

Supporting information

for

Visible-light-induced bromoetherification of alkenols for the synthesis of β -bromotetrahydrofurans and -tetrahydropyrans

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Additional experimental data and ^1H and ^{13}C NMR spectra for products

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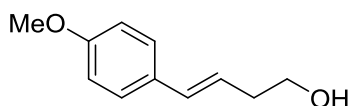
1. General information

All reagents were purchased from commercial sources unless otherwise noted. Solvent was freshly distilled prior to use unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) and visualized by UV-light (254 nm) or by treatment with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^1H NMR spectra were reported in δ ppm referenced to an internal SiMe_4 standard. Chemical shifts for ^{13}C NMR spectra were reported in parts per million relative to the center line signal of the CDCl_3 triplet at 77.0 ppm. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

2. Preparation and characterization of alkenols

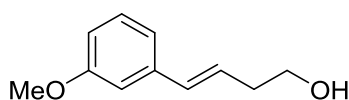
Alkenols **1a-s** were prepared according to reported method^[1].

(*E*)-4-(4-methoxyphenyl)but-3-en-1-ol (**1a**)



^1H NMR (CDCl_3 , 400 MHz): δ 7.27 (d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 6.40 (d, $J = 15.9$ Hz, 1H), 6.03 (dt, $J = 15.7, 7.1$ Hz, 1H), 3.77 (s, 3H), 3.69 (t, $J = 6.4$ Hz, 2H), 2.42 (td, $J = 7.3, 1.0$ Hz, 2H), 2.18 (brs, 1H). Data are consistent with literature values.^[1]

(*E*)-4-(3-methoxyphenyl)but-3-en-1-ol (**1b**)

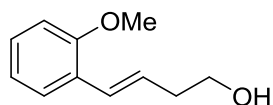


^1H NMR (CDCl_3 , 400 MHz): δ 7.21 (t, $J = 7.9$ Hz, 1H), 6.95 (d, $J = 7.7$ Hz, 1H), 6.89 (s, 1H), 6.77 (dd, $J = 8.2, 2.4$ Hz, 1H), 6.45 (d, $J = 15.9$ Hz, 1H), 6.23-6.16 (m, 1H), 3.80 (s, 1H), 3.74 (t, $J = 6.3$ Hz, 2H), 2.47 (q, $J = 6.5$ Hz, 2H), 1.84 (brs, 1H). Data are

¹ Zeng, X. H.; Miao, C. X.; Wang, S. F.; Xia, C. G.; Sun, W. *Chem. Commun.* 2013, 49, 2418.

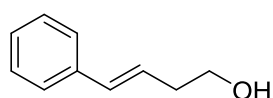
consistent with literature values.^[1]

(E)-4-(2-methoxyphenyl)but-3-en-1-ol (1c)



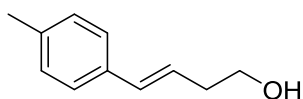
¹HNMR (CDCl₃, 400 MHz): δ 7.43-7.40 (m, 1H), 7.26-7.18 (m, 1H), 6.95-6.79 (m, 3H), 6.19 (dt, $J = 15.9, 7.2$ Hz, 1H), 3.84 (s, 3H), 3.76-3.69 (m, 2H), 2.53-2.47 (m, 2H), 1.68 (brs, 1H). Data are consistent with literature values.^[1]

(E)-4-phenylbut-3-en-1-ol (1d)



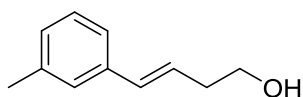
¹HNMR (CDCl₃, 400 MHz): δ 7.36-7.19 (m, 5H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.20 (dt, $J = 15.8, 7.1$ Hz, 1H), 3.76-3.73 (m, 2H), 2.50-2.45 (m, 2H), 1.81 (brs, 1H). Data are consistent with literature values.^[1]

(E)-4-*p*-tolylbut-3-en-1-ol (1e)



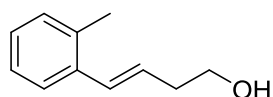
¹HNMR (CDCl₃, 400 MHz): δ 7.16 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.36 (d, $J = 15.9$ Hz, 1H), 6.05 (dt, $J = 15.8, 7.1$ Hz, 1H), 3.64-3.60 (m, 2H), 2.36 (td, $J = 7.3, 0.9$ Hz, 2H), 2.23 (s, 3H), 2.00 (brs, 1H). Data are consistent with literature values.^[1]

(E)-4-*m*-tolylbut-3-en-1-ol (1f)



¹HNMR (CDCl₃, 400 MHz): δ 7.24-7.14 (m, 3H), 7.03 (d, $J = 7.0$ Hz, 1H), 6.46 (d, $J = 15.9$ Hz, 1H), 6.18 (dt, $J = 15.7, 7.1$ Hz, 1H), 3.73 (t, $J = 6.3$ Hz, 2H), 2.49-2.44 (m, 2H), 2.33 (s, 3H), 1.66 (brs, 1H). Data are consistent with literature values.^[1]

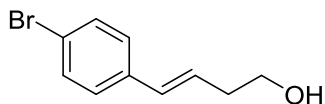
(E)-4-*o*-tolylbut-3-en-1-ol (1g)



¹HNMR (CDCl₃, 400 MHz): δ 7.16-7.12 (m, 4H), 6.68 (d, $J = 15.7$ Hz, 1H), 6.06 (dt,

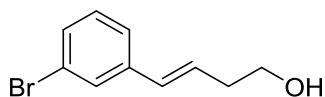
$J = 15.5, 7.2$ Hz, 1H), 3.73 (t, $J = 6.4$ Hz, 2H), 2.49 (td, $J = 7.6, 1.3$ Hz, 2H), 2.33 (s, 3H), 1.81 (brs, 1H). Data are consistent with literature values.^[1]

(E)-4-(4-bromophenyl)but-3-en-1-ol (1h)



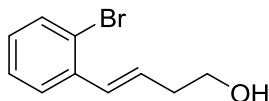
¹HNMR (CDCl₃, 400 MHz): δ 7.41 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 6.41 (d, $J = 15.9$ Hz, 1H), 6.19 (dt, $J = 15.7, 7.1$ Hz, 1H), 3.76-3.73 (m, 2H), 2.48-2.43 (m, 2H), 1.72 (brs, 1H). Data are consistent with literature values.^[1]

(E)-4-(3-bromophenyl)but-3-en-1-ol (1i)



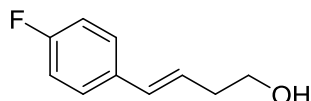
¹HNMR (CDCl₃, 400 MHz): δ 7.50 (s, 1H), 7.32 (d, $J = 7.9$ Hz, 1H), 7.26-7.23 (m, 1H), 7.15 (t, $J = 7.8$ Hz, 1H), 6.40 (d, $J = 15.9$ Hz, 1H), 6.21 (dt, $J = 15.8, 7.1$ Hz, 1H), 3.74 (t, $J = 6.3$ Hz, 2H), 2.47 (td, $J = 7.3, 1.1$ Hz, 1H), 1.83 (brs, 1H). Data are consistent with literature values.^[2]

