The First Planar-Chiral Stable Carbene and Its Metal Complexes

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Starting from (*S*)-*S*-ferrocenyl-*S*-4-tolyl sulfoxide the planar-chiral imidazolium salt (R_p)-1-[2-(trimethylsilyl)ferrocenylmethyl]-3-methylimidazolium iodide was synthesized utilizing the directed *ortho*-metalation strategy. Deprotonation thereof yielded the first planar-chiral carbene, (R_p)-3-methyl-1-[2-(trimethylsilyl)ferrocenylmethyl]imidazolin-2-ylidene, which is stable in tetrahydrofuran at room temperature for several hours. Conversion with sulfur resulted in the formation of the corresponding thiourea derivative. Reaction with the metal precursors $[Rh(COD)Cl]_2$ and $Cr(CO)_6$ gave air-stable complexes. For the latter product an X-ray structural analysis was conducted.

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The isolation and characterization of free and stable carbenes has been an appealing target for a long time.[1] Compound **1** has already been studied by Wanzlick as early as in 1960.[2] Very soon after Öfele and Wanzlick prepared the first transition metal complexes thereof.[3] At that time, however, direct evidence for the existence of free carbenes in solution was unavailable.[4] Finally, in 1991 Arduengo reported on *N*-heterocyclic carbenes (NHCs) such as **2**, which were so stable that their structure could be determined by X-ray diffraction.[5−7] Soon after, the enormous potential of carbenes in mimicking phosphine ligands in catalysis was recognized. A recent prominent example illustrating this concept is the new olefin metathesis catalyst **3**, which shows enhanced performance compared to Grubbs's original system, having tricyclohexylphosphine and a NHC as ligands on ruthenium.[8,9]

Chiral carbenes were first synthesized by Lappert, who introduced compounds with substituents at nitrogen having a stereogenic center.[10] Later, those carbenes have been applied in asymmetric catalysis,[11] and respectable results in terms of activity and enantioselectivity have been achieved in the hydrosilylation of ketones.[12,13] Surprisingly, up to now no planar-chiral carbenes have been described despite the fact that this element of chirality is a vital part of many highly successful ligands, especially those based on the ferrocene scaffold.[14] As part of our ongoing studies on the impact of planar chirality on asymmetric catalysis,[15,16] we have prepared the first planar-chiral free NHC and investigated its reactivity as well as capability to form metal complexes.[17]

The synthetic methodology to generate planar-chiral ferrocenes is well established.[18] Most protocols rely on the directed *ortho*-metalation strategy[19] in combination with a chiral anchoring group. For reasons of flexibility, we chose Kagan's sulfoxide route, which allows the synthesis of a wide range of 1,2-substituted ferrocenes.[20]

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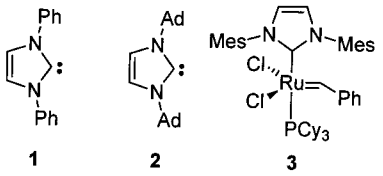
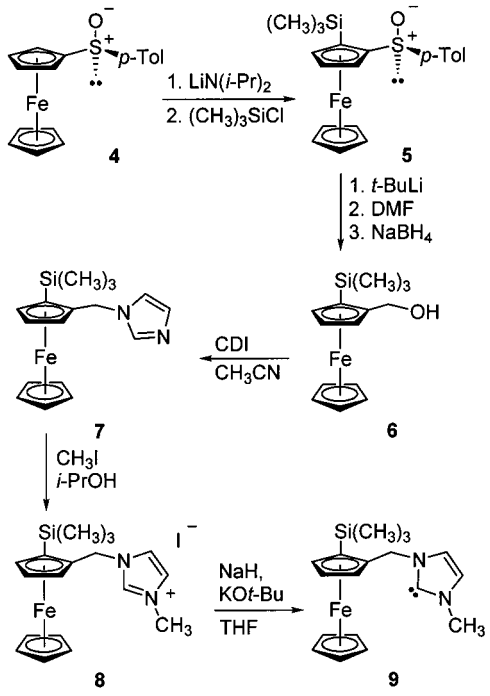


Figure 1.

