

SUPPLEMENTARY INFORMATION

A Cu-incorporated polymeric heterogeneous catalyst: exploring an expedient approach to construct amide bonds and extending its application to triazole hybrid amide synthesis

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1. TEM-EDX images of the polymeric copper catalyst:

The TEM-EDX images of the polymeric copper complex is shown in **Figure 1**. The TEM-EDX analysis has been performed for three different areas of the catalyst. It can be seen that the presence of all the required elements i.e. C, N, O, S and Cu were successfully retained for all the analysed areas of the catalyst.

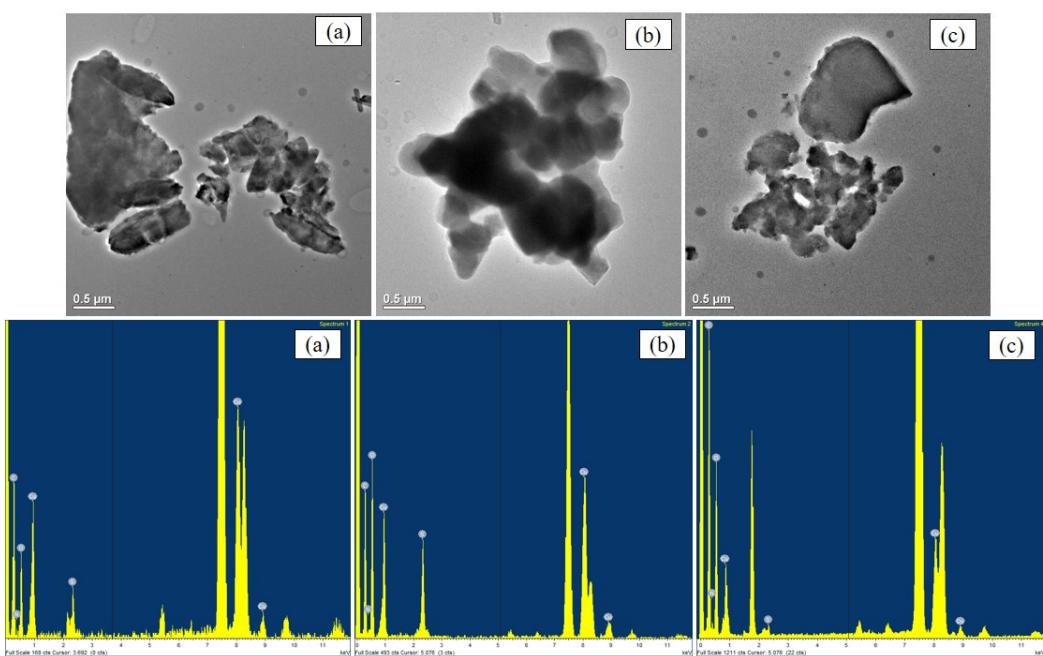
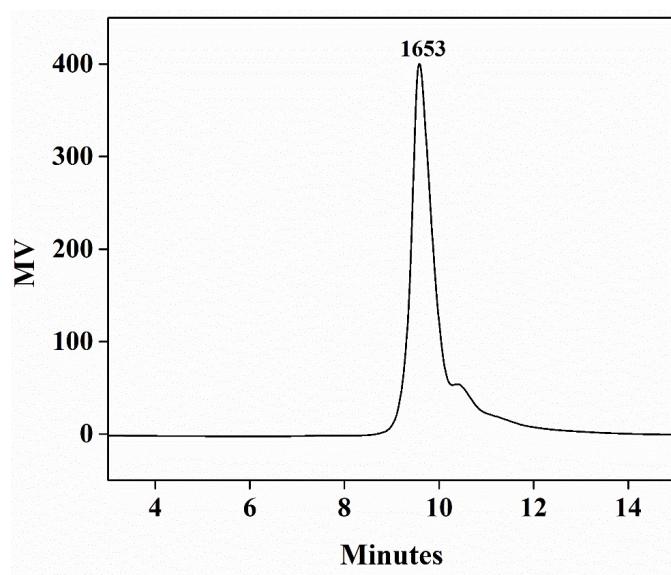
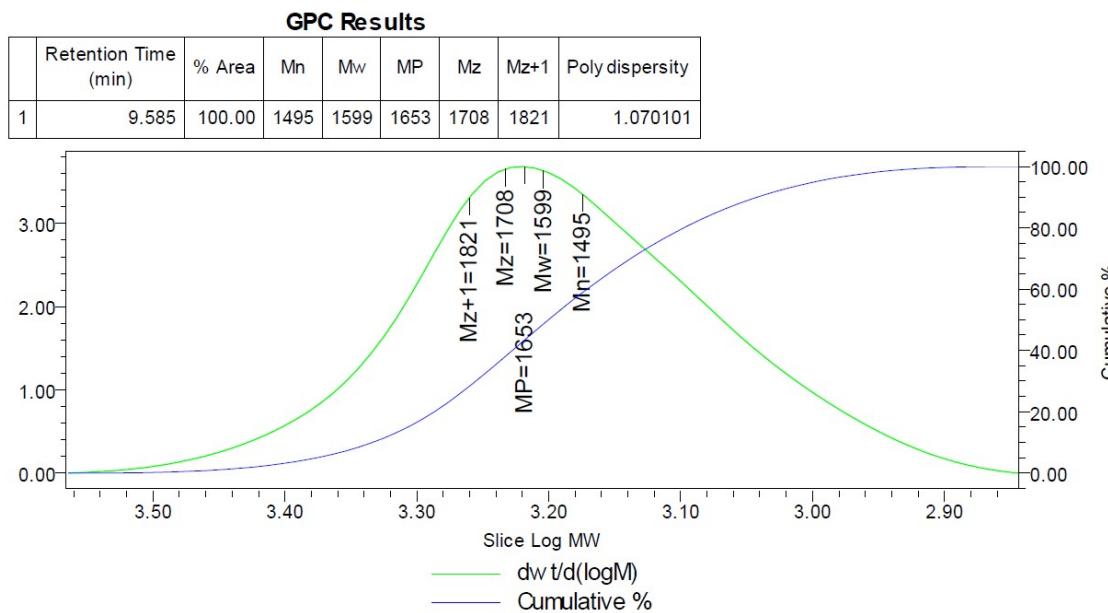


