Supporting Information

Formal Carbene C-H Bond Insertion in the Cu(I)-Catalyzed Reaction of Bis(trimethylsilyl)diazomethane with Benzoazoles and Oxazoles

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1) General methods

All necessary reagents were purchased from commercial suppliers and be used without further purification. The solvents were all distilled prior to use. 200-300 mesh silica gels for the chromatography were used. Chemical shifts for \textsuperscript{1}H NMR (400 MHz) and \textsuperscript{13}C NMR (100 MHz) are reported relative to the chemical shift of tetramethylsilane (TMS): chemical shifts (\(\delta\)) were reported in ppm, and coupling constants (\(J\)) are in Hertz (Hz). IR spectra are reported in wave numbers, cm\(^{-1}\). For HRMS measurements, the mass analyzer is FT-ICR. The substrates 2a, 2b, 2h, 2m, 2n were purchased from commercial suppliers; The substituted benzoxazoles (2c\(^1\), 2d\(^2\), 2e\(^3\), 2f\(^1\), 2g\(^3\), 2i\(^4\), 2j\(^2\), 2k, 2l\(^3\)) were prepared following the literature procedure.\(^4\) The 5-substituted oxazoles (4a\(^5\), 4b\(^6\), 4c\(^5\), 4d\(^6\), 4e\(^5\), 4f\(^7\), 4h, 4g\(^8\), 4i\(^6\), 4m\(^9\), 4n\(^9\)) were prepared following the literature procedure.\(^5\) The 4-substituted oxazoles (4i\(^{10}\), 4j\(^{11}\), 4k\(^{12}\)) were prepared following the literature procedure.\(^6\) The 2 deuterium-labeled substrate \(d\)-2b was prepared following the literature procedure.\(^18\)

2) Preparation of bis(trimethylsilyl)diazomethane 1\(^{13}\)

The reaction was performed under a nitrogen atmosphere in a dried reaction flask. Trimethylsilyldiazomethane (20.0 mmol, 2.0 M solution in hexane, 10 mL) and 20 mL \(n\)-hexane were added to the reaction flask and cooled to -100 \(^\circ\)C. Then \(n\)-BuLi (20.0 mmol, 2.4 M solution in hexane, 8.33 mL) was added dropwise in 1 hour. The resulting solution was stirred for another 15 min at -100 \(^\circ\)C. Trimethylsilyl chloride (20.0 mmol, 2.170 g) was then added dropwise at -80 \(^\circ\)C. The solution was slowly warmed to room temperature over 2 hours and stirred for another 3 hours. The suspension was filtered through a short column filled with basic aluminum oxide twice and the solvent was removed in vacuo. Bis(trimethylsilyl)diazomethane 1 was achieved as yellow liquid (1.985 g, 53%).

3) Preparation of 5-phenyl benzothiazole (2o)

Under nitrogen atmosphere, 5-bromobenzothiazole (2n) (0.5 mmol, 107 mg), phenylboronic acid (0.75 mmol, 92 mg), tetrakis(triphenylphosphine)palladium (0.025 mmol, 29 mg), potassium carbonate (2.0 mmol, 276 mg), toluene (2.5 mL) and water (0.5 mL) were added successively to a 25 mL reaction flask. The mixture was stirred at 80 \(^\circ\)C for 8 hours. The mixture was cooled to room temperature. Then 20 mL water was added to the mixture and extracted with 20 mL ethyl acetate for three times. The organic layer was combined and dried over Na\(_2\)SO\(_4\). Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 20:1). 5-Phenyl benzothiazole 2o was obtained as yellow solid (92 mg, 87%).

4) Optimizing of the reaction conditions: screening of the base\(^a\)

\[ \text{TMS} \quad \text{N} \quad \text{N} \quad \text{TMS} \quad + \quad \text{Me} \quad \text{O} \quad \text{N} \quad \text{H} \quad \xrightarrow{\text{Cul (20 mol \% base (x equiv) \text{solvent (1 mL), } T})} \quad \text{Me} \quad \text{O} \quad \text{TMS} \quad \text{TMS} \]

0.1 mmol
| Entry | Ratio (1:2a) | solvent | x | base | T (°C) | Yield (%)<sup>b</sup> |
|-------|--------------|---------|---|------|--------|------------------------|
| 1     | 2:1          | toluene | 1 | Et₃N | 110    | 0                      |
| 2     | 2:1          | toluene | 1 | tPr₂NH | 110   | trace                  |
| 3     | 2:1          | toluene | 1 | DBU  | 110    | trace                  |
| 4     | 2:1          | toluene | 1 | K₂CO₃ | 110    | 0                      |
| 5     | 2:1          | toluene | 1 | Cs₂CO₃ | 110   | 0                      |
| 6     | 2:1          | toluene | 1 | NaH  | 110    | trace                  |
| 7     | 2:1          | toluene | 1 | LiO'Bu | 110   | 75                     |
| 8     | 2:1          | toluene | 1 | NaO'Bu | 110   | 35                     |
| 9     | 2:1          | toluene | 1 | KO'Bu | 110    | 20                     |

<sup>a</sup>Reaction conditions: bis(trimethylsilyl)diazomethane 1 (0.1 mmol), 2a (0.1 mmol), CuI (0.02 mmol), base (0.1 mmol), solvent (1.0 mL) for 8 h. <sup>b</sup>Isolated yield.

