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CATIONIC Au(I)-CATALYZED CYCLOISOMERIZATION OF *N*-(2-ALKYNYLPHENYL)INDOLINES FOR THE CONSTRUCTION OF INDOLOBENZAZEPINE SKELETON

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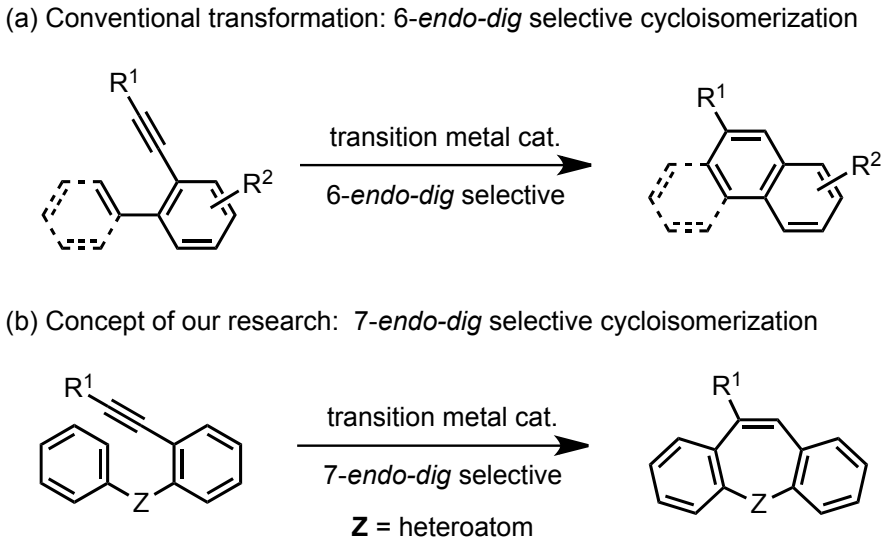
Abstract – An intramolecular reaction of *N*-(2-alkynylphenyl)indolines proceeded efficiently to give indolo[1,7-*ab*][1]benzazepine derivatives in high to excellent yields by cationic Au(I)-catalyzed 7-*endo-dig* selective cycloisomerization along with DDQ oxidation. The present transformation could be used for the intramolecular reaction of *N*-(2-alkynylphenyl)-1,2,3,4-tetrahydroquinoline and *N*-(2-alkynylphenyl)-*N*-methylaniline, and construction of a dibenzazepine skeleton was achieved.

INTRODUCTION

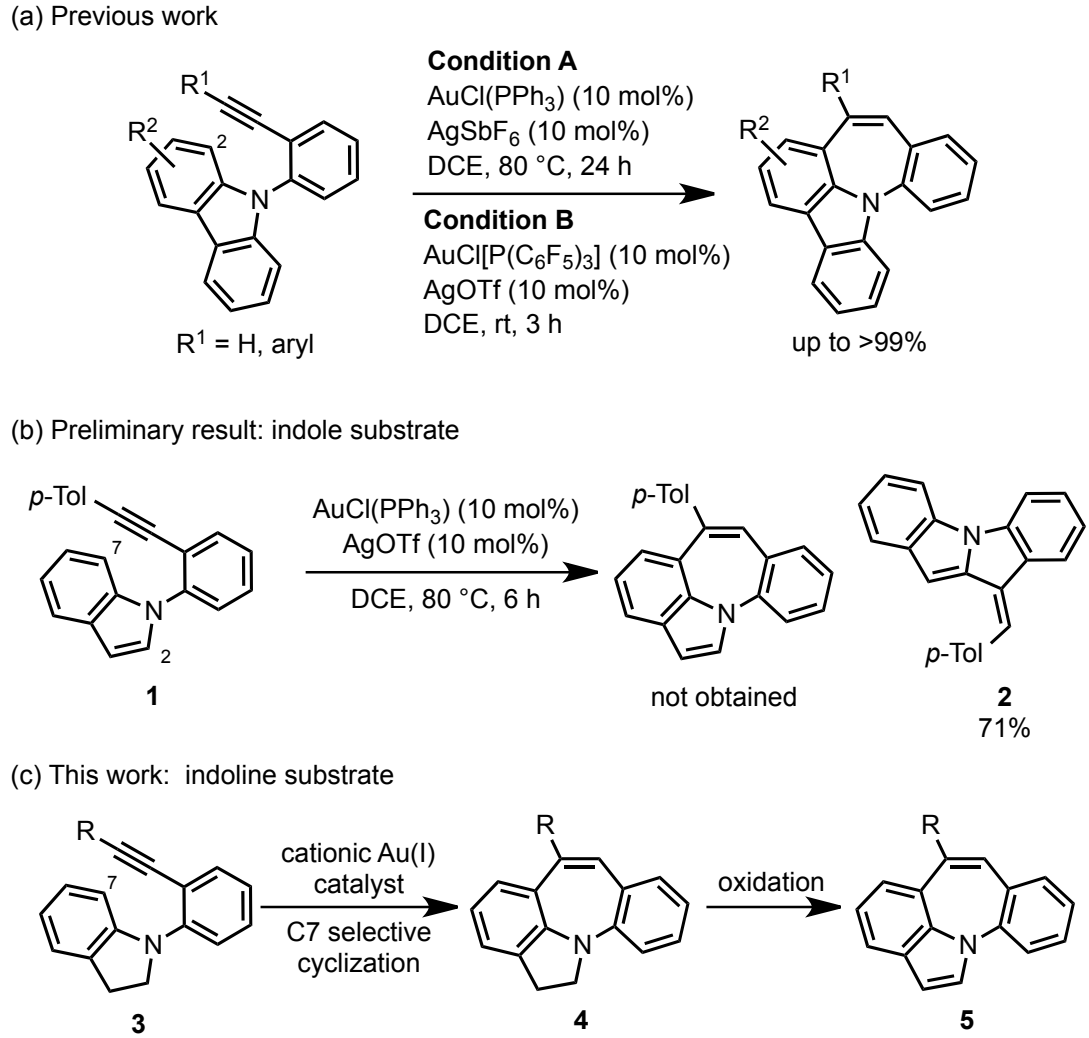
Cycloisomerization of 1,*n*-enynes initiated by the activation of an alkyne moiety using transition metal catalysts is an atom-economical and versatile protocol for the preparation of cyclic compounds.[1] A gold complex is a major player in this reaction,[2] and heteroatom-tethered enynes can be transformed into various types of heterocycles.[3] Among them, *ortho*-phenylene-tethered 1,5-enynes are good substrates, and 6-*endo-dig* selective cycloisomerization gives naphthalene derivatives (Scheme 1a). Other groups and we have previously reported the intramolecular reaction of 2-alkynylbiphenyls, where a part of a benzene ring acts as an ene moiety.[4] Against this background, we designed new substrates by the insertion of a heteroatom (Z) between two benzene rings, and assumed that the intramolecular reaction of the arylalkynes could construct a dibenzoheteropin skeleton by 7-*endo-dig* cycloisomerization (Scheme 1b). We focused on the preparation of dibenzazepine derivatives (Z = NR^2) because they are found in many

biologically active compounds.[5] This is a new strategy for the catalytic synthesis of substituted dibenzazepines.[6-8]



Scheme 1. Concept of this research

We recently reported the Au(I)-catalyzed cycloisomerization of a carbazole-containing substrate, which provided polycyclic conjugated products (Scheme 2a).[9] We considered that the planarity of the carbazole moiety increased the nucleophilicity of the C2 position due to the resonance effect of nitrogen's lone pair and realized 7-*endo-dig* selective cyclization. To expand the substrate scope of this strategy and to evaluate the above speculation, we next subjected indole-containing substrate **1** to cationic Au-catalyzed cycloisomerization (Scheme 2b).[4c] As a result, the reaction proceeded at the undesired C2 position of the indole ring, not the desired C7 position, and tetracyclic product **2** was obtained.[10] To suppress the reactivity of the C2 position, we used indoline-containing substrate **3** and succeeded in C7 selective cyclization for the preparation of dibenzazepine derivatives (Scheme 2c). Subsequent oxidation gave indolo[1,7-*ab*][1]benzazepines.

