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Dedicated to Professor Valer Farcasan on the occasion of his 95th anniversary

SYNTHESIS AND CHARACTERIZATION OF 2-[Mes(Me)NCH$_2$]C$_6$H$_4$Br AND 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br – PRECURSORS FOR NOVEL ONE PENDANT ARM LIGANDS

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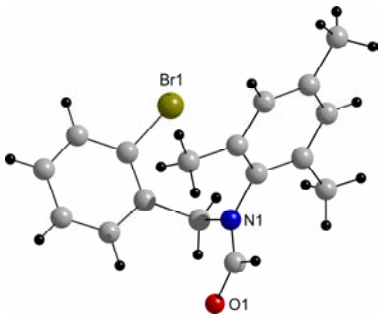
A new secondary amine 2-(MesNHCH$_2$)C$_6$H$_4$Br (**2**) was synthesized starting from imine 2-(MesN=CH)C$_6$H$_4$Br (**1**) and NaBH$_4$. Reaction of **2** with paraformaldehyde and HC(O)OH gave almost quantitatively 2-[Mes(Me)NCH$_2$]C$_6$H$_4$Br (**3**), while treatment of **2** with paraformaldehyde and CH$_3$C(O)OH resulted in **3** as a major product besides a minor amount of the unexpected 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br (**4**) compound. The compounds were characterized by multinuclear NMR and IR spectroscopy, mass spectrometry and the molecular structure of **4** was established by single-crystal X-ray diffraction.



INTRODUCTION

The chemistry of organometallic compounds based on aromatic ligands bearing one or two substituents which contain donor atoms able to provide intramolecular E→M interactions (E = lighter pnicogens – N, P or even As, and chalcogens – O, S) is a topic of high interest with respect to different fundamental as well as applicative aspects.[1,2] Relevant achievements were obtained in (*i*) stabilization of unusual organotin,[3-6] organoantimony and –bismuth,[7-13] or organotellurium[7,14] species; (*ii*) the use of main group metal and metalloid organometallic compounds as ligands for transition metals;[15-19] (*iii*) investigation of hypervalent organoselenium compounds, including their biological activity;[20-24] or (*iv*) the use of heavy organopnicogens (antimony, bismuth) in catalysis and CO_2 fixation.[9,25-28] Most common used are the amine ligands 2-(Me$_2$NCH$_2$)C$_6$H$_4$, 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$ or RN(CH$_2$C$_6$H$_4$)$_2$, and more recently the imine ligands 2-(RN=CH)C$_6$H$_4$ or 2,6-(RN=CH)$_2$C$_6$H$_3$. In a few cases were used ligands with different groups attached to nitrogen atom of the pendant arm, *e.g.* 2-[(*cyclo*-C$_6$H$_{11}$)MeNCH$_2$]C$_6$H$_4$,[20,29] 2-(^{t}BuNHCH$_2$)C$_6$H$_4$,[30] 2-[Me$_2$NCH$_2$CH$_2$(Me)NCH$_2$]C$_6$H$_4$,[31] or 2,6-[^{t}Bu(Me)NCH$_2$]$_2$C$_6$H$_3$.[32]

In order to increase the protection of the metal centre we decided to prepare new proligands with a mesityl group attached to nitrogen of the pendant arm. We report here on the synthesis and the

