# Supporting information

## Selective catalytic oxidation of alcohols by carbon nanotube-gold nanohybrids

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### Calculation of TON and TOF

- Kinetic values were calculated from the results of the reaction depicted in Scheme 1 in the main text.
  For values based on the total amount of gold, the following formulas were used:

  TON = amount of product (mmol) / total amount of gold (mmol)
  = 0.99 / 0.002
  = 495
  TOF = TON / time (h)
  = 495 / 3
  = 165 $h^{-1}$

- The fraction of gold atoms exposed to the surface of AuNP was calculated using the method reported by Boudart and Djega-Mariadassou.[1] The dispersion (fraction of metal atoms exposed) is approximately 0.9/d, where d is the spherical metal particle diameter in nm. Thus gold nanoparticles with a diameter of 3 nm have about 30% (0.9/3 nm) of their atoms lying at the surface of the AuNP. Therefore, adjusted TON and TOF values based on surface atoms are 1648 and 549 $h^{-1}$, respectively.

[1] M. Boudart, G. Djéga-Mariadassou in Kinetics of Heterogeneous Catalytic Reactions, Princeton University Press, Princeton, N. J., 1984, pp26.

**Table S1:** Comparison of different Au-based catalytic systems for the oxidation of benzyl alcohol. Kinetic values are provided based on surface atoms.

| Entry | Catalyst | product | Conds. | Loading | TON | TOF ($h^{-1}$) | Ref |
|---|---|---|---|---|---|---|---|
| 1 | AuCNT | Benzoic acid | 293 K, 1 atm air | 0.2 mol% | 1648 | 549 | This work |
| 2 | Au/Zeolite | Benzaldehyde | 373 K, 2 atm $O_2$ | 2 wt% | NA | 378[a] | [2] |
| 3 | Au/Zeolite | Benzaldehyde | 298 K, $O_2$, light | NA | NA | 2.25 | [3] |
| 4 | Au/hydrotalcite | Benzaldehyde | 393 K, Ar flow | 4 wt% | NA | 800[a] | [4] |
| 5 | $Au/TiO_2$ | Benzaldehyde | 373 K, 10 atm $O_2$ | 7.8 wt% | NA | 300 | [5] |
| 6 | $Au/Ga_2O_3$ | Benzaldehyde | 403 K, 5 atm $O_2$ | 2.5 wt% | NA | 606 | [6] |
| 7 | Au/PVP | Benzoic acid | 295 K, 1 atm air | 1 mol% | NA | 105 | [7] |
| 8 | Au/Polystyrene | Benzaldehyde | 308 K, 1 atm $O_2$ | 2 wt% | NA | 144 | [8,9] |
| 9 | Au foil | Benzaldehyde | 363 K, 5 atm $O_2$ | 76 mol% | NA | 10080 | [9,10] |
| 10 | Au/MgCr–HT | Benzaldehyde | 373 K, 20 mL $min^{-1}$ $O_2$ | 0.32 wt% | NA | 1880 | [11] |
| 11 | $Au/MnO_2$ | Benzaldehyde | 393 K, 3 atm $O_2$ | 5 wt% | NA | 320 | [12] |

[a] *initial reaction rates*

[2] G. Li, D. I. Enache, J. Edwards, A. F. Carley, D. W. Knight, G. J. Hutchings. *Catal. Lett.* 2006, **110**, 7.

[3] X. Zhang, X. Ke, H. Zhu. *Chem. Eur. J.* 2012, **18**, 8048.

[4] W. Fang, J. Chen, Q. Zhang, W. Deng, Y. Wang. *Chem. Eur. J.* 2011, **17**, 1247.

[5] X. Yang, X. Wanga, C. Liang, W. Su, C. Wang, Z. Feng , C. Li, J. Qiu. *Catal. Commun*. 2008, **9**, 2278.

[6] F. Z. Su, M. Chen, L. C. Wang, X. S. Huang, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan. *Catal. Commun.* 2008, **9**, 1027.

[7] Y. Yuan, N. Yan, P. J. Dyson. *Inorg. Chem.* 2011, **50**, 11069.

[8] A. Buonerba, C. Cuomo, S. Ortega Sanchez, P. Canton, A. Grassi. *Chem. Eur. J.* 2012, **18**, 709.

[9] S. E. Davies, M. S. Ide, R. J. Davies. *Green Chem.* 2013, **15**, 17.

[10] H. Guo, A. Al-Hunaiti, M. Kemell, S. Rautiainen, M. Leskela, T. Repo. *ChemCatChem* 2011, **3**, 1872.

[11] P. Liu, Y. Guan, R. A. van Santen, C. Li, E. J. M. Hensen. *Chem. Commun*. 2011, **47**, 11540.

[12] L. C. Wang, L. He, Q. Liu, Y. M. Liu, M. Chen, Y. Cao, H. Y. He, K. N. Fan. *Applied Catalysis A: General* 2008, **344**, 150.

## X-ray photoelectron spectroscopy (XPS)

An aliquot of the AuCNT suspension was filtered through a polypropylene membrane which was then dried under vacuum overnight. XPS analysis showed only the presence metallic gold in the nanohybrid sample (Figure S1).

