

# Site-selective and regioselective Diels–Alder reaction of allenyl aryl ethers

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**Abstract** The site-selectivity and regioselectivity of Diels–Alder reactions of allenyl aryl ethers with cyclopentadiene and acrolein were studied. While cyclopentadiene (as an electron-rich diene) only reacted with the external double bond of allenyl aryl ethers to provide the site-selective normal electron demand Diels–Alder cycloadducts, acrolein (as an electron-deficient diene) reacted with the C<sub>1</sub>–C<sub>2</sub> π bond of allenyl aryl ethers to provide the site- and regioselective hetero-Diels–Alder cycloadducts as exclusive products.

**Keywords** Acrolein · Allenes · Cycloadditions · Cyclopentadiene · Hetero-Diels–Alder · Solvent-free

## Introduction

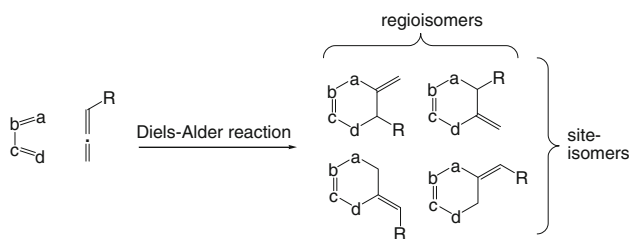
Diels–Alder reactions of allenes as dienophiles provide a valuable approach to cyclic systems with a reactive exo-alkylidene moiety, which is advantageous for further transformations often required in the synthesis of natural products [1–4]. Unfortunately, allene cycloadditions are often hampered by a low periselectivity allowing the [2 + 2] cycloaddition, which competes with the Diels–Alder reaction [5]. In addition the classical variant of this reaction, which is usually conducted under thermal conditions, is restricted in its scope by the necessity of an

appropriate HOMO–LUMO interaction of the reactants as rationalized in terms of the frontier molecular orbital (FMO) theory [6]. This requirement for complementary interacting moieties is fulfilled in the normal electron demand Diels–Alder cycloaddition of electron-deficient allenes with electron-rich dienes [7, 8], and vice versa in the inverse electron demand reaction of electron-rich allenes with electron-deficient dienes [9, 10]. On the other hand, allenes as dipolarophiles [11–18] and dienophiles [19] have attracted less attention in this type of reaction. A possible reason could be that unsymmetrically substituted allenes possess two different double bonds capable of undergoing cycloaddition reactions. Therefore, besides regio-, diastereo-, and enantioselectivity, also site-selectivity of the reaction has to be considered (Fig. 1). The formation of 16 isomeric products is conceivable if unsymmetrical dienes react with monosubstituted allenes.

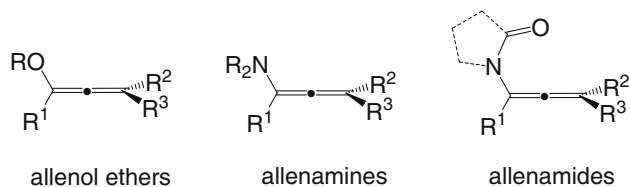
Important subgroups of allenes are those containing heteroatom substitutions such as allenol ethers, allenamines, and allenamides (Fig. 2). The electron-donating ability of the oxygen or nitrogen atom renders them even more synthetically attractive because of the electronic bias imposed by the heteroatoms, allowing site- and regioselective transformations of these molecules.

A review of the literature showed that there have been very limited reports on the development of effective allenyl ether-based methods for Diels–Alder reaction [19]. To the best of our knowledge there is no report on the site- and regioselective reaction of both double bonds of allenyl aryl ethers. It is worth noting that these are the first such processes that employ allenyl aryl ethers in the reaction with cyclopentadiene and that the opposite site-selectivity is produced preferentially as compared with reaction of electron-deficient dienes such as acrolein.

