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Efficient synthesis of benzene-fused 6/7-membered amides *via* Xphos Pd G2 catalyzed intramolecular C–N bond formation†

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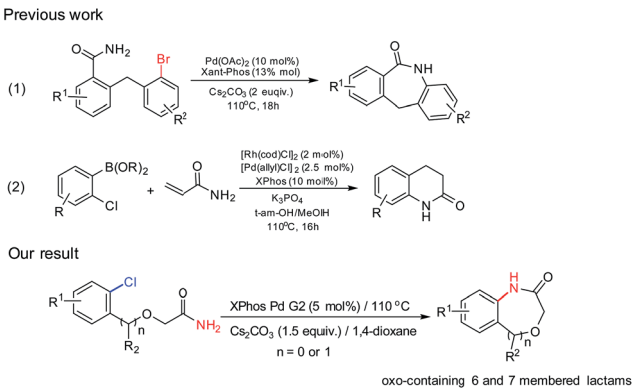
An efficient approach for benzene-fused 6/7-membered amides *via* intramolecular amidation of aryl chlorides catalyzed by a Buchwald–Hartwig second generation Pd catalyst (Xphos Pd G2) has been successfully developed. This catalyst system allows the primary amides which have only modest nucleophilicity to be coupled successfully even with electron rich aryl chlorides in short reaction time. The intramolecular amidation reaction also has good chemoselectivity and excellent functional group compatibility.

Introduction

Benzene-fused amides are important organic compounds commonly encountered in biologically relevant natural or synthetic pharmaceutical compounds.[1–3] Some methods were developed towards the synthesis of these scaffolds which are mainly benzene-fused 6-membered amides known as 2*H*-1,4-benzoxazin-3-(4*H*)-one derivatives.[4–6] However, the substituent diversity in the products is limited and more importantly, it is difficult to synthesize benzene-fused seven-membered amides.

Organic halides are some of the most common industrially used compounds and widely used as starting materials for many chemical transformations. The efficient cleavage of C–X (X = halogen atom) bonds has been actively studied by organic chemists. Among them, palladium catalysts developed by Buchwald and Hartwig proved to be the most useful ones for the C–N bond formation.[7,8] The amination of aryl halogens by transition metal catalyzed coupling methodology has been the subject of significant interest during past few decades, but the amidation reaction has not yet fully studied. Electron-deficient amides have been difficult coupling partners due to their modest nucleophilicity and intolerance of strong base. Although, amidation of aryl bromides and iodides have become the well-established processes in the reaction,[9–12] however, largely absent from the literature on Pd-catalyzed amidation reactions is the description of an efficient method for coupling aryl chlorides.

To the best of our knowledge, there are limited literature reports the intramolecular amidation of aryl chlorides which can construct the valuable molecular structure of benzene-fused amides. Laha *et al.* reported the synthesis of dibenzoazepinones *via* the intramolecular amination of aryl bromide (not aryl chlorides) in 18 h with yield of 68–94%.[13] While, Lautens *et al.* reported the synthesis of 3,4-dihydroquinolinones *via* the reaction between arylboronic acid and acrylamide (Scheme 1).[14]



Scheme 1 Benzene-fused amides: prior arts and design.

As part of our continuing efforts for accessing biologically hetero compounds by metal-catalyzed reactions,[15] herein, we report a facile, efficient, convenient and generally applicable method for the intramolecular amidation of organic halides to synthesize oxo-containing 6/7 membered benzene-fused amides with excellent yield using commerical available XPhos Pd G2 as the catalyst.

Results and discussion

At the outset of our investigation, we employed **1a** as the substrate for the preparation of the desired benzene-fused 7-membered amide **2a**. After considerable amount of efforts on

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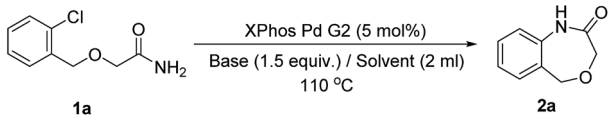
condition discovery and optimization, we were able to obtain **2a** with 97% isolated yield in 5 h.

