First vinyl acetate mediated organocatalytic transesterification of Phenols: A step towards sustainability

Manoj Kumar, Sourav Bagchi and Anuj Sharma*

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, India
(Phone: +91-1332-284751; e-mail: anujsharma.mcl@gmail.com, anujsfcy@iitr.ac.in)

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Experimental detail: S1
Spectral data: S2
Spectra (1c to 32c): S3-S9
S10-S73
**General Experimental Detail.** All NMR spectra were recorded on a Jeol Resonance ECX-400II. Chemical shifts are reported in parts per million and are referenced to TMS. Spectra were processed using MestReNova® software. Mass spectrometry (HRMS) was performed using a Bruker daltronics microTOF-QII® spectrometer using ESI ionization, with less than 5 ppm error for all HRMS analyses. Analytical Thin layer chromatography (TLC) was performed on a silica gel plate (Merck® 60F254). All solvent were distilled prior to use and all chemicals were purchased from sigma-Aldrich® and used without further purification.

**Microwave Irradiation Experiment.** All microwave experiments were carried out in a dedicated Anton Paar Monowave 300 reactor®, operating at a frequency of 2.455 GHz with continuous irradiation power of 0 to 300 W. The reactions were performed in a G-4 Borosilicate glass vial sealed with Teflon septum and placed in a microwave cavity. Initially, microwave of required power was used and temperature was being ramped from room temperature to a desired temperature. Once this temperature was attained, the process vial was held at this temperature for required time. The reactions were continuously stirred. Temperature was measured by an IR sensor. After the experiments a cooling jet cooled the reaction vessel to ambient temperature.

**General procedure for the vinyl acetate based transesterification of phenols.** In a solvent-free condition, phenol 1a (1.0 mmol), vinyl acetate 1b (1.2 mmols) and 1,4-diazabicyclo[2.2.2]octane (30 mol%) were mixed well in a G-4 process vial capped with Teflon septum. After a pre-stirring of 1 or 2 minutes, the vial was subjected to microwave irradiation with the initial ramp time of 1 minute at 70 °C. The temperature was then raised to 140 °C with the holding time of 10 minutes. The reaction mixture was brought to room temperature by cooling jet and dissolved in 10 ml of ethyl acetate. This organic layer was washed with water, saturated brine solution, and dried over anhydrous MgSO₄ and finally evaporated under reduced pressure to give corresponding ester 1c. The product 1c was pure enough for spectral elucidation by ^1^H NMR, ^1^3C NMR and HRMS.
Phenyl acetate (1c). Yield: 99%; whitish yellow solid; mp: 52 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.29 (s, 3H), 7.01 (dd, 2H, $J = 6.0$ & 1.0 Hz), 7.14 (tt, 1H, $J = 6.0$ & 1.1 Hz), 7.23 (t, 2H, $J = 5.9$ Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 20.9, 121.0, 125.2, 129.9, 150.5, 169.7. HRMS (ESI) m/z calcd. for (C$_8$H$_8$O$_2$) [M+ Na]$^+$: 159.0422, found: 159.0419.

2-methoxyphenyl acetate (2c). Yield: 98%; yellow liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.30 (s, 3H), 2.80 (s, 3H), 6.91-6.97 (m, 2H), 7.05 (dd, 1H, $J = 7.8$ & 1.8 Hz), 7.16-7.23 (m, 1H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 20.7, 55.9, 112.5, 120.8, 122.9, 127.0, 139.9, 151.3, 169.1. HRMS (ESI) m/z calcd. for (C$_9$H$_{10}$O$_3$) [M+ Na]$^+$: 189.0528, found: 189.0522.

3-methoxyphenyl acetate (3c). Yield: 97%; yellow liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.22 (s, 3H), 2.31 (s, 3H), 6.81-6.92 (m, 2H), 7.0 (d, 1H, $J = 7.6$ Hz), 7.21 (t, 1H, $J = 7.7$ Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.0, 60.4, 118.6, 122.2, 126.6, 129.2, 139.5, 150.7, 169.6. HRMS (ESI) m/z calcd. for (C$_9$H$_{10}$O$_3$) [M+ Na]$^+$: 189.0528, found: 189.0525.

