

# Molybdenum-mediated diastereoselective synthesis of 2-heterobicyclo[4.4.0]decene derivatives

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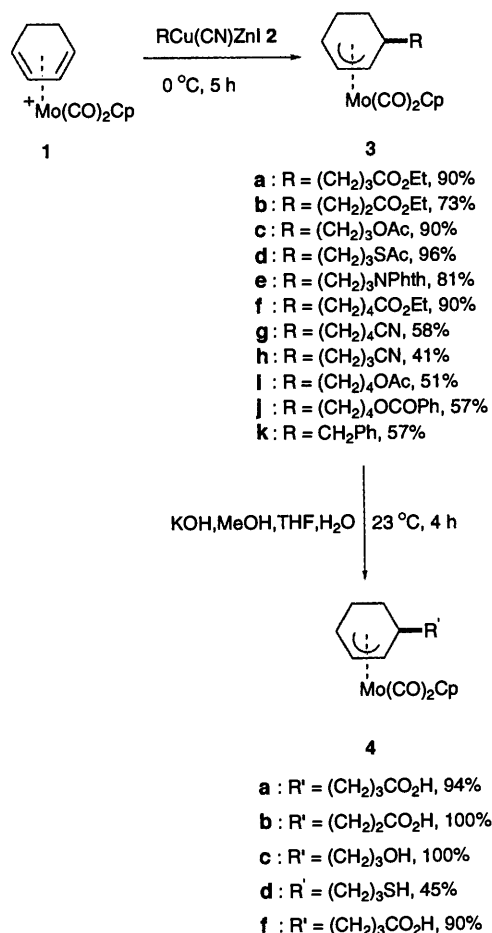
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The addition of a variety of functionalized zinc–copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$  2 to  $(\eta^5\text{-cyclopentadienyl})(\eta^4\text{-cyclohexa-1,3-diene})\text{dicarbonylmolybdenum}$  cation 1 proceeds in a highly regio- and stereo-specific fashion to generate  $(\eta^5\text{-cyclopentadienyl})(\pi\text{-allyl})\text{dicarbonylmolybdenum}$  complexes 3 with a functionalized side-chain at the C-4 position of the ring. Intramolecular cyclization of the  $(\pi\text{-allyl})\text{molybdenum}$  complexes containing a pendant alcohol, carboxylic acid, thiol or amine functionality affords fused 2-heterobicyclo[4.4.0]decene derivatives.

Nucleophilic attack on transition metal-complexed olefin, allyl, diene and dienyl systems is among the most useful of organometallic processes for the synthesis of complex organic molecules.<sup>1</sup> The addition of a wide variety of nucleophiles to  $(\eta^4\text{-diene})\text{tricarbonylmolybdenum}$  cationic complexes have been shown to be both stereo- and regio-specific.<sup>2–5</sup> The subsequent neutral molybdenum  $\pi\text{-allyl}$  intermediates can be re-activated for a second nucleophilic addition by conversion into cationic molybdenum.<sup>3,6–8</sup> This methodology has been developed to bring about stereocontrolled multiple functionalization of six- and seven-membered carbocyclic rings by a sequence of nucleophile additions.<sup>9,10</sup> Cleavage of the ring then allows access to acyclic subunits, which leads to the construction of building blocks for the synthesis of macrolide antibiotics.<sup>11</sup> We have previously demonstrated that addition of highly functionalized zinc–copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$  (also known as Knochel reagents) to the  $[\text{Mo}(\eta^4\text{-cyclohexa-1,3-diene})(\text{CO})_2(\text{Cp})]$  cation 1 occurred at the terminus of the diene system to furnish polyfunctionalized  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2\text{Cp}]$  complexes. Further activation of the resulting neutral  $(\pi\text{-allyl})\text{molybdenum}$  complexes can be accomplished by ligand exchange using  $\text{NOBF}_4$  or by hydride abstraction adding  $\text{Ph}_3\text{CPF}_6$ .<sup>12</sup> Intramolecular cyclization of the new cation containing an acid functionality produced a bicyclic  $\delta$ -lactone as the major product.<sup>12</sup> Here we report in full detail that the intramolecular cyclization can be extended to the  $(\pi\text{-allyl})\text{molybdenum}$  complexes containing an alcohol, thiol or amine functionality. Intramolecular cyclization of the complexes using  $\text{NOBF}_4\text{-Et}_3\text{N}$  furnishes bicyclo[4.4.0]decene derivatives with a hetero-atom at the C-2 position of the bicyclic rings.

Several classes of stabilized lithium enolates as well as non-stabilized enolates of simple esters, keto imines, hydrides, Grignard reagents and the cyano anion have been shown to add to cation 1.<sup>3,13</sup> Among these, the stabilized enolates add most efficiently to the cation. However, the reactions can only introduce a two-carbon atom side-chain at the C-4 position of the  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2(\text{Cp})]$  complexes.<sup>13</sup> Surprisingly, reports on the addition of organocopper derivatives to cation 1 are rare and the reactions proceed in low yields (*ca.* 35%).<sup>14</sup> Furthermore, organocuprates obtained from the corresponding lithium reagents and copper salts do not bear functional groups. With polyfunctional zinc–copper reagents,<sup>15</sup> however, the addition proceeded under mild reaction conditions. Thus, slow addition of a THF solution of the highly functionalized zinc–copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$  (1.2 mol. equiv, generated by transmetalation of the corresponding functionalized zinc organometallic compounds with  $\text{CuCN}\cdot 2\text{LiCl}$  in tetrahydrofuran) to a stirred suspension of cation 1 in THF at 0 °C for 5 h

under nitrogen, followed by work-up with saturated aqueous ammonium chloride, 50% ethyl acetate–hexanes extraction and flash column chromatography on silica yielded the  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2\text{Cp}]$  complexes 3a–k in fair to good yields (41–96%, Scheme 1). In general, the additions proceeded smoothly under

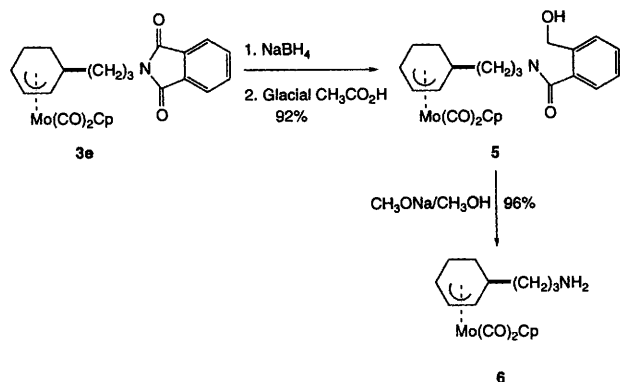


Scheme 1

our reaction conditions. However, the zinc–copper homoenoate of ethyl propionate 2b appeared to be less reactive.<sup>16</sup> However, with an excess of 2b (6.0 mol equiv.) and dimethylformamide (DMF) as solvent, we have successfully performed the addition in 73% yield. The relative stereochemistry at C-4 assigned as *exo* is based on the assumption that

attack of the zinc–copper reagents occurs from the opposite face of the Mo(CO)<sub>2</sub>Cp moiety, and the chemical shift value of  $\delta$  1.71 assigned for the proton at C-4 agrees closely with the values of the *endo* protons of most C-4-substituted [Mo( $\pi$ -allyl)(CO)<sub>2</sub>(Cp)] complexes reported in the literature.<sup>3,9</sup> Further manipulation of the resulting complexes **3** was demonstrated as follows.