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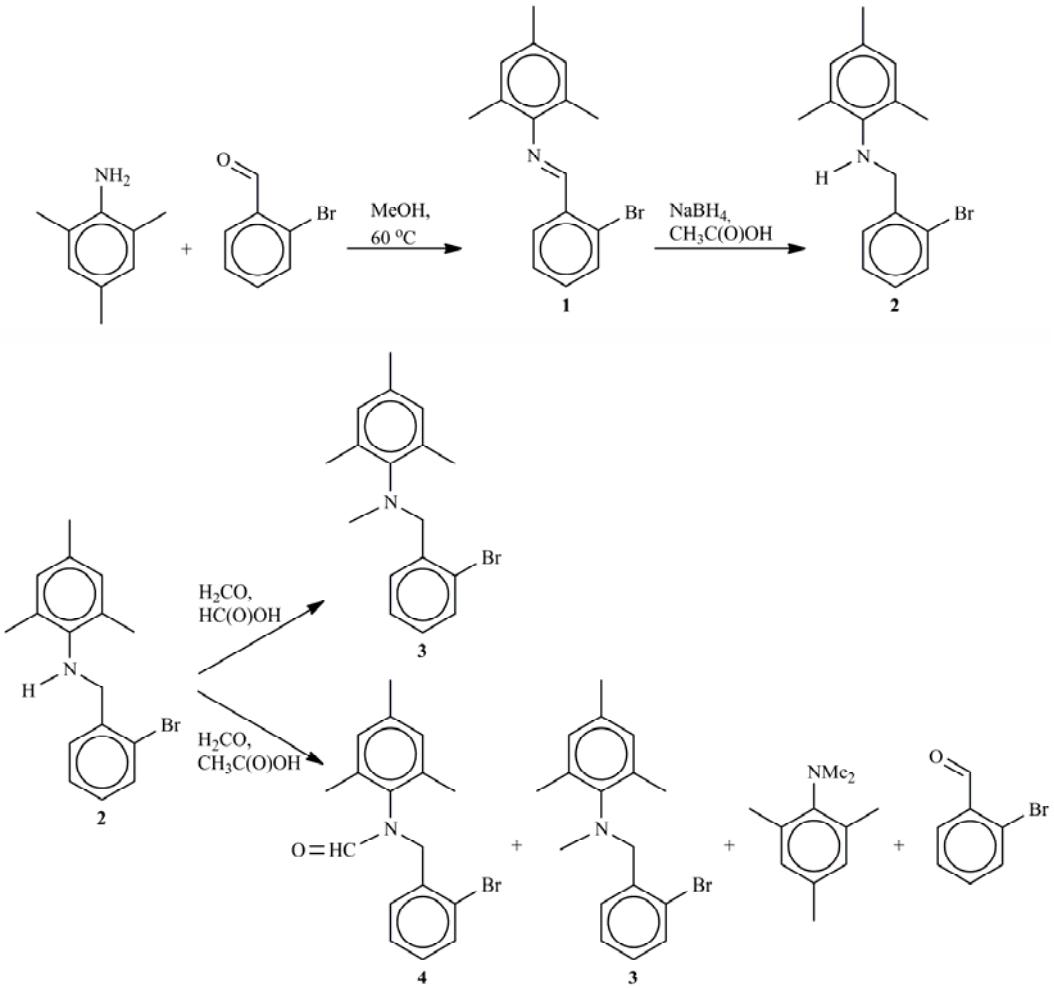
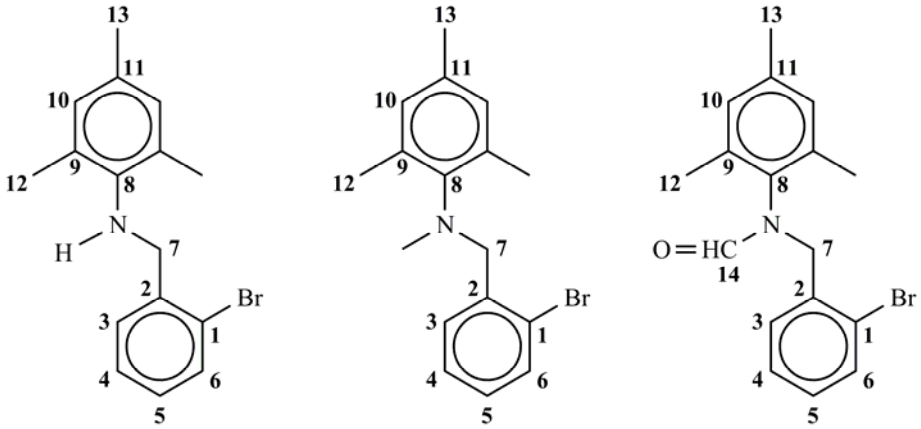
spectroscopic characterization of the amines 2-(MesNHCH$_2$)C$_6$H$_4$Br (**2**) and 2-[Mes(Me)NCH$_2$] C$_6$H$_4$Br (**3**). The unexpected amide derivative 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br (**4**), which might be used as starting material for a new type of one pendant arm ligand through condensation with primary amines, was also isolated and characterized. The crystal and molecular structure of **4** was established by single-crystal X-ray diffraction.

