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Preparation of chiral indenes containing β-pinenyl derived ligand substituents

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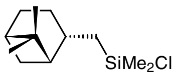
Abstract—A simple procedure for the preparation of new 1-, 2- and 1,3-chirally substituted indenes is described in which indenyllithium or 2-indenylmagnesium bromide is reacted with a β-pinenyl derived chlorosilane. Synthesis of the ethylene bridged bis(indene) analogues of two of the new compounds is also described.

1. Introduction

Chiral group 4 bis(indenyl)metallocenes are desirable reagents and catalysts for a variety of applications ranging from enantioselective transformations of small organic molecules[1] and stereoselective polymerization of alkenes[2] to enantioselective cyclopolymerization of nonconjugated dienes.[3] Commonly employed precatalysts are the C_2-symmetric bridged *ansa*-bis(indenyl) complexes, originally developed by Brintzinger and co-workers,[4] many of which are only accessible in racemic form and thus unsuitable for enantioselective applications.[5] Consequently, synthesis of monosubstituted indenes bearing chiral substituents is of great interest, although relatively few methods for their preparation have been reported in the literature. Earlier examples include the 3-neomenthyl-, neoisomenthyl-, menthyl-, isomenthyl- and neoisopinocamphylindenes and some transition metal complexes of these as reported by Erker and Halterman,[6,7] as well as the corresponding 2-menthyl substituted analogues disclosed by Schumann and Halterman.[7b,8] Synthesis of the 3-substituted indenes was accomplished by reaction of indenyllithium with a chiral terpenyl derived alkylsulfonate. Alternatively, a palladium-catalyzed cross-coupling reaction between menthylmagnesium chloride and 3-indenyl triflate or 2-bromoindene can be utilized for the preparation of 3- and 2-menthylindenes, respectively. Recently, Halterman and Crow described the preparation of chiral annulated indenes by alkylation of nopinone, verbenone and menthone enolates with 2-bromomethylbromobenzene followed by $CrCl_2/NiCl_2$ catalyzed ring closure and subsequent dehydration.[9] Here, we report a facile access to new 1-, 2- and 1,3-chirally substituted indenes and some of their ethylene bridged bis(indenyl) analogues derived from the chiral chlorosilane **1** (Fig. 1), which in turn is readily available by hydrosilylation of β-pinene with dimethylchlorosilane.[10]



1

Figure 1. Chloro{[(1*S*, 2*S*, 5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl} dimethylsilane.

2. Results and discussion

The chiral 2-substituted indene **2** was prepared in 34% isolated yield by reaction of 2-indenylmagnesium bromide[11] with **1** in THF at 66 °C followed by work-up, distillation in vacuo and final purification by column chromatography on silica gel (Scheme 1).[12,13] The corresponding 1-substituted analogue **3a/3b** was obtained in 70% yield by reaction of indenyllithium with **1** in THF at room temperature followed by subsequent work-up and vacuum distillation (Scheme 2).[14] Formation of the 1:1 (1*R*/1*S*) diastereomeric mixture was evidenced by the equal intensities of the diastereomeric

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Keywords: Indene; Indenyl; Chirality; Metallocenes.

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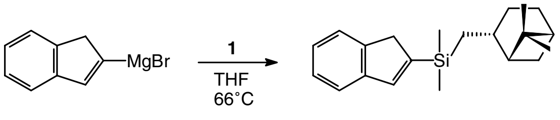
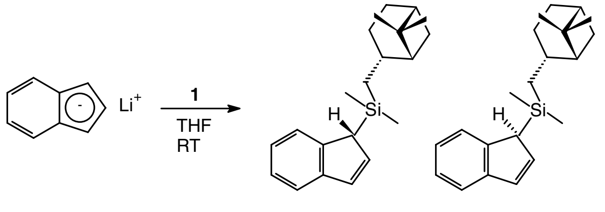


2

Scheme 1. Synthesis of the 2-chirally substituted indene 2.