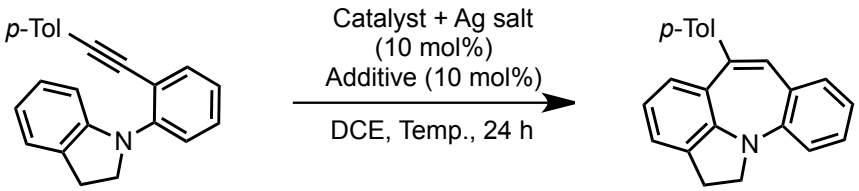


Scheme 2. Our previous and present works

RESULTS AND DISCUSSION

We chose *p*-tolyl-substituted alkyne **3a** as a model substrate and subjected it to cationic Au(I)-catalyzed cycloisomerization in the presence of chloro(triphenylphosphine)gold(I) and silver trifluoromethanesulfonate for 24 h in 1,2-dichloroethane (DCE) (Table 1, Entry 1). As a result, the desired 7-*endo-dig* cycloadduct **4a** was obtained in good NMR yield, but a slight amount of **3a** remained. We considered that the cationic catalyst was unstable under these conditions and became inactive during the reaction. We were pleased to find that the addition of a catalytic amount of pyridine was effective, and tetracyclic compound **4a** was obtained in high NMR yield along with the complete consumption of **3a** (Entry 2). No reaction proceeded in the absence of gold catalyst or silver salt (Entries 3 and 4). These results indicated the cationic gold species was crucial for the present transformation. The counter anion had almost no effect on the results (Entries 2, 5 and 6). Screening of the reaction temperature revealed that the reaction proceeded quantitatively at 40 °C (Entries 2, 7-9).

Table 1. Screening of reaction conditions



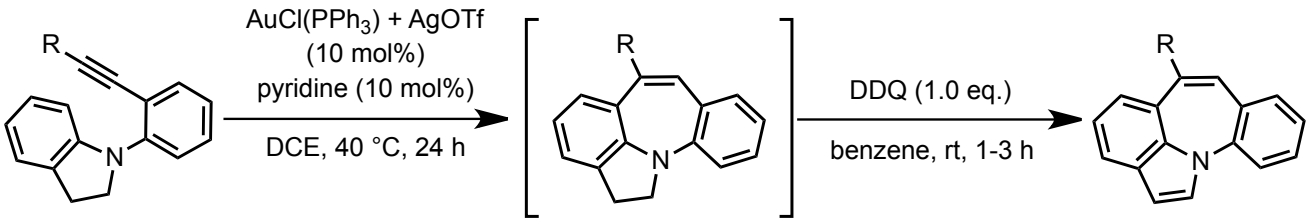
3a **4a**

Entry	Catalyst	Ag salt	Additive	Temp. (°C)	Yield (%)[a]
1	$AuCl(PPh_3)$	AgOTf	none	80	75
2	$AuCl(PPh_3)$	AgOTf	pyridine	80	93
3	none	AgOTf	pyridine	80	N.R.
4	$AuCl(PPh_3)$	none	pyridine	80	N.R.
5	$AuCl(PPh_3)$	$AgBF_4$	pyridine	80	89
6	$AuCl(PPh_3)$	$AgSbF_6$	pyridine	80	92
7	$AuCl(PPh_3)$	AgOTf	pyridine	60	93
8	$AuCl(PPh_3)$	AgOTf	pyridine	40	>99
9	$AuCl(PPh_3)$	AgOTf	pyridine	rt	83

[a] NMR yields were measured by using 1,1,2,2-tetrachloroethane as an internal standard.

Under the reaction conditions for Entry 8 in Table 1, various alkynes were subjected to cationic Au(I)-catalyzed cycloisomerization (Table 2). Since cycloadducts **4** were generally unstable in the silica gel purification step,[11] we isolated and fully characterized indole derivatives **5** after DDQ oxidation.[12] For example, compound **4a** was oxidized without isolation to give the indole derivative **5a** in high yield (Entry 1). Various tolyl- and anisyl-substituted alkynes **3b**-**3f** also provided cycloadducts **5b**-**5f** in high to excellent yields (Entries 2-6). Notably, sterically hindered substrates **3c** and **3f** were also good substrates (Entries 3 and 6). The reaction of phenyl-substituted alkyne **3g** proceeded smoothly to give **5g** quantitatively (Entry 7). While chlorophenyl-substituted alkynes **3h** and **3i** were transformed into **5h** and **5i** in high yield (Entries 8 and 9), the reaction of more electron deficient 4-(trifluoromethyl)phenyl-substituted alkyne **3j** proceeded sluggishly to provide cycloadduct **5j** in moderate yield (Entry 10). More electrophilic gold catalyst prepared from $AuCl[P(C_6F_5)_3]$ and $AgBF_4$ improved the yield, but alkyne **3j** was not completely consumed (Entry 11). 1-Naphthyl and 4-biphenyl-substituted alkynes **3k** and **3l** were also good substrates (Entries 12 and 13). The cycloisomerization of terminal alkyne **3m** was conducted using the more electrophilic gold catalyst because only a trace amount of **5m** was obtained under the optimized conditions. The yield of **5m** was moderate because the oxidation step gave unidentified by-products (Entry 14).[13]

Table 2. Scope of substituents on the alkyne terminus

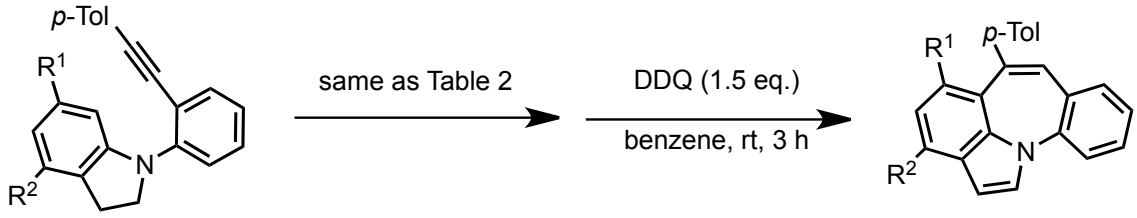


3 **4** **5**

Entry	R	Yield (%)[a]	Entry	R	Yield (%)[a]
1	4-MeC_6H_4 (**3a**)	93 (**5a**)	8	4-ClC_6H_4 (**3h**)	88 (**5h**)
2	3-MeC_6H_4 (**3b**)	98 (**5b**)	9	3-ClC_6H_4 (**3i**)	>99 (**5i**)
3	2-MeC_6H_4 (**3c**)	87 (**5c**)	10	4-$CF_3C_6H_4$ (**3j**)	51 (**5j**)
4	4-$MeOC_6H_4$ (**3d**)	86 (**5d**)	11[b]	4-$CF_3C_6H_4$ (**3j**)	64 (**5j**)
5	3-$MeOC_6H_4$ (**3e**)	96 (**5e**)	12	1-naphthyl (**3k**)	98 (**5k**)
6	2-$MeOC_6H_4$ (**3f**)	88 (**5f**)	13	4-PhC_6H_4 (**3l**)	76 (**5l**)
7	Ph (**3g**)	>99 (**5g**)	14[b]	H (**3m**)	56 (**5m**)

[a] Isolated yield. [b] $AuCl[P(C_6F_5)_3]$ and $AgBF_4$ were used.

Electron-withdrawing and -donating group-substituted indolines **3n** and **3o** were also transformed into tetracyclic compounds **5n** and **5o**, respectively, albeit in moderate yield, because alkynes were not completely consumed.

