Supporting Information

Table of Contents

1. General Information  ........................................................................................................ S2

2. Preparation of TFBen  ..................................................................................................... S2

3. Procedure for the Synthesis of Propargyl Alcohols  ................................................. S2

4. Characterization of TFBen and Substrates  ............................................................... S3

5. General Procedure for Reaction of Propargyl Alcohols with TFBen  .... S12

6. Characterization of Products  ....................................................................................... S13

7. References  ................................................................................................................... S24

8. Spectra of TFBen and Substrates  ............................................................................... S25

9. Spectra of Products  ...................................................................................................... S50
1. General Information

Unless otherwise noted, all reactions were performed under nitrogen protection unless otherwise noted. All reagents were obtained from commercial sources and used as received without further purification. Column chromatography was performed on silica gel (200–300 mesh) using petroleum ether (bp 60–90 °C) and ethyl acetate as eluent. Reactions were followed with TLC (0.25 mm silica gel 20 cm×20 cm). Visualization was accomplished with UV light.\textsuperscript{1}H and \textsuperscript{13}C NMR spectra were taken on 400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl\textsubscript{3} as solvent.

2. Preparation of TFBen

\[
\begin{align*}
\text{HO} & \quad \text{NaOAc (0.5 equiv)} \\
\text{NaOAc (0.5 equiv)} & \quad \text{HCOOH (5.0 equiv), Ac}_2\text{O (4.0 equiv)} \\
r.t. & \quad 4 \text{ h}
\end{align*}
\]

Formic acid (8.4 mL, 222.8 mmol, 5.0 equiv.) was added to acetic anhydride (16.8 mL, 178.2 mmol, 4.0 equiv.) at rt. The mixture was stirred at 60 °C for 1 h and cooled to rt. The resulting solution was poured into a flask containing 1,3,5-trihydroxybenzene (5.62 g, 44.6 mmol, 1.0 equiv.) and NaOAc (1.83 g, 22.3 mmol, 0.5 equiv.). The mixture was stirred for 4 h in a water bath and then diluted with toluene (100 mL), washed with H\textsubscript{2}O (50 mL) twice. Keep the organic phase in fridge (2-8 °C) overnight. Then filtered and dried in vacuo to afford the desired product benzene-1,3,5-triyl triformate (TFBen) (5.1 g, 55%) as a white solid.

3. Procedure for the Synthesis of Propargyl Alcohols\textsuperscript{1}

\[
\begin{align*}
\text{R}^1-\equiv & \rightarrow \quad \text{O} \\
\text{NaH (1 equiv), 0 °C} & \quad \text{DMF, r.t.}
\end{align*}
\]

To a 50 mL round-bottom flask was added an alkyne (7 mmol, 1 equiv.) in DMF (5 mL). The mixture was cooled to 0 °C and stirred for 10 min. Then sodium hydride (7 mmol, 1 equiv.) was added and the reaction continued at 0 °C for 4-6 h. A ketone
(1.2 equiv.) was added and the system was warmed to room temperature for 10 h. After the reaction was completed, the reaction mixture was diluted with saturated sodium bicarbonate solution (60 mL) and extracted with ethyl acetate (40 mL) three times. The combined organic phases were dried with anhydrous Na₂SO₄, concentrated and purified by silica gel column chromatography to obtain the desired propargyl alcohol. (1a, 1b, 1c, 1d, 1f, 1g, 1h, 1i, 1o, 1q, 1r, 1s, 1t, 1u, 1v, 1w)

\[
\begin{array}{ccc}
R_1 & + & R_2 \text{OH} \\
\text{Pd(PPh₃)₄}, \text{CuI, } \text{Et₂NH, DMF, 130°C, 1h} & \rightarrow & R_1 \text{OH}
\end{array}
\]

R₁, R₂, R₃ = alkyl, aryl

An oven-dried 35 mL Schlenk tube equipped with a magnetic stirring bar and a rubber septum was charged with Pd(PPh₃)₄ (57.5 mg, 5 mol%), CuI (19 mg, 1 mol%). After purging the vessel with alternating vacuum and nitrogen cycles, degassed DMF (5 mL), aryl iodides (3 mmol, 1 equiv.), Et₂NH (412 μL, 4.5 mmol, 4 equiv.) and an alkyne (3.6 mmol, 1.2 equiv.) were added and the mixture was stirred at 130 °C for 1 h. After cooling to room temperature, the mixture was diluted with water (20 mL) and extracted with EtOAc (20 mL). Combined organic extracts were washed with H₂O (20 mL), saturated aqueous NaCl (20 mL), dried over MgSO₄ and concentrated in vacuum. The crude product was purified by silica gel chromatography affording the corresponding product. (1j, 1k, 1l, 1m, 1n)

4. Characterization of TFBen and Substrates

\[\text{Benzene-1,3,5-triyl triformate, TFBen}^2\]

White solid, mp. 53.2-55.6 °C.

