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# **Electronic Supplementary Information**

Additive-free Oxychlorination of Unsaturated C-C Bonds with *tert*-Butyl Hypochlorite and Water

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#### 1. General Information

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on a BRUKER AVANCE at 500 and 126 MHz, respectively. Chemical shifts ( $\delta$ ) were reported referenced to an internal tetramethylsilane (TMS) standard or the CDCl<sub>3</sub> residual peak ( $\delta$  7.26) for <sup>1</sup>H-NMR. Chemical shifts of <sup>13</sup>C-NMR were reported relative to CDCl<sub>3</sub> ( $\delta$  77.0). Data were reported in the following order: chemical shift ( $\delta$ ) in ppm; multiplicities were indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) were in Hz. MS were measured by Agilent 7890/7000D GC-MS (EI, 70 eV). Analytical thin-layer chromatography (TLC) was performed on silica gel and visualized with UV light. The purification of organic compounds was carried out by flash chromatography on silica gel (200–300 mesh). Unless otherwise stated, the substrates were prepared according to the literature methods and the products (except **b16**, **b22**, **d11**, **d13'**) were also known compounds and the characterization data were consistent with that of literature. Unless otherwise noted, other commercially available reagents and solvents with analytical grade were purchased from Macklin Inc. (P. R. China) and Energy Chemical (P. R. China) and used without further purification.

#### 2. Experimental Section

- **2.1 Typical experimental procedure for the reaction of alkynes**: alkyne (0.3 mmol) and a mixed solvent of acetone-water (v/v 9/1, 2 mL) were added into a clean glass tube (15 mL), followed by the addition of tBuOCl (4.0 equiv.). Then the mixture was continuously stirred at room temperature for desired time. The reaction was monitored by TLC under UV light. After completion, the reaction mixture was purified by chromatography column on silica gel with EtOAc/petroleum ether to get the desired products.
- **2.2 Typical experimental procedure for the reaction of alkenes**: alkene (0.3 mmol) and a mixed solvent of acetone-water (v/v 9/1, 2 mL) were added into a clean glass tube (15 mL), followed by the addition of tBuOCl (2.2 equiv.). Then the mixture was continuously stirred at room temperature for desired time. The reaction was monitored by TLC under UV light. After completion, the reaction mixture was purified by chromatography column on silica gel with EtOAc/petroleum ether to get the desired products.
- 2.3 Procedure for the <sup>18</sup>O-labelling experiments of alkyne: Follow the typical procedure described in section 2.1 except for the replacement of water by H<sub>2</sub><sup>18</sup>O. After completion, the reaction mixture was injected into GC-MS for MS analysis.
- 2.4 Procedure for the <sup>18</sup>O-labelling experiments of alkene: Follow the typical procedure described in section 2.2 except for the replacement of water by H<sub>2</sub><sup>18</sup>O. After completion, the reaction mixture was injected into GC-MS for MS analysis.

### 3. GC-MS spectra



Scheme S1. The GC-MS spectra of the (a) blank reaction and (b) <sup>18</sup>O-labelling experiments of ethynylbenzene a1.



Scheme S2. The GC-MS spectra of the (a) blank reaction and (b) <sup>18</sup>O-labelling experiments of styrene c1.

#### 4. Characterization data of products

2,2-dichloro-1-phenylethan-1-one  $(b1)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.12 – 8.06 (m, 2H), 7.69 – 7.63 (m, 1H), 7.56 – 7.49 (m, 2H), 6.69 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.90, 134.58, 131.33, 129.76, 128.94, 67.79.

2,2-dichloro-1-(4-methoxyphenyl)ethan-1-one  $(b2)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.11 – 8.04 (m, 2H), 7.02 – 6.95 (m, 2H), 6.65 (s, 1H), 3.90 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 184.60, 164.63, 132.26, 123.91, 114.21, 67.88, 55.66.

 $1-(4-(tert-butyl)phenyl)-2,2-dichloroethan-1-one (b3)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.56 – 7.50 (m, 2H), 6.68 (s, 1H), 1.35 (s, 9H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.53, 158.71, 129.77, 128.60, 125.95, 67.86, 35.37, 30.99.

2,2-dichloro-1-(p-tolyl)ethan-1-one  $(b4)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 2.43 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.56, 145.87, 129.84, 129.66, 128.76, 67.86, 21.85.

