Electronic Supplementary Material (ESI) for Green Chemistry.

Halogen-free water-stable aluminates as replacement for persistent fluorinated weakly-coordinating anions

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Contents

The research results were obtained by Dipl.-Chem. Timo Söhner as part of his PhD studies. B.Sc. Felix Braun, M.Sc. L. Charlotte Over, and B.Sc. Sven Mehlhose contributed scientific results and data in their research internships. Dr. Frank Rominger is responsible for the single-crystal X-ray diffraction analyses. Prof. Dr. Bernd F. Straub contributed the fundamental ideas and the mentoring. The Universität Heidelberg has submitted a German patent application on halogen-free, lipophilic aluminate anions with ethylene-linked bisphenolate ligands (DE 10 2013 004 943.1).

1 General procedures

Chemicals were supplied by Acros, Aldrich, and TCI, and were used without further purification. Reactions involving air-sensitive reagents were carried out under N_2 or argon by using standard Schlenk techniques. Solvents were dried in an Mbraun MB SCS-800 solvent purification system. NMR spectra were recorded at 300 K by using Bruker ARX-250, Bruker Avance 300, Bruker Avance 500, or Bruker Avance 600 spectrometers. Chemical shifts are reported in ppm relative to TMS, and were determined by reference to the ^{13}C or residual ^{1}H solvent peaks. Melting points were determined by using a Gallenkamp hot-stage microscope. THF was dried by an MBRAUN solvent purification system MB SPS-800. The enantiomeric excess was determined by HPLC on a Chiralcel OJ or Chiralcel OD column. Mass spectra were recorded by the Mass Spectrometry Service Facility of the Chemical Department at the Ruprecht-Karls-University Heidelberg. The following machines were employed: Bruker ICR Apex-Qe, Finnigan MAT LCQ and JEOL JMS-700. Elemental analyses were carried out by the Laboratory of Microanalysis in the Department of Chemistry at the Ruprecht-Karls-University Heidelberg. The single crystal X-ray diffraction datasets were collected at 200(2) K on a Bruker APEX diffractometer or a Bruker APEX II Quazar diffractometer equipped with a CCD area detector and a standard sealed tube Mo Kα (λ = 0.71073 Å) radiation source. 0.3° omega-scans covering a whole sphere in reciprocal space were taken in each case, and an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space. Structures were solved by direct methods and refined against F2 with a Full-matrix least-squares algorithm using the SHELXTL-PLUS (6.10) software package.[2]

Lit. 1: (program SADABS 2012/1 for absorption correction)
G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 2012

Lit. 2: (program SHELXL 2014-3 for structure refinement)
Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

2-(Bromomethyl)-4,6-di-*tert*-butylphenol (1a)

A flask was equipped with 51.5 g (0.25 mol) 2,4-di-*tert*-butylphenol in 150 mL acetic acid at room temperature. Paraformaldehyde (8.3 g, 0.27 mol) was added and the suspension was stirred at room temperature for 2 h. 95 mL (0.50 mol) HBr (33 w % in acetic acid) was added within 15 min, and the resulting orange solution was stirred for additional 30 min. After removing of the solvent *in vacuo*, pentane (200 mL) was added and the solution was filtered through a pad of silica gel. The solvent was removed *in vacuo* resulting in a clear yellow oil with a yield of 70.8 g. This oil was used for the synthesis of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) **2a** without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δH (ppm): 1.29 {9H, s, C($\underline{CH_3}$)$_3$}, 1.43 {9H, s, C($\underline{CH_3}$)$_3$}, 4.58 (2H, s, $\underline{CH_2}$), 5.27 (1H, s, OH), 7.10 (1H, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.36 (1H, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

The ^{1}H NMR spectroscopic data is consistent with the literature.[19]

6,6'-(Ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) (2a)

2-(Bromomethyl)-4,6-di-*tert*-butylphenol **1a** (70.8 g, 0.24 mol) was dissolved in 125 mL toluene. A solution of 2.36 g $CuCl_2$ in 375 ml saturated ammonium chloride solution was added whilst stirring. After addition of 23.6 g (0.36 mol) zinc powder, the suspension was stirred vigorously for 16 h at room temperature. The excess of zinc was dissolved with 2 M hydrochloric acid. Diethyl ether was added and the phases were separated. The aqueous phase was extracted twice with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed *in vacuo*. After recrystallisation from acetonitrile, the product was isolated as a colourless powder (yield 38.5 g, 70 %).

^{1}H NMR (600.24 MHz, $CDCl_3$) δH (ppm): 1.32 {18H, s, C($\underline{CH_3}$)$_3$}, 1.47 {18H, s, C($\underline{CH_3}$)$_3$}, 2.86 (4H, s, $\underline{CH_2}$), 5.69 (2H, s, $\underline{OH}$), 7.10 (2H, d, $^{4}J_{HH}$ = 2.3 Hz, Ar-$\underline{H}$), 7.22 (2H, d, $^{4}J_{HH}$ = 2.3 Hz, Ar-$\underline{H}$).

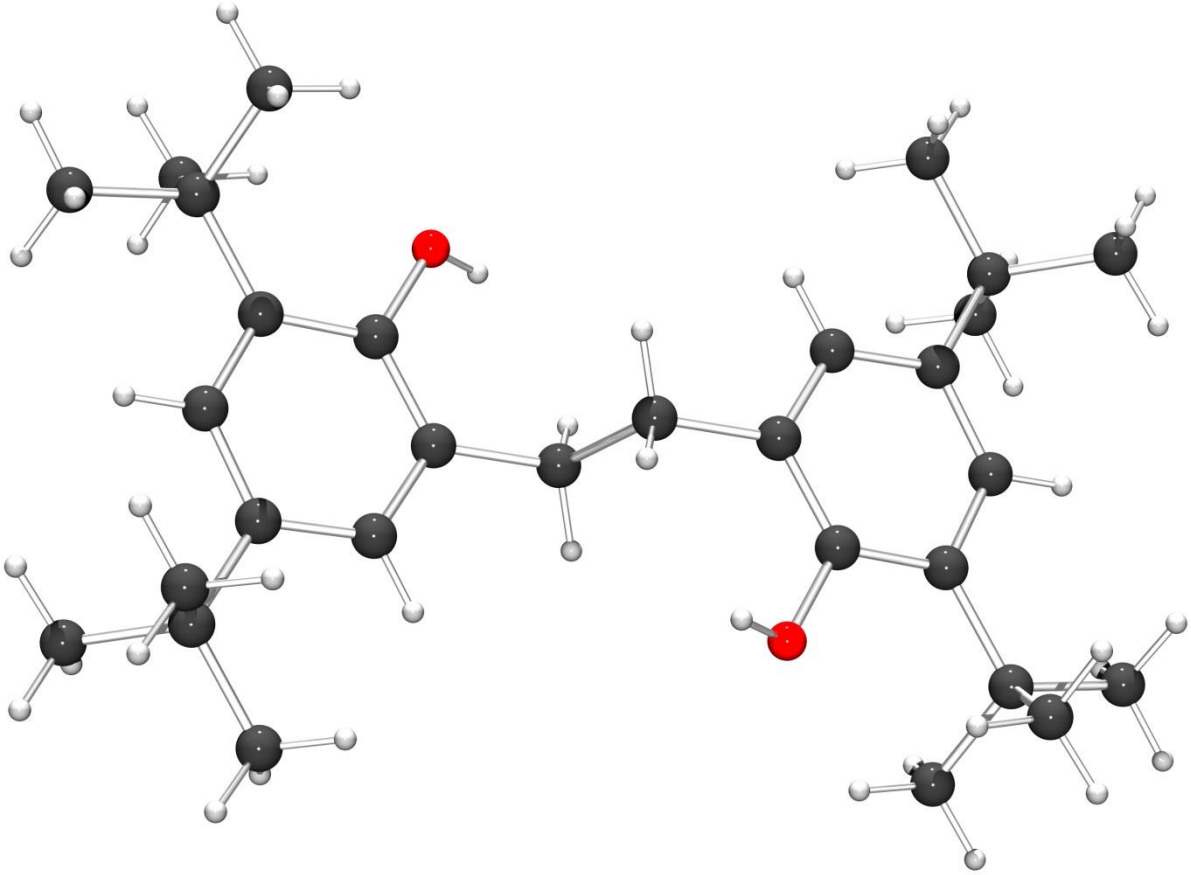
^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$) δC (ppm): 30.3, 31.8, 32.7, 34.4, 34.6, 122.3, 124.9, 127.7, 134.8, 142.6, 150.3.

ES-HRMS (m/z)$^{-}$ [M-H]$^{-}$ calc. mass: 437.34250; found: 437.34196

FTIR (ATR) ν_{max} (cm^{-1}): 3352 (br s), 2957 (m), 2868 (w), 1593 (w), 1477 (m), 1444 (w), 1413 (w), 1391 (w), 1360 (m), 1308 (w), 1277 (w), 1245 (w), 1182 (s), 1146 (w), 1121 (w), 1104 (w), 1024 (w), 942 (w), 904 (w), 876 (m), 822 (w), 807 (w), 762 (w), 721 (w), 651 (w).

$C_{30}H_{46}O_2$: calculated C-82.14%, H-10.57%; found C-82.08%, H-10.79%

Melting point: 175 °C



X-ray diffraction: colourless crystal (needle), dimensions 0.37 x 0.08 x 0.06 mm^3, crystal system triclinic, space group $P\bar{1}$, Z=1, a=5.9662(13) Å, b=10.201(2) Å, c=14.270(3) Å, alpha=101.025(5) deg, beta=93.011(5) deg, gamma=104.712(5) deg, V=819.8(3) $Å^3$, rho=1.055 g/cm^3, T=200(2) K, $Theta_{max}$= 25.02 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.03 and a completeness of 99.5% to a resolution of 0.84Å, 5887 reflections measured, 2874 unique (R(int)=0.0438), 1569 observed (I >2σ (I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space,

mu=0.06mm^{-1}, T_{min}=0.98, T_{max}=1.00, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package[2], 213 parameters refined, hydrogen atoms were treated using appropriate riding models, except H1 of the hydroxy group, which was refined isotropically, goodness of fit 1.06 for observed reflections, final residual values R1(F)=0.070, wR(F^2)=0.152 for observed reflections, residual electron density -0.23 to 0.16 eÅ^{-3}. CCDC 999516 contains the supplementary crystallographic data for this paper.

2-(Bromomethyl)-4,6-di-*tert*-pentylphenol (1b)

A flask was equipped with 58.6 g (0.25 mol) 2,4-di-*tert*-pentylphenol in 150 mL acetic acid at room temperature. Paraformaldehyde (8.3 g, 0.27 mol) was added and the suspension was stirred at room temperature for 2 h. 95 mL (0.50 mol) HBr (33 w % in acetic acid) was added within 15 min and the resulting orange solution was stirred for additional 30 min. After removal of the solvent *in vacuo*, pentane (200 mL) was added and the solution was filtered through a pad of silica gel. Again the solvent was removed *in vacuo*, resulting in a clear yellow oil with a yield of 78.6 g. This oil was used for the synthesis of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-pentylphenol) **2b** without further purification.

^{1}H NMR (400.18 MHz, $CDCl_3$, 300 K) δH (ppm): 0.65 {3H, t, $^3J_{HH}$ = 7.5 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.67 {3H, t, $^3J_{HH}$ = 7.5 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 1.25 {6H, s, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.38 {6H, s, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.58 {2H, q, $^3J_{HH}$ = 7.5 Hz, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.86 {2H, q, $^3J_{HH}$ = 7.5 Hz, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 4.58 (2H, s, $\underline{CH_2}$-Br), 5.22 (1H, s, $\underline{OH}$), 7.02 (1H, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.19 (1H, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 300 K) δC (ppm): 9.2, 9.5, 28.0, 28.5, 33.0, 33.7, 37.0, 37.5, 38.6, 123.2, 125.4, 127.7, 135.3, 141.2, 151.6.

EI-HRMS $(m/z)^+$ $[M]^+$ calc. mass: 328.1224; found: 328.1222.

6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-pentylphenol) (2b)

2-(Bromomethyl)-4,6-di-*tert*-pentylphenol **1b** (78.6 g, 0.24 mol) was dissolved in 125 mL toluene. A solution of 2.36 g $CuCl_2$ in 375 ml saturated ammonium chloride solution was added whilst stirring. After adding of 23.6 g (0.36 mol) zinc powder, the suspension was stirred vigorously for 16 h at room temperature. The excess of zinc metal was dissolved with

2 M hydrochloric acid; then diethyl ether was added and the phases were separated. The aqueous phase was extracted twice with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed *in vacuo*. After recrystallisation from acetonitrile, the product was isolated as a colourless powder (yield 41.5 g, 67%).

^{1}H NMR (400.18 MHz, $CDCl_3$, 300 K) δH (ppm): 0.70 {6H, t, $^{3}J_{HH}$ = 7.5 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.71 {6H, t, $^{3}J_{HH}$ = 7.5 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 1.27 {12H, s, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.42 {6H, s, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.61 {4H, q, $^{3}J_{HH}$ = 7.5 Hz, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.86 {4H, q, $^{3}J_{HH}$ = 7.5 Hz, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 2.84 (4H, s, Ar-$\underline{CH_2}$), 5.58 (2H, s, $\underline{OH}$), 6.98 (2H, d, $^{4}J_{HH}$ = 2.4 Hz, Ar-$\underline{H}$), 7.06 (2H, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

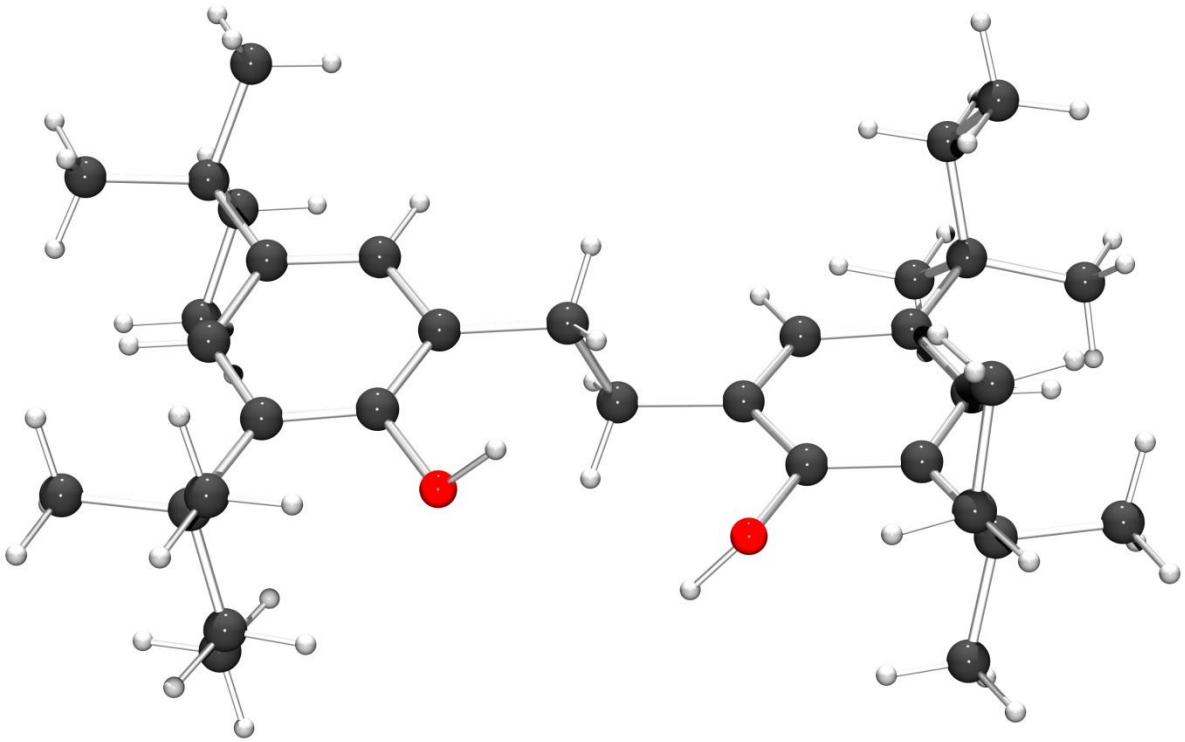
$^{13}C\{^{1}H\}$ NMR (100.62 MHz, $CDCl_3$, 300 K) δC (ppm): 9.3, 9.6, 28.3, 28.7, 32.8, 34.2, 37.2, 37.4, 38.2, 124.3, 125.5, 127.4, 133.0, 140.7, 150.3.

ESI-HRMS $(m/z)^-$ $[M-H]^-$ calc. mass: 493.40376; found: 493.40039.

FTIR (ATR) ν_{max} (cm^{-1}): 3357 (br s), 2963 (m), 2876 (w), 1758 (w), 1590 (w), 1460 (m), 1413 (w), 1377 (w), 1359 (w), 1310 (w), 1277 (w), 1257 (w), 1183 (s), 1119 (w), 1104 (w), 1060 (w), 1004 (w), 948 (w), 929 (w), 904 (w), 873 (m), 797 (w), 775 (w), 761 (w), 711 (w), 654 (w).