\(^1\)H NMR (400 MHz, CDCl₃): δ = 8.24 (s, 3H), 6.97 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl₃): δ = 158.06, 150.30, 112.62.
2-Methyl-4-phenyl-3-butyn-2-ol, 1a
Yellow solid, mp. 49-51 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.41 - 7.43$ (m, 2 H), 7.29 - 7.31 (m, 3 H), 2.33 (s, br, 1 H), 1.62 (s, 6 H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 131.6, 128.2, 128.2, 122.7, 93.8, 82.1, 65.6, 31.4$.

2-Methyl-4-((p-tolyl)but-3-yn-2-ol, 1b
Yellow soild, mp. 49-51 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31$ (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 7.9$ Hz, 2H), 2.57 (s, 1H), 2.34 (s, 3H), 1.61 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 138.2, 131.4, 128.9, 119.6, 93.1, 82.1, 65.5, 31.4, 21.3$.

3-Methyl-4-((o-tolyl)but-3-yn-2-ol, 1c
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.39$ (d, $J = 7.5$ Hz, 1H), 7.23 - 7.17 (m, 2H), 7.12 (t, 1H), 2.41 (s, 3H), 1.63 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 140.1, 131.8, 129.3, 128.2, 125.4, 122.4, 97.9, 81.0, 65.7, 31.6, 20.5$.

2-Methyl-4-((3-methylphenyl)-3-butyn-2-ol, 1d
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.09 - 7.24$ (m, 4 H), 2.32 (s, 3 H), 2.26 (s, br, 1 H), 1.62 (s, 6 H).
$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 137.9, 132.2, 129.1, 128.6, 128.1, 122.5, 93.4, 82.2, 65.5, 31.5, 21.1.$

2-Methyl-4-(4-propylphenyl)but-3-yn-2-ol, 1e
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.32$ (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 2.56 (t, $J = 7.6$ Hz, 2H), 2.21 (s, 1H), 1.64 - 1.58 (m, 8H), 0.91 (t, $J = 7.3$ Hz, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 143.0, 131.5, 128.4, 119.8, 93.1, 82.2, 65.6, 37.8, 31.5, 24.3, 13.7.$

3-(4-(tert-Butyl)phenyl)-2-methylbut-3-yn-2-ol, 1f
White solid, mp. 89-91 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.33$ (q, $J = 8.5$ Hz, 4H), 1.61 (s, 6H), 1.30 (s, 9H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 151.5, 131.5, 125.2, 119.7, 93.1, 82.2, 65.6, 34.7, 31.5, 31.1.$

4-(4-Methoxyphenyl)-2-methylbut-3-yn-2-ol, 1g
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.35 - 7.33$ (m, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 3.78 (s, 3H), 2.51 (s, 1H), 1.60 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 159.4, 133.0, 114.8, 113.8, 92.4, 81.9, 65.5, 55.2, 31.5.$
4-(4-Fluorophenyl)-2-methylbut-3-yn-2-ol, 1h
Yellow oil

$\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.38 \text{ (dd, } J = 8.7, 5.4 \text{ Hz, } 2 \text{H}), 6.98 \text{ (t, } J = 8.7 \text{ Hz, } 2 \text{H}), 2.37 \text{ (s, } 1 \text{H}), 1.61 \text{ (s, } 6 \text{H}).$

$\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 162.4, 133.5, 118.8, 115.4, 93.5, 81.0, 65.5, 31.4.$

4-(4-Chlorophenyl)-2-methylbut-3-yn-2-ol, 1i
Yellow oil

$\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.33 \text{ (d, } J = 8.5 \text{ Hz, } 2 \text{H}), 7.26 \text{ (d, } J = 8.6 \text{ Hz, } 2 \text{H}), 2.31 \text{ (s, } 1 \text{H}), 1.61 \text{ (s, } 6 \text{H}).$

$\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 134.2, 132.8, 128.5, 121.2, 94.7, 81.0, 65.6, 31.4.$

2-Methyl-4-(4'-cyanophenyl)-3-butyn-2-ol, 1j
Yellow solid, mp 65-67 °C.

