**Supplementary information**

Copper supported on acid-activated vermiculite as an efficient and recyclable catalyst for the Biginelli reaction: a green approach

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**Characterization of materials**

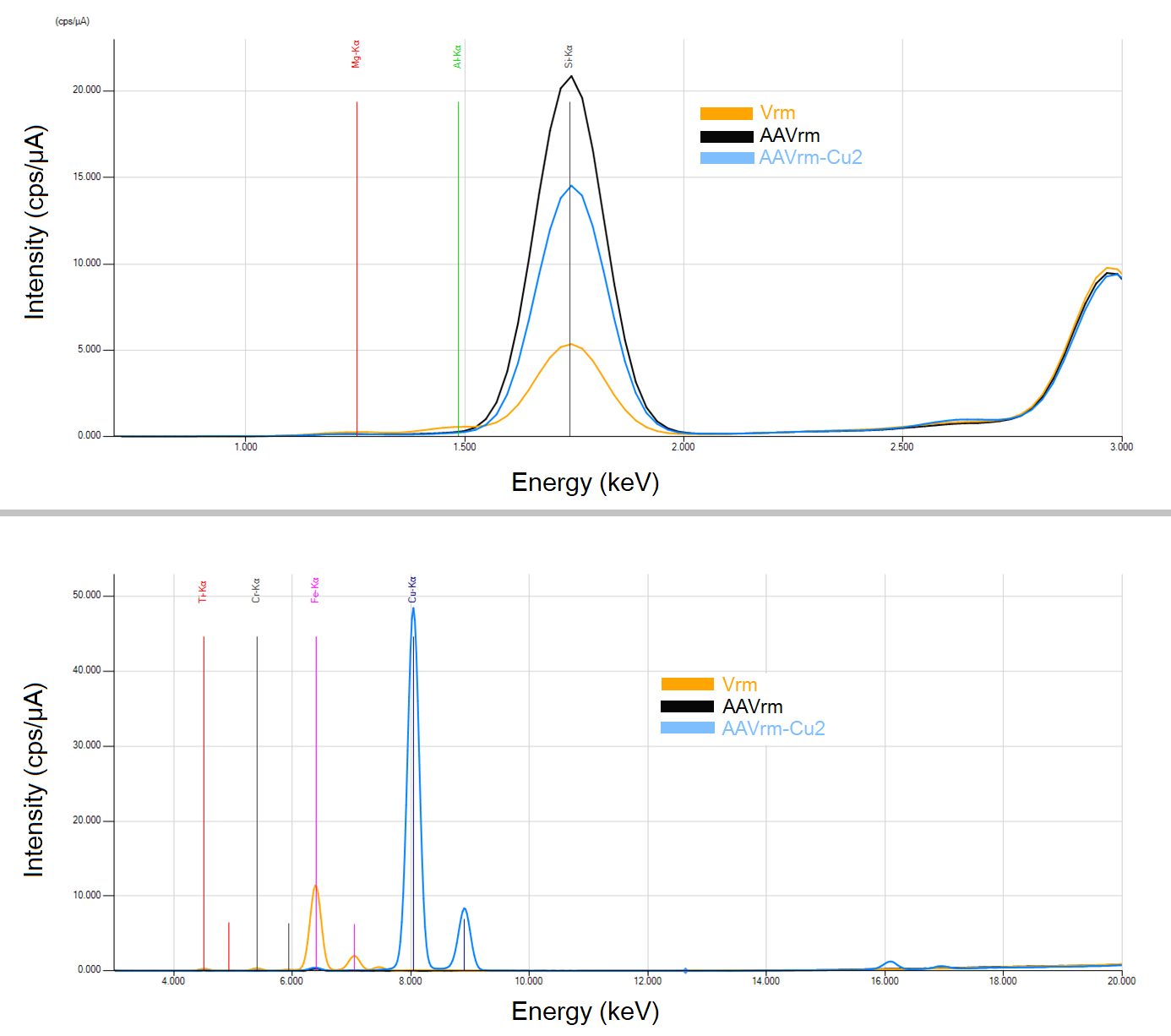


Fig. S1. XRF spectra of Vrm, AAVrm and AAVrm-Cu2.

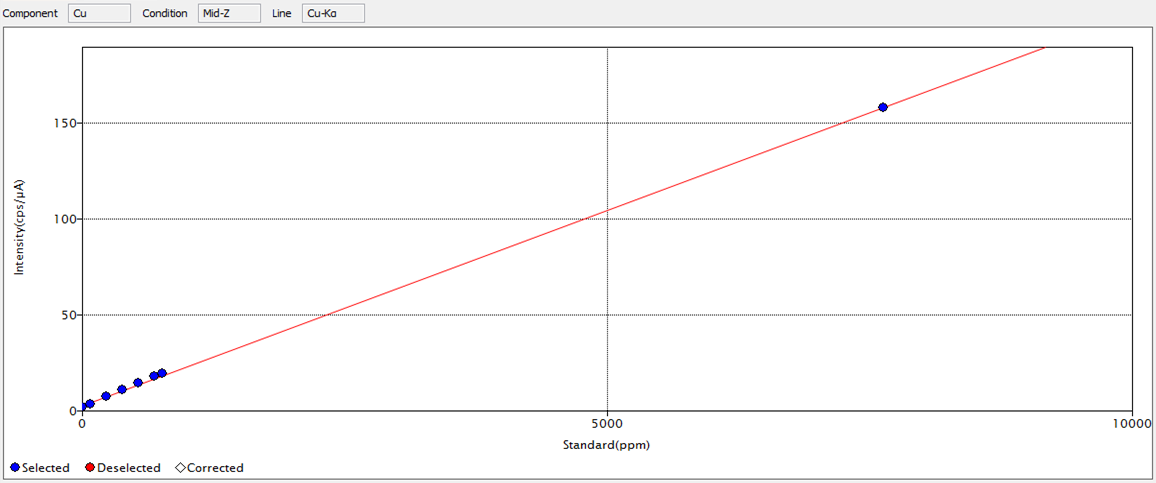
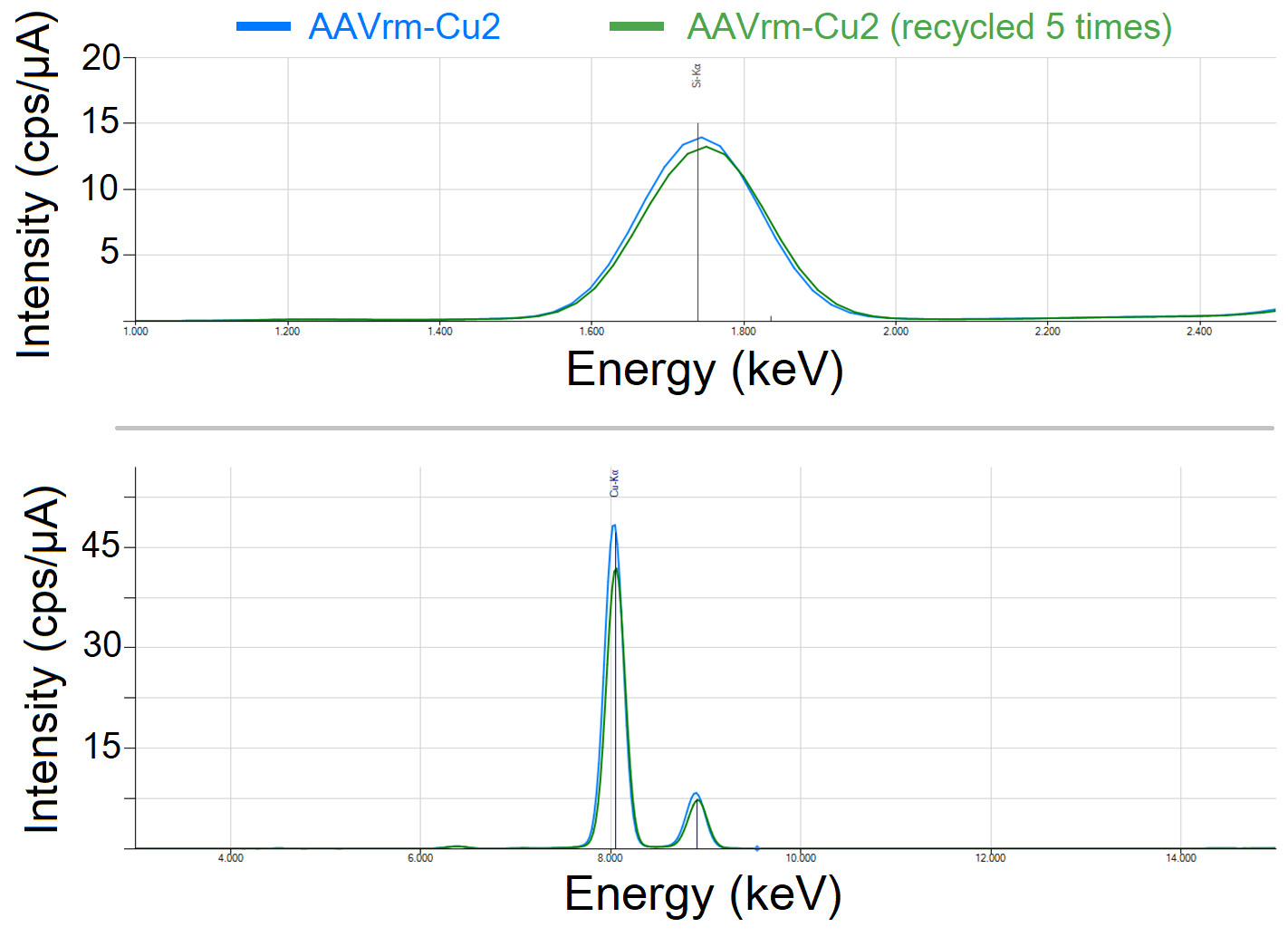


