

Complexes of 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine (fench=NN=CMe)₂C₅H₅N) ligand with molybdenum, tungsten or palladium

Kompleks-kompleks ligan 2,6-diasetilpiridina-di-(1R)-(-)-fenchone diazin (fench=NN=CMe)₂C₅H₅N) dengan molibdenum, tungsten atau paladium

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Abstract

The Schiff-base ligand 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine (**9**) was prepared by heating 2,6-diacetyl-pyridine (**7**) and fenchone hydrazone (**8**) in boiling ethanol in the presence of acetic acid as the catalyst for 28 h. Treatment of (**9**) with [Mo(CO)₄(nbd)] or [W(CO)₄(nbd)] in benzene at 80 °C gave the tetracarbonylmolybdenum(0) (**10**) or tetracarbonyltungsten(0) (**11**). The complexes (**10**) and (**11**) showed that the diazine (**9**) acted as a bidentate chelating ligand bonded through the pyridyl nitrogen and only one of the imino nitrogen donor atoms of the ligand involved in the bonding. However, diazine (**9**) acted as a planar terdentate *N,N,N*-donor-ligand when reacted with palladium(II) to give the cationic products of (**12**), (**13**) and (**15**), respectively.

Keywords Molybdenum complexes, tungsten complexes, palladium complexes; bidentate-*N,N* ligand complexes, terdentate-*N,N,N* ligand complexes, fenchone azine ligand complexes

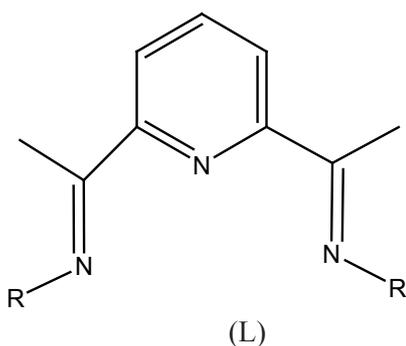
Abstrak

Ligan Schiff-bes 2,6-diasetilpiridina-di-(1R)-(-)-fencen diazin (**9**) telah disediakan dengan memanaskan 2,6-diasetil-piridina (**7**) dengan fencone hidrazin (**8**) di dalam etanol yang mendidih dengan kehadiran asid asetik sebagai mangkin selama 28 J. Tindak balas (**9**) dengan [Mo(CO)₄(nbd)] atau [W(CO)₄(nbd)] di dalam benzena pada 80°C menghasilkan tetrakarbonilmolibdenum(0) (**10**) atau tetrakarboniltungsten(0) (**11**). Kompleks-kompleks (**10**) dan (**11**) menunjukkan diazin (**9**) berlagak sebagai ligan berkelat bidentat dan ikatannya melalui nitrogen piridil dan hanya satu atom nitrogen imino ligan sahaja terlibat dalam ikatan. Walau bagaimana pun, diazine (**9**) berlagak sebagai ligan penderma satah terdenatat-*N,N,N* apabila ditindakbalaskan dengan palladium(II) untuk memberikan hasil-hasil kationik (**12**), (**13**) dan (**15**).

Kata kunci Komplek-kompleks Molibdenum, kompleks-kompleks tungsten, kompleks-kompleks paladium, kompleks-kompleks ligan bidentat-*N,N* ligan, kompleks-kompleks ligan terdentat-*N,N,N*, kompleks-kompleks ligan fencen azin.

Introduction

Terdentate *N,N,N*-donor-ligands (L) generated from 2,6-diacetyl-pyridine have received some attention in recent years (Alyea, Ferguson & Restivo, 1975; Lavery & Nelson, 1984; Naskar *et. al.*, 2005; de Sousa *et. al.*, 2005; Naskar *et. al.*, 2007; Raveendran & Pal, 2007; Panja *et. al.*, 2009; & Subba Rao *et. al.*, 2010). The ligands are readily obtained by Schiff-base condensation of an amine, RNH₂. They usually act as planar tridentate for example in the reactions with nickel(II), copper(II), zinc and cadmium halides, nitrates, perchlorates or tetrafluorobates (Lavery & Nelson, 1984). By reacting such ligands with metal ions, five coordinate [MX₂L] (M = Ni, Zn, or Cd; X = halide) and six coordinate species such as [ML₂]²⁺, [M(η²-NO₃)X(L)], [M(η²-NO₃)NO₃(L)] or [MNO₃(en)(L)]⁺, (M = Ni, Cu, Zn, or Cd; X = halide, en = 1,2-diaminoethane) have been isolated in which the ligands L were tridentate *N,N,N*-donors. Treatment of ligand (1) with nickel(II) nitrate in boiling ethanol gave Ni(NO₃)₂L, the crystal structure of which showed that one nitrate group is monodentate and the other bidentate, with the geometry about nickel atom being distorted octahedral.



