Electronic Supplementary Material (ESI) for CrystEngComm.
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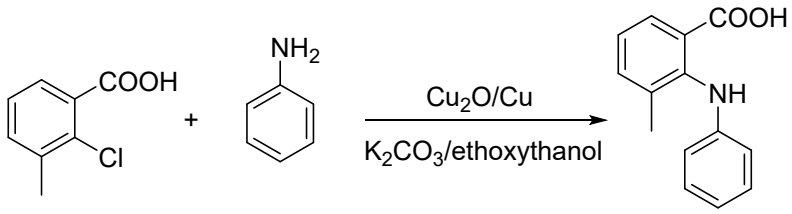
Conformational Flexibility and Substitution Pattern Lead to Polymorphism of Methyl-2-(phenylamino)benzoic acid

Synthesis of MPABAs

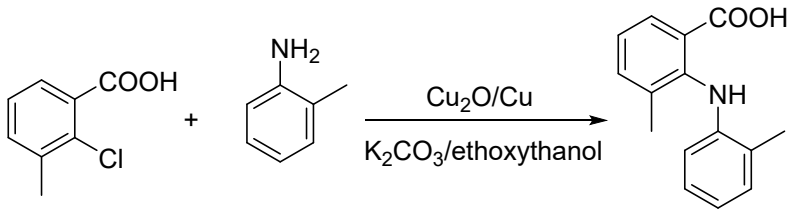
1. ***Synthesis of 3-methyl-2-phenylamino-benzoic acid (1)***



A mixture of 2-chloro-*m*-toluic acid (1 g, 5.86 mmol), *o*-toluidine (640 mg, 5.97 mmol), K_2CO_3 (0.809 g, 5.9 mmol), Cu powder (34 mg, 0.54 mmol), and Cu_2O (38 mg, 0.3 mmol) in 3 mL of 2-ethoxyethanol was refluxed at 130°C under inert atmosphere for 24 h. The cooled reaction mixture was poured into 30 mL of water. The crude product was obtained by precipitation upon acidification of the filtrate with dilute HCl. Then the crude product was purified on column chromatography and recrystallization. The product was obtained as a green solid (0.504 g, yield%: 37.9).

^{1}H NMR (400 MHz, DMSO-d_6) *δppm* 8.53 (s, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 7.0 Hz, 1H), 7.16 (s, 2H), 7.11 (s, 1H), 6.80 (s, 1H), 6.62 (d, J = 7.5 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) *δppm* 169.4, 144.9, 142.5, 136.0, 135.9, 133.2, 129.5, 129.4, 128.4, 123.4, 123.4, 116.9, 115.8, 19.3; mp: 188.9°C.

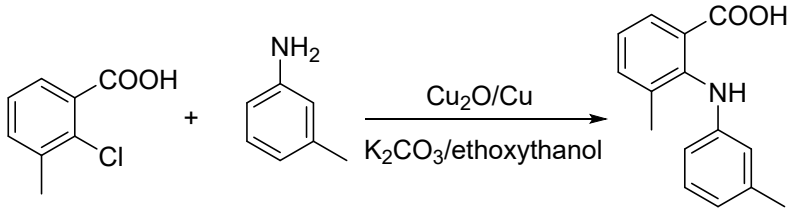
2. ***Synthesis of 3-methyl-2-o-tolylamino-benzoic acid (2)***



The procedure is similar to the preparation of 1 with 2-chloro-*m*-toluic acid (1 g, 5.86 mmol), *o*-toluidine (640 mg, 5.97 mmol), K_2CO_3 (1.38 g, 9.98 mmol), Cu (100 mg, 1.57 mmol), Cu_2O (100 mg, 0.7 mmol), 2-ethoxyethanol (3 mL) to yield green solid (0.3 g, yield%: 21.4).

^{1}H NMR (500 MHz, DMSO-d_6) *δppm* 8.47 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.24 (d, *J* = 7.9 Hz, 1H), 2.30 (s, 3H), 1.96 (d, *J* = 12.3 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) *δppm* 169.8, 144.1, 142.7, 135.8, 132.4, 130.3, 129.2, 126.4, 126.3, 122.2, 121.7, 120.5, 115.4, 18.9, 17.6; mp: 191.8 °C.

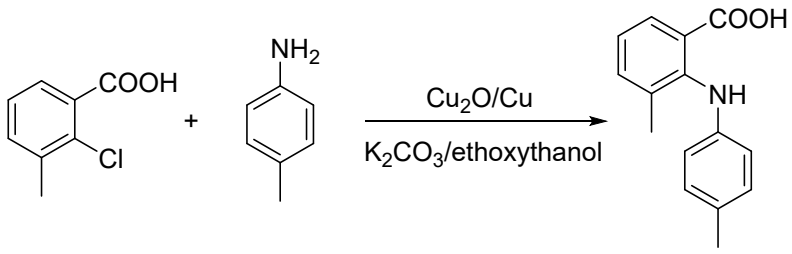
3. ***Synthesis of 3-methyl-2-m-tolylamino-benzoic acid (3)***



The procedure is similar to the preparation of 1 with 2-chloro-*m*-toluic acid (1.5 g, 8.79 mmol), *m*-toluidine (1.9 g, 17.73 mmol), K_2CO_3 (2.43 g, 17.58 mmol), Cu (100 mg, 1.57 mmol), Cu_2O (100 mg, 0.7 mmol), 2-ethoxyethanol (5 mL) to yield green solid (0.36 g, yield%: 17.1).

^{1}H NMR (500 MHz, DMSO-d_6) *δppm* 8.48 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.07 (dt, *J* = 27.7, 7.7 Hz, 2H), 6.63 (d, *J* = 7.4 Hz, 1H), 6.50 – 6.35 (m, 2H), 2.19 (s, 3H), 2.01 (d, *J* = 14.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) *δppm* 169.5, 144.8, 142.7, 138.2, 135.5, 133.2, 129.0, 128.8, 123.2, 122.7, 120.7, 117.1, 113.7, 21.2, 18.9; mp: 172.8 °C.

