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# Boosting Activity of Molecular Oxygen by Pyridinium-based Photocatalysts for Metal-free Alcohol Oxidation

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## Section 1. Experimental section

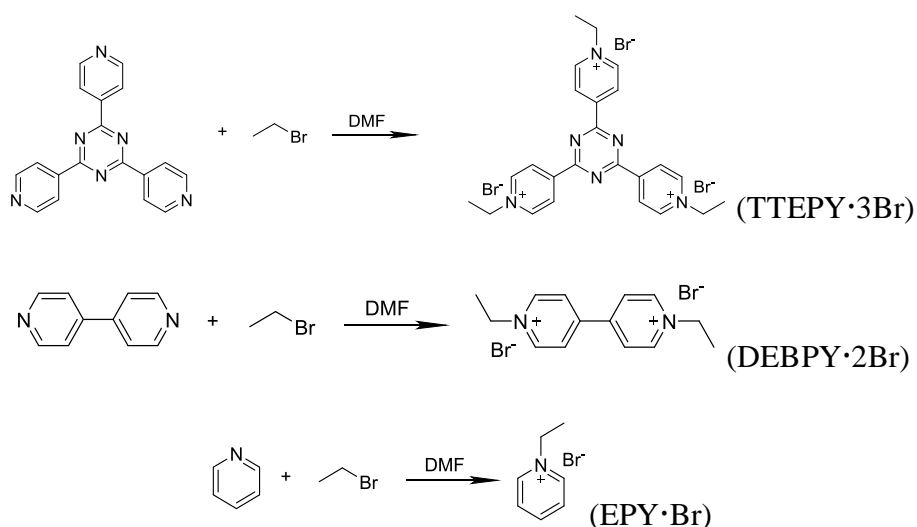
### 1.1 Materials and methods

All of the chemicals were obtained from commercial sources and were used as received unless otherwise stated. IR spectra (KBr pellets) were obtained on a Nicolet IS10 FT-IR spectrometer. The UV-Vis absorption spectra were measured with a Shimadzu UV3600 Spectrometer. The electron spin resonance (ESR) signal was collected with BRUKER ELEXSYS E580 and JES-FA200 ESR Spectrometer.  $^1\text{H}$  NMR spectrum was carried out on a Bruker AV-400 and AV-700 NMR spectrometer. The GC analyses were performed on Shimadzu GC-2014C with an FID detector equipped with an Rtx-5 capillary column. The 395nm light source was obtained by MLED4 system from Zolix Instruments Co.,Ltd. White light-induced catalysis reactions were tested by Beijing Perfectlight Multi-channel photochemical reaction system PCX-50C. The electrochemical analysis was carried out using a CHI 660E electrochemical workstation by Shanghai Chenhua Instrument.

### 1.2 The synthesis of pyridinium-based photocatalysts

TTEPY·3Br, DEBPY·2Br and EPY·Br were synthesized based on a direct Menshutkin reaction of pyridine derivatives and bromoethane. Typically, a mixture of commercially available 2,4,6-tris-(4-pyridyl)-1,3,5-triazine (2.00 g, 6.4 mmol) and bromoethane (2.00 mL, 26.6 mmol) was dissolved in 100 mL of DMF and then stirred at 110 °C for 12 h. After the mixture was cooled to room temperature, the resulting precipitate was collected by filtration, washed with DMF for once and MeCN for three times. After dried in an air oven at 80 °C, TTEPY·3Br is obtained as gold yellow powder 3.19g (yield 77.8%). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3394(s), 3116(w), 3039(m), 1639(m), 1585(w), 1527(s), 1456(w), 1371 (s), 1323(w), 1176(w), 823(m), 748(w), 530(w).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  = 9.26 (d,  $J=6.8$ , 2H), 9.18 (d,  $J=6.9$ , 2H), 4.77 (q,  $J=7.4$ , 2H), 1.69 (t,  $J=7.4$ , 3H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{D}_2\text{O}$ )  $\delta$  168.92, 148.78, 144.97, 126.71, 57.36, 15.09. Yellow solid product DEBPY·2Br was obtained as was TTEPY·3Br, but 4,4'-bipyridine (2.00 g, 12.80 mmol) instead of 2,4,6-tris-(4-pyridyl)-1,3,5-triazine was dissolved in 50 mL of DMF. 2.88g (Yield: 60.1%). IR (KBr pellet,  $\text{cm}^{-1}$ ) for DEBPY·2Br: 3411(m), 3334(w), 3241(w), 3110(w), 3037(m), 2989(s), 2861(w), 1639(s), 1563(m), 1563(m), 1509(s), 1448(s), 1376(m), 1226(m), 1182(s), 1081(m), 856(s), 713(m), 493(m).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  = 9.06 (d,  $J=6.8$ , 2H), 8.47 (d,  $J=6.0$ , 2H), 1.64 (t,  $J=7.4$ , 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ )  $\delta$  150.01, 145.22,

127.03, 57.69, 15.64. White EPY·Br powder was obtained by following step: pyridine (2 mL, 25.8 mmol) and bromoethane (2.00mL, 26.6mmol) was mixed and then stirred at 110 °C for 12 h to give white precipitate. The residual pyridine and bromoethane were removed by rotary evaporator at 80 °C for 4 hours to give EPY·Br. IR (KBr pellet,  $\text{cm}^{-1}$ ) for EPY·Br: 3419(m), 3126(w), 3045(m), 2969(w), 2937(w), 2873(w), 2057(w), 1633(s), 1581(w), 1486(s), 1384(w), 1359(w), 1315(m), 1241(w), 1186(w), 1172(s), 1093(w), 1058(w), 783(s), 682(s), 577(w), 478(w).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  = 8.80 (d,  $J=5.7$ , 2H), 8.47 (t,  $J=7.9$ , 1H), 8.00 (t,  $J=6.9$ , 2H), 4.59 (q,  $J=7.4$ , 2H), 1.58 (t,  $J=7.4$ , 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ )  $\delta$  145.58, 144.05, 128.40, 57.46, 15.93.



**Scheme S1.** Route to synthesize TTEPY·3Br, DEBPY·2Br and EPY·Br

### 1.3 X-ray crystallographic analysis

The X-ray diffraction data of TTEPY·3Br was collected on a Gemini A Ultra diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. The absorption correction was performed by using the multi-scan program and the structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using the SHELXL-2016 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were calculated in ideal positions and refined by riding on their respective carbon atoms.

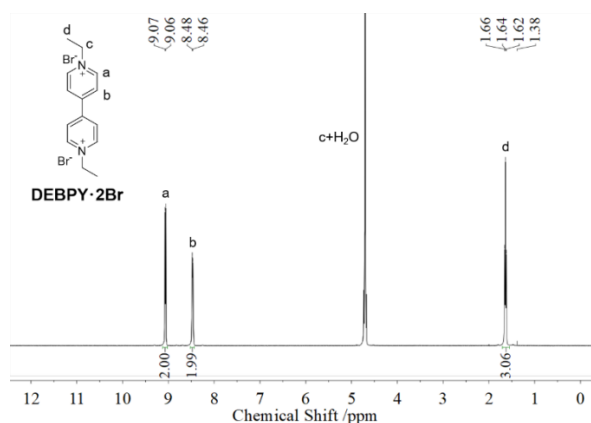
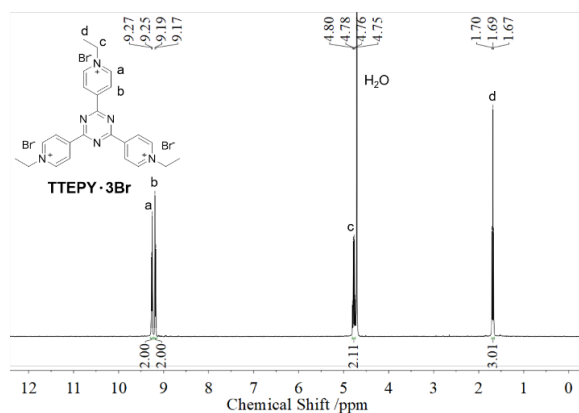
**Crystal data.** C<sub>24</sub>H<sub>27</sub>N<sub>6</sub>Br<sub>3</sub>; *Mr* = 639.25; trigonal R3m *a* = 16.647(3) Å, *b* = 16.647(3) Å, *c* = 7.749(3) Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ , *V* = 1859.6(9) Å<sup>3</sup>; *T* = 293(2) K; *Z* = 3; *D*<sub>calcd</sub> = 1.712 g cm<sup>-3</sup>;  $\mu = 4.906$  mm<sup>-1</sup>; *F*(000) = 954.0; 1042 reflections collected of which 594 unique (*R*<sub>int</sub> = 0.0537); *GOF* = 1.000; *R*<sub>1</sub> = 0.0522 and *wR*<sub>2</sub> = 0.2198 [*I* > 2σ(*I*)]. CCDC 2024746

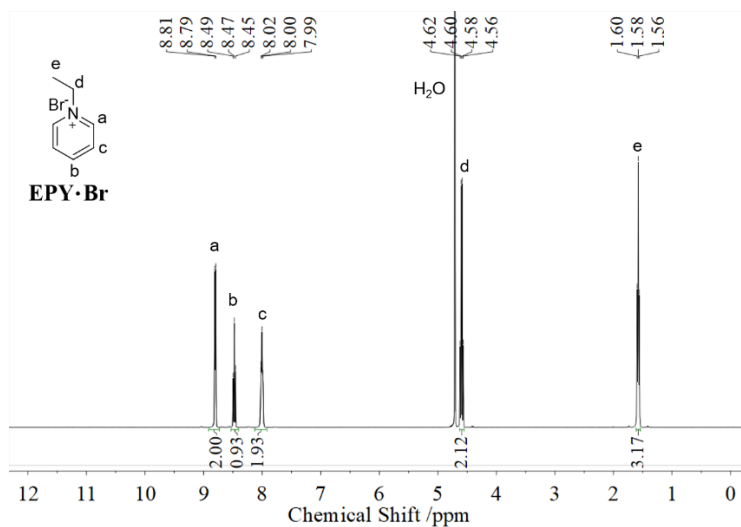
## 1.4 Photocatalytic reaction

In general, a mixture of 2 μmol of TTEPY·3Br (or DEBPY·2Br, EPY·Br), 0.2 mmol alcohols (0.1 mmol for the reactions under white light irradiation) and 2 ml acetonitrile was placed in a quartz tube. The photoinduced oxidation reaction was initiated at room temperature in air atmosphere under light irradiation. The conversion of the product was calculated by GC analysis. The other control experiments were carried out under the same condition except changed of substrate, wavelengths, or exposure to N<sub>2</sub> atmosphere.

