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A Gold(I)-Catalyzed Tandem Cyclization to Benzo[*b*]indeno [1,2-*e*][1,4]diazepines from *o*-Phenylenediamines and Ynones

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Abstract. A gold-catalyzed tandem cyclization of *o*-phenylenediamines with ynones to synthesize benzo[*b*] indeno[1,2-*e*][1,4]diazepine has been developed. The mechanism was explored by control experiments. The method provides a way to access a range of benzo[*b*] indeno[1,2-*e*][1,4]diazepine derivatives in diversity-oriented synthesis aiming at discovering structurally diverse scaffolds.

Keywords: Benzodiazepines; Heterocycles; Gold; Synthetic methods; Domino reactions; Homogeneous catalysis

Introduction

Benzodiazepines are one of attractive frameworks in medicinal chemistry due to their abundance in drugs and high hit rates in lead discovery.[1] The development of structurally diverse benzodiazepines as privileged scaffolds for the preparation of molecular libraries is important in diversity-oriented synthesis.[2] Traditionally, they exhibit significant pharmacological activities on the central nervous system such as antianxiety, sedative, antidepressive and anticonvulsant etc.[3] Recently, as more synthetic compounds are available from novel methodologies, chemists carried out expansive research on their activities in treatment of HIV,[4] cancer,[5] inflammation,[6] lipid peroxidation[7] and malaria.[8] Due to the significance of these molecules, many synthetic strategies have been developed in recent years.[9] For example, in 2012, Dömling and coworkers reported a Ugi four-component reaction strategy to 1,4-benzodiazepine-6-ones (Scheme 1, **a**).[9g] In 2014, Dembinski and coworkers described a catalyst-free microwave-accelerated condensation of alk-3-ynones and *o*-phenylenediamines to access 1,5-benzodiazepines (Scheme 1, **b**).[9h] In the same year, Hajela and coworkers developed a tandem C-2 functionalization/intramolecular azide-alkyne 1,3 dipolar cyclization method to synthesize 9*H*-benzo[*b*]pyrrolo[1,2-*g*][1,2,3]triazolo[1,5-*d*][1,4] diazepines (Scheme 1, **c**).[9i] In 2016, Goggiamani and coworkers advanced a gold-catalyzed hydroamination/cyclization domino process to construct 1,5-benzodiazepines using propargylic alcohol and *o*-phenylenediamines as building blocks (Scheme 1, **d**).[9j] Although these efforts have greatly expanded the diversity of benzodiazepine scaffolds, more synthetic transformations are urgently needed to access complex benzodiazepine derivatives, ideally constructed from relatively simple materials via tandem cyclization.

Recently, homogeneous gold-catalyzed cycloisomerizations have emerged as robust and versatile toolboxes for their atom-economical assembly of a range of compounds from simple noncyclic substrates.[10a,10n] They are featured as mild conditions, high efficiency and excellent selectivity.[10b,10m] Multiple carbon-carbon and carbon-hetero bonds can be formed in one-pot fashion under the catalysis of gold cation species, representing a unique approach to structurally diverse heterocycles.[10c] Therefore, they have been applied in extensive transformations such as the total syntheses of natural products and synthetic methodologies.[10]

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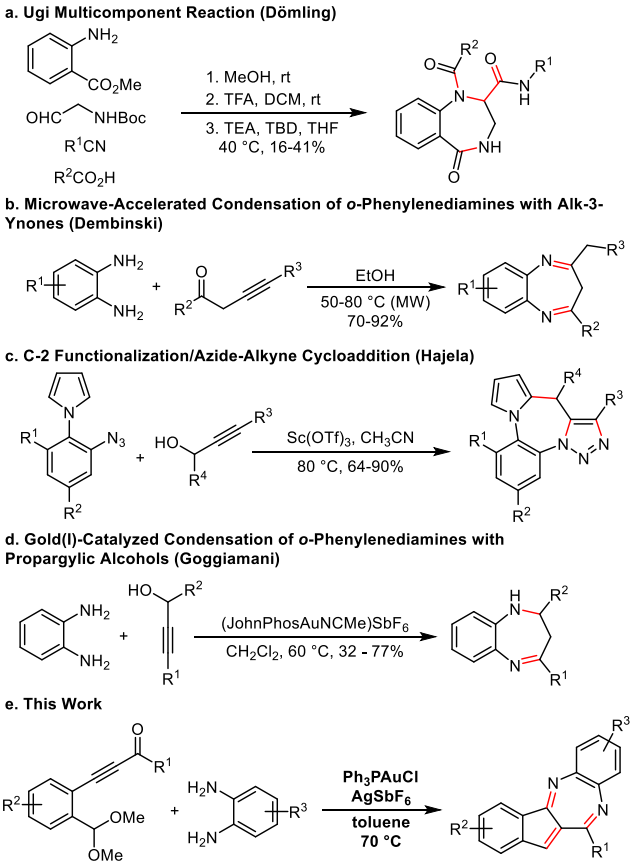
As part of our persistent research interest in constructing structurally diverse heterocyclic molecules via gold-catalyzed cycloisomerizations, we have developed a number of synthetic methods to synthesize heterocycles such as multi-substituted furofuran and furopyran,[11a] indeno-chromen-4-one and indeno-quinolin-4-one,[11b] benzo[*a*]carbazole and indeno[1,2-*c*]quinolone,[11c] 12*H*-benzo[*a*]xanthen-12-one and benzo[*a*]acridin-12(7*H*)-one[11d] etc. Herein we described a gold(I)-catalyzed intramolecular cycloisomerization/ intermolecular Michael addition and condensation cascade process to access a series of structurally novel benzo[*b*]indeno[1,2-*e*][1,4]diazepines using commercially available *o*-phenylenediamines and facilely prepared ynones as building blocks[11b,12,13d] (Scheme 1, **e**).

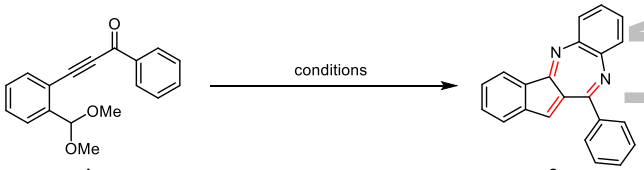


Scheme 1. Representative Methods and Our Tandem Cyclization Strategy to Benzodiazepine Derivatives

Results and Discussion

We envisioned that cycloisomerization of substrate **1** via methoxyl migration/nucleophilic addition under the catalysis of gold(I) species would furnish indenone derivatives.[11b,13] A sequential condensation between the indenone with *o*-phenylenediamine would generate benzo[*b*]indeno[1,2-*e*][1,4]diazepine **2** as a structurally novel hybrid molecule in one pot (Table 1). Based on this synthetic design, we treated substrate **1** with gold catalyst at room temperature followed by addition of *o*-phenylenediamine at 70 °C, which allowed us to isolate the benzo[*b*]indeno[1,2-*e*][1,4]diazepine **2** successfully. We further investigated this cascade process by screening the reaction conditions using substrate **1** and *o*-phenylenediamine under the catalysis of readily available cationic gold(I) catalysts shown in Table 1. Except for Ph_3PAuCl, all of the catalysts allowed the formation of diazepine **2** and the combination of Ph_3PAuCl and $AgSbF_6$ gave the best yield (Table 1, entries 1-6). The control experiment showed that $AgSbF_6$ alone could not catalyze this transformation (Table 1, entry 7). Examination of reaction temperature revealed that 70 °C was the best temperature for the condensation of the two fragments to form diazepine **2** (Table 1, entries 8-9). Decreasing the catalyst loading to 3 mol% led to a lower yield of the desired product (Table 1, entry 10). Increasing the catalyst loading to 10 mol% did not improve the yields (Table 1, entry 11). Investigation on the amounts of *o*-phenylenediamine showed that 3 equivalents afforded the best result (Table 1, entries 12-13). Screening of solvents revealed that toluene was the optimal one among the screened solvents such as tetrahydrofuran (THF), 1,2-dichloroethane (DCE) and acetonitrile (Table 1, entries 14-16). Finally, the optimal condition for the one-pot tandem cyclization was determined as stirring the substrates in the catalysis of $Ph_3PAuCl/AgSbF_6$ in toluene at room temperature followed by heating with *o*-phenylenediamine at 70 °C.

