Journal of Organometallic Chemistry 694 (2009) 3058–3067

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Multiple reactivities of dithranol towards 1-alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (M = Cr, W) – Efficient chemical synthesis of aromatic polyketides

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ARTICLE INFO

Article history:
Received 24 March 2009
Received in revised form 19 May 2009
Accepted 21 May 2009
Available online 27 May 2009

Keywords:
Fischer carbene
Dithranol
Multiple reactivity
Polyketides
Polycarbene

ABSTRACT

Reactions of *anti*-psoriasis drug dithranol with 1-alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (M = Cr, W) were investigated under controlled conditions in which triethylamine-promoted *C*-addition, *O*-addition, electrophilic aromatic substitution, and cyclization consecutively occurred at up to five positions of dithranol. A remarkable solvent effect led to selective formation of polyphenolic organic and organometallic mono- and triscarbene complexes which were efficiently demetalated to the potentially bioactive aromatic polyketides with pyridine-*N*-oxide. All the organic and organometallic products were characterized by methods including X-ray single crystal structural determinations. These results have revealed the novel multiple reactivities of dithranol which might be associated to its clinical side effect, providing a new synthetic methodology to functionalize dithranol for medical purposes, and chemically synthesize aromatic polyketides.

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1. Introduction

Dithranol (1,8-dihydroxy-9(10)-anthracenone) is the most widely used therapeutic drug for treatment of psoriasis, a common chronic inflammatory and scaling skin disease. Apart from the therapeutic benefits, dithranol causes undesirable side effect such as unpleasant inflammation of the skin surrounding the treated psoriatic plaques [1] because it can undergo complex transformations in the human body [2]. Much work has been directed to reduce this clinical side effect by acylation of dithranol at its 10-position [3], and acylation or alkylation of its 1,8-dihydroxys and/or the 9-hydroxy of its tautomer, i.e., 1,8,9-trihydroxyanthracene [3,4]. However, no major advance has been achieved in this aspect, and little effort has been made to explore the unknown reactivities of dithranol which might be associated to this side effect [5]. Thus, chemical insights into the new reactivities of dithranol has been strongly desired to direct functionalization of dithranol for medical purposes. Aromatic polyketides comprise an important class of polyphenols, many of which have been applied in drug development [6]. Based on the structural features, dithranol can be considered as a synthetic building block for aromatic polyketides which are usually biosynthesized by complex procedures (Scheme 1) [7]. To the best of our knowledge, dithranol-based synthesis of aromatic polyketides has never been investigated.

Compounds with a functionalized backbone similar to that of dithranol such as 1,8-dihydroxyanthracene-9,10-dione [8], 9-anthrones [9], and 9-substituted or 9,10-disubstituted anthracenes [10] usually act as dienes to undergo Diels–Alder cycloaddition across their 9,10-positions. Although dithranol presents a molecular structure analogous to those of polyphenols, 9-anthrones, and substituted anthracenes, its multiple functionalization in a single reaction has never been realized. Fischer carbene complexes have been demonstrated versatile reactivities in organic synthesis [11–15], and base-catalyzed Michael-type addition of phenols to 1-alkynyl Fischer carbene complexes has been documented [16]. C–H insertion is also common in the transformations by means of Fischer carbene complexes [16,17]. However, addition of electron-rich polyphenols such as sesamol and phloroglucinol to terminal alkynes can only be realized by Pd(0)-catalyzed C–H insertion [18]. Intrigued by the potential versatile reactivities and structural features of dithranol (**2**), we investigated the multiple reactivities of **2** towards 1-alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (M = Cr, W) (**1**) under controlled conditions, and efficiently synthesized novel dithranol-based aromatic polyketides for the first time.

2. Results and discussion

2.1. Reactions of 1 and 2

In our initial studies, the reactions of **2** and **1** were carried out in different molar ratios in toluene, dichloromethane, diethyl ether or THF at ambient temperature (Eq. (1) and Table 1). No reaction

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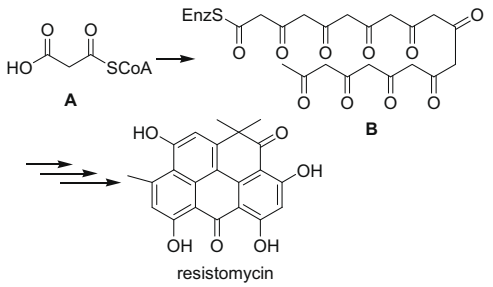
doi:10.1016/j.jorganchem.2009.05.029



Scheme 1. A biosynthesis example of aromatric polyketide (resistomycin) [7].

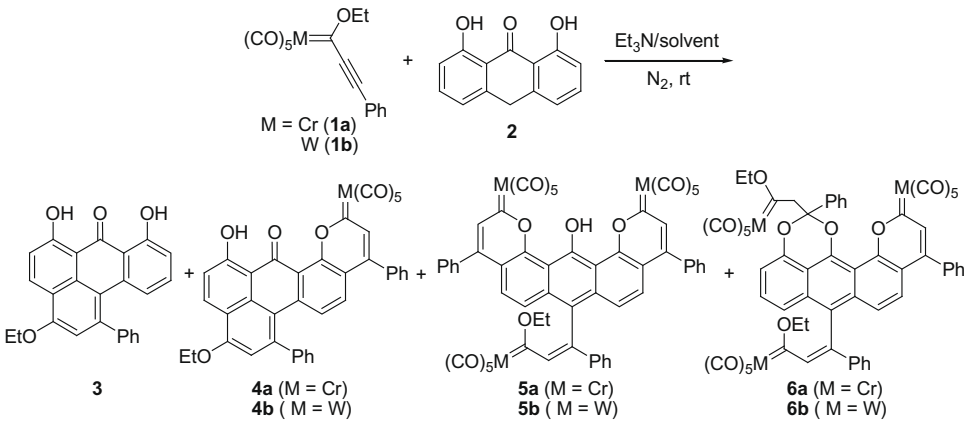
occurred in the absence of a base such as triethylamine except that a very unstable brown species was formed and quickly decomposed from the reactions in THF. Using triethylamine as solvent, the reactions were complicated. However, when suitable amount of triethylamine was used, the reactions of **1** and **2** smoothly proceeded in the organic solvents. The 1:1 molar ratio reaction of **1a** (M = Cr) and **2** formed compound **3** as the major product (10–31%) via a green intermediate which was not successfully isolated, while **2** reacted faster with **1b** (M = W) than with **1a** in all the solvents under the same conditions, affording **3** as the only product (28–46%) (Table 1, entries 1–4). The 2:1 molar ratio reaction of **1a** and **2** formed **4a** as the major product (12–35%), and the same reaction of **1b** and **2** produced both **3** (11–15%) and **4b** (5–25%) as the major products. In the 3:1 molar ratio reactions of **1** and **2**, compounds **3**–**6** were formed in much higher total yields than in those 1:1 and 2:1 molar ratio reactions, and a remarkable solvent effect was observed to direct formation of the products (entries 5–8). In nonpolar toluene, **4** were generated as the major products (49% for **4a**, 44% for **4b**) (entry 5). In the polar solvents CH_2Cl_2 and Et_2O, the same reactions underwent faster, forming one mono- and two triscarbene complexes, i.e., **4–6**, in various yields (10–30%, entries 6 and 7). The 3:1 molar ratio reactions proceeded much faster in THF than in other solvents, producing **4** (21–25%) and **6** (38–51%) as the major products (entry 8). **3** was not isolated from all the 3:1 molar ratio reactions except in that of **1b** and **2** in toluene (5%, entry 5). The 5:1 molar ratio reactions of **1** and **2** underwent in a fashion similar to those 3:1 molar ratio reactions, and the reactions in toluene afforded **4** as the major products (27–32%), and the same reactions in CH_2Cl_2 and THF selectively formed **6** as the major products (26–71%) (entries 9–11).

solution may be the same as that of 9-anthrone. Thus, **3** and/or **4** were preferably formed from the reactions of **1** and **2** in nonpolar solvent toluene, while in polar solvents CH_2Cl_2, Et_2O, and THF, the 9-OH and/or 9-alkoxy-containing triscarbene complexes **5** and/or **6** were favorably generated when >1.0 equiv. of **1** were used. It is obvious that the multiple reactivities of **2** towards **1** are basically solvent- and molar ratio of **1** to **2**-dependent. Hydrogen bonding between the hydroxy and keto groups of the newly formed products and the electron-donating atoms of the solvent molecules of CH_2Cl_2, Et_2O and THF may be another factor to favor the triol tautomer of **2** in the polar solvents, rendering **5** and **6** formed as the major products. The solvent effect is so remarkable that up to five different positions of **2** and its triol tautomer were involved in a single reaction of **2** and **1**, forming multiple-functionalized organic and organometallic dithranol derivatives **3**–**6**.

