

Physical characteristics of compounds

Data associated with particular compounds should be listed after the name (or its equivalent) of the compound concerned, following the description of its preparation.

Alternatively, they can be presented in tabular form.

The suggested order for the presentation of data for a new compound is: *yield, melting point, optical rotation, refractive index, elemental analysis, UV absorptions, IR absorptions, NMR spectra and mass spectra*. The following formats for the citation of each should be followed.

Yield. In parenthesis after the compound name (10.3 g, 72%)

Melting point. In the form 'mp 183 °C (hexane)', *i. e.* the crystallisation solvent in parenthesis.

Optical rotation. The optical rotation due to a solute in solution may be specified by a statement of the type: $[\alpha]_{\text{D}}^{20} + 5.6$ (*c* 1.0, CHCl₃) or $[\alpha]_{589}^{20} + 5.6$ (*c* 1.0, CHCl₃) where concentration is expressed in g/100 cm³ (α and *c* in italics)

Refractive index. In the form ' n_{D}^{22} 1.831'

Elemental analysis. The analytical results of new compounds should be given in the form: *e.g.* compound **1** (Found: C, 80.48; H, 6.19; N, 4.22. Calc. for C₂₂H₂₁NO₂: C, 79.76; H, 6.34; N, 4.23%).

UV absorptions. In the form (λ in italics): $\lambda_{\text{max}}/\text{nm}$ (MeOH) 215 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 35.9×10^3), 273 (17.1×10^3) and 310 (12.3×10^3).

NB: When ϵ values are included, volumes throughout the text must be given in dm³, cm³, mm³, *etc.* for consistency, otherwise, L, mL, μ L, *etc.* are acceptable.

IR absorptions. In the form (ν in italics): $\nu_{\text{max}}/\text{cm}^{-1}$ 2080, 2000 (CO) and 1715 (NO) (Nujol). The type of signal (s, m, vs) can be indicated by appended letters (*e.g.* 2000vs).

NMR data. For all spectra, δ (in italics) should be used, with the nucleus indicated by subscript (*e.g.* δ_{H} , δ_{C} , δ_{P}) if necessary. Instrument frequency and standard should be specified, either in the

general part of the experimental section if they are common to all experiments, or as in the following examples: ^1H NMR (100 MHz, CDCl_3 , standard SiMe_4) and (300 MHz, toluene- d_7 , standard residual toluene at δ 2.1, 223K). When necessary, temperature must be given. Solvent should always be specified. The nature of the coupling (J in italics) should be specified when necessary, *e.g.*: ^1H NMR (CDCl_3) δ 1.18 (t, 3J 7.2 Hz, 3 H, CH_3), 1.58 (s, 1 H, CH), 1.62 (s, 9 H, ^tBu), 3.35 (q, J 7.2 Hz, 2 H, CH_2). A broad signal may be denoted by 'br', *e.g.* δ 2.51 (br, s, 1 H, NH). Coupling constants between different nuclei must be specified as in the following example: $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CDCl_3 , external 85% H_3PO_4 , 298 K) δ 61.0 [dd, $^1J(\text{PtP})$ 5420 and $^2J(\text{PP})$ 24 Hz, P_A], 22.1 [dd, $^1J(\text{PtP})$ 2584 Hz, P_B]. Only unequivocal attributions should be given.

Mass spectrum. The type of spectrum (electron impact, FAB, field desorption, *etc.*) should be indicated in the general part of the experimental. Data should be given in the form: m/z 210 (M^+ , 33%), 195 (67), 167 (9) *etc.* Other possible assignments may be included in the form: m/z 152 ($\text{M}-\text{CH}_3\text{CONH}$, 33). Metastable peaks may be listed as: m^* 160 ($189 \rightarrow 174$), *etc.*

Examples of typical experimental section format.

General

All manipulations and reactions were performed under an atmosphere of dry argon, unless otherwise specified, by using high vacuum-line techniques and Schlenk-type glassware, dried in vacuum prior to use. Solvents were dried, degassed and redistilled before use; CH_2Cl_2 was dried over CaH_2 , hexane over sodium wire and THF over sodium and benzophenone. Purification of the products was carried out by preparative TLC (1 mm thickness glass-backed silica plates 20 x 20 cm, silica gel type GF_{254} , Fluka) and the compounds were extracted from silica with CH_2Cl_2 . The starting material was prepared according to the literature^{ref}.

Elemental analyses were performed on a 2400 CHN-Perkin Elmer instrument. Solution NMR spectra were recorded on a Bruker 300P spectrometer. Standard pulse sequences were used for the NMR experiments. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Deuterated solvents were used as lock and reference [^1H NMR relative to the proton resonance resulting from incomplete deuteration of the CDCl_3 (δ 7.25); ^{13}C NMR relative to the carbon of the CDCl_3 (δ 77.0)] and for ^{31}P NMR, external 85 % H_3PO_4 was used as the reference. Infrared spectra were recorded on a Bomen (FT-IR Michelson) spectrophotometer scanning between 2200 and 1600 cm^{-1} (ν_{CO}) using a CaF_2 liquid cell. Secondary ionisation mass spectra (SIMS) were

obtained on a VG Autospec-Fisons instrument operating between 25 and 30 kV and a current of 40 μ A; *p*-nitrobenzyl alcohol was used as a matrix and was treated by bubbling CO or Ar through it for 0.5 h prior to use. All *m/z* values are referred to ^{193}Ir .

