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Efficient and regioselective chromium(0)-catalyzed reaction of 2-substituted furans with diazo compounds: stereoselective synthesis of (2E,4Z)-2-aryl-hexadienedioic acid diesters ☆

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Dedicated to Professor Christoph Elschenbroich on the occasion of his 65th birthday

Abstract

Pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) catalyzes efficiently reactions of diazo compounds with electron-rich furans. The reaction of 2-methoxyfuran (**2**) with alkyl α-diazoarylacetate (**3a–g**) furnishes the (2E,4Z)-2-aryl-hexadienedioic acid diesters (**4a–g**) in excellent yields. These reactions are highly regioselective. The cyclopropanation intermediates formed from **1** and diazo compounds **3a–g** always arise from a carbene addition to the less substituted C=C bond of **2**. The resulting cyclopropanation product undergoes a ring opening reaction to form the corresponding (2E,4Z)-2-aryl-hexadienedioic acid diesters (**4a–g**). The pentacarbonylchromium(0)-catalyzed reactions of 2-alkylfuran (**5a–b**) with ethyl α-diazophenylacetate (**3a**) and 9-diazo-9H-fluorene (**3h**) produce the 1(E),3(E)-butadienes (**6a–d**) in very good yields.
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Keywords: Diazo compounds; Cyclopropanation; Ring opening reaction; Chromium; Catalysis; Carbene complexes

1. Introduction

The catalytic decomposition of diazo compounds provides a straightforward method for generating reactive carbenes which are very useful intermediates in organic synthesis, e.g., for CH-insertions, OH-insertions, cyclopropanations of olefins and *Buchner* reactions [2]. Especially the cyclopropanation of olefins using the transition metal-catalyzed decomposition of diazo compounds is a powerful and extensively studied process in the chemist's arsenal of synthetic reactions [3]. The cy-

clopropanations can be performed in an either intermolecular way or intramolecular [4] way.

The metal-catalyzed cyclopropanation of enol ethers with α-diazo carbonyl compounds and their application in natural product synthesis [5] has been intensively studied. It became of interest to investigate these reactions with aromatic enol ethers such as furans. These extensive studies of a dirhodium tetraacetate-catalyzed reaction of furan with ethyl diazoacetate revealed that this kind of reaction only furnishes a complex product mixture containing a heterocycle **A**, ring-opened products **B**, **C** and cyclopropane **D** (Scheme 1) [6].

The two dienes **B**, **C** are formed in an oxygen-assisted ring-opening process (Scheme 2). It is remarkable that this crude reaction mixture undergoes an iodine-induced
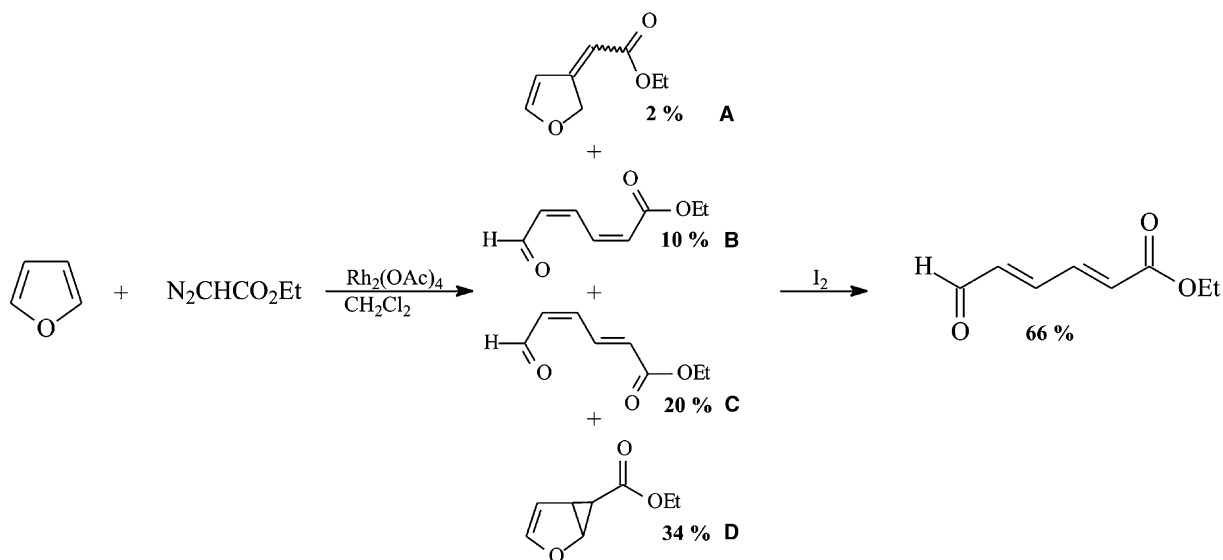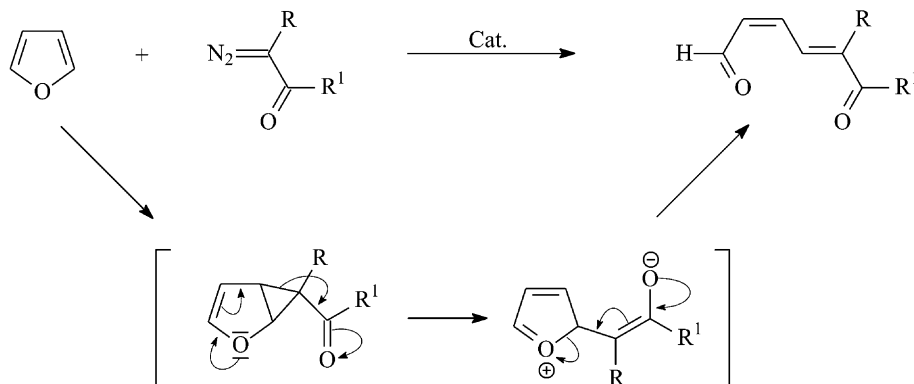

Scheme 1. Dirhodium tetraacetate-catalyzed reaction of furan with ethyl diazoacetate.

Scheme 2. Proposed mechanism of the transition metal-catalyzed reaction of furan with diazo compounds.

product isomerization process yielding (*E*,*E*)-dienes. It offers therefore an elegant "one-pot" reaction for the preparation of such dienes which are used for the synthesis of a number of natural products [7] and heterocyclic systems [8].

The intramolecular version of this transition metal-catalyzed reaction has also been described with compounds containing furan and diazo moieties producing highly functionalized ring systems [9].

The product formation depends on the electronic properties of the substituent at the 2-position in the furan ring. Electron-withdrawing substituents inhibit the ring-opening reaction and allow for the isolation of the cyclopropane products [10]. On the other hand, an electron-rich substituent favors the ring-opening reaction after cyclopropanation. The cyclopropanation process itself seems not to be affected by the electronic properties of the substituent.

This trend is typically observed in the different reaction behaviour of 2-alkylfurans and 2-alkoxyfurans with ethyl diazoacetate under rhodium(II) acetate catalysis.

The first ones react to a product mixture with the 1,3-butadienes as major products [6] whereas the latter are converted completely to the ring-opened products [11].

Pentacarbonylchromium(0) fragments also catalyze the reaction of electron-rich olefins and electron-rich dienes with diazo compounds [1,12]. In this paper, we present a detailed study of the pentacarbonylchromium(0)-catalyzed reaction of diazo compounds with electron-rich furans which has been addressed only in rare examples, so far [6,11]. It represents an efficient regio- and stereoselective methodology for the direct construction of (2*E*,4*Z*)-2-aryl-hexadienedioic acid diesters (**4a–g**) and (2*E*,4*E*)-6-oxo-2-phenyl-octa-2,4-dienedioic acid esters (**6a–b**).

