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Coupling–Isomerization Synthesis of Chalcones

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Dedicated to Professor Barry M. Trost on the occasion of his 65th birthday

Abstract: The Sonogashira coupling of electron-deficient (hetero)aryl halides **1** and (hetero)aryl or alkenyl 1-propargyl alcohols **2** does not terminate at the stage of the expected internal propargyl alcohols, but rather gives rise to the formation of α,β-unsaturated ketones **3** with a variety of acceptor substituents. This new domino reaction, a coupling–isomerization reaction (CIR), can be rationalized as a sequence of rapid Pd/Cu-catalyzed alkynylation followed by a slow amine-base-catalyzed propargyl alcohol–enone isomerization. Performing the CIR in deuterated protic solvents or with a selectively deuterated propargyl alcohol revealed that the base-catalyzed isomerization step proceeds through a formal 1,3-H shift with minimal H/D exchange with the surrounding solvent. Additionally, ^{19}F NMR kinetic measurements on the isomerization step with the fluorinated propargyl alcohol **4r** support the mechanistic rationale.

Keywords: C–C coupling · domino reactions · ketones · kinetics · synthetic methods

Introduction

Chalcones, that is, 1,3-diaryl prop-2-en-1-ones, are an important class of naturally occurring[1] and non-natural biologically active compounds. They cover a wide spectrum of pharmacological activity[2] and their enormous potential ranges from antibacterial, including antimycobacterial, antifungal, antiviral, antiprotozoal, antioxidative, anti-inflammatory, gastroprotective, to antineoplastic agents. A number of these compounds has also proved to be highly active as antiplasmodial,[3] antiviral (e.g., by inhibition of HIV integrase),[4] or antileishmania agents,[5] and as inhibitors of pulmonary carcinogenesis.[6] Chalcones have also found application in materials science. By virtue of $[2\pi+2\pi]$ photocycloaddition, some chalcones are photochromic in merocyanine-containing polymer matrices.[7] While 1-ferrocenyl 3-biaryl propenones are novel types of nonlinear optical (NLO) chromophores,[8] photorefractive polymers doped with push/pull-substituted chalcones show remarkable electrooptic responses,[9] and NLO properties of silylated chalcones in sol–gel matrices have been studied.[10]

In synthetic heterocyclic chemistry, as a consequence of the bifunctional Michael system, 1,3-diaryl prop-2-en-1-ones are important three-carbon building blocks. Among many classes of five-, six-, and seven-membered heterocycles the underlying principle is always the Michael addition–cyclocondensation sequence of chalcones and bifunctional nucleophiles. Furthermore, as dienophiles and dipolarophiles, chalcones can also participate in cycloadditions and furnish in the case of 1,3-dipolar cycloadditions[11] with diazo alkanes pyrazolines,[12] with azides triazolines,[13] with nitrones isoxazolidines,[14] with azomethinylides pyrrolidines,[15] and with nitrile oxides isoxazolines.[16]

The standard synthesis of the important class of chalcones is, as for many other α,β-unsaturated carbonyl compounds, the aldol condensation.[17] Besides a Wittig–Horner access[18] and the fragmentation of oxazolidines by alkylation, Hofmann elimination, and dimethylamine elimination,[19] also stoichiometric organometallic processes such as the vanadium(III)-mediated oxidative coupling of aldehydes and vinyl lithium or vinyl magnesium reagents[20] furnish chalcones. Another option is the isomerization of propargyl alcohols in the acid-catalyzed Meyer–Schuster rearrangement.[21]

Although aldol condensation opens a general route to chalcones, major shortcomings are the strongly basic or acidic additives and reagents and the sometimes vigorous conditions in the condensation step. Therefore, mild reaction conditions as in transition-metal-catalyzed cross-coupling reactions are particularly favorable and promise a high degree

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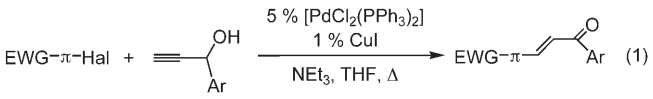
of functional-group tolerance. Conducting cross-coupling in domino fashion, whereby a suitable reactive functionality is generated en route,[22] offers the prospect of extending this methodology to one-pot sequences and paving the way to manifold opportunities for developing novel lead structures of pharmaceuticals, catalysts, and even novel molecule-based materials.

As part of our program to develop new multicomponent methodologies initiated by transition-metal-catalyzed C–C bond formation, we have discovered and developed a new mode of alkyne activation by a detouring outcome of Sonogashira coupling[23] [Eq. (1)].[24] In the past years this new chalcone synthesis has opened an entry to novel consecutive multicomponent syntheses of pharmaceutically relevant heterocycles in a one-pot fashion.[24,25] Here we report synthetic studies on and mechanistic insights into this unusual transformation of electron-deficient halides and (hetero)aryl propargyl alcohols leading to 1,3-di(hetero)aryl propenones under thermal conditions.

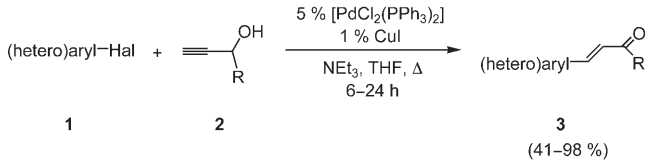


(1)

EWG: electron withdrawing group

Results and Discussion

Synthetic studies: The reaction of sufficiently electron deficient organic and organometallic (hetero)aryl halides **1** that bear electron-withdrawing groups in conjugation with the carbon–halide bond and 1-propargyl alcohols **2** with (hetero)aryl or alkenyl substituents in the 1-position under Sonogashira conditions, that is, in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ and CuI in a boiling mixture of triethylamine and THF, gave rise to formation of 1-substituted 3-(hetero)aryl propenones **3** in good to excellent yields (Scheme 1, Tables 1 and 2). With respect to the outcome of this process this transformation is from now on called a coupling–isomerization reaction (CIR).



Scheme 1. A novel coupling–isomerization reaction (CIR) for the synthesis of 1-substituted 3-(hetero)aryl propenones **3**.

The structures of enones **3** were unambiguously assigned by ^1H, ^{13}C, COSY, and NOESY NMR experiments. Most characteristically, in the ^1H spectra olefinic methine resonances for the newly formed *trans*-configured enone double bonds, indicated by the characteristic appearance of doublets with large vicinal coupling constants (J_{trans} = 15.5–18.9 Hz), are found between δ = 7.03 and 7.88 ppm (as far as they are not superimposed by other aromatic protons). The other (hetero)aromatic, olefinic, or aliphatic protons are detected in the expected regions, whereas the proton signals of the complexed arenes in complexes **3b**, **3c**, **3v**, and **3ab** are found between δ = 5.67 and 6.67 ppm. Indicative for the formation of α,β-unsaturated ketones are the carbonyl resonances in the ^{13}C NMR spectra between δ = 182.4 and 191.0 ppm. Additionally, for fluorine-substituted derivatives **3f**, **3q**, and **3r** the ^1J to ^4J carbon–fluorine couplings can be beneficially used for the unambiguous assignment of further aromatic methine and quaternary carbon nuclei. For the chromium carbonyl complexes **3b**, **3c**, **3v**, and **3ab** the resonances of the carbonyl nuclei bound to the chromium atom can be detected between δ = 233.5 and 233.7 ppm.

In the IR spectra the carbonyl stretching vibrations for the enones can be found between 1656 and 1675 cm^{-1}. In addition, for the chromium carbonyl complexes **3b**, **3c**, **3v**, and **3ab** the diagnostic two carbonyl vibrations appear at 1959–1969 cm^{-1} and 1876–1890 cm^{-1}. Furthermore, the structure of **3** was unambiguously supported by an X-ray crystal structure analysis of **3q** (Figure 1, Table 3).[26]

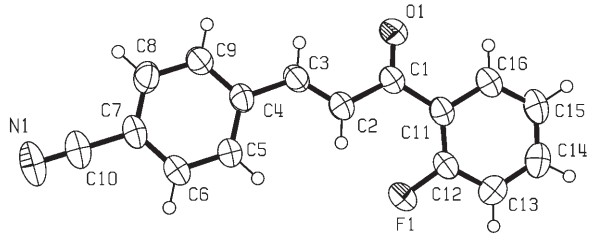
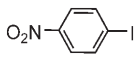
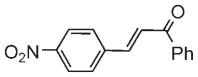
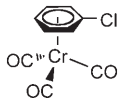
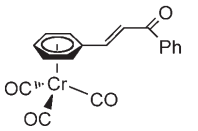
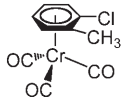
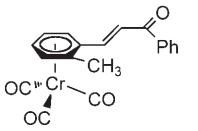
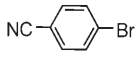
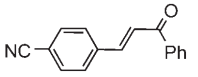
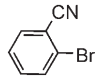
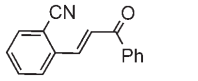
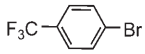
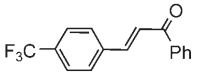
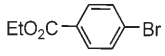
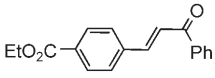
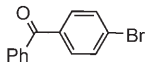
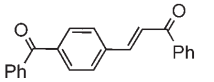
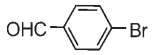
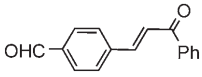
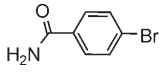
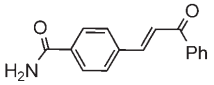
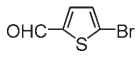
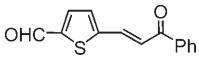
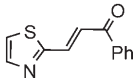
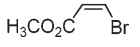
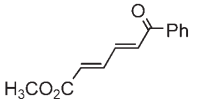
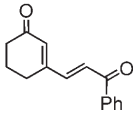


Figure 1. Molecular structure of chalcone **3q** in the solid state.

Abstract in German: *Die Sonogashira-Kupplung von elektronenarmen (Hetero)Arylhalogeniden **1** und (Hetero)Aryl- oder Alkenyl-1-propargylalkoholen **2** endet nicht auf der Stufe der erwarteten Kupplungsprodukte, sondern führt zu α,β-ungesättigten Ketonen **3** mit einer ganzen Palette an Akzeptorsubstituenten. Diese neue Domino-Reaktion, eine Kupplungs-Isomerisierungs-Reaktion (CIR, coupling isomerization reaction), kann als eine Sequenz aus einer raschen Pd-Cu-katalysierten Alkinylierung gefolgt von einer langsamen aminbasekatalysierten Propargylalkohol-Enon-Isomerisierung aufgefasst werden. Führt man die CIR in deuterierten protischen Solventien oder mit einem selektiv deuterierten Propargylalkohol durch, so wird offenbar, dass der basenkatalysierte Isomerisierungsschritt unter einer formalen 1,3-H-Verschiebung und mit minimalem H/D-Austausch mit dem umgebenden protischen Solvens abläuft. ^{19}F NMR-kinetische Messungen des Isomerisierungsschrittes mit dem fluorierten Propargylalkohol **4r** stützen das vorgeschlagene mechanistische Szenario.*

Table 1. Synthesis of 1-phenyl 3-(hetero)aryl propenones **3** by CIR.

Entry	(Hetero)aryl halide **1**		Propargylic alcohol **2**		Enone **3**		Yield [%]
1		**1a**		**2a**		**3a**	82
2		**1b**		**2a**		**3b**	79
3		**1c**		**2a**		**3c**	75
4[a]		**1d**		**2a**		**3d**	96
5		**1e**		**2a**		**3e**	62
6		**1f**		**2a**		**3f**	75
7[a]		**1g**		**2a**		**3g**	58
8[b]		**1h**		**2a**		**3h**	58
9		**1i**		**2a**		**3i**	57
10[a]		**1j**		**2a**		**3j**	77
11		**1k**		**2a**		**3k**	85
12		**1l**		**2a**		**3l**	75
13		**1m**		**2a**		**3m**	89
14		**1n**		**2a**		**3n**	90

[a] In THF/NEt_3 (1:1). [b] In $HNEt_2$.

