ISSN 1070-3632, Russian Journal of General Chemistry, 2024, Vol. 94, No. 12, pp. 3155–3163. © Pleiades Publishing, Ltd., 2024.

Base-Free Fluoride-Mediated Vinylation of Alcohols with Calcium Carbide

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Received October 24, 2024; revised December 3, 2024; accepted December 9, 2024

Abstract—Here, we demonstrate that the reaction between calcium carbide and aliphatic and benzyl alcohols does not require an additional base as a catalyst and can be effectively promoted by readily available potassium fluoride. Potassium fluoride acts as a phase-transferring reagent, activating the calcium hydroxide base released from the reaction of calcium carbide with water. Given this insight, we have developed a novel synthetic pathway for the construction of alkyl vinyl ethers.

Keywords: acetylene, alcohols, vinylation, vinyl ethers, calcium carbide

DOI: 10.1134/S1070363224120041

INTRODUCTION

Vinyl ethers is a specific class of organic compounds: bearing two conjugated functional groups in one molecule (ether and C=C bond), they possess a unique reactivity comparing to the standard alkene moiety [1–3]. The electron-rich character of the *O*-vinyl group has resulted in a significant number of examples of vinyl ethers being used in organic synthesis [4–12] and production of polymeric materials [13–20]. Taking into account the high potential of vinyl ethers for scientific applications and industry, the development of synthetic approaches for the construction of the *O*-vinyl fragment is a demanded goal for modern organic chemistry.

A variety of methods were reported for the synthesis of vinyl ethers. Among them, addition of alcohols to acetylene, elimination processes, vinyl exchange reactions, transition metal-catalyzed vinylation reactions, reduction of acetylenic ethers and even metathesis reactions were used for the construction of *O*-vinyl moiety [1–3, 21]. Addition of alcohols to acetylene (Favorskii–Reppe reaction) is a major industrial process for the synthesis of vinyl ethers [22–27]. Some recent publications reported that acetylene can be replaced with calcium carbide for laboratory use [21, 28–43]. As a rule, both acetylene and carbide processes are performed under superbasic conditions and require the presence of an additional base (Scheme 1) [1, 2, 21–27, 35–41]. Trofimov group has demonstrated the multiple application of a superbasic systems for the synthesis of vinyl ethers from acetylene [22–26, 35], and some research groups performed base-catalyzed vinylation of alcohols and phenols using calcium carbide as acetylene analogue [2, 21, 34–41].

In current work, we demonstrate that aliphatic and benzyl alcohols react with calcium carbide in the presence of potassium fluoride as the sole promoting agent (Scheme 1). In previous studies of the vinylation reaction, a fluoride source was invariably paired with an additional base [2, 7, 24, 36, 37, 44]. Here we demonstrate that potassium fluoride acts as a phase-transferring agent, activating the low-reactive calcium hydroxide, thus allowing to avoid the use of a supplemental base in the

Scheme 1.

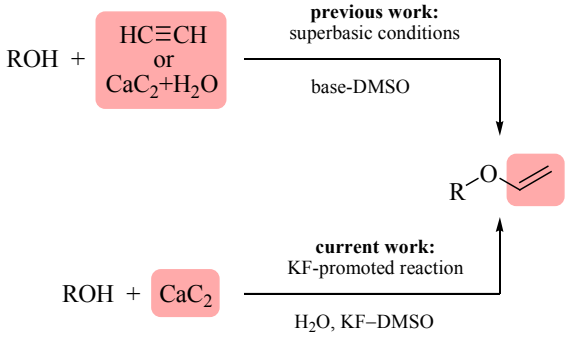
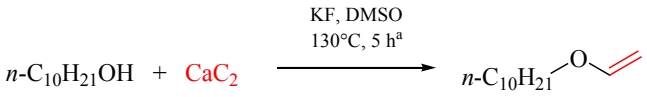


Table 1. Optimization of the reaction conditions.