2. Results and discussion

In our initial studies we focused on the pentacarbonyl (η^2-*cis*-cyclooctene)chromium(0) (**1**)-catalyzed reaction of 2-methoxyfuran (**2**) with alkyl α-diazoarylacetates
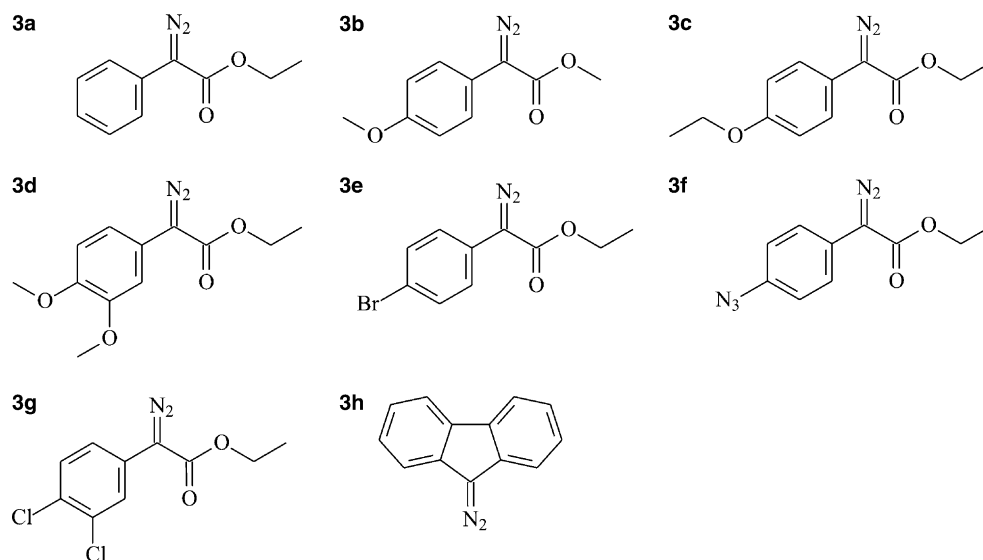
Scheme 3. Diazo compounds **3a–h** applied in the chromium-catalyzed reaction with 2-methoxyfuran (**2**).
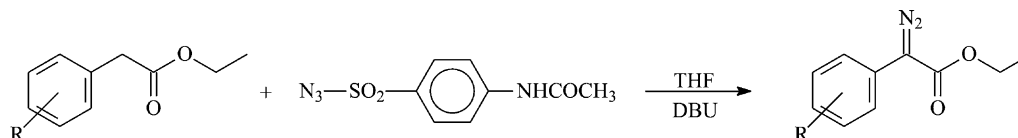
Scheme 4. Synthesis of the ethyl diazoarylacetates **3c–g**.

(**3a–g**), which differ in their electronic properties, and 9-diazo-9*H*-fluorene (**3h**) (Scheme 3).

The new ethyl diazoarylacetates **3c–g** had been prepared in good yields by a slightly modified protocol of a direct diazo transfer reaction established by Davies et al. [13] (Scheme 4).

The solvent has been changed from acetonitrile to THF due to an easier work-up, and the bulky diazabicyclo[5.4.0]undec-7-ene (DBU) base was added in THF over a period of 1 h at room temperature.

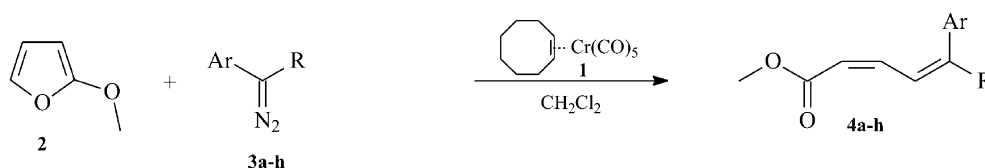### 2.1. Pentacarbonylchromium(0)-catalyzed reaction of 2-methoxyfuran (2) with diazo compounds 3a–h

A solution of the diazo compound **3a–h** in dichloromethane was added over a period of 2 h at 4 °C (**3h** was added at room temperature) to a solution of 2-methoxyfuran (**2**) (molar ratio **2/3a–h** = 2:1) and 2 mol% pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) [14] in dichloromethane, followed by stirring for another 8 h. The (2*E*,4*Z*)-isomers of the electron-poor dienes **4a–h** were obtained as single products in excellent yields (91–99%) after chromatographic work-up (Scheme 5).

In all reactions no side products like carbene dimers or azines could be detected within the accuracy of GC–MS, TLC or NMR spectroscopy in the crude reaction mixture. The configuration of the *E,Z*-dienes was

assigned on the basis of ^{1}H NMR. The double bond hydrogen atoms H-3, H-4 and H-5 of the (2*E*,4*Z*)-isomers reveal characteristic chemical shifts. Especially, H-3 resonating at roughly $\delta = 8.95$ ppm has a strong downfield chemical shift. The $^3J_{HH}$-coupling constants for all double bond protons are ≈ 11.6 Hz. This certifies the *Z*-configuration at the double bond 4-position. It is necessary for the assignment of the configuration of the other double bond to perform a NOESY NMR-experiment. A significant NOE-signal is observable between the *ortho* aromatic proton and H-4 proton for all products. This conclusion has been independently confirmed by a X-ray crystallographic analysis of suitable crystals of compound **4b** (Fig. 1, Table 1).

The crystal structure of **4b** shows that all bond lengths are within the common range of bond lengths for electron-poor 1,4-disubstituted conjugated dienes [15]. Interestingly a bifurcated intramolecular C–H···O hydrogen bonding between H-3 and O-1 and O-6 is observed (Fig. 1). The H···O-distance is in between 2.31 Å (C3–H3···O1) and 2.36 Å (C3–H3···O6) which is a normal distance for this type of bonding [16].

It is remarkable that the pentacarbonylchrom(0)-catalyzed carbene transfer from alkyl diazoarylacetates addresses the less substituted double bond of 2-methoxyfuran with virtually perfect regioselectivity. This is a further improvement compared to the results of

	R	Diazo	Diene	Yield [%]
1	CO$_2$Et		4a	98
2	CO$_2$Me	MeO—	4b	99
3	CO$_2$Et	EtO—	4c	98
4	CO$_2$Et	MeO— , MeO	4d	99
5	CO$_2$Et	Br—	4e	97
6	CO$_2$Et	N$_3$—	4f	91
7	CO$_2$Et	Cl— , Cl	4g	98
8			4h	98

Scheme 5. Reaction of diazo compounds **3a–h** with 2-methoxyfuran (**2**).

Wenkert et al. [6] who observed a regioselectivity of 19:1 in the dirhodium(II)-tetraacetate catalyzed reaction of 2-methylfurans with diazoacetic esters.

2-Methoxyfuran (**2**) reacted with diazo arylacetates (**3a–g**) selectively to the corresponding ring-opened products in quantitative yields. Neither the intermediate cyclopropanation product nor the (2E,4E) isomerization products were detectable in the crude reaction mixture by NMR spectroscopy, GC–MS or TLC. As previously mentioned, electron-rich substituents generally tend to support the ring-opening process. This rule has turned out to be also applicable to this reaction. A notable fact is the full *E*-selectivity in the formation of the new double bond. Ong and co-worker [11] also observed a high *E*-preference in the rhodium(II)-catalyzed reaction of 2-methoxyfuran (**2**) with α-diazoacetophenones.

2.2. Pentacarbonylchrom(0)-catalyzed reaction of 2-alkylfurans (5a,b) with diazo compounds 3a,h

Earlier studies in our group have demonstrated that unsubstituted furan is unreactive towards diazo
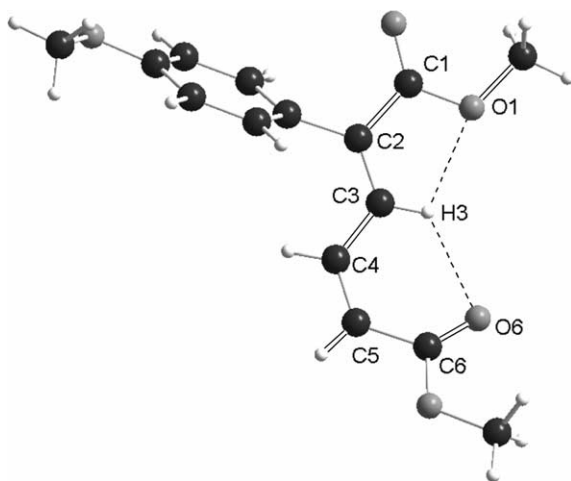
Fig. 1. Diamond plot of the molecular structure of (2*E*,4*Z*)-2-aryl-hexadienedioic acid ester (**4b**). Selected bond lengths (Å) and angles (°) (standard deviations are given in parentheses): C1–C2 1.5027(15), C2–C3 1.3492(16), C3–C4 1.4522(16), C4–C5 1.3447(16), C5–C6 1.4793(16), O1–C1–C2 112.98(9), C3–C2–C1 119.65(10), C2–C3–C4 123.87(10), C5–C4–C3 126.27(11), C4–C5–C6 126.13(10), O6–C6–C5 126.60(11), O1–C1–C2–C3 4.40(14), C1–C2–C3–C4 179.09(10), C2–C3–C4–C5 −170.57(12), C3–C4–C5–C6 0.7(2), C4–C5–C6–O6 −13.3(2). Hydrogen bonds: C3–H3···O1, 2.31; C3–H3···O6, 2.36.

