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FULL PAPER

8-*exo*-dig-Selective Cycloisomerization for the Synthesis of Dibenzo[*b*,*e*][1,4]diazocines Using Cationic Au(I) Catalysts

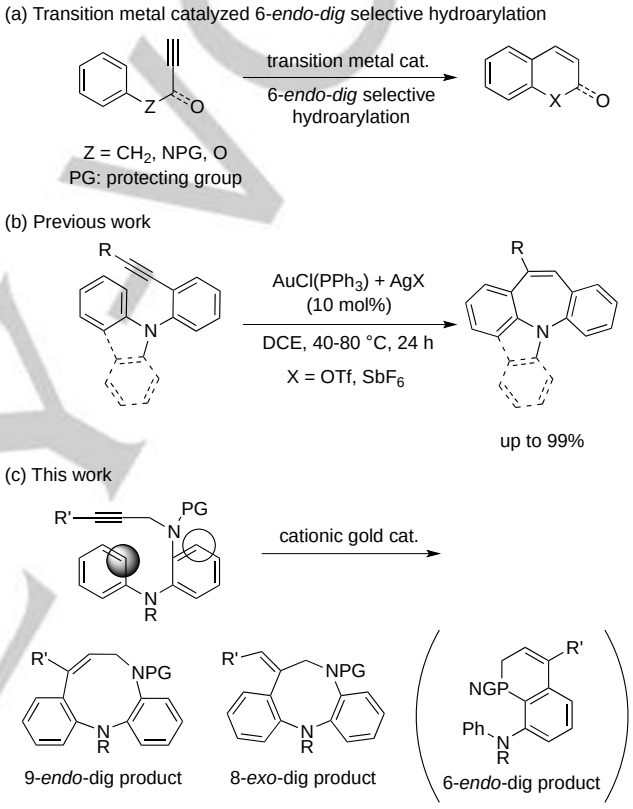
Mamoru Ito,[a] Daisuke Inoue,[a] Asahi Takaki,[a] Kyalo Stephen Kanyiva,[b] and Takanori Shibata*[a]

Dedication ((optional))

Abstract: The cationic Au(I)-catalyzed intramolecular reaction of *N*-propargyl-2-anilinoanilines gave a diazocine skeleton via 8-*exo*-dig-selective cycloisomerization by the suppression of 6-*endo*-dig cycloisomerization. Both terminal and internal alkynes could be used according to the choice of ligand of the Au(I) complex, and various dibenzo[*b*,*e*][1,4]diazocines were obtained. Control experiments suggested that two nitrogen atoms in the tether of substrates were critical in this selective transformation.

Introduction

Among various types of cycloisomerization, intramolecular hydroarylation to alkynes, where part of the benzene ring acts as an ene moiety, is a powerful method for preparing benzannulated carbocycles and heterocycles.[1] For example, there are many reports on the use of 6-*endo*-dig cycloisomerization for the preparation of various bicyclic compounds including dihydroquinolines, quinolinones, chromenes, and coumarins (Scheme 1a).[2] This strategy could also be used for the construction of a seven-membered ring system. Actually, we recently reported the use of 7-*endo*-dig cycloisomerization for the synthesis of benzazepine derivatives fused with a carbazole or indole ring.[3] In these reactions, the electron-donating effect of a nitrogen atom increased the nucleophilicity of its *ortho*-position (black circle), which underwent electrophilic attack by an alkyne moiety activated by a cationic Au(I) catalyst to realize the formation of a seven-membered ring (Scheme 1b). Against this background, we next focused on the construction of a larger ring system by the reactions of *N*-propargyl-2-anilinoanilines. We assumed that dibenzo[*b*,*e*][1,4]diazocine would be formed as an 8-*exo*-product or that dibenzo[*b*,*e*][1,4]diazonine would be formed as a 9-*endo*-product (Scheme 1c). To avoid conventional 6-*endo*-*dig* cycloisomerization, we introduced an electron-withdrawing group to the nitrogen atom of the propargyl amine, which decreased the nucleophilicity of the *ortho* position (white circle).



Scheme 1. Concept of this work.

There are only a few examples of the direct construction of an eight- or nine-membered ring via enyne cycloisomerization (Scheme 2).[4,5] Echavarren and co-workers reported the Au(III)-catalyzed formal 8-*endo*-dig-selective cycloisomerization of alkynylindoles to provide indoloazocines (Scheme 2a).[6] This reaction proceeded via 7-*endo*-*dig* cyclization at the C3 position of indole with a successive 1,2-shift and isomerization. Waldmann and co-workers also achieved Au(I)-catalyzed 8-*endo*-*dig* cyclization of *o*-propargyloxy styrenes to give 2*H*-1-benzo[*b*]oxocines.[7] Sawamura and co-workers reported the 8-*exo*-dig-selective cyclization of acetylene-tethered silyl enol ethers (Scheme 2b).[8] This transformation was achieved by using semi-hollow triethynylphosphane ligands. Toste and co-workers developed the reaction of propargyl ester-containing enynes with a Au(I)-catalyst to give the corresponding cyclopropane-fused eight-membered ring (Scheme 2c).[9] This strategy could be used to construct a nine-membered ring by changing the length of the tether.[10] [2+2] Cycloaddition of enynes has also been used to

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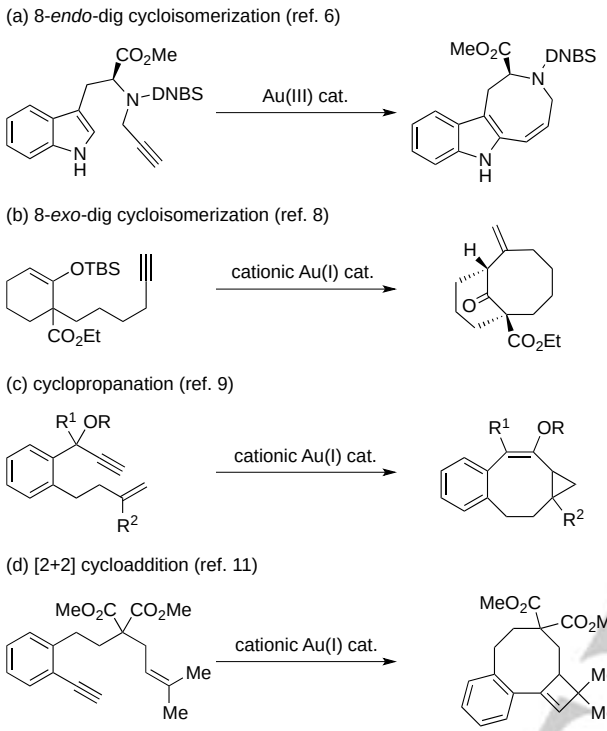
construct a medium-sized ring and macrocycles (Scheme 2d).[11,12] Sawamura and co-workers applied this strategy for the synthesis of cyclobutene-fused eight-membered ring compounds.[11]

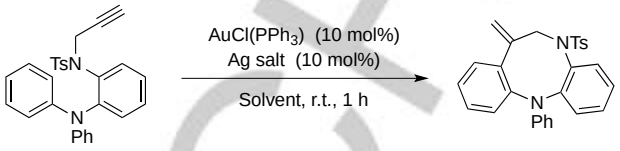


Scheme 2. Examples of eight-membered ring formation via enyne cycloisomerization

Results and Discussion

We chose tosyl as an electron-withdrawing group on the nitrogen and used propargyltosylamine **1a** in the presence of cationic Au(I) catalysts prepared from chloro(triphenylphosphine)gold(I) and silver salt in dichloromethane (DCM) (Table 1, entries 1-3). The reaction proceeded smoothly at room temperature and dibenzo[*b*,*e*][1,4]diazocine derivative **2a** as an 8-*exo*-dig cycloadduct was the only product: a 9-*endo*-dig *or 6-endo*-dig cycloadduct could not be detected. Among the three silver salts examined, $AgSbF_6$ gave the best yield of 90% (entry 1). No reaction proceeded without gold complex or silver salt, which means that the cationic gold complex was critical for this transformation (entries 4 and 5). As a result of solvent screening, chlorobenzene gave the best results, and the reaction proceeded almost quantitatively (entries 6 and 7). When the reaction was conducted using a reduced amount of the catalyst, the yield was decreased, but still good (entry 8).

