

Supporting Information

Neutral Isocyanide-Templated Assembly of Pillar[5]arene [2] and [3]Pseudorotaxanes

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1. Materials and Experimental Methods

All reagents were purchased from Tokyo Chemical Industry (TCI Chemicals) and used without further purifications. Solvents for synthesis were purchased from RCI Labscan and deuterated solvents for NMR analysis were bought from Cambridge Isotope Laboratories.

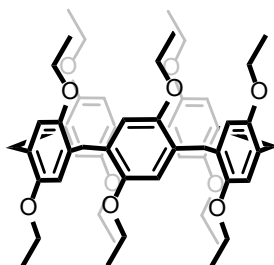
The samples for NMR analysis were prepared as CDCl₃ solutions. Their ¹H NMR spectra were recorded by Bruker AVANCE 400 spectrometer (400 MHz), Bruker AVANCE 500 spectrometer (500 MHz), and Bruker AVANCE 600 spectrometer (600 MHz), while ¹³C NMR spectra were recorded on the same machine (100 MHz) at 298K. The peak assignments were obtained by NMR experiments including ¹H-¹H correlation spectroscopy (COSY), ¹H-¹³C heteronuclear single-quantum coherence (HSQC), 2D Nuclear Over Hauser Enhancement Spectroscopy (NOESY), DEPT-135, and 2D Nuclear Over Hauser Enhancement Spectroscopy (NOESY). The obtained NMR spectral data were processed using Mnova software (Mestrelab Research, S.L.). ¹H-NMR titration experiments of **EtP5A** (2 mM, 0.5ml) with aryl isocyanide guests were carried out by recording spectra at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents of the guest. In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale. Stability constants were obtained by analysis of the resulting data using the online program Bindfit.¹

The diffraction data of **C4@EtP5A**, **C8@EtP5A**, **C10@EtP5A (1:1)**, **C10@(EtP5A)₂ (1:2)** and **Ph-I@EtP5A** were collected on a Rigaku SuperNova diffractometer with a HyPix 3000 detector using CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) at 150 K. Data reduction, scaling, and absorption corrections were performed using CrysAlisPro (version 1.171.40.84a). The structures were solved, and the space groups $P\bar{1}$, $P2_1/n$, $P\bar{1}$, $P2_1/n$ and $P2_1/c$ were determined by intrinsic phasing using ShelXT for **C4@EtP5A**, **C8@EtP5A**, **C10@(EtP5A)₂ (1:2)**, **C10@EtP5A (1:1)** and **Ph-I@EtP5A**, respectively. The structures were refined by full matrix least-squares minimization on F^2 using SHELXL with OLEX² as a graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters, which were 1.2x or 1.5x the equivalent isotropic thermal parameters of their parent carbon or oxygen atoms. In the case of **C10@(EtP5A)₂ (1:2)** diffuse solvent peaks totalling 19.1 electrons were removed using the solvent mask procedure in OLEX² and are consistent with two molecules of water. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) 2167170-2167174. The crystal data and structure refinement are shown in Table S3.

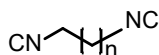
2. Synthesis and Characterisation

2.1 Compounds used in this study

1. Perethylated Pillar[5]arene (EtP5A)



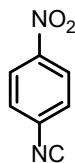
2. Alkyl Isocyanide Guests



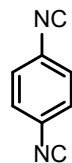
Diisocyanide Guests

n = 1	C2
n = 3	C4
n = 5	C6
n = 7	C8
n = 9	C10

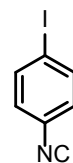
3. Aryl Isocyanide Guests



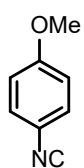
Ph-NO₂



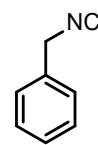
Ph-NC



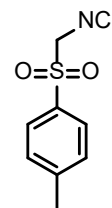
Ph-I



Ph-OMe



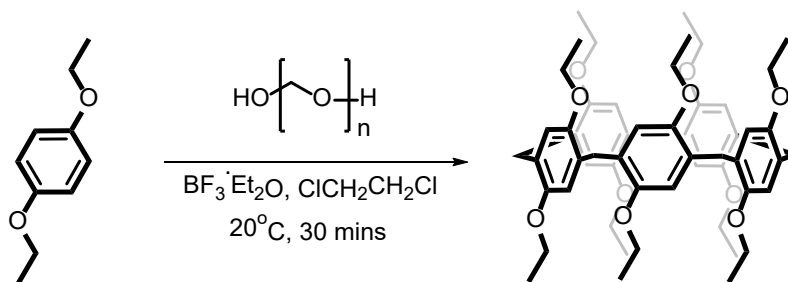
Bn-NC



TOSMIC

Figure S1. Chemical structures of compounds used in this study and their abbreviations

2.2 Perethylated Pillar[5]arene (EtP5A)²



1,4-diethoxybenzene (1.66 g, 10 mmol) was dissolved in DCE (20 ml), followed by addition of finely ground PFA (0.93g, 30 mmol). The suspension was stirred at room temperature. BF₃·Et₂O (1.25 ml, 10 mmol) was subsequently added slowly to produce a greenish solution. The reaction mixture was stirred for 30 mins, then poured into water. The organic residue was extracted into DCM (3x30 ml), washed with water (3x50 ml), and dried over Na₂SO₄. After the solvent was removed, the crude product was purified on a silica gel column using DCM/hexane (3:2 v/v) to afford **EtP5A** as a white powder (Yield: 50%).

¹H NMR [400 MHz, CDCl₃] δ 6.73 (s, 10H), 3.83 (q, J = 7.0 Hz, 20H), 3.77 (s, 10H), 1.27 (t, J = 7.0 Hz, 30H).

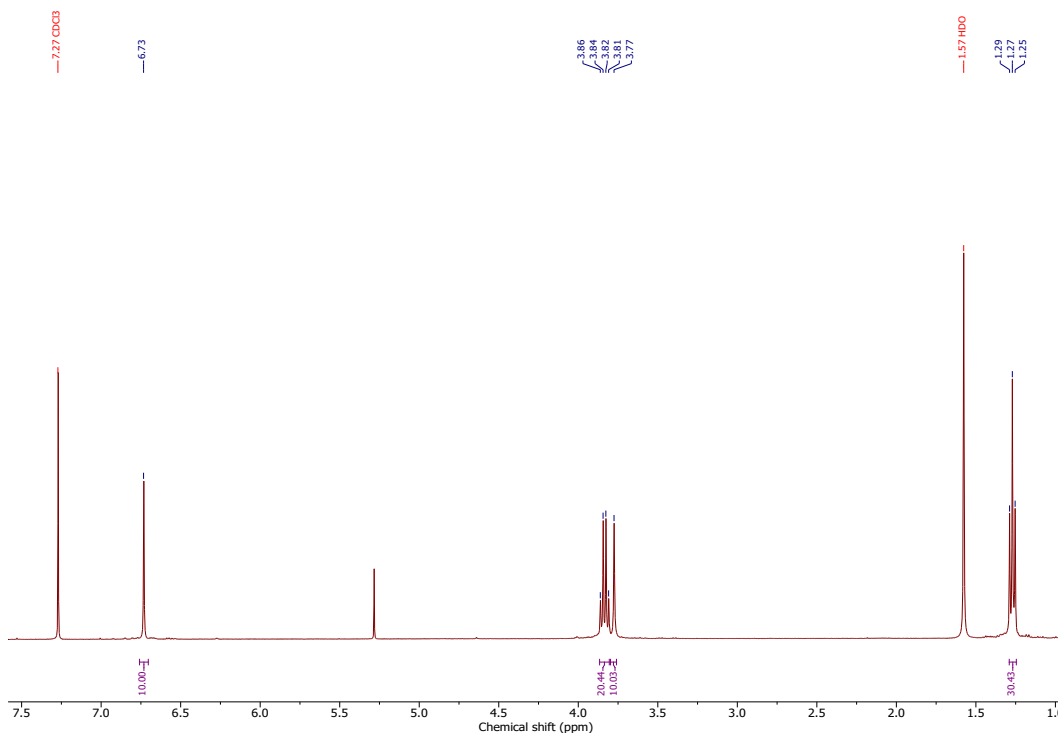
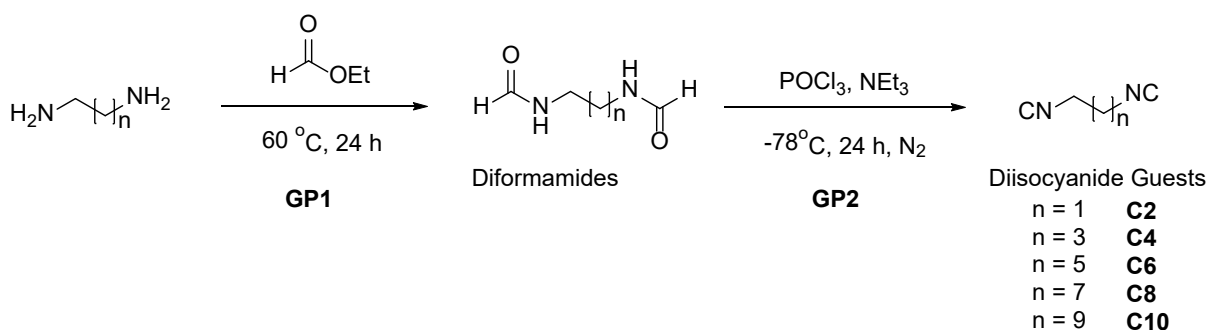


Figure S2. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of EtP5A

2.3 Alkyl Diisocyanide Guests



2.3.1 General procedure for the synthesis diformamide (GP1)

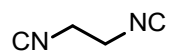
A solution of the selected diamine (1.0 equiv.) in ethyl formate (10.0 equiv.) was refluxed at 60 °C overnight. After cooling to room temperature, a white solid was observed and the solvent was subsequently removed in vacuo to afford the expected diformamide product quantitatively. The product was sufficiently pure for use without further purification.

2.3.2 General procedure for the synthesis diisocyanide (GP2)

The corresponding formamide (1.0 equiv.) was dissolved in dry DCM (approximate concentration around 0.1 - 0.3 M) under a N₂ atmosphere and triethylamine (12.0 equiv.) was added. The solution mixture was cooled to -78 °C and phosphoryl chloride (3.0 equiv.) was subsequently added dropwise, after which the reaction mixture was allowed to warm to room temperature and left stirring overnight. A saturated solution of NaHCO_{3(aq)} was added to quench the reaction, then the organic layer was washed with water followed by brine and dried over Na₂SO₄. The solvent was removed in vacuo to get the crude product which was purified by silica gel column chromatography using DCM to afford a yellow oil of the target isocyanide.

* **Toluenesulfonylmethyl isocyanide (TOSMIC)** is commercially available.

a) 1,2-Diisocyanoethane (C2)



Yield = 86%

^1H NMR [400 MHz, CDCl_3] δ 3.73 (s, 4H).

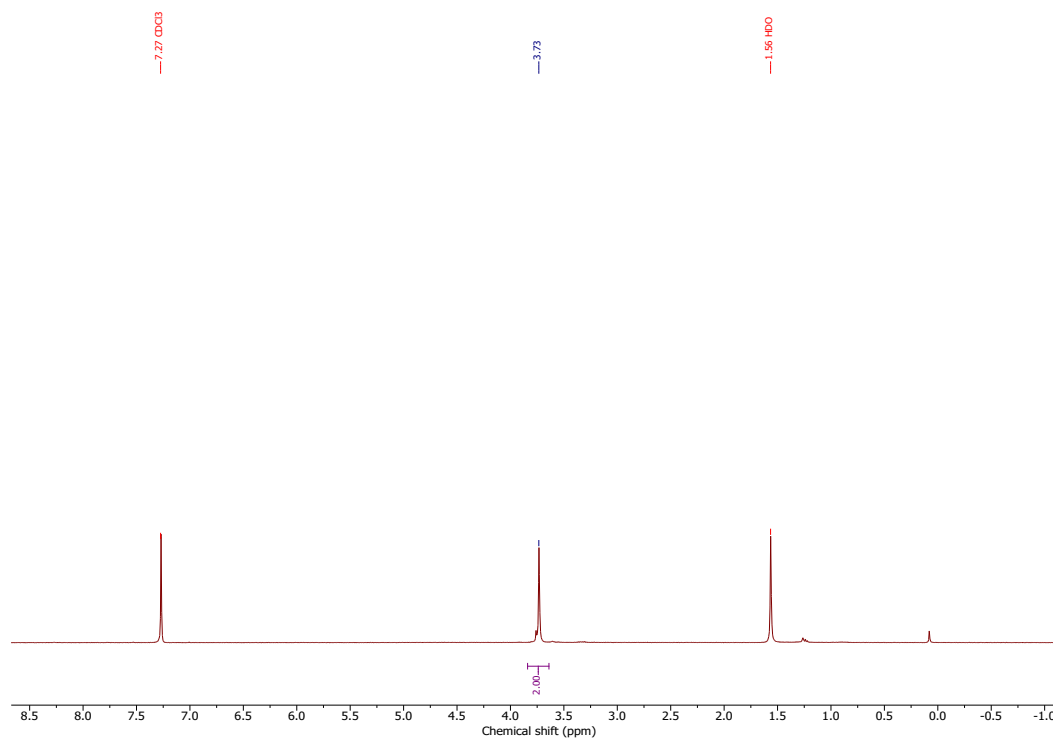
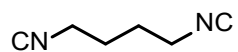


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1,2-diisocyanoethane (C2)**

b) 1,4-diisocyanobutane (C4)



Yield = 93%

^1H NMR [400 MHz, CDCl_3] δ 3.50 (tp, $J = 3.9, 1.9$ Hz, 4H), 1.88 (q, $J = 5.3, 4.2$ Hz, 4H).

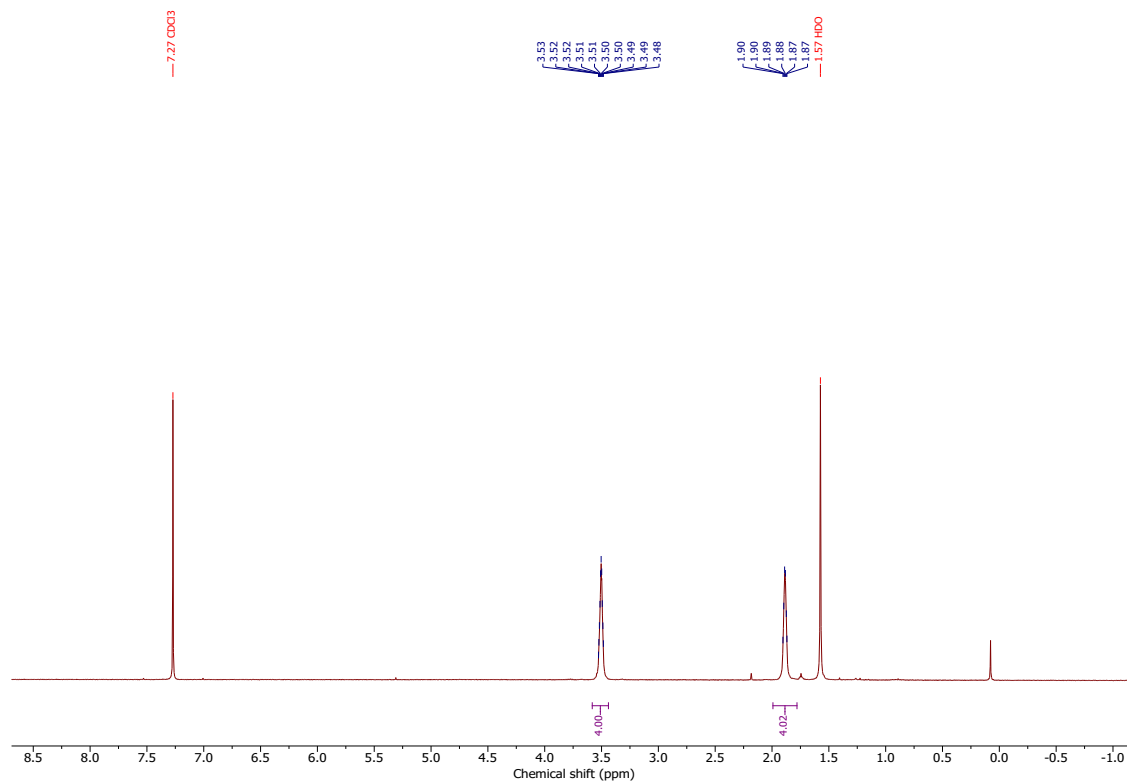
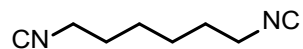


Figure S4. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1,4-diisocyanobutane (C4)**

c) 1,6-diisocyanohexane (C6)



Yield = 92%

^1H NMR [400 MHz, CDCl_3] δ 3.43 (ddt, J = 8.6, 4.1, 2.0 Hz, 4H), 1.72 (s, 4H), 1.54 – 1.49 (m, 4H).

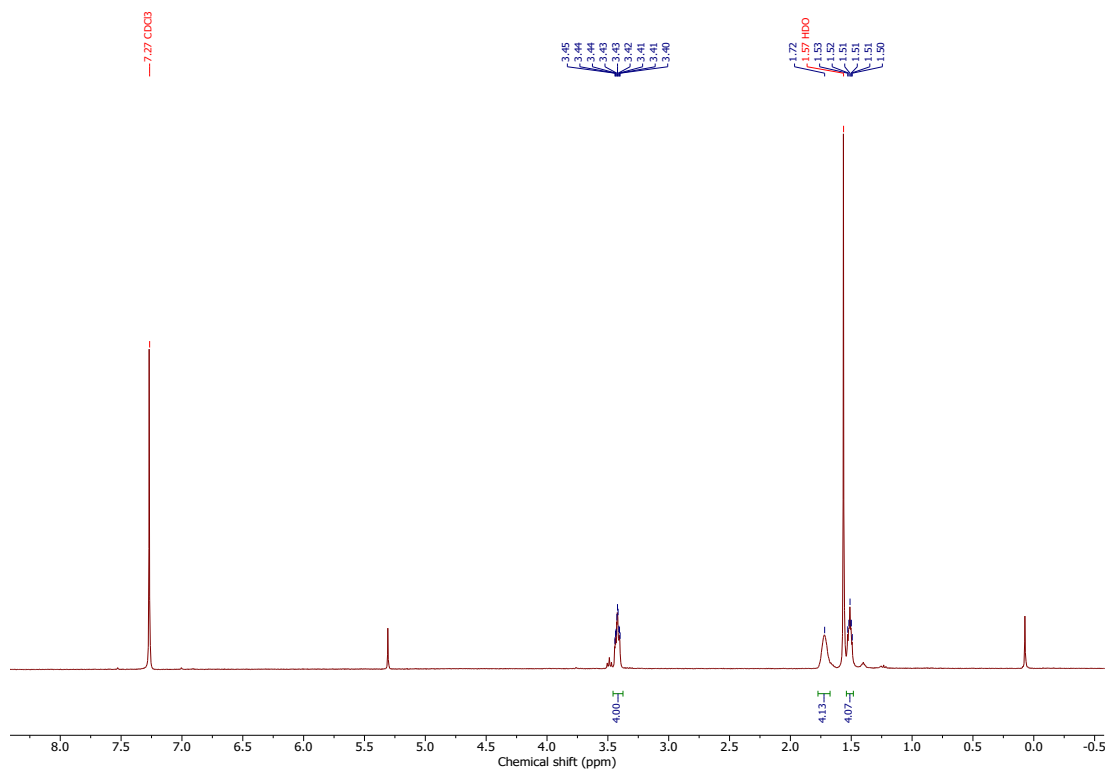
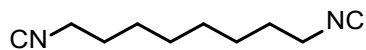


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of 1,6-diisocyanohexane (C6)

d) 1,8-diisocyanooctane (C8)



Yield = 96%

^1H NMR [400 MHz, CDCl_3] δ 3.41 (s, 4H), 1.69 (d, $J = 10.2$ Hz, 4H), 1.47 (s, 4H), 1.38 (d, $J = 7.2$ Hz, 4H).