The scope of this novel enone synthesis is relatively broad. As shown in preliminary experiments[24] a sufficiently electron-withdrawing halide **1** is necessary to trigger the CIR, since in cases in which electroneutral halides were applied the sequence stopped after the Sonogashira coupling. With respect to the electron-deficient halide **1** (Table 1) the scope ranges from strongly electron-withdrawing aryl halides and $Cr(CO)_3$-complexed chloroarenes (entries 2 and 3) to systems with reduced acceptor capacity, such as amides (entry 10), 2-bromothiazole (**1l**) (entry 12), and vinylogous esters and ketones (entries 13 and 14). The other coupling partner, the 1-substituted propargyl alcohol **2**, can be varied in its structure and electronic nature (Table 2). Aryl substituents with various electronic natures (entries 1–5), even with further halide substituents, are tolerated and can be carried through the sequence. Furthermore, electroneutral and electron-rich heterocyclic substituents (entries 6–11) are fully compatible with the CIR, and also alkenyl-substituted propargyl alcohols (entries 12–14) give the expected enones in good yields. As a restriction it became evident that propargyl alcohols with alkyl substituents do not furnish enones, and the reaction halted at the stage of the coupled propargyl alcohol.[24] Besides THF as cosolvent, other solvents such as ethanol, methanol, acetonitrile, DMF (at 50 °C), and toluene can be successfully applied. It is also possible to conduct the CIR in pure base. Amine bases, such as triethylamine, diethylamine, and pyrrolidine, turned out to be favorable. Methodologically, this new enone synthesis is an alternative versatile access to chalcones and related derivatives and has paved the way to consecutive multicomponent syntheses of various heterocycle classes.[24,25]

Prior to our studies, this unusual reaction was only observed and discussed by Minn[27] and Kundu and Das[28] for the coupling of 2-halo-substituted pyrimidines with 1-phenyl propargyl alcohol. Therefore, Kundu and Das speculated on the mechanism by assuming coordination of an intermediate during a hydropalladation–dehydropalladation catalytic cycle to the heterocyclic nitrogen atom.[28b] However, due to a lack of heteroatom coordination in many of our examples, this explanation fails for the formation of enones **3**. Furthermore, we could now show that isomerization exclusively occurs as a base-catalyzed second step.[24] All this prompted us to investigate the CIR mechanistically and propose a reasonable general mechanistic picture of the important sequence.

Table 2. Synthesis of 1-substituted 3-(hetero)aryl propenones **3** by CIR.

Entry	(Hetero)aryl halide **1**	Propargylic alcohol **2**	Enone **3**	Yield [%]
1	**1d**	**2b**	**3o**	98
2	**1a**	**2c**	**3p**	80
3	**1d**	**2d**	**3q**	93
4	**1d**	**2e**	**3r**	96
5[a]	**1d**	**2f**	**3s**	83
6	**1a**	**2g**	**3t**	95
7	**1n**	**2g**	**3u**	95
8	**1b**	**2g**	**3v**	57
9	**1m**	**2g**	**3w**	90
10	**1a**	**2h**	**3x**	84
11[b]	**1d**	**2i**	**3y**	79
12[a]	**1d**	**2j**	**3z**	68
13[c]	**1d**	**2k**	**3aa**	66
14	**1b**	**2l**	**3ab**	41

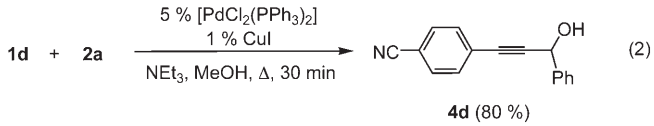
[a] In THF/NEt_3 (1:1). [b] In EtOH/NEt_3 (1:1.8). [c] In CH_3CN/NEt_3 (1:1).

Mechanistic studies: Preliminary studies indicated that the CIR occurs by fast Sonogashira coupling followed by rate-determining base-catalyzed isomerization. After reaction of the halide **1d** and propargyl alcohol **2a** in a boiling mixture of NEt_3 and methanol for 30 min, the presumed coupled propargylic alcohol **4** was isolated in 80% yield [Eq. (2)]. However, analysis of the crude reaction mixture revealed that chalcone **2d** had already formed to some extent. As expected, as isomerization proceeds, the ratio between chalcone **2d** and coupled propargylic alcohol **4d** increases with time. Therefore, it seemed also possible to decouple the fast coupling from the slow isomerization for a thorough investigation of the propargylic alcohol–enone isomerization.

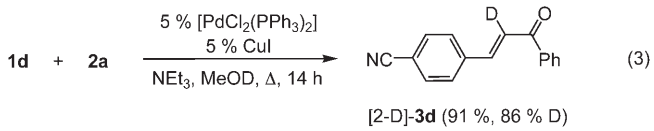
It is reasonable to assume that several intermediates in the CIR are alcohols, which finally furnish an α,β-unsaturated ketone as the end of the sequence. Hence, performing the above reaction under deuterium-exchange conditions could give insight into in which intermolecular H/D exchange processes could be involved. On reaction of *p*-bromobenzonitrile (**1d**) and the propargyl alcohol **2a** in a boiling mixture of NEt_3 and CH_3OD, deuterated chalcone [2-D]-**3d** was obtained in 91% yield [Eq. (3)]. Interestingly, triethylamine-catalyzed isomerization of presumed and actual intermediate **4d** under the same conditions gave [2-D]-**3d** in 93% yield [Eq. (4)]. A Heck-type pathway consisting of an insertion–β-hydride elimination scenario could be excluded, since no substantial transformation of **1d** and **2a** was observed if CuI was omitted from the reaction mixture.

Table 3. Crystal data and structure refinement for **3q**.

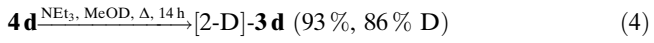
formula	$C_{16}H_{10}FNO$	ρ_{calcd} [g cm^{-3}]	1.339
M_r	251.25	μ [mm^{-1}]	0.094
T [K]	293(2)	crystal size [mm]	0.53 × 0.40 × 0.20
λ [Å]	0.71073	θ range [°]	2.96–23.97
crystal system	triclinic	reflections collected	2117
space group	$P\bar{1}$	independent reflections	1936 (R(int) = 0.0652)
Z	2	absorption correction	semi-empirical from equivalents
a [Å]	6.964(2)	max./min. transmission	0.9914/0.9324
b [Å]	8.6064(12)	refinement method	full-matrix least-squares on F^2
c [Å]	10.536(2)	parameter	172
α [°]	91.367(13)	GOF on F^2	1.014
β [°]	95.30(2)	final R index [$I > 2\sigma(I)$]	0.0494
γ [°]	97.24(2)	$R_w(F^2)$	0.0637
V [Å^3]	623.3(2)	largest diff. peak/hole [e Å^{-3}]	0.190/−0.256



(2)



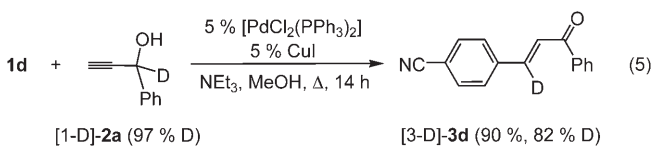
(3)



(4)

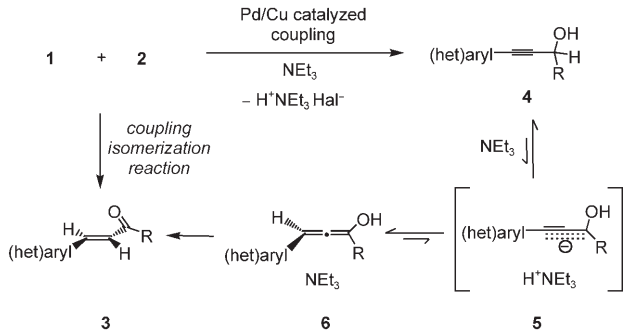
The selectivity of deuteration was finally determined by mass spectrometry. For the CIR and the isomerization step 86% deuterium incorporation was found (along with 9% of bis-deuteration). Interestingly, by integration of the resonance of the residual methine proton in the position α to the carbonyl group at $\delta = 7.59$ ppm in the ^{1}H NMR spectrum of [2-D]-**3d** as a doublet ($^3J = 15.8$ Hz) a 95% degree of deuteration was determined. The connectivity of [2-D]-**3d** was unambiguously established by an HMBC NMR spectrum, in which the resonance of the methine proton in the position β to the carbonyl group appeared at $\delta =$ 7.78 ppm.[29]

As a key experiment to find out to what extent H/D exchange of the propargylic proton is involved in isomerization of the intermediate propargyl alcohol **4d** to enone **3d**, we selectively subjected deuterated propargyl alcohol [1-D]-**2a**[30] (97% deuterium labeling) to CIR with *p*-bromobenzonitrile (**1d**). After reaction of **1d** and propargyl alcohol [1-D]-**2a** in a boiling mixture of NEt_3 and methanol, deuterated chalcone [3-D]-**3d** was obtained in 90% yield with 82% deuteration (determined by mass spectrometry, no bis-deuteration was found) at the position β to the carbonyl group [Eq. (5)].



(5)

A high degree of retention of deuteration in the enone can be interpreted as minimal H/D exchange of the propargylic proton (deuteron) with the protic medium. This is particularly interesting, since the isomerization is an amine-base-catalyzed process, whereas the 1,3-shift of the propargylic proton (deuteron) to become a β-methine proton (deuteron) seems to be the result of an intramolecular proton transfer. As 1,3-H shifts are orbital-symmetry forbidden and concerted suprafacial processes and antarafacial transfer are geometrically not accessible,[31] a plausible explanation for this unusual 1,3-H shift is deprotonation of propargyl alcohol [1-D]-**4d** at the propargylic position to generate contact ion pair **5d** in a solvent cage in which H/D exchange of the triethylammonium cation with the protic medium is considerably slower than reprotonation. Hence, allenol **6d** becomes the short-lived isomerization product that undergoes rapid and irreversible tautomerism to the thermodynamic sink of the isomerization sequence and conclusively rationalizes the generation of chalcone **3d**. Therefore, the mechanistic rationale of the CIR can be described as in Scheme 2. So-



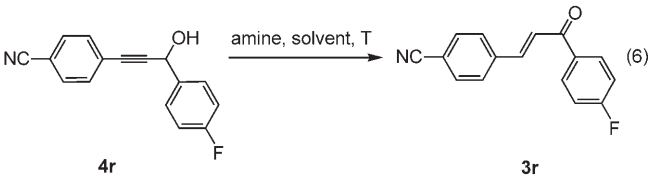
Scheme 2. Mechanistic rationale of the CIR.

nogashira coupling of halide **1** and terminal propargyl alcohol **2** furnishes internal propargyl alcohol **4**, which is deprotonated to give the propargyl anion–triethylammonium contact ion pair **5** as a short-lived intermediate. Protonation of the anion either gives propargyl alcohol **4** or allenol **6**. The latter isomerizes to enone **3**.

Hence, this mechanistic scenario inevitably explains that H/D exchange in deuterated solvents is possible at the stages of alcohols **2**, **4**, and **6**, and therefore selective deuter-

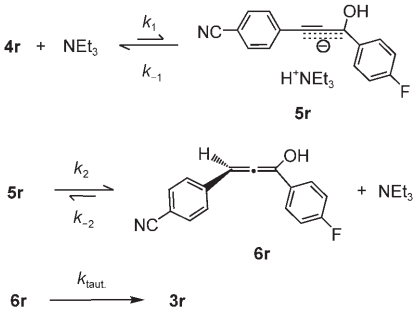
ation in the position α to the carbonyl group becomes evident.

