

Electronic Supplementary Information

An unsymmetrical covalent organic polymer for catalytic amide synthesis

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Fig. S1. Solubility of APC-COP in various solvents viz. (a) DMSO, (b) H₂O, (c) CH₃CN, (d) 1,4-dioxane and (e) CH₃OH.

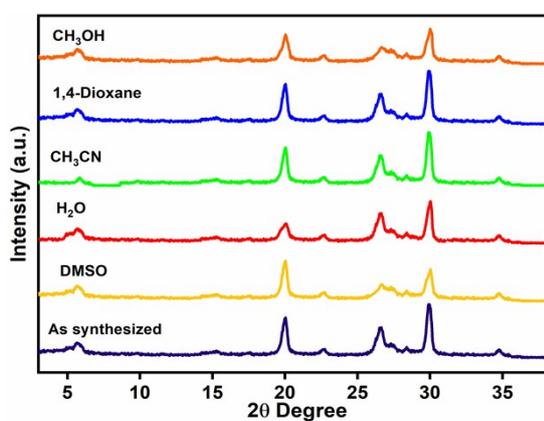


Fig. S2. PXRD patterns of APC-COP after successive treatments in DMSO, H₂O, CH₃CN, 1,4-Dioxane and CH₃OH for 2 days.

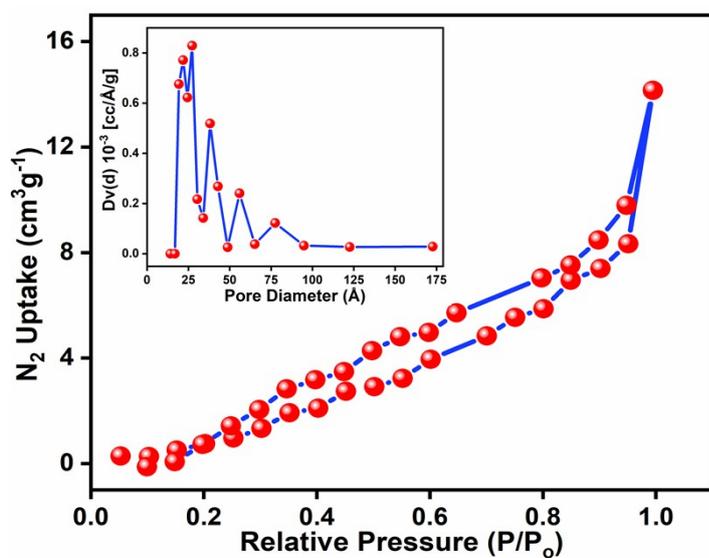


Fig. S3. N₂ adsorption/desorption isotherm and Pore size distribution of APC-COP.

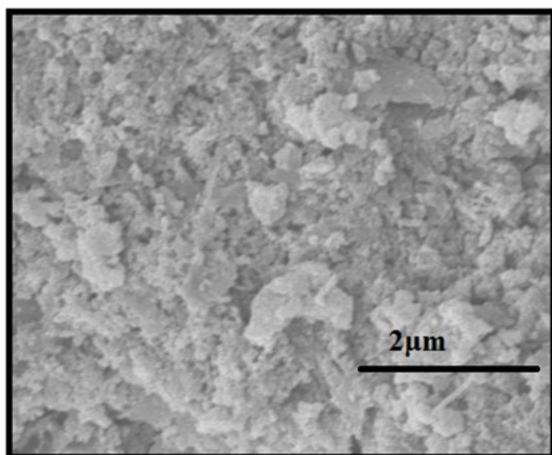


Fig. S4. FESEM image of recovered APC-COP.