Fig. S2. XRF calibration curve of copper standard dissolutions (76–7635 ppm) used to quantify copper fixated in AAVrm-Cu2 and possible copper leachates in the remnant liquid phase of the Biginelli reaction.

 Fig. S3. XRF spectra of catalyst AAVrm-Cu2 and recycled AAVrm-Cu2 (five cycles).

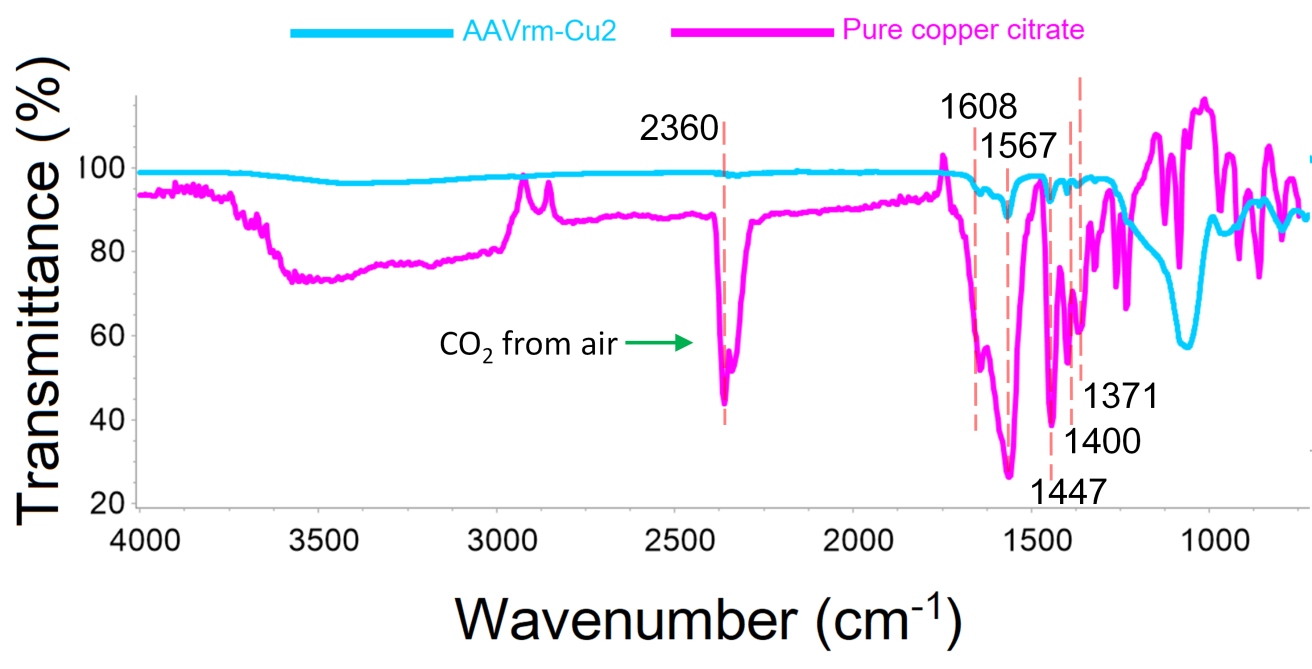


Fig. S4. FTIR spectra of AAVrm-Cu2 and pure copper citrate synthesized in this work.

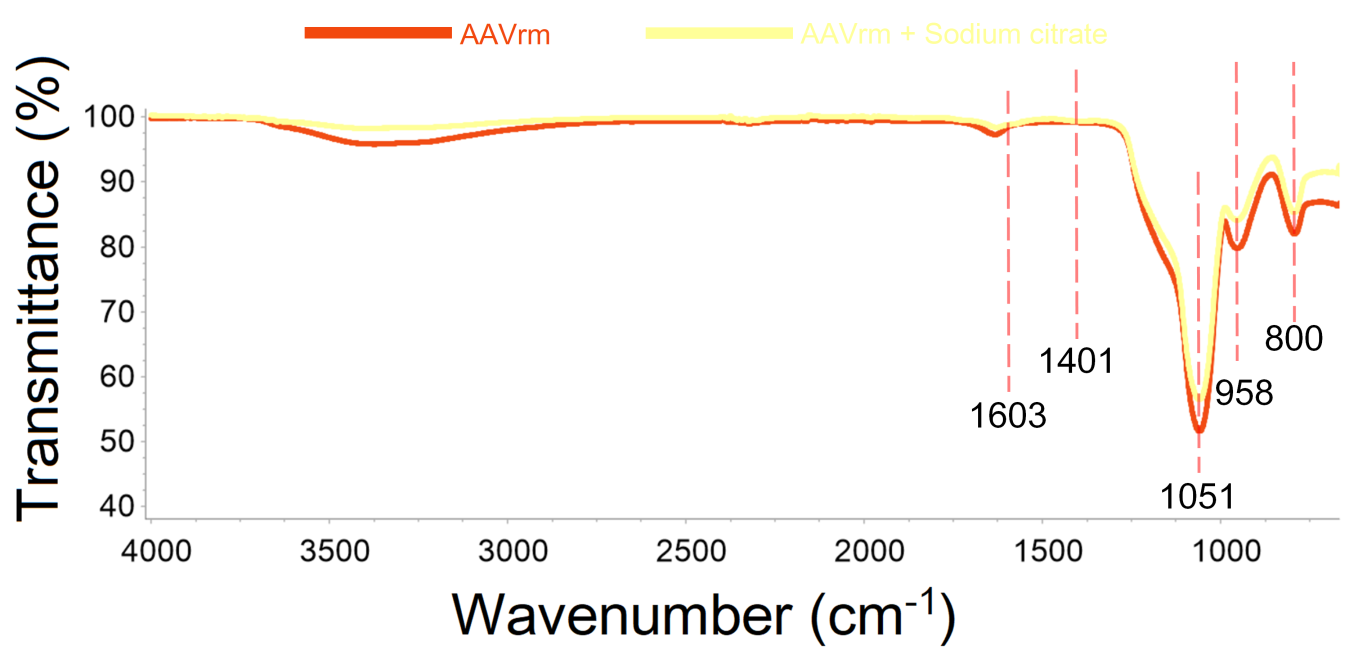


Fig. S5. FTIR spectra of AAVrm and AAVrm + sodium citrate.

