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ARTICLE

Gold-catalyzed formation of aryl-fused pyrazolooxazepines *via* intramolecular regioselective *7-exo-dig* cyclization†

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An efficient method was developed for synthesis of substituted aryl-fused pyrazolooxazepines from *ortho-O*-propargyl aryl pyrazoles by gold-catalysis. In this organic transformation a new C-N bond was formed regioselectively *via 7-exo-dig* cyclization. Moderate to good yields of aryl-fused pyrazolooxazepine derivatives were obtained with significant molecular complexity in one-pot.

Introduction

Medium-sized heterocyclic molecules are important building blocks in medicinal chemistry.[1] Nitrogen containing seven-membered heterocyclic molecules[2] have gained much attention in recent years due to their potential applications in medicinal chemistry and material sciences.[3] The recent literature evidencing that benzooxazepines exhibit a wide range of biological activities such as anticancer,[4a] anti-HIV,[4b] antitumor,[5] anti-inflammatory activities,[6] and also useful for the treatment of Alzheimer's disease.[7]

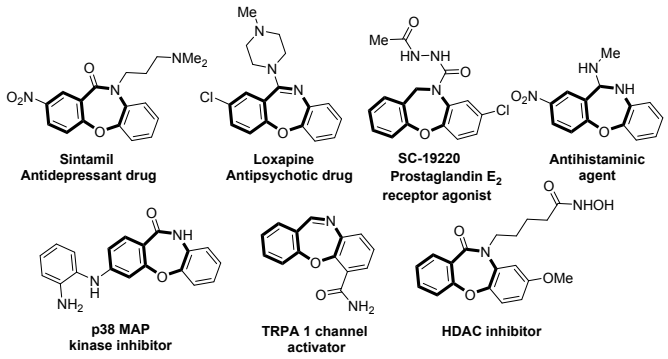

Fig. 1 Selected examples of important molecules containing benzooxazepine core skeleton.

For instance, substituted benzooxazepine derivatives such as Sintamil is a antidepressant drug.[8] Loxapine is antipsychotic drug[9] and SC-19220 acts as prostaglandin E_2 receptor agonist as well as antihistaminic (Figure 1).[10] Further, oxazepine derivatives were used as precursors for synthesis of secoiridoids and monoterpenoid alkaloids.[11]

The gold-catalyzed organic reactions are occupying an important place in synthetic organic chemistry, due to their selectivity and substrate tolerance.[12] Distinctive synthetic methods were discovered by selectively tuning the gold-catalysts,[13] which resulted in the generation of diversified molecular scaffolds.[14]

Regioselective metal-catalyzed organic transformations gained much focus in recent years to construct medium-sized heterocyclic molecules due to their applications in medicinal chemistry. Our current research efforts led to the development of gold-catalyzed regioselective organic transformations.[15] We initiated our investigations for intramolecular synthesis of substituted benzopyrazolooxazepines under gold-catalysis. Recently, gold-catalyzed seven-membered ring formation reactions have been reported by the research groups of Hashmi,[16a] Echavarren[16b] and Sawamura.[16c] Intermolecular synthesis of benzopyrazolooxazepines were reported through Smiles rearrangement,[17a,b] and copper-catalyzed cross coupling reactions.[17c]

Results and discussion

We visualized that 5-phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole **1a** can be converted to the corresponding 5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine **2a** *via 7-exo-dig* cyclization (path a, Scheme 1) or 2-phenyl-7*H*-benzo[*b*]pyrazolo[5,1-*d*][1,5]oxazocine **3a** *via 8-endo-dig*

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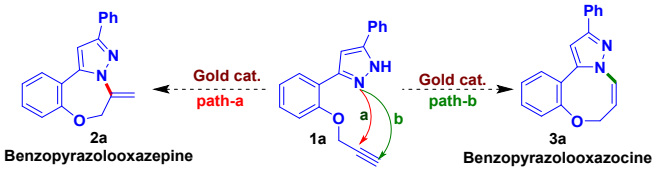
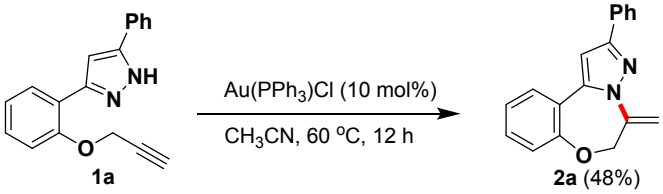
†Electronic Supplementary Information (ESI) available: Experimental details, ^{1}H, ^{13}C NMR spectra, mass for the compounds and *crystallographic data of compound* ***2u*** *in CIF*. (*CCDC 1574971)* See DOI: 10.1039/x0xx00000x

cyclization (path b, Scheme 1) through intramolecular hydroamination under gold-catalysis (Scheme 1).



Scheme 1. Synthetic strategy for the formation of benzopyrazolooxazepine (**2a**) or benzopyrazolooxazocine (**3a**) from **1a**.

Based on the above synthetic approach, a reaction was performed by taking **1a** and 10 mol% of $Au(PPh_3)Cl$ in acetonitrile, which produced 48% yield of product **2a** (Scheme 2).

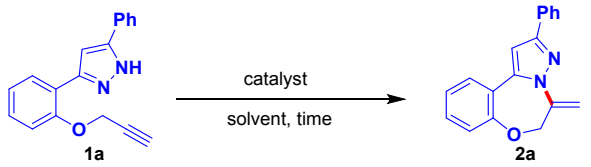


Scheme 2 Conversion of 5-phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole (**1a**) to benzopyrazolooxazepine (**2a**).

This positive result driven us to test this reaction for the yield improvement of product **2a** by utilizing different catalysts, catalyst combinations and reaction conditions. Then, the starting material **1a** was tested without catalyst in acetonitrile; it was observed that the **1a** remained intact (Table 1, entry 2). The substrate **1a** was tested by utilizing various gold-catalysts such as AuCN, AuCl, IPrAuCl, [Au(JohnPhos)(MeCN)][SbF_6], $KAuCl_4$, $AuCl_3$ and $AuBr_3$. Under these reaction conditions the product **2a** was obtained in poor yields (Table 1, entries 3-9). We have conducted experiments by utilizing the substrate **1a** in the presence of different silver catalysts such as $AgSbF_6$, $AgBF_4$, AgOTf and $AgNTf_2$. Moderate yields of product **2a** was observed under these reaction conditions (Table 1, entries 10-13).

