Supplementary Materials for

### Large Transition State Stabilization from a Weak Hydrogen Bond

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#### **1.** General experimental

NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm ( $\delta$ ) referenced to solvent residue. All spectra given for characterization purposes were taken at room temperature. All chemicals and solvents were purchased from commercial suppliers and used as received. Flash chromatography was performed using silica gel from Sorbent Technologies (60 Å, 200 – 400 mesh).

#### 2. Synthesis of the molecular rotors

The molecular rotors were prepared via a thermal condensation between a substituted aniline and a bicyclic anhydride,<sup>1</sup> and anisole rotors were prepared via a subsequent methylation reaction of the corresponding phenol rotors (Scheme S2.1. General route for synthesizing molecular rotors.). Rotor 2 (X = H) and 3 were prepared previously and their synthesis and characterization are not detailed here.<sup>1,2</sup> The rest of the rotors are newly reported compounds and fully characterized.



Scheme S2.1. General route for synthesizing molecular rotors.



cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.61 mmol) and 2aminophenol (73 mg, 0.67 mmol) were added to acetic acid (10 mL) in a round bottom flask with a magnetic stir bar. The round bottom flask was then heated to 120 °C in a silicon oil bath for 12 hours while stirring. After letting the round bottom flask cool to room temperature, the acetic acid was removed *in vacuo*. The crude material was then purified by column chromatography to give rotor **1** (X = H) as a white powder (135 mg, 87%). <sup>1</sup>H NMR (400 MHz, dichloromethane-d<sub>2</sub>)  $\delta$ 7.29 (ddd, *J* = 10.8, 9.0, 3.3 Hz, 1H), 7.04-6.95 (m, 3H), 6.27 (s, 2H), 5.76 (s, 1H), 3.46 (br, 4H), 1.78 (d, *J* = 11.9 Hz, 1H), 1.62 (d, *J* = 11.9 Hz, 1H). <sup>13</sup>C NMR (100 MHz, dichloromethane-d<sub>2</sub>) 177.33, 151.19, 134.86, 130.35, 128.26, 120.95, 120.20, 118.51, 52.27, 46.20, 45.51. HRMS (EI) *m/z* calculated for [C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 255.0895; found 255.0886.



rotor 1 (X = p-NO<sub>2</sub>)

cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.61 mmol) and 2-amino-4nitrophenol (103 mg, 0.67 mmol) were added to acetic acid (10 mL) in a round bottom flask with a magnetic stir bar. The round bottom flask was then heated to 120 °C in a silicon oil bath for 12 hours while stirring. After letting the round bottom flask cool to room temperature, the acetic acid was removed *in vacuo*. The crude material was then purified by column chromatography to give rotor **1** (X = *p*-NO<sub>2</sub>) as an orange powder (123 mg, 67%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  10.06 (br, 1H), 8.07 (dd, *J* = 2.8, 9.0 Hz, 1H), 7.75 (d, *J* = 2.8 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.15 (t, *J* = 1.7 Hz, 1H), 3.45-3.44 (m, 2H), 3.27-3.25 (m, 2H), 1.59-1.55 (m, 2H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)  $\delta$  175.76, 159.40, 140.29, 134.65, 126.05, 125.89, 120.39, 116.80, 51.79, 46.24, 45.12. HRMS (EI) *m/z* calculated for [C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>]<sup>+</sup> (M<sup>+</sup>): 300.0746; found 300.0748.



cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.61 mmol) and 2-amino-5nitrophenol (103 mg, 0.67 mmol) were added to acetic acid (10 mL) in a round bottom flask with a magnetic stir bar. The round bottom flask was then heated to 120 °C in a silicon oil bath for 12 hours while stirring. After letting the round bottom flask cool to room temperature, the acetic acid was removed *in vacuo*. The crude material was then purified by column chromatography to give rotor 1 (X = *m*-NO<sub>2</sub>) as an orange powder (128 mg, 70%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  9.50 (br, 1H), 7.67 (d, *J* = 2.5 Hz, 1H), 7.63 (dd, *J* = 2.5, 8.6 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.13 (t, *J* = 1.8 Hz, 2H), 3.44-3.43 (m, 2H), 3.27-3.25 (m, 2H), 1.56 (t, *J* = 1.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>) 175.65, 154.02, 148.79, 134.64, 130.69, 126.29, 114.32, 111.31, 51.76, 46.24, 45.17. HRMS (EI) *m/z* calculated for [C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>]<sup>+</sup> (M<sup>+</sup>): 300.0746; found 300.0752.



cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.61 mmol) and 2-amino-4chlorophenol (96 mg, 0.67 mmol) were added to acetic acid (10 mL) in a round bottom flask with a magnetic stir bar. The round bottom flask was then heated to 120 °C in a silicon oil bath for 12 hours while stirring. After letting the round bottom flask cool to room temperature, the acetic acid was removed *in vacuo*. The crude material was then purified by column chromatography to give rotor 1 (X = p-Cl) as a white powder (150 mg, 85%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  8.83 (br, 1H), 7.28 (dd, *J* = 2.6, 8.8 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 2.6 Hz, 1H), 6.28 (t, *J* = 1.9 Hz, 2H), 3.53-3.52 (m, 2H), 3.39-3.38 (m, 2H), 1.72-1.67 (m, 2H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)  $\delta$  175.93, 152.48, 134.62, 129.84, 129.11, 123.07, 121.28, 117.98, 51.72, 46.03, 45.10. HRMS *m/z* calculated for [C<sub>15</sub>H<sub>12</sub>ClNO<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 289.0506; found 289.0516.





cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.61 mmol) and 2-amino-5chlorophenol (96 mg, 0.67 mmol) were added to acetic acid (10 mL) in a round bottom flask with a magnetic stir bar. The round bottom flask was then heated to 120 °C in a silicon oil bath for 12 hours while stirring. After letting the round bottom flask cool to room temperature, the acetic acid was removed *in vacuo*. The crude material was then purified by column chromatography to give rotor **1** (X = *m*-Cl) as a white powder (144 mg, 82%).<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  9.01 (br, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.96-6.90 (m, 2H), 6.24 (t, *J* = 1.8 Hz, 2H), 3.52-3.51 (m, 2H), 3.39-3.36 (m, 2H), 1.71-1.66 (m, 2H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)  $\delta$  175.93, 152.48, 134.62, 129.84, 129.11, 123.07, 121.28, 117.98, 51.72, 46.03, 45.10. HRMS *m/z* calculated for [C<sub>15</sub>H<sub>12</sub>ClNO<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 289.0506; found 289.0509.



rotor **1** (X = p-CN)

cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.61 mmol) and 2-amino-4cyanophenol (96 mg, 0.67 mmol) were added to acetic acid (10 mL) in a round bottom flask with a magnetic stir bar. The round bottom flask was then heated to 120 °C in a silicon oil bath for 12 hours while stirring. After letting the round bottom flask cool to room temperature, the acetic acid was removed *in vacuo*. The crude material was then purified by column chromatography to give rotor **1** (X = *p*-CN) as a white powder (123 mg, 72%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  9.81 (br, 1H), 7.68 (dd, *J* = 2.0, 8.6 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.30 (t, *J* = 1.6 Hz, 2H), 3.56-3.55 (m, 2H), 3.40-3.38 (m, 2H), 1.72-1.68 (m, 2H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)  $\delta$  175.85, 157.57, 134.67, 134.35, 134.02, 121.08, 117.96, 117.80, 102.87, 51.70, 46.10, 45.15. HRMS *m/z* calculated for [C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 280.0848; found 280.0860.



Potassium carbonate (223 mg, 1.83 mmol) and iodomethane (0.095 mL, 1.52 mmol) were both added to rotor **1** (X = H) (50 mg, 0.20 mmol) in a round bottom flask with 25 mL of acetone and a stir bar. The round bottom was then stirred at room temperature for 12 hours. The acetone was removed using a rotary evaporator. The crude product was then purified by column chromatography to yield rotor **2** (X = H) as a white powder (52 mg, 99%). <sup>1</sup>H NMR (400 MHz, dichloromethane-d<sub>2</sub>)  $\delta$  7.41-7.28 (m, 1H *folded* and *unfolded*), 7.08-6.91 (m, 3H *folded* and *unfolded*), 6.30 (s, 2H *unfolded*), 6.23 (s, 2H *folded*), 3.80 (s, 3H *folded* and *unfolded*), 3.50-3.43 (m, 4H *folded* and *unfolded*), 1.82-1.77 (m, 1H *folded* and *unfolded*), 1.64-1.59 (m, 1H *folded* and *unfolded*). <sup>13</sup>C NMR has been reported previously.<sup>1</sup> HRMS *m/z* calculated for [C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 269.1052; found 269.1057.



rotor **1** (X = 
$$p$$
-NO<sub>2</sub>)

rotor 2 (X = p-NO<sub>2</sub>)

Potassium carbonate (223 mg, 1.83 mmol) and iodomethane (0.095 mL, 1.52 mmol) were both added to rotor **1** (X = p-NO<sub>2</sub>) (50 mg, 0.17 mmol) in a round bottom flask with 25 mL of acetone and a stir bar. The round bottom was then stirred at room temperature for 12 hours. The acetone was removed using a rotary evaporator. The crude product was then purified by column chromatography to yield rotor **2** (X = p-NO<sub>2</sub>) as a white powder (52 mg, 99%). <sup>1</sup>H NMR (400 MHz, tetrachloroethane-d<sub>2</sub>)  $\delta$  8.36-8.33 (m, 1H *folded* and *unfolded*), 8.03 (d, J = 2.7 Hz, 1H *folded*), 7.83 (d, J = 2.7 Hz, 1H un*folded*), 7.12-7.09 (m, 1H *folded* and *unfolded*), 6.36 (s, 2H *unfolded*), 6.23 (s, 2H *folded*), 3.94 (s, 3H *unfolded*), 3.93 (s, 3H *folded*), 3.55-3.50 (m, 4H *folded* and *unfolded*), 1.86-1.81 (m, 1H *folded* and *unfolded*), 1.66-1.63 (m, 1H *folded* and *unfolded*). <sup>13</sup>C NMR (100 MHz, chloroform-d<sub>1</sub>)  $\delta$  176.02, 175.86, 160.02, 159.89, 141.10, 140.98, 134.77, 134.53, 126.74, 126.65, 126.05, 125.55, 121.17, 121.08, 111.65, 111.64, 56.70, 56.42, 52.51, 52.18, 46.71, 46.23, 45.44, 45.36. HRMS *m/z* calculated for [C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>5</sub>]<sup>+</sup> (M<sup>+</sup>): 314.0903; found 314.0911.



Potassium carbonate (223 mg, 1.83 mmol) and iodomethane (0.095 mL, 1.52 mmol) were both added to rotor **1** (X = *m*-NO<sub>2</sub>) (50 mg, 0.17 mmol) in a round bottom flask with 25 mL of acetone and a stir bar. The round bottom was then stirred at room temperature for 12 hours. The acetone was removed using a rotary evaporator. The crude product was then purified by column chromatography to yield rotor **2** (X = *m*-NO<sub>2</sub>) as a white powder (52 mg, 99%). <sup>1</sup>H NMR (400 MHz, chloroform-d<sub>1</sub>)  $\delta$  7.84-7.79 (m, 1H *folded* and *unfolded*), 7.77-7.76 (m, 1H *folded* and *unfolded*), 7.17 (d, *J* = 8.6 Hz, 1H *folded*), 7.02 (d, *J* = 8.6 Hz, 1H *unfolded*), 6.23 (s, 2H *unfolded*), 6.15 (s, 2H *folded*), 3.83 (s, 3H *folded* and *unfolded*), 3.44-3.39 (m, 4H *folded* and *unfolded*), 1.76-1.71 (m, 1H *folded* and *unfolded*), 1.58-1.53 (m, 1H *folded* and *unfolded*).<sup>13</sup>C NMR (100 MHz, chloroform-d<sub>1</sub>)  $\delta$  175.85, 175.68, 155.44, 155.31, 149.09, 149.03, 134.75, 134.51, 130.21, 129.82, 126.74, 126.67, 115.90, 115.86, 107.39, 107.36, 56.52, 56.28, 52.50, 52.19, 46.77, 46.31, 45.42. HRMS m/z calculated for [C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>5</sub>]<sup>+</sup> (M<sup>+</sup>): 314.0903; found 314.0915.



rotor **1** (X = *p*-Cl)

rotor 2 (X = p-Cl)

Potassium carbonate (223 mg, 1.83 mmol) and iodomethane (0.095 mL, 1.52 mmol) were both added to rotor **1** (X = *p*-Cl) (50 mg, 0.17 mmol) in a round bottom flask with 25 mL of acetone and a stir bar. The round bottom was then stirred at room temperature for 12 hours. The acetone was removed using a rotary evaporator. The crude product was then purified by column chromatography to yield rotor **2** (X = *p*-Cl) as a white powder (52 mg, 99%). <sup>1</sup>H NMR (400 MHz, tetrachloroethane-d<sub>2</sub>)  $\delta$  7.31- 7.28 (m, 1H *folded* and *unfolded*), 6.99 (d, *J* = 2.6 Hz, 1H *folded*), 6.87-6.84 (m, 1H *folded* and *unfolded*), 6.80 (d, *J* = 2.6 Hz, 1H *unfolded*), 6.19 (br, 2H *unfolded*), 6.10 (t, *J* = 1.6 Hz, 1H *folded*), 3.69 (s, 3H *unfolded*), 3.68 (s, 3H *folded*), 3.40-3.32 (m, 4H *folded* and *unfolded*), 1.72-1.67 (m, 1H *folded* and *unfolded*), 1.53-1.48 (m, 1H *folded* and *unfolded*). <sup>13</sup>C NMR (101 MHz, tetrachloroethane -d<sub>2</sub>)  $\delta$  176.43, 176.30, 153.84, 153.74, 134.77, 134.56, 130.62, 130.53, 129.63, 129.13, 125.24, 125.10, 121.80, 121.67, 113.40, 113.36, 56.39, 56.15, 52.57, 52.23, 46.70, 46.18, 45.49, 45.46. HRMS *m/z* calculated for [C<sub>16</sub>H<sub>14</sub>CINO<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 303.0662; found 303.0675.



