Allyl(acetylacetonato)palladium (II) complexes: versatile precursors for the synthesis of dimeric allylpalladium (II) complexes

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The facile synthesis and characterisation of several new dimeric (η^3-allyl)palladium (II) complexes of the type, $[Pd(\mu\text{-}L)_2(\eta^3\text{-}C_3H_4R)_2]$ [R = H or Me; LH = 4-$CH_3C_6H_4SH$; 3,5-R′$_2$pzH (R′ = Bu^t or Ph]; ArNNNHAr (Ar = 4-FC_6H_4); PhNC(Ph)NHPh] are reported.

Keywords: palladium, allyl ligands, NMR spectroscopy

The chemistry of (η^3-allyl)palladium complexes has been widely explored.[1] This is mainly due to their importance as precursors or key intermediates in different palladium catalysed reactions, *viz.,* allylic substitution,[2,3] isomerisations of alkynes to dienes,[4] diene polymerisations[5] and elimination reactions of allylic compounds to dienes.[6] Further, (η^3- allyl)palladium complexes[7] *viz*., $[Pd(\eta^3\text{- allyl})_2]$, $[Pd(\eta^3\text{-}CH_2CHCHMe)_2]$ $[C_PPd(\eta^3\text{-allyl})]$, $[Pd(\eta^3\text{-allyl})(\beta\text{-diketonate})]$[8], $[Pd(\eta^3\text{-allyl})(\text{ketoiminato})]$[9] have been used as precursors for the deposition of high quality palladium thin films under mild conditions. Recently, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ has also been used as precursor for synthesis of palladium nanoparticles.[10]

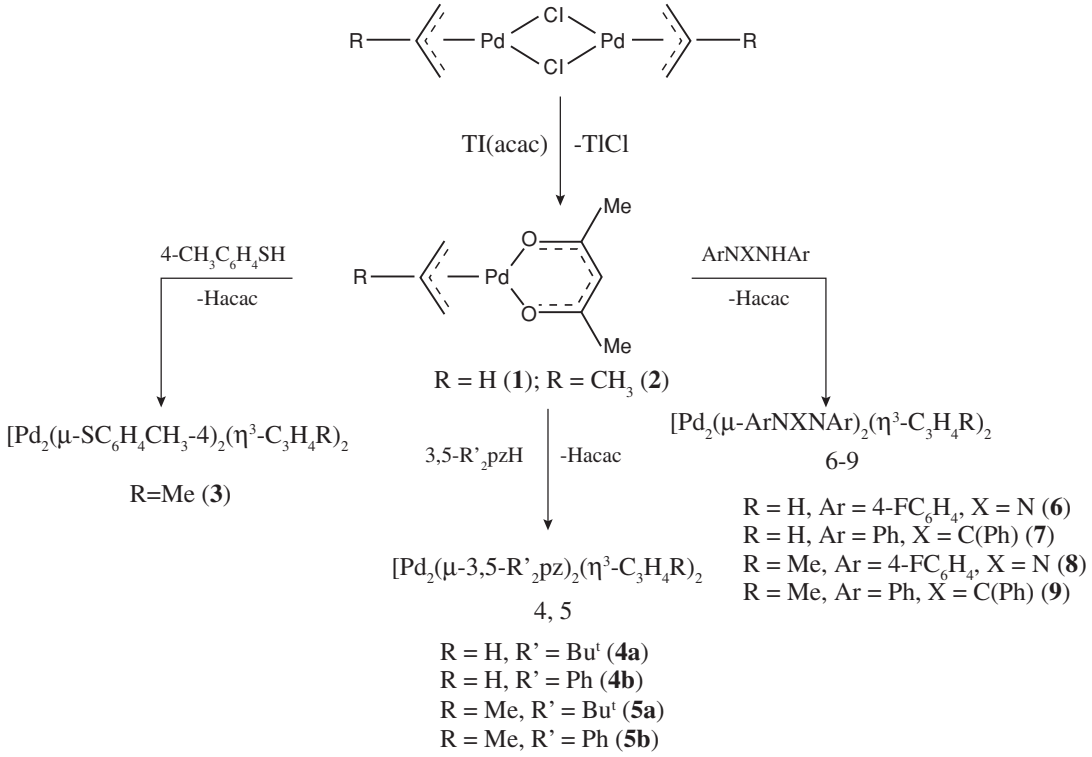
We have been active in the synthesis of dimeric allylpalladium complexes with different bridging ligands and earlier reported synthesis and characterisation of organochalcogenide bridged allylpalladium (II) complexes, which showed interesting thermal behaviour and gave metal rich chalcogenides at moderately low temperatures.[11] As a part of our ongoing research efforts on allylpalladium chemistry, we report here, a general and convenient synthesis of dimeric allylpalladium (II) complexes starting from a (η^3- allyl)(acetylacetonato)palladium complex.