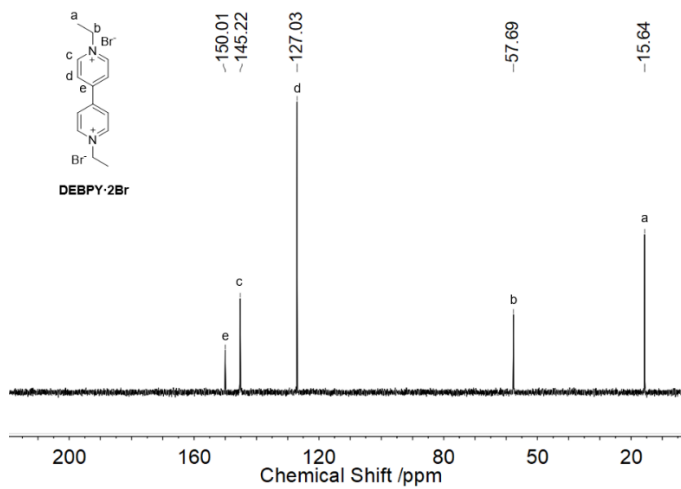
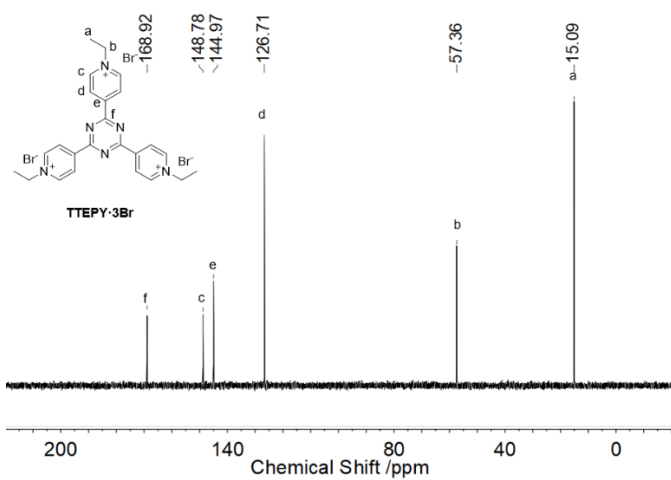
## Section 2. Additional data and figures

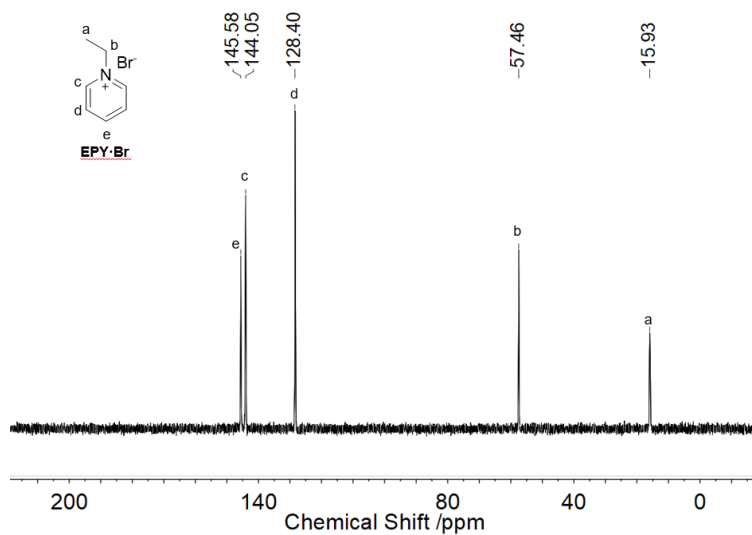
### <sup>1</sup>H NMR



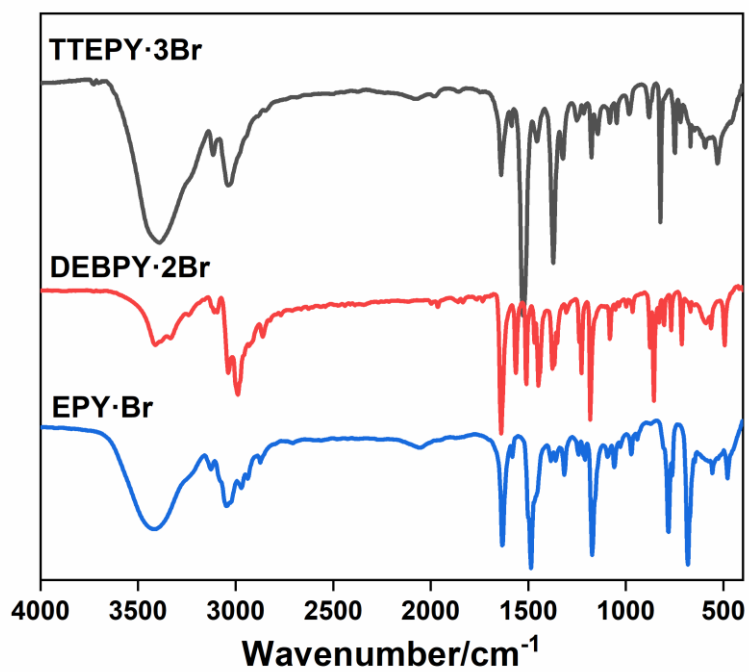


<sup>13</sup>C NMR

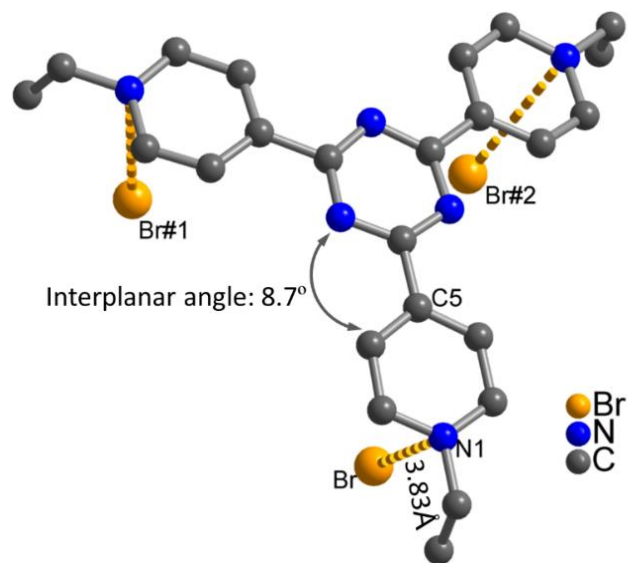




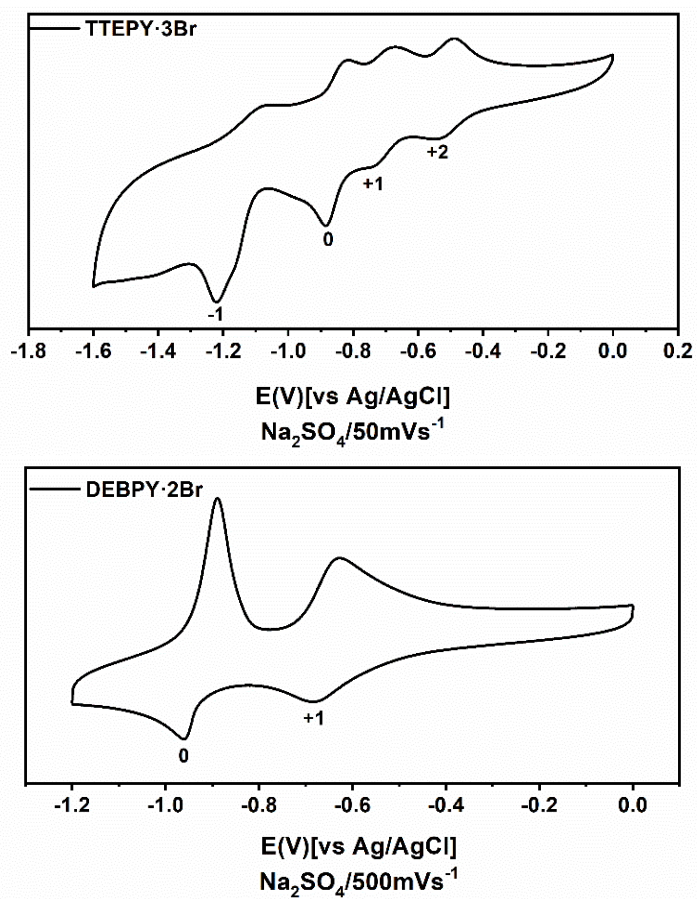
**Figure S1.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of TTEPY·3Br, DEBPY·2Br and EPY·Br in D<sub>2</sub>O.

