Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Self-assembly solvothermal synthesis of $SiMoV_n@[Cu_6O(TZI)_3(H_2O)_6]_4 \cdot nH_2O$ for efficient selective oxidation of various alkylbenzene

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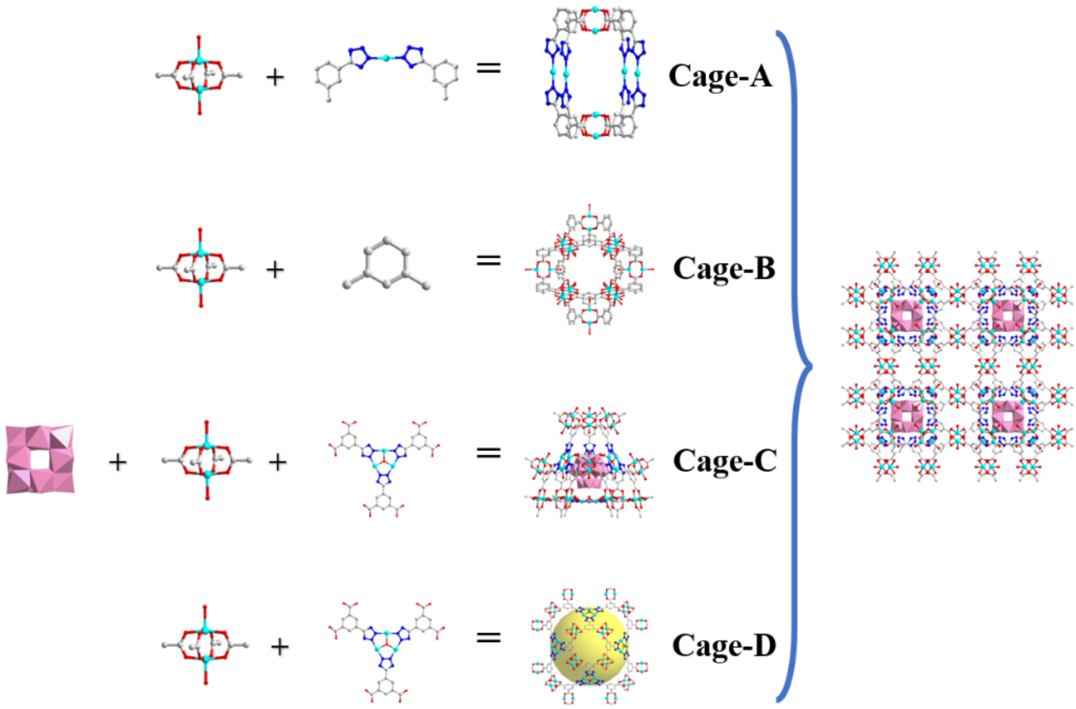


Fig. S1 Composition of four types of cages in complexes **1**-**3**.

Table S1. Crystallographic data for complex **2**.

Parameters	**2**
Empirical formula	$C_{108}H_{36}Cu_{24}Mo_{10}N_{48}O_{118}Si_{1}V_{2}$
CCDC No.	2054498
Formula weight	6476.18
Crystal system	cubic
Space group	$Fm\bar{3}m$
Unit cell	$a=b=c=$ 44.361(5) Å $\alpha=\beta=\gamma=90°$
Volume	87298(30) Å^3
Z	8
Density (Calcd)	0.985 g·cm^{-3}
Temperature	293.00 (2) K
Wavelength	0.71069 Å
Reflections collected	3732
μ	1.512 mm^{-1}
F (000)	25024
Final R_1^a, wR_2^b $[I > 2\sigma(I)]$	0.0858, 0.1140
Final R_1^a, wR_2^b *(all data)*	0.2228, 0.2640
GOF on F^2	1.064

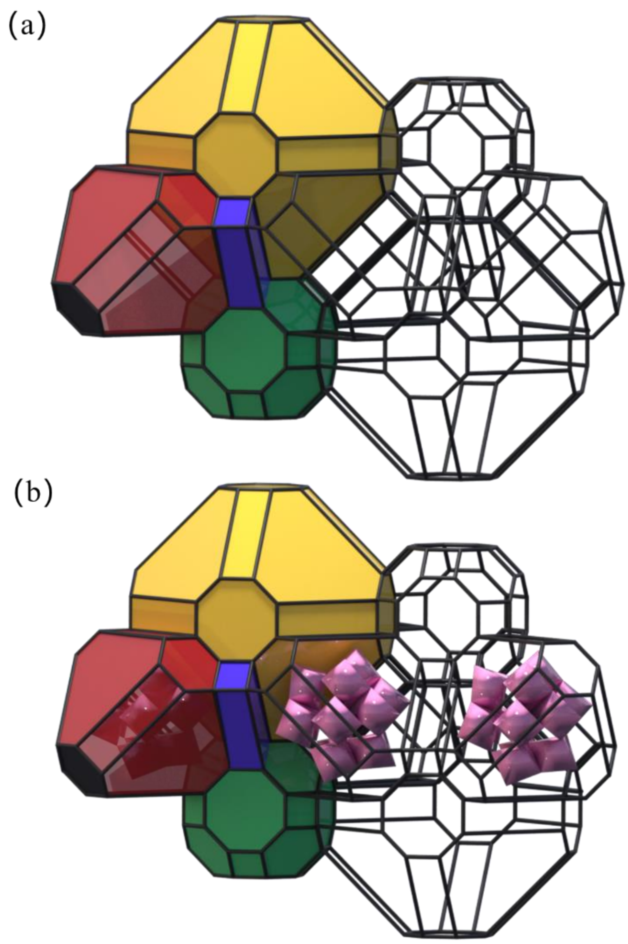


Fig. S2 Complex **2** framework with *lta* topology :(a) Without $SiMoV_2$; (b) Containing $SiMoV_2$.