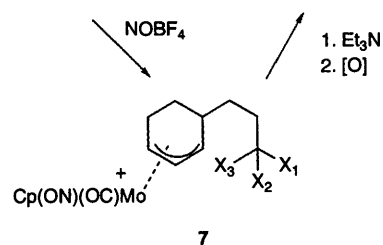
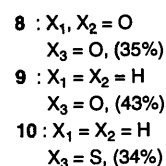
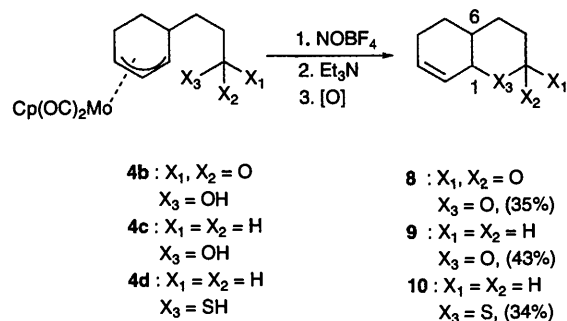
The ester (**3a,b,f**), acetoxy (**3c**) and thioacetoxy (**3d**) functionalities are readily deblocked in a basic solution to give the carboxylic acid (**4a,b,f**), alcohol (**4c**) and thiol (**4d**), respectively. Thus, hydrolysis of **3a–c,f** using potassium hydroxide in MeOH–THF–water at 23 °C gave acids **4a** (94%), **4b** (100%), alcohol **4c** (100%) and acid **4f** (90%), respectively (Scheme 1). However, complex **3d** with a thioacetoxy group was cleaved into the thiol **4d** in only 45% yield under the same reaction conditions. Deprotection of complex **3e** with a phthalimide derivative can be accomplished as follows: treatment of **3e** with 5.0 mol equiv. of sodium borohydride at room temperature under nitrogen for 24 h in propan-2-ol and water (v/v, 6:1) followed by addition of acetic acid gave the *o*-hydroxymethylbenzamide derivative **5** in 92% yield.<sup>17</sup> Reaction of **5** with sodium methoxide in refluxing methanol for 2 h generated the amino complex **6** in 96% yield (Scheme 2).<sup>18</sup>



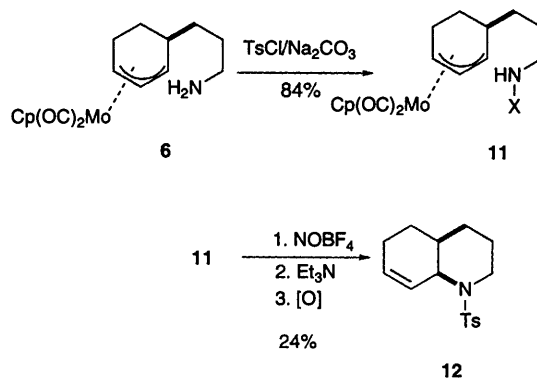
Scheme 2

### Intramolecular cyclizations

Our cyclisation study began with complex **4b**. Complex **4b** was first converted into nitrosyl cyclohexenyl cation **7b** by ligand exchange (NOBF<sub>4</sub>), followed by addition of triethylamine to produce the bicyclo[4.4.0]decene ring skeleton **8** (35%, two steps).<sup>12</sup> The lactone **8** was previously not accessible since the addition of lithium enolates to cation **1**<sup>19</sup> and the palladium-catalysed intramolecular 1,4-addition of cyclohexadiene acid derivatives<sup>20</sup> to give fused 3-oxo-2-azabicyclo[4.3.0]nonene ring systems could only introduce a two-carbon atom side-chain onto the six-membered ring. Alternatively, iodolactonisation of complex **4b** (I<sub>2</sub>; MeCN; 23 °C) also gave the  $\delta$ -lactone **8** in 27% yield. The *cis* stereochemistry of the  $\delta$ -lactone **8** was assigned based upon the coupling constant (5.0 Hz) of the adjacent 1-H and 6-H. This assignment is consistent with that for the *cis*- $\gamma$ -lactones reported by Pearson.<sup>19</sup> Under the same reaction conditions, intramolecular cyclization of the carboxylic acid **4a**, derived from **3a**, however, did not occur. This might be due to the difficulty of formation of the seven-membered ring. The success of intramolecular cyclization of the carboxylic acid **4b** prompted us to investigate the reaction of allylmolybdenum complexes containing an amine, thiol or alcohol group. Thus, complexes **4c** and **4d** after treatment with NOBF<sub>4</sub>, followed by addition of triethylamine, gave the heterobicyclic derivatives **9** (43%) and **10** (34%), respectively (Scheme 3). However, with a reactive amino group, for example complex **6**, intramolecular cyclization failed to occur under the same reaction conditions. The problem, however, can be solved by protection of the reactive amino group. Thus, treatment of **6** with toluenesulfonyl



Scheme 3



Scheme 4

chloride under base conditions generated the less active amide complex **11** in good yield (Scheme 4). Reactivation of **11** using NOBF<sub>4</sub>-generated nitrosyl cation, reacted with Et<sub>3</sub>N to provide bicyclic polyhydroquinoline derivative **12**.

In summary, we have shown that intramolecular molybdenum-mediated cycloaddition can be an effective method for the formation of 2-heterobicyclo[4.4.0]decene derivatives. The ability to achieve exclusive *cis* ring juncture in fused heterobicyclic compounds in a simple reaction may have further applications. Specifically, the preparation of more highly substituted systems for natural product synthesis would be expected to demonstrate still higher levels of stereocontrol.

### Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Tetrahydrofuran (THF) was distilled from a deep blue sodium–benzophenone ketyl solution under nitrogen, prior to use. Acetonitrile, methylene dichloride, hexamethylphosphoramide (HMPA) and *N,N*-dimethylformamide (DMF) were dried by stirring them over CaH<sub>2</sub> under nitrogen for 15 h, after which they were decanted and distilled under reduced pressure before storage over 4 Å molecular sieves under nitrogen. Copper cyanide (CuCN), 3-chloropropyl thioacetate were purchased from Aldrich Chemical Co. and used as received. Zinc particles (purity > 99.9%), ethyl 3-chloropropionate, ethyl 4-chlorobutyrate, ethyl 5-chlorovalerate, 4-chlorobutyronitrile and 5-chlorovaleronitrile were purchased from Merck Co. and used without further purification. Functionalized alkyl iodides are synthesized by refluxing the corresponding alkyl chlorides

with an excess of sodium iodide in refluxing acetone. 4-Iodobutyl benzoate was synthesized by reaction of THF, sodium iodide, and benzoyl chloride.<sup>21</sup> Functionalized zinc–copper reagents<sup>15,22</sup> and cation **1**<sup>3</sup> were prepared according to a literature procedure.<sup>15,22</sup> Flash column chromatography, following the method of Still,<sup>23</sup> was carried out using Merck Kieselgel 60 H silica using the indicated solvent. <sup>1</sup>H NMR nuclear magnetic resonance (NMR) spectra were obtained with a JEOL-EX 400 (400-MHz) spectrometer. Chemical shifts are reported in ppm with either tetramethylsilane (0.00 ppm) or CDCl<sub>3</sub> (7.26 ppm) as internal standard. <sup>13</sup>C NMR spectra were recorded with a JEOL-EX 400 (100.4-MHz) spectrometer with CDCl<sub>3</sub> (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded in the range of 4000–600 cm<sup>-1</sup> using a JASCO IR-700 spectrometer. Mass spectra were measured on a JEOL JMS-D 100 spectrometer at an ionization potential of 30 eV and were reported as mass/charge (*m/z*). High-resolution mass spectra (HRMS) were obtained with an AEI MS-9 double-focusing mass spectrometer at the Department of Chemistry, Northern Instrument Center, Hsin Chu, Taipei, R.O.C.

**General procedure for addition of functionalized zinc–copper reagents to dicarbonyl(η<sup>5</sup>-cyclopentadienyl)(η<sup>5</sup>-cyclohexa-1,3-diene)molybdenum cation **1****

A solution of functionalized zinc–copper reagents<sup>15</sup> (3.0 mol. equiv.) in THF (5.0 ml) was added to a stirred suspension of cation **1**<sup>3</sup> in THF (5.0 ml) at 0 °C under nitrogen. A homogeneous solution was obtained by stirring the reaction mixture at 0 °C for 5 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride at 0 °C and diluted with 50% ethyl acetate–hexanes (100 ml). The resultant solution was washed with water (100 ml × 3) and brine (100 ml × 3), dried (MgSO<sub>4</sub>) (10 g) and concentrated to give the crude mixture.

**Dicarbonyl(η<sup>5</sup>-cyclopentadienyl){ethyl *exo*-4-[(1-3-η)-cyclohex-1-en-4-yl]butyrate}molybdenum **3a****

The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3.0 mmol) to cation **1** (0.44 g, 1.0 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) to give complex **3a** (0.4 g, 90%) as a yellow oil (Found: M<sup>+</sup>, 414.0709. Requires *M*, 414.0728); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3078, 2972, 1934, 1851, 1727, 1606, 1459, 1430, 1375, 1349, 1304, 1241, 1192, 1096, 1029, 934 and 911; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.29 (5 H, s, Cp), 4.16–4.11 (3 H, m, 2-H and 11-H), 3.70 (1 H, m, 1-H or 3-H), 3.63 (1 H, m, 1-H or 3-H), 2.27–2.33 (3 H, m, 4-H and 9-H), 1.95 (1 H, m, 6-H), 1.73–1.42 (5 H, m, 6-H, 7-H and 8-H), 1.25 (3 H, dd, *J* 6.91, 6.78, 12-H), 0.86 (1 H, m, 5-H) and 0.50 (1 H, m, 5-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 236.0 (CO), 235.5 (CO), 173.7 (CO<sub>2</sub>Et), 92.0 (Cp), 60.2 (OCH<sub>2</sub>), 58.6 (2-C), 56.9 (1-C), 55.7 (3-C), 38.8 (6-C), 34.5 (5-C), 31.5 (4-C), 23.5 (12-C), 23.3 (7-C), 18.7 (8-C) and 14.2 (9-C); *m/z* (EI) 414 (M<sup>+</sup>), 386, 358, 356, 297, 115 and 87.

**Dicarbonyl(η<sup>5</sup>-cyclopentadienyl){ethyl *exo*-3-[(1-3-η)-cyclohex-1-en-4-yl]propionate}molybdenum **3b****

The crude mixture obtained from the addition of the corresponding zinc–copper reagent (9.0 mmol) to cation **1** (1.35 g, 3.0 mmol) in DMF (10 ml) was purified by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) to give complex **3b** (0.87 g, 73%) as a yellow oil (Found: M<sup>+</sup>, 400.0576. Requires *M*, 400.0566); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3050, 2936, 1933, 1852, 1726, 1447, 1423, 1373, 1183, 1112, 1071 and 1034; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.26 (5 H, s, Cp), 4.16–4.07 (3 H, m, 2-H and 11-H), 3.68 (1 H, m, 1-H or 3-H), 3.56 (1 H, m, 1-H or 3-H), 2.35 (2 H, t, *J* 7.8, 8-H), 1.93 (m, 1 H, 4-H), 1.82 (1 H, m, 6-H), 1.71 (2 H, m, 6-H and 7-H), 1.67 (1 H, m, 7-H), 1.23 (3 H, t, *J* 7.1, 11-H), 0.79 (1 H, m, 5-H) and 0.46 (1 H, m, 5-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 235.9 (CO), 235.4 (CO), 173.9 (CO<sub>2</sub>Et), 92.1 (Cp), 60.3 (OCH<sub>2</sub>), 57.8 (2-C), 57.0 (1-C), 55.8 (3-C), 34.1 (6-C), 33.1 (5-C), 31.6 (4-C), 23.1 (11-C), 18.7 (7-C) and 14.2 (8-C); *m/z* (EI) 400 (M<sup>+</sup>), 372, 344, 342, 341, 340, 339, 338 and 336.

