Supporting Information

Atom-economic, room-temperature, and high-efficiency synthesis of polyamides via a three-component polymerization involving benzoxazine, odorless isocyanide, and water

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Experimental Section.

Materials. CHCl₃, CH₂Cl₂, THF and toluene were dried and distilled prior to use as well as Et₃N. DMSO, DMF, ethyl ether, octylphosphonic acid (OPA), tosylmethyl isocyanide 2, paraformaldehyde and other reagents and chemicals were purchased from Adamas or Aladdin and used as received. Benzoxazines¹,² and isocyanides³,⁴ were prepared according to the reported procedures.

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III HD NMR spectrometer at 400 MHz and 100 MHz in CDCl₃ or DMSO-d₆ using tetramethylsilane (TMS; δ = 0) as internal standard. FT-IR spectra were performed on a WQF-520 FT-IR spectrometer as thin films on KBr pellets. High resolution mass spectra (HRMS) were measured on a Waters Q-TOF Premier mass spectrometer. Relative weight-average and number-average molecular weights (Mₘ and Mₙ) and polydispersity indices (D, Mₘ/Mₙ) of the polymers were estimated by an Agilent 1260 gel permeation chromatography (GPC) system equipped with a UV detector (eluent: THF, at a flow rate of 1.0 mL/min; calibration standards: polystyrene). Cyclic voltammograms carried out on a CHI650e electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against a saturated calomel reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN).

Monomer Preparation.

Preparation of benzoxazines.

3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (1). In a standard Schlenk tube, phenol (470 mg, 5 mmol), aniline (465 mg, 5 mmol), and paraformaldehyde (300 mg, 10 mmol) were dissolved in 10 mL toluene. The reaction mixture was refluxed for 10 h, afterwards, the mixture was cooled down to room temperature and was washed several times with 0.1 M NaOH solution and distilled water. After this, the solution was dried over anhydrous MgSO₄. The volatile was removed under vacuum and the residue was purified by column chromatography (SiO₂, petroleum ether/EtOAc 30:1).
Benzoxazines 1a, 1b and 1c were prepared according to the synthesis of 1.

**Characterization data of 1:** White powder was obtained (538 mg, 51%). FT-IR (KBr, cm⁻¹): 3009, 2909, 2857, 1602, 1573, 1488, 1225 (C-O-C), 1031, 932 (benzoxazine related band), 755. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.32–7.26 (m, 2H), 7.17–7.11 (m, 3H), 7.06–7.01 (m, 1H), 6.98–6.88 (m, 2H), 6.86–6.82 (m, 1H), 5.39 (s, 2H), 4.66 (s, 2H).

**Characterization data of 1a:** Light yellow solids was obtained (50%). FT-IR (KBr, cm⁻¹): 3035, 2959, 2868, 1613, 1504, 1454, 1237 (C-O-C), 1017, 945 (benzoxazine related band), 829. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.10 (dd, J = 10.8, 4.2 Hz, 9H), 7.02–6.80 (m, 7H), 6.72 (dd, J = 8.4, 3.9 Hz, 2H), 5.30 (s, 4H), 4.57 (s, 4H), 1.70–1.51 (m, 16H), 1.33–1.07 (m, 16H), 0.90–0.49 (m, 18H).

**Characterization data of 1b:** Yellow oil was obtained (35%). FT-IR (KBr, cm⁻¹): 3006, 2963, 2922, 2864, 1614, 1509, 1454, 1236 (C-O-C), 945 (benzoxazine related band), 822. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.55–7.36 (m, 2H), 7.06–6.74 (m, 12H), 5.30 (d, J = 8.3 Hz, 4H), 4.56 (s, 4H), 3.80 (s, 2H), 1.64–0.57 (m, 38H).