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**Fig. 1** Site- and regioselectivity in Diels–Alder reaction of 1,3-dienes with monosubstituted allenes (stereoisomers are not shown)

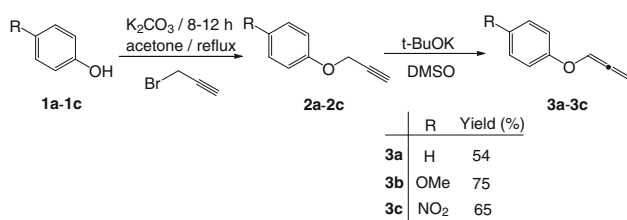


**Fig. 2** Allenol ethers, allenamines, and allenamides as important subgroups of allenes

## Results and discussion

A number of activated allenes, such as dialkyl 2,3-pentadienedioates, alkyl 2,3-butadienoates, various 1,2-propadienyl sulfones [20], and diphenyl(1,2-propadienyl)phosphane oxide [21] have been successfully employed in thermal [4 + 2] cycloadditions with various 1,3-dienes. Surprisingly, the cycloaddition reaction of allenes carrying an electron-donating aryloxy substituent seems to be unknown. The synthesis of allenyl aryl ethers **3a–3c** was performed by classical strategies. The functionalized phenols **1a–1c** were propargylated under basic conditions affording the corresponding propargyl derivatives **2a–2c**. These compounds were converted into the corresponding allenes **3a–3c** in good overall yields by treatment with *t*-BuOK in anhydrous DMSO at ambient temperature (Scheme 1) [22, 23].

The Diels–Alder reaction of compound **3a** with cyclopentadiene was carried out under several sets of reaction conditions. The results are summarized in Table 1. Heating the allene **3a** with cyclopentadiene in toluene at 100 °C (sealed tube) for 5 h afforded a mixture of three compounds. After chromatographic separation, the (*E/Z*) Diels–Alder adducts mixture and the [2 + 2] cycloadduct were



**Scheme 1**

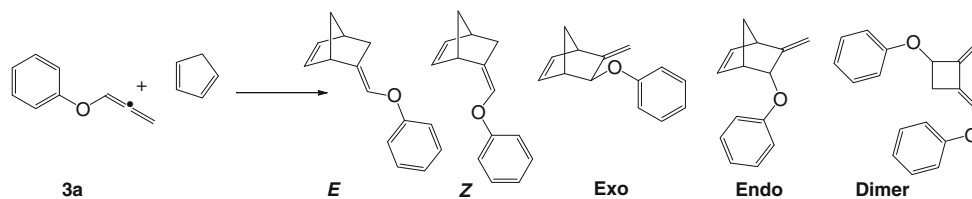
obtained. When the reaction was carried out on the surface of activated silica gel in solvent-free conditions (entry 10), shorter reaction times and an enhancement of the overall yield were observed. No evidence for other adducts besides two adducts was found by TLC and <sup>1</sup>H NMR inspection. The ratio of adducts (major/minor 55:45) was determined by <sup>1</sup>H NMR inspection. The products were isolated in 86% yield (entry 10). This site-selectivity can be reasonably understood by considering the preferential interaction between the HOMO of cyclopentadiene and the LUMO of the external double bond of the allenyl aryl ether **3a**. These results imply that the enol–ether moiety of allenyl aryl ethers simply acts as an electron-withdrawing group.

The conditions of entry 10 (Table 1) were used with the other prepared allenes, and the results are shown in Scheme 2. When the phenyl group of allenyl aryl ether is substituted in the *para* position by a nitro group (as an electron-withdrawing group) and/or a methoxy group (as an electron-donating group), the yield of the reaction is increased. A significant stereoselectivity was not observed under these conditions.