The reaction conditions, as shown in the equation in Table 1, including the use of Xphos Pd G2 as the most effective catalyst, 1,4-dioxane as the optimal solvent, and Cs_2CO_3 as the base. Indeed, other catalysts, such as Ph_3PPdCl, JohnPhos Pd G2, Xphos $PdCl_2$ all fared much worse than Xphos Pd G2 in terms of reaction rate and efficiency (entries 1–3 *vs.* 5). We also performed the reaction with catalysts Xphos Pd G1, Xphos Pd G3 and Xphos Pd G4. All of them gave almost the same result with Xphos Pd G2 (entries 4–7). However, Xphos Pd G2 is the cheapest one. Thus, we chose it as catalyst for further investigation. The combination of $Pd(OAc)_2$ and ligand Xphos cannot proceed the transformation either (entry 8). The reaction can be faster and more efficiency when Cs_2CO_3 was used as the base instead of K_2CO_3 (entry 5 *vs.* entry 9). The best solvent for the reaction is 1,4-dioxane. Toluene is equal efficiency, but DMSO or DMF doesn't work for the reaction (entries 10, 12 and 13). The substrate **1a** can also convert smoothly to product **2a** at 80 °C, but requires longer reaction time (entry 14). Lowering the reaction temperature to 50 °C, the reaction could hardly happen and only trace product observed even prolonging the reaction time to 36 h (entry 15). Substrate concentration has limited effect on the reaction. When the concentration of the substrate was 0.25 M, it gave the best result with 99% yield. Increasing or decreasing the concentration of **1a**, both gave slightly lower yield (entries 16 and 17). Higher the catalyst loading can faster the reaction with same yield (entry 18). Lowering the catalyst loading to 2.5% makes the reaction much difficult to proceed (entry 19). Small amount of water could hinder the reaction and slow down the reaction rate and yield (entry 20).

Table 1 Optimization for the reaction condition[a]

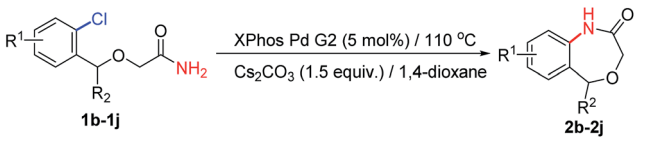


1a 2a

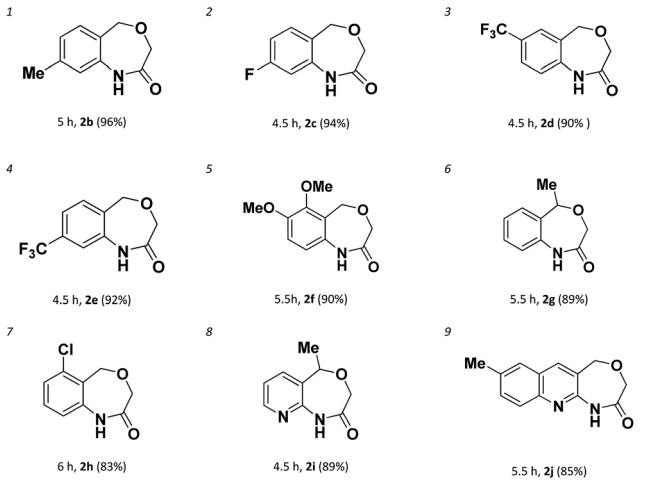
Entry	Catalyst	Base	Solvent	Time	Yield[b]
1	PPh_3PdCl	K_2CO_3	1,4-Dioxane	24 h	NR
2	Johnphos Pd	K_2CO_3	1,4-Dioxane	24 h	18%
3	Xphos $PdCl_2$	K_2CO_3	1,4-Dioxane	24 h	84%
4	Xphos Pd G1	K_2CO_3	1,4-Dioxane	5 h	95%
5	Xphos Pd G2	K_2CO_3	1,4-Dioxane	5 h	97%
6	Xphos Pd G3	K_2CO_3	1,4-Dioxane	5 h	94%
7	Xphos Pd G4	K_2CO_3	1,4-Dioxane	5 h	97%
8	$Pd(OAc)_2$/Xphos	K_2CO_3	1,4-Dioxane	24 h	NR
9	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	2 h	99%
10	XPhos Pd G2	Cs_2CO_3	DMSO	24 h	Trace
11	XPhos Pd G2	Cs_2CO_3	H_2O	24 h	14%
12	XPhos Pd G2	Cs_2CO_3	MePh	8 h	96%
13	XPhos Pd G2	Cs_2CO_3	DMF	24 h	NR
14[c]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	8 h	98%
15[d]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	36 h	Trace
16[e]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	4 h	97%
17[f]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	4 h	96%
18[g]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	2.5 h	97%
19[h]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	12 h	Trace
20[i]	XPhos Pd G2	Cs_2CO_3	1,4-Dioxane	24 h	84%