Table 1. Screening of reaction conditions.[a]

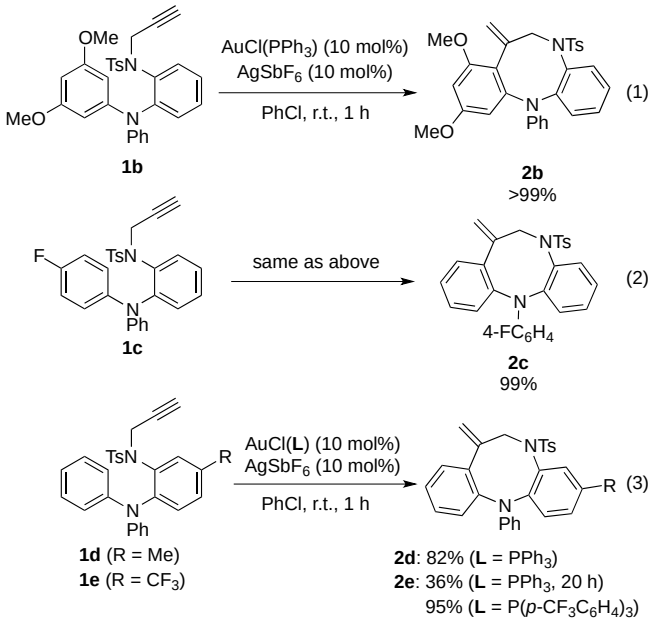


1a **2a**

Entry	Ag salt	Solvent	Yield [%][b]
1	$AgSbF_6$	DCM	90
2	AgOTf	DCM	(47)[c]
3	$AgBF_4$	DCM	(52)[c]
4	none	DCM	NR
5[d]	$AgSbF_6$	DCM	NR
6	$AgSbF_6$	toluene	97
7	$AgSbF_6$	PhCl	99
8[e]	$AgSbF_6$	PhCl	79

[a] Reaction conditions: **1a** (0.05 mmol), $AuCl(PPh_3)$ (10 mol%), silver salt (10 mol%), solvent (0.5 mL), r.t., 1 h. [b] Isolated yield. NMR yield was shown in parentheses. [c] NMR yields were measured by using 1,1,2,2-tetrachloroethane as an internal standard. [d] The reaction was conducted without gold catalyst. [e] Gold complex and silver salt (5 mol%) were used.

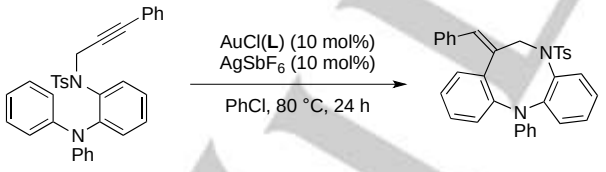
Under the optimized conditions (entry 7 in Table 1), other substrates possessing a substituted aryl group on the nitrogen atom were examined (Scheme 3). The reaction of *N*-(3,5-dimethoxyphenyl)-*N*-phenylaniline derivative **1b** proceeded regioselectively at the more electron-rich arene, and the expected cycloadduct **2b** was obtained quantitatively (Eq. (1)). In contrast, *N*-(4-fluorophenyl)-*N*-phenylaniline derivative **1c** was also a good substrate, and the reaction proceeded at the relatively electron-rich arene to give dibenzodiazocine **2c** almost quantitatively. The substituent could also be introduced on the *ortho*-diamino phenylene tether: the reaction of methyl-substituted substrate **1d** gave the desired product **2d** in high yield. In contrast, trifluoromethyl-substituted substrate **1e** exhibited low reactivity and the yield of **2e** was low even with a longer reaction time because of low conversion. The cationic Au(I) catalyst with a more electron-deficient ligand drastically improved the yield of **2e** up to 95% (Eq. (3)).



Scheme 3. Scope of substituents on the aromatic rings.

When we next perfomed the reaction of phenyl-substituted alkyne **1f** using the optimal cationic Au(I) catalyst, only a trace amount of product **2f** was obtained even at high temperature (Table 2, entry 1). After screening of the ligand, we found that the *N*-heterocyclic carbene (NHC) ligand IPr was effective for the reaction of the internal alkyne (entry 2). We considered that the π-acceptor ability of the NHC ligand efficiently activated the internal alkyne and the bulkiness of IPr made the alkyne accessible to the reaction site of the aryl group.[13] Among other NHC ligands, only IPr-type ligands promoted cycloisomerization (entries 3-6). The product **2f** was obtained as an *E* isomer, which was confirmed by NOESY analysis.

Table 2. Screening of reaction conditions.[a]

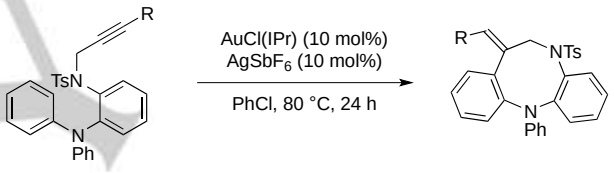


Entry	L	Yield [%][b]
1	PPh_3	trace
2	IPr	94
3	IMes	N.D.
4	SIMes	N.D.
5	SIPr	88
6	IPr^{Me}	71

[a] Reaction conditions: **1f** (0.05 mmol), AuCl(L) (10 mol%), $AgSbF_6$ (10 mol%), solvent (0.5 mL), 80 °C, 24 h. [b] Isolated yield. IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, SIPr = 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene, IMes = 1,3-dimesitylimidazol-2-ylidene, SIMes = 1,3-dimesityl imidazolidin-2-ylidene, IPr^{Me} = 4,5-dimethyl-*N*,*N*'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

Various internal alkynes were subjected to cycloisomerization using cationic Au(I) possessing IPr ligand (Table 3). As for *p*-, *m*-, and *o*-anisyl-substituted alkynes **1g**-**1i,** the corresponding products **2g**-**2i** were obtained, but the yields were moderate because of low conversion (entries 1-3).[14] In contrast, electron-withdrawing group-substituted arylalkynes **1j**-**1l** were good substrates, and cycloadducts **2j**-**2l** with *p*-trifluoromethyl, fluoro, and chlorophenyl groups were obtained in high yield along with the complete consumption of substrates (entries 4-6). In particular, the reaction of ethoxycarbonyl-substituted alkyne **1m** gave the best yield of 98% (entry 7).