The structures of the products were established from their NMR spectroscopic data (<sup>1</sup>H NMR, <sup>13</sup>C NMR, and DEPT) and elemental analysis. The site-selectivity of the Diels–Alder reaction was confirmed by the <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis of **4a–4c**. The characteristic signal for **4a–4c** in the <sup>1</sup>H NMR spectra is a singlet for the =CHOAr group between 6.18 and 6.62 ppm; also the <sup>13</sup>C NMR spectra of compounds **4a–4c** showed two CH<sub>2</sub> groups at 30.6–31.24 and 49.9–51.0 ppm that are in agreement with the proposed structure. The ratio (major/minor) of the products **4a–4c** is based on the integration of their <sup>1</sup>H NMR peaks for the (*E/Z*) isomers.

We also investigated the intermolecular inverse electron demand Diels–Alder cycloaddition reaction of allenyl aryl ethers **3a–3c** with acrolein under thermal and Lewis acid conditions like the previous reactions. When the allenyl aryl ether **3a** was heated with acrolein on activated silica gel under solvent-free conditions at 70 °C for 3 h, the corresponding cycloadduct **5a** was obtained in optimal yield (45%), and is the only regioisomer found in this reaction (Scheme 3). Similar cycloadducts have been reported from the reaction of 1-ethoxy-1,2-propadiene [19], allenamines [24], and allenamides [25].

Furthermore, we also studied the effect of substituents in the *para* position of the phenyl group on the reactivity of allenyl aryl ethers. As shown in Scheme 3, the allenyl aryl ether **3c** with an electron-withdrawing –NO<sub>2</sub> group was much less reactive than the allenyl aryl ether **3b** under the same reaction conditions. These reactivity differences suggest that the electron-withdrawing substitution in the *para* position of the phenyl group in allenyl aryl ether **3c** could considerably decrease delocalization of the oxygen

**Table 1** Diels–Alder reaction of allenyl aryl ether **3a** with cyclopentadiene and ratio of products under different conditions

Entry	Lewis acid	Conditions <sup>a</sup>	Products <sup>b</sup>	Ratio <sup>c</sup>	Overall yield (%) <sup>d</sup>
1	–	Toluene, 100 °C, 5 h	<i>E/Z</i> /dimer	30:48:22	53
2	–	CH <sub>3</sub> CN, 80 °C, 5 h	<i>E/Z</i> /dimer	38:50:12	58
3	ZnO	CH <sub>3</sub> CN, 60 °C, 5 h	<i>E/Z</i>	45:55	40
4	ZnCl <sub>2</sub>	CH <sub>3</sub> CN, 60 °C, 5 h	<i>E/Z</i>	43:57	46
5	CuI	CH <sub>3</sub> CN, 60 °C, 5 h	<i>E/Z</i>	40:60	35
6	Et <sub>2</sub> O·BF <sub>3</sub>	CH <sub>3</sub> CN, 0 °C to RT, 10 h	<i>E/Z</i>	46:54	30
7	SiO <sub>2</sub> <sup>e</sup>	80 °C, 3 h	<i>E/Z</i> /dimer	30:42:28	23
8	SiO <sub>2</sub>	60 °C, 8 h	<i>E/Z</i>	42:58	10
9	SiO <sub>2</sub>	70 °C, 5 h	<i>E/Z</i>	45:55	65
10	Activated SiO <sub>2</sub> <sup>f</sup>	70 °C, 3 h	<i>E/Z</i>	45:55	86

<sup>a</sup> 1 equiv. of allene **3a**, 2.5–3 equiv. of cyclopentadiene, and 1 equiv. of Lewis acid were used