$\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.57 \text{ (d, } J = 8.7 \text{ Hz, } 2 \text{H}), 7.46 \text{ (d, } J = 8.7 \text{ Hz, } 2 \text{H}), 2.39 \text{ (s, } 1 \text{H}), 1.61 \text{ (s, } 6 \text{H}).$

$\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 132.1, 131.9, 127.7, 118.3, 111.5, 98.2, 80.5, 65.5, 31.2.$

Methyl 4-(3-hydroxy-3-methylbut-1-ynyl)benzoate, 1k
Yellow solid, mp. 75-77 °C

$\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.95 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{H}), 7.44 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{H}), 3.90 \text{ (s, } 3 \text{H}), 2.36 \text{ (s, } 1 \text{H}), 1.62 \text{ (s, } 6 \text{H}).$
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.51$ (d, $J = 7.9$ Hz, 2H), 7.46 (d, $J = 7.9$ Hz, 2H), 7.40 (d, $J = 7.9$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 8.2$ Hz, 3H), 1.99 (br, 1H), 1.56 (s, 6H).

$^1$C NMR (100 MHz, CDCl$_3$): $\delta =$ 141.0, 140.3, 132.0, 128.8, 127.6, 127.0, 126.9, 121.6, 94.4, 82.0, 65.7, 31.5.

2-Methyl-4-(naphthalen-1-yl)-3-butyn-2-ol, 1m

Yellow oil

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.30$ (d, $J = 8.1$ Hz, 1 H), 7.83 (t, $J = 8.4$ Hz, 2 H), 7.66 (dd, $J = 7.2$, 1.1 Hz, 1 H), 7.49 – 7.60 (m, 2 H), 7.41 (m, 1 H), 2.27 (s, br, 1 H), 1.74 (s, 6 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 133.2, 133.1, 130.3, 128.7, 128.2, 126.7, 126.3, 126.0, 125.1, 120.3, 98.8, 80.2. 65.9, 31.6.

4-(Furan-3-yl)-2-methylbut-3-yn-2-ol, 1n

Yellow oil

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.62$ (s, 1H), 7.39 (d, $J = 1.7$ Hz, 1H), 6.46 (d, $J = 1.2$ Hz, 2H), 2.26 (s, 2H), 1.63 (s, 13H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 145.6, 142.8, 112.5, 107.0, 95.6, 73.4, 65.6, 31.4.

HRMS (ESI): [M+H$^+$]calcd for C$_9$H$_{11}$O$_2^+$, 151.0754; found, 151.0755.
2-Methyl-4-(thiophen-3-yl)but-3-yn-2-ol, 1o
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.42 - 7.41$ (m, 1H), 7.25 - 7.24 (m, 1H), 7.09 - 7.08 (m, 1H), 1.61 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 129.8, 128.5, 125.2, 121.6, 93.4, 77.2, 65.5, 31.4$.

4-(2,5-Dimethoxyphenyl)-2-methylbut-3-yn-2-ol, 1p
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.85$ (d, $J = 3.0$ Hz, 1H), 6.74 (dd, $J = 9.0, 3.0$ Hz, 1H), 6.69 (d, $J = 9.0$ Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.63 (s, 1H), 1.57 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 154.4, 153.2, 118.2, 115.7, 112.5, 112.2, 98.1, 78.3, 65.6, 56.5, 55.8, 31.5$.

4-Methyl-1-phenylpent-1-yn-3-ol, 1q
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$ (d, $J = 6.6$, 3.0 Hz, 2H), 7.26 - 7.25 (m, 3H), 2.86 (s, 1H), 1.85 - 1.71 (m, 2H), 1.56 (s, 3H), 1.09 (t, $J = 7.5$ Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 131.5, 128.1, 128.0, 122.7, 92.7, 83.2, 68.9, 36.5, 29.1, 9.0$.

