Supporting information

Artificial enzyme of polyoxometalate-supported cobalt complex for isochromans to isochromanones by activating O_2

Xiangyu Ren,[a] Hongrui Tian,[a] Baokuan Chen,*[a] Lingling Dai,[a] Yanfeng Bi,*[a] Guoping Yang,*[b]

[a]*School of Petrochemical Engineering, Liaoning Petrochemical University, 113001, China.*

[b]*School of Chemistry, Biology and Material Science, Jiangxi Province Key Laboratory of Synthetic Chemistry, Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology, Nanchang 330013, China*

E-mail: chenbaokuan@lnpu.edu.cn (B. K. Chen); biyanfeng@lnpu.edu.cn (Y. F. Bi); erick@ecut.edu.cn (G. P. Yang)

1 General Methods

The compounds were obtained from commercial sources and can be used without further purification. The Powder X-ray diffraction (PXRD) was accomplished using Mo Kα radiation (λ = 0.71073 Å) on the Brukerr D8 Advance diffractometer. The fourier transform infrared spectrum (FT-IR) spectra were recorded as the pressed KBr by Bruker ALPHA spectrometer. The thermal gravimetric analyses (TGA) were carried out using the TA Q600 thermal analyzer in a flowing N_2 atmosphere at a heating rate of 10 ℃ min^{-1} from 25 to 900 ℃. The X-ray photoelectron spectrum (XPS) tests were conducted using an ESCALAB 250Xi spectrometer and an Al Kα radiation source (1486.7 eV) as the X-ray energy. ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) spectra were obtained on Bruker AVANCE III 400 instrument.

2 Synthesis of Catalysts

Synthesis of $[Co^{II}(C_7H_{12}N_2)_3][Co^{II}(C_7H_{12}N_2)_4]_2[HPMo^{VI}_4Mo^{V}_4V^{V}_4(V^{IV}O)_2O_{40}]\cdot 3H_2O$ (**PMoV-Co**). NH_4VO_3 (0.116 g, 1 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.145 g, 0.5 mmol), $(NH_4)_2MoO_4$ (0.145 g, 0.73 mmol), H_3PO_3 (0.5 mmol), 1-Butylimidazole (1 mL) and deionized water (10 mL) were contained in a 20 mL Teflon-lined reactor operating at autogenous pressure for 3 days at 140 ℃. After cooling to room temperature, black massive crystals are formed. Yield: 49.3% (based on V). FT-IR (KBr, cm^{-1}): 3439 (s), 3124 (m), 2956 (m), 2928 (m), 2874 (w), 1627 (m), 1519 (m), 1462 (w), 1374 (w), 1233 (m), 1092 (s), 1052 (w), 938 (vs), 790 (s), 658 (w), 530 (vw).

3 Single crystal X-ray diffraction

PMoV-Co single crystal data were acquired using Mo-Kα radiation on a Bruker D8 QUEST system at 273 K. After being handled by utilizing the SQUEEZE function of PLATON,[S1] the structures were solved using the direct technique and refined using full-matrix least-squares on F^2 using the olex 2.[S2] All non-hydrogen atoms were polished anisotropically without the use of lattice water. The hydrogen atoms of the organic ligand were trapped in their prescribed positions. Table S1 provides the crystal information and structural refinement parameters for the **PMoV-Co**. The CCDC number is 2343627.

4 Oxidation of Isochromans to Isochromanones

A typical reaction, isochroman (0.2 mmol), **PMoV-Co** (0.30 mol%), and 1,4-dioxane (2 mL) were put into a 10 mL Shrek tube with an oxygen balloon, which was

heated for 12 h at 80 ℃. After the reaction, the catalyst is filtered and separated for use in cycling tests. The solution was purified via silica gel flash column chromatography, analyze the product by ^{1}H NMR.

5 Characterization of compounds

For **PMoV-Co**, the weight loss during the first process between 25 and 100 ℃ is 2.01% (calcd 1.09%), a result of the **PMoV-Co** losing their isolated water. The weight loss of the second process between 200 and 600 °C is 39.62% (calcd 40.54%), attributed to the loss of 1-butylimidazole in the compounds. The weight loss between 700 and 900 ℃ was thought to be the cause of the collapse of the compound skeletons. The findings of the TG analysis indicated that the compound had thermal stability. (Fig. S1).

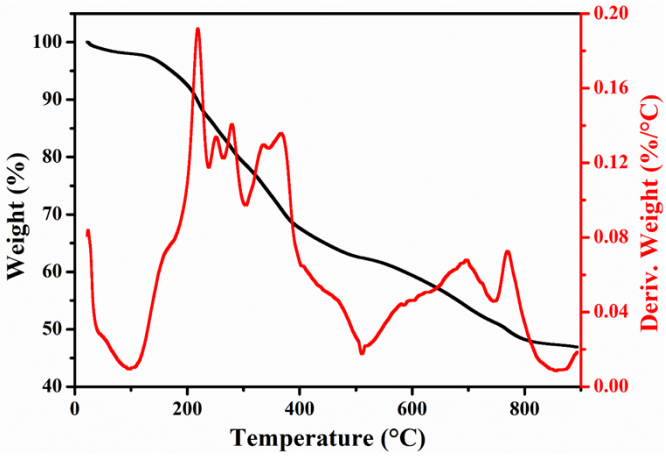


Fig. S1 The TGA curve of **PMoV-Co**

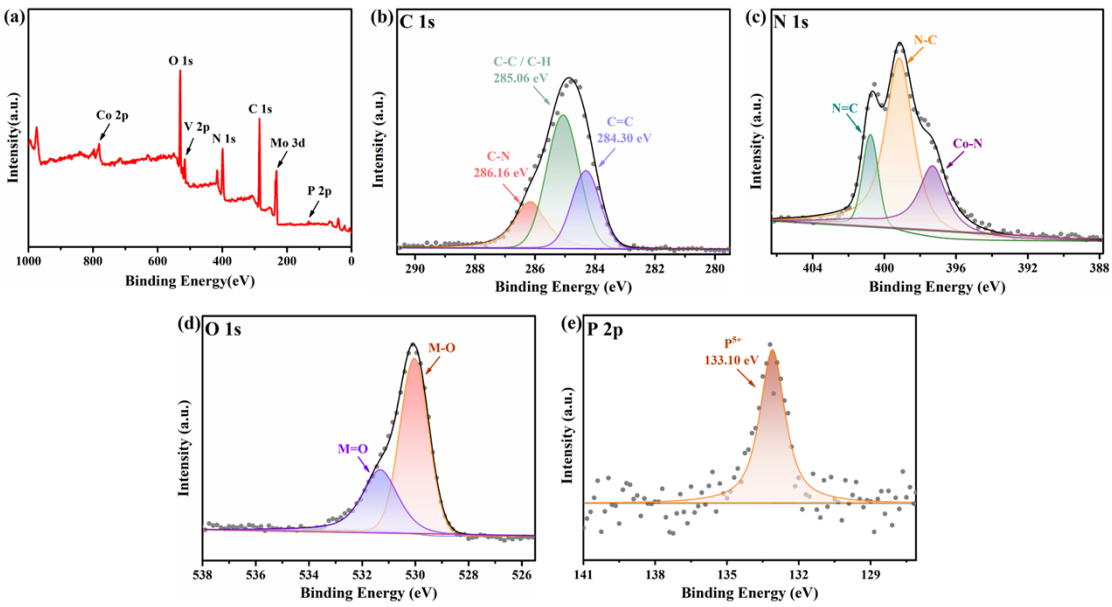


Fig. S2 XPS spectra of **PMoV-Co:** (a) full-scan spectrum; (b) C 1*s*; (c) N 1*s*; (d) O 1*s*; (e) P 2*p*

6 Characterization of other catalysts as a comparison

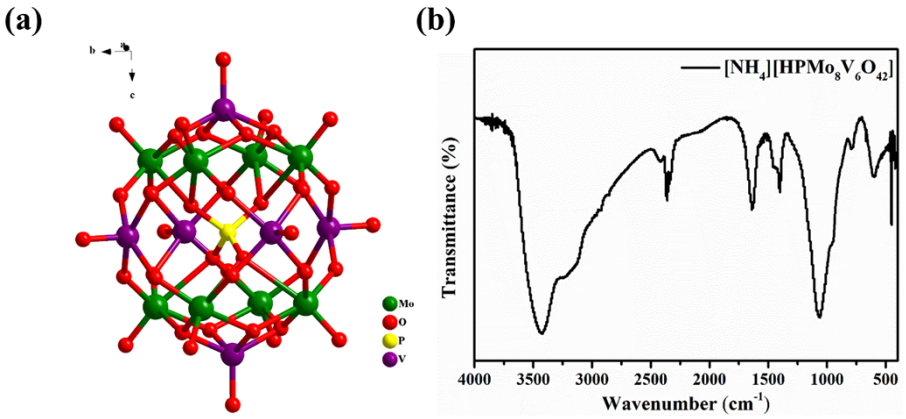


Fig. S3 Ball-and-stick structure and FT-IR spectrum of $[NH_4]_4[HPMo_8V_6O_{42}]$

