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N, N' - Ditritylurea and Analogs as Hosts in Crystalline Clathrate Complexes: Synthesis and Selectivity Studies

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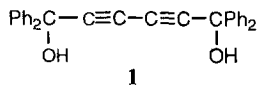
Abstract: Of 38 hosts, most of them new, designed on the 'wheel-and-axle' model, 24 formed clathrate complexes with small molecules; 95 new host/guest combinations are described (Table 6). Selectivity studies (Table 7) show, in some instances, substantial discrimination between guests with similar structures.

Interest in molecular inclusion complexes and molecular recognition via clathrate formation continues at a high level.[1] Among the many topologies developed for clathrate hosts, the design which concerns us here is the so-called 'wheel-and-axle' model we proposed some years ago.[2, 3] It was based on the seminal discovery by Toda[4] that 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol **1** forms well-defined crystalline complexes with a



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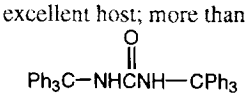
great variety of small molecules. The sp^3 carbons of **1**, with their attached large and rigid aryl substituents were likened to wheels, connected by the diyne chain as the axle. It was proposed that this wheel-and-axle arrangement prevents close packing of the host, thus creating substantial voids that can accommodate guest molecules. In **1**, the hydroxyl groups also provide the opportunity for hydrogen bonding to the guest.

Credence for these ideas was supplied by showing that the molecular shape, and not the specific structure, was responsible for clathrate formation. Thus R—$(C{\equiv}C)_n$—R (n=2,3), R—$(CH_2)_n$—R (n=4,6), $RCH_2CH{=}CHCH_2R$, $RCOCH_2CH_2COR$, RCH=N-N=CHR and R'CH=N-N=CHR', where R = trityl and R' = 9-triptycyl all function as hosts for a variety of hydrocarbons or chlorinated hydrocarbons.[3] The possibility that these complexes could be used for separations was demonstrated with $Ph_3C(CH_2)_6CPh_3$ which, on crystallization from an *o, p*-xylene mixture gave crystals in which only the *p*-xylene was the guest.

To improve these host designs so that polar as well as non-polar guests might be included, a urea moiety was incorporated as the axle. It can act as a donor or acceptor in hydrogen bond formation with guests. The trityl end groups that were retained prevented host-host intermolecular hydrogen bonding.*N,N'* - ditritylurea (DTU), **2**, turned out to be an excellent host; more than 24 complexes with amines, ethers,



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alcohols, aromatic hydrocarbons, amino acid esters, amides and ketones were described.[5, 6] Furthermore, substantial selectivity between certain guest pairs was demonstrated. DTU selected Et_2NH over its isomer *n*-

PrNHMe by 4.6:1 and Et_2O over Et_2NH by >25:1.[6] Factors that may be involved in these selectivities have been discussed.[7]

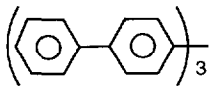
In the present paper we describe the synthesis and properties of a number of new hosts, di-substituted ureas modeled after DTU. We also describe some non-urea but structurally related hosts based on the wheel-and-axle design. Limited studies that illustrate the complexing capabilities of these hosts, and a few selectivity studies between guest pairs are included.

SYNTHESIS OF THE HOSTS

Table 1 lists the new *N,N'*-disubstituted ureas. Except for **6**, all entries were prepared as in eq. 1. For

$$R_1NH_2 + R_2NCO \xrightarrow[\text{reflux}]{t\text{-BuOH}} R_1NHCONHR_2 \qquad (1)$$

the unsymmetric ureas ($R_1 \neq R_2$), the amine-derived R group is written first, then the isocyanate-derived R group. Urea **6** was prepared as in eq. 2. The table lists the yields; other properties (mp, ^1H and ^{13}C NMR,



(2)

IR and mass spectra), as well as the synthesis and properties of the precursor amines and isocyanates are given in the Experimental Section.

To compare with these disubstituted ureas, several monosubstituted analogs (axle with only one wheel) were prepared. These are listed in Table 2. They were obtained by reaction of the appropriate isocyanate with anhydrous ammonia (eq. 3).

$$RNCO + NH_3 \xrightarrow{CH_2Cl_2} RNHCONH_2 \qquad (3)$$

The bis-amides and simple amides in Table 3 also follow the wheel-and-axle design, but offer somewhat different hydrogen-bonding capabilities in the axle.

Most entries were synthesized from tritylamine and the appropriate acyl chloride, using triethylamine as the base. However **32** was prepared by permanganate oxidation of **31**, and **35** was prepared from the naphthoxide and trityl isocyanate.

Finally, the bis-trityl diamines and diethers listed in Table 4 were prepared from the corresponding diamine or diether, trityl chloride and base.

For all entries in Tables 1-4, the structures were clear from the method of synthesis and from the various spectral properties reported in the Experimental Section. For those products which contain two or more chiral centers (**17**, **20-22**, **27**, **32**) no attempt was made to establish stereochemistry, though in each case the compound had a sharp melting point and gave well-defined spectra.

Table 1. *N, N'* - Disubstituted Ureas

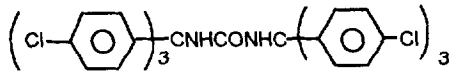
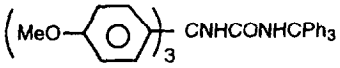
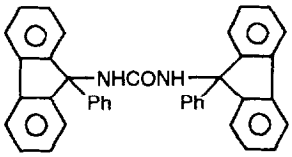
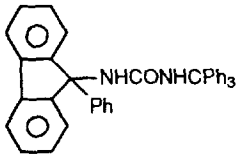
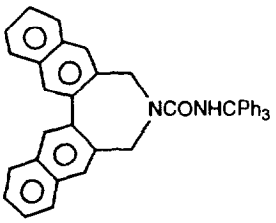
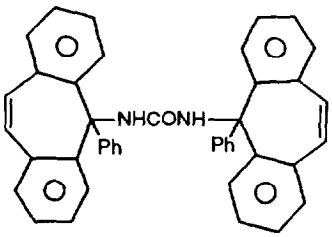
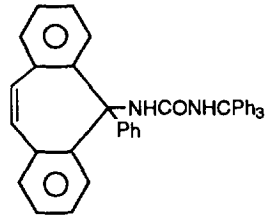
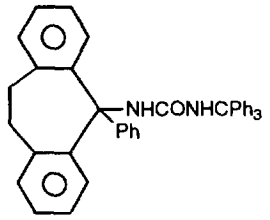
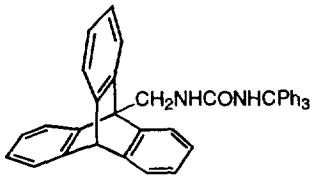
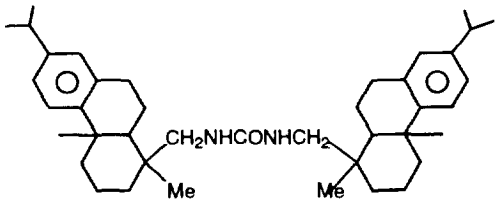
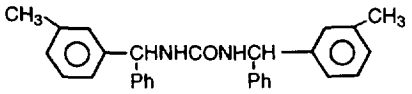
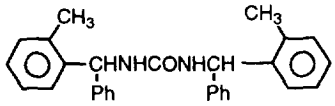
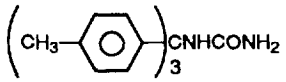
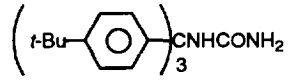
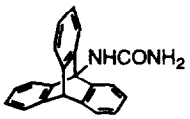
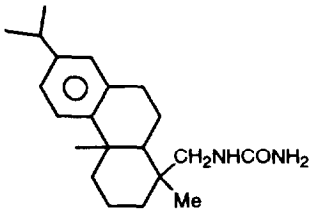
Cpd	Structure	Yield (%)
3		42
4		58
5		39
6		38
7		85
8[a]	$Ph_3CCH_2NHCONHCH_2CPh_3$	79
9[a]	$Ph_3CCH_2NHCONHCPh_3$	75
10		60
11		57
12		53
13		42

Table 1. (continued)

14		54
15		30
16		80
17		65
18[a]	$Ph_2CHNHCONHCHPh_2$	96
19	$Ph_2CHNHCONHCPh_3$	70
20		92
21		76
22		73

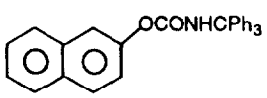
[a]Previously known.

Table 2. *N.*- Substituted Ureas

Cpd	Structure	Yield (%)
23[a]	$Ph_3CNHCONH_2$	91
24		98
25		86
26		95
27		97

[a] Previously known.

Table 3. Bis-amides and Simple Amides

Cpd	Structure	Yield (%)
28[a]	$Ph_3CNHCOCH_2CONHCPh_3$	32
29	$Ph_3CNHCOCH(CH_3)CONHCPh_3$	49
30	$Ph_3CNHCOCH_2CH_2CONHCPh_3$	12
31	$Ph_3CNHCOCH=^{t}CHCONHCPh_3$	65
32	$Ph_3CNHCOCH(OH)-CH(OH)CONHCPh_3$	87
33	$Ph_3CCH_2CONHCPh_3$	77
34	$Ph_3CCH_2CH_2CONHCPh_3$	47
35		26

[a] Previously known.

Table 4. *Bis-trityl Diamines and Diethers*

Cpd	Structure	Yield (%)
36	$Ph_3CNH(CH_2)_3NHCPh_3$	59
37	$Ph_3CNH(CH_2)_4NHCPh_3$	52
38	$Ph_3CNH(CH_2)_5NHCPh_3$	68
39	$Ph_3CNH(CH_2)_6NHCPh_3$	60
40[a]	$Ph_3COCH_2CH_2OCPh_3$	49
41[a]	$Ph_3C(OCH_2CH_2)_2OCPh_3$	56

[a] Previously known.

HOST-GUEST COMPLEXES

DTU Complexes

The literature [5, 6] describes 24 complexes formed by DTU; most are 1:1 but four are 1:2 and one is 2:1. Eight possible guests were found not to form DTU complexes. These results are summarized in Table 5.

For various reasons, we studied a number of other possible guests for DTU. These are listed as 'new' in Table 5. We found 12 additional guests that do form complexes with DTU, and 9 potential guests that do not.

