Supporting Information

Dual-Excitation Polyoxometalate-Based Frameworks for One-Pot Light-Driven Hydrogen Evolution and Oxidative Dehydrogenation

*Wenlong Sun[†], Bowen An[†], Bo Qi[†], Tao Liu[†], Meng Jin[†] and Chunying Duan[†,‡] **

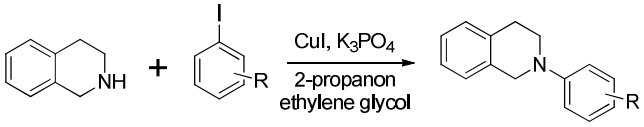
†Chemical School of Zhang Dayu State Key Laboratory of Fine Chemicals Dalian University of Technology Dalian 116024, China

‡Collaborative Innovation Center of Chemical Science and Engineering Tianjin 300071, China

Corresponding Authors

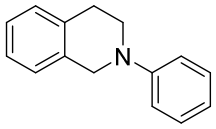
*E-mail: cyduan@dlut.edu.cn.

General procedure for the preparation of starting materials.

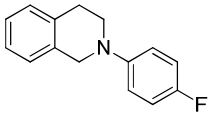


copper(I)iodide (87.4mg, 0.46mmol) and potassium phosphate (2.0g, 9.18mmol) were placed into a Schlenk-tube equipped with a magnetic stirrer. The tube was evacuated and back filled with argon. 2-Propanol (4.6mL), ethylene glycol (0.52mL, 9.18mmol), 1,2,3,4-tetrahydroisoquinoline (1.06mL, 6.88mmol) and 1-tert-Butyl-4-iodobenzene (0.81mL, 4.59mmol) were added successively by microsyringe at room temperature. The reaction mixture was heated at 85°C for 24h and then allowed to cool to room temperature. Diethyl ether (20mL) and water (5mL) were added to the reaction mixture and the organic layer was separated. The aqueous layer was further extracted by diethyl ether (2×5mL) and the combined organic phases were dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography.

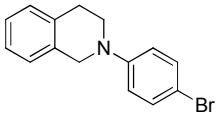
The ^{1}HNMR spectra data of the starting materials.



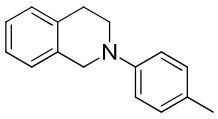
2-Ph-1,2,3,4-tetrahydroisoquinoline: ^{1}HNMR (400MHz, $CDCl_3$): δ 2.94 (t, *J* = 5.6Hz, 2H), 3.51 (t, *J* = 5.6Hz, 2H), 4.37 (s, 2H), 6.75-6.85 (m, 1H), 6.88-7.20 (m, 3H), 7.06-7.19 (m, 3H),7.22-7.32 (m, 2H).



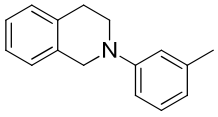
2-(4-F-Ph)-1,2,3,4-tetrahydroisoquinoline: ^{1}HNMR (400MHz, $CDCl_3$): δ 2.98 (t, *J* = 5.6Hz, 2H), 3.48 (t, *J* = 5.6 Hz, 2H), 4.33 (s, 2H), 6.85-7.03 (m, 4H), 7.11-7.23 (m, 4H).



2-(4-Br-Ph)-1,2,3,4-tetrahydroisoquinoline: ^{1}HNMR(400MHz, $CDCl_3$): δ 7.35-7.33 (d, *J* = 9.2 Hz, 2H), 7.24-7.14 (m, 4 H), 6.83-6.81 (d, *J* = 9.2 Hz, 2 H), 4.36 (s, 2 H), 3.53-3.50 (t, *J* = 5.6 Hz, 2 H), 2.98-2.95 (t, *J* = 6.0 Hz, 2 H).



2-(4-Me-Ph)-1,2,3,4-tetrahydroisoquinoline: ^{1}HNMR (400MHz, $CDCl_3$): δ 7.10-7.02 (m, 6 H), 6.84-6.81 (d, *J* = 8.8 Hz, 2 H), 4.25 (s, 2 H), 3.39-3.36 (t, *J* = 6 Hz, 2 H), 2.87-2.84 (t, *J* = 5.6 Hz, 2 H), 2.22 (s, 1 H).



2-(3-Me-Ph)-1,2,3,4-tetrahydroisoquinoline: ^{1}HNMR (500MHz, $CDCl_3$): *δ* 7.22-7.15 (m, 5H), 6.86-6.79 (m, 2H), 6.67-6.65 (m, 1H), 4.41 (s, 2H), 3.56 (t, *J* = 5.85 Hz, 2H), 3.0 (t, *J* = 5.85 Hz, 2H), 2.36 (s, 3H);

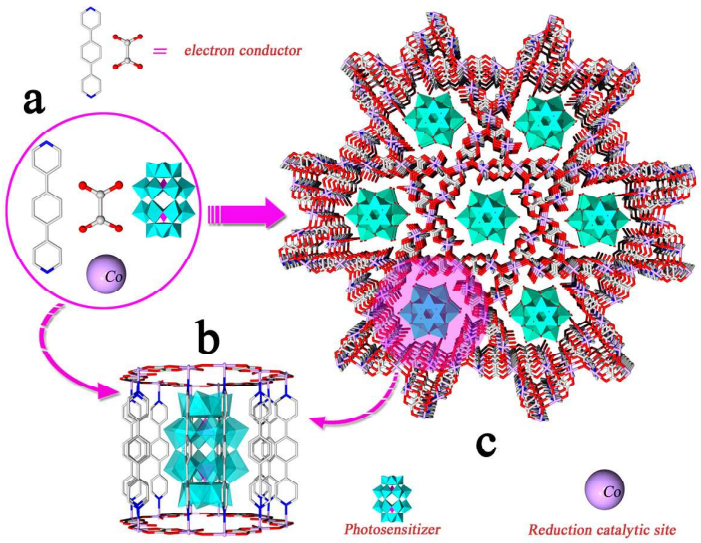


Figure S1. view of the assembly process showing constitute of the three dimensional structures (a) Show of $[P_2W_{18}O_{62}]^{6-}$, OX, Co^{II} and PBPY fragment. (b) A single of molecule cage construction. (c) Face view of the three-dimensional structure, showing the embedded $[P_2W_{18}O_{62}]^{6-}$ units within the pores along the different direction.

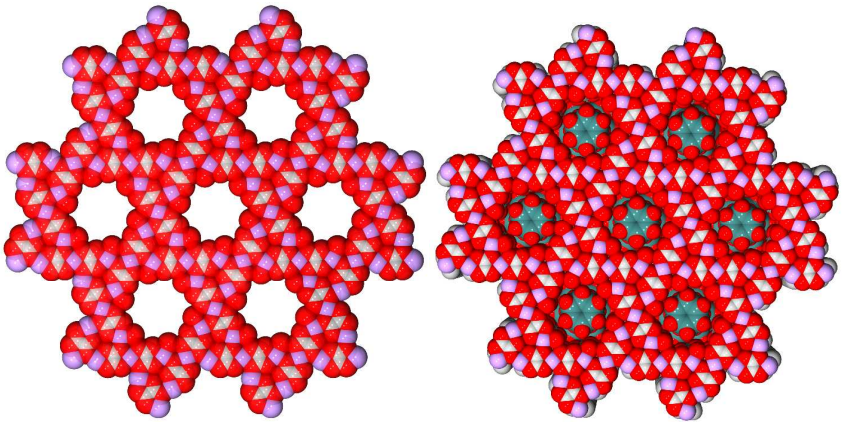


Figure S2. view of the two dimensional sheet constructed by $[P_2W_{18}O_{62}]^{6-}$, OX and cobalt ions.

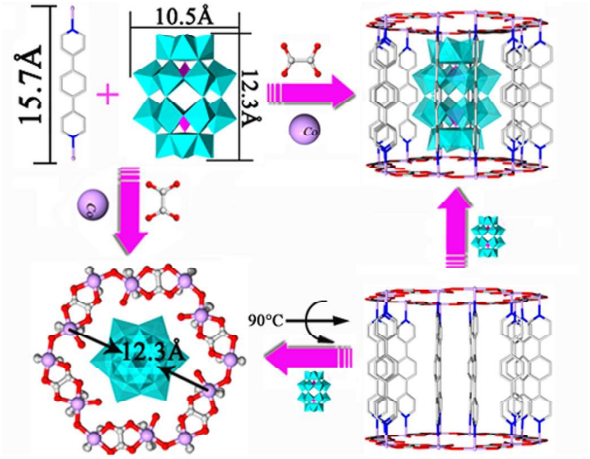


Figure S3. Perspective size of the assembly showing constitutes and structure matching.

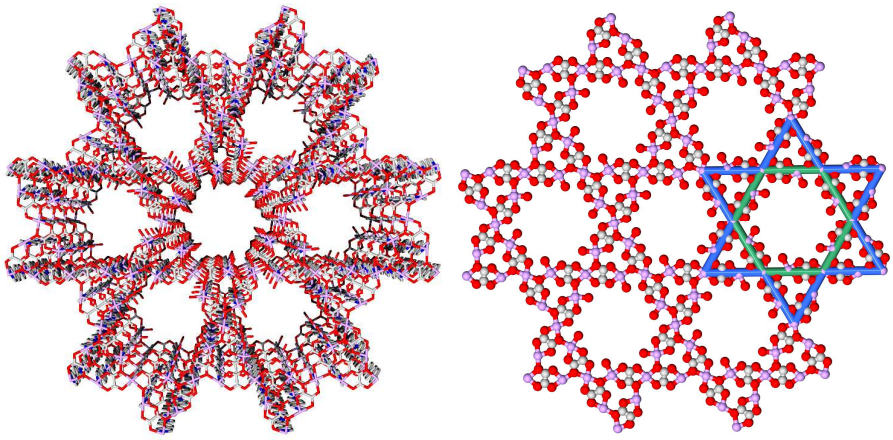


Figure S4. 3D metal organic framework (left picture). 2D metal organic layer with triangular and hexagonal structures (right picture).

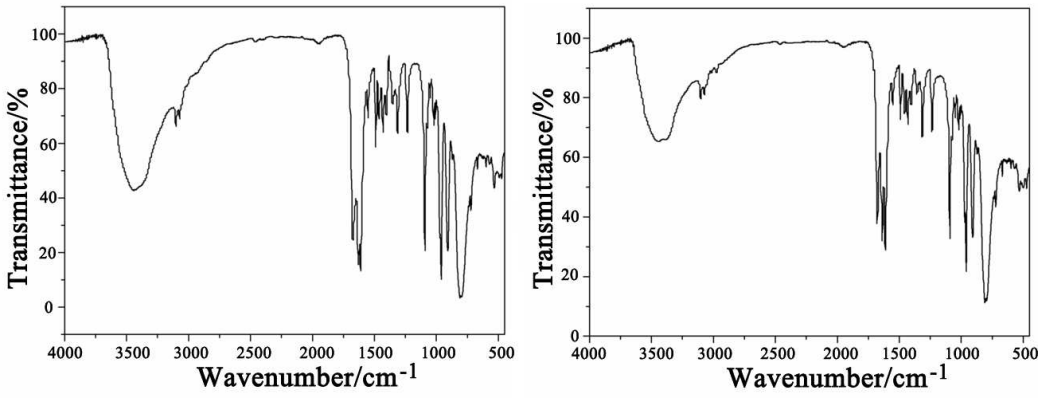


Figure S5. IR spectra of Co-POM (left picture) and Zn-POM (right picture).

