Novel C_3-Symmetric Molecular Scaffolds with Potential Facial Differentiation

Gunther Hennrich, Vincent M. Lynch, and Eric V. Anslyn*[a]

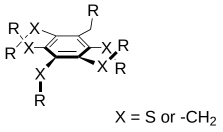
Abstract: The conversion of 1,3,5-substituted benzene and mesitylene by electrophilic aromatic substitution and Sonogashira cross-coupling, respectively, furnished the C_3-symmetric, hexasubstituted benzene derivatives **1** and **2** with an alternating substitution pattern. Based on the molecular scaffolds obtained, the two systems serve as model compounds for novel receptor molecules with distinct geometric features. X-ray structures have been obtained for **1** and **2**, which are discussed in regard to their aptitude as receptor platforms or supramolecular building blocks. By looking at the rotational barriers for the functional groups placed around the molecular scaffolds by variable temperature ^{1}H NMR spectroscopy, **1** and **2** turn out to exist in rapidly interconverting conformations. The alignment of these potential binding groups around the molecular scaffolds should be strongly biased by specific interactions with suitable guest molecules.

Keywords: cross-coupling · ligand design · molecular recognition · receptors · supramolecular chemistry

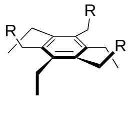
Introduction

During the last few years, an emerging number of supramolecular systems has been reported in which the principle of steric gearing is employed to circumvent the difficulties in synthesis arising form covalent architecture.[1, 2] Here, the suitable preorganization of functional groups and conformational constraint is achieved by controlling the stereochemistry through steric hindrance of the substituents around a rigid platform.[3]

In this context, persubstituted benzenes have been intensely investigated,[4] mainly due to their applications in supramolecular chemistry.[5] However, all of the benzene based conformationally controlled systems are either symmetrically hexasubstituted with the same six functional groups (**A**); or in the case of 1,3,5-triethyl benzene derivatives (**B**), facial segregation is brought about through different functionalities in the 2,4, and 6-positions, while the triethyl-face lacks any function.[6] Nevertheless, both compound classes have found wide application in molecular recognition, and as building blocks in supramolecular assemblies.[7] Yet, when targeting guest molecules or aiming at structurally matching partners, their size is restricted by the phenyl platform.



A

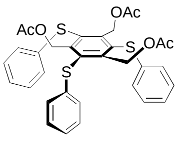


B

We report here new molecular scaffolds that allow the introduction of altered function on either face. The variation of the geometry of the functional groups on the different faces of the benzene core, or the extension of the benzene platform to larger sizes, could lead to molecular receptors that target a whole variety of new potential guest molecules.

Results and Discussion

In this paper, we present two representatives of alternating hexasubstituted benzene scaffolds: 1,3,5-tris(acetoxymethyl)-2,4,6-thiophenyl benzene (**1**) and 1,3,5-tris(acetoxymethyl)-2,4,6-tris(2-ethoxycarbonylphenyl)ethynyl benzene (**2**). The platforms are expected to exist in rapidly interconverting conformations, and are drawn as facially differentiated (see below).



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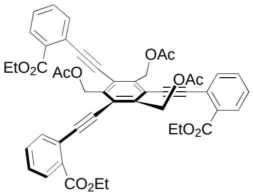

2

Syntheses: The syntheses of both target molecules is conducted in a modular approach. Aryl and acetyl moieties are chosen as representative functionalities that could be easily

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replaced in the synthesis by other similar reactants. By following the pathway depicted in Scheme 1, these functionalities are introduced in the last two steps for both **1** and **2** (Scheme 1). The starting materials **5** and **9** are easily accessible and can be prepared on a large scale. The synthesis of **5** starting from tris-bromomesitylene is straightforward.[8] Bromination of 1,3,5-tris-bromomesitylene (**3**) with elemental bromine gives compound **4**. The threefold substitution of bromine with potassium acetate yields the tris-acetate **5** as a versatile starting material. As shown by Lehn et al., the final nucleophilc substitition by sodium thiophenolate proceeds smoothly under mild conditions by using DMI as solvent.[9] Working in DMF requires harsher conditions and lowers the yield considerably.[10]