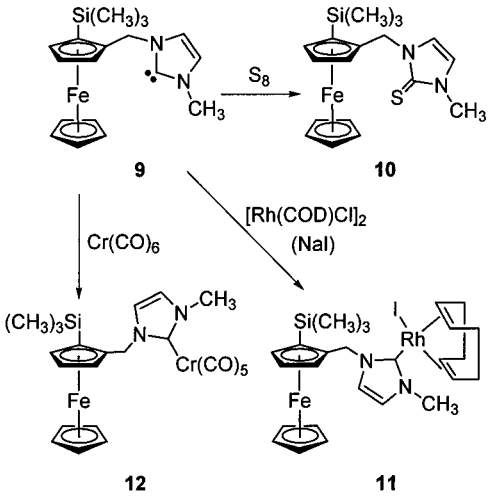
Scheme 1



Starting with *(S)-S*-ferrocenyl-*S*-4-tolyl sulfoxide (**4**), *ortho*-functionalization with lithium diisopropylamide (LDA) and Me_3SiCl afforded **5**. Treatment of **5** with *t*-BuLi replaced the sulfoxide moiety by lithium. The resulting anion was then converted into hydroxymethyl derivative **6** by addition of *N*,*N*-dimethyl formamide followed by reduction of the intermediate aldehyde with sodium borohydride (Scheme 1). Reaction of alcohol **6** with *N*,*N*′-carbonyl diimidazole (CDI)[21] afforded imidazole **7** in excellent yield. As a precursor for stable NHC **9** imidazolium salt **8** was prepared by quaternization of **7** with methyl iodide. Finally, following Arduengo's protocol, the deprotonation of **8** to give NHC **9** was performed in THF at ambient temperature with 5 mol % of KO-*t*-Bu and stoichiometric NaH. All reactions gave good to excellent yields and could be conducted on a multigram scale.

The conversion of **8** into **9** could readily be monitored by observing the evolution of hydrogen. The reaction was usually complete within 60 min. Full conversion was indicated by the change of the initial suspension of NaH in the reaction mixture into a clear solution with precipitated NaI. This result is in contrast with the syntheses of many other free carbenes, where the insolubility of the imidazolium salt precursors requires either longer deprotonation times[6] or the addition of

Scheme 2



liquid ammonia.[22] Since ferrocene **8** is soluble in THF, reduced reaction times are possible.

The resulting planar-chiral free carbene **9** is reasonably stable in THF at room temperature. A proton NMR spectrum of **9** was obtained after conducting the deprotonation of **8** in THF-d_8. In comparison with the corresponding signals of the imidazolium salt the characteristic high-field shift for the two remaining imidazole protons gives evidence for the presence of a free electron pair at the carbene carbon.

To investigate the reactivity of **9**, it was subjected to various carbene-typical reactions (Scheme 2). Treatment with sulfur yielded the expected thiourea derivative **10**. Reactions with $[Rh(COD)Cl]_2$ or $Cr(CO)_6$ led to the formation of air-stable complexes **11** and **12**, respectively. In the former case the formation of diastereomers was observed by NMR spectroscopy, which was attributed to a hindered rotation around the Rh−carbene carbon bond. Furthermore, the chloride at rhodium was exchanged by iodide, which was present in the reaction mixture.

Suitable single crystals for X-ray structure analysis were obtained for chromium carbonyl complex **12**. Its molecular structure in the solid state is depicted in Figure 2.

The structure of **12** in the solid state has been determined by means of single-crystal analysis and is shown in Figure 2. The absolute configuration of **12** has been elucidated using Flack's method.[24] At 2.155(5) Å the Cr=C bond is quite long but still lies in the upper part of the range usually found for chromium carbene complexes. Spatial demands of the bulky ferrocenyl ligand might at least in part account for this bond length.