compounds under chromium(0)-catalysis [17] Nevertheless, we present in this work the successful reaction of strong electron-rich (donating) substituted furans such as 2-methoxyfuran and diazo compounds **3a**–**h** to give the desired disubstituted dienes **4a**–**h**.
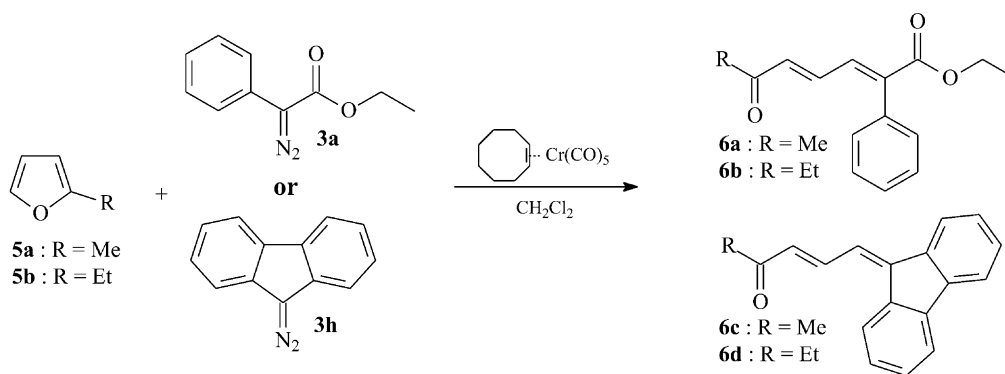
We examined further whether these promising results can be extended to the reaction of 2-alkyl substituted furans (**5a,b**). The diazo compounds ethyl α-diazo-phenyl-acetate (**3a**) and 9-diazo-9*H*-fluorene (**3h**) have been chosen as best suitable for this study, because of their well known characteristics and properties.

A solution of diazo compound **3a** or **3h** in dichloromethane was added at 4 °C (room temperature in the reaction with **3h**) over a period of 4 h to a solution of 2-alkylfuran (**5a,b**) (molar ratio **5a,b**/**3a** or **3h** = 2:1) and 2 mol% pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) in dichloromethane. The resulting mixture was stirred for a further 8 h. The (*E*,*E*)-isomers of the electron-poor dienes **6a**–**d** were obtained as single products in 72–88% yields after chromatographic work-up on silica gel (Scheme 6).

The analysis of the $^3J_{HH}$ coupling constants of H-4 and H-5 in combination with the data obtained in a

Table 1
Crystal data and structure refinement parameters of **4b** and **6d**

Compound	**4b**	**6d**
Methods	The molecular structure was solved by direct methods (SHELXS-97) [23]. The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97) [24]; hydrogen atoms were refined isotropically using a riding model	
Formula	$C_{15}H_{16}O_5$	$C_{19}H_{16}O$
M_r	276.29	260.32
T (K)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	12.9057(2)	15.2330(8)
b (Å)	5.7866(1)	5.5590(3)
c (Å)	18.4481(3)	16.6487(11)
α (°)	90	90
β (°)	102.311(1)	101.522(3)
γ (°)	90	90
V (Å^3)	1346.03(4)	1381.41(14)
Z	4	4
$\rho_{Calc.}$ (g cm^{-3})	1.363	1.252
μ (mm^{-1})	0.103	0.076
$F(000)$	584	552
Crystal size (mm)	0.20×0.15×0.10	0.30×0.08×0.04
Diffractometer	Nonius-κ CCD	Nonius-κ CCD
Radiation	Mo Kα	Mo Kα
θ Range for data collection (°)	3.05–27.48	3.31–25.02
Index range	$-16 \leqslant h \leqslant 16$; $-7 \leqslant k \leqslant 7$; $-23 \leqslant l \leqslant 23$	$-18 \leqslant h \leqslant 18$; $-6 \leqslant k \leqslant 6$; $-19 \leqslant l \leqslant 15$
Collected reflections	18 506	5631
Unique reflections	3072	2407
Parameters/restraints	181/0	181/0
Goodness-of-fit on F^2	1.066	0.873
$R(F)$ for $I > 2\sigma(I)$	0.0364	0.0405
$wR_2(F^2)$ for all data	0.1040	0.0850

	R	Diazo	Diene	Yield [%]
1	Me	3a	6a	78
2	Et	3a	6b	72
3	Me	3h	6c	86
4	Et	3h	6d	88

Scheme 6. Reaction of diazo compounds **3a,h** with 2-alkylfurans (**5a,b**).

NOESY-experiment suggests the formation of (2*E*,4*E*)-isomers. This assignment, which has been independently confirmed by a X-ray crystallographic analysis of suitable single crystals of compound **6d** (Fig. 2, Table 1), is surprising; the ring cleavage of the cyclopropane intermediates formed from 2-alkylfurans (**5a,b**) and (**3a**) under pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) catalysis is rather expected to give the (2*E*,4*Z*)-isomers.

The C4–C5 double bond which is derived from the β-C-atoms in the furan framework is expected to be retained in the *Z*-configuration [18]. However, a *E,E*-configuration is observed for dienes **6a–d** which may be rationalized in terms of an acid-induced isomerization during the chromatographic work-up of the crude reaction mixture on silica gel to give the thermodynamically more stable *trans*-isomer [19].

The crystal structure of **6d** shows a nearly perfect planarity of the molecule; all bond lengths and angles are within the common range for 1,4-disubstituted conjugated dienes.
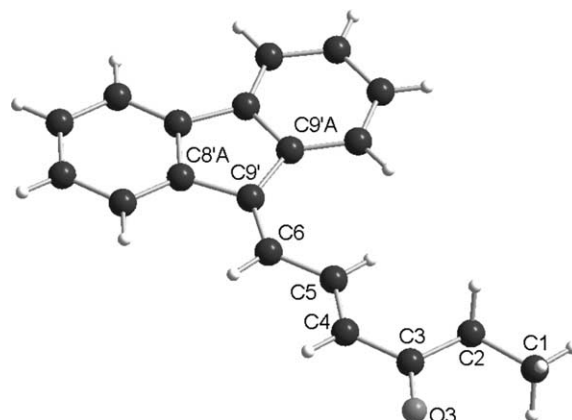

Fig. 2. Diamond plot of the molecular structure of (4*E*)-6-fluoren-9-ylidene-hex-4-en-3-one (**6d**). Selected bond lengths (Å) and angles (°) (standard deviations are given in parentheses): C3–C4 1.472(2), C4–C5 1.340(2), C5–C6 1.440(3), C6–C9′ 1.349(2), C9′–C9′A 1.484(3), C9′–C8′A 1.483(2), O3–C3–C2 121.05(16), C4–C3–C2 119.43(16), C5–C4–C3 125.57(17), C4–C5–C6 122.76(17), C9′–C6–C5 128.80(17), C2–C3–C4–C5 −0.2(3), C3–C4–C5–C6 −179.19(17), C5–C6–C9′–C8′A 175.85(17), C5–C6–C9′–C9′A −1.4(3).

3. Conclusions

The present approach reveals the first stereoselective and general high-yield route to (2E,4Z)-2-aryl-hexadienedioic acid diesters starting from 2-methoxyfuran and alkyl α-diazoarylacetates under pentacarbonyl-chromium(0) catalysis under mild reaction conditions. Furthermore, we established the first highly stereoselective synthesis of (E,E)-1,4-disubstituted dienes (**6a–d**) formed from 2-alkylfurans (**5a,b**) with the diazo compounds **3a,h** in high yields under chromium(0)-catalysis. In this work, we presented a new general method to build up 1,1,4-trisubstituted diene systems.