The preparation of compound **2** is based on the coupling of aryl iodides with free acetylenes under Sonogashira conditions.[11] NBS bromination of **7**, whose synthesis has been described,[12] gives the tris-bromide **7** in reasonable yields. Upon applying a six fold excess of potassium acetate to substitute the methylene bromides in **8**, the acetylene functions are desilylated at the same time to give **9**. Considering the plethora of various literature procedures with sometimes subtle differences in the conditions, the choice of these is crucial in the final coupling reaction of **9** with 2-iodo ethoxybenzoic acid (Table 1). Finally, owing to the electronic deactivation of the aryliodide and the steric hindrance of both the iodide and the alkyne, a 23% yield can be considered satisfactory for a threefold conversion reaction.

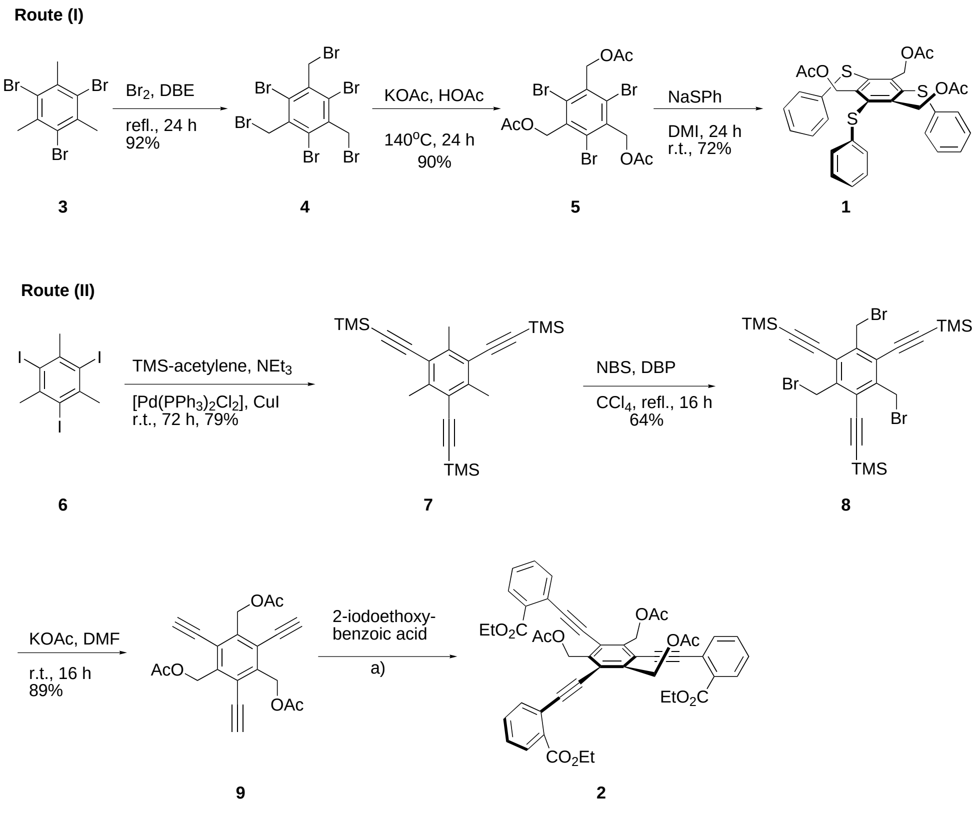
Table 1. Reaction conditions for Sonogashira coupling of acetylene **9** with 2-iodoethoxybenzoic acid.[16]

Run	Catalyst (mol%)	Base/solvent	T [°C]	t [h]	Yield[a] [%]	Ref.
A	$[Pd(PPh_3)_2Cl_2]$ (4), CuI (8)	DIEA[b]/THF	RT	36	8	[13]
B	$[Pd(PPh_3)_2Cl_2]$ (5), CuI (5)	NEt_3	RT	72	15	[14]
C	$[Pd(PPh_3)_4]$ (5), CuI (5)	piperidine	RT	48	23	[15]

[a] Isolated yields, in case of run **C** calculated on the isolated deacylated tris-alcohol compound (**2a**). [b] DIEA: diisopropylamine.