1a **2a**

Entry	Ratio **1a** : CaC_2 : KF	**1a**, mmol	KF, mmol	Solvent	Yield of **2a**, %
1	1:4:0.5	0.75	0.38	DMSO	48
2	1:4:1	0.75	0.75	DMSO	79
3	1:4:2	0.75	1.5	DMSO	93
4	1:4:0	0.75	0	DMSO	0
5	1:3:0.5	1.0	0.5	DMSO	71
6	1:3:1	1.0	1.0	DMSO	83
7	1:3:2	1.0	2.0	DMSO	98 (95)[b]
8	1:2:0.5	1.5	0.75	DMSO	61
9	1:2:1	1.5	1.5	DMSO	78
10	1:2:2	1.5	3.0	DMSO	83
11	1:3:2	1.0	2.0	DMF	Trace
12	1:3:2	1.0	2.0	DX[c]	Trace
13	1:3:2	1.0	2.0	DXM[d]	12

[a] Reaction conditions: **1a**, KF, CaC_2 (3.0 mmol, 210 mg), solvent (1.0 mL), water (7.0 mmol, 127 μL).
[b] Isolated yield given in parentheses.
[c] DX is 1,4-dioxane.
[d] DXM is 1,4-dioxane–DMSO mixture (4 : 1).

reactions with calcium carbide. Using our methodology, a number of alkyl vinyl ethers and benzyl vinyl ethers were synthesized under additional base-free conditions in up to quantitative yields.

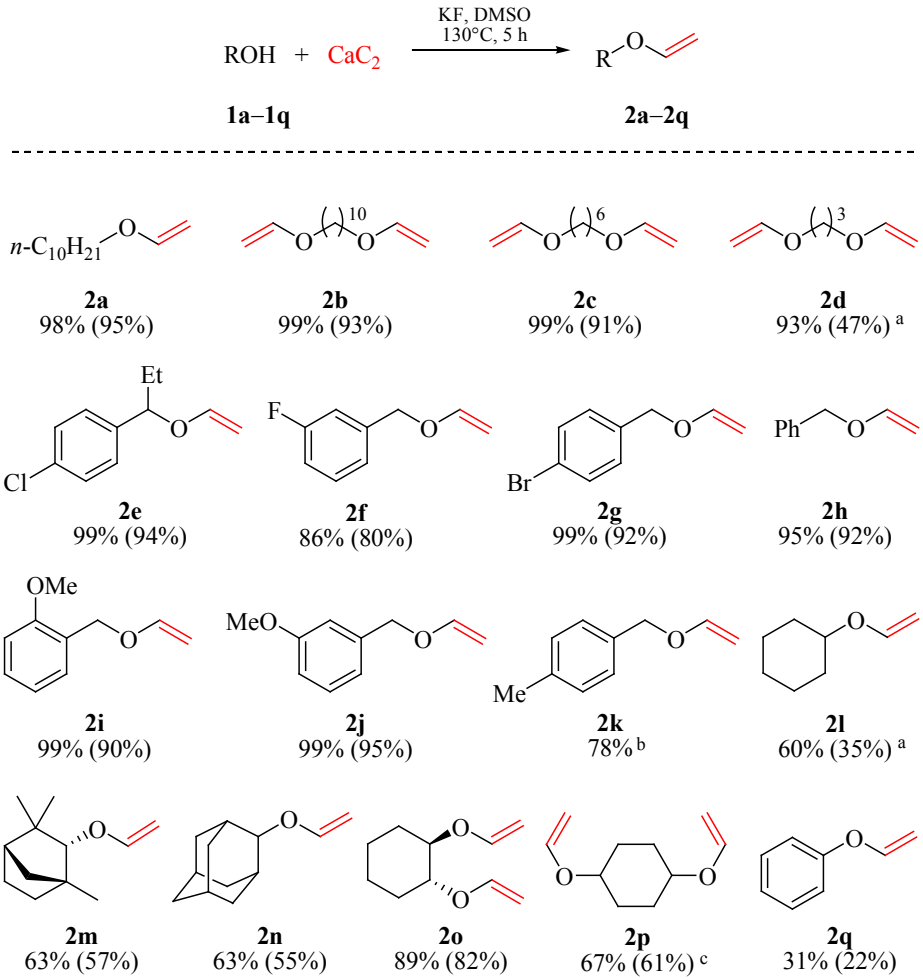
RESULTS AND DISCUSSION

A reaction between *n*-decyl alcohol **1a** and calcium carbide was selected as the model process for our study. We decided to vary the ratio of the components while maintaining a constant acetylene pressure by using 3.0 mmol of calcium carbide per 1.0 mL of dimethyl sulfoxide (solvent). We investigated the influence of the concentration of **1a** and potassium fluoride (Table 1, entries 1–10), and estimated that the optimal conditions for the reaction are 1.0 mmol of **1a** and 2.0 mmol of KF (Table 1, entry 7). Under these optimal conditions, **2a** was synthesized in 95% isolated yield. Dimethylformamide, 1,4-dioxane, and a 1,4-dioxane–DMSO mixture were tested as solvents for the vinylation of **1a** under optimized conditions (Table 1, entries 11–13), the formation of **2a** was observed only in the presence of DMSO.