RESULTS

The imine 2-(MesN=CH)C$_6$H$_4$Br (**1**) was obtained using a slightly modified literature method,[9] *i.e.* the solvent was changed from toluene to methanol and the reaction mixture was refluxed for 3 h. After removal of the solvent the identity of the crude product was checked by NMR spectroscopy and then it was used without further purification. The reduction of the N=C bond in **1** to give the secondary amine 2-(MesNHCH$_2$)C$_6$H$_4$Br (**2**) was achieved by treating a solution of the imine in acetic acid with NaBH$_4$. The reaction should be carried out with caution due to exothermic effect. Further treatment of a solution of **2** in HC(O)OH with paraformaldehyde afforded the tertiary amine 2-[Mes(Me)NCH$_2$]C$_6$H$_4$Br (**3**) (Scheme 1). Both compounds **2** and **3** were isolated in very good yields as yellow oils, soluble in organic solvents. The use of acetic acid as a reaction solvent instead of the formic acid gave a brown oil, soluble in diethyl ether. When stored in the refrigerator the Et$_2$O solution deposited a few yellow crystals of the unexpected amide 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br (**4**) species (Scheme 1). However, the analysis of the ^{1}H NMR spectrum of the crude brown oil suggests that the major product formed is the tertiary amine **3** and, besides the amide **4**, two other compounds were identified as side-products in the mixture, *i.e.* MesNMe$_2$ and 2-(O=CH)C$_6$H$_4$Br.



Scheme 1 – Reaction scheme for the preparation of compounds **2**, **3** and **4**.



Scheme 2 – Numbering schemes for NMR assignments.

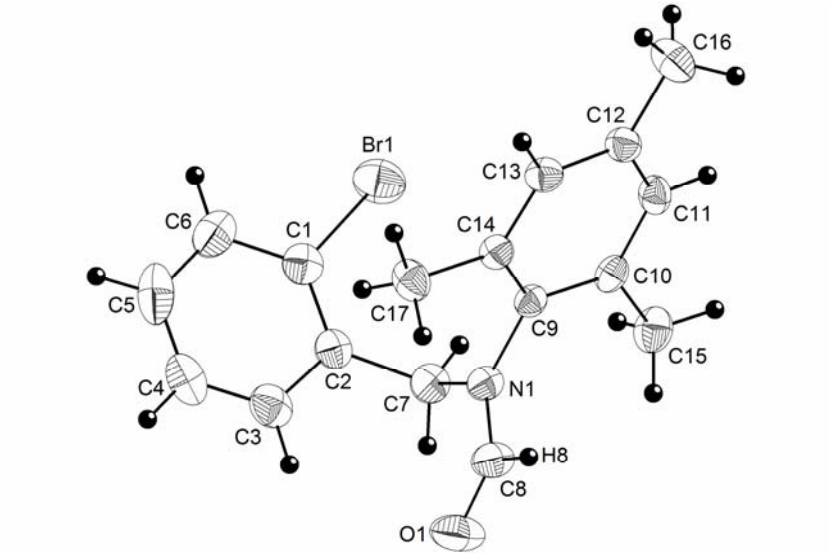


Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for 2-[Mes{(O)CH}NCH_2]C_6H_4Br (*E*-**4** isomer). Selected distances (Å) and angles (deg): Br(1)–C(1) 1.906(4), O(1)–C(8) 1.209(4), N(1)–C(7) 1.466(4), N(1)–C(8) 1.335(4), N(1)–C(9) 1.439(4); C(7)–N(1)–C(8) 119.8(3), C(7)–N(1)–C(9) 120.5(2), C(8)–N(1)–C(9) 119.7(2), Br(1)–C(1)–C(2) 121.0(3), Br(1)–C(1)–C(6) 116.7(3).

The conversion of the secondary amine **2** into the tertiary amine **3** or the amide **4** is reflected in IR spectra: the weak υ(NH) vibration at 3370 cm^{-1} observed for **2** is not present in the spectrum of **3**, while for compound **4** a new, very strong band at 1667 cm^{-1} was observed for υ(CO) vibration.

The compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy in solution. The assignment of the observed resonances was made using 2D experiments according to the numbering scheme shown in Scheme 2. The NMR spectra were recorded in $CDCl_3$ and acetone-d_6 and are consistent with the structure of the title compounds.

