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Dichotomy within 1,4-addition of organolithium and Grignard reagents to α,β-unsaturated Fischer alkoxycarbenes: A new synthesis of Fischer carbenes

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ABSTRACT

The reaction of organolithium and Grignard reagents with pentacarbonyl[(ethoxy)(2-phenylethenyl) carbene]chromium(0) gave, after the quenching of the initially formed product of the 1,4-addition, different products depending on the organometallic and quenching reagents used. The addition of organolithiums, followed by a work-up with acid (AcOH or HCl), afforded the corresponding carbene complexes. In contrast, quenching the reaction mixture with ethanol led to the stereoselective formation of (*Z*)-enol ethers. The usage of Grignard reagents led to the formation of the carbene complexes regardless of which quenching reagent was used.

1. Introduction

The characteristic feature of the Fischer carbene complexes of Group 6 elements, which are already known from 1964 [1], is the strong electron-withdrawing character of the pentacarbonyl metal group. Therefore, it is not surprising that the conjugate addition to the double bond, which is in conjugation with the metal fragment of these complexes, was already attempted in the early seventies. Casey reported a reaction of these compounds with organolithium compounds and lithium enolates. This reaction afforded, depending on the structure of the carbene complex and nucleophile, products of the 1,2 and/or 1,4 addition in low yield (Scheme 1) [2]. Later, it was shown that not only alkenylcarbene complexes, but also (alkoxy)(aryl)carbene complexes, react with organolithiums in the 1,2-, 1,4- or 1,6-fashion, and considerable attention was paid to the addition of lithium enolates [3]. It was shown that the addition of organolithium reagents to optically active Fischer vinylcarbene complexes proceeds with high diastereoselectivity [4]. Later, Iwasawa reported that alkylcerium reagents derived from primary and secondary butyllithium gave almost quantitatively, with α,β-unsaturated carbene complexes, products of a 1,4-addition [5] (Scheme 1). Reactivity of α,β-unsaturated carbene complexes still reminds active area [6]. In connection with our previous experience with metalated Fischer aminocarbene complexes [7], we turned our attention to the reaction of vinylcarbene complexes with organometallic reagents.

2. Results and discussion

In contrast to Casey, who observed the formation of the carbene complex **2a** in low yield together with the enol ether **3**, we observed that the Fischer α,β-unsaturated alkoxycarbene **1b** reacted with *n*-butyllithium, affording the carbene complex **2b** in 91% NMR yield after quenching with dry HCl (Table 1, entry 1). This led us to explore this addition reaction in detail. In contrast to the above result, quenching the reaction of carbene complex **1b** with *n*-butyllithium in dry THF or cyclopentyl methyl ether with ethanol led to the formation of the enol ether **4b** in good yield as the sole product (Table 1, entries 2,3). Casey had already observed the formation of this type of enol ether **4a** in very low yield using an organocopper reagent. Both of our products, carbene **2b** and enol

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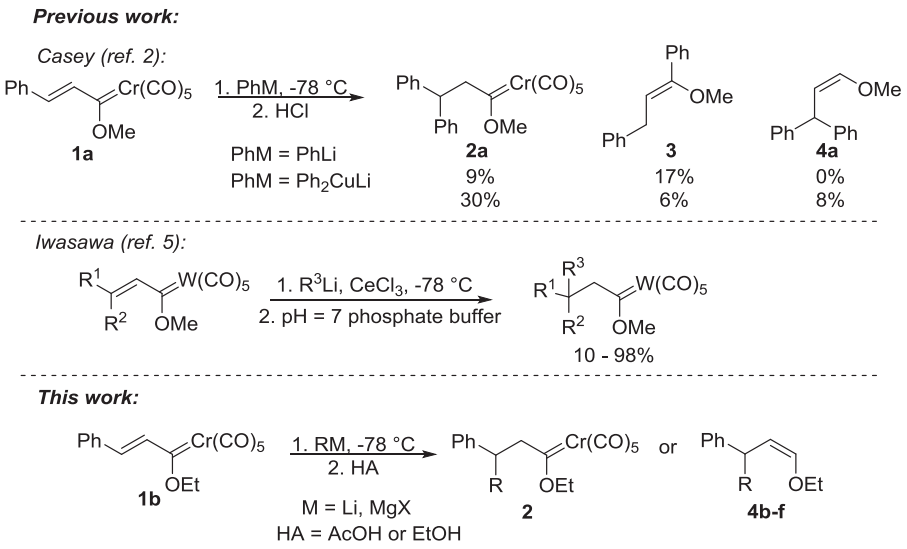
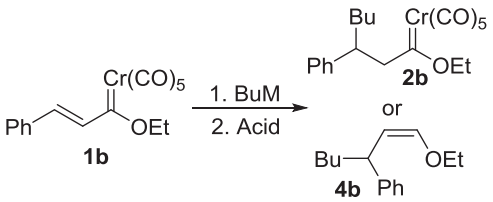


Scheme 1. Reaction of α,β-unsaturated alkoxycarbene complexes with alkyllithium reagents.

Table 1
Addition of organometallic reagents to the carbene **1b**.