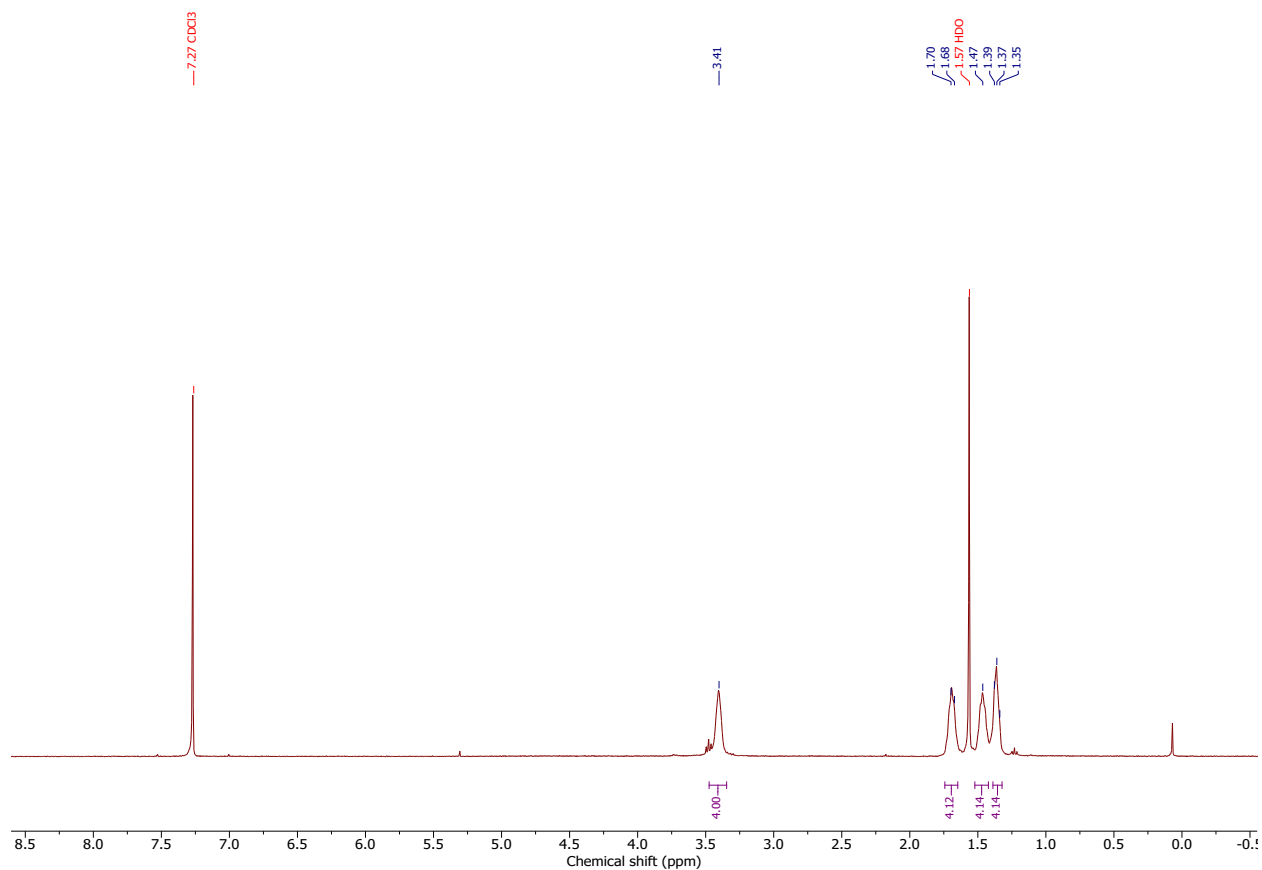
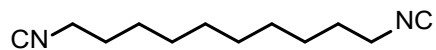


Figure S6. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1,8-diisocyanooctane (C8)**

e) 1,10-diisocyanodecane (C10)



Yield = 93%

^1H NMR [400 MHz, CDCl_3] δ 3.40 (ddt, $J = 6.9, 5.0, 2.1$ Hz, 4H), 1.74 – 1.62 (m, 4H), 1.45 (t, $J = 7.6$ Hz, 4H), 1.33 (s, 8H).

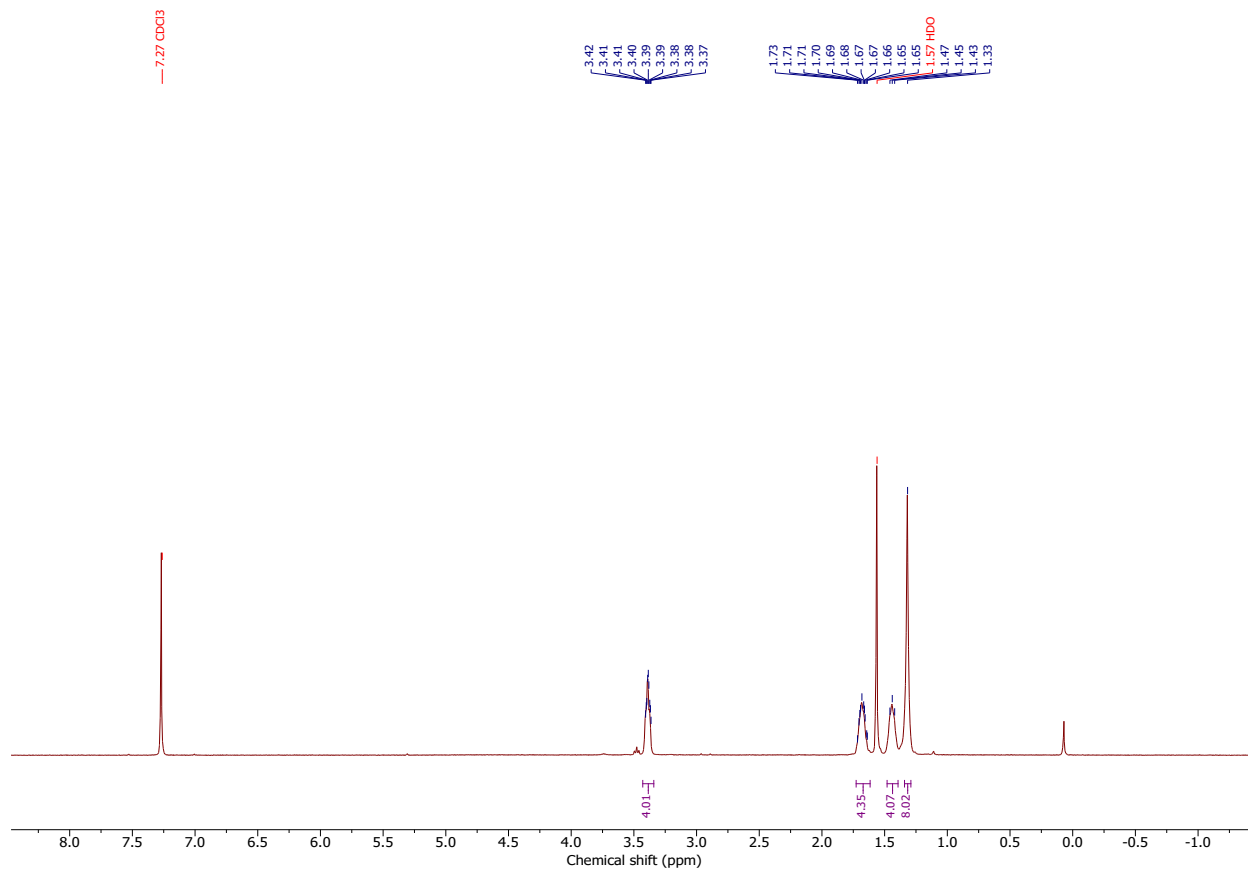
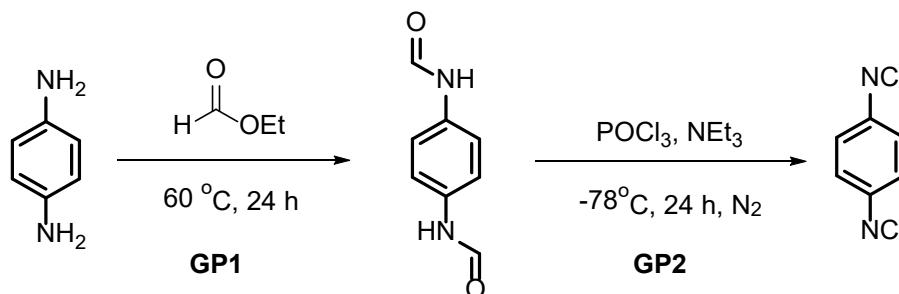


Figure S7. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1,10-diisocyanodecane (C10)**

2.4 Aryl isocyanide Guests

a) 1,4-diisocyanobenzene (Ph-NC)



Synthesis of **Ph-NC** using **GP1** and **GP2**.

Yield = 90%

¹H NMR [400 MHz, CDCl₃] δ 7.45 (s, 4H).

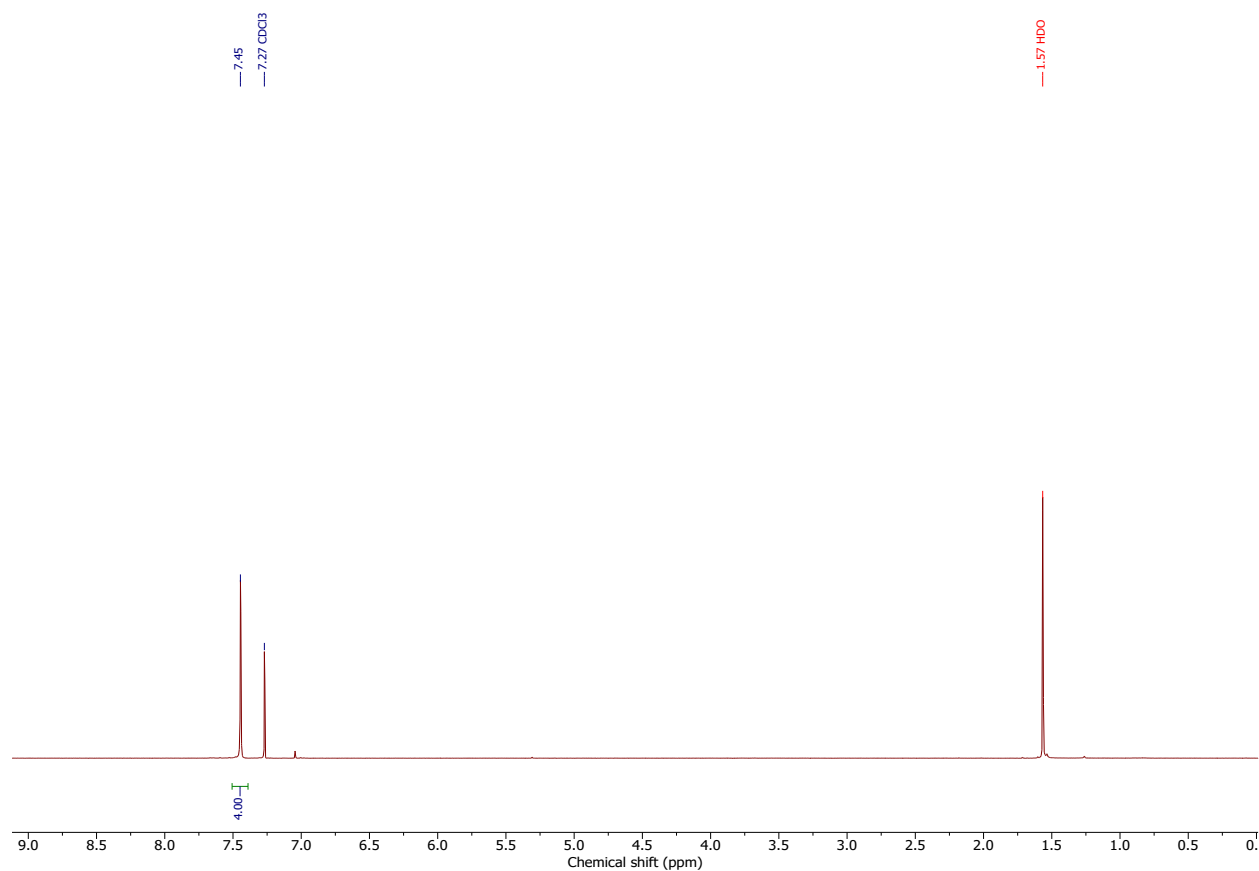
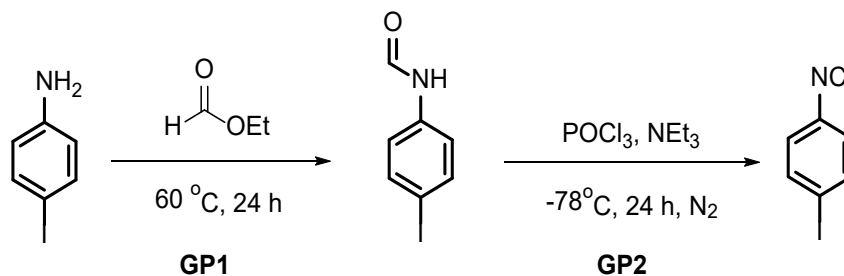


Figure S8. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1,4-diisocyanobenzene**

b) 1-Iodo-4-isocyanobenzene (Ph-I)



Synthesis of **Ph-I** using modified **GP1** and **GP2** procedures; ethyl formate (5.0 equiv.), triethylamine (6.0 equiv.) and phosphoryl chloride (1.5 equiv.). The crude product was purified by silica gel column chromatography using DCM to afford the brown solid of the target isocyanide.

Yield = 79%

^1H NMR [400 MHz, CDCl_3] δ 7.80 – 7.72 (m, 2H), 7.18 – 7.06 (m, 2H).

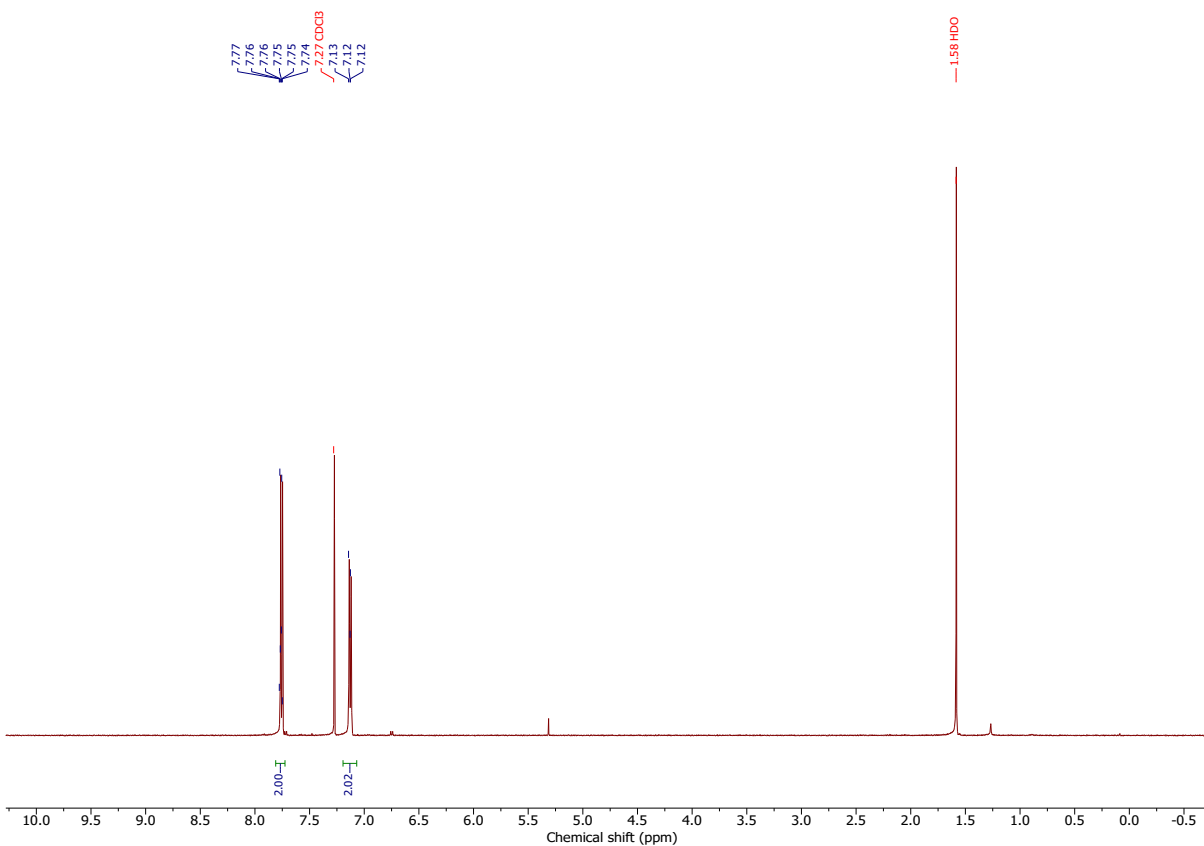
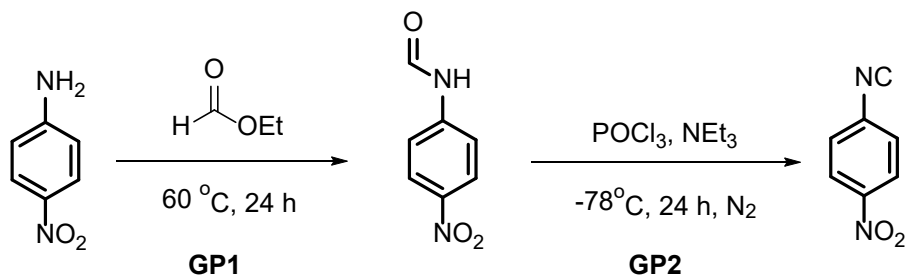


Figure S9. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1-iodo-4-isocyanobenzene**

c) 1-Isocyano-4-nitrobenzene (Ph-NO₂)



Synthesis of **Ph-NO₂** using modified **GP1** and **GP2** procedures; ethyl formate (5.0 equiv.), triethylamine (6.0 equiv.) and phosphoryl chloride (1.5 equiv.). The crude product was purified by silica gel column chromatography using DCM to afford the yellow solid of the target isocyanide.

Yield = 87%

¹H NMR [400 MHz, CDCl₃] δ 8.39 – 8.26 (m, 2H), 7.64 – 7.47 (m, 2H).

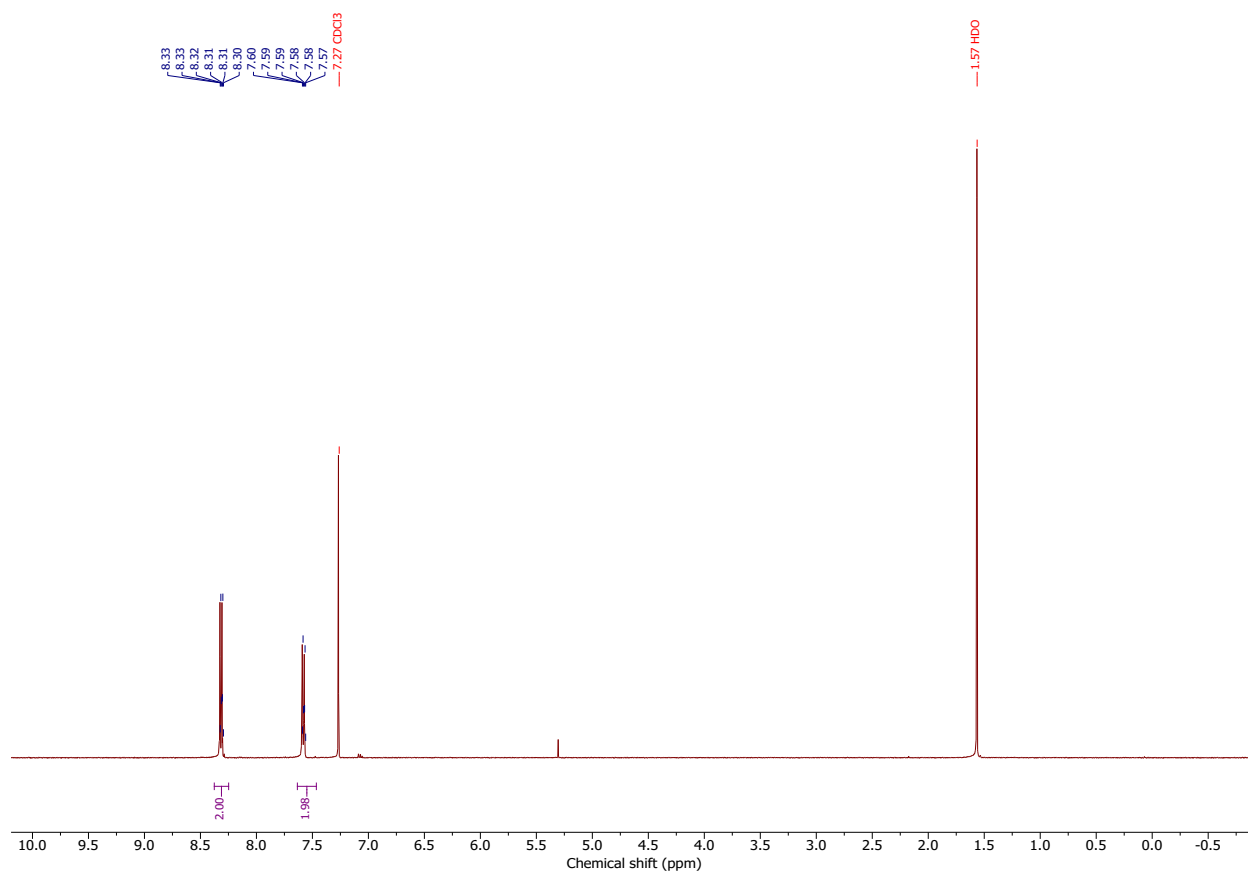
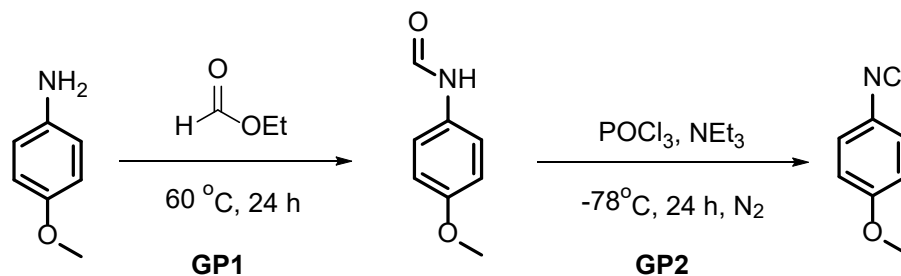


Figure S10. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 1-isocyano-4-nitrobenzene

d) 1-Isocyano-4-methoxybenzene (Ph-OMe)



Synthesis of **Ph-OMe** using modified **GP1** and **GP2** procedures; ethyl formate (5.0 equiv.), triethylamine (6.0 equiv.) and phosphoryl chloride (1.5 equiv.). The crude product was purified by silica gel column chromatography using DCM to afford the target isocyanide as a yellow oil, which solidifies to a green solid upon refrigeration. Note: the product is unstable at room temperature, and needs to be stored in a refrigerator.

