Electronic Supplementary Information

UV light Promoted 'Metal'/'Additive'-free Oxidation of Alcohols: Investigating the Role of Alcohols as Electron Donors

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General Experimental Methods and Materials

Solvents and reagents were purchased from Sigma-Aldrich chemical company and were used without further purification unless otherwise specified. Cyclic Voltammetry studies were performed at room temperature on potentiostat/galvanostat Autolab Instrument (PGSTAT302N) (Netherlands), Metrohm in presence of supporting electrolyte 0.1M tetrabutylammonium perchlorate (Bu_4NClO_4), Ag/AgCl as reference electrode, platinum wire as counter electrode and platinum electrode as working electrode. UV−vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length: 1cm). The cell holder was thermostated at 25°C. ^{1}H NMR and ^{13}C NMR spectra were recorded on, Bruker (Avance II) FT-NMR-AL 500 MHz spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane ($SiMe_4$) as internal standards. Data are reported as follows: multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constant (J/Hz) and integration. Bruker ESI-MS spectrophotometer was used to record mass spectra. A 80 W UV light irradiation source was used for carrying out the photocatalytic reactions. The wavelength of the UV light used is 254 nm. Column chromatography was done using 60–120 mesh silica gel using ethyl acetate (or diethyl ether) and hexane as eluent. Reference for reported products is given before the name of the product.

General Procedure for the UV-light induced oxidation of alcohols to aldehydes or ketones:

A reaction vial containing a stirring bar was charged with the alcohol (1 mmol) and DMSO (4 mL) under aerial conditions. The reaction mixture was stirred under UV light at 30°C. TLC was used to monitor the formation of products. The reaction was stopped after 66 h by turning off the lamp. Then, the resulting mixture underwent an aqueous workup and was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. All the products were purified on silica gel using column chromatography using 1:4 EtOAc:hexane as the eluent. All the products were characterized using ^{1}H NMR spectroscopy. Unreacted alcohols were recovered in all the cases.

General Procedure for the reaction of alcohols with methyl viologen under UV light irradiation:

A reaction vial containing a stirring bar was charged with the alcohol (0.01 mM), DMSO (4 mL) and methyl viologen (0.2 mM) under UV light irradiation and under inert conditions. The reaction mixture was stirred under UV light until the color of the solution changed from colorless to dark blue. Then, the UV-vis spectra of the resulting blue colored solution was recorded.

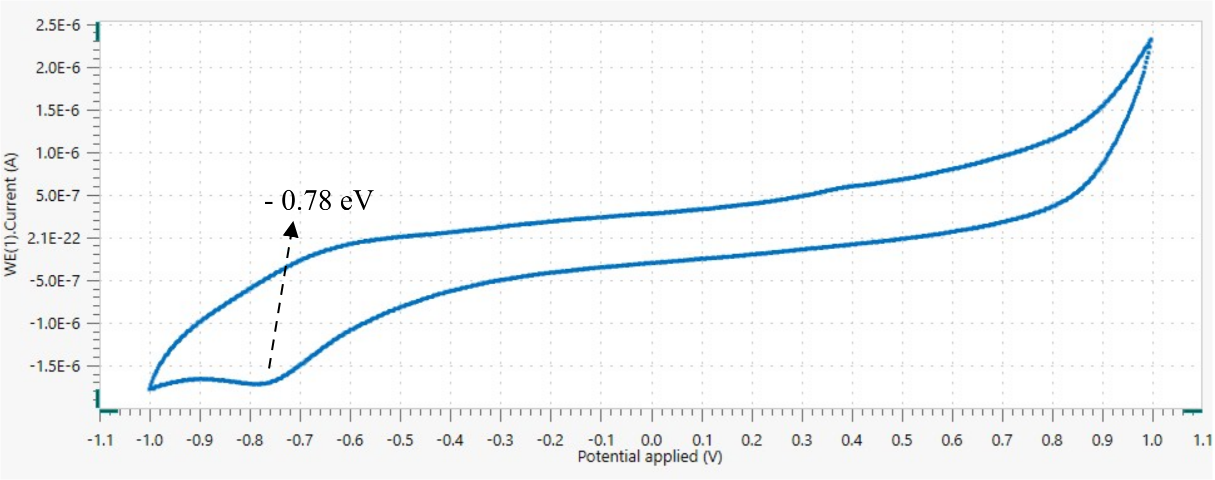

Fig. S1 Cyclic voltammogram of benzyl alcohol in DMSO containing 0.1 M Bu_4NClO_4 (supporting electrolyte) and Ag/AgCl (reference electrode).

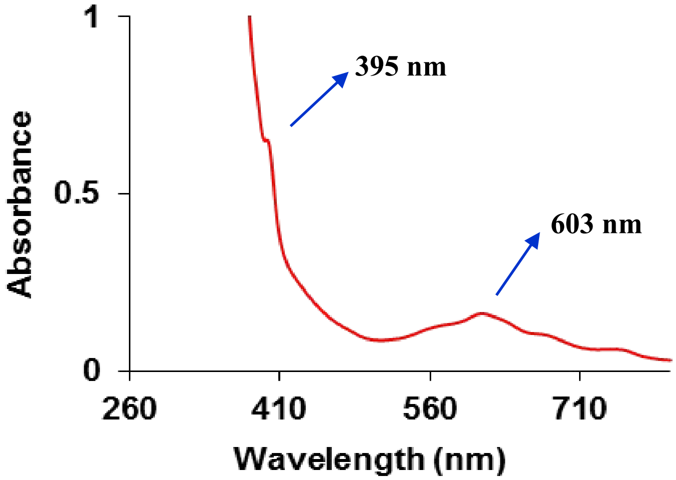

Fig. S2 UV-Vis Spectra of reduced form of methyl viologen ($MV^{\bullet+}$) generated by the reaction of 4-methyl benzyl alcohol (0.01 mM) and methyl viologen dicholoride (MV^{2+}) (0.2 mM) in DMSO under UV light irradiation.

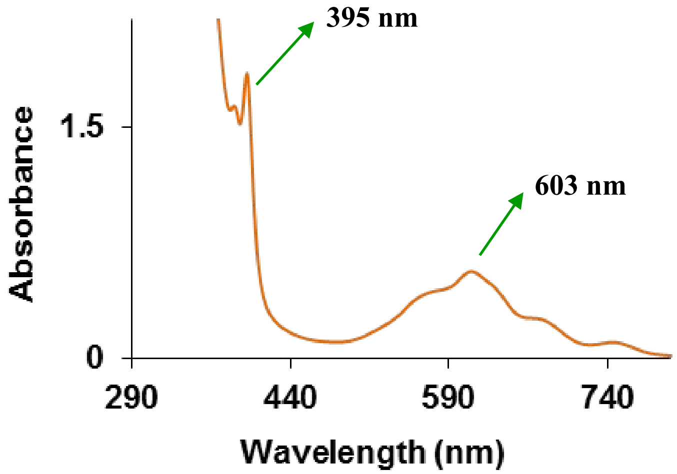

Fig. S3 UV-vis Spectra of reduced form of methyl viologen ($MV^{\bullet+}$) generated by the reaction of 4-methoxybenzyl alcohol (0.01 mM) and methyl viologen dicholoride (MV^{2+}) (0.2 mM) in DMSO under UV light irradiation.

