

Supporting Information

Copper-catalyzed radical cascade oxyalkylation of olefinic amides with simple alkanes: highly efficient access to benzoxazines

Jie Wang, Ruoyu Sang, Xiaolong Chong, Yinuo Zhao, Wenjie Fan, Zejiang Li and
Jincan Zhao*

Index	Page Number
1. General information.....	S2
2. General procedure for the synthesis of alkylated benzoxazines....	S2
3. Characterization data for 3.....	S2
4. HRMS spectrum of TEMPO-cyclohexane adduct.....	S10
5. ¹H and ¹³C NMR spectra of 3.....	S11

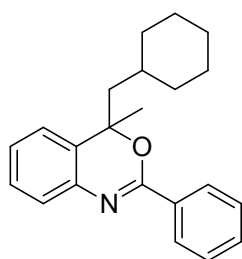
1. General information

All manipulations were carried out under air atmosphere. Commercially available reagents were used as received without purification. Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF–254 with detection by UV. ^1H and ^{13}C NMR spectra were recorded on a Bruker advance III 600M spectrometer. The chemical shift references were as follows: (^1H) CDCl_3 , 7.26 ppm (CHCl_3); (^{13}C) CDCl_3 , 77.00 ppm (CDCl_3). HRMS spectra were carried out at micrOTOF-Q III (ESI). Melting point determination was taken on a Melt–Temp apparatus (X-4) from Beijing Fukai Electro–optic Instrument Plant and was uncorrected.

2. General procedure for the synthesis of alkylated benzoxazines

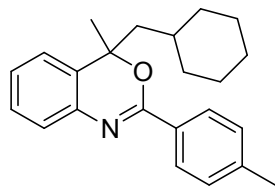
A sealable reaction tube equipped with a magnetic stirrer bar was charged with *N*-(2-(prop-1-en-2-yl)phenyl)benzamide (71 mg, 0.3 mmol), 1,10-phenanthroline (54 mg, 0.3 mmol), K_2CO_3 (41 mg, 0.3 mmol), DTBP (di-*tert*-butyl peroxide, 0.9 mmol, 170 μL), and cyclohexane (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 120 $^\circ\text{C}$. After stirring the mixture at this temperature for 24 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water, dried over MgSO_4 . After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the corresponding product, 4-(cyclohexylmethyl)-4-methyl-2-phenyl-4*H*-benzo[*d*][1,3]oxazine (**3ab**, 78 mg, 82% yield).

3. Characterization data for 3

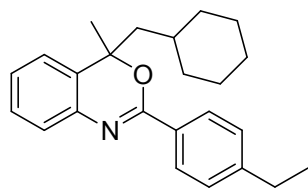


4-(cyclohexylmethyl)-4-methyl-2-phenyl-4*H*-benzo[*d*][1,3]oxazine (3ab): Slight yellow oil. Yield: 78 mg (82%). ^1H NMR (600 MHz, CDCl_3) δ 8.19 – 8.15 (m, 2H), 7.48 (dt, J = 25.0, 7.1 Hz, 3H), 7.33 – 7.25 (m, 2H), 7.18 (td, J = 7.4, 1.4 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 1.99 (dd, J = 14.8, 4.6 Hz, 1H), 1.86 (dd, J = 14.8, 6.0 Hz, 1H), 1.74 – 1.52 (m, 9H), 1.21 – 1.06 (m, 3H), 1.01 – 0.92 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.45, 138.93, 133.15, 131.08, 130.29, 128.25, 128.13, 127.75, 126.30,

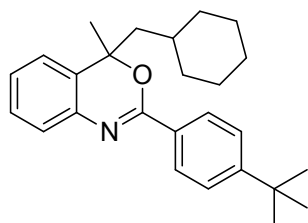
125.16, 122.87, 81.32, 48.15, 34.89, 34.65, 33.63, 28.53, 26.26, 26.17, 26.12. HRMS (ESI) calcd for $C_{22}H_{26}NO$ $[M+H]^+$ 320.2014, found 320.2013.



