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# Supporting Information

## Visible Light-Promoted Oxycarbonylation of Unactivated Alkenes

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## 1. General Information

### Reagents, solvents, and analytical methods:

Unless otherwise noted, all reactions were carried out under carbon monoxide or nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C), dichloromethane and ethyl acetate as eluent. All NMR spectra were recorded at ambient temperature using Bruker Avance III 400 MHz NMR ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$  {1H}, 101 MHz,  $^{19}\text{F}$  376 MHz), Bruker AVANCE III HD 700 MHz NMR spectrometers ( $^1\text{H}$ , 700 MHz;  $^{13}\text{C}$ {1H}, 176 MHz).  $^1\text{H}$  NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ( $\text{CDCl}_3$ : 7.26 ppm;  $\text{d}_6$ -DMSO: 2.50 ppm) whereas  $^{13}\text{C}$ {1H} NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent ( $\text{CDCl}_3$ : 77.0 ppm;  $\text{d}_6$ -DMSO: 39.5 ppm. Data for  $^1\text{H}$  are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd (doublet of doublets), dt (doublet of triplets), qd (quartet of doublets), quint = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. All  $^{13}\text{C}$  NMR spectra were broad-band  $^1\text{H}$  decoupled. All reactions were monitored by GC-FID or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI-TOF) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

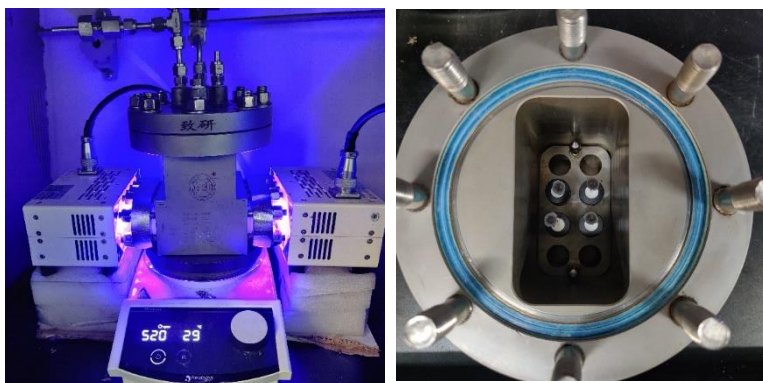
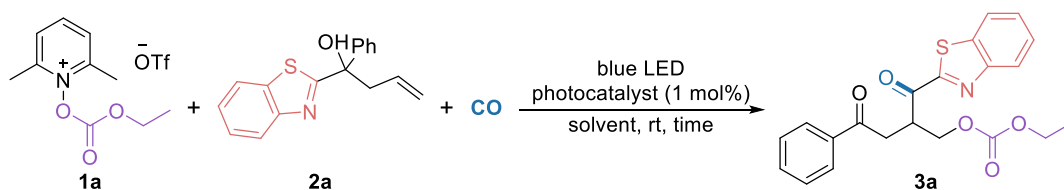


Figure S1. Photochemical Setup

## 2. Optimization of the Reaction Conditions



**Table S1. Optimization of solvent.**

Entry	Solvent	Yield (%)
1	DCM	56
2	DCE	49
3	MeCN	47
4	Acetone	70
5	DMSO	Trace
6	EA	47
7	Toluene	Trace

Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), CO (40 bar) in Solvent (1 mL), irradiation with a 15 W blue LED at rt for 24 hours. The yields were determined by isolated.

**Table S2. Optimization of photocatalysts.**

Entry	Photocatalyst	$E_{1/2}^{P^{+}/P^{*}}$ (V vs. SCE)	$E_{1/2}^{P^{+}/P}$ (V vs. SCE)	$E_{1/2}^{P^{*}/P^{-}}$ (V vs. SCE)	$E_{1/2}^{P/P^{-}}$ (V vs. SCE)	Yield (%)
1	<i>fac</i> -Ir(ppy) <sub>3</sub>	-1.73	+0.77	+0.35	-2.19	Trace
2	4CzIPN	-1.04	+1.52	+1.35	-1.21	51
3	[Ir(dtbbpy)(ppy) <sub>2</sub> ] <sub>2</sub> PF <sub>6</sub>	-0.96	+1.21	+0.66	-1.51	32
4	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	-0.89	+1.69	+1.21	-1.37	70

5	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O	-0.81	+1.29	+0.77	-1.33	Trace
6	Thioxanthone	-1.12	/	+1.18	/	Trace
7	No PC					N.D

Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), Photocatalyst (1 mol%), CO (40 bar) in Acetone (1 mL), irradiation with a 15 W blue LED at rt for 24 hours. The yields were determined by isolated.

**Table S3. Optimization of blue LED.**

Entry	blue LED (w)	Yield (%)
1	7	65
2	15	70
3	30	60

Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), CO (40 bar) in Acetone (1 mL), irradiation with blue LED at rt for 24 hours. The yields were determined by isolated.

**Table S4. Optimization of Density and Time.**

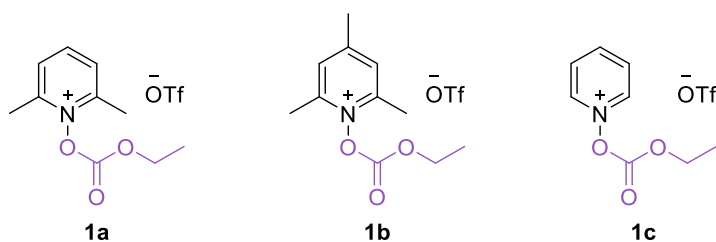
Entry	Acetone (mL)	Time (h)	Yield (%)
1	1	15	56
2	2	24	62
3	1	24	70

Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), CO (40 bar) in Acetone (1 mL), irradiation with a 15 W blue LED at rt for 24 hours. The yields were determined by isolated.

**Table S5. Trifluoromethanesulfonate with different substituents.**

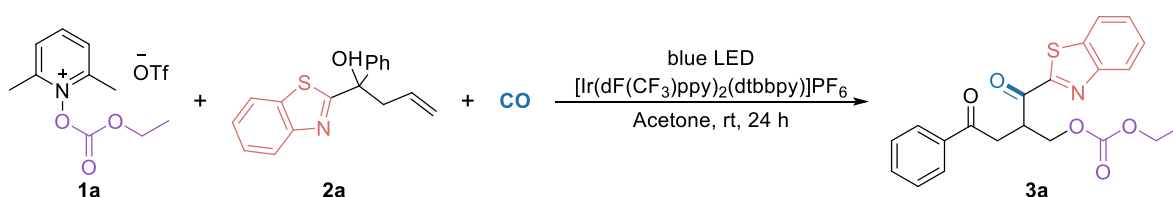
Entry	Trifluoromethanesulfonate	Yield (%)
1	<b>1a</b>	70

2	<b>1b</b>	51
3	<b>1c</b>	20



Reaction conditions: **x** (2 equiv.), **2a** (0.2 mmol), [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), CO (40 bar) in Acetone (1 mL), irradiation with a 15 W blue LED at rt for 24 hours. The yields were determined by isolated.

