Arenes to Substituted Cyclohexadienes: Nucleophile/Electrophile Additions across an Arene Double Bond

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Alkyl-, vinyl- and aryllithium reagents were reacted with tricarbonylchromium–phenyloxazoline and -phenylmethanimine complexes **1** and **2**. The resulting anionic cyclohexadienyl complexes were trapped with primary alkyl, allyl, benzyl, and propargyl bromides to give, after metal removal, 1,3-cyclohexadienes with a 1,5,6-substitution pattern. The results are consistent with *exo*-nucleophilic addition to the *ortho*-position of the arene, followed by addition of the electrophile to the metal center. With allyl, benzyl, and propargyl groups, direct reductive elimination then yielded *trans*-5,6-substituted products. With alkyl halides, reductive elimination was preceeded by CO insertion and acylcyclohexadienes were formed preferentially. In situ deprotonation/alkylation of the acylcyclohexadienes gave products in which three C-substituents had been added across an arene double bond with complete regio- and stereocontrol. The competition between the two pathways is discussed in terms of migratory aptitude to carbonylation and effects of the cyclohexadienyl ligand. Assigned product stereochemistry was confirmed by X-ray structures of two 1,5,6-substituted cyclohexadienes. With complex **2**, an intermediate acetyl enamine cyclohexadiene (**11a**) was isolated and structurally characterized. Its reaction with O_2 gave the corresponding 3,4,5-substituted phenol **12** (X-ray).

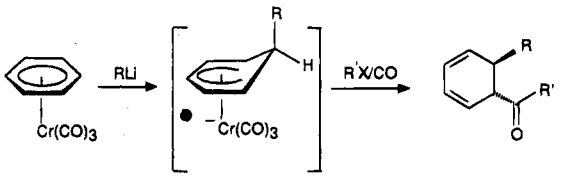
Introduction

We have shown previously that arenes can be transformed stereospecifically into *trans*-disubstituted dihydroarenes *via* temporary complexation of the arene to the electrophilic $Cr(CO)_3$ group (Scheme 1).[1]

Both the complexation and the one-pot procedure of sequential nucleophile/electrophile addition and metal removal are high-yield reactions.[2] This straightforward procedure is of synthetic interest in view of the dearth of methods which allow C-substituents to be added across an arene double bond.[3] An asymmetric version of this reaction sequence would significantly enhance its synthetic potential. No asymmetric double additions have been performed on the benzene ring system.[4] We envisaged an approach which would combine this transition-metal-based transformation with asymmetric methodology based on a chiral auxiliary σ-bound to the arene. The auxiliary would have to direct the incoming nucleophile to one of the two diastereotopic *ortho*-positions. *Ortho*-regioselectivity was considered crucial as it ensures proximity of the reacting center and the chiral auxiliary.[5] In the first part of this study, using achiral auxiliaries, we have shown that phenyloxazoline, phenylmethanimine, and benzaldehyde hydrazone complexes have the desired characteristics (Scheme 2).

These complexes react with a wide range of organolithium compounds to produce cyclohexadienyl interme-

Scheme 1. *trans*-Disubstituted Cyclohexadienes from Benzene *via* Temporary Complexation



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(5) For a very recent report on diastereoselective nucleophilic addition *meta* to a chiral auxiliary in an arene manganese complex, see: Pearson, A. J.; Zhu, P. Y.; Toungs, W. J.; Bradshaw, J. D.; Mc Couville, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 10376.

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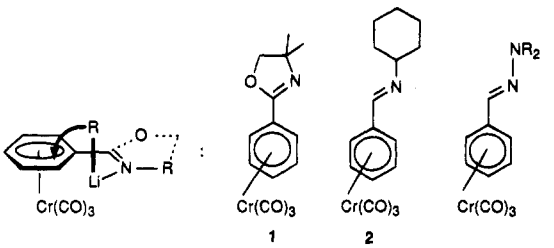
Scheme 2. ortho-Regioselective Nucleophilic Addition *via* Coordination of the Incoming Nucleophile



diates, which upon oxidation, afforded 1,2-substituted arenes in high yield and with good to excellent regioselectivity.[6] In continuation of these studies, this paper describes the results of the sequential reaction of C-nucleophiles and C-electrophiles with complexes **1** and **2**.[7]

Results and Discussion

Nucleophile Addition/Acylation/Alkylation with Oxazoline Complex 1. The cyclohexadienyl intermediate **3** was generated using the previously established protocol for the addition of alkyl-, vinyl-, and phenyllithium reagents to the yellow oxazoline complex **1**.[6b] *In situ* reaction of the orange-red solution of **3a** (R = Me) with methyl iodide under CO (4 bar), and in the presence of HMPA, gave a deep-red reaction mixture from which a crude product was isolated by crystallization. ^{1}H-NMR indicated this to consist of a mixture of **4a**, **6a**, **7a**, and small amounts of aromatic side products (Table 1). On flash chromatography, product **4a** readily isomerized to the enone **5a**. This was associated with the appearance of a red-violet band both on silica and aluminium oxide. The isolated purified product then consisted of a mixture of cyclohexadienes **5a**, **6a**, and **7a** in the approximate ratio of 1:0.5:1 (52% overall yield) (entry 1).

A common feature of the products is the 1,5,6-substitution pattern. We note that C–C bond formation was highly regioselective and that the substitution pattern is different from that of the products of tandem nucleophile/electrophile additions to 1-naphthyloxazolines (Scheme 3). In these reactions, reported by the *Meyers* group, the naphthalene is activated toward nucleophilic addition at C(2). The resulting aza enolate intermediates react with an electrophile at the substituted C(1), yielding 1,2-dihydronaphthalenes with a 1,1,2-substitution pattern.[31]

We then turned our attention to the necessity of reducing the number of products. A likely pathway for the formation of **6a** is alkylation of an intermediate enolate which is generated from **4a** *in situ* by either the excess of MeLi or by the LiOH contained in the commercial organolithium reagent solutions. Indeed, treatment of the reaction mixture with an excess of NaH (3 equiv) and MeI (10 equiv) (−78 °C to room temperature, 4h) (method B) converted products **4a** and **5a** into **6a** (entry 2). ^{1}H-NMR and HPLC analysis of the crude product mixture showed that a single diastereomer was formed. The relative configuration of the two stereogenic centers in **6a** was unambigously established to be as shown in Table 1 by a single crystal X-ray analysis.[7] An ORTEP diagram of **6a** is shown in Figure 1. The diene moiety shows the expected alternance of shorter and longer C–C bonds. Selected bond lengths and angles are given in Table 2.

Conjugation of the diene moiety with the oxazoline C=N double bond is indicated by the near coplanarity of the two systems; the angle between the two planes defined by N,C(7),O,C(11) and C(1),C(2),C(3),C(4) being 6.6(4)°. The substituted C-atoms C(5) and C(6) lie 0.268 Å above and 0.312 Å below the average plane defined by C(1),C(2),C(3),C(4). The acyl group occupies a pseudoequatorial position, whereas the two methyl groups are pseudoaxial.

With a one-pot reaction sequence in hand which regio- and stereoselectively introduces three C substituents across an arene double bond, we focused on improving product selectivity. Readily separable from **6a** by chromatography, cyclohexadiene **7a** accounted for approximately one-third of the yield. Varying conditions by carrying out the reaction in the absence of external CO only marginally increased the proportion of **7a**. In an attempt to suppress its formation, the reaction was repeated without the cosolvent HMPA. HMPA, by decreasing the extent of ion pairing in solution, suppresses migratory insertion of CO in anionic complexes.[8] Therefore the absence of HMPA should favor the formation of **4a** (and products derived thereof) over **7a**. Experiments showed this not to be the case in the reactions under investigation (Table 1, entry 3). Eventually we found that formation of **6a** could be maximized by the addition of the polar cosolvent acetonitrile, which favors carbonylation (entries 4 and 5).

The ^{1}H-NMR spectrum of **7a** showed a near zero vicinal coupling constant between the two protons at the sp^3 C atoms. While this is consistent with a *trans*-configuration of the two new C–C bonds, more tangible proof was obtained by a single-crystal study of the closely related product **7g** (R^1 = Ph, R^2 = allyl)[7] (see below).

With ethyl iodide as electrophile, ketone products **4b**, **5b**, and **6b** were formed exclusively (entry 6). Adding an *in situ* alkylation step afforded **6b** as single product (entry 7). The ^{1}H-NMR spectrum of the crude mixture showed traces of a side product which was tentatively assigned to the epimer of **6b**. The ^{1}H-NMR spectrum showed the diastereomeric ratio of **6b**:*epi*-**6b** to be approximately 95:5.

Nucleophile Addition/Allylation or Propargylation with Oxazoline Complex 1. Product distribution changed radically with allylic, benzylic, and propargylic electrophiles (Table 3). A single product, **7c**, was isolated in 67% yield from the methyllithium/allyl bromide reaction with **1** (entry 1). ^{1}H-NMR of the crude product, however, showed the presence of about 20% ketone product **4c** and, on chromatography, a short-lived red-violet band appeared. On the basis of the observations with alkyl electrophiles, we associate this with the isomerization of **4c** to **5c**. Product instability rendered isolation of either of these secondary products impractical. In the reactions with allylic and benzylic bromides (entries 1–10), the overall crude yield of products was in the 75–85% range with ketone products accounting for 10–20%. In a few cases the ketone products were isolated (**4f**, **5d**, **5e**; see Experimental Section). As

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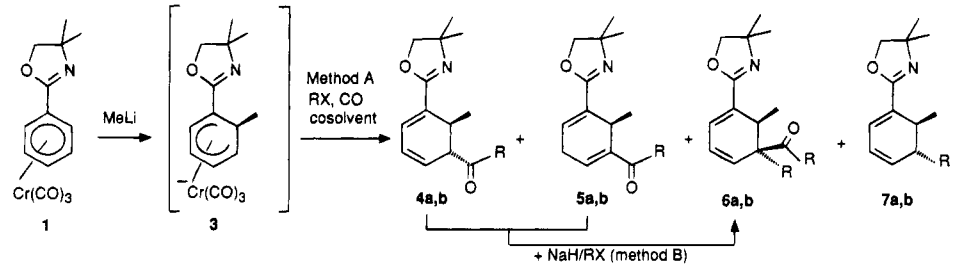
(8) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766.

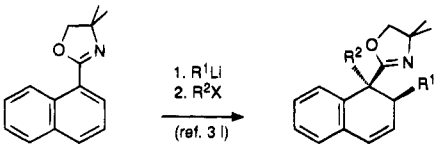
Table 1. Sequential Addition of Methyl Lithium and Alkyl Iodides to the Phenyl Oxazoline Complex 1



entry	RX	cosolvent	method[a]	products	distribution[b] 4	5	6	7	yield[b] (%)
1	MeI	HMPA	A	**4–7a**	0	43	19	38	52
2	MeI	HMPA	B	**4–7a**	0	0	69	31	55
3	MeI		A	**4–7a**	0	33	22	45	55
4	MeI	MeCN[c]	A	**4–7a**	0	18	72	10	62
5	MeI	MeCN[c]	B	**4–7a**	0	0	90	10	58
6	EtI	HMPA	A	**4–7b**	27	12	61	0	83
7	EtI	HMPA	B	**4–7b**	0	0	100	0	59

[a] Method A: Generation of **3a** (1 M in THF), then, at −78 °C, addition of RX (10 equiv), HMPA (10 equiv) or MeCN (large excess), CO (4 bar), followed by warming from −78 °C to rt overnight. Method B: As in Method A, followed by addition of NaH (3 equiv, THF, −78 °C, 0.5 h), then RX (10 equiv) and HMPA (10 equiv) and warming from −78 °C to rt over 4 h. [b] Product distribution and yield after chromatography on SiO_2. [c] Medium was THF/MeCN 1:1.