Good yield (72%) of product **2a** was obtained when **1a** was treated in the presence of $Au(PPh_3)Cl$ (10 mol %) and $AgSbF_6$ (15 mol %) in acetonitrile (Table 1, entry 14). Then we have conducted experiments by using $Au(PPh_3)Cl$ with silver catalysts such as $AgBF_4$, AgOTf and $AgNTf_2$. It was observed that these reactions gave moderate yields of product **2a** (Table 1, entries 15-17). Solvent effect on this reaction was tested by utilising different solvents; moderate to good yields of product **2a** was observed (Table 1, entries 18-21). To check the catalytic effectiveness, we have conducted two experiments by using lower loading of catalysts $Au(PPh_3)Cl/AgSbF_6$ in 2/3 mol % and 5/7.5 mol %. In these cases lower yields of product **2a** was observed (Table 1, entries 22 and 23). Further we have conducted another experiment to check the efficiency of the catalytic combination of $Au(PPh_3)Cl/AgSbF_6$ (10/10 mol %), product **2a** was observed in 66% yield (Table 1, entry 24). A reaction was performed without nitrogen atmosphere, it was observed that 64% yield of product **2a** was isolated (Table 1, entry 25). The substrate **1a** was tested in the presence of different copper catalysts (entries 26-29). Under these reaction conditions, moderate yields of product **2a** was observed.[18]

Table 1. Optimization of reaction conditions[a]



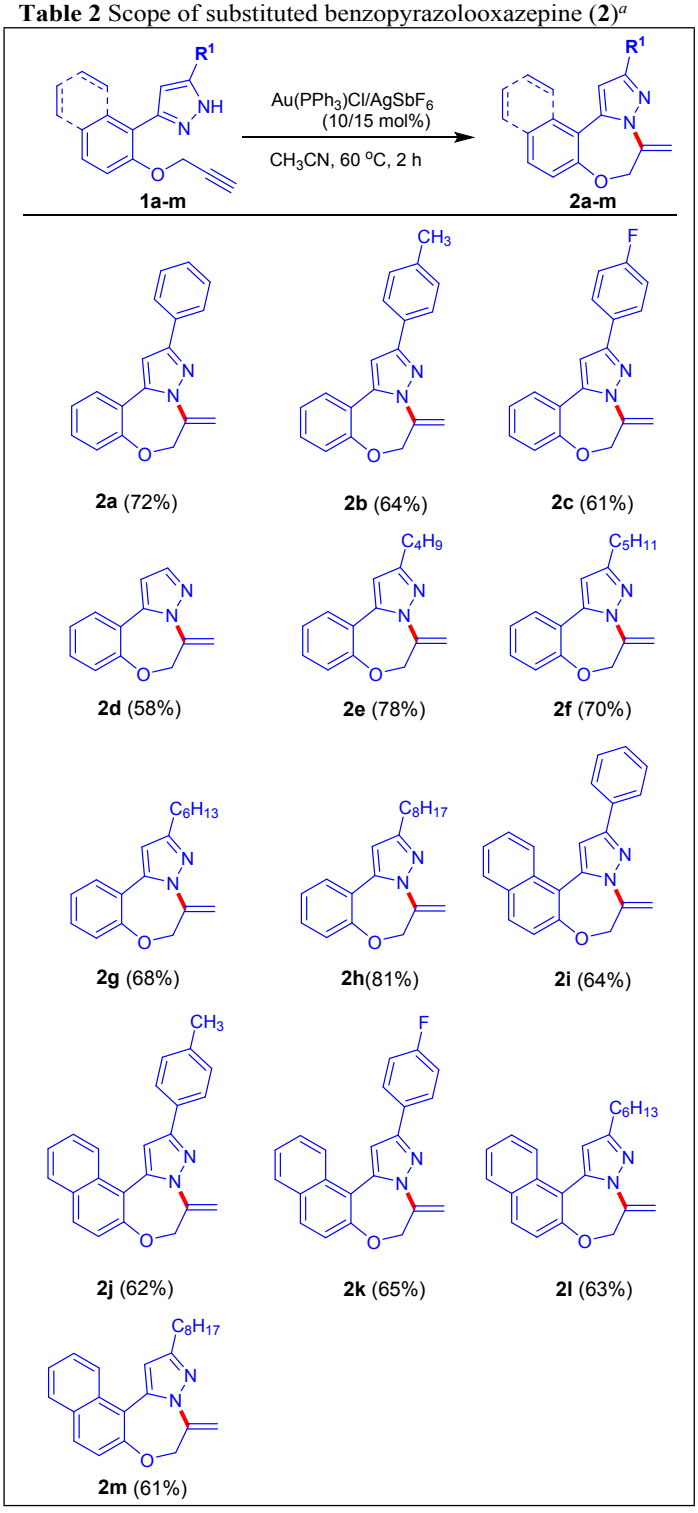
Entry	Catalyst (mol %)	Solvent	Time (h)	Yield(%)[c]
1	$Au(PPh_3)Cl$ (10)	CH_3CN	12	48
2	No Catalyst	CH_3CN	18	nr[b]
3	AuCN (10)	CH_3CN	12	10
4	AuCl (10)	CH_3CN	12	12
5	IPrAuCl (10)	CH_3CN	12	41
6	[Au(JhonPhos)(MeCN)][SbF_6] (10)	CH_3CN	12	43
7	$KAuCl_4$ (10)	CH_3CN	12	11
8	$AuCl_3$ (10)	CH_3CN	12	30
9	$AuBr_3$ (10)	CH_3CN	12	26
10	$AgSbF_6$(10)	CH_3CN	24	32
11	$AgBF_4$ (10)	CH_3CN	24	43
12	AgOTf (10)	CH_3CN	24	46
13	$AgNTf_2$(10)	CH_3CN	24	44
14	**$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (15)**	**CH_3CN**	**2**	**72**
15	$Au(PPh_3)Cl$ (10)/ $AgBF_4$ (15)	CH_3CN	2	50
16	$Au(PPh_3)Cl$ (10)/ AgOTf (15)	CH_3CN	2	56
17	$Au(PPh_3)Cl$ (10)/ $AgNTf_2$ (15)	CH_3CN	2	60
18	$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (15)	Toulene	2	40
19	$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (15)	DCE	2	45
20	$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (15)	THF	2	62
21	$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (15)	MeOH	2	50
22	$Au(PPh_3)Cl$ (2)/ $AgSbF_6$ (3)	CH_3CN	2	25
23	$Au(PPh_3)Cl$ (5)/ $AgSbF_6$ (7.5)	CH_3CN	2	45
24	$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (10)	CH_3CN	2	66
25	$Au(PPh_3)Cl$ (10)/ $AgSbF_6$ (15)	CH_3CN	12	64[d]
26	CuCl (10)	CH_3CN	30	53
27	CuBr (10)	CH_3CN	30	51
28	CuI (10)	CH_3CN	30	42
29	$Cu(OAc)_2$ (10)	CH_3CN	30	39
30	IPrAuCl (10)/ $AgNTf_2$(15)	CH_3CN	12	64
31	IPrAuCl (5)/ $AgNTf_2$ (7.5)	CH_3CN	12	57
32	HCl (10)	CH_3CN	12	cm[e]
33	$HNTf_2$ (10)	CH_3CN	12	cm[e]