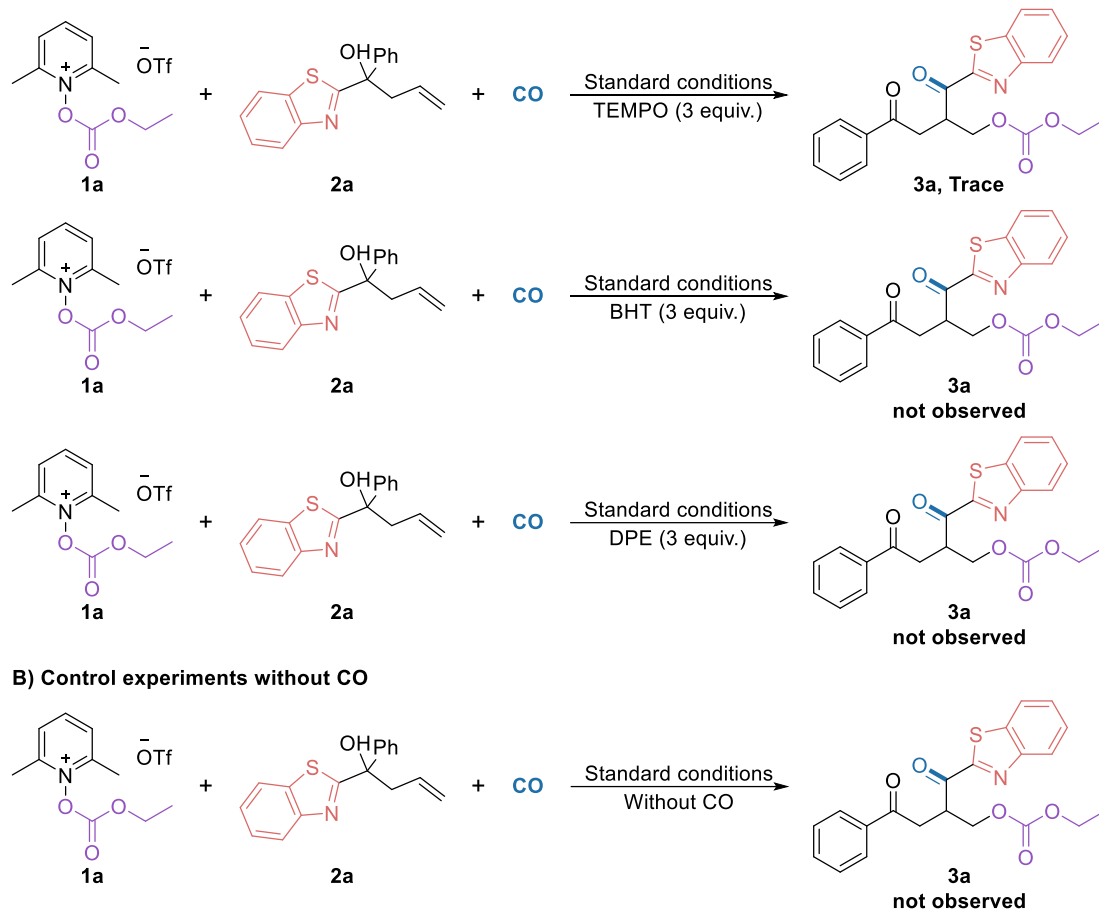
### 3. General Procedure



To a dried 4 mL vial equipped with a magnetic stir bar was added [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (2.3 mg, 1 mol%), **1a** (2 equiv., 0.4 mmol), **2** (0.2 mmol, 1.0 equiv.). The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. The vial was evacuated under vacuum and recharged with argon for three times. After acetone (1 mL) was added with a syringe under nitrogen atmosphere, the vials (usually 8) were placed on an S6 alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows (2 x 10 cm<sup>2</sup>). After the autoclave was flushed three times with CO, it was pressurised with 40 atm of CO and then irradiated with two 15 W blue LEDs (440 nm) at room temperature for 24 h. Upon completion of the reaction, the pressure was carefully released, the reaction was diluted with 20 mL EtOAc. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (silica: 200-300 mesh, eluent: petroleum ether/ethyl acetate (10:1-3:1, v/v) to afford the corresponding pure product **3**.

## 4. Control Experiments

### A) Radical trapping experiments



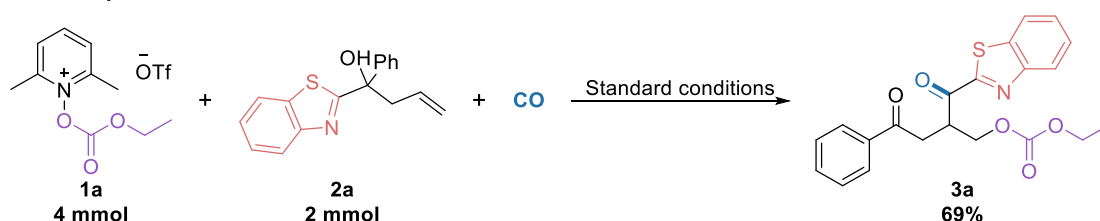
**Eq A, Radical trapping experiments:** To a dried 4 mL vial equipped with a magnetic stir bar was added  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  (2.3 mg, 1 mol%), **1a** (2 equiv., 0.4 mmol), **2a** (0.2 mmol, 1.0 equiv.), radical scavenger (3 equiv.). The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. The vial was evacuated under vacuum and recharged with argon for three times. After acetone (1 mL) was added with a syringe under nitrogen atmosphere, which was transferred into an autoclave with two inserted quartz-glass windows (2 x 10 cm<sup>2</sup>). After the autoclave was flushed three times with CO, it was pressurised with 40 atm of CO and then irradiated with two 15 W blue LEDs (440 nm) at room temperature for 24h. The sample of the reaction

**Eq B, Control experiment without CO:** To a dried 4 mL vial equipped with a magnetic stir bar was added  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  (2.3 mg, 1 mol%), **1a** (2 equiv., 0.4 mmol), **2a** (0.2 mmol, 1.0 equiv.) The vial was closed with a Teflon septum and cap and connected to the atmosphere via a

needle. The vial was evacuated under vacuum and recharged with argon for three times. After acetone (1 mL) was added with a syringe under nitrogen atmosphere, which was transferred into an autoclave with two inserted quartz-glass windows (2 x 10 cm<sup>2</sup>). Without CO and then irradiated with two 15 W blue LEDs (440 nm) at room temperature for 36 h. The sample of the reaction was tested by TLC and GC-MS.