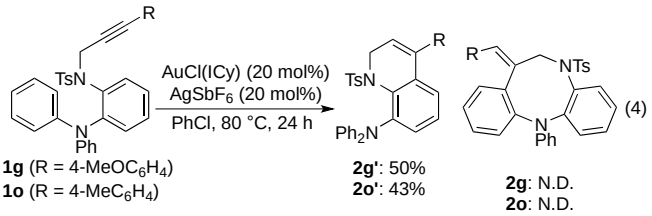
Table 3. Scope of substituents on alkyne terminus.[a]



Entry	R	Yield [%]
1	4-$MeOC_6H_4$ (**1g**)	41 (**2g**)
2	3-$MeOC_6H_4$ (**1h**)	53 (**2h**)
3	2-$MeOC_6H_4$ (**1i**)	50 (**2i**)
4	4-$CF_3C_6H_4$ (**1j**)	85 (**2j**)
5	4-FC_6H_4 (**1k**)	87 (**2k**)
6	4-ClC_6H_4 (**1l**)	93 (**2l**)
7	CO_2Et (**1m**)	98 (**2m**)

[a] Reaction conditions: **1** (0.05 mmol), AuCl(IPr) (10 mol%), $AgSbF_6$ (10 mol%), PhCl (0.5 mL), 80 °C, 24 h.

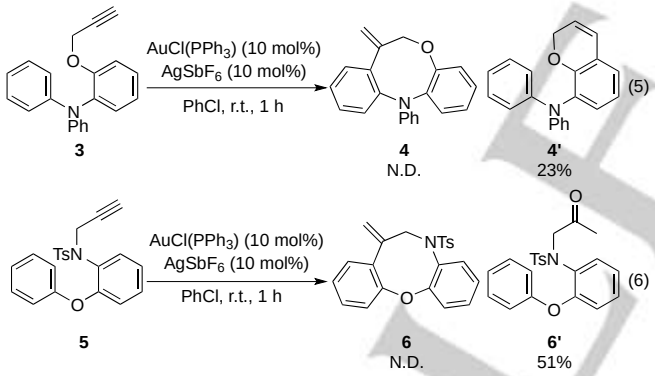
Interestingly, when 1,3-dicyclohexylimidazol-2-ylidene (ICy), instead of IPr, was used as a ligand, the reaction of electron-donating group-substituted alkyne **1g** and **1o** selectively gave 6-*endo*-dig products **2g'** and **2o'**, albeit in low yield, without the formation of 8-*exo*-dig products **2g** and **2o** (Scheme 4).[15] We considered that electron-donating groups and less bulkiness facilitated 6-*endo*-dig cyclization to give **2g'** and **2o'** selectively.



1g (R = 4-MeOC$_6$H$_4$) **2g'**: 50% **2g**: N.D.
1o (R = 4-MeC$_6$H$_4$) **2o'**: 43% **2o**: N.D.

Scheme 4. Undesired 6-*endo*-dig cyclization.

Finally, we next conducted control experiments using *o*-aminophenol-tethered substrates **3** and **5** in place of the parent *o*-diaminobenzene-tethered substrates (Scheme 5). While the reaction of propargyl ether **3** proceeded sluggishly to give conventional 6-*endo*-*dig* product **4'**, albeit in low yield, the formation of 8-*exo*-*dig* product **4** could not be detected at all (Eq. (5)). This result suggested that steric repulsion between the tosyl and diarylamino groups and the electron-withdrawing effect of the tosyl group are important for selective 8-*exo*-*dig* cycloisomerization. In addition, the reaction of propargyl amine **5** with a diphenyl ether moiety gave ketone **6'** by hydration of alkyne moiety without the formation of any cycloadducts (Eq. (6)). This result may suggest that a phenoxy group is more flexible than a diarylamino group and that the alkyne moiety is difficult to access. Therefore, the electron-donating effect of the amino group is responsible for the high reactivity of cycloisomerization.

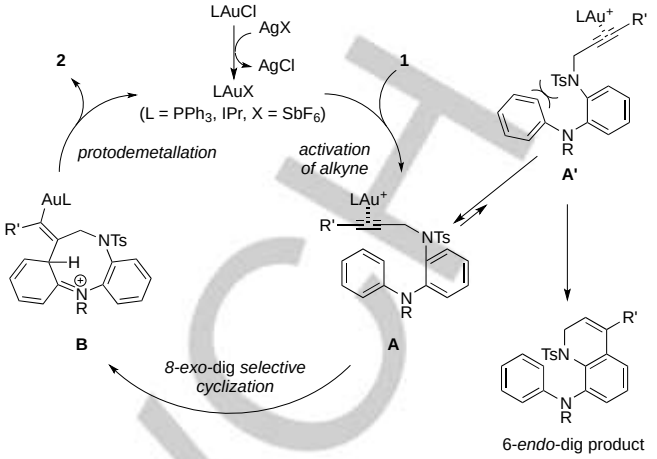


3 **4** N.D. **4'** 23%

5 **6** N.D. **6'** 51%

Scheme 5. Reaction of aminophenol-tethered substrates **3** and **5**.

Regarding the mechanism (Scheme 6), the combination of gold and silver salts gave cationic gold species, which effectively activated the alkyne moiety of **1**. Instead of **A**, we considered rotamer **A'**, which would be transformed into a 6-*endo*-*dig* product. We assume that steric repulsion between tosyl and aryl groups resulted in the favorable formation of rotamer **A**. In addition, the electron-withdrawing tosyl group decreased the nucleophilicity of the 6-*endo*-dig reaction site. As a result, rotamer **A** selectively reacts with an aryl group in an 8-*exo*-dig fashion to provide intermediate **B**. Finally, protodemetallation of **B** provides desired compound **2** along with regeneration of the cationic gold catalysts.



Scheme 6. Plausible reaction mechanism for the selective 8-exo-*dig* cycloisomerization.

Conclusions

We developed a cationic Au(I)-catalyzed 8-*exo*-dig-selective cycloisomerization of *N*-propargyl-2-anilinoanilines to provide dibenzo[*b*,*e*][1,4]diazocines. The reaction of terminal alkynes proceeded smoothly under the mild conditions using PPh_3 as a ligand. In the reaction of internal alkynes, the use of IPr, instead of PPh_3, was important for the high reactivity. Further studies on the construction of a larger ring system are now underway in our laboratory.

Experimental Section

General information: ^{1}H NMR spectra were recorded on JEOL ECX-500 (500 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl3. The coupling constants, *J*, are reported in Hertz (Hz). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; dt, doublet of triplet; m, multiplet; q, quartet. brs, broad singlet. ^{13}C NMR spectra were obtained by JEOL ECX-500 (125 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.16 ppm in CDCl3). CDCl3 was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on a JMS-T100CS with ESI (Electro Spray Ionization) method. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Wakogel B-5F) prepared in our laboratory, and flash column chromatography was performed over silica gel 200-300. All reagents except gold(I) complex and silver salt were weighed and handled in air and backfilled under argon at room temperature. Gold(I) complex and silver salt were weighed under argon in globe box at room temperature. Unless otherwise noted, all reactions were performed under an argon atmosphere. All reagents were purchased from Wako, Kanto, Aldrich, TCI, and Strem and used without further purification.