[a]Reaction conditions: all reactions were carried out at 60 °C under nitrogen atmosphere with **1a** (0.364 mmol), and solvent (3 mL); [b]nr: no reaction; [c]yields are for isolated products; [d]Reaction was conducted without nitrogen atmosphere; [e]Complex mixture was observed.

Reactions were performed by utilizing IPrAuCl in combination of $AgNTf_2$ (entries 30 and 31), good yields of product **2a** were

isolated. Then the substrate **1a** was tested in the presence of HCl and $HNTf_2$ (entries 32 and 33), both the cases complex mixture was observed.

Table 2 Scope of substituted benzopyrazolooxazepine (**2**)[a]



[a]Reaction conditions: all reactions were carried out at 60 °C under nitrogen atmosphere with **1a-1m** (0.364 mmol), $Au(PPh_3)Cl$ (10 mol%)/$AgSbF_6$ (15 mol%) and CH_3CN (3 mL) at 60 °C; yields are for isolated products.

The above experimental results reveal that the catalyst combination of $Au(PPh_3)Cl/AgSbF_6$ (10/15 mol%) in acetonitrile is the best condition for the synthesis of substituted aryl-fused pyrazolooxazepines (Table 1, entry 14). The scope of substrates was studied by utilizing different substituted *ortho-O*-propargyl aryl pyrazoles **1a-1m** (Table 2).

The substrate **1b** which is having electron donating group at R^1 position and **1c** which is containing electron withdrawing group at R^1 position undergoes 7-*exo-dig* cyclization *via* intramolecular hydroamination gave 64% and 61% yield of cyclized products **2b** and **2c**, respectively (Table 2). Substrate **1d** gave 58% yield of desired product **2d**. The substrates having aliphatic functional groups at R^1 position such as **1e**, **1f** and **1g** and **1h** gave the corresponding products **2e**, **2f**, **2g** and **2h** in 78%, 70%, 68% and 81% yields, respectively (Table 2). Naphthyl substituted substrates such as **1i**, **1j**, **1k**, **1l** and **1m** produced good yields of the corresponding products **2i**, **2j**, **2k**, **2l** and **2m**, respectively (Table 2).

The substrate scope was further tested by utilizing different substituted *ortho-O*-propargyl aryl pyrazoles (**1n-1z**) and these results are incorporated in Table 3. Electron donating functional group like di-*tert*-butyl containing substrates such as **1n**, **1o** and **1p** gave 62%, 67% and 65% yields of cyclized products **2n, 2o** and **2p**, respectively (Table 3). Bromo substituted substrates such as **1q**, **1r** and **1s** gave the corresponding products **2q**, **2r** and **2s**, in 76%, 64% and 71% yields, respectively (Table 3). Electron withdrawing functional group like nitro substituted substrates such as **1t**, **1u**, **1v** and **1w** produced the corresponding products **2t**, **2u, 2v** and **2w**, in good yields. Further, the structure of the product 5-methylene-10-nitro-2-(*p*-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine **2u** was confirmed by single crystal X-ray analysis (Figure 2).[19]

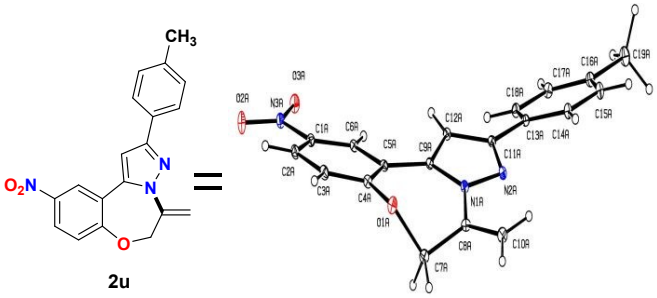
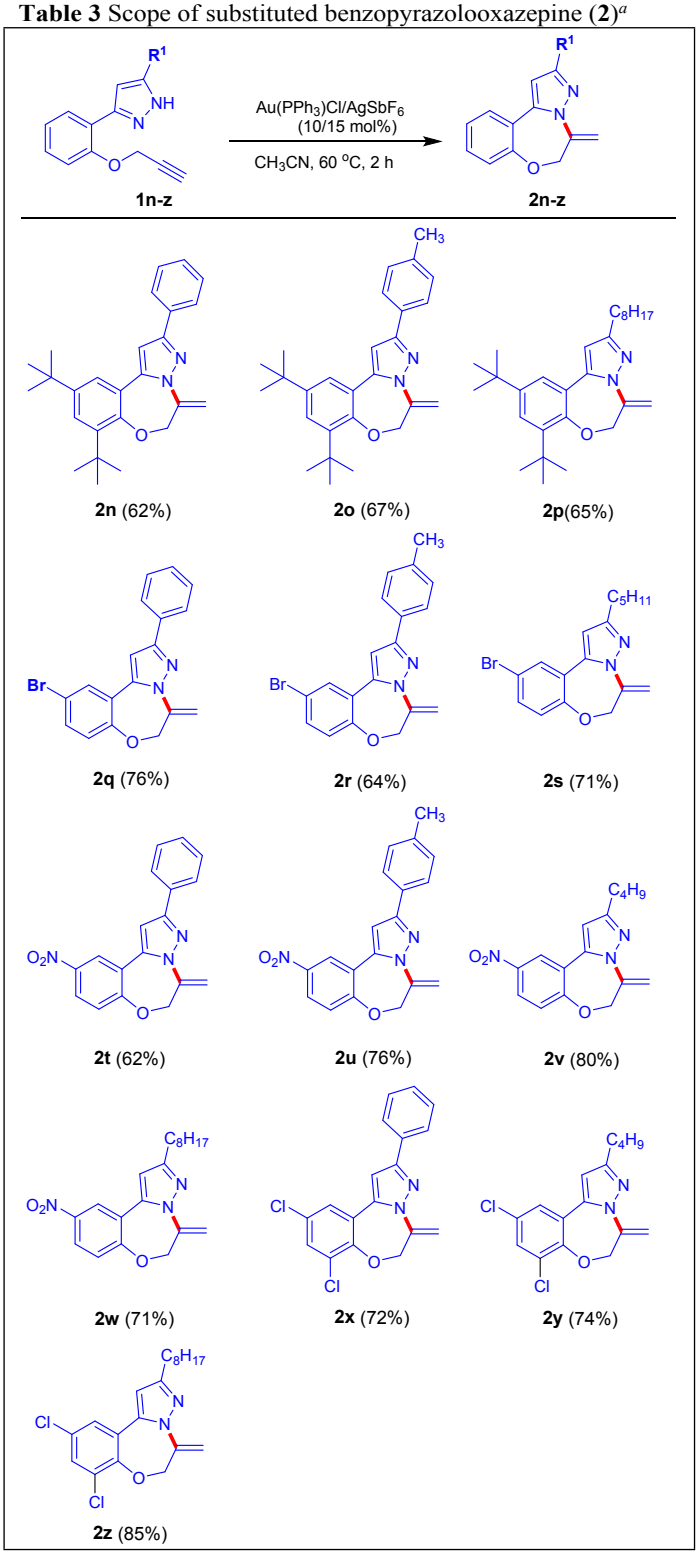


