An excellent Pd-loaded magnetic nanocatalyst on multi-carboxyl and boronic acid bi-ligands

Supporting materials

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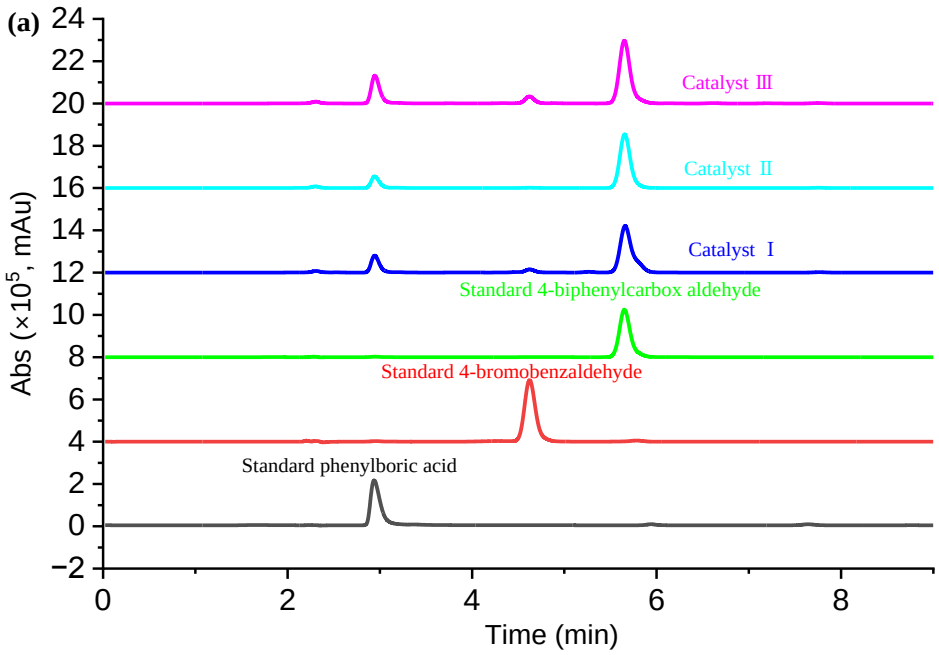
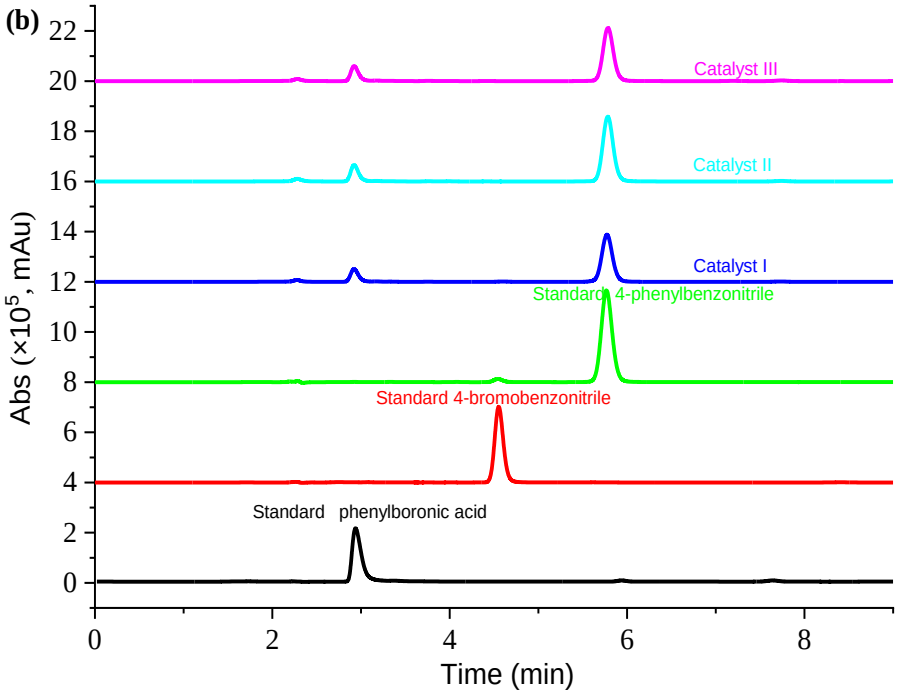
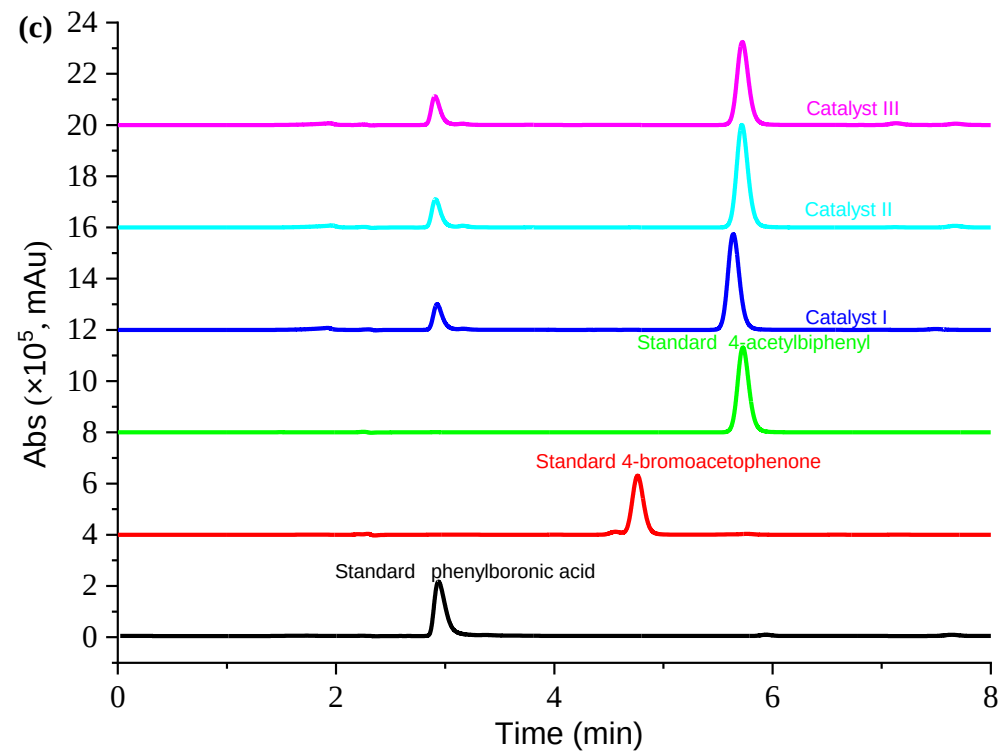
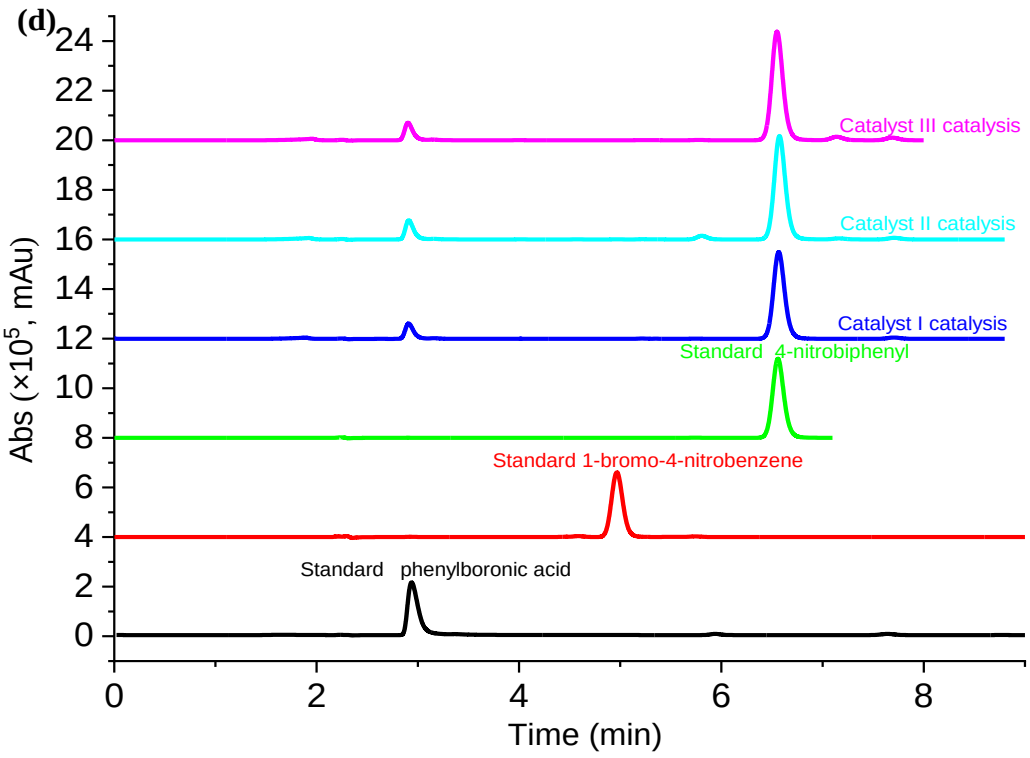
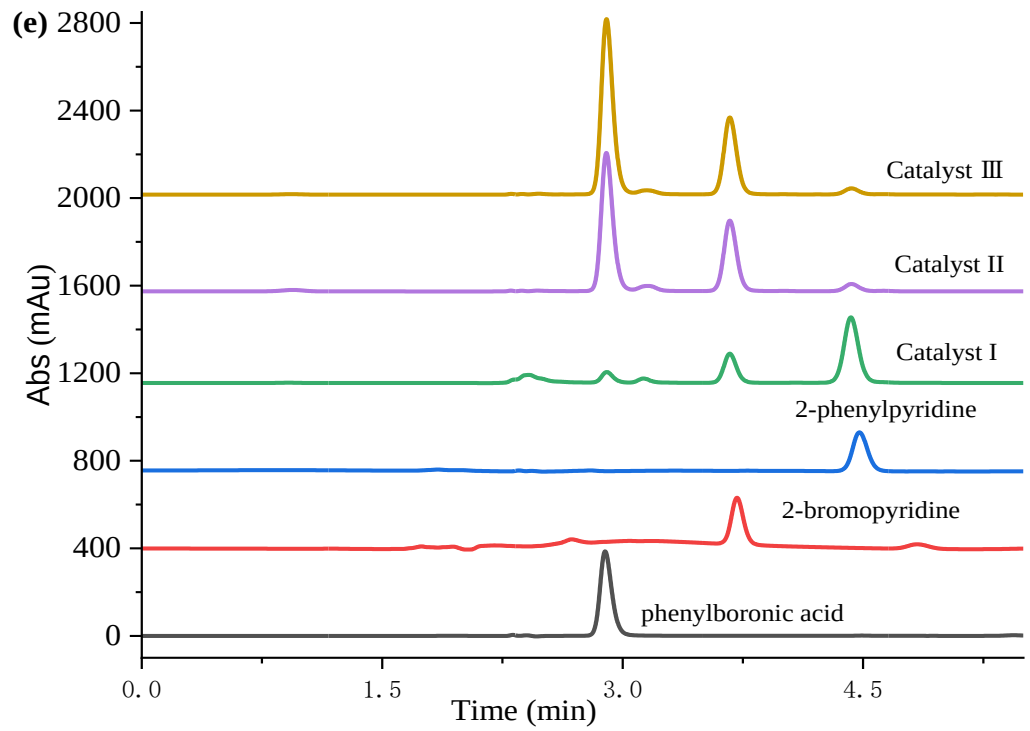
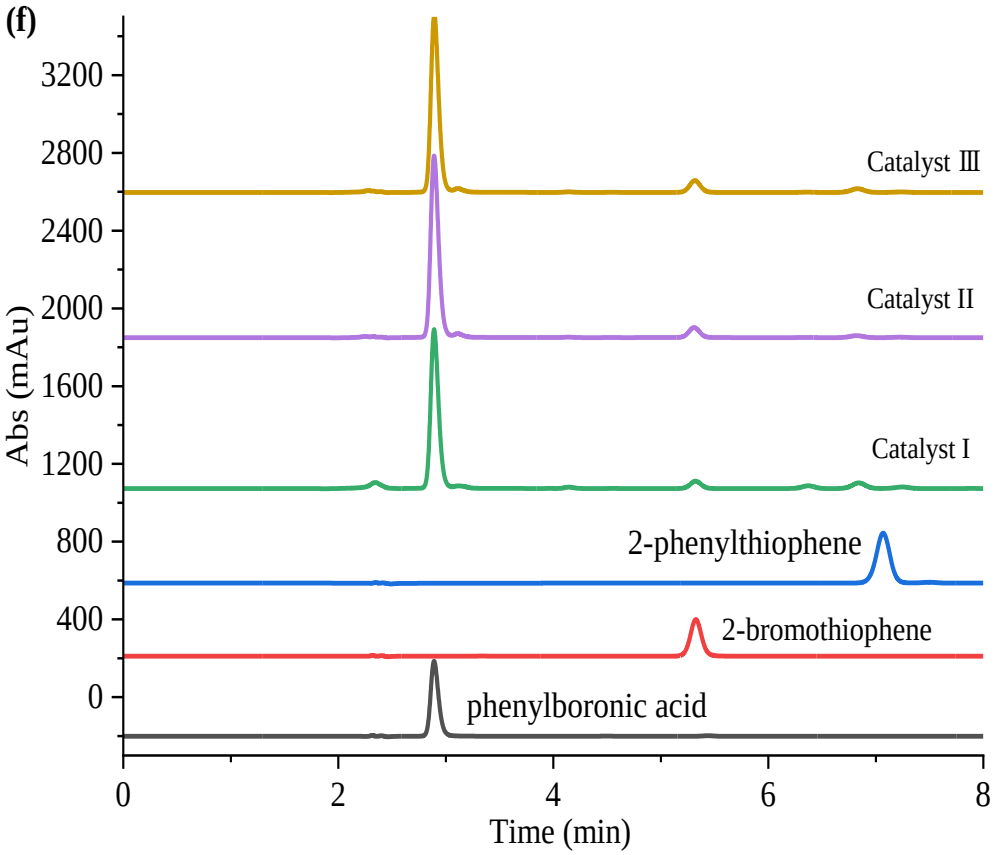