 $1-([1,1'-bipheny1]-4-y1)-2,2-dichloroethan-1-one (b5)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.20 – 8.11 (m, 2H), 7.75 – 7.70 (m, 2H), 7.65 – 7.60 (m, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H), 6.70 (s, 1H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.54, 147.28, 139.35, 130.41, 129.92, 129.10, 128.71, 127.50, 127.34, 67.92.

2,2-dichloro-1-(4-fluorophenyl)ethan-1-one  $(\mathbf{b6})^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.12 (m, 2H), 7.24 – 7.16 (m, 2H), 6.61 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)  $\delta$  183.51, 165.39 (C-F, <sup>1</sup>*J*<sub>C-F</sub> = 259.6 Hz), 131.70 (C-F, <sup>3</sup>*J*<sub>C-F</sub> = 10.1 Hz), 126.46 (C-F, <sup>3</sup>*J*<sub>C-F</sub> = 2.5 Hz), 115.21 (C-F, <sup>2</sup>*J*<sub>C-F</sub> = 21.4 Hz), 66.78.

2,2-dichloro-1-(4-chlorophenyl)ethan-1-one  $(b7)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.02 (m, 2H), 7.53 – 7.47 (m, 2H), 6.60 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 184.93, 141.24, 131.24, 129.47, 129.30, 67.78.

 $1-(4-bromophenyl)-2,2-dichloroethan-1-one (b8)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 2H), 7.71 – 7.65 (m, 2H), 6.59 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.15, 132.30, 131.26, 130.09, 129.88, 67.75.

methyl 4-(2,2-dichloroacetyl)benzoate (b9)<sup>1</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.20 – 8.13 (m, 4H), 6.68 (s, 1H), 3.97 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.47, 165.79, 135.06, 134.56, 129.95, 129.73, 67.80, 52.68.

2,2-dichloro-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**b10**)<sup>1</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 6.62 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.11, 135.62 (C-F,  ${}^{2}J_{C-F} = 32.8$  Hz), 133.98, 130.27, 125.92 (C-F,  ${}^{3}J_{C-F} = 3.8$  Hz), 123.38 (C-F,  ${}^{1}J_{C-F} = 273.4$  Hz), 67.79.

2,2-dichloro-1-(o-tolyl)ethan-1-one  $(b11)^1$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 – 7.28 (m, 2H), 6.66 (s, 1H), 2.53 (s, 3H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.41, 140.64, 132.84, 132.41, 132.36, 128.50, 125.76, 68.97, 21.27.

2,2-dichloro-1-(2-chlorophenyl)ethan-1-one  $(b12)^2$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.39 (td, *J* = 7.3, 1.8 Hz, 1H), 6.79 (s, 1H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.78, 134.35, 133.13, 131.33, 130.59, 130.58, 127.21, 69.32.

2,2-dichloro-1-(naphthalen-1-yl)ethan-1-one (**b13**)<sup>3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.51 (dd, *J* = 8.7, 1.0 Hz, 1H), 8.07 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.98 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.90 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.65 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.82 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.50, 134.46, 134.00, 131.01, 130.29, 128.80, 128.73, 128.25, 127.07, 125.39, 124.11, 69.19.

2,2-dichloro-1-(naphthalen-2-yl)ethan-1-one (**b14**)<sup>1</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.07 (dd, J = 8.7, 1.9 Hz, 1H), 7.98 (dd, J = 8.2, 1.1 Hz, 1H), 7.92 (d, J = 8.7 Hz, 1H), 7.88 (dd, J = 8.2, 1.1 Hz, 1H), 7.65 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.58 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 6.84 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.94, 136.09, 132.25, 131.98, 129.89, 129.53, 128.93, 128.59, 127.90, 127.27, 124.59, 67.90.

2,2-dichloro-1-(thiophen-2-yl)ethan-1-one (b15)<sup>4</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.80 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.21 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.48 (s, 1H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 179.78, 137.09, 136.37, 134.89, 128.57, 68.01.

2-(4,4-dichloro-3-oxobutyl)isoindoline-1,3-dione (b16)



White solid

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.88 (s, 1H), 4.05 (t, *J* = 7.1 Hz, 2H), 3.29 (t, *J* = 7.1 Hz, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 194.52, 167.90, 134.16, 131.92, 123.41, 69.60, 33.49, 33.07.

