indicating strong porphyrin–porphyrin conjugation. Comparing **13**, **15** and **16** shows that the thiophene unit leads to more conjugation than phenylene, but less than anthracene. It is remarkable that the 9,10-diethynylanthracene bridge allows even more electronic communication than the simple butadiyne link in **14**. This implies that longer oligomers of type **2**/**3** should have strong third-order NLO behavior.

## *Experimental Section*

**13**: A solution of **12**[9] (54 mg, 50 μmol) in THF (8 mL) and pyridine (80 μL) was treated with dimethylaminotrimethyltin (41 μL, 250 μmol) at 50 °C for 2 h, then evaporated. To the resulting waxy residue was added THF (8 mL), **8**[11] (11 mg, 25 μmol), tris(dibenzylideneacetone)dipalladium(0) (2.7 mg, 3 μmol), and triphenylphosphane (3.1 mg, 12 μmol) under argon. The mixture was stirred at 50 °C for 24 h. Purification by chromatography on silica (eluting with 50/2/1 petroleum ether (60–80 °C)/ethyl acetate/pyridine) and recrystallization from $CH_2Cl_2$/methanol yielded **13** as a brown solid (27 mg, 46 %).

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[14] Crystals were grown by slow diffusion of *n*-pentane into a solution of **4** in 1 % $C_5H_5N/CHCl_3$, over two weeks. Crystal structure analysis for **4** · $2\,C_5H_5N$: $M_r = 1667.66$, triclinic, space group $P\bar{1}$, $a = 11.052(2)$, $b = 13.110(2)$, $c = 16.970(4)$ Å, $\alpha = 81.88(2)$, $\beta = 89.68(2)$, $\gamma = 77.20(2)^\circ$, $V = 2372.9(8)$ Å$^3$, $Z = 1$, $T = 293$; $\rho_{calc} = 1.167\ g\,cm^{-3}$; $\mu = 0.987\ mm^{-1}$, crystal dimensions 0.25 × 0.35 × 0.45 mm; diffractometer: Enraf-Nonius MACH3; radiation $Cu_{K\alpha}$ ($\lambda = 1.54184$ Å); scan mode: $\omega/2\theta$; range: $3.5 < \theta < 74.6$; measured reflections: 10156; independent reflections: 9712 ($R_{int} = 0.0186$); corrections applied: Lorentz polarization and experimental absorption correction (psi-scans, A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr. A* **1968**, *24*, 351–359) $T_{min}/T_{max}$ 0.7302/0.7839; $R$ values ($I > 2\sigma I$): $R1 = 0.0847$, $wR2 = 0.2492$, all data: $R1 = 0.1344$, $wR2 = 0.2784$. Structure solution with direct methods (SHELXS-86, G. Sheldrick, 1990). Structure refinement (SHELXL-93, G. Sheldrick, 1993): Full-matrix least squares methods against $F^2$; 548 parameters, 28 constraints, max/min residual electron density $0.662/-0.825\ e\,Å^{-3}$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100671. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# The Azide-Nitrilimine Analogy in Aluminum Chemistry**

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Covalent azides of type **A** are well-known 1,3-dipoles that have found widespread application in organic synthesis,[1] and that are also of increasing importance in inorganic chemistry.[2] Aluminum azides possess a rich structural diversity (derivatives **C**–**G**[3]) and constitute valuable single-source

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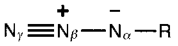
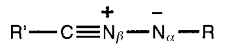


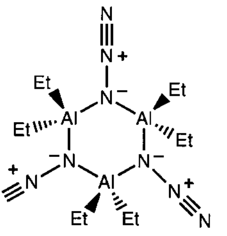
$\overset{+}{N_{\gamma}\equiv N_{\beta}}-\overset{-}{N_{\alpha}}-R$

