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Benzylic functionalization of (η^6-alkylarene)chromium tricarbonyl complexes [1]

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Abstract

A general method for the regioselective benzylic metallation of (η^6-alkylarene)chromium tricarbonyl complexes on the action of lithium amides in THF under very mild conditions has been developed. Transmetallation reactions of the lithium derivatives thus obtained produce the corresponding benzylic organotin, zinc and copper chromium tricarbonyl complexes. Methods for the preparative benzylic functionalization of (η^6-alkylarene)chromium tricarbonyl complexes have been developed, including carboxylation, α-hydroxyalkylation, γ-carbonylation, acylation, arylation, vinylation, heteroarylation and alkylation procedures. 5-Acetoxy-3-benzyl-1,4-methano-2,3,4,5-tetrahydro-*1H*-3-benzazepine has been prepared using the benzylic lithium derivative of the (η^6-alkylarene)chromium tricarbonyl complex at the key step. This compound is a representative of the major class of physiologically active compounds known as *C*-norbenzomorphans.
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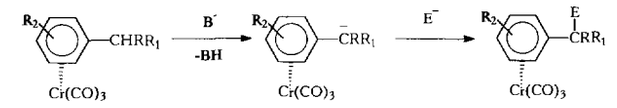
Keywords: (η^6-Arene)chromium tricarbonyl complexes; Metallation; Benzylic functionalization; *C*-norbenzomorphans; Chromium

1. Introduction

Benzylic organometallic derivatives of (η^6-alkylarene)chromium tricarbonyl complexes are widely used for organic synthesis (Scheme 1). The methods for their preparation have been the objective of many researches (for reviews see Refs. [1,2]).

By now a wide range of metallating agents have been used for deprotonation of (η^6-alkylarene)chromium tricarbonyl complexes at the benzylic position. These metallating systems are as follows: ^{t}BuOK in DMF, DMSO or THF; NaH in DMF; KH/18-crown-6 in THF; ^{n}BuLi, ^{t}BuLi or $(Me_3Si)_2NNa$ in THF; $NaNH_2$ in liquid NH_3; R_4NOH. However, the reagents above have a number of essential drawbacks. Almost all of them are applicable only to a limited range of (η^6-alkylarene)chromium tricarbonyl complexes. The yields of the metallated products are often poor. The target metallation reaction at the benzylic position can be accompained by the unwanted side processes of the proton abstraction from the aromatic ring or by the nucleophilic addition of metallating agent to the aromatic ring or to the carbonyl groups in the $Cr(CO_3)$ fragment. Besides, an excess of all metallating agents mentioned (excluding ^{n}BuLi and ^{t}BuLi) is necessary for the preparation of the products in good yield. This leads in some cases to formation of the polysubstituted products.

It should be stressed that only benzylic alkali metal (Li, Na and K) derivatives of (η^6-alkylarene)chromium tricarbonyl complexes have been prepared so far. Their high reactivity and low thermal stability essentially restrict the range of electrophiles that can be used for benzylic functionalization of (η^6-alkylarene)chromium tricarbonyl complexes. So, the electrophiles in use include primarily only alkyl iodides, active alkyl bromides (allylic or benzylic) and unenolizable carbonyl compounds. The benzylic organometallic derivatives of other metals (for example Sn, Zn, Cu) have not yet been described. It is evident that the use of these metal derivatives is very promising for benzylic functionaliza-



Scheme 1. (η^6-Arene)chromium tricarbonyl complexes in organic synthesis.

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[1] Dedicated to Professor Yu.T. Struchkov in recognition of his outstanding contribution to organometallic chemistry.

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tion of alkyl arenes via their chromium tricarbonyl complexes.

2. Results and discussion

2.1. The benzylic metallation of (η^6-alkylarene)chromium tricarbonyl complexes

The metallating system (i.e. metallating agent/solvent/reaction conditions) for the preparative benzylic functionalization of alkyl arenes via benzylic organometallic derivatives of (η^6-alkylarene)chromium tricarbonyl complexes have to satisfy the following requirements.

(1) Generality. (a) The system must be used for benzylic deprotonation of a variety of (η^6-alkylarene)chromium tricarbonyls; (b) it has to provide a possibility for further reactions of benzylic organometallic derivatives of (η^6-alkylarene)chromium tricarbonyl complexes, including those prepared by transmetallation reactions.

(2) Selectivity. The metallating agent must cause proton abstraction only from the benzylic position of the (η^6-alkylarene)chromium tricarbonyl complex.

(3) High yield of the metallation product.

We have found [3] that lithium amides in THF solution are a convenient general metallating system for selective hydrogen abstraction from the benzylic position of (η^6-alkylarene)chromium tricarbonyl complexes. The yields of the corresponding (η^6-alkylarene)chromium tricarbonyl trimethylsilyl derivatives produced on quenching of the reaction mixture with an excess of trimethylsilyl chloride were used as an indicator of both the degree and direction of the metallation process. The results obtained are shown in Table 1.

The most promising metallating agent was found to be lithium diethyl amide, which provided high yields of the target benzylic trimethylsilyl derivatives along with the metallation product when the aromatic ring was absent. It selectively deprotonates the benzylic position of (η^6-alkylarene)chromium tricarbonyl complexes in the case of primary, secondary and tertiary benzylic carbon atoms. However, the yield of the target product (25%) is rather poor in the last case (cumene complex, run 3). On metallation of the chromium tricarbonyl complexes bearing bicyclic ligands, a degree of the metallation depends on the number of methylene groups in the bridge chain (47% and 95% for the indane and tetraline chromium tricarbonyl complexes respectively, runs 5 and 6). Formation of the essential quantities of the aromatic ring substituted products takes place on metallation of the indane and indoline chromium tricarbonyl complexes at 20 °C. However, cooling the reaction mixture to −30 °C increased the selectivity of the reaction, leading to benzylic substitution only (runs 5 and 8).

On the metallation of dialkyl substituted (η^6-arene)chromium tricarbonyl complexes with lithium diethyl amide, deprotonation of only one alkyl group is observed, even with excess metallating agent. Formation of the substitution product at both methyl groups has been observed in the case of the (η^6-*p*-xylene)chromium tricarbonyl complex. However, this disubstitution process can be avoided using less basic lithium *tert*-butyl amide as metallating agent (run 4).

The presence of a nitrogen atom at the bridge aliphatic chain does not prevent the metallation reaction. So, trimethylsilyl derivatives of the chromium tricarbonyl complexes of *N*-methylindoline, *N*-methyl-1,2,3,4-tetrahydroquinoline and *N*-methyl-1,2,3,4-tetrahydroisoquinoline were prepared in high yield.

2.2. The carboxylation reaction of the benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes

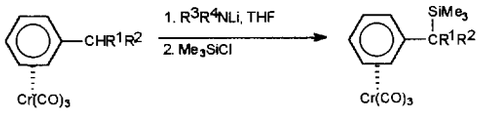
2-Arylcarboxylic acids are of great interest as both anti-inflammatory agents and analgesics [4,5], and much attention is paid to methods for their preparation (for reviews see Refs. [4,6]). A direct carboxylation reaction of benzylic organometallic derivatives of alkylarenes is the most widely used method. It should be stressed that the benzylic organometallic derivatives of (η^6-alkylarene)chromium tricarbonyl complexes were very poorly used in the carboxylation reaction [7,8].

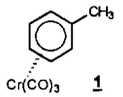
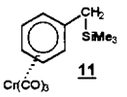
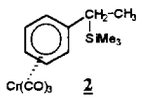
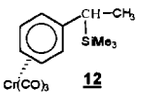
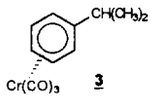
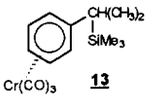
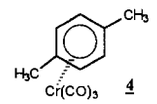
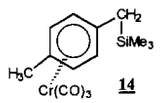
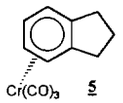
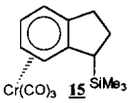
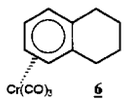
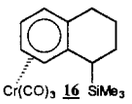
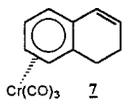
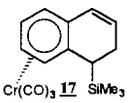
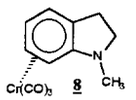
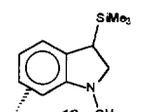
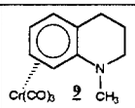
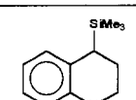
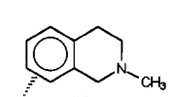
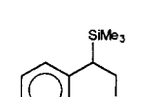
We have found [9,10] that benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes react easily with carbon dioxide, giving after acidification the corresponding chromium tricarbonyl complexes of α-arylcarboxylic acids in good yield. Table 2 shows the starting chromium tricarbonyl complexes and the products obtained, along with their yields. The free acids can be produced from the complexes thus obtained by the usual methods [1,2].

The carboxylation reaction above is applicable to the preparation of various α-arylcarboxylic acid complexes and their esters. In the case of (η^6-alkylarene)chromium tricarbonyl complexes containing a nitrogen atom in the aliphatic chain, the resulting tricarbonyl chromium complexes of carboxylic acids were transformed into the corresponding methyl esters on action of the diazomethane to avoid formation of hardly isolable internal salts of amino acids. (η^6-Tetralol)chromium tricarbonyl complex (run 8), bearing the trimethylsilyl protecting group, should be used as the starting material to prepare (η^6-1-carboxy-4-hydroxy-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl complex. The protecting group is removed on isolation of the product.

The method developed for benzylic carboxylation of (η^6-alkylarene)chromium tricarbonyl complexes is a new route to α-arylcarboxylic acids. It is also the

Table 1
The benzylic metallation of (η^6-alkylarene)chromium tricarbonyl complexes

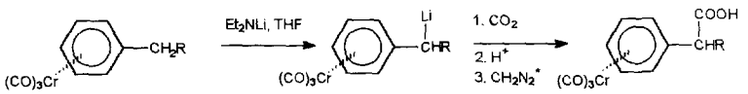


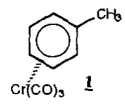
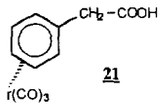
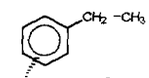
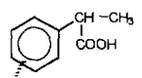
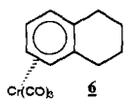
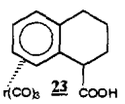
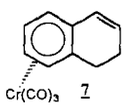
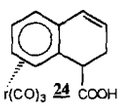
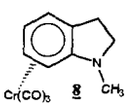
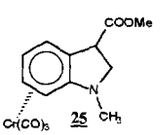
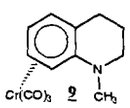
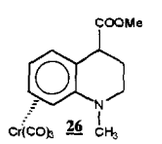
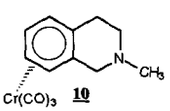
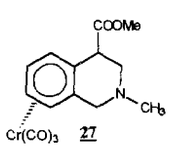
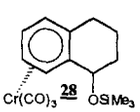
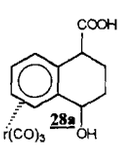
	Starting complex	R^3R^4NLi	Reaction temp., °C	time, min	Product	Yield, %
1	 **1**	Et_2NLi	0	10	 **11**	90
2	 **2**	Et_2NLi	0	10	 **12**	90
3	 **3**	Et_2NLi	20	5	 **13**	25
4	 **4**	t-BuNHLi	-30	3	 **14**	88
5	 **5**	Et_2NLi	-30	5	 **15**	47
6	 **6**	Et_2NLi	20	10	 **16**	95
7	 **7**	Et_2NLi	20	5	 **17**	37
8	 **8**	Et_2NLi	-30	5	 **18**	75
9	 **9**	Et_2NLi	20	3	 **19**	98
10	 **10**	Et_2NLi	20	3	 **20**	92

method for single carbon atom homologization of the benzylic position of alkylarenes. The method permits easy introducion of a carboxylic group directly into the saturated hydrocarbon chain in acyclic, carbocyclic and heterocyclic fragments, in contrast to other methods.

In addition to their pharmacological activity, α-arylcarboxylic acids are also interesting as synthons in fine organic synthesis due to the wide possibilities associated with the simple modification of the carboxylic group.