With the optimized reaction conditions at hand, alcohols **1a**–**1p** were tested in the reaction with calcium carbide (Scheme 2). *n*-Decyl alcohol **1a** and diols **1b**–**1d** demonstrated excellent reactivity: **2a** and divinyl derivatives **2b**–**2d** were synthesized in up to quantitative yields. 1-(4-Chlorophenyl)propan-1-ol **1e** and benzyl alcohols **1g**–**1j** reacted with calcium carbide under optimized conditions producing vinyl ethers **2e** and **2g**–**2j** in quantitative yields. Compounds **2f** and **2k** were synthesized in 86 and 78% yield, respectively. Secondary alcohols **1l**–**1n** demonstrated moderate reactivity towards calcium carbide with vinyl ethers **2l**–**2n** synthesized in 60–63% yields. *rac*-(1*R*,2*R*)-Cyclohexane-1,2-diol **1o** reacted with CaC_2 with the formation of *rac*-(1*R*,2*R*)-1,2-bis(vinyloxy)cyclohexane **2o** in very good yield (89%), and cyclohexane-1,4-diol **1p** produced 1,4-bis(vinyloxy)-cyclohexane **2p** in 67% yield. We also tested phenol **1q** in the reaction, and observed the formation of **2q** in 31% yield.

To investigate the scalability of the developed procedure, gram-scale experiment was performed using **1e** as a substrate (Scheme 3). The reaction of 6.0 mmol of

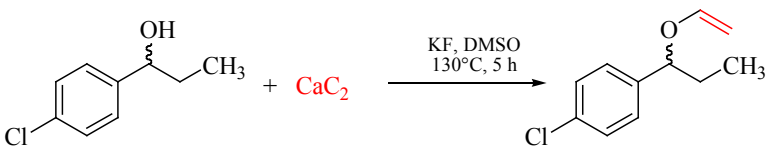
Scheme 2.



2a 98% (95%)
2b 99% (93%)
2c 99% (91%)
2d 93% (47%) [a]
2e 99% (94%)
2f 86% (80%)
2g 99% (92%)
2h 95% (92%)
2i 99% (90%)
2j 99% (95%)
2k 78% [b]
2l 60% (35%) [a]
2m 63% (57%)
2n 63% (55%)
2o 89% (82%)
2p 67% (61%) [c]
2q 31% (22%)

Reaction conditions: **1a–1q** (1.0 mmol), KF (2.0 mmol, 116 mg), CaC_2 (3.0 mmol, 210 mg), DMSO (1.0 mL), water (7.0 mmol, 127 μL). Isolated yield given in parentheses. [a] Due to its high volatility, the product was isolated as a mixture with hexane. [b] The product polymerizes on air and was not isolated in pure form. [c] The mixture of *cis*- and *trans*-bis(vinyl) products.

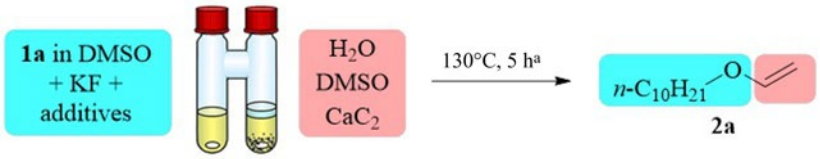
Scheme 3.



1e, 6 mmol, 1.023 g — 18 mmol, 1.260 g — **2e**, 99% (95%), 1.120 g

Reaction conditions: **1e** (6.0 mmol, 1.023 g), KF (12.0 mmol, 0.696 g), CaC_2 (18.0 mmol, 1.260 g), DMSO (6.0 mL), water (42.0 mmol, 0.762 mL). Isolated yield given in parentheses.