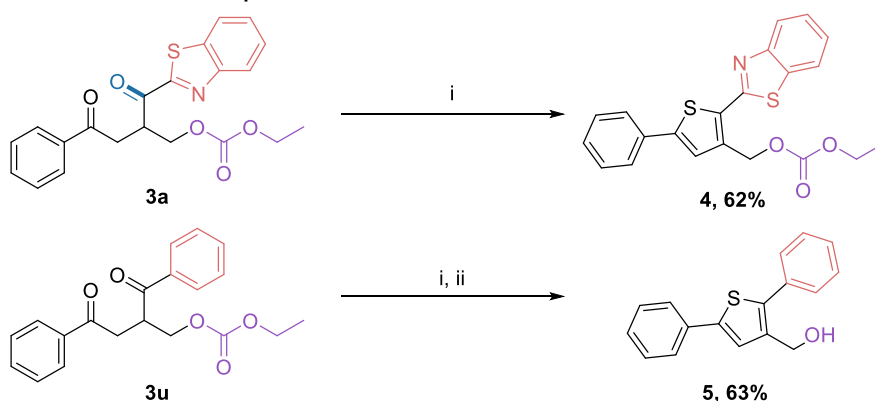
## 5. A scale-up reaction and transformations of the product

### A scale-up reaction



To a dried 4 mL vial equipped with a magnetic stir bar was added [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (11.3 mg, 0.5 mol%), **1a** (2 equiv., 4 mmol, 1380.2 mg), **2a** (1.0 equiv., 2 mmol, 562.2 mg). The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. The vial was evacuated under vacuum and recharged with argon for three times. After acetone (5 mL) was added with a syringe under nitrogen atmosphere, the vials (usually 8) were placed on an S6 alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows (2 x 10 cm<sup>2</sup>). After the autoclave was flushed three times with CO, it was pressurised with 40 atm of CO and then irradiated with two 15 W blue LEDs (440 nm) at room temperature for 24 h. Upon completion of the reaction, the pressure was carefully released, the reaction was diluted with 20 mL EtOAc. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (silica: 200-300 mesh, eluent: petroleum ether/ethyl acetate (10:1-3:1, v/v) to afford the corresponding pure product **3a** (546.6 mg, 69%).

transformations of the product

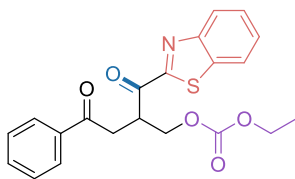


(i) solution of corresponding substrate (0.2 mmol) and Lawesson's Reagent (89 mg, 0.22 mmol) in dichloromethane (3 mL) was stirred at 40 °C under nitrogen for 6 hours. Then EA (20 mL) was added and the reaction mixture was washed with water (10 mL) and saturated sodium bicarbonate solution (10 mL) and dried over sodium sulfate. The solvent of organic layer was removed under reduce pressure and the residue was purified by column chromatography (Hexane:EA = 5:1) to afford the product.

(ii) in a schlenk flask with a stir bar corresponding substrate and 2 mL THF was added. Then 3 mL of 2.0 N aq. NaOH solution was added and basic hydrolysis was performed at 80 °C for 20 h. After cooling, 5 mL brine solution was added and the solvent mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. Purification by column chromatography afforded the desired pure alcohol product.



## 6. Spectroscopic Data of Products



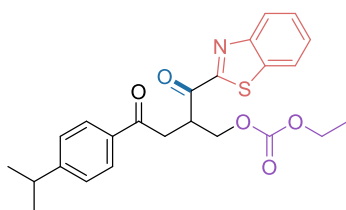
### 2-(benzo[d]thiazole-2-carbonyl)-4-oxo-4-phenylbutyl ethyl carbonate (3a)

55.4 mg, 70% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 3H), 7.60 – 7.50 (m, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.86 (td, *J* = 9.8, 5.2 Hz, 1H), 4.74 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.58 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 18.2, 9.3 Hz, 1H), 3.45 (dd, *J* = 18.2, 4.5 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.1, 193.9, 165.5, 154.8, 153.6, 137.5, 136.1, 133.5, 128.7, 128.2, 127.8, 126.9, 125.7, 122.4, 67.5, 64.3, 42.6, 37.9, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>NO<sub>5</sub>S 398.1057; Found: 398.1056.



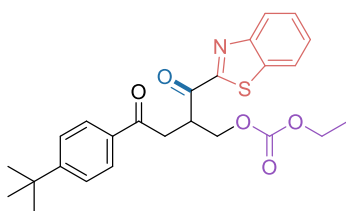
### 2-(benzo[d]thiazole-2-carbonyl)-4-(4-isopropylphenyl)-4-oxobutyl ethyl carbonate (3b)

47.4 mg, 54% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.90 – 4.81 (m, 1H), 4.73 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.56 (dd, *J* = 11.0, 5.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.87 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.43 (dd, *J* = 18.1, 4.5 Hz, 1H), 3.00 – 2.92 (m, 1H), 1.27 – 1.22 (m, 9H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.7, 194.0, 165.6, 155.1, 154.9, 153.6, 137.5, 134.0, 128.5, 127.7, 126.9, 126.8, 125.7, 122.4, 67.5, 64.3, 42.5, 37.8, 34.3, 23.7, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>26</sub>NO<sub>5</sub>S 440.1526; Found: 440.1526.



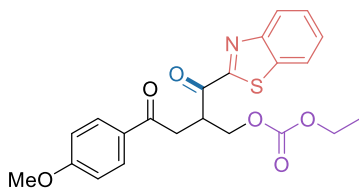
### 2-(benzo[d]thiazole-2-carbonyl)-4-(4-tert-butylphenyl)-4-oxobutyl ethyl carbonate (3c)

46.2 mg, 51% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 4.90 – 4.82 (m, 1H), 4.73 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.57 (dd, *J* = 11.0, 5.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.88 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.44 (dd, *J* = 18.1, 4.5 Hz, 1H), 1.33 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.7, 194.0, 165.6, 157.3, 154.9, 153.6, 137.5, 133.6, 128.2, 127.7, 126.9, 125.7, 125.6, 122.4, 67.5, 64.3, 42.5, 37.8, 35.2, 31.1, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>28</sub>NO<sub>5</sub>S 454.1683; Found: 454.1681.



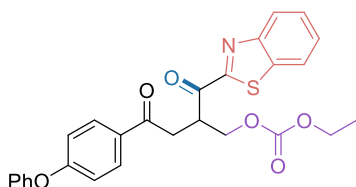
### 2-(benzo[d]thiazole-2-carbonyl)-4-(4-methoxyphenyl)-4-oxobutyl ethyl carbonate (3d)

28.8 mg, 34% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.23 – 8.18 (m, 1H), 8.01 – 7.93 (m, 3H), 7.60 – 7.50 (m, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.89 – 4.81 (m, 1H), 4.72 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.56 (dd, *J* = 10.9, 5.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.89 – 3.80 (m, 4H), 3.41 (dd, *J* = 17.9, 4.6 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 195.5, 194.1, 165.6, 163.8, 154.8, 153.6, 137.5, 130.5, 129.2, 127.7, 126.9, 125.7, 122.4, 113.8, 67.5, 64.3, 55.5, 42.5, 37.6, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>6</sub>S 412.1213; Found: 412.1205.



