Tetrahedron 75 (2019) 130563

Contents lists available at ScienceDirect

Tetrahedron

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

Rh(I)-catalyzed ring-opening of cyclobutanols via C–C bond activation: Synthesis of *cis*-olefin with a remote aldehyde

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ARTICLE INFO

Article history:
Received 15 July 2019
Received in revised form
20 August 2019
Accepted 23 August 2019
Available online 27 August 2019

Keywords:
C–C bond activation
Ring-opening
Cyclobutanols
cis-Olefin
Remote aldehyde

ABSTRACT

A Rh(I)-catalyzed ring-opening of cyclobutanols has been developed with ring opening products bearing *cis*-olefin and a remote aldehyde. Various substrates bearing different substituted aryl groups, heterocyclic groups and alkyl groups were compatible with the mild reaction conditions. A β-C elimination pathway was proposed based on the results of preliminary mechanistic studies.

1. Introduction

Carbon-carbon single bonds are generally thermodynamically stable and kinetically inert. However, significant progress has been made in transition metal catalysis, so much so that numbers of unique synthetic reactions in which a carbon-carbon single bond is cleaved in preference to other seemingly more reactive bonds have increased significantly in the past decades [1]. Cyclobutanols and cyclobutanones are privileged building blocks in this field [2]. For example, in 2016, the Song group developed a Pd-catalyzed ring-opening of 2-alkyenecyclobutanones with arylbornic acids, giving *Z*-selective γ, δ-unsaturated ketones with $Z/E = 40/60–99/1$ (Scheme 1 A) [3]. Last year, the Zhang group reported a rhodium(I)-catalyzed asymmetric [4 + 2] cycloaddition reaction of 2-alkylenecyclobutanols with cyclic enones through C–C bond cleavage, for the efficient synthesis of *trans*-bicyclic compounds; however, the intermediates need to be further converted into the desired products (Scheme 1, B) [4].

cis-Olefin aldehydes and their derivatives are important skeletons in numerous bioactive compounds, flavors, pharmaceuticals and crucial intermediates in organic synthesis [5]. Therefore, efficient syntheses of these thermodynamically less stable *Z*-alkenes are greatly desired. Previously, the olefin aldehydes were prepared from a Wittig-reduction or oxidation of the corresponding alcohols, however, the required reagents (for example PPh_3, DIBALH or Dess-Martin Periodinane) are expensive and the procedures are operationally complex. Generally, these methods produce a mixture of *E* and *Z* products or mainly *E* isomers. During our study concerning the metal-catalyzed chemo- and enantioselective hydrogenation of cyclobutanones [6], we found a highly efficient rhodium(I)-catalyzed ring-opening of cyclobutanols *via* a C (sp^2)-C (sp^3) bond cleavage, leading to a *cis*-olefin product bearing a remote aldehyde (Scheme 1, C). The substrates of the cyclobutanols were obtained from 10% $Ca(OH)_2$ and 60% $NaBH_4$ with moderate or good yields via an operationally simple procedure using inexpensive raw materials. The more important point is that it is an efficient method for obtaining *Z*-alkenes with high selectivity via this catalytic system.

2. Results and discussion

We commenced our study by using **1a** as a model substrate for optimization of the reaction. Initially, the model reaction was carried out in toluene with PPh_3 as a ligand, $[Rh(COD)Cl]_2$ as a catalyst at 110 °C over 12 h. Product **2a** was not detected (Table 1, entry 1). When Na_2CO_3 or ^tBuOK was added as an additive, only a trace

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https://doi.org/10.1016/j.tet.2019.130563
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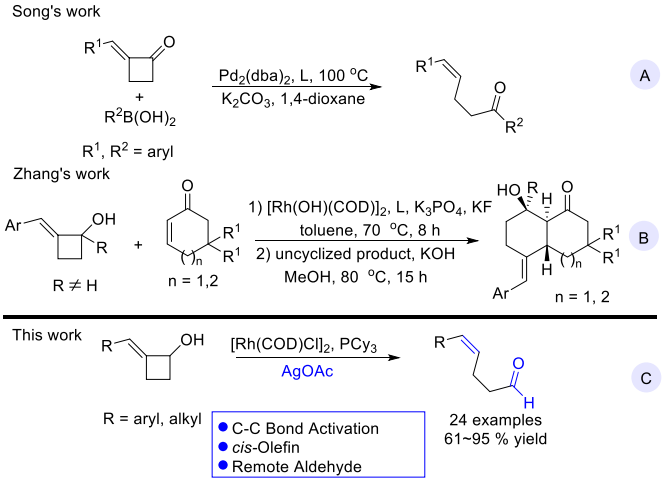
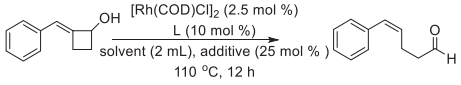


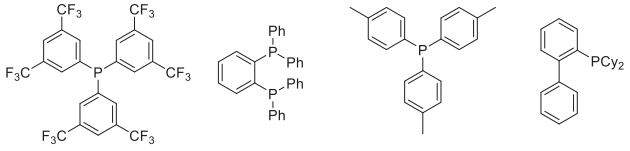
Scheme 1. Methodologies for ring opening of cyclobutanones and cyclobutanols.

amount of **2a** was obtained (Table 1, entries 2 and 3). Subsequently, we found that the use of AgOAc as an additive could give the ring-opened product with 50% yield (Table 1, entry 4). In the absence of any ligand, 2a was obtained in only 9% yield (Table 1, entry 5). However, no further improvement in the yield of 2a was obtained after the solvent was changed to DCM, 1,4-dioxane or o-xylene (Table 1, entries 6–8 vs 4). A better yield of 67% could be achieved by changing the ligand to PCy3 (Table 1, entry 9). Some other monophosphine ligands were also tested, but PCy3 proved to be the most effective ligand (Table 1, entries 10–14 vs 9). In view of the importance of the silver salt, a number of other silver salts were employed in order to enhance the reaction activity. Disappointingly, only low yields were obtained when other silver salts, such as Ag2CO3, AgOTf, AgBF4, AgNTf and AgF, were used in place of AgOAc (Table 1, entries 15–19 vs 9). Use of [Rh(COD)OH]2 also gave the corresponding product 2a in 61% yield (Table 1, entry 20). To our delight, the desired product was obtained in 86% yield by decreasing the amount of AgOAc to 15 mol % (Table 1, entry 21). Further decreasing the amount of AgOAc to 10 mol % only produced 2a in 33% yield (Table 1, entry 22).