2.2. Reaction mechanism

A reaction mechanism is proposed in Scheme 2. Dithranol coexists with its triol tautomer (**2′**) in solution. The 10-position C–H addition of **2** to the C≡C bond of **1** initiates the reaction sequence, forming monocarbene species **C** which undergoes intramolecular nucleophilic aromatic C–H addition to the electronic M=C carbene carbon (or described as electrophilic aromatic substitution) to produce **D** and is followed by reductive elimination/protonation and tautomerization to form the organic product **3**. The initially-generated green intermediate species, presumably **C**, was gradually decomposed to products **3**–**6**. It was observed that only after most of the green intermediate species was consumed, the desired products could be isolated in decent yields. For example, if the reaction mixture was worked up at the time (4–6 h) when **1a** or **1b** was just consumed in the 1:1 molar ratio reaction with **2** in CH_2Cl_2, product **3** could only be isolated in <5% yields, whereas **3** was collected in 31–38% yields after **C** was completely consumed (Table 1, entry 2).

These results have suggested that species **C** is the possible intermediate to **3** and compound **3** was not generated on silica gel during isolation by column chromatography. In the presence of excessive amount of **1**, species **C** undergoes *C*-addition to another molecule of **1**, forming biscarbene species **F** which is then transformed to **4** via species **G** through an intramolecular aromatic C–H addition and cyclization. Both **3** and **4** can not further react with **1** under the reaction conditions, revealing that cyclization



(1)

A solvent-dependent equilibrium can be established between 9-anthrone (the keto tautomer) and its 9-hydroxy tautomer in solution, and the keto form is strongly favored in nonpolar solvents, whereas hydrogen bond acceptor solvents cause the hydroxy form to be slightly preferred [8]. Tautomerism of dithranol in

through the 4(5),10-positions of dithranol deactivates the newly formed polyphenolic systems. **F** is tautomerized to 9-hydroxy biscarbene **H** which further reacts with **1** to form triscarbene species **I** which is eventually cyclized to the triscarbene product **5**. **H** undergoes intermolecular *O*-addition of its 8-hydroxy to **1**

Table 1
Reactions of **1** and **2**.

Entry	**1**:**2**[a]	Solvent	Yield (%)[b] (M = Cr)					Yield (%)[b] (M = W)				
			t (h)	**3**	**4a**	**5a**	**6a**	t (h)	**3**	**4b**	**5b**	**6b**
1	1:1	Toluene	11	25	15			3.5	46			
2	1:1	CH_2Cl_2	24	31				14	38			
3	1:1	Et_2O	18	10	9			10	38			
4	1:1	THF	4	14				4	28			
5	3:1	Toluene	39		49	7	7	11	5	44	4	5
6	3:1	CH_2Cl_2	20		17	15	21	8		30	10	16
7	3:1	Et_2O	17		21	19	26	4		15	22	26
8	3:1	THF	6		21	2	51	4		25	2	38
9	5:1	Toluene	37		32	14	10	9		27	14	8
10	5:1	CH_2Cl_2	19		9	25	33	7.5		12	24	26
11	5:1	THF	3.5		4	8	71	2		4	5	65

Conditions: **2**, 0.3 mmol; **1**, 1.0–5.0 equiv.; Et_3N, 0.45 mmol; solvent, 5 mL; N_2 atmosphere, 0.1 MPa, 26 °C.
[a] Molar ratios of **1** to **2**.
[b] Isolated yields.

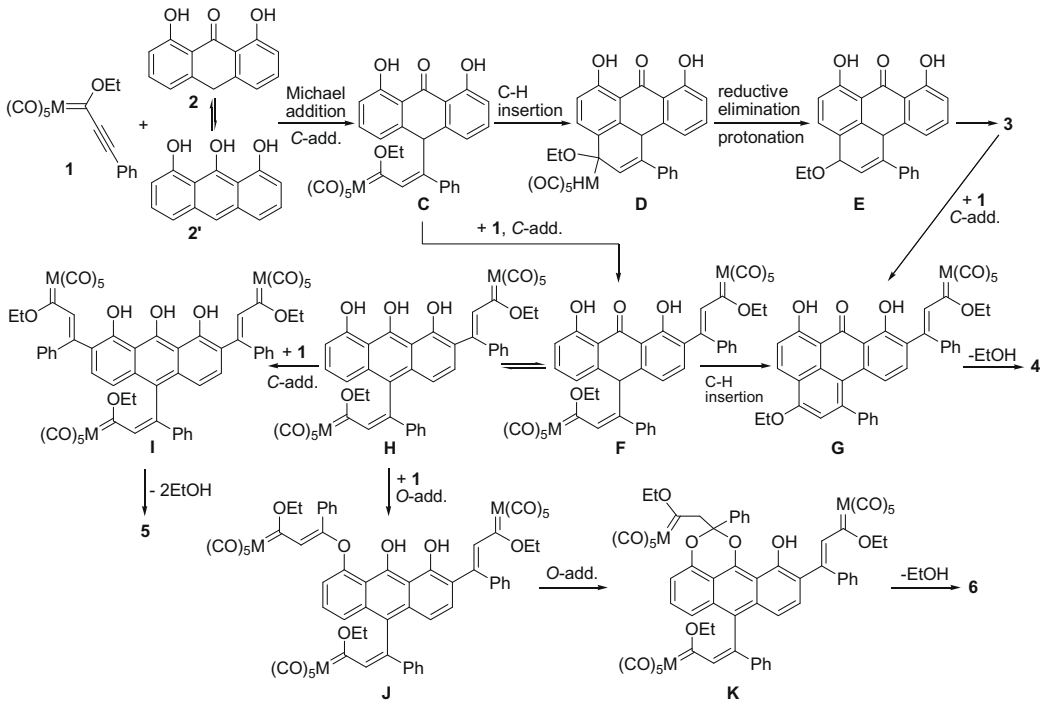
followed by an intramolecular *O*-addition of its 9-hydroxy to the 8-*O*-alkenyl to generate triscarbene intermediates **J** and **K**, respectively, affording the triscarbene product **6**.

2.3. Oxidative demetalation of complexes *4*–*6*

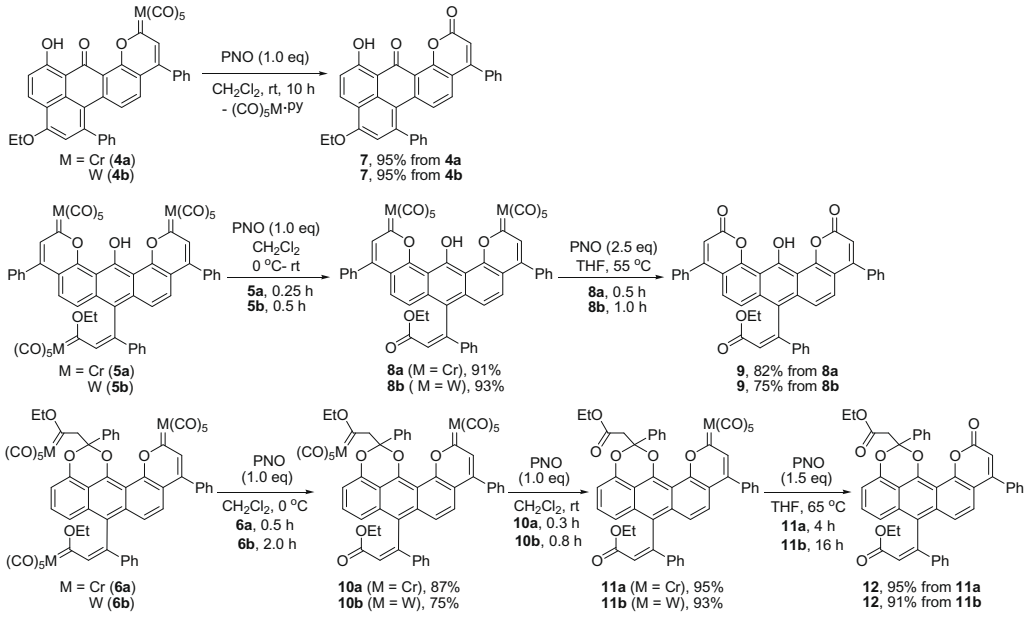
With our previously developed methodologies for demetalation of Fischer carbene complexes [19,20], complexes **4**–**6** were efficiently converted to their corresponding esters, i.e., **7**, **9**, and **12**, with pyridine-N-oxide (PNO) (Scheme 3). Complexes **4** were demetalated to **7** in 95% yields with 1.0 equiv. of PNO. Using 1.0 equiv. of PNO at controlled temperatures (0 °C – r.t.), the $(CO)_5M{=}C$ groups in the 10-alkenyl carbene moieties of **5** and **6** were first demetalated, affording **8** and **10**, respectively. Increasing temperature and using excess of PNO (2.5 equiv.), biscarbene complexes **8** were completely demetalated to triester **9**. With 1.0 equiv. of PNO the $(CO)_5M{=}C$ groups in the 8,9-*O*,*O*-alkylcarbene moieties of **10** were demetalated, producing monocarbene complexes **11** which were further demetalated to triester **12** in 91–95% yields with 1.5 equiv. of PNO at 65 °C. In all the demetalation reactions, the $(CO)_5M$ moieties were transformed to the easily separable complexes pyridine·$M(CO)_5$. The characteristic ^{13}C NMR signals of the M=C carbene carbons in **8**, **10** and **11** were assigned by comparison with the corresponding data of complexes **4**–**6**. The ^{13}C resonances of the Cr=C and $Cr(CO)_5$ moieties appeared at the fields lower than those of their tungsten analogues by about 27 and 20 ppm, respectively. For example, the ^{13}C NMR signals of the three Cr=C bonds in **6a** appeared at 354.1, 333.2, and 283.8 ppm, those of the two Cr=C bonds in **10a** were shown at 354.3 and 283.2 ppm, respectively, while that of the remaining single Cr=C bond in **11a** was at 282.9 ppm. The reactivities of the M=C functionalities in the demetalation reactions follows the order: M=C in the 10-alkenyl carbene moiety > M=C in the *O*,*O*-alkyl carbene moiety > M=C in the cyclic alkenyl carbene moiety.