HRMS (ESI) m/z calcd for C12H9Cl2NO3Na [M+Na]<sup>+</sup> 307.9857, found 307.9853

1,2-bis(4-(tert-butyl)phenyl)-2,2-dichloroethan-1-one (**b17**)<sup>5</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.61 – 7.55 (m, 2H), 7.45 – 7.40 (m, 2H), 7.36 – 7.30 (m, 2H), 1.32 (s, 9H), 1.28 (s, 9H).
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 186.51, 157.12, 153.08, 136.70, 131.24, 129.04, 125.90, 125.79, 125.11, 90.23, 35.15, 34.77, 31.21, 30.98.

2,2-dichloro-1,2-diphenylethan-1-one (**b18**)<sup>3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 2H), 7.68 – 7.64 (m, 2H), 7.50 – 7.45 (m, 1H), 7.45 – 7.38 (m, 3H), 7.31 (t, *J* = 7.9 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 186.69, 139.54, 133.30, 131.71, 131.15, 129.87, 128.99, 128.13, 126.02, 89.91.

1,2-bis(4-bromophenyl)-2,2-dichloroethan-1-one (**b19**)<sup>6</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.68 (m, 2H), 7.58 – 7.54 (m, 2H), 7.51 – 7.47 (m, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.42, 138.30, 132.60, 132.24, 131.67, 130.05, 129.08, 127.85, 124.54, 88.59.

2,2-dichloro-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (**b20**)<sup>5</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.50, 142.39, 134.82 (C-F,  ${}^{2}J_{C-F} = 32.8$  Hz), 134.35, 132.22 (C-F,  ${}^{2}J_{C-F} = 32.8$  Hz), 131.36, 126.95, 126.12 (C-F,  ${}^{3}J_{C-F} = 3.8$  Hz), 125.38 (C-F,  ${}^{3}J_{C-F} = 3.8$  Hz), 123.42 (C-F,  ${}^{1}J_{C-F} = 273.4$  Hz), 123.24 (C-F,  ${}^{1}J_{C-F} = 273.4$  Hz), 87.83.

2,2-dichloro-1,2-di-o-tolylethan-1-one (**b21**)<sup>5</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 8.07 (m, 1H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 2H), 7.19 – 7.13 (m, 1H), 7.07 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.88 (ddd, *J* = 8.4, 6.5, 2.1 Hz, 1H), 2.57 (s, 3H), 2.28 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.37, 140.95, 137.31, 135.71, 132.43, 132.34, 132.10, 131.76, 130.07, 128.89, 126.88, 126.56, 124.62, 92.59, 21.68, 20.94.

2,2-dichloro-1,2-bis(2-chlorophenyl)ethan-1-one (b22)



Pale yellow solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.16 – 8.10 (m, 1H), 7.55 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.34 (ddd, *J* = 7.9, 5.5, 3.4 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.00 (td, *J* = 7.7, 1.2 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 185.46, 136.61, 134.95, 132.49, 132.34, 131.77, 131.71, 131.37, 131.14, 130.24, 129.04, 127.30, 125.23, 88.14.

2,2-dichloro-1-phenylpropan-1-one  $(b23)^2$ 

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.35 – 8.30 (m, 2H), 7.62 – 7.57 (m, 1H), 7.48 (t, J = 7.8 Hz, 2H), 2.36 (s, 3H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.11, 133.60, 131.30, 131.18, 128.12, 82.72, 34.29.

2,2-dichloro-1-phenylbutan-1-one  $(b24)^7$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 2.54 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.48, 133.39, 132.15, 130.94, 128.08, 88.43, 37.85, 9.23.

2,2-dichloro-1-phenylpentan-1-one (**b25**)<sup>8</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 2.52 – 2.43 (m, 2H), 1.79 – 1.68 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.50, 133.39, 132.11, 130.94, 128.08, 87.47, 46.44, 18.25, 13.69.

2,2-dichloro-1-phenylhexan-1-one (b26)<sup>9</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.30 – 8.24 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 – 7.43 (m, 2H), 2.54 – 2.47 (m, 2H), 1.73 – 1.64 (m, 2H), 1.44 (dt, J = 14.8, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 188.54, 133.36, 132.17, 130.92, 128.07,

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) & 188.54, 133.36, 132.17, 130.92, 128.07, 87.70, 44.25, 26.89, 22.34, 13.92.

2,2-dichloro-3-hydroxy-1-phenylpropan-1-one  $(b27)^7$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.32 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 4.27 (s, 2H), 2.97 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 189.21, 134.27, 131.17, 131.10, 128.30, 83.57, 70.63.