Table 2
The carboxylation reaction of the benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes



	Starting complex	Product	Yield, %
1	 1	 21	84
2	 2	 22	57
3	 6	 23	72
4	 7	 24	30
5	 8	 25	51*
6	 9	 26	80*
7	 10	 27	77*
8	 28	 28a	97

* The amino acid obtained was transformed without isolation to the corresponding methyl ester by treatment of the reaction mixture with an excess of diazomethane.

2.3. 1,2-Addition reactions of the benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes to carbonyl compounds

It is well known that benzylic sodium and potassium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes add to activated carbonyl groups in formaldehyde [11,12], benzaldehyde [11,13] and diethyl oxalate [14]. However, the products were obtained in some cases in poor yields [11,13], and the addition products were not obtained if the carbonyl compounds were susceptible to enolization [11,15]. Meanwhile, the benzylic lithium derivatives of (η^6-*N*-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl enter the 1,2-addition reaction to acetone, giving the chromium tricarbonyl complexes of the corresponding alcohol in a yield of 36% [16].

We have found [17] that benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes add smoothly to the carbonyl compounds at −78 °C, producing the corresponding carbinol complexes in good yield. The products thus obtained are shown in Table 3, along with their yields.

The data obtained demonstrate that the lithium derivatives, unlike the sodium and potassium ones, add to the carbonyl groups of both aldehydes and ketones of different type, including the enolizable carbonyl compounds. Two isomers, *exo*- and *endo*-, may be formed from chromium tricarbonyl complexes bearing bicyclic ligands (**6**, **9**, **10**, runs 6–9) in these reactions. However, we really obtained only one product. Relying on the literature data [1,2], these isomers were assigned the *exo*-configurations.

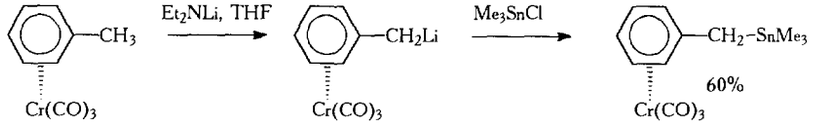
The addition reactions of benzylic lithium derivatives of (η^6-alkylarene) tricarbonylchromium complexes to carbonyl compounds are both another approach to the preparation of α-aryl substituted carbinols and the method for single carbon atom homologization of the benzylic position of alkylarenes.

2.4. Benzylic tin, zinc and copper(I) derivatives of (η^6-alkylarene)chromium tricarbonyl complexes

An application of benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes to the benzylic functionalization of alkyl arenes is essentially limited by two points. The first is unsufficient thermal stability of the lithium derivatives (they are stable for a few minutes at 20 °C). The second point is their high reactivity, requiring the absence of the functional groups in the substrate sensitive to organolithium compounds.

To enhance the synthetic potential of (η^6-alkylarene)chromium tricarbonyl complexes for the benzylic functionalization of alkyl arenes, we first used the corresponding benzylic lithium derivatives as starting materials for the preparation of more stable organometallic compounds. The transmetallation reaction of organolithium compounds with the metal halides produces benzylic tin, mercury, zinc and copper derivatives of (η^6-alkylarene)chromium tricarbonyl complexes.

(η^6-α-Trimethylstannyltoluene)chromium tricarbonyl was prepared by the reaction of the corresponding lithium derivative with trimethyltin chloride



It is well known that both organotin and organosilicon compounds enter the palladium(0) catalysed cross-coupling reactions with aryl halides [18]. In contrast, all our attempts to obtain the cross-coupling products in the reactions of α-trimethylstannyl or α-trimethylsilyl derivatives of (η^6-toluene)chromium tricarbonyl with iodobenzene in the presence of catalytical amounts of $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$ or $PdCl_2(CH_3CN)_2$ failed.

Benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyl complexes have been shown to be the most suitable for the cross-coupling reactions with organic halides [19]. They were prepared from the corresponding lithium derivatives on the action of anhydrous zinc chloride. Unlike the lithium compounds, the zinc ones are much more thermally stable and alive on refluxing in THF for 1 h.

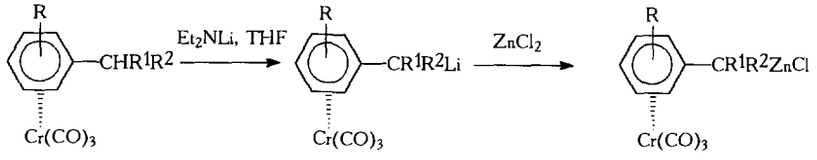
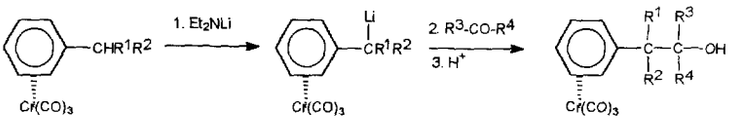


Table 3
1,2-Addition reactions of $(\eta^6\text{-}CHR^1R^2)Cr(CO)_3$ compounds



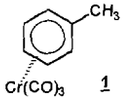
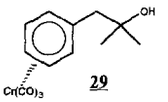
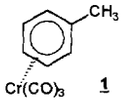
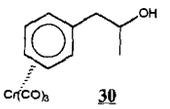
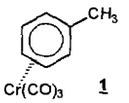
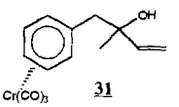
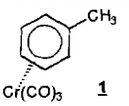
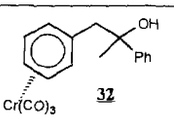
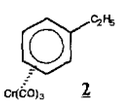
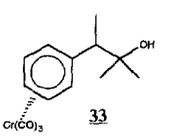
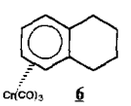
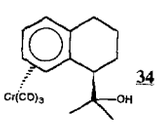
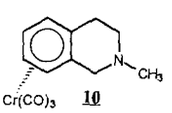
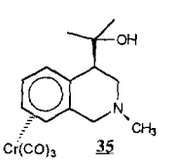
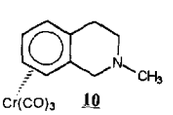
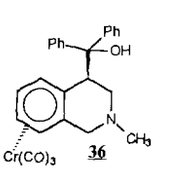
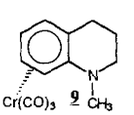
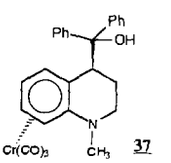
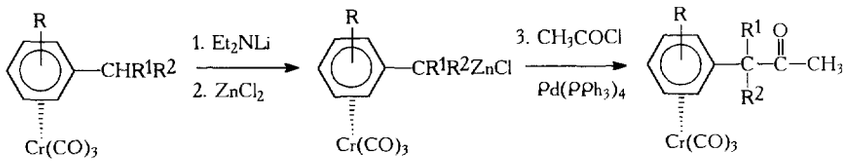
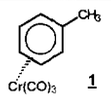
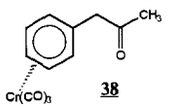
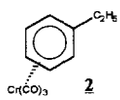
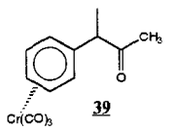
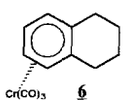
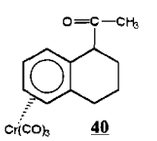
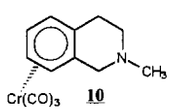
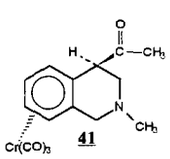
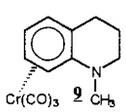
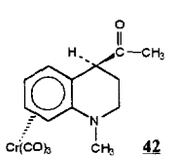
	Starting complex	Carbonyl compound	Product	Yield, %
1	 **1**		 **29**	80
2	 **1**		 **30**	62
3	 **1**		 **31**	69
4	 **1**		 **32**	63
5	 **2**		 **33**	67
6	 **6**		 **34**	82
7	 **10**		 **35**	72
8	 **10**		 **36**	85
9	 **9**		 **37**	71

Table 4
Reactions of benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyl complexes with acetyl chloride



	Starting complex	Product	Yield,%
1	 1	 38	59
2	 2	 39	56
3	 6	 40	71
4	 10	 41	75
5	 9	 42	34

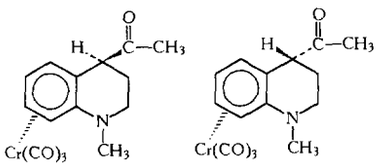
The reaction with acyl chlorides is one of the most usable properties of organozinc reagents [20]. Benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyls react readily with acetyl chloride giving the corresponding ketone complexes, with the presence of palladium catalyst (0.05 equiv. $Pd(PPh_3)_4$), resulting in a 1.5–2-fold increase of the yield. The results obtained are shown in Table 4.

It should be noted that two products were obtained from the η^6-(*N*-methyl-1,2,3,4-tetrahydroquinoline)-

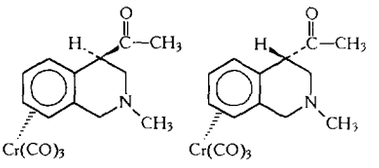
Table 5
^{1}H NMR spectroscopy data for complexes **42** and **41**

	Isomer	Complex **42**			Complex **41**		
		δ (pm)			δ (pm)		
		$CDCl_3$	C_6D_6	$\Delta\delta$	$CDCl_3$	C_6D_6	$\Delta\delta$
benzylic	a	3.56	2.99	0.57	6.65	6.45	0.20
protons	b	3.54	2.82	0.72	6.50	6.05	0.45
acetyl	a	2.26	1.64	0.62	2.14	1.70	0.44
protons	b	2.46	2.10	0.36	2.14	1.84	0.30

chromium tricarbonyl complex (**9**, run 5) on employing the above conditions. These products have been confirmed by ^{1}H NMR spectroscopic data to be the *exo*- and *endo*-isomers of the η^6-(4-acetyl-*N*-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl complex (**42a** and **42b** respectively). The ratio between them has been shown by HLPC to be 51:1.



42a **42b**



41a **41b**

The main product was isolated in a pure form by recrystallization from hexane–diethyl ether (3:1) and identified as the *exo*-isomer **42a** by a method based on measurement of the chemical shifts of 4-benzylic and acetyl protons induced in ^{1}H NMR spectra by an aromatic solvent on passing from $CDCl_3$ to C_6D_6 solution (ASIS effect).

^{1}H NMR spectra of **42a** and **42b** in $CDCl_3$ and C_6D_6 were recorded so as to determine their configuration. The chemical shifts of the 4-benzylic and acetyl protons of these compounds are given in Table 5 for each solvent, along with the difference $\Delta\delta$ between the shifts of the same protons in the two solvents.

The decrease in the chemical shift of the 4-benzylic proton in **42a** on passing from $CDCl_3$ to C_6D_6 solution is less than that for **42b**.

The corresponding changes in chemical shifts for the acyl protons show the opposite tendency. This proves that the 4-benzylic proton occupies a more sterically hindered *endo*-position in **42a** and that the acetyl group has an *exo*-orientation (see Ref. [21]).

Acylation of η^6-(*N*-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl complex (**10**, run 4, Table 4) with acetyl chloride also leads to two isomeric acetyl derivatives (**41a** and **41b**) in the ratio approximately 5:1. The structures of these complexes was elucidated by ^{1}H NMR spectroscopy as described above (see Table 5). These data also indicate the ratio between **41a** and **41b** to be 4.8:1 and 6.1:1 in $CDCl_3$ and C_6D_6 solutions respectively. All our attempts to separate the isomers failed.

We explain the formation of two acylated products in the cases described above in terms of a two-stage process involving the formation of the corresponding *exo*-isomers in the first place followed by rearrangement into the *endo*-products via the enol form. This explanation is also confirmed by the different ratio between **41a** and **41b** in $CDCl_3$ and C_6D_6 solutions when prepared from the same solid material. A possible coordination of the ketone functions with the chromium atoms in the *endo*-isomers would facilitate this process. A distinction in behaviour of the tetrahydroquinoline and tetrahydroisoquinoline complexes is supposed to be due to the different basicity of the nitrogen atoms conjugated or non-conjugated with the aromatic ring. The more basic nitrogen atom in the tetrahydroisoquinoline complex causes a much more effective enolization of the carbonyl group. So, an equilibrium between the *exo*- and *endo*-isomers is reached much more rapidly than in the case of the tetrahydroquinoline derivative.