Potassium carbonate (223 mg, 1.83 mmol) and iodomethane (0.095 mL, 1.52 mmol) were both added to rotor **1** (X = *m*-Cl) (50 mg, 0.17 mmol) in a round bottom flask with 25 mL of acetone and a stir bar. The round bottom was then stirred at room temperature for 12 hours. The acetone was removed using a rotary evaporator. The crude product was then purified by column chromatography to yield rotor **2** (X = *m*-Cl) as a white powder (52 mg, 99%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  7.84-7.80 (m, 1H *folded* and *unfolded*), 7.52 (d, *J* = 2.2 Hz, 1H *folded*), 7.38 (d, *J* = 2.2 Hz, 1H *unfolded*), 7.34-7.29 (m, 1H *folded* and *unfolded*), 6.34 (t, *J* = 1.8 Hz, *unfolded*), 6.18 (t, *J* = 1.8 Hz, *folded*), 3.91 (s, 3H *folded*), 3.89 (s, 3H *unfolded*), 3.58-3.50 (m, 2H *folded* and *unfolded*), 1.72-1.65 (m, 2H *folded* and *unfolded*). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)  $\delta$  175.52, 175.40, 158.88, 158.87, 134.95, 134.69, 134.42, 133.58, 133.18, 122.80, 122.44, 117.83, 117.72, 113.25, 113.19, 103.73, 103.54, 56.00, 55.69, 51.77, 51.65, 46.50, 45.78, 45.23, 45.03. HRMS *m/z* calculated for [C<sub>16</sub>H<sub>14</sub>ClNO<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 303.0662; found 303.0674.



rotor **1** (X = *p*-CN)

rotor 2 (X = p-CN)

Potassium carbonate (223 mg, 1.83 mmol) and iodomethane (0.095 mL, 1.52 mmol) were both added to rotor **1** (X = *p*-CN) (50 mg, 0.18 mmol) in a round bottom flask with 25 mL of acetone and a stir bar. The round bottom was then stirred at room temperature for 12 hours. The acetone was removed using a rotary evaporator. The crude product was then purified by column chromatography to yield rotor **2** (X = *p*-CN) as a white powder (52 mg, 99%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  7.16 (d, *J* = 2.1 Hz, 1H *unfolded*), 7.13 (d, *J* = 2.1 Hz, 1H *folded*), 7.08 (d, *J* = 8.3 Hz, 1H *unfolded*), 7.02-7.00 (m, 1H *folded* and *unfolded*), 6.93 (d, *J* = 8.3 Hz, 1H *folded*), 6.25 (t, *J* = 1.8 Hz, 2H *unfolded*), 6.16 (t, *J* = 1.8 Hz, 2H *folded*), 3.82 (s, 3H, *folded*), 3.81 (s, 3H, *unfolded*), 3.53-3.46 (m, 2H *folded* and *unfolded*), 3.38-3.34 (m, 2H *folded* and *unfolded*), 1.70-1.63 (m, 2H *folded* and *unfolded*). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)  $\delta$  175.73, 175.61, 156.04, 156.03, 135.06, 134.88, 134.56, 134.37, 130.80, 130.48, 120.91, 120.59, 120.30, 120.21, 112.79, 112.75, 55.81, 55.53, 51.81, 51.60, 46.39, 45.67, 45.18, 44.98. HRMS *m/z* calculated for [C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>]<sup>+</sup> (M<sup>+</sup>): 294.1004; found 294.1010.

### 3. <sup>1</sup>H and <sup>13</sup>C NMR spectra



Figure S3.1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 1 (X = H) (400 and 100 MHz, dichloromethane- $d_2$ )



Figure S3.2. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 1 (X = p-NO<sub>2</sub>) (400 and 100 MHz, acetone-d<sub>6</sub>)



Figure S3.3. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 1 (X = m-NO<sub>2</sub>) (400 and 100 MHz, acetone-d<sub>6</sub>)



Figure S3.4. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 1 (X = p-Cl) (400 and 100 MHz, acetone-d<sub>6</sub>)



Figure S3.5. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 1 (X = m-Cl) (400 and 100 MHz, acetone-d<sub>6</sub>)



Figure S3.6. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 1 (X = p-CN) (400 and 100 MHz, acetone-d<sub>6</sub>)



Figure S3.7. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 2 (X = p-NO<sub>2</sub>) (400 and 100 MHz, tetrachloroethane-d<sub>2</sub>)

m-NO<sub>2</sub> anisole Rotor <sup>1</sup>H NMR Spectrum Solvent – chloroform-d<sub>1</sub> Solvent residue signal – 7.19



Figure S3.8. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 2 (X = m-NO<sub>2</sub>) (400 and 100 MHz, chloroform-d<sub>1</sub>)

p-Cl anisole Rotor <sup>1</sup>H NMR Spectrum Solvent – tetrachloroethane-d<sub>2</sub> Solvent residue signal – 5.92



Figure S3.9. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 2 (X = p-Cl) (400 and 100 MHz, acetone-d<sub>6</sub>)

m-Cl anisole Rotor <sup>1</sup>H NMR Spectrum Solvent – acetone-d<sub>6</sub> Solvent residue signal – 2.07



Figure S3.10. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 2 (X = m-Cl) (400 and 100 MHz, acetone-d<sub>6</sub>)





Figure S3.11. <sup>1</sup>H and <sup>13</sup>C NMR spectra of rotor 2 (X = p-CN) (400 and 100 MHz, acetone-d<sub>6</sub>)

#### 4. Experimental measurement of rotational barriers

The rotational barriers of rotors 1 and 2 were determined via coalescence temperature analysis, which was corroborated by NMR line-shape analysis and EXSY experiments of chemically exchanging signals (Table S4.1. Experimental rotational barrier ( $\Delta G_{\pm}^{\pm}$ , kcal/mol) for rotors 1, 2, and 3 via coalescence temperature and line-shape analyses. Table S4.2. Experimental rotational barriers ( $\Delta G^{\ddagger}$ , kcal/mol) for rotors 1, 2, and 3 via EXSY.). These chemical exchange experiments were carried out in accordance with literature precedence.<sup>3–5</sup> The rotational barrier for each rotor was obtained from the coalescence temperature analysis using Equations S1-2. Lineshape analysis was performed using the Bruker Topspin software (Figure S4.1. <sup>1</sup>H NMR exchange line-shape analysis for unsubstituted phenol rotor 1 in dichloromethane-d<sub>2</sub> showing the overlaid experimental (blue lines) and simulated (green lines) traces.). The TS enthalpy ( $\Delta H^{\ddagger}$ ) and entropy  $(\Delta S^{\ddagger})$  for rotors 1, 2, and 3 were obtained from the Eyring plots (Figure S4.2. Eyring plots for rotors 1, 2 and 3 from line-shape analysis) following Equation S3. The rotation barriers were determined by plugging the enthalpy and entropy along with a temperature into Equation S4. Due to the limitation of our equipment, only a single temperature is used to calculated the rotational barrier of rotor 1 via EXSY, however all other rotational barriers that were calculated by lineshape analysis or EXSY have 4 rate measurements or more to construct the Eyring plots from which their rotational barriers were calculated.

Due to the large difference in coalescence temperatures for rotor 1, 2, and 3 two different solvents with similar chemical properties but different melting/boiling temperatures were chosen. Dichloromethane-d<sub>2</sub> (melting point = -95, boiling point = 40 °C) was an appropriate choice as a solvent for rotor 1 which have an average coalescence temperature of -61 °C. Meanwhile, tetrachloroethane-d<sub>2</sub> (melting point = -45, boiling point = 145 °C) was an appropriate choice as a solvent for rotor 2 and 3 which have an average coalescence temperature of 97 °C.

F	Rotor		coalescence temperature			line-shape analysis		
label	Х	$\Delta G^{\ddagger a}$	Temperature (Celsius)	Rate (k <sub>c</sub> )	$\Delta G^{\ddagger ab}$	$\Delta G^{\ddagger ab}$ $\Delta H^{\ddagger a}$ $\Delta S^{\ddagger a}$		k <sub>H</sub> /k <sub>D</sub>
1	Н	10.89	-55	54.40	10.75	10.58	-5.68 x 10 <sup>-4</sup>	
1	Н	10.91	-55	52.26				
1	Н	10.91	-55	52.27				0.926 <sup>e</sup>
1	Н	10.77	-57	56.71				
1	Н	10.87	-55	58.04				
1	p-NO <sub>2</sub>	9.73	-67	202.12				
1	m-NO <sub>2</sub>	9.99	-62	196.26				
1	p-Cl	10.39	-60	97.15				
1	m-Cl	10.08	-65	111.99				
1	p-CN	9.96	-65	147.19				
2	Н	20.77	113	12.89	20.14	20.16	6.19 x 10 <sup>-5</sup>	
2	p-NO <sub>2</sub>	19.35	82	8.98				
2	m-NO <sub>2</sub>	19.58	86	8.98				
2	p-Cl	20.11	98	10.93				
2	m-Cl	20.15	95	8.18				
2	p-CN	20.36	103	11.47				

**Table S4.1.** Experimental rotational barrier ( $\Delta G^{\ddagger}$ , kcal/mol) for rotors 1, 2, and 3 via coalescence temperature and line-shape analyses.

3	Н	21.42	137.5	15.077	19.14	15.04	-1.38 x 10 <sup>-2</sup>		
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*a* energy in kcal/mol. <sup>b</sup> at 298.15 K. <sup>c</sup> mixed with  $H_2O$ . <sup>d</sup> mixed with  $D_2O$ , no phenolic signal was observed in the <sup>1</sup>H NMR spectra. <sup>e</sup> Average isotope effect.

Dotor		rotational barrier (kcal/mol)						Town ougtures (°C)
Kolor		$syn \rightarrow anti$			anti <del>→</del> syr	average $\Delta \mathrm{G}^{\ddagger}$	Temperature (C)	
	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$T\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$T\Delta S^{\ddagger}$		
<b>1</b> <sup>b</sup>	10.91	-	-	11.32	-	-	11.12	-75
2	20.26ª	20.22	-0.036ª	20.14 <sup>a</sup>	20.16	0.017ª	20.20ª	60 to 75
3	21.00 <sup>a</sup>	20.54	-0.46ª	21.01ª	20.18	-0.84ª	21.01ª	70 to 90

**Table S4.2.** Experimental rotational barriers ( $\Delta G^{\ddagger}$ , kcal/mol) for rotors 1, 2, and 3 via EXSY.

<sup>a</sup> at 298.15 K. <sup>b</sup> values calculated based on a single temperature

$$\Delta G^{\dagger} = -R \times T_{c} \times \ln(\frac{k_{c}h}{k_{B}T_{c}})$$
 (Eqn S1)

where

$$k_c = \frac{\pi \times \Delta v}{\sqrt{2}}$$
 (Eqn

$$\ln(\frac{k_{ex}}{T}) = \frac{-\Delta H^{\ddagger}}{R} \times \frac{1}{T} + \ln(\frac{k_{B}}{h}) + \frac{-\Delta S^{\ddagger}}{R} \quad (Eqn \ S3);$$

 $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \times \Delta S^{\ddagger}$ 

 $\Delta G^{*}$ : Gibb's free energy of the rotational barrier

**R**: gas constant

**T**<sub>c</sub> : coalescence temperature (/K) **S2**);  $k_c$  : exchange rate at **T**<sub>c</sub>

 $k_{_B}$ : Boltzmann's constant

 $\Delta v$ : peak difference (/Hz) at a slow exchange regime

 $k_{ex}$  : exchange rate

ΔH<sup>‡</sup> : Ethalpy change in the rotational barrier

(Eqn S4)  $\Delta S^{\dagger}$ : Entropy change in the rotational barrier



Figure S4.1. <sup>1</sup>H NMR exchange line-shape analysis for unsubstituted phenol rotor 1 in dichloromethane- $d_2$  showing the overlaid experimental (blue lines) and simulated (green lines) traces.



Figure S4.2. Eyring plots for rotors 1, 2 and 3 from line-shape analysis

#### 5. Intermolecular hydrogen bond association measurements

The intermolecular hydrogen bond strength between *N*-methylpyrrolidone (NMP) and substituted phenols (*p*-NO<sub>2</sub>, m-NO<sub>2</sub>, p-CN, m-Cl, p-t-Amyl, p-Cl, and H) were measured (Scheme S5.1. Intermolecular hydrogen bond between *N*-methylpyrrolidone (NMP) and a substituted phenol.) in dichloromethane- $d_2$  to gauge the strength of the intramolecular hydrogen bond in rotor **1**. NMP was chosen due to its structural similarity to the hydrogen bond acceptor imide in rotor **1** and its convenience of handling in titration experiment.



Scheme S5.1. Intermolecular hydrogen bond between *N*-methylpyrrolidone (NMP) and a substituted phenol.

