

Electronic supplementary information (ESI)

Cultivation of Cu/HMPC catalyst from hyperaccumulating mustard plant for highly efficient and selective coupling reactions under mild conditions

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Experimental section

Preparation of Hogland nutrient solution. The modified Hoagland's solution was prepared by mixing three different nutrient solutions such as microelement nutrient solution, ferric salt solution and macroelement nutrient solution. At first, stock solution of these three different nutrient solutions were prepared. Then the prepared microelement nutrient solution and ferric salt solution were mixed into macroelement nutrient solution at particular concentration.^{1,2}

The macroelement nutrient solution was prepared in aqueous solution containing calcium nitrate tetrahydrate (945 mg/L), potassium nitrate (506 mg/L), ammonium nitrate (80 mg/L), potassium phosphate monobasic (136 mg/L), magnesium sulphate (493 mg/L), ferric salt solution (2.5 ml), microelement nutrient solution (5 ml, pH=6.0).

The ferric salt solution was prepared by dissolving ferrous sulfate (2.78 g) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 3.73 g) in 0.5 L water.

Similarly, potassium iodide (0.83 mg/L), orthoboric acid (6.2 mg/L), manganese sulphate (22.3 mg/L), zinc sulfate (8.6 mg/L), sodium molybdate dehydrate (0.25 mg/L), copper sulfate (0.025 mg/L), and cobalt chloride (0.025 mg/L) were dissolved in 1L of water to prepare microelement nutrient solution.

Reference

- (1) T. Barac, S. Taghavi, B. Borremans, A. Provoost, L. Oeyen, J. V. Colpaert, J. Vangronsveld, D. van der Lelie, *Nat. Biotechnol.*, 2004, **22**, 583–588.
- (2) D. Ye, T. Li, Z. Zheng, X. Zhang, G. Chen, H. Yu, *Front. Plant. Sci.* 2015, **6**, 1–10.

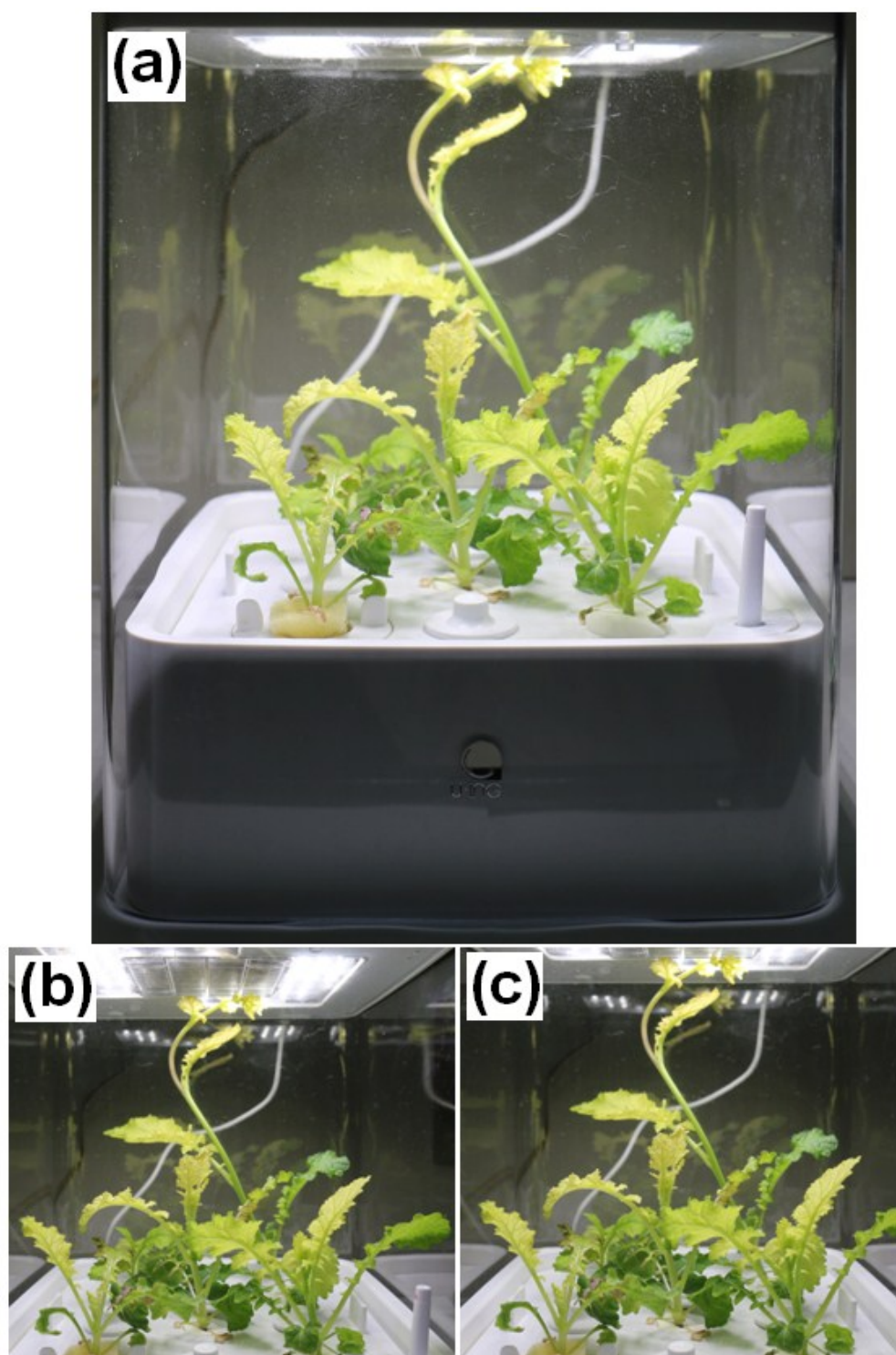


Fig. S1. Cultivation of HMP using Cu^{2+} nutrient solution.



Fig. S2. Optical image of well-grown Cu/HMP plant.

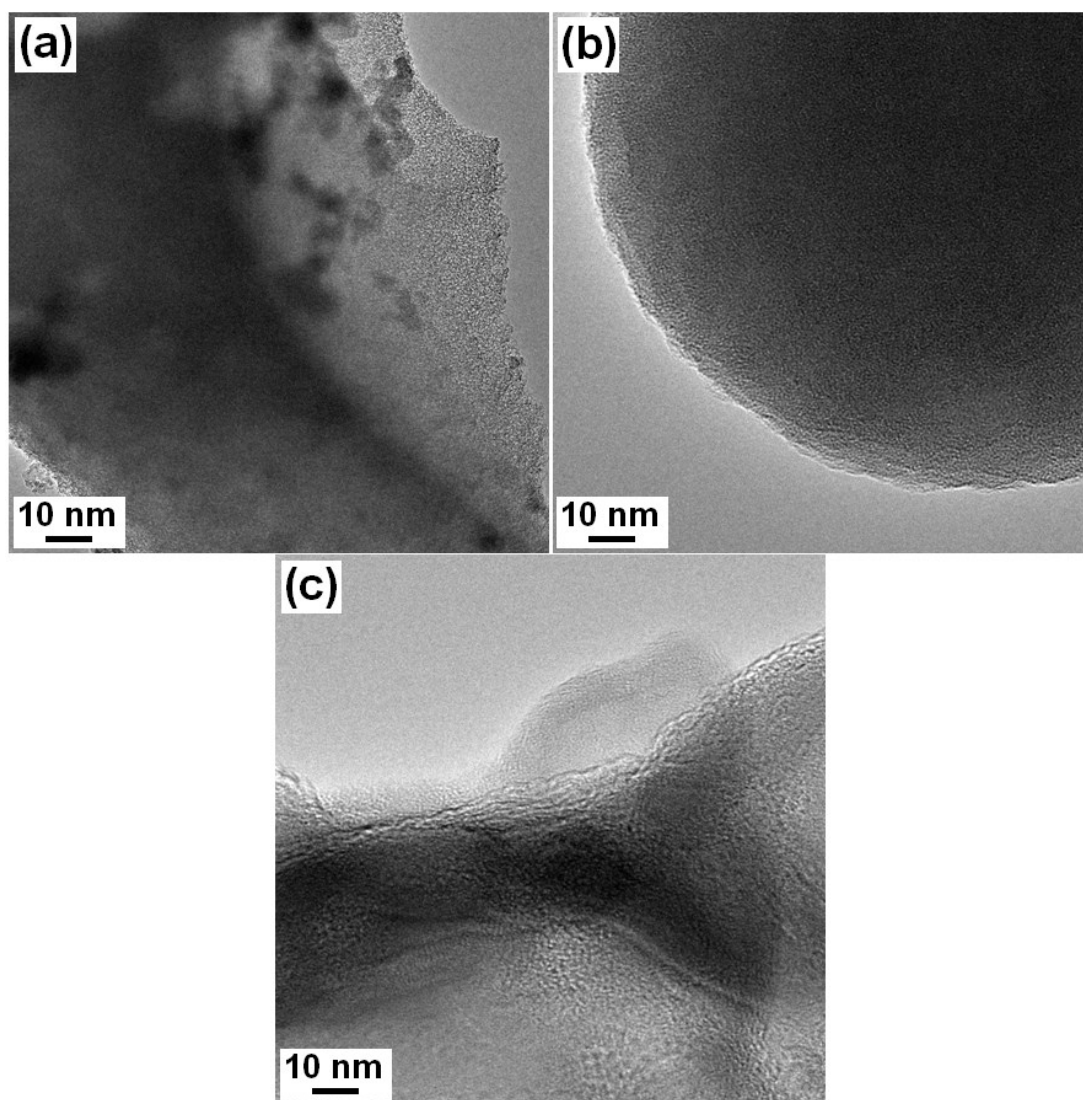


Fig. S3. HR-TEM images of Cu/HMPC.

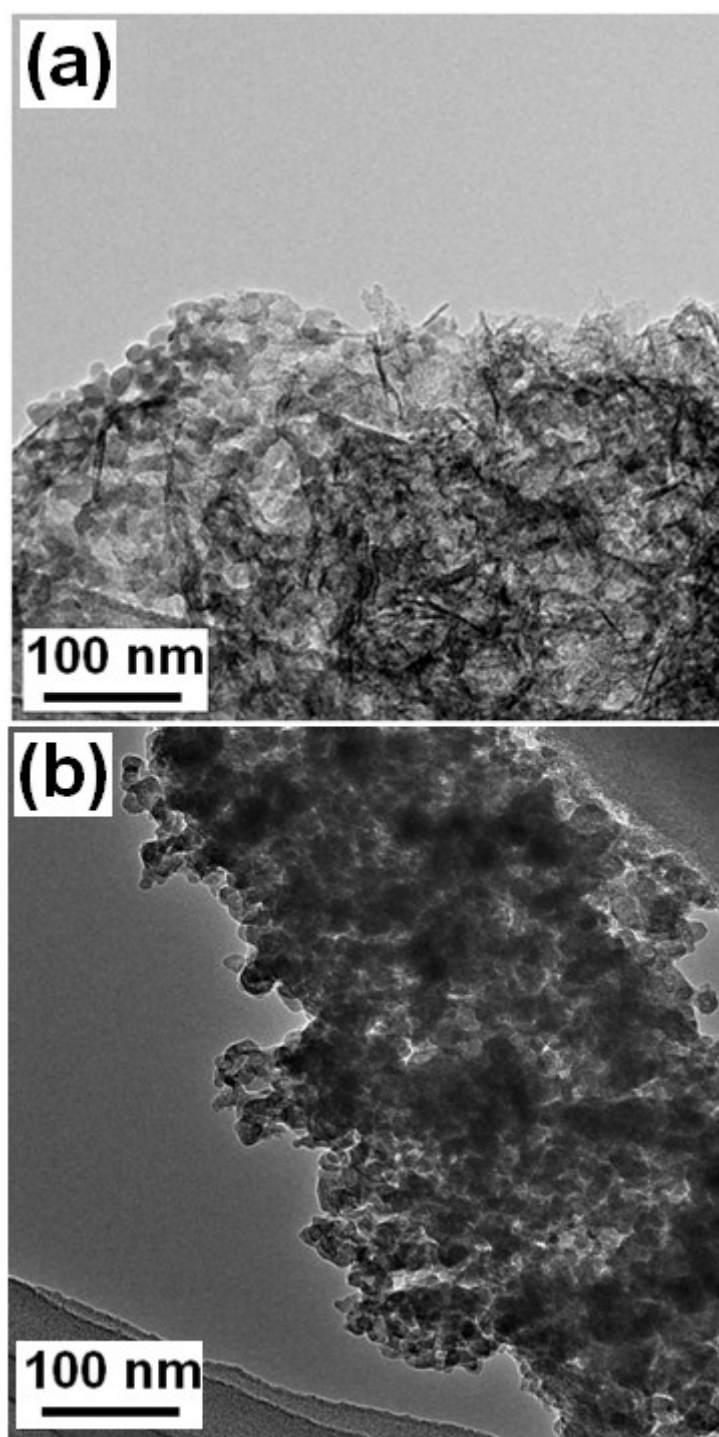


Fig. S4. HR-TEM images of Cu/HMPC show the interconnected 1D, 2D and 3D morphology.

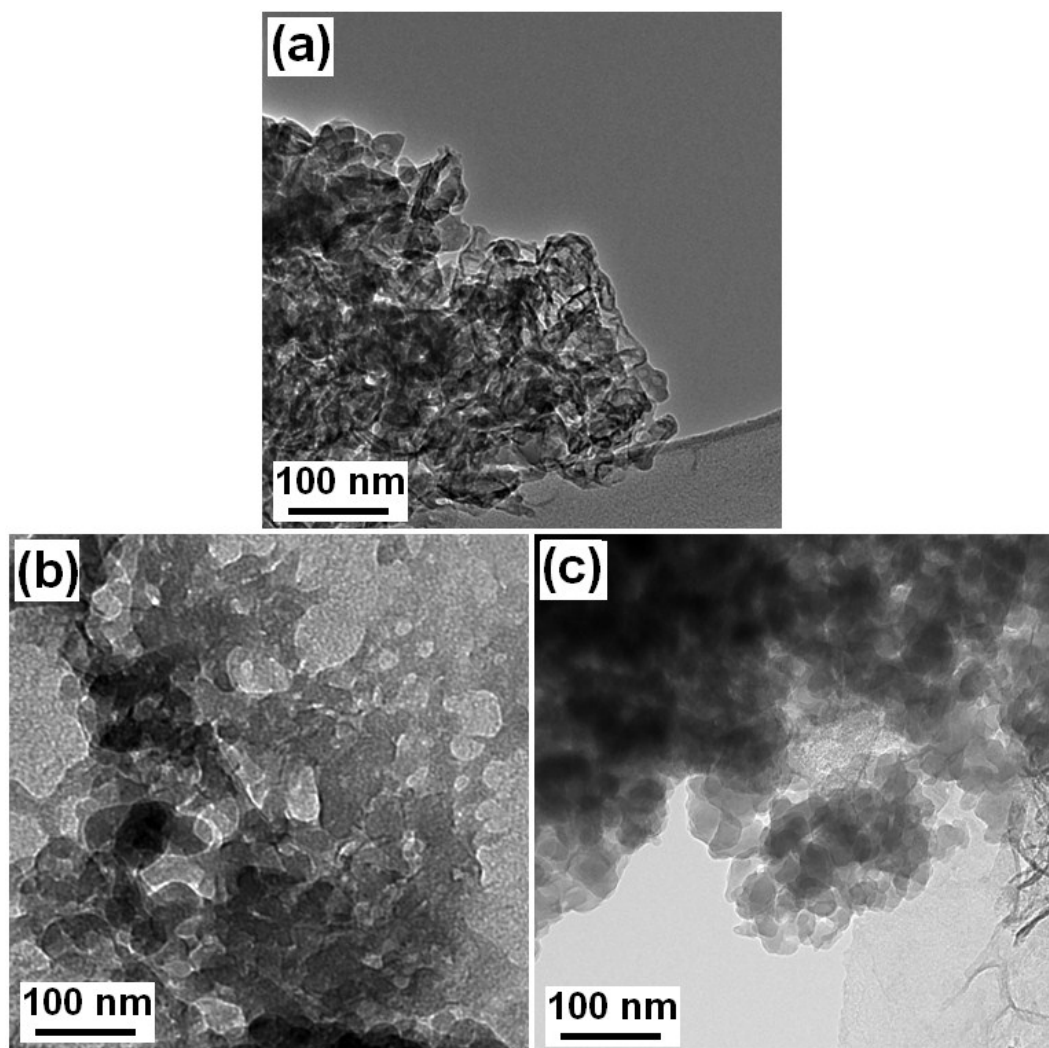


Fig. S5. TEM images of Cu/HMPC.

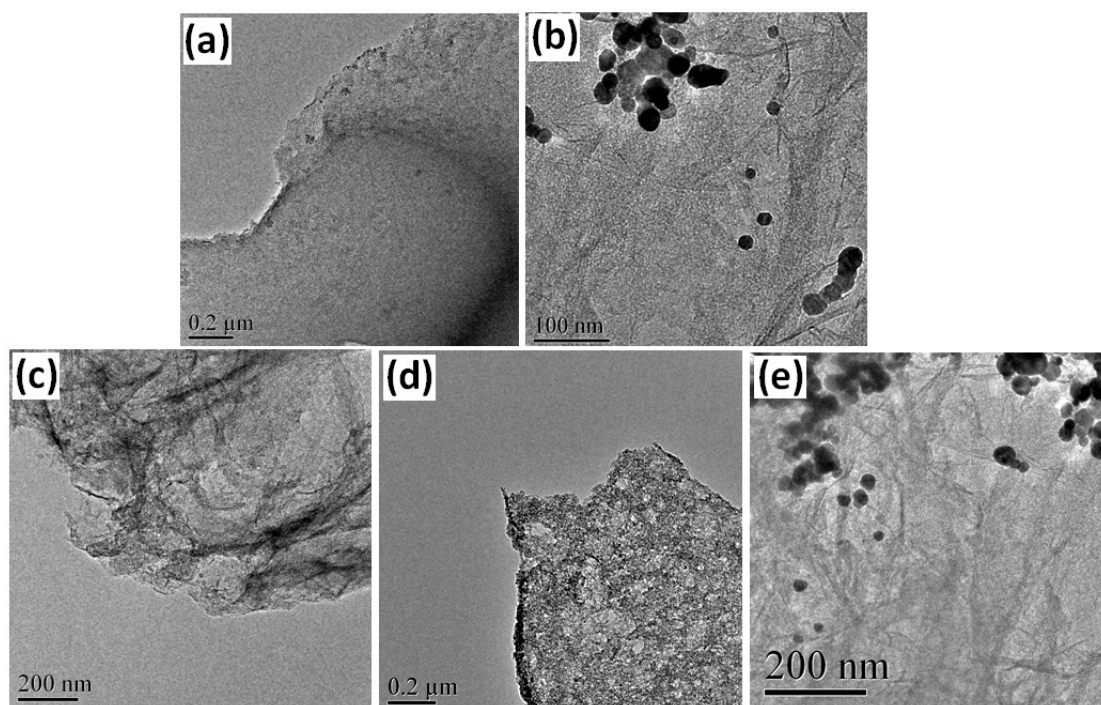


Fig. S6. TEM images of HMPC.

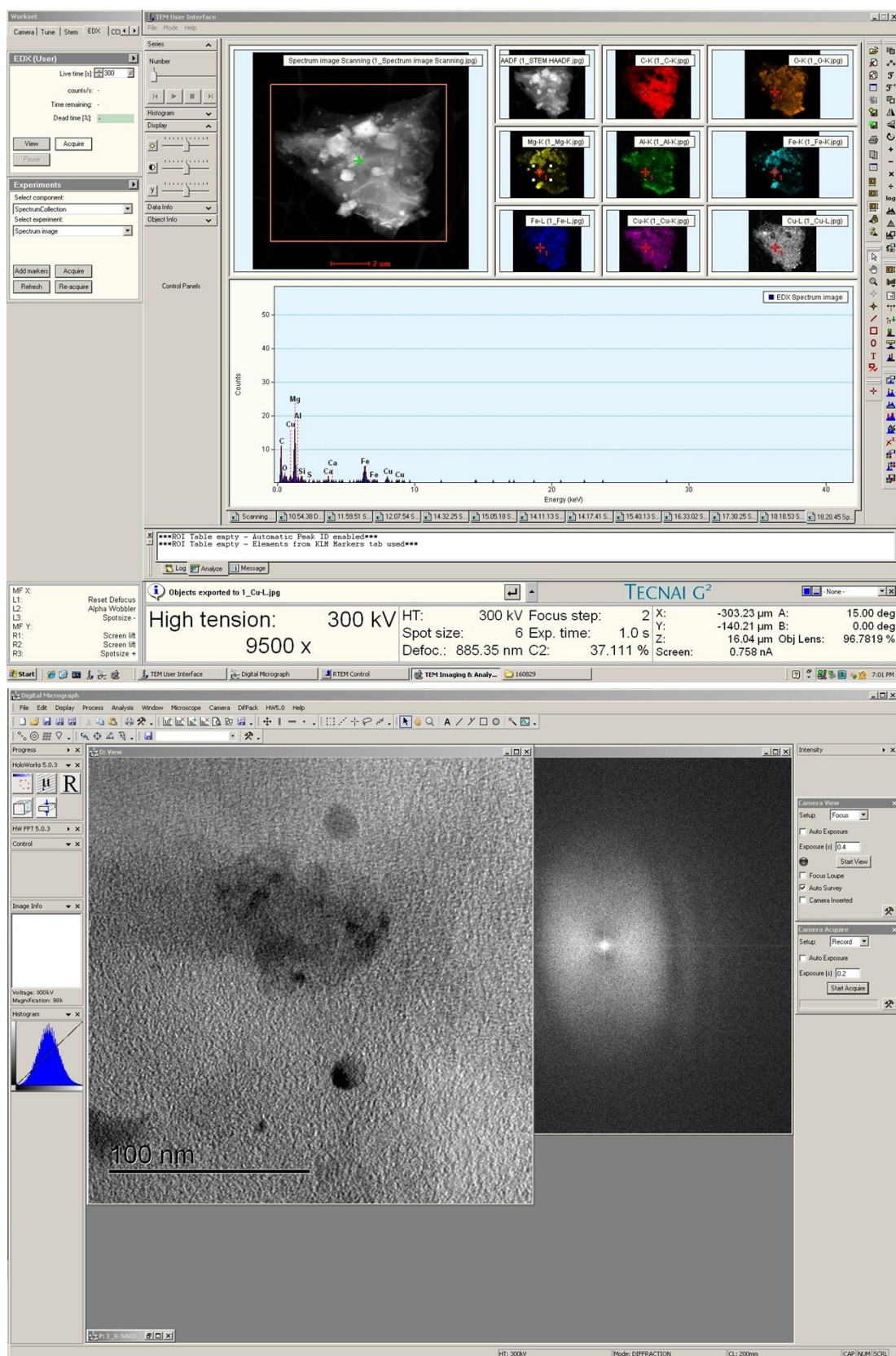


Fig. S7. The screenshot was taken while analysis HR-TEM, SAED and elemental mapping of Cu/HMPC.

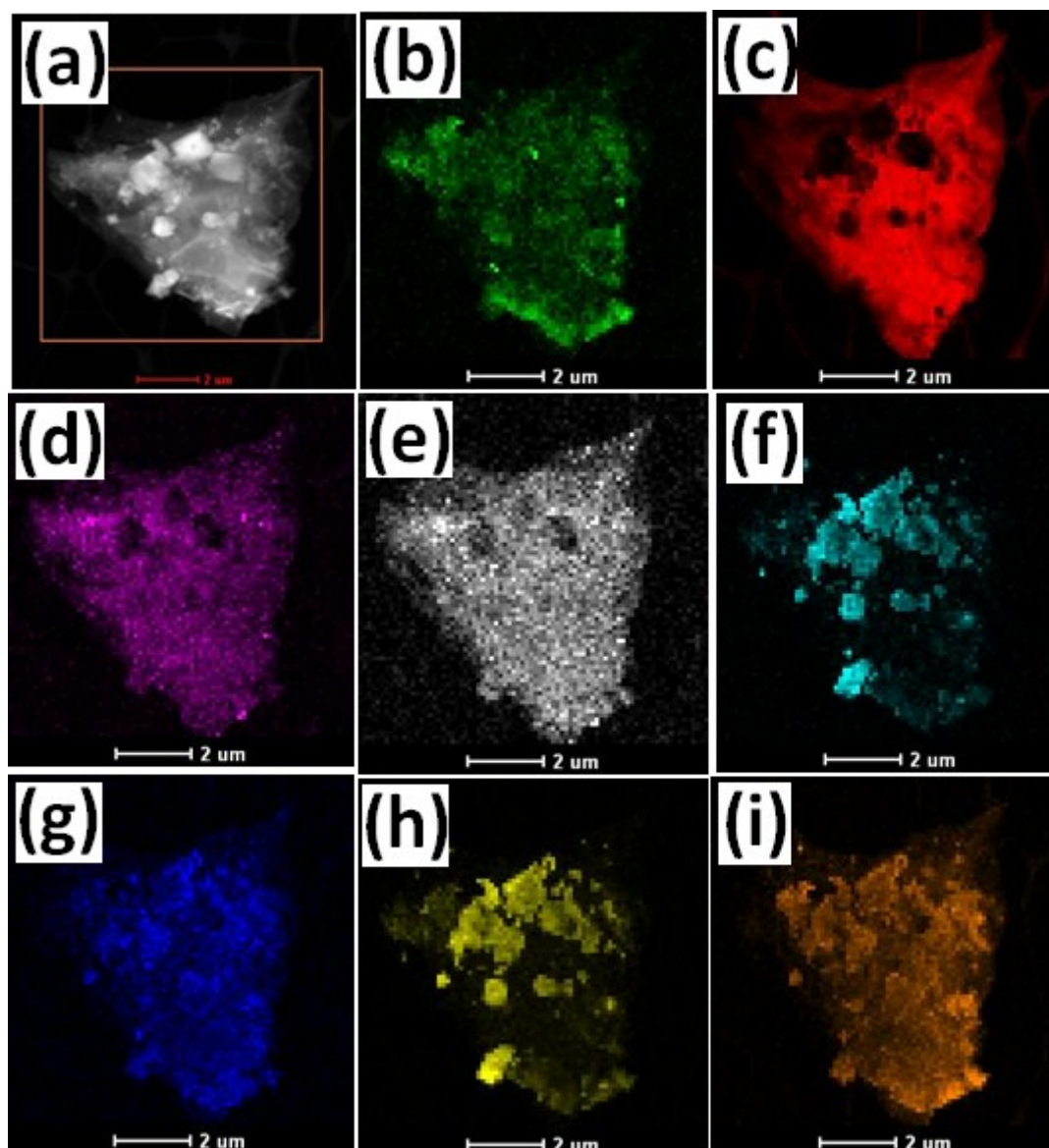


Fig. S8. (a) HRTEM image of Cu/HMPC and corresponding mapping of (b) Al, (c) C, (d) Cu-K, (e) Cu-L, (f) Fe-K, (g) Fe-L, (h) Mg, and (i) O.