(E)-4-(2-bromophenyl)but-3-en-1-ol (1j)



¹HNMR (CDCl₃, 400 MHz): δ 7.33-7.24 (m, 4H), 6.43 (d, $J = 15.9$ Hz, 1H), 6.18 (dt, $J = 15.7, 7.1$ Hz, 1H), 3.75 (t, $J = 6.3$ Hz, 2H), 2.50-2.45 (m, 2H), 1.84 (brs, 1H). Data are consistent with literature values.^[2]

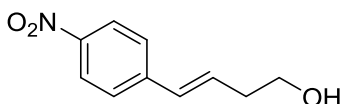
(E)-4-(4-fluorophenyl)but-3-en-1-ol (1k)



¹HNMR (CDCl₃, 400 MHz): δ 7.32-7.29 (m, 2H), 6.98 (t, $J = 8.7$ Hz, 2H), 6.44 (d, $J = 15.9$ Hz, 1H), 6.15-6.07 (m, 1H), 3.74 (t, $J = 6.3$ Hz, 2H), 2.49-2.44 (m, 3H). Data are consistent with literature values.^[1]

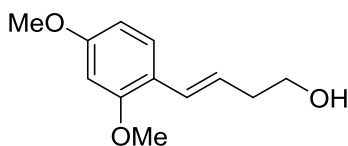
² Zeng, X. H.; Miao, C. X.; Wang, S. F.; Xia, C. G.; Sun, W. *Synthesis*, 2013, 45, 2391.

(E)-4-(4-nitrophenyl)but-3-en-1-ol (1l)



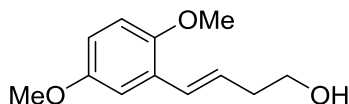
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.14 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 6.56 (d, $J = 16.0$ Hz, 1H), 6.49-6.42 (m, 1H), 3.81 (t, $J = 6.1$ Hz, 2H), 2.54 (q, $J = 6.0$ Hz, 2H), 1.79 (brs, 1H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 146.5, 143.7, 132.1, 130.5, 126.5, 123.9, 61.6, 36.4.

(E)-4-(2,4-dimethoxyphenyl)but-3-en-1-ol (1m)



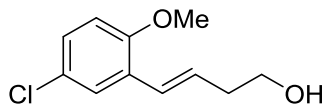
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.35 (d, $J = 8.3$ Hz, 1H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.50-6.45 (m, 2H), 6.10 (dt, $J = 15.9, 7.2$ Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.75 (t, $J = 6.3$ Hz, 2H), 2.53-2.47 (m, 2H), 1.74 (brs, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 160.1, 157.4, 127.2, 127.2, 124.7, 119.4, 104.7, 98.38, 62.1, 55.4, 55.3, 36.8.

(E)-4-(2,5-dimethoxyphenyl)but-3-en-1-ol (1n)



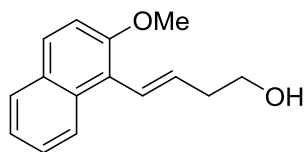
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 6.85 (d, $J = 2.8$ Hz, 1H), 6.78 (dd, $J = 8.5, 5.8$ Hz, 1H), 6.63 (d, $J = 11.6$ Hz, 1H), 5.75 (dt, $J = 11.6, 7.5$ Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.71 (t, $J = 6.4$ Hz, 2H), 2.51 (dd, $J = 7.5, 1.5$ Hz, 2H), 1.72 (brs, 1H).

(E)-4-(5-chloro-2-methoxyphenyl)but-3-en-1-ol (1o)



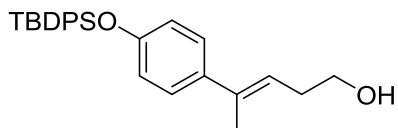
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.38 (d, $J = 2.5$ Hz, 1H), 7.13 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.78-6.72 (m, 2H), 6.23-6.16 (m, 1H), 3.81 (s, 3H), 3.75 (t, $J = 6.3$ Hz, 2H), 2.49 (d, $J = 6.8$ Hz, 2H), 1.67 (brs, 1H).

(E)-4-(2-methoxynaphthalen-1-yl)but-3-en-1-ol (1p)



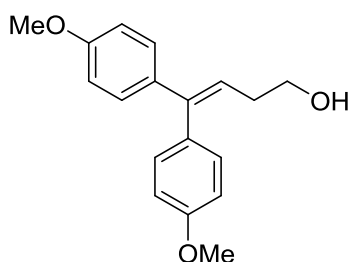
^1H NMR (CDCl_3 , 400 MHz): δ 8.02 (d, $J = 8.6$ Hz, 1H), 7.68 (t, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 9.0$ Hz, 1H), 7.34 (t, $J = 7.2$ Hz, 1H), 7.24 (dd, $J = 12.8, 5.9$ Hz, 1H), 7.16 (t, $J = 8.6$ Hz, 1H), 6.73 (d, $J = 16.1$ Hz, 1H), 6.02 (dt, $J = 15.9, 7.0$ Hz, 1H), 3.82 (s, 3H), 3.70 (t, $J = 6.3$ Hz, 2H), 2.52 (q, $J = 6.2$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 153.0, 131.9, 130.6, 128.2, 127.4, 127.2, 125.3, 124.8, 123.3, 122.4, 119.8, 112.1, 60.8, 55.4, 36.3.

(E)-4-(4-((tert-butyl-diphenylsilyloxy)phenyl)phenyl)pent-3-en-1-ol (1q)



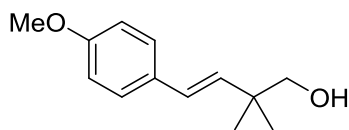
^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (dd, $J = 7.9, 1.4$ Hz, 4H), 7.34 (dd, $J = 5.0, 3.6$ Hz, 2H), 7.29 (t, $J = 7.1$ Hz, 4H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.65 (d, $J = 8.6$ Hz, 2H), 5.30 (td, $J = 7.3, 1.2$ Hz, 1H), 3.50 (t, $J = 6.5$ Hz, 2H), 2.15 (q, $J = 6.5$ Hz, 2H), 1.90 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.3, 139.0, 135.59, 134.2, 133.0, 129.8, 128.7, 127.7, 122.4, 119.3, 62.7, 35.4, 32.6, 26.5, 19.4.

4,4-bis(4-methoxyphenyl)but-3-en-1-ol (1r)



^1H NMR (CDCl_3 , 400 MHz): δ 7.18-7.14 (m, 2H), 7.12-7.09 (m, 2H), 6.92-6.88 (m, 2H), 6.81-6.78 (m, 2H), 5.96 (t, $J = 7.5$ Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.70 (t, $J = 6.6$ Hz, 2H), 2.40 (dd, $J = 14.0, 6.7$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 158.8, 158.6, 143.4, 135.5, 132.3, 131.0, 128.4, 123.2, 113.6, 113.4, 62.7, 55.3, 55.2, 33.3.