Results and discussion

Syntheses and characterisation of complexes

Several new dimeric allylpalladium complexes with different bridging ligands have been prepared by the reaction between the (η^3-allyl)(acetylacetonato)palladium(II) complex, [generated *in situ* by the reaction between **1** or **2** with Tl(acac)], and different organic ligands in acetonitrile as solvent, in good to excellent yields. Recently Jones *et al.*[12] have reported the synthesis of $[Pd(\eta^3\text{-}C_3H_5))(\mu\text{-}3,5\text{-}(CF_3)_2Pz)]_2$ by the reaction between $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and 3,5-($CF_3)_2$PzLi for 12 h at r.t. Our synthetic approach, however, represents a faster and more convenient approach for the preparation of dimeric allylpalladium complexes and is general for a variety of ligands (Scheme 1).

All the complexes, **4–9** could be isolated either as white or yellow crystalline solids (complex **3** is orange coloured) and are readily soluble in common organic solvents. Complexes **1**, **4b**, **5b**, **6–9** are air-stable solids and can be stored at room temperature for several months, whereas **4a** and **5a** tend to decompose after a few days if kept at r.t. and have to be stored under argon below 0 °C to avoid decomposition.



Scheme 1

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The new dimeric complexes **3–9** have been characterised by ^{1}H, ^{13}C{^{1}H} NMR spectroscopy and elemental analyses. The characterisation data are given in the experimental section.

NMR of allylpalladium complexes: At room temperature the ^{1}H NMR spectra of allylpalladium derivatives with different bridging ligands, *viz*., pyrazolato, triazenido- or amidino-ligands ligands show the expected proton ratios for both the ligands. There are four sets of resonances each for *anti* and *syn* protons with both showing up as doublets (*anti* J_{HH} = ~12 Hz*; syn* J_{HH} = ~7 Hz) (see Experimental section). Two/three multiplets appear for the proton bonded to central carbon atom of the allyl ligand in addition to three peaks between 5.8 and 6.8 attributed to the proton bonded to the ring carbon (C-4) of the pyrazolate ring in the case of pyrazolato-bridged derivatives. These data suggest that in solution a mixture of isomers is present. The general occurrence of different isomers in the case of η^3-allyl- pyrazolato,[13] (η^3-allyl)triazenido[14] and –benzamidino-palladium complexes[14] agrees well with the data reported for similar complexes in the literature. For example, the ^{1}H NMR spectra for dimeric palladium(II) allyl derivatives of dimethylpyrazolate, reported by Trofimenko[13] were also found to be more complex than those expected for a molecule of simple C_{2v} symmetry. It was proposed that the NMR data were compatible with a mixture of conformational isomers resulting from different orientation of the allyl groups which may be caused by the rotation of allyl groups or inversion of the entire metallocycle. Figure 1 gives possible conformational isomers for dimeric [(η^3-allyl)(μ-ArNXNAr)]$_2$ [X = N; C(Ph)] complexes. Conformer **I** has stereochemically equivalent allyl groups, while conformer **II** has each set of *syn* and *anti* H's in a different environment. It may be noted that earlier workers have reported one,[14] two,[15] and three isomers[16] for [Pd$_2$(μ-amidino)$_2$(η^3-allyl)$_2$] complexes.

