Postsynthetic modification of single Pd sites into uncoordinated polypyridine groups of a MOF as the highly efficient catalyst for Heck and Suzuki reactions

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(14) The results of GC-MS for the Heck reaction catalyzed by Pd–HoMOF.

(15) The results of GC-MS for the Suzuki–Miyaura reaction catalyzed by Pd–HoMOF.

(1)

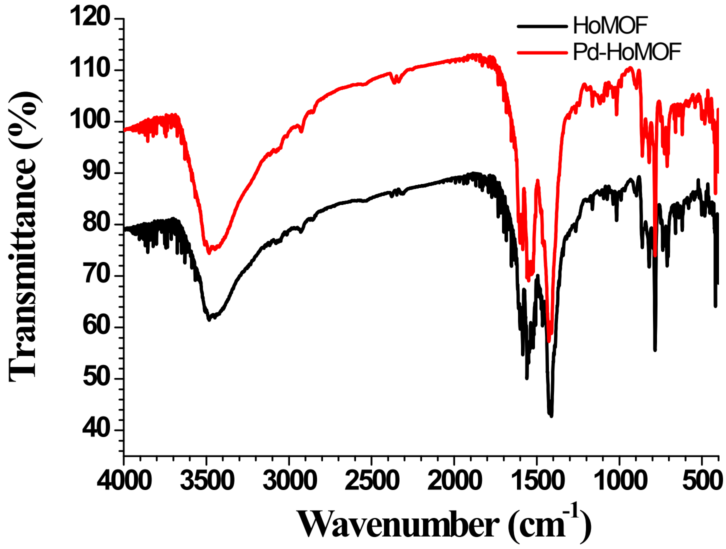


Fig. S1 The IR spectra of **HoMOF** and **Pd-HoMOF**.

(2)

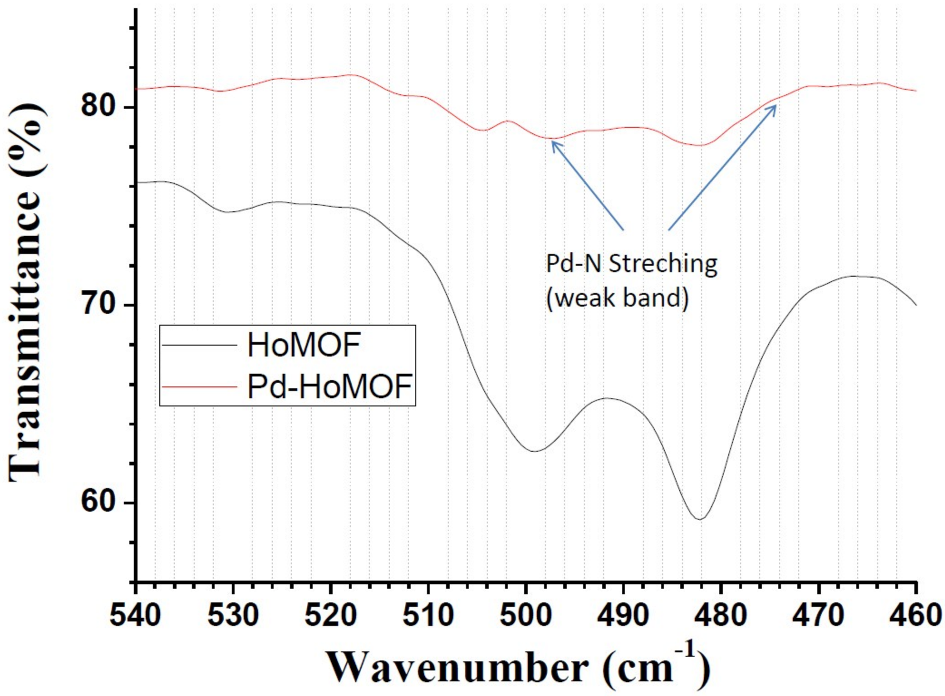


Fig. S2 IR spectra of **HoMOF** (black) and **Pd-HoMOF** (red) demonstrating the two weak Pd–N stretching observed for **Pd-HoMOF**.

(3)

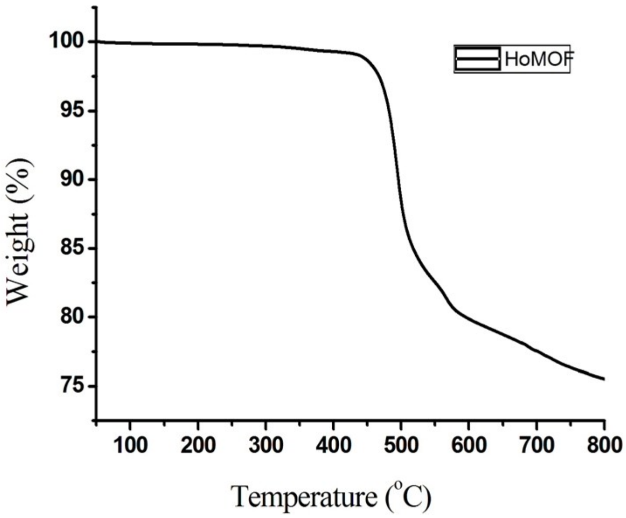


Fig. S3 The TG curve of **HoMOF**.

(4)

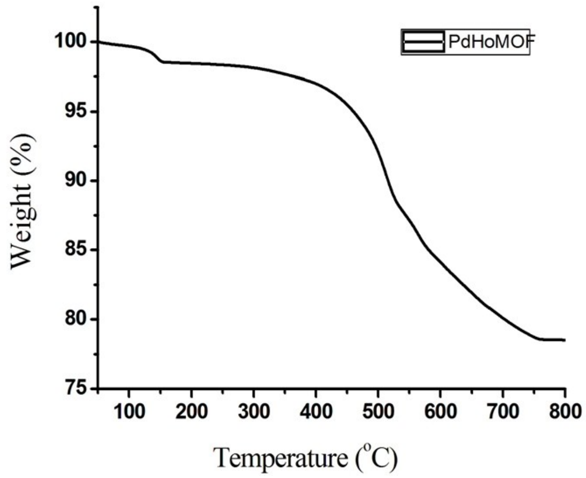


Fig. S4 The TG curve of **PdHoMOF**.

(5)

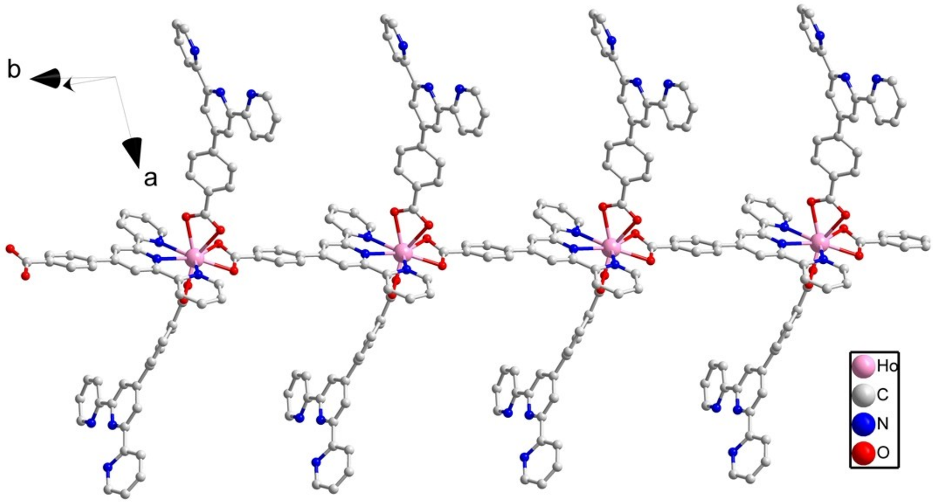


Fig. S5 Side view of one-dimensional chain along the b-axis for compound **HoMOF**.