2-chloro-1-(p-tolyl)ethan-1-ol (d1)<sup>10</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 4.86 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.72 (dd, *J* = 11.2, 3.4 Hz, 1H), 3.63 (dd, *J* = 11.3, 8.7 Hz, 1H), 2.54 (d, *J* = 65.2 Hz, 1H), 2.35 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 138.28, 136.98, 129.35, 125.99, 73.96, 50.92, 21.18.

2-chloro-1-phenylethan-1-ol  $(d2)^{10}$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 5H), 4.90 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.74 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.64 (dd, *J* = 11.3, 8.8 Hz, 1H), 2.50 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 139.92, 128.68, 128.47, 126.06, 74.09, 50.92.

2-chloro-1-(4-fluorophenyl)ethan-1-ol (d3)<sup>11</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.37 (ddd, *J* = 8.5, 5.3, 2.5 Hz, 2H), 7.11 – 7.01 (m, 2H), 4.88 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.71 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.61 (dd, *J* = 11.3, 8.8 Hz, 1H), 2.70 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)  $\delta$  162.67 (C-F, <sup>1</sup>*J*<sub>C-F</sub> = 247.0 Hz), 135.70 (C-

F,  ${}^{3}J_{C-F} = 3.8 \text{ Hz}$ ), 127.81 (C-F,  ${}^{3}J_{C-F} = 7.6 \text{ Hz}$ ), 115.59 (C-F,  ${}^{2}J_{C-F} = 21.4 \text{ Hz}$ ), 73.43, 50.81.

2-chloro-1-(4-chlorophenyl)ethan-1-ol (d4)<sup>10</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 4H), 4.88 (dd, *J* = 8.7, 3.4 Hz, 1H), 3.71 (ddd, *J* = 11.3, 3.5, 1.0 Hz, 1H), 3.60 (ddd, *J* = 11.2, 8.6, 1.0 Hz, 1H), 2.71 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 138.35, 134.24, 128.85, 127.45, 73.37, 50.69.

methyl 4-(2-chloro-1-hydroxyethyl)benzoate (d5)<sup>11</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.05 – 8.00 (m, 2H), 7.48 – 7.43 (m, 2H), 4.95 (dd, J = 8.4, 3.5 Hz, 1H), 3.90 (s, 3H), 3.74 (dd, J = 11.3, 3.5 Hz, 1H), 3.63 (dd, J = 11.3, 8.4 Hz, 1H), 2.96 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 166.72, 144.90, 130.07, 129.85, 126.02, 73.53, 52.16, 50.44.

2-chloro-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (d6)<sup>11</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.63 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.96 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.75 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.63 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.91 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 143.79, 130.62 (C-F,  ${}^{2}J_{C-F} = 32.8$  Hz), 126.45, 125.60 (C-F,  ${}^{3}J_{C-F} = 3.8$  Hz), 123.97 (C-F,  ${}^{1}J_{C-F} = 272.2$  Hz), 73.38, 50.49.

2-chloro-1-(4-nitrophenyl)ethan-1-ol (d7)<sup>12</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.28 – 8.20 (m, 2H), 7.62 – 7.56 (m, 2H), 5.04 (dd, *J* = 8.2, 3.6 Hz, 1H), 3.79 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.64 (dd, *J* = 11.4, 8.2 Hz, 1H), 2.77 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 147.88, 146.93, 127.02, 123.84, 73.01, 50.30.

2-chloro-1-(o-tolyl)ethan-1-ol  $(\mathbf{d8})^{12}$ 



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.51 (dd, J = 7.3, 1.9 Hz, 1H), 7.23 (pd, J = 7.4, 1.7 Hz, 2H), 7.18 – 7.13 (m, 1H), 5.10 (dd, J = 9.2, 3.0 Hz, 1H), 3.69 (dd, J = 11.3, 3.1 Hz, 1H), 3.59 (dd, J = 11.3, 9.2 Hz, 1H), 2.65 (s, 1H), 2.35 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 137.94, 134.78, 130.62, 128.23, 126.49, 125.54, 70.98, 49.93, 19.06.

2-chloro-1-(naphthalen-2-yl)ethan-1-ol (d9)<sup>10</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.92 – 7.76 (m, 4H), 7.47 (ddd, *J* = 16.8, 8.0, 3.2 Hz, 3H), 5.05 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.81 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.72 (dd, *J* = 11.3, 8.8 Hz, 1H), 3.04 – 2.55 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)  $\delta$  137.30, 133.32, 133.22, 128.54, 128.07, 127.75, 126.43, 126.32, 125.30, 123.68, 74.21, 50.82.