4-(cyclohexylmethyl)-4-methyl-2-(p-tolyl)-4H-benzo[d][1,3]oxazine (3bb): Slight yellow oil. Yield: 64 mg (64%). 1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.1$ Hz, 2H), 7.29 – 7.22 (m, 4H), 7.17 – 7.12 (m, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 2.40 (s, 3H), 1.96 (dd, $J = 14.8, 4.7$ Hz, 1H), 1.82 (dd, $J = 14.8, 6.1$ Hz, 1H), 1.71 – 1.51 (m, 9H), 1.19 – 1.03 (m, 3H), 0.98 – 0.90 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.64, 141.48, 139.07, 130.36, 130.31, 128.90, 128.22, 127.77, 126.10, 125.02, 122.84, 81.16, 48.08, 34.90, 34.65, 33.62, 28.43, 26.28, 26.18, 26.13, 21.53. HRMS (ESI) calcd for $C_{23}H_{28}NO$ $[M+H]^+$ 334.2171, found 334.2172.

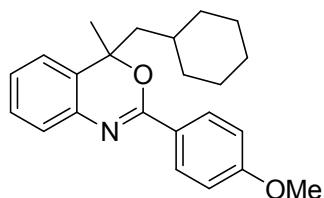


4-(cyclohexylmethyl)-2-(4-ethylphenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3cb): Slight yellow oil. Yield: 74 mg (71%). 1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, $J = 8.2$ Hz, 2H), 7.29 – 7.24 (m, 4H), 7.17 – 7.13 (m, 1H), 7.07 (d, $J = 7.3$ Hz, 1H), 2.70 (q, $J = 7.6$ Hz, 2H), 1.97 (dd, $J = 14.8, 4.7$ Hz, 1H), 1.83 (dd, $J = 14.8, 6.1$ Hz, 1H), 1.72 – 1.51 (m, 9H), 1.26 (t, $J = 7.6$ Hz, 3H), 1.20 – 1.05 (m, 3H), 0.99 – 0.90 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.64, 147.75, 139.11, 130.61, 130.30, 128.21, 127.86, 127.70, 126.08, 125.04, 122.85, 81.16, 48.05, 34.91, 34.65, 33.64, 28.86, 28.52, 26.29, 26.19, 26.15, 15.32. HRMS (ESI) calcd for $C_{24}H_{30}NO$ $[M+H]^+$ 348.2327, found 348.2329.

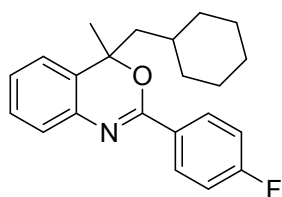


2-(4-(tert-butyl)phenyl)-4-(cyclohexylmethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3db): Slight yellow oil. Yield: 71 mg (63%). 1H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.30 – 7.25 (m, 2H), 7.17 – 7.13 (m, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 1.97 (dd, $J = 14.8, 4.7$ Hz, 1H),

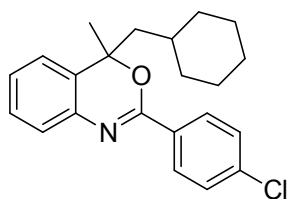
1.85 (dd, $J = 14.8, 6.2$ Hz, 1H), 1.73 – 1.53 (m, 9H), 1.35 (s, 9H), 1.19 – 1.04 (m, 3H), 0.99 – 0.91 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.57, 154.55, 139.11, 130.36, 130.25, 128.20, 127.58, 126.08, 125.13, 125.06, 122.86, 81.15, 47.97, 34.91, 34.89, 34.63, 33.66, 31.19, 28.65, 26.29, 26.19, 26.15. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{34}\text{NO}$ $[\text{M}+\text{H}]^+$ 376.2640, found 376.2639.



4-(cyclohexylmethyl)-2-(4-methoxyphenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3eb): Slight yellow oil. Yield: 76 mg (73%). ^1H NMR (600 MHz, CDCl_3) δ 8.11 – 8.08 (m, 2H), 7.26 (d, $J = 3.9$ Hz, 2H), 7.16 – 7.11 (m, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.96 – 6.92 (m, 2H), 3.85 (s, 3H), 1.96 (dd, $J = 14.8, 4.7$ Hz, 1H), 1.81 (dd, $J = 14.8, 6.1$ Hz, 1H), 1.71 – 1.51 (m, 9H), 1.20 – 1.03 (m, 3H), 0.98 – 0.89 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.11, 156.41, 139.20, 130.24, 129.54, 128.20, 125.87, 125.61, 124.85, 122.81, 113.50, 81.10, 55.33, 48.04, 34.92, 34.67, 33.61, 28.31, 26.28, 26.18, 26.13. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 350.2120, found 350.2123.