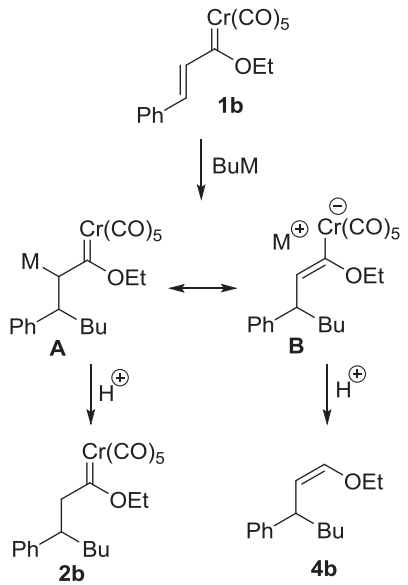
entry	M	solvent/acid	**2b** (%)[a]	**4b** (%)[a]
1	Li	THF/HCl	91, 75[b]	–
2	Li	THF/EtOH	–	73, 61[b]
3	Li	CpOMe/EtOH	–	75
4	Li	Et_2O/EtOH	–	59
5	Li	EtOH,THF/AcOH	91	–
6	MgBr	THF/EtOH	90[b]	–
7	Bu_2CuLi	THF/EtOH	–[c]	–[c]

[a] ^{1}H NMR yield, 1,3,5-trimethoxybenzene was used as the internal standard.
[b] Isolated yield.
[c] A complex mixture of products was formed.

ether **4b**, are the result of a 1,4-addition, while the enol ether **3** observed by Casey results from a 1,2-addition to the α,β-unsaturated carbene [8]. The reduction of α,β-unsaturated alkoxycarbene complexes with $NaBH_4$ is also reported to proceed via 1,2-addition [9]. Running the reaction in diethyl ether dropped the yield of **4b** to 59% (Table 1, entry 4). The work-up of the reaction mixture with acetic acid afforded the same result as that with HCl (Table 1, entry 5). In contrast to *n*-butyllithium, the corresponding Grignard reagent afforded the carbene complex **2b** in 90% isolated yield as the only product when quenched with ethanol (Table 1, entry 6). The Gilman cuprate was shown to be non-effective in this case, affording a complex reaction mixture under the same conditions (Table 1, entry 7). The enol ether **4b** was in all cases obtained exclusively as the (*Z*)-isomer, which follows from the $^3J_{HH}$ coupling constant of the olefin protons (6.25 Hz). Such exclusive formation of (*Z*)-enolether is well known not only as result of 1,2-addition [9,10], but recently also from 1,4-addition [6c,d].

The observed dichotomy of this reaction can be explained by the way in which the initially formed 1,4-adduct of an organometallic reagent to **1b** is protonated. The stronger, and therefore harder, acids prefer protonation on the harder base, which, in this case, is the carbon atom. This results in the formation of the carbene **2b**. In contrast, the softer, weak acids prefer to protonate on the soft metal centre of the aduct, leading, after reductive elimination, to the enol ether **4b**. In the case of the Grignard reagent, the resonance structure **A** prevails in the resonance hybrid because of the more covalent Mg–C bond, while the more electropositive Li atom prefers the ionic resonance structure **B**. The protonation then accordingly leads to the corresponding product **2b** or **4b**. The exclusive formation of the (*Z*)-isomer of **4b** is then a result of steric interactions between bulky $Cr(CO)_5$ and the RCHPh groups, which leads to the (*E*)-configuration of the 1,4-adduct. Protonation on metal and subsequent reductive elimination forms the (*Z*)-**4b** (Scheme 2).

We then began to explore the scope of the transformation of carbene **1b** to the enol ethers **4** (Table 2). Similar results to those



Scheme 2. Formation of **2b** and **4b** by the protonation of the 1,4-adduct of *n*-butyllithium to the α,β-unsaturated carbene **1b**.

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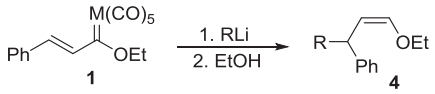
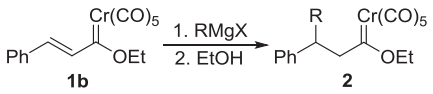
Table 2
Preparation of enol ethers **4** via 1,4-addition of alkyllithium reagents.



entry	R	M	**4**, yield (%)[a]
1	^{n}Bu	Cr	**4b**, 61
2	$PhCH_2CH_2$	Cr	**4c**, 56
3	^{t}Bu	Cr	**4d**, 34
4	$TMSCH_2Li$	Cr	**4e**, 77
5	cycloheptenyl	Cr	**4f**, 72
6	Ph	Cr	**4g**, 44
7	TMSC≡C	Cr	–[b]
8	^{n}Bu	W	**4b**, 54
9	$TMSCH_2Li$	W	**4e**, 75

[a] Isolated yield.
[b] A complex mixture of products was formed.

Table 3
Preparation of carbene complexes **2** by the addition of Grignard reagents to the carbene complex **1b**.

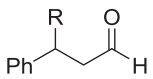


entry	Grignard reagent	**2**, yield (%)[a]
1	BuMgBr	**2b**, 90
2	CpMgCl	**2c**, 97
3	^{t}BuMgCl	**2d**, 97
4	$CH_2{=}CHCH_2MgCl$	**2e**, 47
5	PhMgCl	**2f**, 36, 50[b]
6	$TMSCH_2MgBr$	**2g**, –, 90[c]

[a] Isolated yield.
[b] PhLi was used, and the reaction mixture was quenched with AcOH/EtOH.
[c] $TMSCH_2Li$ was used, and the reaction mixture was quenched with AcOH/EtOH.

with *n*-butyllithium were obtained with phenethyllithium (Table 2, entry 2), while bulkier *tert*-butyllithium afforded the desired enol ether **4d** in low yield (Table 2, entry 3). Trimethylsilylmethyllithium and cycloheptenyllithium reacted smoothly, forming the enol ethers **4e** and **4f** in good yield (Table 2, entries 4,5). The use of phenyllithium, prepared by the reaction of bromobenzene with *tert*-butyllithium, furnished the expected product **4g** in 44% isolated yield (Table 2, entry 6). In contrast, the trimethylsilylethynyllithium failed to react in a reasonably good yield, and a complex reaction mixture was formed in this case (Table 2, entry 7). It is worthwhile to mention that the corresponding tungsten carbene complex **1c** reacted with *n*-butyllithium and trimethylsilylmethyllithium in the same fashion and in similar yields to the chromium carbene **1b** (Table 2, entries 8,9). In all cases, (*Z*)-isomers of the enol ethers 4 were exclusively formed.

