

*Supporting Information for*

**Deoxygenation of carboxylic acids-based radical-polar  
crossover process for modular access to functionalized  
cyclopropanes**

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# 1 General Information

## 1.1 Solvents, reagents, and starting materials

All reactions were carried out in glassware under inert (nitrogen) atmosphere unless otherwise noted. DMF and  $\text{CH}_2\text{Cl}_2$  were dried from CaH. The dehydrated solvents DMSO, DMA and acetonitrile were purchased from Energy Chemical. Alkene were prepared according to our previous report<sup>1</sup> and literature procedures.<sup>2</sup> All known acids are commercially available or prepared via reported procedures.<sup>3</sup> Other photocatalysts and dried solvents were obtained from commercial sources and used without further purification unless otherwise noted.

## 1.2 Instruments

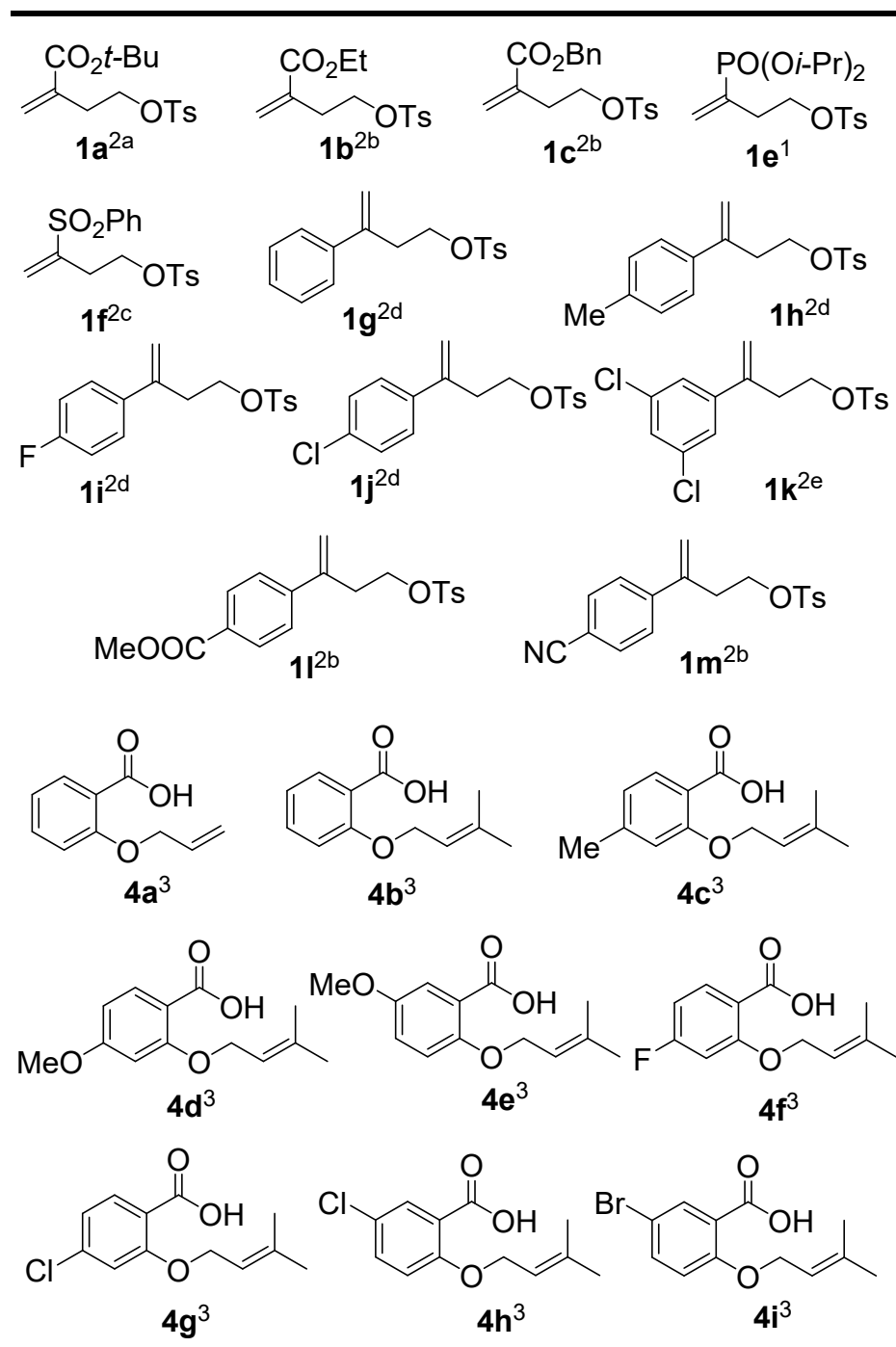
NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane, and calibrated using residue undeuterated solvent ( $\text{CHCl}_3$  at 7.26 ppm  $^1\text{H}$  NMR, 77.0 ppm  $^{13}\text{C}$  NMR). Spectra were reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on an ESI-Q-TOF spectrometer Agilent 6210 ESI/TOF. TLC analyses were performed on precoated GF<sub>254</sub> silica gel plates and were visualized under UV254 nm light, or by  $\text{I}_2$  staining and  $\text{KMnO}_4$  staining solutions. Column chromatography was carried out using 300-400 mesh silica gel and eluted with hexane/ethyl acetate unless otherwise noted.

## 1.3 Picture of a typical reaction setup

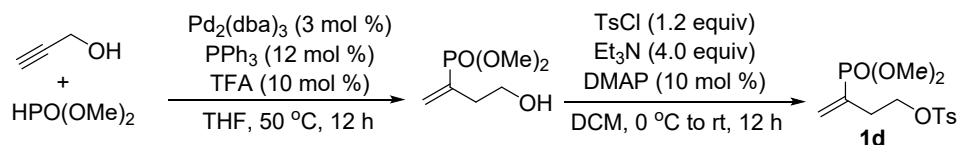


## 2 Synthesis of Starting Materials

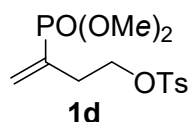
### 2.1 Known compounds<sup>1-3</sup>



## 2.2 Preparation of vinylphosphonate<sup>1</sup>



- (1) Under a nitrogen atmosphere, a Schlenk tube was charged with PPh<sub>3</sub> (0.31 g, 12 mol%) and Pd<sub>2</sub>(dba)<sub>3</sub> (0.27 g, 3 mol%). Then, propargyl alcohol (561 mg, 10 mmol, 1.0 equiv), dimethyl phosphonate (1.1 g, 10 mmol, 1.0 equiv), and THF (40 mL) were added. After stirring for 5 minutes, TFA (80 μL) was added. The reaction was heated to 50 °C and stirred overnight. After the reaction was complete, cooled to room temperature, water was added and was extracted with ethyl acetate. The organic layers were combined and washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuum, flash chromatography over silica gel afforded the product.
- (2) To a Schlenk tube containing methylene chloride (15 mL) was added the homoallyl alcohol (0.9 g, 5 mmol, 1.0 equiv), Et<sub>3</sub>N (2.8 mL, 20 mmol, 4.0 equiv), and DMAP (61 mg, 10 mol%) under nitrogen. The resulting mixture was cooled to 0 °C and then *p*-toluenesulfonyl chloride (6 mmol, 1.2 equiv) was added portionwise. The reaction was allowed to rise to room temperature and stirred for 12 h. After the reaction was complete, H<sub>2</sub>O was added and was extracted with DCM. The organic layers were combined and washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuum, flash chromatography over silica gel afforded the product **1d**.