Yield = 97%

¹H NMR [400 MHz, CDCl₃] δ 7.32 (d, *J* = 8.5 Hz, 2H), 6.88 (dd, *J* = 8.3, 1.4 Hz, 2H), 3.83 (s, 3H).

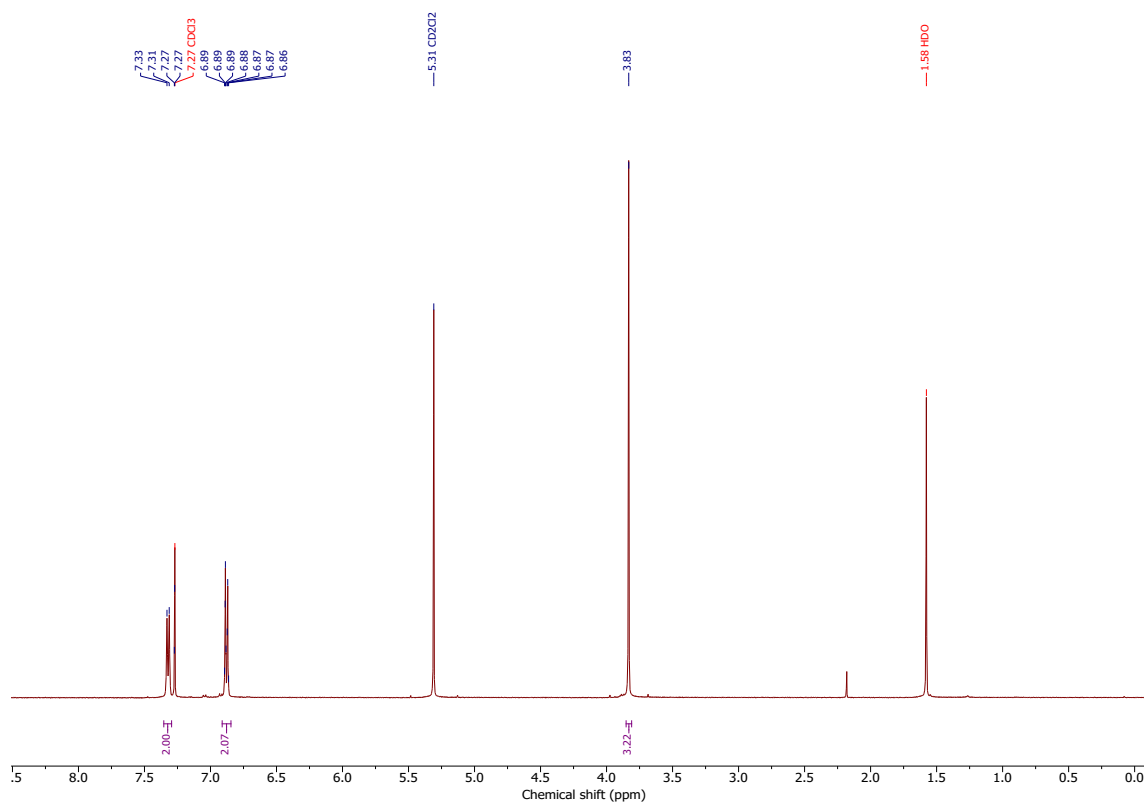
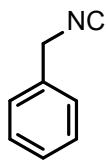


Figure S11. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1-isocyano-4-methoxybenzene**

e) Isocyanomethyl benzene (Bn-NC)



Synthesis of **Bn-NC** using modified **GP1** and **GP2** procedures; ethyl formate (5.0 equiv.), triethylamine (6.0 equiv.) and phosphoryl chloride (1.5 equiv.). The crude product was purified by silica gel column chromatography using DCM to afford the yellow oil of the target isocyanide.

Yield = 82%

¹H NMR [400 MHz, CDCl₃] δ 7.46 – 7.39 (m, 2H), 7.40 – 7.33 (m, 3H), 4.66 (t, J = 2.3 Hz, 2H).

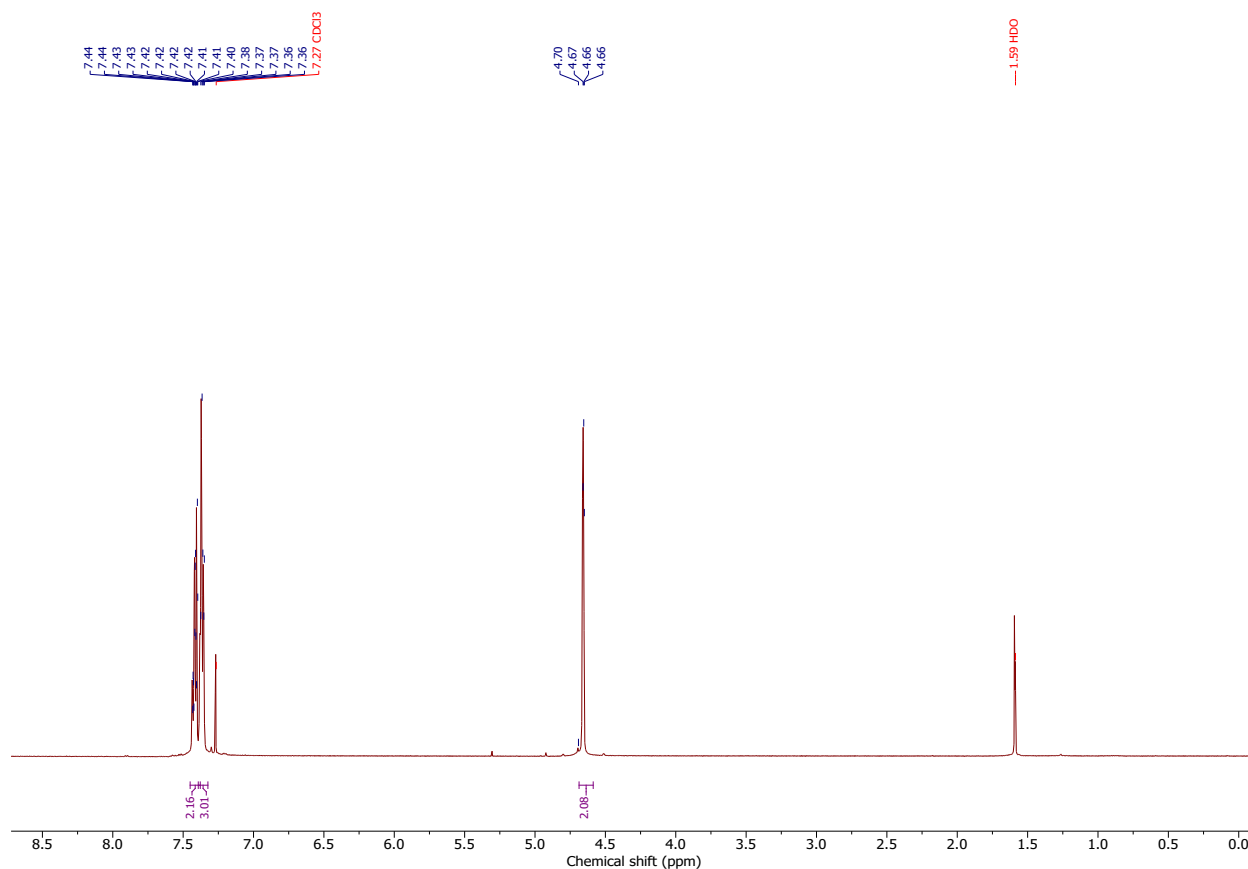
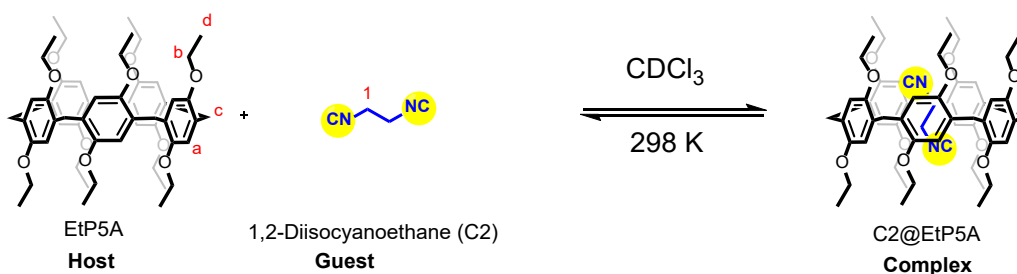


Figure S12. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of Isocyanomethyl benzene

3. Host-Guest Complexation Studies of Alkyl Diisocyanides in CDCl₃

A 10 mM solution of the corresponding isocyanide guest was prepared in CDCl₃ and a portion, 0.5 ml, transferred into an NMR tube capped with a plastic lid. A separate **EtP5A** solution was also prepared at the concentration of 100 mM in a small vial and added in aliquots. The samples were shaken and ¹H NMR spectra were recorded at 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents of **EtP5A**. In the case of **C4** and **C10** complexation, comparative ¹³C NMR, COSY and NOESY spectra of the corresponding complexes were also recorded.

3.1 Evidence of C2@EtP5A complexation in CDCl₃ at 298 K



Scheme S1. Host-guest complexation between **EtP5A** (Host) and **C2** (Guest) in CDCl₃ at 298K.

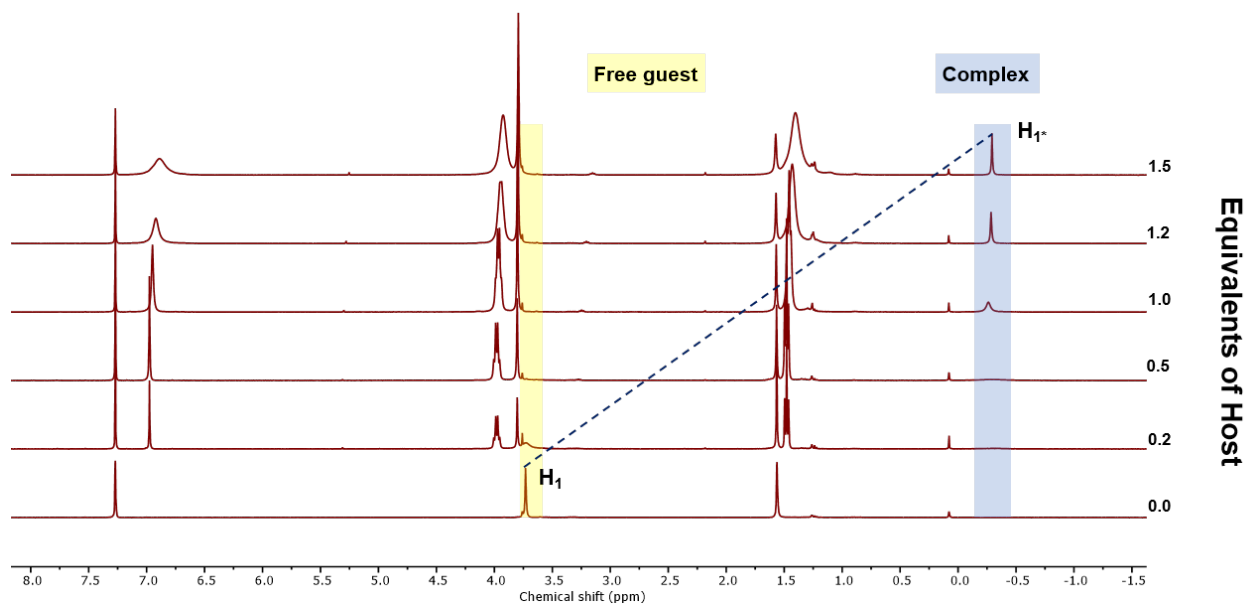
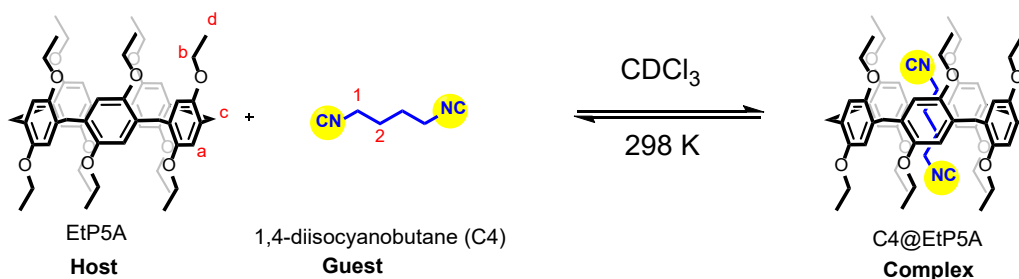


Figure S13. ¹H NMR spectra of **C2** (10 mM, 400 MHz, CDCl₃) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents.

3.2 Evidence of C4@EtP5A complexation in CDCl₃ at 298 K



Scheme S2. Host-guest complexation between **EtP5A** (Host) and **C4** (Guest) in CDCl₃ at 298K.

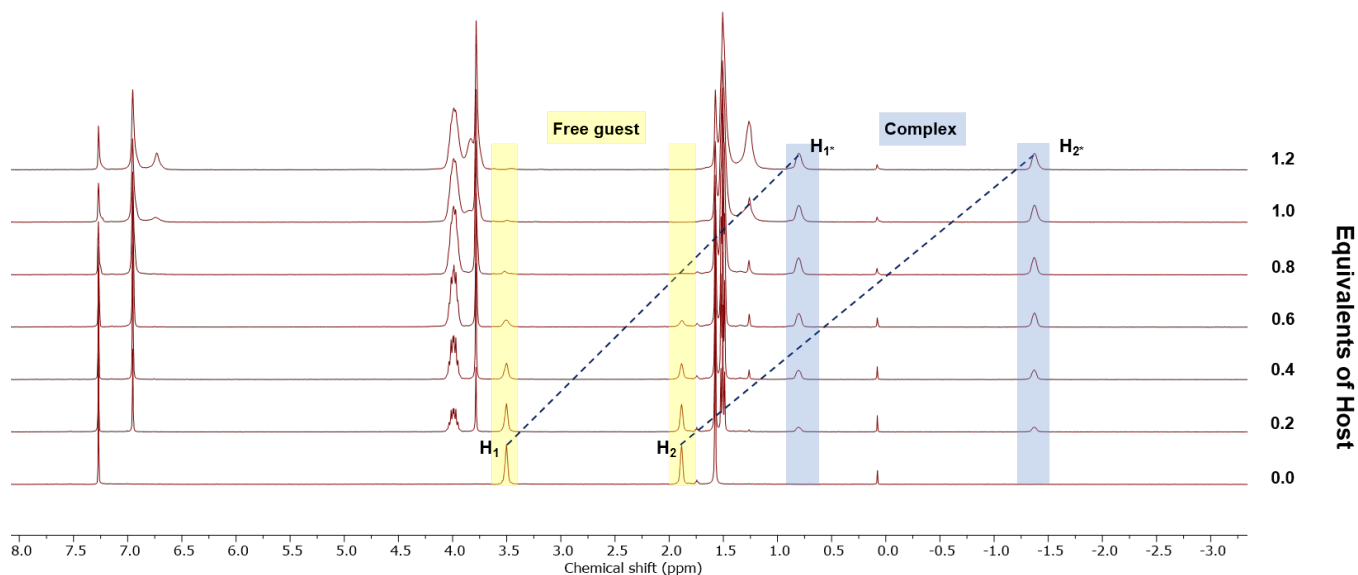


Figure S14. ¹H NMR spectra of **C4** (10 mM, 400 MHz, CDCl₃) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 equivalents

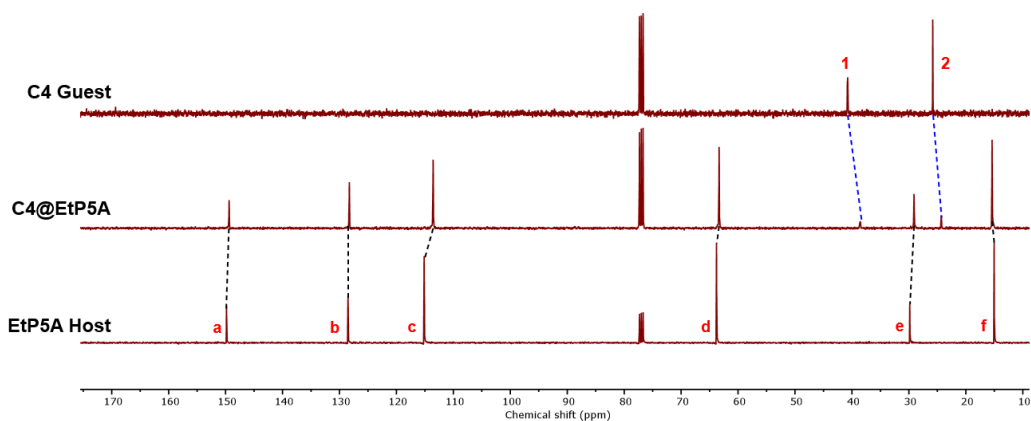


Figure S15. (a) Comparative ¹³C-NMR spectra of **EtP5A** (bottom), a 1:1 complex of **C4@EtP5A** (middle), and a **C4** guest (top) in CDCl₃ (101 MHz, 298K).

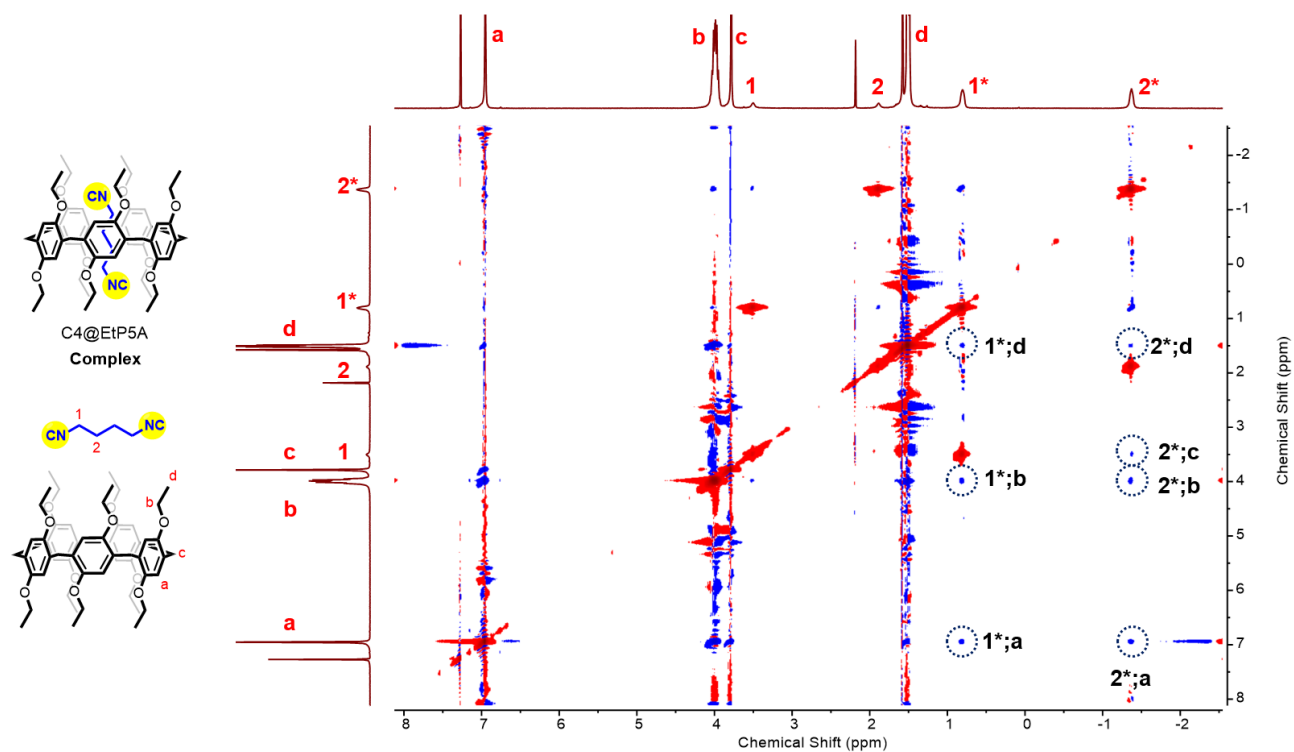
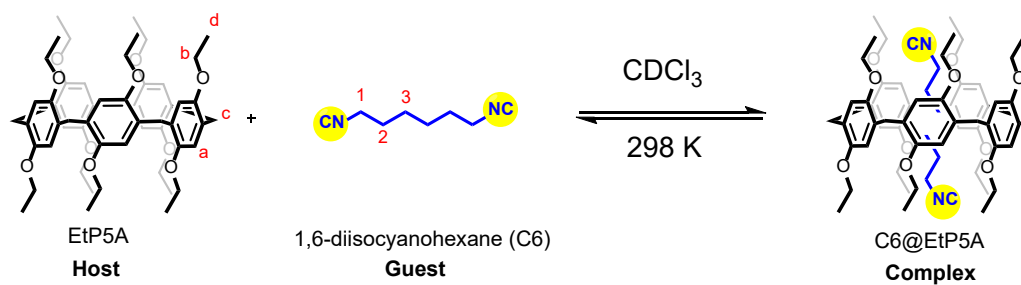


Figure S16. 2D-NOESY (CDCl₃) NMR Spectrum of 1:0.8 mixture of EtP5A and C4.