Scheme 3. Meyers' Methodology for the Sequential Addition of Alkyl Lithium Reagents and Electrophiles to Naphthyl Oxazolines



expected, product distribution varied with changes of reaction conditions. The changes were surprisingly small, however, and this is reflected in the amount of isolated **7c** (entries 1–4). Even under optimal conditions for CO insertion (e.g., by addition of MeCN and in the presence of 4 bar of CO) the major product was the noncarbonylated product **7c** (entry 2). In an attempt to suppress the formation of the ketone products, the electrophile addition reaction was carried out first in THF/toluene (1:10) in the presence of HMPA (entry 3) and thereafter (because the result was the same) in THF under a nitrogen atmosphere (entry 4). The amount of ketone products produced under these conditions was smaller (ca. 10%) and the yield of **7c** increased, but complete suppression of carbonylation was not realized. The conditions of entry 4 were then used in the reactions with alkyl-, vinyl-, and phenyllithium reagents and allyl, methallyl, and benzyl bromide to give products **7d–h** (entries 5–9). Entry 10 describes a slightly different

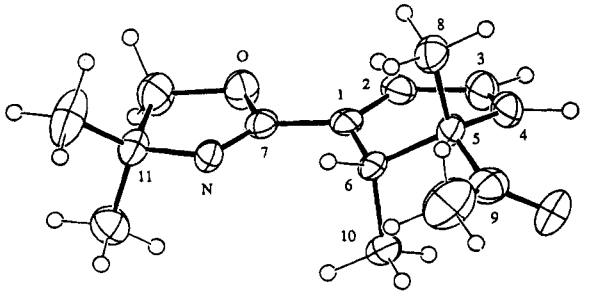


Figure 1. Structure of the cyclohexadiene product **6a**.[7]

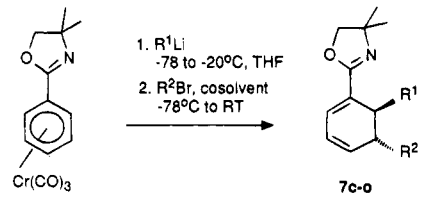
Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsional Angles (deg) for Compounds 6a, 7g, and 11a[a]

	6a	7g	11a
O–C(7)	1.363(7)	1.378(6)	
O–C(8)			1.23(1)
N–C(7)	1.261(8)	1.268(7)	1.35(2)
C(1)–C(2)	1.329(9)	1.332(7)	1.41(2)
C(1)–C(6)	1.513(8)	1.508(7)	1.51(1)
C(1)–C(7)	1.477(9)	1.459(7)	1.35(2)
C(2)–C(3)	1.45(1)	1.470(7)	1.34(2)
C(3)–C(4)	1.33(1)	1.330(9)	1.44(2)
C(4)–C(5)	1.492(9)	1.492(8)	1.32(2)
C(5)–C(6)	1.569(8)	1.578(6)	1.52(2)
C(5)–C(8)	1.575(9)	1.520(8)	1.47(2)
C(5)–C(9)	1.527(9)		
C(6)–C(10)	1.538(9)	1.523(7)	1.55(2)
O–C(7)–N	119.4(6)	116.9(4)	
O–C(7)–C(1)	115.1(5)	116.1(4)	
N–C(7)–C(1)	125.5(5)	126.9(4)	128(1)
O–C(8)–C(5)			122(1)
C(2)–C(1)–C(6)	121.9(6)	123.5(4)	121(1)
C(1)–C(2)–C(3)	119.9(6)	120.5(4)	121(1)
C(2)–C(3)–C(4)	121.3(6)	120.7(5)	121(1)
C(3)–C(4)–C(5)	121.6(6)	122.2(5)	120(1)
C(4)–C(5)–C(6)	111.5(5)	114.1(4)	123(1)
C(1)–C(6)–C(5)	110.0(5)	110.9(4)	109.4(9)
C(2)–C(1)–C(7)–N	177.7(6)	−170.6(5)	178.(1)
C(6)–C(1)–C(7)–N	3.3(9)	10.6(7)	−5.(2)
C(2)–C(1)–C(7)–O	−0.5(9)	9.6(7)	
C(6)–C(1)–C(7)–O	−174.8(5)	−169.1(4)	
C(6)–C(1)–C(2)–C(3)	−4.2(9)	−2.3(8)	10.(2)
C(1)–C(2)–C(3)–C(4)	−13.(1)	−10.6(8)	6.(2)
C(2)–C(3)–C(4)–C(5)	−1.(1)	−1.3(8)	−8.(2)
C(3)–C(4)–C(5)–C(6)	29.2(9)	23.2(7)	−7.(2)
C(3)–C(4)–C(5)–C(8)	−90.4(7)	−102.5(6)	170.(1)
C(3)–C(4)–C(5)–C(9)	152.0(7)		
C(4)–C(5)–C(6)–C(1)	−41.4(7)	−32.0(6)	21.(1)
C(4)–C(5)–C(6)–C(10)	78.5(6)	92.4(5)	−98.(1)

[a] The atomic numbering refers to those in Figures 1–3.

case. In the preceeding examples, nucleophiles always added highly selectively to the *ortho*-position. This is not the case with $LiCH_2CN$, which gives a mixture of regioisomeric intermediates.[6b] After equilibration at 0 °C, which produced the *ortho*-regioisomer exclusively, carbanion dissociation from the anionic cyclohexadienyl

Table 3. Sequential Addition of C-Nucleophiles and Allyl, Benzyl, and Propargyl Bromides to Complex 1



1 7c-o

entry	R^1Li[a]	R^2Br[b]	cosolvent[b]	product[c]	yield[d] (%)
1	MeLi	CH_2=$CHCH_2Br$[e]	HMPA	**7c**	67
2	MeLi	CH_2=$CHCH_2Br$[e]	MeCN[f]	**7c**	51
3	MeLi	CH_2=$CHCH_2Br$	HMPA/ toluene[g]	**7c**	66
4	MeLi	CH_2=$CHCH_2Br$		**7c**	68
5	MeLi	CH_2=$CH(Me)CH_2Br$		**7d**	61
6	MeLi	$PhCH_2Br$		**7e**	52
7	nBuLi	CH=$CHCH_2Br$		**7f**	63
8	PhLi	CH=$CHCH_2Br$		**7g**	67
9	VinylLi[h]	CH=$CHCH_2Br$		**7h**	54
10	$NCCH_2Li$[i]	CH=$CHCH_2Br$	HMPA	**7i**	48
11	MeLi	CH≡CCH_2Br		**7j**	30
12	MeLi	CH≡CCH_2Br	HMPA	**7j**	71
13	nBuLi	CH≡CCH_2Br	HMPA	**7k**	87
14	PhLi	CH≡CCH_2Br	HMPA	**7l**	77
15	VinylLi[h]	CH≡CCH_2Br	HMPA	**7m**	82
16	MeLi	Me_3SiC≡CCH_2Br[j]		**7n**	40
17	MeLi	Me_3SiC≡CCH_2Br[j]	HMPA	**7n**	72
18	VinylLi[h]	Me_3SiC≡CCH_2Br[j]	HMPA	**7o**	88

[a] 1.2–1.5 equiv. [b] 10 equiv. [c] The crude product also contained 10–20% ketone products (see the text). [d] Isolated yield after chromatography. [e] After the addition of allyl bromide, the reaction was placed under CO (4 bar). [f] Medium was THF/MeCN 1:1. [g] Medium was THF/toluene 1:10. [h] Generated from tetravinyltin and MeLi at −78 °C. [i] Reaction mixture was warmed to 0 °C (2 h) before the addition of allyl bromide. [j] 5 equiv.

intermediate was suppressed by addition of HMPA. Allylation then afforded **7i** (entry 10).

Reactions with propargylic bromides gave cyclohexadiene products **7j–o** selectively (entries 11–17). ^{1}H-NMR analysis of the crude reaction mixtures provided no evidence for carbonylated products. Reactions with HMPA as cosolvent gave considerably better yields than those without (compare entries 11 with 12, and 16 with 17). Effects of other addends were not investigated. Yields of **7j–o** (R^2 = propargyl) are 10–20% higher than those of **7c–i** (R^2 = allyl or benzyl), reflecting the absence of ketone products.

A single-crystal X-ray analysis of the solid cyclohexadiene **7g** provided unambiguous evidence for the *trans*-diaxial arrangement of phenyl and allyl groups (Figure 2).[7] On the basis of mechanistic considerations and given the close resemblance of the ^{1}H-NMR spectra, we assign *trans*-stereochemistry to all compounds **7**. Selected bond length and angles for **7g** are listed in Table 2. The oxazoline and cyclohexadiene units are nearly coplanar with an angle of 6.0° between the planes defined by N,C(7),O,C(11) and C(1),C(2),C(3),C(4). The two substituents at the C(5) and C(6) atoms occupy pseudoaxial positions, the most favorable conformation in a ring system with four sp^2 centers. The dihedral angle between the C–H bonds of two pseudoequatorial H is close to 90° and, judging from the very small vicinal coupling ($^3J \approx 0$), this is also the preferred conformation in solution.

Isolation of the Cyclohexadienyl Intermediates 3g and 8a. The common intermediates in the nucleophile/electrophile addition reactions described in this article and the nucleophile addition/oxidation reactions reported earlier[6] are the anionic complexes **3** and **8**. In all reactions described above these were generated and reacted with the electrophiles *in situ*. It is of interest to mention that these intermediates can be isolated and, although air sensitive, are reasonably stable.[9] For example, the reaction of **1** with PhLi followed by solvent removal gave **3g** as red-brown powder. Following literature precedent, the anionic complex was purified further by crystallization from dioxane.[9] Attempts to grow crystals for an X-ray diffraction study have not yet met with success, and structural assignment is based on IR and ^{1}H-NMR spectral data. In the IR, the bands associated with the CO stretching modes are shifted to lower frequencies (1911, 1827 cm^{-1}) as expected for a negatively-charged complex. The ^{1}H-NMR spectrum (DMSO-d_6) agrees with those of other anionic cyclohexadienyl complexes[1c,9] and details are given in the Experimental Section. Similarly, complex **8a** was isolated as a red-brown solid from the reaction of MeLi with complex **2**. Details and ^{1}H-NMR assignment are given in the Experimental Section.

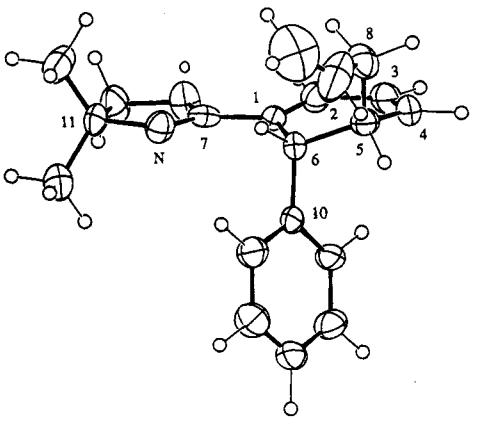


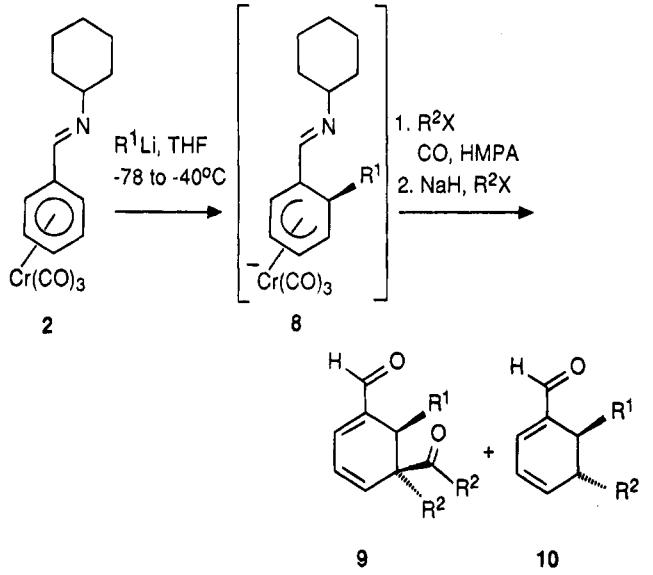
Figure 2. Structure of *trans*-phenylallylcyclohexadiene **7g**.[7]

Nucleophile Addition/Acylation/Alkylation and Nucleophile Addition/Allylation with the Imine Complex 2. Parallel results were obtained with the imine complex **2**. The one-pot reaction shown in Table 4 afforded aldehydes **9**. Modification of the procedure by adding NaH prior to the electrophile in step 2 further shortened the procedure albeit at the cost of a slightly reduced yield (entries 2 and 4). In order to avoid product polimerization, the crude product mixture was chromatographed without aqueous workup and without neutralizing (see Experimental Section). Hydrolysis of the cyclohexylimines then yielded aldehydes **9** and **10**. Analogous to the findings with the oxazoline complex **1**, ketone products **9** were the major or exclusive products in the reaction sequence involving complex **2** and methyl iodide, whereas **10e** was the sole product isolated when the electrophile was allyl bromide (entry 6) and **10f** when it was propargyl bromide (entry 7).