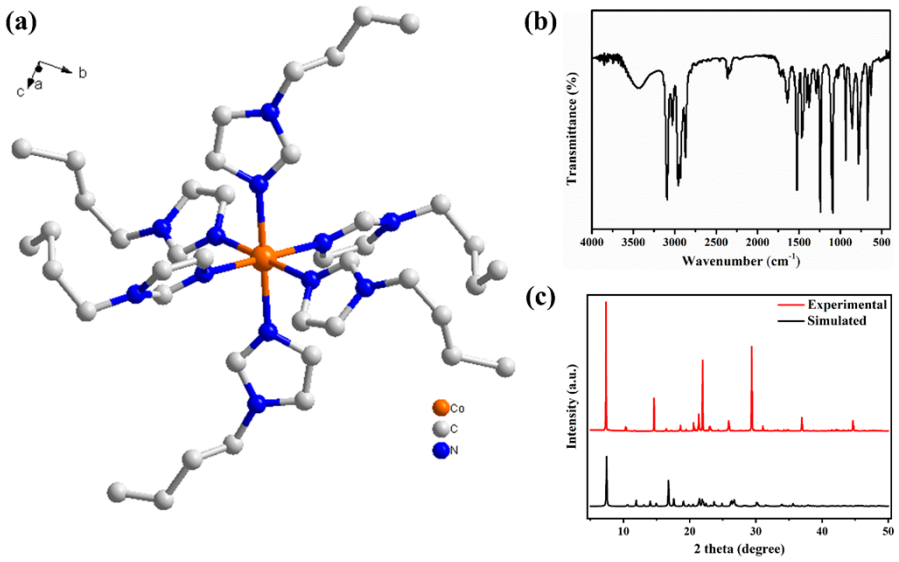


Fig. S4 Ball-and-stick structure, FT-IR spectrum and PXRD of $[Co(C_7H_{12}N_2)_6]\cdot 2Cl$

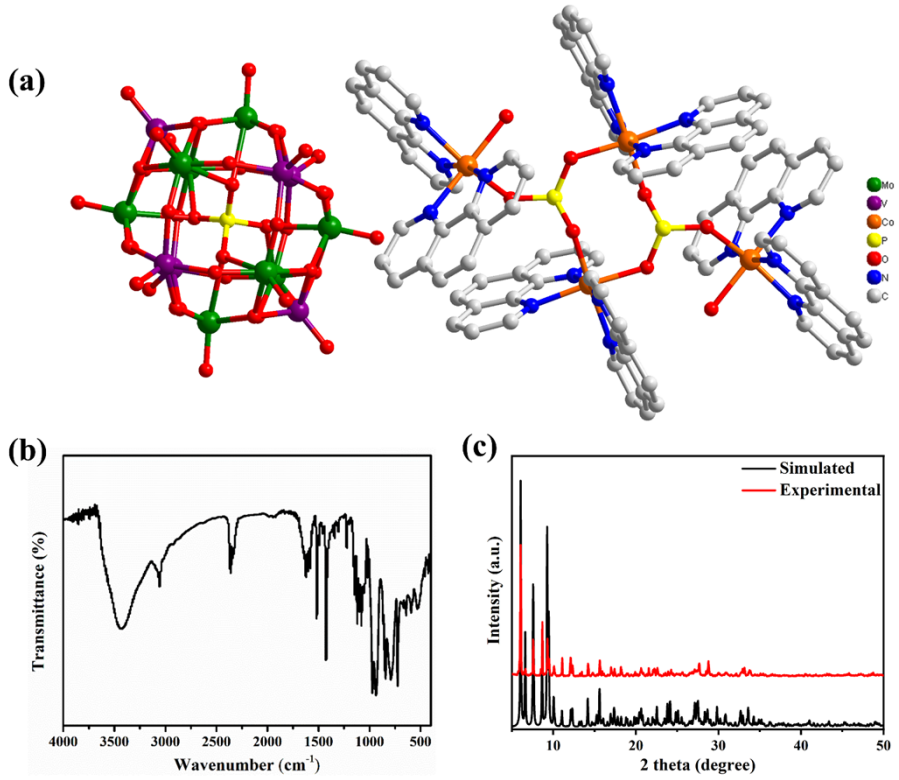


Fig. S5 Ball-and-stick structure, FT-IR spectrum and PXRD of $[Co_4(phen)_8(HPO_3)_2][PMo_8V_6O_{42}]$[S3]

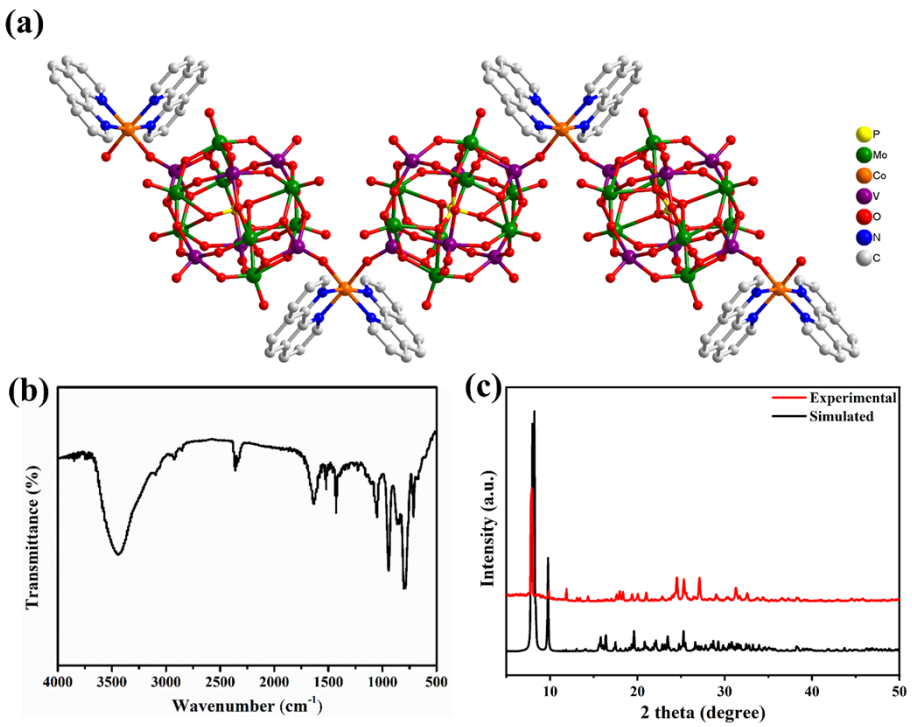


Fig. S6 Ball-and-stick structure, FT-IR spectrum and PXRD of $[PMo_8V_6O_{42}][Co(Phen)_2][Hpy]$[S4]

7 Leaching test (supplement)

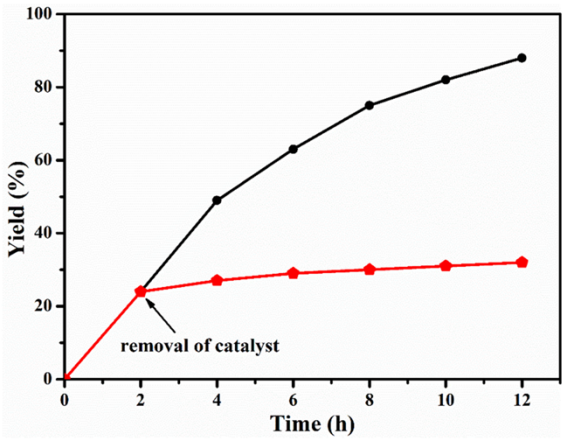


Fig. S7 The heterogeneity test of **PMoV-Co**

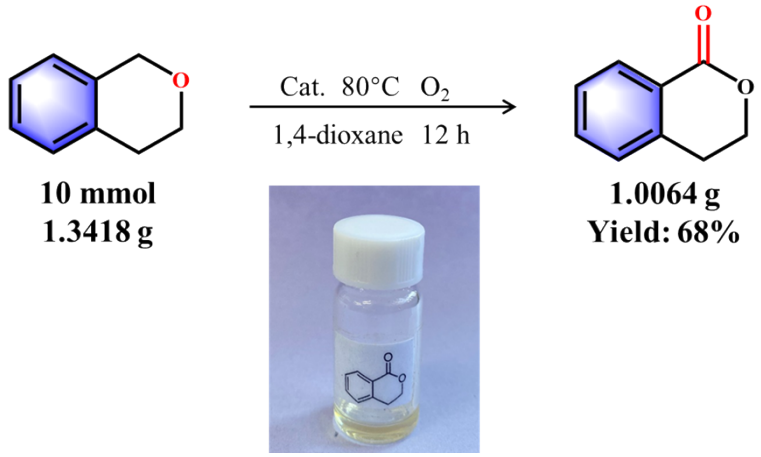


Fig S8. Isochromanone gram scale preparation

8 Radical capture experiment (supplement)

Isochroman (0.2 mmol), **PMoV-Co** (0.003 mmol), (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (2 equiv.)and 1,4-dioxane (2 mL) was put into a 10 mL Shrek tube with an oxygen balloon, which was heated for 12 h at 80 ℃. After the reaction, product 3a was obtained and characterized by ^{1}H NMR (Fig. S9).[S5]