- (1) Ph
- (2) C₆H₄OMe-4
- (3) (CH₂)₃Ph
- (4) C₆H₄Et-4
- (5) (CH₂)CMe₃
- (6) OH

Experimental

All NMR spectra were recorded by using a JEOL FX-90Q spectrometer, A JEOL FX-100 spectrometer, a Bruker ARX-250 or a Bruker AM-400 spectrometer (operating frequencies for ¹H and ¹³C were 400.13 and 100.6 MHz respectively). ¹H and ¹³C chemical shifts are relative to tetramethylsilane and coupling constants are in Hz.

Infrared spectra were recorded by using a Perkin-Elmer model 257 grating spectrometer (4000-600 cm⁻¹) or a Pye Unicam SP2000 (40000-200 cm⁻¹), as Nujol mulls on polyethylene plates, or potassium bromide discs, or as dichloromethane solutions in calcium fluoride cells, with dichloromethane as reference.

Elemental analyses were recorded at the Chemistry Department, University of Leeds UK. As in common with compounds of these types, solvent of crystallisation, particularly CH₂Cl₂ or CHCl₃ was often present and could be removed even by prolonged drying. The solvent could be detected in the ¹H NMR spectrum.

Electrical conductivities were measured by using a Phillips PR 9500/01 Conductance and a Standard Conductance cell at 20°C.

Mass spectra were recorded by Mass Spectroscopy Services at University of Leeds, UK.



A solution containing (1R)-(-)- fenchone hydrazone (779 mg, 4.68 mmol), 2,6-diacetylpyridine (384 mg, 2.14 mmol) and acetic acid (0.1 cm³) in ethanol (10 cm³) was heated at 80°C for 28 h. The reaction mixture was left to stand at ca. 20°C for 1h, after which it was concentrated and cooled at -30°C for 2 d. The required product (**9**) precipitated as a white solid. This was filtered off, washed with cold ethanol and dried. Yield 821 mg, 85%. (Found: C, 75.55; H, 8.85; N, 15.1. Calc. for C₂₉H₄₁N₅ requires C, 75.7; H, 8.9; N, 15.2%). m/z (EI): 459 (M⁺). ¹³C-¹H NMR (62.9 MHz, CDCl₃) δ_c: 22.3 (2C, s, methyl carbon from fench residue), 22.8 (2C, s, methyl carbon from fench residue), 24.3 (2C, s, methyl carbon from fench residue), 48.5 (2C, s, acetyl carbon), 120.4 (2C, s, pyridyl carbon with H) and 136.1 (1C, pyridyl carbon with H).



A solution containing (**9**) (196 mg, 0.43 mmol) and [Mo(CO)₄(nbd)] (128 mg, 0.43 mmol) in benzene (10 cm³) was heated at 80°C for 0.5 h and left to stand at ca. 20°C for 1h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give (**10**) as brown solid. Yield 244 mg, 86%. (Found: C, 58.15; H, 6.3; N, 9.85. Calc. for C₃₃H₄₁MoN₅O₄·1.5CH₃OH requires C, 57.9; H, 6.3; N, 9.7%). m/z (FAB, for ⁹⁸Mo): 670 (M⁺ + 1), 641 (M - CO), 613 (M - 2CO), 584 (M+1-3CO) and 557 (M - 4CO). ¹³C-¹H NMR (62.9 MHz, CDCl₃) δ_c: 15.3 (1C, s, methyl carbon from fench residue), 18.1 (1C, s, methyl carbon from fench residue), 19.3 (1C, s, methyl carbon from fench residue), 26.0 (1C, s, methyl carbon from fench residue), 51.7 (1C, s, acetyl carbon), 52.3 (1C, s, acetyl carbon), 204.8 (1C, s, MoCO), 205.9 (1C, s, MoCO), 221.3 (1C, s, MoCO) and 223.8 (1C, s, MoCO).