4-Methyl-1-phenylhex-1-yn-3-ol, 1r
Yellow oil
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$ (d, $J = 5.0$, 2.2 Hz, 2H), 7.29 - 7.27 (m, 3H),
2.40 (s, 1H), 1.76 – 1.70 (m, 2H), 1.62 – 1.57 (m, 5H), 0.98 (t, J = 7.2 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl₃): δ = 131.6, 128.1, 128.1, 122.7, 92.9, 83.2, 68.5, 45.9, 29.7, 18.1, 14.2.

4-Methyl-1-phenylept-1-yn-3-ol, 1s
Yellow oil
$^1$H NMR (400 MHz, CDCl₃): δ = 7.41 (dd, J = 6.6, 3.0 Hz, 2H), 7.28 (dd, J = 6.4, 3.6 Hz, 3H), 2.52 (s, 1H), 1.861 – 1.69 (m, 2H), 1.60 – 1.48 (m, 5H), 1.42 – 1.33 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl₃): δ = 131.5, 128.1, 128.1, 122.7, 93.0, 83.1, 68.5, 43.4, 29.7, 26.9, 22.7, 14.0.

3-Ethyl-1-phenylpent-1-yn-3-ol, 1t
Yellow oil
$^1$H NMR (400 MHz, CDCl₃): δ = 7.42 (dd, J = 6.5, 2.9 Hz, 2H), 7.29 – 7.27 (m, 3H), 2.26 (s, 1H), 1.83 – 1.69 (m, 4H), 1.10 (t, J = 7.4 Hz, 6H).
$^{13}$C NMR (100 MHz, CDCl₃): δ = 131.6, 128.2, 128.1, 122.8, 91.6, 84.4, 72.5, 34.4, 8.6.

1-(Phenylethynyl)cyclopentan-1-ol, 1u
Yellow oil
$^1$H NMR (400 MHz, CDCl₃): δ = 7.43 – 7.39 (m, 2H), 7.29 – 7.25 (m, 3H), 2.23 (s, 1H), 2.08 – 2.03 (m, 4H), 1.90 - 1.73 (dddd, J = 15.2, 12.2, 11.4, 7.5 Hz, 4H).
$^{13}$C NMR (100 MHz, CDCl₃): δ = 131.5, 128.2, 128.1, 122.8, 92.9, 83.0, 74.8, 42.4, 23.4.
1-(Phenylethynyl)cyclohexan-1-ol, 1v
White solid, mp. 65-67 °C.
\[\text{H NMR (400 MHz, CDCl}_3\]: } \delta = 7.43 - 7.41 \text{ (m, 2H)}, 7.29 \text{ (dd, } J = 6.5, 3.6 \text{ Hz, 3H)}, 2.38 \text{ (s, 1H)}, 2.03 - 1.99 \text{ (m, 2H)}, 1.74 - 1.54 \text{ (m, 7H)}, 1.29 - 1.26 \text{ (m, 1H}).
\[\text{C NMR (100 MHz, CDCl}_3\]: } \delta = 131.6, 128.1, 128.1, 122.8, 92.8, 84.2, 69.0, 39.9, 25.1, 23.3.

1-(Phenylethynyl)cycloheptan-1-ol, 1w
White solid, mp. 79-81 °C.
\[\text{H NMR (400 MHz, CDCl}_3\]: } \delta = 7.43 \text{ (dd, } J = 6.6, 3.0 \text{ Hz, 2H)}, 7.30 - 7.28 \text{ (m, 3H)}, 2.12 \text{ (dd, } J = 13.9, 7.4 \text{ Hz, 3H)}, 1.95 - 1.88 \text{ (m, 2H)}, 1.62 \text{ (dd, } J = 11.5, 7.7 \text{ Hz, 7H}).
\[\text{C NMR (100 MHz, CDCl}_3\]: } \delta = 131.6, 128.2, 128.1, 122.9, 93.8, 83.5, 72.2, 43.1, 27.9, 22.3.