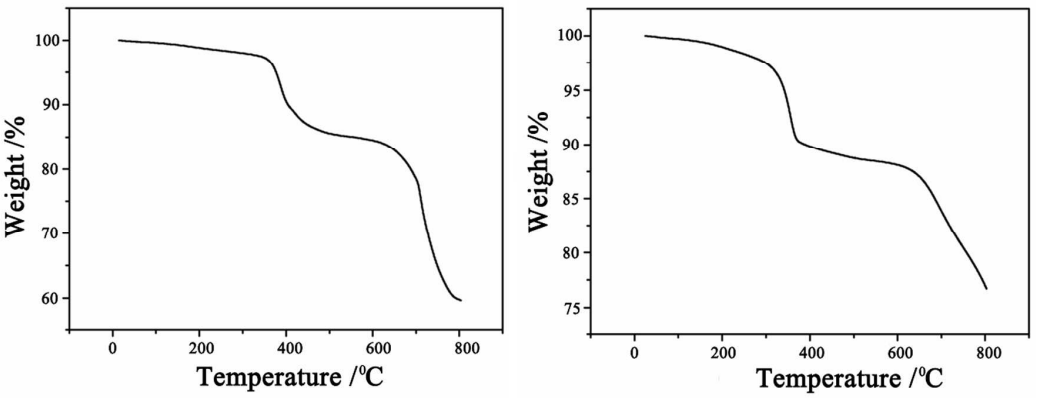


Figure S6. TG curves of Co-POM (left picture) and Zn-POM (right picture) in the flowing N_2 atmosphere, respectively.

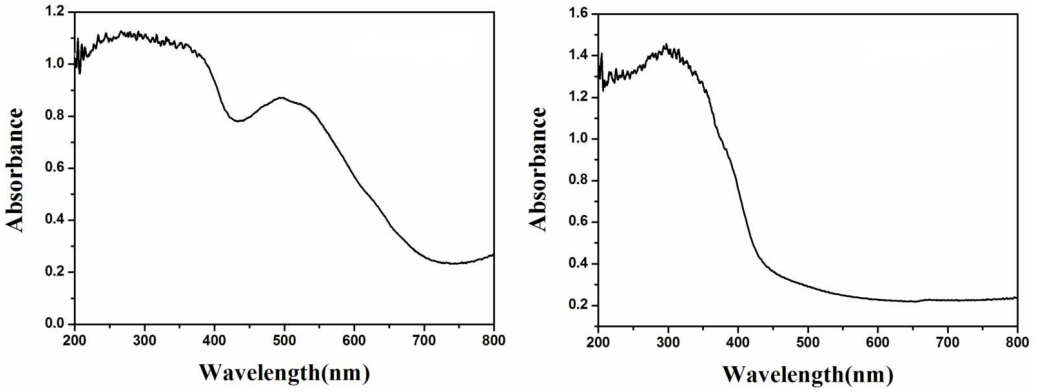


Figure S7. Solid state UV-Vis absorption spectra of Co-POM (left picture) and Zn-POM (right picture), respectively.

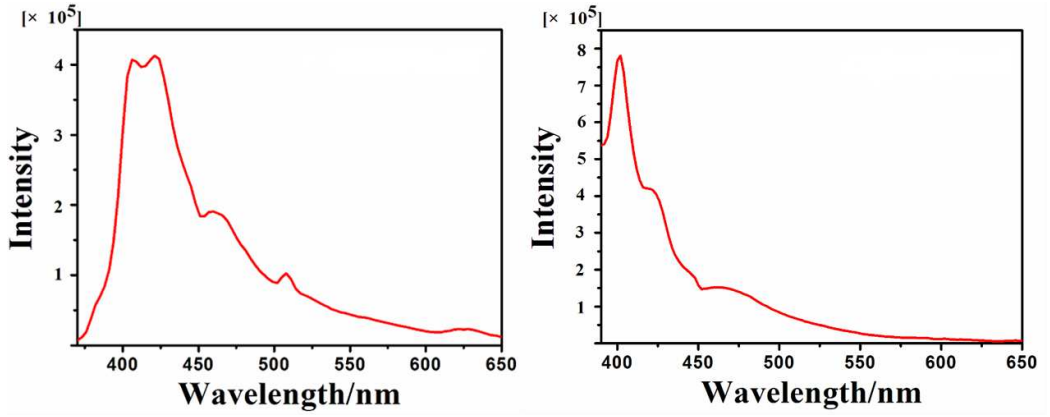


Figure S8. Solid state emission spectra of Co/Zn-POM in MeCN suspension solution.

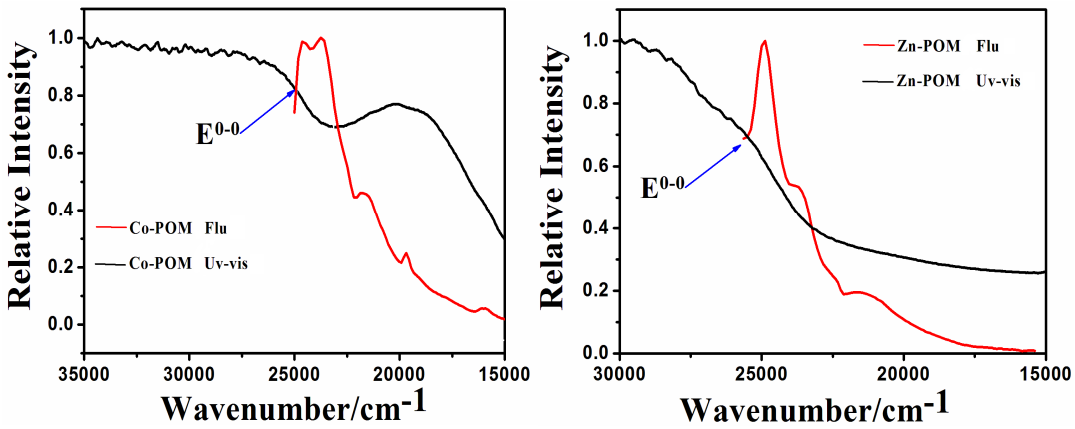


Figure S9. Normalized absorption (black line) and emission spectra (red line) of Co/Zn-POM, excited at 350 nm.

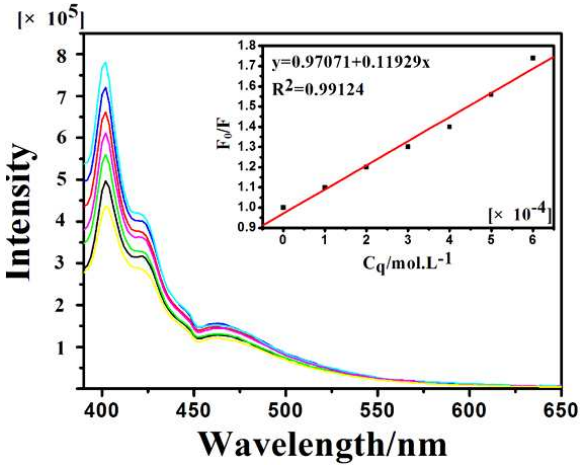


Figure S10. Fluorescence quenching spectra of Zn-POM upon the addition of N-phenyl-tetrahydroisoquinoline and the corresponding simulated stern-volmer curve.

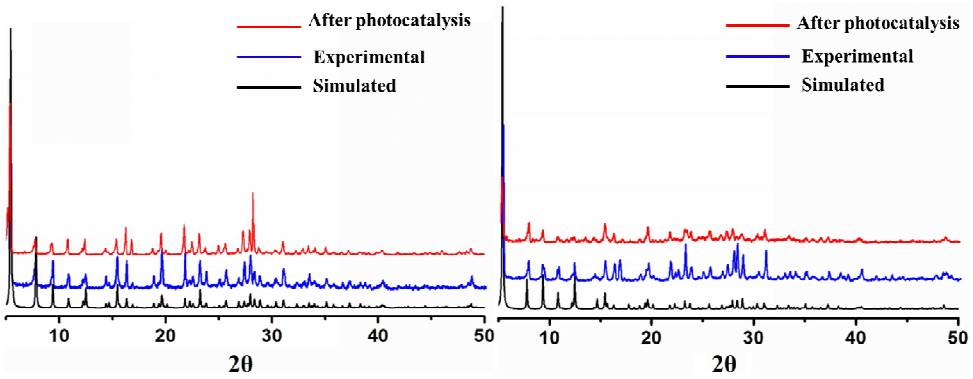


Figure S11. PXRD patterns of Co-POM (left picture) Zn-POM (right picture)**:** its calculated pattern based on the single-crystal simulation(black), the experimental synthesis (blue) and the catalyst after reactions (red).

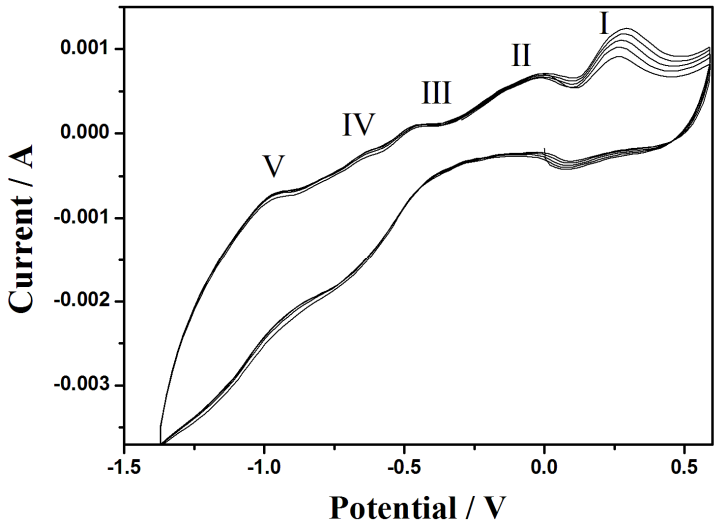
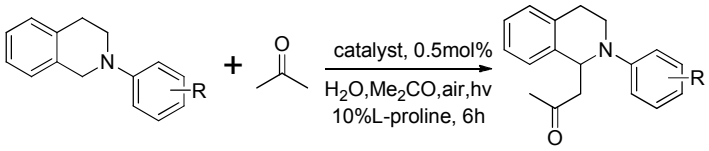


Figure S12. (a) Solid state cyclic voltammetry of Co-POM with a scan rate of 70 mV/s.

Table S1. Photocatalytic Oxidative Mannich Reaction[I]



entry	R	product	t (h)	% Con.
1[a]	4-H-	2a	6	99%
2[b]	4-H-	2a	6	40%
4[c]	4-H-	2a	6	no
5[d]	4-H-	2a	6	no
6[e]	4-H-	2a	6	no

[I]Reaction condition: catalyst (1.5umol, 15mg, 0.5mol%), L-proline (0.03mmol, 10mol%), in an H_2O/acetone solution (1:3), V=5.5mL. Determined by GC areas. 300W Xenon Lamp (λ=350-780nm). [a]after 3th recycle (λ=350-780nm) The catalyst Co-POM were collected by simple centrifugation after each cycle, dried in vacuo and then reused by mixing with fresh reaction solution. [b]no catalyst. [c]No light. [d]Ar atmosphere. [e]light λ=420-780nm.