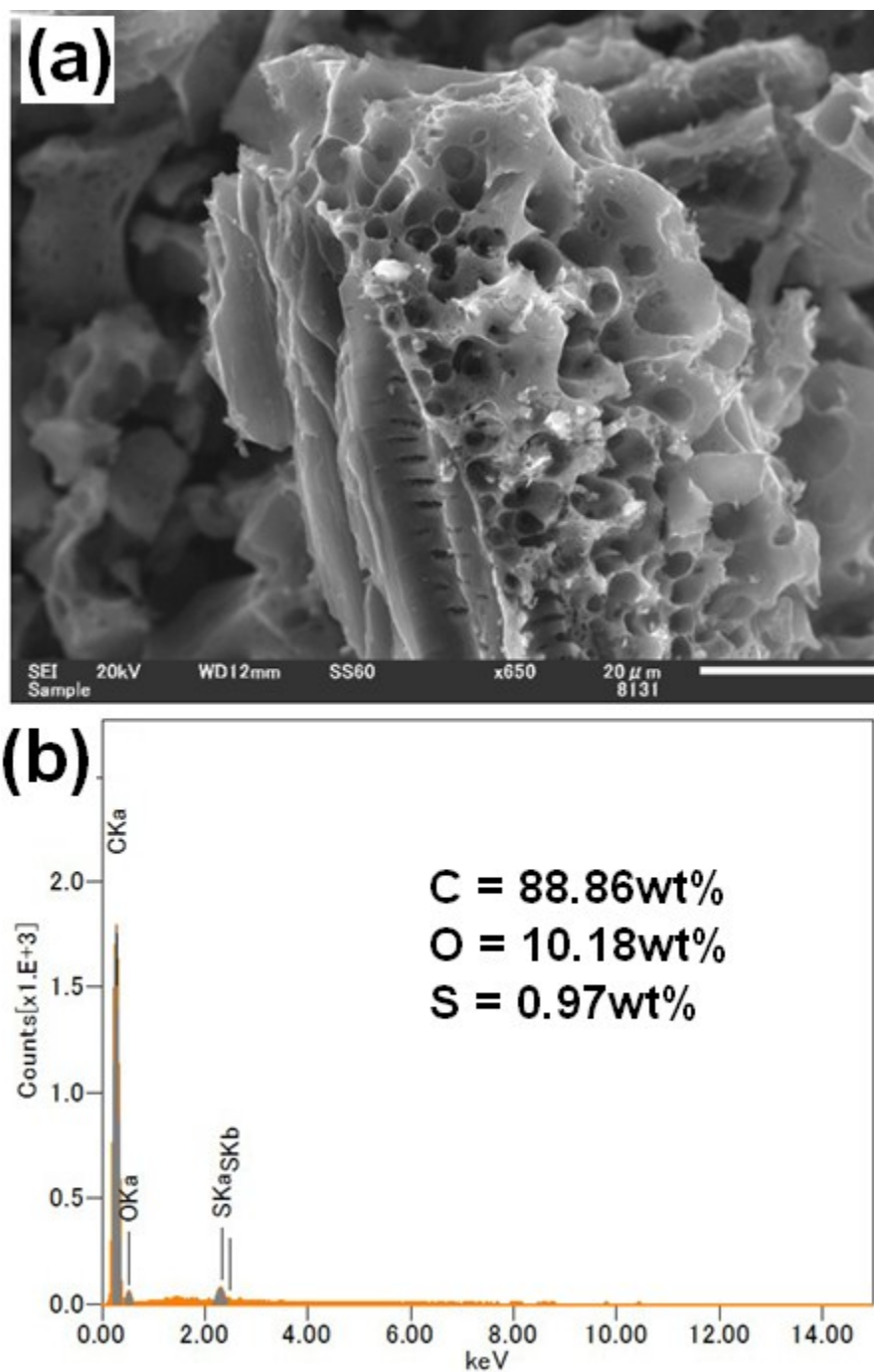


Fig. S9. (a) SEM image and (b) corresponding EDS spectrum of HMPC.

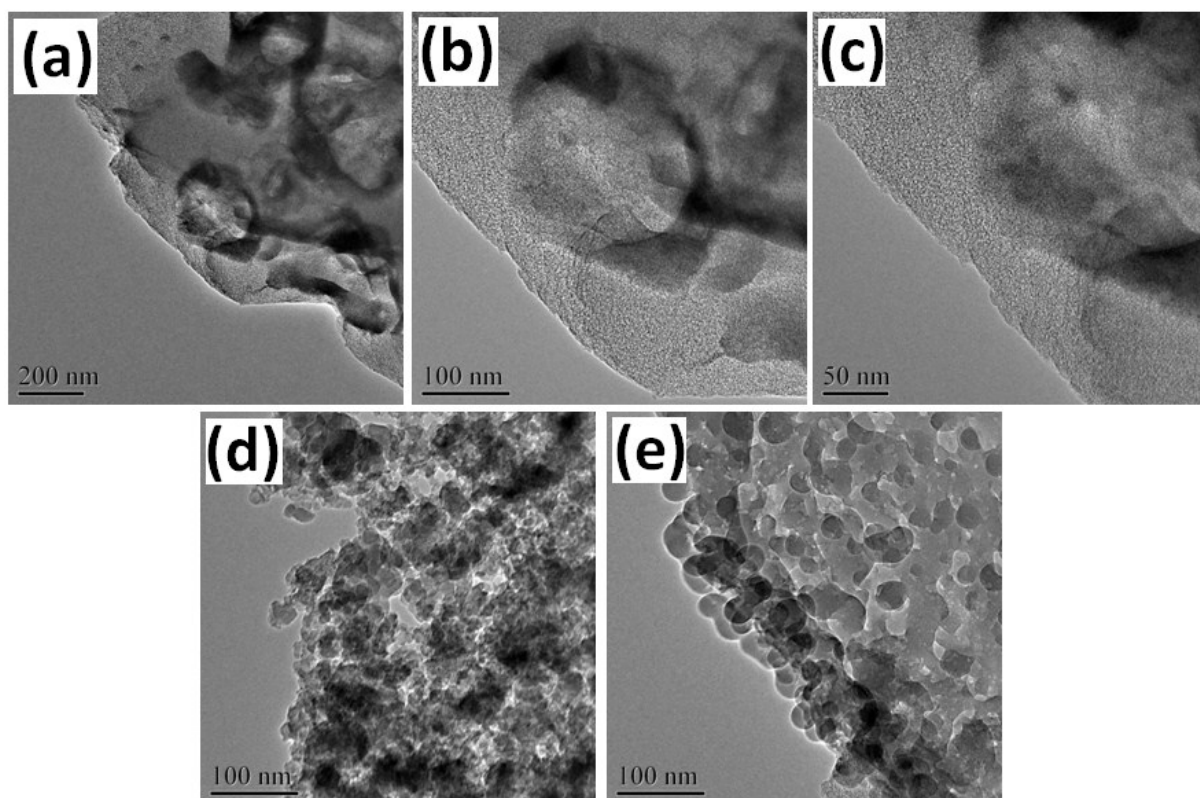


Fig. S10. TEM images of Cu/HMPC-1.

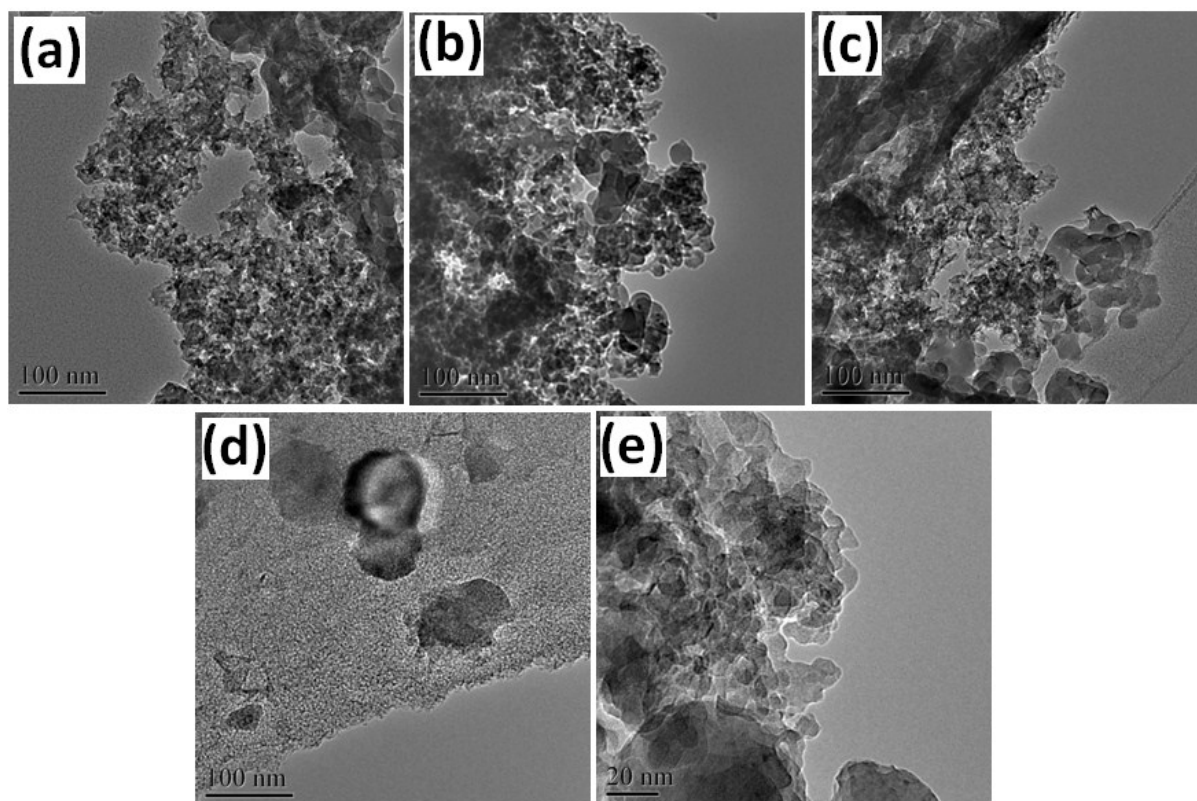


Fig. S11. TEM images of HMPC-1.

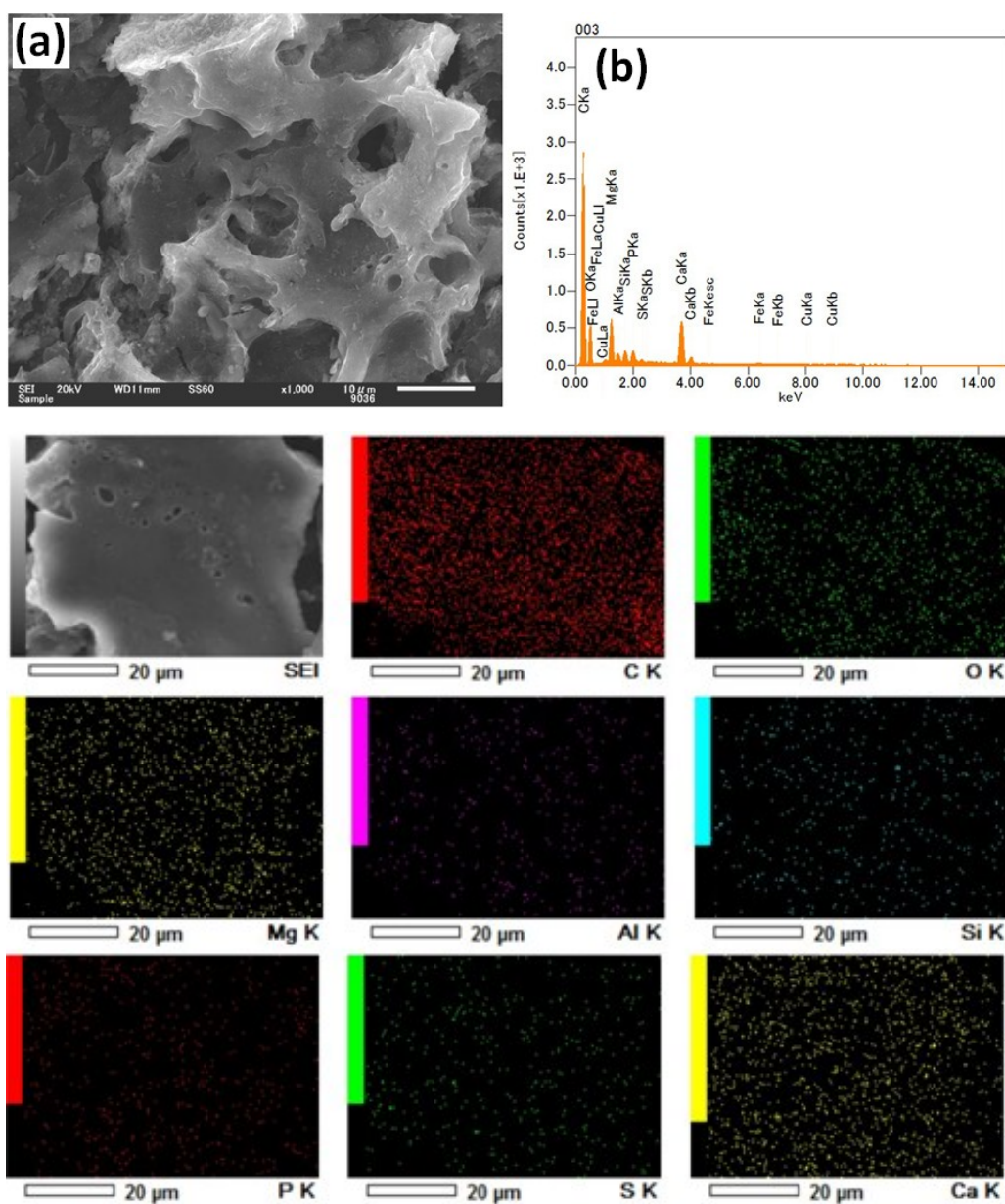


Fig. S12. SEM, EDS and corresponding elemental mapping of Cu/HMPC-1.

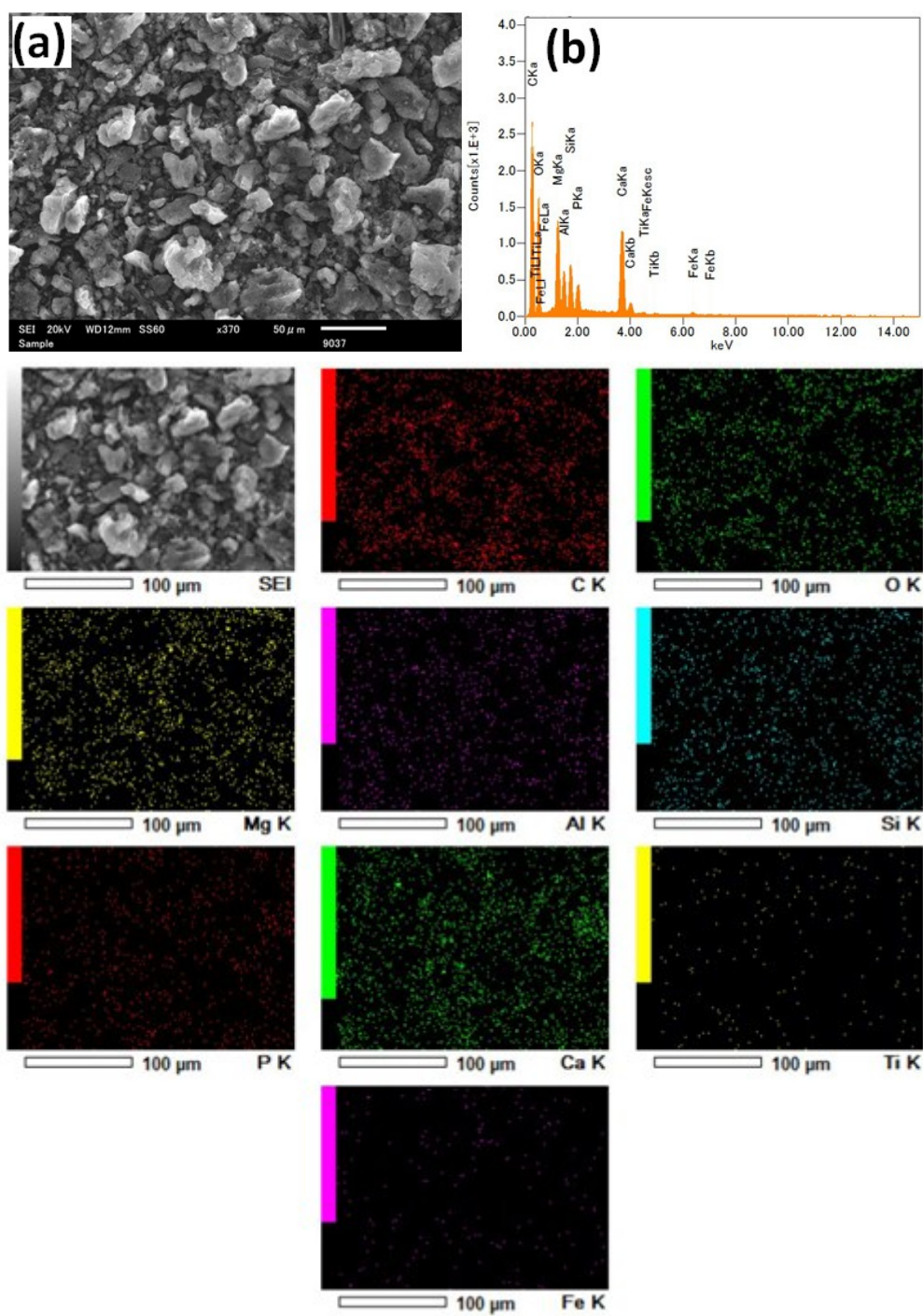


Fig. S13. SEM, EDS and corresponding elemental mapping of HMPC-1.

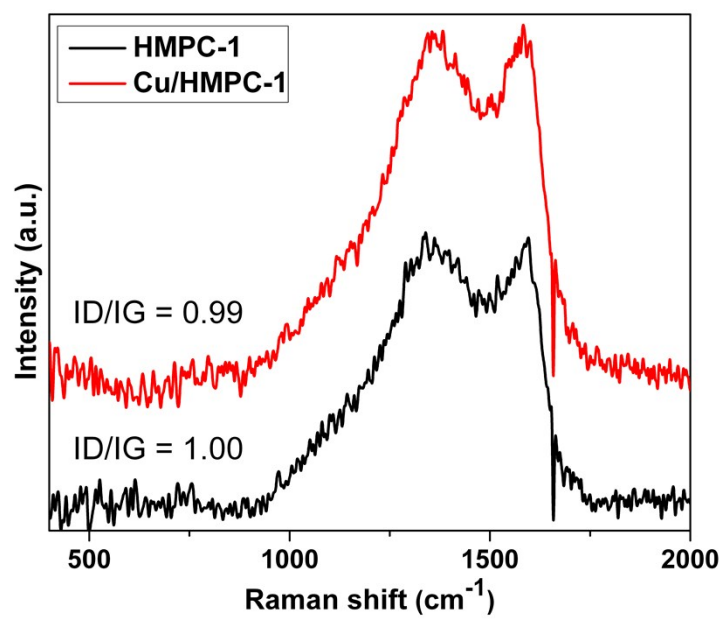


Fig. S14. Raman spectra of HMPC-1 and Cu/HMPC-1.

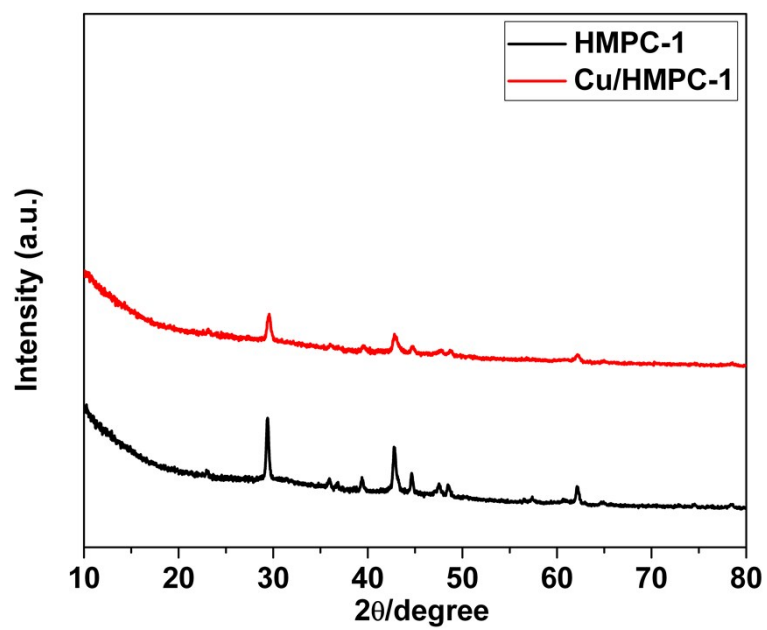


Fig. S15. XRD patterns of HMPC-1 and Cu/HMPC-1.

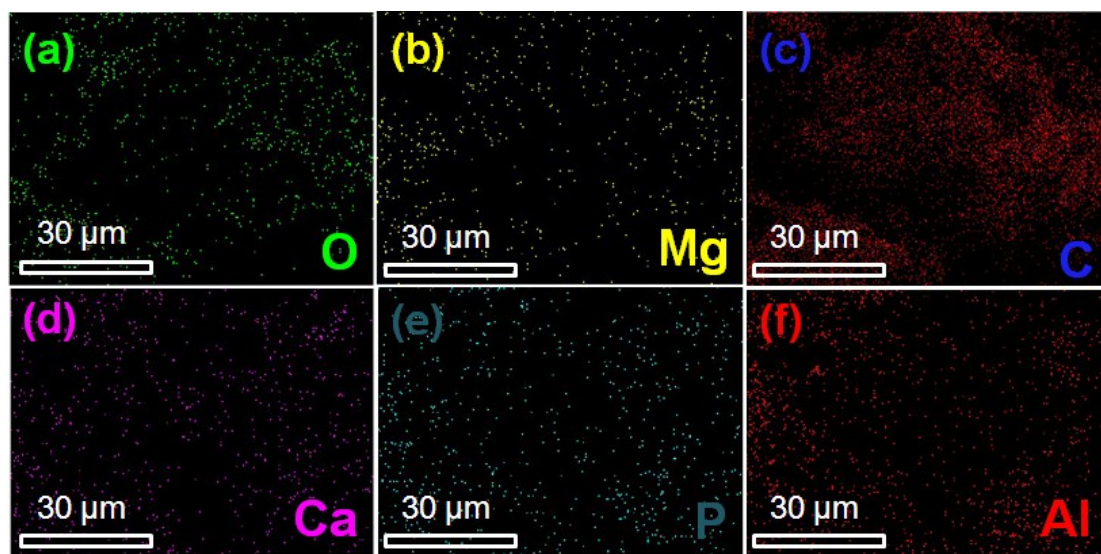
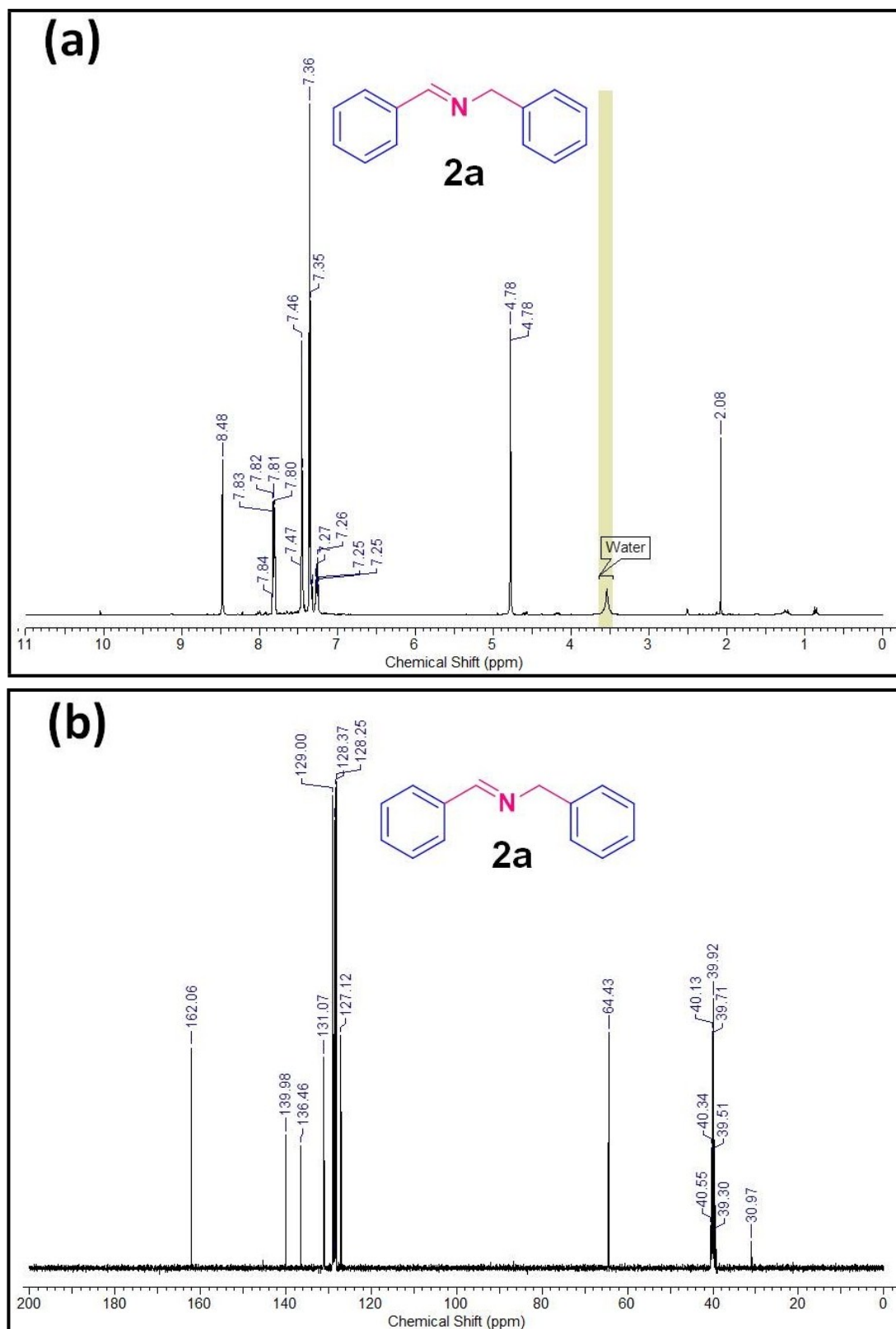


Fig. S16. EDS elemental mappings of used Cu/HMPC.

