Supporting Information

Efficient imidation of C(sp³)–H bonds adjacent to oxygen atoms of aryl ether under metal-free condition

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I. General Remarks:
Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All the reactions were carried out under air atmosphere. $^1$H NMR spectra were recorded at 25°C on a Bruker Ascend$^\text{TM}$ 400 spectrometer, $^{13}$C NMR spectra were recorded at 25°C on a Bruker 100 MHz, and TMS as internal standard. Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. HRMS data were obtained on a Waters LCT Premierxe$^\text{TM}$ (USA). All reactions were monitored by TLC with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

II. General procedure for the synthesis of 3 and 5 (1a as an example).

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\text{Anisole} \; 1a \; (54.0 \; \text{mg}, \; 0.5 \; \text{mmol}), \; \text{saccharin} \; 2 \; (183.0 \; \text{mg}, \; 1.0 \; \text{mmol}) \; \text{were added to Bu}_4\text{NI} \; (18.5 \; \text{mg}, \; 0.05 \; \text{mmol}) \; \text{and TBHP} \; (180.2 \; \text{mg}, \; 2.0 \; \text{mmol}) \; \text{solution. The mixture was stirred at 120}^\circ \text{C for 8.0-12.0 h (monitored by TLC), quenched with water, extracted with dichloromethane} \; (5 \times 3 \; \text{mL}), \; \text{and dried over anhydrous Na}_2\text{SO}_4. \; \text{The solvent was removed under reduced pressure, and the residue was purified by a shot flash silica gel column chromatography (EtOAc/petro ether=1:6) to give compound 3a as a white solid (127.2 mg, 88%).}
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III. The Kinetic Isotope Effect Experiment

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\text{Reaction conditions: The mixture of THF} \; (0.25 \; \text{mmol}), \; \text{THF-d8} \; (0.25 \; \text{mmol}), \; \text{saccharin} \; (1.0 \; \text{mmol}), \; \text{Bu}_4\text{NI} \; (0.05 \; \text{mmol}) \; \text{and TBHP} \; (2.0 \; \text{mmol}) \; \text{was stirred at 120}^\circ \text{C under air atmosphere for 6 h. There is a high kinetic isotope effect} \; (K_H/K_D = 4.0) \; \text{in the deuterated experiment between THF and THF-d8.}
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IV. Analytical data of products obtained in this study

2-(3-oxo-3-phenylpropyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3a
White solid. Mp: 113-115 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.84 (s, 2H), 7.07 (t, J= 7.6 Hz, 1H), 7.14-7.16 (m, 2H), 7.31-7.35 (m, 2H), 7.85-7.94 (m, 3H), 7.95-8.11 (m, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 67.2, 116.7, 121.0, 121.2, 123.1, 125.7, 126.7, 129.6, 134.5, 137.8, 155.9, 158.6. HRMS (ESI-TOF) Calcd for C₁₄H₁₁NO₄S, [M+H]⁺ 290.0487; Found 290.0485.

2-((4-methoxyphenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3b
White solid. Mp: 130-132 °C; ¹H NMR (400 MHz; CDCl₃): δ = 3.77 (s, 3H), 5.76 (s, 2H), 6.85 (dd, J₁= 1.2 Hz, J₂= 8.0 Hz, 2H), 6.87-7.11 (m, 2H), 7.83-7.85 (m, 3H), 7.89 (dd, J₁= 2.0 Hz, J₂= 6.8 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 55.6, 68.2, 114.7, 118.7, 121.1, 125.7, 126.7, 134.5, 135.4, 137.9, 149.9, 155.7, 158.6. HRMS (ESI-TOF) Calcd for C₁₅H₁₃NO₅S, [M+H]⁺ 320.0593; Found 320.0597.
2-((2-methoxyphenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3c
White solid. Mp: 137-139 °C; ¹H NMR (400 MHz; CDCl₃): δ = 3.91 (s, 3H), 5.83 (s, 2H), 6.86 (d, J = 7.6 Hz, 1H), 6.97 (J₁ = 1.6 Hz, J₂ = 8.0 Hz, 1H), 7.09-7.16 (m, 2H), 7.84-7.94 (m, 3H), 8.05 (d, J = 7.6 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 55.9, 68.8, 112.6, 120.9, 121.1, 125.0, 125.6, 126.7, 134.4, 135.3, 137.9, 144.9, 151.6, 158.6. HRMS (ESI-TOF) Calcd for C₁₅H₁₃NO₅S, [M+H]+ 320.0593; Found 320.0591.