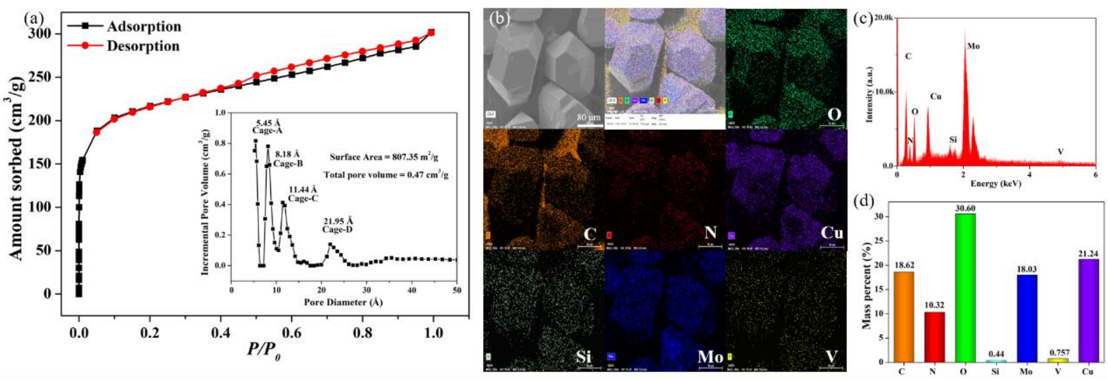


Fig. S3 (a) Nitrogen isothermal adsorption curve and pore size distribution of complex **1**; (b) SEM image and EDS mappings of complex **1**; (c) EDX spectrum; (d) The values of elements of complex **1**.

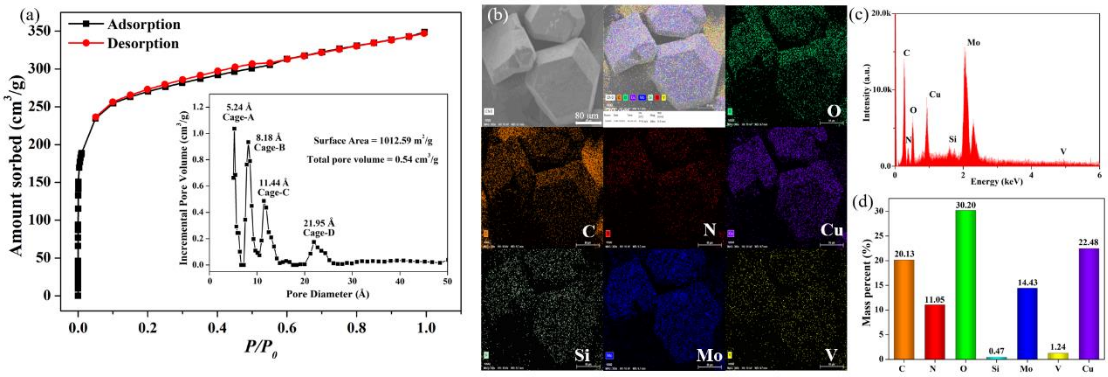


Fig. S4 (a) Nitrogen isothermal adsorption curve and pore size distribution of complex **2**; (b) SEM image and EDS mappings of complex **2**; (c) EDX spectrum; (d) The values of elements of complex **2**.

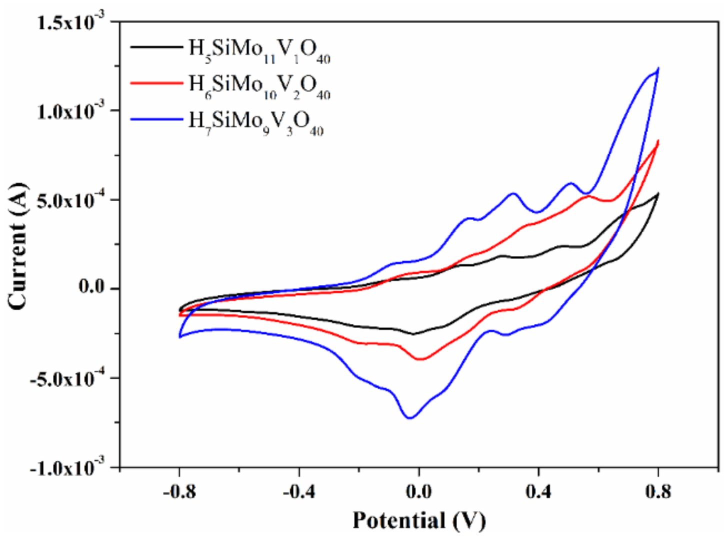
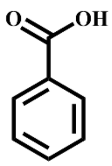


Fig. S5 Cyclic voltammograms of $SiMoV_{1/2/3}$

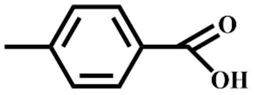
^{1}H NMR , ^{13}C NMR of catalytic oxidation products of complex 3



Benzoic acid

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.97 (s, 1H, -COOH), 7.96 (d, *J* = 8.0 Hz, 2H, Ph-H), 7.60 (t, *J* = 7.3 Hz, 1H, Ph-H), 7.48 (t, *J* = 7.6 Hz, 2H, Ph-H).

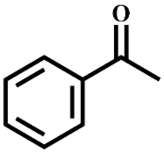
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.8 (-COOH), 133.3 (Ph-C), 131.2 (Ph-C), 129.7 (Ph-C), 129.0 (Ph-C).



p-Toluic acid

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.80 (s, 1H, -COOH), 7.85 (d, *J* = 8.0 Hz, 2H, Ph-H), 7.24 (d, *J* = 8.0 Hz, 2H, Ph-H), 2.32 (s, 3H, $-CH_3$).

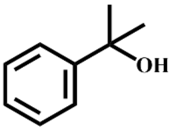
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.8 (-COOH), 143.4 (Ph-C), 129.8 (Ph-C), 129.5 (Ph-C), 128.5 (Ph-C), 21.5 ($-CH_3$).



Acetophenone

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.7 Hz, 2H, Ph-H), 7.43 (t, *J* = 7.3 Hz, 1H, Ph-H), 7.33 (t, *J* = 7.6 Hz, 2H, Ph-H), 2.46 (s, 3H, $-CH_3$).