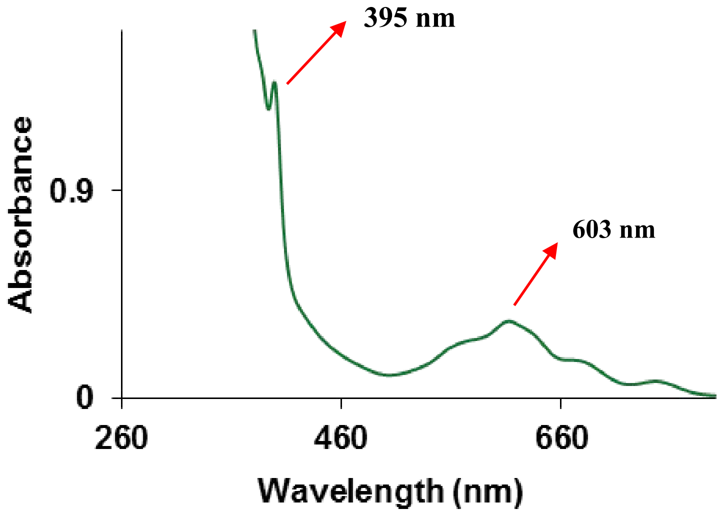

Fig. S4 UV-Vis Spectra of reduced form of methyl viologen ($MV^{\bullet+}$) generated by the reaction of 4-bromobenzyl alcohol (0.01 mM) and methyl viologen dicholoride (MV^{2+}) (0.2mM) in DMSO under UV light irradiation.

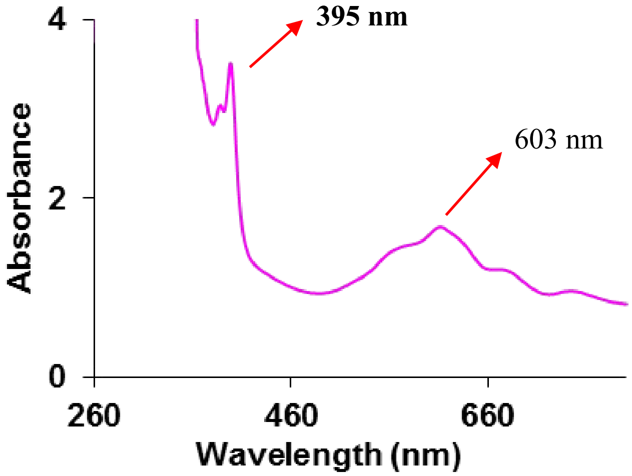

Fig. S5 UV-Vis Spectra of reduced form of methyl viologen ($MV^{\bullet+}$) generated by the reaction of 4-chlorobenzyl alcohol (0.01 mM) and methyl viologen dicholoride (MV^{2+}) (0.2 mM) in DMSO under UV light irradiation.

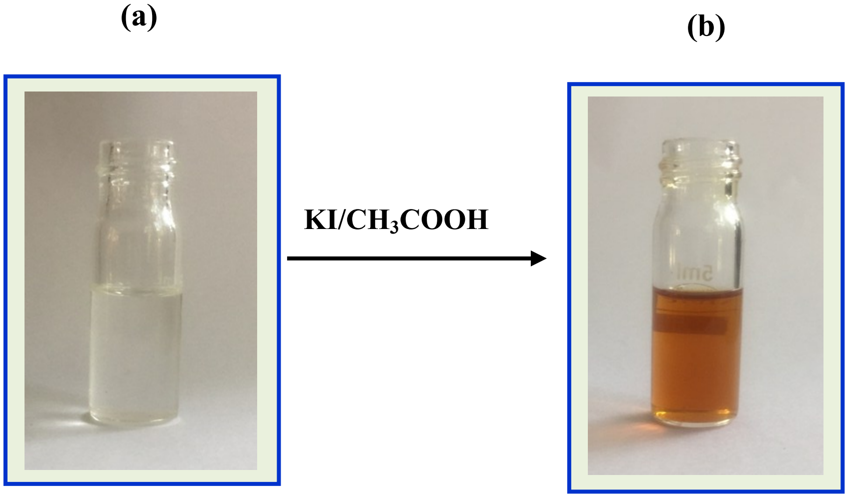

Fig. S6 (a) Reaction mixture of benzyl alcohol (1 mmol) and DMSO**;** (b) After addition of mixture KI (1.0×10^{-1} M), aqueous acetic acid (1.0×10^{-1} M), color of the solution changes to brown.

[2a].[1a] [Benzaldehyde]: (colorless liquid, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 10.02 (s, 1H), 7.88 (d, *J* = 10 Hz, 2H), 7.64-7.61 (m, 1H), 7.54-7.51 (m, 2H).

[2b].[1a] [4-methylbenzaldehyde]: (colorless liquid, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.89 (s, 1H), 7.67 (d, *J* = 5 Hz, 2H), 7.19 (d, *J* = 5 Hz, 2H), 2.27 (s, 3H, CH_3).

[2c].[1a] [4-methoxybenzaldehyde]: (colorless liquid, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.72 (s, 1H), 7.67 (d, *J* =15 Hz, 2H), 6.83 (d, *J* = 10 Hz, 2H), 3.70 (s, 3H, OCH_3)

[2d].[1b] [3-methylbenzaldehyde]: (colorless liquid, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.98 (s, 1H), 7.67 (d, *J* = 10 Hz, 2H), 7.42-7.39 (m, 2H), 2.42 (s, 3H, CH_3).

[2e].[1a] [4-chlorobenzaldehyde]: (white solid, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.98 (s, 1H), 7.82 (d, *J* = 5 Hz, 2H), 7.50 (d, *J* = 5 Hz, 2H).

[2f].[1b] [4-bromobenzaldehyde]: (white solid, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.97 (s, 1H), 7.74 (d, *J* = 10 Hz, 2H), 7.67 (d, *J* = 10 Hz, 2H).

[2h].[1c] [Isophthalaldehyde]: (white solid, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 10.13 (s, 2H), 8.39 (s, 1H), 8.17 (d, *J* = 10 Hz, 2H), 7.75 (t, *J* = 7.5 Hz, 1H).

[2i].[1d] [[1,1'-biphenyl]-4-carbaldehyde]: (white solid, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 10.04 (s, 1H), 7.93 (d, *J* = 10 Hz, 2H), 7.73 (d, *J* = 10 Hz, 2H), 7.62 (d, *J* = 10 Hz, 2H), 7.48-7.45 (m, 2H), 7.42-7.39 (m, 1H).

[2j].[1d] [Acetophenone]: (colorless liquid, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.95 (d, *J* = 10 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 2.59 (s, 3H, CH_3).

[2k].[1a] [benzophenone]: (white solid, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.80 (d, *J* = 5 Hz, 4H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 4H).

[2l].[1e] [9H-fluoren-9-one]: (yellow solid, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.66 (d, *J* = 10 Hz, 2H), 7.53-7.47(m, 4H), 7.31-7.28 (m, 2H).

[2o].[1f] [cyclohexanecarbaldehyde]: (colorless liquid, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.46 (s, 1H), 2.11-2.07 (m, 1H), 1.76-1.71 (m, 2H), 1.60-1.58 (m, 2H), 1.51-1.49 (m, 1H), 1.26-1.10 (m, 5H).

[2p].[1d] [cyclohexanone]: (colorless liquid, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 2.22 – 2.20 (m, 4H), 1.75 – 1.71 (m, 4H), 1.62-1.59 (m, 2H).

[2q].[1f] [thiophene-2-carbaldehyde]: (colorless liquid, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 9.95 (s, 1H), 7.80 (d, *J* = 5 Hz, 1H), 7.78 (d, *J* = 5 Hz, 1H), 7.22 (t, *J* = 5 Hz, 1H).

[2r].[1g][(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl) 1,2,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one]: (white solid, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = ^{1}H NMR (500 MHz, $CDCl_3$) δ= 5.35 (brs, 1H), 3.51 (d, *J* = 15 Hz, 1H), 2.30-2.21 (m, 1H), 2.00 (t, *J* = 15 Hz, 2H), 1.85-1.79 (m, 3H), 1.53 – 1.42 (m, 7H), 1.35-1.23 (m, 4H), 1.15 – 1.05 (m, 7H), 1.01 – 0.96 (m, 5H), 0.95-0.91 (m, 4H), 0.87 (s, 3H), 0.86 (s, 3H), 0.68 (s, 3H).