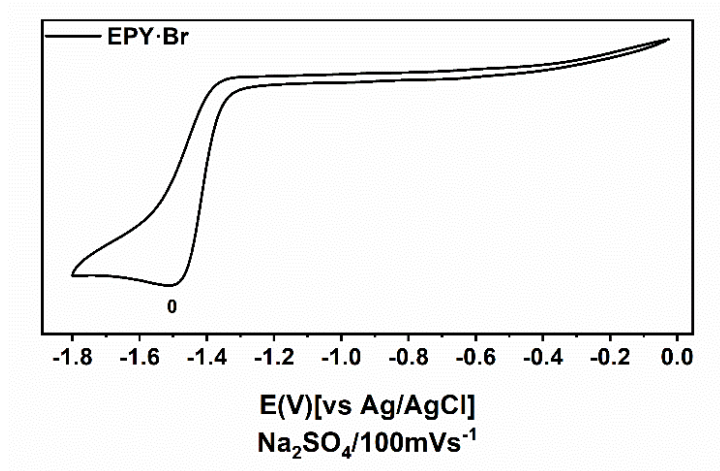


**Figure S2.** FT-IR spectra of TTEPY·3Br, DEBPY·2Br and EPY·Br.

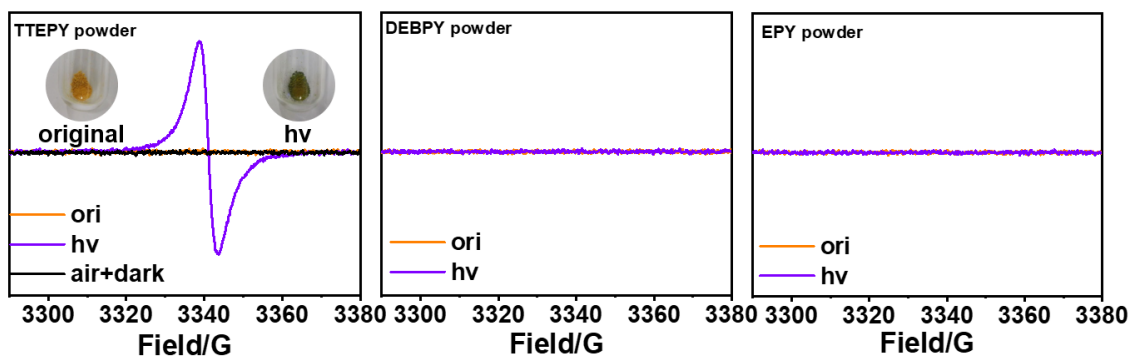


**Figure S3.** The molecular structure of TTEPY·3Br obtained by X-ray single crystal diffraction method.

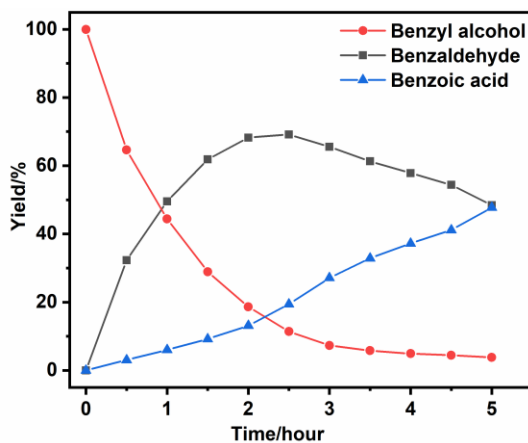




**Figure S4.** The cyclic voltammograms of TTEPY·3Br, DEBPY·2Br and EPY·Br.

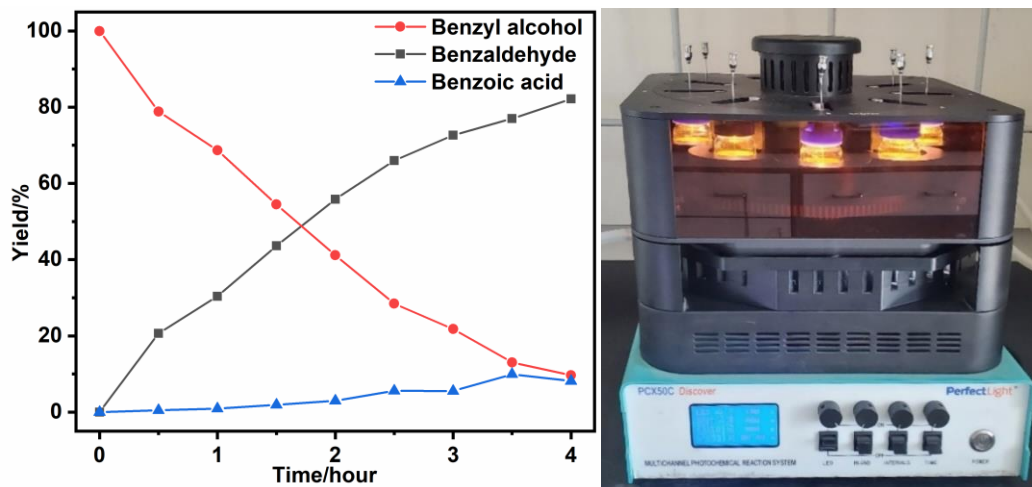


**Figure S5.** The ESR spectra of TTEPY·3Br, DEBPY·2Br and EPY·Br powder under irradiation of 395 nm LED in  $N_2$  condition (tested by BRUKER ELEXSYS E580 ESR Spectrometer). The insets in the figure on the left show the color change of TTEPY·3Br before and after light irradiation.

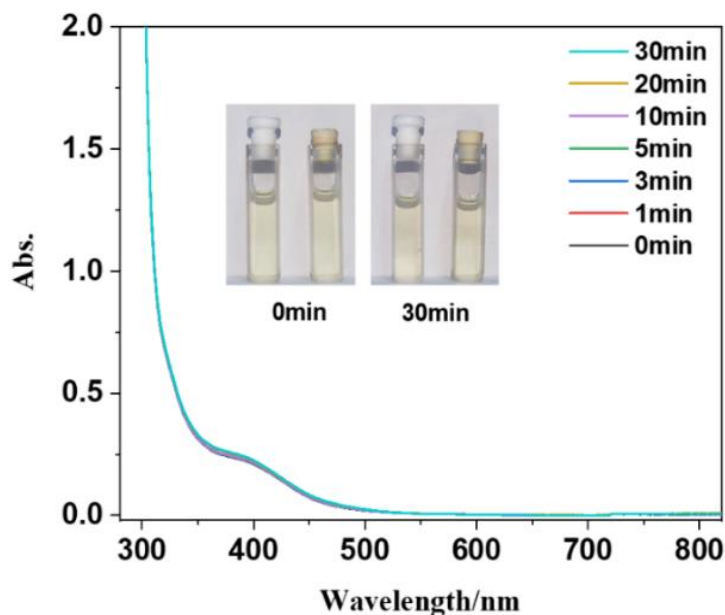


**Figure S6.** Reaction conditions: benzyl alcohol: 0.2 mmol; catalyst: 1 mol%, 2 mL acetonitrile; in air condition; room temperature; light source:  $\lambda = 395$  nm (450 mW).

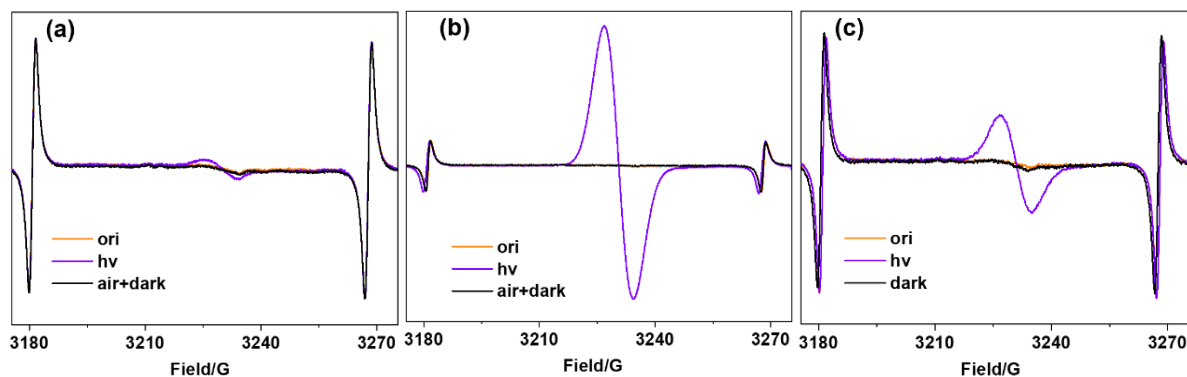




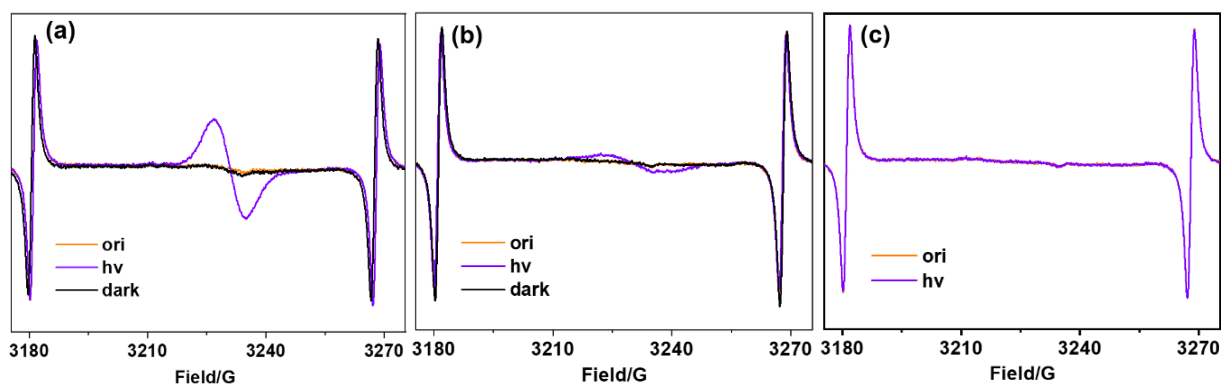
**Figure S7.** (left) Reaction conditions: benzyl alcohol: 0.1 mmol; catalyst: 2 mol%, 2 mL acetonitrile; in air condition; room temperature. (right) The digital photo of the photocatalytic reactor for white light-induced photocatalytic reactions.