Table 1. Optimization of Reaction Conditions



entry[a]	catalyst[b]	additive[c]	solvent	temp. (°C)	yield (%)
1	Ph_3PAuCl		toluene	70	0[d]
2	$Ph_3PAuNTf_2$		toluene	70	37
3	Ph_3PAuCl	$AgBF_4$	toluene	70	48
4	Ph_3PAuCl	AgOTf	toluene	70	64
5	Ph_3PAuCl	$AgSbF_6$	toluene	70	85
6	IPrAuCl	$AgSbF_6$	toluene	70	80
7	$AgSbF_6$		toluene	70	0[d]
8	Ph_3PAuCl	$AgSbF_6$	toluene	80	57
9	Ph_3PAuCl	$AgSbF_6$	toluene	60	73
10	Ph_3PAuCl	$AgSbF_6$	toluene	70	68[e]
11	Ph_3PAuCl	$AgSbF_6$	toluene	70	80[f]
12	Ph_3PAuCl	$AgSbF_6$	toluene	70	61[g]
13	Ph_3PAuCl	$AgSbF_6$	toluene	70	70[h]
14	Ph_3PAuCl	$AgSbF_6$	THF	70	40
15	Ph_3PAuCl	$AgSbF_6$	DCE	70	35
16	Ph_3PAuCl	$AgSbF_6$	CH_3CN	70	26

[a] 3 eq. *o*-phenylenediamine was utilized. [b] 5 mol% catalyst was utilized. [c] 5 mol% additive was utilized. [d] Stirring for 24 h. [e] 3 mol% catalyst and additive were utilized. [f] 10 mol% catalyst and additive were utilized. [g] 1.5 eq. *o*-

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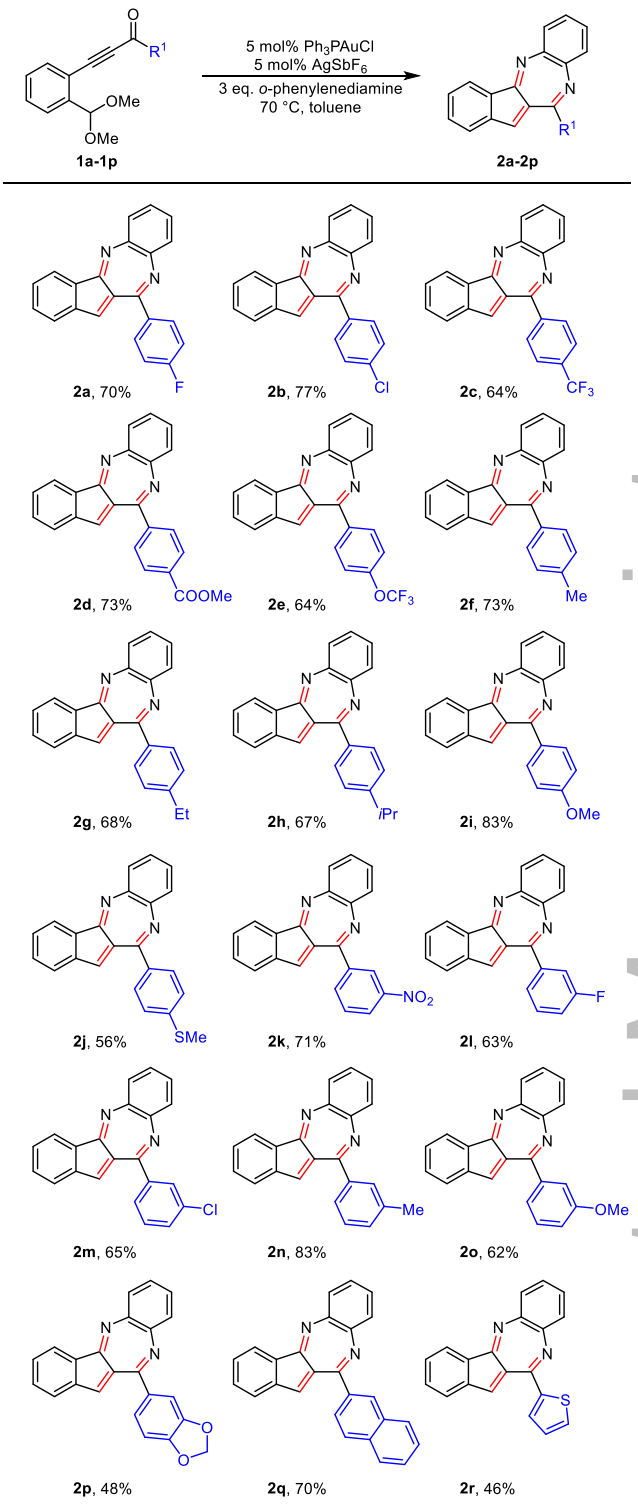
phenylenediamine was utilized. [h] 5 eq. *o*-phenylenediamine was utilized.

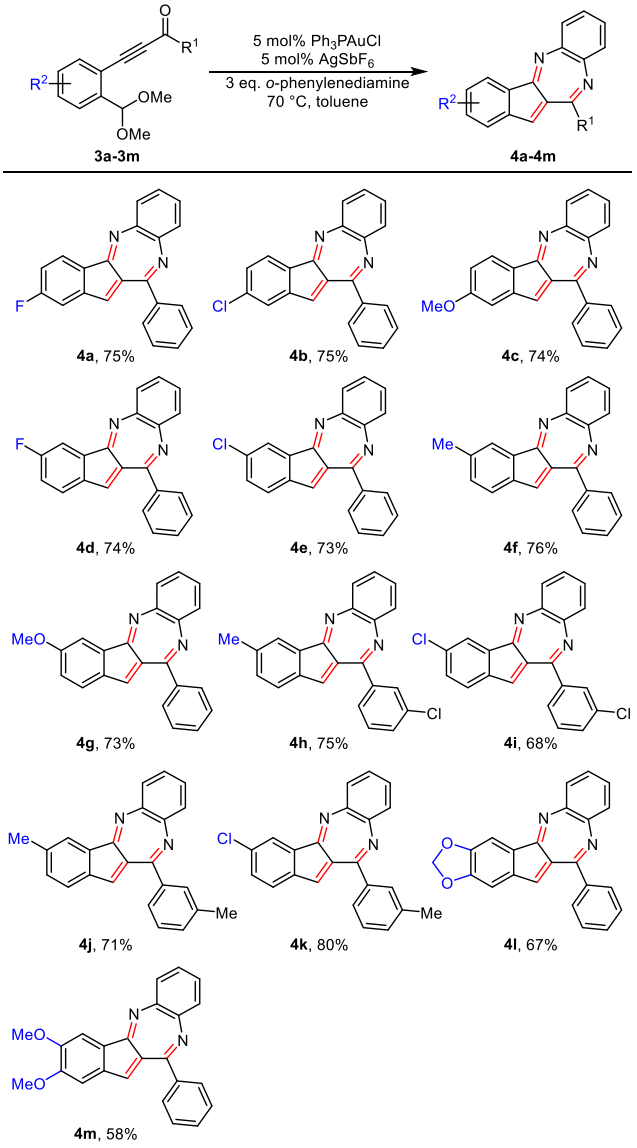
With the optimal conditions in hand, we explored the scope of this tandem transformation systematically by using a variety of ynone substrates and *o*-phenylenediamines. First, the substitutions on the carbonyl group (R^1) were investigated as illustrated in Scheme 2. The substrates with monosubstituted phenyl group on R^1 underwent smoothly to yield benzo[*b*]indeno[1,2-*e*][1,4] diazepines with good to excellent yields regardless of



Scheme 2. Exploring the Scope of Various Substituents at R^1

electron-donating or withdrawing substitutions on phenyl group (Scheme 2, **2a-2i**, **2k-2o**). The substrate bearing sulfur substitution provided relatively lower yield, which might be attributed to the attenuation of gold catalysts by the sulfur atom via coordination (Scheme 2, **2j**). The substrate with multiple electron-donating groups on phenyl ring also gave low yield probably owing to the decreased electrophilic ability of carbonyl group in the substrate (Scheme 2, **2p**). The

