Cs$_2$CO$_3$-promoted defluorination and functionalization of $\alpha$-CF$_3$ carbonyl compounds in the presence of N-, O-, and/or S-nucleophiles

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General Experimental:
The chemicals and reagents were purchased from Acros, Alfa Aesar, and National Chemical Reagent Group Co. Ltd., P. R. China, and used without further purification. Anhydrous solvents (THF, MeOH, DMF, DCM, and CH$_3$CN) used in the reactions were dried and freshly distilled before use. Petroleum ether (PE) used had a boiling range of 60–90 °C. All the reactions were carried out under Ar atmosphere, otherwise stated else. Oxygen and/or moisture sensitive solids and liquids were transferred appropriately. Concentration of solutions in vacuo was accomplished using a rotary evaporator fitted with a water aspirator. Residual solvents were removed under high vacuum (0.1-0.2 mm Hg). The progress of the reactions was monitored by TLC (silica-coated glass plates) and visualized under UV light, and by using iodine, ceric ammonium molybdate stain or phosphomolybdic acid. Melting points were measured on a SGW X-4 microscopy melting point apparatus without correction. $^1$H NMR and $^{13}$C NMR spectra were recorded either on a 400 MHz Varian Instrument at 25 °C or 600 MHz Bruke Instrument at 25 °C, using TMS as an internal standard, respectively. Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, and m for multiplet. Coupling constants (J) are reported in Hertz. $^{13}$C NMR spectra were completely hetero-decoupled and measured at 150 MHz. HRMS spectra were recorded on Finnigan- Mat-95 mass spectrometer, equipped with ESI source. Single crystal X-ray diffraction measurements were performed with a diffractometer working with graphite-monochromated Cu Kα radiation.

Experimental Procedures:
The preparation of compound 3 or 4 in Table 2:

![Chemical reaction](image)

Method a: To a solution of 3,3,3-trifluoropropanoic acid derivatives (1.0 mmol) in THF (5 mL) was added the mono-dentate S-, O-, and N-nucleophiles (2.0 mmol) and Cs$_2$CO$_3$ (2.0 mmol) at 0 °C and then stirred for 2 h at under Ar. The reaction was ended with a saturated aqueous ammonium chloride solution (10 mL) and extracted with CH$_2$Cl$_2$ (DCM, 20 mL*3). After workup, the product was purified by flash chromatography (Petroleum Ether/Ethyl Acetate, PE/EA).

Method c: To a solution of ethyl 3,3,3-trifluoropropanoate (1.0 mmol) in THF (5 mL), was added the mono-dentate S-, O-, and N-nucleophiles (2.0 mmol) and Cs$_2$CO$_3$ (2.0 mmol) at 45 °C for 2 h at under Ar. The reaction was ended with a saturated aqueous ammonium chloride solution (10 mL) and extracted with DCM (20 mL*3). After workup, the product was purified by flash chromatography (PE/EA).

Method d: To a solution of ethyl 3,3,3-trifluoropropanoate (1.0 mmol) in anhydrous DMSO (5 mL), was added the mono-dentate S-, O-, and N-nucleophiles (2.0 mmol) and Cs$_2$CO$_3$ (2.0 mmol) at 45 °C for 2 h at under Ar. The reaction was ended with a saturated aqueous ammonium chloride solution (10 mL) and extracted with DCM (20 mL*3). After workup, the product was purified by flash chromatography (PE/EA).
The preparation of the compounds in Table 3:

To a solution of ethyl 3,3,3-trifluoropropanoate (1.0 mmol) in THF (5 mL), was added the bidentate nucleophiles (1.0 mmol) and Cs$_2$CO$_3$ (2.0 mmol) at 45 °C for 2 h at under Ar. The reaction was ended with a saturated aqueous ammonium chloride solution (10 mL) and extracted with DCM (20 mL*3). After workup, the product was purified by flash chromatography (PE /EA).
Spectral data of all compounds:

*Ethyl 3,3-bis(p-tolylthio)acrylate (3aa).*

![Chemical structure of 3aa](image)

The resultant residue was purified by flash column chromatography (PE/EA=80/1) as a white solid. \(R_f = 0.20\) (PE/EA = 80/1), \(\text{Mp} 85-86 ^\circ\text{C}\).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 (d, \(J = 7.7\) Hz, 2H), 7.09 – 6.88 (m, 6H), 5.03 (s, 1H), 3.92 (q, \(J = 7.1\) Hz, 2H), 2.18 (s, 3H), 2.12 (s, 3H), 1.04 – 0.97 (m, 3H).