(6)

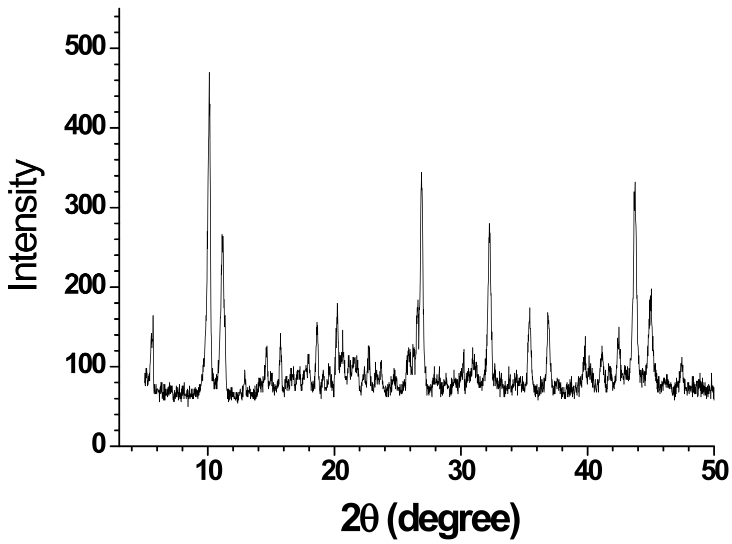


Fig. S6 The XRD patterns after five reaction cycles of **Pd-HoMOF**.

(7)

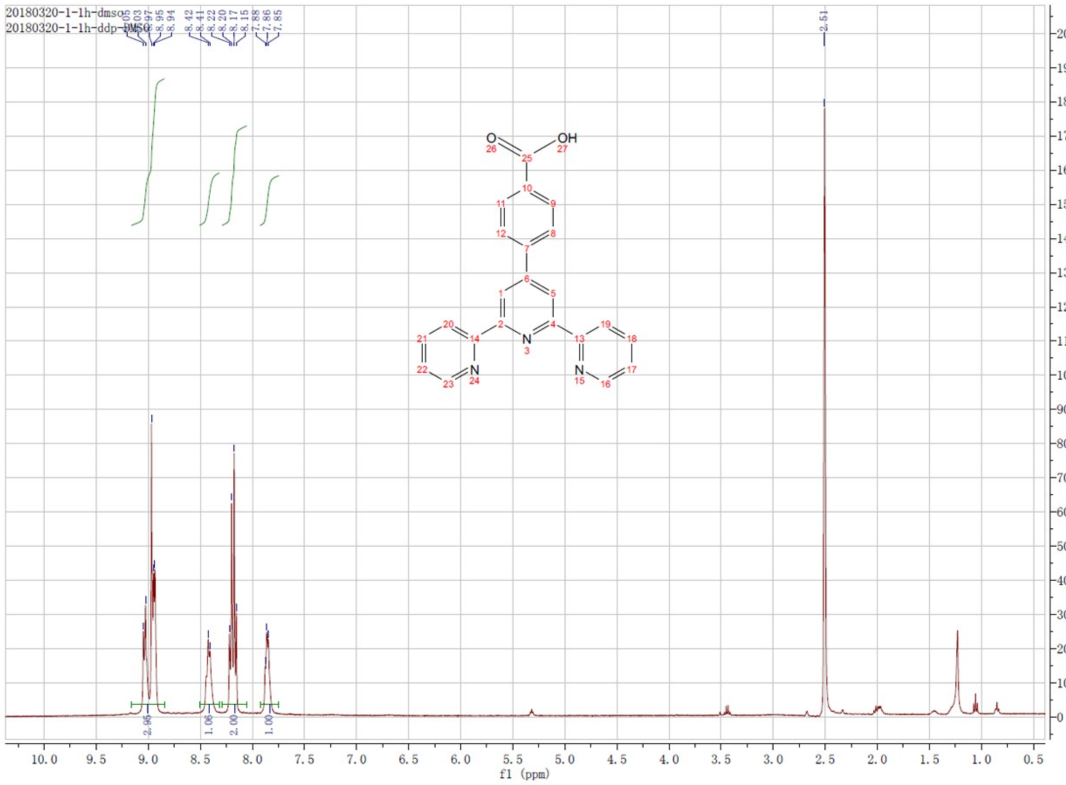
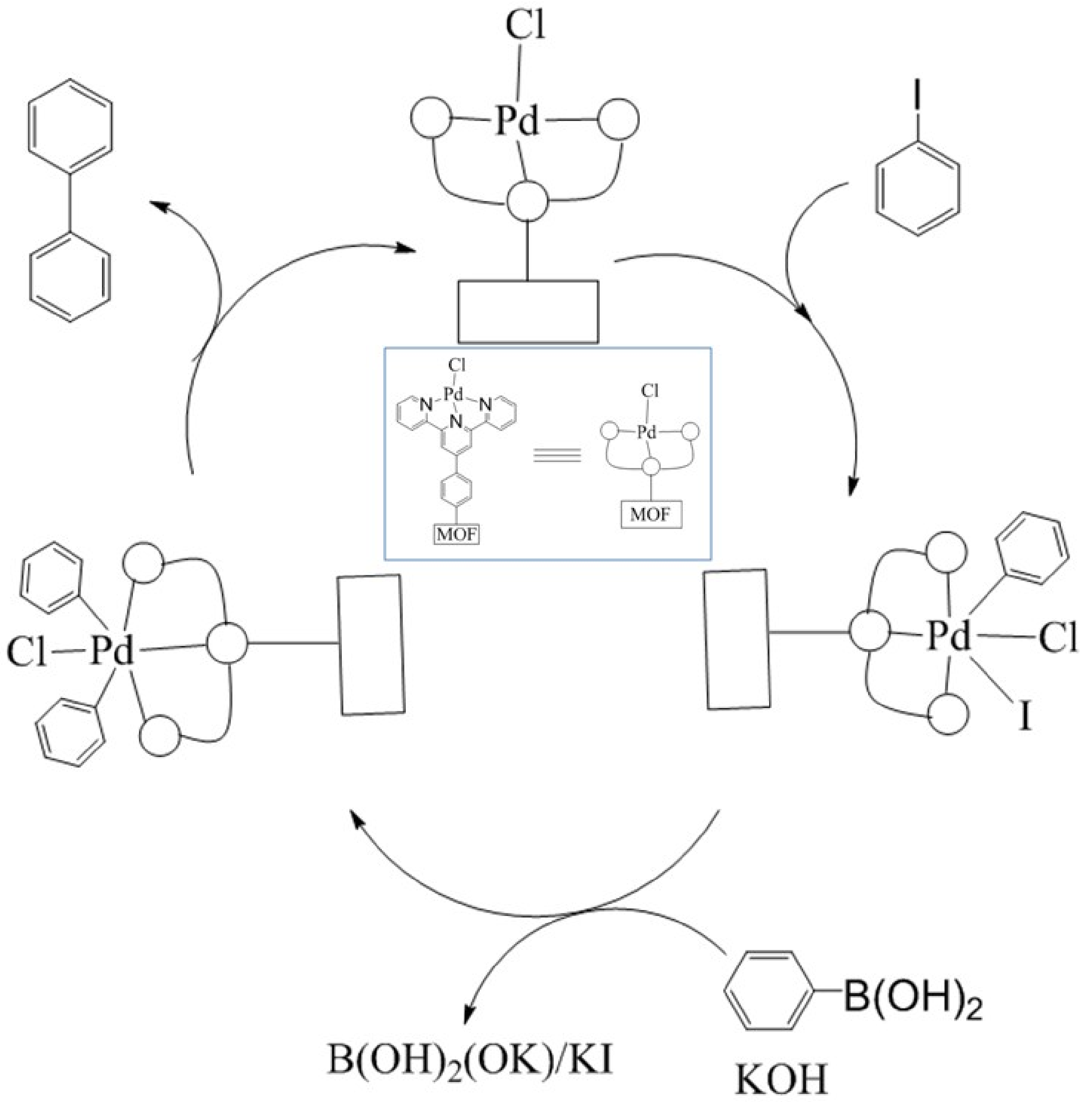


Fig. S7 The ^{1}H NMR analysis for 2-TriPP-COOH.

(8)



Scheme S1 An illustrative sketch of proposed mechanism of the Suzuki–Miyaura reaction of iodobenzene in the presence of Pd-HoMOF catalyst.

(9) Table S1. Crystal data and structure refinement for compound HoMOF.

	1
formula	$C_{66}H_{42}HoN_9O_6$
Fw	1222.01
crystal system	Monoclinic
Space group	C2/c
a, Å	33.823(2)
b, Å	13.7794(10)
c, Å	12.2450(9)
β, °	109.0973(9)
V, Å^3	5392.8(7)
Z	4
D_c, g/cm^3	1.505
μ (Mo K_α), mm^{-1}	1.532
θ_{min}, θ_{max} , °	2.226, 27.484
no. total reflns.	23201
no. uniq. reflns (R_{int})	6113 (0.0278)
no. obs. [I≥2σ(I)]	5684
no. params	373
$R1$,$wR2$ [I≥2σ(I)]	0.0275, 0.0702
$R1$,$wR2$ (all data)	0.0312, 0.0716
GOF	1.083

$R_1 = \Sigma (|F_0|-|F_C|) / \Sigma |F_0|$, $wR_2 = [\Sigma w (|F_0|-|F_C|)^2 / \Sigma w F_0^2]^{1/2}$.