**Dicarbonyl(η<sup>5</sup>-cyclopentadienyl){*exo*-3-[(1-3-η)-cyclohex-1-en-4-yl]propyl acetate}molybdenum **3c****

The crude mixture obtained from the addition of the corresponding zinc–copper reagent (10 mmol) to cation **1** (1.56 g, 3.5 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) to give complex **3c** (1.26 g, 90%) as a yellow oil (Found: M<sup>+</sup>, 400.0566. Requires *M*, 400.0566); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3066, 3050, 2984, 2940, 1934, 1851, 1731, 1653 and 1244; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.29 (5 H, s, Cp), 4.16 (1 H, t, *J* 6.9, 2-H), 4.07 (2 H, t, *J* 6.8, 9-H), 3.71 (1 H, m, 1-H or 3-H), 3.61 (1 H, m, 1-H or 3-H), 2.05 (3 H, s, 11-H), 1.95 (1 H, m, 4-H), 1.75–1.67 (3 H, m, 6-H and 7-H), 1.59–1.40 (3 H, m, 7-H and 8-H), 0.83 (1 H, m, 5-H) and 0.49 (1 H, m, 5-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 235.9 (CO), 235.3 (CO), 171.1, 92.0 (Cp), 64.8 (9-C), 58.4 (2-C), 56.9 (1-C), 55.7 (3-C), 35.5 (6-C), 31.6 (11-C), 27.2 (5-C), 23.2 (4-C), 20.9 (7-C) and 18.7 (8-C); *m/z* (EI) 400 (M<sup>+</sup>), 372, 370, 346, 344, 343, 342, 341, 340 and 338.

**Dicarbonyl(η<sup>5</sup>-cyclopentadienyl){*exo*-3-[(1-3-η)-cyclohex-1-en-4-yl]propylthioacetate}molybdenum **3d****

The crude mixture obtained from the addition of the corresponding zinc–copper reagent (9.0 mmol) to complex **1** (2.2 g, 5.0 mmol, in DMF) (10 ml) was purified by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) to give complex **3d** (1.98 g, 96%) as a yellow oil (Found: M<sup>+</sup>, 416.0340. Requires *M*, 416.0338); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2934, 1935, 1853, 1688, 1609, 1452, 1356 and 1134; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.28 (5 H, s, Cp), 4.15 (1 H, t, *J* 7.0, 2-H), 3.69 (1 H, m, 1-H or 3-H), 3.60 (1 H, m, 1-H or 3-H), 2.87 (2 H, t, *J* 7.3, 9-H), 2.33 (3 H, s, 11-H), 1.94 (1 H, m, 4-H), 1.69–1.41 (6 H, m, 6-H, 7-H, 8-H), 0.86 (1 H, m, 5-H) and 0.49 (1 H, m, 5-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 235.9 (CO), 235.4 (CO), 195.9 (10-C), 92.0 (Cp), 58.4 (2-C), 56.9 (1-C), 55.7 (3-C), 38.4 (9-C), 31.6 (6-C), 30.6 (5-C), 29.4 (4-C), 28.2 (11-C), 23.3 (7-C) and 18.7 (8-C); *m/z* (EI) 416 (M<sup>+</sup>), 415, 414, 413, 412, 410, 390, 362, 360, 359, 358, 357, 356 and 354.

**Dicarbonyl(η<sup>5</sup>-cyclopentadienyl){*exo*-3-[(1-3-η)-1-cyclohex-1-en-4-yl]-*N*-propylphthalimide}molybdenum **3e****

The crude mixture obtained from the addition of the corresponding zinc–copper reagent (5.0 mmol) to cation **1** (0.81 g, 2.1 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) to give complex **3e** (0.80 g, 81%) as a yellow solid (Found: M<sup>+</sup>, 487.0681. Requires *M*, 487.0675); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3059, 3064, 2988, 1935, 1852, 1713, 1615, 1439, 1368, 1260 and 1111; δ<sub>H</sub>(CDCl<sub>3</sub>) 7.85 (2 H, m, 12-H and 15-H), 7.20 (2 H, m, 13-H and 14-H), 5.27 (5 H, s, Cp), 4.14 (1 H, t, *J* 7.0, 2-H), 3.69 (3 H, m, 1-H and 9-H), 3.59 (1 H, m, 3-H), 1.94 (1 H, m, 4-H), 1.81–1.73 (3 H, m, 6-H and 7-H), 1.57–1.41 (3 H, m, 7-H and 8-H), 0.83 (1 H, m, 5-H) and 0.49 (1 H, m, 5-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 168.5 (10-C and 17-C), 133.9 (13-C and 14-C), 132.2 (11-C and 16-C), 123.2 (12-C and 15-C), 92.1 (Cp), 58.3 (2-C), 56.9 (1-C), 55.8 (3-C), 38.3 (9-C), 36.4 (6-C), 31.6 (4-C), 27.3 (5-C), 23.3 (7-C) and 18.7 (8-C); *m/z* (EI) 487 (M<sup>+</sup>), 433, 431, 430, 429, 428, 427 and 425.

**Dicarbonyl(η<sup>5</sup>-cyclopentadienyl){ethyl *exo*-4-[(1-3-η)-cyclohex-1-en-4-yl]pentanoate}molybdenum **3f****

The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3.0 mmol) to cation **1** (0.44 g, 1 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) to give complex **3f** (0.38 g, 90%) as a yellow oil (Found: M<sup>+</sup>, 428.0887. Requires *M*, 428.0885); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2990, 1932, 1849, 1731, 1373, 1242 and 1046; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.28 (5 H, s, Cp), 4.18 (3 H, m, 2-H and 12-H), 3.72 (1 H, m, 1-H or 3-H), 3.63 (1 H, m, 1-H or 3-H), 2.30 (2 H, t, *J* 7.32, 10-H), 1.95 (1 H, m, 6-H), 1.71–1.39 (8 H, m, 4-H, 6-H, 7-H, 8-H and 9-H), 1.26 (3 H, t, *J* 7.32, 13-H), 0.82 (1 H, m, 5-H) and 0.50 (1 H, m, 5-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 236.0 (CO), 235.5 (CO), 173.7 (CO<sub>2</sub>Et), 92.0 (Cp), 60.2 (OCH<sub>2</sub>), 59.0 (2-C), 56.8 (1-C), 55.7 (3-C), 39.0 (6-C), 34.3 (5-C), 31.7 (4-C), 27.7 (10-C),

25.2 (7-C), 23.2 (8-C), 18.7 (9-C) and 14.2 (13-C);  $m/z$  (EI) 428 ( $M^+$ ), 372, 370 and 297.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-4-[(1-3- $\eta$ )-1-cyclohex-1-en-4-yl]valeronitrile}molybdenum 3g**