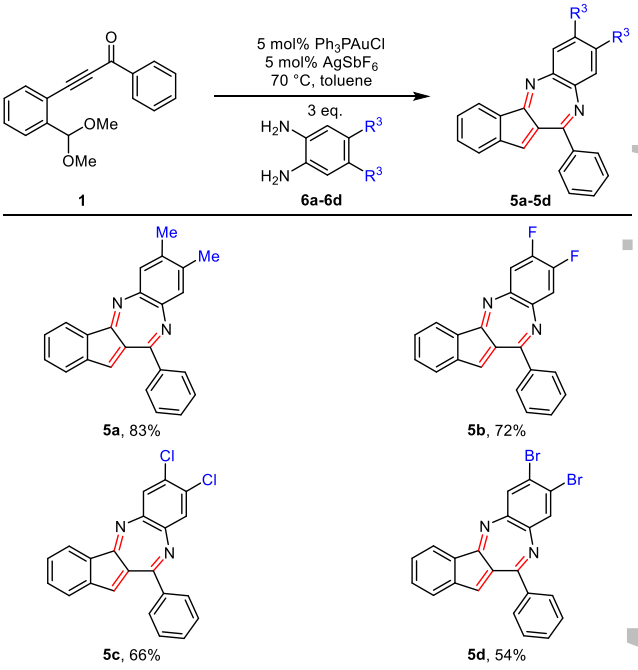
substrate with naphthyl substitution could afford the corresponding product in a satisfactory yield (Scheme 2, **2q**). The reaction was also compatible with the substrates bearing thiophene moieties. However, only moderate yield was achieved due to the instability of the product during isolation (Scheme 2, **2r**). The substrates with aliphatic substitutions on the carbonyl group (R^1) were also investigated; however, no desired products were isolated.



Scheme 3. Exploring the Scope of Various Substituents at R^2

Next, the scope of substituents on the phenyl ring connected to the alkynyl (R^2) was examined. A variety of functional groups such as F, Cl, Me and OMe were well-tolerated and excellent yields were obtained (Scheme 3, **4a-4k**). Gratifyingly, the substrates with multiple electron-donating substituents on this phenyl ring also underwent smoothly to give corresponding products in acceptable yields (Scheme 3, **4l-4m**).

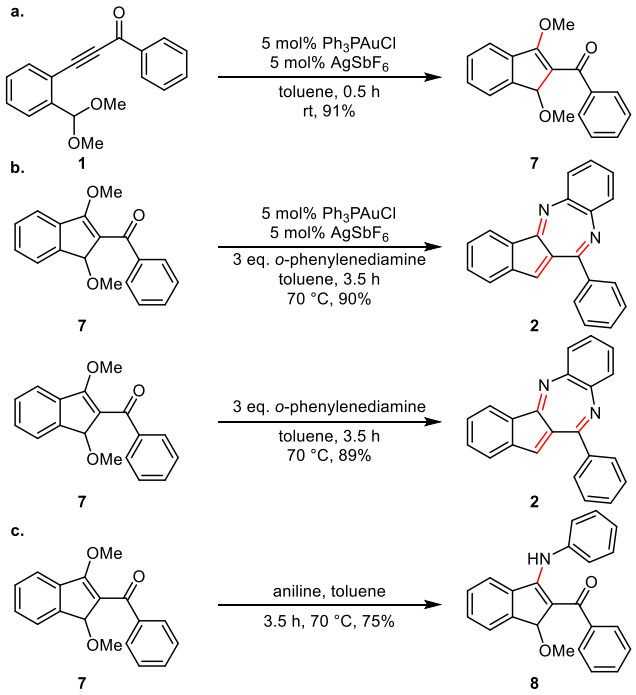
Finally, several substituted *o*-phenylenediamines were investigated (Scheme 4). When the *o*-phenylenediamine with electron-donating substituents was employed, the desired product was obtained in excellent yield (Scheme 4, **5a**). Interestingly, the *o*-phenylenediamines bearing electron-withdrawing substituents were also worked, resulting in acceptable yields (Scheme 4, **5b-5d**). The attempts by utilizing unsymmetrically substituted *o*-phenylenediamines proved unsuccessful because an unisolatable mixture of two regioisomer was obtained.



Scheme 4. Exploring the Scope of Various Substituents at R^3

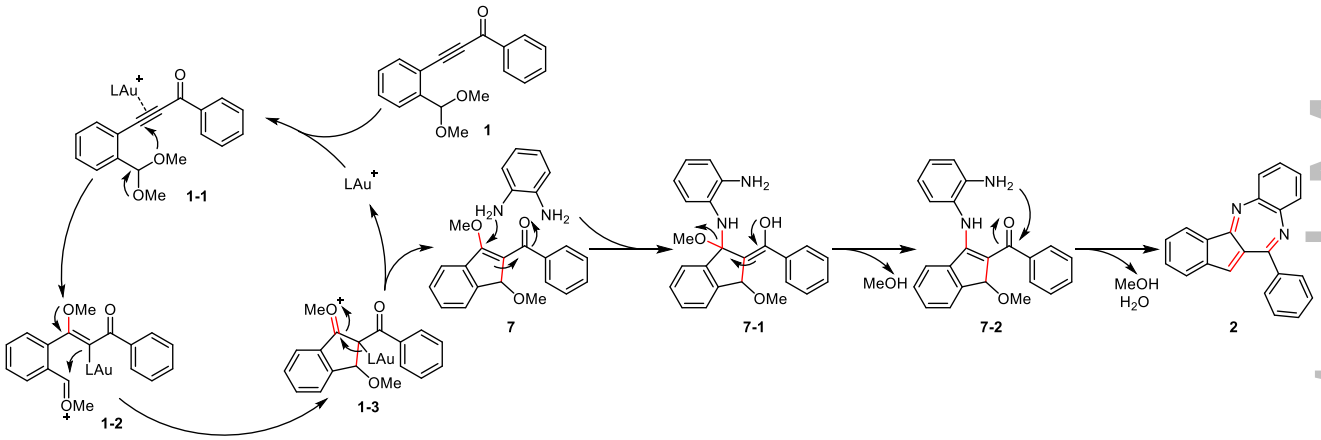
To gain an insight into the possible mechanism of this tandem cyclization, control experiments were carried out based on substrate **1** (Scheme 5). In order to trap the intermediate of the gold-catalyzed reaction, the substrate **1** was treated with gold(I) catalyst in the absence of *o*-phenylenediamine, which resulted in the generation of intermediate **7** via a gold-catalyzed methoxyl rearrangement/cyclization (Scheme 5, **a**). When the isolated intermediate **7** was subjected to the standard conditions, the desired product **2** was obtained in a satisfactory yield. To examine the influence of the gold catalyst in the second cyclization, the isolated intermediate **7** was heated with *o* phenylenediamine without the catalysts, leading to the isolation of the desired product **2** in 89% yield. This result indicated that the gold catalyst did not play a role in the second cyclization (Scheme 5, **b**). Furthermore, to elucidate the detailed process of the diazepine ring construction, we employed aniline in place of *o*-phenylenediamine to capture the possible intermediate. The product **8**, derived from the Michael addition of aniline to the α,β-unsaturated ketone/elimination of methanol was isolated as the only product (Scheme 5, **c**). On the basis of this observation, it could be inferred that the intermolecular Michael addition of amino to

α,β-unsaturated ketone rather than imine formation happened preferentially in the diazepine formation.



Scheme 5. Control Experiments

Based on the experiments above and precedent studies,[9h,11b-11c,13,14] a plausible mechanism for the tandem cyclization was proposed in Scheme 6. The reaction commences with the activation of triple bonds by gold(I) cation species followed by the migration of methoxy group to afford vinylgold species **1-2**. Then the oxonium in **1-2** is attacked by vinyl ether through an intramolecular nucleophilic addition to afford intermediate **1-3**, which is tautomerized into **7**. Upon *o*-phenylenediamine is added, an intermolecular Michael addition of *o*-phenylenediamine to **7** affords the adduct **7-1**. Regeneration of α,β-unsaturated ketone by releasing methanol gives the intermediate **7-2**. Finally, product **2** is achieved through an intramolecular condensation of free amino and carbonyl group followed by a formation of highly conjugated system via subsequent aromatization by release of methanol.