(1) (a) W. Huang, B. C. Ma, H. Lu, R. Li, L. Wang, K. Landfester and K. A. I. Zhang, *ACS Catal.*, 2017, **7**, 5438−5442; (b) R. Ray, S. Chandra, D. Maiti, and G. K. Lahiri, *Chem. Eur. J.*, 2016, **22**, 8814 – 8822; (c) Y. Lin, K. H. Wu, L. Yu, S. Heumann and D. S. Su, *ChemSusChem*, 2017, **10**, 3497-3505; (d) W. Schilling, D. Riemer, Y. Zhang, N. Hatami, and S. Das, *ACS Catal.*, 2018, **8**, 5425−5430; (e) A. Maji, S. Rana, Akanksha and D. Maiti, *Angew. Chem. Int. Ed.*, 2014, **53**, 2428 –2432; (f) J. M. Hoover and S. S. Stahl, *J. Am. Chem. Soc.*, 2011, **133**, 16901–16910; (g) M. G. Coleman, A. N. Brown, B. A. Bolton and H. Guan, *Adv. Synth. Catal.*, 2010, **352**, 967 – 970.

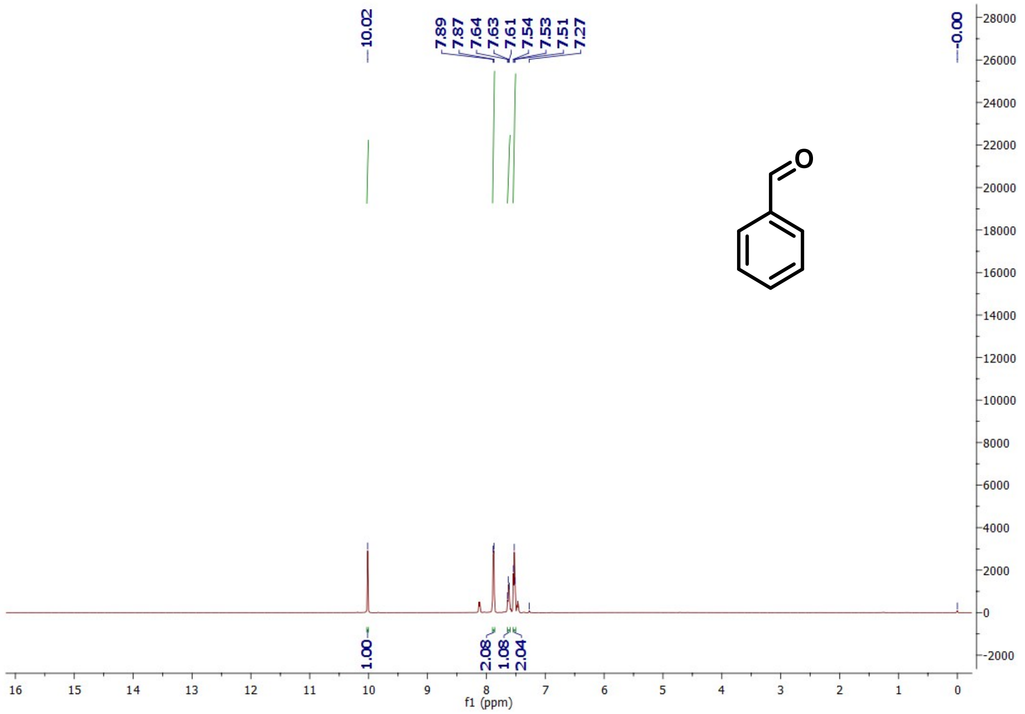

Fig. S7 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2a.

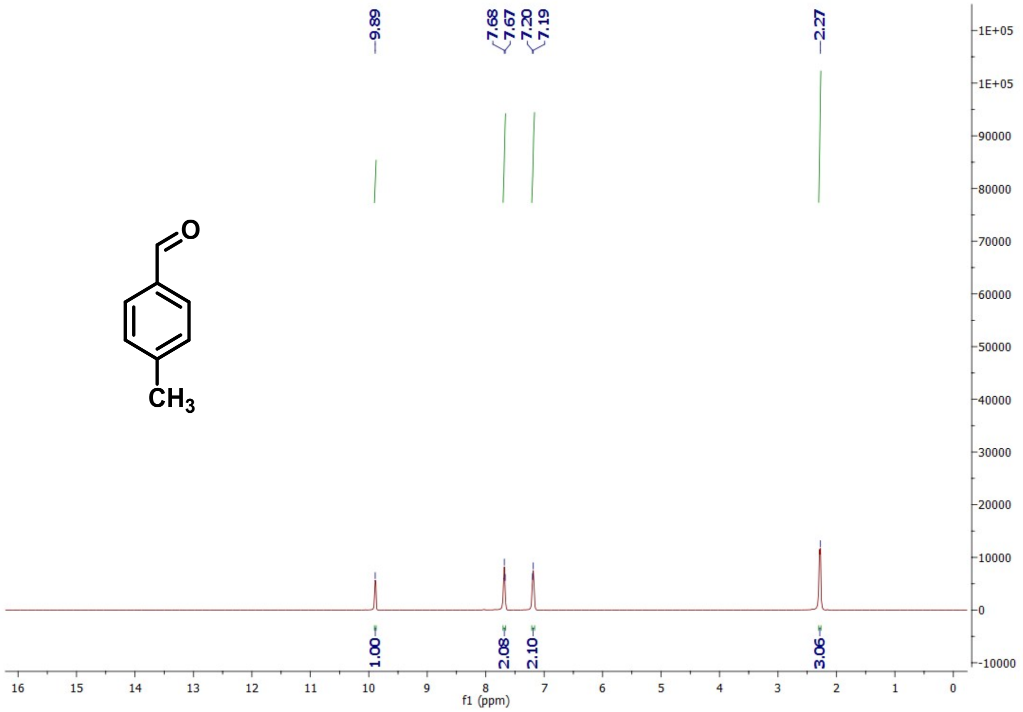

Fig. S8 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2b.