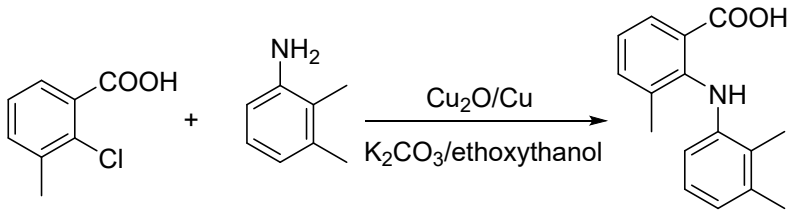
4. ***Synthesis of 3-methyl-2-p-tolylamino-benzoic acid (4)***



The procedure is similar to the preparation of 1 with 2-chloro-*m*-toluic acid (2 g, 11.72 mmol), *p*-toluidine (2.2 g, 20.53 mmol), K_2CO_3 (3.24 g, 23.41 mmol), Cu (100 mg, 1.57 mmol), Cu_2O (100 mg, 0.7 mmol), 2-ethoxyethanol (5 mL) to yield green solid (0.32 g, yield%: 11.4).

^{1}H NMR (500 MHz, DMSO-d_6) *δppm* 8.55 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.1 Hz, 2H), 4.03 (dd, *J* = 14.2, 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) *δppm* 171.6, 166.1, 144.7, 141.9, 137.1, 133.3, 131.2, 130.2, 129.7, 128.4, 122.7, 120.9, 118.6, 20.8, 19.6; mp: 195.4 °C.

5. ***Synthesis of 2-(2,3-mimethyl-phenylamino)-3-methyl-benzoic acid (5)***



The procedure is similar to the preparation of 1 with 2-chloro-*m*-toluic acid (2 g, 11.72 mmol), 2,3-dimethylphenylamine (2.2 g, 18.15 mmol), K_2CO_3 (2.8 g, 20.26 mmol), Cu (100 mg, 1.57 mmol), Cu_2O (100 mg, 0.7 mmol), 2-ethoxyethanol (5 mL) to yield green solid (0.7 g, yield%: 24.1).

^{1}H NMR (500 MHz, DMSO-d_6) *δppm* 8.52 (s, 1H), 7.80 (t, *J* = 12.2 Hz, 1H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 6.9 Hz, 1H), 6.14 (d, *J* = 7.5 Hz, 1H), 2.28 (t, *J* = 34.4 Hz, 6H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) *δppm* 169.84, 144.85, 142.54, 136.80, 135.82, 131.81, 129.13, 125.50, 125.30, 122.76, 121.62, 120.95, 114.36, 20.22, 19.02, 13.10; ESI-MS m/z (M+18) 274.3; mp: 194.1 °C.

Crystal Growth

Example: 250 mg of **1** was suspended in 5 mL methanol. The mixture was stirred overnight and the remaining solid was removed by pipette filtration. A vial containing the clear solution was covered with perforated parafilm. Slow evaporation led to single crystals in about a week.

Crystal Structures

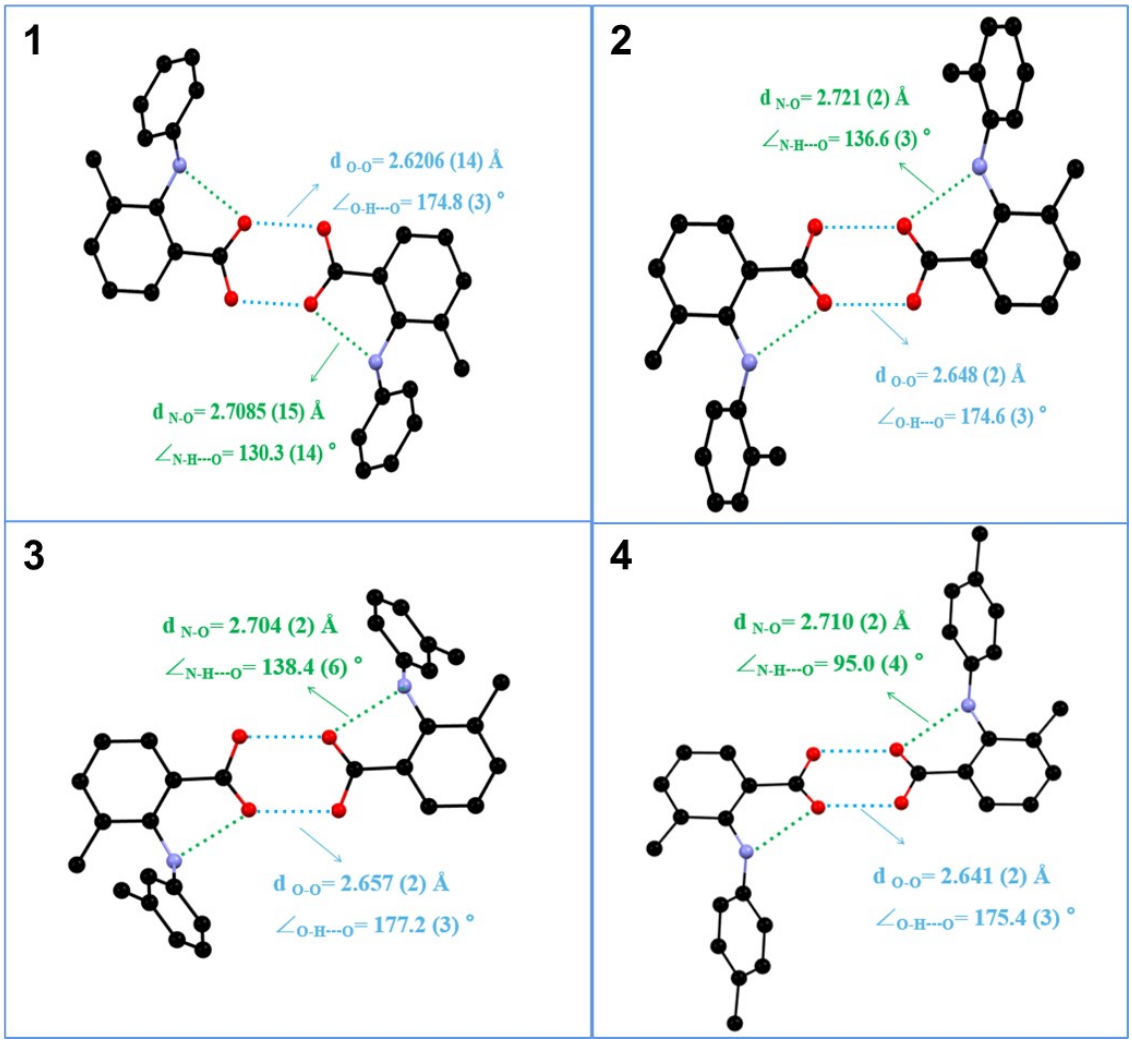


Figure S1 The acid-acid dimer motif in **1-4** (for clarity, H atoms not involved in hydrogen bonding are omitted)