NMR spectra of dimeric methylallyl complexes **3, 5, 8, 9,** on the other hand, show singlets each for the methyl group, *anti* and *syn* protons of the terminal CH_2 groups indicating the presence of only one conformer. The resonances are attributed to conformer **I**. Conformer **III** may be disfavored because of steric interactions between the methyl groups.

Experimental

General experimental details

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. The chloro-bridged allylpalladium dimers, [Pd$_2$(μ-Cl)$_2$(η^3-C$_3$H$_4$R)$_2$)][17] [R = H(**1**) or Me(**2**), 3,5-di-tert-butyl pyrazole,[18] 3,5-diphenyl-pyrazole,[19] 1,3-bis(p-fluorophenyl)triazene,[20] N,N'-diphenylbenz-amidine[21]] were prepared either by following literature procedures or by modification of them. Thus in the preparation of [Pd$_2$(μ-Cl)$_2$(η^3-C$_3$H$_5$)$_2$] from K$_2$PdCl$_4$ and allyl halide, allyl bromide was used instead of allyl chloride and the reaction mixture was refluxed for 3 h, thereby reducing the reaction time from 24 to 3 h. Melting points were determined in sealed capillaries and are uncorrected. C, H, N, S analyses were carried out with a Thermo Finnigan Flash 1112 series elemental analyser. ^{1}H and ^{13}C{^{1}H} were recorded on a Bruker DPX 300 spectrometer. Chemical shifts are referenced to the internal chloroform peak. Most of the carbon resonances have been assigned, but in some cases where it was not possible to assign the resonances unambiguously, quarternary and ternary carbons are indicated as C or CH with the help of DEPT experiments.

Synthesis of complexes: The same general method was used to synthesise complexes **3, 4a–b, 5a–b and 6–9.** It consists of reacting chloro-bridged allylpalladium dimer with Tl(acac) (molar ratio 1:2) in acetonitrile followed by reaction with two equivalents of corresponding ligand. A typical preparation is described below.

Synthesis of [Pd$_2$(μ-3,5-bu$^t_2$Pz)$_2$(η^3-C$_3$H$_5$)$_2$] (**4a**): Solid Tl(acac) (0.760 g, 2.50 mmol) was added to a degassed acetonitrile (50 ml) solution of **1** (0.422 g, 1.15 mmol) at 0 °C. After it was stirred for 30 min at 0 °C, an acetonitrile (5 ml) solution of 3,5-tBu$_2$pzH (0.436 g, 2.42 mmol) was added to it. The resulting mixture was stirred at r.t. for 2 h and then filtered through a bed of Celite. The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallised from hexane at –10 °C to obtain complex **4a** as pale yellow solid.

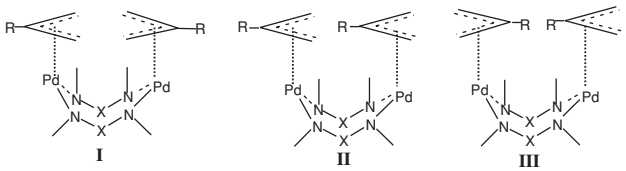

Fig. 1 Conformational isomers possible for Pd complexes **6–9**.

[Pd$_2$(μ-SC$_6$H$_4$CH$_3$-4)$_2$(η^3-C$_4$H$_7$)$_2$] (**3**): Complex **3** has been previously reported by us[22] but here it was obtained by the acac route. Recrystallisation from acetone–hexane mixture. Yield 70%. Dec. pt: 140-142 °C. Anal. Calcd. for C$_{22}$H$_{28}$S$_2$Pd$_2$: C, 46.4; H, 5.0; S, 11.3. Found: C, 46.2; H, 5.0; S, 11.5. ^{1}H NMR: δ 1.95 (s, , 6H CH_3 of 2-methylallyl); 2.29 (s, 6H, CH_3 of ligand); 2.79 (s, 4H, *anti* –H in CH_2); 3.30 (s, 4H, *syn*-H in CH_2); 6.93, 7.53 [each doublet, AB system, ^3J(HH) = 7.7 Hz, 4H, C$_6H_4$,]. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 20.84 (s, *C*H$_3$ of ligand); 23.52 (s, *C*H$_3$ of 2-methylallyl); 64.14 (s, allyl *C*H$_2$); 127.71 (*C*–S); 128.25 (s, *o*-*C*H of the Ph ring); 132.88 (s, *m*-*C*H of the Ph ring); 133.78(C) (s); 134.84 (C); 139.12 (br, ring *C*-CH$_3$).