The crude mixture obtained from the addition of the corresponding zinc-copper reagent (3.0 mmol) to cation **1** (0.44 g, 1.0 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate-90% hexanes) to give complex **3g** (0.23 g, 58%) as a yellow oil (Found:  $M^+$ , 381.0630. Requires  $M$ , 381.0626);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3082, 2932, 2306, 1933, 1851, 1609, 1458, 1275, 1182, 1160, 1113 and 1011;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.29 (5 H, s, Cp), 4.16 (1 H, m, 2-H), 3.69 (1 H, m, 1-H or 3-H), 3.59 (1 H, m, 1-H or 3-H), 2.36 (2 H, t,  $J$  7.32, 10-H), 1.96 (1 H, m, 6-H), 1.78-1.57 (7 H, m, 7-H, 8-H, 9-H and 4-H), 1.25 (1 H, m, 6-H), 0.79 (1 H, m, 5-H) and 0.51 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  235.0 (CO), 234.4 (CO), 118.8 (11-C), 91.1 (Cp), 57.3 (2-C), 55.9 (1-C), 54.7 (3-C), 37.5 (6-C), 30.6 (5-C), 26.2 (4-C), 24.6 (7-C), 22.4 (8-C), 17.8 (9-C) and 16.2 (10-C);  $m/z$  (EI) 381 ( $M^+$ ), 325, 323, 295 and 241.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-4-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]butyronitrile}molybdenum 3h**

The crude mixture obtained from the addition of the corresponding zinc-copper reagent (3.0 mmol) to cation **1** (0.44 g, 1.0 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate-90% hexanes) to give complex **3h** (0.23 g, 41%) as a yellow oil (Found:  $M^+$ , 367.0450. Requires  $M$ , 367.0470);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3060, 2930, 2306, 1935, 1853, 1606, 1423, 1277, 1252, 1160, 1113 and 1011;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.29 (5 H, s, Cp), 4.15 (1 H, m, 2-H), 3.71 (1 H, m, 1-H or 3-H), 3.58 (1 H, m, 1-H or 3-H), 2.34 (2 H, m, 9-H), 1.96 (1 H, m, 6-H), 1.78-1.57 (5 H, m, 7-H, 8-H and 4-H), 1.24 (1 H, m, 6-H), 0.79 (1 H, m, 5-H) and 0.51 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  235.9 (CO), 234.9 (CO), 120.0 (10-C), 92.1 (Cp), 58.0 (2-C), 57.0 (1-C), 55.7 (3-C), 38.2 (6-C), 31.3 (5-C), 24.0 (4-C), 23.2 (7-C), 18.6 (8-C) and 17.4 (9-C);  $m/z$  (EI) 367 ( $M^+$ ), 313, 311, 309, 243, 148, 130, 119 and 79.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){4-*exo*-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]butyl acetate}molybdenum 3i**

The crude mixture obtained from the addition of the corresponding zinc-copper reagent to cation **1** was purified by flash column chromatography (silica gel, 10% ethyl acetate-90% hexanes) to give complex **3i** (0.21 g, 51%) as a yellow oil (Found:  $M^+$ , 414.0739. Requires  $M$ , 414.0729);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3062, 2936, 1934, 1851, 1731, 1606, 1425, 1367, 1240, 1038 and 909;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.30 (5 H, s, Cp), 4.18-4.03 (3 H, m, 2-H and 10-H), 3.71-3.60 (2 H, m, 1-H and 3-H), 2.31 (1 H, m, 4-H), 2.06 (3 H, s, 12-H), 1.95 (1 H, m, 6-H), 1.66-1.22 (7 H, m, 6-H, 7-H, 8-H and 9-H), 0.8 (1 H, m, 5-H) and 0.5 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.0 (CO), 235.6 (CO), 171.2 (11-C), 92.0 (Cp), 64.5 (10-C), 58.9 (2-C), 56.9 (1-C), 55.7 (3-C), 38.9 (6-C), 31.7 (5-C), 28.8 (4-C), 24.5 (12-C), 23.2 (7-C), 21.0 (8-C) and 18.7 (9-C);  $m/z$  (EI) 414 ( $M^+$ ), 358, 356, 243, 210, 152, 94, 91, 80 and 65.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-4-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]butylbenzoate}molybdenum 3j**

The crude mixture obtained from the addition of the corresponding zinc-copper reagent (3.0 mmol) to cation **1** (0.44 g, 1.0 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate-90% hexanes) to give complex **3j** (0.27 g, 57%) as a yellow oil (Found:  $M^+$ , 476.0875. Requires  $M$ , 476.0885);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3085, 2936, 1934, 1851, 1712, 1605, 1439, 1423, 1314, 1254, 1176, 1118, 1071 and 1027;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.05-8.00 (2 H, m, arom.), 7.54-7.39 (3 H, m, arom.), 5.26 (5 H, s, Cp), 4.31 (2 H, dd,  $J$  6.50, 6.59, 10-H), 4.12 (1 H, dd,  $J$  7.18, 7.19, 2-H), 3.68-3.58 (2 H, m, 1-H and 3-H), 1.90 (1 H, m, 6-H), 1.75 (1 H, m, 4-H), 1.58-1.48 (5 H, m, 7-H, 8-H and 9-H), 1.27 (1 H, m, 9-H), 0.86-0.79 (2 H, m, 5-H and 6-

H) and 0.45 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.1 (CO), 235.5 (CO), 166.6 (12-C), 132.8 (13-C), 130.5 (14-C), 129.5 (15-C), 128.3 (16-C), 92.0 (Cp), 64.9 (OCH<sub>2</sub>), 58.9 (2-C), 56.9 (1-C), 55.7 (3-C), 38.9 (6-C), 31.7 (5-C), 28.9 (4-C), 24.6 (7-C), 23.3 (8-C) and 18.7 (9-C);  $m/z$  (EI) 476 ( $M^+$ ), 448, 418, 285, 256, 239, 105 and 91.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-4-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]phenylmethyl}molybdenum 3k**