**Characterization data of 1c:** White solid was obtained (61%). FT-IR (KBr, cm⁻¹): 3002, 2922, 2857, 1607, 1578, 1484, 1222 (C-O-C), 927 (benzoxazine related band), 811. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.27 (dd, J = 8.3, 2.1 Hz, 2H), 7.11 (d, J = 2.1 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 4.89 (s, 4H), 4.03 (s, 4H), 2.80–2.71 (m, 4H), 1.62–1.51 (m, 4H), 1.36–1.26 (m, 12H), 0.88 (t, J = 6.8 Hz, 6H).

**Preparation of isocyanides.**

4-isocyano-1,1'-biphenyl (3). 4-aminobiphenyl (845 mg, 5 mmol) in 10 ml CH₂Cl₂ in a Schlenk tube, added chloroform (407 μL, 5 mmol), tetrabutylammonium hydroxide (26 mg, 0.1 mmol) and 10 mL 50% aqueous solution of sodium hydroxide. The mixture was heated to reflux for 3 hours. Afterwards, cooling down the reaction mixture and washed with distilled water, dried over anhydrous MgSO₄. After the drying agent was filtered off and removed the solvent, the residue was purified by column chromatography (Al₂O₃, petroleum ether/EtOAc 30:1).
Other isocyanides 4a, 4b, 4c, 4d, 4e and 4f were prepared according to the synthesis of 3.

**Characterization data of 3:** Yellow powder was obtained (500 mg, 56%). FT-IR (KBr, cm\(^{-1}\)): 3071, 2963, 2120 (C≡N stretching), 1585, 1473, 845, 761. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.67–7.61 (m, 2H), 7.61–7.55 (m, 2H), 7.53–7.45 (m, 4H), 7.45–7.39 (m, 1H).

**Characterization data of 4a:** Yellow powder was obtained (573 mg, 52%). FT-IR (KBr, cm\(^{-1}\)): 3070, 2125 (C≡N stretching), 1589, 1486, 1245, 837. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.43–7.35 (m, 4H), 7.04–6.98 (m, 4H).

**Characterization data of 4b:** White powder was obtained (477 mg, 47%). FT-IR (KBr, cm\(^{-1}\)): 3030, 2124 (C≡N stretching), 1640, 1486, 816. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.63–7.55 (m, 4H), 7.52–7.44 (m, 4H).

**Characterization data of 4c:** Yellow powder was obtained (455 mg, 25%). FT-IR (KBr, cm\(^{-1}\)): 3020, 2960, 2120 (C≡N stretching), 1604, 1500, 1457, 833. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.31–7.20 (m, 8H), 7.07 (s, 4H), 1.26 (dt, \(J = 11.6, 5.2\) Hz, 12H).

**Characterization data of 4d:** Brown powder was obtained (281 mg, 21%). FT-IR (KBr, cm\(^{-1}\)): 3070, 2135 (C≡N stretching), 1591, 1480, 1300, 1145, 810. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.04–7.97 (m, 2H), 7.95 (s, 2H), 7.68–7.59 (m, 4H).

**Characterization data of 4e:** White powder was obtained (678 mg, 30%). FT-IR (KBr, cm\(^{-1}\)): 3070, 2130 (C≡N stretching), 1583, 1503, 1325, 1250, 1155, 847. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.96–7.89 (m, 4H), 7.44–7.36 (m, 4H), 7.10–7.01 (m, 8H).

**Characterization data of 4f:** Red powder was obtained (320 mg, 20%). FT-IR (KBr, cm\(^{-1}\)): 3020, 2923, 2851, 2115 (C≡N stretching), 1593, 1499, 1318, 1268, 833. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.35–7.28 (m, 6H), 7.09–7.02 (m, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm): 164.55 (s), 146.83 (s), 127.98 (s), 124.74 (s), 122.22 (s). HRMS (MALDI–TOF): \(m/z\) [M+Cl\(^-\)]: calcd for C\(_{21}\)H\(_{12}\)N\(_4\), 320.3201; found 355.0735.

**Preparation of model compounds.**

**Model compound M1.** 1 (0.2 mmol), 2 (0.2 mmol), water (0.2 mmol), and OPA (0.04 mmol) were stirred at room temperature in CHCl\(_3\) (2 mL) for 18 h. Solvent was
removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, petroleum ether/EtOAc 3:1).

