SUPPORTING INFORMATION

Manuscript title: **Hexahomotrioxacalix[3]arene derivatives as ionophores for molecular recognition of dopamine, serotonin and phenylethylamine**

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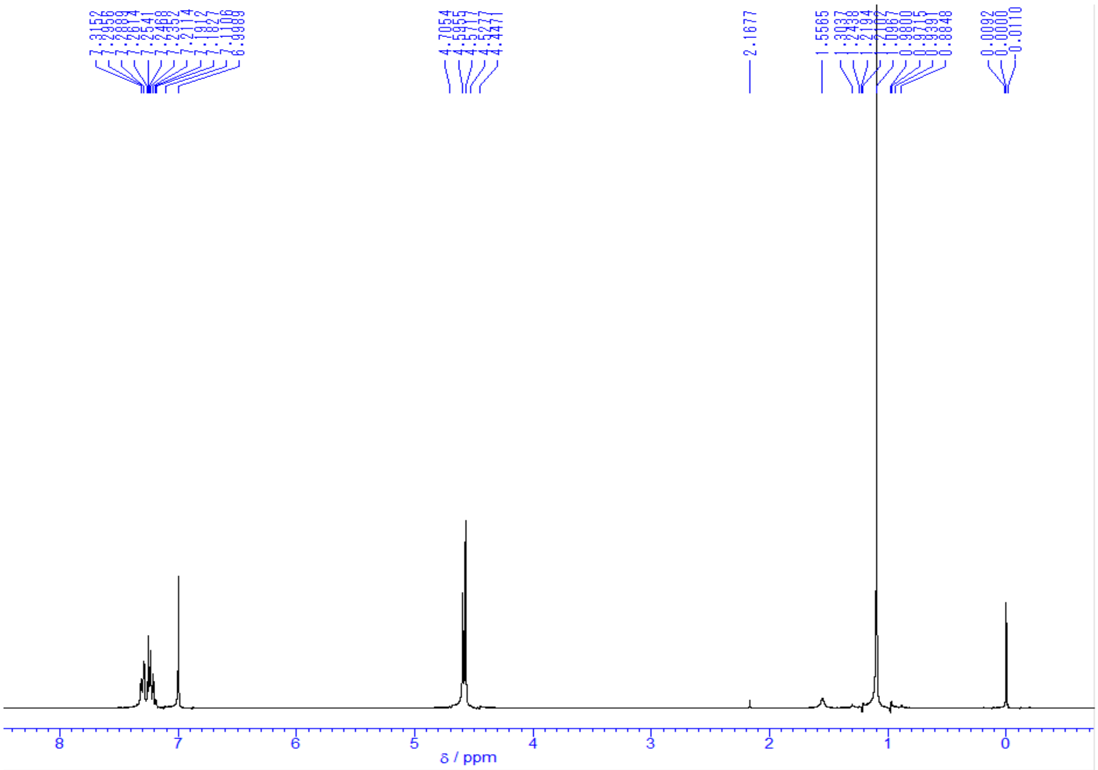


Figure S1. ^{1}H NMR spectra of *cone*-**3** ($CDCl_3$, 300 MHz).

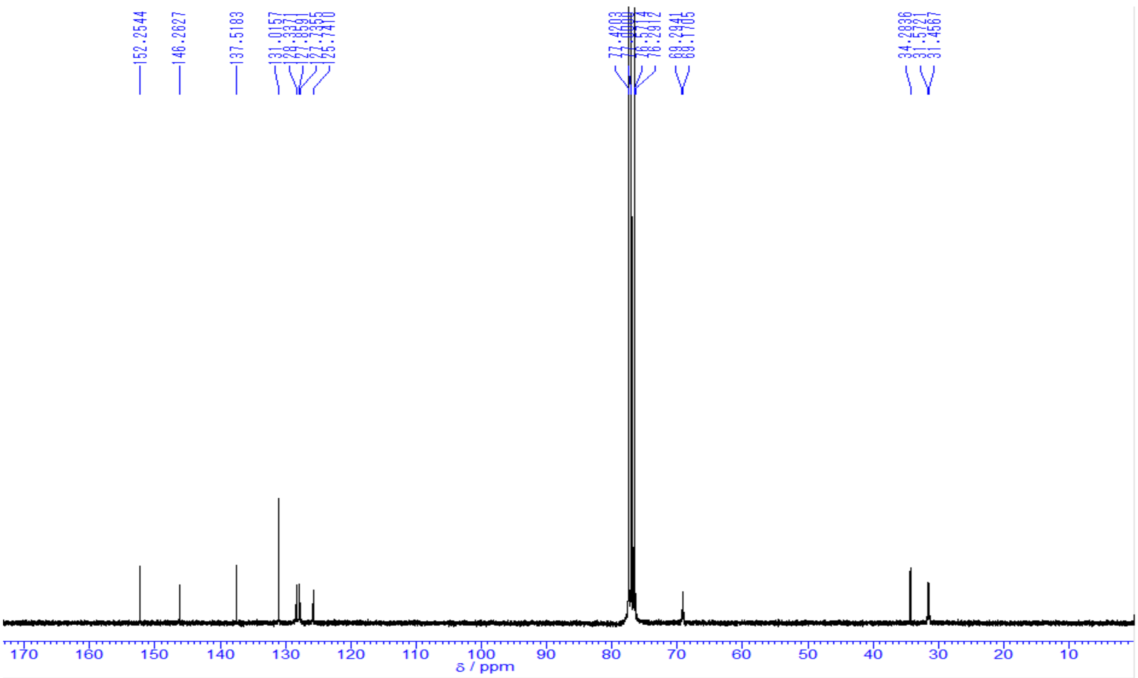


Figure S2. ^{13}C NMR spectra of *cone*-**3** ($CDCl_3$, 300 MHz).