$C_{34}H_{54}O_2$: calculated C-82.53%, H-11.00%; found C-82.42%, H-11.20%

Melting point: 108 °C



X-ray diffraction: colourless crystal (needle), dimensions 0.470 x 0.090 x 0.070 mm^3, crystal system tetragonal, space group $I4_1/a$, Z=8, a=23.87(2) Å, b=23.87(2) Å, c=10.781(9) Å, alpha=90 deg, beta=90 deg, gamma=90 deg, V=6144(12) $Å^3$, rho=1.070 g/cm^3, T=200(2) K, $Theta_{max}$= 21.106 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.91 and a completeness of 59.8% to a resolution of 0.99Å, 8214 reflections measured, 1666 unique (R(int)=0.1496), 947 observed ($I > 2\sigma$ (I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.06mm^{-1}, T_{min}=0.69, T_{max}=0.96, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2013/3) software package[2], 180 parameters refined, hydrogen atoms were treated using appropriate riding models, except H2 at O2, which was refined isotropically, goodness of fit 1.09 for observed reflections, final residual values R1(F)=0.112, wR(F^2)=0.262 for observed reflections, residual electron density -0.34 to 0.21 e$Å^{-3}$. CCDC 999522 contains the supplementary crystallographic data for this paper.

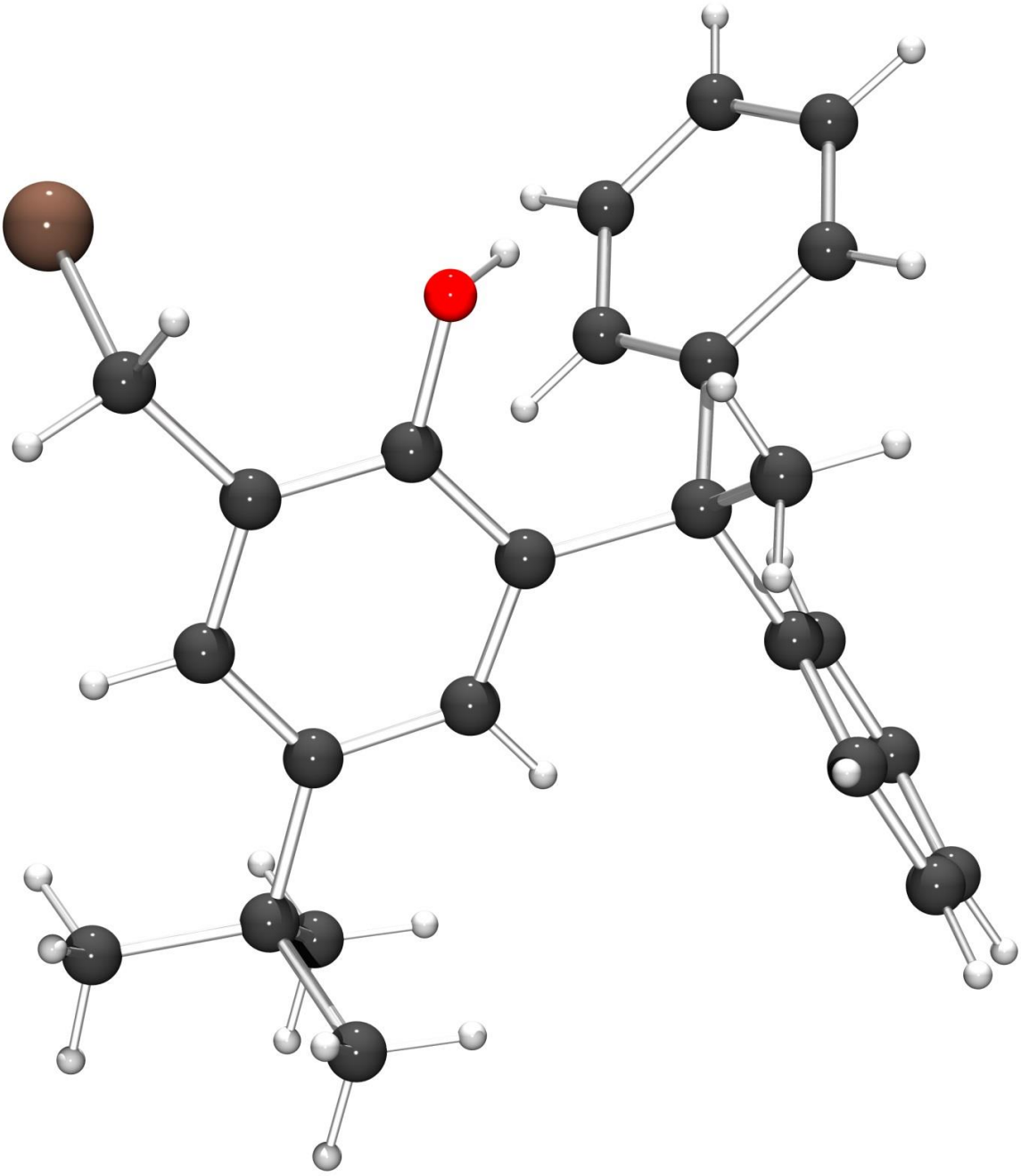
2-(Bromomethyl)-4-*tert*-butyl-6-(1,1-diphenylethyl)phenol (1c)

A flask was equipped with 16.3 g (49.3 mmol) 4-*tert*-butyl-2-(1,1-diphenylethyl)phenol in 60 mL acetic acid at room temperature. Paraformaldehyde (1.63 g, 55.0 mmol) was added and the suspension was stirred at room temperature for 2 h. 18.7 mL (98.6 mol) HBr (33 w % in acetic acid) was added within 15 min and the resulting orange solution was stirred for additional 30 min. After removing of the solvent *in vacuo*, a light yellow solid with a yield of 20.4 g was isolated. This solid was used for the synthesis of 6,6'-(ethane-1,2-diyl)bis[4-*tert*-butyl-2-(1,1-diphenylethyl)phenol] **2c** without further purification.

^{1}H NMR (300.13 MHz, $CDCl_3$, 300 K) δH (ppm): 1.18 {9H, s, C($\underline{CH_3}$)$_3$}, 2.20 (3H, s, $\underline{CH_3}$), 4.53 (2H, s, $\underline{CH_2}$), 4.71 (1H, s, OH), 6.92 (1H, d, $^{4}J_{HH}$ = 2.4 Hz, Ar-$\underline{H}$), 7.22 – 7.44 (11H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (75.46 MHz, $CDCl_3$, 300 K) δC (ppm): 29.0, 31.0, 31.3, 34.4, 51.7, 125.7, 126.7, 127.2, 127.9, 128.5, 128.9, 135.0, 143.3, 146.5, 150.6.

EI-HRMS $(m/z)^+$ $[M]^+$ calc. mass: 424.1245; found: 424.1213.



X-ray diffraction: colourless crystal (needle), dimensions 0.38 x 0.10 x 0.08 mm3, crystal system monoclinic, space group P21/c, Z=4, a=9.971(4) Å, b=11.013(4) Å, c=19.557(8) Å, alpha=90 deg, beta=94.091(14) deg, gamma=90 deg, V=2142.3(15) Å3, rho=1.313 g/cm^3, T=200(2) K, Theta$_{max}$= 21.257 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.53 and a completeness of 61.6% to a resolution of 0.98Å, 8665 reflections measured, 2380 unique (R(int)=0.0812), 1555 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=1.93mm^{-1}, T$_{min}$=0.70, T$_{max}$=0.89, structure solved by direct methods and refined against F2 with a Full-matrix least-

squares algorithm using the SHELXTL (Version 2013/3) software package2, 245 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.04 for observed reflections, final residual values R1(F)=0.052, wR(F2)=0.114 for observed reflections, residual electron density -0.56 to 0.30 $eÅ^{-3}$. CCDC 999519 contains the supplementary crystallographic data for this paper.

6,6'-(Ethane-1,2-diyl)bis[4-*tert*-butyl-2-(1,1-diphenylethyl)phenol] (2c)

2-(Bromomethyl)-4-*tert*-butyl-6-(1,1-diphenylethyl)phenol **1c** (20.4 g, 48.1 mmol) was dissolved in 25 mL toluene. A solution of 0.48 g $CuCl_2$ in 75 ml saturated ammonium chloride solution was added whilst stirring. After adding of 4.8 g (0.36 mol) zinc powder, the suspension was stirred vigorously for 16 h at room temperature. The excess of zinc metal was dissolved with 2 M hydrochloric acid; then dichloromethane was added and the phases were separated. The aqueous phase was extracted twice with dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvent was removed *in vacuo*. After recrystallisation from acetic acid, the product was isolated as a colourless powder (yield 12.7 g, 75%).

^{1}H NMR (400.18 MHz, $CDCl_3$, 300 K) δH (ppm): 1.13 {18H, s, C($\underline{CH_3}$)$_3$}, 2.20 (6H, s, $\underline{CH_3}$), 2.75 (4H, s, $\underline{CH_2}$), 4.88 (2H, s, OH), 6.65 (1H, d, $^4J_{HH}$ = 2.4 Hz, Ar-$\underline{H}$), 7.02 (1H, d, $^4J_{HH}$ = 2.4 Hz, Ar-$\underline{H}$), 7.17 – 7.33 (20H, m, Ar-$\underline{H}$).

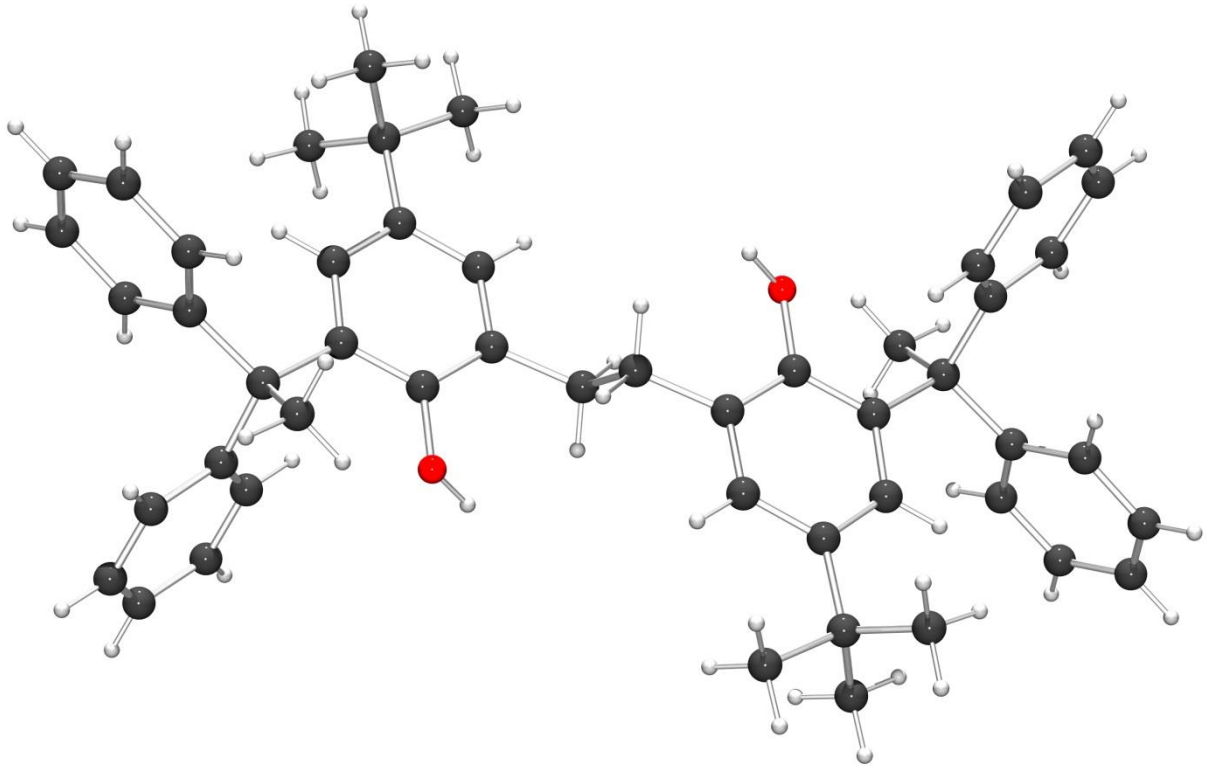
^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 300 K) δC (ppm): 28.7, 31.5, 32.3, 34.3, 51.9, 125.4, 126.3, 126.8, 128.6, 128.7, 128.8, 134.0, 142.5, 147.5, 150.0.

ESI-HRMS $(m/z)^-$ $[M-H]^-$ calc. mass: 685.40510; found: 685.40518.

FTIR (ATR) ν_{max} (cm^{-1}): 3532 (br s), 2961 (w), 2865 (w), 1712 (w), 1597 (w), 1492 (w), 1465 (w), 1444 (m), 1393 (w), 1362 (w), 1320 (w), 1294 (w), 1261 (w), 1202 (w), 1176 (w), 1149 (w), 1115 (w), 1097 (w), 1073 (w), 1025 (w), 1002 (w), 928 (w), 886 (w), 842 (w), 820 (w), 801 (w), 779 (w), 760 (w), 738 (w), 701 (s), 644 (w), 629 (w), 612 (w).

$C_{50}H_{54}O_2$: calculated C-87.42%, H-7.92%; found C-87.33%, H-7.69%

Melting point: 216 °C



X-Ray diffraction: colourless crystal (polyhedron), dimensions 0.380 x 0.320 x 0.160 mm^3, crystal system triclinic, space group $P\bar{1}$, Z=1, a=11.466(3) Å, b=11.745(3) Å, c=11.838(3) Å, alpha=71.639(7) deg, beta=75.918(7) deg, gamma=72.993(7) deg, V=1426.7(7) $Å^3$, rho=1.135 g/cm^3, T=200(2) K, $Theta_{max}$= 25.826 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.60 and a completeness of 99.8% to a resolution of 0.82Å.14178 reflections measured, 5453 unique (R(int)=0.0298), 3789 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.07mm^{-1}, T_{min}=0.89, T_{max}=0.96, structure solved by direct methods and refined against F2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2014-3) software package2, 412 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values R1(F)=0.059, wR(F2)=0.147 for observed reflections, residual electron density -0.34 to 0.37 $eÅ^{-3}$. CCDC 999520 contains the supplementary crystallographic data for this paper.

Tetrakis(tetrahydrofuran)lithium aletbate (3a)

Under inert gas conditions, a solution of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) **2a (**0.87 g, 2.0 mmol) in 6 ml dry THF was added slowly to a solution of $LiAlH_4$ (38 mg, 1.0 mmol) in 1 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 h, and filtered through Celite after cooling to room temperature. After removal of the solvent *in vacuo*, the resulting colourless foam was recrystallised from THF/pentane to give a colourless powder (yield 0.88 g, 75%).

^{1}H NMR (600.24 MHz, d_6-acetone, 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 1.23 – 1.30 {72H, m, C($\underline{CH_3}$)$_3$}, 1.75 – 1.83 (16H, m, thf), 2.27 – 2.36 (4H, m, Ar-$\underline{CH_2}$), 3.53 – 3.70 (20H, major, m, Ar-$\underline{CH_2}$/thf), 3.71 – 3.82 (4H, minor, m, Ar-$\underline{CH_2}$), 6.91 (4H, minor, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.96 (4H, major, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.98 (4H, minor, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 7.00 (4H, major, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.93 MHz, $CDCl_3$, 300 K) δC (ppm): 26.1, 31.0, 31.1, 32.3, 32.4, 34.3, 34.4, 35.3, 35.4, 35.7, 68.0, 121.1, 121.2, 124.2, 124.4, 131.5, 131.6, 136.8, 137.0, 137.2, 156.0, 156.3.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 899.65035; found: 899.64869.

FTIR (ATR) ν_{max} (cm^{-1}): 3421 (br s), 2954 (s), 1622 (w), 1473 (s), 1442 (s), 1416 (m), 1387 (w), 1359 (m), 1320 (m), 1305 (m), 1287 (s), 1238 (m), 1201 (w), 1169 (w), 1135 (w), 1044 (m), 998 (w), 917 (m), 877 (s), 810 (w), 776 (m), 765 (m), 647 (w), 614 (m), 595 (w), 535 (w), 484 (w), 408 (w).

Melting point: 249 °C (decomposition)

X-ray diffraction: colourless crystal (polyhedron), dimensions 0.26 x 0.23 x 0.19 mm^3, crystal system monoclinic, space group $P2_1/n$, Z=4, a=16.4252(10) Å, b=16.4896(10) Å, c=29.6929(18) Å, alpha=90 deg, beta=102.666(1) deg, gamma=90 deg, V=7846.5(8) $Å^3$, rho=1.084 g/cm^3, T=200(2) K, $Theta_{max}$= 26.37 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 8.71 and a completeness of 99.9% to a resolution of 0.80Å, 141901 reflections measured, 16037 unique (R(int)=0.0474), 11230 observed (I >2σ (I)),

intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.14mm^{-1}, T_{min}=0.96, T_{max}=0.97, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package[2], 856 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values R1(F)=0.079, wR(F^2)=0.211 for observed reflections, residual electron density -0.57 to 0.71 eÅ^{-3}. CCDC 999513 contains the supplementary crystallographic data for this paper.