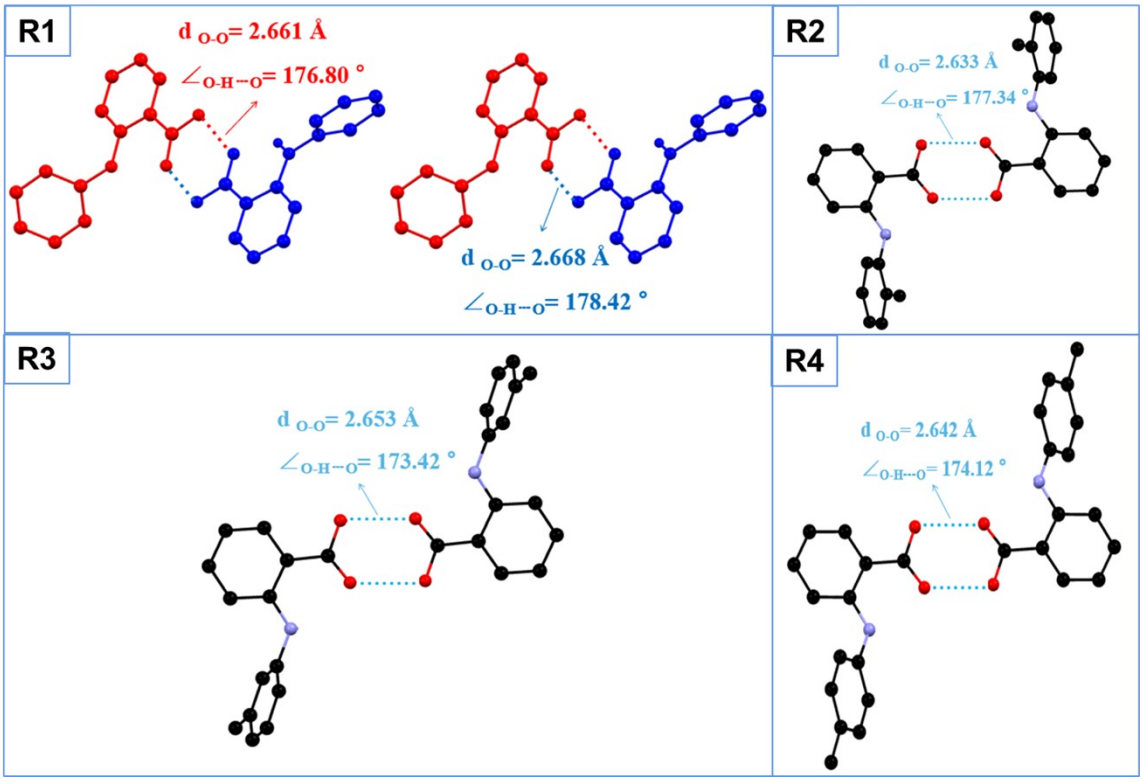


Figure S2 The acid-acid heterodimer motif (A: red; B: blue) in **R1**, and homodimer in **R2-R4** (for clarity, H atoms not involved in hydrogen bonding are omitted)

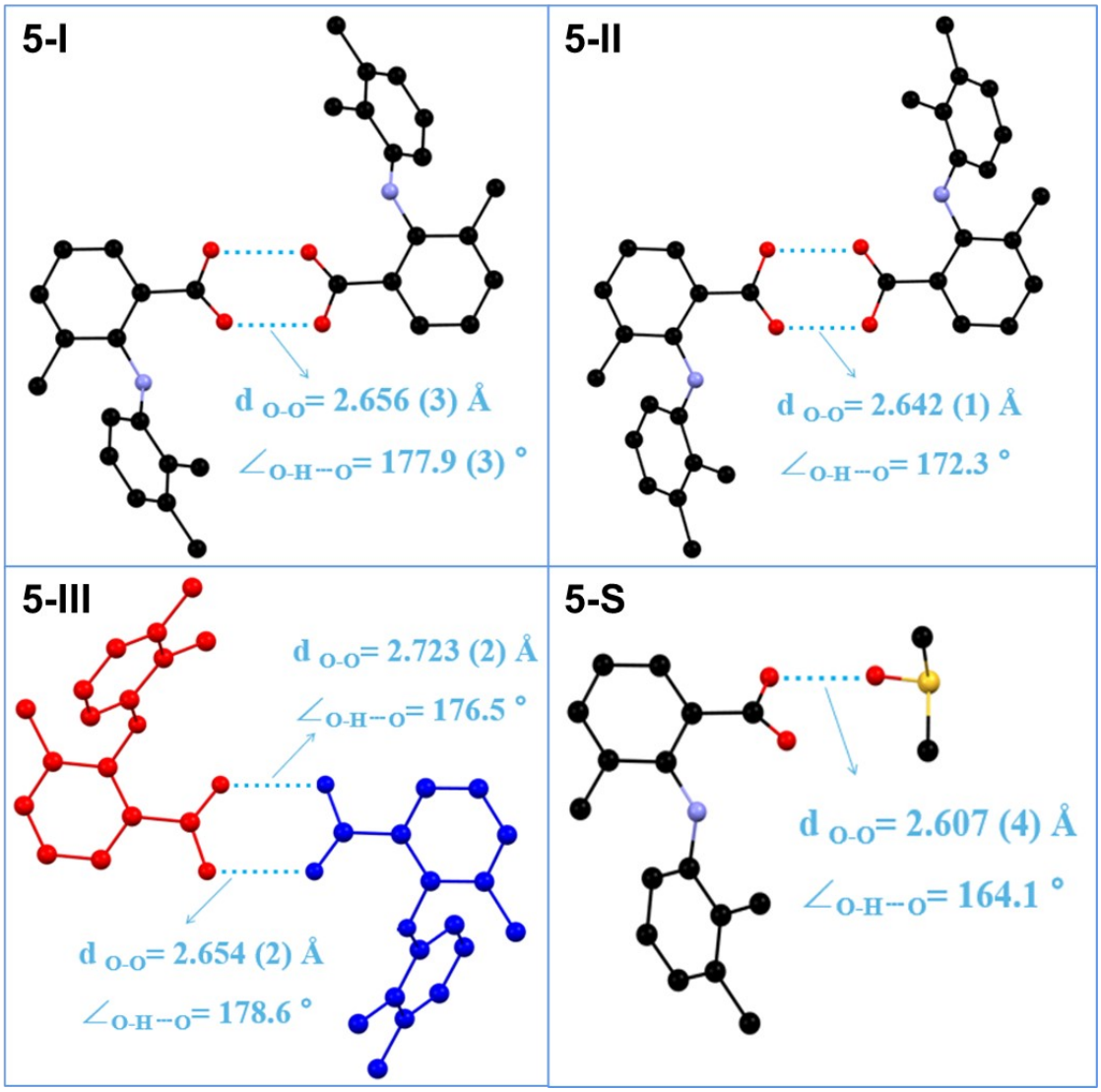


Figure S3 The acid-acid heterodimer motif (A: red; B: blue) in **5-I**, and homodimer in **5-II** and **5-III** (for clarity, H atoms not involved in hydrogen bonding are omitted)