Finally, kinetic investigations were performed to gain more insight into the rate-determining isomerization step. The timescale of the propargyl alcohol–enone isomerization is evidently suited to NMR kinetics studies, and therefore isomerization of fluoro-substituted propargyl alcohol **4r** to enone **3r** became the model of choice [Eq. (6)], since the



^{19}F NMR spectra of **4r** and **3r** display clearly separated singlets at $\delta = -139.1$ (**4r**) and -130.4 ppm (**3r**), and because various amines and solvents without specific labeling can be applied. Initial qualitative kinetic measurements revealed that the isomerization with DBU ($pK_a = 12$) as base was already complete when the sample was placed in the spectrometer. Triethylamine ($pK_a = 10.8$), as used in the synthetic studies, takes several hours for complete conversion, whereas no isomerization was detected even after 12 h when pyridine ($pK_a = 5.2$) was used.

This indicates a strong dependence on the basicity of the applied amine. Therefore, the mechanistic working hypothesis of propargyl alcohol–enone isomerization gives three elementary steps (Scheme 3). Assuming slow deprotonation of



Scheme 3. Presumed elementary steps of the propargyl alcohol–enone isomerization.

4r and of short-lived allenol **6r**, rapid protonation of contact ion pair **5r**, low steady-state concentrations of **5r** and **6r**, that is, Bodenstein's stationary-state approximation,[32] and rapid and irreversible tautomerism of **6r** to give enone **3r** leads to a simplification of the rate law for the decay of the concentration of propargyl alcohol **4r**, which can be monitored by ^{19}F NMR spectroscopy [Eq. (7)].

$$-\frac{d[\mathbf{4r}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{4r}][NEt_3] \quad (7)$$

Now two scenarios can be envisioned depending on the rates of the first two elementary steps. For $k_{-1} \ll k_2$ Equation (7) simplifies to a second-order rate law in which deprotonation of **4r** is the rate-determining step [Eq. (8)]. For $k_{-1} \gg k_2$ Equation (7) turns into a rate law in which rapid deprotonation pre-equilibrium precedes rate-determining protonation of contact ion pair **5r** to give allenol **6r** [Eq. (9)].

$$-\frac{d[\mathbf{4r}]}{dt} = k_1[\mathbf{4r}][NEt_3] \quad (8)$$

$$-\frac{d[\mathbf{4r}]}{dt} = Kk_2[\mathbf{4r}][NEt_3] \quad (9)$$

However, the rate constants for protonation of contact ion pair **5r** to starting material **4r** (k_{-1}) or to allenol **6r** (k_2) should be of comparable magnitude. Therefore, it is reasonable to treat the empirical rate constants in the sense of k_{obs} [Eq. (10)] in which k_{obs} is k_1 or Kk_2.

$$-\frac{d[\mathbf{4r}]}{dt} = k_{obs}[\mathbf{4r}][NEt_3] \quad (10)$$

Further simplification is achieved by using an excess of triethylamine, as in the synthetic studies, which gives a pseudo-first-order rate law with $k_{obs'} = [NEt_3]k_{obs}$ that is suitable for a straightforward mathematical treatment [Eq. (11)].

$$-\frac{d[\mathbf{4r}]}{dt} = k_{obs'}[\mathbf{4r}] \quad (11)$$

Since formation of chalcone **3r** was quantitative in the synthetic studies, integration of the two fluorine resonances was used to determine the concentration of propargyl alcohol **4r** and to monitor its decay. Hence, kinetic studies with a stock solution of **4r** ($c_0(\mathbf{4r}) = 0.20\ mol\,L^{-1}$) furnished the observed rate constants $k_{obs'}$ in dependence on solvent, triethylamine concentration, and temperature (Table 4). Increasing the solvent polarity under pseudo-first-order conditions with respect to triethylamine concentration enhances the rate of the isomerization process by one order of magni-

Table 4. Dependence of rate constants $k_{obs'}$ (kinetics at $c_0(\mathbf{4r}) = 0.20\ mol\,L^{-1}$) on solvent, base concentration, and temperature.

Entry	Solvent	T [K]	$k_{obs'}$ [$mol^2\,L^{-2}\,s^{-1}$]
1	triethylamine (neat)	348	2.27×10^{-5}
2	toluene/triethylamine (1:1)	348	2.42×10^{-5}
3	ethanol/triethylamine (1:1)	348	5.23×10^{-5}
4	acetonitrile/triethylamine (1:1)	348	2.01×10^{-4}
5	acetonitrile/triethylamine (1:1)[a]	348	2.01×10^{-4}
6	acetonitrile/triethylamine (5:1)[b]	348	1.97×10^{-4}
7	acetonitrile/triethylamine (10:1)[c]	348	1.19×10^{-4}
8	acetonitrile/triethylamine (14:1)[d]	348	6.86×10^{-5}
9	acetonitrile/triethylamine (1:1)	328	4.80×10^{-5}
10	acetonitrile/triethylamine (1:1)	338	8.85×10^{-5}
11	acetonitrile/triethylamine (1:1)	348	1.90×10^{-4}
12	acetonitrile/triethylamine (1:1)	358	5.44×10^{-4}

[a] $c(NEt_3) = 6.0\ mol\,L^{-1}$. [b] $c(NEt_3) = 1.2\ mol\,L^{-1}$. [c] $c(NEt_3) = 0.65\ mol\,L^{-1}$. [d] $c(NEt_3) = 0.48\ mol\,L^{-1}$.

tude (entries 1–4). Thus, dipolar aprotic solvents such as acetonitrile are clearly favored over apolar solvents such as toluene or neat triethylamine. Between triethylamine concentrations of 0 and 1.2 mol L^{-1}, a second-order rate law applies best, first-order in the concentration of **4r** and first-order in the concentration of triethylamine, and a reduced rate constant $k_{obs} = 1.66 \cdot 10^{-4}$ mol L^{-1} s^{-1} can be determined (entries 6–8). However, increasing the triethylamine concentration above 1.2 mol L^{-1} leads to the regime of pseudo-first-order conditions (entry 5). As expected, the temperature-dependent kinetics (at 55, 65, 75, and 85 °C) under pseudo-first-order conditions (entries 9–12) is well suited to furnish the desired activation parameters. Thus, the Arrhenius plot[33] gives a pre-exponential factor of $A = 0.69 \times 10^8$ mol^2 L^{-2} s^{-1} and an activation energy of $E_a = 76.6$ kJ mol^{-1}, and the Eyring plot[34] furnishes an activation enthalpy of $\Delta H^{\neq} = 73.7$ kJ mol^{-1} and an activation entropy of $\Delta S^{\neq} = -104.5$ J K^{-1} mol^{-1}. The large negative activation entropy is consistent with a highly ordered late transition state that, according to the Hammond postulate, may well be a contact ion pair in a solvent cage.

Conclusion

Starting from electron-deficient (hetero)aryl halides and (hetero)aryl or alkenyl 1-propargyl alcohols, the Sonogashira coupling–isomerization reaction (CIR) provides general access to α,β-unsaturated ketones with a variety of acceptors, such as esters, amides, ketones, nitriles, nitro, and trifluoromethyl groups; electron-deficient heterocycles; and tricarbonylchromium-complexed arenes. Amines with comparable pK_b, such as $HNEt_2$, NEt_3, and pyrrolidine, can be applied as suitable bases. Favorable solvents for this domino reaction are ethanol, methanol, THF, acetonitrile, DMF (at 50 °C), and toluene, as well as neat amine base. Coupling–isomerization reactions in deuterated protic solvents or with a selectively deuterated propargyl alcohol reveal that the base-catalyzed isomerization step proceeds through a formal 1,3-H shift with minimal H/D exchange with the surrounding solvent. Furthermore, kinetic investigations on the rate-determining isomerization step support the mechanistic rationale. Although the postulated allenol intermediate, which leads to the enone by isomerization, is elusive, further development of CIR as an initiator of new domino processes could be based on the exploitation of allene intermediates. Studies expanding the methodological scope of CIR and the generation of sequences initiated by CIR are currently under investigation.

Experimental Section

General considerations: All reactions involving palladium–copper catalysis were performed in degassed oxygen-free solvents under a nitrogen atmosphere using Schlenk and syringe techniques. Halogen compounds **1**, $[PdCl_2(PPh_3)_2]$, and CuI were purchased in reagent grade from ACROS, Aldrich, Fluka, or Merck and used without further purification. Methyl *cis*-3-bromoacrylate[35] (**1m**) and 3-bromo-cyclohexenone[36] (**1n**) were synthesized by literature procedures. Triethylamine and THF were dried and distilled according to standard procedures.[37] Propargyl alcohols **2** were prepared in analogy to literature procedures[38] by addition of ethynyl magnesium bromide to the corresponding aldehydes. 10-Hexylphenothiazine-3-carbaldehyde was prepared by Vilsmeier formylation.[39] Column chromatography: silica gel 60 M (230–400 mesh), Macherey-Nagel, Düren, or silica gel 60 (70–230 mesh), Merck, Darmstadt. TLC: silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Büchi Melting Point B-540. ^{1}H and ^{13}C NMR spectra: Bruker ARX250, Bruker DRX 300, Bruker ARX 300, Varian VXR 400S, Bruker DRX500, or Bruker AC300 with [D_6]acetone, $CDCl_3$, or [D_6]DMSO as solvent. The assignments of quaternary C, CH, CH_2, and CH_3 were made by using DEPT spectra. IR: Bruker Vector 22 FT-IR or Perkin–Elmer Model Lambda 3. UV/Vis: Hewlett Packard HP8452A. MS: Finnigan MAT 90, MAT 95 Q, Jeol JMS-700, and Finnigan TSQ 700. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, and of the Department Chemie, Ludwig-Maximilians-Universität München.

1-(3-Thienyl)propyn-1-ol (2g): A solution of (trimethylsilyl)acetylene (6.93 mL, 49.0 mmol) in THF (50 mL) was cooled to −78 °C under nitrogen, a 1.6 M solution of *n*BuLi in hexanes (30.7 mL, 49.0 mmol) added dropwise, and the mixture stirred for 60 min at −78 °C. A solution of thiophene-3-carbaldehyde (5.00 g, 44.6 mmol) in THF (10 mL) was added dropwise, and then the mixture was allowed to warm to room temperature over 60 min by removing the cooling bath. A saturated aqueous solution of ammonium chloride (20 mL) was added to the reaction mixture, which was exhaustively extracted with diethyl ether. The combined organic layers were dried with anhydrous magnesium sulfate and the solvents were removed in vacuo.

For desilylation the residue was dissolved in methanol (100 mL) and 2 N sodium hydroxide solution (112 mL) was added. After stirring for 60 min at room temperature the solution was extracted with diethyl ether. The organic phase was washed twice with deionized water, dried with anhydrous magnesium sulfate, and then the solvents were removed in vacuo. The residue was distilled at 88 °C (2.7×10^{-1} mbar) to give 3.96 g (64 %) of **2g** as a colorless solid. M.p. 57–59 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40$ (dd, $J = 3.0$, 0.9 Hz, 1H), 7.30 (dd, $J = 5.0$, 3.0 Hz, 1H), 7.20 (dd, $J = 5.0$, 1.2 Hz, 1H), 5.48 (m, 1H), 2.64 (d, $J = 2.2$ Hz, 1H), 2.38 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 141.1$ (C_{quat}), 126.2 (CH), 126.1 (CH), 122.9 (CH), 83.3 (C_{quat}), 74.0 (CH), 60.3 ppm (CH); IR (KBr): $\tilde{\nu} =$ 3401, 2117, 1781, 1637, 1533 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 138 (100) [M^+]; elemental analysis (%) calcd for C_7H_6OS (138.2): C 60.84, H 4.37, S 23.20; found: C 60.98, H 4.38, S 23.12.