Scheme 6. Proposed Reaction Mechanism

Conclusion

In conclusion, we have developed a gold(I)-catalyzed tandem cyclization strategy to provide a series of benzo[*b*]indeno[1,2-*e*][1,4]diazepines. This one-pot cascade strategy was involved in construction of two rings through cleavage of three chemical bonds and formation of three new double bonds from commercially available *o*-phenylenediamines and readily prepared ynones. The scope of the methodology was examined by a variety of substrates. The possible mechanism of the transformation was probed by isolation of the intermediate and carefully designed control experiments. The study on the bioactivity of the benzo[*b*]indeno[1,2-*e*][1,4] diazepine compounds was ongoing in our lab and will be reported in due course.

Experimental Section

1. General Information

Unless otherwise noted, reagents were obtained commercially and used without further purification. Tetrahydrofuran (THF) was distilled from sodium under a nitrogen atmosphere. Dichloromethane (DCM) was distilled from calcium hydride under a nitrogen atmosphere. Chloroform was distilled from calcium hydride under a nitrogen atmosphere. Toluene was distilled from sodium under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash column chromatography was carried out on Zeoprep 60 (200-300 mesh) silica gel. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers or Bruker Ascend 400 and referenced to $CDCl_3$ and DMSO-d_6. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Bruker IFS 55 spectrometer. Melting points

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(Mp) were tested on Thomas Hoover capillary melting point apparatus.

2. General Procedures for the Preparation of Benzo[*b*]indeno[1,2-*e*][1,4]diazepines 2, 2a-2r, 4a-4m, 5a-5d and Characterization Data

Ph_3PAuCl (0.05 mmol, 25 mg) and $AgSbF_6$ (0.05 mmol, 17 mg) were added in toluene (5 mL) and the mixture was stirred at room temperature for 10 min. Substrates **1**, **1a-1r**, **3a-3m** (1.0 mmol) were then added to the above solution and the mixture was stirred at room temperature for 30 min till TLC showed the consumption of the starting material. *o*-Phenylenediamine (3.0 mmol) was added to the above mixture and the solution was stirred at 70 °C for 3.5 h till TLC showed the consumption of the intermediates. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography (petroleum ether/dichloromethane) on silica gel to afford the products **2**, **2a-2r**, **4a-4m**, **5a-5d**.

11-Phenylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (2)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2** (260 mg) as a red solid with a yield of 85%; Mp 213.2 – 214.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.2 Hz, 1H), 8.12 – 8.06 (m, 1H), 7.96 – 7.89 (m, 1H), 7.85 – 7.73 (m, 2H), 7.67 – 7.61 (m, 1H), 7.61 – 7.54 (m, 5H), 7.54 – 7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 161.4, 142.2, 142.1, 141.8, 139.6, 136.9, 135.4, 135.3, 135.2, 131.4, 130.5, 129.5, 129.0, 128.9, 128.6, 128.5, 127.7, 122.9, 122.7; IR (thin film, cm^{-1}) 2986, 2831, 1609, 1492, 1440, 1400, 1368, 1173, 1006, 799; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{15}N_2$ $[M+H]^+$ 307.1230, Found 307.1232.

11-(4-Fluorophenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2a)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2a** (227 mg) as a red solid with a yield of 70%; Mp 218.6 – 219.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.3 Hz, 1H), 8.12 – 8.06 (m, 1H), 7.93 – 7.88 (m, 1H), 7.82 – 7.77 (m, 2H), 7.65 (td, *J* = 7.3, 1.2 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 (s, 1H), 7.24 – 7.18 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6 (d, *J* = 248.8 Hz) 162.4, 160.2, 142.0, 141.7, 139.5, 138.2 (d, *J* = 3.3 Hz), 136.7, 135.4, 135.3 (d, *J* = 7.1 Hz), 131.5, 130.6, 130.6, 130.5, 129.1, 128.9, 127.9, 122.9, 122.8, 115.6 (d, *J* = 21.4 Hz); IR (thin film, cm^{-1}) 2985, 2923, 2852, 1610, 1492, 1441, 1400, 1366, 1173, 1007, 799; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}FN_2$ $[M+H]^+$ 325.1136, Found 325.1132.

11-(4-Chlorophenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2b)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2b** (262 mg) as a red solid with a yield of 77%; Mp 225.2 – 225.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.4 Hz, 1H), 8.13 – 8.05 (m, 1H), 7.94 – 7.86 (m, 1H), 7.76 – 7.70 (m, 2H), 7.69 – 7.63 (m, 1H), 7.63 – 7.55 (m, 4H), 7.53 – 7.50 (m, 2H), 7.50 – 7.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.1, 142.0, 141.7, 140.5, 139.6, 136.7, 135.5, 135.4, 135.3 (2C), 131.5, 130.6, 130.0, 129.2, 128.8, 128.7, 127.9, 122.9, 122.8; IR (thin film, cm^{-1}) 2985, 2926, 1636, 1603, 1491, 1448, 1368, 1174, 1066, 1011, 799, 764; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}ClN_2$ $[M+H]^+$ 341.0840, Found 341.0840.

11-(4-(Trifluoromethyl)phenyl)benzo[*b*]indeno[1,2-*e*] [1,4]diazepine (2c)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2c** (240 mg) as a red solid with a yield of 64%; Mp 204.4 – 205.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.3 Hz, 1H), 8.17 – 8.07 (m, 1H), 7.95 – 7.86 (m, 3H), 7.81 (s, 1H), 7.79 (s, 1H), 7.71 – 7.62 (m, 2H), 7.62 – 7.56 (m, 3H), 7.49 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 159.9, 145.5, 142.0, 141.7, 139.6, 136.8, 135.5, 135.4, 135.3, 131.6, 131.4 (q, *J* = 32.5 Hz), 130.7, 129.5, 128.9, 128.7, 128.1, 125.7 (q, *J* = 3.8 Hz), 124.2 (d, *J* = 272.1 Hz), 123.0, 122.9; IR (thin film, cm^{-1}) 2923, 2853, 1603, 1463, 1403, 1382, 1332, 1168, 1106, 1066; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{14}F_3N_2$ $[M+H]^+$ 375.1104, Found 375.1100.

Methyl 4-(benzo[*b*]indeno[1,2-*e*][1,4]diazepin-11-yl)benzoate (2d)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2d** (266 mg) as a red solid with a yield of 73%; Mp 208.2 – 210.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.4 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 2H), 8.14 – 8.07 (m, 1H), 7.96 – 7.89 (m, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.65 (td, *J* = 7.4, 1.3 Hz, 1H), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.48 (s, 1H), 3.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 162.4, 160.3, 146.3, 142.1, 141.7, 139.6, 136.8, 135.5, 135.35, 135.26, 131.6, 130.9, 130.6, 130.0, 129.4, 128.7, 128.6, 128.0, 122.9, 122.8, 52.4; IR (thin film, cm^{-1}) 3426, 2922, 2852, 1719, 1628, 1435, 1384, 1278, 1101, 747; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{17}N_2O_2$ $[M+H]^+$ 365.1285, Found 365.1287.

11-(4-(Trifluoromethoxy)phenyl)benzo[*b*]indeno[1,2-*e*] [1,4]diazepine (2e)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2e** (250 mg) as a red solid with a yield of 64%; Mp 175.4 – 175.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.2 Hz, 1H), 8.09 (dd, *J* = 6.0, 3.6 Hz, 1H), 7.90 (dd, *J* = 6.0, 3.6 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.54 (m, 5H), 7.52 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 159.8, 150.0, 142.0, 141.7, 140.7, 139.6, 136.7, 135.4, 135.34, 135.32, 131.5, 130.6, 130.2, 129.3, 128.7, 128.0, 122.9, 122.8, 121.0, 120.7 (q, *J* = 257.8 Hz); IR (thin film, cm^{-1}) 2922, 2853, 2370, 2341, 1627, 1465, 1384, 1270, 1253, 1102; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{14}F_3N_2O$ $[M+H]^+$ 391.1053, Found 391.1051.