Fig. 2 An ORTEP diagram of compound **2u** (CCDC 1574971).

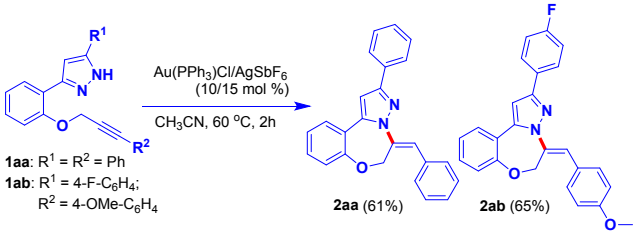
Two electron withdrawing groups like 3,5-dichloro substitutions containing substrates like **1x** ($R^1 = C_6H_5$), **1y** ($R^1 = n\text{-}C_4H_9$) and **1z** ($R^1 = n\text{-}C_8H_{17}$) gave the corresponding product **2x**, **2y** and **2z** in 72%, 74% and 85% yields, respectively (Table 3).

Table 3 Scope of substituted benzopyrazolooxazepine (**2**)[a]



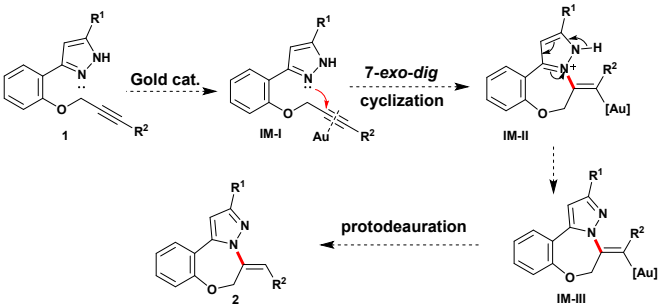
[a]Reaction conditions: all reactions were carried out at 60 °C under nitrogen atmosphere with **1n-1z** (0.364 mmol), $Au(PPh_3)Cl$ (10 mol%)/$AgSbF_6$ (15 mol%) and CH_3CN (3 mL); yields are for isolated products.

Two more experiments were conducted with substrates which are bearing substitutions at R^1 and R^2 position such as **1aa** and **1ab** under the optimized conditions resulted the corresponding products **2aa** and **2ab** in 61% and 65% yields, respectively (Scheme 3).



Scheme 3. Conversion of alkyne disubstituted substrates **1aa**, and **1ab**) to benzopyrazolooxazepine **2aa** and **2ab**.

A tentative reaction mechanism can be proposed for the generation of aryl-pyrazolooxazepines **2** from *ortho-O*-propargyl substituted aryl pyrazoles **1** *via* gold-catalysis (Scheme 4). Substrate **1** would give intermediate-**I (IM-I)** by reacting with gold-catalyst. Then **IM-I** might generate vinyl-gold intermediate-**II (IM-II)** *via* 7-*exo-dig* cyclization.[13] 7-*Exo-dig* preference would be assumed when gold(I) forms a complex with a terminal carbon- carbon triple bond, the internal carbon atom is more positively charged than the external carbon atom, so the nucleophilic attack would driven by this path way.[13f] Subsequently, **IM-II** might produce intermediate-**III (IM-III)**, which would produce substituted aryl-fused pyrazolooxazepines **2** *via* protodeauration.



Scheme 4. A plausible reaction mechanism.

Conclusions

In conclusion, we have established an efficient synthetic protocol for the formation of substituted pyrazolo benzooxazepines and pyrazolo naphthoxazepines from substituted *ortho-O*-propargyl aryl pyrazoles. Significantly, this gold-catalyzed regioselective organic transformation takes place *via* 7-*exo-dig* cyclization. The title compounds were obtained in moderate to good yields.

Experimental Section

General information

Reactions were carried out in oven dried reaction flasks under nitrogen atmosphere and also solvents, reagents were transferred by oven-dried syringes. TLC was performed on Merck silica gel aluminium sheets using

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UV as a visualizing agent and a 0.5% aqueous potassium permanganate solution and heat as developing agents. Solvents were removed under reduced pressure. Columns were packed as slurry of silica gel in hexane and ethyl acetate solvent mixture. The elution was assisted by applying pressure with an air pump. ^{13}C NMR spectra were recorded on 100 MHz and 125 MHz spectrometers. ^{1}HNMR spectra were recorded on 300 MHz, 400 MHz and 500 MHz spectrometers in appropriate solvents using TMS as internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet. All reactions were performed under nitrogen atmosphere with freshly distilled and dried solvents. All solvents were distilled using standard procedures. Unless otherwise noted, reagents were obtained from Aldrich, Alfa Aesar, and TCI used without further purification. Synthesis of aryl-fused pyrazolooxazepines **(1a-1ab)** were prepared by following reported procedures.[20]

X-ray data for the compound KA263 was collected at 100 K on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[21] The structure was solved using intrinsic phasing method[3] and further refined with the SHELXL program and expanded using Fourier techniques.[22] Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

Crystal Data for 2u:[19] $C_{19}H_{15}N_3O_3$ (M =333.35 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.021(9) Å, b = 20.14(3) Å, c = 21.54(3) Å, β = 95.79(2)°, V = 3030(7) Å^3, Z = 8, T = 100.0 K, μ(Mo Kα) = 0.101 mm^{-1}, $Dcalc$ = 1.4612 g/cm^3, 38713 reflections measured (4.46° ≤ 2Θ ≤ 61.62°), 9422 unique (R_{int} = 0.0356, R_{sigma} = 0.0330) which were used in all calculations. The final R_1 was 0.0454 (I>2σ(I)) and wR_2 was 0.1193 (all data). CCDC 1574971 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

Genaeral procedure for synthesis of 5-methylene-5,6-dihydrobenzo[*f*]pyrazolooxazepines 2a-2ab.