Table 2. The experiments in COware



Entry	Additives of *n*-decanol chamber		Yield, %
	$Ca(OH)_2$	Water	
1	✖	✖	0
2	✔	✖	7
3[b]	✖	✔	0
4	✖	✔	0
5	✔	✔	45
6[c]	✖	✔	16

[a] Reaction conditions: first chamber—**1a** (1.0 mmol), KF (2.0 mmol, 116 mg), DMSO (1.0 mL) + additives—$Ca(OH)_2$ (3.0 mmol, 222 mg), water (7.0 mmol, 127 μL); second chamber—CaC_2 (3.5 mmol, 250 mg), DMSO (0.5 mL), water (8.0 mmol, 150 μL).

[b] Water (1.0 mmol, 18 μL) was used as an additive. [c] 20 mg of CaC_2 were added to the alcohol chamber.

alcohol **1e** (1.023 g) and calcium carbide resulted in the formation of 1-chloro-4-[1-(vinyloxy)propyl]benzene **2e** in 99% yield (95% isolated yield), which is comparable with the previous result.

During our optimization studies, we demonstrated that the reaction of decanol-1 **1a** and calcium carbide did not yield *n*-decyl vinyl ether in the absence of potassium fluoride (Table 1, entry 4). This observation led us to propose that KF acts as a phase-transferring reagent in this process. For further mechanistic investigation in this field, we performed the reaction between **1a** and calcium carbide in a two-chamber COware reactor (H-tube), which allows for the separation of the substrate part from the acetylene source (see the inserted picture in Table 2).

We used a larger amount of calcium carbide to maintain acetylene pressure, considering the larger volume of the H-tube compared to the standard 8 mL culture tube. We varied the additives in the substrate chamber, and in the first experiment using potassium fluoride as an additive, we observed only **1a** in the reaction mixture (Table 2, entry 1). In the presence of the KF–$Ca(OH)_2$ mixture, the yield of **2a** was 7% (Table 2, entry 2), and we proposed that vinylation requires the presence of aqueous base. First, by adding 1.0 mmol of water to the mixture with potassium fluoride, vinyl ether **2a** was not obtained (Table 2, entry 3). Increasing the amount of water in the alcohol chamber to 7.0 mmol, still with KF, also did not yield **2a**, whereas in the presence of the KF–$Ca(OH)_2$ mixture **2a** was synthesized in 45% yield (Table 2, entries 4, 5). Interestingly, the addition of 20 mg of calcium carbide to the substrate chamber allowed us to get the product **2a** in 16% yield (Table 2, entry 6).

In summary, the data from Tables 1 and 2 allows us to conclude that in this process, calcium carbide acts both as a source of acetylene and a base, while potassium fluoride serves as a phase-transferring reagent, activating calcium hydroxide. The presence of water in the reaction mixture substantially improves the yield of vinyl ethers.

CONCLUSIONS

To summarize, we developed a convenient and efficient synthetic approach to vinyl derivatives of primary and secondary alcohols, particularly benzyl alcohols. It is based on the reaction of alcohols and acetylene using a mixture of calcium carbide and water as the source of acetylene. A thorough investigation of the vinylation reaction allowed us to avoid the use of an additional base in the reactions between alcohols and calcium carbide. We demonstrated the efficiency of readily available potassium fluoride as the only promoting agent for the vinylation of alcohols. Using the current procedure, vinyl ethers of primary and benzyl alcohols were synthesized in up to

quantitative yield, and secondary alkyl vinyl ethers were synthesized in good to very good yield.

EXPERIMENTAL

Granulated calcium carbide (≥75% gas-volumetric) was purchased from Sigma Aldrich. All chemicals were purchased from Sigma Aldrich, Alfa Aesar and Acros Organics in reagent grade or better quality and used without further purification.

NMR spectra were recorded on Bruker Avance III [400 (^{1}H) and 101 MHz (^{13}C)] spectrometer. High-resolution mass spectra (HRMS) were recorded on a Shimadzu Nexera X2 LCMS-9030 spectrometer using electrospray ionization (ESI). Preparative column chromatography was performed on basic alumina (70–230 mesh) or Merck silica gel 60 (230–400 mesh, pretreated with triethylamine).