Figure 1 TEM (a-c) and EDX (a-c) images of the polymeric copper catalyst.

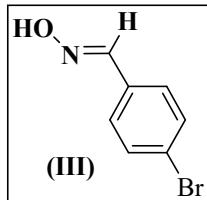
2. GPC chromatogram of imidazole polymer





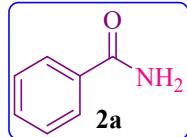
3. Spectral data of the compounds (Intermediate III and 2a-5e).

4-Bromobenzaldehyde oxime¹



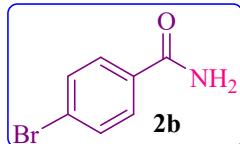
White solid. ¹H NMR (CDCl₃, 400 MHz): δ = 8.1 (s, 1H), 7.55-7.53 (m, 2H), 7.48-7.45 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 149.4, 132.0, 130.9, 128.4, 124.2. Eluent: Ethyl acetate: Hexane (1.5:8.5), R_f = 0.5

1. Benzamide²⁻³



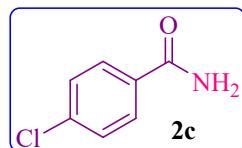
White solid. IR(KBr): 3369, 3172, 1659 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 8.03 (d, J = 7.6 Hz, 2H), 7.74 (t, J = 7.2 Hz, 1H), 7.65 (t, J = 7.4 Hz, 2H), 6.56 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 169.8, 133.4, 131.9, 128.6, 127.3. Eluent: Ethyl acetate: Hexane (5:5), R_f = 0.5

2. 4-bromobenzamide⁴



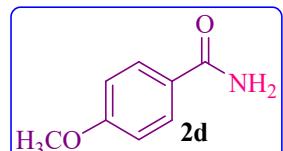
White solid. IR(KBr): 3361, 3176, 1656 cm⁻¹. ¹H NMR (DMSO-d₆, 400 MHz): δ = 8.03 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 168.2, 132.6, 131.2, 131.1, 129.29, 129.26, 125.8. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.5