2,4-diphenylbut-3-yn-2-ol, 1x
Yellow oil
\[\text{H NMR (400 MHz, CDCl}_3\]: } \delta = 7.74-7.72 \text{ (m, 2H)}, 7.90-7.80 \text{ (m, 2H)}, 7.47-7.46 \text{ (m, 2H)}, 7.40-7.24 \text{ (m, 4H)}, 2.53 \text{ (s, 1H)}, 1.87 \text{ (s, 3H}).
\[\text{C NMR (100 MHz, CDCl}_3\]: } \delta = 145.7, 131.7, 128.5, 128.4, 128.3, 127.7, 125.0, 122.6, 92.5, 84.9, 70.4, 33.3.
5. General Procedure for Reaction of Propargyl Alcohols with TFBen

\[
\begin{align*}
\text{R}_1 \text{H} & \quad + \quad \text{TFBen} \\
\text{Et}_3\text{N}, \text{Pd(OAc)}_2, \text{DPPF} & \rightarrow \\
\text{CH}_2\text{Cl}_2, 90^\circ\text{C}, 24\text{h} \\
\end{align*}
\]

\( \text{R}_1, \text{R}_2, \text{R}_3 = \text{alkyl, aryl} \)

Pd(OAc)\(_2\) (5.6 mg, 5 mol%), DPPF (55.4 mg, 20 mol%), TFBen (315 mg, 1.5 mmol, 3.0 equiv.), and a propargyl alcohol (80 mg, 0.5 mmol, 1.0 equiv.) were transferred into an 15 mL tube which was filled with nitrogen. Et\(_3\)N (70 uL, 0.5 mmol, 1.0 equiv.) and DCM (2 mL) were added to the reaction tube. Additionally, in order to increase the yield of 2k, 2p, 2y, it is necessary to add AgOAc (25 mg, 30 mol%). Then the vial was sealed with a screw-top septum cap quickly and placed in a heating block that was preheated to 90°C. After a time period of 24 h, the reaction vial was allowed cooled to room temperature. The reaction mixture was filtered and washed with EtOAc and then concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

6. Characterization of Products

\[\text{O} \quad \text{O} \]

\[\text{2a} \]

\text{5,5-Dimethyl-3-phenylfuran-2(5H)-one}\text{\textsuperscript{3a}}

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (67.7 mg, 72%). mp. 67-69 °C

\(^1\text{H} \text{NMR (400 MHz, CDCl}_3\):} \ \delta = 7.88-7.82 (m, 2H), 7.52 (s, 1H), 7.42-7.35 (m, 3H), 1.54 (s, 6H);

\(^1\text{C} \text{NMR (100 MHz, CDCl}_3\):} \ \delta = 171.2, 153.1, 129.9, 129.6, 129.2, 128.6, 127.1, 83.4, 25.7.
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (75.7 mg, 75%).

**mp. 68-70 °C**

**$^1$H NMR (400 MHz, CDCl$_3$):** δ = 7.75 (d, $J = 8.0$ Hz, 2H), 7.45 (s, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 2.37 (s, 3H), 1.54 (s, 6H);

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ = 170.8, 151.6, 138.8, 129.4, 128.8, 126.5, 126.3, 82.9, 25.3, 20.9.

---

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (56.5 mg, 56%).

**mp. 90-92 °C**

**$^1$H NMR (400 MHz, CDCl$_3$):** δ = 7.36 (d, $J = 7.6$ Hz, 1H), 7.29 (s, 1H), 7.29-7.19 (m, 3H), 2.33 (s, 3H), 1.58 (s, 6H)

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ = 171.0, 151.6, 138.8, 129.4, 129.0, 128.4, 125.4, 83.5, 25.4, 19.9.

---

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow oil (60.6mg, 60%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ = 7.67 (s, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.49 (s, 1H), 7.29 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.19 (d, $J = 7.6$ Hz, 1H), 2.38 (s, 3H), 1.54 (s, 6H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ = 171.1, 152.9, 138.3, 130.1, 130.0, 129.5, 128.5, 127.7, 124.2, 83.4, 25.8, 21.5.
5,5-Dimethyl-3-(4-propylphenyl)furan-2(5H)-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (83.9 mg, 73%). mp. 60-62 °C

^1^H NMR (400 MHz, CDCl₃): δ = 7.77 (d, J = 8.0 Hz, 1H), 7.47 (s, 1H), 7.21 (d, J = 7.9 Hz, 1H), 2.60 (t, J = 7.5 Hz, 1H), 1.64 (dd, J = 14.9, 7.4 Hz, 1H), 0.93 (t, J = 7.3 Hz, 2H).

^1^C NMR (100 MHz, CDCl₃): δ = 171.3, 152.2, 144.1, 129.9, 128.74, 127.0, 83.4, 37.8, 25.8, 24.4, 13.8.


