Au(I)-Catalyzed 6-*endo*-dig Cyclizations of Aromatic 1,5-Enynes to 2-(Naphthalen-2-yl)anilines Leading to Divergent Syntheses of Benzo[*α*]carbazole, Benzo[*c*,*h*]cinnoline and Dibenzo[*i*]phenanthridine Derivatives

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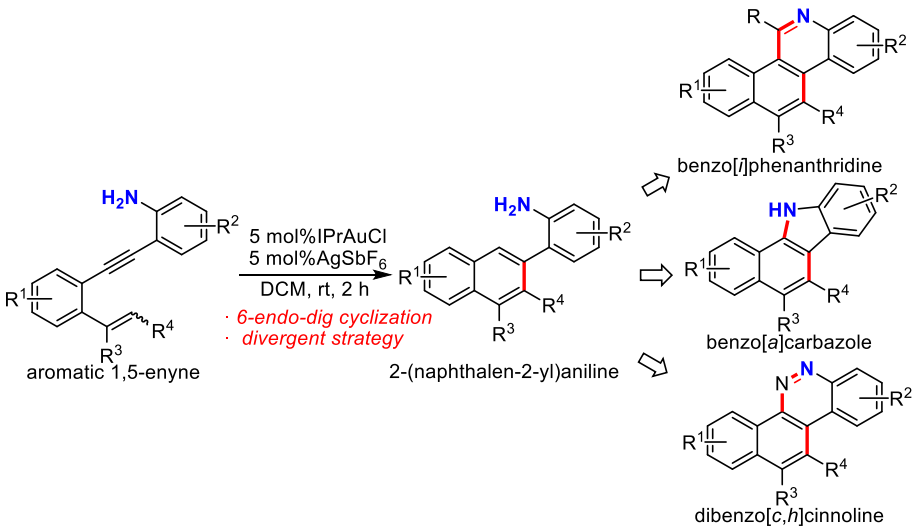
Abstract. A gold(I)-catalyzed 6-*endo*-dig cyclization of aromatic 1,5-enyne was developed to synthesize 2-(naphthalen-2-yl)aniline. The functional group tolerance of this cyclization was examined systematically and a possible mechanism was proposed. The derivatization of 2-(naphthalen-2-yl)aniline was carried out to facile access to benzo[*α*]carbazole, benzo[*c*,*h*]cinnoline and dibenzo[*i*]phenanthridine derivatives in a divergent way.



Introduction

2-(Naphthalen-2-yl)aniline is a significant structural moiety that can be used as a building block in the syntheses of a variety of heterocycles,[1] such as benzo[α]carbazole, benzo[*c*,*h*]cinnoline and dibenzo[*i*]phenanthridine etc. Those heterocycles as privileged structures played pivotal roles in medicinal chemistry,[2] functional organic materials[3] and fluorescent imaging.[4] For example, benzo[*c*,*h*]cinnoline and dibenzo[*i*]phenanthridine derivatives have been identified as topoisomerase I inhibitors with pronounced antitumor activity.[2d] The dibenzo[*i*]phenanthridine derivatives have been developed as a superior probe for NO detection with a novel sensing mechanism.[2b] Benzo[α]carbazole derivatives exhibited antitumor activity against various tumor cell lines.[2a,2c]

A number of synthetic methods for these heterocycles have been developed in an individual fashion.[5] Each method developed so far is limited to access either one of the moieties but never all three. To the best of our knowledge, a unified and divergent synthetic strategy for accessing all of them has never been reported. Herein, a synthetic strategy aiming at the synthesis of 2-(naphthalen-2-yl)aniline, the core structure of those heterocycles was developed based on a gold(I)-catalyzed 6-*endo*-dig cyclization of aromatic 1,5-enynes, which could act as a common intermediate for the

divergent syntheses of these heterocycles.

Transition metal-catalyzed cyclizations of aromatic enynes have become one of the straightforward synthetic strategies in the construction of naphthalene derivatives from simple precursors, due to readily available substrates and mild reaction conditions.[6] Among them, gold-catalyzed cycloisomerizations of aromatic enynes to naphthalenes have drawn much attention recently and a number of elegant pioneering works have been reported up to date[7] including our previous efforts in this field.[7g,7i,7j]

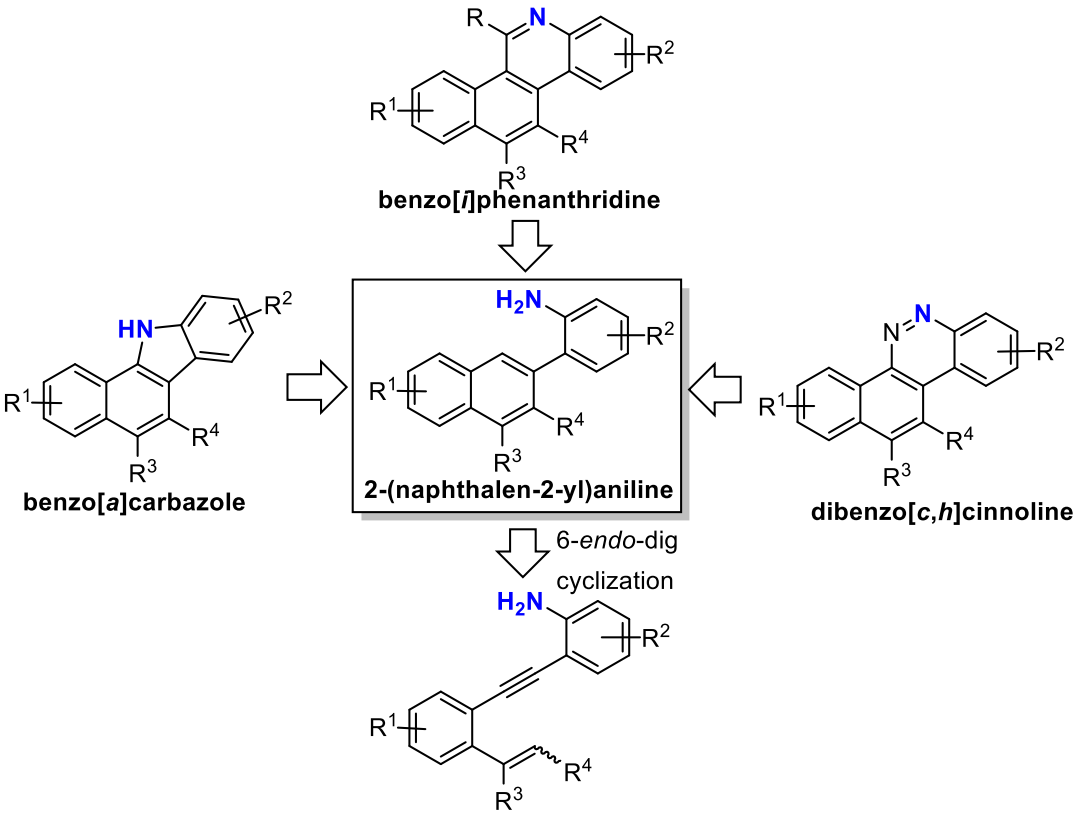


Figure 1. Heterocycles Containing 2-(Naphthalen-2-yl)aniline.

According to the mechanism of cycloisomerization, the reaction of 1,5-enyne substrate could provide the desired naphthalene via a 6-*endo*-dig cyclization or an indene product via a 5-*exo*-dig cyclization. It has been shown by our previous experimental and computational work that the cyclization of aromatic 1,5-enyne substrate with aniline substitution will favor 6-*endo*-dig pathway,

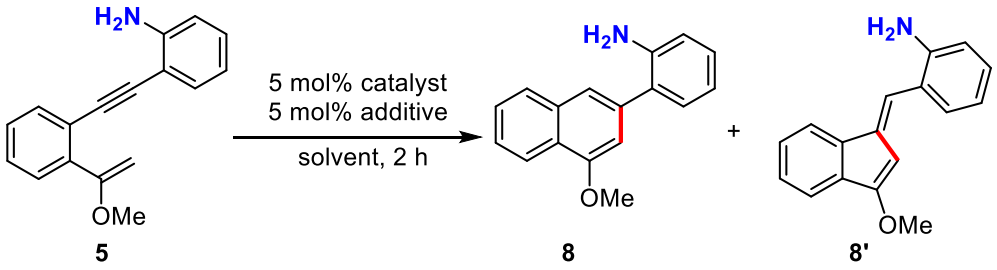
leading to the selective formation of the naphthalene.[7i] It is rationalized that the electron-donating effect of amino group could help to improve the electrophilicity of α-position of the alkyne and stabilize the development of a positive charge at position β of the alkyne upon coordination of the Au^+ complex (Figure 1). The experimental results and a plausible mechanism are presented in the following texts.

Results and Discussion

To evaluate the feasibility of our experimental design, the 1,5-enyne substrate **5** was prepared and subjected to different reaction conditions as listed in Table 1. It was found that triphenylphosphinegold(I) chloride (Ph_3PAuCl) itself was not an effective catalyst to catalyze this transformation (Table 1, entry 1). Examination of several kinds of silver salts illustrated that stirring the substrate **5** with the combination of 5 mol% Ph_3PAuCl and 5 mol% silver hexafluoroantimonate ($AgSbF_6$) in anhydrous dichloromethane (DCM) at room temperature for 2 h gave the desired 6-*endo*-dig product **8** with the highest yield without any 5-*exo*-dig product (Table 1, entries 2-4). Screening of the ligands of the Au(I) catalyst revealed that 5 mol% [1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene] gold (I) chloride (IPrAuCl) combined with 5 mol% $AgSbF_6$ afforded the product **8** with the highest yield of 92% (Table 1, entry 5). An attempt on decreasing the loading of the catalyst to 3 mol% proved unsuccessful, only affording the product in a yield of 78% (Table 1, entry 6). Increasing the loading of the catalyst to 10 mol% did not improve the yield further (Table 1, entry 7). Examination of reaction time revealed that a lower yield was obtained in 1 h and prolonging reaction time was not helpful for the yield improvement (Table 1, entries 8 and 9). Either dropping the temperature to 0 °C or elevating the temperature to 40 °C led to a lower yield (Table 1, entries 10-11). The screening of solvents such as toluene and tetrahydrofuran showed that DCM

remained the optimal solvent for this transformation (Table 1, entries 12-13). The reaction utilizing $AgSbF_6$ as the catalyst did not give any product at all, which proved that gold(I)-catalyst should be the true reactive species (Table 1, entry 14). The control experiment by introducing 2,6-di-*tert*-butylpyridine as the proton scavenger in the IPrAuCl/$AgSbF_6$ system gave the same result with the standard condition, which ruled out the influence of trace amounts of acids on the reaction (Table 1, entry 15). Finally, the optimal reaction conditions were determined as stirring the substrate at the catalysis of 5 mol% IPrAuCl/$AgSbF_6$ in anhydrous DCM at room temperature for 2 h.

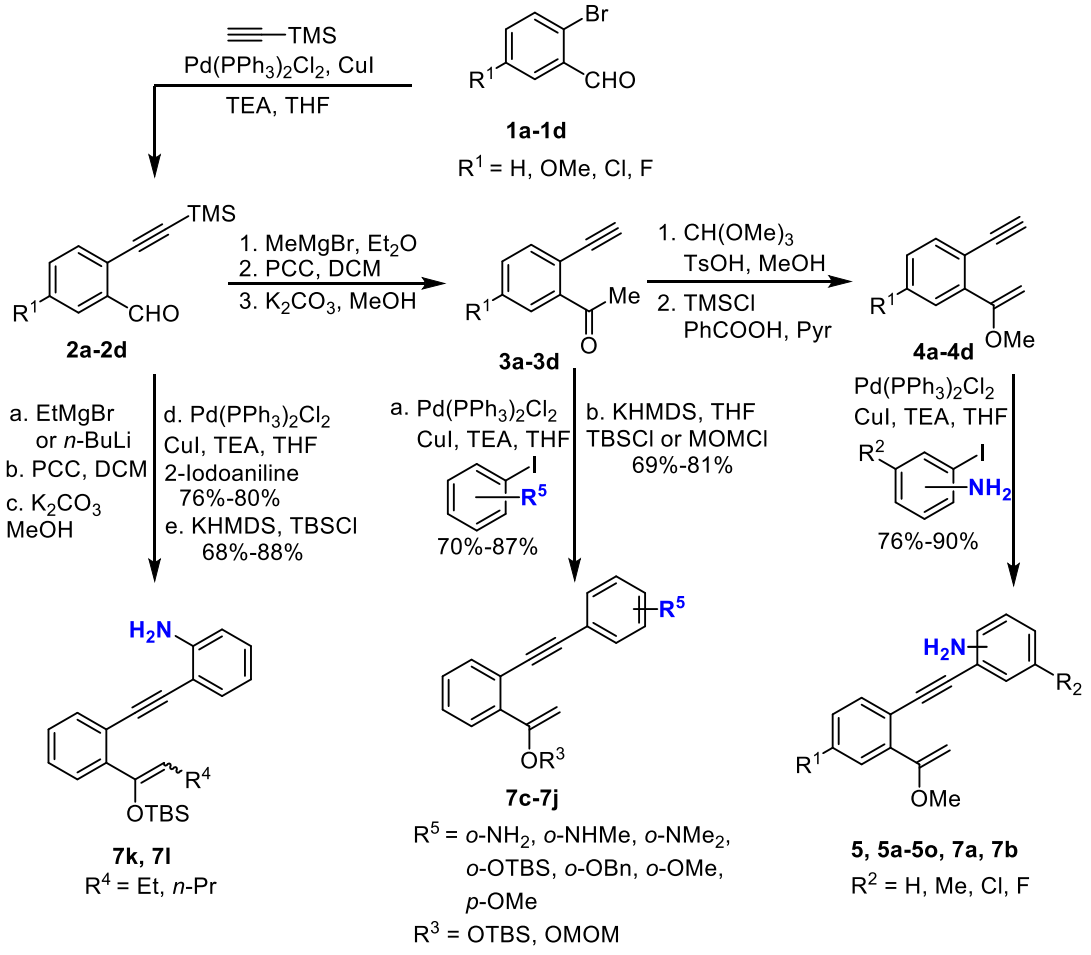
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	additive	T (°C)	yield of **8**(%)	yield of **8'**(%)
1	Ph_3PAuCl	DCM	-	23	0	0
2	Ph_3PAuCl	DCM	AgOTf	23	33	0
3	Ph_3PAuCl	DCM	$AgBF_4$	23	30	0
4	Ph_3PAuCl	DCM	$AgSbF_6$	23	46	0
5	**IPrAuCl**	**DCM**	**$AgSbF_6$**	**23**	**92**	**0**
6	IPrAuCl	DCM	$AgSbF_6$	23	78[b]	0
7	IPrAuCl	DCM	$AgSbF_6$	23	92[c]	0
8	IPrAuCl	DCM	$AgSbF_6$	23	71[d]	0
9	IPrAuCl	DCM	$AgSbF_6$	23	92[e]	0
10	IPrAuCl	DCM	$AgSbF_6$	0	67	0
11	IPrAuCl	DCM	$AgSbF_6$	40	81	0