To a 10 mL round-bottomed flask equipped with magnetic stir bar the substrate 5-phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole **1a** (0.1 g, 0.364 mmol, 1 equiv.) was taken and dissolved in CH_3CN (3 mL). To this reaction mixture Au(PPh_3)Cl (0.017 g, 0.0364 mmol, 10 mol %) and $AgSbF_6$ (0.018 g, 0.0546 mmol, 15 mol %) was added and stirred at 60 °C for 2 hours under nitrogen atmosphere. Progress of the reaction was monitored by using TLC. After completion of the reaction, the reaction mixture was filtered through celite plug and washed the celite plug with Ethyl acetate. The Ethyl acetate layer was concentrated under reduced pressure to get crude residue which was purified by column chromatography through silica gel using hexane and ethyl acetate as eluent (10:1.2) to give product 5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine **2a** (72%). A similar procedure was followed for the synthesis of all substituted pyrazolo fused benzooxazepine and naphthoxazepine derivatives (**2b-2ab**).

5-Methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2a. R_f: 0.65; Hexane: Ethyl acetate mixture (10 : 0.5); Yield: 72%, white solid; Melting Point: 106-108 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.90 (m, 2H), 7.83 (dd, J = 1.5, 7.9 z, 1H), 7.46-7.41 (m, 2H), 7.38-7.33 (m, 1H), 7.30-7.26 (m, 1H), 7.17-7.12 (m, 1H), 7.09 (dd, J = 1.3, 8.1 Hz, 1H), 7.02 (s, 1H), 6.05 (s, 1H), 4.94 (s, 1H), 4.80 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.3, 152.1, 141.4, 132.5, 129.8, 128.8, 128.6, 128.3, 125.9, 123.6, 120.6, 119.4, 103.8, 103.0, 72.4 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 3063, 1649, 1464, 1372, 1344, 1210, 1018, 756, 690 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{18}H_{15}ON_2$ $[M+H]^+$ 275.1178, found 275.1175.

5-Methylene-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2b. R_f: 0.55; Hexane: Ethyl acetate mixture (10 : 0.3); Yield: 64%, white solid; Melting Point: 100-102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.77 (m, 3H), 7.28-7.21 (m, 3H), 7.16-7.10 (m, 1H), 7.07 (dd, J = 0.9, 8.0 Hz, 1H), 6.97 (s, 1H), 6.03 (s, 1H), 4.91 (s, 1H), 4.77 (s, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.2, 152.1, 141.4, 141.2, 138.1, 129.7, 129.3, 128.7, 125.7, 123.5, 120.6, 119.4, 103.6, 102.7, 72.4, 21.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 3019, 1648, 1460, 1213, 1019, 9856, 790, 758 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{19}H_{17}ON_2$ $[M+H]^+$ 289.1335, found 289.1332.

2-(4-Fluorophenyl)-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2c. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 61%, white solid; Melting Point: 116-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.85 (m, 2H), 7.80 (dd, J = 1.5, 7.9 Hz, 1H), 7.30-7.24 (m, 1H), 7.16-7.06 (m, 4H), 6.95 (s, 1H), 6.02 (s, 1H), 4.93 (s, 1H), 4.78 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.9 (d, J = 247.948 Hz, 1C), 157.3, 151.2, 141.5, 141.4, 129.9, 128.7, 127.6 (d, J = 8.174 Hz, 1C), 123.6, 120.7, 119.4, 115.6 (d, J = 20.889 Hz, 2C), 103.6, 103.0, 72.4 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2920, 1649, 1479, 1218, 1020, 840, 760 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{18}H_{14}ON_2F$ $[M+H]^+$ 293.1084, found 293.1082.

5-Methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2d. R_f: 0.5; Hexane: Ethyl acetate mixture (10 : 1); Yield: 58%, white solid; Melting Point: 72-74 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (dd, J = 1.5, 7.9 Hz, 1H), 7.67 (d, J = 1.9 Hz, 1H), 7.28-7.24 (m, 1H), 7.14-7.10 (m, 1H), 7.08 (dd, J = 1.2, 8.0 Hz, 1H), 6.71 (s, 1H), 5.92 (s, 1H), 4.92 (s, 1H), 4.77 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.1, 141.4, 140.8, 140.1, 129.8, 128.7, 123.6, 120.6, 119.3, 106.5, 103.1, 72.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2922, 1650, 1579, 1530, 1464, 1384, 1212, 1018, 922, 759 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{12}H_{11}ON_2$ $[M+H]^+$ 199.0865, found 199.0871.

2-Butyl-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2e. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 78%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73 (dd, J = 1.5, 7.9 Hz, 1H), 7.26-7.22 (m, 1H), 7.12-7.08 (m, 1H), 7.06 (dd, J = 1.2, 8.0 Hz, 1H), 6.52 (s, 1H),

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5.84 (s, 1H), 4.84 (s, 1H), 4.74 (s, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.72-1.66 (m, 2H), 1.47-1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.1, 154.9, 141.3, 140.5, 129.5, 128.7, 123.4, 120.5, 119.6, 105.5, 102.0, 72.5, 31.5, 27.9, 22.5, 13.9 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2956, 1649, 1463, 1382, 1217, 1022, 880, 761 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{16}H_{19}ON_2$ [M+H]$^+$ 255.1491, found 255.1494.

5-Methylene-2-pentyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2f. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 70%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.25-7.21 (m, 1H), 7.12-7.09 (m, 1H), 7.08-7.04 (m, 1H), 6.52 (s, 1H), 5.84 (s, 1H), 4.84 (s, 1H), 4.74 (s, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.75-1.67 (m, 2H), 1.43-1.33 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.1, 154.9, 141.3, 140.4, 129.5, 128.6, 123.4, 120.5, 119.5, 105.5, 102.0, 72.4, 31.6, 29.1, 28.1, 22.4, 14.0 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2954, 1649, 1462, 1379, 1216, 1020, 878, 757 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{17}H_{21}ON_2$ [M+H]$^+$ 269.1648, found 269.1644.