(c)
Abs (×10^5, mAu)
Time (min)
Catalyst III
Catalyst II
Catalyst I
Standard 4-acetylbiphenyl
Standard 4-bromoacetophenone
Standard phenylboronic acid


(d)
Abs (×10^5, mAu)
Time (min)
Catalyst III catalysis
Catalyst II catalysis
Catalyst I catalysis
Standard 4-nitrobiphenyl
Standard 1-bromo-4-nitrobenzene
Standard phenylboronic acid


(e)
2800
2400
2000
1600
1200
800
400
0
Abs (mAu)
Catalyst Ⅲ
Catalyst II
Catalyst I
2-phenylpyridine
2-bromopyridine
phenylboronic acid
0.0
1.5
3.0
4.5
Time (min)


(f)
3200
2800
2400
2000
1600
1200
800
400
0
Abs (mAu)
Catalyst Ⅲ
Catalyst II
Catalyst I
2-phenylthiophene
2-bromothiophene
phenylboronic acid
0
2
4
6
8
Time (min)

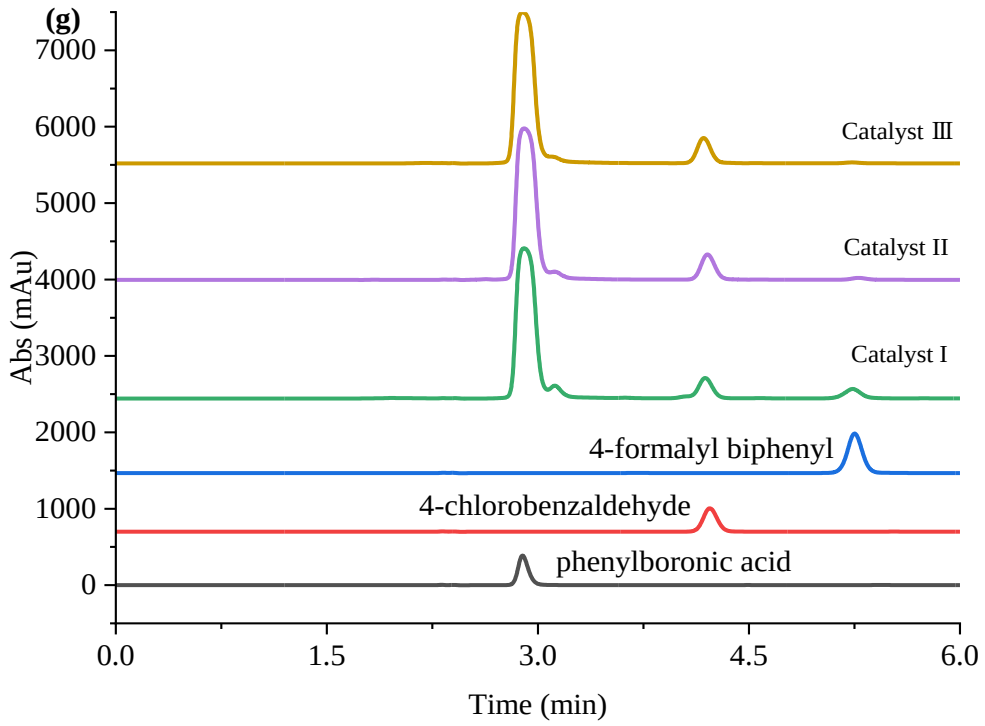
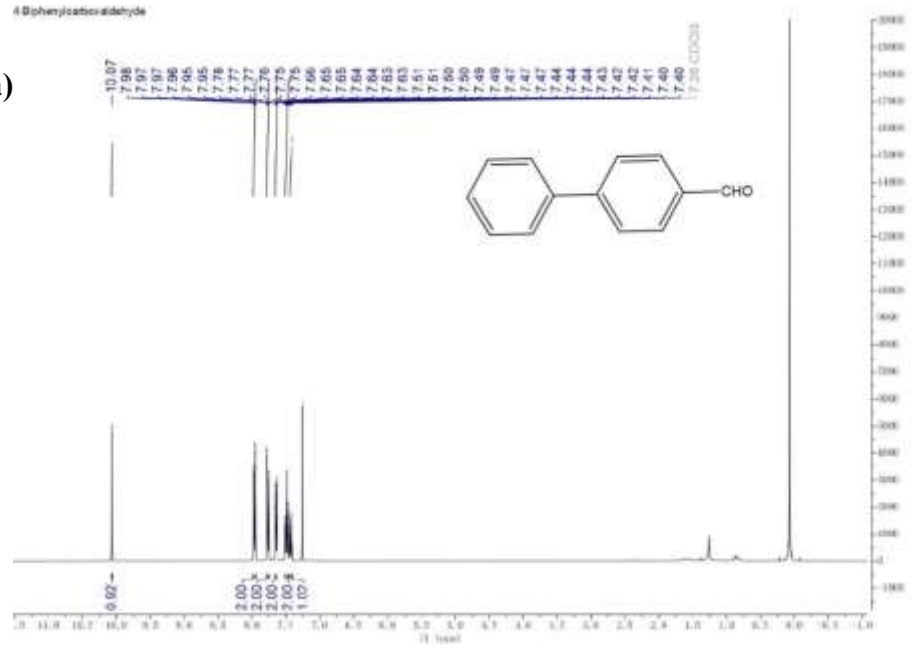


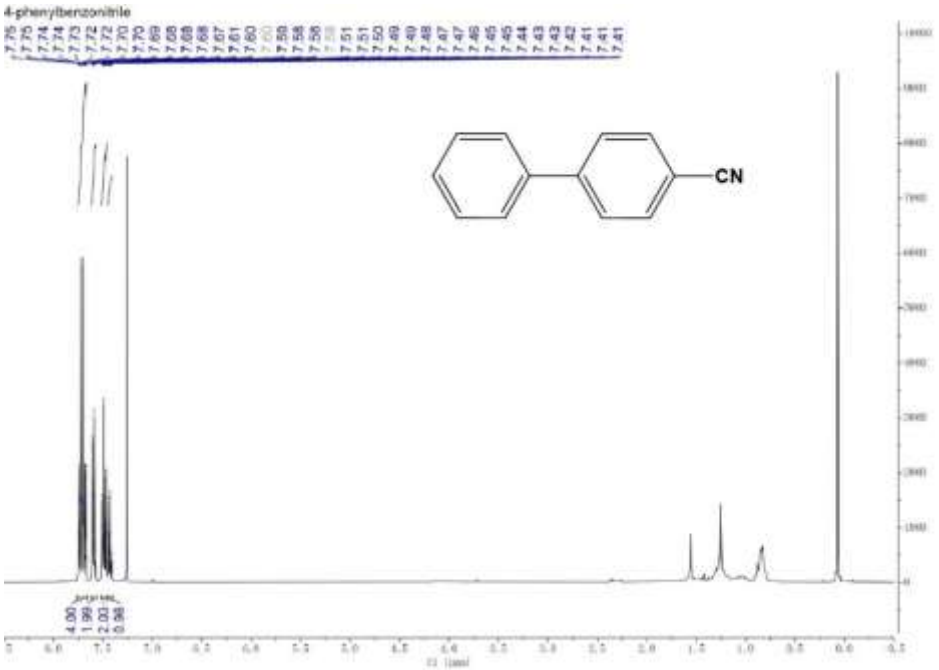
Figure S1 HPLC chromatograms of Suzuki reaction products between phenylboronic acid and 4-bromobenzaldehyde (a), 4-bromobenzonitrile (b), 4-bromoacetophenone (c) and1-bromo-4-nitrobenzene (d), 2-bromopyridine (e), 2-bromothiophene (f) and 4-chlorobenzaldehyde (g) catalyzed by Catalyst I, II and III