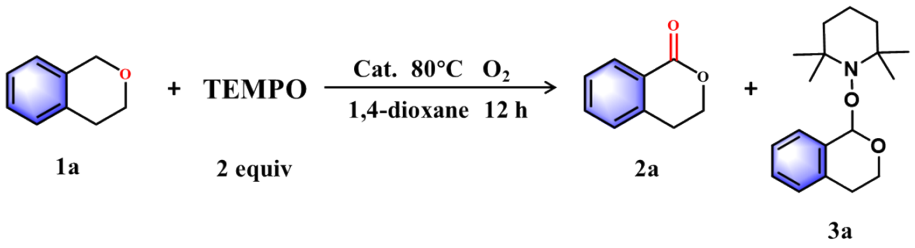
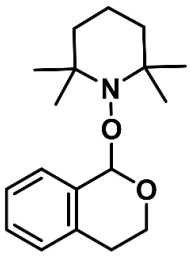
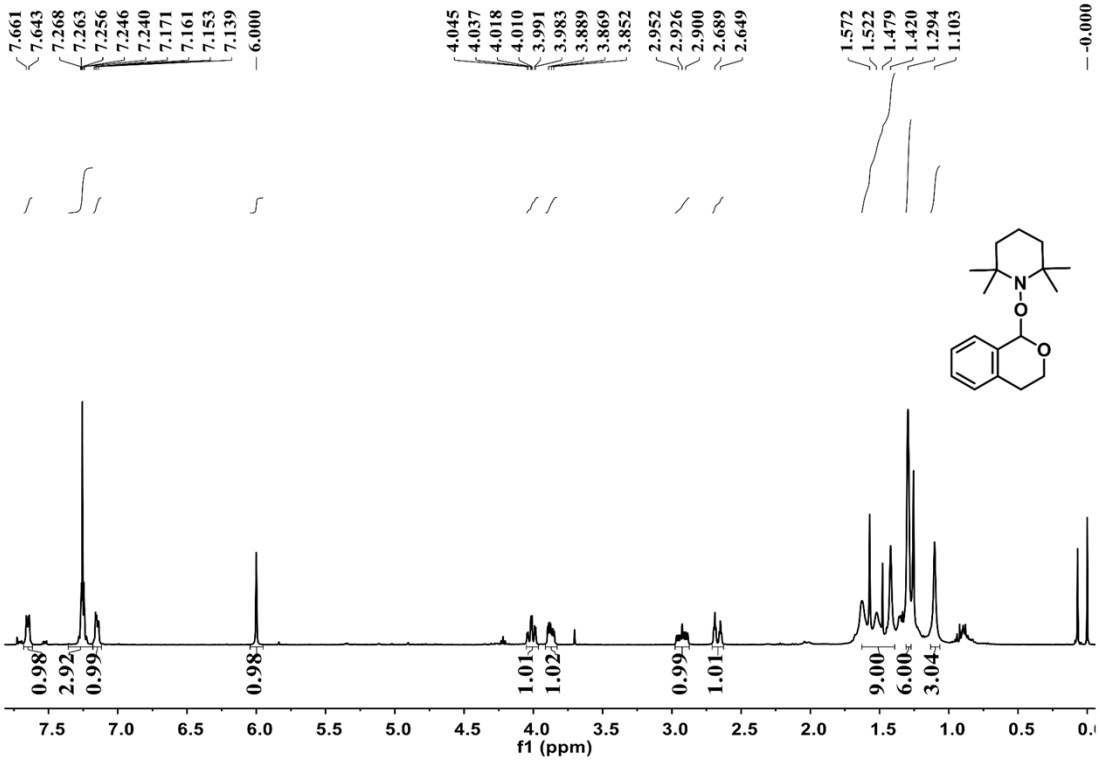


Fig. S9 Radical scavenger experiment of TEMPO



3a, yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 1H), 7.27-7.24 (m, 3H), 7.17-7.15 (m, 1H), 6.00 (s, 1H), 4.05-3.98 (m, 1H), 3.89-3.85 (m, 1H), 2.95-2.90 (m, 1H), 2.69-2.65 (m, 1H), 1.57-1.42 (m, 9H), 1.29 (s, 6H), 1.10 (s, 3H).



9 Catalyst characterization after cycle

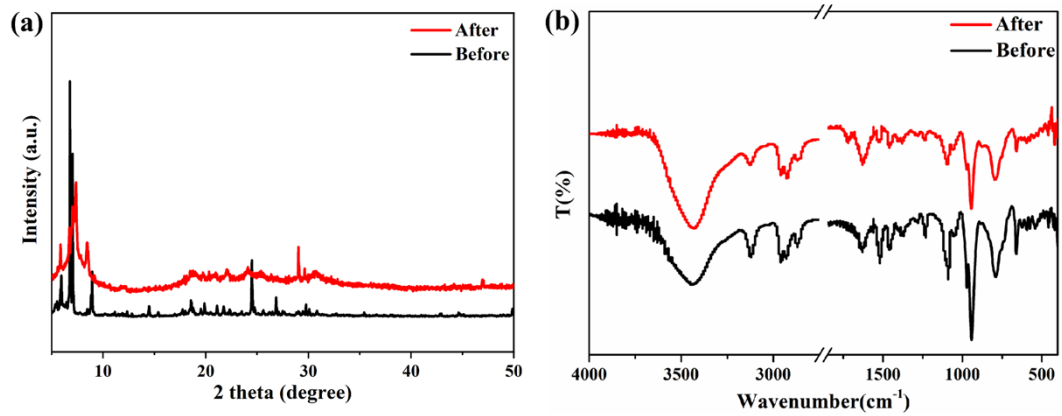


Fig. S10 PXRD patterns and FT-IR for catalyst before and after reaction

From the high resolution of the elements in Fig. S11, it can be seen that the valence states of various elements remain unchanged before and after the photocatalytic cycle reaction of **PMoV-Co**, which proves the stability of the crystal structure of **PMoV-Co**.

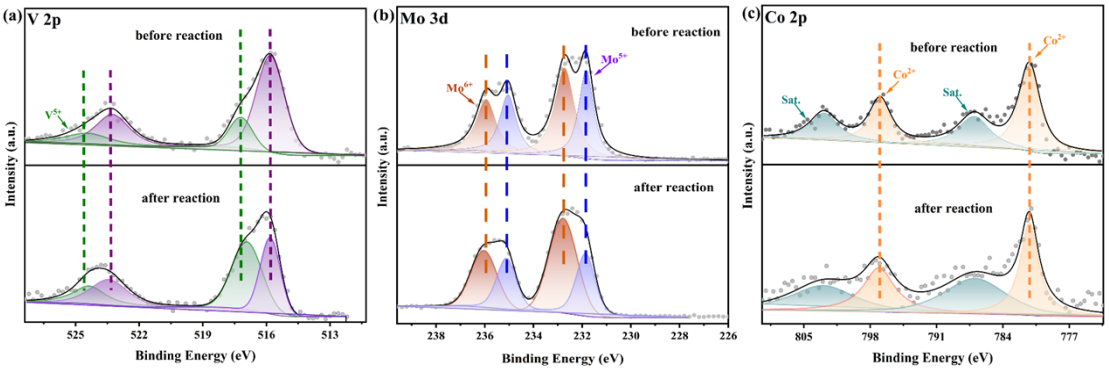


Fig. S11 XPS patterns for catalyst before and after reaction: (a) V 2*p*; (b) Mo 3*d*; (c) Co 2*p*

Table S1 Crystal data

Compounds	**PMoV-Co**
Formula	$C_{77}H_{140}Co_3Mo_8N_{22}O_{46}PV_6$
Formula weight ($g \cdot mol^{-1}$)	3316.93
Crystal	Monoclinic
Space group	*C2/c*
T (K)	273
a (Å)	14.5907 (6)
b (Å)	26.2303 (11)
c (Å)	30.8162 (13)
α (º)	90
β (º)	100.22(4)
γ (º)	90
Volume ($Å^3$)	11606.8 (8)
Z	4
Dc (g/cm3)	1.897
μ (mm^{-1})	1.81
Reflections collected	10292
Unique data	1674
R_{int}	0.043
GOF on F2	1.009
R_1[a]	$R_1 = 0.0715$
wR_2[b] [I > 2σ(I)]	$wR_2 = 0.1874$

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S2. Bond valence sum calculations of PMoV-Co[S6]