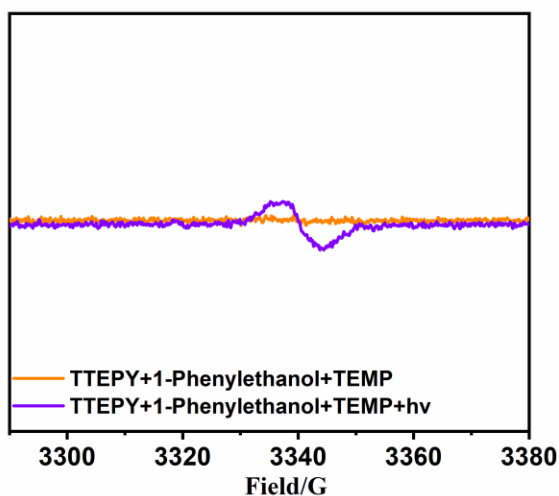
**Figure S8.** UV-vis spectral evolution of TTEPY·3Br in  $N_2$ -saturated MeCN solution upon 395 nm light irradiation. The insets show the image of TTEPY·3Br in  $N_2$ -saturated MeCN solution before and after irradiation. The sample cell on the left in each photo is used for reference without irradiation.



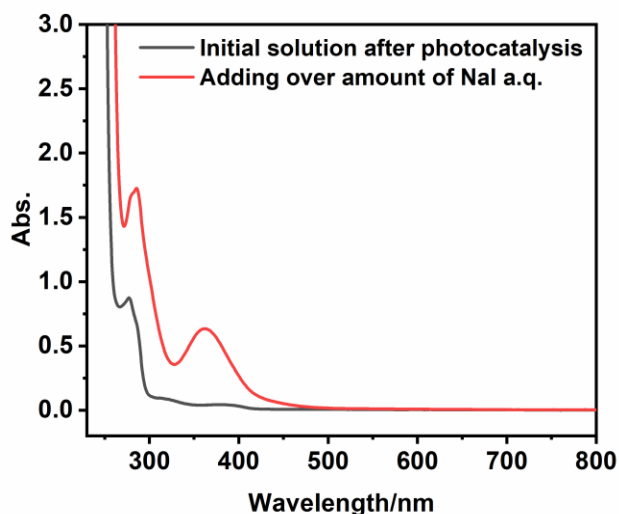
**Figure S9.** (a) The ESR spectral changes of TTEPY·3Br in  $N_2$ -saturated MeCN solution under 395 nm light irradiation for 1 min. (b) The ESR spectral change of TTEPY·3Br and 1-phenylethanol in  $N_2$ -saturated MeCN solution under 395 nm light irradiation for 1 min. (c) The ESR spectral change of TTEPY·3Br and 1-phenylethanol in MeCN solution in an air atmosphere under 395 nm light irradiation for 1 min. (tested by JES-FA200 ESR Spectrometer). The internal standard signals are shown on the two sides for comparison.



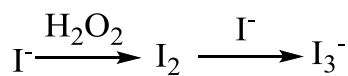
**Figure S10.** The ESR spectra of the mixtures of 1-phenylethanol and TTEPY·3Br (a), 1-phenylethanol and DEBPY·2Br (b), 1-phenylethanol and EPY·Br (c) in MeCN solution under air atmosphere before and after 395 nm light irradiation (tested by JES-FA200 ESR Spectrometer). The internal standard signals are shown on the two sides for comparison.





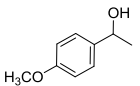
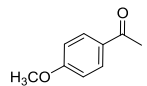
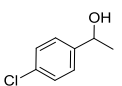
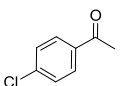
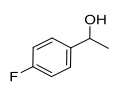
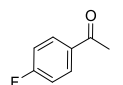
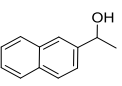
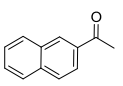


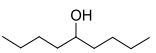
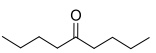
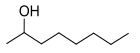
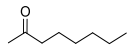




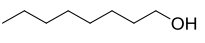
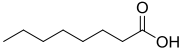
**Figure S11.** ESR spectra of the mixtures of 1-phenylethanol and TTEPY·3Br in presence of TEMP before and after irradiation. (tested by BRUKER ELEXSYS E580 ESR Spectrometer).



**Figure S12.** UV-Vis absorption spectra of the tri-iodide formed by H<sub>2</sub>O<sub>2</sub> oxidation. The formation of H<sub>2</sub>O<sub>2</sub> was confirmed by monitoring tri-iodide (I<sub>3</sub><sup>-</sup>) in aqueous solution. When over amount of NaI was added to the reaction solution, the characteristic peak of I<sub>3</sub><sup>-</sup> ions at ca.360 nm appeared due to the following reactions [ref.: W. Huang, B. C. Ma, H. Lu, R. Li, L. Wang, K. Landfester, K. A. I. Zhang, *ACS Catal.* 2017, **7**, 5438-5442]:



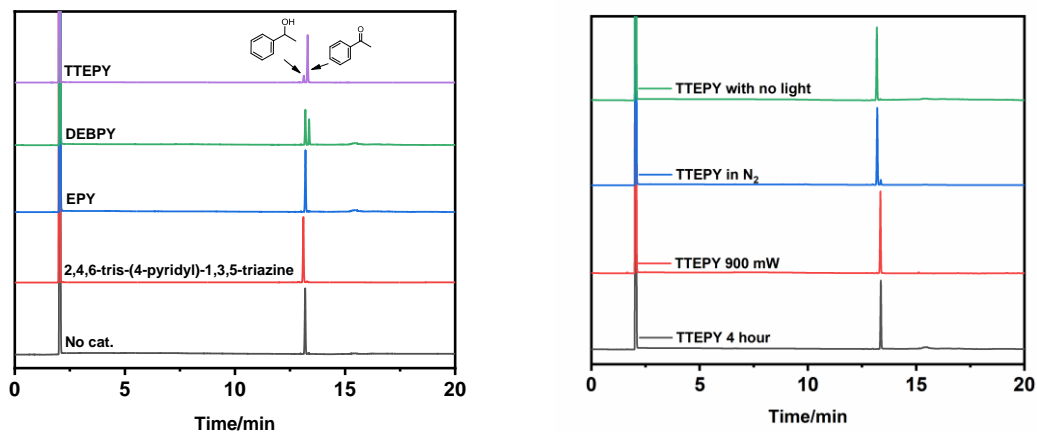
**Table S1.** General substrate scope for the oxidations of alcohols under the irradiation of white light source

Entry <sup>[a]</sup>	Substrate	Product	Time/h	Conv. <sup>[b]</sup> /%	Sel. <sup>[b]</sup> /%
1			6	95	>99
2			6	94	>99
3			6	96	>99
4			6	95	>99
5			8	98	>99
6			12	89	>99
7			12	19	>99
8			12	19	>99
9			12	16	>99
10			12	7	>99
11			12	5	79

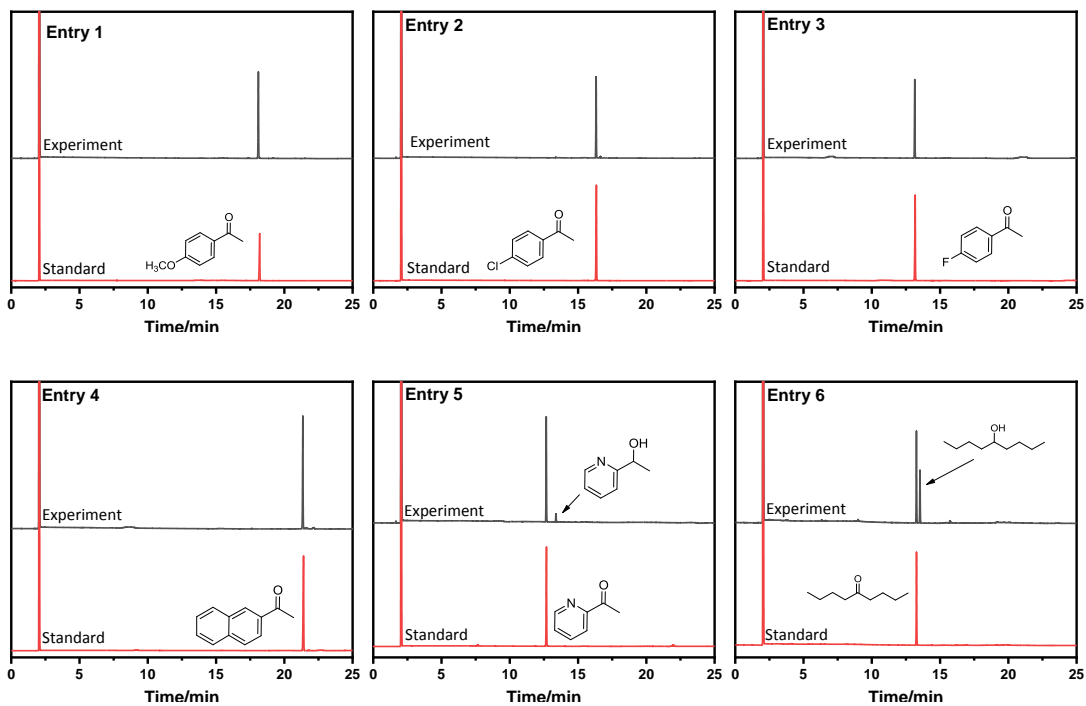
(a) Reaction conditions: irradiation with white light source (180 mW); substrate: 0.1 mmol; catalyst: 2 mol%; 2 mL acetonitrile; in air condition; room temperature. (b) Determined by GC analysis.