In conclusion, we have synthesized the first planar-chiral free carbene and demonstrated its capability to form metal complexes. Currently, we are varying the substitution pattern of the ferrocene backbone by utilizing other *ortho*-directing groups and exploring the potential of planar-chiral carbenes as ligands in asymmetric catalysis.[25]

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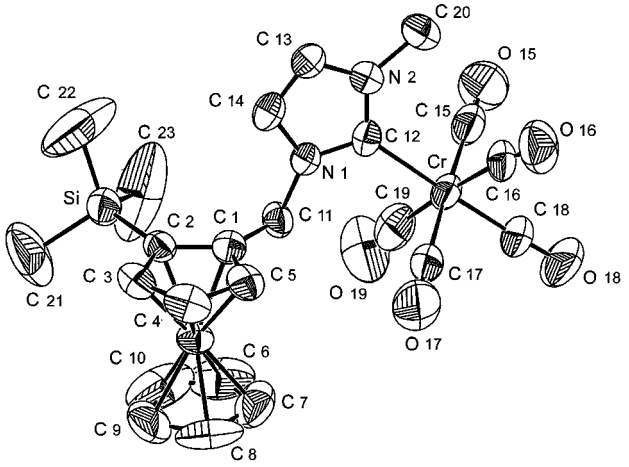

Figure 2. Structure of **12** in the solid state (ORTEP[23] plot). The ellipsoids represent a 50% probability level. Selected bond lengths (Å) und angles (deg): Cr−C12 = 2.155(5), average Fe−C = 2.024(7), average Cr−CO = 1.879(5), average CO = 1.137(7), average C−C in Cp = 1.39(1), C13−C14 = 1.349(6), C12−N1 = 1.359(4), C12−N2 = 1.345(6), N1−C14 = 1.390(6), N2−C13 = 1.358(5); N1−C12−N2 = 103.7(4), N1−C12−Cr = 127.7(3), N2−C12−Cr = 128.6(3), C12−Cr−C18 = 177.5(2).

Experimental Section

General Comments. All manipulations except workup and purification were conducted under an inert atmosphere of Ar using standard Schlenk techniques. Tetrahydrofuran was distilled from sodium/benzophenone ketyl radical and acetonitrile from calcium hydride prior to use. *n*-Butyllithium and *tert*-butyllithium were purchased from Merck Schuchardt as a 1.6 N solution in *n*-hexane, and (*S*)-(−)-4-toluenesulfinic acid menthyl ester (Andersen's reagent) and 1 N KO-*t*-Bu in THF from Aldrich. $[Rh(COD)Cl]_2$ was obtained from Strem Chemicals. Compounds **4** and **5** were prepared according to literature procedures.[20] ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts are given in ppm with internal referencing to the solvent peaks. IR spectra were measured on a Perkin-Elmer 1760 S spectrometer, MS spectra on a Varian MAT 212, and HRMS spectra on a Finnigan MAT 95 mass spectrometer, both with EI ionization. Elemental analyses were carried out at the Institut für Organische Chemie der RWTH Aachen on a Heraeus CHNO-Rapid apparatus. All experiments were conducted at least twice to ensure reproducibility. The descriptors for planar chirality are based on the rules introduced by Schlögl.[26]

(R_p)-[2-(Trimethylsilyl)ferrocenyl]methanol (6). At −78 °C a solution of 1.71 g (4.32 mmol) of (S,S_p)-*S*-4-tolyl-*S*-[(2-trimethylsilyl)ferrocene] (**5**) in 30 mL of THF is treated dropwise with 2.96 mL (1.85 mmol) of *tert*-butyllithium. The dark red solution is stirred at this temperature for 10 min, then 0.99 mL (12.84 mmol) of *N*,*N*-dimethylformamide is injected. After stirring at −78 °C for 1 h water (5 mL) and methanol (10 mL) are added. At ambient temperature 567 mg (14.98 mmol) of $NaBH_4$ is added portionwise, resulting in evolution of hydrogen and a color change to orange. After stirring for 1 h, the reaction mixture is separated between 60 mL of water and 60 mL of diethyl ether. The aqueous layer is extracted with diethyl ether (2 × 50 mL), the combined organic layers are dried ($MgSO_4$), the solvent is evaporated, and the crude product is purified by column chromatography (pentane/diethyl ether, 3:2) to yield 1.00 g (79%) of the title compound as an orange solid: mp 56−58 °C; $[\alpha]_D$ −7° [*c* 1.2, CH_2Cl_2]; ^1H NMR ($CDCl_3$) δ 0.27 (s, 9H), 1.70 (b, 1H), 4.08−4.15 (m, 6H), 4.25−4.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 0.3, 60.8, 68.3, 70.0, 71.5, 71.7, 74.6, 92.3; MS (EI, 70 eV) *m*/*z* (%) 288 (100, M^+), 255 (5), 223 (7), 195 (9), 138 (31); IR (KBr) $\tilde{\nu}$ 3261, 3096, 2956, 2892, 1406, 1304, 1246. Anal. Calcd for $C_{14}H_{20}FeOSi$: C, 58.34; H, 6.99. Found: C, 58.36; H, 6.93.