With the optimized reaction conditions in hand (Table 1, entry 21), the substrate scope was assessed (Table 2). All the cyclobutanols bearing different substituents afforded the desired products in good to excellent yields. Interestingly, when R = aryl, *ortho*-, *meta*-, and *para*-substituted groups on the benzene ring had almost no influence on the selectivity and all gave the *cis*-olefin products with good yields, albeit higher catalyst loadings were required in the reactions of some substrates (**1b-e**, **n**, **s**, **t**). All substrates with substituents on the benzene ring can be tolerated (**2a-p**). Firstly, substrates with different substituents at the 2-position of the aryl ring were examined, and the desired products were obtained in good yields (**2b-c**). Substrates with groups located at the 3-position provide similar results to those bearing a substituent located at the 4-position (**2d-2p**). A 2,4,6-trimethyl substituted substrate gave the best result, providing the corresponding product **2q** in 95% yield. Furthermore, a naphthalene substrate also gave the corresponding product in high yield (81%, **2r**). Heterocyclic cyclobutanols were also good substrates for this transformation, providing the ring opened products **2s-u** in 61%, 88%, and 94% yields, respectively. Alkyl substituted cyclobutanol substrates were employed under the standard conditions, and the corresponding ring opened products **2v-x** were obtained in high yields with *cis*-selectivity. When the reaction was extended to cyclopentanol and cyclohexanol, no corresponding products were obtained [7], suggesting that the strain

Table 1
Optimization of reaction conditions[a]





Entry	Solvent	Additive	L	Yield (%)[b]
1	Toluene	–	PPh_3	N.D.
2	Toluene	Na_2CO_3	PPh_3	trace
3	Toluene	^tBuOK	PPh_3	trace
4	Toluene	AgOAc	PPh_3	50
5	Toluene	AgOAc	–	9
6	DCM	AgOAc	PPh_3	16
7	1,4-dioxane	AgOAc	PPh_3	17
8	*O*-xylene	AgOAc	PPh_3	21
9	Toluene	AgOAc	PCy_3	79
10	Toluene	AgOAc	P (*t*-Bu)$_3$	7
11	Toluene	AgOAc	L1	67
12	Toluene	AgOAc	L2	43
13	Toluene	AgOAc	L3	60
14	Toluene	AgOAc	L4	11
15	Toluene	Ag_2CO_3	PCy_3	4
16	Toluene	AgOTf	PCy_3	21
17	Toluene	$AgBF_4$	PCy_3	trace
18	Toluene	AgNTf	PCy_3	11
19	Toluene	AgF	PCy_3	4
20[c]	Toluene	AgOAc	PCy_3	61
21[d,e]	**Toluene**	**AgOAc**	**PCy_3**	**86 (82)**
22[f]	Toluene	AgOAc	PCy_3	33

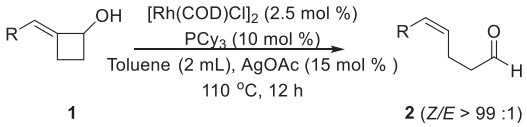
[a] Reaction conditions: substrate **1a** (0.4 mmol, 1.0 equiv.), $[Rh(COD)Cl]_2$ (0.01 mmol, 2.5 mol %), ligand (0.04 mmol, 10 mol %), additive (0.1 mmol, 25 mol %) in sealed tube with 2 ml solvent at 110 °C for 12 h.
[b] Yields were determined by ^1H NMR using CH_2Br_2 as the internal standard.
[c] 2.5 mol % $[Rh(COD)OH]_2$ was used instead of $[Rh(COD)Cl]_2$.
[d] 15 mol % AgOAc.
[e] Number in parenthesis is isolated yield.
[f] 10 mol % AgOAc.

of the four-membered ring is required for this ring-opening reaction.

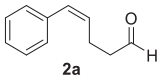
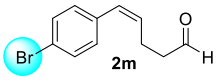
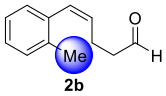
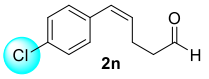
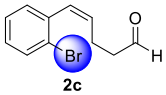
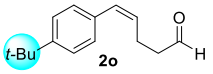
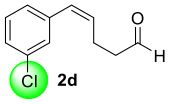
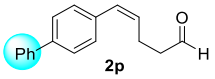
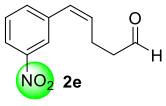
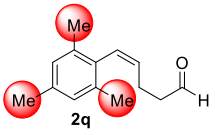
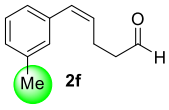
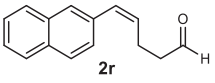
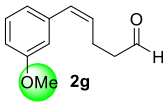
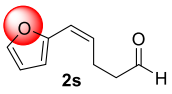
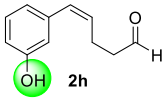
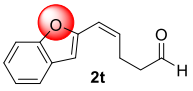
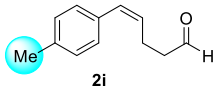
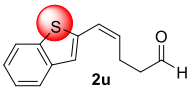
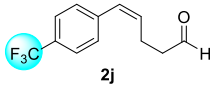
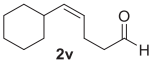
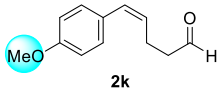
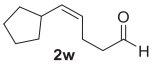
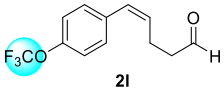
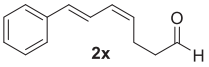
To demonstrate the potential utility of this protocol in synthesis, the catalyst system was employed in a gram-scale reaction of model substrate **1a** to give **2a** in 80% isolated yield (Scheme 2a). The useful olefins **3, 4** and **5** were obtained with ease from **2a** via reduction, witting reaction and alkynylation, respectively, in good yields (Scheme 2a). Some other conversions of **2i** were also performed (Scheme 2b). Product **2i** reacted with PhMgBr to produce unsaturated alcohol **6** in 90% yield, which could be transformed to cyclic ethers **7** [8] and **8** [9], according to literature methods. Furthermore, **6** could be oxidized with Cr_3O to provide **9** in 84% yield. Intermediate **9** could then be transformed to 2,3-bis-substitued unprotected indole **10** [10], cyclic nitrone **11** [3,10] and asymmetric cyclopropane (1*R*,2*R*,1′*R*)-**12** [11], which appear in numerous natural products and medicinally active compounds.