Isolation and Structural Characterization of 11a. Intrigued by this one-pot reaction sequence which adds three C-substituents across an arene bond with excellent regio- and stereocontrol, we explored this process further by focusing on intermediates. When the anionic cyclo-

(9) For previous reports of isolation of anionic cyclohexadienyl–Cr(CO)$_3$ complexes, see ref 1c and (a) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (b) Djukic, J.-P.; Rose-Munch, F.; Rose, E.; Dromzee, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6434.

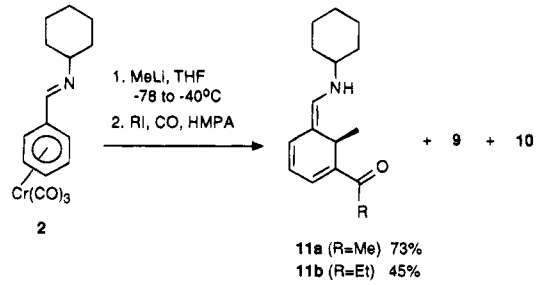
Table 4. Sequential Addition of C-Nucleophiles and C-Electrophiles to Complex 2



entry	R^1Li^a	R^2X^b	products	distribution	yield (%)
1	MeLi	MeI	**9a**[c]:**10a**[c]	90:10	98
2[d]	MeLi	MeI	**9a**[c]:**10a**[c]	90:10	80
3	PhLi	MeI	**9c**		80
4[d]	PhLi	MeI	**9c**		71
5	VinylLi[e]	MeI	**9d**:**10d**	85:15	66
6[f]	MeLi	CH_2=$CHCH_2Br$	**10e**[g]		57
7[f,h]	MeLi	Me_3SiC≡CCH_2Br[i]	**10f**		76

[a] 1.1 equiv of RLi was used. [b] 10 equiv. [c] Initially isolated as the cyclohexylimine derivative **10a'**. [d] NaH, HMPA, and R^2X were all added together. [e] Generated from tetravinyltin and MeLi at −78 °C. [f] Reaction carried out without addition of NaH/R^2X. [g] Isolated as the cyclohexylimine derivative **10e'**. [h] Reaction carried out under N_2 (1 bar, no CO). [i] 5 equiv.

Scheme 4. Alkylation/Acylation of Complex 7 to give Enamine Acetyl Cyclohexadienes 11



hexadienyl intermediate resulting from the reaction of complex **2** with MeLi was treated with CO and MeI, a deep-red solution formed. We found that hydrolysis at this stage with sat. aq NH_4Cl solution only gave intractable polymeric materials. Therefore we attempted to isolate the intermediate by stripping the reaction mixture of volatiles followed by flash chromatography of the resulting red oil. This was successful and gave bordeaux red **11a** as the major product and **9a** and **10a** as minor ones (ratio of separated products was 8:1:1) (Scheme 4). Ethyl iodide gave similar results.

Structural assignment to **11a** is based on the following data. A conjugated enone was indicated by the ν_{CO} absorption at 1685 cm^{-1}. The ^1H-NMR spectrum showed a set of three doublets (at 5.96, 6.32, and 6.72 ppm) and a doublet of doublets (5.48 ppm), accounting for four vinylic protons, and a broad signal at 3.86 ppm. After addition of D_2O the signal at 3.86 ppm disappeared and therefore was assigned to a NH group, and the doublet at 5.96 ppm became a singlet. The mass spectrum of **11a** showed a peak at m/z = 233, corresponding to the loss of a hydrogen atom ($M^+ - 1$), and an absorption at 444 nm (ϵ = 9600) in the UV spectrum accounts for the color. The structural assignment to **11a** was confirmed by an X-ray diffraction study of a crystal obtained by slow crystallization from ether (Figure 3).[7]

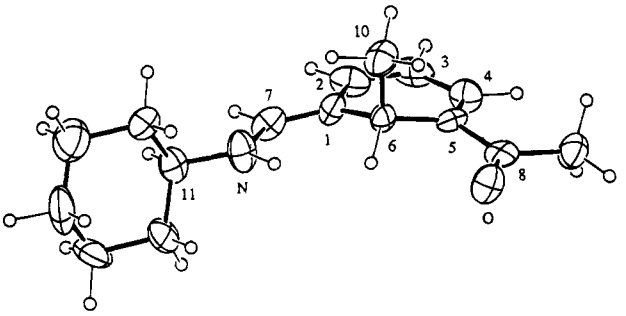
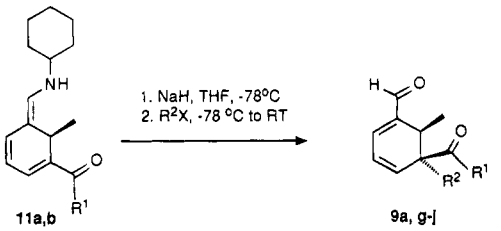


Figure 3. Structure of the acetylcyclohexyl enamine cyclohexadiene **11a**.[7]

Table 5. Regio- and Diastereoselective Alkylation, Allylation, and Propargylation of Enamine 11



entry	R^1	R^2X	product	yield (%)
1	Me	MeI	**9a**	86
2	Me	EtI	**9g**	59
3	Me	CH_2=$CHCH_2Br$	**9h**	79
4	Me	$BrCH_2CO_2Et$[a]	**9i**	50
5	Et	CH_2=$CHCH_2Br$	**9j**	79

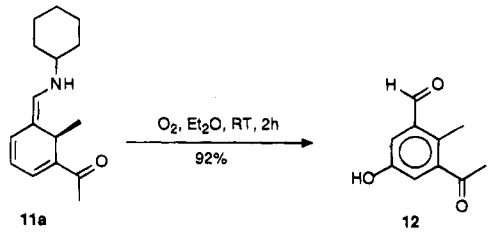
[a] Base used was KOH.

The nine atoms N, C(7), C(1)−C(5), C(8), and O are almost coplanar with deviations of <0.07 Å, except for C(3) (0.09 Å) and C(5) (0.15 Å). The C(6) atom is 0.366 Å above this plane. C=C double bonds are localized, as evidenced by the alternance of shorter bonds (C(2)−C(3), C(4)−C(5), C(1)−C(7) (average distance = 1.33 Å) and longer bonds (C(1)−C(2), C(3)−C(4), C(5)−C(8) (average distance = 1.44 Å). The length of the O−C(8) and N−C(7) bonds (1.23 and 1.35 Å, respectively) is typical of C_{sp^2}=O and C_{sp^2}−N bonds.

Reactivity of Enamine 11a. Enamine **11a** is stable under an inert atmosphere and remained unchanged when kept at low temperature (−78 °C) for several weeks. In solution, treatment with base and MeI afforded **9a** in a highly regio- and diastereoselective reaction (Table 5). This stepwise synthesis of 1,5,6-trisubstituted 1,3-cyclohexadienes gives ready access to products with different R_1 and R_2 groups. Attempts at O- or N-alkylation with hard electrophiles were not successful. **11a** was not stable under acylation conditions and decomposed when reacted with an acylating agent (Ac_2O, $(BOC)_2O$, AcCl, benzoyl chloride) in the presence of a base (Et_3N or pyridine).

We noticed early on that solutions of enamine **11a** were unstable in air. The deep-red solutions lost intensity and

Scheme 5. Oxidation of the Acetyl Enamine Cyclohexadiene 11a



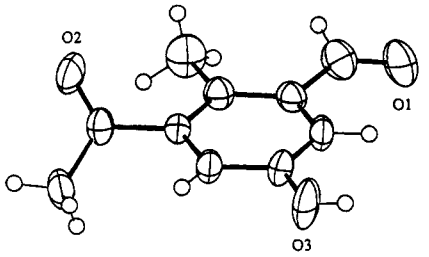
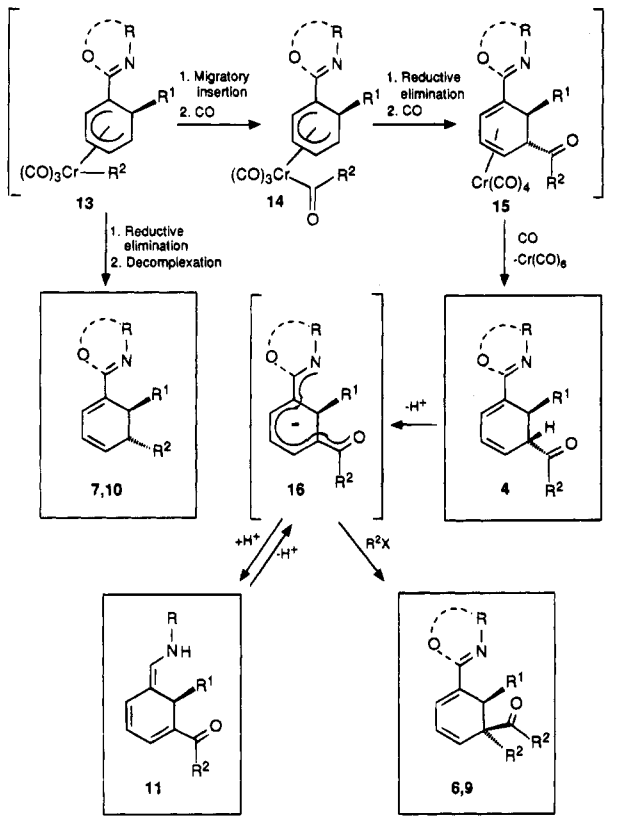


Figure 4. Structure of phenol **12**.

Scheme 6. Proposed Mechanism for the Formation of Cyclohexadienes 4, 6, 7, 9, 10, and 11



eventually turned a pale yellow, accompanied by the formation of a precipitate. In a controlled reaction, **11a** was dissolved in dry ether and a slow stream of dry oxygen was passed through the stirred solution. After 1 h the solution had lost its red color and TLC indicated formation of a new more polar product. Workup and purification afforded the phenol **12** in high yield (Scheme 5). The X-ray structure of **12** is shown in Figure 4.[10]

Mechanistic Considerations. On the basis of the reaction products and the structures of **6a**, **7g**, and **11a** we may explain product formation according to the reaction scheme shown in Scheme 6.

