

Tripodands with Phenyl and Thiophenyl Rings and Nitrogen Bridgehead Atoms

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Dedicated to Professor Manfred Christl on the occasion of his 65th birthday

Keywords: Tripodands / Thiophene / Alkynes / van der Waals forces / Solid state packing / Silver

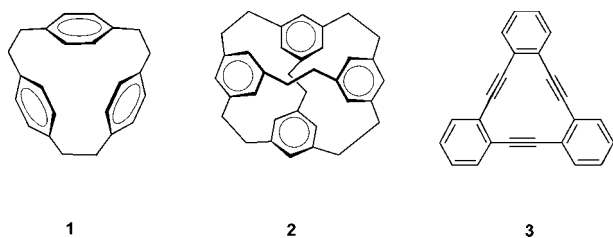
The flexible tripodands **7–9** and **15** with phenyl and thiophenyl rings as “legs” and nitrogen as bridgehead atoms have been synthesized by three-component condensation reactions of the corresponding amine with the aryl halide. The more rigid species **10–14** and **17** were built up from the podands **7–9** as well as from their iodine substitution products **33–35** by a sequence of ethynylation and C–C coupling reactions. Podand **16** was prepared from tris-iodide **36** by Sonogashira coupling with phenylacetylene. In the cases of **7**, **12**, **15–17**, **22**, **24**, **35**, **36**, and **41** the structural parameters were

determined by X-ray studies. With the exception of **7**, **12**, and **17**, all structures show either close intermolecular contacts between heteroatoms (**15**, **22**, **24**, **35**, and **36**), C–H...N hydrogen bonding (**41**), or are closely packed as a result of $\pi\cdots\pi$ stacking (**16**). We were able to isolate silver triflate complexes of **9**, **10**, and **16**, and in the case of **9** we obtained crystals suitable for X-ray diffraction studies.

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Introduction

In host–guest chemistry many cyclic and bicyclic systems are known to be capable of forming host ions.^[1,2] Cations are captured when donor centers, such as nitrogen, oxygen, and sulfur atoms, are available in the compounds. Systems with π donors, such as triple bonds or benzene rings, occur less frequently. Examples of such π donors with a belt-like shape are [2.2.2]paracyclophane (**1**), which was named “ π -prismand” owing to its shape,^[3] other [2.2.2]- and [2.2.1]-cyclophanes,^[4] as well as deltaphane.^[5] With the interconnection of four or more benzene rings by alkane chains, spherical hydrocarbons with an intramolecular cavity (concave hydrocarbons, **2**) have been generated.^[6] The rigid ring system **3** is an example of a π donor with triple bonds^[7] (Scheme 1).



Scheme 1. Examples for π donors providing benzene units (**1**, **2**) and triple bonds (**3**).

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We recently studied a series of bicyclic systems and podands with nitrogen atoms in the bridgehead positions and π donors in the bridges.^[8] As examples we show in Scheme 2 tripodand **4**^[8c] and π -prismand **5**.^[8b] Both form endohedral complexes with silver triflate.^[8b,8c]

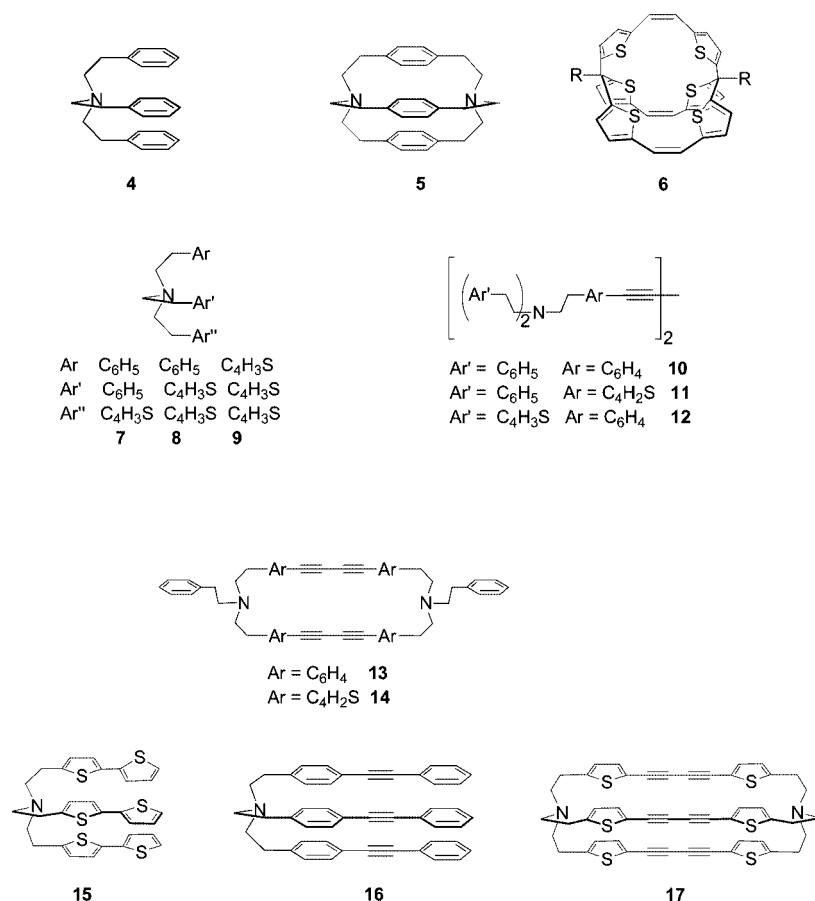
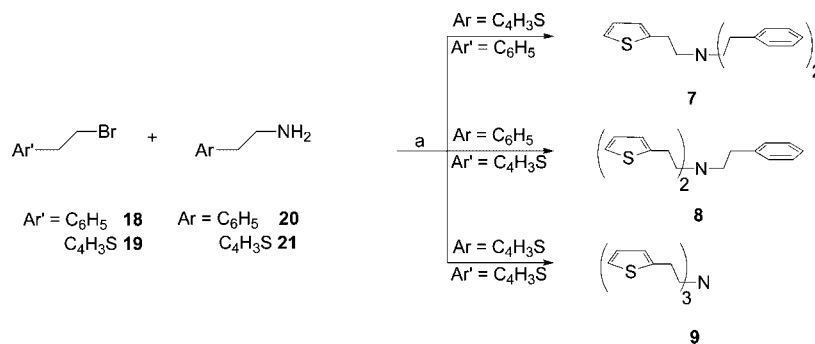
Bicyclic system **6** (Scheme 2) with thiophenyl moieties in the bridges and related tripodands were synthesized by Oda and co-workers.^[9] This, and the good complexation properties of **4** and **5**,^[8b,8c] stimulated us to synthesize simple podands **7–9**, elongated systems **10–16**, and cage compound **17**. In this paper we report the syntheses of **7–17**, some of their molecular structures in the solid state, and the complexes of some of these compounds with silver triflate (Scheme 2).

Results

Syntheses

We synthesized **7–9** commencing with the known reagents (2-bromoethyl)benzene (**18**),^[10] 2-(2-bromoethyl)thiophene (**19**),^[11] (2-phenylethyl)amine (**20**),^[12] and [2-(2-thienylethyl)amine (**21**)]^[13] (Scheme 3). The halide and the amine components were treated with powdered potassium carbonate in acetonitrile to afford podands **7–9** in yields of 60–90%. We rationalized the high yields by assuming a template effect of the potassium ion.

To elongate the aryl part of the podands we synthesized various iodides as summarized in Scheme 4 by treating **7–9** with *n*-butyllithium (*n*BuLi) followed by quenching with

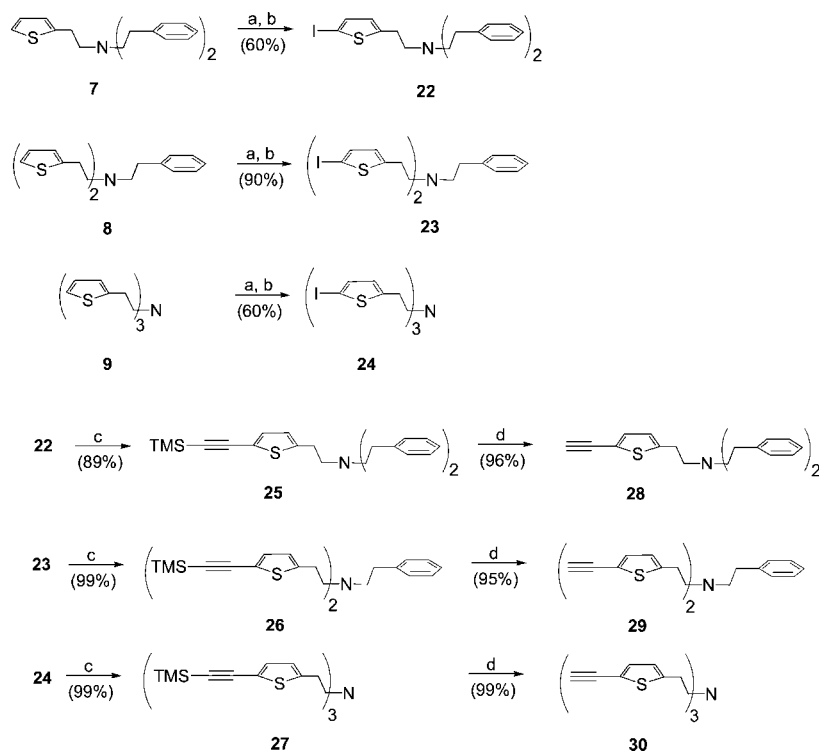
Scheme 2. Tripodand **4**, π -prismand **5**, Oda's bicyclus **6**, and target molecules **7–17**.Scheme 3. Reagents and conditions: a) K_2CO_3 , MeCN, 72 h, reflux.

iodine. This afforded the iodides **22–24** in 60–90% yields. The cross-coupling reactions of **22–24** with trimethylsilylacetylene (TMSA) under Sonogashira conditions^[14] led to **25–27** in excellent yields. The protecting TMS group was removed by treating **25–27** with dilute sodium hydroxide in methanol^[15] affording **28–30** in high yields (Scheme 4).

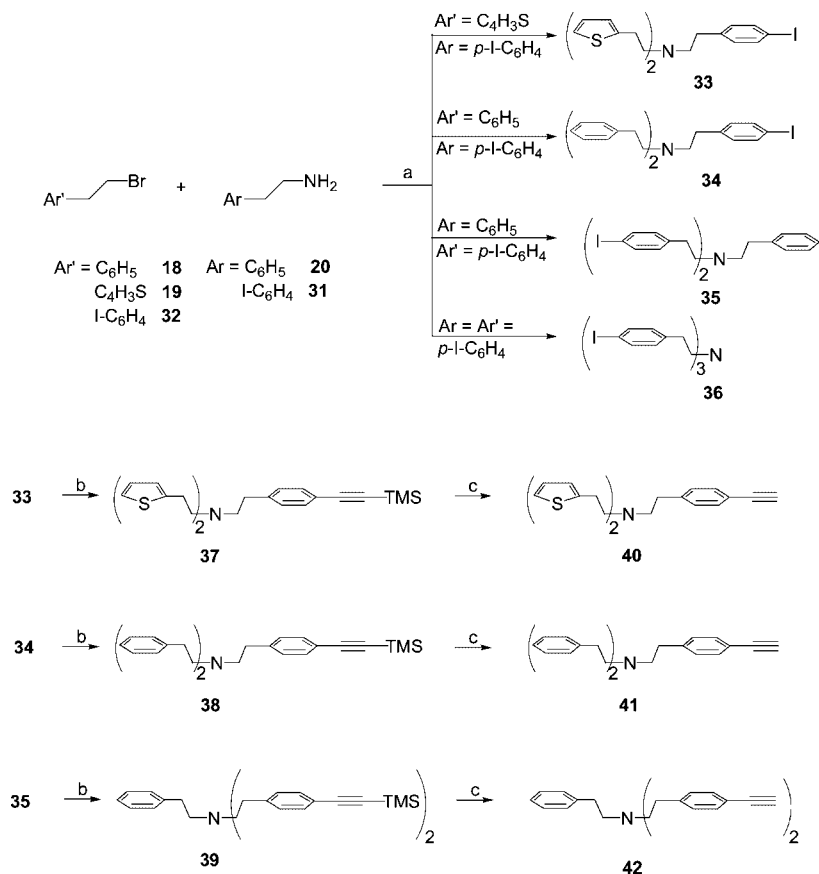
Further intermediates used to obtain larger podands are listed in Scheme 5. They were prepared from **18**, **19**, **20**, 2-(4-iodophenyl)ethylamine (**31**),^[16] and 4-(2-bromoethyl)-iodobenzene (**32**).^[17] The reactions between the amines and the bromides afforded iodo-substituted podands **33–36**

(Scheme 5) in good yields. The cross-coupling reactions of **33–35** with TMSA under Sonogashira conditions^[14] led to intermediates **37–39** in very good yields. The removal of the protecting TMS group was achieved by treatment of **37–39** with a conc. solution of potassium hydroxide in water^[15] to give **40–42** in excellent yields.

Now the stage was set for the preparation of podands **10–14** and cage system **17** (Scheme 6). In all six cases we used the protocol first proposed by Hay.^[18] Reaction of **28–30** and **40–42** with CuCl in the presence of pyridine under aerobic conditions provided podands **10–14** and bicyclic



Scheme 4. Reagents and conditions: a) *n*BuLi, THF, -10°C ; b) I_2 in THF, -70°C ; c) $\text{Pd}(\text{PPh}_3)_4$, CuI, Et_2NH , TMSA in THF, 45°C , 1 h; d) 0.1 N NaOH/ H_2O , 25°C , 2 h.

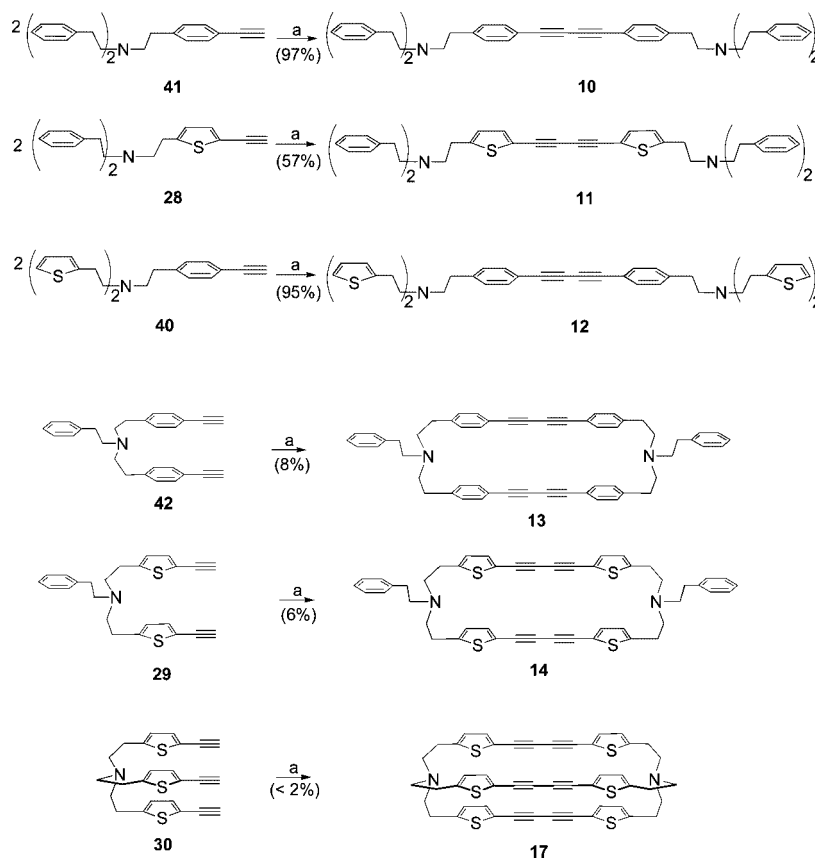


Scheme 5. Reagents and conditions: a) K_2CO_3 , MeCN, 70 h, reflux; b) $\text{Pd}(\text{PPh}_3)_4$, CuI, Et_2NH , TMSA in THF, 45°C , 1 h; c) conc. KOH/ H_2O , 25°C , 2 h.