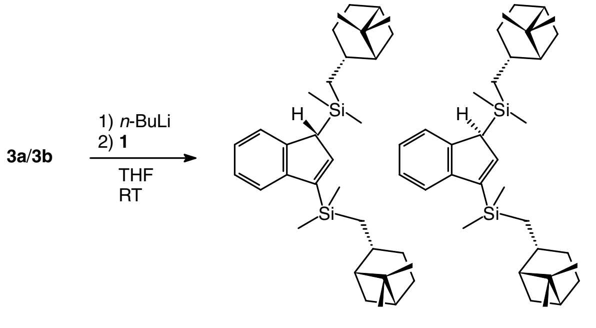


3a 3b

Scheme 2. Synthesis of the diastereomeric 1-chirally substituted indenes 3a and 3b.

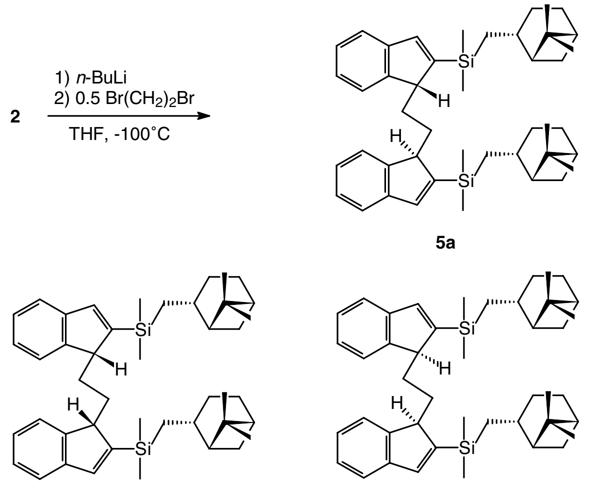
silylmethyl resonances in the ^{1}H NMR analysis. The **3a/3b** mixture was further deprotonated with *n*-BuLi and the lithium derivative obtained added to a solution of **1** in THF at room temperature to provide, after work-up and column chromatography on silica gel, the 1,3-disubstituted indene **4a/4b** in 76% yield as a mixture of two diastereomers (Scheme 3).[15,16]

The ethylene bridged bis(indenyl) analogue of **2** was prepared by addition of 1,2-dibromoethane to the lithium derivative of **2** in THF at −100 °C in a 1:2 molar ratio (Scheme 4). After stirring the reaction mixture at room temperature for 18 h, subsequent work-up and purification by column chromatography on silica gel, a mixture of the diastereomeric bis(indenes) **5a/5b/5c** was obtained in 24% overall yield.[17] Due to the overlapping resonances in the ^{1}H NMR analysis, the exact ratio of the diastereomers formed could not be accurately determined. The analogous ethylene bridged 1,1′-chirally substituted bis(indene) **6** was prepared by reaction of the dilithium derivative of 1,2-bis(3-indenyl)ethane[18] with 2 equiv of **1** in THF at room temperature (Scheme 5).[19] Purification by column chromatography on silica gel provided the **6a/6b/6c** mixture of three diastereomers in 42% isolated yield.[20] All attempts to prepare and isolate the corresponding dimethylsilylene bridged ligand analogues by reaction of the lithium derivatives of either **2** or **3** with 0.5 equiv of dimethyldichlorosilane failed. All successfully prepared compounds **2**–**6** were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, EIMS and polarimetry when applicable. Analytical data is reported in the references and notes section.



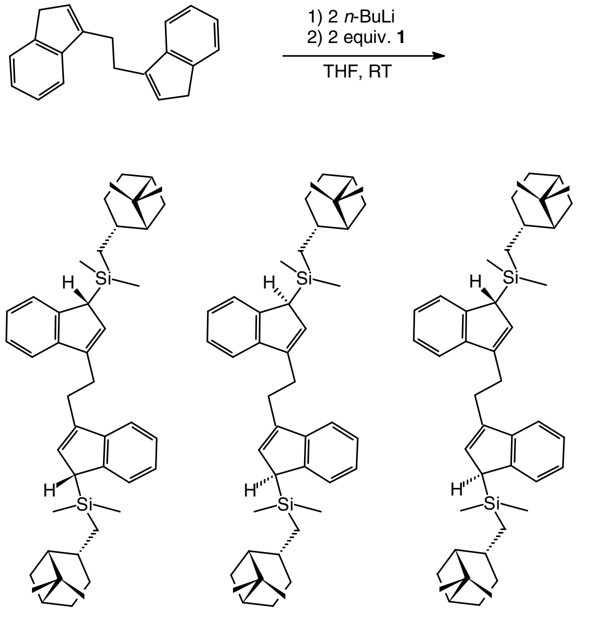
4a 4b

Scheme 3. Synthesis of the diastereomeric 1,3-chirally disubstituted indenes 4a and 4b.