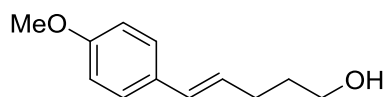
(E)-4-(4-methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (1s)



^1H NMR (CDCl_3 , 400 MHz): δ 7.12 (d, $J = 8.2$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.54 (d, $J = 12.6$ Hz, 1H), 5.50 (d, $J = 12.6$ Hz, 1H), 3.79 (s, 3H), 3.31 (s, 2H), 0.97 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 158.3, 138.2, 129.7, 127.2, 113.9, 113.1, 71.9, 55.1, 39.5, 25.7.

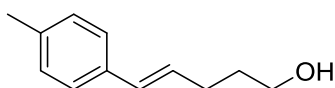
Alkenols **1t-w** were prepared according to reported method.^[3]

(E)-5-(4-methoxyphenyl)pent-4-en-1-ol (1t)



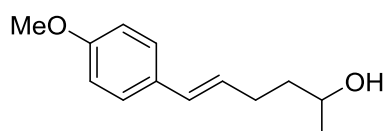
^1H NMR (CDCl_3 , 400 MHz): δ 7.21 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.34 (d, $J = 11.0$ Hz, 1H), 6.06 (dt, $J = 15.8, 6.9$ Hz, 1H), 3.79 (s, 3H), 3.64 (t, $J = 5.7$ Hz, 2H), 3.44 (brs, 1H), 2.43-2.37 (m, 1.8 Hz, 2H), 1.75-1.67 (m, 2H). Data are consistent with literature values.^[4]

(E)-5-*p*-tolylpent-4-en-1-ol (1u)



^1H NMR (CDCl_3 , 400 MHz): δ 7.23 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 2H), 6.38 (d, $J = 15.8$ Hz, 1H), 6.16 (dt, $J = 15.7, 6.9$ Hz, 1H), 3.68 (t, $J = 6.5$ Hz, 2H), 2.33-2.26 (m, 5H), 1.81-1.69 (m, 3H). Data are consistent with literature values.^[5]

(E)-6-(4-methoxyphenyl)hex-5-en-2-ol (1v)



^1H NMR (CDCl_3 , 400 MHz): δ 7.27 (d, $J = 8.1$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.36

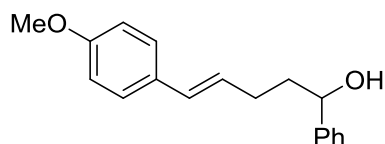
³ Logan, A.W.J.; Parker, J.S.; Hallside, M.S.; Burton J.W. *Org. Lett.* 2012, 14, 2940.

⁴ Belanger, G.; Levesque, F.; Paquet, J.; Barbe, G. *J. Org. Chem.* 2005, 70, 291.

⁵ Crombie, L.; Wyvill, R. D. *J. Chem. Soc. Perkin Trans. 1* 1985, 1983.

(d, $J = 16.0$ Hz, 1H), 6.12-6.04 (m, 1H), 3.88-3.83 (m, 1H), 3.79 (s, 3H), 2.34-2.25 (m, 2H), 1.67-1.57 (m, 2H), 1.47 (brs, 1H), 1.22 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ ^{13}C NMR (101 MHz, CDCl_3) δ 158.7, 130.5, 129.6, 128.1, 127.0, 113.9, 67.6, 55.3, 38.8, 29.3, 23.5.

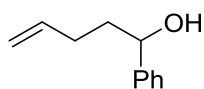
(E)-5-(4-methoxyphenyl)-1-phenylpent-4-en-1-ol (1w)



^1H NMR (CDCl_3 , 400 MHz): δ 7.37-7.25 (m, 7H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.35 (d, $J = 15.8$ Hz, 1H), 6.08 (dt, $J = 15.7, 6.9$ Hz, 1H), 4.74 (t, $J = 6.5$ Hz, 1H), 3.79 (s, 3H), 2.35-2.21 (m, 2H), 2.02-1.85 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 158.7, 144.6, 130.5, 129.8, 128.5, 127.8, 127.6, 127.0, 125.9, 113.9, 74.0, 55.3, 38.6, 29.3.

1x was prepared according to reported method.^[6]

1-phenylpent-4-en-1-ol (1x)



^1H NMR (CDCl_3 , 400 MHz): δ 7.42-7.29 (m, 5H), 5.93-5.83 (m, 1H), 5.11-5.02 (m, 2H), 4.72-4.68 (m, 1H), 2.45-2.08 (m, 3H), 1.97-1.78 (m, 2H). Data are consistent with literature values.^[7]

3. General procedure for photocatalytic bromoetherification of alkenols

General method: To a 10 mL round bottom flask equipped with a magnetic stir bar were added alkenols **1** (0.2 mmol), CBr_4 (132 mg, 0.4 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (4.6 mg, 0.006mmol) and dry DMSO (2 mL). The mixture was irradiated with blue LEDs (1W) at room temperature without degassed for 4 hours. Then water was added and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , concentrated. The residue was purified by flash column chromatography to give the final product **2**.

⁶ Janza, B.; Studer, A. *J. Org. Chem.* 2005, 70, 6991.

⁷ Rawal, V.; Singh, S. P.; Dufour, C.; Michoud, C. *J. Org. Chem.* 1993, 58, 7734.

