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Hydroboration of isoprene and 1,4-cyclooctadiene with N-azolylboranes

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Abstract

The hydroboration of isoprene with N-azolylboranes in THF [az-BH_2–THF: az = N-pyrrolyl (**1a**), N-2,5-dimethylpyrrolyl (**1b**), N-indolyl (**1c**), N-carbazolyl (**1d**)] affords the boracyclopentane derivatives **2a–d**. In the case of **2b,c**, the reduced species **3b,c** with a 2,5-dimethylpyrrolidinyl and a 2,3-dihydroindolyl group respectively attached to the boron atom are also present as side products. The hydroboration of 1,4-cyclooctadiene with **1a–c** leads to mixtures of products containing both the 9-borabicyclo[3.3.1]nonane (**6a–c**) and the 9-borabicyclo[4.2.1]nonane derivative (**7a–c**). In the case of the reaction of **1d** with 1,4-cyclooctadiene, the 9-(N-carbazolyl)-9-borabicyclo[4.2.1]nonane **7d** is formed selectively. The reaction of the corresponding tetraalkyldiboranes(6) with the azoles gives the boracyclopentane derivatives **2** and **4** in higher purity, and in the case of $(H\text{-}9\text{-}BBN)_2$, all 9-(N-azolyl)-9-borabicyclo[3.3.1]nonanes **6a–d** are obtained as the sole products.

Keywords: Boron; Azoles; Hydroboration; Dienes; Isomers; NMR

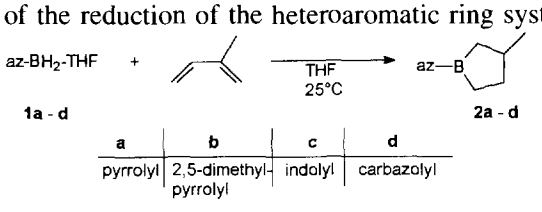
1. Introduction

The so-called cyclic hydroboration [1] of dienes is a well documented reaction, leading to numerous useful organoborane reagents, in particular if the boron atom bears a functional group which can easily be used for further transformations. Such a group could be the N-azolyl group, and it is known that N-pyrrolylborane in THF [2] is a powerful hydroborating agent. In comparison with non-cyclic dienes, it is less straightforward to predict the product distribution resulting from the hydroboration of cyclic dienes. Thus, hydroboration of 1,4-cyclooctadiene has been studied extensively [3–7], and it is agreed that 9-borabicyclo[3.3.1]nonanes are the thermodynamically stable products. However, 9-borabicyclo[4.2.1]nonanes have been identified not only in the initial reaction mixtures resulting from the hydroboration of 1,4-cyclooctadiene with BH_3–THF [3–7]: 9-borabicyclo[4.2.1]nonane is also present (trapped and structurally characterized as an amine adduct [7]) at elevated temperature owing to the equilibrium between 9-borabicyclo[3.3.1]nonane and 9-borabicyclo[4.2.1]-nonane as a result of dehydroboration/hydroboration [5–7]. In this work we report on the formation of N-azolyl-diorganoboranes by the reaction of N-azolylboranes **1a–d** in THF with isoprene and 1,4-cyclooctadiene. A different route is provided by aminolysis of tetraalkyldiboranes(6) [8] which we used to obtain compounds for comparison. Sterically hindered N-azolyl-diorganoboranes are best made from diorganoboronhalides and N-metallated azoles [9].

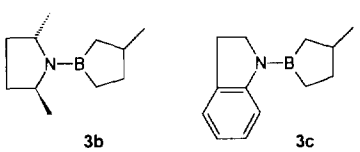
2. Results and discussion

2.1. Hydroboration of isoprene

The reaction of isoprene with N-azolylboranes **1a–d** in THF leads mainly to the 1-(N-azolyl)boracyclopentanes **2a–d** [Eq. (1)]. In the case of **2b,c**, significant amounts of side products **3b,c** are formed as the result of the reduction of the heteroaromatic ring system.