The ^{1}H and ^{13}C NMR spectra for compounds **2** and **3** showed the expected resonances in the aliphatic and the aromatic regions. For compound **4** the ^{1}H and ^{13}C NMR spectra exhibit two sets of resonance signals suggesting the presence of two isomers [designated as isomer **4a** (major product) and isomer **4b** (minor product)] in solution (see subsequent discussion).

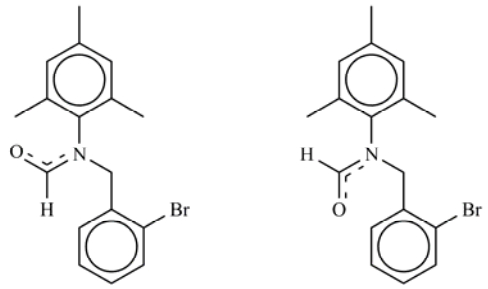
Single crystals of **4** were obtained from petroleum ether at 0 °C and the crystal and molecular structure was established by X-ray diffraction studies. The crystal contains discrete molecules, with no unusual intermolecular interactions. The ORTEP-like view of the

molecular structure, with the atom numbering scheme and selected bond distances and angles, is shown Fig. 1.

DISCUSSION

Solution behavior

For both amines **2** and **3** the NMR spectra exhibit only one set of resonances, which is consistent with one species present in solution. The main difference in the ^{1}H NMR spectra of these compounds resides in the replacement of the broad resonance observed for the hydrogen attached to nitrogen in **2** (δ 3.22 ppm) by a sharp signal for the protons of the methyl group bound to nitrogen in **3** (δ 2.80 ppm).



Z-**4** isomer *E*-**4** isomer

Scheme 3 – Structures of geometric isomers of **4**.

The two sets of ^{1}H and ^{13}C resonances observed in the spectra of the amide **4** suggest the presence of two species in solution. These two species are the geometric isomers *Z*-**4** and *E*-**4** due to the delocalization of the electrons over the OCN system (Scheme 3). This behavior is consistent with the planar NC_3 core observed in solid state structure of **4** (*vide infra*). The two isomers were not separated and using the available NMR data, a definitive assignment of the resonances to a particular isomer was not possible; therefore, in the Experimental part they are designated as isomer **4a** (major product) and isomer **4b** (minor product). The molar ratio between the isomers **4a** and **4b** from samples isolated from different synthetic experiments is practically constant, as established from the integrals of the corresponding ^{1}H resonances obtained from spectra recorded in the same solvent. However, exchange of the solvent resulted in different **4a** / **4b** isomer ratio: 2.1 / 1 in acetone-d_6, 3.3 / 1 in $CDCl_3$, or 4.6 / 1 in C_6D_6. A variable temperature experiment has shown that the molar ratio between the two isomers of **4** is not affected significantly when the ^{1}H NMR spectrum was recorded at 70 °C for a solution in C_6D_6.

Solid state structure

The single-crystal of compound **4** analyzed by X-ray diffraction contains only discrete molecules of the *E*-**4** isomer (Fig. 1), with no intermolecular interactions based on contacts which involve the hydrogen atoms. A delocalization of the electrons over the OCN fragment (amidic ↔ imidic system) resulted in a planar $O(H)CNC_2$ core [deviations from best plane: O(1): –0.007; H(8): 0.006; C(8): 0.001; N(1): 0.003; C(7): 0.003; C(9): –0.006 Å] with all bond angles at the nitrogen atom close to 120°. This electron delocalization is also supported by the magnitude of the bonds at the nitrogen atom. The bond which involves the carbon of the formyl unit [N(1)–C(8) 1.335(4) Å] is considerably shorter (and consequently suggesting increased double bond character) than the other two bonds to aliphatic [N(1)–C(7) 1.466(4) Å] or aromatic [N(1)–C(9) 1.439(4)] carbons. The result is a restriction of free rotation about the carbon-nitrogen bond and the isolation of this amide as a *E*-**4** isomer. The dihedral angle C(2)–C(7)–N(1)–C(9) is 83.7° and this allows a weak intermolecular C–H···π ($Ar_{centroid}$) interaction (*i.e.* H···$Ar_{centroid}$ contact shorter than 3.1 Å, with an angle γ between the normal to the phenyl ring and the line defined by the H atom and $Ph_{centroid}$ smaller than 30º)[33] between a methyl proton of the mesityl group and the other aryl system: C(17)–H(17B)···$Ar_{centroid}${C(1)-C(6)} 2.98 Å; γ = 2.7º.