A solution containing (**9**) (208 mg, 0.44 mmol) and [W(CO)₄(nbd)] (172 mg, 0.44 mmol) in benzene (10 cm³) was heated at 80 °C for 0.5 h and left to stand at ca. 20°C for 1h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give (**10**) as brown solid. Yield 87 mg, 26%. (Found: C, 50.2; H, 4.9; N, 8.95. Calc. for C₃₃H₄₁WN₅O₄ requires C, 52.4; H, 5.4; N, 9.2%). m/z (FAB, for ¹⁸⁴W): 756 (M⁺ + 1), 727 (M - CO) and 643 (M - 4CO).



A solution containing (**9**) (316 mg, 0.69 mmol) and [Na₂PdCl₄H₂O] (253 mg, 0.69 mmol) in methanol (10 cm³) and was boiled for 6 h and left to stand at ca. 20°C for 1h. The solvent was then evaporated to dryness under reduced pressure and solid obtained was collected, washed with water and cold methanol to give (**12**) as an orange solid. Yield 26 mg, 58%. (Found: C, 50.25; H, 6.45; Cl, 10.7; N, 10.15. Calc. for C₂₉H₄₁N₅Cl₂Pd requires C, 54.6; H, 6.5; Cl, 11.1; N, 10.9%). m/z (FAB, for ¹⁰⁶Pd and ³⁵Cl): 602 (M + 2 - Cl) and 564 (M + 1 - 2Cl).



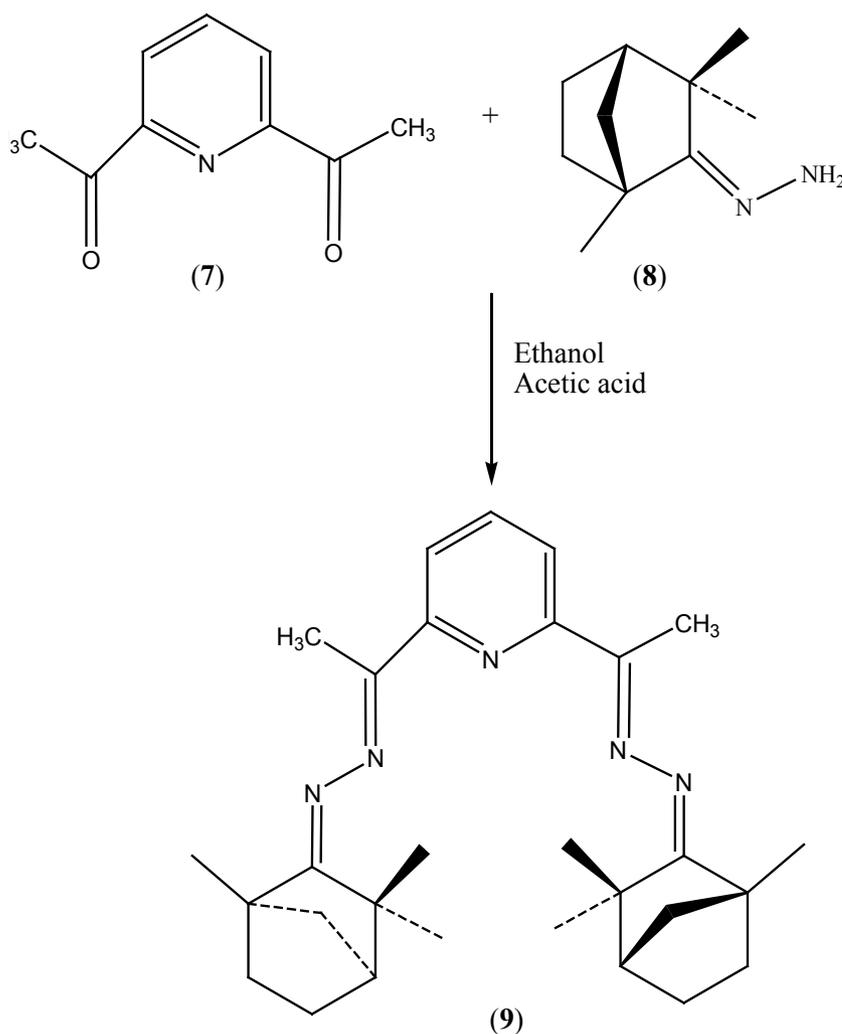
A solution containing (**9**) (672 mg, 1.46 mmol) and [Na₂PdCl₄H₂O] (538 mg, 1.46 mmol) in methanol (25 cm³) and was boiled for 12 h. After allowing the mixture to stand at ca. 20°C for 1h it was treated with NH₄PF₆ (287 mg, 1.77 mmol) to give (**13**) as a yellow solid. Yield 870 mg, 89%. (Found: C, 46.15; H, 5.4; Cl, 4.8; N, 9.3. Calc. for C₂₉H₄₁N₅ClF₆PPd requires C, 46.7; H, 5.5; Cl, 4.75; N, 9.4 %). m/z (FAB, for ¹⁰⁶Pd and ³⁵Cl): 602 (M + 2 - PF₆) and 564 (M - 1 - Cl - PF₆).