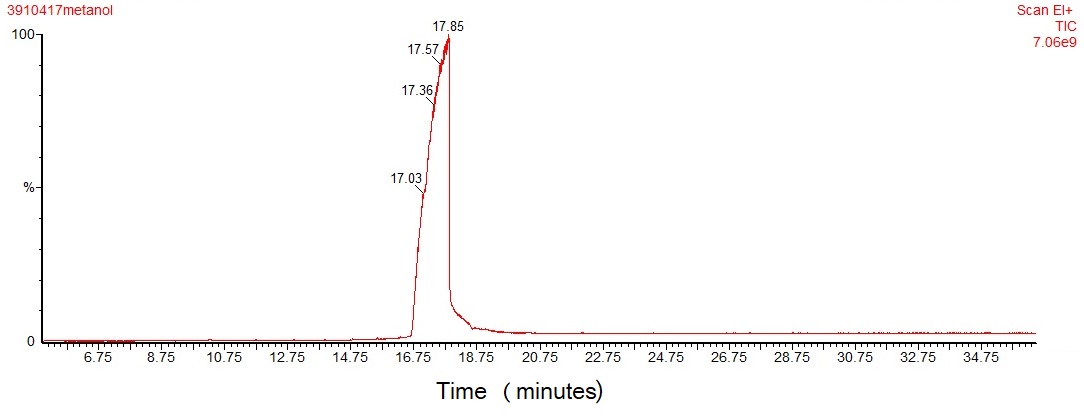


Fig. S6. Chromatogram (GC) of 4a.

Table S1. Spectroscopic data of 4a–4d**.**

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| ***Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a)*** |
| White solid, mp 206-207°C found (208°C reported*)*. 1H NMR (300 MHz, CDCl3): δ ppm) = 8.11 (br, 1H, NH), 7.33 (m, 5H, C6H5), 5.76 (br, 1H, NH), 5.42 (s, 1H, CH3), 4.08 (q, 2H, J = 7.1 Hz), 2.36 (s, 3H, CH3), 1.17 (t, 3H, CH3, J = 7.1 Hz). 13C NMR (75 MHz CDCl3): δ (ppm) = 165.61 (C=O), 153.28 (-NH-C=O-NH-), 146.20 (Calkene), 143.67 (Caromatic), 128.72 (2Caromatic), 127.97 (2Caromatic), 126.60 (Caromatic), 101.42 (Calkene), 60.03 (CH2), 55.77 (CH), 18.69 (CH3), 14.13 (CH3). FTIR-ATR (cm–1): 3,237 (N-H heterocyclic), 3115 (C-H aromatic), 2978 (C-H aliphatic), 1718 (C=O ester), 1643 (C=O heterocyclic), 1217 (C-O ester). MS-EI (m/z): 260 [M], 231, 187, 183 (100 %), 155, 137. |
| ***Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b)*** |
| White solid, mp 206-208°C found (203°C reported). 1H NMR (300 MHz CDCl3): δ (ppm) = 8.21 (d, 2H, J = 8.7 Hz), 7.53 (d, 2H, J = 8.8 Hz), 7.41 (s, 1H, NH), 5.71 (s, 1H, NH), 5.53 (s, 1H, CH), 4.11 (q, 2H, CH2, J = 7.2 Hz), 2.38 (s, 3H, CH3), 1.20 (t, 3H, CH3, J = 7.1 Hz). FTIR-ATR (cm–1): 3226 (N-H heterocycle), 3115 (C-H aromatic), 2976 (C-H aliphatic), 1720 (C=O ester), 1638 (C=O heterocycle), 1208 (C-O ester). DART-MS (m/z): 306 [C14H15N3O5 (M+H)] |
| ***Ethyl 4-[4-(dimethylamino)phenyl]-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c)*** |
| White solid, mp 256-267°C found (261°C reported). 1H NMR (300 MHz, CDCl3): δ (ppm) = 7.18 (d, 2H, Ar, J = 8.3 Hz), 6.96 (s, 1H, NH), 6.65 (d, 2H, Ar, J = 8.2 Hz), 5.31 (s, 1H, N-H), 5.31 (s, 1H, CH), 4.10 (q, 2H, CH2, J = 6.9 Hz), 2.97 (s, 6H, 2CH3), 2.35 (s, 3H, CH3), 1.20 (t, 3H, CH3, J = 7.2 Hz). FTIR-ATR (cm–1): 3,241 (N-H heterocyclic), 3,109 (C-H aromatic), 2,955 (C-H aliphatic), 1,720 (C=O ester), 1,644 (C=O heterocyclic), 1217 (C-O ester). DART-MS (m/z): 304.13[C16H22N3O3 (M+H)]. |
| ***Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d)*** |
| White solid, mp 232-234°C found (236°C reported). 1H NMR (300 MHz DMSO); δ (ppm)= 9.35 (s, 1H, OH), 9.10 (s, br, NH), 7.61 (s, br, NH), 7.02 (d, 2H, J = 8.5 Hz), 6.70 (d, 2H, J = 8.6 Hz), 5.05 (s, 1H, CH), 3.99 (q, 2H, CH2 ester), 2.23 (s, 3H, CH3), 1.10 (t, 3H, CH3, J = 7.1 Hz). 13C NMR (75 MHz DMSO); δ (ppm) = 165.9 (Ccarbonyl ester), 157 (C-OH phenol), 152.7 (-NH-C=O-NH-), 148.2 (Calkene), 128.1, 135.9 (2C, *ipso*-phenyl), ) 127.6 (Caromatic), 115.43 (Caromatic), 100.2 (Calkene), 59.6 (CH2), 54.0 (CH), 18.3 (CH3), 14.4 (CH3). FTIR-ATR (cm–1); 3503 (OH), 3,232 (N-H heterocycle), 3,108 (C-H aromatic), 2,981 (C-H alifatic), 1,680 (C=O ester), 1,640 (C=O heterocycle). DART-MS (m/z): 277.06 [C14H16N2O4 (M+H)]. |

Melting points were compared to the results reported by: Yao N., Lu M., Liu X.B., Tan J. & Hu Y.L. (2018) Copper-doped mesoporous silica supported dual acidic ionic liquid as an efficient and cooperative reusability catalyst for Biginelli reaction. *Journal of Molecular Liquids*, **262**, 328-335.

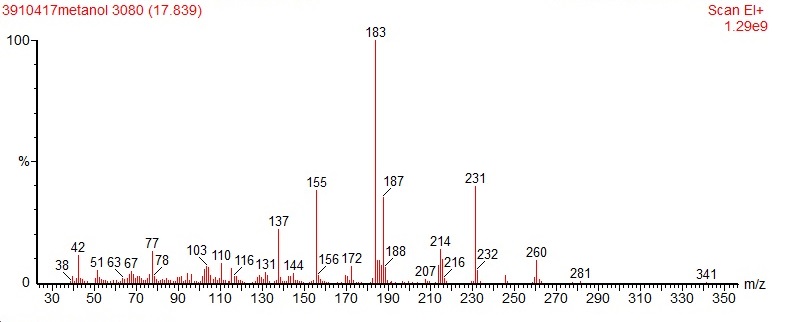


Fig. S7. Mass spectra of 4a.