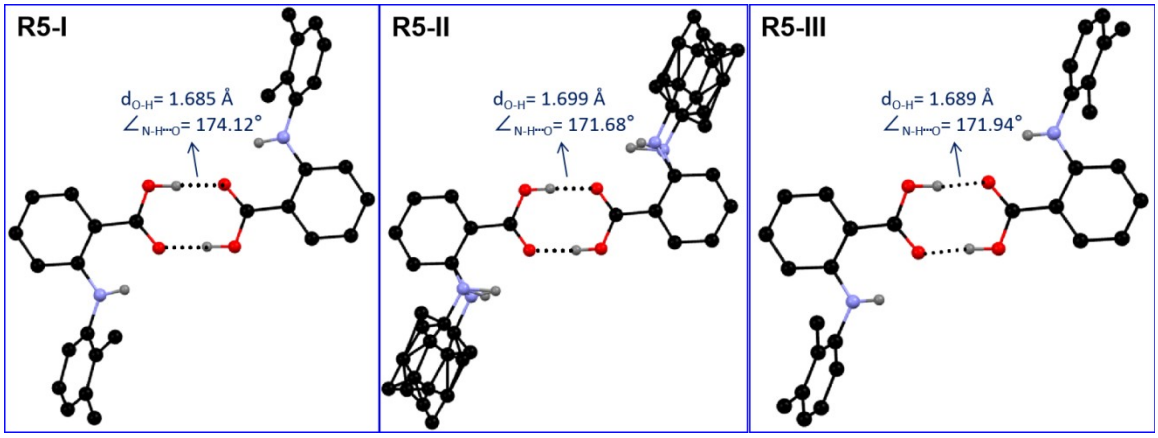


Figure S4 The acid-acid homodimer in **R5-I**, **R5-II** and **R5-III** (for clarity, H's not involved in hydrogen bonding are omitted)

PXRD

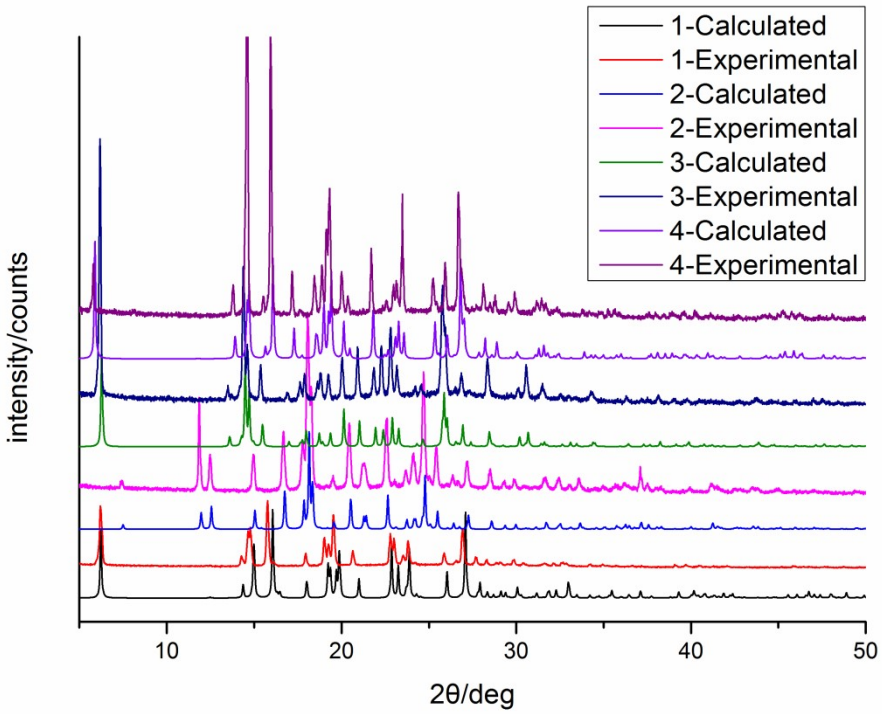


Figure S5 PXRD patterns of compounds **1-4**.