Subsequently, a plausible mechanism has been proposed for this reaction based on literature reports (Scheme 3) [4]. At the start, a well-established rhodium(I) cyclobutanolate **I** is formed and then *β*-C elimination occurs to release the strain of the four-membered ring, affording the vinylrhodium species **II.** Protonation of **II** by **1a** yields the ring opening product **2a** and regenerates the rhodium(I)

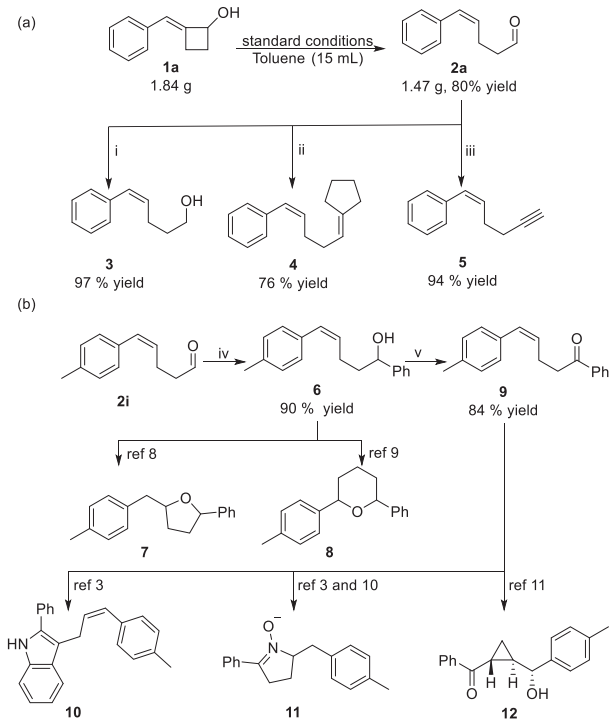
Table 2
Substrate scope[a]



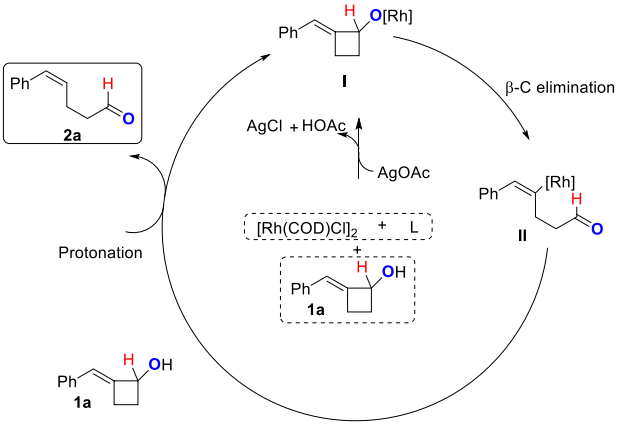
1 **2** (*Z*/*E* > 99 :1)

Entry	Product	Yield (%)[b]	Entry	Product	Yield (%)[b]
1	 **2a**	82	13	 **2m**	91
2[c]	 **2b**	87	14[c]	 **2n**	63
3[c]	 **2c**	84	15	 **2o**	82
4[c]	 **2d**	61	16	 **2p**	66
5[c]	 **2e**	82	17	 **2q**	95
6	 **2f**	77	18	 **2r**	81
7	 **2g**	82	19[c]	 **2s**	61
8	 **2h**	61	20[c]	 **2t**	88
9	 **2i**	64	21	 **2u**	94
10	 **2j**	92	22	 **2v**	93
11	 **2k**	70	23	 **2w**	91
12	 **2l**	81	24	 **2x**	92

[a] Reaction conditions: substrate **1a** (0.4 mmol, 1.0 equiv.), $[Rh(COD)Cl]_2$ (0.01 mmol, 2.5 mol %), AgOAc (0.6 mmol, 15 mol %), ligand (0.04 mmol, 10 mol %) in sealed tube with 2 mL solvent at 110 °C for 12 h.
[b] Isolated yield.
[c] $[Rh(COD)Cl]_2$ is 5.0 mol %.



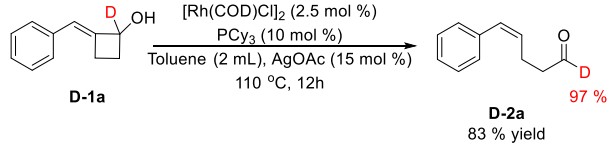
Scheme 2. Synthetic applications and transformations. i) $NaBH_4$, MeOH, 0 °C–RT, 0.5 h. ii) *n*-BuLi, THF, bromo (cyclopentyl) triphenyl-λ^5-phosphane, RT, 24 h iii) K_3PO_4, MeOH, dimethyl-(1-diazo-2-oxopropyl)phosphonate, RT, 24 h. iv) PhMgBr, THF, RT, 12 h. v) $CrO_3/H_2SO_4/H_2O$, acetone, 0 °C – RT, overnight.



Scheme 3. Proposed mechanism.

cyclobutanolate **I**.

The deuterated substrate **D-1a** was tested under standard conditions and it was found that deuterium was incorporated as the aldehyde H (Scheme 4). This result further proves our proposed mechanism.



Scheme 4. The deuterated experiment.

3. Conclusions

In conclusion, we have developed a Rh(I)-catalyzed ring-opening of cyclobutanols, affording various ring opened products bearing *cis*-olefins and remote aldehydes. The synthetic potential of the products was demonstrated via several easy derivatizations. In addition, the strain of the four-membered ring is required for this ring-opening reaction, as verified experimentally. Moreover, preliminary mechanistic studies suggest a *β*-C elimination pathway according to deuterium labeling experiment.

4. Experimental section

4.1. General

All reagents were commercially available and were used without further purification unless otherwise indicated. All solvents were dried and distilled before use according to the standard methods. Analytical thin layer chromatography (TLC) was performed on precoated silica gel F254 plates. Visualization on TLC was achieved with UV light (254 nm) and potassium permanganate as visualization methods. ^{1}H NMR spectra were recorded on Bruker (400 or 500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for tetramethylsilane. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, ddd = double of dd, dt = double of triplet, td = triple of doublet), coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker (101 or 126 MHz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. High resolution mass spectra (HRMS) were obtained with ACQUITYTM UPLC & Q-TOF MS Premier Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. Melting points were measured with SGW X-4 micro melting point apparatus.

4.2. General procedure of Rh(I)-catalyzed ring-opening of cyclobutanols

An oven-dried 25 mL round bottom Schlenk tube was equipped with a magnetic stir bar and charged with substrate (0.4 mmol, 1.0 equiv.), $[Rh(COD)Cl]_2$ (4.9 mg, 0.01 mmol, 2.5 mol %), AgOAc (10.0 mg, 0.06 mmol, 15 mol %), and PCy_3(11.2 mg, 0.04 mmol, 10 mol %) under N_2 atmosphere, then the mixture was dissolved in dry toluene. The solution was stirred at 110 °C for 12 h. After the reaction mixture was cooled to room temperature, and then the product was extracted with EtOAc (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by column chromatography (eluent: petroleum ether/EtOAc = 10/1) to give the corresponding product.

4.2.1. (Z)-5-Phenylpent-4-enal (**2a**)

Yellow oil (53 mg, 82% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 7.33 (t, *J* = 7.0 Hz, 2H), 7.29–7.17 (m, 3H), 6.48 (d, *J* = 11.0 Hz, 1H), 5.61 (dt, *J* = 11.5, 7.0 Hz, 1H), 2.66 (q, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.7, 130.4, 130.0, 128.7, 128.3, 126.9, 43.9, 21.3. HRMS (ESI): calcd. for $C_{11}H_{12}O(M+H)^+$ 161.0961; found 161.0969.