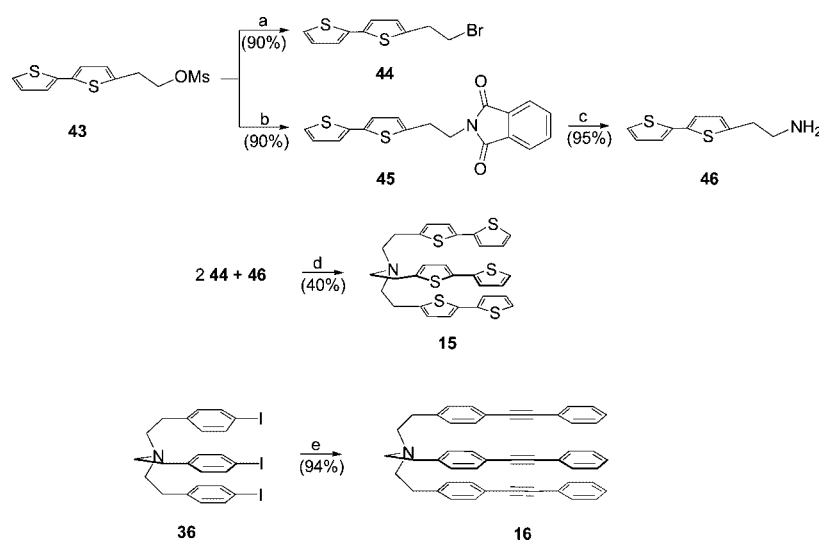
cage **17**. When only one alkyne unit was coupled (**28**, **40**, **41**) the yields varied between 57 and 97%. In the cases of **29**, **30**, and **42**, in which two or three alkyne units were joined, the yields dropped drastically to 2–8%. Cage system **17** with its three 1,3-butadiyne units as rigid spacers is reminiscent of related cages in which 1,1,1-tris(4-hydroxy-

phenyl)ethane units are connected by three hexane-2,4-di-yne units^[19,20] and related species^[21] which allowed the complexation of organic molecules inside the cavity.

The starting point for the preparation of **15** was the mesylate of bithiophenethanol **43**^[22] which was readily converted into bromide **44** through the Finkelstein reaction.^[23]



Scheme 6. Reagents and conditions: a) CuCl, pyridine, air.



Scheme 7. Reagents and conditions: a) LiBr, acetone, 8 h, reflux; b) KPI, DMF, 90 °C; c) N₂H₄·H₂O, NaOEt, EtOH, 4 h, reflux; d) K₂CO₃, MeCN, 64 h, reflux; e) Pd(PPh₃)₄, phenylacetylene, CuI, NEt₃, 80 °C, 1 h.

Reaction of **43** with potassium phthalimide (KPI) led to **45** which was converted to **46** by treatment of **45** with hydrazine hydrate. The reaction of 2 equiv. of bromide **44** with 1 equiv. of amine **46** led in 40% yield to the desired podand **15** (Scheme 7). Podand **16** was prepared by Sonogashira coupling^[14] of **36** with phenylacetylene in 94% yield.

Structural Investigations

The structures of the newly synthesized species were assigned by spectroscopic methods. In the cases of **7**, **12**, **15**–**17**, **22**, **24**, **35**, **36**, and **41** we were able to isolate single crystals that were suitable for X-ray diffraction studies. With the exception of **7**, **12**, and **17**, all the species exhibited either close intermolecular contacts between the heteroatoms (**15**, **22**, **24**, **35**, and **36**), CH $\cdots$ N hydrogen bonding (**41**), or were closely packed as a result of $\pi\cdots\pi$ stacking (**16**).

Of the podands, iodo derivatives **22**, **24**, **35**, and **36** deserve our particular interest owing to intermolecular contacts between the iodine centers or between iodine centers and other heteroatoms. In Figure 1 we show sections of the crystal structure of **35**. Characteristic are the *syn* arrangement of the aryl rings and the *in* position of the lone pairs at the nitrogen atoms.

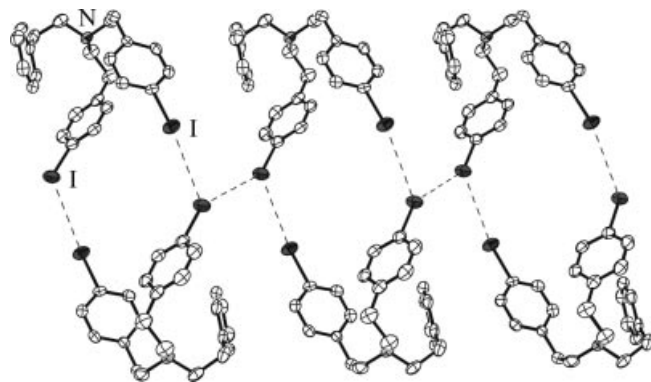


Figure 1. Section of the crystal structure of **35**. The hydrogen atoms have been omitted for the sake of clarity.

This solid-state arrangement was achieved through an intermolecular interaction of the iodine atoms. For **35**, this leads to a structure in which the molecules are connected to pairs forming ribbons to achieve optimal interactions between the iodine centers. The intermolecular distances between the iodine centers are 3.86 and 4.15 Å, respectively. These values are shorter than the sum of the van der Waals radii of two iodine atoms (4.30 Å).^[24]

In the case of **36** we obtained pairs of C_3 symmetric species (S_6) in the solid state in which the aryl rings adopt the *syn* conformation, allowing six symmetry equivalent contacts between the iodine centers, as shown in Figure 2. The intermolecular distances between the iodine centers amount to 4.22 Å. Intermolecular interactions between neutral halogen substituents have been addressed in the literature.^[25,26] Intermolecular distances that are less than the sum of the van der Waals radii of halogen atoms are also

associated with two preferred angular geometries, type I, with $\theta_1 \approx \theta_2 < 180^\circ$, and type II, with $\theta_1 \approx 180^\circ$ and $\theta_2 \approx 90^\circ$. The two angles θ_1 , θ_2 are defined as the two C–X $\cdots$ X (X = halogen) angles.^[26a–c] In our cases, the angles were $\theta_1 = 142.5^\circ$, $\theta_2 = 128.5^\circ$ for **36** and $\theta_1 = 158.4^\circ$, $\theta_2 = 124.2^\circ$ and $\theta_1 = \theta_2 = 150.7^\circ$ for **35**. The interactions between closed-shell systems have previously been interpreted on the basis of donor–acceptor interactions.^[25] Later it was shown by ab initio calculations that correlation effects, that is, induction and dispersion forces, considerably contribute to the bonding.^[27,28]

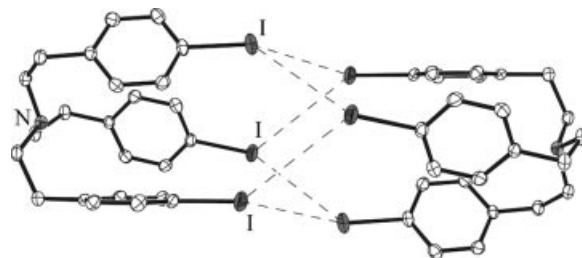


Figure 2. Section of the crystal structure of **36**. The hydrogen atoms have been omitted for the sake of clarity.

In **24**, the three iodine centers prefer close contacts with the sulfur centers of the thiophene rings (Figure 3). As a consequence, a two-dimensional network results with S $\cdots$ I contacts axial with respect to the thiophene rings (3.56, 3.64, and 3.78 Å) and one S $\cdots$ S contact (3.64 Å). All these intermolecular distances are smaller than the sum of the van der Waals radii of sulfur and iodine atoms (4.00 Å)^[24] or two sulfur atoms (3.70 Å).^[24] Recently, the interaction of two sulfur centers was investigated by theoretical means. As stated above, induction and dispersion forces are major contributing factors that account for the attraction between them.^[28]

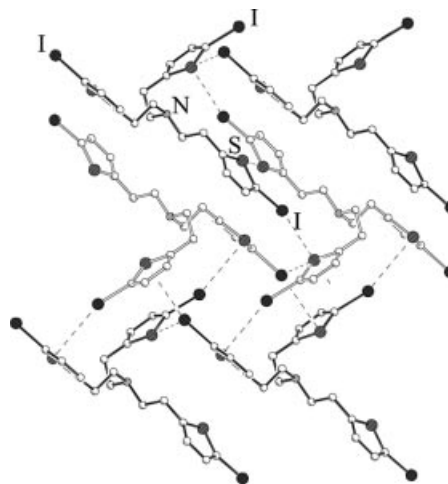


Figure 3. Section of the crystal structure of **24**. Inverted molecules are shown with open bonds and the hydrogen atoms have been omitted for the sake of clarity.

In the solid state of **22**, the molecules form a chain connected by close intermolecular contacts between the iodine and nitrogen centers (3.10 and 3.17 Å) (Figure 4). These

distances are much smaller than the sum of the van der Waals radii of the iodine and nitrogen atoms (3.65 Å).^[24] Intermolecular interactions between lone pairs at nitrogen atoms of sp^3 , sp^2 , and sp character and halogen centers were encountered rather early on in this area of research.^[25,29] This interaction formed the basis for the construction of two- and three-dimensional ensembles in supramolecular chemistry using amines,^[29] azaaromatics,^[29,30a] or nitriles.^[30b]

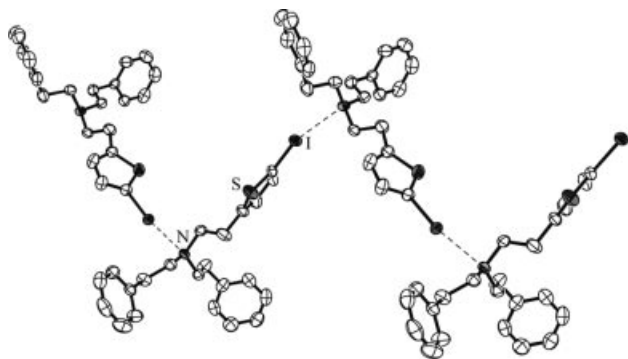


Figure 4. Section of the crystal structure of **22**. The hydrogen atoms have been omitted for the sake of clarity.

A strong intermolecular $S \cdots S$ contact (3.51 Å) between two outer thiophene rings was observed in the solid state of **15**. The $S \cdots S$ contact is about 0.2 Å shorter than the sum of the van der Waals radii of two sulfur centers.

In contrast to the crystal structures with heteroatom contacts, the three nitrogen substituents in **12**, **16**, and **41** are widely spread in their solid state. This leads to a rather close stacking of translational equivalent molecules, resulting in a short lattice constant in the stacking direction. In the case of **16**, close packing of the π units was observed. The acidic hydrogen atoms at the alkyne carbon atoms of **41** form hydrogen bonds with the nitrogen atoms of neighboring molecules, thus connecting parallel stacks through hydrogen bridges (Figure 5). The $C \cdots N$ distance is rather long (3.27 Å) and the $C-H \cdots N$ angle is 150°. Hydrogen bonding between acetylene moieties and N bases have been reported in the literature.^[31]

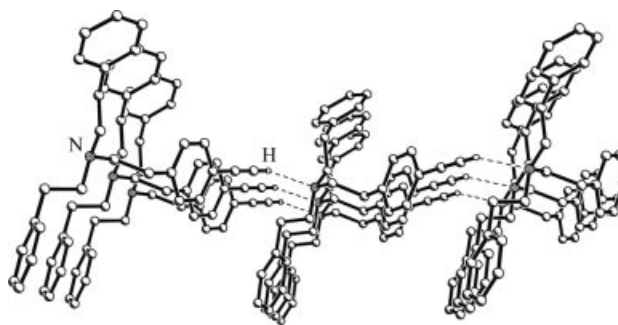


Figure 5. Section of the crystal structure of **41**. With the exception of the alkyne hydrogen atoms all other hydrogen atoms are omitted for the sake of clarity.

Figure 6 reveals the molecular structure of **17** to have a D_3 symmetry in the solid state and an *in/in* conformation at the bridgehead positions. The distance between the nitrogen atoms amounts to 14.7 Å.

Complexation Studies

Podands **7–16** represent π donors with a flexible skeleton. This suggested that these ligands could be used to generate endohedral metal complexes.^[32] In view of several silver complexes of **5** and related π -prismoids^[8] as well as various cyclophanes^[4,5] and related species^[6,33,34] containing benzene rings in the ligand frame, we anticipated the ligand properties for our podands. The reaction of **9**, **10**, and **16** with silver triflate in degassed dichloromethane led to the isolation of the complexes $[9 \cdot Ag]^+ \cdot [CF_3SO_3]^-$, $[10 \cdot 2Ag]^{2+} \cdot 2[CF_3SO_3]^-$, and $[16 \cdot Ag]^+ \cdot [CF_3SO_3]^-$. These complexes could be identified by their analytical data. Especially informative were the 1H - and ^{13}C NMR spectra which show a low-field shift of the methylene protons adjacent to the nitrogen atoms of the complexes relative to the uncomplexed species. In Table 1 we have compared the NMR spectroscopic data of **9**, **10**, and **16** with their silver complexes. The data suggest that in all three complexes the silver ion is situated close to the nitrogen atom and that the lone pair of electrons adopts the *in* conformation. This situation was also found in the complex of **4** with silver triflate.^[8c]

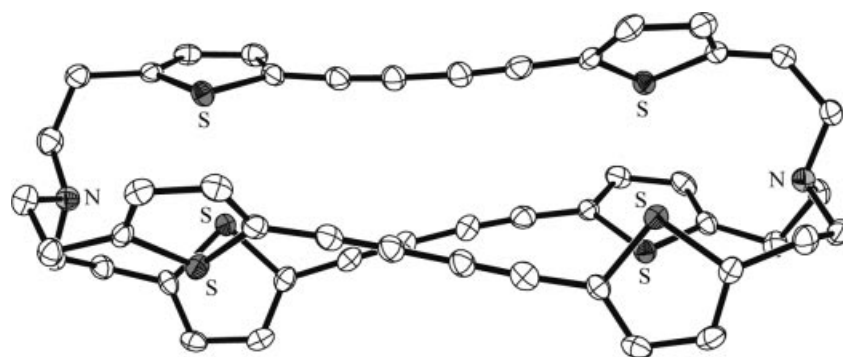
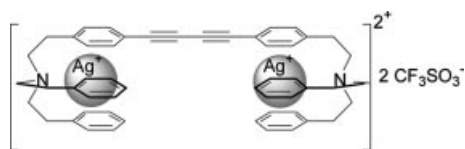


Figure 6. Molecular structure of **17**. The hydrogen atoms have been omitted for the sake of clarity.