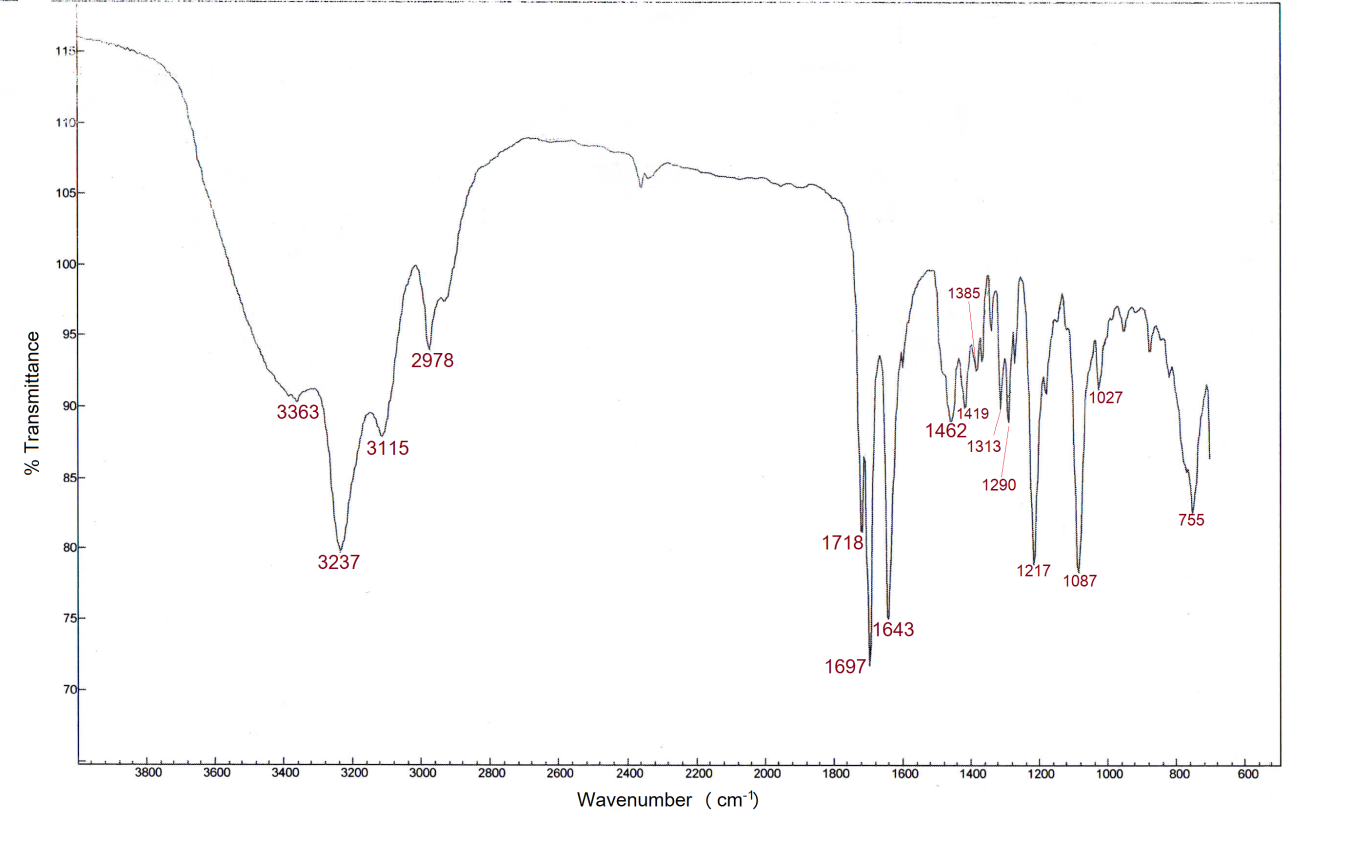


Fig. S8. FTIR-ATR spectra of 4a.

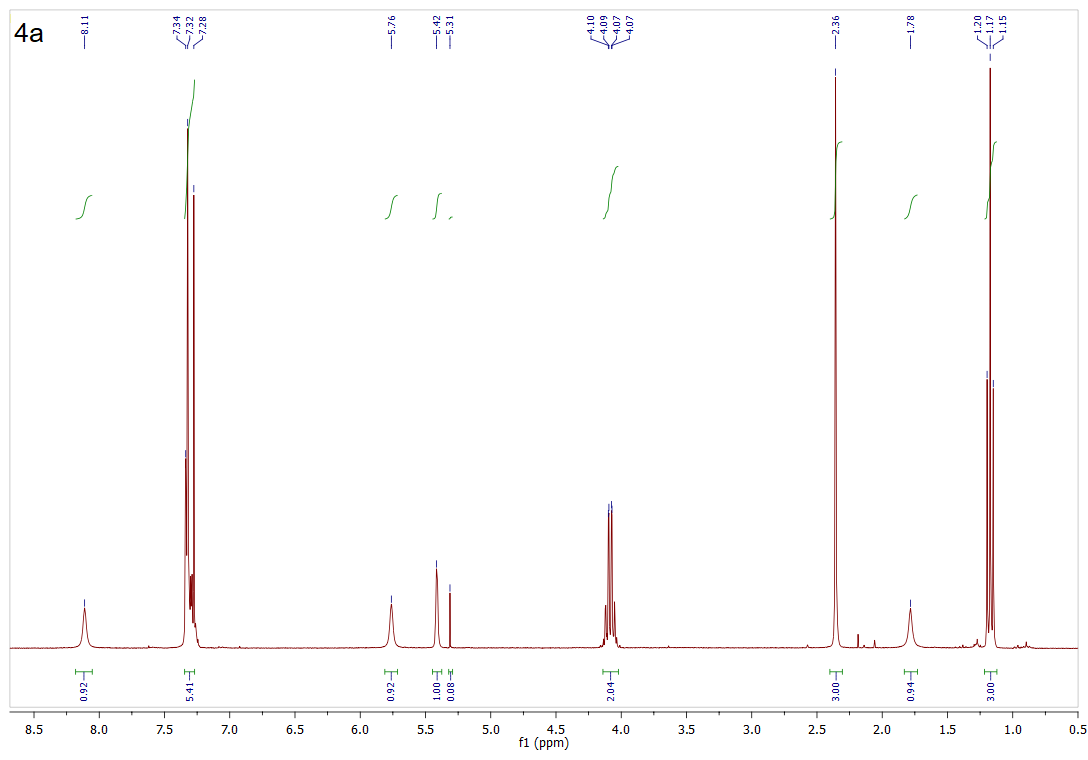


Fig. S9. 1H NMR spectra of 4a.

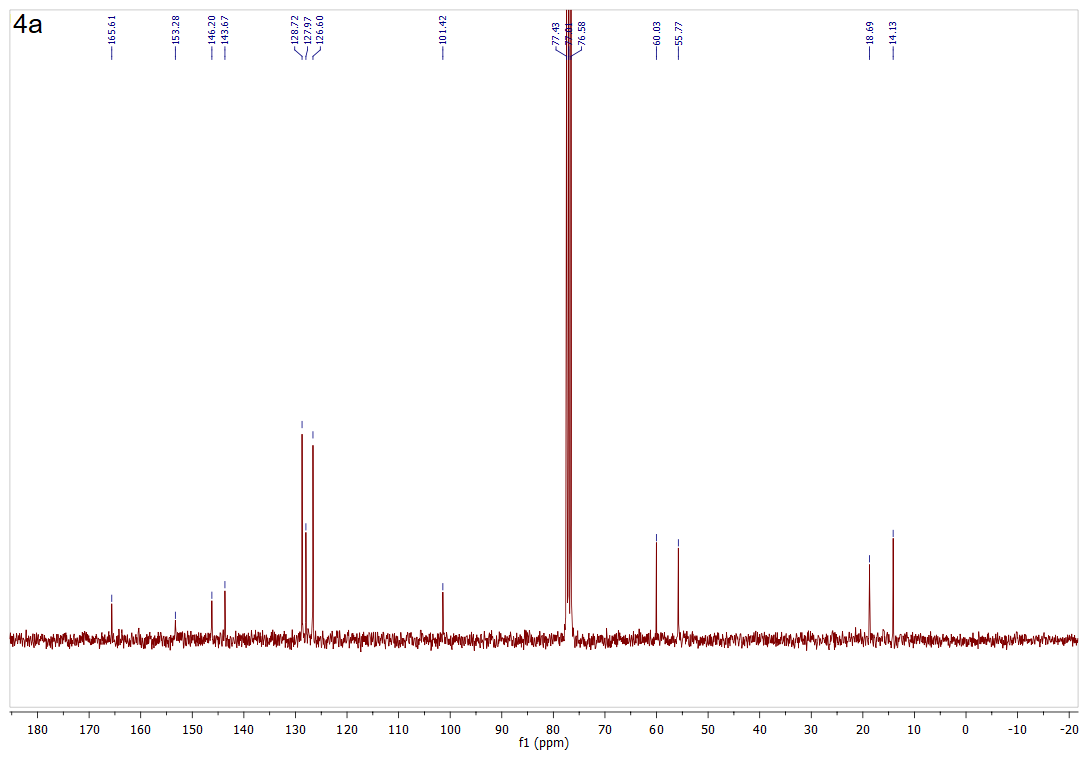


Fig. S10. 13C NMR spectra of 4a.