(R_p)-1-[2-(Trimethylsilyl)ferrocenylmethyl]imidazole (7). A solution of 723 mg (2.51 mmol) of **6** and 1.22 g (7.52 mmol) of 1,1′-carbonyl diimidazole is refluxed for 1 h in 35 mL of acetonitrile. After cooling to ambient temperature the reaction mixture is separated between 100 mL of water and 100 mL of diethyl ether. The aqueous layer is extracted with diethyl ether (2 × 50 mL), the combined organic layers are washed with water (2 × 50 mL) and brine (50 mL) and dried ($MgSO_4$), the solvent is evaporated, and the crude product is purified by column chromatography (dichloromethane/methanol, 95:5) to yield 819 mg (97%) of the title compound as a red oil: $[\alpha]_D$ −16° [*c* 1.3, CH_2Cl_2]; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9H), 3.92−3.98 (m, 6H), 4.21−4.30 (m, 2H), 4.75 (d, J = 14.3 Hz, 1H), 4.83 (d, J = 14.3 Hz, 1H), 6.76 (b, 1H), 6.95 (b, 1H), 7.33 (b, 1H); ^{13}C NMR ($CDCl_3$) δ 0.1, 46.6, 68.6, 70.4, 71.1, 72.4, 74.9, 86.1, 118.4, 128.7, 136.2; MS (EI, 70 eV) *m*/*z* (%) 338 (100, M^+), 271 (38), 188 (9); IR (neat) $\tilde{\nu}$ 3097, 2954, 2895, 1687, 1504, 1403; HRMS calcd for $C_{17}H_{22}FeN_2Si$ 338.0902; found 338.0902.

(R_p)-1-[2-(Trimethylsilyl)ferrocenylmethyl]-3-methylimidazolium Iodide (8). A solution of 720 mg (2.13 mmol) of **7** and 0.147 mL (2.35 mmol) of iodomethane in 2 mL of 2-propanol is heated to 40 °C for 24 h. The solvent is evaporated and the crude product purified by column chromatography (dichloromethane/methanol, 95:5) to yield 881 mg (86%) of the title compound as a red oil: $[\alpha]_D$ −35° [*c* 1.0, CH_2Cl_2]; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 4.10 (s, 3H), 4.20 (b, 1H), 4.23 (s, 5H), 4.48 (b, 1H), 4.72 (b, 1H), 7.19 (b, 1H), 7.73 (b, 1H), 9.60 (b, 1H); ^{13}C NMR ($CDCl_3$) δ 0.1, 36.7, 49.8, 68.8, 71.5, 71.6, 73.2, 75.4, 81.6, 120.5, 123.3, 134.9; IR (neat) $\tilde{\nu}$ 3097, 2954, 2895, 1687, 1504, 1403.

(R_p)-3-Methyl-1-[2-(trimethylsilyl)ferrocenylmethyl]-imidazolin-2-ylidene (9). At ambient temperature 22 mg (0.913 mmol) of sodium hydride and 46 μL of a 1 N solution of KO-*t*-Bu in THF (0.046 mmol, 5 mol %) are added to a solution of 400 mg (0.83 mmol) of **8** (azeotropically dried with benzene prior to the reaction) in 20 mL of THF. Stirring is continued for 60 min, during which time the precipitation of a white solid (NaI) and evolution of hydrogen can be observed.