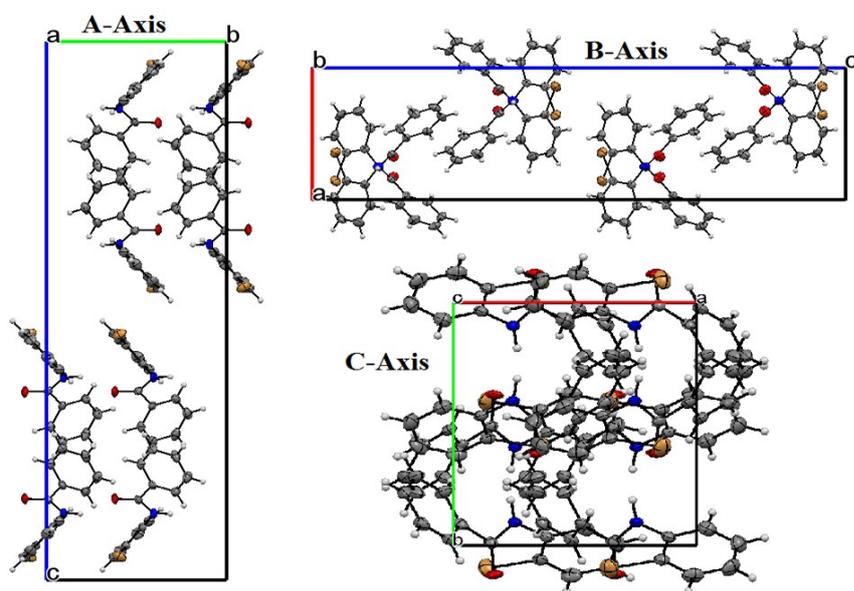


Fig. S5. Crystal packing diagram of **3f** along with a, b and c-axis, respectively. Thermal ellipsoids are at 50% probability level.

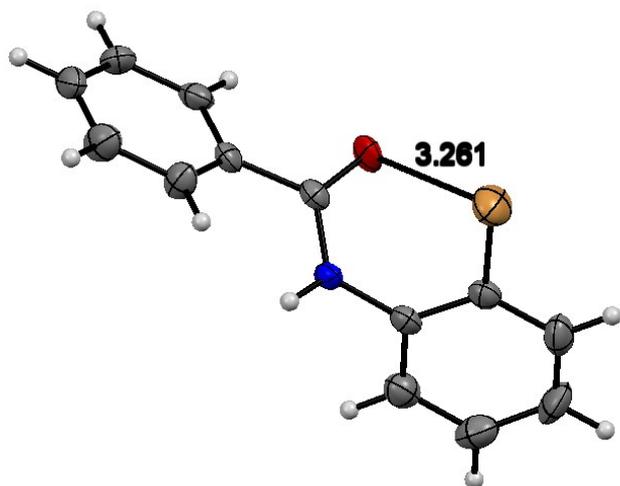


Fig. S6. ORTEP view of halogen interactions between Br...O in **3f**. Thermal ellipsoids are at 50% probability level.

Fig. S7. On-site UV-Vis reaction monitoring catalyzed by **APC-COP** over 30min.

Table S1. Crystallographic parameters for **3f**.

<i>Identification code</i>	3f
<i>CCDC No.</i>	1948701
<i>Empirical formula</i>	$C_{13}H_{10}BrNO$
<i>Formula weight</i>	51.37
<i>Temperature/K</i>	237(80)
<i>Crystal system</i>	Orthorhombic
<i>Space group</i>	Pbca
<i>a/Å</i>	8.1837(8)
<i>b/Å</i>	9.2427(10)
<i>c/Å</i>	30.229(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90