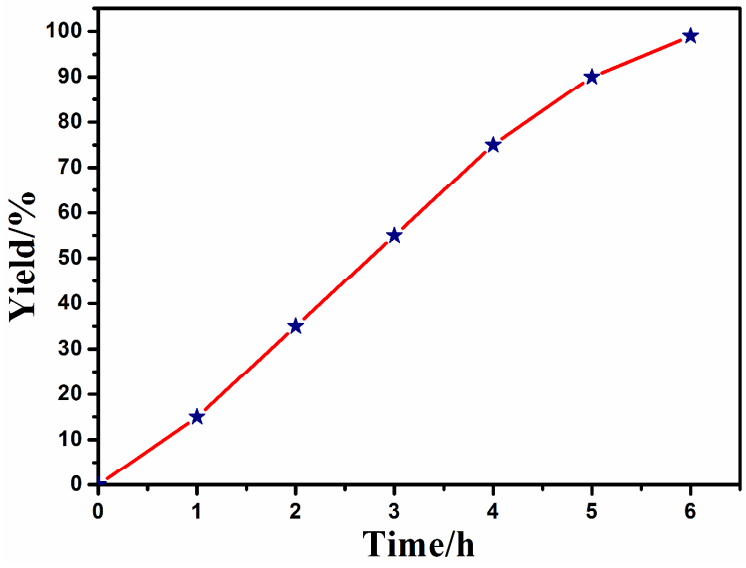
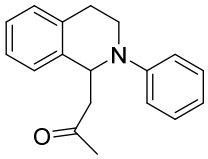
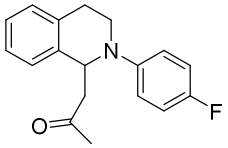


Figure S13. Time-dependence curve of Co-POM photocatalytic N-phenyl-tetrahydroisoquinoline.

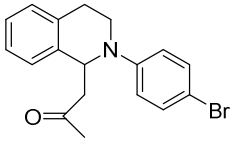
The ^{1}HNMR spectra data of the Mannich Reaction products.



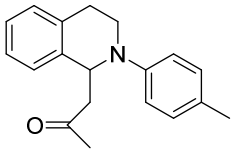
Isolated yield: 95% (Co-POM) and 94% (Zn-POM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.01 (m, 6H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 7.1 Hz, 1H), 5.32 (t, *J* = 6.3 Hz, 1H), 3.62 – 3.52 (m, 1H), 3.50 – 3.36 (m, 1H), 3.03 – 2.92 (m, 2H), 2.76-2.71 (m, 2H), 1.98 (s, 3H).



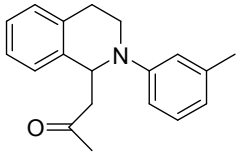
Isolated yield: 93% (Co-POM) and 91% (Zn-POM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.08 (m, 4H), 6.99 – 6.83 (m, 4H), 5.29 (t, *J* = 6.4 Hz, 1H), 3.64 – 3.43 (m, 2H), 3.05-2.99 (m, 2H), 2.85 – 2.72 (m, 2H), 2.08 (s, 3H).



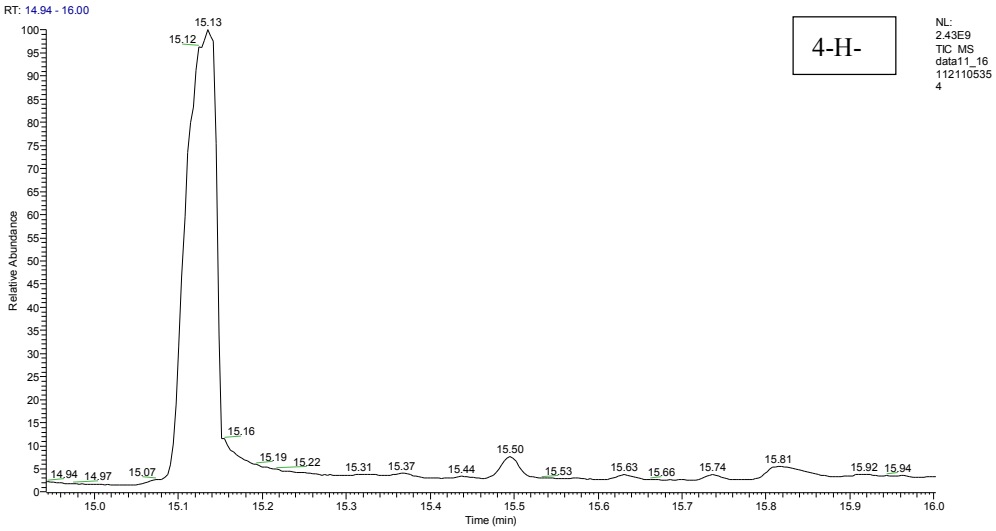
Isolated yield: 91% (Co-POM) and 90% (Zn-POM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.22 – 7.08 (m, 4H), 6.82 (d, *J* = 8.9 Hz, 2H), 5.34 (t, *J* = 6.3 Hz, 1H), 3.62-3.49 (m, 2H), 3.12 – 2.92 (m, 2H), 2.86-2.81 (m, 2H), 2.08 (s, 3H).

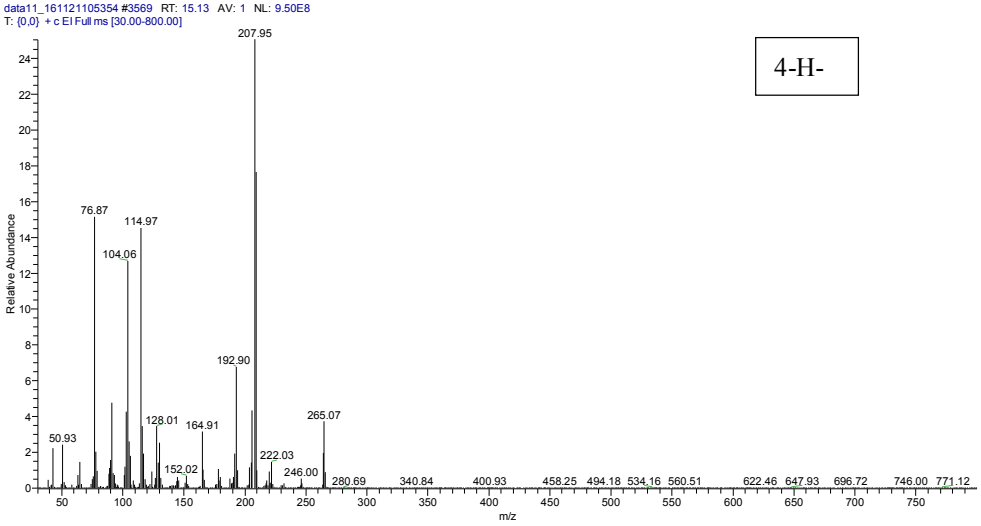


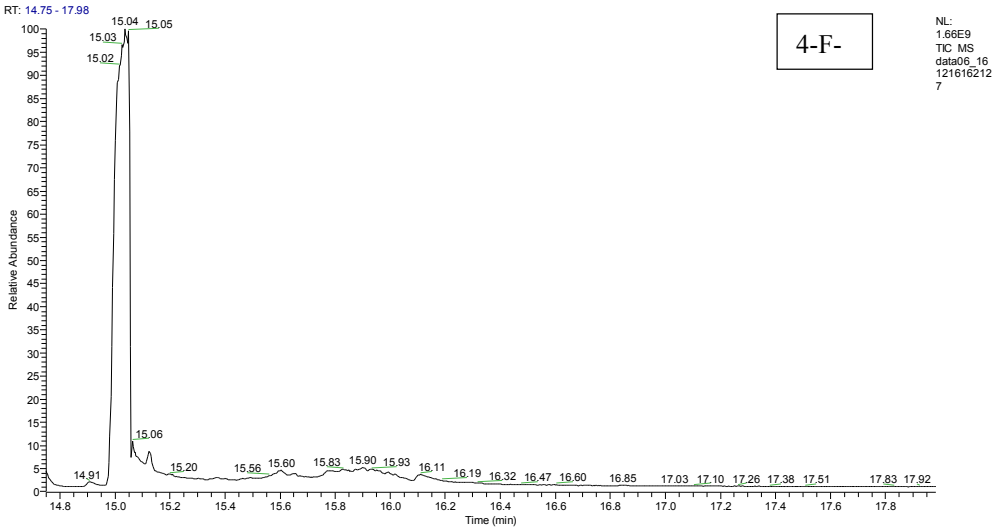
Isolated yield: 93% (Co-POM) and 92% (Zn-POM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.06 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.33 (t, *J* = 6.3 Hz, 1H), 3.66 – 3.52 (m, 1H), 3.53 – 3.40 (m, 1H), 3.11 – 2.93 (m, 2H), 2.82 – 2.69 (m, 2H), 2.23 (s, 3H), 2.04 (s, 3H).

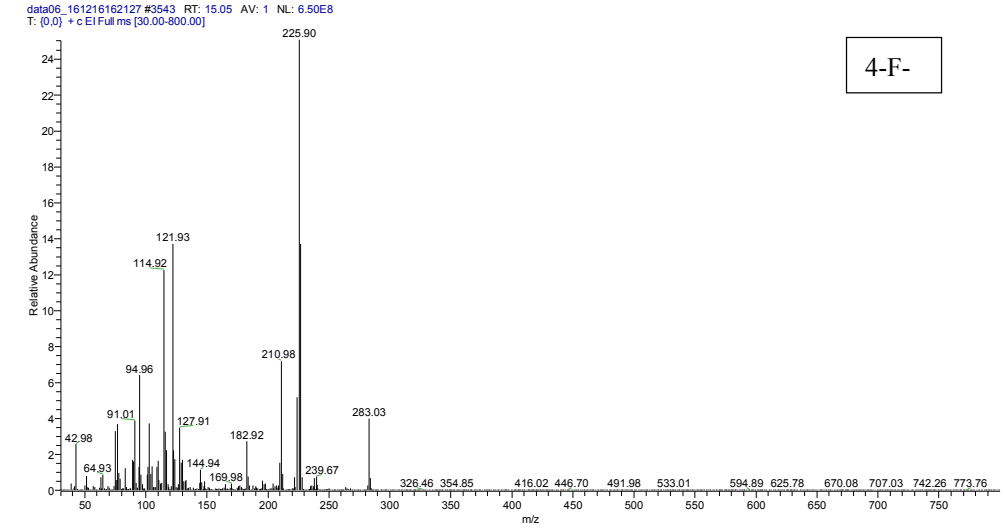


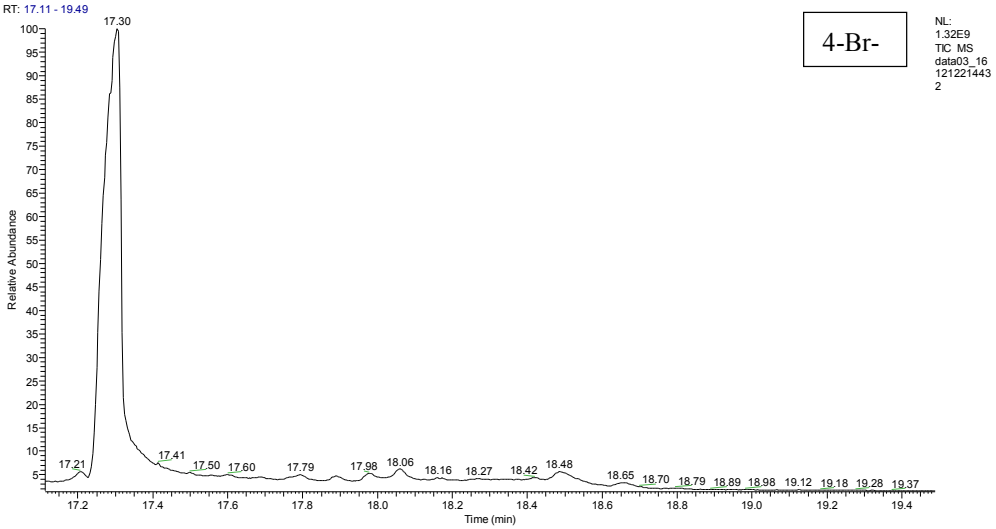
solated yield: 92% (Co-POM) and 90% (Zn-POM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 5H), 6.74 (d, *J* = 9.4 Hz, 2H), 6.60 (d, *J* = 7.3 Hz, 1H), 5.38 (t, *J* = 6.2 Hz, 1H), 3.72 – 3.58 (m, 1H), 3.55-3.48 (m, , 1H), 3.12 – 2.96 (m, 2H), 2.83-2.78 (m, 2H), 2.30 (s, 3H), 2.06 (s, 3H).