DSC

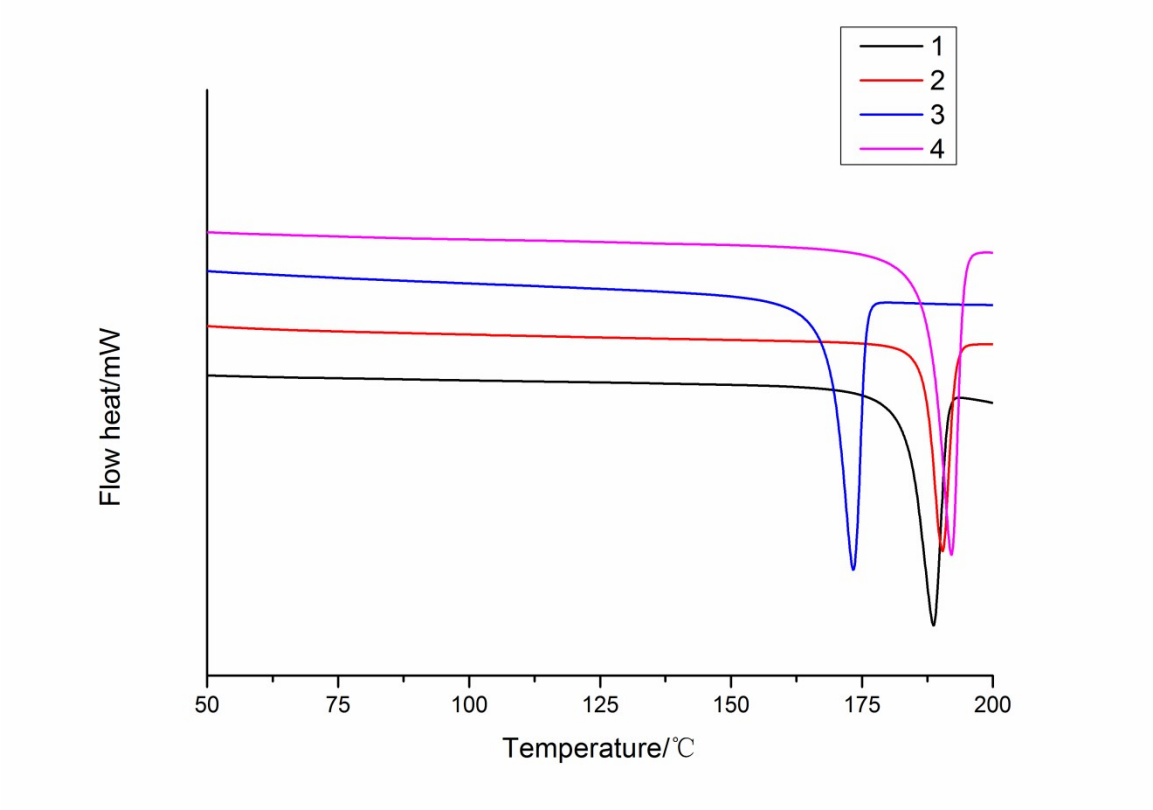


Figure S6 DSC thermograms of compounds **1**-**4**.

IR

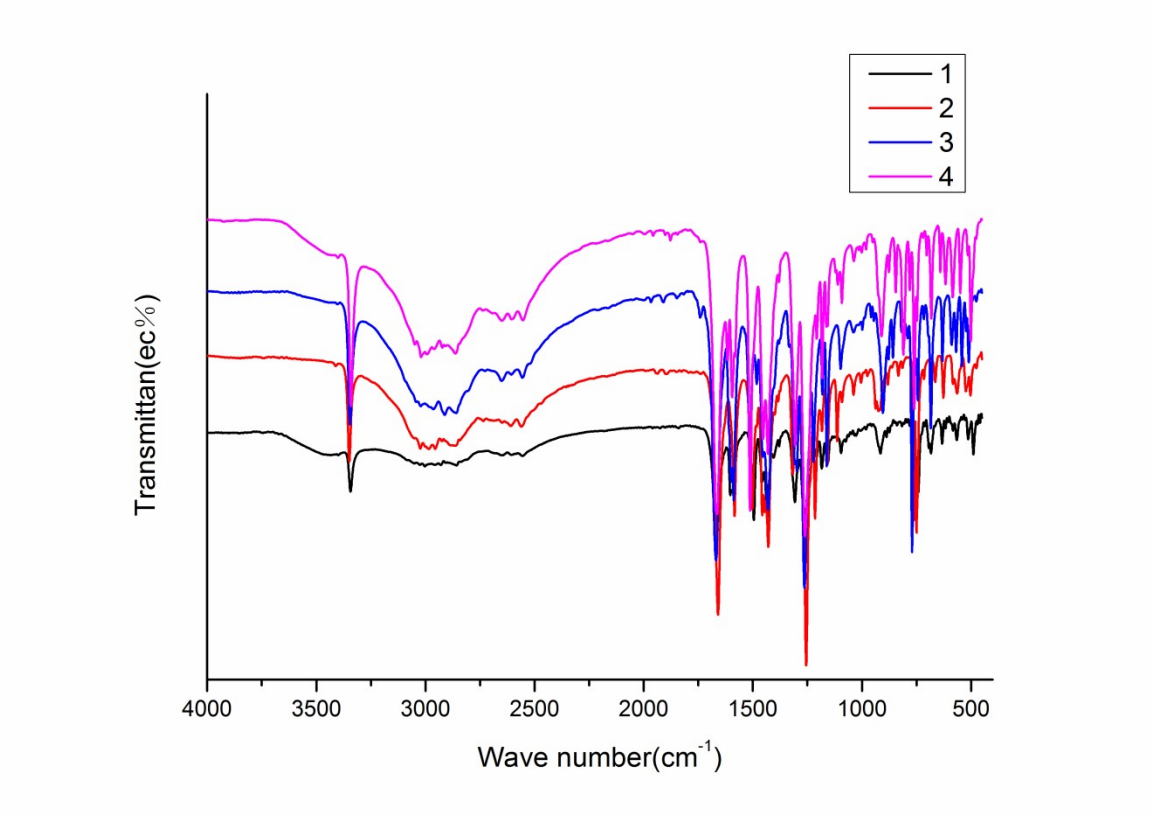


Figure S7 IR spectra of compound **1**-**4**.