<i>Volume/Å³</i>	2286.5(4)
<i>Z</i>	43
<i>ρ_{calc}/cm³</i>	1.6042
<i>μ/mm⁻¹</i>	3.571
<i>F(000)</i>	1102.2
<i>Crystal size/mm³</i>	0.5*0.5*0.5
<i>Radiation</i>	Mo Kα (λ = 0.71073)
<i>2θ range for data collection/°</i>	6.78 to 50
<i>Index ranges</i>	-11 ≤ h ≤ 10, -12 ≤ k ≤ 11, -40 ≤ l ≤ 41
<i>Reflections collected</i>	31290
<i>Independent reflections</i>	2003 [<i>R_{int}</i> = 0.1663, <i>R_{sigma}</i> = 0.1146]
<i>Data/restraints/parameters</i>	2003/0/145
<i>Goodness-of-fit on F²</i>	0.885
<i>Final R indexes [I ≥ 2σ(I)]</i>	<i>R₁</i> = 0.0505, <i>wR₂</i> = 0.1324
<i>Final R indexes [all data]</i>	<i>R₁</i> = 0.0817, <i>wR₂</i> = 0.1584
<i>Largest diff. peak/hole / e Å⁻³</i>	0.62/-0.66

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **3f**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	X	y	z	U(eq)
Br01	6411.6 (8)	4049.0 (7)	5435.0 (2)	46.0 (3)
O002	6693 (4)	3791 (3)	6508.2 (13)	33.3 (9)
N003	7541 (5)	5952 (4)	6235.5 (13)	24.9 (9)
C004	8843 (6)	5345 (5)	5982.3 (16)	25.6 (12)
C005	8571 (6)	4406 (5)	5636.7 (18)	27.1 (12)
C006	4838 (6)	5242 (5)	7155.0 (16)	29.4 (12)
C007	6562 (6)	5106 (5)	6489.7 (16)	24.1 (11)
C008	5314 (6)	5879 (5)	6762.9 (15)	25.5 (12)
C009	4615 (6)	7183 (5)	6640.6 (17)	32.5 (13)
C00A	3719 (6)	5882 (6)	7425.8 (19)	32.8 (14)
C00B	10431 (7)	5694 (5)	6090.1 (18)	35.6 (14)
C00C	3008 (6)	7174 (5)	7297.3 (19)	37.2 (14)

C00D	9859 (8)	3766 (6)	5416.6 (17)	39.1 (15)
C00E	11724 (7)	5067 (6)	5864 (2)	43.7 (15)
C00F	11416 (7)	4094 (6)	5530 (2)	43.5 (17)
C00G	3461 (7)	7817 (6)	6907 (2)	40.0 (14)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3f**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br01	40.7 (5)	54.9 (5)	42.4 (5)	-7.2 (3)	-5.3 (3)	-12.5 (3)
O002	45 (2)	12.3 (19)	43 (2)	5.1 (15)	7.3 (17)	-1.9 (15)
N003	24 (2)	14.2 (19)	36 (3)	-0.7 (16)	6.8 (18)	-1.0 (18)
C004	28 (3)	19 (3)	30 (3)	-4 (2)	1 (2)	0 (2)
C005	31 (3)	21 (3)	29 (3)	-3 (2)	2 (2)	2 (2)
C006	28 (3)	21 (3)	39 (3)	-7 (2)	0 (2)	1 (2)
C007	26 (3)	21 (3)	25 (3)	-3 (2)	-4 (2)	-3 (2)
C008	30 (3)	20 (3)	27 (3)	-5 (2)	-1 (2)	-6 (2)
C009	38 (3)	26 (3)	33 (3)	8 (2)	7 (2)	6 (2)
C00A	34 (3)	30 (3)	35 (3)	-8 (2)	11 (2)	0 (2)
C00B	42 (4)	33 (3)	32 (3)	-6 (2)	0 (3)	0 (2)
C00C	30 (3)	27 (3)	54 (4)	-2 (2)	13 (3)	-10 (3)
C00D	55 (4)	34 (3)	28 (3)	1 (3)	9 (3)	-7 (2)
C00E	33 (3)	48 (4)	50 (4)	-3 (3)	9 (3)	7 (3)
C00F	42 (4)	45 (4)	43 (4)	14 (3)	21 (3)	0 (3)
C00G	42 (3)	27 (3)	51 (4)	8 (2)	10 (3)	8 (3)