4.2.2. (Z)-5-(o-Tolyl)pent-4-enal (**2b**)

Yellow oil (61 mg, 87% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 7.22–7.10 (m, 4H), 6.50 (d, *J* = 11.0 Hz, 1H), 5.68 (dt, *J* = 11.5, 7.0 Hz, 1H), 2.49 (s, 4H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.9, 136.3, 136.2, 129.9, 129.9, 129.7, 128.9, 127.1,

125.5, 43.8, 21.2, 19.9. HRMS (ESI): calcd. for $C_{12}H_{14}O$ $(M + H)^+$ 175.1117; found 175.1120.

*4.2.3. (Z)-5-(2-bromophenyl)pent-4-enal (**2c**)*

Yellow oil (80 mg, 84% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.32–7.23 (m, 2H), 7.12 (td, J = 8.5, 2.5 Hz, 1H), 6.51 (d, J = 11.5 Hz, 1H), 5.73 (dt, J = 11.0, 7.5 Hz, 1H), 2.58–2.53 (m, 2H), 2.52–2.47 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.5, 137.1, 132.7, 131.1, 130.4, 130.0, 128.6, 127.0, 43.5, 21.1. HRMS (ESI): calcd. for $C_{11}H_{11}BrO$ $(M + H)^+$ 239.0066; found 239.0072.

*4.2.4. (Z)-5-(3-chlorophenyl)pent-4-enal (**2d**)*

Yellow oil (47 mg, 61% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 7.30–7.19 (m, 3H), 7.14 (d, J = 7.2 Hz, 1H), 6.41 (d, J = 11.6 Hz, 1H), 5.65 (dt, J = 11.6, 6.8 Hz, 1H), 2.70–2.51 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.4, 138.9, 134.1, 131.4, 129.5, 129.1, 128.7, 126.9, 126.8, 43.7, 21.2. HRMS (ESI): calcd. for $C_{11}H_{11}ClO$ $(M + H)^+$ 195.0571; found 195.0579.

*4.2.5. (Z)-5-(3-nitrophenyl)pent-4-enal (**2e**)*

Yellow oil (67 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.10 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 6.52 (d, J = 11.6 Hz, 1H), 5.86–5.71 (m, 1H), 2.71–2.57 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.0, 148.3, 138.7, 134.6, 133.0, 129.2, 128.1, 123.4, 121.7, 43.5, 21.1. HRMS (ESI): calcd. for $C_{11}H_{11}NO_3$ $(M + H)^+$ 206.0812; found 206.0817.

*4.2.6. (Z)-5-(m-tolyl)pent-4-enal (**2f**)*

Yellow oil (54 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 7.27–7.17 (m, 1H), 7.11–7.00 (m, 3H), 6.45 (d, J = 11.6 Hz, 1H), 5.58 (dt, J = 11.6, 7.2 Hz, 1H), 2.71–2.60 (m, 2H), 2.55 (t, J = 7.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.8, 137.0, 130.5, 129.9, 129.5, 128.2, 127.6, 125.7, 43.9, 21.5, 21.4. HRMS (ESI): calcd. for $C_{12}H_{14}O$ $(M + H)^+$ 175.1117; found 175.1121.

*4.2.7. (Z)-5-(3-methoxyphenyl)pent-4-enal (**2g**)*

Yellow oil (62 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (t, J = 1.6 Hz, 1H), 7.29–7.21 (m, 1H), 6.86 (d, J = 7.6 Hz, 1H), 6.82–6.76 (m, 2H), 6.45 (dt, J = 11.6, 1.6 Hz, 1H), 5.61 (dt, J = 11.6, 7.2 Hz, 1H), 3.81 (s, 3H), 2.70–2.62 (m, 2H), 2.60–2.53 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.7, 159.5, 138.5, 130.3, 130.3, 129.3, 121.2, 114.4, 112.3, 55.2, 43.8, 21.4. HRMS (ESI): calcd. for $C_{12}H_{14}O_2$ $(M + H)^+$ 191.1097; found 191.1091.

*4.2.8. (Z)-5-(3-hydroxyphenyl)pent-4-enal (**2h**)*

Yellow oil (43 mg, 61% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.75 (t, J = 1.6 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.83–6.69 (m, 3H), 6.41 (dt, J = 11.6, 2.0 Hz, 1H), 6.34–6.04 (br, 1H), 5.58 (dt, J = 11.6, 6.8 Hz, 1H), 2.70–2.61 (m, 2H), 2.61–2.53 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.6, 155.8, 138.6, 130.2, 130.1, 129.5, 121.1, 115.5, 114.0, 43.8, 21.4. HRMS (ESI): calcd. for $C_{11}H_{12}O_2$ $(M + H)^+$ 177.0910; found 177.0913.

*4.2.9. (Z)-5-(p-tolyl)pent-4-enal (**2i**)*

Yellow oil (45 mg, 64% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.76 (t, J = 1.5 Hz, 1H), 7.19–7.11 (m, 4H), 6.45 (dt, J = 11.5, 2.0 Hz, 1H), 5.56 (dt, J = 11.5, 7.0 Hz, 1H), 2.70–2.62 (m, 2H), 2.60–2.53 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.9, 136.6, 134.2, 130.3, 129.3, 129.0, 128.6, 43.9, 21.4, 21.2. HRMS (ESI): calcd. for $C_{12}H_{14}O$ $(M + H)^+$ 175.1117; found 175.1114.

*4.2.10. (Z)-5-(4-(trifluoromethyl)phenyl)pent-4-enal (**2j**)*

Yellow oil (84 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.78 (t, J = 1.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.50 (d, J = 11.6 Hz, 1H), 5.72 (dt, J = 11.6, 7.2 Hz, 1H), 2.70–2.54 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.2, 140.6, 132.2, 129.1, 128.9, 128.9 (q, J = 32.6 Hz), 125.2 (q, J = 3.7 Hz), 124.2 (q, J = 272.7 Hz), 43.7, 21.2. HRMS (ESI): calcd. for $C_{12}H_{11}F_3O$ $(M + H)^+$ 229.0835; found 229.0841.

*4.2.11. (Z)-5-(4-methoxyphenyl)pent-4-enal (**2k**)*

Yellow oil (53 mg, 70% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (s, 1H), 7.20 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.41 (d, J = 11.6 Hz, 1H), 5.50 (dt, J = 11.6, 6.8 Hz, 1H), 3.80 (s, 3H), 2.71–2.61 (m, 2H), 2.56 (t, J = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.9, 129.9, 129.8, 128.5, 113.7, 55.3, 44.0, 21.3. HRMS (ESI): calcd. for $C_{12}H_{14}O_2$ $(M + H)^+$ 191.1067; found 191.1071.

*4.2.12. (Z)-5-(4-(trifluoromethoxy)phenyl)pent-4-enal (**2l**)*

Yellow oil (79 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 7.28 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.45 (d, J = 11.6 Hz, 1H), 5.65 (dt, J = 11.2, 7.2 Hz, 1H), 2.71–2.50 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.4, 135.8, 131.0, 130.0, 129.0, 120.8, 120.5 (q, J = 258.0 Hz), 43.7, 21.2. HRMS (ESI): calcd. for $C_{12}H_{11}F_3O_2$ $(M + H)^+$ 245.0784; found 245.0779.