**3-(Dimethoxyphosphoryl)but-3-en-1-yl 4-methylbenzenesulfonate (1d)**. Yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.27 (d *J* = 7.2 Hz, 2H), 6.03

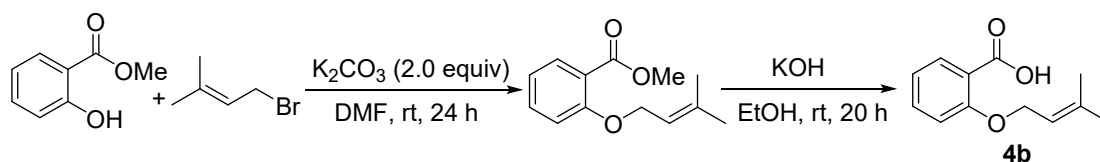
(d,  $J = 22.4$  Hz, 1H), 5.79 (d,  $J = 47.7$  Hz, 1H), 4.10 (t,  $J = 6.5$  Hz, 2H), 3.61 (s, 3H), 3.59 (s, 3H), 2.57 – 2.47 (m, 2H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 133.4 (d,  $J = 8.4$  Hz), 132.9, 132.7 (d,  $J = 176.3$  Hz), 129.8, 127.9, 67.8 (d,  $J = 4.5$  Hz), 52.5 (d,  $J = 5.6$  Hz), 32.1 (d,  $J = 11.8$  Hz), 21.6.

$^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{23}\text{H}_{23}\text{O}_4\text{NaSP}^+$ : 357.0532, found 357.0539.

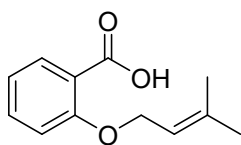
### 2.3 Synthesis of alkenoic acids<sup>3</sup>



(1) Under a nitrogen atmosphere, a Schlenk tube was charged with methyl salicylate (1.52 g, 10 mmol, 1.0 equiv) and  $\text{K}_2\text{CO}_3$  (2.76 g, 20 mmol, 2.0 equiv). Then, 3,3-dimethylallyl bromide (1.79 g, 12 mmol, 1.2 equiv) and anhydrous DMF (20 mL) were added. And the resultant mixture was stirred at room temperature for 24 h. After the reaction was complete, water was added and the mixture was extracted with ethyl acetate. The organic layers were combined and washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , concentrated in vacuum, flash chromatography over silica gel afforded the product.

(2) To a solution of the obtained ester (5 mmol) in EtOH (40 mL) was added a saturated aqueous solution of KOH (1 mL), and the mixture was stirred at room temperature for 20 h. After the solvent ethanol was removed under reduced pressure, saturated sodium chloride aqueous solution (30 mL) was added and the resulting solution was acidified with HCl (10%) until  $\text{pH} = 2$ . Add solid sodium chloride to the aqueous layer, stir for 10 minutes, then extract five times with EtOAc ( $5 \times 20$  mL). The organic layers were combined and washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , concentrated in vacuum, flash chromatography over silica gel

afforded the product.



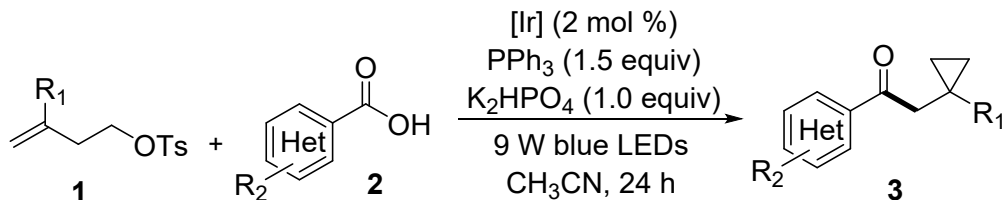
### 2-((3-Methylbut-2-en-1-yl)oxy)benzoic acid **4b**.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.48 (brs, 1H), 8.16 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.15 – 7.07 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 5.55 – 5.49 (m, 1H), 4.75 (d, *J* = 7.1 Hz, 2H), 1.81 (s, 3H), 1.77 (s, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.7, 157.5, 141.8, 134.9, 133.6, 122.0, 117.9, 117.2, 113.0, 66.8, 25.8, 18.2.

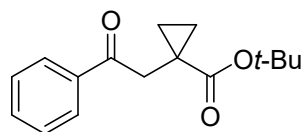
Spectral data matched literature values.<sup>3</sup>

## 3 General Procedure of Photoredox-Catalyzed Cyclopropanation Reactions



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), homoallyl tosylate **1** (0.2 mmol, 1.0 equiv), carboxylic acid **2** (0.36 mmol, 1.8 equiv), PPh<sub>3</sub> (78.7 mg, 0.3 mmol, 1.5 equiv), K<sub>2</sub>HPO<sub>4</sub> (34.8 mg, 0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times, and was charged with degassed CH<sub>3</sub>CN (3 mL). The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowl for 24 h. After the reaction was complete, the reaction solution was quenched by the addition of water (5 mL) and extracted with EtOAc (4 × 10 mL). The organic layers were combined and dried over MgSO<sub>4</sub>, concentrated in vacuum. Flash chromatography over silica gel afforded the product **3**.

## 4 Characterizations of New Compounds

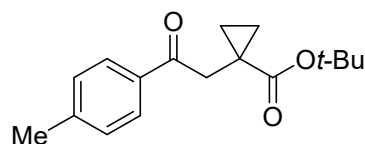


**tert-Butyl 1-(2-oxo-2-phenylethyl)cyclopropanecarboxylate (3a).** Yellow solid (31.8 mg, 61% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.92 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.40 (m, 2H), 3.18 (s, 2H), 1.37–1.32 (m, 2H), 1.35 (s, 9H), 0.78 – 0.73 (m, 2H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 173.5, 137.1, 132.9, 128.5, 127.9, 80.4, 42.9, 27.9, 20.5, 14.7.

**HRMS (ESI)  $[\text{M}+\text{Na}]^+$ :** calculated for  $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Na}^+$ : 283.1305, found 283.1313.

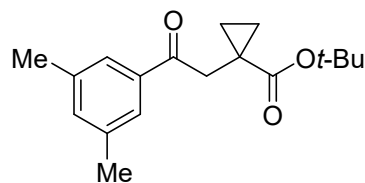


**tert-Butyl 1-(2-(4-methylphenyl)-2-oxoethyl)cyclopropanecarboxylate (3b).** Yellow solid (28.5 mg, 52% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 7.9$  Hz, 2H), 7.24 (d,  $J = 7.9$  Hz, 2H), 3.16 (s, 2H), 2.40 (s, 3H), 1.39 – 1.30 (m, 2H), 1.34 (s, 9H), 0.78 – 0.71 (m, 2H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 173.6, 143.6, 134.7, 129.2, 128.0, 80.3, 42.7, 27.9, 21.6, 20.5, 14.7.