The carbene solution thus obtained is employed without any further purification in the subsequent reactions: ^1H NMR (THF-d_8) δ 0.20 (s, 9H), 3.72 (s, 3H), 4.05 (b, 1H), 4.18 (s, 5H), 4.25 (b, 1H), 4.46 (b, 1H), 5.12 (b, 2H), 6.72 (b, 1H), 6.93 (b, 1H).

(R_p)-3-Methyl-1-[2-(trimethylsilyl)ferrocenylmethyl]-imidazoline-2-thione (10). Carbene **9** (0.42 mmol) in THF is added to a suspension of 13 mg (0.41 mmol) of sulfur in 5 mL of THF. After stirring at ambient temperature for 30 min the reaction is stopped by the addition of 15 mL of water, and resulting mixture is extracted with diethyl ether (3 × 25 mL). The combined organic layers are dried ($MgSO_4$), the solvent is evaporated, and the product is purified by column chromatography (pentane/diethyl ether, 1:1) to yield 104 mg (65%) of the title compound as a yellow solid: mp 150−152 °C; $[\alpha]_D$ −11° [*c* 1.2, CH_2Cl_2]; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 3.61 (s, 3H), 4.13−4.23 (m, 6H), 4.39 (b, 2H), 4.82 (d, J = 14.5 Hz, 1H), 4.96 (d, J = 14.5 Hz, 1H), 6.30 (b, 1H), 6.57 (b, 1H); ^{13}C NMR ($CDCl_3$) δ 0.3, 34.8, 47.9, 69.0, 71.0, 72.2, 73.5, 75.2, 84.7, 115.5, 117.0, 161.3; MS (EI, 70 eV) *m*/*z* (%) 384 (80, M^+), 319 (71), 271 (100), 169 (41); IR (KBr) $\tilde{\nu}$ 2952, 2891, 1565, 1403.

(25) In preliminary studies we already demonstrated the capability of complex **11** to serve as catalyst. Using 1−3 mol % of **11** in the hydrosilylation of acetophenone and propiophenone with Ph_2SiH_2 as reducing agent, ca. 50% conversion was achieved after 24 h at −10 °C. Hydrolysis of the resulting silyl ethers with catalytic amounts of *p*-TosOH afforded the corresponding alcohols, alas as racemates.

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Anal. Calcd for $C_{18}H_{24}FeN_2SSi$: C, 56.24; H, 6.29; N, 7.29. Found: C, 56.12; H, 6.17; N, 7.16.

(R_p)-(η^4-Cyclooctadiene)iodo-3-methyl-{1-[2-(trimethylsilyl)ferrocenylmethyl]imidazolin-2-ylidene}rhodium-(I) (11). Carbene **9** (0.21 mmol) in THF is added to a solution of 51 mg (0.10 mmol) of $[Rh(COD)Cl]_2$ in 5 mL of THF. After stirring at ambient temperature for 24 h the reaction is stopped by the addition of 15 mL of water, and the resulting mixture is extracted with diethyl ether (3 × 25 mL). The combined organic layers are dried ($MgSO_4$), the solvent is evaporated, and the product is purified by column chromatography (pentane/diethyl ether 1:1) to yield 135 mg (93%) of the title compound as a yellow foam (2:1 diastereomeric ratio). Recrystallization (hexane/methyl *tert*-butyl ether, 2:1) yields 90 mg (62%) of the major diastereomer as yellow crystals. Analytical data for the major diastereomer: mp 179 °C (dec); $[\alpha]_D$ −3° [*c* 0.6, CH_2Cl_2]; ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9H), 1.70−2.13 (m, 4H), 2.19−2.50 (m, 4H), 3.40−3.60 (m, 2H), 3.96 (s, 3H), 4.11−4.36 (m, 7H), 4.61 (b, 1H), 5.08 (d, J = 14.2 Hz, 1H), 5.18−5.38 (m, 2H), 5.92 (d, J = 14.2 Hz, 1H), 6.58 (b, 1H), 6.78 (b, 1H); ^{13}C NMR ($CDCl_3$) δ 0.6, 29.2, 30.1, 31.9, 32.8, 50.2, 69.1, 69.2, 70.7 (d, J_{C-Rh} = 13.7 Hz), 71.2, 71.4 (d, J_{C-Rh} = 13.7 Hz), 73.8, 74.5, 86.4, 96.2 (d, J_{C-Rh} = 14.7 Hz), 96.3 (d, J_{C-Rh} = 14.7 Hz), 119.9, 121.7, 181.4 (d, J_{C-Rh} = 48 Hz); MS (EI, 70 eV) *m*/*z* (%) 690 (46, M^+), 582 (48), 382 (100); IR (KBr) $\tilde{\nu}$ 3094, 2952, 2872, 2824, 1453, 1401; HRMS calcd for $C_{26}H_{36}FeIN_2RhSi$ 690.0090; found 690.0089.