^1H NMR spectra, ^{13}C NMR spectra, GC chromatogram, MS(GC) spectra of
catalytic products



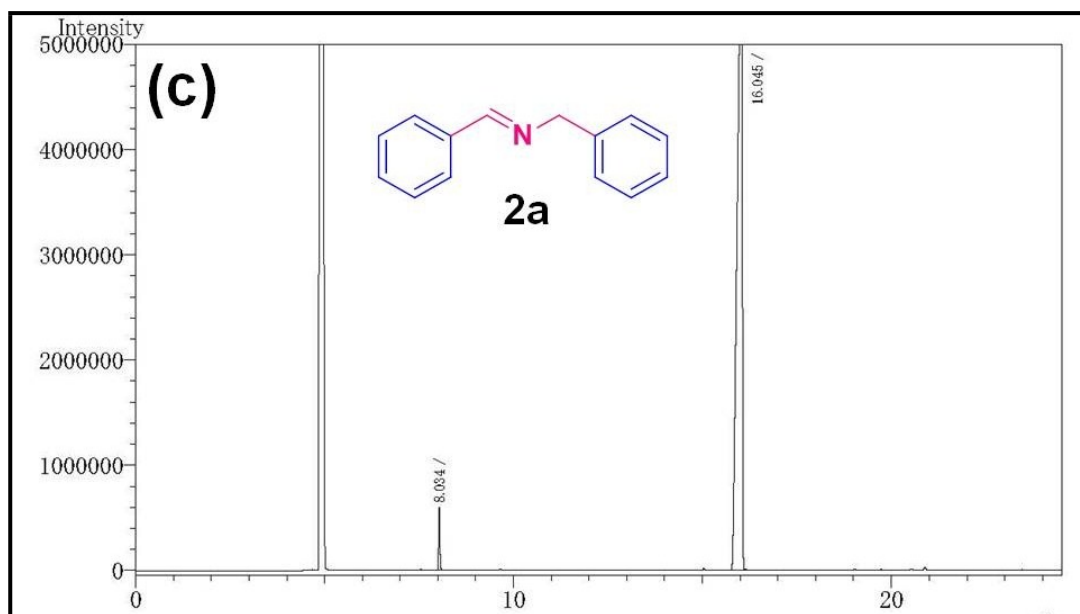
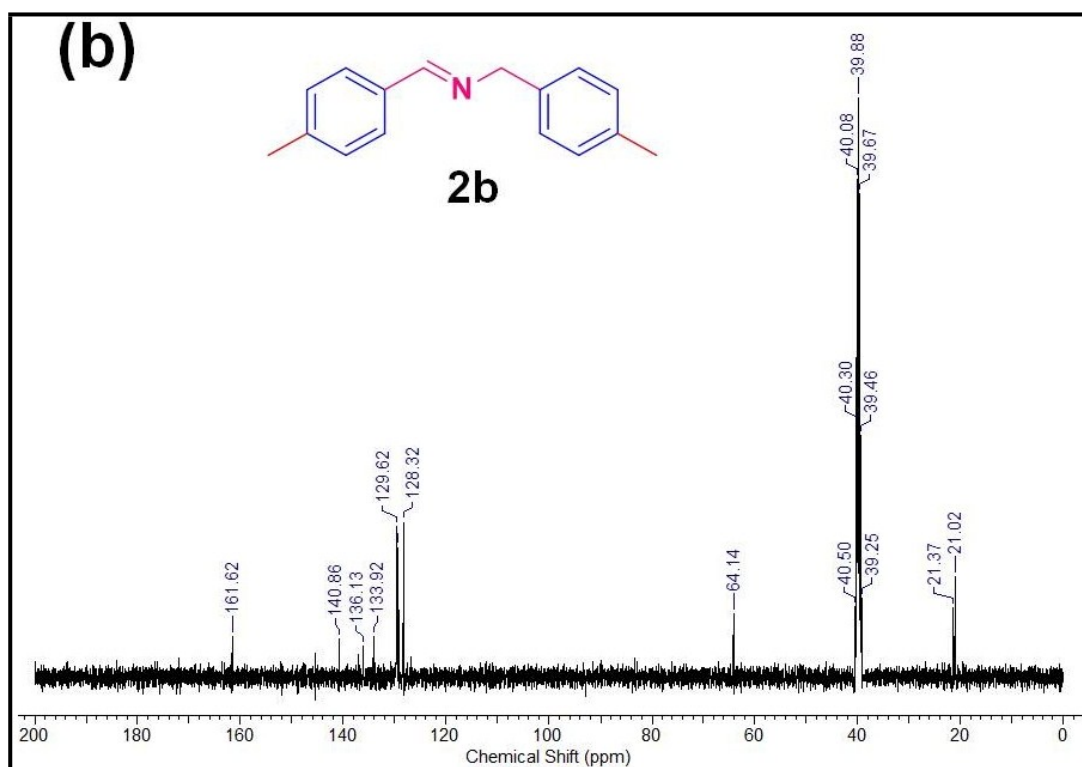
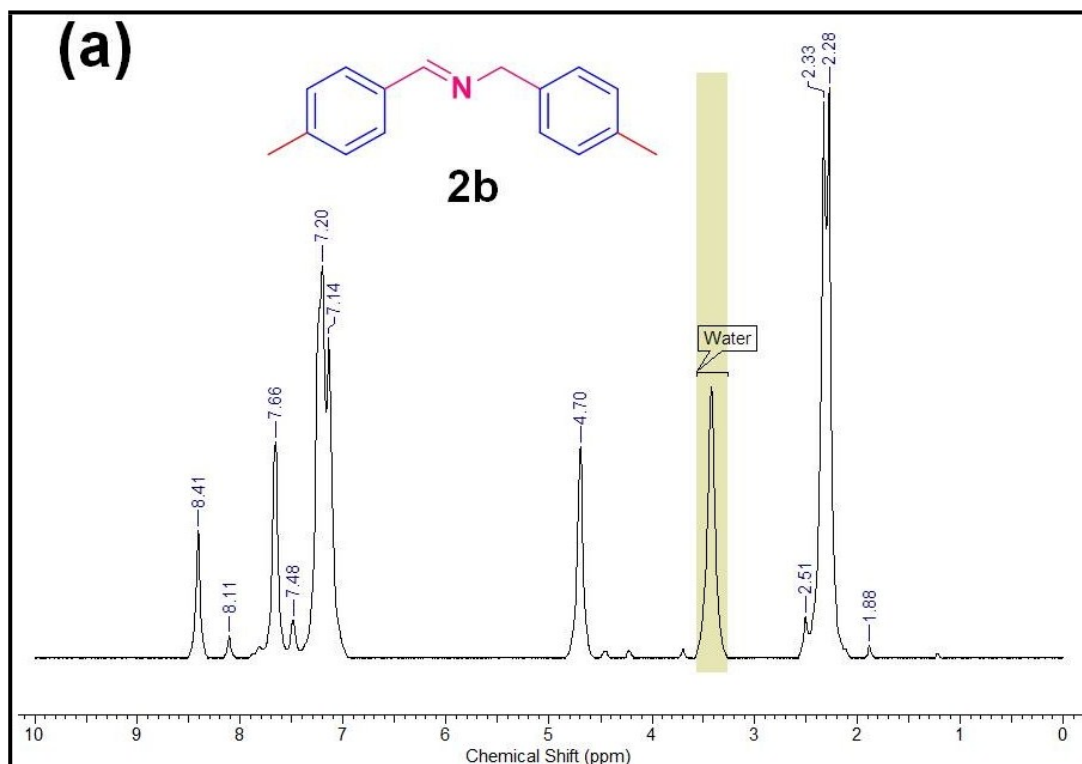


Fig. S17. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-benzylidene-1-phenylmethanamine (**2a**).



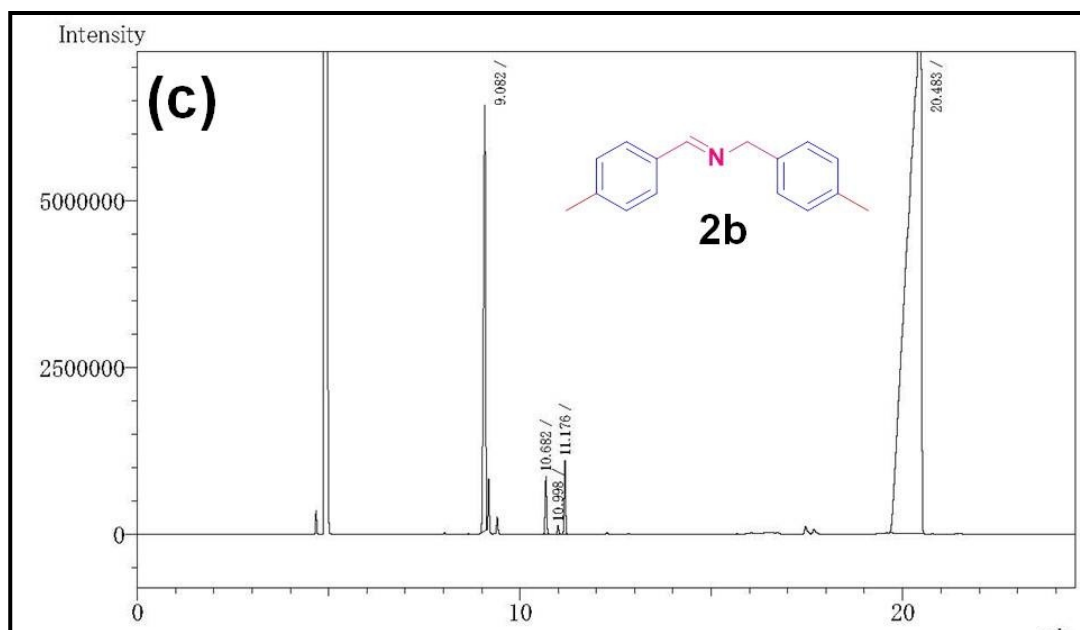
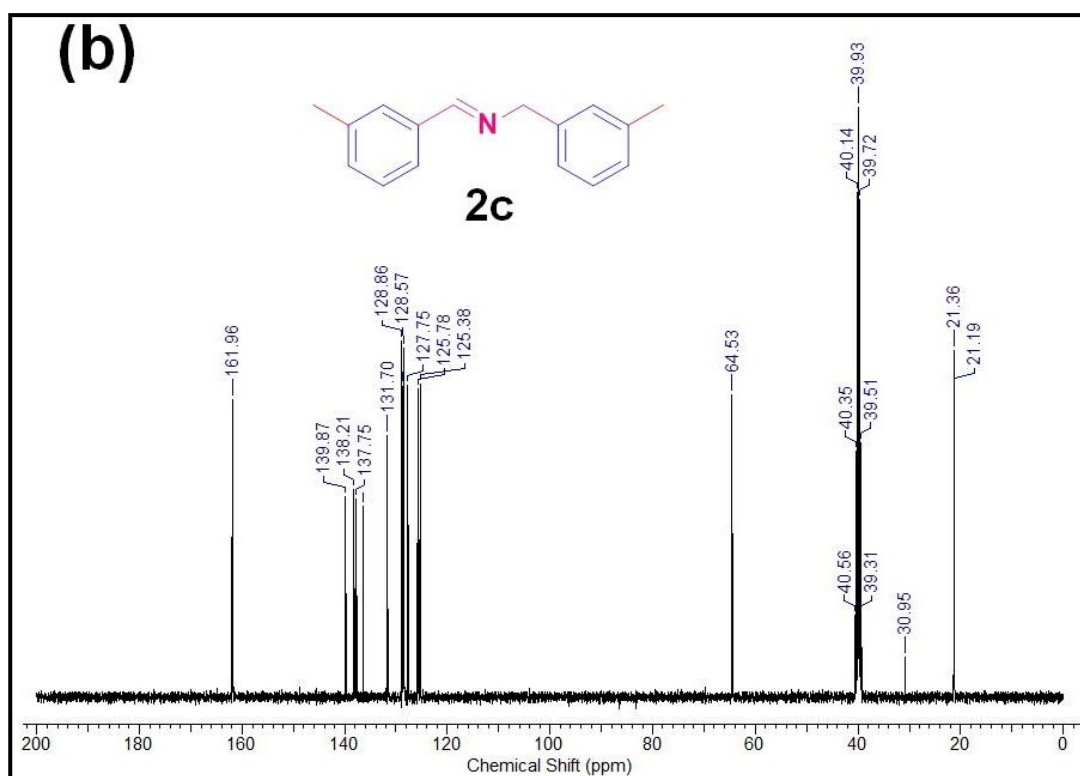
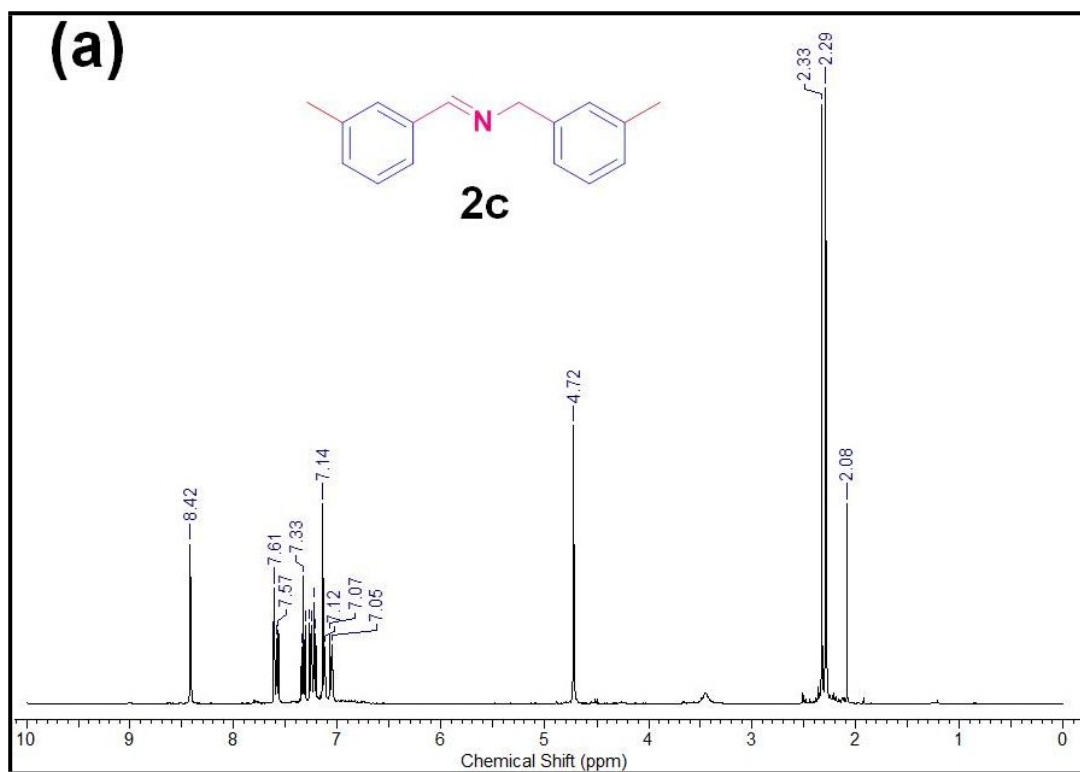


Fig. S18. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(4-methylbenzylidene)-1-(4-tolyl)methanamine (**2b**).



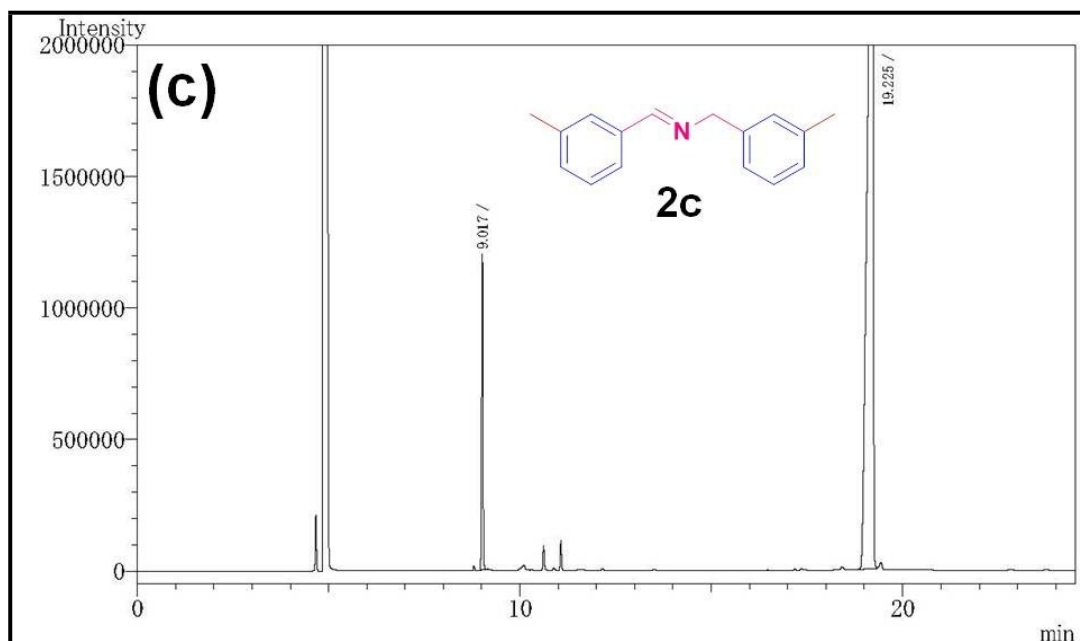
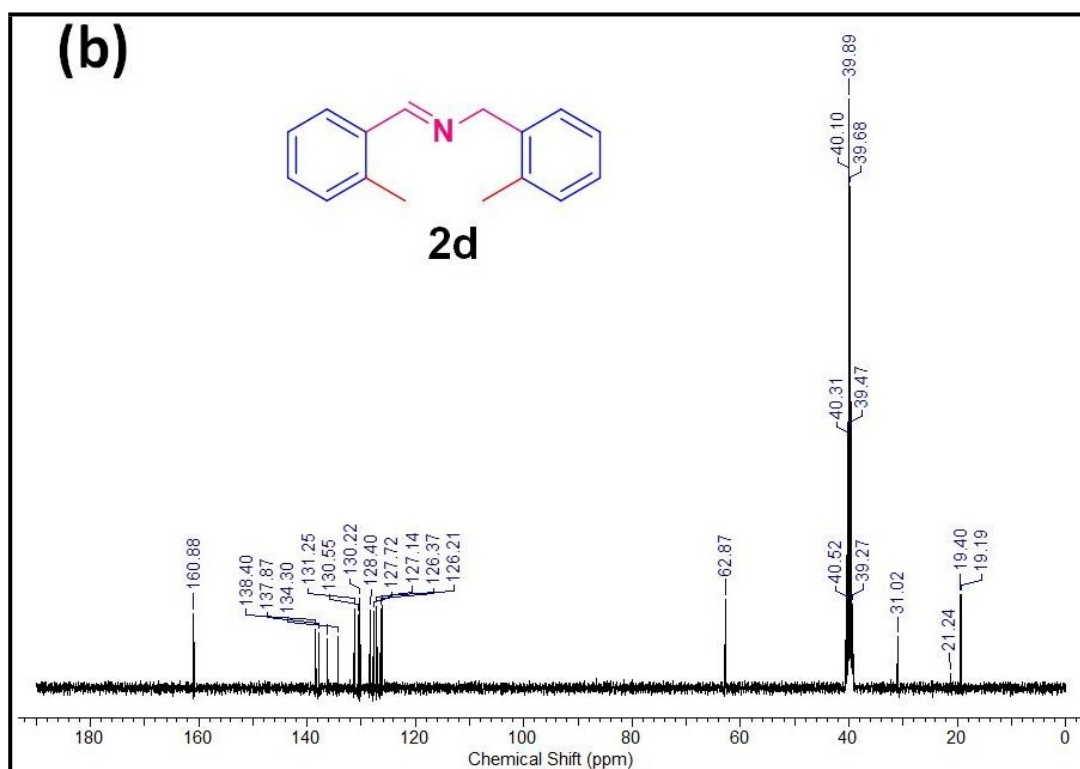
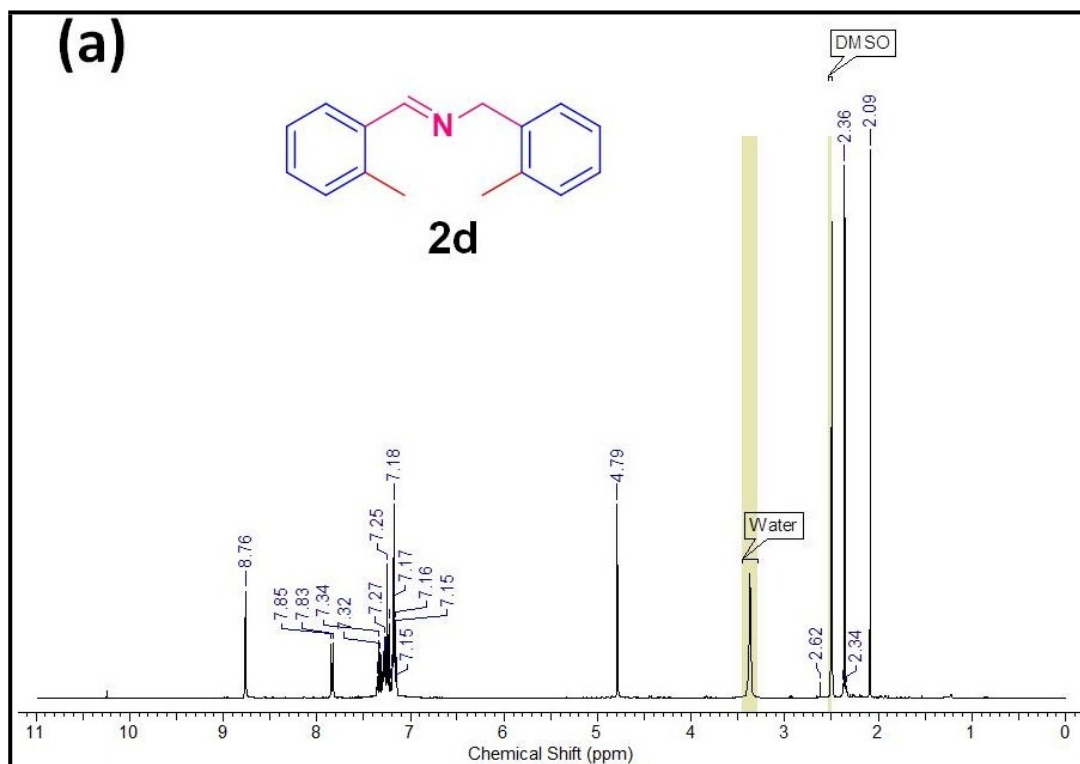


Fig. S19 (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(3-methylbenzyl)-1-(3-tolyl)methanimine (**2c**).



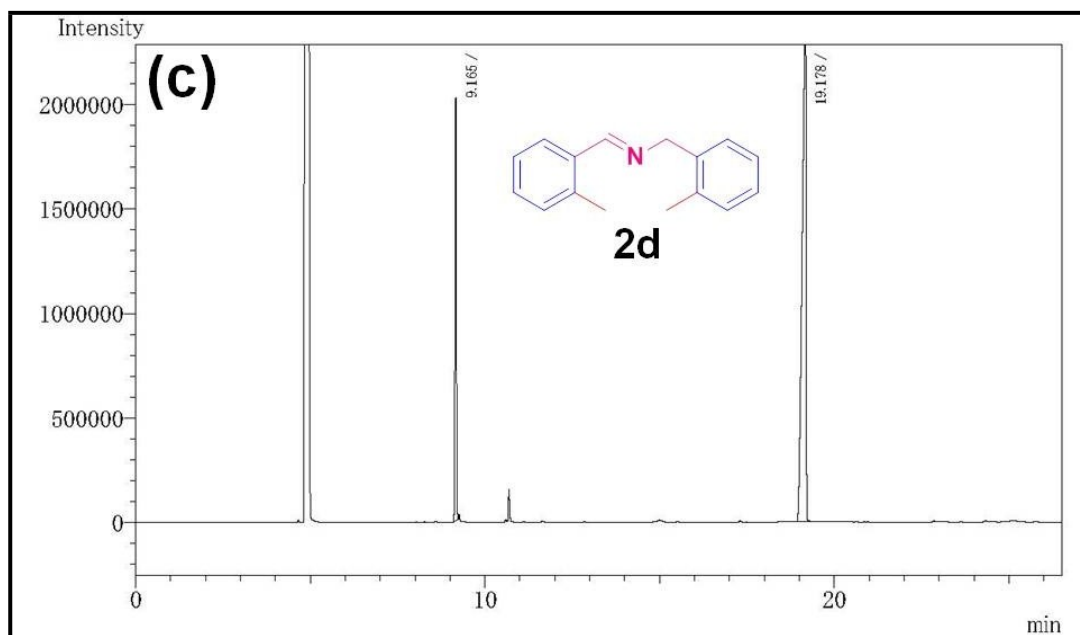
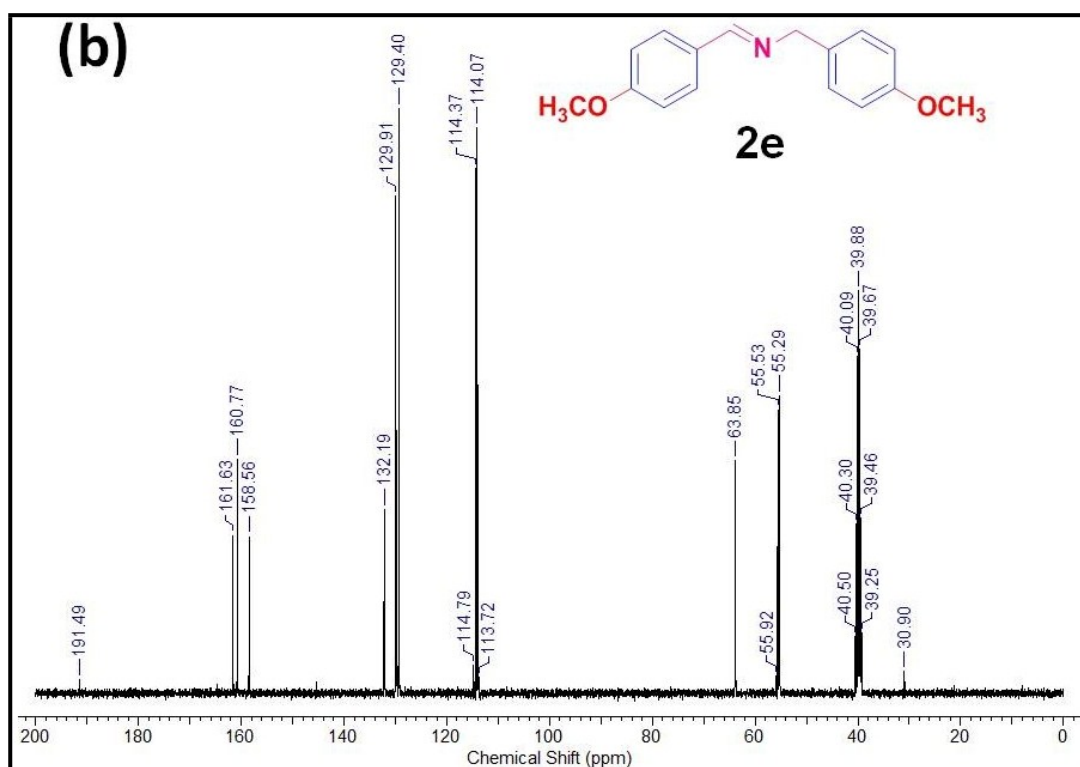
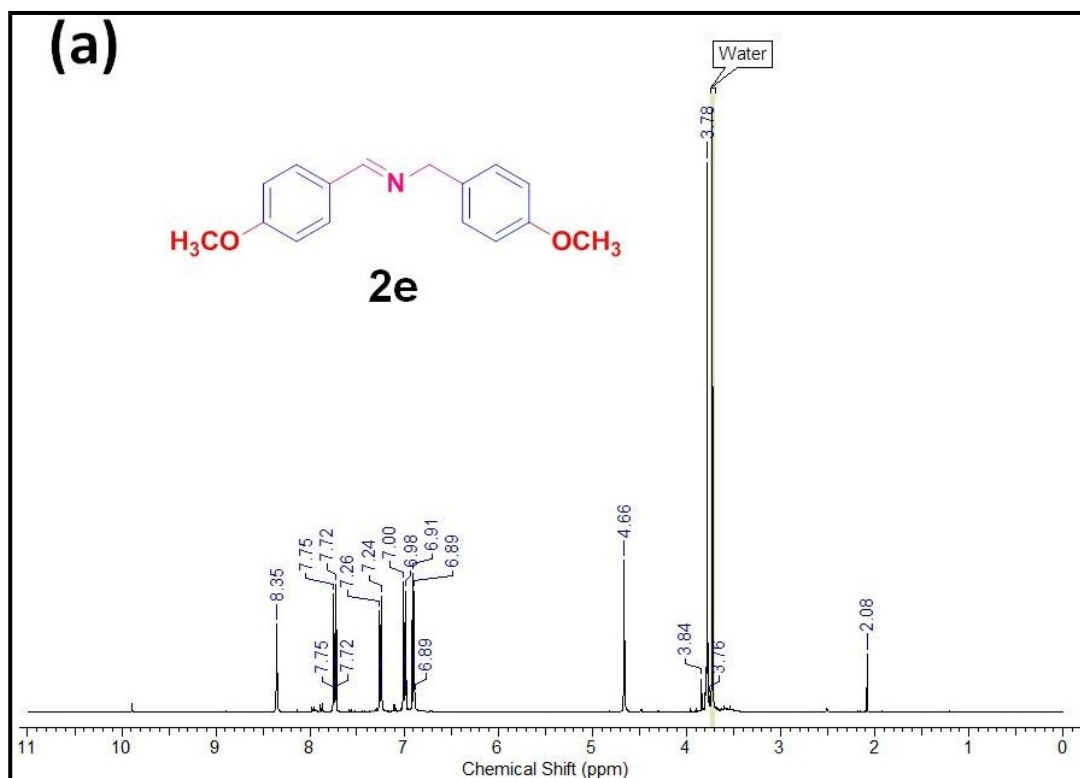


Fig. S20. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(2-methylbenzylidene)-2-methylbenzylamine (**2d**).