5) **Typical procedure for the Cu(I)-catalyzed coupling of bis(trimethylsilyl)diazomethane 1 with benzoxazoles and oxazoles**

Under nitrogen atmosphere, benzoxazole/oxazole (0.2 mmol), cuprous iodide (0.04 mmol, 7.6 mg), lithium tert-butoxide (0.3 mmol, 24 mg) and toluene (1 mL) were mixed in a 10 mL reaction flask. Bis(trimethylsilyl)diazomethane 1 (0.4 mmol, 74 mg) was then added dropwise. The mixture was stirred at 110 °C for 8 hours. Then the mixture was cooled to room temperature and filtered through a short column filled with silica gel. Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give the product.

6) **Typical procedure for the Cu(I)-catalyzed coupling of bis(trimethylsilyl)diazomethane 1 with benzothiazoles**

Under nitrogen atmosphere, benzothiazole (0.2 mmol), cuprous iodide (0.04 mmol, 7.6 mg), lithium tert-butoxide (0.4 mmol, 32 mg) and toluene (1 mL) were mixed in a 10 mL reaction flask. Bis(trimethylsilyl)diazomethane 1 (0.4 mmol, 74 mg) was then added dropwise. The mixture was stirred at 120 °C for 8 hours. Then the mixture was cooled to room temperature and filtered through a short column filled with silica gel. Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give the product.

7) **Typical procedure for the gram scale synthesis**

Under nitrogen atmosphere, benzoxazole (8.0 mmol), cuprous iodide (1.6 mmol, 306 mg), lithium tert-butoxide (12.0 mmol, 960 mg) and toluene (40 mL) were mixed in a 250 mL reaction flask. Bis(trimethylsilyl)diazomethane 1 (16.0 mmol, 2.976 g) was then added dropwise. The mixture was stirred at 110 °C for 8 hours. Then the mixture was cooled to room temperature and filtered through a short column filled with silica gel. Solvent was evaporated
under reduced pressure, and the residue was purified by flash chromatography on silica gel to give the product.

8) Typical Procedure for the desilylation reactions

To a 10 ml flask, 2-(bis(trimethylsilyl)methyl)-5-phenylbenzoxazole 3e (0.2 mmol, 71 mg), TBAF•3H₂O (0.24 mmol, 76 mg) and 1 mL tetrahydrofuran were mixed. The mixture was stirred at 0 °C for 4 hours. Then 20 mL water was added to the mixture and extracted with 20 mL ethyl acetate for three times. The organic layer was combined and dried with Na₂SO₄. Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 30:1). 2-Methyl-5-phenylbenzoxazole 6 was obtained as a white solid (38.2 mg, 91%).

9) Typical Procedure for the Peterson olefination reactions

Under nitrogen atmosphere, substituted 2-(bis(trimethylsilyl)methyl)benzoxazole (0.3 mmol), aldehyde (0.2 mmol), 4 Å molecular sieves (50 mg), CsF (0.2 mmol, 30 mg) and DMF (1 mL) were mixed. The mixture was stirred at 80 °C for 4 hours. The mixture was cooled to room temperature. Then 20 mL water was added to the mixture and extracted with 20 mL ethyl acetate for three times. The organic layer was combined and dried with Na₂SO₄. Solvent was evaporated under reduced pressure, and the residue was purified by planar chromatography on silica gel (petroleum ether: ethyl acetate: DCM = 15:1:1, 1% Et₃N) to give the desire product.

10) Procedure for the KIE and deuterium labeling experiments

Kinetic Isotope measurement

The reaction of 2b and d-2b were carried out in parallel. Under nitrogen atmosphere, 2b/ d-2b (0.2 mmol), cuprous iodide (0.04 mmol, 7.6 mg), lithium tert-butoxide (0.3 mmol, 24 mg) and toluene (1 mL) were mixed in a 10 mL reaction flask. Bis(trimethylsilyl)diazomethane 1 (0.4 mmol, 74 mg) was then added dropwise. The mixture was stirred at 110 °C for 5 min, 10 min, 12 min and 17 min, and quenched by quickly cooled the reaction flask to 0 °C at each time. Then the mixture was filtered through a short column filled with silica gel. Solvent and unreacted 2b or d-2b were evaporated under reduced pressure. The yields were determined by ¹H NMR with CH₃NO₂ as the internal standard.

| time (min) | 5     | 10    | 12    | 15    | 17    |
|------------|-------|-------|-------|-------|-------|
| yield of 3b (%) | 0.8   | 3.6   | 4.4   | 7.0   | 8.2   |
| yield of d-3b (%) | --    | 2.5   | 2.9   | 5.3   | 6.1   |

\[ k_H = 6.22 \times 10^{-3} \text{ min}^{-1} \]
\[ k_D = 5.59 \times 10^{-3} \text{ min}^{-1} \]

Procedure for the Cu(I)-catalyzed coupling of bis(trimethylsilyl)diazomethane 1 and d-2b for the synthesis of deuterium-substituted product 3b

Under nitrogen atmosphere, d-2b (0.2 mmol, 24 mg), cuprous iodide (0.04 mmol, 7.6 mg), lithium tert-butoxide (0.3 mmol, 24 mg) and toluene (1 mL) were mixed in a 10 mL reaction flask. Bis(trimethylsilyl)diazomethane 1 (0.4 mmol, 74 mg) was then added dropwise. The mixture was stirred at 110 °C for 8 hours. Then the mixture was cooled to room temperature and 1 mL D₂O was added. The mixture was stirred for another 1 hour. After that, 20 mL water was added to the mixture and extracted with 20 mL ethyl acetate for three times. The organic
layer was combined and dried with Na$_2$SO$_4$. Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) to give the product $d$-$3b$ as yellow solid (42.4 mg, 76%).