3. 4-chlorobenzamide⁵



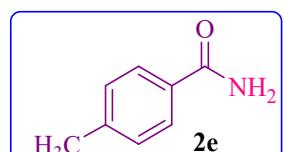
White solid. IR(KBr): 3367, 3177, 1657 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.77 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.06 (brs, 1H), 5.86 (brs, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 168.2, 138.3, 131.6, 128.9, 128.7. Eluent: Ethyl acetate: Hexane (5:5), R_f = 0.5

4. 4-methoxybenzamide^{3,6}



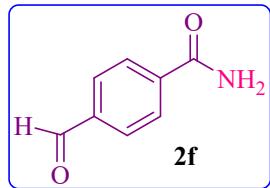
White solid. IR(KBr): 3389, 3168, 1645 cm⁻¹. ¹H NMR (DMSO-d₆, 400 MHz): δ = 7.86-7.83 (m, 3H), 7.17 (brs, 1H), 6.99-6.96 (m, 2H), 3.80 (s, 3H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 168.5, 161.7, 129.1, 125.8, 113.0, 54.9. Eluent: Ethyl acetate: Hexane (5:5), R_f = 0.4

5. 4-methylbenzamide³



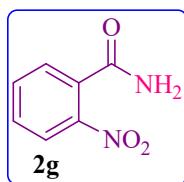
White solid. IR(KBr): 3341, 3164, 1670 cm⁻¹. ¹H NMR (DMSO-d₆, 400 MHz): δ = 7.95 (brs, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.33 (brs, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 168.7, 141.1, 130.6, 128.3, 127.1, 20.8. Eluent: Ethyl acetate: Hexane (5:5), R_f = 0.5

6. 4-formylbenzamide⁷



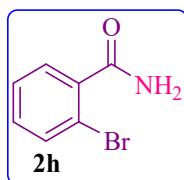
White solid. IR(KBr) 3352, 3192, 1695 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 10.09 (d, *J* = 4.4 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 3H), 7.08 (brs, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 191.9, 168.0, 139.4, 138.0, 129.4, 128.4. Eluent: Ethyl acetate: Hexane (4:6), R_f = 0.5

7. 2-nitrobenzamide³



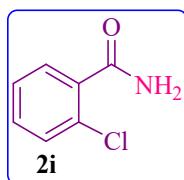
White solid. IR(KBr): 3361, 3176, 1657 cm⁻¹. ¹H NMR (DMSO-d₆, 400 MHz): δ = 8.14 (brs, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.70 (brs, 1H), 7.67-7.60 (m, 2H), 7.63-7.60 (m, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 168.2, 133.3, 133.1, 130.2, 129.0, 124.0. Eluent: Ethyl acetate: Hexane (5:5), R_f = 0.4

8. 2-bromobenzamide⁸



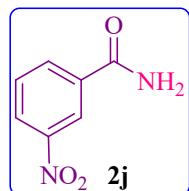
White solid. IR(KBr): 3359, 3181, 1648 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.66-7.61 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.32-7.28 (m, 1H), 6.11 (brs, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 168.9, 136.5, 133.5, 131.7, 129.9, 127.6, 119.1. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.5

9. 2-chlorobenzamide⁶



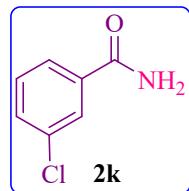
White solid. IR(KBr): 3360, 3179, 1650 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 7.45 (d, *J* = 6.8 Hz, 1H), 7.28-7.12 (m, 3H), 6.85 (brs, 1H), 6.67 (brs, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 168.5, 134.7, 131.3, 130.6, 130.1, 129.9, 126.9. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.4

10. 3-nitrobenzamide⁶



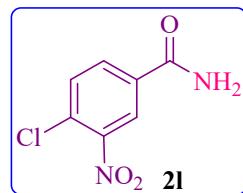
White solid. IR(KBr): 3450, 3341, 1690 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 8.68 (s, 1H), 8.19 (t, *J* = 8.8 Hz, 2H), 7.84 (brs, 1H), 7.52-7.47 (m, 1H), 6.50 (brs, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 166.9, 148.0, 135.4, 133.9, 129.4, 125.9, 122.7. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.4