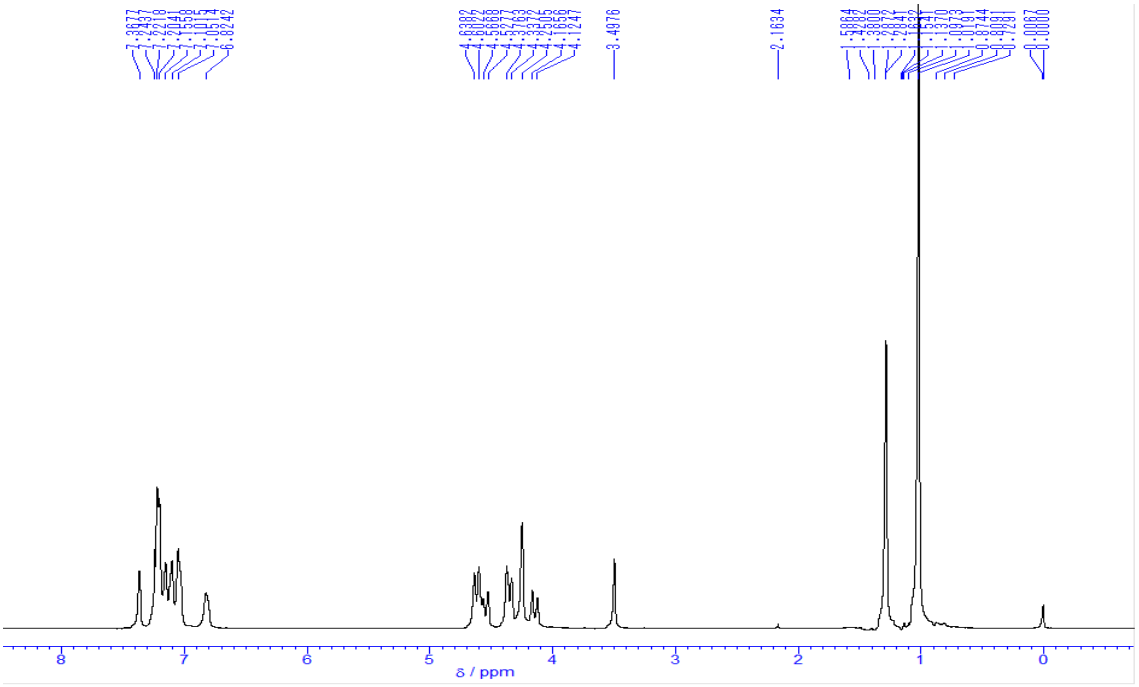


Figure S3. ^{1}H NMR spectra of *partial-cone*-**3** ($CDCl_3$, 300 MHz).

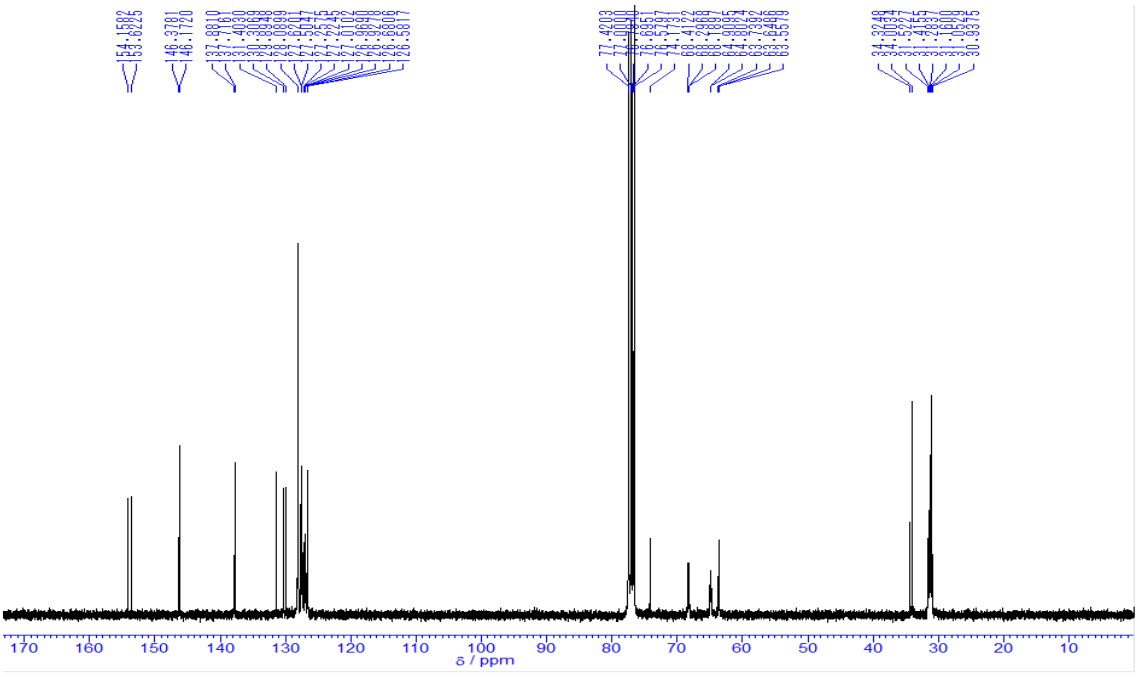


Figure S4. ^{13}C NMR spectra of *partial-cone*-**3** ($CDCl_3$, 300 MHz).

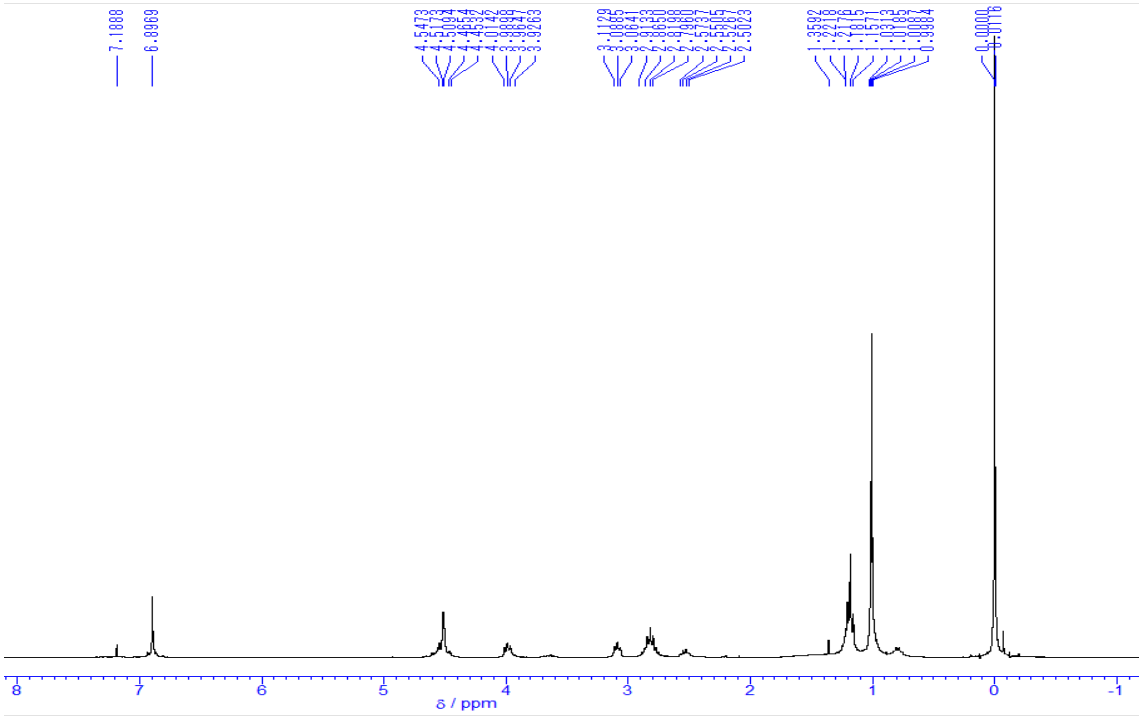


Figure S5. ^{1}H NMR spectra of *cone*-**5** ($CDCl_3$, 300 MHz).

