

## Supplementary Information

### Cycloalkanes and cycloalkenes in dispersive force oriented inclusion crystals by a functionalized acyclic host molecule

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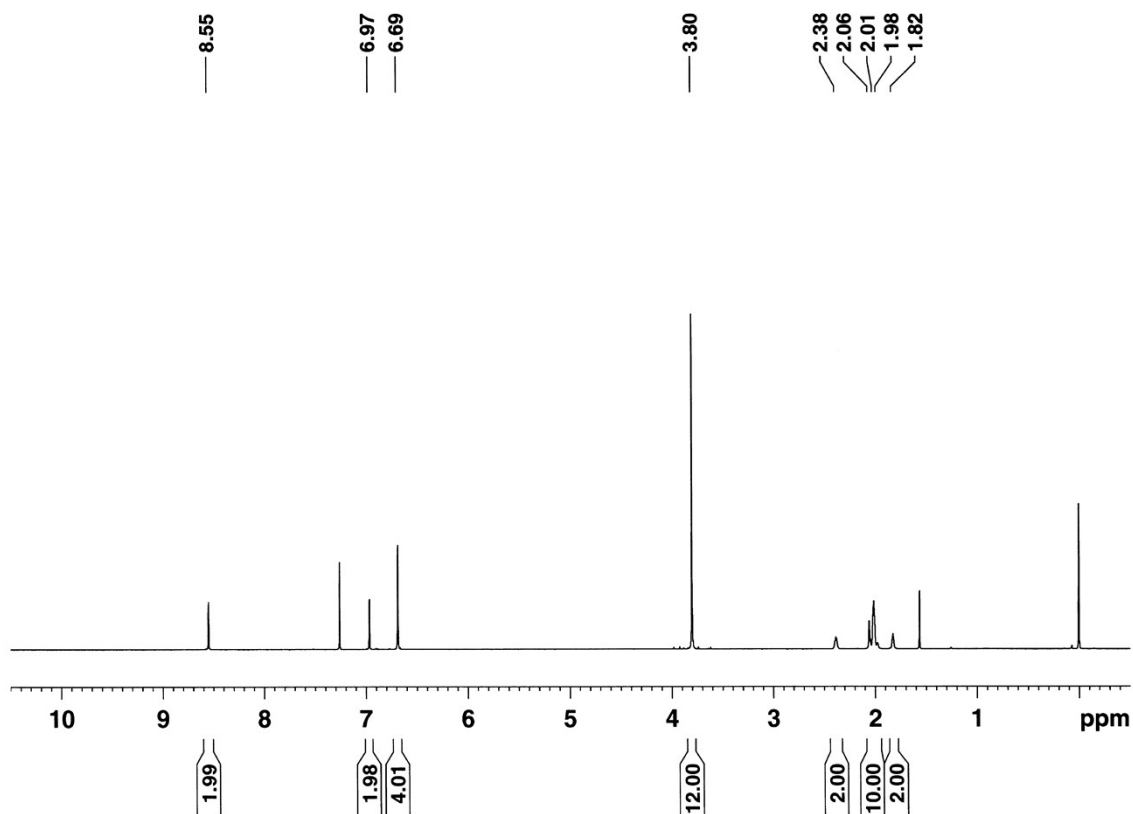
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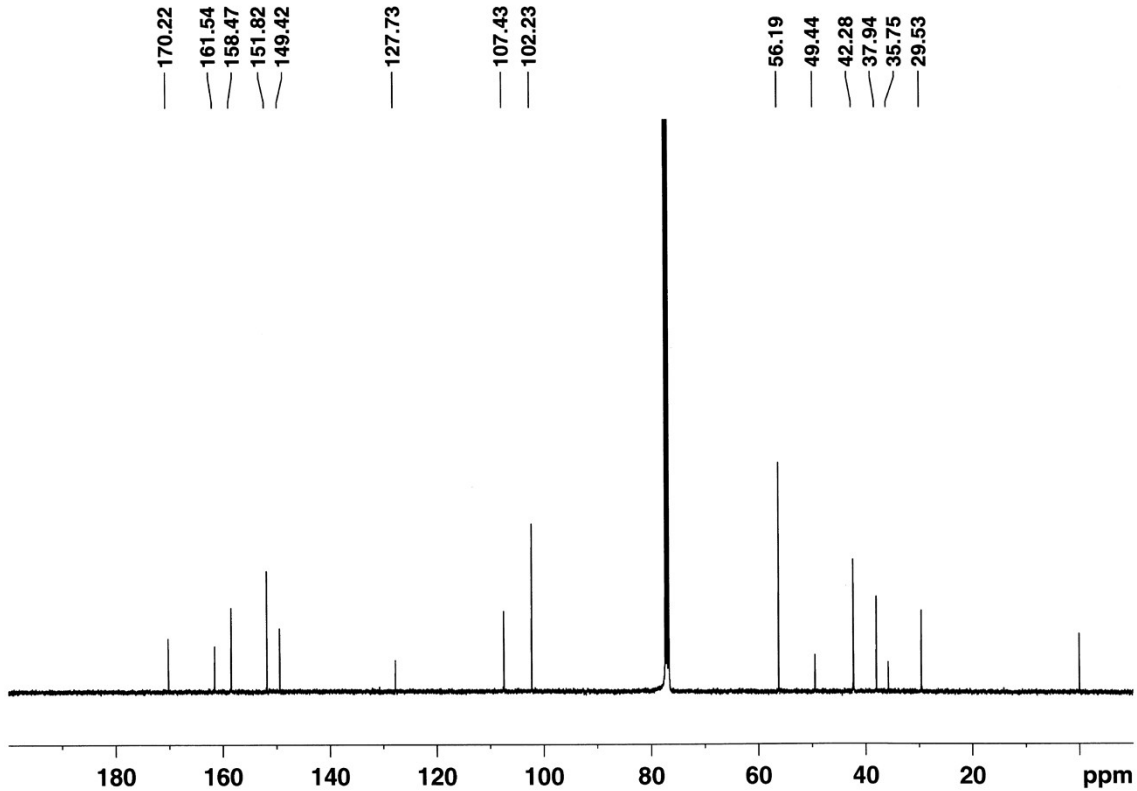