*4.2.13. (Z)-5-(4-bromophenyl)pent-4-enal (**2m**)*

Yellow oil (87 mg, 91% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.76 (t, J = 1.5 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.39 (dt, J = 11.5, 1.5 Hz, 1H), 5.63 (dt, J = 11.5, 6.5 Hz, 1H), 2.65–2.54 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.4, 131.4, 130.9, 130.3, 129.2, 43.7, 21.2. HRMS (ESI): calcd. for $C_{11}H_{11}BrO$ $(M + H)^+$ 239.0066; found 239.0072.

*4.2.14. (Z)-5-(4-chlorophenyl)pent-4-enal (**2n**)*

Yellow ointment (48 mg, 63% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (t, J = 1.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.42 (dt, J = 11.6, 1.6 Hz, 1H), 5.62 (dt, J = 11.6, 6.8 Hz, 1H), 2.70–2.50 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.4, 135.5, 131.1, 130.7, 130.0, 129.2, 128.4, 43.7, 21.2. HRMS (ESI): calcd. for $C_{11}H_{11}ClO$ $(M + H)^+$ 195.0571; found 195.0574.

*4.2.15. (Z)-5-(4-(tert-butyl)phenyl)pent-4-enal (**2o**)*

Yellow oil (71 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (t, J = 1.6 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.45 (dt, J = 11.6, 1.6 Hz, 1H), 5.56 (dt, J = 11.6, 7.2 Hz, 1H), 2.73–2.62 (m, 2H), 2.61–2.52 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.9, 149.8, 134.2, 130.2, 129.4, 128.5, 125.2, 44.0, 34.6, 31.3, 21.4. HRMS (ESI): calcd. for $C_{15}H_{20}O$ $(M + H)^+$ 217.1587; found 217.1585.

*4.2.16. (Z)-5-([1,1′-biphenyl]-4-yl)pent-4-enal (**2p**)*

Yellow oil (63 mg, 66% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 7.58 (t, J = 8.4 Hz, 4H), 7.43 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 3H), 6.50 (d, J = 12.0 Hz, 1H), 5.63 (dt, J = 11.6, 6.8 Hz, 1H), 2.75–2.65 (m, 2H), 2.58 (t, J = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.7, 140.7, 139.7, 136.1, 130.3, 139.0, 129.2, 128.8, 127.3, 127.0, 127.0, 43.9, 21.5. HRMS (ESI): calcd. for $C_{17}H_{16}O$ $(M + H)^+$ 237.1274; found 237.1279.

*4.2.17. (Z)-5-mesitylpent-4-enal (**2q**)*

Yellow oil (77 mg, 95% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.64 (s, 1H), 6.85 (s, 2H), 6.32 (d, J = 11.0 Hz, 1H), 5.70 (dt, J = 11.0, 7.5 Hz, 1H), 2.41 (td, J = 7.0, 1.5 Hz, 2H), 2.27 (s, 3H), 2.18–2.12 (m, 2H), 2.15 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.9, 136.2, 135.8, 133.1, 130.5, 129.2, 128.0, 43.2, 21.5, 21.0, 20.3. HRMS (ESI): calcd. for $C_{14}H_{18}O$ $(M + H)^+$ 203.1430; found 203.1436.

*4.2.18. (Z)-5-(naphthalen-2-yl)pent-4-enal (**2r**)*

Yellow oil (68 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.73 (s, 1H), 7.85–7.74 (m, 3H), 7.69 (s, 1H), 7.50–7.41 (m, 2H), 7.39 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.61 (dt, *J* = 11.6, 2.0 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.72 (qd, *J* = 7.2, 1.6 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.7, 134.7, 133.3, 132.3, 130.5, 130.4, 128.0, 127.8, 127.6, 127.5, 127.0, 126.2, 125.9, 43.9, 21.4. HRMS (ESI): calcd. for $C_{15}H_{14}O$ $(M + H)^+$ 211.1117; found 211.1112.

*4.2.19. (Z)-5-(furan-2-yl)pent-4-enal (**2s**)*

Yellow oil (37 mg, 61% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 1.5 Hz, 1H), 6.40 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.27 (d, *J* = 3.5 Hz, 1H), 6.22 (dt, *J* = 12.0, 1.5 Hz, 1H), 5.50 (dt, *J* = 11.5, 7.5 Hz, 1H), 2.81 (qd, *J* = 7.5, 1.5 Hz, 2H), 2.63 (td, *J* = 7.5, 1.5 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.0, 152.9, 141.8, 127.7, 118.5, 111.1, 109.7, 43.7, 22.0. HRMS (ESI): calcd. for $C_9H_{10}O_2$ $(M + H)^+$ 151.0754; found 151.0758.

*4.2.20. (Z)-5-(benzofuran-2-yl)pent-4-enal (**2t**)*

Yellow ointment (70 mg, 88% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (t, *J* = 1.6 Hz, 1H), 7.56–7.50 (m, 1H), 7.47–7.42 (m, 1H), 7.26 (td, *J* = 7.2, 1.2 Hz, 1H), 7.20 (td, *J* = 7.6, 0.8 Hz, 1H), 6.60 (s, 1H), 6.32 (dt, *J* = 12.0, 1.6 Hz, 1H), 5.71 (dt, *J* = 11.6, 7.6 Hz, 1H), 2.95 (qd, *J* = 7.2, 1.6 Hz, 2H), 2.66 (td, *J* = 7.2, 1.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.8, 154.7, 154.6, 131.7, 128.5, 124.5, 122.9, 120.9, 118.7, 111.1, 106.2, 43.7, 22.3. HRMS (ESI): calcd. for $C_{13}H_{12}O_2$ $(M + H)^+$ 201.0910; found 201.0917.

*4.2.21. (Z)-5-(benzo[b]thiophen-2-yl)pent-4-enal (**2u**)*

Yellow ointment (81 mg, 94% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.80 (t, *J* = 1.5 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 (td, *J* = 7.5, 1.5 Hz, 1H), 7.17 (s, 1H), 6.61 (dt, *J* = 12.0, 2.0 Hz, 1H), 5.65 (dt, *J* = 11.5, 7.5 Hz, 1H), 2.81 (qd, *J* = 7.5, 1.5 Hz, 2H), 2.64 (td, *J* = 7.0, 1.0 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.4, 140.0, 139.9, 139.3, 130.6, 124.5, 124.5, 124.3, 123.7, 123.5, 122.1, 43.5, 21.9. HRMS (ESI): calcd. for $C_{13}H_{12}OS$ $(M + H)^+$ 217.0682; found 217.0687.

