Facile Synthesis of Oxa- and Azacyclic Dienes via Cycloalkenation of Alkynyltungsten Compounds. Stereoselective Construction of Tricyclic Furan and Pyran Derivatives via Intramolecular Diels−Alder Reaction

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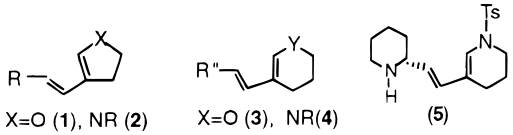
A convenient and short synthesis of functionalized oxacyclic and azacyclic dienes is developed on the basis of organotungsten chemistry. Alkynyltungsten compounds bearing a tethered alcohol and amine are treated with aldehydes and $BF_3{\cdot}Et_2O$ in cold diethyl ether to give tungsten-heterocyclic carbenium salts, further leading to tungsten-heterocyclic dienes via deprotonation with Et_3N. Hydrodemetalation of these tungsten-heterocyclic dienes is performed by the action of anhydrous Me_3NO in CH_3CN. This method is applicable to the synthesis of a number of oxa- and azacyclic dienes, including those tethered with an electron-deficient olefin. The oxacyclic 1,3,8-nonatrienes and 1,3,9-decatrienes undergo intramolecular Diels−Alder reactions upon heating in toluene, yielding tricyclic tetrahydropyran and -furan derivatives with excellent diastereoselectivities.

Introductions

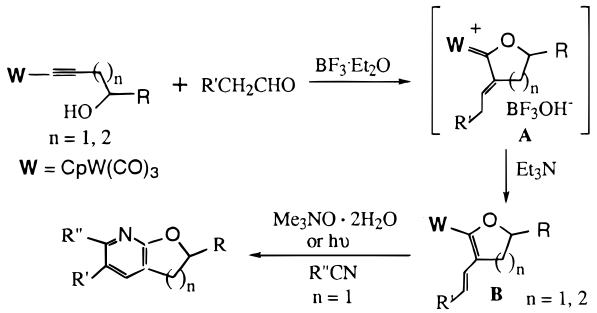
Oxa- and azacyclic dienes **1**−**5** are useful building blocks for complex oxa- and azacyclic compounds.[1−4] Cycloadditions of these heterocyclic dienes with electron-deficient olefins normally proceed with high diastereoselectivities.[1,2] The resulting [4 + 2]-cycloadducts provide a concise approach to naturally occurring compounds. Boeckman and co-workers[3] previously reported a highly convergent synthesis of racemic lycorine through intramolecular [4 + 2]-cycloaddition of 3-vinyl-4,5-dihydropyrrole derivative **2**. Recently, Overman et al.[4] have employed compound **5** as an intermediate for total synthesis of (+)-aloperine. One major problem with the use of these heterocyclic dienes is the diversity of synthetic methods that often require long procedures.[1,2] A general and short synthesis of these heterocyclic dienes will be valuable in synthetic organic chemistry.

Scheme 1



We recently reported that tungsten-alkynol compounds underwent cycloalkenations with aldehydes and $BF_3{\cdot}Et_2O$ to give tungsten-η^1-oxacarbenium salts **A** quantitatively as shown in Scheme 2.[5,6] Further treatment of these carbenium salts with Et_3N led to deprotonation, yielding tungsten-η^1-oxacyclic dienes **B** in excellent yields.[7] If organic nitrile was used as a solvent, the tungsten-η^1-3-vinyl-4,5-dihydrofur-2-yl species **B** underwent cyano-[4 + 2]-cycloaddition, yielding furopyridines in the presence of excess $Me_3NO{\cdot}2H_2O$ or upon photolysis.[7] In this paper, we describe a convenient synthesis of functionalized heterocyclic dienes through hydrodemetalations of tungsten-η^1-oxa- and −azacyclic dienes under appropriate conditions. These heterocyclic dienes can undergo inter- and intramolecular Diels−Alder reactions to give polycyclic furan and pyran derivatives with high diastereoselectivities.

Scheme 2



Results and Discussion

Synthesis of Heterocyclic Dienes. The starting compounds tungsten-η^1-oxacyclic dienes **B** were easily prepared from deprotonation of their corresponding oxa-

(1) (a) Boeckman, R. K. Jr.; Breining, S. R.; Arvanitis, A. *Tetrahedron* **1997**, *53*, 8941. (b) Aelterman, W.; De kimpe, N. *Tetrahedron* **1998**, *54*, 2563. (c) Bigogno, C.; Danieli, B.; Lesma, G.; Passarella, D. *Heterocycles* **1995**, *41*, 973. (d)

(2) (a) Breitmaier, E.; Potthoff, B. *Chem. Ber.* **1986**, *119*, 3204. (b) Breitmaier, E.; Ruffer, U. *Synthesis* **1986**, 584. (c) Breitmaier, E.; Ruffer, U. *Synthesis* **1989**, 623. (d) Cornwall, P.; Dell, C. P.; Knight, D. W. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2395.

(3) Boeckman, R. K. Jr.; Goldstein, S. W.; Walters, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 8250

(4) Brosius, A. D.; Overman, L. E.; Schwink, L. *J. Am. Chem. Soc.* **1999**, *121*, 700.

(5) Liang, K.-W.; Li, W.-T.; Lee, G.-H., Peng S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1997**, *119*, 4404.

(6) Liang, K.-W.; Chandrasekharam, M.; Li, C.-L.; Liu, R.-S. *J. Org. Chem.* **1998**, *63*, 7289.

(7) Li, W,-T.; Lai, F.-C.; Lee, G.-H.; Peng, S.-M.; Liu, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 4520.