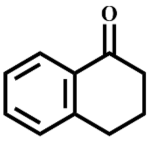
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8 (-CO-), 137.0 (Ph-C), 133.0 (Ph-C), 128.5 (Ph-C), 128.2 (Ph-C), 26.4 ($-CH_3$).



2-phenyl-2-propanol

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (d, *J* = 7.7 Hz, 2H, Ph-H), 7.30 (t, *J* = 7.6 Hz, 2H, Ph-H), 7.19 (t, *J* = 7.0 Hz, 1H, Ph-H), 5.03 (s, 1H, -OH), 1.45 (s, 6H, $-CH_3$).

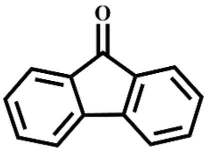
^{13}C NMR (101 MHz, DMSO-d_6) δ 151.0 (Ph-C), 128.2 (Ph-C), 126.3 (Ph-C), 125.0 (Ph-C), 71.1 (C-OH), 32.4 ($-CH_3$).



Tetralone

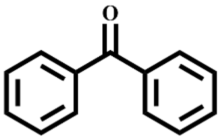
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 9.4 Hz, 1H Ph-H), 7.38 – 7.21 (m, 1H Ph-H), 7.21 – 6.96 (m, 2H Ph-H), 2.92 – 2.65 (m, 2H, $-CH_2$), 2.59 – 2.38 (m, 2H, $-CH_2$), 2.10 – 1.78 (m, 2H, $-CH_2$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9 (-CO-), 144.4 (Ph-C), 133.2 (Ph-C), 132.5 (Ph-C), 128.7 (Ph-C), 126.9 (Ph-C), 126.4 (Ph-C), 39.0 ($-CH_2$), 29.5 ($-CH_2$), 23.2 ($-CH_2$).

 **Fluorenone**

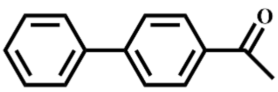
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.3 Hz, 2H, Ph-H), 7.49 (q, *J* = 7.5 Hz, 4H, Ph-H), 7.30 (t, *J* = 7.1 Hz, 2H, Ph-H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.9 (-CO-), 144.4 (Ph-C), 134.7 (Ph-C), 134.1 (Ph-C), 129.1 (Ph-C), 124.3 (Ph-C), 120.3 (Ph-C).

 **Benzophenone**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.8 Hz, 4H, Ph-H), 7.62 (t, *J* = 7.3 Hz, 2H, Ph-H), 7.51 (t, *J* = 7.5 Hz, 4H, Ph-H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.8 (-CO-), 137.6 (Ph-C), 132.5 (Ph-C), 130.1 (Ph-C), 128.3 (Ph-C).

 **4-Phenylacetophenone**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.72 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.66 (d, *J* = 7.6 Hz, 2H, Ph-H), 7.50 (t, *J* = 7.4 Hz, 2H, Ph-H), 7.43 (t, *J* = 7.2 Hz, 1H, Ph-H), 2.67 (s, 3H, $-CH_3$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8 (-CO-), 145.8 (Ph-C), 139.9 (Ph-C), 135.9 (Ph-C), 129.0 (Ph-C), 128.9 (Ph-C), 128.3 (Ph-C), 127.3 (Ph-C), 127.3 (Ph-C), 26.7 ($-CH_3$).