4. Experimental

4.1. General remarks

All reactions were performed in flame-dried glassware and under dry argon atmosphere. Dichloromethane was dried by distillation from calcium hydride and saturated with argon. Silica gel (E. Merck, grade 60, 0.062–0.200 mm) was used for column chromatography. FTIR spectra were recorded on Nicolet Magna 550. Melting-points were determined on Büchi SMP 20 (uncorrected). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 300, AVANCE 400 and DRX 500 instruments. All chemical shifts are given relative to TMS as external standard; δ in ppm, J in Hz. MS (EI) and HR–MS (EI): Kratos MS-50 and Thermoquest MAT 95 XL. GC–MS: Hewlett–Packard 5890 Series-II Gas Chromatograph with 5972 Series-Mass Selective Detector using of HP-5 column (crosslinked 5% PH ME Siloxane, 12 m×0.2 mm×0.33 μm), program: injection temperature 70 °C, heating rate 20 °C/min to 250 °C, hold for 1 min, then 50 °C/min to 280 °C, this was hold for 10 min – TLC: Merck precoated silica gel sheets, 60F$_{254}$.

4.2. Starting materials

Liquid starting compounds were degassed under vacuum and saturated with argon. Pentacarbonyl(η^2-*cis*-cyclooctene) chromium(0) (**1**) [14], ethyl α-diazo-phenyl- acetate (**3a**) [20], methyl α-diazo-(4′-methoxy-phenyl)-acetate (**3b**) [13] and 9-diazo-9*H*-fluorene (**3h**) [21], were prepared according to literature procedures. All other chemicals were used as received from commercial sources.

4.3. General procedure for the preparation of ethyl α-diazoarylacetates

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (4.1 ml, 27.5 mmol) in THF (20 ml) was added to a solution of the ethyl arylacetate (25 mmol) and *p*-acetamidobenzenesulfonylazide (*p*-ABSA) [22] (6.61 g, 27.5 mmol) in

THF (50 ml) over 1 h at room temperature. The reaction mixture was stirred for an additional 12 h, then quenched by addition of saturated aqueous ammonium chloride (50 ml). The aqueous layer was extracted with ethyl acetate (3×75 ml). The combined organic layers were washed with water (2×100 ml) and brine (75 ml), then dried over anhydrous magnesium sulphate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

4.3.1. Ethyl α-diazo-(4′-ethoxy-phenyl)-acetate (3c)

49% yield as a red oil. R_f = 0.38 (eluent: petroleum ether/ethyl acetate, 10:1). IR (film): ν = 3037 cm^{-1} (w, C–H), 2981 cm^{-1} (m, C–H), 2083 cm^{-1} (s, C=N$_2$), 1736 cm^{-1} (s, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.00 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_3$), 1.15 (t, 3H, $^3J_{HH}$ = 6.9 Hz, CH$_3$), 3.62 (q, 2H, $^3J_{HH}$ = 7.1 Hz, O–CH$_2$), 4.07 (q, 2H, $^3J_{HH}$ = 6.9 Hz, O–CH$_2$), 6.83 (d, 2H, $^3J_{HH}$ = 8.9 Hz, Ar–H), 7.42 (d, 2H, $^3J_{HH}$ = 8.9 Hz, Ar–H). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 14.4 (CH$_3$), 14.7 (CH$_3$), 60.7 (O–CH$_2$), 63.3 (O–CH$_2$), 115.4 (2×Ar–C), 117.2 (Ar–C$_q$), 126.0 (2×Ar–C), 157.8 (Ar–C$_q$), 165.2 (C=O). MS (70 eV), *m/z*: 234 (45) [M$^+$], 162 (100) [M$^+$ – N$_2$ – C$_2$H$_4$O], 149 (55) [M$^+$ – N$_2$ – C$_3$H$_5$O], 121 (50) [M$^+$ – N$_2$ – C$_3$H$_5$O – CO]. HR–MS: Calc. 234.1004. Found 234.1007 für [M$^+$].

4.3.2. Ethyl α-diazo-(3′,4′-dimethoxy-phenyl)-acetate (3d)

41% yield as a red crystals; m.p.: 81 °C. R_f = 0.27 (eluent: petroleum ether/ethyl acetate, 6:1). IR (film): ν = 3097 cm^{-1} (w, C–H), 2970 cm^{-1} (m, C–H), 2081 cm^{-1} (vs, C=N$_2$), 1693 cm^{-1} (s, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.00 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_3$), 3.44 (s, 3H, O–CH$_3$), 3.51 (s, 3H, O–CH$_3$), 4.08 (q, 2H, $^3J_{HH}$ = 7.1 Hz, O–CH$_2$), 6.64 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ar–H$_{5′}$), 6.92 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.2 Hz, Ar–H$_{6′}$), 7.31 (d, 1H, $^4J_{HH}$ = 2.2 Hz, Ar–H$_{2′}$). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 14.4 (CH$_3$), 55.6 (O–CH$_3$), 55.7 (O–CH$_3$), 60.7 (O–CH$_2$), 109.4 (Ar–C), 113.0 (Ar–C), 116.8 (Ar–C), 117.8 (Ar–C$_q$), 148.5 (Ar–C$_q$), 150.8 (Ar–C$_q$), 165.2 (C=O). MS (70 eV), *m/z*: 250 (35) [M$^+$], 178 (100) [M$^+$ – N$_2$ – C$_2$H$_4$O], 165 (60), [M$^+$ – N$_2$ – C$_3$H$_5$O], 137 (15) [M$^+$ – N$_2$ – C$_3$H$_5$O – CO]. HR–MS: Calc. 250.0953. Found 250.0947 für [M$^+$].

4.3.3. Ethyl α-diazo-(4′-bromo-phenyl)-acetate (3e)

58% yield as yellow crystals; m.p.: 54 °C. R_f = 0.47 (eluent: petroleum ether/diethyl ether, 8:1). IR (KBr): ν = 3080 cm^{-1} (w, C–H), 2985 cm^{-1} (m, C–H), 2096 cm^{-1} (s, C=N$_2$), 1697 cm^{-1} (s, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.94 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_3$), 3.99 (q, 2H, $^3J_{HH}$ = 7.1 Hz, O–CH$_2$), 7.14 (d, 2H, $^3J_{HH}$ = 8.8

Hz, Ar–H), 7.25 (d, 2H, $^3J_{HH} = 8.8$ Hz, Ar–H). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.3$ (CH_3), 60.9 (O–CH_2), 119.3 (Ar–C_q), 125.3 (Ar–C_q), 125.5 (2×Ar–C), 132.1 (2×Ar–C), 164.1 (C=O). MS (70 eV), m/z: 268 (35) [M^+], 196 (55) [$M^+ - N_2 - C_2H_4O$], 183 (100) [$M^+ - N_2 - C_3H_5O$], 155 (45) [$M^+ - N_2 - C_3H_5O - CO$]. HR–MS: Calc. 267.9847. Found 267.9852 für [M^+].

4.3.4. Ethyl α-diazo-(4′-azido-phenyl)-acetate (3f)

43% yield as red crystals; m.p.: 59 °C. $R_f = 0.41$ (eluent: petroleum ether/ethyl acetate, 8:1). IR (KBr): $v = 3059$ cm^{-1} (w, C–H), 2991 cm^{-1} (m, C–H), 2131 cm^{-1} (vs, $-N_3$), 2075 cm^{-1} (vs, C=N_2), 1691 cm^{-1} (s, C=O). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.96$ (t, 3H, $^3J_{HH} = 7.1$ Hz, CH_3), 4.02 (q, 2H, $^3J_{HH} = 7.1$ Hz, O–CH_2), 6.72 (d, 2H, $^3J_{HH} = 8.8$ Hz, Ar–H), 7.29 (d, 2H, $^3J_{HH} = 8.8$ Hz, Ar–H). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.3$ (CH_3), 60.9 (O–CH_2), 119.8 (2×Ar–C), 122.4 (Ar–C_q), 125.5 (2×Ar–C), 137.7 (Ar–C_q), 164.5 (C=O). MS (70 eV), m/z: 231 (100) [M^+], 203 (20) [$M^+ - N_2$], 131 (90) [$M^+ - N_2 - C_3H_5O - CO$]. HR–MS: Calc. 231.0756. Found 231.0769 für [M^+].