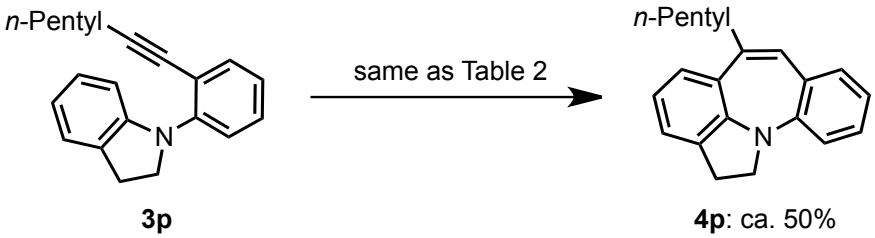


3n (R^1 = F, R^2 = H)
3o (R^1 = H, R^2 = OMe)

5n: 71%
5o: 63%

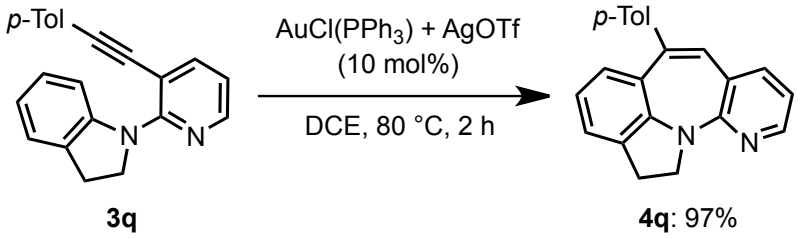
Scheme 3. Reaction of substrates **3n** and **3o** with a substituent on the indoline moiety

Alkyl-substituted alkyne **3p** could be also used in this transformation. Compared with aryl-substituted cycloadducts, *n*-pentyl-substituted one **4p** was stable and characterized without oxidation, but a small amount of unidentified impurities could not be excluded by purification.



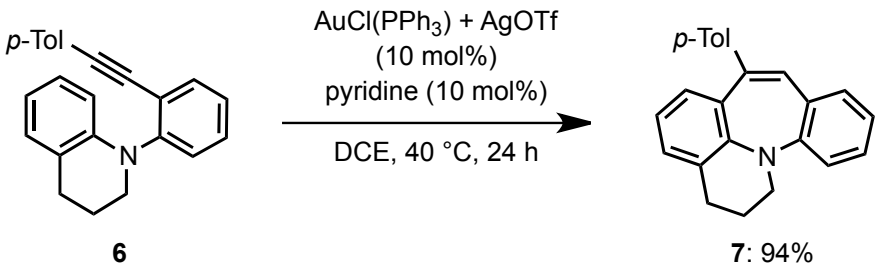
Scheme 4. Reaction of alkyl-substituted alkyne **3p**

The reaction of pyridine-containing substrate **3q** proceeded to give azadibenzazepine derivative **4q** in excellent yield (Scheme 5). While a higher reaction temperature was required, the addition of pyridine was not needed and cycloadduct **4q** possessing an indoline moiety was sufficiently stable to be fully characterized.



Scheme 5. Reaction of pyridine-containing substrate **3q**

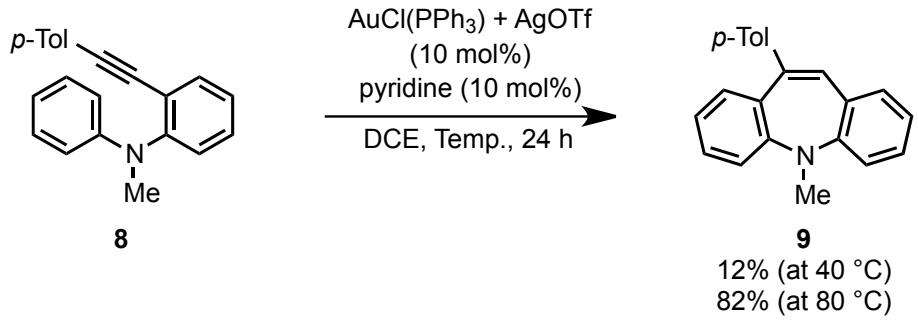
To investigate the effect of the indoline skeleton, we examined more flexible tetrahydroquinoline-containing substrate **6** (Scheme 6). Under the optimized conditions, the reaction proceeded smoothly and cycloadduct **7** could be obtained in high yield. This result indicated that the flexibility around the nitrogen atom does not interfere with the present cycloisomerization.



Scheme 6. Cyclization of tetrahydroquinoline-containing substrate **6**

Finally, we examined the results with the even more flexible *N*-methyldiphenylamine derivative **8** (Scheme 7). Under the optimized conditions, the desired 7-*endo-dig* cycloadduct **9** was obtained, albeit in

low yield due to low conversion.[14] An increase in the reaction temperature to 80 °C realized a high yield of 82%. This result is in contrast to those in the cationic Au(I)-catalyzed cyclization of 1-alkynyl-2-benzylbenzene derivatives, a carbon analogue of **8**, where anthracene derivatives were selectively obtained.[15]



Scheme 7. Cyclization of acyclic substrate **8**

In conclusion, we developed an efficient synthesis of benzazepines fused with indole and tetrahydroquinoline by 7-*endo-dig* selective cycloisomerization. The cationic Au(I)-catalyzed reaction of *N*-(2-alkynylphenyl)indolines and -1,2,3,4-tetrahydroquinolines gave the tetracyclic compounds in good to excellent yields. This strategy could also be used for construction of the parent dibenzazepine skeleton by the reaction of an *N*-(2-alkynylphenyl)aniline derivative. Further studies to expand this protocol for the synthesis of other dibenzoheteropins are now underway in our laboratory.

EXPERIMENTAL

General. ^{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 $CDCl_3$. The coupling constants, *J*, are reported in Hertz (Hz). ^{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 $CDCl_3$). $CDCl_3$ was used as an 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 complexes and silver salts were weighed and handled in air and backfilled under argon at room temperature. Gold complexes and silver salts were weighed and handled under an argon atmosphere in globe box at room temperature. Unless otherwise noted, all reactions were conducted under an argon atmosphere. All reagents were purchased from Wako, Kanto, Aldrich, TCI, and Strem and used without

further purification. Compounds **1**[7a] and **5m**[16] are known and their ^{1}H NMR spectra were accorded with those in literature. The synthetic scheme of compounds **3**, **6** and **8** were described in supporting information.

General procedures for the cycloisomerization in Table 2 and 3: AuCl(PPh$_3$) (0.0050 mmol), AgOTf (0.0050 mmol), and *N*-(2-alkynylphenyl)indoline derivatives **3** (0.050 mmol) were placed in a Schlenk tube under an argon atmosphere in globe box, which was then evacuated and backfilled with argon (×3). To the reaction vessel was added a DCE solution of pyridine (0.0050 mmol) and anhydrous DCE (0.50 mL), then the solution was stirred at 40 °C (bath temperature). The reaction mixture was cooled to room temperature, and the solution was filtered by silica gel. The obtained crude products were subject to the next oxidation without purification under the reported conditions.[12] The crude products and DDQ (0.05 mmol) were placed in a Schlenk tube, which was then evacuated and backfilled with argon (×3). To the reaction vessel was added benzene (1.0 mL), then the solution was stirred at room temperature. After 1 h, the solution was quenched by sat. aqueous $NaHCO_3$, and organic materials were extracted with EtOAc. The organic layer was dried over Na_2SO_4. After removal of solvent, the crude products were purified by PTLC to give **5**.

(*Z*)-10-(4-Methylbenzylidene)indolo[1,2-*a*]indole (2): it was isolated by PTLC (hexane/DCM = 10/1). The title compound was obtained as yellow solid (22.0 mg, 71%). The stereochemistry was determined by the correlation between the singlet proton of the C2 position of the indole ring and aromatic protons of tolyl group in the NOESY spectrum; mp 134-135 °C; ^{1}H NMR δ 8.57 (d, *J* = 8.2 Hz, 1H), 8.48 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.55-7.66 (m, 4H), 7.27-7.43 (m, 5H), 7.07 (s, 1H), 6.85 (s, 1H), 2.44 (s, 3H); ^{13}C NMR δ 138.2, 136.8, 136.2, 136.0, 133.5, 133.1, 130.3, 129.5, 129.0, 128.5, 128.4, 124.8, 123.0, 122.7, 122.0, 122.0, 121.4, 115.4, 114.4, 97.9, 21.5; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{18}N$ ($[M+H]^+$) 308.1434, found 308.1431.

