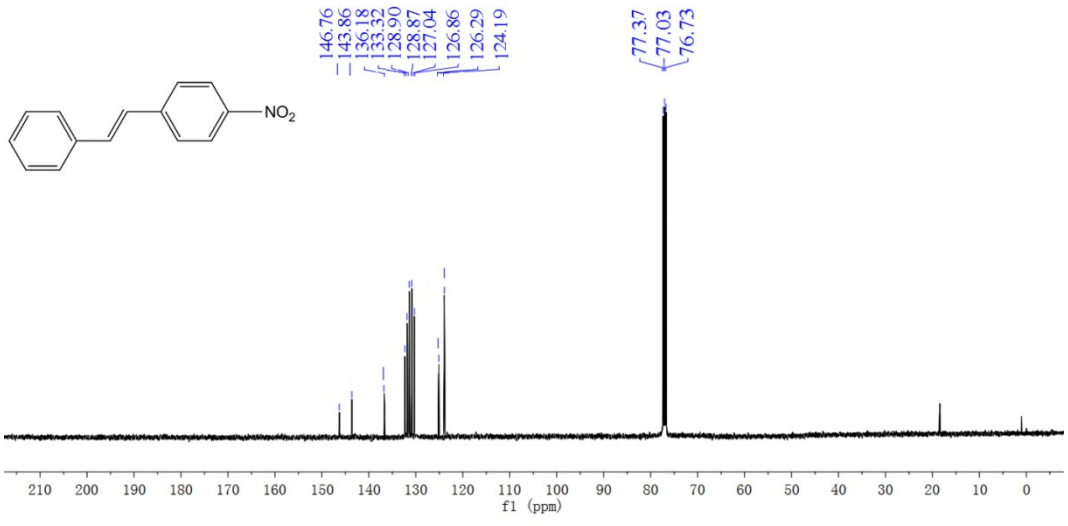
[a] The value referees to the Co^{2+} $2p_{3/2}$ binding energy (eV).

Attached ^{1}H and ^{13}C NMR Spectra of the Heck reaction products

(3a) (*E*)-1-nitro-4-styrylbenzene (Table 2, entry 1)

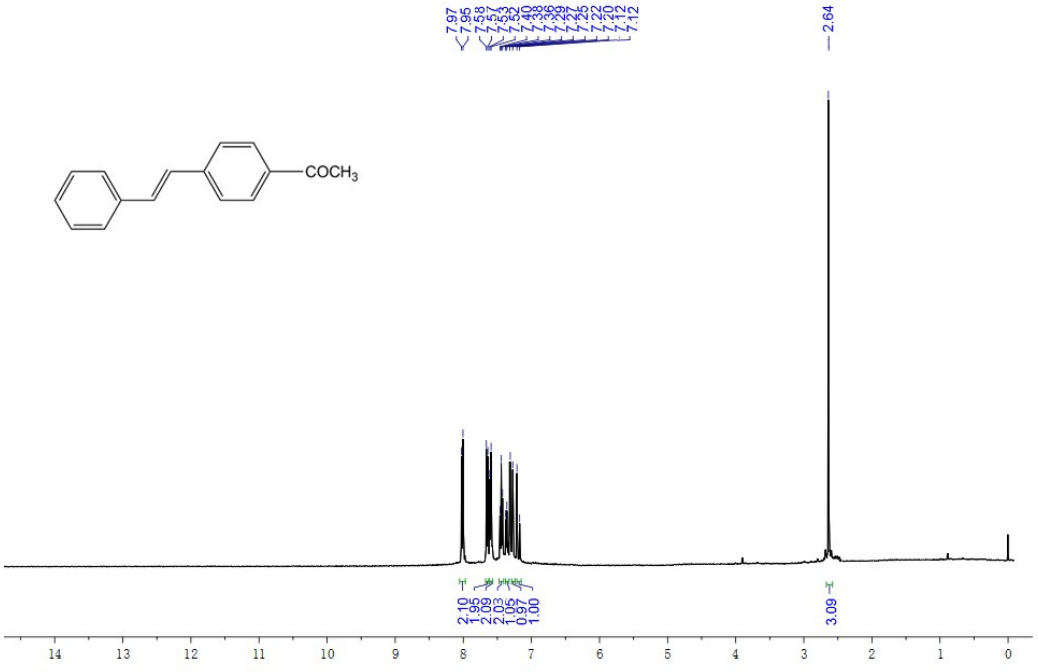
^{1}H-NMR (600M, $CDCl_3$): δ 8.22-8.20 (d, 2H), 7.70-7.65 (d, 2H), 7.56-7.54 (d, 2H), 7.42-7.39 (t, 2H), 7.36-7.34 (t, 1H), 7.28-7.27 (d, 1H), 7.14-7.13 (d, 1H); ^{13}C-NMR (600M, $CDCl_3$): δ 146.76, 143.86, 136.18, 133.32, 128.90, 128.87, 127.04, 126.86, 126.29, 124.19.