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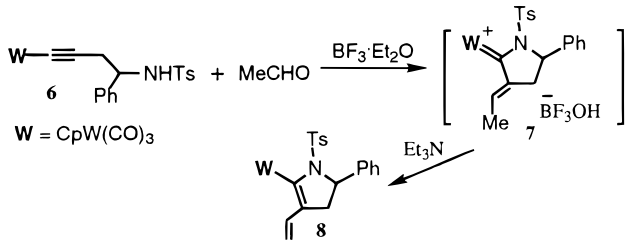
cyclic carbenium salts **A** with Et_3N; the yields normally exceeded 90% (Scheme 2).[7] The tungsten-azacyclic carbenium salt, however, is not available at the present time because cycloalkenation of tungsten-η^1-α,δ-alkynylamines is not known yet. Scheme 3 shows an instance for cycloalkenation of tungsten-alkynylamine compound **6** with acetaldehyde and $BF_3{\cdot}Et_2O$ to yield dark red precipitates, characterized as tungsten-η^1-azacarbenium salt **7**. Sequential treatment of this salt with Et_3N

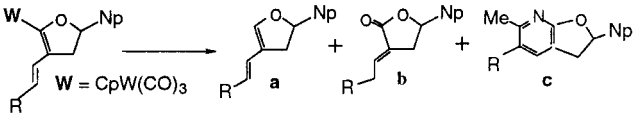
Scheme 3



afforded tungsten-η^1-3-vinyl-4.5-dihydropyrrolyl species **8** in 83% yield based on starting tungsten-η^1-alkynylamine species **6**. The cycloalkenation is not applicable to tungsten-η^1-α,δ-alkynylamine that did not form the corresponding tungsten-piperdinyl salt upon treatment with MeCHO and $BF_3{\cdot}Et_2O$.

Hydrodemetalation of tungsten-heterocyclic dienes was achieved via treatment with Me_3NO, but the yields of the desired heterocyclic dienes depended on the types of tungsten-heterocyclic dienes, the solvents, and the contents of water in Me_3NO. Scheme 4 shows the yields of

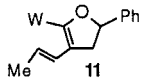
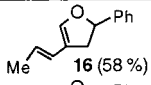
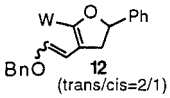
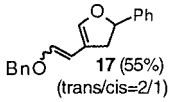
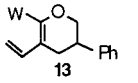
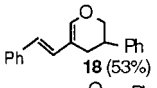
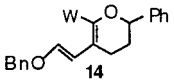
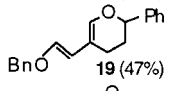
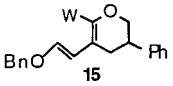
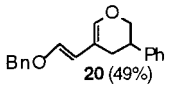
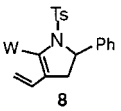
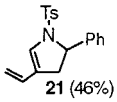
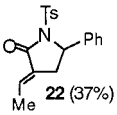
Scheme 4



entry	η^1-diene	Demetallation	solvent	products
1	R =H (**9**)	Me_3NO (5.0 equiv) (23 °C, 2h)	MeCN	**9a** (61%)
2	R =H (**9**)	Me_3NO •0.4 H_2O (5.0 equiv, 23 °C, 10 h)	MeCN	**9a** (35%), **9b** (9%) **9c** (32%)
3	R =H (**9**)	Me_3NO •2H_2O (5.0 equiv, 23 °C, 10 h)	MeCN	**9a** (7%), **9b** (11%) **9c** (58%)
4	R =H (**9**)	Me_3NO (5.0 equiv) (23 °C, 2 h)	CH_2Cl_2	**9a** (11%), **9b** (56%)
5	R = Me (**10**)	Me_3NO •2H_2O (5.0 equiv, 23 °C, 10 h)	MeCN	**10a** (49%)
6	R = Me (**10**)	Me_3NO (5.0 equiv) (23 °C, 2 h)	MeCN	**10a** (56%)

products for demetalation of tungsten-η^1-oxacyclic dienes **9**−**10** under various conditions. Treatment of **9** with anhydrous excess Me_3NO in CH_3CN gave the hydrodemetalation products **9a** in 61% yields. With increasing contents of water in Me_3NO, the yields of unsatuated γ-lactone **9b** and furopyridine **9c** increased steadily together with loss of the yields of oxacyclic diene **9a**. Furopyridine **9c** was formed preferably (58% yield) with the use of excess $Me_3NO{\cdot}2H_2O$. Compound **9c** were also obtained in good yield upon irradiation with UV light in CH_3CN.[7] The role of water for the formation of **9c** seems to enhance the coordination of CH_3CN to tungsten center after one of the CO group was removed by Me_3NO. If the

Table 1. Yields for Demetalation of η^1-Heterocyclic Dienes with Anhydrous Me_3NO[a]

Entries	η^1-Oxacyclic Dienes	Oxacyclic Dienes
1	 **11**	 **16** (58 %)
2	 **12** (trans/cis=2/1)	 **17** (55%) (trans/cis=2/1)
3	 **13**	 **18** (53%)
4	 **14**	 **19** (47%)
5	 **15**	 **20** (49%)
6	 **8**	 **21** (46%)  **22** (37%)

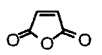
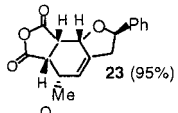
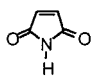
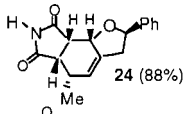
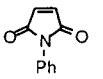
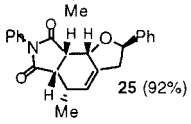
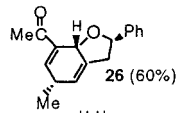
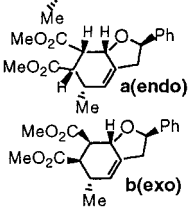
[a] W = CpW(CO)$_3$, Me_3NO (5.0 equiv), CH_3CN, 23 °C, 6 h.

demetalation was performed with anhydrous Me_3NO in CH_2Cl_2 (entry 4), the unsaturated γ-lactone **9b** was formed as the major product (56% yield). Demetalation of tungsten-η^1-oxacyclic diene **10** proceeded more smoothly for the desired oxacyclic diene **10a** (entries 5 and 6), no cyano-[4 + 2]-cycloaddition adduct was formed even though $Me_3NO{\cdot}2H_2O$ was employed.