Table 1. Comparison between the NMR spectroscopic data of **9**, **10**, and **16** with their complexes of silver triflate.

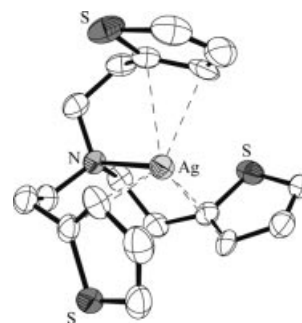
	Multiplicity, δ_{H} [ppm]					
	9	$[\mathbf{9} \cdot \text{Ag}]^+$	10	$[\mathbf{10} \cdot 2\text{Ag}]^{2+}$	16	$[\mathbf{16} \cdot \text{Ag}]^+$
CH_2	t, 2.85	m, 2.88–2.97	m, 2.77–2.80	m, 2.70–2.82	m, 2.73	m, 2.70–2.78
CH_{ar}	t, 2.97		m, 2.80–2.90	m, 2.90–3.02	m, 2.82	m, 2.78–2.85
	dd, 6.81	d, 6.43	d, 7.10	dd, 6.94	d, 7.12	d, 7.03
	dd, 6.90	dd, 7.00	d, 7.17	d, 6.98	m, 7.30–7.35	m, 7.21–7.38
	dd, 7.11	d, 7.41	m, 7.19–7.24	m, 7.35–7.41	d, 7.46	d, 7.47
			m, 7.25–7.33	d, 7.48	dd, 7.53	d, 7.53
			d, 7.45			
	δ_{C} [ppm]					
CH_2	28.3	28.4	33.8	32.9	34.0	33.0
	56.1	58.4	34.0	33.4	55.7	57.3
			55.6	57.4		
			56.0	57.5		
$\text{CH}_{\text{ar}}/\text{C}\equiv\text{C}$	123.4	120.5	73.8	74.8	89.0	88.1
	124.8	126.8	81.6	81.1	89.5	90.8
	126.9	129.0	119.5	120.7	121.0	122.7
	143.4	143.8	126.0	124.2	123.6	122.9
			128.4	126.0	128.3	125.7
			128.9	127.7	128.5	128.7
			129.1	130.6	129.0	128.8
			132.5	133.8	131.6	131.8
			140.6	138.5	131.8	132.9
			142.2	140.6	141.2	138.9

The most interesting result is the fact that **10** complexes with 2 equiv. of silver triflate. As the ^{13}C NMR spectrum of **10** shows only eight signals in the aromatic region (120–140 ppm) we assume a symmetrical structure with one silver atom in each cavity formed by the three aromatic rings and the nitrogen atom, as sketched below (Scheme 8). Other structural possibilities for $[\mathbf{10} \cdot 2\text{Ag}]^{2+}$ cannot be ruled out by our data.

Scheme 8. Assumed structure for $[\mathbf{10} \cdot 2\text{Ag}]^{2+} \cdot 2\text{CF}_3\text{SO}_3^-$.

In the case of $[\mathbf{9} \cdot \text{Ag}]^+ \cdot [\text{CF}_3\text{SO}_3]^-$ we were able to isolate single-crystals that were suitable for X-ray diffraction studies. These studies showed that the thiophene rings adopt a *syn* conformation with the nitrogen lone pair of electrons adopting an *in* conformation (Figure 7).

The silver ion is situated in the center of the cavity spanned by the three thiophene rings. The three thiophene rings in $[\mathbf{9} \cdot \text{Ag}]^+$ are disordered with respect to the sulfur positions, however, all are oriented face-on to the C_3 axis. This conformation brings one edge of the π system of each ring closer to the silver ion. The distances between these atoms and the metal atom (average 2.61 Å) are similar to those found in the silver complexes of **4** (2.47 Å),^[8c] and of various [2.2.2]- and [2.2.1]cyclophanes.^[4,5,33] The distance between the metal and the nitrogen atoms (2.41 Å) is the same as that found in the silver complex of **4**.^[8c]

Figure 7. Molecular structure of $[\mathbf{9} \cdot \text{Ag}]^+ \cdot \text{CF}_3\text{SO}_3^-$. The hydrogen atoms have been omitted for the sake of clarity.

Conclusions

By using a simple three-component condensation procedure paired with catalytic cross-coupling reactions we were able to synthesize podands **7–16** and cage system **17**. The X-ray diffraction studies on **15**, **22**, **24**, **35**, and **36** revealed intermolecular interactions between heteroatoms in the solid state. Interactions between iodine centers (**35**, **36**), between iodine and sulfur atoms (**24**), between iodine and nitrogen atoms (**22**), and between sulfur centers (**15**) are particularly efficient. The intermolecular hydrogen bond between the acetylene moiety and the *tert*-amine function in **41** is also of interest.

In three cases, **9**, **10**, and **16**, we observed complexation between the ligands and silver triflate. In the case of **9**, X-ray diffraction revealed bonding between one edge of each thiophenyl π system and the nitrogen center with the silver ion.

Experimental Section

General Remarks: All melting points are uncorrected using a Büchi apparatus (Dr. Tottoli). Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV/Vis absorption spectra were recorded with a Hewlett-Packard HP 8452A Diode Array spectrometer. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer with the use of the solvent as internal standard (δ). Standard symbols for signal multiplicities are used; p = pseudo. FAB and EI mass spectra were recorded with a JEOL JMS-700 instrument. All reactions were carried out in dried glassware under an atmosphere of argon with the use of dried- and oxygen-free solvents.

General Procedure for the Three-Component Reaction (7–9 and 33–36): For the three-component condensation reaction about 2 equiv. of the bromide and 1 equiv. of amine were dissolved in acetonitrile and refluxed in the presence of potassium carbonate for 64–72 h. The mixture was allowed to cool to room temperature. Subsequently, potassium carbonate was filtered off. After removal of the solvent, the residue was purified by column chromatography.

2-(2-Thienyl)-*N,N*-bis(2-phenylethyl)ethylamine (7): Starting materials: [2-(2-thienyl)ethyl]amine (**21**) (2.02 g, 16.04 mmol), (2-bromoethyl)benzene (**18**) (7.42 g, 40.10 mmol), K_2CO_3 (6.85 g, 49.62 mmol), acetonitrile (200 mL); reaction time: 72 h; column chromatography: silica gel, petroleum ether/diethyl ether (4:1). Yield: 4.79 g (89%) of **7** as a colorless oil. 1H NMR (500 MHz, CD_2Cl_2): δ = 2.74–2.80 (m, 4 H, CH_2), 2.81–2.91 (m, 6 H, CH_2), 2.96–3.00 (m, 2 H, CH_2), 6.83 (d, 3J = 2.3 Hz, 1 H, CH_{ar}), 6.95 (dd, 3J = 4.7 Hz, 3J = 3.1 Hz, 1 H, CH_{ar}), 7.14 (d, 3J = 4.7 Hz, 1 H, CH_{ar}), 7.20 (m, 6 H, CH_{ar}), 7.42 (m, 4 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 28.5 (t, CH_2), 34.0 (t, CH_2), 56.0 (t, N- CH_2), 56.1 (t, N- CH_2), 123.4 (d, C_{ar}), 124.8 (d, C_{ar}), 126.0 (d, C_{ar}), 126.9 (d, C_{ar}), 128.6 (d, C_{ar}), 129.1 (d, C_{ar}), 141.2 (s, C_{ar}), 143.5 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{22}^{1}H_{26}^{14}N_1^{32}S_1$ 336.1786; found 336.1786; calcd. for $^{12}C_{22}^{1}H_{24}^{14}N_1^{32}S_1$ 334.1629; found 334.1638. IR (film): $\tilde{\nu}$ = 3084 (w), 3061 (m), 3025 (m), 2946 (s), 2806 (m), 1943 (w), 1874 (w), 1791 (w), 1700 (w), 1602 (m), 1495 (s), 1450 (s), 1356 (m) cm^{-1} .

2-Phenyl-*N,N*-bis[2-(2-thienyl)ethyl]ethylamine (8): Starting materials: (2-phenylethyl)amine (6.05 g, 50 mmol) (**20**), 2-(2-bromoethyl)-thiophene (**19**) (21.98 g, 115 mmol), K_2CO_3 (19.76 g, 143 mmol), acetonitrile (400 mL); reaction time: 72 h; column chromatography: silica gel, dichloromethane. Yield: 10.62 g (62%) of **8** as a colorless oil. 1H NMR (300 MHz, CD_2Cl_2): δ = 2.78–2.90 (m, 4 H, CH_2), 2.90–2.96 (m, 4 H, CH_2), 3.00–3.09 (m, 4 H, CH_2), 6.86 (d, 3J = 3.3 Hz, 2 H, CH_{ar}), 6.97 (t, 3J = 4.3 Hz, 2 H, CH_{ar}), 7.17 (d, 3J = 5.0 Hz, 2 H, CH_{ar}), 7.26 (d, 3J = 6.9 Hz, 3 H, CH_{ar}), 7.33 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.5 (t, CH_2), 34.2 (t, CH_2), 56.0 (t, N- CH_2), 56.1 (t, N- CH_2), 123.6 (d, CH_{ar}), 125.0 (d, CH_{ar}), 126.2 (d, CH_{ar}), 126.8 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.0 (d, CH_{ar}), 141.0 (s, CH_{ar}), 143.4 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{20}^{1}H_{24}^{14}N_1^{32}S_2$ 342.1350; found 342.1300; calcd. for $^{12}C_{20}^{1}H_{22}^{14}N_1^{32}S_2$ 340.1194; found 340.1206. IR (film): $\tilde{\nu}$ = 3025 (m), 2946 (s), 2809 (s), 1943 (w), 1868 (w), 1791 (w), 1701 (w), 1603 (w), 1495 (m), 1453 (s), 1439 (m), 1159 (m) cm^{-1} . $C_{20}H_{23}NS_2$ (341.53): calcd. C 70.33, H 6.79, N 4.10, S 18.78; found C 70.19, H 6.80, N 4.31, S 18.61.

Tris[2-(2-thienyl)ethyl]amine (9): Starting materials: [2-(2-thienyl)ethyl]amine (**21**) (8.00 g, 62.98 mmol), 2-(2-bromoethyl)thiophene (**19**) (27.66 g, 144.84 mmol), K_2CO_3 (25.36 g, 181.03 mmol), acetonitrile (500 mL); reaction time: 64 h; column chromatography: sil-

ica gel, dichloromethane. Yield: 17.43 g (80%) of **9** as a colorless oil. 1H NMR (500 MHz, CD_2Cl_2): δ = 2.85 (t, 3J = 7.6 Hz, 6 H, CH_2), 2.97 (t, 3J = 7.6 Hz, 6 H, CH_2), 6.81 (dd, 3J = 3.6 Hz, 4J = 1.0 Hz, 3 H, CH_{ar}), 6.90 (dd, 3J = 5.0 Hz, 4J = 3.6 Hz, 3 H, CH_{ar}), 7.11 (dd, 3J = 5.0 Hz, 4J = 1.0 Hz, 3 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 28.3 (t, CH_2), 56.1 (t, CH_2), 123.4 (d, C_{ar}), 124.8 (d, C_{ar}), 126.9 (d, C_{ar}), 143.4 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{18}^{1}H_{22}^{14}N_1^{32}S_3$ 348.0914; found 348.0906; calcd. for $^{12}C_{18}^{1}H_{20}^{14}N_1^{32}S_3$ 346.0758; found 346.0773. IR (film): $\tilde{\nu}$ = 3104 (m), 3068 (m), 2946 (s), 2810 (s), 1535 (m), 1458 (m), 1438 (s), 1363 (m), 1247 (m), 1213 (m), 1221 (m), 1162 (m), 1107 (m) cm^{-1} . $C_{18}H_{21}NS_3$ (347.56): calcd. C 62.20, H 6.09, N 4.03, S 27.68; found C 61.93, H 6.07, N 4.13, S 27.61.

2-(4-Iodophenyl)-*N,N*-bis[2-(2-thienyl)ethyl]ethylamine (33): Starting materials: 2-(4-iodophenyl)ethylamine (**31**) (4.04 g, 16.3 mmol), 2-(2-bromoethyl)thiophene (**19**) (7.19 g, 37.6 mmol), K_2CO_3 (6.44 g, 46.6 mmol), acetonitrile (130 mL); reaction time: 72 h; column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 6.83 g (89.4%) of **33** as a colorless oil. 1H NMR (300 MHz, CD_2Cl_2): δ = 2.69 (m, 2 H, CH_2), 2.81 (m, 6 H, CH_2), 2.93 (m, 4 H, CH_2), 6.77 (dd, 3J = 3.1 Hz, 4J = 1.1 Hz, 2 H, CH_{ar}), 6.91 (m, 4 H, CH_{ar}), 7.11 (dd, 3J = 5.2 Hz, 4J = 1.1 Hz, 2 H, CH_{ar}), 7.59 (dd, 3J = 8.6 Hz, 4J = 2.0 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.5 (t, CH_2), 33.6 (t, CH_2), 55.8 (t, N- CH_2), 56.1 (t, N- CH_2), 91.0 (s, I-C), 123.6 (d, C_{ar}), 125.0 (d, C_{ar}), 126.8 (d, C_{ar}), 131.2 (d, C_{ar}), 137.5 (d, C_{ar}), 140.8 (s, C_{ar}), 143.5 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{20}^{1}H_{23}^{127}I_1^{14}N_1^{32}S_2$ 468.0317; found 468.0295; calcd. for $^{12}C_{20}^{1}H_{21}^{127}I_1^{14}N_1^{32}S_2$ 466.0160; found 466.0154. IR (film): $\tilde{\nu}$ = 3068 (m), 2946 (s), 2808 (s), 1896 (w), 1782 (w), 1637 (w), 1587 (w), 1533 (w), 1484 (s), 1461 (m), 1439 (s), 1399 (m), 1353 (m) cm^{-1} . $C_{20}H_{22}INS_2$ (467.43): calcd. C 51.39, H 4.74, N 3.00, S 13.72, I 27.15; found C 51.44, H 4.78, N 3.18, S 13.72, I 27.32.

