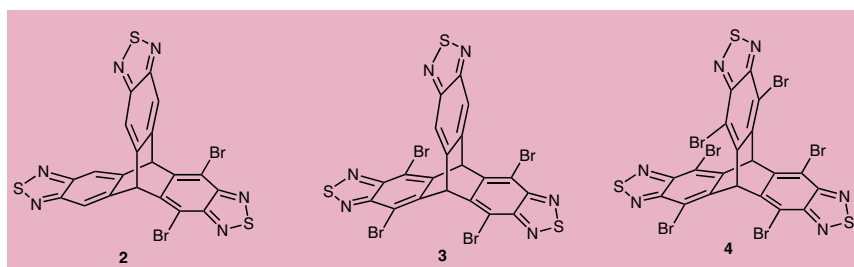
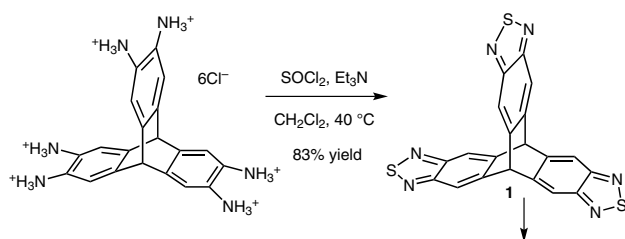


B. KOHL, L. C. OVER, T. LOHR, M. VASYLYEVA, F. ROMINGER, M. MASTALERZ*
(RUPRECHT-KARLS-UNIVERSITÄT HEIDELBERG, GERMANY)
Selective Even-Numbered Bromination of Triptycene Tris(thiadiazoles)
Org. Lett. **2014**, *16*, 5596–5599.

An Unusual Regioselective Di-, Tetra-, and Hexa-Bromination



Reaction Conditions				Isolated Yield (%)			
Additive (equiv)	Br ₂ (equiv)	Time (h)	Temp (°C)	1	2	3	4
Fe (12)	150	14	40	34	31	15	— ^a
Fe (6)	34	2	55	18	32	18	6
Fe (12)	600	140	55	—	—	9	67
HBr (22)	50	140	24	—	—	—	94
FeCl ₃ ·6H ₂ O (6)	50	55	26	—	—	—	97

^a Approximately 7% of hexabromotriptycene has been formed, but not isolated and purified.

Significance: Mastalerz and co-workers report an unusual even-numbered bromination of triptycene tris(thiadiazoles), yielding regioselectively dibromo-, tetrabromo-, and hexabromotriptycenes with two bromines each on the same phenyl ring. These brominated compounds will be useful in the synthesis of π -conjugated polymers of intrinsic microporosity and small electron acceptors.

Comment: Given that the C–C bond lengths of the phenyl rings are alternating, and hence the phenyl rings exhibit more olefinic than aromatic character from X-ray single crystal structure of **1**, the mechanism for this unusual even-numbered bromination is proposed to involve 1,4-addition of Br₂, followed by subsequent re-aromatization of the phenyl ring by oxidation by Br₂ or FeBr₃. It is also proposed that this 1,4-addition–oxidation sequence is favored over electrophilic aromatic substitution. Furthermore, to demonstrate the utility of these monomers in the synthesis of conjugated polymers, dibromotriptycene **2** has been shown to undergo facile Suzuki–Miyaura cross-coupling.

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