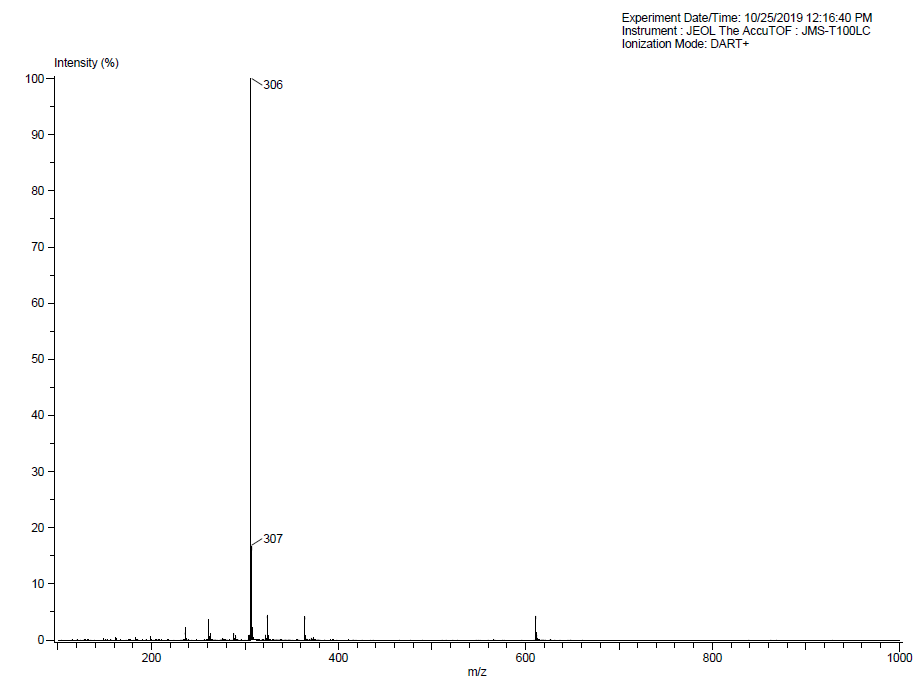


Fig. S11. Mass spectra of 4b.

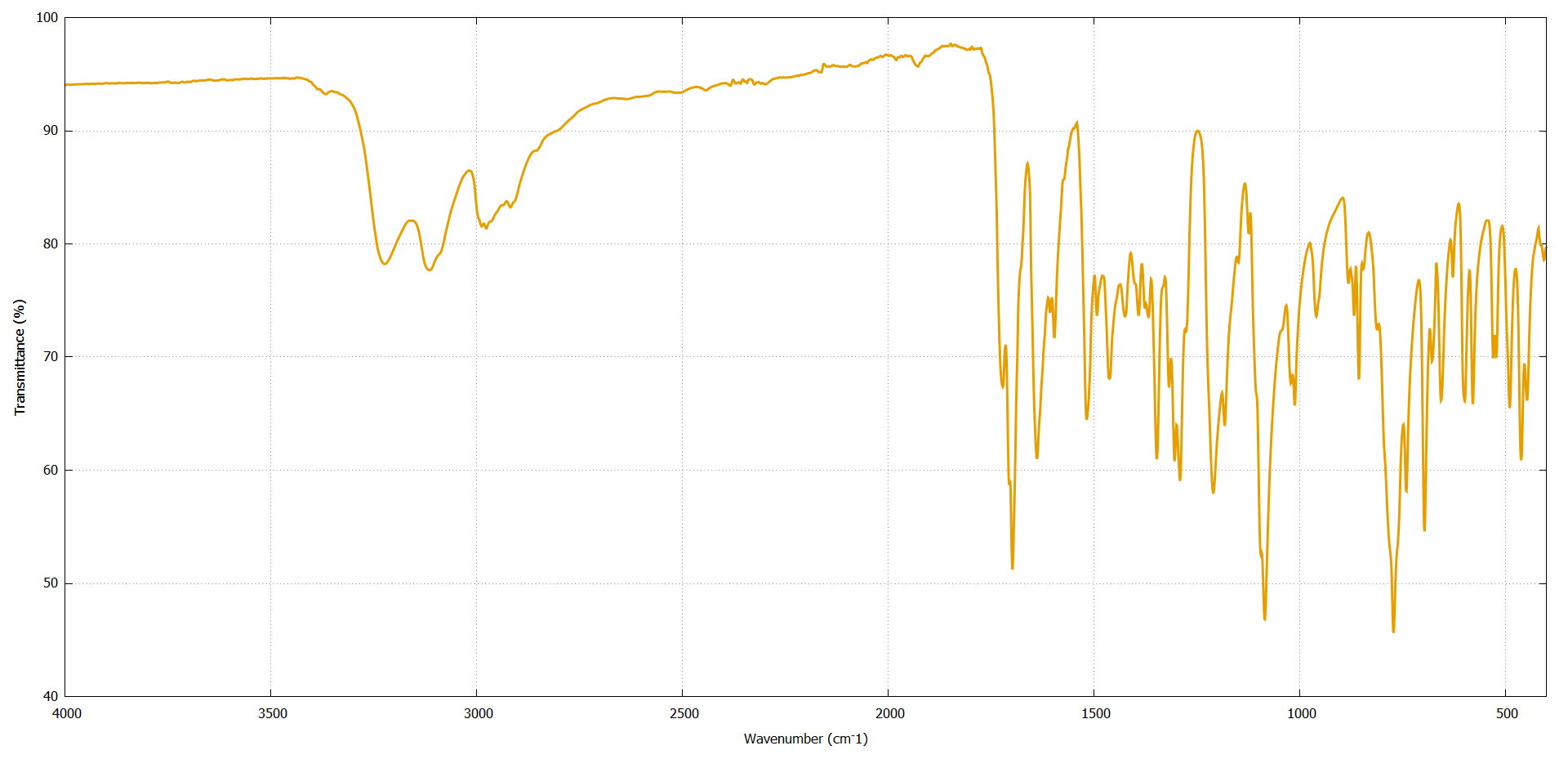


Fig. S12. FTIR-ATR spectra of 4b.