The structures of other acylated chromium complexes containing bicyclic ligands have not been studied in detail.

Palladium(0) catalysed cross-coupling reactions with aryl, heteryl and vinyl halides is another major area of application of organozinc compounds [18].

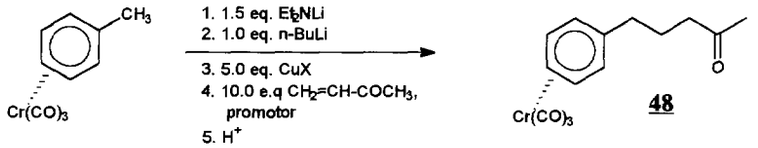
We have found that benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyl complexes undergo reactions with aryl, heteryl and vinyl halides giving the corresponding product [19] (Table 6).

Thus, the use of benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyl complexes in cross-coupling reactions allows the substitution of alkyl arenes at the benzylic position with acyl, aryl, heteryl and vinyl groups.

We have found [17] that the benzylic lithium derivative of the (η^6-toluene)chromium tricarbonyl complex readily enters a transmetallation reaction with copper(I) halides to produce the benzylcopper(I) derivative.

A yellow solution of the benzylic lithium derivative of the (η^6-toluene)chromium tricarbonyl complex in THF turned black on addition of a two-fold excess of

copper(I) halide. The mixture became yellow again when methyl vinyl ketone and the promotor (Me_3SiCl or $BF_3{}^*Et_2O$) were added. Acidic treatment of the reaction mixture gave the only 1,4-addition product **48** of the [η^6-benzylcopper(I)]chromium tricarbonyl complex to methyl vinyl ketone.

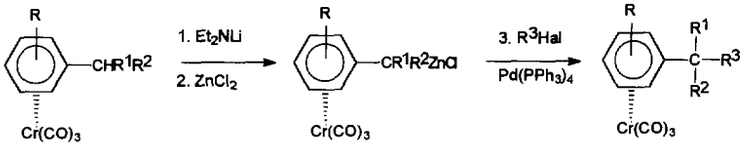


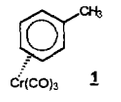
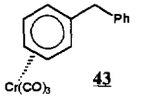
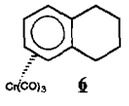
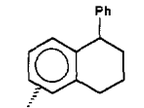
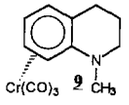
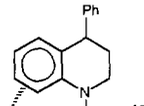
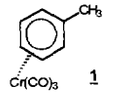
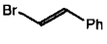
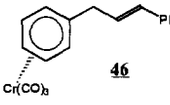
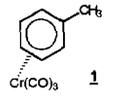
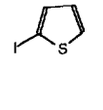
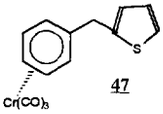
CuX	Promotor	Yield %
CuI	Me_3SiCl	69
CuI	$BF_3{}^*Et_2O$	58
CuBr	$BF_3{}^*Et_2O$	42

Unlike the [η^6-benzylcopper(I)]chromium tricarbonyl complex, the corresponding lithium derivative gives only the 1,2-addition product with methyl vinyl ketone (see Table 3, run 3).

This is the first example of a benzylcopper(I) compound bearing a chromium tricarbonyl group. In contrast to uncomplexed benzylcopper(I) compounds, the benzylcopper(I) derivative of (η^6-toluene)chromium tri-

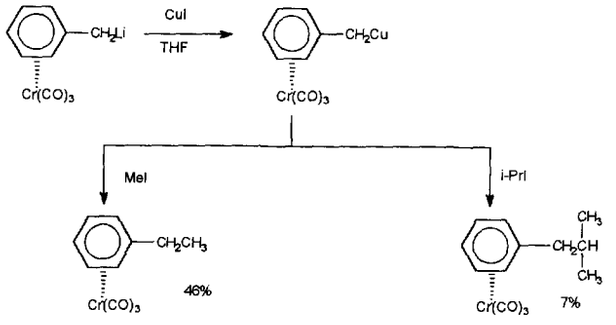
Table 6
Cross-coupling reactions of benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyl complexes with organohalides



	Starting complex	R^3Hal	Product	Yield, %
1	 **1**	Ph J	 **43**	66
2	 **6**	Ph J	 **44**	37
3	 **9**	Ph J	 **45**	27
4	 **1**		 **46**	44
5	 **1**		 **47**	13

carbonyl has increased stability and can be stored for 30 min at 20 °C without decomposition.

The benzylcopper(I) complex undergoes a reaction with alkyl halides. However, the substitution products were obtained in poor yields, with the main product in the case of the reaction with iso-propyl iodide being bis-[(η^6-benzyl)chromium tricarbonyl).



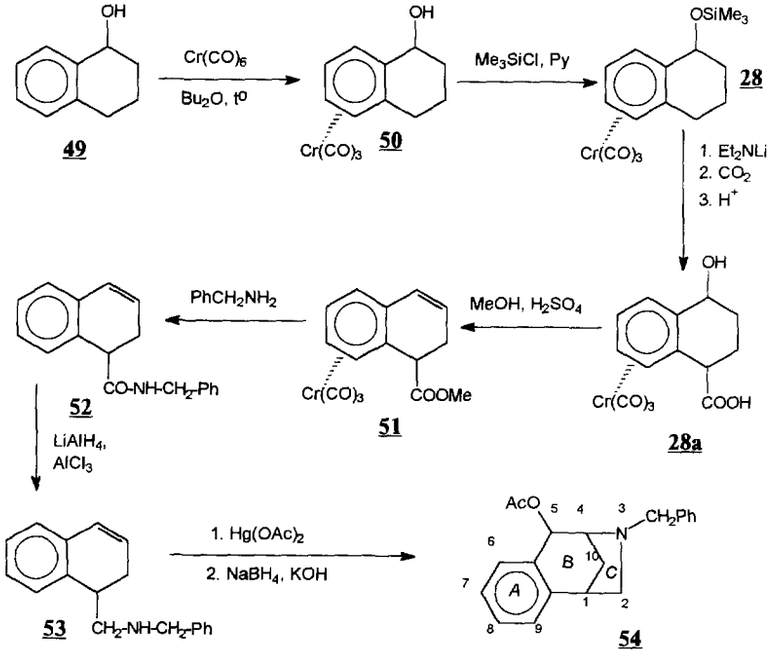
The benzylcopper(I) complex also enters the cross-coupling reaction with iodobenzene in the presence of catalytical quantities of $Pd(PPh_3)_4$. The coupling product was isolated only in 12% yield, in contrast to the 66% yield obtained in the case of the corresponding organozinc complex (see Table 6, run 1).

2.5. A synthesis of 5-acetoxy-3-benzyl-1,4-methano-2,3,4,5-tetrahydro-1H-3-benzazepine

For the nomenclature of benzomorphans, *C*-norbenzomorphans and relative compounds see the review in Ref. [22]. A ring and atom numbering system in 54 is shown in Scheme 2.

The method of benzylic functionalization of alkyl arenes via their chromium tricarbonyl complexes described above can be used for fine organic synthesis. As an example, we have developed a synthesis of 5-acetoxy-3-benzyl-1,4-methano-2,3,4,5-tetrahydro-*1H*-3-benzazepine **54** (Scheme 2). This compound is a representative of the major class of physiologically active compounds known as *C*-norbenzomorphans [22]. This seven-stage procedure includes the carboxylation reaction of the benzylic lithium derivative of the (η^6-arene)chromium tricarbonyl complex for one carbon atom homologization of the benzylic position in the arene as a key step.

C-norbenzomorphan **54** was prepared from easily available 1-tetralol **49**. The synthesis of complex **50** from **49** had been described earlier [23]. The hydroxy function in **50** was protected with a trimethylsilyl group, giving the silyl ether **28**. It is necessary to avoid deprotonation of the hydroxy group on α-metallation of **28**, and to prepare the complex **28a** on carboxylation in good yield. Acid **28a** underwent an esterification reaction by action of methanol in the presence of concentrated sulphuric acid. Under these conditions, sulphuric acid also causes a removal of the trimethylsilyl group



Scheme 2. A total synthesis of 5-acetoxy-3-benzyl-1,4-methano-2,3,4,5-tetrahydro-*1H*-3-benzazepine.

along with the dehydration process, giving the 1,2-dihydronaphthalene derivative **51**. This route to complex **51** is preferable to the esterification of η^6-(1-carboxy-1,2-dihydronaphthalene)chromium tricarbonyl **15** due to the poor yield of the latter on the carboxylation process of the benzylic lithium derivative of the η^6-(1,2-dihydronaphthalene)chromium tricarbonyl complex (see Table 2, run 4).

On heating of **51** with $PhCH_2NH_2$, both a transformation of the ester function into an amide group and removal of the $Cr(CO)_3$ group from the complex take place, producing the amide **52**. The use of amines other than $PhCH_2NH_2$ at this stage offers the possibility of varying the substituent at the nitrogen atom in the *C*-norbenzomorphan framework. A reduction of **52** into **53** is followed by a cyclization process of the latter by the method described earlier [24], giving the target *C*-norbenzomorphan **54**. The acetoxy group at the C(5) carbon atom does not undergo hydrolysis under these conditions.

The nitrogen atom in **54** is *trans* to the acetoxy group. This was proved by the value of ^3J(H(4)H(5)) in the ^{1}H NMR spectrum of **54**, which is 3.2 Hz. This is solely possible for *trans* mutual orientation of the hydrogen atoms H(4) and H(5), because for *cis* orientation this spin–spin decoupled constant must be of value about 6–7 Hz. The values of the dihedral angles between H(4) and H(5) were estimated for the models.

The ^{1}H NMR spectrum data (see Section 3) together with an investigation of the models permit us to identify H(2) and H(10) peaks in the spectrum of **54**. The model experiment shows that the spin–spin decoupled constant between $H_\alpha(10)$ (in contrast to $H_\beta(10)$) and H(1) must be very small in value, due to the corresponding dihedral angle being about 90°. ($H_\alpha(10)$ is a *cis* hydrogen atom to H(1) relative to the B-ring; $H_\beta(10)$ is *trans*.) Similarly, the spin–spin decoupled constant between H(1) and *trans*-H(2) (in contrast to *cis*-H(2)) relative to the C-ring must be very small in value too. So, the peak at δ 1.93 ppm is due to $H_\beta(10)$ (^3J(H(1)–$H_\beta(10)$) = 3.7 Hz), and the peak at δ 2.02 ppm, which shows the spin–spin decoupled constant with H(1) only as a broadening of the signal, is due to $H_\alpha(10)$. Very similarly, the signal at δ 2.85 ppm is due to *cis*-H(2) (^3J(H(1)–*cis*-H(2)) = 4.35 Hz), and the signal at δ 2.77 ppm is due to *trans*-H(2) (^3J(H(1)–*trans*-H(2)) = 0.75 Hz).

3. Experimental section

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an argon atmosphere. THF was dried over sodium benzophenone ketyl and distilled before use.

A 1 M solution of ^{n}BuLi in hexane was used in the reactions. Solid CO_2 was obtained by the formation of a frozen layer of the latter from gaseous CO_2 passed through a layer of P_2O_5. The initial (η^6-alkylarene)chromium tricarbonyl complexes were synthesized by refluxing the arene ligand with $(NH_3)_3Cr(CO)_3$ in dioxane by Mahaffy's method [25].

^{1}H NMR spectra were recorded on Bruker WP-200 SV (with a working frequency of 200 MHz for ^{1}H) and Varian VXR-400 (with a working frequency of 400 MHz for ^{1}H) spectrometers. The chemical shifts are indicated in terms of the δ scale relative to tetramethylsilane. EI-MS spectra (70 eV) were measured on AEI-MS-30 spectrometers. The IR spectra were recorded on a Specord M80 apparatus.