2-((2-chlorophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3d
White solid. Mp: 193-195 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.84 (s, 2H), 7.06 (d, J = 6.4 Hz, 1H), 7.23-7.26 (m, 2H), 7.41 (dd, J₁ = 1.2 Hz, J₂ = 8.0 Hz, 1H), 7.87-7.91 (m, 3H), 7.93 (d, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 68.2, 119.0, 121.2, 124.7, 125.6, 125.8, 126.5, 127.8, 130.7, 134.5, 135.5, 137.8, 152.0, 158.6. HRMS (ESI-TOF) Calcd for C₁₄H₁₀ClNO₄S, [M+H]+ 324.0097; Found 324.0095.

2-((3-chlorophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3e
White solid. Mp: 196-199 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.81 (s, 2H), 7.05 (dd, J₁ = 2.4 Hz, J₂ = 8.0 Hz, 2H), 7.17 (d, J = 6.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.88-7.93 (m, 3H), 7.94 (d, J = 6.0 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 67.0, 114.7, 117.4, 121.2, 123.3, 125.6, 126.5, 130.4, 134.6, 135.0, 135.5, 137.8, 156.6, 158.5. HRMS (ESI-TOF) Calcd for C₁₄H₁₀ClNO₄S, [M+H]+ 324.0097; Found 324.0092.

2-((4-chlorophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3f
White solid. Mp: 192-194 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.81 (s, 2H), 7.08 (dd, J₁ = 2.0 Hz, J₂ = 6.8 Hz, 2H), 7.28 (dd, J₁ = 2.4 Hz, J₂ = 6.8 Hz, 2H), 7.87-7.91 (m, 3H), 7.93 (d, J = 6.4 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 67.4, 118.3, 121.2, 125.8, 126.5, 128.3, 129.6, 134.6, 135.5, 137.8, 154.5, 158.6. HRMS (ESI-TOF) Calcd for C₁₄H₁₀ClNO₄S, [M+H]+ 324.0097; Found 324.0091.
2-(4-methoxybenzyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3g
White solid. Mp: 150-152 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 3.80\) (s, 3H), \(4.87\) (s, 2H), \(6.88\) (d, \(J = 8.8\) Hz, 2H), \(7.46\) (d, \(J = 8.8\) Hz, 2H), \(7.82-7.86\) (m, 3H), \(7.93\) (d, \(J = 6.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 42.3, 55.2, 114.1, 121.0, 125.2, 126.6, 127.4, 130.4, 134.3, 134.7, 137.8, 158.8, 159.6\). HRMS (ESI-TOF) Calcd for C\(_{15}\)H\(_{13}\)NO\(_4\)S, [M+H]\(^+\) 304.0644; Found 304.0639.

2-((4-tert-butylphenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3h
White solid. Mp: 164-166 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 1.30\) (s, 9H), \(5.82\) (s, 2H), \(7.07\) (dd, \(J_1 = 2.0\) Hz, \(J_2 = 6.4\) Hz, 2H), \(7.34\) (dd, \(J_1 = 2.0\) Hz, \(J_2 = 6.4\) Hz, 2H), \(7.84-7.88\) (m, 3H), \(7.90\) (dd, \(J_1 = 1.2\) Hz, \(J_2 = 7.6\) Hz, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 31.4, 34.2, 67.3, 115.9, 121.2, 125.7, 126.4, 126.7, 134.5, 135.4, 137.9, 145.7, 153.7, 158.6\). HRMS (ESI-TOF) Calcd for C\(_{18}\)H\(_{19}\)NO\(_4\)S, [M+H]\(^+\) 346.1113; Found 346.1117.

2-((3-fluorophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3i
White solid. Mp: 148-150 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 5.82\) (s, 2H), \(6.68-6.88\) (m, 1H), \(6.89-6.96\) (m, 2H), \(7.25-7.31\) (m, 1H), \(7.86-7.93\) (m, 3H), \(7.95-8.01\) (m, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 67.0, 104.5, 104.8, 109.8, 110.0, 112.0, 121.2, 125.8, 126.6, 130.4, 130.5, 134.6, 135.0, 135.5, 137.8, 157.1, 157.2, 158.5, 162.2, 164.6\). HRMS (ESI-TOF) Calcd for C\(_{14}\)H\(_{10}\)FNO\(_4\)S, [M+H]\(^+\) 308.0393; Found 308.0391.