The results in Scheme 4 suggest that hydrodemetalation of tungsten-η^1-oxacyclic dienes **9** and **10** was best performed with anhydrous Me_3NO in CH_3CN. The proton (or hydrogen) sources for the resulting dienes **9a** and **10a** were presumbly from either CH_3CN or other reactants.[8] Although the mechanism of hydrodemetalation is not clear at the present stage, it is a reliable tool for the synthesis of a variety of oxa- and azacyclic dienes **16**−**21** as shown in Table 1. The hydrodemetalations of tungsten-η^1-heterocyclic dienes **11**−**15** and **8** were performed exclusively with anhydrous Me_3NO in CH_3CN according to the preceding procedures. The tungsten-η^1-oxacyclic dienes **11**−**15** were prepared from the corresponding tungsten-η^1-α,δ- or −α,ϵ-alkynols and aldehydes according to the synthetic protocol shown in Scheme 2; the yields exceeded 85% in most cases. Entries 1 and 2 show two additional examples for syntheses of 4,5-dihydrofuryl dienes **16** and **17**, and the yields were 58% and 55%, respectively. The Me_3NO-promoted hydrodemetalation is applicable for preparation of six-membered oxacycles including the electron-rich dienes **19** and **20**; the yields were reasonable (47−53% yields). No significant byproducts were found in entries 3−5. In contrast, hydrodemetalation of tungsten-η^1-azacyclic species **8** yielded 4,5-dihydropyrrole **21** (46% yield) in addition to unsaturated γ-lactam **22** (37% yield).

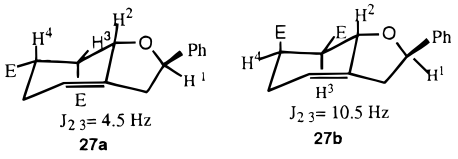
(8) We have performed hydrodemetalation of tungsten-η^1-oxacyclic diene **9** with anhydrous Me_3NO in CD_3CN, and mass analysis of the resulting oxacyclic diene **16** show the deuterium content ca. 25%, indicating that CH_3CN is not the only source for hydrogen (or proton).

Table 2. Cycloadditions of Oxacyclic Diene 16

entry	olefins	react. cond.	products (yields)
1		toluene, 60 °C, 3h	 **23** (95%)
2		toluene, 60 °C, 6h	 **24** (88%)
3		toluene, 60 °C, 6h	 **25** (92%)
4	≡—COMe	toluene, 100 °C, 4h	 **26** (60%)
5	MeO_2C CO_2Me	toluene, 130 °C, 20h	 **a**(endo) **b**(exo) **27** (a/b =56/44, 45%))

Intermolecular Diels−Alder Reaction of 4,5-Dihydrofuryl Diene. Diels−Alder reaction of heterocyclic dienes **1**−**4** have been studied previously over the last two decades for the synthesis of complex heterocyclic compounds.[1−4] The heterocyclic dienes in these studies[1−4] have no substituents on the heterocyclic ring. Heterocyclic dienes **9a**−**10a** and **16**−**22** seem to be more challenging because additional diastereomeric products will form compared to previous studies. Table 2 shows [4 + 2]-cycloadditions for 4,5-dihydrofuryl diene **16** with a number of electron-deficient olefins. The cycloadditions of **16** with maleic anhydride and maleic imide (entries 1−3) proceeded with high diastereoselectivities, and only endo diastereomers **23**−**25** were formed in excellent yields. The stereochemistry of cycloadduct **23** was determined by an ^{1}H NMR NOE effect and further confirmed by X-ray diffraction study.[9] The ORTEP drawing suggests that maleic anhydride approaches the diene moiety in the endo face and opposite the phenyl substituent. One regioisomer is found for the cycloadduct **26** derived from 3-butyn-2-one. The reaction of **16** with dimethyl maleate proceeded very slowly, yielding a mixture of two diastereomers **27a** and **27b** in a 56/44 ratio, which were unseparable by preparative silica plate. The structures

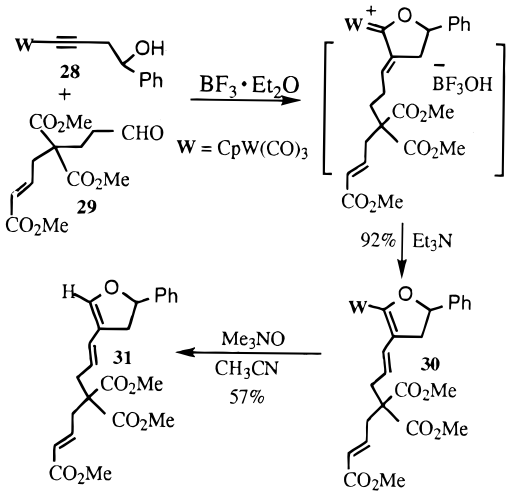
Scheme 5



of these two isomers are determined by an ^{1}H NMR NOE effect, which indicates that both isomers are produced by approach of the diene moiety opposite the phenyl group with **27a** assignable to the endo isomer and **27b** assignable to exo isomer. Diagnostic for the structures are the proton coupling constants J_{23} = 4.5 Hz and J_{23} = 10.5 Hz for **27a** and **27b**, respectively, indicative of axial−equatorial and axial−axial proton couplings. The reaction of oxacyclic diene **16** with less reactive olefins such as methyl vinyl ketone and methyl acrylate proceeded very sluggishly, and that four cycloadducts were formed in equal proportions. No further efforts were made for characterization of these cycloadducts.

Intramolecular Diels−Alder Reactions. The present method is also applicable to the synthesis of oxacyclic dienes bearing an electron-deficient olefin; these functionalized dienes can provide an easy entry to tricyclic oxacycles through intramolecular Diels−Alder reactions.[10] Synthesis of a representative compound **31** is given in Scheme 6. Treatment of tungsten-η^1-alkynol **28**

Scheme 6



with aldehyde **29** with $BF_3{\cdot}Et_2O$ in cold diethyl ether led to formation of insoluble precipitate, presumably oxacarbenium salt that was collected by filtration. Deprotonation of this salt with Et_3N (3.0 equiv) in CH_2Cl_2 delivered tungsten-η^1-oxacyclic diene **30** in 92% yield. Further hydrodemetalation of compound **30** with anhydrous Me_3NO in CH_3CN produced an organic diene **31** in 57% yield. Shown in Table 3 (entries 2−4) are the four oxacyclic dienes **32**−**35** bearing an unsaturated ester. Compounds **32**−**35** were obtained in 56−60% yields by Me_3NO-promoted hydrodemetalation of their corresponding tungsten-η^1-oxacyclic dienes.[11] A scheme showing this process is provided in the Supporting Information. Intramolecular Diels−Alder cycloadditions of these functionalized dienes **31**−**35** proceeded smoothly upon heating in toluene to give only one diastereomeric product **36**−**40** in good yields as shown in Table 3. Determination of the structures of these cycloadducts relied primarily from ^{1}H NMR NOE effect. The NOE-map of the representative compounds **36** is shown in Scheme 7. The NOE maps of the remaining compounds **37**−**40**[12] indicate that these four tricyclic oxacycles (entries 2−5) have trans-fused structures similar to that for compound **36**.