The association constants for the hydrogen bonded complexes of NMP with substituted phenols in dichloromethane-d<sub>2</sub> were measured via <sup>1</sup>H NMR titration experiments. The change in chemical shift ( $\Delta\delta$ ) of phenolic proton was monitored as NMP guest was gradually added into the (substituted) phenol host solution (20 mmol/L) in dichloromethane-d<sub>2</sub>. Subsequent addition of NMP continued until the phenol protons chemical shift remained constant.<sup>6</sup> The association constants (K<sub>a</sub>) were obtained through fitting the experimental binding isotherm using Equations S1-4. An example of the fitted and experimental isotherms for the host-guest complex of *m*-nitrophenol and NMP is shown in Figure S5.1. Experimentally measured and fitted isotherms (in dichloromethane-d<sub>2</sub>) of NMP (guest) binding of *m*-nitrophenol (host) based on chemical shift change ( $\Delta\delta$ ) of the phenolic proton as NMP guest was gradually added.. The Gibbs free association energies ( $\Delta G_{Ka}$ ) of the hydrogen bonded host-guest complexes were then calculated from the measured association constants ( $\Delta G_{Ka} = -R \times T \times \ln K_a$ ) and tabulated in Table S5.1. Gibbs free association energy ( $\Delta G_{Ka}$ , kcal/mol)<sup>*a*</sup> for the hydrogen bonded host-guest complexes of *N*-methyl pyrrolidone and (substituted) phenols in dichloromethane-d<sub>2</sub>

$$\Delta \delta_{i} = \frac{[H]_{free}}{[H]_{i}} \times \Delta \delta_{HG} + \Delta \delta_{HG}$$
 (Eqn S1)

where

$$[\mathbf{H}]_{i} = \frac{[\mathbf{H}]_{o} \times \mathbf{V}_{o}}{\mathbf{V}_{i}}$$
(Eqn S2);

$$[\mathbf{G}]_{i} = \frac{[\mathbf{G}]_{o} \times (\mathbf{V}_{i} - \mathbf{V}_{o})}{\mathbf{V}_{i}}$$
(Eqn S3);

$$[H]_{free} = \frac{\sqrt{b^2 - 4 \times (\frac{K_a}{1000}) \times V_i}}{2 \times (\frac{K_a}{1000})} \qquad (Eqn S4);$$



4.50

4.00

3.50

3.00





Figure S5.1. Experimentally measured and fitted isotherms (in dichloromethane-d<sub>2</sub>) of NMP (guest) binding of *m*-nitrophenol (host) based on chemical shift change ( $\Delta\delta$ ) of the phenolic proton as NMP guest was gradually added.

**Table S5.1.** Gibbs free association energy  $(\Delta G_{Ka}, \text{kcal/mol})^a$  for the hydrogen bonded host-guest complexes of N-methyl pyrrolidone and (substituted) phenols in dichloromethane-d<sub>2</sub>

Host	Substituent on phenol guest	$\Delta G_{Ka}$ (kcal/mol)
NMP	$p-NO_2$	-3.40
NMP	<i>m</i> -NO <sub>2</sub>	-3.09
NMP	p-Cl	-2.05
NMP	<i>m</i> -Cl	-2.71
NMP	<i>p</i> -CN	-2.97
NMP	<i>p-t</i> -Amyl	-2.15
NMP	Н	-1.49

<sup>*a*</sup>  $\Delta G_{Ka}$  values were measured at 25 °C with an error of less than  $\pm 10$  %.

#### 6. Computational studies

#### 6.1 Rotational barrier calculations

Following instructions from a benchmark study on determining the accurate level of theory for rotational barriers, we optimized the ground state and transition state for our rotors using a triple zeta basis set (def2-TZVP) with multiple density functionals and corrected for thermodynamic contributions. Geometries the ground (GS) and transition (TS) states were optimized at B3LYP-D3(BJ)/def2-TZVP level of theory using Turbomole suite of programs (version 6.5).<sup>7-9</sup> The m4 grid was used; convergence criteria were 10<sup>-8</sup> Hartree and 10<sup>-5</sup> atomic units as the maximum norm of the cartesian gradient.<sup>10</sup> Vibrational analysis was also carried out at B3LYP-D3(BJ)/def2-TZVP level with a vibrational scaling factor of 0.965 and the experimentally determined coalescence temperatures. Single-point calculations were carried out on the B3LYP-D3(BJ)-optimized geometries at B2GP-PLYP-D3(BJ)/def2-TZVP level of theory (using ultrafine grid) using Gaussian 09 package (Figure S6.1. Correlation of the calculated ( $\Delta G_{\pm}^{\pm}$ calc.) and experimental ( $\Delta G_{\pm}^{\pm}$  exp.) rotational barriers for the phenol (left) and anisole (right) rotors. Structures were calculated at the B2GP-PLYP-D3(BJ)/def2-TZVP level of theory with thermodynamic corrections. and Table S6.1. Calculated ( $\Delta G^{\ddagger}_{calc.}$ , kcal/mol)<sup>*a*</sup> and experimental  $(\Delta G^{\ddagger}_{exp}, \text{kcal/mol})^{b}$  rotational barrier energies for rotors 1, 2 and 3 as well as the error (kcal/mol)^{c} for the calculations reported as the difference between the calculated and experimental values. -Table S6.2. Statistical values for the error of the calculated (B2GP-PLYP-D3(BJ)/def2-TZVP) rotational barriers for the phenol and anisole rotors.<sup>11–13</sup> The XYZ coordinates for the ground and transition state structures of rotor 1 and rotor 2 are in Table S6.3. XYZ coordinates for the GS synconformer of rotor 2. - Table S6.11. XYZ coordinates for the TS structure of rotor 1 with a constrained hydrogen bond.

To eliminate error in GS energy, the calculated GS energies for the *syn-* and *anti*conformers were averaged. Systematic errors imposed by the averaging should be cancelled out in the difference of the rotational barriers because both the phenol and anisole rotors have the ground states averaged. The hydrogen bond stability in the GS and TS phenol rotors was assessed by comparing the calculated energies for the hydrogen bonding (HB) versus non-hydrogen-bonding (nHB) configurations (Figure S6.2. Calculated rotational barriers for rotor 1 and 2 with ( $\Delta G^{\ddagger}$ ) and without ( $\Delta E^{\ddagger}$ ) thermodynamic corrections.). The non-hydrogen bonding configuration was constructed by freezing the C<sub>(6)</sub>-C<sub>(1)</sub>-O-H dihedral angle to 0° (with C<sub>(2)</sub> being the connection point to the imide moiety) and then re-optimizing the GS structures at the B3LYP-D3(BJ)/def2-TZVP level within this constraint.



**Figure S6.1.** Correlation of the calculated ( $\Delta G^{\ddagger}_{\ddagger}$  calc.) and experimental ( $\Delta G^{\ddagger}_{\ddagger}$  exp.) rotational barriers for the phenol (left) and anisole (right) rotors. Structures were calculated at the B2GP-PLYP-D3(BJ)/def2-TZVP level of theory with thermodynamic corrections.



**Figure S6.2.** Calculated rotational barriers for rotor 1 and 2 with  $(\Delta G^{\ddagger})$  and without  $(\Delta E^{\ddagger})$  thermodynamic corrections.

		$\Delta G^{\ddagger}_{\text{ calc.}}$	$\Delta G^{\ddagger}_{\text{exp.}}$	Temperature	Error
Rotor	substituent	(kcal/mol) <sup>a</sup>	(kcal/mol) <sup>b</sup>	(°C)	(kcal/mol) <sup>c</sup>
1	Н	10.08	10.89	-55	-0.82
1	<i>m</i> -Cl	9.54	10.08	-65	-0.53
1	<i>m</i> -NO <sub>2</sub>	9.51	9.99	-62	-0.49
1	<i>p</i> -Cl	9.84	10.39	-60	-0.54
1	<i>p</i> -CN	9.15	9.96	-65	-0.81
1	p-NO <sub>2</sub>	8.99	9.73	-67	-0.75
2	Н	20.13	20.77	113	-0.64
2	<i>m</i> -Cl	19.60	20.15	95	-0.55
2	<i>m</i> -NO2	18.83	19.58	86	-0.75
2	p-Cl	19.60	20.11	98	-0.51
2	p-CN	19.41	20.36	103	-0.94
2	p-NO2	19.17	19.35	82	-0.19
3	Н	20.30	21.41	137.5	-1.11

**Table S6.1.** Calculated  $(\Delta G^{\ddagger}_{calc.}, \text{ kcal/mol})^a$  and experimental  $(\Delta G^{\ddagger}_{exp.}, \text{ kcal/mol})^b$  rotational barrier energies for rotors 1, 2 and 3 as well as the error (kcal/mol)<sup>c</sup> for the calculations reported as the difference between the calculated and experimental values.

<sup>*a*</sup> B2GP-PLYP-D3(BJ)/def2-TZVP; <sup>*b*</sup> via coalescence temperature; <sup>*c*</sup>  $\Delta G^{\ddagger}_{\text{calc.}}$  -  $\Delta G^{\ddagger}_{\text{exp.}}$ 

**Table S6.2.** Statistical values for the error of the calculated (B2GP-PLYP-D3(BJ)/def2-TZVP) rotational barriers for the phenol and anisole rotors.

Rotors	average error	standard error
1	-0.66	0.14
2	-0.60	0.23
All rotors $(1, 2, and 3)$	-0.66	0.23

Н	0.694200	-2.215100	3.956500
С	0.510500	-1.160600	3.739700
С	1.423500	-0.591800	2.630900
С	0.721900	0.723600	2.350200
С	-0.585300	0.534700	2.534200
C	-0.788700	-0.913000	2.941700
Н	0.555000	-0.577900	4.659300
Н	2.491300	-0.543500	2.822700
Н	1.204600	1.598500	1.941900
Н	-1.384000	1.226000	2.308800
Н	-1.734400	-1.157400	3.416200
C	-0.473900	-1.788500	1.674800
Н	-0.750600	-2.827400	1.853100
C	1.037400	-1.571800	1.463800
Н	1.628200	-2.485200	1.527000
С	1.171100	-0.996100	0.071000
C	-1.130200	-1.314000	0.396600
Ν	-0.116900	-0.887700	-0.471200
0	2.184300	-0.683700	-0.499000
0	-2.307600	-1.290200	0.143700
С	-0.372500	-0.331700	-1.754700
C	-0.847100	0.749000	-4.259500
C	-0.846800	-1.133200	-2.778200
C	-0.145800	1.035000	-1.970100
C	-0.375600	1.566600	-3.237600
C	-1.091800	-0.597900	-4.037100
Н	-1.022500	-2.181400	-2.577500
Н	-0.197300	2.613600	-3.431600
Н	-1.464000	-1.228800	-4.832600
Н	-1.024900	1.178500	-5.237100
0	0.273800	1.750700	-0.900300
C	0.619800	3.111900	-1.090500
Η	1.424100	3.215800	-1.823700
Н	0.963900	3.470300	-0.123300
Н	-0.244100	3.702700	-1.408200

 Table S6.3. XYZ coordinates for the GS syn- conformer of rotor 2.
TADIC SU.T. ATZ COOLUIN	aics			
	Н	0.545500	-1.695200	4.203500
	C	1.051000	-0.775300	3.901800
	C	1.918500	-0.937800	2.633700
	C	2.195900	0.518900	2.308500
	C	1.125200	1.227000	2.672300
	C	0.107300	0.259900	3.250000
	Н	1.609100	-0.364300	4.742400
	Н	2.779900	-1.596700	2.684600
	Η	3.064700	0.872300	1.772300
2	Н	0.939800	2.275700	2.491200
	Н	-0.679100	0.691400	3.861800
	C	-0.427300	-0.606800	2.053500
	Н	-1.272600	-1.216000	2.372000
	C	0.809200	-1.425000	1.632900
	Н	0.674200	-2.503300	1.711400
	C	1.055700	-1.065200	0.184200
	C	-0.821800	0.184700	0.826200
	Ν	0.069500	-0.150100	-0.201400
	0	1.940600	-1.466100	-0.528200
	0	-1.715900	0.984400	0.726700
	C	-0.008800	0.415100	-1.502600
	C	-0.193700	1.528800	-4.029000
	C	0.971300	1.283300	-1.949800
	C	-1.091900	0.078200	-2.326000
	C	-1.182700	0.653200	-3.592000
_	C	0.887500	1.843600	-3.219000
	Н	1.798500	1.514500	-1.292800
	Н	-2.012400	0.417900	-4.241500
	Н	1.656100	2.520600	-3.565700
	Н	-0.275800	1.963900	-5.016800
	0	-1.976400	-0.812100	-1.817500
	C	-3.154000	-1.091900	-2.556600
	Н	-3.734200	-0.181900	-2.730500
	Н	-3.733000	-1.779600	-1.945300
	H	-2.920200	-1.566000	-3.514200

 Table S6.4. XYZ coordinates for the GS anti- conformer of rotor 2.

Table S0.3. ATZ coordinates for the TS structure of fotor Z.				
	Н	4.600500	0.452000	0.194900
	C	3.963200	-0.433100	0.248200
	C	2.821000	-0.308600	1.281300
	C	1.971900	-1.501100	0.889300
	C	2.080400	-1.660500	-0.431000
	C	2.999400	-0.572900	-0.950300
	Н	4.572200	-1.323200	0.401500
	Н	3.086200	-0.222800	2.330900
	Н	1.311500	-2.033100	1.558900
	Н	1.525400	-2.347500	-1.053400
	Н	3.425200	-0.723400	-1.937800
	C	2.230700	0.801100	-0.801500
	Н	2.769900	1.590800	-1.321300
	C	2.125600	0.986600	0.705600
	Н	2.626800	1.873200	1.088400
	C	0.651000	1.108800	0.995000
	C	0.809700	0.762600	-1.290700
	N	-0.076100	0.685500	-0.178500
	0	0.216400	1.555800	2.016300
	0	0.504900	0.799300	-2.457600
	C	-1.445900	0.231300	-0.324000
	C	-4.065200	-0.742100	-0.810600
	C	-1.824400	-0.328800	-1.550800
	C	-2.428100	0.233800	0.702300
	C	-3.717800	-0.229500	0.427500
	C	-3.102300	-0.806600	-1.799500
	Н	-1.108300	-0.369500	-2.348000
	Н	-4.457000	-0.203000	1.212800
	Н	-3.329300	-1.217700	-2.773900
	Н	-5.073800	-1.093500	-0.985500
	0	-2.092100	0.648300	1.938100
	C	-3.069400	0.731900	2.955400
	Н	-3.886100	1.403700	2.674700
	Н	-2.549100	1.136700	3.820200
	H	-3.479700	-0.251900	3.204000

 Table S6.5. XYZ coordinates for the TS structure of rotor 2.