2-Hexyl-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2g. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 68%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73 (dd, *J* = 1.3, 8.0 Hz, 1H), 7.26-7.21 (m, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.06 (dd, *J* = 1.3, 8.0 Hz, 1H), 6.52 (s, 1H), 5.84 (s, 1H), 4.84 (s, 1H), 4.74 (s, 2H), 2.67 (t, *J* = 7.9 Hz, 2H), 1.73-1.66 (m, 2H), 1.44-1.37 (m, 2H), 1.35-1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.1, 155.0, 141.3, 140.5, 129.5, 128.7, 123.4, 120.5, 119.6, 105.5, 102.0, 72.5, 31.6, 29.4, 29.1, 28.2, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2926, 1650, 1463, 1382, 1218, 1022, 880, 760 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{18}H_{23}ON_2$ [M+H]$^+$ 283.1804, found 283.1809.

5-Methylene-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2h. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 81%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.25-7.22 (m, 1H), 7.12-7.08 (m, 1H), 7.06 (dd, *J* = 1.2, 8.0 Hz, 1H), 6.52 (s, 1H), 5.84 (s, 1H), 4.84 (s, 1H), 4.74 (s, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.73-1.66 (m, 2H), 1.44-1.36 (m, 2H), 1.36-1.22 (m, 8H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.1, 154.9, 141.3, 140.5, 129.5, 128.7, 123.4, 120.5, 119.6, 105.5, 102.0, 72.5, 31.8, 29.4, 29.2, 28.2, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2922, 1649, 1462, 1380, 1217, 1021, 878, 758 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{20}H_{27}ON_2$ [M+H]$^+$ 311.2117, found 311.2113.

5-Methylene-2-phenyl-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2i. R_f: 0.5; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 64%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, *J* = 8.3 Hz, 1H), 7.96-7.92 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.58-7.53 (m, 1H), 7.50-7.42 (m, 3H), 7.39-7.33 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.10 (s, 1H), 5.97 (s, 1H), 5.06 (s, 2H), 4.90 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.4, 151.9, 141.8, 139.1, 132.7, 132.3, 131.5, 130.6, 128.6, 128.4, 128.3, 127.1, 125.9, 125.6, 125.0, 120.5, 116.4, 107.9, 101.8, 76.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 3056, 1648, 1462, 1372, 1227, 822, 753 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{22}H_{17}ON_2$ [M+H]$^+$ 325.1335, found 325.1334.

5-Methylene-2-(p-tolyl)-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2j. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 62%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, *J* = 8.1 Hz, 1H), 7.87-7.81 (m, 3H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.50-7.44 (m, 1H), 7.29-7.22 (m, 3H), 7.07 (s, 1H), 5.96 (s, 1H), 5.05 (s, 2H), 4.88 (s, 1H), 2.39 (s, 3H) pm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 152.0, 141.7, 138.9, 138.1, 132.3, 131.4, 130.5, 129.9, 129.3, 128.4, 127.0, 125.9, 125.6, 125.0, 120.5, 116.5, 107.8, 101.5, 76.0, 21.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2921, 1646, 1465, 1396, 1226, 1080, 819, 753 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{23}H_{19}ON_2$[M+H]$^+$ 339.1491, found 339.1490.

2-(4-Fluorophenyl)-5-methylene-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2k. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 65%, white solid; Melting Point: 122-124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, *J* = 8.4 Hz, 1H), 7.94-7.89 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.58-7.53 (m, 1H), 7.51-7.45 (m, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.13 (t, *J* = 8.8 Hz, 2H), 7.05 (s, 1H), 5.95 (s, 1H), 5.06 (s, 2H). 4.90 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.9 (d, *J* = 247.222 Hz, 1C), 157.5, 151.0, 141.7, 139.2, 132.3, 131.5, 130.6, 128.9, 128.5, 127.7 (d, *J* = 8.070 Hz, 1C), 127.1, 125.5, 125.1, 120.5, 116.3, 115.6 (d, *J* = 22.008 Hz, 2C), 107.7, 101.7, 76.0 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 3058, 1647, 1507, 1438, 1370, 1225, 1097, 822, 753 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{22}H_{16}ON_2F$ [M+H]$^+$ 343.1241, found 343.1252.

2-Hexyl-5-methylene-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2l. R_f: 0.75; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 63%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, *J* = 8.6 Hz, 1H), 7.84 (dd, *J* = 1.3, 8.0 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.56-7.49 (m, 1H), 7.48-7.42 (m, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 5.77 (d, *J* = 0.6 Hz, 1H), 5.0 (s, 2H), 4.79 (s, 1H), 2.74 (t, *J* = 7.9 Hz, 2H), 1.78-1.68 (m, 2H), 1.49-1.39 (m, 2H), 1.38-1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.3, 154.6, 141.7, 138.1, 132.3, 131.4, 130.2, 128.3, 126.9, 125.7, 124.9, 120.5, 116.6, 109.8, 100.4, 76.0, 31.7, 29.5, 29.2, 28.4, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2926, 1647, 1447, 1378, 1224, 1002, 818 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{22}H_{25}ON_2$ [M+H]$^+$ 333.1961, found 333.1968.

5-Methylene-2-octyl-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2m. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 61%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 5.78 (s, 1H), 5.01 (s, 2H), 4.80 (s, 1H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.79-1.69 (m, 2H), 1.48-1.39 (m, 2H), 1.37-1.28 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.3, 154.6, 141.7, 138.0, 132.3, 131.4, 130.2, 128.3, 126.8, 125.6, 124.9, 120.5, 116.6, 109.8, 100.4, 76.0, 31.8, 29.5, 29.4, 29.2, 28.3, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2922, 1647, 1509, 1377, 1223, 1096,

1002, 821, 751 cm^{-1}; HRMS (ESI^+) calculated for $C_{24}H_{29}ON_2$ $[M+H]^+$ 361.2274, found 361.2273.