(10) **Table S2**. Selected bond lengths (Å) and angles (º) for compound HoMOF.

Ho(1)-O(3)	2.3721(18)	Ho(1)-O(1)#1	2.467(2)
Ho(1)-O(3)#1	2.3721(18)	Ho(1)-N(4)	2.475(2)
Ho(1)-O(2)#1	2.416(2)	Ho(1)-N(4)#1	2.475(2)
Ho(1)-O(2)	2.416(2)	Ho(1)-N(5)	2.486(3)
Ho(1)-O(1)	2.467(2)		
O(3)-Ho(1)-O(3)#1	55.40(9)	O(2)-Ho(1)-N(4)	66.86(7)
O(3)-Ho(1)-O(2)#1	120.62(8)	O(1)-Ho(1)-N(4)	118.72(7)
O(3)#1-Ho(1)-O(2)#1	87.01(8)	O(1)#1-Ho(1)-N(4)	74.85(7)
O(3)-Ho(1)-O(2)	87.01(8)	O(3)-Ho(1)-N(4)#1	140.34(7)
O(3)#1-Ho(1)-O(2)	120.62(7)	O(3)#1-Ho(1)-N(4)#1	88.65(6)
O(2)#1-Ho(1)-O(2)	150.07(13)	O(2)#1-Ho(1)-N(4)#1	66.86(7)
O(3)-Ho(1)-O(1)	79.13(7)	O(2)-Ho(1)-N(4)#1	100.10(8)

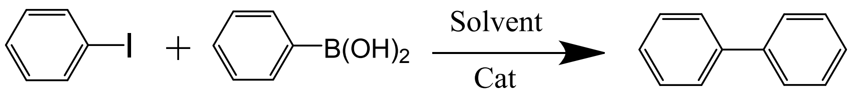
O(3)#1-Ho(1)-O(1)	74.24(7)	O(1)-Ho(1)-N(4)#1	74.85(7)
O(2)#1-Ho(1)-O(1)	137.58(8)	O(1)#1-Ho(1)-N(4)#1	118.72(7)
O(2)-Ho(1)-O(1)	52.84(7)	N(4)-Ho(1)-N(4)#1	130.14(9)
O(3)-Ho(1)-O(1)#1	74.24(7)	O(3)-Ho(1)-N(5)	152.30(4)
O(3)#1-Ho(1)-O(1)#1	79.12(7)	O(3)#1-Ho(1)-N(5)	152.30(4)
O(2)#1-Ho(1)-O(1)#1	52.84(7)	O(2)#1-Ho(1)-N(5)	75.04(6)
O(2)-Ho(1)-O(1)#1	137.58(8)	O(2)-Ho(1)-N(5)	75.04(6)
O(1)-Ho(1)-O(1)#1	149.87(11)	O(1)-Ho(1)-N(5)	105.07(6)
O(3)-Ho(1)-N(4)	88.65(6)	O(1)#1-Ho(1)-N(5)	105.07(6)
O(3)#1-Ho(1)-N(4)	140.34(7)	N(4)-Ho(1)-N(5)	65.07(5)
O(2)#1-Ho(1)-N(4)	100.10(8)	N(4)#1-Ho(1)-N(5)	65.07(5)

Symmetry transformations used to generate equivalent atoms for **1**: #1: -x+1,y,-z+3/2.

(11) **Table S3**. Reusability of Pd–HoMOF catalyst in the Heck reaction. Reaction time = 1 h.

Reaction Runs	1	2	3	4	5
Yield (%)	99	99	99	98.3	98.0

(12) **Table S4**. Optimization of Suzuki–Miyaura reaction.[a]



Entry	Base	Solvent	T(℃)	Time(h)	Yield(%)[b]
1	KOH	EtOH	80	1	25.4
2	KOH	H_2O	100	1	18.4
3	KOH	Dioxane	100	1	45
4	K_2CO_3	DMF	100	1	51
5	Cs_2CO_3	DMF	100	1	62.8
6	KOH	DMF	80	1	91.6
7	**KOH**	**DMF**	**100**	**1**	**>99**
8	KOH	DMF	100	4	>99
9[c]	KOH	DMF	100	1	none
10[d]	KOH	DMF	100	1	90.8

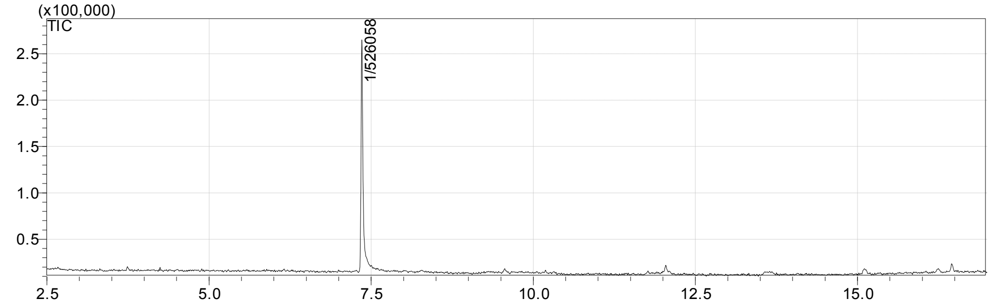
[a]Reaction conditions: Ph–I (0.5 mmol), phenylboronic acid (0.75mmol), base (1.5 mmol), Pd–HoMOF (0.4 mol% Pd). [b]Yield determined by GC-MS analysis. [c]Parent HoMOF as the catalyst. [d]$PdCl_2(CH_3CN)_2$ as the catalyst (0.4 mol% Pd).

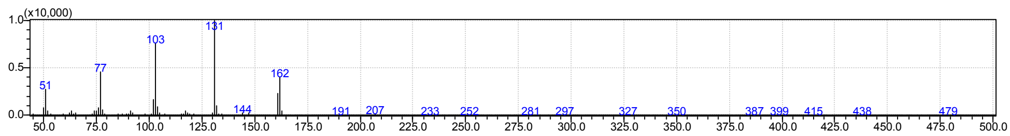
(13) **Table S5**. Reusability of Pd–HoMOF catalyst in the Suzuki reaction. Reaction time = 1 h.

Reaction Runs	1	2	3	4	5
Yield (%)	99	99	99	99	99

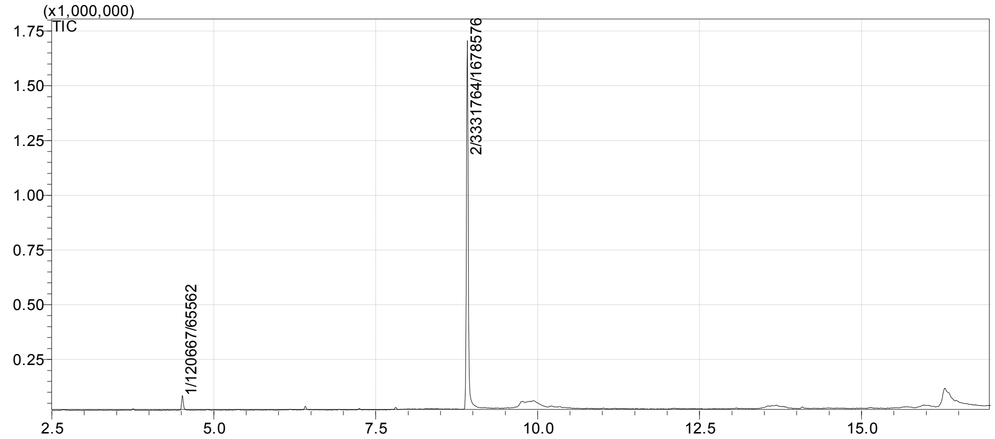
(14) The results of GC-MS for the Heck reaction catalyzed by Pd–HoMOF

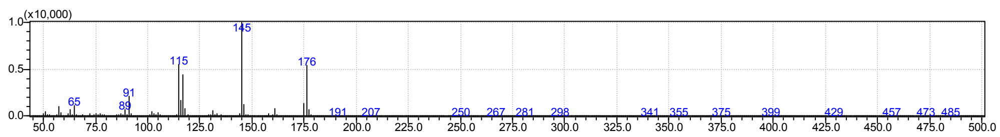
1. The results of GC (up) and MS (down) for iodobenzene and methyl acrylate