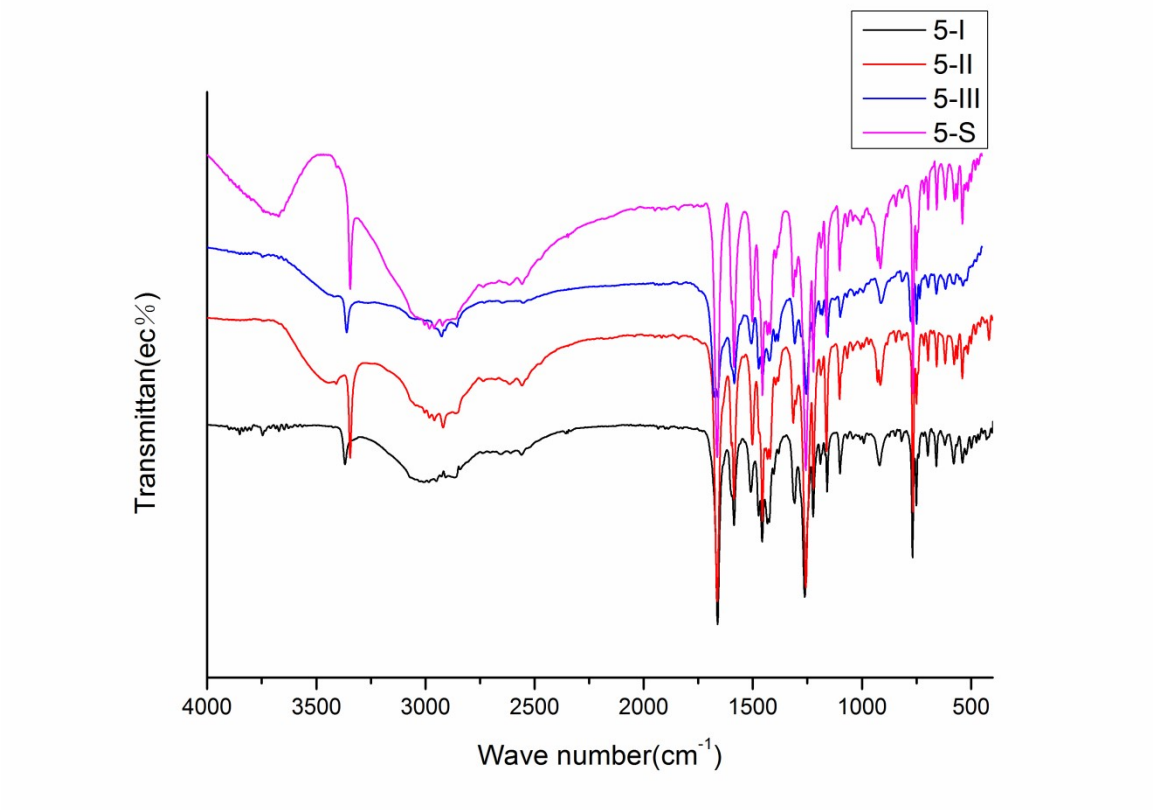
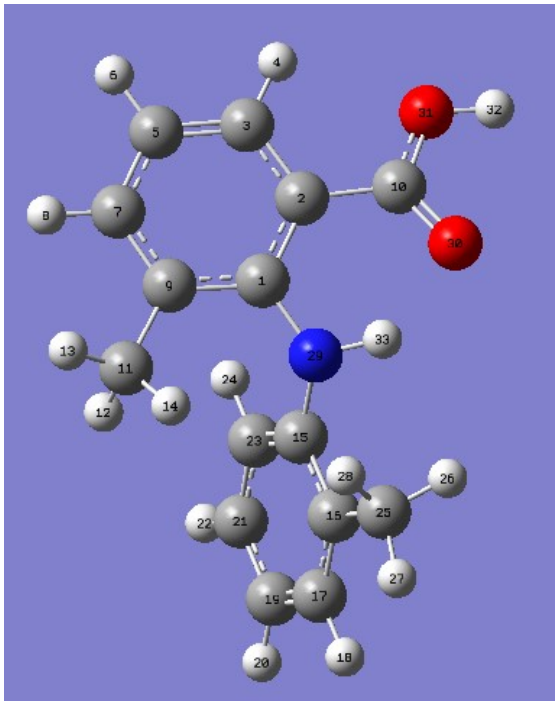


Figure S8 IR spectra of the three polymorphs and solvate of compound **5**.

Bond composition and bond order

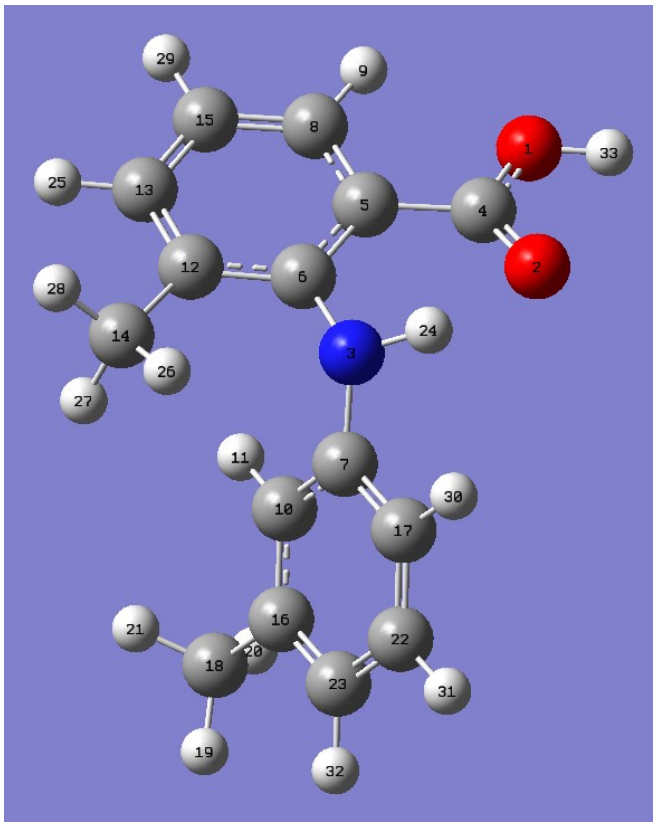
2



Bond composition: $\sigma_{CBAN} = 0.627(sp^{2.59})_C + 0.778(sp^{1.87})_N$; $\sigma_{CbenzeneN} = 0.622(sp^{2.72})_C + 0.783(sp^{1.95})_N$

Bond order: $C_{BA}N$ 0.981; $C_{benzene}N$ 0.976

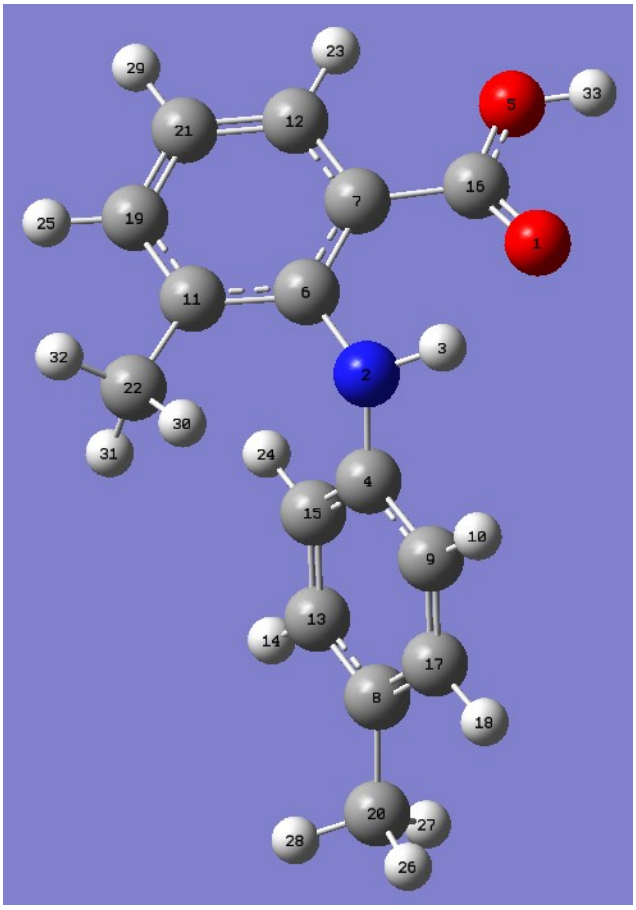
3



Bond composition: $\sigma_{CBAN} = 0.629(sp^{2.62})_C + 0.778(sp^{1.90})_N$; $\sigma_{CbenzezeN} = 0.623(sp^{2.71})_C + 0.782(sp^{1.91})_N$