11) Spectra Data for the Products

Bis(trimethylsilyl)diazomethane (1)$^{13}$

![Bis(trimethylsilyl)diazomethane (1)](image)

Yield 53% (1.9846 g); yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.17 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ -0.3, 16.6; IR (film): 2960, 2045, 1699, 1251, 1227, 930, 839 cm$^{-1}$.

benzo[$d$]oxazole-2-$d$ ($d$-$2b$)$^{18}$

![benzo[$d$]oxazole-2-$d$ ($d$-$2b$)](image)

White solid, m.p. = 31-32 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (s, 0.06 H, 94% D), 7.81-7.79 (m, 1H), 7.60-7.58 (m, 1H), 7.41-7.35 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 152.5, 149.9, 140.0, 125.5, 124.5, 120.6, 110.9; IR (film): 2083, 1688, 1473, 1450, 1235, 1060 cm$^{-1}$.

7-bromobenzo[$d$]oxazole (2k)

![7-bromobenzo[$d$]oxazole (2k)](image)

Yield 89% (353.1 mg, petroleum ether (PE): ethyl acetate (EA) = 100:1); orange solid, m.p. 41-43 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.54 (d, $J$ = 7.9 Hz, 1H), 7.28-7.24 (m, 1H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 152.5, 148.3, 140.8, 128.9, 125.9, 119.8, 103.0; IR (film): 3095, 1476, 1421, 1078, 897, 785 cm$^{-1}$; HRMS (ESI) calcd for C$_7$H$_4$NO$^{79}$Br [M]$^+$ 196.9471; found 196.9470.

5-phenylbenzo[$d$]thiazole (2o)

![5-phenylbenzo[$d$]thiazole (2o)](image)
Yield 87% (92.0 mg, PE: EA = 20:1); yellow solid, m.p. 65-66 °C; ^1H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 8.36 (s, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.69-7.67 (m, 3H), 7.49-7.46 (m, 2H), 7.40-7.36 (m, 1H); ^13C{^1H} NMR (100 MHz, CDCl₃) δ 154.6, 154.1, 140.6, 139.9, 132.7, 129.0, 127.6, 127.5, 125.2, 122.1, 121.9; IR (film): 1437, 899, 833, 814, 759, 698 cm⁻¹; HRMS (ESI) calcd for C₁₃H₉NS [M]+ 211.0450; found 211.0448.

2-(bis(trimethylsilyl)methyl)-5-methylbenzo[d]oxazole (3a)

Yield 89% (51.5 mg, PE: EA = 200:1); yellow oil; ^1H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 7.25 (d, J = 8.3 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H), 2.11 (s, 1H), 0.12 (s, 18H); ^13C{^1H} NMR (100 MHz, CDCl₃) δ 169.7, 149.0, 142.5, 133.3, 124.0, 118.7, 109.0, 23.6, 21.4, 0.0; IR (film): 2955, 1543, 1252, 842, 796, 689 cm⁻¹; HRMS (ESI) calcd for C₁₅H₂₆NOSi₂ [M+H]+ 292.1547; found 292.1549.

2-(bis(trimethylsilyl)methyl)benzo[d]oxazole (3b)

Yield 78% (42.9 mg, PE: EA = 200:1); yellow solid, m.p. = 74-76 °C; ^1H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.23-7.14 (m, 2H), 2.10 (s, 1H), 0.12 (s, 18H); ^13C{^1H} NMR (100 MHz, CDCl₃) δ 169.5, 150.8, 142.3, 123.6, 123.0, 118.6, 109.6, 23.6, 0.0; IR (film): 2957, 1539, 1457, 1251, 846, 743 cm⁻¹; HRMS (ESI) calcd for C₁₄H₂₄NOSi₂ [M+H]+ 278.1391; found 278.1388.

2-(bis(trimethylsilyl)methyl-d)benzo[d]oxazole (d-3b)

Yield 76% (42.4 mg, PE: EA = 200:1); yellow solid, m.p. = 76-78 °C; ^1H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.24-7.15 (m, 2H), 2.08 (s, 0.28H, 72% D), 0.12 (s, 18H); ^13C{^1H} NMR (100 MHz, CDCl₃) δ 169.6, 150.8, 142.3, 123.6, 123.0, 118.6, 109.6, 23.6, 0.0; IR (film): 2956, 1539, 1457, 1251, 846, 743 cm⁻¹; HRMS (ESI) calcd for C₁₄H₂₃DNOSi₂ [M+H]+ 279.1454; found 279.1449.

2-(bis(trimethylsilyl)methyl)-5-fluorobenzo[d]oxazole (3c)
Yield 59% (35.0 mg, PE: EA = 200:1); white solid, m.p. = 41-43 °C; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.30-7.22 (m, 2H), 6.89 (td, \( J = 9.0, 2.2 \) Hz, 1H), 2.07 (s, 1H), 0.12 (s, 18H); \( ^{13} \)C\( \{^1 \)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.6, 159.8 (d, \( J = 239 \) Hz), 147.1, 143.3 (d, \( J = 13 \) Hz), 110.2 (\( J = 22 \) Hz), 109.6 (d, \( J = 10 \) Hz), 105.3 (d, \( J = 26 \) Hz), 23.9, 0.0; IR (film): 2957, 1539, 1478, 1253, 1135, 844 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{14}\)H\(_{23}\)FNOSi\(_2\) [M+H]\(^+\) 296.1297; found 296.1289.