**HRMS (ESI)  $[\text{M}+\text{Na}]^+$ :** calculated for  $\text{C}_{17}\text{H}_{22}\text{O}_3\text{Na}^+$ : 297.1461, found 297.1471.



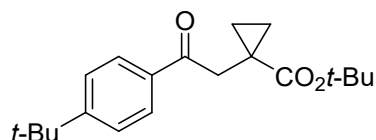
**tert-Butyl 1-(2-(3,5-dimethylphenyl)-2-oxoethyl)cyclopropanecarboxylate (3c).** Yellow solid (35.8 mg, 62% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (s, 2H), 7.18 (s, 1H), 3.16 (s, 2H), 2.36 (s, 6H),

1.35 (s, 9H), 1.35 – 1.31 (m, 2H), 0.76 – 0.71 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 173.6, 138.1, 137.2, 134.5, 125.7, 80.3, 43.0, 27.9, 21.2, 20.5, 14.7.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}^+$ : 311.1618, found 311.1624.



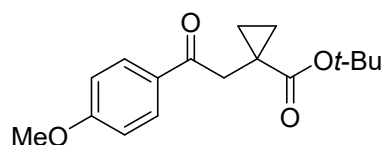
**tert-Butyl 1-(2-(4-tert-butylphenyl)-2-oxoethyl)cyclopropanecarboxylate (3d).**

Yellow solid (42.4 mg, 67% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.6$  Hz, 2H), 7.46 (d,  $J = 8.5$  Hz, 2H), 3.17 (s, 2H), 1.35 (s, 9H), 1.35 – 1.31 (m, 2H), 1.33 (s, 9H), 0.77 – 0.72 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 173.6, 156.5, 134.6, 127.8, 125.4, 80.3, 42.8, 35.0, 31.1, 27.9, 20.5, 14.7.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{Na}^+$ : 339.1931, found 339.1939.



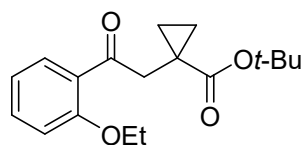
**tert-Butyl 1-(2-(4-methoxyphenyl)-2-oxoethyl)cyclopropanecarboxylate (3e).**

White solid (26.7 mg, 46% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.9$  Hz, 2H), 6.92 (d,  $J = 8.9$  Hz, 2H), 3.86 (s, 3H), 3.14 (s, 2H), 1.34 (s, 9H), 1.34 – 1.31 (m, 2H), 0.78 – 0.71 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 173.7, 163.3, 130.3, 130.1, 113.6, 80.3, 55.4, 42.5, 27.9, 20.6, 14.7.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{17}\text{H}_{22}\text{O}_4\text{Na}^+$ : 313.1410, found 313.1418.



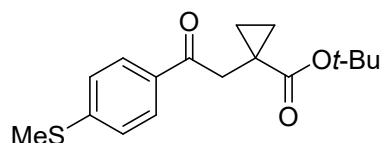
**tert-Butyl 1-(2-(2-ethoxyphenyl)-2-oxoethyl)cyclopropanecarboxylate (3f).** Yellow

oil (32.9 mg, 54% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.71 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.43 – 7.37 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.22 (s, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.36 (s, 9H), 1.30 – 1.26 (m, 2H), 0.74 – 0.68 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 199.9, 173.8, 157.8, 133.1, 130.2, 128.4, 120.4, 112.2, 80.0, 63.9, 48.4, 27.9, 20.8, 14.7(2), 14.7(0).

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>18</sub>H<sub>24</sub>O<sub>4</sub>Na<sup>+</sup>: 327.1567, found 327.1575.

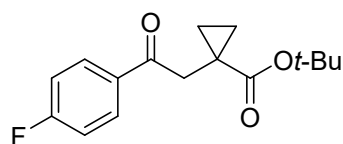


**tert-Butyl 1-(2-(4-(methylsulfanyl)phenyl)-2-oxoethyl)cyclopropanecarboxylate (3g)**. White solid (23.3 mg, 38% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 3.14 (s, 2H), 2.52 (s, 3H), 1.34 (s, 9H), 1.36 – 1.32 (m, 2H), 0.77 – 0.73 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 196.8, 173.6, 145.5, 133.5, 128.3, 125.0, 80.4, 42.6, 27.9, 20.6, 14.8, 14.7.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>NaS<sup>+</sup>: 329.1182, found 329.1187.



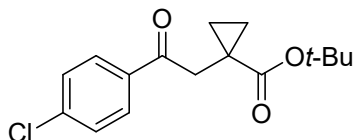
**tert-Butyl 1-(2-(4-fluorophenyl)-2-oxoethyl)cyclopropanecarboxylate (3h)**. Yellow solid (33.4 mg, 60% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.02 – 7.95 (m, 2H), 7.15 – 7.08 (m, 2H), 3.14 (s, 2H), 1.37 – 1.31 (m, 2H), 1.34 (s, 9H), 0.78 – 0.74 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 196.2, 173.5, 165.6 (d, *J* = 130.9 Hz), 133.5 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 9.2 Hz), 115.6 (d, *J* = 21.9 Hz), 80.5, 42.8, 27.9, 20.6, 14.7.

**<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -105.7.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>16</sub>H<sub>19</sub>O<sub>3</sub>NaF<sup>+</sup>: 301.1210, found 301.1220.

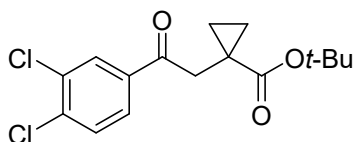


**tert-Butyl 1-(2-(4-chlorophenyl)-2-oxoethyl)cyclopropanecarboxylate (3i).** Yellow solid (36.6 mg, 62% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.6$  Hz, 2H), 7.42 (d,  $J = 8.5$  Hz, 2H), 3.14 (s, 2H), 1.37 – 1.31 (m, 2H), 1.34 (s, 9H), 0.79 – 0.72 (m, 2H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.6, 173.4, 139.3, 135.4, 129.3, 128.8, 80.5, 42.8, 27.9, 20.5, 14.7.

**HRMS (ESI)  $[\text{M}+\text{Na}]^+$ :** calculated for  $\text{C}_{16}\text{H}_{19}\text{O}_3\text{NaCl}^+$ : 317.0915, found 317.0924.

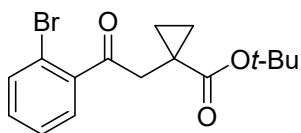


**tert-Butyl 1-(2-(3,4-dichlorophenyl)-2-oxoethyl)cyclopropanecarboxylate (3j).** Yellow solid (46.1 mg, 70% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 2.1$  Hz, 1H), 7.77 (dd,  $J = 8.4, 2.1$  Hz, 1H), 7.53 (d,  $J = 8.3$  Hz, 1H), 3.11 (s, 2H), 1.37 – 1.33 (m, 2H), 1.34 (s, 9H), 0.78 – 0.74 (m, 2H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 173.3, 137.4, 136.6, 133.2, 130.7, 130.0, 127.0, 80.6, 42.8, 27.9, 20.5, 14.7.