2.4. X-ray crystallographic studies

The molecular structures of **3**, **4b**, **5a** and **12** were further confirmed by X-ray crystallographic studies (Figs. 1–4, Tables 2 and 3). Compound **3** exists in a keto-configuration in the solid state (Fig. 1) and intramolecular hydrogen bonds (1.70 Å) are present between the 9-keto oxygen atom and the 1,8-dihydroxy hydrogens. Complex **4b** features a monocarbene structure with the keto-configuration of **2** remaining in the complex molecule (Fig. 2) and complex **5a** presents a triscarbene structure with a pentacyclic backbone (Fig. 3). The three Cr=C bond lengths in **5a** are in the region of 1.90–2.04 Å and a longer intramolecular hydrogen bond O–H···O (1.86 Å) is present between the 9-OH and one of the O–C=Cr oxygen atoms. Compound **12** features a triester structure which was generated from its triscarbene precursors **6** (Fig. 4). The organic compounds **3** and **7** present molecular structures typical of the structural architectures of aromatic polyketides which are clinically useful and usually biosynthesized via complex pathways [7,21]. Compound **7** may also act as a versatile bioactive agent through hydrolysis of its lactone group [22] and in fact the pentangular structure of **7** is very similar to that of antitumor agents benastatins [23]. The polyphenolic derivatives **9** and **12**, and their



Scheme 2. A proposed reaction mechanism.



Scheme 3. Oxidative demetalation of complexes **4**–**6** with PNO.

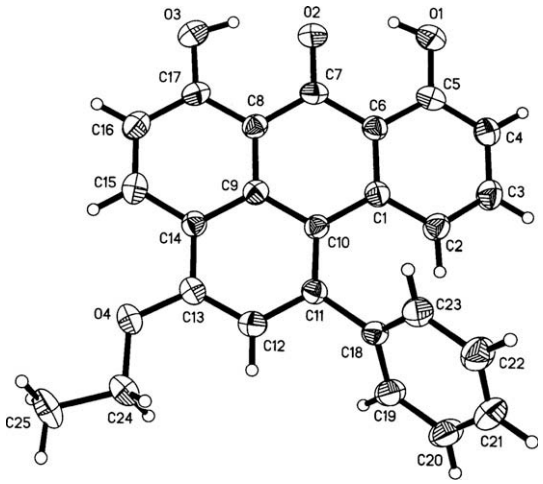


Fig. 1. Molecular structure of **3**.

possible hydrolyzed forms also exhibit structures analogous to the substructures of many natural aromatic polyketide-derived products or bioactive agents [24–26].

3. Summary

In summary, solvent-dependent multiple reactivities of dithranol have been unveiled. These results might be associated to the clinic side effect of dithranol and provide a new synthetic methodology for functionalization of dithranol for medical purposes and chemical synthesis of aromatic polyketides.

4. Experimental

4.1. General considerations

All the manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reaction solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a 400 MHz NMR spectrometer

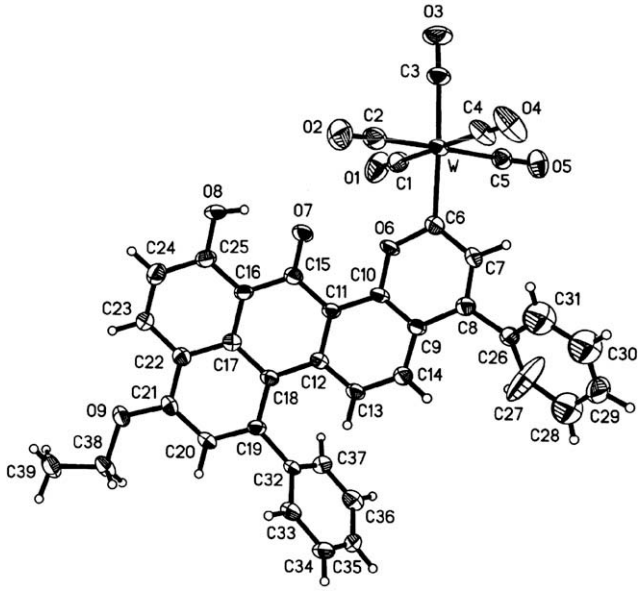
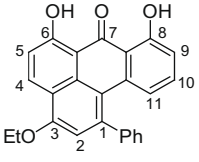


Fig. 2. Molecular structure of **4b**.

and all chemical shift values refer to $\delta_{TMS} = 0.00$ ppm or $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). All the melting points were uncorrected.

4.2. Synthesis and characterization of compounds *3*–*6*

In a similar fashion, the reactions of **1** and **2** in various molar ratios were carried out in toluene, dichloromethane, diethyl ether, and THF at room temperature. The products **3–6** were isolated by flash silica gel column chromatography and fully characterized.



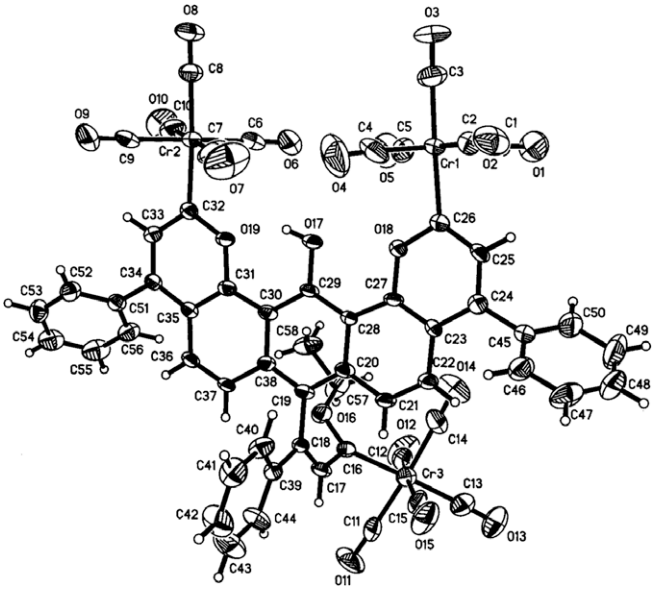


Fig. 3. Molecular structure of **5a**.

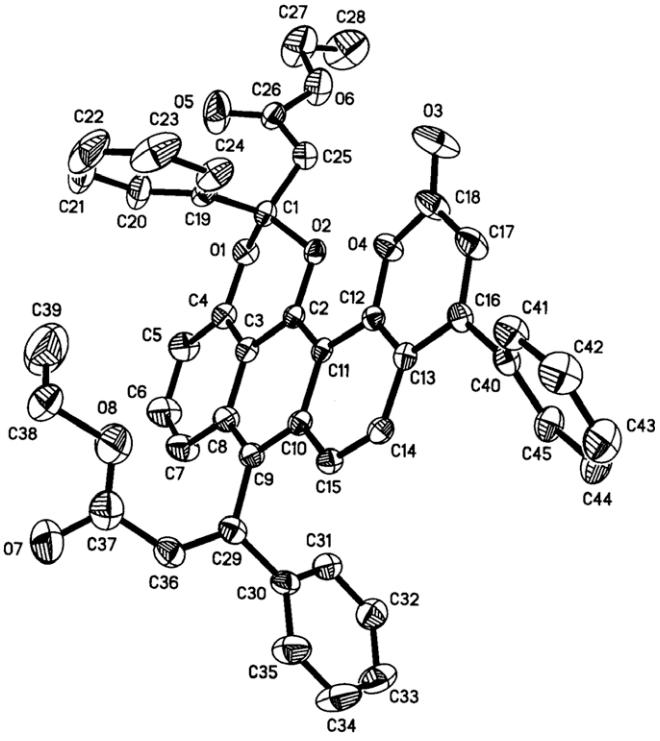


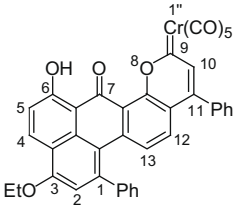
Fig. 4. Molecular structure of **12**.