4.3.5. Ethyl α-diazo-(3′,4′-dichloro-phenyl)-acetate (3g)

56% yield as yellow crystals; m.p.: 76 °C. $R_f = 0.41$ (eluent: petroleum ether/diethyl ether, 10:1). IR (KBr): $v = 3099$ cm^{-1} (m, C–H), 2983 cm^{-1} (m, C–H), 2102 cm^{-1} (vs, C=N_2), 1689 cm^{-1} (s, C=O). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.94$ (t, 3H, $^3J_{HH} = 7.1$ Hz, CH_3), 3.97 (q, 2H, $^3J_{HH} = 7.1$ Hz, O–CH_2), 6.90 (dd, 1H, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.3$ Hz, Ar–H$_{6'}$), 7.02 (d, 1H, $^3J_{HH} = 8.6$ Hz, Ar–H$_{5'}$), 7.59 (d, 1H, $^4J_{HH} = 2.3$ Hz, Ar–H$_{2'}$). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.2$ (CH_3), 61.1 (O–CH_2), 122.8 (Ar–C), 125.5 (Ar–C), 126.7 (Ar–C_q), 129.4 (Ar–C_q), 130.4 (Ar–C), 133.4 (Ar–C_q), 163.7 (C=O). MS (70 eV), m/z: 258 (20) [M^+], 186 (40) [$M^+ - N_2 - C_2H_4O$], 173 (100) [$M^+ - N_2 - C_3H_5O$], 145 (40) [$M^+ - N_2 - C_3H_5O - CO$]. HR–MS: Calc. 257.9963. Found 257.9963 für [M^+].

4.4. General procedure for the chromium(0)-catalyzed reactions of diazo compounds 3a–h with 2-methoxyfuran (2)

A solution of the diazo compound 3a–h (3 mmol) in 20 ml CH_2Cl_2 was added over a period of 2 h at 4 °C (3h was added at room temperature) to a stirred solution containing 2 eq. 2-methoxyfuran (2) and 2 mol% of yellow cyclooctene complex 1 in 5 ml of CH_2Cl_2. Evolution of N_2 was accompanied by a colour change of the reaction mixture from yellow to orange, red or violet typical for the relevant chromium carbene intermediate. After stirring for a further 8 h followed by removal of the solvent under reduced pressure, work-up was performed by column chromatography.

4.4.1. (2E,4Z)-2-phenyl-hexa-2,4-dienedioic acid 1-ethyl-ester-6-methyl ester (4a)

Reaction of 3 mmol 3a (0.57 g) with 6 mmol 2 (0.59 g) in the presence of 1 (18 mg, 0.06 mmol, 2 mol%) gave 0.77 g (98%) of 4a after work-up (eluent: dichloromethane/petroleum ether, 4:1, $R_f = 0.28$) as an orange oil. GC–MS: $t_{Ret} = 9.32$ min – IR (film): $v = 3059$ cm^{-1} (m, C–H), 2983 cm^{-1} (s, C–H), 1705 cm^{-1} (b vs, C=O). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.94$ (t, 3H, $^3J_{HH} = 7.1$ Hz, CH_3), 3.37 (s, 3H, O–CH_3), 3.99 (q, 2H, $^3J_{HH} = 7.1$ Hz, O–CH_2), 5.60 (dd, 1H, $^3J_{HH} = 11.4$ Hz, $^4J_{HH} = 1.2$ Hz, H-5), 6.43 (dd, 1H, $^3J_{HH} = 11.4$ Hz, $^3J_{HH} = 11.6$ Hz, H-4), 7.05–7.2 (m, 5H, Ar–H), 8.98 (dd, 1H, $^3J_{HH} = 11.6$ Hz, $^4J_{HH} = 1.2$ Hz, H-3). ^{13}C NMR (75 MHz, C_6D_6): $\delta = 14.1$ (CH_3), 51.0 (O–CH_3), 61.2 (O–CH_2), 123.7(C-5), 133.9 (C-3), 139.3 (C-4), 140.5 (C_q-2), 2×128.1, 128.4 2×130.7, (5×Ar–C), 134.8 (Ar–C_q), 165.8 (C-1), 166.6 (C-6). MS (70 eV), m/z: 260 (10) [M^+], 201 (25) [$M^+ - C_2H_3O_2$], 187 (100) [$M^+ - C_3H_5O_2$], 173 (30) [$M^+ - C_2H_3O_2 - C_2H_4$] 155 (40) [$M^+ - C_3H_5O_2 - CH_4O$], 127 (40) [$M^+ - C_3H_5O_2 - CH_4O - CO$]. HR–MS: Calc. 260.1049. Found 260.1053 für [M^+].

4.4.2. (2E,4Z)-2-(4′-methoxy-phenyl)-hexa-2,4-dienedioic acid dimethyl ester (4b)

Reaction of 3 mmol 3b (0.62 g) with 6 mmol 2 (0.59 g) in the presence of 1 (18 mg, 0.06 mmol, 2 mol%) gave 0.82 g (99%) of 4b after work-up (eluent: cyclohexane/ethyl acetate, 5:1, $R_f = 0.30$) as pale yellow crystals; m.p.: 79 °C. Crystals for X-ray structural analysis were grown from benzene. GC–MS: $t_{Ret} = 10.35$ min – IR (KBr): $v = 3048$ cm^{-1} (m, C–H), 2981 cm^{-1} (s, C–H), 1711 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 3.43$ (s, 3H, O–CH_3), 3.46 (s, 3H, O–CH_3), 3.47 (s, 3H, O–CH_3), 5.72 (dd, 1H, $^3J_{HH} = 11.4$ Hz, $^4J_{HH} = 1.2$ Hz, H-5), 6.58 (dd, 1H, $^3J_{HH} = 11.6$ Hz, $^3J_{HH} = 11.6$ Hz, H-4), 6.80 (d, 2H, $^3J_{HH} = 8.7$ Hz, Ar–H), 7.73 (d, 2H, $^3J_{HH} = 8.7$ Hz, Ar–H), 8.95 (dd, 1H, $^3J_{HH} = 11.6$ Hz, $^4J_{HH} = 1.2$ Hz, H-3). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 51.1$ (O–CH_3), 51.9 (O–CH_3), 54.9 (O–CH_3), 123.3 (C-5), 133.5 (C-3), 139.6 (C-4), 139.9, (C_q-2), 113.7 (2×Ar–C), 132.2 (2×Ar–C), 126.8 (Ar–C_q), 160.3 (Ar–C_q), 166.0 (C-1), 167.0 (C-6). MS (70 eV), m/z: 276 (40) [M^+], 245 (10) [$M^+ - CH_3O$], 217 (100) [$M^+ - C_2H_3O_2$], 202 (20) [$M^+ - C_2H_3O_2 - CH_3$], 185 (60) [$M^+ - C_2H_3O_2 - CH_4O$], 158 (20) [$M^+ - C_2H_3O_2 - C_2H_3O_2$], 121 (25) [$C_8H_9O^+$]. HR–MS: Calc. 276.0998. Found 276.0996 für [M^+].

4.4.3. (2E,4Z)-2-(4′-ethoxy-phenyl)-hexa-2,4-dienedioic acid 1-ethylester-6-methyl ester (4c)

Reaction of 3 mmol 3c (0.70 g) with 6 mmol 2 (0.59 g) in the presence of 1 (18 mg, 0.06 mmol, 2 mol%) gave 0.89 g (98%) of 4c after work-up (eluent: cyclohexane/ethyl acetate, 5:1, $R_f = 0.34$) as yellow solid;

m.p.: 62 °C. GC–MS: t_{Ret} = 10.84 min – IR (KBr): v = 3041 cm^{-1} (m, C–H), 2987 cm^{-1} (s, C–H), 1698 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.03 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, CH$_3$), 1.17 (t, 3H, $^{3}J_{HH}$ = 7.0 Hz, CH$_3$), 3.44 (s, 3H, O–CH$_3$), 3.67 (q, 2H, $^{3}J_{HH}$ = 7.0 Hz, O–CH$_2$), 4.08 (q, 2H, $^{3}J_{HH}$ = 7.1 Hz, O–CH$_2$), 5.72 (dd, 1H, $^{3}J_{HH}$ = 11.4 Hz, $^{4}J_{HH}$ = 1.2 Hz, H-5), 6.63 (dd, 1H, $^{3}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 11.6 Hz, H-4), 6.82 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, Ar–H), 7.18 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, Ar–H), 9.02 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz, $^{4}J_{HH}$ = 1.2 Hz, H-3). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 14.1 (CH$_3$), 14.7 (CH$_3$), 51.0 (O–CH$_3$), 61.1 (O–CH$_2$), 63.4 (O–CH$_2$), 123.1 (C-5), 133.2 (C-3), 139.8 (C-4), 140.3, (C$_q$-2), 114.2 (2×Ar–C), 132.2 (2×Ar–C), 126.8 (Ar–C$_q$), 159.7 (Ar–C$_q$), 165.9 (C-1), 167.0 (C-6). MS (70 eV), m/z: 304 (45) [M$^+$], 273 (10) [M$^+$ – CH$_3$O], 245 (20) [M$^+$ – C$_2$H$_3$O$_2$], 231 (100) [M$^+$ – C$_3$H$_5$O$_2$], 217 (20) [M$^+$ – C$_2$H$_3$O$_2$ – C$_2$H$_4$], 199 (50) [M$^+$ – C$_3$H$_5$O$_2$ – CH$_4$O], 171 (20) [M$^+$ – C$_3$H$_5$O$_2$ – CH$_4$O – CO]. HR–MS: Calc. 304.1311. Found 304.1316 für [M$^+$].