Addition of R^1Li to the *exo*-face of the complexed arene in **1** and **2**, in accord with literature precedence,[9] gives the anionic cyclohexadienyl intermediates **3** and **8**. Reaction with a primary iodide, allylic, benzylic or propargylic bromide then results in **13**. Depending on the nature of the R^2 group and reaction conditions, **13** evolves *via* one of the two pathways shown. The first pathway, observed predominantly or exclusively when R^2 = alkyl, is migraton of R^2 in **13** to a *cis*-carbonyl ligand followed by CO filling the vacant coordination site. The resulting acyl intermediate **14** then undergoes acyl transfer by reductive elimination to the *syn*-face of the cyclohexadienyl moiety. Ligand displacement of the labile diene complex **15** affords the *trans*-substituted cyclohexadiene **4**. Formation of the carbonylated product is common in these reactions and can be ascribed to reversible migratory insertion and a higher rate of reductive elimination of ketones from acylalkyl–transition-metal complexes compared to reductive coupling of two alkyl ligands to afford alkanes.[11] The direct reductive elimination from **13** to give the *trans*-substituted cyclohexadienes **7** and **10** was unexpected because of our previous finding that the reaction of $[(C_6H_6)Cr(CO)_3]$ with 2-lithio-2-methyl-1,3-dithiane as nucleophile and alkyl, allyl, or benzyl halides as electrophiles always gave acyl products exclusively.[1a] Reductive elimination not preceeded by CO insertion is the preferred pathway with complexes **1** and **2** when R^2 is allyl or benzyl and is the exclusive pathway when R^2 is propargyl. Therefore reductive elimination and migratory CO insertion have competitive rates in **13**, and this effect must be attributed to the oxazoline and imine substituents. Geometric requirements aside, the major factor accelerating reductive elimination is electron withdrawal.[12] In complex **13** the electron-withdrawing oxazoline and imine substituents destabilize intermediate **13** and accelerate reductive elimination. Oxazoline and imine groups also contribute to the easy deprotonation of **4** to give **16**. Regio- and diastereoselective C-alkylation of the extensively delocalized enolate **16** from the less hindered face affords **6** or **9**. Interestingly, in the imine case, the hard electrophile H^+ preferentially reacts at the hard N center to give the enamine **11**.

Product distribution, as detailed by the data in Tables 1, 3, and 4, indicates migratory aptitudes of the σ-bound R^2 groups in **13** to carbonyl insertion to follow the order: ethyl > methyl > benzyl, allyl ≫ propargyl. This ranking checks with that observed in kinetic studies of CO migratory insertion reactions in a number *of* other

(10) *X-ray Crystal Structure Determination of* **12**:[20] Yellow crystals were obtained by slow evaporation from hexane/ether solution. Crystal data: $C_{10}H_{10}O_3$, $M_r = 178.2$; $\mu = 0.094$ mm^{-1}, $F(000) = 188$, $d_x = 1.35$ g cm^{-3}, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.013(2)$ Å, $b = 7.944(2)$ Å, $c = 8.180(2)$ Å, $\alpha = 82.01(2)°$, $\beta = 84.93(2)°$, $\gamma = 75.90(2)°$, $V = 437.0(2)$ Å^3. Cell dimensions and intensities were measured at room temperature on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), ω–2θ scans, scan width $1.2° + 0.25 \tan\theta$, and scan speed 0.02–0.14°/s. Two reference reflections measured every 100 reflections showed variation less than 3.5 $\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption. A total of 1715 unique reflections were measured ($(\sin\theta)/\lambda)_{max} = 0.62$ Å^{-1}), of which 1237 were observable ($|F_o| > 4\sigma(F_o)$). The structure was solved by direct methods using MULTAN 87;[17] all other calculations used XTAL system[18] and ORTEP programs.[19] All coordinates of the hydrogen atoms were observed and refined with isotropic displacement parameters fixed to 0.05 Å^2. The final R factor was 0.057 ($R = \omega R$, $\omega = 1$). Hydrogen bonds occur in the molecular packing: $O(3)\cdots O(2)_{x,y,z-1} = 2.713(3)$ Å.

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transition-metal complexes.[13] Alkyl R^2 groups in **13** readily undergo carbonylation and favor this pathway rather than direct reductive elimination. An important solvent effect is observed when R^2 = Me. In THF/HMPA, the two pathways leading to **4–6a** and **7a** have comparable rates (Table 1, entry 1). Addition of MeCN favors the formation of **4–6a** rather than **7a**, in keeping with the established role of donor solvents on the rate of migratory insertion.[14] In a situation where the two processes migratory CO insertion (**13** → **14**) and reductive elimination (**13** → **7,10**) become competitive, the reduced migratory aptitude of allyl, benzyl, and propargyl groups tilts the balance in favor of the latter process. The rate differences are large enough to make the transformations remarkably selective, and as a result we can direct the reactions to desired products by selecting the appropiate electrophile.

Summary and Conclusions

The oxazoline and imine substituents in complexes **1** and **2** efficiently direct the incoming nucleophile to the *ortho*-carbon. Reductive elimination always occurs to the unsubstituted terminal of the cyclohexadienyl intermediates **3** and **8**. In accord with the migratory aptitute of the R^2 groups to carbonyl insertion, either the acylcyclohexadienes **6** and **9** or the allyl-, benzyl-, and propargylcyclohexadienes **7** and **10** are formed in a one-pot reaction sequence with good to excellent selectivity. First, promising results have been obtained in an asymmetric version of this methodology using enantiomerically pure phenyl oxazoline complexes.[15] We have also shown that SAMP–hydrazone benzaldehyde complexes undergo highly diastereoselective *ortho*-addition in reactions with C-nucleophiles.[16] Details and extensions of these studies will be the subject of a forthcoming paper.

Experimental Section

1. General. General procedures are identical with those in a previous paper.[6b] The UV spectra of **11a** and **12** were recorded on a Kontron Uvikon 860 spectrometer. MeI, EtI, allyl bromide, methallyl bromide, benzyl bromide, propargyl bromide, 3-(trimethylsilyl)propargyl bromide, and ethyl bromoacetate were obtained from Fluka and distilled over P_2O_5 before use. *cis*-2-Ethoxyvinyl bromide (Fluka) was used as received. Commercial solutions of MeLi, PhLi, and nBuLi were used after titration. *cis*-(Ethoxyvinyl)lithium was prepared according to a literature method.[15] Vinyllithium and acetonitrile lithium were prepared as described previously.[6b]

2. Preparation and ^{1}H-NMR Characterization of Cyclohexadienyl Complexes 3g and 8a. Complex 3g. PhLi (1.71 M in cyclohexane/Et_2O, 1.313 mL, 2.246 mmol, 1.1 equiv) was added to a solution of **1** (635.6 mg, 2.042 mmol) in dry THF (20 mL) at −78 °C. After warming to −10 °C in 4 h, the reaction mixture was taken to dryness under vacuum. Toward the end of the evaporation, the cooling bath was replaced by a water bath at 40 °C. The dark-yellow solid was taken up in 20 mL of dioxane at 50 °C and the solution was slowly cooled to ambient temperature. After several days **13** precipitated as a yellow-brown powdery solid which was separated and washed with 3 × 10 mL of pentane. IR (THF): 1911 (s), 1827 (s). ^{1}H-NMR (DMSO-d_6: 1.05 and 1.14 (2 s, 6 H), 3.09 (br dd, 1 H, J = 5 and 7 Hz), 3.68 (m, 2 H), 4.08 (br d, 1H, J = 5 Hz), 4.67 (br t, 1H, J = 5 and 7 Hz), 4.99 (br t, 1 H, J = 5 Hz), 5.27 (br d, 1 H, J = 5 Hz), 6.94–7.02 (m, 3 H), 7.05–7.12 (m, 2 H).

Complex 8a. MeLi (1.6 M in ether, 0.425 mL, 0.68 mmol) was added to a solution of **2** (200 mg, 0.620 mmol) in dry THF (10 mL) at −78 °C. The stirred solution was warmed slowly (2 h) to −40 °C and then kept at this temperature for an additional 2 h. The reaction mixture was taken to dryness under vacuum at −20 °C. The red-brown solid was washed with dry ether and dried under vacuum at room temperature. ^{1}H-NMR (DMSO-d_6): 0.18 (d, 3H, J = 6.4 Hz), 1.10–1.18 (m, 10 H), 2.60–2.80 (m, 2H), 2.93 (dq, 1H, J = 5.8, 6.4 Hz), 4.48 (dd, 1H, J = 5.1, 5.8 Hz), 4.59 (d, 1H, J = 5.1 Hz), 4.98 (t, 1H, J = 5.1 Hz), 7.03 (s, 1H).

3. Nucleophile/Electrophile Addition Reactions with Complex 1. (a) General Procedures: Method A. The reaction was carried out in a heavy-walled 80-mL Schlenk tube fitted with a 8-mm O-ring tap (Youngs) and a rubber septum. A solution of RLi (1.1–1.2 equiv) was added dropwise *via* syringe to a solution of complex **1** (0.25–1 mmol) in THF (3–10 mL) at −78 °C. After warming to −20 °C over a period of 3 h, the orange-red solution was recooled to −78 °C and HMPA (10 equiv) and the electrophile (10 equiv) were added. The rubber septum was replaced by an adapter with a small pressure gauge. After a freeze/pump cycle, CO (4 bar) was pressed onto the mixture at −78 °C, and the magnetically stirred solution was warmed up to ambient temperature overnight. Excess CO was vented, and volatiles were removed *in vacuo*. The residue was dissolved in Et_2O (50 mL) and the solution washed sequentially with H_2O (2x, 10 mL) and aq NaCl solution (sat., 10 mL). The aqueous phases were combined and extracted with Et_2O (3x, 10 mL). The organic phases were dried ($MgSO_4$), exposed to sunlight (3 h) until colorless, and filtered over Celite. After evaporation of the solvent (rotavapor), the crude products were purified by flash chromatography on silica gel (hexane/ether).

Method B. The reaction was carried out exactly as before except for the following additional step. The crude product mixture was dissolved in dry THF (3–10 mL) under N_2. The resulting solution was cooled to −78 °C and transferred *via* cannula into a dispersion of NaH (3 equiv, prewashed with dry pentane, 5 × 10 mL) in dry THF at the same temperature. After 0.5 h the same carbon electrophile (10 equiv) and HMPA (10 equiv, if not already present) were added. After warming to ambient temperature over a period of several hours, the reaction was quenched by careful dropwise addition of aq NH_4Cl solution (sat.) at 0 °C. Workup was as in method A.

(b) Reactions of Complex 1 with MeLi and MeI: Method A. Starting with 159 mg (0.51 mmol) of **1** yielded 26 mg of **5a** (22%), 15 mg (12%) of **6a**, and 21 mg (20%) of **7a**.

1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-6-methyl-1,4-cyclohexadien-1-yl]ethanone (5a). IR (CH_2Cl_2): 1680 (vs), 1667 (vs), 1638 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.13 (d, 3 H, J = 6.8 Hz), 1.29 and 1.30 (2 s, 6 H), 2.31 (s, 3 H), 2.98–3.08 (m, 2 H), 3.75–3.98 (m, 3 H), 6.52–6.59 (m, 1 H), 6.79–6.86 (m, 1 H). MS: 233 (15), 218 (20), 204 (100), 190 (60).

***cis*-1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-1,6-dimethyl-2,4-cyclohexadien-1-yl]ethanone (6a).** Mp 66–67 °C. IR (CH_2Cl_2): 1704 (vs), 1652 (m), 1610 (vs), 1570 (w), 1455 (m), 1404 (m), 1367 (s), 1292 (m), 1244 (m), 1207 (s), 1011 (s).

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(20) The author has deposited atomic coordinates for structure **12** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

^{1}H-NMR ($CDCl_3$, 400 MHz,): 0.88 (d, 3 H, J = 7.0 Hz), 1.25, 1.31 and 1.37 (3 s, 9 H), 2.22 (s, 3 H), 3.04 (q, 1 H, J = 7.0 Hz), 3.97 (m, 2 H), 6.02 (dd, 1 H, J = 5.2, 9.6 Hz), 6.39 (d, 1 H, J = 9.6 Hz), 6.62 (d, 1 H, J = 5.2 Hz). MS: 247 (18), 232 (12), 204 (70), 190 (20). Anal. Calcd for $C_{15}H_{21}NO_2$ (247.33): C, 72.84; H, 8.56; N, 5.66. Found: C, 72.66; H, 8.50; N, 5.52.

***trans*-4,5-Dihydro-4,4-dimethyl-2-(5,6-dimethyl-1,3-cyclohexadien-1-yl)-oxazole (7a).** IR (CH_2Cl_2): 1652 (s), 1611 (vs), 1463 (m), 1363 (m), 1348 (m), 1315 (m), 1296 (m), 1281 (m), 1211 (m), 1055 (m), 1044 (m), 1026 (m), 1015 (m), 1000 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.93 (d, 3 H, J = 7.0 Hz), 1.01 (d, 3 H, J = 7.0 Hz), 1.29 and 1.33 (2 s, 6 H), 2.05–2.22 (m, 1 H), 2.63 (q, 1 H), 3.88–3.99 (m, 2 H), 5.91–5.98 (m, 2 H), 6.55–6.60 (m, 1 H). MS: 205 (90), 190 (100). HR-MS: calcd for $C_{13}H_{19}NO$ 205.1466, found 205.1456.