1-(2-(2-(4-Methylphenyl)ethynyl)phenyl)indoline (3a): it was isolated by flash column chromatography (hexane/EtOAc = 10/1). The title compound was obtained as white solid (305.8 mg, 92%); mp 66-68 °C; ^{1}H NMR δ 7.56 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.40 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.29 (ddd, *J* = 1.7, 7.4, 7.4 Hz, 1H), 7.14-7.20 (m, 3H), 7.06-7.12 (m, 3H), 7.02 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.74 (ddd, *J* = 1.0, 7.3, 7.3 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.11 (t, *J* = 8.3 Hz, 2H), 3.16 (t, *J* = 8.3 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR δ 148.6, 146.9, 138.4, 134.0, 131.3, 130.9, 129.2, 126.9, 124.8, 123.9, 122.2, 120.6, 118.9, 118.7, 110.0, 95.6, 87.6, 54.2, 29.1, 21.6 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{20}N$ ($[M+H]^+$) 310.1590, found 310.1588.

1-(2-(2-(3-Methylphenyl)ethynyl)phenyl)indoline (3b): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as brown oil (77.4 mg, 74%); ^{1}H NMR δ 7.56 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.40 (dd, *J* = 1.1, 8.1 Hz, 1H), 7.29 (ddd, *J* = 1.7, 7.4, 7.4 Hz, 1H), 7.18 (dd, *J* = 6.4, 6.4 Hz, 1H),

7.15 (d, *J* = 7.6 Hz, 1H), 7.06-7.12 (m, 3H), 7.00-7.05 (m, 2H), 6.75 (ddd, *J* = 1.1, 7.4, 7.4 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 4.11 (t, *J* = 8.5 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR δ 148.6, 146.9, 138.1, 134.0, 132.1, 130.9, 129.3, 129.2, 128.5, 128.3, 126.9, 124.8, 123.9, 123.4, 122.2, 118.8, 118.7, 110.0, 95.6, 87.9, 54.2, 29.1, 21.4; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{20}N$ ($[M+H]^+$) 310.1590, found 310.1590.

1-(2-(2-(2-Methylphenyl)ethynyl)phenyl)indoline (3c): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as brown oil (78.8 mg, 73%); ^{1}H NMR δ 7.60 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.40 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.29-7.33 (m, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.06-7.20 (m, 5H), 7.01 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.72 (ddd, *J* = 1.0, 7.4, 7.4 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.09 (t, *J* = 8.4 Hz, 2H), 3.15 (t, *J* = 8.4 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR δ 148.7, 146.5, 140.0, 134.0, 131.8, 130.7, 129.4, 129.2, 128.2, 120.8, 125.5, 124.7, 123.9, 123.3, 122.1, 119.4, 118.6, 109.7, 93.9, 91.7, 54.1, 29.0, 20.4; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{20}N$ ($[M+H]^+$) 310.1590, found 310.1590.

1-(2-(2-(4-Methoxyphenyl)ethynyl)phenyl)indoline (3d): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as brown oil (79.9 mg, 56%); ^{1}H NMR δ 7.57 (dd, *J* = 1.6, 7.9 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.30 (ddd, *J* = 1.6, 7.7, 7.7 Hz, 1H), 7.17-7.23 (m, 3H), 7.10 (ddd, *J* = 1.1, 7.4, 7.4 Hz, 1H), 7.00-7.06 (m, 1H), 6.79-6.83 (m, 2H), 6.69-6.77 (m, 2H), 4.12 (t, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 3.18 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 159.7, 148.6, 146.7, 133.6, 132.9, 130.8, 129.0, 126.9, 124.8, 123.9, 122.3, 119.1, 118.7, 115.8, 114.1, 110.0, 95.4, 86.9, 55.4, 54.2, 29.1; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{20}NO$ ($[M+H]^+$) 326.1539, found 326.1539.

1-(2-(2-(3-Methoxyphenyl)ethynyl)phenyl)indoline (3e): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as brown oil (123.4 mg, 71%); ^{1}H NMR δ 7.57 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.27-7.32 (m, 1H), 7.14-7.18 (m, 2H), 7.09 (ddd, *J* = 1.2, 7.5, 7.5 Hz, 1H), 7.02 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.80-6.84 (m, 1H), 6.68-6.75 (m, 3H), 4.09 (t, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 3.15 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 159.5, 148.5, 146.9, 134.1, 130.9, 129.5, 129.5, 126.9, 124.9, 124.7, 124.0, 123.9, 122.2, 118.8, 118.6, 115.9, 115.2, 110.1, 95.5, 88.1, 55.5, 54.2, 29.3; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{19}NNaO$ ($[M+Na]^+$) 348.1359, found 348.1359.

1-(2-(2-(2-Methoxyphenyl)ethynyl)phenyl)indoline (3f): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as brown oil (121.3 mg, 80%); ^{1}H NMR δ 7.60 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.43 (dd, *J* = 0.7, 7.9 Hz, 1H), 7.19-7.28 (m, 3H), 7.15 (d, *J* = 7.1 Hz, 1H), 7.06 (ddd, *J* = 0.9, 7.6, 7.6 Hz, 1H), 7.01 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.80-6.87 (m, 2H), 6.69-6.76 (m, 2H), 4.18 (t, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 3.15 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 159.8, 148.5, 146.8, 134.1, 133.2, 130.8, 129.6, 129.0, 126.7, 124.7, 123.6, 121.7, 120.4, 118.9, 118.5, 112.8, 110.6, 109.8, 92.0, 91.4, 55.7, 53.9, 29.0; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{19}NNaO$ ($[M+Na]^+$) 348.1359, found 348.1359.

1-(2-(2-Phenylethynyl)phenyl)indoline (3g): it was isolated by PTLC (hexane/EtOAc = 20/1). The title

compound was obtained as brown oil (68.0 mg, 40%); ^{1}H NMR δ 7.57 (dd, *J* = 1.8, 7.7 Hz, 1H), 7.40 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.29 (ddd, *J* = 1.7, 7.3, 7.3 Hz, 1H), 7.26 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.09 (ddd, *J* = 0.9, 7.8, 7.8 Hz, 1H), 7.02 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.74 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.10 (t, *J* = 8.3 Hz, 2H), 3.16 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 148.5, 146.9, 134.1, 131.4, 130.9, 129.4, 128.4, 128.2, 126.9, 124.9, 123.9, 123.6, 122.2, 118.8, 118.7, 110.0, 95.4, 88.2, 54.2, 29.1; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{18}N$ ($[M+H]^+$) 296.1434, found 296.1430.

1-(2-(2-(4-Chlorophenyl)ethynyl)phenyl)indoline (3h): it was isolated by PTLC (hexane/DCM = 10/1). The title compound was obtained as brown oil (62.8 mg, 63%); ^{1}H NMR δ 7.56 (dd, *J* = 1.6, 7.7 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.29-7.35 (m, 1H), 7.07-7.16 (m, 3H), 7.17-7.26 (m, 3H), 7.02 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.75 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.08 (t, *J* = 8.5 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 148.3, 146.9, 134.2, 133.9, 132.6, 130.8, 129.6, 128.7, 126.8, 124.8, 123.8, 122.2, 122.0, 118.8, 118.2, 109.9, 94.4, 89.1, 54.2, 29.0; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{17}{}^{35}ClN$ ($[M+H]^+$) 330.1044, found 330.1044.