\(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 165.4, 163.0, 140.5, 137.0, 135.4, 130.7, 129.6, 126.7, 125.5, 107.1, 59.8, 21.5, 21.4, 14.4.

\(\text{HRMS-ESI (m/z)}: \text{[M+H]}^+\) caled for C\(_{19}\)H\(_{21}\)O\(_2\)S\(_2\) 345.0978; found 345.0973.

*Ethyl 3,3-bis(m-tolylthio)acrylate (3ab).*

![Chemical structure of 3ab](image)

The resultant residue was purified by flash column chromatography (PE/EA=100/1) as a pale yellow liquid. \(R_f = 0.20\) (PE/EA = 100/1).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (d, \(J = 7.5\) Hz, 2H), 7.23 – 6.98 (m, 6H), 5.21 (d, \(J = 1.4\) Hz, 1H), 4.03 (qd, \(J = 7.1, 1.4\) Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 1.12 (td, \(J = 7.1, 1.4\) Hz, 4H).

\(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 165.5, 161.9, 139.8, 138.7, 137.5, 135.8, 134.1, 132.4, 130.9, 130.9, 130.2, 129.7, 129.0, 128.7, 108.4, 60.1, 21.4, 21.3, 14.5.

\(\text{HRMS-ESI (m/z)}: \text{[M+H]}^+\) caled for C\(_{19}\)H\(_{21}\)O\(_2\)S\(_2\) 345.0978; found 345.0969.

*Ethyl 3,3-bis(o-tolylthio)acrylate (3ac)*

![Chemical structure of 3ac](image)
The resultant residue was purified by flash column chromatography (PE/EA=60/1) as a white solid. $R_f = 0.20$ (PE/EA = 60/1), $M_p$ 84-85°C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J = 7.7$ Hz, 1H), 7.47 – 7.08 (m, 7H), 5.11 (s, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.59 (s, 3H), 2.32 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.7, 160.9, 144.6, 143.0, 138.2, 136.7, 131.4, 130.9, 130.9, 130.6, 129.4, 128.8, 127.4, 126.6, 106.6, 60.0, 21.4, 20.4, 14.5.

HRMS-ESI ($m/z$): [M + H]$^+$ calcd for C$_{19}$H$_{21}$O$_2$S$_2$ 345.0978; found 345.0974.

Ethyl 3,3-bis((4-methoxyphenyl)thio)acrylate (3ad)

The resultant residue was purified by flash column chromatography (PE/EA=20/1) as a pale yellow liquid. $R_f = 0.21$ (PE/EA = 20/1).

$^1$H NMR (400 MHz, CDCl$_3$) $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.69 – 7.57 (m, 2H), 7.30 (d, $J = 8.7$ Hz, 2H), 6.99 – 6.84 (m, 4H), 5.14 (s, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.83 (d, $J = 9.8$ Hz, 6H), 1.23 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.7, 164.7, 161.5, 161.2, 138.9, 137.4, 120.8, 119.7, 115.6, 114.5, 106.5, 60.0, 55.5, 14.6.

HRMS-ESI ($m/z$): [M + H]$^+$ calcd for C$_{19}$H$_{21}$O$_4$S$_2$ 377.0876; found 377.0868.

