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Consecutive Michael-Addition-Olefination Sequences with $Cr(CO)_3$-Complexed Aryl Allenylphosphonates - An Efficient Synthesis of Heterocyclic Substituted Arene Complexes

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Dedicated to Prof. Dr. Klaus Hafner on the occasion of his 70th birthday

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Summary: The Michael-Addition of 1,2 and 1,3-difunctional carbonyl compounds **6** to $Cr(CO)_3$-complexed aryl allenylphosphonates **5** followed by an intramolecular Horner-Emmons-Wadsworth olefination in boiling THF gives rise to arene $Cr(CO)_3$ substituted heterocycles **7** in moderate to good yields.

INTRODUCTION

Among numerous reactions mediated by $Cr(CO)_3$-complexed arenes sidechain functionalizations[1] represent the most intriguing synthetic options. In addition to steric effects of the bulky chromiumcarbonyl tripod $Cr(CO)_3$ complexation alters the electronic properties of arenes significantly. As a consequence of the net electron withdrawing properties of the chromium carbonyl tripod complexed arenes are able to stabilize benzylic anions very efficiently.[1c] Remarkably, some nucleophiles can be added to styrene complexes to give stable benzylic carbanions, however, the scope of this useful synthesis is limited only to stabilized carbanions.[1a,c] Since quite a number of nucleophiles are known to react readily with acceptor substituted allenes at the central carbon atom[2,3] we suggest the use of allenyl substituted arene $Cr(CO)_3$-complexes[4] which upon nucleophilic addition generate stabilized allyl anions for further functionalization. Furthermore, acceptor substituted allenes are key building blocks in the synthesis of five- and six-membered heterocycles.[3a] Recently, we could show that $Cr(CO)_3$-complexed benzylphosphonate anions react in a Horner-Emmons-Wadsworth (HEW) reaction with aldehydes to give alkenyl substituted arene $Cr(CO)_3$-complexes in good yields.[5] Thus, complexed aryl allenyl phosphonates could be suitable substrates for Michael addition-olefination sequences giving rise to dienyl, carbo or heterocyclic substituents on arene $Cr(CO)_3$-complexes

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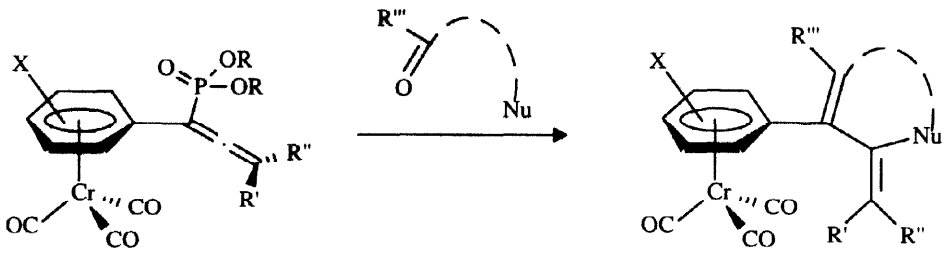
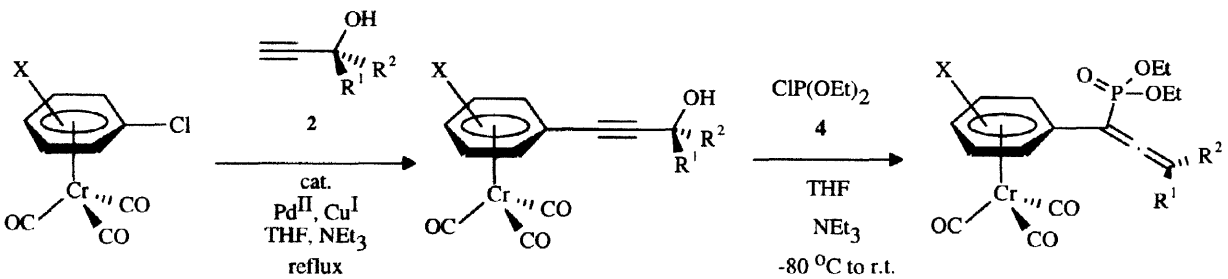
(see Scheme 1). Here, we report our preliminary results on a novel metal template directed synthesis of arene $Cr(CO)_3$ susbtituted heterocycles via a consecutive Michael addition-HEW olefination sequence with allenylphosphonate substituted chromium carbonyl arene complexes.



Scheme 1

RESULTS AND DISCUSSION

The allenylphosphonate arene complexes **5** are easily accessible from the chloroarene complexes **1** in a two step sequence (see Scheme 2).[4] The Sonogashira coupling of **1**[6] with the propargylic alcohols **2** furnishes the η^6-aryl propargylic alcohols **3** as yellow crystals in good to excellent yields. The complexes **3** react in a displacement rearrangement with diethoxy chlorophosphane (**4**) to give the allenylphosphonate arene complexes **5** as yellow crystalline solids or oils, respectively, in good yields.



1a: X = H
1b: X = *o*-Me
1c: X = *m*-Me
1d: X = *p*-Me

3a: X = H, $R^1 = R^2$ = Me; 90 %
3b: X = H, R^1 = H, R^2 = Et; 69 %
3c: X = *o*-Me, $R^1 = R^2$ = Me; 77 %
3d: X = *m*-Me, $R^1 = R^2$ = Me; 82 %
3e: X = *p*-Me, $R^1 = R^2$ = Me; 100 %

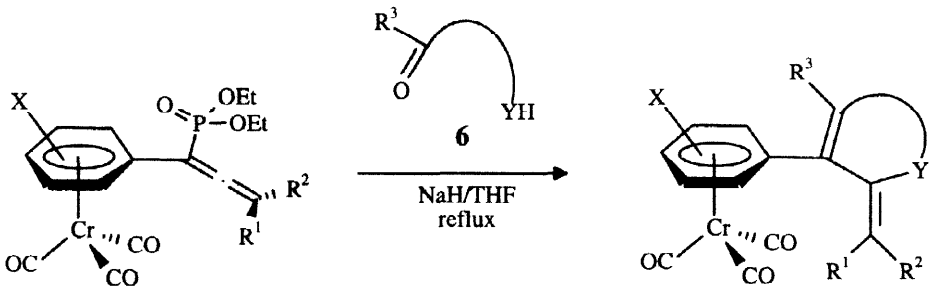
5a: X = H, $R^1 = R^2$ = Me; 80 %
5b: X = H, R^1 = H, R^2 = Et; 68 %
5c: X = *o*-Me, $R^1 = R^2$ = Me; 79 %
5d: X = *m*-Me, $R^1 = R^2$ = Me; 69 %
5e: X = *p*-Me, $R^1 = R^2$ = Me; 71 %