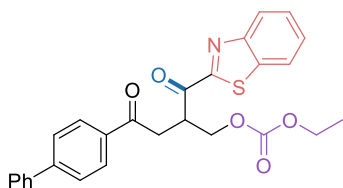
### 2-(benzo[d]thiazole-2-carbonyl)-4-oxo-4-(4-phenoxyphenyl)butyl ethyl carbonate (3e)

40.6 mg, 41% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.5 Hz, 1H), 7.97 (t, *J* = 8.4 Hz, 3H), 7.61 – 7.51 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.90 – 4.82 (m, 1H), 4.73 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.57 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.86 (dd, *J* = 18.0, 9.4 Hz, 1H), 3.41 (dd, *J* = 18.0, 4.5 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 195.6, 194.0, 165.5, 162.3, 155.4, 154.8, 153.6, 137.5, 130.8, 130.6, 130.1, 127.8, 126.9, 125.7, 124.7, 122.4, 120.3, 117.3, 67.5, 64.3, 42.6, 37.7, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>24</sub>NO<sub>6</sub>S 490.1319; Found: 490.1325.



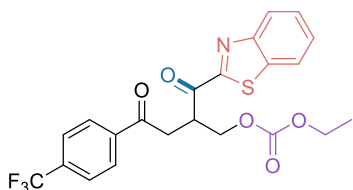
**4-([1,1'-biphenyl]-4-yl)-2-(benzo[d]thiazole-2-carbonyl)-4-oxobutyl ethyl carbonate (3f)**

46.4 mg, 49% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 7.1 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.51 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.37 (m, 1H), 4.89 (td, *J* = 9.4, 4.4 Hz, 1H), 4.77 (dd, *J* = 11.0, 5.1 Hz, 1H), 4.60 (dd, *J* = 10.9, 5.5 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.94 (dd, *J* = 18.1, 9.4 Hz, 1H), 3.49 (dd, *J* = 18.1, 4.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.7, 194.0, 165.5, 154.9, 153.6, 146.1, 139.8, 137.5, 134.8, 129.0, 128.9, 128.3, 127.8, 127.3, 127.3, 127.0, 125.7, 122.5, 67.5, 64.4, 42.6, 37.9, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>24</sub>NO<sub>5</sub>S 474.1370; Found: 474.1369.



**2-(benzo[d]thiazole-2-carbonyl)-4-oxo-4-(4-(trifluoromethyl)phenyl)butyl ethyl carbonate (3g)**

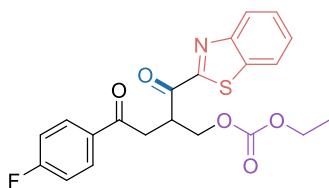
58.6 mg, 63% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.7 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.52 (m, 2H), 4.91 – 4.83 (m, 1H), 4.77 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.59 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.93 (dd, *J* = 18.3, 9.4 Hz, 1H), 3.44 (dd, *J* = 18.3, 4.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.3, 193.6, 165.2, 154.8, 153.5, 138.7, 137.5, 134.7 (q, *J*<sub>C-F</sub> = 32.7 Hz), 128.6, 127.9, 127.1, 125.8 (q, *J*<sub>C-F</sub> = 5.1 Hz), 123.6 (q, *J*<sub>C-F</sub> = 272.8 Hz), 122.5, 67.3, 64.4, 42.6, 38.0, 14.2.

**<sup>19</sup>F NMR (56 MHz, CDCl<sub>3</sub>)** δ -63.1.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>5</sub>S 466.0931; Found: 466.0934.



**2-(benzo[d]thiazole-2-carbonyl)-4-(4-fluorophenyl)-4-oxobutyl ethyl carbonate (3h)**

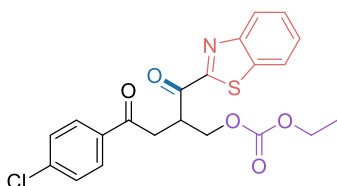
49.8 mg, 60% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.19 (d, *J* = 7.4 Hz, 1H), 8.06 – 7.95 (m, 3H), 7.60 – 7.50 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 4.89 – 4.81 (m, 1H), 4.74 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.57 (dd, *J* = 11.0, 5.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.87 (dd, *J* = 18.1, 9.5 Hz, 1H), 3.40 (dd, *J* = 18.1, 4.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 195.5, 193.8, 166.0 (d, *J*<sub>C-F</sub> = 255.3 Hz), 165.4, 154.8, 153.5, 137.5, 132.6 (d, *J*<sub>C-F</sub> = 3.0 Hz), 130.9 (d, *J*<sub>C-F</sub> = 9.4 Hz), 127.8, 127.0, 125.7, 122.4, 115.8 (d, *J*<sub>C-F</sub> = 21.9 Hz), 67.4, 64.4, 42.6, 37.7, 14.2.

**<sup>19</sup>F NMR (56 MHz, CDCl<sub>3</sub>)** δ -104.4.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>FNO<sub>5</sub>S 416.0962; Found: 416.0964.



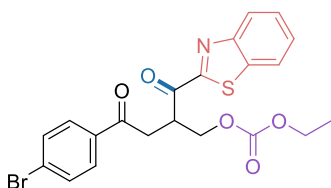
### 2-(benzo[d]thiazole-2-carbonyl)-4-(4-chlorophenyl)-4-oxobutyl ethyl carbonate (3i)

42.2 mg, 49% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.51 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 4.89 – 4.81 (m, 1H), 4.74 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.57 (dd, *J* = 11.0, 5.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.87 (dd, *J* = 18.2, 9.4 Hz, 1H), 3.40 (dd, *J* = 18.2, 4.4 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 195.9, 193.7, 165.3, 154.8, 153.5, 140.0, 137.5, 134.4, 129.7, 129.0, 127.8, 127.0, 125.7, 122.5, 67.4, 64.4, 42.6, 37.8, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>ClNO<sub>5</sub>S 432.0667; Found: 432.0668.



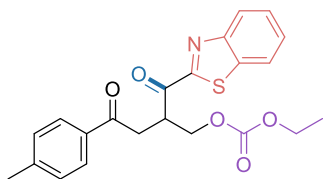
### 2-(benzo[d]thiazole-2-carbonyl)-4-(4-bromophenyl)-4-oxobutyl ethyl carbonate (3j)

67.5 mg, 71% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.63 – 7.51 (m, 4H), 4.89 – 4.80 (m, 1H), 4.74 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.57 (dd, *J* = 11.0, 5.3 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.86 (dd, *J* = 18.2, 9.4 Hz, 1H), 3.39 (dd, *J* = 18.2, 4.4 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.2, 193.7, 165.3, 154.8, 153.5, 137.5, 134.8, 132.0, 129.8, 128.8, 127.8, 127.0, 125.7, 122.5, 67.4, 64.4, 42.5, 37.7, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>BrNO<sub>5</sub>S 476.0162; Found: 476.0168.



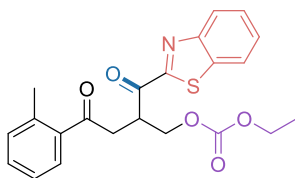
**2-(benzo[d]thiazole-2-carbonyl)-4-oxo-4-(*p*-tolyl)butyl ethyl carbonate (3k)**

46.8 mg, 57% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.49 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 4.89 – 4.81 (m, 1H), 4.73 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.56 (dd, *J* = 10.9, 5.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.86 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.43 (dd, *J* = 18.1, 4.5 Hz, 1H), 2.41 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.6, 194.0, 165.6, 154.8, 153.6, 144.4, 137.5, 133.7, 129.3, 128.4, 127.7, 126.9, 125.7, 122.4, 67.5, 64.3, 42.5, 37.8, 21.7, 14.2.