		5 I 6 I 6 I 6 G	~_~	
	Н	-0.044600	-3.904900	-1.875500
	C	0.276700	-3.667100	-0.859200
	C	1.335700	-2.544800	-0.794100
	C	1.318100	-2.239200	0.692900
	C	0.072800	-2.431100	1.131100
	C	-0.770900	-2.868800	-0.052200
	Н	0.596400	-4.574200	-0.348100
	Н	2.306700	-2.729900	-1.242900
	Н	2.147400	-1.823800	1.246500
	Н	-0.317000	-2.206300	2.113100
	Н	-1.717200	-3.350000	0.175200
	C	-0.912000	-1.618700	-0.996400
	Н	-1.637900	-1.816300	-1.784600
	C	0.522900	-1.397900	-1.503300
S	Н	0.631300	-1.466600	-2.585300
	C	0.889100	-0.008500	-1.054400
	C	-1.286500	-0.338100	-0.289700
	N	-0.187800	0.554200	-0.387700
	0	1.968200	0.533000	-1.209000
	0	-2.318300	-0.094500	0.273900
	C	-0.206500	1.860100	0.195800
	C	-0.396800	4.345000	1.429200
	C	-1.319400	2.670500	-0.019500
	C	0.839700	2.310400	1.015100
	C	0.723900	3.556800	1.629000
	C	-1.419600	3.908500	0.592500
	H	-2.115700	2.310300	-0.653800
	Н	1.540600	3.884400	2.258100
	Н	-2.291700	4.524600	0.421100
	Н	-0.467400	5.308300	1.917700
	0	1.951300	1.573900	1.269800
	H	2.230900	1.149400	0.434400

 Table S6.6. XYZ coordinates for the GS syn- conformer of rotor 1.

и	0 207200	5 3 20 4 0 0	0.583000
	-0.397300	-5.529400	-0.383000
	-0.112200	-3.000000	0.437700
C	0.910000	-3.910/00	0.515/00
C	0.842100	-3.585000	1.994400
C	-0.408200	-3.810200	2.402200
C	-1.205700	-4.288700	1.202700
Н	0.220900	-5.955500	0.971900
Н	1.898700	-4.073000	0.095700
Н	1.647600	-3.143500	2.563200
Н	-0.829800	-3.592900	3.372800
Η	-2.143000	-4.795000	1.411600
C	-1.357500	-3.057100	0.234700
Н	-2.056700	-3.286800	-0.568200
C	0.082600	-2.803900	-0.240100
Н	0.221200	-2.896700	-1.316600
C	0.391300	-1.390800	0.177500
C	-1.784700	-1.777400	0.912800
Ν	-0.698000	-0.868500	0.857600
0	1.424100	-0.786800	-0.044000
0	-2.844600	-1.549100	1.429000
C	-0.730900	0.411600	1.495500
C	-0.969200	2.882300	2.747700
C	-1.219600	0.497000	2.797800
C	-0.324500	1.572800	0.822000
C	-0.457900	2.803600	1.463400
C	-1.340700	1.725000	3.425700
Н	-1.524100	-0.406600	3.304100
Н	-0.142500	3.687300	0.925200
Н	-1.727000	1.777800	4.434500
Н	-1.066600	3.848200	3.226600
0	0.162700	1.560600	-0.444600
Н	0.770600	0.799100	-0.528000

Table S6.7. XYZ coordinates for the GS anti- conformer of rotor 1.

	Н	4.429200	0.836400	-0.484600
	C	3.968700	-0.014200	0.022500
	C	2.899200	0.393000	1.060200
	C	2.248800	-0.952200	1.323200
	C	2.290600	-1.652200	0.188800
	C	2.966700	-0.789700	-0.860800
	Н	4.739500	-0.657700	0.445400
	H	3.220100	0.957800	1.930400
	Н	1.727100	-1.212600	2.231700
	Н	1.815400	-2.601400	-0.011100
	H	3.348900	-1.300200	-1.739700
	C	1.969800	0.379500	-1.194100
	H	2.323100	0.947300	-2.054600
	C	1.928300	1.191200	0.115800
	H	2.267700	2.221100	0.009100
	C	0.477300	1.194000	0.543000
	C	0.542400	-0.057200	-1.441700
	N	-0.246900	0.454800	-0.403600
	0	-0.003400	1.727900	1.508400
	0	0.128600	-0.727100	-2.353100
	C	-1.642000	0.207700	-0.290700
	C	-4.368600	-0.260000	-0.060700
	C	-2.528200	0.779300	-1.191900
-	C	-2.119000	-0.620800	0.727600
	C	-3.488900	-0.839700	0.842800
	C	-3.892400	0.547300	-1.086600
	H	-2.132500	1.406900	-1.978900
	H	-3.861300	-1.473200	1.640400
	H	-4.575600	0.996000	-1.794500
	H	-5.430500	-0.443500	0.039500
	0	-1.211700	-1.187300	1.567200
	H	-1.671600	-1.733300	2.214300

**Table S6.8.** XYZ coordinates for the GS *syn-* conformer of rotor 1 with a constrained hydrogen bond.

	Η	-0.888800	-4.359800	-0.791300
	C	-0.053600	-4.026300	-0.171700
	C	0.841800	-2.972900	-0.861600
	C	1.662400	-2.497800	0.324200
	C	0.883600	-2.557600	1.406000
	C	-0.475700	-3.072900	0.968500
	Н	0.510200	-4.886600	0.187500
	Н	1.395800	-3.273100	-1.745900
3	Н	2.656400	-2.080600	0.253600
	Н	1.113100	-2.201600	2.400000
	Н	-1.121200	-3.463800	1.749200
	C	-1.140000	-1.936200	0.110700
	Н	-2.179200	-2.182000	-0.105800
	C	-0.239800	-1.867700	-1.138800
	Н	-0.763500	-2.072000	-2.072100
	C	0.295800	-0.453500	-1.171300
	C	-1.080000	-0.555500	0.726400
T 7	N	-0.251200	0.233800	-0.079200
	0	1.072200	0.019600	-1.959600
	0	-1.622700	-0.178600	1.733600
	C	0.044800	1.595000	0.199100
	C	0.628900	4.257000	0.712300
	C	0.824300	1.938500	1.293000
	C	-0.462000	2.588400	-0.641000
	C	-0.155300	3.921300	-0.383000
	C	1.117800	3.269100	1.558700
	H	1.195000	1.149000	1.932300
	Н	-0.538800	4.693900	-1.040200
	H	1.724800	3.530800	2.414300
	H	0.856200	5.297800	0.903100
	0	-1.245500	2.196800	-1.680900
	H	-1.533200	2.970000	-2.178500

**Table S6.9.** XYZ coordinates for the GS *anti*- conformer of rotor **1** with a constrained hydrogen bond.

<b>Table S0.10.</b> A Y Z COC	brainates	for the 13	s structure	e of rotor <b>I</b> .
	H	0.007800	-3.963800	-1.850000
	C	0.350800	-3.681100	-0.852500
	C	1.356700	-2.509000	-0.854600
	C	1.375300	-2.164000	0.622400
	C	0.154800	-2.399200	1.108300
	C	-0.705600	-2.907300	-0.032900
	H	0.730000	-4.556600	-0.327200
	H	2.319100	-2.657300	-1.334200
	H	2.207500	-1.704500	1.135700
	H	-0.210900	-2.170000	2.098600
	H	-1.623100	-3.420100	0.238200
	C	-0.930000	-1.695500	-1.016100
	H	-1.677200	-1.951000	-1.765900
	C	0.458300	-1.426100	-1.568700
	H	0.546300	-1.516400	-2.650400
	C	0.769400	-0.013100	-1.176100
	C	-1.342500	-0.416200	-0.342500
	N	-0.267500	0.541700	-0.420100
	0	1.816400	0.515700	-1.505500
	0	-2.417800	-0.263300	0.171800
	C	-0.305400	1.858900	0.232400
	C	-0.603100	4.328000	1.595700
	C	-1.459700	2.181400	0.967800
	C	0.731400	2.833900	0.199200
	C	0.540500	4.042500	0.885200
_	C	-1.616000	3.380700	1.636600
	H	-2.260800	1.472000	1.012700
	H	1.357800	4.748500	0.825500
	H	-2.531600	3.562800	2.182600
	H	-0.701600	5.275900	2.109100
	0	1.921800	2.761000	-0.414400
	H	2.008900	1.911100	-0.910800

Table S6.10. XYZ coordinates for the TS structure of rotor 1

Η	-1.677100	4.947600	-6.177500
C	-1.750500	3.914400	-5.831500
C	-0.477400	3.411000	-5.116200
C	-1.001600	2.128400	-4.498800
C	-2.283000	2.325800	-4.182500
C	-2.643300	3.743900	-4.582400
Η	-2.051900	3.266900	-6.653700
Η	0.440800	3.337600	-5.690400
Η	-0.394300	1.266100	-4.264800
Η	-2.933200	1.657100	-3.637500
Η	-3.700800	3.972500	-4.670800
C	-1.871500	4.709200	-3.603600
Η	-2.219500	5.733100	-3.730800
C	-0.413200	4.484600	-3.961700
H	0.117200	5.373000	-4.301400
C	0.229400	3.992700	-2.699700
C	-1.983000	4.340500	-2.150200
N	-0.708400	3.866600	-1.670600
0	1.422200	3.748900	-2.654300
0	-3.004300	4.441000	-1.524900
C	-0.499600	3.326700	-0.318800
C	-0.351300	2.308500	2.324100
C	-1.615500	3.277000	0.535300
C	0.731400	2.833900	0.199200
C	0.759800	2.342200	1.512700
C	-1.555800	2.782700	1.824500
H	-2.557600	3.641300	0.179200
H	1.720000	1.982500	1.856900
H	-2.453900	2.775200	2.427000
H	-0.277400	1.918200	3.331000
0	1.921800	2.761000	-0.414400
 H	2.602000	2.368700	0.185400

Table S6.11. XYZ coordinates for the TS structure of rotor 1 with a constrained hydrogen bond.

## 6.2 Symmetry adapted perturbation theory calculations

The origins of the amplified catalyzing effect (ACE) of the transition state hydrogen bond in rotor **1** were investigated symmetry adapted perturbation theory (SAPT(CCSD)/cc-pVTZ). SAPT calculations can deconstruct interaction energy of an intermolecular complex into four fundamental energy terms: electrostatics ( $E_{elst}$ ), exchange-repulsion ( $E_{exch}$ ), induction/polarization ( $E_{ind}$ ) and London dispersion ( $E_{disp}$ ). The SAPT calculations were carried out on a simple bimolecular complex comprised of NMP and phenol in *two* distinct configurations of the NMPphenol complex, i.e., hydrogen bonding (**HB**) and non-hydrogen bonding (**nHB**) (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right).) using the Q-Chem<sup>14</sup> software package.

To mimic the transition state in the rotors, the NMP amide (-NCH<sub>3</sub>-CO-CH<sub>2</sub>-) motif and phenol were kept coplanar to each other by a dihedral constraint of 0° between the residing planes. The ∠OHO was locked at 180° for the configuration with a hydrogen bond (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right)., left). The O-to-O distances (**D**) was systematically altered from 3.00 to 2.00 Å (over 11 steps of 0.1 Å intervals) to generate a potential energy profile using the M06-2X/6-31G\* level of theory. The complex without a hydrogen bond (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right)., right) was made by freezing all the atoms in the complex with a hydrogen bond at each discrete **D** except the phenolic hydrogen, which had a dihedral angle constrained to 0° with the carbon ortho to the hydroxyl group. The geometry of the complex without a hydrogen bond was then optimized at the M06-2X/6-31G\* level of theory for each discrete **D** with constraints on all the frozen atoms except the phenolic hydrogen.

The component terms ( $E_{elst}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$ ) for the NMP-phenol **HB** and **nHB** configurations (Figure S6.4. SAPT energies for the NMP-phenol complex between 2.0 and 3.0 Å in the configurations with (**A**) and without (**B**) hydrogen bond as well as the corresponding energy difference (**C**).) at 11 discrete O-to-O distances (**D**) between 2.0 and 3.0 Å were obtained and tabulated in Table S6.12. SAPT total ( $E_{total}$ , kcal/mol) and component energies ( $E_{elst}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$ , kcal/mol) for the NMP-phenol complex in two configurations (Figure S6.3) at 11 different O-to-O distances (**D**) as well as the differences in energy ( $\Delta E = E^{HB} - E^{nHB}$ ) between the two configurations. The ACE's were characterized as the difference ( $\Delta E = E^{HB} - E^{nHB}$ ) in the calculated total and component energy terms between the NMP-phenol **HB** and **nHB** configurations. The xyz coordinates of the NMP-phenol complex in both configurations at 11 different O-to-O distances are listed in Table S6.13. XYZ coordinates for NMP-phenol HB complex (D = 2.0 Å). - Table **S6.34.** XYZ coordinates for NMP-phenol nHB complex (D = 3.0 Å).





non-hydrogen bonding (nHB)





**Figure S6.3.** Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right).

**Table S6.12.** SAPT total ( $E_{total}$ , kcal/mol) and component energies ( $E_{elst}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$ , kcal/mol) for the NMP-phenol complex in two configurations (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right).) at 11 different O-to-O distances (**D**) as well as the differences in energy ( $\Delta E = E^{HB} - E^{nHB}$ ) between the two configurations.