Stuctural investigations: As seen by X-ray crystallography, the thiophenyl rings of **1** are positioned above or below the central phenyl plane. The phenyl substituents are oriented nearly aligned with the S to central benzene bond, instead of being perpendicular to it. The C(Ar)-S-C(Ar) angles are in the range of 103–104° (Figure 1). As a consequence of this, two molecules of **1** form a dimer, interlocking with two thiophenyl groups each (Figure 1b). The two free thiophenyl moieties place each dimer into a packing superstructure. This packing creates the *two-up-one-down* configuration of the acetoxymethyl and the thiophenyl groups in the solid state.[17]

Molecule **2** is almost planar with the acetoxylmethyl groups pointing perpendicular out of the plane. The *two-up-one-down* conformation of these substituents is attributed to the crystal packing. The expected unbiased conformational preference of the aryl groups around the triple bonds in solution is reflected in the positioning of the ethoxycarbonyl functions towards or away from each other in the solid state (Figure 2a). The distance between the three arylcarbonyl functions, analogous for potential binding sites, is approximately 7 Å



Scheme 1. Syntheses of tris(thiophenyl) compound **1** (route I) and tris(arylacetylene) compound **2** (route II). a) See Table 1 for reaction conditions. DBE: 1,2-dibromoethane; DMI: 1,3-dimethyl-2-imidazolidone; DBP: dibenzoylperoxide.

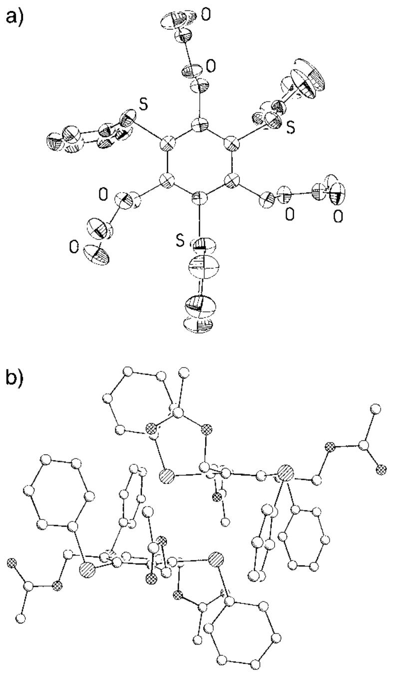


Figure 1. a) Top view of 1. Displacement ellipsoids are scaled to the 30 % probability level. The hydrogen atoms are omitted for clarity. b) Molecules of **1** form tightly packed dimers around crystallographic inversion centers at 0, 0, ½.

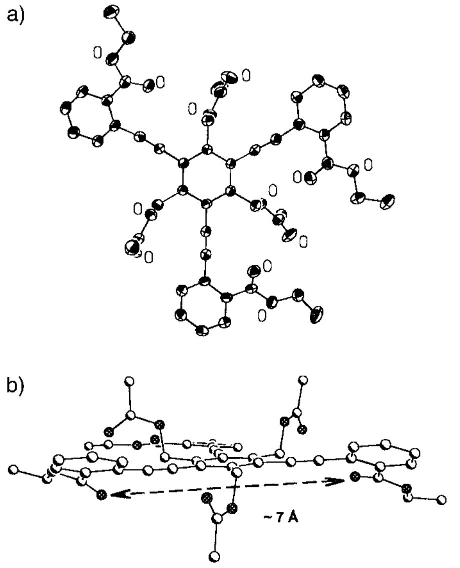


Figure 2. a) Top view of **2**. Displacement ellipsoids are scaled to the 30 % probability level. The hydrogen atoms are omitted for clarity. b) Side view of **2**. The arrow indicates the distance between two arylcarboxy functions.