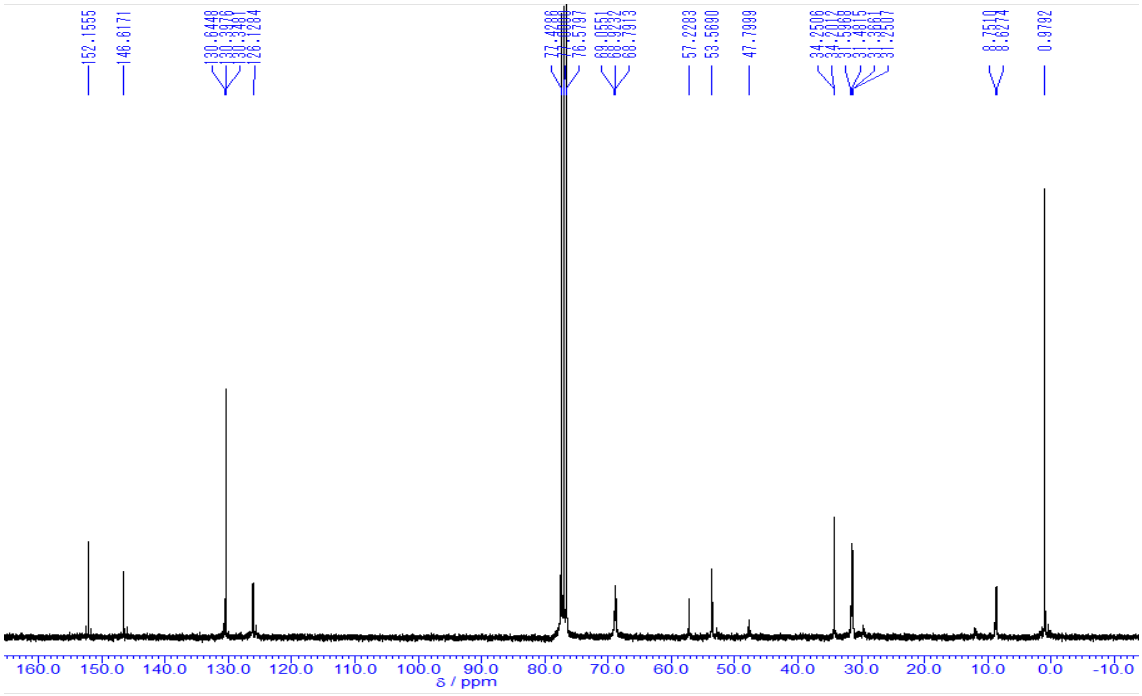


Figure S6. ^{13}C NMR spectra of *cone*-**5** ($CDCl_3$, 300 MHz).

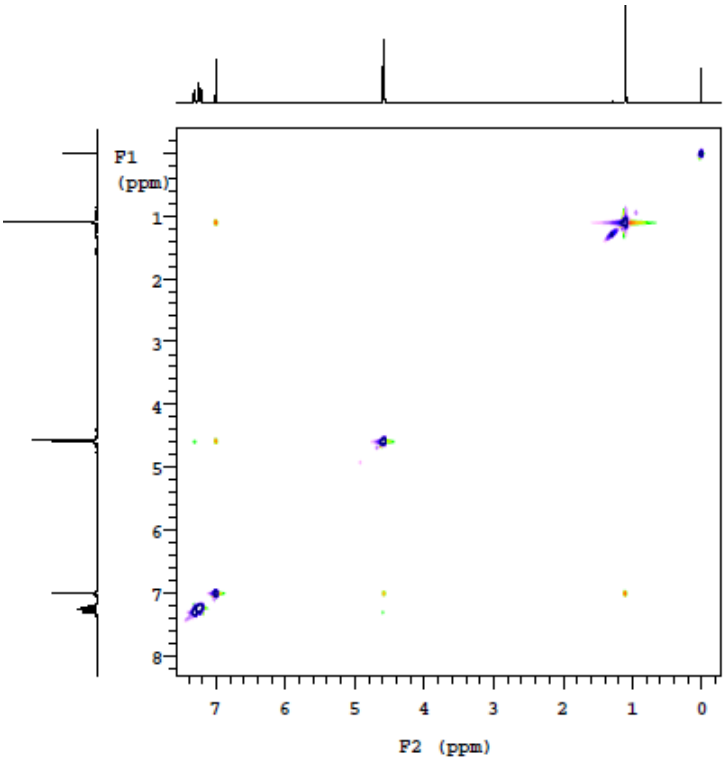


Figure S7. NOESY spectra of *cone*-**3** (4.0 mM) in $CDCl_3$ at 300 K, 400 MHz.

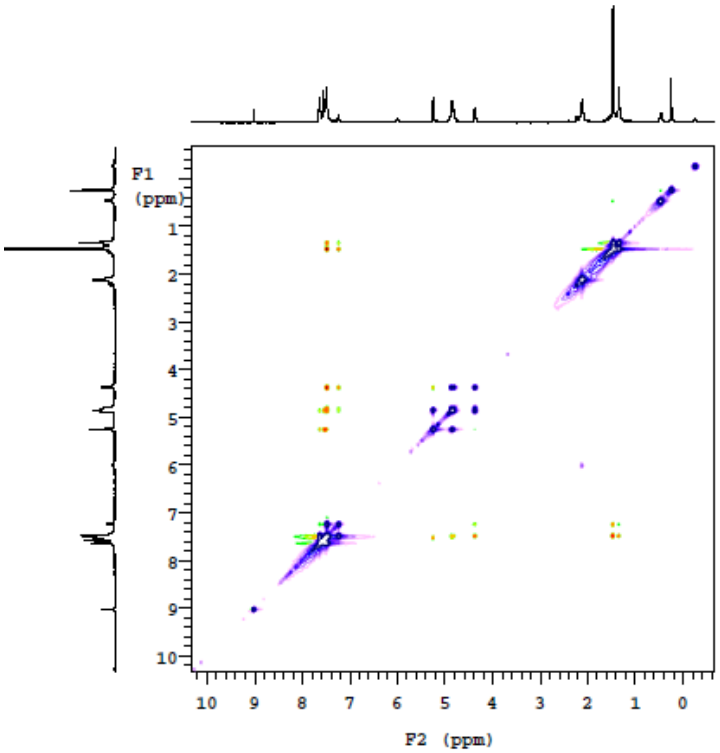


Figure S8. NOESY spectra of *cone*-**3** (4.0 mM) with *n*-butylammonium ion (H/G = 1:1) in $CDCl_3/CD_3CN$ (10:1, v/v) at 300 K, 400 MHz.