[a] The reactions were carried in Schlenk flasks. **1a** (0.5 mmol), Pd* (5 mol%), solvent (2 ml), base (1.5 equiv.), 110 °C. [b] Isolated yield. [c] The reaction temperature is 80 °C. [d] The reaction temperature is 50 °C. [e] Substrate concentration is 0.25 M. [f] Substrate concentration is 0.5 M. [g] The catalyst loading is 7.5 mol%. [h] The catalyst loading is 2.5 mol%. [i] H_2O (5 μl) was added.

Table 2 Formation of benzene-fused 7-membered amide: reaction scopes.[a,b]

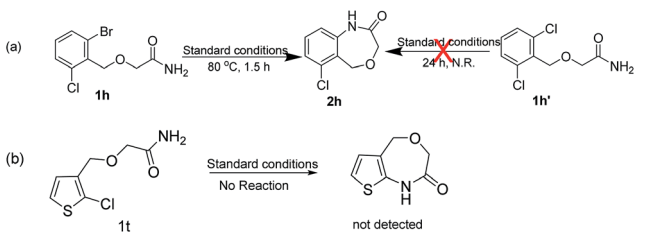


1b-1j 2b-2j

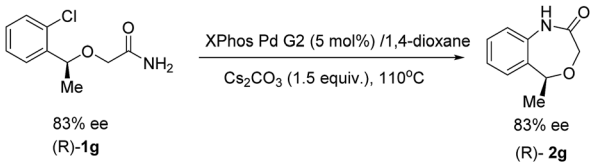


[a] The reactions were carried in Schlenk flask under Ar. **1b–1j** (0.5 mmol), Xphos Pd G2 (5 mol%), 1,4-dioxane (2 ml), Cs_2CO_3 (1.5 equiv.), 110 °C. [b] Isolated yield.

With the optimal conditions (Table 1, entry 9) in hand, we then set out to explore the substrate scope of the reaction for constructing benzene-fused 7-membered amides. As shown in Table 2, even electron-rich aryl chlorides can furnish the transformation in short time. A methyl (entry 1), a fluoro (entry 2), a trifluoromethyl (entries 3 and 4) or methoxyls (entry 5) substitution at the benzene ring were readily allowed and these reactions proceeded smoothly to afford the corresponding benzene-fused amides in good to excellent yields. In the case of



Scheme 2 (a) Chemoselectivity of the reaction. (b) Unsuccessful example.



Scheme 3 (*R*)-**2g** was formed without detectable ee erosion.

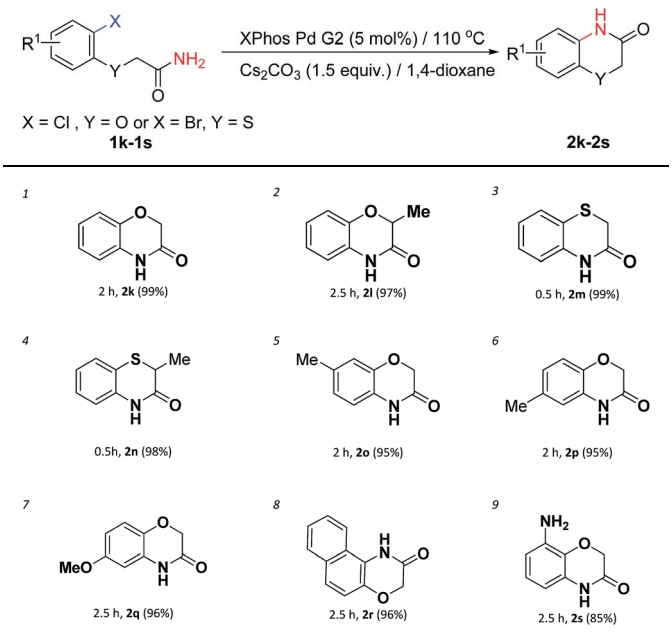
2-(1-phenylethoxy)acetamide as the substrate, **2g** could be obtained with 89% yield in 5.5 h, which the reaction time was longer than that of **2a**.