Bond order: $C_{BA}N$ 0.980; $C_{benzene}N$ 0.975

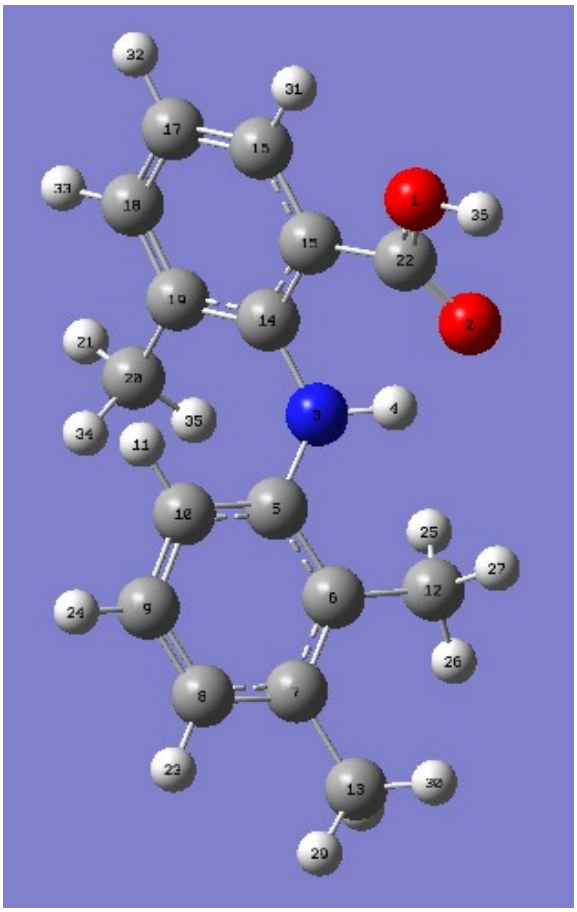
4



Bond composition: $\sigma_{CBAN} = 0.629(sp^{2.61})_C + 0.777(sp^{1.91})_N$; $\sigma_{CbenzeneN} = 0.624(sp^{2.62})_C + 0.782(sp^{1.90})_N$

Bond order: $C_{BA}N$ 0.980; $C_{benzene}N$ 0.976

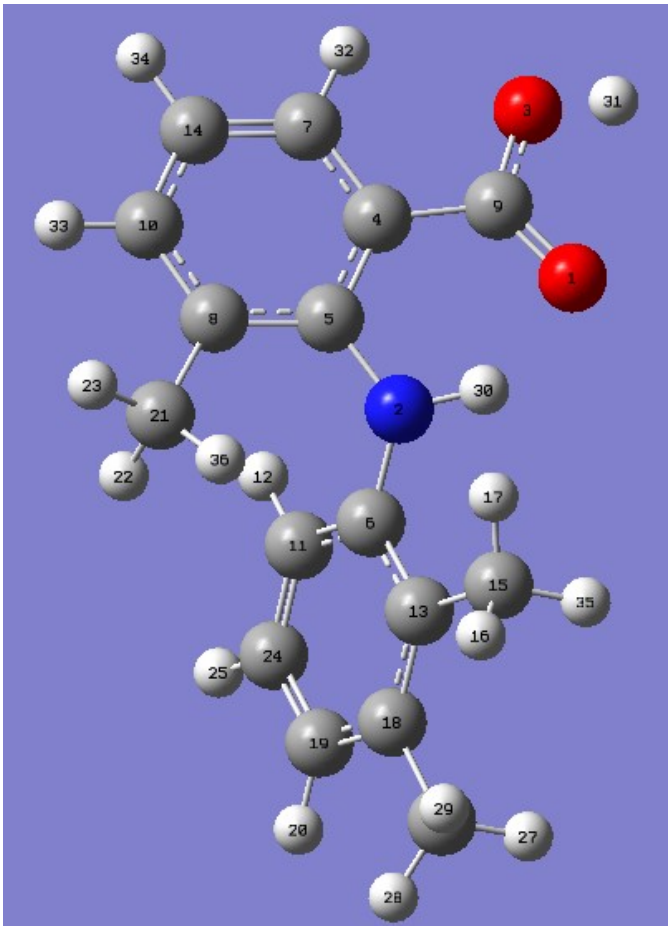
5-I



Bond composition: $\sigma_{CBAN} = 0.628(sp^{2.62})_C + 0.778(sp^{1.93})_N$; $\sigma_{CbenzeneN} = 0.622(sp^{2.73})_C + 0.783(sp^{1.88})_N$