4-methoxyphenyl acetate (4c). Yield: 98%; yellow liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.24 (s, 3H), 3.75 (s, 3H), 6.86 (dt, 2H, $J = 9.1$ & 3.6 Hz), 6.98 (dt, 2H, $J = 9.2$ & 3.5 Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.1, 55.6, 114.5, 122.4, 144.3, 157.3, 170.0. HRMS (ESI) m/z calcd. for (C$_9$H$_{10}$O$_3$) [M+ Na]$^+$: 189.0528, found: 189.0523.

2,3-dimethylphenyl acetate (5c). Yield: 98%; brown liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.26 (d, 6H, $J = 6.0$ Hz), 2.29 (s, 3H), 6.84 (dd, 1H, $J = 8.0$ & 2.4 Hz), 6.90 (br s, 1H), 7.14 (d, 2H, $J = 8.1$ Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 19.3, 20.0, 21.2, 118.7, 122.6, 130.5, 134.3, 138.0, 148.7, 170.0. HRMS (ESI) m/z calcd. for (C$_{10}$H$_{12}$O$_2$) [M+ Na]$^+$: 187.0735, found: 187.0730.
4-tert-butylphenyl acetate (6c). Yield: 99%; brown liquid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 1.25 (s, 9H), 2.22 (s, 3H), 6.90-6.99 (m, 2H), 7.28-7.38 (m, 2H). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 14.2, 31.4, 34.5, 120.9, 126.3, 148.4, 171.5. HRMS (ESI) m/z calcd. for (C\(_{12}\)H\(_{16}\)O\(_2\)) [M+ Na\(^+\)]: 215.1048, found: 215.1041.

4-chlorophenyl acetate (7c). Yield: 96%; yellow liquid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.21 (s, 3H), 6.97 (dt, 2H, \(J = 8.7 \text{ & } 3.2\) Hz), 7.27 (dt, 2H, \(J = 8.8 \text{ & } 3.2\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 20.1, 123.0, 129.5, 131.1, 149.2, 169.2. HRMS (ESI) m/z calcd. for (C\(_8\)H\(_7\)ClO\(_2\)) [M+ Na\(^+\)]: 193.0033, found: 193.0028.

2,6-dichlorophenyl acetate (8c). Yield: 96%; yellow solid; mp: 108-110 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.32 (s, 3H), 7.05 (d, 1H, \(J = 8.7\) Hz), 7.23 (dd, 1H, \(J = 8.7 \text{ & } 2.4\) Hz), 7.43 (d, 2H, \(J = 2.4\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 20.6, 124.7, 128.0, 129.2, 130.2, 132.0, 135.8, 168.4. HRMS (ESI) m/z calcd. for (C\(_8\)H\(_6\)Cl\(_2\)O\(_2\)) [M+ Na\(^+\)]: 226.9643, found: 226.9638.

3-(trifluoromethyl)phenyl acetate (9c). Yield: 97%; yellow liquid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.30 (s, 3H), 7.24-7.30 (m, 1H), 7.37 (br s, 1H), 7.48 (d, 2H, \(J = 5.2\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 21.0, 119.0 (q, \(J = 3.8\) Hz), 122.3, 122.7 (q, \(J = 3.8\) Hz), 125.0, 125.3 (q, \(J = 1.0\) Hz), 130.1, 150.8, 169.2. HRMS (ESI) m/z calcd. for (C\(_9\)H\(_7\)F\(_3\)O\(_2\)) [M+ Na\(^+\)]: 227.0296, found: 227.0290.