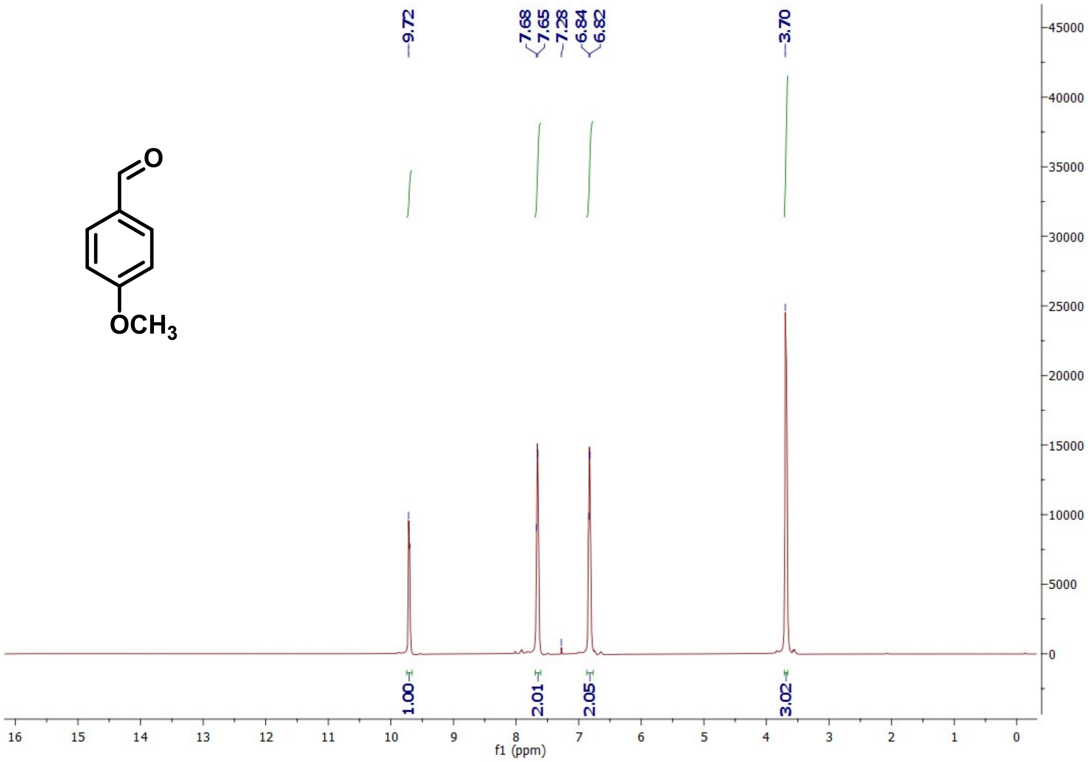

Fig. S9 ^{1}**H NMR Spectra (**$CDCl_3$**, 500 MHz, ppm) of compound 2c.**

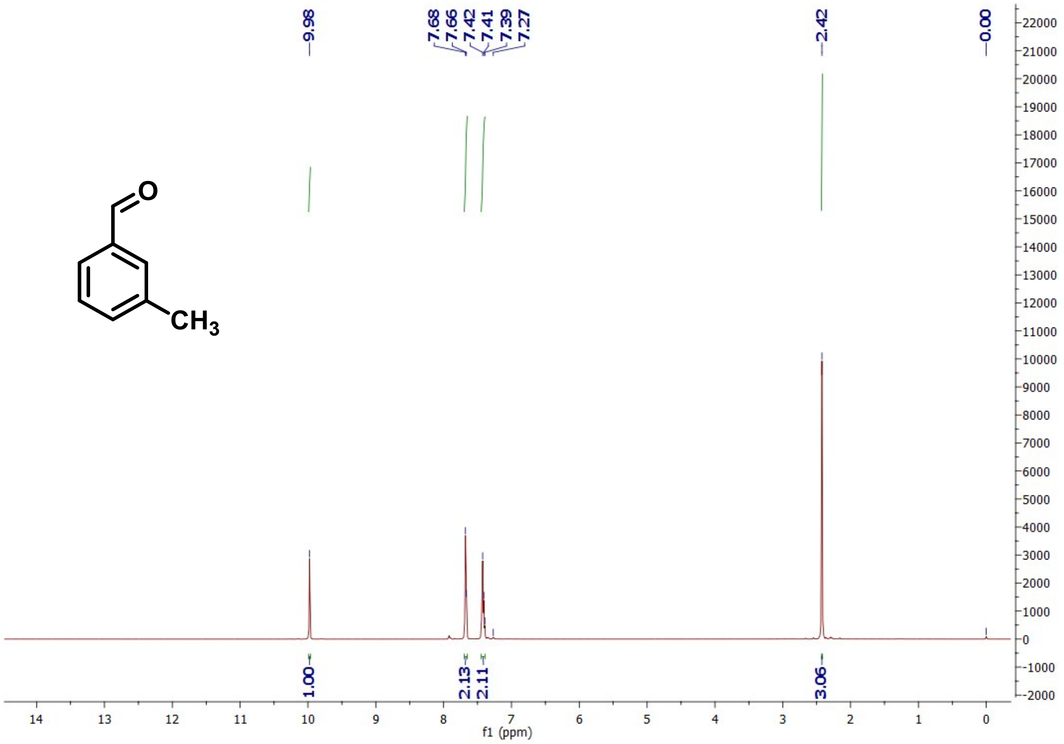

Fig. S10 ^{1}**H NMR Spectra (**$CDCl_3$**, 500 MHz, ppm) of compound 2d.**

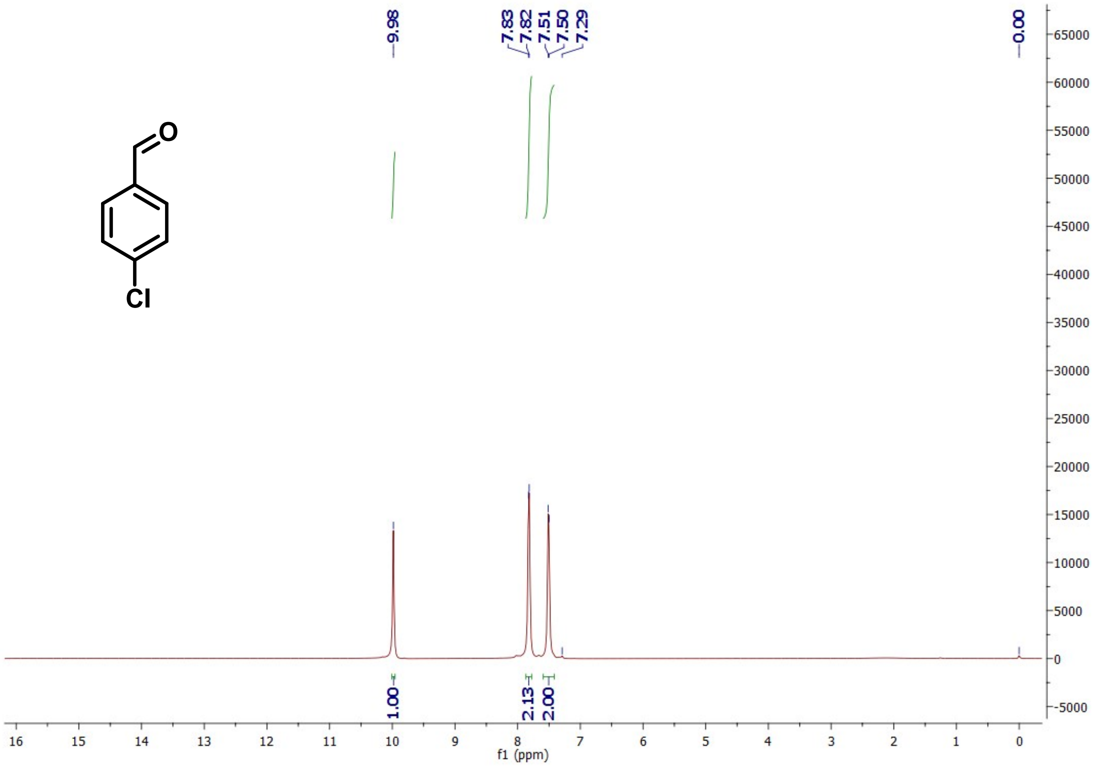

Fig. S11 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2e.