**Model compound M2.** 1 (0.2 mmol), 3 (0.2 mmol), water (0.2 mmol) and OPA (0.04 mmol) stirred at room temperature in CHCl₃ (2 mL) for 6 h. After removed solvent under reduced pressure and the crude product was purified by column chromatography (SiO₂, petroleum ether/EtOAc 8:1).

**Characterization data of M1:** White powder was obtained (65 mg, 77%). FT-IR (KBr, cm⁻¹): 3496(-OH), 3243(-NH), 3040, 2923, 1668, 1570, 1326, 1230, 1140, 754. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.61 (s, 1H), 8.95 (t, J = 6.6 Hz, 1H), 7.70 (dd, J = 24.8, 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.14–7.00 (m, 3H), 6.91 (d, J = 7.4 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.68 (t, J = 7.4 Hz, 1H), 6.62 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 8.2 Hz, 2H), 4.68 (d, J = 6.6 Hz, 2H), 4.36 (s, 2H), 3.94 (s, 2H), 2.40 (d, J = 10.6 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ (ppm): 170.51 (s), 155.39 (s), 148.68 (s), 145.02 (s), 134.95 (s), 130.19 (s), 129.23 (s), 129.01 (s), 128.02 (s), 127.73 (s), 124.41 (s), 119.26 (s), 116.71 (s), 115.39 (s), 112.39 (s), 60.69 (s), 54.07 (s), 50.77 (s), 21.60 (s). HRMS (MALDI−TOF): m/z [M+H⁺]: calcd for C₂₃H₂₄N₂O₄S, 424.1457; found 425.1498.

**Characterization data of M2:** White powder was obtained (60 mg, 73%). FT-IR (KBr, cm⁻¹): 3279, 3069, 2956, 1640, 1530, 1497, 1450, 1312, 837. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 10.06 (s, 1H), 9.64 (s, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.64 (dd, J = 7.8, 4.6 Hz, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.10 (dt, J = 23.8, 8.2 Hz, 4H), 6.85 (d, J = 7.8 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 8.5 Hz, 3H), 4.59 (s, 2H), 4.24 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ (ppm): 169.50 (s), 155.39 (s), 149.05 (s), 149.04 (s), 140.13 (s), 138.79 (s), 135.46 (s), 135.43 (s), 129.37 (s), 128.07 (s), 127.50 (s), 127.38 (s), 126.71 (s), 124.77 (s), 120.11 (s), 119.34 (s), 116.75 (s), 115.46 (s), 112.49 (s), 55.24 (s), 51.29 (s). HRMS (MALDI−TOF): m/z [M+H⁺]: calcd for C₂₇H₂₄N₂O₂, 408.4682; found 409.1919.

**Polymer Synthesis.** The polymerization reactions were carried out using a standard Schlenk technique under nitrogen atmosphere and a typical synthetic method for the
preparation of P1 (1a/4a) was given as an example: 1a (0.25 mmol), 4a (0.25 mmol), water (0.5 mmol) and OPA (0.1 mmol) was stirred at room temperature in 5 mL CHCl₃ for 6 h. A portion of CHCl₃ was removed from the mixture and the residue was added dropwise into 200 mL ethyl ether, the precipitate was collected by filtration and dried under vacuum at 40 °C to a constant weight.

**Characterization data of P1 (1a+4a):** Yellow powder was obtained (204 mg, 75%). FT-IR (KBr, cm⁻¹): 3301, 3035, 2963, 2922, 2868, 1672, 1611, 1501, 1302, 1214, 822. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.17 (hydroxyl protons), 7.23–6.17 (aromatic protons), 4.25 (CH₂ protons), 3.84 (CH₂ protons), 2.03–0.21 (CH₂ and CH₃ protons).

**Characterization data of P2 (1a+4b):** Yellow powder was obtained (153 mg, 57%). FT-IR (KBr, cm⁻¹): 3315, 3032, 2963, 2922, 2865, 1668, 1607, 1505, 1316, 822. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.34 (O-H), 9.15 (N-H), 8.42–7.30 (aromatic protons), 7.21–5.55 (aromatic protons), 4.49 (CH₂ protons), 3.82 (CH₂ protons), 2.15–0.16 (CH₂ and CH₃ protons).