(a)



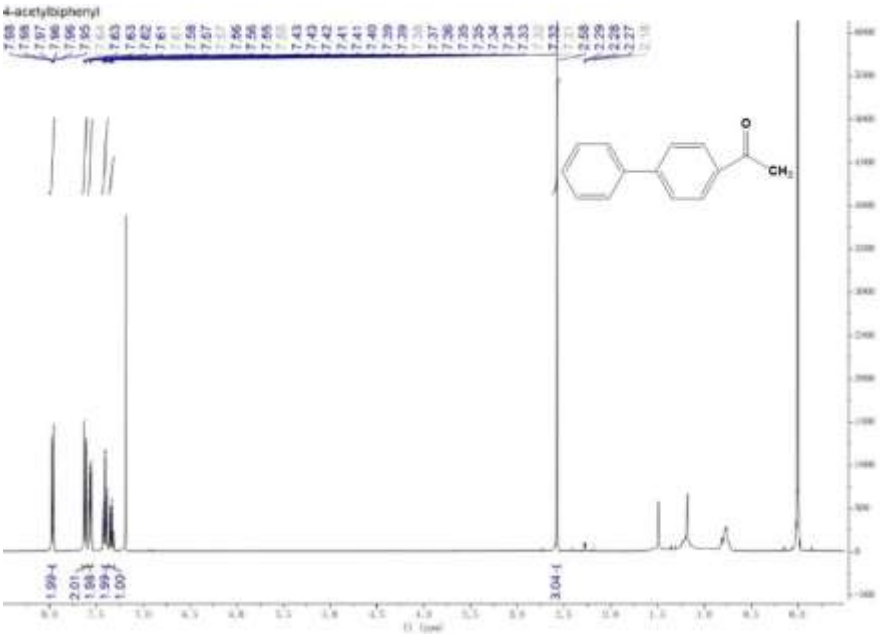
^{1}H NMR (400 MHz, Chloroform-*d*) : δ 10.07 (s, 1H), 7.98-7.94 (m, 2H), 7.78-7.74 (m, 2H), 7.66-7.62 (m, 2H), 7.51-7.47 (m, 2H), 7.45-7.40 (m, 1H)

(b)



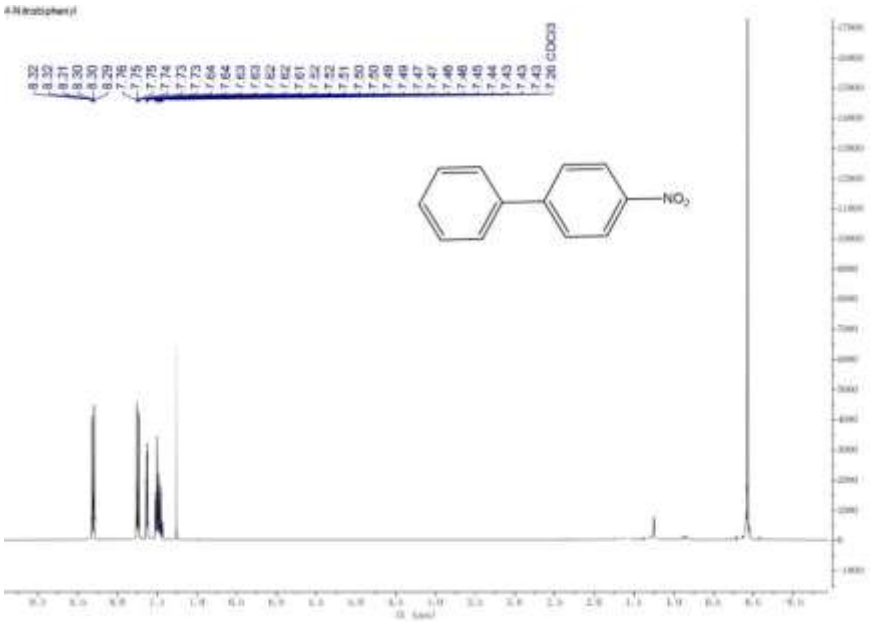
^{1}H NMR data (400 MHz, Chloroform-d) : δ 7.76-7.66 (m, 4H), 7.62-7.57 (m, 2H), 7.52-7.46 (m, 2H), 7.45-7.39 (m, 1H)

(c)



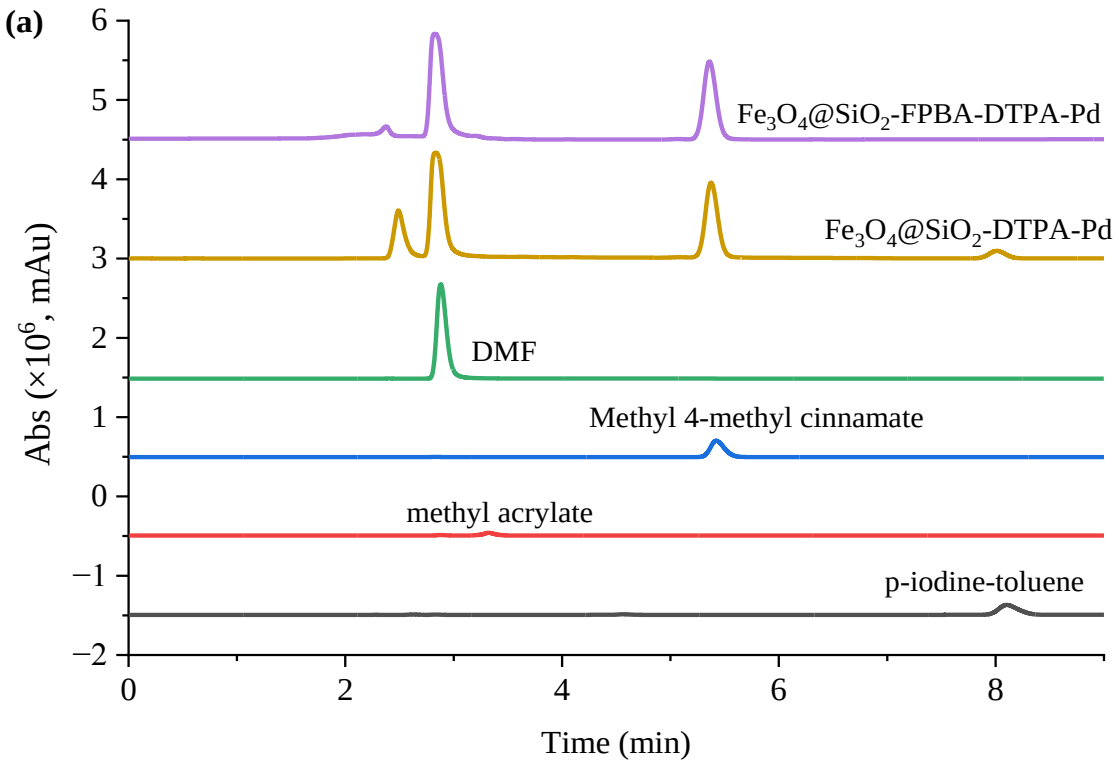
^{1}H NMR (400 MHz, Chloroform-d) : δ 7.63-7.58 (m, 2H), 7.48-7.41 (m, 2H), 7.39-7.33 (m, 2H), 7.19 (ddd, J = 7.6, 1.7, 1.0 Hz, 1H), 7.14 (dd, J = 2.6, 1.6 Hz, 1H), 6.91 (ddd, J = 8.2, 2.6, 1.0 Hz, 1H), 3.88 (s, 3H)

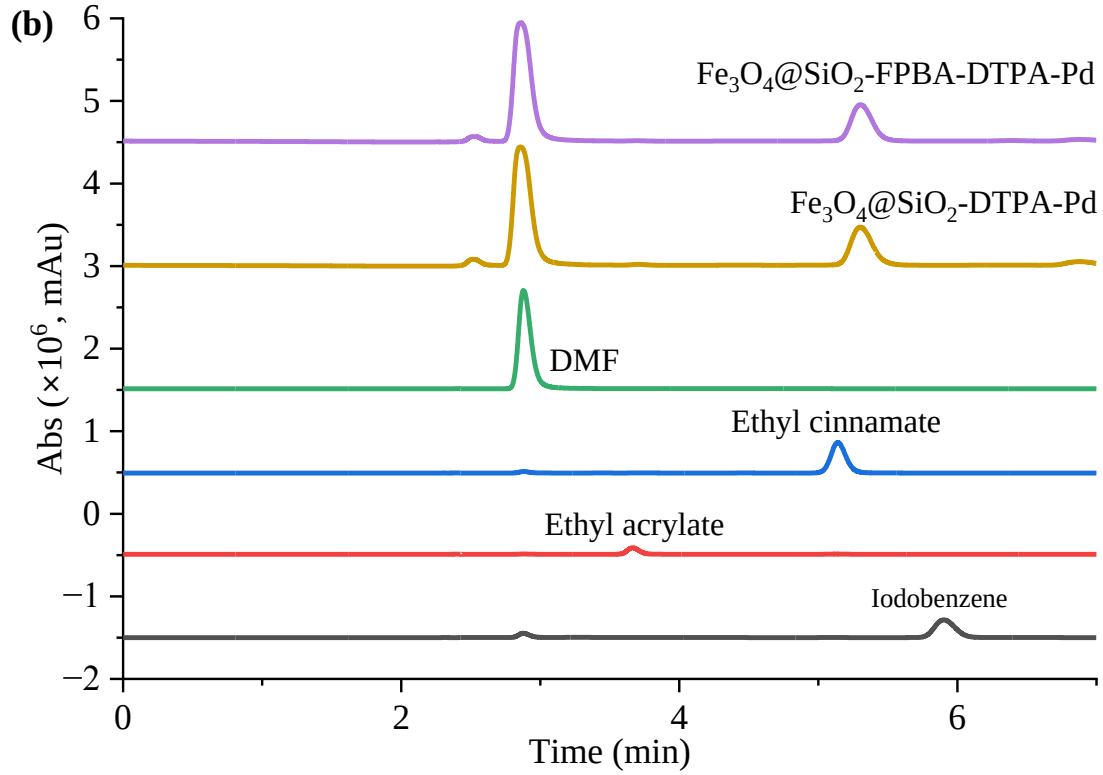
(d)