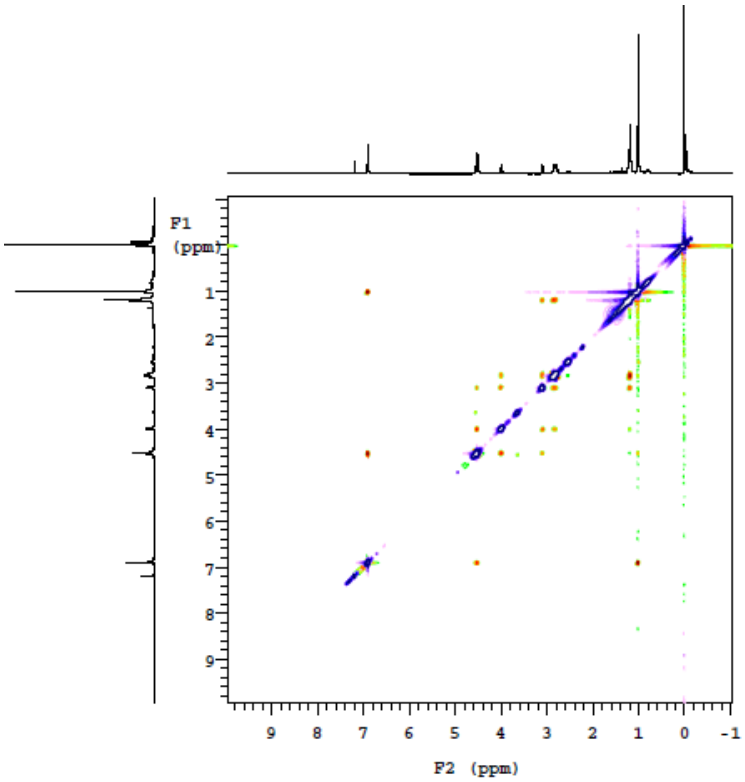


Figure S9. NOESY spectra of *cone*-**5** (4.0 mM) in $CDCl_3$ at 300 K, 400 MHz.

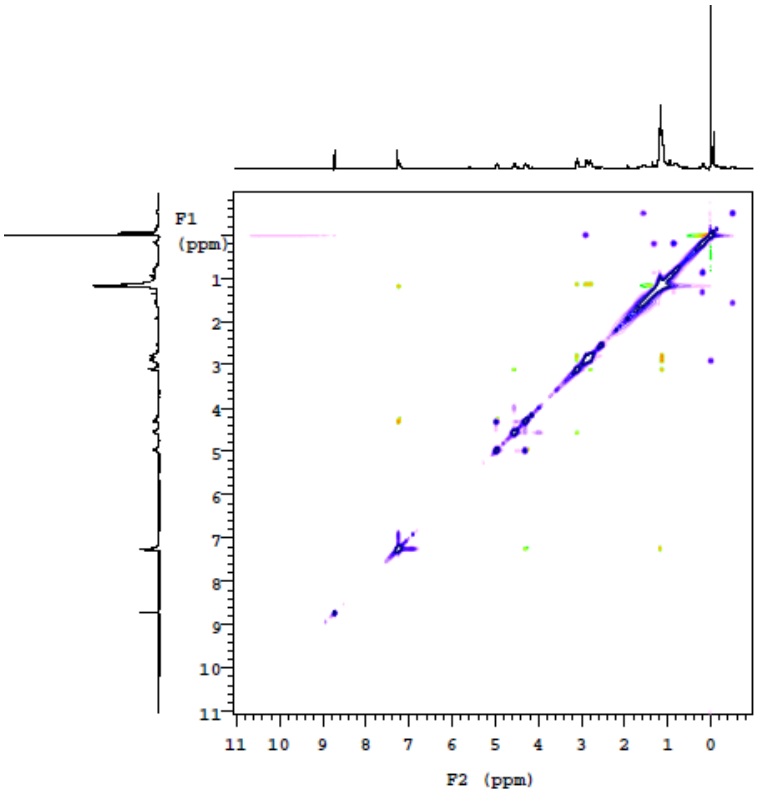


Figure S10. NOESY spectra of *cone*-**5** (4.0 mM) with *n*-butylammonium ion (H/G = 1:1) in $CDCl_3/CD_3CN$ (10:1, v/v) at 300 K, 400 MHz.

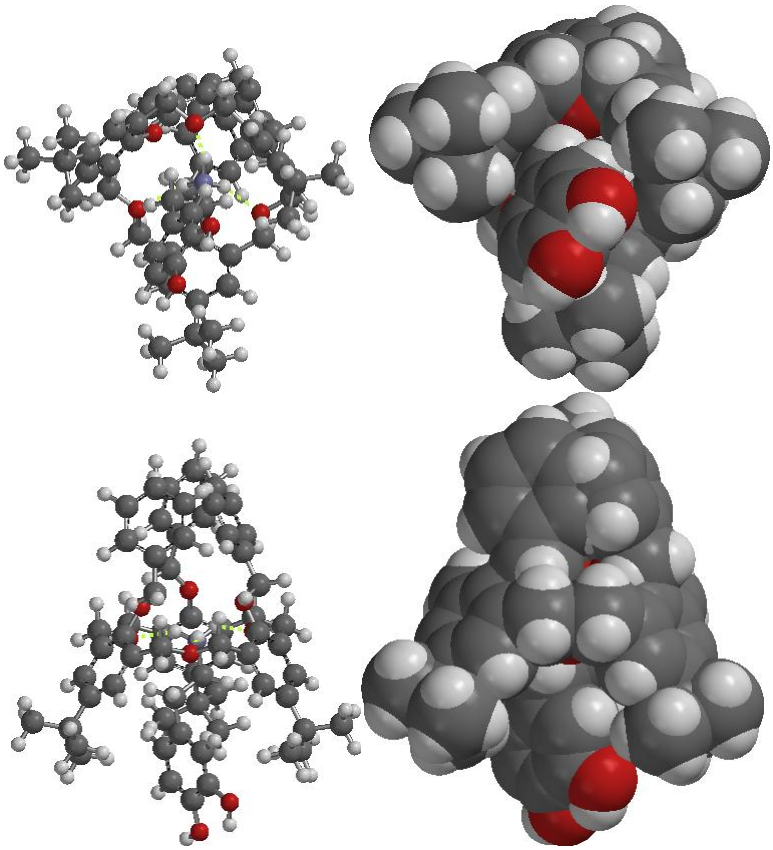


Figure S11. Computer-generated energy-minimized (MMFF) models of the complex between *cone*-**3** and dopamine. Top left and right: Ball-and-stick and space-filling representations, respectively, of the complex viewed from the wide rim face in which the guest dopamine ammonium cationic centre is in the cavity and is hydrogen-bonded to the bridge ether oxygen's of the host. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, showing the dopamine guest which is located into the cavity of the host *cone*-**3**.[1]