CO Atmosphere/MeCN/Method B. This reaction was carried out as described in the general procedure except that HMPA was replaced by MeCN (10 mL). The crude product mixture was analyzed by HPLC (Silica spheri 5 μm, 250 × 10 mm column; hexane/AcOEt 3:1; 5 mL/min; UV detector at 280 nm). Starting with 1 mmol of **1**, 146 mg (59%) of **6a** and 13 mg (6.5%) of **7a** were obtained.

(c) Reactions of Complex 1 with MeLi and EtI: Method A. Starting with 89 mg (0.287 mmol) of **1** yield 16 mg (22%) of **4b**, 7 mg (10%) of **5b**, and 35 mg (51%) of **6b**.

***trans*-1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-6-methyl-2,4-cyclohexadien-1-yl]-1-propanone (4b).** IR (CH_2Cl_2): 1710 (s), 1650 (m), 1612 (s), 1463 (m), 1405 (m), 1381 (m), 1375 (m), 1301 (m), 1292 (m), 1273 (m), 1212 (m), 1187 (m), 1025 (m), 969 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.95 (t, 3 H, J = 7.0 Hz, CH_2CH_3), 1.11 (d, 3 H, J = 7.0 Hz), 1.28 and 1.33 (2 s, 6 H), 2.42–2.55 (dq, 2 H, J = 1.3, 7.0 Hz), 2.97 (d, 1H, J = 6.3 Hz), 3.37 (bq, 1 H, J = 7.0 Hz), 3.87–3.99 (m, 2 H), 5.96 (ddt, 1 H, J = 0.9, 6.3, 9.5 Hz), 6.16 (ddd, 1 H, J = 0.9, 5.4, 9.5 Hz), 6.56 (dd, 1 H, J = 0.9, 5.4 Hz). MS: 247 (45), 246 (88), 232 (47), 218 (22), 190 (100), 176 (86), 160 (48). HR-MS: calcd for $C_{15}H_{21}O_2N$ 241.1572, found 241.1562.

1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-6-methyl-1,4-cyclohexadien-1-yl]-1-propanone (5b). IR (CH_2Cl_2): 1692 (s), 1680 (s), 1663 (s), 1618 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.09 (t, 3 H, J = 7.0 Hz), 1.14 (d, 3 H, J = 6.8 Hz), 1.30 and 1.31 (2 s, 6 H), 2.60–2.78 (m, 2 H), 2.94–3.08 (m, 2H), 3.80–4.05 (m, 3 H), 6.54–6.62 (m, 1 H), 6.77–6.83 (m, 1 H). MS: 246 (M − 1) (10), 232 (3), 218 (8), 190 (18), 57 (100).

***cis*-1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-1-ethyl-6-methyl-2,4-cyclohexadien-1-yl]-1-propanone (6b).** IR (CH_2Cl_2): 1704 (vs), 1653 (m), 1611 (vs), 1574 (w), 1456 (m), 1400 (w), 1381 (m), 1366 (m), 1348 (m), 1292 (m), 1208 (m), 1189 (m), 1056 (m). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.72 (t, 3 H, J = 7.5 Hz), 0.81 (d, 3 H, J = 7.0 Hz), 1.06 (t, 3 H, J = 7.0 Hz), 1.29 and 1.35 (2 s, 6 H), 1.62–1.72 and 1.88–1.98 (m, 2 H), 2.37–2.48 and 2.59–2.7 (m, 2 H), 2.96 (dq, 1 H, J = 7.0 Hz), 3.91–3.99 (m, 2 H), 6.05 (dd, 1 H, J = 5.5, 10.0 Hz), 6.47 (bd, 1 H, J = 10.0 Hz), 6.59 (dd, 1 H, J = 5.5 Hz). MS: 275 (3), 249 (12), 218 (100). HR-MS: calcd for $C_{17}H_{25}O_2N$ 275.1885, found 275.1890.

CO Atmosphere (Method B). The reaction was carried out with 314 mg (1.01 mmol) of **1** to give 164 mg (59%) of **6b**.

(d) Reactions of Complex 1 with MeLi and Allyl Bromide (Method A). Starting with 84 mg (0.270 mmol) of **1** gave 41 mg (65%) of **7c**. Repeating the reaction with 315 mg (1.01 mmol) of **1** but without adding HMPA and CO afforded 159.3 mg (68%) of **7c**.

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-methyl-5-(2-propenyl)-1,3-cyclohexadien-1-yl)oxazole (7c).** IR (CH_2Cl_2): 1652 (w), 1609 (s), 1470 (w), 1440 (w), 1405 (w), 1367 (m), 1348 (m), 1292 (m), 1207 (m), 1040 (m), 1022 (m), 996 (m), 988 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.10 (d, 3 H, J = 7.2 Hz), 1.30 and 1.31 (2 s, 6 H), 1.90–2.24 (m, 3 H), 2.75 (bq, 1 H, J = 7.2 Hz), 3.89–3.99 (m, 2 H), 4.89–4.96 (m, 1 H), 4.99 (bs, 1 H), 5.65–6.04 (m, 2 H), 6.55–6.60 (m, 1 H). MS: 231 (13), 190 (100), 174 (8), 119 (74). HR-MS: calcd for $C_{15}H_{21}NO$ 231.1623, found 231.1649.

(e) Reaction of Complex 1 with MeLi and Methallyl Bromide. Using method A with 90 mg (0.289 mmol) of **1** gave 42 mg (59%) of **7d** and 12 mg (13%) of **5d**. Using method A but without adding HMPA and CO (N_2 atmosphere), the reaction with **1** (322 mg,1.035 mmol) gave **7d** (155.2 mg, 61%). A small amount of **5d** was also formed but not isolated.

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-methyl-5-(2-methyl-2-propenyl)-1,3-cyclohexadien-1-yl]oxazole (7d).** IR (CH_2Cl_2): 1648 (s), 1607 (vs), 1574 (m), 1455 (m), 1405 (m), 1362 (m), 1348 (m), 1330 (w), 1292 (s), 1211 (m), 1188 (w), 1044 (m), 1026 (s), 1011 (s), 985 (m), 962 (m), 904 (m), 888 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.03 (d, 3 H, J = 7.0 Hz, CH_3-C(6')), 1.29 and 1.31 (2 s, 6 H), 1.69 (br s, 3 H), 1.85–2.12 (m, 2 H), 2.17–2.30 (m, 1 H), 2.73 (q, 1 H, J = 7.0 Hz), 3.89–3.98 (m, 2 H), 4.57–4.62 (m, 1 H), 4.74–4.79 (m, 1 H), 5.88–6.03 (m, 2 H), 6.56–6.62 (m, 1H). MS: 245 (10), 190 (35), 174 (12), 119 (75), 91 (57), 55 (100). HR-MS calcd for $C_{16}H_{23}ON$ 245.1779, found 245.1771.

1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-6-methyl-1,4-cyclohexadien-1-yl]-3-methyl-3-buten-1-one (5d). IR (CH_2Cl_2): 1680 (s), 1655 (s), 1652 (s), 1610 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.14 (d, 3 H, J = 6.8 Hz), 1.29 and 1.30 (2 s, 6 H), 1.74 (br s, 3 H), 2.98–3.10 (m, 2 H), 3.28–3.48 (m, 2 H), 3.78–3.98 (m, 3 H), 4.76 (br s, 1 H), 4.90 (br s, 1 H), 6.56 (m, 1 H), 6.87 (m, 1 H). MS: 272 (M − 1, 8), 258 (5), 244 (14), 232 (15), 55 (100).

Reactions of Complex 1 with MeLi and Benzyl Bromide. Using method A and starting with **1** (93 mg, 0.299 mmol) gave **7e** (45 mg, 54%) and **5e** (13 mg, 15%). Repeating the preparation on a 1-mmol scale without CO or HMPA gave 52% of **7e** and 13% of **5e**.

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-methyl-5-(phenylmethyl)-1,3-cyclohexadien-1-yl]oxazole (7e).** IR (CH_2Cl_2): 1652 (m), 1611 (s), 1574 (w), 1496 (w), 1455 (m), 1404 (w), 1367 (m), 1352 (m), 1292 (m), 1207 (m), 1185 (w), 1037 (m), 1022 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.99 (d, 3 H, J = 7.0 Hz), 1.30 and 1.36 (2 s, 6 H), 2.25–2.83 (m, 4 H), 3.96 (s, 2 H), 5.86 (ddt, 1 H, J = 1.0, 5.5, 9.4 Hz), 6.02 (dd, 1 H, J = 5.5, 9.4 Hz), 6.62 (dd, 1 H, J = 1.0, 5.5 Hz). MS: 281 (1), 190 (44), 119 (62), 91 (100). HR-MS: calcd for $C_{19}H_{23}NO$ 281.1779, found 281.1745.

1-[5-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)-6-methyl-1,4-cyclohexadien-1-yl]-2-phenylethanone (5e). IR (CH_2Cl_2): 1685 (s), 1663 (s), 1637 (m), 1614 (s), 1500 (m), 1455 (m), 1400 (m), 1367 (m), 1348 (m), 1300 (m), 1207 (w), 1177 (m), 1022 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.10 (d, 3 H, J = 7.0 Hz), 1.29 and 1.30 (2 s, 6H), 2.99–3.08 (m, 2 H), 3.80–4.80 (m, 3 H), 3.99 (s, 2 H), 6.52–6.58 (m, 1 H), 6.89–6.95 (m, 1 H), 7.10–7.40 (m, 5 H). MS: 309 (1), 218 (10), 190 (9), 91 (100). HR-MS: calcd for $C_{13}H_{16}NO_2$ (M − $PhCH_2$) 218.1181, found 218.1137.

(g) Reactions of Complex 1 with RLi and Allyl Bromide, Propargyl Bromide, or 3-(Trimethylsilyl)propargyl Bromide. All reactions in section g, yielding **7f–o**, were carried out in THF under an N_2 atmosphere (Method A without CO and HMPA (unless specified). This apart the procedure and workup were those of method A.

BuLi/Allyl Bromide. Starting with 320 mg (1.028 mmol) of **1** yielded **7f** (178 mg, 63%) and **4f** (59 mg, 18%).

***trans*-2-[6-Butyl-5-(2-propenyl)-1,3-cyclohexadien-1-yl]-4,5-dihydro-4,4-dimethyloxazole (7f).** IR (CH_2Cl_2): 1648 (m), 1610 (s), 1570 (w), 1463 (w), 1440 (w), 1363 (w), 1352 (m), 1293 (m), 1274 (m), 1263 (m), 1207 (m), 1033 (s), 989 (m), 963 (m), 920 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.80–0.90 (m, 3 H), 1.27 and 1.31 (2 s, 6 H), 1.10–1.50 (m, 6 H), 1.92–2.34 (m, 3 H), 2.62–2.75 (bt, 1 H, J = 6.5 Hz), 3.86–3.99 (m, 2 H), 4.90–4.97 (m, 1 H), 4.98–5.04 (m, 1 H), 5.66–6.02 (m, 3 H), 6.58–6.62 (m, 1 H). MS: 273 (13), 232 (100), 176 (52), 161 (26), 160 (23). HR-MS: calcd for $C_{18}H_{27}NO$ 273.2092, found 273.2059.

1-[6-Butyl-5-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)-2,4-cyclohexadien-1-yl]-3-buten-1-one (4f). IR (CH_2Cl_2): 1711 (s), 1652 (m), 1611 (s), 1466 (m), 1422 (w), 1403 (m), 1382 (w), 1363 (m), 1348 (m) , 1296 (m), 1270 (m), 1210 (m), 1033 (s), 992 (m), 962 (m), 926 (m), 911 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.80–0.92 (m, 3 H), 1.10–1.60 (m, 6H), 1.26 and 1.31 (2 s, 3H), 3.16 (bd, 1 H, J = 6.0 Hz), 3.22–3.55 (m, 3 H), 3.86–3.99 (m, 2 H), 4.94–5.22 (m, 2 H), 5.77–5.99 (m, 2 H), 6.17 (ddd, 1 H, J = 1.0, 6.0, 9.0 Hz), 6.59 (dd, 1 H, J = 1.0, 6.0 Hz).