(1)



3b 3c

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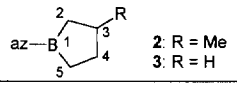
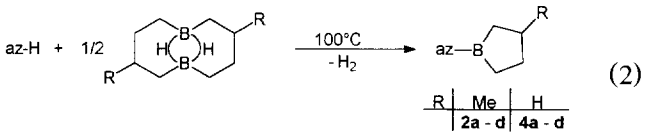
Table 1
^{11}B and ^{13}C NMR data [a] of the 3-methylborolane rings of **2a–d**, **4a–d**, **5c**



No.	az	$\delta^{11}B$	$\delta^{13}C$				
			C-2	C-3	C-4	C-5	Me
2a	pyrrolyl	62.8	29.4 [br]	35.6	35.1	19.4 [br]	22.6
2b	2,5-dimethylpyrrolyl	61.7	33.8 [br]	35.6	35.2	23.9 [br]	22.6
2c	indolyl	60.8	30.8 [br]	35.0/36.4 [b]	34.6/35.8 [b]	20.8 [br]	22.7/22.8 [b]
2d	carbazolyl	61.2	33.5 [br]	35.8	35.3	23.9 [br]	22.6
4a	pyrrolyl	62.9	20.0 [br]	27.5	27.5	20.0 [br]	—
4b	2,5-dimethylpyrrolyl	61.7	24.2 [br]	27.3	27.3	24.2 [br]	—
4c	indolyl	60.7	21.7 [br]/27.4 [br] [b]	27.1/28.7 [b]	27.1/28.7 [b]	21.7 [br]/27.4 [br] [b]	—
4d	carbazolyl	61.7	24.0 [br]	27.3	27.3	24.0 [br]	—
5c	2,3-dihydroindole	54.0	20.5 [br]	28.8/29.6 [b]	28.8/29.6 [b]	20.5 [br]	—

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J[^{13}C,^{11}B]$.
[b] Rotational barrier at room temperature.

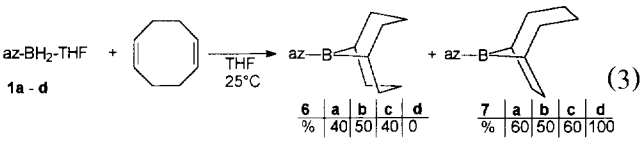
The compounds **2a–d** or **4a–d** can also be obtained from the reaction of the azoles with the corresponding tetraalkyldiborane(6) as shown in Eq. (2). This reaction affords the N-azolylboranes in higher purity, but in the case of the preparation of **2c** and **4c**, the compounds **3c** and **5c** bearing a 2,3-dihydroindolyl group are again obtained as side products in changing amounts (between 5% and 25%).



(2)

2.2. Hydroboration of 1,4-cyclooctadiene

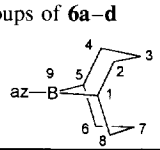
As shown in Eq. (3), the reaction of the N-azolylboranes **1a–c** with 1,4-cyclooctadiene leads to mixtures of two isomers, 9-borabicyclo[3.3.1]nonanes **6a–c** and 9-borabicyclo[4.2.1]nonane derivatives **7a–c**. The reaction of N-pyrrolylborane-triethylamine with 1,4-cyclooctadiene did not give **7a** [6]. However, N-carbazolylborane (**1d**) reacts selectively with 1,4-cyclooctadiene to give solely the 9-(N-carbazolyl)-9-borabicyclo[4.2.1]nonane (**7d**). This opens the most convenient access to this particular bicyclic system, since other routes require cumbersome fractional crystallization procedures [7]. Side products analogous to **3b,c** can also be detected.