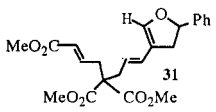
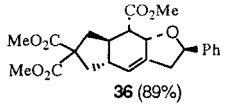
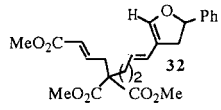
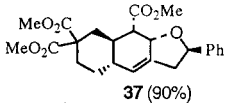
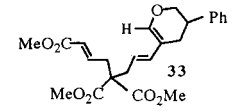
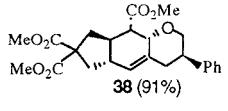
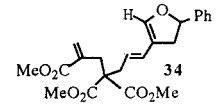
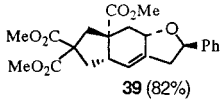
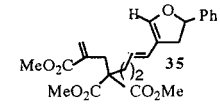
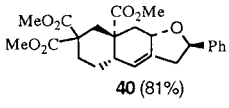
(9) Crystal data for **23**: monoclinic, space group $P2_1/n$, a = 9.1021(1) Å, b = 9.2417(1) Å, c = 17.6166(3) Å, β = 102.092(20)°, V = 1449.0(5) Å^3, Z = 4; final R = 0.0431 and R_w = 0.0466. The X-ray data of **23** is provided in the Supporting Information.

(10) Review article of intramolecular Diels−Alder reaction, see: Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, p 513.

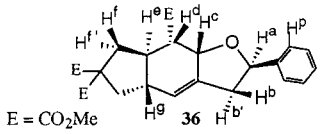
(11) Details in the syntheses of oxacyclic dienes **32**−**35** are provided in the Supporting Information.

(12) The NOE maps of the compounds **37**−**40** are given in the Experimental Section.

Table 3. Synthesis of Tricyclic Oxacycles via Intramolecular Diels–Alder Reaction

entry	olefins	react. cond.	products (yields)
1	 **31**	toluene, 110 °C, 2h	 **36** (89%)
2	 **32**	toluene, 110 °C, 2h	 **37** (90%)
3	 **33**	toluene, 110 °C,2h	 **38** (91%)
4	 **34**	toluene, 120 °C, 3h	 **39** (82%)
5	 **35**	toluene, 120 °C, 4h	 **40** (81%)

Scheme 7

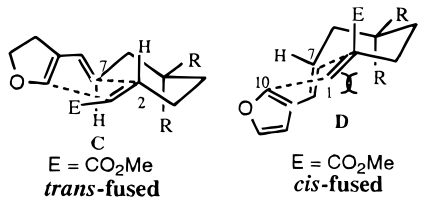


E = CO_2Me **36**

irradiation	intensities increase
H^a	$H^{b'}$(4.8%), H^p(3.1%), H^c(0 %), H^b(0 %),
H^c	H^d(12.5%), H^p(2.0%),
H^d	H^c(11.5%), H^e(0%)
H^e	$H^{f'}$(8.9%), H^g(0 %), H^d(0 %),
H^g	H^f(6.2%), H^e(0 %), H^d(2.4 %),

Intramolecular Diels–Alder cycloadditions have been studied extensively,[12–16] and stereoselection of cis- or trans-fused products depends on both electronic and steric effects. Scheme 8 shows the two transition states

Scheme 8



C E = CO_2Me ***trans*-fused**

D E = CO_2Me ***cis*-fused**

C and **D** for cis- and trans-fused stereoselections for decatriene according to the Houk's concept of "twist asynchronicity".[13] In this concept, stereoselection is controlled by the timing of bond formation in the transition state. A generally accepted interpretation is that a terminally activating group CO_2Me on decatriene prefers trans-fused stereoselection because of the polarization effect of the double bond, which enhances the interaction of the C(2)- and C(7)-carbons.[14–16] This model accounts well for the observed trans-stereoselection for intramolecular cycloaddition of the nona- and decatrienes **31**–**33**. On the other hand, an internal activating group CO_2Me on decatriene-like state **D** generally prefers cis-fused products because it increases the C(1) coefficient of the LUMO orbital to enhance its C(1)–C(10) interaction;[14–16] this speculation contradicts with our observations (entries 4 and 5, Table 3). We envision that the trans selectivities of cycloadducts **39** and **40** may have two reasons according to related studies in the literatures.[15,16] First, two substituents (R=CO_2Me) at the C(5)-carbon destabilizes the structure of state **E** through increasing steric interaction with the axial C(7)=C(8) bond.[17] Furthermore, the C(10)-oxygen atom is expect to decrease the C(10) coefficient of the diene HOMO orbital to make the C(1)–C(10) interaction less pronounced,[18] diminishing the preference for cis-stereoselection.

Conclusion. In this study, we have successfully developed a short and convenient synthesis of functionalized oxa- and azacyclic dienes based on cycloalkenations of alkynyltungsten compounds. The key step in the syntheses is the dehydrodemetalation of tungsten-heterocyclic dienes via treatment with anhydrous Me_3NO in CH_3CN. This method is applicable to the syntheses of oxacyclic dienes including those tethered with an electron-deficient olefin. Intramolecular Diels–Alder reactions of these oxacyclic trienes afforded tricyclic furan and pyran derivatives with high diastereoselectivities.

Experimental Section

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, sodium, dicyclopentadiene, propargyl bromide, methanesulfonamide, *p*-toluenesulfoamide, and benzaldehyde were obtained commercially and used without purification. Spectral data of compounds **9**, **9b**, **9c**, **10**, **11**, and **28** were published previously.[5,7] Spectral data of compounds **10**, **10a**, **13**–**22**, **24**–**27**, and **32**–**35** in repetitive experiments are provided in the Supporting Information.