2-(bis(trimethylsilyl)methyl)-5-(tert-butyl)benzo[d]oxazole (3d)

Yield 83% (55.3 mg, PE: EA = 200:1); yellow oil; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.60-7.58 (m, 1H), 7.30-7.21 (m, 2H), 2.11 (s, 1H), 1.33 (s, 9H), 0.12 (s, 18H); \( ^{13} \)C\( \{^1 \)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 169.6, 148.7, 147.0, 142.1, 120.5, 115.3, 108.7, 34.8, 31.8, 23.5, 0.0; IR (film): 2960, 1544, 1481, 1252, 844, 776 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{32}\)NOSi\(_2\) [M+H]\(^+\) 334.2017; found 334.2015.

2-(bis(trimethylsilyl)methyl)-5-phenylbenzo[d]oxazole (3e)

Yield 68% (41.7 mg, PE: EA = 200:1); yellow oil; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.77 (s, 1H), 7.56-7.54 (m, 2H), 7.42-7.37 (m, 4H), 7.30-7.27 (m, 1H), 2.19 (s, 1H), 0.13 (s, 18H); \( ^{13} \)C\( \{^1 \)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.4, 150.2, 142.7, 141.4, 137.6, 128.7, 127.4, 127.0, 122.6, 117.2, 109.6, 23.8, 0.0; IR (film): 2956, 1542, 1252, 844, 776, 698 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{20}\)H\(_{28}\)NOSi\(_2\) [M+H]\(^+\) 354.1704; found 354.1694.

2-(bis(trimethylsilyl)methyl)-5-bromobenzo[d]oxazole (3f)

Yield 52% (36.8 mg, PE: EA = 200:1); colorless oil; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.70-7.69 (m, 1H), 7.56-7.54 (m, 2H), 7.42-7.37 (m, 4H), 7.30-7.24 (m, 2H), 2.08 (s, 1H), 0.12 (s, 18H); \( ^{13} \)C\( \{^1 \)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.1, 149.8, 144.1, 126.0, 121.7, 116.5, 110.8, 23.8, 0.0; IR (film): 2955, 1537, 1447, 1254,
842, 683 cm⁻¹; HRMS (ESI) calcd for C_{14}H_{23}^{79}BrNOSi₂ [M+H]^+ 356.0496; found 356.0504.

2-(bis(trimethylsilyl)methyl)-5-methoxybenzo[d]oxazole (3g)

![Structure of 3g]

Yield 77% (47.2 mg, PE: EA = 50:1); yellow oil; ^1H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 8.7 Hz, 1H), 7.09 (d, J = 2.3 Hz, 1H), 6.76 (dd, J = 8.8, 2.5 Hz, 1H), 3.80 (s, 3H), 2.09 (s, 1H), 0.12 (s, 18H); ^13C{¹H} NMR (100 MHz, CDCl₃) δ 170.5, 156.8, 145.3, 143.1, 111.0, 109.6, 102.3, 55.9, 23.7, 0.0; IR (film): 2955, 1540, 1482, 1252, 1197, 844 cm⁻¹; HRMS (ESI) calcd for C_{15}H_{26}NO₂Si₂ [M+H]^+ 308.1497; found 308.1488.

2-(bis(trimethylsilyl)methyl)-6-methylbenzo[d]oxazole (3h)

![Structure of 3h]

Yield 85% (49.2 mg, PE: EA = 200:1); yellow solid, m.p. = 75-77 °C; ^1H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.0 Hz, 1H), 7.22 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 2.45 (s, 3H), 2.11 (s, 1H), 0.14 (s, 18H); ^13C{¹H} NMR (100 MHz, CDCl₃) δ 169.0, 151.0, 140.0, 133.2, 124.7, 118.0, 110.0, 23.5, 21.6, 0.0; IR (film): 2957, 1547, 1253, 844, 809, 686 cm⁻¹; HRMS (ESI) calcd for C_{15}H_{26}NO₂Si₂ [M+H]^+ 292.1547; found 292.1550.

2-(bis(trimethylsilyl)methyl)-6-chlorobenzo[d]oxazole (3i)

![Structure of 3i]

Yield 67% (41.6 mg, PE: EA = 200:1); yellow oil; ^1H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.20 (dd, J = 8.4, 1.8 Hz, 1H), 2.09 (s, 1H), 0.12 (s, 18H); ^13C{¹H} NMR (100 MHz, CDCl₃) δ 170.4, 150.9, 141.1, 128.7, 124.2, 119.0, 110.4, 23.7, 0.0; IR (film): 2955, 1544, 1463, 1253, 919, 843 cm⁻¹; HRMS (ESI) calcd for C_{14}H_{23}^{35}ClNOSi₂ [M+H]^+ 312.1001; found 312.1001.

2-(bis(trimethylsilyl)methyl)-7-methylbenzo[d]oxazole (3j)
Yield 80% (46.9 mg, PE: EA = 200:1); orange solid, m.p. = 50-52 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J$ = 7.8 Hz, 1H), 7.13 (t, $J$ = 7.7 Hz, 1H), 6.99 (d, $J$ = 7.5 Hz, 1H), 2.48 (s, 3H), 2.14 (s, 1H), 0.15 (s, 18H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 169.1, 149.9, 141.8, 124.1, 123.5, 120.0, 116.0, 23.6, 15.0, 0.0; IR (film): 2955, 1543, 1252, 847, 782, 745 cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{26}$NOSi$_2$ [M+H]$^+$ 292.1547; found 292.1556.