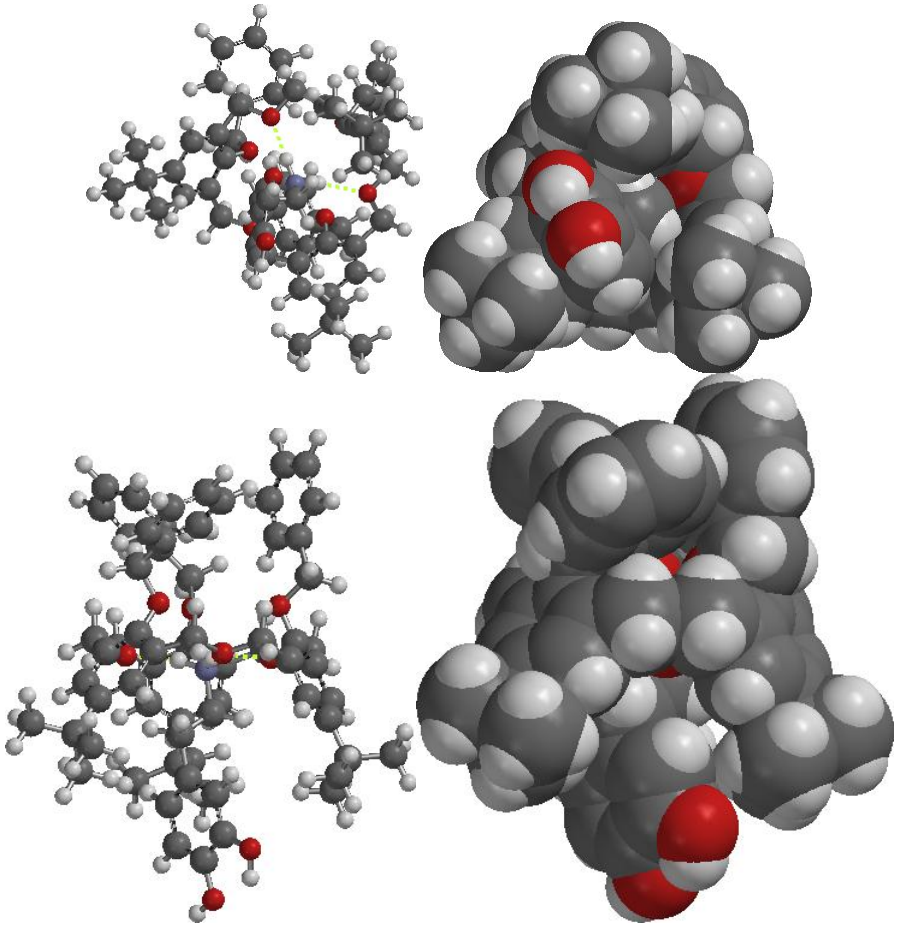


Figure S12. Computer-generated PM3 model of the complex between *cone*-**3** and the dopamine. Top left and right: Ball-and- stick and space-filling representations, respectively, of the complex as viewed from the face in which the wide rim and the guest dopamine in the cavity and guest NH_3^+ ion formed hydrogen bonding with bridge ether oxygen of $ArCH_2OCH_2Ar$,can be seen. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, seeing dopamine into the cavity of the host *cone*-**3**.[1]

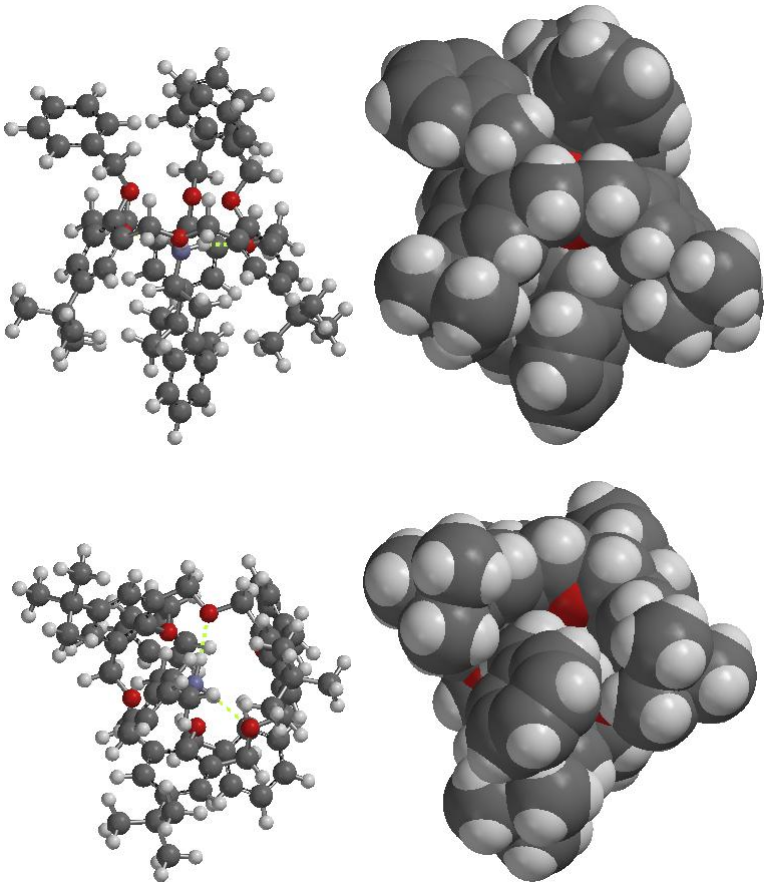


Figure S13. Computer-generated PM3 model of the complex between *cone*-**3** and the phenylethylamine. Top left and right: Ball-and- stick and space-filling representations, respectively, of the complex as viewed from the face in which the wide rim and the guest phenylethylamine in the cavity and guest NH_3^+ ion formed hydrogen bonding with bridge ether oxygen of $ArCH_2OCH_2Ar$,can be seen. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, seeing phenylethylamine into the cavity of the host *cone*-**3**.[1]