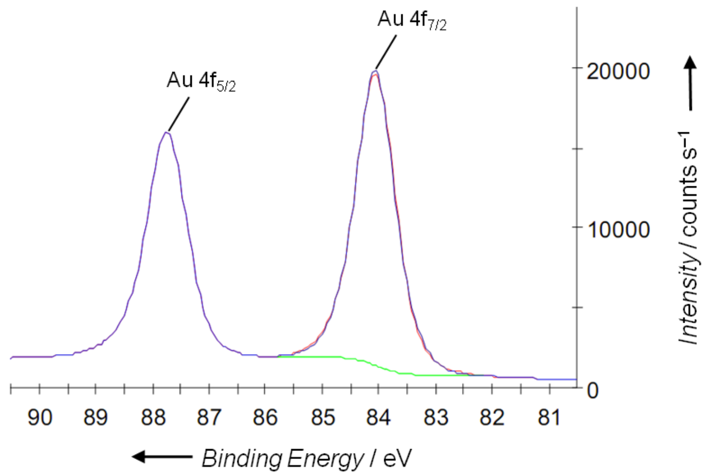


**Figure S1.** Narrow scan XPS analysis of AuCNT nanohybrids.

## Copies of $^1H$ NMR spectra

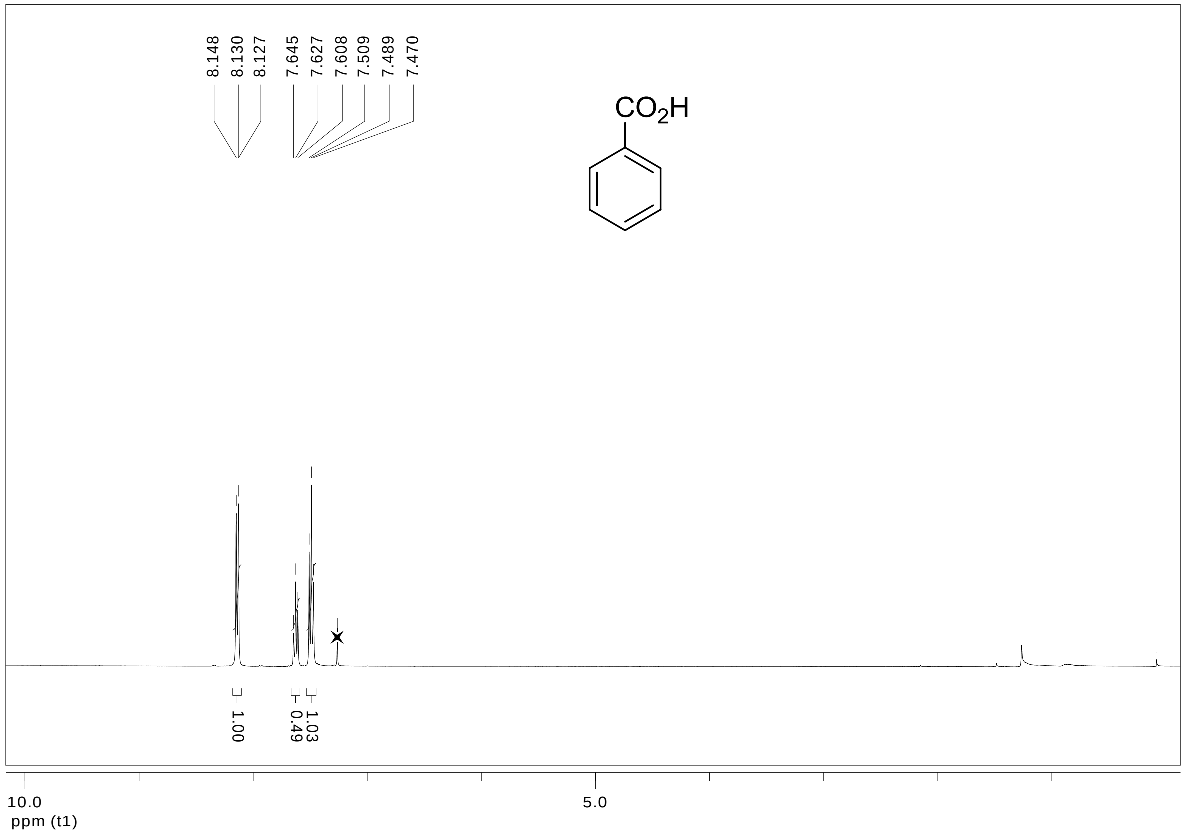


**Fig. S1** Benzoic acid (**2a**).

$^1H$ NMR (400 MHz, $CDCl_3$) 7.61 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 2H).

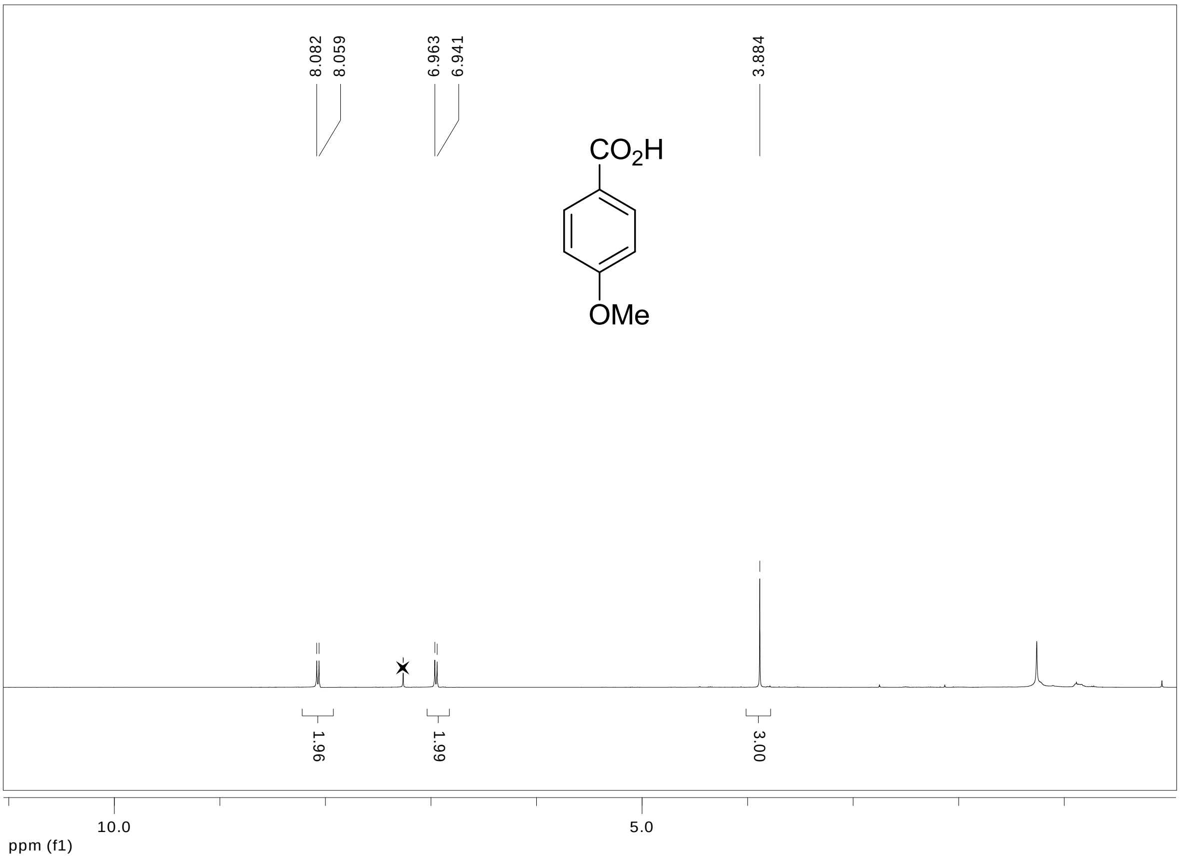


**Fig. S2** 4-Methoxybenzoic acid (**2b**).

$^1$H NMR (400 MHz, $CDCl_3$) 3.88 (s, 3H), 6.95 (d, *J* = 8.9 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 2H).