The chemoselectivity of the system was also briefly explored. When there are more than one chloro-groups on the ring, the reaction can hardly proceed. For example, as shown in Scheme 2, when **1h′** was used as the substrate, only trace of **2h** was observed by NMR. Fortunately, when **1h** was used instead of **1h′**, **2h** could be achieved successfully with 83% yield (entry 7) which indicated that the reaction had good chemoselectivity.

Unfortunately, when we explored this chemistry with thiophene substrate, no expected product was observed (Scheme 2b). For other heteroaromatic amides **1i-1j**, the amidation reaction could proceed smoothly. When (1-(pyridin-3-yl)ethoxy) acetamide **1i** was used, **2i** could be obtained with 89% yield in 4.5 h (entry 8). Oxazepino[5,6-*b*]quinolin-2(3*H*)-one **2j** was also obtained with good yield (entry 9).

When Table 2, entry 6 was performed using the (*R*)-substrate (83% ee) under the optimal conditions, (*R*)-**2g** was formed without detectable ee erosion (Scheme 3).

Table 3 Formation of benzene-fused 6-membered amide: reaction scopes.[a,b]



[a] The reactions were carried in Schlenk flask under Ar. Substrate **1k–1s** (0.5 mmol), Xphos Pd G2 (5 mol%), 1,4-dioxane (2 ml), Cs_2CO_3 (1.5 equiv.), 110 °C. [b] Isolated yield.

With the success in the formations of benzene-fused seven membered rings, we subsequently turned to explore the 6-membered ring formation. As expected, the benzene-fused 6-membered rings are much easier formed than the seven membered ones both in efficiency and yields. We found a broad range of 6-membered ring amides possessing various functional groups could be achieved with high yields in short reaction times (Table 3).

However, it needs to point out that the substrate used for the formation of **2n** is aryl bromide (entry 4). The intramolecular amidation reaction could not proceed when the corresponding aryl chloride was used. Electron-rich aryl chlorides can also couple with amides successfully in short time affording the products in excellent yields (entries 5–7). For the sterically hindered aryl chloride, the amidation reaction was successfully proceeded affording **2r** in 96% yield (entry 8). Even for 2-(2-aminophenoxy)acetamide which has a very strong electron donating amino-group which deactivated the C–Cl bond could also undergo the intramolecular amidation and gives product **2s** in 85% yield (entry 9).

Conclusions

In conclusion, an efficient protocol for C–N cross-coupling reactions has been described. This catalyst system allows the primary amides which have only modest nucleophilicity could couple successfully even with electron rich aryl chlorides which can afford valuable benzene-fused 6/7-membered amides with high yield in short reaction time. The catalyst system also has good chemoselectivity and excellent functional group compatibility which supplies an important alternative way to the synthesis of benzene-fused 6/7-membered amides.

Experimental section

General experimental methods

Commercially available reagents were used without further purification. The solvents used for experiment research were all through pretreatment on condition of anaerobic and without water. Reactions were monitored by thin layer chromatography (TLC) using silicycle precoated silica gel plates. Flash column chromatography was performed over silicycle silica gel (300–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on JMTC-400/54/SS 400 MHz spectrometers using residue solvent peaks as internal standards ($CHCl_3$, ^{1}H: 7.26 ppm; ^{13}C: 77.00 ppm). Infrared spectra were recorded with a PerkinElmer Spectrum Two FT-IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with MicroTof-II using electron spray ionization (MeOH or CH_3CN as solvent) or Waters GCT Premier time-of-flight mass spectrometer with a field ionization (FI) ion source.