Scheme 2

The η^6-arene complexation of **5** is supported by the considerable upfield shift of the arene proton and carbon resonances in the ^1H and ^{13}C NMR spectra, respectively. In the ^{13}C NMR spectra the characteristic allene resonances for the α-carbon atom (δ = 90 - 94), central β-carbon atom (δ = 208) and the γ-carbon atom (δ = 98 - 102) appear within the expected margin.[7] The unambiguous assignments of the quaternary α- and γ-carbon

resonances can be made due to the large phosphorus-carbon couplings ($J_{P,\alpha C}$ = 192 Hz; $J_{P,\beta C}$ = 14 Hz) in the proton decoupled carbon NMR spectra. Besides the strong terminal CO-stretching bands in the IR spectra of **5** at $\tilde{\nu}$ = 1960 and 1880 cm^{-1}, respectively, in the fingerprint region the strong absorptions at $\tilde{\nu}$ = 1250, 1050 and 1025 cm^{-1} represent the PO-stretching bands. The CC-deformation bands characteristic for the allene skeleton appear at $\tilde{\nu}$ = 970 cm^{-1}.

The complexes **5** react smoothly in boiling THF with a number of 1,2- and 1,3-difunctional carbonyl compounds **6** in the presence of sodium hydride in a one-pot reaction to furnish a number of arene$Cr(CO)_3$ substituted heterocycles **7** as yellow to orange crystalline solids in moderate to good yields (see Scheme 3 and Table 1).

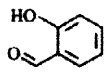
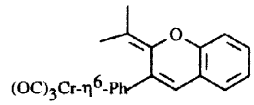
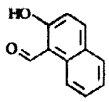
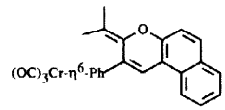
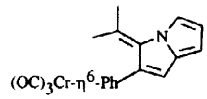
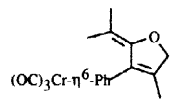
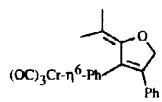
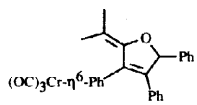
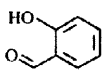
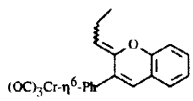
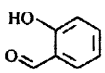
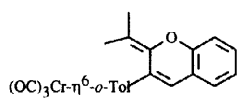
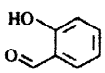
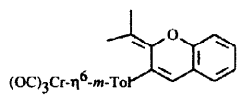
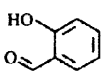
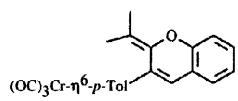
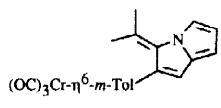


5 **7**

Scheme 3

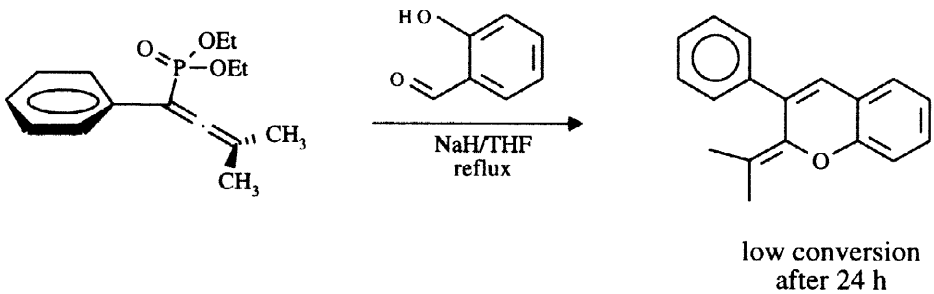
All $Cr(CO)_3$ complexed arene fragments can be easily identified due to the upfield shift of the arene proton and carbon resonances in the NMR spectra. Furthermore, the carbon NMR spectroscopic data support the formation of a heterocyclic framework attached to an arene complex due to two quaternary resonances at relative downfield (δ = 134 - 154). For the complex **5b** bearing a racemic allenyl substituent a 1:2 mixture of *E* and *Z* isomers of **7g** is formed (entry 7). This can be reasonably explained considering the relative stability of the diastereomeric allyl anions formed upon nucleophilic addition. The 1,3-strain between the arene chromium carbonyl substituent and the ethyl substituent in the *syn*-configurated allyl anion leading to the *E*-configurated double bond is obviously slightly higher than in the *anti*-configurated isomer causing the formation of the *Z*-double bond. According to the fragmentation pattern in the mass spectra the newly formed arene complexed heterocycles behave similarly to other arene complexes with π-substitutents as indicated by the appearance of the M^+-CO- and M^+-3CO-fragments.

Table 1. AreneCr(CO)$_3$ substituted heterocycles **7** by addition-olefination reactions of the allenyl phosphonate complexes **5** with the difunctional carbonyl compounds **6**.

entry	complex **5**	difunctional carbonyl compound **6**	arene Cr(CO)$_3$ substituted heterocycle **7**	isolated yield (%)
1	**5a**		 **7a**	87
2	**5a**		 **7b**	38
3	**5a**		 **7c**	54
4	**5a**		 **7d**	56
5	**5a**		 **7e**	52
6	**5a**		 **7f**	48
7	**5b**		 **7g**	54 E/Z = 1:2
8	**5c**		 **7h**	0
9	**5d**		 **7i**	92
10	**5e**		 **7j**	82
11	**5d**		 **7k**	64

Compared to aldehydes the reactivity of ketones is somewhat lower as reflected by the slightly lower yields (entries 4-6) obtained under otherwise similar conditions. A clear limitation of this novel metal template mediated heterocycle synthesis are *ortho*-substituted complexes as **5c** (entry 8) which do not cyclize even after prolonged heating in THF. The steric strain of the allyl anion formed upon nucleophilic addition of the phenolate minimizes a sufficient overlap with the electron withdrawing arene chromium carbonyl fragment. To rule out an electronic bias which could arise from the electron donating *ortho*-methyl group the *para*-substituted complex **5e** (entry 10) was applied in the addition-cyclization sequence. It smoothly reacts with the anion of salicylic aldehyde to give the desired chromene derivative **7j** in good yield. Fortunately, *meta*-substituted complexes as **5d** (entries 9 and 11) readily form the expected heterocycles. Thus, also planar chiral complexes are accessible by this methodology.