EXPERIMENTAL

Solvents were distilled prior to use. Other starting materials such as 2,4,6-trimethylaniline, 2-(O=CH)C_6H_4Br, $NaBH_4$, HC(O)OH, $CH_3C(O)OH$ and paraformaldehyde were obtained from Aldrich or Merck and were used as received. ^{1}H and ^{13}C NMR spectra, including 2D experiments, were recorded at room temperature on Bruker Avance III 400 or Bruker Avance III 600 instruments. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent [$CHCl_3$, 7.26 ppm; $CD_3C(O)CD_2H$, 2.05 ppm]. The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent [$CDCl_3$, 77.16 ppm; $(CD_3)_2CO$, 29.84 ppm].[34] ^{1}H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC). The NMR spectra were processed using the *MestReC* and *MestReNova* software.[35] MS APCI(+) spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer. Data analysis and calculations of the theoretical isotopic

patterns were carried out with the Xcalibur software package.[36] Infrared spectra were recorded in the range 4000–250 cm^{-1} on a Bruker Vector 22 spectrometer.

Synthesis of N-[(2-bromophenyl)methyl]-2,4,6-trimethylaniline, 2-(MesNHCH$_2$)C$_6$H$_4$Br **(2)**

$NaBH_4$ (1.10 g, 29.10 mmol) was added in small portions to a solution of **1** (4.41 g, 14.59 mmol) in $CH_3C(O)OH$ (20 mL) at 5°C (warning: the reaction is exothermic!), under argon. The reaction mixture was allowed to reach room temperature and then 20 mL of methanol were added dropwise (caution: exothermic reaction as well!). Over the reaction mixture cold water was added and the mixture was extracted with CH_2Cl_2 (3x30 mL). The organic fractions were combined and washed with a solution of K_2CO_3 (5 g in 100 mL H_2O) and water (100 mL). After the removal of CH_2Cl_2, the title compound **2** was obtained as an yellow oil. Yield = 3.9 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (9H, s, br, C*H*$_3$), 3.22 (1H, s, br, -N*H*), 4.19 (2H, s, H-7), 6.86 (2H, s, H-10), 7.16 (1H, ddd, H-5, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.8 Hz), 7.28 (1H, ddd, H-4, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2 Hz), 7.41 (1H, dd, H-3, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.7 Hz), 7.59 (1H, dd, H-6, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.40 (s, *C*-12), 20.74 (s, *C*-13), 52.90 (s, *C*-7), 123.97 (s, *C*-1), 127.67 (s, *C*-4), 128.89 (s, *C*-5), 129.56 (s, *C*-10), 130.34 (s, *C*-3), 130.53 (s, *C*-9), 131.95 (s, *C*-11), 132.85 (s, *C*-6), 139.58 (s, *C*-2), 142.75 (s, *C*-8). IR (KBr pellet, cm^{-1}): υ 3370(w) (NH). MS (APCI+, MeOH): *m/z* (%) 302.05 (30) $[M–H]^+$, 222.12 (12) $[M–Br–3H]^+$, 135.1 (100) $[MesNH_2]^+$. HRMS (APCI+): Calc. for $[C_{16}H_{17}BrN]^+$ 302.05389. Found: 302.05432.

Synthesis of N-[(2-bromophenyl)methyl]-N,2,4,6-tetramethylaniline, 2-[Mes(Me)NCH$_2$]C$_6$H$_4$Br **(3)**