Tetrakis(tetrahydrofuran)lithium aletpate (3b)

Under inert gas conditions, a solution of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-pentylphenol) **2b (**4.95 g, 10.0 mmol, 2 eq) in 20 ml dry THF was added slowly to a solution of $LiAlH_4$ (0.19 g, 5.0 mmol) in 10 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 h, and filtered through Celite after cooling to room temperature. After removal of the solvent *in vacuo*, the resulting colourless foam was recrystallised from THF/pentane to give a colourless powder (yield 4.40 g, 67%).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) δH (ppm): 0.30 {12H, major, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.41 {12H, minor, t, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.64 {12H, major, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.66 {12H, minor, t, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$},1.14 – 1.37 {48H, m, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.52 – 1.63 {8H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.65 – 1.88 {24H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$/thf}, 2.22 – 2.38 (4H, m, Ar-$\underline{CH_2}$), 3.55 – 3.65 (20H, minor, m, Ar-$\underline{CH_2}$/thf) 3.74 -3.92 (4H, major, m, Ar-$\underline{CH_2}$), 6.83 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.84 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.86 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.88 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

$^{13}C\{^1H\}$ NMR (100.66 MHz, d_6-acetone, 300 K) δC (ppm): 9.6, 10.0, 26.1, 28.5, 28.6, 29.0, 29.4, 33.6, 33.6, 35.3, 35.8, 37.5, 37.6, 38.0, 38.1, 38.7, 38.8, 68.0, 123.1, 123.3, 124.9, 125.2, 131.6, 134.6, 134.7, 135.8, 135.8, 156.1, 156.4.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 1011.77555; found: 1011.77393.

FTIR (ATR) ν_{max} (cm^{-1}): 2959 (m), 2874 (m), 1739 (w), 1708 (w), 1620 (w), 1469 (s), 1440 (m), 1416 (m), 1374 (w), 1358 (w), 1321 (m), 1288 (s), 1249 (m), 1235 (w), 1216 (w), 1166

(w), 1133 (w), 1042 (s), 1002 (w), 933 (w), 911 (m),894 (m), 873 (s), 789 (m), 775 (m), 746 (m), 672 (w), 650 (w), 613 (m).

Melting point: 196 °C (decomposition)

Tetrakis(tetrahydrofuran)lithium alphetbate (3c)

Under inert gas a solution of 6,6'-(ethane-1,2-diyl)bis[4-*tert*-butyl-2-(1,1-diphenylethyl)-phenol] **2c (**1.5 g, 2.0 mmol) in 9 ml dry THF was added slowly to a solution of $LiAlH_4$ (58 mg, 1.0 mmol) in 1 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 d and filtered through Celite after cooling to room temperature. After removal of the solvent *in vacuo*, methanol was added and the suspension was stirred for 1 h. The suspension was filtered and the solvent of the filtrate was removed *in vacuo*. The resulting colourless foam was recrystallised from THF/pentane to give a colourless powder (yield 1.05 g, 62%).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) alphetbate major : minor conformer ratio (2:1) δH (ppm): 1.05 {36H, minor, s, C($\underline{CH_3}$)$_3$}, 1.07 {36H, major, s, C($\underline{CH_3}$)$_3$}, 1.72 – 1.85 (20H, m, Ar-$\underline{CH_2}$/thf), 1.95 (12H, major, s, CPh$_2\underline{CH_3}$), 2.02 (12H, minor, s, CPh$_2\underline{CH_3}$), 2.80 – 3.00 (4H, m, Ar-$\underline{CH_2}$), 3.58 – 3.66 (16H, m, thf), 6.18 – 8.23 (4H, m, Ar-$\underline{H}$), 6.75 – 7.30 (44H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (100.62 MHz, d_6-acetone, 300 K) δC (ppm): 26.1, 29.3, 30.0, 32.1, 34.0, 34.6, 35.3, 54.0, 68.0, 124.8, 124.9, 125.2, 125.3, 125.4, 125.5, 127.5, 127.7, 128.3, 128.7, 129.2, 129.6, 129.9, 130.1, 132.4, 132.7, 134.7, 134.9, 135.9, 152.2, 152.5, 153.3, 156.6, 156.7.

ES-HRMS (m/z)$^-$ [M]$^-$ calc. mass: 1395.77555; found: 1395.77311.

FTIR (ATR) ν_{max} (cm^{-1}): 3055 (w), 3028 (w), 2948 (w), 2900 (w), 2863 (w), 1813 (w), 1598 (m), 1471 (m), 1440 (m), 1414 (w), 1390 (m), 1359 (w), 1302 (m), 1217 (w), 1187 (w), 1154 (w), 1137 (w), 1072 (m), 1027 (w), 997 (w), 923 (w), 869 (w), ,838 (w), 803 (w), 769 (m), 757 (m), 724 (m), 696 (s), 632 (m).

Melting point: 201 °C (decomposition)

Bis(tetrahydrofuran)sodium aletbate (4a)

Under inert gas conditions, a solution of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) **2a (**17.4 g, 40.0 mmol) in 110 ml dry THF was added slowly to a solution of $NaAlH_4$ (1.20 g, 20.0 mmol) in 10 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 h, and filtered through Celite after cooling to room temperature. After removal of the solvent *in vacuo*, pentane was added and the suspension was stirred for 30 min. After filtration, the colourless powder was dried *in vacuo* (yield 19.5 g, 83%).

^{1}H NMR (600.24 MHz, d_6-acetone, 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 1.23 – 1.30 {72H, m, C($\underline{CH_3}$)$_3$}, 1.75 – 1.83 (8H, m, thf), 2.27 – 2.37 (4H, m, Ar-$\underline{CH_2}$), 3.55 – 3.65 (20H, major, m, Ar-$\underline{CH_2}$/thf), 3.73 – 3.81 (4H, minor, m, Ar-$\underline{CH_2}$), 6.91 (4H, minor, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.96 (4H, major, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.98 (4H, minor, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.00 (4H, major, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.93 MHz, $CDCl_3$, 300 K) δC (ppm): 26.1, 31.0, 31.1, 32.3, 32.4, 34.3, 34.4, 35.3, 35.4, 35.7, 68.0, 121.0, 121.2, 124.2, 124.4, 131.5, 131.6, 136.8, 137.0, 137.2, 156.0, 156.3.

ESI-HRMS (m/z)$^-$ [M]$^-$ calc. mass: 899.65035; found: 899.64839.

FTIR (ATR) ν_{max} (cm^{-1}): 2950 (s), 2902 (m), 2866 (m), 1760 (w), 1605 (m), 1472 (s), 1442 (s), 1414 (m), 1389 (w), 1359 (m), 1316 (m), 1303 (m), 1282 (s), 1254 (m), 1236 (m), 1201 (m), 1168 (m), 1133 (w), 1114 (w), 995 (w), 912 (w), 876 (s), 855 (w), 810 (w), 772 (w), 647 (w), 611 (m).

$C_{68}H_{104}NaAlO_6$: calculated C-76.51%, H-9.82%; found C-76.29%, H-10.07%

Melting point: 278 °C (decomposition)

X-ray diffraction: colourless crystal (needle), dimensions 0.12 x 0.08 x 0.07 mm^3, crystal system monoclinic, space group C2/c, Z=4, a=11.081(2) Å, b=23.961(6) Å, c=24.439(6) Å, alpha=90 deg, beta=101.533(7) deg, gamma=90 deg, V=6358(2) Å^3, rho=1.115 g/cm^3, T=200(2) K, Theta$_{max}$= 18.00 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean

redundancy of 5.52 and a completeness of 100.0% to a resolution of 1.15Å, 12355 reflections measured, 2197 unique (R(int)=0.1252), 1430 observed (I >2σ (I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.09mm^{-1}, T_{min}=0.99, T_{max}=0.99, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2014-3) software package[2], 419 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.10 for observed reflections, final residual values R1(F)=0.131, wR(F^2)=0.314 for observed reflections, residual electron density -0.45 to 0.45 eÅ^{-3}. CCDC 999518 contains the supplementary crystallographic data for this paper.

Tetrakis(tetrahydrofuran)sodium aletbate

This compound was obtained by crystallization of bis(tetrahydrofuran)sodium aletbate **4a** from THF / pentane. It has only been characterized by X-ray diffraction. By removing excess solvent *in vacuo*, only bis(tetrahydrofuran)sodium aletbate **4a** has been obtained.

X-ray diffraction: colourless crystal (polyhedron), dimensions 0.11 x 0.10 x 0.08 mm3, crystal system triclinic, space group $P\bar{1}$, Z=2, a=14.1898(2) Å, b=14.7188(3) Å, c=19.3540(4) Å, alpha=83.112(1) deg, beta=89.299(1) deg, gamma=71.328(1) deg, V=3800.35(12) Å^3, rho=1.059 g/cm^3, T=200(2) K, $Theta_{max}$= 22.72 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.49 and a completeness of 100.0% to a resolution of 0.92Å, 45713 reflections measured, 10197 unique (R(int)=0.0540), 6499 observed (I >2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.08mm^{-1}, T_{min}=0.99, T_{max}=0.99, structure solved by direct methods and refined against F2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package2, 831 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.04 for observed reflections, final residual values R1(F)=0.070, wR(F2)=0.179 for observed reflections, residual electron density -0.32 to 0.51 eÅ^{-3}. CCDC 999514 contains the supplementary crystallographic data for this paper.

Bis(tetrahydrofuran)sodium aletpate (4b)

Under an inert gas atmosphere, a solution of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-pentylphenol) **2b (**4.08 g, 8.2 mmol) in 20 ml dry THF was slowly added to a solution of $NaAlH_4$ (0.22 g, 4.1 mmol) in 5 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 h, and filtered through Celite after cooling to room temperature. After removal of the solvent *in vacuo*, pentane was added and the suspension was stirred for 30 min. After filtration the colourless powder was dried *in vacuo* (yield 4.40 g, 67%).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) aletpate major : minor conformer rartio (63:37) δH (ppm): 0.30 {12H, major, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.41 {12H, minor, t, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.62 – 0.70 {12H, m, $C(CH_3)_2(CH_2\underline{CH_3})$}, 1.08 – 1.35 {48H, m, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.52 – 1.62 {8H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.65 – 1.86 {16H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$/thf}, 2.22 – 2.37 (4H, m, $\underline{CH_2}$-Ar), 3.57 – 3.67 (12H, minor, m, Ar-$\underline{CH_2}$/thf), 3.84 -3.90 (4H, major, m, Ar-$\underline{CH_2}$), 6.83 (4H, major, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.84 (4H, major, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.86 (4H, minor, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.88 (4H, minor, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$).

$^{13}C\{^1H\}$ NMR (150.33 MHz, $CDCl_3$, 300 K) δC (ppm): 9.5, 10.0, 26.1, 28.4, 28.5, 28.9, 29.3, 29.4, 33.4, 33.6, 35.1, 35.7, 37.5, 37.9, 38.0, 38.6, 38.7, 68.0, 123.0, 123.2, 124.8, 125.1, 131.4, 131.5 134.5, 134.6, 135.7, 135.8, 156.0, 156.3.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 1011.77555; found: 1011.78139.

FTIR (ATR) ν_{max} (cm^{-1}): 2949 (m), 2901 (m), 2868 (m), 1753 (w), 1657 (w), 1604 (w), 1471 (m), 1440 (m), 1416 (w), 1388 (w), 1358 (w), 1319 (m), 1286 (s), 1251 (m), 1237 (w), 1201 (w), 1169 (w), 1135 (w), 1043 (s), 999 (w), 915 (m), 873 (s), 810 (w), 789 (w), 775 (m), 765 (m), 668 (w), 646 (w), 614 (s).

$C_{76}H_{120}AlNaO_4$: calculated C-77.37%, H-10.25%; found C-76.41%, H-10.41%

Melting point: 260 °C (decomposition)

Bis(tetrahydrofuran)sodium alphetbate (4c)

Under inert gas conditions, a solution of 6,6'-(ethane-1,2-diyl)bis[4-*tert*-butyl-2-(1,1-diphenylethyl)phenol] **2c** (3.0 g, 4.4 mmol) in 9 ml dry THF was added slowly to a solution of $LiAlH_4$ (120 mg, 2.0 mmol) in 1 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 d and filtered through Celite after cooling to room temperature. After removal of the solvent *in vacuo*, methanol was added and the suspension was stirred for 1 h. The suspension was filtered and the solvent of the filtrate was removed *in vacuo*. The resulting colourless foam was recrystallised from THF/pentane to give a colourless powder (yield 1.76 g, 52%).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) alphetbate major : minor conformer ratio (2:1) δH (ppm): 1.05 {36H, minor, s, C($\underline{CH_3}$)$_3$}, 1.07 {36H, major, s, C($\underline{CH_3}$)$_3$}, 1.74 – 1.90 (12H, m, Ar-$\underline{CH_2}$/thf), 1.95 (12H, major, s, CPh$_2\underline{CH_3}$), 2.02 (12H, minor, s, CPh$_2\underline{CH_3}$), 2.86 – 3.00 (4H, m, Ar-$\underline{CH_2}$), 3.60 – 3.66 (8H, m, thf), 6.17 – 6.23 (4H, m, Ar-$\underline{H}$), 6.73 – 7.20 (44H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (100.62 MHz, d_6-acetone, 300 K) δC (ppm): 26.1, 29.2, 30.0, 32.0, 34.0, 34.5, 35.2, 53.9, 68.0, 124.7, 124.9, 125.2, 125.3, 125.4, 127.5, 127.7, 128.2, 128.6, 128.7, 129.1, 129.5, 129.8, 130.0, 132.3, 132.6, 134.6, 134.9, 135.8, 152.1, 152.4, 153.2, 156.5, 156.7.

ES-HRMS (m/z)$^-$ [M]$^-$ calc. mass: 1395.77555; found: 1395.78337.

FTIR (ATR) ν_{max} (cm^{-1}): 3056 (w), 3029 (w), 2951 (m), 2867 (w), 1763 (w), 1598 (w), 1471 (m), 1443 (m), 1414 (w), 1391 (w), 1360 (w), 1292 (m), 1215 (m), 1155 (w), 1136 (w), 1051 (w), 1028 (m), 996 (w), 923 (w), 915 (w), 874 (m), 761 (m), 729 (w), 698 (s), 651 (w), 633 (w), 612 (s).

Melting point: 185 °C (decomposition)

Sodium aletbate (5a)

This compound was obtained by elimination of the thf ligands at 150 °C and 0.1 mbar over 24 h in the solid state. The product was obtained as a colourless solid in quantitative yield.

^{1}H NMR (600.24 MHz, CD_2Cl_2, 300 K) δH (ppm): 1.22 – 1.26 {36H, br. s, C($\underline{CH_3}$)$_3$}, 1.28 {36H, s, C($\underline{CH_3}$)$_3$}, 2.32 – 2.82 (4H, br. s, Ar-$\underline{CH_2}$), 3.06 – 3.73 (4H, br. s, Ar-$\underline{CH_2}$), 7.04 (4H, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.10 (4H, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, CD_2Cl_2, 300 K) δC (ppm): 30.5, 31.8, 34.3, 35.0, 35.1, 122.5, 125.1,131.3, 136.8, 140.1 153.7.

ESI-HRMS (m/z)$^-$ [M]$^-$ calc. mass: 899.64794; found: 899.64834.

FTIR (ATR) ν_{max} (cm^{-1}): 3613 (w), 2952 (m), 2867 (w), 1617 (w), 1470 (s), 1440 (s), 1413 (m), 1390 (w), 1360 (m), 1316 (m), 1271 (s), 1235 (s), 1202 (w), 1167 (w), 1134 (w), 1025 (w), 996 (w), 912 (m), 865 (s), 810 (w), 763 (m), 648 (w), 615 (s).

Melting point: 275 °C

Sodium aletpate (5b)

This compound was obtained by elimination of the thf ligands at 150 °C and 0.1 mbar over 24 h in the solid state. The product was obtained as a colourless solid in quantitative yield.

^{1}H NMR (600.24 MHz, CD_2Cl_2, 300 K) δH (ppm): 0.43 {12H, br s, C(CH_3)$_2$($CH_2\underline{CH_3}$)}, 0.67 {12H, t, $^{3}J_{HH}$ = 7.2 Hz, C(CH_3)$_2$($CH_2\underline{CH_3}$)}, 1.24 {48H,br s, C($\underline{CH_3}$)$_2$(CH_2CH_3)}, 1.59 {8H, q, $^{3}J_{HH}$ = 7.2 Hz, C(CH_3)$_2$($\underline{CH_2}CH_3$)}, 1.62 {8H, br s, C(CH_3)$_2$($\underline{CH_2}CH_3$)}, 2.52 (4H, br s, Ar-$\underline{CH_2}$), 3.22 – 3.63 (4H, m, Ar-$\underline{CH_2}$), 6.97 (4H, br s, Ar-H), 6.98 (4H, br s, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, CD_2Cl_2, 300 K) δC (ppm): 9.3, 9.4, 27.8, 28.9, 33.8, 34.8, 35.2, 37.4, 37.5, 38.5, 124.3, 125.7, 126.0, 131.1, 135.4, 135.9, 138.1, 153.7.

ESI-HRMS (m/z)$^-$ [M]$^-$ calc. mass: 1011.77555; found: 1011.77444.

FTIR (ATR) ν_{max} (cm^{-1}): 3600 (w), 3516 (w), 2961 (s), 2874 (m), 1739 (w), 1712 (w), 1616 (w), 1468 (s), 1442 (s), 1414 (m), 1374 (w), 1360 (w), 1277 (s), 1216 (m), 1164 (w), 1133 (w), 1058 (w), 1005 (w), 934 (w), 912 (m), 895 (m), 876 (s), 856 (s), 782 (m), 744 (m), 653 (w), 631 (w), 611 (m).
Melting point: 271 °C (decomposition)

Sodium alphetbate (5c)

This compound was obtained by elimination of the thf ligands at 150 °C and 0.1 mbar over 24 h in the solid state. The product was obtained as a colourless solid in quantitative yield.