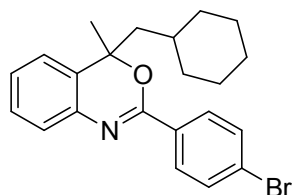


4-(cyclohexylmethyl)-2-(4-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3fb): Slight yellow oil. Yield: 71 mg (70%). ^1H NMR (600 MHz, CDCl_3) δ 8.14 (dd, $J = 8.8, 5.5$ Hz, 2H), 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 1H), 7.11 (t, $J = 8.7$ Hz, 2H), 7.07 (d, $J = 7.6$ Hz, 1H), 1.96 (dd, $J = 14.9, 4.7$ Hz, 1H), 1.82 (dd, $J = 14.9, 6.1$ Hz, 1H), 1.69 – 1.52 (m, 9H), 1.20 – 1.04 (m, 3H), 0.99 – 0.89 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 164.77 (d, $J = 251.4$ Hz), 155.57, 138.80, 130.15, 129.95 (d, $J = 8.8$ Hz), 129.31 (d, $J = 2.9$ Hz), 128.32, 126.37, 125.10, 122.91, 115.19 (d, $J = 21.8$ Hz), 81.52, 48.18, 34.90, 34.66, 33.64, 28.48, 26.26, 26.17, 26.11. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{FNO}$ $[\text{M}+\text{H}]^+$ 338.1920, found 338.1918.



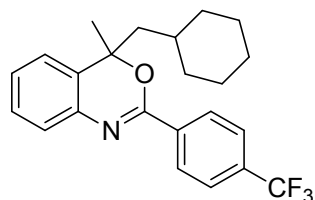
2-(4-chlorophenyl)-4-(cyclohexylmethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3gb): Slight yellow oil.

Yield: 77 mg (73%). ^1H NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 1.96 (dd, $J = 14.9, 4.7$ Hz, 1H), 1.81 (dd, $J = 14.9, 6.1$ Hz, 1H), 1.69 – 1.63 (m, 4H), 1.62 – 1.51 (m, 5H), 1.18 – 1.03 (m, 3H), 0.98 – 0.89 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.52, 138.67, 137.28, 131.63, 130.19, 129.08, 128.43, 128.35, 126.56, 125.18, 122.93, 81.61, 48.22, 34.88, 34.64, 33.64, 28.51, 26.25, 26.16, 26.10. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{ClNO}$ $[\text{M}+\text{H}]^+$ 354.1625, found 354.1626.



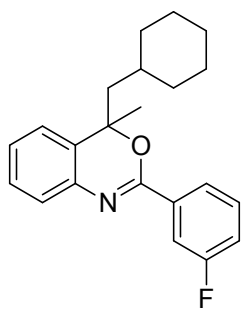
2-(4-bromophenyl)-4-(cyclohexylmethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3hb): Slight yellow oil.

Yield: 100 mg (84%). ^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, $J = 8.6$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 1.95 (dd, $J = 14.9, 4.8$ Hz, 1H), 1.80 (dd, $J = 14.9, 6.1$ Hz, 1H), 1.69 – 1.63 (m, 4H), 1.62 – 1.52 (m, 5H), 1.18 – 1.03 (m, 3H), 0.98 – 0.89 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.60, 138.63, 132.07, 131.39, 130.19, 129.28, 128.35, 126.59, 125.82, 125.19, 122.94, 81.62, 48.21, 34.87, 34.63, 33.63, 28.51, 26.25, 26.15, 26.09. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{BrNO}$ $[\text{M}+\text{H}]^+$ 398.1120, found 398.1120.