3.3 Evidence of C6@EtP5A complexation in CDCl₃ at 298 K



Scheme S3. Host-guest complexation between **EtP5A** (Host) and **C6** (Guest) in CDCl₃ at 298K.

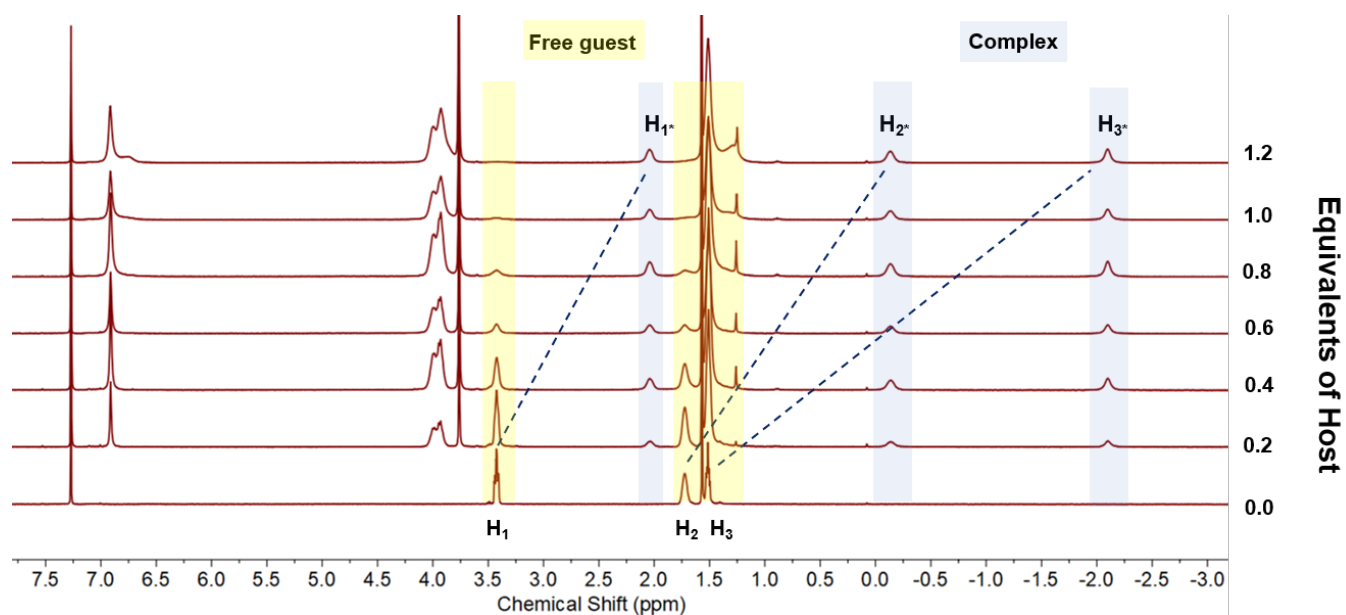
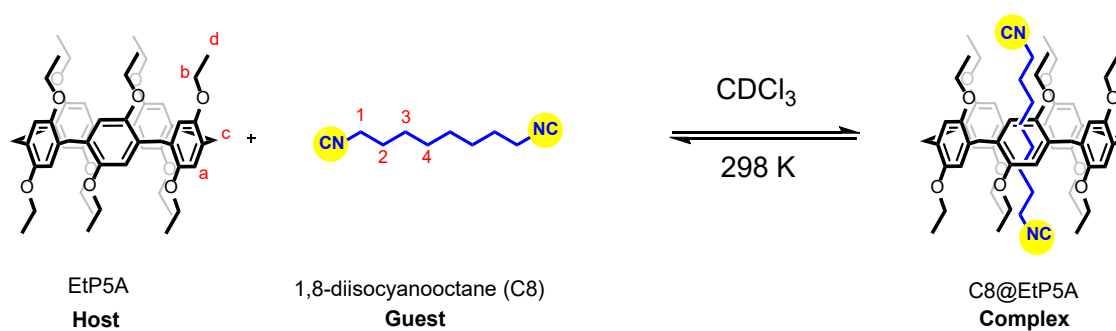


Figure S17. ¹H NMR spectra of **C6** (10 mM, 400 MHz, CDCl₃) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents.

3.4 Evidence of C8@EtP5A complexation in CDCl₃ at 298 K



Scheme S4. Host-guest complexation between **EtP5A** (Host) and **C8** (Guest) in CDCl₃ at 298K.

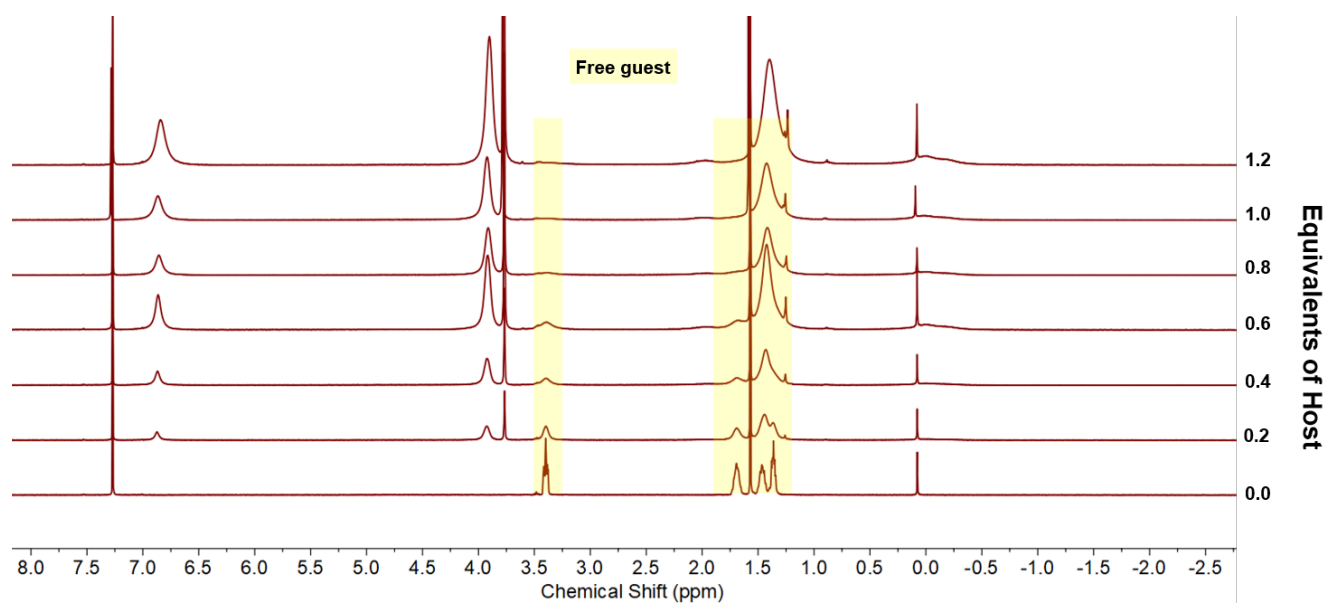
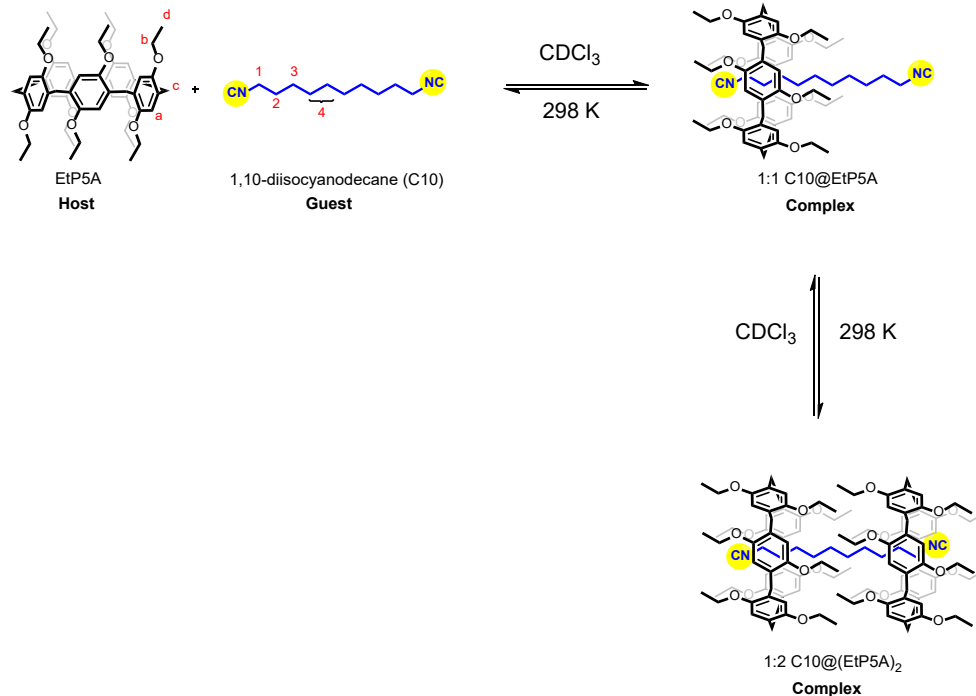


Figure S18. ¹H NMR spectra of **C8** (10 mM, 400 MHz, CDCl₃) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents.

3.5 Evidence of C10@EtP5A complexation in CDCl₃ at 298 K



Scheme S5. Host-guest complexation between **EtP5A** (Host) and **C10** (Guest) in CDCl₃ at 298K.

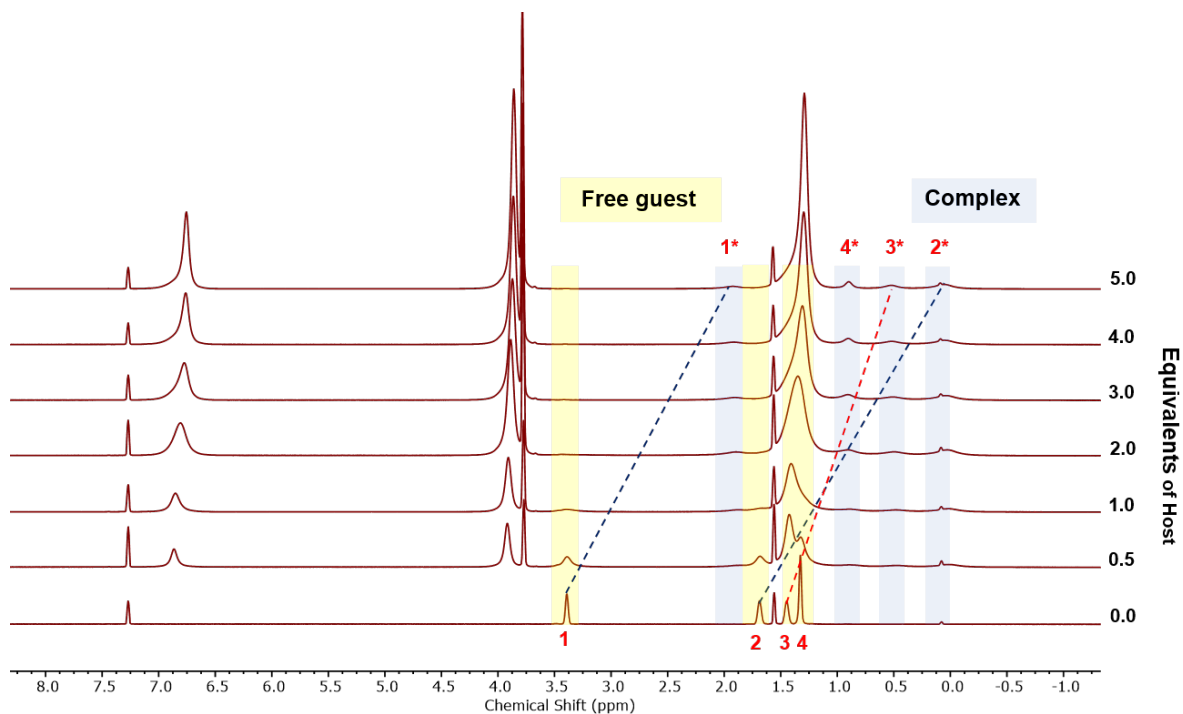


Figure S19. ¹H NMR spectra of **C10** (10 mM, 400 MHz, CDCl₃) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 equivalents.

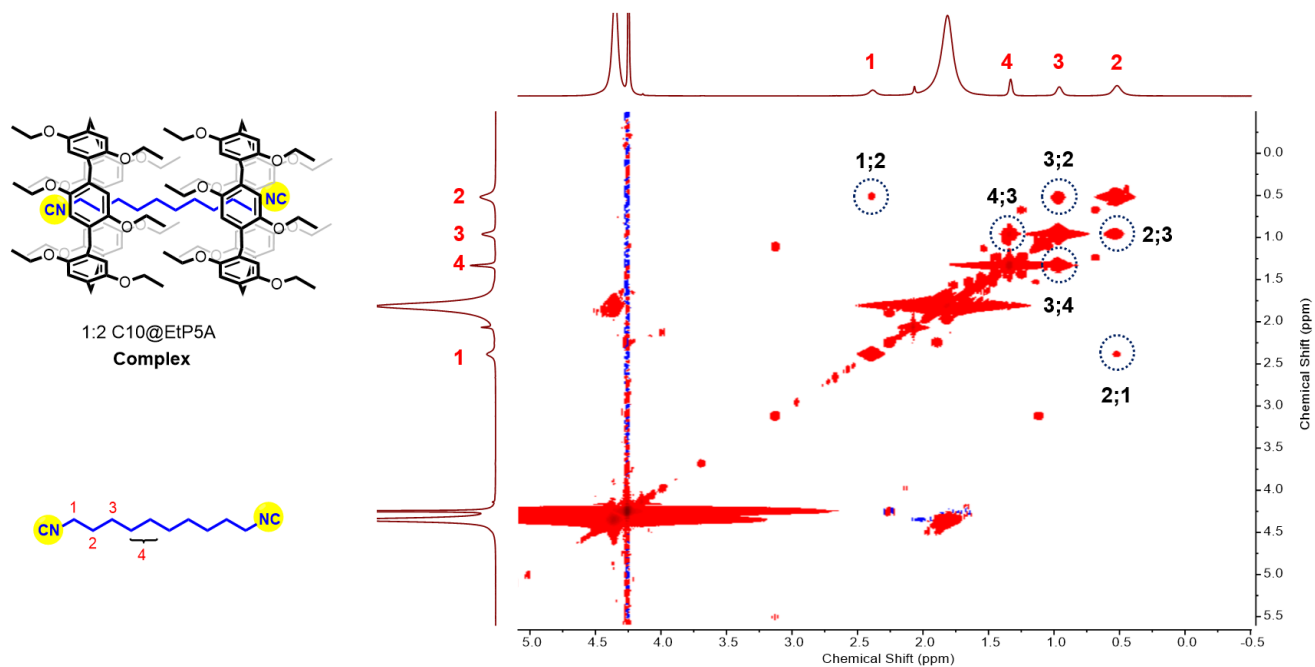


Figure S20. ^1H - ^1H COSY (CDCl_3) of 2:1 mixture of EtP5A and C10.

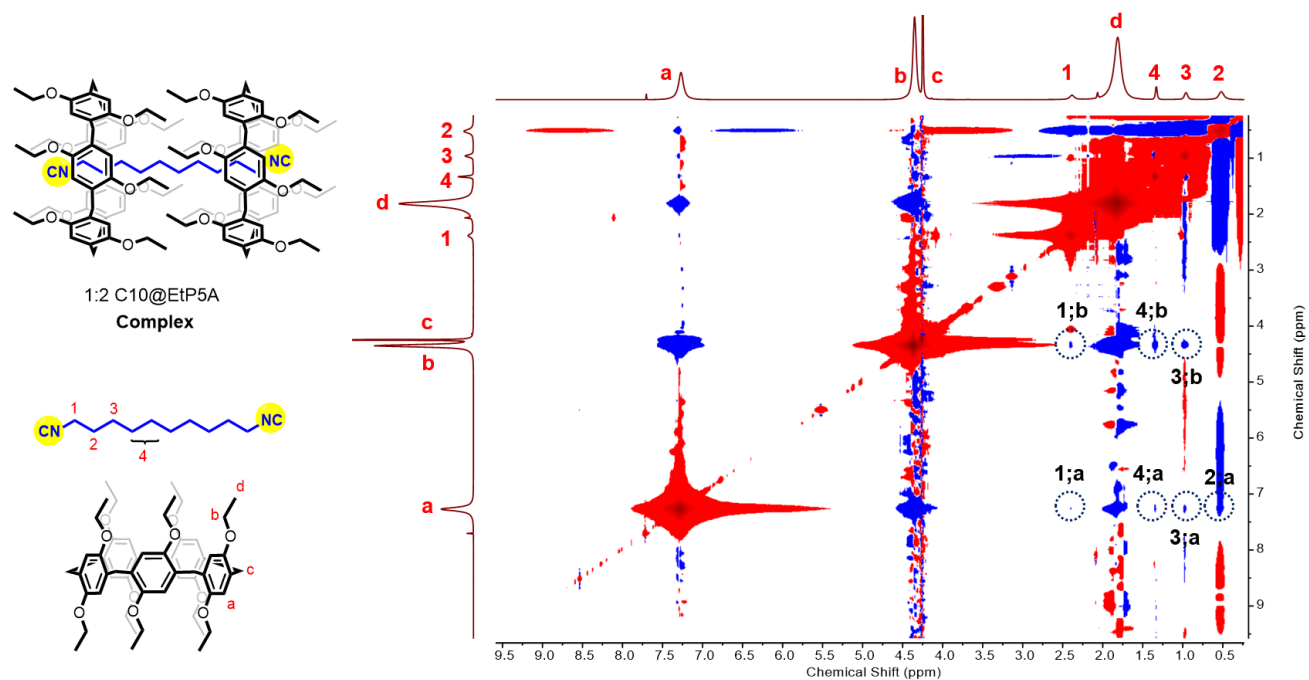
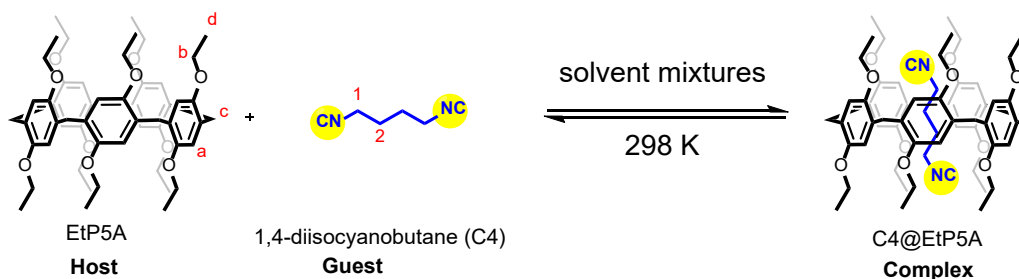


Figure S21. 2D-NOESY (CDCl_3) NMR Spectrum of 2:1 mixture of EtP5A and C10.

4. Host-Guest Complexation Studies of C4@EtP5A in Solvent Mixtures



Scheme S6. Host-guest complexation between **EtP5A** (Host) and **C4** (Guest) in solvent mixtures at 298 K.