Table S4. Bond Lengths for **3f**.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
Br01	C005	1.898 (5)	C007	C008	1.495 (7)
O002	C007	1.222 (5)	C008	C009	1.384 (6)
N003	C004	1.427 (6)	C009	C00G	1.372 (7)
N003	C007	1.358 (6)	C00A	C00C	1.384 (7)
C004	C005	1.376 (7)	C00B	C00E	1.387 (8)
C004	C00B	1.378 (7)	C00C	C00G	1.373 (8)
C005	C00D	1.380 (8)	C00D	C00F	1.354 (9)
C006	C008	1.380 (6)	C00E	C00F	1.374 (8)
C006	C00A	1.363 (7)			

Table S5. Bond Angles for **3f**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C007	N003	C004	121.2 (4)	C007	C008	C006	117.6 (4)
C005	C004	N003	122.3 (4)	C009	C008	C006	119.0 (5)
C00B	C004	N003	119.0 (4)	C009	C008	C007	123.4 (4)
C00B	C004	C005	118.6 (5)	C00G	C009	C008	120.0 (5)
C004	C005	Br01	120.3 (4)	C00C	C00A	C006	119.3 (5)
C00D	C005	Br01	118.8 (4)	C00E	C00B	C004	120.4 (5)
C00D	C005	C004	120.9 (5)	C00G	C00C	C00A	120.1 (5)
C00A	C006	C008	121.3 (5)	C00F	C00D	C005	120.0 (5)
N003	C007	O002	123.2 (4)	C00F	C00E	C00B	119.7 (6)
C008	C007	O002	120.7 (4)	C00E	C00F	C00D	120.4 (5)
C008	C007	N003	116.1 (4)	C00C	C00G	C009	120.4 (5)

Table S6. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **3f**.

Atom	X	y	z	U(eq)
H00D	9658 (8)	3109 (6)	5189.9 (17)	47.0 (18)
H00F	12281 (7)	3659 (6)	5382 (2)	52 (2)
H00E	12795 (7)	5304 (6)	5938 (2)	52.4 (18)
H00B	10637 (7)	6353 (5)	6315.8 (18)	42.7 (16)
H009	4928 (6)	7629 (5)	6378.2 (17)	39.0 (15)
H00G	2983 (7)	8687 (6)	6822 (2)	47.9 (17)
H00C	2222 (6)	7607 (5)	7475.8 (19)	44.6 (17)
H00A	3437 (6)	5456 (6)	7693.8 (19)	39.4 (16)
H006	5290 (6)	4358 (5)	7236.3 (16)	35.3 (15)
H003	7373 (5)	6870 (4)	6227.0 (13)	29.9 (11)

Table S7. Reusability of **APC-COP**.^a

Number of Cycles	1	2	3	4	5	6	7	8	9
Yield (%)	98	98	97	97	96	95	95	94	94

^aReaction conditions: benzoic acid (1 mmol), *p*-anisidine (1 mmol), **APC-COP** (10 mg), 1,4-dioxane (3 mL).

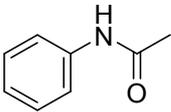
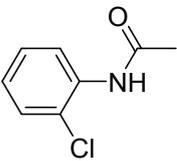
Table S8. Reaction profiles for three different carboxylic acids with different pK_a .^a

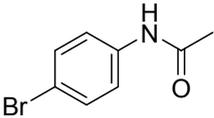
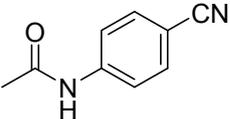
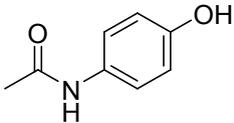
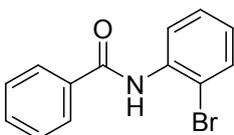
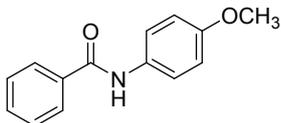
Time (min)	% Yield ^b		
	CCl_3COOH	HCCl_2COOH	ClCH_2COOH
0	0	0	0
5	15	55	40
10	38	69	52