Finally, the electronic influence of the chromiumcarbonyl complexation on the relative reaction rate was qualitatively studied. The comparison of complexed aryl allenyl phosphonates with the free ligand (see Scheme 4) clearly points out the electronic influence of the chromium carbonyl arene substituents on the reactivity. In the absence of the electronically activating chromium carbonyl tripod only a low conversion was observed after 24 h of heating in THF. Thus, the $Cr(CO)_3$-complexed arene enhances the rate of HEW-cyclization considerably.



Scheme 4

CONCLUSION

The Michael addition-intramolecular HEW-olefination sequence of 1,2- and 1,3-difunctionalized carbonyl compounds and arene $Cr(CO)_3$-substituted allenyl phosphonates represents a facile and selective metal template directed one-pot synthesis of a number of arene $Cr(CO)_3$-substituted heterocycles. The electron withdrawing property of the $Cr(CO)_3$ tripod is necessary for reasonable reaction rates. In addition, electron releasing substituents placed in *meta*- or in *para*-position to the allenyl substituent are compatible with the general reaction profile. Thus, the introduction of benzoid substituents to the core of alkylidene chromenes, pyrrolizines and dihydrofurans can be accomplished in a straight forward manner. Further

methodological studies on functionalizations of these novel organometallic heterocycles and their application to the synthesis of more complex heterocyclic systems are currently underway.

EXPERIMENTAL

General

All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures.[8] - Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 70-230. TLC: silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar. - The chlorobenzene complexes **1** were prepared by literature methods.[9] Bis(triphenylphosphane)palladium(II) dichloride, copper(I) iodide, the propargylic alcohols **2**, chlorodiethoxyphosphane (**4**), the difunctionalized carbonyl compounds **6** and sodium hydride (97%) were purchased from Merck, Aldrich or Fluka, and used without further purification. The η^6-aryl propargylic alcohol complexes **3** were prepared in analogy to our published protocol.[4] - ^1H, ^{13}C and ^{31}P NMR spectra: Bruker ARX 300, Varian VXR 400S [D_6]DMSO. - IR: Perkin Elmer FT-IR spectrometer 1000. The samples were pressed into KBr pellets. - UV/Vis: Perkin Elmer Models Lambda 16. - MS: Finnigan MAT 90 and MAT 95 Q. - Elemental analyses were carried out in the Microanalytical Laboratory of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

General Procedure (GP) for the displacement rearrangement of complexed propargylic alcohols 3 with chlorodiethoxyphosphane (4) to complexed aryl allenylphosphonates 5

To a degassed solution of 1 equivalent of **3** and 1.1 equivalents of triethylamine in 15 ml of THF, cooled to -78 °C was added dropwise a solution of 1 equivalent of chlorodiethoxyphosphane (**4**) in 5 ml of THF over a period of 5 min. The reaction mixture was stirred at -78 °C for 1 h then the mixture was allowed to come to room temperature overnight. After the addition of 30 ml of water the mixture was extracted several times with dichloromethane. The organic phases were dried over magnesium sulfate. After evaporation of the solvents in vacuo the residue was chromatographed on silica gel (diethyl ether/pentane (1:1), diethyl ether and methanol/ dichloromethane (1:10)). The intense yellow orange band was collected. Further purification for solid allenyl phosphonates was achieved by recrystallization from dichloromethane/pentane.

Tricarbonyl{η^6-[1-(diethoxyphosphoryl)-3-methylbuta-1,2-dien-1-yl]benzene}chromium(0) **(5a):** According to the GP 2.00 g (6.75 mmol) of **3a**, 1.01 ml (7.1 mmol) of **4** and 1.03 ml (7.4 mmol) of triethylamine

furnished 2.24 g (80 %) of **5a** as yellow crystals, m.p. 65-67 °C. - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.22 (t, J = 6.6 Hz, 6 H), 1.85 (d, $J_{P,H}$ = 6.0 Hz, 6 H), 4.02 (m, 4 H), 5.66 (t, J = 6.0 Hz, 1 H), 5.77 (t, J = 6.2 Hz, 2 H), 5.88 (d, J = 6.4 Hz, 2 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.2 (CH$_3$, $J_{P,C}$ = 6.4 Hz), 19.2 (CH$_3$, $J_{P,C}$ = 5.9 Hz), 62.7 (CH$_2$, $J_{P,C}$ = 6.1 Hz), 91.7 (C$_{quat.}$, $J_{P,C}$ = 192.6 Hz), 94.1 (CH), 94.3 (CH, $J_{P,C}$ = 4.7 Hz), 94.4 (CH), 102.2 (C$_{quat.}$, $J_{P,C}$ = 13.9 Hz), 104.5 (C$_{quat.}$, $J_{P,C}$ = 13.9 Hz), 208.3 (C$_{quat.}$, $J_{P,C}$ = 3.8 Hz), 233.6 (C$_{quat.}$, CO). - ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 13.57. - MS (EI), m/z (%): 360 (M$^+$ - 2 CO, 16), 332 (M$^+$ - 3 CO, 100), 52 (Cr$^+$, 6). - IR (KBr): $\tilde{\nu}$ = 1965 cm^{-1}, 1895, 1873, 1441, 1357, 1256, 1048, 1026, 970, 792, 748, 660, 630, 572, 533. - UV/Vis (DMSO): λ_{max} (ε) = 324 nm (37300). - $C_{18}H_{21}CrO_6P$ (416.3) calcd. C 51.93, H 5.08; found C 51.85, H 5.21.