2-benzylphenyl acetate (10c). Yield: 95%; yellow liquid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.25 (s, 3H), 3.99 (s, 2H), 7.14 (d, 1H, \(J = 8.2\) Hz), 7.22-7.24 (m, 1H), 7.24-7.26 (m, 3H), 7.27-7.33 (m, 2H), 7.35 (dt, 2H, \(J = 7.6 \text{ & } 0.6\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 21.0, 36.6, 115.6, 120.6, 122.7, 126.4, 126.5, 127.8, 128.7, 129.0, 131.2, 133.1, 139.8, 149.2, 169.7. HRMS (ESI) m/z calcd. for (C\(_{15}\)H\(_{14}\)O\(_2\)) [M+ Na\(^+\)]: 249.0892, found: 249.0882.
4-benzylphenyl acetate (11c). Yield: 94%; brown liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.35 (s, 3H), 4.08 (s, 2H), 7.15 (dt, 2H, $J = 8.6$ & $2.7$ Hz), 7.29-7.36 (m, 5H), 7.39-7.45 (m, 2H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.3, 41.5, 115.6, 121.8, 126.5, 128.8, 128.9, 130.1, 139.0, 141.0, 149.2, 170.0. HRMS (ESI) m/z calcd. for (C$_{15}$H$_{14}$O$_2$) [M+ Na]$^+$: 249.0892, found: 249.0887.

4-(benzyloxy)phenyl acetate (12c). Yield: 96%; whitish solid; mp: 120 °C (decomp); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.29 (s, 3H), 5.05 (s, 2H), 7.0 (qt, 4H, $J = 10.1$ & $2.9$ Hz), 7.34 (tt, 1H, $J = 7.0$ & $1.6$ Hz), 7.37-7.47 (m, 4H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.2, 70.5, 115.5, 122.5, 127.6, 128.1, 128.7, 136.9, 144.5, 156.5, 170.0. HRMS (ESI) m/z calcd. for (C$_{15}$H$_{14}$O$_3$) [M+ Na]$^+$: 263.0841, found: 263.0836.

Benzo[d][1,3]dioxol-5-yl acetate (13c). Yield: 98%; brown solid; mp: 106-109 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.19 (s, 3H), 5.88 (s, 2H), 6.48 (dd, 1H, $J = 8.4$ & $2.4$ Hz), 6.58 (d, 1H, $J = 2.32$ Hz), 6.72 (d, 1H, $J = 8.4$ Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.0, 101.8, 103.8, 108.0, 114.0, 145.1, 145.4, 148.1, 169.8. HRMS (ESI) m/z calcd. for (C$_9$H$_8$O$_4$) [M+ Na]$^+$: 203.0321, found: 203.0318.

1,2-benzenediol 1,2-diacetate (14c). Yield: 92%; brown liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.25 (s, 6H), 7.13-7.19 (m, 2H), 7.19-7.25 (m, 2H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 20.7, 123.5, 126.5, 142.2, 168.4. HRMS (ESI) m/z calcd. for (C$_{10}$H$_{10}$O$_4$) [M+ Na]$^+$: 217.0477, found: 217.0470.

1,3-benzenediol 1,3-diacetate (15c). Yield: 94%; yellow liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.27 (s, 6H), 6.86 (t, 1H, $J = 1.1$ Hz), 6.92 (dd, 2H, $J = 6.0$ & $1.2$ Hz), 7.22 (t, 1H, $J = 6.0$ Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 20.9, 115.4, 119.2, 131.2, 151.6, 169.7. HRMS (ESI) m/z calcd. for (C$_{10}$H$_{10}$O$_4$) [M+ Na]$^+$: 217.0477, found: 217.0471.