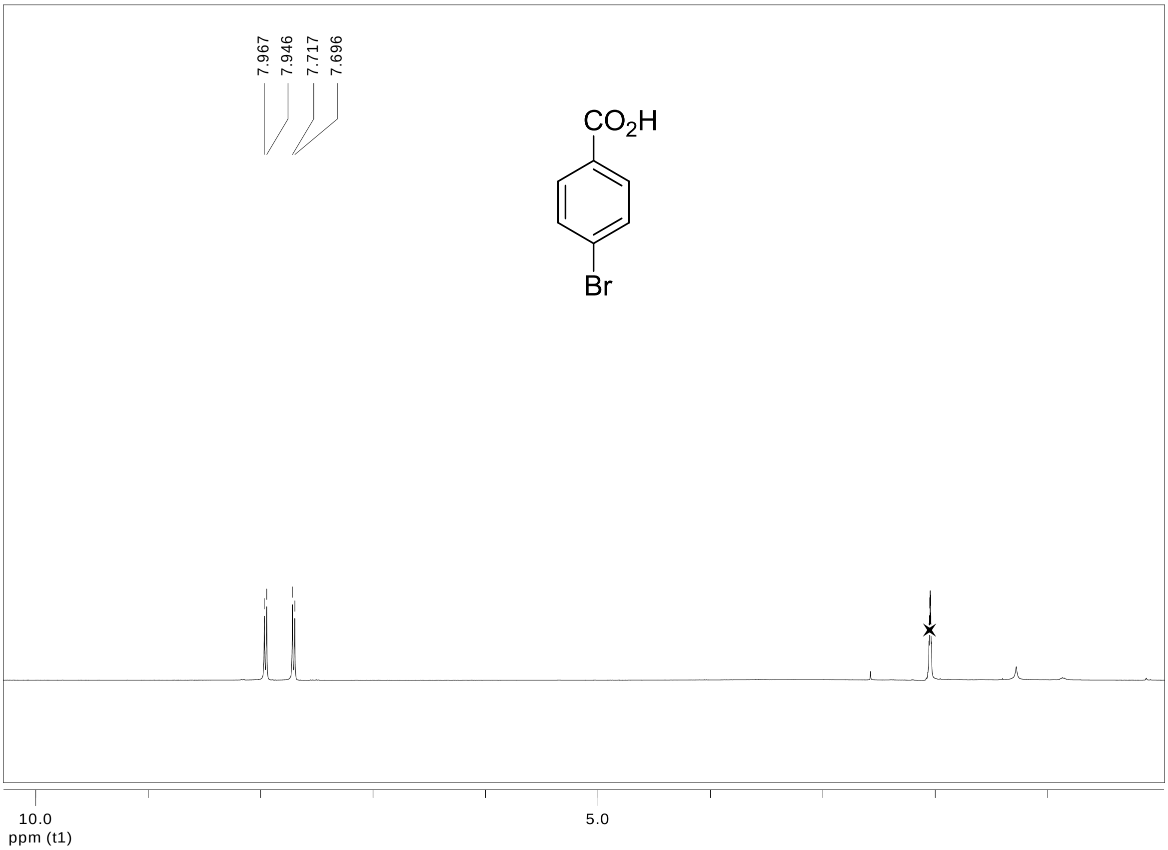


**Fig. S3** 4-Bromobenzoic acid (**2c**).

$^1$H NMR (400 MHz, Acetone-$d_6$) 7.70 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H).

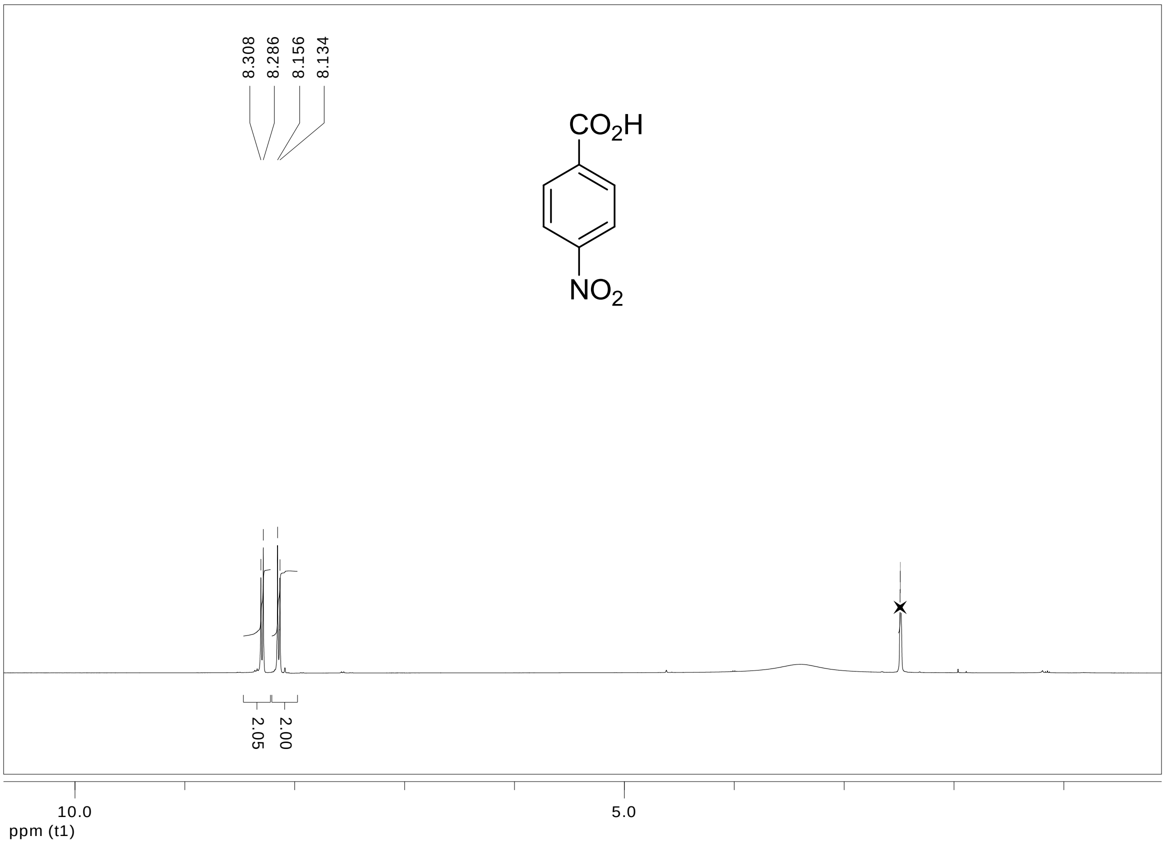


**Fig. S4** 4-Nitrobenzoic acid (**2d**).

$^1$H NMR (400 MHz, DMSO-d$_6$) 8.14 (d, *J* = 8.8 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H).