(3)

The first step of the hydroboration of 1,4-cyclooctadiene with N-azolylboranes in THF leads presumably to compounds of type **A** which may adopt the conformation as shown for further intramolecular hydroboration. It is concievable that the preferred approach of the B–H moiety towards the remaining C=C bond depends on repulsive interactions between the N-azolyl group and the C_8 ring. Considering the bulkiness of **A**, it is unlikely that the reaction proceeds through intermediates in which two C_8 rings are attached to boron. Such

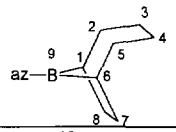
Table 2
^{11}B and ^{13}C NMR data [a] of the 9-borabicyclo[3.3.1]nonane groups of **6a–d**



No.	az	$\delta^{11}B$	$\delta^{13}C$		
			C-1/5	C-2/4/6/8	C-3/7
6a	pyrrolyl	59.9	25.7 [br]	34.0	23.5
6b	2,5-dimethylpyrrolyl	60.7	28.0 [br]	33.7	23.1
6c	indolyl	59.7	27.3 [br]/25.7 [br] [b]	34.0/33.8/33.6/33.4 [b]	23.4
6d	carbazolyl	58.6	27.0 [br]	33.5	23.3

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J[^{13}C,^{11}B]$.
[b] Rotational barrier at room temperature.

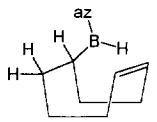
Table 3
^{11}B and ^{13}C NMR data [a] of the 9-borabicyclo[4.2.1]nonane groups of **7a–d**



No.	az	$\delta^{11}B$	$\delta^{13}C$		
			C-1/6	C-2/5/7/8	C-3/4
7a	pyrrolyl	61.3	28.0 [br]	31.6/32.8	26.7
7b	2,5-dimethylpyrrolyl	64.2	29.3 [br]	31.6/32.8	27.4
7c	indolyl	n.o.	29.5 [br]	30.8/31.8/32.0/32.9 [b]	26.8
7d	carbazolyl	59.5	30.1 [br]	31.3 (2 signals)	27.2

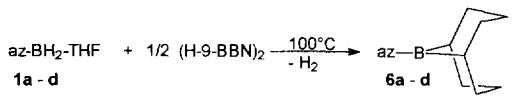
[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J[^{13}C,^{11}B]$.
[b] Rotational barrier at room temperature.

intermediates have to be assumed for the reaction between BH_3–THF and 1,4-cyclooctadiene [4–7], where the situation is sterically much less crowded after the first step of the hydroboration, and the BH_2 group is ready for further intra- and also intermolecular hydroboration.



A

Pure samples of 9-(N-azolyl)-9-borabicyclo[3.3.1]nonanes **6a–d** can be obtained from the reaction of $(H\text{-}9\text{-}BBN)_2$ with the azoles [Eq. (4)], analogous to the reaction shown in Eq. (2). Side products corresponding to **3** and **5** are formed in minor quantities (< 5%).



(4)

2.3. NMR spectroscopic results

The ^{11}B and ^{13}C NMR data of the boracyclopentanes **2** and **4** [Eqs. (1) and (2)] are listed in Table 1, and Tables 2 and 3 contain ^{11}B and ^{13}C NMR data of the