**Characterization data of P3 (1a+4c):** Yellow powder was obtained (160 mg, 52%). FT-IR (KBr, cm⁻¹): 3307, 3026, 2959, 2923, 2864, 1665, 1603, 1505, 1404, 1315, 826. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.66 (hydroxyl protons), 7.16–6.49 (aromatic protons), 4.50 (CH₂ protons), 3.77 (CH₂ protons), 1.91–0.30 (CH₂ and CH₃ protons).

**Characterization data of P4 (1a+4d):** Red powder was obtained (70 mg, 25%). FT-IR (KBr, cm⁻¹): 3286, 3025, 2922, 2861, 1672, 1601, 1509, 1418, 1302, 822. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.21 (hydroxyl protons), 7.89–7.33 (aromatic protons), 7.21–6.47 (aromatic protons), 4.51 (CH₂ protons), 3.83 (CH₂ protons), 1.78–0.21 (CH₂ and CH₃ protons).

**Characterization data of P5 (1a+4e):** Light yellow powder was obtained (240 mg, 73%). FT-IR (KBr, cm⁻¹): 3293, 3027, 2963, 2922, 2864, 1672, 1596, 1501, 1418, 1302, 822. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.98 (hydroxyl protons), 8.03–7.54 (aromatic protons), 7.22–6.35 (aromatic protons), 4.52 (CH₂ protons), 4.10 (CH₂ protons), 1.81–0.15 (CH₂ and CH₃ protons).
Characterization data of P6 (1b+4a): Brown powder was obtained (141 mg, 60%). FT-IR (KBr, cm\(^{-1}\)): 3293, 3028, 2959, 2922, 2864, 1669, 1611, 1504, 1415, 1305, 1211, 822. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.20 (hydroxyl protons), 7.19–5.98 (aromatic protons), 4.40 (CH\(_2\) protons), 3.82 (CH\(_2\) protons), 1.97–0.17 (CH\(_3\) and CH\(_2\) protons).

Characterization data of P7 (1c+4a): White powder was obtained (60 mg, 35%). FT-IR (KBr, cm\(^{-1}\)): 3275, 3046, 2955, 2923, 2854, 1663, 1611, 1494, 1410, 1305, 1229, 826. \(^1\)H NMR (400 MHz, CDCl\(_3\)/CD\(_3\)OD=20:1) \(\delta\) (ppm): 7.78–6.52 (aromatic protons), 4.38 (CH\(_2\) protons), 3.81 (CH\(_2\) protons), 3.36 (CH\(_2\) protons), 2.6 (CH\(_2\) protons), 1.97–0.56 (CH\(_3\) and CH\(_2\) protons). We envisaged that the peaks of active protons (O-H and N-H) not appeared in the existence of CD\(_3\)OD and the peaks of CH\(_2\) protons splitting in the mixed deuterated reagents.

Characterization data of P1-air (1a+4a): Yellow powder was obtained (135 mg, 50%). FT-IR (KBr, cm\(^{-1}\)): 3297, 3039, 2963, 2922, 2864, 1665, 1607, 1501, 1305, 1214, 822. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.17 (hydroxyl protons), 7.23–6.13 (aromatic protons), 4.45 (CH\(_2\) protons), 3.86 (CH\(_2\) protons), 1.99–0.20 (CH\(_3\) and CH\(_2\) protons).

Characterization data of P8 (1a+4a/4f=10:1): Red powder was obtained (120 mg, 57%). FT-IR (KBr, cm\(^{-1}\)): 3297, 3039, 2963, 2926, 2864, 1665, 1607, 1501, 1309, 1214, 818. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.11 (hydroxyl protons), 7.22–6.11 (aromatic protons), 4.40 (CH\(_2\) protons), 3.83 (CH\(_2\) protons), 2.00–0.15 (CH\(_3\) and CH\(_2\) protons).