^{1}H NMR , ^{13}C NMR and MS spectra for catalytic products of complex 3

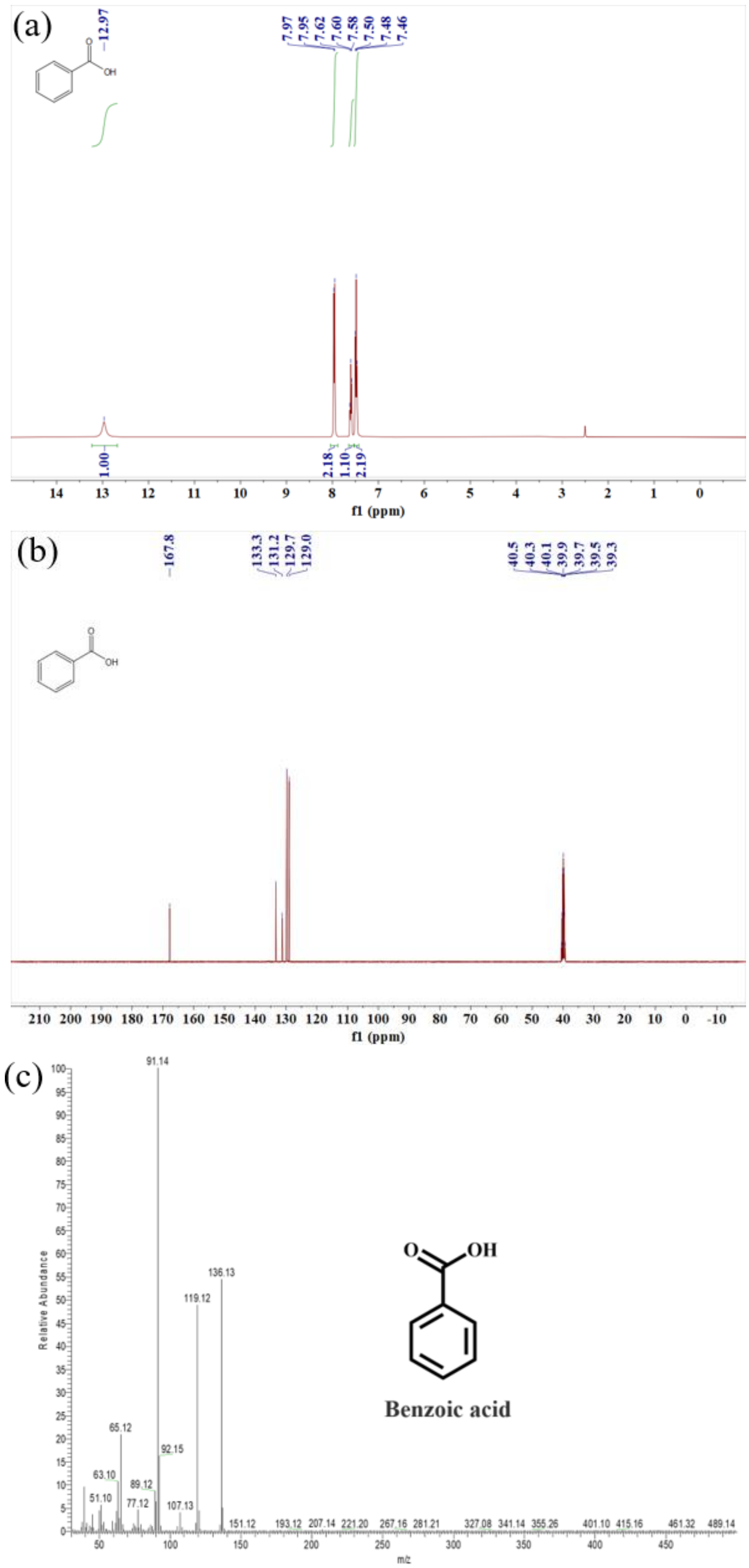


Fig. S6 ^{1}H NMR (a), ^{13}C NMR (b) and MS (c) spectra of benzoic acid