2-chloro-1-(naphthalen-1-yl)ethan-1-ol (d10)<sup>13</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.00 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.73 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.58 – 7.45 (m, 3H), 5.67 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.94 (dd, *J* = 11.5, 2.8 Hz, 1H), 3.73 (dd, *J* = 11.5, 9.2 Hz, 1H), 2.87 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 135.32, 133.77, 130.18, 129.15, 128.93, 126.59, 125.79, 125.49, 123.70, 122.37, 71.32, 50.53.

(8R,9S,13S,14S)-3-(2-chloro-1-hydroxyethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16decahydro-17H-cyclopenta[a]phenanthren-17-one (**d11**)



White solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.30 (d, J = 8.0 Hz, 1H), 7.18 – 7.11 (m, 2H), 4.84 (dd, J = 8.8, 3.4 Hz, 1H), 3.74 (dd, J = 11.2, 3.4 Hz, 1H), 3.69 – 3.61 (m, 1H), 2.93 (dd, J = 9.1, 4.3 Hz, 2H), 2.51 (dd, J = 18.9, 8.8 Hz, 1H), 2.43 (dt, J = 12.9, 3.9 Hz, 1H), 2.30 (ddt, J = 17.2, 10.7, 4.8 Hz, 1H), 2.22 – 1.93 (m, 5H), 1.70 – 1.57 (m, 2H), 1.57 – 1.40 (m, 4H), 0.91 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 140.10, 137.41, 136.95, 126.64, 126.63, 125.69, 123.52, 123.49, 73.91, 73.84, 50.88, 50.52, 47.97, 44.39, 38.08, 35.85, 31.59, 29.45, 29.42, 26.44, 25.71, 21.59, 13.85.

HRMS (ESI) m/z calcd for C20H25ClO2Na [M+Na]<sup>+</sup> 355.1441, found 355.1425

2-chloro-1-(pyridin-3-yl)ethan-1-ol (d12)<sup>14</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.62 – 8.44 (m, 2H), 7.79 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.33 (dd, *J* = 7.9, 4.9 Hz, 1H), 4.96 (dd, *J* = 7.7, 4.2 Hz, 1H), 4.24 (s, 1H), 3.78 – 3.64 (m, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 149.08, 147.58, 136.42, 134.38, 123.72, 71.65, 50.12.

2-(3-chloro-2-hydroxypropyl)isoindoline-1,3-dione (d13)<sup>15</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.87 (dt, *J* = 7.1, 3.6 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.18 (dq, *J* = 7.3, 4.7 Hz, 1H), 4.00 – 3.85 (m, 2H), 3.72 – 3.58 (m, 2H), 2.86 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 168.67, 134.28, 131.84, 123.56, 69.74, 47.28, 41.60.

2-(2-chloro-3-hydroxypropyl)isoindoline-1,3-dione (d13')



White solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dt, *J* = 7.1, 3.6 Hz, 2H), 7.80 – 7.74 (m, 2H), 4.31 (p, *J* = 5.7 Hz, 1H), 4.18 – 4.03 (m, 2H), 3.78 (qd, *J* = 12.6, 5.2 Hz, 2H), 2.92 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 168.46, 134.44, 131.66, 123.70, 63.90, 58.83, 39.98.

HRMS (ESI) m/z calcd for C11H10ClNO3Na [M+Na]<sup>+</sup> 262.0247, found 262.0242

1-chloro-3-(phenylsulfonyl)propan-2-ol (d14)<sup>16</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 4.46 – 4.35 (m, 1H), 3.67 – 3.58 (m, 2H), 3.46 – 3.31 (m, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 139.01, 134.30, 129.56, 127.98, 66.22, 59.58, 47.54.

2-chloro-3-(phenylsulfonyl)propan-1-ol (d14')<sup>16</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.95 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 4.45 (dq, *J* = 12.0, 6.8, 5.9 Hz, 1H), 4.02 – 3.88 (m, 2H), 3.73 (dd, *J* = 14.6, 7.1 Hz, 1H), 3.54 (dd, *J* = 14.6, 5.8 Hz, 1H), 2.26 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)  $\delta$  139.11, 134.30, 129.53, 128.12, 65.66,

59.64, 54.87.

anti-2-chloro-1-phenylpropan-1-ol (d15)<sup>10</sup>

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H), 4.94 (d, *J* = 3.8 Hz, 1H), 4.31 (qd, *J* = 6.7, 3.8 Hz, 1H), 2.46 (s, 1H), 1.38 (dd, *J* = 6.7, 2.7 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 139.59, 128.38, 128.06, 126.39, 77.17, 62.79, 18.04.