**A**

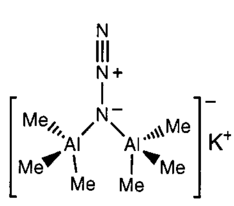


$R'-C\equiv\overset{+}{N_{\beta}}-\overset{-}{N_{\alpha}}-R$

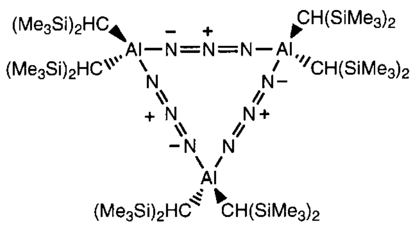
**B**



**C**



**D**



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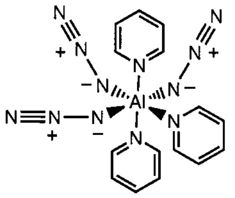
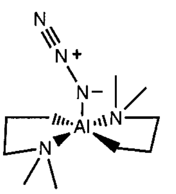
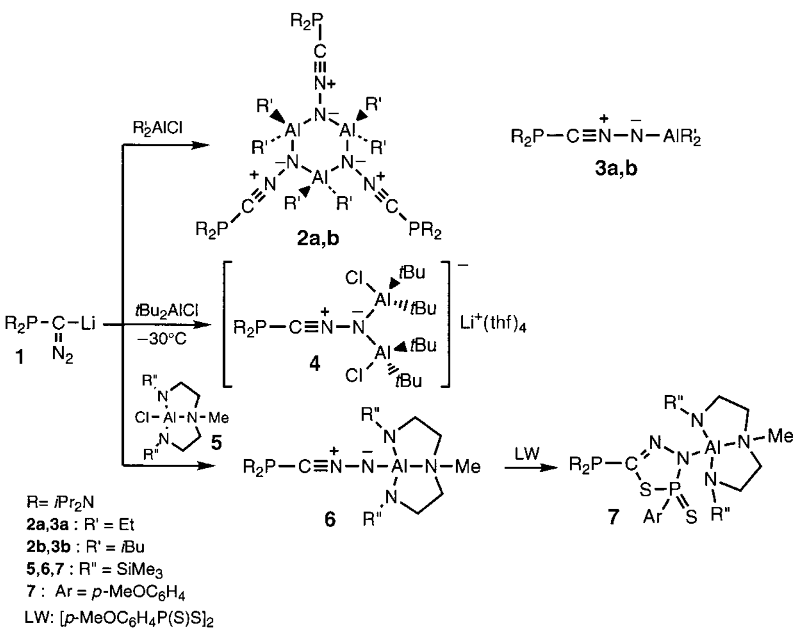


**F**



**G**



Scheme 1. Reactions of the lithium salt **1** with various aluminum chlorides.

precursors to AlN semiconducting phases.[4] For many years, the development of the chemistry of the isolobal nitrilimines of type **B** was hampered because of their potential instability and the lack of suitable preparative methods. In recent years, efficient routes have been established for preparing stable nitrilimines[5] and, just as for the azides, the $N_{\alpha}-N_{\beta}$ bond can be cleaved.[6] Here we report the synthesis of various aluminum–nitrogen derivatives featuring the nitrilimine skeleton.