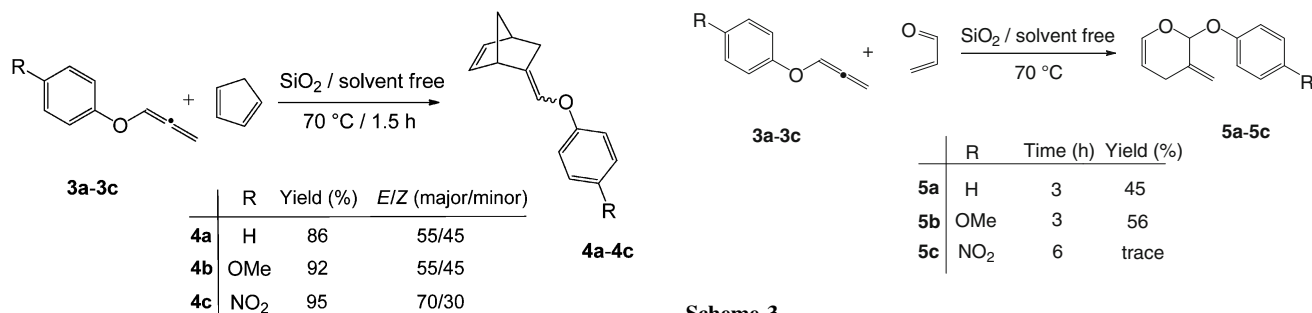
<sup>b</sup> Based on <sup>1</sup>H NMR spectra of crude products

<sup>c</sup> Determined by column chromatography

<sup>d</sup> Cumulative yield of isolated mixture of products

<sup>e</sup> Silica gel 2.5–3 weight equiv. was used

<sup>f</sup> Merck silica gel 70–230 mesh was activated at 150 °C in vacuum for 5 h



## Scheme 2

lone pairs of the ether, thereby reducing the ability to donate electron density towards the allene moiety and diminishing their reactivity. However, the allenyl aryl ether **3b** was the most reactive among the three allenyl aryl ethers, providing the cycloadduct **5b** in good yield in 3 h.

## Conclusion

The present results have demonstrated an interesting periselectivity in cycloaddition reaction of allenyl aryl ethers **3a–3c**. While the external double bond of allenyl aryl

## Scheme 3

ethers **3a–3c** undergoes the Diels–Alder reaction with electron-rich 1,3-dienes (cyclopentadiene), the internal double bond of the allenyl aryl ethers **3a–3c** undergoes the Diels–Alder reaction with electron-deficient 1,3-dienes (acrolein) as a dienophile. The reactions proceed in a highly site- and regioselective manner. Further development of the synthetic utility of these reactions is in progress in our laboratory.

## Experimental

Diels–Alder reactions were carried out under nitrogen using flame-dried glassware in sealed tubes. Cyclopentadiene was

obtained by cracking of the dimer (Sigma–Aldrich) directly before use. Acrolein was dried over  $\text{CaSO}_4$  and then distilled before use. Merck silica gel 70–230 mesh was activated (dried) at  $150^\circ\text{C}$  in vacuum for 5 h.  $\text{SiO}_2$  TLC plates 60 F<sub>254</sub> were purchased from Merck. Chromatography columns were prepared from Merck silica gel 70–230 mesh.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded by using a Bruker DRX-500 Avance spectrometer operating at 500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ . In the  $^{13}\text{C}$  NMR spectra signals corresponding to CH,  $\text{CH}_2$ , or  $\text{CH}_3$  groups were assigned from DEPT. Chemical shifts are given in ppm relative to  $\text{Me}_4\text{Si}$  as internal standard.  $\text{CDCl}_3$  was used as solvent at ambient temperature. Elemental analysis (C, H, N) was performed on a Perkin Elmer 2004 (II) CHN analyzer. Results agreed within standard errors with calculated values.

#### Preparation of propargyl ethers **2a–2c**

A mixture of phenol derivative **1a–1c** (50 mmol) and  $5.6\text{ cm}^3$  propargyl bromide (75 mmol) was stirred in  $40\text{ cm}^3$  acetone in the presence of 8.3 g  $\text{K}_2\text{CO}_3$  (60 mmol) for 8–10 h at reflux temperature. After completion of the reaction as monitored by TLC,  $120\text{ cm}^3$  ice-cold water was added to the reaction mixture. The reaction mixture was extracted with diethyl ether ( $3 \times 40\text{ cm}^3$ ), and the ether layer was washed with brine and dried with anhydrous  $\text{MgSO}_4$ . Evaporation of the solvent gave propargyl ethers **2a–2c**. The propargyl ethers were used without further purification for the next stage.