	$E^{\mathbf{HB}}$ for the co	onfiguration w	ith hydrogen	bond	
D (Å)	E <sup>HB</sup> <sub>elst</sub>	$E_{\rm exch}^{\rm HB}$	$E_{\rm ind}^{\rm HB}$	E <sup>HB</sup> disp	$E_{ m total}^{ m HB}$
3.0	-8.75	4.42	-1.28	-3.19	-8.80
2.9	-10.05	6.51	-1.56	-3.78	-8.87
2.8	-11.68	9.55	-1.93	-4.50	-8.56
2.7	-13.73	13.94	-2.47	-5.39	-7.65
2.6	-16.33	20.24	-3.26	-6.52	-5.87
2.5	-19.65	29.17	-4.51	-7.94	-2.93
2.4	-23.90	41.73	-6.58	-9.82	1.43
2.3	-29.29	59.18	-10.16	-12.08	7.65
2.2	-35.99	83.08	-16.47	-15.09	15.54
2.1	-43.94	115.26	-27.60	-18.97	24.75
2.0	-52.44	157.62	-47.13	-24.00	34.04
	$E^{\mathbf{nHB}}$ for the con	nfiguration wi	thout hydrog	en bond	
D (Å)	E <sup>nHB</sup> <sub>elst</sub>	E <sup>nHB</sup> <sub>exch</sub>	E <sup>nHB</sup> ind	E <sup>nHB</sup> disp	$E_{ m total}^{ m nHB}$
3.0	1.95	1.64	-0.58	-2.30	0.72
2.9	1.99	2.36	-0.66	-2.66	1.04
2.8	1.98	3.41	-0.76	-3.09	1.54
2.7	1.86	4.93	-0.88	-3.59	2.31
2.6	1.58	7.14	-1.03	-4.20	3.48
2.5	1.04	10.35	-1.23	-4.94	5.22
2.4	-0.12	14.98	-1.50	-5.85	7.51
2.3	-1.40	22.29	-1.89	-6.96	12.05
2.2	-3.80	31.01	-2.51	-8.33	16.37
2.1	-7.51	44.22	-3.55	-10.06	23.11
2.0	-13.11	62.63	-5.36	-12.23	31.93
		$\Delta E = E^{\mathbf{HB}} - E$	<sup>7</sup> nHB		
D (Å)	$\Delta E_{\rm elst}$	$\Delta E_{\rm exch}$	$\Delta E_{\rm ind}$	$\Delta E_{\rm disp}$	$\Delta E_{ m total}$
3.0	-10.70	2.77	-0.70	-0.89	-9.51
2.9	-12.04	4.14	-0.89	-1.11	-9.91
2.8	-13.65	6.14	-1.17	-1.41	-10.10
2.7	-15.58	9.01	-1.58	-1.80	-9.96
2.6	-17.91	13.09	-2.23	-2.31	-9.35
2.5	-20.70	18.82	-3.28	-3.00	-8.15
2.4	-23.78	26.75	-5.09	-3.97	-6.09
2.3	-27.89	36.88	-8.28	-5.12	-4.41
2.2	-32.19	52.07	-13.96	-6.75	-0.83
2.1	-36.43	71.04	-24.05	-8.92	1.63
2.0	-39.33	94.99	-41.77	-11.77	2.12



**Figure S6.4.** SAPT energies for the NMP-phenol complex between 2.0 and 3.0 Å in the configurations with (A) and without (B) hydrogen bond as well as the corresponding energy difference (C).

С	-2.925187	1.666576	0.664758
Н	-3.051441	1.676828	-0.425183
С	-1.762255	2.574389	1.048332
Η	-1.646690	3.403127	0.345873
С	-0.569087	1.649635	0.997023
С	-2.470926	0.293722	1.117578
Ν	-1.044427	0.346526	0.929937
0	0.598166	2.000901	1.058326
С	5.356258	0.070336	0.902502
С	3.335517	1.967545	1.018898
С	5.685838	1.431683	0.966394
С	4.015045	-0.341775	0.896678
С	3.000196	0.616124	0.955564
С	4.664291	2.381321	1.024679
Н	6.720771	1.766301	0.971569
Η	3.746713	-1.394857	0.846888
Н	1.960334	0.297147	0.950486
Н	4.901141	3.441048	1.074424
С	-0.208932	-0.810533	1.147248
Н	-0.248635	-1.079846	2.206450
Η	0.826404	-0.587101	0.875706
Н	-0.578668	-1.638996	0.537702
Н	-1.871113	2.952892	2.069240
Η	-3.872936	1.972689	1.116193
Η	-2.679500	0.130458	2.180374
Н	-2.909650	-0.510614	0.520836
0	2.369896	2.928600	1.076906
Η	1.504867	2.475682	1.067835
Н	6.154011	-0.679807	0.856781

**Table S6.13.** XYZ coordinates for NMP-phenol HB complex (D = 2.0 Å).

Í	С	-2.958647	1.683265	0.664756
	Η	-3.084884	1.694877	-0.425173
	С	-1.787159	2.579992	1.048376
	Н	-1.663825	3.407708	0.346034
	С	-0.602785	1.644014	0.996831
	С	-2.517341	0.306111	1.117330
	Ν	-1.090421	0.345464	0.929584
	0	0.567739	1.984227	1.058094
	С	5.396388	0.054364	0.902526
	С	3.393670	1.970563	1.019373
	С	5.738820	1.412527	0.966600
	С	4.051341	-0.345056	0.896745
	С	3.045592	0.622379	0.955859
	С	4.726295	2.371765	1.025111
	Η	6.776868	1.737352	0.971744
	Н	3.773067	-1.395548	0.846815
	Н	2.002761	0.313242	0.950815
	Η	4.973150	3.429199	1.075000
	С	-0.265878	-0.819470	1.146651
	Н	-0.308041	-1.088559	2.205815
	Н	0.771502	-0.605788	0.875061
	Η	-0.643472	-1.644310	0.537008
	Н	-1.892357	2.959349	2.069351
	Н	-3.903426	1.998249	1.116313
	Н	-2.727365	0.144662	2.180117
	Н	-2.963691	-0.493953	0.520500
	Ο	2.437177	2.940688	1.077605
	Η	1.567906	2.495965	1.068533
	Н	6.187015	-0.703276	0.856627

**Table S6.14.** XYZ coordinates for NMP-phenol HB complex (D = 2.1 Å).

C	-2.992360	1.699382	0.664759
Н	-3.118572	1.712305	-0.425158
C	-1.812702	2.585318	1.048415
Н	-1.681870	3.411976	0.346183
C	-0.636928	1.638572	0.996638
C	-2.563612	0.318190	1.117098
N	-1.136407	0.344538	0.929241
0	0.536658	1.968073	1.057856
C	5.436904	0.038951	0.902545
C	3.451777	1.973340	1.019832
C	5.791729	1.393921	0.966789
C	4.088265	-0.348169	0.896815
C	3.091397	0.628401	0.956151
C	4.788010	2.362357	1.025521
Н	6.832700	1.709252	0.971896
Н	3.800406	-1.396069	0.846755
Н	2.045787	0.328800	0.951146
Н	5.044515	3.417485	1.075544
C	-0.322519	-0.827908	1.146073
Н	-0.367053	-1.096756	2.205201
Н	0.716747	-0.623668	0.874430
Н	-0.707678	-1.649176	0.536341
Н	-1.914350	2.965471	2.069453
Н	-3.934187	2.022914	1.116438
Н	-2.775017	0.158510	2.179878
Н	-3.017297	-0.477678	0.520187
0	2.504187	2.952151	1.078283
Н	1.630891	2.515386	1.069217
Н	6.220576	-0.725870	0.856472

**Table S6.15.** XYZ coordinates for NMP-phenol HB complex (D = 2.2 Å).

С	-3.026323	1.714948	0.664767
Н	-3.152504	1.729136	-0.425138
С	-1.838860	2.590382	1.048448
Н	-1.700792	3.415951	0.346320
С	-0.671494	1.633301	0.996444
С	-2.609748	0.329962	1.116880
Ν	-1.182382	0.343737	0.928910
0	0.504961	1.952420	1.057612
С	5.477797	0.024076	0.902561
С	3.509834	1.975898	1.020278
С	5.844575	1.375852	0.966963
С	4.125794	-0.351122	0.896888
С	3.137590	0.634201	0.956440
С	4.849450	2.353102	1.025911
Η	6.888290	1.681981	0.972028
Η	3.828691	-1.396434	0.846707
Η	2.089375	0.343844	0.951480
Η	5.115263	3.405918	1.076058
С	-0.378858	-0.835879	1.145513
Η	-0.425678	-1.104470	2.204608
Η	0.662149	-0.640784	0.873813
Η	-0.771301	-1.653630	0.535699
Η	-1.937065	2.971276	2.069547
Η	-3.965221	2.046719	1.116568
Η	-2.822469	0.172007	2.179655
Η	-3.070490	-0.461787	0.519897
0	2.570926	2.963028	1.078941
Н	1.693808	2.533990	1.069886
Н	6.254683	-0.747627	0.856318

**Table S6.16.** XYZ coordinates for NMP-phenol HB complex (D = 2.3 Å).

С	-3.060534	1.729984	0.664780
Н	-3.186678	1.745393	-0.425113
С	-1.865609	2.595199	1.048477
Η	-1.720556	3.419652	0.346446
С	-0.706460	1.628194	0.996251
С	-2.655760	0.341433	1.116676
Ν	-1.228344	0.343047	0.928590
0	0.472681	1.937251	1.057363
С	5.519059	0.009719	0.902573
С	3.567838	1.978254	1.020709
С	5.897368	1.358306	0.967122
С	4.163901	-0.353924	0.896962
С	3.184149	0.639791	0.956726
С	4.910626	2.344008	1.026281
Η	6.943659	1.655514	0.972140
Η	3.857882	-1.396654	0.846668
Н	2.133494	0.358393	0.951814
Η	5.185421	3.394510	1.076544
С	-0.434901	-0.843414	1.144971
Η	-0.483926	-1.111735	2.204035
Η	0.607711	-0.657176	0.873211
Η	-0.834360	-1.657704	0.535082
Η	-1.960476	2.976783	2.069634
Η	-3.996529	2.069698	1.116701
Η	-2.869735	0.185159	2.179448
Η	-3.123292	-0.446275	0.519627
0	2.637396	2.973354	1.079579
Η	1.756647	2.551821	1.070541
Η	6.289325	-0.768582	0.856164

**Table S6.17.** XYZ coordinates for NMP-phenol HB complex (D = 2.4 Å).

С	-3.094987	1.744510	0.664796
Η	-3.221089	1.761097	-0.425084
C	-1.892927	2.599781	1.048502
Η	-1.741130	3.423096	0.346562
C	-0.741807	1.623245	0.996058
C	-2.701655	0.352607	1.116484
Ν	-1.274289	0.342459	0.928280
0	0.439851	1.922548	1.057111
C	5.560679	-0.004141	0.902581
C	3.625788	1.980422	1.021126
C	5.950115	1.341269	0.967267
C	4.202564	-0.356582	0.897038
C	3.231056	0.645182	0.957008
C	4.971550	2.335076	1.026632
Н	6.998824	1.629826	0.972236
Н	3.887942	-1.396743	0.846640
Η	2.178113	0.372469	0.952148
Н	5.255014	3.383267	1.077004
C	-0.490652	-0.850539	1.144447
Н	-0.541803	-1.118580	2.203480
Н	0.553440	-0.672882	0.872622
Н	-0.896871	-1.661427	0.534489
Н	-1.984556	2.982006	2.069715
Н	-4.028107	2.091884	1.116838
Н	-2.916825	0.197972	2.179255
Η	-3.175724	-0.431138	0.519376
0	2.703599	2.983164	1.080199
Н	1.819398	2.568918	1.071181
Н	6.324489	-0.788769	0.856011

**Table S6.18.** XYZ coordinates for NMP-phenol HB complex (D = 2.5 Å).

C	-3.129679	1.758546	0.664816
Н	-3.255735	1.776270	-0.425052
C	-1.920793	2.604141	1.048523
Н	-1.762483	3.426302	0.346668
C	-0.777515	1.618447	0.995866
C	-2.747441	0.363491	1.116305
N	-1.320217	0.341964	0.927979
0	0.406501	1.908294	1.056855
C	5.602648	-0.017523	0.902586
C	3.683682	1.982420	1.021531
C	6.002825	1.324725	0.967400
C	4.241761	-0.359103	0.897116
C	3.278291	0.650383	0.957286
C	5.032235	2.326311	1.026965
Н	7.053806	1.604895	0.972315
Н	3.918835	-1.396712	0.846620
Н	2.223202	0.386090	0.952483
Н	5.324067	3.372198	1.077438
C	-0.546117	-0.857283	1.143939
Н	-0.599320	-1.125033	2.202945
Н	0.499338	-0.687939	0.872048
Н	-0.958852	-1.664827	0.533918
Н	-2.009281	2.986964	2.069789
Н	-4.059957	2.113309	1.116978
Н	-2.963751	0.210452	2.179076
Н	-3.227805	-0.416371	0.519143
0	2.769538	2.992489	1.080800
Н	1.882055	2.585321	1.071807
Н	6.360162	-0.808222	0.855858

**Table S6.19.** XYZ coordinates for NMP-phenol HB complex (D = 2.6 Å).

С	-3.164604	1.772111	0.664839
Н	-3.290611	1.790933	-0.425016
С	-1.949186	2.608291	1.048540
Η	-1.784582	3.429283	0.346766
С	-0.813566	1.613794	0.995674
С	-2.793125	0.374091	1.116138
Ν	-1.366126	0.341552	0.927689
0	0.372660	1.894471	1.056596
С	5.644956	-0.030446	0.902589
С	3.741519	1.984259	1.021922
С	6.055503	1.308661	0.967521
С	4.281468	-0.361494	0.897194
С	3.325836	0.655403	0.957561
С	5.092691	2.317713	1.027282
Н	7.108620	1.580697	0.972379
Η	3.950526	-1.396569	0.846607
Н	2.268736	0.399276	0.952816
Н	5.392604	3.361307	1.077849
С	-0.601303	-0.863668	1.143447
Н	-0.656486	-1.131120	2.202427
Η	0.445408	-0.702381	0.871487
Н	-1.020319	-1.667927	0.533369
Η	-2.034626	2.991669	2.069857
Η	-4.092074	2.134003	1.117120
Η	-3.010523	0.222607	2.178909
Н	-3.279554	-0.401966	0.518928
0	2.835216	3.001358	1.081383
Η	1.944611	2.601065	1.072420
Н	6.396330	-0.826972	0.855707

**Table S6.20.** XYZ coordinates for NMP-phenol HB complex (D = 2.7 Å).

С	-3.199759	1.785223	0.664865
Н	-3.325713	1.805107	-0.424977
С	-1.978084	2.612241	1.048554
Η	-1.807400	3.432055	0.346855
С	-0.849944	1.609279	0.995484
С	-2.838715	0.384413	1.115981
Ν	-1.412016	0.341215	0.927408
0	0.338355	1.881064	1.056336
С	5.687594	-0.042929	0.902589
С	3.799299	1.985952	1.022301
С	6.108157	1.293061	0.967631
С	4.321667	-0.363762	0.897274
С	3.373677	0.660252	0.957831
С	5.152929	2.309285	1.027583
Η	7.163280	1.557208	0.972430
Η	3.982983	-1.396326	0.846603
Η	2.314689	0.412044	0.953149
Η	5.460648	3.350599	1.078238
С	-0.656215	-0.869718	1.142970
Η	-0.713310	-1.136865	2.201926
Η	0.391650	-0.716240	0.870939
Η	-1.081291	-1.670753	0.532841
Η	-2.060567	2.996137	2.069919
Η	-4.124457	2.153997	1.117264
Η	-3.057152	0.234445	2.178754
Η	-3.330989	-0.387917	0.518728
0	2.900638	3.009800	1.081950
Н	2.007062	2.616183	1.073018
Н	6.432982	-0.845051	0.855557