3.1. Reactions of benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes with chlorotrimethylsilane

*3.1.1. (η^6-α-Trimethylsilyltoluene)chromium tricarbonyl (**11**)*

A two-necked 50 ml flask was charged with 20 ml of THF, after which 0.27 ml (2.6 mmol) of diethylamine and 2.6 ml (2.6 mmol) of ^{n}BuLi solution were added and the contents cooled to 0 °C. After 5 min, 0.3 g (1.32 mmol) of (η^6-toluene)chromium tricarbonyl was added and the mixture stirred for 10 min at 0 °C. 0.67 ml (5.26 mmol) of chlorotrimethylsilane was added to the mixture and the latter heated to 20 °C followed by stirring for 30 min. After an addition of 1 ml water, THF was distilled away in vacuo, the residue dissolved in chloroform and the solution filtered through a layer of Al_2O_3 (1 cm). The solvent was distilled away in vacuo and the product purified by thin layer chromatography on Al_2O_3 using a 1:9 ether–pentane mixture as eluent and subsequent crystallization. This afforded 0.35 g (90%) **11** as yellow crystals, m.p. 141.5–143 °C. ^{1}H NMR ($CDCl_3$): 0.04 (s, 9H, $3CH_3$); 1.84 (s, 2H, CH_2); 4.97 (m), 5.07 (m), 5.43 (m, 5H, C_6H_5). Anal. Found: C, 51.96; H, 5.64; Si, 8.98; Cr, 17.67. $C_{13}H_{16}CrO_3Si$ Calc.: C, 51.98; H, 5.38; Si, 9.35; Cr, 17.31%.

*3.1.2. [η^6-α-(Trimethylsilyl)ethylbenzene]chromium tricarbonyl (**12**)*

12 was obtained by the procedure described for **11** from 0.26 ml (2.5 mmol) of diethylamine, 2.5 ml (2.5 mmol) of ^{n}BuLi solution, 0.3 g (1.2 mmol) of (η^6-ethylbenzene)chromium tricarbonyl and 0.63 ml (5.0 mmol) of chlorotrimethylsilane after metallation for 10 min at 20 °C. Yield 0.33 g (85%), m.p. 68–69.5 °C. ^{1}H NMR ($CDCl_3$): 0.01 (s, 9H, $3CH_3$); 1.27 (d, 3H, CH_3); 1.89 (m, 1H, CH); 4.97–5.41 (m, 5H, C_6H_5). Anal. Found: C, 53.59; H, 5.47; Si, 8.78; Cr, 16.42. $C_{14}H_{18}CrO_3Si$ Calc.: C, 53.48; H, 5.78; Si, 8.93; Cr, 16.54%.

3.1.3. [η⁶-1-Methyl-1-(trimethylsilyl)ethylbenzene]-chromium tricarbonyl (13)

13 was obtained by the procedure described for **11** from 0.16 ml (1.56 mmol) of diethylamine, 1.56 ml (1.56 mmol) of ^{n}BuLi solution, 0.2 g (0.78 mmol) of (η⁶-*iso*-propylbenzene)chromium tricarbonyl and 0.4 ml (3.31 mmol) of chlorotrimethylsilane after metallation for 5 min at 20 °C. Yield 0.08 g (31%), m.p. 111–112.5 °C. ^{1}H NMR ($CDCl_3$): −0.04 (s, 9H, $3CH_3$); 1.29 (s, 6H, $2CH_3$); 5.19–5.38 (m, 5H, C_6H_5). Anal. Found: C, 54.84; H, 6.25; Si, 8.32; Cr, 15.56. $C_{15}H_{20}CrO_3Si$ Calc.: C, 54.85; H, 6.15; Si, 8.55; Cr, 15.83%.

3.1.4. [η⁶-4-Methyl-1-(trimethylsilyl)methylbenzene]-chromium tricarbonyl (14)

14 was obtained by the procedure described for **11** from 0.17 ml (1.65 mmol) of *tert*-butylamine, 1.65 ml (1.65 mmol) of ^{n}BuLi solution, 0.2 g (0.83 mmol) of (η⁶-1,4-dimethylbenzene)chromium tricarbonyl and 0.42 ml (3.31 mmol) of chlorotrimethylsilane after metallation for 3 min at −30 °C. Yield 0.23 g (88%), m.p. 94.5–95.5 °C. ^{1}H NMR ($CDCl_3$): 0.04 (s, 9H, $3CH_3$); 1.71 (s, 2H, CH_2); 2.11 (s, 3H, CH_3); 5.06 (d), 5.29 (d, 4H, C_6H_4). Anal. Found: C, 53.56; H, 5.74; Si, 8.53; Cr, 16.90. $C_{14}H_{18}CrO_3Si$ Calc.: C, 53.48; H, 5.78; Si, 8.93; Cr, 15.54%.

3.1.5. [η⁶-1-(Trimethylsilyl)indane]chromium tricarbonyl (15)

15 was obtained by the procedure described for **11** from 0.18 ml (1.78 mmol) of diethylamine, 1.78 ml (1.78 mmol) of ^{n}BuLi solution, 0.2 g (0.89 mmol) of (η⁶-indane)chromium tricarbonyl and 0.45 ml (3.56 mmol) of chlorotrimethylsilane after metallation for 5 min at −30 °C. Yield 0.12 g (47%), m.p. 77.5–78.5 °C. ^{1}H NMR ($CDCl_3$): 0.05 (s, 9H, $3CH_3$); 1.94–2.11 (m), 2.20–2.51 (m), 2.57–2.83 (m, 5H, CH_2–CH_2–CH); 5.16 (m), 5.29 (m), 5.49 (m, 4H, C_6H_4). Anal. Found: C, 55.19; H, 5.66; Si, 8.32; Cr, 15.46. $C_{15}H_{18}CrO_3Si$ Calc.: C, 55.19; H, 5.57; Si, 8.61; Cr, 15.93%.

3.1.6. (η⁶-1-Trimethylsilyl-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl (16)

16 was obtained by the procedure described for **11** from 0.15 ml (1.5 mmol) of diethylamine, 1.5 ml (1.5 mmol) of ^{n}BuLi solution, 0.2 g (0.75 mmol) of (η⁶-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl and 0.38 ml (3.0 mmol) of chlorotrimethylsilane after metallation for 10 min at 20 °C. Yield 0.24 g (95%), m.p. 108–108.5 °C. ^{1}H NMR ($CDCl_3$): 0.04 (s, 9H, $3CH_3$); 1.60–2.17 (m), 2.31–2.69 (m, 7H, CH_2–CH_2–CH_2–CH); 5.06–5.34 (m, 4H, C_6H_4). Anal. Found: C, 55.26; H, 5.83; Si, 8.02; Cr, 15.27. $C_{16}H_{20}CrO_3Si$ Calc.: C, 56.44; H, 5.93; Si, 8.25; Cr, 15.27%.

3.1.7. (η⁶-1-Trimethylsilyl-1,2-dihydronaphthalene)-chromium tricarbonyl (17)

17 was obtained by the procedure described for **11** from 0.23 ml (2.26 mmol) of diethylamine, 2.26 ml (2.26 mmol) of ^{n}BuLi solution, 0.3 g (1.13 mmol) of (η⁶-1,2-dihydronaphthalene)chromium tricarbonyl and 0.57 ml (4.57 mmol) of chlorotrimethylsilane after metallation for 5 min at 20 °C. Yield 0.14 g (37%), m.p. 94.5–95.5 °C. ^{1}H NMR ($CDCl_3$): 0.06 (s, 9H, $3CH_3$); 2.10 (d, 1H, CH); 2.30–2.50 (m), 2.71–3.00 (m, 2H, CH_2); 5.06–5.40 (m, 4H, C_6H_4); 6.00 (m, 2H, CH=CH). Anal. Found: C, 56.83; H, 5.33; Si, 7.95; Cr, 13.71. $C_{16}H_{18}CrO_3Si$ Calc.: C, 56.78; H, 5.37; Si, 8.30; Cr, 15.37%.

3.1.8. [η⁶-N-methyl-3-(trimethylsilyl)indoline]chromium tricarbonyl (18)

18 was obtained by the procedure described for **11** from 0.076 ml (0.74 mmol) of diethylamine, 0.74 ml (0.74 mmol) of ^{n}BuLi solution, 0.1 g (0.37 mmol) of (η⁶-*N*-methyl-indoline)chromium tricarbonyl and 0.19 ml (1.49 mmol) of chlorotrimethylsilane after metallation for 5 min at −30 °C. Yield 0.09 g (71%), m.p. 98–99 °C. ^{1}H NMR ($CDCl_3$): 0.06 (s, 9H, $3CH_3$); 2.28 (d, 1H, CH); 2.63 (s, 3H, CH_3); 3.34 (dd), 3.54 (m, 2H, CH_2); 4.74 (d), 4.91 (td), 5.29 (td), 5.40 (d, 4H, C_6H_4). Anal. Found: C, 52.44; H, 5.89; N, 3.77; Si, 8.23; Cr, 14.67. $C_{15}H_{19}NCrO_3Si$ Calc.: C, 52.76; H, 5.62; N, 4.10; Si, 8.23; Cr, 15.23%.

3.1.9. (η⁶-N-methyl-4-trimethylsilyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl (19)

19 was obtained by the procedure described for **11** from 0.15 ml (1.41 mmol) of diethylamine, 1.41 ml (1.41 mmol) of ^{n}BuLi solution, 0.2 g (0.71 mmol) of (η⁶-*N*-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl and 0.36 ml (2.82 mmol) of chlorotrimethylsilane after metallation for 3 min at 20 °C. Yield 0.25 g (98%), m.p. 130.5–131.5 °C. ^{1}H NMR ($CDCl_3$): 0.06 (s, 9H, $3CH_3$); 1.80–2.40 (m, 3H, CH_2–CH); 2.86 (s, 3H, CH_3); 3.14–3.31 (m, 2H, N–CH_2); 4.71–5.00, 5.41–5.57 (m, 4H, C_6H_4). Anal. Found: C, 54.10; H, 6.24; N, 4.00; Si, 7.43; Cr, 13.66. $C_{16}H_{21}NCrO_3Si$ Calc.: C, 54.06; H, 5.97; N, 3.94; Si, 7.90; Cr, 14.63%.

3.1.10. (η⁶-N-methyl-4-trimethylsilyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl (20)

20 was obtained by the procedure described for **11** from 0.15 ml (1.41 mmol) of diethylamine, 1.41 ml (1.41 mmol) of ^{n}BuLi solution, 0.2 g (0.71 mmol) of (η⁶-*N*-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl and 0.36 ml (2.82 mmol) of chlorotrimethylsilane after metallation for 3 min at 20 °C. Yield 0.23 g (92%), m.p. 85–86 °C. ^{1}H NMR ($CDCl_3$): 0.03 (s, 9H, $3CH_3$); 1.95 (m, 1H, CH); 2.30 (s, 3H, CH_3); 2.50–2.68

(m), 2.75–2.86 (m, 2H, CH_2–CH); 3.18–3.30 (m), 3.48–3.65 (m, 2H, CH_2–N); 5.00–5.30 (m, 4H, C_6H_4). Anal. Found: C, 54.02; H, 5.96; N, 3.93; Si, 7.46; Cr, 14.53. $C_{16}H_{21}NCrO_3Si$ Calc.: C, 54.06; H, 5.97; N, 3.94; Si, 7.90; Cr, 14.63%.

3.2. Reactions of benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes with carbon dioxide

3.2.1. [(η^6-Phenyl)chromiumtricarbonyl]acetic acid (21)

A two-necked 50 ml flask was charged with 20 ml of THF after which 0.27 ml (2.63 mmol) of diethylamine and 2.63 ml (2.63 mmol) of ^{n}BuLi solution were added and the contents cooled to 0 °C. After 5 min, 0.3 g (1.32 mmol) of (η^6-toluene)chromium tricarbonyl was added and the mixture stirred for 10 min at 0 °C. Next, the reaction mixture was poured onto solid CO_2. 20 min after the evaporation of CO_2, THF was removed in vacuo. The residue was dissolved in 50 ml of 5% NaOH solution, the alkaline solution washed with ether (3 × 20 ml) and acidified with concentrated HCl to pH 1. The product was extracted from the resulting mixture with ether (3 × 20 ml). The combined ether extracts were dried over Na_2SO_4, ether was evaporated and the product was recrystallized from a 2:1 ether–hexane mixture. This afforded 0.3 g (84%) of **21** as yellow crystals, m.p. 133–135 °C (134–135.5 °C [26]).