The lithium salt of the [bis(diisopropylamino)phosphanyl]diazomethane **1**[7] was allowed to react in THF, at −78 °C, with one equivalent of $ClAlEt_2$ and $ClAl(iBu)_2$. After workup at room temperature, compound **2a** and **2b** were isolated in 85 and 90% yield,[8] respectively (Scheme 1). The IR absorption at 2140 $cm^{-1}$, the $^{14}N$ chemical shift of the $N_{\beta}$ center (**2a**: −203 ($\nu_{1/2} = 147$ Hz); **2b**: −203 ($\nu_{1/2} = 118$ Hz)), and the observation of doublet for the PC carbon atom (**2a**: 62.89 ($J_{P,C} = 74.3$ Hz); **2b**:63.21 ($J_{P,C} = 62.5$ Hz)) in the $^{13}C$ NMR spectrum were consistent with nitrilimine structures **3a**, **b**. However, derivatives **2a**, **b** are inert toward the Lawesson's reagent, one of the most effective 1,3-dipolarophiles.[9] Single crystals of **2b** suitable for an X-ray analysis[10] were grown from a solution in pentane at −30 °C (Figure 1). Compound **2b** is a trimer of nitrilimine **3b**, and is the first structurally characterized six-membered Al–N heterocycle in which the nitrogen and aluminum atoms possess different coordination numbers[11] (an X-ray diffraction study performed of poor quality crystals of **2a** also reveals a six-membered Al–N core). The central six-membered $(AlN_{\alpha})_3$ heterocycle features a twisted conformation, in contrast to the planar geometry postulated from IR and Raman data for the analogous azide derivative **C**.[3a] The mean endocyclic ring angles at the $N_{\alpha}$ (119.6°) and Al (109.6°) atoms reflect the $sp^2$ and $sp^3$ hybridization, respectively. The $Al-N_{\alpha}$ bond lengths (1.89–1.93 Å) are much longer than those observed for the only known aromatic alumazene **H** (1.78 Å),[11] which contains three-coordinate Al and N centers, but are comparable to those of tris(aminoalanes) **I** (1.95 Å),[12] which contain four-coordinate Al and N centers. The N-N-C fragments are almost linear (177.5–179.7°), as are the P-C-N angles (163.1–169.1°), reflecting the sp hybridization of the C and $N_{\beta}$ atoms. The $N_{\alpha}-N_{\beta}$ bond

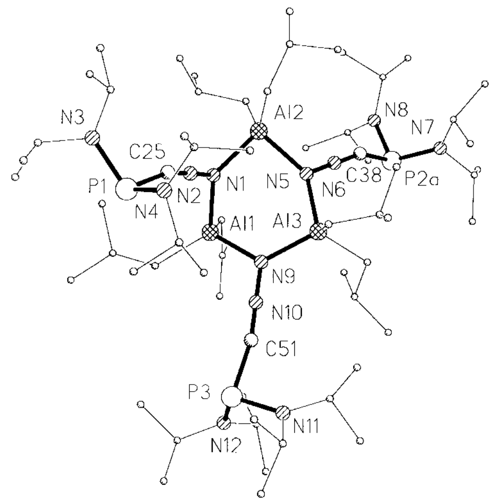
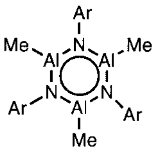
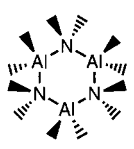


Figure 1. Molecular structure of **2b** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C25 1.804(7), C25–N2 1.144(7), N2–N1 1.287(6), N1–Al1 1.918(5), N1–Al2 1.893(5); P1-C25-N2 163.1(6), C25-N2-N1 177.9(6), N2-N1-Al1 114.5(4), N2-N1-Al2 119.2(4), Al1-N1-Al2 123.6(3), N1-Al1-N9 98.2(2).



**H**



**I**

lengths (1.26–1.29 Å) are half way between those for a double and a single N–N bond, and the $N_\beta$–C bond lengths (1.14–1.16 Å) are typical for a C–N triple bond. Taken together, these data support a heteropropargylic canonical structure for the C-N-N fragment, in contrast to most of the known nitrilimines, which feature a cumulenic structure.[13]

The same reaction was carried out with the more sterically hindered $ClAl(tBu)_2$ in the hope of stabilizing a monomeric nitrilimine. After workup at below −30 °C, highly air- and moisture-sensitive crystals of **4** (Scheme 1) suitable for an X-ray crystallographic study were obtained from the pentane solution at −30 °C (Scheme 1; Figure 2).[10] Compound **4** is a nitrilimine analogue of the azido complex **D**,[3b] featuring a 1,1-$\mu$-$N_\alpha$ bridging mode. In both cases, the $Al_2N_2E$ (E = C or N) fragment is planar (maximum deviation: **4**: 0.006 Å; **C**: 0.01 Å), indicating an $sp^2$ hybridization for the bridging $N_\alpha$ nitrogen, while the $N_\beta$ atom is sp-hybridized (**4:** C-N-N: 178.9°; **C**: N-N-N: 178°). The Al–N distances lie in the same range (**4**: 1.96 and 1.95 Å; **C**: 2.03 Å], the N–N bond length (1.29 Å) lies between the values for a double and a single bond, and the C–N bond length (1.16 Å) is typical for a C–N triple bond. The P-C-N fragment is almost linear (168.9°). Again these data as a whole support a heteropropargylic canonical structure for the C-N-N fragment. Compound **4** is one of the very rare examples of a lithium salt featuring an Al–Cl bond;[14] at temperatures above −20 °C, it decomposes rapidly leading to a complicated mixture of products.