5a 5b 5c

Scheme 4. Synthesis of the ethylene bridged 2,2′-chirally substituted bis(indenyl) diastereomers 5a, 5b and 5c.



6a 6b 6c

Scheme 5. Synthesis of the ethylene bridged 1,1′-chirally substituted bis(indenyl) diastereomers 6a, 6b and 6c.

In summary, we have devised a simple route to a series of new chiral indenes and bridged bis(indenes) containing a β-pinenyl derived ligand substituent. The easy preparation of this new family of chirally substituted indenes further broadens the scope of chiral cyclopentadienyl ligand precursors, potentially providing access to a series of new chiral transition metal complexes. This topic is currently under investigation in the authors' laboratories.

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References and Notes

1. Hoveyda, A. H.; Morken, J. P. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, pp 625–683.
2. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1346.
3. Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91–98.
4. (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233–247; (b) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63–67; (c) Schäfer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1987**, *328*, 87–99.
5. (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965–994; (b) Halterman, R. L. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, pp 455–544.
6. (a) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590–4601; (b) Erker, G.; Aulbach, M.; Krüger, C.; Werner, S. *J. Organomet. Chem.* **1993**, *450*, 1–7; (c) Knickmeier, M.; Erker, G.; Fox, T. *J. Am. Chem. Soc.* **1996**, *118*, 9623–9630.
7. (a) Schumann, H.; Stenzel, O.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 1743–1751; (b) Schumann, H.; Stenzel, O.; Dechert, S.; Halterman, R. L. *Organometallics* **2001**, *20*, 1983–1991; (c) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 2215–2225.
8. (a) Halterman, R. L.; Fahey, D. R.; Bailly, E. F.; Dockter, D. W.; Stenzel, O.; Shipman, J. L.; Khan, M. A.; Dechert, S.; Schumann, H. *Organometallics* **2000**, *19*, 5464–5470; (b) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 5360–5368; (c) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Blum, J.; Gelman, D.; Halterman, R. L. *Eur. J. Inorg. Chem.* **2002**, 211–219.
9. (a) Halterman, R. L.; Crow, L. D. *Tetrahedron Lett.* **2003**, *44*, 2907–2909; (b) See also: Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276–2277.
10. (a) Wang, D.; Chan, T. H. *Tetrahedron Lett.* **1983**, *24*, 1573–1576; (b) Aoki, T.; Shinohara, K.; Oikawa, E. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 565–570.
11. (a) Davison, A.; Rakita, P. E. *J. Organomet. Chem.* **1970**, *23*, 407–426; (b) McEwen, I.; Rönnqvist, M.; Ahlberg, P. *J. Am. Chem. Soc.* **1993**, *115*, 3989–3996.
12. Compound **2**: 5.69 g (34%) of a yellow oil. FC eluent: hexane. $[\alpha]_{\mathrm{D}}^{23}$ −3.0 (*c* 0.0464 g/mL, $CHCl_3$). EIMS calcd for $C_{21}H_{30}Si$ 310.2117, found 310.2113. ^{1}H NMR ($CDCl_3$, 400.0 MHz, δ): 7.47 (md, $J = 7.40$ Hz, 1H, arom CH); 7.39 (md, $J = 7.48$ Hz, 1H, arom CH); 7.25 (mt, $J = 7.44$ Hz, 1H, arom CH); 7.16 (mt, $J = 7.32$ Hz, 1H, arom CH); 7.08 (m, 1H, olefinic CH); 3.43 (dd, $J = 1.95$ Hz, 0.50 Hz, 2H, CH_2 in five-membered ring); 2.15 (m, 1H, pinen); 2.01 (m, 1H, pinen); 1.83 (m, 1H, pinen); 1.7 (m, 3H, pinen); 1.63 (dt, $J = 5.61$ Hz, 1.30 Hz, 1H, pinen); 1.37 (d, $J = 9.92$ Hz,1H, pinen); 1.24 (m, 1H, pinen); 1.16 (s, 3H, pinen CH_3); 