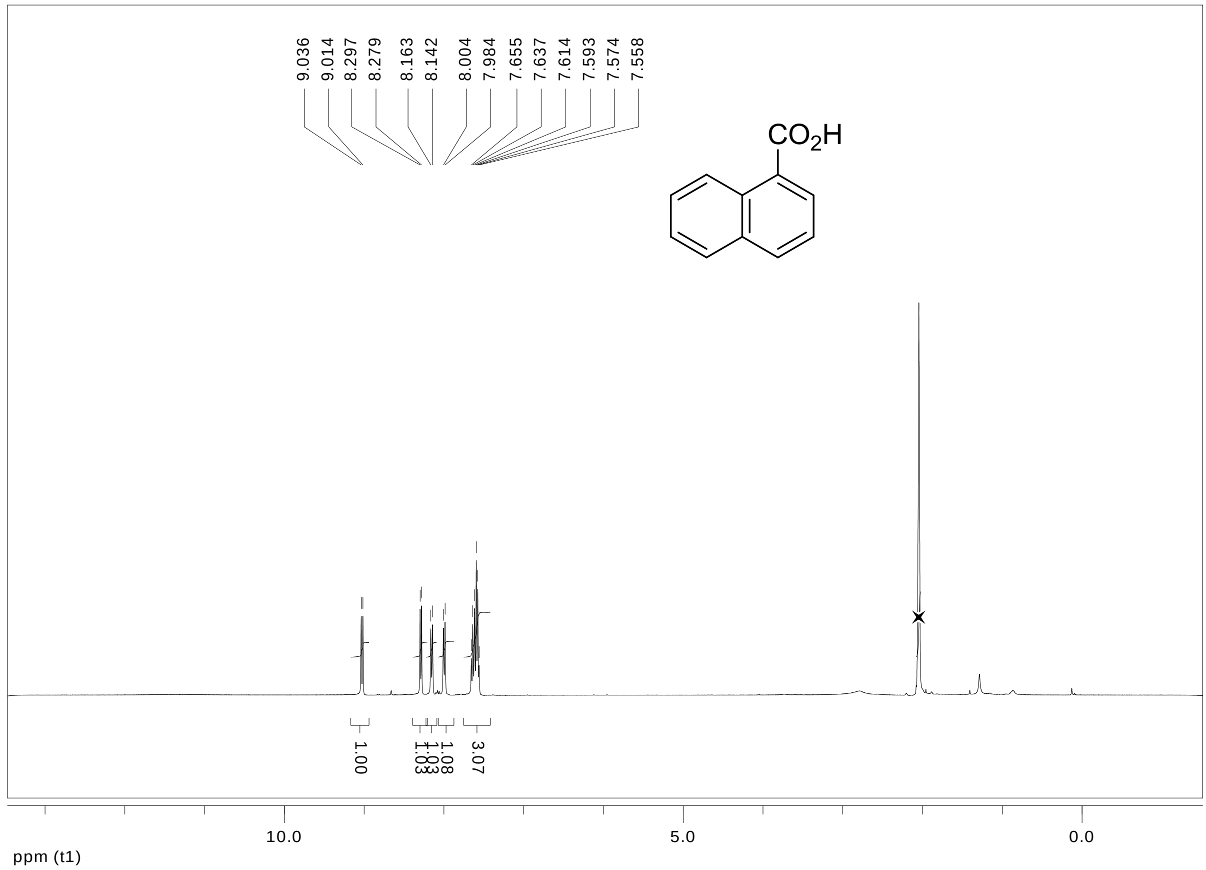


**Fig. S5** 1-Naphthenic acid (**2e**).

$^1$H NMR (400 MHz, Acetone-$d_6$) 7.56-7.65 (m, 3H), 7.99 (d, J = 8.6 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 8.28 (d, J = 7.2 Hz, 1H), 9.02 (d, J = 8.6 Hz, 1H).

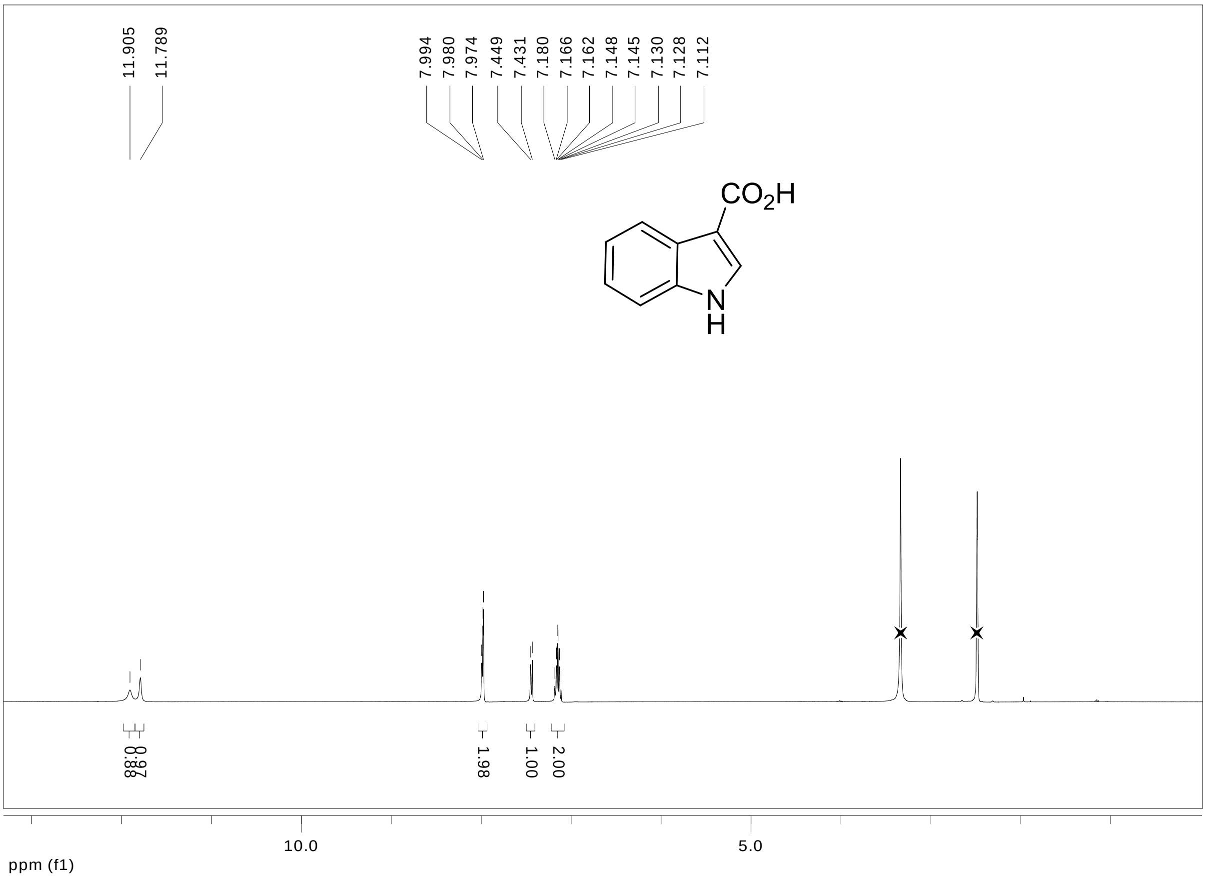


**Fig. S6** Indole-3-carboxylic acid (**2f**).

$^{1}H$ NMR (400 MHz, DMSO-$d_6$) 7.14 (m, 2H), 7.44 (dd, J = 7.0, 1.3 Hz, 1H), 7.97-7.99 (m, 2H), 11.78 (s, 1H), 11.90 (s, 1H).