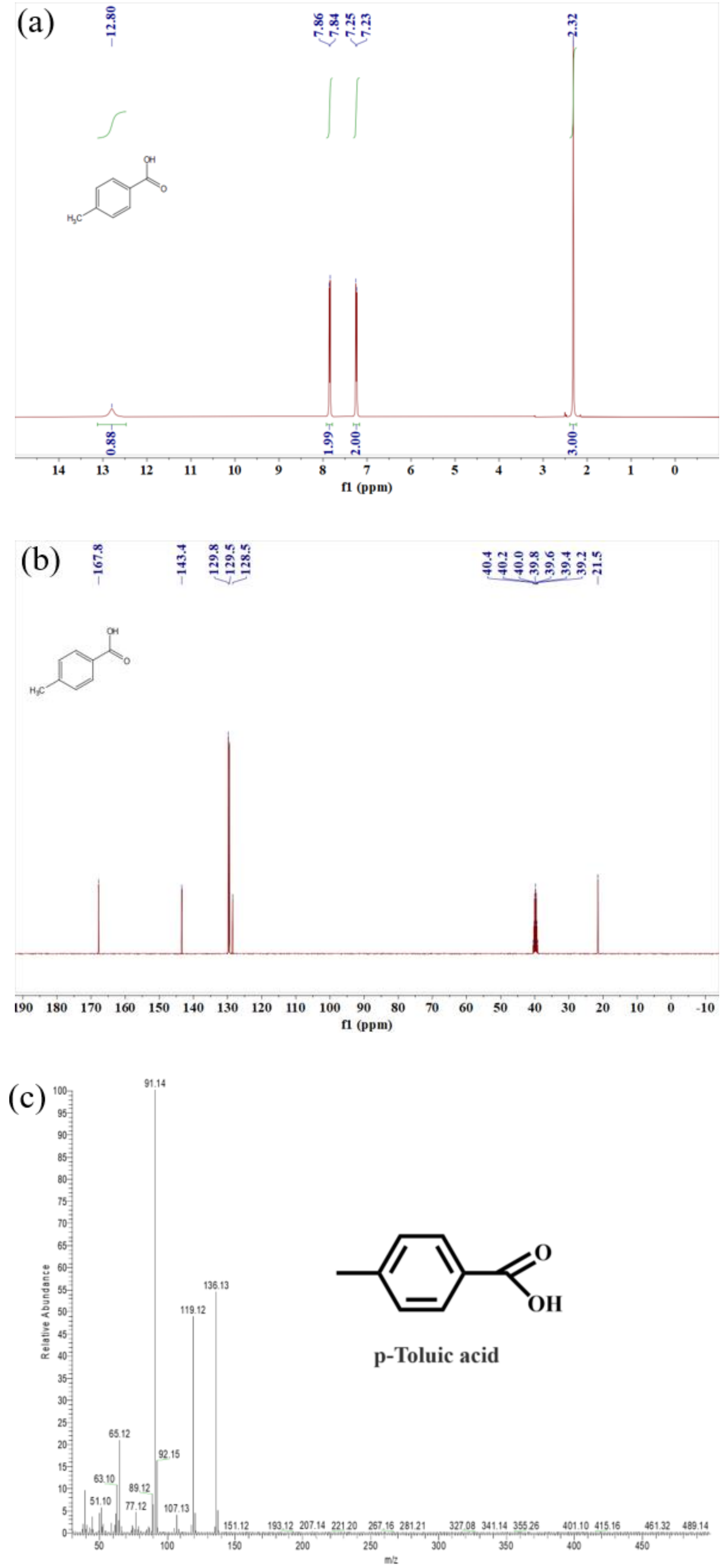


Fig. S7 ^{1}H NMR (a), ^{13}C NMR (b) and MS (c) spectra of p-toluic-acid

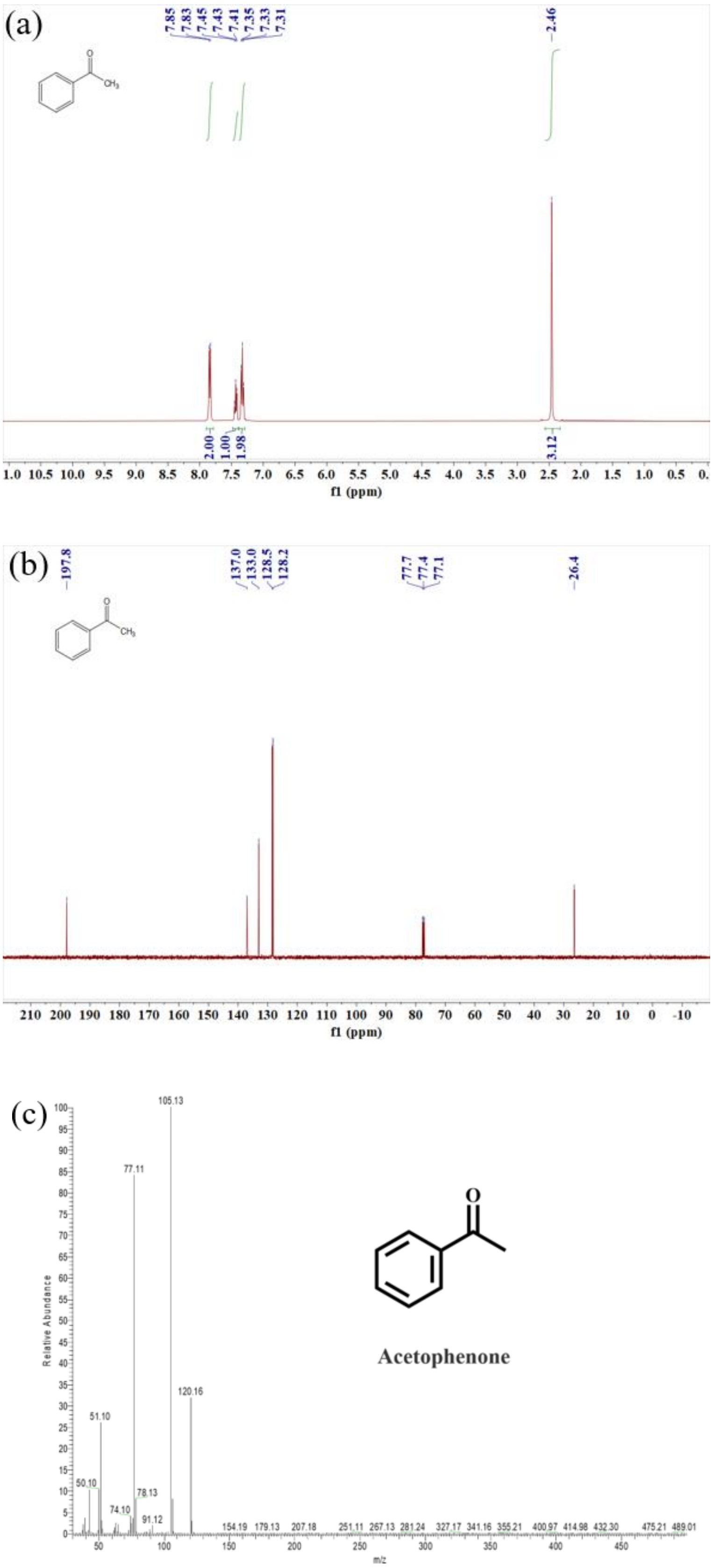


Fig. S8 ^{1}H NMR (a), ^{13}C NMR (b) and