Tungsten-η^1-4-phenyl-4-tosylaminobut-1-yne (6). To a diethylamine solution (25 mL) of $CpW(CO)_3Cl$ (3.00 g, 8.15 mmol) and CuI (0.16 g, 0.82 mmol) was added 4-phenyl-3-tosylamino-1-butyne (2.31 g, 7.74 mmol), and the mixture was stirred at 23 °C for 6 h. The solution was concentrated to ca. 3.0 mL and eluted through a silica column to yield a yellow band that afforded compound **6** as a yellow solid (3.18 g, 5.03 mmol, 65%): IR (neat, cm^{-1}) ν(CO) 2027(vs), 1934(vs), $\nu(SO_2)$ 1349(s); ^1H NMR (300 MHz, $CDCl_3$) δ 7.10–7.56 (9H, m), 5.50 (5H, s), 5.31 (s, br s), 4.38 (1H, dd, J = 11.8, 4.9 Hz), 2.71 (2H, m, J = 15 Hz), 2.34 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.9, 212.2, 212.1, 142.9, 140.4, 137.5, 129.3, 127.9, 127.2, 127.0,

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(15) (a) Ichihara, A.; Miki, M.; Tazaki, H.; Sakamura, S. *Tetrahedron Lett.* **1987**, *28*, 1175. (b) Burke, S. D.; Piscopio, A. D.; Buchana, J. L. *Tetrahedron Lett.* **1988**, *29*, 2757. (c) Matikainen, J. K. T.; Kaltia, S. A. A.; Hase, T. A. *Tetrahedron Lett.* **1988**, *29*, 2685.

(16) (a) Marshall, J. A.; Audia, J. E.; Crote, J. *J. Org. Chem.* **1984**, *49*, 5277. (b) Marshall, J. A.; Audia, J. E.; Crote, J. *J. Am. Chem. Soc.* **1988**, *110*, 1290.

(17) Trost, B. M.; Lautens, M.; Hung, M.-H.; Carmichael, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 7641.

(18) (a) Burke, S. D.; Magnin, D. R.; Oplinger, J. A.; Baker, J. P.; Abdelmagid, A. *Tetrahedron Lett.* **1984**, *25*, 19. (b) Hashimoto, S.; Sakata, S.; Sonegawa, M.; Ikegami, S. *J. Am. Chem. Soc.* **1988**, *110*, 3760.

126.7, 122.5, 91.4, 63.9, 56.7, 31.3, 21.4; MS (EI, *m*/*z*) 631 (M^+), 603 ($M^+ - CO$), 547 ($M^+ - 3CO$). Anal. Calcd for $WC_{25}H_{21}SNO_5$: C, 47.54; H, 3.25; N, 2.23. Found: C, 47.54; H, 3.52; N, 2.29.

Tungsten-η^1-pyrrolylidenium Salt (7). To a diethyl ether solution of alkynyltungsten compound **6** (0.80 g, 1.27 mmol) at −78 °C were added acetaldehyde (1.0 mL) and $BF_3{\cdot}Et_2O$ (0.16 mL, 1.30 mmol), and the solution was warmed to 23 °C over a period of 8 h. During this period, a red precipitate of tungsten−η^1-azacyclic carbenium salt **7** was slowly deposited, collected by filtration, and washed with diethyl ether. The yield was 91% (0.86 g, 1.15 mmol): IR (neat, cm^{-1}) υ(CO) 1991(vs), 1920(s); ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C) δ anti-form, 7.50−6.90 (10H, m), 6.01 (5H, s), 4.89 (1H, dd, J = 9.4, 4.9 Hz), 3.63 (1H, dd, J = 15.9, 9.4 Hz), 2.74 (1H, dd, J = 15.9, 4.9 Hz), 2.65 (3H, s), 2.10 (3H, d, J = 6.3 Hz), syn-form, δ 7.50−6.90 (10H, m), 6.06 (5H, s), 5.39 (1H, dd, J = 9.4, 4.9 Hz), 3.48 (1H, dd, J = 15.9, 9.4 Hz), 3.10 (1H, dd, J = 15.9, 4.9 Hz), 2.35 (3H, s), 2.10 (3H, d, J = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, −30 °C) anti-form δ 259.9, 235.5, 230.2, 228.5, 152.6, 150.1, 148.4, 147.3, 136.9, 131.2, 129.4, 127.9, 127.2, 126.8, 94.8, 69.6, 38.2, 22.3, 18.4, syn-form δ 262.0, 235.5, 234.6, 231.5, 152.7, 146.3, 146.1, 130.1, 128.9, 128.4, 127.6, 127.0, 124.2, 94.4, 69.2, 37.4, 21.9, 18.7. Anal. Calcd for $C_{27}H_{24}WSNO_6BF_3$: C, 43.66; H, 3.26; N, 1.89. Found: C, 43.61; H, 3.25; N, 1.86.

CpW(CO)$_3$(η^1-1-tosyl-3-vinyl-5-phenyl-4,5-dihydropyrrol-2-yl) (8). To a CH_2Cl_2 solution of azacyclic carbenium salt **7** (0.30 g, 0.40 mmol) was added Et_3N (0.081 mL, 0.80 mmol) at 0 °C, and the mixture was stirred for 1 h. The residues were chromatographed through a short alumina column to give a yelow band to afford **8** as a yellow solid (0.23 g, 0.36 mmol, 89%): IR (neat, cm^{-1}): υ(CO) 2025(vs) 1922(s), $\upsilon(SO_2)$ 1332-(s); ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C) anti-form δ 7.04−7.40 (9H, m, 2 Ph), 6.50 (1H, dd, J = 17.0, 10.8 Hz), 5.58 (5H, s), 5.30 (1H, dd, J = 8.3, 7.5 Hz), 5.14 (1H, d, J = 10.8 Hz), 5.01 (1H, d, J = 17.1 Hz), 3.30 (1H, m, J = 8.3 Hz), 2.87 (3H, s), 2.51 (1H, d, J = 7.5 Hz), syn-form 7.12−7.47 (5H, m), 6.43 (1H, dd, J = 17.4, 10.7 Hz), 5.69 (5H, s), 5.30 (1H, overlapped with that of anti isomer), 5.08 (2H, m), 3.16 (1H, m), 2.82 (3H, s), 2.69 (1H, m); MS (EI, *m*/*e*) 657. Anal. Calcd for $C_{27}H_{23}WNSO_5$: C, 49.31; H, 3.53. Found: C, 49.04; H, 3.66.