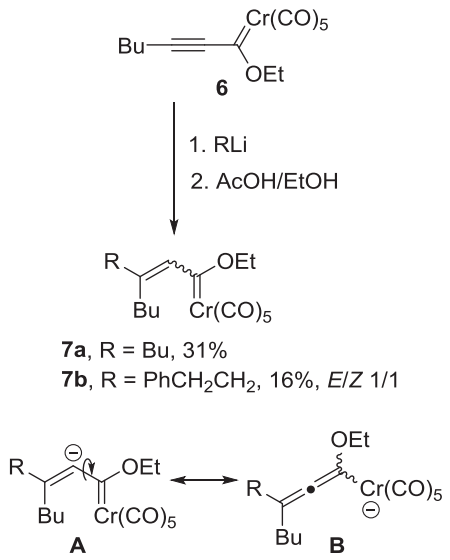
The obtained enol ethers can be easily hydrolysed to the corresponding β-substituted aldehydes. This was demonstrated on the enol ethers **4b**, **e** and **f**. Their treatment with 1M aqueous hydrochloric acid in acetone afforded the desired aldehydes **5b**, **e** and **5f** in high yield.



5b R = Bu, 89%
5e R = $TMSCH_2$, 98%
5f R = cycloheptenyl, 94%

The reaction of alkoxycarbene **1b** with Grignard reagents was explored next. This reaction, which was accomplished under the same conditions as the reaction with organolithiums, was more sluggish, requiring about 30 min to finish. This was easily followed by the colour change from deep red to yellow. Butylmagnesium bromide gave the carbene **2b** in almost quantitative yield (Table 3, entry 1), just as did the cyclopentyl and *tert*-butylmagnesium chlorides (Table 3, entries 2,3). A moderate yield of the corresponding carbene **2e** was observed in the reaction of **1b** with allylmagnesium chloride (Table 3, entry 4). Similar results were also obtained with phenylmagnesium chloride, but in this case, the addition reaction had to be carried out at 0 °C to achieve the complete conversion of the starting **1b**. Here, the better yield of the carbene **2f** was obtained when phenyllithium was used instead of the Grignard reagent and the reaction mixture was quenched with acetic acid in ethanol (Table 3, entry 5). Trimethylsilylmethyl magnesium bromide failed to give the corresponding carbene complex **2g**, and the formation of a complex reaction mixture was observed instead (Table 3, entry 6). However, using trimethylsilylmethyllithium, followed by quenching with a solution of acetic acid in ethanol, afforded the desired carbene complex **2g** in 90% yield (Table 3, entry 6). Other tested Grignard reagents, including 2-thienylmagnesium bromide, phenethyl magnesium iodide and vinylmagnesium chloride, failed to give the expected alkoxycarbenes, and the formation of a complex reaction mixture was instead observed.

In addition, the analogous reaction of Fischer carbene **6**, containing a conjugated triple bond with organolithiums, was briefly tested. The carbene complex **6** was treated with *n*-butyllithium at −78 °C, and acetic acid was subsequently added. In this case, the crude reaction mixture was more complicated compared to the reactions with the previously studied alkenylcarbenes. Despite that, we were able to isolate the expected unsaturated carbene **7a** in 31% yield by chromatography (Scheme 3). The reaction with phenethyllithium proceeded with even lower yield (16%) and was not stereoselective, giving an approximately 1:1 mixture of *E*/*Z* isomers (Scheme 3). The loss of stereoselectivity can be attributed to the low rotational barrier around the C–C bond in the resonance hybrid **A**↔**B** (Scheme 3) and the similar steric interactions of the ethoxycarbene moiety with the butyl and the R groups in the primary product of the addition.



Scheme 3. Addition of alkyllithiums to alkynylcarbene complex **6**.

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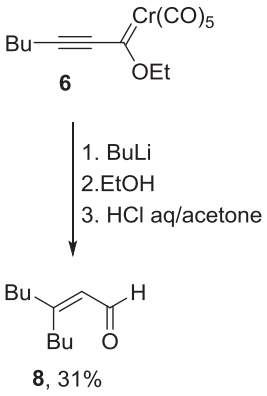

Scheme 4. One-pot conversion of alkynylcarbene **6** to 3-butylhept-2-enal **8**.

As with alkenylcarbene **1b**, when the reaction of the alkynylcarbene **6** with organolithium was quenched with ethanol, the corresponding allenyl enol ethers were formed. These enol ethers were not isolated. Evidence of their formation comes from the hydrolysis of the crude reaction mixture of **1b** with BuLi, which afforded 3-butylhept-2-enal **8** in low yield (Scheme 4).

3. Conclusions

The 1,4-addition of organometallic reagents to the α,β-unsaturated alkoxycarbene complexes of chromium gives different products depending on the organometallic reagent and/or the method of quenching used. The addition of organolithium reagents followed by acidic (HCl or AcOH) work-up gives carbene complexes, products of conjugated addition. This reaction represents new synthetic approach to certain alkoxycarbene complexes. In contrast, quenching the reaction mixture with ethanol leads to the loss of the metal and to the formation of enol ethers as the only products. These enol ethers are formed exclusively as (*Z*)-isomers. In contrast to the lithium reagents, the Grignard reagents afford carbenes in high yield regardless of whether HCl or ethanol is used for the quenching.