4. Stereochemical determination of β -bromotetrahydrofuran 2a

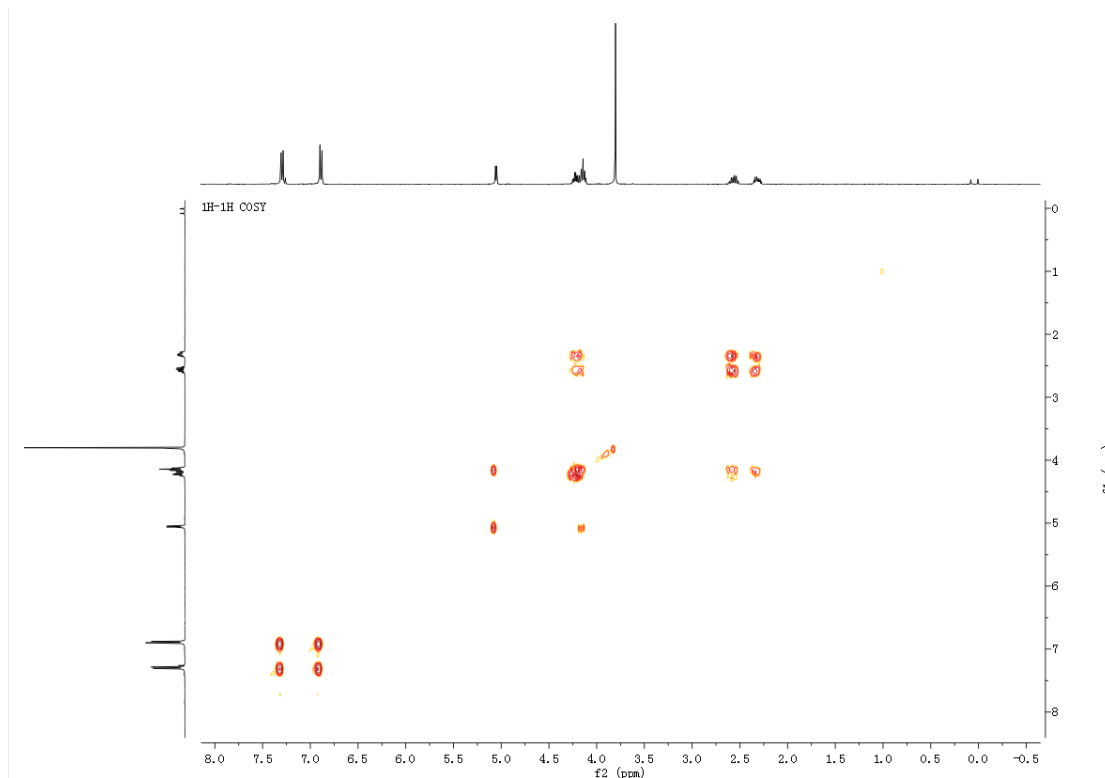


Fig. 1 COSY spectrum of the product **2a**.

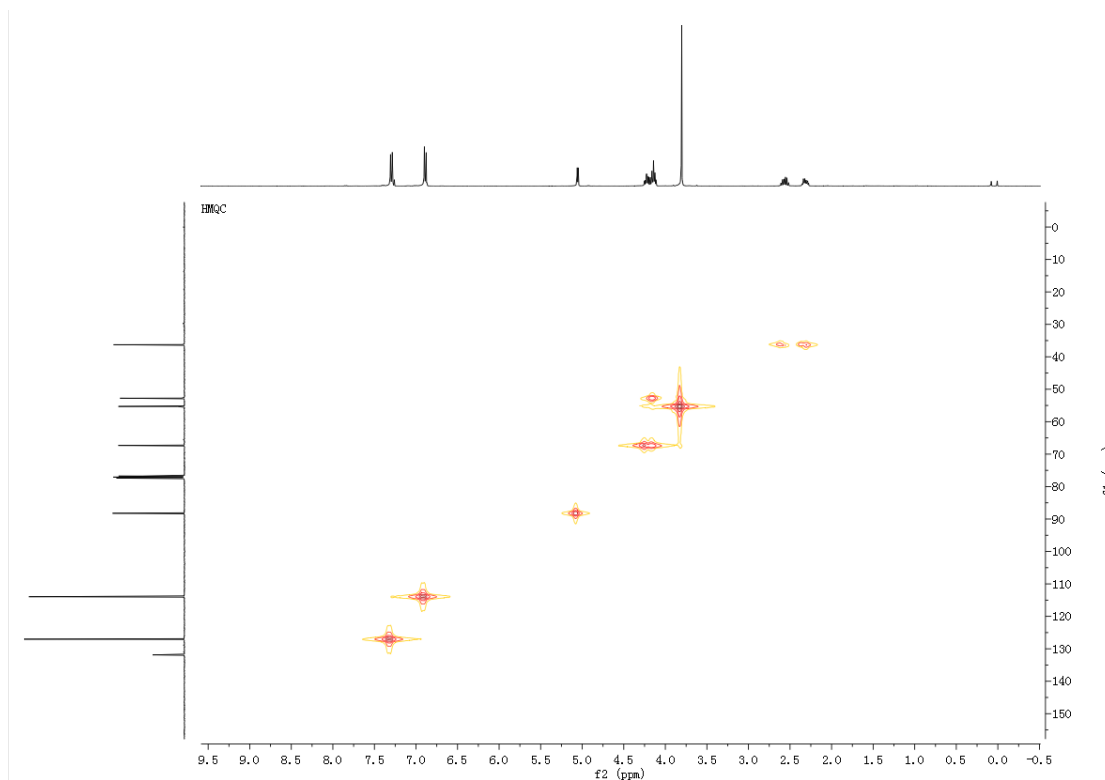


Fig. 2 HMQC spectrum of the product **2a**.

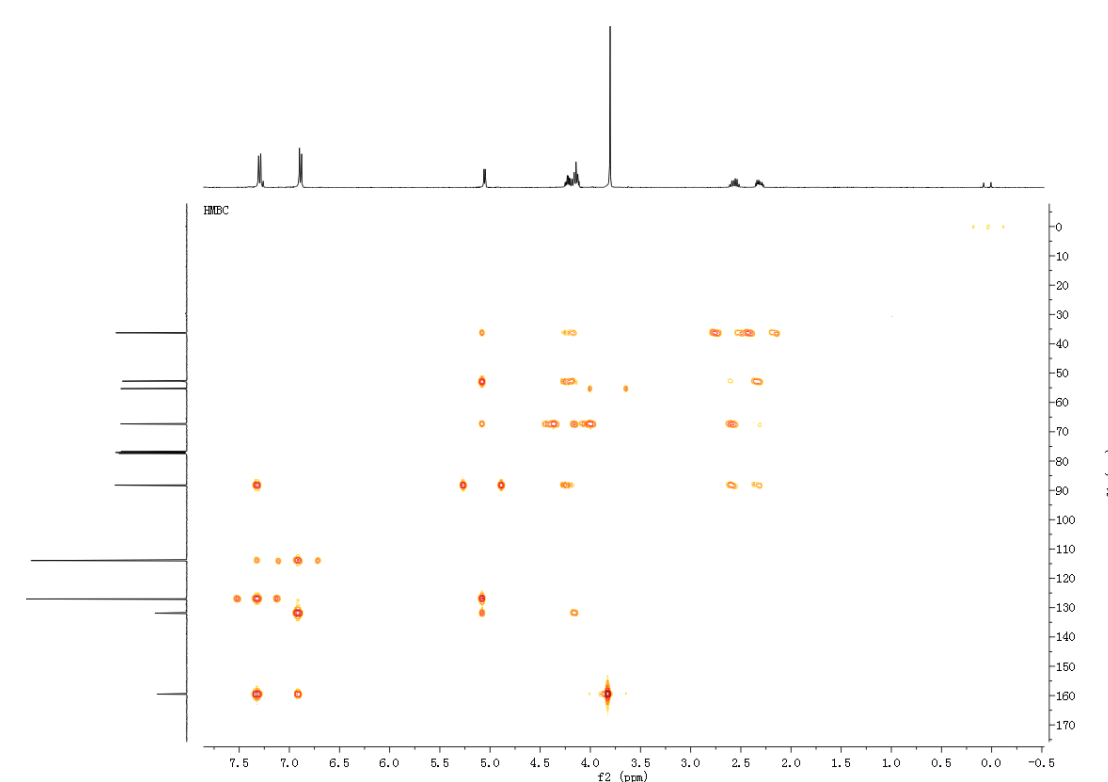


Fig. 3 HMBC spectrum of the product **2a**.