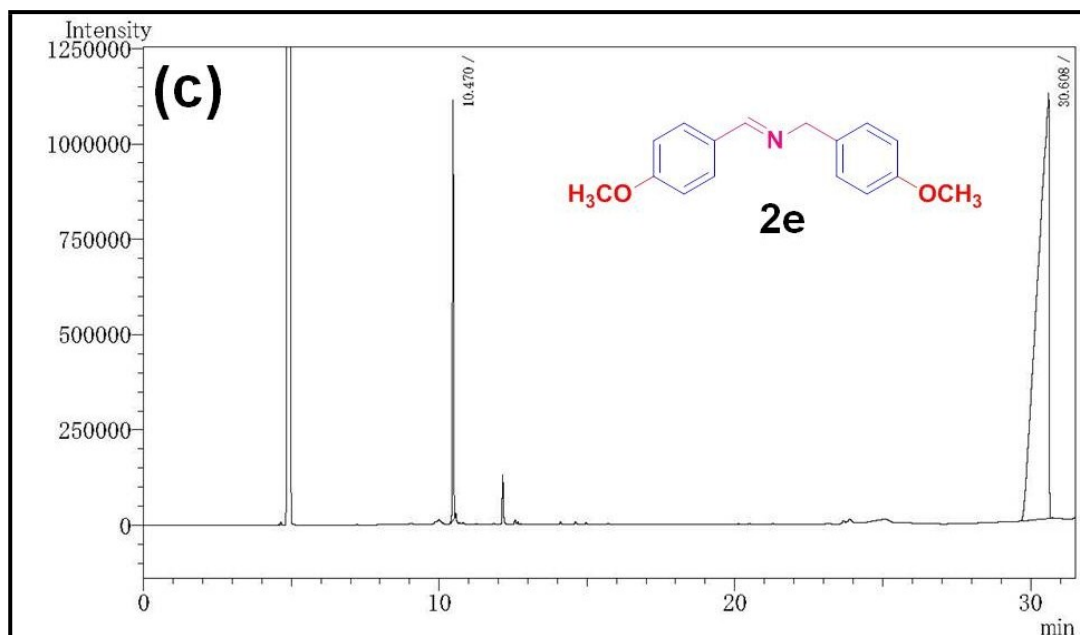
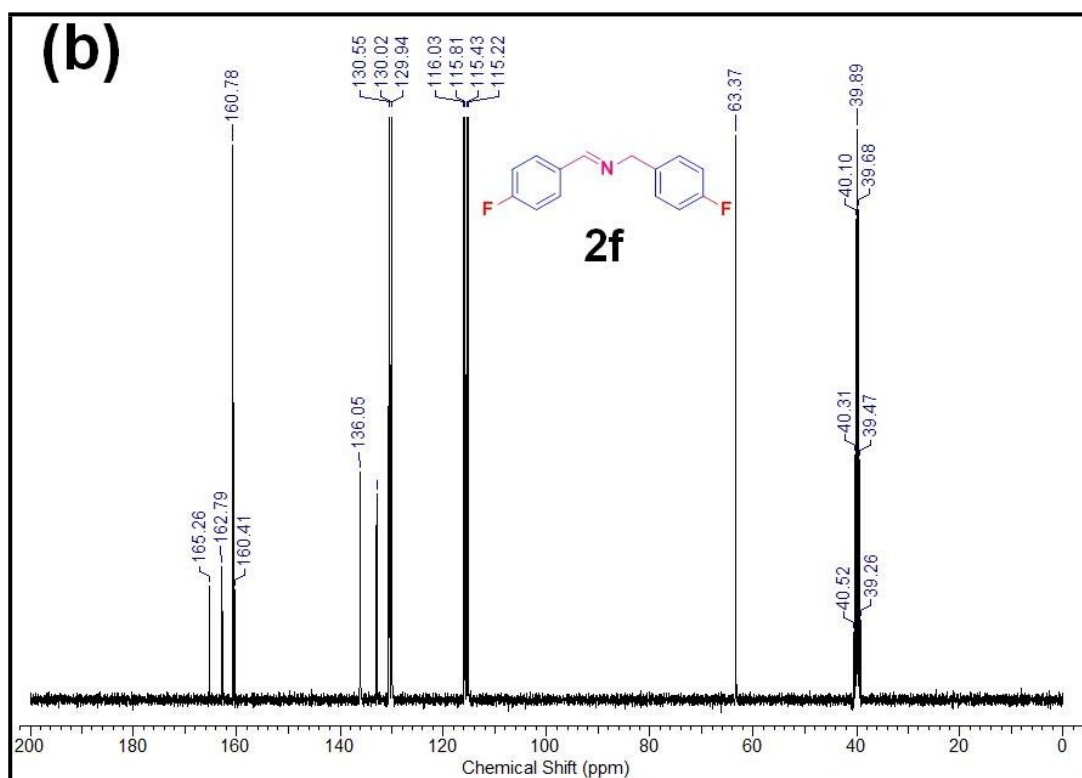
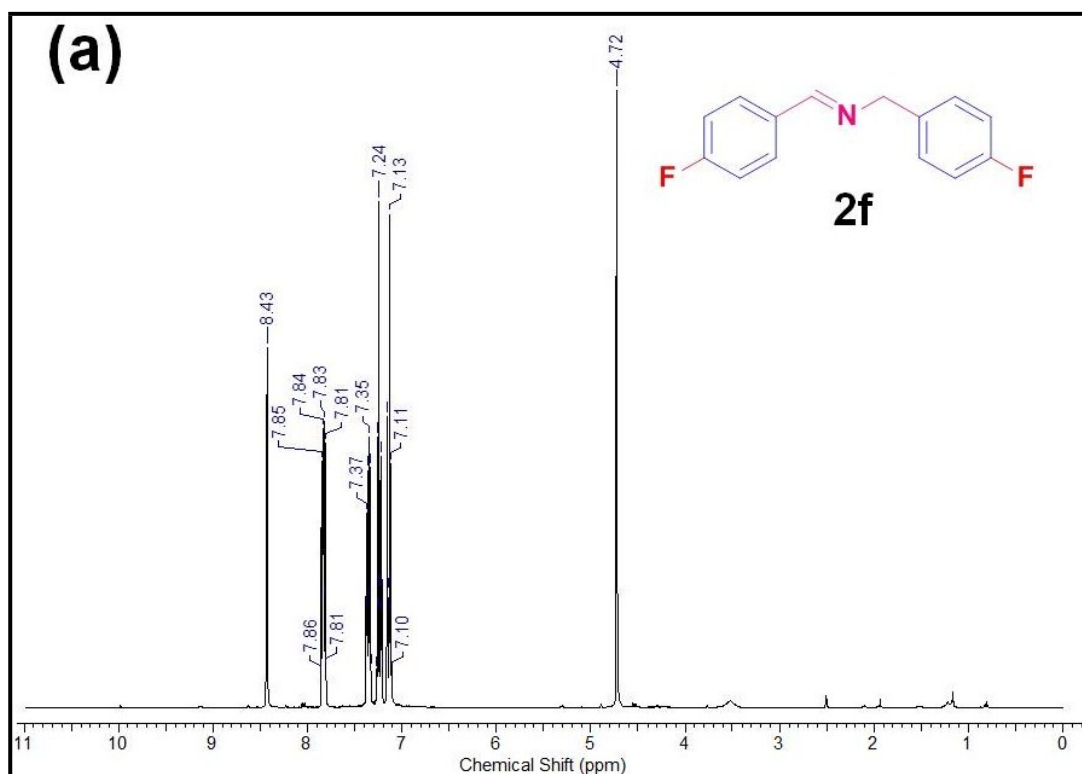


Fig. S21. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine (**2e**).



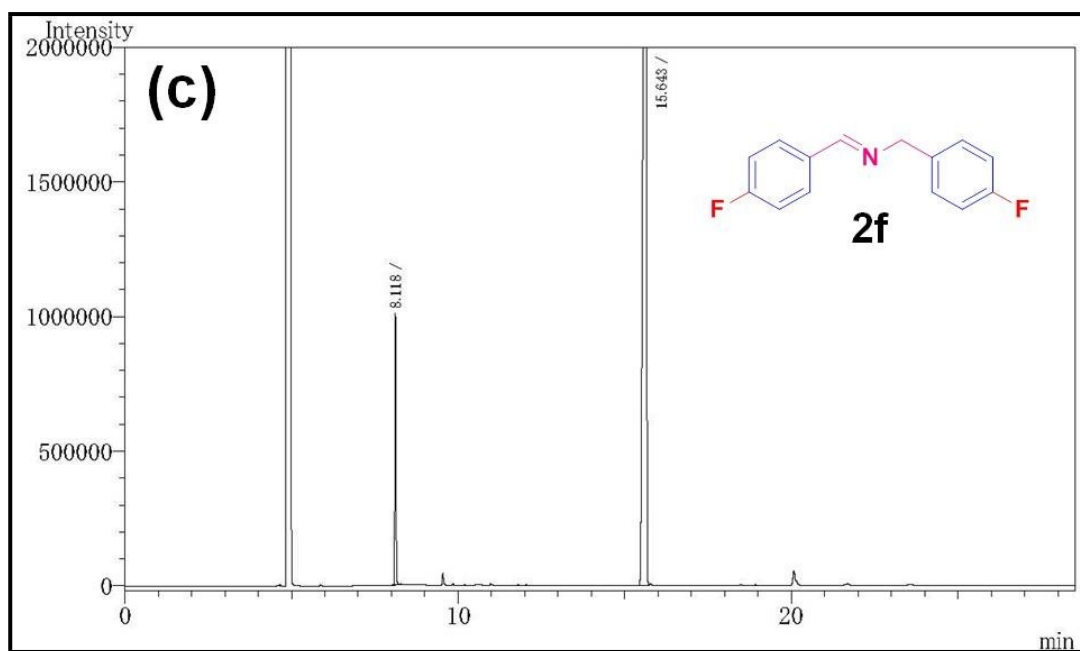
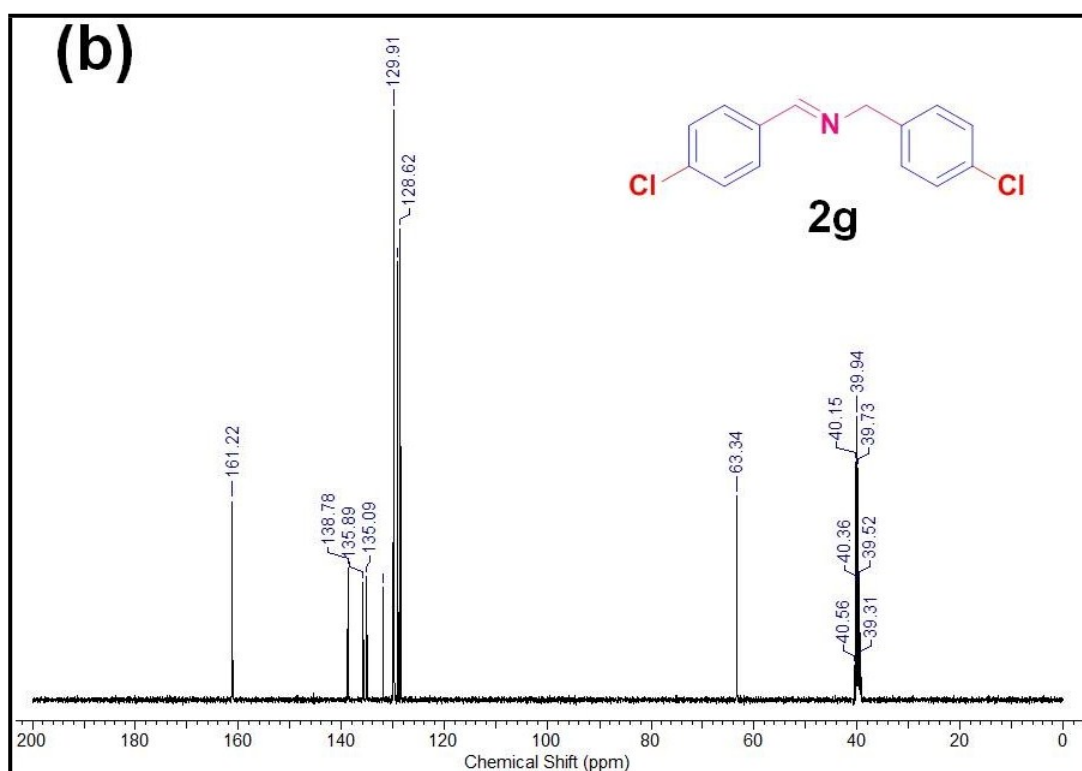
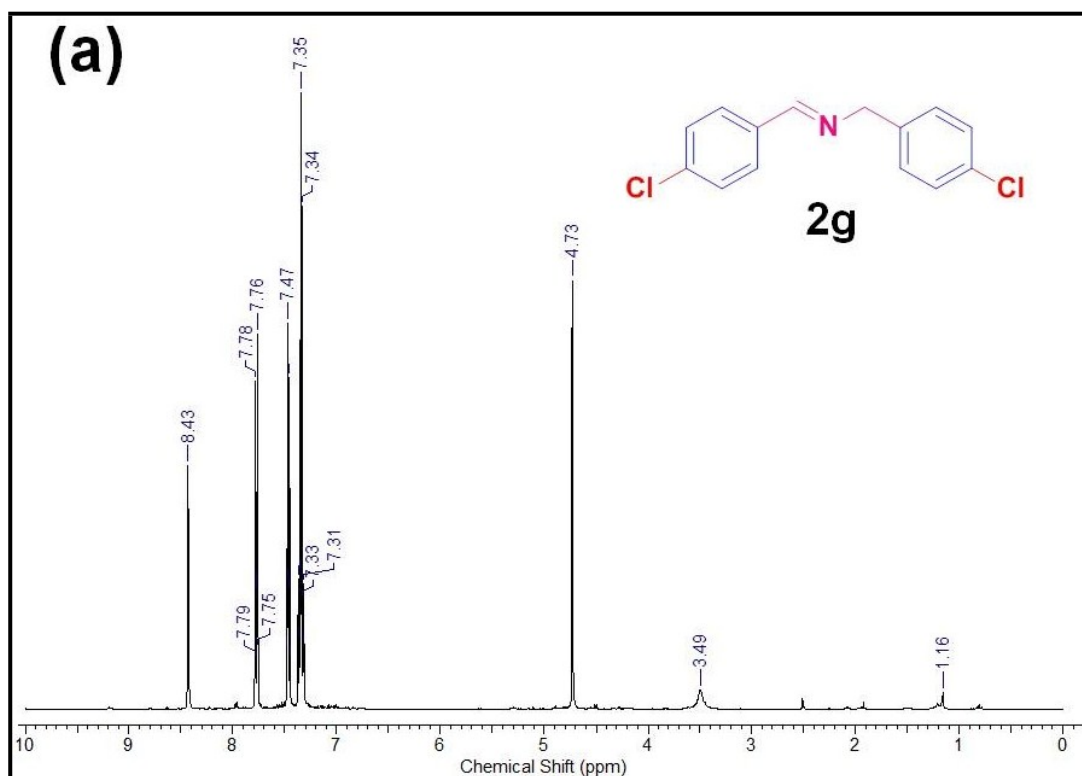


Fig. S22. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(4-fluorobenzylidene)-1-(4-fluorophenyl)methanamine (**2f**).



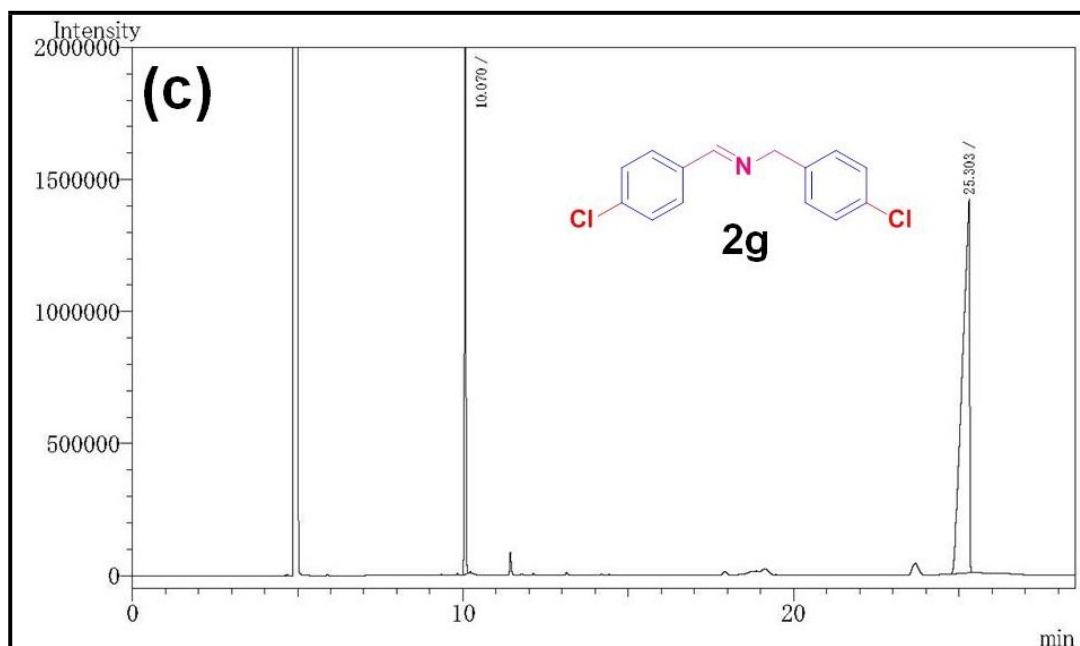
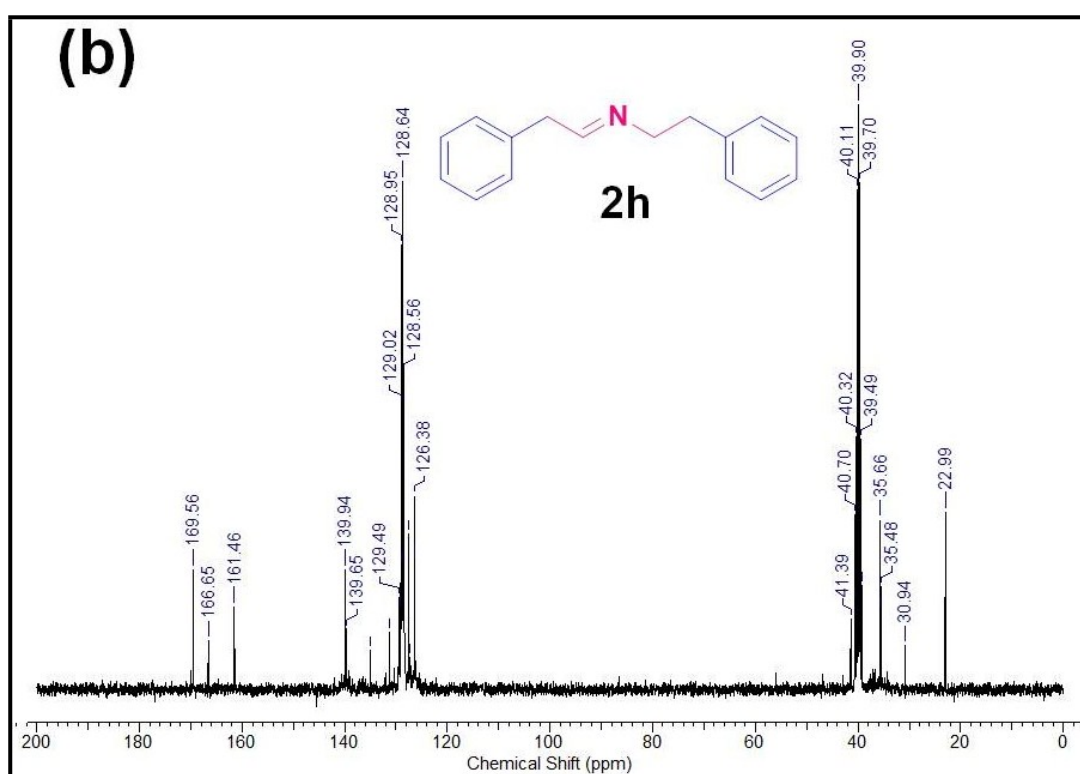
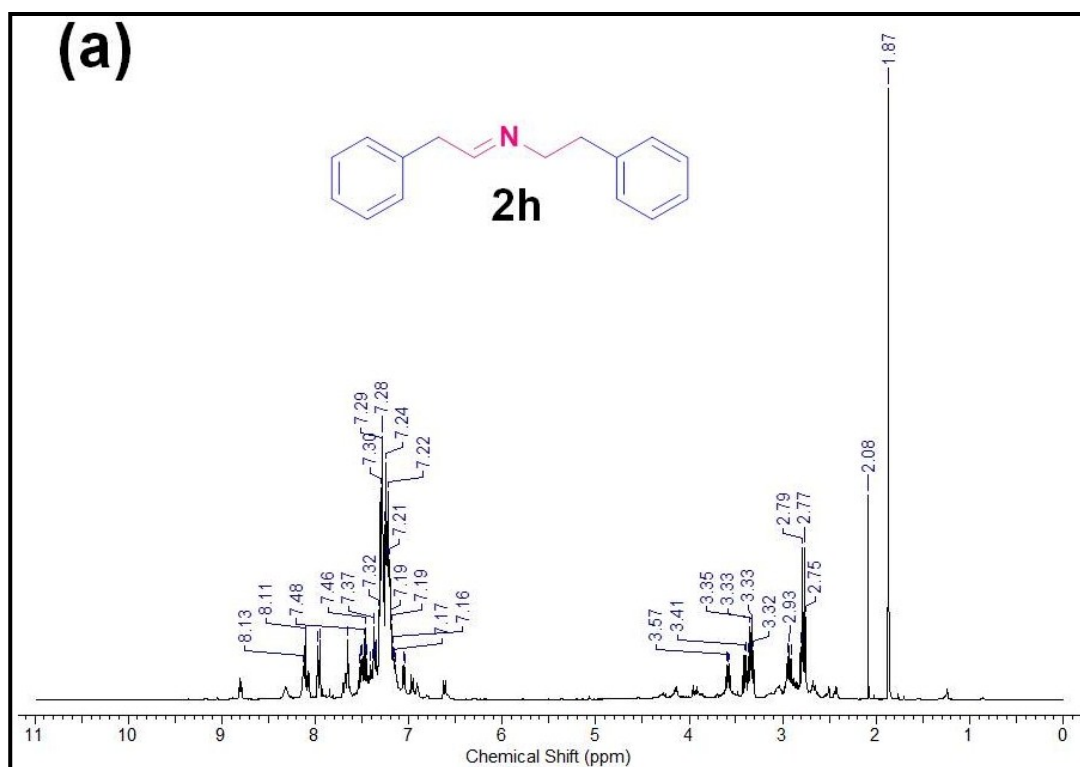


Fig. S23. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(4-Chlorobenzylidene)-1-(4-chlorophenyl)methanamine (**2g**).



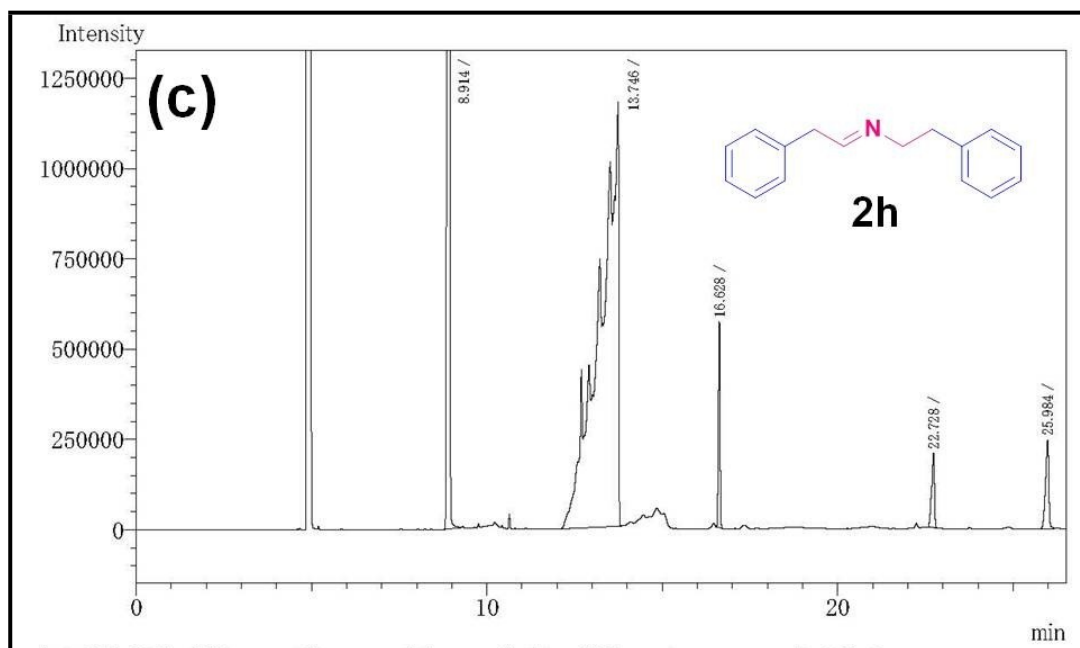
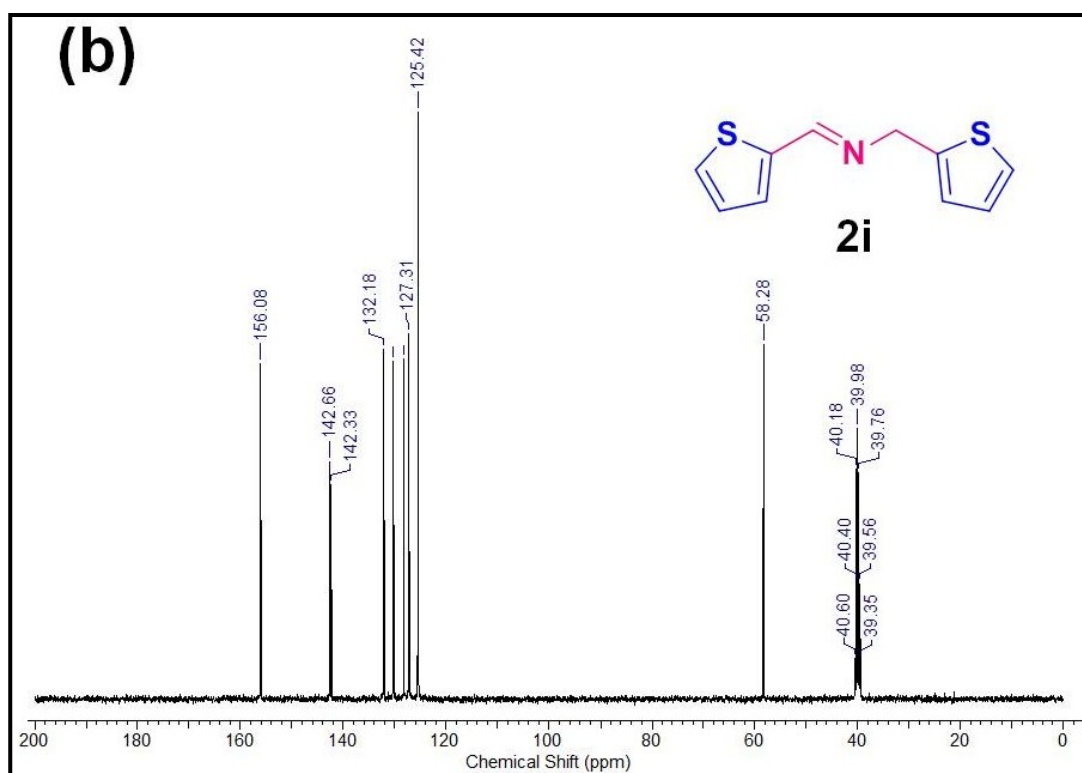
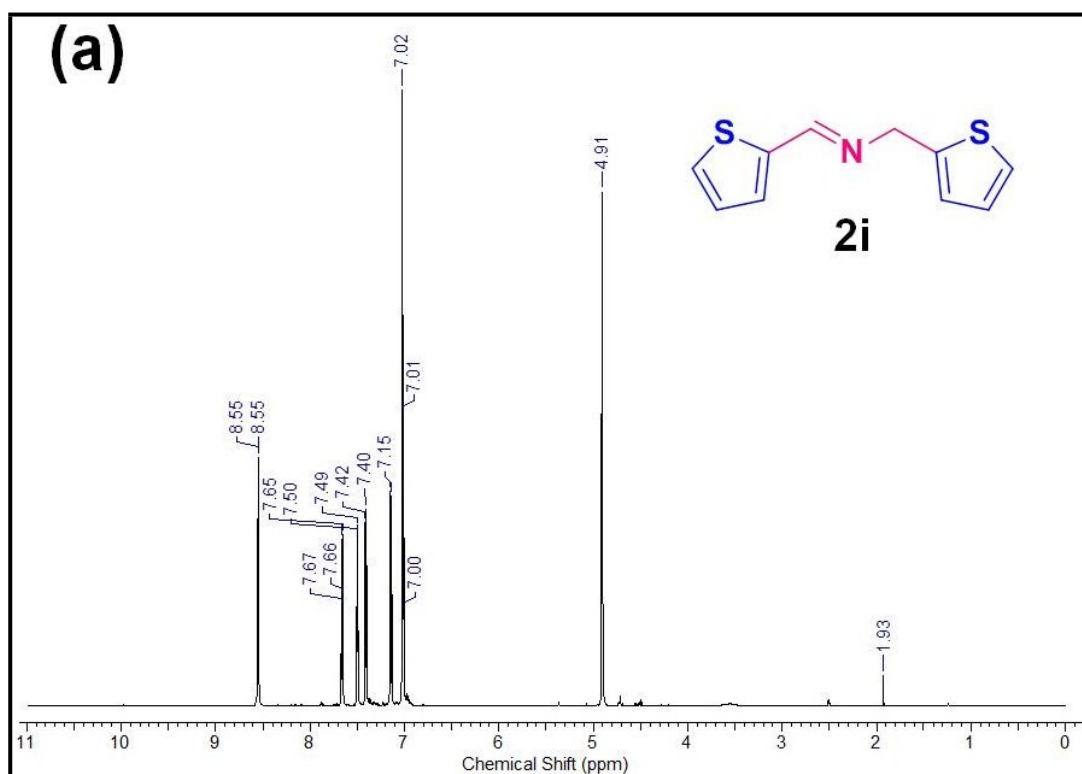


Fig. S24. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of 2-phenyl-*N*-(2-phenylethylidene)ethanamine (**2h**).