4.1 Complexation in a 1:1 CDCl₃/d₆-Acetone

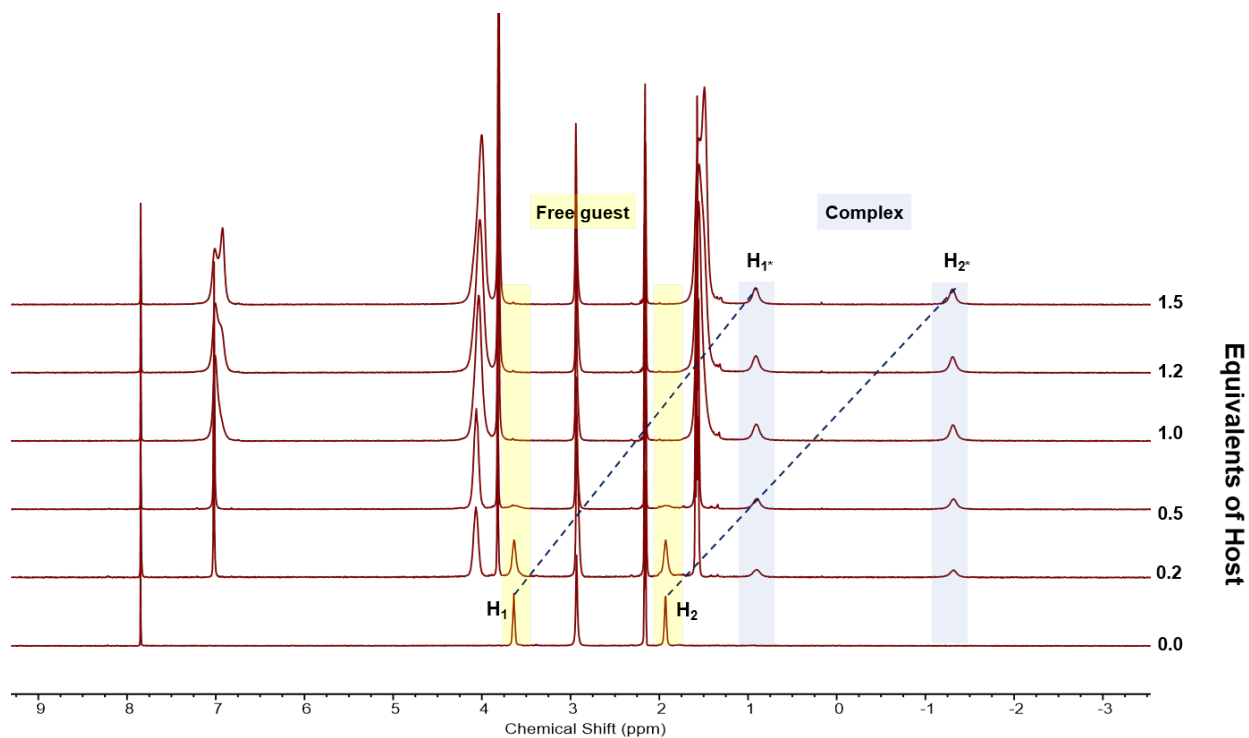


Figure S22. ¹H NMR spectra of **C4** (10 mM, 400 MHz, 1:1 CDCl₃/d₆-acetone) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents.

4.2 Complexation in a 1:1 CDCl₃/d₄-Methanol

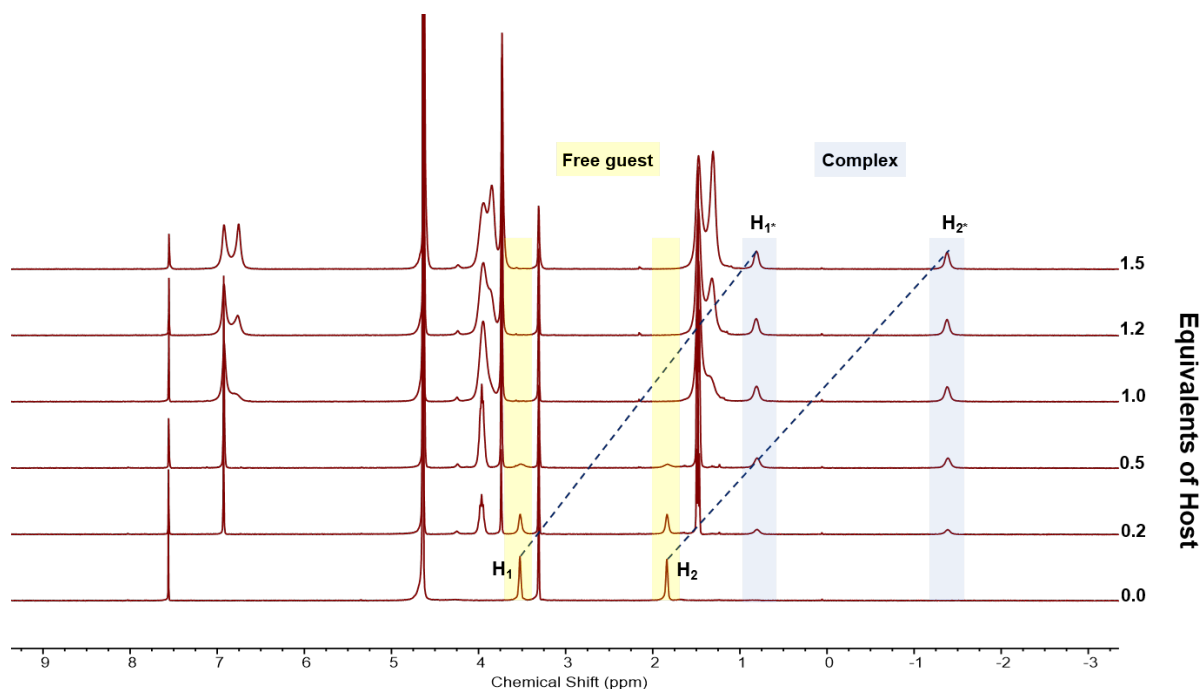


Figure S23. ¹H NMR spectra of **C4** (10 mM, 400 MHz, 1:1 CDCl₃/d₄-methanol) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents.

4.3 Complexation in a 1:1 CDCl₃/d₆-DMSO

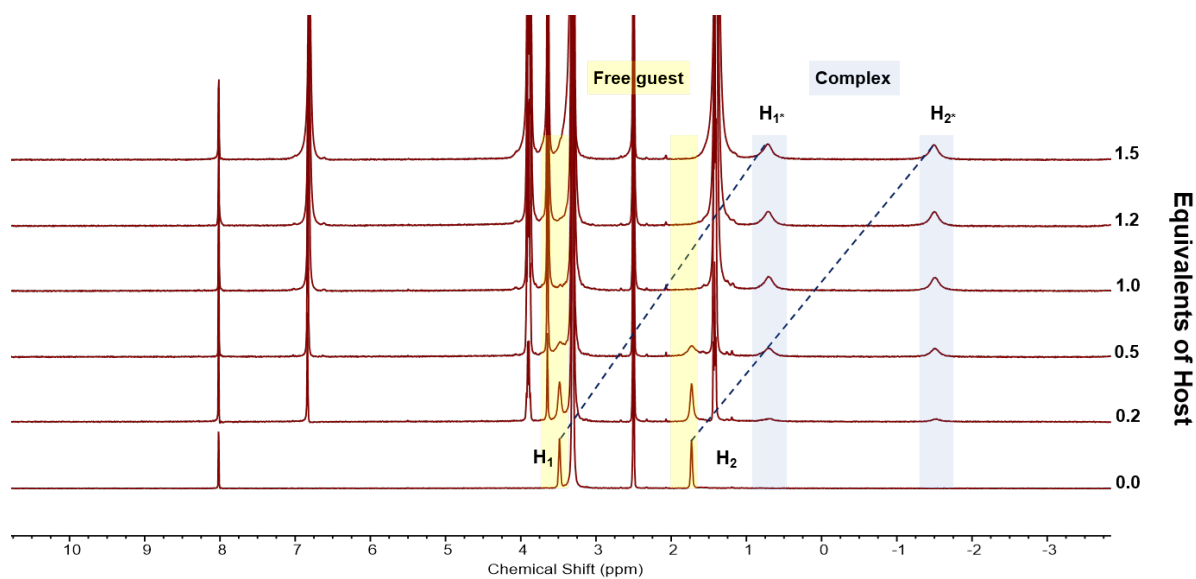


Figure S24. ¹H NMR spectra of **C4** (10 mM, 400 MHz, 1:1 CDCl₃/d₆-DMSO) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.2, 0.5, 1.0, 1.2, and 1.5 equivalents.

4.4 Complexation in a 1:1 CDCl₃/d₃-MeCN

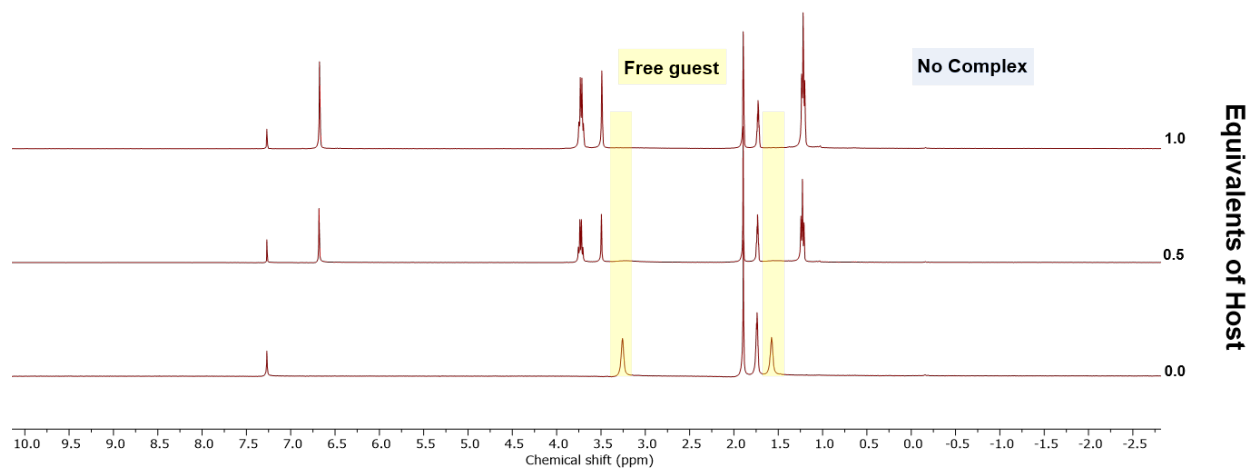


Figure S25. ¹H NMR spectra of **C4** (10 mM, 400 MHz, 1:1 CDCl₃/d₃-MeCN) in the presence of increasing amounts of **EtP5A**; from bottom to top: 0.0, 0.5, and 1.0 equivalents

5. Host-Guest Complexation Studies of Aryl Isocyanide in CDCl₃

5.1 1,4-diisocyanobenzene (Ph-NC)

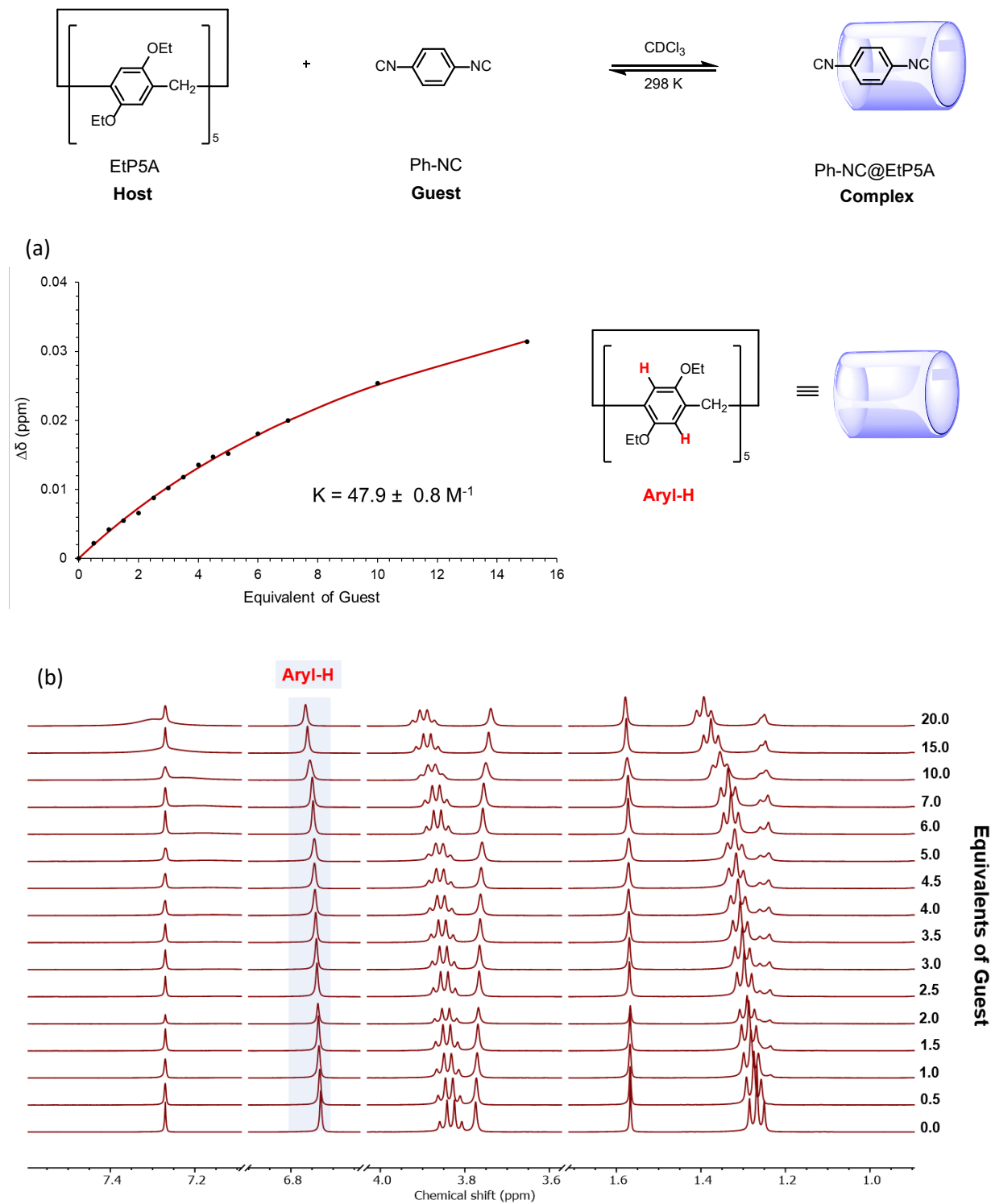


Figure S26. (a) Non-linear fitting curve of ¹H NMR titration with EtP5A (host) and Ph-NC (guest); (b) ¹H NMR spectra of EtP5A (10 mM) with the increasing ratio of Ph-NC from 0.0 to 20.0 eq. in CDCl₃ at 298 K

5.2 1-Isocyano-4-nitrobenzene (Ph-NO₂)

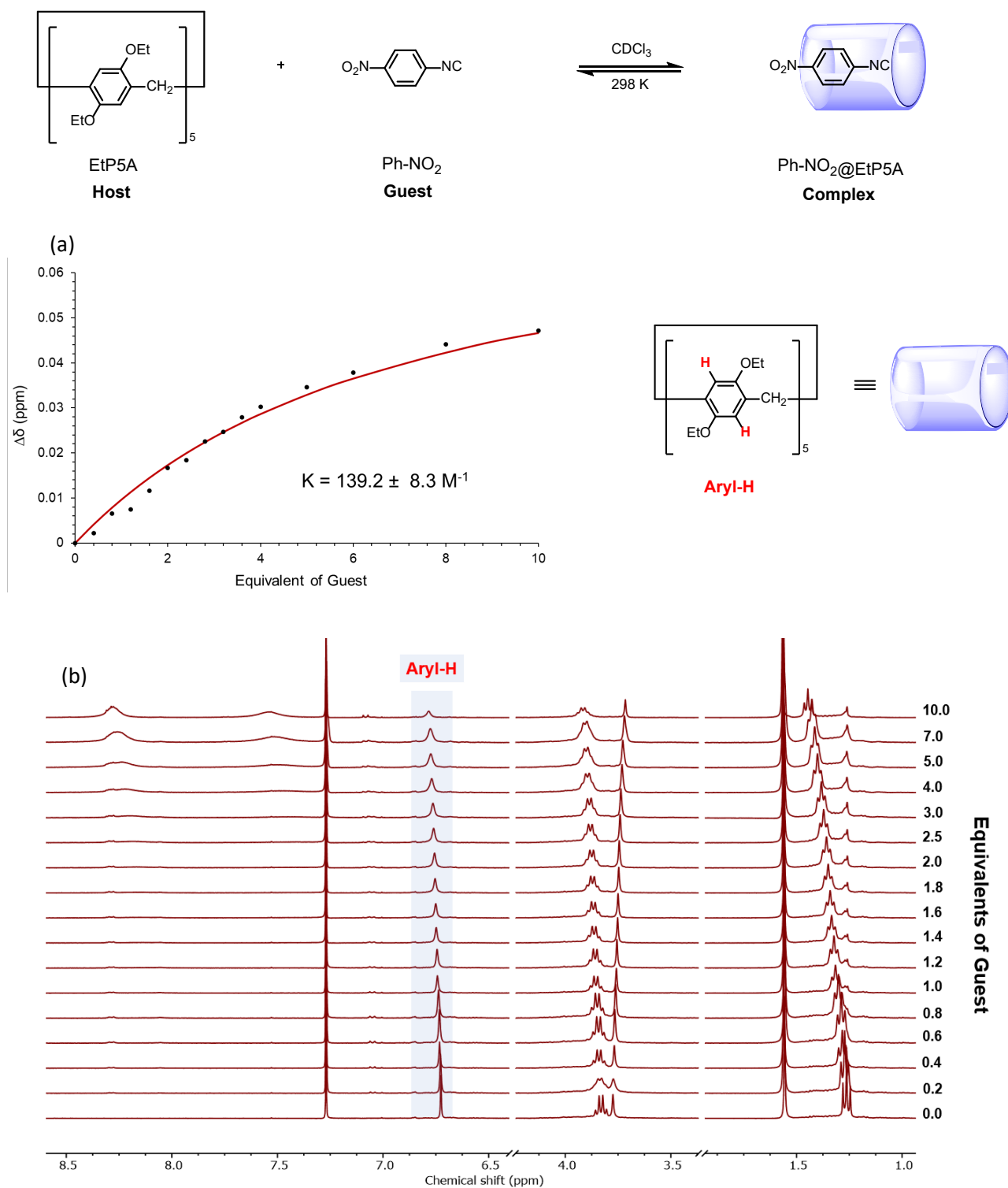


Figure S27. (a) Non-linear fitting curve of ¹H NMR titration with EtP5A (host) and Ph-NO₂ (guest); (b) ¹H NMR spectra of EtP5A (10 mM) with the increasing ratio of Ph-NO₂ from 0.0 to 10.0 eq. in CDCl₃ at 298 K

5.3 1-Iodo-4-isocyanobenzene (Ph-I)

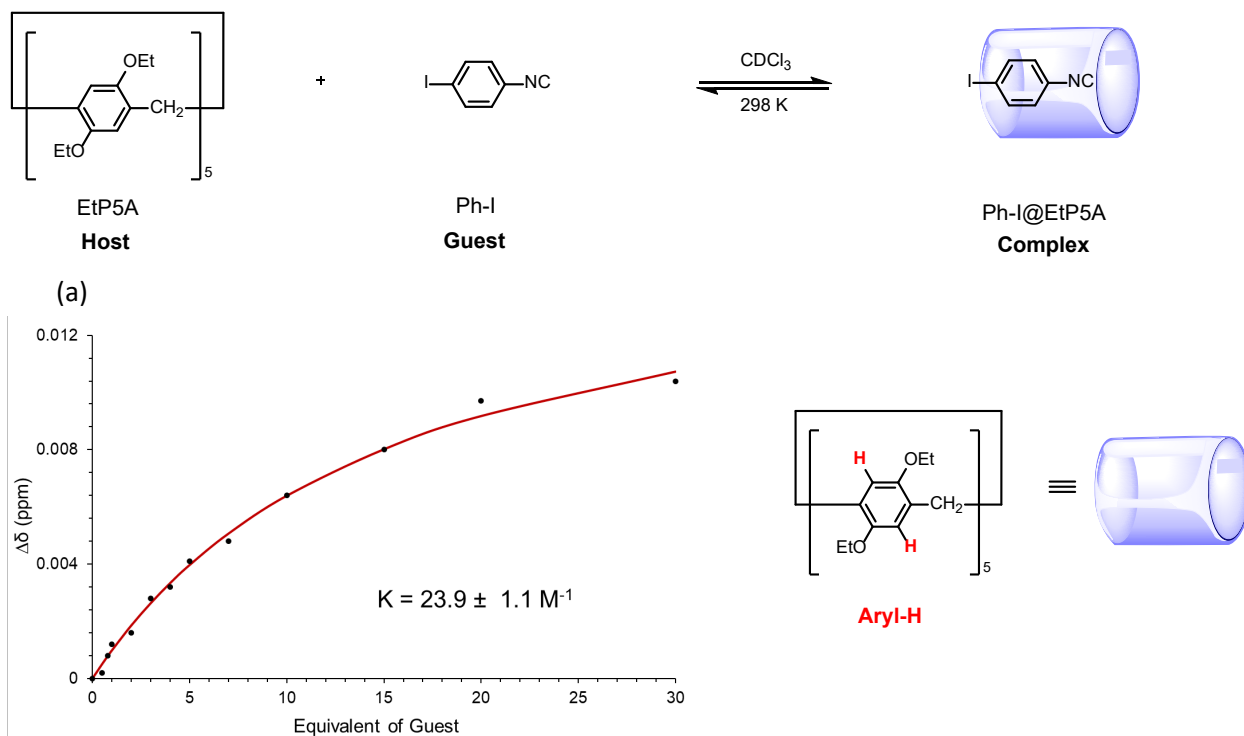


Figure S28. (a) Non-linear fitting curve of ^1H NMR titration with **EtP5A** (host) and **Ph-I** (guest); (b) ^1H NMR spectra of **EtP5A** (10 mM) with the increasing ratio of **Ph-I** from 0.0 to 20.0 eq. in CDCl_3 at 298 K