**HRMS (ESI)  $[\text{M}+\text{Na}]^+$ :** calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_3\text{NaCl}_2^+$ : 351.0525, found 351.0531.



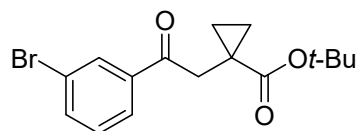
**tert-Butyl 1-(2-(2-bromophenyl)-2-oxoethyl)cyclopropanecarboxylate (3k).** Yellow oil (44.8 mg, 66% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.45 (dd,  $J = 7.6, 1.8$  Hz, 1H), 7.38 – 7.33 (m, 1H), 7.30 – 7.24 (m, 1H), 3.11 (s, 2H), 1.39 (s, 9H), 1.34 –

1.30 (m, 2H), 0.83 – 0.75 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  201.6, 173.3, 141.7, 133.5, 131.3, 128.6, 127.3, 118.4, 80.6, 47.0, 27.9, 20.7, 14.9.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{16}\text{H}_{19}\text{O}_3\text{BrNa}^+$ : 361.0410, found 361.0420.

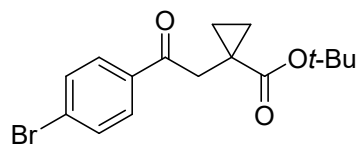


**tert-Butyl 1-(2-(3-bromophenyl)-2-oxoethyl)cyclopropanecarboxylate (3l).** Yellow solid (43.4 mg, 64% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 8.04 (m, 1H), 7.87 (d,  $J = 7.9$  Hz, 1H), 7.67 (d,  $J = 7.9$  Hz, 1H), 7.33 (t,  $J = 7.9$  Hz, 1H), 3.13 (s, 2H), 1.37 – 7.31 (m, 2H), 1.34 (s, 9H), 0.78 – 0.72 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 173.3, 138.8, 135.7, 131.0, 130.1, 126.4, 122.9, 80.5, 42.9, 27.9, 20.5, 14.7.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{16}\text{H}_{19}\text{O}_3\text{NaBr}^+$ : 361.0410, found 361.0419.

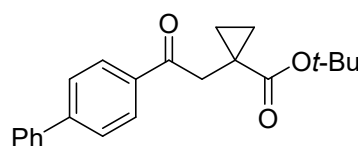


**tert-Butyl 1-(2-(4-bromophenyl)-2-oxoethyl)cyclopropanecarboxylate (3m).** Yellow solid (34.6 mg, 51% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.6$  Hz, 2H), 7.59 (d,  $J = 8.6$  Hz, 2H), 3.13 (s, 2H), 1.37 – 1.30 (m, 2H), 1.35 (s, 9H), 0.79 – 0.71 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.8, 173.4, 135.8, 131.8, 129.4, 128.0, 80.5, 42.8, 27.9, 20.5, 14.7.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{16}\text{H}_{19}\text{O}_3\text{NaBr}^+$ : 361.0410, found 361.0419.

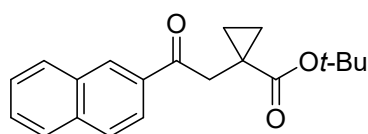


**tert-Butyl 1-(2-oxo-2-(4-phenylphenyl)ethyl)cyclopropanecarboxylate (3n).** White solid (35.7 mg, 53% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.22 (s, 2H), 1.40 – 1.34 (m, 2H), 1.36 (s, 9H), 0.83 – 0.79 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.4, 173.6, 145.5, 139.9, 135.8, 128.9, 128.5, 128.2, 127.2(4), 127.1(7), 80.4, 42.9, 27.9, 20.6, 14.7.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>Na<sup>+</sup>: 359.1618, found 359.1625.



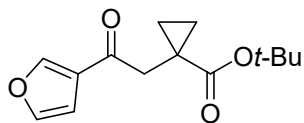
**tert-Butyl 1-(2-(naphthalen-2-yl)-2-oxoethyl)cyclopropanecarboxylate (3o).**

Yellow solid (39.7 mg, 64% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.47 (s, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 8.5 Hz, 2H), 7.62 – 7.52 (m, 2H), 3.33 (s, 2H), 1.40 – 1.37 (m, 2H), 1.35 (s, 9H), 0.83 – 0.79 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.7, 173.6, 135.5, 134.5, 132.5, 129.5, 129.4, 128.4, 128.3, 127.8, 126.7, 123.8, 80.4, 43.0, 27.9, 20.6, 14.8.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>Na<sup>+</sup>: 333.1461, found 333.1470.

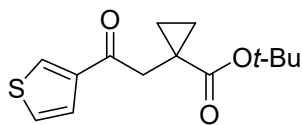


**tert-Butyl 1-(2-(furan-3-yl)-2-oxoethyl)cyclopropanecarboxylate (3p).** Yellow solid (34.5 mg, 69% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.04 (s, 1H), 7.42 (t, *J* = 1.7 Hz, 1H), 6.79 – 6.75 (m, 1H), 2.94 (s, 2H), 1.34 (s, 9H), 1.33 – 1.29 (m, 2H), 0.79 – 0.74 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 192.6, 173.5, 146.9, 144.0, 127.7, 108.6, 80.5, 44.4, 27.9, 20.4, 14.8.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>Na<sup>+</sup>: 273.1097, found 273.1107.

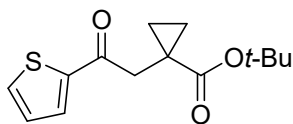


**tert-Butyl 1-(2-oxo-2-(thiophen-3-yl)ethyl)cyclopropanecarboxylate (3q)**. Yellow solid (37.8 mg, 71% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.07 – 8.02 (m, 1H), 7.57 – 7.52 (m, 1H), 7.32 – 7.28 (m, 1H), 3.09 (s, 2H), 1.34 (s, 9H), 1.34 – 1.31 (m, 2H), 0.78 – 0.74 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 192.2, 173.5, 142.3, 131.5, 126.9, 126.2, 80.5, 43.9, 27.8, 20.5, 14.8.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>NaS<sup>+</sup>: 289.0870, found 289.0870.

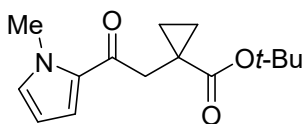


**tert-Butyl 1-(2-oxo-2-(thiophen-2-yl)ethyl)cyclopropanecarboxylate (3r)**. Yellow solid (35.7 mg, 67% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.72 (d, *J* = 3.7 Hz, 1H), 7.61 (d, *J* = 4.9 Hz, 1H), 7.11 (t, *J* = 4.4 Hz, 1H), 3.11 (s, 2H), 1.33 (s, 9H), 1.33 – 1.31 (m, 2H), 0.81 – 0.77 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 190.7, 173.4, 144.3, 133.2, 131.5, 127.9, 80.6, 43.3, 27.8, 20.7, 14.8.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>NaS<sup>+</sup>: 289.0870, found 289.0878.