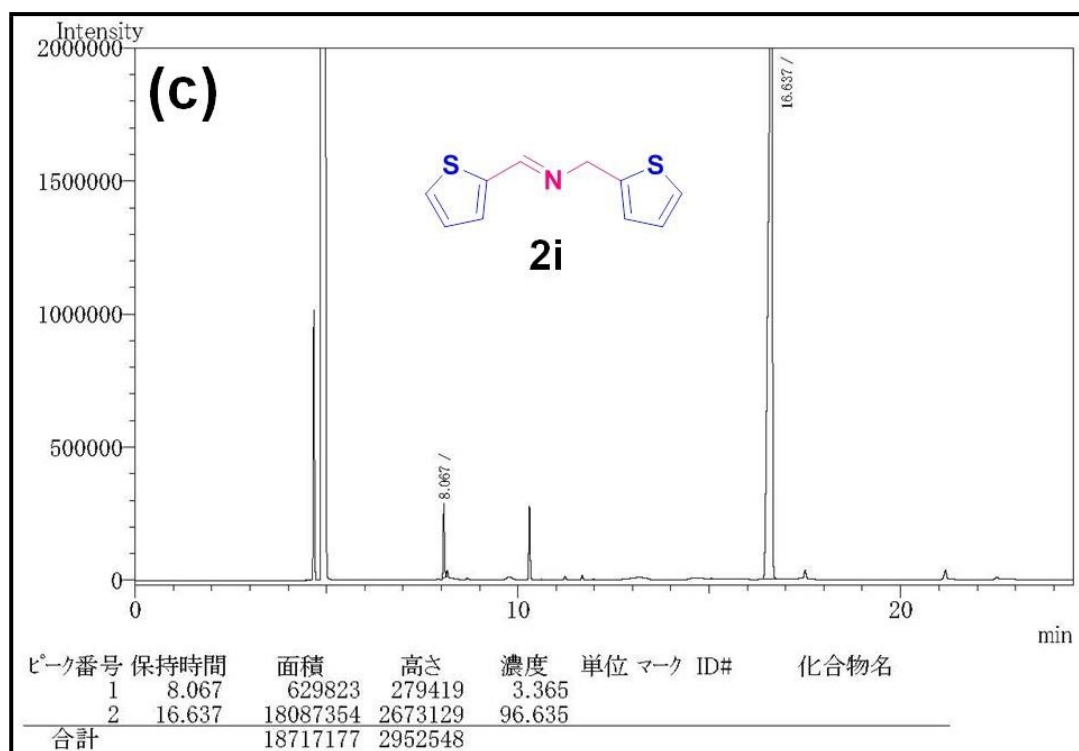


Fig. S25. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(thiophen-2-yl)-1-(thiophen-2-yl)methanamine (**2i**).

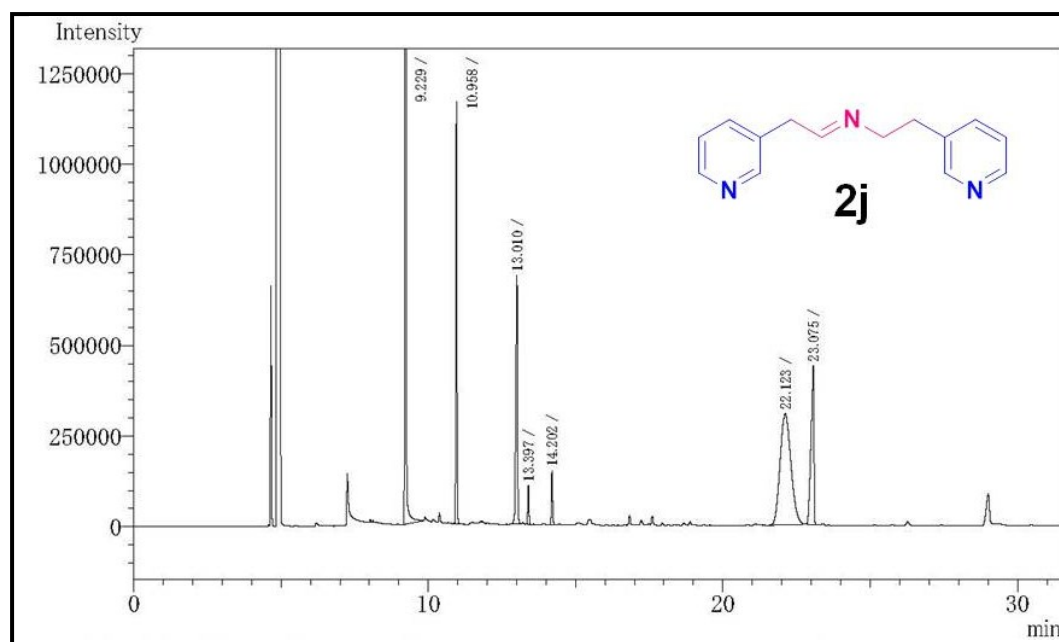


Fig. S26. GC chromatogram of 2-(pyridin-3-yl)-*N*-(2-(pyridin-3-yl)ethylidene)ethanamine (2j).

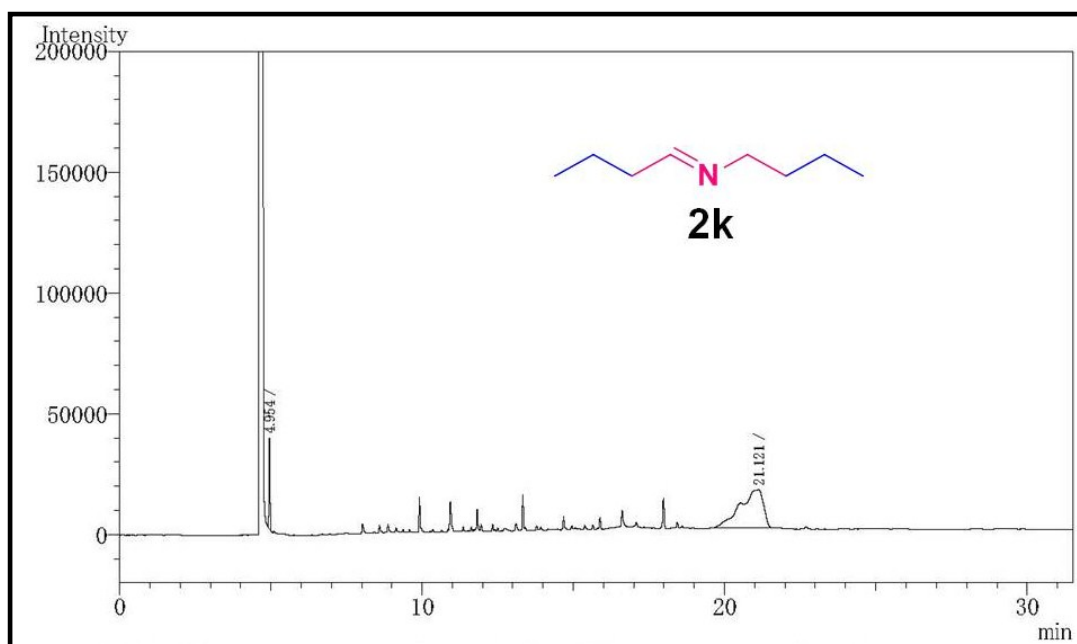
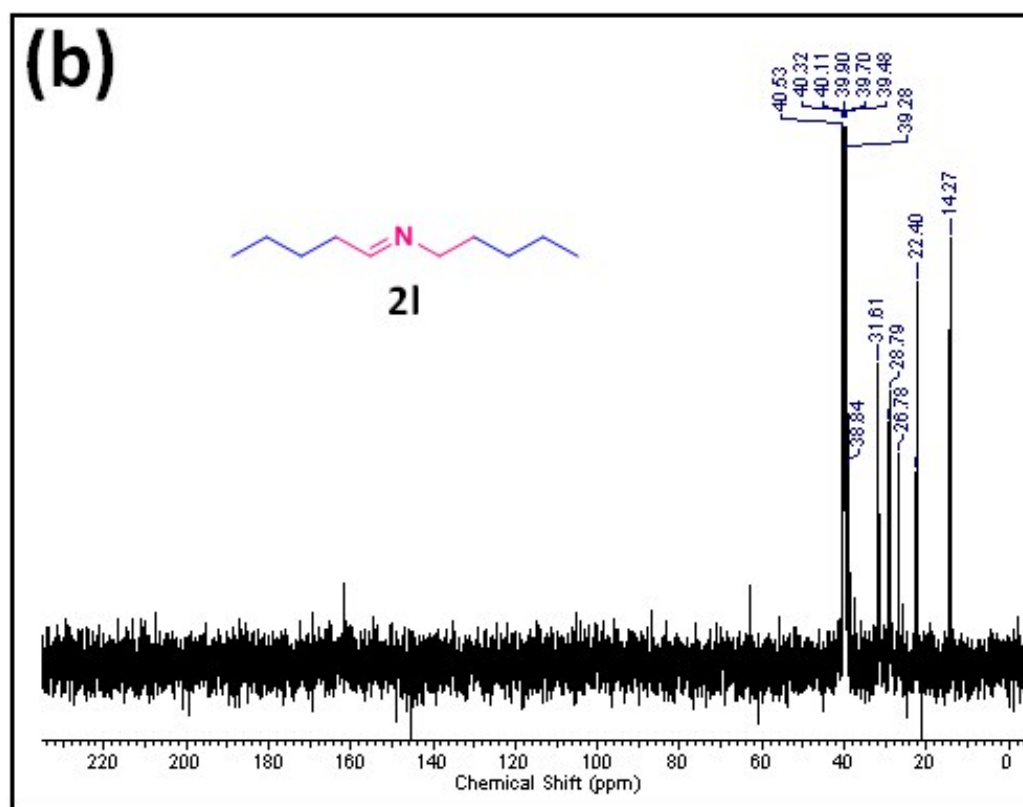
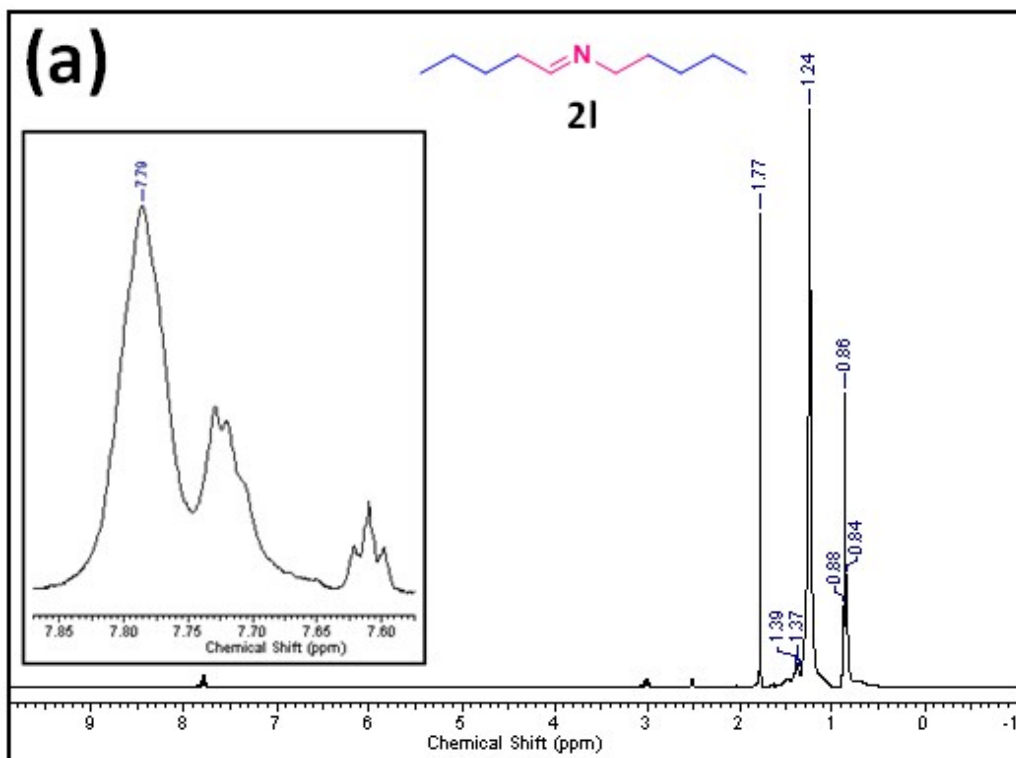


Fig. S27. GC chromatogram of *N*-butylidenebutan-1-amine (**2k**).



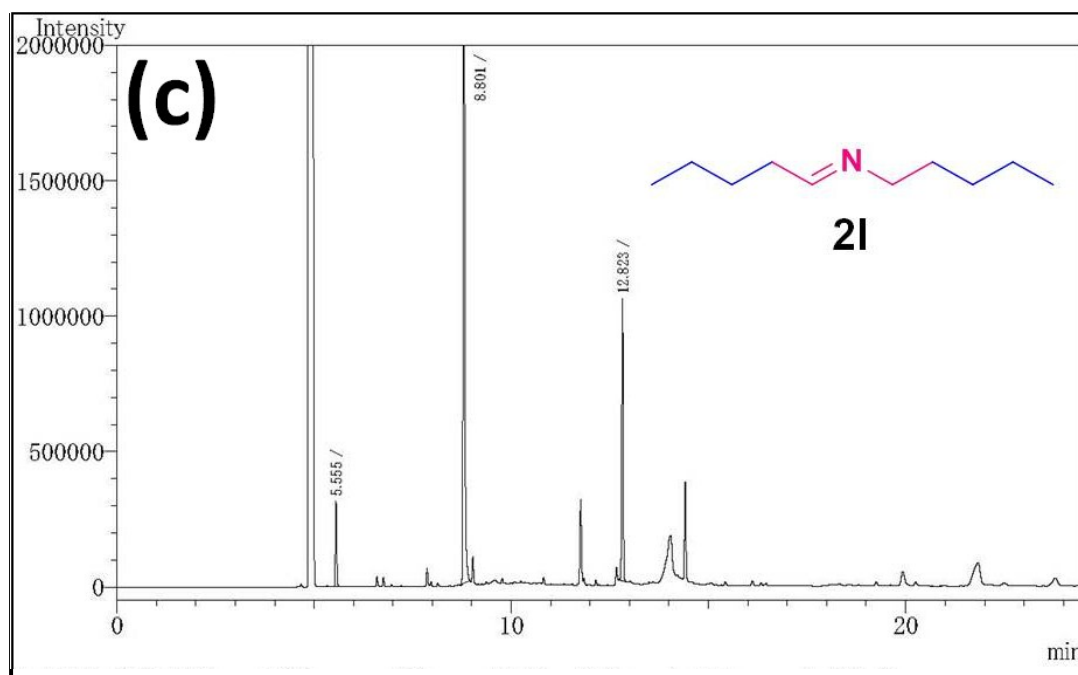
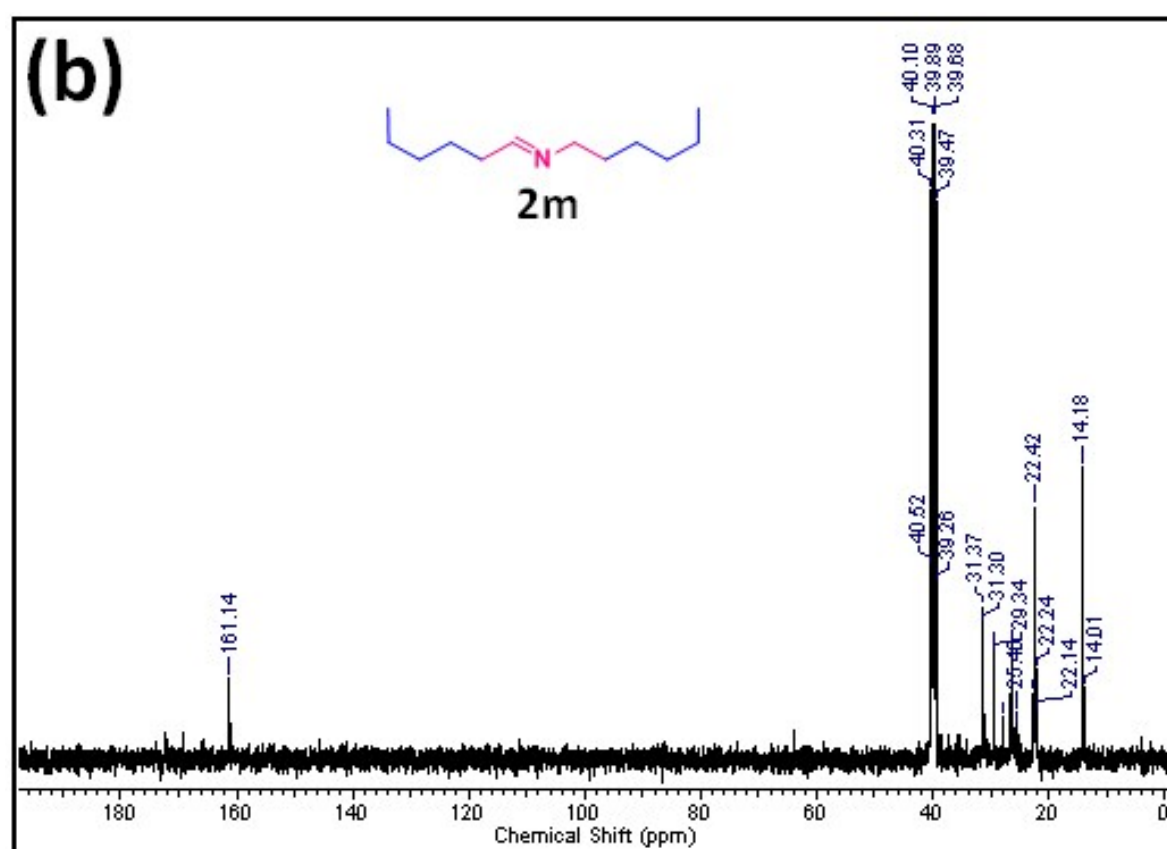
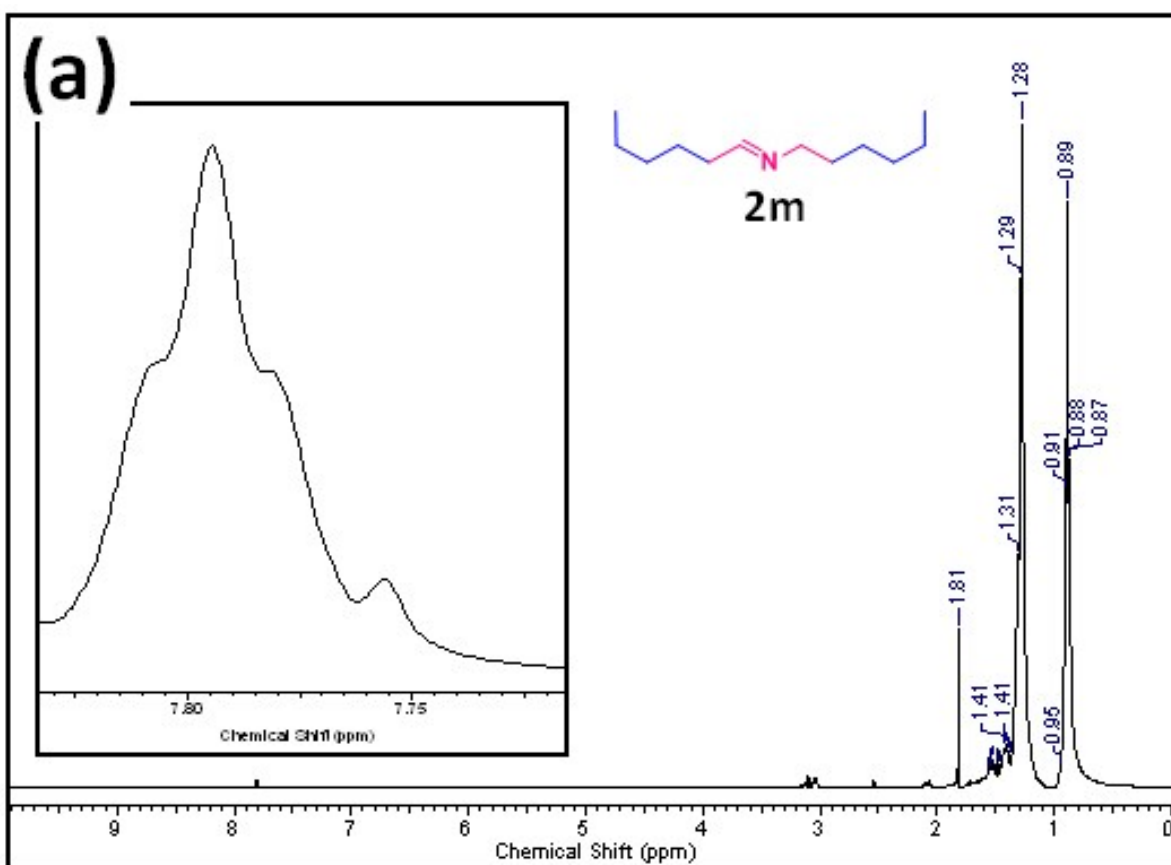


Fig. S28. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-pentylidenepentan-1-amine (**2I**).