11. 3-chlorobenzamide⁹



White solid. IR(KBr): 3359, 3178, 1658 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 7.09 (s, 1H), 7.00-6.96 (m, 2H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.55-6.51 (m, 1H), 6.03 (brs, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 167.3, 135.4, 133.4, 130.7, 129.1, 127.3, 125.5. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.5

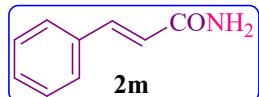
12. 4-chloro-3-nitro-benzamide¹⁰



White solid. IR(KBr) 3374, 3190, 1665 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 8.42 (d, *J* = 2.4 Hz, 1H), 8.20-8.17 (dd, *J* = 2.6, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.52

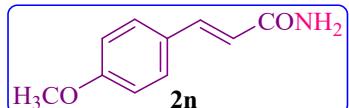
(brs, 1H), 7.12 (brs, 1H). ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 100 MHz): $\delta = 166.4, 145.9, 137.7, 136.8, 131.1, 125.0, 124.3$. Eluent: Ethyl acetate: Hexane (6:4), $R_f = 0.4$

13. Cinnamide¹⁰



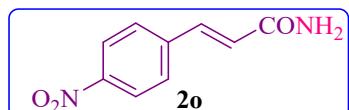
White solid. IR(KBr): 3380, 3165, 1668 cm^{-1} . ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 400 MHz): $\delta = 7.51\text{-}7.46$ (m, 4H), 7.39-7.32 (m, 3H), 6.87 (brs, 1H), 6.65 (d, $J = 15.6$ Hz, 1H). ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 100 MHz): $\delta = 167.5, 139.8, 135.1, 129.5, 129.0, 127.7, 122.2$. Eluent: Ethyl acetate: Hexane (6:4), $R_f = 0.5$

14. (E)-3-(4-methoxyphenyl)acrylamide



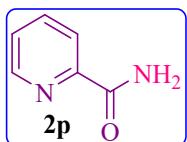
Yellow solid. IR(KBr): 3442, 2928, 1662 cm^{-1} . ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 400 MHz): $\delta = 7.46\text{-}7.38$ (m, 4H), 6.92 (d, $J = 7.6$ Hz, 2H), 6.86 (brs, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 100 MHz): $\delta = 167.7, 160.6, 139.4, 129.2, 127.7, 119.7, 114.4, 55.4$. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2$ [$\text{M} + \text{H}]^+$ 178.0868, found: 178.0859. Eluent: Ethyl acetate: Hexane (6:4), $R_f = 0.4$

15. (E)-3-(4-nitrophenyl)acrylamide



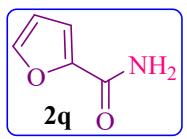
Yellow solid. IR(KBr): 3430, 2923, 1667 cm^{-1} . ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 400 MHz): $\delta = 8.24$ (d, $J = 8.0$ Hz, 2H), 7.77 (brs, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 16.0$ Hz, 1H), 7.54 (brs, 1H), 6.83 (d, $J = 16.0$ Hz, 2H). ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 100 MHz): $\delta = 166.6, 147.5, 141.2, 137.5, 128.0, 125.3, 123.6$. HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_8\text{N}_2\text{O}_3$ [$\text{M} + \text{H}]^+$ 193.0613, found: 193.0597. Eluent: Ethyl acetate: Hexane (6:4), $R_f = 0.4$

16. Picolinamide⁶



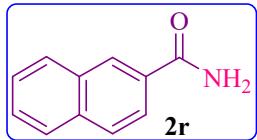
White solid. IR(KBr): 3182, 3208, 1682 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 8.66 (d, *J* = 4.4 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.02 (brs, 1H), 7.95-7.91 (m, 1H), 7.54-7.51 (m, 1H), 6.72 (brs, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 167.1, 149.5, 148.3, 137.2, 126.4, 122.3. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.5