1,4-benzenediol 1,4-diaceate (16c). Yield: 92%; brown liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.26 (s, 6H), 7.07 (s, 4H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.1, 122.5, 148.1, 169.4. HRMS (ESI) m/z calcd. for (C$_{10}$H$_{10}$O$_4$) [M+ Na]$^+$: 217.0477, found: 217.0468.
Naphthalen-1-yl acetate (17c). Yield: 90%; brown solid; mp: 88 °C; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.48 (s, 3H), 7.31 (d, 1H, \(J = 8.0\) Hz), 7.50 (t, 1H, \(J = 8.0\) Hz), 7.52-7.60 (m, 2H), 7.78 (d, 1H, \(J = 8.2\) Hz), 7.92 (t, 2H, \(J = 7.3\) Hz). \(^1^C\) NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 21.2, 118.3, 121.3, 125.6, 126.2, 126.6, 126.9, 128.2, 134.7, 146.7, 169.7. HRMS (ESI) m/z calcd. for (C\(_{12}\)H\(_{10}\)O\(_2\)) [M+ Na]: 209.0579, found: 209.0573.

Naphthalen-2-yl acetate (18c). Yield: 99%; brown solid; mp: 96-98 °C; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.37 (s, 3H), 7.25-7.34 (m, 2H), 7.59 (d, 1H, \(J = 7.6\) Hz), 7.60-7.70 (m, 2H). \(^1^C\) NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 21.3, 118.7, 121.3, 125.9, 126.7, 127.8, 127.9, 129.6, 131.6, 133.9, 148.4, 169.9. HRMS (ESI) m/z calcd. for (C\(_{12}\)H\(_{10}\)O\(_2\)) [M+ Na]: 209.0579, found: 209.0574.

2,3-naphthalenediol-2,3-diacetate (19c). Yield: 98%; white solid; mp: 110-112 °C; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.34 (s, 6H), 7.45-7.50 (m, 2H), 7.68 (s, 2H), 7.76-7.82 (m, 2H). \(^1^C\) NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 20.9, 121.1, 126.6, 127.6, 131.7, 141.1, 168.8. HRMS (ESI) m/z calcd. for (C\(_{14}\)H\(_{12}\)O\(_4\)) [M+ Na]: 267.0634, found: 267.0621.

2,6-naphthalenediol-2,6-diacetate (20c). Yield: 97%; yellow liquid; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.34 (s, 6H), 7.24 (d, 2H, \(J = 6.6\) & 2.1 Hz), 7.56 (d, 2H, \(J = 2.3\) Hz), 7.80 (d, 2H, \(J = 8.8\) Hz). \(^1^C\) NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 21.2, 118.6, 122.1, 129.2, 131.8, 148.4, 169.7. HRMS (ESI) m/z calcd. for (C\(_{14}\)H\(_{12}\)O\(_4\)) [M+ Na]: 267.0634, found: 267.0630.

6-bromonaphthalen-2-yl acetate (21c). Yield: 96%; white solid; mp: 112 °C; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.35 (s, 3H), 7.22 (dd, 1H, \(J = 8.9\) & 2.3 Hz), 7.49-7.54 (m, 2H), 7.62 (d, 1H, \(J = 8.9\) Hz), 7.71 (d, 1H, \(J = 8.9\) Hz), 7.96 (d, 1H, \(J = 1.8\) Hz). \(^1^C\) NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 21.3, 118.8, 119.7, 122.4, 128.6, 129.1, 129.9, 130.1, 132.2, 132.5, 148.6, 169.7. HRMS (ESI) m/z calcd. for (C\(_{12}\)H\(_9\)BrO\(_2\)) [M+ Na]: 286.9684, found: 286.9682.
1,5-naphthalenediol-1,5-diacetate (22c). Yield: 99%; white solid; mp: 128-130 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 2.27 (s, 6H), 6.82 (dd, 2H, \(J = 6.0 \& 1.1\) Hz), 7.25 (t, 2H, \(J = 6.0\) Hz), 7.44 (dd, 2H, \(J = 5.9 \& 1.1\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 20.9, 117.5, 121.2, 125.1, 125.6, 145.4, 170.2. HRMS (ESI) m/z calcd. for (C\(_{14}\)H\(_{12}\)O\(_4\)) \([\text{M+ Na}]^+\): 267.0634, found: 267.0630.