The crude mixture obtained from the addition of the corresponding zinc-copper reagent (3.0 mmol) to cation **1** (0.44 g, 1.0 mmol) was purified by flash column chromatography (silica gel, 10% ethyl acetate-90% hexanes) to give complex **3k** (0.22 g, 57%) as a yellow oil (Found:  $M^+$ , 390.0511. Requires  $M$ , 390.0517);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3060, 2930, 1935, 1852, 1606, 1425, 1253 and 1010;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.26-7.08 (5 H, m, arom.), 5.22 (5 H, s, Cp), 4.12 (1 H, dd,  $J$  7.18, 7.14, 2-H), 3.67 (1 H, m, 1-H or 3-H), 3.45 (1 H, m, 1-H or 3-H), 2.68 (1 H, m, 7-H), 1.99-1.92 (2 H, m, 4-H and 6-H), 1.57 (1 H, m, 6-H), 0.77 (1 H, m, 5-H) and 0.38 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  235.9 (CO), 235.4 (CO), 141.2 (8-C), 129.2 (9-C), 128.2 (10-C), 125.8 (11-C), 92.0 (Cp), 58.4 (2-C), 56.7 (1-C), 55.9 (3-C), 45.7 (6-C), 34.0 (5-C), 22.9 (4-C) and 18.6 (7-C);  $m/z$  (EI) 390 ( $M^+$ ), 362, 334, 243, 241, 91, 80 and 79.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-4-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]butanoic acid}molybdenum 4a**

A solution of the ester complex **3a** (0.42 g, 1.0 mmol) in 1:1 methanol-THF (10 ml) was stirred while a solution of potassium hydroxide (0.33 g) in water (5 ml) was added. Stirring was continued for 4 h, whilst the progress of the reaction was monitored by TLC. The reaction mixture was poured onto 10% HCl-ice and the product was extracted with ethyl acetate-hexanes (1:1; 100 ml  $\times$  3). The combined extracts were washed with water (100 ml  $\times$  3), dried ( $\text{MgSO}_4$ ) and concentrated to give the crude mixture. This was purified by flash column chromatography (silica gel, 33% ethyl acetate-67% hexanes) to give the acid **4a** (0.36 g, 0.9 mmol, 94%) as a yellow solid (Found:  $M^+$ , 386.0423. Requires  $M$ , 386.0416);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3022, 2938, 1935, 1852, 1714, 1620, 1524, 1425, 1234, 1130, 1083 and 1013;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.28 (5 H, s, Cp), 4.15 (1 H, dd,  $J$  7.32, 7.36, 2-H), 3.70 (1 H, m, 1-H or 3-H), 3.62 (1 H, m, 1-H or 3-H), 2.37 (2 H, t,  $J$  7.32, 9-H), 1.98 (1 H, m, 6-H), 1.75-1.69 (3 H, m, 4-H and 8-H), 1.55-1.45 (3 H, m, 6-H and 7-H), 0.80 (1 H, m, 5-H) and 0.50 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.0 (CO), 235.5 (CO), 179.5 (10-C), 92.1 (Cp), 58.4 (2-C), 56.9 (1-C), 55.8 (3-C), 34.2 (6-C), 32.2 (9-C), 32.0 (5-C), 31.6 (4-C), 23.3 (7-C) and 18.7 (8-C);  $m/z$  (EI) 386 ( $M^+$ ), 358, 330, 324, 278, 243, 241, 180, 162, 79 and 65.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-3-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]propanoic acid}molybdenum 4b**

The crude mixture obtained from the hydrolysis of the corresponding complex **3b** (0.23 g, 0.57 mmol) was purified by flash column chromatography (silica gel, 33% ethyl acetate-67% hexanes) to give complex **4b** (0.23 g, 100%) as a yellow oil (Found:  $M^+$ , 372.0255. Requires  $M$ , 372.0254);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3085, 2932, 1934, 1852, 1707, 1606, 1422, 1292 and 1131;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.29 (5 H, s, Cp), 4.17 (1 H, t,  $J$  7.0, 2-H), 3.70 (1 H, m, 1-H or 3-H), 3.58 (1 H, m, 1-H or 3-H), 2.44 (2 H, t,  $J$  8.0, 8-H), 1.97 (1 H, m, 4-H), 1.84 (1 H, m, 6-H), 1.72 (2 H, m, 6-H and 7-H), 1.60 (1 H, m, 7-H), 0.81 (1 H, m, 5-H) and 0.51 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  235.9 (CO), 235.3 (CO), 179.4 (9-C), 92.1 (Cp), 57.4 (2-C), 57.0 (1-C), 55.8 (3-C), 33.8 (6-C), 32.7 (5-C), 31.5 (8-C), 23.1 (4-C) and 18.7 (7-C);  $m/z$  (EI) 372 ( $M^+$ ), 316, 314, 313, 312, 311, 310 and 308.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-3-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]propanol}molybdenum 4c**

The crude mixture obtained from the hydrolysis of the corresponding complex **3c** (1.22 g, 3.07 mmol) was purified by flash column chromatography (silica gel, 33% ethyl acetate-67% hexanes) to give complex **4c** (1.10 g, 3.07 mmol, 100%) as a

yellow oil (Found:  $M^+$ , 358.0461. Requires  $M$ , 358.0308);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3072, 3048, 2938, 1933, 1850, 1653, 1425 and 1051;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.29 (5 H, s, Cp), 4.16 (1 H, t,  $J$  7.0, 2-H), 3.70–3.63 (4 H, m, 1-H, 3-H and 9-H) 1.97 (1 H, m, 4-H), 1.70–1.41 (6 H, m, 6-H, 7-H and 8-H), 0.84 (1 H, m, 5-H) and 0.49 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.1 (CO), 235.4 (CO), 92.0 (Cp), 63.1 (9-C), 58.8 (2-C), 56.9 (1-C), 55.7 (3-C), 35.3 (6-C), 31.6 (5-C), 31.3 (4-C), 20.9 (7-C) and 18.7 (8-C);  $m/z$  (EI) 358 ( $M^+$ ), 356, 304, 302, 301, 300, 299, 298 and 296.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-3-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]propanethiol}molybdenum 4d**

The crude mixture obtained from the hydrolysis of the corresponding complex **3d** (0.37 g, 0.89 mmol) was purified by flash column chromatography (silica gel, 33% ethyl acetate–67% hexanes) to give complex **4d** (0.15 g, 40 mmol, 45%) as a yellow oil (Found:  $M^+$ , 374.0236. Requires  $M$ , 374.0233);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3056, 2988, 2932, 1933, 1852, 1611, 1453 and 1111;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.29 (5 H, s, Cp), 4.16 (1 H, t,  $J$  7.0, 2-H), 3.70 (1 H, m, 1-H or 3-H), 3.61 (1 H, m, 1-H or 3-H), 2.68 (2 H, t,  $J$  7.1, 9-H), 1.97 (1 H, m, 4-H), 1.81–1.44 (6 H, m, 6-H, 7-H and 8-H), 0.84 (1 H, m, 5-H) and 0.50 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.1 (CO), 235.4 (CO), 92.0 (Cp), 58.6 (2-C), 56.9 (1-C), 55.7 (3-C), 39.2 (6-C), 38.0 (9-C), 31.6 (5-C), 27.7 (4-C), 23.2 (7-C) and 18.7 (8-C);  $m/z$  (EI) 374 ( $M^+$ ), 320, 318, 317, 316, 315, 314 and 312.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*N*-(*o*-hydroxymethylbenzoyl)-*exo*-3-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]propylamine}molybdenum 5**