1-(2-(2-(3-Chlorophenyl)ethynyl)phenyl)indoline (3i): it was isolated by flash column chromatography (hexane/EtOAc = 40/1). The title compound was obtained as brown oil (108.9 mg, 79%); ^{1}H NMR δ 7.55 (dd, *J* = 1.4, 7.9 Hz, 1H), 7.39 (dd, *J* = 1.0, 8.2 Hz, 1H), 7.31 (ddd, *J* = 1.7, 7.3, 7.3 Hz, 1H), 7.15-7.24 (m, 4H), 7.07-7.12 (m, 2H), 7.02 (dd, *J* = 7.7, 7.7 Hz, 1H), 6.76 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 4.08 (t, *J* = 8.4 Hz, 2H), 3.16 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 148.3, 147.1, 134.2, 134.1, 131.3, 130.9, 129.8, 129.6, 129.5, 128.5, 126.9, 125.4, 125.0, 123.9, 122.3, 119.0, 118.1, 110.0, 94.2, 89.5, 54.3, 29.2; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{17}{}^{35}ClN$ ($[M+H]^+$) 330.1044, found 330.1044.

1-(2-(2-(4-Trifluoromethylphenyl)ethynyl)phenyl)indoline (3j): it was isolated by flash column chromatography (hexane/EtOAc = 10/1). The title compound was obtained yellow solid (59.6 mg, 59%); mp 86-87 °C; 7.58 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.39 (dd, *J* = 1.1, 8.4 Hz, 1H), 7.34 (ddd, *J* = 1.7, 7.4, 7.4 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 6.3 Hz, 1H), 7.08-7.14 (m, 1H), 7.02 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.76 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 4.09 (t, *J* = 8.5 Hz, 2H), 3.17 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 148.2, 147.1, 134.1, 131.6, 130.9, 130.0, 129.9, 129.7, 127.4 (q, *J* = 1.68 Hz), 126.8, 125.2 (q, *J* = 3.83 Hz), 124.9, 123.9, 122.2, 119.0, 117.8, 110.0, 94.2, 90.6, 54.3, 29.1; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}F_3N$ ($[M+H]^+$) 364.1308, found 364.1305.

1-(2-(2-(1-Naphthyl)ethynyl)phenyl)indoline (3k): it was isolated by flash column chromatography (hexane/EtOAc = 40/1). The title compound was obtained as brown oil (72.4 mg, 33%); ^{1}H NMR δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 8.8, 8.8 Hz, 2H), 7.70 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.52 (dd, *J* = 1.0, 7.2 Hz, 1H), 7.30-7.46 (m, 5H), 7.22 (dd, *J* = 1.1, 7.5 Hz, 1H), 7.14 (ddd, *J* = 1.3, 7.4, 7.4 Hz, 1H), 7.02 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.71-6.77 (m, 2H), 4.11 (t, *J* = 8.4 Hz, 2H), 3.17 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 149.0, 146.8, 134.1, 133.3, 133.3, 130.8, 130.3, 129.6, 128.7, 128.2, 127.0, 126.8, 126.4, 125.3, 124.9, 124.3,

122.5, 121.3, 119.6, 118.9, 109.7, 93.4, 92.9, 54.3, 29.2 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI, positive): *m/z* calcd. for $C_{26}H_{20}N$ ($[M+H]^+$) 346.1590, found 346.1587.

1-(2-(2-(4-Phenylphenyl)ethynyl)phenyl)indoline (3l): it was isolated by flash column chromatography (hexane/EtOAc = 40/1). The title compound was obtained as white solid (30.5 mg, 12%); mp 160-161 °C; ^{1}H NMR δ 7.55-7.61 (m, 3H), 7.49-7.53 (m, 2H), 7.40-7.45 (m, 3H), 7.28-7.36 (m, 4H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.11 (ddd, *J* = 1.2, 7.4, 7.4 Hz, 1H), 7.04 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.76 (ddd, *J* = 0.9, 7.4, 7.4 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.12 (t, *J* = 8.4 Hz, 2H), 3.18 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 148.5, 146.9, 140.9, 140.5, 134.1, 131.8, 130.9, 129.4, 129.0, 127.7, 127.1, 127.1, 126.9, 124.9, 123.9, 122.5, 122.2, 118.8, 118.7, 110.0, 95.4, 89.0, 54.3, 29.1; HRMS (ESI, positive): *m/z* calcd. for $C_{28}H_{22}N$ ($[M+H]^+$) 372.1747, found 372,1747.

1-(2-Ethynylphenyl)indoline (3m): it was isolated by flash column chromatography (hexane/EtOAc = 30/1). The title compound was obtained as brown solid (60.6 mg, 68%); mp 43-44 °C; ^{1}H NMR δ 7.55 (dd, *J* = 1.6, 7.9 Hz, 1H), 7.42 (dd, *J* = 1.0, 8.5 Hz, 1H), 7.28-7.31 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.07 (ddd, *J* = 1.1, 7.4, 7.4 Hz, 1H), 7.02 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.74 (ddd, *J* = 1.0, 7.3, 7.3 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 4.05 (t, *J* = 8.6 Hz, 2H), 3.27 (s, 1H), 3.15 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 148.7, 148.0, 135.0, 130.9, 129.9, 126.9, 125.0, 124.0, 122.0, 119.0, 118.0, 110.0, 82.6, 82.2, 54.2, 29.1; HRMS (ESI, positive): *m/z* calcd. for $C_{16}H_{14}N$ ($[M+H]^+$) 220.1121, found 220.1119.

6-Fluoro-1-(2-(2-(4-methylphenyl)ethynyl)phenyl)indoline (3n): it was isolated by flash column chromatography (hexane/EtOAc = 5/1). The title compound was obtained as brown oil (23.4 mg, 18%); ^{1}H NMR δ 7.57 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.38 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.32 (ddd, *J* = 1.6, 7.3, 8.1 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.14 (ddd, *J* = 1.3, 7.6, 7.6 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.00-7.06 (m, 1H), 6.39 (ddd, *J* = 2.3, 8.0, 9.3 Hz, 1H), 6.34 (dd, *J* = 2.3, 10.5 Hz, 1H), 4.12 (t, *J* = 8.4 Hz, 2H), 3.11 (t, *J* = 8.4, 2H), 2.33 (s, 3H); ^{13}C NMR δ 163.1 (d, *J* = 240.2 Hz), 150.5 (d, *J* = 11.9 Hz), 145.8, 138.6, 134.1, 131.4, 129.3, 129.2, 125.9 (d, *J* = 2.4 Hz), 124.9 (d, *J* = 10.4 Hz), 124.7, 122.9, 120.4, 119.5, 104.4 (d, *J* = 22.7 Hz), 97.7 (d, *J* = 27.7 Hz), 95.8, 87.1, 55.0, 28.3, 21.6; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{19}FN$ ($[M+H]^+$) 328.1496, found 328.1494.

4-Methoxy-1-(2-(2-(4-methylphenyl)ethynyl)phenyl)indoline (3o): it was isolated by flash column chromatography (hexane). The title compound was obtained as brown oil (77.1 mg, 54%); ^{1}H NMR δ 7.55 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.41 (dd, *J* = 0.4, 8.2 Hz, 1H), 7.26 (ddd, *J* = 1.5, 7.2, 8.0 Hz, 1H), 7.19-7.24 (m, 2H), 7.05-7.10 (m, 3H), 7.00 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 8.2 Hz, 1H), 4.13 (t, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 3.11 (t, *J* = 8.6 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR δ 156.6, 150.4, 147.1, 138.4, 134.0, 131.3, 129.2, 129.1, 128.3, 123.9, 122.6, 120.6, 119.1, 117.3, 103.9, 101.8, 95.3, 87.5, 55.4, 54.6, 26.1, 21.6; HRMS (ESI, positive): *m/z* calcd. for $C_{24}H_{22}NO$ ($[M+H]^+$) 340.1696, found 340.1696.