General procedures for the cycloisomerization in Tables 1, and 2: 2-propargyltosylaminodiphenylaniline derivative **1** (0.050

mmol) was placed in a Schlenk tube in air. This reaction vessel was evacuated and backfilled with argon (×3), and then gold(I) complex (10 mol%) and silver salt (10 mol%) were placed to the reaction vessel in globe box. After solvent (0.5 ml) was added, the solution was stirred at room temperature for 1 h. The solution was filtered by silica gel. After removal of solvent, the crude products were filtered by short column, and purified by PTLC to give desired cyclized product **2**.

***N*-(2-(Diphenylamino)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1a)**: Isolated by silica gel column chromatography (hexane/ethyl acetate = 3/1). The title compound was obtained as a brown solid, 16% in total yield; mp 193-195 °C; ^{1}H NMR δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.35-7.27 (m, 2H), 7.25-7.18 (m, 7H), 7.08-7.02 (m, 5H), 6.99 (dd, *J* = 7.4, 7.4 Hz, 2H), 3.98 (brs, 1H), 3.03 (brs, 1H), 2.40 (s, 3H), 1.99 (dd, *J* = 2.3, 2.5 Hz, 1H); ^{13}C NMR δ 148.0, 147.8, 143.6, 137.0, 135.4, 131.7, 129.9, 129.6, 129.2, 129.2, 128.6, 124.9, 123.7, 122.7, 78.5, 73.8, 38.3, 21.7; HRMS (ESI, positive): *m/z* calcd. For $C_{28}H_{24}N_2NaO_2S$ ([M+Na]$^+$) 475.1451, found 475.1451.

***N*-(2-((3,5-Dimethoxyphenyl)(phenyl)amino)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as red oil, 27% in total yield; ^{1}H NMR δ 7.66-7.61 (m, 2H), 7.35-7.28 (m, 2H), 7.25-7.19 (m, 5H), 7.10-7.04 (m, 3H), 7.02-6.96 (m, 1H), 6.23 (d, *J* = 2.1 Hz, 2H), 6.15 (t, *J* = 2.2 Hz, 1H), 4.01 (brs, 1H), 3.69 (s, 6H), 3.14 (brs, 1H), 2.41 (s, 3H), 1.99 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR δ 161.3, 149.9, 147.7, 147.5, 143.6, 137.0, 135.6, 131.6, 129.9, 129.8, 129.2, 129.1, 128.7, 125.2, 124.0, 122.9, 102.3, 95.2, 78.6, 73.8, 55.5, 38.4, 21.7; HRMS (ESI, positive): *m/z* calcd for $C_{30}H_{28}N_2NaO_4S$([M+Na]$^+$)535.1661, found 535.1662.

***N*-(2-((4-Fluorophenyl)(phenyl)amino)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a light yellow solid, 17% in total yield; mp 180 °C; ^{1}H NMR δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.36-7.14 (m, 7H), 7.10-6.86 (m, 8H), 4.01 (brs, 1H), 3.01 (brs, 1H), 2.42 (s, 3H), 1.99 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR δ 158.9 (d, *J* = 241.8 Hz), 148.3, 147.9, 144.2 (d, *J* = 2.6 Hz), 143.7, 136.9, 135.2, 131.6, 130.0, 129.3, 129.2, 128.6, 125.7 (d, *J* = 8.2 Hz), 124.9, 123.3, 122.7, 115.9 (d, *J* = 22.5 Hz), 78.4, 73.9, 53.6, 38.4, 21.7; HRMS (ESI, positive): *m/z* calcd for $C_{28}H_{23}FN_2NaO_2S$ ([M+Na]$^+$) 493.1357, found 493.1356.

***N*-(2-(Diphenylamino)-5-methylphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1d)**: Isolated by recrystallization (hexane/dichloromethane). The title compound was obtained as a white solid, 8% in total yield; mp 150-152 °C; ^{1}H NMR δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.24-7.17 (m, 7H), 7.12 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.06-7.00 (m, 5H), 6.96 (dd, *J* = 7.4, 7.4 Hz, 2H), 3.91 (brs, 1H), 3.08 (brs, 1H), 2.40 (s, 3H), 2.25 (s, 3H), 2.01 (dd, *J* = 2.4, 2.4 Hz, 1H); ^{13}C NMR δ 148.0, 144.7, 143.6, 137.0, 135.3, 135.2, 132.2, 130.7, 129.6, 129.1, 129.1, 128.6, 123.3, 122.4, 78.5, 73.7, 38.3, 21.7, 20.9; HRMS (ESI, positive): *m/z* calcd. For $C_{29}H_{26}N_2NaO_2S$ ([M+Na]$^+$) 489.1607, found 489.1608

***N*-(2-(Diphenylamino)-5-(trifluoromethyl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)**

benzenesulfonamide (1e): Isolated by silica gel column chromatography (hexane/ethyl acetate = 10/1). The title compound was obtained as a white solid, 9% in total yield; mp 121-122 °C; ^{1}H NMR δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 2.1, 8.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.35-7.22 (m, 7H), 7.14-7.04 (m, 6H), 3.97 (brs, 1H), 2.92 (brs, 1H), 2.42 (s, 3H), 2.01 (dd, *J* = 2.4, 2.4 Hz, 1H); ^{13}C NMR δ 151.7, 147.7, 144.2, 136.2, 134.4, 129.5, 129.4 (q, *J* = 3.9 Hz), 129.3, 128.6, 128.6, 126.6 (q, *J* = 3.3 Hz,), 125.6 (q, *J* = 33.4 Hz), 124.6, 123.9, 123.7 (q, *J* = 272.4 Hz), 77.9, 74.5, 38.0, 21.7; HRMS (ESI, positive): *m/z* calcd. For $C_{29}H_{23}F_3N_2NaO_2S$ ([M+Na]$^+$) 543.1325, found 543.1326

***N*-(2-(Diphenylamino)phenyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1f)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a white solid, 58%; mp 159 °C; ^{1}H NMR δ 7.68 (d, *J* = 7.1 Hz, 2H), 7.39-7.29 (m, 2H), 7.29-7.20 (m, 8H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 4H), 7.08-7.03 (m, 3H), 7.01 (dd, *J* = 6.9, 6.9 Hz, 2H), 4.18 (brs, 1H), 3.15 (brs, 1H), 2.34 (s, 3H); ^{13}C NMR δ 148.2 148.2, 143.4, 137.4, 135.8, 131.5, 131.4, 129.9, 129.5, 129.3, 129.2, 128.7, 128.4, 128.3, 124.9, 123.9, 122.7, 122.6, 85.4, 84.1, 39.3, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{34}H_{28}N_2NaO_2S$ ([M+Na]$^+$) 551.1765, found 551.1764.

***N*-(2-(Diphenylamino)phenyl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1g)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a light yellow solid, 56%; mp 114 °C; ^{1}H NMR δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.39-7.27 (m, 2H), 7.27-7.21 (m, 5H), 7.20-7.14 (m, 2H), 7.11 (dd, *J* = 0.7, 7.7 Hz, 3H), 7.07-6.96 (m, 6H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.16 (brs, 1H), 3.79 (s, 3H), 3.13 (br, 1H), 2.35 (s, 3H); ^{13}C NMR δ 159.7, 148.2, 148.2, 143.3, 137.4, 135.8, 132.9, 131.5, 129.9, 129.5, 129.3, 129.2, 128.7, 124.9, 123.9, 122.7, 114.7, 113.9, 85.3, 82.6, 55.4, 39.4, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1869, found 581.1869.