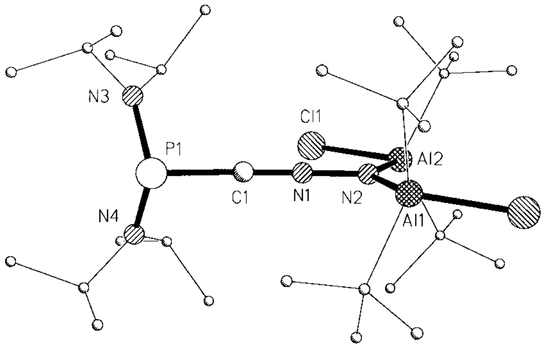


Figure 2. Molecular structure of the anion of **4** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.800(3), C1–N1 1.161(3), N1–N2 1.293(3), N2–Al1 1.954(3), N2–Al2 1.958(3); P1-C1-N1 168.9(3), C1-N1-N2 178.9(3), N1-N2-Al1 107.8(2), N1-N2-Al2 114.5(2), Al1-N2-Al2 137.7(1).

We have recently shown that the tridentate diamidoamine ligand $[(Me_3SiNCH_2CH_2)_2NR]^{2-}$ allows the preparation of a variety of monomeric aluminum(III) derivatives.[15] Therefore, the lithium salt of **1** was allowed to react with the aluminum chloride **5**. After workup at room temperature, nitrilimine **6**[8] was isolated as an orange oil in 91 % yield (Scheme 1). The $^{31}$P (48.51) and $^{13}$C (61.17 (d, $J_{\mathrm{P,C}} = 83.5$ Hz)) NMR signals for the P-C-N-N skeleton are comparable to those observed for compounds **2a**, **b**, but the IR absorption is shifted to lower frequency ($\tilde{\nu} = 2076\ \mathrm{cm}^{-1}$; $\Delta\tilde{\nu} = 64\ \mathrm{cm}^{-1}$/**2a**, **b**). The simplicity of the NMR spectra for the diamidoamine part is in agreement with a monomeric structure.[15] Interestingly, in contrast to derivatives **2**, compound **6** reacted with the Lawesson's reagent,[9] affording the expected [3+2] adduct **6** as an orange oil in 63 % yield.

The only example of four-coordinate "monomeric" aluminum azide features intermolecular hydrogen bonding involving the $N_\alpha$ and $N_\gamma$ atoms in the solid state.[3d] In contrast, the azide **8**,[8] which is analogous to nitrilimine **6**, prepared in 85 % yield by treatment of the aluminum chloride **5** with $NaN_3$, is monomeric as proved by a single-crystal X-ray diffraction study[10] (Figure 3). These results clearly show that nitrilimines of type **B** can indeed exhibit a comparable coordination behavior to that of covalent azides **A**.