3-Vinyl-5-naphthyl-4,5-dihydrofuran (9a). To a CH_3CN solution (5.0 mL) of tungsten-4,5-dihydrofuryl **9** (400 mg, 0.72 mmol) was added anhydrous Me_3NO (229 mg, 3.60 mmol), and the mixture was stirred for 2 h. To this solution was added saturated NH_4Cl (3.0 mL), and the organic layer was extracted with diethyl ether, eluted through a preparative silica plate to give compound **10a** as a colorless oil (95.5 mg, 0.43 mmol, 61%): IR (neat,cm^{-1}) υ(C=C) 1651 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.48 (7H, m), 6.65 (1H, s), 6.55 (1H, dd, J = 17.3, 10.5 Hz), 5.78 (1H, dd, J = 10.5, 8.4 Hz), 4.91 (1H, d, J = 10.5 Hz), 4.83 (1H, d, J = 17.3 Hz), 3.24 (1H, dd, J = 14.2, 10.5 Hz), 2.80 (1H, dd, J = 14.2, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 139.7, 133.2, 133.1, 128.7, 128.6, 128.0, 127.7, 126.2, 126.0, 124.5, 123.6, 116.4, 110.2, 83.9, 37.2; Mass (EI, *m*/*e*) 222 (M^+); HRMS calcd for $C_{16}H_{14}O$ 222.1045, found 222.1041.

Cycloaddition of Oxacyclic Diene 16 with Maleic Anhydride. To a toluene solution of compound **16** (46 mg, 0.25 mmol) was added maleic anhydride (26 mg, 0.27 mmol), and the solution was heated for 60 °C for 3 h. The solution was dried in vacuo and eluted through a preparative silica plate to yield **23** as a colorless solid (66 mg, 0.23 mmol, 95%): IR (neat, cm^{-1}) υ(C0) 1753 (w), υ(C=C) 1673 (w); ^{1}H NMR (300 MHz,$CDCl_3$) δ 7.34 (5H, m), 5.61 (1H, s), 5.13 (1H, dd, J = 9.1, 6.4 Hz), 4.67 (1H, d, J = 8.8 Hz), 3.74 (1H, t, J = 8.8 Hz), 3.20 (1H, d, J = 8.8, 6.2 Hz), 2.90 (1H, dd, J = 14.4, 6.4 Hz), 2.63 (1H, dd, J = 14.4, 9.1 Hz), 2.44 (1H, m),1.45 (3H, d, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0, 169.4, 142.5, 141.0, 128.4, 127.9, 126.0, 123.5, 82.0, 74.8, 45.2, 45.0, 37.9, 30.6,16.8; HRMS (*m*/*z*) calcd for $C_{17}H_{16}O_4$ 284.1049, found 284.1047.

CpW(CO)$_3$[η^1-trimethyl(1*E*,6*E*)-7-(5-phenyl-4,5-dihydrofuran-3-yl)hepta-1,6-diene-1,4,4-tricarboxylate] (30). To a diethyl ether solution (20 mL) of tungsten-η^1-alkynol **28** (711 mg, 1.49 mmol) were added aldehyde **29** (512 mg, 1.79 mmol) and $BF_3{\cdot}Et_2O$ (1.22 mL, 1.79 mmol) at −60 °C, and the mixture was stirred for 8 h. The solution was warmed to 23 °C, and the resulting orange precipitates (937 mg, 96%) were collected by filtration. The solids were redissolved in CH_2Cl_2 (10 mL) and treated with Et_3N (1.03 mL, 7.45 mmol). The solution was evaporated to dryness and eluted through a basic Al_2O_3 column to yield tungsten-η^1-4,5-dihydrofuryltriene **30** (899 mg, 1.21 mmol, 92%): IR (neat, cm^{-1}) 2025 (s), 1927 (s), 1726 (s), 1601 (m), 1498 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.18 (5H, m), 6.77 (1H, dt, J = 15.0, 7.6 Hz), 6.07 (1H, d, J = 15.0 Hz), 5.82 (1H, d, J = 15.8 Hz), 5.55 (5H, s), 5.39 (1H, dd, J = 10.4, 7.4 Hz), 4.79 (1H, dt, J = 15.8, 7.5 Hz), 3.65 (9H, s), 3.00 (1H, dd, J = 14.2, 10.4 Hz), 2.73−2.67 (4H, m), 2.46 (1H, dd, J = 14.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 227.2, 215.8, 170.7, 166.1, 150.5, 144.3, 143.0, 132.7, 128.2, 127.8, 127.0, 125.2, 124.3, 115.3, 91.7, 83.7, 57.8, 52.3, 51.2, 39.9, 37.0, 35.0. MS (EI, *m*/*e*) 746 (M^+). Anal. Calcd for $C_{31}H_{30}WO_{10}$: C, 49.88; H, 4.05. Found: C, 49.89; H, 4.03.

Trimethyl(1*E*,6*E*)-7-(5-phenyl-4,5-dihydrofuran-3-yl)-hepta-1,6-diene-1,4,4-tricarboxylate] (31). To a CH_3CN (10 mL) solution of compound **30** (113 mg, 0.15 mmol) was added Me_3NO (45.6 mg, 0.61 mmol), and the mixture was stirred for 3 h before a saturated NH_4Cl solution was added. The organic layer was extracted with diethyl ether and eluted through a preparative silica gel column to yield compound **31** as a colorless oil (35 mg, 0.090 mmol, 57%): IR (neat, cm^{-1}) 2954 (w), 1731 (s), 1436 (m), 1267 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.19 (5H, m), 6.74 (1H, dt, J = 16.1, 7.6 Hz), 6.47 (1H, s), 6.18 (1H, d, J = 15.3 Hz), 5.80 (1H, d, J = 16.1 Hz), 5.51 (1H, t, J = 9.4 Hz), 4.96 (1H, dt, J = 15.3, 7.6 Hz), 3.63 (3H, s), 3.04 (1H, t, J = 9.4 Hz), 2.69 (1H, d, J = 7.6 Hz), 2.62 (1H, d, J = 7.6 Hz), 2.57−2.55 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 165.9, 144.1, 142.7, 142.2, 128.5, 128.3, 127.5, 126.5, 124.4, 118.7, 114.8, 83.3, 57.5, 52.1, 51.3, 37.4, 36.4, 35.2; MS (EI, *m*/*e*) 414 (M^+); HRMS(EI) calcd for $C_{23}H_{26}O_7$ 414.1679, found 414.1676.