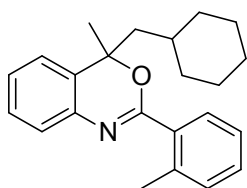
4-(cyclohexylmethyl)-4-methyl-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazine (3ib): Slight

yellow oil. Yield: 91 mg (78%). ^1H NMR (600 MHz, CDCl_3) δ 8.27 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 1.99 (dd, $J = 14.9, 4.8$ Hz, 1H), 1.85 (dd, $J = 14.9, 6.1$ Hz, 1H), 1.68 (s, 4H), 1.63 – 1.53 (m, 5H), 1.20 – 1.04 (m, 3H), 1.00 – 0.91 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.04, 138.45, 136.53, 132.60 (q, $J = 32.5$ Hz), 130.22, 128.43, 128.00, 126.96, 125.44, 125.12 (q, $J = 3.6$ Hz), 123.01, 81.89, 48.31, 34.87, 34.64, 33.69, 28.68, 26.25, 26.16, 26.09. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{25}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 388.1888, found 388.1889.

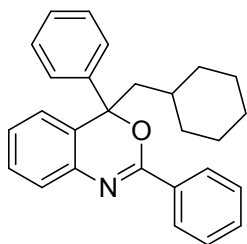


4-(cyclohexylmethyl)-2-(3-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3jb): Slight yellow oil.

Yield: 72 mg (71%). ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, $J = 7.8$ Hz, 1H), 7.85 – 7.81 (m, 1H), 7.42 – 7.37 (m, 1H), 7.29 – 7.26 (m, 2H), 7.20 – 7.15 (m, 2H), 7.07 (d, $J = 7.6$ Hz, 1H), 1.96 (dd, $J = 14.9$, 4.8 Hz, 1H), 1.82 (dd, $J = 14.9$, 6.1 Hz, 1H), 1.70 – 1.63 (m, 4H), 1.62 – 1.51 (m, 5H), 1.17 – 1.04 (m, 3H), 0.99 – 0.90 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.67 (d, $J = 245.4$ Hz), 155.27 (d, $J = 3.2$ Hz), 138.57, 135.50 (d, $J = 8.0$ Hz), 130.22, 129.66 (d, $J = 7.9$ Hz), 128.35, 126.68, 125.29, 123.39 (d, $J = 2.8$ Hz), 122.95, 117.99 (d, $J = 21.4$ Hz), 114.62 (d, $J = 23.5$ Hz), 81.71, 48.19, 34.88, 34.62, 33.64, 28.59, 26.24, 26.15, 26.09. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{FNO}$ $[\text{M}+\text{H}]^+$ 338.1920, found 338.1921.

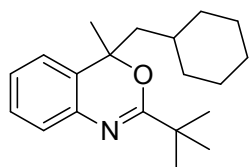


4-(cyclohexylmethyl)-4-methyl-2-(o-tolyl)-4H-benzo[d][1,3]oxazine (3kb): Slight yellow oil. Yield: 55 mg (55%). ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 7.6$ Hz, 1H), 7.28 – 7.22 (m, 1H), 7.28 – 7.22 (m, 4H), 7.19 – 7.16 (m, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 2.63 (s, 3H), 1.97 (dd, $J = 14.8$, 4.7 Hz, 1H), 1.87 (dd, $J = 14.8$, 5.9 Hz, 1H), 1.69 – 1.63 (m, 4H), 1.58 – 1.51 (d, $J = 10.7$ Hz, 5H), 1.18 – 1.03 (m, 3H), 0.98 – 0.86 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.47, 138.80, 137.94, 133.22, 131.28, 130.02, 129.55, 129.30, 128.26, 126.40, 125.63, 125.13, 122.99, 81.68, 48.36, 34.81, 34.69, 33.71, 29.22, 26.30, 26.21, 26.14, 21.48. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$ 334.2171, found 334.2173.

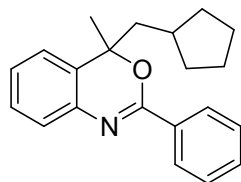


4-(cyclohexylmethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3lb): Slight yellow oil. Yield: 67 mg (59%). ^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 7.1$ Hz, 2H), 7.52 – 7.44 (m, 3H), 7.35 – 7.29 (m,

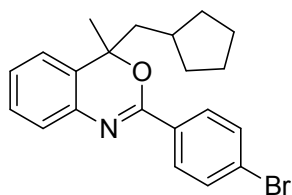
4H), 7.26 – 7.21 (m, 4H), 7.17 (dd, $J = 10.4, 4.0$ Hz, 1H), 2.30 (d, $J = 4.9$ Hz, 2H), 1.85 (d, $J = 12.5$ Hz, 1H), 1.73 – 1.67 (m, 2H), 1.63 – 1.53 (m, 3H), 1.20 – 1.01 (m, 5H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.49, 144.66, 139.72, 132.80, 131.26, 128.69, 128.32, 128.19, 128.15, 127.81, 127.50, 126.14, 125.49, 125.42, 124.65, 84.73, 48.03, 35.12, 34.52, 34.29, 26.35, 26.21, 26.18. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$ 382.2171, found 382.2171.