4. Experimental

4.1. General information

All reactions were performed under an argon atmosphere. The NMR spectra were measured on a Varian Gemini 300 (^{1}H, 300.07 MHz, ^{13}C, 75.46 MHz), a Bruker DRX 500 Avance (^{1}H, 500.13 MHz, ^{13}C, 125.78 MHz) and a Bruker 600 Avance III (^{1}H, 600.13 MHz, ^{13}C, 150.92 MHz) spectrometer at 298 K. The mass spectra were measured on a ZAB-SEQ (VG Analytical). The dry and degassed solvents were prepared with PureSolv MD7 silica gel (Merck, Silica Gel 60, 40–63 μm), and aluminium oxide 90 standardized (Merck, 0.063–0.200 mm) was used for the column chromatography. BuLi (2.5 M solution in hexane) and other compounds were purchased. Phenethyllithium [11], pentacarbonyl[ethoxy(phenylethenyl)carbene]chromium(0) (**1b**) [12] and pentacarbonyl[ethoxy(hept-1-ynyl)carbene]chromium(0) (**6**) [13] were prepared according to the procedure in the literature; other compounds were purchased. A concentration of *n*-BuLi, *t*-BuLi, was determined by titration using menthol and 1,10-phenanthroline before use. The concentration of Grignard reagents was determined by titration using iodine.

4.1.1. Cycloheptenyllithium

t-BuLi (1.18 mL, 2.0 mmol) was added to a solution of 1-bromocyclohept-1-ene in dry ether (3 mL) cooled to −78 °C. The resultant mixture was stirred for 30 min at −78 °C, then the mixture was warmed to ambient temperature and the cycloheptenyllithium was used as prepared.

4.1.2. Pentacarbonyl[ethoxy(phenylethenyl)carbene]tungsten(0)

(***1c***) was prepared by modified literature procedure [9]. Triethylamine (13.35 mL, 96 mmol), trimethylsilyl chloride (11.0 mL, 87 mmol) and benzaldehyde (2.52 g, 24.0 mmol) were added to the solution of pentacarbonyl[ethoxy(methyl)carbene]tungsten(0) (6.230 g, 15.73 mmol) in dry ether (30 mL). The resultant mixture was stirred for 48 h at ambient temperature. Then 10 g of alumina was added, solvents were removed under reduce pressure, and column chromatography (hexane, $R_f = 0.30$) afforded the title compound 2.55 g (33%) as black solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.68 (t, $J = 7.2$ Hz, 3H), 4.95 (q, $J = 7.2$ Hz, 2H), 7.20 (d, $J = 15.6$ Hz, 1H), 7.41–7.43 (m, 3H), 7.61–7.63 (m, 2H), 7.88 (d, $J = 15.6$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.0, 78.9, 129.2, 129.3, 130.9, 134.1, 134.6, 143.6, 197.6 ($^1J_{W\text{-}C} = 127$ Hz), 203.9 ($^1J_{W\text{-}C} = 116$ Hz), 305.2 ($^1J_{W\text{-}C} = 104$ Hz). HRMS (ESI) calcd for $C_{16}H_{11}O_6W$ $[M\text{-}H]^-$: 483.0070. Found: 483.0076.

4.2. General procedure for the reaction of alkoxycarbene 1b with Grignard reagents – formation of carbene complexes

A solution of Grignard reagent (1.5 equiv) was added to the solution of the carbene **1b** (1.0 equiv) in dry THF (9 mL/mmol) cooled to −78 °C. The resulting mixture was stirred for 30 min at −78 °C followed by the addition of EtOH (6 mL/mmol). The mixture was then stirred for 15 min at −78 °C, warmed to ambient temperature and concentrated under reduce pressure. Column chromatography on silica gel afforded the target compound.

4.2.1. Pentacarbonyl[ethoxy(2-phenylhexyl)methylene] chromium(0) (***2b***)

The general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), butylmagnesium bromide (0.42 mL, 0.90 mmol), dry THF (6 mL), and EtOH (4 mL) afforded after column chromatography (hexane $R_f = 0.55$, PMA detection) the title compound 0.222 g (90%) as a yellow oil. Alternatively, the title compound was prepared from the carbene **1b** (0.053 g, 0.15 mmol), butyllithium (0.09 mL, 0.023 mmol), dry THF (3 mL) and HCl (0.5 mL, 1.5 mmol of 3M solution in CpOMe). Column chromatography afforded the title compound 0.092 g (75%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.86 (t, $J = 7.2$ Hz, 3H, CH_3^{Hex}), 1.11–1.16 (m, 2H, CH_2 ^{Hex}), 1.24–1.34 (m, 2H, CH_2 ^{Hex}), 1.44 (t, $J = 7.0$ Hz, 3H, CH_3^{EtO}), 1.57–1.64 (m, 2H, CH_2 ^{Hex}), 3.14 (m, 1H, CHPh), 3.63 (dd, $J = 8.8$, 15.1 Hz, 1H, $\underline{CH_2}$C(OEt)Cr(CO)$_5$), 3.72 (dd, $J = 5.7$, 15.1 Hz, 1H, $\underline{CH_2}$C(OEt)Cr(CO)$_5$), 4.94–4.95 (m, 2H, CH_2^{EtO}), 7.13–718 (m, 2H, CH^{Ph}), 7.20–7.21 (m, 1H, CH^{Ph}), 7.28–7.30 (m, 2H, CH^{Ph}). ^{13}C NMR (151 MHz, $CDCl_3$): δ 13.9 (CH_3^{Hex}), 14.7 (CH_3^{EtO}), 22.5 (CH_2^{Hex}), 29.6 (CH_2^{Hex}), 36.1 (CH_2^{Hex}), 43.5 ($\underline{CH}$Ph), 70.0 ($\underline{CH_2}$C(OEt)Cr(CO)$_5$), 77.9 (CH_2^{EtO}), 126.3 (CH^{Ph}), 127.5 (CH^{Ph}), 128.3 (CH^{Ph}), 144.1 (C_q^{Ph}), 216.4 (CO), 223.1 (CO), 359.1 (C=Cr). HRMS (ESI) calcd for $C_{20}H_{21}CrO_6$ $[M\text{-}H]^-$: 409.0749. Found: 409.0775.