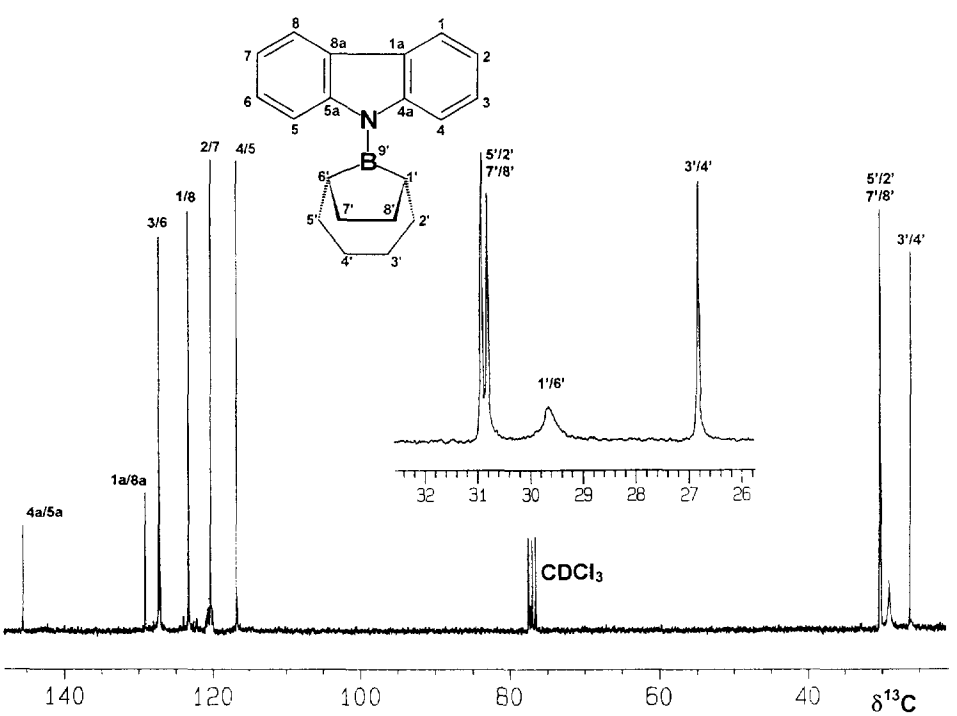


Fig. 1. 67.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **7d** in $CDCl_3$ (15%, 25 °C). The 9-borabicyclo[4.2.1]nonane system (extended part) is evident from the aliphatic region. Note the broad ^{13}C NMR signal of the boron bonded ^{13}C nuclei.

bicyclic N-azolylboranes **6** and **7** [Eq. (3)]. ^{1}H NMR data are given in the experimental part.

The NMR data are fully consistent with the proposed structures. The δ^{11}B data are typical for these structural fragments [10]. The boron atoms are deshielded by approximately 10 ppm compared with corresponding aminoboranes and BN(pp)π interactions must be rather weak, as has been concluded for other N-azolylboranes [11,12]. This is also evident from the δ^{13}C values for the heteroaromatic ring systems which cover only a small range, even if substituents at the boron atom other than organyl groups are present [9,10]. The 9-borabicyclo[4.2.1]nonane structure is readily identified by the characteristic pattern in the aliphatic region of the ^{13}C NMR spectrum as shown for **7d** in Fig. 1.

3. Conclusions

N-azolylboranes in THF proved to be useful hydroborating agents for dienes. The formation of the side products **3b,c**, **5c** as a result of the reduction of the heteroaromatic ring system is somewhat unexpected for the hydroboration reactions. The most interesting result for the synthesis and application of organoboron compounds concerns the highly selective formation of the 9-bora-bicyclo[4.2.1]nonane system in **7d**.

4. Experimental details

All preparative work and handling of samples was carried out under an atmosphere of dry N_2, using oven-dried glassware and dry solvents. Starting materials were prepared by literature procedures [1,2:1,2-bis(1,4-butane-diyl)diborane(6) [13], 1,2:1,2-bis(2-methyl-1,4-butane-diyl)diborane(6) [13], $(H\text{-}9\text{-}BBN)_2$ [14], N-pyrrolylborane–THF-adduct, N-2,5-dimethyl-pyrrolylborane–THF-adduct, N-indolyl-borane–THF-adduct, N-carbazolyl-borane–THF-adduct [2,11]]. Mass spectra (EI-MS; 70 eV) were recorded with a VARIAN-MAT CH 7 instrument with direct inlet. NMR spectra were recorded by using Jeol EX270 (^{1}H, ^{13}C) and Bruker ARX 250 and AM 500 spectrometers (^{1}H, ^{11}B, ^{13}C, ^{14}N). Chemical shifts are given with respect to Me_4Si [δ^1H($CHCl_3/CDCl_3$) = 7.24, (C_6D_6) = 7.15; δ^{13}C($CDCl_3$) = 77.0, (C_6D_6) = 128.0], Et_2O–BF_3 [δ^{11}B with $\Xi(^{11}B)$ = 32.083971 MHz] and neat $MeNO_2$ [δ^{14}N with $\Xi(^{14}N)$ = 7.223656 MHz; δ^{15}N with $\Xi(^{15}N)$ = 10.136767 MHz].