2-((4-fluorophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3j
White solid. Mp: 108-110 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 5.78\) (s, 2H), \(6.97-7.02\) (m, 2H), \(7.09-7.13\) (m, 2H), \(7.86-7.92\) (m, 3H), \(7.93\) (d, \(J = 6.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 68.1, 116.0, 116.2, 118.6, 118.7, 121.2, 125.7, 126.5, 134.6, 135.5, 137.8, 151.9, 157.6, 158.6, 159.9\). HRMS (ESI-TOF) Calcd for C\(_{14}\)H\(_{10}\)FNO\(_4\)S, [M+H]\(^+\) 308.0393; Found 308.0389.
2-((4-bromophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3k
White solid. Mp: 167-170 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.81 (s, 2H), 7.05 (dd, J₁ = 2.0 Hz, J₂ = 6.8 Hz, 2H), 7.34 (dd, J₁ = 2.4 Hz, J₂ = 6.8 Hz, 2H), 7.85-7.91 (m, 3H), 7.92 (d, J = 6.4 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 67.2, 115.7, 118.7, 121.2, 125.8, 126.5, 132.6, 134.6, 135.5, 137.8, 155.0, 158.6. HRMS (ESI-TOF) Calcd for C₁₄H₁₀BrNO₄S, [M+H]⁺ 367.9592; Found 367.9596.

2-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methoxy)benzonitrile 3l
White solid. Mp: 116-118 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.93 (s, 2H), 7.13-7.17 (m, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.56-7.60 (m, 2H), 7.61-7.63 (m, 3H), 7.87 (t, J = 6.4 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 67.3, 104.4, 115.4, 115.6, 121.3, 123.3, 125.9, 126.4, 134.1, 134.2, 134.6, 135.7, 137.8, 157.6, 158.6. HRMS (ESI-TOF) Calcd for C₁₅H₁₀N₂O₄S, [M+H]⁺ 315.0440; Found 315.0445.

2-((4-nitrophenoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3m
White solid. Mp: 207-209 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.92 (s, 2H), 7.25 (d, J = 9.2 Hz, 2H), 7.90-7.95 (m, 3H), 7.96 (d, J = 6.8 Hz, 1H), 8.12-8.26 (m, 2H). ¹³C NMR (100 MHz; CDCl₃): δ = 67.0, 114.8, 117.4, 121.2, 123.3, 125.8, 126.6, 133.4, 134.6, 135.0, 135.5, 156.6, 158.5. HRMS (ESI-TOF) Calcd for C₁₄H₁₁N₂O₆S, [M+H]⁺ 335.0338; Found 335.0386.

2-((phenylthio)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 3o
White solid. Mp: 110-112 °C; ¹H NMR (400 MHz; CDCl₃): δ = 5.17 (s, 2H), 7.33-7.60 (m, 3H), 7.62 (dd, J₁ = 1.2 Hz, J₂ = 6.8 Hz, 2H), 7.83-7.91 (m, 3H), 8.03 (d, J = 7.6 Hz, 1H). ¹³C NMR (100 MHz; CDCl₃): δ = 44.4, 121.0, 125.4, 126.9, 127.4, 128.4, 129.4, 132.8, 134.4, 135.0, 137.9, 158.3. HRMS (ESI-TOF) Calcd for C₁₅H₁₂NO₃S₂, [M+H]⁺ 306.0259; Found 306.0255.
5-(4-chlorophenyl)-4-methyl-2-(phenoxymethyl)isothiazol-3(2H)-one 1,1-dioxide 3p
White solid. Mp: 76-79 °C; $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 2.19$ (s, 3H), 5.75 (s, 2H), 7.08 (t, $J$=7.6 Hz, 1H), 7.14 (d, $J$= 8.0 Hz, 2H), 7.32-7.36 (m, 2H), 7.51-7.54 (m, 2H), 7.61-7.64 (m, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 10.2$, 67.6, 116.6, 122.9, 123.1, 129.7, 129.8, 129.9, 130.3, 130.4, 132.3, 144.4, 155.9, 160.6. HRMS (ESI-TOF) Calcd for C$_{17}$H$_{12}$NCIO$_4$S [M+H]$^+$ 364.0410; Found 364.0419.

5-(4-fluorophenyl)-4-methyl-2-(phenoxymethyl)isothiazol-3(2H)-one 1,1-dioxide 3q
White solid. Mp: 81-84 °C; $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 2.19$ (s, 3H), 5.75 (s, 2H), 7.08 (t, $J$=7.2 Hz, 1H), 7.14 (d, $J$= 7.6 Hz, 2H), 7.15-7.26 (m, 2H), 7.32-7.36 (m, 2H), 7.67-7.70 (m, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 10.2$, 67.6, 116.6, 116.8, 117.0, 120.6, 123.1, 129.7, 131.4, 131.5, 131.9, 144.5, 155.9, 160.7, 163.2, 165.7. HRMS (ESI-TOF) Calcd for C$_{17}$H$_{12}$NOF$_4$S [M+H]$^+$ 348.0706; Found 348.0701.