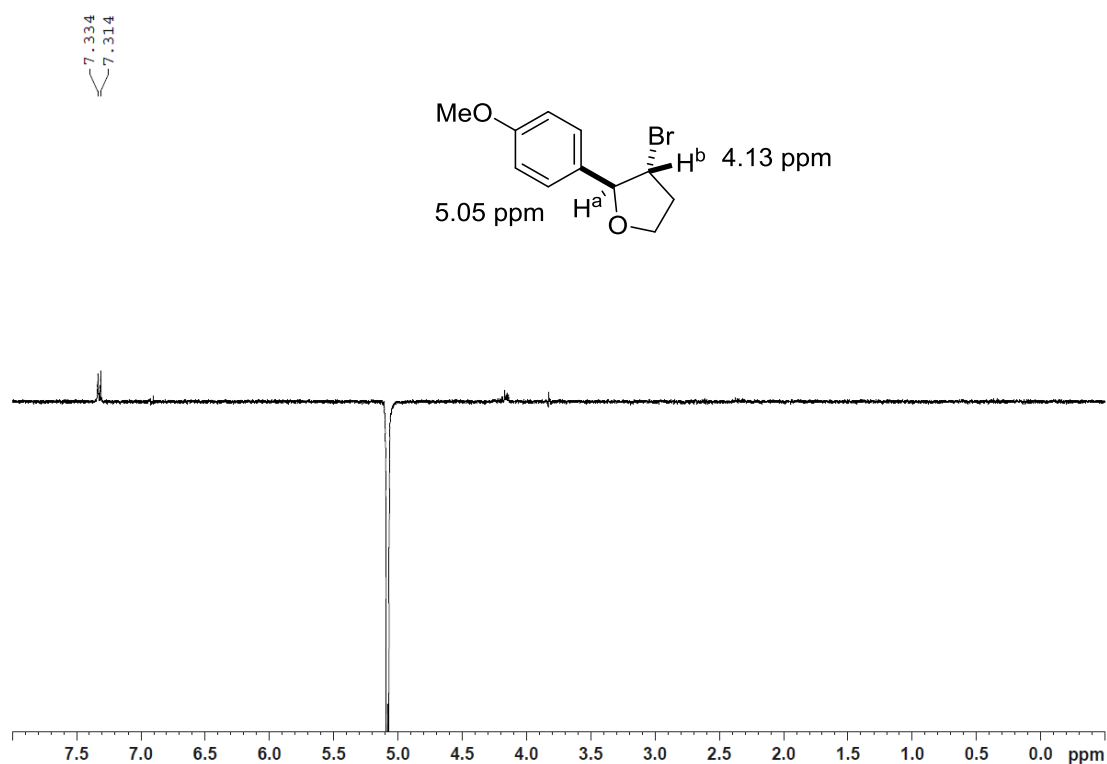
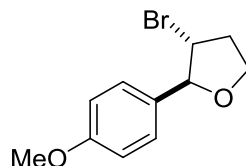


Fig. 4 NOE spectrum of the product **2a**. (There is no NOE between H^a and H^b .)

The NOE data indicate that product **2a** should be *trans* configuration. The stereochemistry of all other products was inferred by analogy.

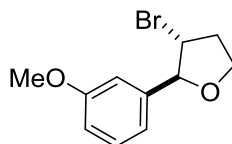
5. Characterization of photocatalytic bromoetherification products

3-bromo-2-(4-methoxyphenyl)tetrahydrofuran (2a)



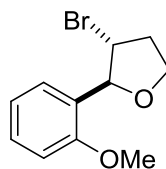
^1H NMR (CDCl_3 , 400 MHz): δ 7.30 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 5.05 (d, $J = 5.0$ Hz, 1H), 4.23 (td, $J = 8.2, 4.1$ Hz, 1H), 4.19-4.10 (m, 2H), 3.80 (s, 3H), 2.56 (dd, $J = 13.7, 7.3$ Hz, 1H), 2.37-2.26 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.5, 131.9, 127.0, 114.0, 88.2, 67.3, 55.3, 52.8, 36.3. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{BrO}_2$ 257.0177, found 257.0176.

3-bromo-2-(3-methoxyphenyl)tetrahydrofuran (2b)



^1H NMR (CDCl_3 , 400 MHz): δ 7.27 (t, $J = 7.9$ Hz, 2H), 6.94 (dd, $J = 13.5, 4.8$ Hz, 2H), 6.84 (dd, $J = 8.1, 2.5$ Hz, 1H), 5.13 (d, $J = 4.5$ Hz, 1H), 4.29 – 4.15 (m, 3H), 3.82 (s, 3H), 2.54 (dd, $J = 13.7, 7.0$ Hz, 1H), 2.39 – 2.26 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.8, 141.8, 129.6, 117.9, 113.5, 111.2, 88.4, 67.5, 55.3, 52.7, 36.2. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{BrO}_2$ 257.0177, found 257.0175.

3-bromo-2-(2-methoxyphenyl)tetrahydrofuran (2c)



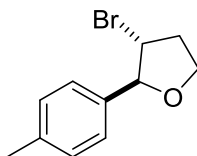
^1H NMR (CDCl_3 , 400 MHz): δ 7.35-7.28 (m, 1H), 7.29-7.23 (m, 1H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 5.52 (s, 1H), 4.50-4.41 (m, 1H), 4.37-4.23 (m, 2H), 3.88 (s, 3H), 2.44-2.29 (m, 1H), 2.28-2.17 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 156.2, 129.4, 128.9, 126.1, 120.5, 110.2, 85.2, 67.7, 55.4, 53.3, 35.3. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{BrO}_2$ 257.0177, found 257.0177.

3-bromo-2-phenyltetrahydrofuran (2d)



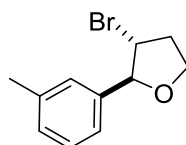
^1H NMR (CDCl_3 , 400 MHz): δ 7.43-7.33 (m, 4H), 7.32 (dd, $J = 5.8, 2.9$ Hz, 1H), 5.14 (d, $J = 4.7$ Hz, 1H), 4.26 (td, $J = 8.2, 4.0$ Hz, 1H), 4.23-4.15 (m, 2H), 2.56 (dd, $J = 13.8, 7.2$ Hz, 1H), 2.40-2.26 (m, 1H), 2.28-2.17 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 140.0, 128.5, 128.1, 125.6, 88.5, 67.5, 52.7, 36.2. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{12}\text{BrO}$ 227.0072, found 227.0070. Data are consistent with literature values.[⁸]

3-bromo-2-*p*-tolyltetrahydrofuran (2e)



^1H NMR (CDCl_3 , 400 MHz): δ 7.26 (d, $J = 7.9$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 5.10 (d, $J = 4.7$ Hz, 1H), 4.30-4.20 (m, 1H), 4.20-4.12 (m, 2H), 2.64-2.45(m, 1H), 2.35 (s, 3H), 2.33-2.27 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 137.8, 137.0, 129.2, 125.5, 88.4, 67.4, 52.8, 36.2, 21.1. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{BrO}$ 241.0228, found 241.0230.