Ethyl 3,3-bis((4-nitrophenyl)thio)acrylate (3ae)
The resultant residue was purified by flash column chromatography (PE/EA=80/1) as a white foamy solid. $R_f=0.20$ (PE/EA = 80/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 – 8.08 (m, 4H), 7.65 – 7.55 (m, 2H), 7.40 (dd, $J$ = 8.9, 2.1 Hz, 2H), 6.10 (s, 1H), 4.23 (q, $J$ = 7.1 Hz, 6H), 1.30 (t, $J$ = 7.1 Hz, 5H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 164.4, 151.4, 148.3, 147.9, 139.9, 138.8, 135.6, 132.8, 127.0, 124.5, 124.2, 123.6, 119.7, 61.1, 14.4.

HRMS-ESI ($m/z$): [M + H]$^+$ calcld for C$_{17}$H$_{15}$N$_2$O$_6$S$_2$ 407.0372; found 407.0378.

Ethyl 3,3-bis((4-chlorophenyl)thio)acrylate (3af)

The resultant residue was purified by flash column chromatography (PE/EA=100/1) as a pale yellow liquid. $R_f=0.20$ (PE/EA = 100/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 – 7.44 (d, $J$ = 8.0 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.31 – 7.21 (d, $J$ = 8.0 Hz, 2H), 5.37 (s, 1H), 4.15 (q, $J$ = 7.2 Hz, 2H), 1.24 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.2, 159.6, 138.0, 136.8, 136.6, 136.3, 130.2, 129.2, 128.8, 127.7, 110.1, 60.3, 14.5.

HRMS-ESI ($m/z$): [M + H]$^+$ calcld for C$_{17}$H$_{15}$Cl$_2$O$_2$S$_2$ 384.9885; found 384.9887.

Ethyl 3,3-bis(butylthio)acrylate (3ag)

The resultant residue was purified by flash column chromatography (PE/EA=100/1) as a clear liquid. $R_f=0.21$ (PE/EA = 100/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.63 (s, 1H), 4.17 (q, $J$ = 7.2 Hz, 2H), 3.02 (t, $J$ = 6.8 Hz, 2H), 2.87 (t, $J$ = 6.8 Hz, 2H), 1.79 – 1.58 (m, 4H), 1.47 (m, 4H), 1.28 (tt, $J$ = 7.6, 1.7 Hz, 3H), 0.95 (qd, $J$ = 7.6, 3.6 Hz, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.3, 160.6, 106.3, 59.9, 33.8, 31.5, 31.4, 29.64, 22.3, 22.2, 14.7, 13.8, 13.8.

HRMS-ESI ($m/z$): [M + H]$^+$ calcld for C$_{13}$H$_{25}$O$_2$S$_2$ 277.1291; found 277.1286.
**Benzyl 3,3-bis(p-tolylthio)acrylate (3ba)**

The resultant residue was purified by flash column chromatography (PE/EA=60/1) as a white solid. \( R_f = 0.25 \) (PE/EA = 60/1). \( \text{Mp} \) 123-124°C.

\({}^{1}\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.59 (dd, \( J = 8.1, 2.2 \text{ Hz}, 2\text{H} \)), 7.40 – 7.06 (m, 11H), 5.24 (s, 1H), 5.11 (s, 2H), 2.40 (s, 3H), 2.34 (s, 3H).

\({}^{13}\text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 164.6, 163.5, 140.0, 139.9, 136.4, 135.7, 134.8, 130.1, 129.0, 127.9, 127.9, 125.8, 124.8, 105.9, 65.1, 20.9, 20.7.

**HRMS-ESI \( (m/z) \):** \([M + H]^+\) calcd for C\(_{24}\)H\(_{23}\)O\(_2\)S\(_2\) 407.1134; found 407.1130.

**Naphthalen-2-yl 3,3-bis(p-tolylthio)acrylate (3ca)**

The resultant residue was purified by flash column chromatography (PE/EA=20/1) as a white solid. \( R_f = 0.20 \) (PE/EA = 20/1). \( \text{Mp} \) 121-122°C.

\({}^{1}\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.75 (dd, \( J = 22.1, 8.0 \text{ Hz}, 2\text{H} \)), 7.52 – 7.45 (m, 2H), 7.41 (d, \( J = 5.5 \text{ Hz} \), 1H), 7.24 – 7.16 (m, 4H), 7.18 – 7.06 (m, 6H), 5.49 (s, 1H), 2.32 (s, 3H), 2.28 (s, 3H).