***N*-(2-(Diphenylamino)phenyl)-*N*-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1h)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a yellow solid, 50%; mp 114 °C; ^{1}H NMR δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.38-7.34 (m, 1H), 7.33-7.28 (m, 1H), 7.28-7.17 (m, 7H), 7.16-7.08 (m, 5H), 7.07-6.98 (m, 3H), 6.83 (dd, *J* = 2.4, 8.3 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.59 (s, 1H), 4.17 (brs, 1H), 3.77 (s, 3H), 3.13 (brs, 1H), 2.35 (s, 3H); ^{13}C NMR δ 159.3, 148.2, 148.2, 143.5, 137.3, 135.8, 131.4, 129.9, 129.5, 129.3, 129.3, 129.2, 128.7, 124.9, 124.0, 123.9, 123.6, 122.7, 117.0, 114.4, 85.3, 84.0, 55.4, 39.2, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1869, found 581.1869.

***N*-(2-(Diphenylamino)phenyl)-*N*-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1i)**

Isolated by pTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a light red solid, 51%; mp 189 °C; ^{1}H NMR δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.40-7.33 (m, 2H), 7.32-7.27 (m, 1H), 7.27-7.21 (m, 5H), 7.15-7.07 (m, 6H), 7.06-6.97 (m, 3H), 6.95 (dd, *J* = 1.8, 7.7 Hz, 1H), 6.86-6.77 (m, 2H), 4.23 (brs, 1H), 3.77 (s, 3H), 3.14(brs, 1H), 2.27 (s, 3H); ^{13}C NMR δ 160.1, 148.3, 148.2, 143.2, 137.2, 135.8, 133.3, 131.8, 129.8, 129.8, 129.3, 129.2, 129.1, 128.8, 124.7, 123.9, 122.7, 120.3, 111.9, 110.5, 88.1, 82.1, 55.6, 39.6, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1868, found 581.1869.

***N*-(2-(Diphenylamino)phenyl)-4-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (1j)**

Isolated by pTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a white solid, 62%; mp 154 °C; ^{1}H NMR δ 7.67 (d, *J* = 6.7 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.39-7.30 (m, 2H), 7.22-7.29 (m, 5H), 7.17 (dd, *J* = 7.4, 7.7 Hz, 4H), 7.13-7.04 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 2H), 4.18 (brs, 1H), 3.19 (brs, 1H), 2.35 (s, 3H); ^{13}C NMR δ 148.2, 148.1, 143.5, 137.3, 135.7, 131.7, 131.3, 130.2 (q, *J* = 33.1 Hz), 130.1, 129.7, 129.3, 129.2, 128.7, 126.4 (q, *J* = 1.5 Hz), 125.2 (q, *J* = 3.9 Hz), 124.9, 123.9, 123.9 (q, *J* = 271.8 Hz), 122.8, 86.8, 84.1, 39.1, 21.6 HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{27}F_3N_2NaO_2S$ ([M+Na]$^+$) 619.1634, found 619.1638.

***N*-(2-(Diphenylamino)phenyl)-*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1k)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a white solid, 28%; mp 147 °C; ^{1}H NMR δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.38-7.29 (m, 2H), 7.28-7.20 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 4H), 7.07-6.98 (m, 5H), 6.93 (dd, *J* = 8.7, 8.7 Hz, 2H), 4.13 (brs, 1H), 3.14(brs, 1H), 2.34 (s, 3H); ^{13}C NMR δ 162.6 (d, *J* = 250.0 Hz), 148.2, 148.2, 143.4, 137.4, 135.8, 133.4 (d, *J* = 8.3 Hz), 131.4, 129.9, 129.6, 129.3, 129.2, 128.7, 124.9, 123.9, 122.8, 118.7 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 22.1 Hz), 84.4, 83.8 (d, *J* = 1.5 Hz), 39.2, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{34}H_{27}FN_2NaO_2S$ ([M+Na]$^+$) 569.1669, found 569.1669.

***N*-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-*N*-(2-(diphenylamino)phenyl)-4-methylbenzenesulfonamide (1l)**

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a light yellow solid, 79%; mp 165 °C; ^{1}H NMR δ 7.70-7.62 (m, 2H), 7.39-7.29 (m, 2H), 7.27-7.14 (m, 9H), 7.13-7.08 (m, 4H), 7.07-7.03 (m, 1H), 7.03-6.93 (m, 4H), 4.13 (brs, 1H), 3.14 (brs, 1H), 2.35 (s, 3H); ^{13}C NMR δ 148.2, 148.2, 143.5, 137.3, 135.7, 134.5, 132.7, 131.3, 130.0, 129.6, 129.3, 129.2, 128.7, 128.6, 124.9, 123.9, 122.8, 121.1, 85.2, 84.3, 39.2, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{34}H_{27}ClN_2NaO_2S$ ([M+Na]$^+$) 585.1374, found 585.1374.

Ethyl 4-((*N*-(2-(diphenylamino)phenyl)-4-methylphenyl)sulfonamido)but-2-ynoate (1m)

Isolated by PTLC (dichloromethane). The title compound is obtained as a white solid, 34%; mp 128 °C; ^{1}H NMR δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.36-7.29 (m, 2H), 7.27-7.20 (m, 7H), 7.10-7.02 (m, 6H), 7.00 (dd, *J* = 7.4, 7.4 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.07(brs, 1H), 3.03(brs, 1H), 2.41(s, 3H), 1.27(t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 152.9, 148.2, 148.1, 143.9, 136.4, 135.0, 131.5, 130.3, 129.6, 129.5, 129.3, 128.6, 125.2, 123.8, 122.9, 82.2, 77.3, 62.1, 38.3, 21.7, 14.1, ; HRMS (ESI, positive): *m/z* calcd for $C_{31}H_{28}N_2NaO_4S$([M+Na]$^+$)547.1663, found 547.1662.

***N*-(2-(Diphenylamino)phenyl)-4-methyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1o)**

Isolated by PTLC (hexane/dichloromethane = 1/2) The title compound is obtained as a white solid, 53%; mp 159 °C; ^{1}H NMR δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.37-7.33 (m, 1H), 7.33-7.28 (ddd, *J* = 1.6, 7.3, 7.3 Hz, 1H), 7.28-7.21 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 0.7, 8.1 Hz, 4H), 7.03-6.97 (m, 5H), 6.95 (d, *J* = 7.9 Hz, 2H), 4.18 (brs, 1H), 3.12 (brs, 1H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR δ 148.2, 148.2, 143.4, 138.6, 137.4, 135.8, 131.5, 131.4, 129.9, 129.5, 129.3, 129.2, 129.0, 128.7, 124.9, 123.9, 122.7, 119.5, 85.5, 83.4, 39.3, 21.6, 21.6; HRMS (ESI, positive):*m/z* calcd for $C_{35}H_{30}N_2NaO_2S$ ([M+Na]$^+$) 565.1924, found 565.1920.