To a stirred solution of **3e** (0.52 g, 1.07 mmol) in propan-2-ol (12.0 ml) and water (2.0 ml) was added  $\text{NaBH}_4$  (8.0 mmol). The mixture was stirred for 24 h, after which TLC indicated complete consumption of starting material. Excess of hydride was then decomposed with glacial acetic acid (2.0 ml). The reaction mixture was concentrated *in vacuo*, diluted with water and filtered to give complex **5** (0.48 g, 92%) as a yellow solid (Found:  $M^+$ , 473.0889. Requires  $M$ , 473.0882);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3437, 3056, 2936, 1935, 1852, 1647, 1526, 1424, 1278 and 1105;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.54–7.35 (4 H, m, 12-H, 13-H, 14-H and 15-H), 6.47 (1 H, m, NH), 5.29 (5 H, s, Cp), 4.60 (2 H, d,  $J$  6.3, 9-H), 4.48 (1 H, m, OH), 4.17 (1 H, t,  $J$  7.0, 2-H), 3.71 (1 H, m, 1-H or 3-H), 3.63 (1 H, m, 1-H or 3-H), 3.46 (2 H, m, 17-H), 1.96 (1 H, m, 4-H), 1.72–1.48 (6 H, m, 6-H, 7-H, 8-H), 0.84 (1 H, m, 5-H) and 0.52 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.1 (CO), 235.4 (CO), 170.0 (16-C), 140.1 (11-C), 135.9 (14-C), 131.2 (10-C), 130.8 (13-C), 128.2 (12-C), 127.5 (15-C), 92.1 (Cp), 64.7 (17-C), 58.4 (2-C), 56.9 (3-C), 55.7 (1-C), 40.5 (9-C), 36.6 (6-C), 31.8 (5-C), 28.3 (4-C), 23.3 (7-C), 18.7 (8-C);  $m/z$  (EI) 473 ( $M^+$ ), 447, 445, 444, 443, 442, 441, 439, 419, 417, 416, 415, 414, 413 and 411.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*exo*-3-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]propylamine}molybdenum 6**

The complex **5** (0.74 g, 1.5 mmol) was dissolved in a solution of  $\text{MeONa-MeOH}$  [sodium (0.16 g, 7.0 mmol) in  $\text{MeOH}$  (15 ml)] and the mixture refluxed for 2 h. It was then poured onto 10% aq.  $\text{HCl}$ -ice and extracted with ethyl acetate–hexanes (1 : 1; 100 ml  $\times$  2). The combined extracts were washed with water (100 ml  $\times$  2), dried ( $\text{MgSO}_4$ ), and concentrated to give the crude mixture. The crude mixture was purified by flash column chromatography (silica gel, 33% ethyl acetate–67% hexanes) to give the complex **6** (0.71 g, 96%) as a yellow oil (Found:  $M^+$ , 357.0643. Requires  $M$ , 357.0621);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3378, 3057, 2932, 2851, 1932, 1850, 1671, 1580, 1453, 1402, 1269 and 1113;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.29 (5 H, s, Cp), 4.15 (3 H, m, 2-H and 9-H), 3.70 (1 H, m, 1-H or 3-H), 3.62 (1 H, m, 1-H or 3-H), 2.78 (2 H, m,  $\text{NH}_2$ ), 1.97–1.94 (2 H, m, 6-H), 1.69–1.43 (5 H, m, 4-H, 7-H, 8-H), 0.83 (1 H, m, 5-H) and 0.53 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.0 (CO), 235.4 (CO), 92.2 (Cp), 58.6 (2-C), 56.9 (1-C), 55.8 (3-C), 53.5 (9-C), 36.4 (6-C), 31.7 (5-C), 29.0 (4-C), 23.3 (7-C) and 18.7 (8-C);  $m/z$  (EI) 357 ( $M^+$ ), 303, 301, 300, 299, 298, 297 and 295.

**General procedure for intramolecular cyclization of complexes 4b–d**

**Synthesis of 2-heterobicyclo[4.4.0]decene derivatives 8–10.** To a stirred solution of each of complexes **4b–d** in  $\text{Me}_3\text{CN}$  (10 ml) at 0 °C was added  $\text{NOPF}_6$  (1.5 mol equiv.) in one portion. The resultant mixture was stirred for 15 min after which it was treated dropwise with  $\text{Et}_3\text{N}$  (1.5 mol equiv.) and stirring continued for a further 15 min. The mixture was poured into water (50 ml) and extracted with 50% ethyl acetate–hexanes (50  $\times$  2 ml). The combined extracts were washed with brine (50 ml), 10% aqueous  $\text{HCl}$  (50 ml) and water (50  $\times$  2 ml), dried ( $\text{MgSO}_4$ ), and evaporated to give the crude mixture.

(1*R*\*,6*R*\*)-2-Oxa-3-oxobicyclo[4.4.0]dec-9-ene **8**.—The crude mixture from the intramolecular cyclization of complex **4b** (0.06 g, 0.16 mmol) and  $\text{NOBF}_4$  (0.03 g, 0.24 mmol) in  $\text{Et}_3\text{N}$  (0.03 ml) was purified by flash column chromatography (silica gel, 25% ethyl acetate–75% hexanes) to afford lactone **8** (8.4 mg, 35%) (Found:  $M^+$ , 152.0928. Requires  $M$ , 152.0834);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3022, 2930, 1724, 1432, 1360, 1335, 1206 and 1048;  $\delta_{\text{H}}(\text{CDCl}_3)$  6.02 (1 H, m, 4-H), 5.82 (1 H, m, 3-H), 4.78 (1 H, m, 2-H), 2.52 (2 H, m, 8-H), 2.21–2.00 (4 H, m, 5-H, 1-H and 6-H) and 1.73–1.60 (3 H, m, 6-H and 7-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  172.1 (9-C), 132.7 (3-C or 4-C), 124.5 (3-C or 4-C), 74.9 (2-C), 30.9 (1-C), 28.3 (8-C), 24.1 (5-C), 24.0 (6-C) and 23.7 (7-C);  $m/z$  (EI) 152 ( $M^+$ ), 124, 96, 80, 67 and 55.