8,10-Di-tert-butyl-5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo [1,5-*d*][1,4]oxazepine: 2n. R_f: 0.7; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 62%, white solid; Melting Point: 168-170 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 7.0 Hz, 2H), 7.64 (d, J = 2.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.39-7.32 (m, 2H), 6.91 (s, 1H), 6.01 (s, 1H), 4.84 (s, 1H), 4.80 (s, 2H), 1.42 (s, 9H), 1.37 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.4, 15.9, 145.7, 142.8, 141.9, 140.5, 132.7, 128.6, 128.2, 125.9, 124.7, 123.8, 121.2, 104.6, 100.3, 73.0, 35.2, 34.6, 31.5, 30.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2966, 1648, 1467, 1380, 1021, 869, 763, 693 cm^{-1}; HRMS (ESI^+) calculated for $C_{26}H_{31}ON_2$ $[M+H]^+$ 387.2430, found 387.2443.

8,10-Di-tert-butyl-5-methylene-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo [1,5-*d*][1,4]oxazepine: 2o. R_f: 0.65; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 67%, white solid; Melting Point: 162-164 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 6.88 (s, 1H), 6.0 (s, 1H), 4.83 (s, 1H), 4.79 (s, 2H), 2.39 (s, 3H), 1.42 (s, 9H), 1.37 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.4, 152.0, 145.6, 142.7, 141.9, 140.4, 138.1, 129.9, 129.3, 125.9, 124.7, 123.8, 121.3, 104.4, 100.1, 73.0, 35.2, 34.6, 31.5, 30.3, 21.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2961, 1648, 1446, 1370, 1019, 877, 756 cm^{-1}; HRMS (ESI^+) calculated for $C_{27}H_{33}ON_2$ $[M+H]^+$ 401.2587, found 401.2586.

8,10-Di-tert-butyl-5-methylene-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2p. R_f: 0.7; Hexane: Ethyl acetate mixture (10 : 0.3); Yield: 65%, Yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 2.4 Hz, 1H), 6.42 (s, 1H), 5.79 (s, 1H), 4.74 (s, 1H), 4.73 (s, 2H), 2.67 (t, J = 7.9 Hz, 2H), 1.75-1.66 (m, 2H), 1.48-1.41 (m, 2H), 1.40 (s, 9H), 1.34 (s, 9H), 1.33-1.21 (m, 10 H), 0.88 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.3, 154.9, 145.5, 141.9, 141.8, 140.3, 124.4, 123.7, 121.3, 106.3, 99.2, 73.1, 35.1, 34.5, 31.9, 31.4, 30.3, 29.7, 29.5, 29.49, 29.4, 29.2, 28.3, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2954, 1650, 1540, 1380, 1224, 1022, 877, 792, 722 cm^{-1}; HRMS (ESI^+) calculated for $C_{28}H_{43}ON_2$ $[M+H]^+$ 423.3369, found 423.3375.

10-Bromo-5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2q. R_f: 0.7; Hexane: Ethyl acetate mixture (10 : 0.3); Yield: 76%, white solid; Melting Point: 128-130 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.89 (m, 3H), 7.44 (t, J = 7.5 Hz, 2H), 7.39-7.33 (m, 2H), 7.01 (s, 1H), 6.97 (d, J = 8.6 Hz, 1H), 6.06 (s, 1H), 4.96 (s, 1H), 4.77 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.3, 152.2, 141.0, 139.9, 132.4, 132.2, 131.1, 128.6, 128.5, 125.9, 122.5, 121.3, 116.0, 104.3, 103.7, 72.5 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 3062, 1649, 1440, 1372, 1210, 1018, 765, 690 cm^{-1}; HRMS (ESI^+) calculated for $C_{18}H_{14}ON_2$ $[M+H]^+$ 353.0284, found 353.0283.

10-Bromo-5-methylene-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2r. R_f: 0.65; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 64%, Yellow liquid; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, J = 2.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 2.2, 8.6 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.98 (s, 1H), 6.96 (d, J = 9.6 Hz, 1H), 6.05 (s, 1H), 4.94 (s, 1H), 4.77 (s, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.2, 152.2, 140.9, 139.8, 138.3, 132.3, 131.0, 129.4, 129.3, 125.8, 122.4, 121.3, 115.9, 104.1, 103.5, 72.5, 21.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2917, 1649, 1475, 1342, 1116, 1019, 824, 669 cm^{-1}; HRMS (ESI^+) calculated for $C_{19}H_{16}ON_2Br$ $[M+H]^+$ 367.0440, found 367.0453.

10-Bromo-5-methylene-2-pentyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2s. R_f: 0.5; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 71%, Yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 2.4 Hz, 1H), 7.31 (dd, J = 2.4, 8.6 Hz, 1H), 6.93 (d, J = 8.6 Hz, 1H), 6.52 (s, 1H), 5.86 (s, 1H), 4.86 (s, 1H), 4.71 (s, 2H), 2.66 (t, J = 7.9 Hz, 2H), 1.75-1.66 (m, 2H), 1.42-1.34 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.1, 155.1, 140.9, 139.0, 132.1, 131.0, 122.4, 121.4, 115.9, 106.1, 102.7, 72.5, 31.6, 29.1, 28.2, 22.5, 14.0 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2954, 1649, 1482, 1379, 1218, 1018, 876, 791, 726 cm^{-1}; HRMS (ESI^+) calculated for $C_{17}H_{20}ON_2Br^{79}$ 347.0753, found 347.0764 and $C_{17}H_{20}ON_2Br^{81}$ [M+2] 349.0733, found 349.0740.

5-Methylene-10-nitro-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2t. R_f: 0.45; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 62%, white solid; Melting Point: 148-150 °C; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.75 (d, J = 2.5 Hz, 1H), 8.12 (dd, J = 2.7, 9.0 Hz 1H), 7.94-7.91 (m, 2H), 7.48-7.43 (m, 2H), 7.41-7.36 (m, 1H), 7.19 (d, J = 9.0 Hz, 1H), 7.17 (s, 1H), 6.12 (s, 1H), 5.07 (s, 1H), 4.85 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.2, 152.5, 143.5, 140.0, 139.1, 131.9, 128.7, 125.9, 124.8, 124.5, 121.8, 119.4, 105.3, 104.8, 72.2 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2927, 1653, 1520, 1344, 1085, 764, 693 cm^{-1}; HRMS (ESI^+) calculated for $C_{18}H_{14}O_3N_3$ $[M+H]^+$ 320.1029, found 320.1028.