11-(p-Tolyl)benzo[*b*]indeno[1,2-*e*][1,4]diazepine (2f)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2f** (234 mg) as a red solid with a yield of 73%; Mp 188.6 – 189.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.4 Hz, 1H), 8.11 – 8.06 (m, 1H), 7.97 – 7.89 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.64 (td, *J* = 7.3, 1.2 Hz, 1H), 7.61 – 7.57 (m, 3H), 7.57 – 7.53 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 161.4, 142.3, 141.8, 139.58, 139.57, 139.3, 136.8, 135.37, 135.35, 135.2, 131.3, 130.5, 129.2, 129.1, 128.8, 128.5, 127.7, 122.8, 122.7, 21.6.; IR (thin film, cm^{-1}) 2986, 2831, 1609, 1492, 1440, 1400, 1367, 1173, 1006, 799, HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2$ $[M+H]^+$ 321.1386, Found 321.1389.

11-(4-Ethylphenyl)benzo[*b*]indeno[1,2-*e*][1,4]diazepine (2g)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2g** (227 mg) as a red solid with a yield of 68%; Mp 148.6 – 150.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.3 Hz, 1H), 8.15 – 8.03 (m, 1H), 7.97 – 7.89 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.57 – 7.50 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 161.5, 145.9, 142.3, 141.9, 139.60, 139.59, 136.9, 135.42, 135.38, 135.2, 131.4, 130.5, 129.1, 128.8, 128.6, 128.1, 127.7, 122.9, 122.7, 29.0, 15.7; IR (thin film, cm^{-1}) 2959, 2923, 2853, 1603, 1548, 1463, 1377, 1332, 1182, 1114, 764; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1543, Found 335.1540.

11-(4-Isopropylphenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2h)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2h** (233 mg) as a red solid with a yield of 67%; Mp 158.0 – 159.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.2 Hz, 1H), 8.14 – 8.04 (m, 1H), 8.00 – 7.89 (m, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.61 (t, *J* = 10.1 Hz, 4H), 7.57 – 7.53 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 3.02 (hept, *J* = 6.9 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 161.5, 150.5, 142.3, 141.9, 139.7, 139.6, 136.9, 135.41, 135.35, 135.2, 131.3, 130.4, 129.1, 128.8, 128.6, 127.7, 126.6, 122.8, 122.7, 34.3, 24.1; IR (thin film, cm^{-1}) 2955, 2923, 2852, 1604, 1549, 1464, 1403, 1375, 1334, 1092, 766, 751; HRMS (ESI): *m/z* Calcd. for $C_{25}H_{21}N_2$ $[M+H]^+$ 349.1699, Found 349.1701.

11-(4-Methoxyphenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2i)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2i** (279 mg) as a red solid with a yield of 83%; Mp 206.6 – 206.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.30 (m, 1H), 8.11 – 8.03 (m, 1H), 7.95 – 7.88 (m, 1H), 7.83 – 7.75 (m, 2H), 7.66 – 7.61 (m, 2H), 7.61 – 7.50 (m, 4H), 7.09 – 7.00 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.82, 160.81, 142.2, 141.8, 139.5, 136.6, 135.4, 135.23, 135.15, 134.7, 131.3, 130.4, 130.2, 129.0, 128.6, 127.7, 122.8, 122.6, 113.9, 55.6; IR (thin film, cm^{-1}) 3047, 2986, 2922, 2831, 1607, 1492, 1441, 1367, 1253, 1174, 1007, 761; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2O$ $[M+H]^+$ 337.1335, Found 337.1333.

11-(4-(Methylthio)phenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2j)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2j** (197 mg) as a red solid with a yield of 56%; Mp 201.9 – 202.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dq, *J* = 7.2, 0.9 Hz, 1H), 8.12 – 8.04 (m, 1H), 7.94 – 7.86 (m, 1H), 7.77 – 7.71 (m, 2H), 7.67 – 7.62 (m, 1H), 7.62 – 7.52 (m, 5H), 7.43 – 7.34 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.7, 142.2, 141.8, 140.6, 139.5, 138.7, 136.7, 135.35, 135.32, 135.2, 131.4, 130.5, 129.1, 128.88, 128.86, 127.8, 126.2, 122.9, 122.7, 15.7; IR (thin film, cm^{-1}) 2921, 2852, 1590, 1545, 1463, 1366, 1331, 1185, 1088, 763; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2S$ $[M+H]^+$ 353.1107, Found 353.1108.

11-(3-nitrophenyl)benzo[*b*]indeno[1,2-*e*][1,4]diazepine (2k)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2k** (249 mg) as a red solid with a yield of 71%; Mp 244.1 – 244.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.43 – 8.33 (m, 2H), 8.18 – 8.08 (m, 2H), 7.94 – 7.88 (m, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.48 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 158.5, 148.5, 143.6, 141.8, 141.6, 139.5, 136.5, 135.5, 135.4, 135.2, 134.6, 131.7, 130.8, 129.72, 129.77, 128.3, 128.2, 124.2, 123.8, 123.03, 122.99; IR (thin film, cm^{-1}) 3423, 2923, 2853, 1627, 1522, 1466, 1436, 1346, 1099, 759; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}N_3O_2$ $[M+H]^+$ 352.1081, Found 352.1085.

11-(3-Fluorophenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2l)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2l** (204 mg) as a red solid with a yield of 63%; Mp 212.8 – 213.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.33 (m, 1H), 8.19 – 8.04 (m, 1H), 7.99 – 7.87 (m, 1H), 7.70 – 7.62 (m, 1H), 7.61 – 7.55 (m, 5H), 7.55 (s, 1H), 7.54 – 7.44 (m, 2H), 7.21 (tdd, *J* = 8.4, 2.6, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.7 Hz), 162.4, 159.8 (d, *J* = 2.4 Hz), 144.1 (d, *J* = 7.3 Hz), 142.0, 141.7, 139.6, 136.9, 135.4, 135.3 (2C), 131.5, 130.6, 130.2 (d, *J* = 8.1 Hz), 129.3, 128.6, 127.9, 124.2 (d, *J* = 3.0 Hz), 122.9, 122.8, 116.4 (d, *J* = 21.2 Hz), 115.8 (d, *J* = 22.5 Hz); IR (thin film, cm^{-1}) 3048, 2986, 2831, 1609, 1492, 1439, 1400, 1368, 1173, 1006, 798; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}FN_2$ $[M+H]^+$ 325.1136, Found 325.1138.

11-(3-Chlorophenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2m)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2m** (222 mg) as a red solid with a yield of 65%; Mp 196.3 – 197.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.3 Hz, 1H), 8.10 (dt, *J* = 6.0, 3.7 Hz, 1H), 7.96 – 7.86 (m, 1H), 7.77 (s, 1H), 7.68 – 7.63 (m, 2H), 7.63 – 7.55 (m, 4H), 7.51 (s, 1H), 7.52 – 7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 159.8, 143.7, 142.0, 141.7, 139.6, 136.8, 135.4, 135.32, 135.29, 134.6, 131.5, 130.6, 129.9, 129.6, 129.3, 128.75, 128.67, 128.0, 126.6, 122.9, 122.8; IR (thin film, cm^{-1}) 2986, 2922, 2831, 1609, 1492, 1440, 1401, 1367, 1173, 1006, 799, 774; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}ClN_2$ $[M+H]^+$ 341.0840, Found 341.0843.

11-(m-Tolyl)benzo[*b*]indeno[1,2-*e*][1,4]diazepine (2n)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2n** (266 mg) as a red solid with a yield of 83%; Mp 174.3 – 174.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 – 8.35 (m, 1H), 8.12 – 8.07 (m, 1H), 7.97 – 7.91 (m, 1H), 7.65 (td, *J* = 7.3, 1.2 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.57 – 7.51 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 161.8, 142.3, 142.1, 141.8, 139.7, 138.4, 137.1, 135.4 (2C), 135.2, 131.4, 130.5, 130.2, 129.2, 129.1, 128.9, 128.4, 127.8, 125.5, 122.9, 122.7, 21.7; IR (thin film, cm^{-1}) 2986, 2831, 1608, 1492, 1440, 1400, 1366, 1173, 1006, 799; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2$ $[M+H]^+$ 321.1386, Found 321.1390.