1-(10-Hexyl-10*H*-phenothiazin-3-yl)-prop-2-yn-1-ol (2i): According to the literature procedure[38] **2i** (4.11 g, 76 %) was obtained as an orange-red resin. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.10$–7.14 (m, 2H), 6.87–6.93 (m, 1H), 6.81–6.86 (m, 2H), 5.35 (d, $J = 2.2$ Hz, 1H), 3.80–3.85 (m, 2H), 2.65 (d, $J = 2.2$ Hz, 1H), 1.37–1.44 (m, 2H), 1.25–1.31 (m, 6H), 0.87 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 145.4$ (C_{quat}), 144.8 (C_{quat}), 133.9 (C_{quat}), 127.2 (CH), 127.1 (CH), 125.5 (CH), 125.5 (CH), 125.1 (C_{quat}), 124.3 (C_{quat}), 122.3 (CH), 115.2 (CH), 115.0 (CH), 83.2 (C_{quat}), 74.6 (CH), 63.5 (CH), 47.3 (CH_2), 31.2 (CH_2), 26.6 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 13.7 ppm (CH_3); IR (neat): $\tilde{\nu} = 1604$, 2856, 2928, 2954, 3292 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 308 (6200), 260 nm (30 500 mol^{-1} m^3 cm^{-1}); MS (FAB, NBA): *m*/*z* (%): 337 (100) [M^+], 320 (14) [M^+−OH], 266 (12) [M^+−C_5H_{11}], 252 (11) [M^+−C_6H_{13}]; HRMS (FAB, NBA) calcd for $C_{21}H_{23}NOS$: 337.1500; found: 337.1465.

1-(4-Bromophenyl)prop-2-yn-1-ol (2j): According to the literature procedure[38] **2j** (6.58 g, 78 %) was obtained as beige crystals. M.p. 48–49 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.50$ (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J =$ 8.5 Hz, 2H), 5.41 (s, 1H), 2.67 (d, $J = 2.2$ Hz, 1H), 2.47 ppm (br, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 139.0$ (C_{quat}), 131.7 (CH), 128.3 (CH), 122.5 (C_{quat}), 83.0 (C_{quat}), 75.2 (CH), 63.7 ppm (CH); IR (KBr): $\tilde{\nu} = 1590$, 2122, 3284 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 212 (34) [^{81}Br-M^+], 210 (46) [^{79}Br-M^+], 188 (18) [^{81}Br-M^+−C≡C], 186 (18) [^{79}Br-M^+−C≡C], 131 (68) [M^+−Br], 53 (100) [C≡C−CO^+]; elemental analysis (%) calcd for

C_9H_7BrO (211.1): C 51.22, H 3.34, Br 37.86; found: C 51.18, H 3.32, Br 37.65.

General procedure for the synthesis of chalcones 3 by CIR: $[PdCl_2(PPh_3)_2]$ (14.0 mg, 0.02 mmol) and CuI (1.9 mg, 0.01 mmol) were added to a degassed solution of a (hetero)aryl halide **1** (1.00 mmol) and a propargylic alcohol **2** (1.05 mmol) in a mixture of the solvent indicated and triethylamine (or other amine base). The reaction mixture was heated to reflux for 14 h. After cooling to room temperature the formed triethylammonium salt was precipitated with diethyl ether (15 mL). After filtration the solvents were removed in vacuo and the residue was purified by recrystallization and/or chromatography on silica gel (for experimental details see Table 5).

3-(4-Nitrophenyl)-1-phenylprop-2-en-1-one (3a): This compound was prepared according to the general procedure; purification by trituration with ethanol and recrystallization from ethanol gave a yellow powder. M.p. 163–164 °C (lit.[40] 164 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.26$ (d, $J = 8.8$ Hz, 2H); 8.01–8.04 (m, 2H), 7.81 (d, $J = 15.6$ Hz, 1H), 7.78 (d, $J = 8.7$ Hz, 2H), 7.64 (d, $J = 15.7$ Hz, 1H), 7.59–7.64 (m, 1H), 7.49–7.55 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 189.6$ (C_{quat}), 148.6 (C_{quat}), 141.5 (CH), 141.0 (C_{quat}), 137.5 (C_{quat}), 133.3 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 125.7 (CH), 124.2 ppm (CH).

Tricarbonyl{η^6-[(*E*)-3-phenylprop-1-en-3-onyl]benzene}chromium(0) (3b): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) and crystallization from pentane/diethyl ether gave an orange-red solid. M.p. 156–159 °C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta = 8.12$ (d, $J = 7.3$ Hz, 2H), 7.86 (d, $J = 15.6$ Hz, 1H), 7.67 (t, $J = 7.3$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.36 (d, $J = 15.6$ Hz, 1H), 6.40 (d, $J = 6.3$ Hz, 2H), 5.87 (t, $J = 6.1$ Hz, 1H), 5.80 ppm (t, $J = 5.9$ Hz, 2H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): $\delta =$ 233.5 (C_{quat}, CO), 188.7 (C_{quat}), 141.5 (CH), 137.3 (C_{quat}), 133.6 (CH), 129.0 (CH), 128.7 (CH), 123.2 (CH), 101.4 (C_{quat}), 95.9 (CH), 95.9 (CH), 94.0 ppm (CH); IR (KBr): $\tilde{\nu} = 3079$, 2924, 2853, 1966, 1608, 1577, 1504, 1447, 1384, 1332, 1287, 1217, 1179, 1159, 1033, 1018, 995, 817, 777, 704, 685, 658, 629, 617 cm^{-1}; UV/Vis (DMSO): λ_{max} (ε) = 452 (5100), 274 nm (21 300 mol^{-1} dm^3 cm^{-1}); MS (EI): *m*/*z* (%): 344 (13) [M^+], 288 (6) [$M^+ - 2$CO], 260 (100) [$M^+ - 3$CO], 208 (8) [$M^+ - Cr(CO)_3$], 52 (28) [Cr^+]; elemental analysis (%) calcd for $C_{18}H_{12}CrO_4$ (344.3): C 62.79, H 3.51. Found: C 63.28, H 3.43.

Tricarbonyl{η^6-[(*E*)-3-phenylprop-1-en-3-onyl]-2-methylbenzene}chromium(0) (3c): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) and crystallization from pentane/diethyl ether gave an orange-red solid. M.p. 90–93 °C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta = 8.13$ (d, $J =$ 7.5 Hz, 2H), 7.87 (d, $J = 15.3$ Hz, 1H), 7.67 (t, $J = 7.3$ Hz, 1H), 7.57 (t, $J =$ 7.4 Hz, 2H), 7.55 (d, $J = 15.0$ Hz, 1H), 6.67 (d, $J = 6.8$ Hz, 1H), 5.96 (t, $J = 6.3$ Hz, 1H), 5.67–5.69 (m, 2H), 2.34 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): $\delta = 233.7$ (C_{quat}), 188.6 (C_{quat}), 138.3 (CH), 137.3 (C_{quat}), 133.6 (CH), 128.8 (CH), 129.0 (CH), 124.1 (CH), 96.9 (CH), 100.1 (C_{quat}), 91.8 (CH), 94.5 (CH), 95.4 (CH), 18.8 ppm (CH_3); IR (KBr): $\tilde{\nu} =$ 1574, 1588, 1661, 1876, 1959 cm^{-1}; UV/Vis (DMSO): λ_{max} (ε) = 452 (5200), 275 nm (19 600 mol^{-1} dm^3 cm^{-1}); MS (EI): *m*/*z* (%): 358 (14) [M^+], 302 (5) [$M^+ - 2$CO], 274 (100) [$M^+ - 3$CO], 222 (5) [$M^+ - Cr(CO)_3$], 52 (25) [Cr^+]; elemental analysis (%) calcd for $C_{19}H_{14}CrO_4$ (358.3): C 63.69, H 3.94; found: C 64.00, H 4.11.

3-(4-Cyanophenyl)-1-phenylprop-2-en-1-one (3d): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave a colorless fluffy solid. M.p. 159–160 °C (lit.[46] 156–157 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.00$–8.04 (m, 2H), 7.76 (d, $J = 15.8$ Hz, 1H), 7.67–7.73 (m, 4H), 7.59 (d, $J = 15.8$ Hz, 1H), 7.57–7.64 (m, 1H), 7.48–7.54 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 189.7$ (C_{quat}), 142.0 (CH), 139.2 (C_{quat}), 137.6 (C_{quat}), 133.2 (CH), 132.6 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 125.1 (CH), 118.3 (C_{quat}), 113.5 ppm (C_{quat}); MS (FD$^+$): *m*/*z* (%): 235 (5) [M^+], 234 (22) [M^+], 233 (100) [M^+].

[2-D]-3-(4-Cyanophenyl)-1-phenylprop-2-en-1-one ([2-D]-3d): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave a colorless fluffy solid. M.p. 159 °C (lit. for all-proton **3d**[46] 156–157 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta =$

Table 5. Experimental details for CIR enone synthesis.

Entry	(Hetero)aryl halide **1**	Propargylic alcohol **2**	Solvent	Base	Yield of chalcone **3**
1	**1a** (253 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3a**, 82 % (208 mg)
2[a]	**1b** (250 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3b**, 79 % (272 mg)
3[b]	**1c** (260 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3c**, 75 % (270 mg)
4	**1d** (182 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (2.5 mL)	NEt_3 (2.5 mL)	**3d**, 96 % (223 mg)
5	**1e** (182 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3e**, 62 % (145 mg)
6	**1f** (225 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (6.0 mL)	$HNEt_2$ (3.5 mL)	**3f**, 75 % (206 mg)
7	**1g** (229 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (2.5 mL)	NEt_3 (2.5 mL)	**3g**, 58 % (163 mg)
8	**1h** (261 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)		$HNEt_2$ (6 mL)	**3h**, 58 % (179 mg)
9[c]	**1i** (370 mg, 2.00 mmol)	**2a** (270 mg, 2.10 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3i**, 57 % (270 mg)
10	**1j** (200 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (2.5 mL)	NEt_3 (2.5 mL)	**3j**, 77 % (193 mg)
11[d]	**1k** (192 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3k**, 85 % (206 mg)
12	**1l** (164 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3l**, 75 % (161 mg)
13[e]	**1m** (165 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3m**, 89 % (192 mg)
14[e]	**1n** (175 mg, 1.00 mmol)	**2a** (135 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3n**, 90 % (210 mg)
15	**1d** 182 mg, 1.00 mmol)	**2b** (235 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3o**, 98 % (320 mg)
16	**1a** (253 mg, 1.00 mmol)	**2c** (170 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3p**, 80 % (226 mg)
17	**1d** (182 mg, 1.00 mmol)	**2d** (150 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3q**, 93 % (234 mg)
18	**1d** (182 mg, 1.00 mmol)	**2e** (150 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3r**, 96 % (240 mg)
19	**1d** (182 mg, 1.00 mmol)	**2f** (354 mg, 1.05 mmol)	THF (2.5 mL)	NEt_3 (2.5 mL)	**3s**, 83 % (258 mg)
20[c]	**1a** (250 mg, 1.00 mmol)	**2g** (145 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3t**, 95 % (260 mg)
21	**1n** (175 mg, 1.00 mmol)	**2g** (145 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3u**, 95 % (220 mg)
22[e]	**1b** (250 mg, 1.00 mmol)	**2g** (145 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3v**, 57 % (200 mg)
23[e]	**1m** (165 mg, 1.00 mmol)	**2g** (145 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3w**, 90 % (200 mg)
24	**1a** (253 mg, 1.00 mmol)	**2h** (128 mg, 1.05 mmol)	THF (6.0 mL)	NEt_3 (3.5 mL)	**3x**, 84 % (203 mg)
25	**1d** (182 mg, 1.00 mmol)	**2i** (354 mg, 1.05 mmol)	EtOH (2.0 mL)	NEt_3 (3.5 mL)	**3y**, 79 % (347 mg)
26	**1d** (182 mg, 1.00 mmol)	**2j** (116 mg, 1.05 mmol)	THF (2.5 mL)	NEt_3 (2.5 mL)	**3z**, 68 % (143 mg)
27	**1d** (182 mg, 1.00 mmol)	**2k** (101 mg, 1.05 mmol)	MeCN (2.5 mL)	NEt_3 (2.5 mL)	**3aa**, 66 % (130 mg)
28[a]	**1b** (250 mg, 1.00 mmol)	**2l** (170 mg, 1.05 mmol)	THF (10 mL)	NEt_3 (5 mL)	**3ab**, 41 % (152 mg)

[a] Reaction time: 6 h. [b] Reaction time: 48 h. [c] Reaction time: 9 h. [d] Reaction time: 15 h. [e] Reaction time: 8 h.