Characterization data of P9 (1a+4a/4f=5:1): Red powder was obtained (110 mg, 52%). FT-IR (KBr, cm\(^{-1}\)): 3296, 3038, 2962, 2926, 2865, 1668, 1607, 1501, 1309, 1215, 821. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.15 (hydroxyl protons), 7.25–6.12 (aromatic protons), 4.43 (CH\(_2\) protons), 3.81 (CH\(_2\) protons), 1.92–0.15 (CH\(_3\) and CH\(_2\) protons).
Scheme S1. Proposed reaction mechanism of CLOBERT reaction.\textsuperscript{5}

\begin{align*}
\text{Scheme S2. The mechanism for Ugi 4CR and Ugi 3CR.}\textsuperscript{6}
\end{align*}
Scheme S3. Synthetic route of benzoxazines 1, 1a, 1b and 1c.
Scheme S4. Synthetic route of isocyanides 3, 4a, 4b, 4c, 4d and 4e.
Figure S1. FT-IR spectra of 1, 2 and M1.

Figure S2. FT-IR spectra of 1, 3 and M2.
Figure S3. FT-IR spectra of 1a, 4a, P1 and P1-air.

Figure S4. FT-IR spectra of 1a, 4b and P2.
Figure S5. FT-IR spectra of 1a, 4c and P3.

Figure S6. FT-IR spectra of 1a, 4d and P4.
Figure S7. FT-IR spectra of 1a, 4e and P5.

Figure S8. FT-IR spectra of 1b, 4a and P6.
Figure S9. FT-IR spectra of 1c, 4a and P7.

Figure S10. FT-IR spectra of 4f, P1, P8 and P9.
**Figure S11.** In-situ $^1$H NMR study of the polymerization between 1a and 4a in CDCl$_3$ under room temperature.

**Figure S12.** $^1$H NMR spectrum of 1 in CDCl$_3$. 
Figure S13. $^1$H NMR spectrum of $1a$ in CDCl$_3$.

Figure S14. $^1$H NMR spectrum of $1b$ in CDCl$_3$. 
Figure S15. $^1$H NMR spectrum of 1e in CDCl$_3$.

Figure S16. $^1$H NMR spectrum of 4 in CDCl$_3$. 
Figure S17. $^1$H NMR spectrum of 4a in CDCl$_3$.

Figure S18. $^1$H NMR spectrum of 4b in CDCl$_3$. 
Figure S19. $^1$H NMR spectrum of 4c in CDCl$_3$.

Figure S20. $^1$H NMR spectrum of 4d in CDCl$_3$. 
Figure S21. $^1$H NMR spectrum of 4e in CDCl$_3$.

Figure S22. $^1$H NMR spectrum of 4f in CDCl$_3$. 
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Figure S24. High resolution mass spectrum of 4f.
Figure S25. High resolution mass spectrum of model compound M1.

Figure S26. High resolution mass spectrum of model compound M2.
Figure S27. $^1$H NMR spectrum of P2 in CDCl$_3$.

Figure S28. $^1$H NMR spectrum of P3 in CDCl$_3$. 

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Figure S29. $^1$H NMR spectrum of P4 in CDCl$_3$.

Figure S30. $^1$H NMR spectrum of P5 in DMSO-$d_6$.  

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Figure S31. $^1$H NMR spectrum of P6 in CDCl$_3$.

Figure S32. $^1$H NMR spectrum of P7 in CDCl$_3$/CD$_3$OD (20:1, v:v).
Figure S33. $^1$H NMR spectra of P1 (A), P8 (B) and P9 (C) in CDCl$_3$.

Figure S34. GPC curves of other polymers (P2-P9 and P1-air).
**Figure S35.** TG (A) and DSC thermograms (B) of P1 (recorded under nitrogen with the heating rate of 10 °C/min).

**Figure S36.** Cyclic voltammograms of polymer films coated on platinum electrodes in 0.1 M Bu4NPF6, CH3CN solution.
References