^{1}H NMR (400.33 MHz, CD_2Cl_2, 300 K) δH (ppm): 1.16 {36H, s, C($\underline{CH_3}$)$_3$}, 1.86 (12H, s, CPh$_2$$\underline{CH_3}$), 2.31 – 3.20 (8H, br s, Ar-$\underline{CH_2}$), 6.44 (4H, d, $^{4}J_{HH}$ = 2.4 Hz, Ar-$\underline{H}$), 6.76 – 6.91 (16H, m, Ar-$\underline{H}$), 7.04 (4H, d, $^{4}J_{HH}$ = 2.4 Hz, Ar-$\underline{H}$), 7.06 – 7.16 (16H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, CD_2Cl_2, 300 K) δC (ppm): 28.8, 31.6, 34.0, 35.0, 53.0, 125.4, 126.1, 128.2, 128.8, 129.0, 131.8, 135.5, 139.3, 150.9, 153.8.

ESI-HRMS (m/z)$^{-}$ [M]$^{-}$ calc. mass: 1011.77555; found: 1011.77519.

Tetraphenylphosphonium aletbate (6a)

a) Solvent acetone

PPh_4Br (98 mg, 0.23 mmol) was added to a solution of 250 mg (0.23 mmol) bis(tetrahydrofuran)sodium aletbate **4a** in 20 mL acetone. Colourless NaBr precipitated. After stirring at room temperature for 60 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removal of the solvent and crystallisation from acetone / pentane, the product was obtained as a colourless solid. (yield 275 mg, 93%).

b) Solvent ethyl acetate

PPh_4Br (98 mg, 0.23 mmol) was added to a solution of 250 mg (0.23 mmol) bis(tetrahydrofuran)sodium aletbate **4a** in 20 mL ethyl acetate. Colourless NaBr precipitated. After stirring at room temperature for 60 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removing of the solvent and crystallisation from ethylacetate / pentane, the product was obtained as a colourless solid. (yield 220 mg, 76%).

c) Solvent toluene

PPh_4Br (98 mg, 0.23 mmol) was added to a solution of 250 mg (0.23 mmol) bis(tetrahydrofuran)sodium aletbate **4a** in 20 mL toluene. Colourless NaBr precipitated. After stirring at room temperature for 60 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removal of the solvent and crystallisation from toluene / pentane, the product was obtained as a colourless solid. (yield 40 mg, 13%).

d) Solvent CH_2Cl_2

Under inert gas conditions, PPh_4Br (82 mg, 0.2 mmol) in 3 mL dichloromethane was slowly added to a solution of bis(tetrahydrofuran)sodium aletbate **4a** (210 mg, 0.20 mmol) in 7 mL dichloromethane whilst stirring. A colourless solid (NaBr) precipitated. After stirring for 30 min at room temperature, the suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from dichloromethane / pentane gave the title product as a colourless solid. (yield 240 mg, 96 %).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 1.23 – 1.28 {72H, m , C($\underline{CH_3}$)$_3$}, 2.25 – 2.39 (4H, m, Ar-$\underline{CH_2}$), 3.52 – 3.66 (4H, major, m, Ar-$\underline{CH_2}$), 3.70 – 3.84 (4H, minor, m, Ar-$\underline{CH_2}$), 6.90 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.95 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.97 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.00 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.81 – 7.91 (16H, m, Ar-$\underline{H}$), 7.96 – 8.05 (4H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm): 31.1, 32.3, 32.4, 34.4, 35.3, 35.4, 35.8, 119.0 (d, $^1J_{PC}$ = 89.5 Hz), 121.1, 121.2, 124.2, 124.4, 131.4 (d, $^2J_{PC}$ = 12.8 Hz), 131.6, 131.6, 135.6 (d, $^3J_{PC}$ = 10.4 Hz), 136.4 (d, $^4J_{PC}$ = 3.0 Hz), 136.9, 137.0, 137.1, 137.3, 156.0, 156.4.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 899.65035; found: 899.64935 $[M^+]$ calc. mass: 339.13026; found: 339.12981.

FTIR (ATR) ν_{max} (cm^{-1}): 3444 (br), 2951 (s), 2865 (m), 2043 (w), 1993 (w), 1587 (w), 1473 (s), 1442 (s), 1416 (m), 1387 (w), 1359 (m), 1320 (m), 1306 (m), 1288 (s), 1238 (m), 1201 (w), 1169 (w), 1135 (w), 1109 (s), 1027 (w), 998 (w), 917 (w), 877 (s), 810 (w), 776 (w), 764 (w), 724 (m), 690 (m), 647 (w), 613 (m), 594 (w), 527 (s), 484 (w).

$C_{84}H_{108}AlO_4P$: calculated C-81.38%, H-8.78%; found C-81.44%, H-8.66%

Melting point: > 300°C

X-ray diffraction: colourless crystal (polyhedron), dimensions 0.23 x 0.15 x 0.13 mm^3, crystal system monoclinic, space group C2/c, Z=8, a=27.1582(14) Å, b=28.5362(13) Å, c=24.0085(11) Å, alpha=90 deg, beta=113.8690(10) deg, gamma=90 deg, V=17015.0(14) $Å^3$, rho=1.134 g/cm^3, T=200(2) K, $Theta_{max}$= 19.78 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.28 and a completeness of 99.9% to a resolution of 1.05Å, 33346 reflections measured, 7693 unique (R(int)=0.0692), 4514 observed (I >2σ (I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.25mm^{-1}, T_{min}=0.95, T_{max}=0.97, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package[2], 1119 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values R1(F)=0.084, $wR(F^2)$=0.223 for observed reflections, residual electron density -0.29 to 0.39 $eÅ^{-3}$. CCDC 999512 contains the supplementary crystallographic data for this paper.

Tetraphenylphosphonium aletpate (6b)

Under inert gas conditions, PPh_4Br (140 mg, 0.33 mmol) in 3 mL dichloromethane was slowly added to a solution of bis(tetrahydrofuran)sodium aletpate **4b** (400 mg, 0.33 mmol) in 7 mL dichloromethane whilst stirring. A colourless solid (NaBr) precipitated. After stirring for 30 min at room temperature, the suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from dichloromethane / pentane gave the title product as a colourless solid. (yield 388 mg, 87 %).

^{1}H NMR (600.24 MHz, d_6-acetone, 300 K) aletpate major : minor conformer ratio (63:37) δH (ppm): 0.26 {12H, major, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.40 {12H, minor, t, $^3J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.62 – 0.68 {12H, m, $C(CH_3)_2(CH_2\underline{CH_3})$}, 1.08 – 1.36 {48H, m, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.52 – 1.60 {8H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.66 – 1.82 {16H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 2.24 – 2.34 (4H, Ar-$\underline{CH_2}$), 3.57 – 3.65 (4H, minor, m, Ar-$\underline{CH_2}$), 3.78 -3.85 (4H, major, m, Ar-$\underline{CH_2}$), 6.83 (4H, major, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.84 (4H, major, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.86 (4H, minor, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.88 (4H, minor, d, $^4J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 7.81 – 7.89 (16H, m, Ar-$\underline{H}$), 7.96 – 8.01 (4H, m, Ar-$\underline{H}$).

$^{13}C\{^1H\}$ NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm): 8.7, 9.2, 27.6, 27.7, 28.1, 28.5, 32.7, 32.8, 34.3, 34.9, 36.7, 37.1, 37.2, 37.8, 37.9, 118.1 (d, $^1J_{C\text{-}P}$ = 89.4 Hz), 122.2, 122.4, 124.0, 124.3, 130.5 (d, $^2J_{C\text{-}P}$ = 12.9 Hz), 130.6, 130.7, 133.8, 134.7 (d, $^3J_{C\text{-}P}$ = 10.4 Hz), 134.9, 135.0, 135.5 (d, $^2J_{C\text{-}P}$ = 2.7 Hz), 155.2, 155.5.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 1011.77555; found: 1011.77462 $[M]^+$ calc. mass: 339.12971; found: 339.12940.

FTIR (ATR) ν_{max} (cm^{-1}): 2961 (m), 2873 (m), 1742 (w), 1587 (w), 1468 (s), 1468 (s), 1438 (m), 1416 (w), 1379 (w), 1358 (w), 1320 (s), 1288 (s), 1250 (w), 1216 (w), 1166 (w), 1133 (w), 1058 (w), 998 (w),967 (m), 934 (m), 896 (m), 873 (s), 859 (w), 788 (w), 776 (m), 747 (m), 723 (s), 689 (s), 651 (w), 616 (m).

$C_{92}H_{124}AlO_4P$: calculated C-81.73%, H-9.24%; found C-81.71%, H-9.18%

Melting point 298 °C

X-ray diffraction: colourless crystal (plate), dimensions 0.18 x 0.12 x 0.03 mm^3, crystal system triclinic, space group $P\bar{1}$, Z=8, a=23.163(2) Å, b=27.127(3) Å, c=30.989(3) Å, alpha=115.645(2) deg, beta=99.092(3) deg, gamma=100.786(3) deg, V=16604(3) $Å^3$, rho=1.082 g/cm^3, T=200(2) K, $Theta_{max}$= 19.81 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.55 and a completeness of 99.5% to a resolution of 1.05Å, 76557 reflections measured, 30030 unique (R(int)=0.0888), 15579 observed (>2σ (I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, mu=0.09mm^{-1}, T_{min}=0.98, T_{max}=1.00, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2013/3) software package[2], 3529 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values R1(F)=0.095, wR(F^2)=0.248 for observed reflections, residual electron density -0.45 to 0.82 e$Å^{-3}$. CCDC 999521 contains the supplementary crystallographic data for this paper.

Tetraphenylphosphonium alphetbate (6c)

Under inert gas conditions, PPh_4Br (84 mg, 0.2 mmol) in 3 mL dichloromethane was slowly added to a solution of bis(tetrahydrofuran)sodium alphetbate **4c** (340 mg, 0.20 mmol) in 7 mL dichloromethane whilst stirring. A colourless solid (NaBr) precipitated. After stirring for 30 min at room temperature, the suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from dichloromethane / pentane gave the title product as a colourless solid. (yield 270 mg, 80 %).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) alphetbate major : minor conformer ratio (2:1) δH (ppm): 1.05 {36H, minor, s, C($\underline{CH_3}$)$_3$}, 1.07 {36H, major, s, C($\underline{CH_3}$)$_3$}, 1.74 – 1.90 (12H, m, Ar-$\underline{CH_2}$/thf), 1.96 (12H, major, s, $CPh_2\underline{CH_3}$), 2.05 (12H, minor, s, $CPh_2\underline{CH_3}$), 2.86 – 3.00 (4H, m, Ar-$\underline{CH_2}$), 3.60 – 3.66 (8H, m, thf), 6.17 – 6.23 (4H, m, Ar-$\underline{H}$), 6.73 – 7.20 (44H, m, Ar-$\underline{H}$), 7.79 – 7.88 (16H, m, Ar-$\underline{H}$), 7.94 – 8.00 (4H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm): 29.4, 30.0, 32.1, 34.1, 34.7, 35.3, 54.0, 118.9 (d, $^1J_{C\text{-}P}$ = 89.2 Hz), 124.8, 124.9, 125.3, 125.4, 125.5, 127.5, 127.6, 127.7, 128.4, 128.8, 129.2, 129.6, 129.9, 130.0, 131.4 (d, $^2J_{C\text{-}P}$ = 12.9 Hz), 132.5, 132.7, 134.7, 134.9, 135.6 (d, $^3J_{C\text{-}P}$ = 10.5 Hz), 135.9, 136.4 (d, $^4J_{C\text{-}P}$ = 3.0 Hz), 152.3, 152.4, 153.3, 156.1, 156.8.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 1395.77555; found: 1395.77297 $[M^+]$ calc. mass: 339.12971; found: 339.12967.

FTIR (ATR) ν_{max} (cm^{-1}): 3055 (w), 2951 (m), 2867 (w), 1751 (w), 1705 (m), 1598 (w), 1472 (s), 1443 (m), 1415 (m), 1390 (w), 1360 (w), 1302 (m), 1236 (w), 1217 (w), 1154 (w), 1137 (w), 1044 (w), 1028 (m), 999 (w), 923 (w), 869 (m), 859 (w), 770 (m), 759 (m), 729 (w), 698 (s), 650 (w), 632 (w), 611 (w).

Melting point: 245°C

X-Ray diffraction: colourless crystal (plate), dimensions 0.440 x 0.440 x 0.080 mm^3, crystal system monoclinic, space group $P2_{1/c}$, Z=4, a=14.8662(15) Å, b=33.789(4) Å, c=27.090(3) Å, alpha=90 deg, beta=94.019(4) deg, gamma=90 deg, V=13574(2) $Å^3$, rho=1.003 g/cm^3, T=200(2) K, $Theta_{max}$= 22.464 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.93 and a completeness of 96.1% to a resolution of 0.95Å, 52178 reflections measured, 16987 unique (R(int)=0.0633), 10464 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.15mm^{-1}, T_{min}=0.82, T_{max}=0.96, structure refined against F2 with a Full-matrix least-squares algorithm using the SHELXL (Version 2013-4) software 2, 1315 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.23 for observed reflections, final residual values R1(F)=0.106, $wR(F^2)$=0.311 for observed reflections, residual electron density -1.01 to 0.92 $eÅ^{-3}$. CCDC 999523 contains the supplementary crystallographic data for this paper.

Tetrabutylammonium aletbate 7a

a) Solvent acetone

NBu_4Br (75 mg, 0.23 mmol) was added to a solution of 250 mg (0.23 mmol) bis(tetrahydro-furan)sodium aletbate **4a** in 20 mL acetone. A colourless precipitate of NaBr formed slowly. After stirring at room temperature for 60 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removing of the solvent and crystallisation from acetone / pentane, the product was obtained as a colourless solid. (yield 250 mg, 94%).

b) Solvent ethyl acetate

NBu_4Br (75 mg, 0.23 mmol) was added to a solution of 250 mg (0.23 mmol) bis(tetrahydrofuran)sodium aletbate **4a** in 20 mL ethyl acetate. Colourless NaBr precipitated. After stirring at room temperature for 60 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removing of the solvent and crystallisation from ethyl acetate / pentane, the product was obtained as a colourless solid. (yield 242 mg, 90%).

c) Solvent toluene

NBu_4Br (75 mg, 0.23 mmol) was added to a solution of 250 mg (0.23 mmol) bis(tetrahydrofuran)sodium aletbate **4a** in 20 mL toluene. Colourless NaBr precipitated. After stirring at room temperature for 60 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removing of the solvent and crystallisation from toluene / pentane, the product was obtained as a colourless solid. (yield 240 mg, 90%).

d) Solvent CH_2Cl_2

Under inert gas conditions, a solution of 64 mg (0.2 mmol) NBu_4Br in 3 mL dichloromethane was added to a solution of 210 mg (0.2 mmol) bis(tetrahydrofuran)sodium aletbate **4a** in 7 mL dichloromethane. Colourless NaBr precipitated. After stirring at room temperature for 30 min the suspension was filtered through Celite, resulting in a clear colourless solution. After removing of the solvent and crystallisation from dichloromethane / pentane, the product was obtained as a colourless solid. (yield 210 mg, 97%).

^{1}H NMR (600.24 MHz, d_6-acetone 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 0.98 (12H, t, $^3J_{HH}$ = 7.3 Hz, $\underline{CH_3}$), 1.21 – 1.31 {72H, m, C($\underline{CH_3}$)$_3$}, 1.39 – 1.48 (8H, m, $\underline{CH_2}$), 1.80 – 1.88 (8 H, m, $\underline{CH_2}$), 2.27 – 2.37 (4H, m, Ar-$\underline{CH_2}$), 3.43 – 3.49 (8H, m, N-$\underline{CH_2}$), 3.54 – 3.66 (4H, major, m, Ar-$\underline{CH_2}$), 3.72 – 3.83 (4H, minor, m, Ar-$\underline{CH_2}$), 6.91 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.96 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.98 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.00 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm): 13.8, 20.3 (t, $^2J_{C\text{-}N}$ = 1.6 Hz), 24.5, 31.0, 31.1, 32.3, 32.4, 34.3, 34.4, 35.3, 35.4, 35.7, 59.3 (t, $^1J_{C\text{-}N}$ = 2.9 Hz), 121.0, 121.2, 124.2, 124.4, 131.5, 131.6, 136.8, 137.0, 137.2, 156.0, 156.3.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 899.65035; found: 899.64866, $[M]^+$ calc. mass: 242.28423; found: 242.28434.

FTIR (ATR) ν_{max} (cm^{-1}): 3418 (br), 2950 (s), 2866 (m), 1616 (w), 1474 (s), 1441 (m), 1417 (m), 1386 (w), 1359 (m), 1320 (m), 1305 (m), 1287 (s), 1238 (m), 1201 (w), 1169 (w), 1135 (w), 1025 (w), 998 (w), 917 (m), 876 (s), 776 (m), 764 (m), 647 (w), 613 (m), 593 (w), 535 (w), 484 (w), 407 (w).