General procedure for the synthesis of benzene-fused 6/7-membered amides

2-((2-chlorobenzyl)oxy)acetyl chloride **1** (0.25 mmol), Cs_2CO_3 (122.65 mg, 0.375 mmol) and Pd Xphos G2 (9.8 mg, 0.0125

mmol) were added into Schlenk tube. The mixture was stirred under argon and dry 1,4-dioxane (1 ml) was added and heated to 110 °C. The reaction was monitored by TLC. After the reaction finished, the product was isolated with column chromatography.

3,5-Dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2a

99% yield, m.p. 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.58 (s, 2H), 4.75 (s, 2H), 6.87 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.26–7.27 (m, 1H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 72.8, 73.5, 119.2, 123.7, 128.6, 128.7, 129.2, 135.7, 173.2; IR ν (cm^{-1}): 3357.3, 3171.4, 1635.8, 1431.5, 1377.8; HRMS calcd for $C_9H_9NO_2$ $(M - H)^+$ 162.0555, found 162.0559.

8-Methyl-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2b

96% yield, m.p. 154–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.33 (s, 3H), 4.57 (s, 2H), 4.70 (s, 2H), 6.79 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 8.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 21.0, 72.5, 73.3, 119.9, 124.5, 125.9, 128.4, 135.7, 139.3, 173.5; IR ν (cm^{-1}): 3377.0, 3184.2, 2962.5, 1656.5, 1259.5; HRMS calcd for $C_{10}H_{11}NO_2$ $(M + Na)^+$ 200.0687, found 200.0673.

8-Fluoro-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2c

94% yield, m.p. 166–167 °C; ^{1}H NMR (400 MHz, d^6-DMSO): δ ppm 4.43 (s, 2H), 4.65 (s, 2H), 6.79 (dt, J^1 = 8.0 Hz, J^2 = 2.4 Hz, 1H), 6.92 (dd, J^1 = 10.4 Hz, J^2 = 2.4 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 10.30 (s, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ ppm 71.7, 73.8, 106.2 (d, J = 25.8 Hz), 109.4 (d, J = 21.1 Hz), 126.0 (d, J = 2.8 Hz), 130.6 (d, J = 9.6 Hz), 139.1 (d, J = 10.5 Hz), 162.3 (d, J = 41.4 Hz), 173.4; ^{19}F NMR: −113.9; IR ν (cm^{-1}): 3194.0, 3066.2, 1661.0, 1603.5, 1372.5; HRMS calcd for $C_9H_8FNO_2$ $(M + Na)^+$ 204.0437, found 204.0430.

7-(Trifluoromethyl)-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(1*H*)-one 2d

90% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.62 (s, 2H), 4.78 (s, 2H), 7.24–7.31 (m, 3H), 8.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 70.1, 70.2, 123.9 (q, J = 3.9 Hz), 124.5 (q, J = 267.2 Hz), 126.2 (q, J = 3.9 Hz), 129.3, 131.8 (q, J = 32.6 Hz), 133.5, 138.6, 171.6; ^{19}F NMR: δ ppm 78.8; IR ν (cm^{-1}): 2979.8, 1663.7, 1334.6, 1121.5; HRMS calcd for $C_{10}H_8F_3NO_2$ (M − H) 230.0427, found 230.0425.

8-(Trifluoromethyl)-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2e

92% yield, m.p. 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.56 (s, 2H), 4.77 (s, 2H), 7.09 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 9.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 72.9, 74.0, 119.6, 123.9 (q, J = 270.2 Hz), 125.7 (q, J = 32.6 Hz), 125.7 (q, J = 3.9 Hz), 126.4 (q, J = 3.9 Hz), 129.2, 138.9, 174.5; ^{19}F NMR: δ ppm 62.1; IR ν (cm^{-1}): 2919.9, 1658.6, 1447.8, 1084.8, 656.7; HRMS calcd for $C_{10}H_8F_3NO_2$ $(M - H)^+$ 230.0427, found 230.0429.