2-(4-Iodophenyl)-*N,N*-bis(2-phenylethyl)ethylamine (34): Starting materials: 2-(4-iodophenyl)ethylamine (**31**) (13.4 g, 52.8 mmol), (2-bromoethyl)benzene (**18**) (22.47 g, 122 mmol), K_2CO_3 (20.82 g, 151 mmol), acetonitrile (420 mL); reaction time: 72 h; column chromatography: silica gel, dichloromethane. Yield: 15.4 g (64%) of **34** as a pale yellow oil. 1H NMR (300 MHz, CD_2Cl_2): δ = 2.66–2.90 (m, 12 H, CH_2), 6.92 (d, 3J = 8.1 Hz, 2 H, CH_{ar}), 7.20 (t, 3J = 7.4 Hz, 6 H, CH_{ar}), 7.31 (t, 3J = 7.4 Hz, 4 H, CH_{ar}), 7.62 (d, 3J = 8.1 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 33.6 (t, CH_2), 34.0 (t, CH_2), 55.9 (t, N- CH_2), 56.2 (t, N- CH_2), 91.0 (s, CH_{ar} -I), 126.1 (d, CH_{ar}), 128.6 (d, CH_{ar}), 129.1 (d, CH_{ar}), 131.2 (d, CH_{ar}), 137.4 (d, CH_{ar}), 141.07 (s, CH_{ar}), 141.20 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{24}^{1}H_{27}^{14}N_1^{127}I_1$ 456.1188; found 456.1189; calcd. for $^{12}C_{24}^{1}H_{26}^{14}N_1^{127}I_1$ 455.1110; found 455.1075; calcd. for $^{12}C_{24}^{1}H_{25}^{14}N_1^{127}I_1$ 454.1032; found 454.1030. IR (film): $\tilde{\nu}$ = 3060 (m), 3024 (s), 2947 (s), 2859 (m), 2802 (s), 1597 (m), 1494 (s), 1484 (s), 1462 (s), 1452 (s), 1400 (m), 1354 (m), 1120 (s) cm^{-1} . $C_{24}H_{26}IN$ (455.37): calcd. C 63.30, H 5.75, N 3.08, I 27.87; found C 63.03, H 5.74, N 3.18, I 27.63.

***N,N*-Bis[2-(4-iodophenyl)ethyl]-2-phenylethylamine (35):** Starting materials: (2-phenylethyl)amine (**20**) (3.86 g, 31.9 mmol), 4-(2-bromoethyl)iodobenzene (**32**) (22.82 g, 73.4 mmol), K_2CO_3 (12.62 g, 91.3 mmol), acetonitrile (260 mL); reaction time: 72 h; column chromatography: silica gel, dichloromethane. Yield: 11.7 g (63%) of **35** as a pale yellow solid; m.p. 39 °C. 1H NMR (500 MHz, CD_2Cl_2): δ = 2.62 (t, 3J = 7.4 Hz, 4 H, CH_2), 2.65 (m, 2 H, CH_2), 2.72 (t, 3J = 7.4 Hz, 6 H, CH_2), 6.86 (d, 3J = 8.0 Hz, 4 H, CH_{ar}), 7.10 (d, 3J = 7.4 Hz, 2 H, CH_{ar}), 7.16 (t, 3J = 7.3 Hz, 1 H, CH_{ar}), 7.23 (t, 3J = 7.4 Hz, 2 H, CH_{ar}), 7.57 (d, 3J = 8.0 Hz, 4 H,

CH_{ar}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ = 33.6 (t, CH₂), 34.0 (t, CH₂), 55.8 (t, N-CH₂), 56.2 (t, N-CH₂), 91.0 (s, CH_{ar}-I), 126.1 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.2 (d, CH_{ar}), 131.3 (d, CH_{ar}), 137.5 (d, CH_{ar}), 141.1 (s, CH_{ar}), 141.2 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₂₄¹H₂₆¹⁴N₁¹²⁷I₂ 582.0155; found 582.0161; calcd. for ¹²C₂₄¹H₂₄¹⁴N₁¹²⁷I₂ 579.9998; found 580.009. IR (film): ν̄ = 3024 (m), 2947 (s), 2802 (m), 1484 (vs), 1462 (m), 1400 (m), 1201 (m), 1121 (s) cm⁻¹. C₂₄H₂₅I₂N (581.27): calcd. C 49.59, H 4.34, N 2.41, I 43.66; found C 49.33, H 4.45, N 2.47, I 43.83.

Tris[2-(4-iodophenyl)ethyl]amine (36): Starting materials: 2-(4-iodophenyl)ethylamine (31) (6.2 g, 25.09 mmol), 4-(2-bromoethyl)iodobenzene (32) (17.33 g, 55.73 mmol), K₂CO₃ (9.90 g, 71.73 mmol), acetonitrile (200 mL); reaction time: 72 h; column chromatography: silica gel, dichloromethane. Yield: 8.34 g (47%) of **36** as a white solid; m.p. 81 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.61 (t, ³J = 6.0 Hz, 6 H, CH₂), 2.72 (t, ³J = 6.0 Hz, 6 H, CH₂), 6.82 (d, ³J = 8.0 Hz, 6 H, CH_{ar}), 7.57 (d, ³J = 8.0 Hz, 6 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 33.5 (t, CH₂), 55.6 (t, CH₂), 91.1 (s, I-C_{ar}), 131.0 (d, C_{ar}), 137.4 (d, C_{ar}), 140.3 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₂₄¹H₂₅¹²⁷I₃¹⁴N₁ 707.9121; found 707.9161; calcd. for ¹²C₂₄¹H₂₃¹²⁷I₃¹⁴N₁ 705.8965; found 705.9005. IR (KBr): ν̄ = 3440 (b), 2950 (m), 2804 (m), 2106 (w), 1893 (w), 1482 (s), 1452 (m), 1399 (m), 1273 (m), 1213 (m) cm⁻¹. C₂₄H₂₄I₃N (707.17): calcd. C 40.76, H 3.42, N 1.98, I 53.84; found C 40.53, H 3.53, N 2.09, I 53.63.

Tris[2-[5-(2-thienyl)-2-thienyl]ethyl]amine (15): Starting materials: **46** (0.85 g, 4.06 mmol), **44** (2.55 g, 9.33 mmol), K₂CO₃ (1.66 g, 12.01 mmol), acetonitrile (100 mL); reaction time: 64 h; column chromatography: silica gel, petroleum ether/diethyl ether (3:1). Yield: 0.96 g (40%) of **15** as a colorless waxy solid; m.p. 50 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.91 (t, ³J = 6.2 Hz, 2 H, CH₂), 3.01 (t, ³J = 6.2 Hz, 2 H, CH₂), 6.70 (pd, ³J = 3.5 Hz, 3 H, CH_{ar}), 6.98 (d, ³J = 2.8 Hz, 3 H, CH_{ar}), 7.00 (d, ³J = 2.8 Hz, 3 H, CH_{ar}), 7.10 (pd, ³J = 3.5 Hz, 3 H, CH_{ar}), 7.16 (pd, ³J = 5.0 Hz, 3 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 28.5 (t, CH₂), 55.7 (t, CH₂), 123.2 (d, C_{ar}), 123.5 (d, C_{ar}), 124.0 (d, C_{ar}), 125.6 (d, C_{ar}), 127.7 (d, C_{ar}), 135.7 (s, C_{ar}), 137.8 (s, C_{ar}), 142.1 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₃₀¹H₂₈¹⁴N₁³²S₆ 594.0546; found 594.0530. IR (film): ν̄ = 3104 (m), 3067 (m), 2945 (s), 2812 (ms), 1784 (w), 1733 (w), 1588 (w), 1517 (s), 1470 (m), 1426 (s), 1351 (m), 1263 (m) cm⁻¹. C₃₀H₂₇NS₆ (593.93): calcd. C 60.67, H 4.58, N 2.36, S 32.39; found C 60.73, H 4.88, N 2.52, S 32.15.

General Procedure for the Iodination Reaction – Synthesis of 22–24: A three-necked flask was charged with dry tetrahydrofuran and the thiophene compound. The solution was cooled to 0 °C and then 1.6 M *n*BuLi was added through a syringe. The mixture was warmed to room temperature and stirred for 30 min until a brown precipitate formed. Subsequently, the mixture was cooled to –78 °C and under vigorous stirring a solution of iodine in tetrahydrofuran was added dropwise ensuring the temperature did not rise above –70 °C. The reaction mixture was allowed to reach room temperature overnight. For work up hexane was added. The organic layer was washed with a sodium thiosulfate solution and water, dried (MgSO₄), filtered, and the solvent evaporated under reduced pressure. The residue was purified by column chromatography.

2-[2-(5-Iodo-2-thienyl)ethyl]-N,N-bis(2-phenylethyl)ethylamine (22): Starting materials: **7** (4.0 g, 11.94 mmol), 1.6 M *n*BuLi (14.9 mL, 23.84 mmol), iodine (6.07 g, 23.84 mmol), tetrahydrofuran (200 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 3.27 g (59.4%) of **22** as a white solid; m.p. 46–50 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.77–2.84 (m, 4 H, CH₂), 2.84–2.90 (m, 6 H, CH₂), 2.94–3.01 (m, 2 H, CH₂),

6.48 (d, ³J = 3.5 Hz, 1 H, CH_{ar}), 7.07 (d, ³J = 3.5 Hz, 1 H, CH_{ar}), 7.21 (m, 6 H, CH_{ar}), 7.32 (m, 4 H, CH_{ar}) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 28.8 (t, CH₂), 33.6 (t, CH₂), 55.4 (t, N-CH₂), 55.9 (t, N-CH₂), 70.7 (s, I-C_{ar}), 126.2 (d, C_{ar}), 126.6 (d, C_{ar}), 128.4 (d, C_{ar}), 128.9 (d, C_{ar}), 136.4 (d, C_{ar}), 140.5 (s, C_{ar}), 149.2 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₂₂¹H₂₅¹²⁷I₁¹⁴N₁³²S₁ 462.0752; found 462.0755; calcd. for ¹²C₂₂¹H₂₃¹²⁷I₁¹⁴N₁³²S₁ 460.0596; found 460.0594. IR (KBr): ν̄ = 3441 (b), 3083 (w), 3062 (w), 2952 (s), 2930 (s), 2860 (m), 2820 (m), 2214 (w), 1639 (m), 1534 (m), 1453 (m) cm⁻¹.

N,N-Bis[2-(5-iodo-2-thienyl)ethyl]-2-phenylethylamine (23): Starting materials: **8** (6.22 g, 18.22 mmol), 1.6 M *n*BuLi (45.6 mL, 72.96 mmol), iodine (18.37 g, 72.96 mmol), tetrahydrofuran (460 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 8.07 g (87%) of **23** as a yellow oil. ¹H NMR (300 MHz, CD₂Cl₂): δ = 2.81 (m, 8 H, CH₂), 2.94 (t, ³J = 7.3 Hz, 4 H, CH₂), 6.50 (d, ³J = 3.4 Hz, 2 H, CH_{ar}), 7.05 (d, ³J = 3.4 Hz, 2 H, CH_{ar}), 7.18 (t, ³J = 7.3 Hz, 3 H, CH_{ar}), 7.29 (m, 2 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CD₂Cl₂): δ = 28.9 (t, CH₂), 33.8 (t, CH₂), 55.3 (t, N-CH₂), 55.8 (t, N-CH₂), 70.5 (s, I-CH_{ar}), 126.1 (d, CH_{ar}), 126.9 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.0 (d, CH_{ar}), 136.6 (d, CH_{ar}), 140.9 (s, CH_{ar}), 149.8 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₂₀¹H₂₂¹²⁷I₂¹⁴N₁³²S₂ 593.9283; found 593.9260; calcd. for ¹²C₂₀¹H₂₀¹²⁷I₂¹⁴N₁³²S₂ 591.9127; found 591.9137. IR (film): ν̄ = 3024 (m), 2947 (s), 2810 (s), 1602 (w), 1495 (m), 1453 (s), 1432 (s) cm⁻¹.

Tris[2-(5-iodo-2-thienyl)ethyl]amine (24): Starting materials: **9** (5.00 g, 14.40 mmol), 1.6 M *n*BuLi (54.0 mL, 86.45 mmol), iodine (21.93 g, 86.45 mmol), tetrahydrofuran (700 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 6.39 g (61%) of **24** as a white solid; m.p. 76 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.78 (t, ³J = 7.2 Hz, 6 H, CH₂), 2.93 (t, ³J = 7.2 Hz, 6 H, CH₂), 6.47 (d, ³J = 3.3 Hz, 3 H, CH_{ar}), 7.05 (d, ³J = 3.3 Hz, 3 H, CH_{ar}) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 28.5 (t, CH₂), 55.4 (t, CH₂), 70.7 (s, C_{ar}), 126.6 (d, C_{ar}), 136.6 (d, C_{ar}), 149.0 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₁₈¹H₁₉¹²⁷I₃¹⁴N₁³²S₃ 725.7814; found 725.7792; calcd. for ¹²C₁₈¹H₁₇¹²⁷I₃¹⁴N₁³²S₃ 723.7657; found 723.7667. IR (KBr): ν̄ = 3435 (b), 2946 (s), 2841 (s), 2810 (s), 2726 (w), 1456 (m), 1430 (s), 1346 (m), 1221 (m), 1165 (m) cm⁻¹. C₁₈H₁₈I₃NS₃ (725.25): calcd. C 29.81, H 2.50, N 1.93, S 13.26, I 52.49; found C 30.08, H 2.53, N 2.02, S 13.42, I 52.21.

General Procedure for the Sonogashira Coupling Reaction with TMSA – Synthesis of 25–27 and 37–39: The iodides, tetrakis(triphenylphosphane)palladium(0), and copper(I) iodide were suspended in diethylamine and ethynyltrimethylsilane (solution in THF) was added. The reaction mixture was heated at 45 °C for 1 h. For work up the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

2-[5-(Trimethylsilylethynyl)-2-thienyl]-N,N-bis(2-phenylethyl)ethylamine (25): Starting materials: **22** (2.50 g, 5.42 mmol), ethynyltrimethylsilane (1.30 g, 5.8 mmol, 40% solution in THF), tetrakis(triphenylphosphane)palladium(0) (313 mg, 0.27 mmol), copper(I) iodide (103 mg, 0.54 mmol), diethylamine (50 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 2.1 g (88.8%) of **25** as a pale yellow oil. ¹H NMR (500 MHz, CD₂Cl₂): δ = 0.22 (s, 3 H, Si-CH₃), 2.70–2.78 (m, 4 H, CH₂), 2.79–2.84 (m, 6 H, CH₂), 2.87–2.93 (m, 2 H, CH₂), 6.23 (d, ³J = 3.6 Hz, 1 H, CH_{ar}), 7.02 (d, ³J = 3.6 Hz, 1 H, CH_{ar}), 7.17 (m, 6 H, CH_{ar}), 7.26 (m, 4 H, CH_{ar}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ = 0.0 (q, Si-CH₃), 28.9 (t, CH₂), 34.0 (t, CH₂), 55.6 (t, N-CH₂), 56.1 (t, N-CH₂), 98.0 (s, C≡C), 98.2 (s, C≡C), 121.2 (s,

C_{ar}), 125.0 (d, C_{ar}), 126.0 (d, C_{ar}), 128.6 (d, C_{ar}), 129.1 (d, C_{ar}), 132.7 (d, C_{ar}), 141.1 (s, C_{ar}), 146.2 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{27}^{1}H_{34}^{14}N_1^{32}S_1^{28}Si_1$ 432.2181; found 432.2187.