3.2.2. 2-[(η^6-Phenyl)chromiumtricarbonyl]propionic acid (22)

22 was obtained by the procedure described for **21** from 0.22 ml (2.16 mmol) of diethylamine, 2.16 ml (2.16 mmol) of ^{n}BuLi solution and 0.25 g (1.08 mmol) of (η^6-ethylbenzene)chromium tricarbonyl after metallation for 10 min at 20 °C. Yield 0.17 g (57%), m.p. 150–151 °C (with decomposition). ^{1}H NMR ($CDCl_3$): 1.41 (d, 3H, CH_3); 3.47 (m, 1H, CH); 5.21–5.59 (m, 5H, C_6H_5). Anal. Found: C, 50.45; H, 3.81; Cr, 18.37. $C_{12}H_{10}CrO_5$ Calc.: C, 50.35; H, 3.53; Cr, 18.17%.

3.2.3. [(η^6-1,2,3,4-Tetrahydronaphthalene)-1-carboxylic acid]chromium tricarbonyl (23)

23 was obtained by the procedure described for **21** from 0.39 ml (3.73 mmol) of diethylamine, 3.73 ml (3.73 mmol) of ^{n}BuLi solution and 0.5 g (1.87 mmol) of (η^6-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl after metallation for 5 min at 20 °C. Yield 0.42 g (72%), m.p. 150–151 °C (with decomposition). ^{1}H NMR ($CDCl_3$): 1.78 (m), 2.12 (m), 2.67 (m, 6H, $(-CH_2-)_3$); 3.70 (m, 1H, CH); 5.17–5.50 (m, 4H, C_6H_4). Anal. Found: C, 54.17; H, 3.96; Cr, 16.48. $C_{14}H_{12}CrO_5$ Calc.: C, 53.85; H, 3.88; Cr, 16.65%.

3.2.4. [(η^6-1,2-Dihydronaphthalene)-1-carboxylic acid]chromium tricarbonyl (24)

24 was obtained by the procedure described for **21** from 0.23 ml (2.26 mmol) of diethylamine, 2.26 ml (2.26 mmol) of ^{n}BuLi solution, and 0.3 g (1.13 mmol) of (η^6-1,2-dihydronaphthalene)chromium tricarbonyl after metallation for 10 min at 0 °C. Yield 0.11 g (30%), m.p. 177–180 °C (with decomposition). ^{1}H NMR ($CDCl_3$): 2.66–3.00 (m, 2H, CH_2); 3.52 (m, 1H, CH); 5.16–5.55 (m, 4H, C_6H_5); 6.16 (M, 2H, CH=CH). Anal. Found: C, 54.34; H, 3.64; Cr, 16.70. $C_{14}H_{10}CrO_5$ Calc.: C, 54.20; H, 3.26; Cr, 16.76%.

3.2.5. [(η^6-N-Methylindoline)-3-carboxylic acid methyl ester]chromium tricarbonyl (25)

A 50 ml flask was charged with 20 ml of THF, 0.23 ml (2.23 mmol) of diethylamine and 2.23 ml (2.23 mmol) of ^{n}BuLi solution and cooled to −30 °C. 0.3 g (1.12 mmol) of (η^6-*N*-methylindoline)chromium tricarbonyl was added. After stirring for 5 min at −30 °C, the mixture was poured onto solid CO_2. 30 min after the evaporation of CO_2, 1 ml of conc. HCl was added to the mixture, THF was evaporated in vacuo, and the residue treated with an excess of CH_2N_2 solution in ether. After evolution of nitrogen had ceased, the mixture was filtered through a 2 cm layer of Al_2O_3. The products were eluted with ether. The solvent was evaporated and the residue recrystallized from a 1:3 ether–hexane mixture. This afforded 0.19 g (51%) of **25** as yellow crystals, m.p. 127–129 °C. ^{1}H NMR ($CDCl_3$): 2.75 (s, 3H, N–CH_3); 2.67 (m, 2H, CH_2); 2.90 (s, 3H, O–CH_3); 4.05 (m, 1H, CH); 4.70 (m), 4.80 (m), 5.50 (m), 5.90 (m, 4H, C_6H_5). Anal. Found: C, 51.39; H, 4.14; N, 4.29; Cr, 15.11. $C_{14}H_{13}CrNO_5$ Calc.: C, 51.38; H, 4.01; N, 4.28; Cr, 15.89%.

3.2.6. [(η^6-N-Methyl-1,2,3,4-tetrahydroquinoline)-4-carboxylic acid methyl ester]chromium tricarbonyl (26)

26 was obtained by the procedure described for **25** from 0.15 ml (1.41 mmol) of diethylamine, 1.41 ml (1.41 mmol) of ^{n}BuLi solution, and 0.2 g (0.71 mmol) of (η^6-*N*-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl after metallation for 5 min at 20 °C. Yield 0.19 g (80%), m.p. 88 °C. ^{1}H NMR ($CDCl_3$): 2.29 (m, 2H, N–CH_2–); 2.93 (s, 3H, N–CH_3); 3.11–3.57 (m, 3H, $CHCH_2$); 3.75 (s, 3H, OCH_3); 4.79–4.89 (m), 5.57–5.75 (m, 2H + 2H, C_6H_4). Anal. Found: C, 53.05; H, 4.92; N, 4.23; Cr, 15.12. $C_{15}H_{15}CrNO_5$ Calc.: C, 52.78; H, 4.44; N, 4.11; Cr, 15.24%.

3.2.7. [(η^6-N-Methyl-1,2,3,4-tetrahydroisoquinoline)-4-carboxylic acid methyl ester]chromium tricarbonyl (27)

27 was obtained by the procedure described for **25** from 0.15 ml (1.41 mmol) of diethylamine, 1.41 ml

(1.41 mmol) of ^{n}BuLi solution, and 0.2 g (0.71 mmol) of (η^6-*N*-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl after metallation for 5 min at 20 °C. Yield 0.19 g (80%) as a yellow oil. ^{1}H NMR ($CDCl_3$): 2.40 (s, 3H, NCH_3); 2.60–2.73 (m, 1H, CH); 3.20–3.37 (m, 2H, CH_2NCH_2CH); 3.50–3.73 (m, 2H, CH_2NCH_2CH); 5.20–5.50 (m, 4H, C_6H_4). Anal. Found: C, 52.44; H, 4.49; N, 4.20; Cr, 15.39. $C_{15}H_{15}CrNO_5$ Calc.: C, 52.78; H, 4.44; N, 4.11; Cr, 15.24%.

3.3. 1,2-Addition reaction of benzylic lithium derivatives of (η^6-alkylarene)chromium tricarbonyl complexes to carbonyl compounds

3.3.1. (η^6-2-Methyl-1-phenylpropan-2-ol)chromium tricarbonyl (29)

A two-necked 50 ml flask was charged with 20 ml of THF, after which 0.068 ml (0.66 mmol) of diethylamine and 0.66 ml (0.66 mmol) of ^{n}BuLi solution were added and the contents cooled to 0 °C. After 5 min, 0.1 g (0.44 mmol) of (η^6-toluene)chromium tricarbonyl was added and the mixture stirred for 10 min at 0 °C. The mixture was cooled to −30 °C and 0.44 ml (0.44 mmol) of ^{n}BuLi solution was added. The mixture was stirred again for 5 min at −30 °C and cooled to −70 °C. Next, 0.16 ml (2.19 mmol) of acetone was added to the mixture, followed by stirring again for 30 min. The mixture was heated to 20 °C. After the addition of 2 ml of saturated aqueous NH_4Cl solution, THF was distilled away in vacuo, the residue was dissolved in chloroform, and the solution was filtered through a layer of Al_2O_3 (1 cm). The solvent was distilled away in vacuo and the product was purified by thin layer chromatography on Al_2O_3 using a 1:5 ether–pentane mixture as eluent and subsequent crystallization. This afforded 0.1 g (80%) **29** as yellow crystals, m.p. 72–73.5 °C. ^{1}H NMR ($CDCl_3$): 1.25 (s, 6H, $2CH_3$); 1.35 (s, 1H, OH); 2.45 (s, 2H, CH_2); 5.15–5.45 (m, 5H, C_6H_5). Anal. Found: C, 54.24; H, 4.73; Cr, 18.32. $C_{13}H_{14}CrO_4$ Calc.: C, 54.54; H, 4.93; Cr, 18.16%.

3.3.2. (η^6-1-Phenylpropan-2-ol)chromium tricarbonyl (30)

30 was obtained by the procedure described for **29** from 0.45 ml (4.39 mmol) of diethylamine, 4.39 ml (4.39 mmol) of ^{n}BuLi solution, 0.5 g (2.19 mmol) of (η^6-toluene)chromium tricarbonyl, 2.19 ml (2.19 mmol) of ^{n}BuLi solution and 0.61 ml (10.96 mmol) of acetaldehyde. Yield 0.34 g (62%), m.p. 69.5–70 °C. ^{1}H NMR ($CDCl_3$): 1.30 (d, 3H, CH_3); 1.60 (d, 1H, OH); 2.45 (m, 2H, CH_2); 4.00 (m, 1H, CH); 5.15–5.50 (m, 5H, C_6H_5). Anal. Found: C, 53.13; H, 4.44; Cr, 19.25. $C_{12}H_{12}CrO_4$ Calc.: C, 52.94; H, 4.45; Cr, 19.09%.

3.3.3. (η^6-2-Methyl-1-phenylbut-3-en-2-ol)chromium tricarbonyl (31)

31 was obtained by the procedure described for **29** from 0.27 ml (2.63 mmol) of diethylamine, 2.63 ml (2.63 mmol) of ^{n}BuLi solution, 0.3 g (1.32 mmol) of (η^6-toluene)chromium tricarbonyl, 1.32 ml (1.32 mmol) of ^{n}BuLi solution and 0.55 ml (7.86 mmol) of methyl vinyl ketone. Yield 0.27 g (69%), m.p. 76–77 °C. ^{1}H NMR ($CDCl_3$): 1.35 (s, 3H, CH_3); 1.45 (s, 1H, OH); 2.50 (s, 2H, CH_2); 5.10–5.40 (m, 7H, C_6H_5 and $=CH_2$); 5.95 (m, 1H, –CH=). Anal. Found: C, 55.72; H, 4.62; Cr, 17.90. $C_{14}H_{14}CrO_4$ Calc.: C, 56.37; H, 4.73; Cr, 17.43%.

3.3.4. 2-Phenyl-1-[(η^6-phenyl)chromium tricarbonyl]-propan-2-ol (32)

32 was obtained by the procedure described for **29** from 0.45 ml (4.39 mmol) of diethylamine, 4.39 ml (4.39 mmol) of ^{n}BuLi solution, 0.5 g (2.19 mmol) of (η^6-toluene)chromium tricarbonyl, 2.19 ml (2.19 mmol) of ^{n}BuLi solution and 1.28 ml (10.96 mmol) of acetophenone. Yield 0.48 g (63%), m.p. 89–89.5 °C. ^{1}H NMR ($CDCl_3$): 1.70 (s, 3H, CH_3); 1.80 (s, 1H, OH); 2.75 (s, 2H, CH_2); 5.05–5.45 (m, 5H, $C_6H_5[Cr(CO)_3]$); 7.30 (m, 5H, C_6H_5). Anal. Found: C, 61.74; H, 4.66; Cr, 15.24. $C_{18}H_{16}CrO_4$ Calc.: C, 62.06; H, 4.63; Cr, 14.92%.