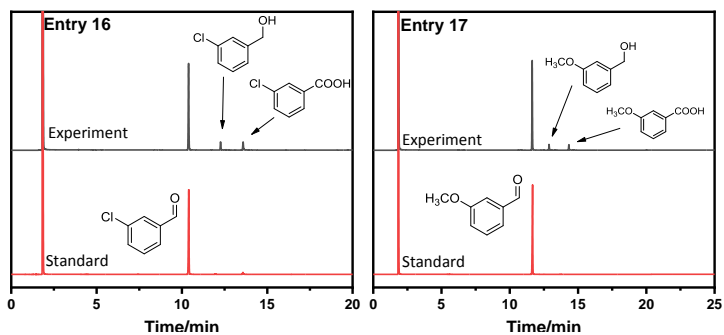
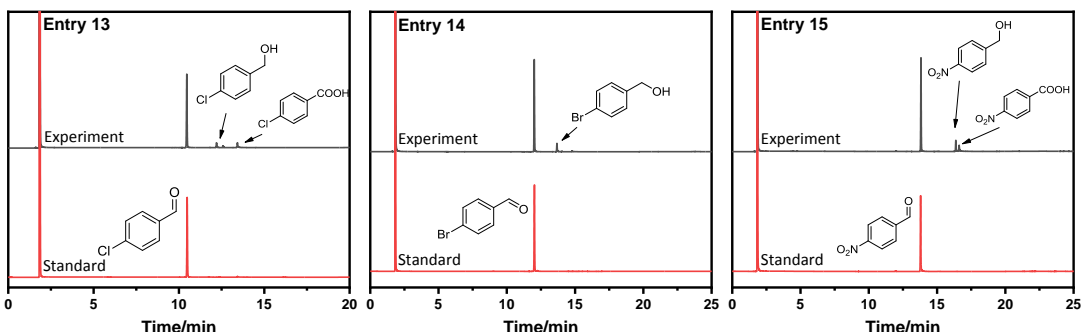
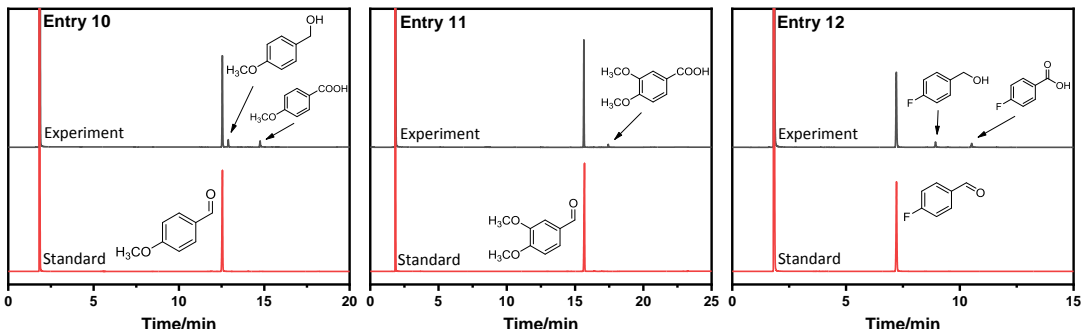
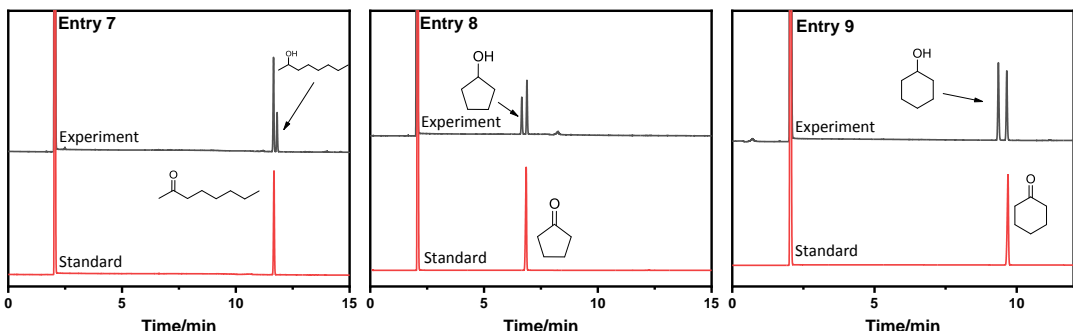
### Section 3. Gas chromatography details

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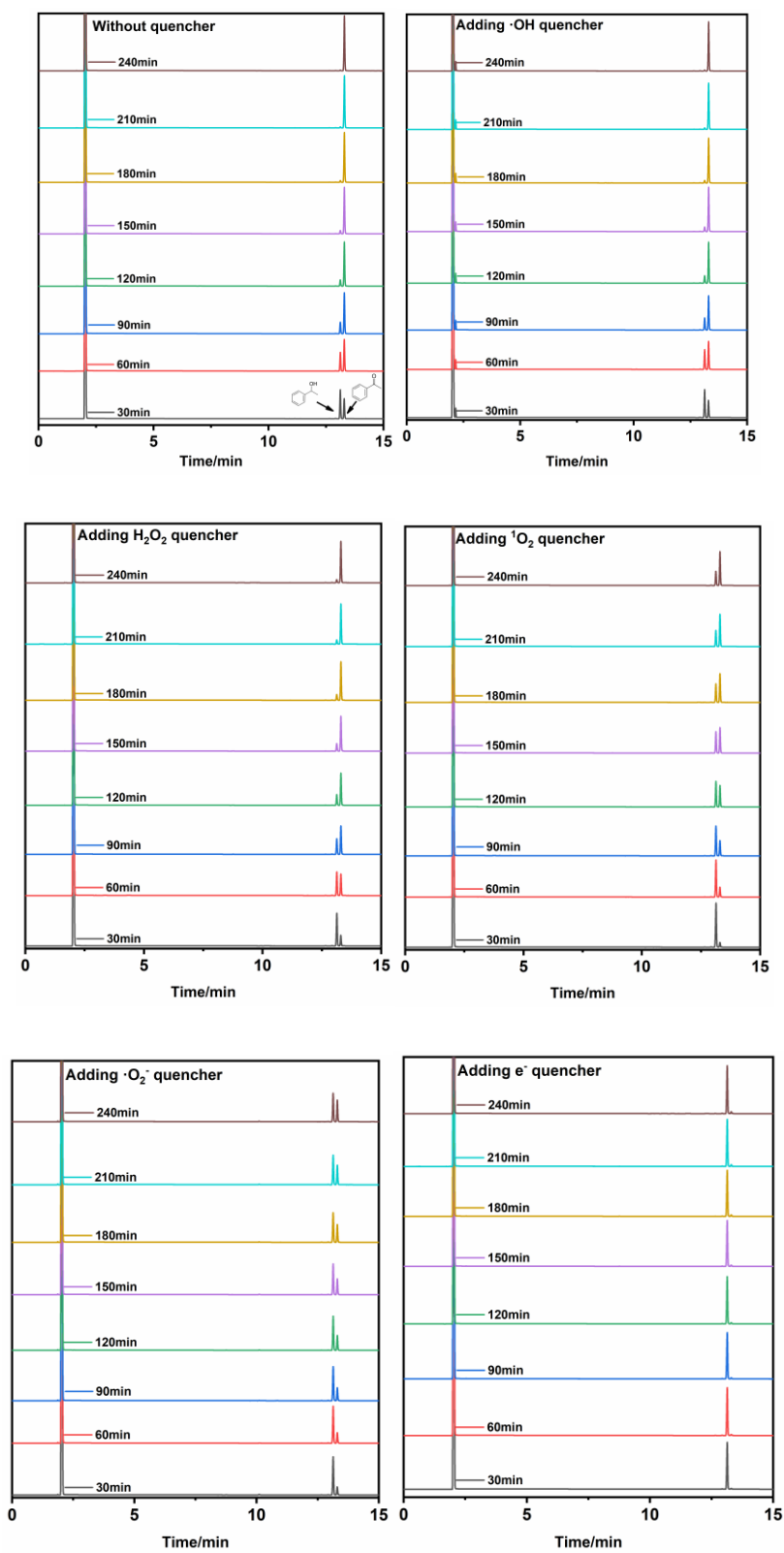


Gas chromatography details of Table 1:

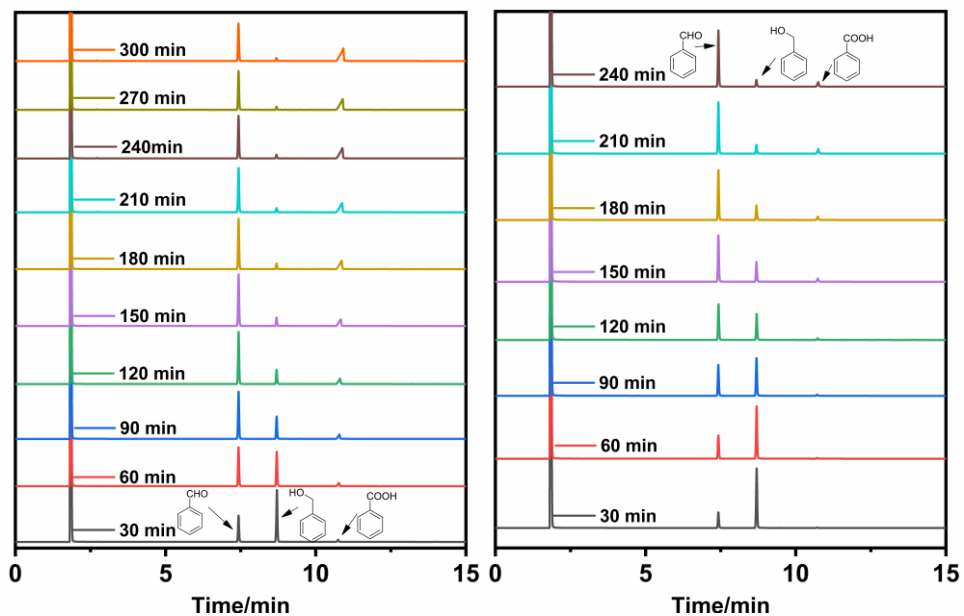




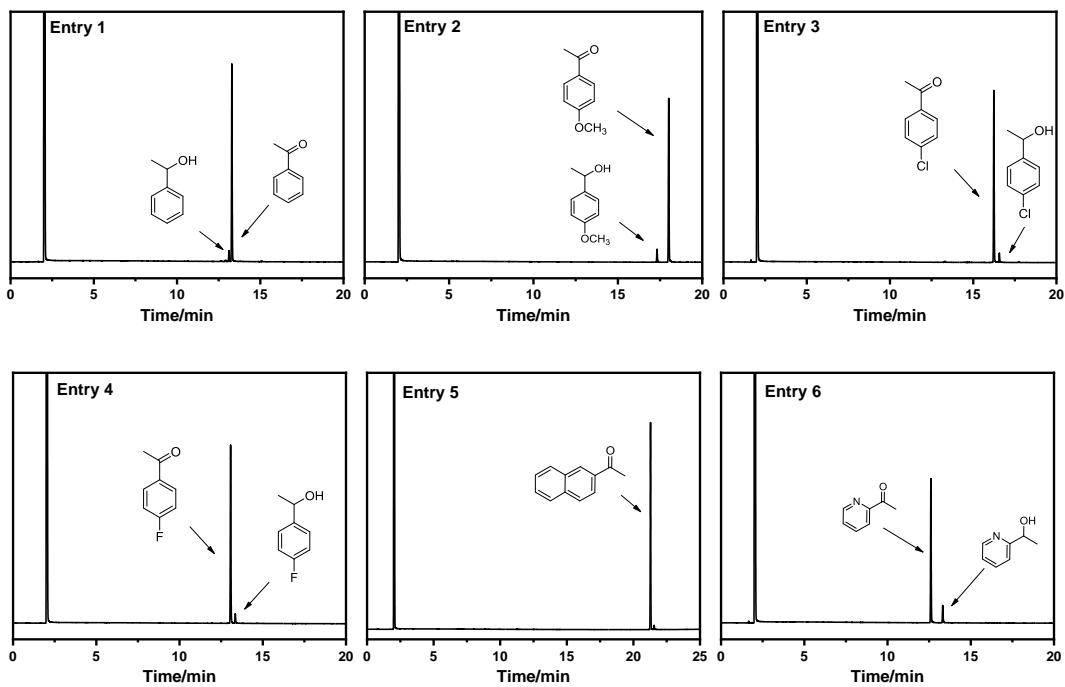
Gas chromatography details of Figure 3:



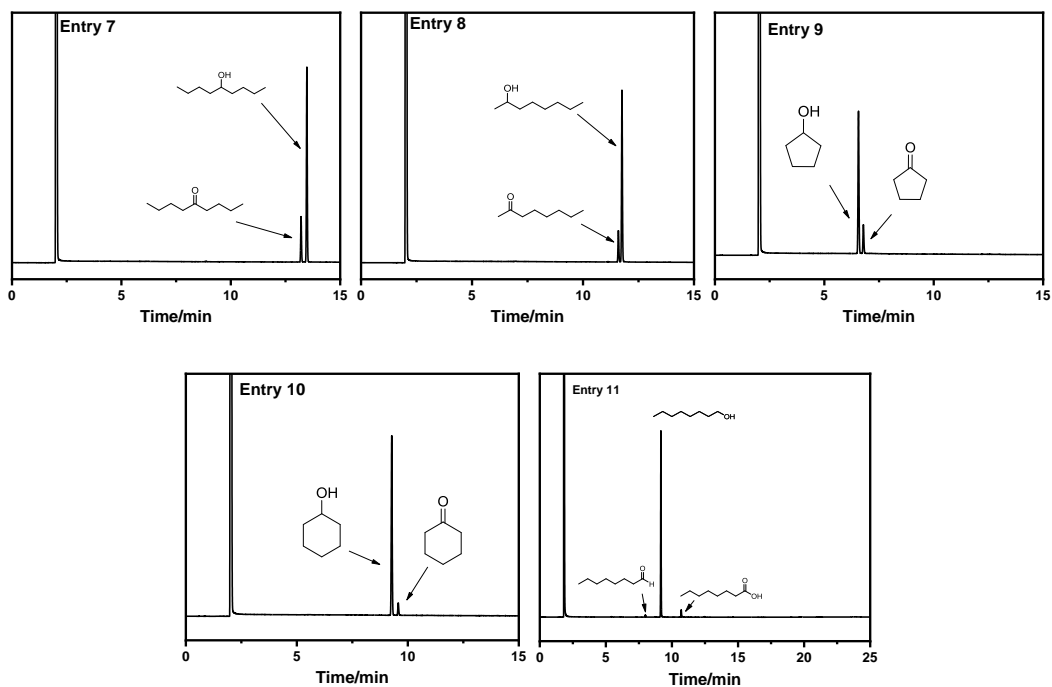
Gas chromatography details of Figure S6 (left), and Figure S7 (right):



Gas chromatography details of Table S1:



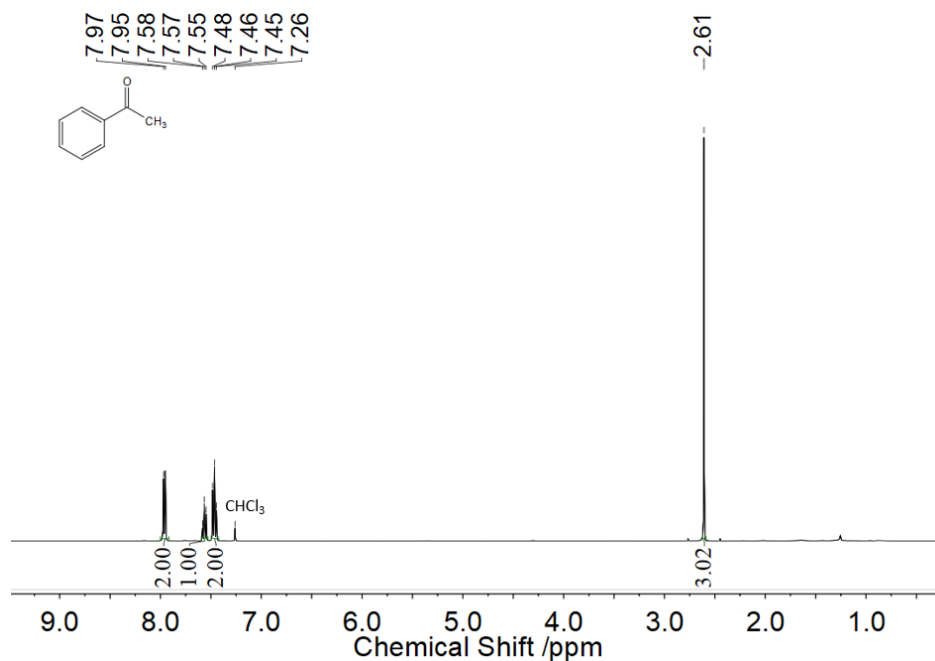




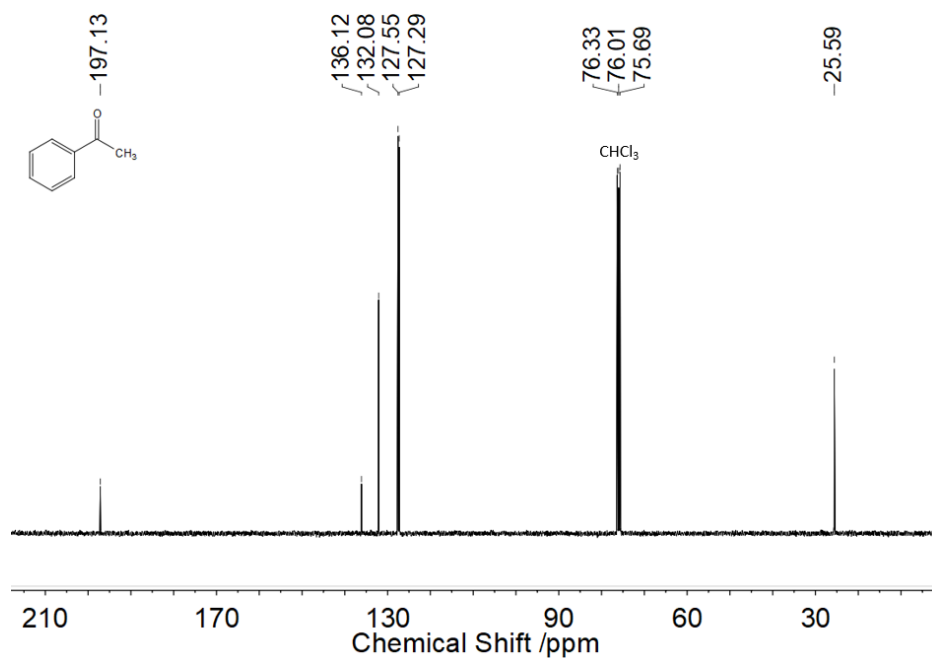
## Section 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR details for isolated products

Acetophenone

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.5$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 2.61 (s, 3H).