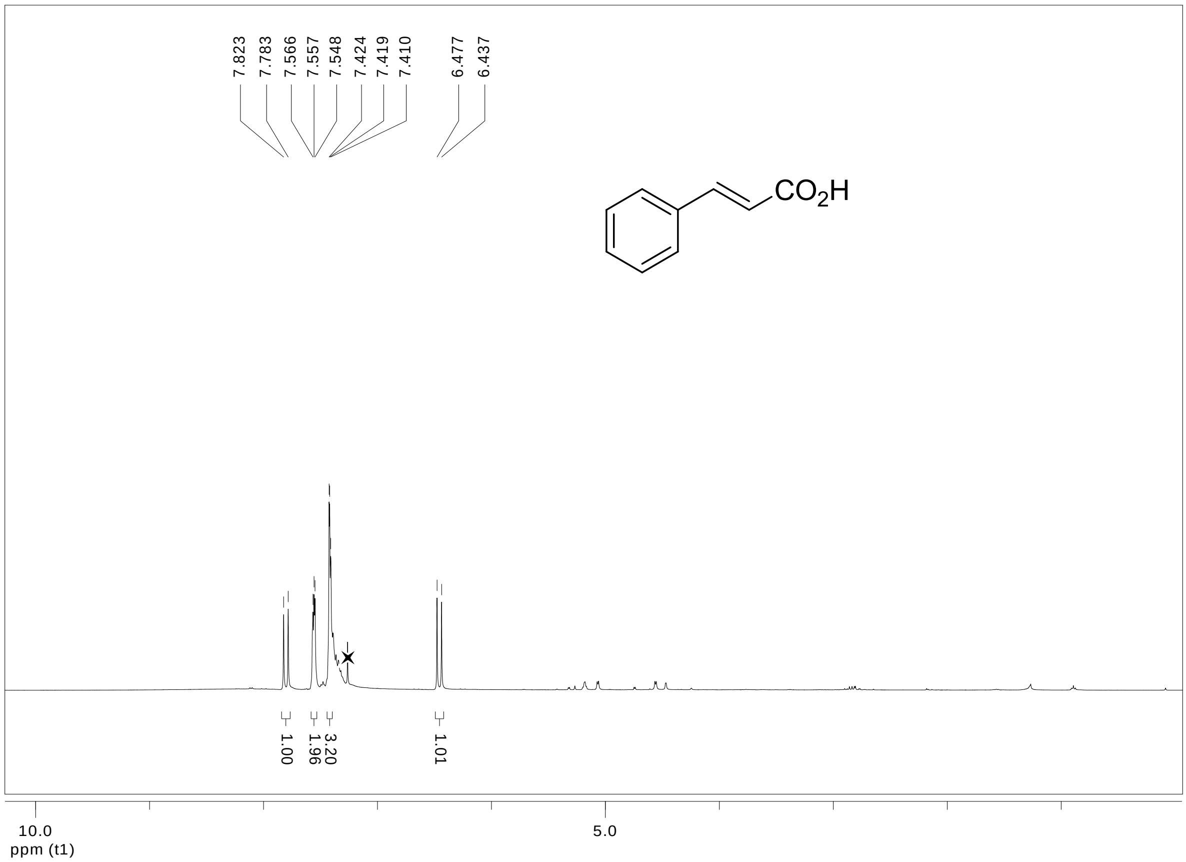


**Fig. S7** Cinnamic acid (**2g**).

$^1$H NMR (400 MHz, $CDCl_3$) 6.45 (d, *J* = 16.0 Hz, 1H), 7.36-7.42 (m, 3H), 7.54-7.56 (m, 2H), 7.80 (d, *J* = 16.0 Hz, 1H).

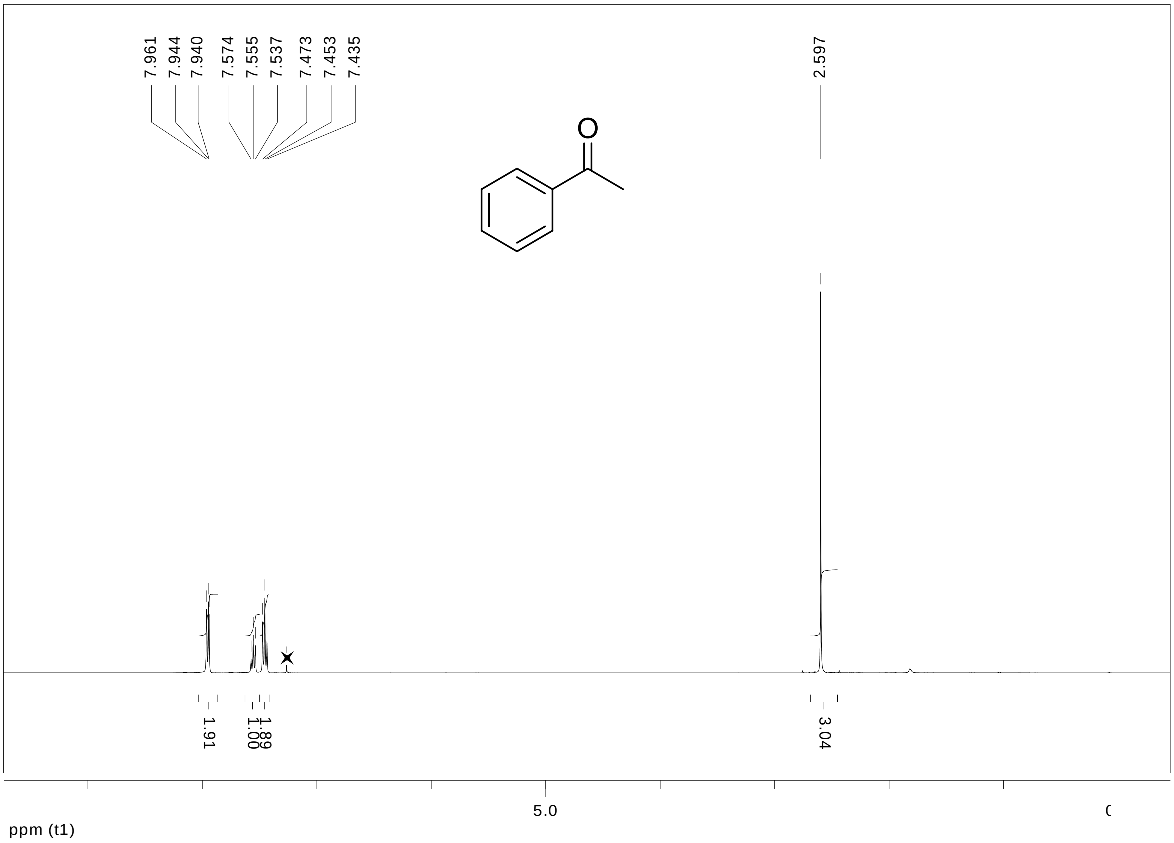


**Fig. S8** Acetophenone (**4a**).

[1]H NMR (400 MHz, $CDCl_3$) 2.59 (s, 3H), 7.45 (t, *J* = 7.6, 7,4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H).