4.1. Hydroborations

4.1.1. General procedure

Isoprene or 1,5-cyclooctadiene (10 mmol) was added without any further solvent to a solution of 10 mmol of the respective N-azolylborane–THF-adduct at room temperature. The solution was stirred for 2 days. Then the solvent was removed in vacuo and the residue was distilled. In the case of the preparation of **7d**, the residue was extracted with hexane, the solvent was removed from the extract, and the unreacted carbazole was sublimed in vacuo at 150 °C. The residue was identified as pure **7d**.

2a: 1.1 g (70%) of a colourless oil (b.p. 32 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.81 (m) (H-2/5); 6.34 (m) (H-3/4); 1.84 (m) (H-3′); 1.32 (m) (H-4′); 1.09 (m) (H-2′); 1.00 (d) (Me); 0.55 (m) (H-5′). EI-MS: m/z (%) = 147 (15) [M^+]; 132 (10) [M^+ − Me]; 81 (8) [M^+ − pyrrolyl]; 69 (100) [$C_5H_9^+$].

2b / 3b-mixture: 0.2 g (11%) of a colourless oil (b.p. 51 °C/0.1 Torr). **2b** (95%): ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 5.95 (s) (H-3/4); 2.12 (s) (Me/pyrrole); 1.81 (m) (H-3′); 1.45 (m) (H-4′); 1.05 (d) (Me); 1.02 (m) (H-2′); 0.68 (m) (H-5′). EI-MS: m/z (%) = 175 (48) [M^+]; 94 (76) [$C_6H_8N^+$]; 69 (100) [$C_5H_9^+$]. **3b** (5%): ^{13}C NMR (C_6D_6; 62.9 MHz): δ^{13}C = 70.1 (C-2/5); 33.7 (C-3/4); 17.3 (Me). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 2.41 (m) (H-3/4); the other resonances overlap with signals from **2b**.

2c / 3c-mixture: 1.0 g (50%) of a colourless oil (b.p. 92 °C/0.1 Torr). **2c** (70%): ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.50 (m) (H-8); 7.46 (m) (H-7); 7.18 (m) (H-4/5); 6.93 (m) (H-2); 6.47 (m) (H-3); 1.88 (m) (H-2′/3′); 1.50 (m) (H-4′); 1.16 (m) (H3′); 1.12 (d) (Me); 0.60 (H-5′). EI-MS: m/z (%) = 197 (20) [M^+]; 117 (70) [$C_8H_7^+$]. **3c** (30%): ^{13}C NMR (C_6D_6; 62.9 MHz): δ^{13}C = 51.2 (C-2); 27.3 (C-3); 133.8 (C-3a); 125.3 (C-4); 127.6 (C-5); 122.0 (C-6); 114.5 (C-7); 149.6 (C-7a). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.05 (m); 7.00 (m); 6.95 (m); 6.38 (m); 3.33 (m) (H-2′); 2.56 (m) (H3′); 1.91 (m) (H-2′/3′); 1.32 (m); 1.18 (m) (H-3′); 1.24 (d) (Me); 0.70 (m) (H-5′).

2d: 1.4 g (57%) of a colourless solid (m.p. 148 °C; b.p. 169 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.76 (m); 7.51(m); 7.24–7.01 (m); 1.90–1.48 (m); 1.27–0.93 (m); 1.03 (d) (Me); 0.85–0.70 (m).

6a / 7a: 0.4 g (22%) of a colourless oil (b.p. 63 °C/0.1 Torr). **4a**: ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.10 (m) (H-2/5); 6.36 (m) (H-3/4); 2.00–1.60 (m); 1.26 (m). EI-MS: m/z (%) = 187 (100) [M^+]; 145 (30) [$M^+ - C_3H_6$]; 67 (10) [$C_4H_5N^+$]. **5a**: ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.89 (m) (H-2/5); 6.42 (m) (H-3/4); 1.60–1.40 (m); 1.38 (m); 1.10 (m).