MS (c) spectra of acetophenone

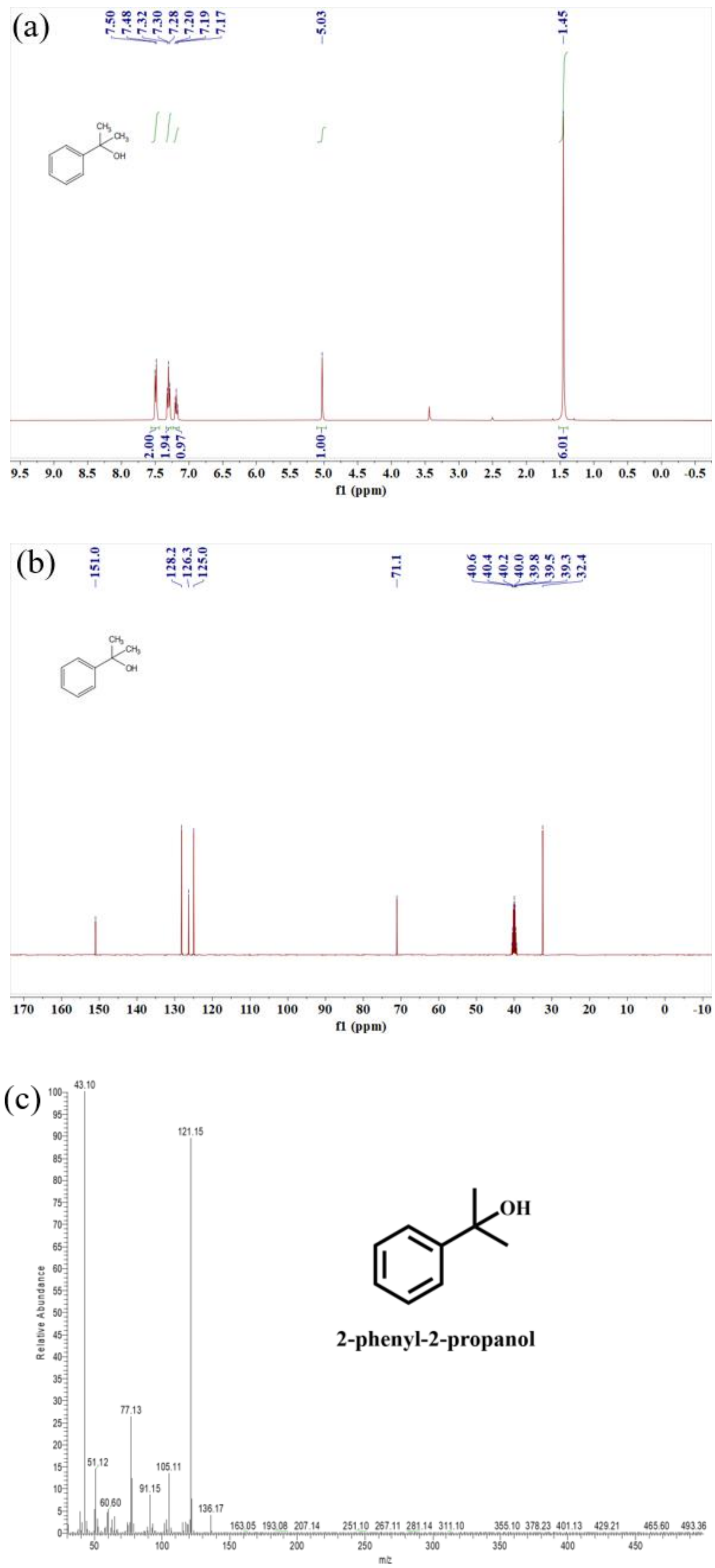


Fig. S9 [1]H NMR (a), [13]C NMR (b) and MS (c) spectra of 2-phenyl-2-propanol

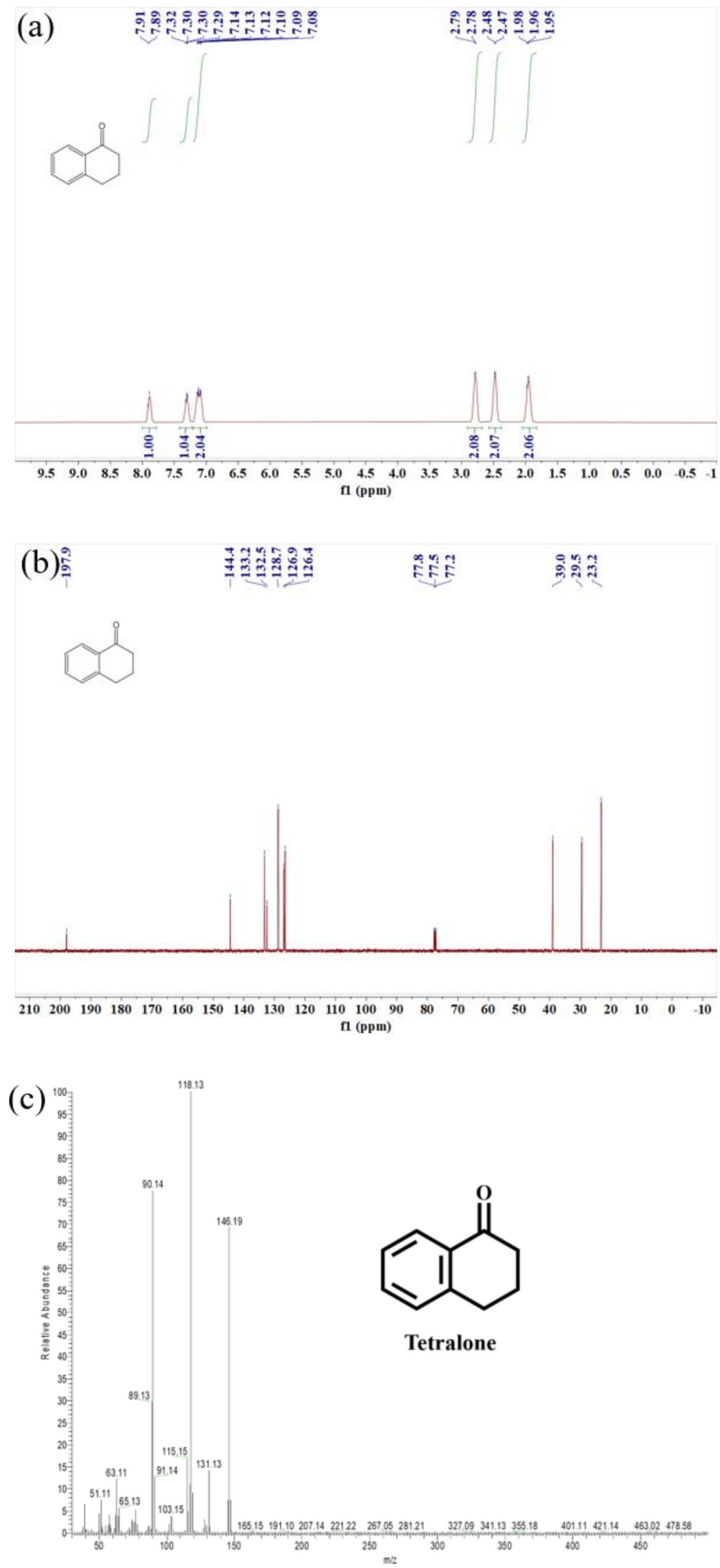