Table 5. DTU Complexes (DTU:guest)

1:1[6]	[a]Et_2O, *n*-PrOMe, [a]Et_2NH, *n*-PrNHMe, [b]Me_2CO, CH_2=$CHCH_2OH$, $HCONMe_2$, [c]$EtCONH_2$, *i*-$PrCONH_2$, [b]*t*-$BuCONH_2$, $PhCONH_2$, [b]CH_2Cl_2, $PhCH_3$, [b]$MeCO_2Et$, THF, ethyl esters of [c]*N*-acetylglycine, [d]alanine, [e]methionine, aspartic acid
1:1(new)	[b]MeCHO, *m*-$(CH_3)_2C_6H_4$, PhH, $PhOCH_3$, $MeOCH_2CH_2OMe$, MeNHCONHMe
1:2[6]	MeOH, EtOH, *n*-PrOH, BuOH
1:2(new)	[b]MeCN
2:1[6]	$Me_2NCOCH_2CH_2CONMe_2$
2:1(new)	$MeNO_2$, $HOCH_2CH_2OH$, $HOCH_2CH_2NH_2$, $MeOCH_2CH_2OH$
3:2(new)	$MeNHCH_2CH_2NH_2$
no complex[6]	2-BuOH, Et_3N, cyclohexanone, camphor, Et esters of *N*-acetylproline, serine, phenylalanine, glutamic acid
no complex(new)	$PhNO_2$, PhSH, $PhSO_2NH_2$, Et_2S, $H_2N(CH_2)_4NH_2$, cyclohexene oxide, pyridine, 4-picoline, ephedrine

X-ray structures as follows: [a]ref 6 [b]ref 9 [c]ref 5 [d]ref 10 [e]ref 11

So far, X-ray structures of 6 DTU complexes have been reported in the literature.[5,6,10,11] We have determined the structures of 6 additional DTU complexes (Table 5).[9] The patterns which emerge from these structures will be described in a separate paper.

Complexes with New Wheel-and-axle Hosts

The complexing capabilities of each host were studied in the following way. A small sample of the potential host was dissolved in hot ethyl acetate[8] to give an approximately 0.05-0.1M solution; excess guest (10-20 fold) was added, the solution was cooled and the resulting crystals were collected and dried under reduced pressure. The stoichiometric host/guest ratio was then determined by ^{1}H NMR integration.

Table 6 summarizes the results. For easy comparison, selected data on DTU (**2**) and on *N*-tritylurea (NTU, **23**) are included. Y indicates that a complex was formed, 1:1 unless otherwise designated; N indicates that no complex was formed. Host-guest combinations that were not explored are indicated by blank spaces. Guests are listed across the top of the table in decreasing number of complexes observed, but no great significance should be attached to this sequence, because some highly effective guests were under-tested. For example, DMSO was tested with only 4 hosts, but gave a 1:1 complex in each case, and likely would give complexes with other hosts listed in the Table.

Table 6 (excluding entries under **2** and **23**, whose host properties have already been described) lists 95 new host-guest complexes out of 234 combinations tested. Of the 38 potential hosts that were synthesized, only 14 were ineffective with all the guests tried (it should be kept in mind, however, that only 3-5 potential guests were tried in each of these cases).

To best examine how structural variations on the DTU pattern affect complex formation, it is useful to examine certain groups of compounds; for this reason, the hosts in Table 6 are listed according to structural type.

DTU-Type Hosts with Larger End Groups

In compounds **3-6**, the DTU structure (**2**) has been modified by substituting various groups (R=Me,*t*-Bu,Cl,Ph) in the *para* positions of the phenyl groups. It was thought that increasing the size of the 'wheels' might allow complex formation with larger guest molecules. However, although methyl (**3**) or chloro (**5**) substitution gave molecules with host properties comparable to those of DTU itself, *t*-butyl (**4**) or phenyl (**6**) substitution sharply diminished the host capability, at least with those guests tested. Even with **3** and **5**, some differences from DTU were observed. Thus **3** did not form complexes with toluene or methylene chloride, and **5** did not form a complex with methanol, allyl alcohol or *t*-butyl alcohol; DTU formed complexes with each of these guests.

Table 6. Host-Guest Complexes[a].

Host	$Me_2C=O$	DMF	Et_2O	MeCN	MeOH	$MeCONH_2$	THF	EtOH	DMSO	Et_2NH	Other Complexes	No Complexes
2	Y	Y	Y	Y[b]	Y[b]		Y	Y[b]		Y	Table 5	Table 5
3	Y	Y	Y		Y	Y		Y		Y	allyl alcohol, *n*-PrOH, MeCHO, *i*-PrOH, *t*-$BuCONH_2$	toluene, CH_2Cl_2
4	N		N		N							
5	Y	Y	Y	Y	N	Y		Y		Y	*t*-$BuCONH_2$, MeNH-*n*Pr, *n*-PrOH,*i*-PrOH	allyl alcohol, EtOAc, *t*-BuOH, *i*-$PrNH_2$
6	N	Y[b]	N		N		N	N				toluene, CH_2Cl_2
13	Y	Y[b]	Y[c]	Y[d]								EtOAc
10	N	Y	N	N								EtOAc
18, 20-22	N	N			N							
7	Y	Y[c]	Y	Y[c]	N	Y		Y	Y	Y	$MeNO_2$	toluene, *t*-$BuCONH_2$, *n*-PrOH, MeO-*n*Pr, *i*Pr_2NH, CH_2Cl_2
11	Y[d]	Y	Y[e]	N	N	Y[d]			Y			
14	N	Y	Y[e]	N	N	Y[c]			Y			
15	Y	Y	Y[e]	N	Y[c]	Y			Y	Y		toluene
12		N	N		N			N				
19	N	N	N		N							
9	Y	Y	Y	Y[f]	Y	Y	Y	Y		N	$MeNO_2$[b]	EtOAc, *i*-PrOH, toluene, *t*-$BuCONH_2$,
8	N	Y	N	N	N	N		N				$MeNO_2$
16	Y		Y	N	Y		Y	Y			CH_2Cl_2	EtOAc
17	N		N	N	Y[c]						EtOAc[g]	$MeNO_2$
33	Y		Y	Y[f]	Y[d]						CH_2Cl_2[c]	EtOAc, toluene
34	N			N	N							EtOAc, toluene
35	N			Y	N							EtOAc, toluene
23		Y[c]									MeCON(Me_2)[c], toluene	
24	Y[d]		N	N	N						EtOAc[d]	
25,27	N	N	N	N	N							EtOAc
26	Y[d]	Y[d]		Y				N			EtOAc[c]	
28	N			Y[c]	N							CH_2Cl_2
29,30	N			N	N							CH_2Cl_2
31,32	Y[d]			N	N							CH_2Cl_2
36	N				N		Y				*p*-xylene	toluene
37	Y[d]				N		Y				*p*-xylene, toluene[c], CH_2Cl_2[c]	
38	N				N		N					*p*-xylene, CH_2Cl_2
39	N						Y					*p*-xylene, CH_2Cl_2
40	N				N						toluene	*p*-xylene, *m*-xylene
41	N											toluene,*p*-xylene, *i*-PrOH

[a]All complexes are 1:1 unless otherwise indicated. [b]1:2 [c]2:1 [d]3:1 [e]3:2 [f]2:3 [g]4:1

DTU-Type Hosts with Rigid End Groups

The three aryl rings on each 'wheel' of DTU are free to rotate, which may be important in conformational adaptation to guests. It was thought that by decreasing these degrees of freedom somewhat one might increase selectivity. The decrease was accomplished by connecting two of the rings, either with a two-carbon link as in **13** or with a zero-carbon link as in **10**. As seen from Table 6, **13** was an effective host for several guests, though the host:guest ratio in 3 of 4 cases differed from the 1:1 observed with DTU. Compound **10**, however, was only effective with 1 of 5 guests tried. It seems reasonable to conclude that the more successful hosts of this type will have flexible end groups.

Ureas with Smaller End Groups

The effect of changing the triarylmethyl end groups of DTU to diarylmethyl groups was tested with **18** and **20-22**. Somewhat surprisingly, these compounds were totally ineffective as hosts toward 3 guests that gave good complexes with DTU and its triarylmethyl analogs **3** and **5**. One possible explanation is that replacing one phenyl by hydrogen may allow the end group of a neighboring host molecule to pack closely from the less hindered side, thus diminishing or eliminating the void.

Unsymmetric Urea Hosts

Examples discussed so far had identical end groups. The result of keeping one end group trityl but varying the other end group is given in the next batch of hosts in Table 6 (*i.e.* **7**, **11**, **12**, **14**, **15**, **19**).

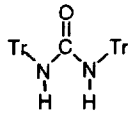
The minor modification of tri-*p*-anisyl for triphenyl at one end still left a very effective host (**7**), though not as good as DTU itself. Directly connecting two of the phenyl groups, as in **11**, diminished the host properties, and as already seen, these properties diminished drastically when both ends of the molecule were so altered (*i.e.*, **2** >**11**>>**10**). On the other hand, connecting the phenyls with a 2-carbon bridge, as in **14** and **15**, was not nearly as destructive. Indeed with the more flexible saturated bridge (**15**) the host properties were quite good. We can conclude that the less rigid structures, which can adapt conformationally to various guests, afford the better hosts.

Neither **12** nor **19** afforded complexes with the guests tried. Comparison of **2** with **19** and **18** shows that even converting just one trityl end group to a diphenylmethyl group vastly diminishes the host properties of these ureas. Apparently the bulkier end group is an important requirement to prevent host-host close interactions.

Ureas with Longer Axles

Comparison of the host properties of **2**, **9**, and **8** is striking. Inserting one methylene group between the trityl and urea nitrogen, as in **9**, still leaves a very effective host. However, inserting a methylene at *each* end of the urea, as in **8**, almost entirely destroys the host properties; of 8 guests that formed complexes with **9**, only one (DMF) formed a complex with **8**.

One possible explanation may be associated with the observation from X-ray structures of DTU complexes[5-7] that guest hydrogen bonding to the N-H bonds of the urea moiety is involved. In the extended form of the axle, these bonds are readily accessible in DTU (**2**) and in **9**, but not in **8**, where they are blocked by the trityl groups.



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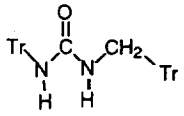
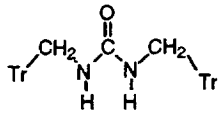


9



8

Comparison of **9** with **16**, in which the tritylmethylene group is replaced by a triptycylmethyl group shows that this conformational restriction has relatively little effect; both compounds function well as hosts. Urea **17** is an alicyclic analog of **8**, and like it, is not a very effective host.