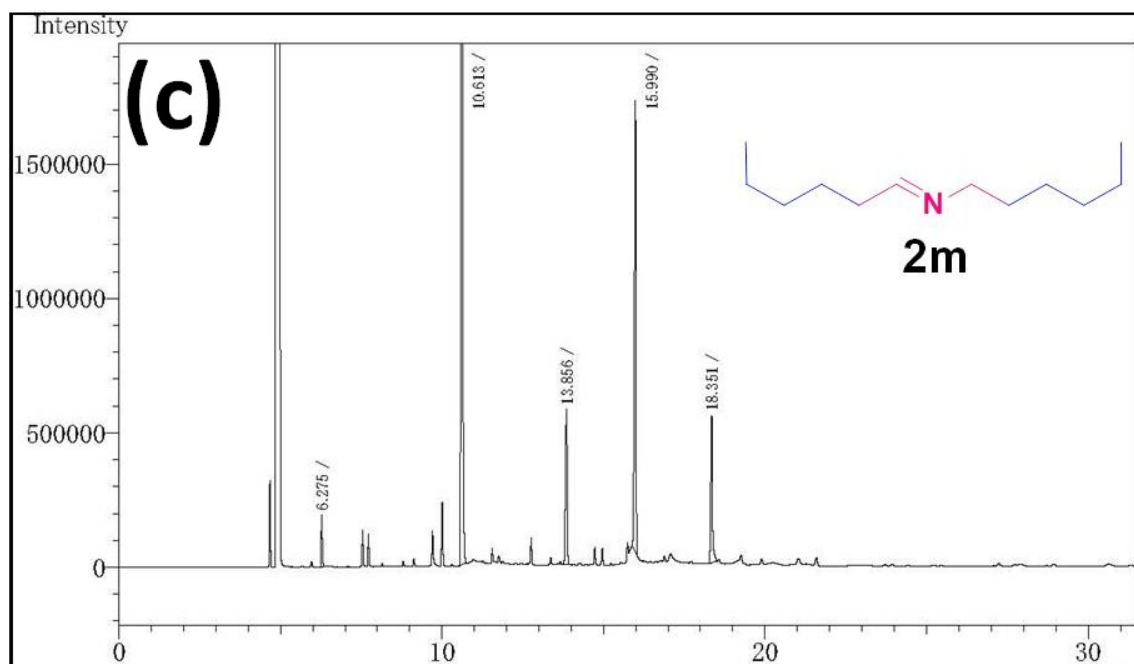
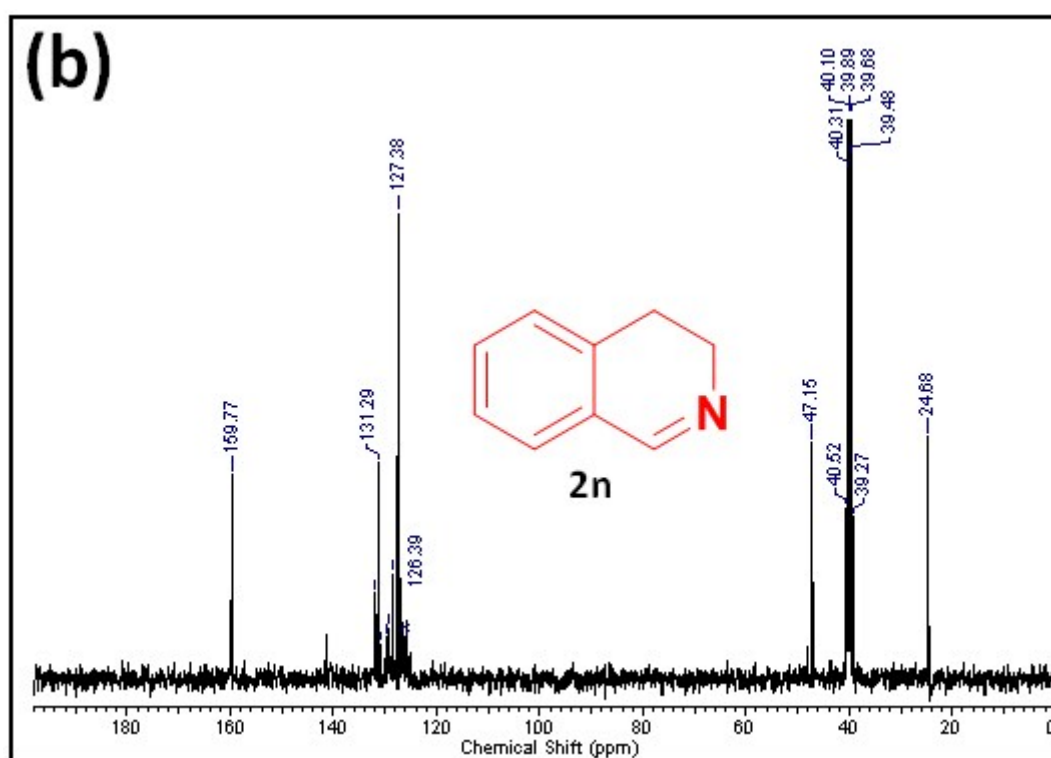
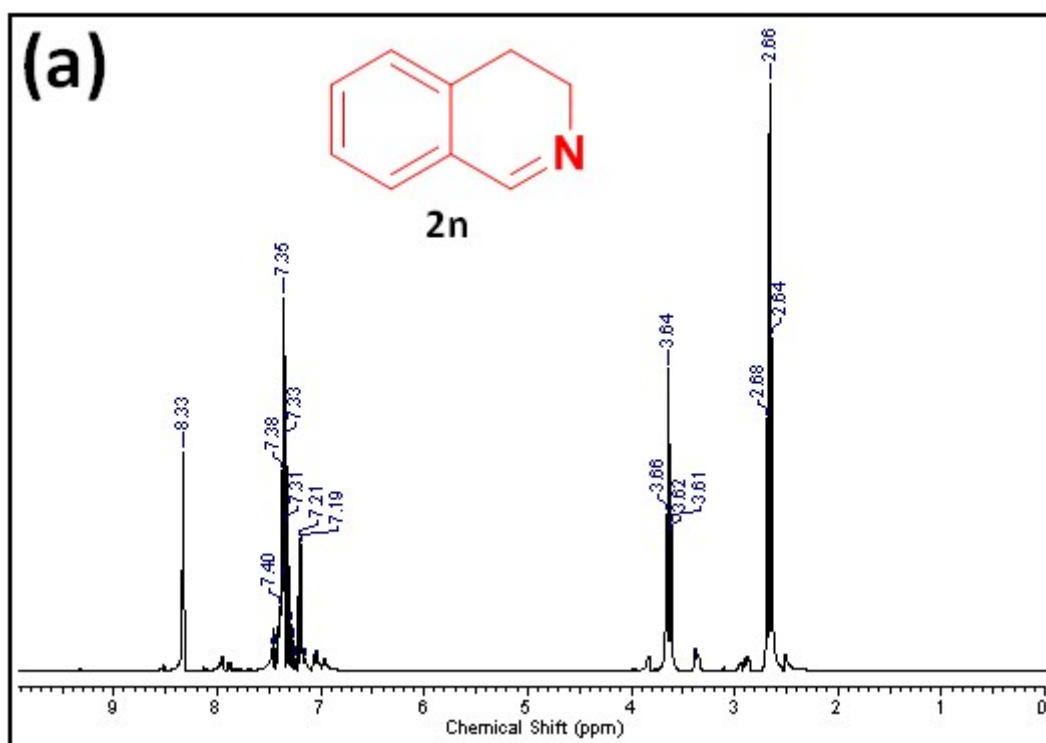


Fig. S29. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-hexylidenehexan-1-amine (**2m**).



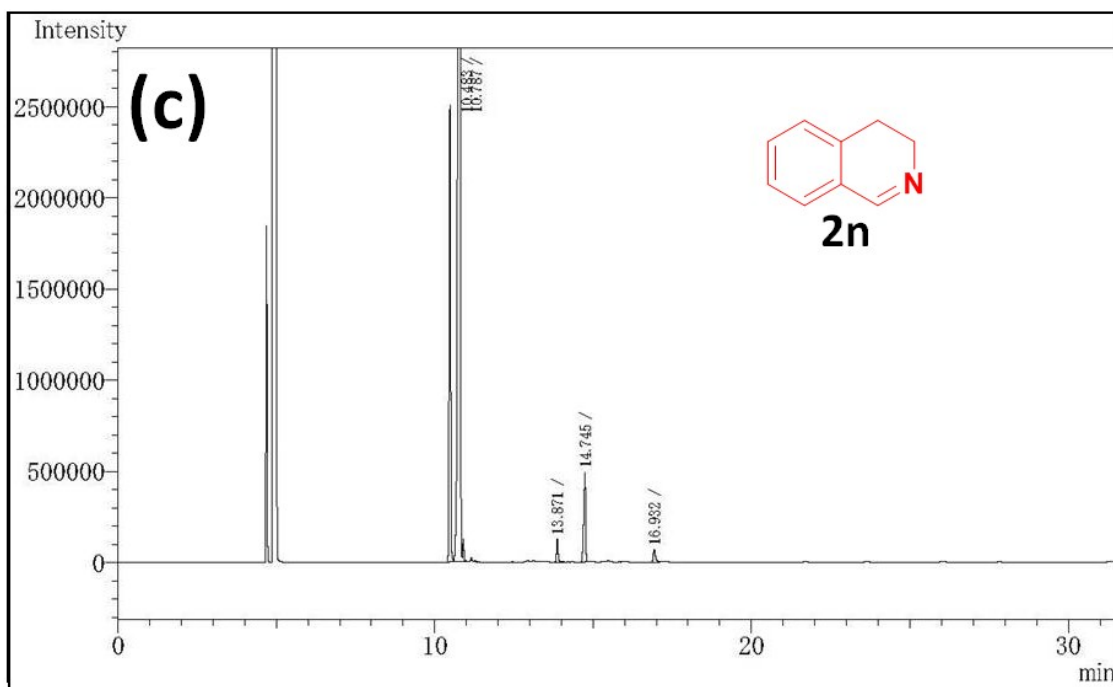
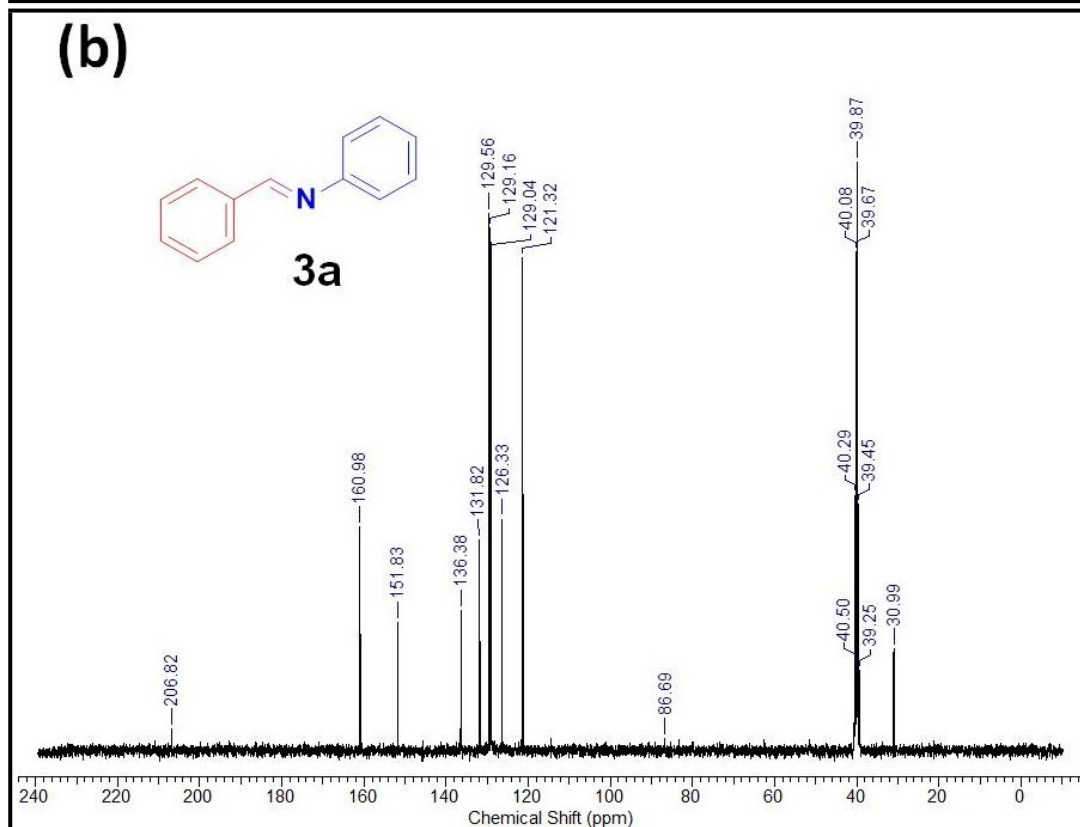
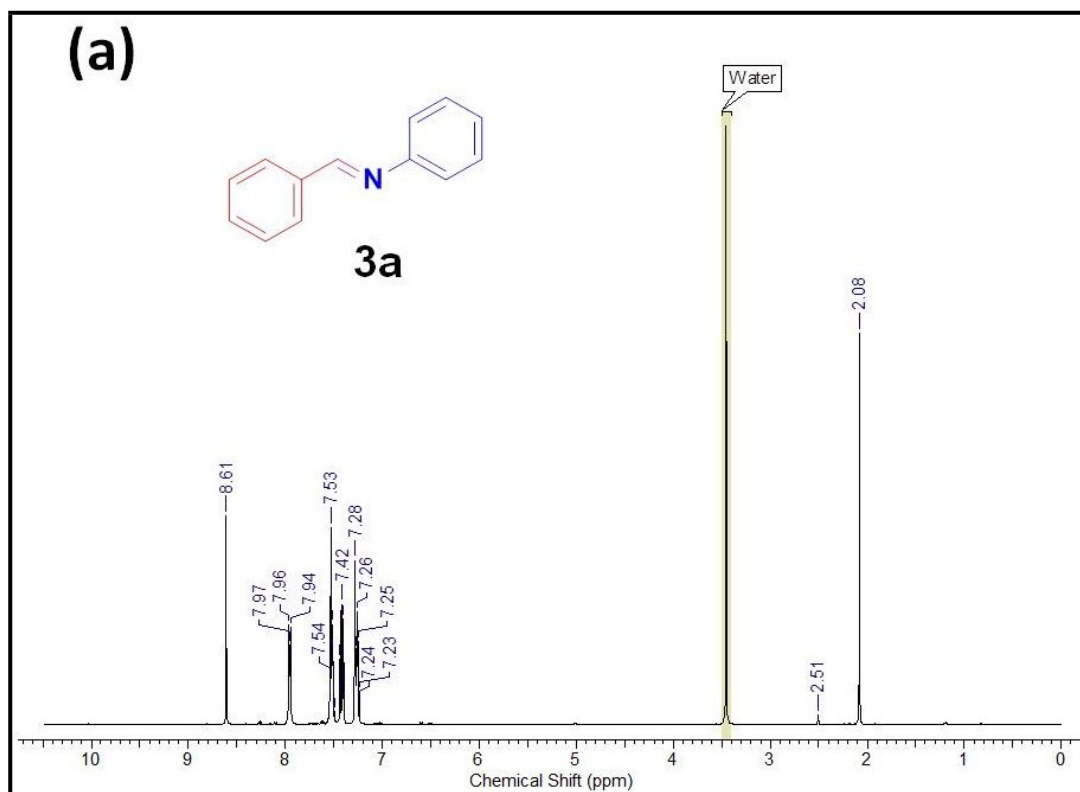


Fig. S30. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of 3,4-dihydroisoquinoline (**2n**).



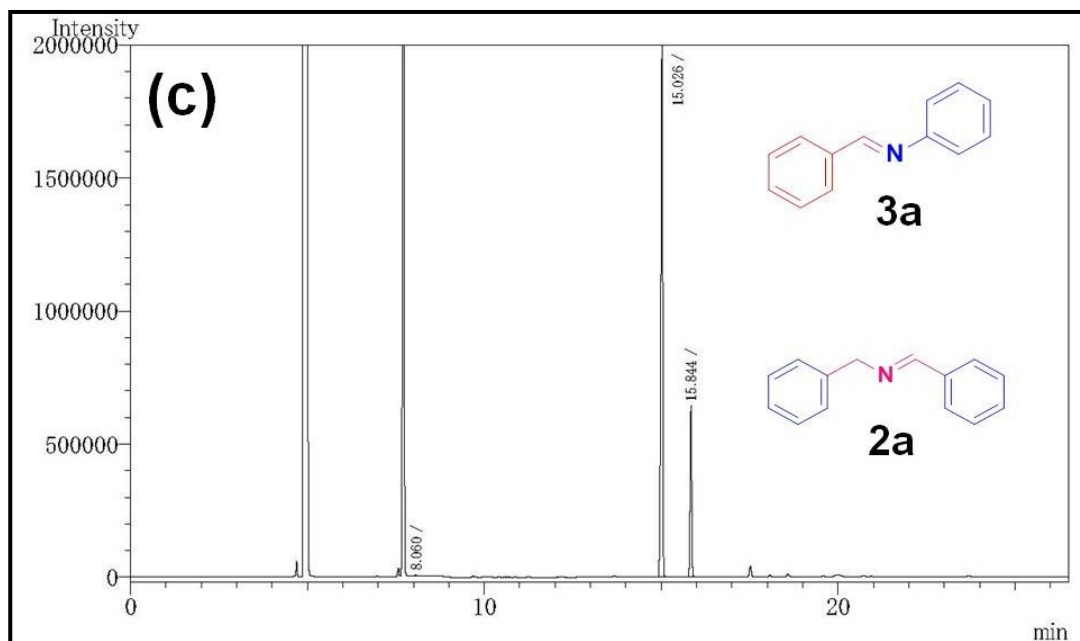
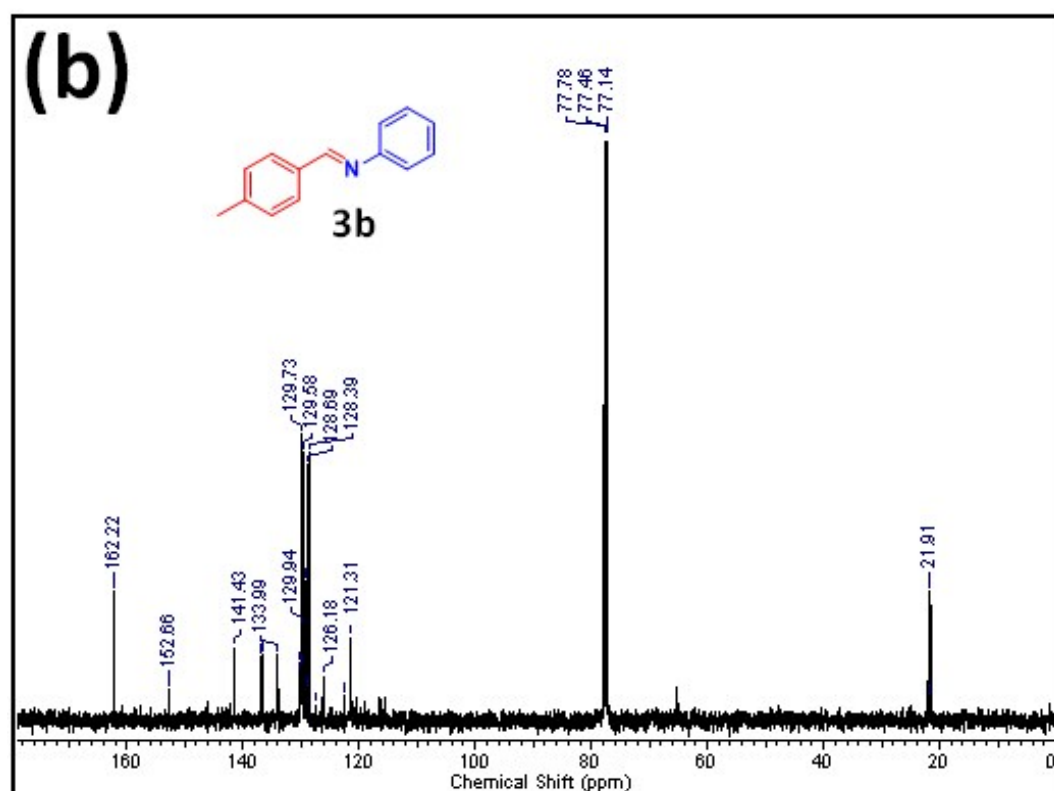
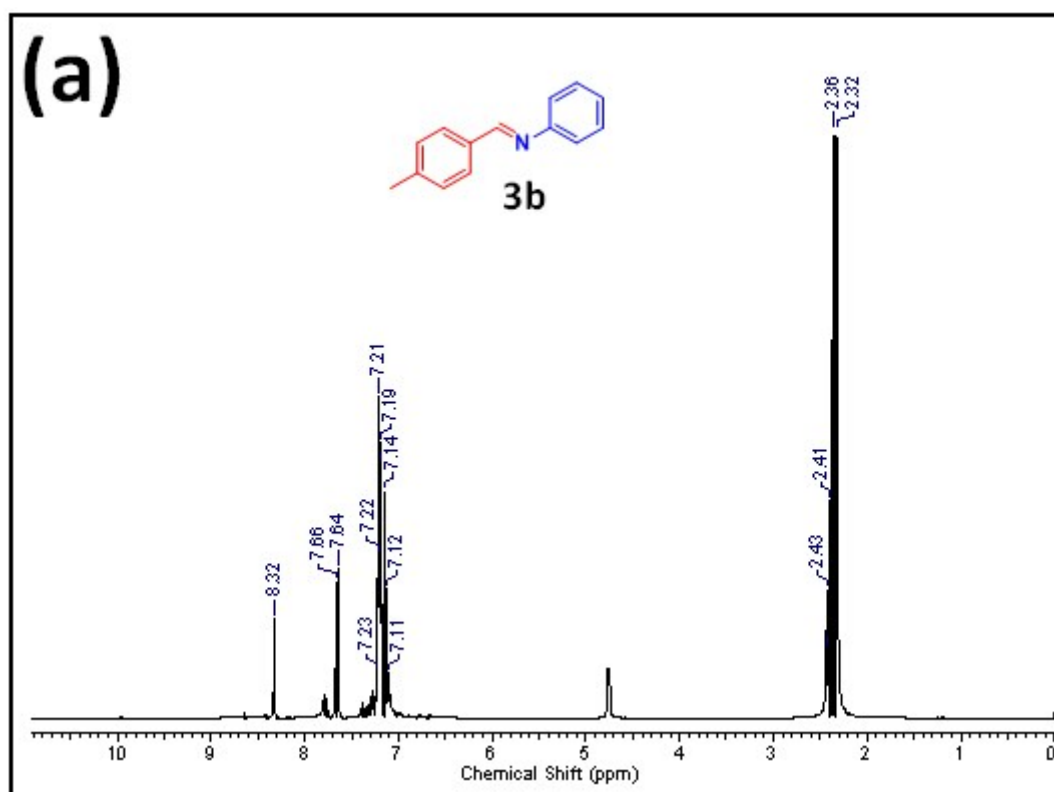


Fig. S31. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-benzylideneaniline (**3a**).



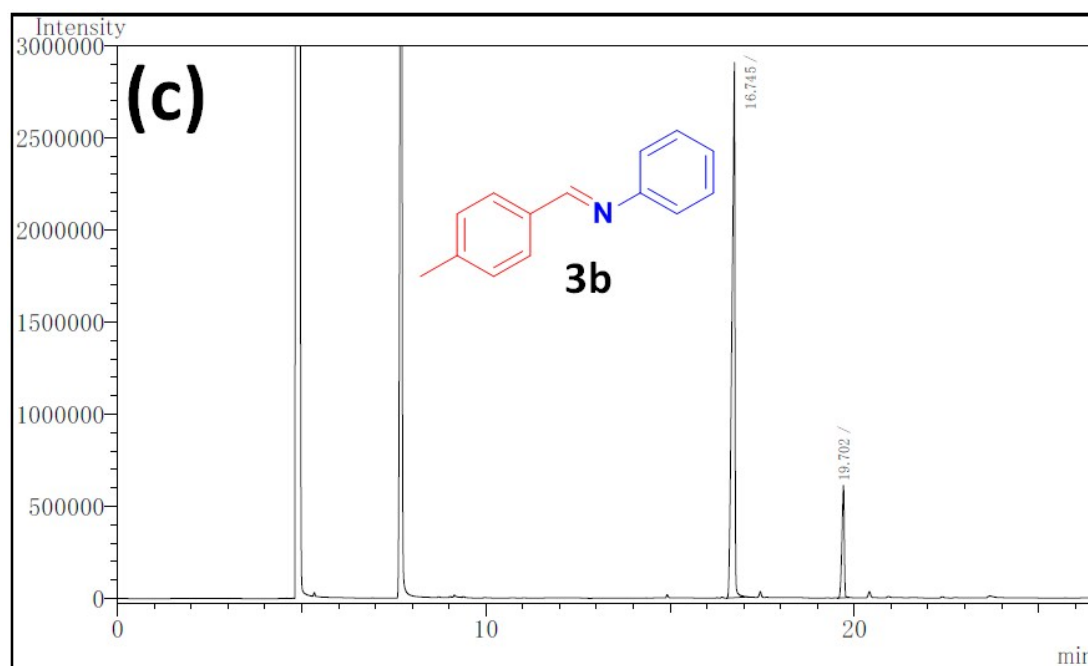
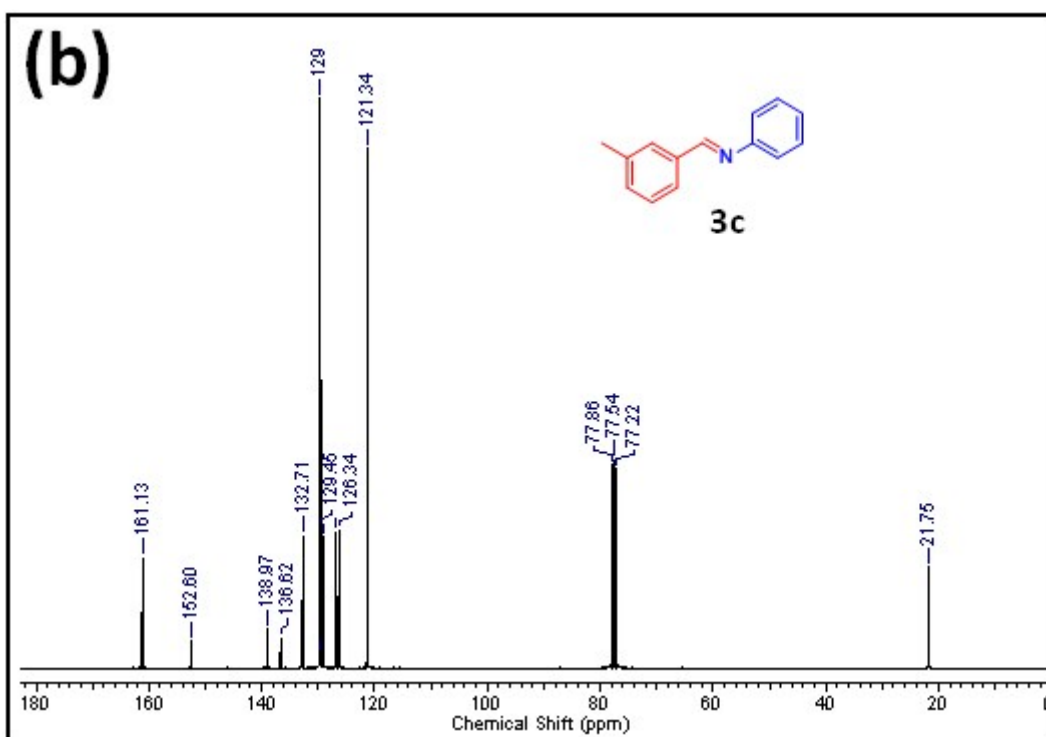
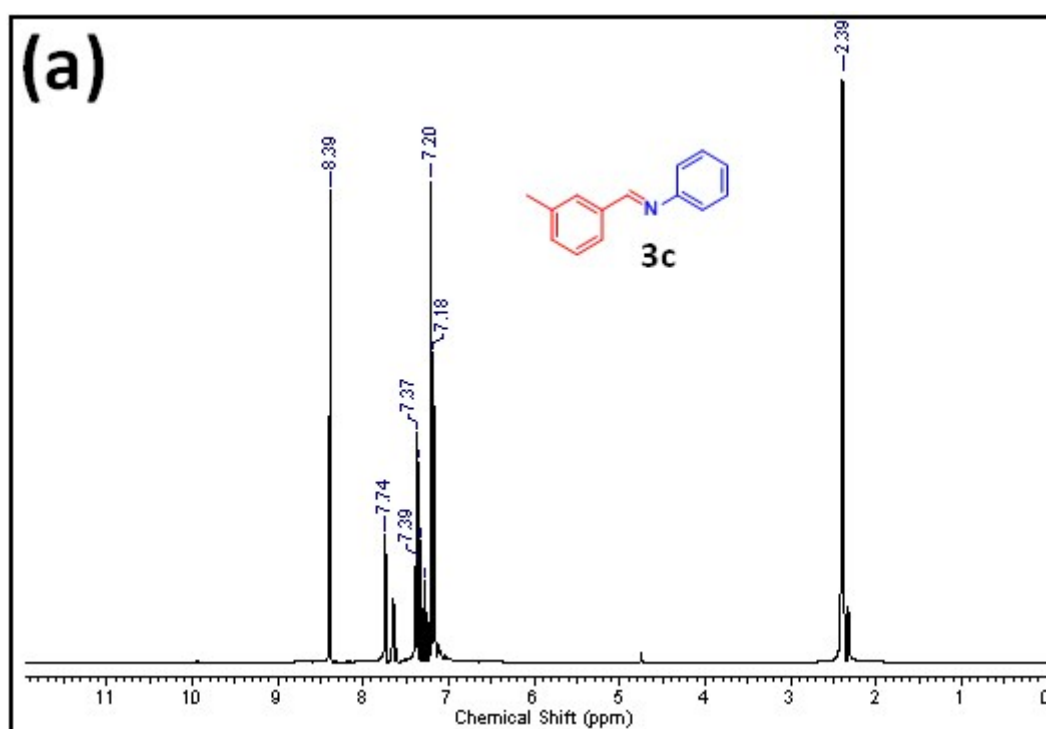


Fig. S32. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(4-Methylbenzylidene)aniline (**3b**).