12	IPrAuCl	toluene	$AgSbF_6$	23	83	0
13	IPrAuCl	THF	$AgSbF_6$	23	87	0
14	-	DCM	$AgSbF_6$	23	0	0
15	IPrAuCl	THF	$AgSbF_6$	23	90[f]	0

[a)] isolated yields. [b)] 3 mol% IPrAuCl and 3 mol% $AgSbF_6$ were used. [c)] 10 mol% IPrAuCl and 10 mol% $AgSbF_6$ were used. [d)] The reaction was run for 1 h. [e)] The reaction was run for 3 h. [f)] 5 mol% 2,6-diterbutylpyridine was added. IPr = [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]



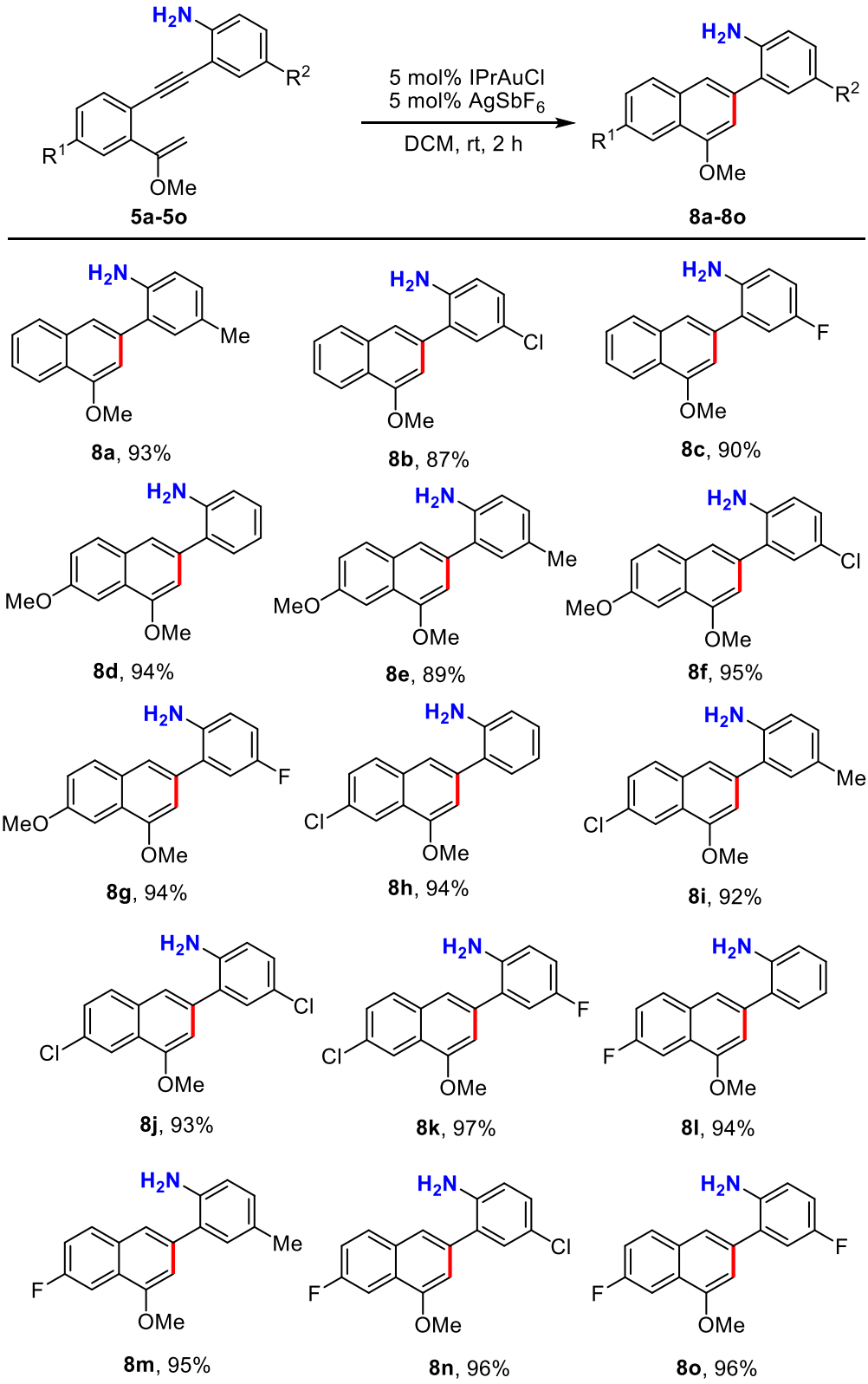
Scheme 1. The Preparation of the Substrates.

With the optimal conditions in hand, we began to synthesize a series of substrates as shown in Scheme 1 to examine the substrate scope.[7i,8] All the substrates were prepared starting from commercially available 2-bromobenzaldehydes **1a-1d**. A Sonogashira coupling reaction of **1a-1d** with (trimethylsilyl)acetylene provided the alkyne-substituted aromatic aldehydes **2a-2d**, which was

converted to alkyne-substituted aromatic ketones **3a-3d** via a three-step functional group transformation. Enolization of ketones **3a-3d** was achieved by a two-step sequence to give enol ethers **4a-4d**, from which the substrates **5a-5o** and **7a-7b** were obtained via a Sonogashira coupling. The substrates **7c-7j** were synthesized from ketones **3a-3d** via a two-step reaction and the substrates **7k-7l** were prepared from alkyne-substituted aromatic aldehydes **2a-2d** via a five-step functional group transformation (Scheme 1).

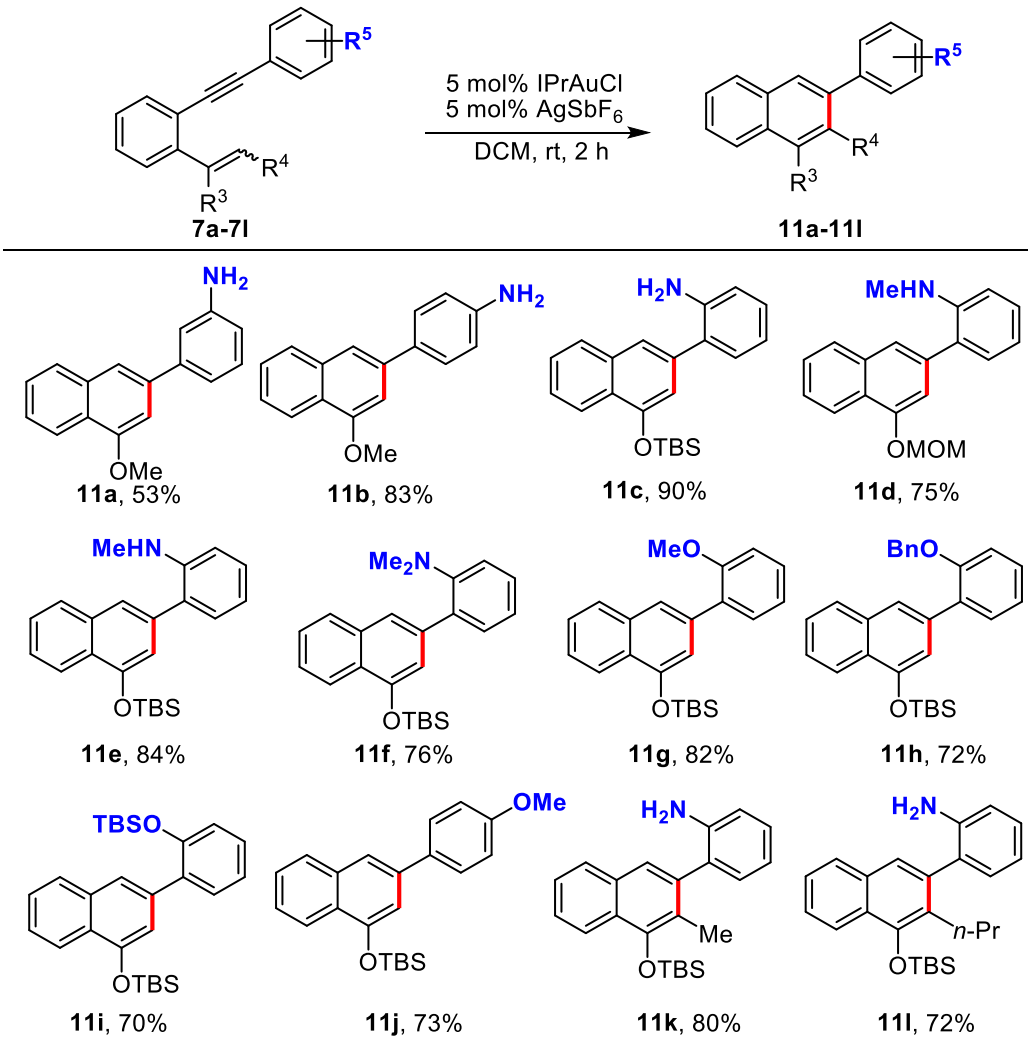
Next, the functional group tolerances of this reaction were examined with the synthetic substrates **5a-5o**. The reaction exhibited an excellent functional group tolerance as shown in Scheme 2. All the examined substrates provided the desired 6-*endo*-dig cyclization products under the standard reaction conditions with excellent yields regardless of the substrates with electron-donating or electron-withdrawing substitutions on both aromatic rings.

In the following exploration of substrate scope, to examine the influence of electronic effect of the amino group, the substrate **7a** with meta-amino group substitution and substrate **7b** with para-amino group substitution were examined under the standard condition. The yield of the substrate **7a** with meta-amino group substitution was much lower than that of the substrate **7b** with para-amino group substitution (Scheme 3, **7a**-**7b**). The substrates with methoxymethyl (MOM)-ether and silyl ether could tolerate the reaction conditions well and provided moderate to excellent yields (Scheme 3, **7c**-**7d**). The steric effect of the substitution was also examined by synthesizing the substrates bearing amino, methylamino and dimethylamino groups, which showed that more sterically hindered substitutions led to lower yields (Scheme 3, **7d**-**7f**). The substrates with *ortho*-methoxy, *ortho*-benzyloxy and *ortho*-silyloxy substitutions could also give the products with good yields. The same patten was observed that when the substitutions were more sterically hindered, the lower yields

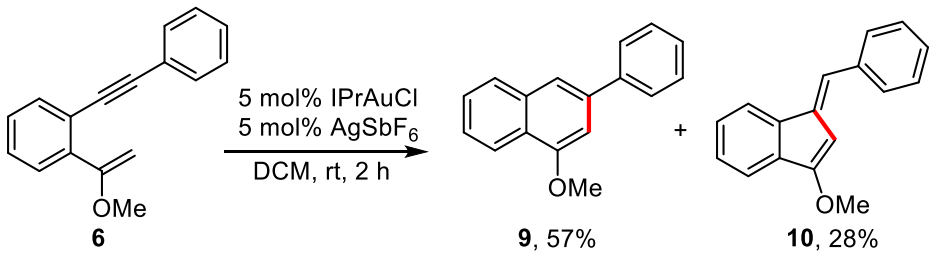


Scheme 2. Functional Group Tolerance of 1,5-Enyne with Aniline Substitution in the Au(I)-Catalyzed 6-*endo*-dig Cyclization.

were obtained (Scheme 3, **7g-7i**). The yield of the substrate bearing *ortho*-methoxy substitution was better than that of the substrate bearing *para*-methoxy substitution (Scheme 3, **7g**, **7j**). The substrates with alkyl substituted alkene were also examined under the reaction condition and acceptable yields were obtained (Scheme 3, **7k-7l**).