while the acetoxy functions encircle a binding site of the same dimension as in similar systems.[6] Hence, the two-faced platform contains a wider upper and a narrower lower "rim" poised to distinguish between guests with not only different functionalities but also of different sizes (Figure 2b).[18]

As revealed by variable temperature ^1H NMR experiments (in [D$_8$]toluene and [D$_6$]DMSO, respectively), for both molecules **1** and **2** the respective acetyl or thiophenyl groups are placed statistically above or below the central benzene core and are freely rotating. Even at −70 °C, no rotational barriers for these substituents can be determined as evidenced by no broadening of the ^1H NMR signals. Similarly, a rapid rotation of the ethoxycarbonylbenzene moieties around the acetylenic bonds is observed at this temperature. In support, calculations have shown for different tolane systems, that the energetic barrier for the rotation of the phenyl groups around the acetylene bond is in the order of 0.3 kcal mol^{-1}.[19]

In the presence of suitable guest structures, we expect the substituents to adopt a *three-up-three-down* conformation of the binding groups around the benzene plane of **1** and around the triple-bond expanded platform of **2**.

Conclusion

Versatile synthetic routes for two novel molecular scaffolds have been worked out that allow the introduction of various functionalities onto a central core. Considering the low rotational barriers of the "masked" binding substituents around the core structure, the directing input of a suitable guest should easily align the functional groups and therefore induce and bias a two-face preorganisation of the scaffold. For both **1** and **2**, a selective face-dependent interaction is envisioned by the use of different binding groups as well as the matching with the different geometries of both faces.

Experimental Section

General methods: All reagents and solvents, which were of the highest purity available, were obtained from Aldrich. Column chromatography was carried out with silica gel 60 (No. 7731, Merck). For characterization of the substances, NMR data were recorded at 25 °C on a Bruker AC-250 spectrometer, CDCl$_3$ was used as solvent with chemical shifts reported as ppm and CDCl$_3$ serving as solvent internal standard. Low and high resolution mass spectra were measured on a Finnigan TSQ70 and a VG analytical ZAB2-E mass spectrometer, respectively. The variable temperature ^1H NMR experiments were carried out on a Bruker AMX-500 spectrometer. The temperature was varied in 20 °C increments from −70 °C to 90 °C in [D$_8$]toluene as solvent for **1** and **2**, and additionally for **1** from 20 to 100 °C in [D$_6$]DMSO.

Materials

1,3,5-Tris(bromo)-2,4,6-tris(bromomethyl) benzene (4): Bromine (9.8 g, 3.14 mL, 0.06 mol) was added over a period of 1 h to a refluxing solution of 1,3,5-tris-bromomesitylene (**3**, 10 g, 0.012 mol) in 1,2-dibromoethane (40 mL) and the reaction mixture was refluxed for another 24 h. The solid precipitating from the cold solution was filtered, washed several times with water and recrystallized from ethanol/benzene (2:1) to give pure **4** as colorless crystals (4.85 g, 68 %). M.p. 218 °C; ^1H NMR: $\delta = 4.90$ (s, 6H; C*H*$_2$); ^{13}C NMR: $\delta = 137.40$, 128.47 (Ar), 35.50 (Ar-*C*H$_2$); CI$^+$-MS: *m*/*z* (%): 594 (3) [*M*]$^+$, 513 (100), 435(5); HRMS: calcd for $C_9H_6Br_6$: 587.5569; found: 587.5559.