0.79 (s, 3H, pinen CH_3); 0.79 (dd, $J = 8.47$ Hz, 14.50 Hz, 1H, SiCH); 0.69 (dd, $J = 5.95$ Hz, 14.57 Hz, 1H, SiCH); 0.21 (s, 3H, $SiCH_3$); 0.21 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 149.39 (C_q attached to Si); 146.85 (arom C_q); 145.78 (arom C_q); 140.70 (olefinic CH); 126.30 (arom CH); 124.66 (arom CH); 123.65 (arom CH); 120.80 (arom CH); 49.42 (pinen CH); 42.65 (CH_2 in five-membered ring); 40.76 (pinen CH); 39.64 (pinen C_q); 31.34 (pinen CH); 27.03 (pinen CH_3); 25.69 (pinen CH_2); 24.88 (pinen CH_2); 24.04 ($SiCH_2$); 23.10 (pinen CH_2); 20.13 (pinen CH_3); −1.52 ($SiCH_3$); −1.70 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, δ): −8.33.
13. For the preparation of 2-(trimethylsilyl)indene, see: (a) Davison, A.; Rakita, P. E. *J. Organomet. Chem.* **1970**, *23*, 407–426; (b) Grimmer, N. E.; Coville, N. J.; de Koning, C. B.; Smith, J. M.; Cook, L. M. *J. Organomet. Chem.* **2000**, *616*, 112–127.
14. Diastereomeric mixture of compounds **3a** and **3b**: 11.46 g (70%) of a yellow oil; bp 113–119 °C/0.33 mbar. EIMS calcd for $C_{21}H_{30}Si$ 310.2117, found 310.2117. The ^{1}H and ^{13}C NMR signals of the two diastereomers overlap almost completely, except for the proton and carbon resonances originating from the Si bound methyl groups and the carbon resonances from the carbon atoms next to the chiral centre in the β-pinenyl part. Amounts of the protons are given as the sum of the protons from both diastereomers. ^{1}H NMR ($CDCl_3$, 400.0 MHz, δ): 7.52 (m, 2+2H, arom CH); 7.27 (m, 2+2H, arom CH); 6.98 (m, 1+1H, olefinic CH); 6.72 (m, 1+1H, olefinic CH); 3.59 (m, 1+1H, CH in five-membered ring); 2.08 (m, 2+2H, pinen CH); 1.90 (m, 1+1H, pinen CH); 1.74 (m, 3+3H, pinen CH); 1.62 (m, 1+1H, pinen CH); 1.39 (m, 1+1H, pinen CH); 1.25 (m, 1+1H, pinen CH); 1.24 (m, 3+3H, pinen CH_3); 0.87 (m, 3+3H, pinen CH_3); 0.58 (m, 2+2H, $SiCH_2$); 0.06 (s, 3H, $SiCH_3$); 0.02 (s, 3H, $SiCH_3$); 0.01 (s, 3H, $SiCH_3$); −0.05 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 145.48 (2C, C_q); 144.26 (2C, C_q); 135.89 (2C, olefinic CH); 128.89 (2C, olefinic CH); 124.78 (2C, arom CH); 123.61 (2C, arom CH); 122.79 (2C, arom CH); 121.05 (2C, arom CH); 49.36 (pinen CH); 49.21 (pinen CH); 46.34 (2C, CH in five-membered ring); 40.66 (2C, pinen CH); 39.60 (2C, pinen C_q); 31.08 (2C, pinen CH); 26.99 (2C, pinen CH_3); 25.67 (pinen CH_2); 25.53 (pinen CH_2); 24.80 (2C, pinen CH_2); 23.02 (2C, pinen CH_2); 22.56 (2C, $SiCH_2$); 20.09 (2C, pinen CH_3); −2.70 ($SiCH_3$); −2.96 ($SiCH_3$); −2.99 ($SiCH_3$); −3.14 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, δ): 4.231, 4.192.
15. Diastereomeric mixture of compounds **4a** and **4b**: 2.79 g (76%) of a yellow oil. FC eluent: hexane. EIMS calcd for $C_{33}H_{52}Si_2$ 504.3608, found 504.3619. The ^{1}H and ^{13}C NMR signals of the two diastereomers overlap almost completely, except for the proton resonances originating from the Si bound methyl groups (Si attached to an aliphatic carbon) and the carbon resonances from quaternary carbon atoms and some of the carbons in the β-pinenyl part. Amounts of the protons are given as the sum of the protons from both diastereomers. ^{1}H NMR ($CDCl_3$, 400.0 MHz, δ): 7.50 (m, 1+1H, arom CH); 7.42 (m, 1+1H, arom CH); 7.21 (m, 1+1H, arom CH); 7.13 (m, 1+1H, arom CH); 6.79 (m, 1+1H, olefinic CH); 3.56 (m, 1+1H, CH in five-membered ring); 1.97 (m, 2+2H, pinen); 1.81 (m, 2+2H, pinen); 1.64 (m, 6+6H, pinen); 1.26 (m,