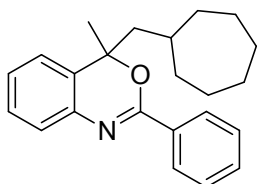
2-(tert-butyl)-4-(cyclohexylmethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3mb): Slight yellow solid (recrystallization from hexane / EtOAc (v/v = 10:1)), mp 61–63 °C. Yield: 57 mg (63%). ^1H NMR (600 MHz, CDCl_3) δ 7.21 (td, $J = 7.8, 1.2$ Hz, 1H), 7.16 – 7.13 (m, 1H), 7.11 (td, $J = 7.5, 1.1$ Hz, 1H), 6.99 (dd, $J = 7.6, 0.8$ Hz, 1H), 1.89 (dd, $J = 14.7, 4.6$ Hz, 1H), 1.79 (dd, $J = 14.8, 6.4$ Hz, 1H), 1.68 (d, $J = 11.5$ Hz, 1H), 1.63 – 1.52 (m, 4H), 1.48 (s, 4H), 1.25 (s, 9H), 1.19 – 1.05 (m, 3H), 0.98 – 0.86 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 167.60, 138.91, 129.62, 128.01, 125.81, 124.82, 122.85, 80.26, 47.68, 37.13, 34.89, 34.62, 33.66, 29.13, 27.49, 26.37, 26.22, 26.20. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{30}\text{NO}$ $[\text{M}+\text{H}]^+$ 300.2327, found 300.2326.



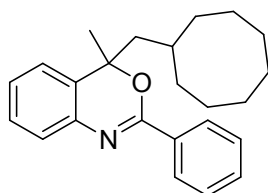
4-(cyclopentylmethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3aa): Slight yellow oil. Yield: 73 mg (80%). ^1H NMR (600 MHz, CDCl_3) δ 8.17 – 8.13 (m, 2H), 7.48 – 7.40 (m, 3H), 7.29 – 7.23 (m, 2H), 7.15 (td, $J = 7.5, 1.3$ Hz, 1H), 7.06 (dd, $J = 7.6, 0.9$ Hz, 1H), 2.14 (dd, $J = 14.6, 5.6$ Hz, 1H), 2.00 (dd, $J = 14.6, 7.0$ Hz, 1H), 1.94 – 1.86 (m, 1H), 1.74 – 1.64 (m, 5H), 1.50 (dt, $J = 10.8, 5.9$ Hz, 2H), 1.42 – 1.33 (m, 2H), 1.13 – 1.06 (m, 1H), 1.05 – 0.98 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.42, 138.90, 133.10, 131.01, 129.95, 128.21, 128.07, 127.70, 126.25, 125.10, 122.97, 81.29, 47.41, 36.02, 34.15, 33.95, 28.74, 24.92, 24.77. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$ 306.1858, found 306.1856.



2-(4-bromophenyl)-4-(cyclopentylmethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3ha): Slight yellow oil. Yield: 90 mg (78%). ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 3.2 Hz, 2H), 7.11 – 7.07 (m, 1H), 6.99 (d, J = 7.6 Hz, 1H), 2.05 (dd, J = 14.6, 5.6 Hz, 1H), 1.90 (dd, J = 14.6, 7.0 Hz, 1H), 1.84 – 1.77 (m, 1H), 1.65 – 1.56 (m, 5H), 1.47 – 1.40 (m, 2H), 1.34 – 1.27 (m, 2H), 1.05 – 0.90 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.61, 138.68, 132.11, 131.37, 129.92, 129.29, 128.35, 126.56, 125.78, 125.19, 123.06, 81.65, 47.57, 36.05, 34.20, 33.99, 28.79, 24.96, 24.81. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{BrNO}$ $[\text{M}+\text{H}]^+$ 384.0963, found 384.0967.