1-(2-(Hept-1-yn-1-yl)phenyl)indoline (3p): it was isolated by flash chromatography (hexane/EtOAc = 10/1). The title compound was obtained as brown oil; ^{1}H NMR δ 7.45 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.36 (dd, *J* = 0.9, 8.1 Hz, 1H), 7.23 (ddd, *J* = 1.6, 7.3, 7.3 Hz, 1H), 7.14 (dd, *J* = 0.7, 7.3 Hz, 1H), 6.97-7.07 (m, 2H), 6.70 (ddd, *J* = 1.0, 7.3, 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.02 (t, *J* = 8.4 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 2H), 2.33 (t, *J* = 8.4 Hz, 2H), 1.46 (quin, *J* = 7.3 Hz, 2H), 1.22-1.36 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 148.9, 146.9, 134.1, 130.7, 128.5, 126.8, 124.8, 124.0, 122.3, 120.1, 118.5, 109.8, 96.4, 79.0, 54.0, 31.2, 29.0, 28.4, 22.4, 19.8, 14.1; HRMS (ESI, positive): *m/z* calcd. for $C_{21}H_{24}N$ ($[M+H]^+$) 290.1903, found 290.1901.

1-(3-(2-(4-Methylphenyl)ethynyl)pyridin-2-yl)indoline (3q): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as white solid (75.1 mg, 48%); mp 93-94 °C; ^{1}H NMR δ 8.26 (dd, *J* = 1.9, 4.8 Hz, 1H), 7.79 (dd, *J* = 2.0, 7.7 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.15-7.22 (m, 3H), 7.07-7.11 (m, 3H), 6.90 (dd, *J* = 4.8, 7.6 Hz, 1H), 6.85 (ddd, *J* = 0.9, 7.4, 7.4 Hz, 1H), 4.38 (t, *J* = 8.3 Hz, 2H), 3.16 (t, *J* = 8.3 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR δ 156.7, 147.4, 145.5, 142.5, 138.8, 131.8, 131.2, 129.3, 126.5, 124.6, 120.6, 120.2, 116.7, 113.7, 109.3, 97.3, 86.4, 52.8, 29.1, 21.7; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{19}N_2$ ($[M+H]^+$) 311.1543, found 311.1543.

6-(4-Methylphenyl)indolo[1,7-*ab*][1]benzazepine (5a): it was isolated by PTLC (hexane/toluene = 10/1). The title compound was obtained as yellow solid (14.1 mg, 93%); mp 108-111 °C; ^{1}H NMR δ 7.39 (d, *J* = 3.7 Hz, 1H), 7.15 (m, 5H), 7.06 (dd, *J* = 7.2 Hz, 1H), 6.86 (m, 3H), 6.70 (dd, *J* = 7.7, 7.7 Hz, 1H), 6.50 (d, *J* = 3.5 Hz, 1H), 6.34 (dd, *J* = 1.1, 7.6 Hz, 1H), 6.02 (s, 1H), 2.37 (s, 3H); ^{13}C NMR δ 143.7, 143.2, 141.6, 140.6, 137.3, 133.6, 131.8, 131.7, 130.2, 129.7, 129.1, 129.0, 127.7, 125.6, 125.1, 124.8, 122.0, 120.9, 120.8, 106.5, 21.4; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}N$ ($[M]^+$) 307.1356, found 307.1356.

6-(3-Methylphenyl)indolo[1,7-*ab*][1]benzazepine (5b): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as yellow oil (15.8 mg, 98%); ^{1}H NMR δ 7.41 (d, *J* = 3.6 Hz, 1H), 7.26 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.12-7.18 (m, 2H), 7.06-7.12 (m, 3H), 6.82-6.92 (m, 3H), 6.72 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.51 (d, *J* = 3.5 Hz, 1H), 6.32 (dd, *J* = 0.9, 7.5 Hz, 1H), 6.02 (s, 1H), 2.37 (s, 3H); ^{13}C NMR δ 143.5, 143.3, 143.2, 141.4, 138.0, 133.5, 131.7, 131.5, 130.2, 129.6, 129.5, 128.2, 128.1, 127.6, 126.0, 125.5, 125.0, 124.7, 121.9, 120.7, 120.7, 106.3, 21.5; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}N$ ($[M]^+$) 307.1356, found 307.1356.

6-(2-Methylphenyl)indolo[1,7-*ab*][1]benzazepine (5c): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as yellow oil (13.8 mg, 87%); ^{1}H NMR δ 7.41 (d, *J* = 3.5 Hz, 1H), 7.23-7.30 (m, 3H), 7.16-7.19 (m, 1H), 7.06-7.13 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 1.0, 7.4 Hz, 1H), 6.78 (dd, *J* = 1.4, 7.7 Hz, 1H), 6.63 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.50 (d, *J* = 3.5 Hz, 1H), 6.02 (dd, *J* = 0.7, 7.4 Hz, 1H), 5.89 (s, 1H), 2.30 (s, 3H); ^{13}C NMR δ 142.6, 142.6, 141.4, 136.6, 133.8, 131.7,

131.5, 130.5, 130.2, 129.6, 129.5, 127.6, 127.3, 126.2, 125.2, 125.2, 123.8, 122.2, 120.9, 120.6, 106.3, 19.6 (a pair of peaks at the aromatic reagion was overlapped.); HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}N$ ($[M]^+$) 307.1356, found 307.1356.

6-(4-Methoxylphenyl)indolo[1,7-*ab*][1]benzazepine (5d): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as yellow oil (13.8 mg, 86%); ^{1}H NMR δ 7.41 (d, *J* = 3.6 Hz, 1H), 7.18-7.23 (m, 2H), 7.17 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.08 (ddd, *J* = 1.9, 7.1, 8.1 Hz, 1H), 6.83-6.93 (m, 5H), 6.73 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.37 (dd, *J* = 0.7, 7.6 Hz, 1H), 6.04 (s, 1H), 3.84 (s, 3H); ^{13}C NMR δ 159.0, 143.6, 142.7, 141.4, 135.7, 133.3, 131.6, 131.5, 130.1, 130.0, 129.6, 127.7, 125.6, 125.0, 124.7, 121.8, 120.8, 120.7, 113.7, 106.4, 55.3; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}NO$ ($[M]^+$) 323.1305, found 323.1305.

6-(3-Methoxylphenyl)indolo[1,7-*ab*][1]benzazepine (5e): it was isolated by PTLC (hexane/toluene = 10/1). The title compound was obtained as yellow oil (15.6 mg, 96%); ^{1}H NMR δ 7.42 (d *J* = 3.4 Hz, 1H), 7.29 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.08-7.13 (m, 1H), 6.84-6.92 (m, 6H), 6.72 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.52, (d, *J* = 3.6 Hz, 1H), 6.35 (d, *J* = 7.3 Hz, 1H), 6.05 (s, 1H), 3.81 (s, 3H); ^{13}C NMR δ 159.8, 144.9, 143.6, 143.1, 141.6, 133.7, 131.9, 131.7, 130.4, 129.6, 129.5, 127.5, 125.6, 125.1, 124.8, 122.1, 121.5, 120.9, 120.9, 114.6, 113.2, 106.5, 55.4; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}NO$ ($[M]^+$) 323.1305, found 323.1306.

6-(2-Methoxylphenyl)indolo[1,7-*ab*][1]benzazepine (5f): it was isolated by PTLC (hexane/toluene = 3/1). The title compound was obtained as yellow solid (14.3 mg, 88%); mp 127-128 °C; ^{1}H NMR δ 7.39 (d, *J* = 3.6 Hz, 1H), 7.33 (ddd, *J* = 1.8, 7.8, 7.8 Hz, 1H), 7.20 (dd, *J* = 1.8, 7.4 Hz, 1H), 7.04-7.12 (m, 2H), 7.00 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.78 (dd, *J* = 1.6, 7.7 Hz, 1H), 6.64 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.48 (d, *J* = 3.5 Hz, 1H), 6.11 (d, *J* = 7.4 Hz, 1H), 5.94 (s, 1H), 3.73 (s, 3H); ^{13}C NMR δ 157.4, 142.4, 141.5, 140.1, 133.9, 132.3, 132.2, 131.5, 130.9, 130.4, 129.5, 129.0, 127.3, 125.1, 125.0, 123.7, 122.0, 121.0, 120.7, 120.4, 111.3, 106.2, 55.9; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{17}NNaO$ ($[M+Na]^+$) 346.1202, found 346.1203.