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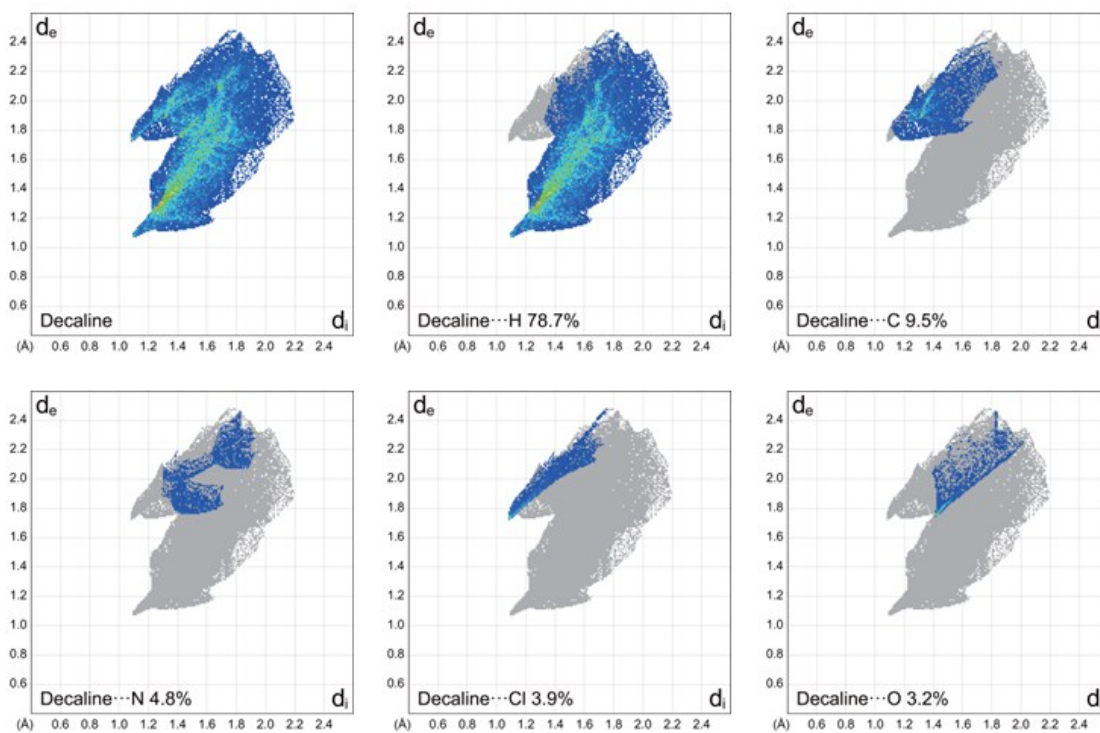
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$^1\text{H}$  NMR spectrum of **1** (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR spectrum of **1** (100 MHz,  $\text{CDCl}_3$ )





**Fig. S1** The 2D fingerprint plots focusing on the specific interactions of *trans*-decahydronaphthalene in crystal **1a**.