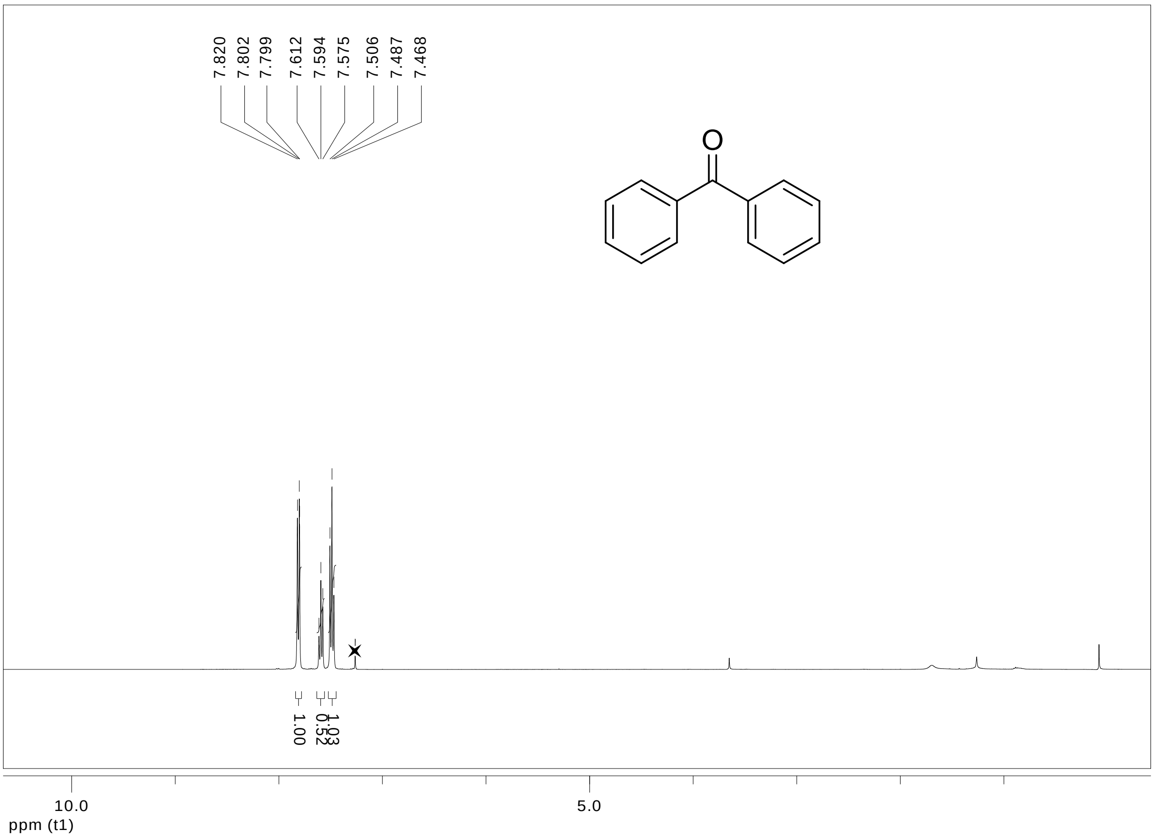


**Fig. S9** Benzophenone (**4b**).

$^1$H NMR (400 MHz, $CDCl_3$) 7.48 (dd, *J* = 7.6, 7.3 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 4H).

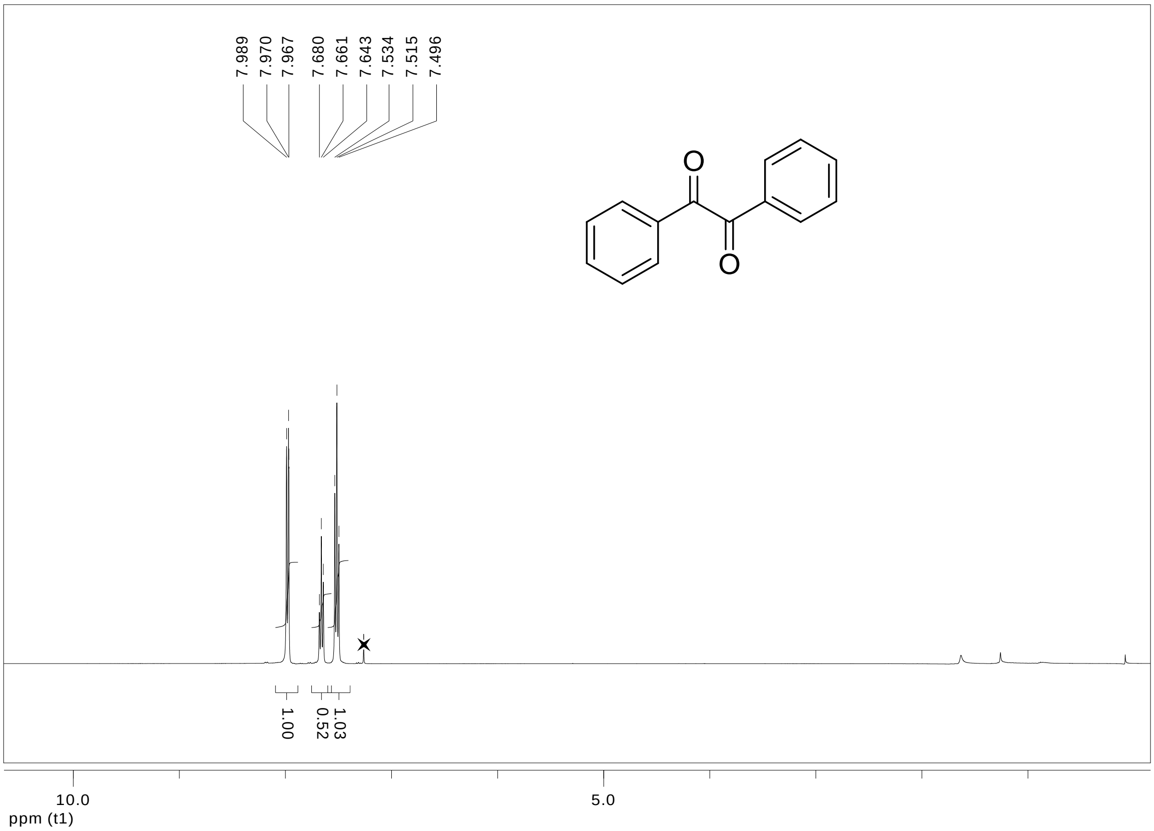


**Fig. S10** Benzil (**4c**).

$^{1}$H NMR (400 MHz, $CDCl_3$) 7.51 (dd, *J* = 7.8, 7.5 Hz, 4H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 4H).