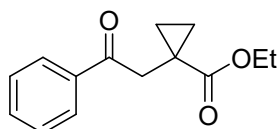
**tert-Butyl 1-(2-(1-methyl-1H-pyrrol-2-yl)-2-oxoethyl)cyclopropanecarboxylate (3s)**. Yellow solid (40.0 mg, 76% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 6.93 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.77 (t, *J* = 2.1 Hz, 1H),

6.09 (dd,  $J = 4.1, 2.5$  Hz, 1H), 3.93 (s, 3H), 3.02 (s, 2H), 1.35 (s, 9H), 1.31 – 1.28 (m, 2H), 0.77 – 0.72 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  188.8, 173.8, 130.6, 130.5, 118.5, 107.7, 80.2, 42.8, 37.6, 27.9, 20.6, 14.5.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}^+$ : 286.1414, found 286.1424.

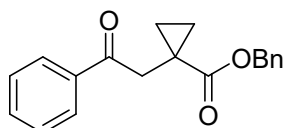


**Ethyl 1-(2-oxo-2-phenylethyl)cyclopropanecarboxylate (3t).** Yellow solid (29.3 mg, 63% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 7.0$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.7$  Hz, 2H), 4.08 (q,  $J = 7.1$  Hz, 2H), 3.24 (s, 2H), 1.45 – 1.40 (m, 2H), 1.14 (t,  $J = 7.1$  Hz, 3H), 0.85 – 0.80 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.7, 174.4, 137.0, 133.0, 128.5, 127.9, 60.7, 42.7, 19.8, 15.0, 14.0.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Na}^+$ : 255.0992, found 255.1001.

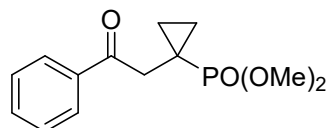


**Benzyl 1-(2-oxo-2-phenylethyl)cyclopropanecarboxylate (3u).** Yellow solid (43.5 mg, 74% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.92 (m, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.8$  Hz, 2H), 7.30 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 5.08 (s, 2H), 3.27 (s, 2H), 1.51 – 1.46 (m, 2H), 0.89 – 0.83 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5, 174.2, 136.8, 136.0, 133.0, 128.5, 128.3, 127.9, 127.7, 66.4, 42.7, 19.8, 15.2.

HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{Na}^+$ : 317.1148, found 317.1157.



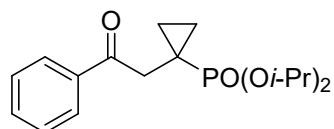
**Dimethyl (1-(2-oxo-2-phenylethyl)cyclopropyl)phosphonate (3v).** Yellow oil (29.0 mg, 54% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 3H), 3.16 (s, 1H), 3.13 (s, 1H), 1.32 – 1.26 (m, 2H), 0.90 – 0.80 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.3, 137.1, 133.2, 128.6, 128.1, 52.8 (d, *J* = 6.4 Hz), 40.7 (d, *J* = 5.4 Hz), 10.6 (d, *J* = 193.8 Hz), 10.3 (d, *J* = 2.7 Hz).

**<sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>)** δ 33.7.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>NaP<sup>+</sup>: 291.0757, found 291.0766.



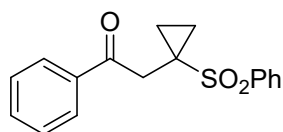
**Dipropan-2-yl(1-(2-oxo-2-phenylethyl)cyclopropyl)phosphonate (3w).** Yellow oil (44.1 mg, 68% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.97 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.69 – 4.58 (m, 2H), 3.15 (s, 1H), 3.12 (s, 1H), 1.27 (d, *J* = 6.2 Hz, 6H), 1.23 (d, *J* = 6.2 Hz, 6H), 1.22 – 1.15 (m, 2H), 0.88 – 0.80 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.7, 137.4, 133.0, 128.5, 128.4, 70.6 (d, *J* = 6.4 Hz), 39.3 (d, *J* = 4.6 Hz), 23.9 (m), 12.7 (d, *J* = 196.0 Hz), 10.0 (d, *J* = 2.7 Hz).

**<sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>)** δ 28.8.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>17</sub>H<sub>25</sub>O<sub>4</sub>NaP<sup>+</sup>: 347.1383, found 347.1392.



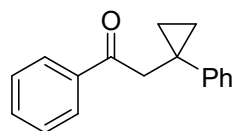
**1-Phenyl-2-(1-(phenylsulfonyl)cyclopropyl)ethenone (3x).** Yellow solid (28.2 mg,

47% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.85 – 7.82 (m, 2H), 7.77 – 7.72 (m, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 3.41 (s, 2H), 1.76 – 1.70 (m, 2H), 1.15 – 1.08 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 195.2, 138.4, 136.5, 133.6(3), 133.5(6), 129.1, 128.8, 128.7, 128.2, 38.7, 37.6, 11.5.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>NaS<sup>+</sup>: 323.0712, found 323.0720.

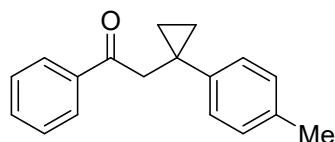


**1-Phenyl-2-(1-phenylcyclopropyl)ethanone (3y)**. Yellow solid (20.8 mg, 44% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.85 – 7.79 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 3.31 (s, 2H), 1.04 – 0.99 (m, 2H), 0.94 – 0.89 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 198.6, 144.8, 137.3, 132.8, 128.6, 128.4, 128.1, 128.0, 126.1, 48.1, 22.1, 13.4.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>17</sub>H<sub>16</sub>ONa<sup>+</sup>: 259.1093, found 259.1091.

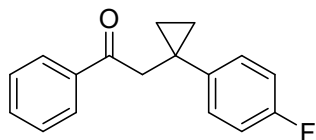


**2-(1-(4-Methylphenyl)cyclopropyl)-1-phenylethanone (3z)**. Yellow oil (21.0 mg, 42% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.85 – 7.80 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.29 (s, 2H), 2.27 (s, 3H), 1.00 – 0.96 (m, 2H), 0.89 – 0.86 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 198.6, 141.8, 137.4, 135.6, 132.8, 128.8, 128.6, 128.4, 128.1, 48.2, 21.6, 20.9, 13.3.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>18</sub>H<sub>18</sub>ONa<sup>+</sup>: 273.1250, found 273.1259.