6+6H, pinen); 1.16 (m, 6+6H, pinen $\mathrm{CH_3}$); 0.84 (m, 4+4H, pinen); 0.75 (m, 6+6H, pinen $\mathrm{CH_3}$); 0.48 (m, 2+2H, pinen); 0.28 (m, 6+6H, olefinic $\mathrm{SiCH_3}$); −0.06 (s, 3H, $\mathrm{SiCH_3}$); −0.09 (s, 3H, $\mathrm{SiCH_3}$); −0.12 (s, 3H, $\mathrm{SiCH_3}$); −0.15 (s, 3H, $\mathrm{SiCH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 100.6 MHz, δ): 147.59 ($\mathrm{C_q}$); 146.45 ($\mathrm{C_q}$); 145.63 ($\mathrm{C_q}$); 145.59 ($\mathrm{C_q}$); 141.29 ($\mathrm{C_q}$); 141.25 ($\mathrm{C_q}$); 124.45 (2C), 124.41 (2C), 123.15 (2C), 122.73 (2C), 122.12 (2C) (arom CH and olefinic CH); 49.33, 49.31, 49.19, 49.06, 48.42, 48.40, 40.66, 40.58, 39.52, 31.58, 31.30, 31.25, 31.05, 30.90, 30.53, 26.91, 26.90, 26.57, 25.68, 25.61, 25.54, 25.43, 24.78, 24.72, 24.70, 23.97, 23.93, 23.02, 22.96, 22.93, 22.66, 22.47, 20.05, 20.01 (42C, pinen and CH in five-membered ring); −1.62 (4C, olefinic $\mathrm{SiCH_3}$); −3.01 (4C, $\mathrm{SiCH_3}$). ^{29}Si NMR ($\mathrm{CDCl_3}$, 79.5 MHz, δ): 4.19, 4.14 (aliphatic Si); −9.24, −9.37 (olefinic Si).