2-(bis(trimethylsilyl)methyl)-7-bromobenzo[d]oxazole (3k)

Yield 58% (40.7 mg, PE: EA = 200:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J$ = 7.8 Hz, 1H), 7.33 (d, $J$ = 7.8 Hz, 1H), 7.12 (t, $J$ = 7.9 Hz, 1H), 2.14 (s, 1H), 0.16 (s, 18H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.0, 148.9, 143.1, 126.2, 124.9, 117.6, 101.7, 23.7, 0.0; IR (film): 2957, 1544, 1424, 1253, 848, 737 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{23}$BrNOSi$_2$ [M+H]$^+$ 356.0496; found 356.0491.

2-(bis(trimethylsilyl)methyl)-4-methylbenzo[d]oxazole (3l)

Yield 97% (56.4 mg, PE: EA = 200:1); white solid, m.p. = 48-50 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24-7.22 (m, 1H), 7.10-7.03 (m, 2H), 2.56 (s, 3H), 2.16 (s, 1H), 0.14 (s, 18H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 168.6, 150.6, 141.4, 128.9, 124.3, 122.6, 107.0, 23.6, 16.6, 0.0; IR (film): 2958, 1547, 1251, 1070, 846, 737 cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{26}$NOSi$_2$ [M+H]$^+$ 292.1547; found 292.1538.

2-(bis(trimethylsilyl)methyl)benzo[d]thiazole (3m)
Yield 65% (38.3 mg, PE: EA = 200:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 7.9$ Hz, 1H), 7.37-7.33 (m, 1H), 7.24-7.21 (m, 1H), 2.28 (s, 1H), 0.13 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 167.0, 153.4, 135.6, 125.9, 124.7, 122.4, 121.4, 29.7, 20.1; IR (film): 2956, 1497, 1436, 1251, 843, 758 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{24}$NSSi$_2$ [M+H]$^+$ 294.1163; found 294.1154.

2-(bis(trimethylsilyl)methyl)-5-bromobenzo[d]thiazole (3n)

Yield 79% (58.5 mg, PE: EA = 200:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 1.8$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.36 (dd, $J = 8.4$, 1.9 Hz, 1H), 2.25 (s, 1H), 0.13 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 174.7, 155.3, 133.8, 126.5, 124.5, 121.9, 119.0, 31.1, 0.0; IR (film): 2955, 1491, 1429, 1254, 1080, 847 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{23}$BrNSSi$_2$ [M+H]$^+$ 372.0268; found 372.0277.

2-(bis(trimethylsilyl)methyl)-5-phenylbenzo[d]thiazole (3o)

Yield 82% (60.8 mg, PE: EA = 100:1), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.65 (d, $J = 7.4$ Hz, 1H), 7.50-7.41 (m, 3H), 7.33 (t, $J = 7.3$ Hz, 1H), 2.28 (s, 1H), 0.14 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 173.3, 154.7, 141.1, 139.0, 134.0, 128.8, 127.3, 127.1, 122.9, 121.0, 120.0, 30.8, 0.0; IR (film): 2956, 1495, 1445, 1251, 846, 760 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{28}$NSSi$_2$ [M+H]$^+$ 370.1476; found 370.1483.

5-(2-bromophenyl)oxazole (4h)
Yield 68% (PE: EA = 100:1); yellow solid, m.p. = 59-60 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1H), 7.80 (t, $J$ = 1.7 Hz, 1H), 7.59-7.57 (m, 1H), 7.48-7.45 (m, 1H), 7.38 (s, 1H), 7.31-7.21 (m, 1H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 150.8, 150.1, 131.6, 130.5, 129.6, 127.3, 123.1, 122.9, 122.5; IR (film): 3113, 2921, 2849, 1111, 1045, 781, 736, 681 cm$^{-1}$; HRMS (ESI) calcd for C$_9$H$_6$NO$_7$Br [M]$^+$ 222.9627; found 222.9628.

2-(bis(trimethylsilyl)methyl)-5-phenyloxazole (5a)

Yield 83% (50.4 mg, PE: EA = 50:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 7.4 Hz, 2H), 7.40 (t, $J$ = 7.6 Hz, 2H), 7.29-7.26 (m, 1H), 7.19 (s, 1H), 2.08 (s, 1H), 0.15 (s, 18H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 149.8, 149.7, 128.9, 128.7, 127.6, 123.5, 122.1, 22.9, 0.0; IR (film): 2957, 1528, 1252, 847, 814, 692 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{26}$NOSi$_2$ [M+H]$^+$ 304.1547; found 304.1555.

2-(bis(trimethylsilyl)methyl)-5-(p-tolyl)oxazole (5b)

Yield 63% (38.9 mg, PE: EA = 50:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J$ = 8.1 Hz, 2H), 7.20 (d, $J$ = 8.0 Hz, 2H), 7.12 (s, 1H), 2.36 (s, 3H), 2.01 (s, 1H), 0.14 (s, 18H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 166.0, 149.9, 137.5, 129.6, 126.1, 123.5, 121.4, 22.8, 21.4, 0.0; IR (film): 2955, 1531, 1100, 846, 814, 692 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{28}$NOSi$_2$ [M+H]$^+$ 318.1704; found 318.1708.