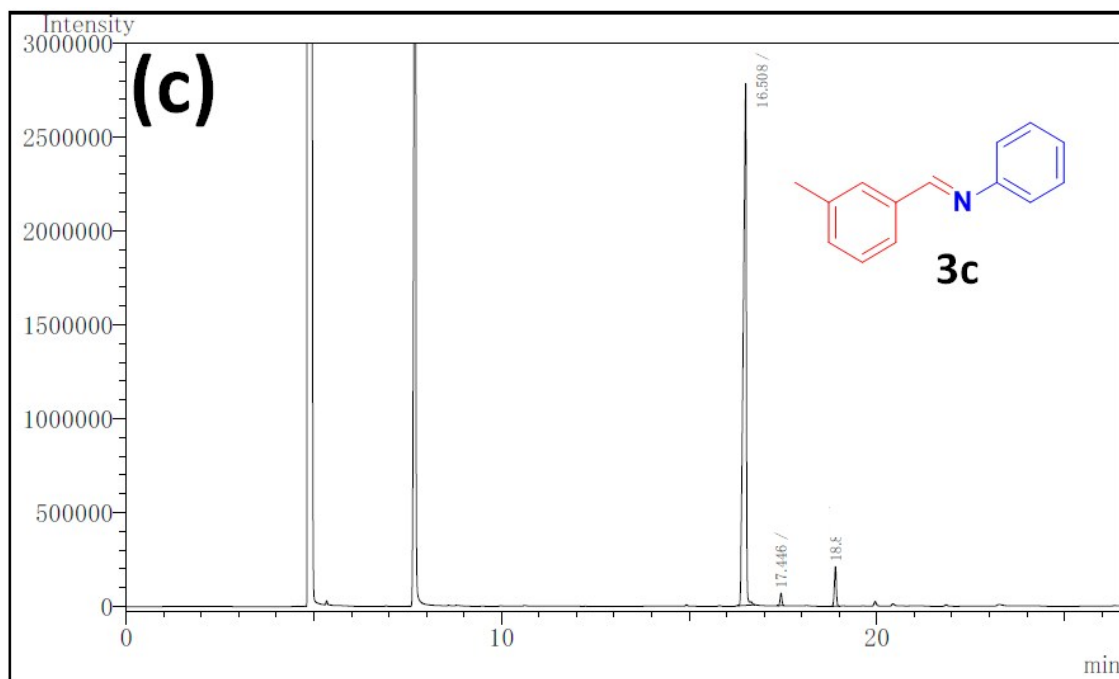
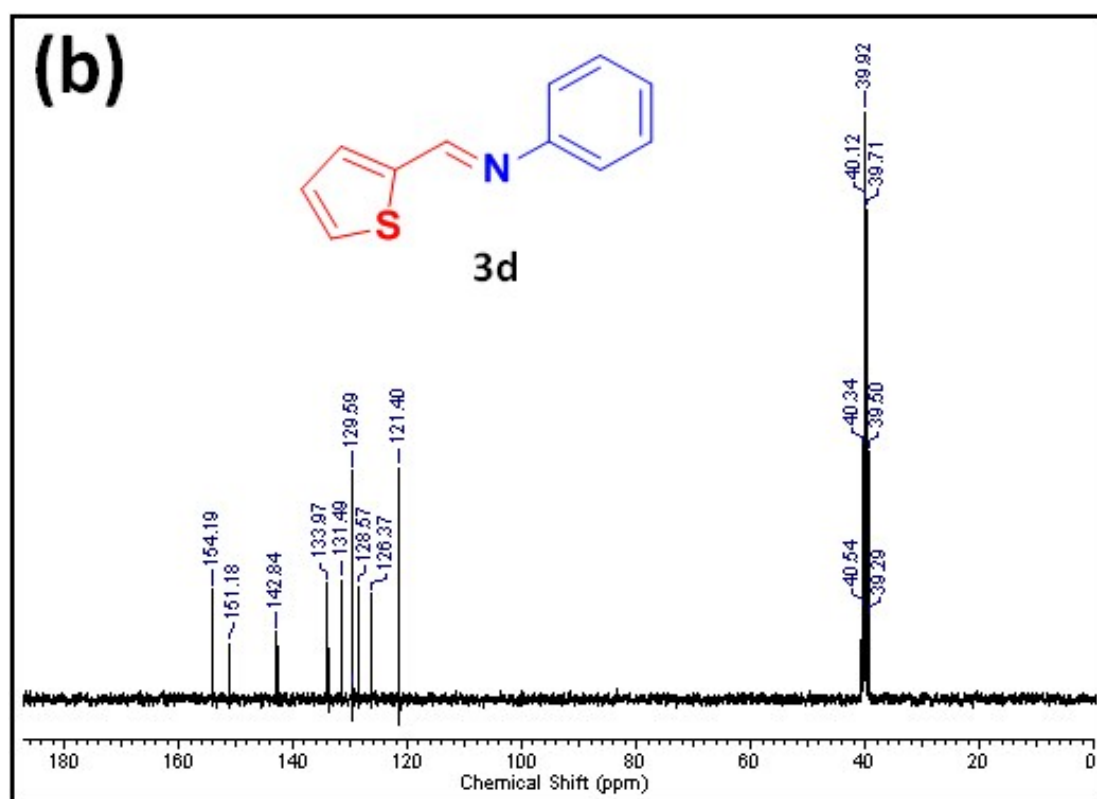
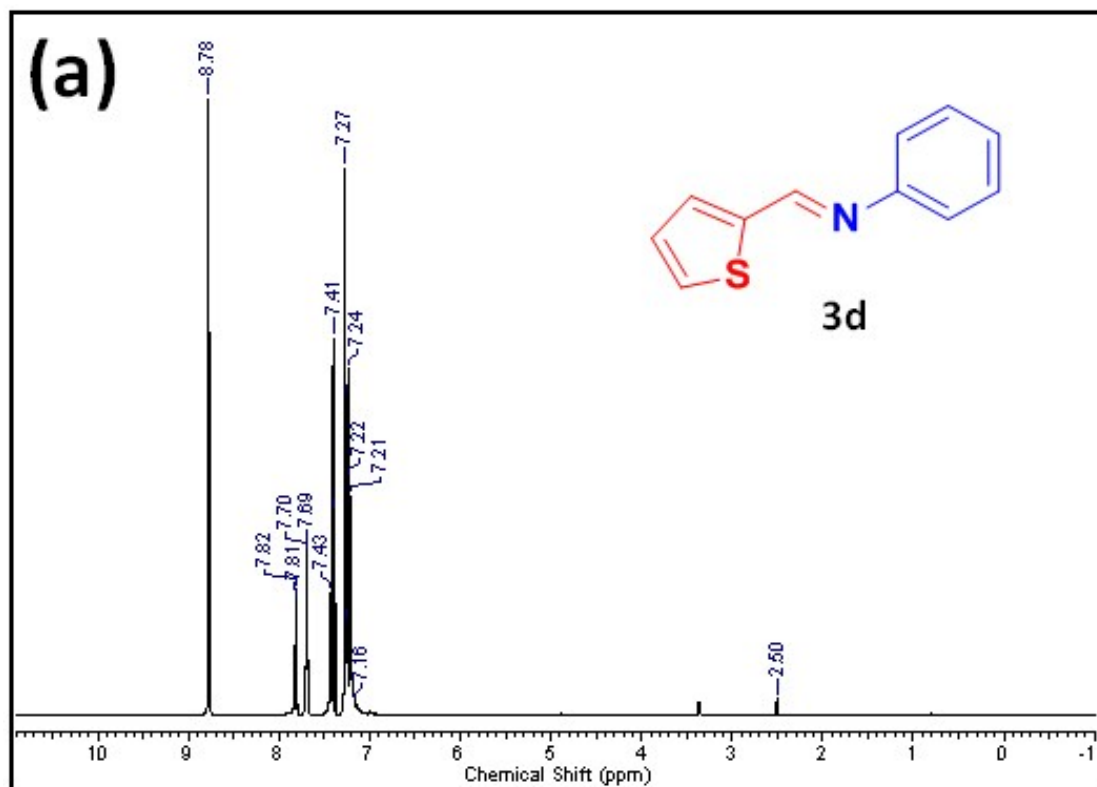


Fig. S33. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-phenyl-1-(*m*-tolyl)methanimine (**3c**).



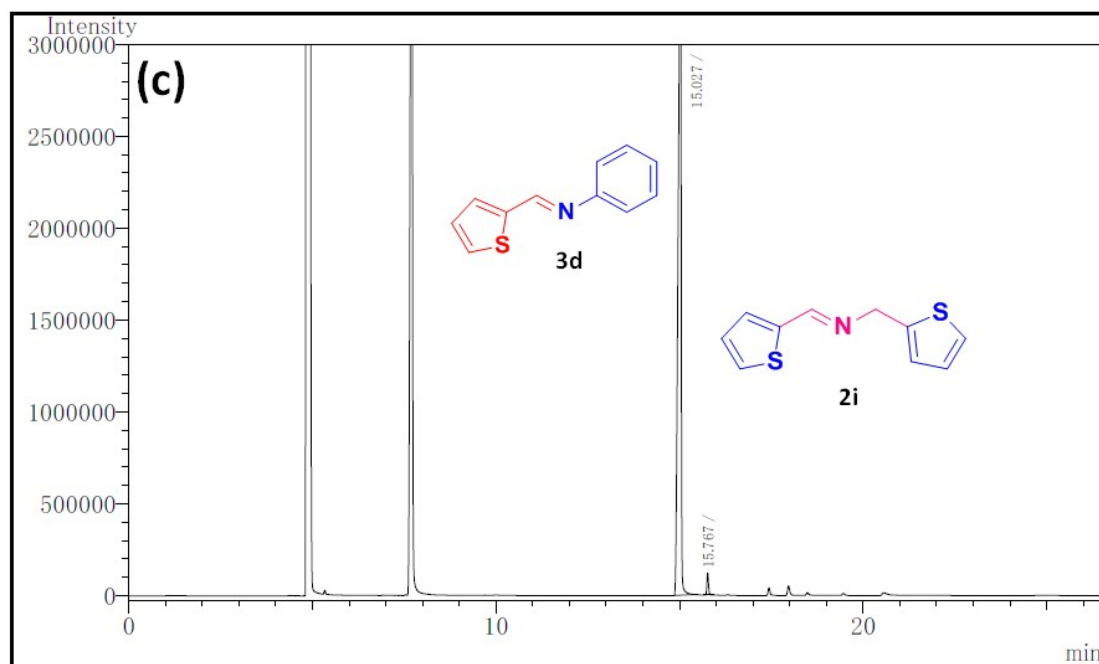
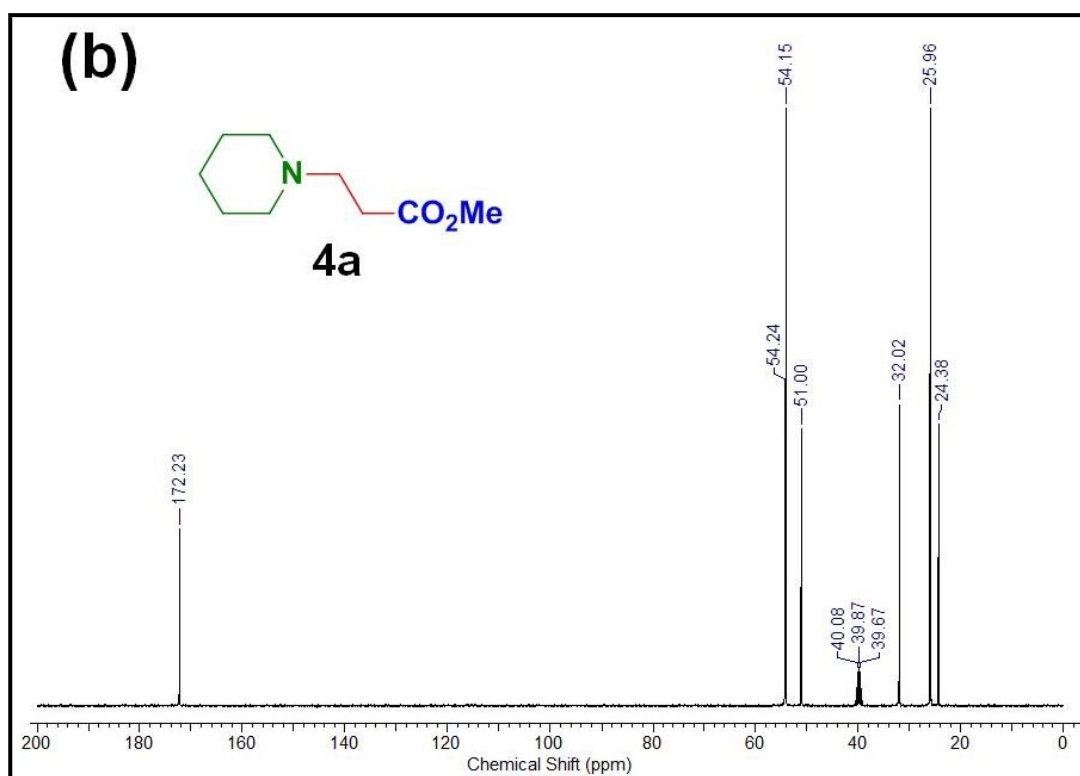
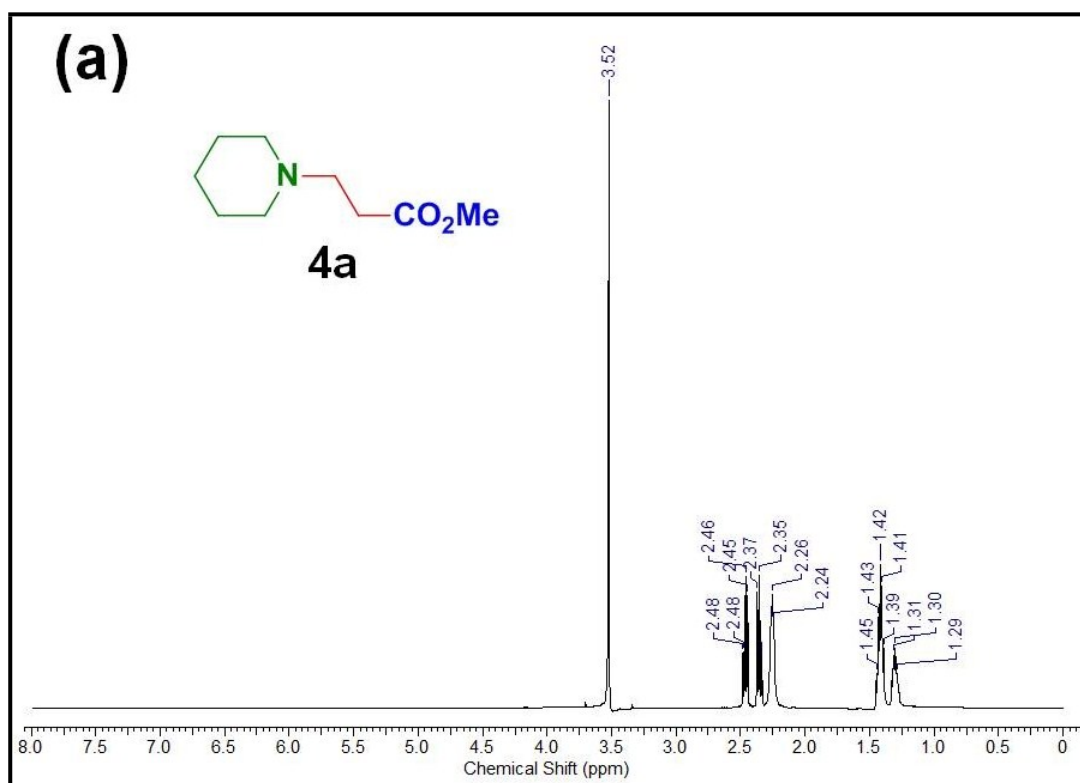


Fig. S34. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of *N*-(thiophen-2-yl)-1-methanamine (**3d**).



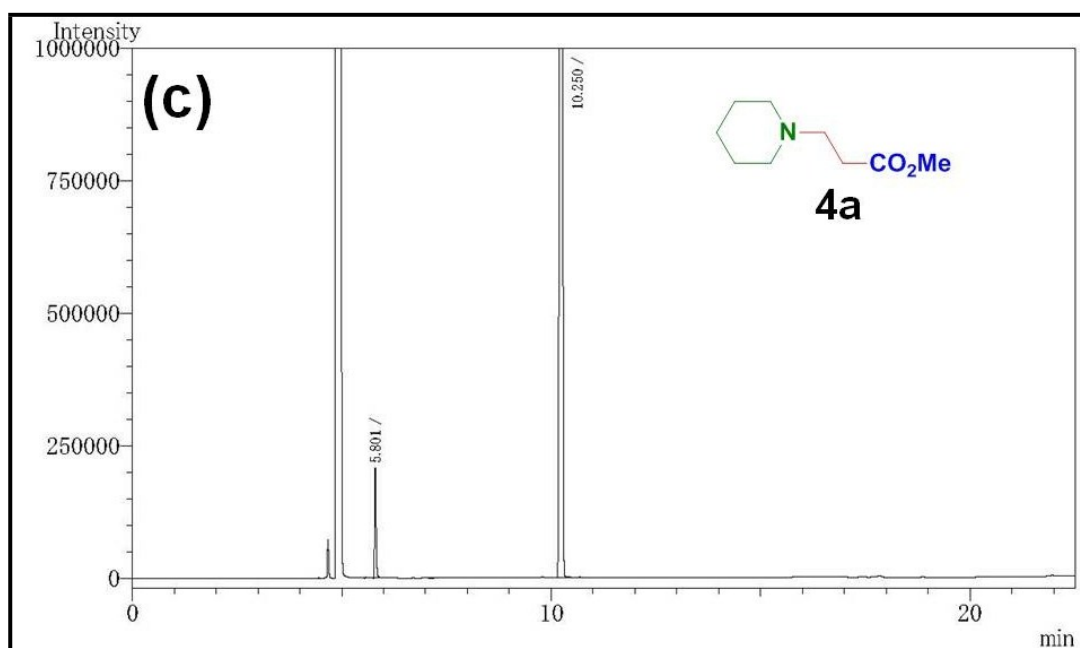
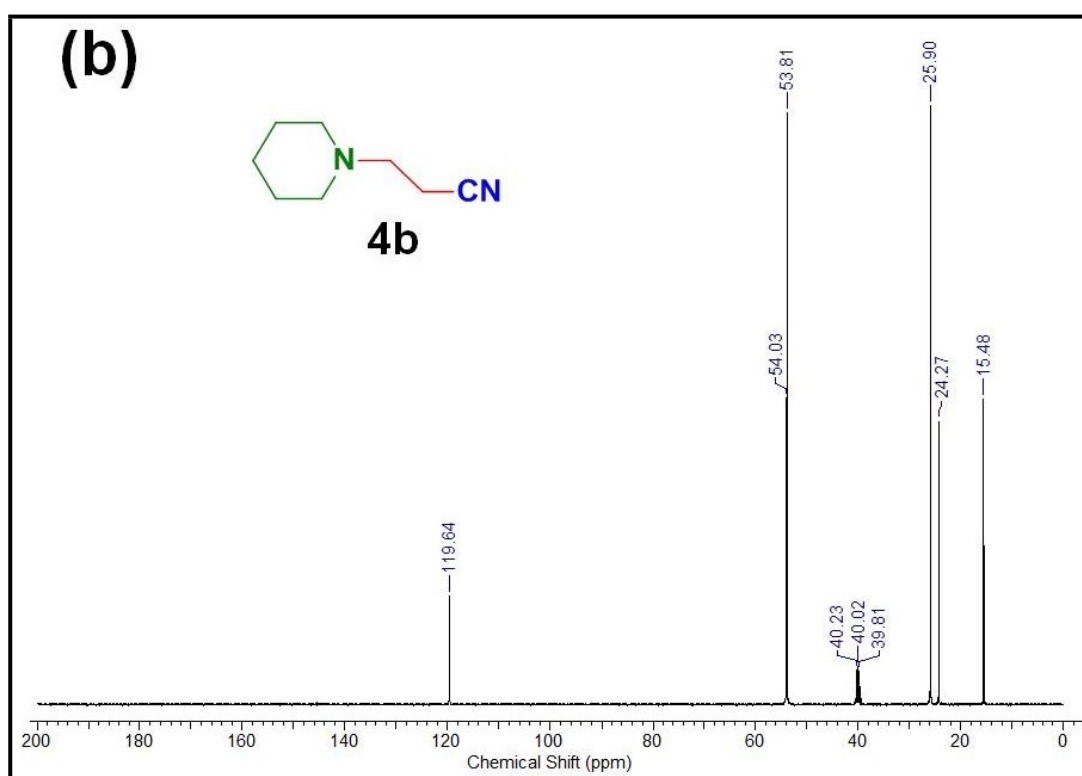
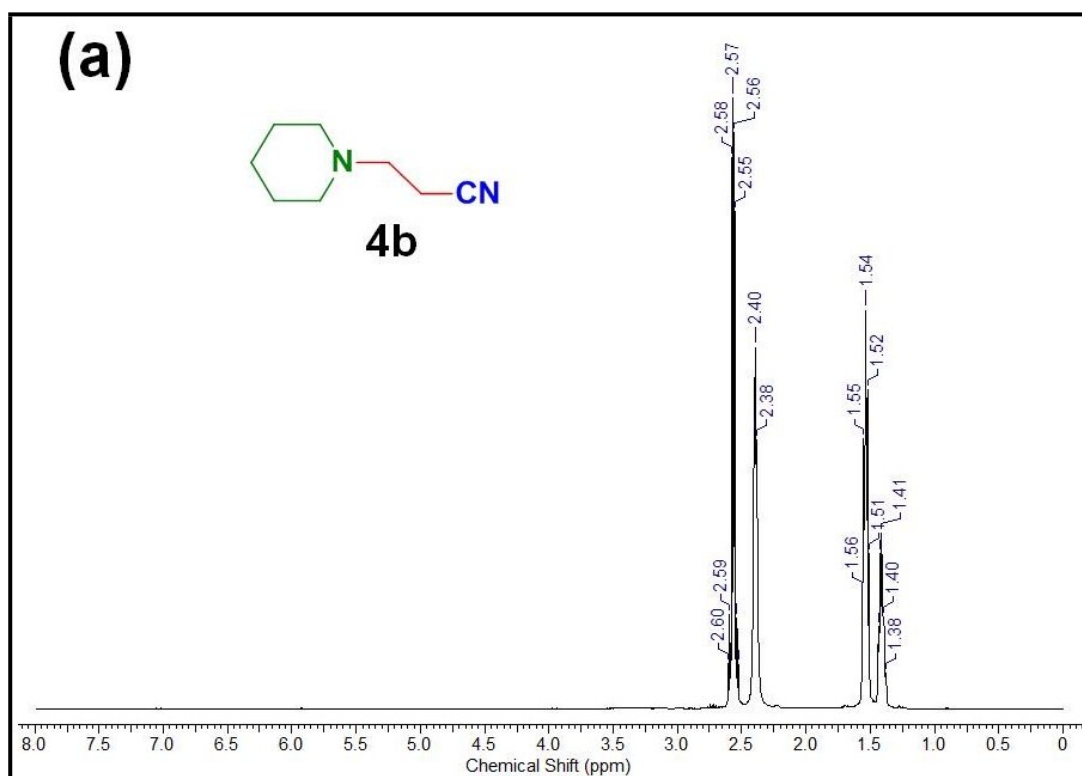


Fig. S35. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of methyl 3-(piperidin-1-yl)propanoate (**4a**).



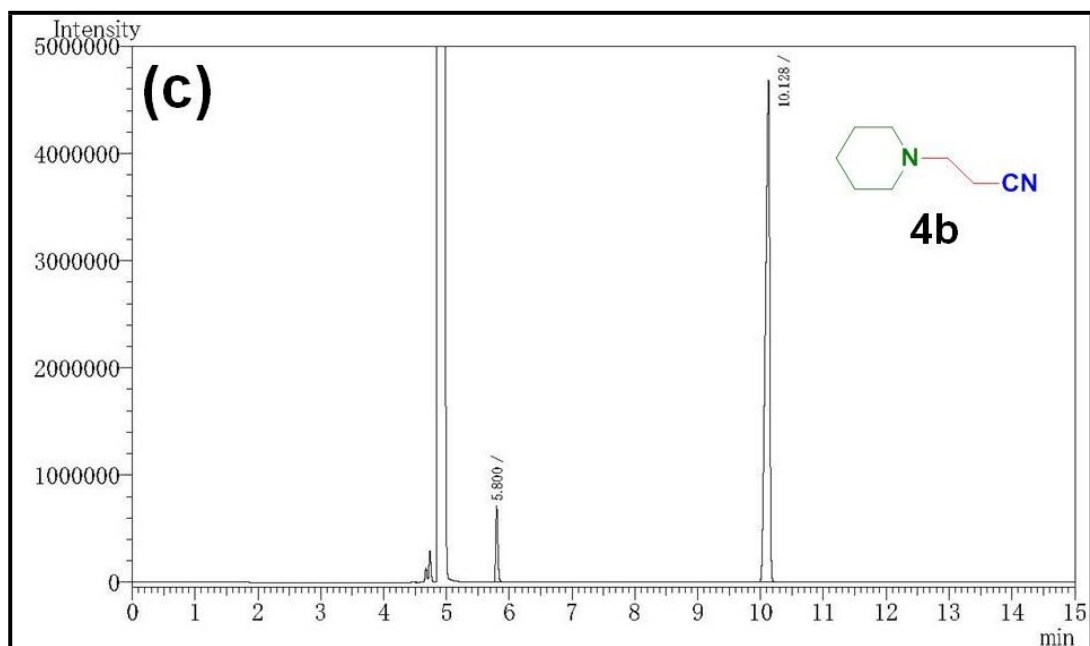
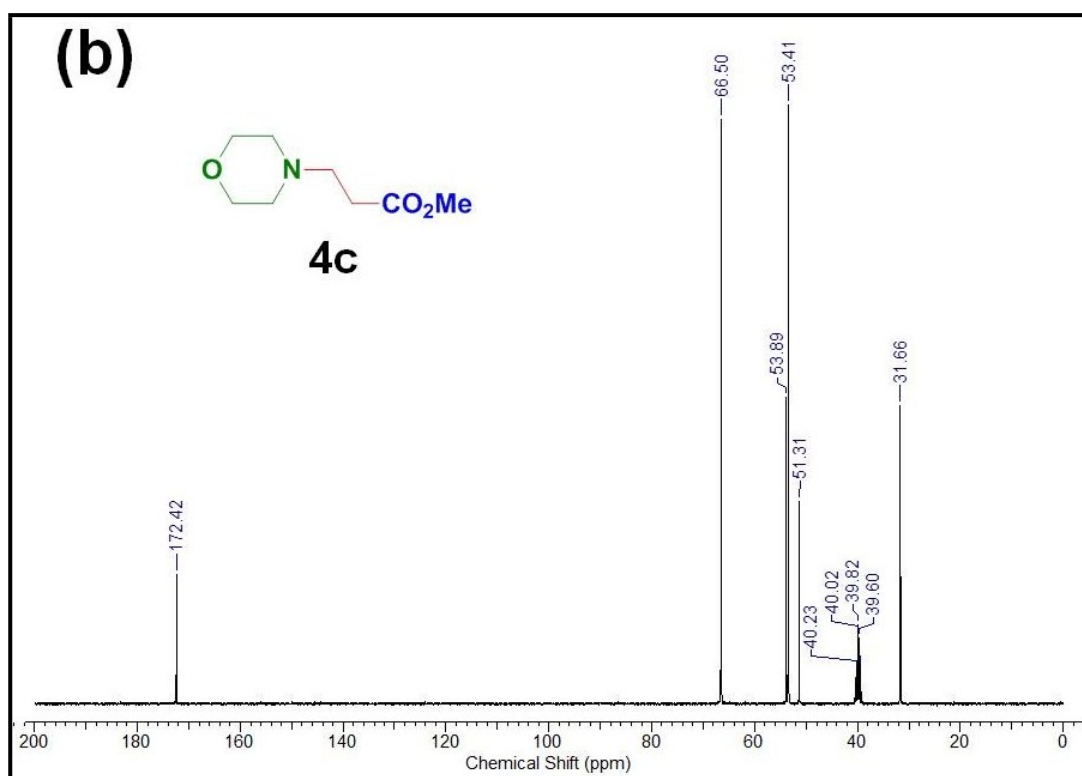
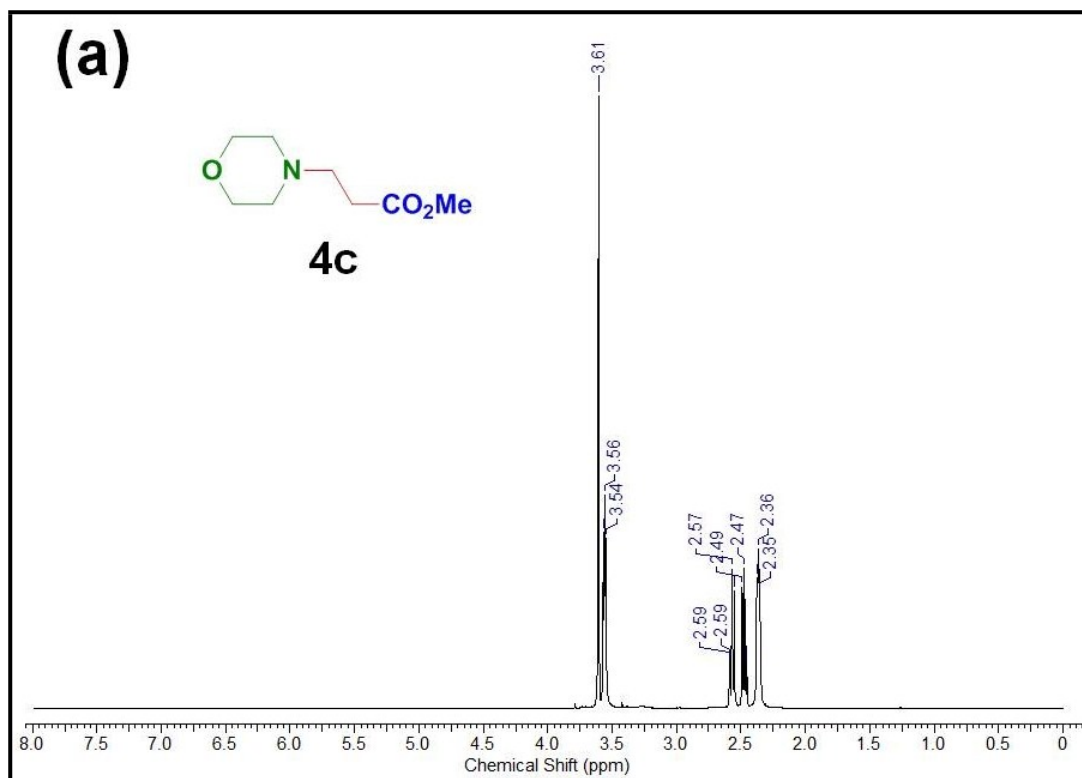


Fig. S36. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of 3-(piperidin-1-yl)propanenitrile (**4b**).