7-Methylene-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b,e*][1,4]diazocine (2a): Isolated by PTLC (dichloromethane). The title compound was obtained as a brown solid 99%; mp 146-148 °C; ^{1}H NMR δ 7.80-7.74 (m, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.28-7.22 (m, 3H), 7.20-7.16 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.04 (dd, *J* = 8.1, 8.1 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.78 (dd, *J* = 7.2, 7.2 Hz, 1H) 6.42 (d, *J* = 8.6 Hz, 2H), 5.38 (s, 1H), 5.20 (s, 1H), 4.54 (s, 2H), 2.29 (s, 3H); ^{13}C NMR δ 147.8, 143.6, 143.3, 131.8, 139.7, 139.6, 137.0, 136.0, 131.2, 130.4, 129.5, 129.4, 129.0, 128.5, 127.7, 127.4, 126.8, 126.7, 126.6, 119.2, 117.8, 115.4, 54.7, 21.6; HRMS (ESI, positive): *m/z* calcd. For $C_{28}H_{24}N_2NaO_2S$ ([M+Na]$^+$) 475.1451, found 475.1452.

8,10-Dimethoxy-7-methylene-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b,e*][1,4]diazocine (2b)

Isolated by PTLC (hexane/ethyl acetate = 5/1). The title compound is obtained as a light yellow solid, >99%; mp 146 °C; ^{1}H NMR δ7.71 (d, *J* = 7.6 Hz, 1H), 7.28-7.22 (m, 2H), 7.20-7.12 (m, 3H), 7.04 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.79 (dd, *J* = 6.9 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 5.40 (s, 1H), 5.34 (s, 1H), 4.36 (s, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 2.30 (s, 3H); ^{13}C NMR δ 160.4, 159.2, 147.6, 144.4, 143.0, 139.9, 137.3, 136.8, 135.5, 130.7, 129.4, 129.0, 127.7, 127.4, 126.8, 126.7, 121.4, 120.4, 119.5, 116.2, 104.0, 97.1, 56.3, 55.9, 55.5, 21.6; HRMS (ESI, positive):*m/z* calcd for $C_{30}H_{28}N_2NaO_4S$ ([M+Na]$^+$) 535.1662, found 535.1662.

12-(4-Fluorophenyl)-7-methylene-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b,e*][1,4]diazocine (2c)

Isolated by PTLC (hexane/ethyl acetate = 5/1). The title compound is obtained as yellow oil, 99%; ^{1}H NMR δ 7.79-7.74 (m, 1H), 7.41 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.23-7.11 (m, 7H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.72-6.64 (m, 2H), 6.39-6.28 (m, 2H), 5.37 (s, 1H), 5.21 (s, 1H), 4.55 (s, 2H), 2.29 (s, 3H); ^{13}C NMR δ 156.9 (d, *J* = 237.9 Hz), 144.2 (d, *J* = 1.9 Hz), 143.5, 142.9, 142.6, 139.7, 139.0, 137.5, 136.0, 131.4, 130.3, 129.5, 129.4, 128.5, 127.5, 127.0 (d, *J* = 5.0 Hz), 126.2, 118.9, 116.9, 116.9, 115.6, 115.4, 54.5, 21.5; HRMS (ESI, positive):*m/z* calcd for $C_{28}H_{23}FN_2NaO_2S$ ([M+Na]$^+$) 493.1357, found 493.1356.

3-Methyl-7-methylene-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b,e*][1,4]diazocine (2d): Isolated by pTLC (hexane/diethyl ether = 1/1). The title compound was obtained as brown oil, 82%; ^{1}H NMR δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 1.6, 7.3 Hz, 1H), 7.42-7.33 (m, 4H), 7.18 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.10-7.02 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.81 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 2H), 5.37 (s, 1H), 5.19 (s, 1H), 4.56 (s, 2H), 2.28 (s, 3H), 1.55 (s, 3H); ^{13}C NMR δ 147.9, 143.3, 143.3, 142.3, 139.2, 139.2, 136.9, 135.9, 134.4, 131.0, 130.3, 129.4, 129.4, 129.0, 128.2, 128.1, 127.7, 126.2, 119.0, 118.3, 115.5, 54.5, 21.6, 21.4 (a pair of aromatic peaks was overlapped) ; HRMS (ESI, positive): *m/z* calcd. For $C_{29}H_{26}N_2NaO_2S$ ([M+Na]$^+$) 489.1607, found 489.1606.

7-Methylene-12-phenyl-5-tosyl-3-trifluoromethyl-5,6,7,12-tetrahydrodibenzo[*b,e*][1,4]diazocine (2e): It was isolated by pTLC (hexane/diethylether = 1/1). The title compound was

obtained as a brown solid, 95%; mp 149-151 °C; ^{1}H NMR δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 1.7, 7.4 Hz, 1H), 7.42-7.33 (m, 4H), 7.81 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.09-7.02 (m, 4H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.80 (dd, *J* = 7.4 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 2H), 5.36 (s, 1H), 5.19 (s, 1H), 4.56 (s, 2H), 2.28 (s, 3H); ^{13}C NMR δ 147.3, 144.1, 144.0, 140.3, 140.2, 140.0, 139.2, 135.3, 130.9, 130.8, 129.8, 129.7, 129.5, 129.2, 128.0, 127.7, 124.7 (q, *J* = 21.5 Hz), 123.7 (q, *J* = 272.7 Hz), 123.5 (q, *J* = 4.5 Hz), 123.0 (q, *J* = 3.9 Hz), 119.9, 116.5, 115.4, 54.7, 21.6; HRMS (ESI, positive): *m/z* calcd. For $C_{29}H_{23}F_3N_2NaO_2S$ ([M+Na]$^+$) 543.1325, found 543.1326.

(*E*)-7-Benzylidene-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2f)

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a yellow solid, 94%; mp 196 °C; ^{1}H NMR δ 7,71-7.62 (m, 1H), 7.32-7.24 (m, 2H), 7.23-7.13 (m, 4H), 7.13-7.03 (m, 7H), 6.97-6.86 (m, 3H), 6.85-6.74 (m, 3H), 6.60 (d, *J* = 8.6 Hz, 2H), 6.53 (s, 1H), 4.54 (brs, 1H), 4.43 (brs, 1H), 2.28 (s, 3H); ^{13}C NMR 147.8, 143.5, 143.3, 139.7, 137.7, 136.7, 136.1, 135.1, 135.1, 133.0, 132.3, 130.8, 129.5, 129.2, 129.0, 128.9, 128.0, 128.0, 127.7, 127.6, 127.2, 126.9, 126.8, 124.9, 119.9, 116.8, 57.0, 21.6; HRMS (ESI, positive):*m/z* calcd for $C_{34}H_{28}N_2NaO_2S$ ([M+Na]$^+$) 551.1764, found 551.1764.

(*E*)-7-(4-Methoxybenzylidene)-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2g)

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as colorless oil, 41%; ^{1}H NMR δ 8.24 (s, 1H), 7.78 (dd, *J* = 1.4, 7.9 Hz, 1H), 7.65 (dd, *J* = 1.5, 8.2 Hz, 1H), 7.40 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.22-7.18 (m, 2H), 7.18-7.12 (m, 4H), 7.12-7.00 (m, 5H), 6.91-6.88 (m, 2H), 6.82 (s, 1H), 6.79 (d, *J* = 8.2 Hz, 2H), 4.08 (s, 2H), 3.81 (s, 3H), 2.20 (s, 3H); ^{13}C NMR δ 158.3, 148.7, 148.1, 143.2, 142.8, 136.6, 136.0, 135.8, 134.6, 132.6, 132.2, 130.5, 129.9, 129.3, 129.2, 128.6, 128.0, 127.4, 126.9, 125.3, 125.0, 124.8, 123.6, 123.4, 120.1, 114.2, 55.4, 42.8, 21.5; HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1870, found 581.1869.