4.4.4. (2E,4Z)-2-(3′,4′-dimethoxy-phenyl)-hexa-2,4-dienedioic acid 1-ethylester-6-methyl ester (4d)

Reaction of 3 mmol **3d** (0.75 g) with 6 mmol **2** (0.59 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.95 g (99%) of **4d** after work-up (eluent: cyclohexane/ethyl acetate, 5:1, R_f = 0.23) as a pale yellow oil. GC–MS: t_{Ret} = 11.28 min – IR (film): v = 3078 cm^{-1} (w, C–H), 2982 cm^{-1} (m, C–H), 1716 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.04 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, CH$_3$), 3.46 (s, 3H, O–CH$_3$), 3.47 (s, 3H, O–CH$_3$), 3.49 (s, 3H, O–CH$_3$), 4.10 (q, 2H, $^{3}J_{HH}$ = 7.1 Hz, O–CH$_2$), 5.76 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz, $^{4}J_{HH}$ = 1.2 Hz, H-5), 6.63 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz, Ar–H$_{5'}$), 6.68 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz, $^{3}J_{HH}$ = 11.6 Hz, H-4), 6.81 (dd, 1H, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 2.0 Hz, Ar–H$_{6'}$), 6.83 (d, 1H, $^{4}J_{HH}$ = 2.0 Hz, Ar–H$_{2'}$), 9.02 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz, $^{4}J_{HH}$ = 1.2 Hz, H-3). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 14.2 (CH$_3$), 51.0 (O–CH$_3$), 55.5 (O–CH$_3$), 55.6 (O–CH$_3$), 61.2 (O–CH$_2$), 123.1 (C-5), 133.4 (C-3), 139.9 (C-4), 140.5, (C$_q$-2), 111.5 (Ar–C), 114.8 (Ar–C), 123.8 (Ar–C), 127.2 (Ar–C$_q$), 149.6 (Ar–C$_q$), 150.4 (Ar–C$_q$), 166.0 (C-1), 167.0 (C-6). MS (70 eV), m/z: 320 (20) [M$^+$], 261 (10) [M$^+$ – C$_2$H$_3$O$_2$], 247 (15) [M$^+$ – C$_3$H$_5$O$_2$], 215 (50) [M$^+$ – C$_3$H$_5$O$_2$ – CH$_4$O], 165 (100) [C$_9$H$_9$O$_3$$^+$], 151 (35) [C$_9H_{11}O_2$$^+$], 137 (15) [C$_8H_9O_2$$^+$]. HR–MS: Calc. 320.1260. Found 320.1255 für [M$^+$].

4.4.5. (2E,4Z)-2-(4′-bromo-phenyl)-hexa-2,4-dienedioic acid 1-ethylester-6-methyl ester (4e)

Reaction of 3 mmol **3e** (0.81 g) with 6 mmol **2** (0.59 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.99 g (97%) of **4e** after work-up (eluent: cyclohexane/ethyl acetate, 8:1, R_f = 0.43) as a pale yellow oil. GC–MS: t_{Ret} = 11.01 min – IR (film): v = 3069 cm^{-1} (w, C–H), 2981 cm^{-1} (m, C–H), 1713 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.04 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, CH$_3$), 3.40 (s, 3H, O–CH$_3$), 4.06 (q, 2H, $^{3}J_{HH}$ = 7.1 Hz, O–CH$_2$), 5.71 (d, 1H, $^{3}J_{HH}$ = 11.6 Hz, H-5), 6.35 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz, $^{3}J_{HH}$ = 11.7 Hz, H-4), 6.76 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, Ar–H), 7.08 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, Ar–H), 9.01 (d, 1H, $^{3}J_{HH}$ = 11.7 Hz, H-3). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 14.3 (CH$_3$), 51.0 (O–CH$_3$), 61.2 (O–CH$_2$), 123.4 (C-5), 134.2 (C-3), 139.6 (C-4), 140.7, (C$_q$-2), 117.9 (2×Ar–C), 132.1 (2×Ar–C), 132.7 (Ar–C$_q$), 138.1 (Ar–C$_q$), 165.4 (C-1), 166.1 (C-6). MS (70 eV), m/z: 338 (30) [M$^+$], 307 (10) [M$^+$ – CH$_3$O], 279 (25) [M$^+$ – C$_2$H$_3$O$_2$], 265 (100) [M$^+$ – C$_3$H$_5$O$_2$], 251 (25) [M$^+$ – C$_2$H$_3$O$_2$ – C$_2$H$_4$], 233 (65) [M$^+$ – C$_3$H$_5$O$_2$ – CH$_4$O], 205 (65) [M$^+$ – C$_3$H$_5$O$_2$ – CH$_4$O – CO], 171 (30) [C$_7$H$_6$Br$^+$]. HR–MS: Calc. 338.0154. Found 338.0156 für [M$^+$].

4.4.6. (2E,4Z)-2-(4′-azido-phenyl)-hexa-2,4-dienedioic acid 1-ethylester-6-methyl ester (4f)

Reaction of 3 mmol **3f** (0.69 g) with 6 mmol **2** (0.59 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.82 g (91%) of **4f** after work-up (eluent: cyclohexane/ethyl acetate, 8:1, R_f = 0.46) as orange solid; m.p.: 85 °C. GC–MS: t_{Ret} = 11.13 min – IR (KBr): v = 3045 cm^{-1} (w, C–H), 2987 cm^{-1} (m, C–H), 2128 cm^{-1} (s, –N$_3$), 1703 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.01 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, CH$_3$), 3.42 (s, 3H, O–CH$_3$), 4.05 (q, 2H, $^{3}J_{HH}$ = 7.1 Hz, O–CH$_2$), 5.73 (d, 1H, $^{3}J_{HH}$ = 11.5 Hz, H-5), 6.44 (dd, 1H, $^{3}J_{HH}$ = 11.5 Hz, $^{3}J_{HH}$ = 11.5 Hz, H-4), 6.72 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, Ar–H), 7.01 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, Ar–H), 9.04 (d, 1H, $^{3}J_{HH}$ = 11.5 Hz, H-3). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 14.1 (CH$_3$), 51.1 (O–CH$_3$), 61.3 (O–CH$_2$), 123.8 (C-5), 134.0 (C-3), 139.1 (C-4), 140.5, (C$_q$-2), 118.8 (2×Ar–C), 132.3 (2×Ar–C), 131.2 (Ar–C$_q$), 139.4 (Ar–C$_q$), 165.7 (C-1), 166.4 (C-6). MS (70 eV), m/z: 301 (20) [M$^+$], 273 (100) [M$^+$ – N$_2$], 214 (20) [M$^+$ – N$_2$ – C$_2$H$_3$O$_2$], 228 (15) [M$^+$ – C$_3$H$_5$O$_2$], 200 (20) [M$^+$ – N$_2$ – C$_3$H$_5$O$_2$]. HR–MS: Calc. 301.1063. Found 301.1063 für [M$^+$].