**Table S6.21.** XYZ coordinates for NMP-phenol HB complex (D = 2.8 Å).

C	-3.235138	1.797900	0.664894
Η	-3.361036	1.818810	-0.424936
C	-2.007469	2.616004	1.048565
Η	-1.830907	3.434632	0.346936
C	-0.886632	1.604897	0.995296
C	-2.884217	0.394464	1.115834
Ν	-1.457885	0.340947	0.927136
0	0.303611	1.868057	1.056075
C	5.730552	-0.054988	0.902586
C	3.857021	1.987511	1.022669
C	6.160793	1.277912	0.967732
C	4.362336	-0.365914	0.897354
C	3.421797	0.664937	0.958098
C	5.212959	2.301025	1.027869
Η	7.217803	1.534404	0.972468
Η	4.016174	-1.395991	0.846605
Η	2.361037	0.424411	0.953479
Η	5.528221	3.340077	1.078606
C	-0.710862	-0.875454	1.142509
Η	-0.769802	-1.142290	2.201441
Η	0.338065	-0.729545	0.870405
Η	-1.141782	-1.673323	0.532333
Η	-2.087082	3.000381	2.069977
Η	-4.157101	2.173319	1.117409
Η	-3.103646	0.245972	2.178610
Η	-3.382126	-0.374216	0.518543
0	2.965809	3.017839	1.082499
H	2.069403	2.630709	1.073602
H	6.470104	-0.862486	0.855408

**Table S6.22.** XYZ coordinates for NMP-phenol HB complex (D = 2.9 Å).

ſ	С	-3.270735	1.810161	0.664925
	Н	-3.396575	1.832062	-0.424892
l	С	-2.037322	2.619587	1.048573
	Н	-1.855076	3.437026	0.347009
l	С	-0.923614	1.600643	0.995109
	С	-2.929638	0.404251	1.115697
	Ν	-1.503732	0.340742	0.926872
l	Ο	0.268451	1.855435	1.055813
	С	5.773822	-0.066643	0.902581
	С	3.914685	1.988947	1.023025
	С	6.213414	1.263198	0.967822
	С	4.403456	-0.367955	0.897434
	С	3.470182	0.669467	0.958360
	С	5.272791	2.292934	1.028141
	Η	7.272199	1.512263	0.972494
	Η	4.050067	-1.395572	0.846613
l	Н	2.407760	0.436394	0.953807
	Η	5.595343	3.329742	1.078954
	С	-0.765249	-0.880895	1.142062
	Н	-0.825971	-1.147416	2.200973
	Η	0.284654	-0.742327	0.869883
l	Η	-1.201811	-1.675659	0.531844
l	Η	-2.114149	3.004413	2.070029
	Η	-4.190002	2.191998	1.117555
	Η	-3.150014	0.257197	2.178477
	Η	-3.432980	-0.360855	0.518372
	0	3.030733	3.025499	1.083032
	Η	2.131631	2.644673	1.074173
	Η	6.507683	-0.879308	0.855261

**Table S6.23.** XYZ coordinates for NMP-phenol HB complex (D = 3.0 Å).

C	-2.968730	1.620656	0.663104
Η	-3.094984	1.630908	-0.426837
C	-1.805797	2.528469	1.046677
Н	-1.690233	3.357206	0.344218
C	-0.612629	1.603715	0.995368
C	-2.514469	0.247802	1.115924
Ν	-1.087970	0.300605	0.928283
0	0.554623	1.954981	1.056671
C	5.312715	0.024415	0.900847
C	3.291974	1.921625	1.017243
C	5.642295	1.385763	0.964740
C	3.971503	-0.387695	0.895023
C	2.956654	0.570203	0.953910
C	4.620749	2.335401	1.023024
Η	6.677228	1.720381	0.969914
Н	3.703170	-1.440777	0.845233
Η	1.916791	0.251227	0.948831
Η	4.857598	3.395128	1.072770
C	-0.252475	-0.856453	1.145594
Η	-0.292178	-1.125767	2.204796
Η	0.782862	-0.633021	0.874052
Η	-0.622211	-1.684917	0.536048
Η	-1.914655	2.906971	2.067585
Η	-3.916479	1.926768	1.114538
Η	-2.723043	0.084538	2.178719
Η	-2.953193	-0.556535	0.519182
0	2.326353	2.882679	1.075251
H	2.724063	3.761451	1.114167
Η	6.110469	-0.725728	0.855126

**Table S6.24.** XYZ coordinates for NMP-phenol nHB complex (D = 2.0 Å).

С	-3.002659	1.637761	0.663098
Н	-3.128896	1.649372	-0.426831
С	-1.831172	2.534487	1.046718
Н	-1.707837	3.362204	0.344377
С	-0.646798	1.598510	0.995173
С	-2.561354	0.260607	1.115672
Ν	-1.134434	0.299959	0.927926
0	0.523726	1.938723	1.056437
С	5.352375	0.008859	0.900868
С	3.349657	1.925058	1.017715
С	5.694807	1.367023	0.964943
С	4.007328	-0.390560	0.895088
С	3.001579	0.576874	0.954201
С	4.682283	2.326261	1.023454
Η	6.732855	1.691847	0.970086
Η	3.729054	-1.441053	0.845158
Н	1.958749	0.267738	0.949157
Η	4.929137	3.383695	1.073342
С	-0.309891	-0.864975	1.144994
Η	-0.352054	-1.134064	2.204157
Η	0.727489	-0.651292	0.873403
Η	-0.687485	-1.689814	0.535350
Η	-1.936369	2.913844	2.067693
Η	-3.947438	1.952744	1.114655
Η	-2.771378	0.099157	2.178459
Η	-3.007704	-0.539457	0.518842
0	2.393164	2.895184	1.075947
Н	2.800263	3.770090	1.114949
Н	6.143002	-0.748780	0.854969

**Table S6.25.** XYZ coordinates for NMP-phenol nHB complex (D = 2.1 Å).

С	-3.036821	1.654284	0.663099
Н	-3.163033	1.667208	-0.426818
С	-1.857163	2.540220	1.046755
Н	-1.726332	3.366879	0.344523
С	-0.681390	1.593474	0.994977
С	-2.608073	0.273092	1.115437
Ν	-1.180869	0.299441	0.927581
0	0.492197	1.922975	1.056196
С	5.392442	-0.006147	0.900885
С	3.407315	1.928243	1.018172
С	5.747267	1.348824	0.965129
С	4.043804	-0.393267	0.895155
С	3.046935	0.583303	0.954491
С	4.743549	2.317259	1.023861
Н	6.788239	1.664155	0.970236
Η	3.755945	-1.441167	0.845095
Н	2.001325	0.283703	0.949486
Н	5.000053	3.372387	1.073884
С	-0.366980	-0.873006	1.144413
Η	-0.411514	-1.141853	2.203541
Η	0.672286	-0.668766	0.872770
Η	-0.752139	-1.694274	0.534680
Η	-1.958811	2.920373	2.067793
Η	-3.978648	1.977816	1.114778
Η	-2.819479	0.113412	2.178218
Η	-3.061758	-0.522775	0.518527
0	2.459725	2.907053	1.076622
Н	2.875814	3.778120	1.115703
Н	6.176114	-0.770968	0.854812

**Table S6.26.** XYZ coordinates for NMP-phenol nHB complex (D = 2.2 Å).

C	-3.071213	1.670248	0.663105
Н	-3.197395	1.684436	-0.426800
C	-1.883750	2.545682	1.046786
H	-1.745682	3.371251	0.344658
C	-0.716384	1.588601	0.994782
C	-2.654639	0.285262	1.115217
N	-1.227273	0.299037	0.927248
0	0.460071	1.907720	1.055950
C	5.432907	-0.020624	0.900898
C	3.464944	1.931198	1.018615
C	5.799685	1.331152	0.965300
C	4.080903	-0.395822	0.895226
C	3.092700	0.589501	0.954778
C	4.804560	2.308402	1.024249
Н	6.843400	1.637281	0.970365
Н	3.783801	-1.441134	0.845044
Η	2.044485	0.299144	0.949817
Н	5.070373	3.361218	1.074396
C	-0.423748	-0.880579	1.143851
Н	-0.470569	-1.149170	2.202946
Н	0.617258	-0.685484	0.872151
Н	-0.816192	-1.698330	0.534037
Н	-1.981955	2.926576	2.067885
Н	-4.010112	2.002019	1.114905
Н	-2.867360	0.127307	2.177993
Н	-3.115380	-0.506487	0.518234
0	2.526036	2.918328	1.077278
Н	2.950736	3.785590	1.116431
H	6.209793	-0.792327	0.854655

**Table S6.27.** XYZ coordinates for NMP-phenol nHB complex (D = 2.3 Å).

С	-3.105834	1.685673	0.663116
Η	-3.231978	1.701082	-0.426777
C	-1.910909	2.550888	1.046813
Η	-1.765856	3.375341	0.344782
C	-0.751760	1.583883	0.994587
C	-2.701060	0.297121	1.115012
Ν	-1.273644	0.298736	0.926926
0	0.427381	1.892940	1.055699
C	5.473759	-0.034593	0.900909
C	3.522538	1.933942	1.019045
C	5.852068	1.313995	0.965458
C	4.118601	-0.398235	0.895298
C	3.138849	0.595480	0.955062
C	4.865326	2.299696	1.024617
Н	6.898359	1.611202	0.970476
Н	3.812582	-1.440966	0.845004
Н	2.088194	0.314082	0.950150
Η	5.140121	3.350198	1.074880
C	-0.480201	-0.887725	1.143307
Η	-0.529226	-1.156046	2.202371
Η	0.562411	-0.701487	0.871547
Η	-0.879660	-1.702016	0.533418
Η	-2.005776	2.932471	2.067970
Η	-4.041829	2.025387	1.115037
Η	-2.915035	0.140848	2.177784
Η	-3.168592	-0.490586	0.517963
0	2.592096	2.929043	1.077915
Η	3.025047	3.792542	1.117133
Η	6.244025	-0.812893	0.854500

**Table S6.28.** XYZ coordinates for NMP-phenol nHB complex (D = 2.4 Å).

С	-3.140678	1.700578	0.663131
Н	-3.266781	1.717165	-0.426750
С	-1.938619	2.555849	1.046837
Н	-1.786822	3.379164	0.344897
С	-0.787498	1.579313	0.994392
С	-2.747346	0.308675	1.114819
Ν	-1.319981	0.298527	0.926614
Ο	0.394159	1.878616	1.055445
С	5.514987	-0.048073	0.900916
С	3.580096	1.936490	1.019461
С	5.904423	1.297337	0.965602
С	4.156873	-0.400514	0.895373
С	3.185364	0.601250	0.955342
С	4.925859	2.291144	1.024967
Η	6.953133	1.585894	0.970570
Н	3.842250	-1.440675	0.844974
Η	2.132421	0.328537	0.950483
Η	5.209322	3.339335	1.075338
С	-0.536343	-0.894471	1.142781
Н	-0.587495	-1.162512	2.201815
Н	0.507748	-0.716814	0.870957
Н	-0.942563	-1.705359	0.532824
Н	-2.030248	2.938074	2.068049
Н	-4.073799	2.047952	1.115173
Н	-2.962516	0.154040	2.177590
Η	-3.221416	-0.475070	0.517711
0	2.657907	2.939232	1.078533
Η	3.098768	3.799016	1.117810
Н	6.278797	-0.832701	0.854345

**Table S6.29.** XYZ coordinates for NMP-phenol nHB complex (D = 2.5 Å).

С	-3.175745	1.714984	0.663149
Н	-3.301802	1.732709	-0.426718
С	-1.966860	2.560579	1.046857
Н	-1.808549	3.382740	0.345002
С	-0.823581	1.574885	0.994199
С	-2.793507	0.319930	1.114639
Ν	-1.366284	0.298402	0.926313
0	0.360435	1.864732	1.055188
С	5.556581	-0.061085	0.900920
С	3.637616	1.938858	1.019864
С	5.956758	1.281164	0.965734
С	4.195694	-0.402664	0.895450
С	3.232224	0.606821	0.955620
С	4.986169	2.282749	1.025299
Η	7.007740	1.561334	0.970649
Η	3.872769	-1.440273	0.844953
Н	2.177135	0.342528	0.950817
Η	5.278000	3.328636	1.075772
С	-0.592184	-0.900844	1.142272
Η	-0.645387	-1.168594	2.201278
Η	0.453272	-0.731501	0.870381
Η	-1.004918	-1.708389	0.532252
Η	-2.055348	2.943402	2.068123
Η	-4.106024	2.069747	1.115312
Η	-3.009817	0.166891	2.177409
Η	-3.273872	-0.459933	0.517477
0	2.723471	2.948927	1.079134
Н	3.171918	3.805047	1.118464
Н	6.314095	-0.851784	0.854192

**Table S6.30.** XYZ coordinates for NMP-phenol nHB complex (D = 2.6 Å).

C	-3.211029	1.728910	0.663172
Н	-3.337036	1.747733	-0.426683
C	-1.995611	2.565091	1.046873
Н	-1.831007	3.386083	0.345099
C	-0.859991	1.570593	0.994007
C	-2.839550	0.330891	1.114471
N	-1.412552	0.298352	0.926022
0	0.326235	1.851271	1.054929
C	5.598530	-0.073646	0.900922
C	3.695094	1.941058	1.020255
C	6.009078	1.265461	0.965854
C	4.235043	-0.404694	0.895527
C	3.279411	0.612203	0.955894
C	5.046266	2.274513	1.025615
Н	7.062194	1.537497	0.970712
Н	3.904101	-1.439770	0.844941
Н	2.222311	0.356076	0.951149
Н	5.346179	3.318107	1.076182
C	-0.647728	-0.906868	1.141780
Н	-0.702911	-1.174320	2.200760
Н	0.398982	-0.745581	0.869820
Н	-1.066745	-1.711128	0.531702
Н	-2.081051	2.948469	2.068190
Н	-4.138499	2.090803	1.115453
Н	-3.056948	0.179407	2.177242
Н	-3.325979	-0.445166	0.517261
0	2.788791	2.958158	1.079716
Н	3.244518	3.810669	1.119095
Н	6.349905	-0.870172	0.854040