1,3,5-Tris(acetoxymethyl)-2,4,6-tris(bromomethyl) benzene (5): Compound **4** (2.0 g, 3.4 mmol) and potassium acetate (2.2 g, 0.022 mol) in glacial acetic acid (40 mL) were heated for 16 h at 140 °C in a sealed tube. The solvent was removed and the remaining solid was stirred with water (50 mL) and dichloromethane (50 mL) for 15 min. The phases were separated. The organic phase was washed subsequently with saturated bicarbonate solution, water, and brine (50 mL each). After drying over Na$_2$SO$_4$, the solvent was removed in vacuo and the remaining solid was recrystallized from ethanol to give pure **5** as colorless crystals (1.62 g, 90 %). M.p. 154 °C; ^1H NMR: $\delta = 5.52$ (s, 6H; C*H*$_2$), 2.08 (s, 9H; C*H*$_3$);

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^{13}C NMR: $\delta = 170.43$ ($C{=}O$), 135.63, 131.44 (Ar), 68.09 (Ar-CH_2), 20.60 (CH_3); CI$^+$-MS: m/z (%): 533 (3) $[M+H]^+$, 471 (100), 445 (64), 417 (19), 393 (14), 365 (3); HRMS: calcd for $C_{15}H_{16}O_6Br_3$: 528.8497; found: 528.8480.

1,3,5-Tris(acetoxymethyl)-2,4,6-thiophenyl benzene (1): Compound **5** (500 mg, 0.94 mmol mmol) and sodium thiophenolate (621 mg, 4.7 mmol) were stirred in DMI (5 mL) under argon at room temperature for 24 h. The solvent was removed by Kugelrohr distillation. To the remaining solid water (20 mL) was added, and the suspension was extracted with dichloromethane (3 × 10 mL). The organic phase was dried ($MgSO_4$). The solvent was removed in vacuo and the remaining solid was recrystallized from cyclohexane to give pure **1** as colorless crystals (418 mg, 72 %). M.p. 136–138 °C; ^{1}H NMR: $\delta = 7.21-6.90$ (m, 15H; Ar), 5.65 (s, 6H; CH_2), 1.52 (s, 9H; CH_3); ^{13}C NMR: $\delta = 170.14$ ($C{=}O$), 148.23, 139.46, 137.29, 128.97, 126.93, 125.45 (Ar), 65.29 (Ar-CH_2), 20.07 (CH_3); CI$^+$-MS: m/z (%): 618 (23) $[M]^+$, 559 (100), 529 (9), 499 (6), 439 (14); HRMS: calcd for $C_{33}H_{30}O_6S_3$: 618.1205; found: 618.1209.

1,3,5-Tris(bromomethyl)-2,4,6-tris(trimethylsilylethynyl) benzene (8): 1,3,5-Tris(trimethylsilylethynyl) mesitylene (**7**, 2.0 g, 4.9 mmol), *N*-bromosuccinimide (0.026 mmol, 4.6 g) and dibenzoyl peroxide (200 mg, 0.8 mmol) were heated in CCl_4 (40 mL) at reflux for 16 h. The solution was cooled, filtered, and the filtrate was concentrated in vacuo. The remaining yellow oil was purified by column chromatography (hexanes/benzene 10:1, $R_f = 0.60$) and the resulting solid was recrystallized from methanol/ethanol (1:1) to give pure **8** as colorless needles (2.05 g, 64 %). M.p. 184–188 °C; ^{1}H NMR: $\delta = 4.82$ (s, 6H; CH_2), 0.31 (s, 27H; CH_3); ^{13}C NMR: $\delta = 141.99$, 124.10 (Ar), 108.78, 98.04 ($C{\equiv}C$), 30.08 (Ar-CH_2), -0.47 (CH_3); CI$^+$-MS: m/z (%): 647 (26) $[M+H]^+$, 631 (48), 573 (20), 565 (100), 521 (14), 493 (36); HRMS: calcd for $C_{24}H_{34}Si_3Br_3$: 642.9518; found: 642.9507.