Tricarbonyl{η^6-[1-(diethoxyphosphoryl)-penta-1,2-dien-1-yl]benzene}chromium(0) **(5b):** According to the GP 0.40 g (1.35 mmol) of **3b**, 0.20 ml (1.40 mmol) of **4** and 0.21 ml (1.50 mmol) of triethylamine furnished 0.38 g (68 %) of **5b** as a yellow orange oil. - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.07 (t, J = 7.2 Hz, 6 H), 1.26 (m, 6 H), 2.18 (m, 2 H), 4.03 (m, 4 H), 5.69-5.94 (m, 5 H), 6.15 (m, 1 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 13.2 (CH$_3$), 16.2 (CH$_3$, $J_{P,C}$ = 6.6 Hz), 21.1 (CH$_2$, $J_{P,C}$ = 5.3 Hz), 62.7 (CH$_2$, $J_{P,C}$ = 6.0 Hz), 62.8 (CH$_2$, $J_{P,C}$ = 6.0 Hz), 93.9 (CH, $J_{P,C}$ = 5.3 Hz), 94.2 (CH, $J_{P,C}$ = 4.0 Hz), 94.3 (CH, double intensity), 94.4 (C$_{quat.}$, $J_{P,C}$ = 192.4 Hz), 98.8 (CH, $J_{P,C}$ = 13.9 Hz), 103.7 (C$_{quat.}$, $J_{P,C}$ = 11.9 Hz), 209.6 (C$_{quat.}$, $J_{P,C}$ = 4.0 Hz), 233.8 (C$_{quat.}$, CO). - MS (EI), m/z (%): 388 (M$^+$ - CO, 1), 360 (M$^+$ - 2 CO, 25), 332 (M$^+$ - 3 CO, 100), 280 (M$^+$ - Cr(CO)$_3$, 2), 52 (Cr$^+$, 6). - IR (KBr): $\tilde{\nu}$ = 1963 cm^{-1}, 1883, 1457, 1368, 1252, 1048, 1024, 969, 814, 757, 658, 629, 576, 531. - UV/Vis (DMSO): λ_{max} (ε) = 324 nm (8200). - $C_{19}H_{23}CrO_6P$ (416.3) calcd. C 51.93, H 5.08; found C 52.21, H 5.09.

Tricarbonyl{η^6-1-[1-(diethoxyphosphoryl)-3-methylbuta-1,2-dien-1-yl]-2-methylbenzene}chromium(0) **(5c):** According to the GP 0.67 g (2.16 mmol) of **3c**, 0.34 ml (2.38 mmol) of **4** and 0.37 ml (2.66 mmol) of triethylamine furnished 0.73 g (79 %) of **5c** as a yellow orange oil. - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.21 (m, 6 H), 1.80 (d, $J_{P,H}$ = 6.0 Hz, 6 H), 2.21 (s, 3 H), 4.02 (m, 4 H), 5.43 (t, J = 6.2 Hz, 1 H), 5.49 (d, J = 6.3 Hz, 1 H), 5.84 (t, J = 6.3 Hz, 1 H), 5.93 (d, J = 6.3 Hz, 1 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.3 (CH$_3$, $J_{P,C}$ = 6.0 Hz), 18.5 (CH$_3$, $J_{P,C}$ = 6.0 Hz), 19.2 (CH$_3$), 19.3 (CH$_3$, $J_{P,C}$ = 6.0 Hz), 62.6 (CH$_2$, $J_{P,C}$ =

6.6 Hz), 89.4 (CH), 90.2 ($C_{quat.}$, $J_{P,C}$ = 191.7 Hz), 92.7 (CH), 97.5 ($C_{quat.}$, $J_{P,C}$ = 14.6 Hz), 97.8 (CH), 100.3 (CH), 106.7 ($C_{quat.}$, $J_{P,C}$ = 14.6 Hz), 113.0 ($C_{quat.}$, $J_{P,C}$ = 3.9 Hz), 209.6 ($C_{quat.}$, $J_{P,C}$ = 5.3 Hz), 233.8 ($C_{quat.}$, CO). - MS (EI), m/z (%): 430 (M^+, 1), 402 (M^+ - CO, 1), 374 (M^+ - 2 CO, 8), 346 (M^+ - 3 CO, 100), 294 (M^+ - $Cr(CO)_3$, 2), 52 (Cr^+, 10). - IR (KBr): $\tilde{\nu}$ = 1959 cm^{-1}, 1878, 1444, 1367, 1245, 1050, 1025, 968, 851, 797, 752, 666, 627, 568, 535. - UV/Vis (DMSO): λ_{max} (ε) = 324 nm (6100). - $C_{19}H_{23}CrO_6P$ (430.4) calcd. C 53.02, H 5.38; found C 51.98, H 5.84.

Tricarbonyl{η^6-1-[1-(diethoxyphosphoryl)-3-methylbuta-1,2-dien-1-yl]-3-methylbenzene}chromium(0) **(5d):** According to the GP 0.53 g (2.01 mmol) of **3d**, 0.31 ml (2.22 mmol) of **4** and 0.37 ml (2.66 mmol) of triethylamine furnished 0.60 g (69 %) of **5d** as yellow orange crystals, m.p. 75-77 °C. - ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 1.24 (m, J = 6.9 Hz, 6 H), 1.86 (d, $J_{P,H}$ = 6.0 Hz, 6 H), 2.17 (s, 3 H), 4.02 (m, 4 H), 5.55 (d, J = 6.3 Hz, 1 H), 5.72 (s, 1 H), 5.76 (d, J = 6.3 Hz, 1 H), 5.88 (pt, J = 6.5 Hz, 1 H). - ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 16.3 (CH_3, $J_{P,C}$ = 6.0 Hz), 19.2 (CH_3, $J_{P,C}$ = 6.0 Hz), 19.3 (CH_3, $J_{P,C}$ = 6.0 Hz), 20.6 (CH_3), 62.7 (CH_2, $J_{P,C}$ = 6.0 Hz), 91.4 (CH, $J_{P,C}$ = 4.6 Hz), 91.7 ($C_{quat.}$, $J_{P,C}$ = 192.4 Hz), 93.9 (CH), 94.0 (CH, $J_{P,C}$ = 8.0 Hz), 95.8 (CH), 102.3 ($C_{quat.}$, $J_{P,C}$ = 13.9 Hz), 105.9 ($C_{quat.}$, $J_{P,C}$ = 13.9 Hz), 110.7 ($C_{quat.}$), 208.6 ($C_{quat.}$, $J_{P,C}$ = 3.3 Hz), 234.3 ($C_{quat.}$, CO). - ^{31}P NMR ([D_6]DMSO, 121 MHz) : δ = 13.64. - MS (EI), m/z (%): 430 (M^+, 1), 402 (M^+ - CO, 1), 374 (M^+ - 2 CO, 8), 346 (M^+ - 3 CO, 100), 294 (M^+ - $Cr(CO)_3$, 2), 52 (Cr^+, 10). - IR (KBr): $\tilde{\nu}$ = 1963 cm^{-1}, 1882, 1444, 1238, 1054, 1028, 970, 667, 630, 576, 536. - UV/Vis (DMSO): λ_{max} (ε) = 324 nm (7100). - $C_{19}H_{23}CrO_6P$ (430.4) calcd. C 53.02, H 5.38; found C 54.77, H 5.73.