*4.2.22. (Z)-5-cyclohexylpent-4-enal (**2v**)*

Yellow oil (62 mg, 93% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 5.32–5.16 (m, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.38 (q, *J* = 7.0 Hz, 2H), 1.76–1.51 (m, 8H), 1.22–1.18 (m, 1H), 1.06 (qd, *J* = 13.0, 3.0 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.3, 137.7, 125.2, 44.1, 36.3, 33.2, 30.3, 26.0, 25.9, 20.3, 15.4. HRMS (ESI): calcd. for $C_{11}H_{18}O$ $(M + H)^+$ 167.1430; found 167.1439.

*4.2.23. (Z)-5-cyclopentylpent-4-enal (**2w**)*

Colorless oil (55 mg, 91% yield).^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.77 (t, *J* = 1.5 Hz, 1H), 5.36 (tt, *J* = 11.0, 1.5 Hz, 1H), 5.26 (dt, *J* = 11.0, 7.5 Hz, 1H), 2.75–2.64 (m, 1H), 2.52–2.45 (m, 2H), 2.43–2.36 (q, *J* = 7.2 Hz, 2H), 1.83–1.72 (m, 2H), 1.71–1.62 (m, 2H), 1.61–1.50 (m, 2H), 1.29–1.14 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.3, 137.0, 125.6, 44.0, 38.1, 33.7, 25.4, 20.4. HRMS (ESI): calcd. for $C_{10}H_{16}O$ $(M + H)^+$ 153.1274; found 153.1279.

*4.2.24. (4Z,6E)-7-phenylhepta-4,6-dienal (**2x**)*

Yellow oil (68 mg, 92% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.79 (t, *J* = 1.0 Hz, 1H), 7.44–7.38 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25–7.19 (m, 1H), 7.04 (ddd, *J* = 15.5, 11.0, 1.0 Hz, 1H), 6.55 (d, *J* = 15.5 Hz, 1H), 6.19 (t, *J* = 11.0 Hz, 1H), 5.46 (dt, *J* = 10.5, 7.0 Hz, 1H), 2.66–2.51 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.7, 137.3, 133.2, 130.1, 129.8, 128.7, 127.7, 126.5, 123.7, 43.7, 20.7. HRMS (ESI): calcd. for $C_{13}H_{14}O$ $(M + H)^+$ 187.1117; found 187.1114.

4.3. Deuteration experiments

*4.3.1. (E)-2-benzylidenecyclobutan-1-d-1-ol (**D-1a**)*

To a 50 mL round-bottomed flask, $NaBD_4$ (3.6 mmol, 0.6 equiv.) was added to a stirred solution of **S-1a** (6.0 mmol, 1 equiv.) in MeOH (10 mL) at 0 °C. After stirring at 0 °C for 1 h and additional 3 h at room temperature, the reaction was quenched by addition of water. The MeOH was removed by rotary evaporation and the remaining aqueous phase was extracted with DCM (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by column chromatography to give corresponding deuterated substrate **D-1a**.

White solid (0.8 g, 84% yield). Mp 75–76 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.29 (m, 2H), 7.26 (d, *J* = 6.0 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.43 (t, *J* = 2.4 Hz, 1H), 2.85–2.73 (m, 1H), 2.72–2.59 (m, 1H), 2.55–2.43 (m, 1H), 1.95 (q, *J* = 9.6 Hz, 1H), 1.77–1.42 (br, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.8, 128.5, 127.8, 126.7, 120.1, 71.8 (t, *J* = 23.6 Hz), 31.8, 25.2. HRMS (ESI): calcd. for $C_{11}H_{11}DO$ $(M + H)^+$ 162.1024; found 162.1029.

*4.3.2. (Z)-5-phenylpent-4-enal-1-d (**D-2a**)*

An oven-dried 25 mL round bottom Schlenk tube was equipped with a magnetic stir bar and charged with substrate **D-1a** (0.4 mmol, 1.0 equiv.), $[Rh(COD)Cl]_2$ (4.9 mg, 0.01 mmol, 2.5 mol %), AgOAc (10.0 mg, 0.06 mmol, 15 mol %), and PCy_3(11.2 mg, 0.04 mmol, 10 mol %) under N_2 atmosphere, then the mixture was dissolved in dry toluene. The solution was stirred at 110 °C for 12 h. After the reaction mixture was cooled to room temperature, and then the product was extracted with EtOAc (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by column chromatography (eluent: petroleum ether/EtOAc = 10/1) to give the corresponding product **D-2a**.

Yellow oil (53 mg, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.30 (m, 2H), 7.29–7.20 (m, 3H), 6.48 (dt, *J* = 11.6, 2.0 Hz, 1H), 5.60 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.71–2.61 (m, 2H), 2.59–2.51 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.4 (t, *J* = 26.5 Hz), 137.1, 130.4, 130.1, 128.7, 128.3, 126.9, 43.7 (t, *J* = 3.7 Hz), 21.3. HRMS (ESI): calcd. for $C_{11}H_{11}DO$ $(M + H)^+$ 162.1024; found 162.1021.

4.4. Applications and transformations

*4.4.1. (Z)-5-phenylpent-4-en-1-ol (**3**)*

To a 25 mL round-bottomed flask, $NaBH_4$ (0.24 mmol, 0.6 equiv.) was added to a stirred solution of **2a** (0.4 mmol, 1.0 equiv.) in MeOH (2 mL) at 0 °C. After stirring at 0 °C for 10 min and an additional 20 min at room temperature, the reaction was quenched by the addition of water. The MeOH was removed by rotary evaporation and the remaining aqueous phase was extracted with DCM (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by column chromatography to give the corresponding product **3**.

Yellow oil (62 mg, 97% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.24 (m, 4H), 7.19 (tt, *J* = 7.2, 1.6 Hz, 1H), 6.42 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.22 (dt, *J* = 16.0, 6.8 Hz, 1H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.37–2.25 (m, 2H), 1.81–1.70 (m, 2H), 1.70–1.54 (br, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.6, 130.4, 130.1, 128.5, 127.0, 126.0, 62.4, 32.3, 29.3. HRMS (ESI): calcd. for $C_{11}H_{14}O$ $(M + H)^+$ 163.1117; found 163.1121.

*4.4.2. (Z)-(5-cyclopentylidenepent-1-en-1-yl)benzene (**4**)*

To a dry THF solution (5 mL) of cyclopentyltriphenylphosphonium bromide (987 mg, 2.4 mmol) cooled at 0 °C in an ice-

bath was slowly added a hexane solution of n-BuLi (2.5 M, 1.2 mL, 3.0 mmol). The mixture was stirred at room temperature for 1 h. Then a dry THF solution (5 mL) of **2a** (320 mg, 2.0 mmol) was added to the mixture. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the mixture was quenched with saturated aqueous NH_4Cl, and then the product was extracted with EtOAc (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by column chromatography (eluent: petroleum ether/EtOAc = 10/1) to give corresponding product **4**.