3.3.5. (η^6-2-Methyl-3-phenylbutan-2-ol)chromium tricarbonyl (33)

33 was obtained by the procedure described for **29** from 0.26 ml (2.48 mmol) of diethylamine, 2.48 ml (2.48 mmol) of ^{n}BuLi solution, 0.3 g (1.24 mmol) of (η^6-ethylbenzene)chromium tricarbonyl, 1.24 ml (1.32 mmol) of ^{n}BuLi solution and 0.45 ml (6.20 mmol) of acetone. Yield 0.25 g (67%), m.p. 46–47 °C. ^{1}H NMR ($CDCl_3$): 1.20 (d, 3H, $CH–CH_3$); 1.25 (s, 6H, $2CH_3$); 2.45 (m, 1H, CH); 5.10–5.45 (m, 5H, C_6H_5). Anal. Found: C, 56.00; H, 5.37; Cr, 17.46. $C_{14}H_{16}CrO_4$ Calc.: C, 55.99; H, 5.37; Cr, 17.31%.

3.3.6. [η^6-1-(2-Hydroxyprop-2-yl)-1,2,3,4-tetrahydronaphthalene]chromium tricarbonyl (34)

34 was obtained by the procedure described for **29** from 0.23 ml (2.24 mmol) of diethylamine, 2.24 ml (2.24 mmol) of ^{n}BuLi solution, 0.3 g (1.12 mmol) of (η^6-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl, 1.12 ml (1.12 mmol) of ^{n}BuLi solution and 0.4 ml (5.60 mmol) of acetone. Yield 0.3 g (82%), m.p. 110–111 °C. ^{1}H NMR ($CDCl_3$): 1.10 (s, 3H, CH_3); 1.35 (s, 3H, CH_3); 1.45 (s, 1H, OH); 1.55–2.15 (m, 4H, $CH–CH_2–CH_2$); 2.45–2.55 (m, 2H, CH_2); 2.80 (m, 1H, CH); 5.25 (m, 3H), 6.15 (m, 1H, C_6H_4). Anal. Found: C, 58.83; H, 5.47; Cr, 15.94. $C_{16}H_{18}CrO_4$ Calc.: C, 58.88; H, 5.56; Cr, 15.93%.

3.3.7. [η^6-N-Methyl-4-(2-hydroxyprop-2-yl)-1,2,3,4-tetrahydroisoquinoline]chromium tricarbonyl (35)

35 was obtained by the procedure described for **29** from 0.22 ml (2.12 mmol) of diethylamine, 2.12 ml (2.12 mmol) of ^{n}BuLi solution, 0.3 g (1.06 mmol) of (η^6-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl, 1.06 ml (1.06 mmol) of ^{n}BuLi solution and 0.39 ml (5.30 mmol) of acetone. Yield 0.26 g (72%), m.p. 143–144.5 °C. ^{1}H NMR ($CDCl_3$): 1.30 (s, 3H, CH_3); 1.40 (s, 3H, CH_3); 2.30 (m, 1H, CH); 2.40 (s, 3H, N–CH_3); 2.70 (dd, 1H), 3.25 (d, 1H, ABX system, J_{AB} = 13 Hz, J_{AX} = 3 Hz, CH–CH_2); 3.30, 3.80 (dd, AB system, J_{AB} = 16 Hz, 2H, CH_2); 5.10–5.45 (m, 4H, C_6H_4); 6.35 (s, 1H, OH). Anal. Found: C, 56.13; H, 5.57; Cr, 15.28. $C_{16}H_{19}CrNO_4$ Calc.: C, 56.29; H, 5.61; Cr, 15.23%.

3.3.8. (η^6-N-Methyl-4-hydroxydiphenylmethyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl (36)

36 was obtained by the procedure described for **29** from 0.22 ml (2.12 mmol) of diethylamine, 2.12 ml (2.12 mmol) of ^{n}BuLi solution, 0.3 g (1.06 mmol) of (η^6-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl, 1.06 ml (1.06 mmol) of ^{n}BuLi solution and 0.96 g (5.30 mmol) of benzophenone. Yield 0.42 g (85%), m.p. 187–188 °C. ^{1}H NMR ($CDCl_3$): 2.20 (s, 3H, CH_3); 2.70 (dd, 1H), 3.25 (d, 1H, ABX system, J_{AB} = 12 Hz, J_{AX} = 3 Hz, CH–CH_2); 3.30, 3.85 (dd, AB system, J_{AB} = 16 Hz, 2H, CH_2); 3.50 (m, 1H, CH); 4.20 (m, 1H), 4.70 (m, 1H), 5.25 (m, 2H, C_6H_4); 7.10–7.75 (m, 10H, $2C_6H_5$). Anal. Found: C, 67.36; H, 5.09; Cr, 11.06. $C_{26}H_{23}CrNO_4$ Calc.: C, 67.68; H, 4.98; Cr, 11.17%.

3.3.9. (η^6-N-Methyl-4-hydroxydiphenylmethyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl (37)

37 was obtained by the procedure described for **29** from 0.22 ml (2.12 mmol) of diethylamine, 2.12 ml (2.12 mmol) of ^{n}BuLi solution, 0.3 g (1.06 mmol) of (η^6-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl, 1.06 ml (1.06 mmol) of ^{n}BuLi solution and 0.96 g (5.30 mmol) of benzophenone. Yield 0.35 g (71%), m.p. 187–188 °C. ^{1}H NMR ($CDCl_3$): 2.00–2.20 (m, 2H, CH–CH_2); 2.70 (s, 1H, OH); 2.85 (s, 3H, CH_3); 3.00–3.25 (m, 2H, N–CH_2); 3.60 (m, 1H, CH); 4.40 (m, 1H), 4.80 (m, 1H), 4.95 (m, 1H), 5.50 (m, 1H, C_6H_4); 7.15–7.65 (m, 10H, $2C_6H_5$). Anal. Found: C, 67.24; H, 5.18; Cr, 10.06. $C_{26}H_{23}CrNO_4$ Calc.: C, 67.68; H, 4.98; Cr, 11.17%.

3.4. Cross-coupling reactions of benzylic derivatives of (η^6-alkylarene)chromium tricarbonyl complexes with acetyl chloride

3.4.1. (η^6-1-Phenylpropan-2-on)chromium tricarbonyl (38)

A two-necked 50 ml flask was charged with 20 ml of THF, after which 0.16 ml (1.5 mmol) of diethylamine and 1.5 ml (1.5 mmol) of ^{n}BuLi solution were added, and the contents cooled to 0 °C. After 5 min, 0.23 g (1.0 mmol) of (η^6-toluene)chromium tricarbonyl was added and the mixture was stirred for 10 min at 0 °C. The mixture was cooled to −30 °C and 1.0 ml (1.0 mmol) of ^{n}BuLi solution was added. The mixture was stirred again for 5 min at −30 °C. Next, 0.34 g (2.5 mmol) of $ZnCl_2$ was added to the mixture and the latter was heated to 0 °C. The mixture was stirred again for 15 min at 0 °C, then 0.71 ml (10 mmol) of acetyl chloride and 0.06 g (0.05 mmol) of $Pd(PPh_3)_4$ were added, and the mixture was stirred again for 2 h at 0 °C. After the addition of 1 ml of saturated aqueous NH_4Cl solution, the THF was distilled away in vacuo, the residue was dissolved in chloroform, and the solution was filtered through a layer of Al_2O_3 (1 cm). The solvent was distilled away in vacuo and the product was purified by thin layer chromatography on SiO_2 using a 1:3 ether–pentane mixture as eluent and subsequent crystallization. This afforded 0.16 g (59%) **38** as yellow crystals, m.p. 56–57 °C. ^{1}H NMR ($CDCl_3$): 2.28 (s, 3H, CH_3); 3.45 (s, 2H, –CH_2–); 5.08–5.48 (m, 5H, C_6H_5). Anal. Found: C, 53.34; H, 4.03; Cr, 19.37. $C_{12}H_{10}CrO_4$ Calc.: C, 53.34; H, 3.73; Cr, 19.24%.

3.4.2. (η^6-3-Phenylbutan-2-on)chromium tricarbonyl (39)

39 was obtained by the procedure described for **38** from 0.21 ml (2.0 mmol) of diethylamine, 2.0 ml (2.0 mmol) of ^{n}BuLi solution, 0.24 g (1.0 mmol) of (η^6-ethylbenzene)chromium tricarbonyl, 1.0 ml (1.0 mmol) of ^{n}BuLi solution, 0.41 ml (3.0 mmol) of $ZnCl_2$, 0.71 ml (10 mmol) of acetyl chloride and 0.06 g (0.05 mmol) of $Pd(PPh_3)_4$. Yield 0.16 g (56%) as a yellow oil. ^{1}H NMR ($CDCl_3$): 1.44 (d, 3H, CH–CH_3); 2.25 (s, 3H, C(O)CH_3); 3.50 (m, 1H, CH–CH_3); 5.20–5.44 (m, 5H, C_6H_5). Anal. Found: C, 55.04; H, 4.45; Cr, 18.54. $C_{13}H_{12}CrO_4$ Calc.: C, 54.94; H, 4.26; Cr, 18.29%.

3.4.3. (η^6-1-Acetyl-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl (40)

40 was obtained by the procedure described for **38** from 0.21 ml (2.0 mmol) of diethylamine, 2.0 ml (2.0 mmol) of ^{n}BuLi solution, 0.24 g (1.0 mmol) of (η^6-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl, 1.0 ml (1.0 mmol) of ^{n}BuLi solution, 0.41 ml (3.0 mmol) of $ZnCl_2$, 0.71 ml (10 mmol) of acetyl chloride and 0.06 g (0.05 mmol) of $Pd(PPh_3)_4$. Yield 0.22 g (71%), m.p. 78–79 °C. ^{1}H NMR ($CDCl_3$): 1.24–1.51, 1.51–2.05, 2.05–2.37 (m, 4H, CH–CH_2–CH_2–CH_2); 2.32 (s, 3H, C(O)CH_3); 2.66 (t, 2H, CH–CH_2–CH_2–CH_2); 3.78 (t, 1H, CH–CH_2–CH_2–CH_2); 5.12–5.32 (m, 4H, C_6H_4). Anal. Found: C, 58.06; H, 4.53; Cr, 16.62. $C_{15}H_{14}CrO_4$ Calc.: C, 58.07; H, 4.55; Cr, 16.76%.

*3.4.4. (η^6-4-Acetyl-N-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl (**41**)*

41 was obtained by the procedure described for **38** from 0.21 ml (2.0 mmol) of diethylamine, 2.0 ml (2.0 mmol) of ^{n}BuLi solution, 0.24 g (1.0 mmol) of (η^6-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl, 1.0 ml (1.0 mmol) of ^{n}BuLi solution, 0.41 ml (3.0 mmol) of $ZnCl_2$, 0.71 ml (10 mmol) of acetyl chloride and 0.06 g (0.05 mmol) of $Pd(Ph_3)_4$. Yield 0.22 g (71%, a mixture of *exo*- and *endo*-isomers). The ratio between *exo*- and *endo*-isomers was shown by ^{1}H NMR to be 4.8:1 in $CDCl_3$ and 6.1:1 in C_6D_6.

3.4.4.1. exo-(η^6-4-Acetyl-N-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl. ^{1}H NMR ($CDCl_3$): 2.14 (s, 3H, C(O)CH_3); 3.08 (s, 3H, N–CH_3); 3.96, 4.90 (1H + 1H, AB system, J_{AB} = 15.3 Hz, CH_2–N–CH_2–CH); 5.25–5.70 (m, 4H, C_6H_4); 5.48 (1H, H_A), 5.66 (1H, H_B), 6.66 (1H, H_X) (ABX system, J_{AB} = 0 Hz, J_{AX} = 11.5 Hz, J_{BX} = 17.2 Hz, CH_2–N–CH_AH_B–CH_X). ^{1}H NMR (C_6D_6): 1.70 (s, 3H, C(O)CH_3); 2.36 (s, 3H, N–CH_3); 3.62, 4.68 (1H + 1H, AB system, J_{AB} = 15.3 Hz, CH_2–N–CH_2–CH); 4.48–4.58, 4.84–4.87, 5.07–5.11 (m, 2H + 1H + 1H, C_6H_4); 5.30 (1H, H_A), 5.23 (1H, H_B), 6.45 (1H, H_X) (ABX system, J_{AB} = 0 Hz, J_{AX} = 10.9 Hz, J_{BX} = 17.4 Hz, CH_2–N–CH_AH_B–CH_X).