\({}^{13}\text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 167.6, 164.0, 148.7, 141.1, 141.0, 137.2, 135.8, 134.0, 131.5, 131.1, 123.0, 129.3, 127.9, 127.8, 126.6, 125.6, 125.4, 121.7, 118.8, 105.5, 21.7, 21.6.

**HRMS-ESI \( (m/z) \):** \([M + H]^+\) calcd for C\(_{27}\)H\(_{25}\)O\(_2\)S\(_2\) 443.1134; found 443.1142.

**3,3,3-Trifluoro-N-methyl-N-(p-tolyl)propenamide (3da)**
The resultant residue was purified by flash column chromatography (PE/EA=15/1) as a white solid. $R_f = 0.20$ (PE/EA = 15/1). \textbf{Mp} 144-145°C.

$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 7.7$ Hz, 2H), 7.11 (d, $J = 7.7$ Hz, 2H), 6.89 (m, 4H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.73 (d, $J = 7.6$ Hz, 2H), 4.98 (s, 1H), 3.15 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 165.5, 157.4, 141.5, 140.2, 139.5, 137.0, 135.3, 130.1, 129.9, 129.6, 127.5, 127.0, 110.2, 36.9, 21.6, 21.5, 21.3.

\textbf{HRMS-ESI} (m/z): [M + H]$^+$ calcd for C$_{24}$H$_{24}$NOS$_2$ 406.1294; found 406.1319.

\textit{N-(p-tolyl)-3,3-bis(p-tolylthio)acrylamide (3fa).}

The resultant residue was purified by flash column chromatography (PE/EA=8/1) as a white solid. $R_f = 0.21$ (PE/EA = 8/1). \textbf{Mp} 116-117°C.

$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.6$ Hz, 2H), 7.39 (s, 2H), 7.25 (dd, $J = 35.3$, 7.6 Hz, 6H), 7.06 (d, $J = 8.3$ Hz, 2H), $\delta$ 5.30 (s, 1H), 2.39 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 163.2, 158.0, 140.5, 136.4, 135.8, 135.6, 133.6, 130.8, 129.8, 129.6, 127.5, 119.7, 112.4, 21.6, 21.6, 21.1.

\textbf{HRMS-ESI} (m/z): [M + H]$^+$ calcd for C$_{24}$H$_{24}$NOS$_2$ 406.1294; found 406.1319.

\textit{Ethyl 3,3-bis(p-tolyloxy)acrylate (3ai)}
The resultant residue was purified by flash column chromatography (PE/EA=40/1) as a clear liquid. $R_f = 0.20$ (PE/EA = 40/1).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.21 – 7.03 (m, 6H), 6.93 (d, $J = 8.3$ Hz, 2H), 4.49 (s, 1H), 4.10 (q, $J = 7.1$ Hz, 2H), 2.33 – 2.32 (m, 6H), 1.20 (t, $J = 7.1$ Hz, 3H).

**13C NMR** (150 MHz, CDCl$_3$) δ 166.4, 166.1, 151.9, 150.5, 136.1, 134.4, 130.7, 130.2, 120.6, 119.0, 80.8, 59.8, 21.1, 21.0, 14.6.

**HRMS-ESI** ($m/z$): [M + H]$^+$ calcld for C$_{19}$H$_{21}$O$_3$ 313.1434; found 313.1441.

*Ethyl (Z)-3-fluoro-3-(N-(p-tolyl)acetamido)acrylate (4ak)*

![4ak](image)

The resultant residue was purified by flash column chromatography (PE/EA=4/1) as a clear liquid. $R_f = 0.25$ (PE/EA = 4/1).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.26 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 5.40 (d, $J = 27.1$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 2.39 (s, 4H), 2.13 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H).