*4.2.1. A typical procedure for the 1:1 molar ratio reactions of **1** and **2** – synthesis of 3-ethoxy-6,8-dihydroxy-1-phenyl-benzo[de]anthracen-7-one (**3**)*

Under a nitrogen atmosphere and at ambient temperature, to a mixture of complex **1b** (241 mg, 0.5 mmol) and **2** (114 mg, 0.5 mmol) in 5 mL toluene was added triethylamine (104 μL, 0.75 mmol) with stirring. The reaction was monitored by TLC analysis on silica gel. A green intermediate was initially formed and then gradually decomposed to form the product. After the green intermediate disappeared over a period of 3.5 h, all the volatiles were evaporated under reduced pressure and the resulting residue was subject to purification by flash silica gel chromatography with petroleum ether (30–60 °C)/dichloromethane as the eluent (v/v, 2:1, R_f = 0.45) to afford the organic product **3** (88 mg, 46%). Red single crystals were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 5/1) at room temperature. M.p.: 213–215 °C. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 14.75 (s, 1H, O*H*), 13.15 (s, 1H, O*H*), 8.55 (d, 1H, *J* = 9.2 Hz), 7.46 and 7.37 (m each, 3:2H, Ph), 7.15 (d, 1H, *J* = 9.2 Hz), 7.06 (t, 1H), 6.78 (m, 3H), 4.25 (q, 2H, OCH_2), 1.57 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 189.76 (Cq, C=O), 169.04, 162.91, 156.32, 146.53, 144.81, 137.90, 134.12, 134.07, 129.79, 129.40, 128.86, 127.92, 120.31, 118.13, 116.77, 115.93, 115.66, 113.87, 110.48, 109.19, 64.50 (OCH_2), 14.83 (CH_3). HRMS calcd for $C_{25}H_{18}O_4$: *m/z* 382.1205. Found: 382.1207.

*4.2.2. A typical procedure for the 3:1 molar ratio reactions of **1** and **2** – the 3:1 molar ratio reactions of **1** and **2** in diethyl ether*

Under a nitrogen atmosphere and at ambient temperature, to a mixture of complex **1** (1.00 mmol) and **2** (0.33 mmol) in 5 mL diethyl ether was added triethylamine (70 μL, 0.50 mmol) with stirring. The reaction was monitored by TLC analysis on silica gel. A green intermediate was initially formed and then gradually decomposed to form the products. After the green intermediate disappeared over a period of 17 h for the reaction of **1a** and **2**, and 4 h for the reaction of **1b** and **2**, all the volatiles were removed under reduced pressure and the resultant residue was purified by flash silica gel chromatography using petroleum ether (30–60 °C)/dichloromethane (v/v, 4/1) as the eluent, affording complexes **4**, **5**, and **6**, respectively. In the reactions, **3** was only detected and no measurable amount was formed.



*4.2.3. 9-(1,1,1,1,1-Pentacarbonyl-1-chroma)-3-ethoxy-6-hydroxy-1,11-diphenyl-8-oxa-benzo[hi]chrysene-7-one (**4a**)*

R_f = 0.50 (petroleum ether (30–60 °C)/dichloromethane, v/v = 2:1). Green crystals (48 mg, 21%) were obtained from recrystallization in *n*-pentane/dichloromethane (v/v, 4/1) at −20 °C. M.p.: 170 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 16.90 (s, 1H, O*H*), 8.67 (d, 1H, *J* = 9.6 Hz), 8.15 (s, 1H), 7.54 (m, 3H), 7.46 (m, 5H), 7.41 (m, 4H), 7.33 (d, 1H, *J* = 9.6 Hz), 6.93 (s, 1H), 4.35 (q, 2H, OCH_2), 1.61 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 291.12(Cq, Cr=C), 225.70 and 217.49 (Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 184.56 (Cq, C=O), 171.62, 162.63, 158.25, 147.87, 143.98, 141.38, 137.87, 137.53, 134.78, 133.62, 130.65, 130.14, 129.60, 129.53, 129.20, 128.57, 128.30, 127.16, 119.56, 118.86, 117.75, 115.94, 114.71, 111.10, 110.72, 64.87 (OCH_2), 14.83 (CH_3). Anal. Calc. for $C_{39}H_{22}O_9Cr$: C, 68.22; H, 3.23. Found: C, 68.34; H, 3.18%.

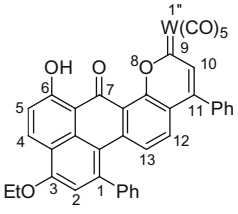


Table 2
Crystallographic data and refinement details for **3**, **4b**, **5a** and **12**.

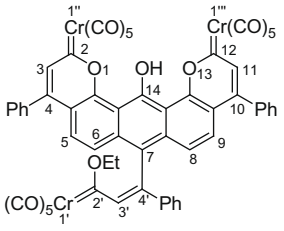
	3	**4b**·CH_2Cl_2	**5a**	**12**
Empirical formula	$C_{25}H_{18}O_4$	$C_{40}H_{24}Cl_2O_9W$	$C_{58}H_{28}Cr_3O_{19}$	C_{45} $H_{34}O_8$
Formula weight	382.39	903.34	1184.80	702.72
T (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$
a (Å)	7.7505(12)	16.7332(10)	12.939(8)	11.9871(8)
b (Å)	10.2733(17)	15.8904(9)	13.410(8)	11.8034(8)
c (Å)	23.498(4)	14.3263(8)	18.779(8)	25.5997(17)
α (°)	90	90	75.318(10)	90
β (°)	98.476(3)	109.4100(10)	76.947(9)	102.5320(10)
γ (°)	90	90	64.017(9)	90
V (Å^3)	1850.6(5)	3592.8(4)	2809(3)	3535.8(4)
Z	4	4	2	4
D_c (g cm^{-3})	1.373	1.670	1.401	1.320
μ (mm^{-1})	0.093	3.421	0.644	0.090
F(0 0 0)	800	1776	1200	1472
Crystal size (mm^3)	0.51 × 0.47 × 0.05	0.30 × 0.16 × 0.10	0.32 × 0.27 × 0.07	0.40 × 0.35 × 0.29
θ limits (°)	1.75–27.00	1.82–26.00	1.90–26.50	1.91–25.50
No. of data collected	10 493	19 389	12 466	18 286
No. of unique data	3993	7054	10 415	6562
[$R_{(int)}$]	0.1524	0.0802	0.0623	0.0371
No. of data observed with $I > 2\sigma(I)$	1671	5056	4106	3754
No. of refined parameters	272	441	723	500
Goodness-of-fit (GOF) on F^2	0.790	0.990	0.878	0.930
R (all data/observed data)	0.1346/0.0644	0.0793/0.0539	0.1990/0.0928	0.0976/0.0541
wR^2 (all data/observed data)	0.1678/0.1426	0.1445/0.1332	0.2556/0.2082	0.1475/0.1308
Residual ρ_{max} (e Å^{-3})	0.290 (−0.257)	1.524 (−0.919)	0.747 (−0.593)	0.309 (−0.229)

Table 3
Selected bond distances (Å) and angles (°) for **3**, **4b**, **5a** and **12**.