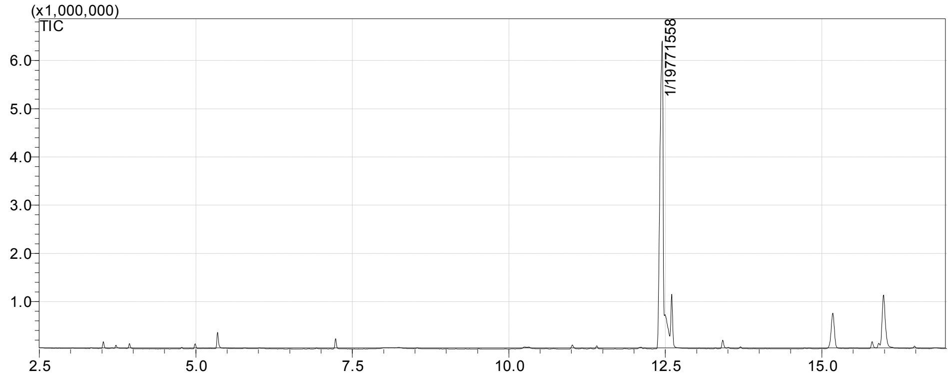


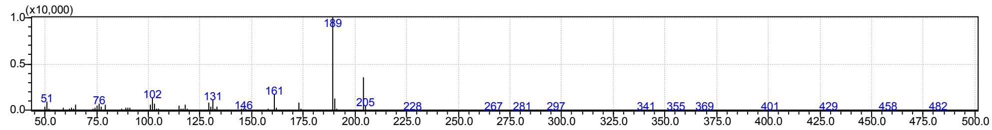
2. The results of GC (up) and MS (down) for 4-methyliodobenzene and methyl acrylate



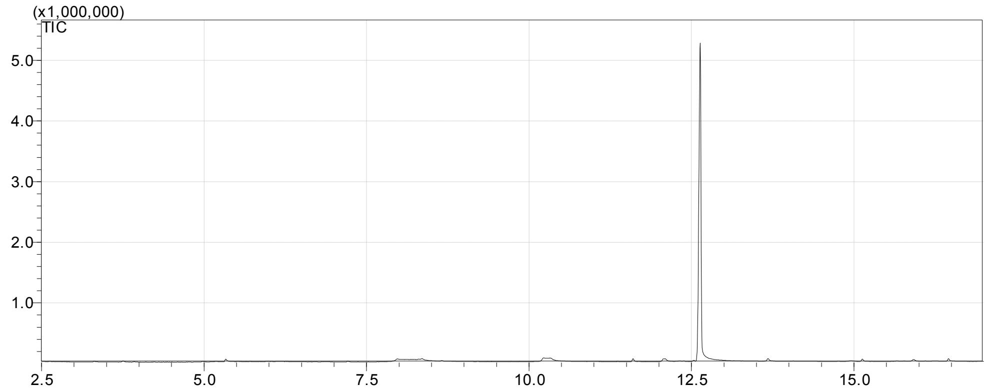


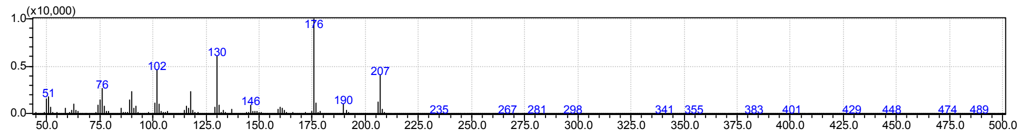
3. The results of GC (up) and MS (down) for 4-iodoacetophenone and methyl acrylate



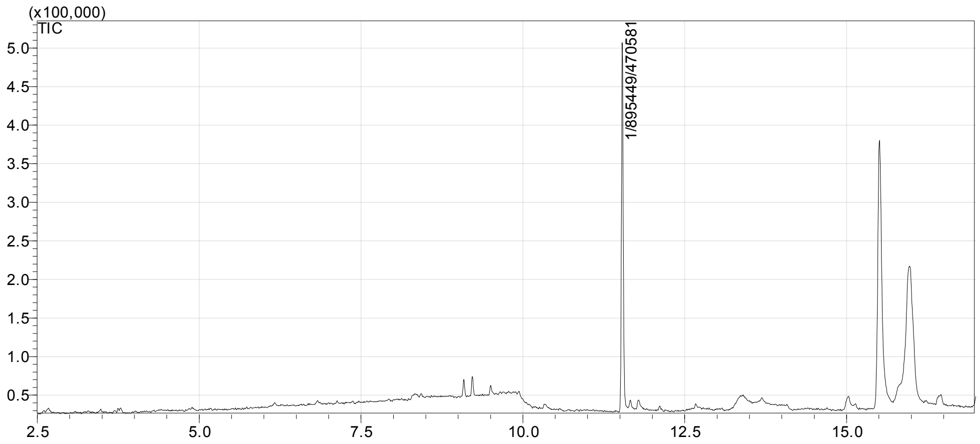


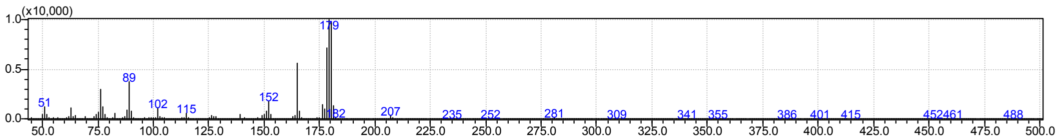
4. The results of GC (up) and MS (down) for 4-iodonitrobenzene and methyl acrylate



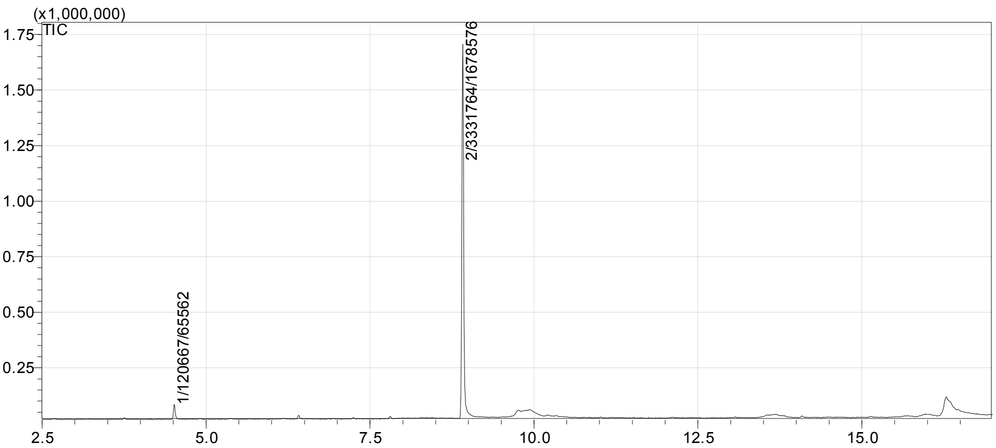


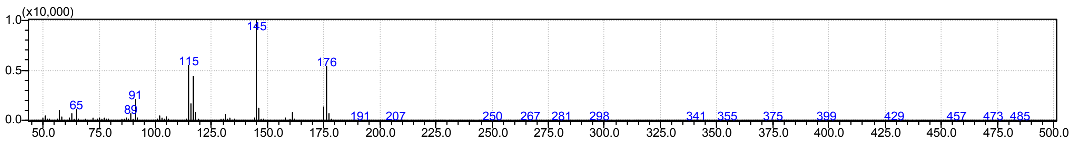
5. The results of GC (up) and MS (down) for iodobenzene and styrene