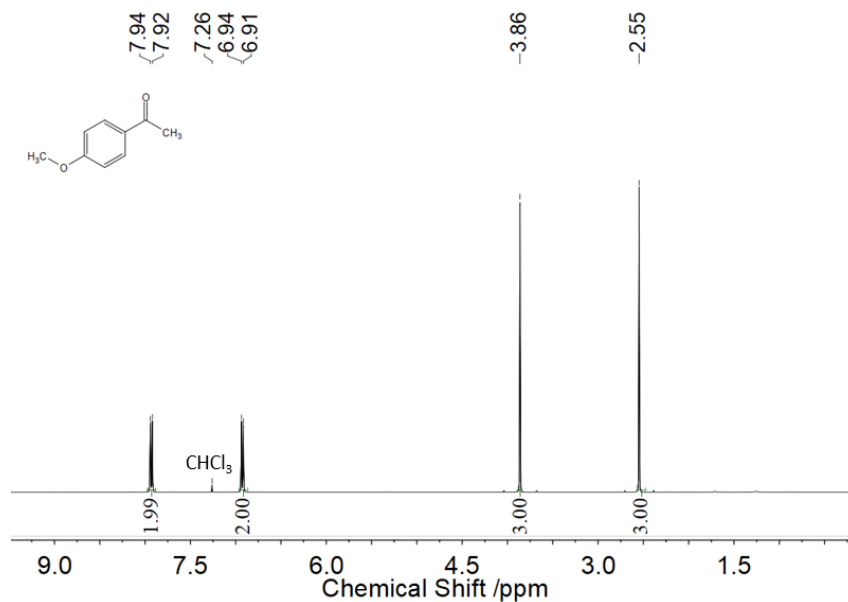


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.13, 136.12, 132.08, 127.55, 127.29, 25.59.

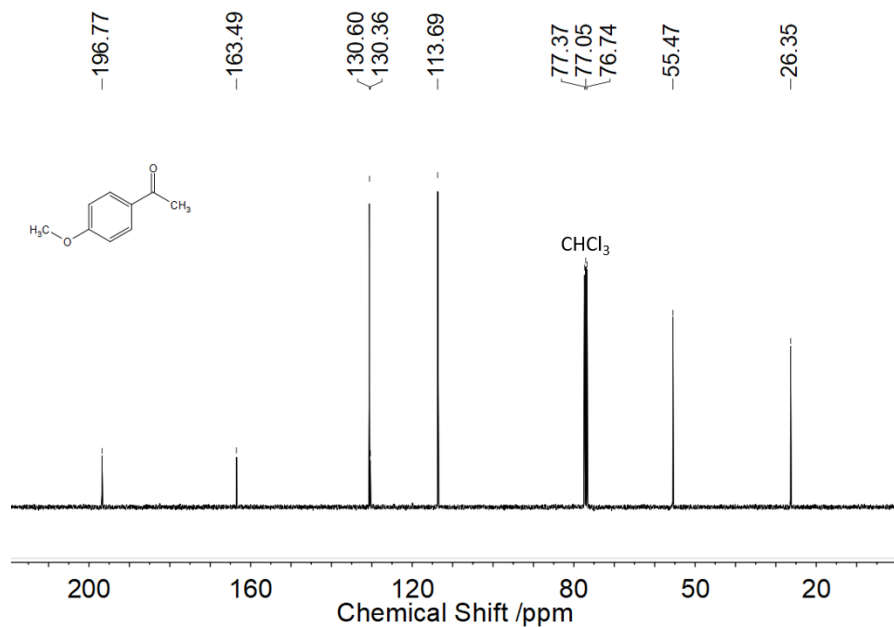


1-(4-methoxyphenyl)ethan-1-one

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.9$  Hz, 2H), 6.92 (d,  $J = 8.9$  Hz, 2H), 3.86 (s, 3H), 2.55 (s, 3H).

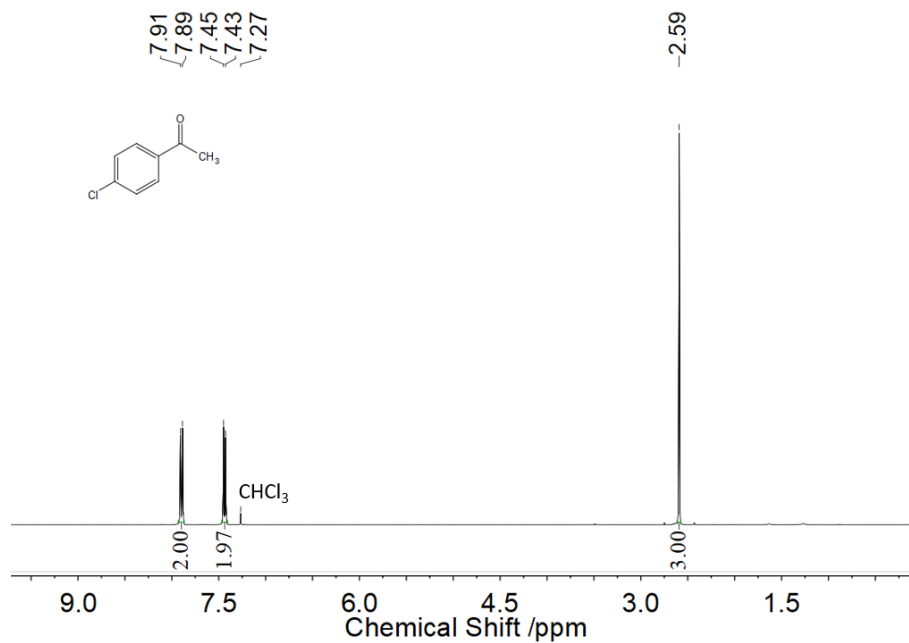


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.77, 163.49, 130.60, 130.36, 113.69, 55.47, 26.35.

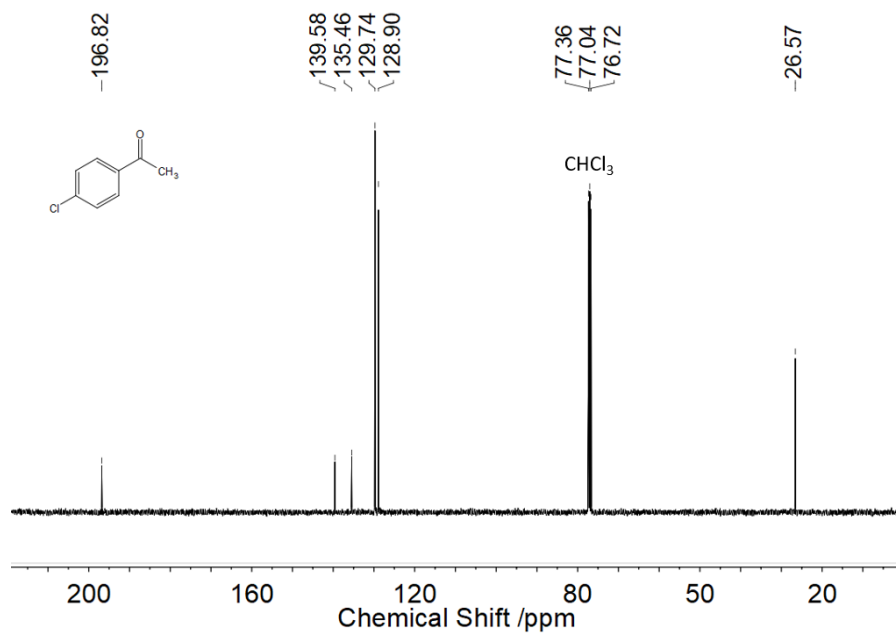


1-(4-chlorophenyl)ethan-1-one

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.9$  Hz, 2H), 6.93 (d,  $J = 8.9$  Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H).

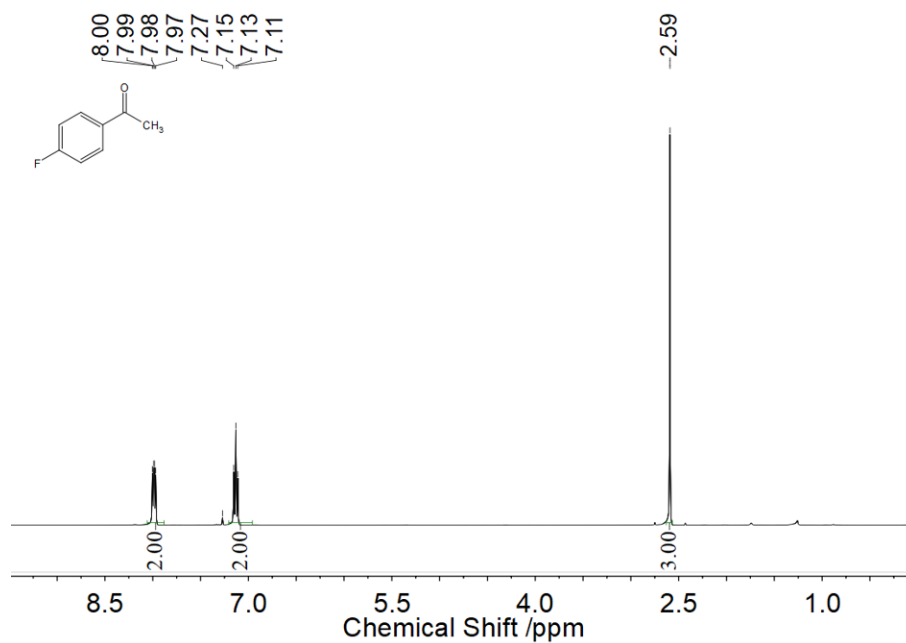


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.82, 139.58, 135.46, 129.74, 128.90, 26.57.