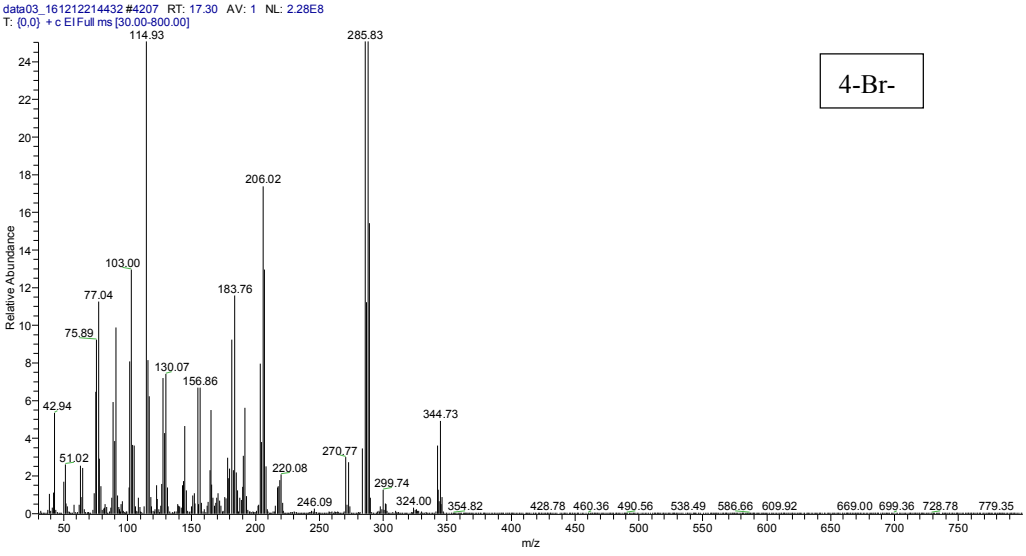

RT: 14.94 - 16.00
4-H-
NL:
2.43E9
TIC MS
data11_16
112110535
4
Relative Abundance
Time (min)

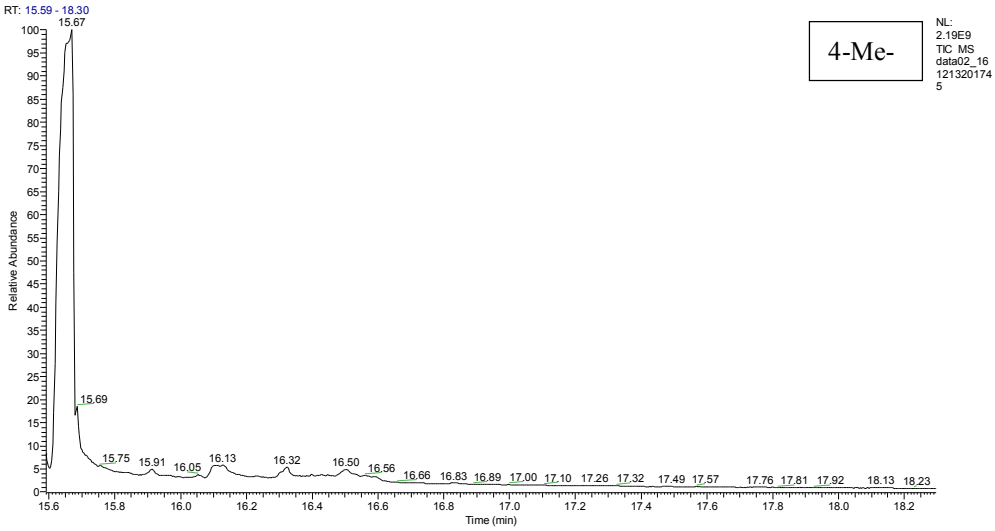

data11_161121105354 #3569 RT: 15.13 AV: 1 NL: 9.50E8
T: {0,0} + c EI Full ms [30.00-800.00]
4-H-
Relative Abundance
m/z

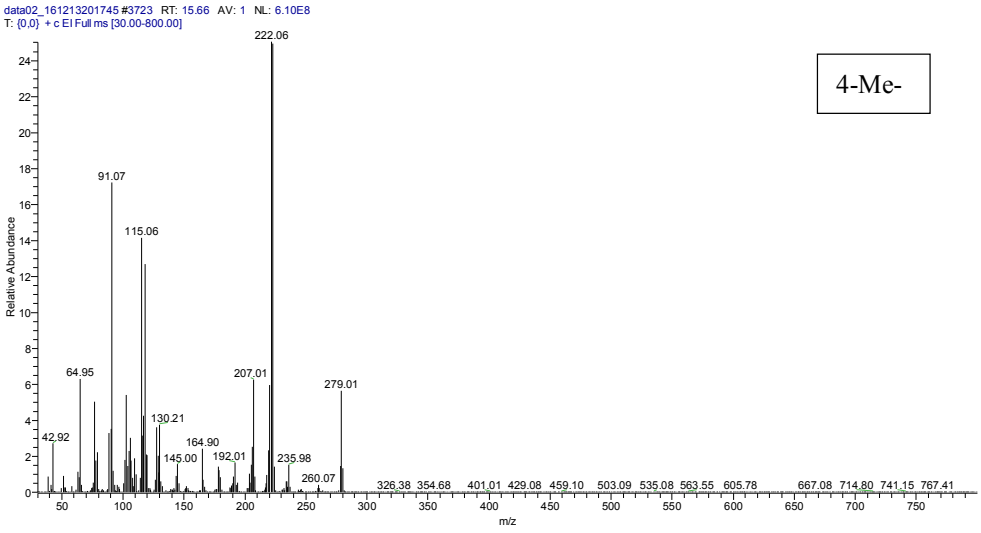

RT: 14.75 - 17.98
4-F-
NL:
1.66E9
TIC MS
data06_16
121616212
7
Relative Abundance
Time (min)

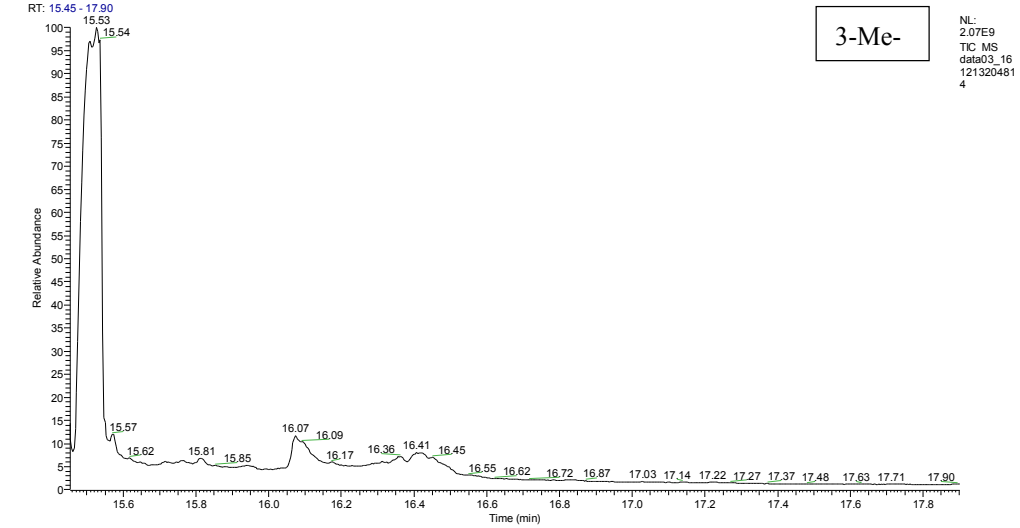

data06_161216162127 #3543 RT: 15.05 AV: 1 NL: 6.50E8
T: {0,0} + c EI Full ms [30.00-800.00]
4-F-
Relative Abundance
m/z


RT: 17.11 - 19.49
4-Br-
NL:
1.32E9
TIC MS
data03_16
121221443
2
Relative Abundance
Time (min)


data03_161212214432 #4207 RT: 17.30 AV: 1 NL: 2.28E8
T: {0,0} + c EI Full ms [30.00-800.00]
4-Br-
Relative Abundance
m/z


RT: 15.59 - 18.30
4-Me-
NL:
2.19E9
TIC MS
data02_16
121320174
5
Relative Abundance
Time (min)


data02_161213201745 #3723 RT: 15.66 AV: 1 NL: 6.10E8
T: {0,0} + c EI Full ms [30.00-800.00]
4-Me-
Relative Abundance
m/z


RT: 15.45 - 17.90
3-Me-
NL:
2.07E9
TIC MS
data03_16
121320481
4
Relative Abundance
Time (min)