***N,N*-Bis{2-[5-(trimethylsilyl)ethynyl]-2-thienyl}ethyl}-2-phenylethylamine (26):** Starting materials: **23** (2.32 g, 3.91 mmol), ethynyltrimethylsilane (1.74 g, 17.67 mmol, 44% solution in THF), tetrakis(triphenylphosphane)palladium(0) (444 mg, 0.38 mmol), copper(I) iodide (146 mg, 0.77 mmol), diethylamine (50 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 2.1 g (99%) of **26** as a yellow oil. 1H NMR (300 MHz, CD_2Cl_2): δ = 0.23 (s, 18 H, Si-CH₃), 2.74–2.80 (m, 4 H, CH₂), 2.81–2.84 (m, 4 H, CH₂), 2.86–2.94 (m, 4 H, CH₂), 6.64 (d, 3J = 3.5 Hz, 2 H, CH_{ar}), 7.04 (d, 3J = 3.5 Hz, 2 H, CH_{ar}), 7.18 (m, 3 H, CH_{ar}), 7.27 (t, 3J = 9.2 Hz, 4J = 5.5 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = –0.1 (q, Si-CH₃), 28.7 (t, CH₂), 34.0 (t, CH₂), 55.5 (t, N-CH₂), 56.1 (t, N-CH₂), 98.2 (s, C≡C), 98.3 (s, C≡C), 121.3 (s, CH_{ar}), 125.0 (d, CH_{ar}), 126.3 (d, CH_{ar}), 128.7 (d, CH_{ar}), 129.1 (d, CH_{ar}), 132.8 (d, CH_{ar}), 140.8 (s, CH_{ar}), 146.0 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{30}^{1}H_{40}^{14}N_1^{32}S_2^{28}Si_2$ 534.2141; found 534.2138; calcd. for $^{12}C_{30}^{1}H_{38}^{14}N_1^{32}S_2^{28}Si_2$ 532.1984; found 532.2029. IR (KBr): $\tilde{\nu}$ = 3441 (m), 3025 (w), 2953 (s), 2815 (s), 2141 (vs), 1943 (w), 1532 (m), 1497 (m), 1453 (s), 1439 (m), 1248 (s) cm^{-1} . $C_{30}H_{39}NS_2Si_2$ (533.94): calcd. C 67.48, H 7.36, N 2.62; found C 67.48, H 7.52, N 2.86.

Tris{2-[5-(trimethylethylsilyl)ethynyl]-2-thienyl}ethyl}amine (27): Starting materials: **24** (1.81 g, 2.50 mmol), ethynyltrimethylsilane (2.01 g, 8.23 mmol, 44% solution in THF), tetrakis(triphenylphosphane)palladium(0) (372 mg, 0.32 mmol), copper(I) chloride (158 mg, 0.83 mmol), diethylamine (85 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 1.56 g (99%) of **27** as a white solid; m.p. 94 °C. 1H NMR (500 MHz, $CDCl_3$): δ = 0.24 (s, 27 H, CH₃), 2.81 (t, 3J = 7.1 Hz, 6 H, CH₂), 2.91 (t, 3J = 7.1 Hz, 6 H, CH₂), 6.60 (d, 3J = 3.4 Hz, 3 H, CH_{ar}), 7.05 (d, 3J = 3.4 Hz, 3 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.1 (q, Si-CH₃), 28.7 (t, CH₂), 55.4 (t, CH₂), 98.0 (s, C≡C), δ = 98.2 (s, C≡C), 121.4 (s, C_{ar}), 124.9 (d, C_{ar}), 132.6 (d, C_{ar}), 145.1 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{33}^{1}H_{46}^{14}N_1^{32}S_2^{28}Si_3$ 636.2100; found 636.2070; calcd. for $^{12}C_{33}^{1}H_{44}^{14}N_1^{32}S_2^{28}Si_3$ 634.1944; found 634.1923. IR (KBr): $\tilde{\nu}$ = 3451 (b), 2955 (m), 2924 (m), 2824 (w), 2140 (s), 1533 (w), 1459 (m), 1248 (s), 1172 (m), 1158 (m) cm^{-1} . $C_{33}H_{45}NS_3Si_3$ (636.17): calcd. C 62.31, H 7.13, N 2.20, S 15.12; found C 62.52, H 7.29, N 2.37, S 15.11.

2-[4-(Trimethylsilyl)ethynyl]phenyl]-*N,N*-bis[2-(2-thienyl)ethyl]ethylamine (37): Starting materials: **33** (5.00 g, 10.71 mmol), ethynyltrimethylsilane (3.04 g, 13.39 mmol, 44% solution in THF), tetrakis(triphenylphosphane)palladium(0) (309 mg, 0.27 mmol), copper(I) iodide (102 mg, 0.54 mmol), diethylamine (60 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 4.6 g (98%) of **37** as a pale yellow oil. 1H NMR (300 MHz, CD_2Cl_2): δ = 0.28 (s, Si-CH₃), 2.72–2.92 (m, 8 H, CH₂), 2.94–3.05 (m, 4 H, CH₂), 6.82 (d, 3J = 3.0 Hz, 2 H, CH_{ar}), 6.94 (dd, 3J = 5.1 Hz, 3J = 3.0 Hz, 2 H, CH_{ar}), 7.14 (m, 4 H, CH_{ar}), 7.40 (d, 3J = 8.0 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 0.1 (q, Si-CH₃), 28.6 (t, CH₂), 34.2 (t, CH₂), 55.8 (t, N-CH₂), 56.0 (t, N-CH₂), 93.7 (s, C≡C), 105.6 (s, C≡C), 121.0 (s, C_{ar}), 123.6 (d, C_{ar}), 125.0 (d, C_{ar}), 127.0 (d, C_{ar}), 129.2 (d, C_{ar}), 132.0 (d, C_{ar}), 142.0 (s, C_{ar}), 143.5 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{25}^{1}H_{32}^{14}N_1^{32}S_2^{28}Si_1$ 438.1745; found 438.1723; calcd. for $^{12}C_{25}^{1}H_{30}^{14}N_1^{32}S_2^{28}Si_1$ 436.1589; found 436.1604. IR (film): $\tilde{\nu}$ = 3069 (m), 2954 (s), 2808 (s), 2157 (s), 1506 (s), 1461 (m), 1439 (s), 1399 (m), 1353 (m), 1249 (s), 1223 (m) cm^{-1} . $C_{25}H_{31}NS_2Si$ (437.36):

calcd. C 68.60, H 7.14, N 3.20, S 14.65; found C 68.58, H 7.19, N 3.37, S 14.77.

2-[4-(Trimethylsilyl)ethynyl]phenyl]-*N,N*-bis(2-phenylethyl)ethylamine (38): Starting materials: **34** (1.73 g, 3.80 mmol), ethynyltrimethylsilane (1.16 g, 4.74 mmol, 40% solution in THF), tetrakis(triphenylphosphane)palladium(0) (254 mg, 0.22 mmol), copper(I) iodide (84 mg, 0.44 mmol), diethylamine (40 mL); column chromatography: silica gel, petroleum ether/diethyl ether (10:1). Yield: 1.6 g (95%) of **38** as a colorless oil. 1H NMR (300 MHz, CD_2Cl_2): δ = 0.24 (s, 9 H, CH₃), 2.71 (m, 6 H, CH₂), 2.80 (m, 6 H, CH₂), 7.10 (d, 3J = 7.1 Hz, 2 H, CH_{ar}), 7.17 (d, 3J = 7.5 Hz, 4 H, CH_{ar}), 7.20 (t, 3J = 7.5 Hz, 2 H, CH_{ar}), 7.28 (t, 3J = 7.4 Hz, 4 H, CH_{ar}), 7.36 (d, 3J = 8.1 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 0.0 (q, CH₃), 34.1 (t, CH₂), 34.2 (t, CH₂), 55.9 (t, N-CH₂), 56.2 (t, N-CH₂), 93.7 (s, C≡C), 105.4 (s, C≡C), 120.1 (s, C_{ar}), 126.0 (d, C_{ar}), 128.6 (d, C_{ar}), 129.1 (d, C_{ar}), 129.2 (d, C_{ar}), 132.0 (d, C_{ar}), 141.2 (s, C_{ar}), 142.2 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{29}^{1}H_{36}^{14}N_1^{28}Si_1$ 426.2617; found 426.2596; calcd. for $^{12}C_{29}^{1}H_{34}^{14}N_1^{28}Si_1$ 424.2461; found 424.2467. IR (film): $\tilde{\nu}$ = 3026 (s), 2954 (vs), 2861 (m), 2803 (s), 2156 (vs), 1506 (s), 1496 (s), 1453 (s), 1249 (s), 1223 (m), 1121 (s). $C_{29}H_{35}NSi$ (425.68): C 81.82, H 8.29, N 3.29; found C 81.97, H 8.41, N 3.54.

***N,N*-Bis{2-[4-(trimethylsilyl)ethynyl]phenyl}ethyl}-2-phenylethylamine (39):** Starting materials: **35** (4.71 g, 8.10 mmol), ethynyltrimethylsilane (4.60 g, 18.83 mmol, 44% solution in THF), tetrakis(triphenylphosphane)palladium(0) (468 mg, 0.41 mmol), copper(I) iodide (154 mg, 0.81 mmol), diethylamine (50 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 4.11 g (97%) of **39** as a colorless oil. 1H NMR (500 MHz, CD_2Cl_2): δ = 0.23 (s, 18 H, Si-CH₃), 2.67 (m, 6 H, CH₂), 2.76 (m, 6 H, CH₂), 7.06 (d, 3J = 8.1 Hz, 4 H, CH_{ar}), 7.14 (d, 3J = 7.0 Hz, 2 H, CH_{ar}), 7.17 (t, 3J = 7.3 Hz, 1 H, CH_{ar}), 7.27 (t, 3J = 7.0 Hz, 2 H, CH_{ar}), 7.35 (d, 3J = 8.1 Hz, 4 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 0.0 (q, Si-CH₃), 34.1 (t, CH₂), 34.2 (t, CH₂), 55.2 (t, N-CH₂), 55.9 (t, N-CH₂), 93.6 (s, C≡C), 105.3 (s, C≡C), 120.9 (s, CH_{ar}), 126.0 (d, CH_{ar}), 128.6 (d, CH_{ar}), 129.1 (d, CH_{ar}), 129.2 (d, CH_{ar}), 132.0 (d, CH_{ar}), 141.2 (s, CH_{ar}), 142.0 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{34}^{1}H_{44}^{14}N_1^{28}Si_2$ 522.3012; found 522.2976; calcd. for $^{12}C_{34}^{1}H_{42}^{14}N_1^{28}Si_2$ 520.2856; found 520.2818.

Tris{2-[4-(phenylethynyl)phenyl]ethyl}amine (16): Compound **36** (1.34 g, 1.90 mmol), tetrakis(triphenylphosphane)palladium(0) (134 mg, 0.108 mmol), and copper(I) iodide (54 mg, 0.28 mmol) were suspended in triethylamine (60 mL) and 1-ethynylbenzene (1.16 g, 11.36 mmol) was added. The reaction mixture was heated at 80 °C for 1 h. For work up the solvent was evaporated under reduced pressure and the residue was purified by column chromatography [deactivated silica gel, petroleum ether/diethyl ether (3:1)]. Yield: 1.13 g (94%) of **16** as a white solid; m.p. 106 °C. 1H NMR (500 MHz, $CDCl_3$): δ = 2.73 (m, 6 H, CH₂), 2.82 (m, 6 H, CH₂), 7.12 (d, 3J = 8.0 Hz, 6 H, CH_{ar}), 7.30–7.35 (m, 9 H, CH_{ar}), 7.46 (d, 3J = 8.0 Hz, 6 H, CH_{ar}), 7.53 (dd, 3J = 7.1 Hz, 4J = 2.0 Hz, 6 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.0 (t, CH₂), 55.7 (t, CH₂), 89.0 (s, C≡C), 89.5 (s, C≡C), 121.0 (s, C_{ar}), 123.6 (s, C_{ar}), 128.3 (d, C_{ar}), 128.5 (d, C_{ar}), 129.0 (d, C_{ar}), 131.6 (d, C_{ar}), 131.8 (d, C_{ar}), 141.2 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}C_{48}^{1}H_{40}^{14}N_1$ 630.3161; found 630.3145. IR (KBr): $\tilde{\nu}$ = 3447 (b), 3028 (w), 2949 (w), 2791 (w), 2214 (w), 1639 (m), 1510 (s), 1441 (m), 1121 (s). $C_{48}H_{39}N$ (629.83): C 91.53, H 6.24, N 2.22; found C 91.36, H 6.31, N 2.45.

General Procedure for Removal of the TMS Group – Synthesis of 28–30: The TMS-protected compounds were dissolved in tetra-

hydrofuran and an aqueous solution of sodium hydroxide (0.1 N) was added dropwise. After 2 h, the reaction mixture was transferred to a separating funnel and diethyl ether was added to give a clear phase separation. The aqueous phase was extracted with diethyl ether. The organic phases were dried (MgSO_4), filtered, and the solvent evaporated under reduced pressure.

2-(5-Ethynyl-2-thienyl)-*N,N*-bis(2-phenylethyl)ethylamine (28): Starting materials: **25** (2.08 g, 4.81 mmol), 0.1 N solution of sodium hydroxide in water (47.5 mL, 4.75 mmol), tetrahydrofuran (150 mL). Yield: 1.63 g (96%) of **28** as a brown oil. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.84 (m, 12 H, CH_2), 3.30 (s, 1 H, $\text{C}\equiv\text{CH}$), 6.32 (d, 3J = 2.5 Hz, 1 H, CH_{ar}), 7.08 (d, 3J = 3.5 Hz, 1 H, CH_{ar}), 7.18 (m, 6 H, CH_{ar}), 7.28 (m, 4 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 28.6 (t, CH_2), 33.9 (t, CH_2), 55.3 (t, N- CH_2), 55.8 (t, N- CH_2), 77.6 (C $\equiv\text{C}$), 80.7 (C $\equiv\text{C}$), 120.2 (s, C_{ar}), 124.8 (d, C_{ar}), 126.2 (d, C_{ar}), 128.4 (d, C_{ar}), 128.7 (d, C_{ar}), 133.0 (d, C_{ar}), 140.5 (s, C_{ar}), 145.6 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{24}^{1}\text{H}_{26}^{14}\text{N}_1^{32}\text{S}_1$ 360.1786; found 360.1794; calcd. for $^{12}\text{C}_{24}^{1}\text{H}_{24}^{14}\text{N}_1^{32}\text{S}_1$ 358.1629; found 358.1638.