A solution containing (9) (672 mg, 1.36 mmol) and $[\text{Na}_2\text{PdCl}_4\text{H}_2\text{O}]$ (502 mg, 1.36 mmol) in methanol (25 cm^3) and was boiled for 6 h. After allowing the mixture to stand at ca. 20°C for 1h it was treated with NaBPh_4 (504 mg, 1.47 mmol) to give (14) as a yellow solid. Yield 966 mg, 77%. (Found: C, 68.3; H, 6.4; Cl, 4.0; N, 7.65. Calc. for $\text{C}_{53}\text{H}_{61}\text{BClN}_5\text{Pd}\cdot\text{CH}_3\text{OH}$ requires C, 68.1; H, 6.9; Cl, 3.75; N, 7.4 %). m/z (FAB, for ^{106}Pd and ^{35}Cl): 600 (M - BPh_4) and 564 (M - 1 - Cl - BPh_4).

Result and Discussion

We prepared 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine (9) by heating 2,6-diacetylpyridine (7) and fenchone hydrazone (8) in boiling ethanol in the presence of acetic acid as the catalyst for 28 h (Scheme 1). The product (9) was a white solid and was obtained in 85% yield. The Schiff-base type ligand (9) was characterized by (i) elemental analysis (C, H, N); (ii) the infrared spectrum, which showed a band at 1660 cm^{-1} due to (C=N) (Table 1); (iii) mass spectrometry, which

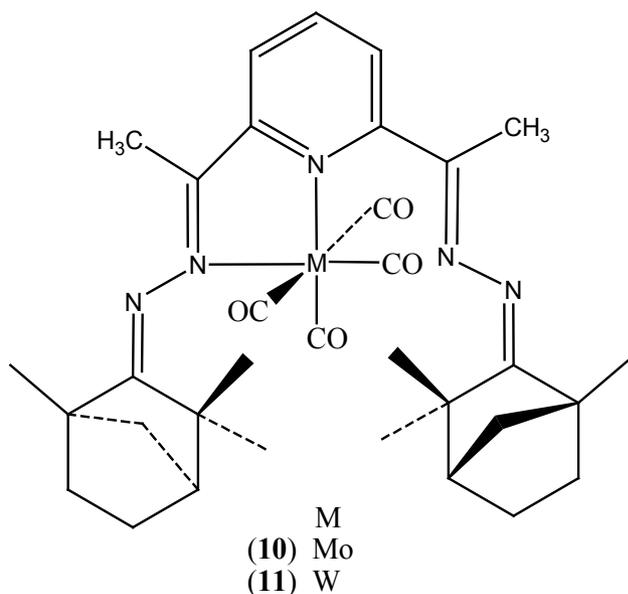


Scheme 1

showed a parent molecular ion at $m/z = 459$ and (iv) the ^1H NMR spectrum (Table 2).

In the ^1H NMR spectrum of **(9)** the resonance of the $\text{CH}_3\text{C}=\text{N}$ protons was a singlet at 2.35 ppm and the pyridyl protons resonated as a triplet at 7.69 ppm and a doublet at 8.12 ppm. The protons from the fenchone residue were assigned by comparison with (1R)-(-)-fenchone (Kolehmainen *et. al.*, 1990). The resonances of the methyl protons were singlet at 1.19, 1.22 and 1.33, respectively. The ^{13}C - $\{^1\text{H}\}$ NMR spectrum of **(9)** was also recorded and was assigned with the aid of an Attached Proton Test (APT), and DEPT-135 experiments; the assignments for the carbons from the fenchone residue were after comparison with the literature values (Kolehmainen *et. al.*, 1990). The resonance of the $\text{CH}_3\text{C}=\text{N}$ carbons was a singlet at 48.5 ppm and the resonances of the methyl carbons from the fenchone residue were singlet at 22.3, 22.8 and 24.5 ppm respectively. Two singlets at 120.40 and 136.1 ppm correspond to resonances of the pyridyl carbons bonded to a hydrogen atom.