The reaction of *trans*- $\beta$ -methyl styrene (inseparable on silicon chromatography)

*syn*-2-chloro-1-phenylpropan-1-ol (**d15'**)<sup>10</sup>

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.27 (m, 5H), 4.58 (d, *J* = 7.5 Hz, 1H), 4.25 – 4.17 (m, 1H), 2.54 (d, *J* = 259.5 Hz, 1H), 1.37 (ddd, *J* = 6.7, 3.6, 1.0 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 139.63, 139.61, 128.59, 126.88, 126.41, 79.12, 64.52, 21.55.

The reaction of cis- $\beta$ -methyl styrene (inseparable on silicon chromatography)

anti-2-chloro-1,2-diphenylethan-1-ol (d16)<sup>10</sup>

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 10H), 5.05 (dd, *J* = 34.8, 6.5 Hz, 2H), 2.48 – 2.20 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 139.49, 137.24, 128.73, 128.47, 128.38, 128.35, 128.19, 127.08, 78.20, 66.91.

*syn*-2-chloro-1,2-diphenylethan-1-ol (**d16'**)<sup>10</sup>

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.05 (m, 10H), 5.06 – 4.90 (m, 2H), 3.04 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 138.72, 137.70, 128.55, 128.32, 128.20, 128.14, 127.98, 126.97, 78.78, 70.68.

2,2-dichloro-1-(2-chlorophenyl)ethan-1-ol (**b12'**)<sup>2,3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.41 – 7.28 (m, 3H), 6.09 (d, *J* = 3.2 Hz, 1H), 5.50 (d, *J* = 3.3 Hz, 1H), 2.97 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 135.10, 132.19, 129.95, 129.46, 128.81, 127.11, 75.11, 74.97. 1-chloro-2-(2,2-dichloro-1-(4-chlorophenyl)ethyl)benzene (b12")<sup>2,3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.33 – 7.26 (m, 5H), 7.21 (td, *J* = 7.7, 1.7 Hz, 1H), 6.36 (d, *J* = 8.7 Hz, 1H), 5.18 (d, *J* = 8.6 Hz, 1H).
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 137.20, 136.76, 134.23, 133.64, 130.27,

130.25, 128.82, 128.80, 128.42, 127.13, 73.76, 57.22.

2,2-dichloro-1-(2-fluorophenyl)ethan-1-one (b28)<sup>2,3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.98 (td, J = 7.5, 1.8 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.32 (td, J = 7.6, 1.1 Hz, 1H), 7.20 (ddd, J = 11.3, 8.4, 1.1 Hz, 1H), 6.82 (d, J = 1.9 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 184.38, 184.35, 162.16, 160.13, 136.27, 136.20, 132.25, 132.23, 125.18, 125.15, 121.13, 121.04, 116.90, 116.71, 70.28, 70.19.

2,2-dichloro-1-(2-fluorophenyl)ethan-1-ol (b28')<sup>2,3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.56 (td, *J* = 7.5, 1.8 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (ddd, *J* = 10.6, 8.3, 1.2 Hz, 1H), 5.98 (dd, *J* = 4.5, 1.3 Hz, 1H), 5.33 (d, *J* = 4.5 Hz, 1H), 2.93 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 160.90, 158.94, 130.52, 130.45, 128.54,

128.51, 124.87, 124.77, 124.44, 124.41, 115.51, 115.33, 75.40, 75.38, 73.20, 73.19.

1-(2,2-dichloro-1-(4-chlorophenyl)ethyl)-2-fluorobenzene (**b28**")<sup>2,3</sup>



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.23 (m, 6H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (ddd, *J* = 10.6, 8.2, 1.2 Hz, 1H), 6.44 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 9.2 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 161.21, 159.25, 137.29, 133.67, 129.86, 129.85, 129.48, 129.42, 129.34, 129.31, 128.93, 127.06, 126.95, 124.51, 124.48, 116.20, 116.02, 73.45, 73.42, 56.57, 56.56.

2-(2-bromo-4-nitro-1H-imidazol-1-yl)-1-phenylethan-1-ol (d2')<sup>17</sup>



<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.51 (s, 1H), 7.41 – 7.35 (m, 4H), 7.35 – 7.28 (m, 1H), 5.90 (d, *J* = 4.5 Hz, 1H), 4.97 (dt, *J* = 8.4, 4.2 Hz, 1H), 4.26 – 4.08 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  146.41, 141.77, 128.82, 128.28, 126.38, 125.38, 121.73, 71.18, 55.71.