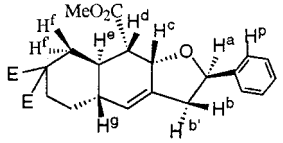
Trimethyl (1*E*,6*E*)-7-(5-Phenyl-4,5-dihydrofuran-3-yl)-hepta-1,6-diene-1,3,3-tricarboxylate (32). This compound was prepared according to a procedure similar to that for **31**; the yield was 57%: IR (neat, cm^{-1}) 2953 (w), 2917 (w), 1731 (s), 1435 (w), 1266 (w), 1171 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29−7.20 (5H, m), 6.73 (1H, dt, J = 15.5, 7.8 Hz), 6.45 (1H, s), 6.14 (1H, d, J = 15.5 Hz), 5.83 (1H, d, J = 15.5 Hz), 5.51 (1H, dd, J = 10.7, 8.1 Hz), 5.16−5.12 (1H, m), 3.65 (3H, s), 3.64 (6H, s), 3.07 (1H, dd, J = 13.3, 10.7 Hz), 2.75 (1H, d, J = 8.2 Hz), 2.60 (1H, dd, J = 13.3, 8.1 Hz), 1.96−1.89 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 165.9, 143.1, 142.5, 142.4, 128.3, 127.5, 125.3, 124.9, 124.4, 122.7, 114.8, 83.0, 56.8, 52.3, 51.3, 37.5, 35.3, 32.5, 27.2; MS (EI, 75 *m*/*e*) 428 (M^+); HRMS (EI) calcd for $C_{24}H_{28}O_7$ 428.1835, found 428.1837.

Trimethyl (2*R,4a*S**,7a*R**,8*S**,8a*S**)-2-Phenyl-3,4a,5,6,7,-7a,8,8a-octahydro-2*H*-indeno[5,6-*b*]furan-6,6,8-tricarboxylate (36).** A toluene solution of compound **31** (35 mg, 0.090 mmol) was heated for 60 °C for 3 h. The solution was dried in vacuo and eluted through a preparative silica plate to yield **36** as a colorless solid (32 mg, 0.082 mmol, 92%): IR (neat, cm^{-1}) 2953 (w), 2926 (w), 2854 (w), 1732 (s), 1436 (m), 1266 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.25 (5H, m), 5.85 (1H, d, J = 2.1 Hz), 4.93 (1H, dd, J = 9.6, 6.0 Hz), 4.74 (1H, d, J = 8.8 Hz), 3.72 (3H, s), 3.71 (3H, s), 3.70 (3H, s), 2.89 (1H, dd, J = 10.8, 8.8 Hz), 2.87 (1H, dd, J = 14.0, 6.0 Hz), 2.72−2.64 (2H, m), 2.57 (1H, dd, J = 14.0, 9.6 Hz) 2.15−2.04 (1H, m), 1.97 (1H, t, J = 12.8 Hz), 1.96−1.89 (1H, m), 1.84 (1H, t, J = 12.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.5, 172.3, 142.8,140.3, 128.3, 127.2, 125.3, 122.6, 80.0, 74.2, 59.4, 52.7, 51.6, 49.1, 44.0, 42.0, 38.8, 37.9, 37.8; MS (EI, 75 eV, *m*/*e*) 414 (M^+); HRMS (EI) calcd for $C_{23}H_{26}O_7$ 414.1679, found 414.1677.

Trimethyl (2*R,4a*S**,8a*R**,9*S**,9a*S**)-2-Phenyl-2,3,4a,-5,6,7,8,8a,9,9a-decahydronaphtho[2,3-*b*]furan-7,7,9-tricarboxylate (37).** This compound was prepared similarly by heating **32** in toluene; the yield was 90%: IR (neat, cm^{-1}) 2953 (w), 1732 (s), 1450 (m), 1435 (m), 1253 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.20 (5H, m), 5.47 (1H, d, J = 1.7 Hz), 4.90 (1H, dd, J = 9.2, 6.0 Hz), 4.54 (1H, d, J = 9.0 Hz), 3.74 (3H,

s), 3.65 (3H, s), 3.64 (3H, s), 2.84−2.76 (2H, m), 2.58−2.45 (3H, m), 2.31−2.21 (1H, m), 1.95 (1H, dd, J = 12.3, 8.5 Hz), 1.72−1.34 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 172.4, 171.0, 142.9, 139.4, 128.3, 127.3, 125.7, 124.5, 80.1, 73.3, 55.3, 52., 52.6, 51.6, 51.3, 39.3, 37.5, 37.5, 36.5, 30.9, 29.1; MS (EI, 75 eV, *m/e*) 428 (M^+); HRMS (EI) calcd for $C_{24}H_{28}O_7$ 428.1835, found 428.1833.

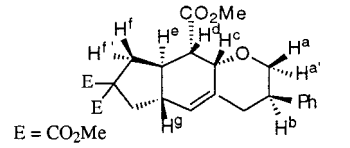
^{1}H-NOE-map of compound 37



irradiation	intensities increase
H^a	$H^{b'}$(8.5%), H^p(2.9%), H^c(0 %), H^b(1.5 %),
H^c	H^d(10.8%), H^p (1.9%), H^a(0 %)
H^d	H^c(11.2%), H^e(0%), H^g (2.0%)
H^e	$H^{f'}$(8.9%), H^g(0 %), H^d(0 %),
H^g	H^f (2.2%), H^e(0 %), H^d(2.4 %),