We have studied the Schiff-base type ligand **(9)** as a ligand for group 6 metal carbonyls. Treatment of $[\text{Mo}(\text{CO})_4(\text{nbd})]$ with **(9)** in benzene at 80°C gave the molybdenum(0) complex **(10)** in which the ligand **(9)** behaves as a bidentate-*N,N* donor ligand. The isolated product was fully characterized. The infrared absorption bands at 2010, 1912 and 1849 cm^{-1} were in the expected region for tetracarbonyl (Lu & Selbin 1987; & Albon *et. al.*, 1989). The structure was further supported by mass spectroscopic data which revealed four sequential losses of carbonyl ligands that is peaks at $641(\text{M} - \text{CO})$, $613(\text{M} - 2\text{CO})$, $584(\text{M} + 1 - 3\text{CO})$ and $557(\text{M} - 4\text{CO})$.



The ^1H NMR spectrum of **(10)** showed that the $\text{CH}_3\text{C}=\text{N}$ protons were inequivalent and resonated as two singlets at 2.34 and 2.58 ppm, respectively (Table 1.2). The resonances of the methyl protons of the the fenchone residue were broad overlapping singlets in the region of 1.30-1.33 ppm . The ^{13}C - $\{^1\text{H}\}$ NMR spectrum of **(10)** the resonances of the $\text{CH}_3\text{C}=\text{N}$ carbons were singlets at 51.7 and 52.3 ppm, respectively. The resonances of the carbonyl carbons were singlets at 204.0, 205.9, 2221.3 and 223.8 ppm, respectively which again supported the evidence for the formation of the tetracarbonyl complex **(10)**.

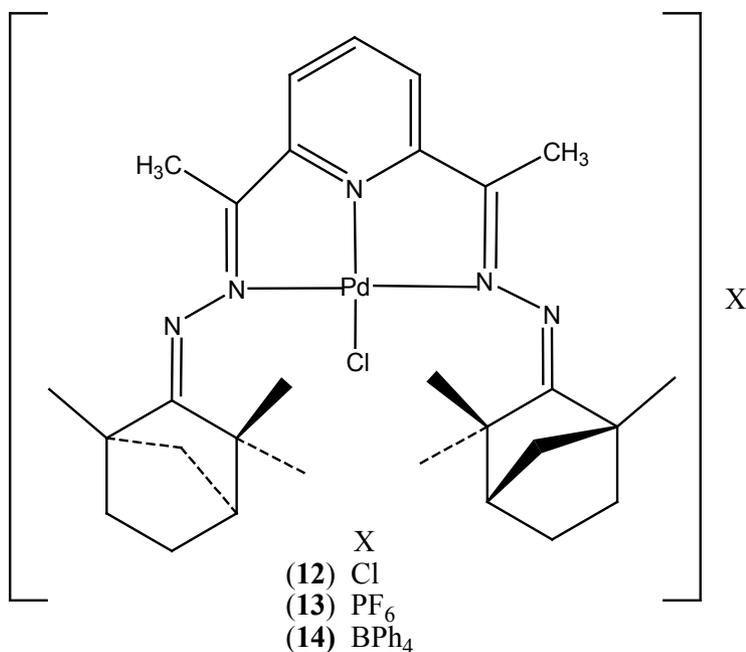
From the above observation we suggest that the ligand **(9)** is acting as the bidentate chelating

ligand bonding through the pyridyl nitrogen and only one of the imino nitrogen donor atoms, similar to that reported by Lu & Selbin (1987).

Treatment of (9) with $[\text{W}(\text{CO})_4(\text{nbid})]$ in benzene at 80°C gave the tetracarbonyl tungsten(0) complex (11). The ^1H NMR, $^{13}\text{C}\{-^1\text{H}\}$, mass spectral and infrared data of (11) were analogous to those of the molybdenum complex (5) thus we envisage the complex to have an analogous structure.