16. The analogous 1,3-bis(trimethylsilyl)indenyl derived anion was recently complexed with zirconium, see: Bradley, C. A.; Lobkovsky, E.; Chirik, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 8110–8111.
17. Diastereomeric mixture of compounds **5a**, **5b** and **5c**: 1.15 g (24%) of a pale yellow oil. FC eluent: hexane. EIMS calcd for $\mathrm{C_{44}H_{62}Si_2}$ 646.4390, found 646.4391. The ^{1}H NMR signals of the three diastereomers overlap completely. Amounts of the protons are given as the sum of the protons from the three diastereomers. ^{1}H NMR ($\mathrm{CDCl_3}$, 400.0 MHz, δ): 7.73–7.16 (m, 10+10+10H, overlapping signals from arom and olefinic CH); 3.75 (m, 2+2+2H, CH in five-membered ring); 2.24–1.38 (m, 22+22+22H, overlapping signals from the protons in pinen part and ethylene bridge); 1.39 (m, 6+6+6H, pinen $\mathrm{CH_3}$); 1.01 (m, 6+6+6H, pinen $\mathrm{CH_3}$); 0.87 (m, 4+4+4H, $\mathrm{SiCH_2}$); 0.42–0.24 (m, 12+12+12H, overlapping signals from $\mathrm{SiCH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 100.6 MHz, δ): 153.35, 153.22, 153.15, 150.36, 150.34, 150.25, 145.13, 145.02, 141.04, 140.59, 126.42, 126.38, 124.67, 124.64, 123.32, 123.15, 123.12, 120.72, 120.68 (16+16+16C, overlapping arom and olefinic carbons); 54.65, 54.57, 54.09, 54.07, 49.33, 49.24, 49.20, 49.12, 40.62, 39.52, 39.49, 31.59, 31.20, 31.16, 31.11, 27.69, 26.91, 26.87, 25.58, 25.50, 25.46, 25.34, 24.77, 24.26, 24.18, 24.00, 23.89, 23.74, 23.01, 22.66 (24+24+24C, overlapping aliphatic carbons); −0.76, −1.00, −1.21, −1.33, −1.41, −1.50, −1.74 (4+4+4C, $\mathrm{SiCH_3}$). ^{29}Si NMR ($\mathrm{CDCl_3}$, 79.5 MHz, δ): −8.47, −8.54, −8.61, −8.75.
18. Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501–1505.
19. Spaleck, W.; Antberg, M.; Aulbach, M.; Bachmann, B.; Dolle, V.; Haftka, S.; Küber, F.; Rohrmann, J.; Winter, A. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, Heidelberg, 1995; pp 83–97.
20. Diastereomeric mixture of compounds **6a**, **6b** and **6c**: 7.48 g (42%) of a yellow oil. FC eluent: hexane. EIMS calcd for $\mathrm{C_{44}H_{62}Si_2}$ 646.4390, found 646.4395. The ^{1}H NMR signals of the three diastereomers overlap completely. Amounts of the protons are given as the sum of the protons from the three diastereomers. ^{1}H NMR ($\mathrm{CDCl_3}$, 400.0 MHz, δ): 7.44 (m, 4+4+4H, arom CH); 7.26 (m, 2+2+2H, arom CH); 7.17 (m, 2+2+2H, arom CH); 6.39 (m, 2+2+2H, olefinic CH); 3.41 (m, 2+2+2H, aliphatic CH in five-membered ring); 2.99 (m, 4+4+4H, $\mathrm{CH_2}$ in the ethylene bridge); 1.98 (m, 4+4+4H, pinen); 1.81 (m, 2+2+2H, pinen); 1.60 (m, 8+8+8H, pinen); 1.28 (m, 4+4+4H, pinen); 1.14 (m, 6+6+6H, pinen $\mathrm{CH_3}$); 0.76 (m, 6+6+6H, pinen $\mathrm{CH_3}$); 0.49 (m, 4+4+4H, $\mathrm{SiCH_2}$); −0.07 (m, 12+12+12H, $\mathrm{SiCH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 100.6 MHz, δ): 146.24, 144.47, 144.44, 141.50, 141.43, 141.41, 130.00, 129.99, 124.56, 124.52, 123.59, 122.91, 118.95, 118.93 (16+16+16C, overlapping arom and olefinic carbons); 49.32, 49.14, 44.43, 40.59, 39.52, 31.59, 31.05, 27.17, 27.13, 27.03, 26.91, 25.61, 25.47, 24.74, 24.72, 22.96, 22.66, 22.61, 22.55, 22.51, 20.02, 15.28, 14.12 (24+24+24C, overlapping aliphatic carbons); −2.59, −2.84, −2.92, −2.96, −3.13, −3.17 (4+4+4C, $\mathrm{SiCH_3}$). ^{29}Si NMR ($\mathrm{CDCl_3}$, 79.5 MHz, δ): 4.18.