$C_{84}H_{140}AlNO_4$: calculated C-79.88%, H-10.94% N-1.23%; found C-79.84%, H-11.09% N-1.09%

Melting point 272 °C

X-ray diffraction: colourless crystal (plate), dimensions 0.21 x 0.09 x 0.03 mm^3, crystal system orthorhombic, space group Pbca, Z=8, a=24.3711(15) Å, b=24.6465(15) Å, c=25.3492(15) Å, alpha=90 deg, beta=90 deg, gamma=90 deg, V=15226.3(16) $Å^3$, rho=1.071 g/cm^3, T=200(2) K, $Theta_{max}$= 20.82 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 10.86 and a completeness of 99.9% to a resolution of 1.0Å, 89697 reflections measured, 7971 unique (R(int)=0.1334), 4935 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.14mm^{-1}, T_{min}=0.97, T_{max}=1.00, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package[2], 785 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.02 for observed reflections, final residual values R1(F)=0.079, $wR(F^2)$=0.176 for observed reflections, residual electron density -0.50 to 0.41 $eÅ^{-3}$. CCDC 999515 contains the supplementary crystallographic data for this paper.

Tetrabutylammonium aletpate 7b

Under inert gas a solution of 105 mg (0.31 mmol) tetrabutylammonium bromide in 3 mL dichloromethane was added to a solution of 350 mg (0.31 mmol) bis(tetrahydrofuran)sodium aletpate **4b** in 7 mL dichloromethane. A colourless precipitate of NaBr was formed. After stirring at room temperature for 30 min the suspension was filtered through Celite resulting a

clear colourless solution. After removing of the solvent and crystallisation from dichloromethane / pentane the product was obtained as a colourless solid. (yield 350 mg, 89%).

^{1}H NMR (600.24 MHz, d_6-acetone 300 K) aletpate major : minor conformer ratio (63:37) δH (ppm): 0.26 {12H, major, $^{3}J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.40 {12H, minor, t, $^{3}J_{HH}$ = 7.4 Hz, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.62 – 0.69 {12H, m, $C(CH_3)_2(CH_2\underline{CH_3})$}, 0.97 (12H, t, $^{3}J_{HH}$ = 7.3 Hz, $\underline{CH_3}$), 1.08 – 1.32 {48H, m, $C(\underline{CH_3})_2(CH_2CH_3)$}, 1.40 – 1.47 (8H, m, $\underline{CH_2}$), 1.53 – 1.60 {8H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.66 – 1.80 {8H, m, $C(CH_3)_2(\underline{CH_2}CH_3)$}, 1.81 – 1.87 (8 H, m, $\underline{CH_2}$), 2.25 – 2.34 (4H, m, Ar-$\underline{CH_2}$), 3.43 – 3.48 (8H, m, N-$\underline{CH_2}$), 3.57 – 3.65 (4H, minor, m, Ar-$\underline{CH_2}$) 3.78 -3.85 (4H, major, m, Ar-$\underline{CH_2}$), 6.83 (4H, major, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.84 (4H, major, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.86 (4H, minor, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$), 6.88 (4H, minor, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-$\underline{H}$).

$^{13}C\{^{1}H\}$ NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm):9.5, 10.0, 13.8, 20.3 (t, $^{3}J_{C\text{-}N}$ = 1.4 Hz), 24.3, 28.4, 28.5, 28.9, 29.3, 33.4, 33.6, 35.1, 35.7, 37.5, 37.9, 38.0, 38.6, 38.7, 59.3 (t, $^{2}J_{C\text{-}N}$ = 3.1 Hz) , 123.0, 123.2, 124.8, 125.1, 131.4, 131.5 134.5, 134.6, 135.7, 135.8, 156.0, 156.3.

ESI-HRMS $(m/z)^{-}$ $[M]^{-}$ calc. mass: 1011.77555; found: 1011.77595, $[M]^{+}$ calc. mass: 242.28423; found: 242.28419.

FTIR (ATR) ν_{max} (cm^{-1}): 2958 (m), 2871 (m), 1741 (m), 1611 (w), 1466 (s), 1374 (m), 1360 (w), 1290 (s), 1214 (m), 1164 (w), 1130 (w), 1057 (w), 1002 (w), 867 (s), 780 (m), 744 (m), 653 (w).

$C_{84}H_{140}AlNO_4$: calculated C-80.39%, H-11.24% N-1.12%; found C-79.83%, H-11.36% N-1.00%

Melting point 189 °C

Tetrabutylammonium alphetbate (7c)

Under inert gas, tetrabutylammonium bromide (32 mg, 0.1 mmol) in 2 mL dichloromethane was slowly added to a solution of bis(tetrahydrofuran)sodium alphetbate **4c** (165 mg,

0.1 mmol) in 4 mL dichloromethane whilst stirring. A colourless solid (NaBr) precipitated. After stirring for 30 min at room temperature, the suspension was filtered through Celite and the solvent was removed *in vacuo*. Diethyl ether (1 mL) was added and the solution was stirred for 10 min. A colourless solid was formed; then pentane was added. After filtration the product was obtained as a colourless solid. (yield 150 mg, 90 %).

^{1}H NMR (300.51 MHz, d_6-acetone, 300 K) alphetbate major : minor conformer ratio (2:1) δH (ppm): 0.98 (12H, t, $^{3}J_{HH}$ = 7.4 Hz, $\underline{CH_3}$), 1.05 {36H, minor, s, C($\underline{CH_3}$)$_3$}, 1.07 {36H, major, s, C($\underline{CH_3}$)$_3$}, 1.39 – 1.50 (8H, m, $\underline{CH_2}$), 1.78 – 1.91 (12H, m, $\underline{CH_2}$/Ar-$\underline{CH_2}$), 1.94 (12H, major, s, CPh$_2\underline{CH_3}$), 2.02 (12H, minor, s, CPh$_2\underline{CH_3}$), 2.86 – 3.04 (4H, m, Ar-$\underline{CH_2}$), 3.43 – 3.50 (8H, m, N-$\underline{CH_2}$), 6.18 – 6.24 (4H, m, Ar-$\underline{H}$), 6.72 – 7.20 (44H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm): 13.8, 20.3 (t, $^{3}J_{C\text{-}N}$ = 1.4 Hz), 24.4, 29.4, 30.0, 32.1, 34.0, 34.6, 35.3, 54.0 (t, $^{2}J_{C\text{-}N}$ = 2.8 Hz), 59.4, 124.8, 124.9, 125.2, 125.3, 125.4, 125.5, 127.5, 127.7, 128.3, 128.7, 129.2, 129.6, 129.9, 130.1, 132.4, 132.7, 134.7, 134.9, 135.9, 152.2, 152.5, 153.3, 156.6, 156.7.

ESI-HRMS (m/z)$^{-}$ [M]$^{-}$ calc. mass: 1395.77555; found: 1395.77649 [M^{+}] calc. mass: 242.28423; found: 242.28409.

FTIR (ATR) ν_{max} (cm^{-1}): 3055 (w), 3027 (w), 2960 (m), 2874 (w), 1598 (w), 1471 (s), 1444 (m), 1415 (m), 1359 (w), 1302 (m), 1217 (w), 1154 (w), 1138 (w), 1071 (w), 1028 (w), 999 (w), 924 (w), 870 (m), 838 (w), 769 (m), 759 (m), 728 (w), 697 (s), 633 (w), 611 (w).

Melting point: 210°C

[Bis-1,3-(2,6-diisopropylphenyl)imidazole-2-ylidene](dimethylsulfide)gold aletbate (8a)

Under inert gas a solution of sodium aletbate **5a** (100 mg 0.1 mmol) in 10 mL dry dichloromethane was added to a solution of (IPr)AuCl (66 mg, 0.11 mmol) and dimethylsulfide (0.4 ml, 0.50 mmol) in 5 mL dichloromethane at room temperature whilst stirring. A colourless solid (NaCl) precipitated. The resulting suspension was stirred for an additional 2 h at room temperature. The suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from dichloromethane / pentane gave the title compound as a colourless solid (yield 120 mg, 75%).

^{1}H NMR (600.24 MHz, d_6-acetone 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 1.22 – 1.28 {84 H, m, C(CH_3)$_3$ / CH(CH_3)$_2$}, 1.35 {12H, d, $^{3}J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$} 2.28 – 2.37 (4H, m, Ar-CH_2), 2.40 {6H, s, S(CH_3)$_2$}, 2.60 (4H, sept, $^{3}J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$}, 3.55 – 3.64 (4H, major, m, Ar-CH_2), 3.72 – 3.81 (4H, minor, m, Ar-CH_2), 6.90 (4H, minor, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-H), 6.96 (4H, major, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-H), 6.97 (4H, minor, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-H), 7.00 (4H, major, d, $^{4}J_{HH}$ = 2.6 Hz, Ar-H).7.48 – 7.66 (6H, m, Ar-H), 8.05 (2H, s, Ar-H).

^{13}C{^{1}H} NMR (150.93 MHz, d_6-acetone, 300 K) δC (ppm): 22.9, 24.2, 25.0, 29.5, 31.1, 31.2, 32.4, 32.5, 34.4, 34.5, 35.4, 35.5, 35.9, 121.2, 121.3, 124.3, 124.5, 125.0, 125.1, 125.6, 126.3, 131.5, 131.6, 131.7, 132.1, 134.5, 136.9, 137.1, 137.7, 146.6, 146.7, 146.8, 156.1, 156.4, 177.3.

ESI-HRMS (m/z)$^{-}$ $[M]^{-}$ calc. mass: 899.65035; found: 899.64845, $[M]^{+}$ calc. mass: 642.27342; found: 642.27247.

FTIR (ATR) ν_{max} (cm^{-1}): 3450 (br), 3154 (w), 3114 (w), 2960 (s), 2868 (m),1618 (w), 1473 (s),1442 (s), 1417 (m), 1387 (w), 1359 (m),1286 (s), 1238(s), 1202 (m),1169 (w), 1135 (w), 1060 (w), 917 (m), 876 (s), 805 (m), 777 (m), 761 (m), 703 (m), 614 (m),485 (w).

$C_{89}H_{130}AlAuN_2O_4S$: calculated C-67.70%, H-8.15% N-1.86%; found C-67.09%, H-8.21% N-1.96%

Melting point: 200 °C (decomposition).

X-ray diffraction: colourless crystal (plate), dimensions 0.22 x 0.18 x 0.02 mm^3, crystal system orthorhombic, space group $Pca2_1$, Z=4, a=24.5162(13) Å, b=14.2702(7) Å, c=27.0151(13) Å, alpha=90 deg, beta=90 deg, gamma=90 deg, V=9451.3(8) Å^3, rho=1.139 g/cm^3, T=200(2) K, $Theta_{max}$= 22.21 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 9.36 and a completeness of 100.0% to a resolution of 0.94Å, 58906 reflections measured, 11694 unique (R(int)=0.1234), 8458 observed (I >2σ (I)), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was

applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=1.63mm^{-1}, T_{min}=0.72, T_{max}=0.97, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package[2], 958 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter -0.004(8), goodness of fit 1.02 for observed reflections, final residual values R1(F)=0.059, wR(F^2)=0.107 for observed reflections, residual electron density -1.28 to 1.42 eÅ^{-3}. CCDC 999517 contains the supplementary crystallographic data for this paper.

[Bis-1,3-(2,6-diisopropylphenyl)imidazole-2-ylidene](dimethylsulfide)gold aletpate (8b)

Under inert gas conditions, a solution of sodium aletpate **5b** (200 mg 0.19 mmol) in 20 mL dry dichloromethane was added to a solution of (IPr)AuCl (120 mg, 0.19 mmol) and dimethylsulfide (0.8 ml, 1.0 mmol) in 5 mL dichloromethane at room temperature whilst stirring. A colourless solid (NaCl) precipitated. The resulting suspension was stirred for an additional 2 h at room temperature. The suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from dichloromethane / pentane gave the title product as a colourless solid. (yield 270 mg, 84%)

^{1}H NMR (600.24 MHz, CD_2Cl_2, 300 K) aletpate major : minor conformer ratio (63:37) δH (ppm): 0.26 {12H, major, $^3J_{HH}$ = 7.4 Hz, C(CH$_3$)$_2$(CH$_2$<u>CH$_3$</u>)}, 0.40 {12H, minor, t, $^3J_{HH}$ = 7.4 Hz, C(CH$_3$)$_2$(CH$_2$<u>CH$_3$</u>)}, 0.66 {12H, , major, t, $^3J_{HH}$ = 7.4 Hz, C(CH$_3$)$_2$(CH$_2$<u>CH$_3$</u>)}, 0.69 (12H, minor, t, $^3J_{HH}$ = 7.4 Hz, C(CH$_3$)$_2$(CH$_2$<u>CH$_3$</u>)}, 1.26 {12H, d, $^3J_{HH}$ = 6.9 Hz, CH(<u>CH$_3$</u>)$_2$}, 1.29 {12H, d, $^3J_{HH}$= 6.9 Hz, CH(<u>CH$_3$</u>)$_2$}, (1.06 – 1.32 {48H, m, C(<u>CH$_3$</u>)$_2$(CH$_2$CH$_3$)}, 1.49 – 1.68 (16H, m, <u>CH$_2$</u>), 2.19 {6H, s, S(<u>CH$_3$</u>)$_2$}, 2.27 – 2.35 (4H, m, Ar-<u>CH$_2$</u>), 2.47 {4H, sep, $^3J_{HH}$= 6.9 Hz, C<u>H</u>(CH$_3$)$_2$}, 3.43 – 3.49 (4H, minor, m, Ar-<u>CH$_2$</u>) 3.63 -3.71 (4H, major, m, Ar-<u>CH$_2$</u>), 6.83 (4H, major, d, $^4J_{HH}$ = 2.5 Hz, Ar-<u>H</u>), 6.84 (4H, major, d, $^4J_{HH}$ = 2.5 Hz, Ar-<u>H</u>), 6.88 (4H, minor, d, $^4J_{HH}$ = 2.5 Hz, Ar-<u>H</u>), 6.89 (4H, minor, d, $^4J_{HH}$ = 2.5 Hz, Ar-<u>H</u>), 7.31 (2H, s, Ar-<u>H</u>), 7.37 (4H, d, $^3J_{HH}$ = 7.8 Hz, Ar-H), 7.58 (2H, t, $^3J_{HH}$ = 7.8 Hz, Ar-<u>H</u>).

^{13}C{^{1}H} NMR (150.33 MHz, CD_2Cl_2, 300 K) δC (ppm): 9.4, 9.6, 23.1, 24.0, 25.0, 27.4, 27.7, 27.8, 28.2, 28.9, 29.0, 29.2, 33.0, 33.2, 34.4, 34.9, 37.2, 37.5, 37.6, 38.2, 38.3, 122.9, 123.1, 124.5, 124.8, 124.9, 125.0, 131.0, 131.1, 131.7, 133.3, 134.8, 135.8, 135.9, 145.9, 146.0, 155.5, 155.8, 176.5.

ESI-HRMS (m/z)$^-$ $[M]^-$ calc. mass: 1011.77555; found: 1011.77478, $[M]^+$ calc. mass: 642.27342; found: 642.27305.

FTIR (ATR) ν_{max} (cm^{-1}): 3114 (w), 2960 (m), 2872 (w), 1742 (w), 1597 (w), 1550 (w), 1468 (s), 1416 (m), 1382 (w), 1358 (w), 1287 (m), 1251 (s), 1216 (w), 1165 (w), 1132 (w), 1059 (w), 1002 (w), 988 (w), 935 (w), 911 (w), 896 (w), 873 (w), 859 (m), 803 (w), 777 (w), 757 (w), 746 (w), 704 (w), 669 (w), 650 (w), 614 (m).

$C_{97}H_{146}AlAuN_2O_4S$: calculated C-70.17%, H-8.86 % N-1.69 found C-69.82 %, H-8.68% N-1.68.

Melting point: 179 °C (decomposition).

Ir(PHOX1)(cod) aletbate (9)

A solution of 256 mg (0.66 mmol) (S)-4-*tert*-butyl-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-1,3-oxazol and 250 mg (0.33 mmol) $[Ir(cod)Cl]_2$ in 12 ml of dry dichloromethane was heated under reflux conditions for 2 h. After cooling to room temperature, 608 mg (0.66 mmol) sodium aletbate **5a** was added. A colourless precipitate was formed immediately and the suspension was stirred for 1 h. The suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from diethyl ether / pentane gave the title product as an orange solid (yield 980 mg, 91%).

^{1}H NMR (600.24 MHz, d_6-acetone, 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 0.76 {9H, s, PHOX-C($\underline{CH_3}$)$_3$}, 1.24 – 1.26 {72H, m, C($\underline{CH_3}$)$_3$}, 1.53 (1H, m, cod), 1.73 (1H, m, cod), 2.11 (1H, m, cod), 2.32 (4H, m, Ar-$\underline{CH_2}$), 2.47 (3H, m, cod), 2.68 (3H, m, cod), 3.08 (1H, s, cod), 3.61 (1H, s, cod), 3.53 – 3.63 (4H, major, m, Ar-$\underline{CH_2}$) 3.71 – 3.79 (4H, minor, m, Ar-$\underline{CH_2}$), 4.37 (1H, d, $^3J_{HH}$ = 8.9 Hz, O-$\underline{CH_2}$), 4.73 (1H, dd, $^2J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 9.4 Hz, N-$\underline{CH}$), 4.92 (1H, dd, $^2J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 9.4 Hz, O-$\underline{CH_2}$), 5.02 (1H, m, cod), 5.42 (1H, s, cod), 6.90 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.95 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.96 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.99 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.01 (1H, s, Ar-$\underline{H}$), 7.26 (1H, m, Ar-$\underline{H}$), 7.53 – 7.66, (9H, m Ar-H), 7.81 (1H, m, Ar-$\underline{H}$), 7.89 (1H, m, Ar-$\underline{H}$), 8.38 (1H, m, Ar-$\underline{H}$).