**Table S6.31.** XYZ coordinates for NMP-phenol nHB complex (D = 2.7 Å).

С	-3.246527	1.742375	0.663198
Н	-3.372481	1.762259	-0.426645
C	-2.024853	2.569394	1.046887
Н	-1.854168	3.389208	0.345187
C	-0.896712	1.566431	0.993817
C	-2.885484	0.341565	1.114314
N	-1.458785	0.298368	0.925740
0	0.291586	1.838216	1.054669
C	5.640825	-0.085776	0.900921
C	3.752530	1.943105	1.020634
C	6.061389	1.250214	0.965964
C	4.274898	-0.406609	0.895606
C	3.326908	0.617404	0.956164
C	5.106160	2.266437	1.025916
Н	7.116512	1.514360	0.970762
Н	3.936214	-1.439174	0.844935
Η	2.267920	0.369196	0.951481
Н	5.413879	3.307752	1.076571
C	-0.702984	-0.912565	1.141303
Н	-0.760078	-1.179712	2.200258
H	0.344881	-0.759087	0.869272
Н	-1.128059	-1.713600	0.531174
H	-2.107336	2.953290	2.068252
H	-4.171225	2.111150	1.115596
H	-3.103920	0.191597	2.177087
Н	-3.377757	-0.430764	0.517061
0	2.853869	2.966952	1.080282
H	3.316587	3.815912	1.119704
H	6.386213	-0.887898	0.853890

**Table S6.32.** XYZ coordinates for NMP-phenol nHB complex (D = 2.8 Å).

C	-3.282236	1.755397	0.663226
Н	-3.408134	1.776307	-0.426603
C	-2.054567	2.573500	1.046897
Н	-1.878005	3.392128	0.345268
C	-0.933729	1.562394	0.993628
C	-2.931315	0.351960	1.114167
N	-1.504983	0.298444	0.925468
0	0.256513	1.825553	1.054408
C	5.683455	-0.097492	0.900919
C	3.809923	1.945008	1.021001
C	6.113695	1.235408	0.966064
C	4.315238	-0.408417	0.895686
C	3.374699	0.622434	0.956430
C	5.165861	2.258522	1.026202
Н	7.170705	1.491900	0.970800
Н	3.969076	-1.438494	0.844937
Η	2.313940	0.381907	0.951812
Н	5.481123	3.297573	1.076938
C	-0.757960	-0.917957	1.140841
Н	-0.816900	-1.184793	2.199774
Н	0.290967	-0.772049	0.868737
Н	-1.188880	-1.715827	0.530666
Н	-2.134180	2.957878	2.068309
Н	-4.204199	2.130816	1.115741
Н	-3.150744	0.203469	2.176943
Н	-3.429223	-0.416719	0.516876
0	2.918711	2.975335	1.080832
H	3.388145	3.820804	1.120292
H	6.423006	-0.904990	0.853741

**Table S6.33.** XYZ coordinates for NMP-phenol nHB complex (D = 2.9 Å).

C	-3.318149	1.767993	0.663258
Н	-3.443989	1.789894	-0.426559
C	-2.084736	2.577420	1.046905
Н	-1.902490	3.394858	0.345342
C	-0.971028	1.558475	0.993441
C	-2.977052	0.362083	1.114030
N	-1.551146	0.298574	0.925205
0	0.221037	1.813267	1.054146
C	5.726409	-0.108810	0.900914
C	3.867272	1.946779	1.021357
C	6.166000	1.221030	0.966155
C	4.356042	-0.410122	0.895767
C	3.422769	0.627299	0.956692
C	5.225377	2.250766	1.026474
Н	7.224785	1.470095	0.970827
Н	4.002653	-1.437739	0.844946
Н	2.360346	0.394226	0.952140
Н	5.547930	3.287574	1.077286
C	-0.812662	-0.923063	1.140394
Н	-0.873385	-1.189584	2.199306
Н	0.237240	-0.784494	0.868216
Н	-1.249225	-1.717827	0.530176
Н	-2.161562	2.962245	2.068362
Н	-4.237416	2.149830	1.115888
Н	-3.197428	0.215030	2.176810
Н	-3.480394	-0.403023	0.516705
0	2.983319	2.983331	1.081365
Н	3.459210	3.825370	1.120860
H	6.460269	-0.921475	0.853594

**Table S6.34.** XYZ coordinates for NMP-phenol nHB complex (D = 3.0 Å).

The relative insensitivity of the ACE's in substituted phenol rotors against electrostatic alterations was examined via a series of similar SAPT calculations on bimolecular complexes comprised of NMP and substituted phenols (X = H, p-NO<sub>2</sub>, m-NO<sub>2</sub>, p-CN, p-Cl, and m-Cl). In this study, the O-to-O distance (**D**) at 2.5 Å is the only distance used to mimic the transition state geometries of the phenol and control rotors. The geometric constraints described previously for the unsubstituted phenol were applied on the NMP-substituted phenol complexes in the configurations with and without (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right).) hydrogen bond. The geometric optimizations and SAPT calculations were carried out at the same levels of theory as described above. The component terms ( $E_{elst}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$ ) for the six bimolecular complexes of NMP and substituted phenols with and without hydrogen bond were obtained and tabulated in Table S6.35. SAPT total ( $E_{total}$ , kcal/mol) and component energies ( $E_{elst}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$ , kcal/mol) for the NMP-phenol complex in two configurations (Figure S6.3) at 2.5 Å as well as the differences in energy ( $E^{\Lambda} = E^{HB} - E^{nHB}$ ) between the two configurations.

The hydrogen bond ACE's were characterized similarly as above. The ACE for each hydrogen bond was based on the difference ( $\Delta E = E^{HB} - E^{nHB}$ ) in the calculated total ( $\Delta E_{total}$ ) and component energy terms ( $\Delta E_{elst}$ ,  $\Delta E_{exch}$ ,  $\Delta E_{ind}$ , and  $\Delta E_{disp}$ ) between the configurations of with and without hydrogen bond for the six bimolecular complexes ( $X = H, p-NO_2, m-NO_2, p-CN, p-Cl$ , and m-Cl). These energy differences were plotted against the measured association energies  $(\Delta G_{\rm Ka})$  to explore the origins of the relatively constant ACE's observed in substituted phenol rotors (Figure S6.5. Correlations of the calculated hydrogen bond ACE total ( $\Delta E_{total}$ , kcal/mol) and component energy terms ( $\Delta E_{elst}$ ,  $\Delta E_{exch}$ ,  $\Delta E_{ind}$ , and  $\Delta E_{disp}$  kcal/mol) with the experimentally measured association energies ( $\Delta G_{Ka}$ , kcal/mol) in the bimolecular complexes of NMP and substituted phenols. The calculated total and component terms were tabulated in Table S6.35, and the experimentally measured association energies were tabulated in Table S5.1). The electrostatic term ( $\Delta E_{elst}$ ) of the hydrogen bond ACE was relatively constant despite the presence of EWG substituents, resulting a flat trend line in the correlation plot against the measured association energy (Figure S6.5. Correlations of the calculated hydrogen bond ACE total ( $\Delta E_{total}$ , kcal/mol) and component energy terms ( $\Delta E_{elst}$ ,  $\Delta E_{exch}$ ,  $\Delta E_{ind}$ , and  $\Delta E_{disp}$  kcal/mol) with the experimentally measured association energies ( $\Delta G_{Ka}$ , kcal/mol) in the bimolecular complexes of NMP and substituted phenols. The calculated total and component terms were tabulated in Table S6.35, and the experimentally measured association energies were tabulated in Table S5.1, A). However, moderate changes were observed in the exchange ( $\Delta E_{exch}$ ) and induction ( $\Delta E_{ind}$ ) terms as well as the total energy ( $\Delta E_{\text{total}}$ ) of the hydrogen bond ACE's upon introducing EWG substituents. Nevertheless, these changes were significantly less in comparison to the observed changes in association energy for the host-guest complex of NMP and substituted phenols in solution.
**Table S6.35.** SAPT total ( $E_{total}$ , kcal/mol) and component energies ( $E_{elst}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$ , kcal/mol) for the NMP-phenol complex in two configurations (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right).) at 2.5 Å as well as the differences in energy ( $E^{\Delta} = E^{\text{HB}} - E^{\text{nHB}}$ ) between the two configurations.

$E^{\text{HB}}$ for the configuration with hydrogen bond						
Fundamental energy	Н	p-NO <sub>2</sub>	m-NO <sub>2</sub>	p-Cl	m-Cl	p-CN
$E_{ m elst}^{ m HB}$	-19.65	-21.72	-21.32	-20.43	-20.32	-21.31
$E_{\rm exch}^{\rm HB}$	29.17	28.54	28.68	28.93	28.89	28.69
$E_{\rm indu}^{\rm HB}$	-4.51	-5.13	-5.02	-4.73	-4.71	-5.01
$E_{ m dips}^{ m HB}$	-7.94	-7.84	-7.85	-7.91	-7.91	-7.87
$E_{\rm total}^{\rm HB}$	-2.93	-6.16	-5.51	-4.15	-4.05	-5.49
$E^{\mathbf{nHB}}$ for the configuration without hydrogen bond						
	Н	p-NO <sub>2</sub>	m-NO <sub>2</sub>	p-Cl	m-Cl	p-CN
$E_{\rm elst}^{{f nHB}}$	1.04	-1.02	-0.65	0.26	0.36	-0.61
$E_{\mathrm{exch}}^{\mathbf{nHB}}$	10.35	10.17	10.23	10.25	10.31	10.21
$E_{\mathrm{indu}}^{\mathbf{nHB}}$	-1.23	-1.23	-1.26	-1.23	-1.23	-1.23
$E_{\mathrm{disp}}^{\mathbf{nHB}}$	-4.94	-4.91	-4.90	-4.94	-4.95	-4.92
$E_{\rm total}^{{f nHB}}$	5.22	3.00	3.42	4.33	4.49	3.44
$\Delta E = E^{\mathbf{HB}} - E^{\mathbf{nHB}}$						
	Н	p-NO <sub>2</sub>	m-NO <sub>2</sub>	p-Cl	m-Cl	p-CN
$\Delta E_{\rm elst.}$	-20.70	-20.70	-20.67	-20.69	-20.68	-20.69
$\Delta E_{\mathrm{exch.}}$	18.82	18.38	18.44	18.68	18.58	18.48
$\Delta E_{ m ind.}$	-3.28	-3.90	-3.76	-3.50	-3.49	-3.77
$\Delta E_{\rm disp.}$	-3.00	-2.93	-2.94	-2.97	-2.96	-2.95
$\Delta E_{\rm total}$	-8.15	-9.16	-8.93	-8.48	-8.54	-8.93



**Figure S6.5.** Correlations of the calculated hydrogen bond ACE total ( $\Delta E_{\text{total}}$ , kcal/mol) and component energy terms ( $\Delta E_{\text{elst}}$ ,  $\Delta E_{\text{exch}}$ ,  $\Delta E_{\text{ind}}$ , and  $\Delta E_{\text{disp}}$  kcal/mol) with the experimentally measured association energies ( $\Delta G_{\text{Ka}}$ , kcal/mol) in the bimolecular complexes of NMP and substituted phenols. The calculated total and component terms were tabulated in Table S6.35. SAPT total ( $E_{\text{total}}$ , kcal/mol) and component energies ( $E_{\text{elst}}$ ,  $E_{\text{exch}}$ ,  $E_{\text{ind}}$ , and  $E_{\text{disp}}$ , kcal/mol) for the NMP-phenol complex in two configurations (Figure S6.3. Two configurations of the bimolecular complex of NMP and phenol (X=H) used for SAPT analysis: hydrogen bonding (**HB**, left) and non-hydrogen bonding (**nHB**, right).) at 2.5 Å as well as the differences in energy ( $E^{\Lambda} = E^{\text{HB}} - E^{\text{nHB}}$ ) between the two configurations., and the experimentally measured association energies were tabulated in Table S5.1. Gibbs free association energy ( $\Delta G_{\text{Ka}}$ , kcal/mol)<sup>*a*</sup> for the hydrogen bonded host-guest complexes of *N*-methyl pyrrolidone and (substituted) phenols in dichloromethane-d<sub>2</sub>.

## 7. Crystallographic structures

### 7.1 X-ray structure determination for phenol rotor 1 (X = H), $C_{15}H_{13}NO_3$

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.<sup>15,16</sup> Final unit cell parameters were determined by least-squares refinement of 9106 reflections taken from the data set. The structure was solved with SHELXT.<sup>17,18</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2016<sup>17,18</sup> using OLEX2.<sup>19</sup>

The compound crystallizes in the space group  $P2_1/n$  of the monoclinic system. The asymmetric unit consists of one  $C_{15}H_{13}NO_3$  molecule, which is disordered. The  $-C_6H_4OH$  substituent is disordered over two orientations *via* a 180° rotation about the N1-C10 bond. Only the hydroxyl group atoms are affected; all other atoms are exactly superimposed. The major component occupancy fraction (atom label suffixes A) refined to 0.685(3). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in Fourier difference maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C) for methine hydrogen atoms and d(C-H) = 0.99 Å and Uiso(H) = 1.2Ueq(C) for methylene hydrogens. Hydroxyl hydrogen atoms were located in difference maps. They were refined isotropically with a similar distance restrains (SHELX SADI). The largest residual electron density peak in the final difference map is  $0.39 \text{ e}^-/\text{Å}^3$ , located 0.75 Å from C5.