**13C NMR** (150 MHz, CDCl$_3$) δ 170.2, 164.0, 159.1, 157.2, 139.5, 136.1, 130.8, 127.7, 94.7, 94.6, 60.7, 23.9, 23.8, 21.3, 14.4.

**HRMS-ESI** ($m/z$): [M + Na]$^+$ calcld for C$_{14}$H$_{16}$FNNaO$_3$ 288.1006; found 288.0987.

*1-Phenyl-3,3-bis(p-tolylthio)prop-2-en-1-one (3ga)*

![3ga](image)

The resultant residue was purified by flash column chromatography (PE/EA=45/1) as a white solid. $R_f = 0.20$ (PE/EA = 45/1). **Mp** 141-142°C.

**1H NMR** (400 MHz, CDCl$_3$) δ 7.62 (td, $J = 5.8$, 4.0, 2.0 Hz, 4H), 7.50 – 7.38 (m, 1H), 7.39 – 7.29 (m, 4H), 7.29 – 7.19 (m, 4H), δ 6.41 (s, 1H), 2.41 (s, 3H), 2.40 (s, 3H).

**13C NMR** (150 MHz, CDCl$_3$) δ 186.3, 167.8, 140.9, 140.8, 139.2, 136.9, 135.7, 131.9, 130.9, 129.9, 128.5, 128.0, 127.4, 126.4, 112.0, 21.7, 21.6.

**HRMS-ESI** ($m/z$): [M + H]$^+$ calcld for C$_{23}$H$_{21}$OS$_2$ 377.1028; found 377.1031.

*Ethyl 2-(benzo[d][1,3]dioxol-2-yliod)acetate (5am)*

![5am](image)
The resultant residue was purified by flash column chromatography (PE/Et = 20/1) as a pale yellow solid. R_{f} = 0.20 (PE/Et = 20/1), Mp 84-85 °C.

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.35 - 7.22 \ (m, 1H), 7.16 - 7.15 \ (m, 3H), 5.01 \ (s, 1H), 4.22 \ (q, J = 7.2 \text{ Hz, 2H}), 1.31 \ (t, J = 7.2 \text{ Hz, 3H}). \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3) \delta 167.6, 166.4, 145.3, 143.8, 124.8, 124.6, 110.7, 109.9, 70.7, 59.9, 14.7. \]

HRMS-ESI (m/z): [M + H]^+ calcd for C_{11}H_{11}O_{2} 207.0652; found 207.0645.

Ethyl (Z)-2-(benzo[d][1,3]oxathiol-2-ylidene)acetate (5an)

The resultant residue was purified by flash column chromatography (PE/Et = 75/1) as a white solid. R_{f} = 0.23 (PE/Et = 75/1), Mp 115-116 °C.

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.49 - 7.37 \ (m, 1H), 7.30 - 7.10 \ (m, 3H), 5.87 \ (d, J = 1.3 \text{ Hz, 1H}), 4.25 \ (q, J = 7.1 \text{ Hz, 2H}), 1.43 - 1.21 \ (m, 3H). \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3) \delta 171.6, 168.5, 152.3, 127.0, 124.7, 124.6, 122.0, 111.3, 89.2, 60.3, 14.7. \]

HRMS-ESI (m/z): [M + H]^+ calcd for C_{11}H_{11}O_{3}S 223.0423; found 223.0422.

Ethyl 3,3-bis((2-aminophenyl)thio)acrylate (3ao)

The resultant residue was purified by flash column chromatography (PE/Et = 75/1) as a white solid. R_{f} = 0.23 (PE/Et = 75/1), Mp 115-116 °C.