Atom	Bond	Distance / Å	Bond Valence	Bond Valence Sum (BVS)
Mo1	Mo01 - O20	1.669 (7)	1.798	4.829
	Mo01 - O18	1.782 (7)	1.325	
	Mo01 - O8	2.04 (7)	0.660	
	Mo01 - O9	2.06 (7)	0.625	
	Mo01 - O3	2.435 (14)	0.227	
	Mo01 - O6^{ii}	2.489 (12)	0.196	
Mo2	Mo02 - O13	1.670 (7)	1.793	4.803
	Mo02 - O4	1.786 (8)	1.310	
	Mo02 - O14	2.041 (7)	0.658	
	Mo02 - O9	2.064 (7)	0.618	
	Mo02 - O7^{ii}	2.418 (13)	0.237	
	Mo02 - O6^{ii}	2.507 (12)	0.187	
Mo3	Mo03 - O15	1.668 (6)	0.223	5.913
	Mo03 - O5	1.780 (8)	1.332	
	Mo03 - O21	1.793 (7)	0.630	
	Mo03 - O17	2.051 (7)	1.803	
	Mo03 - O8	2.057 (7)	0.640	
	Mo03 - O2^{ii}	2.441 (12)	1.286	
Mo4	Mo04 - O12	1.659 (6)	1.847	5.941
	Mo04 - O23	1.784 (8)	1.317	
	Mo04 - O1	1.788 (8)	1.303	
	Mo04 - O17^{ii}	2.046 (7)	0.649	
	Mo04 - O14^{ii}	2.059 (7)	0.627	
	Mo04 - O2	2.485 (13)	0.198	
Co1	Co1 - N9	2.029 (8)	0.600	2.499
	Co1 - N9i	2.029 (8)	0.600	
	Co1 - N9i	2.029 (8)	0.600	
	Co1 - O11i	2.081 (6)	0.349	
	Co1 - O11	2.081 (6)	0.349	
Co2	Co2 - N7	1.994 (9)	0.656	2.472
	Co2 - N1	2.017 (8)	0.620	
	Co2 - N5	2.050 (9)	0.567	
	Co2 - N3	2.123 (9)	0.465	
	Co2 - O10	2.362 (7)	0.164	

Atom	Bond	Distance / Å	Bond Valence	Bond Valence Sum (BVS)
V1	V1 - O1	1.902 (8)	0.765	4.694
	V1 - O5	1.915 (8)	0.739	
	V1 - O10	1.599 (7)	1.736	
	V1 - O18	1.920 (7)	0.729	
	V1 - O19	1.922 (7)	0.725	
V2	V2 - O17	1.922 (7)	0.725	4.482
	V2 - O8	1.919 (7)	0.731	
	V2 - O9	1.919 (7)	0.731	
	V2 - O11	1.638 (6)	1.562	
	V2 - O14	1.918 (7)	0.733	
V3	V3 - O16	1.565 (7)	1.903	4.958
	V3 - O4	1.906 (8)	0.757	
	V3 - O21	1.904 (7)	0.761	
	V3 - O22	1.906 (8)	0.757	
	V3 - O23	1.895 (7)	0.780	

Symmetry transformations used to generate equivalent atoms: i: x, y, 1/2-z

Reference

S1. Bruker, A. X. S. Inc., APEX3 Package, APEX3, SAINT and SADABS, Madison, Wisconsin, USA, 2016.

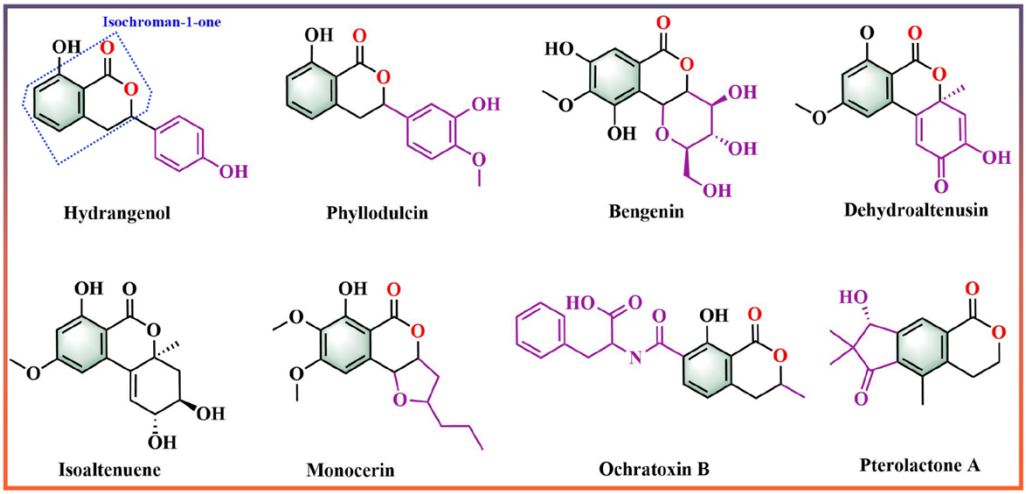
S2. (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339-341; (b) G. M. Sheldrick, SHELXT-Integrated space-group and crystal-structure determination. *Acta Cryst.*, 2015, **A71**, 3-8.

S3. S. Y. Shi, Y. C. Zou, X. B. Cui, J. N. Xu, Y. Wang, G. W. Wang, G. D. Yang, J. Q. Xu, T. G. Wang and Z. M. Gao, 0D and 1D dimensional structures based on the combination of polyoxometalates, transition metal coordination complexes and organic amines, *CrystEngComm*, 2010, **12**, 2122-2128.

S4. M. Yuan, Y. G. Li, E. B. Wang, Y. Lu, C. W. Hu, H. N. Hu and H. Q. Jia, Hydrothermal synthesis and crystal structure of a hybrid material based on $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$ and a highly reduced polyoxoanion, *J. Chem. Soc. Dalton Trans.*, 2002, 2916-2920.

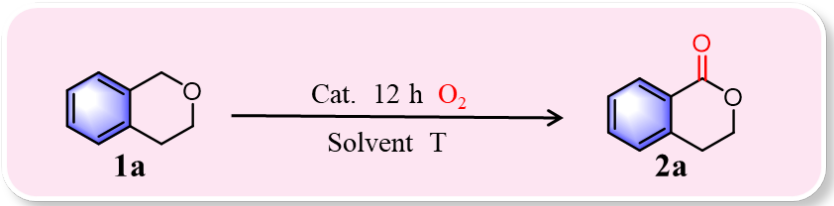
S5. Z. G. Yan, C. Jin, B. Sun and W. K. Su, (Diacetoxyiodo)benzene-Mediated Transition-Metal-Free Amination of C(sp^3) –H Bonds Adjacent to Heteroatoms with Azoles: Synthesis of N-Alkylated Azoles, *Synlett*, 2018, **29**, 2432-2436.

S6. N. E.Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B*,1991, **47**, 192-197.



Scheme S1 Representative naturally occurring isochromanones.

Table S3 Optimization of the Reaction Conditions[a]

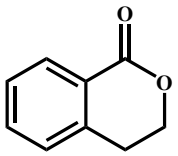


entry	catalyst (mol%)	solvent	temperature (°C)	yield (%)[b]
1	none	1,4-dioxane	80	21
2	**PMoV-Co** (0.15)	1,4-dioxane	80	53
3	**PMoV-Co** (0.30)	1,4-dioxane	80	88
4	**PMoV-Co** (0.45)	1,4-dioxane	80	90
5	**PMoV-Co** (0.60)	1,4-dioxane	80	89
6	**PMoV-Co** (0.30)	1,4-dioxane	40	36
7	**PMoV-Co** (0.30)	1,4-dioxane	60	63
8	**PMoV-Co** (0.30)	1,4-dioxane	80	92(88)[c]
9	**PMoV-Co** (0.30)	1,4-dioxane	100	72
10	**PMoV-Co** (0.30)	CH_3OH	80	Trace
11	**PMoV-Co** (0.30)	CH_3CH_2OH	80	3
12	**PMoV-Co** (0.30)	H_2O	80	19
13	**PMoV-Co** (0.30)	CH_3CN	80	37
14	**PMoV-Co** (0.30)	DMF	80	Trace
15	**PMoV-Co** (0.30)	DMSO	80	8
16	**PMoV-Co** (0.30)	DCM	80	55

[a] Reaction conditions: **1a** (0.2 mmol), catalyst, solvent (2 mL), O_2 balloon, 12h. [b] Yields determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. [c] isolated yield.

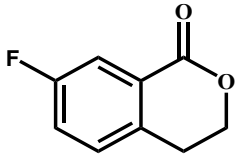
8 Characterization of the products

Isochroman-1-one (**2a**)



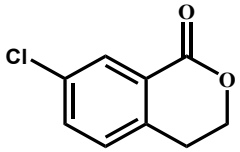
Yield 88%, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J*= 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 4.54 (t, *J* = 8.0 Hz, 2H), 3.04 (t, *J*= 6.0 Hz, 2H).

7-Fluoroisochroman-1-one (2b)



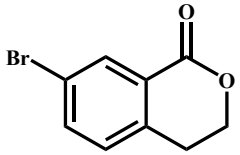
Yield 71%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.2 Hz, 1H), 7.27-7.25 (m, 2H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H).

7- Chloroisochroman-1-one (2c)



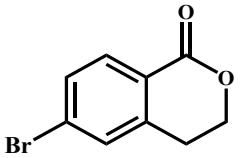
Yield 73%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H).

7-Bromoisochroman-1-one (2d)



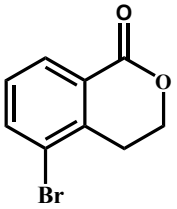
Yield 84%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.4 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.03 (t, *J* = 6.0 Hz, 2H).