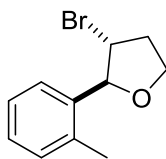
3-bromo-2-*m*-tolyltetrahydrofuran (2f)



^1H NMR (CDCl_3 , 400 MHz): δ 7.28 (dd, $J = 6.7, 4.7$ Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 1H), 7.17 (d, $J = 8.9$ Hz, 2H), 7.12 (d, $J = 7.4$ Hz, 1H), 5.11 (d, $J = 4.6$ Hz, 1H), 4.26 (td, $J = 8.2, 4.0$ Hz, 1H), 4.22-4.16 (m, 2H), 2.55 (dt, $J = 15.1, 8.0$ Hz, 1H), 2.36 (s, 3H), 2.35-2.24 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 139.9, 138.2, 128.8, 128.4, 126.2, 122.8, 88.6, 67.5, 52.8, 36.2, 21.4. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{BrO}$ 241.0228, found 241.0230.

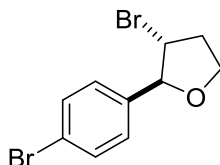
⁸ Crich, D.; Sartillo-Piscil, F.; Quintero-Cortes, L.; Wink, D. J. *J. Org. Chem.* 2002, 67, 3360-3364.

3-bromo-2-*o*-tolyltetrahydrofuran (2g)



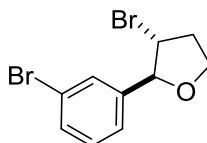
^1H NMR (CDCl_3 , 400 MHz): δ 7.33 (dd, $J = 5.1, 3.9$ Hz, 1H), 7.20 (dd, $J = 5.9, 3.3$ Hz, 2H), 7.17 (dd, $J = 8.1, 3.7$ Hz, 2H), 5.44 (d, $J = 2.5$ Hz, 1H), 4.38 (td, $J = 8.2, 2.2$ Hz, 1H), 4.33-4.22 (m, 2H), 2.54-2.44 (m, 1H), 2.24 (s, 3H), 2.28 (ddt, $J = 13.9, 5.7, 2.3$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 139.2, 134.9, 130.4, 127.8, 126.1, 124.9, 86.7, 67.9, 52.9, 35.6, 19.6. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{BrO}$ 241.0228, found 241.0227.

3-bromo-2-(4-bromophenyl)tetrahydrofuran (2h)



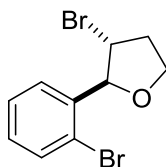
^1H NMR (CDCl_3 , 400 MHz): δ 7.48 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 5.05 (d, $J = 5.1$ Hz, 1H), 4.23 (td, $J = 8.2, 4.3$ Hz, 1H), 4.17 (dd, $J = 15.5, 8.2$ Hz, 1H), 4.08 (dt, $J = 7.0, 4.9$ Hz, 1H), 2.54 (td, $J = 15.1, 7.7$ Hz, 1H), 2.39-2.25 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 139.0, 131.8, 127.4, 122.0, 87.8, 67.5, 52.1, 36.3. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}$ 306.9156, found 306.9158.

3-bromo-2-(3-bromophenyl)tetrahydrofuran (2i)



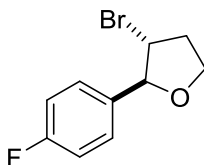
^1H NMR (CDCl_3 , 400 MHz): δ 7.54 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.31 (d, $J = 7.7$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 2H), 5.08 (d, $J = 4.8$ Hz, 1H), 4.31-4.08 (m, 3H), 2.53 (dt, $J = 15.0, 7.5$ Hz, 1H), 2.39-2.27 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 142.4, 131.2, 130.1, 128.7, 124.4, 122.8, 87.7, 67.6, 52.2, 36.3. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}$ 306.9156, found 306.9153.

3-bromo-2-(2-bromophenyl)tetrahydrofuran (2j)



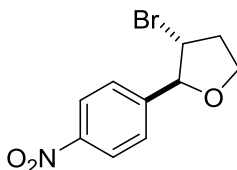
^1H NMR (CDCl_3 , 400 MHz): δ 7.56 (d, $J = 7.9$ Hz, 1H), 7.43-7.27 (m, 2H), 7.21-7.12 (m, 1H), 5.54 (s, 1H), 4.50-4.32 (m, 3H), 2.54-2.20 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 140.7, 132.9, 129.4, 127.5, 127.1, 121.8, 88.5, 68.5, 53.0, 34.7. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}$ 306.9156, found 306.9157.

3-bromo-2-(4-fluorophenyl)tetrahydrofuran (2k)



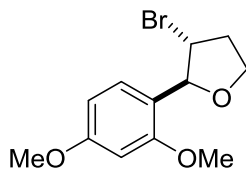
^1H NMR (CDCl_3 , 400 MHz): δ 7.36 (dd, $J = 8.5, 5.4$ Hz, 2H), 7.04 (t, $J = 8.7$ Hz, 2H), 5.06 (d, $J = 5.2$ Hz, 1H), 4.28-4.20 (m, 1H), 4.20-4.13 (m, 1H), 4.10 (dt, $J = 7.0, 5.0$ Hz, 3H), 2.56 (dd, $J = 13.7, 7.4$ Hz, 1H), 2.38-2.25 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 163.8, 161.3, 135.6, 135.5, 127.5, 127.4, 115.5, 115.3, 87.8, 67.4, 52.3, 36.3. ^{19}F NMR (376MHz, CDCl_3): δ -114.2 (s). HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{11}\text{BrFO}$ 244.9977, found 244.9980.

3-bromo-2-(4-nitrophenyl)tetrahydrofuran (2l)



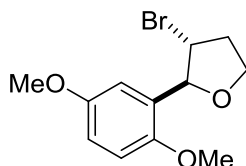
^1H NMR (CDCl_3 , 400 MHz): δ 8.23 (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 8.3$ Hz, 2H), 5.16 (d, $J = 5.0$ Hz, 1H), 4.30-4.19 (m, 2H), 4.08 (dd, $J = 11.0, 5.7$ Hz, 1H), 2.62-2.53 (m, 1H), 2.41-2.33 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.8, 147.0, 126.5, 123.8, 87.3, 67.8, 51.3, 36.4. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{11}\text{BrNO}_3$ 271.9922, found 271.9922.