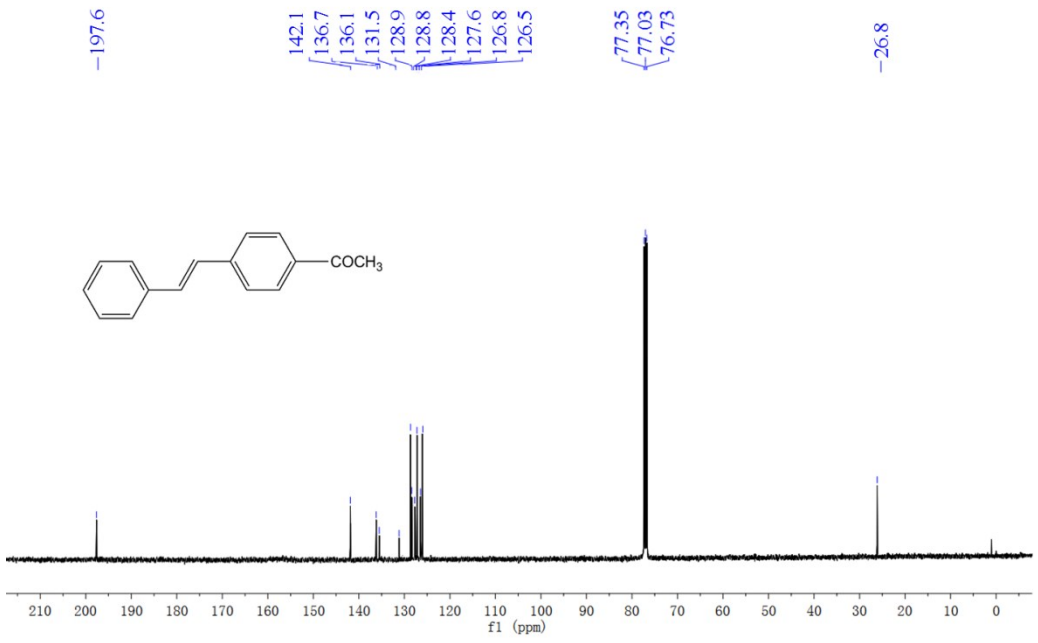




(3b) (*E*)-1-(4-styrylphenyl) ethanone (Table 2, entry 2)

^{1}H-NMR (600M, $CDCl_3$): δ 7.97-7.95 (d, 2H), 7.58-7.57 (d, 2H), 7.53-7.52 (d, 2H), 7.40-7.36 (t, 2H), 7.29-7.25 (t, 1H), 7.22-7.20 (d, 1H), 7.12 (d, 1H), 2.64 (s, 3H); ^{13}C-NMR (600M, $CDCl_3$): δ 197.6, 142.1, 136.7, 136.1, 131.5, 128.9, 128.8, 128.4, 127.6, 126.8, 126.5, 26.8.