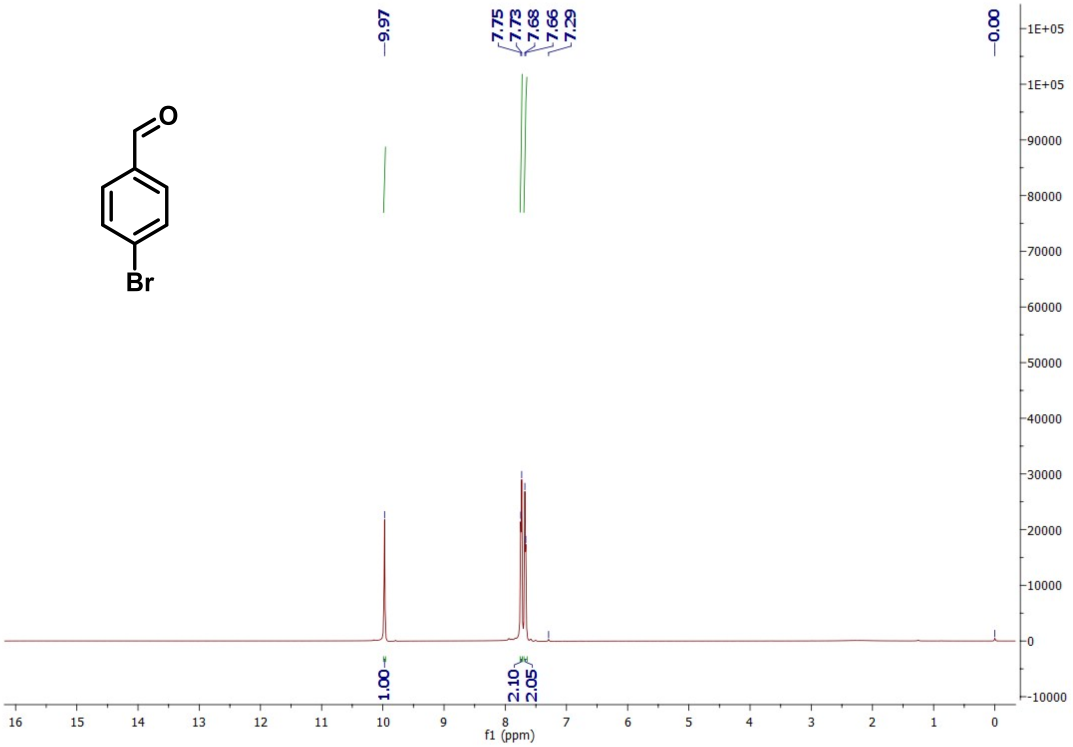

Fig. S12 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2f.

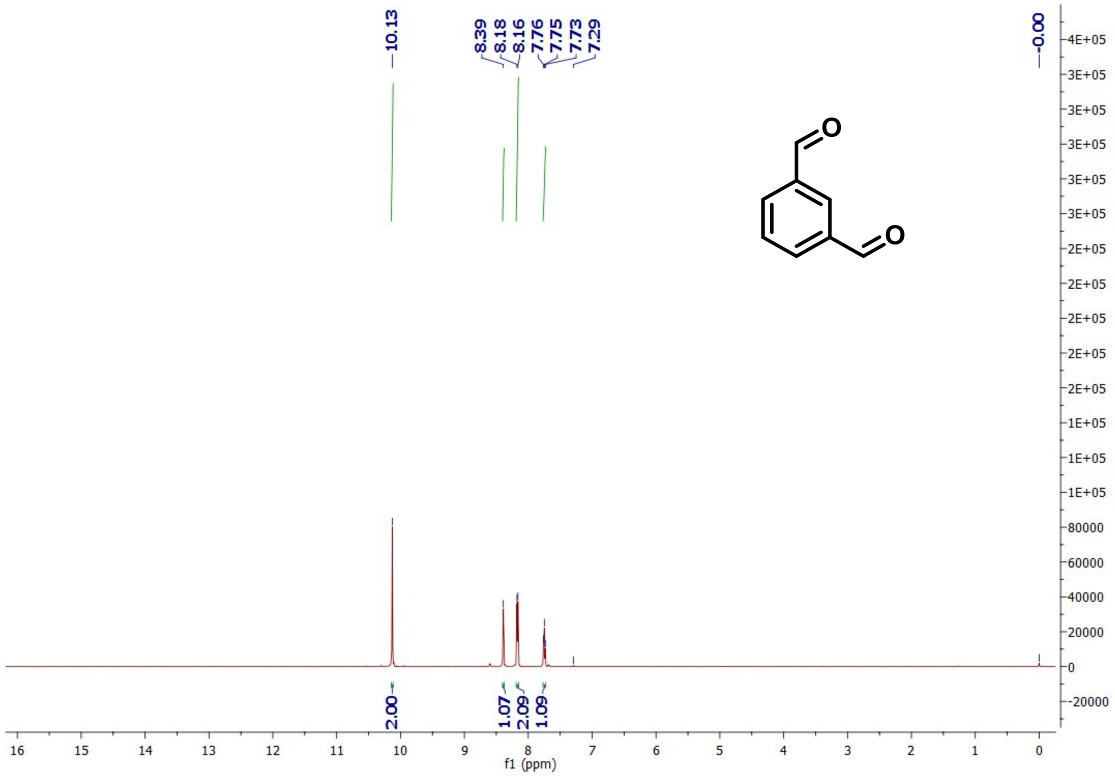

Fig. S13 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2h.

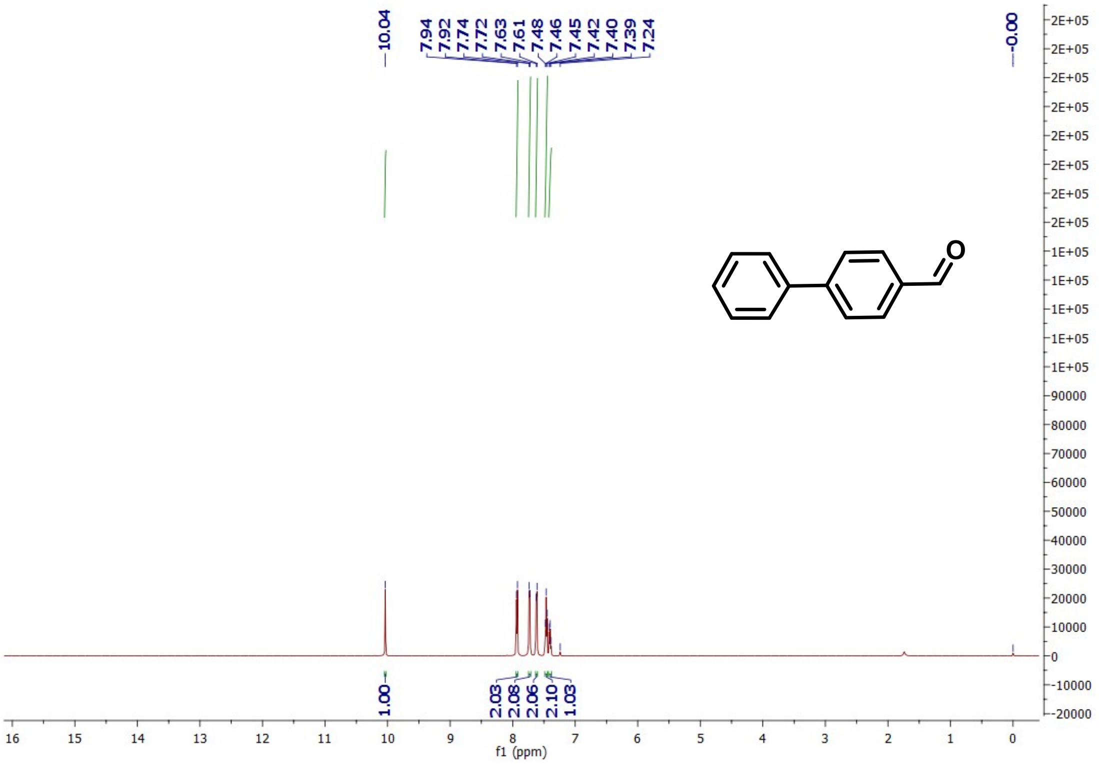

Fig. S14 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2i.