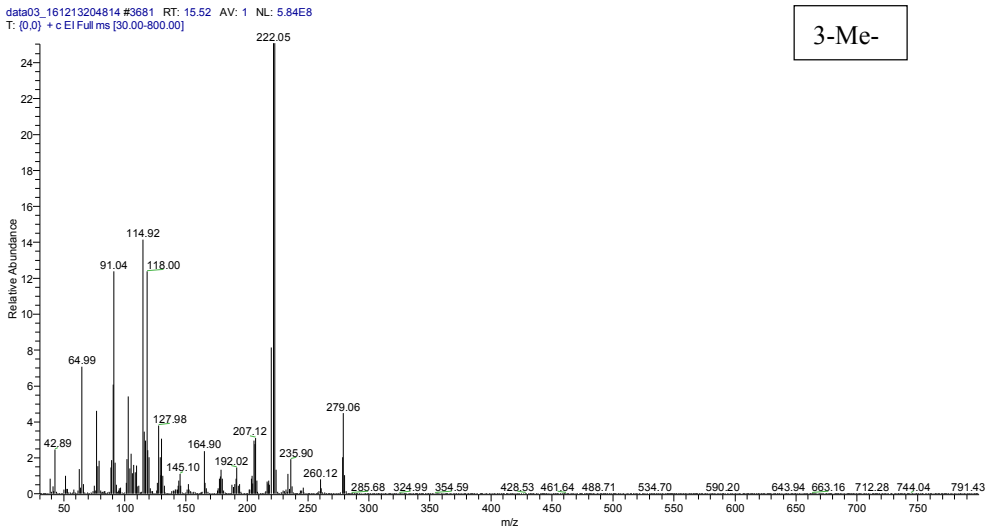
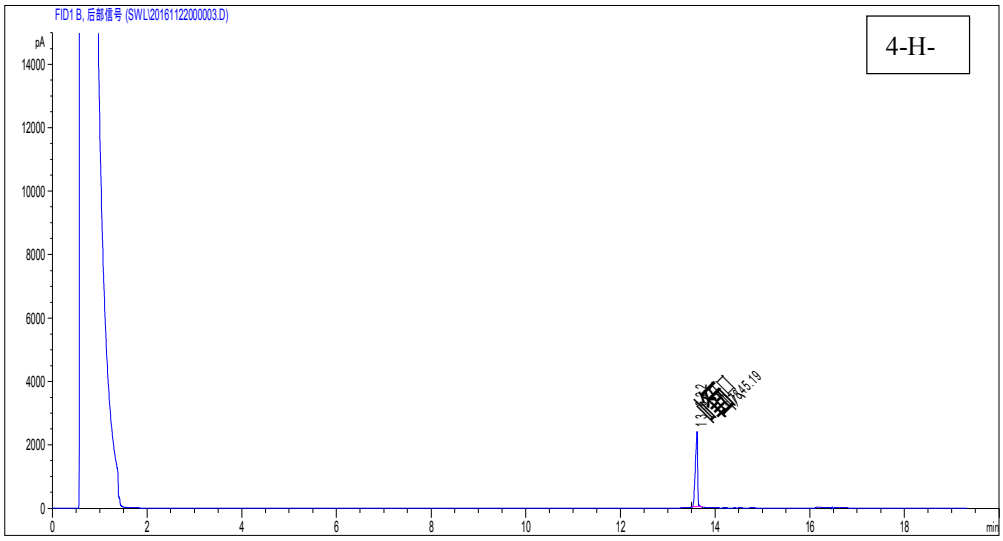
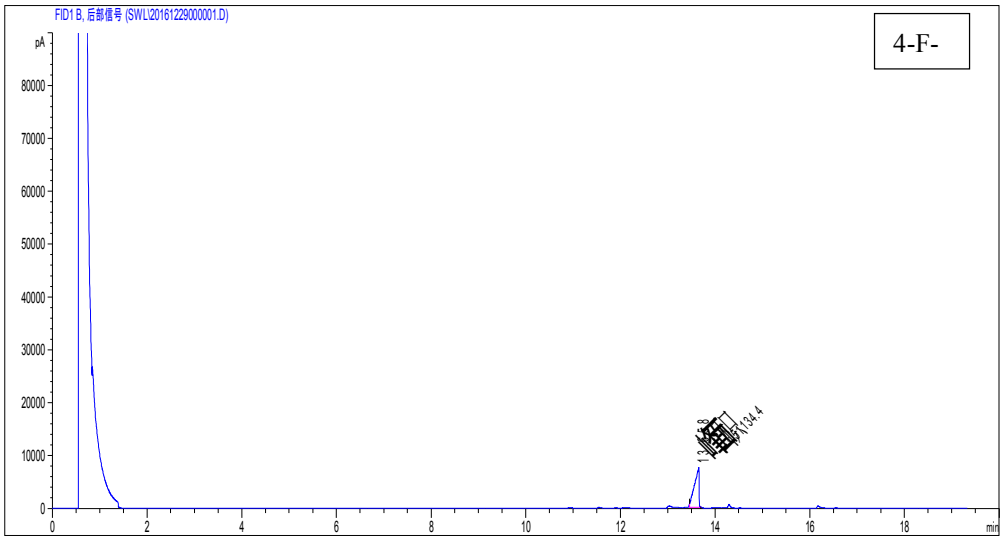
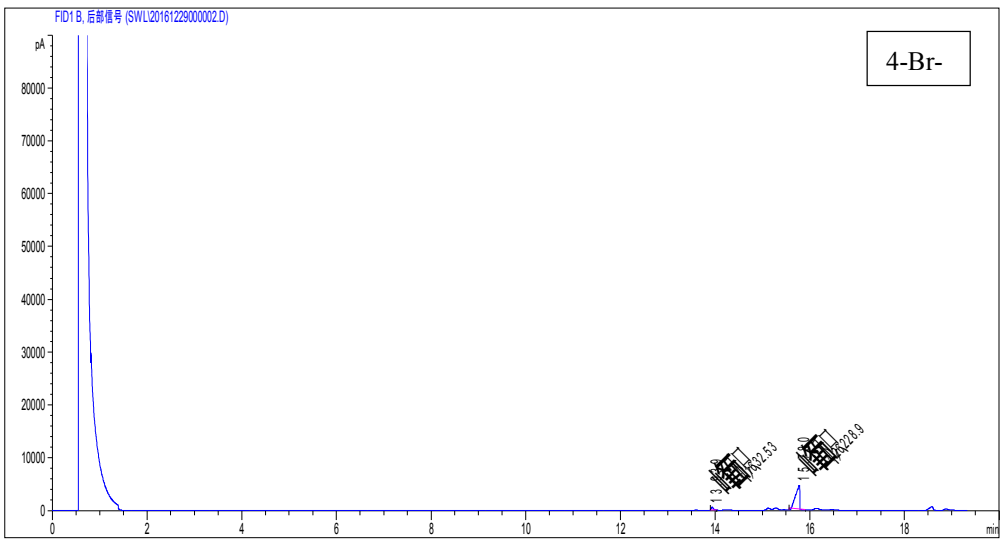


Figure S14. GC-MS spectrum of the mannich reaction mixture after photocatalysis.


FID1 B, 后部信号 (SWL\20161122000003.D)
pA
14000
12000
10000
8000
6000
4000
2000
0
0
2
4
6
8
10
12
14
16
18
min
4-H-


FID1 B, 后部信号 (SWL\20161229000001.D)
pA
80000
70000
60000
50000
40000
30000
20000
10000
0
0
2
4
6
8
10
12
14
16
18
min
4-F-


FID1 B, 后部信号 (SWL\20161229000002.D)
pA
80000
70000
60000
50000
40000
30000
20000
10000
0
0
2
4
6
8
10
12
14
16
18
min
4-Br-

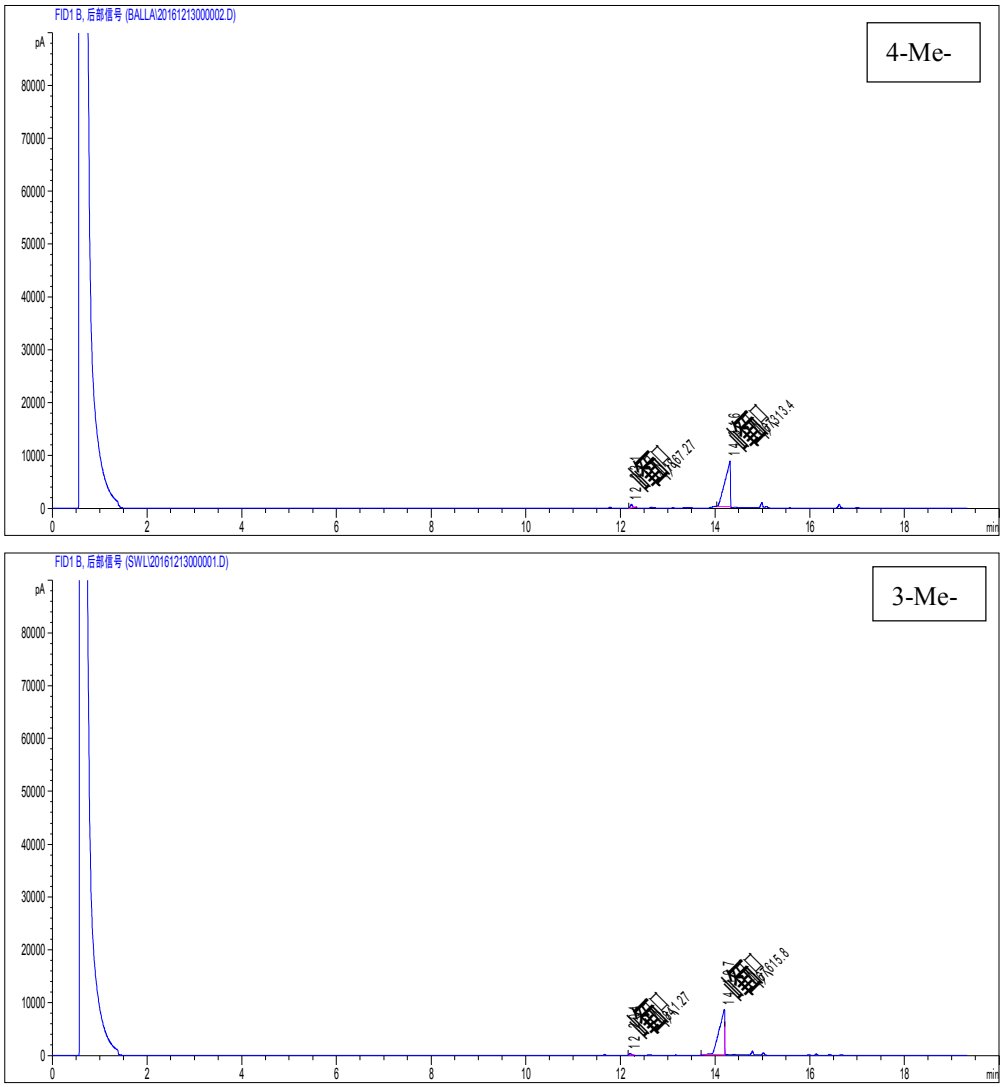
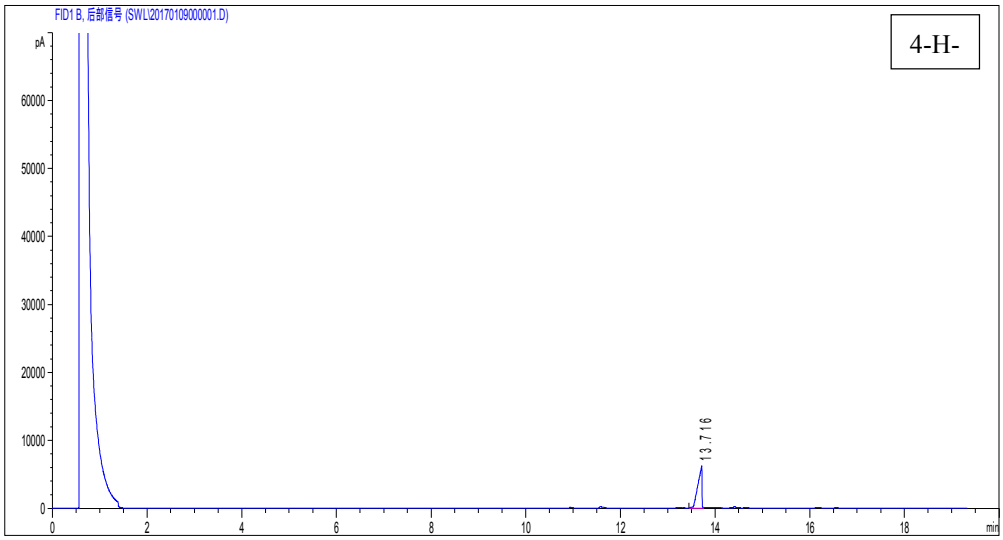
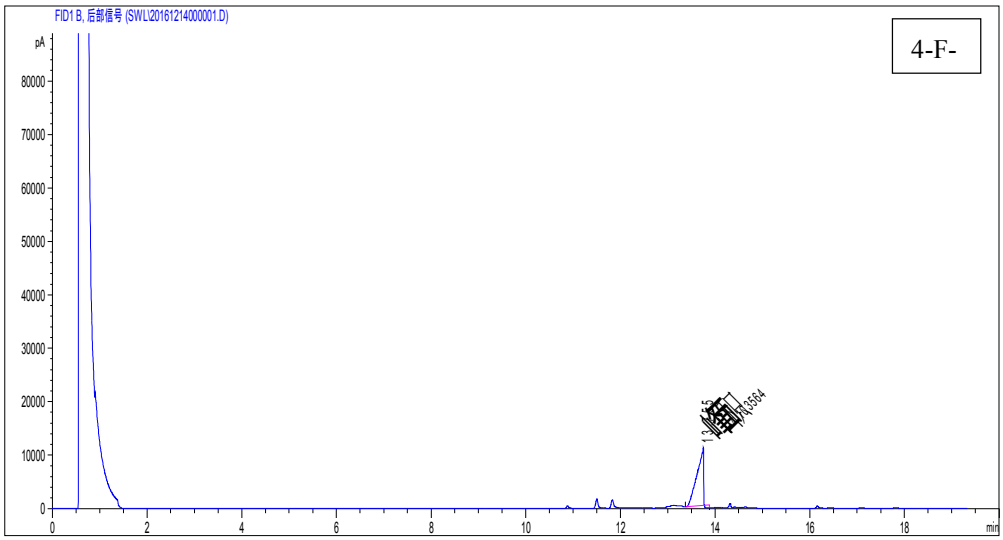
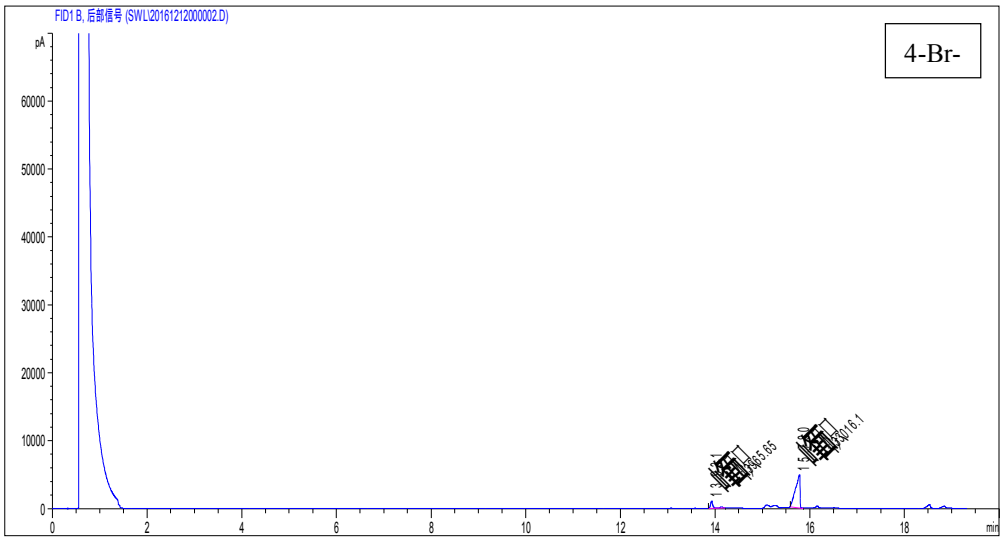