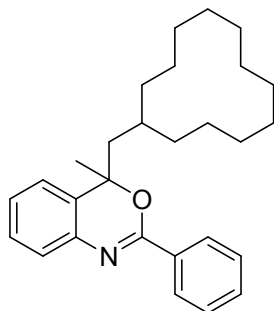


4-(cycloheptylmethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3ac): Slight yellow oil. Yield: 68 mg (68%). ^1H NMR (600 MHz, CDCl_3) δ 8.17 – 8.14 (m, 2H), 7.51 – 7.46 (m, 1H), 7.44 (dd, J = 11.4, 4.4 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.20 – 7.16 (m, 1H), 7.09 (d, J = 7.3 Hz, 1H), 1.98 (dd, J = 14.7, 4.5 Hz, 1H), 1.89 (dd, J = 14.7, 6.1 Hz, 1H), 1.85 – 1.78 (m, 1H), 1.70 (s, 3H), 1.68 – 1.60 (m, 2H), 1.54 – 1.46 (m, 4H), 1.45 – 1.38 (m, 2H), 1.35 – 1.19 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.50, 138.99, 133.11, 131.10, 130.31, 128.28, 128.14, 127.76, 126.33, 125.15, 122.91, 81.49, 48.87, 36.58, 36.03, 35.13, 28.52, 28.25, 28.22, 26.10, 25.96. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$ 334.2171, found 334.2170.

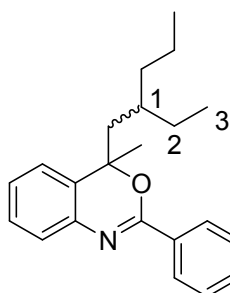


4-(cyclooctylmethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3ad): Slight yellow oil. Yield: 82 mg (79%). ^1H NMR (600 MHz, CDCl_3) δ 8.17 – 8.12 (m, 2H), 7.45 (dt, J = 26.2, 7.2 Hz, 3H), 7.30 – 7.25 (m, 2H), 7.16 (td, J = 7.6, 1.8 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 1.99 – 1.94 (m, 1H), 1.88 (t, J = 8.7 Hz, 2H), 1.69 (s, 3H), 1.63 – 1.58 (m, 1H), 1.55 – 1.37 (m, 9H), 1.35 – 1.25 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.47, 138.98, 133.12, 131.08, 130.24, 128.28, 128.13, 127.74, 126.31, 125.17,

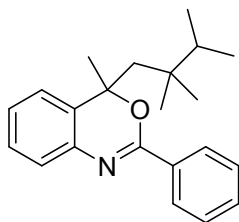
122.94, 81.57, 48.80, 33.95, 33.17, 32.98, 28.37, 27.39, 27.22, 26.21, 25.26, 24.80. HRMS (ESI) calcd for $C_{24}H_{30}NO$ $[M+H]^+$ 348.2327, found 348.2326.



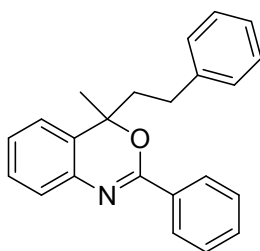
4-(cyclododecylmethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3ae): Slight yellow oil. Yield: 85 mg (70%). 1H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.27 (dd, $J = 12.9, 6.2$ Hz, 2H), 7.18 – 7.13 (m, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 1.93 – 1.84 (m, 2H), 1.74 – 1.68 (m, 4H), 1.32 – 1.13 (m, 19H), 1.12 – 1.04 (m, 2H), 1.00 – 0.94 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.45, 138.97, 133.13, 131.05, 130.08, 128.31, 128.07, 127.78, 126.30, 125.16, 123.18, 81.59, 47.03, 31.04, 30.98, 29.25, 28.48, 23.98, 23.91, 23.59, 23.49, 23.45, 23.38, 23.35, 21.91, 21.86. HRMS (ESI) calcd for $C_{28}H_{38}NO$ $[M+H]^+$ 404.2953, found 404.2951.