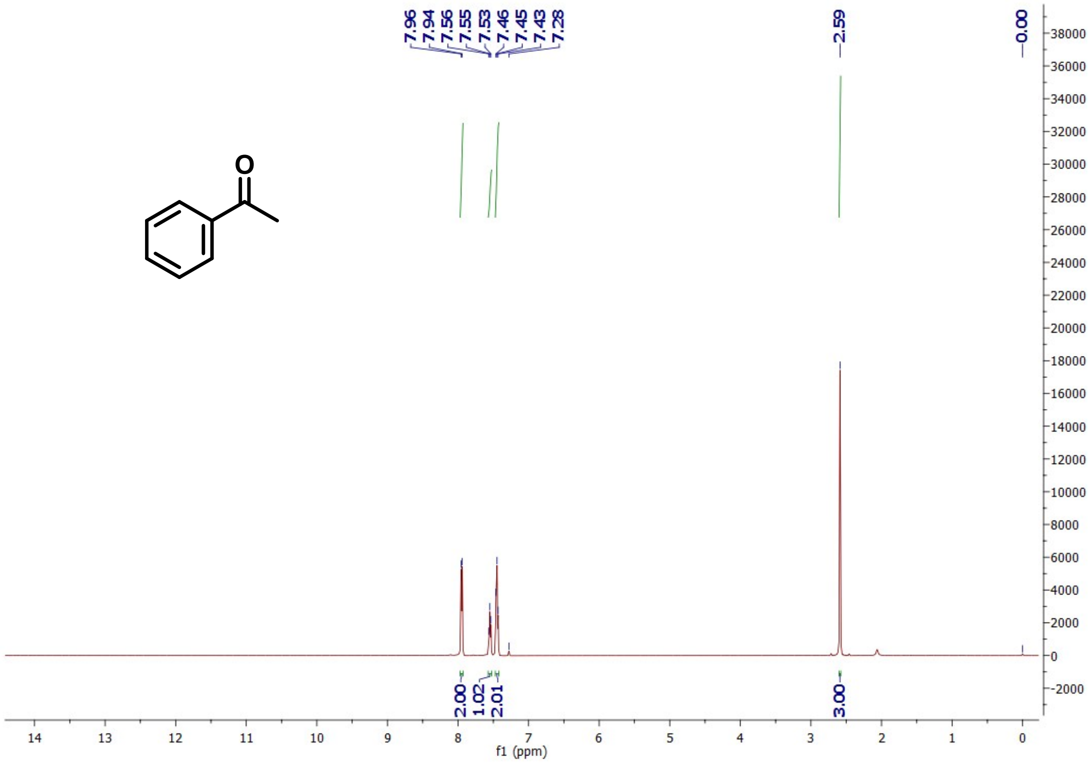

Fig. S15 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2j.

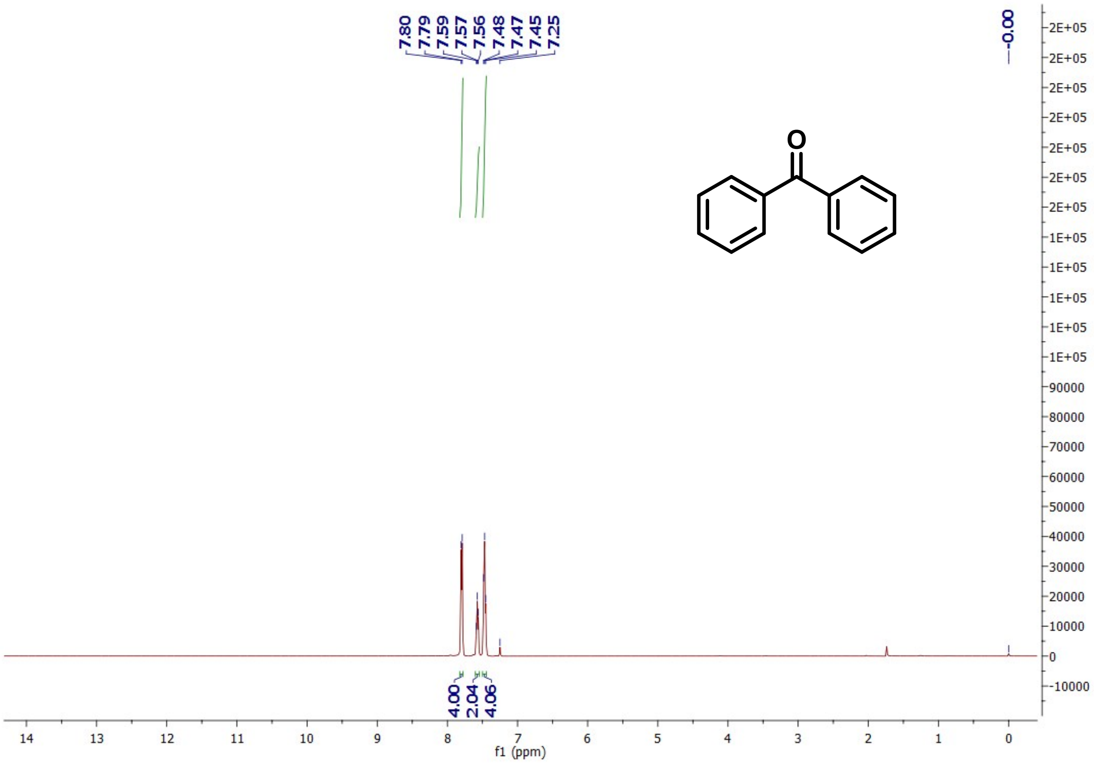

Fig. S16 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2k.

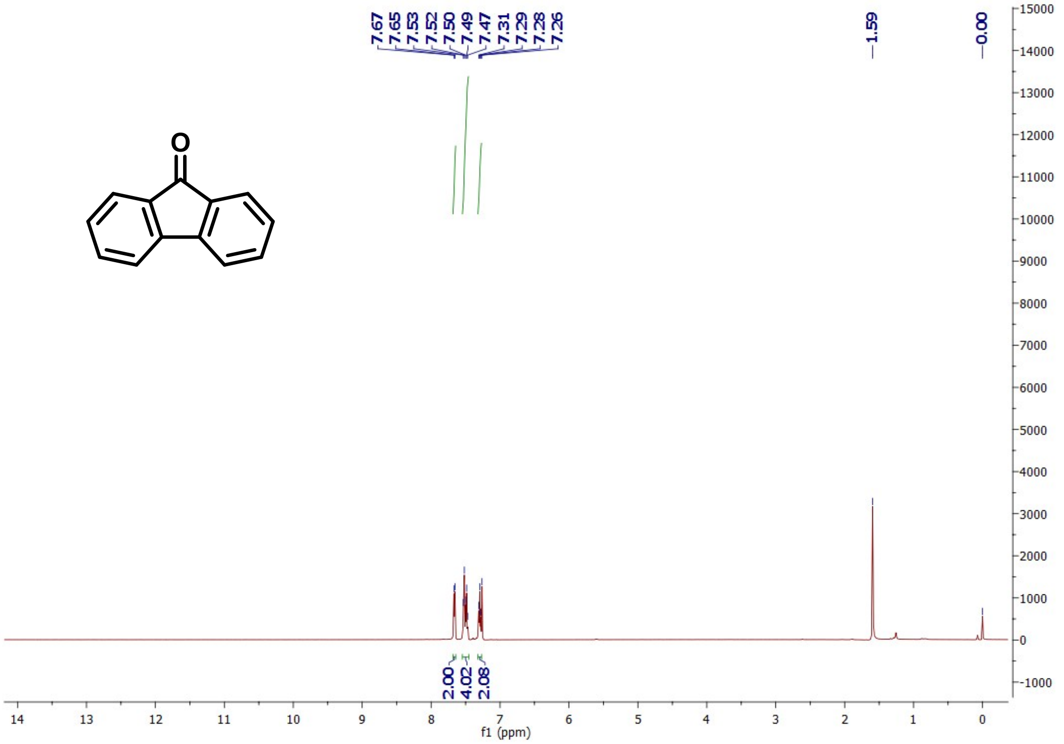

Fig. S17 ^{1}H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 2l.