Synthesis of [Ir₄(CO)₁₁{Fe(η^5 -P₃C₂^tBu₂)(η^5 -C₅H₅)}] (1)

A solution of NBu₄[Ir₄(CO)₁₁] (50 mg, 0.045 mmol) and [Fe(η^5 -P₃C₂^tBu₂)(η^5 -C₅H₅)] (16 mg, 0.045 mmol) in CH₂Cl₂ (10 cm³ or mL, see above) was stirred at room temperature for 24 h. The solution was concentrated under vacuum to 1 cm³ and the mixture separated by TLC using CH₂Cl₂/hexane (3:7 v/v) as eluent to afford orange product **1**, which was recrystallised from the same solvent system (38 mg, 60%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CO) 2091s, 2058vs, 2035s, 2024s, 1970w, 1888w, 1854m and 1830m (hexane); ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 5.3 (s, 5H, C₅H₅), 1.6 (s, 9H, ^tBu) and 1.3 (s, 9H, ^tBu); ³¹P{¹H} NMR (121.4 MHz CD₂Cl₂/CS₂, 85 % H₃PO₄, -105 °C) δ (major isomer:1) -18.3 (d, ¹J(P₁P₂) 457 Hz, P₁), 8.9 (d, P₂) and 16.7 (s, P₃) and δ (minor isomer:0.15) -47.1 (d, ¹J(P₁P₂) 450Hz, P₁) 20.7 (d, P₂), 14.8 (d, P₃); ¹³C{¹H} NMR except CO region (75.4 MHz, CDCl₃ 25 °C) δ 76.1 (s, 5C, Cp), 38.8 [dd, ²J(CP) 17.4 and ³J(CP) 5.8 Hz, 1C, CMe₃], 38.3 [dd, ²J(CP) 15.3 and ³J(CP) 4.4 Hz, 1C, CMe₃], 35.8 [dd, ³J(CP) 10.9 and ³J(CP) 4.4 Hz, 3C, CCH₃], 35.5 [t, ³J(CP) 9.4 Hz, 3C, CCH₃]; *m/z* 1432 (M⁺, 34%), 1404 (30, M – CO) 1376 (13, M – 2CO), 1348 (17, M – 3CO), 1320 (31, M – 4CO), 1292 (23, M – 5CO), 1264 (18, M – 6CO), 1236 (100, M – 7CO), 1208 (34, M – 8CO), 1180 (9, M – 9CO), 1152 (12, M – 10CO) and 1124 (9, M – 11CO).

General procedure for the reduction of N-Boc 2-piperidinones

To a solution of the lactam (1.0 mmol) in THF (2.0 cm³) stirred at 0 °C was added borane dimethylsulfide complex (1.0 mmol). The reaction mixture was stirred for 18 h at room temperature and then quenched with methanol (5.0 cm³). The reaction mixture was concentrated under reduced pressure and repeatedly (4 \times) dissolved in methanol (3.0 cm³) and evaporated under reduced pressure. The product was purified by column chromatography on silica gel (eluent indicated for each case).

(2*RS*,5*RS*)-1-(*tert*-Butoxycarbonyl)-2,5-dimethylpiperidine (**19**). Eluent: hexane/ethyl acetate 2:1 (v/v); (0.183 g, 86%); colorless oil; IR $\nu_{\text{max}}/\text{cm}^{-1}$ 2966, 2933, 2861, 1692, 1475, 1310, 1261, 1155, 1078, 874 (film); ¹H NMR (CDCl₃, 300 MHz) δ 4.35 (m, 1H), 3.63 (d, ³J 13.4 Hz, 1H), 3.05 (dd, ³J 13.4 and 3.2 Hz, 1H), 1.7-1.9 (m, 3H), 1.45 (s, 9H), 1.25 (m, 2H), 1.13 (d, ³J 7.0 Hz,

3H), 0.97 (d, 3J 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 155.6, 78.9, 46.2, 43.7, 28.5, 27.9, 24.9, 24.8, 16.6, 16.2; HRMS (M^+) Found: 213.1725. Calc. for $\text{C}_{12}\text{H}_{23}\text{NO}_2$: 231.1729.

(*2RS,5SR*)-1-(*tert*-Butoxycarbonyl)-2-methyl-5-benzylpiperidine (**2I**). Eluent: hexane/ethyl acetate (1:1); (0,159 g, 55%); white solid, m.p. 48.5-50.0 °C (hexane); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3086, 3060, 2934, 2861, 1689, 1496, , 1363, 1150, 1056, 739, 700 (film); ^1H NMR (CDCl_3 , 500 MHz) δ 7.1-7.3 (m, 5H), 4.41 (m, 1H), 3.76 (d, 3J 13.7 Hz, 1H), 2.99 (dd, 3J 13.7 and 3.6 Hz, 1H), 2.74 (dd, 3J 13.6 and 8.3 Hz, 1H), 2.57 (dd, 3J 13.6 and 7.0 Hz, 1H), 1.95 (m, 2H), 1.75 (m, 1H), 1.46 (s, 9H), 1.3-1.5 (m, 2H), 1.14 (d, 3J 6.9 Hz, 3H). ^{13}C NMR (CDCl_3 , 125.7 MHz) δ 155.4, 141.1, 129.1, 128.2, 125.8, 79.1, 46.0, 41.2, 36.7, 35.5, 28.5, 25.0, 22.9, 16.0; HRMS (M^+) Found: 289.2041. Calc. for $\text{C}_{18}\text{H}_{27}\text{NO}_2$: 289.2042.