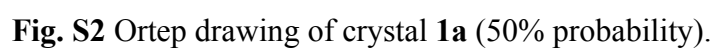
### Single crystal X-ray diffraction experiment for 1a

The colorless prismatic crystal ( $0.100 \times 0.080 \times 0.050 \text{ mm}^3$ ), obtained from chloroform/*trans*-decahydronaphthalene, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$  :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>39</sub>H<sub>43</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub>,  $M_r = 734.67$ ; triclinic, space group  $P-1$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.374 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 10.0070(5)$ ,  $b = 13.2653(7)$ ,  $c = 15.0577(8) \text{ \AA}$ ,  $\alpha = 80.234(2)$ ,  $\beta = 71.193(2)$ ,  $\gamma = 70.137(2)^\circ$ ,  $V = 1775.50(16) \text{ \AA}^3$ , 24164 measured and 7255 independent [ $I > 2\sigma(I)$ ] reflections, 464 parameters, final  $R_1 = 0.0647$ ,  $wR_2 = 0.1855$ ,  $S = 1.035$  [ $I > 2\sigma(I)$ ]. CCDC 1880544

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically placed on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms.

The *trans*-decahydronaphthalene molecule lied on the crystallographic symmetric center was firstly refined with the free variable and finally fixed with the site occupancy factor of 100%.