3.4.4.2. endo-(η^6-4-Acetyl-N-methyl-1,2,3,4-tetrahydroisoquinoline)chromium tricarbonyl. ^{1}H NMR ($CDCl_3$): 2.14 (s, 3H, C(O)CH_3); 2.98 (s, 3H, N–CH_3); 6.66 (m, 1H, CH_2–N–CH_2–C*H*). ^{1}H NMR (C_6D_6): 1.84 (s, 3H, C(O)CH_3); 2.78 (s, 3H, N–CH_3); 6.05 (m, 1H, CH_2–N–CH_2–C*H*).

Anal. Found: C, 54.95; H, 5.15; N, 4.12; Cr, 16.02. $C_{15}H_{15}CrNO_4$ Calc.: C, 55.39; H, 4.65; N, 4.31; Cr, 15.98%.

*3.4.5. exo-(η^6-4-Acetyl-N-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl (**42**)*

42 was obtained by the procedure described for **38** from 0.21 ml (2.0 mmol) of diethylamine, 2.0 ml (2.0 mmol) of ^{n}BuLi solution, 0.24 g (1.0 mmol) of (η^6-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl, 1.0 ml (1.0 mmol) of ^{n}BuLi solution, 0.41 ml (3.0 mmol) of $ZnCl_2$, 0.71 ml (10 mmol) of acetyl chloride and 0.06 g (0.05 mmol) of $Pd(PPh_3)_4$. Yield 0.11 g (34%), m.p. 114–115 °C.

3.4.5.1. exo-(η^6-4-Acetyl-N-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl. ^{1}H NMR ($CDCl_3$): 2.08–2.42 (m, 2H, N–CH_2–CH_2–CH); 2.26 (s, 3H, C(O)CH_3); 2.87 (s, 3H, N–CH_3); 3.13–3.25 (m, 2H, N–CH_2–CH_2–CH); 3.56 (t, 1H, N–CH_2–CH_2–C*H*); 4.75–4.88, 5.41–5.64 (m, 4H, C_6H_4). ^{1}H NMR (C_6D_6): 1.46–1.62, 1.68–2.00 (m, 2H, N–CH_2–CH_2–CH); 1.64 (s, 3H, C(O)CH_3); 2.11 (s, 3H, N–CH_3); 2.39–2.76 (m, 2H, N–CH_2–CH_2–CH); 2.99 (t, 1H, N–CH_2–CH_2–C*H*); 4.07–4.27, 4.91–5.00 (m, 4H, C_6H_4).

3.4.5.2. endo-(η^6-4-Acetyl-N-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl. ^{1}H NMR ($CDCl_3$): 1.88–2.08, 2.10–2.37 (m, 2H, N–CH_2–CH_2–CH); 2.46 (s, 3H, C(O)CH_3); 2.87 (s, 3H, N–CH_3); 3.12–3.29, 3.43–3.61 (m, 2H, N–CH_2–CH_2–CH); 3.54 (t, 1H, N–CH_2–CH_2–C*H*); 4.62–4.90, 5.52–5.64 (m, 4H, C_6H_4). ^{1}H NMR (C_6D_6): 1.00–1.30, 1.73–2.00 (m, 2H, N–CH_2–CH_2–CH); 2.10 (s, 3H, C(O)CH_3); 2.25 (s, 3H, N–CH_3); 2.25–2.53, 2.90–3.05 (m, 2H, N–CH_2–CH_2–CH); 2.82 (t, 1H, N–CH_2–CH_2–C*H*); 3.94 (d, 1H), 4.09 (m, 1H), 4.88–5.00 (d, 1H, C_6H_4).

Anal. Found: C, 56.04; H, 4.94; N, 4.24; Cr, 16.81. $C_{15}H_{15}CrNO_4$ Calc.: C, 55.39; H, 4.65; N, 4.31; Cr, 15.98%.

3.5. Cross-coupling reactions of benzylic zinc derivatives of (η^6-alkylarene)chromium tricarbonyl complexes with organic halides

*3.5.1. (η^6-1-Diphenylmethane)chromium tricarbonyl (**43**)*

A two-necked 50 ml flask was charged with 20 ml of THF, after which 0.17 ml (1.5 mmol) of diethylamine and 1.65 ml (1.65 mmol) of ^{n}BuLi solution were added and the contents cooled to 0 °C. After 5 min, 0.25 g (1.1 mmol) of (η^6-toluene)chromium tricarbonyl was added and the mixture was stirred for 10 min at 0 °C. The mixture was cooled to −30 °C and 1.1 ml (1.1 mmol) of ^{n}BuLi solution was added. The mixture was stirred again for 5 min at −30 °C. Next, 0.34 g (2.5 mmol) of $ZnCl_2$ was added to the mixture, and the latter was heated to 20 °C. The mixture was stirred again for 15 min at 20 °C, and added dropwise to a boiling solution of 0.62 ml (5.5 mmol) of PhI and 0.06 g (0.05 mmol) of $Pd(PPh_3)_4$ in 10 ml of THF. After an additional reflux for 1 h and cooling to room temperature, 1 ml of saturated aqueous NH_4Cl solution was added. THF was distilled away in vacuo, the residue was dissolved in chloroform and the solution was filtered through a layer of Al_2O_3 (1 cm). The solvent was distilled away in vacuo and the product was purified by thin layer chromatography on SiO_2 using a 1:3 ether–pentane mixture as eluent and subsequent crystallization. This afforded 0.22 g (66%) **43** as yellow crystals, m.p. 101 °C (100 °C [27]).

*3.5.2. 1-Phenyl-(η^6-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl (**44**)*

44 was obtained by the procedure described for **43** from 0.15 ml (1.11 mmol) of diethylamine, 1.11 ml (1.11 mmol) of ^{n}BuLi solution, 0.2 g (0.74 mmol) of (η^6-1,2,3,4-tetrahydronaphthaline)chromium tricar-

bonyl, 0.74 ml (0.74 mmol) of ^{n}BuLi solution, 0.25 g (1.85 mmol) of $ZnCl_2$, 0.42 ml (3.70 mmol) of PhI and 0.03 g (0.04 mmol) of $Pd(PPh_3)_4$. Yield 0.095 g (37%), m.p. 119–121 °C. ^{1}H NMR ($CDCl_3$): 0.63–0.97, 2.10–2.30, 2.63–2.93 (m, 6H, CH_2–CH_2–CH_2–CH); 4.00 (t, 1H, CH); 5.00–5.40 (m, 4H, C_6H_4); 7.07–7.43 (m, 5H, C_6H_5). Anal. Found: C, 66.10; H, 4.88; Cr, 14.96. $C_{19}H_{16}CrO_3$ Calc.: C, 66.28; H, 4.68; Cr, 15.10%.

*3.5.3. 4-Phenyl-(η^6-N-methyl-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl (**45**)*

45 was obtained by the procedure described for **43** from 0.27 ml (2.65 mmol) of diethylamine, 2.65 ml (2.65 mmol) of ^{n}BuLi solution, 0.5 g (1.77 mmol) of (η^6-1,2,3,4-tetrahydroquinoline)chromium tricarbonyl, 1.77 ml (1.77 mmol) of ^{n}BuLi solution, 0.6 g (4.42 mmol) of $ZnCl_2$, 0.99 ml (8.83 mmol) of PhI and 0.2 g (0.18 mmol) of $Pd(PPh_3)_4$. Yield 0.17 g (27%), m.p. 137–138 °C. ^{1}H NMR ($CDCl_3$): 1.68–1.94, 1.94–2.24 (m, 2H, CH_2–CH); 2.68 (s, 3H, CH_3); 2.82–3.15 (m, 2H, CH_2–N); 3.74 (t, 1H, CH); 4.50, 4.68, 5.09, 5.29 (m, 1H + 1H + 1H + 1H, C_6H_4); 6.79–7.24 (m, 5H, C_6H_5). Anal. Found: C, 63.46; H, 4.88; N, 3.76; Cr, 14.33. $C_{19}H_{17}CrNO_3$ Calc.: C, 63.51; H, 4.77; N, 3.90; Cr, 14.47%.

*3.5.4. [1-Phenyl-3-(η^6-phenyl)-prop-1-en]chromium tricarbonyl (**46**)*

46 was obtained by the procedure described for **43** from 0.34 ml (3.29 mmol) of diethylamine, 3.29 ml (3.29 mmol) of ^{n}BuLi solution, 0.5 g (2.19 mmol) of (η^6-toluene)chromium tricarbonyl, 2.19 ml (2.19 mmol) of ^{n}BuLi solution, 0.75 g (5.48 mmol) of $ZnCl_2$, 0.85 ml (6.58 mmol) of β-bromostyrene and 0.25 g (0.22 mmol) of $Pd(PPh_3)_4$. Yield 0.32 g (44%), m.p. 116–117.5 °C. ^{1}H NMR ($CDCl_3$): 3.35 (d, 2H, CH_2–CH=); 5.25, 5.40 (m, 5H, [$C_6H_5Cr(CO)_3$]); 6.43 (dt, 1H, CH_2–CH=CH–); 6.53 (d, 1H, CH_2–CH=CH–); 7.28–7.48 (m, 5H, C_6H_5). Anal. Found: C, 65.50; H, 4.43; Cr, 15.37. $C_{18}H_{14}CrO_3$ Calc.: C, 65.45; H, 4.27; Cr, 15.74%.

*3.5.5. [(2-Thienyl)(η^6-phenyl)methane]chromium tricarbonyl (**47**)*

47 was obtained by the procedure described for **43** from 0.34 ml (3.29 mmol) of diethylamine, 3.29 ml (3.29 mmol) of ^{n}BuLi solution, 0.5 g (2.19 mmol) of (η^6-toluene)chromium tricarbonyl, 2.19 ml (2.19 mmol) of ^{n}BuLi solution, 0.75 g (5.48 mmol) of $ZnCl_2$, 0.73 ml (6.58 mmol) of 2-iodothiophene and 0.51 g (0.44 mmol) of $Pd(PPh_3)_4$. Yield 0.09 g (13%), m.p. 92–93 °C. ^{1}H NMR ($CDCl_3$): 3.93 (s, 2H, CH_2); 5.22, 5.39 (m, 5H, C_6H_5); 6.95, 7.24 (m, 3H, C_4H_3S). Anal. Found: C, 54.41; H, 3.24; S, 9.96; Cr, 16.78. $C_{14}H_{10}CrO_3S$ Calc.: C, 54.19; H, 3.25; S, 10.33; Cr, 16.76%.

3.6. A 1,4-addition reaction of [η^6-benzylcopper(I)]chromium tricarbonyl to methyl vinyl ketone

*3.6.1. 5-[(η^6-Phenyl)chromium tricarbonyl]-pentan-2-one (**48**)*

3.6.1.1. Method A. A two-necked 50 ml flask was charged with 20 ml of THF, after which 0.068 ml (0.66 mmol) of diethylamine and 0.66 ml (0.66 mmol) of ^{n}BuLi solution were added and the contents cooled to 0 °C. After 5 min, 0.1 g (0.44 mmol) of (η^6-toluene)chromium tricarbonyl was added and the mixture was stirred for 10 min at 0 °C. The mixture was cooled to −30 °C and 0.44 ml (0.44 mmol) of ^{n}BuLi solution was added. The mixture was stirred again for 5 min at −30 °C and cooled to −70 °C. Next, 0.42 g (2.19 mmol) of CuI was added to the mixture, and the latter was heated to 20 °C. The mixture was stirred again for 10 min at 20 °C and cooled to −70 °C. 0.36 ml (4.38 mmol) of methyl vinyl ketone and 0.56 ml (4.38 mmol) of chlorotrimethylsilane were added. The mixture was stirred again for 10 min at −70 °C. After an additional stirring for 2 h at 20 °C, 1 ml of 10% aqueous HCl solution was added. THF was distilled away in vacuo, the residue was dissolved in chloroform and the solution was filtered through a layer of Al_2O_3 (1 cm). The solvent was distilled away and the product was purified by thin layer chromatography on SiO_2 using a 1:3 ether–pentane mixture as eluent and subsequent crystallization. This afforded 0.09 g (69%) of **48** as yellow crystals, m.p. 62–63.5 °C. ^{1}H NMR ($CDCl_3$): 1.84 (m, 2H, CH_2–CH_2–CH_2); 2.16 (s, 3H, CH_3); 2.33 (t, 2H, CO–CH_2); 2.52 (t, 2H, CH_2–CH_2–CH_2–CO); 5.18–5.45 (m, 5H, C_6H_5). Anal. Found: C, 56.23; H, 4.66; Cr, 17.03. $C_{14}H_{14}CrO_4$ Calc.: C, 56.37; H, 4.73; Cr, 17.43%.