$^{13}C\{^{1}H\}$ NMR (150.33 MHz, d_6-acetone, 300 K) δC (ppm): 25.8, 31.2, 32.5, 33.7, 34.5, 35.5, 35.9, 63.1, 63.6, 71.4, 75.4, 94.7, 94.8, 99.3, 99.4, 121.1, 121.3, 124.3, 124.5, 129.7, 130.7, 131.6, 131.7, 132.8, 133.4, 133.7, 134.4, 134.7, 134.8, 135.3, 135.4, 135.5, 135.6, 136.1, 137.0, 156.1, 165.1.

ESI-HRMS $(m/z)^-$ $[M]^-$ calc. mass: 899.65035; found: 899.64864, $[M]^+$ calc. mass: 688.23163; found: 688.23084.

FTIR (ATR) ν_{max} (cm^{-1}): 3437 (br), 2950 (s), 2864 (m), 1716 (w), 1593 (m), 1564 (w), 1473 (s), 1438 (s), 1416 (m), 1386 (w), 1359 (m), 1320 (s), 1305 (s), 1287 (m), 1254 (s), 1238 (m), 1201 (m), 1169 (m), 1124 (m), 1097 (m), 1061 (w), 1027 (w), 999 (w), 966 (w), 917 (m), 876 (s), 810 (w), 776 (m), 764 (m), 746 (w), 698 (m), 647 (w), 613 (w), 594 (m), 546 (w), 512 (m), 493 (w), 459 (w).

$C_{93}H_{126}AlIrNO_5P$: calculated C-70.33%, H-8.00%, N-0.88%; found C-70.56%, H-8.18%, N-0.64%

Melting point: 210 °C (decomposition)

Ir(PHOX2)(cod) aletbate (10)

A solution of 125 mg (0.30 mmol) (S)-4-*tert*-butyl-2-[2-(di-o-tolylphosphino)phenyl]-4,5-dihydro-1,3-oxazol and 100 mg (0.15 mmol) $[Ir(cod)Cl]_2$ in 6 ml of dry dichloromethane was heated under reflux conditions for 2 h. After cooling to room temperature, 360 mg (0.39 mmol) sodium aletbate **5a** was added. A colourless precipitate formed immediately. The suspension was stirred for 1 h. The suspension was filtered through Celite and the solvent was removed *in vacuo*. Recrystallisation from diethyl ether / pentane gave the title product as an orange solid (yield 430 mg, 82 %).

^{1}H NMR (400.18 MHz, d_6-acetone 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 0.67 {9H, s, PHOX-C($\underline{CH_3}$)$_3$}, 1.24 – 1.26 {72H, m, C($\underline{CH_3}$)$_3$}, 1.55 (1H, m, cod), 1.67 (1H, m, cod), 2.11 (1H, m, cod), 2.29 – 2.47 (12H, m, cod /Ar-$\underline{CH_3}$/Ar-$\underline{CH_2}$), 3.00 (1H, s, cod), 3.19 (3H, s, Ar-$\underline{CH_3}$), 3.45 (1H, s, cod), 3.56 – 3.63 (4H, major, m, Ar-$\underline{CH_2}$) 3.73 – 3.81 (4H, minor, m, Ar-$\underline{CH_2}$),4.34 (1H, d, $^{3}J_{HH}$ = 7.4 Hz, O-$\underline{CH_2}$), 4.74 (1H, dd, $^{2}J_{HH}$ =

2.1 Hz, $^{3}J_{HH}$ = 9.4 Hz, N-CH), 4.88 (1H, dd, $^{2}J_{HH}$ = 2.1 Hz, $^{3}J_{HH}$ = 9.4 Hz, O-CH_2), 5.03 (1H, m, cod), 5.37 (1H, s, cod), 6.63 (1H, m, Ar-H), 6.92 (4H, minor, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-H), 6.97 (4H, major, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-H), 6.98 (4H, minor, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-H), 7.00 (4H, major, d, $^{4}J_{HH}$ = 2.5 Hz, Ar-H), 7.01 (1H, s Ar-H), 7.16 (1H, m, Ar-H), 7.34 – 7.61, (6H, m Ar-H), 7.81 (1H, m, Ar-H), 7.89 (1H, m, Ar-H), 8.36 (1H, m, Ar-H)

$^{13}C\{^{1}H\}$ NMR (100.66, MHz, d_6-acetone, 300 K) δC (ppm): 25.1, 25.5, 25.8, 26.0, 26.1, 28.7, 31.2, 32.5, 33.8, 34.6, 35.1, 35.5, 35.9, 36.6, 67.1 67.2, 71.5, 75.5, 91.8, 97.1, 120.6, 121.0, 121.2, 121.2, 124.3, 124.6, 128.0, 128.1, 131.7, 131.8, 133.0, 133.3, 133.7, 134.6, 134.7, 134.8, 135.5, 136.0, 137.0, 137.2, 137.4, 142.5, 144.4, 156.1, 156.5, 165.0.

ESI-HRMS (m/z)$^{-}$ $[M]^{-}$ calc. mass: 899.65035; found: 899.64775, $[M]^{+}$ calc. mass: 716.26295; found: 716.26246.

FTIR (ATR) ν_{max} (cm^{-1}): 2943 (m), 2864 (m), 1749 (w), 1594 (w), 1564 (w), 1472 (s), 1440 (s), 1416 (m), 1384 (m), 1358 (m), 1318 (m), 1305 (s), 1284 (m), 1237 (m), 1201 (w), 1169 (m), 1234 (w), 1062 (w), 1017 (w), 999 (w), 965 (w), 916 (m), 872 (s), 808 (w), 776 (m), 763 (m), 732 (w), 715 (w), 682 (w), 647 (w), 612 (m)

$C_{95}H_{130}AlIrNO_5P$: calculated C-70.60%, H-8.11% N-0.87%; found C-70.17%, H-8.08% N-0.73%

$[\alpha]_D$ = -118.5° ($CDCl_3$, c = 0.2, 23 °C)

Melting point: 190 °C

(E)-N-(1-Phenylethyliden)aniline (11)

Aniline (5.5 mL, 60 mmol) and acetophenone (5.8 mL, 50 mmol) were dissolved in toluene (30 mL). Molecular sieves (20 g, 3 Å) were added and the suspension was stirred for 70 h at room temperature. After filtration over Celite, the solvent was removed *in vacuo*. The product was purified by bulb-to-bulb distillation (0.03 mbar, 130 °C). Yield: 6.2 g (64 %).

^{1}H NMR (400.18 MHz, $CDCl_3$, 300 K) δH (ppm): 2.27 (3H, s, $\underline{CH_3}$), 6.84 – 6.86 (2H, m, Ar-$\underline{H}$), 7.11 – 7.15 (1H, m, Ar-$\underline{H}$), 7.37 – 7.41 (2H, m, Ar-$\underline{H}$), 7.46 – 7.52 (3H, m, Ar-$\underline{H}$), 8.01 – 8.03 (2H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33, MHz, $CDCl_3$, 300 K) δH (ppm): 17.4, 119.5, 123.3, 127.2, 128.4, 129.0, 130.5, 139.5, 151.8, 165.5.

The spectroscopic data is consistent with the literature.[30c]

(R)-*N*-(1-Phenylethyl)aniline (12)

A mixture of complex **9** or **10** (0.0025 mmol, 1 mol %) and substrate 13 (0.25 mmol) were dissolved in dichloromethane under argon atmosphere in a flask. The reaction mixture was pressurised with hydrogen (1 bar). The reaction mixture was stirred at room temperature for 24 h. The conversion of the reaction was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography over silica gel (hexanes / ethyl acetate 100:1). Enantiomer ratios were analyzed with HPLC using a Chiralcel column.

^{1}H NMR (600.24 MHz, $CDCl_3$, 300 K) δH (ppm): 1.52 (3H, d, $^{3}J_{HH}$ = 6.7 Hz, $\underline{CH_3}$), 4.48 (1H, q, $^{3}J_{HH}$ = 6.7 Hz, $\underline{CH}$),), 6.51 (2H, d, $^{3}J_{HH}$ = 7.7 Hz, Ar-$\underline{H}$), 6.64 (1H, d, $^{3}J_{HH}$ = 7.3 Hz, Ar-$\underline{H}$), 7.08 – 7.10 (2H, m, Ar-$\underline{H}$), 7.22 – 7.24 (1H, m, Ar-$\underline{H}$), 7.31 – 7.33 (2H, m, Ar-$\underline{H}$), 7.37 – 7.38 (2H, m, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33, MHz, $CDCl_3$, 300 K) δH (ppm): 25.2, 53.55, 113.3, 117.3, 125.9, 127.0, 128.8, 129.2, 145.3, 147.4.

77% *ee*, $[\alpha]_D$ = -3.9 (c = 1.00, $CHCl_3$), HPLC separation conditions: Chiralcel OD-H III, 210 nm, 90:10 hexane / iPrOH; 0.5 mL min^{-1}, t_R = 13.2 and 15.1 min.

The spectroscopic data is consistent with the literature.[30c]

(E)-2-Methyl-1-phenylpent-1-en-3-one (13)

3-Pentanone (4.3 g, 50 mmol) and benzaldehyde (5.3 g, 50 mmol), and 15 mL concentrated HCl were added to a 50 mL flask. The mixture was heated under reflux conditions for 4 h.

After cooling to room temperature, ether (100 mL) was added and the water layer was extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with water (2 × 30 mL) and aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 9:1, Rf = 0.39) to yield **13** as a colourless solid.

^{1}H NMR (400.18 MHz, d_6-acetone 300 K) δH (ppm): 1.17 (3H, t, $^3J_{HH}$ = 7.2 Hz, $CH_2C\underline{H}_3$), 2.06 (3H, d, $^4J_{HH}$ = 1.2 Hz, PhHC=CR-$\underline{CH}_3$), 2.84 (2H, q, $^3J_{HH}$ = 7.2 Hz, $C\underline{H}_2CH_3$), 7.30 – 7.38 (1H, m, Ar-$\underline{H}$), 7.39 – 7.45 (4H, m, Ar-$\underline{H}$), 7.52 (1H, d, $^4J_{HH}$ = 1.2 Hz, Ph$\underline{H}$C=CR-CH_3).

The spectroscopic data is consistent with the literature.[31a]

(S)-2-Methyl-1-phenylpentan-3-one (14)

A mixture of complex **9** or **10** (0.0025 mmol, 1 mol %) and substrate **13** (0.25 mmol) was dissolved in dichloromethane under an argon atmosphere. The reaction mixture was pressurised with hydrogen (1 bar). The reaction mixture was stirred at room temperature for 24 h. The conversion of the reaction was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 9:1, Rf = 0.39) Enantiomer ratios were analyzed with HPLC using a Chiralcel column.

^{1}H NMR (600.24 MHz, $CDCl_3$, 300 K) δH (ppm): 0.97 (3H, t, $^3J_{HH}$ = 7.3 Hz, $CH_2\underline{CH}_3$), 1.08 (3H, d, $^3J_{HH}$ = 7.0 Hz, $CH\underline{CH}_3$), 2.26 (1H, dq, $^2J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 7.3 Hz, $C\underline{H}CH_3$), 2.44 (1H, dq, $^2J_{HH}$ =17.9 Hz, $^3J_{HH}$ = 7.3 Hz), 2.57 (1H, dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.4 Hz), 2.83 – 2.90 (1H, m), 2.97 (1H, dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.3 Hz), 7.14 (2H, d, $^3J_{HH}$ = 7.2 Hz, Ar-$\underline{H}$); 7.19 (1H, t, $^3J_{HH}$ = 7.4 Hz, Ar-$\underline{H}$), 7.27 (2H, t, $^3J_{HH}$ = 7.4 Hz, Ar-$\underline{H}$).

^{13}C{^{1}H} NMR (150.33, MHz, $CDCl_3$, 300 K) δH (ppm): 7.7, 16.8, 35.3, 39.4, 48.0, 126.3, 128.5, 129.0, 139.9, 215.1.

99% *ee*, [α]D_{23} = +70.5 (c = 1.1, $CHCl_3$); HPLC separation conditions: Chiralcel OJ-H 2, 210 nm, 99:1 hexane / iPrOH; 0.5 mL min^{-1}, t_R = 17.4 and 19.4 min.

The spectroscopic data is consistent with the literature.[31a]

2 Hydrolysis studies

2.1) Aletbate anion

A homogenous solution of 13.2 mg (0.01 mmol) tetrabutylammonium aletbate **8a** in d_4-methanol showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 12.4 mg (0.01 mmol) tetraphenylphosphonium aletbate **7a** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 15.4 mg (0.01 mmol) tetraphenylphosphonium aletbate **7a** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 15 µL (0.11 mmol) triethylamine showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 12.5 mg (0.01 mmol) tetraphenylphosphonium aletbate **7a** in a mixture of d_8-tetrahydrofuran and D_2O (0.58 : 0.12 mL) with 0.05 mL (0.11 mmol) 1 M NaOH showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 12.4 mg (0.01 mmol) tetraphenylphosphonium aletbate **7a** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 30 mg (0.50 mmol) acetic acid indicated about 1.6 % decomposition of the aluminate after 7 d at room temperature in the ^{1}H NMR spectra.

A homogenous solution of 12.4 mg (0.01 mmol) tetraphenylphosphonium aletbate **7a** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 0.01 mL (0.11 mmol) trifluoroacetic acid indicated a decomposition of the aluminate of 6 % after 1 h, 44 % after 19 h and 90 % after 67 h at room temperature in the ^{1}H NMR spectra.

2.2) Aletpate anion

A homogenous solution of 20.1 mg (0.01 mmol) tetrabutylammonium aletpate **8b** in d_4-methanol showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 18.0 mg (0.01 mmol) tetraphenylphosphonium aletpate **7b** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 21.0 mg (0.01 mmol) tetraphenylphosphonium aletpate **7b** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 16 µL (0.11 mmol) triethylamine showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 22.0 mg (0.01 mmol) tetraphenylphosphonium aletpate **7b** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 0.05 mL (0.11 mmol) 1 M NaOH showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 22.4 mg (0.01 mmol) tetraphenylphosphonium aletpate **7b** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 9.4 mg (0.16 mmol) acetic acid indicated about 3% decomposition of the aluminate after 7 d at room temperature in the ^{1}H NMR spectra.

A homogenous solution of 22.4 mg (0.01 mmol) tetraphenylphosphonium aletpate **7b** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 10.7 µL (0.11 mmol) trifluoroacetic acid indicated a decomposition of the aluminate of 10 % after 3 h, 38 % after 7 h and 84 % after 24 h at room temperature in the ^{1}H NMR spectra.

2.3) Alphetbate anion

A homogenous solution of 16.2 mg (0.01 mmol) tetrabutylammonium aletbate **8c** in d_4-methanol showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 17.5 mg (0.01 mmol) tetraphenylphosphonium alphetbate **7c** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 17.5 mg (0.01 mmol) tetraphenylphosphonium alphetbate **7c** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 16 µL (0.11 mmol) triethylamine

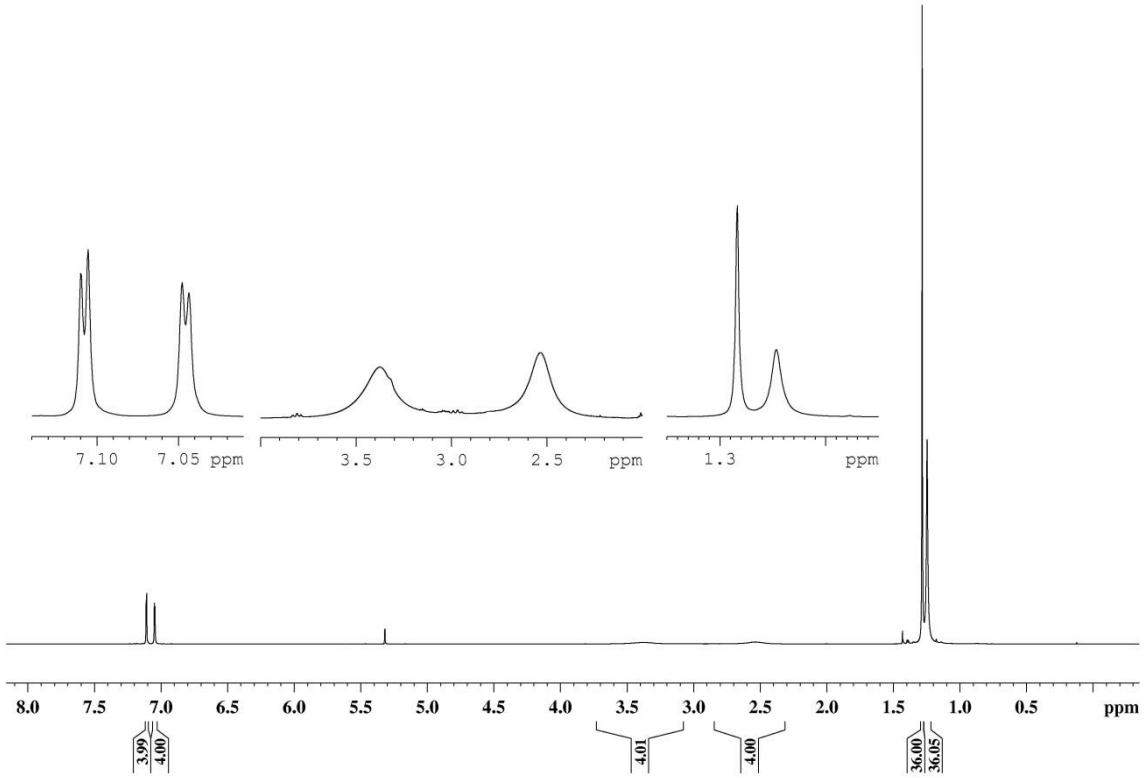
showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

A homogenous solution of 21.0 mg (0.01 mmol) tetraphenylphosphonium alphetbate **7c** in a mixture of d_8-tetrahydrofuran and D_2O (0.48 : 0.12 mL) with 0.05 mL (0.11 mmol) 1 M NaOH showed no products of aluminate hydrolysis after 7 d at room temperature as detected by ^{1}H NMR spectroscopy.