A solution of **2** (19.50 g, 64.10 mmol) in formic acid (38.36 g, 833.30 mmol) was heated to 70 °C on an oil bath. Paraformaldehyde (2.80 g, 93.32 mmol) was added in small portions and the temperature of the oil bath was raised to 95 °C. The reaction progress was monitored by TLC. A solution of K_2CO_3 (115.16 g, 833.30 mmol) in 200 mL distilled water was added to the reaction mixture cooled at room temperature. The product was extracted with CH_2Cl_2 (3x30 mL) and the combined organic fractions were further washed with distilled water (2x50 mL). Removal of CH_2Cl_2 afforded 18.91 g (93%) of **3** as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.30 (3H, s, H-13, C*H*$_3$), 2.39 (6H, s, H-12, C*H*$_3$), 2.80 (3H, s, NC*H*$_3$), 4.31 (2H, s, H-7), 6.89 (2H, s, H-10), 7.15 (1H, dd, H-5, $^3J_{HH}$ = 7.8 Hz), 7.35 (1H, dd, H-4, $^3J_{HH}$ = 7.5 Hz), 7.58 (1H, d, H-6, $^3J_{HH}$ = 7.9 Hz), 7.64 (1H, d, H-3, $^3J_{HH}$ = 7.7 Hz). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.69 (s, *C*-12), 20.84 (s, *C*-13), 40.34 (s, N*C*H$_3$), 60.05 (s, *C*-7), 124.18 (s, *C*-1), 127.32 (s, *C*-4), 128.18 (s, *C*-5), 129.86 (s, *C*-10), 130.16 (s, *C*-3), 132.76 (s, *C*-6), 134.79 (s, *C*-11), 137.04 (s, *C*-9), 139.61 (s, *C*-2), 147.31 (s, *C*-8). MS (APCI+, MeOH): *m/z* (%) 318.09 (100) $[M+H]^+$, 302.05 (20) $[M–Me]^+$. HRMS (APCI+): Calc. for $[C_{17}H_{21}BrN]^+$ 318.08519. Found: 318.08544.

Synthesis of N-[(2-bromophenyl)methyl]-N-(2,4,6-trimethylphenyl) formamide, 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br **(4)**

A solution of **2** (3.05 g, 10.02 mmol) in acetic acid (7.82 g, 130.26 mmol) was heated to 70 °C on an oil bath. Paraformaldehyde (0.44 g, 14.58 mmol) was added in small portions and the temperature of the mixture–was raised to 95 °C, the reaction being monitored by TLC. Then the reaction mixture was cooled at room temperature and a solution of K_2CO_3 (18 g, 130.26 mmol) in 50 mL distilled water was added. The product was extracted with CH_2Cl_2 (3x30 mL) and the combined organic fractions were further washed with distilled water (2x50 mL). The organic solution was dried on anhydrous Na_2SO_4, then filtered. The removal of the solvent afforded 2.96 g of brown oil. A few yellow crystals appeared in the oil when left at room temperature for some minutes. Diethyl ether was added until the oil and the crystals were completely dissolved and the solution was kept in the refrigerator for 2 h when yellow crystals formed. They were separated from the solution by filtration and dried *in vacuo* to obtain the title compound **4**. Yield = 0.35 g (11%). M.p. = 138-140 °C. ^{1}H NMR [600 MHz, $(CD_3)_2CO$]: δ 1.83 (6H, s, H-12b, C*H*$_3$), 1.92 (6H, s, H-12a, C*H*$_3$), 2.21 (3H, s, H-13b, C*H*$_3$), 2.25 (3H, s, H-13a, C*H*$_3$), 4.84 (2H, s, H-7b), 4.95 (2H, s, H-7a), 6.82 (2H, s, H-10b), 6.90 (2H, s, H-10a), 6.99 (1H, dd, H-3b, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.8 Hz), 7.21 (2H, m, H-4b + H-5a), 7.25 (1H, ddd, H-5b, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.9 Hz), 7.32 (1H, ddd, H-4a, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.3 Hz), 7.50 (1H, dd, H-6a, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.3 Hz), 7.55 (1H, dd, H-3a, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.7 Hz), 7.61 (1H, dd, H-6b, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.4 Hz), 8.00 [1H, s, H-14a, C*H*(O)], 8.70 [1H, s, H-14b, C*H*(O)]. ^{13}C NMR [151 MHz, $(CD_3)_2CO$]: δ 17.87 (s, *C*-12b), 18.01 (s, *C*-12a), 20.92 (s, *C*-13b), 20.93 (s, *C*-13a), 48.00 (s, *C*-7a), 53.35 (s, *C*-7b), 125.22 (s, *C*-1a), 125.90 (s, *C*-1b), 128.43 (s, *C*-4b), 128.61 (s, *C*-4a), 129.76 (s, *C*-10b), 130.14 (s, *C*-10a), 130.52 (s, *C*-5a), 130.96 (s, *C*-5b), 133.44 (s, *C*-6a), 133.63 (s, *C*-3b), 133.77 (s, *C*-6b), 133.93 (s, *C*-3a), 134.46 (s, *C*-8b), 136.13 (s, *C*-2b), 136.22 (s, *C*-8a), 136.98 (s, *C*-9b), 137.55 (s, *C*-2a), 137.86 (s, *C*-9a), 138.02 (s, *C*-11b), 138.86 (s, *C*-11a), 162.72 (s, *C*-14b), 163.68 (s, *C*-14a). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.85 (6H, s, H-12b, C*H*$_3$), 1.91 (6H, s, H-12a, C*H*$_3$), 2.23 (3H, s, H-13b, C*H*$_3$), 2.27 (3H, s, H-13a, C*H*$_3$), 4.72 (2H, s, H-7b), 4.96 (2H, s, H-7a), 6.78 (1H, dd, H-3b, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.8 Hz), 6.82 (2H, s, H-10b), 6.85 (2H, s, H-10a), 7.11 (2H, m, H-4b + H-5a), 7.16 (1H, ddd, H-5b, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.8 Hz), 7.23 (1H, ddd, H-4a, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.3 Hz), 7.43 (1H, dd, H-6a, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.3 Hz), 7.56 (2H, m, H-3a + H-6b), 8.04 [1H, s, H-14a, C*H*(O)], 8.70 [1H, s, H-14b, C*H*(O)]. ^{13}C NMR (151 MHz, $CDCl_3$): δ 17.69 (s, *C*-12b), 17.92 (s, *C*-12a), 21.05 (s, *C*-13a), 21.07 (s, *C*-13b), 47.78 (s, *C*-7a), 53.36 (s, *C*-7b), 124.90 (s, *C*-1a), 125.52 (s, *C*-1b), 127.54 (s, *C*-4b), 127.75 (s, *C*-4a), 129.52 (s, *C*-10a), 129.54 (s, *C*-5a, *C*-10b), 130.16 (s, *C*-5b), 132.49 (s, *C*-3b), 132.71 (s, *C*-8b), 132.74 (s, *C*-6a), 133.13 (s, *C*-3a), 133.22 (s, *C*-6b), 134.33 (s, *C*-2b), 135.17 (s, *C*-8a), 135.87 (s, *C*-9b), 136.26 (s, *C*-2a), 137.03 (s, *C*-9a), 138.00 (s, *C*-11b), 138.41 (s, *C*-11a), 162.52 (s, *C*-14b), 163.71 (s, *C*-14a) [resonances with "a" for isomer **4a** (major) and "b" for isomer **4b** (minor)]. IR (KBr pellet, cm^{-1}): υ 1667(vs) (CO). MS (APCI+, MeCN): 665.11 (13) $[2M+H]^+$, 332.06 (100) $[M+H]^+$. HRMS (APCI+): Calc. for $[C_{17}H_{19}BrNO+H]^+$ 332.06465. Found: 332.06464.