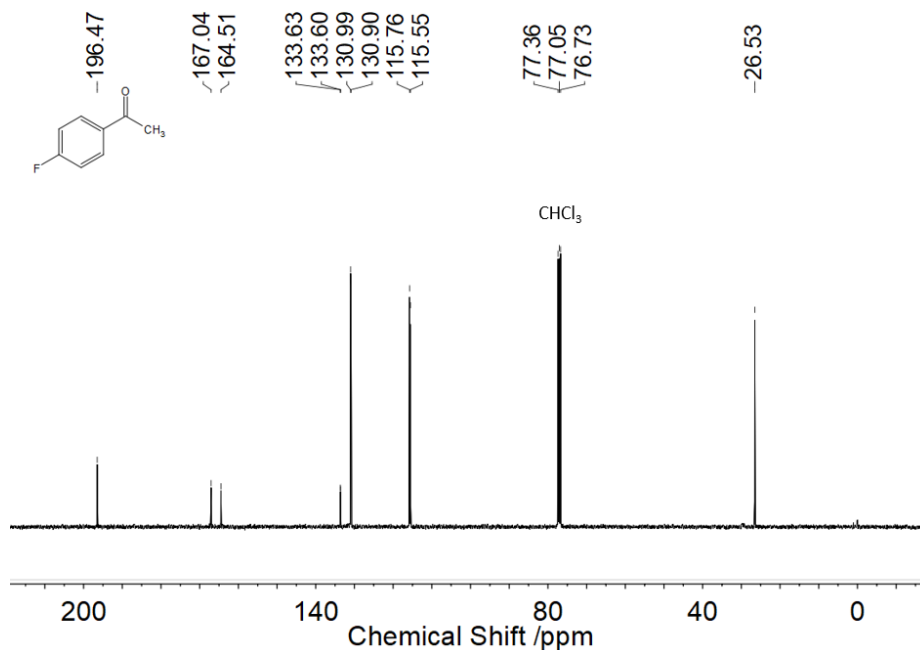


1-(4-fluorophenyl)ethan-1-one

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.96-7.21(m, 2H), 7.13 (t,  $J = 8.6$  Hz, 2H), 2.59 (s, 3H).

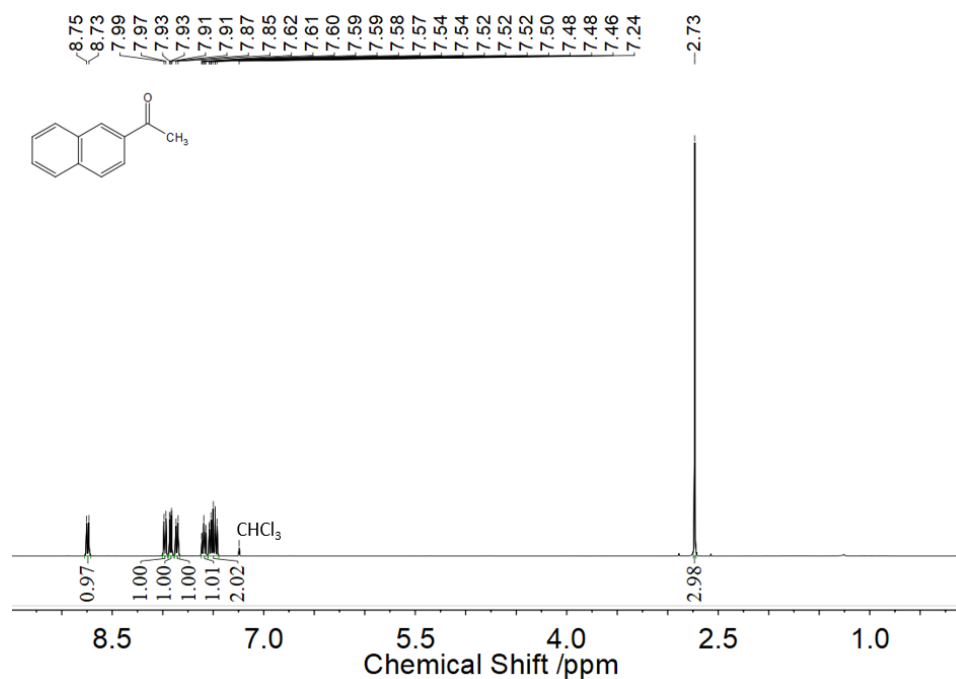


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.47, 165.78(d,  $J_{\text{C-F}}=254.6$  Hz), 133.62 (d,  $J_{\text{C-F}}=2.9$ Hz), 130.95 (d,  $J_{\text{C-F}}=9.3$ Hz), 115.66 (d,  $J_{\text{C-F}}=21.8$ Hz), 26.53.

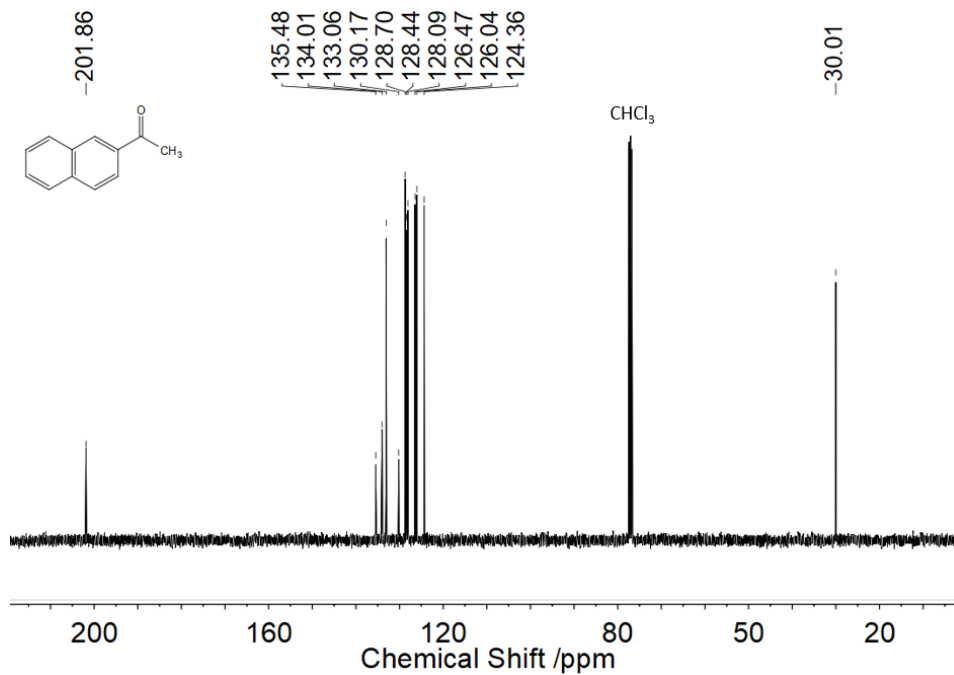


1-(naphthalen-2-yl)ethan-1-one

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74 (d,  $J = 8.7$  Hz, 1H), 7.98 (d,  $J = 8.2$  Hz, 1H), 7.89-7.94 (m, 1H), 7.86 (d,  $J = 8.1$  Hz, 1H), 7.56-7.61 (m, 1H), 7.55-7.44 (m, 2H), 2.73 (s, 3H).

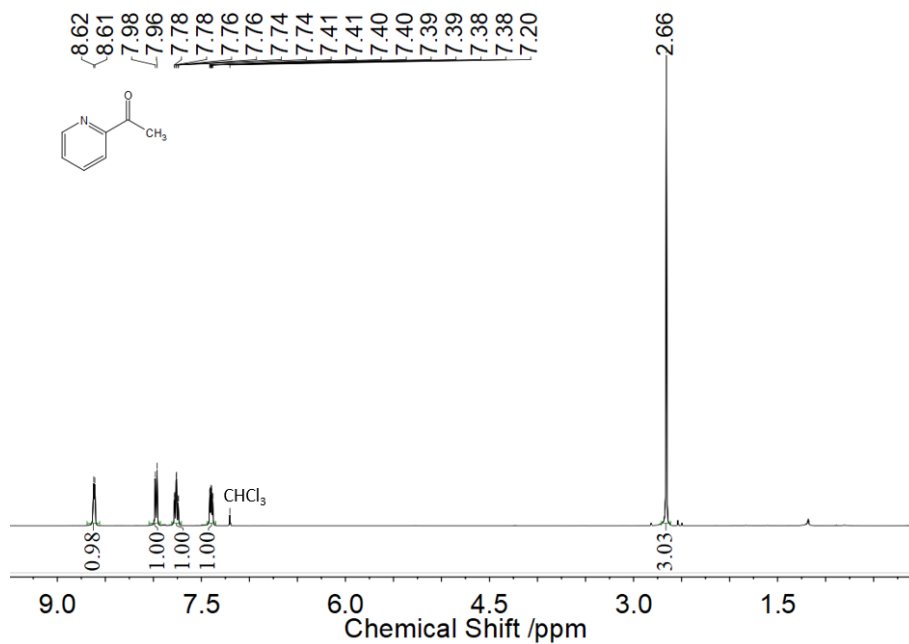


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.86, 135.48, 134.01, 133.06, 130.17, 128.70, 128.44, 128.09, 126.47, 126.04, 124.36, 30.01.



1-(pyridin-2-yl)ethan-1-one

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (d,  $J = 4.3$  Hz, 1H), 7.97 (d,  $J = 7.9$  Hz, 1H), 7.71-7.81 (m, 1H), 7.34-7.44 (m, 1H), 2.66 (s, 3H).



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.10, 152.59, 147.97, 135.81, 126.06, 120.63, 24.76.