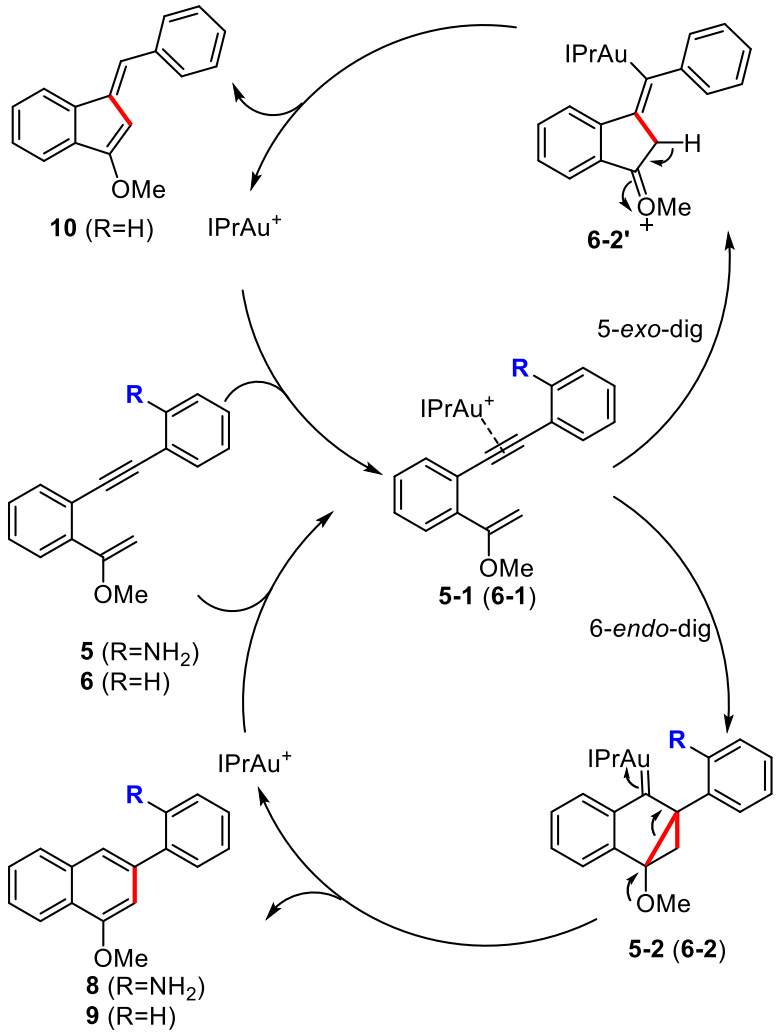


Scheme 3. Further Substrate Scope in the Au(I)-Catalyzed 6-*endo*-dig Cyclization.



Scheme 4. Au(I)-Catalyzed Cyclization of Amino-Free Substrate.

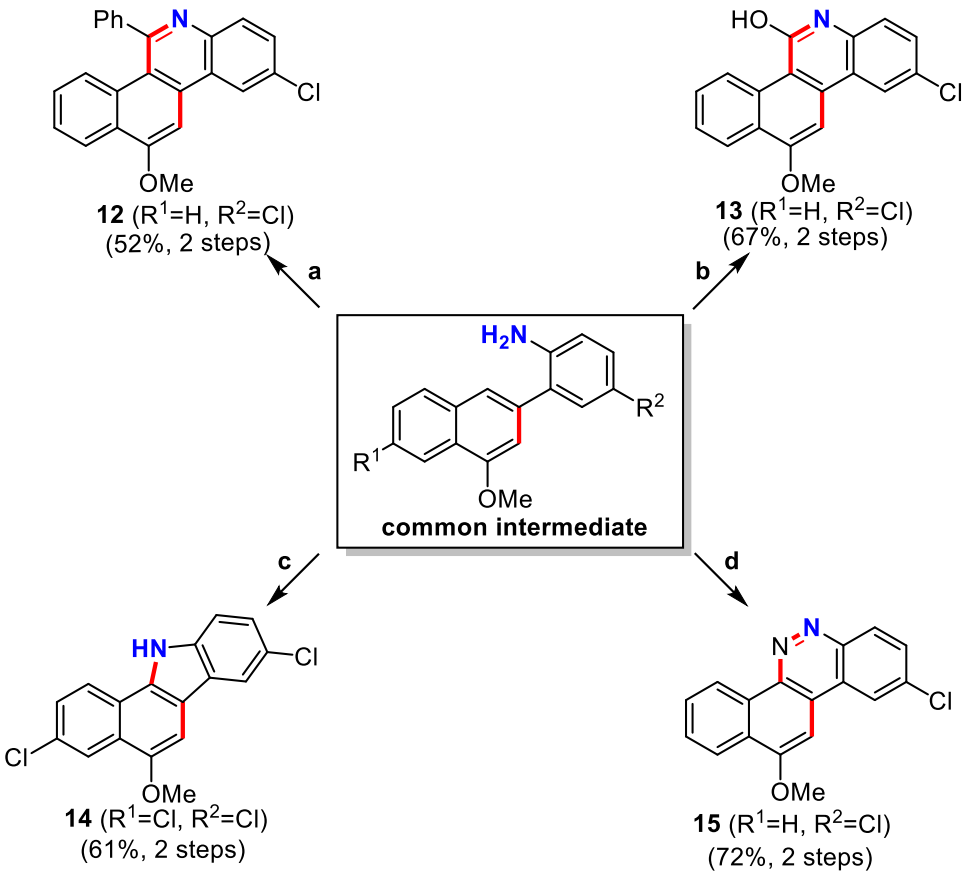
To study the influence of the electron-donating amino group on the selectivity of the cyclization, the amino-free substrate **6** was synthesized and subjected to the standard reaction condition. The reaction provided a mixture of naphthalene product **9** and indene product **10** with a ratio of 2:1 (Scheme 4). This result indicated that the electron-donating group in the substrate was essential in increasing the selectivity of the cyclization.



Scheme 5. Proposed Reaction Mechanism.

Based on the data of the control experiments above and the existing literature,[9] a possible mechanism of the reaction was proposed in Scheme 5. For the substrate **6**, the 5-*exo*-dig and 6-*endo*-dig pathways were competitive leading to the formation of a mixture of naphthalene **9** and indene **10** via intermediates **6-2** and **6-2'**. For the substrate **5**, the amino group acted as an electron-donating

group to increase the electrophilicity of the α position of the alkyne via conjugate effect, which prompted the nucleophilic addition of vinyl ether to the activated β position of the alkyne via a 6-*endo*-dig cyclization resulting in the formation of cyclopropylcarbene intermediate **5-2** exclusively. Finally, the naphthalene product **8** was generated as the only product after tautomerization and protodeauration (Scheme 5, blue cycle).



a. (i) PhCHO, $MgSO_4$, DCM; (ii) CF_3COOH, O_2, DCM. b. (i) BTC, TEA, DCE; (ii) $AlCl_3$.c. (i) TsCl, pyr, DCM; (ii) $Pd(OAc)_2$, oxone, DMF/*t*-BuOH. d. (i) $NaNO_2$, EtOH, H_2O, HCl; (ii) 60 °C, DCM.

Scheme 6. Divergent Syntheses of Benzo[*α*]carbazole, Benzo[*c*,*h*]cinnoline and Dibenzo[*i*]phenanthridine Derivatives.

The derivatization of 2-(naphthalen-2-yl)aniline product afforded a divergent access to a series of heterocycles as shown in Scheme 6.[10] For example, under Mannich reaction conditions, it could be transformed into benzo[*c*,*h*]cinnoline derivatives **12** after oxidative aromatization of the

product.[10b] By treating the product with triphosgene and aluminum chloride, a benzo[*c*,*h*]cinnoline compound **13** was obtained.[10c] A benzo[α]carbazole derivatives **14** was also synthesized via a palladium-catalyzed oxidative C-N bond formation.[10d] And the dibenzo[*i*]phenanthridine **15** was generated by a diazo-compound formation and subsequent cyclization under thermal conditions.[10a]

Conclusions

In conclusion, a unique synthetic strategy for 2-(naphthalen-2-yl)anilines based on 6-*endo*-dig cyclization of aromatic 1,5-enynes have been developed. The amino-group in the substrates acted as both a directing group for the cyclization and a functional group for the derivatization of the products. The 2-(naphthalen-2-yl)aniline product of this methodology afforded a common intermediate for the divergent syntheses of benzo[α]carbazole, benzo[*c*,*h*]cinnoline and dibenzo[*i*]phenanthridine derivatives.

Experimental Section

1. General Experimental Methods. Unless otherwise noted, reagents were obtained commercially and used without further purification. Tetrahydrofuran and diethyl ether were distilled from sodium under a nitrogen atmosphere. Dichloromethane and dichloroethane were 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 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 were tested on Thomas Hoover capillary melting point apparatus.

2. General Procedures for the Preparation of Substrates 4a-4d.

A magnetically stirred emulsion of 2-bromobenzaldehydes **1a-1d** (2.70 mmol), $Pd(Ph_3P)_2Cl_2$ (94.8 mg, 0.13 mmol) and CuI (51.4 mg, 0.27 mmol) in degassed THF (20 mL) at 60 °C under an atmosphere of nitrogen was treated with TEA (1.9 mL, 13.51 mmol) and trimethylsilylacetylene (1.2 mL, 8.10 mmol). The resulted mixture was stirred for 0.5-2 h sequentially. After the consumption of the starting materials, the emulsion was filtered through Celite. The filtrate was concentrated under reduced pressure to get the crude products **2a-2d**.[11]

To a solution of compounds **2a-2d** (7.8 mmol) in dry Et_2O (35 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 2.6 mL) at −78 °C with stirring under a nitrogen atmosphere. After the drop was completed, the reaction solution was allowed to warm to room temperature, and stirring was continued for 3 h. After the completion of the reaction, it was quenched with a saturated aqueous solution of NH_4Cl, extracted with EtOAc and washed with water. The organic layers were washed with brine, dried over anhydrous Na_2SO_4. Then the organic layers were filtered and concentrated under reduced pressure to give the crude product, which was used in the next step without further purification.

To a solution of PCC (952 mg, 4.1 mmol) in dry DCM (30 mL) was added a solution of crude product obtained in the last step (2.7 mmol) in DCM at 0 °C with stirring under a nitrogen atmosphere. After the drop was completed, the reaction solution was allowed to warm to room temperature and stirred overnight. After the reaction was completed, the reaction solution was passed through a sand funnel to obtain crude product and evaporated to dryness.

To a solution of the crude product obtained above (2.23 mmol) in methanol (40 mL) was added K_2CO_3 (0.370 g, 2.7 mmol) and the resulted mixture was stirred at room temperature for 3 h. After

completion of the reaction, it was quenched with saturated aqueous solution of NH_4Cl, extracted with DCM and washed with water. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness to give the crude products **3a-3d**.[12]

The mixture of the compounds **3a-3d** (17.2 mmol), trimethyl orthoformate (4.56 g, 43 mmol), TsCl (654 mg, 3.44 mmol) in methanol (40 mL) was stirred at room temperature for 3.5 h. After completion of the reaction, it was quenched with TEA, extracted with EtOAc and washed with water. The organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and evaporated to dryness to give the crude product. The solution of the crude product (6 mmol), trimethylchlorosilane (7.2 mL, 65 mmol), benzoic acid (88 mg, 0.72 mmol) in pyridine (30 mL) was stirred at 80 °C overnight. After the completion of the reaction, a 15% aqueous solution of NaOH was added to the reaction solution at 0 °C, which was extracted with EtOAc. The organic layers were washed with a saturated aqueous solution of $CuSO_4$ and brine, dried over anhydrous Na_2SO_4, and evaporated to dryness to give the crude products **4a-4d**.

3. General Procedures for the Preparation of Substrates 5, 5a-5o, 6, 7a-7b and Characterization Data

A magnetically stirred emulsion of iodoanilines (2.28 mmol) or iodobenzenes (0.45 g, 2.20 mmol) $Pd(Ph_3P)_2Cl_2$ (80 mg, 0.11 mmol) and CuI (43 mg, 0.23 mmol) in degassed THF (20 mL) at room temperature under an atmosphere of nitrogen was treated with Et_3N (1.6 mL, 11.41 mmol) and **1a-1d** (6.60 mmol) in THF (6 mL). The resulted mixture was stirred until the terminal alkyne was completely consumed. After the reaction was completed, the reaction solution was concentrated and subjected to a flash column chromatography on silica gel to give products **5**, **5a-5o**, **6, 7a-7b**.