Yellow oil (323 mg, 76% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.24 (m, 4H), 7.23–7.15 (m, 1H), 6.41 (d, *J* = 12.0 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.6 Hz, 1H), 5.23 (t, *J* = 5.6 Hz, 1H), 2.45–2.33 (m, 2H), 2.27–2.07 (m, 6H), 1.71–1.53 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.0, 137.9, 132.9, 129.1, 128.9, 128.2, 126.5, 119.4, 33.7, 30.1, 28.9, 28.8, 26.6, 26.5. HRMS (ESI): calcd. for $C_{16}H_{20}O$ $(M + H)^+$ 213.1638; found 213.1632.

*4.4.3. (Z)-hex-1-en-5-yn-1-ylbenzene (**5**)*

To a 25 mL round-bottomed flask, which was equipped with a magnetic stir bar, was added **2a** (1 mmol, 1.0 equiv.) and K_3PO_4 (2.0 mmol, 2.0 equiv.) under a N_2 atmosphere. The mixture was dissolved in dry MeOH. Then a dry MeOH solution of dimethyl (1-diazo-2-oxopropyl)phosphonate (1.2 mmol, 1.2 equiv.) was added to the mixture. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the product was extracted with EtOAc (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by column chromatography (eluent: petroleum ether/EtOAc = 10/1) to give corresponding product **5**.

Yellow oil (147 mg, 94% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36–7.30 (m, 2H), 7.30–7.25 (m, 2H), 7.25–7.20 (m, 1H), 6.51 (dt, *J* = 12.0, 2.0 Hz, 1H), 5.72 (dt, *J* = 11.5, 7.0 Hz, 1H), 2.57 (qd, *J* = 7.5, 2.0 Hz, 2H), 2.31 (td, *J* = 7.0, 2.5 Hz, 2H), 1.98 (t, *J* = 3.0 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.3, 130.4, 130.3, 128.8, 128.2, 126.8, 83.8, 68.9, 27.6, 18.9. HRMS (ESI): calcd. for $C_{12}H_{12}$ $(M + H)^+$ 157.1012; found 157.1020.

*4.4.4. (Z)-1-phenyl-5-(p-tolyl)pent-4-en-1-ol (**6**)*

To a solution of **2i** (400 mg, 2.3 mmol) in dry THF (10 mL), PhMgBr (0.9 mL, 3 M, 2.8 mmol) was slowly added at −78 °C. The mixture was stirred for 15 min at −78 °C and then warmed to room temperature and stirred for another 6 h. Upon completion of the reaction, the mixture was quenched by addition of saturated aqueous NH_4Cl. The product was extracted with EtOAc (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated. The residue was purified by column chromatography (eluent: petroleum ether/EtOAc = 5/1) to give the corresponding product **6**.

Yellow oil (522 mg, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28–7.15 (m, 5H), 7.07 (q, *J* = 8.4 Hz, 4H), 6.35 (d, *J* = 11.6 Hz, 1H), 5.55 (dt, *J* = 11.6, 7.2 Hz, 1H), 4.53 (t, *J* = 6.8 Hz, 1H), 2.46 (br, 1H), 2.38–2.30 (m, 2H), 2.28 (s, 3H), 1.91–1.67 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.7, 136.3, 134.8, 131.5, 129.5, 129.1, 128.8, 128.5, 127.6, 126.1, 74.1, 39.3, 25.2, 21.4. HRMS (ESI): calcd. for $C_{17}H_{18}O$ $(M + H)^+$ 239.1430; found 239.1437.

*4.4.5. (Z)-1-phenyl-5-(p-tolyl)pent-4-en-1-one (**9**)*

To a 5 mL round-bottomed flask, Cr_3O (213 mg, 0.74 mmol), H_2SO_4 (0.22 mL) and H_2O (0.5 mL) were added, and the mixture was stirred for 30 min at room temperature. To a solution of **6** (239 mg, 1 mmol) in acetone, the resulting $Cr_3O/H_2SO_4/H_2O$ mixture was slowly added at 0 °C. The mixture was warmed to room temperature and stirred overnight. Upon completion of the reaction, the mixture was quenched by the addition saturated aqueous of NH_4Cl and the product was extracted with EtOAc (10 ml x3). The combined organic phase was washed with brine (10 ml x3), dried over anhydrous Na_2SO_4 and evaporated. The residue was purified by column chromatography (eluent: petroleum ether/EtOAc = 5/1) to give corresponding product **9**.

Yellow oil (147 mg, 84% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96–7.90 (m, 2H), 7.56–7.49 (m, 1H), 7.47–7.39 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 11.6 Hz, 1H), 5.65 (dt, *J* = 11.6, 7.2 Hz, 1H), 3.11–3.02 (m, 2H), 2.77 (qd, *J* = 7.6, 1.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.4, 136.9, 136.4, 134.5, 133.1, 130.3, 129.9, 129.0, 128.7, 128.6, 128.1, 38.7, 23.4, 21.2. HRMS (ESI): calcd. for $C_{17}H_{16}O$ $(M + H)^+$ 237.1274; found 237.1280.

Acknowledgments

We would like to thank National Natural Science Foundation of China (Nos. 21702134, 21772119 and 21620102003), Science and Technology Commission of Shanghai Municipality (No. 17ZR1415200) and Shanghai Municipal Education Commission (No. 201701070002E00030) for financial support. We thank the Instrumental Analysis Center of SJTU for characterization.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.130563.