General procedure for the synthesis of 2a–2q. A 8 mL culture tube equipped with a screw cap was loaded with potassium fluoride (116 mg, 2.0 mmol), CaC_2 (210 mg, 3.0 mmol), **1a**–**1q** (1.0 mmol), and 1.0 mL of DMSO. Then water (127 μL, 7.0 mmol) was carefully added, the tube was thoroughly sealed and heated to 130°C for 5 h. After, the reaction mixture was cooled to the room temperature, compounds **2a**–**2q** were extracted with hexane directly from the reaction tube. **Extraction procedure:** 1.0 mL of hexane was added to the reaction vessel, which was then closed and shaken. The hexane layer was subsequently separated with a Pasteur pipette (the procedure should be repeated 3 to 7 times). After that, the combined hexane extracts were washed three times with water, dried over Na_2SO_4, and evaporated to get pure **2a**–**2q**. If necessary, a product was purified with column chromatography (Et_3N-pretreated SiO_2 or basic Al_2O_3) using hexane as an eluent.

Gram-scale synthesis of 1-chloro-4-[1-(vinyloxy)-propyl]benzene 2e. A 32 mL reaction tube was loaded with potassium fluoride (12.0 mmol, 0.696 g), calcium carbide (18.0 mmol, 1.260 g), 1-(4-chlorophenyl)propan-1-ol **1e** (6.0 mmol, 1.023 g), and 6.0 mL of DMSO. Then, 0.762 mL of water were added carefully, and the tube was immediately sealed. The mixture was stirred at 130°C for 5 h. After that, the reaction mixture was cooled to room temperature and extracted with hexane as described previously. The solvent from hexane extract was evaporated to get 1.120 g (95%) of pure 1-chloro-4-(1-(vinyloxy)propyl)benzene **2e** as a colorless oil.

***n*-Decyl vinyl ether (2a)** [7]. Yield 175 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.48 d. d (1H, OCH=, *J* 14.3, 6.8 Hz), 4.15 d. d (1H, =CH_2, *J* 14.3, 1.7 Hz), 3.93 d. d (1H, =CH_2, *J* 6.8, 1.7 Hz), 3.64 t (2H, OCH_2, *J* 6.5 Hz), 1.61–1.54 m (2H), 1.33–1.25 m (14H), 0.86 t (3H, CH_3, *J* 6.8 Hz). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 151.9 (OCH=), 86.5 (=CH_2), 67.5 (OCH_2), 31.3 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.72 (CH_2), 28.66 (CH_2), 28.5 (CH_2), 25.4 (CH_2), 22.1 (CH_2), 13.9 (CH_3). Mass spectrum (LCMS ESI), *m/z*: 185.1899 [*M* + H]$^+$ (calcd for $C_{12}H_{25}O^+$: 185.1900).

1,10-Bis(vinyloxy)decane (2b) [7]. Yield 105 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) δ 6.48 d. d (2H, 2OCH=, *J* 14.3, 6.8 Hz), 4.15 d. d (2H, =CH_2, *J* 14.3, 1.7 Hz), 3.94 d. d (2H, =CH_2, *J* 6.8, 1.7 Hz), 3.64 t (4H, OCH_2, *J* 6.5 Hz), 1.57 quint (4H, *J* 6.8 Hz), 1.33–1.26 m (12H). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 152.0 (2OCH=), 86.5 (2=CH_2), 67.5 ($2OCH_2$), 28.9 ($2CH_2$), 28.7 ($2CH_2$), 28.5 ($2CH_2$), 25.4 ($2CH_2$). Mass spectrum (LCMS ESI), *m/z*: 227.2007 [*M* + H]$^+$ (calcd for $C_{14}H_{27}O_2^+$: 227.2006).

1,6-Bis(vinyloxy)hexane (2c). Yield 77 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.48 d. d (2H, OCH=, *J* 14.3, 6.8 Hz), 4.16 d. d (2H, =CH_2, *J* 14.3, 1.7 Hz), 3.94 d. d (2H, =CH_2, *J* 6.8, 1.7 Hz), 3.65 t (4H, $2OCH_2$, *J* 6.5 Hz), 1.59 quint (4H, *J* 6.9 Hz), 1.36–1.33 m (4H). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 151.9 (2OCH=), 86.5 (2=CH_2), 67.4 ($2OCH_2$), 28.4 ($2CH_2$), 25.2 ($2CH_2$). Mass spectrum (LCMS ESI), *m/z*: 171.1377 [*M* + H]$^+$ (calcd for $C_{10}H_{19}O_2^+$: 171.1380).