We also studied the coordination behaviour of ligand (9) with palladium. The cationic chloropalladium(II) complex (12) was obtained as a yellow solid when we treated the Schiff-base ligand (4) with $\text{Na}_2\text{PdCl}_4 \cdot 4\text{H}_2\text{O}$ in boiling methanol. The infrared spectrum of the product (12) showed a band at 350 cm^{-1} due to $\nu(\text{Pd}-\text{Cl})$ (Table 1.0). The mass spectrum showed the losses of the chloride atoms with peaks at 620 ($\text{M} - \text{Cl}$), and 567 ($\text{M} - 2\text{Cl}$). Electrical conductivity measurements of (12) at 20°C in acetone solution showed it to be 1:1 electrolyte (molar conductivity, $\Lambda_m = 109\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$) (Geary, W. J., 1971). In the NMR spectrum of (12) the resonance for the $\text{CH}_3\text{C}=\text{N}$ protons were a singlet at 2.55 ppm. The resonances of the methyl protons from the fenchone residue were singlets at 1.20, 1.25 and 1.29 ppm, respectively. The pyridyl protons gave resonances in the range of 8.70-8.79 ppm.

Treatment of the cationic salt (12) with NH_4PF_6 gave the hoped for PF_6 salt (13). The infrared spectrum showed a band at 345 cm^{-1} due to $\nu(\text{Pd}-\text{Cl})$. The molar conductivity measurements taken in acetone at 20°C showed it to be 1:1 electrolyte (molar conductivity, $\Lambda_m = 168\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$). The ^1H NMR spectrum of (8) displayed a similar pattern to that of the chloride salt (7). The resonance of the $\text{CH}_3\text{C}=\text{N}$ protons was a singlet at 2.38 ppm and the pyridyl protons resonated as two multiplets at 7.94 and 8.40 ppm.



Similarly, treatment of the chloride salts (12) with BBPh_4 gave the hoped for BPh_4 salt (14). The infrared spectrum showed a band at 345 cm^{-1} due to $\nu(\text{Pd}-\text{Cl})$ and the molar conductivity measurements taken in acetone at 20°C showed it to be 1:1 electrolyte (molar conductivity, Λ_m

= 96 ohm⁻¹ mol⁻¹ cm²) [8]. The ¹H NMR spectrum of (9), the resonance of the CH₃C=N protons overlapped with those of other protons in the fenchone residue; this gave broad peaks in the range of 1.90–2.01 ppm. The methyl protons from fenchone residue were singlets at 1.70, 1.77 and 1.80 ppm.

We observed that (9) acted as planar terdentate-*N,N,N* donor ligand when reacted with palladium(II), similar to that reported by Alyea, Ferguson & Restivo (1995).

Table 1 Infrared data

Compound	IR bands (cm ⁻¹)		
	ν(C=N) ^a	ν(M–Cl) ^b	ν(C≡O) ^c
(9)	1660 (s)	–	–
(10)	1653(m)	–	2010, 1912, 1849
(11)	1650 (m)	–	2004,1904,1849
(12)	1645 (m)	350 (m)	–
(13)	1635 (m)	345 (m)	–
(14)	1638 (m)	345 (m)	–
(13)	1658(s)	–	–
(14)	1560 (m)	350 (s)	–

^a As KBR disc. ^b In nujol. ^cIn CH₂Cl₂, all carbonyl bands are strong

Table 2 Proton NMR data^a

Compound	δ(acetyl)	δ(pyridyl)	δ(fenchone methyl)
(9)	2.35 (6H, s)	7.69 (1H, t)	1.19 (3H,s)
	-	8.12 (2H, d)	1.22 (3H, s)
	-	-	1.33 (3H, s)
(10)	2.34 (3H, s)	7.36-7.98 (3H, m)	1.30-1.33 (9H, br)
	2.58 (3H, s)	-	-
(11)	2.28 (3H, s)	7.37-7.93 ((3H, m)	1.24-1.27 (6H, br)
	2.54 (3H, s)	-	1.50 (3H, s)
	2.55 (6H, s)	8.71-8.79 ((3H, br)	1.20 (3H, s)
(12)	-	-	1.25 (3H, s)
	-	-	1.29 (3H, s)
	2.38 (6H, s)	7.94 (1H, m)	1.25-1.29 (6H, br)
(13)	-	8.40 (2H, m)	1.57 (3H, s)
	1.80 (6H, s)	7.36-7.49 (3H, m)	1.70 (3H, s)
	-	-	1.77 (3H, s)
(14)	-	-	1.80 (3H, s)
	-	-	-

^a Proton NMR recorded at 400 MHz, chemical shift δ relative to SiMe₄, solvent CDCl₃ unless stated; s = singlet, d = doublet, m = multiplet, t = triplet

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