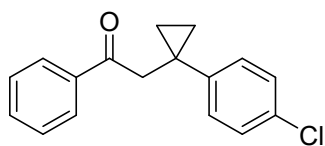
**2-(1-(4-Fluorophenyl)cyclopropyl)-1-phenylethanone (3aa).** White solid (27.5 mg, 54% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.83 – 7.78 (m, 2H), 7.51 (t,  $J$  = 7.4 Hz, 1H), 7.39 (t,  $J$  = 7.8 Hz, 2H), 7.35 – 7.29 (m, 2H), 6.92 – 6.87 (m, 2H), 3.27 (s, 2H), 0.99 – 0.93 (m, 2H), 0.93 – 0.87 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  198.5, 161.2 (d,  $J$  = 244.8 Hz), 140.5 (d,  $J$  = 3.2 Hz), 137.2, 132.9, 130.5 (d,  $J$  = 8.1 Hz), 128.5, 128.0, 114.8 (d,  $J$  = 21.7 Hz), 48.4, 21.6, 13.3.

**<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)**  $\delta$  -116.8.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>17</sub>H<sub>15</sub>ONaF<sup>+</sup>: 277.0999, found 277.1003.

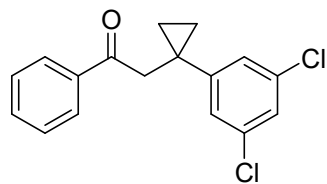


**2-(1-(4-Chlorophenyl)cyclopropyl)-1-phenylethanone (3ab).** Yellow solid (28.2 mg, 52% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.84 – 7.80 (m, 2H), 7.52 (t,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 2H), 3.29 (s, 2H), 1.00 – 0.96 (m, 2H), 0.92 – 0.89 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  198.2, 143.3, 137.2, 133.0, 131.7, 130.2, 128.5, 128.2, 128.0, 48.1, 21.4, 13.5.

**HRMS (ESI) [M+H]<sup>+</sup>:** calculated for C<sub>17</sub>H<sub>16</sub>OCl<sup>+</sup>: 271.0884, found 271.0885.

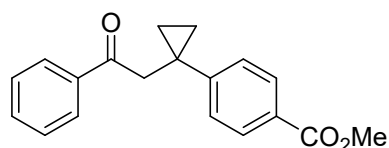


**2-(1-(3,5-Dichlorophenyl)cyclopropyl)-1-phenylethanone (3ac).** Yellow oil (42.1 mg, 69% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.87 – 7.82 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 7.24 (s, 1H), 7.23 (s, 1H), 7.13 (t,  $J$  = 1.9 Hz, 1H), 3.31 (s, 2H), 1.03 – 1.00 (m, 2H), 0.93 – 0.90 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  197.6, 148.4, 136.9, 134.4, 133.1, 128.6, 127.9, 127.3, 126.3, 47.7, 21.5, 13.8.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>17</sub>H<sub>14</sub>ONaCl<sub>2</sub><sup>+</sup>: 327.0314, found 327.0322.

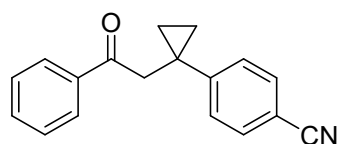


**Methyl 4-(1-(2-oxo-2-phenylethyl)cyclopropyl)benzoate (3ad).** Yellow solid (43.0 mg, 73% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.90 (d,  $J$  = 8.4 Hz, 2H), 7.86 – 7.82 (m, 2H), 7.52 (t,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.8 Hz, 2H), 7.36 (d,  $J$  = 8.5 Hz, 2H), 3.87 (s, 3H), 3.36 (s, 2H), 1.09 – 1.05 (m, 2H), 0.98 – 0.94 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  198.0, 167.0, 150.3, 137.0, 133.0, 129.5, 128.5, 128.0, 127.9, 127.7, 51.9, 47.5, 21.6, 14.3.

**HRMS (ESI) [M+Na]<sup>+</sup>:** calculated for C<sub>19</sub>H<sub>18</sub>O<sub>3</sub>Na<sup>+</sup>: 317.1148, found 317.1157.

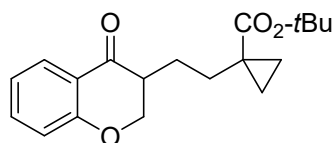


**4-(1-(2-Oxo-2-phenylethyl)cyclopropyl)benzotrile (3ae).** Yellow solid (30.3 mg, 58% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.88 – 7.82 (m, 2H), 7.57 – 7.49 (m, 3H), 7.45 – 7.38 (m, 4H), 3.37 (s, 2H), 1.10 – 1.05 (m, 2H), 1.01 – 0.97 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.7, 150.5, 136.8, 133.2, 132.0, 128.9, 128.6, 127.9, 119.0, 109.6, 47.5, 21.6, 14.5.

**HRMS (ESI) [M+H]<sup>+</sup>**: calculated for C<sub>18</sub>H<sub>16</sub>NO<sup>+</sup>: 262.1226, found 262.1219.

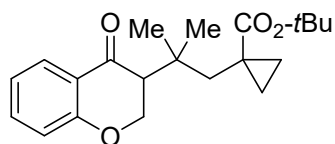


**tert-Butyl** **1-(2-(4-oxo-3,4-dihydro-2H-chromen-3-yl)ethyl)cyclopropanecarboxylate (5a)**. Yellow solid (47.4 mg, 75% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.04 – 6.97 (m, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 4.53 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.28 (dd, *J* = 11.4, 8.7 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.07 – 1.97 (m, 1H), 1.71 – 1.65 (m, 2H), 1.57 – 1.47 (m, 1H), 1.39 (s, 9H), 1.16 – 1.11 (m, 2H), 0.70 – 0.61 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 194.4, 174.1, 161.4, 135.7, 127.4, 121.3, 120.6, 117.6, 80.2, 70.6, 45.9, 31.6, 28.0, 24.6, 24.0, 15.6, 15.2.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>19</sub>H<sub>24</sub>O<sub>4</sub>Na<sup>+</sup>: 339.1567, found 339.1572.



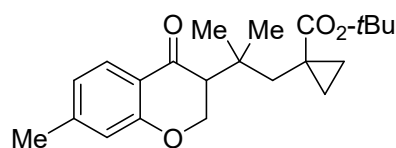
**tert-Butyl** **1-(2-methyl-2-(4-oxo-3,4-dihydro-2H-chromen-3-yl)propyl)cyclopropanecarboxylate (5b)**. Yellow oil (50.9 mg, 74% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.86 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 – 7.40 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.68 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.52 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.48 (t, *J* = 4.8 Hz, 1H), 2.05 (d, *J* = 14.7 Hz, 1H), 1.77 (d, *J* = 14.7 Hz, 1H), 1.40 (s, 9H), 1.19 – 1.15 (m, 4H), 1.06 (s, 3H), 1.06 – 1.01 (m, 1H), 0.86 – 0.79 (m, 1H), 0.71 – 0.62 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 194.1, 174.3, 161.3, 135.6, 127.1, 122.4, 121.2,

117.5, 80.1, 68.8, 54.5, 42.9, 37.7, 27.8, 26.6, 26.4, 22.2, 15.0, 14.1.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>Na<sup>+</sup>: 367.1880, found 367.1887.