**HRMS (ESI-TOF) *m/z*:** [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>5</sub>S 412.1213; Found: 412.1205.



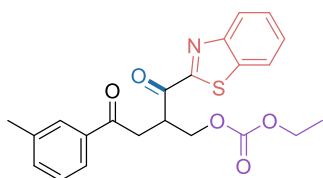
**2-(benzo[d]thiazole-2-carbonyl)-4-oxo-4-(*o*-tolyl)butyl ethyl carbonate (3l)**

46.1 mg, 56% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.39 (t, *J* = 6.9 Hz, 1H), 7.30 – 7.22 (m, 2H), 4.86 – 4.79 (m, 1H), 4.74 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.57 (dd, *J* = 10.9, 5.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.86 (dd, *J* = 18.1, 9.4 Hz, 1H), 3.34 (dd, *J* = 18.2, 4.4 Hz, 1H), 2.45 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 200.6, 193.9, 165.5, 154.9, 153.6, 138.7, 137.5, 136.6, 132.1, 131.8, 129.0, 127.8, 127.0, 125.8, 125.7, 122.4, 67.5, 64.3, 42.9, 40.3, 21.5, 14.2.

**HRMS (ESI-TOF) *m/z*:** [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>5</sub>S 412.1213; Found: 412.1217.



**2-(benzo[d]thiazole-2-carbonyl)-4-oxo-4-(*m*-tolyl)butyl ethyl carbonate (3m)**

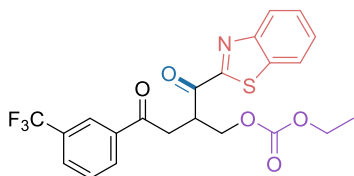
47.6 mg, 58% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 6.7 Hz, 2H), 7.60 – 7.49 (m, 2H), 7.41 – 7.31 (m, 2H), 4.91 – 4.81 (m, 1H), 4.74 (dd, *J* = 11.0, 5.1 Hz, 1H),

4.57 (dd,  $J = 10.9, 5.6$  Hz, 1H), 4.15 (q,  $J = 7.1$  Hz, 2H), 3.89 (dd,  $J = 18.2, 9.4$  Hz, 1H), 3.44 (dd,  $J = 18.2, 4.5$  Hz, 1H), 2.39 (s, 3H), 1.24 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 194.0, 165.5, 154.8, 153.6, 138.5, 137.5, 136.1, 134.3, 128.8, 128.5, 127.8, 126.9, 125.7, 125.5, 122.4, 67.5, 64.3, 42.5, 38.0, 21.4, 14.2.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{22}\text{NO}_5\text{S}$  412.1213; Found: 412.1210.



### 2-(benzo[*d*]thiazole-2-carbonyl)-4-oxo-4-(3-(trifluoromethyl)phenyl)butyl ethyl carbonate (3n)

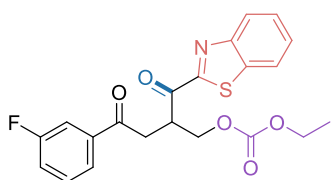
55.8 mg, 60% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 – 8.14 (m, 3H), 7.99 (d,  $J = 7.8$  Hz, 1H), 7.84 (d,  $J = 7.8$  Hz, 1H), 7.66 – 7.50 (m, 3H), 4.92 – 4.83 (m, 1H), 4.77 (dd,  $J = 11.0, 5.2$  Hz, 1H), 4.59 (dd,  $J = 11.0, 5.2$  Hz, 1H), 4.15 (q,  $J = 7.1$  Hz, 2H), 3.93 (dd,  $J = 18.2, 9.4$  Hz, 1H), 3.44 (dd,  $J = 18.2, 4.3$  Hz, 1H), 1.25 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 193.6, 165.2, 154.8, 153.5, 137.5, 136.6, 131.4, 131.3 (q,  $J_{\text{C-F}} = 32.9$  Hz), 129.9 (q,  $J_{\text{C-F}} = 3.6$  Hz), 129.4, 127.9, 127.1, 125.7, 125.1 (q,  $J_{\text{C-F}} = 3.8$  Hz), 123.6 (q,  $J_{\text{C-F}} = 272.7$  Hz), 122.5, 67.3, 64.4, 42.6, 37.8, 14.2.

$^{19}\text{F}$  NMR (56 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.8.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{19}\text{F}_3\text{NO}_5\text{S}$  466.0931; Found: 466.0933.



### 2-(benzo[*d*]thiazole-2-carbonyl)-4-(3-fluorophenyl)-4-oxobutyl ethyl carbonate (3o)

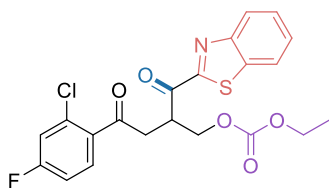
53.1 mg, 64% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J = 7.7$  Hz, 1H), 7.99 (d,  $J = 7.6$  Hz, 1H), 7.78 (d,  $J = 7.8$  Hz, 1H), 7.66 (d,  $J = 8.8$  Hz, 1H), 7.62 – 7.51 (m, 2H), 7.49 – 7.42 (m, 1H), 7.31 – 7.26 (m, 1H), 4.89 – 4.82 (m, 1H), 4.75 (dd,  $J = 11.0, 5.2$  Hz, 1H), 4.58 (dd,  $J = 11.0, 5.4$  Hz, 1H), 4.15 (q,  $J = 7.1$  Hz, 2H), 3.89 (dd,  $J = 18.2, 9.4$  Hz, 1H), 3.40 (dd,  $J = 18.2, 4.4$  Hz, 1H), 1.25 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 193.7, 165.3, 162.8 (d,  $J_{\text{C-F}} = 248.1$  Hz), 154.8, 153.5, 138.2 (d,  $J_{\text{C-F}} = 6.3$  Hz), 137.5, 130.4 (d,  $J_{\text{C-F}} = 7.7$  Hz), 127.9, 127.0, 125.7, 124.0 (d,  $J_{\text{C-F}} = 3.0$  Hz), 122.5, 120.6 (d,  $J_{\text{C-F}} = 21.5$  Hz), 115.0 (d,  $J_{\text{C-F}} = 22.4$  Hz), 67.4, 64.4, 42.6, 37.9, 14.2.

$^{19}\text{F}$  NMR (56 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.6.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{19}\text{FNO}_5\text{S}$  416.0962; Found: 416.0964.