Crystal structure determination

A block colorless crystal of **4** was attached on a cryoloop. The details of the crystal structure determination and refinement are given in Table 1. Data collection and processing was carried at room temperature on a Bruker SMART APEX system using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[38] The figure was created with the Diamond program.[39]

Table 1

Crystallographic data for compound **4**

Molecular formula	$C_{17}H_{18}BrNO$	$F(000)$	680
M	332.23	μ(Mo-Kα)/mm^{-1}	2.666
Crystal system	Monoclinic	Crystal size (mm^3)	0.60 x 0.50 x 0.40
Space group	$P2_1/c$	θ range for data collection (º)	1.76 to 25.00
Temperature (K)	297(2)	Reflections collected	14279
a/Å	11.8231(12)	Independent reflections	2700 [R_{int} = 0.0386]
b/Å	8.3733(8)	Absorption correction	Multi-Scan[37]
c/ Å	15.8867(16)	Maximum and minimum transmissions	0.4152 and 0.2976
α/º	90	Data / restraints / parameters	2700 / 0 / 184
β/º	101.893(2)	Goodness-of-fit on F^2	1.053
γ/º	90	Final R indices [$I>2\sigma(I)$]	R_1 = 0.0429 wR_2 = 0.1115
V/Å^3	1539.0(3)	R indices (all data)	R_1 = 0.0647 wR_2 = 0.1194
Z	4	Largest difference peak and hole (e Å^{-3})	0.328 and –0.295
D_{calc}/gcm^{-3}	1.434		

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis of **4** have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1044167). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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