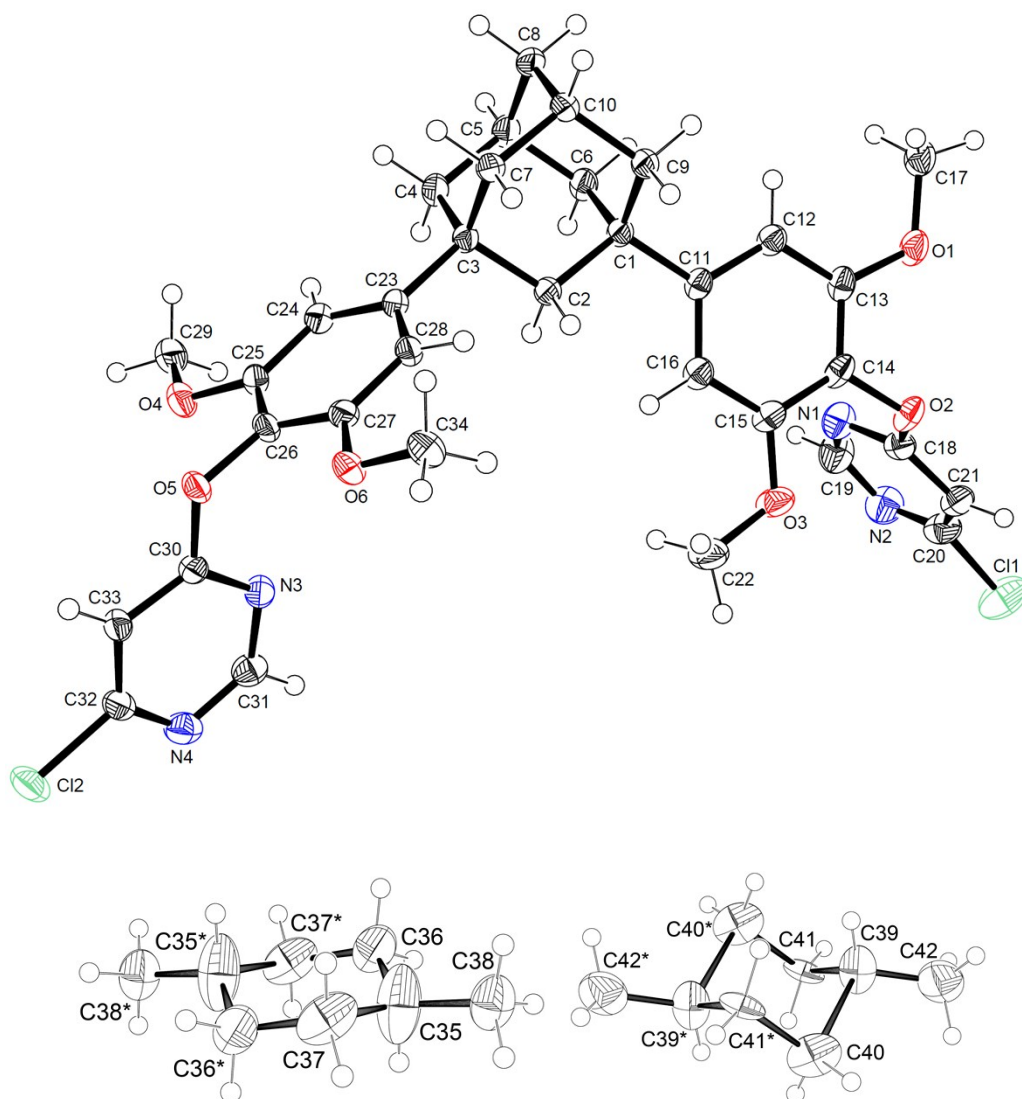


### Single crystal X-ray diffraction experiment for 1b

The colorless prismatic crystal ( $0.100 \times 0.090 \times 0.050$  mm<sup>3</sup>), obtained from chloroform/*trans*-1,4-dimethylcyclohexane, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>38</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub>,  $M_r = 721.65$ ; triclinic, space group  $P-1$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.374$  g·cm<sup>-3</sup>,  $a = 9.9163(5)$ ,  $b = 13.1401(7)$ ,  $c = 14.9925(8)$  Å,  $\alpha = 78.987(2)$ ,  $\beta = 71.536(2)$ ,  $\gamma = 71.106(2)^\circ$ ,  $V = 1744.60(16)$  Å<sup>3</sup>, 23873 measured and 7105 independent [ $I > 2\sigma(I)$ ] reflections, 496 parameters, final  $R_1 = 0.0475$ ,  $wR_2 = 0.1308$ ,  $S = 1.042$  [ $I > 2\sigma(I)$ ]. CCDC 1880545

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. A couple of overlapped and disordered *trans*-1,4-dimethylcyclohexane molecules (C35, C36, C37 and C38, and C39, C40, C41 and C42) riding on a symmetry center were firstly refined with each free variable and finally refined with PART n/-n. The occupancy ratio was 67/33.



**Fig. S3** Ortep drawing of crystal **1b** (50% probability).

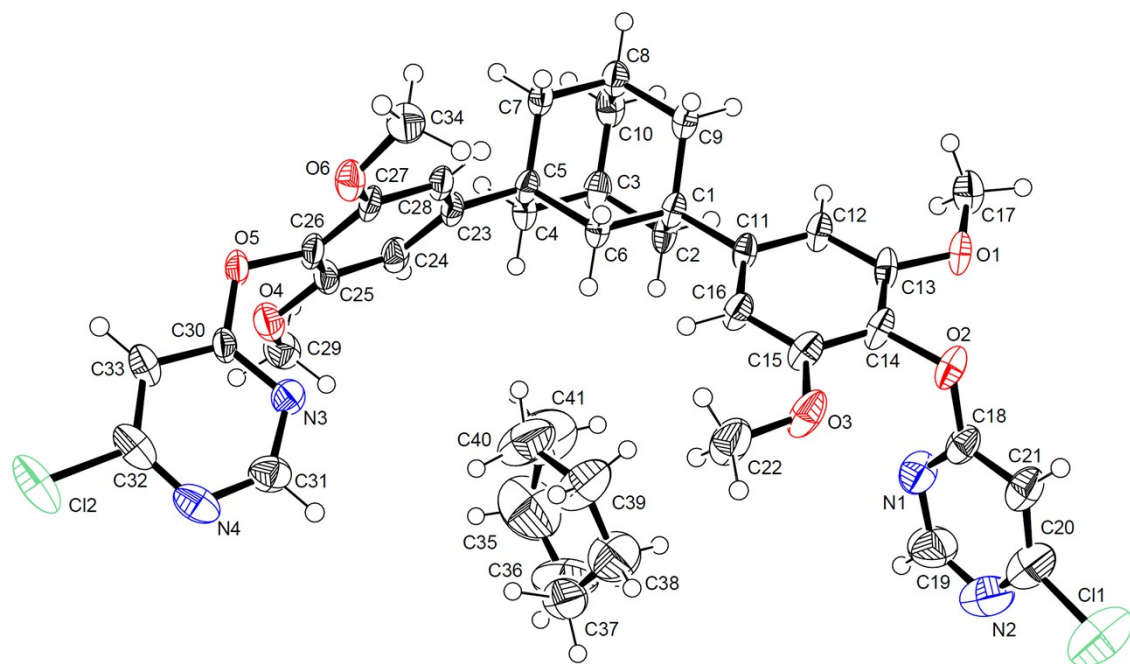
### Single crystal X-ray diffraction experiment for 1c