2-((2-(1-Methoxyvinyl)phenyl)ethynyl)aniline (5) Brown oily liquid (448 mg, 1.8 mmol, 79%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.68–7.60 (m, 1H), 7.51–7.34 (m, 3H), 7.23–7.17 (m, 1H), 7.13–7.03 (m, 1H), 6.78–6.68 (m, 1H), 6.54 (s, 1H), 5.45 (s, 2H), 4.64–4.59 (m, 1H), 4.51 (d, *J* = 2.5 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.95, 150.00, 138.85, 133.06, 132.01, 130.40, 128.93, 128.75, 128.54, 121.47, 116.41, 114.27, 106.22, 93.71, 90.60, 86.86, 55.77; IR (thin film, cm^{-1}): 2947, 2206, 1616, 1494, 1308, 1194, 1134, 1090, 1016, 749; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1229.

2-((2-(1-Methoxyvinyl)phenyl)ethynyl)-4-methylaniline (5a) Brown oily liquid (480 mg, 1.82 mmol, 80%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.64–7.61 (m, 1H), 7.44 (s, 1H), 7.40–7.35 (m, 2H), 7.01 (s, 1H), 6.91 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 5.24 (s, 2H), 4.62 (d, *J* = 2.4 Hz, 1H), 4.51 (d, *J* = 2.5 Hz, 1H), 3.68 (s, 3H), 2.15 (d, *J* = 5.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.11, 149.98, 140.98, 135.26, 134.06, 133.50, 131.13, 130.93, 130.69, 127.11, 123.72, 116.71, 108.43, 95.72, 93.04, 89.07, 57.98, 22.51; IR (thin film, cm^{-1}): 3465, 3367, 2926, 2197, 1617, 1499, 1307, 1143, 813, 761; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, Found 264.1386.

4-Chloro-2-((2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5b) Brown oily liquid (542 mg, 1.92 mmol, 84%) (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.70 – 7.65 (m, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 5.63 (s, 2H), 4.62 (d, *J* = 2.5 Hz, 1H), 4.53 (d, *J* = 2.5 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.74, 149.01, 138.98, 133.29, 130.68, 130.23, 128.94, 128.74, 120.94, 119.13, 115.82, 107.58, 94.68, 89.10, 87.04, 55.79; IR (thin film, cm^{-1}): 3473, 3027,

2022, 1615, 1491, 1288, 1135, 1045, 811, 759; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}ClNO$ $[M+H]^+$ 284.0837, Found 284.0840.

4-Fluoro-2-((2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5c) Brown solid (530 mg, 1.98 mmol, 87%) (EtOAc/petroleum ether = 1:30); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.69–7.62 (m, 1H), 7.49–7.43 (m, 1H), 7.43–7.36 (m, 2H), 7.03–6.94 (m, 2H), 6.76–6.68 (m, 1H), 5.38–5.32 (m, 2H), 4.61 (t, *J* = 7.0 Hz, 1H), 4.52 (d, *J* = 2.5 Hz, 1H), 3.69 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.80, 153.81 (d, *J* = 231.6 Hz), 146.90, 139.04, 133.23, 128.97, 128.91, 128.78, 120.99, 117.72 (d, *J* = 22.5 Hz), 117.16 (d, *J* = 23.0 Hz), 115.38 (d, *J* = 8.0 Hz), 106.52 (d, *J* = 9.3 Hz), 94.35, 89.49 (d, *J* = 3.0 Hz), 87.00, 55.79; IR (thin film, cm^{-1}): 3467, 3370, 3037, 2936, 2202, 1495, 1285, 1116, 811, 739; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}FNO$ $[M+H]^+$ 268.1132, Found 268.1132.

2-((4-Methoxy-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5d) Yellow oily liquid (496 mg, 1.78 mmol, 78%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.59 – 7.55 (m, 1H), 7.16 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.99 – 6.94 (m, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.53 (t, *J* = 7.4 Hz, 1H), 5.37 (d, *J* = 21.3 Hz, 2H), 4.66 (t, *J* = 4.3 Hz, 1H), 4.51 (d, *J* = 2.5 Hz, 1H), 3.81 (d, *J* = 7.9 Hz, 3H), 3.68 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.61, 159.28, 149.70, 140.34, 134.65, 131.75, 129.96, 116.39, 114.87, 114.18, 113.98, 113.58, 106.74, 93.74, 88.97, 87.01, 55.84, 55.78; IR (thin film, cm^{-1}): 3469, 2958, 2161, 1613, 1499, 1307, 1226, 1142, 929, 817; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, Found 280.1330.

2-((4-Methoxy-2-(1-methoxyvinyl)phenyl)ethynyl)-4-methylaniline (5e) Brown oily liquid (508 mg, 1.73 mmol, 76%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.55 (dd, *J* = 5.8, 5.1 Hz, 1H), 7.00 – 6.94 (m, 3H), 6.89 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 2H), 4.67 (t, *J* = 5.5 Hz, 1H), 4.52 (d, *J* = 2.5 Hz, 1H), 3.81 – 3.79 (m, 3H), 3.68 (d, *J* = 5.9

Hz, 3H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.57, 159.25, 147.46, 140.26, 134.64, 131.64, 130.83, 124.88, 114.87, 114.42, 113.96, 113.64, 106.77, 93.55, 89.21, 87.00, 55.83, 55.77, 20.32; IR (thin film, cm^{-1}): 3462, 3006, 2928, 2196, 1598, 1454, 1301, 1080, 1035, 814; HRMS (ESI): *m/z* Calcd. for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.1489, Found 294.1493.

4-Chloro-2-((4-methoxy-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5f) Brown oily liquid (585 mg, 1.87 mmol, 82%) (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.62 – 7.60 (m, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.73 (d, *J* = 8.7 Hz, 1H), 5.57 (s, 2H), 4.67 (d, *J* = 2.5 Hz, 1H), 4.53 (d, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.43, 159.57, 148.71, 140.53, 134.91, 130.43, 129.77, 119.12, 115.69, 114.91, 113.97, 113.03, 108.14, 94.83, 87.57, 87.17, 55.87, 55.80; IR (thin film, cm^{-1}): 3465, 3367, 2936, 2838, 1597, 1490, 1300, 1224, 1034, 720; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ 314.0943, Found 314.0940.

4-Fluoro-2-((4-methoxy-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5g) Yellow oily liquid (575 mg, 1.94 mmol, 85%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.61 – 7.57 (m, 1H), 7.01 – 6.92 (m, 4H), 6.70 (dd, *J* = 8.9, 5.0 Hz, 1H), 5.30 (s, 2H), 4.65 (d, *J* = 2.5 Hz, 1H), 4.52 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.50, 159.55, 153.87 (d, *J* = 231.5 Hz), 146.56, 140.59, 134.85, 117.20 (d, *J* = 22.4 Hz), 116.95 (d, *J* = 23.0 Hz), 115.25 (d, *J* = 8.1 Hz), 114.91, 114.03, 113.08, 107.12 (d, *J* = 9.3 Hz), 94.50, 87.95 (d, *J* = 3.0 Hz), 87.14, 55.87, 55.80; IR (thin film, cm^{-1}): 3463, 2939, 2200, 1596, 1457, 1304, 1278, 1079, 922, 812; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}FNO_2$ $[M+H]^+$ 298.1238, Found 298.1242.

2-((4-Chloro-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5h) Yellow solid (548 mg, 1.93 mmol, 85%) (EtOAc/petroleum ether = 1:25); Mp 82.1 – 83.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.71

(t, *J* = 7.0 Hz, 1H), 7.48 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.19 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.54 (dd, *J* = 11.0, 3.9 Hz, 1H), 5.49 (s, 2H), 4.76 (d, *J* = 2.7 Hz, 1H), 4.58 (d, *J* = 2.7 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.28, 150.15, 140.22, 134.88, 133.00, 132.13, 130.64, 128.90, 128.32, 120.37, 116.40, 114.38, 105.82, 92.64, 91.97, 87.85, 55.91; IR (thin film, cm^{-1}): 3470, 3372, 2931, 2846, 2205, 1616, 1304, 1041, 821, 748; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}ClNO$ $[M+H]^+$ 284.0837, Found 284.0841.

2-((4-Chloro-2-(1-methoxyvinyl)phenyl)ethynyl)-4-methylaniline (5i) Brown solid (562 mg, 1.89 mmol, 83%) (EtOAc/petroleum ether = 1:20); Mp 79.3 – 80.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.00 (d, *J* = 1.4 Hz, 1H), 6.92 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 5.28 (s, 2H), 4.77 (d, *J* = 2.7 Hz, 1H), 4.59 (d, *J* = 2.8 Hz, 1H), 3.69 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.23, 147.95, 140.13, 134.88, 132.93, 131.92, 131.56, 128.89, 128.28, 124.89, 120.41, 114.61, 105.81, 92.45, 92.23, 87.86, 55.91, 20.29; IR (thin film, cm^{-1}): 3465, 3371, 2954, 2194, 1721, 1618, 1498, 1299, 1110, 814; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{18}ClNO$ $[M+H]^+$ 298.0993, Found 298.0989.

4-Chloro-2-((4-chloro-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5j) Brown solid (650 mg, 2.05 mmol, 90%) (EtOAc/petroleum ether = 1:40); Mp 66.1 – 67.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 5.67 (s, 2H), 4.76 (d, *J* = 2.7 Hz, 1H), 4.61 (t, *J* = 6.4 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.07, 149.16, 140.37, 135.11, 133.42, 130.76, 130.47, 128.94, 128.31, 119.84, 119.10, 115.94, 107.15, 93.56, 90.42, 88.05, 55.93; IR (thin film, cm^{-1}): 3473, 3373, 2929, 2202, 1716, 1617, 1487, 1302, 1192, 816; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}Cl_2NO$ $[M+H]^+$ 318.0447, Found 318.0448.

2-((4-Chloro-2-(1-methoxyvinyl)phenyl)ethynyl)-4-fluoroaniline (5k) Brown solid (542 mg, 1.80 mmol, 79%) (EtOAc/petroleum ether = 1:40); Mp 76.5 – 77.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 (d, J = 8.2 Hz, 1H), 7.49 (dd, J = 8.2, 2.2 Hz, 2H), 6.99 (dd, J = 14.2, 5.9 Hz, 2H), 6.72 (dd, J = 8.6, 4.8 Hz, 1H), 5.40 (s, 2H), 4.75 (d, J = 2.8 Hz, 1H), 4.59 (d, J = 2.8 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.15, 153.78 (d, J = 231.7 Hz), 147.05, 140.43, 135.05, 133.40, 128.96, 128.36, 119.88, 118.01 (d, J = 22.5 Hz), 117.21 (d, J = 23.0 Hz), 115.52 (d, J = 7.9 Hz), 106.09 (d, J = 9.3 Hz), 93.23, 90.78 (d, J = 3.0 Hz), 88.01, 55.93; IR (thin film, cm^{-1}): 3468, 3363, 2927, 2202, 1725, 1617, 1495, 1300, 1113, 871; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}ClFNO$ $[M+H]^+$ 302.0743, Found 302.0745.

2-((4-Fluoro-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5l) Brown oily liquid (517 mg, 1.94 mmol, 85%) (EtOAc/petroleum ether = 1:30); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.73 (dd, J = 10.1, 5.1 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.19 (dd, J = 7.7, 1.4 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.57 – 6.52 (m, 1H), 5.46 (s, 2H), 4.78 (t, J = 4.4 Hz, 1H), 4.58 (d, J = 2.7 Hz, 1H), 3.68 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.72 (d, J = 247.4 Hz), 159.38 (d, J = 1.9 Hz), 150.02, 140.83 (d, J = 8.3 Hz), 135.50 (d, J = 8.5 Hz), 132.03, 130.42, 117.88 (d, J = 3.1 Hz), 116.39, 116.16 (d, J = 21.8 Hz), 115.47 (d, J = 23.3 Hz), 114.34, 106.09, 92.69, 90.56, 87.74, 55.87; IR (thin film, cm^{-1}): 3371, 3074, 2955, 2205, 1717, 1611, 1492, 1201, 820, 748; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}FNO$ $[M+H]^+$ 268.1132, Found 268.1130.

2-((4-Fluoro-2-(1-methoxyvinyl)phenyl)ethynyl)-4-methylaniline(5m) Brown solid (512 mg, 1.82 mmol, 80%) (EtOAc/petroleum ether = 1:25); Mp 82.4 – 83.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.71 (dd, J = 8.4, 5.9 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.00 (d, J = 1.3 Hz, 1H), 6.91 (dd, J = 8.3, 1.8 Hz, 1H), 6.64 (d, J = 8.3 Hz, 1H), 5.25 (s, 2H), 4.79 (d, J = 2.7 Hz, 1H), 4.59 (d, J = 2.7 Hz, 1H),

3.69 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.68 (d, J = 247.3 Hz), 159.32 (d, J = 1.8 Hz), 147.79, 140.74 (d, J = 8.2 Hz), 135.50 (d, J = 8.5 Hz), 131.85, 131.32, 124.89, 117.91 (d, J = 3.1 Hz), 116.17 (d, J = 21.8 Hz), 115.44 (d, J = 23.3 Hz), 114.57, 106.08, 92.48, 90.80, 87.76, 55.89, 20.29; IR (thin film, cm^{-1}): 3369, 2926, 2199, 1611, 1497, 1308, 1199, 1078, 877, 817; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}FNO$ $[M+H]^+$ 282.1289, Found 282.1292.