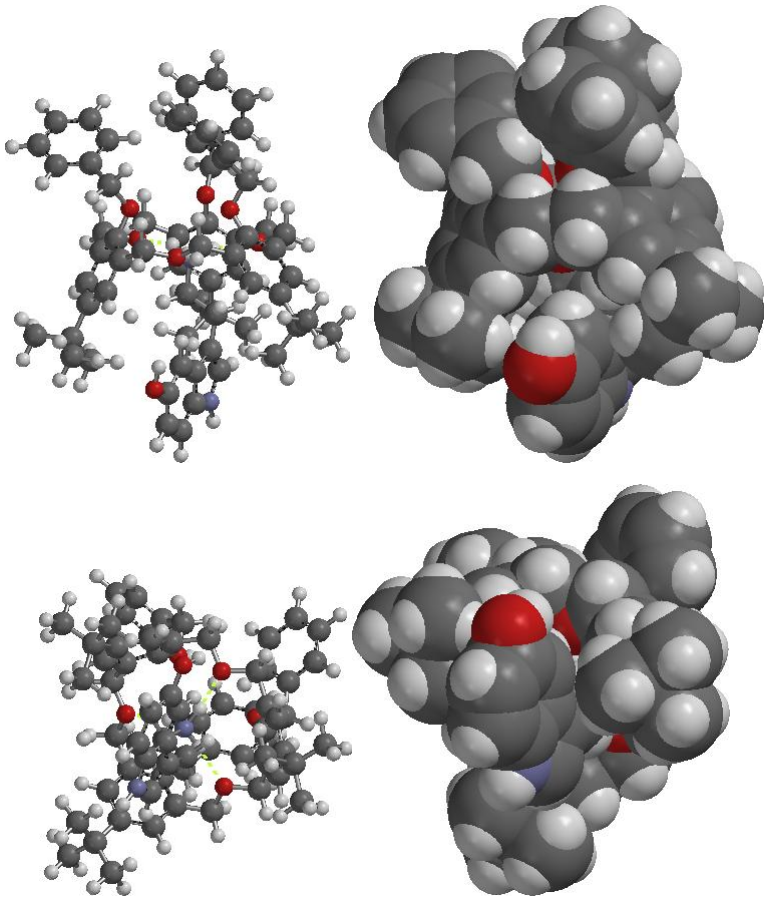


Figure S14. Computer-generated PM3 model of the complex between *cone*-**3** and the serotonin. Top left and right: Ball-and- stick and space-filling representations, respectively, of the complex as viewed from the face in which the wide rim and the guest serotonin in the cavity and guest NH_3^+ ion formed hydrogen bonding with bridge ether oxygen of $ArCH_2OCH_2Ar$,can be seen. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, seeing serotonin into the cavity of the host *cone*-**3**.[1]

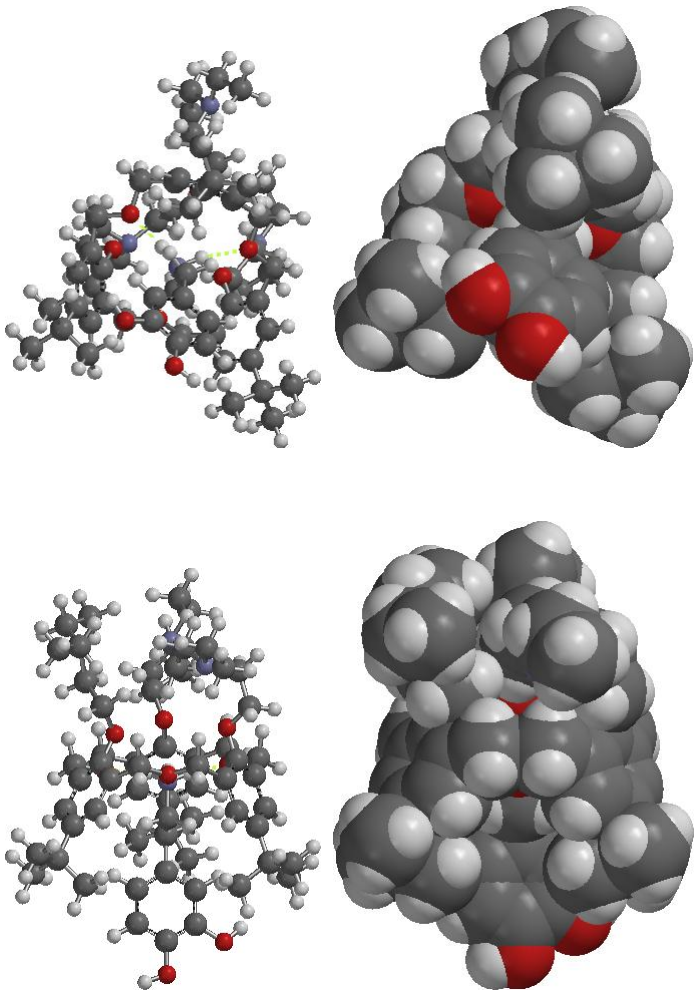


Figure S15. Computer-generated PM3 model of the complex between *cone*-**5** and the dopamine. Top left and right: Ball-and- stick and space-filling representations, respectively, of the complex as viewed from the face in which the wide rim and the guest dopamine in the cavity and guest NH_3^+ ion formed hydrogen bonding with bridge ether oxygen of $ArCH_2OCH_2Ar$,can be seen. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, seeing dopamine into the cavity of the host *cone*-**5**.[1]

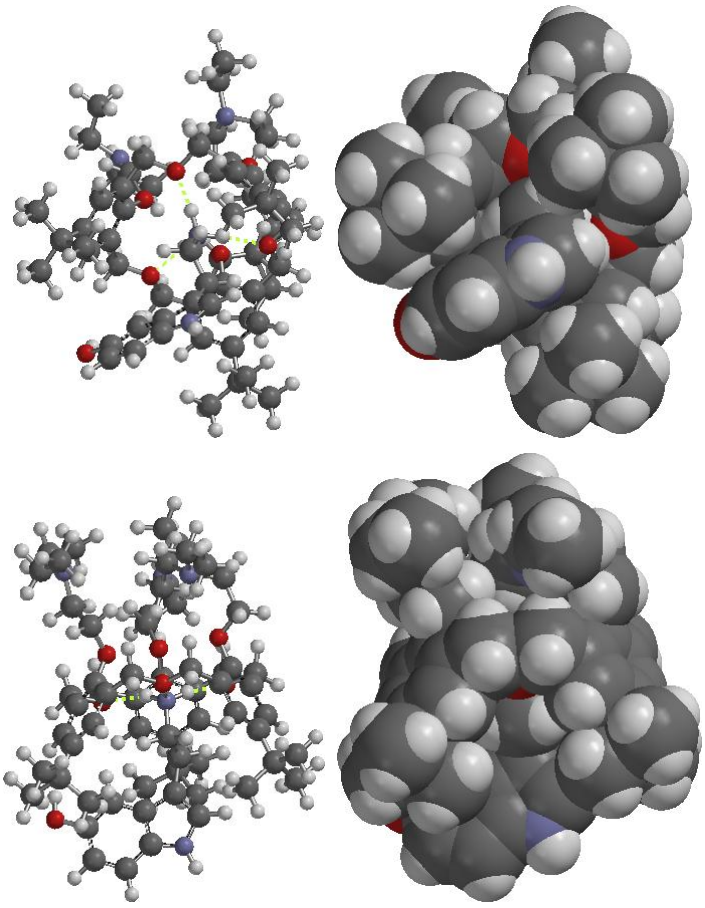


Figure S16. Computer-generated PM3 model of the complex between *cone*-**5** and serotonin. Top left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the face in which the wide rim and the guest serotonin.in the cavity and guest NH_3^+ ion formed hydrogen bonding with bridge ether oxygen of $ArCH_2OCH_2Ar$,can be seen. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, seeing serotonin into the cavity of the host *cone*-**5**.[1]