8.00–8.04 (m, 2H), 7.76 (s, 1H), 7.67–7.73 (m, 4H), 7.59 (5% residual signal), 7.57–7.64 (m, 1H), 7.48–7.54 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.7 (C_{quat}), 142.0 (CH), 139.2 (C_{quat}), 137.6 (C_{quat}), 133.2 (CH), 132.6 (CH), 128.7 (CH), 128.6 (CH), 113.5 (C_{quat}), 128.5 (CH), 125.1 (br, residual signal), 118.3 ppm (C_{quat}); MS (FD$^+$): *m/z* (%): 236 (5) [D-M^++D], 235 (32) [D-M^++H], 234 (100) [D-M^+], 233 (5) [M^+], that is, 5% undeuterated product, 86% monodeuteration, and 9% bis-deuteration.

[3-D]-3-(4-Cyanophenyl)-1-phenylprop-2-en-1-one ([3-D]-3d): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave a colorless fluffy solid. M.p. 158 °C (lit. for all-proton **3d**[46] 156–157 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00–8.04 (m, 2H), 7.76 (8%, residual signal), 7.67–7.73 (m, 4H), 7.59 (s, 1H), 7.57–7.64 (m, 1H), 7.48–7.54 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.7 (C_{quat}), 142.0 (br, residual signal), 139.2 (C_{quat}), 137.6 (C_{quat}), 133.2 (CH), 132.6 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 125.1 (CH), 118.3 (C_{quat}), 113.5 ppm (C_{quat}); MS (FD$^+$): *m/z* (%): 236 (3) [D-M^++D], 235 (20) [D-M^++H], 234 (100) [D-M^+], 233 (21) [D-M^+], that is, 18% undeuterated product and 82% monodeuteration.

3-(2-Cyanophenyl)-1-phenylprop-2-en-1-one (3e): This compound was prepared according to general procedure; purification by chromatography on silica gel (petroleum ether/ethyl acetate 4:1) and recrystallization from ethanol gave a yellow solid. M.p. 133–134 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.98–8.05 (m, 3H), 7.72–7.83 (m, 3H), 7.58–7.69 (m, 2H), 7.47–7.55 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.9 (C_{quat}), 139.5 (CH), 137.9 (C_{quat}), 137.5 (C_{quat}), 133.8 (CH), 133.3 (CH), 133.0 (CH), 130.1 (CH), 128.8 (CH), 128.7 (CH), 128.1 (CH), 126.8 (CH), 117.5 (C_{quat}), 112.5 ppm (C_{quat}); IR (KBr): $\tilde{\nu}$ = 3064, 2223, 1664, 1613, 1592, 1577, 1477, 1448, 1340, 1317, 1281, 1213, 1183, 1159, 1034, 1015, 970, 896, 862, 816, 783, 767, 728, 691, 654, 596 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 295 nm (20700 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): *m/z* (%): 233 (100) [M^+], 204 (65), 156 (26) [M^+−Ph], 128 (24) [M^+−PhCO], 105 (84) [PhCO$^+$], 101 (13), 77 (57) [Ph$^+$]; elemental analysis (%) calcd for $C_{16}H_{11}NO$ (233.3): C 82.38, H 4.75, N 6.00; found: C 81.99, H 4.72, N 5.92.

3-(4-Trifluoromethylphenyl)-1-phenylprop-2-en-1-one (3f): This compound was prepared according to the general procedure; purification by trituration with pentane and recrystallization from ethanol gave yellow crystals. M.p. 128–129 °C (lit.[41] 116–118 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.02–8.05 (m, 2H), 7.82 (d, *J* = 18.9 Hz, 1H), 7.66–7.77 (m, 4H), 7.49–7.65 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 190.0 (C_{quat}), 142.7 (q, ^5J(C,F) = 0.6 Hz, CH), 138.3 (q, ^4J(C,F) = 1.4 Hz, C_{quat}), 137.8 (C_{quat}), 133.1 (CH), 131.9 (q, ^2J(C,F) = 32.6 Hz, C_{quat}), 128.7 (CH), 128.6 (CH), 128.5 (CH), 125.9 (q, ^3J(C,F) = 3.8 Hz, CH), 124.3 (CH), 123.8 ppm (q, ^1J(C,F) = 272.3 Hz, C_{quat}).

Ethyl 4-(3-oxo-3-phenylprop-1-en-1-yl)benzoate (3g): This compound was prepared according to the general procedure; purification by trituration with 2-propanol and recrystallization from 2-propanol gave a beige solid. M.p. 82–83 °C (lit.[42] 83–84 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.01–8.09 (m, 4H), 7.81 (d, *J* = 15.5 Hz, 1H), 7.68–7.71 (m, 2H), 7.49–7.62 (m, 4H), 4.39 (q, *J* = 6.9 Hz, 2H), 1.41 ppm (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 190.0 (C_{quat}), 165.7 (C_{quat}), 143.1 (CH), 138.8 (C_{quat}), 137.7 (C_{quat}), 132.8 (CH), 131.7 (C_{quat}), 129.9 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 123.9 (CH), 61.0 (CH_2), 14.1 ppm (CH_3).

4-(3-Oxo-3-phenylprop-1-en-1-yl)-benzophenone (3h): This compound was prepared according to the general procedure; purification by trituration with diethyl ether and recrystallization from 2-propanol gave a beige solid. M.p. 173–174 °C (lit.[43] 174 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.04–8.06 (m, 2H), 7.80–7.87 (m, 5H), 7.74–7.76 (m, 2H), 7.62–7.66 (m, 3H), 7.48–7.59 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.8 (C_{quat}), 190.1 (C_{quat}), 143.2 (CH), 138.9 (C_{quat}), 138.6 (C_{quat}), 137.9 (C_{quat}), 137.3 (C_{quat}), 133.0 (CH), 132.6 (CH), 130.6 (CH), 130.0 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 124.1 ppm (CH).

4-[(*E*)-3-Oxo-3-phenylpropenyl]-benzaldehyde (3i): This compound was prepared according to the general procedure; purification by trituration with diethyl ether and recrystallization from 2-propanol gave a beige solid. M.p. 125 C (lit.[44] 125 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.0 (s, 1H), 8.04 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 15.0 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 15.9 Hz, 1H), 7.53 (m, 2H), 7.23 ppm (t, *J* = 6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 191.4 (CH), 189.9 (C_{quat}), 142.7 (CH), 140.5 (C_{quat}), 137.7 (C_{quat}), 137.2 (C_{quat}), 133.1 (CH), 130.1 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 124.7 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1566, 1603, 1659, 1697 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 315 nm (26200 mol^{-1} dm^3 cm^{-1}); MS (EI): *m/z* (%): 236 (100) [M^+]; HRMS calcd for $C_{16}H_{12}O_2$: 236.0837; found: 236.0832.

4-(3-Oxo-3-phenylprop-1-en-1-yl)benzamide (3j): This compound was prepared according to the general procedure; purification by trituration with 2-propanol and recrystallization from 2-propanol gave a beige solid. M.p. 117–118 °C (no melting point available[45]); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.16–8.19 (m, 2H), 8.01–8.04 (m, 2H), 7.93–7.96 (m, 3H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.51–7.75 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.9 (C_{quat}), 168.3 (C_{quat}), 143.6 (CH), 138.9 (C_{quat}), 138.7 (C_{quat}), 136.7 (C_{quat}), 133.8 (CH), 129.6 (CH), 129.3 (CH), 129.3 (CH), 129.0 (CH), 124.4 ppm (CH).

5-[(*E*)-3-Oxo-3-phenylpropenyl]thiophene-2-carbaldehyde (3k): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) gave a pale yellow solid. M.p. 87–90 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.93 (s, 1H), 7.99–8.02 (m, 2H), 7.88 (d, *J* = 15.5 Hz, 1H), 7.72 (d, *J* = 3.9 Hz, 1H), 7.46–7.56 (m, 2H), 7.56–7.64 (m, 1H), 7.51 (d, *J* = 15.4 Hz, 1H), 7.40 ppm (d, *J* = 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.1 (C_{quat}), 182.8 (CH), 148.5 (C_{quat}), 144.6 (C_{quat}), 137.5 (C_{quat}), 136.6 (CH), 135.6 (CH), 133.3 (CH), 131.6 (CH), 128.8 (CH), 128.6 (CH), 124.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1664, 1598, 1589, 1576, 1448, 1347, 1268, 1222, 1203, 1048, 1032, 1014, 970, 855, 817, 774, 763, 693, 666, 614 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 349 nm (25300 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): *m/z* (%): 242 (100) [M^+]; elemental analysis (%) calcd for $C_{14}H_{10}O_2S$ (242.3): C 69.40, H 4.15, S 13.23; found: C 69.20, H 4.07, S 13.00.

1-Phenyl-3-(2-thiazolyl)prop-2-en-1-one (3l): This compound was prepared according to the general procedure; purification by chromatography on silica gel (petroleum ether/ethyl acetate 4:1) and recrystallization from ethanol gave a light brown solid. M.p. 92 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.06 (m, 2H), 7.98 (d, *J* = 3.2 Hz, 1H), 7.98 (m, 2H), 7.59–7.64 (m, 1H), 7.49–7.54 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.6 (C_{quat}), 164.0 (C_{quat}), 144.9 (CH), 137.5 (C_{quat}), 134.9 (CH), 133.3 (CH), 128.8 (CH), 128.7 (CH), 125.9 (CH), 121.8 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1603, 1665 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 328 (17000), 256 nm (7200 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): *m/z* (%): 215 (21) [M^+], 186 (100), 138 (11) [M^+−Ph], 110 (11) [M^+−C_6H_5CO], 105 (13) [$C_6H_5CO^+$], 77 (19) [Ph$^+$]; elemental analysis (%) calcd for $C_{12}H_9NOS$ (215.3): C 66.95, H 4.201, N 6.51, S 14.89; found: C 66.87, H 4.28, N 6.55, S 14.89.

(2*E*,4*E*)-6-Oxo-6-phenylhexa-2,4-dienoic acid methyl ester (3m): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) gave a pale yellow solid. M.p. 138–140 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96 (d, *J* = 7.2 Hz, 2H), 7.29–7.62 (m, 6H), 6.34 (m, 1H), 3.77 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.7 (C_{quat}), 166.4 (C_{quat}), 141.7 (CH), 140.4 (C_{quat}), 137.4 (C_{quat}), 133.3 (CH), 131.8 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 51.9 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 1599, 1623, 1661, 1708 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 291 nm (28500 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): *m/z* (%): 216 (35) [M^+]; elemental analysis (%) calcd for $C_{13}H_{12}O_3$ (216.2): C 72.21, H 5.59; found: C 71.74, H 5.57.