3-(4-(tert-Butyl)phenyl)-5,5-dimethylfuran-2(5H)-one^3a
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (84.0 mg, 75%). mp. 91-93 °C

^1^H NMR (400 MHz, CDCl₃): δ = 7.81-7.76 (m, 2H), 7.47 (s, 1H), 7.45-7.40 (m, 2H), 1.54 (s, 6H), 1.33 (s, 9H)

^1^C NMR (100 MHz, CDCl₃): δ = 170.8, 152.0, 151.8, 129.4, 126.4, 126.3, 125.1, 82.9, 34.2, 30.7, 25.3.

3-(4-Methoxyphenyl)-5,5-dimethylfuran-2(5H)-one^3a
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow solid (85.0 mg, 78%). mp. 57-59 °C

^1^H NMR (400 MHz, CDCl₃): δ = 7.84-7.80 (m, 2H), 7.38 (s, 1H), 6.94-6.90 (m, 2H), 3.83 (s, 3H), 1.54 (s, 6H).

^1^C NMR (100 MHz, CDCl₃): δ = 171.0, 159.8, 150.3, 128.9, 128.0, 121.7, 113.5, 82.8, 54.8, 25.4.

S13
3-(4-Fluorophenyl)-5,5-dimethylfuran-2(5H)-one<sup>3a</sup>

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 5:1) to give the product as a **white solid** (58.7mg, 57%). mp. 82-84 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.89-7.82 (m, 2H), 7.47 (s, 1H), 7.13-7.05 (m, 2H), 1.55 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 170.5, 162.7 (d, <i>J</i><sub>C-F</sub> = 248 Hz), 152.0 (d, <i>J</i><sub>C-F</sub> = 1.6 Hz), 128.6 (d, <i>J</i><sub>C-F</sub> = 8.2 Hz), 128.5, 125.2 (d, <i>J</i><sub>C-F</sub> = 3.4 Hz), 115.2 (d, <i>J</i><sub>C-F</sub> = 21.5 Hz), 83.0, 25.3.

---

3-(4-Chlorophenyl)-5,5-dimethylfuran-2(5H)-one<sup>3a</sup>

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 5:1) to give the product as a **white solid** (66.6mg, 60%). mp. 89-91 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.82-7.79 (m, 2H), 7.52 (s, 1H), 7.39-7.36 (m, 2H), 1.56 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 170.4, 162.7, 152.7, 134.8, 128.5, 128.4, 127.9, 127.5, 83.1, 25.2.

---

4-(5,5-Dimethyl-2-oxo-2,5-dihydrofuran-3-yl)benzonitrile

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 2:1) to give the product as a **white solid** (66.0mg, 62%). mp. 165-167 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.04 (d, <i>J</i> = 1.6 Hz, 1H), 8.02 (d, <i>J</i> = 1.9 Hz, 2H), 7.75 (d, <i>J</i> = 1.7 Hz, 1H), 7.73 (d, <i>J</i> = 1.8 Hz, 1H), 7.71 (s, 1H), 1.62 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 173.5, 158.9, 137.2, 135.7, 134.7, 132.0, 131.0, 121.7, 116.1, 87.2, 28.9.

HRMS (ESI): [M+H]<sup>+</sup>calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub><sup>+</sup>, 214.0863; found, 214.0849.
Methyl 4-(5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)benzoate
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 2:1) to give the product as a white solid (98.4mg, 80%). mp. 135-137 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.02 (d, $J = 7.9$ Hz, 2H), 7.90 (d, $J = 8.2$ Hz, 2H), 7.63 (s, 1H), 3.89 (s, 3H), 1.53 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.6, 166.5, 154.9, 133.9, 130.5, 129.8, 129.2, 127.0, 83.7, 52.2, 25.6.
HRMS (ESI): [M+H$^+$]calcd for C$_{14}$H$_{15}$O$_4$, 247.0965; found, 247.0974.

3-((1,1'-Biphenyl)-4-yl)-5,5-dimethylfuran-2(5$H$)-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow solid (108.4mg, 82%). mp. 148-150 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.95 (d, $J = 8.4$ Hz, 2H), 7.71 – 7.58 (m, 4H), 7.55 (s, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.3$ Hz, 1H), 1.57 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.1, 152.7, 142.0, 140.3, 129.7, 128.9, 128.5, 127.7, 127.5, 127.3, 127.0, 83.5, 25.8.
HRMS (ESI): [M+H$^+$]calcd for C$_{18}$H$_{17}$O$_2$, 265.1223; found, 265.1229.