References

[1] (For selected reviews on C-C bond activation, see:) (a) W.D. Jones, Nature 364 (1993) 676;
(b) B. Rybtchinski, D. Milstein, Angew. Chem. Int. Ed. 38 (1999) 870;
(c) M. Murakami, Y. Ito, Top. Organomet. Chem. 3 (1999) 97;
(d) C. Perthuisot, B.L. Edelbach, D.L. Zubris, N. Simhai, C.N. Iverson, C. Muller, T. Satoh, W.D. Jones, J. Mol. Catal. 189 (2002) 157;
(e) C.H. Jun, Chem. Soc. Rev. 33 (2004) 610;
(f) D. Nečas, M. Kotora, Curr. Org. Chem. 11 (2007) 1566;
(g) Y.J. Park, J.W. Park, C.H. Junn, Acc. Chem. Res. 41 (2008) 222;
(h) C. Aïssa, Synthesis 21 (2011) 3389;
(i) M. Murakami, T. Matsuda, Chem. Commun. 47 (2011) 1100;
(j) K. Ruhland, Eur. J. Org. Chem. 14 (2012) 2683;
(k) A. Korotvička, D. Nečas, M. Kotora, Curr. Org. Chem. 16 (2012) 1170;
(l) C–C bond activation, in: G. Dong (Ed.), Topics in Current Chemistry, vol. 346, Springer-Verlag, Berlin, 2014;
(m) F. Chen, T. Wang, N. Jiao, Chem. Rev. 114 (2014) 8613;
(n) A. Dermenci, J.W. Coe, G. Dong, Org. Chem. Front. 1 (2014) 567;
(o) L. Souillart, N. Cramer, Chem. Rev. 115 (2015) 9410;
(p) I. Marek, A. Masarwa, P.O. Delaye, M. Leibeling, Angew. Chem. Int. Ed. 54 (2015) 414;
(q) Y. Xia, G. Lu, P. Liu, G. Dong, Nature 359 (2016) 546;
(r) G. Fumagalli, S. Stanton, J.F. Bower, Chem. Rev. 117 (2017) 9404;
(s) P. Chen, B.A. Billett, T. Tsukamoto, G. Dong, ACS Catal. 7 (2017) 1340;
(t) J. Zhu, J. Wang, G. Dong, Nat. Chem. 11 (2019) 45.
[2] (a) T. Nishimura, K. Ohe, S. Uemura, J. Am. Chem. Soc. 121 (1999) 2645;
(b) T. Matsuda, M. Makino, M. Murakami, Org. Lett. 6 (2004) 1257;
(c) M. Murakami, M. Makino, S. Ashida, T. Matsuda, Bull. Chem. Soc. Jpn. 79 (2006) 1315;
(d) T. Seiser, N. Cramer, Angew. Chem. Int. Ed. 47 (2008) 9294;
(e) T. Seiser, N. Cramer, Org. Biomol. Chem. 7 (2009) 2835;
(f) M. Shigeno, T. Yamamoto, M. Murakami, Chem. Eur J. 15 (2009) 12929;
(g) T. Seiser, O.A. Roth, N. Cramer, Angew. Chem. Int. Ed. 48 (2009) 6320;
(h) T. Seiser, N. Cramer, J. Am. Chem. Soc. 132 (2010) 5340;
(i) T. Seiser, T. Saget, D.N. Tran, N. Cramer, Angew. Chem. Int. Ed. 50 (2011) 7740;
(j) T. Xu, H.M. Ko, N.A. Savage, G. Dong, J. Am. Chem. Soc. 134 (2012) 20005;
(k) T. Xu, G. Dong, Angew. Chem. Int. Ed. 51 (2012) 7567;
(l) N. Ishida, S. Sawano, Y. Masuda, M. Murakami, J. Am. Chem. Soc. 134 (2012) 17502;
(m) N. Ishida, Y. Nakanishi, M. Murakami, Angew. Chem. Int. Ed. 52 (2013) 11875;
(n) T. Matsuda, N. Miura, Org. Biomol. Chem. 11 (2013) 3424;
(o) L. Souillart, N. Cramer, Chem. Sci. 5 (2014) 837;

(p) Y. Xia, Z. Liu, Z. Liu, R. Ge, F. Ye, M. Hossain, Y. Zhang, J. Wang, J. Am. Chem. Soc. 136 (2014) 3013;
(q) A. Yada, S. Fujita, M. Murakami, J. Am. Chem. Soc. 136 (2014) 7217;
(r) T. Xu, G. Dong, Angew. Chem. Int. Ed. 53 (2014) 10733;
(s) H. Min, G. Dong, Nat. Chem. 6 (2014) 739;
(t) T. Xu, N.A. Savage, G. Dong, Angew. Chem. Int. Ed. 53 (2014) 1891;
(u) P. Chen, T. Xu, G. Dong, Angew. Chem. Int. Ed. 53 (2014) 1674;
(v) R. Ren, H. Zhao, L. Huan, C. Zhu, Angew. Chem. Int. Ed. 54 (2015) 12692;
(w) H. Zhao, X. Fan, J. Yu, C. Zhu, J. Am. Chem. Soc. 137 (2015) 3490;
(x) N. Ishida, N. Ishikawa, S. Sawano, Y. Masuda, M. Murakami, Chem. Commun. 51 (2015) 1882;
(y) X. Zhou, G. Dong, J. Am. Chem. Soc. 137 (2015) 13715;
(z) P. Chen, J. Sieber, C.H. Senanayake, G. Dong, Chem. Sci. 6 (2015) 5440;
(aa) G. Lu, C. Fang, T. Xu, G. Dong, P. Liu, J. Am. Chem. Soc. 137 (2015) 8274;
(ab) J. Yu, H. Yan, C. Zhu, Angew. Chem. Int. Ed. 55 (2016) 1143;
(ac) R. Ren, Z. Wu, Y. Xu, C. Zhu, Angew. Chem. Int. Ed. 55 (2016) 2866;
(ad) Q. Tian, B. Chen, G. Zhang, Green Chem. 18 (2016) 6236;
(ae) C. Zhao, L.C. Liu, J. Wang, C. Jiang, Q.W. Zhang, W. He, Org. Lett. 18 (2016) 328;
(af) R. Guo, G. Zhang, J. Am. Chem. Soc. 139 (2017) 12891;
(ag) S. Okumura, F. Sun, N. Ishida, M. Murakami, J. Am. Chem. Soc. 139 (2017) 12414;
(ah) L. Deng, M. Chen, G. Dong, J. Am. Chem. Soc. 140 (2018) 9652;
(ai) T. Sun, Y. Zhang, B. Qiu, Y. Wang, Y. Qin, G. Dong, Angew. Chem. Int. Ed. 57 (2018) 2859;
(aj) Z. Zhu, X. Li, S. Chen, P. Chen, B.A. Billett, Z. Huang, G. Dong, ACS Catal. 8 (2018) 845.
[3] Y. Zhu, C. Rao, Q. Song, Org. Lett. 18 (2016) 4000.
[4] X. Zheng, R. Guo, G. Zhang, D. Zhang, Chem. Sci. 9 (2018) 1873.
[5] (a) A. Furstner, O. Guth, A. Rumbo, G. Seidel, J. Am. Chem. Soc. 121 (1999) 11108;
(b) V.N. Odinokov, Chem. Nat. Compd. 36 (2000) 11;
(c) N. Winssinger, S. Barluenga, Chem. Commun. (2007) 22;
(d) M. Fouche, L. Rooney, A.G.M. Barrett, J. Org. Chem. 77 (2012) 3060.
[6] (a) J. Xia, Y. Nie, Y. Liu, I.D. Gridnev, W. Zhang, Chin. J. Chem. 36 (2018) 612;
(b) J. Li, Y. Lu, Y. Zhu, Y. Nie, J. Shen, Y. Liu, D. Liu, W. Zhang, Org. Lett. 21 (2019) 4331.
[7] (See supporting information for more details).
[8] E. Pérez-Mayoral, I. Matos, I. Fonseca, I. Čejka, Chem. Eur J. 16 (2010) 12079.
[9] (a) L. Coulombel, E. Duñach, Green Chem. 6 (2004) 499;
(b) C.G. Yang, N.W. Reich, Z. Shi, C. He, Org. Lett. 7 (2005) 4553;
(c) I.N. Francesco, B. Cacciuttolo, M. Pucheault, S. Antoniotti, Green Chem. 17 (2015) 837.
[10] X. Peng, B. Tong, H. Hirao, S. Chiba, Angew. Chem. Int. Ed. 53 (2014) 1959.
[11] T. Boesen, D.J. Fox, W. Galloway, D.S. Pedersen, C.R. Tyzack, S. Warren, Org. Biomol. Chem. 3 (2005) 630.