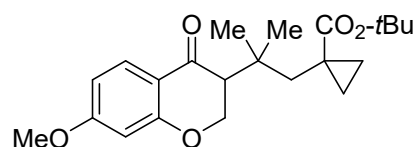


**tert-Butyl**                      **1-(2-methyl-2-(7-methyl-4-oxo-3,4-dihydro-2H-chromen-3-yl)propyl)cyclopropanecarboxylate (5c)**. Yellow oil (48.8 mg, 68% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.75 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.71 (s, 1H), 4.67 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.49 (dd, *J* = 12.1, 4.3 Hz, 1H), 2.43 (t, *J* = 4.7 Hz, 1H), 2.34 (s, 3H), 2.05 (d, *J* = 14.7 Hz, 1H), 1.77 (d, *J* = 14.7 Hz, 1H), 1.41 (s, 9H), 1.19 – 1.12 (m, 4H), 1.05 (s, 3H), 1.04 – 0.98 (m, 1H), 0.83 – 0.77 (m, 1H), 0.67 – 0.61 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7, 174.3, 161.4, 147.0, 127.0, 122.6, 120.2, 117.5, 80.1, 68.8, 54.4, 42.9, 37.7, 27.8, 26.6, 26.4, 22.2, 21.9, 15.0, 14.1.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>Na<sup>+</sup>: 381.2036, found 381.2046.

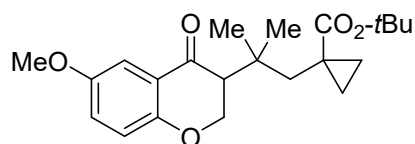


**tert-Butyl**                      **1-(2-(7-methoxy-4-oxo-3,4-dihydro-2H-chromen-3-yl)-2-methylpropyl)cyclopropanecarboxylate (5d)**. Yellow oil (36.7 mg, 49% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.80 (d, *J* = 8.8 Hz, 1H), 6.55 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.35 (d, *J* = 2.3 Hz, 1H), 4.68 (dd, *J* = 12.1, 4.7 Hz, 1H), 4.49 (dd, *J* = 12.1, 4.4 Hz, 1H), 3.82 (s, 3H), 2.39 (t, *J* = 4.5 Hz, 1H), 2.05 (d, *J* = 14.6 Hz, 1H), 1.76 (d, *J* = 14.7 Hz, 1H), 1.40 (s, 9H), 1.19 – 1.12 (m, 4H), 1.05 (s, 3H), 1.03 – 0.97 (m, 1H), 0.84 – 0.77 (m, 1H), 0.67 – 0.60 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 192.6, 174.3, 165.7, 163.2, 128.8, 116.3, 109.7, 100.3, 80.0, 69.2, 55.5, 54.1, 42.9, 37.8, 27.8, 26.6, 26.4, 22.2, 15.0, 14.1.

**HRMS (ESI) [M+H]<sup>+</sup>**: calculated for C<sub>22</sub>H<sub>31</sub>O<sub>5</sub><sup>+</sup>: 375.2166, found 375.2174.

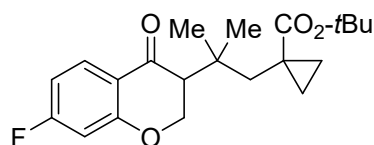


**tert-Butyl**                      **1-(2-(6-methoxy-4-oxo-3,4-dihydro-2H-chromen-3-yl)-2-methylpropyl)cyclopropanecarboxylate (5e)**. Yellow oil (40.0 mg, 53% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.30 (d, *J* = 3.2 Hz, 1H), 7.05 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 4.65 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.47 (dd, *J* = 12.1, 4.3 Hz, 1H), 3.79 (s, 3H), 2.49 – 2.42 (m, 1H), 2.05 (d, *J* = 14.7 Hz, 1H), 1.77 (d, *J* = 14.7 Hz, 1H), 1.41 (s, 9H), 1.19 – 1.13 (m, 4H), 1.06 (s, 3H), 1.03 – 0.98 (m, 1H), 0.83 – 0.77 (m, 1H), 0.68 – 0.61 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 194.1, 174.3, 156.1, 154.0, 124.8, 122.1, 118.8, 107.5, 80.1, 68.9, 55.7, 54.3, 42.9, 37.8, 27.8, 26.7, 26.4, 22.2, 15.0, 14.1.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>22</sub>H<sub>30</sub>O<sub>5</sub>Na<sup>+</sup>: 397.1986, found 397.1994.



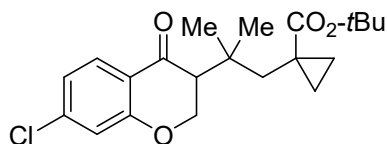
**tert-Butyl**                      **1-(2-(7-fluoro-4-oxo-3,4-dihydro-2H-chromen-3-yl)-2-methylpropyl)cyclopropanecarboxylate (5f)**. Yellow oil (58.7 mg, 81% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.88 (dd, *J* = 8.8, 6.6 Hz, 1H), 6.71 (td, *J* = 8.5, 2.4 Hz, 1H), 6.60 (dd, *J* = 9.8, 2.4 Hz, 1H), 4.71 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.53 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.46 (t, *J* = 4.7 Hz, 1H), 2.04 (d, *J* = 14.7 Hz, 1H), 1.75 (d, *J* = 14.7 Hz, 1H), 1.40 (s, 9H), 1.19 – 1.13 (m, 4H), 1.06 – 0.99 (m, 4H), 0.82 – 0.75 (m, 1H), 0.67 – 0.61 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 192.6, 174.2, 167.2 (d, *J* = 256.3 Hz), 162.9 (d, *J* = 13.6 Hz), 129.6 (d, *J* = 11.0 Hz), 119.3 (d, *J* = 2.7 Hz), 109.6 (d, *J* = 22.7 Hz), 104.2 (d, *J* = 24.5 Hz), 80.1, 69.3, 54.2, 42.9, 37.7, 27.8, 26.6, 26.4, 22.2, 15.0, 14.1.

**<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -101.3.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>21</sub>H<sub>27</sub>O<sub>4</sub>NaF<sup>+</sup>: 385.1786, found 385.1794.

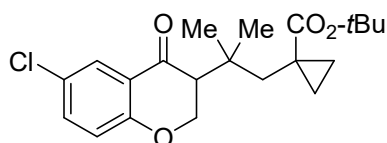


***tert*-Butyl**                      **1-(2-(7-chloro-4-oxo-3,4-dihydro-2*H*-chromen-3-yl)-2-methylpropyl)cyclopropanecarboxylate (5g)**. Yellow oil (54.6 mg, 72% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.80 (d, *J* = 8.4 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 4.71 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.52 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.03 (d, *J* = 14.7 Hz, 1H), 1.74 (d, *J* = 14.7 Hz, 1H), 1.40 (s, 9H), 1.19 – 1.13 (m, 4H), 1.06 – 0.99 (m, 4H), 0.82 – 0.75 (m, 1H), 0.67 – 0.61 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.0, 174.2, 161.7, 141.4, 128.4, 122.0, 120.9, 117.7, 80.1, 69.2, 54.3, 42.8, 37.8, 27.8, 26.6, 26.4, 22.2, 15.0, 14.1.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>21</sub>H<sub>27</sub>O<sub>4</sub>NaCl<sup>+</sup>: 401.1490, found 401.1497.