#### Isomerisation of propargyl ethers **2a–2c** into allenyl aryl ethers **3a–3c**

To 5 mmol of the prepared propargyl ether **2** was added 2.5 mmol of finely powdered potassium *tert*-butoxide (*t*-BuOK) in  $10\text{ cm}^3$  anhydrous DMSO at ambient temperature using a flame-dried flask. The reaction was slightly exothermic. The reaction mixture was stirred for 1.5 h. Subsequently the brown reaction mixture was poured on ice water. The reaction mixture was extracted with  $3 \times 20\text{ cm}^3$   $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  and the combined extracts were dried with  $\text{MgSO}_4$ . Evaporation of the solvent and column chromatography of the product on silica gel gave the pure products. The allenyl aryl ethers **3a–3c** were identified by comparison of their spectra with those of authentic samples [23].

#### General procedure for Diels–Alder reaction of allenyl aryl ethers **3a–3c** with cyclopentadiene and acrolein

A mixture of 2.5 equiv. (5 mmol) of cyclopentadiene (or acrolein) and 1 equiv. (2 mmol) of the allenyl aryl ether **3** was prepared at room temperature. Silica gel (2.5–3 weight

equiv.) was added, and the reaction vessel was shaken vigorously. The mixture was allowed to stand at the temperature and time indicated for each compound. Work-up method A: a suitable solvent such as  $\text{CHCl}_3$  was added and the silica gel was removed by filtration. The filtrate was washed with additional solvent. The combined filtrates were evaporated and the residue was separated by column chromatography. Work-up method B: the volatile materials were removed under reduced pressure, and the solid powder was separated by column chromatography to afford the pure compounds.

#### (5*E/Z*)-5-(Phenoxymethylene)bicyclo[2.2.1]hept-2-ene (**4a**, $\text{C}_{14}\text{H}_{14}\text{O}$ )

$T = 70^\circ\text{C}$ ,  $t = 1.5\text{ h}$ , work-up method B, eluent: petroleum ether/ethyl acetate (20:1);  $R_f = 0.69$ ; pale yellow oil; yield 0.34 g (86%).

Major isomer (55%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.48$  (d,  $J = 8.1\text{ Hz}$ , 1H), 1.67–1.69 (m, 1H), 1.94 (dt,  $J = 15.1, 2.3\text{ Hz}$ , 1H), 2.43 (dm,  $J = 14.5\text{ Hz}$ , 1H), 3.09 (s, 1H), 3.33 (s, 1H), 6.14–6.17 (m, 1H), 6.20–6.25 (m, 1H), 6.59 (s, 1H), 7.01–7.07 (m, 3H), 7.30–7.36 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 31.04$  ( $\text{CH}_2$ ), 42.22 (CH), 46.70 (CH), 51.03 ( $\text{CH}_2$ ), 116.40 (CH), 122.34 (CH), 127.53 (C), 129.95 (CH), 132.55 (CH), 134.61 (CH), 137.00 (CH), 158.45 (C) ppm.

Minor isomer (45%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.45$  (d,  $J = 8.2\text{ Hz}$ , 1H), 1.63–1.65 (m, 1H), 1.87 (d,  $J = 13.9\text{ Hz}$ , 1H), 2.43 (dm,  $J = 14.5\text{ Hz}$ , 1H), 3.09 (s, 1H), 3.80 (s, 1H), 6.14–6.17 (m, 1H), 6.20–6.25 (m, 1H), 6.25 (s, 1H), 7.01–7.07 (m, 3H), 7.30–7.36 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 30.80$  ( $\text{CH}_2$ ), 42.11 (CH), 44.55 (CH), 50.02 ( $\text{CH}_2$ ), 116.30 (CH), 122.27 (CH), 127.89 (C), 129.94 (CH), 132.05 (CH), 134.65 (CH), 136.88 (CH), 158.78 (C) ppm.