Finally in this series, we might compare the simple trityl amides **33** and **34** with their urea analogs. Amide **33**, an analog of DTU (replace one NH by CH_2) formed complexes with 5 of 7 guests tried, whereas no complexes were observed with **34**, in which the axle is lengthened by one more methylene group. Urethane **35**, which only formed one complex, probably has a structure that allows close host-host hydrogen bonding, thus not creating large voids for guests.

Monamides

It has been shown by X-ray studies that NTU (**23**) forms complexes in quite a different manner from DTU (**2**).[5] With only one of the two amide nitrogens substituted, host-host close approach with hydrogen bonding between them becomes possible, the host molecules being arranged in a head-to-tail fashion. Two-to-one complexes are formed in which guests fit in the interstices created by the bulky trityl groups, and are held not by hydrogen bonds but by interaction with the π-systems of the aryl rings.

It was of interest to examine other monoamides, analogs of NTU. Complexes were formed with **24** (but not the bulkier **25** or **27**) and with the triptycyl amide **26**; it will be interesting to compare their X-ray structures with those of the NTU complexes.

Bis-Amides, Amines and Ethers

The effect of lengthening the 'axle' between trityl end groups was examined with a number of potential hosts (**28-32**, **36-39** and **40**, **41**). To encourage hydrogen bonding, carbonyl groups, amide and amine nitrogens and ether oxygens were included in the 'axle.' Although several complexes were observed, in general these compounds were not particularly effective hosts. In the series of diamines $TrNH(CH_2)_nNH$ Tr, the diamine with n=4 was alone in forming complexes with 5 of 6 guests tried. Analogs with one less or one more methylene group were less effective (for n=3, complexes with 2 of 5 guests tried, and for n=5, 0 of 5 guests tried).

The long 'axles' in these molecules no doubt permit close host-host interactions; the molecules are not rigid enough to create the voids necessary for good host activity.

SELECTIVITY STUDIES

Selectivity studies between certain guest pairs were carried out for three hosts, DTU (**2**), its p-tolyl analog **3**, and to a lesser extent, NTU (**23**). Measurements were performed as follows. To a solution of the host in hot ethyl acetate was added an excess of a similar solution of the guest mixture. After cooling, the guest ratio in the collected and dried crystals was determined by ^{1}H NMR. The selectivities, listed in Table 7, are for competition between equimolar amounts of the two guests. Studies with the Et_2O:Et_2NH and Et_2O :*n*-PrOMe mixtures and DTU as host showed that over the range of guest ratios from 2:1 and 1:2 the selectivity was constant $\pm$0.4. However, the selectivity was somewhat dependent on the host concentration, being highest at low host concentrations; the ranges are indicated for first two entries in Table 7.

One can make several generalizations from the results. The selectivities of **2** and **3** are comparable, though in most instances **2** is somewhat the more selective host. This may be due to the larger voids in the lattice of **3** as a consequence of the methyl substituents.

Especially striking is the reversal in selectivity for the acetamide-dimethylformamide pair between the ditritylurea hosts (**2**, **3**) and the monotrityl urea **23**. The specific H-bonding between guest and host in the former type as contrasted with the lack thereof in the latter[5,6] provides a clear explanation.

Since the guests can easily be recovered from these host-guest complexes, the data in Table 7 show that useful separations might be achieved.

Table 7. Selectivities [a]

Guest 1	Guest 2	Hosts 2	3	23
Et_2O	Et_2NH	3.6-6.4	1.3	
Et_2O	*n*-PrOMe	8.8-12.5		
n-PrOMe	*n*-PrNHMe	2.1		
$MeCONH_2$	DMF	>20	>20	<0.1
$MeCONH_2$	Et_2NH	>20		
$MeCONH_2$	*t*-$BuCONH_2$	>20	>20	
Me_2CO	MeCHO	15	8.1	
MeOH	EtOH	2.3	2.6	
CH_2=$CHCH_2OH$	1-PrOH	3.1	1.5	
MeCN	$MeNO_2$			1.6
DMF	MeCN			>10

[a]The ratio is always Guest 1/Guest 2

Ethers are preferred over amines due to the stronger hydrogen bond forming capacity of oxygen over nitrogen, with the N-H bonds in the urea moiety of the host.[5,6] Reasons for the selectivity of other guest pairs await X-ray structure determinations.

EXPERIMENTAL SECTION

Typical Procedure for Amines. Tri (*p*-chlorophenyl) methylamine (42). Into a stirred solution of 0.5 g (1.31 mmol) of tri-*p*-chlorophenyl)methyl chloride[12] was bubbled anhydrous ammonia gas over 3 h. A 10% sodium hydroxide solution (100 mL) was added and the aqueous layer was extracted (2X) with methylene chloride. Combined organic layers were washed with water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent and column chromatography of the residue over silica gel, eluting with 7:3 methylene chloride/hexane, gave 0.38 g (80%) of **42**, mp 96-100 °C; mass spectrum, *m/e* (relative intensity) 362 (M^+, 2), 361 (5), 347 (3), 345 (7), 252 (61), 250 (100), 140 (13), 139 (17), 138 (37), 111 (16); ^1H NMR ($CDCl_3$) δ 2.22 (br s, 2 H), 7.17 (dd, 12H); IR (KBr) 3472, 3399 cm^{-1}.

Tri(*p*-*t*-butylphenyl)methylamine (43). From 0.3 g (0.67 mmol) of tri(*p*-*t*-butylphenyl)methyl chloride[13] in 50 mL of dry methylene chloride and anhydrous ammonia gas was obtained 0.26 g (91%) of **43**, mp 238-240 °C; ^1H NMR ($CDCl_3$) : δ 1.30 (s, 27H), 2.21 (br s, 2H), 7.22 (dd, 12H); mass spectrum, *m/e* (relative intensity) 427 (M^+, 6), 411 (6), 295 (25), 294 (100); IR (KBr) 3447, 3285 cm^{-1}.

5-Amino-5-phenyl-5H-dibenzo[a,d]cycloheptene (44). From 0.7 g (2.31 mmol) of 5-chloro-5-phenyl-5H-dibenzo[a,d]cycloheptene[14] in 50 mL of dry methylene chloride treated with ammonia (1.5 h) gave, after chromatography over silica gel, eluting with 1:1 CH_2Cl_2/hexane, 0.45 g (69%) of **44**, mp 173-174 °C (lit.[15] 170-171.5 °C): ^1H NMR ($CDCl_3$) δ 1.95 (br s, 2H), 6.47-6.53 (m, 2H), 6.68 (s, 2H), 6.96-7.09 (m,

3H), 7.03-7.32 (m, 4 H), 7.45-7.52 (m, 2H), 8.08 (d, 2 H); mass spectrum, *m/e* (relative intensity) 283 ($M^{+\cdot}$, 100), 282 (30), 267 (16), 254 (20), 206 (28), 178 (16), 105 (34), 104 (51), 77 (22); IR (KBr) 3451, 3391 cm^{-1}.

Tri (*p*-methoxyphenyl)methylamine (45). From 3.7 g (10 mmol) of tri(*p*-methoxyphenyl)methyl chloride[16] in 150 mL of dry methylene chloride treated with anhydrous ammonia (3 h) there was obtained after chromatography over silica gel, eluting with 7:3 hexane/ethyl acetate, 2.5 g (71%) of **45**, mp 110-112 °C: ^1H NMR ($CDCl_3$) δ 2.19 (br s, 2 H), 3.78 (s, 9 H), 6.97 (dd, 12 H); mass spectrum, *m/e* (relative intensity) 349 (M^+, 25), 334 (15), 333 (36), 318 (11), 243 (23), 242 (100), 134 (14); IR (KBr) 3374, 3300 cm^{-1}.

5-Amino-5-phenyl-dibenzo[a,d][1,4]-cycloheptane (46). Into a stirred solution of 8.3 g (30 mmol) of 5-phenyl-dibenzo[a,d][1,4]cycloheptadien-5-ol[17] in 150 mL of anhydrous ether was bubbled dry HCl gas for 1.5 h. Vacuum removal of the solvent gave a solid which was dissolved in CH_2Cl_2 (150 mL). Treatment with anhydrous ammonia (3 h), removal of the solvent under reduced pressure, and chromatography of the residue over silica gel, eluting with 1:1 hexane/methylene chloride, gave 5.3 g (64%) of **46**, mp 155-156.5 °C: ^1H NMR ($CDCl_3$) δ 2.01 (br s, 2H), 2.64-2.91 (m, 4H), 6.91-6.95 (m, 2H), 7.05-7.09 (m, 2H), 7.16-7.28 (m, 7 H), 7.91-7.94 (m, 2 H); mass spectrum, *m/e* (relative intensity) 285 (M^+, 70), 284 (56), 268 (27), 209 (15), 208 (100), 191 (19), 178 (15), 165 (16), 106 (30), 105 (49), 104 (50), 77 (26); IR (KBr) 3325, 3296 cm^{-1}.

2,7-Dihydrodinaphtho[2,1-c:1',2'-e] azepine (47)[18]. A stirred solution of 6.3 g (14.3 mmol) of 2,2'-bisbromoethyl-1,1'-dinaphthyl[19] in a mixture of CH_2Cl_2 (200 mL) and MeOH (105 mL) was treated with anhydrous ammonia for 3 h. Aqueous sodium hydroxide (10%, 50 mL) was added and the organic layer was washed with water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent and chromatography of the oily residue over silica gel, eluting with 7:3 ethyl acetate/methanol gave 2.2 g (52%) of **47** as white needles, mp 149-151 °C: ^1H NMR ($CDCl_3$) δ 2.41 (br s, 1 H), 3.52 (d, 2 H, *J*=12.2 Hz), 3.85 (d, 2 H, *J*=12.2 Hz), 7.23-7.29 (m, 2 H), 7.43-7.49 (m, 4 H), 7.56-7.59 (m, 2 H), 7.92-7.98 (m, 4 H) ; ^{13}C NMR ($CDCl_3$) δ 46.0, 126.4, 126.5, 127.3, 127.6, 128.5, 129.2, 129.7, 131.3, 134.0, 135.3; mass spectrum, *m/e* (relative intensity) 295 (M^+, 21), 294 (11), 267 (26), 266 (100), 265 (35), 252 (12); IR (KBr) 3335 cm^{-1}.