Fig. S10 ^{1}H NMR (a), ^{13}C NMR (b) and MS (c) spectra of tetralone

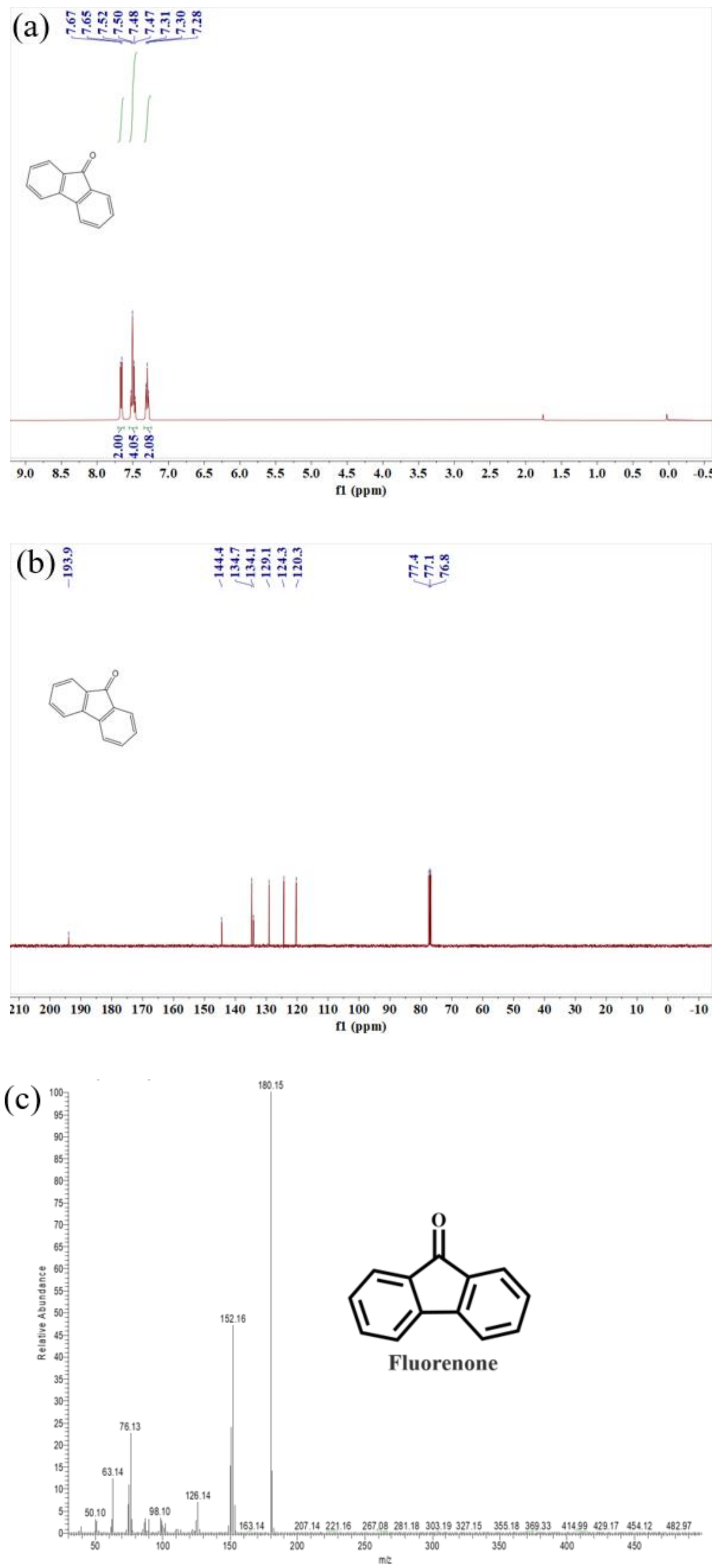
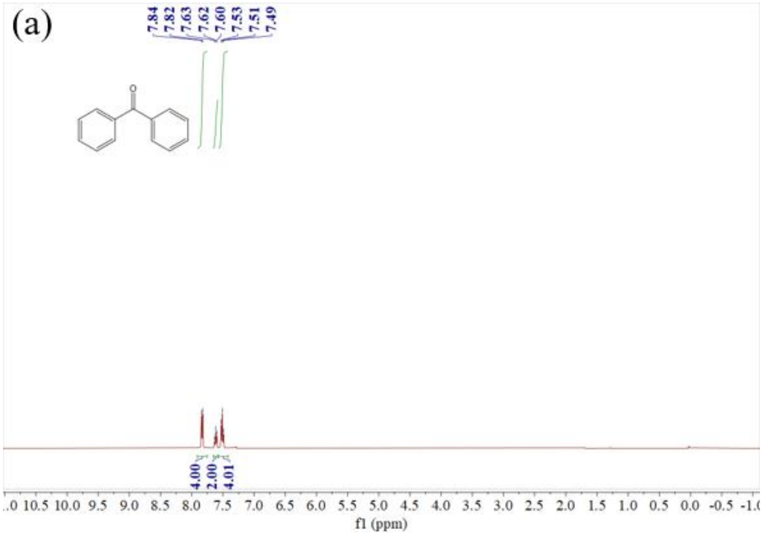
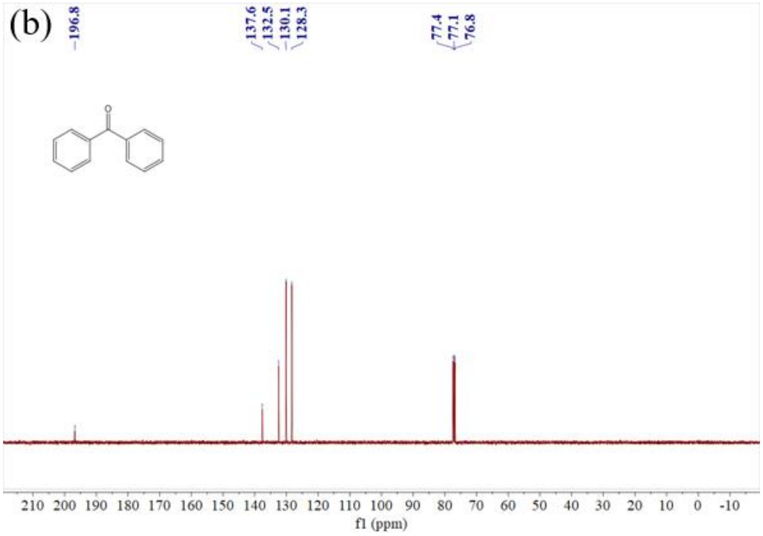