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4.2.2. Pentacarbonyl[ethoxy(2-phenyl-2-cyclopentylethyl) methylene]chromium(0) (**2c**)

This compound was prepared according to the general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), cyclopentyl magnesium bromide (0.45 mL, 0.90 mmol), dry THF (6 mL), and EtOH (4 mL). Column chromatography (hexane $R_f = 0.60$, PMA detection) afforded the title compound 0.246 g (97%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92–1.03 (m, 1H), 1.19–1.69 (m, 9H), 1.90–2.04 (m, 2H), 2.88 (dt, $J = 4.5$, 10.5 Hz, 1H), 3.66–3.86 (m, 2H), 4.79–4.85 (m, 2H), 7.06–7.23 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$): δ 14.5, 24.7, 25.2, 31.4, 31.5, 46.4, 49.2, 68.9, 77.8, 126.1, 127.7, 128.1, 144.0, 216.3, 223.0, 358.9. HRMS (ESI) calcd for $C_{21}H_{21}CrO_6$[M-H]$^-$: 421.0749. Found: 421.0768.

4.2.3. Pentacarbonyl[ethoxy(2-phenyl-2-tert-butylethyl)methylene] chromium(0) (**2d**)

The general procedure starting from the carbene **1b** (0.196 g, 0.56 mmol), *tert*-butylmagnesium chloride (0.45 mL, 0.90 mmol), dry THF (6 mL), and EtOH (4 mL) afforded after column chromatography (hexane $R_f = 0.60$, PMA detection) the title compound 0.223 g (97%) as a red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (s, 9H), 1.24 (t, $J = 6.9$ Hz), 2.95 (dd, $J = 3.6$, 11.4 Hz, 1H), 3.66 (dd, $J = 3.9$, 16.2 Hz, 1H), 4.13 (dd, $J = 11.1$, 16.2 Hz, 1H), 4.75–4.82 (m, 2H), 7.07–7.09 (m, 2H), 7.15–7.25 (m, 3H). ^{13}C NMR (76 MHz, $CDCl_3$): δ 14.4, 28.0, 33.8, 52.5, 64.1, 78.1, 126.1, 127.5, 129.2, 141.7, 216.4, 222.9, 358.4. HRMS (ESI) calcd for $C_{20}H_{21}CrO_6$ [M-H]$^-$: 409.0749. Found: 409.0769.

4.2.4. Pentacarbonyl[ethoxy(2-phenylpent-4-enyl)methylene] chromium(0) (**2e**)

The general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), allylmagnesium chloride (0.50 mL, 0.90 mmol), dry THF (6 mL), and EtOH (4 mL) afforded after column chromatography (hexane/DCM 9/1 $R_f = 0.25$, PMA detection) the title compound 0.110 g (47%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (t, $J = 7.2$ Hz, 3H), 2.24–2.40 (m, 2H), 3.16–3.24 (m, 1H), 3.67–3.70 (m, 2H), 4.89–5.04 (m, 4H), 5.56–5.67 (m, 1H), 7.10–7.30 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$): δ 14.6, 40.8, 43.1, 68.8, 77.9, 116.9, 126.4, 127.4, 128.4, 136.0, 143.5, 216.3, 223.0, 358.5. HRMS (ESI) calcd for $C_{19}H_{17}CrO_6$ [M-H]$^-$: 393.0436. Found: 393.0458.

4.2.5. Pentacarbonyl[ethoxy(2,2-diphenylethyl)methylene] chromium(0) (**2f**)

Prepared according to the general procedure starting from the carbene **1b** (0.106 g, 0.30 mmol), phenylmagnesium chloride (0.45 mL, 0.24 mmol), dry THF (3 mL). The reaction mixture was stirred for 30 min at 0 °C before EtOH (4 mL) was added. Column chromatography (hexane, $R_f = 0.40$, PMA detection) afforded the title compound 0.046 g (36%). Analogously, the starting compound was prepared from the carbene **1b** (0.212 g, 0.60 mmol), phenyllithium (3.0 mL, 1.0 mmol), dry THF (6 mL). The reaction mixture was stirred for 15 min at −78 °C, quenched by addition of a solution of acetic acid (0.240 g, 4.0 mmol) in EtOH (4 mL). After 15 min at −78 °C the reaction mixture was warmed to ambient temperature, concentrated under reduce pressure, and column chromatography (hexane/DMC 9/1, $R_f = 0.15$, PMA detection) afforded the title compound 0.130 g (50%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (t, $J = 7.0$ Hz, 3H), 4.21 (d, $J = 7.7$ Hz, 2H), 4.58 (t, $J = 7.7$ Hz), 4.98 (q, $J = 7.0$ Hz, 2H), 7.23–7.25 (m, 6H), 7.30–7.34 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.5, 48.1, 68.4, 78.2, 126.5, 127.7, 128.6, 143.3, 216.3, 222.9, 356.5. HRMS (ESI) calcd for $C_{22}H_{17}CrO_6$ [M-H]$^-$: 429.0436. Found: 429.0461.

4.2.6. Pentacarbonyl{ethoxy[2-phenyl-3-(trimethylsilylmethyl) propyl]methylene}chromium(0) (**2g**)

The general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), trimethylsilylmethyllithium (3.0 mL, 1.0 mmol), dry THF (6 mL) was followed. The reaction mixture was stirred for 15 min at −78 °C, quenched by addition of a solution of acetic acid (0.240 g, 4.0 mmol) in EtOH (4 mL). After 15 min at −78 °C the reaction mixture was warmed to ambient temperature, concentrated under reduce pressure, and column chromatography (hexane $R_f = 0.55$, PMA detection) afforded the title compound 0.238 g (90%) as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ −0.24 (s, 9H), 0.83 (dd, $J = 4.8$ Hz, 1H), 1.04 (dd, $J = 11.1$, 14.1 Hz, 1H), 1.40 (t, $J = 6.9$ Hz, 3H), 3.27–3.33 (m, 1H), 3.59 (dd, $J = 9.0$, 14.7 Hz, 1H), 3.70 (dd, $J = 6.0$, 14.7 Hz, 1H), 4.90 (q, $J = 6.9$ Hz, 2H), 7.11–7.18 (m, 3H), 7.22–7.26 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ −1.3, 14.6, 25.0, 40.0, 73.5, 77.8, 126.4, 127.4, 128.3, 145.1, 216.4, 223.1, 359.1. HRMS (ESI) calcd for $C_{20}H_{23}CrO_6Si$ [M-H]$^-$: 439.0675. Found: 439.0699.