The colorless prismatic crystal ( $0.050 \times 0.050 \times 0.030 \text{ mm}^3$ ), obtained from chloroform/cycloheptane, was immersed in Paraton-N oil and placed in the  $\text{N}_2$  cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE,  $\text{CuK}\alpha$  :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

$\text{C}_{37.5}\text{H}_{41}\text{Cl}_2\text{N}_4\text{O}_6$ ,  $M_r = 714.64$ ; triclinic, space group  $P-1$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.367 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 9.9369(5)$ ,  $b = 13.0256(7)$ ,  $c = 14.9773(8) \text{ \AA}$ ,  $\alpha = 78.670(3)$ ,  $\beta = 71.719(3)$ ,  $\gamma = 71.595(3)^\circ$ ,  $V = 1736.34(16) \text{ \AA}^3$ , 21375 measured and 7109 independent [ $I > 2\sigma(I)$ ] reflections, 482 parameters, 42 restraints, final  $R_1 = 0.0890$ ,  $wR_2 = 0.2603$ ,  $S = 1.046$  [ $I > 2\sigma(I)$ ]. CCDC 1880546

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The cycloheptane lied on a symmetric center was firstly refined with free variable and finally fixed with the occupancy of 50% (combination with PART -n). The restraint SIMU was applied to C35, C36, C37, C38, C39, C40 and C41.





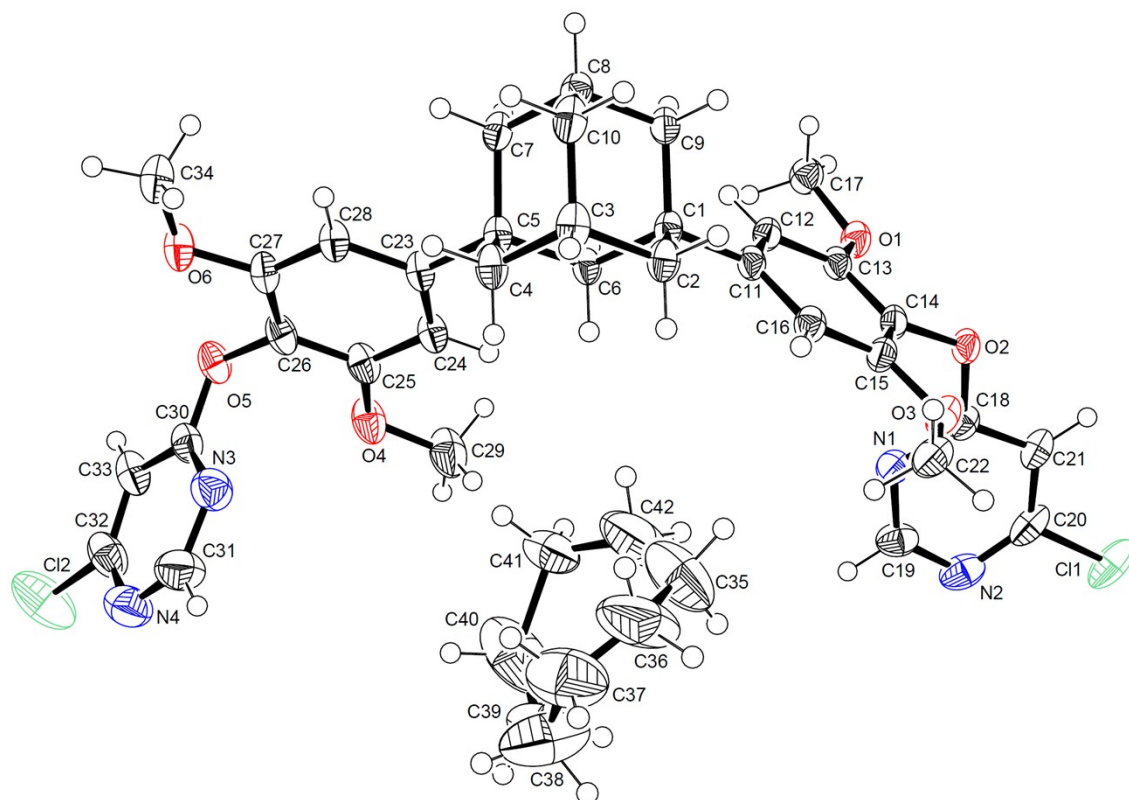
**Fig. S4** Ortep drawing of crystal **1c** (50% probability).