Tricarbonyl{η^6-1-[1-(diethoxyphosphoryl)-3-methylbuta-1,2-dien-1-yl]-4-methylbenzene}chromium(0) **(5e):** According to the GP 1.00 g (3.80 mmol) of **3**, 0.59 ml (4.19 mmol) of **4** and 0.64 ml (4.61 mmol) of triethylamine furnished 1.16 g (71 %) of **5e** as yellow orange crystals, m.p. 78-80 °C. - ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 1.24 (t, J = 7.1 Hz, 6 H), 1.84 (d, $J_{P,H}$ = 6.0 Hz, 6 H), 2.11 (s, 3 H), 4.01 (m, 4 H), 5.65 (m, J = 6.7 Hz, 2 H), 5.96 (m, J = 6.7 Hz, 2 H). - ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 16.2 (CH_3, $J_{P,C}$ = 6.3 Hz), 19.4 (CH_3, $J_{P,C}$ = 6.3 Hz), 19.9 (CH_3), 62.7 (CH_2, $J_{P,C}$ = 6.3 Hz), 91.3 ($C_{quat.}$, $J_{P,C}$ = 192.4 Hz), 94.3 (CH), 95.6 (CH, $J_{P,C}$ = 5.0 Hz), 101.5 ($C_{quat.}$, $J_{P,C}$ = 14.6 Hz), 101.9 ($C_{quat.}$, $J_{P,C}$ = 14.3 Hz), 110.6 ($C_{quat.}$), 208.0

($C_{quat.}$, $J_{P,C}$ = 3.9 Hz), 234.1 ($C_{quat.}$, CO). - ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 13.62. - MS (EI), m/z (%): 430 (M^+, 1), 402 (M^+ - CO, 1), 374 (M^+ - 2 CO, 8), 346 (M^+ - 3 CO, 100), 294 (M^+ - $Cr(CO)_3$, 2), 52 (Cr^+, 10). - IR (KBr): $\tilde{\nu}$ = 1961 cm^{-1}, 1881, 1248, 1033, 970, 667, 629, 534. - UV/Vis (DMSO): λ_{max} (ε) = 325 nm (7300). - $C_{19}H_{23}CrO_6P$ (430.4) calcd. C 53.02, H 5.38; found C 52.70, H 5.54.

General Procedure (GP) for the synthesis of the heterocycles 7

To a degassed suspension of 0.6 mmol of sodium hydride (97%) in 10 ml of THF a solution of 0.5 mmol of the difunctional carbonyl compound in 2 ml of THF is added under nitrogen. After stirring for 2 min at r.t. 0.5 mmol of **5** in 5 ml of THF is added to the suspension. The reaction mixture is heated to reflux temperature for 1-3 h. After cooling to r.t. the mixture is diluted with 5 ml of water. The aqueous layer is extracted twice with 10 ml of ether. The combined organic phases are dried over magnesium sulfate and the solvents are removed in vacuo. The residue is chromatographed on silica gel (diethyl ether/pentane 1:3) to give the pure product **7**.

Tricarbonyl[η^6-(2-isopropylidene-2H-chromen-3-yl)benzene]chromium(0) **(7a):** According to the GP 200 mg (0.48 mmol) of **5a**, 51 µl (0.48 mmol) of salicylic aldehyde and 14 mg (0.57 mmol) of sodium hydride furnished 160 mg (87 %) of **7a** as orange crystals, m.p. = 140-141 °C (diethyl ether/pentane). - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.11 (s, 3 H), 1.34 (s, 3 H), 5.70 (t, *J* = 6.1 Hz, 1 H), 5.85 (pt, *J* = 6.4 Hz, 2 H), 6.00 (d, *J* = 6.4 Hz, 2 H), 6.89 (s, 1 H), 6.97 (m, 2 H), 7.24 (m, 2 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 18.4 (CH_3), 21.1 (CH_3), 94.4 (CH), 94.5 (CH), 95.5 (CH), 112.3 ($C_{quat.}$), 114.7 (CH), 115.4 ($C_{quat.}$), 122.2 ($C_{quat.}$), 122.5 (CH), 127.2 (CH), 128.8 ($C_{quat.}$), 129.2 (CH), 130.4 (CH), 139.9 ($C_{quat.}$), 154.1 ($C_{quat.}$), 234.0 ($C_{quat.}$, CO). - MS (EI), m/z (%): 384 (M^+, 38), 328 (M^+ - 2 CO, 38), 300 (M^+ - 3 CO, 100), 248 (M^+ - $Cr(CO)_3$, 6), 52 (Cr^+, 21). - IR (KBr): $\tilde{\nu}$ = 1962 cm^{-1}, 1889, 1866. - UV/Vis (DMSO): λ_{max} (ε) = 332 nm (9400). - $C_{21}H_{16}CrO_4$ (384.4) calcd. C 65.62, H 4.19; found C 66.00, H 4.27.