1,3-Bis(vinyloxy)propane (2d) [45]. Yield 30 mg (recalculated taking hexane into account), colorless oil. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.46 d. d (2H, OCH=, *J* 14.3, 6.8 Hz), 4.20 d. d (2H, CH_2, *J* 14.3, 2.0 Hz), 4.00 d. d (2H, =CH_2, *J* 6.8, 2.0 Hz), 3.80 t (4H, $2OCH_2$, *J* 6.2 Hz), 2.02 quint (2H, CH_2, *J* 6.2 Hz). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 151.8 (2OCH=), 86.8 (2=CH_2), 64.2 ($2OCH_2$), 28.2 (CH_2). Mass spectrum (LCMS ESI), *m/z*: 129.0911 [*M* + H]$^+$ (calcd for $C_7H_{13}O_2^+$: 129.0910).

1-Chloro-4-(1-(vinyloxy)propyl)benzene (2e). Yield 185 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 7.41 d ($2H_{Ar}$, *J* 8.5 Hz), 7.32 d ($2H_{Ar}$, *J* 8.5 Hz), 6.37 d. d (1H, OCH=, *J* 14.1, 6.6 Hz), 4.79 t [1H, O<u>CH</u>(Et), *J* 6.5 Hz], 4.16 d. d (1H, =CH_2, *J* 14.2, 1.5 Hz), 3.93 d. d (1H, =CH_2, *J* 6.7, 1.5 Hz), 1.85–1.63 m (2H, <u>CH_2</u>CH_3), 0.82 t (3H, CH_3, *J* 7.4 Hz). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 150.9 (OCH=),

140.5 (C), 131.9 (C), 128.3 (2CH), 128.1 (2CH), 89.1 (=CH_2), 80.8 [O<u>CH</u>(Et)], 29.8 (<u>CH_2</u>CH_3), 9.6 (CH_3). Mass spectrum (LCMS ESI), *m/z*: 304.9691 $[M + Ag]^+$ (calcd for $C_{11}H_{13}ClOAg^+$: 304.9695).

3-Fluorobenzyl vinyl ether (2f). Yield 121 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.33 t. d (1H_{Ar}, *J* 7.9, 5.8 Hz), 7.13–7.06 m (2H_{Ar}), 7.00 t. d (1H_{Ar}, *J* 8.5, 2.6 Hz), 6.55 d. d (1H, OCH=, *J* 14.3, 6.8 Hz), 4.76 s (2H, OCH_2), 4.30 d. d (1H, =CH_2, *J* 14.3, 2.3 Hz), 4.11 d. d (1H, =CH_2, *J* 6.8, 2.3 Hz). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 163.1 d (CF, J_{CF} 246.0 Hz), 151.6 (OCH=), 139.7 d (C_{Ar}, J_{CF} 7.4 Hz,), 130.2 d (CH_{Ar}, J_{CF} 8.2 Hz), 122.9 d (CH_{Ar}, J_{CF} 3.0 Hz), 114.9 d (CH_{Ar}, J_{CF} 21.1 Hz), 114.4 d (CH_{Ar}, J_{CF} 22.0 Hz), 87.9 (=CH_2), 69.4 d (OCH_2, J_{CF} 2.0 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$): δ_F –113.00 ppm. Mass spectrum (LCMS ESI), *m/z*: 258.9684 $[M + Ag]^+$ (calcd for $C_9H_9OFAg^+$: 258.9683).

4-Bromobenzyl vinyl ether (2g) [7]. Yield 195 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.49 d (2H_{Ar}, *J* 8.4 Hz), 7.23 d (2H_{Ar}, *J* 8.4 Hz), 6.54 d. d (1H, OCH=, *J* 14.3, 6.8 Hz), 4.71 s (2H, OCH_2), 4.29 d. d (1H, =CH_2, *J* 14.3, 2.3 Hz), 4.10 d. d (1H, =CH_2, *J* 6.8, 2.2 Hz). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 151.6 (OCH=), 136.1 (C), 131.8 (2CH_{Ar}), 129.3 (2CH_{Ar}), 122.0 (C), 87.8 (=CH_2), 69.4 (OCH_2). Mass spectrum (LCMS ESI), *m/z*: 320.8872 $[M + Ag]^+$ (calcd for $C_9H_9OBrAg^+$: 320.8865).