### Single crystal X-ray diffraction experiment for 1d

The colorless prismatic crystal ( $0.100 \times 0.100 \times 0.060$  mm<sup>3</sup>), obtained from chloroform/cyclooctane, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>38</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub>,  $M_r = 721.65$ ; triclinic, space group  $P-1$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.366$  g·cm<sup>-3</sup>,  $a = 9.9249(9)$ ,  $b = 13.0873(12)$ ,  $c = 15.1023(14)$  Å,  $\alpha = 78.486(3)$ ,  $\beta = 71.671(3)$ ,  $\gamma = 71.466(3)^\circ$ ,  $V = 1754.7(3)$  Å<sup>3</sup>, 22489 measured and 7155 independent [ $I > 2\sigma(I)$ ] reflections, 491 parameters, 12 restraints, final  $R_1 = 0.0625$ ,  $wR_2 = 0.1851$ ,  $S = 1.064$  [ $I > 2\sigma(I)$ ]. CCDC 1880547

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The cyclooctane lied on a symmetric center was firstly refined with free variable and finally fixed with the occupancy of 50% (combination with PART -n). The restraint SIMU was applied to C36, C37, C38, C39 and C40.



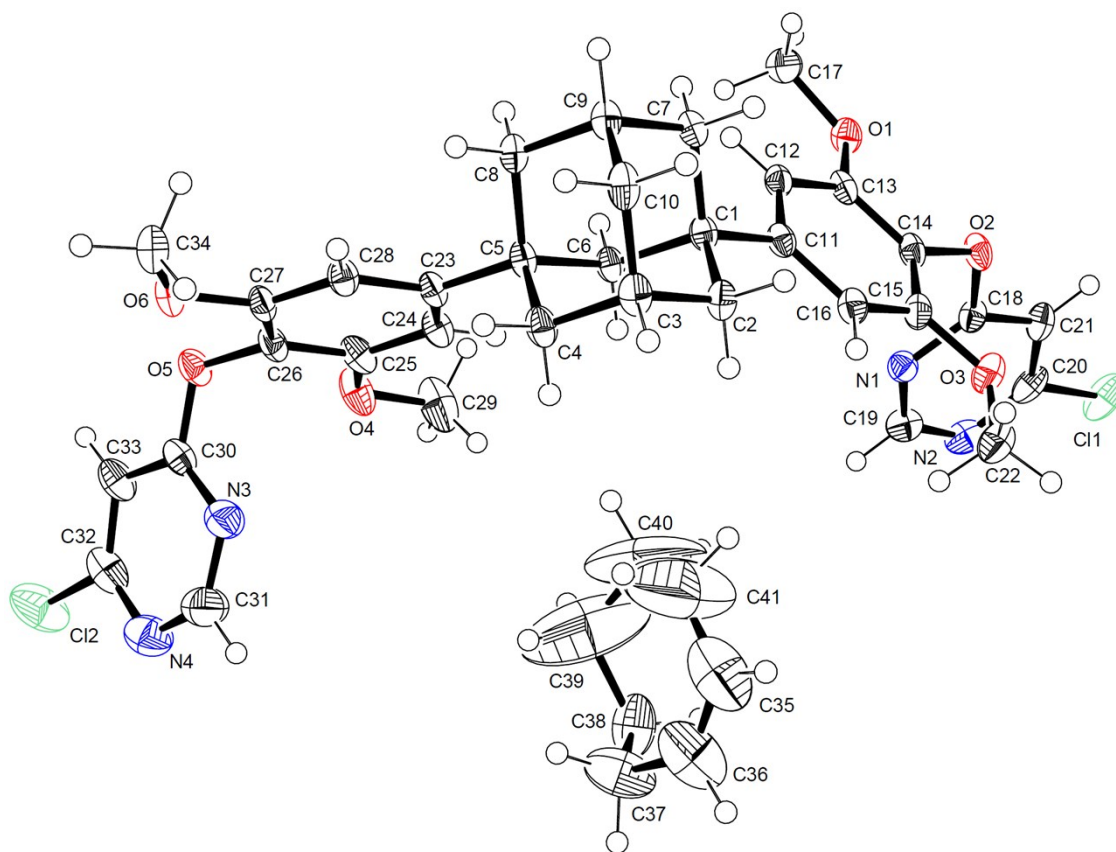
**Fig. S5** Ortep drawing of crystal **1d** (50% probability).