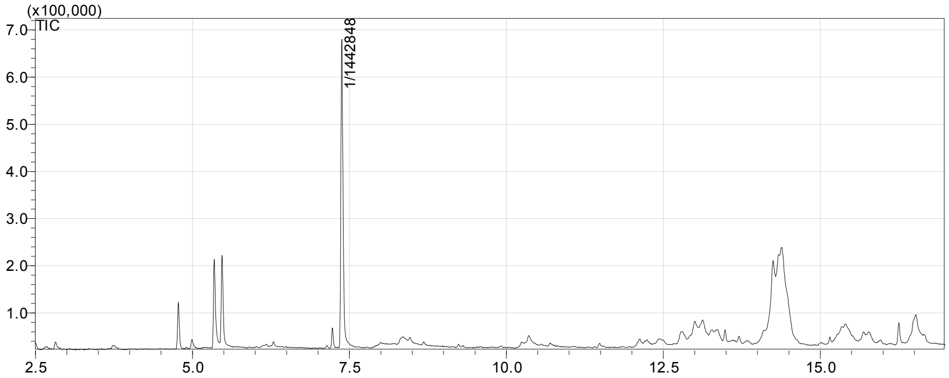


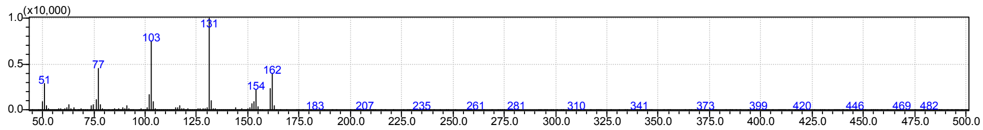
6. The results of GC (up) and MS (down) for 4-methyliodobenzene and styrene



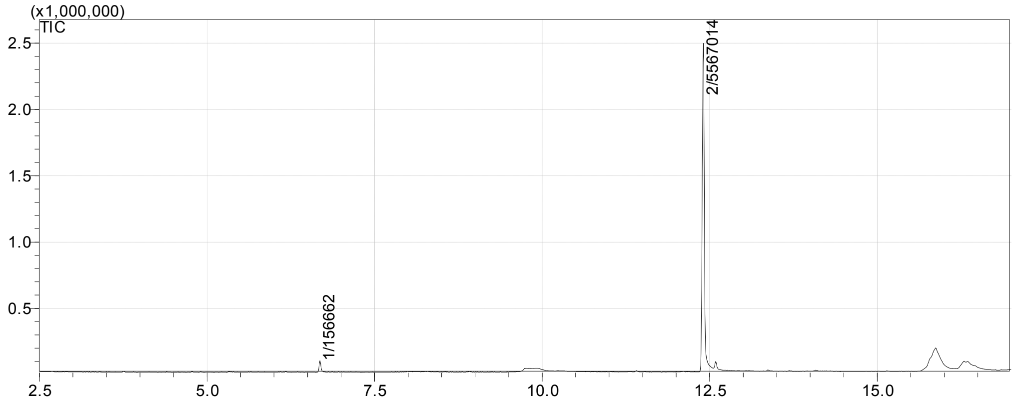


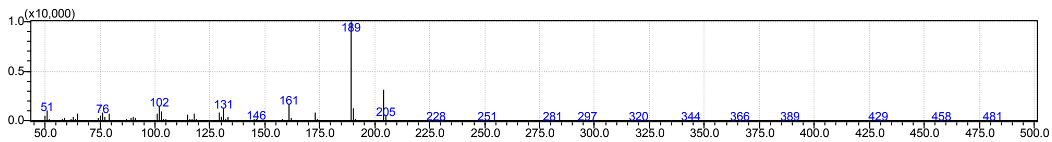
7. The results of GC (up) and MS (down) for bromobenzene and methyl acrylate



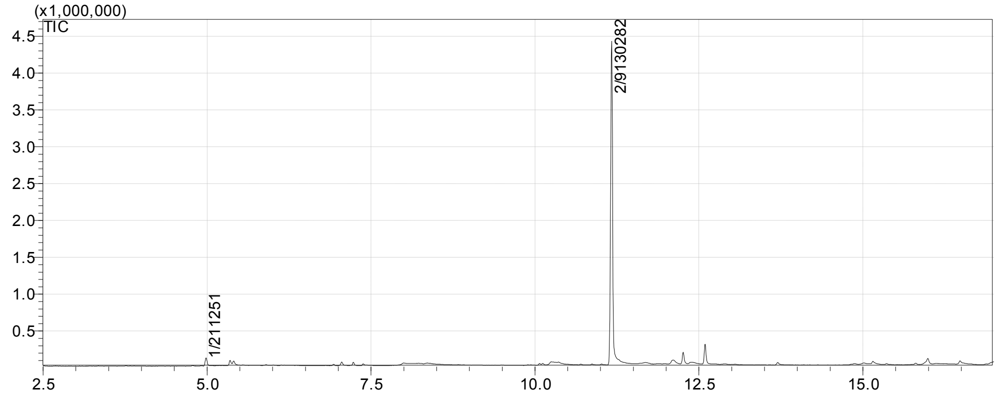


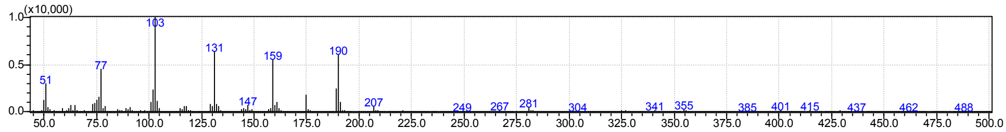
8. The results of GC (up) and MS (down) for 4-bromoacetophenone and methyl acrylate



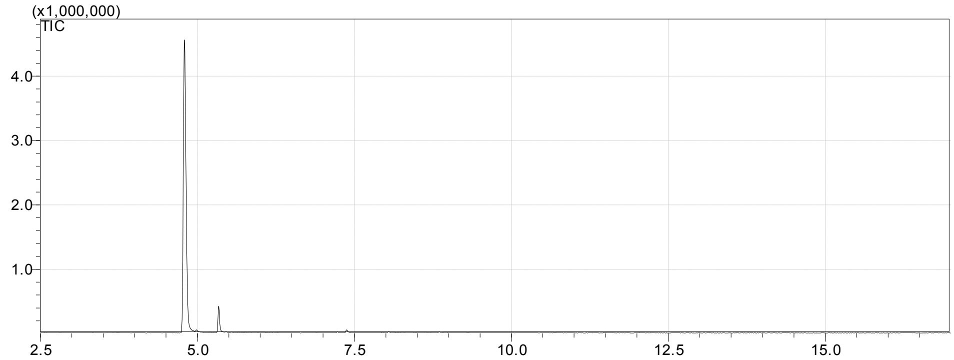


9. The results of GC (up) and MS (down) for 4-bromobenzaldehyde and methyl acrylate

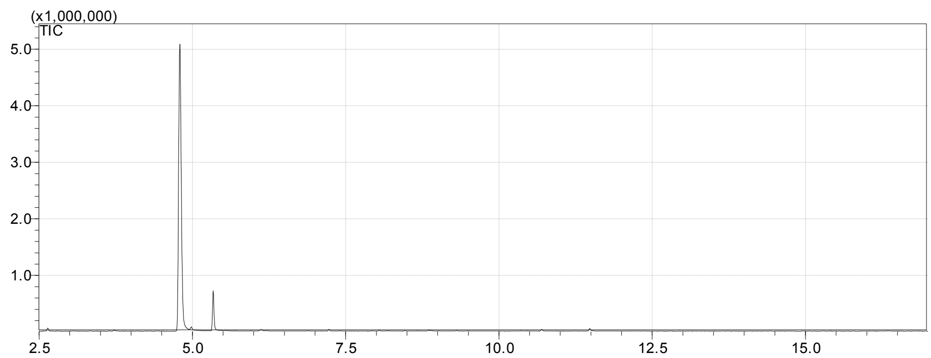




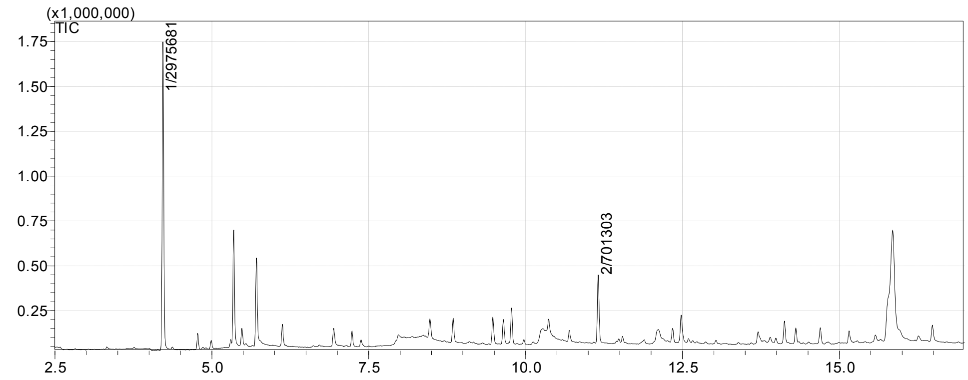
10. The results of GC for chlorobenzene and methyl acrylate