11-(3-Methoxyphenyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2o)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2o** (209 mg) as a red solid with a yield of 62%; Mp 160.5 – 160.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.4 Hz, 1H), 8.10 (dd, *J* = 6.1, 3.3 Hz, 1H), 8.00 – 7.89 (m, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.62 – 7.54 (m, 5H) 7.43 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (s, 1H), 7.05 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 161.2, 159.8, 143.4, 142.2, 141.8, 139.7, 137.1, 135.41, 135.35, 135.2, 131.4, 130.5, 129.6, 129.02, 128.99, 127.8, 122.9, 122.8, 120.8, 115.3, 114.0, 55.6; IR (thin film, cm^{-1}) 3048, 2987, 2924, 2831, 1599, 1552, 1490, 1463, 1368, 1333, 1269, 1174, 1045, 1006, 764; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2O$ $[M+H]^+$ 337.1335, Found 337.1339.

11-(Benzo[*d*][1,3]dioxol-5-yl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2p)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to

give the product **2p** (168 mg) as a red solid with a yield of 48%; Mp 133.6 – 134.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.32 (m, 1H), 8.11 – 8.04 (m, 1H), 7.92 – 7.86 (m, 1H), 7.66 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.57 – 7.51 (m, 2H), 7.37 – 7.29 (m, 2H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.4, 148.8, 147.8, 142.0, 141.7, 139.5, 136.7, 136.2, 135.4, 135.23, 135.18, 131.3, 130.5, 128.84, 128.79, 127.7, 122.83, 122.75, 122.7, 109.4, 108.2, 101.5; IR (thin film, cm^{-1}) 2923, 2853, 1604, 1462, 1384, 1259, 1236, 1103, 1038, 802; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{15}N_2O_2$ $[M+H]^+$ 351.1128, Found 351.1130.

11-(Naphthalen-2-yl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (2q)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2q** (249 mg) as a red solid with a yield of 70%; Mp 186.9 – 188.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.36 (m, 1H), 8.28 (s, 1H), 8.16 – 8.08 (m, 1H), 8.00 (d, J = 8.5 Hz, 1H), 8.00 – 7.90 (m, 3H), 7.89 (dd, J = 8.4, 1.7 Hz, 1H), 7.68 – 7.60 (m, 3H), 7.60 – 7.54 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 161.4, 142.3, 141.9, 139.7, 139.5, 137.1, 135.45, 135.41, 135.3, 134.0, 133.2, 131.4, 130.6, 129.2, 129.0, 128.7, 128.4, 127.94, 127.89, 127.8, 126.9, 126.6, 126.3, 122.9, 122.8; IR (thin film, cm^{-1}) 3046, 2922, 2852, 1599, 1463, 1383, 1331, 1183, 1101, 756; HRMS (ESI): *m/z* Calcd. for $C_{26}H_{17}N_2$ $[M+H]^+$ 357.1386, Found 357.1383.

11-(Thiophen-2-yl)benzo[*b*]indeno[1,2-*e*][1,4]diazepine (2r)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **2r** (144 mg) as a red solid with a yield of 46%; Mp 133.1 – 133.7 ° C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.4 Hz, 1H), 8.11 (s, 1H), 8.05 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.81 (d, *J* = 3.2 Hz, 1H), 7.66 (d, *J* = 4.1 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.58 – 7.50 (m, 3H), 7.17 (dd, *J* = 5.1, 3.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 153.1, 146.4, 141.7, 141.4, 139.2, 135.3, 135.1, 134.9, 134.8, 131.2, 130.3, 129.1, 128.6, 128.1, 127.7, 127.3, 127.2, 122.7, 122.6; IR (thin film, cm^{-1}) 2922, 2852, 1602, 1463, 1421, 1384, 1327, 1117, 1101, 762, 704; HRMS (ESI): *m/z* Calcd. for $C_{20}H_{13}N_2S$ $[M+H]^+$ 313.0794, Found 313.0790.

2-Fluoro-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (4a)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4a** (243 mg) as a red solid with a yield of 75%; Mp 232.1 – 232.9 ° C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, J = 8.1, 5.2 Hz, 1H), 8.14 – 8.06 (m, 1H), 8.00 – 7.92 (m, 1H), 7.80 – 7.74 (m, 2H), 7.62 – 7.57 (m, 2H), 7.56 – 7.51 (m, 3H), 7.50 (s, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (d, J = 250.7 Hz), 161.0, 160.9, 143.8 (d, J = 9.9 Hz), 142.1, 141.9, 139.5, 135.6, 135.23, 135.2 (d, J = 3.0 Hz), 131.1 (d, J = 2.4 Hz), 130.6, 130.1, 129.6, 129.2, 128.7, 128.5, 124.6 (d, J = 9.7 Hz), 114.8 (d, J = 24.0 Hz), 109.6 (d, J = 23.9 Hz); IR (thin film, cm^{-1}) 3051, 3024, 2986, 2831, 1610, 1492, 1440, 1400, 1365, 1173, 1005, 799, 774, 700; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}FN_2$ $[M+H]^+$ 325.1136, Found 325.1135.

2-Chloro-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (4b)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4b** (256 mg) as a red solid with a yield of 75%; Mp 221.5 – 222.5 ° C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.13 – 8.05 (m, 1H), 7.99 – 7.91 (m, 1H), 7.82 – 7.71 (m, 2H), 7.62 – 7.57 (m, 2H), 7.57 – 7.54 (m, 2H), 7.54 – 7.50 (m, 3H), 7.48 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 161.0, 143.0, 142.1, 141.8, 139.4, 137.3, 135.5, 135.2, 135.0, 133.3, 130.7, 129.8, 129.5, 129.1, 128.5, 128.4, 127.6, 123.8, 122.6; IR (thin film, cm^{-1}) 2921, 2852, 1620, 1598, 1549, 1521, 1461, 1419, 1357, 1191, 1102, 1063, 761, 698; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}ClN_2$ $[M+H]^+$ 341.0840, Found 341.0841.

2-Methoxy-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (4c)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4c** (249 mg) as a red solid with a yield of 74%; Mp 179.1 – 180.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 8.11 – 8.06 (m, 1H), 7.98 – 7.92 (m, 1H), 7.78 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.54 – 7.49 (m, 3H), 7.48 (s, 1H), 7.10 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.06 (d, *J* = 2.2 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.0, 161.5, 160.8, 143.9, 142.2, 142.1, 139.7, 136.1, 135.4, 134.9, 129.9, 129.8, 129.4, 128.9, 128.56, 128.55, 128.1, 124.3, 114.1, 107.5, 55.8; IR (thin film, cm^{-1}) 3049, 2986, 2956, 2923, 2831, 1603, 1492, 1439, 1400, 1364, 1232, 1173, 1156, 1006, 799, 770, 698; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2O$ $[M+H]^+$ 337.1335, Found 337.1132.

3-Fluoro-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (4d)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4d** (240 mg) as a red solid with a yield of 74%; Mp 182.9 – 183.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.01 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.91 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.82 – 7.73 (m, 2H), 7.60 – 7.54 (m, 2H), 7.54 – 7.50 (m, 4H), 7.50 (s, 1H), 7.32 (td, *J* = 8.9, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8 (d, *J* = 248.8 Hz), 161.6 (d, *J* = 3.1 Hz), 161.4, 142.3, 141.9 139.3, 137.61 (d, *J* = 2.0 Hz), 137.55, 135.9 (d, *J* = 2.0 Hz), 135.44, 135.38, 131.0, 129.60, 129.55 (d, *J* = 4.6 Hz), 129.0, 128.6, 128.4, 123.9 (d, *J* = 8.5 Hz), 118.4 (d, *J* = 23.9 Hz), 110.2 (d, *J* = 24.2 Hz); IR (thin film, cm^{-1}) 2986, 2919, 2849, 1607, 1550, 1492, 1458, 1440, 1369, 1263, 1191, 1173, 1095, 1005, 770, 696; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}FN_2$ $[M+H]^+$ 325.1136, Found 335.1140.