#### (5*E/Z*)-5-[4-Methoxyphenoxy)methylene]bicyclo[2.2.1]hept-2-ene (**4b**, $\text{C}_{15}\text{H}_{16}\text{O}_2$ )

$T = 70^\circ\text{C}$ ,  $t = 1.5\text{ h}$ , work-up method B, eluent: petroleum ether/ethyl acetate (5:1);  $R_f = 0.42$ ; pale yellow oil; yield 0.42 g (92%).

Major isomer (55%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.44$  (d,  $J = 8.2\text{ Hz}$ , 1H), 1.61–1.66 (m, 1H), 1.84 (d,  $J = 13.9\text{ Hz}$ , 1H), 2.40–2.44 (dm,  $J = 14.1\text{ Hz}$ , 1H), 3.08 (s, 1H), 3.79 (s, 1H), 3.82 (s, 3H), 6.12–6.20 (m, 2H), 6.18 (s, 1H), 6.86–6.89 (m, 2H), 6.94–6.97 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 30.64$  ( $\text{CH}_2$ ), 41.99 (CH), 44.34 (CH), 49.93 ( $\text{CH}_2$ ), 56.15 ( $\text{CH}_3$ ), 115.03 (CH), 117.37 (CH), 126.82 (C), 132.79 (CH), 134.59 (CH), 136.78 (CH), 152.70 (C), 155.14 (C) ppm.

Minor isomer (45%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.46$  (d,  $J = 8.2\text{ Hz}$ , 1H), 1.61–1.66 (m, 1H), 1.92 (d,  $J = 15.1\text{ Hz}$ , 1H), 2.40–2.44 (dm,  $J = 14.1\text{ Hz}$ , 1H), 3.08 (s, 1H), 3.30 (s, 1H), 3.82 (s, 3H), 6.12–6.20 (m, 2H), 6.50

(s, 1H), 6.86–6.89 (m, 2H), 6.94–6.97 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 30.87 ( $\text{CH}_2$ ), 42.13 (CH), 46.53 (CH), 50.91 ( $\text{CH}_2$ ), 56.15 ( $\text{CH}_3$ ), 115.00 (CH), 117.21 (CH), 126.31 (C), 133.40 (CH), 134.59 (CH), 136.86 (CH), 152.40 (C), 155.08 (C) ppm.

(5*E/Z*)-5-[4-Nitrophenoxy)methylene]bicyclo[2.2.1]-hept-2-ene (**4c**,  $\text{C}_{14}\text{H}_{13}\text{NO}_3$ )

$T = 70\text{ }^\circ\text{C}$ ,  $t = 1.5\text{ h}$ , work-up method B, eluent: petroleum ether/ethyl acetate (5:1);  $R_f = 0.53$ ; yellow oil; yield 0.46 g (95%).

Major isomer (70%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.48 (d,  $J = 8.3\text{ Hz}$ , 1H), 1.69–1.71 (m, 1H), 1.94 (dt,  $J = 15.3, 2.3\text{ Hz}$ , 1H), 2.36–2.40 (dm,  $J = 15.2\text{ Hz}$ , 1H), 3.09 (s, 1H), 3.37 (s, 1H), 6.12–6.14 (m, 1H), 6.22–6.24 (m, 1H), 6.62 (dd,  $J = 2.0, 1.6\text{ Hz}$ , 1H), 7.04–7.10 (m, 2H), 7.21–7.26 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 31.24 ( $\text{CH}_2$ ), 41.98 (CH), 46.64 (CH), 50.96 ( $\text{CH}_2$ ), 115.87 (CH), 126.31 (CH), 130.80 (CH), 131.53 (C), 134.19 (CH), 137.62 (CH), 142.60 (C), 163.09 (C) ppm.