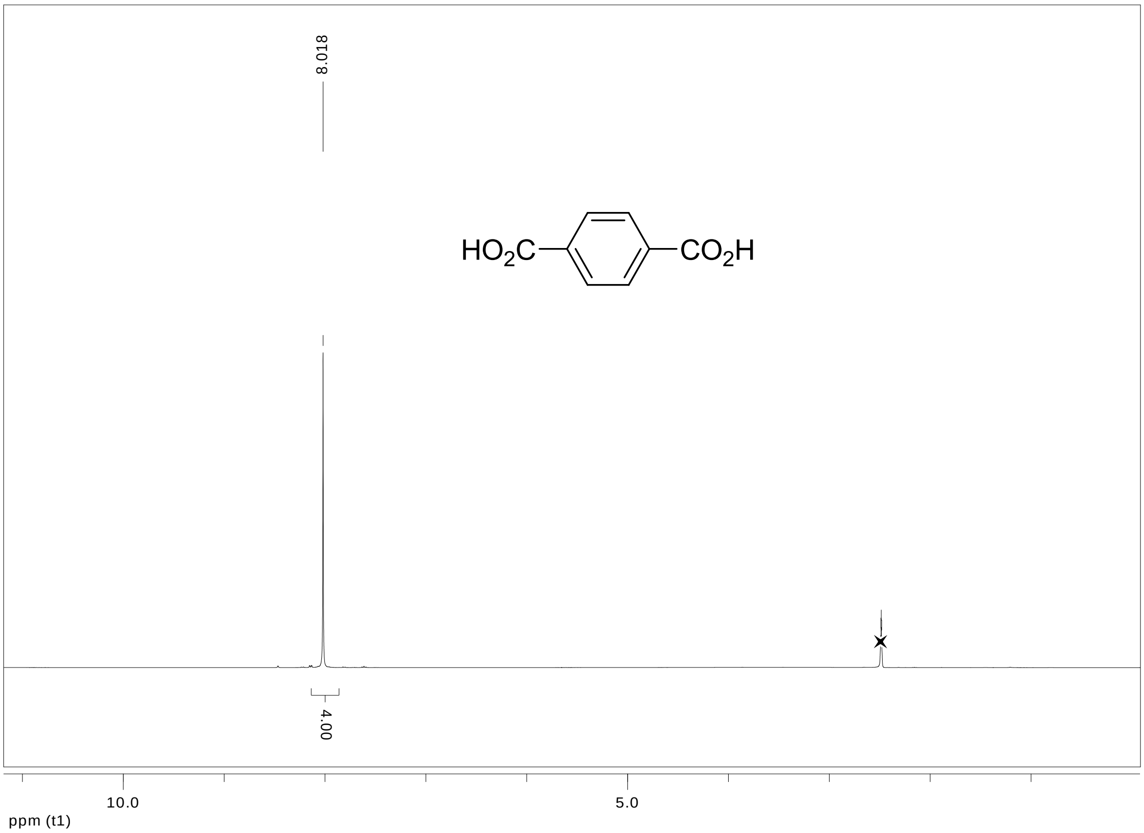


**Fig. S11** Terephthalic acid (**2i**).

[1]H NMR (400 MHz, DMSO-$d_6$) 8.02 (s, 4H).

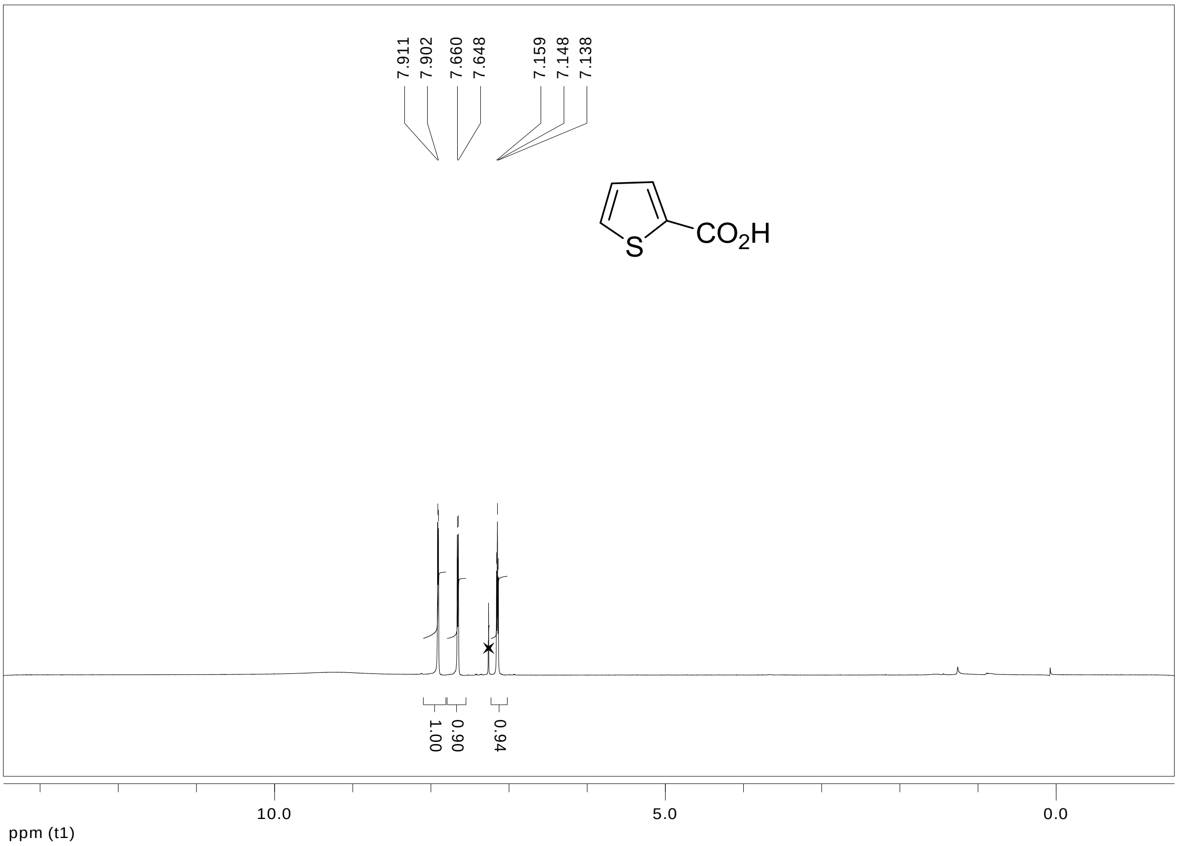


**Fig. S12** 2-Thiophenecarboxylic acid (**2j**).

$^{1}$H NMR (400 MHz, $CDCl_3$) 7.14 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.65 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 3.6 Hz, 1H).