5.4 1-Isocyano-4-methoxybenzene (Ph-OMe)

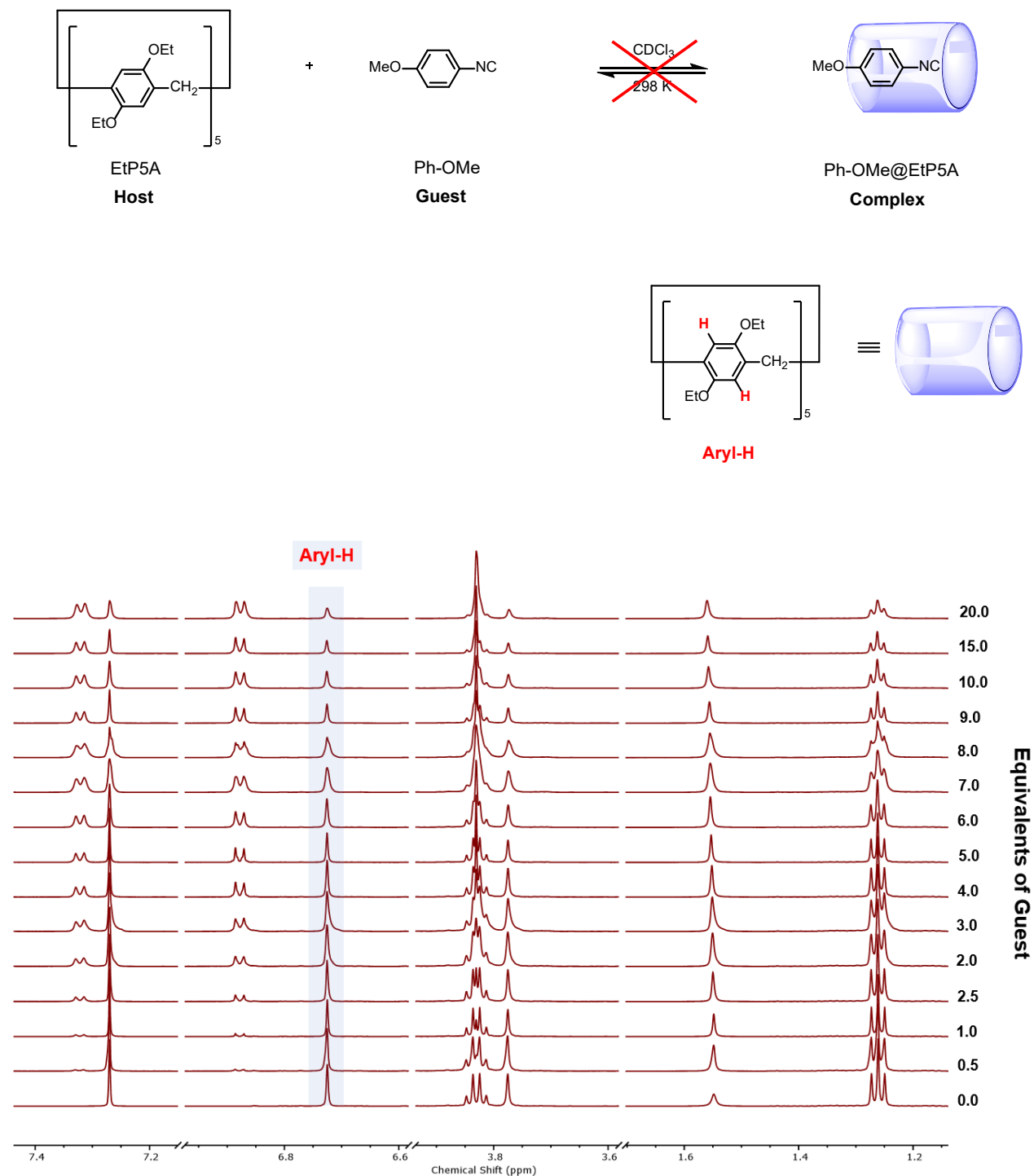


Figure S29. ¹H NMR spectra of EtP5A (10 mM) with the increasing ratio of Ph-OMe from 0.0 to 20.0 eq. in CDCl₃ at 298 K.

5.5 Isocyanomethyl benzene (Benzyl isocyanide)

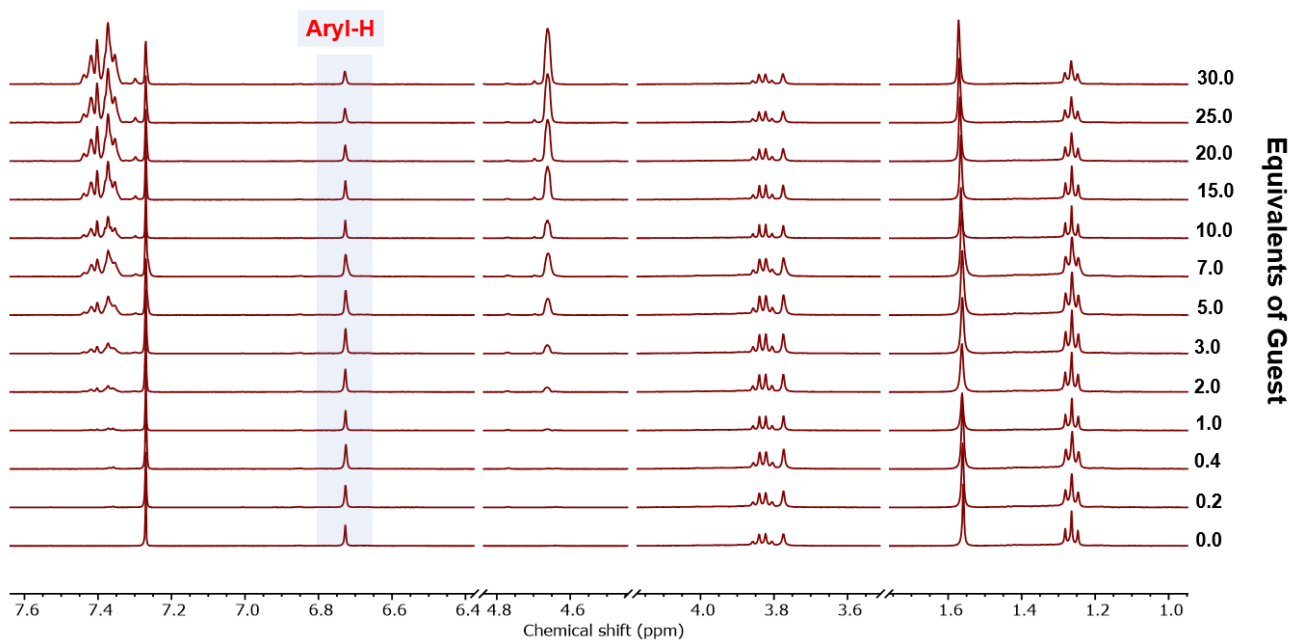
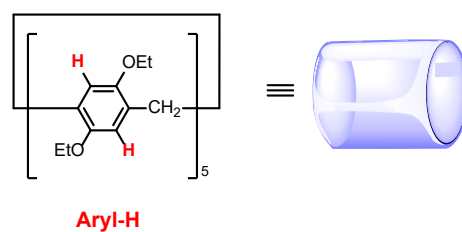
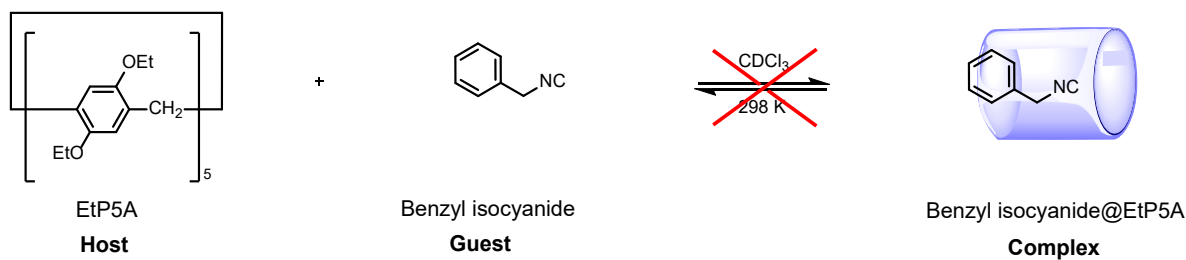


Figure S30. ^1H NMR spectra of **EtP5A** (10 mM) with the increasing ratio of **Benzyl isocyanide** from 0.0 to 30.0 eq. in CDCl_3 at 298 K.

5.6 Toluenesulfonylmethyl isocyanide (TOSMIC)

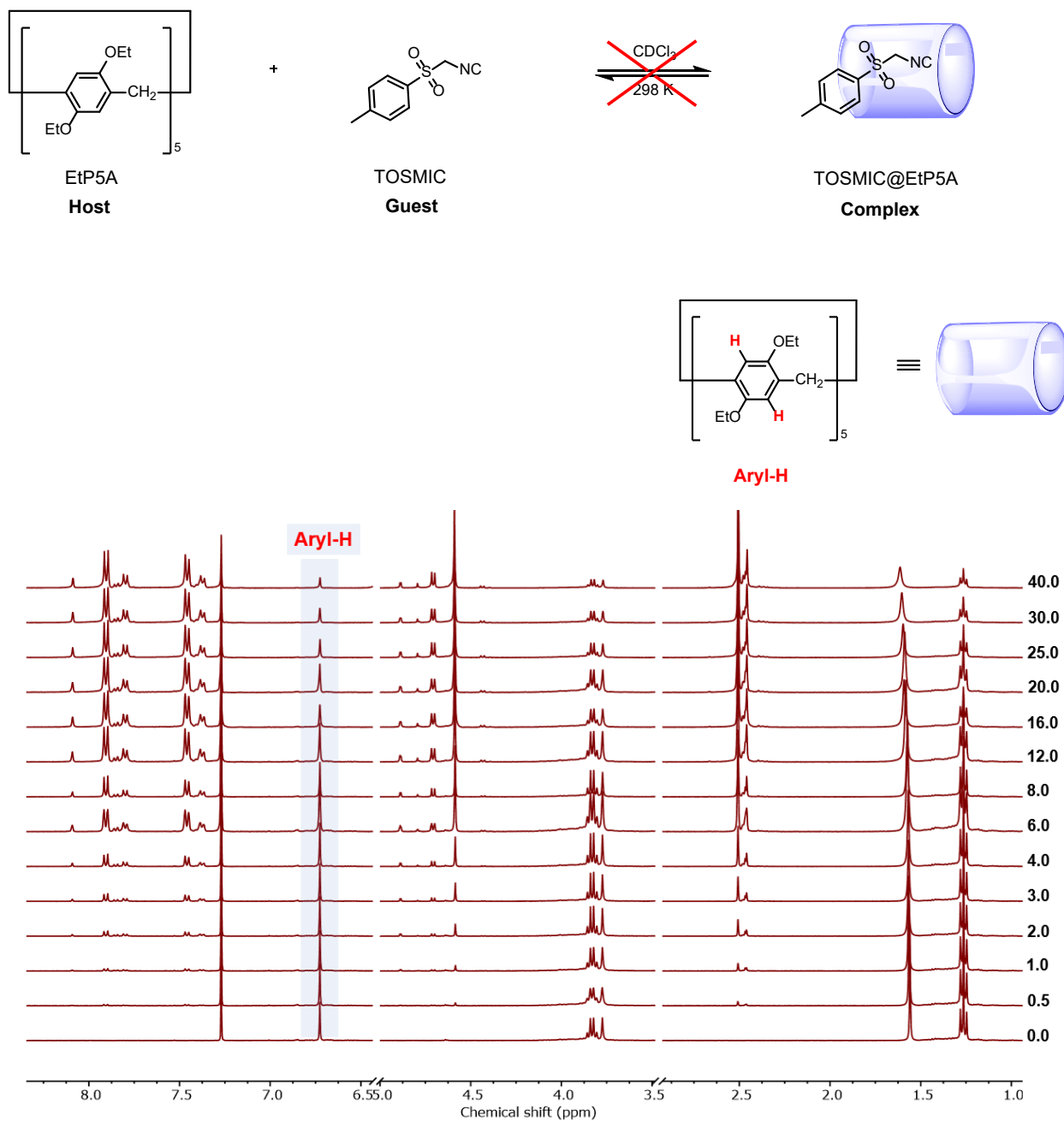
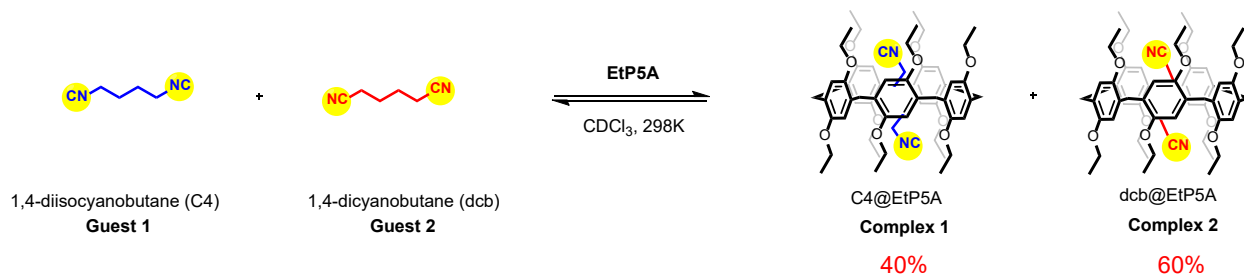


Figure S31. ¹H NMR spectra of EtP5A (10 mM) with the increasing ratio of TOSMIC from 0.0 to 40.0 eq. in CDCl₃ at 298 K.

6. Competitive Host-Guest Complexation Studies

6.1 EtP5A with two isoelectronic guests, 1,4-diisocyanobutane (**C4**) and 1,4-dicyanobutane (**dcb**) in CDCl_3 .



Scheme S7. Competitive Host-Guest Complexation of EtP5A (Host) with **C4** (Guest) and **dcb** (Guest) by the addition of EtP5A to a 1:1 mixture of **C4** and **dcb**.

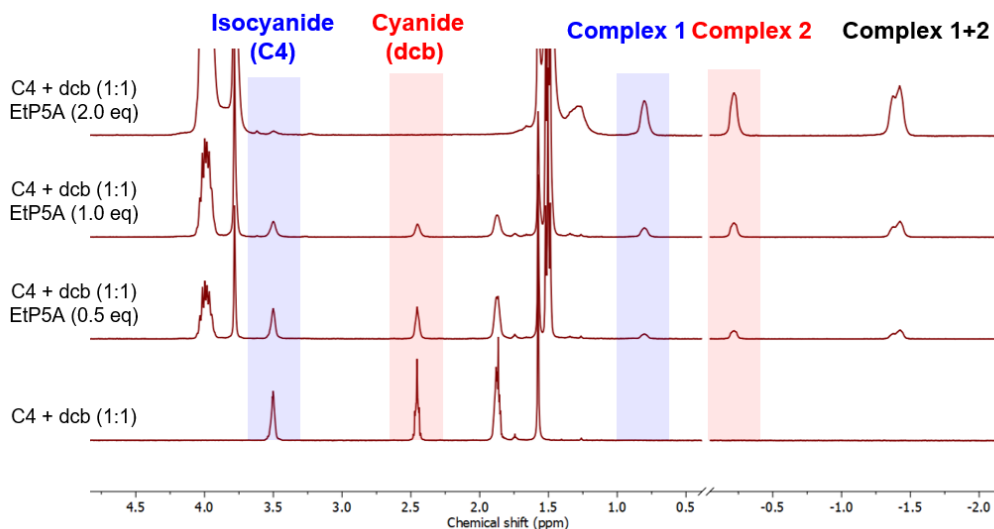


Figure S32. ^1H NMR spectra of **C4** and **dcb** 1:1 ratio (400 MHz, CDCl_3) in the presence of increasing amounts of EtP5A; from bottom to top: 0.0, 0.5, 1.0, and 2.0 equivalents.

Table S1. ¹H-NMR integration of complexed and free guest at EtP5A 1.0 equivalent

¹ H-NMR Integration				
Free guest		Complex		
C4	dcb	C4@EtP5A	dcb@EtP5A	total
2.20	1.82	1.64	2.39	4.03

Method 1

$$\% \text{Complexation} = \frac{\text{integration of complex}}{\text{integration of complex} + \text{free guest}} \times 100$$

Percentage of C4@EtP5A

$$\text{Complexation} = \frac{\text{integration of complex}}{\text{integration of complex} + \text{free guest}} \times 100$$

$$= \frac{1.64}{1.64 + 2.20} \times 100$$

$$= 42.7\%$$

Percentage of dcb@EtP5A

$$\text{Complexation} = \frac{\text{integration of complex}}{\text{integration of complex} + \text{free guest}} \times 100$$

$$= \frac{2.39}{2.39 + 1.82} \times 100$$

$$= 56.7\%$$

Method 2

$$\% \text{Complexation} = \frac{\text{integration of complex 1}}{\text{integration of complex 1} + \text{complex 2}} \times 100$$

Percentage of C4@EtP5A

$$\text{Complexation} = \frac{\text{integration of complex 1}}{\text{integration of complex 1} + \text{complex 2}} \times 100$$

$$= \frac{1.64}{1.64 + 2.39} \times 100$$

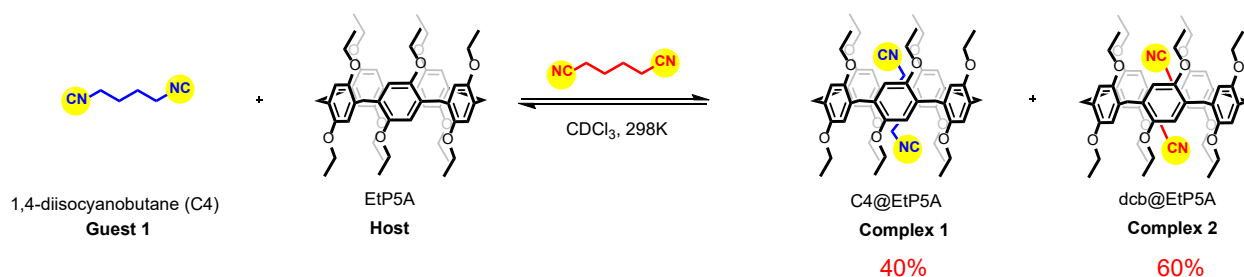
$$= 40.6\%$$

Percentage of dcb@EtP5A

$$\text{Complexation} = \frac{\text{integration of complex 1}}{\text{integration of complex 1} + \text{complex 2}} \times 100$$

$$= \frac{2.39}{1.64 + 2.39} \times 100$$

$$= 59.3\%$$



Scheme S8. Competitive Host-Guest Complexation of EtP5A (Host) with C4 (Guest) and dcb (Guest) by the addition of dcb to a 1:1 mixture of EtP5A and C4.

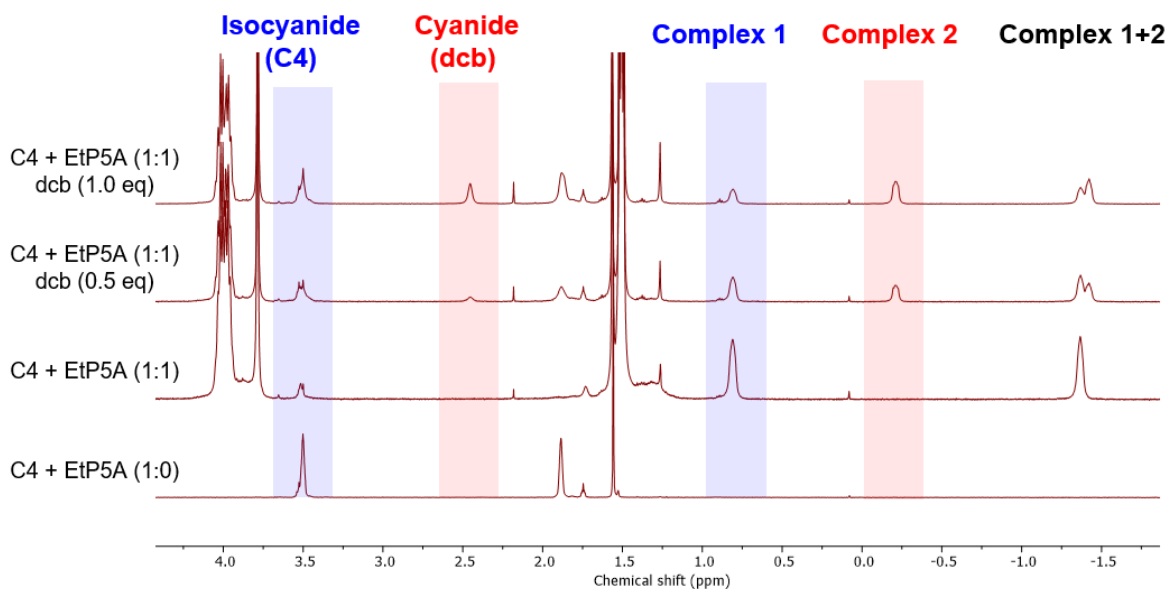


Figure S33. ^1H NMR spectra of C4 and EtP5A 1:1 ratio (400 MHz, CDCl_3) in the presence of increasing amounts of dcb; from bottom to top: 0.0, 0.5, and 1.0 equivalents.