Bond order: $C_{BA}N$ 0.979; $C_{benzene}N$ 0.975

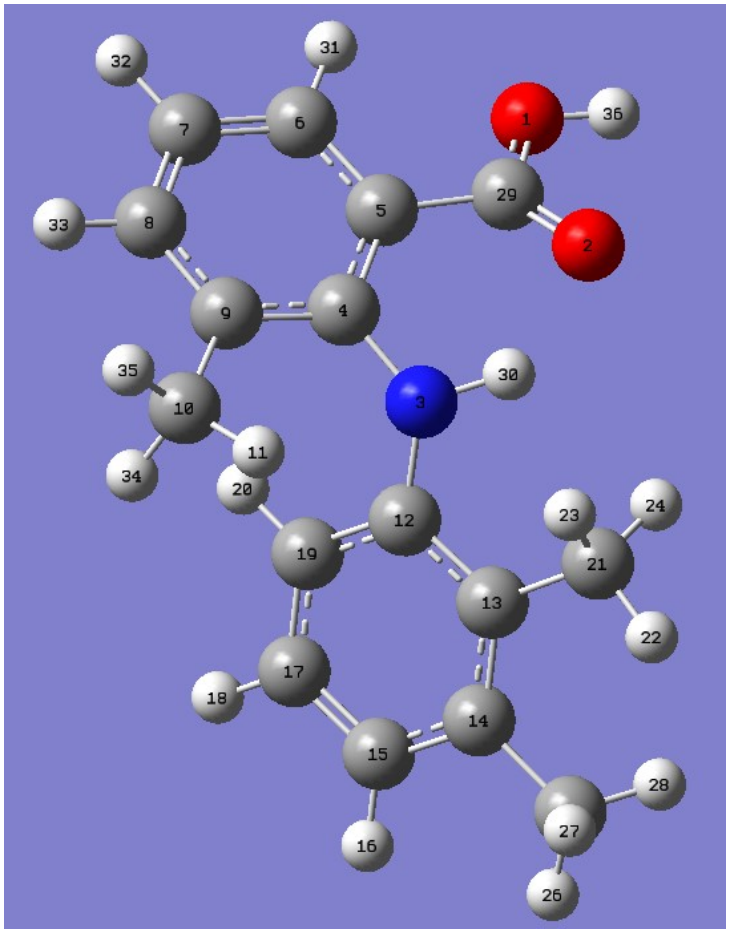
5-II



Bond composition: $\sigma_{CBAN} = 0.628(sp^{2.55})_C + 0.778(sp^{1.85})_N$; $\sigma_{CbenzeneN} = 0.621(sp^{2.75})_C + 0.784(sp^{1.92})_N$

Bond order: $C_{BA}N$ 0.981; $C_{benzene}N$ 0.976

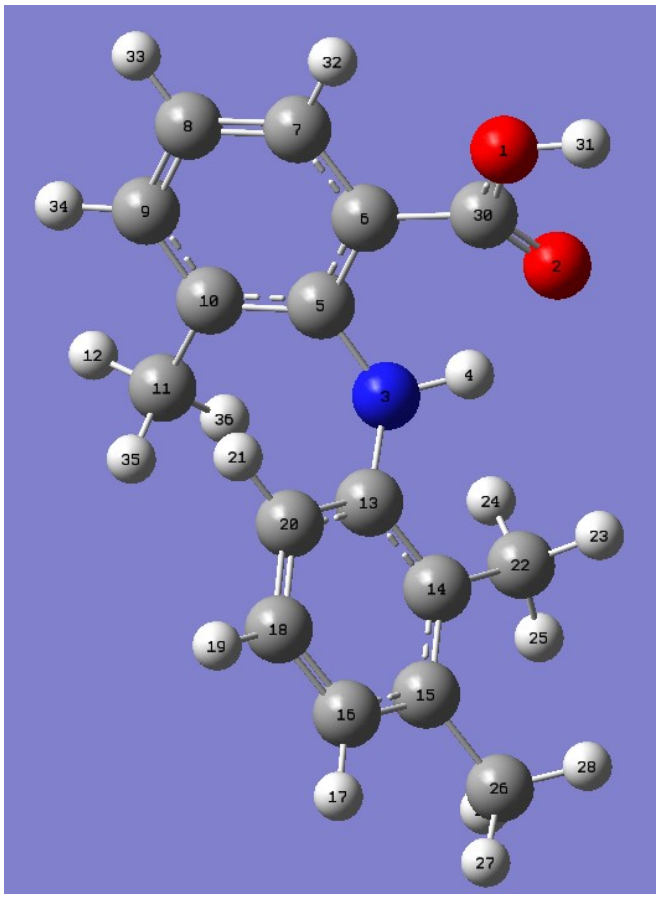
5-IIIA



Bond composition: $\sigma_{CBAN} = 0.628(sp^{2.58})_C + 0.778(sp^{1.88})_N$; $\sigma_{CbenzeneN} = 0.621(sp^{2.77})_C + 0.784(sp^{1.91})_N$

Bond order: $C_{BA}N$ 0.981; $C_{benzene}N$ 0.975

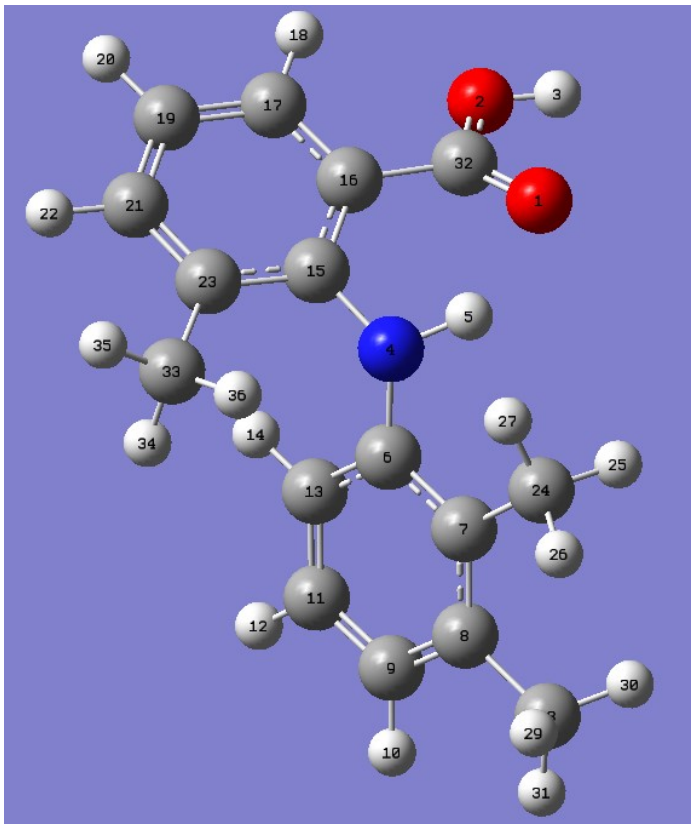
5-IIIB



Bond composition: $\sigma_{CBAN} = 0.629(sp^{2.62})_C + 0.777(sp^{1.94})_N$; $\sigma_{CbenzeneN} = 0.622(sp^{2.72})_C + 0.783(sp^{1.89})_N$

Bond order: $C_{BA}N$ 0.980; $C_{benzene}N$ 0.975

5-S



Bond composition: $\sigma_{CBAN} = 0.629(sp^{2.64})_C + 0.778(sp^{1.92})_N$; $\sigma_{CbenzeneN} = 0.621(sp^{2.75})_C + 0.784(sp^{1.84})_N$

Bond order: $C_{BA}N$ **0.980;** $C_{benzene}N$ **0.976**

Figure S9 **Bond composition and bond order of the two N-C bonds of compounds 2-5**