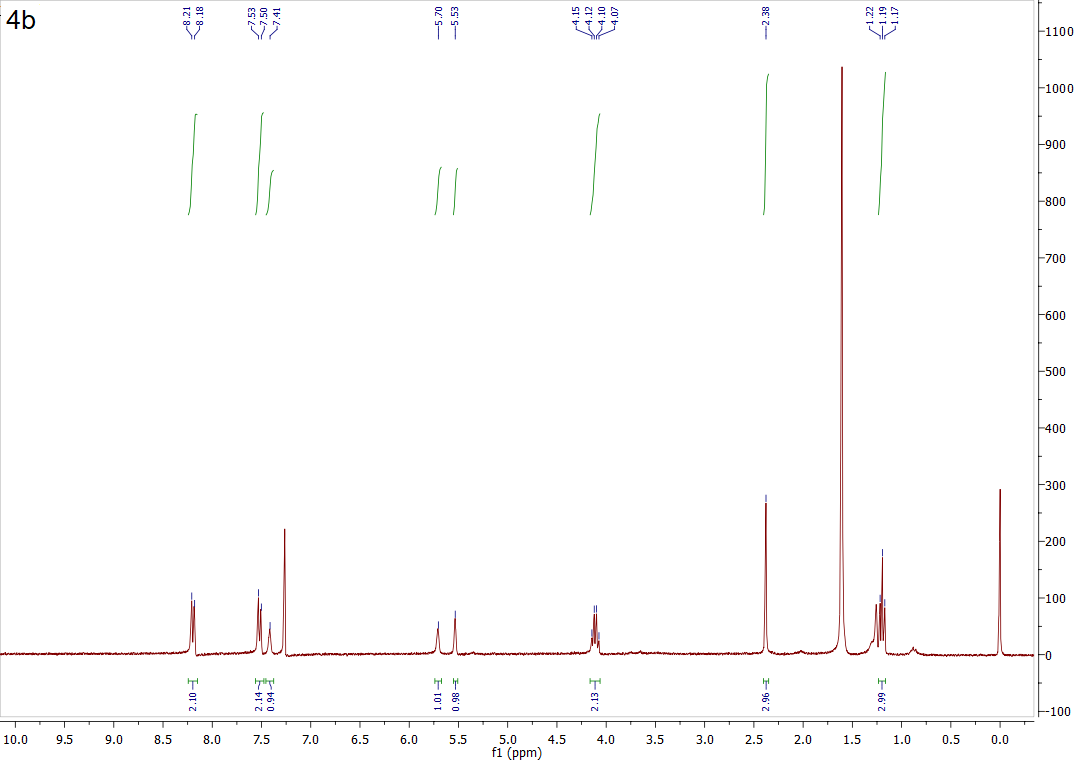


Fig. S13. 1H NMR spectra of 4b.

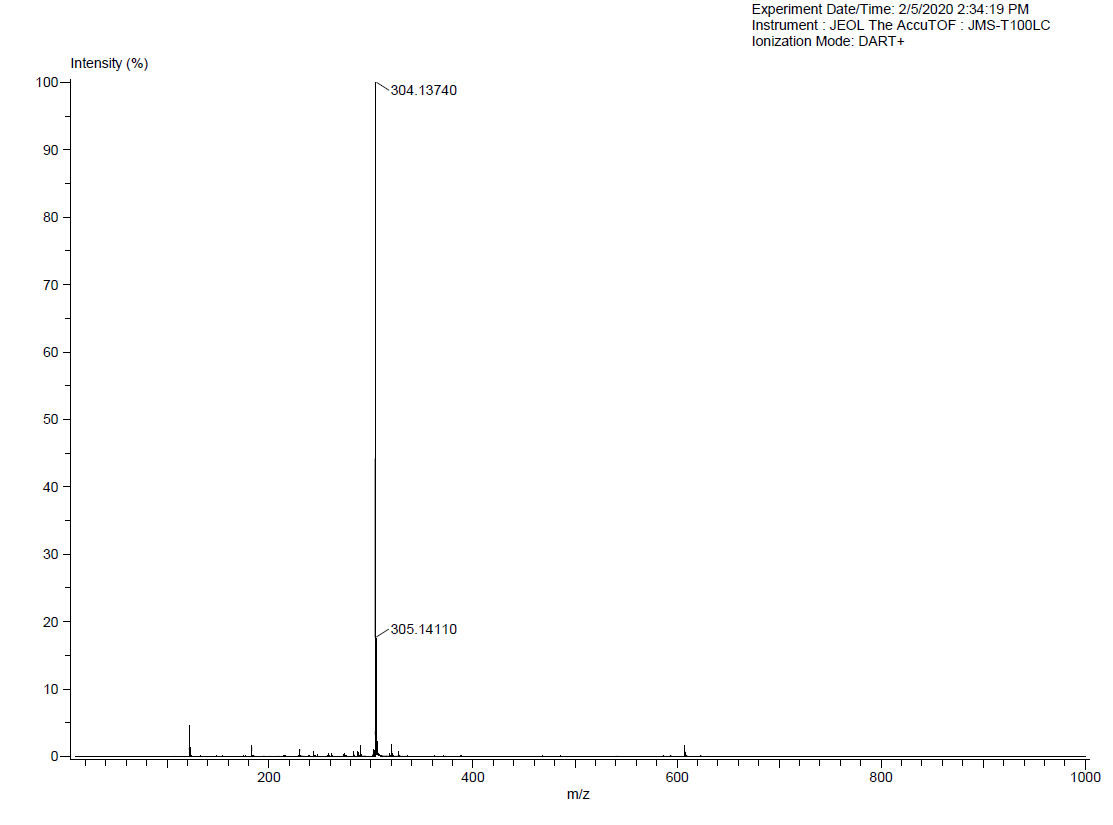


Fig. S14. Mass spectra of 4c.

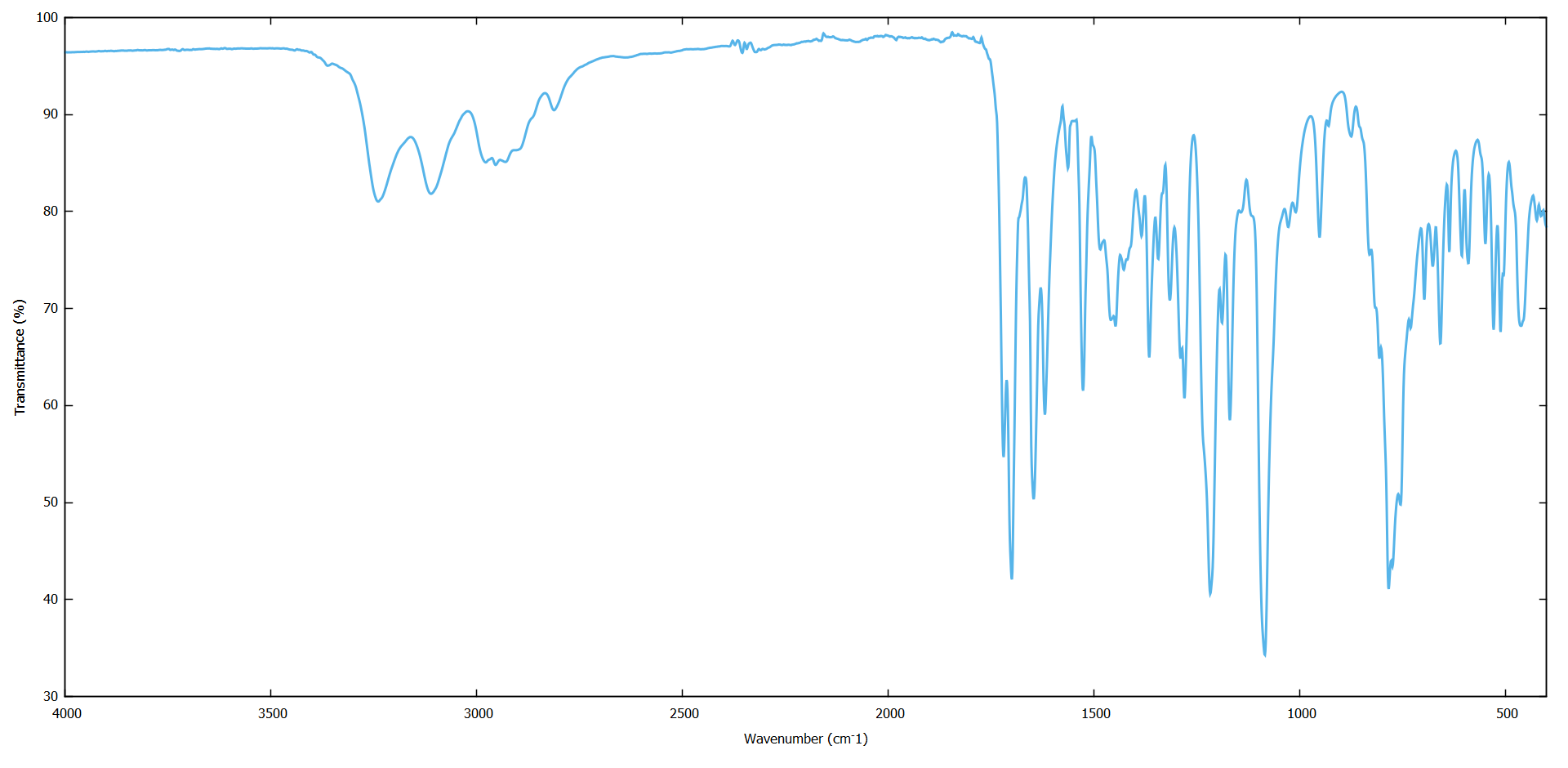


Fig. S15. FTIR-ATR spectra of 4c.