Tricarbonyl[η^6-(3-isopropylidene-3H-benzo[f]chromen-2-yl)benzene]chromium(0) **(7b):** According to the GP 200 mg (0.48 mmol) of **5a**, 82 mg (0.48 mmol) of 1-formyl 2-naphthol and 14 mg (0.57 mmol) of sodium hydride furnished 80 mg (38 %) of **7b** as orange crystals, m.p. = 197 - 200 °C (diethyl ether/pentane). - ^{1}H ([D$_6$]DMSO, 300 MHz): δ = 1.39 (s, 3 H), 1.90 (s, 3 H), 5.71 (t, *J* = 6.2 Hz, 1 H), 5.90 (pt, *J* = 6.4 Hz, 2 H), 6.24 (d, *J* = 6.5 Hz, 2 H), 7.29 (d, *J* = 8.8 Hz, 1 H), 7.43 (dd, *J* = 7.2 Hz, 1 H), 7.57-7.63 (m, 2 H), 7.85-7.89 (m, 2 H), 8.25 (d, *J* = 8.4 Hz, 1 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 18.0 (CH_3), 21.0 (CH_3), 94.4

(CH), 94.8 (CH), 95.4 (CH), 111.9 ($C_{quat.}$), 115.3 ($C_{quat.}$), 115.4 ($C_{quat.}$), 116.3 (CH), 122.3 (CH), 124.7 (CH), 125.9 (CH), 127.2 ($C_{quat.}$), 127.7 (CH), 128.8 (CH), 129.4 ($C_{quat.}$), 129.4 ($C_{quat.}$), 131.1 (CH), 139.6 ($C_{quat.}$), 152.8 ($C_{quat.}$), 234.2 ($C_{quat.}$, CO). - MS (EI), m/z (%): 434 (M^+, 25), 378 (M^+ - 2 CO, 17), 350 (M^+ - 3 CO, 100), 298 (M^+ - $Cr(CO)_3$, 25), 52 (Cr^+, 3). - **IR** (KBr): $\tilde{\nu}$ = 1962 cm^{-1}, 1873. - UV/Vis (DMSO): λ_{max} (ε) = 299 nm (12500), 396 (6300). - $C_{25}H_{18}CrO_4$ (434.4) calcd. C 69.12 H 4.17; found C 69.17, H 4.23.

Tricarbonyl[η⁶-(3-isopropylidene-3H-pyrrolizin-2-yl)benzene]chromium(0) **(7c):** According to the GP 300 mg (0.72 mmol) of **5a**, 69 mg (0.72 mmol) of pyrrole-2-carbaldehyde and 21 mg (0.86 mmol) of sodium hydride furnished 140 mg (54 %) of **7c** as yellow crystals, m.p. = 155 - 158 °C (diethyl ether/pentane). - ^1H NMR ([D_6]DMSO, 300 MHz): δ = 1.85 (s, 3 H), 2.06 (s, 3 H), 5.69 (t, *J* = 6.5 Hz, 2 H), 5.83 (t, *J* = 6.4 Hz, 1 H), 6.00 (d, *J* = 6.5 Hz, 2 H), 6.08 (d, *J* = 3.4 Hz, 1 H), 6.25 (pt, *J* = 2.9 Hz, 1 H), 6.69 (s, 1 H), 7.22 (d, *J* = 2.6 Hz, 1 H). - ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 23.5 (CH_3), 23.6 (CH_3), 92.3 (CH), 96.5 (CH), 99.1 (CH), 100.6 (CH), 110.2 ($C_{quat.}$), 113.0 (CH), 119.3 (CH), 123.7 ($C_{quat.}$), 125.4 (CH), 131.5 ($C_{quat.}$), 133.8 ($C_{quat.}$), 136.3 ($C_{quat.}$), 233.9 ($C_{quat.}$, CO). - MS (EI), m/z (%): 357 (M^+, 29), 301 (M^+ - 2 CO, 14), 273 (M^+ - 3 CO, 100), 221 (M^+ - $Cr(CO)_3$, 27), 52 (Cr^+, 7). - IR (KBr): $\tilde{\nu}$ = 1963 cm^{-1}, 1890. - UV/Vis (DMSO): λ_{max} (ε) = 314 nm (19000). - $C_{19}H_{15}CrNO_3$ (357.3) calcd. C 63.86 H 4.23, N 3.92; found C 63.52, H 4.29, N 3.95.

Tricarbonyl[η⁶-(2-isopropylidene-4-methyl-2,5-dihydro-furan-3-yl)benzene]chromium(0) **(7d):** Accor-ding to the GP 200 mg (0.48 mmol) of **5a**, 33 µl (0.48 mmol) of 2-hydroxy acetone and 14 mg (0.57 mmol) of sodium hydride furnished 90 mg (56 %) of **7d** as (56 %), yellow crystals, m.p. = 145 - 148 °C (diethyl ether/pentane). - ^1H NMR ([D_6]DMSO, 300 MHz): δ = 1.32 (s, 3 H), 1.64 (s, 3 H), 2.01 (s, 3 H), 4.77 (s, 2 H), 5.69 (t, *J* = 6.4 Hz, 2 H), 5.78 (d, *J* = 6.4 Hz, 2 H), 5.83 (t, *J* = 6.2 Hz, 1 H). - ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 11.9 (CH_3), 19.2 (CH_3), 19.4 (CH_3), 77.3 (CH_2), 92.7 (CH), 96.2 (CH), 97.7 ($C_{quat.}$), 98.6 (CH), 106.0 ($C_{quat.}$), 125.1 ($C_{quat..}$), 142.3 ($C_{quat.}$), 154.2 ($C_{quat.}$), 233.9 ($C_{quat.}$, CO). - MS (EI), m/z (%): 336 (M^+, 26), 280 (M^+ - 2 CO, 12), 252 (M^+ - 3 CO, 100), 200 (M^+ - $Cr(CO)_3$, 8), 52 (Cr^+, 12). - IR (KBr): $\tilde{\nu}$ = 1969 cm^{-1}, 1888, 1875. - UV/Vis (DMSO): λ_{max} (ε) = 317 nm (11100). - $C_{17}H_{16}CrO_4$ (336.3) calcd. C 60.71, H 4.79, found C 60.21, H 4.83.