4-Chloro-2-((4-fluoro-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5n) Brown oily liquid (604 mg, 2.00 mmol, 88%) (EtOAc/petroleum ether = 1:30); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.79 – 7.73 (m, 1H), 7.28 (dd, J = 13.4, 5.7 Hz, 2H), 7.17 (d, J = 2.5 Hz, 1H), 7.11 (dd, J = 8.7, 2.5 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 5.64 (s, 2H), 4.77 (d, J = 2.7 Hz, 1H), 4.60 (d, J = 2.7 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.93 (d, J = 247.8 Hz), 159.15 (d, J = 1.7 Hz), 149.04, 141.03 (d, J = 8.3 Hz), 135.79 (d, J = 8.6 Hz), 130.68, 130.26, 119.07, 117.35 (d, J = 3.2 Hz), 116.23 (d, J = 21.9 Hz), 115.87, 115.48 (d, J = 23.4 Hz), 107.40, 93.63, 89.05, 87.95, 55.91; IR (thin film, cm^{-1}): 3470, 3372, 3074, 2851, 1609, 1491, 1308, 1201, 878, 818; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}FClNO$ $[M+H]^+$ 302.0743, Found 302.0744.

4-Fluoro-2-((4-fluoro-2-(1-methoxyvinyl)phenyl)ethynyl)aniline (5o) Brown solid (578 mg, 2.03 mmol, 89%) (EtOAc/petroleum ether = 1:30); Mp 100.3 – 101.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.78 – 7.72 (m, 1H), 7.29 (d, J = 2.6 Hz, 2H), 7.02–6.94 (m, 2H), 6.72 (dd, J = 8.8, 5.0 Hz, 1H), 5.35 (d, J = 32.1 Hz, 2H), 4.76 (d, J = 2.8 Hz, 1H), 4.59 (d, J = 2.8 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.92 (d, J = 247.8 Hz), 159.24 (d, J = 1.9 Hz), 153.80 (d, J = 231.6 Hz), 146.91, 141.09 (d, J = 8.3 Hz), 135.72 (d, J = 8.6 Hz), 117.75 (d, J = 22.5 Hz), 117.40 (d, J = 3.1 Hz), 117.16 (d, J = 23.1 Hz), 116.24 (d, J = 21.8 Hz), 115.62, 115.47 (d, J = 2.1 Hz), 115.42, 106.36 (d, J = 9.3 Hz), 93.31, 87.91, 55.90; IR (thin film, cm^{-1}): 3465, 3369, 2930, 2203, 1604,

1495, 1309, 1194, 873, 818; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1038, Found 286.1040.

1-(1-Methoxyvinyl)-2-(phenylethynyl)benzene (6) Brown oily liquid (371 mg, 1.58 mmol, 72%) (EtOAc/petroleum ether = 1:50); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.60 – 7.57 (m, 1H), 7.54 – 7.49 (m, 3H), 7.44 – 7.35 (m, 5H), 4.70 (d, J = 2.6 Hz, 1H), 4.54 (d, J = 2.6 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.88, 138.90, 132.72, 131.16, 128.68, 128.43, 128.08, 122.63, 120.33, 92.59, 88.71, 86.38, 55.15; ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.36, 145.89, 136.73, 136.50, 134.66, 129.23, 128.94, 128.46, 127.57, 127.54, 127.34, 126.53, 125.77, 123.20, 85.45, 55.84; IR (thin film, cm^{-1}): 3078, 2854, 1666, 1583, 1452, 1381, 1010, 863, 779, 694; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}O$ $[M+H]^+$ 235.1118, Found 235.1116.

3-((2-(1-Methoxyvinyl)phenyl)ethynyl)aniline (7a) Brown oily liquid (426 mg, 1.71 mmol, 75%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.56 – 7.52 (m, 1H), 7.50 – 7.46 (m, 1H), 7.40 – 7.35 (m, 2H), 7.05 (t, J = 7.8 Hz, 1H), 6.73 – 6.70 (m, 1H), 6.66 – 6.63 (m, 1H), 6.61 (m, J = 8.1, 2.3, 1.0 Hz, 1H), 5.26 (s, 2H), 4.67 (d, J = 2.5 Hz, 1H), 4.53 (d, J = 2.6 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.92, 148.84, 138.74, 132.66, 129.20, 128.43, 128.30, 128.06, 122.77, 120.63, 118.70, 116.03, 114.60, 93.67, 87.23, 86.37, 55.23; IR (thin film, cm^{-1}): 3439, 2923, 1619, 1514, 1465, 1383, 1306, 1192, 1045, 766; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1230.

4-((2-(1-Methoxyvinyl)phenyl)ethynyl)aniline (7b) Brown oily liquid (426 mg, 1.71 mmol, 75%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.49 – 7.46 (m, 1H), 7.46 – 7.44 (m, 1H), 7.35 – 7.29 (m, 2H), 7.20 – 7.15 (m, 2H), 6.60 – 6.56 (m, 2H), 5.58 (s, 2H), 4.69 (d, J = 2.5 Hz, 1H), 4.52 (d, J = 2.5 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.98,

149.56, 138.07, 132.45, 132.16, 128.29, 127.92, 127.41, 121.45, 113.66, 108.48, 94.83, 86.21, 85.98, 55.14; IR (thin film, cm^{-1}): 3380, 2926, 2207, 1620, 1514, 1465, 1305, 1133, 1045, 755; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1228.

4. Procedures for the Preparation of Intermediate 7c-1 to 7k-1, 7c-7l and Characterization Data

A magnetically stirred emulsion of iodobenzenes (2.28 mmol), $Pd(Ph_3P)_2Cl_2$ (80 mg, 0.11 mmol) and CuI (43 mg, 0.23 mmol) in degassed THF (20 mL) at room temperature under an atmosphere of nitrogen was treated with Et_3N (1.6 mL, 11.41 mmol) and **3a** (1.0 g, 6.85 mmol) in THF (10 mL). The resulted mixture was stirred until the terminal alkyne was completely consumed. After the reaction was completed, the reaction solution was concentrated and subjected to a flash column chromatography on silica gel to give products **7c-1** to **7i-1**.

1-(2-((2-Aminophenyl)ethynyl)phenyl)ethan-1-one (7c-1) Brown solid (439 mg, 1.87 mmol, 82%) (EtOAc/petroleum ether = 1:10); Mp 87.0 – 88.5 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.8, 0.4 Hz, 1H), 7.67 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.50 (m, *J* = 7.6, 1.1 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.17 – 7.13 (m, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 5.03 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.80, 149.87, 138.14, 134.28, 132.19, 131.95, 130.42, 129.91, 127.58, 122.66, 117.21, 114.24, 107.19, 94.44, 92.05, 28.83; IR (thin film, cm^{-1}): 3437, 2851, 2313, 1516, 1466, 1384, 1271, 1031, 757, 520; HRMS (ESI): *m/z* Calcd. for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, Found 236.1074.

1-(2-((2-(Methylamino)phenyl)ethynyl)phenyl)ethan-1-one (7d-1) Brown solid (494 mg, 1.98 mmol, 87%) (EtOAc/petroleum ether = 1:15); Mp 91.4 – 92.1 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.50 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.37 (m, *J* = 5.5,

2.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.62 (dd, *J* = 7.8, 5.7 Hz, 2H), 6.14 (s, 1H), 3.06 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.58, 151.76, 137.87, 134.23, 132.07, 131.96, 130.79, 130.02, 127.40, 122.73, 115.39, 108.80, 106.70, 94.99, 92.38, 30.19, 28.79; IR (thin film, cm^{-1}): 3422, 3312, 2401, 2304, 2150. 1248, 1121, 781, 500, 483; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1231.

1-(2-((2-(Dimethylamino)phenyl)ethynyl)phenyl)ethan-1-one (7e-1) Brown oily liquid (480 mg, 1.82 mmol, 80%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.64 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (m, *J* = 7.7, 1.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.91 (td, *J* = 7.5, 0.9 Hz, 1H), 2.99 (s, 6H), 2.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.87, 155.07, 140.60, 134.34, 133.64, 131.32, 129.90, 128.72, 128.08, 122.44, 120.66, 117.21, 114.92, 94.94, 93.60, 43.73, 30.16; IR (thin film, cm^{-1}): 3440, 3375, 2314, 2168, 1244, 1135, 838, 756, 504, 478; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, Found 264.1385.

1-(2-((2-Methoxyphenyl)ethynyl)phenyl)ethan-1-one (7f-1) Brown oily liquid (445 mg, 1.78 mmol, 78%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.44 (m, *J* = 7.6, 1.1 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.34 – 7.29 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.05, 160.29, 140.77, 133.90, 133.39, 131.25, 130.36, 128.62, 128.18, 122.15, 120.57, 112.13, 110.74, 92.44, 92.21, 55.68, 30.34; IR (thin film, cm^{-1}): 3427, 2921, 2345, 2171, 1494, 1466, 1104, 1026, 520, 467; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067, Found 251.1070.

1-(2-((2-Hydroxyphenyl)ethynyl)phenyl)ethan-1-one (7g-1) White oily liquid (387 mg, 1.64 mmol,

72%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.99 (s, 1H), 7.77 (dd, J = 7.8, 1.0 Hz, 1H), 7.65 (dd, J = 7.7, 0.9 Hz, 1H), 7.58 (m, J = 7.6, 1.3 Hz, 1H), 7.49 (m, J = 7.6, 1.3 Hz, 1H), 7.41 (dd, J = 7.6, 1.6 Hz, 1H), 7.25 (m, J = 8.3, 7.5, 1.7 Hz, 1H), 6.94 (dd, J = 8.2, 0.6 Hz, 1H), 6.85 (td, J = 7.5, 1.0 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 200.19, 158.65, 140.19, 133.38, 132.76, 131.63, 130.61, 128.75, 128.44, 120.99, 119.26, 115.58, 109.49, 91.96, 91.84, 29.93; IR (thin film, cm^{-1}): 3374, 3068, 2178, 1922, 1266, 1243, 830, 756, 480, 444; HRMS (ESI): *m/z* Calcd. for $C_{16}H_{13}O_2$ $[M+H]^+$ 237.0910, Found 237.0913.

1-(2-((2-(Benzyloxy)phenyl)ethynyl)phenyl)ethan-1-one (7h-1) Yellow oily liquid (557 mg, 1.71 mmol, 75%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.8, 1.1 Hz, 1H), 7.62 (dd, J = 7.7, 0.7 Hz, 1H), 7.56 (dd, J = 7.5, 1.6 Hz, 1H), 7.49 (d, J = 7.3 Hz, 2H), 7.44 (m, J = 7.6, 1.3 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.31 (m, J = 8.4, 1.7 Hz, 1H), 6.98 (dd, J = 13.7, 7.8 Hz, 2H), 5.16 (s, 2H), 2.73 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.89, 159.42, 140.61, 136.58, 133.97, 133.48, 131.22, 130.26, 128.60, 128.59, 128.14, 128.05, 127.48, 127.45, 122.19, 120.89, 112.73, 112.43, 92.63, 92.32, 70.49, 30.31; IR (thin film, cm^{-1}): 3062, 3031, 2514, 2212, 1381, 1357, 1102, 1005, 597, 531; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{19}O_2$ $[M+H]^+$ 327.1380, Found 327.1379.

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)ethan-1-one (7i-1) Yellow oily liquid (399 mg, 1.60 mmol, 70%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 0.8 Hz, 1H), 7.61 (d, J = 7.1 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.38 (m, J = 7.7, 1.1 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.69, 160.20, 140.73, 133.84, 133.18, 131.43, 128.82, 128.06, 122.27, 115.14, 114.29, 95.43, 87.51, 77.37, 77.16, 76.95, 55.50, 30.19; IR (thin film, cm^{-1}): 3415, 2994, 2131, 1482, 1398, 1121, 1012, 513, 460; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{13}O_2$ $[M+H]^+$ 251.1067, Found 251.1065.

A magnetically stirred solution of substrate **7c-1** to **7i-1** (0.62 mmol) in degassed THF (10 mL) maintained at −78 °C under an atmosphere of nitrogen was added a solution of KHMDS (0.93 mL, 0.93 mmol, 1.0 M) in THF dropwise and then the mixture was stirred at room temperature for 1 h. To the reaction mixture was added a solution of the TBSCl (140 mg, 0.93 mmol) or MOMCl (75 mg, 0.93 mmol) in THF (5 mL) at −78 °C and the reaction was stirred for 2 h at room temperature. The reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with EtOAc (30 mL x 3). The combined organic layers were washed with brine (20 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel to afford the products **7c-7j**.

2-((2-(1-((tert-Butyldimethylsilyl)oxy)vinyl)phenyl)ethynyl)aniline (7c) Yellow oily liquid (234 mg, 0.67 mmol, 79%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.64 (dd, J = 7.3, 1.3 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.40 – 7.32 (m, 2H), 7.19 (d, J = 6.8 Hz, 1H), 7.08 (dd, J = 11.3, 4.1 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 6.54 (t, J = 7.4 Hz, 1H), 5.50 (s, 2H), 4.99 (s, 1H), 4.72 (s, 1H), 0.88 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.60, 150.11, 140.02, 133.13, 131.96, 130.38, 128.66, 128.45, 128.15, 121.03, 116.31, 114.31, 106.19, 97.21, 93.91, 91.26, 26.01, 18.42, 4.27; IR (thin film, cm^{-1}): 3474, 3374, 2954, 2856, 1616, 1458, 1304, 1124, 834, 472; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{28}NOSi$ $[M+H]^+$ 350.1935, Found 350.1938.