Figure S15. GC spectrum of the reaction mixture after photocatalysis (Co-POM in Table 1).


FID1 B, 后部信号 (SWL\20170109000001.D)
4-H-
pA
60000
50000
40000
30000
20000
10000
0
13.716
0
2
4
6
8
10
12
14
16
18
min


FID1 B, 后部信号 (SWL\20161214000001.D)
4-F-
pA
80000
70000
60000
50000
40000
30000
20000
10000
0
13.564
0
2
4
6
8
10
12
14
16
18
min


FID1 B, 后部信号 (SWL\20161212000002.D)
4-Br-
pA
60000
50000
40000
30000
20000
10000
0
13.665
15.916.1
0
2
4
6
8
10
12
14
16
18
min

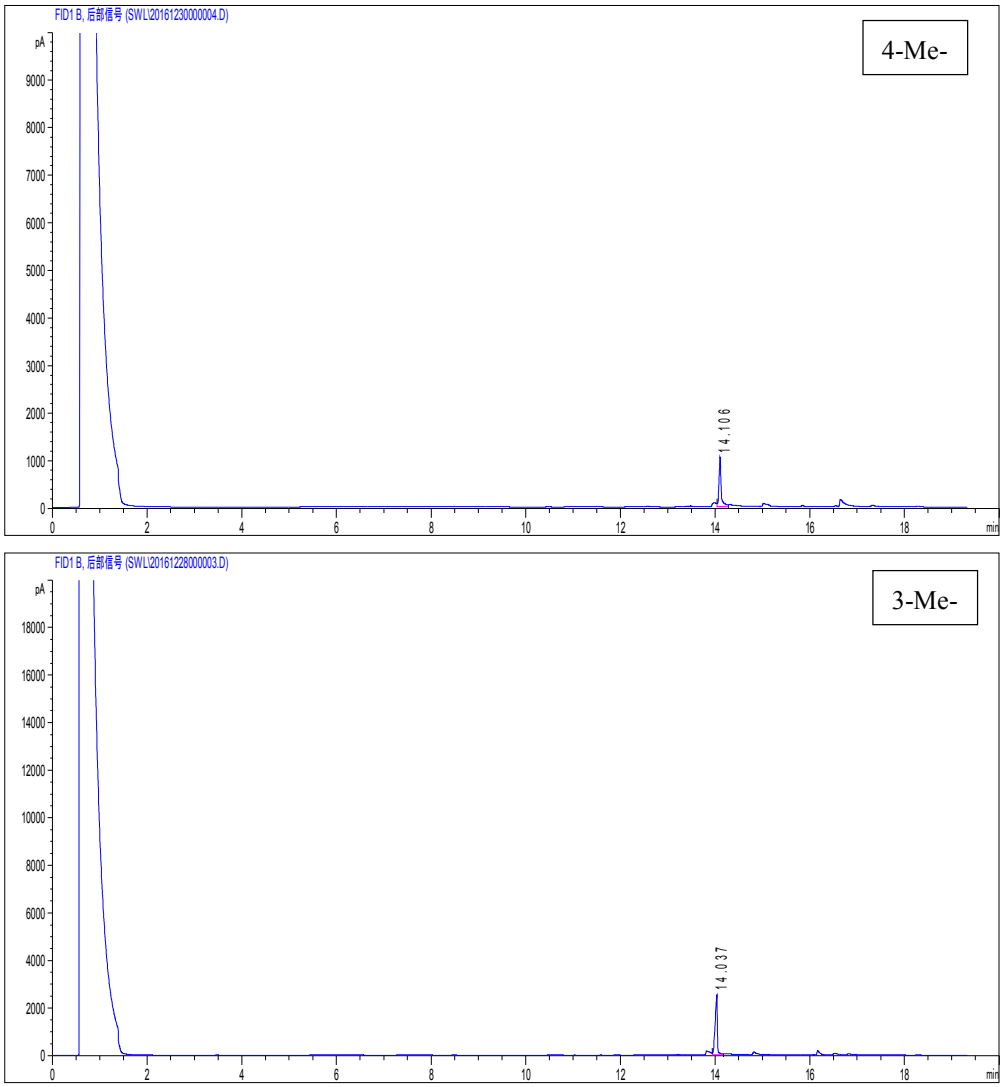


Figure S16. GC spectrum of the reaction mixture after photocatalysis (Zn-POM in Table 1).

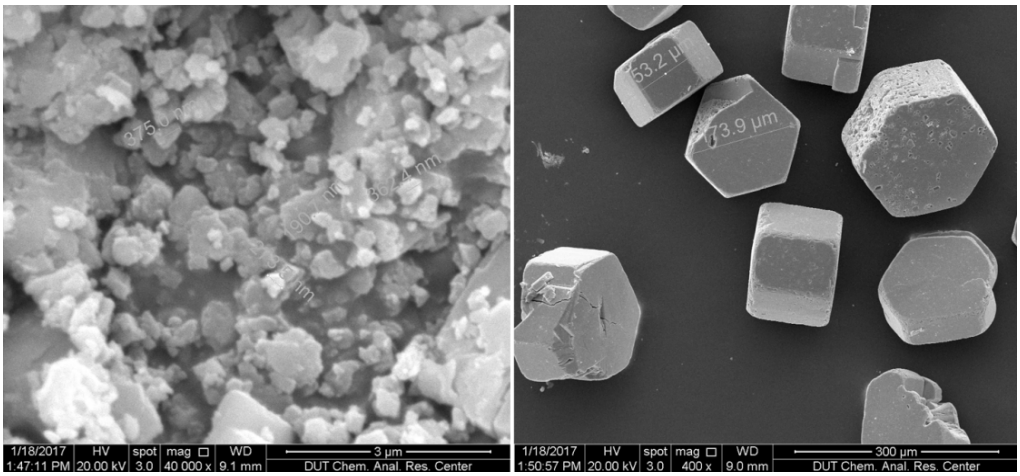


Figure S17. SEM image of the initial Co-POM crystals with size of 0.19~0.37μm, with which the catalytic yield is 98% in six hour (left); right is the well-grounded Co-POM crystals whose size is 0.15-0.17mm, with that the catalytic yield is 72% in six hour. These results demonstrated the surface area is the crucial factor for high yield.

Table S2. Photoreductive Hydrogen Production.[a]

catalytic	catalytic	Light (λ/nm)	electron donor	Time	TON
Co-POM	0.3umol	350-780	TEA	21h	700
Co-POM	0.3umol	420-780	TEA	21h	no
Co-POM	0.3umol	350-400	TEA	21h	trace
Co-POM[b]	0.3umol	Hg-lamp	TEA	21h	450
Co-POM	0.3umol	no	TEA	21h	no
Co-POM	0.3umol	350-780	no	21h	no
Co-POM	0.3umol	350-780	TPA	21h	400
Zn-POM	0.3umol	350-780	TEA	21h	trace
$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$	0.3umol	350-780	TEA	21h	trace
no catalyst	0umol	350-780	TEA	21h	no
$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$, $Co(NO_3)_2$	0.3umol	350-780	TEA	21h	150
Co-POM (1st run)	0.3umol	350-780	TEA	10h	275
Co-POM (2nd run)	0.3umol	350-780	TEA	10h	270
Co-POM (3rd run)	0.3umol	350-780	TEA	10h	270

[a]reaction condition: the solution total volume of 5.5mL, and triethylamine/tripropylamine (TEA/TPA) (9% v:v) in a H_2O/Me_2CO (1:3 in volume) solution at 25°C resulted in the light irradiation. [b]300W Hg lamp. The catalyst Co-POM were recycled utilization by removing acetone and TEA solvent, and add the fresh acetone and TEA after each cycle for avoiding catalyst loss.

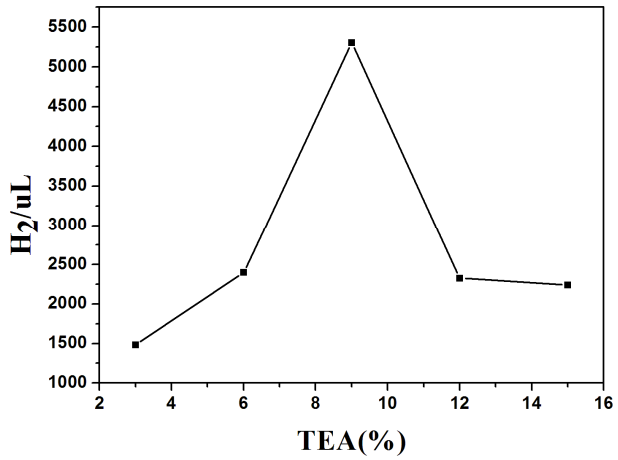


Figure S18. Photocatalytic H_2 evolution in 3:1 Me_2CO/H_2O of the systems containing Co-POM (0.3μM) and at the various TEA concentration.