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.53 \ (d, J = 7.7 \text{ Hz, 1H}), 7.28 \ (dd, J = 12.8, 5.5 \text{ Hz, 1H}), 7.22 \ (d, J = 7.3 \text{ Hz, 2H}), 6.79 \ (d, J = 7.7 \text{ Hz, 2H}), 6.70 \ (q, J = 7.7 \text{ Hz, 2H}), 5.35 \ (s, 1H), 4.43 \ (brs, 4H), 4.13 \ (q, J = 7.3 \text{ Hz, 2H}), 1.24 \ (t, J = 7.1 \text{ Hz, 3H}). \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3) \delta 165.8, 159.2, 150.4, 149.1, 138.5, 137.6, 132.6, 132.5, 119.0, 118.9, 115.8, 115.6, 112.5, 112.0, 107.7, 60.2, 14.6. \]

HRMS-ESI (m/z): [M + Na]^+ calcd for C_{17}H_{18}N_{2}NaO_{2}S_{2} 369.0702; found 369.0700.
Ethyl 2-(benzo[d]oxazol-2-yl)acetate (5aq)

The resultant residue was purified by flash column chromatography (PE/EA=20/1) as a white solid. \( R_f = 0.20 \) (PE/EA = 20/1), \( \text{Mp} 56-57 \) °C.
\[^1H\text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.72 \ (d, \ J = 3.6 \text{ Hz}, 1\text{H}), 7.71 \ (d, \ J = 3.6 \text{ Hz}, 1\text{H}), 7.35-7.10 \ (m, 2\text{H}), 4.25 \ (q, \ J = 7.1 \text{ Hz}, 2\text{H}), 4.03 \ (s, 2\text{H}), 1.29 \ (t, \ J = 7.1 \text{ Hz}, 3\text{H}).\]
\[^{13}C\text{ NMR} \ (150 \text{ MHz, CDCl}_3) \delta 167.2, 159.7, 151.3, 141.3, 125.3, 124.6, 120.2, 110.8, 62.1, 35.5, 14.2.\]
HRMS-ESI (m/z): \([\text{M + H}]^+\) calcd for C\(_{11}\)H\(_{12}\)NO\(_3\) 206.0812; found 206.0813.

Ethyl 2-(6-methylbenzo[d]oxazol-2-yl)acetate (5as)

The resultant residue was purified by flash column chromatography (PE/EA=18/1) as a yellow liquid. \( R_f = 0.20 \) (PE/EA = 18/1).
\[^1H\text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.57 – 7.46 \ (s, 1\text{H}), 7.46 – 7.37 \ (d, \ J = 8.4 \text{ Hz}, 1\text{H}), 7.15 \ (d, \ J = 8.4 \text{ Hz}, 1\text{H}), 4.40 – 4.13 \ (q, \ J = 7.2 \text{ Hz}, 2\text{H}), 4.00 \ (s, 2\text{H}), 2.46 \ (s, 3\text{H}), 1.28 \ (t, \ J = 7.2 \text{ Hz}, 3\text{H}).\]
\[^{13}C\text{ NMR} \ (150 \text{ MHz, CDCl}_3) \delta 167.3, 159.8, 149.6, 141.5, 134.5, 126.4, 120.1, 110.2, 62.1, 35.6, 21.6, 14.3.\]
HRMS-ESI (m/z): \([\text{M + H}]^+\) calcd for C\(_{12}\)H\(_{14}\)NO\(_3\) 220.0968; found 220.0967.

Ethyl 2-(5-methylbenzo[d]oxazol-2-yl)acetate (5at)

The resultant residue was purified by flash column chromatography (PE/EA=18/1) as a pale yellow solid. \( R_f = 0.20 \) (PE/EA = 18/1), \( \text{Mp} 58-59 \) °C.
\[^1H\text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.49 \ (s, 1\text{H}), 7.39 \ (d, \ J = 8.4 \text{ Hz}, 1\text{H}), 7.14 \ (d, \ J = 8.3 \text{ Hz}, 1\text{H}), 4.24 \ (q, \ J = 7.1 \text{ Hz}, 2\text{H}), 3.99 \ (s, 2\text{H}), 2.46 \ (s, 3\text{H}), 1.28 \ (t, \ J = 7.1 \text{ Hz}, 3\text{H}).\]
\[^{13}C\text{ NMR} \ (150 \text{ MHz, CDCl}_3) \delta 167.3, 159.2, 151.6, 139.1, 135.7, 125.8, 119.5, 110.9, 62.1, 35.5, 21.9, 14.3.\]
HRMS-ESI (m/z): \([\text{M + H}]^+\) calcd for C\(_{12}\)H\(_{14}\)NO\(_3\) 220.0968; found 220.0969.