**2-(benzo[d]thiazole-2-carbonyl)-4-(2-chloro-4-fluorophenyl)-4-oxobutyl ethyl carbonate (3p)**

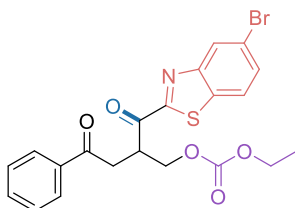
63.7 mg, 71% yield, brown oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.69 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.17 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.08 – 7.02 (m, 1H), 4.86 – 4.79 (m, 1H), 4.76 (dd, *J* = 10.9, 5.1 Hz, 1H), 4.58 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.85 (dd, *J* = 18.4, 9.3 Hz, 1H), 3.40 (dd, *J* = 18.4, 4.3 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 193.5, 165.2, 163.9 (d, *J*<sub>C-F</sub> = 257.4 Hz), 154.8, 153.5, 137.5, 134.1 (d, *J*<sub>C-F</sub> = 3.6 Hz), 133.3 (d, *J*<sub>C-F</sub> = 10.8 Hz), 131.9 (d, *J*<sub>C-F</sub> = 9.5 Hz), 127.9, 127.0, 125.7, 122.4, 118.3 (d, *J*<sub>C-F</sub> = 24.8 Hz), 114.5 (d, *J*<sub>C-F</sub> = 21.3 Hz), 67.4, 64.4, 43.2, 41.6, 14.2.

**<sup>19</sup>F NMR (56 MHz, CDCl<sub>3</sub>)** δ -105.8.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>18</sub>ClFNO<sub>5</sub>S 450.0573; Found: 450.0579.



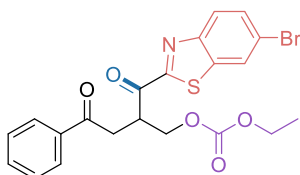
**2-(5-bromobenzo[d]thiazole-2-carbonyl)-4-oxo-4-phenylbutyl ethyl carbonate (3q)**

68.4 mg, 72% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.13 (d, *J* = 1.7 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.67 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.86 – 4.77 (m, 1H), 4.72 (dd, *J* = 11.0, 5.1 Hz, 1H), 4.54 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 18.2, 9.5 Hz, 1H), 3.45 (dd, *J* = 18.2, 4.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.0, 193.7, 166.0, 154.8, 152.3, 139.0, 136.0, 133.6, 130.7, 128.7, 128.2, 126.7, 125.0, 122.0, 67.4, 64.4, 42.5, 38.0, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>BrNO<sub>5</sub>S 476.0162; Found: 476.0156.



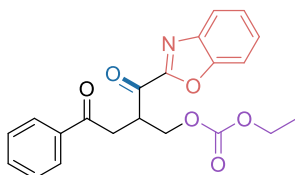
**2-(6-bromobenzo[d]thiazole-2-carbonyl)-4-oxo-4-phenylbutyl ethyl carbonate (3r)**

48.4 mg, 51% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.35 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.85 – 4.77 (m, 1H), 4.72 (dd, *J* = 11.0, 5.1 Hz, 1H), 4.55 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 18.2, 9.5 Hz, 1H), 3.46 (dd, *J* = 18.2, 4.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.0, 193.7, 167.1, 154.8, 154.6, 136.2, 136.0, 133.6, 130.9, 128.7, 128.3, 128.2, 123.5, 120.6, 67.3, 64.4, 42.5, 38.0, 14.2.

**HRMS (ESI-TOF) *m/z*:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>BrNO<sub>5</sub>S 476.0162; Found: 476.0168.



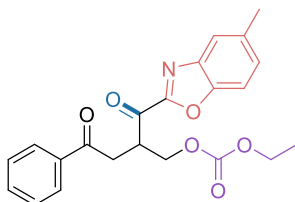
**2-(benzo[*d*]oxazole-2-carbonyl)-4-oxo-4-phenylbutyl ethyl carbonate (3s)**

39.6 mg, 52% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 3H), 4.77 – 4.69 (m, 2H), 4.53 (dd, *J* = 12.8, 7.6 Hz, 1H), 4.15 (q, *J* = 5.6 Hz, 2H), 3.89 (dd, *J* = 18.3, 9.1 Hz, 1H), 3.48 (dd, *J* = 18.3, 3.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.9, 189.0, 157.0, 154.8, 150.9, 140.7, 135.9, 133.6, 128.7, 128.6, 128.2, 125.8, 122.5, 112.0, 67.3, 64.4, 43.2, 38.2, 14.2.

**HRMS (ESI-TOF) *m/z*:** [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>NO<sub>6</sub> 382.1285; Found: 382.1281.



**ethyl (2-(5-methylbenzo[*d*]oxazole-2-carbonyl)-4-oxo-4-phenylbutyl) carbonate (3t)**

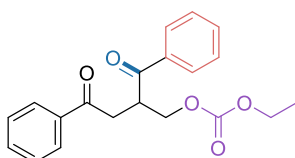
37.1 mg, 47% yield, slight yellow solid. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.68 (s, 1H), 7.61 – 7.52 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 9.8 Hz, 1H), 4.75 – 4.67 (m, 2H), 4.57 – 4.49 (m, 1H), 4.18 – 4.11 (m, 2H), 3.89 (dd, *J* = 18.2, 9.3 Hz, 1H), 3.47 (dd, *J* = 18.3, 4.1 Hz, 1H), 2.51 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.9, 188.9, 157.1, 154.8, 149.2, 140.9, 135.9, 135.8, 133.6, 130.1, 128.7, 128.2, 122.0, 111.4, 67.3, 64.4, 43.2, 38.1, 21.6, 14.2.

**HRMS (ESI-TOF) *m/z*:** [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>6</sub> 396.1442; Found: 396.1438.





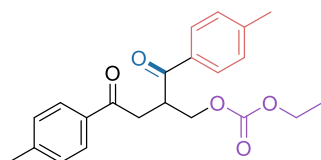
### 2-benzoyl-4-oxo-4-phenylbutyl ethyl carbonate (3u)

35.3 mg, 52% yield, 95% purity, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.10 (d, *J* = 7.3 Hz, 2H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.63 – 7.54 (m, 2H), 7.53 – 7.43 (m, 4H), 4.60 – 4.49 (m, 2H), 4.24 (dd, *J* = 10.3, 6.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.78 (dd, *J* = 18.1, 8.5 Hz, 1H), 3.35 (dd, *J* = 18.1, 4.1 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 199.7, 197.4, 154.8, 136.2, 136.2, 133.5, 128.8, 128.7, 128.2, 67.6, 64.4, 41.4, 38.2, 14.2.

**HRMS (ESI-TOF) m/z:** [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>Na 363.1203; Found: 363.1202.



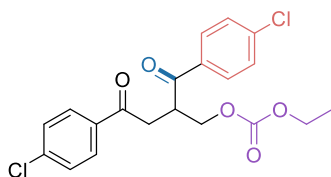
### ethyl (2-(4-methylbenzoyl)-4-oxo-4-(*p*-tolyl)butyl) carbonate (3v)

19.9 mg, 27% yield, slight yellow solid. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.57 – 4.47 (m, 2H), 4.26 – 4.19 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.71 (dd, *J* = 18.1, 8.3 Hz, 1H), 3.31 (dd, *J* = 18.0, 4.2 Hz, 1H), 2.41 (d, *J* = 7.4 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 199.3, 197.0, 154.8, 144.3, 144.3, 133.8, 133.8, 129.5, 129.3, 128.8, 128.3, 67.7, 64.3, 41.2, 38.1, 21.7, 21.7, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>25</sub>O<sub>5</sub> 369.1697; Found: 369.1699.