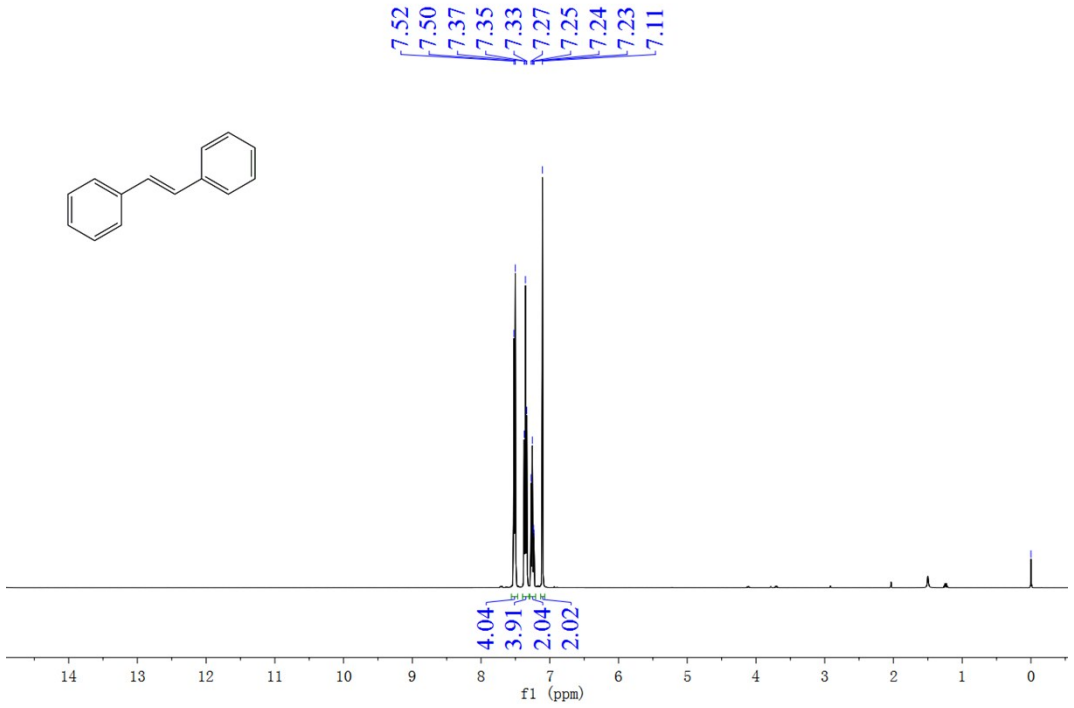


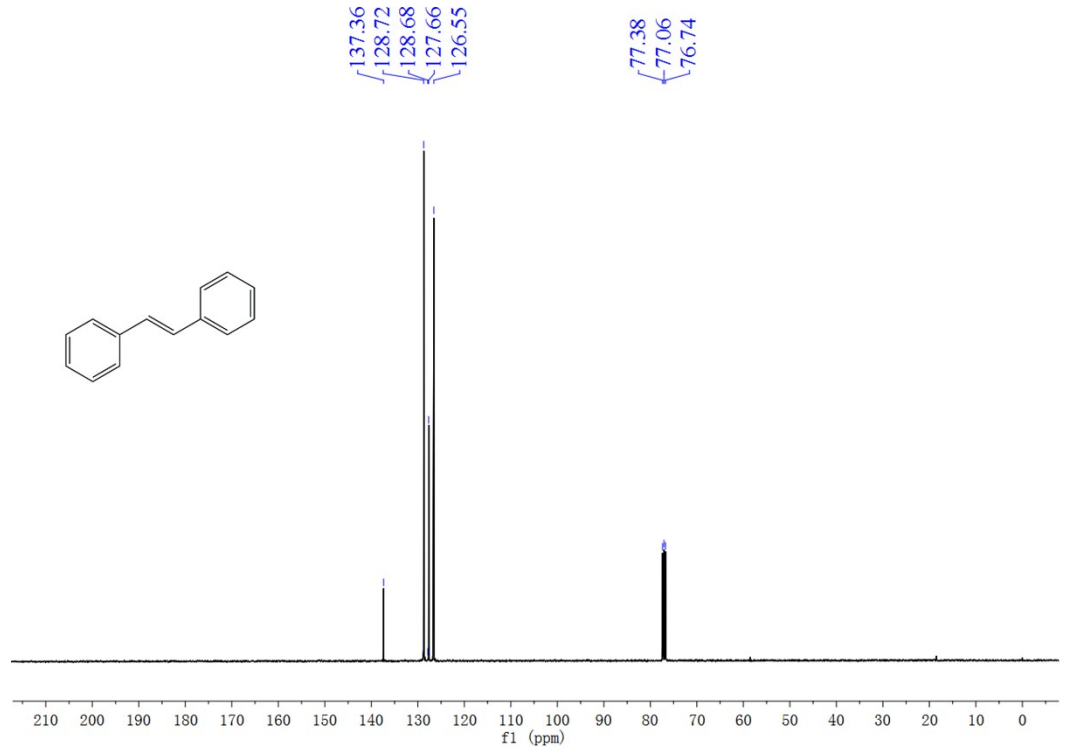


(3c) (*E*)-1,2-diphenylethene(Table 2, entries 3, 8 and 10)