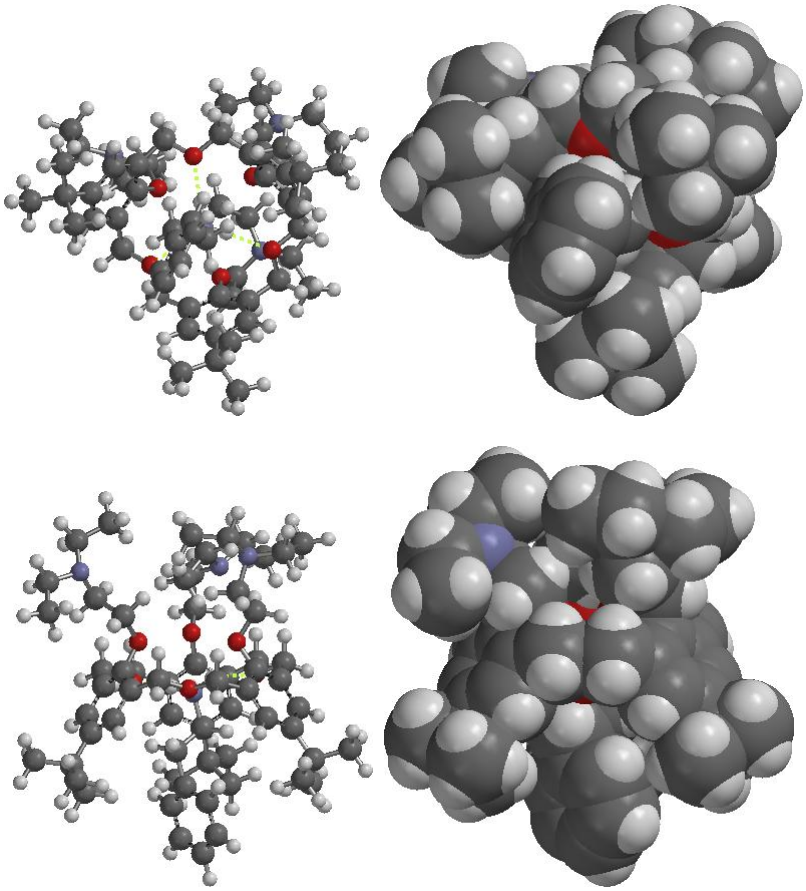
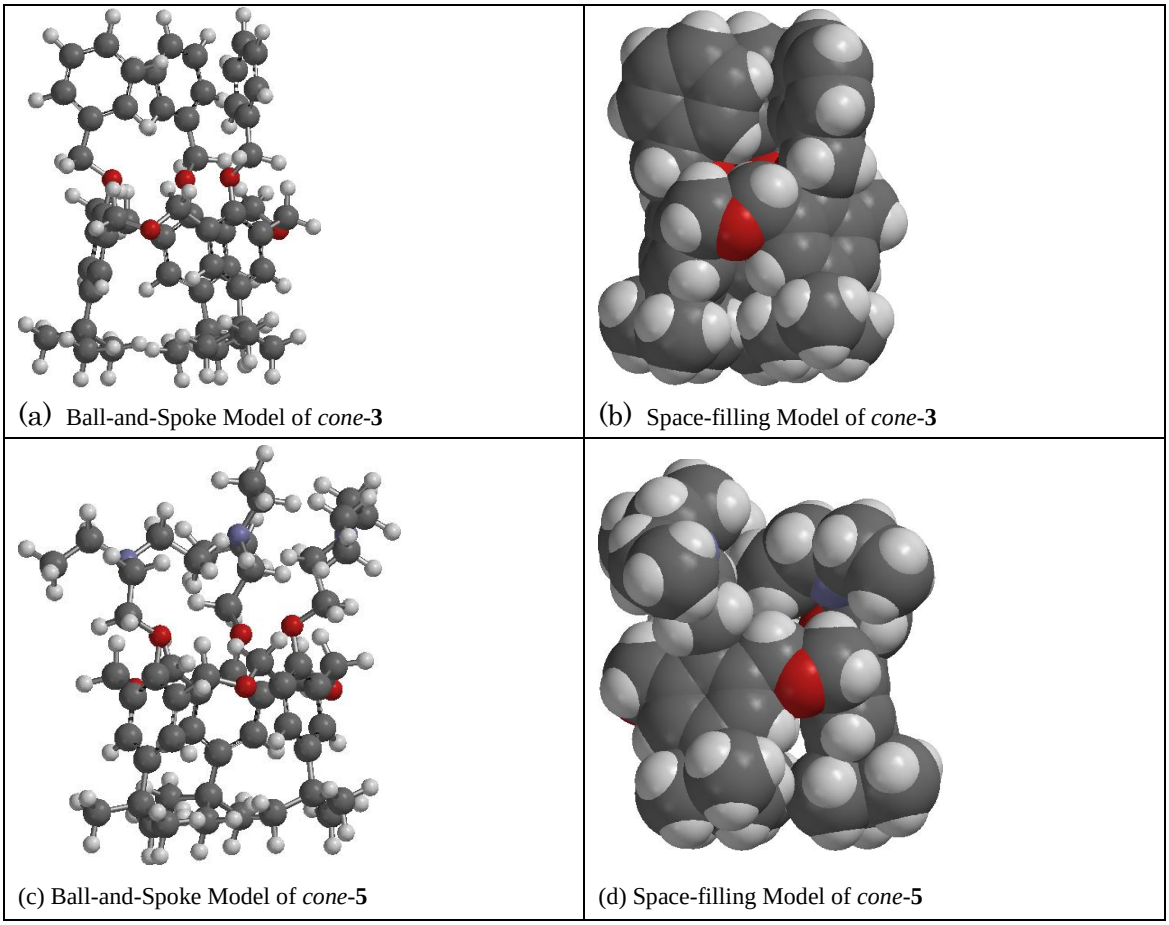


Figure S17. Computer-generated PM3 model of the complex between *cone*-**5** and phenylethylamine. Top left and right: Ball-and- stick and space-filling representations, respectively, of the complex as viewed from the face in which the wide rim and the guest phenylethylamine in the cavity and guest NH_3^+ ion formed hydrogen bonding with bridge ether oxygen of $ArCH_2OCH_2Ar$,can be seen. Bottom left and right: Ball-and-stick and space-filling representations, respectively, of the complex as viewed from the side face, seeing phenylethylamine cation into the cavity of the host *cone*-**5**.[1]