4.3. General procedure for the reaction of alkoxycarbenes 1b and 1c with alkyllithium reagents – formation of enolethers

A solution of alkyllithium (1.5 equiv) was added to a solution of carbene **1b** or **1c** (1.0 equiv) in dry THF (9 mL/mmol) cooled to −78 °C. The resulting mixture was stirred for 15 min at −78 °C followed by the addition of EtOH (6 mL/mmol). The mixture was stirred for 15 min at −78 °C, warmed to ambient temperature and concentrated under reduce pressure. Column chromatography (silica gel) afforded the target compound.

4.3.1. (Z)-1-Ethoxy-3-phenylhept-1-ene (**4b**)

This compound was prepared according to the general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), BuLi (0.38 mL, 0.9 mmol), dry THF (6 mL), and EtOH (4 mL). Column chromatography (hexane/DCM 1/9, $R_f = 0.35$, PMA detection) afforded the title compound 0.080 g (61%) as a colorless oil. The title compound was also prepared from the tungsten carbene complex **1c** (0.290 g, 0.60 mmol) according to the general procedure. Column chromatography (hexane/DCM 1/9, $R_f = 0.35$, PMA detection) afforded the title compound 0.070 g (54%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.1$ Hz, 3H, CH_3^{Hept}), 1.28 (t, $J = 7.1$ Hz, 3H, CH_3^{EtO}), 1.35–1.38 (m, 4H, CH_2^{Hept}), 1.62–1.77 (m, 2H, CH_2^{Hept}), 3.80–3.85 (m, 3H, 2H CH_2^{EtO} + 1H $\underline{CH}$Ph), 4.56 (dd, $J = 6.2$, 9.6 Hz, 1H, =CH−), 6.02 (d, $J = 6.2$ Hz, 1H, =$\overline{CH}$−O), 7.19–7.22 (m, 1H, CH^{Ph}), 7.28–7.32 (m, 4H, CH^{Ph}). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.1 (CH_3^{Hept}), 15.3 (CH_3^{EtO}), 22.7 (CH_2^{Hept}), 29.8 (CH_2^{Hept}), 36.6 (CH_2^{Hept}), 40.3 (CH^{Ph}), 67.6 (CH_2^{EtO}), 111.3 (=CH−), 125.6 (CH^{Ph}), 127.3 (CH^{Ph}), 128.3 (CH^{Ph}), 144.3 (=CH−O), 146.5 (C_q^{Ph}). HRMS (ESI) calcd for $C_{15}H_{23}O$ [M+H]$^+$: 219.1743. Found: 219.1742.

4.3.2. (Z)-1-Ethoxy-3,5-diphenylpent-1-ene (**4c**)

The general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), phenethyllithium (3.1 mL, 1.0 mmol), dry THF (6 mL), and EtOH (4 mL) afforded after column chromatography (hexane/DCM 4/1, $R_f = 0.30$, PMA detection) the title compound 0.090 g (56%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (t, J = 7.1 H, 3H), 2.00–2.08 (m, 2H), 2.60–2.65 (m, 1H), 2.70–2.75 (m, 1H), 3.84–3.93 (m, 3H), 4.62 (dd, $J = 6.2$, 9.60 Hz, 1H), 6.09 (d, $J = 6.2$ Hz, 1H), 7.21–7.25 (m, 4H), 7.31–7.36 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.4, 34.0, 38.7, 40.2, 67.7, 110.7, 125.6, 125.8, 127.3, 128.2, 128.4, 128.5, 142.6, 144.7, 146.0. HRMS (EI) [M]$^+$ calcd for $C_{19}H_{22}O$: 266.1665. Found: 266.1645.

4.3.3. (Z)-1-Ethoxy-3-phenyl-4,4-dimethylpent-1-ene (**4d**)

The compound was prepared according to the general

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procedure starting from carbene **1b** (0.212 g, 0.60 mmol), *tert*-butyllithium (0.53 mL, 0.90 mmol), dry THF (6 mL), and EtOH (4 mL). Column chromatography (hexane/DCM 9/1, $R_f = 0.35$, PMA detection) afforded the title compound 0.045 g (34%) as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (s, 9H), 1.22 (t, $J = 7.1$ Hz, 3H), 3.68 (d, $J = 10.7$ Hz, 1H), 3.78 (q, $J = 7.1$ Hz, 2H), 4.89 (dd, $J = 6.4$, 10.7 Hz, 1H), 6.06 (d, $J = 6.4$ Hz, 1H), 7.20–7.30 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.3, 27.8, 34.3, 50.5, 67.5, 107.5, 125.6, 127.5, 129.4, 143.5, 144.8. HRMS (EI) $[M]^+$ calcd for $C_{14}H_{19}O$: 203.1430. Found: 203.1419.

4.3.4. (Z)-Trimethyl(4-ethoxy-2-phenylbut-3-enyl)silane (**4e**)

The general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), trimethylsilylmethyllithium (0.90 mL, 0.90 mmol), dry THF (6 mL), and EtOH (4 mL) afforded after column chromatography (hexane/DCM 9/1, $R_f = 0.40$, PMA detection) the title compound 0.115 g (77%) as a yellow oil. The title compound was also prepared from the tungsten carbene complex **1c** (0.290 g, 0.60 mmol) by the same procedure. Column chromatography (hexane/DCM 1/9, $R_f = 0.40$, PMA detection) afforded the title compound 0.111 g (75%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.02 (s, 9H), 1.07 (d, $J = 7.8$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H), 3.83 (q, $J = 7.0$ Hz, 2H), 4.03 (m, 1H), 4.56 (dd, $J = 6.2$, 9.7 Hz, 1H), 5.92 (d, $J = 6.2$ Hz, 1H), 7.18–7.20 (m, 1H), 7.30–7.34 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.4, 25.3, 36.2, 67.6, 113.6, 125.6, 126.9, 128.3, 143.0, 148.7. HRMS (EI) $[M]^+$ calcd for $C_{15}H_{24}OSi$: 248.1591. Found: 248.1586.