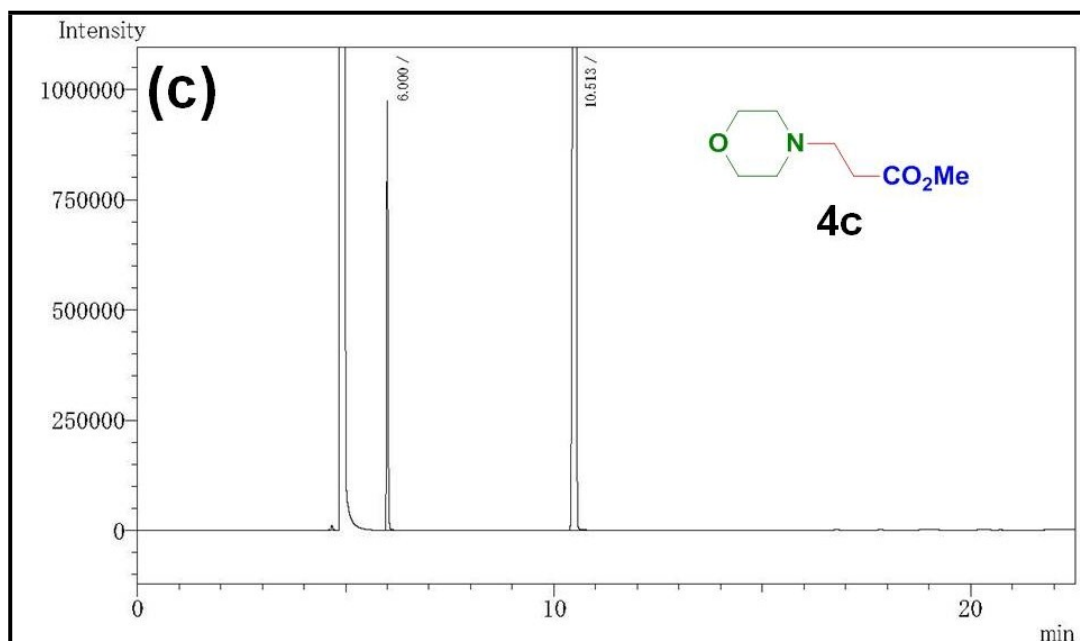
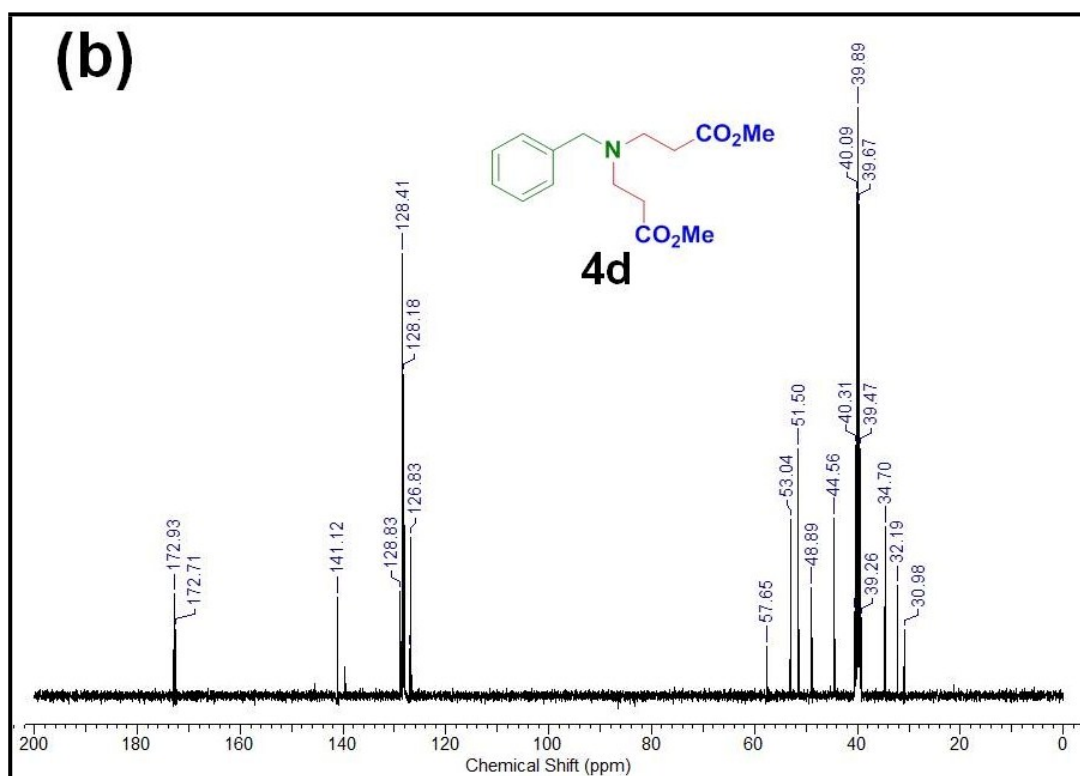
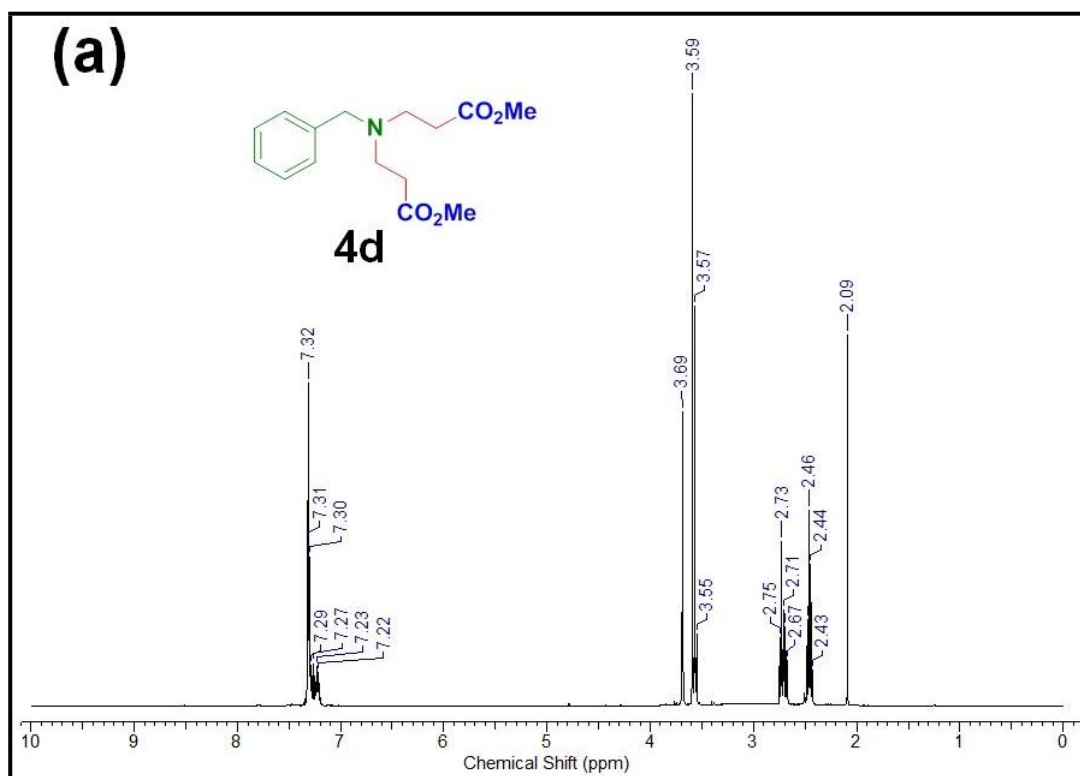


Fig. S37. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of methyl 3-morpholinopropanoate (**4c**).



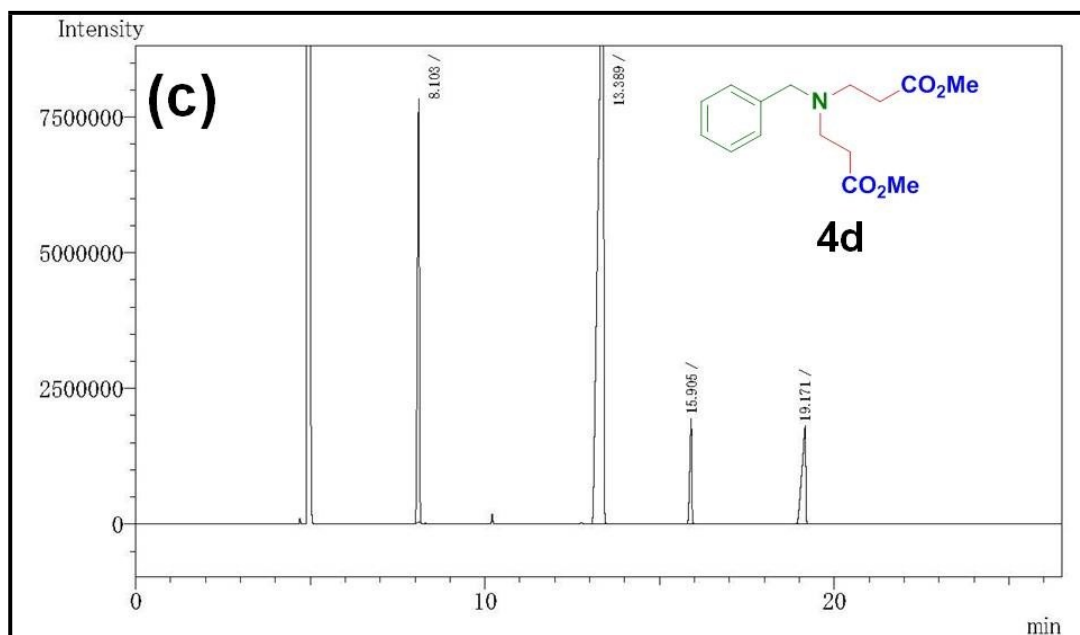
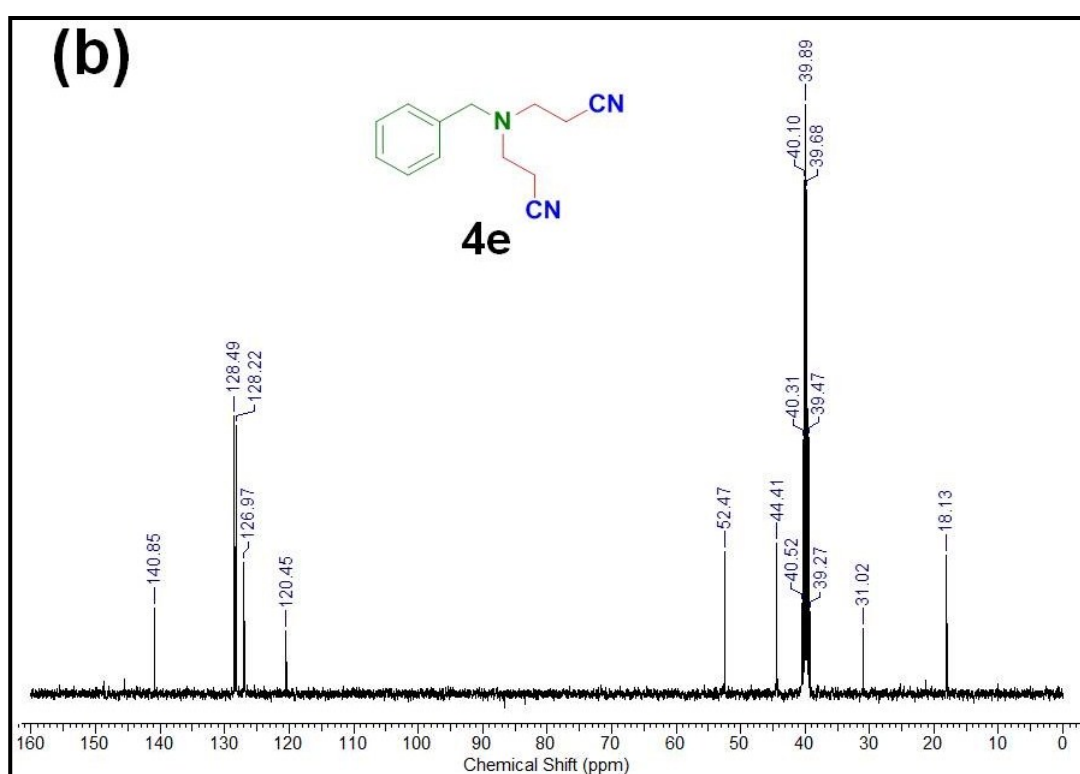
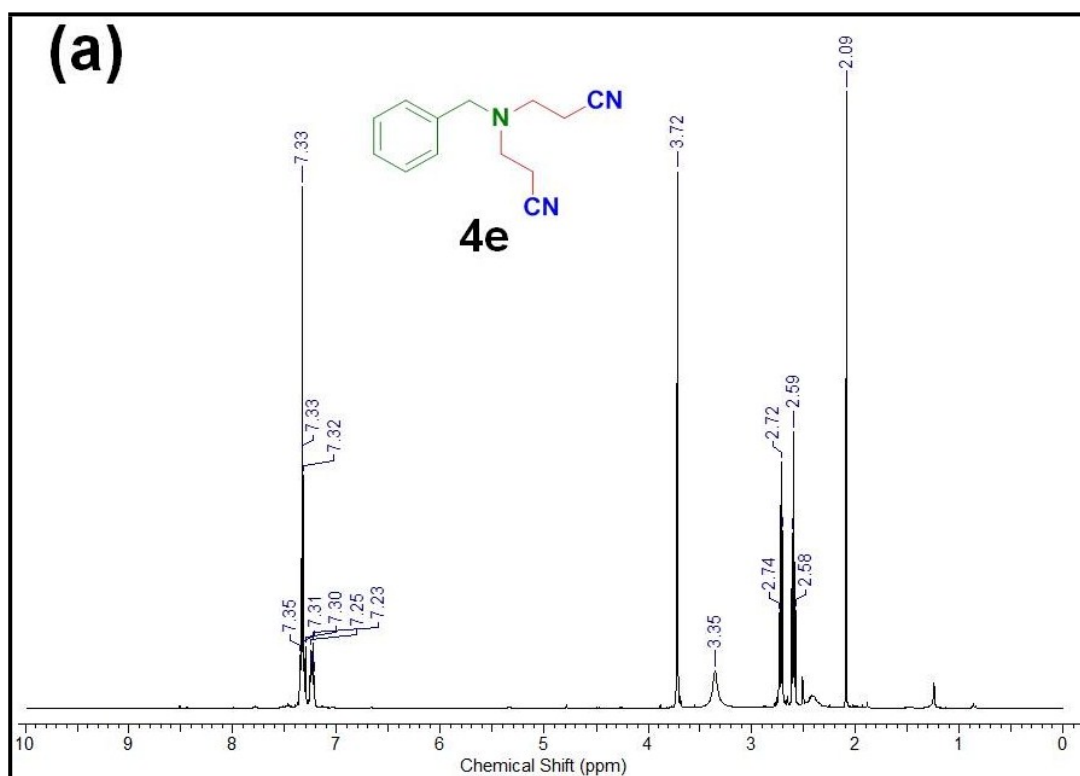


Fig. S38. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of 3,3'-(*N*-benzylimino)dipropionic acid dimethyl ester (**4d**).



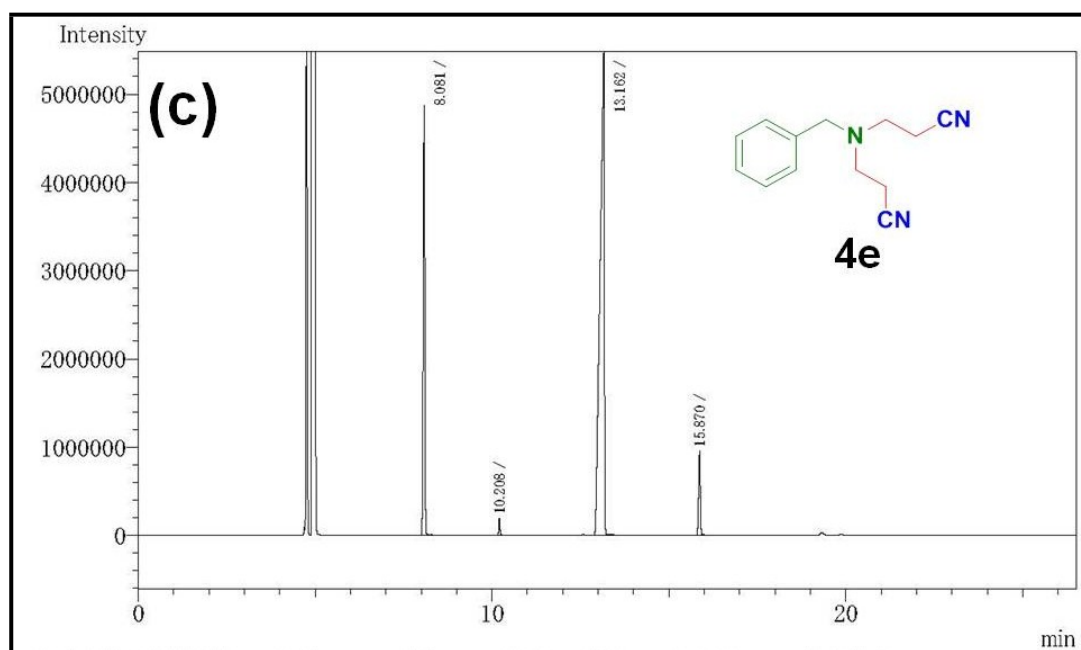


Fig. S39. (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum and (c) GC chromatogram of 3,3'-(benzylazanediyl)dipropanenitrile (**4e**).

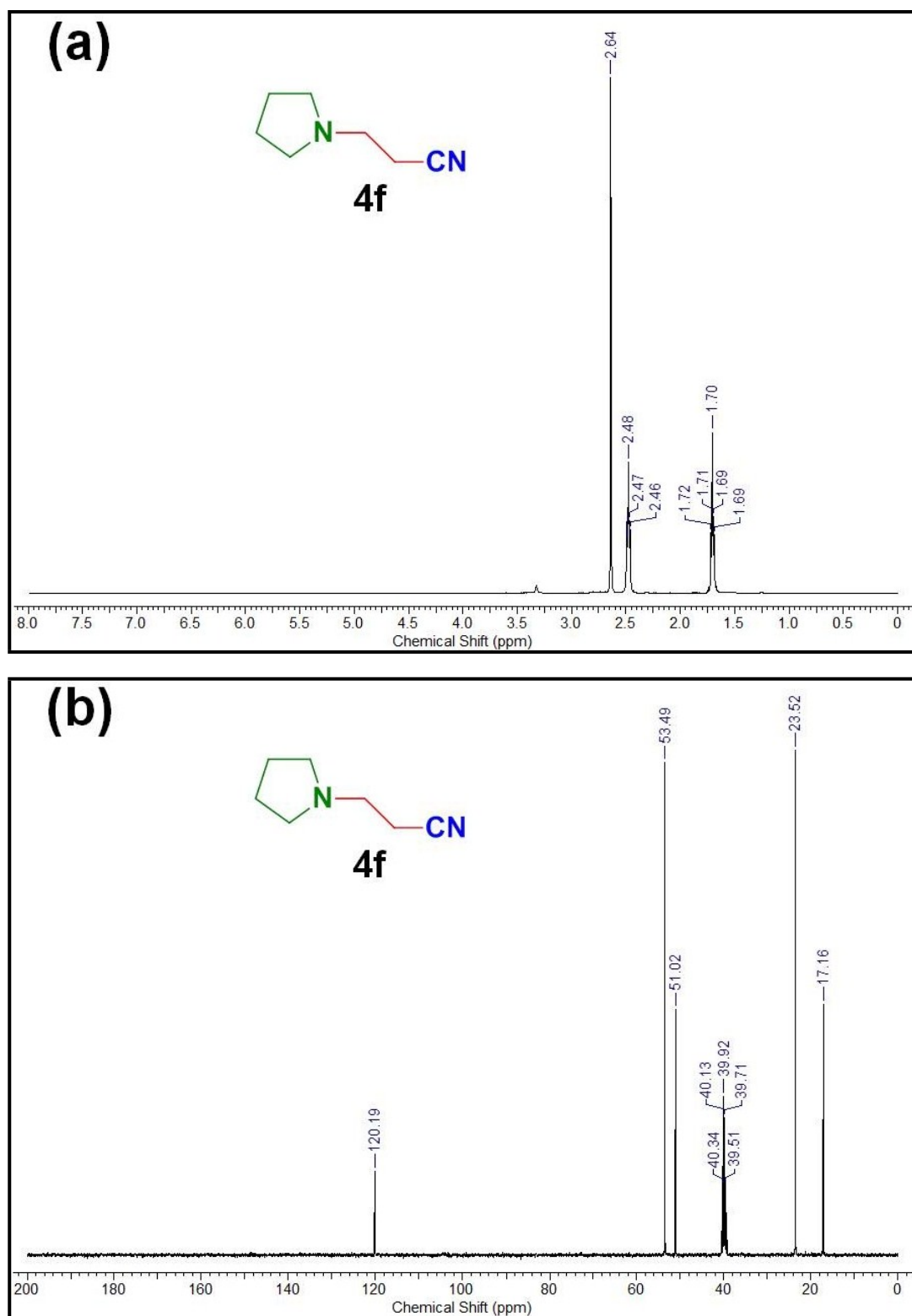


Fig. S40 (a) ¹H and (b) ¹³C NMR spectrum of 3-(pyrrolidin-1-yl)propanenitrile (**4f**).

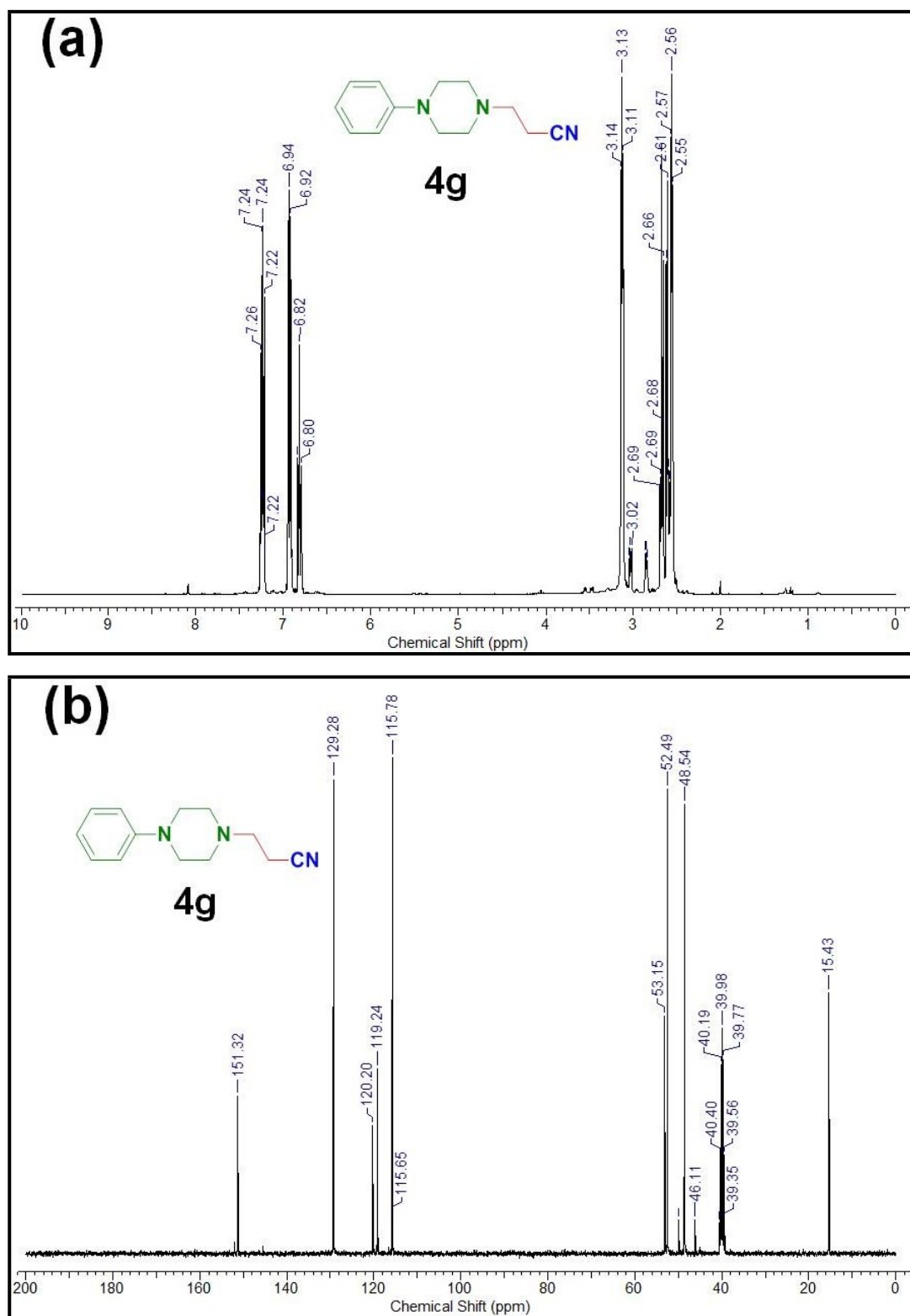


Fig. S41. (a) ¹H and (b) ¹³C NMR spectrum of 3-(4-phenylpiperazin-1-yl) propanenitrile (**4g**).