Typical Procedure for Isocyanates. Tri (*p*-tolyl)methyl Isocyanate (48). A suspension of 1.5 g (4.68 mmol) of tri(*p*-tolyl) methyl chloride[12] and 1.5 g (18.5 mmol) of potassium cyanate in 75 mL of dry acetone was refluxed for 3 h under argon. The resulting white precipitate was filtered, extracted with acetone (3X), and the combined extracts were dried (Na_2SO_4). Vacuum removal of the solvent gave 1.0 g (65%) of **48**, mp 125-129 °C: mass spectrum; *m/e* (relative intensity) 327 (M^+, 58), 312 (11), 286 (26), 285 (100), 237 (12), 236 (61), 211 (30), 182 (13), 178 (12), 119 (50), 91 (52); IR (KBr) 2262 cm^{-1}.

Tri(*p*-chlorophenyl)methyl isocyanate (49). From 0.5 g (1.30 mmol) of tri(*p*-chlorophenyl)methyl chloride[12] and 0.5 g (6.16 mmol) of potassium cyanate in 50 mL of dry acetone there was obtained 0.21 g (42%) of **49** as a semi-solid: mass spectrum, *m/e* (relative intensity) 389 (38), 387 (M^+, 46), 345 (100); IR (neat) 2253 cm^{-1}.

Tri(*p*-*t*-butylphenyl)methyl isocyanate (50). From 2.5 g (5.6 mmol) of tri(*p*-*t*-butylphenyl)methyl chloride[13] and 2.5 g (3.07 mmol) of potassium cyanate in 100 mL of dry acetone there was obtained 1.8 g (71%) of **50**, mp 245-250 °C: mass spectrum, *m/e* (relative intensity) 453 (M^+, trace), 411 (13), 320 (6), 43 (100); ^1H NMR ($CDCl_3$) δ 1.31 (s, 27 H), 7.21 (dd, 12 H); IR (KBr) 2388 cm^{-1}.

5-Phenyl-5H-dibenzo[a,d]cycloheptenyl-5-isocyanate (51). From 1 g (3.3 mmol) of 5-chloro-5-phenyl-5H-dibenzo[a,d]cycloheptene[14] and 1.2 g (14.8 mmol) of potassium isocyanate in 75 mL of dry acetone there was obtained 0.7 g (69%) of **51** as a yellow solid, mp 107-117 °C: mass spectrum, *m/e* (relative intensity) 309 (M^+, 75), 284 (12), 267 (24), 232 (10), 178 (42), 43 (100); IR (KBr) 2342 cm^{-1}.

9-Phenyl-9-fluorenyl isocyanate (52). From 1 g (6.68 mmol) of silver isocyanate[20] and 1.9 g (6.67 mmol) of 9-chloro-9-phenyl fluorene[21] in 100 mL of anhydrous acetone there was obtained 1.71 g (90%) of **52** as a yellow oil: mass spectrum, *m/e* (relative intensity) 283 (M^+, 82) 242 (22), 241 (100), 206 (20), 181 (12); IR (neat) 2241 cm^{-1}.

Typical Procedure for Isocyanates from Amines and Phosgene. Phenyl-*p*-tolylmethyl isocyanate (53). To a stirred solution of phenyl-*p*-tolylmethylamine[22] (0.9 g, 4.57 mmol) in 75 mL of dry toluene under argon was added 0.90 g (9.14 mmol) of phosgene in 15 mL of dry toluene over 10 min. The reaction mixture was stirred at room temperature (8 h), then at 50°C (2 h). Vacuum removal of the solvent gave 0.86 g (84%) of **53** as an oil; mass spectrum, *m/e* (relative intensity) 223 (M^+, 100), 208 (68), 194 (24), 181 (79), 180 (22), 166 (31), 165 (41), 146 (31), 91 (33), 77 (34); IR (neat) 2248 cm^{-1}.

Phenyl-*m*-tolylmethyl isocyanate (54). From 0.25 g (1.27 mmol) phenyl-*m*-tolylmethylamine[22] in 25 mL of dry toluene and 0.25 g (2.45 mmol) of phosgene in 10 mL of dry toluene there was obtained 0.25 g (88%) of **54** as an oil: mass spectrum, *m/e* (relative intensity) 223 (M^+, 100), 194 (13), 181 (46), 180 (20), 166 (20), 165 (27), 146 (15), 91 (20), 77 (21); IR (neat) 2253 cm^{-1}.

Phenyl-*o*-tolylmethyl isocyanate (55). From phenyl-*o*-tolylmethylamine[22] (0.67 g, 3.4 mmol) in 75 mL of dry toluene and 0.67 g (6.8 mmol) of phosgene in 15 mL of toluene there was obtained 0.71 g (93.6% of **55** as an oil: mass spectrum, *m/e* (relative intensity) 223 (M^+, 15), 208 (22), 194 (10), 181 (40), 180 (100), 179 (32), 165 (37), 146 (18), 91 (25), 77 (34); IR (neat) 2252 cm^{-1}.

Isocyanate of Dehydroabietylamine (56)[23]. From 1.7 g (5.95 mmol) of dehydroabietylamine[24] in 50 mL of dry toluene and 1.18 g (11.9 mmol) of phosgene in 30 mL dry toluene there was obtained 1.7 g (92%) of **56** as an oil: mass spectrum, *m/e* (relative intensity) 311 (M^+, 4), 296 (20), 223 (10), 92 (66), 91 (100); IR (neat) 2264 cm^{-1}.

Typical Procedure for Ureas from Amines and Isocyanates. *N,N'*-Bis(triphenylmethyl) urea (DTU, 2). A suspension of 4 g (15.4 mmol) of trityl amine[25] and 4.40 g (15.4 mmol) of trityl isocyanate[26] in 100 mL of *t*-butanol was heated at reflux for 24 h under Ar. Vacuum removal of the solvent gave an oil which was triturated with ether to give 5.41 g (64%) of **2**. Recrystallization from ethyl acetate gave white crystals, mp 260-261 °C (lit.[26] 252 °C).

***N,N'* -Bis[tri(*p*-methylphenyl)methyl]urea (3).** From 0.9 g (2.75 mmol) of **48** and 0.8 g (2.66 mmol) of tri(*p*-methylphenyl)methylamine[27] in 50 mL of *t*-butanol refluxed for 36 h there was obtained, after recrystallization from acetonitrile, 0.71 g (42%) of white crystals, mp 229-230 °C (dec): ^1H NMR ($CDCl_3$) δ 2.29 (s, 18 H), 5.36 (s, 2 H), 6.99-7.02 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 69.3, 128.6 (overlap), 136.3, 141.9, 155.9; mass spectrum (30 eV), *m/e* (relative intensity) 628 (M^+, trace), 344 (30), 343 (100), 285 (40), 210 (45); IR (KBr) 3419, 1666 cm^{-1}. Anal. Calcd for $C_{45}H_{44}N_2O$: C, 85.95; H, 7.05. Found: C, 86.01; H, 7.14.

***N,N'*-Bis[tri(*p*-t-butylphenyl)methyl]urea (4).** To a stirred solution of amine **43** in 25 mL of dry THF at -78 °C under Ar was added *n*-BuLi (0.84 mmol) in 20 mL of THF. After 10 min, there was added isocyanate **50** (0.4 g, 0.88 mmol) in 10 mL of dry THF over 10 min. After 1 h, the solution was warmed to room temperature and stirred for an additional 2 h. Vacuum removal of the solvent gave a residue which was triturated with ether to yield 0.42 g (58%) of **4**. Recrystallization from a $CH_3OH/CHCl_3$ mixture gave white crystals, mp 272-273 °C: ^1H NMR ($CDCl_3$) δ 1.28 (s, 54H), 5.44 (s, 2 H), 6.85-7.07 (m, 12 H), 7.15 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 31.3, 34.3, 69.2, 124.5, 128.4, 141.9, 149.3, 155.9; mass spectrum, *m/e* (relative intensity) 880 (M^+, trace), 469 (71), 411 (26), 294 (49), 57 (100); IR (KBr) 3407, 1702 cm^{-1}. Anal. Calcd for $C_{63}H_{80}N_2O$: C, 85.94; H, 9.16. Found : C, 86.02; H, 9.11.

***N,N'* -Bis[tri-(*p*-chlorophenyl)methyl]urea (5).** Reaction of isocyanate **49** (0.2 g, 0.51 mmol) with amine **42** (0.2 g, 0.55 mmol) in 35 mL of *t*-butanol, 8 h reflux, gave 0.15 g (38.9%) of **5**, recrystallized from acetone; mp 267-269 °C (dec): ^1H NMR ($CDCl_3$) δ 5.51 (s, 2 H), 6.94 (d, 12 H, *J*=8.5 Hz), 7.20 (d, 12 H, *J*=8.5 Hz) ; ^{13}C NMR ($CDCl_3$) δ 68.9, 128.3, 129.8, 133.4, 142.4, 155.5; mass spectrum (30 eV), *m/e* (relative intensity) 405 (M^+-343, 35), 403 (40), 347 (37), 345 (33), 278 (19), 276 (29), 252 (55), 250 (100), 139 (31), 138 (28), 111 (13); IR (KBr) 3395, 1632 cm^{-1}. Anal. Calcd for $C_{39}H_{26}Cl_6N_2O.C_3H_6O$(acetone): C, 62.32; H, 3.98. Found: C, 62.18; H, 4.02.

***N, N'*-Bis[tri-(4-biphenyl)methyl]urea (6).** The solution of 4.88 g (9.63 mmol) of tri(4-biphenyl)methyl chloride[28] and 0.25 g (4.16 mmol) of urea in 200 mL of dry pyridine was refluxed for 10 h. The reaction was quenched with 500 mL of 10% HCl and extracted with CH_2Cl_2(3x 100 mL). Combined organic layers were washed with 10% HCl (2x 50 mL), water, saturated NaCl solution, and dried ($MgSO_4$). Vacuum removal of the solvent gave 1.6 g (38%) of **6** which was recrystallized from acetone, mp 277-278 °C : ^1H NMR ($CDCl_3$) δ 5.67 (s, 2 H), 7.25-7.55 (m, 54 H); ^{13}C NMR (DMSO-d_6) δ 68.3, 125.5, 126.4, 127.2, 128.8, 129.0, 137.9, 139.5, 144.7, 155.9; mass spectrum, *m/e* (relative intensity) 513 (M^+ -487, 12), 487 (12), 471 (54), 334 (100); IR (KBr) 3412, 1671 cm^{-1}. Anal. Calcd for $C_{75}H_{56}N_2O$: C, 89.97; H,5.64. Found: C, 89.98; H, 5.82.