Fig. S11 ^{1}H NMR (a), ^{13}C NMR (b) and MS (c) spectra of fluorenone





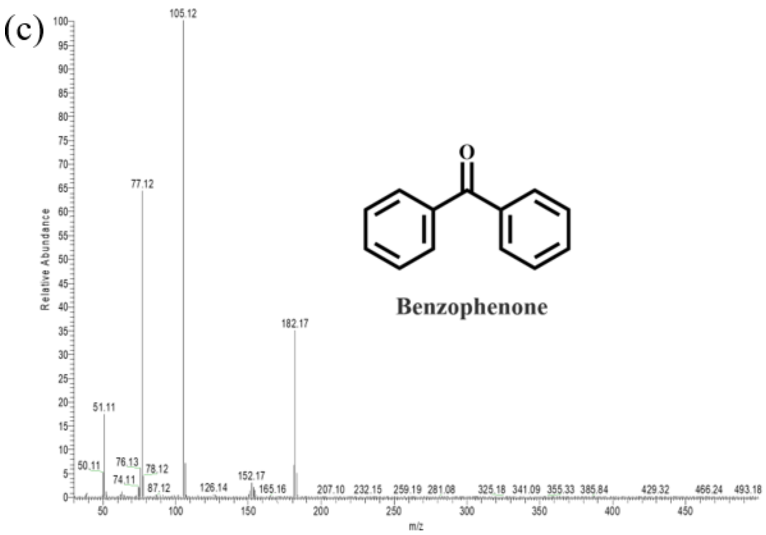


Fig. S12 [1]H NMR (a), [13]C NMR (b) and MS (c) spectra of benzophenone

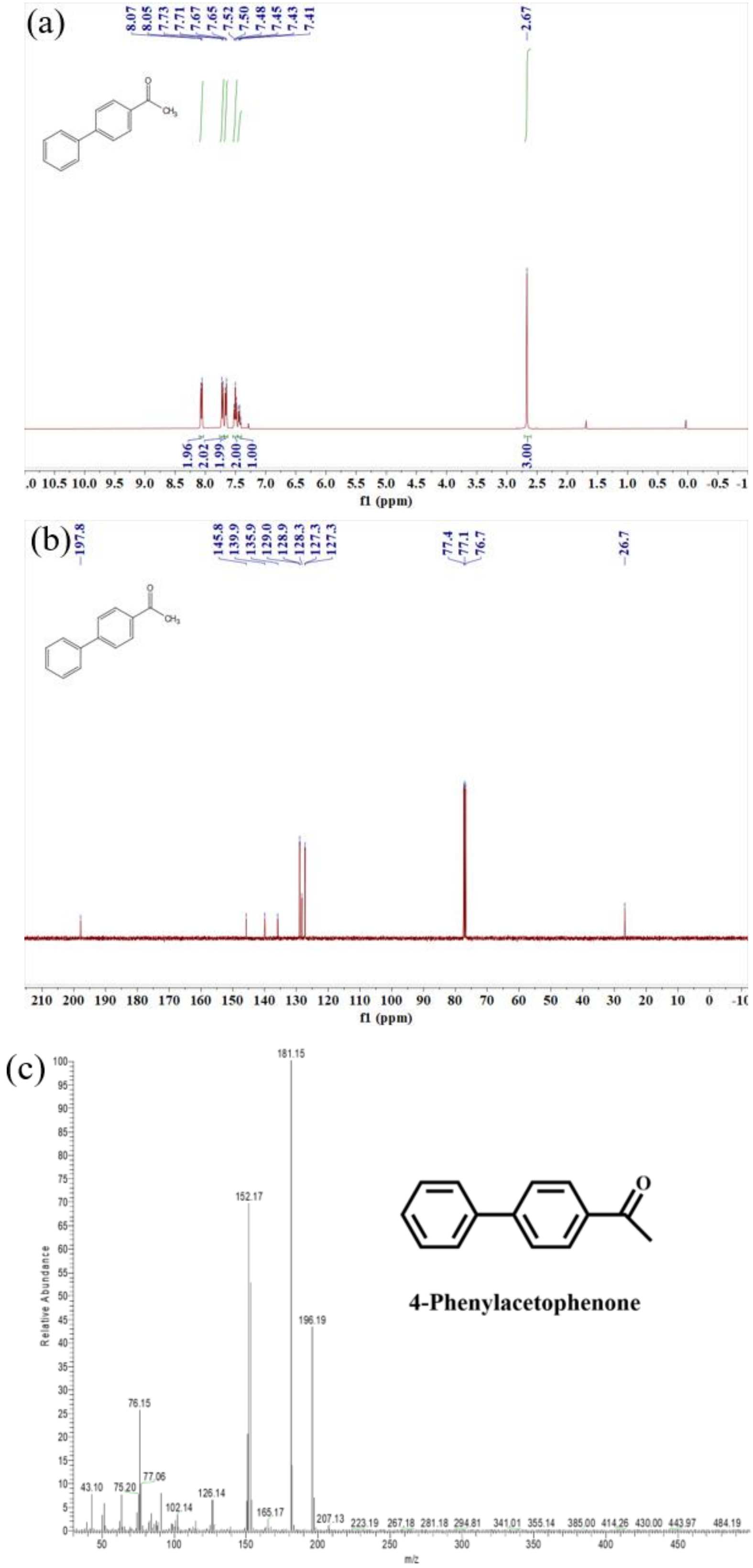


Fig. S13 ^{1}H NMR (a), ^{13}C NMR (b) and MS (c) spectra of 4-phenylacetophenone

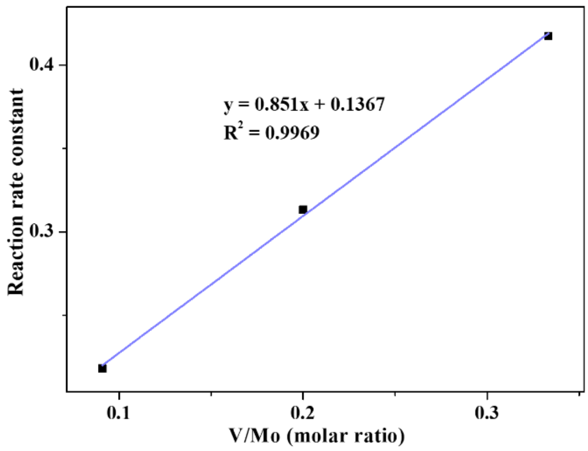


Fig. S14 Reaction rates as a function of V/Mo molar ratio in complexes **1-3**.

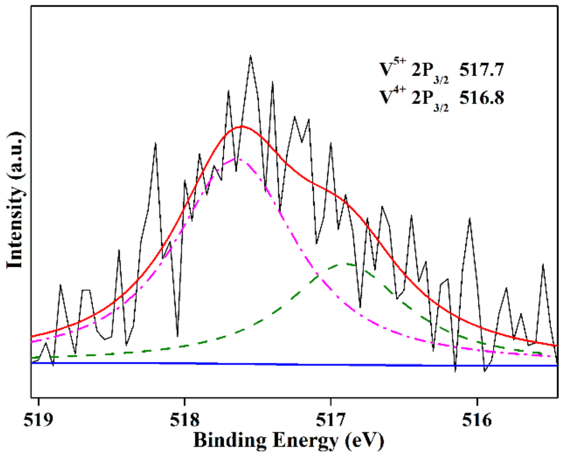


Fig. S15 Fluxion of V^{5+} and V^{4+} ions evidenced by XPS spectrum.