Tricarbonyl[η^6-(2-isopropylidene-4-phenyl-2,5-dihydro-furan-3-yl)benzene]chromium(0) **(7e):** Accor-ding to the GP 200 mg (0.48 mmol) of **5a**, 65 mg (0.48 mmol) of α-hydroxy acetophenone and 14 mg (0.57 mmol) of sodium hydride furnished 100 mg (52 %) of **7e** as yellow crystals, m.p. = 136 - 139 °C (diethyl ether/pentane). - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.27 (s, 3 H), 1.69 (s, 3 H), 5.13 (s, 2 H), 5.53 (m, 2 H), 5.82 (m, 3 H), 7.37 (m, 5 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 19.3 (CH_3), 19.6 (CH_3), 77.3 (CH_2), 91.5 (CH), 95.8 (CH), 99.6 (CH), 100.4 ($C_{quat.}$), 105.7 ($C_{quat.}$), 126.6 ($C_{quat.}$), 128.1 (CH), 128.8 (CH), 129.5 (CH), 131.6 ($C_{quat.}$), 144.2 ($C_{quat.}$), 155.7 ($C_{quat.}$), 232.9 ($C_{quat.}$, CO). - MS (EI), m/z (%): 398 (M^+, 12), 314 (M^+ - 3 CO, 100), 262 (M^+ - $Cr(CO)_3$, 9), 52 (Cr^+, 12). - IR (KBr): $\tilde{\nu}$ = 1969 cm^{-1}, 1908, 1891,1876, 1857. - UV/Vis (DMSO): λ_{max} (ε) = 316 nm (13700). - $C_{22}H_{18}CrO_4$ (398.4) calcd. C 66.33, H 4.55; found C 66.62 H 4.70.

Tricarbonyl[η^6-(2-isopropylidene-4,5-diphenyl-2,5-dihydro-furan-3-yl)benzene]chromium(0) **(7f):** According to the GP 200 mg (0.48 mmol) of **5a**, 102 mg (0.48 mmol) of benzoin and 14 mg (0.57 mmol) of sodium hydride furnished 110 mg (48 %) of **7f** as yellow crystals, m.p. = 130 - 132 °C (diethyl ether/pentane). - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.35 (s, 3 H), 1.72 (s, 3 H), 5.52 (m, *J* = 6.6 Hz, 2 *m*-H), 5.75 (m, *J* = 7.5 Hz, 1 *o*-H, 1 *p*-H), 6.05 (d, *J* = 6.6 Hz, 1 *o*-H), 6.31 (s, 1 H), 7.13-7.26 (m, 10 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 19.5 (CH_3), 19.8 (CH_3), 88.8 (CH), 91.0 (CH), 91.2 (CH), 96.0 (CH), 98.6 (CH), 100.6 (CH), 101.1 ($C_{quat.}$), 105.4 ($C_{quat.}$), 127.3 (CH), 127.4 (CH), 127.8 (CH), 128.6 (CH), 129.9 (CH, double intensity), 131.8 ($C_{quat.}$, double intensity), 139.4 ($C_{quat.}$), 146.9 ($C_{quat.}$), 154.4 ($C_{quat.}$), 232.8 ($C_{quat.}$, CO). - MS (EI), m/z (%): 474 (M^+, 8), 390 (M^+ - 3 CO, 100), 338 (M^+ - $Cr(CO)_3$, 6), 52 (Cr^+, 3). - IR (KBr): $\tilde{\nu}$ = 1967 cm^{-1}, 1896. - UV/Vis (DMSO): λ_{max} (ε) = 317 nm (16100). - $C_{28}H_{22}CrO_4$ (474.5) calcd. C 70.88 H 4.67; found C 71.16, H 4.77.

E/Z-Tricarbonyl{η^6-[2-(1-propylidene)-2H-chromen-3-yl]benzene}chromium(0) **(7g):** According to the GP 400 mg (1.10 mmol) of **5b**, 110 µl (1.10 mmol) of salicylic aldehyde and 31 mg (1.3 mmol) of sodium hydride furnished 230 mg (54 %) of **7g** as yellow crystals, m.p. = 102-104 °C (diethyl ether/pentane). - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 0.80 (t, *J* = 7.5 Hz, 1 H), 0.96 (t, *J* = 7.2 Hz, 2 H), 1.58 (dt, *J* = 7.5 Hz, 0.66 H), 2.18 (dt, *J* = 7.2, 7.5 Hz, 1.34 H), 4.75 (t, *J* = 7.2 Hz, 0.66 H), 5.09 (t, *J* = 7.8 Hz, 0.33 H), 5.74 (m, 2 H), 5.82 (m, 1 H), 5.96 (d, *J* = 6.3 Hz, 1.34 H), 6.04 (d, *J* = 6.3 Hz, 0.66 H), 6.64 (s, 0.66 H), 6.83 (s, 0.33 H),

6.89-6.99 (m, J = 7.1 Hz, 2 H), 7.20-7.40 (m, J = 7.2 Hz, 2 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 14.0 (CH_3), 18.0 (CH_2), 93.4 (CH), 96.5 (CH), 97.2 (CH), 109.3 (CH), 109.8 ($C_{quat.}$), 114.5 (CH), 120.6 ($C_{quat.}$), 122.9 (CH), 125.9 (CH), 127.4 (CH), 129.3 ($C_{quat.}$), 130.6 (CH), 147.4 ($C_{quat.}$), 152.7 ($C_{quat.}$), 233.7 ($C_{quat.}$, CO); additional signals for the *E*-isomer: 14.6 (CH_3), 20.8 (CH_2), 93.7 (CH), 95.3 (CH), 95.9 (CH), 111.9 ($C_{quat.}$), 113.4 (CH), 114.5 (CH), 121.2 ($C_{quat.}$), 122.6 (CH), 127.0 ($C_{quat.}$), 127.4 (CH), 130.2 (CH), 130.8 (CH), 145.2 ($C_{quat.}$), 153.8 ($C_{quat.}$), 233.8 ($C_{quat.}$, CO). - MS (EI), m/z (%): 384 (M^+, 28), 328 (M^+ - 2 CO, 11), 300 (M^+ - 3 CO, 100), 248 (M^+ - $Cr(CO)_3$, 15), 52 (Cr^+, 32). - IR (KBr): $\tilde{\nu}$ = 1969 cm^{-1}, 1884. - UV/Vis (DMSO): λ_{max} (ε) = 333 nm (9300). - $C_{21}H_{16}CrO_4$ (384.4) calcd. C 65.62, H 4.19; found C 65.78, H 4.02.