***N*-Tri(*p*-methoxyphenyl)methyl-*N'*-triphenylmethylurea (7).** From trityl isocyanate[26] (2 g, 7.02 mmol) and amine **45** (1.5 g, 4.29 mmol) in 60 mL of *t*-butanol (10 h reflux) there was obtained 2.3 g (84%) of **7** which was recrystallized from ethyl acetate, mp 215-216.5 °C: ^1H NMR ($CDCl_3$) δ 3.76 (s, 9 H), 5.37 (s, 1H), 5.46 (s, 1 H), 6.72 (d, 6 H), 6.96-7.23 (m, 21H); ^{13}C NMR ($CDCl_3$) δ 55.2, 68.7, 69.9, 113.2, 126.8, 127.8, 128.7, 129.8, 137.1, 144.7, 155.7, 158.3; mass spectrum, *m/e* (relative intensity) 634 (M^+, 2), 392 (21), 391 (83), 334 (27), 333 (100), 302 (13), 243 (19), 242 (39), 208 (12), 182 (30); IR (KBr) 3417, 3346, 1661 cm^{-1}. Anal. Calcd for $C_{42}H_{38}N_2O_4$: C,79.47; H, 6.03. Found: C, 79.55; H, 6.23.

***N,N'*-Bis(2,2,2-triphenylethyl)urea (8)[29].** To a suspension of 2,2,2-triphenylethylamine hydrochloride (0.412 g, 1.33 mmol) and triethylamine (0.135 g, 1.34 mmol) in 100 mL of CH_2Cl_2(stir 10 min.) was added dropwise 0.3 g (1.0 mmol) of 2,2,2-triphenylethyl isocyanate in 25 mL of CH_2Cl_2. The mixture was stirred (10 h), then washed with 10% HCl (2 x 50 mL), water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent gave 0.45 g (78%) of **8** which was recrystallized from methanol, mp 240-241 °C (lit.[30] 218.5-219 °C). ^1H NMR ($CDCl_3$) δ 3.75 (t, 2 H), 4.21 (d, 4 H), 7.13-7.29 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ 49.1, 57.0, 126.6, 128.2, 129.2, 145.2, 156.9; mass spectrum,*m/e* (relative intensity) 572

(M^+, 26), 329 (8), 300 (1), 272 (1), 256 (13), 244 (20), 243 (100), 179 (13), 178 (12), 165 (61); IR (KBr) 3314, 1640 cm^{-1}. Anal. Calcd for $C_{41}H_{36}N_2O$: C, 85.98; H, 6.34. Found : C, 86.07; H, 6.29.

***N*-2,2,2-Triphenylethyl-*N'*-triphenylmethyl urea (9).** Reaction of 2,2,2-triphenylethylamine hydrochloride[30] (1.5 g, 4.84 mmol) with triethylamine (1.45 g, 1.42 mmol) in 100 mL of CH_2Cl_2 and 1.38 g (4.84 mmol) of trityl isocyanate in 100 mL of CH_2Cl_2 gave 2.03 g (75%) of **9** which was recrystallized from ethyl acetate, mp 225-226.5 °C: ^1H NMR ($CDCl_3$) δ 3.89 (t, 1 H), 4.18 (d, 2 H), 5.74 (s, 1 H), 6.95-7.14 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ 49.0, 56.7, 69.1, 126.2, 127.1, 128.0, 128.2, 128.4, 129.1, 143.9, 145.2, 157.0; mass spectrum, *m/e* (relative intensity) 558 (M^+, 1), 315 (16), 285 (1), 243 (100), 165 (41); IR (KBr) 3415, 3203, 1644 cm^{-1}. Anal. Calcd for $C_{40}H_{34}N_2O.C_3H_6O$: C, 85.82; H, 6.53. Found: C, 85.79; H, 6.68.

***N,N'*-Bis(9-phenyl-9-fluorenyl)urea (10).** Reaction of isocyanate **52** (2.5 g, 8.83 mmol) with 9-amino-9-phenyl fluorene[21] (1.95 g, 7.58 mmol) in 100 mL of *t*-butanol at reflux for 8 h gave, after column chromatography over silica gel, eluting with 7:3 methylene chloride/hexane, 2.47 g (60%) of **10**, mp 253-254 °C: ^1H NMR ($CDCl_3$) δ 5.14 (s, 2 H), 6.91-6.94 (m, 4 H), 7.08-7.33 (m, 18 H), 7.54-7.57 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 69.5, 120.1, 125.1, 125.2, 127.2, 128.1, 128.4, 128.5, 139.5, 142.6, 148.5, 156.5; mass spectrum, *m/e* (relative intensity) 540 (M^+, 5), 299 (50), 283 (18), 257 (10), 256 (13), 241 (54), 239 (29), 180 (100), 119 (17), 91 (18); IR (KBr) 3346, 1666 cm^{-1}. Anal. Calcd for $C_{39}H_{28}N_2O$: C, 86.64; H, 5.22. Found: C, 86.56; H, 5.30.

***N*-(9-phenyl-9-fluorenyl)-*N'*-triphenylmethyl urea (11).** Reaction of 9-amino-phenylfluorene[21] (0.45 g, 1.76 mmol) with 0.5 g (1.75 mmol) of trityl isocyante[26] in 100 mL of *t*-butanol at reflux for 12 h gave 0.542 g (57%) of **11** which was recrystallized from acetone, mp 235-237 °C: ^1H NMR ($CDCl_3$) δ 5.34 (s, 2 H), 6.87 (m, 6 H), 7.12-7.55 (m, 22 H); ^{13}C NMR ($CDC\ l_3$) δ 69.9, 126.7, 127.5, 127.7, 128.4, 128.5, 128.6, 128.8, 139.5, 143.0, 144.6, 148.5, 156.0 (one peak overlap); mass spectrum, *m/e* (relative intensity) 542 (M^+, 3), 302 (20), 301 (100), 299 (19), 243 (14), 241 (35), 182 (54), 180 (19), 104 (44); IR (KBr) 3411, 3204, 1668 cm^{-1}. Anal. Calcd for $C_{39}H_{30}N_2O$: C, 86.32; H, 5.57. Found: C, 86.44; H, 5.54.

***N*-[2,7-Dihydrodinaphtho(2,1-c:1',2'-e) azepenyl]-*N'*-triphenylmethyl urea (12).** Reaction of amine **47** (2.4 g, 8.14 mmol) with trityl isocyanate (3 g, 10.5 mmol) in 150 mL of *t*-butanol at reflux for 4 days gave, after column chromatography over silica gel, eluting with 7:3 methylene chloride/hexane, 2.45 g (52%) of **12** which was recrystallized from chloroform/ethanol mp 263-265 °C (dec): ^1H NMR ($CDCl_3$) δ 3.72 (d, 2 H), 4.83 (d, 2 H), 5.71 (s, 1 H), 7.23-7.28 (m, 17 H), 7.44-7.52 (m, 4 H), 7.58-7.61 (d, 2 H), 7.95-8.00 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 48.4, 70.2, 125.8, 126.1, 126.8, 127.4, 127.8, 128.3, 128.7, 129.2, 131.4, 133.3 (overlap), 134.9, 145.5, 155.9 (one peak overlap); mass spectrum, *m/e* (relative intensity) 337 (M^+-243, trace), 295 (13), 285 (27), 267 (17), 266 (22), 265 (20), 243 (29), 208 (100), 165 (34), 105 (15), 77 (50); IR (KBr) 3418, 1668 cm^{-1}. Anal. Calcd for $C_{42}H_{32}N_2O$: C, 86.87; H, 5.55. Found C, 86.79; H, 5.52.

***N,N'*-Bis(5-phenyl-dibenzo[a,d]-5-cycloheptenyl)urea (13).** In a procedure similar to that used for **4**, reaction of amine **44** (1.83 g, 6.46 mmol) with *n*-butyllithium (6.75 mmol) in 50 mL of THF and isocyanate **51** (1.42 g, 4.59 mmol) in 50 mL of THF gave, after column chromatography over silica gel, eluting with CH_2Cl_2 1.15 g (42%) of **13**, which was recrystallized from toluene, mp 266-268 °C: ^1H NMR ($CDCl_3$) δ5.96 (br s, 2 H), 6.61 (m, 8 H), 6.95 (m, 6 H), 7.26 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 67.8, 124.6, 126.6, 126.7, 128.0, 128.5, 129.3, 129.4, 131.6, 134.1, 139.5, 142.5 (overlap), 156.4; mass spectrum, *m/e* (relative intensity)

592 (M^+, 1), 325 (16), 310 (14), 309 (59), 284 (22), 283 (100), 282 (18), 268 (22), 267 (94), 254 (21), 232 (16), 206 (41), 179 (13), 178 (46), 105 (38), 104 (41); IR (KBr) 3419, 1667 cm^{-1}. Anal. Calcd for $C_{43}H_{32}N_2O.2(C_3H_7NO)$: C, 79.65; H, 6.27. Found: C, 79.79; H, 6.34.

***N*-5-Phenyl-dibenzo[a,d]-5-cycloheptenyl-*N'*-triphenylmethyl urea (14).** Reaction of amine **44** (0.98 g, 3.46 mmol) with *n*-butyllithium (3.64 mmol) in 50 mL of dry THF and trityl isocyanate (1.1 g, 3.86 mmol) in 20 mL of dry THF gave, after column chromatography over silica gel, eluting with 9:1 hexane/ethyl acetate, 1.06 g (54%) of **14**, mp 238-240 °C: ^1H NMR ($CDCl_3$) δ 5.46 (br s, 1 H), 5.58 (br s, 1 H), 6.46-6.66 (m, 4 H), 6.87-7.36 (m, 26 H); ^{13}C NMR ($CDCl_3$) δ 69.9, 70.2, 123.9, 126.3, 127.0, 127.2, 127.9, 128.1, 128.8 (overlap), 129.1 (overlap), 131.4, 133.8, 139.2, 144.4, 156.0; mass spectrum (CI), *m/e* (relative intensity) 569 (M^++1, 18), 267 (99), 243 (100); IR (KBr) 3416 (overlap NH), 1671 cm^{-1}. Anal. Calcd for $C_{41}H_{32}N_2O.C_4H_{10}O$: C, 84.08; H, 6.59. Found: C, 83.86; H, 6.75.