Compound **3**					
O(2)–C(7)	1.277(3)	C(10)–C(11)	1.397(3)	C(11)–C(12)	1.404(3)
C(11)–C(18)	1.499(3)	C(12)–C(13)	1.379(3)	C(13)–C(14)	1.402(3)
C(10)–C(11)–C(12)	21.1(2)	C(11)–C(12)–C(13)		121.3(2)	
C(12)–C(13)–C(14)	119.6(2)	O(1)–H···O(2)	1.77(3)	O(3)–H···O(2)	1.69(2)
Complex **4b**					
W–C(6)	2.172(7)	O(7)–C(15)	1.244(8)	C(18)–C(19)	1.412(9)
C(19)–C(20)	1.402(9)	C(20)–C(21)	1.394(10)	C(21)–C(22)	1.381(10)
C(18)–C(19)–C(20)	119.6(6)	C(19)–C(20)–C(21)		121.7(7)	
O(8)–H···O(7)	1.79				
Complex **5a**					
Cr(1)–C(26)	2.038(7)	Cr(2)–C(32)	2.048(7)	Cr(3)–C(12)	1.901(11)
O(17)–C(29)	1.331(7)	C(16)–C(17)	1.432(9)	C(17)–C(18)	1.354(9)
C(18)–C(19)	1.512(9)				
C(17)–C(18)–C(19)	121.4(6)	C(24)–C(25)–C(26)		124.7(7)	
C(32)–C(33)–C(34)	123.0(6)	O(17)–H···O(19)		1.86	
Compound **12**					
C(1)–O(1)	1.425(2)	C(1)–O(2)	1.443(2)	C(1)–C(25)	1.505(3)
C(2)–O(2)	1.370(2)	C(9)–C(29)	1.498(3)	O(1)–C(1)–O(2)	109.27(16)
C(9)–C(29)–C(36)	123.4(2)	C(1)–C(25)–C(26)		117.3(2)	

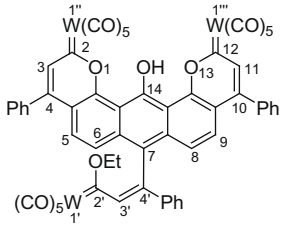
*4.2.4. 9-(1,1,1,1,1-Pentacarbonyl-1-tungsta)-3-ethoxy-6-hydroxy-1,11-diphenyl-8-oxa-benzo[hi]chrysene-7-one (**4b**)*

R_f = 0.50 (petroleum ether (30-60 °C)/dichloromethane, v/v = 2:1). Deep blue crystals (40 mg, 15%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 4/1) at −20 °C. M.p.: 200 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 16.88 (s, 1H, O*H*), 8.68 (d, 1H, J = 9.6 Hz), 8.15 (s, 1H), 7.53 (m, 3H), 7.46 (m, 5H), 7.41 (m, 4H), 7.34 (d, 1H, J = 9.6 Hz), 6.93 (s, 1H), 4.35 (q, 2H, OCH_2), 1.61 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 263.92 (Cq, W=C), 205.74 and 198.48 (Cq each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 184.48, 171.69, 161.83, 158.34, 147.92, 143.99, 141.80, 141.24, 141.06, 134.98, 133.70, 130.69, 130.18, 129.63, 129.24, 129.19, 128.60, 128.05, 127.40, 119.66, 119.27, 118.02, 116.01, 114.83, 111.16, 110.80, 64.90 (OCH_2), 14.85 (CH_3). Anal. Calc. for $C_{39}H_{22}O_9W$: C, 57.23; H, 2.71. Found: C, 57.47; H, 2.74%.



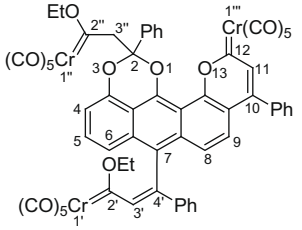
*4.2.5. 2,12-Bis(2-(1,1,1,1,1-pentacarbonyl-1-chroma))-7-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-chroma-buta-1,3-dien-4-yl)-4,10-diphenyl-2H,12H-1,13-dioxa-dibenzo[a,j]anthracen-14-ol (**5a**)*

R_f = 0.60 (petroleum ether (30–60 °C)/dichloromethane, v/v = 2:1). Brown crystals (74 mg, 19%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 5/1) at −20 °C. M.p.: 190 °C, dec. ^{1}H NMR (CD_2Cl_2, 23 °C, 400 MHz) δ 11.66 (s, 1H, O*H*), 8.57 (s, 1H), 8.30 (s, 2H), 7.72 (d, 2H, *J* = 9.3 Hz), 7.64 (d, 2H, *J* = 9.3 Hz), 7.56 (m, 10H), 7.31 (m, 3H), 7.24 (m, 2H), 4.33 (q, 2H, OCH_2), 0.31 (t, 3H, CH_3); $^{13}C\{^1H\}$NMR (CD_2Cl_2, 23 °C, 100 MHz) δ 333.56 and 285.89 (Cq each, 1:2, Cr=C, C2′ and C2/C12), 224.46 and 217.09 (Cq each, 1:4, *trans*- and *cis*-CO, C2/C12–$Cr(CO)_5$), 223.72 and 216.39 (Cq each, 1:4, *trans*- and *cis*-CO, C2′–$Cr(CO)_5$), 165.72, 157.52, 141.84, 139.25, 139.01, 138.85, 134.68, 133.22, 130.88, 130.49, 130.40, 129.56, 129.38, 128.28, 125.90, 125.57, 124.95, 118.46, 110.16, 76.89 (OCH_2), 13.85 (CH_3). Anal. Calc. for $C_{58}H_{28}O_{19}Cr_3$: C, 58.80; H, 2.38. Found: C, 59.78; H, 2.60%.



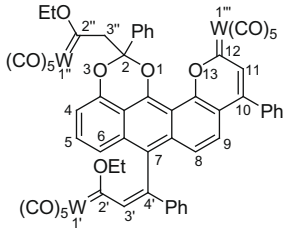
*4.2.6. 2,12-Bis(2-(1,1,1,1,1-pentacarbonyl-1-tungsta))-7-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-buta-1,3-dien-4-yl)-4,10-diphenyl-2H,12H-1,13-dioxa-dibenzo[a,j]anthracen-14-ol (**5b**)*

R_f = 0.60 (petroleum ether (30–60 °C)/dichloromethane, v/v = 2:1). Brown crystals (115 mg, 22%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 5/1) at −20 °C. M.p.: 200 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 11.60 (s, 1H, O*H*), 8.53 (s, 1H), 8.30 (s, 2H), 7.75 (d, 2H, *J* = 9.6 Hz), 7.69 (d, 2H, *J* = 9.6 Hz), 7.59 (m, 6H), 7.56 (m, 4H), 7.33 (m, 5H), 4.15 (q, 2H, OCH_2), 0.37 (t, 3H, CH_3); $^{13}C\{^1H\}$NMR ($CDCl_3$, 23 °C, 100 MHz) δ 306.82 and 258.71 (Cq each, 1:2, W=C, C2′ and C2/C12), 204.57 and 198.08 (Cq each, 1:4, *trans*- and *cis*-CO, C2/C12–$W(CO)_5$), 203.30 and 197.19 (Cq each, 1:4, *trans*- and *cis*-CO, C2′–$W(CO)_5$), 164.45, 157.46, 145.90, 142.33, 142.16, 138.87, 134.88, 133.97, 133.23, 130.54, 129.68, 129.52, 129.43, 129.20, 128.02, 126.39, 125.49, 125.24, 119.04, 110.37, 79.16 (OCH_2), 14.21 (CH_3). Anal. Calc. for $C_{58}H_{28}O_{19}W_3$: C, 44.08; H, 1.79. Found: C, 44.06; H, 1.82%.



*4.2.7. 2-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-chroma-1-propen-3-yl)-7-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-chroma-buta-1,3-dien-4-yl)-12-(1,1,1,1,1-pentacarbonyl-1-chroma)-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracene (**6a**)*

R_f = 0.65 (petroleum ether (30–60 °C)/dichloromethane, v/v = 2:1). Deep green crystals (105 mg, 26%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 10/1) at −20 °C. M.p.: 175 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 8.38 (s, 1H), 8.31 (s, 1H), 7.55–7.41(m, 15H), 7.14 (m, 5H), 5.47 and 4.49 (d each, 1:1H, *J* = 14.0 Hz, CH_2), 5.09 and 4.96 (s and br each, 1:1H, OCH_2), 3.80 and 3.27 (s and br each, 1:1H, OCH_2), 1.35 and −0.36 (s and br each, 3:3H, 2 × CH_3); $^{13}C\{^1H\}$NMR ($CDCl_3$) δ 354.07, 333.24 and 283.79 (Cq each, 1:1:1, Cr=C, C2″, C2′ and C12), 224.06 and 218.13 (Cq each, 1:4, *trans*- and *cis*-CO, C2″–$Cr(CO)_5$), 223.81 and 216.29 (Cq each, 1:4, *trans*- and *cis*-CO, C2′–$Cr(CO)_5$), 223.71 and 216.17 (Cq each, 1:4, *trans*- and *cis*-CO, C12–$Cr(CO)_5$), 165.44, 148.65, 147.78, 141.66, 139.65, 139.59, 139.36, 139.02, 134.92, 132.04, 130.47, 130.29, 130.10, 129.59, 129.38, 129.24, 129.03, 128.76, 128.61, 128.44, 129.19, 127.87, 127.50, 125.68, 122.62, 119.52, 118.51, 112.59, 109.67, 108.44, 104.22, 78.25 and 76.09 (2 × OCH_2), 71.22 (CH_2), 14.73 and 13.59 (2 × CH_3). Anal. Calc. for $C_{60}H_{34}O_{20}Cr_3$: C, 58.55; H, 2.78. Found: C, 58.29; H, 2.88%.