6-Phenylindolo[1,7-*ab*][1]benzazepine (5g): it was isolated by PTLC (hexane/DCM = 5/1). The title compound was obtained as yellow solid (14.6 mg, >99%); mp 136-137 °C; ^{1}H NMR δ 7.42 (d, *J* = 3.5 Hz, 1H), 7.32-7.40 (m, 3H), 7.28-7-31 (m, 2H), 7.17 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.08-7.12 (m, 1H), 6.85-6.93 (m, 3H), 6.72 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H), 6.32 (dd, *J* = 0.9, 7.1 Hz, 1H), 6.04 (s, 1H); ^{13}C HMR δ 143.6, 143.4, 143.2, 141.5, 133.6, 132.0, 131.6, 130.3, 129.6, 129.1, 128.4, 127.6, 127.5, 125.6, 125.1, 124.8, 122.0, 120.8, 106.5 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{15}N$ ($[M]^+$) 293.1199, found 293.1198.

6-(4-Chlorophenyl)indolo[1,7-*ab*][1]benzazepine (5h): it was isolated by PTLC (hexane/DCM = 5/1). The title compound was obtained as yellow solid (14.2 mg, 88%); mp 126-127 °C; ^{1}H NMR δ 7.42 (d, *J* =

3.5 Hz, 1H), 7.33-7.37 (m, 2H), 7.20-7.24 (m, 2H), 7.17 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.11 (ddd, *J* = 1.7, 7.6, 8.1 Hz, 1H), 6.91 (ddd, *J* = 1.0, 7.4, 7.4 Hz, 1H), 6.84-6.89 (m, 2H), 6.72 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 6.27 (dd, *J* = 0.6, 7.3 Hz, 1H), 6.01 (s, 1H); ^{13}C NMR δ 143.7, 142.1, 141.9, 141.6, 133.7, 133.4, 132.3, 131.8, 130.6, 130.5, 129.4, 128.7, 127.3, 125.7, 125.2, 124.6, 122.1, 121.1, 121.0, 106.6; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{14}{}^{35}ClN$ ($[M]^+$) 327.0809, found 327.0810.

6-(3-Chlorophenyl)indolo[1,7-*ab*][1]benzazepine (5i): it was isolated by PTLC (hexane/DCM = 5/1). The title compound was obtained as yellow oil (16.6 mg, >99%); ^{1}H NMR δ 7.40 (d, *J* = 3.7 Hz, 1H), 7.26-7.34 (m, 3H), 7.13-7.20 (m, 2H), 7.10 (dd, *J* = 1.7, 7.4 Hz, 1H), 6.82-6.92 (m, 3H), 6.73 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.52 (d, *J* = 3.8 Hz, 1H), 6.26 (d, *J* = 7.4 Hz, 1H), 6.01 (s, 1H); ^{13}C NMR δ 145.2, 143.6, 141.9, 141.6, 134.4, 133.8, 132.5, 131.8, 130.7, 129.8, 129.3, 129.2, 127.7, 127.4, 127.2, 125.7, 125.2, 124.6, 122.1, 121.1, 121.0, 106.6; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{14}{}^{35}ClN$ ($[M]^+$) 327.0809, found 327.0810.

6-(4-Trifluoromethylphenyl)indolo[1,7-*ab*][1]benzazepine (5j): it was isolated by PTLC (hexane/DCM = 10/1). The title compound was obtained as yellow solid (9.1 mg, 51%); mp 119-120 °C; ^{1}H NMR δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.38-7.44 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (ddd, *J* = 1.7, 7.7, 7.7 Hz, 1H), 6.84-6.95 (m, 3H), 6.73 (ddd, *J* = 2.0, 7.6, 7.6 Hz, 1H), 6.52-6.55 (m, 1H), 6.22 (d, *J* = 7.4 Hz, 1H), 6.01 (s, 1H); ^{13}C NMR δ 147.1 (q, *J* = 1.44 Hz), 143.7, 142.0, 141.6, 133.8, 132.7, 131.9, 130.8, 129.8, 129.5, 129.2, 127.1, 125.8, 125.7, 125.5 (q, *J* = 3.83 Hz), 125.2, 124.5, 122.1, 121.2, 121.0, 106.6; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{14}F_3N$ ($[M]^+$) 361.1073, found 361.1073.

6-(1-Naphthyl)indolo[1,7-*ab*][1]benzazepine (5k): it was isolated by PTLC (hexane/DCM = 5/1). The title compound was obtained as yellow solid (17.0 mg, 98%); mp 138-140 °C; ^{1}H NMR δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.86 (dd, *J* = 8.5, 8.5 Hz, 2H), 7.35-7.54 (m, 5H), 7.06-7.15 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.88 (ddd, *J* = 1.9, 7.4, 7.4 Hz, 1H), 6.78 (dd, *J* = 1.5, 7.6 Hz, 1H), 6.49-.6.54 (m, 2H), 6.06 (s, 1H), 5.96 (d, *J* = 7.3, 1H); ^{13}C NMR δ 142.2, 141.4, 141.3, 140.6, 133.8, 133.7, 132.9, 132.1, 131.4, 130.5, 129.3, 128.2, 127.8, 126.5, 126.2, 126.2, 125.9, 125.8, 125.1, 125.1, 124.6, 122.1, 120.8, 120.5, 106.2 (a pair of peaks at the aromatic region was overlapped): *m/z* calcd. for $C_{26}H_{17}N$ ($[M]^+$) 343.1356, found 343.1356.

6-(4-Phenylphenyl)indolo[1,7-*ab*][1]benzazepine (5l): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as yellow solid (14.0 mg, 76%); mp 163-164 °C; ^{1}H NMR δ 7.59-7.67 (m, 4H), 7.42-7.49 (m, 3H), 7.34-7.40 (m, 3H), 7.19 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.12 (ddd, *J* = 2.1, 7.3, 7.9 Hz, 1H), 6.86-6.95 (m, 3H), 6.76 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.54 (d, *J* = 3.4 Hz, 1H), 6.42 (dd, *J* = 0.8, 7.4 Hz, 1H), 6.11 (s, 1H); ^{13}C NMR δ 143.7, 142.9, 142.5, 141.6, 140.9, 140.4, 133.6, 132.0, 132.0, 131.7, 130.4, 129.6, 129.5, 128.9, 127.5, 127.4, 127.2, 125.7, 125.1, 124.8, 122.0, 120.9, 120.9, 106.5; HRMS (ESI, positive): *m/z* calcd. for $C_{28}H_{19}N$ ($[M]^+$) 369.1512, found 369.1514.

5-Fluoro-6-(4-methylphenyl)indolo[1,7-*ab*][1]benzazepine (5n): it was isolated by PTLC

(hexane/toluene = 10/1). The title compound was obtained as yellow solid (12.3 mg, 71%); mp 119-121 °C; ^{1}H NMR δ 7.40 (d, *J* = 3.5 Hz, 1H), 7.20-7.25 (m, 1H), 7.11-7.17 (m, 5H), 7.03 (dd, *J* = 1.9, 7.6 Hz, 1H), 7.00 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.66 (dd, *J* = 8.4, 11.6 Hz, 1H), 6.56 (d, *J* = 3.5 Hz, 1H), 6.36 (s, 1H), 2.36 (s, 3H); ^{13}C NMR 157.6 (d, *J* = 247.46 Hz), 147.7 (d, *J* = 7.75 Hz), 142.5, 141.4 (d, *J* = 3.28 Hz), 139.9, 137.0, 133,3, 132.6, 130.0, 129.5, 128.9, 127.9, 127.5 (d, *J* = 3.28 Hz), 126.7 (d, *J* = 2.68 Hz), 125.1, 121.9, 121.2 (d, *J* = 11.03 Hz), 124.9 (d, *J* = 13.41 Hz), 112.4 (d, *J* = 25.63 Hz), 107.0, 21.3; HRMS (ESI, positive): *m/z* calcd. for $C_{23}H_{16}FN$ ($[M]^+$) 325.1261, found 325.1262.