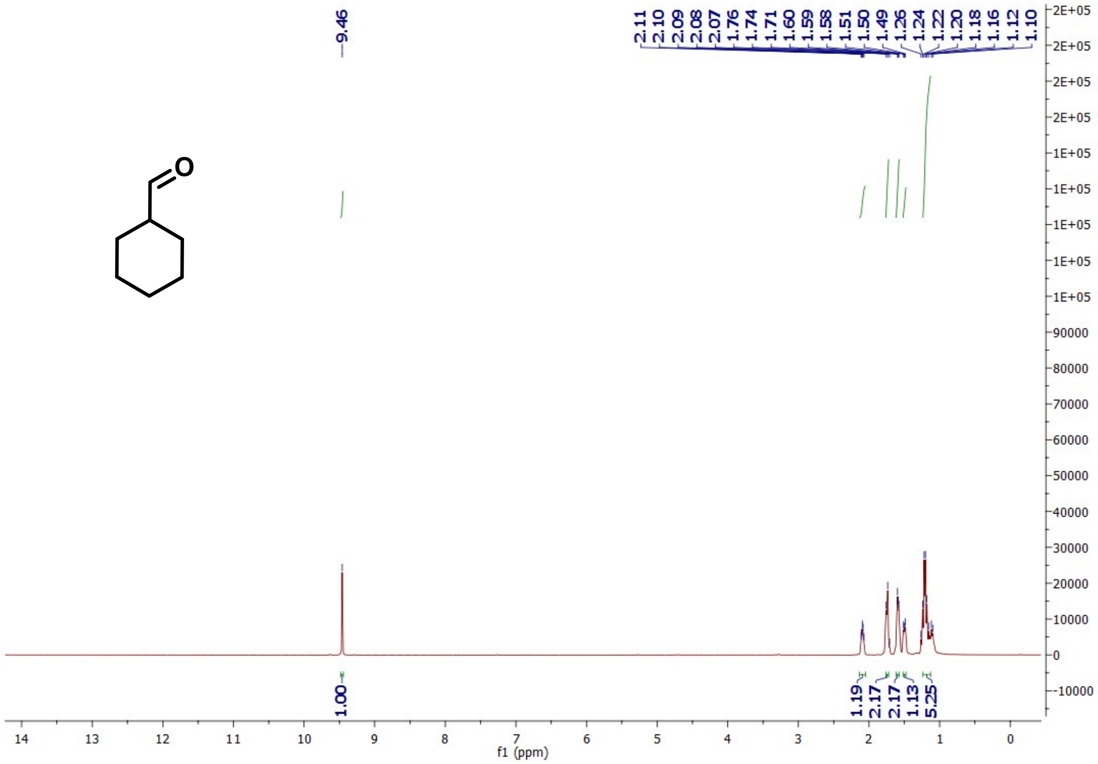

Fig. S18 ^{1}H NMR Spectra (CDCl$_3$,500 MHz, ppm) of compound 2o.

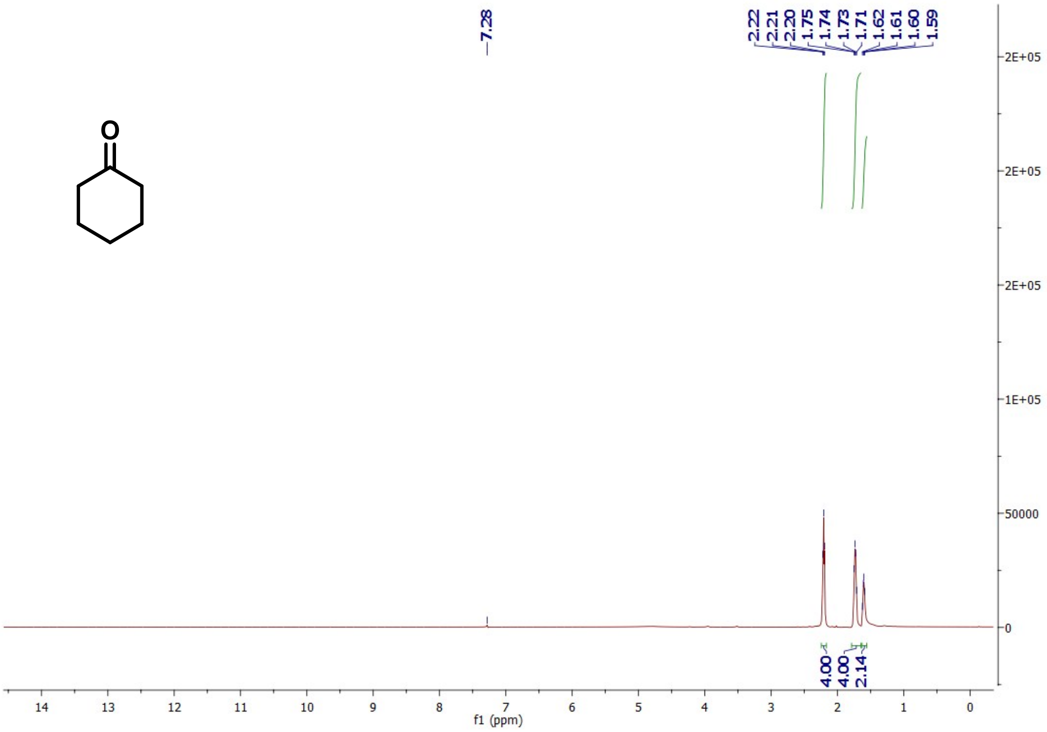

Fig. S19 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2p.

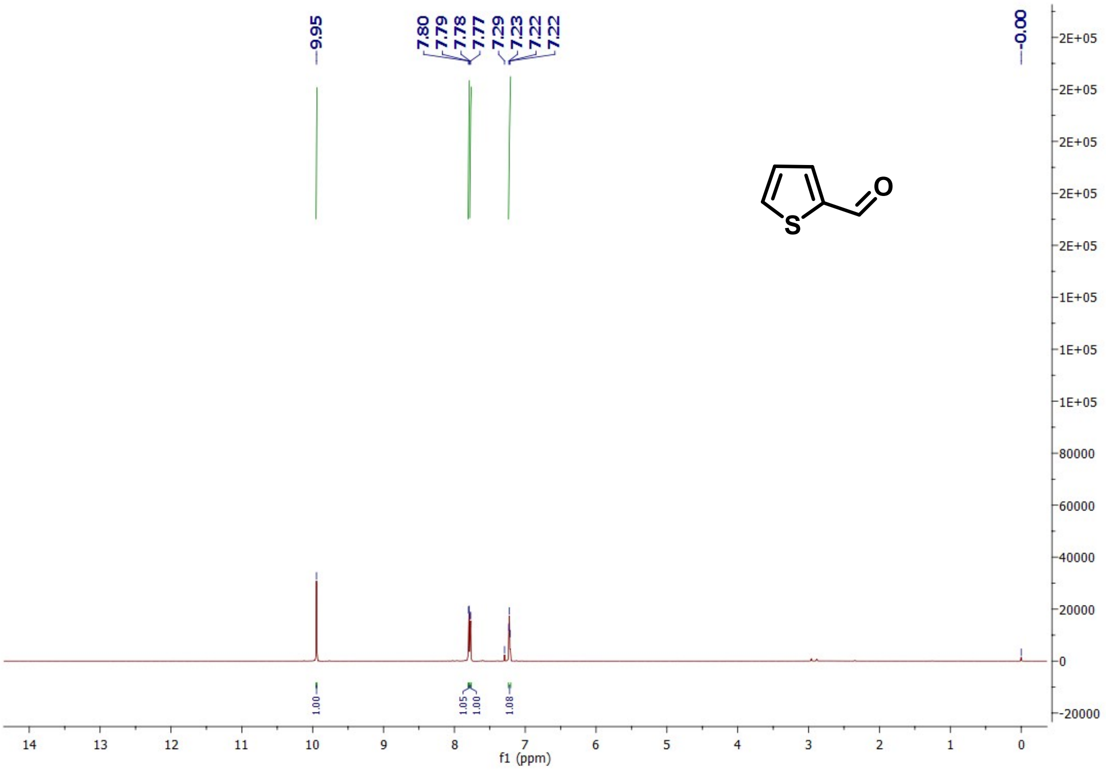

Fig. S20 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2q.