[Pd$_2$(μ-3,5-bu$^t_2$Pz)$_2$(η^3-C$_3$H$_5$)$_2$] (**4a**): Yield : 72%. M.p. 134–136 °C. Anal. Calcd. for C$_{28}$H$_{48}$N$_4$Pd$_2$: C, 51.5; H, 7.4; N, 8.6. Found: C, 51.8; H, 7.8; N, 9.1. ^{1}H NMR: δ 1.30, 1.34, 1.39, 1.45 [each s, 36 H, C(CH_3)$_3$)]; 2.62 (d, 12.2 Hz, 1H), 2.72 (d, 12.2 Hz, 1H), 2.82 (d, 12.2 Hz, 1H), 3.21 (d, 12.2 Hz, 1H) [*anti*-H in CH_2,), 3.66 (d, 7.0 Hz, 1H), 3.74 (d, 7.0 Hz, 1H), 3.79 (d, 7.0 Hz, 1H), 3.88 (d, 7.0 Hz, 1H) [*syn* –H in CH_2]; 5.18 (septet, 7.0 Hz), 5.27–5.52 (m) [2H, allyl C*H*]; 5.88(s), 5.90 (s) [*H*-4 pz ring). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 30.50 (s, pyrazolato C(*C*H$_3$)$_3$; 31.93 (s, pyrazolato *C*(CH$_3$)$_3$; 56.82 (s), 57.35 (s), 58.06 (s), [allyl *C*H$_2$]; 97.56 (s), 98.20 (s), 98.50 (s) [pz ring *C*H]; 110.45 (s), 111.40 (s), 112.16 (s)[allyl *C*H]; 160.45 (s), 160.68 (s), 160.82 (s)[C_3+ C_5 of pz ring].

[Pd$_2$(μ-3,5-Ph$_2$Pz)$_2$(η^3-C$_3$H$_5$)$_2$] (**4b**): White crystalline complex, recrystallisation from CH$_2$Cl$_2$–hexane mixture. Yield 74%. M.p. 200–202 °C. Anal Calcd. for C$_{36}$H$_{32}$N$_4$Pd$_2$: C, 59.0; H, 4.4; N, 8.2. Found: C, 58.0; H, 4.3; N, 7.9. ^{1}H NMR: δ 1.90 (d, 12.4 Hz, 1H, anti-H in CH_2); 2.01 (d, 12.4 Hz, 1H, anti-H in CH_2); 2.38 (d, 12.4 Hz, 1H, *anti*-H in CH_2); 2.51 (d, 12.4 Hz, 1H, *anti*-H in CH_2); 2.85 (d, 6.8 Hz, 1H, *anti*-H in CH$_2$); 2.96 (d, 6.8 Hz, 1H, *syn*-H in CH_2); 3.16 (d, 6.8 Hz, 1H, *syn*-H in CH_2); 3.27 (d, 6.8 Hz, 1H, *syn*-H in CH$_2$); 4.99 (m, 2H) (allyl C*H*); 6.69 (s) 6.75 (s); 6.81 (s); 6.87 (s)[*H*-4 Pz]; 7.36-7.52 (m, 12H, Ph); 7.75 (d, 7.0 Hz, 3H, Ph); 8.03-8.20 (m, 5H, Ph).^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 57.56 (s), 57.90 (s) [allyl *C*H$_2$]; 102.74 (s), 102.90 (s), [*C*H, pz ring]; 114.61 (s), 115.24 (s), [allyl CH]; 125.75 (CH); 127.14 (CH); 127.30 (CH) [m-CH of Ph ring); 127.71 (CH); 127.96 (CH) [p-CH of Ph ring]; 128.20 (s, CH); 128.95 (s, CH) [o-CH of the Ph ring]; 135.70 (s), 136.04 (s) [ipso C of Ph ring]; 155.14 (s), 154.88 (s) [C-Ph].