Ethyl 2-(6-nitrobenzo[d]oxazol-2-yl)acetate (5au)
The resultant residue was purified by flash column chromatography (PE/EA=13/1) as a pale yellow solid. Rf = 0.20 (PE/EA = 13/1), Mp 77-79 °C.

\[ \text{1H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \:\text{H} \]

- 8.46 (dt, \( J = 6.3, 2.4 \text{ Hz, 1H} \)),
- 8.32 (dq, \( J = 8.9, 1.7 \text{ Hz, 1H} \)),
- 7.83 (dd, \( J = 8.9, 1.7 \text{ Hz, 1H} \)),
- 4.28 (q, \( J = 7.0 \text{ Hz, 2H} \)),
- 4.10 (s, 2H),
- 1.31 (t, \( J = 7.0 \text{ Hz, 3H} \)).

\[ \text{13C NMR} \ (150 \text{ MHz, CDCl}_3) \delta \:\text{C} \]

- 166.4, 164.5, 150.4, 146.5, 145.6, 120.8, 120.4, 107.6, 62.5, 35.7, 14.3.

\[ \text{HRMS-ESI} \ (m/z): [\text{M} + \text{H}]^+ \text{ calcd for C}_{11}\text{H}_{11}\text{N}_2\text{O}_5 251.0662; \text{ found } 251.0665. \]

**Ethyl 2-(5-nitrobenzo[d]oxazol-2-yl)acetate (5av)**

The resultant residue was purified by flash column chromatography (PE/EA=20/1) as a pale yellow solid. Rf = 0.20 (PE/EA = 20/1), Mp 87-88 °C.

\[ \text{1H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \:\text{H} \]

- 8.46 (d, \( J = 2.1 \text{ Hz, 1H} \)),
- 8.32 (d, \( J = 8.9 \text{ Hz, 1H} \)),
- 7.91 – 7.78 (m, 1H),
- 4.27 (q, \( J = 7.0 \text{ Hz, 2H} \)),
- 4.10 (s, 2H),
- 1.31 (t, \( J = 7.0 \text{ Hz, 3H} \)).

\[ \text{13C NMR} \ (150 \text{ MHz, CDCl}_3) \delta \:\text{C} \]

- 166.1, 159.6, 150.6, 139.3, 130.3, 124.6, 120.0, 110.7, 61.4, 34.6, 13.5.

\[ \text{HRMS-ESI} \ (m/z): [\text{M} + \text{H}]^+ \text{ calcd for C}_{11}\text{H}_{10}\text{N}_2\text{O}_5 251.0662; \text{ found } 251.0663. \]

**Ethyl 2-(6-chlorobenzo[d]oxazol-2-yl)acetate (5aw)**

The resultant residue was purified by flash column chromatography (PE/EA=15/1) as a black solid. Rf = 0.21 (PE/EA = 15/1), Mp 85-86 °C.

\[ \text{1H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \:\text{H} \]

- 7.63 (dt, \( J = 8.5, 1.9 \text{ Hz, 1H} \)),
- 7.55 (q, \( J = 1.9, 1.5 \text{ Hz, 1H} \)),
- 7.33 (dt, \( J = 8.5, 1.5 \text{ Hz, 1H} \)),
- 4.25 (q, \( J = 7.1 \text{ Hz, 2H} \)),
- 4.01 (s, 2H),
- 1.29 (t, \( J = 7.1 \text{ Hz, 3H} \)).

\[ \text{13C NMR} \ (150 \text{ MHz, CDCl}_3) \delta \:\text{C} \]

- 166.1, 159.6, 150.6, 139.3, 130.3, 124.6, 120.0, 110.7, 61.4, 34.6, 13.5.

\[ \text{HRMS-ESI} \ (m/z): [\text{M} + \text{H}]^+ \text{ calcd for C}_{11}\text{H}_{11}\text{ClN}_2\text{O}_3 240.0422; \text{ found } 240.0419. \]

**Ethyl 2-(5-chlorobenzo[d]oxazol-2-yl)acetate (5ax)**
The resultant residue was purified by flash column chromatography (PE/EA = 30/1) as a pale yellow solid. R_t = 0.23 (PE/EA = 30/1), Mp 85-86 °C.