4-methyl-2-(phenoxymethyl)-5-(p-tolyl)isothiazol-3(2H)-one 1,1-dioxide 3r
White solid. Mp: 73-76 °C; $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 2.20$ (s, 3H), 2.44 (s, 3H), 5.75 (s, 2H), 7.08 (t, $J$=7.6 Hz, 1H), 7.14 (d, $J$= 7.2 Hz, 2H), 7.32 (d, $J$= 6.0 Hz, 3H), 7.58 (d, $J$= 8.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 10.3$, 21.6, 67.5, 116.6, 121.6, 122.9, 128.9, 129.0, 129.6, 130.1, 130.9, 142.3, 145.5, 156.0, 161.1. HRMS (ESI-TOF) Calcd for C$_{18}$H$_{18}$NO$_3$S [M+H]$^+$ 344.0957; Found 344.0952.

5-ethyl-4-methyl-2-(phenoxymethyl)isothiazol-3(2H)-one 1,1-dioxide 3s
White solid. Mp: 55-57 °C; $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 1.36$ (t, $J$= 6.0 Hz, 3H), 2.04 (s, 3H), 2.70 (q, $J$= 7.6 Hz, 2H), 5.66 (s, 2H), 7.08 (d, $J$= 7.2 Hz, 1H), 7.09 (d, $J$= 8.0 Hz, 2H), 7.30-7.34 (m, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 8.8$, 12.1, 17.6, 67.3, 116.5, 122.9, 129.6, 132.1,
148.6, 155.9, 160.9. HRMS (ESI-TOF) Calcd for C$_{13}$H$_{16}$NO$_4$S, [M+H]$^+$ 282.0800; Found 282.0801.

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\text{2-((2-methoxyethoxy)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 5a}
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White solid. Mp: 105-107 °C; $^1$H NMR (400 MHz; CDCl$_3$): δ = 3.38 (s, 3H), 3.58-3.60 (m, 2H), 3.83-3.85 (m, 2H), 7.87-7.90 (m, 3H), 7.93 (dd, $J_1= 1.2$ Hz, $J_2= 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): δ = 59.0, 69.4, 70.0, 71.4, 121.1, 125.5, 126.9, 134.5, 135.3, 137.9, 159.2. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{13}$NO$_5$S, [M+H]$^+$ 272.0593; Found 272.0599.

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\text{2-(1,2-dimethoxyethyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 5a'}
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White solid. Mp: 90-92 °C; $^1$H NMR (400 MHz; CDCl$_3$): δ = 3.45 (s, 3H), 3.57 (s, 3H), 3.97 (d, $J= 6.0$ Hz, 2H), 5.62 (t, $J= 6.0$ Hz, 1H), 7.85-7.94 (m, 3H), 8.08 (t, $J= 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): δ = 57.7, 59.4, 71.6, 85.6, 120.8, 125.5, 126.6, 134.3, 135.1, 138.1, 159.2. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{13}$NO$_5$S, [M+H]$^+$ 272.0593; Found 272.0596.

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\text{2-(tetrahydrofuran-2-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 5b}
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White solid. Mp: 107-110 °C; $^1$H NMR (400 MHz; CDCl$_3$): δ = 2.25 (t, $J= 6.8$ Hz, 2H), 3.93 (t, $J= 7.2$ Hz, 2H), 4.31 (t, $J= 6.4$ Hz, 2H), 7.86-7.95 (m, 3H), 8.10 (m, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): δ = 27.4, 36.0, 60.8, 121.0, 125.2, 127.3, 134.4, 134.9, 137.7, 158.9, 160.8. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{11}$NO$_5$S, [M+H]$^+$ 254.0487; Found 254.0481.

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\text{2-(1,4-dioxan-2-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide 5c}
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White solid. Mp: 161-163 °C; $^1$H NMR (400 MHz; CDCl$_3$): δ = 3.79-3.93 (m, 2H), 4.02 (dd, $J_1= 2.8$ Hz, $J_2= 7.6$ Hz, 1H), 4.11 (d, $J= 7.6$ Hz, 2H), 4.36 (m, 1H), 5.70 (dd, $J_1= 2.8$ Hz, $J_2= 8.8$ Hz, 1H), 7.85-7.93 (m, 3H), 8.07 (t, $J= 7.2$ Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): δ = 65.9, 66.5, 66.7, 78.9, 120.9, 125.5, 126.4, 134.4, 135.3, 137.9, 158.5. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{11}$NO$_5$S, [M+H]$^+$ 270.0436; Found 270.0433.
V. $^1$H NMR and $^{13}$C NMR spectra copies of compounds 3, 5 and H.