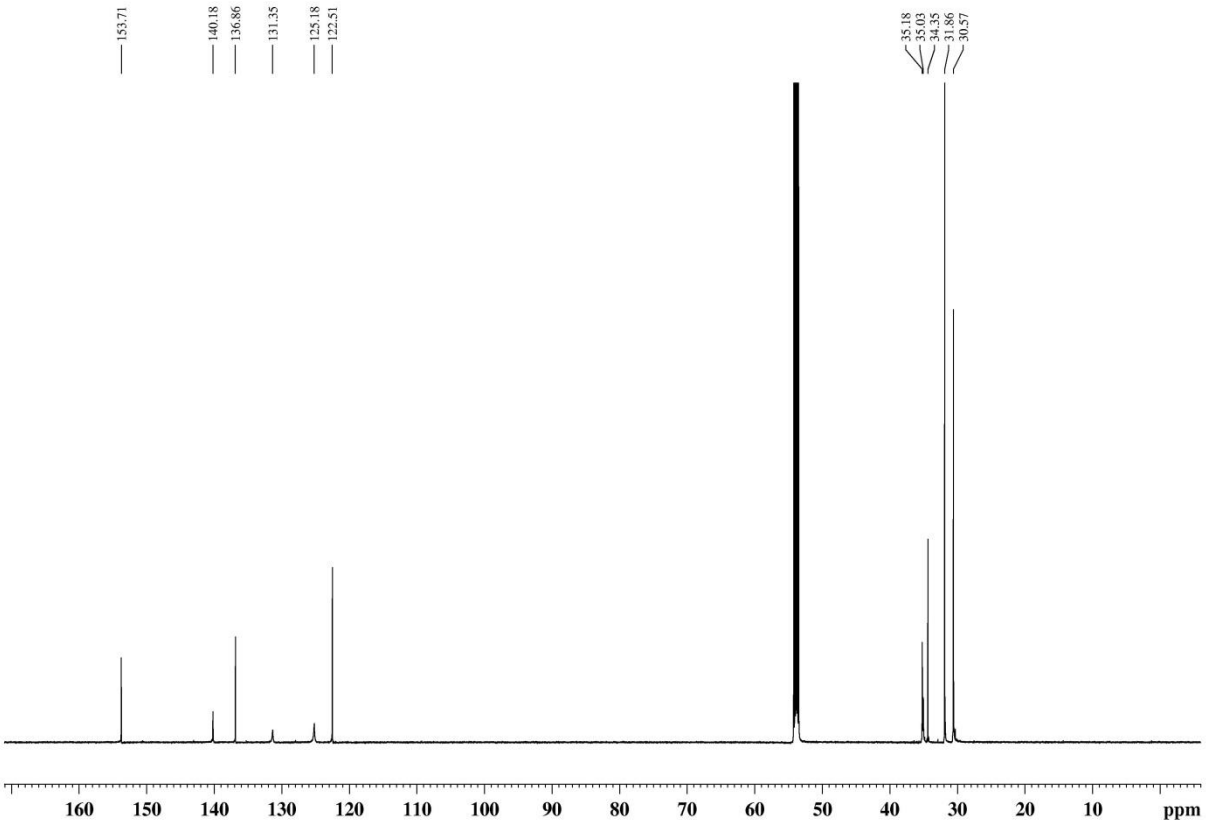
A homogenous solution of 12.4 mg (0.01 mmol) tetraphenylphosphonium alphetbate **7c** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 7 mg (0.11 mmol) acetic acid indicated about 30 % decomposition of the aluminate after 6 d at room temperature in the ^{1}H NMR spectra.

A homogenous solution of 24.3 mg (0.01 mmol) tetraphenylphosphonium alphetbate **7c** in a mixture of d_8-tetrahydrofuran and D_2O (0.4 : 0.1 mL) with 0.01 mL (0.11 mmol) trifluoroacetic acid indicated a decomposition of the aluminate of 31 % after 1 h, 49 % after 3 h and 100 % after 16 h at room temperature in the ^{1}H NMR spectra.

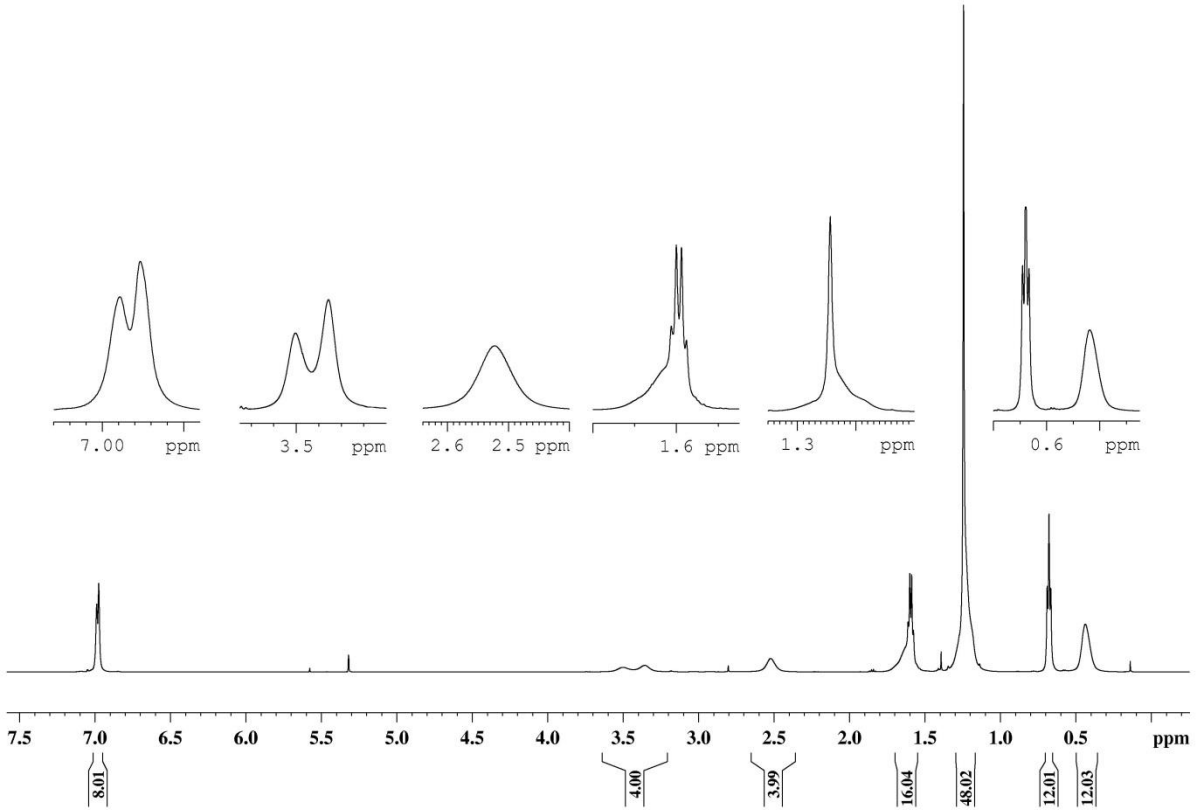
3 NMR Spectra



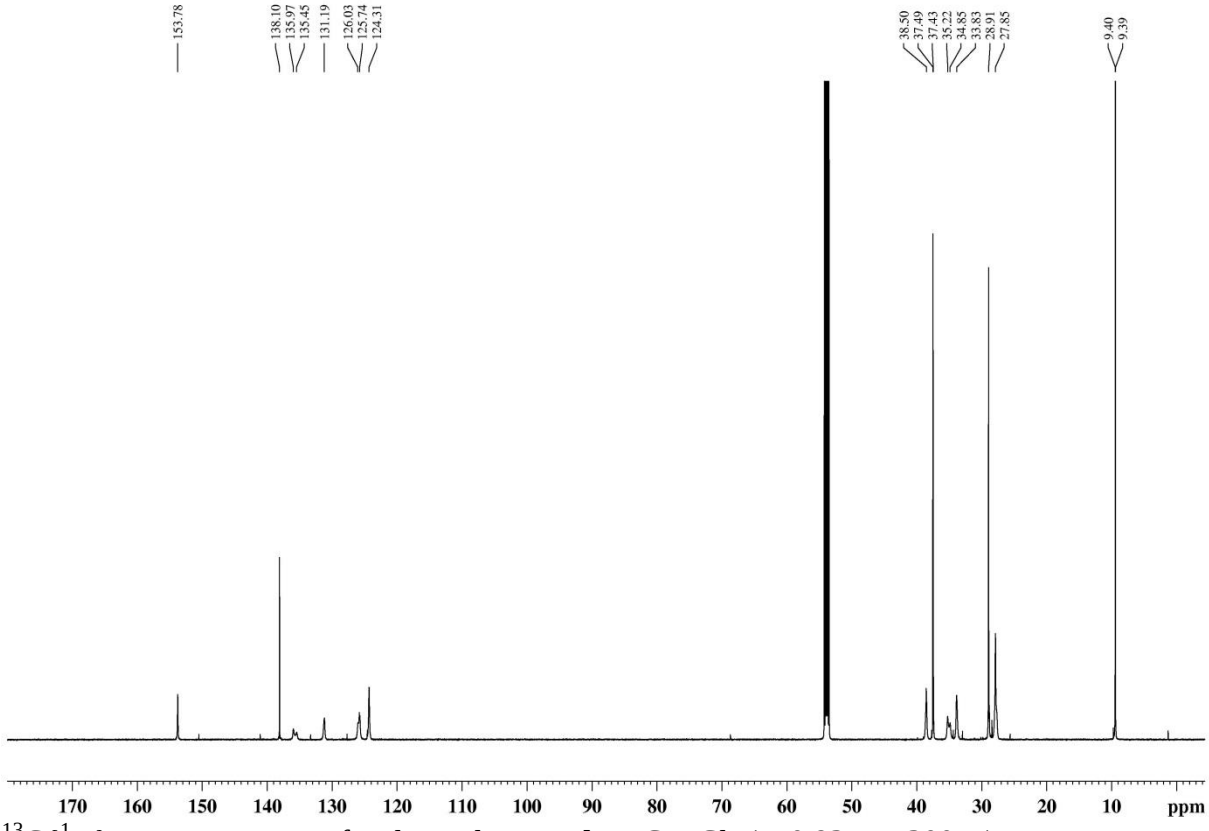
^{1}H NMR spectrum of sodium aletbate **5a** in CD_2Cl_2 (600.24 Hz, 300 K)



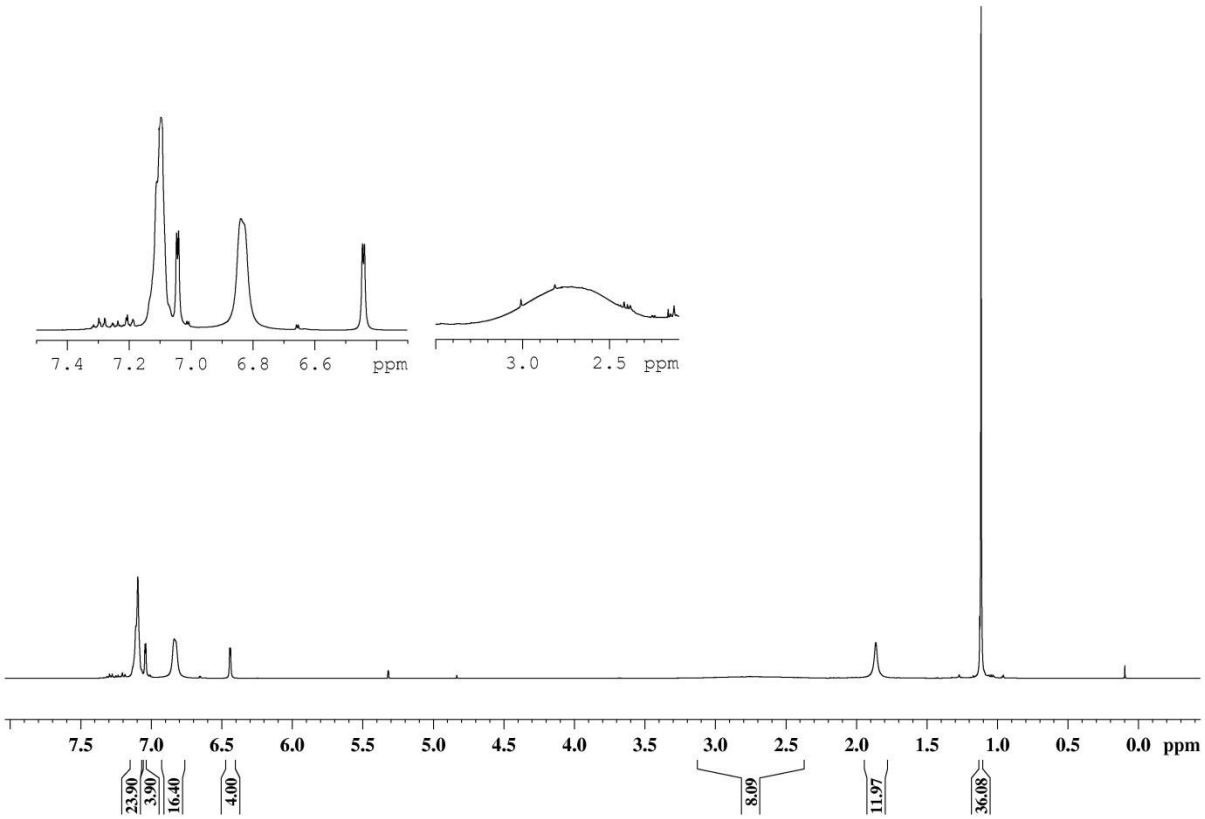
^{13}C{^{1}H} NMR spectrum of sodium aletbate **5a** in CD_2Cl_2 (150.33 Hz, 300 K)



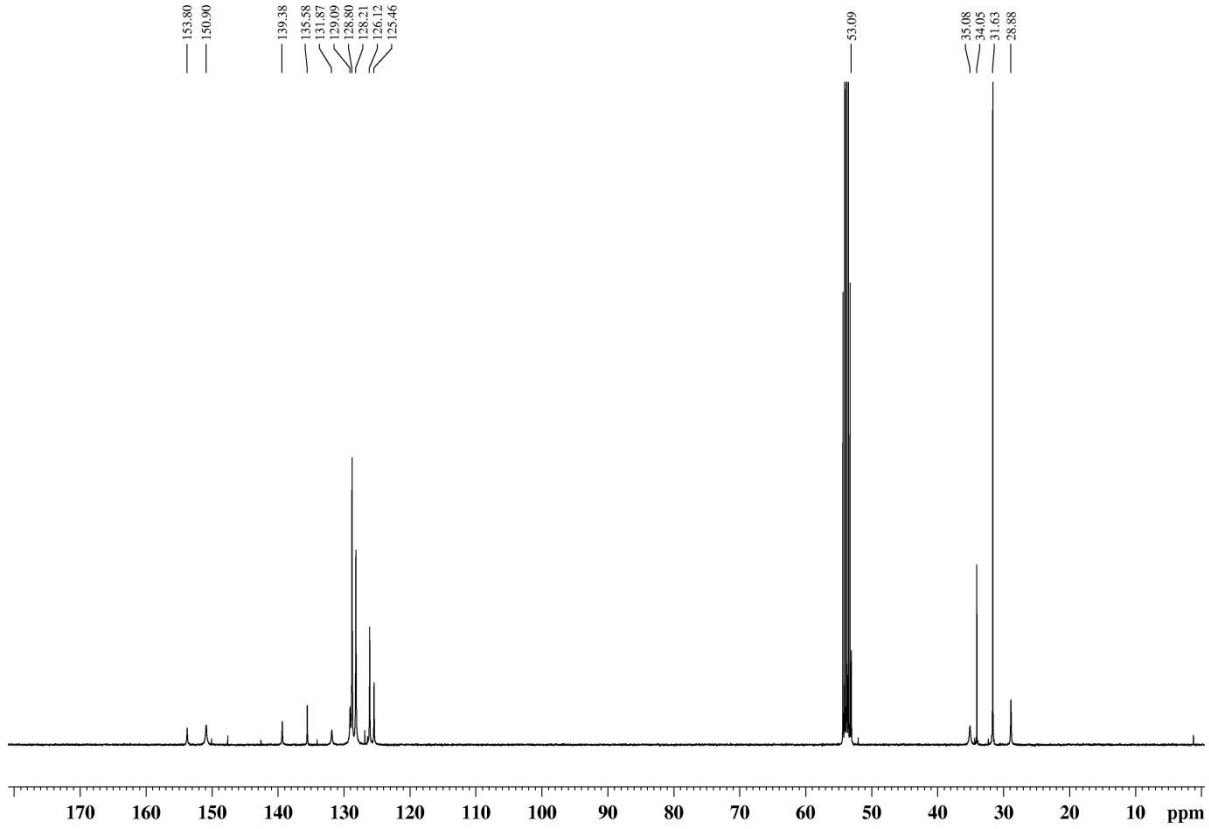
^{1}H NMR spectrum of sodium aletpate **5b** in CD_2Cl_2 (600.24 Hz, 300 K)