3-bromo-2-(2,4-dimethoxyphenyl)tetrahydrofuran (2m)



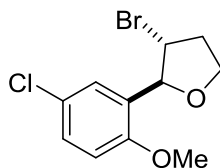
93%, $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.20 (d, $J = 7.9$ Hz, 1H), 6.50-6.41 (m, 2H), 5.42 (d, $J = 1.9$ Hz, 1H), 4.46-4.38 (m, 1H), 4.34-4.20 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.38 (d, $J = 9.9$ Hz, 1H), 2.23 (d, $J = 5.8$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 160.7, 157.3, 127.0, 121.7, 103.9, 98.4, 85.1, 67.5, 55.4, 55.4, 53.2, 35.3. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{16}\text{BrO}_3$ 287.0283, found 287.0280.

3-bromo-2-(2,5-dimethoxyphenyl)tetrahydrofuran (2n)



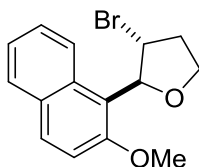
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 6.91 (m, 1H), 6.78 (d, $J = 2.3$ Hz, 2H), 5.48 (s, 1H), 4.44 (d, $J = 5.4$ Hz, 1H), 4.31 (m, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 2.41-2.28 (m, 1H), 2.26-2.17 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 153.7, 150.4, 130.7, 112.9, 112.7, 111.1, 85.4, 67.8, 55.9, 55.8, 53.3, 35.2. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{16}\text{BrO}_3$ 287.0283, found 287.0280.

3-bromo-2-(5-chloro-2-methoxyphenyl)tetrahydrofuran (2o)



$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.28 (d, $J = 2.4$ Hz, 1H), 7.21 (dd, $J = 8.7, 2.6$ Hz, 1H), 6.78 (d, $J = 8.7$ Hz, 1H), 5.46 (s, 1H), 4.39 (d, $J = 5.4$ Hz, 1H), 4.35 (td, $J = 8.2, 1.9$ Hz, 1H), 4.32-4.24 (m, 1H), 3.86 (s, 3H), 2.31 (ddd, $J = 10.3, 8.3, 5.4$ Hz, 1H), 2.22 (dd, $J = 13.9, 5.6$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 154.8, 131.4, 128.5, 126.2, 125.8, 111.4, 84.7, 67.9, 55.7, 52.8, 35.3. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{13}\text{BrClO}_2$ 290.9787, found 290.9785.

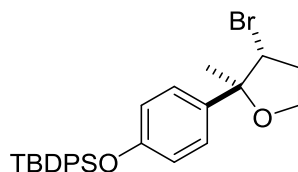
3-bromo-2-(2-methoxynaphthalen-1-yl)tetrahydrofuran (2p)



^1H NMR (CDCl_3 , 400 MHz): δ 8.15 (d, $J = 8.7$ Hz, 1H), 7.81 (dd, $J = 18.3, 8.7$ Hz, 2H), 7.53-7.41 (m, 1H), 7.39-7.22 (m, 2H), 6.01 (d, $J = 6.9$ Hz, 1H), 4.84-4.73 (m, 1H), 4.39-4.27 (m, 1H), 4.21-4.09 (m, 1H), 3.96 (s, 3H), 2.99-2.81 (m, 1H), 2.57-2.44 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 156.3, 132.7, 130.8, 129.6, 128.8, 126.7, 123.5, 123.3, 118.1, 114.0, 83.0, 67.3, 57.0, 50.4, 38.2. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{16}\text{BrO}_2$ 307.0334, found 307.0330.

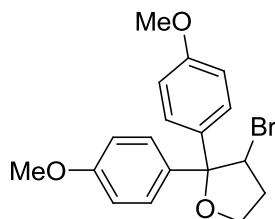
(4-(3-bromo-2-methyltetrahydrofuran-2-yl)phenoxy)(*tert*-butyl)diphenylsilane

(2q)



^1H NMR (CDCl_3 , 400 MHz): δ 7.77-7.66 (m, 4H), 7.43 (dd, $J = 8.4, 6.2$ Hz, 2H), 7.36 (dd, $J = 11.0, 4.1$ Hz, 4H), 7.14-7.06 (m, 2H), 6.75-6.68 (m, 2H), 4.50 (dd, $J = 5.6, 3.2$ Hz, 1H), 4.18 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.98 (td, $J = 8.4, 3.7$ Hz, 1H), 2.37-2.30 (m, 1H), 2.26-2.20 (m, 1H), 1.6 (s, 3H), 1.1 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 154.7, 137.7, 135.5, 132.9, 129.9, 127.7, 125.5, 119.5, 86.4, 65.5, 58.7, 36.4, 28.0, 26.5, 19.4. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{32}\text{BrO}_2\text{Si}$ 495.1355, found 495.1358.

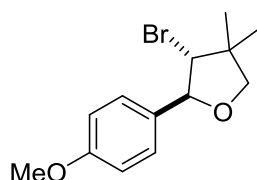
3-bromo-2,2-bis(4-methoxyphenyl)tetrahydrofuran (2r)



^1H NMR (CDCl_3 , 400 MHz): δ 7.38 (dd, $J = 20.5, 8.8$ Hz, 4H), 6.82 (dd, $J = 14.0, 8.8$ Hz, 4H), 5.20 (dd, $J = 4.5, 2.6$ Hz, 1H), 4.39 (q, $J = 8.0$ Hz, 1H), 4.05 (td, $J = 8.2, 4.4$

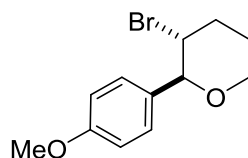
Hz, 1H), 3.75 (d, $J = 5.2$ Hz, 6H), 2.45 (dd, $J = 7.8, 4.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 158.7, 158.3, 136.9, 136.3, 127.3, 126.4, 114.0, 113.0, 90.5, 65.2, 57.3, 55.3, 55.1, 36.58. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{20}\text{BrO}_3$ 363.0596, found 363.0598.

3-bromo-2-(4-methoxyphenyl)-4,4-dimethyltetrahydrofuran (2s)



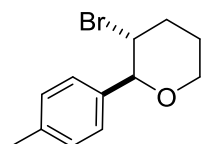
^1H NMR (CDCl_3 , 400 MHz): δ 7.35 (d, $J = 8.6$ Hz, 2H), 6.9 (d, $J = 8.7$ Hz, 1H), 4.92 (d, $J = 9.1$ Hz, 1H), 3.92-3.85 (m, 2H), 3.81 (s, 3H), 3.77 (d, $J = 9.1$ Hz, 1H), 1.26 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.6, 131.8, 127.4, 113.8, 85.6, 78.7, 65.3, 55.2, 42.7, 23.9, 23.7. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{18}\text{BrO}_2$ 285.0490, found 285.0492.