5,5-Dimethyl-3-(naphthalen-2-yl)furan-2(5$H$)-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (101.2mg, 85%). mp. 106-108 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.59 (s, 1H), 7.94-7.88 (m, 1H), 7.85 (d, $J = 8.8$ Hz,
1H), 7.83-7.79 (m, 1H), 7.76 (dd, J = 8.8, 2.0 Hz, 1H), 7.61 (s, 1H), 7.52-7.47 (m, 2H), 1.58 (s, 6H).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.22 (s, 1H), 7.48 (t, $J = 1.6$ Hz, 1H), 7.28 (s, 1H), 6.63 – 6.61 (m, 1H), 1.56 (s, 6H).

$^1$H NMR (100 MHz, CDCl$_3$): δ = 171.1, 149.7, 143.4, 142.5, 123.8, 115.2, 108.2, 84.9, 25.8.

HRMS (ESI): [M+H$^+$]calcd for C$_{10}$H$_{11}$O$_3^+$, 179.0703; found, 179.0704.

5,5-Dimethyl-[3,3′-bifuran]-2(5H)-one

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow oil (66.7 mg, 75%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.83-7.79 (m, 1H), 7.76 (dd, J = 8.8, 2.0 Hz, 1H), 7.61 (s, 1H), 7.52-7.47 (m, 2H), 1.58 (s, 6H).

$^1$H NMR (100 MHz, CDCl$_3$): δ = 170.7, 152.5, 132.9, 132.7, 129.3, 128.3, 127.8, 127.1, 126.5, 126.4, 126.3, 126.0, 123.7, 83.0, 25.3.

HRMS (ESI): [M+H$^+$]calcd for C$_{10}$H$_{11}$O$_3^+$, 179.0703; found, 179.0704.

5,5-Dimethyl-3-(thiophen-3-yl)furan-2(5H)-one

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (46.5 mg, 48%). mp. 102-104 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.15 (d, $J = 1.1$ Hz, 1H), 7.35 (d, $J = 1.8$ Hz, 2H), 7.34 (s, 1H), 1.53 (s, 6H).

$^1$H NMR (100 MHz, CDCl$_3$): δ = 171.1, 150.5, 130.3, 126.1, 125.9, 125.7, 125.2, 84.0, 25.8.

HRMS (ESI): [M+H$^+$]calcd for C$_{10}$H$_{11}$O$_3^+$, 195.0474; found, 195.0479.
3-(2,5-Dimethoxyphenyl)-5,5-dimethylfuran-2(5H)-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 5:1) to give the product as a yellow oil (62.0mg, 50%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.90$ (s, 2H), 6.88 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 1.54 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.8$, 157.4, 153.4, 152.2, 124.8, 119.1, 115.6, 114.6, 111.9, 83.1, 55.9, 55.8, 25.7.

HRMS (ESI): [M+H$^+$]calcd for C$_{14}$H$_{17}$O$_4$$^+$, 249.1121; found, 249.1123.

5-Ethyl-5-methyl-3-phenylfuran-2(5H)-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow oil (76.7mg, 76%). mp. 69-71 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.90$ (dd, $J = 7.2$, 1.0 Hz, 2H), 7.51 (s, 1H), 7.47 – 7.39 (m, 3H), 1.98 – 1.83 (m, 2H), 1.55 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.3$, 152.1, 130.9, 129.7, 129.2, 128.6, 127.1, 86.1, 31.7, 23.8, 8.2.

HRMS (ESI): [M+H$^+$]calcd for C$_{13}$H$_{15}$O$_2$$^+$, 203.1067; found, 203.1070.

5-Methyl-3-phenyl-5-propylfuran-2(5H)-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow oil (79.9mg, 74%).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 6.6$ Hz, 2H), 7.47 (s, 1H), 7.38-7.42 (m, $J = 7.6$ Hz, 3H), 1.94 – 1.70 (m, 2H), 1.52 (s, 3H), 1.44 – 1.25 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.3$, 152.2, 130.6, 129.7, 129.2, 128.6, 127.1, 85.0, 40.9, 24.3, 17.3, 14.2.

HRMS (ESI): [M+H$^+$]calcd for C$_{14}$H$_{17}$O$_2^+$, 217.1223; found, 217.1225.