2-((2-(1-(Methoxymethoxy)vinyl)phenyl)ethynyl)-N-methylaniline (7d) Yellow oily liquid (131 mg, 0.45 mmol, 72%) (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 – 7.68 (m, 1H), 7.51 – 7.48 (m, 1H), 7.43 – 7.37 (m, 2H), 7.27 (dd, J = 7.8, 1.6 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.60 (dd, J = 7.8, 5.9 Hz, 2H), 5.41 (q, J = 4.8 Hz, 1H), 5.11 (s, 2H), 4.79 (d, J = 2.1 Hz, 1H), 4.77 (d, J = 2.1 Hz, 1H), 3.39 (s, 3H), 2.83 (d, J = 5.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-

d$_6$) δ 157.81, 150.47, 138.43, 133.21, 132.17, 130.85, 128.95, 128.80, 128.64, 121.51, 115.97, 109.50, 106.76, 94.43, 94.20, 91.03, 90.52, 56.37, 30.18; IR (thin film, cm^{-1}): 3353, 3076, 2829, 2359, 1615, 1430, 1203, 1179, 816, 768; HRMS (ESI): *m/z* Calcd. for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.1489, Found 294.1492.

2-((2-(1-((tert-Butyldimethylsilyl)oxy)vinyl)phenyl)ethynyl)-N-methylaniline (7e) Yellow oily liquid (162 mg, 0.45 mmol, 72%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.68 – 7.63 (m, 1H), 7.48 – 7.45 (m, 1H), 7.39 – 7.34 (m, 2H), 7.24 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.23 – 7.18 (m, 1H), 6.61 – 6.56 (m, 2H), 5.46 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.97 (d, *J* = 0.9 Hz, 1H), 4.78 (d, *J* = 0.9 Hz, 1H), 2.82 (d, *J* = 5.0 Hz, 3H), 0.87 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 155.26, 149.98, 139.68, 132.60, 131.49, 130.34, 128.19, 128.06, 127.73, 120.50, 115.46, 108.99, 106.35, 96.69, 94.08, 90.41, 29.75, 25.46, 17.94, -4.82; IR (thin film, cm^{-1}): 3395, 3061, 2816, 2204, 1514, 1463, 1077, 1016, 596, 477; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{30}NOSi$ $[M+H]^+$ 364.2091, Found 364.2093.

2-((2-(1-((tert-Butyldimethylsilyl)oxy)vinyl)phenyl)ethynyl)-N,N-dimethylaniline (7f) Yellow oily liquid (157 mg, 0.42 mmol, 67%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.48 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.30 (m, *J* = 7.6, 1.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 6.95 – 6.88 (m, 2H), 5.28 (d, *J* = 1.1 Hz, 1H), 4.79 (d, *J* = 1.2 Hz, 1H), 3.02 (s, 6H), 0.97 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.65, 154.63, 140.01, 134.47, 133.14, 129.27, 127.82, 127.78, 127.58, 121.23, 120.46, 116.98, 115.61, 97.03, 94.70, 92.96, 43.73, 25.91, 18.39, 1.18, -4.48; IR (thin film, cm^{-1}): 3437, 2926, 1627, 1464, 1384, 1077, 836, 751, 619; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{32}NOSi$ $[M+H]^+$ 378.2248, Found 378.2245.

tert-Butyl((1-(2-((2-methoxyphenyl)ethynyl)phenyl)vinyl)oxy)dimethylsilane (7g) Yellow oily

liquid (173 mg, 0.46 mmol, 74%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.54 (m, J = 7.7, 2.9, 1.1 Hz, 2H), 7.41 (m, J = 8.3, 5.0, 2.5 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.37 – 7.33 (m, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.98 (m, J = 7.5, 0.8 Hz, 1H), 5.26 (d, J = 1.5 Hz, 1H), 4.75 (d, J = 1.5 Hz, 1H), 3.84 (s, 3H), 0.90 (s, 9H), 0.13 (d, J = 3.0 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.74, 153.66, 139.30, 133.17, 132.77, 130.36, 128.32, 128.05, 127.34, 120.46, 119.94, 111.61, 111.38, 96.83, 92.62, 90.21, 55.62, 25.58, 17.92, -4.77; IR (thin film, cm^{-1}): 3361, 3089, 1621, 1562, 1193, 1158, 924, 801, 531, 429; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{32}NOSi$ $[M+H]^+$ 378.2248, Found 378.2245.

((1-(2-((2-(Benzyloxy)phenyl)ethynyl)phenyl)vinyl)oxy)(tert-butyl)dimethylsilane (7h) Brown oily liquid (196 mg, 0.45 mmol, 72%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.8, 0.8 Hz, 1H), 7.45 (dd, J = 7.6, 1.0 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.26 (t, J = 7.5 Hz, 2H), 7.19 (m, J = 10.2, 8.9, 4.3 Hz, 2H), 7.16 – 7.09 (m, 2H), 6.83 (dd, J = 15.6, 8.0 Hz, 2H), 5.28 (d, J = 1.5 Hz, 1H), 5.06 (s, 2H), 4.51 (d, J = 1.5 Hz, 1H), 0.85 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.34, 154.07, 139.86, 137.05, 133.73, 133.52, 129.65, 128.60, 127.96, 127.88, 127.62, 127.48, 127.42, 120.93, 120.86, 113.81, 112.75, 97.25, 93.79, 90.35, 70.55, 25.94, 25.87, 18.38, -4.48; IR (thin film, cm^{-1}): 3838, 2924, 1462, 1385, 1246, 1110, 837, 756, 471, 420; HRMS (ESI): *m/z* Calcd. for $C_{29}H_{33}O_2Si$ $[M+H]^+$ 440.2172, Found 440.2175.

tert-Butyl((1-(2-((2-((tert-butyldimethylsilyl)oxy)phenyl)ethynyl)phenyl)vinyl)oxy)dimethylsilane (7i) Yellow oily liquid (198 mg, 0.43 mmol, 69%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.8, 1.1 Hz, 1H), 7.39 (dd, J = 7.6, 1.2 Hz, 1H), 7.28 (dd, J = 7.6, 1.7 Hz, 1H), 7.14 (m, J = 7.6, 1.4 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.06 – 7.02 (m, 1H), 6.78 (m, J = 7.5, 1.0 Hz, 1H), 6.70 (dd, J = 8.2, 0.7 Hz, 1H), 5.09 (d, J = 1.2 Hz, 1H), 4.62 (d,

J = 1.2 Hz, 1H), 0.91 – 0.89 (m, 9H), 0.81 – 0.79 (m, 9H), 0.11 (s, 6H), 0.00 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.32, 154.61, 140.43, 133.67, 133.06, 129.48, 127.83, 127.82, 127.57, 121.32, 121.06, 119.94, 116.42, 97.08, 92.91, 91.08, 25.95, 25.93, 18.48, 18.41, -4.05, -4.46; IR (thin film, cm^{-1}): 3374, 2202, 1674, 1609, 1356, 1296, 1017, 954, 527, 48; HRMS (ESI): *m/z* Calcd. for $C_{28}H_{41}O_2Si_2$ $[M+H]^+$ 465.2640, Found 465.2639.

tert-Butyl((1-(2-((4-methoxyphenyl)ethynyl)phenyl)vinyl)oxy)dimethylsilane (7j) Brown oily liquid (183 mg, 0.50 mmol, 81%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.41–7.37 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 5.02 (s, 1H), 4.73 (s, 1H), 3.79 (s, 3H), 0.89 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 202.28, 162.53, 142.85, 136.14, 135.68, 134.35, 131.58, 131.10, 123.44, 117.20, 96.94, 90.04, 58.03, 32.33, 28.51, 20.51, 0.49; IR (thin film, cm^{-1}): 3005, 2828, 2170, 2089, 1666, 1472, 1290, 1157, 1056, 801; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{29}O_2Si$ $[M+H]^+$ 365.1932, Found 365.1935.

To a solution of compound **2a** (1.58 g, 7.8 mmol) in dry THF (30 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 2.6 mL) or *n*-BuLi (1.6 M in hexanes, 4.9 mL) at –78 °C with stirring under a nitrogen atmosphere. After the drop was completed, the reaction solution was allowed to warm to room temperature, and stirring was continued for 3 h. After the completion of the reaction, it was quenched with a saturated aqueous solution of NH_4Cl, extracted with EtOAc and washed with water. The organic layers were washed with brine, dried over anhydrous Na_2SO_4. Then the organic layers were filtered and concentrated under reduced pressure to give the crude product, which was used in the next step without further purification.

To a solution of PCC (952 mg, 4.1 mmol) in dry DCM (30 mL) was added a solution of the crude

product obtained above (2.7 mmol) in DCM at 0 °C with stirring under a nitrogen atmosphere. After the drop was completed, the reaction solution was allowed to warm to room temperature and stirred overnight. After the reaction was completed, the reaction solution was passed through a sand funnel and concentrated to obtain the crude ketone product.

To a solution of the crude ketone product (2.23 mmol) in methanol (40 mL) was added K_2CO_3 (0.370 g, 2.7 mmol) and the resulted mixture was stirred at room temperature for 3 h. After completion of the reaction, it was quenched with a saturated aqueous solution of NH_4Cl, extracted with DCM and washed with water. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness to give the crude product **3e** or **3f**.

A magnetically stirred emulsion of 2-iodoaniline (591 mg, 2.70 mmol), $Pd(Ph_3P)_2Cl_2$ (80 mg, 0.11 mmol) and CuI (43 mg, 0.23 mmol) in degassed THF (20 mL) maintained at room temperature under an atmosphere of nitrogen was treated with TEA (1.6 mL, 11.41 mmol) and **3e**, **3f** (3.0 mmol) in THF (10 mL). The resulted mixture was stirred until the terminal alkyne was completely consumed. After the reaction was completed, the reaction solution was concentrated and subjected to a flash column chromatography on silica gel to give compound **7j-1** or **7k-1**.

1-(2-((2-Aminophenyl)ethynyl)phenyl)propan-1-one (7j-1) Brown oily liquid (511 mg, 2.05 mmol, 76%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.66 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.48 (m, *J* = 7.6, 1.2 Hz, 1H), 7.37 (m, *J* = 15.0, 7.6, 1.3 Hz, 2H), 7.17 – 7.13 (m, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.70 – 6.65 (m, 1H), 4.98 (s, 2H), 3.04 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.23, 149.78, 138.77, 134.11, 132.17, 131.50, 130.36, 128.86, 127.61, 122.41, 117.23, 114.25, 107.25, 94.24, 91.64, 77.37, 77.16, 76.95, 34.12, 8.63; IR (thin film, cm^{-1}): 3461, 3359, 2373, 2202, 1379, 1314, 1079, 950, 620, 480; HRMS

(ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1228.

1-(2-((2-Aminophenyl)ethynyl)phenyl)pentan-1-one (7k-1) Brown oily liquid (598 mg, 2.16 mmol, 80%) (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.66 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.48 (m, *J* = 7.6, 1.2 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.17 – 7.13 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.69 – 6.64 (m, 1H), 4.98 (s, 2H), 3.03 – 2.98 (m, 2H), 1.75 – 1.69 (m, 2H), 1.40 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.05, 149.78, 138.94, 134.05, 132.11, 131.44, 130.31, 128.88, 127.55, 122.37, 117.15, 114.20, 107.20, 94.18, 91.60, 77.37, 77.16, 76.95, 40.71, 26.78, 22.55, 14.05; IR (thin film, cm^{-1}): 3451, 3390, 2366, 2182, 1396, 1381, 1072, 961, 599, 473; HRMS (ESI): *m/z* Calcd. for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1540, Found 278.1538.

A magnetically stirred solution of substrate **7j-1** or **7k-1** (0.62 mmol) in degassed THF (5 mL) maintained at −78 °C under an atmosphere of nitrogen was added a solution of KHMDS (0.93 mL, 0.93 mmol, 1.0 M) in THF dropwise and then the mixture was stirred at room temperature for 1 h. To the reaction mixture was added a solution of the TBSCl (140 mg, 0.93 mmol) in THF (5 mL) at −78 °C and the reaction was stirred for 2 h at room temperature. The reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with EtOAc (30 mL x 3). The combined organic layers were washed with brine (20 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel to afford the product **7k** or **7l**.