4.3.5. (Z)-1-(3-ethoxy-1-phenylallyl)cyclohept-1-ene (**4f**)

The general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), cycloheptenyllithium (3.0 mL, 1.0 mmol), dry THF (6 mL), and EtOH (4 mL) afforded after column chromatography (hexane/DCM 9/1, $R_f = 0.40$, PMA detection) the title compound 0.110 g (72%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (t, $J = 7.1$ Hz, 3H), 1.37–1.42 (m, 2H), 1.51–1.55 (m, 2H), 1.71–1.75 (m, 2H), 2.04–2.07 (m, 2H), 2.18–2.22 (m, 2H), 3.81–3.87 (m, 2H), 4.55 (d, $J = 9.8$ Hz, 1H), 4.70 (dd, $J = 6.2$, 9.8 Hz, 1H), 5.80 (t, $J = 6.4$ Hz, 1H), 6.09 (d, $J = 6.2$ Hz, 1H), 7.20–7.22 (m, 1H), 7.30–7.31 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.4, 27.2, 27.3, 28.5, 31.8, 32.7, 48.7, 67.7, 108.2, 125.8, 127.0, 128.06, 128.10, 144.0, 144.3, 146.2. HRMS (ESI) calcd for $C_{18}H_{25}O$ $[M+H]^+$: 257.1900. Found: 257.1899.

4.3.6. (Z)-1-Ethoxy-3,3-diphenylprop-1-ene (**4g**)

This compound was prepared according to the general procedure starting from the carbene **1b** (0.212 g, 0.60 mmol), phenyllithium (3.0 mL, 1.0 mmol), dry THF (6 mL), and EtOH (4 mL). Column chromatography (hexane → hexane/DCM 9/1, $R_f = 0.35$, PMA detection) afforded the title compound 0.063 g (44%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (t, $J = 7.0$ Hz, 3H), 3.87 (q, $J = 7.0$ Hz, 2H), 4.95 (dd, $J = 6.3$, 9.9 Hz, 1H), 5.31 (d, $J = 9.9$ Hz, 1H), 6.18 (d, $J = 6.3$ Hz, 1H), 7.21–7.24 (m, 2H), 7.27–7.28 (m, 4H), 7.30–7.34 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.4, 45.3, 67.8, 109.3, 126.0, 128.2, 128.3, 144.7, 145.1. HRMS (EI) $[M]^+$ calcd for $C_{17}H_{18}O$: 238.1352. Found: 238.1347.

4.3.7. Pentacarbonyl[ethoxy(2-butyl-hex-1-enyl)methylene] chromium(0) (**7a**)

This compound was prepared according to the general procedure starting from the carbene **5** (0.165 g, 0.50 mmol), *n*-butyllithium (0.31 mL, 0.75 mmol) in dry THF (5 mL). The reaction mixture was stirred for 15 min at −78 °C, quenched by addition of a solution of acetic acid (0.240 g, 4.0 mmol) in EtOH (4 mL). After 15 min at −78 °C the reaction mixture was warmed to ambient temperature, concentrated under reduce pressure, and column chromatography (hexane $R_f = 0.50$, PMA detection) afforded the title compound 0.060 g (31%) as a red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89–0.95 (m, 6H), 1.32–1.51 (m, 8H), 1.65 (t, $J = 6.9$ Hz, 3H), 2.08–2.18 (m, 4H), 5.06 (q, $J = 6.9$ Hz, 2H), 7.20 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.9, 14.0, 15.2, 22.6, 23.3, 30.3, 31.2, 33.8, 38.5, 76.8, 140.9, 147.3, 216.9, 224.1, 337.0. HRMS (ESI) calcd for $C_{18}H_{23}CrO_6$ $[M-H]^-$: 387.09052. Found: 387.09045.

4.3.8. (E) and (Z)-Pentacarbonyl[ethoxy(2-phenethyl-hex-1-enyl) methylene]chromium(0) (**7b**)

The carbene was prepared according to the general procedure starting from the carbene **5** (0.195 g, 0.591 mmol), phenethyllithium (3.0 mL, 1.0 mmol), dry THF (6 mL). The reaction mixture was stirred for 15 min at −78 °C, quenched by addition of a solution of acetic acid (0.240 g, 4.0 mmol) in EtOH (4 mL). After 15 min at −78 °C the reaction mixture was warmed to ambient temperature, concentrated under reduce pressure, and column chromatography (hexane $R_f = 0.35$, PMA detection) afforded the title compound 0.040 g (16%) as a 1/1 mixture of *E*/*Z* isomers in form of a red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92–0.98 (m, 6H), 1.35–1.45 (m, 6H), 1.51–1.56 (m, 2H), 1.63 (t, $J = 7.1$ Hz, 3H), 1.67 (t, $J = 7.1$ Hz, 3H), 2.14 (t, $J = 7.8$ Hz, 2H, CH_2^Z), 2.21 (t, $J = 8.2$ Hz, 2H, CH_2^E), 2.47 (t, $J = 7.9$ Hz, 2H CH_2^E), 2.55 (t, $J = 7.7$ Hz, 2H, CH_2^Z), 2.74 (t, $J = 8.6$ Hz, 2H, CH_2^Z), 2.85 (t, $J = 8.3$ Hz, 2H, CH_2^E), 5.04–5.08 (m, 4H, CH_2), 7.18–7.34 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.9, 14.0, 15.2, 15.4, 22.5, 23.2, 30.3, 31.1, 33.7, 34.6, 34.9, 35.2, 38.4, 40.1, 76.8, 76.9, 126.19, 126.23, 128.1, 128.3, 128.52, 128.53, 140.9, 141.0, 141.2, 141.3, 216.81, 216.82, 224.0, 337.4, 338.4. HRMS (ESI) calcd for $C_{22}H_{23}CrO_6$ $[M-H]^-$: 435.09052. Found: 435.09057.