6-Bromoisochroman-1-one (2e)



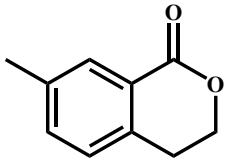
Yield 87%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 4.53 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H).

8-Bromoisochroman-1-one (2f)



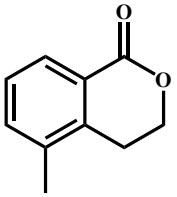
Yield 84%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 4.55 (t, *J* = 6.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H).

7-Methylisochroman-1-one (2g)



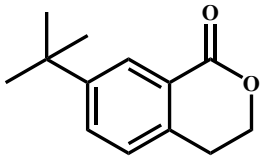
Yield 73%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* =8.0 Hz, 1H), 4.51 (t, *J* = 6.0 Hz, 2H), 3.01 (t, *J* = 6.0 Hz, 2H), 2.38 (s, 3H).

8-Methylisochroman-1-one (2h)



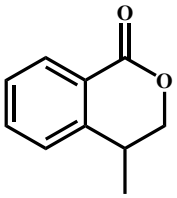
Yield 91%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 6.4 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 2.95 (t, *J* = 6.0 Hz, 2H).

7-(Tert-butyl)isochroman-1-one (2i)



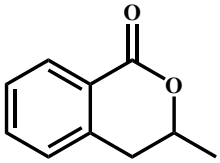
Yield 75%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 7.20 (d, *J* =8.0 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 3.03 (t, *J* = 6.0 Hz, 2H), 1.34 (s, 9H).

4-Methylisochroman-1-one (2j)



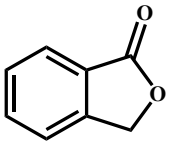
Yield 80%, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 4.53 (dd, *J* = 10.8 Hz, 4.0 Hz, 1H), 4.25 (dd, *J* = 10.8Hz, 6.4 Hz, 1H), 3.19-3.15 (m, 1H), 1.38 (d, *J* = 8.0 Hz, 3H).

3-Methylisochroman-1-one (2k)



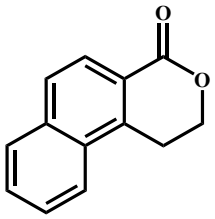
Yield 74%, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 4.73-4.65 (m, 1H), 2.99-2.89 (m, 2H), 1.53 (d, *J* = 8.0 Hz, 3H).

Isobenzofuran-1(3H)-one (2l)



Yield 80%, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 6.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 6.0 Hz, 1H), 5.33 (s, 2H).

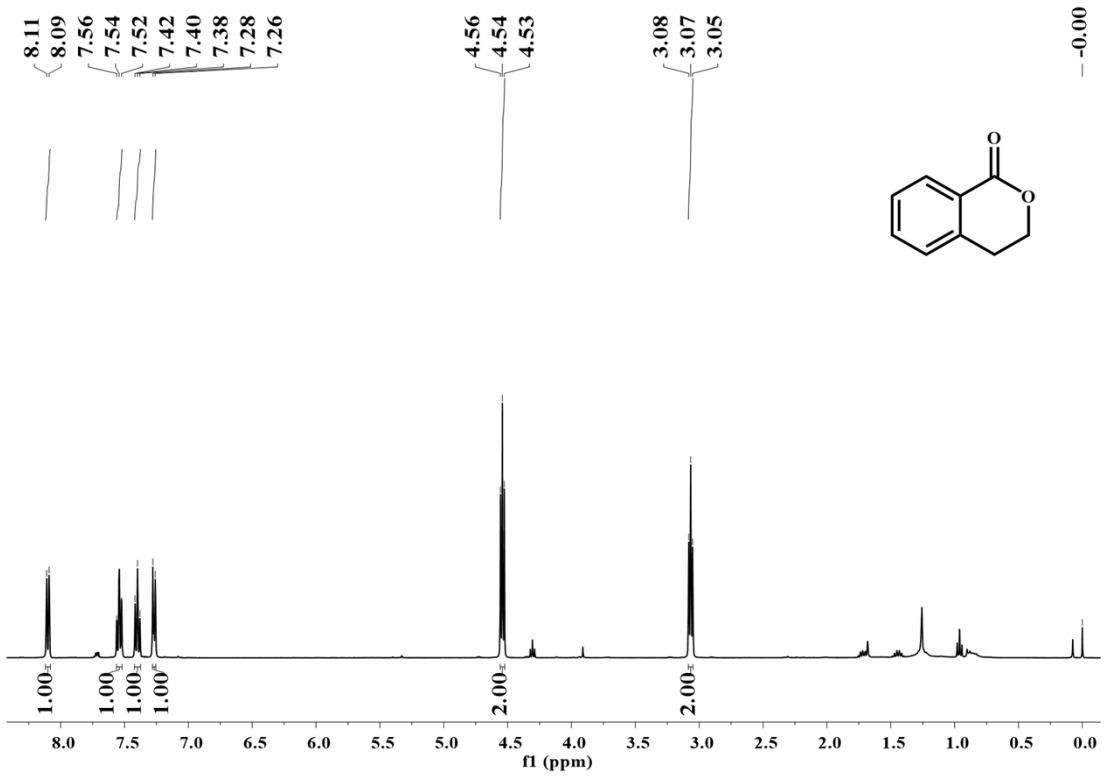
1,2-Dihydro-4H-benzo[f]isochromen-4-one (2m)



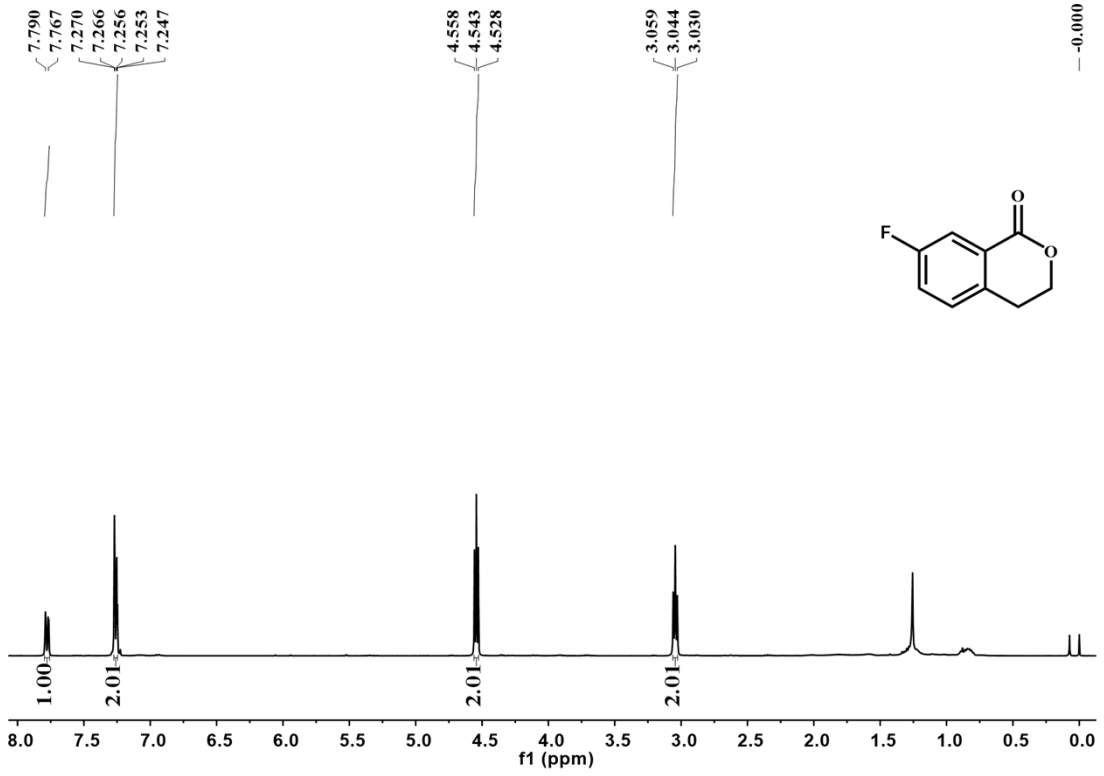
Yield 71%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.67-7.61 (m, 2H), 4.68 (t, J = 6.0 Hz, 2H), 3.45 (t, J = 6.0 Hz, 2H).