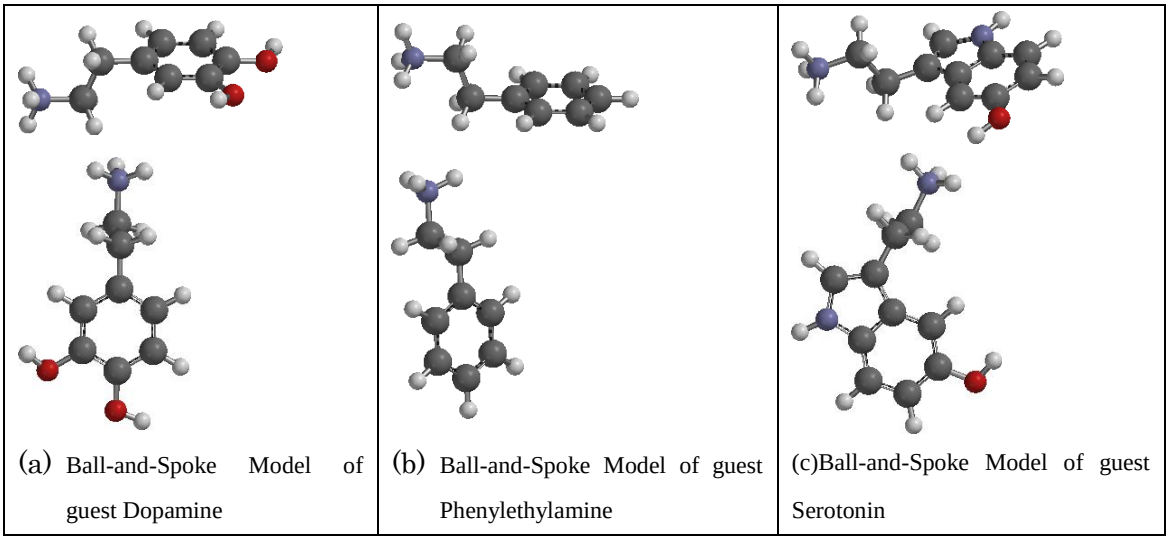
(a) Ball-and-Spoke Model of *cone*-**3**

(b) Space-filling Model of *cone*-**3**

(c) Ball-and-Spoke Model of *cone*-**5**

(d) Space-filling Model of *cone*-**5**

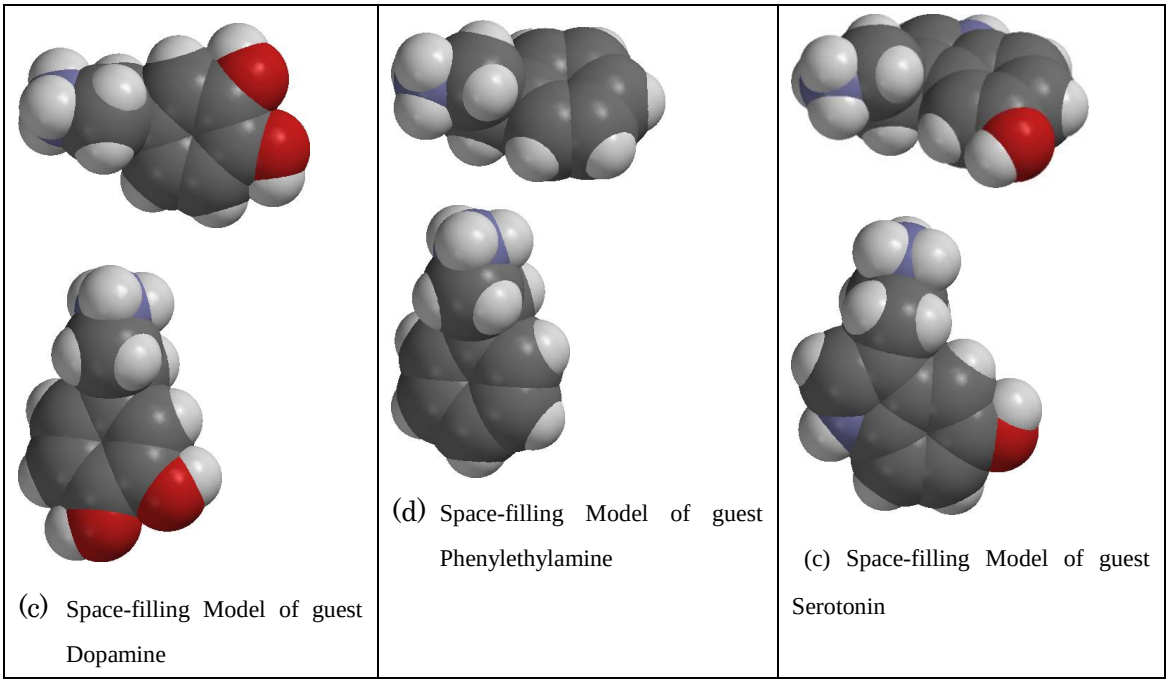
Figure S18. Space-filling and Ball-and-spoke models for the free host molecules of *cone*-**3** and *cone*-**5**, as generated by Spartan' 10 V1.1.0.



(a) Ball-and-Spoke Model of guest Dopamine

(b) Ball-and-Spoke Model of guest Phenylethylamine

(c)Ball-and-Spoke Model of guest Serotonin



(c) Space-filling Model of guest Dopamine

(d) Space-filling Model of guest Phenylethylamine

(c) Space-filling Model of guest Serotonin

Figure S19. Space-filling Ball-and-spoke models of the supramolecular free guest molecules, as generated by Spartan' 10 V1.1.0.

Table 1. Energy minimized for the free host, free guest and complexes of *cone*-**3** and *cone*-**5** with guest dopamine, serotonin and phenyl ethylamine, as generated by Spartan' 10 V1.1.0.

Free host and guest	**Before complex Energy minimized KJ/mole(free host and guest)**	**After complex with guest (Energy minimized KJ/mole)**
Free *cone*-**3**	988.2015 KJ/mole	*cone*-**3**⊃Dopamine, 776.191 KJ/mole *cone*-**3**⊃Serotonin, 758.205 KJ/mole *cone*-**3**⊃Phenyl ethylamine, 826.0482 KJ/mole
Free *cone*-**5**	937.1964 KJ/ mole	*cone*-**5**⊃Dopamine, 787.165 KJ/mole *cone*-**3**⊃Serotonin, 727.672 KJ/mole *cone*-**3**⊃Phenyl ethylamine, 790.630 KJ/mole
Free Dopamine	132.136 KJ/mole	
Serotonin	71.304 KJ/mole	
Free Phenyl- ethylamine	128.228 KJ/mole	

References

1. Molecular modeling (MMFF) was conducted using Spartan 10 (V1.1.0) Molecular Modeling Software from Wavefunction, Inc. www.wavefun.com (http://www.wavefun.com/).