17. Furan-2-carboxamide¹¹



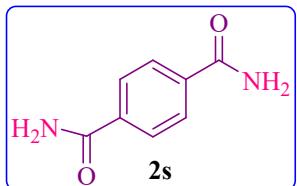
White solid. IR(KBr): 3161, 3078, 1648 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 7.51 (d, *J* = 9.2 Hz, 1H), 7.13-7.10 (m, 1H), 6.97 (brs, 1H), 6.88 (brs, 1H), 6.51-6.48 (m, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 160.4, 147.7, 144.3, 114.4, 112.0. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.4

18. 2-naphthamide⁶



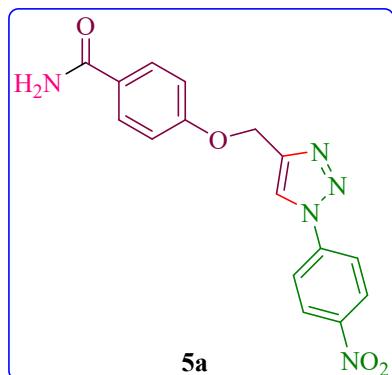
White solid. IR(KBr): 3378, 3196, 1656 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 8.40 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 3H), 7.51-7.44 (m, 2H), 6.74 (brs, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 168.6, 134.0, 131.8, 130.7, 128.3, 127.6, 127.3, 127.0, 126.9, 125.9, 123.8. Eluent: Ethyl acetate: Hexane (5:5), R_f = 0.5

19. Terephthalamide¹⁰



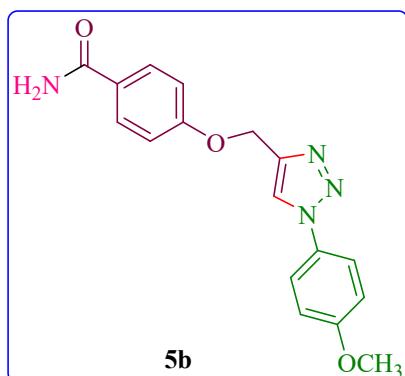
White solid. IR(KBr): 3449, 1642 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 11.08 (s, 2H), 8.09-8.07 (m, 2H), 7.583-7.571 (m, 4H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 147.9, 133.9, 126.8. Eluent: Ethyl acetate: Hexane (6:4), R_f = 0.5

20. 4-((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methoxy)benzamide



Yellow solid. IR(KBr): 3642, 3425, 3223, 1599, 1294, 1246, 750 cm⁻¹. m.p = 192-196 °C. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 7.48 (d, J = 8.4 Hz, 1H), 7.17 (s, 2H), 6.91 (s, 2H), 6.80 (d, J = 5.6 Hz, 1H), 6.43 (d, J = 8.8 Hz, 1H), 6.29 (s, 2H), 5.78 (s, 2H), 4.16 (d, J = 7.2 Hz, 1H), 4.07 (d, J = 5.6 Hz, 1H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 157.9, 146.6, 145.9, 143.7, 140.1, 127.0, 125.4, 124.4, 121.7, 119.6, 113.9, 60.4. HRMS (ESI): *m/z* calcd for C₁₆H₁₃N₅O₄ [M+ H]⁺ 340.1046, found: 340.0854. Eluent: Ethyl acetate: Hexane (8:2), R_f = 0.4

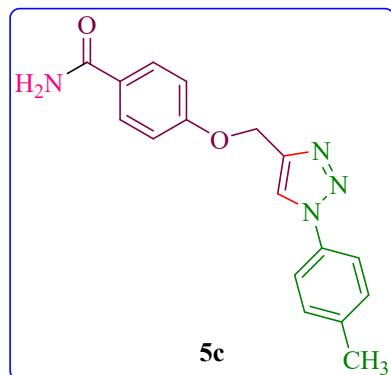
21. 4-((1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)methoxy)benzamide



Yellow solid. IR(KBr): 3164, 2881, 1606, 1514, 1248, 959, 829 cm⁻¹. m.p = 180-182 °C. ¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 10.59 (brs, 1H), 8.17 (s, 1H), 7.94 (s, 1H), 7.60 (t, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 6.96 (t, J = 8.0 Hz, 4H), 5.18 (s, 2H), 3.78 (s, 3H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 159.3, 158.6, 147.5, 143.4, 129.8, 127.6, 125.8,