8,9-Dimethoxy-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2f

90% yield, m.p. 148–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 3.87 (s, 3H), 3.88 (s, 3H), 4.61 (s, 2H), 4.67 (s, 2H), 6.58 (d, J = 8.8 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 8.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 55.9, 60.8, 72.9, 74.1, 106.6, 121.8, 122.8, 129.5, 136.8, 152.3, 172.4; IR: ν (cm^{-1}): 3195.3, 1661.6, 1391.6, 1112.3. HRMS calcd for $C_{11}H_{13}NO_4$ $(M + Na)^+$ 246.0742, found 246.0736.

5-Methyl-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2g

89% yield, m.p. 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.64 (d, J = 6.4 Hz, 3H), 4.54 (d, J = 2.4 Hz, 2H), 4.78 (q, J = 6.4 Hz, 1H), 6.99 (dd, J^1 = 8.4H, J^2 = 0.4 Hz, 1H), 7.01 (td, J^1 = 7.6 Hz, J^2 = 0.4 Hz, 1H), 7.23–7.29 (m, 2H), 8.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 19.0, 71.1, 75.2, 120.0, 123.9, 125.9, 128.8, 132.7, 136.0, 173.7; IR ν (cm^{-1}): 3196.7, 3065.5, 2997.0, 2903.1, 1656.9; HRMS calcd for $C_{10}H_{11}NO_2$ $(M - H)^+$ 176.0721, found 176.0725. For corresponding chiral *R*-**2g**: −78° (*c* 0.10, acetone), 83% ee (determined by a chiral AD-H column, ^{i}PrOH/hexane = 10/90, t_{major} = 14.26 min, t_{minor} = 15.40 min).

6-Chloro-3,5-dihydrobenzo[*e*][1,4]oxazepin-2(*H*)-one 2h

83% yield, m.p. 172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.52 (s, 2H), 4.99 (s, 2H), 6.78 (d, J = 7.6 Hz, 1H), 7.11–7.19 (m, 2H), 7.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 69.8, 73.1, 118.2, 124.9, 126.6, 129.2, 133.7, 137.5, 173.0; IR ν (cm^{-1}): 3246.6, 2918.9, 1671.0, 1480.4, 1258.1; HRMS calcd for $C_9H_8ClNO_2$ $(M + Na)^+$ 220.0141, found 220.0143.

5-Methyl-3,5-dihydropyrido[2,3-*e*][1,4]oxazepin-2(*H*)-one 2i

89% yield, m.p. 106–106.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.64 (d, J = 6.4 Hz, 3H), 4.64 (d, J = 6.0 Hz, 2H), 4.73 (q, J = 6.4 Hz, 1H), 7.04 (dd, J^1 = 7.6 Hz, J^2 = 4.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 4.8 Hz, 1H), 9.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 18.9, 72.2, 75.0, 118.7, 127.4, 134.7, 147.6, 149.1, 173.0; IR ν (cm^{-1}): 3180.4, 1662.7, 1634.3, 1401.8, 1315.7; HRMS calcd for $C_9H_{10}N_2O_2$ $(M + Na)^+$ 201.0640, found 201.0623.

8-Methyl-3,5-dihydro-[1,4]oxazepino[5,6-*b*]quinolin-2(*H*)-one 2j

85% yield, m.p. 134–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.51 (s, 3H), 4.69 (s, 2H), 4.85 (s, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 8.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 21.5, 72.2, 74.3, 123.3, 125.0, 126.1, 127.2, 132.8, 135.7, 145.0, 147.6, 172.3; IR ν (cm^{-1}): 2919.9, 1658.6, 1447.8, 1084.8, 656.7; HRMS calcd for $C_{13}H_{12}N_2O_2$ $(M - H)^+$ 227.0821, found 227.0848.

2*H*-Benzo[*b*][1,4]oxazin-3(4*H*)-one 2k[6a,16,17]

Known compound, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.63 (s, 2H), 6.82–6.98 (m, 4H), 8.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 67.2, 116.0, 116.8, 122.7, 124.3, 126.0, 143.6, 165.9.