9 ^{1}H NMR spectra

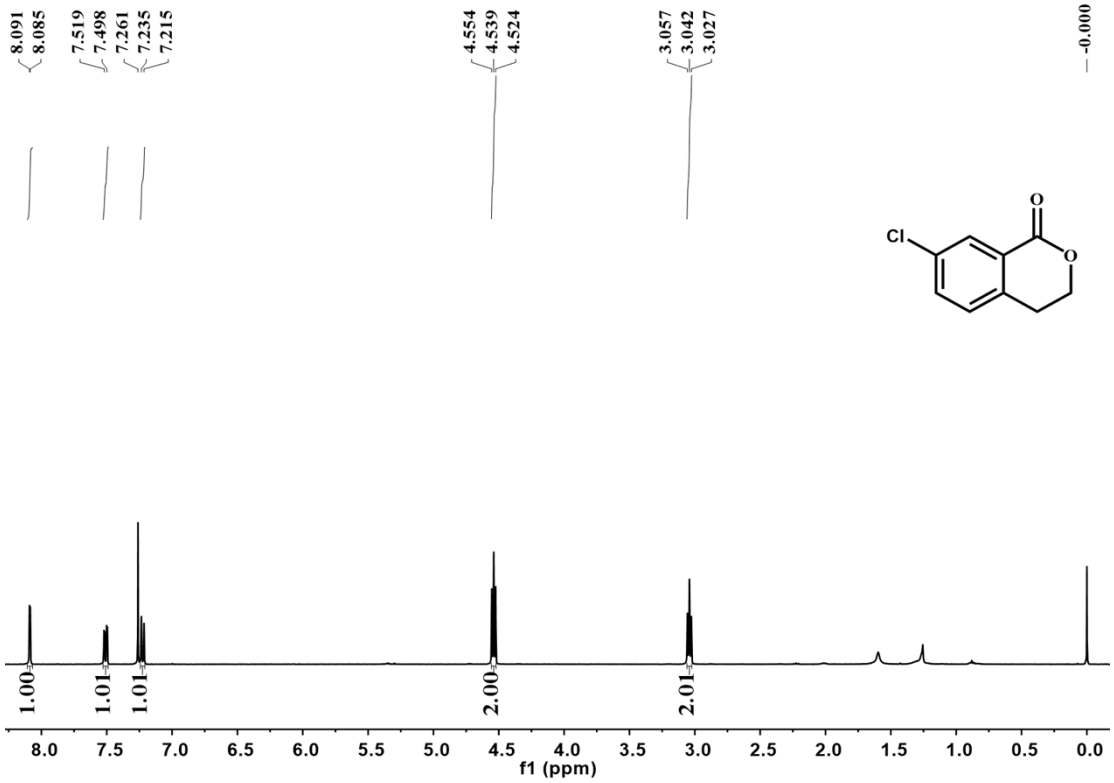
Isochroman-1-one (2a)



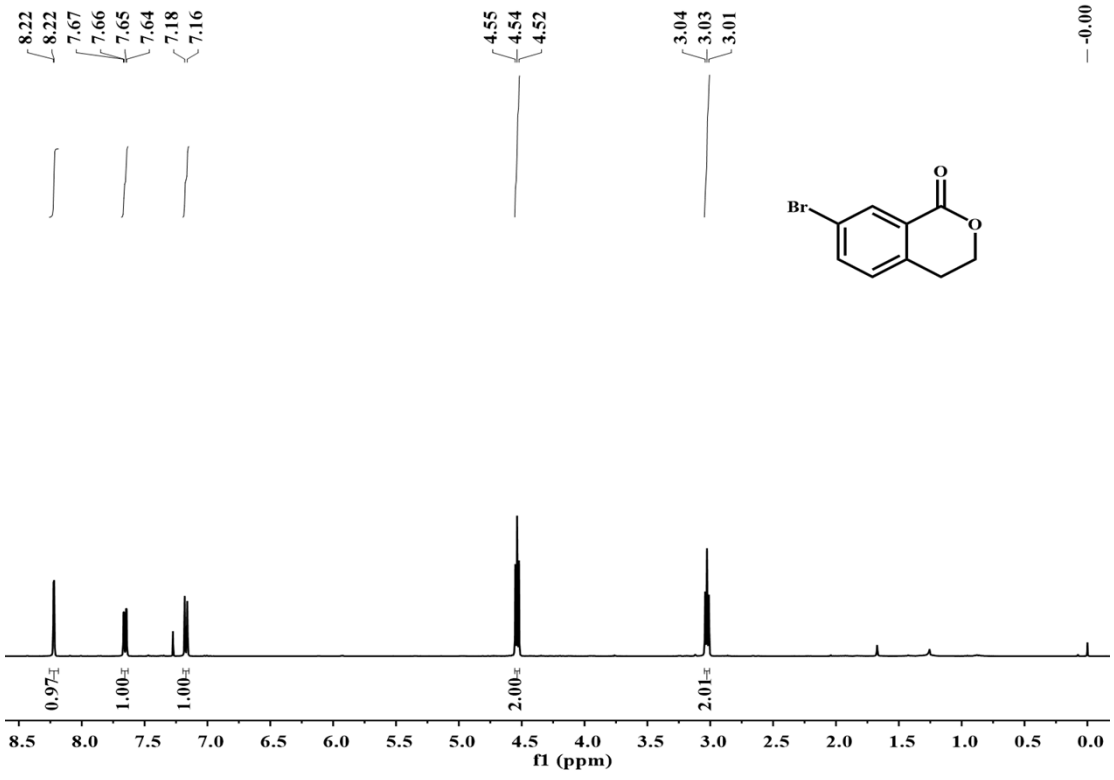
7-Fluoroisochroman-1-one (2b)



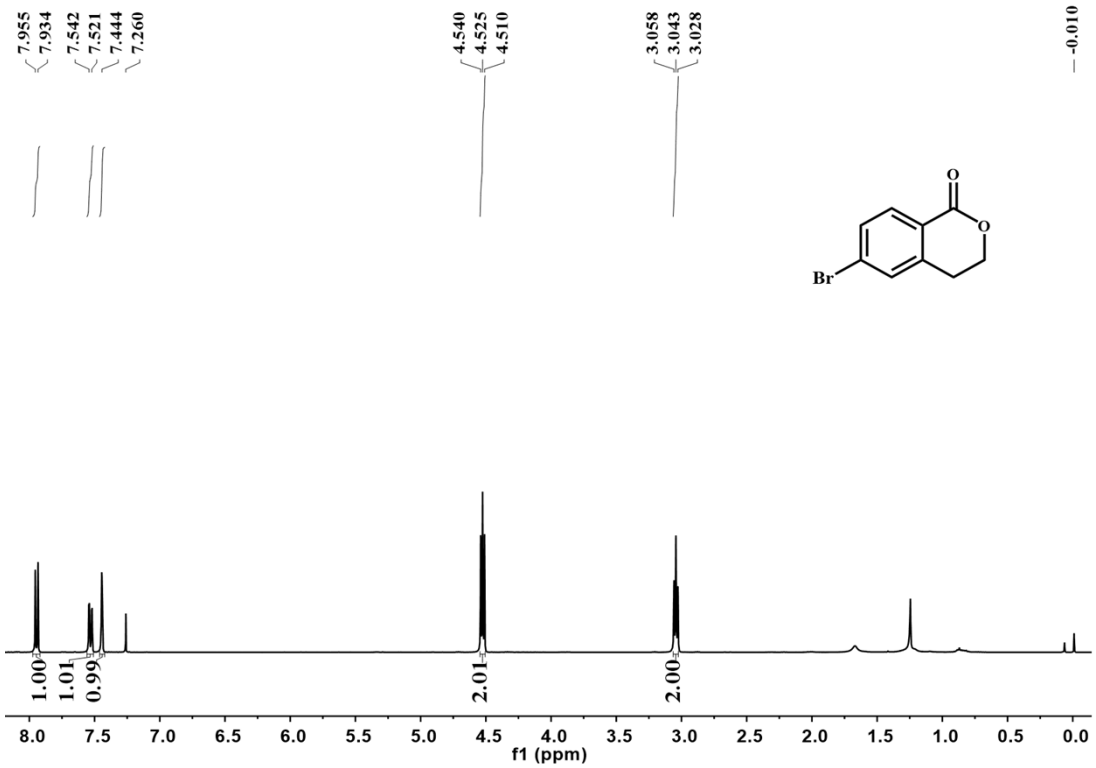
7-Fluoroisochroman-1-one (2c)



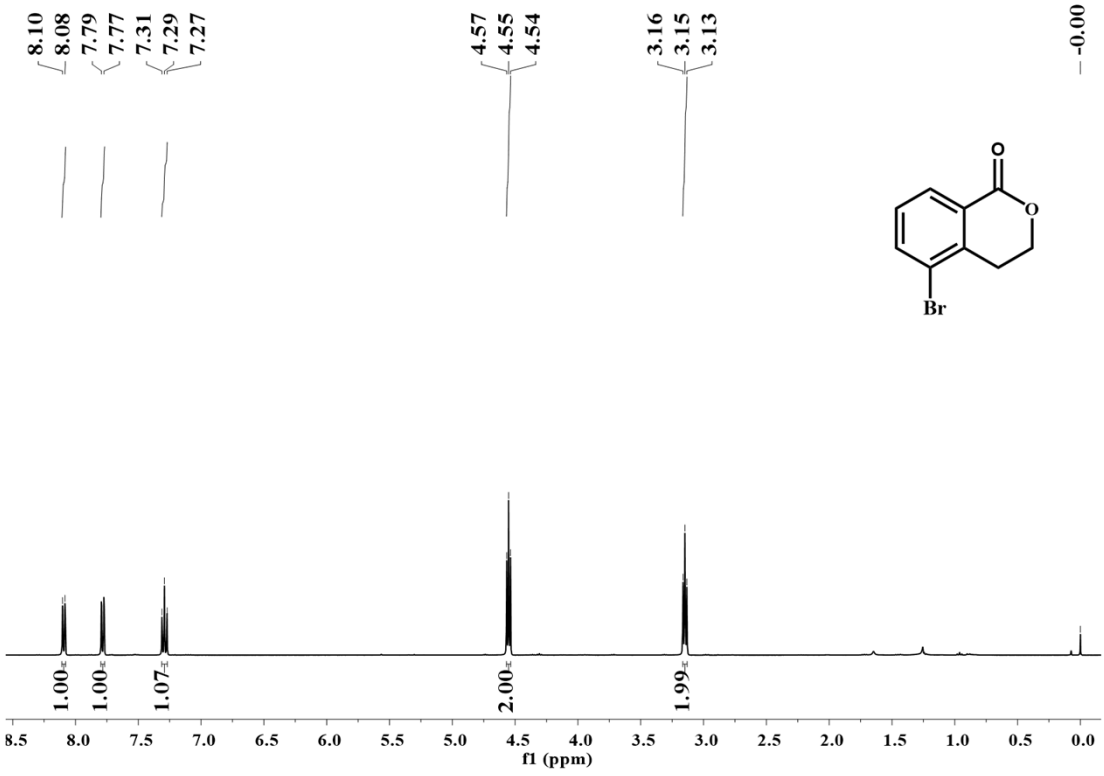
7-Bromoisochroman-1-one (2d)