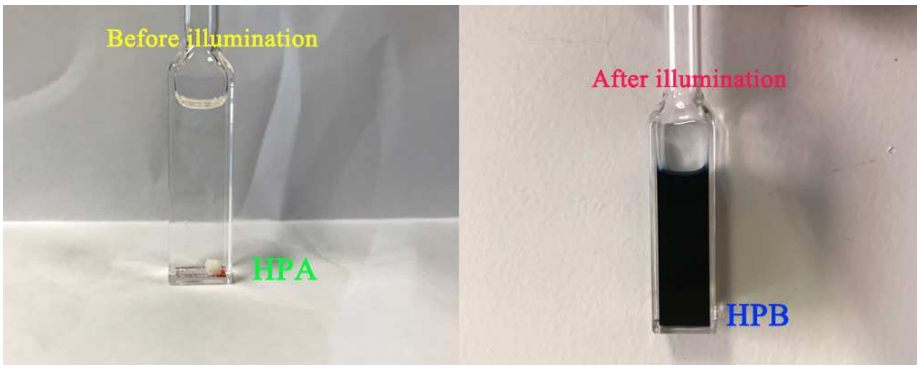


Figure S19. Optical image: heteropolyacid (HPA) of Co-POM solution before irradiation (left picture), heteropoly blue (HPB) of Co-POM solution after irradiation (right picture).

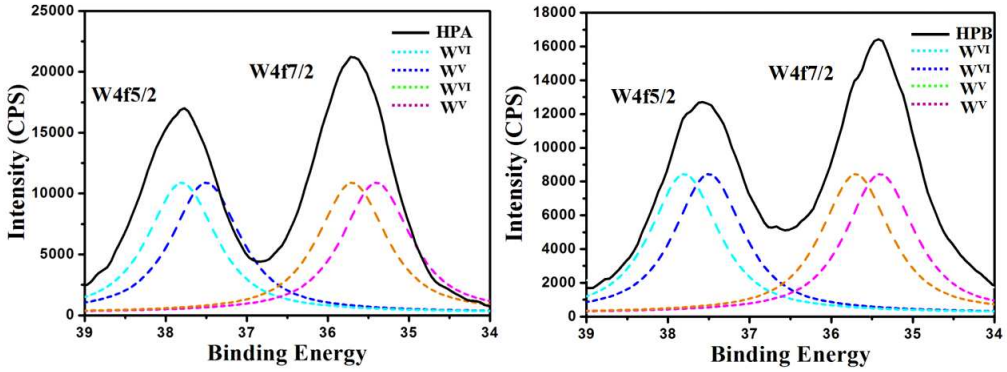


Figure S20. XP spectra of W4f in HPA before photoirradiation (left picture) and HPB after photoirradiation (right picture).

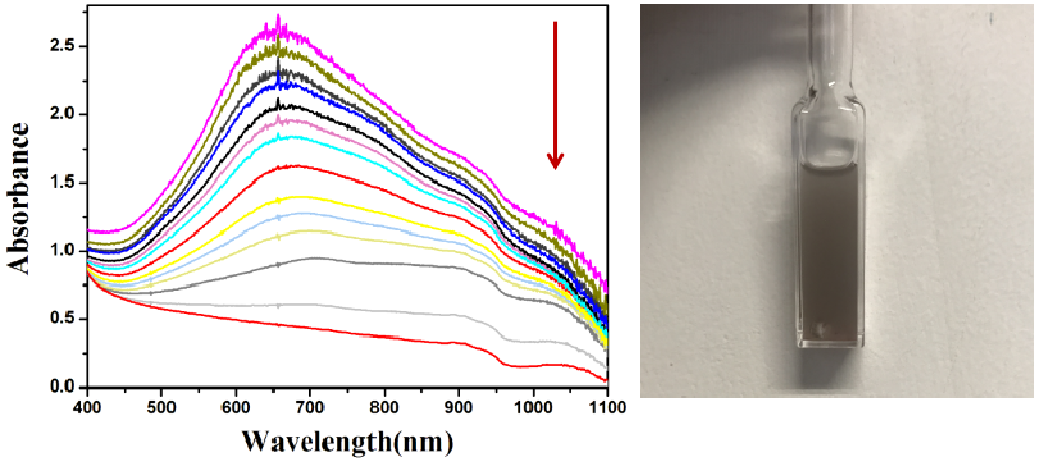


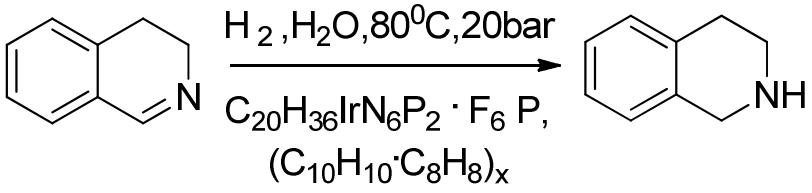
Figure S21. Absorb curve of HPB under O_2 atmosphere time. O_2 time: 0-30min (left picture); Optical image: HPB turn to HPA of Co-POM solution after expose O_2 (right picture).

Table S3. Photocatalytic Oxidation and Reduction Coupling.[a]

catalytic	catalytic	Light (λ/nm)	Time	TON (H_2)
Co-POM	0.1umol	350-780	68h	90
Co-POM (2nd run)	0.1umol	350-780	68h	90
Co-POM (3rd run)	0.1umol	350-780	68h	85
Zn-POM	0.1umol	350-780	68h	trace
Zn-POM[b]	0.1umol	350-780	68h	trace
Co/Zn-POM[c]	0.1umol	350-780	68h	trace

[a]reaction condition: tetrahydroisoquinoline (1mmol) in a Me_2CO (5.5mL) solution. [b]reaction condition: tetrahydroisoquinoline (1mmol) in a H_2O/Me_2CO (1:3 in volume, 5.5mL) solution. [c]3,4-Dihydroiso-quinoline (1mmol) in a Me_2CO (5.5mL) or a H_2O/Me_2CO (1:3 in volume, 5.5mL) solution at 25°C. The catalyst Co-POM were recycled utilization by centrifugation dried in vacuum, and add the fresh solution after each cycle. Determined by GC areas, 300W xenon lamp (λ=350-780nm).

Scheme S1. Hydrogenation of 3,4-Dihydroisoquinoline and isoquinoline.[S1]



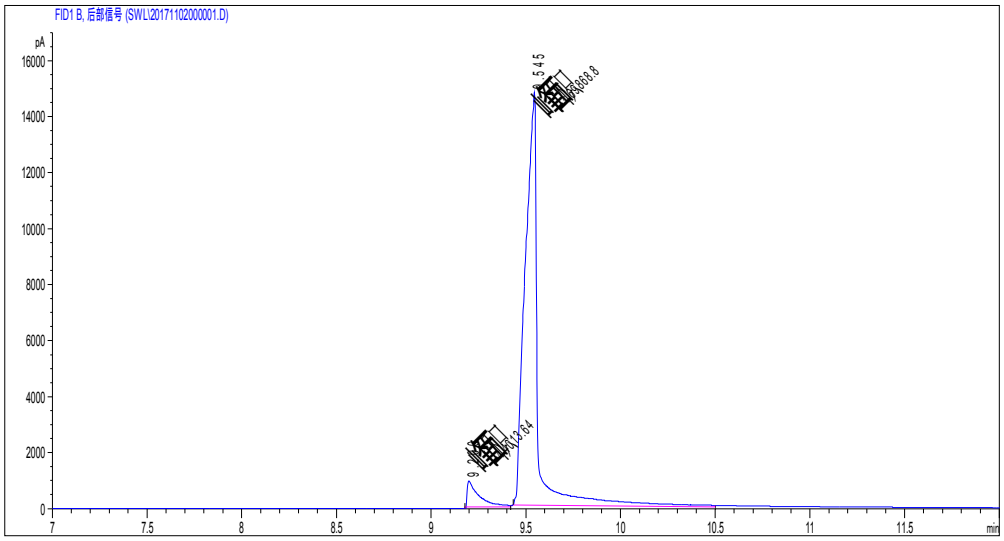
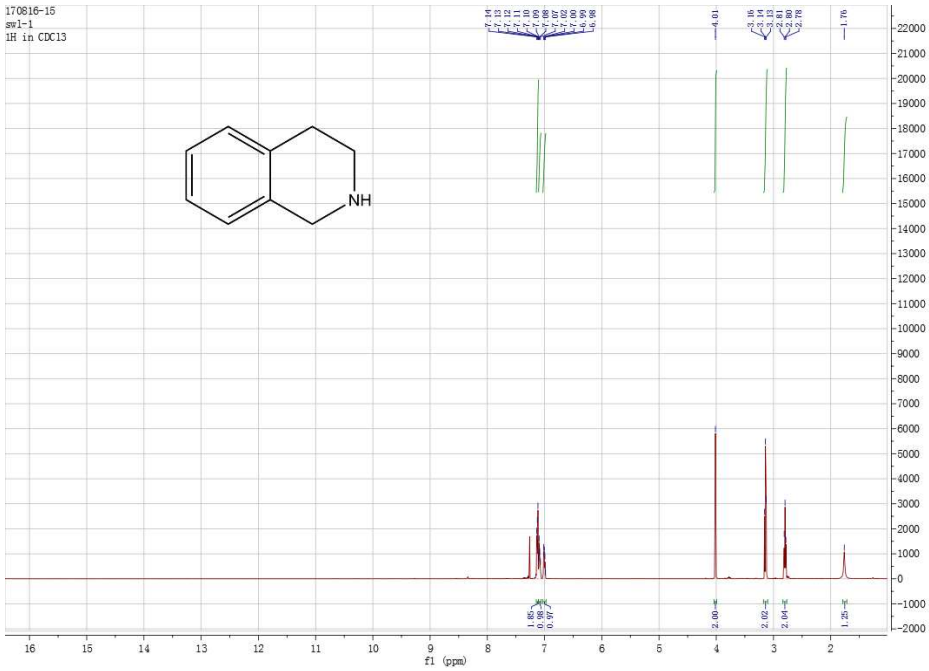
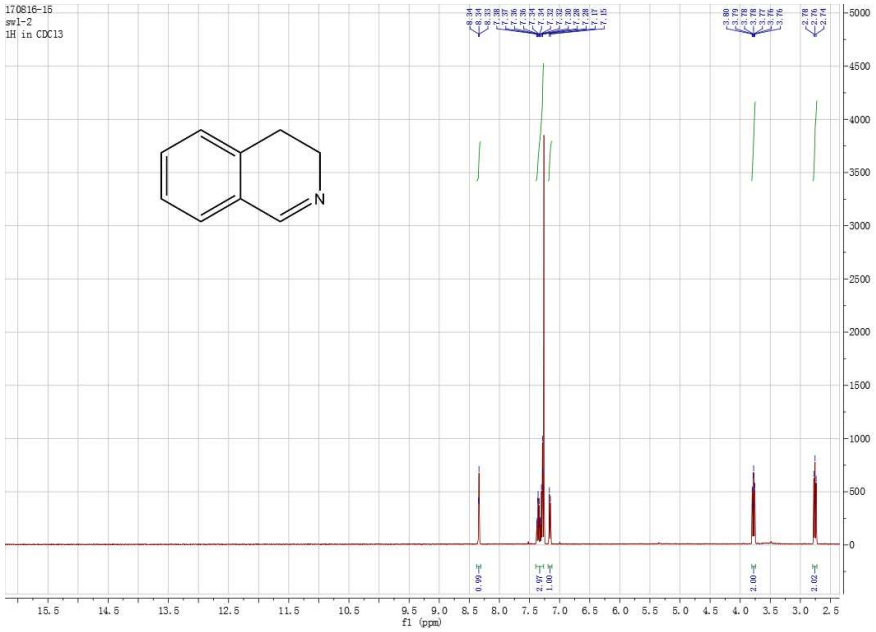