Empirical formula	C <sub>15</sub> H <sub>13</sub> NO <sub>13</sub>
Formula weight	255.26
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	10.7032(5)
b/Å	6.6627(3)
c/Å	16.9382(8)
α/°	90
β/°	92.303(2)
$\gamma/^{\circ}$	90
Volume/Å <sup>3</sup>	1206.92(10)
Ζ	4
$ ho_{calc}g/cm^3$	1.405
µ/mm <sup>-1</sup>	0.099
F(000)	536.0
Crystal size/mm <sup>3</sup>	0.52  imes 0.26  imes 0.2
Radiation	MoKa ( $\lambda = 0.71073$ )
2Θ range for data collection/°	4.422 to 60.36
Index ranges	$-15 \le h \le 15, -9 \le k \le 9, -23 \le l \le 23$
Reflections collected	56388
Independent reflections	$3575 [R_{int} = 0.0454, R_{sigma} = 0.0223]$
Data/restraints/parameters	3575/1/191
Goodness-of-fit on F <sup>2</sup>	1.046
Final R indexes [I>=2 $\sigma$ (I)]	$R_1 = 0.0401, wR_2 = 0.0967$
Final R indexes [all data]	$R_1 = 0.0525, wR_2 = 0.1027$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.39/-0.21

**Table S7.1.** Crystal data and structure refinement for rotor 1 (X = H).

# 7.2 X-ray structure determination for phenol rotor 1 (X = p-Cl), C<sub>15</sub>H<sub>12</sub>ClNO<sub>3</sub>

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.<sup>15,16</sup> Final unit cell parameters were determined by least-squares refinement of 9958 reflections taken from the data set. The structure was solved with SHELXT.<sup>17,20</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2017<sup>17,20</sup> using OLEX2.<sup>19</sup>

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space group  $P2_1/c$ , which was verified by structure solution. The asymmetric unit consists of two crystallographically independent but chemically identical molecules. The molecules were numbered identically except for label suffixes A or B. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in Fourier difference maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C)for methine hydrogen atoms, d(C-H) = 0.95 Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogen atoms, d(C-H) = 0.99 Å and Uiso(H) = 1.2Ueq(C) for methylene hydrogen atoms, and d(C-H) =0.98 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The two independent hydroxy hydrogen atoms were located in difference Fourier maps and refined freely. The largest residual electron density peak in the final difference map is  $0.42 \text{ e}^{-1}$ Å<sup>3</sup>, located 0.74 Å from C6A.



Empirical formula	C <sub>15</sub> H <sub>12</sub> CINO <sub>3</sub>
Formula weight	289.71
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	21.3570(9)
b/Å	6.8190(3)
c/Å	20.0691(8)
α/°	90
β/°	115.0080(10)
γ/°	90
Volume/Å <sup>3</sup>	2648.72(19)
Ζ	8
$ ho_{calc}g/cm^3$	1.453
µ/mm <sup>-1</sup>	0.295
F(000)	1200.0
Crystal size/mm <sup>3</sup>	0.6 imes 0.14 imes 0.08
Radiation	MoKa ( $\lambda = 0.71073$ )
2@ range for data collection/°	4.48 to 60.106
Index ranges	$-30 \le h \le 29, -9 \le k \le 9, -28 \le l \le 28$
Reflections collected	61497
Independent reflections	7769 [ $R_{int} = 0.0490, R_{sigma} = 0.0344$ ]
Data/restraints/parameters	7769/0/370
Goodness-of-fit on F <sup>2</sup>	1.017
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0426, wR_2 = 0.0909$
Final R indexes [all data]	$R_1 = 0.0669, wR_2 = 0.1019$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.42/-0.47

**Table S7.2.** Crystal data and structure refinement for rotor 1 (X = p-Cl).

#### 7.3 X-ray structure determination for phenol rotor 1 (X = m-Cl), C<sub>15</sub>H<sub>12</sub>ClNO<sub>3</sub>

X-ray intensity data from a colorless plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.<sup>15,16</sup> Final unit cell parameters were determined by least-squares refinement of 9909 reflections taken from the data set. The structure was solved with SHELXT.<sup>18,20</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2016<sup>18,20</sup> using OLEX2.<sup>19</sup>

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space groups Ia and I2/a. A reasonable solution and refinement was obtained in I2/a. The refinement was hampered by whole-molecule disorder present in the crystal. This was suggested by the appearance of diffuse streaking between Bragg peaks in the area detector diffraction pattern images of several surveyed crystals, both at low and at room temperature. Initial structure solutions returned a pattern of electron density consistent with one molecule in the asymmetric unit. A single molecule model refined poorly, giving high Rvalues and a pattern of residual electron density eventually seen to correspond to another complete molecule in a different orientation, but partially overlapped with the main molecule. The two disorder components are related by an apparent non--crystallographic mirror plane perpendicular to the b axis at y = 0.25. The whole-molecular disorder was also observed in the lower symmetry space groups Ia and I2. Examination of the diffraction pattern for an alternative unit cell or for twinning was fruitless. The disordered asymmetric unit in I2/a consists of one C<sub>15</sub>H<sub>12</sub>ClNO<sub>3</sub> molecule, with disorder population fractions of 0.879(2) (no atom label suffix) and 0.121(2) (atom label suffixes B). A further structural complication is that the -C<sub>6</sub>H<sub>3</sub>ClOH substituent of each disorder component is itself disordered over two conformations within each component. This is manifested only in the position of the -OH group. For stability, -OH group occupancies were fixed at values providing the most reasonable displacement parameter values, and are: main wholemolecule component, O3A/O3C = 50/50 (0.44/0.44), minor component O3B/O3D = 60/40(0.07/0.05). A total of 64 restraints were used in the disorder modeling. The geometry of the minor component was restrained to be similar to that of the major using SHELX SAME instructions. The two N1-C10 distances and all C-O(hydroxyl) distances between components were further

restrained to be similar to those of the same type. All nonhydrogen atoms of the major disorder component were refined with anisotropic displacement parameters. Those of the minor were refined isotropically except when they were nearly superimposed with an atom from the major component, in which case both atoms were refined with equal anisotropic displacement parameters. Hydrogen atoms bonded to carbon placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C) for methine hydrogen atoms, d(C-H) = 0.95 Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogen atoms and d(C-H) = 0.99 Å and Uiso(H) =1.2Ueq(C) for methylene hydrogen atoms. Hydroxyl hydrogen atoms could not be reliably located and were not calculated. The largest residual electron density peak in the final difference map is 0.35 e<sup>-</sup>/Å<sup>3</sup>, located 0.91 Å from O3B.



Empirical formula	C <sub>15</sub> H <sub>12</sub> CINO <sub>3</sub>
Formula weight	289.71
Temperature/K	100(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	17.4699(12)
b/Å	6.8917(5)
c/Å	22.137(2)
α/°	90
β/°	103.5700(16)
γ/°	90
Volume/Å <sup>3</sup>	2590.8(3)
Ζ	8
$\rho_{calc}g/cm^3$	1.485
µ/mm <sup>-1</sup>	0.301
F(000)	1200.0
Crystal size/mm <sup>3</sup>	0.28  imes 0.22  imes 0.06
Radiation	MoKa ( $\lambda = 0.71073$ )
20 range for data collection/°	4.798 to 55.446
Index ranges	$-22 \le h \le 22, -9 \le k \le 9, -28 \le l \le 28$
Reflections collected	49286
Independent reflections	$3036 [R_{int} = 0.0385, R_{sigma} = 0.0153]$
Data/restraints/parameters	3036/64/272
Goodness-of-fit on F <sup>2</sup>	1.301
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0524, wR_2 = 0.1264$
Final R indexes [all data]	$R_1 = 0.0557, wR_2 = 0.1277$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.35/-0.29

**Table S7.3.** Crystal data and structure refinement for rotor (X = *m*-Cl).

### 7.4 X-ray structure determination for anisole rotor 2 (X = p-NO<sub>2</sub>), C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>5</sub>

X-ray intensity data from a colorless block were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.<sup>15,16</sup> Final unit cell parameters were determined by least-squares refinement of 9963 reflections taken from the data set. The structure was solved with SHELXT.<sup>17,20</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2017<sup>17,20</sup> using OLEX2.<sup>19</sup>

The compound crystallizes in the triclinic system. The space group *P*-1 (No. 2) was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C) for methine hydrogen atoms, d(C-H) = 0.95 Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogen atoms, and d(C-H) = 0.98 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is  $0.38 e^{-1}$ Å<sup>3</sup>, located 0.62 Å from C14.



Empirical formula	$C_{16}H_{14}N_2O_5$
Formula weight	314.29
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.7842(5)
b/Å	9.7899(6)
c/Å	10.0423(6)
α/°	81.677(2)
β/°	82.193(2)
γ/°	67.584(2)
Volume/Å <sup>3</sup>	697.29(8)
Ζ	2
$\rho_{calc}g/cm^3$	1.497
µ/mm <sup>-1</sup>	0.113
F(000)	328.0
Crystal size/mm <sup>3</sup>	$0.54 \times 0.44 \times 0.36$
Radiation	MoKα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	4.524 to 60.384
Index ranges	$-11 \le h \le 11, -13 \le k \le 13, -14 \le l \le 14$
Reflections collected	31746
Independent reflections	4121 [ $R_{int} = 0.0480, R_{sigma} = 0.0333$ ]
Data/restraints/parameters	4121/0/210
Goodness-of-fit on F <sup>2</sup>	1.029
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0440, wR_2 = 0.1003$
Final R indexes [all data]	$R_1 = 0.0645, wR_2 = 0.1111$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.38/-0.31

**Table S7.4.** Crystal data and structure refinement for rotor **2** (X = p-NO<sub>2</sub>).

#### 7.5 X-ray structure determination for anisole rotor 2 (X = m-NO<sub>2</sub>), C<sub>16</sub>H<sub>14</sub>ClNO<sub>3</sub>

X-ray intensity data from a colorless block were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.<sup>15,16</sup> Final unit cell parameters were determined by least-squares refinement of 9800 reflections taken from the data set. The structure was solved with SHELXT.<sup>17,20</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2017<sup>17,20</sup> using OLEX2.<sup>19</sup>

The compound crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was consistent with the space group  $P2_12_12_1$ , which was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in Fourier difference maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C) for methine hydrogen atoms, d(C-H) = 0.95Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogen atoms, d(C-H) = 0.99 Å and Uiso(H) =1.2Ueq(C) for methylene hydrogen atoms, and d(C-H) = 0.98 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is  $0.26 \text{ e-/Å}^3$ , located 0.68 Å from C13. The absolute structure (Flack) parameter after the final refinement cycle was 0.013(13), indicating the correct absolute structure and the absence of racemic twinning.



Empirical formula	C <sub>16</sub> H <sub>14</sub> CINO <sub>3</sub>
Formula weight	303.73
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	9.8726(5)
b/Å	10.9075(5)
c/Å	12.7229(6)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1370.07(11)
Ζ	4
$\rho_{calc}g/cm^3$	1.473
µ/mm <sup>-1</sup>	0.288
F(000)	632.0
Crystal size/mm <sup>3</sup>	0.48  imes 0.42  imes 0.3
Radiation	MoKα ( $\lambda$ = 0.71073)
20 range for data collection/°	4.92 to 60.168
Index ranges	$-13 \le h \le 13, -15 \le k \le 15, -17 \le l \le 17$
Reflections collected	49019
Independent reflections	4021 [R <sub>int</sub> = 0.0391, R <sub>sigma</sub> = 0.0199]
Data/restraints/parameters	4021/0/192
Goodness-of-fit on F <sup>2</sup>	1.029
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0272, wR_2 = 0.0636$
Final R indexes [all data]	$R_1 = 0.0309, wR_2 = 0.0655$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.26/-0.20
Flack parameter	0.013(13)

**Table S7.5.** Crystal data and structure refinement for rotor **2** (X = m-NO<sub>2</sub>).

### 7.6 X-ray structure determination for anisole rotor 2 (X = p-CN), C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>

X-ray intensity data from a colorless rectangular plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.<sup>15,16</sup> Final unit cell parameters were determined by least-squares refinement of 9963 reflections taken from the data set. The structure was solved with SHELXT.<sup>17,20</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2017<sup>17,20</sup> using OLEX2.<sup>19</sup>

The compound crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was consistent with the space groups  $Pna2_1$  and Pnma. Intensity statistics suggested an acentric structure.  $Pna2_1$  was assigned by SHELXT and was confirmed by structure refinement and with ADDSYM.<sup>21–24</sup> The asymmetric unit consists of one molecule. All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in Fourier difference maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C) for methine hydrogen atoms, d(C-H) = 0.95 Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogen atoms, and d(C-H) =0.98 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. Though lacking any atoms heavier then oxygen, the final absolute structure (Flack) parameter of 0.11(14) suggests the correct absolute structure has been established. This was aided by the high-quality, relatively high resolution data ( $d_{max} = 0.71$  Å). The largest residual electron density peak in the final difference map is  $0.28 \text{ e}^-/\text{Å}^3$ , located 0.70 Å from C11.



Empirical formula	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>
Formula weight	294.30
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pna2 <sub>1</sub>
a/Å	25.6129(11)
b/Å	7.2650(3)
c/Å	7.5367(3)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1402.41(10)
Ζ	4
$\rho_{calc}g/cm^3$	1.394
μ/mm <sup>-1</sup>	0.097
F(000)	616.0
Crystal size/mm <sup>3</sup>	0.36  imes 0.2  imes 0.1
Radiation	MoKα ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/°	5.828 to 60.164
Index ranges	$-36 \le h \le 36, -10 \le k \le 10, -10 \le l \le 10$
Reflections collected	73700
Independent reflections	4118 [R <sub>int</sub> = 0.0300, R <sub>sigma</sub> = 0.0125]
Data/restraints/parameters	4118/1/201
Goodness-of-fit on F <sup>2</sup>	1.032
Final R indexes [I>=2 $\sigma$ (I)]	$R_1 = 0.0278, wR_2 = 0.0735$
Final R indexes [all data]	$R_1 = 0.0298, wR_2 = 0.0748$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.28/-0.17
Flack parameter	0.11(13)

**Table S7.6.** Crystal data and structure refinement for rotor **2** (X = p-CN).

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