3-[(*E*)-3-Oxo-3-phenylpropenyl]cyclohex-2-enone (3n): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) gave a pale yellow solid. M.p. 113–115 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 (dd, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 15.8 Hz, 1H), 7.32 (d, *J* = 15.7 Hz, 1H), 6.24 (s, 1H), 2.61 (m, 2H), 2.48 (m, 2H), 2.12 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 199.5 (C_{quat}), 189.7 (C_{quat}), 154.1 (C_{quat}), 144.0 (CH), 137.3 (C_{quat}), 133.2 (CH), 133.0 (CH), 128.7 (CH), 128.5 (CH), 121.2 (CH), 37.6 (CH_2), 24.9 (CH_2), 22.0 ppm (CH_2); IR (KBr): $\tilde{\nu}$ = 1602, 1664 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 299 nm (25400 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): *m/z* (%): 226 (78) [M^+]; elemental analysis (%) calcd for $C_{15}H_{14}O_2 \times 0.33\ H_2O$ (226.3 + 6.0): C 77.56, H 6.36; found: C 77.68, H 6.14.

3-(4-Cyanophenyl)-1-(4-phenoxyphenyl)prop-2-en-1-one (3o): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave light beige crystals. M.p. 178–179 °C (lit.[46] 175–177 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00–8.05 (m, 2H), 7.77 (d, J = 15.8 Hz, 1H), 7.68–7.71 (m, 4H), 7.59 (d, J = 15.6 Hz, 1H), 7.38–7.44 (m, 2H), 7.19–7.24 (m, 1H), 7.03–7.10 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 188.4 (C_{quat}), 162.7 (C_{quat}), 155.7 (C_{quat}), 142.0 (CH), 139.7 (C_{quat}), 133.1 (CH), 132.5 (C_{quat}), 131.3 (CH), 130.5 (CH), 129.0 (CH), 125.3 (CH), 125.2 (CH), 120.6 (CH), 118.8 (C_{quat}), 117.9 (CH), 113.8 ppm (C_{quat}).

1-(4-Methoxyphenyl)-3-(4-nitrophenyl)-prop-2-en-1-one (3p): This compound was prepared according to the general procedure; purification by chromatography on silica gel (petroleum ether/ethyl acetate 4:1) and recrystallization from ethanol gave a red-brown solid. M.p. 168–169 °C (lit.[47] 168–169 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (d, J = 8.9 Hz, 2H), 8.04 (d, J = 8.9 Hz, 2H), 7.78 (d, J = 15.9 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 15.7 Hz, 1H), 6.98 (d, J = 8.9 Hz, 2H), 3.89 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 187.6 (C_{quat}), 163.7 (C_{quat}), 148.2 (C_{quat}), 141.1 (C_{quat}), 140.5 (CH), 131.1 (CH), 130.8 (C_{quat}), 128.6 (CH), 125.5 (CH), 124.0 (CH), 113.8 (CH), 55.5 ppm (CH_3).

3-(4-Cyanophenyl)-1-(2-fluorophenyl)prop-2-en-1-one (3q): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave pale yellow crystals. M.p. 121–122 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (dt, J = 1.9, 7.6 Hz, 1H), 7.72 (dd, J = 1.7, 15.8 Hz, 1H), 7.70 (m, 4H), 7.55–7.60 (m, 1H), 7.48 (dd, J = 3.0, 15.8 Hz, 1H), 7.30 (dd, J = 0.9, 7.7 Hz, 1H), 7.19 ppm (ddd, J = 0.9, 8.3, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 188.5 (d, ^3J(C,F) = 2.6 Hz, C_{quat}, CO), 161.9 (d, ^1J(C,F) = 252.7 Hz, C_{quat}), 142.2 (d, ^5J(C,F) = 1.5 Hz, CH), 139.5 (C_{quat}), 135.0 (d, ^3J(C,F) = 8.7 Hz, CH), 133.1 (CH), 131.5 (d, ^4J(C,F) = 2.6 Hz, CH), 129.2 (CH), 128.9 (d, ^3J(C,F) = 7.3 Hz, CH), 126.9 (d, ^2J(C,F) = 12.8 Hz, C_{quat}), 125.1 (d, ^4J(C,F) = 3.5 Hz, CH), 118.7 (C_{quat}), 117.0 (d, ^2J(C,F) = 23.0 Hz, CH), 114.0 ppm (C_{quat}); IR (KBr): $\tilde{\nu}$ = 1602, 1611, 1660, 2228 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 305 nm (30900 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): m/z (%): 251 (100) [M^+], 222 (17), 156 (18), 128 (13) [$M^+ - FC_6H_4CO$], 123 (22) [$FC_6H_4CO^+$], 95 (13) [$C_6H_4F^+$]; elemental analysis (%) calcd for $C_{16}H_{10}NOF$ (251.3): C 76.48, H 4.01, N 5.57; found: C 76.38, H 4.00, N 5.56.

3-(4-Cyanophenyl)-1-(4-fluorophenyl)prop-2-en-1-one (3r): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave light beige crystals. M.p. 151–152 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.07 (dd, J = 8.8, 5.4 Hz, 2H), 7.78 (d, J = 15.7 Hz, 1H), 7.72 (m, 4H), 7.58 (d, J = 15.6 Hz, 1H), 7.20 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 188.4 (C_{quat}), 166.3 (d, ^1J(C,F) = 254.0 Hz, C_{quat}), 142.7 (CH), 139.5 (C_{quat}), 134.4 (d, ^4J(C,F) = 2.9 Hz, C_{quat}), 133.1 (CH), 131.6 (d, ^3J(C,F)$_=$ 9.3 Hz, CH), 129.1 (CH), 125.0 (CH), 118.7 (C_{quat}), 116.4 (d, ^2J(C,F) = 21.6 Hz, CH), 114.0 ppm (C_{quat}); ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −130.4 ppm; IR (KBr): $\tilde{\nu}$ = 1610, 1663, 2230 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 305 nm (23200 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): m/z (%): 251 (100) [M^+], 222 (15), 156 (12) [$M^+ - FC_6H_4^+$], 128 (10) [$M^+ - C_6H_4CO$], 123 (28) [$FC_6H_4CO^+$], 95 (21) [$C_6H_4F^+$]; elemental analysis (%) calcd for $C_{16}H_{10}FNO$ (251.3): C 76.49, H 4.01, N 5.57; found: C 76.43, H 3.64, N 5.62.

1-(4-Bromophenyl)-3-(4-cyanophenyl)prop-2-en-1-one (3s): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave a beige solid. M.p. 168 °C (lit. [48] 167 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.87–7.90 (m, 2H), 7.78 (d, J = 15.7 Hz, 1H), 7.70–7.72 (m, 4H), 7.64–7.67 (m, 2H), 7.54 ppm (d, J = 15.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 188.4 (C_{quat}), 142.4 (CH), 138.8 (C_{quat}), 136.1 (C_{quat}), 132.5 (CH), 131.9 (CH), 129.8 (CH), 128.5 (CH), 128.3 (C_{quat}), 124.3 (CH), 118.1 (C_{quat}), 113.5 ppm (C_{quat}).

(*E*)-3-(4-Nitrophenyl)-1-thiophen-3-ylpropenone (3t): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) and crystallization from ethanol gave a pale yellow solid. M.p. 182–185 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (d, J = 8.7 Hz, 2H), 8.21 (dd, J = 1.1, 2.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.67 (dd, J 1.1, 5.2 Hz, 1H), 7.50 (d, J = 15.6 Hz, 1H), 7.39 ppm (dd, J = 2.8, 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 183.0 (C_{quat}), 148.5 (C_{quat}), 142.6 (C_{quat}), 140.9 (C_{quat}), 140.8 (CH), 132.8 (CH), 128.9 (CH), 127.3 (CH), 126.9 (CH), 126.4 (CH), 124.2 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1593, 1606, 1658 cm^{-1}; UV/Vis (DMSO): λ_{max} (ε) = 317 nm (22400 mol^{-1} dm^3 cm^{-1}); MS (EI): m/z (%): 259 (100) [M^+]; elemental analysis (%) calcd for $C_{13}H_9NO_3S \cdot 0.33\,CH_3CH_2OH$ (259.3 + 15.5): C 59.77, H 4.04, N 5.10, S 11.67; found: C 59.67, H 3.74, N 4.71, S 11.32.

3-[(*E*)-3-Oxo-3-thiophen-3-ylpropenyl]cyclohex-2-enone (3u): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) gave a pale yellow solid. M.p. 127–130 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13 (dd, J = 1.3, 2.9 Hz, 1H), 7.62 (dd, J = 1.2, 5.1 Hz, 1H), 7.46 (d, J = 16.1 Hz, 1H), 7.38 (dd, J = 2.9, 5.2 Hz, 1H), 7.18 (dd, J = 0.5, 15.6 Hz, 1H), 6.25 (s, 1H), 2.60 (m, 2H), 2.49 (m, 2H), 2.13 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 199.6 (C_{quat}), 183.1 (C_{quat}), 154.1 (C_{quat}), 143.4 (CH), 142.5 (C_{quat}), 133.0 (CH), 132.7 (CH), 127.8 (CH), 127.3 (CH), 126.8 (CH), 37.7 (CH_2), 25.0 (CH_2), 22.0 ppm (CH_2); IR (KBr): $\tilde{\nu}$ = 1580, 1594, 1661 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 299 nm (30300 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): m/z (%): 232 (82) [M^+]; elemental analysis (%) calcd for $C_{13}H_{12}O_2S$ (232.3): C 67.21, H 5.20; found: C 66.91, H 5.28.

Tricarbonyl{η^6-[(*E*)-3-oxo-3-(3-thienyl)prop-1-enyl]benzene} chromium(0) (3v): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) and crystallization from pentane/diethyl ether gave an orange-red solid. M.p. 141–143 °C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.78 (s, 1H), 7.76 (d, J = 15.5 Hz, 1H), 7.64–7.68 (m, 2H), 7.32 (d, J = 15.4 Hz, 1H), 6.36 (d, J = 6.1 Hz, 2H), 5.79–5.86 ppm (m, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 233.5 (C_{quat}), 182.4 (C_{quat}), 142.7 (C_{quat}), 140.5 (CH), 134.9 (CH), 128.1 (CH), 127.2 (CH), 124.3 (CH), 101.6 (C_{quat}), 95.8 (CH), 95.7 (CH), 94.1 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1598, 1656, 1883, 1969 cm^{-1}; UV/Vis (DMSO): λ_{max} (ε) = 446 (4700), 276 nm (18600 mol^{-1} dm^3 cm^{-1}); MS (EI): m/z (%): 350 (17) [M^+], 294 (11) [$M^+ - 2CO$], 266 (100) [$M^+ - 3CO$], 214 (14) [$M^+ - Cr(CO)_3$], 52 (24) [Cr^+]; elemental analysis (%) calcd for $C_{16}H_{10}CrO_4S$ (350.3): C 54.85, H 2.87, S 9.15; found: C 55.59, H 3.26, S 9.49.