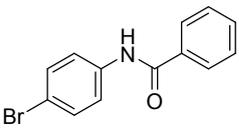
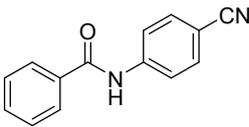
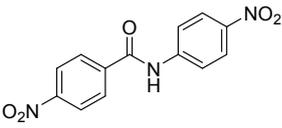
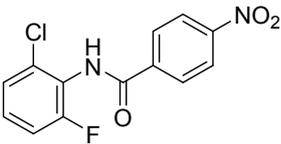
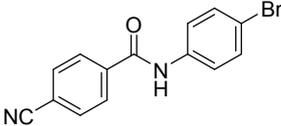
15	44	88	65
20	62	92	72
25	75	95	78
30	94	99	88

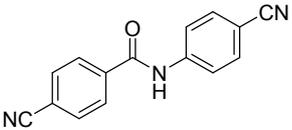
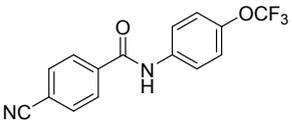
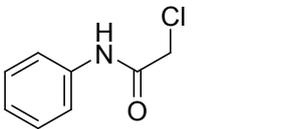
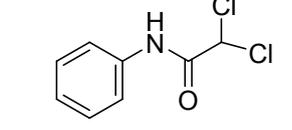
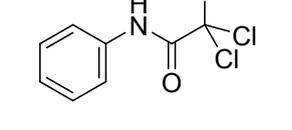
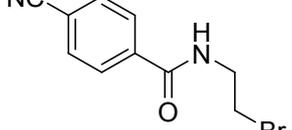
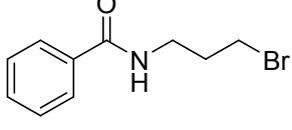
^aReaction conditions: Carboxylic Acid (1 mmol), *p*-aniline (1mmol), **APC-COP** (10 mg), 1,4-dioxane (3 mL). ^b% yield was calculated using ¹H NMR spectroscopy.

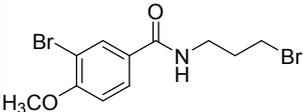
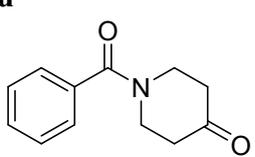
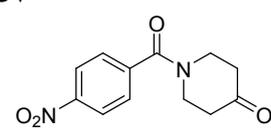
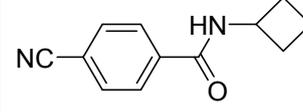
¹H and ¹³C NMR chemical shifts for **3a-w**.

<p>3a</p> 	<p>¹H-NMR (400 MHz, CDCl₃) δ 9.74 (s, 1H), 7.33 (d, <i>J</i> = 8.0 Hz, 2H), 7.12 (d, <i>J</i> = 8.1 Hz, 2H), 7.05 (t, <i>J</i> = 8.0 Hz, 1H), 2.08 (s, 3H)</p> <p>¹³C-NMR (101 MHz, DMSO-<i>d</i>₆) δ 169.13, 139.50, 130.29, 127.21, 122.53, 24.50</p>
<p>3b</p> 	<p>¹H-NMR (400 MHz, DMSO-<i>d</i>₆) δ 9.48 (s, 1H), 7.68 (d, <i>J</i> = 7.7 Hz, 1H), 7.43 (d, <i>J</i> = 8.0 Hz, 1H), 7.26 (t, <i>J</i> = 7.7 Hz, 1H), 7.13 (t, <i>J</i> = 7.6 Hz, 1H), 2.07 (s, 3H)</p> <p>¹³C-NMR (101 MHz, DMSO-<i>d</i>₆) δ 169.21, 135.35, 129.91, 127.81,</p>