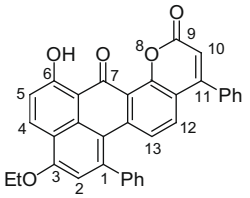
*4.2.8. 2-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-tungsta-1-propen-3-yl)-7-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-buta-1,3-dien-4-yl)-12-(1,1,1,1,1-pentacarbonyl-1-tungsta)-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracene (**6b**)*

R_f = 0.65 (petroleum ether (30–60 °C)/dichloromethane, v/v = 2:1). Deep green crystals (140 mg, 26%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 10/1) at −20 °C. M.p.: >280 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 8.35 (s, 1H), 8.32 (s, 1H), 7.57 (m, 9H), 7.44 (m, 2H), 7.32 (d, 1H, *J* = 4.0 Hz), 7.24 (m, 5H), 7.15 (s, 3H), 5.38 and 4.20 (d each, 1:1H, *J* = 13.2 Hz, CH_2), 4.81 and 4.57 (q each, 1:1H, OCH_2), 3.60 and 3.19 (q each, 1:1H, OCH_2), 1.20 and −0.45 (t each, 3:3H, 2 × CH_3); $^{13}C\{^1H\}$NMR ($CDCl_3$, 23 °C, 100 MHz) δ 327.07, 306.73 and 257.33 (Cq each, 1:1:1, W=C, C2″, C2′ and C12), 204.40 and 198.99 (Cq each, 1:4, *trans*- and *cis*-CO, C2″–$W(CO)_5$), 204.02 and 197.42 (Cq each, 1:4, *trans*- and *cis*-CO, C2′–$W(CO)_5$), 203.50 and 197.11 (Cq each, 1:4, *trans*- and *cis*-CO, C12–$W(CO)_5$), 164.24, 148.60, 147.83, 145.42, 143.14, 142.18, 139.31, 139.07, 135.06, 135.00, 131.98, 130.53, 130.43, 130.37, 130.23, 129.31, 128.88, 128.49, 127.97, 127.86, 125.91, 122.52, 119.60, 119.02, 112.63, 109.94, 108.56, 104.23, 80.67 and 78.59 (2 × OCH_2), 73.54 (CH_2), 14.26, 13.17. Anal. Calc. for $C_{60}H_{34}O_{20}W_3$: C, 44.31; H, 2.11. Found: C, 44.46; H, 2.15%.

*4.3. Oxidative demetalation of **4**–**6***

*4.3.1. A typical procedure for oxidative demetalation of complexes **4***

Complex **4a** or **4b** (0.20 mmol) was reacted with pyridine *N*-oxide (0.20 mmol, 1.0 equiv.) in 3 mL of dichloromethane at room temperature for 10 h. After **4** was completely consumed, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silical gel chromatography using petroleum ether (30–60 °C)/diethyl ether (v/v, 2/1) as the eluent to afford compound **7** as the product.

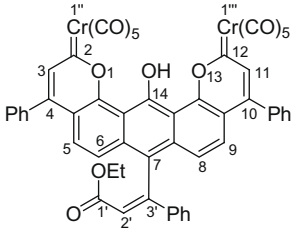


*4.3.2. 3-Ethoxy-6-hydroxy-1,11-diphenyl-8-oxa-benzo[hi]chrysene-7,9-dione (**7**)*

R_f = 0.50 (100% dichloromethane). Orange crystals (130 mg from **4a**, 95%; 130 mg from **4b**, 95%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 4/1) at −20 °C. M.p.: 276–278 °C. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 16.48 (s, 1H, O*H*), 8.67 (d, 1H, *J* = 9.2 Hz), 7.50 (m, 3H), 7.43 (m, 3H), 7.39 (m, 4H), 7.25 (m, 2H), 7.17 (d, 1H, *J* = 9.2 Hz), 6.84 (s, 1H), 6.41 (s, 1H), 4.30 (q, 2H, OCH_2), 1.60 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 185.23 (Cq, C=O), 170.72 (Cq, C=O), 160.29, 157.48, 155.40, 154.68, 147.06, 144.28, 141.43, 135.42, 133.37, 130.31, 129.74, 129.52, 129.08, 129.05, 128.64, 128.30, 128.19, 125.14, 119.16, 118.02, 116.20, 116.04, 114.84, 114.66, 110.73, 110.56, 64.70 (OCH_2), 14.83 (CH_3). HRMS calcd for $C_{34}H_{22}O_5$: 510.1467. Found: 510.1464.

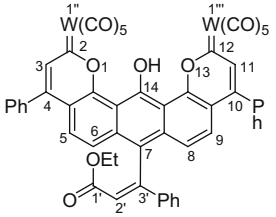
*4.3.3. A typical procedure for stepwise oxidative demetalation of complexes **5***

Complex **5a** or **5b** (0.20 mmol) was reacted with pyridine *N*-oxide (0.20 mmol) in 3 mL of dichloromethane with stirring at ambient temperature, and the reaction was monitored by TLC analysis on silica gel. After **5** was completely consumed within 15–20 min, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel chromatography using petroleum ether (30–60 °C)/dichloromethane as the eluent (v/v, 1/1) to afford complex **8a** or **8b**. Complex **8a** or **8b** (0.20 mmol) was reacted with pyridine *N*-oxide (0.50 mmol, 2.5 equiv.) in 3 mL of THF at 55 °C for 0.5–1.0 h. After **8** was completely consumed, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel chromatography using dichloromethane/diethyl ether as the eluent (v/v, 1/1) to afford compound **9**. In a similar fashion, copmplex **5a** or **5b** (0.20 mmol) was reacted with excess of pyridine *N*-oxide (0.70 mmol, 3.5 equiv.) in 3 mL of THF at 55 °C for 0.5–1.0 h also afforded compound **9**.



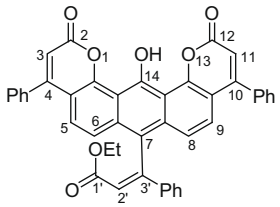
*4.3.4. 3-[2,12-Bis(2-(1,1,1,1,1-pentacarbonyl-1-chroma))-4,10-diphenyl-14-hydroxy-2H,12H-1,13-dioxa-dibenzo[a,j]anthracen-7-yl]-3-phenyl-acrylic acid ethyl ester (**8a**)*

R_f = 0.50 (petroleum ether (30–60 °C)/dichloromethane, v/v = 1:1). Brown crystals (183 mg, 91%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 4/1) at −20 °C. M.p.: 185 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 11.71 (s, 1H, O*H*), 8.27 (s, 2H), 7.74 (d, 2H, *J* = 9.4 Hz), 7.64 (d, 2H, *J* = 9.4 Hz), 7.56 (m, 10H), 7.33 (m, 5H), 7.08 (s, 1H), 3.86 (q, 2H, OCH_2), 1.01 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 284.94 (Cq, Cr=C, C2/C12), 224.59 and 217.10 (Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 166.07 (Cq, C=O), 164.88, 158.00, 151.89, 139.01, 138.26, 134.87, 133.01, 130.68, 130.32, 129.55, 129.30, 129.25, 127.25, 125.42, 125.26, 124.76, 121.37, 118.53, 110.47, 60.48 (OCH_2), 14.16 (CH_3). Anal. Calc. for $C_{53}H_{28}O_{15}Cr_2$: C, 63.10; H, 2.80. Found: C, 62.73; H, 2.84%.



*4.3.5. 3-[2,12-Bis(2-(1,1,1,1,1-pentacarbonyl-1-tungsta))-4,10-diphenyl-14-hydroxy-2H,12H-1,13-dioxa-dibenzo[a,j]anthracen-7-yl]-3-phenyl-acrylic acid ethyl ester (**8b**)*

R_f = 0.50 (petroleum ether (30–60 °C)/dichloromethane, v/v = 1:1). Brown crystals (236 mg, 93%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 4/1) at −20 °C. M.p.: >280 °C. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 11.60 (s, 1H, O*H*), 8.29 (s, 2H), 7.74 (d, 2H, *J* = 9.2 Hz), 7.66 (d, 2H, *J* = 9.2 Hz), 7.58 (m, 10H), 7.33 (m, 5H), 7.09 (s, 1H), 3.86 (q, 2H, OCH_2), 1.02 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 258.01 (Cq, W=C, C2/C12), 204.69 and 198.08 (Cq each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 164.85, 164.79, 157.91, 151.85, 142.36, 142.04, 138.22, 135.06, 133.21, 130.71, 130.36, 129.28, 129.20, 127.25, 125.53, 125.34, 125.00, 121.38, 119.06, 110.67, 60.50 (OCH_2), 14.17 (CH_3). Anal. Calc. for $C_{53}H_{28}O_{15}W_2$: C, 50.03; H, 2.22. Found: C, 50.59; H, 2.25%.