2-(bis(trimethylsilyl)methyl)-5-(4-methoxyphenyl)oxazole (5c)
Yield 73\% (48.7 mg, PE: EA = 100:1); yellow solid, m.p. = 40-42 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 8.9\) Hz, 2H), 7.03 (s, 1H), 6.93 (d, \(J = 8.9\) Hz, 2H), 3.82 (s, 3H), 1.99 (s, 1H), 0.13 (s, 18H); \(^13\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.7, 159.2, 149.7, 125.0, 121.8, 120.5, 114.4, 55.4, 22.7, 0.0; IR (film): 2954, 1504, 1251, 1176, 1031, 832 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{28}\)NO\(_2\)Si\(_2\) [M+H]\(^+\) 334.1653; found 334.1661.

2-(bis(trimethylsilyl)methyl)-5-(4-chlorophenyl)oxazole (5d)

Yield 94\% (62.1 mg, PE: EA = 100:1); yellow solid, m.p. = 48-50 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (d, \(J = 8.7\) Hz, 2H), 7.35 (d, \(J = 8.7\) Hz, 2H), 7.16 (s, 1H), 2.02 (s, 1H), 0.13 (s, 18H); \(^13\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.2, 148.8, 133.2, 129.1, 127.2, 124.7, 122.6, 22.9, 0.0; IR (film): 2957, 1528, 1485, 1252, 1095, 850 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{25}\)ClNOSi\(_2\) [M+H]\(^+\) 338.1158; found 338.1150.

2-(bis(trimethylsilyl)methyl)-5-(4-bromophenyl)oxazole (5e)

Yield 92\% (69.5 mg, PE: EA = 50:1); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 8.5\) Hz, 2H), 7.41 (d, \(J = 8.5\) Hz, 2H), 7.18 (s, 1H), 2.03 (s, 1H), 0.14 (s, 18H); \(^13\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.8, 148.8, 132.1, 127.6, 125.0, 122.8, 121.2, 22.9, 0.0; IR (film): 2955, 1526, 1252, 1103, 846, 734 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{25}\)BrNOSi\(_2\) [M+H]\(^+\) 382.0653; found 382.0646.

2-(bis(trimethylsilyl)methyl)-5-(4-(trifluoromethyl)phenyl)oxazole (5f)
Yield 99% (72.9 mg, PE: EA = 50:1); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67-7.62 (m, 4H), 7.31 (s, 1H), 2.13 (s, 1H), 0.15 (s, 18H); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.7 (q, \(J = 6.4\) Hz), 148.4, 131.9, 129.2 (q, \(J = 32.6\) Hz), 126.0 (q, \(J = 3.7\) Hz), 124.2, 124.1 (q, \(J = 271.9\) Hz), 123.5, 23.1, 0.0; IR (film): 2955, 1526, 1325, 1253, 1127, 843 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{25}\)F\(_3\)NOSi\(_2\) [M+H]\(^+\) 372.1421; found 372.1415.

2-(bis(trimethylsilyl)methyl)-5-(4-(methylthio)phenyl)oxazole (5g)

Yield 80% (55.7 mg, PE: EA = 50:1); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 8.4\) Hz, 2H), 7.29 (d, \(J = 8.4\) Hz, 2H), 7.15 (s, 1H), 2.51 (s, 3H), 2.03 (s, 1H), 0.15 (s, 18H); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.3, 149.4, 137.9, 127.0, 125.7, 123.9, 121.8, 22.8, 15.9, 0.0; IR (film): 2954, 1527, 1251, 1100, 847, 693 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{28}\)NOSSi\(_2\) [M+H]\(^+\) 350.1425; found 350.1422.

2-(bis(trimethylsilyl)methyl)-5-(2-bromophenyl)oxazole (5h)

Yield 73% (55.1 mg, PE: EA = 50:1); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.69 (t, \(J = 1.7\) Hz, 1H), 7.48 (d, \(J = 7.8\) Hz, 1H), 7.40-7.38 (m, 1H), 7.28-7.26 (m, 1H), 7.21 (s, 1H), 2.04 (s, 1H), 0.15 (s, 18H); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.1, 148.2, 130.7, 130.5, 130.4, 126.4, 123.3, 123.1, 122.0, 22.9, 0.0; IR (film): 2956, 1526, 1252, 847, 780, 683 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{25}\)BrNOSi\(_2\) [M+H]\(^+\) 382.0653; found 382.0645.

2-(bis(trimethylsilyl)methyl)-4-phenyloxazole (5i)
Yield 84% (50.8 mg, PE: EA = 100:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77-7.74 (m, 3H), 7.42-7.39 (m, 2H), 7.32-7.28 (m, 1H), 2.05 (s, 1H), 0.15 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 167.0, 140.5, 132.1, 131.9, 128.7, 127.6, 125.5, 22.6, 0.0; IR (film): 2957, 1547, 1252, 845, 732, 693 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{26}$NOSi$_2$ [M+H]$^+$ 304.1547; found 304.1556.

2-(bis(trimethylsilyl)methyl)-4-(p-tolyl)oxazole (5j)

Yield 57% (36.2 mg, PE: EA = 100:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (s, 1H), 7.61 (d, $J$ = 8.1 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 2.36 (s, 3H), 2.02 (s, 1H), 0.12 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 166.9, 140.5, 137.4, 131.6, 129.4, 129.1, 125.4, 22.6, 21.4, 0.0; IR (film): 2954, 1546, 1326, 1252, 853, 742 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{28}$NOSi$_2$ [M+H]$^+$ 318.1704; found 318.1695.