5-Methylene-10-nitro-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2u. R_f: 0.45; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 76%, white solid; Melting Point: 162-164 °C; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.53 (d, J = 2.7 Hz, 1H), 8.11 (dd, J = 2.7, 9.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 9.0 Hz, 1H), 7.13 (s, 1H), 6.10 (s, 1H), 5.06 (s, 1H), 4.84 (s, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.2, 152.5, 143.4, 140.0, 138.9, 138.6, 129.4, 129.0, 125.8, 124.5, 121.8, 119.6, 105.1, 104.7, 72.2 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2921, 1651, 1512, 1343, 1079, 896, 791 cm^{-1}; HRMS (ESI^+) calculated for $C_{19}H_{16}O_3N_3$ $[M+H]^+$ 334.1186, found 334.1183.

2-Butyl-5-methylene-10-nitro-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2v. R_f: 0.65; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 80%, white solid; Melting Point: 69-71 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.66 (d, J = 2.7 Hz, 1H), 8.09 (dd, J = 2.7, 9.0 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 6.69 (s, 1H), 5.93 (s, 1H), 4.99 (s, 1H), 4.79 (s, 2H), 2.69 (t, J = 7.7 Hz, 2H), 1.77-1.63 (m, 2H), 1.52-1.36 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.1, 155.3, 143.4, 139.9, 138.2, 124.7, 124.3, 121.7, 119.6, 106.7, 104.4, 72.3, 31.4, 27.8, 22.4, 13.8 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2956, 1651, 1546, 1344, 1126, 1017, 927, 804 cm^{-1}; HRMS (ESI^+) calculated for $C_{16}H_{18}O_3N_3$ $[M+H]^+$ 300.1342, found 300.1338.

5-Methylene-10-nitro-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2w. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 71%, white solid; Melting Point: 76-78 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.66 (d, J = 2.6 Hz, 1H), 8.09 (dd, J = 2.7, 9.0 Hz, 1H), 7.16 (d, J = 9.0 Hz, 1H), 6.68 (s, 1H), 4.98 (s, 1H), 4.79 (s, 2H), 2.68 (t, J = 7.6 Hz, 2H), 1.75-1.68 (m, 2H), 1.44-1.38 (m, 2H), 1.36-1.27 (m, 8H), 0.88 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.1, 155.4, 139.9, 138.2, 124.8, 124.3, 121.7, 119.6, 106.7, 104.4, 72.3, 31.8, 29.3, 29.2, 28.1, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2924, 1652, 1520, 1344, 1256, 1092, 882 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{20}H_{26}O_3N_3$[M+H]$^+$ 356.1968, found 356.1967.

8,10-Dichloro-5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2x. R_f: 0.65; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 72%, white solid; Melting Point: 139-141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 1.4 Hz, 1H), 7.89 (d, J = 1.4 Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.47-7.42 (m, 2H), 7.40-7.35 (m, 2H), 7.01 (s, 1H), 6.09 (s, 1H), 5.0 (s, 1H), 4.87 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.2, 151.8, 140.4, 139.3, 132.0, 129.6, 128.7, 128.6, 128.5, 126.9, 126.7, 125.9, 122.3, 105.0, 104.0, 73.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2923, 1648, 1540, 1444, 1370, 993, 878, 761, 686 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{18}H_{13}ON_2Cl_2$ [M+H]$^+$ 343.0399, found 343.0409.

2-Butyl-8,10-dichloro-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2y. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.4); Yield: 74%, white solid; Melting Point: 76-78 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 6.52 (s, 1H), 5.90 (s, 1H), 4.90 (s, 1H), 4.81 (s, 2H), 2.67 (t, J = 7.6 Hz, 2H), 1.72-1.65 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.1, 151.7, 140.3, 138.4, 129.3, 128.3, 126.8, 126.7, 122.4, 106.9, 103.1, 73.2, 31.4, 27.8, 22.4, 13.9 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2956, 1650, 1382, 1231, 999, 848 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{26}H_{17}ON_2Cl_2$ [M+H]$^+$ 323.0712, found 323.0711.

8,10-Dichloro-5-methylene-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2z. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 85%, white solid; Melting Point: 59-61 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, J = 2.5 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 6.52 (s, 1H), 5.89 (s, 1H), 4.90 (s, 1H), 4.80 (s, 2H), 2.66 (t, J = 7.9 Hz, 2H), 1.73-1.65 (m, 2H), 1.42-1.36 (m, 2H), 1.33-1.25 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 151.7, 140.3, 138.4, 129.3, 128.3, 126.8, 126.7, 122.4, 106.9, 103.1, 73.2, 31.8, 29.4, 29.3, 29.2, 28.1, 22.6, 14.1 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2924, 1652, 1382, 1231, 1017, 848, 793 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{20}H_{25}ON_2Cl_2$[M+H]$^+$ 379.1338, found 379.1341.

(*E*)-5-Benzylidene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2aa. R_f: 0.6; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 61%, Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.80 (m, 2H), 7.42-7.21 (m, 10H), 6.99 (d, J = 7.5 Hz, 2H), 6.72 (s, 1H), 6.31 (t, J = 8.0 Hz, 1H), 4.87-4.75 (m, 1H), 4.70-4.60 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.4, 154.1, 146.6, 146.2, 134.8, 133.6, 132.8, 130.8, 129.7, 128.6, 128.4, 128.2, 127.0, 125.8, 121.2, 120.4, 117.3, 117.1, 104.9, 64.9 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2924, 1603, 1469, 1211, 1046, 760, 689 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{24}H_{19}ON_2$ [M+H]$^+$ 351.1491, found 351.1501.

(*E*)-2-(4-Fluorophenyl)-5-(4-methoxybenzylidene)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: 2ab. R_f: 0.45; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 65%, white solid; Melting Point: 164-166 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.78 (m, 2H), 7.32-7.24 (m, 4H), 7.07 (t, J = 8.8 Hz, 2H), 7.01-6.94 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.65 (s, 1H), 6.20 (t, J = 8.1 Hz, 1H), 4.81-4.73 (m, 1H), 4.67-4.60 (m, 1H), 3.80 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (d, J = 246.481 Hz, 1C), 160.8, 154.5, 153.1, 146.6, 145.9, 133.6, 130.8, 129.1, 129.0, 128.5, 127.5 (d, J = 8.069 Hz, 1C), 127.2, 121.1, 120.4, 116.9, 115.5 (d, J = 22.007 Hz, 2C), 115.2, 113.9, 104.7, 64.9, 55.3 ppm; IR(CH_2Cl_2): $\tilde{\upsilon}$ = 2924, 1604, 1512, 1448, 1252, 1020, 837, 754 cm^{-1}; HRMS (ESI$^+$) calculated for $C_{25}H_{20}FN_2O_2$ [M+H]$^+$ 399.1503, found 399.1513.

Conflicts of interest

There are no conflicts to declare.

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