3-Chloro-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (4e)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4e** (249 mg) as a red solid with a yield of 73%; Mp 194.0 – 194.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.9 Hz, 1H), 8.12 – 8.03 (m, 1H), 7.96 – 7.89 (m, 1H), 7.81 – 7.72 (m, 2H), 7.61 – 7.55 (m, 3H), 7.55 – 7.51 (m, 3H), 7.50 – 7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (2C), 142.3, 141.9, 139.9, 139.4, 136.8, 135.7, 135.5, 135.4, 133.8, 131.2, 131.0, 129.6, 129.4, 129.2, 128.6, 128.4, 123.6, 123.1; IR (thin film, cm^{-1}) 2921, 2852, 1626, 1591, 1550, 1440, 1382, 1253, 1059, 1002, 763; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{14}ClN_2$ $[M+H]^+$ 341.0840, Found 341.0840.

3-Methyl-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (4f)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4f** (244 mg) as a red solid with a yield of 76%; Mp 153.7 – 155.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.11 – 8.04 (m, 1H), 7.95 – 7.88 (m, 1H), 7.82 – 7.73 (m, 2H), 7.58 – 7.52 (m, 3H), 7.52 – 7.48 (m, 3H), 7.45 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 161.6, 142.4, 142.2, 139.6, 139.3, 138.3, 137.2, 135.7, 135.4, 135.1, 132.3, 130.4, 129.4, 128.8, 128.7, 128.6, 128.5, 123.4, 122.5, 22.1; IR (thin film, cm^{-1}) 3046, 2986, 2920,

2852, 1610, 1551, 1492, 1441, 1440, 1368, 1173, 1127, 1008, 865, 799, 760, 703; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2$ $[M+H]^+$ 321.1386, Found 312.1390.

3-Methoxy-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (4g)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4g** (246 mg) as a dark green solid with a yield of 73%; Mp 174.6 – 174.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.76 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.51 – 7.45 (m, 4H), 7.20 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 161.7, 160.4, 142.6, 142.2, 139.4, 137.5, 137.2, 135.3, 135.2, 134.9, 130.6, 129.4, 128.65, 128.57, 128.4, 128.2, 123.8, 118.8, 107.0, 56.0; IR (thin film, cm^{-1}) 3051, 3024, 2986, 2831, 1610, 1492, 1440, 1400, 1365, 1173, 1005, 799, 774; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{17}N_2O$ $[M+H]^+$ 337.1335, Found 337.1333.

11-(3-Chlorophenyl)-3-methylbenzo[*b*]indeno[1,2-*e*][1,4]diazepine (4h)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4h** (266 mg) as a red solid with a yield of 75%; Mp 159.8 – 160.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 0.7 Hz, 1H), 8.10 – 8.03 (m, 1H), 7.93 – 7.84 (m, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.64 (dt, *J* = 7.1, 1.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.51 – 7.42 (m, 5H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 159.9, 143.8, 142.1, 139.6, 139.2, 138.5, 137.0, 135.6, 135.4, 135.2, 134.6, 132.4, 130.5, 129.8, 129.5, 129.1, 128.7, 128.2, 126.6, 123.4, 122.6, 22.1; IR (thin film, cm^{-1}) 3063, 2986, 2919, 2851, 2831, 1610, 1492, 1363, 1322, 1173, 1079, 1006, 893, 873, 775, 761, 701; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{16}ClN_2$ $[M+H]^+$ 335.0997, Found 335.0995.

3-Chloro-11-(3-chlorophenyl)benzo[*b*]indeno[1,2-*e*][1,4]diazepine (4i)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4i** (255 mg) as a red solid with a yield of 68%; Mp 178.6 – 180.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.9 Hz, 1H), 8.14 – 8.01 (m, 1H), 7.98 – 7.83 (m, 1H), 7.75 (t, *J* = 1.9 Hz, 1H), 7.63 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.51 – 7.47 (m, 2H), 7.47 – 7.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 159.6, 143.5, 142.0, 139.7, 139.4, 136.7, 135.53, 135.48, 134.7, 134.0, 131.3, 131.1, 129.9, 129.7, 129.5, 128.9, 128.7, 126.6, 123.7, 123.1; IR (thin film, cm^{-1}) 2922, 2852, 1551, 1511, 1440, 1418, 1360, 1320, 1253, 1060, 768; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{13}Cl_2N_2$ $[M+H]^+$ 375.0450, Found 375.0449.

3-Methyl-11-(m-tolyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (4j)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4j** (237 mg) as a red solid with a yield of 71%; Mp 148.2 – 149.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.09 – 8.05 (m, 1H), 7.94 – 7.89 (m, 1H), 7.57 (s, 1H), 7.56 – 7.52 (m, 3H), 7.51 (s, 1H), 7.48 – 7.43 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 2.58 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 161.9, 142.4, 142.1, 139.7, 139.3, 138.4, 138.3, 137.3, 135.7, 135.4, 135.2, 132.3, 130.4, 130.2, 129.1, 128.78, 128.77, 128.4, 125.5, 123.4, 122.5, 22.1, 21.7.; IR (thin film, cm^{-1}) 2986, 2919, 2852, 2831, 1588, 1489, 1438, 1396, 1357, 1171, 1107, 1006, 876, 797, 774, 761; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1543, Found 335.1547.

3-Chloro-11-(m-tolyl)benzo[*b*]indeno[1,2-*e*][1,4] diazepine (4k)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4k** (284 mg) as a red solid with a yield of 80%; Mp 153.7 – 154.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 1.9 Hz, 1H), 8.10 – 8.02 (m, 1H), 7.97 – 7.90 (m, 1H), 7.61 – 7.51 (m, 5H), 7.51 – 7.45 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 161.2, 142.3, 141.8, 139.8, 139.4, 138.4, 136.7, 135.6, 135.43, 135.35, 133.7, 131.1, 130.9, 130.3, 129.4, 129.02, 129.01, 128.4, 125.4, 123.5, 123.0, 21.7; IR (thin film, cm^{-1}) 2922, 2852, 1603, 1550, 1511, 1440, 1383, 1361, 1320, 1253, 1059, 773; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{16}ClN_2$ $[M+H]^+$ 355.0997, Found 355.0993.

11-Phenyl-[1,3]dioxolo[4',5':5,6]indeno[1,2-*e*]benzo[*b*] [1,4]diazepine (4l)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4l** (235 mg) as a red solid with a yield of 67%; Mp 259.0 – 261.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 8.02 – 7.91 (m, 1H), 7.83 (s, 1H), 7.80 – 7.73 (m, 2H), 7.61 – 7.54 (m, 2H), 7.54 – 7.49 (m, 3H), 7.47 (s, 1H), 7.02 (s, 1H), 6.13 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 160.7, 151.2, 148.3, 142.4, 142.3, 139.3, 137.9, 135.7, 135.3, 135.2, 130.3, 130.2, 129.4, 128.6, 128.6, 128.5, 127.9, 103.6, 102.9, 102.2; IR (thin film, cm^{-1}) 2923, 2852, 1550, 1521, 1466, 1440, 1381, 1320, 1233, 1140, 1036, 767; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{15}N_2O_2$ $[M+H]^+$ 351.1128, Found 351.1125.

2,3-Dimethoxy-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (4m)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **4m** (213 mg) as a brown solid with a yield of 58%; Mp 174.6 – 175.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 1H), 7.98 – 7.93 (m, 1H), 7.90 (s, 1H), 7.80 – 7.75 (m, 2H), 7.59 – 7.54 (m, 2H), 7.54 – 7.47 (m, 4H), 7.07 (s, 1H), 4.10 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6, 160.7, 152.7, 149.7, 142.4, 139.2, 136.12, 136.09, 135.3, 134.9, 130.1, 129.3, 128.6 (3C), 128.5, 128.4, 128.3, 127.7, 105.4, 105.0, 56.5, 56.4; IR (thin film, cm^{-1}) 2922, 2851, 1584, 1518, 1471, 1320, 1238, 1213, 1156, 1116, 762; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{19}N_2O_2$ $[M+H]^+$ 367.1441, Found 367.1445.