3,4,4a,5,6,8a-Hexahydro-(4a $\alpha$ ,8a $\alpha$ )-2H-benzo[b]pyran **9**.—The crude mixture from intramolecular cyclization of complex **4c** (0.65 g, 1.84 mmol) and  $\text{NOBF}_4$  (0.23 g, 1.84 mmol) in  $\text{Et}_3\text{N}$  (0.3 ml) was purified by flash column chromatography (silica gel, 25% ethyl acetate–75% hexanes) to afford a single pyran **9** (0.11 g, 43%) (Found:  $M^+$ , 138.1047. Requires  $M$ , 138.1041);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3064, 3030, 2936, 2858, 1652, 1444, 1435, 1095 and 1064;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.87 (1 H, m, 7-H), 5.70 (1 H, m, 8-H), 3.84 (2 H, m, 2-H and 8a-H), 3.44 (1 H, m, 2-H), 2.12–1.61 (7 H, m, 4a-H, 6-H, 5-H, 4-H) and 1.38 (2 H, m, 3-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  132.0 (7-C or 8-C), 127.1 (7-C or 8-C), 71.9 (8a-C), 67.3 (2-C), 33.2 (4a-C), 27.9 (6-C), 25.4 (5-C), 22.9 (4-C) and 22.5 (3-C);  $m/z$  (EI) 138 ( $M^+$ ), 137, 122, 109, 97, 69, 55, 41 and 28.

3,4,5,6,8a-Hexahydro-(4a $\alpha$ ,8a $\alpha$ )-2H-benzo[b]thiopyran **10**.—The crude mixture from intramolecular cyclization of complex **4d** (0.4 g, 1.06 mmol) and  $\text{NOBF}_4$  (0.19 g, 1.62 mmol) in  $\text{Et}_3\text{N}$  (0.3 ml) was purified by flash column chromatography (silica gel, 25% ethyl acetate–75% hexanes) to afford a single thiopyran **10** (0.06 g, 34%) (Found:  $M^+$ , 154.0814. Requires  $M$ , 154.0813);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3029, 2928, 2856, 1603, 1439 and 1097;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.76 (1 H, m, 7-H), 5.67 (1 H, m, 8-H), 3.50 (1 H, m, 8a-H), 2.54 (2 H, m, 2-H), 2.22–2.03 (4 H, m, 4a-H, 6-H and 5-H) and 1.82–1.41 (5 H, m, 5-H, 4-H, 3-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.8 (7-C or 8-C), 128.0 (7-C or 8-C), 40.6 (8a-C), 33.5 (2-C), 30.1 (4a-C), 28.4 (6-C), 24.8 (5-C), 24.1 (4-C) and 23.6 (3-C);  $m/z$  (EI) 154 ( $M^+$ ), 118, 90, 76, 55, 41 and 28.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl){*N*-(*p*-tolylsulfonyl)-*exo*-3-[(1-3- $\eta$ )-cyclohex-1-en-4-yl]propylamine}molybdenum 11**

Treatment of complex **6** (0.25 g, 0.70 mmol) and saturated aqueous sodium carbonate (3 ml) in chloroform (5 ml) with toluene-*p*-sulfonyl chloride (0.27 g, 1.4 mmol) under nitrogen at 25 °C for 24 h gave complex **11** (0.3 g, 84%) as a yellow oil after purification of the crude mixture by flash column chromatography (silica gel, 10% ethyl acetate–90% hexanes) (Found:  $M^+$ , 511.0716. Requires  $M$ , 511.0708);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3376, 3055, 2936, 1935, 1852, 1601, 1424, 1331 and 1161;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.72 (2 H, d,  $J$  8.3, 11-H and 15-H), 7.25 (2 H, d,  $J$  8.3, 12-H and 14-H), 5.20 (5 H, s, Cp), 4.73 (1 H, m, NH), 4.13 (1 H, t,  $J$  7.3, 2-H), 3.59 (1 H, m, 1-H or 3-H), 3.47 (1 H, m, 1-H or 3-H), 2.86 (2 H, q,  $J$  6.4, 9-H), 2.36 (3 H, s, 16-H), 1.98 (1 H, m, 4-H), 1.60–1.34 (6 H, m, 6-H, 7-H, 8-H), 0.70 (1 H, m, 5-H) and 0.37 (1 H, m, 5-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  236.0 (CO), 235.4 (CO), 143.3 (10-C), 136.9 (13-C), 129.7 (12-C and 14-C), 127.0 (11-C and 15-C), 92.0 (Cp),

58.2 (2-C), 56.8 (1-C), 55.6 (3-C), 43.4 (9-C), 36.0 (6-C), 31.4 (5-C), 28.1 (4-C), 23.2 (16-C), 21.5 (7-C) and 18.6 (8-C);  $m/z$  (EI) 511 ( $M^+$ ), 457, 455, 454, 453, 452, 451 and 449.

#### **cis-1,2,3,4,4a,5,6,8a-Octahydro-1-(*p*-tolylsulfonyl)quinoline 12**

The crude mixture from intramolecular cyclization of **11** (0.18 g, 0.34 mmol) with  $\text{NOBF}_4$  (0.07 g) and  $\text{Et}_3\text{N}$  (0.2 ml) was purified by flash column chromatography (silica gel, 25% ethyl acetate–75% hexanes) to afford a single quinoline derivative **12** (24 mg, 24%) as a colourless oil (Found:  $M^+$ , 291.1302. Requires  $M$ , 291.1287;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3398, 3054, 2932, 2861, 1649, 1601, 1495, 1451, 1396, 1333 and 1157;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.71 (2 H, d,  $J$  8.3, 10-H and 14-H), 7.28 (2 H, d,  $J$  7.8, 11-H and 13-H), 5.68 (1 H, m, 7-H), 5.12 (1 H, d,  $J$  10.2, 8-H), 4.60 (1 H, m, 8a-H), 3.76 (2 H, d,  $J$  11.7, 2-H), 2.76 (1 H, t,  $J$  11.3, 4a-H), 2.42 (3 H, s, 15-H) and 1.92–1.43 (8 H, m, 6-H, 5-H, 4-H, 3-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  142.8 (9-C), 138.8 (12-C), 130.5 (11-C and 13-C), 129.6 (7-C or 8-C), 126.9 (7-C or 8-C), 126.3 (10-C and 14-C), 53.4 (8a-C), 41.0 (2-C), 32.1 (4a-C), 27.0 (6-C), 24.9 (5-C), 23.1 (4-C), 21.5 (15-C) and 20.6 (3-C);  $m/z$  (EI) 291 ( $M^+$ ), 227, 136, 91, 69, 55, 41 and 28.

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