	126.93, 126.76, 126.65, 23.41
3c 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.38 (s, 1H), 7.79 (t, $J = 1.6$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 1H), 7.12 (t, $J = 8.0$ Hz, 1H), 2.16 (s, 3H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 169.57, 139.42, 130.31, 127.33, 123.24, 122.56, 118.74, 24.51.
3d 	$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 9.40 (s, 1H), 7.37 (d, $J = 8.5$ Hz, 2H), 6.61 (d, $J = 8.5$ Hz, 2H), 2.09 (s, 3H) $^{13}\text{C-NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 153.48, 134.24, 121.21, 119.48, 113.46, 96.13, 24.37
3e 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.56 (s, 1H), 8.93 (s, 1H), 7.19 (d, $J = 7.6$ Hz, 2H), 6.70 (d, $J = 7.3$ Hz, 2H), 2.05 (s, 3H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 168.49, 153.36, 131.27, 122.19, 115.85, 23.52
3f 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.54 (d, $J = 8.2$ Hz, 1H), 8.47 (s, 1H), 7.93 (d, $J = 7.3$ Hz, 2H), 7.54 (dt, $J = 26.0, 7.2$ Hz, 4H), 7.36 (t, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 165.34, 135.90, 134.66, 132.35, 129.05, 128.64, 127.20, 125.39, 121.86, 113.88
3g 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.39 (s, 1H), 8.10 (d, $J = 7.4$ Hz, 2H), 7.57 (d, $J = 7.4$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 1H), 6.76 (d, $J = 8.9$ Hz, 2H), 6.71 (d, $J = 8.9$ Hz, 2H), 3.73 (s, 3H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 170.76, 153.48, 133.22, 130.66, 130.11, 128.46, 117.39, 114.92, 55.79

<p>3h</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.06 (s, 1H), 8.52 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 7.4$ Hz, 2H), 7.58 (t, $J = 7.1$ Hz, 2H), 7.50-7.53 (m, 2H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 8.2$ Hz, 1H)</p> <p>$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 165.34, 135.90, 134.64, 132.31, 129.05, 128.64, 127.21, 125.39, 121.89</p>
<p>3i</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.16 (s, $J = 8.3$, 1H), 8.46 (s, 1H), 7.91 (d, $J = 8.0$ Hz, 2H), 7.46-7.57 (m, 4H), 7.31-7.35 (m, 1H), 6.96-7.00 (m, 1H)</p> <p>$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 165.65, 135.88, 134.79, 132.31, 129.05, 128.60, 127.21, 125.44, 121.98, 113.62</p>
<p>3j</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.67 (s, 1H), 8.19 (d, $J = 1.9$ Hz, 2H), 8.16 (d, $J = 1.9$ Hz, 2H), 8.07 (d, $J = 8.7$ Hz, 2H), 7.76 (d, $J = 8.9$ Hz, 2H)</p> <p>$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.03, 150.32, 145.44, 130.89, 128.95, 123.58, 122.35, 115.64</p>
<p>3k</p> 	<p>$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 10.14 (s, 1H), 8.09-8.24 (m, 1H), 7.73-7.80 (m, 2H), 7.51-7.56 (m, 2H), 7.47 (d, $J = 7.7$ Hz, 2H)</p> <p>$^{13}\text{C-NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 164.94, 150.45, 137.04, 136.72, 130.83, 126.69, 123.63, 115.94, 115.75, 111.54, 102.23</p>
<p>3l</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.09 (s, 1H), 8.08 (d, $J = 8.7$ Hz, 2H), 7.67 (d, $J = 8.7$ Hz, 2H), 7.15 (d, $J = 8.8$ Hz, 2H), 6.51 (d, $J = 8.8$ Hz, 2H)</p> <p>$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.17, 145.30, 134.81, 132.22, 131.99, 130.38, 118.45, 116.67, 115.99, 110.16</p>