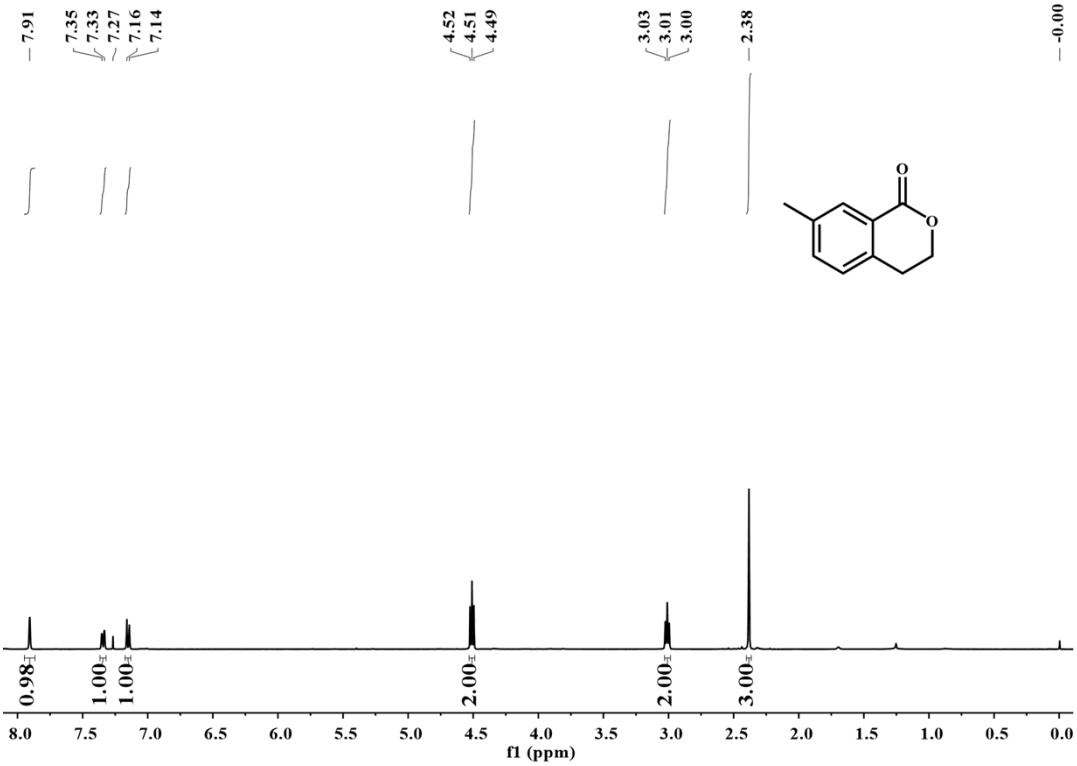
6-Bromoisochroman-1-one (2e)



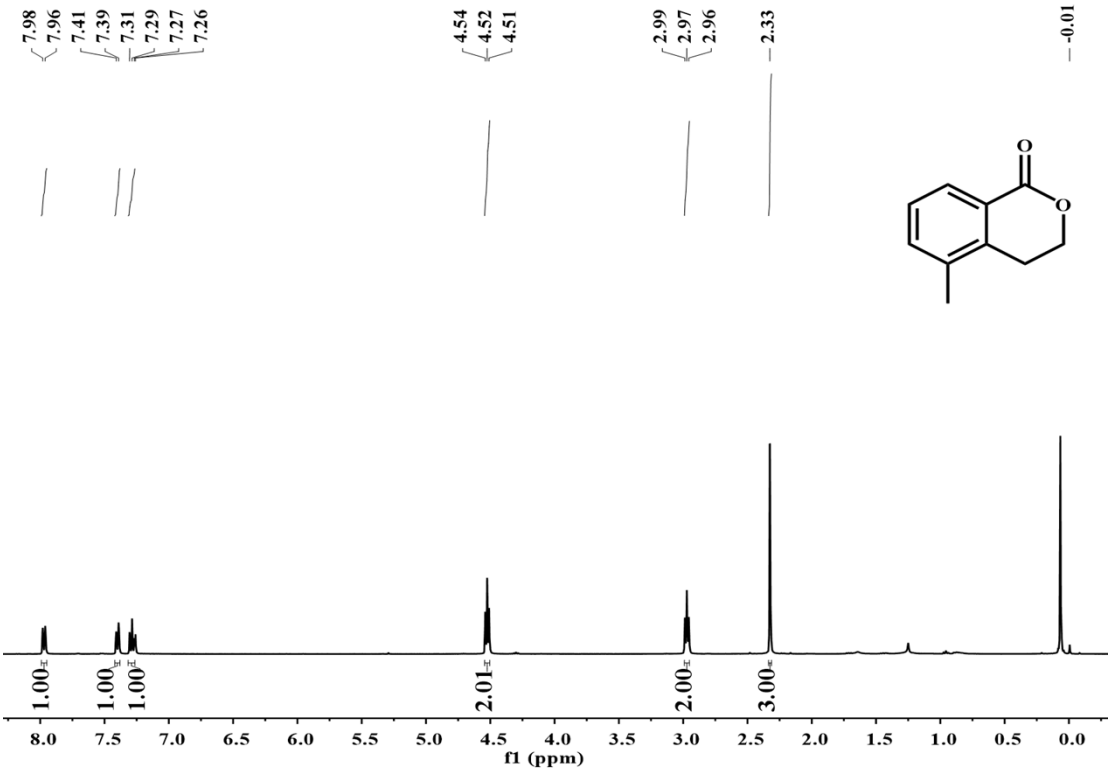
8-Bromoisochroman-1-one (2f)



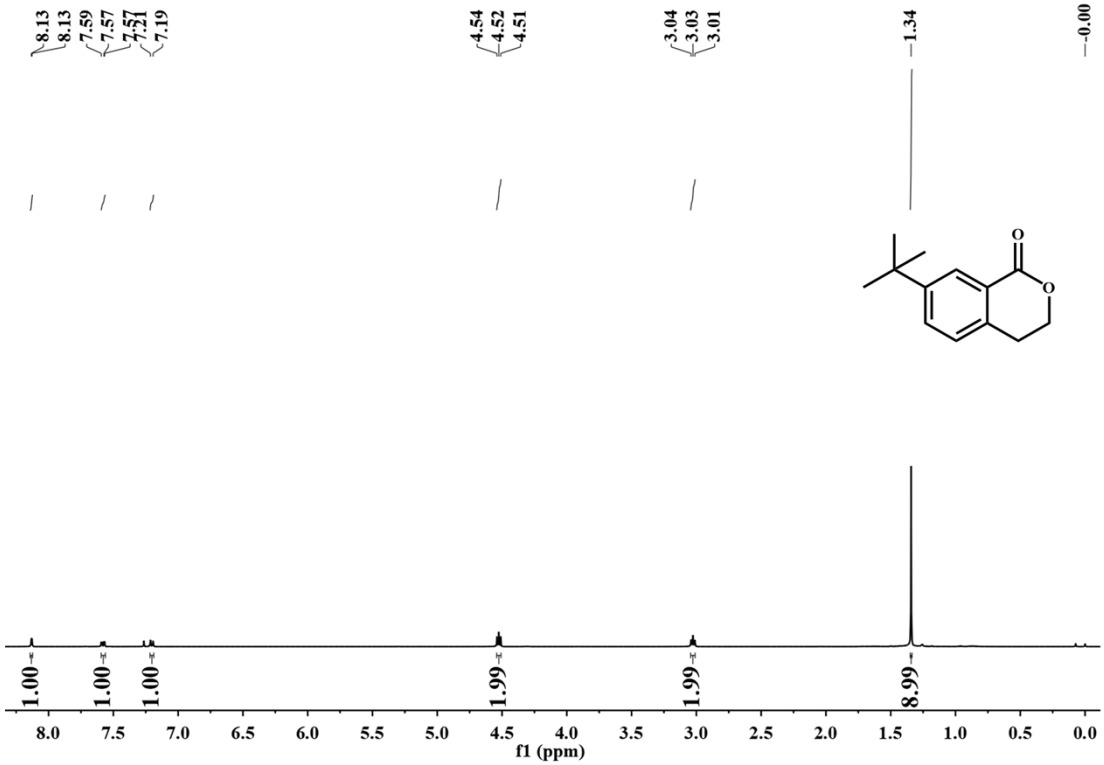
7-Methylisochroman-1-one (2g)