[Pd$_2$(μ-3,5-bu$^t_2$Pz)$_2$(η^3-C$_4$H$_7$)$_2$] (**5a**): Pale yellow complex recrystallisation from CH$_2$Cl$_2$–hexane mixture. Yield: 81%. M.p. 108–110 °C. Anal. Calcd. for C$_{30}$H$_{52}$N$_4$Pd$_2$: C, 52.9; H, 7.7; N, 8.2. Found: C, 52.6; H, 8.1; N, 7.9. ^{1}H NMR: δ 1.37 (s, 36H, C(CH_3)$_3$); 2.14 (s, 6H, CH_3 of 2-methyl allyl); 2.70 (s, 4H, *anti*-H in CH_2); 3.62 (s, 4H, *syn*-H in CH_2) 5.88 (s, 2H, H-4 of pz ring). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 22.92 (s, *C*H$_3$ of 2-methylallyl); 30.50 (*C*H$_3$ t-butyl); 31.92 (s, *C*(CH$_3$)$_3$ 57.32 (s, allyl *C*H$_2$); 98.23 (s, *C*-4, pz ring)); 127.35 (s, allyl central *C*); 160.51 (br, C_3+ C_5 pz ring).

[Pd$_2$(μ-3,5-Ph$_2$pz)$_2$(η^3-C$_4$H$_7$)] (**5b**): Colourless crystalline complex, recrystallisation from CH$_2$Cl$_2$–hexane mixture Yield 76%. M.p. 195–198 °C. Anal. Calcd. for C$_{38}$H$_{36}$N$_4$Pd$_2$: C, 59.9; H, 4.8, N, 7.6. Found C, 60.2; H, 4.9; N, 7.9. ^{1}H NMR: δ 1.64 (s, 6H. CH_3 of 2-methylallyl); 2.50 (s, 4H, *anti*-H in CH_2); 2.98 (s, 4H, *syn*-H in CH_2); 6.78 (s, 2H, *H-4* pz); 7.34–7.38 (m, 4H, Ph), 7.46–7.51 (m, 8H, Ph), 8.08 (d, 7.4 Hz, 8H, Ph).^{13}C{1H} NMR (75 MHz, CDCl$_3$): δ 22.51 (s, CH$_3$ of 2-methylallyl); 56.95(s, allyl CH$_2$); 102.80 (s, pz ring *C*H); 126.90 (s, *m- C*H of Ph ring); 127.61 (s, *p*-*C*H of Ph ring); 128.17 (s, *o*-*C*H of Ph ring); 130.81(s, central allyl carbon); 135.89 (s, *ipso-C* of Ph ring); 154.72 (s, *C*-Ph).

[Pd$_2$(μ-FC$_6$H$_4$NNNFC$_6$H$_4$)$_2$(η^3-C$_3$H$_5$)$_2$] (**6**): Bright yellow complex, recrystallised from CH$_3$CN–(C$_2$H$_5$)$_2$O mixture. Yield 71%. Dec. pt.: 155–158 °C. Anal. Calcd. for C$_{30}$H$_{26}$F$_4$N$_6$Pd$_2$: C, 47.5; H, 3.4; N, 11.1. Found: C, 47.4; H, 4.0; N, 11.3 ^{1}H NMR: δ 2.79 (d, 12.6 Hz, 1H); 2.88(d, 12.6 Hz, 2H); 3.05 (d, 12.6 Hz, 1H)[*anti*-H in CH$_2$); 3.73 (d, 7.0 Hz, 1H); 3.81 (d, 7.0 Hz, 2H); 3.90 (d, 7.0 Hz, 1H) (*syn*-

H in CH_2]; 5.09 (septet, 7.0 Hz, 0.5 H); 5.59-5.85 (m, 1.5 H) (allyl CH); 6.83-7.00 (m, 8H, C_6H_4); 7.31–7.53 (m, 8H, C_6H_4). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) : δ 55.82 (s), 56.96 (s), 58.16 (s) (allyl CH_2); 112.76 (s), 113.80 (s) [allyl CH]; 115.24 (d, 22 Hz, *m-C*H of Ph ring); 121.99 (br), 122.72 (br) [*o-C*H of the Ph ring]; 149.44 (s), 149.89 (s) [ring *C*-N]; 161.40 (d, 243 Hz)[ring *C*-F].