2-((2-(1-((tert-Butyldimethylsilyl)oxy)prop-1-en-1-yl)phenyl)ethynyl)aniline (7k) Brown oily liquid (198 mg, 0.55 mmol, 88%) (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.57 – 7.54 (m, 1H), 7.35 – 7.30 (m, 3H), 7.18 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.71

(d, J = 7.7 Hz, 1H), 6.53 (m, J = 7.6, 0.9 Hz, 1H), 5.56 (s, 2H), 5.10 (d, J = 6.7 Hz, 1H), 1.72 (d, J = 6.7 Hz, 3H), 0.86 (s, 9H), -0.10 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 149.75, 148.95, 141.12, 131.69, 131.28, 129.84, 128.41, 127.87, 127.82, 121.26, 115.71, 113.65, 107.77, 105.66, 93.54, 90.36, 39.94, 39.80, 39.66, 39.52, 39.38, 39.24, 39.10, 25.53, 17.95, 11.23, -4.51; IR (thin film, cm^{-1}): 2955, 2926, 2375, 2316, 1315, 1255, 858, 838, 544, 472; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{30}NOSi$ $[M+H]^+$ 364.2091, Found 364.2093.

2-((2-(1-((tert-Butyldimethylsilyl)oxy)pent-1-en-1-yl)phenyl)ethynyl)aniline (7l) Brown oily liquid (165 mg, 0.42 mmol, 68%) (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.59 – 7.54 (m, 1H), 7.36 – 7.30 (m, 3H), 7.17 (dd, J = 7.6, 1.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.72 (d, J = 8.1 Hz, 1H), 6.52 (dd, J = 10.9, 4.0 Hz, 1H), 5.54 (s, 2H), 5.01 (t, J = 7.2 Hz, 1H), 2.18 (q, J = 7.3 Hz, 2H), 1.46 – 1.38 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H), 0.85 (s, 9H), -0.11 (s, 6H); ^{13}C NMR (150 MHz, DMSO d_6) δ 149.76, 148.31, 141.12, 131.80, 131.26, 129.80, 128.57, 127.88, 127.82, 121.40, 115.64, 113.68, 113.52, 105.65, 93.47, 90.35, 39.94, 39.80, 39.66, 39.52, 39.38, 39.24, 39.10, 27.50, 25.52, 22.33, 17.96, 13.93, -4.51; IR (thin film, cm^{-1}): 3437, 2923, 1464, 1410, 1384, 1108, 837, 618, 471; HRMS (ESI): *m/z* Calcd. for $C_{25}H_{34}NOSi$ $[M+H]^+$ 392.2404, Found 392.2404.

5. General Procedures for the Preparation of 8, 8a-8o, 9, 10, 11a-11l and Characterization Data

A magnetically stirred solution of 1,5-enyne substrates **5**, **5a-5o**, **6, 7a-7l** (1 mmol) in dry DCM (10 mL) at room temperature under an atmosphere of nitrogen was treated with the gold catalyst, which was generated by stirring the mixture of IPrAuCl (30 mg, 0.05 mmol) and $AgSbF_6$ (17 mg, 0.05 mmol) in dry DCM (10 mL) at room temperature for 30 min. The resulted mixture was stirred at room temperature for 2 h and concentrated under reduced pressure. The residues were purified by a flash column chromatography (EtOAc/petroleum ether) on silica gel to afford the products **8**, **8a-**

8o, **9**, **10**, **11a-11l**.

2-(4-Methoxynaphthalen-2-yl)aniline (8) Yellow oily liquid (229 mg, 0.92 mmol, 92%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.14 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.51–7.46 (m, 2H), 7.13 (dd, J = 7.5, 1.5 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.99 (d, J = 1.1 Hz, 1H), 6.79 (dd, J = 8.0, 0.9 Hz, 1H), 6.67 (dd, J = 7.4, 1.1 Hz, 1H), 4.93 (d, J = 16.7 Hz, 2H), 4.00 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.30, 145.70, 138.18, 134.69, 130.66, 128.74, 128.18, 127.13, 126.32, 125.64, 124.29, 121.76, 119.83, 117.05, 115.69, 106.22, 56.03; IR (thin film, cm^{-1}): 3060, 2957, 2929, 1721, 1617, 1397, 1290, 991, 751; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1230.

2-(4-Methoxynaphthalen-2-yl)-4-methylaniline (8a) Yellow oily liquid (245 mg, 0.93 mmol, 93%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.14 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.50 – 7.45 (m, 2H), 7.00 – 6.94 (m, 2H), 6.90 (dd, J = 8.1, 1.7 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.70 (s, 2H), 4.00 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150MHz, DMSO-d_6) δ 155.24, 143.19, 138.32, 134.68, 131.03, 129.27, 128.15, 127.11, 126.40, 125.59, 125.46, 124.24, 121.76, 119.80, 115.95, 106.23, 56.04, 20.59； IR (thin film, cm^{-1}): 2957, 2862, 1723, 1625, 1504, 1455, 1286, 1147, 848, 748; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, Found 264.1385.

4-Chloro-2-(4-methoxynaphthalen-2-yl)aniline (8b) Brown oily liquid (246 mg, 0.87 mmol, 87%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.99 (dd, J = 9.0, 5.8 Hz, 1H), 7.74 (dd, J = 10.7, 2.7 Hz, 1H), 7.54 (s, 1H), 7.48 – 7.41 (m, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 6.92 – 6.88 (m, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.71 (s, 2H), 4.00 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.45, 144.92, 136.74, 134.63, 129.78, 128.31, 127.71, 127.22, 125.90, 124.51,

121.78, 120.05, 117.08, 105.88, 56.09; IR (thin film, cm^{-1}): 2954, 2858, 1718, 1557, 1491, 1228, 1146, 993, 914, 777; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}ClNO$ $[M+H]^+$ 284.0837, Found 284.0841.

4-Fluoro-2-(4-methoxynaphthalen-2-yl)aniline (8c) Yellow oily liquid (240 mg, 0.90 mmol, 90%) (EtOAc/petroleum ether = 1:10); ^1H NMR (600 MHz, DMSO-d_6) δ 8.15 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.57 – 7.48 (m, 3H), 7.02 – 6.97 (m, 2H), 6.94 (dd, J = 8.6, 3.0 Hz, 1H), 6.79 (dd, J = 8.8, 5.2 Hz, 1H), 4.83 (s, 2H), 4.01 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.41, 155.06 (d, J = 229.5 Hz), 142.33, 137.01, 134.58, 128.29, 127.23, 127.04 (d, J = 7.1 Hz), 125.90, 124.45, 121.77, 119.99, 116.63, 116.53 (d, J = 15.8 Hz), 115.17 (d, J = 21.8 Hz), 105.96, 56.09； IR (thin film, cm^{-1}): 3459, 3372, 1587, 1500, 1284, 1258, 1110, 951, 777, 752; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}FNO$ $[M+H]^+$ 268.1132, Found 268.1134.

2-(4,6-Dimethoxynaphthalen-2-yl)aniline (8d) Yellow oily liquid (262 mg, 0. 94 mmol, 94%) (EtOAc/petroleum ether = 1:15); ^1H NMR (600 MHz, DMSO-d_6) δ 7.82 (d, J = 8.9 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.19 (dd, J = 10.6, 5.3 Hz, 1H), 7.12 (dd, J = 7.5, 1.4 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.98 (d, J = 1.0 Hz, 1H), 6.82 – 6.76 (m, 1H), 6.66 (dd, J = 7.4, 1.0 Hz, 1H), 4.88 (s, 2H), 4.00 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 157.47, 154.43, 145.68, 135.56, 130.66, 129.96, 128.53, 126.47, 125.19, 119.73, 119.41, 117.07, 115.64, 106.68, 100.31, 55.96, 55.62； IR (thin film, cm^{-1}): 2957, 1721, 1498, 1393, 1289, 1216, 1122, 1074, 962, 745; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, Found 280.1330.

2-(4,6-Dimethoxynaphthalen-2-yl)-4-methylaniline (8e) Yellow oily liquid (261 mg, 0.89 mmol, 89%) (EtOAc/petroleum ether = 1:20); ^1H NMR (600 MHz, DMSO-d_6) δ 7.81 (d, J = 8.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.18 (dd, J = 8.9, 2.6 Hz, 1H), 6.95 (dd, J = 17.5, 1.4 Hz, 2H), 6.88 (dd, J = 8.1, 1.7 Hz, 1H), 6.69 (d, J = 8.1 Hz, 1H), 4.66 (s, 2H), 3.99 (s, 3H), 3.88 (s, 3H), 2.20 (s, 3H); ^{13}C

NMR (150 MHz, DMSO-d_6) δ 157.43, 154.38, 143.15, 135.70, 131.05, 129.93, 129.05, 126.55, 125.46, 125.14, 119.70, 119.39, 115.89, 106.68, 100.31, 55.97, 55.61, 20.59; IR (thin film, cm^{-1}): 3480, 1719, 1621, 1602, 1461, 1328, 1253, 1180, 997, 811; HRMS (ESI): *m/z* Calcd. for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.1489, Found 294.1493.

4-Chloro-2-(4,6-dimethoxynaphthalen-2-yl)aniline (8f) Brown oily liquid (297 mg, 0.95 mmol, 95%) (EtOAc/petroleum ether = 1:15); ^1H NMR (600 MHz, DMSO-d_6) δ 7.84 (d, J = 8.9 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.20 (dd, J = 8.9, 2.6 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.96 (d, J = 1.0 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 5.07 (s, 2H), 4.00 (d, J = 5.4 Hz, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 153.98, 151.20, 138.98, 138.36, 132.52, 130.04, 129.93, 127.10, 126.36, 124.42, 120.21, 119.33, 116.63, 115.36, 114.65, 106.98, 55.78, 55.41; IR (thin film, cm^{-1}): 3368, 2360, 1724, 1606, 1494, 1255, 1290, 1218, 1098, 814; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ 314.0943, Found 314.0943.

2-(4,6-Dimethoxynaphthalen-2-yl)-4-fluoroaniline (8g) Brown oily liquid (279 mg, 0.94 mmol, 94%) (EtOAc/petroleum ether = 1:15); ^1H NMR (600 MHz, DMSO-d_6) δ 7.83 (d, J = 8.9 Hz, 1H), 7.48 (s, 1H), 7.45 (d, J = 2.6 Hz, 1H), 7.20 (dd, J = 8.9, 2.6 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.95 – 6.90 (m, 1H), 6.78 (dd, J = 8.8, 5.2 Hz, 1H), 4.82 (s, 2H), 4.00 (d, J = 6.3 Hz, 3H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 157.65, 155.11 (d, J = 229.5 Hz), 154.52, 142.23, 134.40, 130.03, 129.87, 125.40, 119.88, 119.51, 116.61, 116.54, 116.47, 114.92 (d, J = 21.7 Hz), 106.40, 100.31, 56.02, 55.64; IR (thin film, cm^{-1}): 3359, 2923, 1604, 1464, 1380, 1257, 1220, 1140, 954, 811; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}FNO_2$ $[M+H]^+$ 298.1238, Found 298.1242.

2-(6-Chloro-4-methoxynaphthalen-2-yl)aniline (8h) Brown oily liquid (266 mg, 0.94 mmol, 94%) (EtOAc/petroleum ether = 1:20); ^1H NMR (600 MHz, DMSO-d_6) δ 8.10 (d, J = 2.1 Hz, 1H), 7.96

(d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.15 – 7.05 (m, 3H), 6.82 – 6.78 (m, 1H), 6.67 (dd, *J* = 7.4, 1.0 Hz, 1H), 4.95 (s, 2H), 4.01 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 154.47, 145.74, 138.91, 133.07, 130.67, 130.53, 130.33, 128.92, 127.56, 125.88, 124.86, 120.66, 119.73, 117.06, 115.77, 107.49, 56.23; IR (thin film, cm^{-1}): 3466, 2956, 1772, 1615, 1453, 1290, 1228, 1148, 881, 751; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}ClNO$ $[M+H]^+$ 284.0837, Found 284.0838.

2-(6-Chloro-4-methoxynaphthalen-2-yl)-4-methyl aniline (8i) Brown oily liquid (273 mg, 0.92 mmol, 92%) (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.10 (d, *J* = 2.1 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.53 (dd, *J* = 7.9, 3.0 Hz, 2H), 7.06 (d, *J* = 0.9 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.73 (s, 2H), 4.00 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 154.42, 143.23, 139.06, 133.06, 131.02, 130.47, 130.28, 129.47, 127.53, 125.99, 125.51, 124.82, 120.67, 119.70, 116.05, 107.48, 56.22, 20.56; IR (thin film, cm^{-1}): 2940, 2833, 1622, 1589, 1503, 1453, 1294, 1120, 1020, 842; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}ClNO$ $[M+H]^+$ 298.0993, Found 298.0991.

4-Chloro-2-(6-chloro-4-methoxynaphthalen-2-yl)aniline (8j) Yellow oily liquid (295 mg, 0.93 mmol, 93%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.10 (d, *J* = 2.2 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.16 – 7.09 (m, 2H), 7.05 (d, *J* = 1.2 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 5.14 (s, 2H), 4.02 (d, *J* = 9.7 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 154.61, 144.93, 137.43, 133.00, 130.61, 129.79, 128.50, 127.64, 127.27, 125.09, 120.70, 120.14, 119.92, 117.17, 107.13, 56.28; IR (thin film, cm^{-1}): 2955, 2836, 1614, 1404, 1292, 1195, 1018, 916, 807, 693；HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}Cl_2NO$ $[M+H]^+$ 318.0447, Found 318.0451.