(2*E*,4*E*)-6-Oxo-6-thiophen-3-yl-hexa-2,4-dienoic acid methyl ester (3w): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) gave a pale yellow solid. M.p. 137–138 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.11 (dd, J = 1.2, 2.8 Hz, 1H), 7.61 (dd, J = 1.3, 5.1 Hz, 1H), 7.43 (dd, J = 2.9, 10.2 Hz, 1H), 7.43 (d, J = 10.7 Hz, 1H), 7.37 (dd, J = 2.8, 5.1 Hz, 1H), 7.13 (m, 1H), 6.29 (m, 1H), 3.80 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 183.1 (C_{quat}), 166.4 (C_{quat}), 142.5 (C_{quat}), 141.5 (CH), 139.7 (CH), 132.7 (CH), 132.5 (CH), 128.7 (CH), 127.3 (CH), 126.8 (CH), 51.9 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 1594, 1624, 1653, 1709 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 290 nm (25500 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV): m/z (%): 222 (83) [M^+]; elemental analysis (%) calcd for $C_{11}H_{10}O_2S$ (222.3): C 59.44, H 4.53, S 14.42; found: C 59.89, H 4.78, S 13.56.

1-(2-Furyl)-3-(4-nitrophenyl)prop-2-en-1-one (3x): This compound was prepared according to the general procedure; purification by recrystallization from ethanol/THF gave a beige powder. M.p. 232 °C (lit. [49] 238 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.27 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 15.9 Hz, 1H), 7.79 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 1,1 Hz, 1H), 7.56 (d, J = 15.8 Hz, 1H), 7.39 (d, J = 3.6 Hz, 1H), 6.63 ppm (dd, J = 1.7, 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 186.0 (C_{quat}), 147.0 (CH), 140.9 (C_{quat}), 140.8 (CH), 129.0 (CH), 128.6 (C_{quat}), 124.9 (CH), 124.2 (CH), 123.7 (C_{quat}), 118.3 (CH), 112.9 ppm (CH).

3-(4-Cyanophenyl)-1-(10-hexyl-10*H*-phenothazin-3-yl)prop-2-en-1-one (3y): This compound was prepared according to the general procedure; purification by chromatography on silica gel (petroleum ether/ethyl acetate 3:1) and recrystallization from ethanol gave an orange-red solid. M.p. 123 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86 (dd, J = 2.3, 8.5 Hz, 1H), 7.78 (d, J = 1.7 Hz, 1H), 7.68–7.74 (m, 5H), 7.57 (d, J = 15.7 Hz, 1H), 7.11–7.21 (m, 2H), 6.95–6.99 (m, 1H), 6.89 (d, J = 8.3 Hz, 2H), 3.89 (t, J = 6.9 Hz, 2H), 1.78–1.88 (m, 2H), 1.41–1.48 (m, 2H), 1.28–1.37 (m, 4H), 0.89 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 186.7 (C_{quat}), 149.6 (C_{quat}), 143.3 (C_{quat}), 141.0 (CH), 139.2 (C_{quat}), 132.4 (CH), 131.5 (C_{quat}), 128.5 (CH), 128.4 (CH), 127.6 (CH), 127.6 (CH), 127.3 (CH), 124.5 (CH), 124.4 (C_{quat}), 123.5 (C_{quat}), 123.2 (CH), 118.2 (C_{quat}), 115.6 (CH), 114.4 (CH), 113.1 (C_{quat}), 47.7 (CH_2), 31.2 (CH_2), 26.5 (CH_2),

26.3 (CH_2), 22.3 (CH_2), 13.7 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 1570, 1605, 1656, 2227 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 438 (9800), 306 (37800), 258 nm (25200 $mol^{-1}dm^3cm^{-1}$); MS (EI, 70 eV): *m/z* (%): 438 (100) [M^+], 367 (79) [$M^+-C_5H_{11}$], 353 (91) [$M^+-C_6H_{13}$]; elemental analysis (%) calcd for $C_{28}H_{26}N_2OS$ (438.6): C 76.68, H 5.98, N 6.39, S 7.31; found: C 76.87, H 5.98, N 6.54, S 7.28.

1-(4-Cyanophenyl)-4-methylene-hex-1-en-3-one (3z): This compound was prepared according to the general procedure; purification by recrystallization from ethanol gave a colorless solid. M.p. 111 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.63–7.68 (m, 4H), 7.59 (d, *J* = 15.8 Hz, 1H), 7.31 (d, *J* = 15.8 Hz, 1H), 6.05 (s, 1H), 5.84 (t, *J* = 1.4 Hz, 1H), 2.41 (q, *J* = 7.4 Hz, 2H), 1.08 ppm (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 191.0 (C_{quat}), 151.0 (C_{quat}), 140.6 (CH), 139.1 (C_{quat}), 132.4 (CH), 128.3 (CH), 124.9 (CH), 123.1 (CH_2), 118.2 (C_{quat}), 113.1 (C_{quat}), 24.0 (CH_2), 12.3 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 1559, 1602, 1656, 2225 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 300 nm (18800 $mol^{-1}dm^3cm^{-1}$); MS (EI, 70 eV): *m/z* (%): 211 (65) [M^+], 196 (34) [M^+-CH_3], 156 (100) [$M^+-CH_2{=}C{-}C_2H_5$], 154 (14), 128 (51) [$M^+-CH_2{=}C(CO)C_2H_5$], 101 (15); elemental analysis (%) calcd for $C_{14}H_{13}NO$ (211.3): C 79.59, H 6.20, N 6.63; found: C 79.37, H 6.23, N 6.61.

1-(4-Cyanophenyl)hexa-1,4-dien-3-one (3aa): This compound was prepared according to the general procedure; purification by chromatography on silica gel (petroleum ether/ethyl acetate 4:1) gave a yellow solid. M.p. 112–113 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.68 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 15.9 Hz, 1H), 7.03 (d, *J* = 15.9 Hz, 1H), 7.05 (dq, *J* = 15.5, 6.9 Hz, 1H), 6.44 (dq, *J* = 15.5, 1.5 Hz, 1H), 1.98 ppm (dd, *J* = 1.5, 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 188.1 (C_{quat}), 144.3 (CH), 140.1 (CH), 139.0 (C_{quat}), 132.4 (CH), 130.7 (CH), 128.3 (CH), 127.3 (CH), 118.1 (C_{quat}), 113.1 (C_{quat}), 18.3 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 1559, 1594, 1633, 1661, 1675, 2226 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 300 nm (31300 $mol^{-1}dm^3cm^{-1}$); MS (EI, 70 eV): *m/z* (%): 197 (7) [M^+], 69 (23) [$CH_3CH{=}CHCO^+$], 41 (37) [$CH_3CH{=}CH^+$], 39 (100) [$CH_3C{\equiv}C^+$]; elemental analysis (%) calcd for $C_{13}H_{11}NO$ (197.2): C 79.17, H 5.62, N 7.10; found: C 78.93, H 5.71, N 7.10.

Tricarbonyl(η^6-{(*E*)-3-[(*E*)-2-phenylethenyl)]prop-1-en-3-onyl]benzene)-chromium(0) (3ab): This compound was prepared according to the general procedure; purification by chromatography on silica gel (pentane/diethyl ether) and crystallization from pentane/diethyl ether gave an orange-red solid. M.p. 68 °C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.80–6.30 (m, 5H), 7.18–7.83 ppm (m, 9H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 233.5 (C_{quat}), 188.1 (C_{quat}), 143.7 (CH), 140.3 (CH), 134.7 (C_{quat}), 130.9 (CH), 129.2 (CH), 128.7 (CH), 126.5 (CH), 125.7 (CH), 101.8 (C_{quat}), 95.8 (CH), 95.5 (CH), 94.2 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1618, 1651, 1886, 1965 cm^{-1}; UV/Vis (DMSO): λ_{max} (ε) = 445 (2800), 311 nm (16600 $mol^{-1}dm^3cm^{-1}$); MS (EI): *m/z* (%): 370 (19) [M^+], 314 (15) [M^+-2CO], 286 (100) [M^+-3CO], 234 (17) [$M^+-Cr(CO)_3$], 52 (49) [Cr^+]; HRMS calcd for $C_{20}H_{14}CrO_4$: 370.0297; found: 370.0296.

3-(4-Cyanophenyl)-1-(4-fluorophenyl)-prop-2-yn-1-ol (4r): [$PdCl_2(PPh_3)_2$] (28.0 mg, 0.04 mmol) and CuI (3.8 mg, 0.02 mmol) were added to a degassed solution of **1d** (364 mg, 2.00 mmol) and **2e** (315 mg, 2.10 mmol) in triethylamine (5.0 mL) and THF (5.0 mL). The mixture was heated to reflux for 20 min and then cooled to room temperature. Then diethyl ether (15 mL) was added to precipitate the triethylammonium bromide. The mixture was filtered and the solvents were removed from the filtrate in vacuo. The residue was subjected to chromatography on silica gel (hexane/acetone 3:1) and after crystallization from diethyl ether/pentane 373 mg (74%) of **4r** were obtained as intense yellow crystals. M.p. 68–69 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.51–7.61 (m, 6H), 7.04–7.12 (m, 2H), 5.68 (s, 1H), 2.51 ppm (br, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.8 (d, *J* = 246.0 Hz, C_{quat}), 135.9 (d, *J* = 3.3 Hz, C_{quat}), 132.2 (CH), 132.0 (CH), 128.5 (d, *J* = 8.4 Hz, CH), 127.1 (C_{quat}), 118.2 (C_{quat}), 115.6 (d, *J* = 21.8 Hz, CH), 112.1 (C_{quat}), 92.9 (C_{quat}), 85.0 (C_{quat}), 64.3 ppm (CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −139.1 ppm; IR (KBr): $\tilde{\nu}$ = 1604, 2227 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 274 nm (25300), 262 (25800 $mol^{-1}dm^3cm^{-1}$); MS (EI, 70 eV): *m/z* (%): 251 (96) [M^+], 250 (100) [M^+-H], 234 (34) [M^+-OH], 232 (23) [M^+-F], 149 (14) [$C{\equiv}CCH(OH)C_6H_4F^+$], 127 (17) [$NCC_6H_4C{\equiv}CH^+$], 123 (27) [$FC_6H_4CO^+$]; elemental analysis (%) calcd for $C_{16}H_{10}NOF$ (251.3): C 76.49, H 4.01, N 5.57; found: C 76.17, H 4.40, N 5.51.

Kinetic studies: All reactions were carried out in NMR tubes. Compound **4r** (30 mg, 0.12 mmol) was dissolved in a total volume of 0.6 mL of solvents (c_0(**4r**) = 0.20 mol L^{-1}). The reaction was then monitored by recording ^{19}F NMR spectra. The ^{19}F NMR signals were observed at δ = −139.1 ppm (**4r**) and δ = −130.4 ppm (**3r**). The obtained data were processed by logarithmic and linear regression analyses furnishing time–conversion plots, slopes, and axis intercepts (Tables 6–18).

Table 6. Kinetics in triethylamine as a solvent, c_0(**4r**) = 0.20 mol L^{-1}, *T* = 348 K.[a]

t [s]	Percentage **4r**	Percentage **3r**	[**4r**]$_t$ [mol L^{-1}]	ln([**4r**]$_t$/[**4r**]$_0$)
9600	90.89	9.11	0.1808	0.0956
12600	81.54	18.46	0.1623	0.2041
16500	69.39	30.61	0.1381	0.3654
20100	66.37	33.63	0.1321	0.4099
22740	65.19	34.81	0.1297	0.4279
26520	61.34	38.66	0.1221	0.4887

[a] Evaluation from 9 to 40% conversion, since **3r** started to precipitate. Slope: $k_{obs'} = 2.27\times10^{-5}$ $mol^2L^{-2}s^{-1}$. r^2 = 0.92.