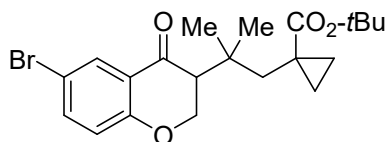


***tert*-Butyl**                      **1-(2-(6-chloro-4-oxo-3,4-dihydro-2*H*-chromen-3-yl)-2-methylpropyl)cyclopropanecarboxylate (5h)**. Yellow oil (48.5 mg, 64% yield).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.82 (d, *J* = 2.7 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.69 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.51 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.49 – 2.45 (m, 1H), 2.03 (d, *J* = 14.7 Hz, 1H), 1.74 (d, *J* = 14.8 Hz, 1H), 1.40 (s, 9H), 1.19 – 1.13 (m, 4H), 1.06 – 1.00 (m, 4H), 0.82 – 0.73 (m, 1H), 0.67 – 0.61 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 192.9, 174.2, 159.8, 135.4, 126.7, 126.5, 123.1, 119.3, 80.1, 68.9, 54.2, 42.8, 37.8, 27.8, 26.6, 26.4, 22.2, 15.0, 14.1.

**HRMS (ESI) [M+Na]<sup>+</sup>**: calculated for C<sub>21</sub>H<sub>27</sub>O<sub>4</sub>NaCl<sup>+</sup>: 401.1490, found 401.1499.



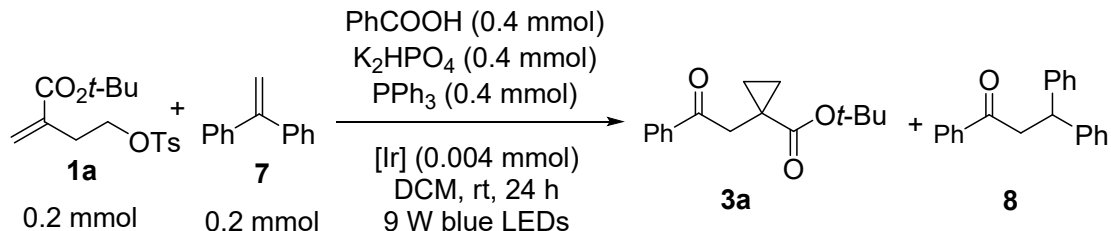
**tert-Butyl** **1-(2-(6-bromo-4-oxo-3,4-dihydro-2H-chromen-3-yl)-2-methylpropyl)cyclopropanecarboxylate (5i)**. Yellow oil (59.3 mg, 70% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 2.5$  Hz, 1H), 7.50 (dd,  $J = 8.8, 2.6$  Hz, 1H), 6.82 (d,  $J = 8.7$  Hz, 1H), 4.69 (dd,  $J = 12.3, 5.3$  Hz, 1H), 4.50 (dd,  $J = 12.3, 4.4$  Hz, 1H), 2.47 (t,  $J = 4.8$  Hz, 1H), 2.03 (d,  $J = 14.7$  Hz, 1H), 1.74 (d,  $J = 14.6$  Hz, 1H), 1.40 (s, 9H), 1.19 – 1.12 (m, 4H), 1.06 – 1.00 (m, 4H), 0.81 – 0.75 (m, 1H), 0.67 – 0.61 (m, 1H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  192.8, 174.2, 160.2, 138.2, 129.6, 123.6, 119.6, 113.9, 80.1, 68.9, 54.2, 42.8, 37.8, 27.8, 26.6, 26.4, 22.2, 15.0, 14.1.

**HRMS (ESI)  $[\text{M}+\text{Na}]^+$** : calculated for  $\text{C}_{21}\text{H}_{27}\text{O}_4\text{NaBr}$ : 445.0985, found 445.0990.

## 5 Mechanistic Study



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (4.5 mg, 0.004 mmol), homoallyl tosylate **1a** (65.2 mg, 0.2 mmol), 1,1-diphenylethylene **7** (36 mg, 0.2 mmol), benzoic acid **2a** (48.8 mg, 0.4 mmol),  $\text{PPh}_3$  (157.4 mg, 0.4 mmol),  $\text{K}_2\text{HPO}_4$  (69.6 mg, 0.4 mmol) were added. The tube was evacuated and filled with nitrogen for 3 times, and was charged with degassed  $\text{CH}_2\text{Cl}_2$  (4 mL). The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h. After the reaction was complete, the reaction solution was quenched by the addition of water (5 mL) and extracted with EtOAc ( $4 \times 10$  mL). The organic layers were combined and dried over  $\text{MgSO}_4$ , concentrated in vacuum. Flash

chromatography over silica gel afforded the product **3a** (15.6 mg, 30% yield) and **8** (13.7 mg, 24% yield).

**1,3,3-Triphenylpropan-1-one (8).**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.94 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.47 – 7.42 (m, 2H), 7.27 (d, *J* = 4.4 Hz, 8H), 7.20 – 7.15 (m, 2H), 4.83 (t, *J* = 7.3 Hz, 1H), 3.75 (d, *J* = 7.3 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 198.0, 144.1, 137.1, 133.1, 128.6, 128.5, 128.0, 127.8, 126.4, 45.9, 44.7.

Spectral data matched literature values.<sup>4</sup>

## 6 References

[1] W. Luo, Y. Yang, Y. Fang, X. Zhang, X. Jin, G. Zhao, L. Zhang, Y. Li, W. Zhou, T. Xia and B. Chen, *Adv. Synth. Catal.*, 2019, **361**, 4215.

[2] (a) M. Fischer, K. Kloiber, J. Häusler, K. Ledolter, R. Konrat and W. Schmid, *ChemBioChem*, 2007, **8**, 610; (b) H. Li, Y. Zhang, X. Yang, Z. Deng, Z. Zhu, P. Zhou, X. Ouyang, Y. Yuan, X. Chen, L. Yang, M. Liu and C. Shu, *Angew. Chem. Int. Ed.*, 2023, **62**, e202300159; (c) Z. Tian, D. He, J. Liang, Q. Liu, M. Ye, L. Hai, G. Lv and Y. Wu, *Adv. Synth. Catal.*, 2025, **367**, e70045; (d) C.-J. Li, M.-Y. Liu, Z.-L. Wei and W.-W. Liao, *J. Org. Chem.*, 2024, **89**, 18769; (e) X. Ouyang, B. Shi, Y. Zhao, Z. Zhu,

Y. Yang and C. Shu, *Chem. Sci.*, 2024, **15**, 11092.

[3] Y. Ding, S. Yu, M. Ren, J. Lu, Q. Fu, Z. Zhang, Q. Wang, J. Bai, N. Hao, L. Yang, S. Wei, D. Yi and J. Wei, *Front. Chem.*, 2022, **10**, 1059792.

[4] A. Devineau, G. Pousse, C. Taillier, J. Blanchet, J. Rouden and V. Dalla, *Adv. Synth. Catal.*, 2010, **352**, 2881.

# 7 NMR Spectra of New Compounds