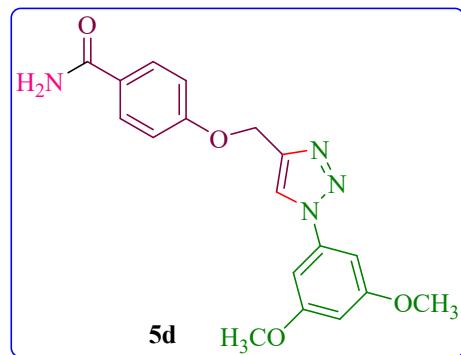
121.6, 121.4, 114.4, 114.3, 61.2, 55.1. HRMS (ESI): m/z calcd for C₁₇H₁₆N₄O₃ [M+ H]⁺: 325.1301, found: 325.1281. Eluent: Ethyl acetate: Hexane (8:2), R_f= 0.4

22. 4-((1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)methoxy)benzamide



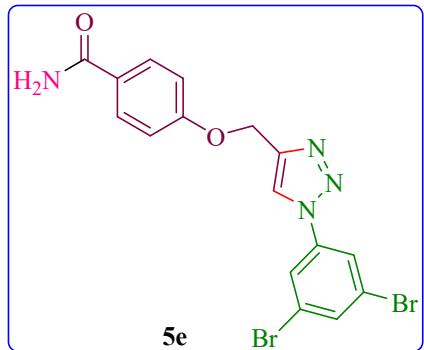
Yellow solid. IR(KBr): 3169, 2781, 1609, 1511, 1254, 954, 833, 729 cm⁻¹. m.p = 185-187 °C.
¹H NMR (CDCl₃ + DMSO-d₆, 400 MHz): δ = 10.74 (brs, 1H), 8.45 (d, *J* = 3.6 Hz, 1H), 7.99-7.98 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.49-7.47 (m, 2H), 7.31 (s, 2H), 7.00-6.98 (m, 2H), 5.24-5.22 (m, 2H), 2.39 (t, *J* = 2.8 Hz, 3H). ¹³C NMR (CDCl₃ + DMSO-d₆, 100 MHz): δ = 157.9, 146.6, 142.7, 137.5, 133.4, 129.0, 126.8, 125.1, 120.9, 119.1, 113.7, 60.4, 19.8. HRMS (ESI): m/z calcd for C₁₇H₁₆N₄O₂ [M+ H]⁺: 309.1352, found: 309.1324. Eluent: Ethyl acetate: Hexane (8:2), R_f= 0.4

23. 4-((1-(3,5-dimethoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)benzamide



White solid. IR(KBr): 3438, 1730, 1514, 1256, 789 cm⁻¹. m.p = 174-178 °C.
¹H NMR (DMSO-d₆, 400 MHz): δ = 11.01 (s, 1H), 9.30 (s, 1H), 8.70 (d, *J* = 1.6 Hz, 2H), 8.51 (t, *J* = 1.4 Hz, 1H), 8.08 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 5.29 (s, 2H), 3.95 (s, 6H). ¹³C NMR (DMSO-d₆, 100 MHz): δ = 164.9, 159.2, 148.0, 144.5, 137.6, 132.4, 128.3, 126.5, 124.8, 123.9, 115.4, 61.4, 53.3. Eluent: Ethyl acetate: Hexane (9:1), R_f= 0.4.

24. 4-((1-(3,5-dibromophenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)benzamide



Pale yellow solid. IR(KBr): 3280, 3071, 1607, 1512, 1245, 746 cm⁻¹. m.p = 148-152 °C.¹H NMR (DMSO-d₆, 400 MHz): δ = 11.01 (s, 1H), 9.09 (s, 1H), 8.24 (d, *J* = 1.6 Hz, 2H), 8.08 (s, 1H), 7.99 (t, *J* = 1.4 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.27 (s, 2H). ¹³C NMR (DMSO-d₆, 100 MHz): δ = 159.1, 148.0, 144.4, 138.7, 133.9, 128.3, 126.5, 123.8, 123.7, 122.3, 115.4, 61.4. Eluent: Ethyl acetate: Hexane (9:1), R_f = 0.4