Table S2. ^1H -NMR integration of complexed and free guest at dcb 1.0 equivalent

^1H -NMR Integration				
Free guest		Complex		
C4	dcb	C4@EtP5A	dcb@EtP5A	total
2.48	1.65	1.66	2.37	4.03

Method 1

$$\% \text{Complexation} = \frac{\text{integration of complexed guest}}{\text{integration of complexed guest} + \text{free guest}} \times 100$$

Percentage of C4@EtP5A

$$\text{Complexation} = \frac{\text{integration of complexed guest}}{\text{integration of complexed guest} + \text{free guest}} \times 100$$

$$= \frac{1.66}{1.66 + 2.48} \times 100$$

$$= 40.1\%$$

Percentage of dcb@EtP5A

$$\text{Complexation} = \frac{\text{integration of complexed guest}}{\text{integration of complexed guest} + \text{free guest}} \times 100$$

$$= \frac{2.37}{2.37 + 1.65} \times 100$$

$$= 58.9\%$$

Method 2

$$\% \text{Complexation} = \frac{\text{integration of complex 1}}{\text{integration of complex 1} + \text{complex 2}} \times 100$$

Percentage of C4@EtP5A

$$\text{Complexation} = \frac{\text{integration of complex 1}}{\text{integration of complex 1} + \text{complex 2}} \times 100$$

$$= \frac{1.66}{1.66 + 2.37} \times 100$$

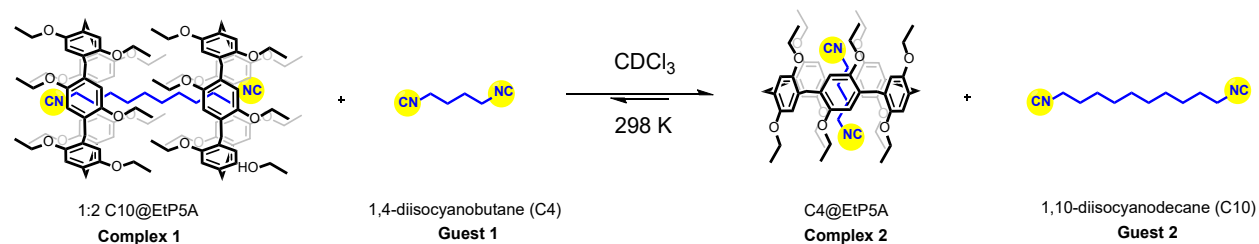
$$= 41.2\%$$

Percentage of dcb@EtP5A

$$\text{Complexation} = \frac{\text{integration of complex 1}}{\text{integration of complex 1} + \text{complex 2}} \times 100$$

$$= \frac{2.37}{1.66 + 2.37} \times 100$$

$$= 58.8\%$$



Scheme S9. Competitive Host-Guest Complexation of **EtP5A** (Host) with **C4** (Guest) and **C10** (Guest).

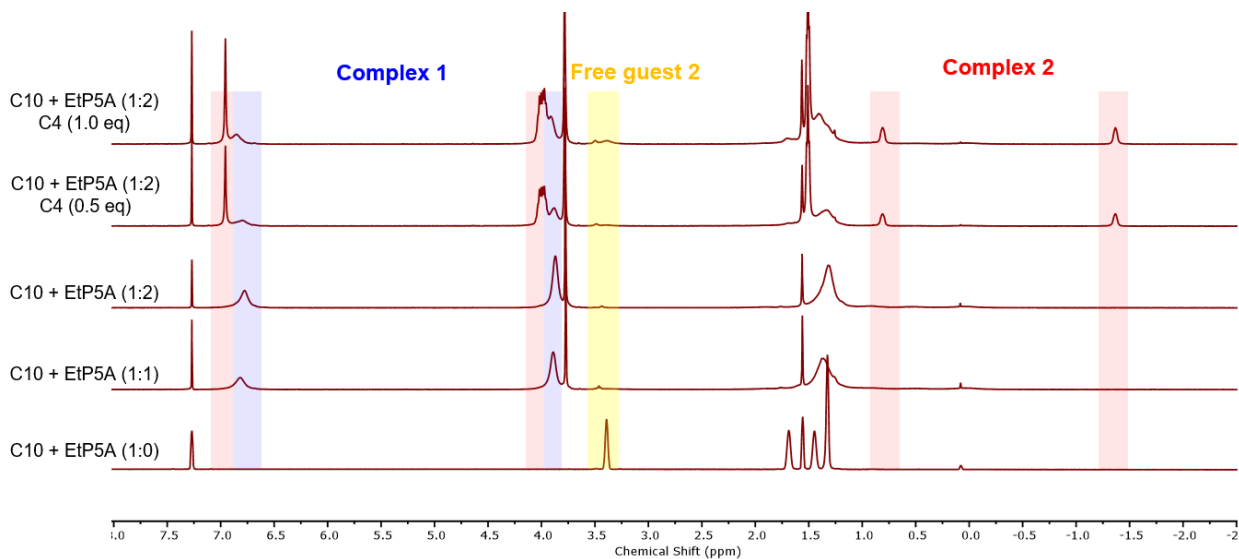


Figure S34. ¹H NMR spectra of **C10** and **EtP5A** 1:2 ratio (400 MHz, CDCl₃) in the presence of increasing amounts of **C4**; from bottom to top: 0.0, 0.5, and 1.0 equivalents.

7. X-Ray Crystallographic Data

Structural description

The structures are all broadly similar with the diisocyanide sitting inside the EtP5A host (Figure S35-S44). In the case of **C4@EtP5A** the asymmetric unit contains two independent EtP5A molecules with disordered diisocyanide guests. For molecule 1, at both ends of the pillararene there are C-H...C interactions that involve the ethoxy hydrogens and the isocyanide carbon of the guest. For molecule 2, these interactions are only found at one of the terminal carbons. The packing in this structure involves strips of the molecules with the pillararenes connected via C-H... π interactions (Figure S39).

In **C8@EtP5A** and **C10 @EtP5A (1:1)** the diisocyanide guests are, unusually, not disordered with a gauche conformation of the carbon atoms at the protruding end of the diisocyanide. At the other end there are again interactions involving the rim of the pillararene that keep the guest in a fixed position. The dangling isocyanide carbon forms C-H...C interactions with a neighbouring pillararene resulting in very similar packing diagrams (Figures S40 and S42).

The structure of **C10@EtP5A (1:2)** is unique in this series with two host pillararenes and the diisocyanide guest. Remarkably, the guest is completely ordered with an anti-conformation of the C10 chain. The pillararenes are slightly angled such that the central part of the pseudo[3]rotaxane is larger in the middle than at the ends. As in **C4@EtP5A**, C-H...C interactions involving the ethoxy hydrogens and the isocyanide carbon hold the guest in place. The neighbouring pseudo[3]rotaxanes are linked by C-H... π interactions resulting in a structure with channels that are coincident with the crystallographic [111] axis (Figure S47).

The structure of **Ph-I@EtP5A** reveals that the iodophenylisocyanide guest is very slightly disordered in a 96:4 ratio. The aromatic isocyanide sits within the pillararene and is held in place by significant C-H... π interactions (Figure S9). The large iodine atom causes one end of the pillararene to be more open than the other. Interestingly, the iodophenylisocyanide guests all point in one direction creating a 1D chain (Figure S44). This raises the possibility of an interaction between the iodine and isocyanide C atom, although with a I...C distance of 4.16 Å this seems unlikely.

Table S3. Crystallographic data and refinement parameters for **C4@EtP5A**, **C8@EtP5A** and **C10@EtP5A** (**1:2**), **C10@EtP5A (1:1)** and **Ph-I@EtP5A**

	C4@EtP5A	C8@EtP5A
Empirical formula	C ₆₁ H ₇₈ N ₂ O ₁₀	C ₆₅ H ₈₆ N ₂ O ₁₀
Formula weight	999.25	1055.35
Temperature/K	150.0(1)	150.0(1)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	13.2167(3)	13.31350(9)
<i>b</i> /Å	20.9569(3)	22.57704(13)
<i>c</i> /Å	21.2096(3)	20.66232(13)
α /°	102.1610(10)	90
β /°	90.262(2)	102.1000(6)
γ /°	92.131(2)	90
Volume/Å ³	5738.39(18)	6072.69(7)
<i>Z</i>	4	4
ρ_{calc} /cm ³	1.157	1.154
μ /mm ⁻¹	0.622	0.612
<i>F</i> (000)	2152.0	2280.0
Crystal size/mm ³	0.279 × 0.235 × 0.204	0.221 × 0.161 × 0.134
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 θ range for data collection/°	4.262 to 137.14	5.87 to 137.07
Index ranges	-15 ≤ <i>h</i> ≤ 15, -23 ≤ <i>k</i> ≤ 25, -25 ≤ <i>l</i> ≤ 24	-15 ≤ <i>h</i> ≤ 16, -27 ≤ <i>k</i> ≤ 27, -24 ≤ <i>l</i> ≤ 24
Reflections collected	86474	61927
Independent reflections	20971 [<i>R</i> _{int} = 0.0382, <i>R</i> _{sigma} = 0.0293]	11112 [<i>R</i> _{int} = 0.0570, <i>R</i> _{sigma} = 0.0382]
Data/restraints/parameters	20971/83/1391	11112/3/704
Goodness-of-fit on <i>F</i> ²	1.033	1.062
Final <i>R</i> indexes [<i>I</i> 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0811, <i>wR</i> ₂ = 0.2498	<i>R</i> ₁ = 0.0480, <i>wR</i> ₂ = 0.1285
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0965, <i>wR</i> ₂ = 0.2663	<i>R</i> ₁ = 0.0544, <i>wR</i> ₂ = 0.1335
Largest diff. peak/hole / e Å ⁻³	0.61/-0.33	0.36/-0.34
CCDC No.	2167174	2167170

	C10@(EtP5A)₂ (1:2)	C10@EtP5A (1:1)
Empirical formula	C ₁₂₂ H ₁₆₄ N ₂ O ₂₂	C ₆₇ H ₉₀ N ₂ O ₁₀
Formula weight	2010.54	1083.40
Temperature/K	149.9(2)	150.0(1)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	13.02310(10)	13.23130(10)
<i>b</i> /Å	14.51270(10)	22.6354(2)
<i>c</i> /Å	15.24250(10)	20.6987(2)
α /°	89.0960(10)	90
β /°	86.1870(10)	100.5510(10)
γ /°	83.0700(10)	90
Volume/Å ³	2853.37(4)	6094.36(9)
<i>Z</i>	1	4
ρ_{calc} /cm ³	1.170	1.181
μ /mm ⁻¹	0.635	0.621
<i>F</i> (000)	1086.0	2344.0
Crystal size/mm ³	0.33 × 0.25 × 0.128	0.384 × 0.303 × 0.167
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 θ range for data collection/°	5.812 to 137.176	5.84 to 137.104
Index ranges	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 17, -18 ≤ <i>l</i> ≤ 18	-12 ≤ <i>h</i> ≤ 15, -27 ≤ <i>k</i> ≤ 26, -24 ≤ <i>l</i> ≤ 24
Reflections collected	57277	48466
Independent reflections	10461 [<i>R</i> _{int} = 0.0440, <i>R</i> _{sigma} = 0.0274]	11105 [<i>R</i> _{int} = 0.0466, <i>R</i> _{sigma} = 0.0320]
Data/restraints/parameters	10461/0/659	11105/55/722
Goodness-of-fit on <i>F</i> ²	1.051	1.054
Final <i>R</i> indexes [<i>I</i> 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0413, <i>wR</i> ₂ = 0.1108	<i>R</i> ₁ = 0.0602, <i>wR</i> ₂ = 0.1686
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0467, <i>wR</i> ₂ = 0.1150	<i>R</i> ₁ = 0.0668, <i>wR</i> ₂ = 0.1750
Largest diff. peak/hole / e Å ⁻³	0.20/-0.22	0.71/-0.49
CCDC No.	2167171	2167173

Ph-I@EtP5A

Empirical formula	C ₆₃ H ₇₅ Cl ₃ IINO ₁₀
Formula weight	1239.49
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	11.60810(10)
<i>b</i> /Å	21.52620(10)
<i>c</i> /Å	27.6794(3)
α /°	90
β /°	120.0360(10)
γ /°	90
Volume/Å ³	5987.67(10)
<i>Z</i>	4
ρ_{calc} /cm ³	1.375
μ /mm ⁻¹	5.902
<i>F</i> (000)	2576.0
Crystal size/mm ³	0.414 × 0.318 × 0.238
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	5.518 to 137.102
Index ranges	-13 ≤ <i>h</i> ≤ 14, -25 ≤ <i>k</i> ≤ 25, -33 ≤ <i>l</i> ≤ 33
Reflections collected	48172
Independent reflections	10951 [<i>R</i> _{int} = 0.0620, <i>R</i> _{sigma} = 0.0398]
Data/restraints/parameters	10951/263/774
Goodness-of-fit on <i>F</i> ²	1.039
Final <i>R</i> indexes [<i>I</i> 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0465, <i>wR</i> ₂ = 0.1222
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0494, <i>wR</i> ₂ = 0.1245
Largest diff. peak/hole / e Å ⁻³	2.18/-0.70
CCDC No.	2167172

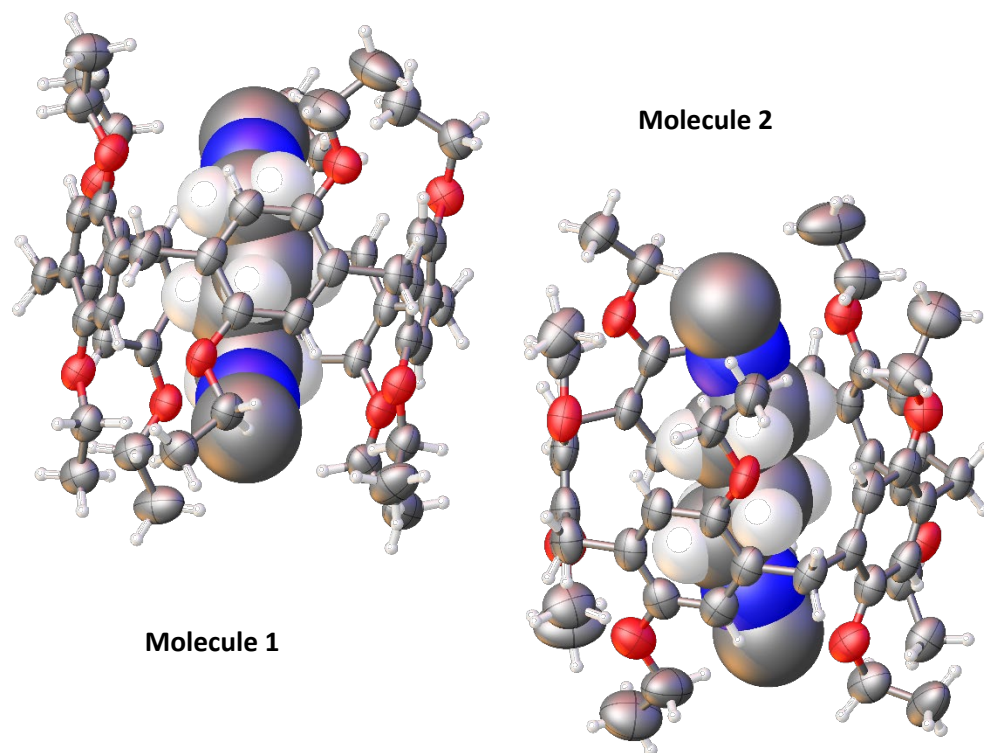


Figure S35. View of the asymmetric unit in **C4@EtP5A**. Ellipsoids are drawn at 50%. For clarity, only the major parts of the disordered isocyanides are shown as spacefill models.

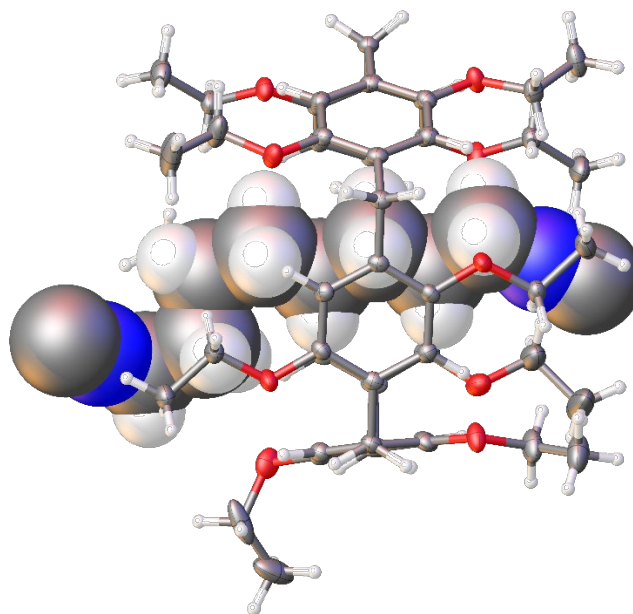


Figure S36. View of the asymmetric unit in **C8@EtP5A**. Ellipsoids are drawn at 50% with the diisocyanide shown as a spacefill model.

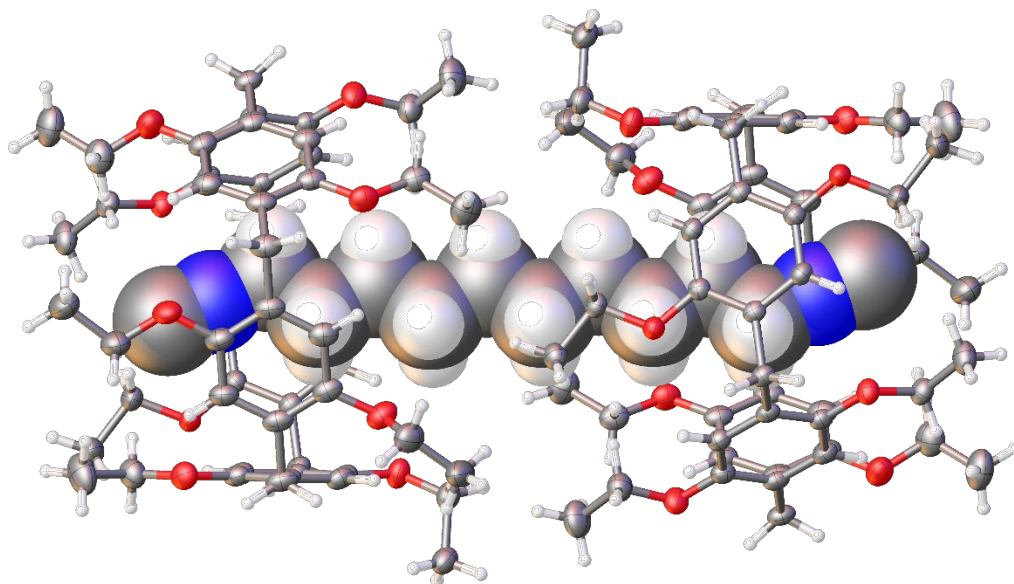


Figure S37. View of the pseudo[3]rotaxane in **C10@EtP5A**₂ (**1:2**). Ellipsoids are drawn at 50% with the diisocyanide shown as a spacefill model.

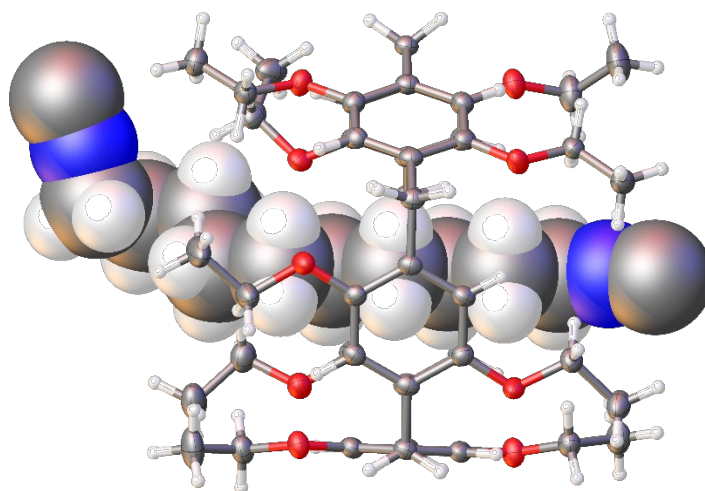


Figure S38. View of the asymmetric unit in **C10@EtP5A** (**1:1**). Ellipsoids are drawn at 50% with the diisocyanide shown as a spacefill model.