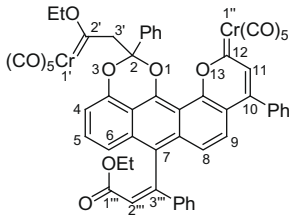
*4.3.6. 3-(14-Hydroxy-2,12-dioxo-4,10-diphenyl-2H,12H-1,13-dioxa-dibenzo[a,j]anthracen-7-yl)-3-phenyl-acrylic acid ethyl ester (**9**)*

R_f = 0.50 (diethyl ether/dichloromethane, v/v = 1:1). Yellow crystals (108 mg from **8a**, 82%; 98 mg from **8b**, 75%) were obtained by recrystallization from dichloromethane/*n*-pentane (v/v, 1/4) at room temperature. M.p.: >250 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 11.09 (s, 1H, O*H*), 7.54 (d, 2H, *J* = 9.3 Hz), 7.50 (m, 6H), 7.43 (m, 4H), 7.36 (d, 2H, *J* = 9.3 Hz), 7.30 (m, 3H), 7.25 (m, 2H), 7.00 (s, 1H), 6.47 (s, 2H), 3.80 (q, 2H, OCH_2), 0.88 (t, 3H, CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 165.07, 159.26, 156.88, 156.49, 154.78, 152.50, 138.75, 135.81, 132.97, 130.33, 129.77, 129.14, 129.02, 128.61, 127.28, 124.70, 124.01, 122.09, 121.35, 113.58, 113.24, 110.36, 60.25 (OCH_2), 14.04 (CH_3). HRMS calcd for $C_{43}H_{28}O_7$: 656.1835. Found: 656.1844.

*4.3.7. A typical procedure for stepwise oxidative demetalation of complexes **6***

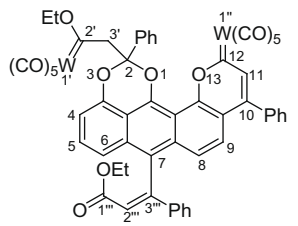
Complex **6a** or **6b** (0.20 mmol) was reacted with pyridine *N*-oxide (0.20 mmol) in 3 mL of dichloromethane at ambient tem-

perature, and the reaction was monitored by TLC analysis on silica gel. After **6** was completely consumed over a period of 0.5 (for **6a**) – 2 h (for **6b**), all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel chromatography using hexanes/dichloromethane as the eluent (v/v, 1/1) to afford complex **10a** or **10b** (R_f = 0.50 (petroleum ether (30–60 °C)/dichloromethane, v/v = 1:2) as the product. In a similar fashion, complex **10a** or **10b** (0.20 mmol) was reacted with pyridine *N*-oxide (0.20 mmol) in 3 mL of dichloromethane at ambient temperature for 20 (for **10a**) – 50 (for **10b**) min. All the volatiles were removed under reduced pressure and the resultant residue was purified by flash silica gel chromatography using petroleum ether (30–60 °C)/diethyl ether (v/v, 2/1) as the eluent to afford complex **11a** or **11b** (R_f = 0.50, 100% dichloromethane). Complex **11a** or **11b** (0.20 mmol) was further reacted with pyridine *N*-oxide (0.30 mmol) in 3 mL of THF at 66 °C. After **11** was completely consumed over a period of 4 (for **11a**) – 16 (for **11b**) h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel chromatography using dichloromethane/diethyl ether (v/v, 1/1) as the eluent to afford triester **12** (R_f = 0.50). Treatment of complex **6** (0.20 mmol) with excess of pyridine *N*-oxide (0.70 mmol, 3.5 equiv.) in 3 mL of THF at 66 °C (4 h for **6a** and 16 h for **6b**) also afforded compound **12**.



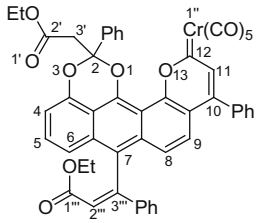
*4.3.8. 3-[2-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-chroma-1-propen-3-yl)-12-(1,1,1,1,1-pentacarbonyl-1-chroma)-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracen-7-yl]-3-phenyl-acrylic acid ethyl ester (**10a**)*

R_f = 0.65 (petroleum ether (30–60 °C)/dichloromethane (v/v, 1/2)). Green crystals (183 mg, 87%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 10/1) at −20 °C. M.p.: 150 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 8.30 (s, 1H), 7.58 (m, 8H), 7.45 (m, 3H), 7.27 (m, 5H), 7.12 (m, 4H), 6.93 (s, 1H), 5.41 and 4.51 (d each, 1:1H, J = 14.0 Hz, CH_2), 5.10 and 4.98 (q each, 1:1H, OCH_2), 3.11 (q, 2H, OCH_2), 1.37 and −0.14 (t each, 3:3H, 2 × CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 354.33 and 283.22 (Cq each, 1:1, Cr=C, C2′ and C12), 224.16 and 216.18 (Cq each, 1:4, *trans*- and *cis*-CO, C2′–$Cr(CO)_5$), 223.76 and 218.13 (Cq each, 1:4, *trans*- and *cis*-CO, C12–$Cr(CO)_5$), 165.66, 165.55, 150.69, 148.56, 148.18, 139.80, 139.30, 139.24, 138.86, 135.03, 132.09, 130.21, 130.16, 130.09, 129.59, 129.19, 129.10, 128.80, 128.34, 127.77, 127.25, 125.55, 122.55, 122.24, 119.28, 118.55, 112.73, 109.45, 108.47, 104.25, 78.22 and 71.14 (2 × OCH_2), 59.88 (CH_2), 14.73 and 13.26 (2 × CH_3). Anal. Calc. for $C_{55}H_{34}O_{16}Cr_2$: C, 62.62; H, 3.25. Found: C, 62.55; H, 3.30%.



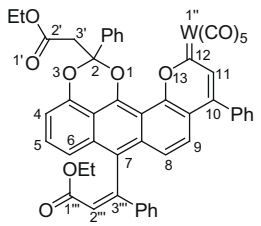
*4.3.9. 3-[2-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-tungsta-1-propen-3-yl)-12-(1,1,1,1,1-pentacarbonyl-1-tungsta)-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracen-7-yl]-3-phenyl-acrylic acid ethyl ester (**10b**)*

R_f = 0.65 (petroleum ether (30–60 °C)/dichloromethane (v/v, 1/2)). Green crystals (198 mg, 75%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 10/1) at −20 °C. M.p.: 176 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 8.33 (s, 1H), 7.62 (d, 1H, J = 9.60 Hz), 7.56 and 7.52–7.41 (m each, 5:5H), 7.27–7.17 and 7.11 (m each, 6:3H), 6.93 (s, 1H), 5.31 and 4.22 (d each, 1:1H, J = 12.8 Hz, CH_2), 4.81 and 4.56 (q each, 1:1H, OCH_2), 3.11 (q, 2H, OCH_2), 1.19 and −0.20 (t each, 3:3H, 2 × CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 327.36 and 256.79 (Cq each, 1:1, W=C, C2′ and C12), 204.48 and 198.99 (Cq each, 1:4, *trans*- and *cis*-CO, C2′–$W(CO)_5$), 204.06 and 197.44 (Cq each, 1:4, *trans*- and *cis*-CO, C12–$W(CO)_5$), 165.50, 164.44, 150.58, 148.55, 148.17, 143.27, 142.01, 139.05, 138.82, 135.09, 132.17, 130.24, 130.18, 129.30, 129.21, 129.09, 128.87, 128.38, 127.75, 127.45, 127.24, 125.86, 122.40, 122.24, 119.34, 119.04, 112.78, 109.71, 108.57, 104.24, 80.66 (CH_2), 73.52 and 59.87 (2 × OCH_2), 14.24 and 13.16 (2 × CH_3). Anal. Calc. for $C_{55}H_{34}O_{16}$ W_2: C, 50.10; H, 2.60. Found: C, 50.23; H, 2.65%.