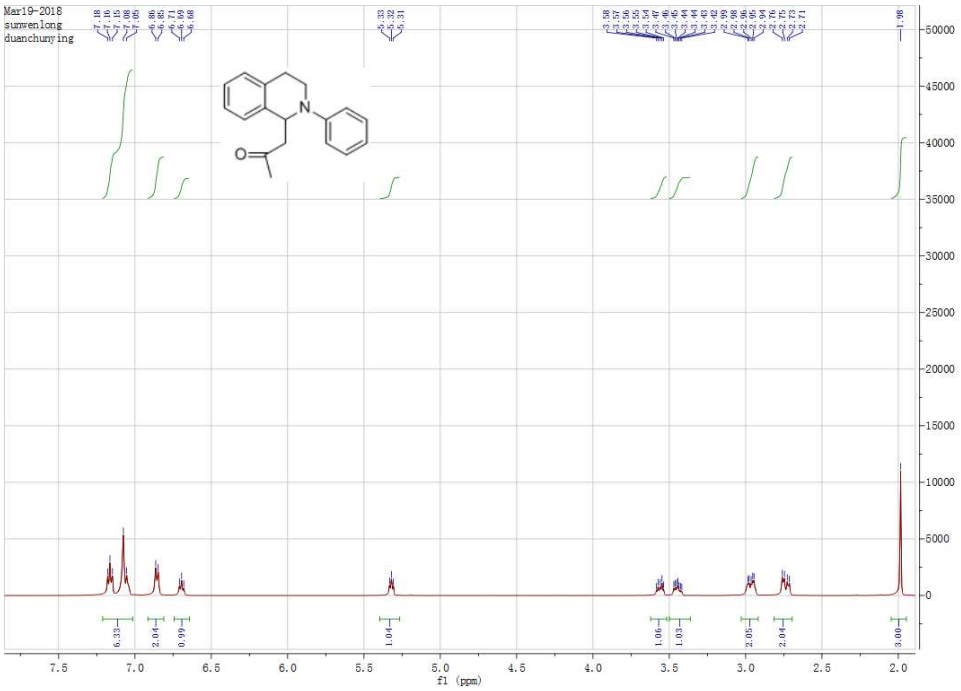
Figure S22. GC spectrum of the reaction mixture after photocatalytic Co-POM (0.1 μmol) and tetrahydroisoquinoline (3 mmol) in H_2O/Me_2CO (1:3 by volume 5.5ml) .

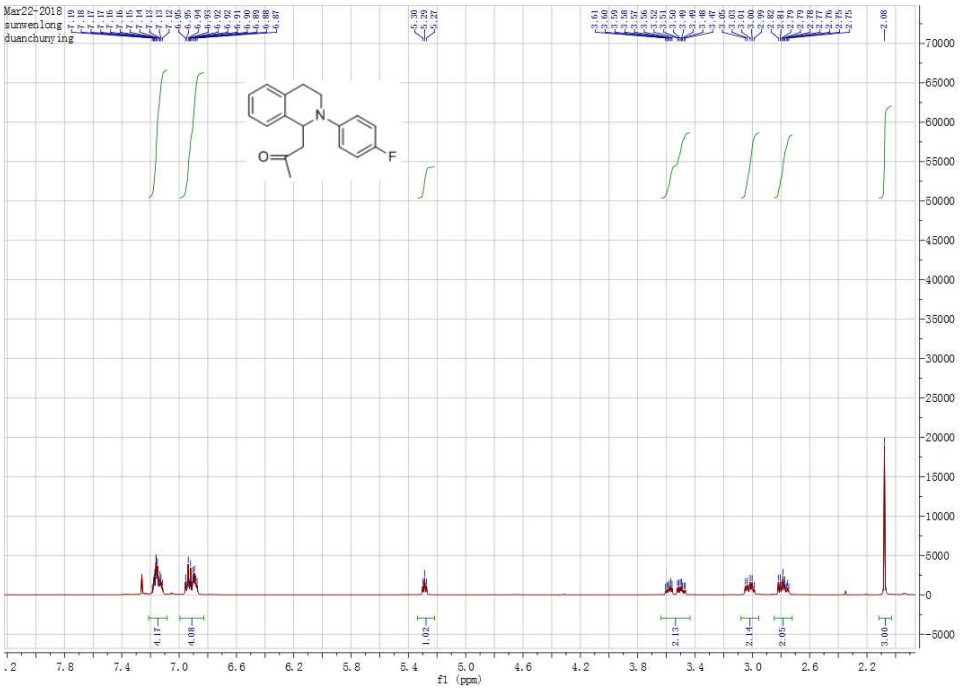


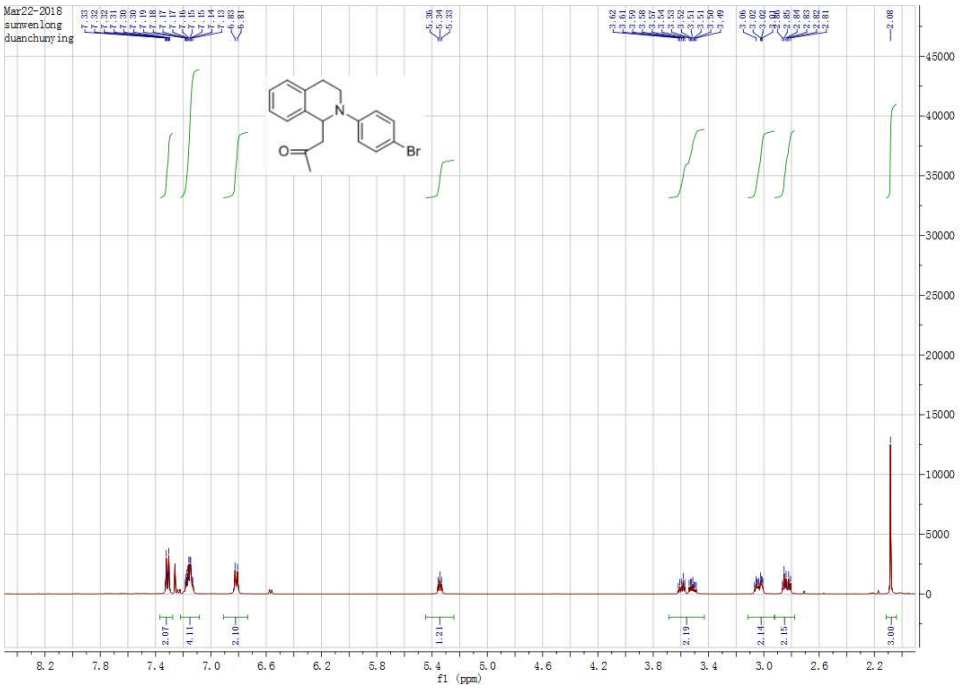
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 –7.10 (m, 2H), 7.09 (dd, *J* = 8.4, 4.4 Hz, 1H),7.03 – 6.99 (m, 1H), 4.01 (s, 2H), 3.14 (t, *J* = 6.0 Hz, 2H), 2.80 (t, *J* = 6.0Hz, 2H), 1.76 (s, 1H).

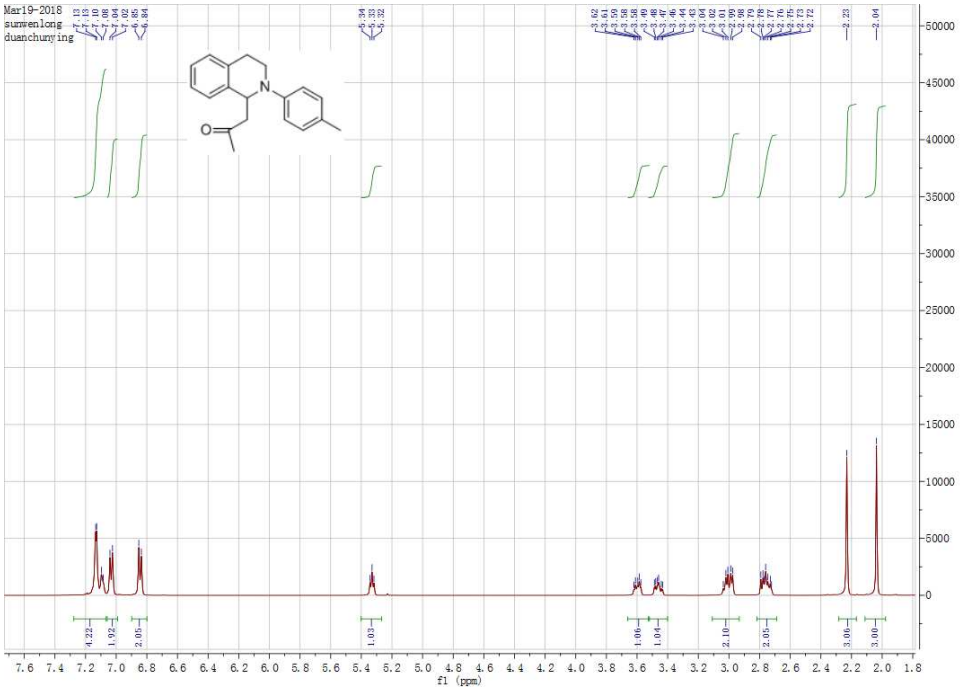


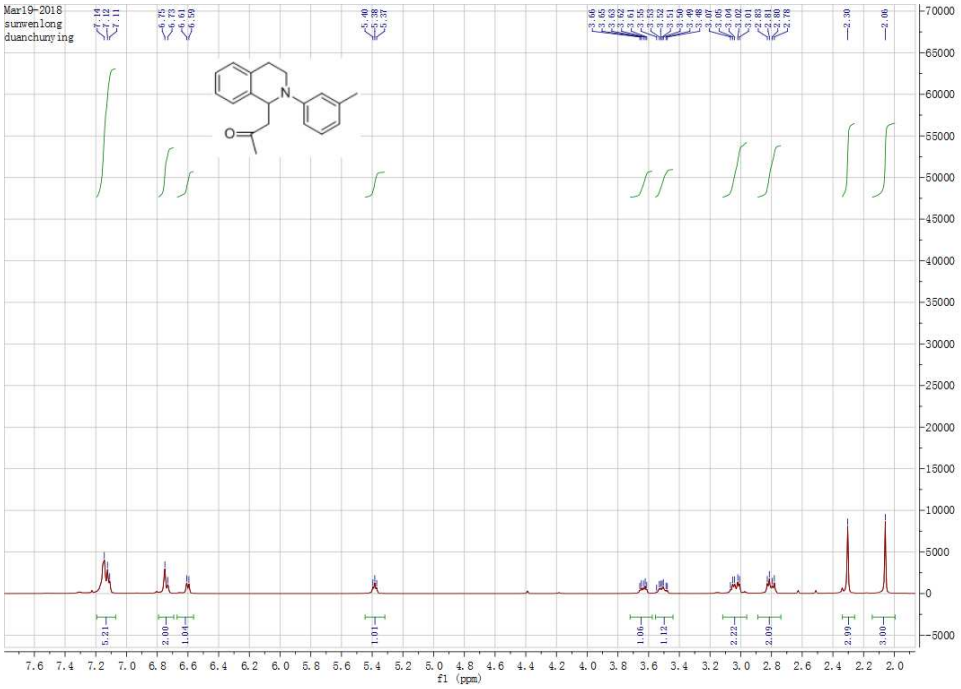
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (t, *J* =2.0 Hz, 1H), 7.38-7.28 (m, 3H), 7.16 (d, *J* = 7.3 Hz, 1H), 3.80-3.76 (m, 2H), 2.76 (t, *J*= 7.9 Hz, 2H);




Mar22-2018
sunwenlong
duanchunying
O
N
F
f1 (ppm)


Mar22-2018
sunwenlong
duanchunying
O
N
Br
f1 (ppm)





[S1] Barbaro, P.; Gonsalvi, L.; Guerriero, A.; Liguori, F. Facile heterogeneous catalytic hydrogenations of C=N and C=O bonds in neat water: anchoring of water-soluble metal complexes onto ion-exchange resins. *Green Chem*. **2012**, *14*, 3211−3219.