4-heptyl-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3af, C1), 4-methyl-4-(2-methylhexyl)-2-phenyl-4H-benzo[d][1,3]oxazine(3af, C2), 4-(2-ethylpentyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3af, C3): Slight yellow oil. Yield: 39 mg (40%). 1H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, $J = 7.3$ Hz, 2H), 7.50 – 7.41 (m, 3H), 7.31 – 7.25 (m, 2H), 7.17 (dd, $J = 9.5, 4.5$ Hz, 1H), 7.08 (dd, $J = 11.5, 7.5$ Hz, 1H), 2.10 (d, $J = 3.1$ Hz, 0.16H), 2.07 (d, $J = 3.2$ Hz, 0.16H), 1.95 (dt, $J = 15.1, 4.8$ Hz, 0.64H), 1.91 (d, $J = 4.5$ Hz, 0.16H), 1.90 – 1.84 (m, 0.64H), 1.83 (d, $J = 5.9$ Hz, 0.16H), 1.79 – 1.65 (m, 4.49H), 1.59 – 1.54 (m, 0.46H), 1.30 – 1.09 (m, 7.41H), 0.90 – 0.69 (m, 6.49H). HRMS (ESI) calcd for $C_{22}H_{28}NO$ $[M+H]^+$ 322.2171, found 322.2170.

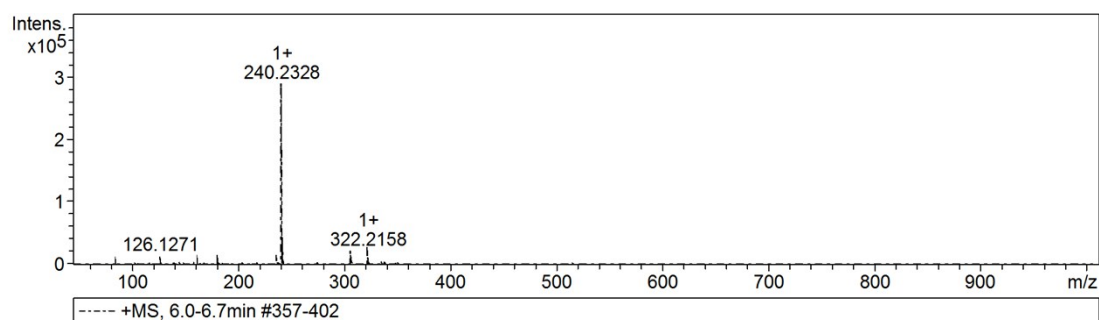


4-methyl-2-phenyl-4-(2,2,3-trimethylbutyl)-4H-benzo[d][1,3]oxazine (3ag): Slight yellow oil. Yield: 43 mg (45%). ^1H NMR (600 MHz, CDCl_3) δ 8.17 – 8.14 (m, 2H), 7.49 – 7.42 (m, 3H), 7.27 – 7.22 (m, 2H), 7.16 – 7.08 (m, 2H), 2.14 (d, $J = 15.3$ Hz, 1H), 2.01 (d, $J = 15.3$ Hz, 1H), 1.69 (s, 3H), 1.46 (dt, $J = 13.6, 6.8$ Hz, 1H), 0.94 (s, 3H), 0.85 (d, $J = 6.8$ Hz, 3H), 0.80 (d, $J = 6.8$ Hz, 3H), 0.71 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.81, 138.26, 133.20, 131.06, 130.68, 128.15, 128.14, 127.77, 126.06, 125.46, 123.52, 81.85, 47.86, 38.89, 36.24, 32.74, 26.44, 25.38, 17.53, 17.48. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$ 322.2171, found 322.2170.



4-methyl-4-phenethyl-2-phenyl-4H-benzo[d][1,3]oxazine (3ah): Slight yellow oil. Yield: 44 mg (45%). ^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, $J = 7.3$ Hz, 2H), 7.53 (dt, $J = 14.9, 7.2$ Hz, 3H), 7.37 (dt, $J = 6.9, 5.0$ Hz, 2H), 7.30 – 7.23 (m, 3H), 7.22 – 7.14 (m, 4H), 2.84 – 2.71 (m, 2H), 2.44 – 2.28 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.58, 141.60, 139.05, 132.97, 131.25, 129.46, 128.53, 128.38, 128.23, 128.21, 127.81, 126.57, 125.85, 125.32, 122.77, 80.63, 43.34, 30.19, 27.77. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$ 328.1701, found 328.1703.

4. HRMS spectrum of TEMPO-cyclohexane adduct



5. ^1H and ^{13}C NMR spectra of 3