7,8-Dimethyl-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (5a)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **5a** (278 mg) as a brown solid with a yield of 83%; Mp 158.0 – 159.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.3 Hz, 1H), 7.88 (s, 1H), 7.78 – 7.73 (m, 2H), 7.73 (s, 1H), 7.62 (td, *J* = 7.3, 1.2 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.55 – 7.46 (m, 4H), 2.44 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6, 160.7, 142.4, 141.7, 140.2, 140.1, 138.2, 137.6, 136.2, 135.9, 135.8, 135.4, 131.1, 129.3, 129.1, 128.6, 128.5, 127.4, 122.7, 122.5, 19.6, 19.4; IR (thin film, cm^{-1}) 2920, 2852, 1604, 1547, 1522, 1463, 1442, 1383, 1367, 1307, 1261, 1100, 1027; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1543, Found 335.1543.

7,8-Difluoro-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (5b)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **5b** (246 mg) as a brown solid with a yield of 72%; Mp 201.9 – 202.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.4 Hz, 1H), 7.86 (dd, *J* = 11.3, 8.6 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.72 – 7.65 (m, 2H), 7.64 – 7.57 (m, 3H), 7.56 – 7.49 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9 (d, *J* = 3.3 Hz), 162.0 (d, *J* = 2.8 Hz), 150.8 (dd, *J* =

150.9, 13.7 Hz), 149.1 (dd, *J* = 149.2, 13.7 Hz), 141.8, 141.6, 139.9 (dd, *J* = 9.2, 3.1 Hz), 137.7, 136.8 (dd, *J* = 8.5, 3.0 Hz), 135.1, 131.8, 129.8, 128.8, 128.7, 128.4, 128.1, 123.05, 122.96, 122.7 (d, *J* = 17.9 Hz), 122.4 (d, *J* = 17.5 Hz); IR (thin film, cm^{-1}) 2922, 2852, 1594, 1564, 1484, 1463, 1381, 1308, 1254, 1192, 889; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{13}F_2N_2$ $[M+H]^+$ 343.1041, Found 343.1044.

7,8-Dichloro-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (5c)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **5c** (248 mg) as a brown solid with a yield of 66%; Mp 236.9 – 238.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.4 Hz, 1H), 8.15 (s, 1H), 8.00 (s, 1H), 7.78 – 7.72 (m, 2H), 7.67 (td, *J* = 7.4, 1.2 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.56 – 7.49 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 162.7, 141.8, 141.58, 141.57, 138.9, 138.8, 136.1, 135.7, 135.2, 133.6, 132.0, 131.8, 129.9, 128.8, 128.7, 128.45, 128.36, 123.14, 123.10; IR (thin film, cm^{-1}) 2922, 2853, 1626, 1581, 1545, 1460, 1383, 1327, 1256, 1100; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{13}Cl_2N_2$ $[M+H]^+$ 375.0450, Found 375.0452.

7,8-Dibromo-11-phenylbenzo[*b*]indeno[1,2-*e*][1,4] diazepine (5d)

Purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as an eluent to give the product **5d** (251 mg) as a brown solid with a yield of 54%; Mp 197.8 – 198.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 – 8.29 (m, 2H), 8.17 (s, 1H), 7.77 – 7.73 (m, 2H), 7.67 (td, *J* = 7.4, 1.2 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.61 – 7.58 (m, 1H), 7.55– 7.50 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 162.9, 142.0, 141.8, 141.6, 139.4, 139.3, 138.9, 138.8, 135.3, 132.0, 129.9, 128.9, 128.7, 128.43, 128.41, 126.0, 124.0, 123.2, 123.1; IR (thin film, cm^{-1}) 2958, 2919, 2853, 1599, 1459, 1372, 1325, 1261, 1096, 1029, 802; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{13}Br_2N_2$ $[M+H]^+$ 462.9440, Found 462.9441.

3. Procedures for the Preparation of Intermediate 7 and Characterization Data

Ph_3PAuCl (0.05 mmol, 25 mg) and $AgSbF_6$ (0.05 mmol, 17 mg) were added in toluene (5 mL) and the mixture was stirred at room temperature for 10 min. Substrate 1 (1.0 mmol, 280 mg) was then added to the above solution and mixture was stirred at room temperature for 30 min till TLC showed the consumption of the starting material. The solvent was removed in vacuo and the residue was purified by a flash column chromatography (EtOAc/petroleum ether) on silica gel to afford the intermediate **7**.

(1,3-Dimethoxy-1H-inden-2-yl)(phenyl)methanone (7)

Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as an eluent to give the product **7** (255 mg) as a yellow solid with a yield of 91%; Mp 87.8 – 88.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.59 – 7.55 (m, 1H), 7.53 – 7.49 (m, 2H), 7.49 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 5.67 (s, 1H), 3.85 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 194.0, 162.8, 141.7, 140.1, 138.5, 132.9, 129.25, 129.16 (3C), 128.7, 124.3, 120.8, 116.5, 83.1, 61.3, 52.9; IR (thin film, cm^{-1}) 1639, 1599, 1576, 1447, 1367, 1332, 1248, 1204, 1069; HRMS (ESI): *m/z* Calcd. For $C_{18}H_{16}O_3Na$ $[M+Na]^+$ 303.0992, Found 303.0996.

4. Procedures for the Preparation of Product 2 from Intermediate 7

4.1 Standard Conditions

Ph_3PAuCl (0.05 mmol, 25 mg) and $AgSbF_6$ (0.05 mmol, 17 mg) were added in toluene (5 mL) and the mixture was stirred at room temperature for 10 min. Substrate **7** (1.0 mmol, 280 mg) was then added to the solution and the mixture was stirred at room temperature for 10 min before *o*-phenylenediamine (3.0 mmol, 324 mg) was added. The resulting solution was stirred at 70 °C for 3.5 h till TLC showed the consumption of **7**. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography (dichloromethane/petroleum ether) on silica gel to afford product **2** (276 mg) in 90% yield.

4.2 Conditions in the Absence of Catalysts

Substrate **7** (1.0 mmol, 280 mg) and *o*-phenylenediamine (3.0 mmol, 324 mg) were dissolved in toluene (5 mL) and the mixture was stirred at 70 °C for 3.5 h till TLC showed the consumption of **7**. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography (dichloromethane/petroleum ether) on silica gel to afford product **2** (273 mg) in 89% yield.

5. Procedures for the Preparation of (1-Methoxy-1-(phenylamino)-1*H*-inden-2-yl)(phenyl)methanone (8) from Intermediate 7 and Characterization Data

Substrate **7** (1.0 mmol, 280 mg) and aniline (3.0 mmol, 279 mg) were dissolved in toluene (5 mL) and the mixture was stirred at 70 °C for 3.5 h till TLC showed the consumption of **7**. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as an eluent to give the product **8** (256 mg) as a yellow solid with a yield of 75%; Mp 73.5 – 74.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.42 (s, 1H), 7.98 – 7.88 (m, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.40 (m, 5H), 7.42 – 7.33 (m, 4H), 7.10 (td, *J* = 7.7, 1.2 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.79 (s, 1H), 2.87 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 191.6, 161.6, 146.5, 141.7, 138.8, 135.5, 130.9, 130.2, 129.4, 128.3, 128.2, 127.5, 127.2, 126.4, 124.9, 124.8, 108.7, 79.5, 50.5; IR (thin film, cm^{-1}) 3448, 1611, 1595, 1543, 1533, 1452, 1437, 1383, 1304, 1263, 1204, 1066, 746; HRMS (ESI): *m/z* Calcd. For $C_{23}H_{19}NO_2Na$ $[M+Na]^+$ 364.1308, Found 364.1310.

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FULL PAPER

A Gold(I)-Catalyzed Tandem Cyclization to Benzo[*b*]indeno [1,2-*e*][1,4]diazepines from o-Phenylenediamines and Ynones

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