***N,N*-Bis[2-(5-ethynyl-2-thienyl)ethyl]-2-phenylethylamine (29):** Starting materials: **26** (1.0 g, 1.87 mmol), 0.1 N solution of sodium hydroxide in water (37.0 mL, 3.7 mmol), tetrahydrofuran (60 mL). Yield: 692 mg (95%) of **29** as a brown oil. ^1H NMR (300 MHz, CD_2Cl_2): δ = 2.74–2.87 (m, 8 H, CH_2), 2.87–2.96 (m, 4 H, CH_2), 3.35 (s, 2 H, $\text{C}\equiv\text{CH}$), 6.64 (d, 3J = 3.6 Hz, 2 H, CH_{ar}), 7.09 (d, 3J = 3.6 Hz, 2 H, CH_{ar}), 7.18 (dd, 3J = 7.1 Hz, 4J = 5.0 Hz, 3 H, CH_{ar}), 7.25 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.7 (t, CH_2), 34.0 (t, CH_2), 55.6 (t, N- CH_2), 56.1 (t, N- CH_2), 77.5 (C $\equiv\text{C}$), 80.6 (C $\equiv\text{C}$), 120.0 (s, CH_{ar}), 125.1 (d, CH_{ar}), 126.3 (d, CH_{ar}), 128.7 (d, CH_{ar}), 129.1 (d, CH_{ar}), 133.3 (d, CH_{ar}), 140.8 (s, CH_{ar}), 146.2 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{24}^{1}\text{H}_{24}^{14}\text{N}_1^{32}\text{S}_2$ 390.1350; found 390.1320; calcd. for $^{12}\text{C}_{24}^{1}\text{H}_{22}^{14}\text{N}_1^{32}\text{S}_2$ 388.1194; found 388.1183.

Tris[2-(5-ethynyl-2-thienyl)ethyl]amine (30): Starting materials: **27** (1.40 g, 2.20 mmol), 0.1 N solution of sodium hydroxide in water (66.0 mL, 6.6 mmol), tetrahydrofuran (480 mL). Yield: 0.92 g (99%) of **30** as an orange oil. ^1H NMR (500 MHz, CDCl_3): δ = 2.83 (t, 3J = 7.0 Hz, 6 H, CH_2), 2.93 (t, 3J = 7.0 Hz, 6 H, CH_2), 3.30 (s, 3 H, $\text{C}\equiv\text{C-H}$), 6.64 (d, 3J = 3.4 Hz, 3 H, CH_{ar}), 7.08 (d, 3J = 3.4 Hz, 3 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 28.6 (t, CH_2), 55.3 (t, CH_2), 77.5 (C $\equiv\text{C}$), 80.8 (C $\equiv\text{C}$), 120.2 (s, C_{ar}), 124.8 (d, C_{ar}), 133.0 (d, C_{ar}), 145.0 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{24}^{1}\text{H}_{22}^{14}\text{N}_1^{32}\text{S}_3$ 420.0914; found 420.0869; calcd. for $^{12}\text{C}_{24}^{1}\text{H}_{20}^{14}\text{N}_1^{32}\text{S}_3$ 418.0758; found 418.0744.

General Procedure for Removal of the TMS Group – Synthesis of 40–42: The TMS-protected compounds were dissolved in a mixture of methanol and tetrahydrofuran. Subsequently a concentrated solution of potassium hydroxide was added. After 2 h the reaction mixture was transferred to a separating funnel and the organic layer was washed with water. Diethyl ether was added to give a clear phase separation. The aqueous phase was extracted with diethyl ether. The organic phases were dried (MgSO_4), filtered, the solvent evaporated under reduced pressure, and the residue purified by column chromatography.

2-(4-Ethynylphenyl)-*N,N*-bis[2-(2-thienyl)ethyl]ethylamine (40): Starting materials: **37** (4.0 g, 9.15 mmol), potassium hydroxide (767 mg, 13.69 mmol), tetrahydrofuran (35 mL), methanol (500 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 2.66 g (66.5%) of **40** as a brown oil. ^1H NMR (300 MHz, CD_2Cl_2): δ = 2.72–2.80 (m, 4 H, CH_2), 2.81–2.88 (m, 4 H, CH_2), 2.90–3.00 (m, 4 H, CH_2), 3.09 (s, 1 H, $\text{C}\equiv\text{CH}$), 6.78 (d, 3J = 3.2 Hz, 2 H, CH_{ar}), 6.90 (dd, 3J =

5.1 Hz, 3J = 3.2 Hz, 2 H, CH_{ar}), 7.12 (m, 4 H, CH_{ar}), 7.39 (d, 3J = 8.1 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.5 (t, CH_2), 34.0 (t, CH_2), 55.9 (t, N- CH_2), 56.0 (t, N- CH_2), 76.7 (d, $\text{C}\equiv\text{CH}$), 84.0 (s, $\text{C}\equiv\text{C}$), 119.7 (s, C_{ar}), 123.6 (d, C_{ar}), 125.0 (d, C_{ar}), 126.8 (d, C_{ar}), 129.1 (d, C_{ar}), 132.2 (d, C_{ar}), 142.2 (s, C_{ar}), 143.5 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{22}^{1}\text{H}_{24}^{14}\text{N}_1^{32}\text{S}_2$ 366.1350; found 366.1308; calcd. for $^{12}\text{C}_{22}^{1}\text{H}_{22}^{14}\text{N}_1^{32}\text{S}_2$ 364.1194; found 364.1186. IR (film): $\tilde{\nu}$ = 3289 (s), 3105 (w), 3068 (w), 3027 (w), 2947 (s), 2808 (s), 2106 (w), 1909 (w), 1792 (w), 1607 (w), 1507 (s), 1460 (m), 1353 (m), 1248 (s), 1223 (m), 1160 (m) cm^{-1} . $\text{C}_{22}\text{H}_{23}\text{NS}_2$ (365.56): calcd. C 72.28, H 6.34, N 3.83, S 17.54; found C 72.27, H 6.42, N 3.93, S 17.35.

2-(4-Ethynylphenyl)-*N,N*-bis(2-phenylethyl)ethylamine (41): Starting materials: **38** (1.17 g, 2.75 mmol), potassium hydroxide (193 mg, 3.44 mmol), tetrahydrofuran (45 mL), methanol (125 mL); column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 0.88 g (91%) of **41** as a white solid; m.p. 38 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.73 (m, 6 H, CH_2), 2.80 (m, 6 H, CH_2), 3.10 (s, 1 H, $\text{C}\equiv\text{CH}$), 7.11 (d, 3J = 7.8 Hz, 2 H, CH_{ar}), 7.17 (d, 3J = 7.5 Hz, 4 H, CH_{ar}), 7.20 (pd, 3J = 7.1 Hz, 2 H, CH_{ar}), 7.28 (t, 3J = 7.4 Hz, 4 H, CH_{ar}), 7.40 (d, 3J = 7.9 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 34.06 (t, CH_2), 34.1 (t, CH_2), 55.7 (t, N- CH_2), 56.2 (t, N- CH_2), 76.7 (d, $\text{C}\equiv\text{CH}$), 83.8 (s, $\text{C}\equiv\text{C}$), 119.6 (s, C_{ar}), 126.0 (d, C_{ar}), 128.4 (d, C_{ar}), 129.1 (d, C_{ar}), 129.2 (d, C_{ar}), 132.1 (d, C_{ar}), 141.2 (s, C_{ar}), 142.5 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{26}^{1}\text{H}_{28}^{14}\text{N}_1$ 354.2222; found 354.2232; calcd. for $^{12}\text{C}_{26}^{1}\text{H}_{26}^{14}\text{N}_1$ 352.2065; found 352.2080. IR (film): $\tilde{\nu}$ = 3289 (s), 3061 (m), 3026 (s), 2947 (s), 2860 (m), 2804 (s), 2106 (w), 1602 (m), 1496 (s), 1452 (s), 1354 (m), 1121 (s) cm^{-1} . $\text{C}_{26}\text{H}_{27}\text{N}$ (353.50): calcd. C 88.34, H 7.70, N 3.96; found C 88.25, H 7.69, N 4.14.

***N,N*-Bis[2-(4-ethynylphenyl)ethyl]-2-phenylethylamine (42):** Starting materials: **39** (2.00 g, 3.82 mmol), potassium hydroxide (538 mg, 9.58 mmol), tetrahydrofuran (10 mL), methanol (200 mL). Yield: 1.36 g (94%) of **42** as a brown oil. ^1H NMR (300 MHz, CD_2Cl_2): δ = 2.70 (m, 6 H, CH_2), 2.77 (m, 6 H, CH_2), 3.08 (s, 2 H, $\text{C}\equiv\text{CH}$), 7.09 (d, 3J = 8.1 Hz, 4 H, CH_{ar}), 7.23 (d, 3J = 7.2 Hz, 2 H, CH_{ar}), 7.19 (t, 3J = 7.2 Hz, 1 H, CH_{ar}), 7.25 (t, 3J = 7.2 Hz, 2 H, CH_{ar}), 7.37 (d, 3J = 8.1 Hz, 4 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 34.11 (t, CH_2), 34.13 (t, CH_2), 55.7 (t, N- CH_2), 56.0 (t, N- CH_2), 76.7 (d, $\text{C}\equiv\text{CH}$), 83.8 (s, $\text{C}\equiv\text{C}$), 119.8 (s, CH_{ar}), 126.2 (d, CH_{ar}), 128.6 (d, CH_{ar}), 129.1 (d, CH_{ar}), 129.2 (d, CH_{ar}), 132.3 (d, CH_{ar}), 141.2 (s, CH_{ar}), 142.3 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{28}^{1}\text{H}_{28}^{14}\text{N}_1$ 378.2222; found 378.2208; calcd. for $^{12}\text{C}_{28}^{1}\text{H}_{26}^{14}\text{N}_1$ 376.2065; found 376.2041.

General Procedure for Alkyne–Alkyne Coupling – Synthesis of 10–12: Copper(I) chloride was suspended in pyridine and the components to be coupled were added. Afterwards air was bubbled through the suspension for 24 h. For work up the pyridine was removed and the residue was purified by column chromatography.

1,4-Bis(4-{2-[bis(2-phenylethyl)amino]ethyl}phenyl)buta-1,3-diyne (10): Starting materials: **41** (3.5 g, 9.90 mmol), copper(I) chloride (386 mg, 3.90 mmol), pyridine (400 mL). Column chromatography: deactivated silica gel, petroleum ether/diethyl ether (1:1). Yield: 3.42 g (97%) of **10** as a colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 2.77–2.80 (m, 12 H, CH_2), 2.80–2.90 (m, 12 H, CH_2), 7.10 (d, 3J = 7.4 Hz, 4 H, CH_{ar}), 7.17 (d, 3J = 6.2 Hz, 8 H, CH_{ar}), 7.19–7.24 (m, 4 H, CH_{ar}), 7.25–7.33 (m, 8 H, CH_{ar}), 7.45 (d, 3J = 7.4 Hz, 4 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 33.8 (t, CH_2), 34.0 (t, CH_2), 55.6 (t, N- CH_2), 56.0 (t, N- CH_2), 73.8 (s, $\text{C}\equiv\text{C}$), 81.6 (s, $\text{C}\equiv\text{C}$), 119.5 (s, C_{ar}), 126.0 (d, C_{ar}), 128.4 (d, C_{ar}), 128.9 (d, C_{ar}), 129.1 (d, C_{ar}), 132.5 (d, C_{ar}), 140.6 (s, C_{ar}), 142.2 (s, C_{ar}) ppm.

HRMS (FAB+): calcd. for $^{12}\text{C}_{52}^{1}\text{H}_{53}^{14}\text{N}_2$ 705.4209; found 705.4244. IR (film): $\tilde{\nu}$ = 3061 (m), 3026 (s), 2947 (s), 2860 (m), 2804 (s), 2115 (w), 2145 (w), 1603 (s), 1495 (s), 1453 (s), 1354 (m), 1265 (m), 1177 (m), 1121 (s) cm^{-1} . $\text{C}_{52}\text{H}_{52}\text{N}_2$ (704.98): calcd. C 88.59, H 7.43, N 3.97; found C 88.50; H 7.46, N 4.11.

1,4-Bis(5-{2-[bis(2-phenylethyl)amino]ethyl}-2-thienyl)buta-1,3-diyne (11): Starting materials: **28** (1.63 g, 4.53 mmol), copper(I) chloride (159 mg, 1.61 mmol), pyridine (200 mL). Column chromatography: deactivated silica gel, petroleum ether/diethyl ether (5:1). Yield: 0.924 g (56.9%) of **11** as a yellow solid; m.p. 53–55 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.74 (m, 8 H, CH_2), 2.81 (m, 12 H, CH_2), 2.91 (t, 3J = 6.7 Hz, 4 H, CH_2), 6.66 (d, 3J = 3.5 Hz, 2 H, CH_{ar}), 7.17 (m, 14 H, CH_{ar}), 7.26 (m, 8 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 29.0 (t, CH_2), 34.0 (t, CH_2), 55.3 (t, N- CH_2), 56.1 (t, N- CH_2), 77.4 (s, $\text{C}\equiv\text{C}$), 77.5 (s, $\text{C}\equiv\text{C}$), 120.0 (s, C_{ar}), 125.4 (d, C_{ar}), 126.2 (d, C_{ar}), 128.6 (d, C_{ar}), 129.1 (d, C_{ar}), 134.6 (d, C_{ar}), 141.1 (s, C_{ar}), 148.3 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{48}^{1}\text{H}_{49}^{14}\text{N}_2^{32}\text{S}_2$ 717.3337; found 717.3280; calcd. for $^{12}\text{C}_{48}^{1}\text{H}_{47}^{14}\text{N}_2^{32}\text{S}_2$ 715.3181; found 715.3176. IR (KBr): $\tilde{\nu}$ = 3447 (b), 3023 (m), 2942 (s), 2859 (m), 2824 (s), 2136 (m), 1600 (m), 1496 (m), 1451 (s), 1352 (m), 1319 (s) cm^{-1} . $\text{C}_{48}\text{H}_{48}\text{N}_2\text{S}_2$ (717.04): calcd. C 80.40, H 6.75, N 3.91, S 8.94; found C 80.27, H 6.63, N 3.98, S 9.08.