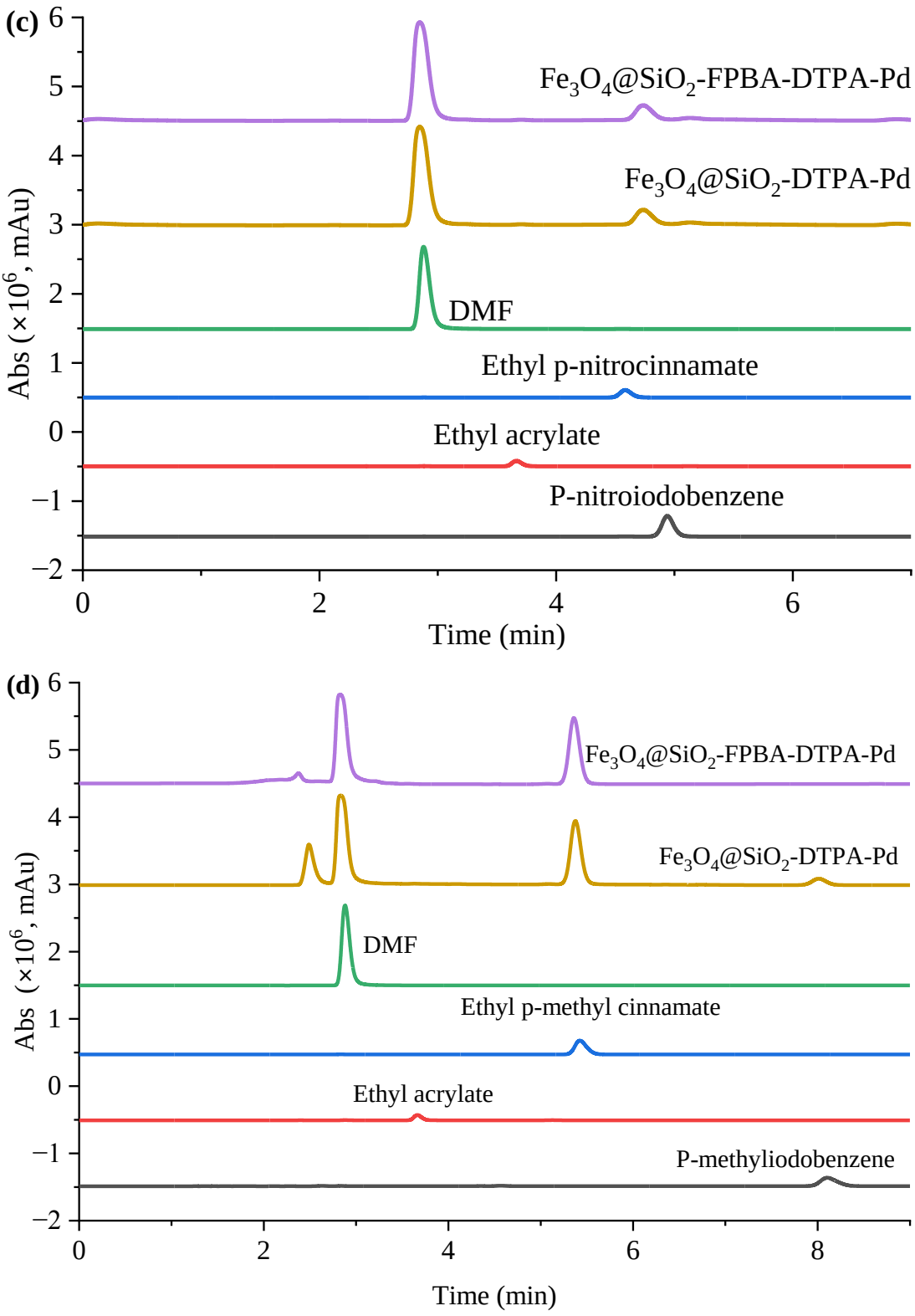


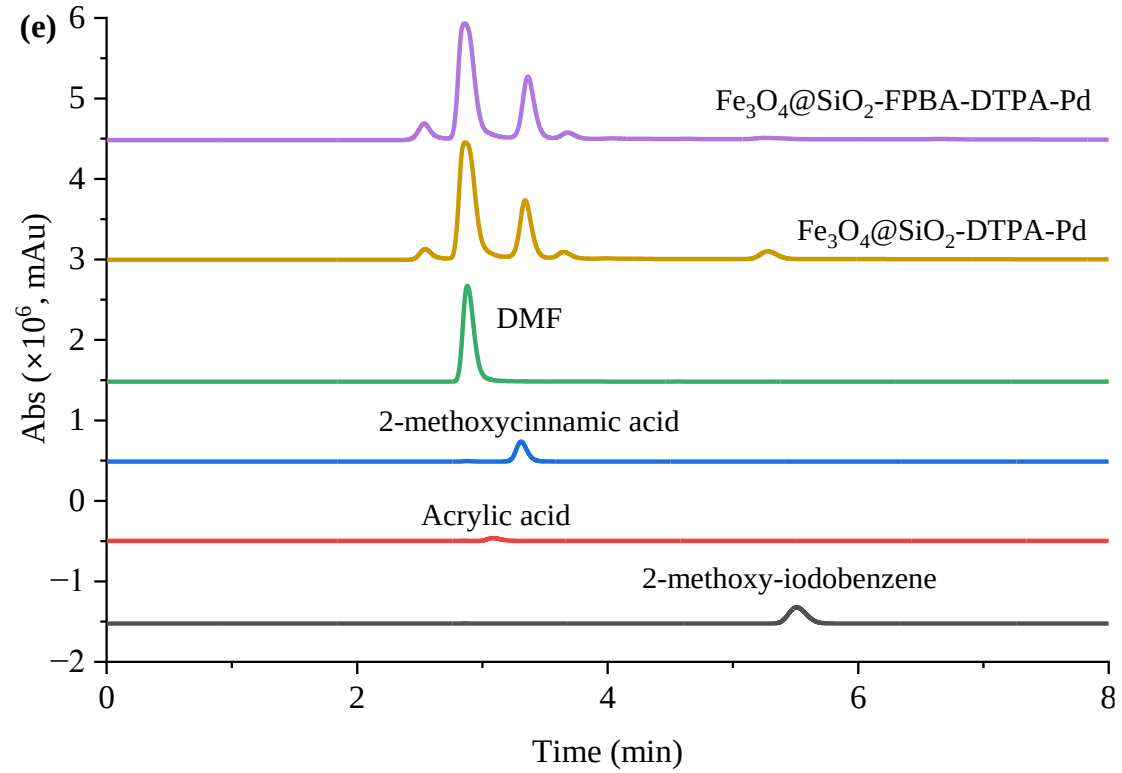
^{1}H NMR (400 MHz, Chloroform-*d*) : δ 8.33-8.27 (m, 2H), 7.76-7.72 (m, 2H), 7.65-7.61 (m, 2H), 7.53-7.48 (m, 2H), 7.47-7.43 (m, 1H)

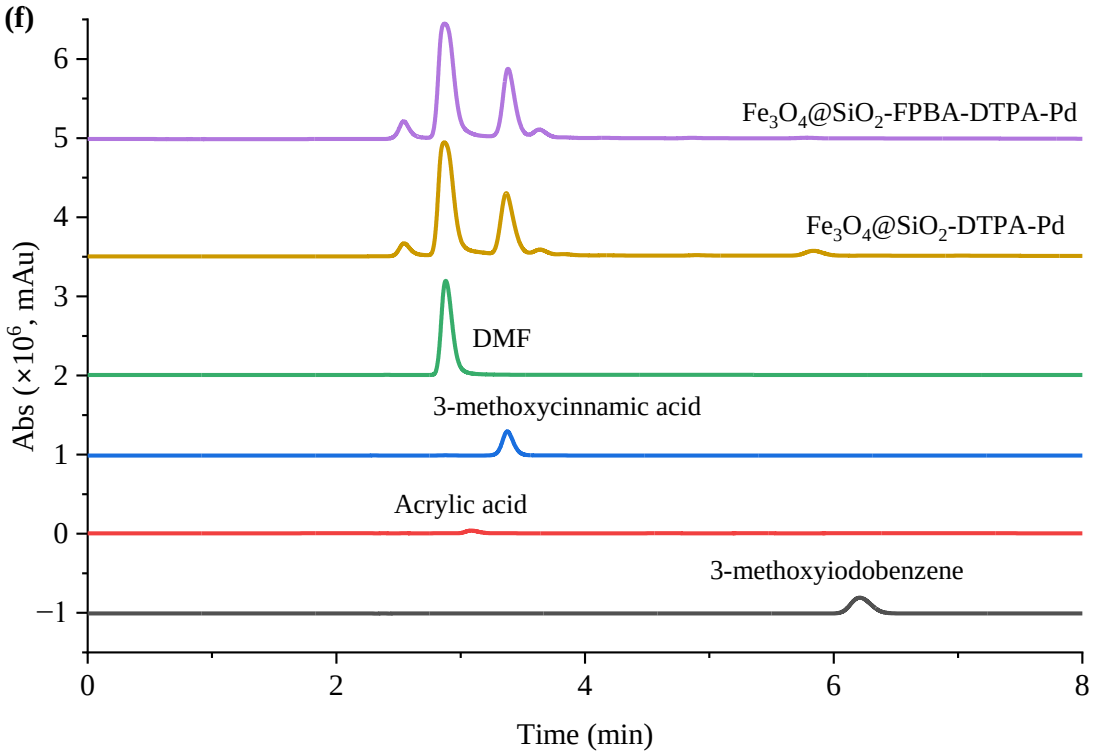
Figure S2 ^{1}H NMR spectra of Suzuki product of 4-biphenylcarboxaldehyde (a), 4-phenylbenzonitrile (b), 4-acetylbiphenyl (c) and 4-nitrobiphenyl (d)

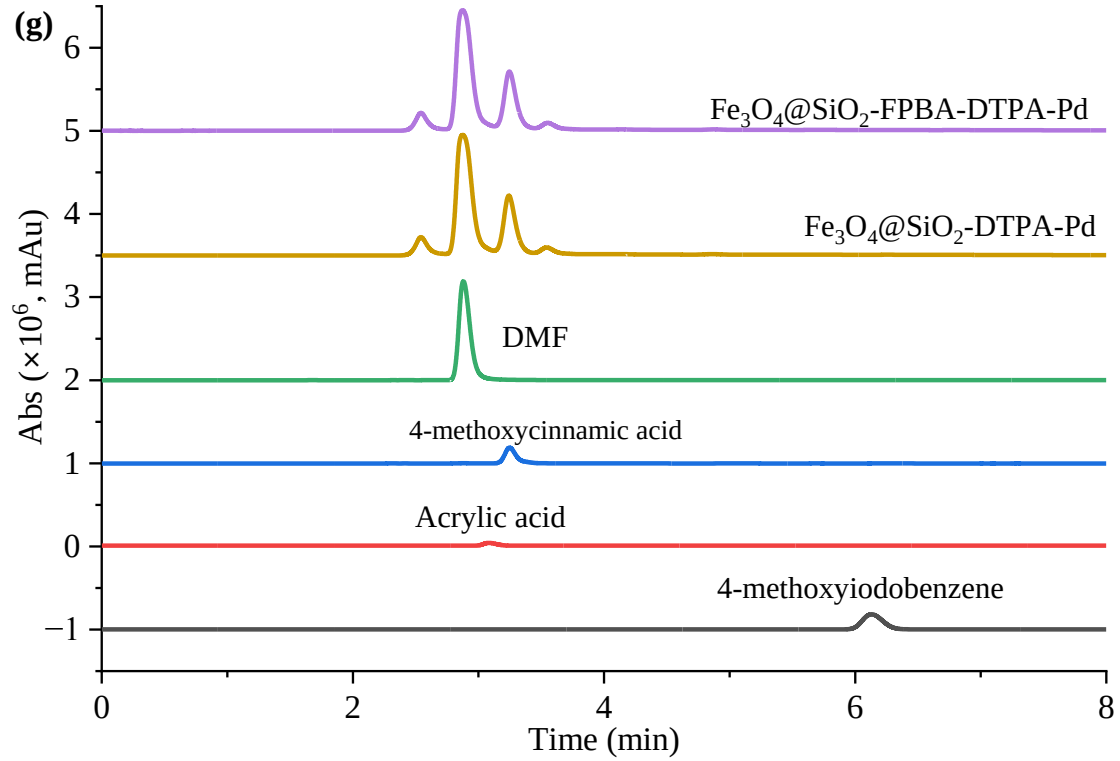

(a)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
Methyl 4-methyl cinnamate
methyl acrylate
p-iodine-toluene
Abs (×10^6, mAu)
Time (min)