MS: 301 (3), 260 (5), 244 (13), 232 (15), 202 (10), 176 (100). HR-MS: calcd for $C_{19}H_{27}NO_2$ 301.2041, found 301.2023.

PhLi/Allyl Bromide. Starting with 1.051 mmol of **1** yielded 207 mg (67%) of **7g**.

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-phenyl-5-(2-propenyl)-1,3-cyclohexadien-1-yl]oxazole (7g).** Mp 67–69 °C. IR (CH_2Cl_2): 1652 (m), 1640 (m), 1611 (vs), 1574 (w), 1492 (m), 1459 (w), 1448 (m), 1440 (w), 1405 (m), 1367 (m), 1348 (m), 1325 (w), 1296 (m), 1207 (m), 1040 (s), 1011 (m), 100 (m), 985 (m), 962 (m), 918 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.10 and 1.26 (2 s, 6H), 2.10–2.60 (m, 3 H), 3.82–3.91 (m, 2 H), 3.99 (br s, 1 H), 5.00–5.06 (m, 1 H), 5.08–5.12 (m, 1 H), 5.74–5.96 (m, 2 H), 6.10 (dd, 1 H, J = 6.9 Hz), 6.91 (d, 1 H, J = 6.0 Hz), 7.10–7.30 (m, 5 H). MS: 293 (15), 292 (19), 252 (100), 181 (43). Anal. Calcd for $C_{20}H_{23}NO$ (293.40): C, 81.87; H, 7.90; N, 4.77. Found: C, 81.68; H, 7.79; N, 4.70.

Vinyllithium/Allyl Bromide. To a stirred solution of tetravinyltin (0.133 mL, 0.73 mmol) in 10 mL of dry THF was added dropwise MeLi (1.62 M in Et_2O, 1.358 mL, 2.2 mmol) at −78 °C under a nitrogen atmosphere. After 1 h, complex **1** (311 mg, 1.00 mmol) was added as a solid, and the resulting solution was gradually warmed to −20 °C over a period of 3h. The solution was recooled to −78 °C and allyl bromide (0.865 mL, 10 equiv) was added. The solution was slowly warmed to room temperature and stirred overnight. After usual workup, flash chromatography (SiO_2, hexane/Et_2O 5:1 to Et_2O) gave **7h** (131 mg, 54%) of as a colorless oil.

***trans*-4,5-Dihydro-4,4-dimethyl-2-(6-ethenyl-5-(2-propenyl)-1,3-cyclohexadien-1-yl)oxazole (7h).** IR (CH_2Cl_2): 1650 (s), 1609 (vs), 1348 (m), 1294 (s), 1205 (s), 1305 (s), 994 (m), 962 (m), 918 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.25 and 1.30 (2 s, 6 H), 1.95–2.42 (m, 3 H), 3.37 (d, 1 H, J = 6.4 Hz), 3.87–3.97 (m, 2 H), 4.88–5.10 (m, 4 H), 5.66–5.88 (m, 2 H), 5.92–6.06 (m, 2 H), 6.67–6.72 (m, 1 H). MS: 243 (20), 242 (45), 228 (10), 202 (100), 200 (70), 188 (15), 148 (35), 131 (85), 130 (48). HR-MS: calcd for $C_{16}H_{21}NO$ 243.1623, found 243.1618.

Lithiumacetonitrile/Allyl Bromide. To a stirred solution of lithium acetonitrile (0.397 mmol) in dry THF (3 mL) was added complex **1** (82.3 mg, 0.264 mmol) as a solid at −90 °C. After stirring at 0 °C for 2 h, the solution was recooled to −90 °C, and HMPA (0.9 mL) and allyl bromide (10 equiv) were added. Following the usual procedure, flash chromatography on silica gel using hexane/ether 2.5:1 afforded **7i** (32 mg, 48%).

***trans*-2-[6-(2-Propenyl)-2-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)-2,4-cyclohexadien-1-yl]acetonitrile (7i).** IR (CH_2Cl_2): 1651 (s), 1610 (vs), 1404 (m), 1365 (m), 1351 (s), 1303 (s), 1206 (s), 1050 (s), 1015 (m), 986 (m), 962 (m), 920 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.28 and 1.30 (2 s, 6 H), 1.93–2.26 (m, 2 H), 2.28–2.60 (m, 2 H, AB part of ABX system, J = 16.5, 10.0, 5.0 Hz), 2.47–2.58 (m, 1 H), 3.11 (dd, 1 H, X part of ABX system, J = 5.0, 10.0 Hz), 3.95 (s, 2H), 4.93–5.08 (s, 2 H), 5.63–5.86 (m, 1 H), 6.00–6.12 (m, 2 H), 6.68–6.74 (m, 1 H). MS: 256 (20), 241 (10), 215 (72), 199 (20), 160 (30), 144 (100), 116 (41). HR-MS: calcd for $C_{16}H_{20}N_2O$ 256.1575, found 256.1565.

MeLi/Propargyl Bromide. Sequential reaction of complex **1** (1.244 g, 4 mmol) with MeLi and propargyl bromide in THF/HMPA (10 equiv) gave **7j** (645 mg, 71%). An analogous reaction without HMPA yielded **7j** in 30% yield.

***trans*-4,5-Dihydro-4,4-dimethyl-2-(6-methyl-5-(2-propynyl)-1,3-cyclohexadien-1-yl)oxazole (7j).** Mp 55–57 °C (hexane/ether). IR (CH_2Cl_2): 1650 (m), 1610 (s), 1422 (s), 1273 (vs), 1209 (w), 1024 (m), 896 (s). ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.07 (d, 3 H, J = 7.4 Hz), 1.31 and 1.35 (2 s, 6 H), 1.96 (t, 1 H, J = 2.5 Hz), 2.12 (ddd, 1 H, J = 2.5, 7.4, 10.0 Hz), 2.23 (ddd, 1 H, J = 2.5, 7.7, 10.0 Hz), 2.29–2.35 (m, 1 H), 2.86 (q, 1 H, J = 7.4 Hz), 3.91–4.00 (m, 2 H, AB system, J = 7.7 Hz), 6.03–6.11 (m, 2 H), 6.62 (bd, 1 H, J = 3.0 Hz). MS: 229 (M + 1, 8), 228 (7), 190 (74), 174 (10), 160 (13), 136 (21), 120 (11), 119 (100), 118 (48), 91 (74). HR-MS: calcd for $C_{15}H_{18}NO$ 228.1388, found 228.1371. Anal. Calcd for $C_{15}H_{18}NO$ (228.14): C, 72.79; H, 8.68; N, 4.47. Found: C, 72.26; H, 8.62; N, 4.42.

(f) BuLi/Propargyl Bromide. In the medium THF/HMPA (10 equiv), the reaction was carried out with **1** (311 mg, 1 mmol) to give **7k** (236 mg, 87%).

2-(6-Butyl-5-(2-propynyl)-1,3-cyclohexadien-1-yl)-4,5-dihydro-4,4-dimethyloxazole (7k). IR (CH_2Cl_2): 1610 (s), 1349 (m), 1293 (m), 1206 (m), 1034 (s), 947 (w), 963 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.80–0.90 (m, 3 H), 1.15–1.50 (m, 6 H), 1.27 and 1.31 (2 s, 6 H), 1.95 (t, 1 H, J = 2.6 Hz), 2.03–2.32 (m, 2 H, J = 2.6, 7.4, 16.3 Hz), 2.41–2.52 (m, 1 H), 2.71–2.80 (m, 1 H), 3.86–3.98 (m, 2 H), 5.88–6.11 (m, 2 H), 6.60–6.63 (m, 1 H). MS: 272 (M + 1, 30), 271 (17), 232 (100), 228 (10), 214 (20), 202 (13), 176 (99), 161 (35), 105 (76). HR-MS: calcd for $C_{18}H_{25}NO$ 271.1936, found 271.1899.

PhLi/Propargyl Bromide. In the medium THF/HMPA (10 equiv), the reaction was carried out with **1** (311 mg, 1 mmol) to give **7l** (224 mg, 77%).

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-phenyl-5-(2-propynyl)-1,3-cyclohexadien-1-yl]oxazole (7l).** Mp 116–117 °C. IR (CH_2Cl_2): 1651 (m), 1612 (s), 1576 (w), 1494 (m), 1365 (m), 1349 (m), 1295 (m), 1207 (m), 1038 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.09 and 1.26 (2 s, 6 H), 2.05 (t, 1 H, J = 2.7 Hz), 2.35 (dt, 1 H, J = 2.7, 7.6 Hz), 2.63–2.75 (m, 1 H), 3.80–3.92 (m, 2 H, AB system, J_{AB} = 7.9 Hz), 4.10 (br s, 1 H), 5.99 (dd, 1 H, J = 5.6, 9.5 Hz), 6.15 (dd, 1 H, J = 5.4, 9.5 Hz), 6.95 (d, 1 H, J = 5.4 Hz), 7.10–7.30 (m, 5H). MS: 252 (M − C_3H_3, 100), 181 (62), 180 (40), 165 (20), 152 (35), 115 (18), 105 (21), 77 (40). Anal. Calcd for $C_{20}H_{21}NO$ (291.39): C, 82.44; H, 8.68; N, 4.47. Found: C, 81.98; H, 7.25; N, 4.84.

Vinyllithium/Propargyl Bromide. The reaction was carried out with 1.244 g (4.0 mmol) of complex **1** and yielded 792 mg (82%) of **7m**.

***trans*-4,5-Dihydro-4,4-dimethyl-2-(6-ethynyl-5-(2-propynyl)-1,3-cyclohexadien-1-yl]oxazole (7m).** Mp 39 °C. IR (CH_2Cl_2):1651 (s), 1635 (m), 1611 (s), 1575 (m), 1476 (w), 1463 (m), 1427 (m), 1413 (m), 1401 (m), 1387 (w), 1364 (m), 1348 (s), 1326 (m), 1294 (s), 1208 (s), 1037 (s), 1010 (m), 991 (m), 962 (m), 919 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.22 and 1.28 (2 s, 6 H), 1.95 (t, 1 H, J = 2.6 H), 2.05–2.33 (m, 2 H, J = 2.6, 7.8, 10.5 Hz), 2.46–2.58 (m, 1 H), 3.44 (bd, 1 H, J = 6.1 Hz), 3.84–3.96 (m, 2 H, AB system, J = 7.9 Hz), 4.92 (dt, 1 H), 5.02 (dt, 1 H, J = 1.6, 15.7 Hz), 5.75 (ddd, 1H, J = 6.1, 10.2, 15.7 Hz), 5.95–6.10 (m, 2 H), 6.67–6.71 (m, 1 H). MS: 242 (M + 1, 80), 202 (81), 287 (51), 164 (33), 160 (20), 131 (75), 105 (100), 77 (45), 55 (60). Anal. Calcd for $C_{16}H_{19}NO$ (241.33): C, 79.63; H, 7.93; N, 5.80. Found: C, 79.02; H, 7.92; N, 5.79.

MeLi/3-(Trimethylsilyl)propargyl Bromide. The reaction was carried out with 311 mg (1.0 mmol) of complex **1** and yielded 217 mg (72%) of **7n**.

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-methyl-5-(3-(trimethylsilyl)-2-propynyl)-1,3-cyclohexadien-1-yl]oxazole (7n).** IR (CH_2Cl_2): 1561 (m), 1610 (s), 1042 (m), 1022 (s), 845 (vs). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.13 (s, 9 H), 1.05 (d, 3 H, J = 7.1 Hz), 1.29 and 1.33 (2 s, 6 H), 2.12–2.37 (m, 3H), 2.80 (q, 1H, J = 7.1 Hz), 3.88–3.99 (m, 2 H, AB system (m), J_{AB} = 7.9 Hz), 6.03–6.08 (m, 2H), 6.56–6.62 (m, 1H). MS: 301 (11), 286 (7), 190 (100), 160 (15), 119 (40), 104 (25), 96 (60), 91 (100), 83 (40), 73 (25), 55 (18). HR-MS: calcd for $C_{18}H_{27}NOSi$ 301.1861, found 301.1850.