4.4. General procedure for hydrolysis of enolethers

Hydrochloric acid (1 M solution in water, 4.5 mL/mmol) was added to a solution of enolether **4** in acetone (15 mL/mmol). The resultant mixture was stirred for 2 h at ambient temperature. Then acetone was removed under reduce pressure, water layer was diluted with ether, water layer was removed, and organic layer was washed with K_2CO_3 (aq), and brine. Organic phase was then dried over $MgSO_4$, concentrated under reduce pressure and column chromatography afforded the expected product.

4.4.1. 3-Phenylheptanal (**5b**)

The general procedure starting from enol ether **4b** (0.077 g, 0.35 mmol), HCl (1.5 mL, 1M aq solution) and acetone (5 mL) afforded after column chromatography (hexane/DCM 4/1, $R_f = 0.15$, PMA detection) the title compound 0.060 g (89%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (t, $J = 6.9$ Hz, 3H, CH_3^{Hept}), 1.10–1.32 (m, 4H, CH_2^{Hept}), 1.59–1.68 (m, 2H, CH_2^{Hept}), 2.69–2.72 (m, 2H, $\underline{CH_2}CHO$), 3.16 (p, $J = 7.8$ Hz, 1H, $\underline{CH}Ph$), 7.17–7.33 (m, 5H, CH^{Ph}), 9.66 (t, $J = 2.4$ Hz, 1H, CHO). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.0 (CH_3^{Hept}), 22.6 (CH_2^{Hept}), 29.5 (CH_2^{Hept}), 36.4 (CH_2^{Hept}), 40.1 (CH_2^{Hept}), 50.7 ($\underline{CH}Ph$), 126.5 (CH^{Ph}), 127.5 (CH^{Ph}), 128.6 (CH^{Ph}), 144.0 (C_q^{Ph}), 202.1 (CHO). HRMS (EI) $[M]^+$ calcd for $C_{13}H_{18}O$: 190.1352. Found: 190.1350.

4.4.2. 3-Phenyl-4-(trimethylsilyl)butanal (**5e**)

The general procedure starting from the enol ether **4e** (0.092 g, 0.37 mmol), HCl (1.5 mL, 1M aq solution) and acetone (5 mL) afforded after column chromatography (hexane/DCM 4/1, $R_f = 0.20$, PMA detection) the title compound 0.080 g (98%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.15 (s, 9H), 0.98–1.10 (m, 2H), 2.70–2.82 (m, 2H), 3.33–3.39 (m, 1H), 7.22–7.34 (m, 5H), 9.67 (t, $J = 2.1$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ −1.2, 25.1, 36.8, 54.4, 126.7, 127.4, 128.6, 145.3, 202.2. HRMS (ESI) calcd for $C_{13}H_{20}ONaSi$ $[M+Na]^+$: 243.11756. Found: 243.11757.

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*4.4.3. 3-Phenyl-3-(cyclohepten-1-yl)propanal (**5f**)*

The general procedure starting from the enol ether **4f** (0.099 g, 0.39 mmol), HCl (1.5 mL, 1M aq solution) in acetone (5 mL) afforded after column chromatography (hexane/DCM 4/1, $R_f = 0.20$, PMA detection) the title compound 0.083 g (94%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20–1.30 (m, 2H), 1.42–1.48 (m, 2H), 1.62–1.70 (m, 2H), 1.95–1.99 (m, 2H), 2.12–2.17 (m, 2H), 2.69–2.88 (m, 2H), 3.86 (t, $J = 7.5$ Hz, 1H), 5.77 (t, J = 6. Hz, 1H), 7.18–7.32 (m, 5H), 9.69 (t, $J = 2.2$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.7, 27.0, 28.3, 31.8, 32.6, 47.0, 48.4, 126.6, 127.7, 127.9, 128.4, 141.9, 145.0, 202.2. HRMS (ESI) calcd for $C_{16}H_{20}NaO$ $[M+Na]^+$: 251.14064. Found: 251.14058.

*4.4.4. 3-Butylhept-3-enal (**8**)*

A solution of *n*-butyllithium (0.86 mL, 2.07 mmol) was added to the solution of carbene **5** (0.456 g, 1.38 mmol) in dry THF (13 mL) cooled to −78 °C. The resulting mixture was stirred for 15 min at −78 °C followed by the addition of EtOH (10 mL). The mixture was then stirred for 15 min at −78 °C, warmed to ambient temperature and concentrated under reduce pressure. The isolated crude product was dissolved in acetone (10 mL) and 1M aqueous HCl (6 mL) was added. The resultant mixture was stirred for 2 h at ambient temperature. Then acetone was removed under reduce pressure, water layer was diluted with ether, water layer was removed, and organic layer was washed with K_2CO_3 (aq), and brine. Organic phase was then dried over $MgSO_4$, concentrated under reduce pressure and column chromatography (hexane/EtOAc 20/1, $R_f = 0.40$) afforded the title compound 0.071 g (31%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90–0.96 (m, 6H), 1.26–1.56 (m, 8H), 2.22 (t, $J = 8.4$ Hz, 2H), 2.55 (t, $J = 7.5$ Hz, 2H), 5.85 (d, $J = 8.1$ Hz, 1H), 9.99 (d, $J = 8.1$ Hz, 1H), in accordance with reference [14].

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.02.038.

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