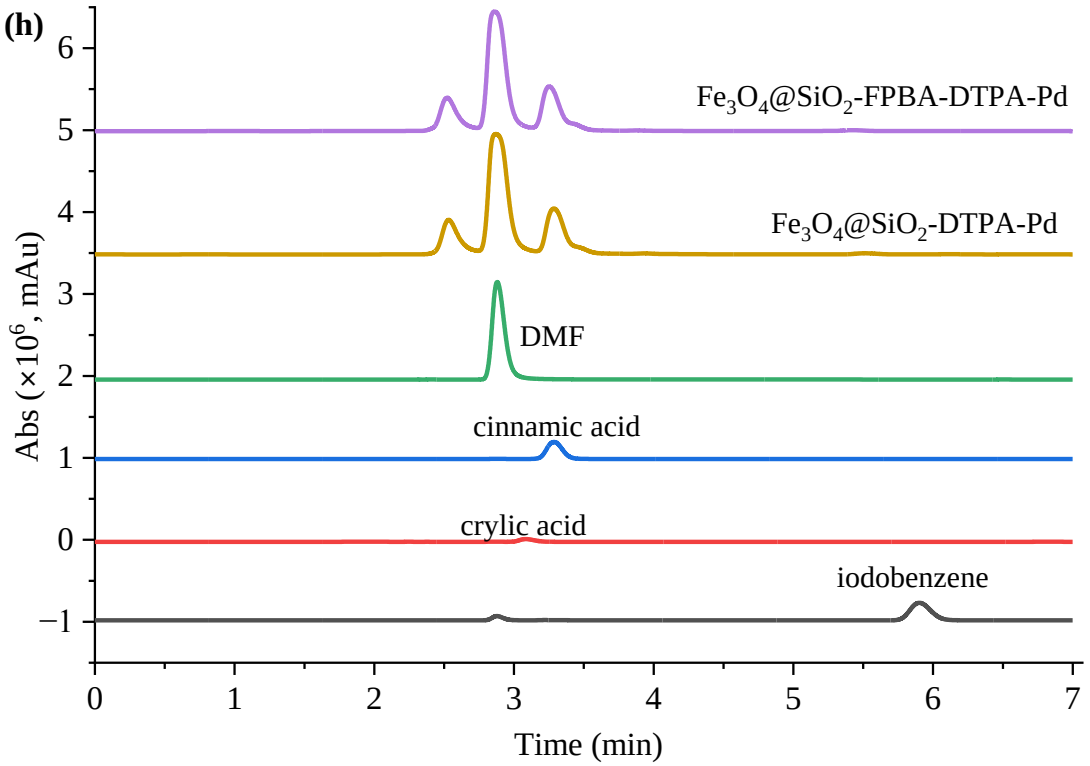

(b)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
Ethyl cinnamate
Ethyl acrylate
Iodobenzene
Abs (×10^6, mAu)
Time (min)

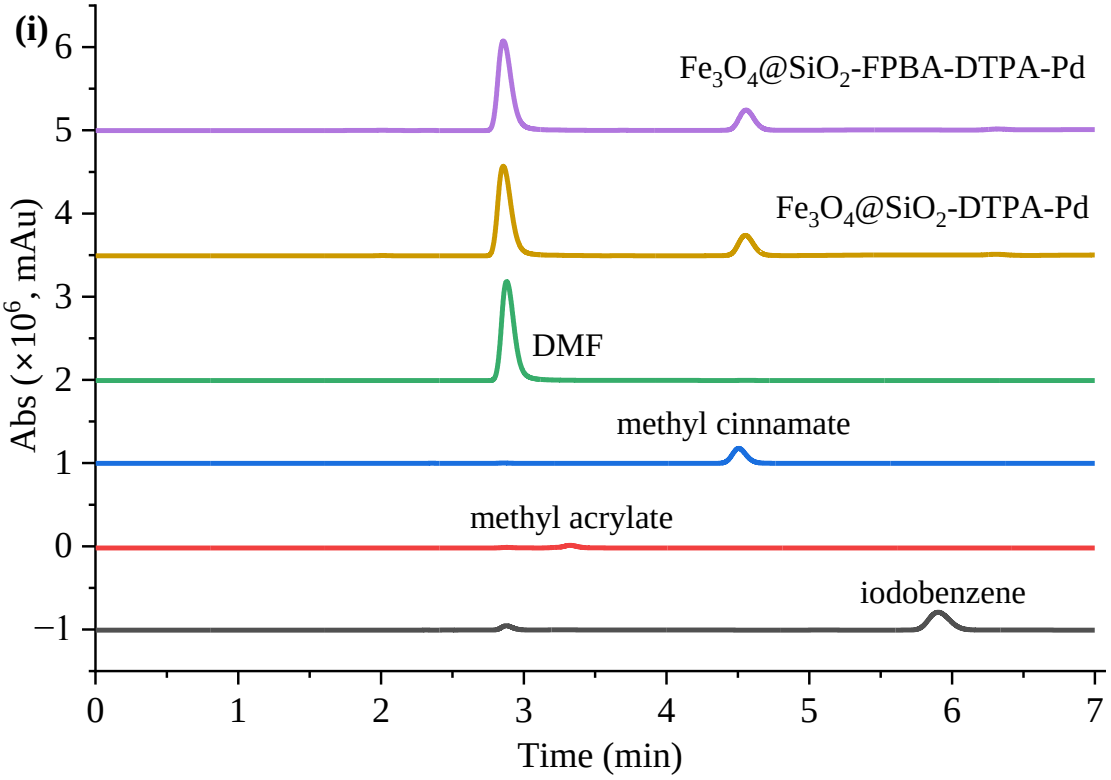

(c)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
Ethyl p-nitrocinnamate
Ethyl acrylate
P-nitroiodobenzene
Abs (×10^6, mAu)
Time (min)
(d)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
Ethyl p-methyl cinnamate
Ethyl acrylate
P-methyliodobenzene
Abs (×10^6, mAu)
Time (min)

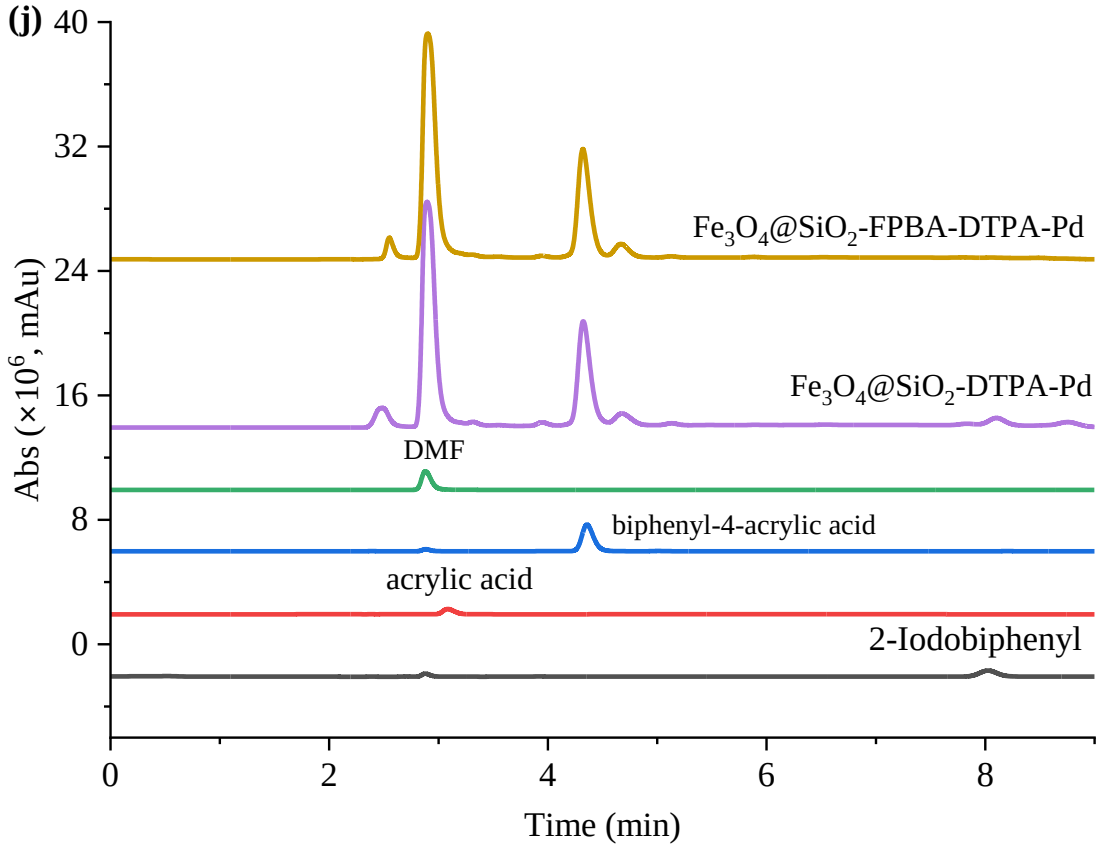

(e)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
2-methoxycinnamic acid
Acrylic acid
2-methoxy-iodobenzene
Abs (×10^6, mAu)
Time (min)