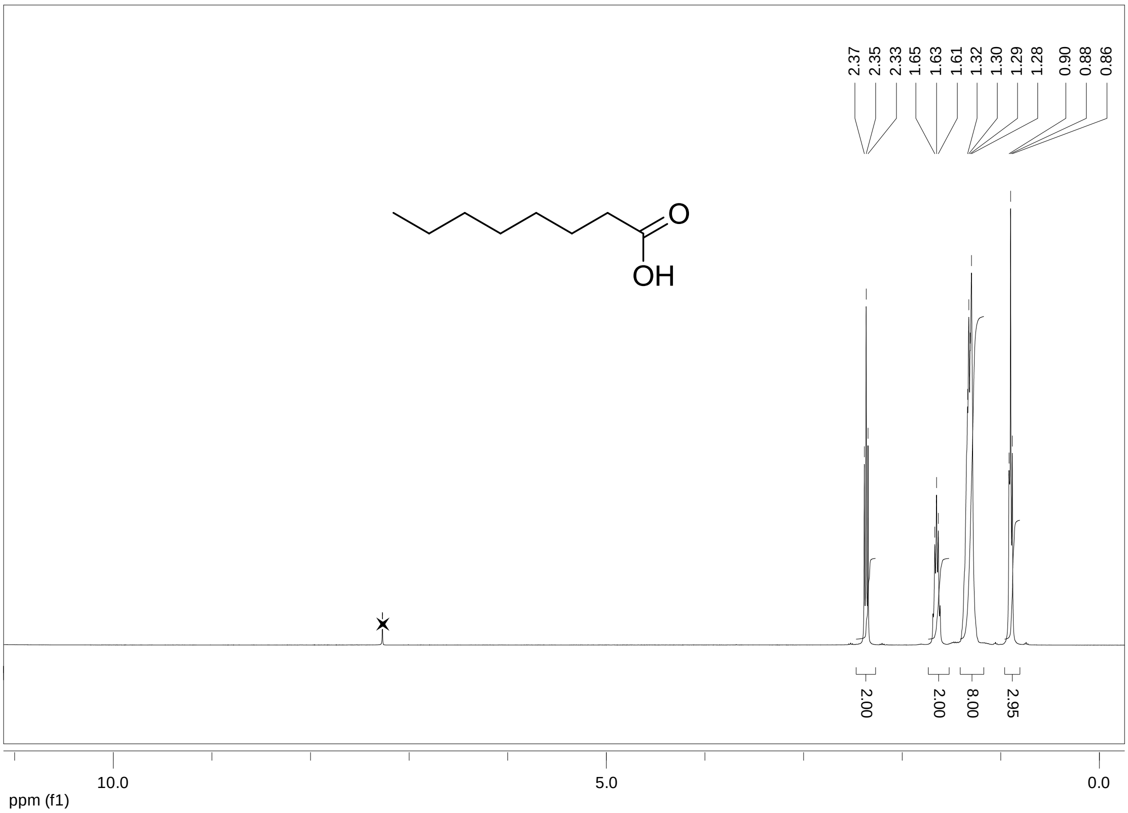


**Fig. S13** Octanoic acid (**2k**).

$^{1}$H NMR (400 MHz, $CDCl_3$) 0.88 (t, *J* = 7.1 Hz, 3H), 1.26-1.32 (m, 8H), 1.63 (m, , 2H), 2.35 (t, *J* = 7.3 Hz, 2H).

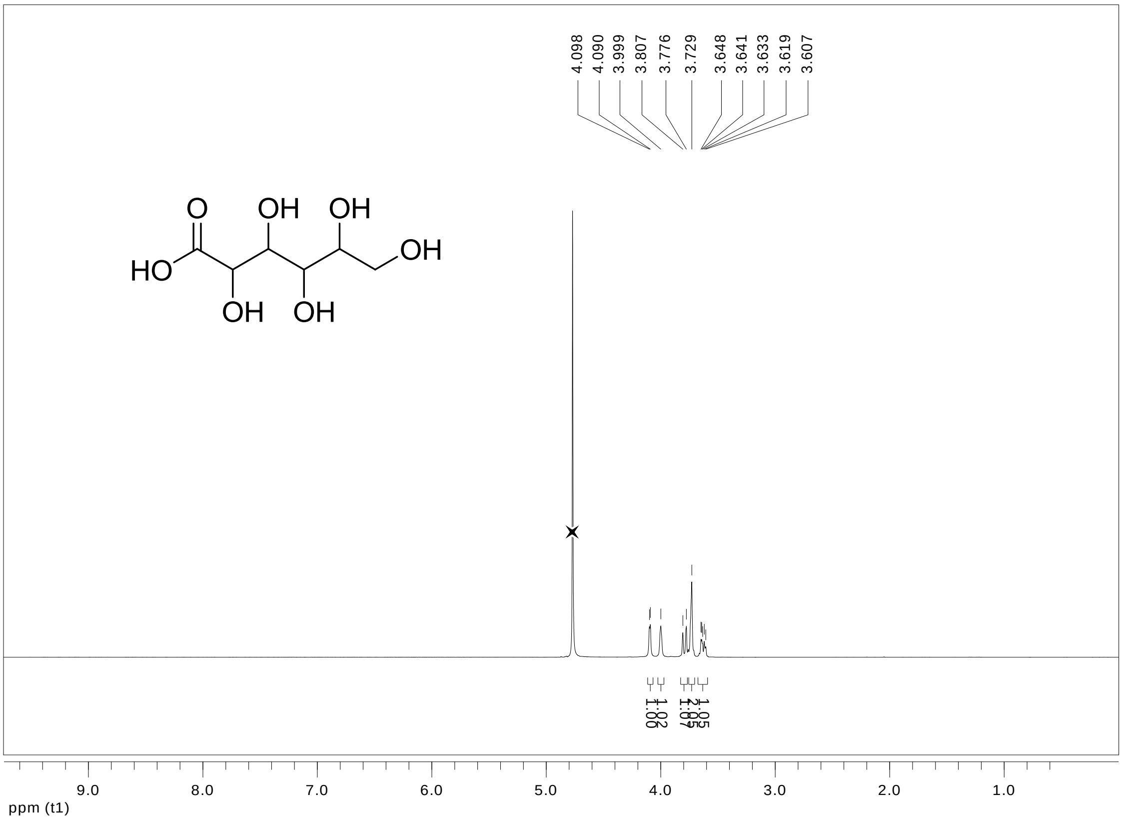


**Fig. S14** Gluconic acid (**2l**).

$^1$H NMR (400 MHz, $D_2O$) 3.61-3.65 (m, 1H), 3.72-3.79 (m, 3H), 3.99 (broad s, 1H), 4.09 (d, *J* = 3.0 Hz, 1H).