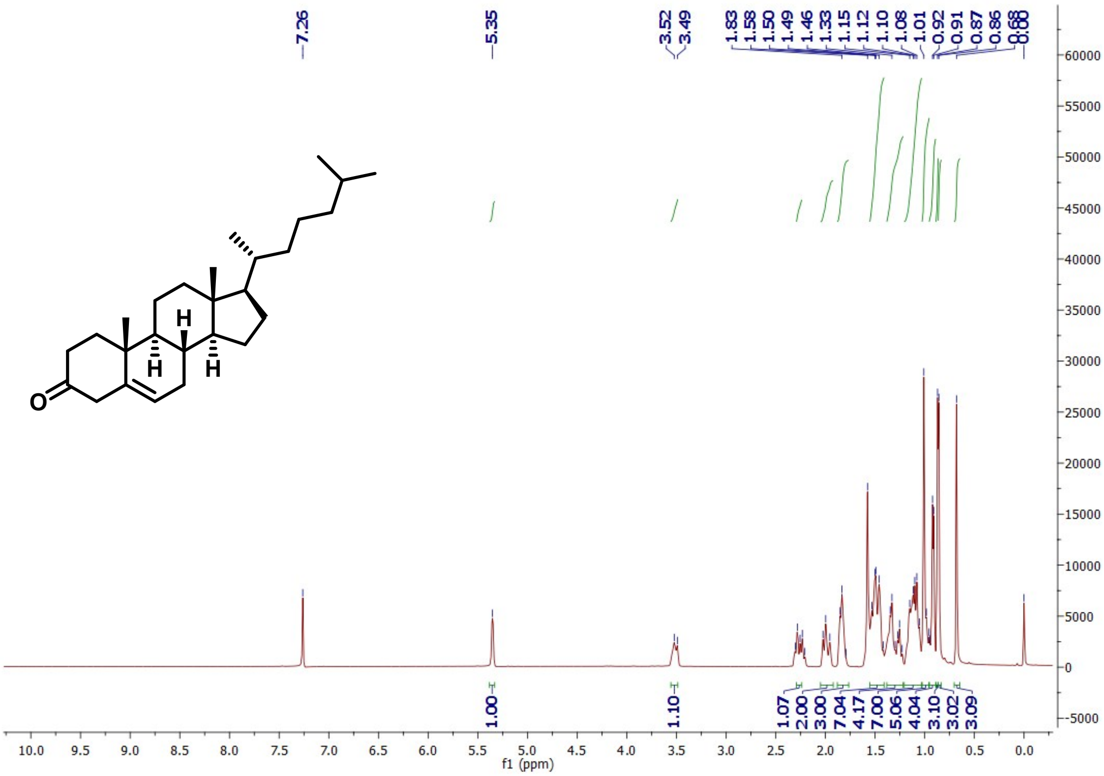

Fig. S21 ^{1}H NMR Spectra ($CDCl_3$, 500 MHz, ppm) of compound 2r.

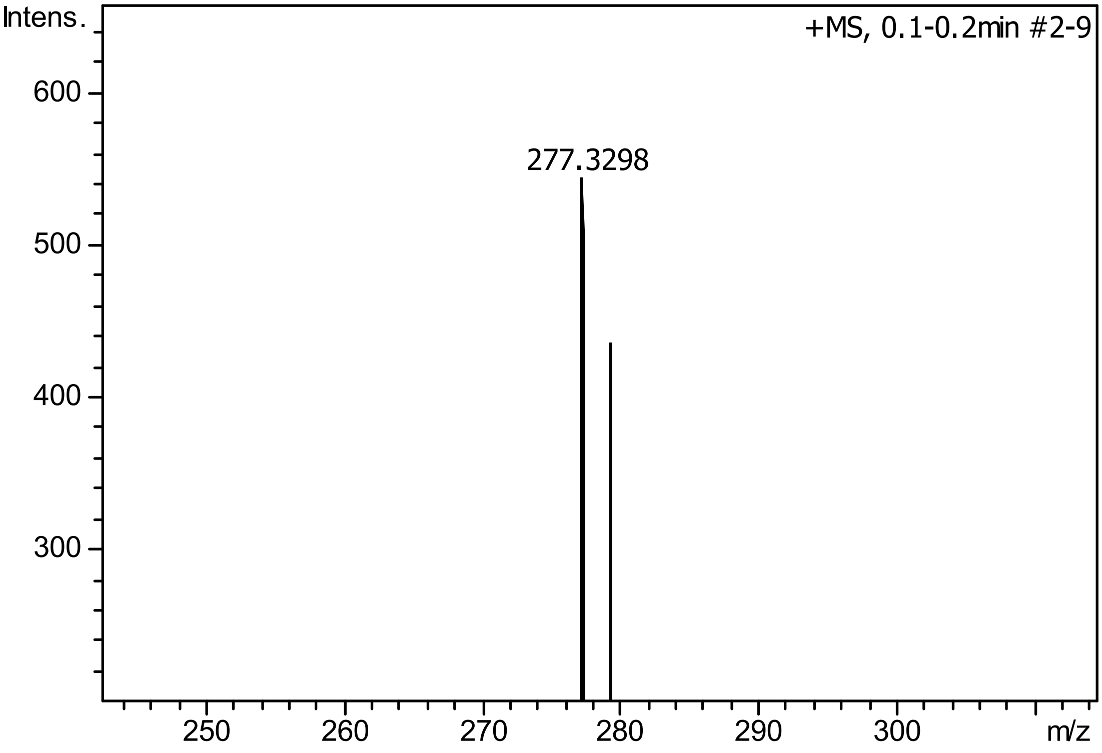

Fig. S22 ESI-MS of adduct between 4-methylbenzylalcohol and TEMPO.

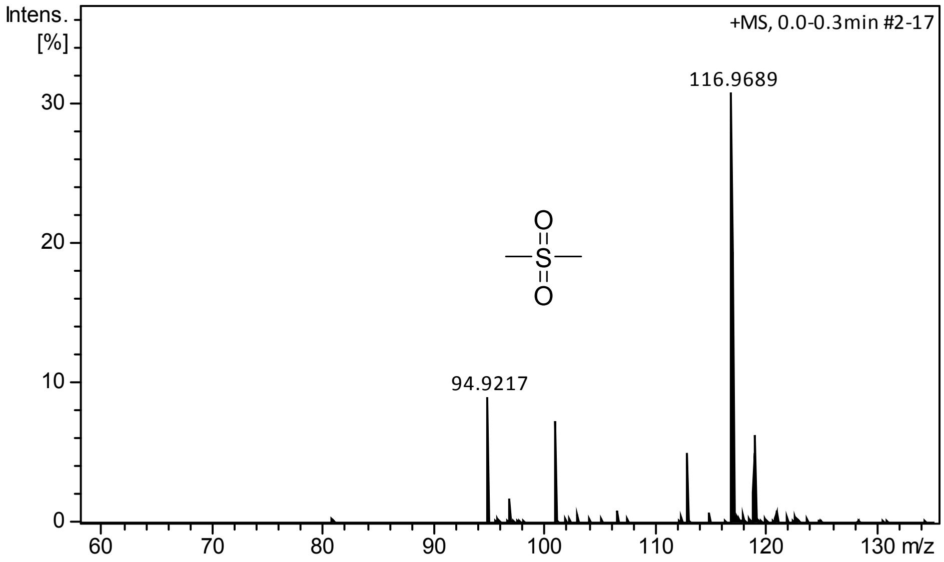

Fig. S23 ESI-MS of $DMSO_2$ as a byproduct.