Table 7. Kinetics in toluene/triethylamine (1:1), c_0(**4r**) = 0.20 mol L^{-1}, *T* = 348 K.[a]

t [s]	Percentage **4r**	Percentage **3r**	[**4r**]$_t$ [mol L^{-1}]	ln([**4r**]$_t$/[**4r**]$_0$)
13500	84.49	15.51	0.1681	0.1685
18300	80.38	19.62	0.1600	0.2184
21000	76.30	23.71	0.1518	0.2706
24780	64.14	35.86	0.1276	0.4441
27300	61.10	38.90	0.1216	0.4926
29100	55.94	44.06	0.1113	0.5809
33600	55.86	44.14	0.1112	0.5823
34800	51.37	48.63	0.1022	0.6662
39000	50.59	49.41	0.1007	0.6814
42600	44.18	55.82	0.08792	0.8168
46200	36.67	63.32	0.07297	1.003
48900	37.30	62.70	0.07422	0.9862

[a] Evaluation from 15 to 63% conversion, since **3r** started to precipitate. Slope: $k_{obs'} = 2.42\times10^{-5}$ $mol^2L^{-2}s^{-1}$. r^2 = 0.97.

Table 8. Kinetics in ethanol/triethylamine (1:1), c_0(**4r**) = 0.20 mol L^{-1}, *T* = 348 K.[a]

t [s]	Percentage **4r**	Percentage **3r**	[**4r**]$_t$ [mol L^{-1}]	ln([**4r**]$_t$/[**4r**]$_0$)
8100	72.98	27.02	0.1452	0.3149
11100	65.95	34.05	0.1312	0.4163
14400	57.38	42.62	0.1142	0.5555
15900	52.58	47.42	0.1046	0.6429
17580	43.94	56.06	0.0874	0.8224
19200	38.08	61.92	0.0758	0.9655
21900	33.89	66.11	0.0674	1.082
23880	33.86	66.14	0.0674	1.083
25620	34.29	65.71	0.0682	1.070
28200	27.20	72.80	0.0541	1.302
29880	27.14	72.86	0.0540	1.304
32700	20.20	79.80	0.0402	1.600
35700	17.00	83.00	0.0338	1.772
38280	16.65	83.35	0.0331	1.793
43380	11.11	88.89	0.0221	2.197

[a] Evaluation from 27 to 89% conversion. Slope: $k_{obs'} = 5.23\times10^{-5}$ $mol^2L^{-2}s^{-1}$. r^2 = 0.98.

Table 9. Kinetics in acetonitrile/triethylamine (1:1), $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 348$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
960	86.55	13.45	0.1722	0.1444
2640	58.00	42.00	0.1154	0.5447
6780	31.96	68.04	0.06360	1.141
7920	27.14	72.86	0.05402	1.304
9120	18.62	81.38	0.03705	1.681
9720	17.42	82.58	0.03467	1.747
10860	11.54	88.46	0.02297	2.159
11340	10.29	89.71	0.02048	2.274
12480	8.11	91.90	0.01613	2.513

[a] Evaluation from 13 to 92% conversion. Slope: $k_{obs'} = 2.01 \times 10^{-4}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.98$.

Table 10. Kinetics in acetonitrile/triethylamine (1:1), $c(\mathrm{NEt_3}) = 6.0\ \mathrm{mol\,L^{-1}}$, $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 348$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
960	86.55	13.45	0.1722	0.1444
2640	58.00	42.00	0.1154	0.5447
6780	31.96	68.04	0.06360	1.141
7920	27.14	72.86	0.05402	1.304
9120	18.62	81.38	0.03705	1.681
9720	17.42	82.58	0.03467	1.747
10860	11.54	88.46	0.02297	2.159
11340	10.29	89.71	0.02048	2.274
12480	8.105	91.89	0.01613	2.513

[a] Evaluation from 13 to 92% conversion. Slope: $k_{obs'} = 2.01 \times 10^{-4}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.98$.

Table 11. Kinetics in acetonitrile/triethylamine (5:1), $c(\mathrm{NEt_3}) = 1.2\ \mathrm{mol\,L^{-1}}$, $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 348$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
1980	64.92	35.08	0.1292	0.4321
2520	64.50	35.50	0.1284	0.4385
3600	46.93	53.07	0.0934	0.7564
4140	41.55	58.45	0.0827	0.8782
5760	31.63	68.37	0.0629	1.1512
6300	28.35	71.65	0.0564	1.2604
7380	24.09	75.91	0.0479	1.4233
8520	18.78	81.22	0.0374	1.6724
9600	15.22	84.78	0.0303	1.8828
10680	12.41	87.59	0.0247	2.0863

[a] Evaluation from 35 to 88% conversion. Slope: $k_{obs'} = 1.97 \times 10^{-4}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.996$.

Table 12. Kinetics in acetonitrile/triethylamine (10:1), $c(\mathrm{NEt_3}) = 0.65\ \mathrm{mol\,L^{-1}}$, $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 348$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
1380	83.77	16.23	0.1667	0.1771
2940	68.15	31.85	0.1356	0.3835
4080	58.69	41.31	0.1168	0.5329
6240	45.60	54.40	0.0907	0.7853
7980	37.65	62.35	0.0749	0.9767
9360	35.25	64.75	0.0702	1.0426
10620	29.78	70.22	0.0593	1.2113
11700	22.83	77.17	0.0454	1.4773
12780	23.92	76.08	0.0476	1.4306
15000	14.91	85.09	0.0297	1.9030

[a] Evaluation from 16 to 85% conversion. Slope: $k_{obs'} = 1.20 \times 10^{-4}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.98$.

Table 13. Kinetics in acetonitrile/triethylamine (14:1), $c(\mathrm{NEt_3}) = 0.48\ \mathrm{mol\,L^{-1}}$, $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 348$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
1920	75.50	24.50	0.1502	0.2810
2400	71.19	28.81	0.1417	0.3398
3300	70.34	29.66	0.1400	0.3519
3840	62.62	37.38	0.1246	0.4680
5460	60.40	39.60	0.1202	0.5042
7140	50.21	49.79	0.0999	0.6889
11460	39.30	60.70	0.0782	0.9340
13740	32.44	67.56	0.0645	1.1259
15060	29.68	70.32	0.0591	1.2146
16200	26.32	73.68	0.0524	1.3350
17400	21.76	78.24	0.0433	1.5252
20700	24.42	75.58	0.0486	1.4098

[a] Evaluation from 24 to 76% conversion. Slope: $k_{obs'} = 6.86 \times 10^{-5}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.97$.

Table 14. Kinetics in acetonitrile/triethylamine (1:1), $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 328$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
5640	82.84	17.16	0.1649	0.1882
10260	65.41	34.59	0.1302	0.4245
14820	59.44	40.56	0.1183	0.5203
19440	47.40	52.60	0.09433	0.7465
22020	44.10	55.90	0.08776	0.8187
25740	32.80	67.20	0.06527	1.115
29340	27.86	72.14	0.05543	1.278
30780	22.54	77.46	0.04485	1.490
32640	24.32	75.68	0.04841	1.414
34380	22.67	77.33	0.04511	1.484
36060	19.75	80.25	0.03930	1.622

[a] Evaluation from 17 to 80% conversion. Slope: $k_{obs'} = 4.80 \times 10^{-5}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.98$.

Table 15. Kinetics in acetonitrile/triethylamine (1:1), $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 338$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
4740	63.54	36.46	0.1264	0.4535
6540	53.83	46.17	0.1071	0.6194
8460	45.41	54.59	0.09037	0.7894
12840	28.45	71.55	0.05661	1.257
14160	26.42	73.58	0.05257	1.331
16860	19.52	80.48	0.03885	1.634
18600	21.79	78.21	0.04335	1.524
20340	18.18	81.82	0.03618	1.705
21240	19.36	80.64	0.03854	1.642
27180	10.55	89.45	0.02099	2.249
27720	5.50	94.50	0.01094	2.901

[a] Evaluation from 36 to 95% conversion. Slope: $k_{obs'} = 8.85 \times 10^{-5}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.93$.

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Table 16. Kinetics in acetonitrile/triethylamine (1:1), $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 348$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
960	86.55	13.45	0.1722	0.1444
2640	58.00	42.00	0.1154	0.5447
6780	31.96	68.04	0.06360	1.141
7920	27.14	72.86	0.05402	1.304
9120	18.62	81.38	0.03705	1.681
9720	17.42	82.58	0.03467	1.747
10860	11.54	88.46	0.02297	2.159
11340	10.29	89.71	0.02048	2.274
12480	8.105	91.89	0.01613	2.513

[a] Evaluation from 13 to 92% conversion. Slope: $k_{obs'} = 1.90 \times 10^{-4}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.976$.

Table 17. Kinetics in acetonitrile/triethylamine (1:1), $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$, $T = 358$ K.[a]

t [s]	Percentage **4r**	Percentage **3r**	$[\mathbf{4r}]_t$ [mol L^{-1}]	$\ln([\mathbf{4r}]_t/[\mathbf{4r}]_0)$
1440	63.54	36.46	0.1264	0.4535
2040	45.24	54.76	0.09003	0.7932
2640	34.23	65.77	0.06813	1.072
3120	32.80	67.20	0.06527	1.115
3660	18.49	81.51	0.03680	1.688
4200	11.54	88.46	0.02297	2.159
4740	12.23	87.77	0.02433	2.102

[a] Evaluation from 36 to 88% conversion. Slope: $k_{obs'} = 5.44 \times 10^{-4}\ \mathrm{mol^2\,L^{-2}\,s^{-1}}$. $r^2 = 0.952$.

Table 18. Temperature-dependent kinetics in acetonitrile/triethylamine (1:1), $c_0(\mathbf{4r}) = 0.20\ \mathrm{mol\,L^{-1}}$.

T [K]	$1/T$ [K^{-1}]	$k_{obs'}$ [mol^2 L^{-2} s^{-1}]	$\ln k_{obs'}$[a]	$k_{obs'}/T$ [mol^2 L^{-2} s^{-1} K^{-1}]	$\ln(k_{obs'}/T)$[b]
358	0.00279	5.44×10^{-4}	−7.52	1.52×10^{-6}	−13.40
348	0.00287	1.90×10^{-4}	−8.57	5.45×10^{-7}	−14.42
338	0.00296	8.85×10^{-5}	−9.33	2.62×10^{-7}	−15.16
328	0.00305	4.80×10^{-5}	−9.95	1.46×10^{-7}	−15.74

[a] Arrhenius plot: $r^2 = 0.978$, x axis: $\ln A = 18.04$; $A = 0.69 \times 10^8$, slope: $-E_a/R = -9215.2$ K; $E_a = 76.6\ \mathrm{kJ\,mol^{-1}}$. [b] Eyring plot: $r^2 = 0.976$, x axis: $\ln(k_B h^{-1}) + \Delta S^{\neq}/R = 11.197$; $\Delta S^{\neq} = -104.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$, slope: $-\Delta H^{\neq}/R = -8868.9$; $\Delta H^{\neq} = 73.7\ \mathrm{kJ\,mol^{-1}}$.

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the carbonyl carbon nucleus at $\delta = 190$ ppm and the methine carbon atom in *meta* position to the cyano group appearing at $\delta = 129$ ppm.
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[34] From the Eyring equation $k_{obs'} = \frac{k_B T}{h} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/R}$, the linear logarithmic expression $\ln(k_{obs}/T) = \ln(k_B/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT$ is applied to establish a linear correlation between $\ln(k_{obs}/T)$ and reciprocal temperature. The slope of the linear equation ($r^2 = 0.976$) is $-\Delta H^{\neq}/R = -8868.9$ K, and thus the activation enthalpy is $\Delta H^{\neq} = 73.7\ \mathrm{kJ\,mol^{-1}}$. The axis intercept is $\ln(k_B h^{-1}) + \Delta S^{\neq}/R = 11.197$, and thus the activation entropy calculates to $\Delta S^{\neq} = -104.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
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