***N*-(5-Phenyl-dibenzo[a,d][1,4]-5-cycloheptanyl-*N'*-triphenylmethyl urea (15).** Reaction of amine **46** (0.2 g, 0.70 mmol) with *n*-butyllithium (0.75 mmol) in 25 mL of dry THF and triphenylmethyl isocyanate (0.3 g, 1.05 mmol) in 10 mL of dry THF gave, after column chromatography over silica gel, eluting with 8.5:1.5 hexane/ethyl acetate, 0.12 g (30%) of **15**, mp 225-227 °C: ^1H NMR ($CDCl_3$) δ 2.65-2.75 (m, 2 H), 2.92-3.02 (m, 2 H), 5.29 (s, 1 H), 5.36 (s, 1 H), 6.85 (m, 8 H), 7.02-7.31 (m, 18 H), 7.88 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.8,69.8, 70.9, 126.4, 126.5, 127.3, 127.6, 128.0, 128.1, 128.5, 130.55, 130.59, 140.5, 142.1, 144.8, 147.3, 155.1 (one peak overlaps with other peaks); mass spectrum, *m/e* (relative intensity) 570 (M^+, 1), 327 (40), 302 (23), 301 (100), 243 (12), 182 (48), 165 (23); IR (KBr) 3429, 3227, 1668 cm^{-1}. Anal. Calcd for $C_{41}H_{34}N_2O$: C, 84.04; H, 6.41. Found: C, 84.15; H, 6.42.

***N*-Triphenylmethyl-*N'*-9-triptycylmethyl urea (16).** In a procedure similar to that used for **8**, reaction of 9-triptycylmethyl amine hydrochloride[30] (0.62 g, 1.94 mmol) with triethylamine (0.363 g, 3.58 mmol) in 100 mL of CH_2Cl_2 and 0.5 g (1.75 mmol) of trityl isocyanate in 25 mL of CH_2Cl_2 gave 0.8 g (80%) of **16**, which was recrystallized from ethyl acetate, mp 264-266 °C (dec): ^1H NMR ($CDCl_3$) δ 4.71 (s, 3 H), 5.24(s, 1 H), 5.89 (br s, 1 H), 6.77-7.30 (m, 27 H); ^{13}C NMR ($CDCl_3$) δ 38.6, 52.7, 54.2, 69.7, 122.1, 123.3, 124.9, 125.1, 127.3, 128.1, 128.6,144.0, 146.3, 157.5 (one peak overlap); mass spectrum, *m/e* (relative intensity) 568 (M^+, 23), 265 (13), 252 (22), 243 (29), 182 (100), 165 (61); IR (KBr) 3437, 3320, 1656 cm^{-1}. Anal. Calcd for $C_{41}H_{32}N_2O$: C, 86.59; H, 5.67. Found: C, 86.77; H, 5.62.

***N,N'*-Bis(dehydroabietyl)urea (17).** To a stirred solution of 1.8 g (5.79 mmol) of isocyanate **56** in 50 mL of CH_2Cl_2 under Ar was added dropwise of 2.0 g (7.02 mmol) of dehydroabietylamine[24] in 50 mL of CH_2Cl_2. After an additional 8 h at room temperature, vacuum removal of the solvent gave an oil which was triturated with ether to give 2.23 g (65%) of **17**. Recrystallization from acetone gave needles, mp 169-171 °C: ^1H NMR ($CDCl_3$) δ 0.85 (s, 6H), 1.18-1.41 (m, 26 H), 1.54-1.85 (m, 8 H), 2.21-2.26 (m, 8 H), 2.72-2.91 (m, 6H), 3.01-3.04 (d, 4H), 4.36 (t, 2 H), 6.87 (m, 2 H), 6.94-6.97 (m, 2 H), 7.13-7.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.6, 18.8, 24.0, 25.2, 30.1, 33.4, 36.0, 37.4, 38.4, 44.9, 50.7, 123.8, 124.1, 126.8, 134.8, 145.5, 147.3, 158.5 (3 peaks overlapped); mass spectrum, *m/e* (relative intensity) 596 (M^+, 3), 239 (11), 173 (37), 131 (11), 88 (100); IR (KBr) 3460, 1633 cm^{-1}. Anal. Calcd for $C_{41}H_{60}N_2O$: C, 82.50; H, 10.13. Found: C, 82.55; H, 9.98.

***N,N'*-Bis(diphenylmethyl)urea (18).** To a suspension of 1.5 g (5.9 mmol) of diphenylmethylamine hydrochloride in 100 mL of CH_2Cl_2 under Ar was added 0.6 g (5.91 mmol) of triethylamine. The solution was stirred for 10 min, after which was added dropwise 1.33 g (5.46 mmol) of diphenylmethyl isocyanate in 100 mL of CH_2Cl_2. After 10 h, the solution was washed with HCl(2 x 50 mL), water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent gave 2.05 g (96%) of **18** which was recrystallized from acetone, mp 272-273 °C (dec)(lit[31] 272-273 °C): ^{1}H NMR ($CDCl_3$) δ 4.98 (d, 2 H), 5.92 (d, 2 H), 7.15-7.32 (m, 18 H); ^{13}C NMR (DMSO-d_6) δ 56.9, 126.7 (overlap), 128.3, 143.5, 156.3; mass spectrum, *m/e* (relative intensity) 392 (M^+, 29), 225 (34), 183 (14), 182 (100), 167 (26), 152 (14), 106 (16), 104 (33), 77 (20); IR (KBr) 3317, 1630 cm^{-1}.

***N*-Diphenylmethyl-*N'*-triphenylmethyl urea(19).** In a procedure similar to that used for **18**, reaction of 1 g (4.56 mmol) of diphenylmethylamine hydrochloride in 50 mL of CH_2Cl_2 with 0.47 g (4.58 mmol) of triethylamine and 1.1 g (3.86 mmol) of trityl isocyanate in 25 mL of CH_2Cl_2 gave 1.45 g (70%) of **19** which was recrystallized from ethyl acetate, mp 240-241 °C (lit.[32] 226-227 °C): ^{1}H NMR ($CDCl_3$) δ 4.73 (d, 1 H), 5.79 (s, 1 H), 5.95 (d, 1 H), 6.79-7.33 (m, 25 H); ^{13}C NMR ($CDCl_3$) δ 57.8, 69.7, 126.9, 127.2, 127.4, 128.3, 128.7 142.1, 144.4, 156.5; mass spectrum, *m/e* (relative intensity) 468 (M^+, 2), 301 (18), 225 (49), 182 (100), 106 (29), 105 (22), 77 (66). Anal. Calcd for $C_{33}H_{28}N_2O$: C, 84.58; H, 6.02. Found: C, 84.44; H, 5.99.

***N,N'*-Bis[(phenyl-*p*-tolyl)methyl]urea (20).** In a procedure similar to that used for **18**, reaction of (phenyl-*p*-tolyl)methylamine hydrochloride[22] (2.3 g, 9.85 mmol) with triethylamine (1.0 g, 9.85 mmol) in 100 mL of CH_2Cl_2 and 2 g (8.96 mmol) of isocyanate **53** in 25 mL of CH_2Cl_2 gave 3.45 g (92%) of **20** which was recrystallized from acetone, mp 261-262 °C: ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 6 H), 4.98 (d, 2 H), 5.86 (d, 2 H), 7.01-7.29 (m, 18 H); ^{13}C NMR (DMSO-d_6) δ 20.5, 56.6, 126.7 (overlap), 128.3, 128.9, 135.8, 140.6, 143.8, 156.3; mass spectrum, *m/e* (relative intensity) 420 (M^+, 19), 239 (47), 197 (18), 196 (100), 181 (21), 166 (18), 165 (24), 120 (17), 118 (12), 106 (12), 104 (29), 91 (17), 77 (13); IR (KBr) 3307, 1631 cm^{-1}. Anal. Calcd for $C_{29}H_{28}N_2O$: C, 82.82; H, 6.71. Found: C, 82.95; H, 6.75.

***N,N'*-Bis[(phenyl-*m*-tolyl)methyl]urea (21).** In a procedure similar that used for **18**, reaction of (phenyl-*m*-tolyl)methylamine hydrochloride[22] (1.6 g, 6.85 mmol) with triethylamine (0.69 g, 6.85 mmol) in 25 mL of CH_2Cl_2 and 1.6 g (7.17 mmol) of isocyanate **54** gave2.2 g (76%) of **21** which was recrystallized from methanol, mp 251-252 °C: ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 6 H), 5.00 (d, 2 H), 5.86 (d, 2 H), 6.93-7.28 (m, 18 H); ^{13}C NMR (DMSO-d_6) δ 21.0, 56.9, 123.9, 126.7, 127.3, 127.4, 128.25 (overlap), 128.30, 137.4, 143.5, 143.7, 156.3; mass spectrum, *m/e*(relative intensity) 420 (M^+, 22), 239 (36), 197 (15), 196 (100), 181 (16), 166 (19), 165 (17), 104 (19), 91 (15), 77 (12); IR (KBr) 3330, 1630 cm^{-1}. Anal. Calcd for $C_{29}H_{28}N_2O$: C, 82.82; H, 6.71. Found: C, 82.67; H, 6.69.

***N, N'*-Bis[(phenyl-*o*-tolyl)methyl]urea (22).** In a procedure similar to that used for **18**, reaction of (phenyl-*o*-tolyl)methylamine hydrochloride[22] (2.0 g, 8.56 mmol) with triethylamine (0.87 g, 8.58 mmol) in 100 mL of CH_2Cl_2 and 1.27 g (5.7 mmol) of isocyanate **55** in 25 mL of CH_2Cl_2 gave 2.62 g (73%) of **22** which was recrystallized from acetone, mp 266-267 °C (dec): ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 6 H), 4.83 (d, 2 H), 6.13 (d, 2 H), 7.03-7.31 (m, 18 H); ^{13}C NMR (DMSO-d_6) δ 18.9, 53.6, 125.9, 126.5, 126.8, 127.0, 128.3, 130.3 135.2, 141.5, 142.7, 156.2; mass spectrum, *m/e* (relative intensity) 420 (M^+, 24), 239 (21), 197 (15), 196

(100), 181 (26), 180 (28), 179 (21), 166 (20), 165 (25), 120 (19), 106 (27), 104 (33), 91 (22); IR (KBr) 3332, 1637 cm^{-1}. Anal. Calcd for $C_{29}H_{28}N_2O$: C, 82.82; C, 6.71. Found: C, 82.72; H, 6.79.