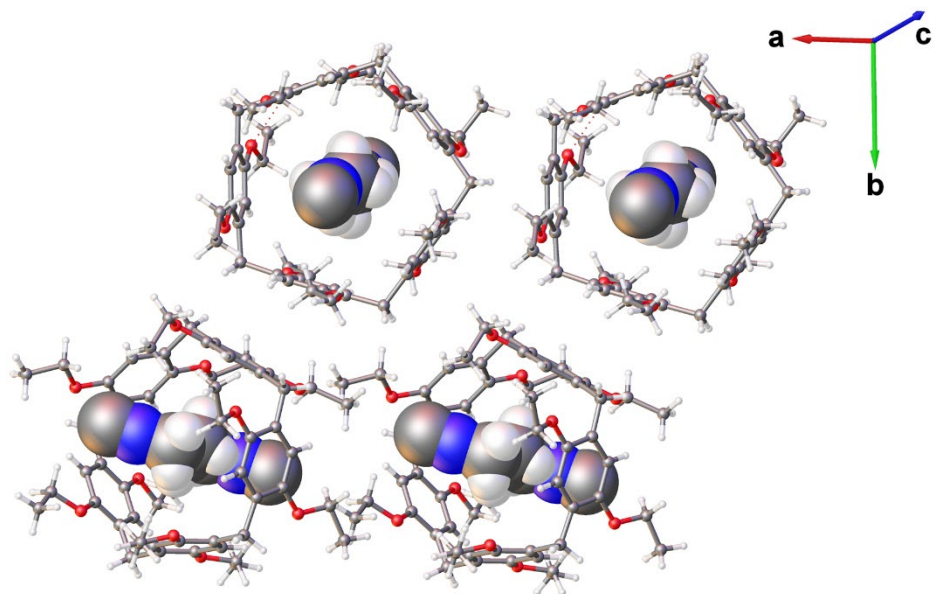


Figure S39. View of the packing in **C4@EtP5A**. The upper pillararenes contains only molecule 1, while the lower pillararenes contain only molecule 2.

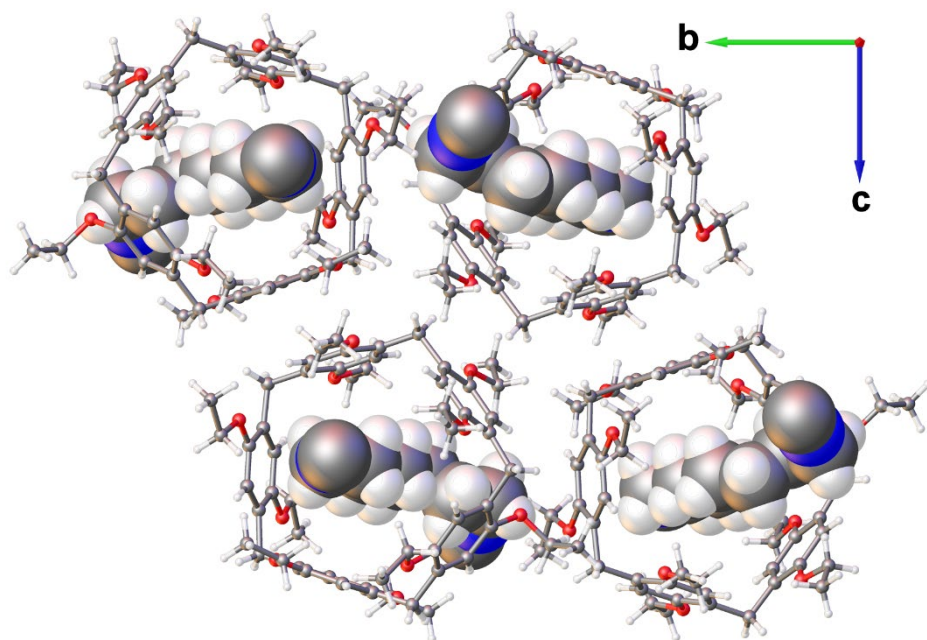


Figure S40. View of the packing in **C8@EtP5A**. The protrusion of one end of the diisocyanide is clearly visible.

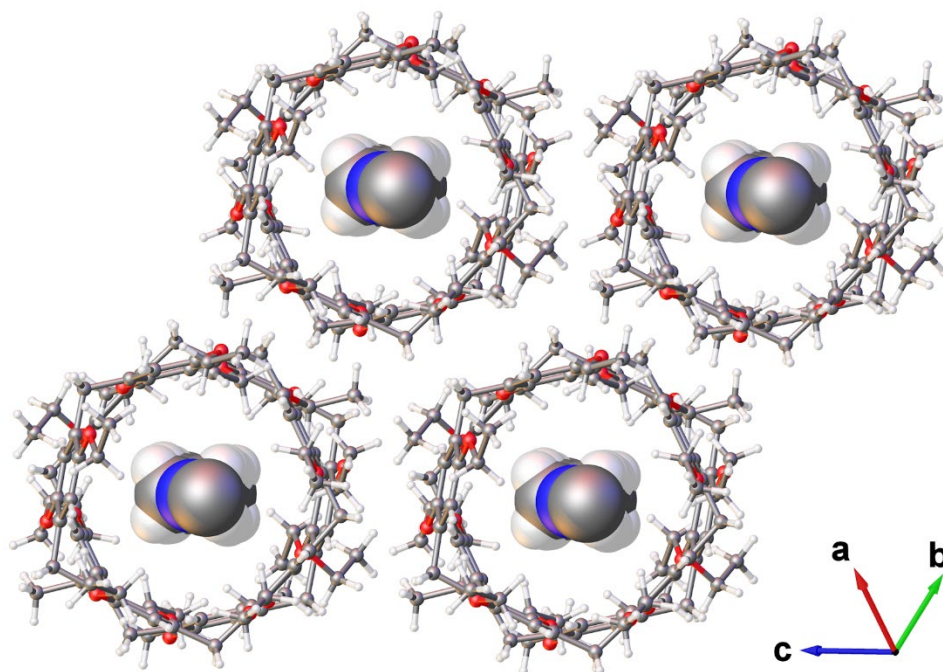


Figure S41. View of the packing in **C10@EtP5A₂** (**1:2**) showing the 1D channels that are coincident with the crystallographic [111] axis.

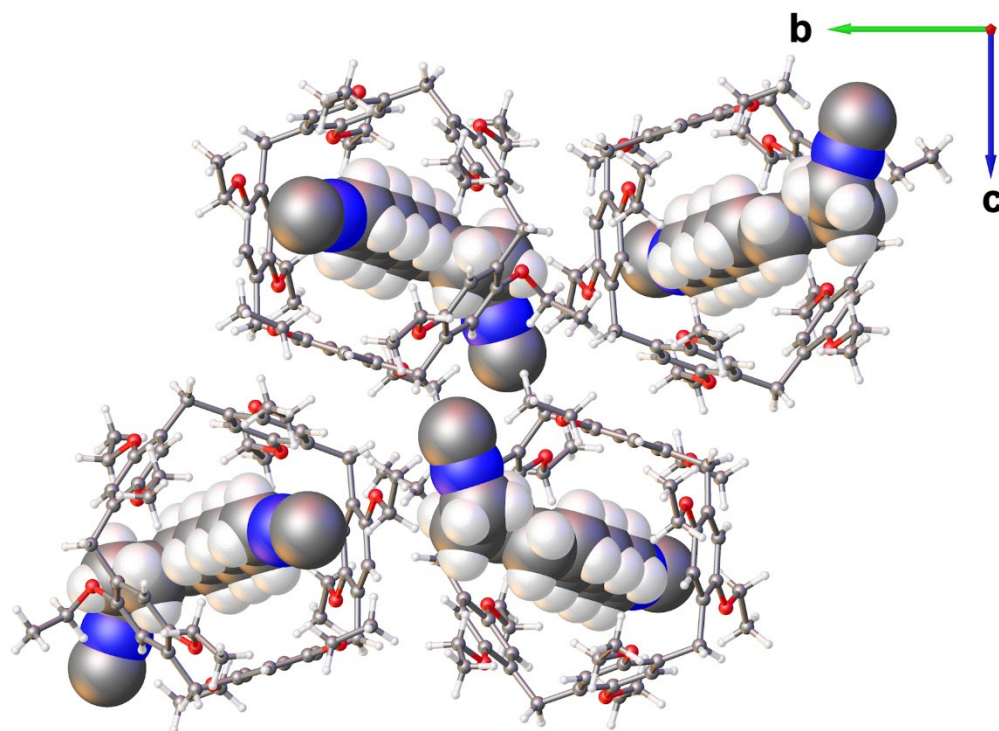


Figure S42. View of the packing in **C10@EtP5A** (**1:1**). The protrusion of one end of the diisocyanide is clearly visible.

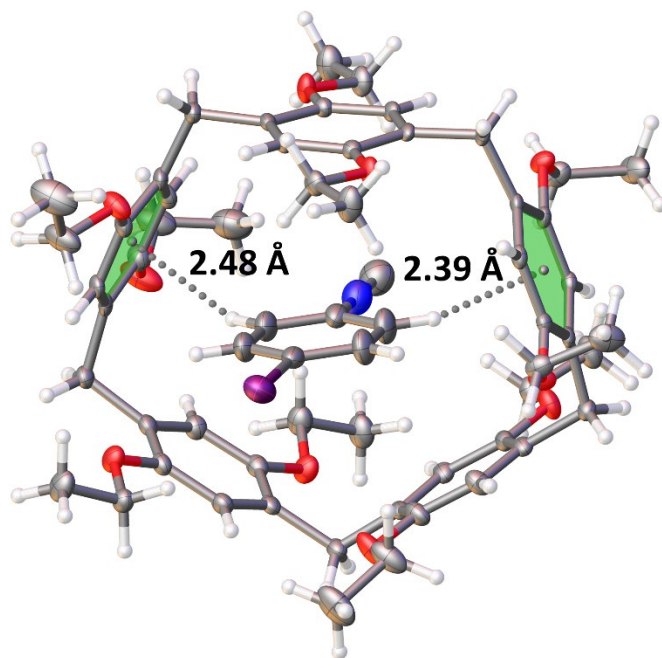


Figure S43. View of the C-H... π interactions in **Ph-I@EtP5A**, only the only the major part is shown in the interests of clarity.

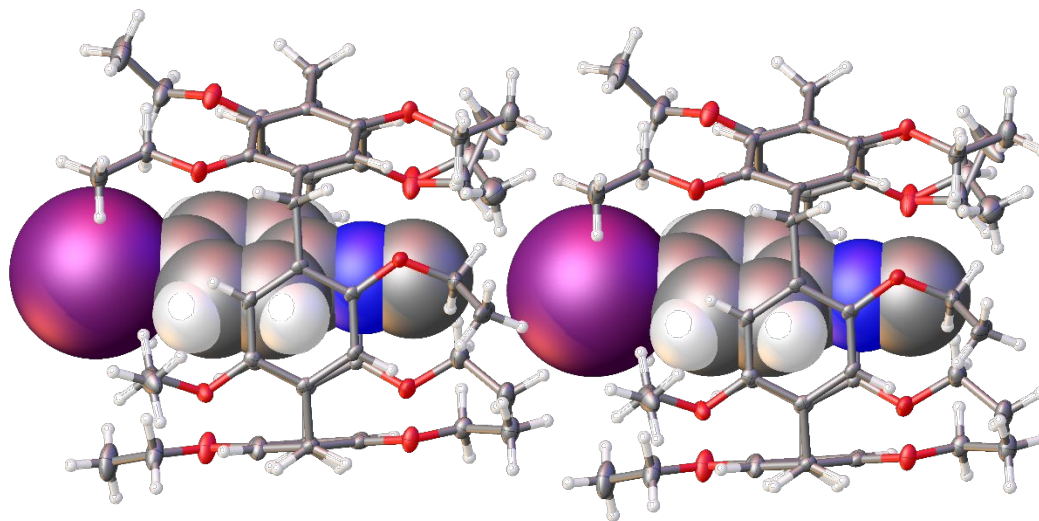


Figure S44. View of the 1D chain in **Ph-I@EtP5A**, only the major part is shown in the interests of clarity. Ellipsoids are drawn at 50% with the guest shown as a spacefill model.

8. Computational data

Computational Details.

All calculations were performed by Gaussian 09 program.³ The calculations on the isolated systems were performed at the DFT level with the RB3LYP exchange-correlation functional.⁴⁻⁵ The 6-31++G(D,P) all-electron basis set was used for the C, H, and N atoms. Display charge distribution type Mulliken with the color scale from -0.550 (red) to 0.550 (green). The molecular electrostatic potential (MEP) was plotted over electron density surface with an isovalue of 0.004 au. The color scale is ranged from $-4.743e^{-2}$ (red) to $4.743e^{-2}$ (blue) au.

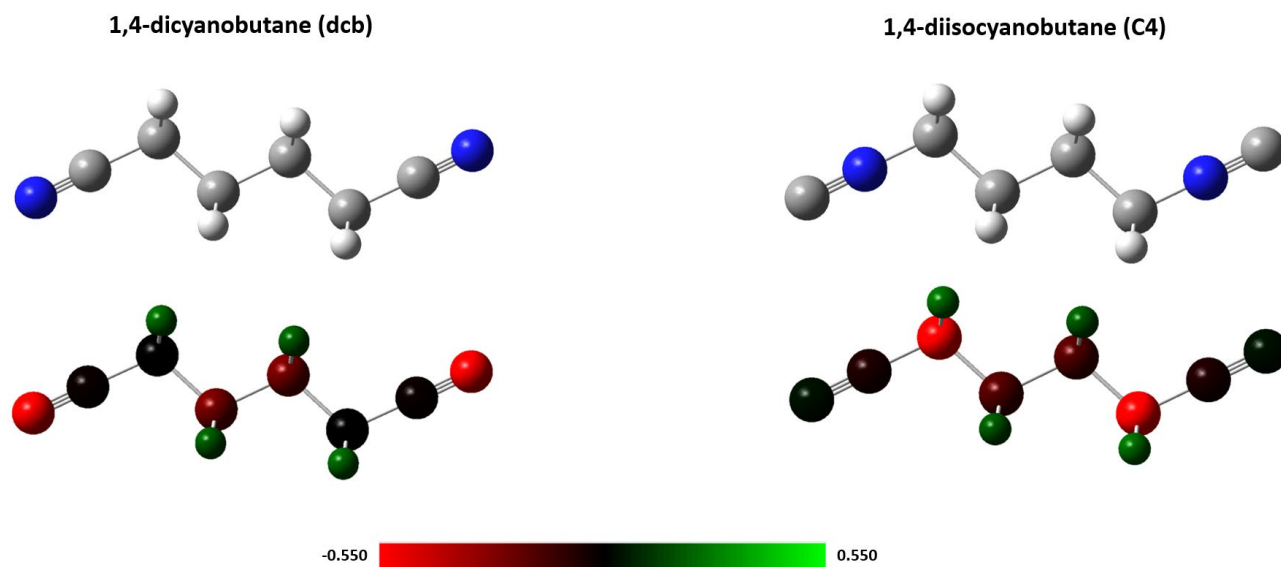


Figure S45. Display charge distribution type Mulliken of **dcb** and **C4** with the color scale from -0.550 (red) to 0.550 (green).

1,4-dicyanobutane (dcb)

1,4-diisocyanobutane (C4)

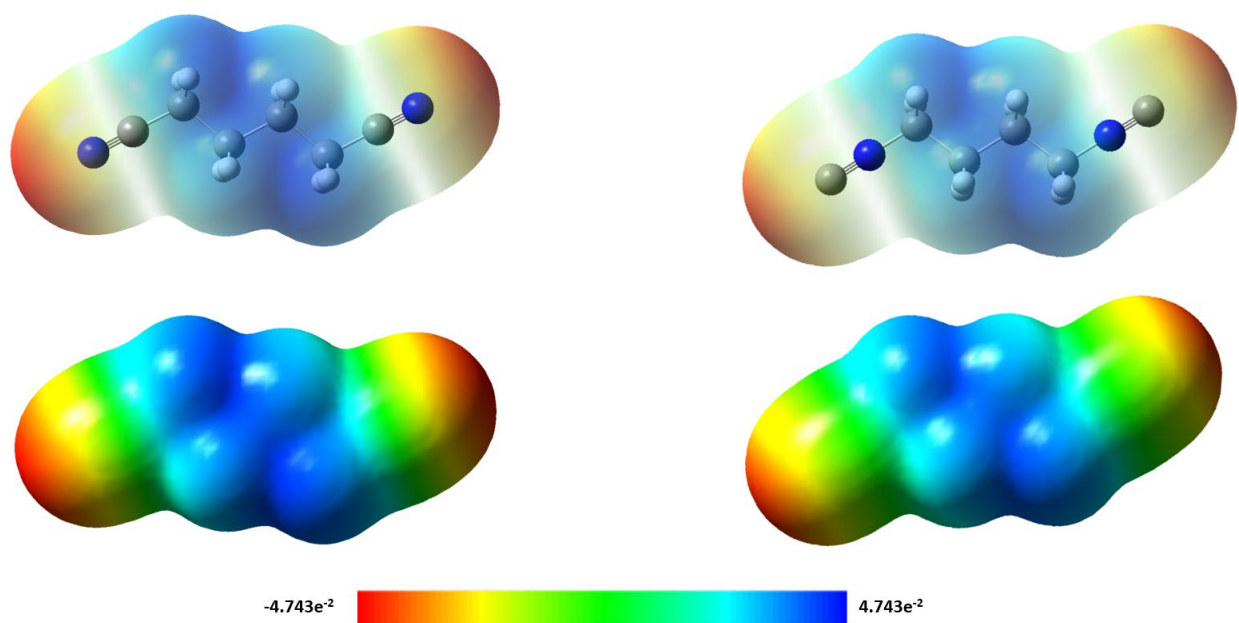


Figure S46. Electrostatic potential plots (ESPs) were mapped over electron density surfaces with isodensity of 0.004 au with the color scale from $-4.743e^{-2}$ (red) to $4.743e^{-2}$ (blue) au for **dcb** and **C4**.

Cartesian coordinates of the optimized structures

1,4-dicyanobutane (dcb)

16

scf done: -342.946492082

1	C	1.612554	-0.519436	-0.006800
2	H	1.969209	-1.528246	-0.006800
3	H	0.542554	-0.519423	-0.006800
4	C	2.125896	0.206520	1.250605
5	H	3.195895	0.204813	1.251584
6	H	1.770840	1.215893	1.249628
7	C	2.125896	0.206520	-1.264205
8	H	3.195896	0.206834	-1.264016
9	H	1.768935	1.215222	-1.264394
10	C	1.612997	-0.519750	-2.521609
11	H	0.542997	-0.520136	-2.521755
12	H	1.970027	-1.528427	-2.521462
13	C	1.610257	-0.517809	2.508008
14	C	2.126241	0.206275	-3.779014
15	N	1.226340	-1.057106	3.444202
16	N	2.508374	0.746835	-4.715209

Mulliken charges: 1

1	C	0.232145
2	H	0.174755
3	H	0.174867
4	C	-0.051275
5	H	0.190899
6	H	0.190850
7	C	-0.232147
8	H	0.174859
9	H	0.174763
10	C	-0.051269
11	H	0.190892
12	H	0.190856
13	C	0.043873
14	C	0.043866
15	N	-0.491823
16	N	-0.491822

1,4-diisocyanobutane (C4)

16

scf done: -342.842500546

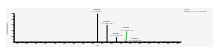
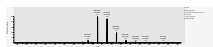
1	C	0.551061	0.319923	-0.187143
2	H	0.907734	0.824321	0.686509
3	H	0.907734	0.824321	-1.060794
4	C	-0.988939	0.319942	-0.187143
5	H	-1.345612	-0.184440	-1.060804
6	H	-1.345612	-0.184473	0.686499
7	C	-1.502254	1.771874	-0.187115
8	H	-1.145574	2.276269	0.686535
9	H	-1.145601	2.276284	-1.060768
10	C	-3.042254	1.771874	-0.187090
11	H	-3.398934	1.267479	-1.060741
12	H	-3.398907	1.267463	0.686562
13	N	1.041044	-1.066012	-0.187143
14	N	-3.532254	3.157803	-0.187069
15	C	-3.963454	4.377421	-0.187050
16	C	1.472229	-2.285635	-0.187143

Mulliken charges: 1

1	C	-0.521976
2	H	0.203975
3	H	0.203974
4	C	-0.174430
5	H	0.168293
6	H	0.168291
7	C	-0.174432
8	H	0.168293
9	H	0.168295
10	C	-0.521973
11	H	0.203975
12	H	0.203976
13	N	-0.097117
14	N	-0.097116
15	C	0.048985
16	C	0.048988

9. High Resolution Mass Spectra of EtP5A and C4@EtP5A

9.1 EtP5A



10. References

1. "BindFit v0.5 | Supramolecular," can be found under <http://app.supramolecular.org/bindfit/>.
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3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, *et al.*, *Gaussian 09, Revision B.01*, 2009.
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