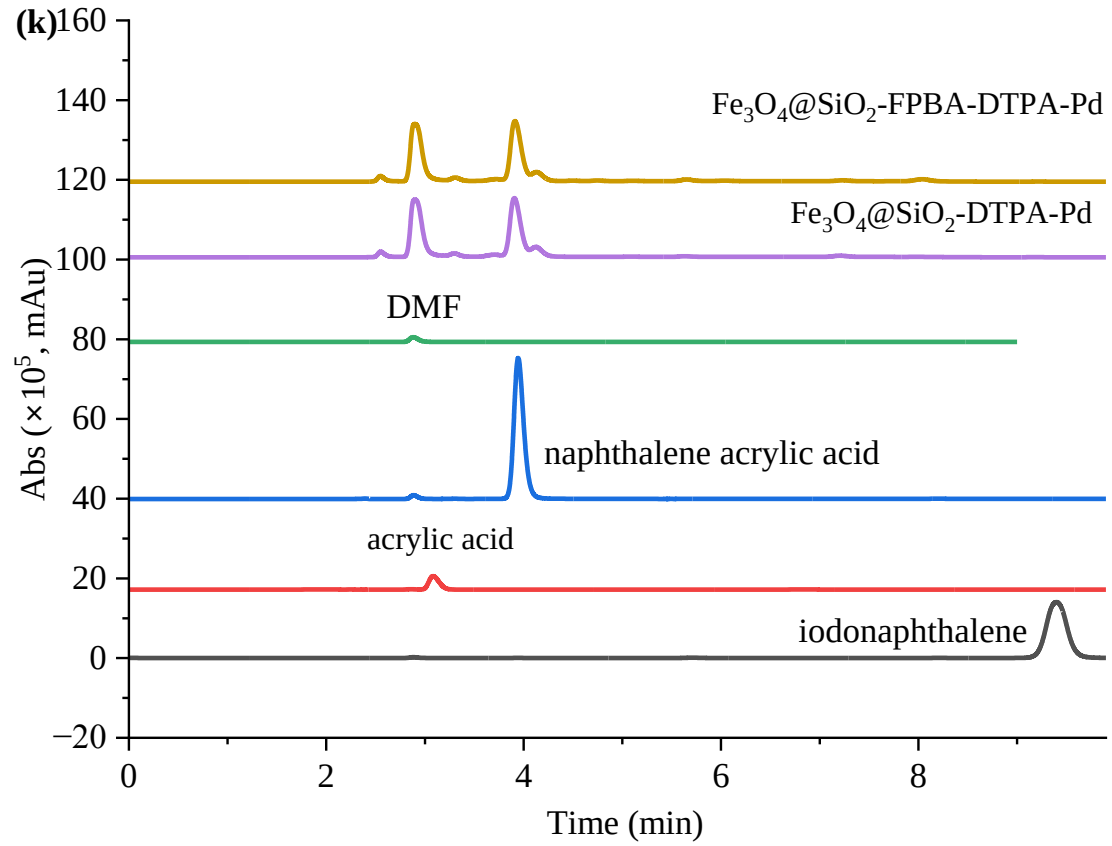

(f)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
3-methoxycinnamic acid
Acrylic acid
3-methoxyiodobenzene
Abs (×10^6, mAu)
Time (min)

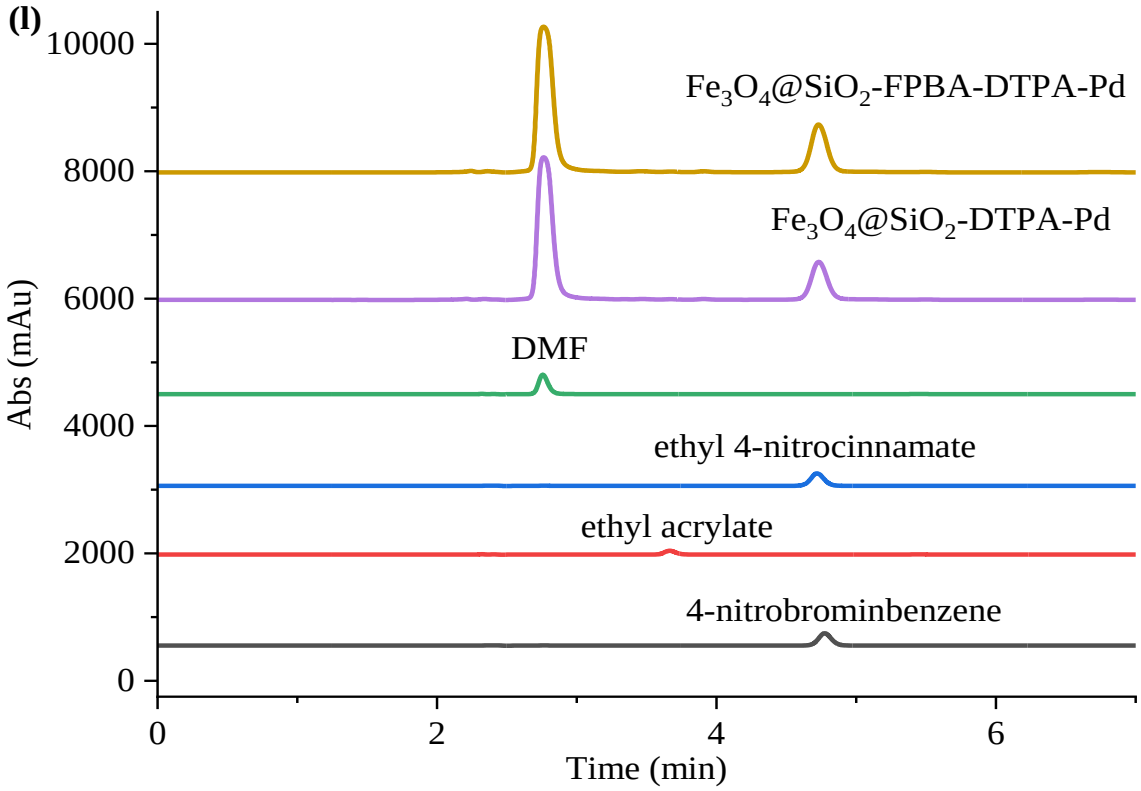

(g)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
4-methoxycinnamic acid
Acrylic acid
4-methoxyiodobenzene
Abs (×10^6, mAu)
Time (min)


(h)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
cinnamic acid
crylic acid
iodobenzene
Abs (×10^6, mAu)
Time (min)


(i)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
methyl cinnamate
methyl acrylate
iodobenzene
Abs (×10^6, mAu)
Time (min)


(j)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
biphenyl-4-acrylic acid
acrylic acid
2-Iodobiphenyl
Abs (×10^6, mAu)
Time (min)


(k)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
naphthalene acrylic acid
acrylic acid
iodonaphthalene
Abs (×10^5, mAu)
Time (min)


(l)
Fe3O4@SiO2-FPBA-DTPA-Pd
Fe3O4@SiO2-DTPA-Pd
DMF
ethyl 4-nitrocinnamate
ethyl acrylate
4-nitrobrominbenzene
Abs (mAu)
Time (min)

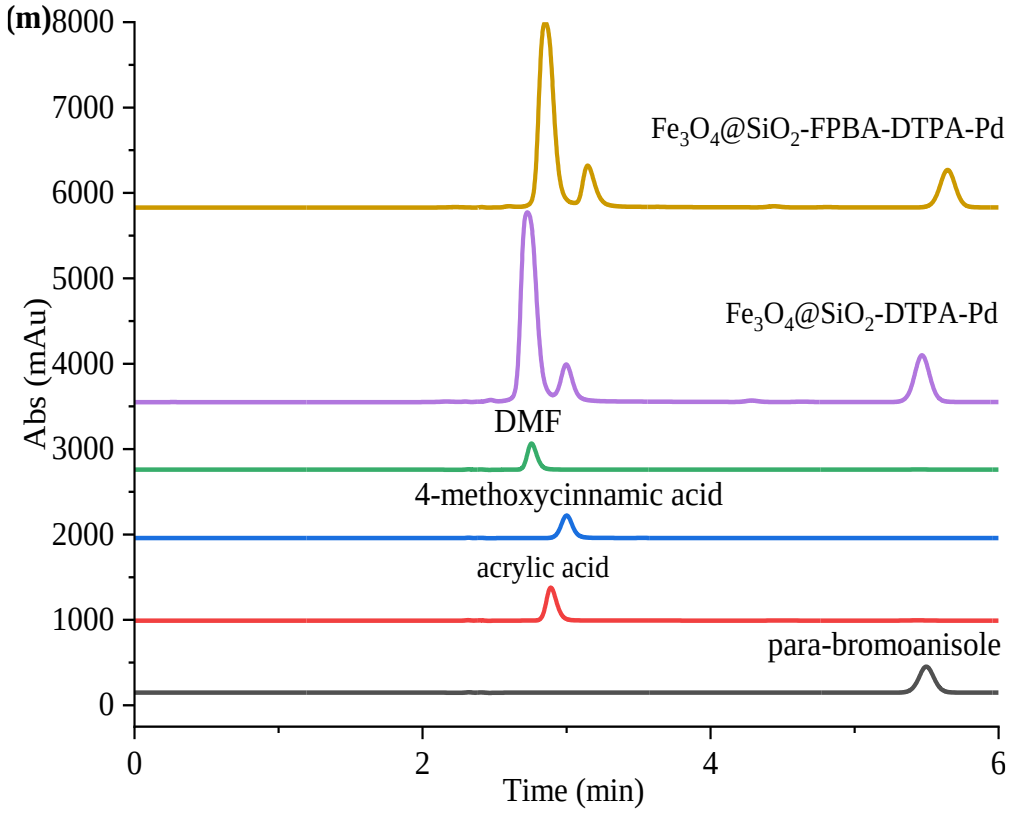
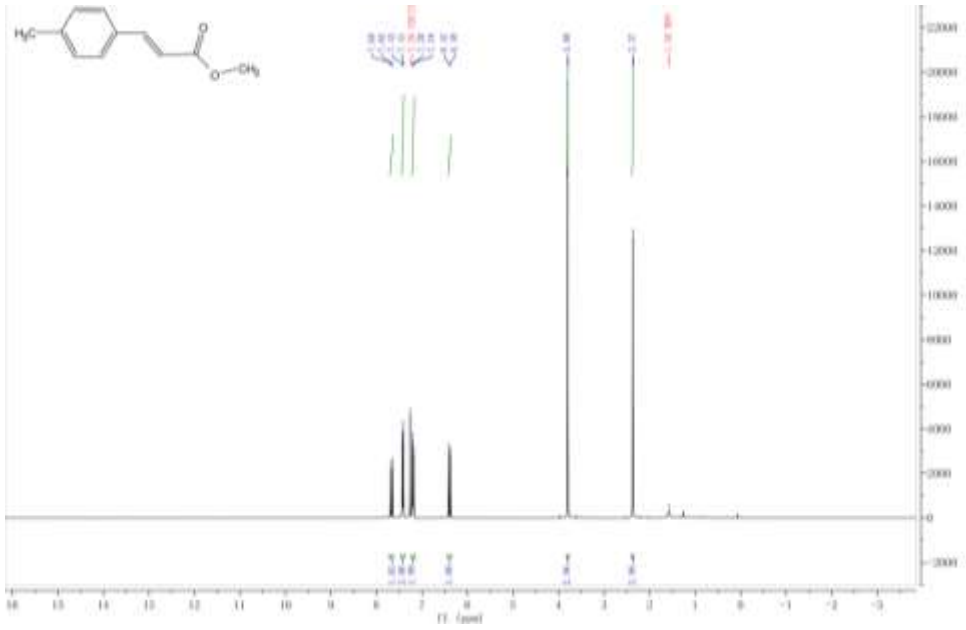