^{1}H-NMR (600M, $CDCl_3$): δ 7.52-7.50 (d, 4H), 7.37-7.33 (t, 4H), 7.27-7.23 (t, 2H), 7.11 (s, 2H);

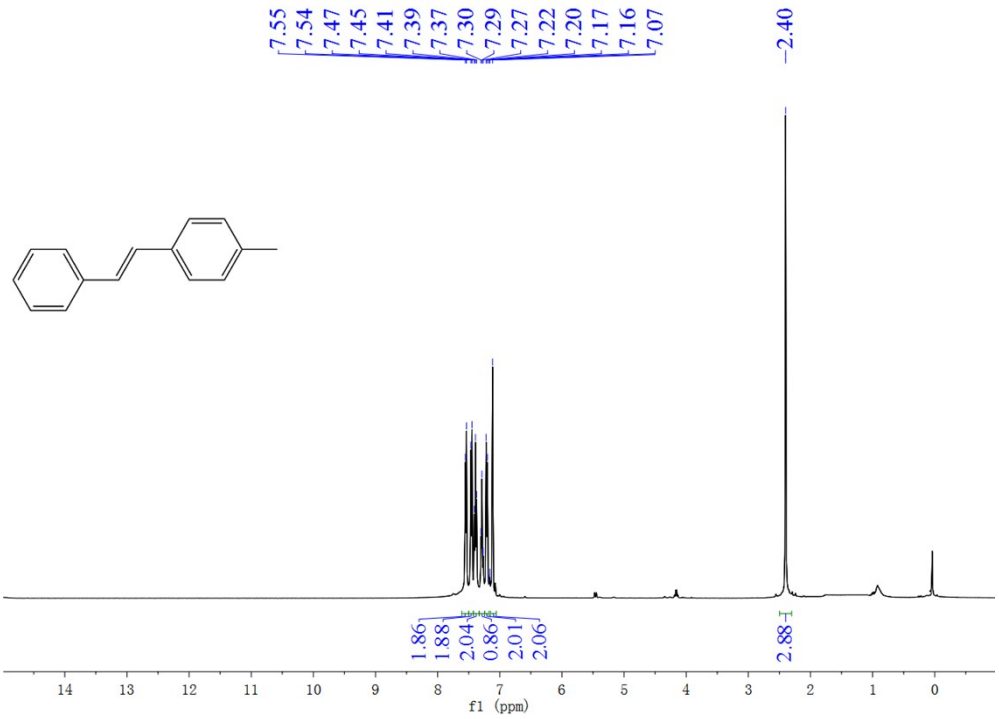
^{13}C-NMR (600M, $CDCl_3$): δ 137.36, 128.72, 128.68, 127.66, 126.55.