### Single crystal X-ray diffraction experiment for 1e

The colorless prismatic crystal ( $0.100 \times 0.050 \times 0.050$  mm<sup>3</sup>), obtained from chloroform/cycloheptene, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>37.5</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub>,  $M_r = 713.63$ ; triclinic, space group  $P-1$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.367$  g·cm<sup>-3</sup>,  $a = 9.9312(5)$ ,  $b = 13.0381(7)$ ,  $c = 14.9669(8)$  Å,  $\alpha = 78.504(2)$ ,  $\beta = 71.545(2)$ ,  $\gamma = 71.592(2)^\circ$ ,  $V = 1733.59(16)$  Å<sup>3</sup>, 23329 measured and 7107 independent [ $I > 2\sigma(I)$ ] reflections, 482 parameters, 14 restraints, final  $R_1 = 0.0563$ ,  $wR_2 = 0.1629$ ,  $S = 1.044$  [ $I > 2\sigma(I)$ ]. CCDC 1880548

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The cycloheptene lied on a symmetric center was firstly refined with free variable and finally fixed with the occupancy of 50% (combination with PART -n). The restraint DELU was applied to C35, C36, C37, C38, C39, C40 and C41. The sight of double bond of the cycloheptene was determined as follows. After careful comparison with each bond distance with anisotropically refined atoms, the bond distance of C35-C36 was significantly shorter than the others. In addition, C41, C35, C36 and C37 was almost planar, and C35 and C36 may interact with the pyrimidine ring by  $\pi$ - $\pi$  interaction. Hydrogen atoms of the methylene moiety (C37, C38, C39, C40 and C41) were refined with HFIX 23 one-by-one in sequence. The bond distance of C35-C36 was watched whether the distance drastically changes or not during refinement. Finally, hydrogen atoms of C35 and C36 were refined with HFIX 43.



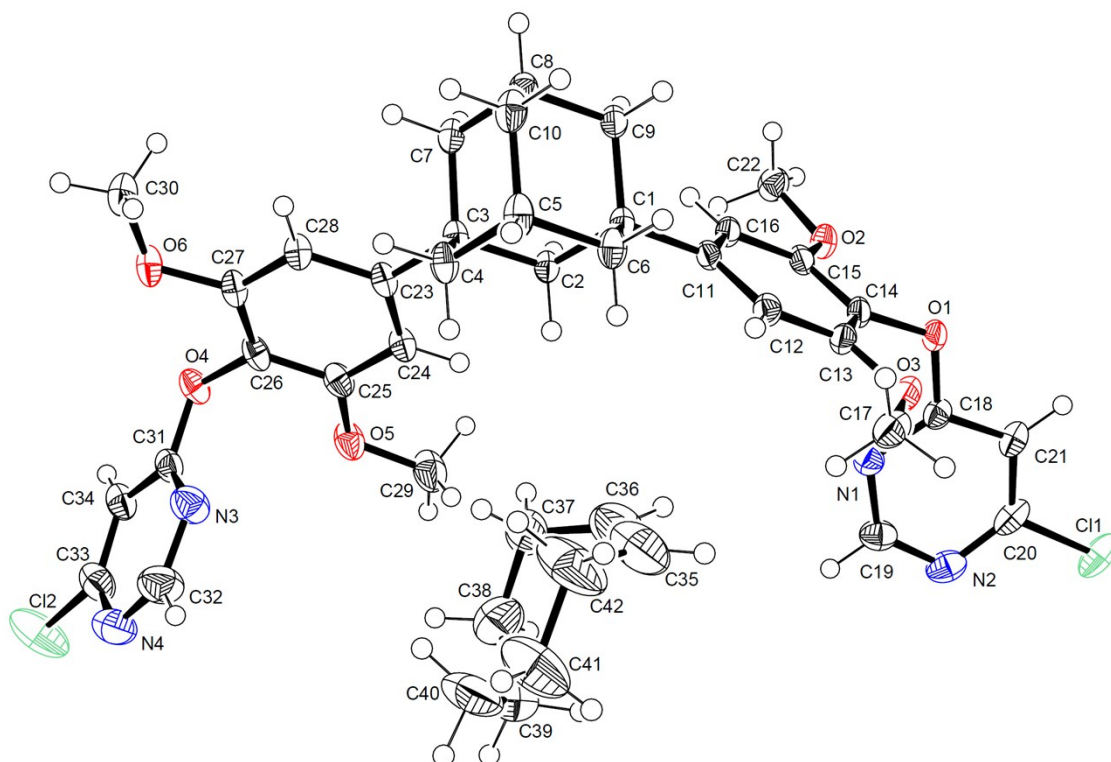
**Fig. S6** Ortep drawing of crystal **1e** (50% probability).