Benzyl vinyl ether (2h) [41]. Yield 123 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 7.40–7.30 m (5H_{Ph}), 6.59 d. d (1H, OCH=, *J* 14.2, 6.7 Hz), 4.77 s (2H, Ph<u>CH_2</u>), 4.31 d. d (1H, =CH_2, *J* 14.2, 1.9 Hz), 4.05 d. d (1H, =CH_2, *J* 6.7, 1.9 Hz). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 151.7 (OCH=), 137.0 (C), 128.3 (2CH_{Ph}), 127.7 (CH_{Ph}), 127.6 (2CH_{Ph}), 87.7 (=CH_2), 69.6 (CH_2). Mass spectrum (LCMS ESI), *m/z*: 135.0807 $[M + H]^+$ (calcd for $C_9H_{11}O^+$: 135.0804).

2-Methoxybenzyl vinyl ether (2i) [41]. Yield 137 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 7.33–7.29 m (2H_{Ar}), 7.02 d (1H_{Ar}, *J* 8.4 Hz), 6.95 t (1H_{Ar}, *J* 7.4 Hz), 6.58 d. d (1H, OCH=, *J* 14.2, 6.7 Hz), 4.74 s (2H, OCH_2), 4.28 d. d (1H, =CH_2, *J* 14.2, 1.8 Hz), 4.02 d. d (1H, =CH_2, *J* 6.7, 1.8 Hz), 3.80 s (3H, OCH_3). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 156.8 (C), 151.9 (OCH=), 129.3 (CH), 129.0 (CH), 124.7 (C), 120.2 (CH), 110.8 (CH), 87.3 (=CH_2), 65.0 (CH_2), 55.3 (CH_3). Mass spectrum (LCMS ESI), *m/z*: 270.9878 $[M + Ag]^+$ (calcd for $C_{10}H_{12}O_2Ag^+$: 270.9883).

3-Methoxybenzyl vinyl ether (2j) [12]. Yield 144 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 7.28 t (1H_{Ar}, *J* 8.1 Hz), 6.94–6.92 m (2H_{Ar}), 6.89–6.87 m (1H_{Ar}), 6.58 d. d (1H, OCH=, *J* 14.2, 6.7 Hz), 4.74 s (2H, OCH_2), 4.30 d. d (1H, =CH_2, *J* 14.2, 1.9 Hz), 4.05 d. d (1H, =CH_2, *J* 6.7, 1.9 Hz), 3.75 s (3H, OCH_3). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm:159.3 (C), 151.7 (OCH=), 138.6 (C), 129.4 (CH), 119.6 (CH), 113.3 (CH), 112.9 (CH), 87.7 (=CH_2), 69.5 (CH_2), 55.0 (CH_3). Mass spectrum (LCMS ESI), *m/z*: 270.9886 $[M + Ag]^+$ (calcd for $C_{10}H_{12}O_2Ag^+$: 270.9883).

(Vinyloxy)cyclohexane (2l) [46]. Yield 37 mg (recalculated taking hexane into account), colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.39 d. d (1H, OCH=, *J* 14.1, 6.6 Hz), 4.19 d. d (1H, =CH_2, *J* 14.1, 1.1 Hz), 3.92 d. d (1H, =CH_2, *J* 6.6, 1.1 Hz), 3.81–3.75 m (1H, <u>CH</u>OC_2H_3), 1.85–1.80 m (2H), 1.69–1.62 m (2H), 1.51–1.46 m (1H), 1.36–1.18 m (5H). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 150.8 (OCH=), 87.9 (=CH_2), 76.5 (<u>CH</u>OC_2H_3), 31.5 (2CH_2), 25.0 (CH_2), 23.1 (2CH_2). Mass spectrum (LCMS ESI), *m/z*: 127.1118 $[M + H]^+$ (calcd for $C_8H_{15}O^+$: 127.1117).

(1*R*,2*R*,4*S*)-1,3,3-Trimethyl-2-(vinyloxy) bicyclo[2.2.1]heptane (2m) [47]. Yield 103 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.39 d. d (1H, OCH=, *J* 14.0, 6.5 Hz), 4.20 d. d (1H, =CH_2, *J* 14.0, 1.4 Hz), 3.90 d. d (1H, =CH_2, *J* 6.5, 1.4 Hz), 3.42 d (1H, <u>CH</u>OC_2H_3, *J* 1.6 Hz,), 1.72–1.59 m (3H), 1.52 d. q (1H, *J* 10.1, 2.1 Hz,), 1.44–1.34 m (1H), 1.11 d. d (1H, *J* 10.1, 1.6 Hz,), 1.06–0.96 m (7H), 0.81 s (3H, CH_3). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 153.4 (OCH=), 91.4 (<u>CH</u>OC_2H_3), 87.4 (=CH_2), 48.6 (C), 47.9 (CH), 40.6 (CH_2), 39.4 (C), 30.5 (CH_3), 25.8 (CH_2), 25.5 (CH_2), 20.3 (CH_3), 19.4 (CH_3). Mass spectrum (LCMS ESI), *m/z*: 137.1329 $[M - OC_2H_3]^+$ (calcd for $C_{10}H_{17}^+$: 137.1325).