(*E*)-7-(3-Methoxybenzylidene)-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2h)

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a yellow solid, 53%; mp 91 °C; ^{1}H NMR δ 7.66 (dd, *J* = 1.6, 8.8 Hz, 1H), 7.30-7.26 (m, 1H), 7.25-7.04 (m, 9H), 7.00 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.96-6.89 (m, 3H), 6.82 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.63 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.59 (d, *J* = 4.0 Hz, 2H), 6.51 (s, 1H), 6.43 (d, *J* = 4.0 Hz, 1H), 6.27 (s, 1H), 4.54 (brs, 1H), 4.42 (brs, 1H), 3.54 (s, 3H), 2.29 (s, 3H); ^{13}C NMR δ 159.2, 147.9, 143.5, 143.3, 139.8, 138.1, 137.8, 136.7, 136.2, 135.4, 133.1, 132.4, 130.8, 129.5, 129.2, 129.1, 129.0, 128.1, 127.8, 127.6, 126.9, 126.9, 124.9, 121.7, 120.0, 116.9, 113.8, 113.6, 57.0, 55.1, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1869, found 581.1869.

(*E*)-7-(2-Methoxybenzylidene)-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2i)

Isolated by pTLC (hexane/dichloromethane = 1/2). The title compound is obtained as brown oil, 50%; ^{1}H NMR δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25-7.11 (m, 6H), 7.06 (dd, *J* = 8.0, 8.0 Hz, 3H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.81 (q, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 4.3 Hz, 1H), 6.68 (s, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.45 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.04 (d, *J* = 7.7 Hz, 1H), 4.69 (brs, 1H), 4.26 (brs, 1H), 3.81 (s, 3H), 2.29 (s, 3H); ^{13}C NMR δ 157.6, 147.8, 144.0, 143.1, 140.2, 137.8, 136.6, 136.2, 133.9, 132.7, 131.6, 130.2, 129.8, 129.5, 129.2, 128.8, 128.5, 127.7, 127.4, 127.1, 126.6, 125.9, 124.4, 120.0, 119.8, 116.9, 110.4, 56.8, 55.5, 21.6 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1868, found 581.1869.

(*E*)-12-Phenyl-5-tosyl-7-(4-(trifluoromethyl)benzylidene)-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2j)

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a white solid, 85%; mp 172 °C**;** ^{1}H NMR δ 7.64 (dd, *J* = 1.5, 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.31-7.23 (m, 4H), 7.20-7.01 (m, 6H), 6.86-6.98 (m, 5H), 6.83 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.52 (s, 1H), 4.54 (brs, 1H), 4.51 (brs, 1H), 2.30 (s, 3H); ^{13}C NMR δ 147.8, 143.7, 143.5, 140.4, 139.7, 138.2, 137.7, 136.2, 136.1, 133.0, 130.7, 130.1, 129.5, 129.5, 129.2, 129.2, 129.0 (q, *J* = 32.2 Hz), 128.1, 127.8, 127.7, 127.0, 126.9, 125.3, 125.1 (q, *J* = 3.9 Hz), 124.6 (q, *J* = 237.5 Hz), 120.2, 116.9, 56.9, 21.6 HRMS (ESI, positive): *m/z* calcd for $C_{35}H_{27}F_3N_2NaO_2S$ ([M+Na]$^+$) 619.1635, found 619.1638.

(*E*)-7-(4-Fluorobenzylidene)-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2k)

Isolated by PTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a yellow solid, 87%; mp 193 °C**;** ^{1}H NMR δ 7.65 (dd, *J* = 1.4, 8.0 H, 1H), 7.30-7.20 (m, 4H), 7.20-7.11 (m, 3H), 7.08 (dd, *J* = 7.7, 7.7 Hz, 3H), 6.97-6.88 (m, 3H), 6.82 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 4H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 4.52 (brs, 1H), 4.42 (brs, 1H), 2.29 (s, 3H); ^{13}C NMR δ 162.0 (d, *J* = 217.8 Hz), 147.8, 143.7, 143.4, 139.8, 137.7, 136.1, 136.5, 135.3 (d, *J* = 1.2 Hz), 132.9, 132.8, 132.8, 131.0, 130.8, 130.6 (d, *J* = 8.1 Hz), 129.5, 129.2, 129.1, 128.0, 127.8, 126.9 (d, *J* = 4.2 Hz), 125.0, 120.0, 116.9, 115.1 (d, *J* = 21.5 Hz), 57.0, 21.6 (a pair of peaks at the aromatic region was overlapped.); HRMS (ESI, positive): *m/z* calcd for $C_{34}H_{27}FN_2NaO_2S$ ([M+Na]$^+$) 569.1669, found 569.1669.

(*E*)-7-(4-Chlorobenzylidene)-12-phenyl-5-tosyl-5,6,7,12-tetrahydrodibenzo[*b*,*e*][1,4]diazocine (2l)

Isolated by pTLC (hexane/dichloromethane = 1/2). The title compound is obtained as a yellow solid, 89%; mp 210 °C**;** ^{1}H NMR δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.32-7.21 (m, 4H), 7.20-7.10 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 3H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.96-6.89 (m, 3H), 6.82 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 8.2 Hz, 2H), 6.45 (s, 1H), 4.52 (brs, 1H), .4.44 (brs, 1H), 2.29 (s, 3H); ^{13}C NMR δ 147.8, 143.6, 143.4, 139.7, 137.7, 136.4, 136.2, 136.1, 135.2, 133.0, 132.9, 130.8, 130.7, 130.3, 129.5, 129.5, 129.2, 128.3, 127.9, 127.9, 127.7, 126.9, 126.9, 125.1, 120.1, 116.9, 57.0, 21.6; HRMS (ESI, positive): *m/z* calcd for $C_{34}H_{27}O_2ClNaO_2S$ ([M+Na]$^+$) 585.1373, found 585.1374.

Ethyl (*E*)-2-(12-phenyl-5-tosyl-5,12-dihydrodibenzo[b,e][1,4]diazocin-7(6H)-ylidene)acetate (2m)

Isolated by PTLC (dichloromethane). The title compound is obtained as yellow oil, 98%; ^{1}H NMR δ 7.62 (dd, *J* = 1.5, 7.7 Hz, 1H),7.31-7.51 (m, 4H), 7.17 (dd, *J* = 1.1, 8.0 Hz, 1H), 6.99-7.14 (m, 8H), 6.76 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 5.73 (s, 1H), 4.88 (brs, 1H), 4.20 (brs, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ 165.1, 154.6, 147.4, 143.9, 140.8, 139.2, 137.4, 137.1, 136.3, 134.0, 130.8,

129.6, 129.6, 129.6, 128.9, 127.9, 126.5, 126.4, 125.9, 125.1, 119.6, 116.9, 115.1, 60.1, 56.4, 21.6, 14.2; HRMS (ESI, positive): *m/z* calcd for $C_{31}H_{28}N_2NaO_4S$ ([M+Na]$^+$) 547.1661, found 547.1662.