Trimethyl 3-Phenyl-3,4,5a,6,8,8a,9,9a-octahydrocyclopenta[*g*]chromene-7,7,9(2*H*)-tricarboxylate (38). This compound was prepared similarly by heating **33** in toluene; the yield was 91%: IR (neat, cm^{-1}) 2916 (w), 2848 (w), 1734 (s), 1464 (w), 1257 (w); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31−7.11 (5H, m), 5.29 (1H, s), 4.13 (2H, m), 3.98 (1H, dd, J = 12.0, 2.4 Hz), 3.66 (3H, s), 3.66 (3H, s), 3.65 (3H, s), 2.94 (1H, br), 2.88 (1H, dd, J = 12.4, 6.0 Hz), 2.81 (1H, m), 2.73 (1H, dd, J = 12.0, 6.0 Hz), 2.41 (1H, dd, J = 12.4, 6.0 Hz), 2.28 (1H, d, J = 10.8 Hz), 2.07−1.93 (2H, m), 1.85 (1H, t, J = 12.4 Hz), 1.71 (1H, t, J = 10.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 172.7, 171.8, 144.3, 133.6, 128.2, 127.3, 126.1, 125.0, 75.9, 71.9, 58.8, 52.5, 51.4, 50.9, 43.6, 42.5, 40.3, 39.8, 38.3, 37.8; MS (EI, 75 eV, *m/e*) 428 (M^+); HRMS (EI) calcd for $C_{24}H_{28}O7$ 428.1835, found 428.1837.

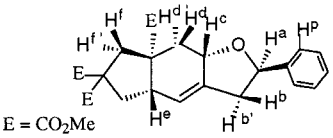
^{1}H-NOE-map of compound 38



irradiation	intensities increase
H^a	H^c(2.9%), $H^{a'}$(22.3%), H^b(0 %)
$H^{a'}$	H^b(6.8%), H^a(23.1%),
H^c	H^d(6.2%), H^a(2.0%),
H^d	H^c(5.2%), H^e (0%)
H^e	H^d (0%), H^g (0%)
H^g	H^e (0%), H^d(2.2 %),

Trimethyl (2*R,4a*S**,7a*R**,8a*S**)-2-Phenyl-3,4a,5,6,7,-7a,8,8a-octahydro-2*H*-indeno[5,6-*b*]furan-6,6,7a-tricarboxylate (39).** This compound was prepared similarly by heating **34** in toluene; the yield was 82%: IR (neat, cm^{-1}) 2958 (w), 1647 (w), 1600 (m), 1440 (w), 1233 (w); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.15 (5H, m), 5.48 (1H, d, J = 2.5 Hz), 4.91 (1H, dd, J = 9.4, 6.2 Hz), 4.27−4.25 (1H, m), 3.66 (3H, s), 3.66 (3H, s), 3.65 (3H, s), 3.18−3.13 (1H, br), 2.90 (1H, d, J = 14.6 Hz), 2.83 (1H, dd, J = 14.5, 6.2 Hz), 2.67−2.54 (2H, m), 2.53 (1H, dd, J = 14.5, 9.4 Hz), 2.65 (1H, d, J = 14.6 Hz), 2.00 (1H, t, J = 13.0 Hz), 1.46 (1H, t, J = 11.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 171.8, 171.5, 142.7, 140.4, 128.4, 127.5, 125.8, 119.0, 79.9, 74.5, 60.1, 52.9, 52.8, 52.4, 50.3, 45.0, 41.2, 40.2, 40.1, 37.2; MS (EI, *m/e*) 414 (M^+); HRMS (EI) calcd for $C_{23}H_{26}O_7$ 414.1679, found 414.1675.

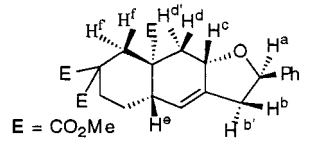
^{1}H-NOE-map of compound 39



irradiation	intensities increase
H^a	$H^{b'}$(8.9%), H^p(2.3%), H^c(0 %), H^b(1.6 %),
H^c	H^d(10.8%), H^p (1.9%), $H^{d'}$(1.4 %)
H^d	H^c(8.2%), $H^{d'}$ (26.6%), OMe (0%)
$H^{d'}$	H^d (27.9%), H^c(0 %), OMe(2.0 %),
H^e	H^f (2.3%), H^d(2.0 %),

Trimethyl (2*R,4a*S**,8a*R**,9a*S**)-2-phenyl-2,3,4a,5,6,7,8,-8a,9,9a-decahydronaphtho[2,3-*b*]furan-7,7,8a-tricarboxylate (40):** IR (neat, cm^{-1}) 2950 (w), 1731 (s), 1450 (m), 1434 (m), 1245 (m); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26−7.17 (5H, m), 5.44 (1H, d, J = 1.7 Hz), 4.84 (1H, dd, J = 9.3, 6.3 Hz), 4.28−4.26 (1H, m), 3.73 (3H, s), 3.63 (3H, s), 3.63 (3H, s), 2.71 (1H, dd, J = 14.1, 6.3 Hz), 2.62−2.57 (1H, m), 2.53 (1H, dd, J = 14.4, 2.1 Hz), 2.49−2.47 (1H, m), 2.35 (1H, ddd, J = 14.1, 5.5, 2.5 Hz), 2.27 (1H, dd, J = 11.9, 5.8 Hz), 2.12 (1H, d, J = 14.4 Hz), 1.75 (1H, ddd, J = 14.1, 8.2, 3.9 Hz), 1.56−1.44 (2H, m), 1.35 (1H, dd, J = 11.9, 10.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 172.1, 171.4, 143.1, 137.2, 128.4, 127.4, 125.7, 122.9, 79.9, 74.9, 52.9, 52.6, 52.3, 45.4, 40.1, 38.8, 36.4, 31.8, 30.4, 26.8; MS (EI, 75 eV, *m/e*) 428 (M^+); HRMS (EI) calcd for $C_{24}H_{28}O_7$ 428.1835, found 428.1834.

^{1}H-NOE-map of compound 40



irradiation	intensities increase
H^a	$H^{b'}$(5.5%), H^c(0 %), H^b(0 %),
H^c	H^d(5.8%), H^a (0%),
H^d	H^c(6.2%), H^e (2.0%), $H^{d'}$ (22.4%)
H^e	H^f (2.0%), H^d(2.3 %),

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Supporting Information Available: Syntheses and spectral data of compounds **10**, **10a**, **13**−**22**, **24**−**27**, and **32**−**35** in repetitive experiments; tables of crystal data, atomic coordinates, bond distances and angles of compound **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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