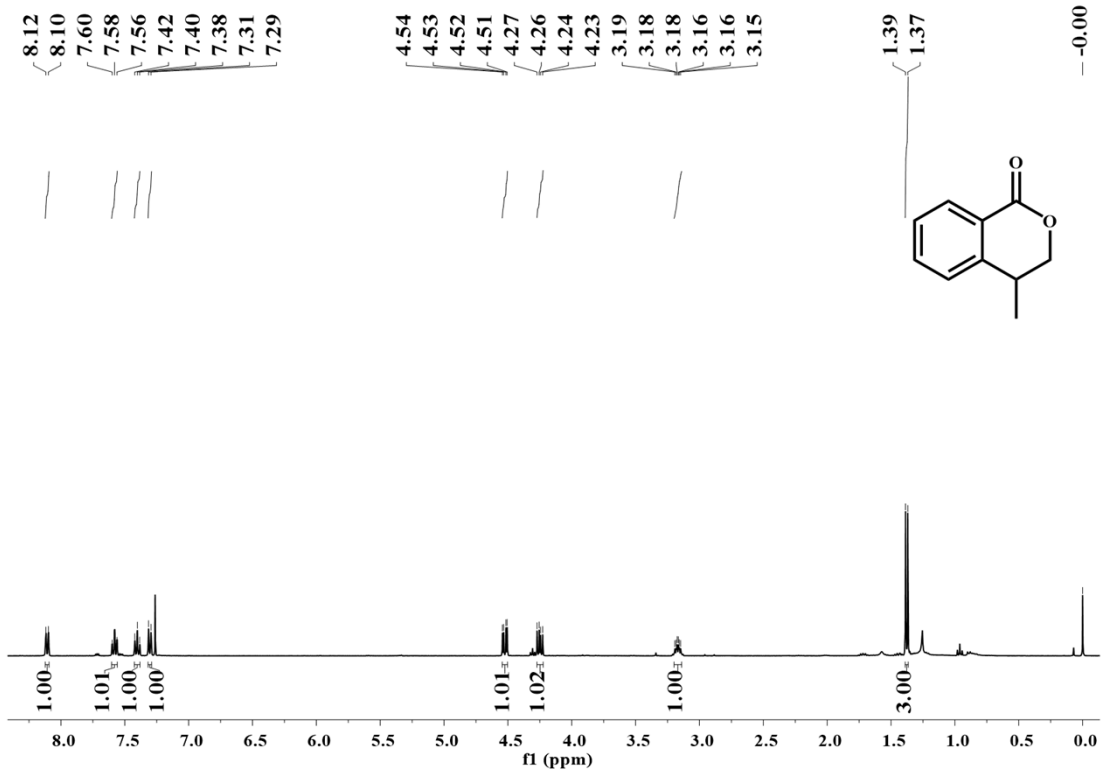
8-Methylisochroman-1-one (2h)



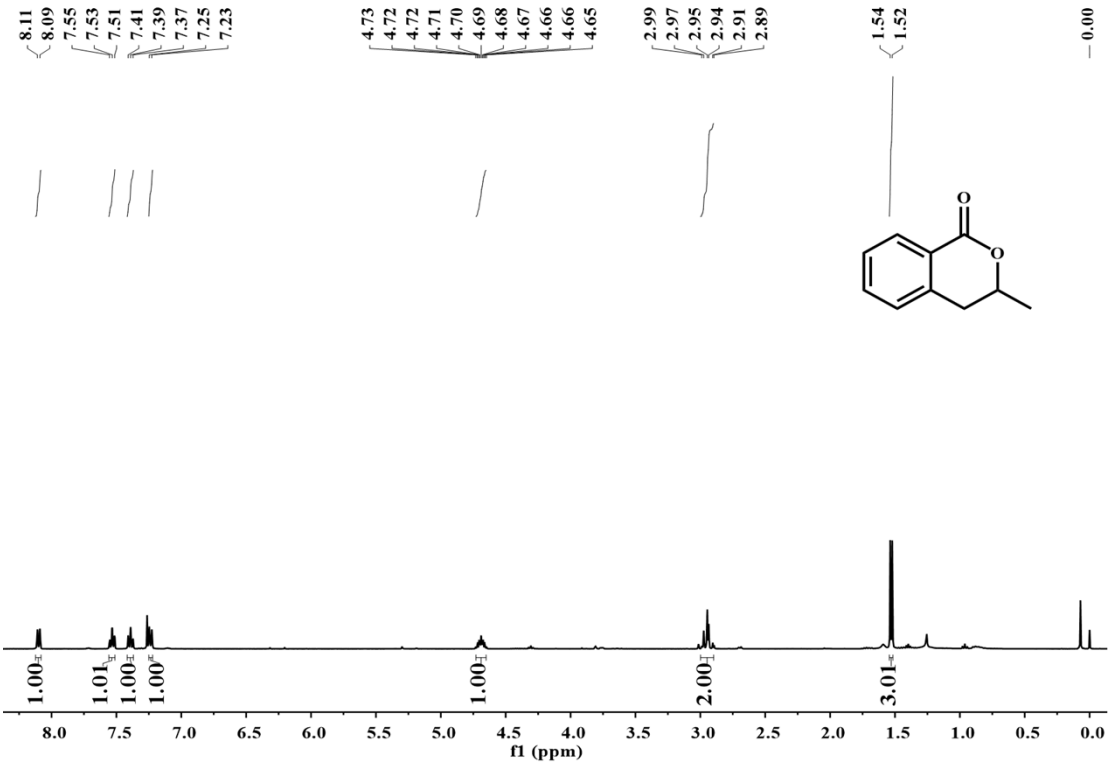
7-(Tert-butyl)isochroman-1-one (2i)



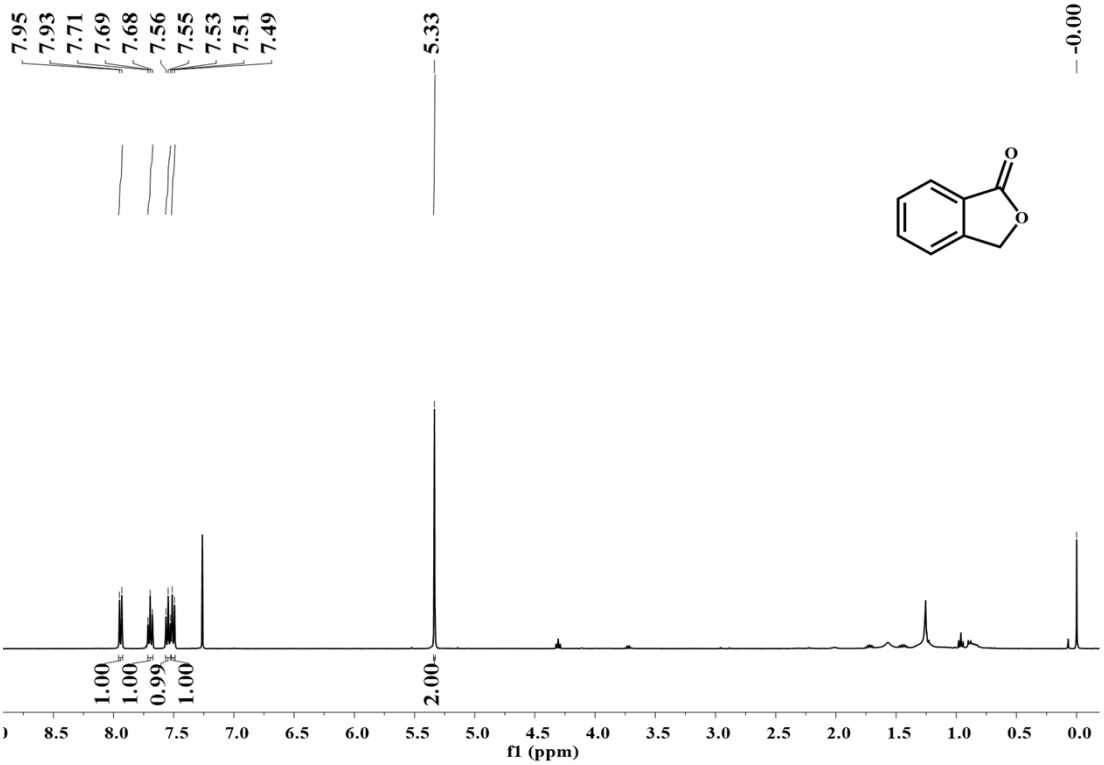
4-Methylisochroman-1-one (2j)



8-Methylisochroman-1-one (2k)



Isobenzofuran-1(3H)-one (2l)



1,2-Dihydro-4H-benzo[f]isochromen-4-one (2m)