Minor isomer (30%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.44 (d,  $J = 8.3\text{ Hz}$ , 1H), 1.64–1.66 (m, 1H), 1.94 (dt,  $J = 15.3, 2.3\text{ Hz}$ , 1H), 2.42–2.46 (dm,  $J = 15.3\text{ Hz}$ , 1H), 3.11 (s, 1H), 3.74 (s, 1H), 6.08–6.10 (m, 1H), 6.22–6.24 (m, 1H), 6.29 (s, 1H), 7.04–7.10 (m, 2H), 7.21–7.26 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 30.92 ( $\text{CH}_2$ ), 41.92 (CH), 44.66 (CH), 49.97 ( $\text{CH}_2$ ), 115.82 (CH), 126.31 (CH), 130.25 (CH), 131.71 (C), 134.02 (CH), 137.62 (CH), 142.60 (C), 163.49 (C) ppm.

3-Methylene-2-phenoxy-3,4-dihydro-2H-pyran (**5a**,  $\text{C}_{12}\text{H}_{12}\text{O}_2$ )

$T = 70\text{ }^\circ\text{C}$ ,  $t = 3\text{ h}$ , work-up method A, eluent: petroleum ether/ethyl acetate (10:1);  $R_f = 0.52$ ; colorless oil; yield 0.17 g (45%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.78 (ddd,  $J = 18.9, 4.7, 0.6\text{ Hz}$ , 1H), 3.23 (dm,  $J = 18.9\text{ Hz}$ , 1H), 4.95–4.97 (m, 1H), 5.18 (d,  $J = 2.5\text{ Hz}$ , 1H), 5.25 (d,  $J = 2.3\text{ Hz}$ , 1H), 5.90 (s, 1H), 6.30–6.32 (m, 1H), 7.09 (t,  $J = 7.3\text{ Hz}$ , 1H), 7.16 (d,  $J = 7.7\text{ Hz}$ , 2H), 7.36 (t,  $J = 7.5\text{ Hz}$ , 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 25.89 ( $\text{CH}_2$ ), 98.15 (CH), 101.91 (CH), 113.72 ( $\text{CH}_2$ ), 117.49 (CH), 122.79 (CH), 129.90 (CH), 139.11 (C), 140.20 (CH), 157.08 (C) ppm.

2-(4-Methoxyphenoxy)-3-methylene-3,4-dihydro-2H-pyran (**5b**,  $\text{C}_{13}\text{H}_{14}\text{O}_3$ )

$T = 70\text{ }^\circ\text{C}$ ,  $t = 3\text{ h}$ , work-up method A, eluent: petroleum ether/ethyl acetate (7:1);  $R_f = 0.45$ ; colorless oil; yield 0.24 g (56%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.78 (dd,  $J = 18.9, 4.5\text{ Hz}$ , 1H), 3.23 (dm,  $J = 18.9\text{ Hz}$ , 1H), 3.82

(s, 3H), 4.94–4.96 (m, 1H), 5.16 (d,  $J = 1.6\text{ Hz}$ , 1H), 5.22 (d,  $J = 1.7\text{ Hz}$ , 1H), 5.75 (s, 1H), 6.30–6.31 (m, 1H), 6.89 (d,  $J = 9.0\text{ Hz}$ , 2H), 7.08 (d,  $J = 9.0\text{ Hz}$ , 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 25.90 ( $\text{CH}_2$ ), 56.08 ( $\text{CH}_3$ ), 99.22 (CH), 101.92 (CH), 113.02 ( $\text{CH}_2$ ), 114.98 (CH), 119.09 (CH), 139.29 (C), 140.16 (CH), 150.99 (C), 155.59 (C) ppm.

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