2-(bis(trimethylsilyl)methyl)-4-(4-bromophenyl)oxazole (5k)

Yield 75% (56.9 mg, PE: EA = 100:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.58 (d, $J$ = 8.6 Hz, 2H), 7.49 (d, $J$ = 8.6 Hz, 2H), 2.00 (s, 1H), 0.12 (s, 18H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 139.6, 132.3, 131.8, 130.9, 127.1, 121.3, 22.7, 0.0; IR (film): 2953, 1252, 1074, 942, 845, 745 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{25}$BrNOSi$_2$ [M+H]$^+$ 382.0653; found 382.0644.

2-(bis(trimethylsilyl)methyl)-5-(naphthalen-1-yl)oxazole (5l)
Yield 89% (63.3 mg, PE: EA = 50:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31-8.25 (m, 1H), 7.86-7.78 (m, 2H), 7.66 (d, $J = 7.2$ Hz, 1H), 7.53-7.45 (m, 3H), 7.29 (s, 1H), 2.19 (s, 1H), 0.15 (s, 18H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 166.8, 148.8, 133.8, 129.8, 128.7, 128.6, 126.7, 126.0, 125.9, 125.5, 125.3, 125.0, 22.8, 0.0; IR (film): 2954, 1527, 1251, 799, 773 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{28}$NOSi$_2$ [M$+$H]$^+$ 354.1704; found 354.1711.

2-(bis(trimethylsilyl)methyl)-5-(furan-2-yl)oxazole (5m)

Yield 56% (33.1 mg, PE: EA = 50:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.42 (m, 1H), 7.07 (s, 1H), 6.48-6.45 (m, 2H), 2.01 (s, 1H), 0.12 (s, 18H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 155.1, 144.5, 142.4, 142.2, 122.2, 111.4, 105.7, 22.7, 0.0; IR (film): 2957, 1544, 1252, 1009, 847, 732 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{24}$NO$_2$Si$_2$ [M$+$H]$^+$ 294.1340; found 294.1348.

2-(bis(trimethylsilyl)methyl)-5-(thiophen-2-yl)oxazole (5n)

Yield 71% (44.1 mg, PE: EA = 50:1); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J = 5.0$ Hz, 1H), 7.18 (d, $J = 3.5$ Hz, 1H), 7.05-7.03 (m, 2H), 2.05 (s, 1H), 0.13 (s, 18H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 145.3, 130.9, 127.8, 124.5, 122.8, 121.8, 22.7, 0.0; IR (film): 2956, 1533, 1251, 1098, 1024, 846 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{24}$NOSSi$_2$ [M$+$H]$^+$ 310.1112; found 310.1116.

5-(tert-butyl)-2-methylbenzo[d]oxazole (6d)$^{15}$
Yield 93% (35.1 mg, PE: EA = 30:1); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.66 (s, 1H), 7.39-7.33 (m, 2H), 2.61 (s, 3H), 1.37 (s, 9H); \(^{13}\)C \({}^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.8, 148.9, 147.5, 141.4, 122.0, 115.9, 109.2, 34.8, 31.7, 14.5; IR (film): 2959, 1581, 1482, 1270, 1180, 918 cm\(^{-1}\).

2-methyl-5-phenylbenzo[d]oxazole (6e)\(^{16}\)

Yield 91% (38.2 mg, PE: EA = 30:1); white solid, m.p. = 56-57 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (s, 1H), 7.61-7.59 (m, 2H), 7.50 (s, 2H), 7.46-7.43 (m, 2H), 7.37-7.33 (m, 1H), 2.65 (s, 3H); \(^{13}\)C \({}^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.5, 150.6, 142.2, 141.1, 138.0, 127.5, 127.2, 124.1, 118.0, 110.2, 14.6; IR (film): 3060, 1579, 1469, 1264, 1204, 763 cm\(^{-1}\).

5-bromo-2-methylbenzo[d]oxazole (6f)\(^{17}\)

Yield 88% (35.7 mg, PE: EA = 30:1); yellow solid, m.p. = 60-61 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J\) = 16.3 Hz, 1H), 7.41-7.39 (m, 2H), 7.35-7.32 (m, 1H), 2.64 (s, 3H); \(^{13}\)C \({}^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.1, 149.9, 143.1, 127.4, 122.4, 116.8, 111.4, 14.5; IR (film): 1567, 1456, 1263, 1167, 900, 800 cm\(^{-1}\).

\((E)\)-2-(4-chlorostyryl)-5-methylbenzo[d]oxazole (7a)

Yield 63% (31.9 mg, PE: DCM = 15:1:1, 1% Et\(_3\)N); white solid, m.p. = 150-151 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.70 (d, \(J\) = 16.3 Hz, 1H), 7.52-7.50 (m, 3H), 7.40-7.37 (m, 3H), 7.00-6.98 (m, 1H), 7.00 (s, 1H), 2.63 (s, 3H); IR (film): 1660, 1628, 1596, 1536, 1494, 1460, 1417, 1353, 1305, 1229, 1180, 1140, 1101, 1057, 1007, 962, 918, 820, 753 cm\(^{-1}\).
7.15 (d, J = 8.1 Hz, 1H), 7.02 (d, J = 16.3 Hz, 1H), 2.47 (m, 3H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 162.6, 148.7, 142.3, 137.6, 135.5, 134.5, 133.7, 129.2, 128.7, 126.5, 119.9, 114.7, 109.7, 21.5; IR (film): 2920, 1643, 1531, 1263, 1097, 965, 812 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{13}$ClNO [M+H]$^+$ 270.0680; found 270.0674.