4.4.7. (2E,4Z)-2-(3′,4′-dichloro-phenyl)-hexa-2,4-dienedioic acid 1-ethylester-6-methyl ester (4g)

Reaction of 3 mmol **3g** (0.78 g) with 6 mmol **2** (0.59 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.97 g (98%) of **4g** after work-up (eluent: cyclohexane/ethyl acetate, 5:1, R_f = 0.48) as a pale yellow oil. GC–MS: t_{Ret} = 10.93 min – IR (film): v = 3088 cm^{-1} (w, C–H), 2977 cm^{-1} (m, C–H), 1704 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.00 (t, 3H, $^{3}J_{HH}$ = 7.0 Hz, CH$_3$), 3.43 (s, 3H, O–CH$_3$), 4.02 (q, 2H, $^{3}J_{HH}$ = 7.0 Hz, O–CH$_2$), 5.69 (dd, 1H, $^{3}J_{HH}$ = 11.4 Hz, $^{4}J_{HH}$ = 1.3 Hz, H-5), 6.21 (dd, 1H, $^{3}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 11.6 Hz, H-4), 6.71 (dd, 1H, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 2.0 Hz, Ar–H$_{6'}$), 7.08 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz, Ar–H$_{5'}$), 7.18 (d, 1H, $^{4}J_{HH}$ = 2.0 Hz, Ar–H$_{2'}$), 8.95 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz,

$^4J_{HH} = 1.3$ Hz, H-3). ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 14.1$ (CH$_3$), 51.2 (O–CH$_3$), 61.5 (O–CH$_2$), 124.8 (C-5), 132.5 (C-3), 138.2 (C-4), 137.6, (C$_q$-2), 130.1 (Ar–C), 130.2 (Ar–C), 134.9 (Ar–C), 128.3 (Ar–C$_q$), 132.8 (Ar–C$_q$), 134.6 (Ar–C$_q$), 165.6 (C-1), 165.7 (C-6). MS (70 eV), *m/z*: 328 (10) [M$^+$], 269 (20) [M$^+$ – C$_2$H$_3$O$_2$], 255 (100) [M$^+$ – C$_3$H$_5$O$_2$], 241 (25) [M$^+$ – C$_2$H$_3$O$_2$ – C$_2$H$_4$], 223 (20) [M$^+$ – C$_3$H$_5$O$_2$ – CH$_4$O], 173 (25) [C$_8$H$_7$Cl$_2$$^+$]. HR–MS: Calc. 328.0269. Found 328.0276 für [M$^+$].

4.4.8. (2Z)-4-fluoren-9′-ylidene-but-2-enoic acid methyl ester (4h)

Reaction of 3 mmol **3h** (0.58 g) with 6 mmol **2** (0.59 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.77 g (98%) of **4h** after work-up (eluent: dichloromethane/petroleum ether, 4:1, $R_f = 0.42$) as bright yellow crystals; m.p.: 175 °C. GC–MS: $t_{Ret} = 12.28$ min – IR (film): $v = 3049$ cm^{-1} (m, C–H), 2953 cm^{-1} (m, C–H), 1709 cm^{-1} (vs, C=O). ^{1}H NMR (500 MHz, C$_6$D$_6$): $\delta = 3.42$ (s, 3H, O–CH$_3$), 5.83 (d, 1H, $^3J_{HH} = 11.2$ Hz, H-2), 6.96 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 7.7$ Hz, Ar–H), 6.99 (dd, 1H, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.6$ Hz, Ar–H), 7.06 (dd, 1H, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, Ar–H), 7.09 (dd, 1H, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, Ar–H), 7.10 (d, 1H, $^3J_{HH} = 7.5$ Hz, Ar–H), 7.38 (d, 1H, $^3J_{HH} = 7.5$ Hz, Ar–H), 7.41 (dd, 1H, $^3J_{HH} = 11.4$ Hz, $^3J_{HH} = 11.2$ Hz, H-3), 7.53 (d, 1H, $^3J_{HH} = 7.7$ Hz, Ar–H), 7.71 (d, 1H, $^3J_{HH} = 7.6$ Hz, Ar–H), 8.79 (d, 1H, $^3J_{HH} = 11.4$ Hz, H-4). ^{13}C NMR (125 MHz, C$_6$D$_6$): $\delta = 50.9$ (O–CH$_3$), 119.9 (Ar–C), 120.3 (Ar–C), 121.0(C-2), 121.8 (Ar–C), 121.9 (Ar–C), 126.3 (C-4), 127.3 (Ar–C), 127.7 (Ar–C), 129.3 (Ar–C), 129.4 (Ar–C), 136.8, (C-9′), 139.1 (Ar–C$_q$), 139.8 (Ar–C$_q$), 140.1 (Ar–C$_q$), 142.3 (Ar–C$_q$), 142.3 (C-3), 166.3 (C-1). MS (70 eV), *m/z*: 262 (35) [M$^+$], 203 (100) [M$^+$ – C$_2$H$_3$O$_2$], 152 (20) [M$^+$ – C$_2$H$_3$O$_2$ – C$_4$H$_3$]. HR–MS: Calc. 262.0994. Found 262.0990 für [M$^+$].

4.5. General procedure for the chromium(0)-catalyzed reactions of ethyl α-diazo-phenylacetate (3a) with 2-alkylfurans (5a,b)

A solution of ethyl α-diazo-phenylacetate (**3a**) in 20 ml CH$_2$Cl$_2$ was added over a period of 4 h at 4 °C to a stirred solution containing 2 eq. of 2-alkylfurans (**5a,b**) and 2 mol% of cyclooctene complex **1** in 5 ml of CH$_2$Cl$_2$. Evolution of N$_2$ was accompanied by a colour change of the reaction mixture from yellow to dark red. After stirring for a further 8 h followed by removal of the solvent under reduced pressure, work-up was performed by column chromatography.

4.5.1. (2E,4E)-6-oxo-2-phenyl-hepta-2,4-dienedioic acid ethyl ester (6a)

Reaction of 3 mmol **3a** (0.57 g) with 6 mmol 2-methylfuran (**5a**) (0.49 g) in the presence of **1** (18 mg,

0.06 mmol, 2 mol%) gave 0.57 g (78%) of **6a** after work-up (eluent: dichloromethane/petroleum ether, 4:1, $R_f = 0.37$) as an orange oil. GC–MS: $t_{Ret} = 9.08$ min – IR (film): $v = 3067$ cm^{-1} (w, C–H), 2981 cm^{-1} (s, C–H), 1721 cm^{-1} (b vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.99$ (t, 3H, $^3J_{HH} = 7.1$ Hz, CH$_3$), 1.71 (s, 3H, H-7), 4.07 (q, 2H, $^3J_{HH} = 7.1$ Hz, O–CH$_2$), 6.10 (dd, 1H, $^3J_{HH} = 15.6$ Hz, $^4J_{HH} = 0.6$ Hz, H-5), 7.09 (dd, 1H, $^3J_{HH} = 15.6$ Hz, $^3J_{HH} = 11.7$ Hz, H-4), 7.12–7.23 (m, 5H, Ar–H), 7.56 (d, 1H, $^3J_{HH} = 11.6$ Hz, H-3). ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 14.1$ (CH$_3$), 27.1 (C-7), 61.3 (O–CH$_2$), 2×128.2 (Ar–C), 128.6 (C-5), 2×130.7 (Ar–C), 134.7 (Ar–C$_q$), 136.5 (Ar–C), 137.0 (C-3), 137.2 (C-4), 140.4, (C$_q$-2), 166.2 (C-1), 196.3 (C-6). MS (70 eV), *m/z*: 244 (10) [M$^+$], 215 (20) [M$^+$ – C$_2$H$_5$], 201 (90) [M$^+$ – C$_2$H$_3$O], 173 (55) [M$^+$ – C$_2$H$_3$O – C$_2$H$_4$], 171 (100) [M$^+$ – C$_3$H$_5$O$_2$], 128 (25) [M$^+$ – C$_3$H$_5$O$_2$ – C$_2$H$_3$O], 91 (10) [C$_7$H$_7$$^+$], 77 (15) [C$_6H_5$$^+$]. HR–MS: Calc. 244.1099. Found 244.1097 für [M$^+$].