**1H NMR** (400 MHz, CDCl_3) δ 7.70 (q, J = 2.0 Hz, 1H), 7.45 (dt, J = 8.7, 1.8 Hz, 1H), 7.32 (dq, J = 8.7, 2.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 3H), 4.01 (s, 3H), 1.29 (t, J = 7.1 Hz, 5H).

**13C NMR** (150 MHz, CDCl_3) δ 166.9, 161.2, 149.9, 142.4, 130.2, 125.7, 120.3, 111.6, 62.3, 35.5, 14.3.

**HRMS-ESI (m/z):** [M + H]^+ calcd for C_{11}H_{11}ClNO_3 240.0422; found 240.0419.

**Ethyl 2-(5-methoxybenzo[d]oxazol-2-yl)acetate (5ay)**

The resultant residue was purified by flash column chromatography (PE/EA = 30/1) as a white liquid. R_t = 0.21 (PE/EA = 10/1).

**1H NMR** (400 MHz, CDCl_3) δ 7.40 (dd, J = 8.9, 1.4 Hz, 1H), 7.19 (d, J = 1.4 Hz, 1H), 7.01 – 6.86 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.99 (s, 2H), 3.85 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

**13C NMR** (150 MHz, CDCl_3) δ 167.2, 160.5, 157.4, 146.0, 142.2, 113.9, 110.9, 103.2, 62.1, 56.1, 35.6, 14.3.

**HRMS-ESI (m/z):** [M + H]^+ calcd for C_{12}H_{14}NO_4 236.0917; found 236.0916.

**Dimethyl 2,2’-(((3-ethoxy-3-oxoprop-1-ene-1,1-diyl)bis(oxy))bis(2,1-phenylene))diacetate (3az)**

The resultant residue was purified by flash column chromatography (PE/EA = 5/1) as a clear liquid. R_t = 0.21 (PE/EA = 5/1).

**1H NMR** (400 MHz, CDCl_3) δ 7.48 – 6.83 (m, 8H), 3.72 (s, 1H), 4.03 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 3.53 (s, 3H), 3.44 (s, 2H), 1.12 (t, J = 7.1 Hz, 3H).

**13C NMR** (150 MHz, CDCl_3) δ 171.5, 170.9, 165.7, 164.9, 151.8, 150.7, 132.0, 131.4, 129.3, 128.5, 126.7, 126.6, 125.4, 121.2, 119.8, 79.9, 59.7, 52.2, 35.4, 35.3, 14.5.

**HRMS-ESI (m/z):** [M + H]^+ calcd for C_{23}H_{25}O_8 429.1544; found 429.1550.

**Methyl 3,3-bis(p-tolylthio)acrylate (3ha)**
The resultant residue was purified by flash column chromatography (PE/EA=15/1) as a white foamy solid. $R_f$ = 0.21 (PE/EA = 15/1). $\textbf{Mp}$ 82-83 °C.

$^1\text{H\ NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 8.1 Hz, 2H), 7.35 – 6.93 (m, 6H), 5.19 (s, 1H), 3.65 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H).

$^{13}\text{C\ NMR}$ (150 MHz, CDCl$_3$) $\delta$ 166.0, 163.8, 140.8, 140.7, 137.2, 135.7, 130.9, 129.9, 126.9, 125.6, 106.8, 51.3, 21.7, 21.5.

$\textbf{HRMS-ESI}$ ($m/z$): [M + H]$^+$ calcld for C$_{18}$H$_{18}$O$_2$S$_2$ 331.0821; found 331.0826.
Copies of $^1$H NMR and $^{13}$C NMR spectra of all compound:
3ah

4ah