1,4-Bis[4-(2-{bis[2-(2-thienyl)ethyl]amino}ethyl)phenyl]buta-1,3-diyne (12): Starting materials: **40** (2.00 g, 2.75 mmol), copper(I) chloride (110 mg, 1.10 mmol), pyridine (110 mL). Column chromatography: deactivated silica gel, petroleum ether/diethyl ether (4:1). Yield: 1.91 g (95.3%) of **12** as a pale yellow solid; m.p. 49 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ = 2.82 (m, 16 H, CH_2), 2.96 (m, 8 H, CH_2), 6.78 (d, 3J = 3.3 Hz, 4 H, CH_{ar}), 6.92 (dd, 3J = 5.1 Hz, 4J = 3.3 Hz, 4 H, CH_{ar}), 7.13 (dd, 3J = 5.1 Hz, 4J = 1.0 Hz, 4 H, CH_{ar}), 7.16 (d, 3J = 8.1 Hz, 4 H, CH_{ar}), 7.42 (d, 3J = 8.1 Hz, 4 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.3 (t, CH_2), 34.2 (t, CH_2), 55.8 (t, N- CH_2), 56.1 (t, N- CH_2), 73.5 (s, $\text{C}\equiv\text{C}$), 81.7 (s, $\text{C}\equiv\text{C}$), 119.4 (s, C_{ar}), 123.4 (d, C_{ar}), 125.0 (d, C_{ar}), 126.9 (d, C_{ar}), 129.4 (d, C_{ar}), 132.7 (d, C_{ar}), 143.0 (s, C_{ar}), 143.3 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{44}^{1}\text{H}_{45}^{14}\text{N}_2^{32}\text{S}_4$ 729.2466; found 729.2397; calcd. for $^{12}\text{C}_{44}^{1}\text{H}_{43}^{14}\text{N}_2^{32}\text{S}_4$ 727.2309; found 727.2310. IR (KBr): $\tilde{\nu}$ = 3440 (b), 3068 (w), 2947 (s), 2933 (s), 2808 (s), 2210 (w), 2144 (w), 1913 (w), 1792 (w), 1628 (m), 1602 (m), 1503 (s), 1438 (s), 1349 (m), 1247 (m) cm^{-1} . $\text{C}_{42}\text{H}_{44}\text{N}_2\text{S}_4$ (729.09): calcd. C 72.48, H 6.08, N 3.84, S 17.59; found C 72.27, H 6.05, N 3.98, S 17.53.

General Procedure for Alkyne–Alkyne Coupling – Synthesis of 13, 14, and 17: Copper(I) chloride was suspended in pyridine and the components to be coupled were dissolved in pyridine (20 mL) and added to the suspension within 24 h while air was bubbled through. For work up the pyridine was removed and the residue was purified by column chromatography.

1,12-Bis(2-phenylethyl)-1,12-diaza-4,9,15,20(1,4)-tetrabenzenacyclocosaphane-5,7,16,18-tetrayne (13): Starting materials: **42** (1.00 g, 2.65 mmol), copper(I) chloride (210 mg, 2.12 mmol), pyridine (200 mL). Column chromatography: basic alumina, activity III, hot toluene. Yield: 73 mg (8%) of **13** as a pale yellow waxy solid. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.70 (m, 12 H, CH_2), 2.79 (m, 12 H, CH_2), 7.12 (m, 10 H, CH_{ar}), 7.17 (t, 3J = 7.2 Hz, 4 H, CH_{ar}), 7.27 (m, 4 H, CH_{ar}), 7.43 (d, 3J = 7.2 Hz, 8 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 34.0 (t, CH_2), 34.1 (t, CH_2), 55.7 (t, N- CH_2), 56.0 (t, N- CH_2), 73.7 (s, $\text{C}\equiv\text{C}$), 81.7 (d, $\text{C}\equiv\text{C}$), 119.2 (s, CH_{ar}), 126.2 (d, CH_{ar}), 128.6 (d, CH_{ar}), 129.1 (d, CH_{ar}), 129.4 (d, CH_{ar}), 132.7 (d, CH_{ar}), 141.0 (s, CH_{ar}), 143.0 (s, CH_{ar}) ppm.

HRMS (FAB+): calcd. for $^{12}\text{C}_{56}^{1}\text{H}_{51}^{14}\text{N}_2$ 751.4052; found 751.4070; calcd. for $^{12}\text{C}_{56}^{1}\text{H}_{49}^{14}\text{N}_2$ 749.3896; found 749.3942.

1,12-Bis(2-phenylethyl)-1,12-diaza-4,9,15,20(2,5)-tetrathiophenacyclocosaphane-5,7,16,18-tetrayne (14): Starting materials: **29** (700 mg, 1.85 mmol), copper(I) chloride (72 mg, 0.73 mmol), pyridine (60 mL). Column chromatography: basic alumina, activity III, dichloromethane. Yield: 21 mg (6%) of **14** as a brown waxy solid. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.73–2.85 (m, 16 H, CH_2), 2.86–2.97 (m, 8 H, CH_2), 6.62–6.70 (m, 4 H, CH_{ar}), 7.14–7.21 (m, 10 H, CH_{ar}), 7.27 (pd, 3J = 6.8 Hz, 4 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 29.0 (t, CH_2), 33.8 (t, CH_2), 55.4 (t, N- CH_2), 55.8 (t, N- CH_2), 77.3 (s, $\text{C}\equiv\text{C}$), 77.5 (s, $\text{C}\equiv\text{C}$), 120.0 (s, CH_{ar}), 125.4 (d, CH_{ar}), 126.1 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.0 (d, CH_{ar}), 134.6 (d, CH_{ar}), 140.7 (s, CH_{ar}), 148.0 (s, CH_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{48}^{1}\text{H}_{43}^{14}\text{N}_2^{32}\text{S}_4$ 775.2309; found 775.2223.

1,12-Diaza-4,9,15,20,25,30(2,5)-hexathiophenabicyclo[10.10.10]-dotriacontaphane-5,7,16,18,26,28-hexayne (17): Starting materials: **30** (920 g, 2.19 mmol), copper(I) chloride (320 mg, 3.23 mmol), pyridine (400 mL). Column chromatography: basic alumina, activity III, dichloromethane. Yield: 18 mg (<2%) of **17** as a brown solid. ^1H NMR (500 MHz, CDCl_3): δ = 2.58 (m, 12 H, CH_2), 2.75 (m, 12 H, CH_2), 6.51 (d, 3J = 3.7 Hz, 6 H, CH_{ar}), 7.10 (d, 3J = 3.7 Hz, 6 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 27.7 (t, CH_2), 55.4 (t, CH_2), 76.4 (s, $\text{C}\equiv\text{C}$), 76.8 (s, $\text{C}\equiv\text{C}$), 120.3 (s, C_{ar}), 124.1 (d, C_{ar}), 134.1 (d, C_{ar}), 147.4 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{48}^{1}\text{H}_{39}^{14}\text{N}_2^{32}\text{S}_6$ 835.1437; found 835.1281; calcd. for $^{12}\text{C}_{48}^{1}\text{H}_{37}^{14}\text{N}_2^{32}\text{S}_6$ 833.1281; found 833.1303.

2-{2-[5-(2-Thienyl)-2-thienyl]ethyl}isoindoline-1,3-dione (45): Potassium phthalimide (6.75 g, 36.44 mmol) and **43** (8.75 g, 30.40 mmol) were suspended in dimethylformamide (250 mL) and heated at 90 °C for 4 h. After cooling to room temperature the mixture was poured into water and the precipitate was filtered off and washed with water. The white solid was dried with silica gel in an exsiccator. Yield: 9.27 g (90%) of **45** as a white solid; m.p. 146 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.18 (t, 3J = 7.2 Hz, 2 H, CH_2), 3.96 (t, 3J = 7.2 Hz, 2 H, CH_2), 6.76 (d, 3J = 3.6 Hz, 1 H, CH_{ar}), 6.96 (pt, 3J = 3.6 Hz, 2 H, CH_{ar}), 7.08 (dd, 3J = 3.6 Hz, 4J = 1.0 Hz, 1 H, CH_{ar}), 7.15 (dd, 3J = 5.0 Hz, 4J = 1.0 Hz, 1 H, CH_{ar}), 7.70 (dd, 3J = 5.5 Hz, 3J = 3.1 Hz, 2 H, CH_{ar}), 7.83 (dd, 3J = 5.5 Hz, 4J = 3.0 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 28.8 (t, CH_2), 39.1 (t, CH_2), 123.4 (d, C_{ar}), 123.5 (d, C_{ar}), 123.6 (d, C_{ar}), 124.2 (d, C_{ar}), 126.5 (d, C_{ar}), 127.7 (d, C_{ar}), 132.0 (s, C_{ar}), 134.0 (d, C_{ar}), 136.3 (s, C_{ar}), 137.5 (s, C_{ar}), 139.4 (s, C_{ar}), 168.2 (s, CO) ppm. HRMS (FAB+): calcd. for $^{12}\text{C}_{18}^{1}\text{H}_{14}^{14}\text{N}_1^{16}\text{O}_2^{32}\text{S}_2$ 340.0466; found 340.0447; calcd. for $^{12}\text{C}_{18}^{1}\text{H}_{13}^{14}\text{N}_1^{16}\text{O}_2^{32}\text{S}_2$ 339.0388; found 339.0404. IR (KBr): $\tilde{\nu}$ = 3459 (b), 3102 (w), 2933 (w), 1773 (m), 1713 (vs), 1444 (s), 1428 (s), 1332 (w), 1084 (s) cm^{-1} . $\text{C}_{18}\text{H}_{13}\text{NO}_2\text{S}_2$ (339.43): calcd. C 63.69, H 3.86, N 4.13; found C 63.51, H 3.88, N 4.33.

2-[5-(2-Thienyl)-2-thienyl]ethylamine (46): Hydrazine hydrate (3.5 mL, 72.76 mmol) was added to a solution of **45** (9.27 g, 27.31 mmol) in ethanol (300 mL) and the mixture was then refluxed for 4 h. After cooling the mixture to room temperature, sodium ethoxide (1.86 g, 27.33 mmol) was added and the mixture was refluxed for another 30 min. Subsequently, the reaction mixture was cooled in an ice bath and the precipitating solid was filtered off. Water was added to the filtrate and the mixture was extracted with dichloromethane several times. The organic phases were dried with magnesium sulfate and the solvent was evaporated. Yield: 5.45 g (95.4%) of **46** as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.33 (s, 2 H, NH_2), 2.92 (m, 2 H, CH_2), 2.98 (t, 3J =

5.7 Hz, 2 H, CH₂), 6.72 (d, ³J = 3.5 Hz, 1 H, CH_{ar}), 6.98 (m, 2 H, CH_{ar}), 7.09 (d, ³J = 3.5 Hz, 1 H, CH_{ar}), 7.16 (d, ³J = 5.1 Hz, 1 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 34.4 (t, CH₂), 43.7 (t, CH₂), 123.2 (d, C_{ar}), 123.5 (d, C_{ar}), 124.1 (d, C_{ar}), 126.0 (d, C_{ar}), 127.7 (d, C_{ar}), 135.6 (s, C_{ar}), 137.8 (s, C_{ar}), 141.9 (s, C_{ar}) ppm.

2-(2-Bromoethyl)-5-(2-thienyl)thiophene (44): Compound **43** (3.0 g, 10.43 mmol) and lithium bromide (1.81 g, 20.83 mmol) were dissolved in acetone (100 mL) and refluxed for 12 h. The mixture was cooled to room temperature and poured into water. The phases were separated and the aqueous phase was extracted with dichloromethane several times. The organic phases were dried with magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography (silica gel, petroleum ether). Yield: 2.57 g (90.3%) of **44** as a pale green oil. ¹H NMR (300 MHz, CDCl₃): δ = 3.35 (t, ³J = 7.2 Hz, 2 H, CH₂), 3.59 (t, ³J = 7.2 Hz, 2 H, CH₂), 6.80 (d, ³J = 3.1 Hz, 1 H, CH_{ar}), 7.01 (m, 2 H, CH_{ar}), 7.14 (d, ³J = 3.0 Hz, 1 H, CH_{ar}), 7.20 (d, ³J = 5.0 Hz, 1 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 32.2 (t, CH₂), 33.7 (t, CH₂), 123.626 (d, C_{ar}), 123.632 (d, C_{ar}), 124.4 (d, C_{ar}), 126.6 (d, C_{ar}), 127.9 (d, C_{ar}), 136.4 (s, C_{ar}), 137.5 (s, C_{ar}), 140.2 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₁₀¹H₉⁷⁹Br¹³²S₂ 273.9309; found 273.9319; calcd. for ¹²C₁₀¹H₉⁷⁹Br¹³²S₂ 271.9329; found 271.9351. IR (KBr): ν̄ = 3102 (w), 3068 (w), 2962 (w), 1522 (w), 1471 (w), 1431 (m), 1270 (m), 1215 (s) cm⁻¹.

General Procedure for the Preparation of Silver(I) Triflates of 9, 10, and 16: The reactions were carried out in Schlenk flasks within a glove box under an argon atmosphere. Silver triflate was dissolved in dry degassed dichloromethane and afterwards the ligand was added. The mixture was stirred for 2 h. The reaction flask was protected with aluminium foil to exclude light. For work up, the solution was filtered off and the solvent was removed under reduced pressure.

{Ag⁺·C[Tris[2-(2-thienyl)ethyl]amine}trifluoromethanesulfonate [9·AgCF₃SO₃]: Starting materials: **9** (100 mg, 0.288 mmol), silver(I) triflate (77 mg, 0.300 mmol), dichloromethane (40 mL). Yield: 174 mg (100%) of [9·AgCF₃SO₃] as colorless crystals. ¹H NMR (500 MHz, CD₂Cl₂): δ = 2.88–2.97 (m, 12 H, CH₂), 6.43 (d, ³J = 3.1 Hz, 3 H, CH_{ar}), 7.00 (dd, ³J = 4.6 Hz, ⁴J = 3.1 Hz, 3 H, CH_{ar}), 7.41 (d, ³J = 4.6 Hz, 3 H, CH_{ar}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ = 28.4 (t, CH₂), 58.4 (t, CH₂), 120.5 (s, C_{ar}), 126.8 (d, C_{ar}), 129.0 (d, C_{ar}), 143.8 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₁₈¹H₂₁¹⁴N₁³²S₃¹⁰⁹Ag₁ 455.9884; found 455.9914; calcd. for ¹²C₁₈¹H₂₁¹⁴N₁³²S₃¹⁰⁷Ag₁ 453.9887; found 453.9904.

[Ag⁺·2,1,4-Bis(4-{2-[bis(2-phenylethyl)amino]ethyl}phenyl)buta-1,3-diyne]bis(trifluoromethanesulfonate) [10·2AgCF₃SO₃]: Starting materials: **10** (100 mg, 0.142 mmol), silver(I) triflate (84 mg, 0.325 mmol), dichloromethane (50 mL). Yield: 173 mg (100%) of [10·2AgCF₃SO₃] as a pale brown solid. ¹H NMR (300 MHz, CD₂Cl₂): δ = 2.70–2.82 (m, 12 H, CH₂), 2.90–3.02 (m, 12 H, CH₂), 6.94 (dd, ³J = 6.3 Hz, ⁴J = 2.8 Hz, 8 H, CH_{ar}), 6.98 (d, ³J = 8.0 Hz, 4 H, CH_{ar}), 7.35–7.41 (m, 12 H, CH_{ar}), 7.48 (d, ³J = 8.0 Hz, 4 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CD₂Cl₂): δ = 32.9 (t, CH₂), 33.4 (t, CH₂), 57.4 (t, N-CH₂), 57.5 (t, N-CH₂), 74.8 (s, C≡C), 81.1 (s, C≡C), 120.7 (s, C_{ar}), 124.2 (d, C_{ar}), 126.0 (d, C_{ar}), 127.7 (d, C_{ar}), 130.6 (d, C_{ar}), 133.8 (d, C_{ar}), 138.5 (s, C_{ar}), 140.6 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₅₃¹H₅₂¹⁹F₃¹⁴N₂¹⁶O₃³²S₁¹⁰⁹Ag₂ 1071.1741; found 1071.1792; calcd. for ¹²C₅₃¹H₅₂¹⁹F₃¹⁴N₂¹⁶O₃³²S₁¹⁰⁷Ag₂ 1069.1749; found 1069.1809; calcd. for ¹²C₅₃¹H₅₂¹⁹F₃¹⁴N₂¹⁶O₃³²S₁¹⁰⁷Ag₂ 1067.1749; found 1067.1768.