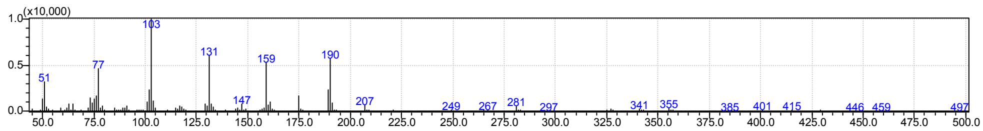


11. The results of GC for 4-methylchlorobenzene and methyl acrylate



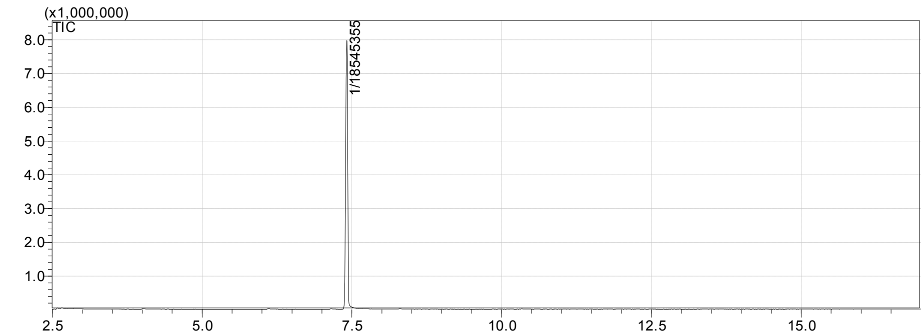
12. The results of GC (up) and MS (down) for 4-chlorobenzaldehyde and methyl acrylate

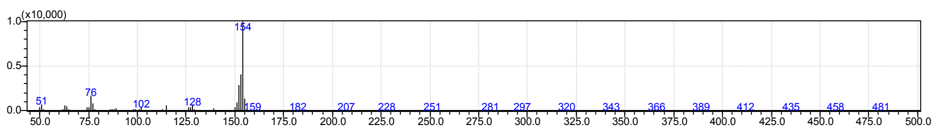




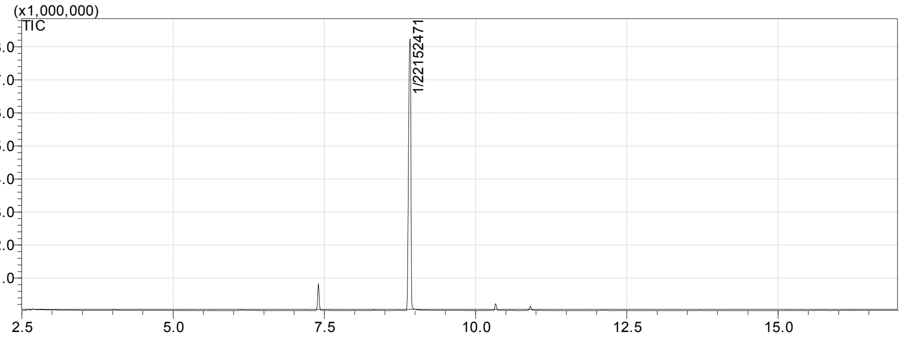
(15) The results of GC-MS for the Suzuki–Miyaura reaction catalyzed by Pd–HoMOF

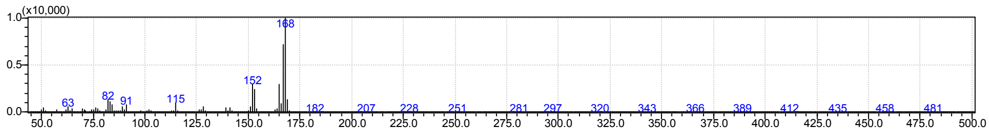
1. The results of GC (up) and MS (down) for iodobenzene and phenylboronic acid



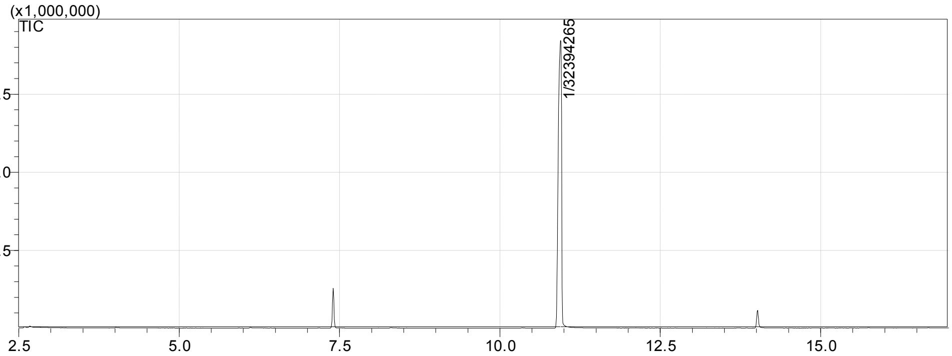


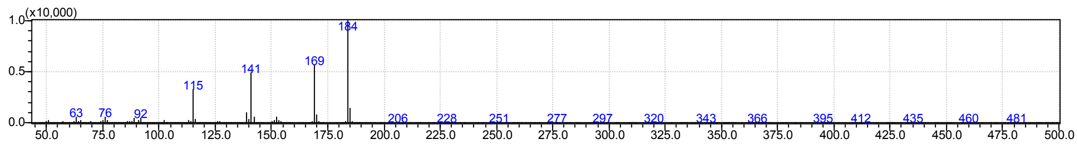
2. The results of GC (up) and MS (down) for 4-methyliodobenzene and phenylboronic acid



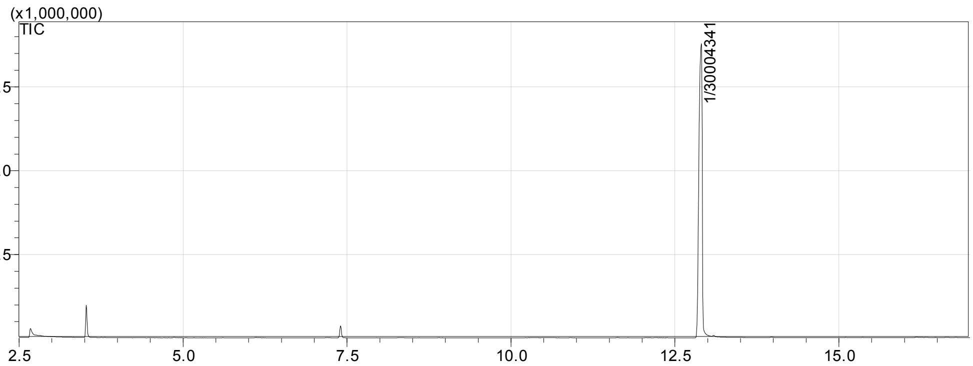


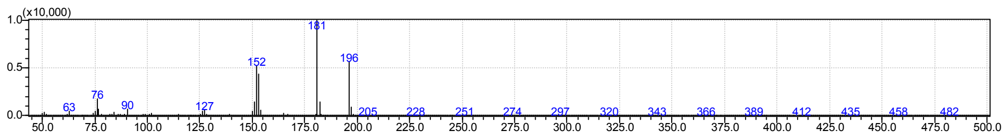
3. The results of GC (up) and MS (down) for 4-methoxyiodobenzene and phenylboronic acid



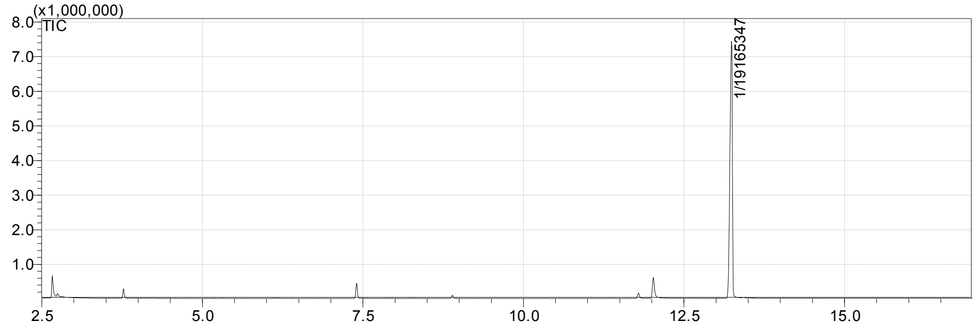


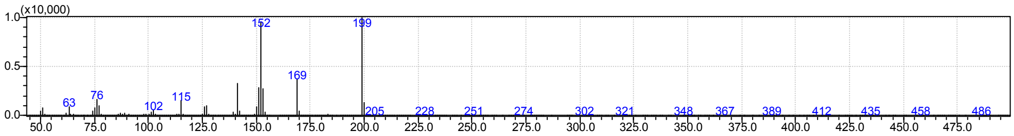
4. The results of GC (up) and MS (down) for 4-iodoacetophenone and phenylboronic acid