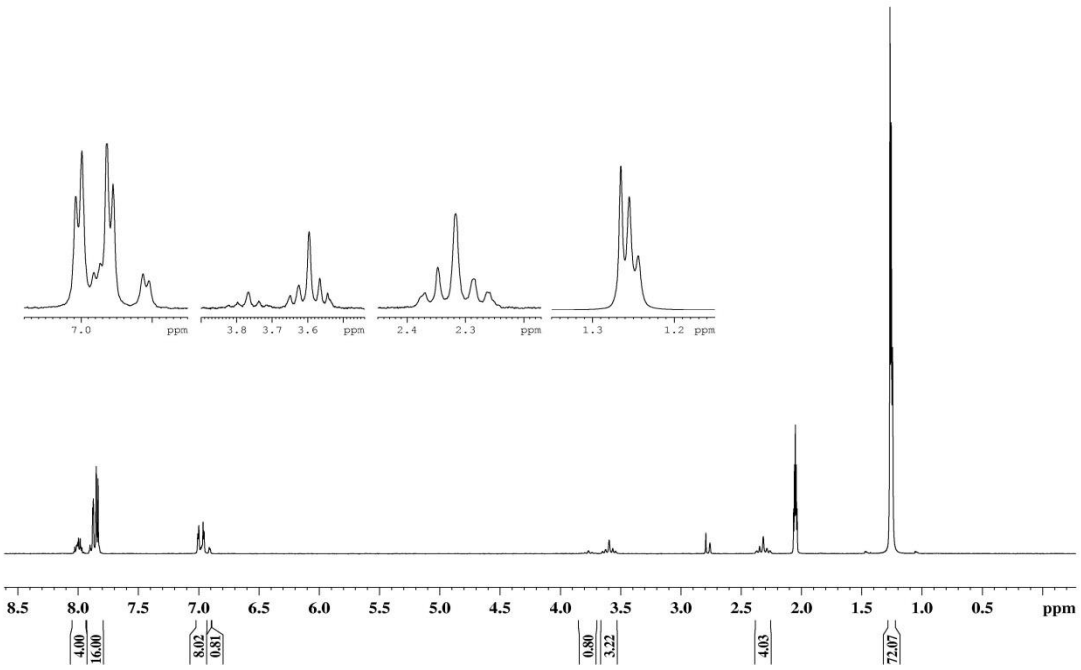
^{13}C{^{1}H} NMR spectrum of sodium aletpate **5b** in CD_2Cl_2 (150.93 Hz, 300 K)



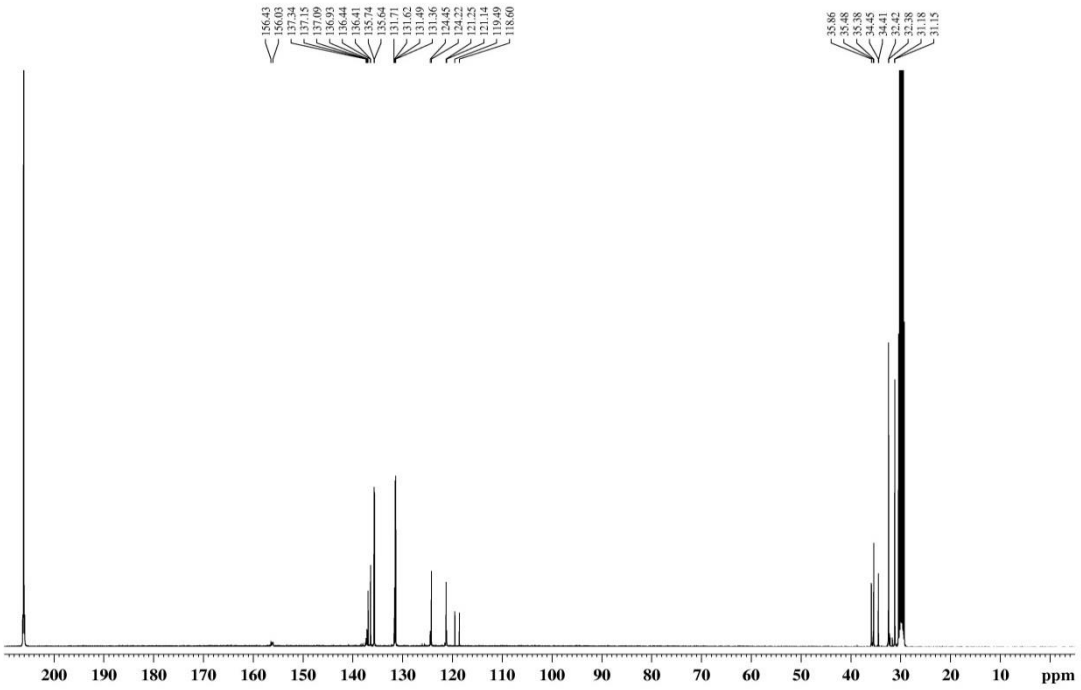
^{1}H NMR spectrum of sodium alphetbate **5c** in CD_2Cl_2 (400.33 Hz, 300 K)



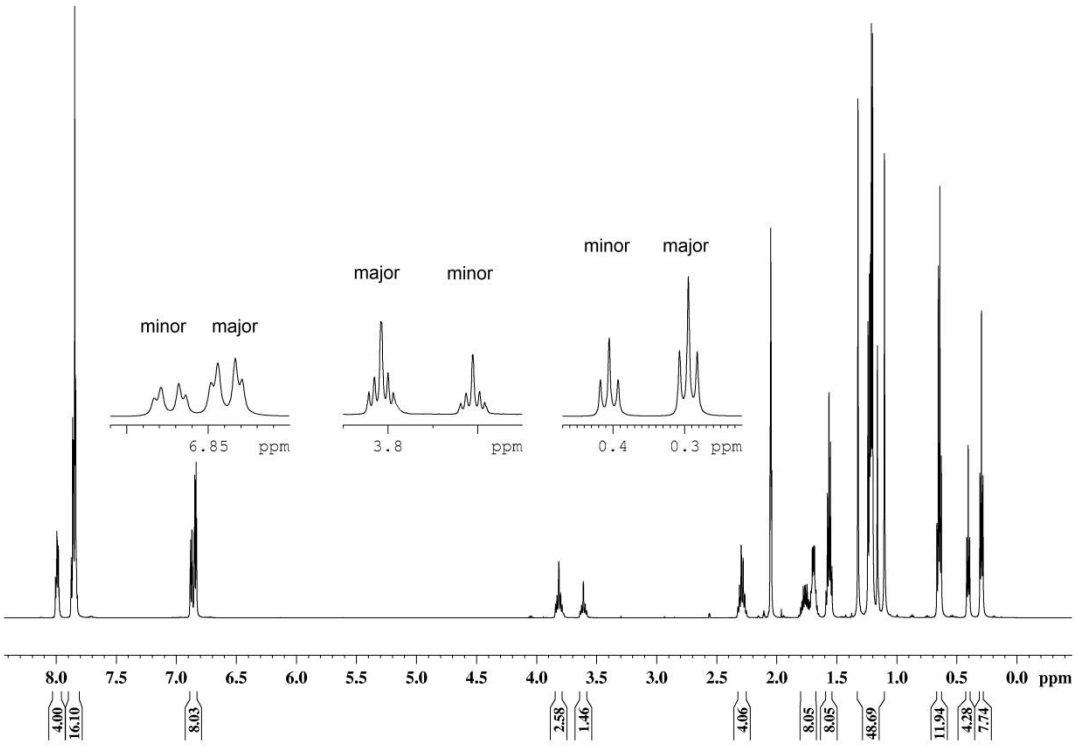
^{13}C{^{1}H} NMR spectrum of sodium alphetbate **5c** in CD_2Cl_2 (100.66 Hz, 300 K)



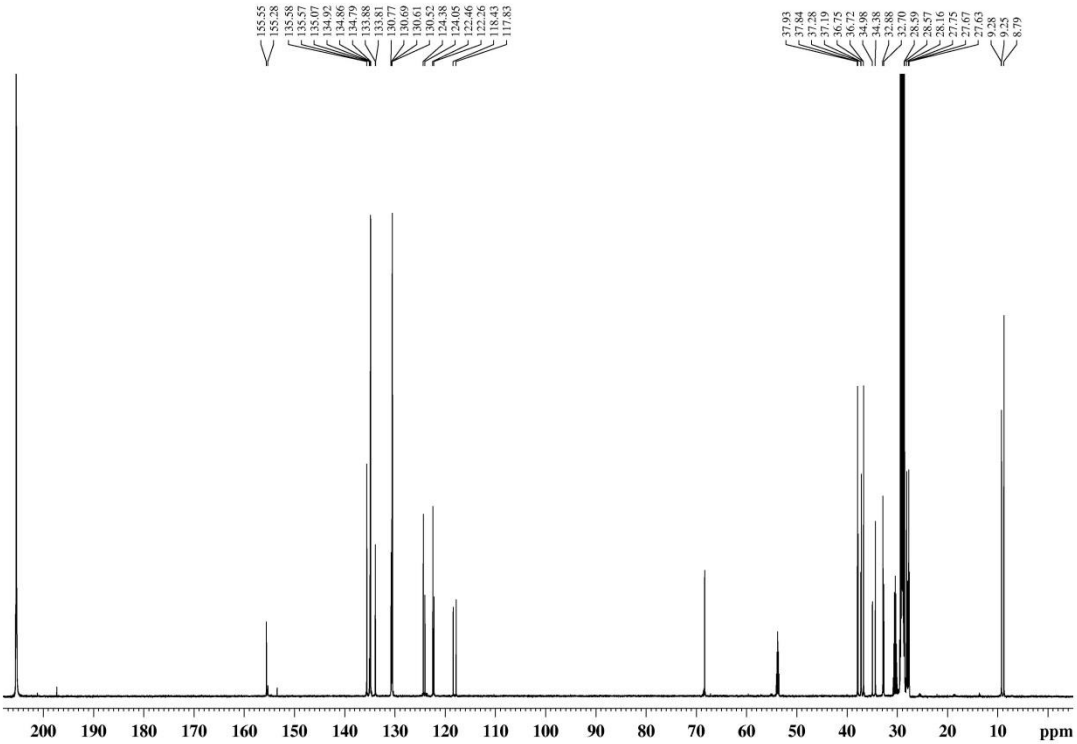
^{1}H NMR spectrum of PPh_4 aletbate **6a** in d_6-acetone (300.51 Hz, 300 K)



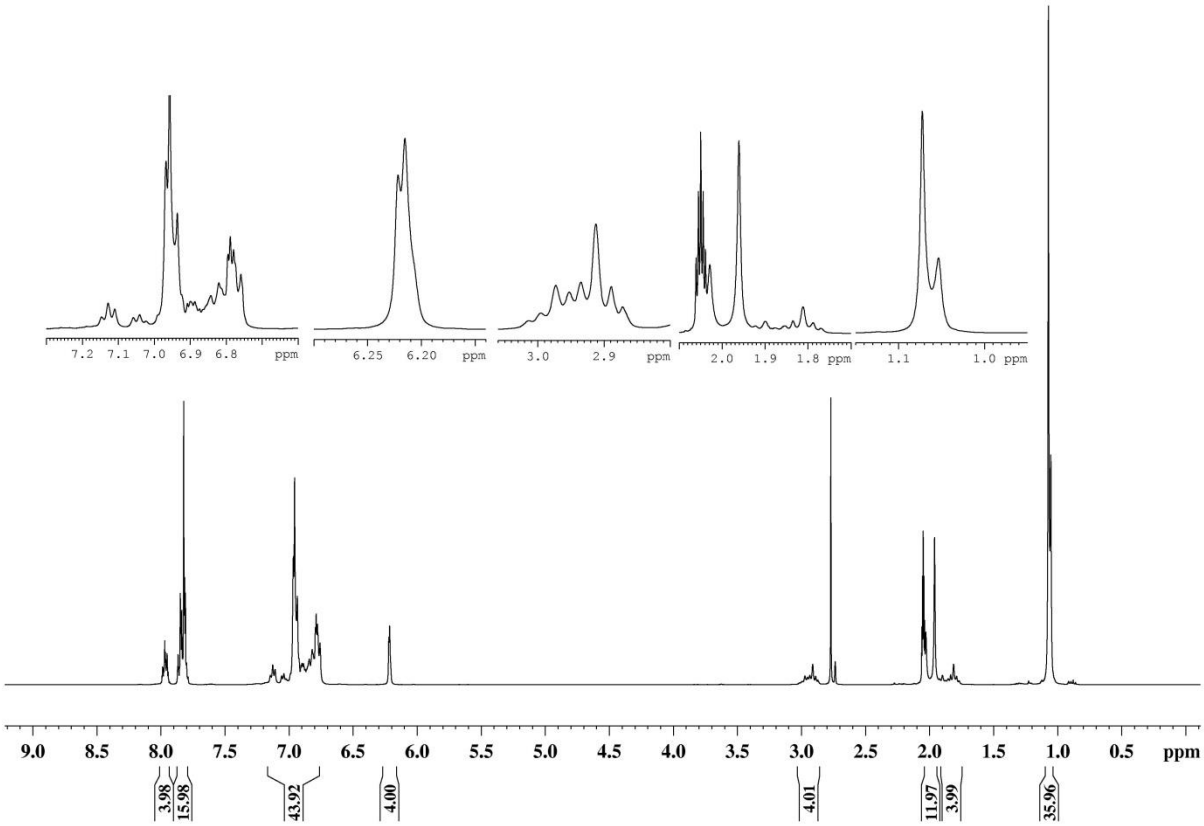
$^{13}C\{^{1}H\}$ NMR spectrum of PPh_4 aletbate **6a** in d_6-acetone (150.33 Hz, 300 K)



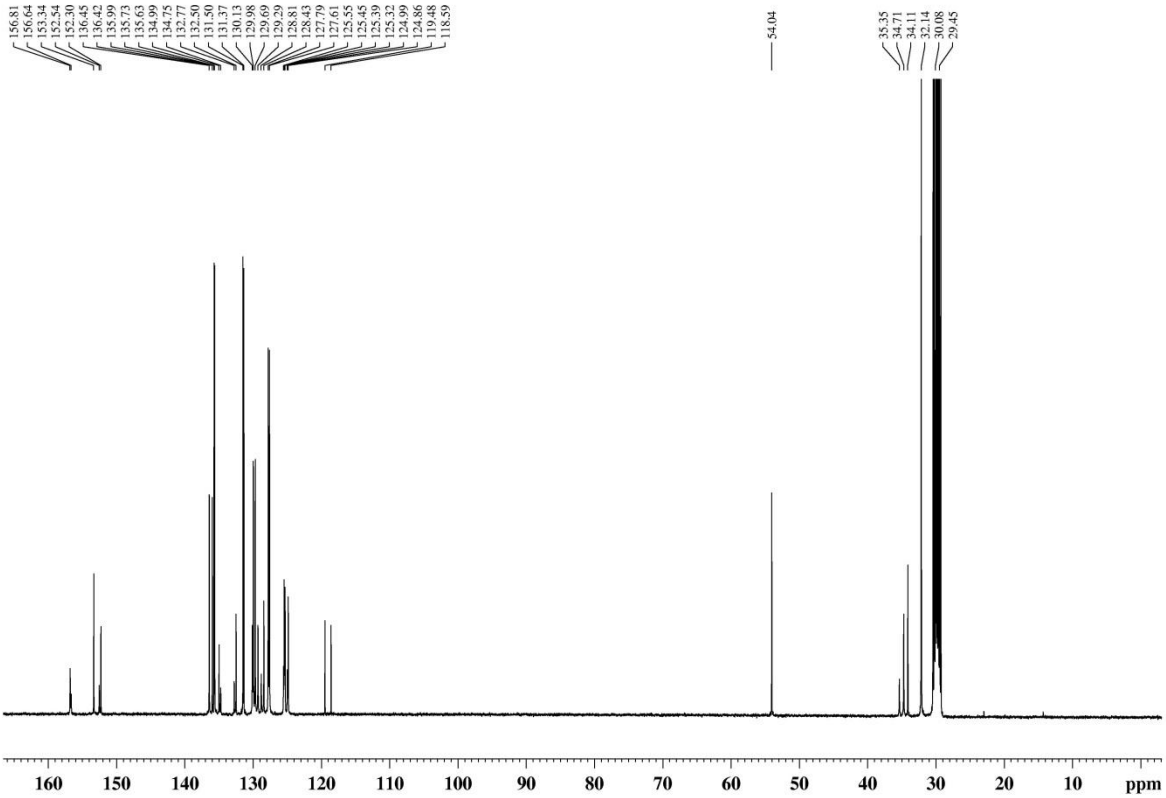
^{1}H NMR spectrum of PPh_4 aletpate **6b** in d_6-acetone (600.24 Hz, 300 K)



^{13}C{^{1}H} NMR spectrum of PPh_4 aletpate **6b** in d_6-acetone (150.33 Hz, 300 K)



^{1}H NMR spectrum of PPh_4 alphetbate **6c** in d_6-acetone (400.18 Hz, 300 K)



^{13}C{^{1}H} NMR spectrum of PPh_4 alphetbate **6c** in d_6-acetone (100.62 Hz, 300 K)