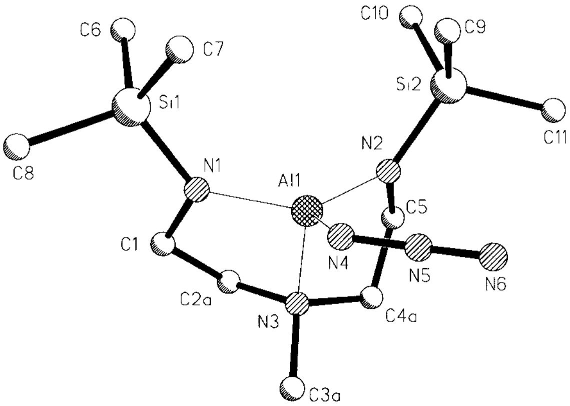


Figure 3. Molecular structure of **8** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] Al1–N1 1.805(4), Al1–N2 1.807(4), Al1–N3 1.970(4), Al1–N4 1.837(5), N4–N5 1.212(6), N5–N6 1.137(6); Al1-N4-N5 129.9(4), N4-N5-N6 176.6(5).

## *Experimental Section*

In a typical experiment a solution of $Et_2AlCl$ (1M, 1.9 mL) in hexane was added dropwise at −78 °C to a solution (10 mL) of **1** (prepared by addition at −78 °C of a solution of BuLi (1.9 mmol) in hexane to the bis(diisopropylamino)phosphanyldiazomethane (0.52 g, 1.9 mmol)) in THF. The solution was allowed to warm to room temperature, stirred for 1 h, and the solvent was removed under vacuum. The residue was treated with pentane and filtered (10 mL). Compound **2a** was obtained from a pentane solution at −30 °C as colorless crystals (0.64 g).

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[8] Selected spectroscopic data: **2a**: M.p. 98 °C; $^{31}$P NMR ($C_6D_6$): $\delta = 43.2$(s); **2b**: M.p. 142 °C; $^{31}$P NMR ($C_6D_6$): $\delta = 44.4$ (s); **6**: $^{1}$H NMR ($C_6D_6$): $\delta = 0.37$ (s; SiMe$_3$), 1.16 (d, $J = 6.7$ Hz; CHC$H_3$), 1.29 (d, $J = 6.7$ Hz; CHC$H_3$), 1.87 (dt, $J = 11.5$, 5.6 Hz; CH$_2$), 1.94 (s; NCH$_3$), 2.20 (dt, $J = 11.5$, 5.8 Hz; CH$_2$), 2.79 (dd, $J = 5.6$, 5.8 Hz; 2CH$_2$), 3.46 (septd, $J = 6.7$, 6.7 Hz; C$H$CH$_3$), 3.52 (septd, $J = 6.7$, 6.7 Hz; C$H$CH$_3$); **7**: $^{31}$P NMR ($C_6D_6$): $\delta = 49.1$ (d, $J = 4.3$ Hz), 104.7 (d, $J = 4.3$ Hz); $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 134.5$ (dd, $J = 59.4$, 13.4 Hz; PCSP); IR (pentane): $\tilde{\nu} = 1594$ cm$^{-1}$; **8**: $^{1}$H NMR ($C_6D_6$): $\delta = 0.48$ (s; SiCH$_3$), 1.96 (s; NCH$_3$), 1.99 (dt, $J = 11.7$, 5.8 Hz; CH$_2$), 2.34 (dt, $J = 11.7$, 5.7 Hz; CH$_2$), 2.91 (dd, $J = 5.7$, 5.8 Hz; 2 CH$_2$); $^{27}$Al NMR ($C_6D_6$): $\delta = +118$ ($\nu_{1/2} = 3800$ Hz); $^{14}$N NMR ($C_6D_6$): $\delta = -138.9$ ($\nu_{1/2} = 70$ Hz), $-202.9$ ($\nu_{1/2} = 15$ Hz), $-224.5$ ($\nu_{1/2} = 25$ Hz); IR (THF): $\tilde{\nu} = 2125$ cm$^{-1}$.