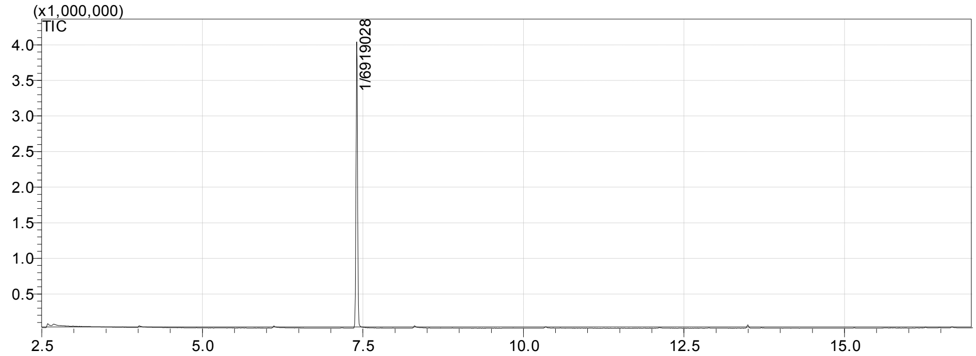


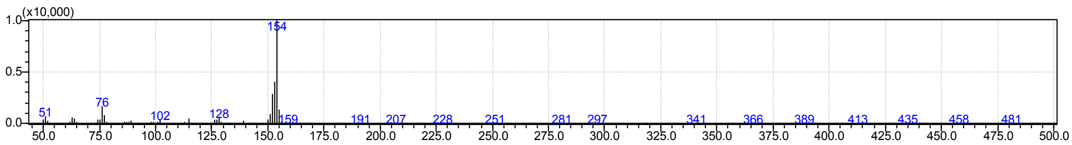
5. The results of GC (up) and MS (down) for 4-iodonitrobenzene and phenylboronic acid



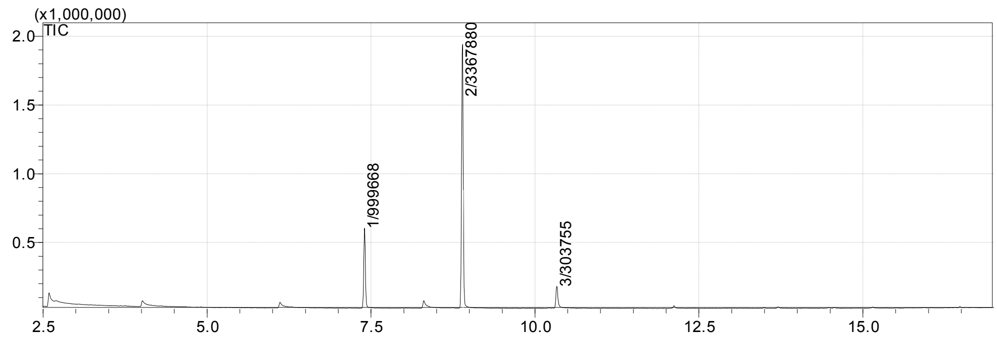


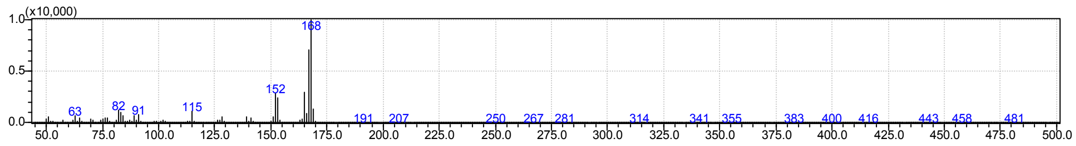
6. The results of GC (up) and MS (down) for bromobenzene and phenylboronic acid



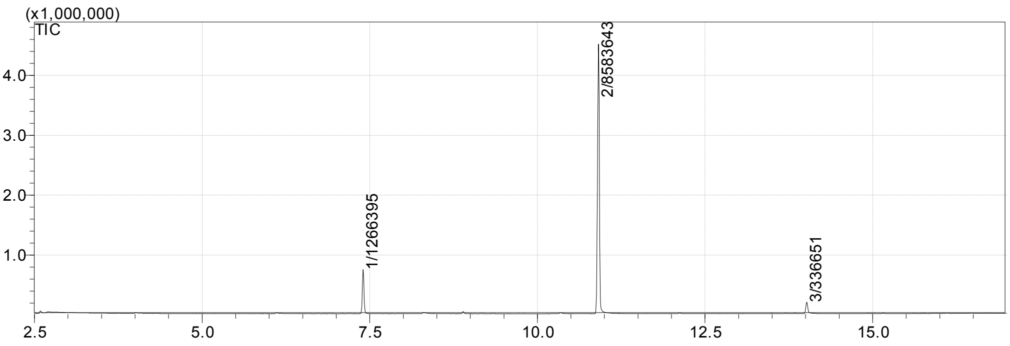


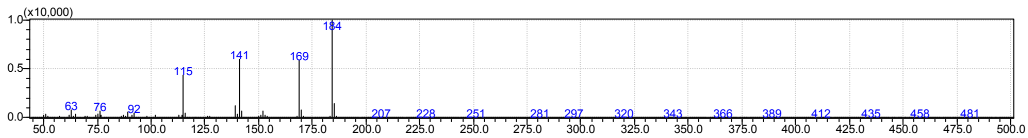
7. The results of GC (up) and MS (down) for 4-methylbromobenzene and phenylboronic acid



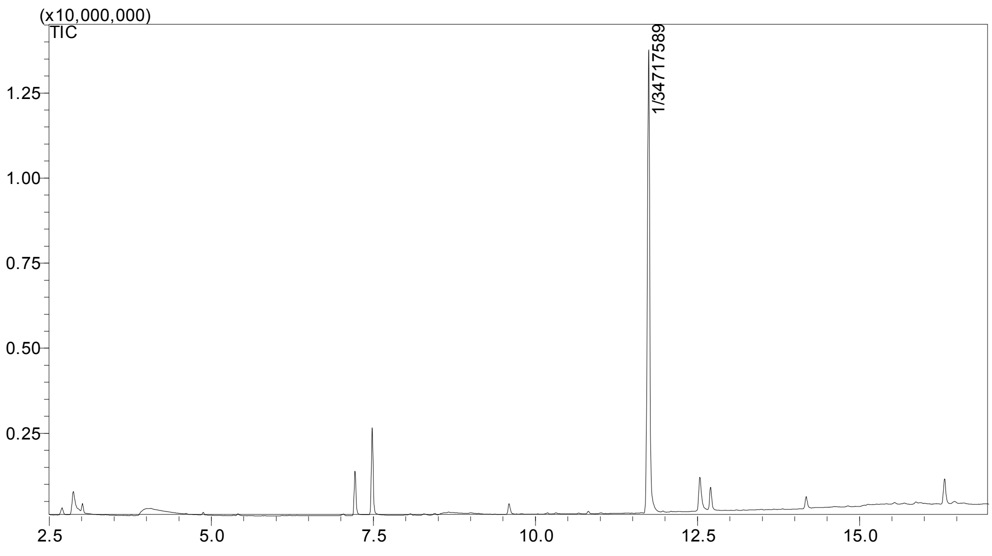


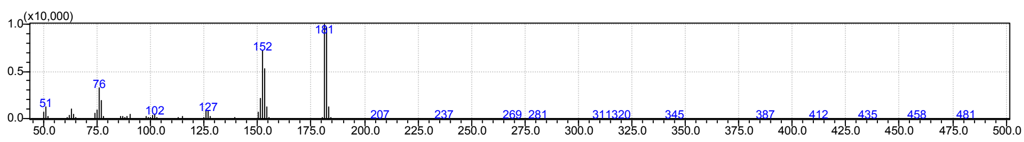
8. The results of GC (up) and MS (down) for 4-methoxybromobenzene and phenylboronic acid