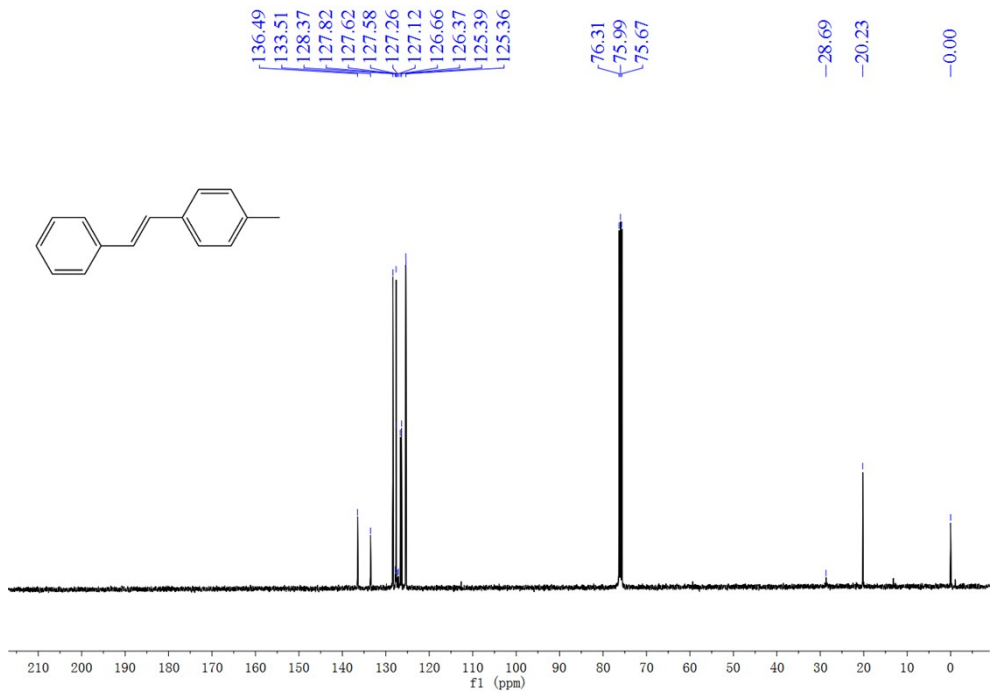




(3d) (E)-1-methyl-4-styrylbenzene (Table 2, entry 4)

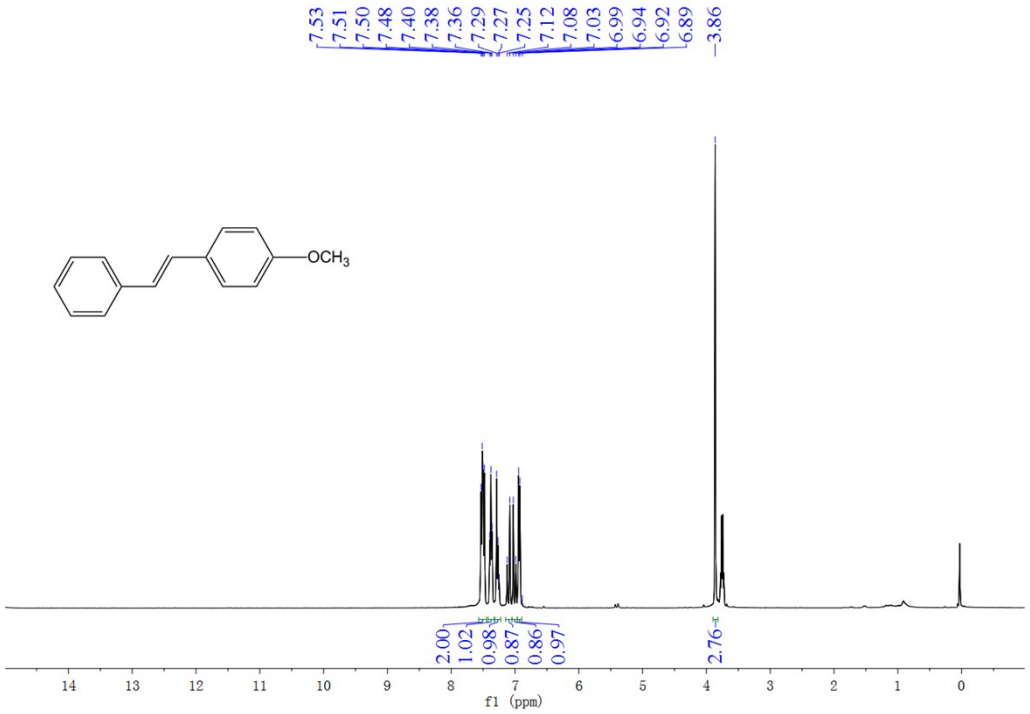
^{1}H-NMR (600M, $CDCl_3$): δ 7.55-7.54 (d, 2H), 7.47-7.45 (d, 2H), 7.41-7.37 (t, 2H), 7.30-7.27 (t, 1H), 7.22-7.20 (d, 2H), 7.07 (s, 2H), 2.40 (s, 3H); ^{13}C-NMR (600M, $CDCl_3$): δ 136.49, 133.51, 128.37, 127.82, 127.62, 126.66, 126.37, 125.39, 125.36, 20.23.