Tricarbonyl[η^6-1-(2-isopropylidene-2H-chromen-3-yl)-3-methylbenzene]chromium(0) **(7i):** According to the GP 200 mg (0.46 mmol) of **5d**, 48 µl (0.46 mmol) of salicylic aldehyde and 14 mg (0.57 mmol) of sodium hydride furnished 170 mg (92 %) of **7i** as yellow crystals, m.p. = 130-133 °C (diethyl ether/pentane). - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.34 (s, 3 H), 1.87 (s, 3 H), 2.25 (s, 3 H), 5.56 (d, J = 6.0 Hz, 1 H), 5.79 (d, J = 6.0 Hz, 1 H), 5.92 (s, 1 H), 5.94 (m, 1 H), 6.95-7.00 (m, 3 H), 7.24-7.29 (m, 2 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 18.2 (CH_3), 20.2 (CH_3), 21.1 (CH_3), 92.2 (CH), 93.9 (CH), 95.3 (CH), 110.8 ($C_{quat.}$), 114.5 ($C_{quat.}$), 115.4 ($C_{quat.}$), 122.1 ($C_{quat.}$), 122.3 (CH), 127.1 (CH), 128.5 ($C_{quat.}$), 129.4 (CH), 130.2 (CH), 139.5 ($C_{quat.}$), 154.1 ($C_{quat.}$), 234.3 ($C_{quat.}$, CO). - MS (EI), m/z (%): 398 (M^+, 28), 342 (M^+ - 2 CO, 25), 314 (M^+ - 3 CO, 100), 262 (M^+ - $Cr(CO)_3$, 12), 52 (Cr^+, 12). - IR (KBr): $\tilde{\nu}$ = 1960 cm^{-1}, 1877. - UV/Vis (DMSO): λ_{max} (ε) = 332 nm (9500). - $C_{22}H_{18}CrO_4$ (398.4) calcd. C 66.33, H 4.55; found C 66.58, H 4.48.

Tricarbonyl[η^6-1-(2-isopropylidene-2H-chromen-3-yl)-4-methylbenzene]chromium(0) **(7j):** According to the GP 200 mg (0.46 mmol) of **5e**, 48 µl (0.46 mmol) of α-salicylic aldehyde and 14 mg (0.57 mmol) of sodium hydride furnished 150 mg (82 %) of **7j** as yellow crystals, m.p. = 130-133 °C (diethyl ether/pentane). - ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.28 (s, 3 H), 1.79 (s, 3 H), 2.09 (s, 3 H), 5.66 (d, J = 6.6 Hz, 2 H), 6.05 (d, J = 6.6 Hz, 2 H), 6.21 (s, 1 H), 6.91 (m, J = 6.3 Hz, 2 H), 7.16 (m, J = 6.9 Hz, 2 H). - ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 18.5 (CH_3), 20.1 (CH_3), 21.3 (CH_3), 94.2 (CH), 97.0 (CH), 109.4 ($C_{quat.}$), 111.2

($C_{quat.}$), 114.7 (CH), 115.3 ($C_{quat.}$), 122.2 ($C_{quat.}$), 122.5 (CH), 127.1 (CH), 128.6 (CH), 128.9 ($C_{quat.}$), 130.3 (CH), 140.1 ($C_{quat.}$), 154.1 ($C_{quat.}$), 234.2 ($C_{quat.}$, CO). - MS (EI), m/z (%): 398 (M^+, 57), 342 (M^+ - 2 CO, 36), 314 (M^+ - 3 CO, 100), 262 (M^+ - $Cr(CO)_3$, 6), 52 (Cr^+, 2). - IR (KBr): $\tilde{\nu}$ = 1967 cm^{-1}, 1956, 1877. - UV/Vis (DMSO): λ_{max} (ε) = 336 nm (9500). - $C_{22}H_{18}CrO_4$ (398.4) calcd. C 66.33, H 4.55; found C 66.31, H 4.64.

Tricarbonyl[η^6-1-(3-isopropylidene-3H-pyrrolizin-2-yl)-3-methylbenzene]chromium(0) **(7k):** According to the GP 180 mg (0.41 mmol) of **5d**, 39 mg (0.41 mmol) of pyrrole-2-carbaldehyde and 12 mg (0.50 mmol) of sodium hydride furnished 100 mg (64 %) of **7k** as yellow crystals, m.p. = 152 - 154 °C (diethyl ether/pentane). - ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 1.85 (s, 3 H), 2.06 (s, 3 H), 2.19 (s, 3 H), 5.70 (m, 1 H), 5.81 (m, 2 H), 5.94 (s, 1 H), 6.07 (d, *J* = 3.3 Hz, 1 H), 6.24 (pt, *J* = 3.4 Hz, 1 H), 6.74 (s, 1 H), 7.22 (m,1 H). - ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 20.2 (CH_3), 23.6 (CH_3), 23.9 (CH_3), 93.8 (CH), 95.9 (CH), 96.0 (CH), 99.0 (CH), 100.7 (CH), 109.0 ($C_{quat.}$), 111.7 ($C_{quat.}$), 113.1 (CH), 119.4 (CH), 123.8 ($C_{quat.}$), 125.4 (CH), 131.4 ($C_{quat.}$), 133.8 ($C_{quat.}$), 136.4 ($C_{quat.}$), 234.4 ($C_{quat.}$, CO). - MS (EI), m/z (%): 371 (M^+, 53), 315 (M^+ - 2 CO, 24), 287 (M^+ - 3 CO, 100), 235 (M^+ - $Cr(CO)_3$, 7). - IR (KBr): $\tilde{\nu}$ = 1962 cm^{-1}, 1881. - UV/Vis (DMSO): λ_{max} (ε) = 315 nm (18200). - $C_{20}H_{17}CrNO_3$ (371.4) calcd. C 64.68 H 4.61, N 3.77; found C 64.61, H 4.80, N 3.77.

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