6b / 7b: 0.6 g (27%) of a colourless oil (b.p. 98 °C/0.1 Torr). **4b**: ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 5.99 (s) (H-3/4); 2.26 (s) (Me); 2.00–1.60 (m); 1.45–1.25 (m). **5b**: ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 5.94 (s) (H-3/4); 2.28 (s) (Me); 1.70 (m); 1.55 (m); 1.10 (m).

6c / 7c: 0.44 g (19%) of a colourless oil (b.p. 125 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.84 (m); 7.56 (m); 7.31 (m); 7.21 (m); 6.57 (m); 2.49 (m); 1.84 (m); 1.27 (m). EI-MS: m/z (%) = 237 (18) [M^+]; 131 (100) [$C_9H_8N^+$]; 117 (31) [$C_8H_7N^+$].

7d: 2.6 g (90%) of a colourless solid (m.p. 115 °C). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.80 (m); 7.56 (m); 7.24 (m); 2.42 (m); 1.89 (m); 1.62 (m); 1.64–1.34 (m); 1.09 (m). EI-MS: m/z (%) = 287 (1) [M^+]; 259 (7) [$M^+ - C_2H_4$], 167 (100) [$C_{12}H_9N^+$].

4.2. Aminolyses

4.2.1. General procedure

The tetraalkyldiborane(6) (10 mmol) was added to 10 mmol of the respective azole. The mixture was stirred for 2 days at 110 °C and after that distilled in vacuo.

With indole mixtures with the 2,3-dihydro derivatives **3c**, **5c** were obtained; **6d** cannot be distilled, its purification is similar to **7d**.

2a: 1.1 g (75%). **2b**: 1.2 g (69%) of colourless crystals (m.p. 34 °C). **2c / 3c**-mixture 1.2 g (62%). **2d**: 1.8 g (74%). **6a**: 1.0 g (52%). **6b**: 0.8 g (38%). **6c**: 1.4 g (59%). ^{1}H NMR and EI-MS s. 4.1.

6d: 2.0 g (70%) of a colourless solid (m.p. 180 °C). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.98–7.75 (m); 7.34–7.15 (m); 7.03 (m); 1.87 (m); 1.89 (m); 1.36 (m). EI-MS: m/z (%) = 287 (6.7) [M^+]; 258 (100) [$M^+ - C_2H_5$]; 167 (58) [$C_8H_7N^+$].

4a: 0.64 g (48%) of a colourless oil (b.p. 120 °C/720 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.81 (m) (H-2/5); 6.32 (m) (H-3/4); 1.62 (m) (H-3′/4′); 1.07 (m) (H2′/5′). EI-MS: m/z (%) = 133 (80) [M^+]; 104 (100) [$M^+ - C_2H_5$].

4b: 1.3 g (82%) of a colourless crystals (m.p. 64 °C; b.p. 70 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 5.91 (s) (H-3/4); 2.13 (s) (Me); 1.58 (m) (H-3′/4′); 1.17 (m) (H-2′/5′). EI-MS: m/z (%) = 161 (77) [M^+]; 107 (100) [$M^+ - C_4H_6$]; 94 (60) [$C_6H_8N^+$].

4c / 5c-mixture: 1.0 g (58%) of a colourless oil (b.p. 90 °C/0.1 Torr). **4c** (90%): ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.50 (m) (H-4/7); 7.15 (m) (H-5/6); 6.81 (m) (H-2); 6.47 (m) (H-3); 1.60 (m) (H-3′/4′); 1.20 (m) (H-2′5′). **5c** (10%): ^{13}C NMR (C_6D_8; 62.9 MHz): δ^{13}C = 51.3 (C-2); 27.3 (C-3); 133.8 (C-3a); 125.3 (C-4); 127.1 (C-5); 122.2 (C-6); 114.4 (C-7); 149.2 (C-7a). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 3.32 (m) (H-2); 2.51 (m) (H-3); the other resonances overlap with signals from **4c**.

4d: 2.1 g (90%) of a white solid (m.p. 187 °C). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.78 (m) (H-1); 7.49 (m) (H-4); 7.21 (m) (H-2/3); 1.61 (m) (H-3′/4′); 1.30 (m) (H2′/5).

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