### Single crystal X-ray diffraction experiment for 1f

The colorless prismatic crystal ( $0.100 \times 0.080 \times 0.060$  mm<sup>3</sup>), obtained from chloroform/cyclooctene, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>38</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub>, *Mr* = 720.65; triclinic, space group *P*-1, *Z* = 2, *D*<sub>calc</sub> = 1.374 g·cm<sup>-3</sup>, *a* = 9.9494(7), *b* = 13.0577(10), *c* = 15.0470(11) Å,  $\alpha$  = 78.907(2),  $\beta$  = 71.437(2),  $\gamma$  = 70.820(2)°, *V* = 1741.8(2) Å<sup>3</sup>, 23211 measured and 7110 independent [*I* > 2σ(*I*)] reflections, 491 parameters, final *R*<sub>1</sub> = 0.0479, *wR*<sub>2</sub> = 0.1344, *S* = 1.052 [*I* > 2σ(*I*)]. CCDC 1880549

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The cyclooctene lied on a symmetric center was firstly refined with free variable and finally fixed with the occupancy of 50% (combination with PART -n). The site of double bond of the cyclooctene was determined as follows. After careful comparison with each bond distance with anisotropically refined atoms, the bond distance of C35-C36 was apparently shorter than the others. Hydrogen atoms of methylene moiety (C39, C40, C38, C41, C37 and C42) were refined with HFIX 23 one-by-one in sequence. The bond distance of C35-C36 was always watched whether the distance drastically changes or not during refinement. Finally, hydrogen atoms of C35 and C36 were refined with HFIX 43.



**Fig. S7** Ortep drawing of crystal **1f** (50% probability).

### Single crystal X-ray diffraction experiment for 1

The colorless prismatic crystal ( $0.120 \times 0.100 \times 0.100$  mm<sup>3</sup>), obtained from acetonitrile/chloroform, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>34</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub>,  $M_r = 665.55$ ; monoclinic, space group  $C2/c$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.421$  g·cm<sup>-3</sup>,  $a = 19.6020(17)$ ,  $b = 10.4596(9)$ ,  $c = 15.8952(14)$  Å,  $\beta = 107.358(2)^\circ$ ,  $V = 3110.6(5)$  Å<sup>3</sup>, 19081 measured and 3239 independent [ $I > 2\sigma(I)$ ] reflections, 211 parameters, final  $R_1 = 0.0527$ ,  $wR_2 = 0.1531$ ,  $S = 1.042$  [ $I > 2\sigma(I)$ ]. CCDC 1880550

C4 and C5 were lied on two-fold axis and half a molecule was determined. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically and geometrically placed on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms.

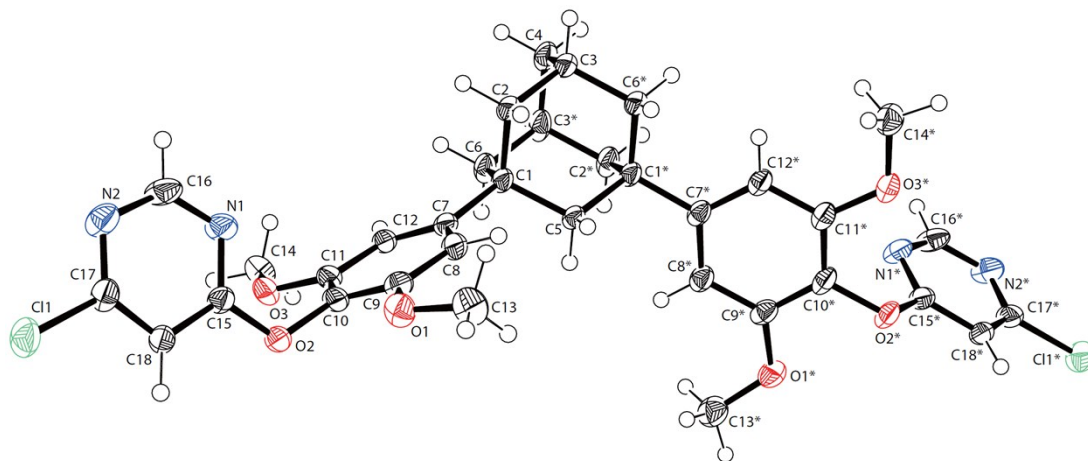


Fig. S8 Ortep drawing of crystal 1 (50% probability).

- (1) G. M. Sheldrick, (1996). *SADABS*. University of Göttingen, Germany.
- (2) G. M. Sheldrick, *Acta. Cryst.*, 2015, **A71**, 3–8.
- (3) G. M. Sheldrick, *Acta. Cryst.*, 2015, **C71**, 3–8.