4-(4-methoxyphenyl)-*N*,*N*-diphenyl-1-tosyl-1,2-dihydroquinolin-8-amine (2g')

Isolated by PTLC (hexane/dichloromethane = 1/2) The title compound is obtained as white solid, 70%; mp 237 °C; ^{1}H NMR δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.30-7.14 (m, 9H), 7.09-6.99 (m, 5H), 6.79-6.73 (m, 2H), 6.70-6.60 (m, 3H), 5.36 (dd, *J* = 2.6, 6.0 Hz, 1H), 4.26 (dd, *J* = 6.0, 18.2 Hz, 1H), 3.80 (s, 3H), 3.26 (dd, *J* = 2.6, 18.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR δ 159.2, 146.5, 143.2, 138.5, 137.3, 134.9, 130.5, 129.9, 129.2, 129.2, 129.1, 128.9, 128.6, 128.2, 127.7, 127.5, 122.7, 121.5, 113.3, 55.4, 53.6, 44.1, 21.5; HRMS (ESI, positive):*m/z* calcd for $C_{35}H_{30}N_2NaO_3S$ ([M+Na]$^+$) 581.1870, found 581.1869.

***N*,*N*-diphenyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydroquinolin-8-amine (2o')**

Isolated by PTLC (hexane/dichloromethane = 1/2) The title compound is obtained as light yellow oil, 43%; ^{1}H NMR δ 7.44-7.40 (m, 2H), 7.30-7.15 (m, 9H), 7.08-6.99 (m, 7H), 6.66-6.59 (m, 3H), 5.39 (dd, *J* = 2.5, 6.0 Hz, 1H), 4.27 (dd, *J* = 6.0, 18.3 Hz, 1H), 3.27 (dd, *J* = 2.3, 18.4 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR δ146.5, 143.2, 138.9, 137.4, 137.2, 135.2, 134.8, 129.7, 129.5, 129.3, 129.0, 128.9, 128.7, 128.6, 128.5, 128.1, 127.6, 127.5, 123.0, 121.6, 44.1, 21.5, 21.3; HRMS (ESI, positive):*m/z* calcd for $C_{35}H_{30}N_2NaO_2S$ ([M+Na]$^+$) 565.1920, found 565.1920.

***N*,*N*-Diphenyl-2-(prop-2-yn-1-yloxy)aniline (3)**

Isolated by flash column chromatography (hexane/ethyl acetate = 9/1). The title compound was obtained as brown oil, 81%; ^{1}H NMR δ 7.24-7.16 (m, 6H), 7.12 (dd, *J* = 0.9, 7.9 Hz, 1H), 7.05-6.97 (m, 5H), 6.93 (dd, *J* = 7.3, 7.3 Hz, 2H), 4.48 (d, *J* = 2.4 Hz, 2H), 2.40 (dd, *J* = 2.4 Hz, 1H); ^{13}C NMR δ 154.0, 147.7, 136.8, 130.2, 129.0, 126.5, 123.2, 122.0, 121.8, 116.6, 78.8, 75.4, 56.8; HRMS (ESI, positive): m/z calcd. For $C_{21}H_{17}NNaO$ ([M+Na]$^+$) 322.1202, found 322.1202.

***N*,*N*-Diphenyl-2H-chromen-8-amine (4')**

Isolated by PTLC (hexane/ethyl acetate = 15/1). The title compound was obtained as orange oil, 59%; ^{1}H NMR δ 7.23-7.15 (m, 4H), 7.07-7.00 (m, 4H),7.00-6.98 (m, 3H), 6.83 (d, *J* = 4.9 Hz, 2H), 6.41 (dt, J_t= 1.8 Hz, J_d = 9.9 Hz, 1H), 5.72 (dt, J_t = 3.5, J_d = 9.9 Hz, 1H), 4.52 (dd, *J* = 1.8, 3.5 Hz, 2H); ^{13}C NMR 150.0, 147.7, 134.3, 129.7, 129.0, 124.7, 124.5, 124.0, 122.8, 121.9, 121.8, 121.7, 65.2; HRMS (ESI, positive): *m/z* calcd. For $C_{21}H_{18}NO$ ([M+H]$^+$) 300.1383, found 300.1383.

4-Methyl-*N*-(2-oxopropyl)-*N*-(2-phenoxyphenyl)benzenesulfonamide (5)

Isolated by PTLC (hexane/ethyl acetate = 4/1). The title compound was obtained as a white solid, 22% in total yield; mp 100-102 °C; ^{1}H NMR δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.45 (dd, *J* = 1.7, 7.9 Hz, 1H), 7.29-7.16 (m, 5H), 7.12-7.07 (m, 1H), 7.05 (ddd, *J* = 1.4, 7.7, 7.7 Hz, 1H), 6.77-6.71 (m, 3H), 4.51 (d, *J* = 1.8 Hz, 2H), 2.38 (s, 3H), 2.18 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR δ 155.7, 155.1, 143.5, 137.1, 133.5, 130.0, 129.8, 129.5, 128.2, 127.9, 124.1, 123.0, 119.6, 118.1, 78.5, 73.5, 40.2, 21.6; HRMS (ESI, positive): *m/z* calcd. For $C_{22}H_{19}NNaO_3S$ ([M+Na]$^+$) 400.0978, found 400.0979.

4-Methyl-*N*-(2-oxopropyl)-*N*-(2-phenoxyphenyl)benzenesulfonamide (6')

Isolated by PTLC (hexane/ethyl acetate = 3/1). The title compound was obtained as a brown solid, 72%; mp 88-89 °C; ^{1}H NMR δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (d, 8.1 Hz, 2H), 7.25 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.22-7.15 (m, 3H), 7.12-7.03 (m, 2H), 6.66 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 2H), 4.41 (s, 2H), 2.37 (s, 3H), 2.30 (s, 3H); ^{13}C NMR δ 204.9, 155.1, 154.3, 143.7, 136.5, 133.5, 129.9, 129.5, 128.8, 127.9, 124.3, 123.1, 119.5, 117.6, 60.3, 27.3, 21.7 (a pair of aromatic region was overlapped); HRMS (ESI, positive): m/z calcd. For $C_{22}H_{21}NNaO_4S$ ([M+Na]$^+$) 418.1084, found 418.1080.

Acknowledgements

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Keywords: dibenzodiazocine • NHC ligand • 8-*exo*-dig • gold • hydroarylation

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[14] The reaction of **1a** gave 5% of **2g'** as byproduct.

[15] In both reactions, starting materials **1g** and **1o** were consumed.

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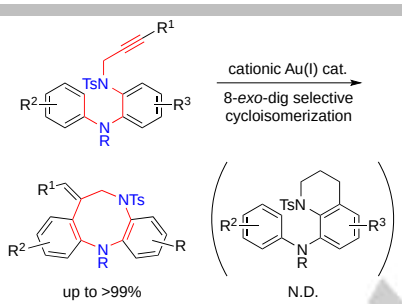
FULL PAPER

The cationic Au(I)-catalyzed intramolecular reaction of *N*-propargyl-2-anilinoanilines gave a diazocine skeleton via 8-*exo*-dig-selective cycloisomerization. Both terminal and internal alkynes could be used according to the choice of ligand of the Au(I) complex. Two nitrogen atoms in the tether of substrates were critical in this selective transformation.



up to >99% N.D.

*M. Ito, D. Inoue, A. Takaki, K. S. Kanyiva and T. Shibata**

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8-*exo*-dig-Selective Cycloisomerization for the Synthesis of Dibenzo[*b*,*e*][1,4]diazocines Using Cationic Au(I) catalysts