2-(2-methoxy-4-nitro-1H-imidazol-1-yl)-1-phenylethan-1-ol (d2")<sup>17</sup>



<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.05 (s, 1H), 7.40 – 7.24 (m, 6H), 5.80 (d, *J* = 4.5 Hz, 1H), 4.90 (dt, *J* = 7.3, 4.7 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.88 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  151.35, 142.23, 141.80, 128.64, 128.04, 126.38, 120.66, 71.01, 58.02, 52.07.

### 5. Characterization data of products



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2,2-dichloro-1-(4-methoxyphenyl)ethan-1-one (b2)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

1-(4-(tert-butyl)phenyl)-2,2-dichloroethan-1-one (b3)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2,2-dichloro-1-(p-tolyl)ethan-1-one (b4)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



### 1-([1,1'-biphenyl]-4-yl)-2,2-dichloroethan-1-one (**b5**)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2,2-dichloro-1-(4-fluorophenyl)ethan-1-one (b6)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

## 2,2-dichloro-1-(4-chlorophenyl)ethan-1-one (b7)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

## 1-(4-bromophenyl)-2,2-dichloroethan-1-one (b8)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

methyl 4-(2,2-dichloroacetyl)benzoate (b9)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2,2-dichloro-1-(4-(trifluoromethyl)phenyl)ethan-1-one (b10)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2,2-dichloro-1-(o-tolyl)ethan-1-one (b11)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)





<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)


### 2,2-dichloro-1-(naphthalen-1-yl)ethan-1-one (**b13**)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

### 2,2-dichloro-1-(naphthalen-2-yl)ethan-1-one (b14)





2,2-dichloro-1-(thiophen-2-yl)ethan-1-one (b15)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)





<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



### 1,2-bis(4-(tert-butyl)phenyl)-2,2-dichloroethan-1-one (b17)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



# 2,2-dichloro-1,2-diphenylethan-1-one (b18)







<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)





<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2,2-dichloro-1,2-di-o-tolylethan-1-one (**b21**)





### 2,2-dichloro-1,2-bis(2-chlorophenyl)ethan-1-one (**b22**)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2,2-dichloro-1-phenylpropan-1-one (**b23**)







<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2,2-dichloro-1-phenylpentan-1-one (b25)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



# 2,2-dichloro-1-phenylhexan-1-one (b26)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2,2-dichloro-3-hydroxy-1-phenylpropan-1-one (**b27**)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2-chloro-1-(p-tolyl)ethan-1-ol (d1)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

3.75 3.75 3.73 3.73 3.73 3.72 3.65 3.65 3.65 3.65 3.65 3.65 3.65 2.50 J || ſ 5.00H 1.02 0.95H 1.00 1.97<sup>2</sup> 5.0 4.5 f1 (ppm) 7.5 4.0 3.5 3.0 2.5 2.0 9.5 9.0 8.5 8.0 7.0 6.5 6.0 5.5 1.5 1.0

- 16000 - 15000 - 14000 - 13000 - 12000

-1000





<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2-chloro-1-(4-fluorophenyl)ethan-1-ol (d3)





2-chloro-1-(4-chlorophenyl)ethan-1-ol (d4)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



methyl 4-(2-chloro-1-hydroxyethyl)benzoate (d5)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2-chloro-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (d6)







2-chloro-1-(4-nitrophenyl)ethan-1-ol (**d7**)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

2-chloro-1-(o-tolyl)ethan-1-ol (d8)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2-chloro-1-(naphthalen-2-yl)ethan-1-ol (**d9**)





2-chloro-1-(naphthalen-1-yl)ethan-1-ol (d10)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



(8R,9S,13S,14S)-3-(2-chloro-1-hydroxyethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16decahydro-17H-cyclopenta[a]phenanthren-17-one (**d11**)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



# 2-(3-chloro-2-hydroxypropyl)isoindoline-1,3-dione (d13)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



# 2-(2-chloro-3-hydroxypropyl)isoindoline-1,3-dione (d13')

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



# 1-chloro-3-(phenylsulfonyl)propan-2-ol (d14)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2-chloro-3-(phenylsulfonyl)propan-1-ol (d14')



anti-2-chloro-1-phenylpropan-1-ol (d15)

The reaction of *trans*-β-methyl styrene (inseparable on silicon chromatography)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)