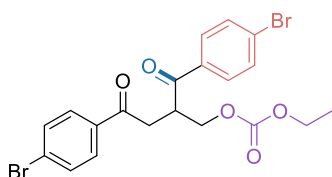
### 2-(4-chlorobenzoyl)-4-(4-chlorophenyl)-4-oxobutyl ethyl carbonate (3w)

40.8 mg, 50% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.46 (q, *J* = 5.8 Hz, 2H), 4.23 – 4.11 (m, 3H), 3.74 (dd, *J* = 18.1, 8.7 Hz, 1H), 3.29 (dd, *J* = 18.2, 3.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.5, 196.2, 154.8, 140.0, 140.0, 134.7, 134.4, 130.1, 129.6, 129.1, 129.0, 67.4, 64.5, 41.5, 38.3, 14.2.

**HRMS (ESI-TOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>Cl<sub>2</sub>O<sub>5</sub> 409.0604; Found: 409.0608.



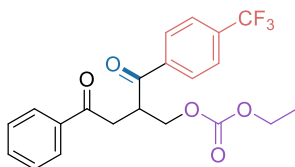
**2-(4-bromobenzoyl)-4-(4-bromophenyl)-4-oxobutyl ethyl carbonate (3x)**

49.6 mg, 50% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 4.50 – 4.41 (m, 2H), 4.25 – 4.12 (m, 3H), 3.73 (dd, *J* = 18.1, 8.9 Hz, 1H), 3.33 – 3.25 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.7, 196.4, 154.8, 135.1, 134.8, 132.1, 132.0, 130.1, 129.7, 128.8, 67.4, 64.5, 41.4, 38.3, 14.2.

HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>Br<sub>2</sub>O<sub>5</sub> 496.9594; Found: 496.9592.



**ethyl (4-oxo-4-phenyl-2-(4-(trifluoromethyl)benzoyl)butyl) carbonate (3y)**

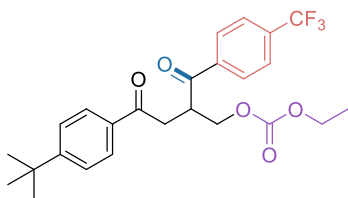
48.9 mg, 60% yield, 95% purity, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.55 – 4.46 (m, 2H), 4.26 (dd, *J* = 10.2, 6.3 Hz, 1H), 4.15 (q, *J* = 6.9 Hz, 2H), 3.81 (dd, *J* = 18.2, 9.2 Hz, 1H), 3.38 (dd, *J* = 18.1, 3.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.3, 197.3, 154.8, 139.3, 135.9, 134.5 (q, *J*<sub>C-F</sub> = 32.7 Hz), 133.7, 129.0, 128.7, 128.2, 125.9 (q, *J*<sub>C-F</sub> = 3.7 Hz), 123.6 (q, *J*<sub>C-F</sub> = 272.7 Hz), 67.4, 64.5, 41.7, 38.6, 14.2.

<sup>19</sup>F NMR (56 MHz, CDCl<sub>3</sub>) δ -63.1.

HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>F<sub>3</sub>O<sub>5</sub> 409.1257; Found: 409.1251.



**4-(4-(tert-butyl)phenyl)-4-oxo-2-(4-(trifluoromethyl)benzoyl)butyl ethyl carbonate (3z)**

46.8 mg, 56% yield, 95% purity, colorless oil. Eluent: pentane/ethyl acetate = 5:1-3:1

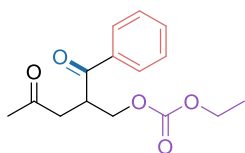
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 4.55 – 4.44 (m, 2H), 4.26 (dd, *J* = 10.3, 6.3 Hz, 1H), 4.15 (q, *J* = 7.0 Hz,

2H), 3.77 (dd,  $J = 18.1, 9.1$  Hz, 1H), 3.36 (dd,  $J = 18.1, 3.7$  Hz, 1H), 1.33 (s, 9H), 1.25 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4, 196.9, 157.5, 154.8, 139.4, 134.5 (q,  $J_{\text{C-F}} = 32.6$  Hz), 133.4, 129.0, 128.2, 125.8 (q,  $J_{\text{C-F}} = 3.7$  Hz), 125.7, 123.6 (q,  $J_{\text{C-F}} = 272.5$  Hz), 67.5, 64.5, 41.7, 38.6, 35.2, 31.1, 14.2.

$^{19}\text{F}$  NMR (56 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.1.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{28}\text{F}_3\text{O}_5$  465.1883; Found: 465.1886.



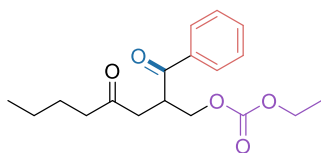
### 2-benzoyl-4-oxopentyl ethyl carbonate (3ab)

12.7 mg, 23% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.3$  Hz, 2H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 7.7$  Hz, 2H), 4.43 (dd,  $J = 10.6, 5.6$  Hz, 1H), 4.38 – 4.30 (m, 1H), 4.17 – 4.10 (m, 3H), 3.20 (dd,  $J = 18.3, 8.5$  Hz, 1H), 2.77 (dd,  $J = 18.3, 4.6$  Hz, 1H), 2.18 (s, 3H), 1.25 (d,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.0, 199.5, 154.8, 136.1, 133.5, 128.8, 128.6, 67.4, 64.3, 42.6, 41.3, 30.0, 14.2.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_5$  279.1227; Found: 279.1223.



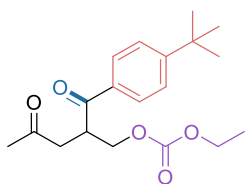
### 2-benzoyl-4-oxooctyl ethyl carbonate (3ac)

14.7 mg, 23% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 7.2$  Hz, 2H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 2H), 4.46 – 4.33 (m, 2H), 4.18 – 4.10 (m, 3H), 3.16 (dd,  $J = 18.1, 8.5$  Hz, 1H), 2.73 (dd,  $J = 18.1, 4.5$  Hz, 1H), 2.44 (dd,  $J = 7.9, 6.8$  Hz, 2H), 1.58 – 1.48 (m, 2H), 1.26 (t,  $J = 7.1$  Hz, 5H), 0.88 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.5, 199.7, 154.8, 136.2, 133.4, 128.8, 128.6, 67.5, 64.3, 42.5, 41.8, 41.2, 25.8, 22.3, 14.2, 13.9.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_5\text{Na}$  343.1516; Found: 343.1510.



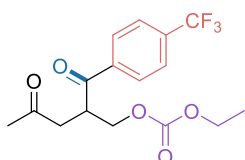
### 2-(4-(*tert*-butyl)benzoyl)-4-oxopentyl ethyl carbonate (3ad)

16.1 mg, 24% yield, 95% purity, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.5$  Hz, 2H), 7.49 (d,  $J = 8.5$  Hz, 2H), 4.45 (dd,  $J = 10.7$ , 5.5 Hz, 1H), 4.38 – 4.31 (m, 1H), 4.18 – 4.09 (m, 3H), 3.19 (dd,  $J = 18.2$ , 8.5 Hz, 1H), 2.76 (dd,  $J = 18.3$ , 4.6 Hz, 1H), 2.18 (s, 3H), 1.34 (s, 9H), 1.27 (s, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.1, 198.9, 157.3, 154.8, 133.4, 128.6, 125.8, 67.5, 64.3, 42.5, 41.2, 35.2, 31.1, 30.0, 14.2.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{27}\text{O}_5$  335.1853; Found: 335.1858.