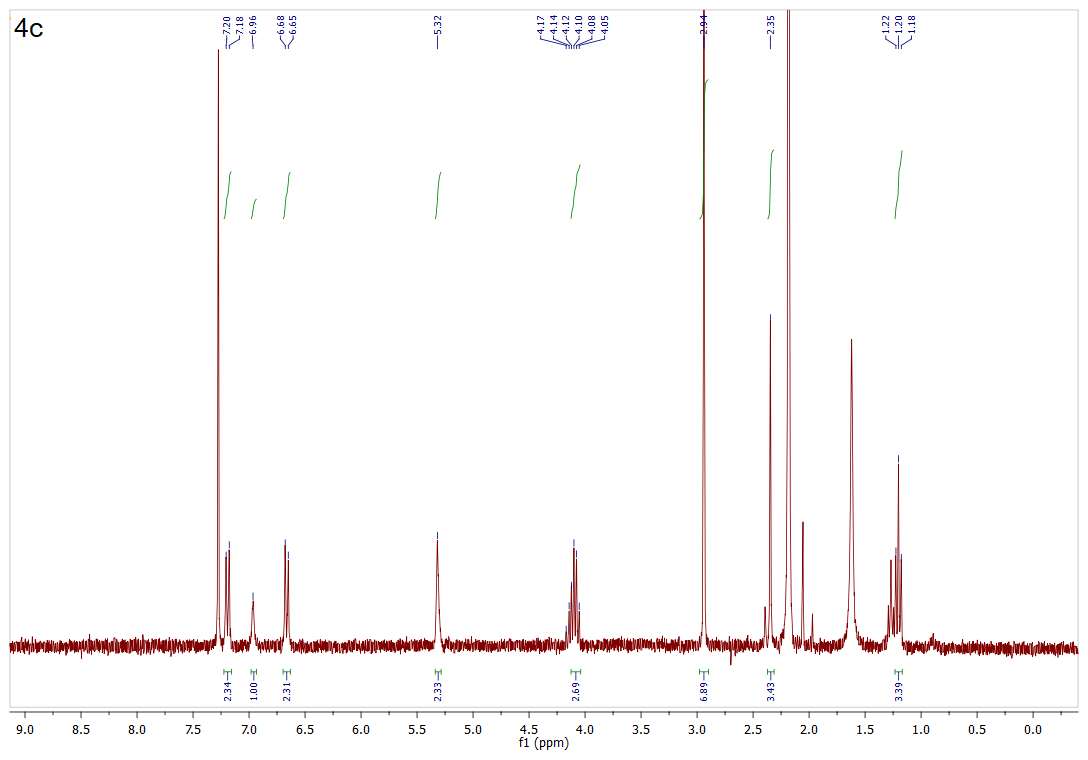


Fig. S16. 1H NMR spectra of 4c.

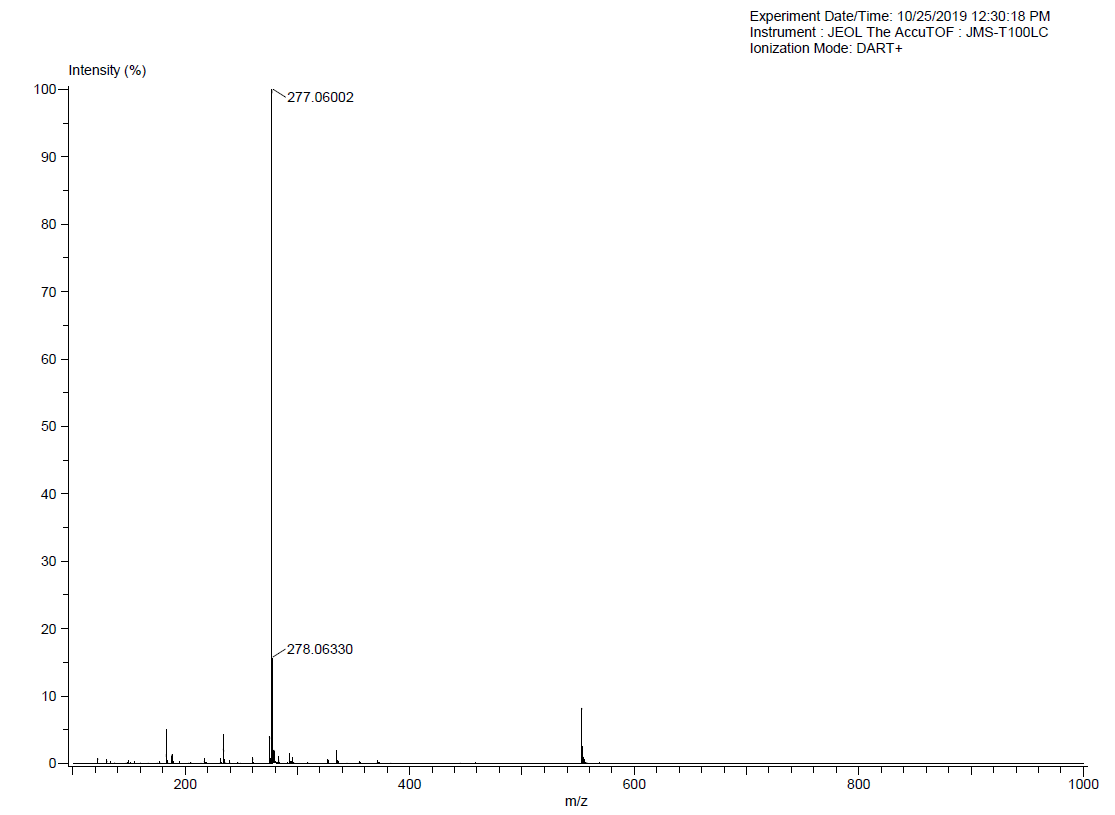


Fig. S17. Mass spectra of 4d.