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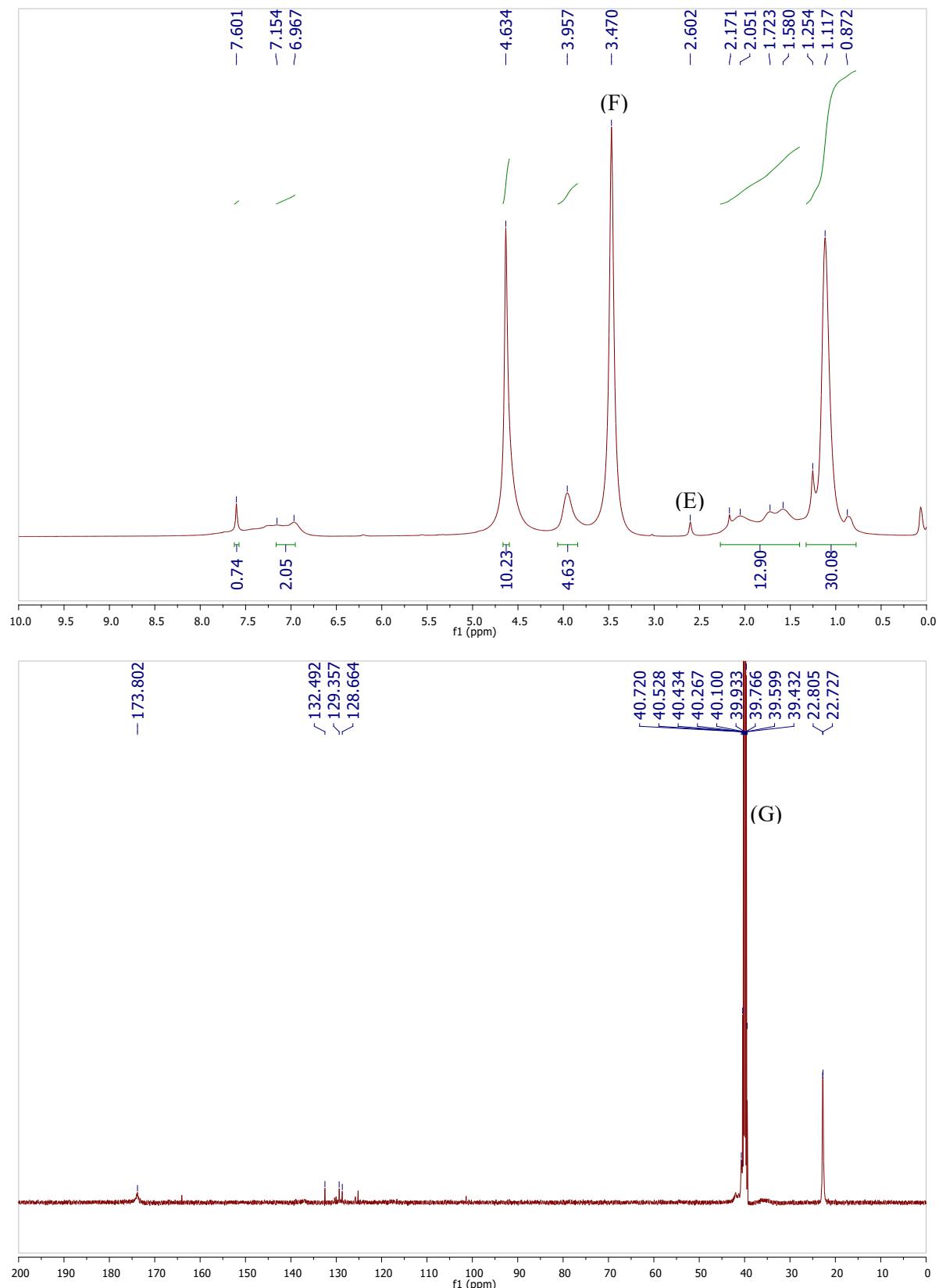
5. ¹H and ¹³C NMR spectra of Polymer (I) and intermediate (III)

Note: The labelled peaks for ¹H NMR spectroscopy are due to:

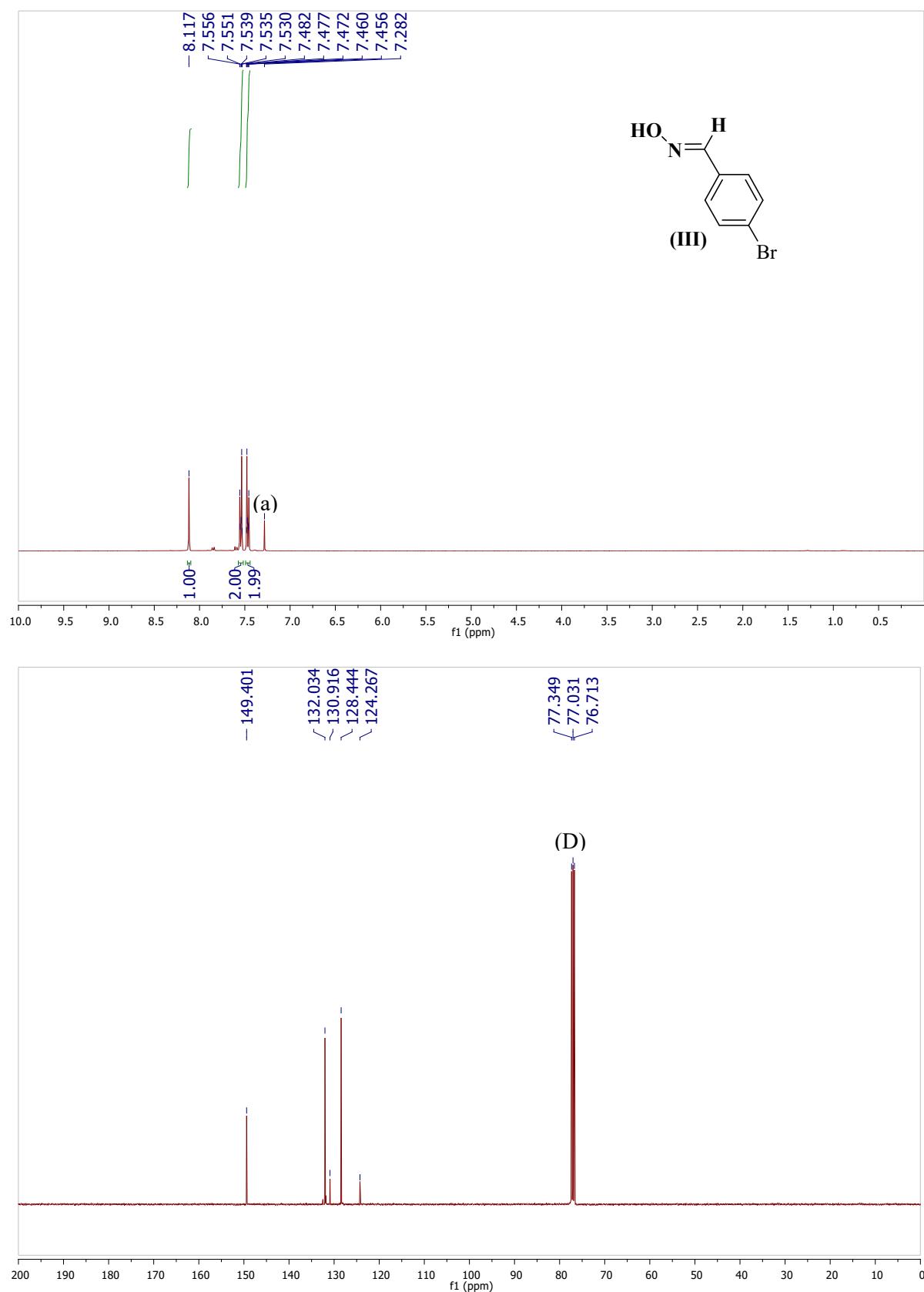
A = Grease, a = CDCl₃, B = CDCl₃+H₂O, C = impurities, E = DMSO-d₆, F = DMSO-d₆+H₂O. The labelled peaks for ¹³C NMR spectroscopy are due to:

D = CDCl₃, G = DMSO-d₆

¹H and ¹³C NMR spectra of Polymer (I)



¹H and ¹³C NMR spectra of intermediate (III)



6. ^1H and ^{13}C NMR spectra of compounds (2a-5e)