Phenyl benzoate (23c). Yield: 97%; yellow liquid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 7.03 (tt, 1H, \(J = 5.9 \& 1.3\) Hz), 7.17 (dd, 2H, \(J = 6.1 \& 1.2\) Hz), 7.30 (t, 2H, \(J = 6.0\) Hz), 7.42 (t, 2H, \(J = 6.1\) Hz), 7.50 (tt, 1H, \(J = 5.9 \& 1.2\) Hz), 8.10 (dd, 2H, \(J = 6.0 \& 1.0\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 123.7, 128.1, 132.0, 132.6, 132.7, 133.8, 136.5, 153.9, 170.0. HRMS (ESI) m/z calcd. for (C\(_{13}\)H\(_{10}\)O\(_2\)) \([\text{M+ Na}]^+\): 221.0579, found: 221.0575.

4-chlorophenyl benzoate (24c). Yield: 95%; yellow liquid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 7.13 (d, 2H, \(J = 6.0\) Hz), 7.39 (d, 2H, \(J = 6.0\) Hz), 7.50 (t, 2H, \(J = 6.0\) Hz), 7.57 (tt, 1H, \(J = 6.0 \& 1.1\) Hz), 8.17 (dd, 2H, \(J = 5.9 \& 1.2\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 123.5, 131.0, 131.5, 131.7, 132.9, 133.3, 135.6, 152.1, 169.1. HRMS (ESI) m/z calcd. for (C\(_{13}\)H\(_{9}\)ClO\(_2\)) \([\text{M+ Na}]^+\): 255.0189, found: 255.0183.

Benzo[d][1,3]dioxol-5-yl benzoate (25c). Yield: 95%; brown solid; mp: 120-121 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 5.90 (s, 2H), 6.67 (dd, 1H, \(J = 6.0 \& 1.1\) Hz), 6.72 (d, 1H, \(J = 1.2\) Hz), 6.76 (d, 1H, \(J = 6.0\) Hz), 7.43 (t, 2H, \(J = 6.0\) Hz), 7.50 (tt, 1H, \(J = 6.0 \& 1.1\) Hz), 8.11 (dd, 2H, \(J = 5.9 \& 1.2\) Hz). \(^{13}\)C NMR: (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 102.1, 102.6, 110.9, 115.3, 129.1, 129.7, 131.0, 133.6, 146.8, 147.8, 149.8, 167.2. HRMS (ESI) m/z calcd. for (C\(_{14}\)H\(_{10}\)O\(_4\)) \([\text{M+ Na}]^+\): 265.0477, found: 265.0472.

Naphthalen-2-yl benzoate (26c). Yield: 98%; brown solid; mp: 126-127 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 7.2 (t, 1H, \(J = 1.1\) Hz), 7.36-7.48 (m, 5H), 7.53 (tt, 1H, \(J = 6.0 \& 1.1\) Hz), 7.58 (dd, 1H, \(J = 6.0 \& 1.0\) Hz), 7.78 (tt, 2H, \(J = 5.3 \& 1.2\) Hz), 8.14 (dd, 2H, \(J = 5.9 \& 1.2\) Hz). \(^{13}\)C NMR: (100 MHz,
DMSO-$d_6$: $\delta$ (ppm) 117.9, 122.7, 125.4, 128.6, 128.7, 130.1, 130.5, 130.6, 131.1, 132.3, 132.5, 133.0, 136.5, 151.7, 168.6. HRMS (ESI) m/z calcd. for (C$_{17}$H$_{12}$O$_2$) [M+ Na$^+$]: 271.0735, found: 271.0730.

1,4-benzenediol 1,4-dibenzoate (27c). Yield: 93%; yellow liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.19 (s, 4H), 7.44 (t, 4H, $J = 6.0$ Hz), 7.52 (tt, 2H, $J = 6.0$ & 1.2 Hz), 8.03 (dd, 4H, $J = 6.0$ & 1.0 Hz). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 123.0, 129.8, 130.5, 131.7, 134.4, 149.9, 167.9. HRMS (ESI) m/z calcd. for (C$_{20}$H$_{14}$O$_4$) [M+ Na$^+$]: 341.0790, found: 341.0784.