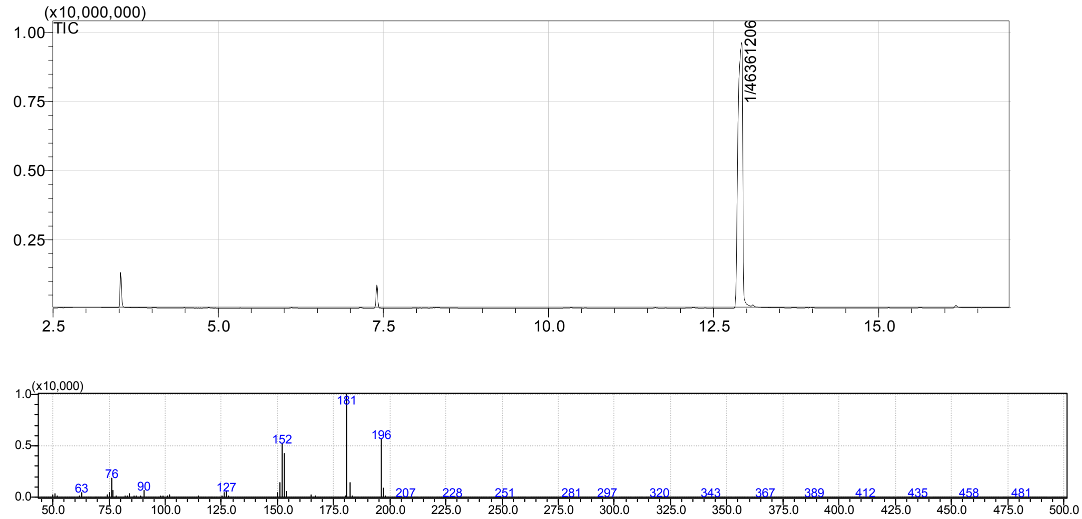


9. The results of GC (up) and MS (down) for 4-bromobenzaldehyde and phenylboronic acid

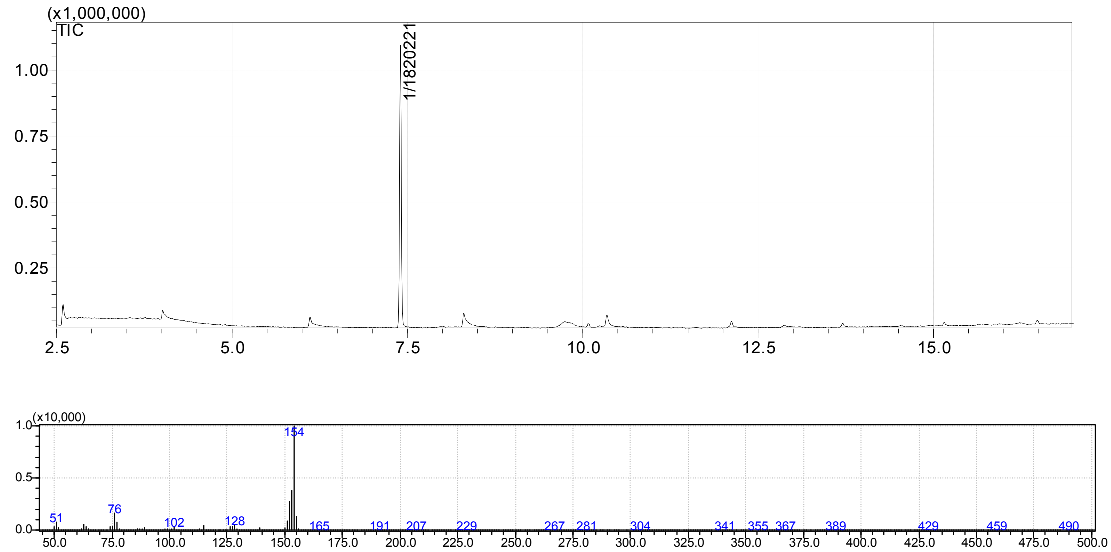




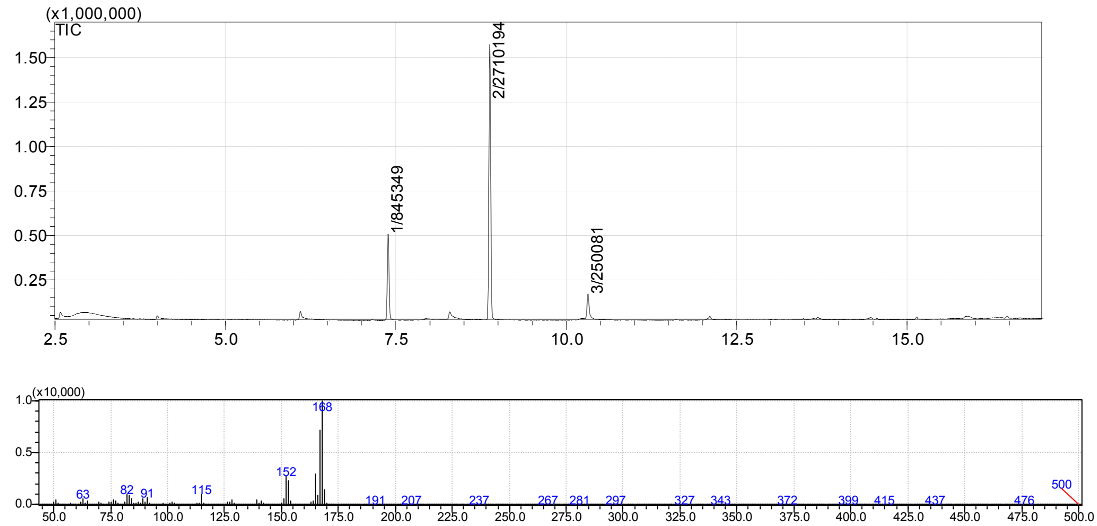
10. The results of GC (up) and MS (down) for 4-bromoacetophenone and phenylboronic acid



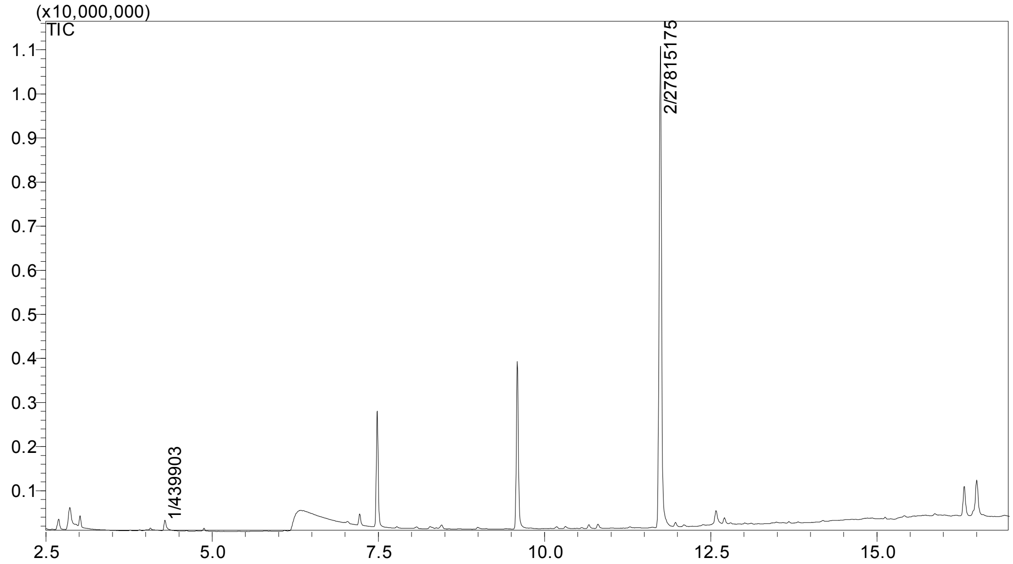
11. The results of GC (up) and MS (down) for chlorobenzene and phenylboronic acid



12. The results of GC (up) and MS (down) for 4-methylchlorobenzene and phenylboronic acid



13. The results of GC (up) and MS (down) for 4-chlorobenzaldehyde and phenylboronic acid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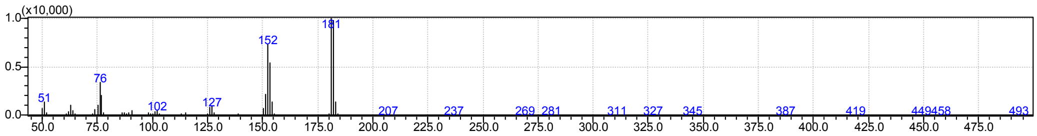
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