(R_p)-Pentacarbonyl-{3-methyl-1-[2-(trimethylsilyl)ferrocenylmethyl]imidazolin-2-ylidene}chromium(0) (12). Carbene **9** (0.23 mmol) in THF is added to a solution of 46 mg (0.21 mmol) of $Cr(CO)_6$ in 5 mL of THF. After stirring at ambient temperature for 24 h the solvent is evaporated and the product purified by column chromatography (pentane/diethyl ether, 1:1) to yield 78 mg (68%) of the title compound as a yellow syrup crystallizing slowly: mp 135 °C (dec); $[\alpha]_D$ −141° [*c* 1.6, CH_2Cl_2]; ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 9H), 3.87 (s, 3H), 4.15−4.27 (m, 7H), 4.35−4.45 (m, 2H), 4.96 (d, J = 14.2 Hz, 1H), 5.46 (d, J = 14.2 Hz, 1H), 6.62 (b, 1H), 6.82 (b, 1H); ^{13}C NMR ($CDCl_3$) δ 0.5, 39.2, 51.7, 69.1, 69.2, 71.6, 72.6, 73.2, 75.1, 85.3, 120.7, 122.7, 189.8, 218.1, 221.5; MS (EI, 70 eV) *m*/*z* (%) 544 (11, M^+), 404 (100), 266 (21), 198 (28); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2957, 2053, 1966, 1907, 1440; HRMS calcd for $C_{23}H_{24}CrFeN_2O_5Si$ 544.0209; found 544.0207.

X-ray Crystal Structure Analysis of 12. Single crystals of **12** have been obtained from methyl *tert*-butyl ether at 298 K. The complex crystallizes in triclinic space group *P*1 (No. 1) with a = 7.2543(6) Å, b = 9.1986(7) Å, c = 10.3309(8) Å, α = 103.215(2)°, β = 104.883(2)°, and γ = 90.391(2)°, resulting in a cell volume of V = 647.03(9) Å^3. At Z = 1 and M_r = 544.39 the calculated density amounts to d_{cal} = 1.397 g cm^{-3}. A total number of 9007 reflections have been collected at room temperature in the range $-9 < h < 9$, $-12 < k < 12$, $-13 < l < 12$ on a Bruker Smart APEX CCD diffractometer employing Mo Kα radiation (λ = 0.71073 Å). Diffraction data have been corrected for absorption effects (μ = 1.048 mm^{-1}) employing the empirical SADABS method[27] (max. and min. effective transmission are 1.000 and 0.656, respectively). The structure has been solved employing direct methods as implemented in the Xtal3.7 package[28] of crystallographic routines using GENSIN[29] to generate structure invariant relationships and GENTAN[30] for the general tangent phasing procedure. All non-hydrogen atoms have been subjected to an anisotropic full-matrix least-squares refinement on F including 289 parameters and 5006 observed reflections ($F > 4\sigma(F)$) terminating at R (R_w) = 0.041 (0.044, $w = (\sigma^2(F) + 0.0004F^2)^{-1}$, a goodness of fit of S = 1.038, and a final residual electron density of −0.41/+0.30 e Å^{-3}. Some hydrogen atoms could be located. The remaining ones have been calculated in idealized positions. Their isotropic displacement parameters have been fixed at 1.5U of the relevant heavy atom. All hydrogen parameters have been fixed in the refinement process. A separate calculation resulted in an absolute structure parameter of X_{abs} = 0.13(3) for the structure shown in Figure 2. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 167668.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds and crystallographic data concerning the X-ray structure of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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