$\text{N-}(\text{pyridine-2yl})\text{acetamide (28c).}$ Yield: 97%; brown solid; mp: 108-109 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.17 (s, 3H), 6.97-7.06 (m, 1H), 7.68 (td, 1H, $J = 7.9$ & 2.0 Hz), 8.15-8.32 (m, 2H), 9.38 (s, 1H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 24.7, 114.6, 119.8, 138.7, 147.5, 151.9. HRMS (ESI) m/z calcd. for (C$_7$H$_8$N$_2$O) [M+ Na$^+$]: 159.0535, found: 159.0529.

$\text{N-}(\text{pyridine-2yl})\text{benzamide (29c).}$ Yield: 96%; brown solid; mp: 118 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.55 (td, 1H, $J = 6.0$ & 1.1 Hz), 7.73 (t, 2H, $J = 5.5$ Hz), 7.78 (tt, 1H, $J = 5.8$ & 1.4 Hz), 7.99 (td, 1H, $J = 6.0$ & 1.1 Hz), 8.15 (dd, 2H, $J = 5.9$ & 1.2 Hz), 8.35 (dd, 1H, $J = 6.0$ & 1.1 Hz), 8.73 (dd, 1H, $J = 6.0$ & 1.3 Hz), 9.38 (s, 1H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 116.9, 120.0, 129.2, 129.6, 132.7, 136.0, 140.7, 148.9, 153.2, 168.5. HRMS (ESI) m/z calcd. for (C$_{12}$H$_{10}$N$_2$O) [M+ Na$^+$]: 221.0691, found: 221.0687.

$\text{N-}(4\text{-methylpyridine-2yl})\text{acetamide (30c).}$ Yield: 98%; brown solid; mp: 122-124 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.63 (s, 3H), 2.85 (s, 3H), 7.47 (dd, 1H, $J = 6.0$ & 1.1 Hz), 8.65 (d, 1H, $J = 1.1$ Hz), 8.82 (d, 1H, $J = 6.0$ Hz), 9.38 (s, 1H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.2, 23.8, 114.8, 121.8, 149.4, 155.2, 170.5. HRMS (ESI) m/z calcd. for (C$_8$H$_{10}$N$_2$O) 173.0691 [M+ Na$^+$], found: 173.0689.
N-(5-bromopyridine-2yl)actamide (31c). Yield: 92%; brown solid; mp: 126 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ (ppm) 2.21 (s, 3H), 8.25 (dd, 1H, $J = 6.0$ & 1.1 Hz), 8.54 (d, 1H, $J = 6.0$ Hz), 8.59 (d, 1H, $J = 1.1$ Hz), 9.38 (s, 1H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): δ (ppm) 20.2, 106.9, 115.3, 134.9, 147.3, 148.9, 166.8. HRMS (ESI) m/z calcd. for (C$_7$H$_7$BrN$_2$O) [M+ Na]$^+$: 236.9640, found: 236.9636.

N-(5-bromopyridine-2yl)benzamide (32c). Yield: 90%; brown solid; mp: 132-134 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ (ppm) 7.44 (t, 2H, $J = 5.8$ Hz), 7.49 (tt, 1H, $J = 5.8$ & 1.2 Hz), 7.86 (dd, 2H, $J = 5.8$ & 1.0 Hz), 8.09 (dd, 1H, $J = 6.0$ & 1.1 Hz), 8.32 (d, 1H, $J = 6.0$ Hz), 8.54 (d, 1H, $J = 1.1$ Hz), 9.44 (s, 1H). $^{13}$C NMR: (100 MHz, DMSO-$d_6$): δ (ppm) 113.2, 121.8, 128.5, 128.8, 132.0, 135.2, 139.7, 150.4, 151.7, 167.7. HRMS (ESI) m/z calcd. for (C$_{12}$H$_9$BrN$_2$O) [M+ Na]$^+$: 298.9796, found: 298.9792.