[Ag⁺·C[Tris[2-[4-(phenylethynyl)phenyl]ethyl]amine]trifluoromethanesulfonate [16·AgCF₃SO₃]: Starting materials: **16** (50 mg, 0.079 mmol), silver(I) triflate (23 mg 0.090 mmol), dichloromethane

(35 mL). Yield: 70 mg (100%) of [16·AgCF₃SO₃] as a pale brown solid. ¹H NMR (300 MHz, CD₂Cl₂): δ = 2.70–2.78 (m, 6 H, CH₂), 2.78–2.85 (m, 6 H, CH₂), 7.03 (d, ³J = 7.5 Hz, 6 H, CH_{ar}), 7.21–7.38 (m, 9 H, CH_{ar}), 7.47 (d, ³J = 6.8 Hz, 6 H, CH_{ar}), 7.53 (d, ³J = 7.5 Hz, 6 H, CH_{ar}) ppm. ¹³C NMR (75 MHz, CD₂Cl₂): δ = 33.0 (t, CH₂), 57.3 (t, CH₂), 88.1 (s, C≡C), 90.8 (s, C≡C), 122.7 (s, C_{ar}), 122.9 (s, C_{ar}), 125.7 (d, C_{ar}), 128.7 (d, C_{ar}), 128.8 (d, C_{ar}), 131.8 (d, C_{ar}), 132.9 (d, C_{ar}), 138.9 (s, C_{ar}) ppm. HRMS (FAB+): calcd. for ¹²C₄₈¹H₃₉¹⁴N₁¹⁰⁷Ag₁ 738.2130; found 738.2129; calcd. for ¹²C₄₈¹H₃₉¹⁴N₁¹⁰⁹Ag₁ 736.2133; found 736.2112.

X-ray Structure Analyses: The reflections were collected with a Bruker Smart CCD diffractometer at 200 K (**22**, **24**, **35**, **41**, [9·Ag]⁺) or 233 K (**12**) and with a Bruker APEX diffractometer (**7**, **15**, **16**, **17**, **36**) at 100 K. Mo-K_α radiation was used and sets of 0.3° ω scans were recorded, covering a whole sphere in reciprocal space in all cases. Intensities were corrected for Lorentzian and polarization effects, and empirical absorption corrections were applied using SADABS^[35] based on the Laue symmetry of the reciprocal space. Structures were solved by direct methods and refined against F² with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package.^[36] Hydrogen atoms were treated using appropriate riding models (**7**, **12**, **22**, **24**, **35**, **36**, **41**, [9·Ag]⁺) or refined isotropically (**16**, **17**).

CCDC-606494–CCDC-606504 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7: Colorless crystal (irregular), dimensions 0.26 × 0.25 × 0.23 mm, crystal system triclinic, space group *P* $\bar{1}$, *Z* = 2, *a* = 9.8690(14), *b* = 11.8611(16), *c* = 12.0762(16) Å, *α* = 93.516(3), *β* = 108.503(3), *γ* = 106.151(3)°, *V* = 1270.1(3) Å³, *ρ* = 1.194 g cm⁻³, *T* = 100(2) K, *Θ*_{max} = 23.25°, 8511 reflections measured, 3563 unique [*R*(int) = 0.0272], 2815 observed [*I* > 2σ(*I*)], *μ* = 0.15 mm⁻¹, *T*_{min} = 0.96, *T*_{max} = 0.97, 376 parameters refined, the position of the thiophenyl group was evenly interchanged with the position of a phenyl group, a stoichiometric amount of 2-phenylethylamine was found to have co-crystallized, goodness of fit = 1.05 for observed reflections, final residual values *R*₁(*F*) = 0.056, *wR*(*F*²) = 0.150 for observed reflections, residual electron density −0.56 to 0.33 e Å⁻³. CCDC-606494.

12: Colorless crystal (lamina), dimensions 0.66 × 0.24 × 0.02 mm, crystal system monoclinic, space group *P*₂₁/*c*, *Z* = 4, *a* = 20.9767(5), *b* = 6.0647(2), *c* = 15.1831(1) Å, *β* = 102.786(2)°, *V* = 1883.66(8) Å³, *ρ* = 1.285 g cm⁻³, *T* = 233(2) K, *Θ*_{max} = 21.53°, 11023 reflections measured, 2172 unique [*R*(int) = 0.0470], 1572 observed [*I* > 2σ(*I*)], *μ* = 0.29 mm⁻¹, *T*_{min} = 0.83, *T*_{max} = 0.99, 260 parameters refined, one of the thiophene arms was found to be disordered, which was handled using a superposition with a different orientation, goodness of fit = 1.03 for observed reflections, final residual values *R*₁(*F*) = 0.048, *wR*(*F*²) = 0.115 for observed reflections, residual electron density −0.28 to 0.31 e Å⁻³. CCDC-606495.

15: Colourless crystal (irregular), dimensions 0.09 × 0.08 × 0.03 mm, crystal system monoclinic, space group *P*₂₁, *Z* = 2, *a* = 5.7826(4), *b* = 28.092(2), *c* = 8.7687(6) Å, *β* = 102.156(2)°, *V* = 1392.5(2) Å³, *ρ* = 1.416 g cm⁻³, *T* = 100(2) K, *Θ*_{max} = 28.28°, 14358 reflections measured, 6682 unique [*R*(int) = 0.0385], 6243 observed [*I* > 2σ(*I*)], *μ* = 0.51 mm⁻¹, *T*_{min} = 0.96, *T*_{max} = 0.98, 446 parameters refined, Flack absolute structure parameter = 0.06(7), two of the terminal thiophenyl groups were found to be superimposed by thiophenyl rings with a reversed orientation with occupations for the minor component of 10%, the two hydrogen atoms of the disordered carbon atoms were treated using appropriate riding models, the rest

of the hydrogen atoms were refined isotropically, goodness of fit = 1.11 for observed reflections, final residual values $R_1(F) = 0.048$, $wR(F^2) = 0.103$ for observed reflections, residual electron density -0.29 to $0.44 \text{ e \AA}^{-3}$. CCDC-606496.

16: Colourless crystal (irregular), dimensions $0.32 \times 0.23 \times 0.15 \text{ mm}$, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 18.681(1)$, $b = 5.8936(3)$, $c = 33.275(2) \text{ \AA}$, $\beta = 101.204(1)^\circ$, $V = 3593.7(3) \text{ \AA}^3$, $\rho = 1.243 \text{ g cm}^{-3}$, $T = 100(2) \text{ K}$, $\theta_{\text{max}} = 24.71^\circ$, 27318 reflections measured, 6087 unique [$R(\text{int}) = 0.0398$], 4822 observed [$I > 2\sigma(I)$], $\mu = 0.14 \text{ mm}^{-1}$, $T_{\text{min}} = 0.96$, $T_{\text{max}} = 0.98$, 625 parameters refined, co-crystallization of 0.5 mol of dichloromethane disordered over a center of inversion was observed, goodness of fit = 1.04 for observed reflections, final residual values $R_1(F) = 0.049$, $wR(F^2) = 0.113$ for observed reflections, residual electron density -0.76 to $0.23 \text{ e \AA}^{-3}$. CCDC-606497.

17: Red-brown crystal (polyhedron), dimensions $0.21 \times 0.20 \times 0.09 \text{ mm}$, crystal system cubic, space group $P2_13$, $Z = 4$, $a = 16.0060(3) \text{ \AA}$, $V = 4100.6(1) \text{ \AA}^3$, $\rho = 1.350 \text{ g cm}^{-3}$, $T = 100(2) \text{ K}$, $\theta_{\text{max}} = 28.23^\circ$, 42784 reflections measured, 3398 unique [$R(\text{int}) = 0.0849$], 2990 observed [$I > 2\sigma(I)$], $\mu = 0.37 \text{ mm}^{-1}$, $T_{\text{min}} = 0.93$, $T_{\text{max}} = 0.97$, 217 parameters refined, Flack absolute structure parameter = $-0.02(9)$, goodness of fit = 1.09 for observed reflections, final residual values $R_1(F) = 0.047$, $wR(F^2) = 0.107$ for observed reflections, residual electron density -0.26 to $0.55 \text{ e \AA}^{-3}$. CCDC-606498.

22: Colorless crystal (polyhedron), dimensions $0.38 \times 0.18 \times 0.10 \text{ mm}$, crystal system monoclinic, space group $P2_1$, $Z = 4$, $a = 6.3456(1)$, $b = 16.9623(3)$, $c = 19.1141(2) \text{ \AA}$, $\beta = 91.201(1)^\circ$, $V = 2056.91(5) \text{ \AA}^3$, $\rho = 1.490 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, $\theta_{\text{max}} = 27.49^\circ$, 21288 reflections measured, 9358 unique [$R(\text{int}) = 0.0338$], 7668 observed [$I > 2\sigma(I)$], $\mu = 1.66 \text{ mm}^{-1}$, $T_{\text{min}} = 0.57$, $T_{\text{max}} = 0.85$, 451 parameters refined, Flack absolute structure parameter = $0.006(15)$, goodness of fit = 1.04 for observed reflections, final residual values $R_1(F) = 0.032$, $wR(F^2) = 0.064$ for observed reflections, residual electron density -0.55 to $0.59 \text{ e \AA}^{-3}$. CCDC-606499.

24: Colorless crystal (lamina), dimensions $0.24 \times 0.20 \times 0.02 \text{ mm}$, crystal system triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8.9099(1)$, $b = 10.3450(1)$, $c = 13.2216(1) \text{ \AA}$, $\alpha = 73.2360(10)$, $\beta = 83.2770(10)$, $\gamma = 72.6650(10)^\circ$, $V = 1113.234(19) \text{ \AA}^3$, $\rho = 2.164 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, $\theta_{\text{max}} = 27.49^\circ$, 11643 reflections measured, 5086 unique [$R(\text{int}) = 0.0376$], 4106 observed [$I > 2\sigma(I)$], $\mu = 4.50 \text{ mm}^{-1}$, $T_{\text{min}} = 0.41$, $T_{\text{max}} = 0.92$, 226 parameters refined, goodness of fit = 1.09 for observed reflections, final residual values $R_1(F) = 0.031$, $wR(F^2) = 0.070$ for observed reflections, residual electron density -1.16 to $0.49 \text{ e \AA}^{-3}$. CCDC-606500.

35: Colorless crystal (polyhedron), dimensions $0.12 \times 0.10 \times 0.06 \text{ mm}$, crystal system monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.7918(4)$, $b = 8.8544(4)$, $c = 26.4962(11) \text{ \AA}$, $\beta = 98.6640(10)^\circ$, $V = 2271.02(17) \text{ \AA}^3$, $\rho = 1.700 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, $\theta_{\text{max}} = 22.99^\circ$, 15781 reflections measured, 3157 unique [$R(\text{int}) = 0.0600$], 2311 observed [$I > 2\sigma(I)$], $\mu = 2.78 \text{ mm}^{-1}$, $T_{\text{min}} = 0.73$, $T_{\text{max}} = 0.85$, 244 parameters refined, goodness of fit = 1.03 for observed reflections, final residual values $R_1(F) = 0.032$, $wR(F^2) = 0.060$ for observed reflections, residual electron density -0.87 to $0.70 \text{ e \AA}^{-3}$. CCDC-606501.

36: Colorless crystal (polyhedron), dimensions $0.15 \times 0.14 \times 0.05 \text{ mm}$, crystal system rhombohedral, space group $R\bar{3}$, $Z = 6$, $a = 12.5687(8)$, $c = 27.338(3) \text{ \AA}$, $V = 3740.0(5) \text{ \AA}^3$, $\rho = 1.997 \text{ g cm}^{-3}$, $T = 100(2) \text{ K}$, $\theta_{\text{max}} = 28.34^\circ$, 12202 reflections measured, 2074 unique [$R(\text{int}) = 0.0300$], 2000 observed [$I > 2\sigma(I)$], $\mu = 3.88 \text{ mm}^{-1}$, $T_{\text{min}} = 0.59$, $T_{\text{max}} = 0.83$, 112 parameters refined, co-crystallization

of 0.5 mol of dichloromethane disordered over a $\bar{3}$ center was observed, goodness of fit = 1.27 for observed reflections, final residual values $R_1(F) = 0.030$, $wR(F^2) = 0.076$ for observed reflections, residual electron density -0.53 to $0.96 \text{ e \AA}^{-3}$. CCDC-606502.

41: Colorless crystal (polyhedron), dimensions $0.40 \times 0.20 \times 0.10 \text{ mm}$, crystal system monoclinic, space group Cc , $Z = 4$, $a = 18.6354(5)$, $b = 6.6054(2)$, $c = 17.4674(6) \text{ \AA}$, $\beta = 96.4930(10)^\circ$, $V = 2136.34(11) \text{ \AA}^3$, $\rho = 1.099 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, $\theta_{\text{max}} = 24.10^\circ$, 8098 reflections measured, 3397 unique [$R(\text{int}) = 0.0245$], 3021 observed [$I > 2\sigma(I)$], $\mu = 0.06 \text{ mm}^{-1}$, $T_{\text{min}} = 0.98$, $T_{\text{max}} = 0.99$, 245 parameters refined, Flack absolute structure parameter = $-1(3)$, goodness of fit = 1.03 for observed reflections, final residual values $R_1(F) = 0.032$, $wR(F^2) = 0.078$ for observed reflections, residual electron density -0.13 to $0.20 \text{ e \AA}^{-3}$. CCDC-606503.

[9-Ag](CF₃SO₃): Colorless crystal (polyhedron), dimensions $0.2 \times 0.2 \times 0.12 \text{ mm}$, crystal system orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 13.2610(2)$, $b = 13.8087(2)$, $c = 14.4501(1) \text{ \AA}$, $V = 2646.06(6) \text{ \AA}^3$, $\rho = 1.731 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, $\theta_{\text{max}} = 27.48^\circ$, 27690 reflections measured, 6043 unique [$R(\text{int}) = 0.0437$], 5192 observed [$I > 2\sigma(I)$], $\mu = 1.32 \text{ mm}^{-1}$, $T_{\text{min}} = 0.78$, $T_{\text{max}} = 0.86$, 358 parameters refined, Flack absolute structure parameter = $-0.01(3)$, co-crystallization of 1 mol of dichloromethane was observed, the thiophenyl rings were found to be superimposed by thiophenyl rings with a reversed orientation with occupations for the minor components of 10, 20, and 45%, goodness of fit = 1.02 for observed reflections, final residual values $R_1(F) = 0.032$, $wR(F^2) = 0.069$ for observed reflections, residual electron density -0.56 to $0.52 \text{ e \AA}^{-3}$. CCDC-606504.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft for financial support. We thank Mrs. P. Krämer for typing and drawings.

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Received: June 13, 2006

Published Online: October 10, 2006