***N*-Triphenylmethylurea (23)[26].** Into a stirred solution of 4 g (14.0 mmol) of trityl isocyanate in 100 mL of CH_2Cl_2 was bubbled anhydrous ammonia gas for 3 h. Vacuum removal of the solvent gave 3.85 g (91%) of **23**, recrystallized from ethyl acetate to give white crystals, mp 251-252 °C. (lit.[26] 242 °C).

***N*-Tri(*p*-tolyl)methylurea (24).** In a procedure similar to that used for **23**, treatment of isocyanate **48** (0.36 g, 1.1 mmol) in 50 mL of CH_2Cl_2 with anhydrous ammonia for 3 h gave 0.37 g (98%) of **24**, which was recrystallized from acetonitrile, mp 235-236 °C: ^1H NMR ($CDCl_3$) δ 2.33 (s, 9 H), 4.16 (s, 2 H), 5.78 (s, 1 H), 7.09-7.18 (m, 12 H); ^{13}C NMR (DMSO-d_6) δ 20.4, 67.8, 127.8, 128.3, 135.0, 143.4, 157.6; mass spectrum, *m/e* (relative intensity) 344 (M^+, 23), 285 (23), 210 (72), 118 (100); IR (KBr) 3423, 3398, 1654 cm^{-1}. Anal. Calcd for $3(C_{23}H_{24}N_2O)$. C_3H_6O (acetone) : C, 79.23; H, 7.20. Found : C, 79.14; H, 7.28.

***N*-Tri(*p*-*t*-butylphenyl)methylurea (25).** In a procedure similar to that used for **23**, treatment of isocyanate **50**, (0.92 g, 2.03 mmol) with ammonia gas in 50 mL of CH_2Cl_2 gave 0.82 g (86%) of **25** which was recrystallized from acetone, mp 252-254 °C: ^1H NMR ($CDCl_3$) δ 1.29 (s, 27 H), 4.19 (s, 2 H), 5.85 (s, 1 H), 7.25 (dd, 12 H); ^{13}C NMR ($CDCl_3$) δ 31.3, 34.4, 69.1, 125.0, 128.3, 141.6, 150.0, 158.6; mass spectrum, *m/e* (relative intensity) 470 (M^+, 4), 453 (2), 411 (27), 294 (100), 104 (100); IR (KBr) 3477, 3350, 1655 cm^{-1}. Anal. Calcd for $C_{32}H_{42}N_2O$: C, 81.65; H, 8.99. Found: C, 81.70; H, 8.99.

***N*-9-Triptycylurea (26).** Into a solution of 9-triptycyl isocyanate[33] (0.65 g, 2.20 mmol) in 50 mL of CH_2Cl_2 was bubbled anhydrous ammonia for 1.5 h. The white precipitate (0.65, 95%) of **26** was filtered and recrystallized from ethanol, mp 314-315 °C: ^1H NMR (DMSO-d_6) δ 5.59 (s, 1 H), 6.24 s, 3 H), 6.98-7.02 (m, 6 H), 7.36-7.48 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 52.1, 65.7, 121.9, 123.1, 124.1, 124.9, 144.3, 144.5, 157.9; mass spectrum, *m/e* (relative intensity) 312 (M^+, 21), 295 (7), 268 (29), 267 (31), 252 (100), 165 (14); IR (KBr) 3601, 3333, 1649 cm^{-1}. Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75, H, 5.16. Found: C, 80.60; H, 5.25.

***N*-Dehydroabietylurea (27).** In a procedure similar to that used for **23**, treatment of isocyanate **56** with anhydrous ammonia in 100 mL of CH_2Cl_2 gave 4.1 g (97%) of **27** which was recrystallized from acetone, mp 190-191 °C. ^1H NMR ($CDCl_3$) δ 0.91 (s, 3 H), 1.20-1.46 (m, 13 H), 1.59-1.88 (m, 4 H), 2.24-2.29 (m, 1 H), 2.76-3.13 (m, 5 H), 4.40 (s, 2 H), 4.78 (t, 1 H), 6.88 (s, 1 H), 6.96-6.99 (m, 1 H), 7.14-7.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.6, 18.8, 24.0, 25.2, 30.1, 33.4, 36.0, 37.4, 38.4, 45.0, 50.8, 123.8, 124.2, 126.8, 134.8, 145.5, 147.2, 159.5 (3 peaks overlapped); mass spectrum, *m/e* (relative intensity) 328 (M^+, 4), 173 (36), 74 (100); IR (KBr) 3472, 3337, 1632 cm^{-1}. Anal. Calcd for $C_{21}H_{32}N_2O$: C, 76.78; H, 9.82. Found : C, 76.87; H, 9.62.

***N,N'*-Ditritylmalonamide (28).** To a stirred solution of 2.59 g (10 mmol) of triphenylmethylamine[27] in 10 mL of toluene under Ar was added dropwise 0.26 g (1.85 mmol) of malonyl chloride in 20 mL of toluene. After 10 min 1.01 g (10 mmol) of triethylamine was added. The solution was heated at reflux for 10 h, then filtered. Solvent was removed under reduced pressure and the solid residue was extracted with CH_2Cl_2 (3X) Combined organic extracts were washed with dil. HCl(2X 100 mL), water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent and recrystallization from acetone gave 0.35 g (32%) of white needles, mp 293-294 °C (lit.[34], 302 °C): ^1H NMR ($CDCl_3$) δ 3.28 (s, 2 H), 7.11-7.35 (m, 30 H), 7.74 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 46.4, 70.7, 127.1, 128.0, 128.6, 144.2, 166.1; mass spectrum, *m/e*

(relative intensity) 586 (M^+, 21), 343 (88), 243 (88), 182 (47), 165 (100), 104 (53), 77 (60), 50 (42), 40 (82); IR (KBr) 3365, 3300, 1665 cm^{-1}.

***N,N'*-Dityrityl-2-methylmalonamide (29).** In a procedure similar to that used for **28**, reaction of 1.847 g (7.13 mmol) of triphenylmethyamine[27] in 100 mL of toluene with 0.05 g (3.5 mmol) of 2-methylmalonyl choride[35] in 10 mL of toluene and 1.44 g (14.26 mmol) of triethylamine gave, after recrystallization from acetonitrile, 1.06 g (49%) of white needles, mp 299-300 °C (dec): ^1H NMR ($CDCl_3$) δ 1.49 (d, 3 H), 3.10 (q, 1 H), 7.14-7.28 (m, 30 H), 7.63 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.0, 51.0, 70.4, 127.0, 128.0, 128.5, 144.3, 170.0; mass spectrum, *m/e* (relative intensity) 600 (M^+, 16), 357 (63), 243 (75), 182 (21), 165 (100), 104 (37), 85 (56), 77 (39), 40 (54); IR (KBr) 3492, 3298, 1660 cm^{-1}. Anal. Calcd for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04. Found : C, 84.01; H, 6.15.

***N,N'*-Dititylsuccinamide (30).** In a procedure similar to that used for **28,** reaction of 5.2 g (20 mmol) of triphenylmethylamine[27] in 150 mL of dry toluene, with 1.55 g (10 mmol) of succinoyl chloride in 25 mL of toluene and 4.06 g (40.2 mmol) of triethylamine gave, after recrystallization from acetonitrile, 0.7 g (11.6%) of **30** mp 302-303 °C (dec): ^{1}NMR ($CDCl_3$) δ 2.62 (s, 4 H), 6.97 (s, 2 H), 7.16-7.20 (m, 30 H); (^{13}C NMR not available due to poor solubility); mass spectrum, *m/e* (relative intensity) 600 (M^+, 4), 357 (15), 263 (25), 244 (16), 243 (58), 182 (39), 166 (19), 165 (83), 104 (23), 85 (100); IR (KBr) 3300, 1651 cm^{-1}. Anal. Calcd for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04. Found C, 83.85; H, 6.19.

***N,N'*-Dititylfumaramide (31).** In a procedure similar to that used for **28**, reaction of 2.59 g (100 mmol) of triphenylmethylamine in 250 mL of toluene with 5.37 g (35.1 mmol) of fumaryl chloride in 50 mL of toluene and 7.09 g (70.2 mmol) of triethylamine gave, after recrystallization from acetonitrile 13.6 g (65%) of needles, mp 307-308 °C: ^1H NMR ($CDCl_3$) δ 6.89 (s, 2 H), 6.93 (s, 2 H), 7.23 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ 71.0, 127.3, 128.1, 128.6, 134.2, 144.1, 163.0; mass spectrum, *m/e* (relative intensity) 598 (M^+, 8), 417 (3), 355 (54), 261 (48), 243 (100), 182 (64), 165 (78), 104 (32), 77 (36), 40 (50); IR (KBr) 3422, 3390, 1667 cm^{-1}. Anal. Calcd for $C_{42}H_{34}N_2O_2$: C, 84.25; H, 5.72. Found: C, 84.38; H, 5.82.

***N,N'*-Dititryltartaramide (32).** To a stirred solution of 2.5 g (4.18 mmol) of **31** in 225 mL of dry pyridine at 0 °C, was added 2.26 g (6.19 mmol) of tetrabutylammonium permanganate[36] in 100 mL of dry pyridine dropwise over 30 min. After 8 h at room temperature, the solution was poured into 100 mL of 10% HCl and 100 mL of 20% aqueous sodium bisulfate. The resulting solid was filtered, dissolved in CH_2Cl_2 (150 mL) and washed with HCl (2X 50 mL), water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent and recrystallization from CH_2Cl_2 gave 2.3 g (87%) of white needles, mp 278-279 °C: ^1H NMR ($CDCl_3$) δ 4.31 (dd, 2 H), 5.00 (dd, 2 H), 7.14-7.26 (m, 30 H), 8.35 (s, 2 H); (^{13}C NMR not available due to poor solubility); mass spectrum, *m/e* (relative intensity) 632 (M^+, 2), 389 (2), 346 (3), 243 (100), 165 (13); IR (KBr) 3374, 3357, 1679, 1660 cm^{-1}. Anal. Calcd for $3(C_{42}H_{36}N_2O_4)$. C_3H_6O : C, 79.20; H, 5.87; N, 4.30. Found: C, 79.05; H, 5.87; N, 4.47.