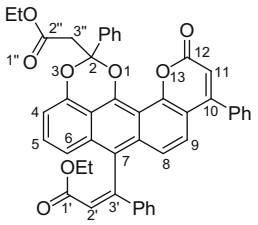
*4.3.10. 3-[2-(2-Ethoxycarbonylmethyl)-12-(1,1,1,1,1-pentacarbonyl-1-chroma)-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracen-7-yl]-3-phenyl-acrylic acid ethyl ester (**11a**)*

R_f = 0.50 (100% dichloromethane). Green crystals (167 mg, 95%) were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 10/1) at −20 °C. M.p.: 158 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 8.31 (s, 1H), 7.68 (m, 2H), 7.62–7.57 (m, 6H), 7.49-7.40 (m, 3H), 7.30–7.22 (m, 6H), 7.12 (m, 3H), 6.94 (s, 1H), 4.13 (m, 2H, OCH_2), 4.02 and 3.85 (d each, 1:1H, J = 14.4 Hz, CH_2), 3.12 (q, 2H, OCH_2), 1.18 and −0.16 (t each, 3:3H, 2 × CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 282.90 (Cq, Cr=C), 224.61 and 217.97 (Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 167.73, 167.66, 165.71, 165.55, 151.75, 150.69, 148.75, 148.42, 139.94, 139.25, 139.16, 138.89, 138.76, 138.29, 135.15, 135.04, 132.18, 130.15, 129.59, 129.42, 129.18, 129.08, 129.02, 128.87, 128.28, 128.13, 127.82, 127.34, 127.26, 127.21, 125.63, 125.36, 122.48, 122.25, 121.57, 119.24, 118.97, 118.57, 112.93, 110.00, 109.92, 108.53, 103.68, 60.94 (CH_2), 59.92 and 47.92 (2 × OCH_2), 14.14 and 13.21 (2 × CH_3). Anal. Calc. for $C_{50}H_{34}O_{12}Cr$: C, 68.34; H, 3.90. Found: C, 68.46; H, 3.96%.



*4.3.11. 3-[2-(2-Ethoxycarbonylmethyl)-12-(1,1,1,1,1-pentacarbonyl-1-tungsta)-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracen-7-yl]-3-phenyl-acrylic acid ethyl ester (**11b**)*

R_f = 0.50 (100% dichloromethane). Brown crystals (188 mg, 93%) were obtained by recrystallization from dichloromethane/*n*-pentane (v/v, 1/10) at −20 °C. M.p.: 145–147 °C. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 8.34 (s, 1H), 7.67–7.62 and 7.57 (m each, 3:6H), 7.52–7.38 (m, 4H), 7.32–7.17 (m, 4H), 7.15–7.09 (m, 3H), 6.94 (s, 1H), 4.10 (m, 2H, OCH_2), 3.99 and 3.82 (d each, 1:1H, J = 14.0 Hz, CH_2), 3.12 (m, 2H, OCH_2), 1.15 and −0.20 (t each, 3:3H, 2 × CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 256.68 (Cq, W=C), 204.72 and 198.89 (Cq each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 167.60, 165.52, 164.47, 150.58, 148.75, 148.40, 143.34, 141.97, 138.85, 138.17, 135.11, 132.24, 130.28, 130.15, 129.32, 129.21, 129.08, 128.33, 128.20, 127.74, 127.49, 127.25, 125.88, 122.35, 122.26, 119.27, 119.02, 112.91, 109.99, 108.59, 103.62, 60.93, 59.91, 48.22, 14.09, 13.12. Anal. Calc. for $C_{50}H_{34}O_{12}W$: C, 59.42; H, 3.39. Found: C, 59.35; H, 3.32%.



*4.3.12. 3-[2-(2-Ethoxycarbonylmethyl)-12-oxo-2,10-diphenyl-12H-1,3,13-trioxa-dibenzo[a,kl]anthracen-7-yl)]-3-phenyl-acrylic acid ethyl ester (**12**)*

R_f = 0.50 (dichloromethane/diethyl ether, v/v, 1/1). Yellow crystals (133 mg from M = Cr, 95%; 128 mg from M = W, 91%). Single crystals were obtained by recrystallization from *n*-pentane/dichloromethane (v/v, 4/1) at room temperature. M.p.: 250 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.90 (s, 1H), 7.88 (s, 1H), 7.50–7.44 (m, 6H), 7.38 (m, 2H), 7.25–7.12 (m, 10H), 6.91 (s, 1H), 6.50 (s, 1H), 4.12 (m, 2H, OCH_2), 3.62 and 3.51 (d each, 1:1H, J = 14.5 Hz, CH_2), 3.33 and 3.19 (m each, 1:1H, OCH_2), 1.16 and −0.16 (t each, 3:3H, 2 × CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$, 23 °C, 100 MHz) δ 167.76, 165.65, 160.78, 156.42, 153.49, 151.02, 148.33, 146.58, 139.27, 139.19, 135.97, 131.31, 131.07, 129.97, 129.62, 129.17, 128.99, 128.95, 128.66, 128.53, 127.32, 127.27, 126.32, 122.96, 122.20, 122.03, 119.05, 113.93, 113.48, 111.86, 109.23, 108.78, 102.24, 60.94, 59.89, 47.53, 14.16, 12.86. HRMS calcd for $C_{45}H_{34}O_8$: 702.2254. Found: 702.2247.

4.4. X-ray crystallographic studies

Single crystal for X-ray diffraction studies for compounds **3**, **4b**, **5a**, and **12** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for these compounds are summarized in Table 2, and the selected bond distances and angles are listed in Table 3.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (20772124) and the National Basic Research Program of China (2009CB825300) for support of this research.

Appendix A. Supplementary material

CCDC 701684, 701685, 701686 and 701687 contain the supplementary crystallographic data for **3**, **4b**, **5a** and **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.029.

References

[1] I. Orojan, L. Bakota, K. Gulya, Neurochem. Int. 52 (2008) 265.
[2] A. Ferlan, S. Perca, M. Schara, Pharmazie 58 (2003) 475.
[3] K. Müller, R. Altmann, H. Prinz, Eur. J. Med. Chem. 33 (1998) 209.
[4] K. Müller, H. Reindl, K. Breu, J. Med. Chem. 44 (2001) 814.
[5] R. Shabana, L.S. Boulos, Y.M. Shaker, Heteroatom Chem. 10 (1999) 25.
[6] C. Hertweck, A. Luzhetskyy, Y. Rebets, A. Bechthold, Nat. Prod. Rep. 24 (2007) 162.
[7] K. Fritzsche, K. Ishida, C. Hertweck, J. Am. Chem. Soc. 130 (2008) 8307.
[8] M. Koerner, B. Rickborn, J. Org. Chem. 56 (1991) 1373.
[9] C. Wang, L.Y. Zhu, J.F. Xiang, Y.X. Yu, D.Q. Zhang, Z.G. Shuai, D.B. Zhu, J. Org. Chem. 72 (2007) 4306.
[10] J.C.C. Atherton, S. Jones, Tetrahedron 59 (2003) 9039.
[11] J.W. Herndon, Coord. Chem. Rev. 253 (2009) 86.
[12] J. Huang, C.R. Wu, W.D. Wulff, J. Am. Chem. Soc. 129 (2007) 13366.
[13] J. Barluenga, M.G. Suero, I. Perez-Sanchez, J. Florez, J. Am. Chem. Soc. 130 (2008) 2708.
[14] J. Barluenga, M.A. Fernandez-Rodriguez, E. Aguilar, J. Organomet. Chem. 690 (2005) 539.
[15] M.A. Sierra, Chem. Rev. 100 (2000) 3591.
[16] R. Aumann, R. Fröhlich, S. Kotila, Organometallics 15 (1996) 4842.
[17] J. Barluenga, S. Martínez, A.L. Suárez-Sobrino, M. Tomás, Organometallics 25 (2006) 2337.
[18] B.M. Trost, F.D. Toste, K. Greenman, J. Am. Chem. Soc. 125 (2003) 4518.
[19] Z.Y. Zheng, J.Z. Chen, N. Luo, Z.K. Yu, X.W. Han, Organometallics 25 (2006) 5301.
[20] Z.Y. Zheng, J.Z. Chen, N. Luo, Z.K. Yu, X.W. Han, J. Organomet. Chem. 691 (2006) 3679.
[21] K. Ishida, K. Fritzsche, C. Hertweck, J. Am. Chem. Soc. 129 (2007) 12648.
[22] W. Zhang, B.I. Wilke, J. Zhan, K. Watanabe, C.N. Boddy, Y. Tang, J. Am. Chem. Soc. 129 (2007) 9304.
[23] A. Schenk, Z.L. Xu, C. Pfeiffer, C. Steinbeck, C. Hertweck, Angew. Chem., Int. Ed. 46 (2007) 7035.
[24] M.K. Kharel, L. Zhu, T. Liu, J. Rohr, J. Am. Chem. Soc. 129 (2007) 3780.
[25] K.C. Nicolaou, Y.H. Lim, J.L. Piper, C.D. Papageorgiou, J. Am. Chem. Soc. 129 (2007) 4001.
[26] C. Leimkuhler, M. Fridman, T. Lupoli, S. Walker, C.T. Walsh, D. Kahne, J. Am. Chem. Soc. 129 (2007) 10546.