2-(Vinyloxy)adamantane (2n). Yield 98 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.41 d. d (1H, OCH=, *J* 14.1, 6.5 Hz), 4.24 d. d (1H, =CH_2, *J* 14.1, 0.9 Hz), 3.96–3.94 m (2H, 1H, =CH_2 and <u>CH</u>OC_2H_3), 1.98–1.92 m (4H), 1.82–1.75 m (4H), 1.70–1.68 m (4H), 1.48–1.45 m (2H). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 150.5 (OCH=), 88.3 (=CH_2), 80.7 (<u>CH</u>OC_2H_3), 36.9 (CH_2), 35.6 (2CH_2), 31.3 (2CH), 30.9 (2CH_2), 26.6 (CH), 26.5 (CH). Mass spectrum (LCMS ESI), *m/z*: 179.1429 $[M + H]^+$ (calcd for $C_{12}H_{19}O^+$: 179.1430).

(1*R*,2*R*)-1,2-Bis(vinyloxy)cyclohexane (2o) [38]. Yield 69 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.39 d. d (2H, 2OCH=, *J* 14.0, 6.5 Hz), 4.20 d. d (2H, =CH_2, *J* 14.0, 0.8 Hz), 3.91 d. d (2H, =CH_2, *J* 6.5, 0.8 Hz), 3.77–3.71 m (2H, $\underline{CH}OC_2H_3$), 1.97–1.92 m (2H), 1.62–1.59 m (2H), 1.32–1.21 m (4H). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 151.6 (2OCH=), 87.9 (2=CH_2), 79.9 ($\underline{CH}OC_2H_3$), 29.5 (2CH_2), 22.6 (2CH_2). Mass spectrum (LCMS ESI), *m/z*: 275.0205 [*M* + Ag]$^+$ (calcd for $C_{10}H_{13}OAg^+$: 275.0196).

1,4-Bis(vinyloxy)cyclohexane (2p). Yield 51 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 6.42–6.36 m (2H, 2OCH=), 4.25–4.20 m (2H, =CH_2), 3.97–3.84 m (4H, =CH_2 and 2$\underline{CH}OC_2H_3$), 1.93–1.87 m (3H), 1.69–1.60 m (3H), 1.44–1.35 m (2H). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 150.7 and 150.6 (2OCH=), 88.3 and 88.2 (2=CH_2), 75.3 and 74.0 ($\underline{CH}OC_2H_3$), 27.9 (2CH_2), 26.8 (2CH_2). Mass spectrum (LCMS ESI), *m/z*: 223.1308 [*M* + MeOH + Na]$^+$ (calcd for $C_{11}H_{17}ONa^+$: 223.1305).

Phenyl vinyl ether (2q) [38]. Yield 26 mg, colorless oil. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 7.36 d. d (2H_{Ph}, *J* 8.7, 7.4 Hz,), 7.12–7.04 m (3H_{Ph}), 6.86 d. d (1H, OCH=, *J* 13.6, 6.0 Hz), 4.72 d. d (1H, =CH_2, *J* 13.6, 1.5 Hz,), 4.47 d. d (1H, =CH_2, *J* 6.1, 1.5 Hz). ^{13}C NMR spectrum (101 MHz, DMSO-d_6), δ_C, ppm: 156.2 (C), 148.2 (OCH=), 129.8 (2CH), 123.1 (CH), 116.6 (2CH), 95.1 (=CH_2). Mass spectrum (LCMS ESI), *m/z*: 121.0649 [*M* + H]$^+$ (calcd for $C_8H_9O^+$: 121.0648).

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ACKNOWLEDGMENTS

The authors express their gratitude to the Resource Centres "Magnetic Resonance Research Centre" and "Chemical Analysis and Materials Research Centre" of the St. Petersburg State University.

FUNDING

This work was financially supported by the Russian Science Foundation and St. Petersburg Science Foundation (project no. 24-23-20144).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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