<p>3m</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.26 (s, 1H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.47-7.58 (m, 6H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 166.27, 141.87, 138.61, 133.91, 130.80, 128.77, 128.42, 125.30, 119.83, 114.53, 109.77</p>
<p>3n</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.47 (s, 1H), 8.18 (d, $J = 51.8$ Hz, 2H), 7.73-7.80 (m, 2H), 7.51-7.56 (m, 2H), 7.47 (d, $J = 7.7$ Hz, 2H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 166.80, 145.31, 133.84, 129.59, 120.69, 117.05, 110.47, 108.61</p>
<p>3o</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.93 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.1$ Hz, 2H), 7.04 (t, $J = 8.0$ Hz, 1H), 4.20 (s, 2H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 170.99, 141.37, 132.16, 129.07, 124.39, 42.77</p>
<p>3p</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.18 (s, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.12 (t, $J = 8.0$ Hz, 1H), 6.11 (s, 1H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 172.48, 142.86, 133.65, 130.57, 125.89, 63.24</p>
<p>3q</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.45 (s, 1H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.12 (t, $J = 8.0$ Hz, 1H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 161.57, 138.84, 129.63, 127.11, 122.37, 89.62</p>
<p>3r</p> 	<p>$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.89 (s, 1H), 8.04 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.2$, 2H), 4.00 (t, $J = 7.1$ Hz, 3H), 3.71 (t, $J = 7.1$ Hz, 2H) $^{13}\text{C-NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 171.60, 140.24, 136.77, 134.71, 122.64, 120.48, 52.93, 28.24</p>
<p>3s</p> 	<p>$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.46 (s, 1H), 7.87 (d, $J = 5.5$ Hz, 2H), 7.25-7.36 (m, 3H), 3.91 (t, $J = 7.0$ Hz, 2H), 1.84 (t, $J = 3.6$ Hz, 2H), 1.05-1.08 (m, 2H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 168.67, 132.70, 130.83, 129.70, 128.24,</p>

	60.19, 20.99, 14.15
3t 	$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.61 (s, 1H), 7.99 (s, 1H), 7.72 (d, $J = 8.7$ Hz, 1H), 6.79 (d, $J = 8.7$ Hz, 1H), 3.96 (q, $J = 7.1$ Hz, 2H), 3.80-3.83 (m, 5H), 1.87-1.93 (m, 2H) $^{13}\text{C-NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 167.85, 158.46, 133.07, 129.18, 126.70, 124.41, 111.38, 56.40, 34.18, 29.27, 20.65
3u 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.12 (d, $J = 8.7$ Hz, 2H), 7.52-7.57 (m, 1H), 7.45 (d, $J = 7.8$ Hz, 2H), 4.01 (t, $J = 6.1$ Hz, 4H), 2.40 (t, $J = 6.1$ Hz, 4H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 208.40, 171.13, 133.62, 130.20, 128.67, 128.52, 46.62, 40.47
3v 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.5$ Hz, 2H), 7.74 (d, $J = 8.7$ Hz, 2H), 3.77 (t, $J = 8.8$ Hz, 4H), 2.39 (t, $J = 8.6$ Hz, 4H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 206.62, 170.80, 153.42, 141.46, 133.81, 121.08, 54.66, 43.60
3w 	$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.47 (s, 1H), 8.08 (d, $J = 6.7$ Hz, 2H), 7.67 (d, $J = 6.7$ Hz, 2H), 2.99 (d, $J = 8.2$ Hz, 1H), 1.74-1.78 (m, 2H), 1.08-1.33 (m, 4H) $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 170.43, 142.12, 131.27, 129.44, 118.49, 112.96, 47.68, 32.75, 13.91

^1H and ^{13}C NMR spectra