***N*-Triphenylmethyl-3,3',3''-propanamide (33).** To a stirred solution of 3,3'3''-triphenylpropanoyl chloride[29] (1 g, 3.12 mmol) in 30 mL of anhydrous THF under Ar was added dropwise 0.9 g (3.47 mmol) of tritylamine in 20 mL of dry THF. After 5 min, there was added 0.363 g(3.58 mmol) of triethylamine. After 10 h, the solution was washed with 10% HCL (2X 50 mL), water, saturated NaCl and dried ($MgSO_4$). Vacuum removal of the solvent gave an oil which was triturated with ether to give 1.3 g (77%) of **33**.

Recrystallization from ethanol gave white needles, mp 169-170 °C: ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 2 H), 6.21 (s, 1 H), 6.82-6.86 (m, 6 H), 7.13-7.24 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 50.3, 56.0, 70.6, 126.5, 126.6, 127.6, 128.2, 128.6, 129.4, 144.3, 146.2, 169.0; mass spectrum, *m/e* (relative intensity) 543 (M^+, 2), 301 (23), 300 (100), 244 (12), 243 (54), 182 (23), 85 (18); IR (KBr) 3403, 1667 cm^{-1}. Anal. Calcd for $C_{40}H_{33}NO$: C, 85.99; H, 5.01. Found: C, 86.06; H, 5.03.

***N*-Triphenylmethyl-4,4',4''triphenylbutanamide (34).** In a procedure similar to that used for **33**, reaction of 4,4',4''-triphenyl-1-butanoyl chloride[37] (0.6 g, 1.78 mmol) in 30 mL of anhydrous THF with 0.55 g (2.12 mmol) of tritylamine in 20 mL of anhydrous THF and 0.29 g (2.86 mmol) of triethylamine gave 0.47 g (47%) of **34** which was recrystallized from acetone, mp 263-265 °C (dec): ^{1}H NMR ($CDCl_3$) δ 2.04 (m, 2 H), 2.94 (m, 2 H), 6.29 (s, 1 H), 7.11-7.29 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ 34.3, 35.3, 56.2, 70.5, 126.0, 127.0, 127.9, 128.0, 128.7, 129.2, 144.8, 146.9, 171.6; mass spectrum, *m/e* (relative intensity) 557 (M^+, 6), 244 (21), 243 (100), 182 (20), 167 (15), 165 (29); IR (KBr) 3359, 1661 cm^{-1}. Anal. Calcd for $C_{41}H_{35}NO$: C, 88.29; H, 6.33. Found: C, 88.37; H, 6.32.

***O*-2-Naphthyl-*N*-tritylcarbamate (35).** To a suspension of 0.84 g (35 mmol) of NaH in 125 mL of dry THF under Ar was added dropwise of 5.05 g (35 mmol) of β-naphthol in 125 mL of dry THF. After 30 min, there was added dropwise trityl isocyanate (5 g, 17.5 mmol) in 50 mL of THF. After 48 h, the reaction was quenched with water and extracted with ether (3X). Combined organic extracts were washed with saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent gave an oil that was chromatographed over silica gel, eluting with 7:3 chloroform/hexane to give 2.0 g (26%) of **35**, which was recrystallized from ethyl acetate, mp 196-198 °C: ^{1}H NMR ($CDCl_3$) δ 6.39 (s, 1 H), 7.32 (m, 19 H), 7.75 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 70.3, 118.1, 121.2, 125.3, 126.3, 127.2, 127.6, 128.1, 128.6, 129.0, 131.1, 133.7, 144.5, 148.6, 152.9; mass spectrum, *m/e* (relative intensity) 286 (M^+-143,8), 285 (39), 244 (12), 243 (49), 208 (100), 165 (39), 144 (82); IR (KBr) 3292, 1704 cm^{-1}. Anal. Calcd for $C_{30}H_{32}NO_2$: C, 83.89; H, 5.39. Found: C, 83.86; H, 5.41.

***N,N'*-Dityrityl-1,3-diaminopropane (36).** To a stirred solution of trityl chloride (4 g, 14.4 mmol) in 100 mL of CH_2Cl_2 under Ar was added dropwise 1,3-diaminopropane (0.53 g, 7.18 mmol) in 20 mL of CH_2Cl_2. After 10 min, triethylamine (1.45 g, 14.4 mmol) was added and the solution was stirred for 10 h. The precipitate was filtered and the organic layer was washed with 10% HCl (2X 100 mL), water, saturated NaCl solution and dried ($MgSO_4$). Vacuum removal of the solvent and trituration with ether gave **36** that was recrystallized from chloroform/petroleum ether (30-60 °C) to give 2.38 g (59%) of white crystals, mp 179-181 °C: ^{1}H NMR ($CDCl_3$)δ 1.66 (t, 2 H), 1.89 (br s, 2 H), 2.21 (t, 4 H), 7.13-7.28 (m, 18 H), 7.41-7.45 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 31.4, 42.5, 71.0, 126.2, 127.8, 128.9, 146.2; mass spectrum, *m/e* (relative intensity) 243 (M^+-315, 100), 165 (46), 73 (22), 44 (41), 43 (14); IR (KBr) 3400 cm^{-1}. Anal. Calcd for $C_{41}H_{38}N_2$: C, 88.13; H, 6.85. Found: C, 88.26; H, 6.85.

***N,N'*-dityrityl-1,4-diaminobutane (37).** In a procedure similar to that used for **36**, reaction of trityl chloride (4 g, 14.4 mmol) in 100 mL of CH_2Cl_2 with 1,4-diaminobutane (0.625 g, 7.09 mmol) in 20 mL of methylene chloride and triethylamine (1.45 g, 14.4 mmol) gave, after recrystallization from acetone, 2.1 g (52%) of white needles, mp 154-155 °C: ^{1}H NMR ($CDCl_3$) δ 1.49 (m, 6 H), 2.07 (m, 4 H), 7.12-7.27 (m, 18 H), 7.42-7.46 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 28.6, 43.5, 70.8, 126.1, 127.7, 128.6, 146.3; mass spectrum,

m/e (relative intensity) 315 (M^+-257, 1), 244 (23), 243 (100), 165 (26); IR (KBr) 3316 cm^{-1}. Anal. Calcd for $C_{42}H_{40}N_2$: C, 88.07; H, 7.04. Found: C, 87.81; H, 7.28.

***N,N'*-Dityityl-1,5-diaminopentane (38).** In a procedure similar to that used for **36**, reaction of trityl chloride (6.5 g, 23.3 mmol) in 100 mL of CH_2Cl_2 with 1,5-diaminopentane (1.02 g, 10 mmol) in 25 mL of dry methylene chloride and triethylamine (2.22 g, 22 mmol) gave, after recrystallization from acetone, 4.01 g (68%) of white crystals, mp 148-149 °C: ^1H NMR ($CDCl_3$) δ 1.32 (m, 8 H), 2.08 (t, 4 H), 7.13-7.28 (m, 18 H), 7.44-7.47 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 25.1, 30.8, 43.5, 70.9, 126.2, 127.8, 128.7, 146.4; mass spectrum, *m/e* (relative intensity) 343 (M^+-243, 1), 258 (1), 244 (22), 243 (100); IR (KBr) 3329 cm^{-1}. Anal. Calcd for $C_{43}H_{42}N_2$: C, 88.01; H, 7.21. Found: C, 88.07; H, 7.29.

***N, N'*-Dityityl-1,6-diaminohexane (39).** In a procedure similar to that used for **36**, reaction of trityl chloride (4.1 g, 14.7 mmol) in 100 mL of CH_2Cl_2 with 1,6-diaminohexane (0.854 g, 7.36 mmol) in 25 mL of dry methylene chloride and triethylamine (1.49 g, 14.7 mmol) gave 2.64 g (60%) of **39**, which was recrystallized from acetone, mp 188-189 °C: ^1H NMR ($CDCl_3$) δ 1.23 (m, 4 H), 1.46 (m, 6 H), 2.08 (t, 4 H), 7.13-7.28 (m, 18 H), 7.45-7.47 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 27.3, 30.8, 43.4, 70.8, 126.1, 127.7, 128.6, 146.3; mass spectrum, *m/e* (relative intensity) 600 (M^+, trace), 357 (2), 258 (6), 244 (25), 243 (100), 165 (16); IR (KBr) 3320 cm^{-1}. Anal. Calcd for $C_{44}H_{44}N_2$: C, 87.96; H, 7.38. Found: C, 87.94; H, 7.42.

Ethyleneglycol bis(triphenylmethyl) ether (40)[39]. A stirred solution of ethylene glycol (1.08 g, 17.5 mmol), and 9.75 g (35 mmol) of triphenylmethyl chloride in 80 mL of dry pyridine was heated at reflux for 30 min, then cooled and poured into 1000 mL of 10% HC l. Filtration gave, after recrystallization from toluene, 4.68 g (49%) of **40**, mp 188-189 °C (lit.[39] 188 °C).

Diethylene Glycol bis(triphenylmethyl) ether (41)[40]. In a procedure similar to that used for **40,** reaction of 1.69 g (15.9 mmol) of diethylene glycol and 8.9 g (31.9 mmol) of triphenylmethyl chloride in 80 mL of dry pyridine gave, after recrystallization from toluene 5.28 g (56%) of white crystals, mp 157-158 °C (lit.[40] 158 °C).

Typical Procedure for Inclusion Studies. The host (for **2**, 0.2 g; for other hosts, 0.05-0.10 g) was dissolved in 3 mL of hot ethyl acetate in a 25 mL erlenmeyer flask. The flask was sealed with a rubber septum and 20 mmol equiv. of liquid guest was added via syringe (for solid guests, 2 mmol equiv. was added directly). If no crystals formed on cooling to room temperature, the solution was further cooled to 5 °C. The precipitated crystals were filtered, dried at room temperature at 0.5-1.5 torr for 10 h. The host/guest ratio was determined by ^1H NMR.

Typical Procedure for Selectivity Studies. DTU (0.2 g) was dissolved in 3 mL of hot ethyl acetate, and the flask was sealed with a rubber septum. A solution of the 1:1 guest mixture (for example, 0.2 equiv. each of $(CH_3)_3CCONH_2$ and CH_3CONH_2) in 3 mL of ethyl acetate was added via syringe. After cooling, collecting and drying the crystals, the guest ratio was determined by ^1H NMR.

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