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[10] Crystal data: **2b**: $C_{63}H_{138}Al_3N_{12}P_3$, orthorhombic, $P2_12_12_1$, $a = 13.701(7)$, $b = 14.354(7)$, $c = 41.008(15)$ Å, $V = 8065(6)$ Å$^3$, $Z = 4$, with 665 parameters refined on 11282 reflections with $F > 2\sigma(F_o)$], $R1 = 0.063$ and $wR2 = 0.196$; **4**: $C_{45}H_{87}Al_2Cl_2LiN_4O_4P$, monoclinic, $P2_1/c$, $a = 17.490(5)$, $b = 11.458(2)$, $c = 28.904(7)$ Å, $\beta = 92.67(2)°$, $V = 5786.1(24)$ Å$^3$, $Z = 4$, with 584 parameters refined on 9514 reflections with $F > 2\sigma(F_o)$], $R1 = 0.065$ and $wR2 = 0.200$; **8**: $C_{11}H_{29}AlN_6Si_2$, monoclinic, $P2_1/n$, $a = 9.366(1)$, $b = 8.123(1)$, $c = 25.794(3)$ Å, $\beta = 93.76(1)°$, $V = 1958.1(4)$ Å$^3$, $Z = 4$, with 217 parameters refined on 2490 reflections with $F > 2\sigma(F_o)$], $R1 = 0.078$ and $wR2 = 0.185$. The structures were solved by direct methods[16a] and refined by full-matrix least squares on $F^2$ [16b].Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100758. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# Direct Observation of Radical Intermediates While Investigating the Redox Behavior of Thiamin Coenzyme Models[**]

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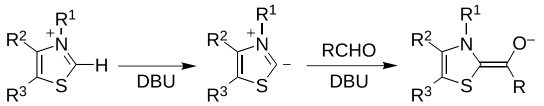
Thiamin diphosphate (ThDP) is the coenzyme for a number of important biochemical reactions, including the decarboxylation of pyruvic acid to acetaldehyde. The conjugate base of 2-hydroxyethyl-ThDP, which is an acyl carbanion equivalent and called an "active aldehyde", plays a key role in the catalysis of ThDP-dependent enzymes.[1] The active aldehyde is able to reduce various physiological electron acceptors, for example the lipoamide in the pyruvate dehydrogenase multienzyme complex,[2] the flavin adenine dinucleotide (FAD) in pyruvate oxidase,[3] and the $Fe_4S_4$ cluster in pyruvate-ferredoxin oxidoreductase.[4] Simple thiazolium ions have been studied extensively as models of the thiamin coenzyme, and valuable information about the elementary step of ThDP-dependent enzymatic reactions was provided.[5–10] The active aldehyde, however, readily undergoes acyloin-type condensation with a second pyruvate or aldehyde molecule in the absence of oxidizing agents.[1, 11] Such instability of the active aldehydes has precluded the direct determination of the most fundamental properties of the intermediates, such as oxidation potentials.[12] Therefore, no direct observation of the radical intermediates derived from thiamin coenzyme models has been described so far. Here we report the direct observation of radical intermediates of active aldehydes $\mathbf{2}^-$ with low-temperature cyclic voltammetry and EPR spectroscopy. Active aldehydes $\mathbf{2}^-$ are derived from 3-benzylthiazolium salts **1** and simple aldehydes such as acetaldehyde and benzaldehyde in the presence of 1,8-diazabicylco[5.4.0]undec-7-ene (DBU).

A cyclic voltammogram (CV) of the active aldehyde $\mathbf{2a}^-$—which is prepared in situ by adding neat DBU ($1.0 \times 10^{-2}$ M) to a deaerated solution of 3-benzylthiazolium ion **1a** ($5.0 \times$



**1** $\mathbf{1}^-$ $\mathbf{2}^-$

**a** $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = H$, R = Me
**b** $R^1 = PhCH_2$, $R^2 = R^3 = Me$, R = Me
**c** $R^1 = PhCH_2$, $R^2 = R^3 = H$, R = Me
**d** $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = H$, R = Ph
**e** $R^1 = PhCH_2$, $R^2 = R^3 = Me$, R = Ph
**f** $R^1 = PhCH_2$, $R^2 = R^3 = H$, R = Ph
**g** $R^1 = PhCD_2$, $R^2 = Me$, $R^3 = H$, R = Me
**h** $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = H$, R = $CD_3$
**i** $R^1 = PhCD_2$, $R^2 = Me$, $R^3 = H$, R = Ph

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