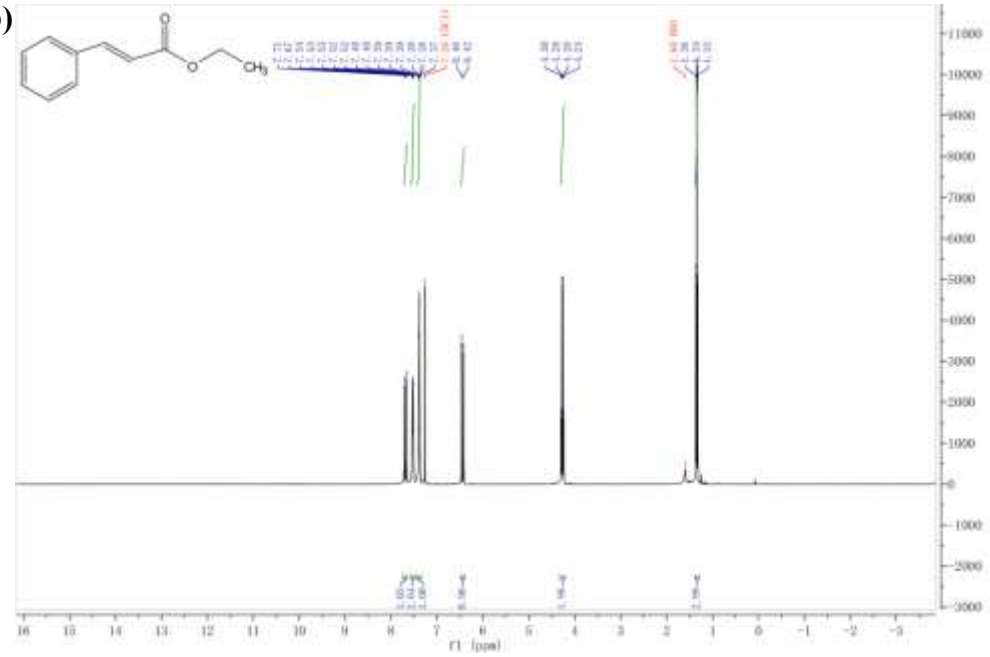
Figure S3 HPLC chromatograms of Heck reaction products between p-methyl iodobenzene and methyl acrylate (a), iodobenzene and ethyl acrylate (b), p-nitroiodobenzene and ethyl acrylate (c), p-methyl iodobenzene and ethyl acrylate (d), 2-methoxyiodobenzene and acrylic acid (e), 3-methoxyiodobenzene and acrylic acid (f), 4-methoxyiodobenzene and acrylic acid (g), iodobenzene and acrylic acid (h), and iodobenzene and methyl acrylate (i), 2-iodobiphenyl and acrylic acid (j), iodonaphthalene and acrylic acid (k), 4-nitrobrominbenzene and ethyl acrylate (l), para-bromoanisole and acrylic acid (m)

(a)



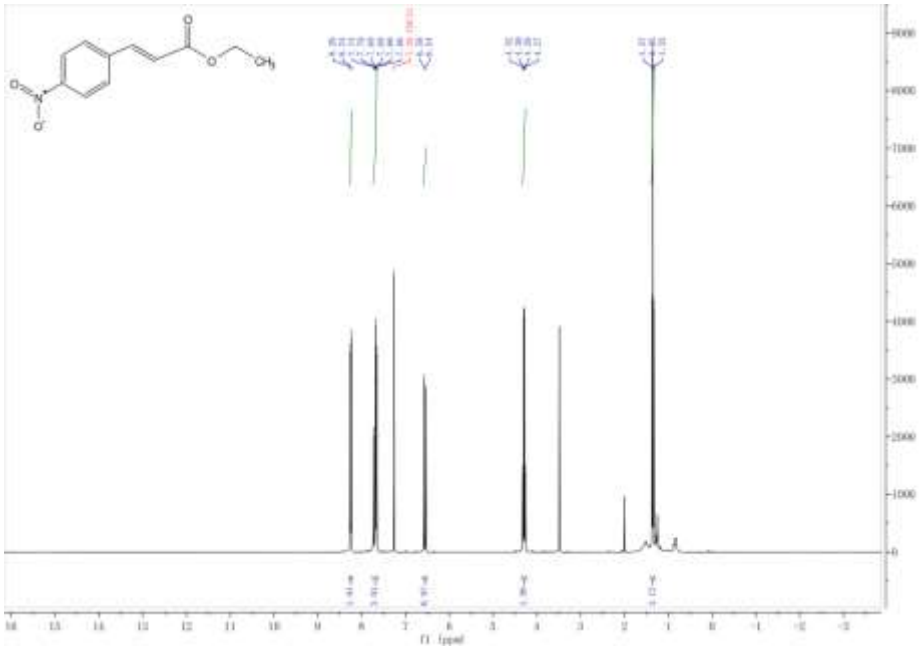
^{1}H NMR (400 MHz, Chloroform-d) : δ 7.67 (d, J = 15.9 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.40 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H)

(b)



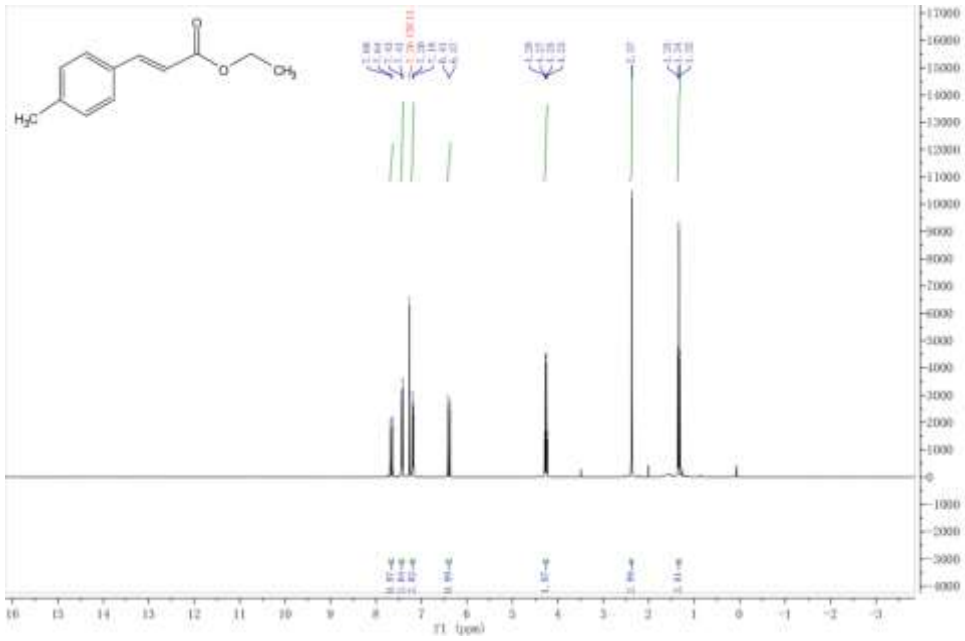
^{1}H NMR (400 MHz, Chloroform-d) : δ 7.69 (d, J = 16.0 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.44 – 7.34 (m, 3H), 6.44 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H)

(c)



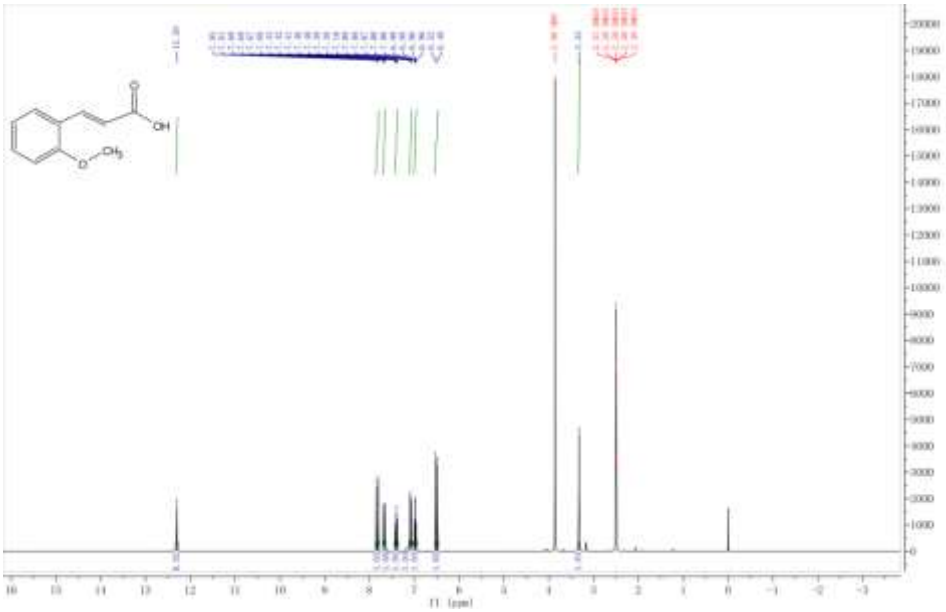
^{1}H NMR (400 MHz, Chloroform-d) : δ 8.25 (d, J = 8.8 Hz, 2H), 7.75 – 7.63 (m, 3H), 6.56 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H)

(d)



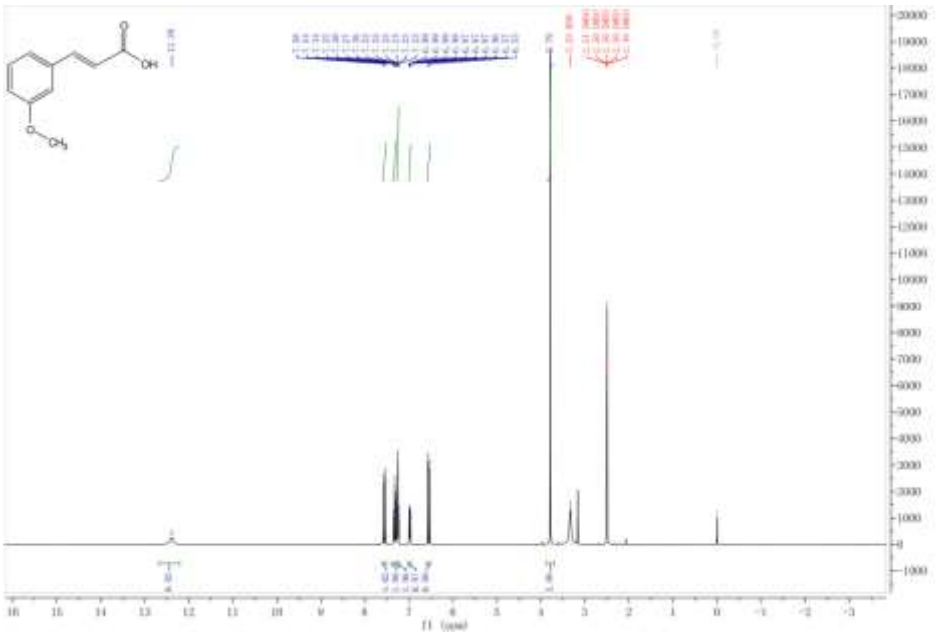
^{1}H NMR (400 MHz, Chloroform-*d*) : δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H)

(e)