[Pd_2(μ-PhNC(Ph)NPh)$_2$(η^3-C_3H_5)$_2$] (**7**): Yellow complex, recrystallisation from CH_2Cl_2–hexane mixture. Yield 74%. Dec. pt.: 145–148 °C. Anal. Calcd. for $C_{44}H_{40}N_4Pd_2$: C, 63.1; H, 4.8; N, 6.7. Found: C, 62.9; H, 4.8; N, 6.7. ^1H NMR: δ 2.77 (d, 12.2 Hz, 1H), 2.79 (d, 12.2 Hz, 1H), 2.79 (d, 12.2 Hz, 2H) (*anti*-H in CH_2); 3.20 (d, 7.0 Hz, 1H); 3.29 (d, 7.0 Hz, 2H); 3.44 (d, 7 Hz, 0.5 H); 3.52 (d, 0.5 H, 7.0 Hz) (*syn*-H in CH_2); 5.20 (m, 1H); 5.68 (m, 1H) [allyl CH]; 6.12 (d, 7.4 Hz, 1H, Ph); 6.26 (d, 7.2 Hz, 1H, Ph); 6.65-7.02 (m, 28H, Ph). $^{13}C\{^1H\}$ NMR 75 MHz, $CDCl_3$): δ 55.42 (s), 55.85 (s), 56.42 (s), 56.61 [allyl CH_2]; 109.96 (s); 111.10 (s), 113.2 (s) [allyl CH]; 120.57 (CH); 120.90 (CH); 126.47 (CH);126.82 (CH); 127.31 (CH); 131.49 (CH), 132.10 (CH); 137.01 (C); 153.82 (C), 154.00(C); 169.59 (C).

[Pd_2(μ-$FC_6H_4NNNFC_6H_4$)$_2$(η^3-C_4H_7)$_2$] (**8**): Bright yellow complex, recrystallisation from CH_2Cl_2–hexane mixture. Yield 78%. Dec. pt: 160–162 °C. Anal. Calcd. for $C_{32}H_{30}F_4N_6Pd_2$: C, 48.8; C, 3.8; N, 10.7. Found: C, 49.1; H, 3.8; N, 10.2. ^1H NMR: δ 2.26 (s, 6H CH_3 of 2-methylallyl); 2.80 (s, 4H, *anti*-H in CH_2); 3.58(s, 4H, *syn*-H in CH_2); 6.86–6.97 (m, 8H, C_6H_4), 7.35–7.41 (m, 8H, C_6H_4).$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 23.40 (s, CH_3 allyl); 56.77 (s, allyl CH_2); 114.99 (d, 22.1 Hz, *m-C*H of the Ph ring); 122.21 (s, *o-C*H of Ph ring), 129.26 (s, central allyl carbon); 149.60 (s, ring *C*–N); 161.74 (d, 243 Hz, ring *C*–F).

[Pd_2(μ-PhNC(Ph)NPh)$_2$(η^3-C_4H_7)$_2$] (**9**): Yellow complex, recrystallisation from $CHCl_3$–hexane mixture. Yield 82%. Dec. pt: 176–178 °C. Anal. Calcd. for $C_{46}H_{44}N_4Pd_2$: C, 63.8; H, 5.1; N, 6.5. Found C, 63.1; H, 4.8; N, 6.7. ^1H NMR: δ 2.26 (s, 6H, CH_3 of 2-methylallyl); 2.74 (s, 4H, *anti*-H in CH_2); 3.10(s, 4H, *syn*-H in CH_2); 6.15 (d, 7.2 Hz, 3H, Ph), 6.62–6.97 (m, 27H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 23.84 (s, CH_3 of 2-methylallyl); 55.98 (s, allyl CH_2); 120.40 (CH); 126.71 (CH); 126.90 (CH); 127.10 (CH); 127.24 (CH); 127.27 (CH); 131.46 (CH); 132.24 (CH); 137.05 (s, C); 154.11 (s, C); 169.28 (s, C).

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