3-bromo-2-(4-methoxyphenyl)tetrahydro-2H-pyran (2t)



^1H NMR (CDCl_3 , 400 MHz): δ 7.31 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.28 (d, $J = 10$ Hz, 1H), 4.14-4.01 (m, 2H), 3.80 (s, 3H), 3.63 (td, $J = 12.0, 2.2$ Hz, 1H), 2.61-2.56 (m, 1H), 2.17-2.06 (m, 1H), 1.99-1.87 (m, 1H), 1.75-1.71 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.6, 132.0, 128.7, 113.6, 85.1, 68.7, 55.2, 52.7, 36.2, 28.4. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{16}\text{BrO}_2$ 271.0334, found 271.0330.

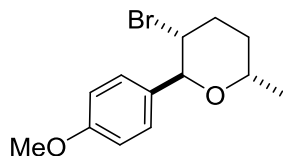
3-bromo-2-p-tolyltetrahydro-2H-pyran (2u)



^1H NMR (CDCl_3 , 400 MHz): δ 7.27 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 4.29 (d, $J = 10.0$ Hz, 1H), 4.14-4.03 (m, 2H), 3.63 (td, $J = 12.0, 2.2$ Hz, 1H), 2.61-2.55 (m, 1H), 2.35 (s, 3H), 2.12 (ddd, $J = 24.8, 13.0, 4.2$ Hz, 1H), 2.06-1.84 (m, 1H), 1.74 (dd,

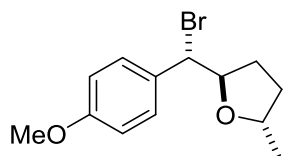
$J = 13.7, 2.3$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 138.2, 136.7, 129.0, 127.4, 85.4, 68.7, 52.5, 36.2, 28.4, 21.3. Data are consistent with literature values.^[9]

3-bromo-2-(4-methoxyphenyl)-6-methyltetrahydro-2H-pyran (2v)



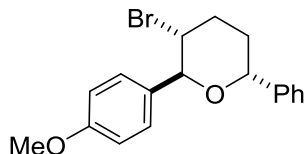
^1H NMR (CDCl_3 , 400 MHz): δ 7.30 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.73 (d, $J = 8.4$ Hz, 1H), 4.23 (ddd, $J = 14.3, 9.5, 5.1$ Hz, 2H), 3.80 (s, 3H), 2.31 (d, $J = 5.2$ Hz, 2H), 2.04-1.91 (m, 1H), 1.75-1.64 (m, 1H), 1.37 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.4, 132.0, 128.5, 113.8, 68.8, 55.3, 53.0, 30.9, 30.3, 17.4. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{18}\text{BrO}_2$ 285.0490, found 285.0492.

2-(bromo(4-methoxyphenyl)methyl)-5-methyltetrahydrofuran (3v)



^1H NMR (CDCl_3 , 400 MHz): δ 7.31 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 8.1$ Hz, 2H), 4.34 (d, $J = 10.0$ Hz, 1H), 4.07-3.91 (m, 1H), 3.80 (s, 3H), 3.72 (dd, $J = 10.6, 5.7$ Hz, 1H), 2.54 (d, $J = 13.4$ Hz, 1H), 2.15 (qd, $J = 13.0, 3.6$ Hz, 1H), 1.77 (d, $J = 13.3$ Hz, 1H), 1.58 (d, $J = 12.0$ Hz, 1H), 1.21 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.5, 132.2, 128.7, 113.6, 84.7, 74.6, 55.2, 53.0, 36.2, 35.5, 21.6. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{18}\text{BrO}_2$ 285.0490, found 285.0492.

3-bromo-2-(4-methoxyphenyl)-6-phenyltetrahydro-2H-pyran (2w)

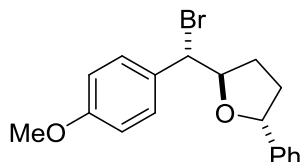


^1H NMR (CDCl_3 , 400 MHz): δ 7.51-7.38 (m, 4H), 7.33 (dd, $J = 8.4, 5.3$ Hz, 3H), 6.95-6.88 (m, 2H), 5.10 (s, 1H), 4.64 (d, $J = 8.2$ Hz, 1H), 4.42 (td, $J = 9.0, 4.1$ Hz, 1H), 3.82 (s, 3H), 2.44 (ddd, $J = 15.7, 10.1, 5.0$ Hz, 2H), 2.33-2.12 (m, 2H); ^{13}C

⁹ S. E. Denmark, M. T. Burk, *Org. Lett.*, 2012, 14, 256-259.

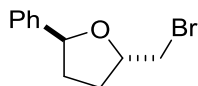
NMR (CDCl₃, 100 MHz): δ 159.5, 139.8, 131.6, 128.8, 128.5, 127.4, 126.6, 113.9, 77.8, 73.5, 55.3, 52.3, 30.9, 28.4. HRMS-ESI (m/z): [M+H]⁺ calculated for C₁₈H₂₀BrO₂ 347.0647, found 347.0648.

2-(bromo(4-methoxyphenyl)methyl)-5-phenyltetrahydrofuran (3w)



¹HNMR (CDCl₃, 400 MHz): δ 7.32 (ddd, J = 27.5, 18.9, 7.3 Hz, 8H), 6.89 (d, J = 8.7 Hz, 2H), 4.65 (dd, J = 11.2, 2.0 Hz, 1H), 4.53 (d, J = 10.0 Hz, 1H), 4.14- 4.02 (m, 1H), 3.80 (s, 3H), 2.66 (dd, J = 13.2, 3.7 Hz, 1H), 2.33 (ddd, J = 25.3, 13.1, 4.2 Hz, 1H), 2.14-2.00 (m, 1H), 1.90 (ddd, J = 25.0, 13.6, 3.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ ¹³C NMR (101 MHz, CDCl₃) δ 159.6, 141.8, 132.0, 128.83 (s), 128.3, 127.6, 125.8, 113.5, 85.1, 80.2, 55.2, 52.8, 36.6, 36.1. HRMS-ESI (m/z): [M+H]⁺ calculated for C₁₈H₂₀BrO₂ 347.0647, found 347.0648.

2-(bromomethyl)-5-phenyltetrahydrofuran (3x)



¹HNMR (CDCl₃, 400 MHz): δ 7.40-7.30 (m, 4H), 5.15-5.05 (m, 1H), 4.58-4.44 (m, 1H), 3.55 (dd, J = 10.1, 4.7 Hz, 1H), 3.46 (dd, J = 10.1, 6.8 Hz, 1H), 2.41 (dt, J = 11.3, 5.6 Hz, 1H), 2.31-2.14 (m, 1H), 2.02-1.76 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 142.7, 128.4, 127.4, 125.6, 81.54 (s), 78.7, 36.0, 35.2, 31.2. Data are consistent with literature values.^[10]

¹⁰ M. Greb, J. Hartung, F. Köhler, K. Spehar, R. Kluge, R. Csuk, *Eur. J. Org. Chem.* **2004**, 3799-3812.

6. ^1H and ^{13}C NMR spectra