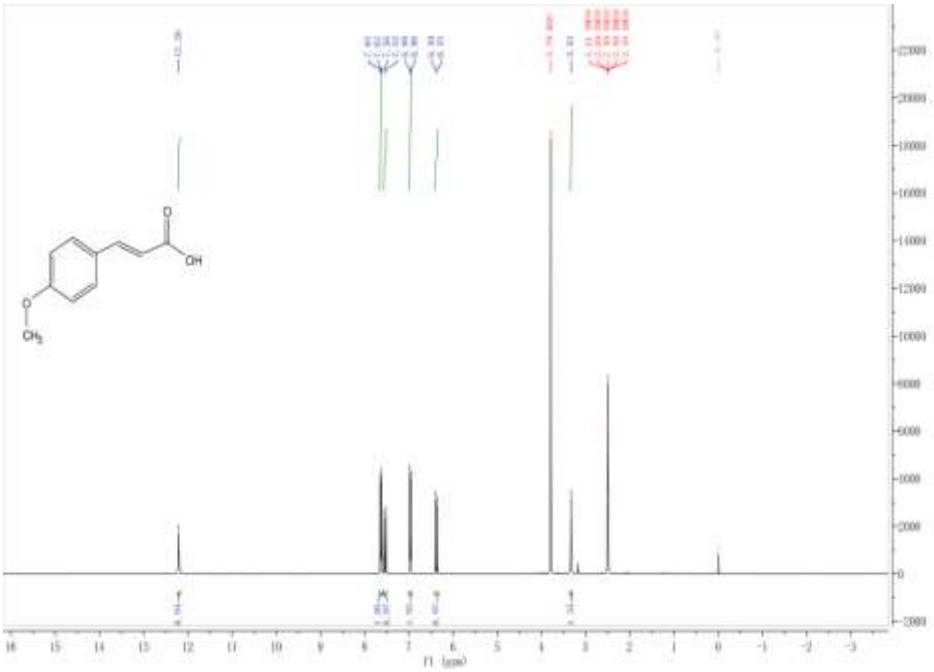
^{1}H NMR (400 MHz, DMSO-d_6) : δ 12.30 (s, 1H), 7.83 (d, J = 16.2 Hz, 1H), 7.67 (dd, J = 7.7, 1.7 Hz, 1H), 7.40 (ddd, J = 8.8, 7.4, 1.7 Hz, 1H), 7.08 (dd, J = 8.4, 1.0 Hz, 1H), 6.98 (td, J = 7.5, 1.0 Hz, 1H), 6.50 (d, J = 16.1 Hz, 1H), 3.33 (s, 3H)

(f)



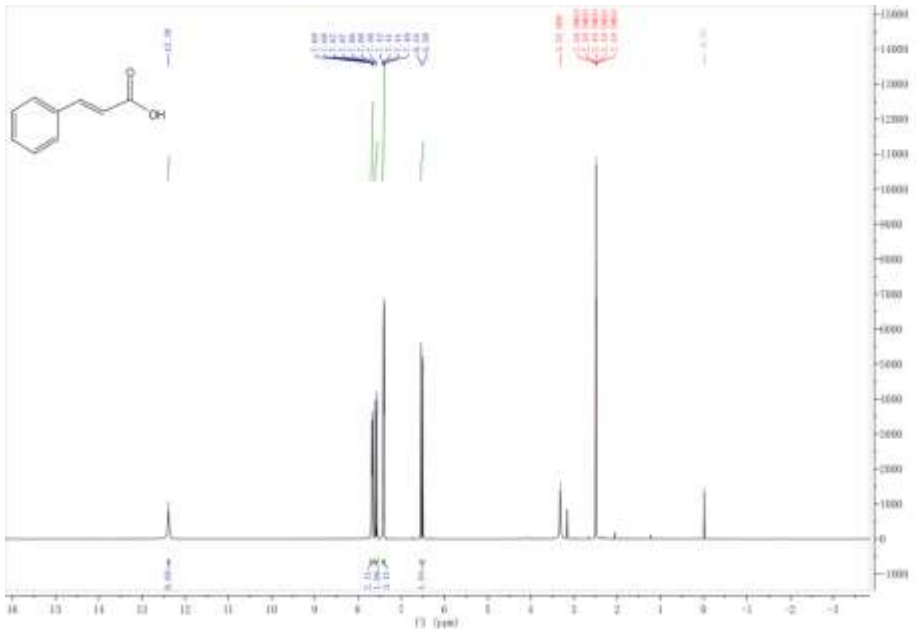
^{1}H NMR (400 MHz, DMSO-d_6) : δ 12.39 (s, 1H), 7.56 (d, J = 16.0 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.98 (ddd, J = 8.1, 2.5, 1.0 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 3.79 (s, 3H)

(g)



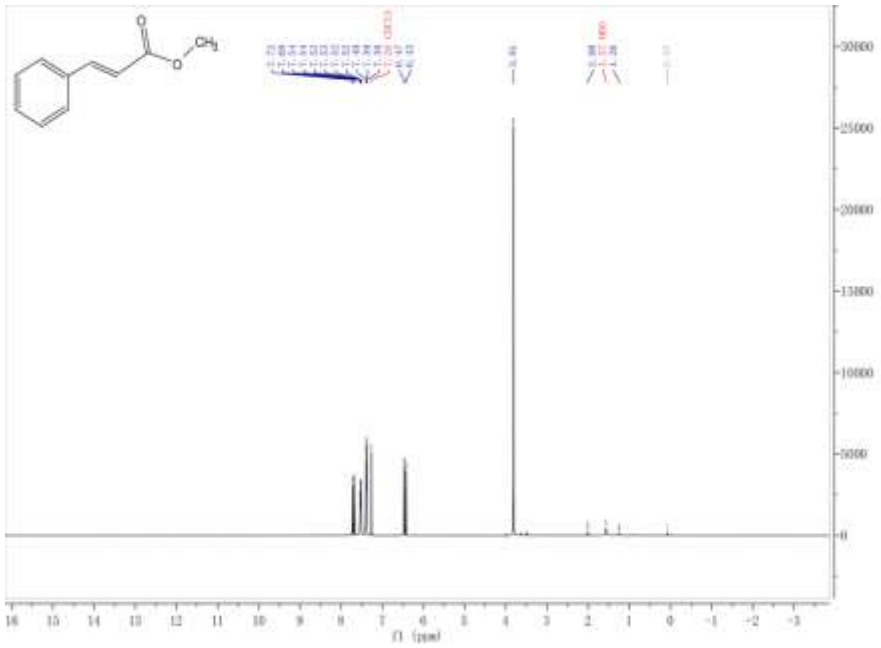
^{1}H NMR (400 MHz, DMSO-d_6) : δ 12.20 (s, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 15.9 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 16.0 Hz, 1H), 3.33 (s, 3H)

(h)



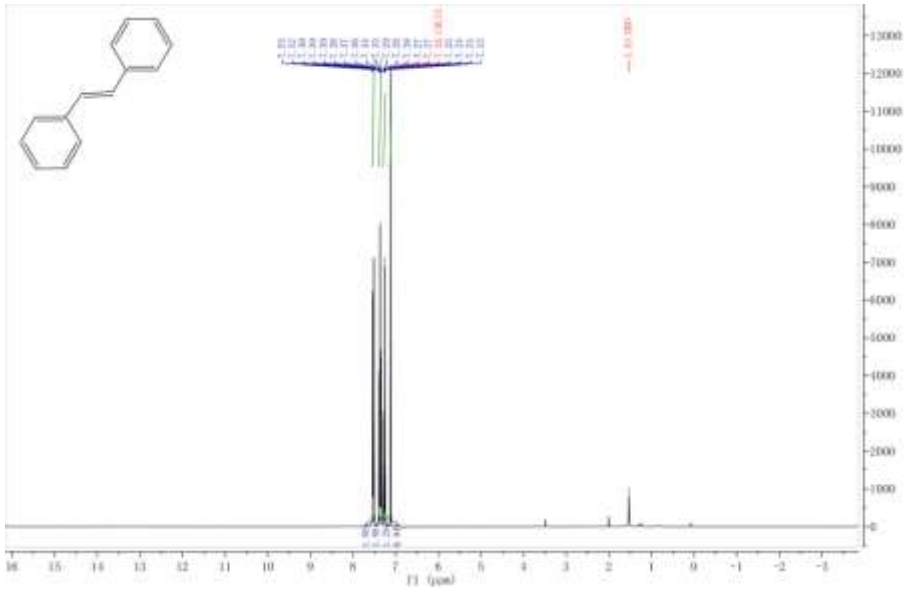
^{1}H NMR (400 MHz, DMSO-d_6) : δ 12.39 (s, 1H), 7.67 (dd, J = 6.7, 3.0 Hz, 2H), 7.58 (d, J = 16.0 Hz, 1H), 7.45 – 7.37 (m, 3H), 6.52 (d, J = 16.0 Hz, 1H)

(i)



^{1}H NMR (400 MHz, Chloroform-*d*) : δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.42 – 7.36 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H)

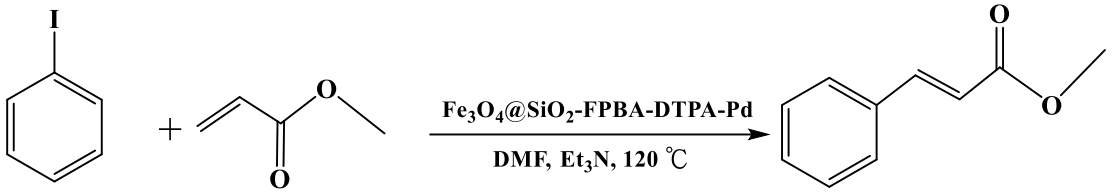
(j)



^{1}H NMR (400 MHz, Chloroform-*d*) : δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.32 (m, 2H), 7.31 – 7.22 (m, 1H), 7.12 (s, 1H)

Figure S4 1H NMR spectra of Heck product of Methyl p-methylcinnamic acid (a), ethyl cinnamic acid (b), ethyl p-nitrocinnamic acid (c), ethyl p-methylcinnamic acid (d), 2-methoxycinnamic acid (e), 3-methoxycinnamic acid (f), 4-methoxycinnamic acid (g), cinnamic acid (h), methyl cinnamic acid (i) and trans -1, 2-stilbenes (j)

Table S1 Conditions optimization of the Heck reaction model of iodobenzene with methyl acrylate catalyzed by two catalysts



Entry	Time (min)	Catalyst (mol%)	Yeild(%)	
			Fe_3O_4@SiO_2-FPBA-DTPA-Pd	Fe_3O_4@SiO_2-DTPA-Pd
1	15	1.00	70	73
2	30	1.00	81	82
3	45	1.00	84	77
4	60	1.00	91	85
5	90	1.00	96	91
6	120	1.00	98	88
7	120	0.34	88	69
8	120	0.50	97	90
9	120	0.80	97	85

Conditions: 0.5 mmol iodobenzene, 0.75 mmol styrene, 1.0 mmol triethylamine as base, and 3 mL DMF as solvent, 120 ^{o}C