5-Butyl-5-methyl-3-phenylfuran-2(5H)-one

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a brown oil (82.8 mg, 72%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 6.5$ Hz, 2H), 7.47 (s, 1H), 7.43 – 7.35 (m, 3H), 1.89 – 1.74 (m, 2H), 1.52 (s, 3H), 1.38 – 1.23 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.3$, 152.2, 130.7, 129.7, 129.1, 128.6, 127.1, 85.8, 38.5, 26.0, 24.3, 22.8, 13.9.

HRMS (ESI): [M+H$^+$]calcd for C$_{15}$H$_{19}$O$_2^+$, 231.1380; found, 231.1384.

5,5-Diethyl-3-phenylfuran-2(5H)-one

According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow oil (88.5 mg, 82%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.86$ (d, $J = 4.6$ Hz, 2H), 7.41 (s, 1H), 7.40 – 7.38 (m, 3H), 1.98 – 1.78 (m, 4H), 0.90 (t, $J = 7.5$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.5$, 150.8, 131.9, 129.7, 129.2, 128.6, 127.1, 88.8, 30.0, 7.9.

HRMS (ESI): [M+H$^+$]calcd for C$_{15}$H$_{19}$O$_2^+$, 231.1380; found, 231.1384.
3-Phenyl-1-oxaspiro[4.4]non-3-en-2-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a yellow solid (55.6 mg, 52%). mp. 64-66 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85 (d, $J$ = 4.5 Hz, 2H), 7.48 (s, 1H), 7.42 – 7.34 (m, 3H), 2.10 – 1.80 (m, 8H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.2, 150.8, 130.4, 129.7, 129.1, 128.6, 127.0, 93.8, 37.2, 24.7.

3-Phenyl-1-oxaspiro[4.5]dec-3-en-2-one$^{3b}$
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (82.1 mg, 72%). mp. 97-99 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.84–7.87 (m, 2H), 7.57 (s, 1H), 7.34–7.43 (m, 3H), 1.67–1.87 (m, 9H), 1.36–1.45 (m, 1H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.1, 152.4, 130.1, 129.7, 129.0, 128.5, 127.0, 85.3, 34.8, 24.6, 22.4.

3-Phenyl-1-oxaspiro[4.6]undec-3-en-2-one
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (72.6 mg, 60%). mp. 100-102 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.84 (d, $J$ = 6.5 Hz, 2H), 7.59 (s, 1H), 7.42 – 7.33 (m, 3H), 2.03 – 1.55 (m, 12H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.2, 153.4, 129.8, 129.3, 129.1, 128.6, 127.1, 88.7, 38.0, 28.9, 22.8.
HRMS (ESI): [M+H$^+$]calcd for C$_{16}$H$_{19}$O$_2^+$, 243.1380; found, 243.1382.
5-Methyl-3,5-diphenylfuran-2(5H)-one\textsuperscript{3a}
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a white solid (76.2 mg, 61%). mp. 73-75 °C
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.88-7.84 (m, 2H), 7.74 (s, 1H), 7.46-7.42 (m, 2H), 7.41-7.35 (m, 5H), 7.34-7.31 (m, 1H), 1.88 (s, 3H)
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 171.1, 152.1, 139.8, 129.4, 129.3, 128.9, 128.7, 128.3, 127.2, 124.9, 85.9, 26.7.

5-Ethyl-3-phenylfuran-2(5H)-one\textsuperscript{3b}
According to general procedure for reaction, the crude residue was purified by flash chromatography (PE/EtOAc = 10:1) to give the product as a brown oil (65.8 mg, 70%).
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.85 (d, J = 6.3 Hz, 1H), 7.55 (s, 1H), 7.41 – 7.37 (m, 3H), 5.04 – 4.86 (m, 1H), 1.95 – 1.73 (m, 2H), 1.06 (t, J = 7.4 Hz, 4H).
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 171.7, 147.7, 131.8, 129.6, 129.3, 128.6, 127.0, 81.5, 26.7, 9.2.

7. References
8. Spectra of TFBen and Substrates
1b
1c
1f
1h

S29
1i
**1k**

![NMR Spectrum](image)

**S32**
1p

![NMR Spectra](image)

S37
1r
1w
9. Spectra of Products

2a
2e

S50
2j

[Chemical structure and NMR spectra]

S55
2k
2p

S61
2v

S67