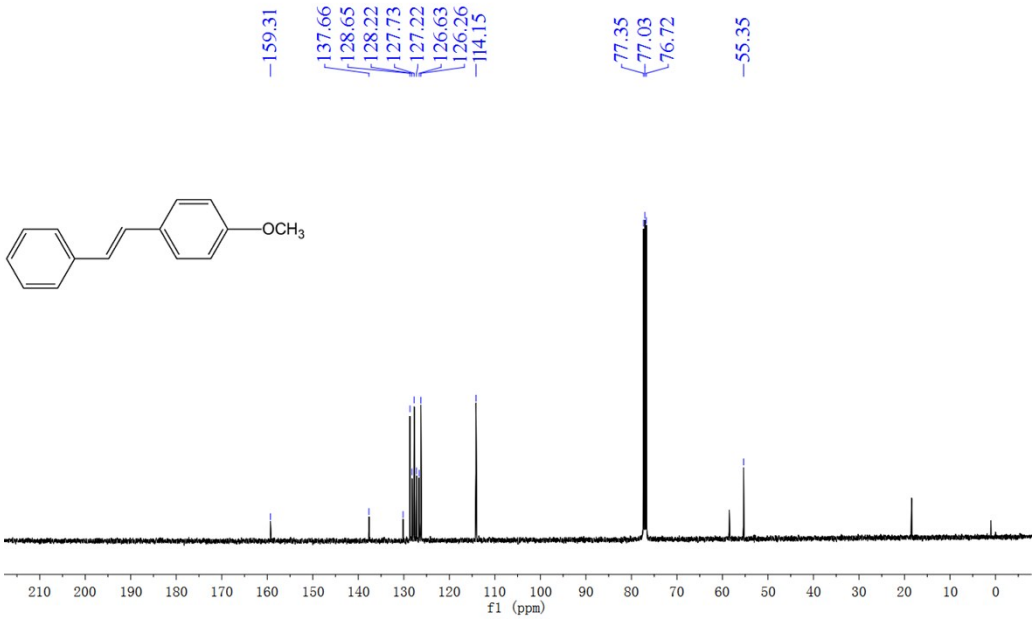




(3e) (*E*)-1-methoxy-4-styrylbenzene (Table 2, entry 5)

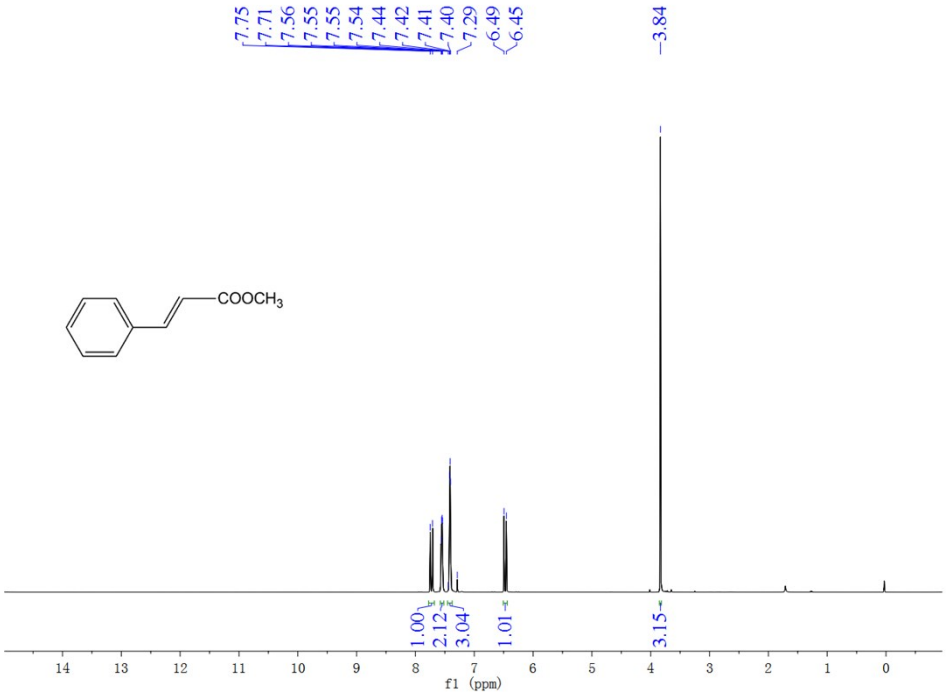
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53-7.48 (m, 4H), 7.40-7.36 (t, 2H), 7.29-7.25 (t, 1H), 7.12-7.08 (d, 1H), 7.03-6.99 (d, 1H), 6.94-6.92 (d, 2H), 3.86 (s, 3H); ^{13}C NMR (600 MHz, $CDCl_3$): δ 159.31, 137.66, 128.65, 128.22, 127.73, 127.22, 126.63, 126.26, 114.15, 55.35.