### ethyl (4-oxo-2-(4-(trifluoromethyl)benzoyl)pentyl) carbonate (3ae)

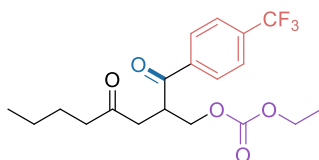
31.1 mg, 45% yield, 95% purity, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J = 8.2$  Hz, 2H), 7.75 (d,  $J = 8.3$  Hz, 2H), 4.38 (dd,  $J = 10.6$ , 6.0 Hz, 1H), 4.34 – 4.26 (m, 1H), 4.18 – 4.11 (m, 3H), 3.23 (dd,  $J = 18.4$ , 9.1 Hz, 1H), 2.80 (dd,  $J = 18.4$ , 4.1 Hz, 1H), 2.18 (s, 3H), 1.25 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.8, 199.2, 154.7, 134.6 (q,  $J_{\text{C-F}} = 32.6$  Hz), 129.9, 128.9, 125.8 (q,  $J_{\text{C-F}} = 3.8$  Hz), 123.6 (q,  $J_{\text{C-F}} = 272.6$  Hz), 67.2, 64.5, 42.8, 41.6, 29.7, 14.1.

$^{19}\text{F NMR}$  (56 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.2.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{F}_3\text{O}_5$  347.1101; Found: 347.1099.



### ethyl (4-oxo-2-(4-(trifluoromethyl)benzoyl)octyl) carbonate (3af)

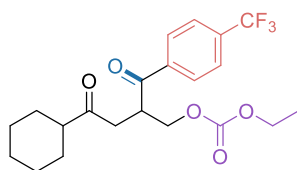
32.6 mg, 42% yield, slight yellow solid. Eluent: pentane/ethyl acetate = 5:1-3:1

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J = 8.1$  Hz, 2H), 7.75 (d,  $J = 8.2$  Hz, 2H), 4.40 – 4.28 (m, 2H), 4.19 – 4.09 (m, 3H), 3.20 (dd,  $J = 18.2$ , 9.0 Hz, 1H), 2.77 (dd,  $J = 18.2$ , 4.0 Hz, 1H), 2.44 (t,  $J = 7.4$  Hz, 2H), 1.57 – 1.50 (m, 2H), 1.31 – 1.22 (m, 5H), 0.91 – 0.86 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.4, 199.4, 154.7, 139.3, 134.5 (q,  $J_{\text{C-F}} = 32.7$  Hz), 128.9, 125.8 (q,  $J_{\text{C-F}} = 3.7$  Hz), 123.6 (q,  $J_{\text{C-F}} = 272.9$  Hz), 67.3, 64.4, 42.3, 42.1, 41.5, 25.8, 22.2, 14.2, 13.8.

$^{19}\text{F NMR}$  (56 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.2.

**HRMS (ESI-TOF) m/z:**  $[M + H]^+$  Calcd for  $C_{19}H_{24}F_3O_5$  389.1570; Found: 389.1571.



**4-cyclohexyl-4-oxo-2-(4-(trifluoromethyl)benzoyl)butyl ethyl carbonate (3ag)**

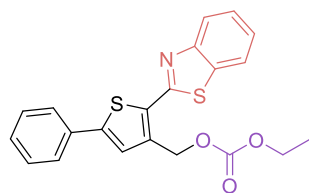
28.1 mg, 34% yield, slight yellow oil. Eluent: pentane/ethyl acetate = 5:1-3:1

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.12 (d,  $J = 8.2$  Hz, 2H), 7.74 (d,  $J = 8.3$  Hz, 2H), 4.40 – 4.27 (m, 2H), 4.19 – 4.10 (m, 3H), 3.23 (dd,  $J = 18.2, 9.0$  Hz, 1H), 2.79 (dd,  $J = 18.2, 4.0$  Hz, 1H), 2.42 – 2.31 (m, 1H), 1.87 – 1.64 (m, 5H), 1.35 – 1.20 (m, 8H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  211.4, 199.5, 154.7, 139.3, 134.5 (q,  $J_{C-F} = 32.6$  Hz), 128.9, 125.8 (q,  $J_{C-F} = 3.7$  Hz), 123.6 (q,  $J_{C-F} = 273.0$  Hz), 67.4, 64.4, 505, 41.4, 40.2, 28.4, 28.3, 25.8, 25.6, 14.2.

**$^{19}F$  NMR (56 MHz,  $CDCl_3$ )**  $\delta$  -63.2.

**HRMS (ESI-TOF) m/z:**  $[M + H]^+$  Calcd for  $C_{21}H_{26}F_3O_5$  415.1727; Found: 415.1723.



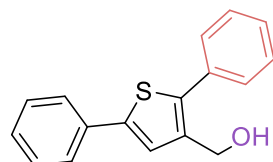
**(2-(benzo[d]thiazol-2-yl)-5-phenylthiophen-3-yl)methyl ethyl carbonate (4)**

49 mg, 62% yield, colorless solid. Eluent: pentane/ethyl acetate = 5:1-3:1

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.06 (d,  $J = 8.1$  Hz, 1H), 7.86 (d,  $J = 7.9$  Hz, 1H), 7.65 (d,  $J = 7.2$  Hz, 2H), 7.49 (t,  $J = 7.2$  Hz, 1H), 7.45 (s, 1H), 7.43 – 7.32 (m, 4H), 5.64 (s, 2H), 4.28 (q,  $J = 7.1$  Hz, 2H), 1.35 (t,  $J = 7.1$  Hz, 3H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  159.5, 155.1, 153.5, 146.6, 137.6, 135.0, 133.1, 132.6, 129.1, 128.6, 126.6, 125.9, 125.8, 125.3, 123.2, 121.4, 64.4, 64.0, 14.3.

**HRMS (ESI-TOF) m/z:**  $[M + H]^+$  Calcd for  $C_{21}H_{18}NO_3S_2$  396.0723; Found: 396.0719.



**(2,5-diphenylthiophen-3-yl)methanol (5)**

63% yield, colorless solid. Eluent: pentane/ethyl acetate = 5:1-3:1

**$^1H$  NMR (400 MHz, DMSO)**  $\delta$  7.70 – 7.64 (m, 2H), 7.57 (dd,  $J = 5.3, 3.1$  Hz, 3H), 7.52 – 7.37 (m, 5H), 7.33 (t,  $J = 7.4$  Hz, 1H), 5.31 (t,  $J = 5.4$  Hz, 1H), 4.49 (d,  $J = 5.4$  Hz, 2H).

**$^{13}C$  NMR (101 MHz, DMSO)**  $\delta$  141.6, 140.5, 138.5, 133.9, 133.8, 129.7, 129.4, 129.0, 128.3, 128.2, 127.1, 125.5, 57.7.

## 7. The NMR Spectrum