1,3,5-Tris(acetoxymethyl)-2,4,6-tris(ethynyl) benzene (9): Compound **8** (500 mg, 0.78 mmol) and potassium acetate (495 mg, 5.0 mmol) were stirred in dry DMF (5 mL) at room temperature for 16 h. The solvent was removed. To the remaining solid, water (20 mL) was added, and the suspension was extracted with dichloromethane (3 × 10 mL). The organic phase was dried ($MgSO_4$), the solvent was removed in vacuo, and the remaining solid was recrystallized from cyclohexane to give pure **9** as colorless crystals (254 mg, 72 %). M.p. 157–160 °C; ^{1}H NMR: $\delta = 5.42$ (s, 6H; CH_2), 3.56 (s, 3H; $C{\equiv}CH$), 2.04 (s, 9H; CH_3); ^{13}C NMR: $\delta = 170.58$ ($C{=}O$), 140.77, 125.86 (Ar), 87.87 (Ar-$C{\equiv}C$-), 77.14 ($C{\equiv}CH$), 63.23 (Ar-CH_2), 20.44 (CH_3); CI$^+$-MS: m/z (%): 366 (2) $[M]^+$, 343 (2), 307 (100), 265 (8); HRMS: calcd for $C_{21}H_{18}O_6$: 366.1103; found: 366.1099.

1,3,5-Tris(acetoxymethyl)-2,4,6-tris(2-ethoxycarbonylphenyl)ethynyl benzene (2): 2-Iodoethoxybenzoic acid (497 mg, 1.8 mmol) was stirred together with palladium(II)-bis(triphenylphosphine)dichloride (51 mg, 0.072 mmol) and copper(I) iodide (15 mg, 0.072 mmol) in dry degassed triethyl amine (5 mL) under argon for 30 min, before **9** (175 mg, 0.48 mmol) was added. The suspension was stirred at room temperature for 72 h. After removing the solvent, an ammonium hydroxide solution (1N, 25 mL) was added to the solid residue and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed in vacuo. The remaining solid was purified by column chromatography (hexanes/ethyl acetate 1:1, $R_f = 0.27$) and finally by recrystallisation from cyclohexane/benzene (2:1) to give pure **2** as orange crystals (58 mg, 15 %). M.p. 154 °C; ^{1}H NMR: $\delta = 7.98-7.95$ (m, 3H; Ar), 7.67–7.64 (m, 3H; Ar), 7.54–7.36 (m, 6H; Ar), 5.75 (s, 6H; CH_2), 4.38 (q, $J = 7$ Hz, 6H; CH_2CH_3), 2.05 (s, 9H; CO-CH_3), 1.36 (t, $J = 7$ Hz, 9H; CH_2-CH_3); ^{13}C NMR: $\delta = 170.97$ (CH_3-$C{=}O$), 165.37 (CH_3CH_2-$C{=}O$), 139.42, 134.40, 131.99, 131.78, 130.24, 128.56, 127.44, 122.93 (Ar), 97.82, 88.44 (Ar-$C{\equiv}C$), 64.02 (Ar-CH_2), 61.21 (CH_2CH_3) 20.92 (CO-CH_3), 14.26 (CH_3CH_2); CI$^+$-MS: m/z (%): 685 (15) $[M]^+$, 524 (16), 519 (14), 515 (14), 447 (76), 335 (69), 305 (20), 299 (10), 263 (100), 253 (22), 185 (43); HRMS: calcd for $C_{42}H_{37}O_9$: 685.2438; found: 685.2446.