Vinyllithium/3-(Trimethylsilyl)propargyl Bromide. The reaction was carried out with 311 mg (1.0 mmol) of complex **1** and yielded 277 mg (88%) of **7o**.

***trans*-4,5-Dihydro-4,4-dimethyl-2-[6-ethenyl-5-(3-trimethylsilyl-2-propynyl)-1,3-cyclohexadien-1-yl]oxazole (7o).** Mp 53–54.5 °C. IR (CH_2Cl_2): 1651 (m), 1611 (s), 1364 (m), 1294 (m), 1252 (s), 1207 (m), 1036 (s), 991 (m), 962 (m), 918 (m), 845 (vs). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.13 (s, 9 H), 1.25 and 1.31 (2 s, 6 H), 4.14–2.40 (m, AB part of ABX system, 2 H, J = 7.4, 7.9, 16.4 Hz), 2.48–2.60 (m, 1 H), 3.42–3.48 (m, 1H), 3.88–3.98 (m, 2 H, AB system, J_{AB} = 8.0 Hz), 4.95 (dt, 1 H, J = 2.0, 10.0 Hz), 5.04 (dt, 1 H, J = 2.0, 10.0 Hz), 5.78 (ddd, 1 H, J = 6.0, 10.0, 18.0 Hz), 6.00–6.12 (m, 2 H), 6.68–6.76 (m, 1 H). MS: 313 (5), 240 (7), 215 (12), 202 (100), 200 (39), 187 (49), 148 (36), 146 (12), 132 (15), 131 (92), 130 (46), 115 (18), 105 (40). Anal. Calcd for $C_{19}H_{27}NOSi$ (313.51): C, 78.56; H, 8.35; N, 6.11. Found: C, 78.01; H, 8.24; N, 6.09.

4. Nucleophile/Electrophile Addition Reactions with Complex 2. (a) General Procedures: Method A. The reaction was carried out in a heavy-walled 80-mL Schlenk tube

fitted with a 8-mm O-ring tap (Youngs) and a rubber septum. A solution of the organolithium reagent (1.1 equiv) was added dropwise *via* syringe to a solution of complex **2** (1 mmol) in THF (10 mL) at −78 °C. After warming to −40 °C in 2 h, stirring was continued at this temperature for an additional 2 h. The red solution was recooled to −78 °C, and HMPA (10 equiv) and the electrophile (10 equiv) were added. The rubber septum was replaced by an adapter with a small pressure gauge. After a freeze/pump cycle, CO (4 bar) was pressed onto the mixture at −78 °C, and the magnetically stirred solution left to warm up to ambient temperature overnight. Excess CO was vented, and volatiles were removed *in vacuo*. The red oily residue was purified by flash chromatography on silica gel (hexane/Et_2O).

Method B. The reaction was carried out exactly as before except for the following additional step. The red residue was dissolved in dry THF (10 mL) under N_2 atmosphere. The resulting solution was cooled to −78 °C and transferred *via* cannula into a dispersion of NaH (10 equiv, prewashed with dry pentane, 5 × 10 mL) in dry THF at the same temperature. After 0.5 h the carbon electrophile (10 equiv) was added. The temperature was allowed to raise slowly to 20 °C, and the solution was stirred overnight. After evaporation of volatiles, the crude product mixture was purified by flash chromatography on silica gel (hexane/Et_2O).

(b) MeLi/MeI (Method A). The reaction was carried out with 1.00 g (3.1 mmol) of complex **2**. Flash chromatography first eluted **11a** (551 mg, 73%) followed by the cyclohexylimine derivative of **9a** (73 mg, 9%), and the cyclohexylimine derivative of **10a** (55 mg, 8%). Treatment of an ether solution of the cyclohexylimine derivative of **9a** with sat. aq NH_4Cl afforded aldehyde **9a** quantitatively.

1-[5-((Cyclohexylamine)methylene)-6-methyl-1,3-cyclohexadienyl]ethanone (11a). IR ($CHCl_3$): 1685 (s), 1635 (m), 1450 (s), 1220 (m), 1200 (m), 1110 (m), 1080 (m). ^{1}H-NMR (C_6D_6, 200 MHz): 0.70−1.05 (m, 5 H), 1.30 (d, 3 H, J = 7.0 Hz), 1.45−1.59 (m, 5 H), 2.15 (s, 3 H), 2.42−2.51 (m, 1 H), 3.78−3.88 (m, 1H), 4.35 (q, 1 H), 5.49 (dd, 1 H, J = 6.3, 8.5 Hz), 6.07 (d, 1 H, J = 13.2 Hz), 6.36 (d, 1 H, J = 8.5 Hz), 6.78 (d, 1 H, J = 6.3 Hz). ^{13}C-NMR (C_6H_6, 100 MHz): 19.4, 24.9, 25.2, 25.2, 28.2, 34.0, 34.4, 56.3, 111.1, 112.6, 134.4, 136.1, 138.1, 139.7, 195.6. MS: 244 (3), 230 (1), 216 (8), 176 (77), 162 (10), 134 (21), 55 (100). UV (hexane): λ_{max} 254 nm (ϵ 17 400), 444 nm (ϵ 9600).

***cis*-5-Acetyl-5,6-dimethyl-1,3-cyclohexadienecarbaldehyde (9a).** IR (CH_2Cl_2): 1705 (vs), 1668 (vs), 1569 (s), 1412 (s), 1378 (s), 1355 (s), 1255 (s), 1177 (vs), 1154 (s), 1097 (m), 896 (m). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.81 (*d*, 3 H, J = 7.2 Hz), 1.19 (s, 3 H), 2.23 (s, 3 H), 3.08 (q, 1 H, J = 7.2 Hz), 6.21 (dd, 1 H, J = 5.2, 9.6 Hz), 6.69 (d, 1 H, J = 9.6 Hz), 6.74 (d, 1 H, J = 5.2 Hz), 9.55 (s, 1 H). MS: 136 (89), 121 (77), 107 (100), 91 (92). HR-MS: calcd for $C_9H_{11}O$ ($M^+ - COCH_3$) 135.0810, found 135.0766.

***trans*-5,6-Dimethylcyclohexa-1,3-dienecarbaldehyde Cyclohexylimine (10a').** IR ($CHCl_3$): 1670 (w), 1645 (m), 1610 (s), 1565 (m), 1450 (s). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (d, 3 H, J = 7.2 Hz), 0.97 (d, 3 H, J = 7.4 Hz), 1.20−1.84 (m, 10 H), 2.09−2.15 (m, 1 H), 2.75 (q, 1 H, J = 7.4 Hz), 2.99−3.07 (m, 1 H), 5.92−6.00 (m, 2 H), 6.08−6.10 (m, 1 H), 7.84 (s, 1 H). MS: 217 (95), 202 (78), 188 (38), 134 (65), 120 (97), 105 (34), 84 (100). HR-MS: calcd for $C_{15}H_{23}N$ 217.1831, found 217.1840.

(c) MeLi/MeI (Method B). The reaction was carried out with 300 mg (0.93 mmol) of **2** to give **9a** (146 mg, 88%) and **10a** (20 mg, 10%).

(d) MeLi/EtI (Method A). Starting with 500 mg (1.55 mmol) of **2** yielded 181 mg (45%) of **11b**, 70 mg (28%) of **9b**, and 11 mg (3%) of **10b**.

1-[5-((Cyclohexylamino)methylene)-6-methyl-1,3-cyclohexadienyl]-1-propanone (11b). IR (hexane): 1680 (s), 1650 (s), 1625 (vs), 1510 (s), 1460 (m), 1440 (s), 1370 (m), 1300 (w), 1270 (m), 1225 (m), 1190 (m), 1150 (m). ^{1}H-NMR (C_6D_6, 200 MHz): 0.45−1.85 (m, 10 H), 1.17 (t, 3 H, J = 7.1 Hz), 1.29 (d, 3 H, J = 6.6 Hz), 2.25−2.55 (m, 1 H), 2.48 (q, 2 H, J = 7.1 Hz), 3.92 (dd, 1 H, J = 13.0 Hz, NH, signal changed to d on irradiation at 5.98, signal disappeared on addition of D_2O), 4.32 (dq, 1 H, J = 1.1, 6.6 Hz), 5.50 (dd, 1 H, J = 6.2, 8.7 Hz), 5.98 (d, 1 H, J = 13.0 Hz), signal changed to s on irradiation at 3.92), 6.32 (d, 1 H, J = 8.7 Hz), 6.78 (d, 1 H, J = 6.2 Hz). MS: 259 (1), 244 (8), 230 (3), 216 (2), 190 (19), 176 (5), 162 (21), 57 (100).

***cis*-5-Ethyl-6-methyl-5-propionyl-1,3-cyclohexadienecarbaldehyde (9b).** IR (CH_2Cl_2): 1705 (vs), 1672 (vs), 1455 (m), 1425 (m) 1275 (s), 1160 (m), 1150 (m), 890 (m). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.71−0.76 (m, 6 H), 1.11 (t, 3 H, J = 7.0 Hz), 1.62−1.84 (m, 2 H), 2.47−2.60 (m, 2 H), 3.04 (dq, 1 H, J = 1.5, 7.0 Hz), 6.26 (dd, 1 H, J = 5.2, 10.0 Hz), 6.72 (dd, 1 H, J = 1.0, 5.2 Hz), 6.79 (dt, 1 H, J = 1.0, 10.0 Hz), 9.52 (s, 1 H). MS: 206 (12), 191 (45), 177 (100), 163 (86), 150 (40), 57 (100). HR-MS: calcd for $C_{11}H_{12}O$ ($M^+ - C_2H_4$) 178.1357, found 178.1351.

(e) PhLi/MeI (Method B). The reaction was carried out with 100 mg (0.31 mmol) of **2** to yield **9c** (59 mg, 80%).

***cis*-5-Acetyl-5-methyl-6-phenyl-1,3-cyclohexadienecarbaldehyde (9c).** IR ($CHCl_3$): 1673 (vs), 1580 (m), 1490 (s), 1450 (s), 1350 (s), 1200 (m), 1175 (m). ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.37 (s, 3 H), 1.88 (s, 3 H), 4.15 (s, 1 H), 6.35 (dd, 1 H, J = 5.6, 9.6 Hz), 6.84 (d, 1 H, J = 5.6 Hz), 6.92 (d, 1 H, J = 9.6 Hz), 7.14−7.18 (m, 3 H), 7.29−7.33 (m, 2 H), 9.51 (s, 1 H). MS: 240 (10), 198 (100), 183 (32), 169 (60), 154 (30), 91 (25). HR-MS: calcd for $C_{14}H_{14}O$ ($M^+ - COCH_2$) 198.1045, found 198.1016.

(f) Vinyllithium/MeI (Method B). To a stirred solution of tetravinyltin (82.6 μL, 0.454 mmol) in THF (10 mL) was added dropwise MeLi (1.6 M in Et_2O, 0.85 mL, 1.36 mmol) at −78 °C. After stirring at this temperature for 1 h, a precooled (−78 °C) solution of **2** (200 mg, 0.62 mmol) in THF (10 mL) was added *via* cannula. Following the usual procedure afforded **9d** (68 mg, 58%) and **10d** (7 mg, 8%).