The reaction of *cis*-β-methyl styrene (inseparable on silicon chromatography) - 11000 1.38 1.37 1.37 1.37 1.37 1.37 1.36 1.36 민 10000 9000 8000 1 1 11 7000 6000 5000 4000 3000 2000 1000 5.16 J 3.00H 0.31 ⊾ 0.62 € 0.32 € 0.64 ₹ 0.90--1000 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 f1 (ppm) 1.5 1.0 0.5 10.5 10.0 7.5 2.0 9.0 8.5 8.0 7.0 6.5 0.0 9.5 <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) 79.12 77.31 CDC13 77.17 77.16 77.06 CDC15 76.81 CDC13 64.52 64.52 - 2400 2300 139.63 139.61 128.59 128.53 128.38 128.38 128.05 128.88 126.88 126.41 ~ 21.55 ~ 18.08 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 100 300 200 100 -100 -200 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 f1 (ppm) 20 10 0 -10 60 50 40 30

syn-2-chloro-1-phenylpropan-1-ol (d15')

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



### anti-2-chloro-1,2-diphenylethan-1-ol (d16)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)





<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



2,2-dichloro-1-(2-chlorophenyl)ethan-1-ol (b12')




<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)



<sup>13</sup>C NMR (126 MHz, Chloroform-d)



<sup>13</sup>C NMR (126 MHz, Chloroform-d)



<sup>13</sup>C NMR (126 MHz, Chloroform-d)



2-(2-bromo-4-nitro-1H-imidazol-1-yl)-1-phenylethan-1-ol (**d2**')

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)



2-(2-methoxy-4-nitro-1H-imidazol-1-yl)-1-phenylethan-1-ol (d2")

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)

## 6. References

- X. Zhang, Y. Wu, Y. Zhang, H. Liu, Z. Xie, S. Fu, F. Liu, *Tetrahedron* 2017, 73, 4513–4518.
- 2) Y. Li, T. Mou, L. Lu, X. Jiang, Chem. Commun. 2019, 55, 14299–14302.
- 3) V. P. Charpe, M. Gupta, K. C. Hwang, ChemSusChem 2022, 15, e202200957.
- Z. Zhang, J. Yang, K. Wu, R. Yu, J. Bu, Z. Huang, S. Li, X. Ma, *Tetrahedron Lett.* 2022, 88, 153575.
- 5) E. Cho, M. Kim, A. Jayaraman, J. Kim, S. Lee, Eur. J. Org. Chem. 2018, 781-784.
- G. Choi, H. E. Kim, S. Hwang, H. Jang, W.-J. Chung, Org. Lett. 2020, 22, 4190– 4195.
- N. Chaisan, S. Ruengsangtongkul, C. Thongsornkleeb, J. Tummatorn, S. Ruchirawat, *Synlett* 2022, *33*, 1426–1430.
- Z. Li, Q. Sun, P. Qian, K. Hu, Z. Zha, Z. Wang, Chin. Chem. Lett. 2020, 31, 1855– 1858.
- 9) G. A. Hiegel, C. D. Bayne, B. Ridley, Synth. Commun. 2003, 33, 1997–2002.
- 10) P. Swamy, M. A. Kumar, M. M. Reddy, M. Naresh, K. Srujana, N. Narender, RSC Adv. 2014, 4, 26288–26294.
- 11) C. Yin, W. Wu, Y. Hu, X. Tan, C. You, Y. Liu, Z. Chen, X.-Q. Dong, X. Zhang, Adv. Synth. Catal. 2018, 360, 2119–2124.
- 12) T. von Keutz, D. Cantillo, C. O. Kappe, Org. Lett. 2020, 22, 7537–7541.
- 13) C. K. Blasius, V. Vasilenko, L. H. Gade, Angew. Chem. Int. Ed. 2018, 57, 10231– 10235.
- 14) M. G. Perrone, E. Santandrea, E. Giorgio, L. Bleve, A. Scilimati, P. Tortorella, *Bioorg. Med. Chem.* 2006, 14, 1207–1214.
- 15) L. Ielo, M. Miele, V. Pillari, R. Senatore, S. Mirabile, R. Gitto, W. Holzer, A. R. Alcántara, V. Pace, Org. Biomol. Chem. 2021,19, 2038–2043.
- 16) J. Muzart, A, Riahi, J. Organomet. Chem. 1992, 433, 323-336.
- 17) S.-H. Lee, S. Kim, M.-H. Yun, Y. S. Lee, S.-N. Cho, T. Oh, P. Kim, *Bioorg. Med. Chem. Lett.* 2011, 21, 1515-1518.