4.5.2. (2E,4E)-6-oxo-2-phenyl-octa-2,4-dienedioic acid ethyl ester (6b)

Reaction of 3 mmol **3a** (0.57 g) with 6 mmol 2-ethyl-furan (**5b**) (0.58 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.56 g (72%) of **6b** after work-up (eluent: dichloromethane/petroleum ether, 4:1, $R_f = 0.40$) as an orange oil. GC–MS: $t_{Ret} = 9.60$ min – IR (film): $v = 3057$ cm^{-1} (m, C–H), 2972 cm^{-1} (m, C–H), 1718 cm^{-1} (b vs, C=O). ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 0.88$ (t, 3H, $^3J_{HH} = 7.3$ Hz, H-8), 0.98 (t, 3H, $^3J_{HH} = 7.1$ Hz, CH$_3$), 2.00 (q, 2H, $^3J_{HH} = 7.3$ Hz, H-7), 4.05 (q, 2H, $^3J_{HH} = 7.1$ Hz, O–CH$_2$), 6.10 (dd, 1H, $^3J_{HH} = 15.5$ Hz, $^4J_{HH} = 0.7$ Hz, H-5), 7.20 (dd, 1H, $^3J_{HH} = 15.5$ Hz, $^3J_{HH} = 11.7$ Hz, H-4), 7.08–7.25 (m, 5H, Ar–H), 7.54 (dd, 1H, $^3J_{HH} = 11.7$ Hz, $^4J_{HH} = 0.7$ Hz, H-3). ^{13}C NMR (75 MHz, C$_6$D$_6$): $\delta = 7.9$ (C-8), 14.1 (CH$_3$), 34.0 (C-7), 61.2 (O–CH$_2$), 2×128.2 (Ar–C), 128.6(C-5), 2×130.5 (Ar–C), 134.7 (Ar–C$_q$), 135.8 (Ar–C), 136.1 (C-3), 137.3 (C-4), 140.3, (C$_q$-2), 166.3 (C-1), 198.8 (C-6). MS (70 eV), *m/z*: 258 (10) [M$^+$], 215 (20) [M$^+$ – C$_2$H$_5$], 201 (100) [M$^+$ – C$_2$H$_5$ – CO], 185 (90) [M$^+$ – C$_3$H$_5$O$_2$], 173 (55) [M$^+$ – C$_2$H$_5$ – CO – C$_2$H$_4$], 128 (25) [M$^+$ – C$_3$H$_5$O$_2$ – C$_3$H$_5$O], 91 (10) [C$_7$H$_7$$^+$], 77 (15) [C$_6H_5$$^+$]. HR–MS: Calc. 258.1256. Found 258.1263 für [M$^+$].

4.6. General procedure for the chromium(0)-catalyzed reactions of 9-diazo-9h-fluorene (3h) with 2-alkylfurans (5a,b)

A solution of 9-diazo-9*H*-fluorene (**3h**) in 20 ml CH$_2$Cl$_2$ was added over a period of 8 h at room temperature to a stirred solution containing 2 eq. of 2-alkylfuran (**5a,b**) and 2 mol% of cyclooctene complex **1** in 5 ml of CH$_2$Cl$_2$. Evolution of N$_2$ was accompanied by a

colour change of the reaction mixture from yellow to violet. After stirring for a further 8 h followed by removal of the solvent under reduced pressure, work-up was performed by column chromatography.

4.6.1. (3E)-5-fluoren-9′-ylidene-pent-3-en-2-one (6c)

Reaction of 3 mmol **3h** (0.58 g) with 6 mmol 2-methylfuran (**5a**) (0.49 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.64 g (86%) of **6c** after work-up (eluent: dichloromethane/petroleum ether, 2:1, $R_f = 0.31$) as bright yellow crystals; m.p.: 124 °C. GC–MS: $t_{Ret} = 12.16$ min – IR (film): $v = 3033$ cm^{-1} (w, C–H), 2971 cm^{-1} (m, C–H), 1716 cm^{-1} (vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 1.97$ (s, 3H, H-1), 6.14 (dd, 1H, $^3J_{HH} = 15.2$ Hz, $^4J_{HH} = 0.9$ Hz, H-3), 6.86 (dd, 1H, $^3J_{HH} = 12.1$ Hz, $^4J_{HH} = 0.9$ Hz, H-5), 7.02 (dt, 1H, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.1$ Hz, Ar–H), 7.11 (dt, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.1$ Hz, Ar–H), 7.12 (dt, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.0$ Hz, Ar–H), 7.17 (dt, 1H, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.0$ Hz, Ar–H), 7.43 (dd, 3H, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, Ar–H), 7.89 (d, 1H, $^3J_{HH} = 7.6$ Hz, Ar–H), 8.21 (dd, 1H, $^3J_{HH} = 12.1$ Hz, $^3J_{HH} = 15.2$ Hz, H-4). ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 27.8$ (C-1), 120.1 (Ar–C), 120.4 (Ar–C), 121.2 (C-3), 123.9 (Ar–C), 126.2 (C-5), 127.4 (Ar–C), 127.7 (Ar–C), 2×129.5 (Ar–C), 134.3 (Ar–C), 136.6 (C-4), 136.9 (C-9′), 139.3 (Ar–C$_q$), 140.4 (Ar–C$_q$), 142.0 (Ar–C$_q$), 142.5 (Ar–C$_q$), 196.1 (C-2). MS (70 eV), m/z: 246 (100) [M$^+$], 231 (60) [M$^+$ – CH$_3$], 203 (100) [M$^+$ – CH$_3$ – CO], 165 (10) [C$_{13}$H$_9^+$]. HR–MS: Calc. 246.1045. Found 246.1051 für [M$^+$].

4.6.2. (4E)-6-fluoren-9′-ylidene-hex-4-en-3-one (6d)

Reaction of 3 mmol **3h** (0.58 g) with 6 mmol 2-ethyl-furan (**5b**) (0.58 g) in the presence of **1** (18 mg, 0.06 mmol, 2 mol%) gave 0.69 g (88%) of **6d** after work-up (eluent: dichloromethane/petroleum ether, 2:1, $R_f = 0.36$) as bright yellow crystals; m.p.: 116 °C. Crystals for X-ray structural analysis were grown from *n*-pentane. GC–MS: $t_{Ret} = 12.79$ min – IR (film): $v = 3048$ cm^{-1} (w, C–H), 2983 cm^{-1} (m, C–H), 1709 cm^{-1} (vs, C=O). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 1.11$ (t, 3H, $^3J_{HH} = 7.3$ Hz, H-1), 2.27 (q, 2H, $^3J_{HH} = 7.3$ Hz, H-2), 6.17 (dd, 1H, $^3J_{HH} = 15.1$ Hz, $^4J_{HH} = 0.9$ Hz, H-4), 6.90 (dd, 1H, $^3J_{HH} = 12.3$ Hz, $^4J_{HH} = 0.9$ Hz, H-6), 7.01 (dt, 1H, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.1$ Hz, Ar–H), 7.11 (dt, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 0.9$ Hz, Ar–H), 7.12 (dt, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.1$ Hz, Ar–H), 7.17 (dt, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.1$ Hz, Ar–H), 7.43 (d, 1H, $^3J_{HH} = 7.6$ Hz, Ar–H), 7.43 (d, 1H, $^3J_{HH} = 7.5$ Hz, Ar–H), 7.46 (d, 1H, $^3J_{HH} = 7.5$ Hz, Ar–H), 7.95 (d, 1H, $^3J_{HH} = 7.6$ Hz, Ar–H), 8.36 (dd, 1H, $^3J_{HH} = 12.3$ Hz, $^3J_{HH} = 15.1$ Hz, H-5). ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 8.2$ (C-1), 34.6 (C-2), 120.1 (Ar–C), 120.3 (Ar–C), 121.2 (C-4), 124.0 (Ar–C), 126.3 (C-6), 127.4 (Ar–C), 127.7 (Ar–C), 2×129.4 (Ar–C), 133.5 (Ar–C),

135.8 (C-5), 137.0 (C-9′), 139.3 (Ar–C$_q$), 140.4 (Ar–C$_q$), 142.0 (Ar–C$_q$), 142.4 (Ar–C$_q$), 198.8 (C-3). MS (70 eV), m/z: 260 (60) [M$^+$], 231 (100) [M$^+$ – C$_2$H$_5$], 203 (40) [M$^+$ – C$_2$H$_5$ – CO]. HR–MS: Calc. 260.1201. Found 260.1203 für [M$^+$].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 233891 for compound **6d** and No. 233892 for compound **4b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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