(E)-2-(4-bromostyryl)-5-methylbenzo[d]oxazole (7b)

Yield 58% (34.5 mg), PE: EA: DCM = 15:1:1, 1% Et$_3$N); white solid, m.p. = 148-149 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, J = 16.3 Hz, 1H), 7.56-7.50 (m, 3H), 7.45 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.3 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 16.3 Hz, 1H), 2.48 (s, 3H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 162.6, 148.7, 142.3, 137.7, 134.5, 134.2, 132.2, 128.9, 126.6, 123.8, 119.9, 114.8, 109.7, 21.5; IR (film): 2919, 2851, 1532, 1073, 964, 805 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{13}$ClNO [M+H]$^+$ 314.0175; found 314.0175.

(E)-6-chloro-2-styrylbenzo[d]oxazole (7c)

Yield 45% (22.9 mg), PE: EA: DCM = 15:1:1, 1% Et$_3$N); white solid, m.p. = 87-89 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, J = 16.3 Hz, 1H), 7.62-7.59 (m, 3H), 7.53 (d, J = 1.8 Hz, 1H), 7.45-7.37 (m, 3H), 7.31 (dd, J = 8.5, 1.9 Hz, 1H), 7.04 (d, J = 16.3 Hz, 1H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 163.5, 150.6, 141.0, 140.1, 135.0, 130.8, 130.0, 129.0, 127.7, 125.2, 120.3, 113.5, 111.0; IR (film): 2919, 1643, 1460, 1264, 930, 758 cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{11}$BrNO [M+H]$^+$ 256.0524; found 256.0522.

12) References

1. Lee, J. J.; Kin, J.; Jun, Y. M.; Lee, B. M.; Kim, B. H. Tetrahedron 2009, 65, 8821-8831.
2. Zhao, X.; Ding, F.; Li, J.; Lu, X.; Wang, B.; Yu, P. Tetrahedron Lett. 2015, 56, 511-513.
3. Cho, S. H.; Kim, J. Y.; Lee, S. Y.; Chang, S. Angew. Chem., Int. Ed. 2009, 48, 9127-9130.
4. Wertz, S.; Kodama, S.; Studer, A. Angew, Chem., Int. Ed. 2011, 50, 11511-11515.
5. Besselièvre, F.; Mahuteau-Betzer, F.; Grierson, D. S; Piguel, S. J. Org. Chem. 2008, 73, 3278-3280.
6. Vinay Kumar, K. S.; Swaroop, T. R.; Rajeev, N.; Vinayaka, A. C.; Lingaraju, G. S.; Rangappa, K. S.; Sadashiva, M, P. Synlett 2016, 27, 1363-1366.
7. Matsuyama, N.; Hirano, K.; Satoh, T.; Miura, M. Org. Lett. 2009, 11, 4156-4159.

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8. Tanaka, C. *Yakugaku Zasshi* 1965, 85, 186-192.
9. Pippel, D. J.; Mapes, C. M.; Mani, N. S. *J. Org. Chem.* 2007, 72, 5828-5831.
10. Whitney, S. E.; Winters, M.; Rickborn, B. *J. Org. Chem.* 1990, 55, 929-935.
11. Amaike, K.; Itami, K.; Yamaguchi, J. *Chem. Eur. J.* 2016, 22, 4384-4388.
12. Bürli, R. W.; Luckhurst, C. A.; Aziz, O.; Matthews, K. L.; Yates, D.; Lyons, K. A.; Beconi, M.; McAllister, G.; Breccia, P.; Stott, A. J.; Penrose, S. D.; Wall, M.; Lamers, M.; Philip, L.; Müller, I.; Richardson, C. M.; Jarvis, R.; Stones, L.; Hughes, S.; Wishart, G.; Haughan, A. F.; O’Connell, C.; Mead, T.; NeNeil, H.; Vann, J.; Mangette, J.; Maillard, M.; Beaumont, V.; Munoz-Sanjuan, I.; Dominguez, C. *J. Med. Chem.* 2013, 54, 9934-9954.
13. Ibad, M. F.; Langer, P.; Reiß, F.; Schulz, A.; Villinger, A. *J. Am. Chem. Soc.* 2012, 134, 17757-17768.
14. Das, M.; Manvar, A.; Jacolot, M.; Blangetti, M.; Johes, R. C.; O’Shea, D. F. *Chem. Eur. J.* 2015, 21, 8737-8740.
15. Li, K.-H.; Du, Z.-B.; Guo, C.-C.; Chen, Q.-Y. *J. Org. Chem.* 2009, 74, 3286-3292.
16. Hua, X.; Masson-Makdissi, J.; Sullivan, R. J.; Newman, S. G. *Org. Lett.* 2016, 18, 5312-5315.
17. Zhang, X.; Huang, R.; Marrot, J.; Coeffard, V.; Xiong, Y. *Tetrahedron* 2015, 71, 700-708.
18. Tan, G.; He, S.; Huang, X.; Liao, X.; Cheng, Y.; You, J. *Angew. Chem., Int. Ed.* 2016, 55, 10414-10418.
13) $^1$H and $^{13}$C NMR spectra