1,3,5-Tris(hydroxymethyl)-2,4,6-tris(2-ethoxycarbonylphenyl)ethynyl benzene (2a): 2-Iodoethoxybenzoic acid (552 mg, 2.0 mmol) was stirred together with palladium(II)-tetrakis-(triphenylphosphine) (116 mg, 0.1 mmol) and copper(I) iodide (19 mg, 0.1 mmol) in dry degassed piperidine (3 mL) under argon for 30 min, before **9** (245 mg, 0.67 mmol) was added. The suspension was stirred at 80 °C for 48 h. The solvent was removed and the remaining solid was purified by column chromatography (hexanes/ethyl acetate 5:1, then 1:1); $R_f = 0.42$ (hexanes/ethyl acetate 5:2) and finally by recrystallisation from methanol to give pure **2a** as bright yellow crystals (102 mg, 23 %). M.p. 96–98 °C; ^{1}H NMR: $\delta = 7.91-7.88$ (m, 3H; Ar), 7.51–7.10 (m, 9H; Ar), 4.61 (s, 6H; CH_2), 4.31 (q, $J = 7$ Hz, 6H; CH_2CH_3), 1.7 (brs, 3H; OH), 1.32 (t, $J = 7$ Hz; 9H, CH_2-CH_3); ^{13}C NMR: $\delta = 167.61$ (CH_3CH_2-$C{=}O$), 147.37, 138.40, 134.84, 134.49, 132.10, 130.62, 130.00, 129.51, 127.56, 126.58 (Ar), 115.46, 110.95 (Ar-$C{\equiv}C$), 61.04 (Ar-CH_2), 31.91 (CH_2CH_3), 14.23 (CH_3CH_2); CI$^+$-MS: m/z (%): 810 (8) $[M]^+$, 795 (7), 751 (100), 737 (5), 723 (5), 709 (32), 693 (5); HRMS: calcd for $C_{48}H_{42}O_{12}$: 810.2676; found: 810.2687.

CCDC-175643 (**1**) and -175644 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors gratefully acknowledge Prof. Yves Rubin for helpful discussion on the synthetic pathway involving compounds **3**–**5** and the financial support by the Beckman Foundation and the National Science Foundation.

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[17] Crystallographic summary for **1**: Colorless prisms were grown from ethanol, triclinic, $P\bar{1}$ (No. 2), $Z = 2$ in a cell of dimensions: $a = 10.9063(2)$, $b = 12.0443(3)$, $c = 12.9586(3)$ Å, $\alpha = 75.062(1)$, $\beta = 81.897(1)$, $\gamma = 67.011(1)°$, $V = 1512.52(6)$ Å^3, $\rho_{\mathrm{calcd}} = 1.24$ g cm^{-3}, $\mu = 0.289$ mm^{-1}, $F(000) = 792$. A total of 10351 reflections were measured, 6894 unique ($R_{\mathrm{int}} = 0.026$), on a Nonus Kappa CCD using graphite monochromatized $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 153 K. The structure was refined on F^2 to an $R_w = 0.123$, with a conventional $R = 0.0486$ (4500 reflections with $F_o > 4[\sigma(F_o)]$), and a goodness of fit = 1.02 for 380 refined parameters.

[18] Crystallographic summary for **2**: Colorless laths were grown by slow evaporation from a 3:1 solution of ethanol/benzene, monoclinic, $P2_1/n$ (No. 14), $Z = 4$ in a cell of dimensions: $a = 19.6827(4)$, $b = 8.9314(2)$, $c = 23.8162(5)$ Å, $\beta = 99.020(1)°$, $V = 4134.97(15)$ Å^3, $\rho_{\mathrm{calcd}} = 1.30$ g cm^{-3}, $\mu = 0.094$ mm^{-1}, $F(000) = 1704$. A total of 15166 reflections were measured, 9426 unique ($R_{\mathrm{int}} = 0.079$), on a Nonus Kappa CCD using graphite monochromatized $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Åat 153 K. The structure was refined on F^2 to an $R_w = 0.171$, with a conventional $R = 0.0827$ (3989 reflections with $F_o > 4[\sigma(F_o)]$), and a goodness of fit = 1.14 for 542 refined parameters.

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Received: December 13, 2001 [F3737]