3-Methoxy-6-(4-methylphenyl)indolo[1,7-*ab*][1]benzazepine (5o): it was isolated by PTLC (hexane/toluene = 10/1). The title compound was obtained as yellow oil (8.0 mg, 62%); ^{1}H NMR δ 7.32 (d, *J* = 3.5 Hz, 1H), 7.17-7.19 (m, 4H), 7.05 (dd, *J* = 1.7, 7.5 Hz, 1H), 6.86-6.91 (m, 2H), 6.81 (dd, *J* = 1.6, 7.6 Hz, 1H), 6.61 (d, 3.5 Hz, 1H), 6.27 (d, 8.3 Hz, 1H), 6.12 (d, 8.4 Hz, 1H), 5.86 (s, 1H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR δ 153.2, 144.3, 143.1, 140.9, 140.9, 137.2, 133.4, 130.1, 129.7, 129.3, 129.1, 129.0, 125.9, 125.3, 124.3, 122.5, 121.3, 120.7, 103.3, 101.0, 55.4, 21.4; HRMS (ESI, positive): *m/z* calcd. for $C_{24}H_{19}NO$ ($[M]^+$) 337.1461, found 337.1462.

6-Pentyl-1,2-dihydrobenzo[6,7]azepino[3,2,1-*hi*]indole (4p): it was isolated by flash chromatography (hexane/EtOAc = 10/1). The title compound was obtained as brown oil; ^{1}H NMR δ 7.02-6.91 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.68-6.76 (m, 3H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.17 (s, 1H), 3.78 (t, *J* = 8.2 Hz, 2H), 2.94 (t, *J* = 8.2 Hz, 2H), 2.39 (t, *J* = 7.8 Hz, 2H), 1.48-1.57 (m, 2H), 1.30-1.40 (m, 4H) 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 141.2, 132.5, 131.3, 130.5, 130.0, 128.9, 125.5, 124.6, 122.6, 121.9, 117.8, 115.5, 49.7, 37.0, 31.9, 28.8, 28.5, 22.7, 14.2 (two pairs of peaks at the aromatic region were overlapped); HRMS (ESI, positive): *m/z* calcd. for $C_{21}H_{24}N$ ($[M+H]^+$) 290.1903, found 290.1898.

6-(4-Methylphenyl)pyrido[3',2':6,7]azepino[3,2,1-*hi*]indoline (4q): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as yellow solid (30.5 mg, 97%); mp 130 °C (decomp.); ^{1}H NMR δ 7.84 (dd, *J* = 1.7, 4.9 Hz, 1H), 7.13-7.20 (m, 4H), 6.92 (dd, *J* = 1.3, 7.3 Hz, 2H), 6.50-6.60 (m, 2H), 6.36 (d, *J* = 7.8, 1H), 5.94 (s, 1H), 4.19 (dd, *J* = 8.4 Hz, 2H), 2.91 (t, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR δ 160.0, 151.3, 146.7, 143.4, 139.9, 138.9, 137.5, 133.8, 130.2, 129.4, 129.1, 128.8, 127.7, 125.9, 124.3, 122.5, 117.1, 47.3, 27.6, 21.3; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{19}N_2$ ($[M+H]^+$) 310.1541, found 310.1543.

1-(2-(2-(4-Methylphenyl)ethynyl)phenyl)-1,2,3,4-tetrahydroquinoline (6): it was isolated by flash column chromatography (hexane/toluene = 5/1). The title compound was obtained as white solid (66.6 mg, 57%); mp 81-83 °C; ^{1}H NMR δ 7.58 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.27-7.35 (m, 2H), 7.18 (ddd, *J* = 1.7, 7.7, 7.7 Hz, 1H), 7.12-7.15 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.03 (dd, *J* = 1.2, 7.5 Hz, 1H), 6.89 (ddd, *J* = 1.6, 7.0, 7.0 Hz, 1H), 6.65 (ddd, *J* = 1.1, 7.3, 7.3 Hz, 1H), 6.40 (dd, 0.9, 8.0 Hz, 1H) 3.69 (m, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 3H), 2.04-2.11 (m, 2H); ^{13}C NMR δ 149.8, 145.0, 138.4, 133.9, 131.3, 123.0,

129.4, 129.1, 128.4, 126.9, 125.4, 123.0, 122.4, 120.5, 117.9, 115.1, 94.7, 85.9, 51.2, 28.1, 22.6, 21.8; HRMS (ESI, positive): *m/z* calcd. for $C_{24}H_{22}N$ ($[M+H]^+$) 324.1747, found 324.1745.

7-(4-Methylphenyl)-2,3-dihydrobenzo[6,7]azepino[3,2,1-*ij*]quinoline (7): it was isolated by PTLC (hexane/EtOAc = 10/1). The title compound was obtained as yellow solid (15.3 mg, 94%); mp 68-70 °C; ^{1}H NMR δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.12-7.22 (m, 4H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.92-7.02 (m, 2H), 6.84 (s, 1H), 6.79 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 4.00-4.08 (m, 1H), 3.53-3.63 (m, 1H), 2.90-3.00 (m, 2H), 2.39-2.50 (m, 1H), 2.37 (s, 3H), 1.96-2.05 (m, 1H); ^{13}C NMR δ 153.5, 150.7, 144.8, 141.4, 137.1, 134.6, 133.1, 131.0, 130.1, 130.1, 129.0, 129.0, 128.9, 128.9, 128.4, 122.8, 122.6, 117.7, 48.8, 27.1, 21.2, 20.6; HRMS (ESI, positive): *m/z* calcd. for $C_{24}H_{22}N$ ($[M+H]^+$) 324.1747, found 324.1742.

***N*-Methyl-*N*-phenyl-2-(2-(4-methylphenyl)ethynyl)benzenamine (8):** it was isolated by flash column chromatography (hexane/toluene = 3/1). The title compound was obtained as brown oil (99.6 mg, 72%); ^{1}H NMR δ 7.56 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.31 (ddd, *J* = 1.6, 7.5, 8.1 Hz, 1H), 7.13-7.26 (m, 4H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.72-6.80 (m, 3H), 3.36 (s, 3H), 2.30 (s, 3H); ^{13}C NMR δ 150.2, 149.2, 138.4, 133.9, 131.5, 129.5, 129.0, 128.9, 127.7, 125.2, 122.0, 120.3, 118.1, 114.9, 95.0, 86.7, 39.9, 21.6; HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{20}N$ ($[M+H]^+$) 298.1590, found 298.1588.

5-Methyl-10-(4-methylphenyl)dibenz[*b*,*f*]azepine (9): it was isolated by PTLC (hexane/toluene = 3/1). The title compound was obtained as yellow solid (12.2 mg, 82%); mp 128-129 °C; ^{1}H NMR δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.21-7.30 (m, 2H), 7.18 (dd, *J* = 0.5, 8.4 Hz, 2H), 7.15 (dd, *J* = 8.1, 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 7.00 (ddd, *J* = 1.1, 7.4, 7.4 Hz, 1H), 6.97 (s, 1H), 6.90 (ddd, *J* = 1.1, 7.9, 7.9 Hz, 1H), 6.87 (dd, *J* = 2.1, 7.7 Hz, 1H), 3.39 (s, 3H), 2.39 (s, 3H); ^{13}C NMR δ 153.9, 153.0, 144.3, 140.9, 137.3, 134.7, 132.9, 130.7, 130.3, 129.6, 129.2, 129.1, 129.0, 128.5, 123.2, 118.8, 117.9, 38.8, 21.3 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI, positive): *m/z* calcd. for $C_{22}H_{20}N$ ($[M+H]^+$) 298.1590, found 298.1590.

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