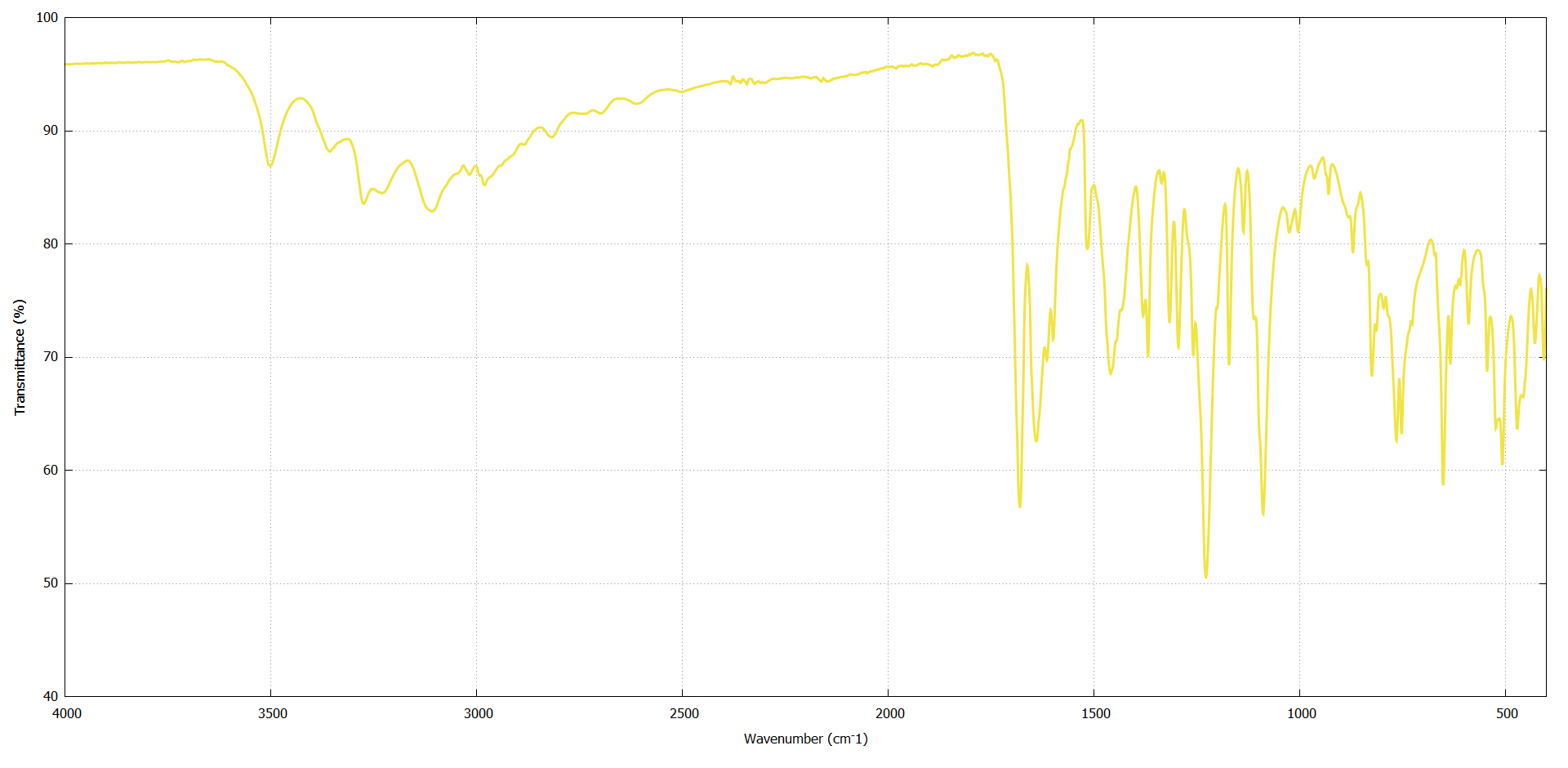


Fig. S18. FTIR-ATR spectra of 4d.

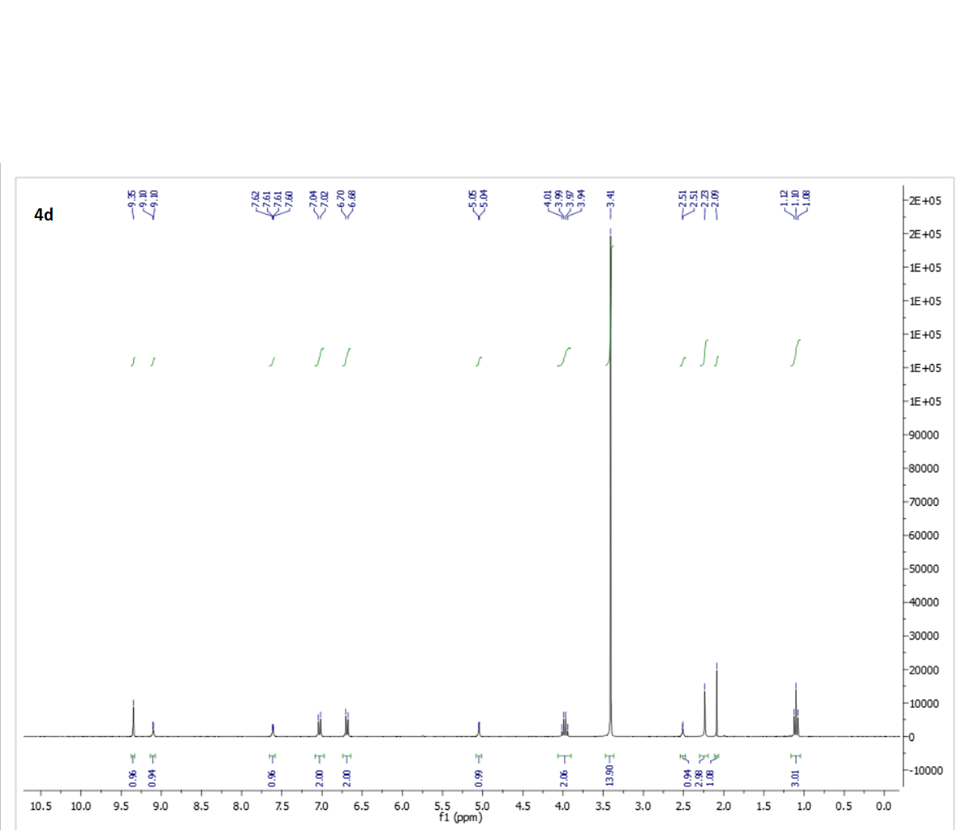


Fig. S19. 1H NMR spectra of 4d.

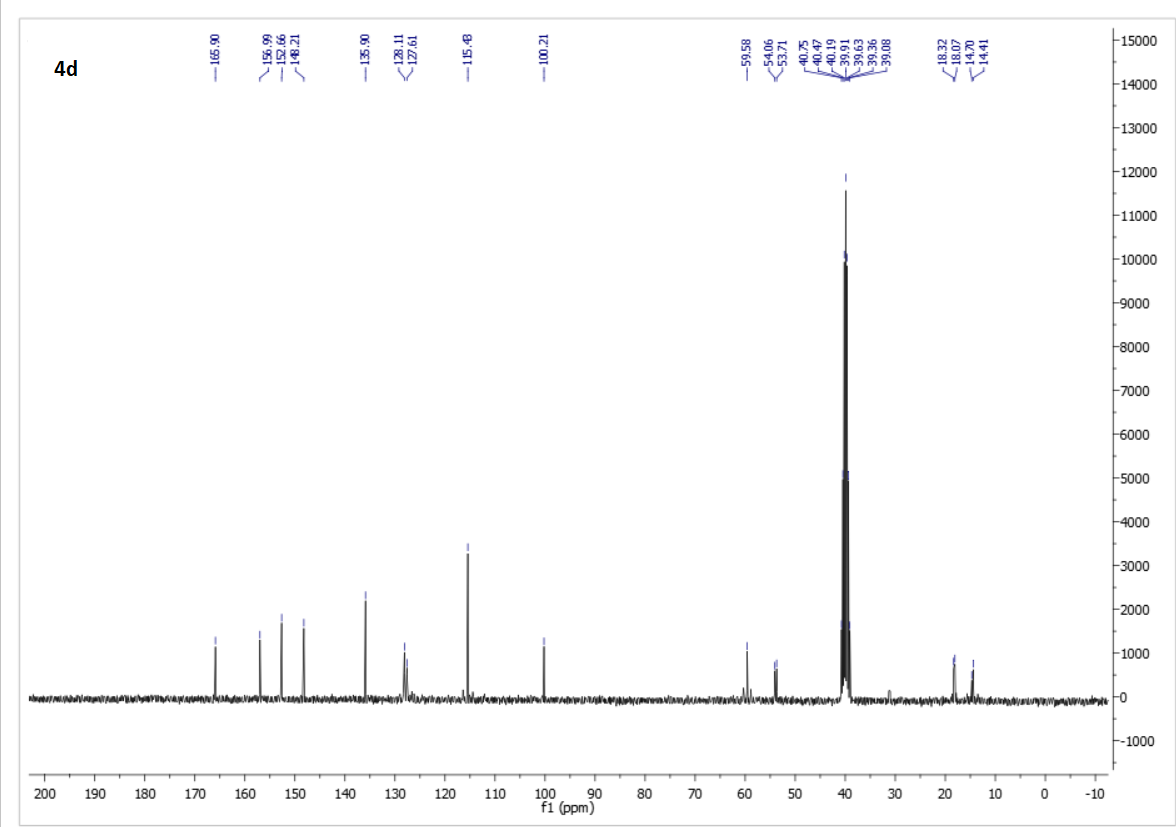


Fig. S20. 13C NMR spectra of 4d