3.6.1.2. Method B. **36** was obtained by the procedure described for Method A from 0.068 ml (0.66 mmol) of diethylamine, 0.66 ml (0.66 mmol) of ^{n}BuLi solution, 0.1 g (0.44 mmol) of (η^6-toluene)chromium tricarbonyl, 0.44 ml (0.44 mmol) of ^{n}BuLi solution, 0.42 g (2.19 mmol) of CuI, 0.36 ml (4.38 mmol) of methyl vinyl ketone, 0.54 ml (4.38 mmol) of $BF_3 \cdot Et_2O$. Yield 0.075 g (58%), m.p. 63–63.5 °C.

3.6.1.3. Method C. **36** was obtained by the procedure described for Method A from 0.068 ml (0.66 mmol) of diethylamine, 0.66 ml (0.66 mmol) of ^{n}BuLi solution, 0.1 g (0.44 mmol) of (η^6-toluene)chromium tricarbonyl, 0.44 ml (0.44 mmol) of ^{n}BuLi solution, 0.37 g (2.19 mmol) of CuBr, 0.36 ml (4.38 mmol) of methyl vinyl ketone, 0.54 ml (4.38 mmol) of $BF_3 \cdot Et_2O$. Yield 0.055 g (42%), m.p. 63–63.5 °C.

3.7. The total synthesis of 5-acetoxy-3-benzyl-1,4-methano-2,3,4,5-tetrahydro-1H-3-benzazepine

3.7.1. η^6-(1-Trimethylsilyloxy-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl (28)

A 100 ml flask was charged with 50 ml of THF, 5.0 g (17.6 mmol) of η^6-(1-hydroxy-1,2,3,4-tetrahydronaphthalene)chromium tricarbonyl (**50**), 2.6 ml (20.3 mmol) of chlorotrimethylsilane and 1.65 ml (20.3 mmol) of pyridine. The mixture was stirred for 1.5 h at room temperature and then filtered through a layer of Al_2O_3 (2 cm). The products were eluted with ether. The solvent was evaporated in vacuo and the residue recrystallized from ether on cooling to −40 °C, which afforded 5.7 g (91%) of **28** as yellow crystals, m.p. 96 °C. ^{1}H NMR ($CDCl_3$): 0.24 (s, 9H, $Si(CH_3)_3$); 1.50–1.85 (m, 2H, O–CH–CH_2–CH_2–CH_2); 1.85–2.11 (m, 2H, O–CH–CH_2–CH_2–CH_2); 2.49–2.81 (m, 2H, O–CH–CH_2–CH_2–CH_2); 4.48–4.62 (m, 1H, O–CH–); 5.00–5.70 (m, 4H, C_6H_4). Anal. Found: C, 53.97; H, 5.63; Cr, 14.60; Si, 7.79. $C_{16}H_{20}CrO_4Si$ Calc.: C, 53.91; H, 5.67; Cr, 14.59; Si, 7.88%.

3.7.2. (η^6-4-Hydroxy-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid)chromium tricarbonyl (28a)

28a was obtained by the procedure described for **21** from 0.29 ml (2.81 mmol) of diethylamine, 2.81 ml (2.81 mmol) of ^{n}BuLi solution, and 0.5 g (1.40 mmol) of complex **28** after metallation for 5 min at 0 °C. Yield 0.44 g (96%), m.p. 101–102 °C. ^{1}H NMR ($CDCl_3$): 1.59–2.41 (m, 4H, $-CH_2$ $-CH_2-$); 3.68 (m, 1H, C*H*–COOH); 4.50 (m, 1H, C*H*–OH); 5.11–5.77 (m, 4H, C_6H_4). *m/z* 328, M^+. Anal. Found: C, 49.66; H, 4.07; Cr, 14.09. $C_{14}H_{12}CrO_6$ Calc.: C, 51.22; H, 3.69; Cr, 15.84%.

3.7.3. η^6-(1,2-Dihydronaphthalene-1-carboxylic acid methyl ester)chromium tricarbonyl (51)

A 100 ml flask was charged with 50 ml of CCl_4, 5.0 ml of MeOH, 5 ml of concentrated H_2SO_4 and 2.63 g of complex **28a**. The mixture was refluxed for 2 h and treated with 30 ml of water. The organic layer was separated, washed with water (2 × 30 ml) and filtered through a layer of Al_2O_3 (2 cm), eluting the products with ether. The solvent was evaporated in vacuo and the residue recrystallized from 1:3 ether–hexane mixture, which afforded 1.4 g (60%) of **51** as yellow crystals, m.p. 114–116 °C. ^{1}H NMR ($CDCl_3$): 2.66–3.00 (m, 2H, CH_2); 3.50 (m, 1H, –CH–); 3.72 (s, 3H, CH_3); 5.14–5.21 (m), 5.21–5.59 (m, 2H + 2H, C_6H_4); 6.14 (m, 2H, CH=CH). Anal. Found: C, 55.57; H, 4.15; Cr, 16.19. $C_{15}H_{12}CrO_5$ Calc.: C, 55.56; H, 3.74; Cr, 16.04%.

3.7.4. N-Benzylamide of 1,2-dihydronaphthalene-1-carboxylic acid 52

A 25 ml flask was charged with 5 ml of benzylamine, 0.2 g of NH_4Cl and 1.8 g (5.56 mmol) of complex **51**. The mixture was heated for 9 h at 150 °C. After cooling, the reaction mixture was dissolved in 50 ml of $CHCl_3$. The resulting solution was washed with 10% aqueous HCl solution (3 × 20 ml) and the solvent evaporated in vacuo. The residue was extracted with hot heptane (5 × 25 ml) and the solvent evaporated in vacuo. The residue was chromatographed on a 30 cm Al_2O_3 column (eluent 1:10 ether–hexane mixture), which afforded 0.71 g (52%) of **52** as colourless fine crystals, m.p. 85–87 °C. ^{1}H NMR ($CDCl_3$): 2.55–2.71 (m), 3.00–3.19 (m, 1H + 1H, CH–CH_2); 3.61–3.71 (m, 1H, CH); 4.29–4.55 (m, 2H, CH_2N); 5.65 (m, 1H, NH). 6.00–6.13 (m), 6.50–6.56 (m, 1H + 1H, CH=CH); 7.07–7.39 (m, 9H, C_6H_4 and C_6H_5). Anal. Found: C, 82.05; H, 6.25; N, 5.34. $C_{18}H_{17}NO$ Calc.: C, 82.09; H, 6.52; N, 5.32%.

3.7.5. Benzyl[(1,2-dihydronaphthyl-1)methyl]amine 53

A 50 ml flask was charged with 15 ml of ether and cooled to −10 °C. 5.1 g (38.2 mmol) of $AlCl_3$ was added to the flask and dissolved on stirring. 14.7 ml of 1.55 M solution (22.9 mmol) of $LiAlH_4$ in ether was added to the mixture. The mixture was stirred for 30 min at room temperature and treated with 0.67 g (2.54 mmol) of amide **52**. After stirring for 60 h at 20 °C, 50 ml of 10% NaOH solution was added and the reaction products were extracted with ether (5 × 30 ml). The ether extract was treated with 10% HCl solution (3 × 10 ml). The combined acid solutions were treated with conc. NaOH solution (to pH 14) and the product was extracted with ether (5 × 20 ml). The ether was evaporated and the residue chromatographed on a 20 cm SiO_2 column (eluent $CHCl_3$–MeOH–25% aqueous ammonia mixture (99:1:0.1)), which afforded 0.44 g (69%) of **53** as colourless oil. ^{1}H NMR ($CDCl_3$): 2.30–2.50 (m, 2H, CHCH_2CH=CH); 2.62–2.90 (m, 3H, $CHCH_2N$); 3.68, 3.81 (1H + 1H, AB system, J_{AB} = 14 Hz, $CH_2C_6H_5$); 5.82 (m), 6.33 (m, 1H + 1H, CH=CH); 6.90–7.30 (m, 9H, C_6H_4 and C_6H_5). The product was dissolved in 5 ml of ether and treated with 2 equiv. of HCl solution in ethyl alcohol. The precipitated deposit of the hydrochloride was filtered off and recrystallized from a 1:3 ether–ethanol mixture, affording a product with m.p. 205–207 °C. Anal. Found: C, 75.09; H, 6.90; Cl, 12.11; N, 4.80. $C_{18}H_{20}ClN$ Calc.: C, 75.63; H, 7.07; Cl, 12.40; N, 4.90%.

3.7.6. 5-Acetoxy-3-benzyl-1,4-methano-2,3,4,5-tetrahydro-1H-3-benzazepine (54)

A 50 ml flask was charged with a solution of 0.45 g (1.41 mmol) of mercury(II) acetate in 23 ml of water and a solution of 0.31 g (1.21 mmol) of amine **53** in 45 ml of THF. The mixture was stirred for 7 h at room temperature, cooled to 0 °C and treated with a solution of 0.25 g of $NaBH_4$ in 10 ml of 10% KOH solution. The mixture was stirred for 1 h at room temperature. The

product was extracted with ether (5 × 20 ml). The solvent extracts were combined and dried over anhydrous Na_2SO_4. The ether was evaporated and the residue chromatographed on a 20 cm SiO_2 column (eluent $CHCl_3$–MeOH–25% aqueous ammonia mixture (99:1:0.1)), which afforded 0.13 g (35%) of **54** as colourless oil. ^{1}H NMR ($CDCl_3$): 1.93 (m, 1H, β-H(10), ^2J = 11.61 Hz, $^3J_{H(1),H(10)}$ = 3.7 Hz. $^3J_{H(4),H(10)}$ = 5.64 Hz); 2.02 (d, 1H, α-H(10), ^2J = 11.61 Hz); 2.06 (s, 3H, CH_3); 2.77 (dd, 1H, *trans*-H(2) relative to H(1) in *C* ring, ^2J = 8.65 Hz, $^3J_{H(1),H(2)}$ = 0.75 Hz); 2.85 (dd, 1H, *cis*-H(2) relative to H(1) in *C* ring, ^2J = 8.65 Hz, $^3J_{H(1),H(2)}$ = 4.35 Hz); 3.27 (m, 1H, H(1)); 3.53 (dd, 1H, H(4), $^3J_{H(4),H(5)}$ = 3.05 Hz, $^4J_{H(4),\beta\text{-}H(10)}$ = 5.64 Hz); 3.95, 3.99 (1H + 1H, AB system, PhCH_2, J_{AB} = 13.4 Hz); 5.78 (d, 1H, H(5), $^3J_{H(4),H(5)}$ = 3.05 Hz); 7.06–7.44 (m, 9H, C_6H_5 and C_6H_4). ^{13}C NMR ($CDCl_3$): 21.345, 41.391, 61.135, 72.007 (C(1), C(4), C(5), CO*C*H_3), 29.955, 59.378, 60.192 (C(2), C(10), *C*H_2Ph); 128.150, 128.464 (*o*-CH and *m*-CH in Ph); 126.538, 126.850, 126.956, 127.922, 130.521 (aromatic CH, except *o*-CH and *m*-CH in Ph); 132.994, 139.676, 143.458 (aromatic C); 170.373 (C=O). IR spectrum ($CHCl_3$; λ (cm^{-1})): 1732 (C=O). *m/z* 307, M^+. Anal. Found: C, 78.05; H, 6.70; N, 4.57. $C_{20}H_{21}NO_2$ Calc.: C, 78.13; H, 6.90; N, 4.56%.

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