2-Methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one 2l[17]

Known compound, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.59 (d, $J = 6.8$ Hz, 3H), 4.67 (q, $J = 6.8$ Hz, 1H), 6.88–6.89 (m, 1H), 6.96–6.97 (m, 3H), 9.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 16.2, 73.2, 115.9, 117.0, 122.6, 124.1, 126.4, 143.1, 168.9.

2*H*-Benzo[*b*][1,4]thiazin-3(4*H*)-one 2m[18,19]

Known compound, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 3.44 (s, 2H), 6.90 (d, $J = 8.0$ Hz, 1H), 7.01 (dt, $J^1 = 8.0$ Hz, $J^2 = 1.2$ Hz, 1H), 7.17 (dt, $J^1 = 7.6$ Hz, $J^2 = 1.2$ Hz, 1H), 7.31 (d, $J = 7.8$ Hz, 1H), 9.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 29.9, 117.4, 119.9, 123.9, 127.2, 127.8, 136.3, 166.4;

2-Methyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one 2n[18,19]

Known compound, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.50 (d, $J = 7.2$ Hz, 3H), 3.56 (q, $J = 7.2$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 7.02 (t, $J = 6.8$ Hz, 1H), 7.18 (t, $J = 8.0$ Hz, 1H), 7.30–7.31 (m, 1H), 8.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.4, 37.0, 116.9, 119.4, 123.8, 127.1, 128.1, 136.0, 168.9.

7-Methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one 2o[18]

Known compound, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.28 (s, 3H), 4.60 (s, 2H), 6.67 (s, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 9.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 20.7, 67.2, 116.5, 116.7, 120.3, 124.7, 125.8, 132.5, 166.6.

6-Methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one 2p[18,19]

Known compound, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.28 (s, 3H), 4.60 (s, 2H), 6.67 (s, 1H), 6.78 (dd, $J^1 = 8.4$ Hz, $J^2 = 1.2$ Hz, 1H), 6.86 (d, $J = 7.6$ Hz, 1H), 9.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 20.6, 67.2, 116.4, 116.5, 124.7, 125.7, 132.5, 141.4, 166.7.

6-Methoxy-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one 2q[18,19]

Known compound, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 3.76 (s, 3H), 4.57 (s, 2H), 6.40 (d, $J = 2.4$ Hz, 1H), 6.50 (dd, $J^1 = 8.6$ Hz, $J^2 = 3.2$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 1H), 8.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 55.8, 67.4, 102.1, 108.8, 117.2, 126.8, 137.6, 155.3, 166.6.

1*H*-Naphtho[2,1-*b*][1,4]oxazin-2(3*H*)-one 2r

96% yield, m.p. 207–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.76 (s, 2H), 7.22 (d, $J = 8.2$ Hz, 1H), 7.43 (td, $J^1 = 7.8$ Hz, $J^2 = 0.8$ Hz, 1H), 7.54 (d, $J = 9.2$ Hz, 1H), 7.58 (td, $J^1 = 7.8$ Hz, $J^2 = 1.2$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 9.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 67.5, 117.4, 118.7, 119.0, 123.0, 124.3, 124.7, 127.0, 128.7, 130.0, 140.6, 166.0; IR ν (cm^{-1}): 3189.9, 2961.3, 2877.5, 1681.8, 1458.9; HRMS calcd for $C_{12}H_9NO_2$ $(M + Na)^+$ 222.0531, found 222.0527.

8-Amino-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one 2s[20]

Known compound, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.73 (s, 2H), 6.73 (dd, $J^1 = 8.0$ Hz, $J^2 = 1.2$ Hz, 1H), 6.90 (t, $J = 8.0$ Hz, 1H), 7.06 (dd, $J^1 = 8.0$ Hz, $J^2 = 1.2$ Hz, 1H), 8.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 67.4, 114.3, 122.2, 122.9, 125.1, 127.1, 139.8, 165.4.

Conflicts of interest

There are no conflicts to declare.

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