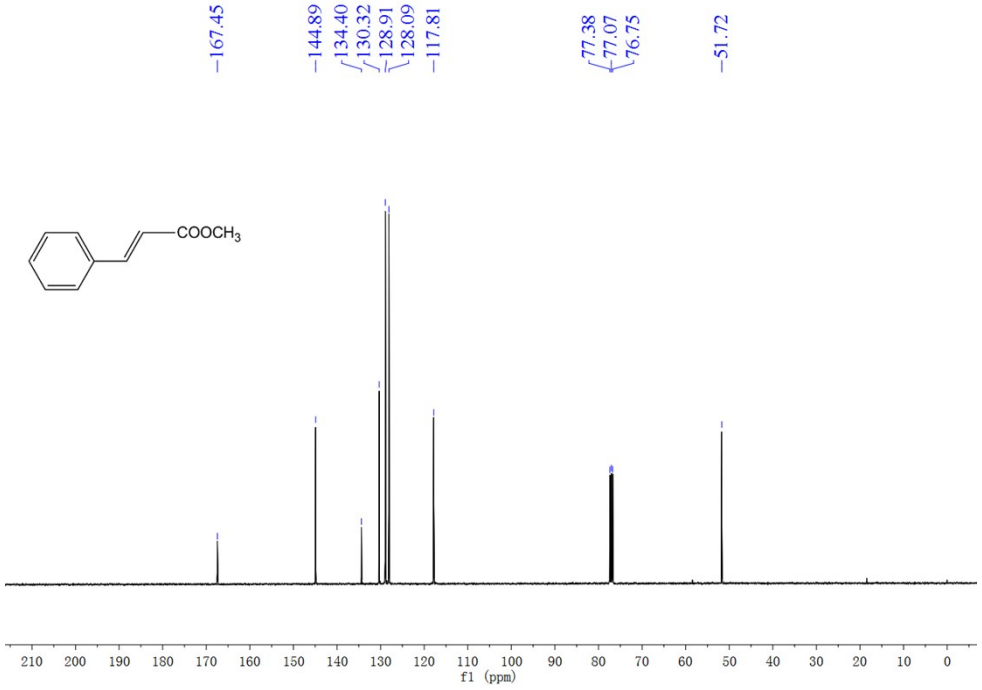




(3f) (*E*)-methyl cinnamate (Table 2, entries 6 and 9)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75-7.71 (d, 1H), 7.56-7.54 (m, 2H), 7.44-7.40 (m, 3H), 6.49-6.45(d, 1H), 3.84(s, 3H); ^{13}C NMR ($CDCl_3$): δ 167.45, 144.89, 134.40, 130.32, 128.91, 128.09, 117.81, 51.72.





(3g) (*E*)-ethyl cinnamate (Table 2, entry 7)

^{1}H NMR (600 MHz, $CDCl_3$); δ 7.74-7.70 (d, 1H), 7.56-7.42 (m, 2H), 7.41-7.29(m, 2H), 6.49-6.45(d, 1H), 4.32-4.27(m, 2H), 1.39-1.35(t, 3H); ^{13}C NMR (600 MHz, $CDCl_3$): δ 167.03, 144.60, 134.48, 130.23, 128.89, 128.06, 118.29, 60.52, 14.35.