***cis*-5-Acetyl-6-ethenyl-5-methyl-1,3-cyclohexadienecarbaldehyde (9d).** IR (CH_2Cl_2): 1708 (vs), 1677 (vs), 1670 (s), 1450 (m), 1360 (s), 1250 (m), 1175 (s), 1100 (m), 1000 (m), 970 (s), 920 (s). ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.23 (s, 3 H), 2.20 (s, 3 H), 3.63 (d, 1 H, J = 9.0 Hz), 4.99 (dd, 1 H , J = 1.2, 10.0 Hz), 5.23 (d, 1 H, J = 16.8 Hz), 5.57 (ddd, 1 H, J = 9.0, 10.0, 16.8 Hz), 6.23 (dd, 1 H, J = 5.4, 9.8 Hz), 6.74 (d, 1 H, J = 9.8 Hz), 6.78 (d, 1 H, J = 5.4 Hz), 9.55 (s, 1 H). MS: 190 (2), 161 (2), 148 (33), 133 (32), 119 (66), 105 (32), 91 (100). HR-MS: calcd for $C_{10}H_{12}O$ ($M^+ - COCH_2$) 148.0888, found 148.0867.

***trans*-5-Methyl-6-ethenyl-1,3-cyclohexadienecarbaldehyde (10d).** IR (CH_2Cl_2): 1680 (vs), 1580 (m), 1280 (m), 1250 (m), 1180 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.96 (d, 3 H, J = 7.2 Hz), 2.38−2.55 (m, 1 H), 3.25 (d, 1 H, J = 7.2 Hz), 4.93 (dt, 1 H, J = 1.4, 10.2 Hz), 5.02 (dt, 1 H, J = 1.4, 17.1 Hz), 5.72 (ddd, 1 H, J = 7.0, 10.2, 17.1 Hz), 6.14 (dd, 1 H, J = 5.2, 9.4 Hz), 6.27 (dd, 1 H, J = 5.2, 9.4 Hz), 6.79 (dd, 1 H, J = 1.0, 5.2 Hz), 9.54 (s, 1 H). MS: 148 (19), 133 (27), 119 (60), 105 (85), 91 (100).

(g) MeLi/Allyl Bromide (Method A). The reaction was carried out with 200 mg (0.62 mmol) of **2** to yield **10e** (86 mg, 57%).

***trans*-5-Allyl-6-methyl-1,3-cyclohexadiencarbaldehyde Cyclohexylimine (10e').** IR (CH_2Cl_2): 1669 (s), 1638 (s), 1611 (s), 1568 (m), 1422 (vs), 917 (s), 896 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.96 (d, 3 H, J = 7.1 Hz), 1.20−2.20 (m, 13 H), 2.90 (q, 1 H, J = 7.1 Hz), 2.93−3.10 (m, 1 H), 4.85−5.00 (m, 2 H), 5.64−6.10 (m, 4 H), 7.80 (s, 1 H). MS: 243 (35), 202 (69), 187 (17), 160 (10), 120 (100), 83 (81). HR-MS: calcd for $C_{17}H_{25}N$ 243.1987, found 243.1969.

(h) MeLi/3-(Trimethylsilyl)propargyl Bromide. MeLi (1.27 N in ether, 1.2 mmol, 0.945 mL) was added to a solution of the imine complex **2** (1.0 mmol) in THF (10 mL) at −78 °C. After warming to −40 °C during 4 h the solution was cooled to −78 °C, and HMPA (1.7 mL) and 3-(trimethylsilyl)propargyl bromide (5 mmol, 0.7 mL) were added. The reaction mixure was slowly warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo*, and the residue was purified by flash chromatography (SiO_2, hexane/ether 30:1 to 20:1) to yield 197.8 mg (76%) of aldehyde **10f**.

6-Methyl-5-(3-(trimethylsilyl)prop-2-ynyl)-1,3-cyclohexadienecarbaldehyde (10f). IR (CH_2Cl_2): 1672 (vs), 1570

(s), 1453 (m), 1425 (m), 1406 (m), 1364 (m), 1327 (m), 1248 (s), 1181 (s), 1163 (s), 1121 (m), 1032 (s), 999 (m), 841 (vs). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.12 (s, 9H, $(CH_3)_3Si$), 0.96 (t, 3H, J = 7.2 Hz), 2.01–2.13 (m, B part of ABX system, 1H, J = 7.6, 16.5 Hz), 2.14–2.27 (m, A part of ABX system, 1H, J =7.3, 16.5 Hz), 2.32–2.43 (m, 1H, J = 7.3, 7.6 Hz), 2.86 (tq, 1H, J = 1.0, 7.2 Hz), 6.17–6.25 (m, 1H, J = 5.0, 9.4 Hz), 6.26–6.34 (m, 1H, J = 1.0, 5.1, 9.4 Hz), 6.80 (dd, 1H, J = 1.3, 5.0 Hz), 9.47 (s, 1H). MS: 232 (5), 203 (15), 121 (10), 93 (85), 73 (100). HR-MS: calcd for $C_{14}H_{20}OSi$ 232.1283, found 232.1270.

5. Deprotonation/Alkylation Reactions of 11. General Procedure: A 0.02–0.06 M solution of **11** in THF was added to a dispersion of NaH (3–10 equiv, prewashed with pentane, 5 × 10 mL) in THF (10 mL) at −78 °C. After 0.5 h the electrophile (3–10 equiv) was added. The mixture was kept for 0.5 h at −78 °C and then warmed slowly to ambient temperature and stirred overnight. The solvent was evaporated, the residue dissolved in Et_2O (50 mL) and the solution carefully treated with aq NH_4Cl solution (sat., 10 mL). The phases were separated, and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic phases were combined, washed with brine, and dried ($MgSO_4$), and the solvent was evaporated. The products were purified by flash chromatography on silica gel (hexane/ether 4:1).

(a) Reaction of 11a with MeI. The reaction was carried out with 76 mg (0.31 mmol) of **11a** as described in the general procedure, except for warming to 0 °C over a period of 3 h. Chromatography afforded **9a** (48 mg, 86%).

(b) Reaction of 11a with EtI. The reaction was carried out with 39 mg (0.16 mmol) of **11a** to give **9g** (17.5 mg, 59%).

***cis*-5-Acetyl-5-ethyl-6-methyl-1,3-cyclohexadienecarbaldehyde (9g).** IR (CH_2Cl_2): 1707 (vs), 1672 (vs), 1571 (m), 1460 (w), 1370 (w), 1350 (w), 1190 (m), 1110 (w). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.74 (t, 3 H, J = 7.5 Hz), 0.78 (d, 3 H, J = 6.7 Hz), 1.50–1.90 (m, 2 H), 2.20 (s, 3 H), 3.03 (dq, 1 H, J = 1.1, 6.7 Hz), 6.24 (dd, 1 H, J = 5.2, 9.7 Hz), 6.71 (d, 1 H, J = 5.2 Hz), 6.77 (dd, 1 H, J = 9.7 Hz), 9.60 (s, 1 H). MS: 193 (0.3), 177 (1), 163 (1), 150 (27), 135 (26), 121 (43), 93 (100), 91 (33). HR-MS: calcd for $C_{10}H_{14}O$ ($M^+ - COCH_2$) 150.1045, found 150.1015.

(c) Reaction of 11a with Allyl Bromide. Starting with 41 mg (0.17 mmol) of **11a** gave **9h** (27.0 mg, 78%).

***cis*-5-Acetyl-6-methyl-5-(2-propenyl)-1,3-cyclohexadienecarbaldehyde (9h).** IR (CH_2Cl_2): 1707 (vs), 1672 (vs), 1570 (m), 1361 (m), 1170 (s), 925 (m), 910 (m), 770 (m), 730 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.79 (d, 3 H, J = 7.0 Hz), 2.20 (s, 3 H), 2.22–2.54 (m, 2 H), 3.06 (dq, 1 H, J = 1.1, 7.0 Hz), 4.92–5.10 (m, 2 H), 5.42–5.64 (m, 1 H), 6.30 (dd, 1 H, J = 5.4, 9.8 Hz), 6.67–6.78 (m, 2 H), 9.54 (s, 1 H). MS: 205 (5), 162 (38), 147 (30), 121 (91), 105 (74), 91 (100). HR-MS: calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1159.

(d) Reaction of 11a with $BrCH_2CO_2Et$. To a solution of **11a** (549 mg, 2.24 mmol) in THF (30 mL) was added KOH (10 equiv, 1.25 g, 22.3 mmol) at −78 °C. The mixture was stirred for 30 min. $BrCH_2CO_2Et$ (10 equiv, 2.5 mL, 22.3 mmol) was then added at −78 °C. The mixture was warmed slowly to ambient temperature and stirred overnight. Usual workup and chromatography (hexane/ether 20:1, then 5.1) gave **9i** (335 mg, 60%).

(1-Acetyl-5-formyl-6-methylcyclohexa-2,4-dienyl)acetic Acid Ethyl Ester (9i). IR (CH_2Cl_2): 1731 (vs), 1709 (s), 1674 (vs), 1570 (m), 1456 (m), 1408 (m), 1372 (m), 1353 (m), 1341 (m), 1166 (s), 1033 (m). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.82 (d, 1 H, J = 6.8 Hz), 1.20 (t, 3 H, J = 6.8 Hz), 2.34 (s, 3 H), 2.65 (AB d, 1 H, J = 16.5 Hz), 2.85 (AB d, 1 H, J = 16.5 Hz), 2.91 (q, 1 H, J = 6.8 Hz), 4.05 (q, 2 H, J = 6.8 Hz), 6.32 (dd, 1 H, J = 5.2, 9.6 Hz), 6.73–6.77 (m, 2 H), 9.53 (s, 1 H). MS: 250 (0.2), 205 (12), 163 (14), 121 (19), 105 (100), 91 (39). HR-MS: calcd for $C_{12}H_{15}O_3$ ($M - COCH_3$) 207.1021, found 207.0992.

(e) Reaction of 11b with Allyl Bromide. The reaction was carried out with 55 mg (0.21 mmol) of **11b** to give **9j** (36 mg, 79%).

***cis*-5-Propionyl-5-(2-propenyl)-6-methyl-1,3-cyclohexadienecarbaldehyde (9j).** IR (CH_2Cl_2): 1708 (vs), 1673 (vs), 1568 (s), 1410 (m), 1175 (s), 940 (m), 930 (m), 910 (m). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.76 (d, 3 H, J = 7.0 Hz), 1.09 (t, 3 H, J = 7.2 Hz), 2.33–2.39 (m, 1 H), 2.43–2.50 (m, 1 H), 2.51 (dq, 1 H, J = 7.2, 18.0 Hz), 2.62 (dq, 1 H, J = 7.2, 18.0 Hz), 3.08 (dq, 1 H, J = 1.2, 7.0 Hz), 4.95–5.02 (m, 2 H), 5.48–5.59 (m, 1 H), 6.30 (dd, 1 H, J = 5.5, 10.0 Hz), 6.72–6.76 (m, 2 H), 9.79 (s, 1 H). MS: 177 (1), 162 (7), 147 (8), 121 (14), 105 (11), 91 (15), 57 (100). HR-MS: calcd for $C_{11}H_{14}O$ ($M^+ - COCH_2$-CH_2) 162.1045, found 162.1036.

6. Reaction of 11a with O_2. In the dark, a slow stream of dry oxygen gas was passed through a stirred solution of **11a** (115 mg, 0.47 mmol) in dry ether (10 mL) at 23 °C. The initially red solution turned yellow after 1 h, and after 2 h, TLC showed the starting material to have been consumed. The mixture was taken to dryness under vacuum. Flash chromatography on silica (hexane/ether 2:1) gave **12** (77 mg, 92%). Mp 165–166 °C. IR ($CHCl_3$): 3010 (s), 2950 (s), 2875 (s), 1683 (s), 1650 (m), 1640 (m), 1635 (m), 1605 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.05–1.95 (m, 10 H), 2.41 (s, 3 H), 2.51 (s, 3 H), 3.05–3.18 (m, 1 H), 7.02 (s, 1 H), 7.42 (s, 1 H), 8.65 (s, 1 H). MS: 178 (6), 177 (14), 176 (100), 162 (13), 134 (24), 91(10). HR-MS: calcd for $C_{10}H_{10}O_3$ 178.0629, found 178.0635.

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Supplementary Material Available: ^{1}H-NMR spectra of **6a,b**, **7c–l,n,o**, **9a–d,g,i**, **10f**, **11a**, and **12** (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.