2-(6-Chloro-4-methoxynaphthalen-2-yl)-4-fluoroaniline (8k) Brown oily liquid (292 mg, 0.97

mmol, 97%) (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10 (d, J = 2.1 Hz, 1H), 7.95 (t, J = 9.5 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.08 (d, J = 1.0 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.79 (dd, J = 8.8, 5.2 Hz, 1H), 4.86 (s, 2H), 4.02 (s, 3H; ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.06 (d, J = 229.5 Hz), 154.57, 142.37 (d, J = 1.1 Hz), 137.73, 132.96, 130.62, 130.60, 127.66, 126.58 (d, J = 7.0 Hz), 125.03, 120.68, 119.91, 116.72 (d, J = 7.5 Hz), 116.56 (d, J = 22.1 Hz), 115.37 (d, J = 21.8 Hz), 107.24, 56.29; IR (thin film, cm^{-1}): 2922, 2396, 1724, 1587, 1496, 1453, 1288, 1256, 1082, 849; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}ClFNO$ $[M+H]^+$ 302.0743, Found 302.0741.

2-(6-Fluoro-4-methoxynaphthalen-2-yl)aniline (8l) Yellow oily liquid (251 mg, 0.94 mmol, 94%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10 (d, J = 2.1 Hz, 1H), 7.95 (t, J = 9.5 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.08 (d, J = 1.0 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.79 (dd, J = 8.8, 5.2 Hz, 1H), 4.86 (s, 2H), 4.02 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.28 (d, J = 242.9 Hz), 154.81 (d, J = 5.3 Hz), 145.74, 137.63 (d, J = 2.3 Hz), 131.84, 131.21 (d, J = 8.8 Hz), 130.68, 128.80, 126.04, 124.85 (d, J = 8.7 Hz), 119.84, 117.09 (d, J = 25.5 Hz), 117.05, 115.72, 107.27, 105.44 (d, J = 22.2 Hz), 56.17; IR (thin film, cm^{-1}): 2957, 1719, 1499, 1387, 1290, 1130, 1028, 997, 875, 749； HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}FNO$ $[M+H]^+$ 268.1132, Found 268.1136.

2-(6-Fluoro-4-methoxynaphthalen-2-yl)-4-methyl aniline (8m) Brown oily liquid (267 mg, 0.95 mmol, 95%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.99 (dd, J = 9.0, 5.8 Hz, 1H), 7.74 (dd, J = 10.7, 2.7 Hz, 1H), 7.54 (s, 1H), 7.48 – 7.41 (m, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 6.92 – 6.88 (m, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.71 (s, 2H), 4.00 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.25 (d, J = 242.9 Hz), 154.74 (d, J = 5.2 Hz), 143.22, 137.78 (d, J = 2.5 Hz), 131.82, 131.18 (d, J = 8.8 Hz), 131.05, 129.34, 126.11, 125.46, 124.79 (d, J = 8.7 Hz), 119.80, 117.07 (d, J = 25.0 Hz), 115.98, 107.26, 105.43 (d, J = 22.2 Hz), 56.17, 20.57; IR (thin film, cm^{-1}):

2927, 1607, 1504, 1462, 1386, 1291, 1187, 1090, 933, 867; HRMS (ESI): *m/z* Calcd. for $C_{18}H_{17}FNO$ $[M+H]^+$ 282.1289, Found 282.1289.

4-Chloro-2-(6-fluoro-4-methoxynaphthalen-2-yl)aniline (8n) Brown solid (289 mg, 0.96 mmol, 96%) (EtOAc/petroleum ether = 1:15); Mp 76.1 – 77.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 9.0, 5.8 Hz, 1H), 7.76 (dd, *J* = 10.6, 2.5 Hz, 1H), 7.58 (d, *J* = 11.6 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.03 (s, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 5.12 (s, 1H), 4.01 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.42 (d, *J* = 243.3 Hz), 154.92 (d, *J* = 5.1 Hz), 144.96, 136.18, 131.77, 131.37 (d, *J* = 8.9 Hz), 129.80, 128.39, 127.38, 125.10 (d, *J* = 8.8 Hz), 120.03, 117.20 (d, *J* = 25.0 Hz), 117.09, 106.93, 105.47 (d, *J* = 22.2 Hz), 56.24; IR (thin film, cm^{-1}): 2952, 2851, 1607, 1507, 1462, 1293, 1227, 1013, 875, 691; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}ClFNO$ $[M+H]^+$ 302.0743, Found 302.0746.

4-Fluoro-2-(6-fluoro-4-methoxynaphthalen-2-yl)aniline (8o) Yellow oily liquid (274 mg, 0.96 mmol, 96%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 9.0, 5.7 Hz, 1H), 7.76 (dd, *J* = 10.6, 2.6 Hz, 1H), 7.60 (s, 1H), 7.47 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.06 (s, 1H), 7.01 – 6.92 (m, 2H), 6.79 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.84 (s, 2H), 4.01 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.41 (d, *J* = 243.2 Hz), 155.04 (d, *J* = 231.0 Hz), 154.89 (d, *J* = 5.2 Hz), 142.37, 136.47, 131.73, 131.35 (d, *J* = 8.9 Hz), 126.73 (d, *J* = 7.0 Hz), 125.05 (d, *J* = 8.8 Hz), 120.01, 117.21 (d, *J* = 25.0 Hz), 116.65 (d, *J* = 2.1 Hz), 116.56 (d, *J* = 16.8 Hz), 115.24 (d, *J* = 21.8 Hz), 107.00, 105.47 (d, *J* = 22.2 Hz), 56.23; IR (thin film, cm^{-1}): 3365, 2924, 2201, 1725, 1605, 1501, 1287, 1193, 996, 811; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1038, Found 286.1042.

1-Methoxy-3-phenylnaphthalene (9) Yellow oily liquid (13.3 mg, 0.057 mmol, 57%)

(EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.14 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.3 Hz, 2H), 7.78 (s, 1H), 7.58 – 7.54 (m, 1H), 7.53 – 7.48 (m, 3H), 7.41 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 1.1 Hz, 1H), 4.08 (s, 3H). Data are in agreement with those reported in literature.[13]

1-Benzylidene-3-methoxy-1H-indene (10) Yellow oily liquid (6.6 mg, 1:1 *E/Z* 0.028mmol, 28%) (EtOAc/petroleum ether = 1:15); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.56 – 7.54 (m, 1H, *E* + 1H, *Z*), 7.51 – 7.48 (m, 2H, *E* + 2H, *Z*), 7.47 – 7.45 (m, 1H, *E* + 1H, *Z*), 7.43 (s, 1H, *E*), 7.45 (s,1H, *Z*), 7.11 – 7.09 (m, 1H, *E* + 1H, *Z*), 7.06 – 7.02 (m, 2H, *E* + 2H, *Z*), 6.78 – 6.73 (m, 2H, *E* + 2H, *Z*), 5.12 (s, 1H, *E*), 5.10 (s, 1H, *Z*), 3.15 (s, 3H, *E* + 3H, *Z*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.36 (*E*), 145.89(*Z*), 143.92 (*E*), 142.66(*Z*), 141.79 (*E*), 138.67(*Z*), 136.73 (*E*), 136.50(*Z*), 134.67 (*E*), 129.23(*Z*), 128.94 (*E*), 128.46(*Z*), 128.34 (*E*), 128.09(*Z*), 127.57 (*E*), 127.54(*Z*), 127.34 (*E*), 127.19(*Z*), 126.53 (*E*), 125.77(*Z*), 124.83 (*E*), 123.21(*Z*), 120.40 (*E*), 120.01(*Z*), 85.45 (*E*), 76.93(*Z*), 55.84 (*E*), 50.59(*Z*); IR (thin film, cm^{-1}): 3010, 2792, 1732, 1503, 1349, 1299, 1222, 901, 853, 742; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{15}O$ $[M+H]^+$ 235.1118, Found 235.1120.

3-(4-Methoxynaphthalen-2-yl)aniline (11a) Brown oily liquid (132 mg, 0.53 mmol, 53%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.59 (s, 1H), 7.53 – 7.43 (m, 2H), 7.26 (dd, J = 13.0, 5.1 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.74 – 6.68 (m, 1H), 4.05 (s, 3H), 3.77 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.78, 146.90, 143.01, 139.25, 134.67, 129.85, 127.90, 126.90, 125.29, 124.95, 122.02, 118.41, 118.08, 114.36, 114.26, 104.02, 77.37, 77.16, 76.95, 55.74; IR (thin film, cm^{-1}): 3451, 2955, 2926, 1464, 1380, 1364, 1305, 892, 763; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{14}NO$ $[M+H]^+$ 250.1227, Found 250.1229.

4-(4-Methoxynaphthalen-2-yl)aniline (11b) Yellow oily liquid (206 mg, 0.83 mmol, 83%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.54 – 7.49 (m, 1H), 7.46 (m, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.06 (d, *J* = 1.2 Hz, 1H), 6.84 – 6.78 (m, 2H), 4.08 (s, 3H), 3.76 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.77, 146.11, 138.97, 134.85, 131.93, 128.37, 127.68, 126.81, 124.85, 124.47, 121.96, 117.22, 115.49, 103.68, 55.65; IR (thin film, cm^{-1}): 3425, 3301, 2938, 1261, 1243, 829, 759, 532, 501; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1227, Found 250.1227.

2-(4-((tert-Butyldimethylsilyl)oxy)naphthalen-2-yl)aniline (11c) Yellow oily liquid (314 mg, 0.90 mmol, 90%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 1H), 7.56 – 7.50 (m, 1H), 7.26 (s, 1H), 7.24 – 7.18 (m, 2H), 6.96 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.73 (s, 1H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.50 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.54 (s, 2H), 0.84 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.09, 143.80, 137.33, 135.21, 130.59, 128.63, 127.84, 127.69, 127.07, 126.73, 125.37, 122.65, 120.98, 118.73, 115.72, 114.08, 26.01, 18.57, -4.08; IR (thin film, cm^{-1}): 3466, 3378, 1954, 2929, 1296, 1256, 835, 750, 532, 499; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{28}NOSi$ $[M+H]^+$ 350.1935, Found 350.1937.

2-(4-(Methoxymethoxy)naphthalen-2-yl)-N-methyl aniline (11d) Brown oily liquid (240 mg, 0.82 mmol, 82%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.10 – 7.07 (m, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 5.45 (s, 2H), 4.95 (q, *J* = 4.8 Hz, 1H), 3.47 (s, 3H), 2.68 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.45, 146.40, 137.16, 134.34, 129.97, 128.77, 127.88, 126.66, 126.58, 125.49, 124.36, 121.31, 120.86, 115.88, 109.72, 109.67, 94.63, 55.99; IR (thin film, cm^{-1}): 3324, 2930, 2816, 1623, 1431, 943, 832, 523, 422; HRMS (ESI): *m/z*

Calcd. for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.1489, Found 294.1491.

2-(4-((tert-Butyldimethylsilyl)oxy)naphthalen-2-yl)-N-methylaniline (11e) Yellow oily liquid (305 mg, 0.84 mmol, 84%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.9 Hz, 1H), 7.84 (d, *J* = 6.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 6.99 (s, 1H), 6.86 (t, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.21 (s, 1H), 2.85 (s, 3H), 1.15 (s, 9H), 0.35 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.15, 146.34, 137.25, 135.28, 130.18, 128.95, 127.84, 127.77, 127.11, 126.74, 125.41, 122.67, 121.29, 117.07, 114.37, 110.09, 30.93, 26.01, 18.58, -4.11; IR (thin film, cm^{-1}): 3428, 3049, 2856, 2812, 1313, 1256, 931, 835, 628, 420; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{30}NOSi$ $[M+H]^+$ 364.2091, Found 364.2090.

2-(4-((tert-Butyldimethylsilyl)oxy)naphthalen-2-yl)-N,N-dimethylaniline (11f) Yellow oily liquid (287 mg, 0.76 mmol, 76%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 6.3, 3.1 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.60 (s, 1H), 7.54 – 7.48 (m, 2H), 7.42 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.12 (dd, *J* = 15.4, 7.8 Hz, 2H), 2.62 (s, 6H), 1.17 (s, 9H), 0.36 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.43, 151.25, 140.27, 135.43, 134.35, 131.93, 128.36, 127.88, 127.05, 126.25, 125.04, 122.61, 121.86, 120.08, 117.81, 114.28, 43.46, 26.08, 18.58, -4.24; IR (thin film, cm^{-1}): 3438, 3052, 2778, 1318, 1255, 1155, 928, 836, 626, 428; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{32}NOSi$ $[M+H]^+$ 378.2248, Found 378.2250.

tert-Butyl((3-(2-methoxyphenyl)naphthalen-1-yl)oxy) dimethylsilane (11g) Yellow oily liquid (299 mg, 0.82 mmol, 82%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 1H), 7.84 – 7.80 (m, 1H), 7.56 (s, 1H), 7.46 (m, *J* = 11.5, 6.9 Hz, 3H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 1.12 (s, 9H), 0.33 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.75, 150.87, 136.64, 134.96, 131.14, 130.93, 128.85,

128.00, 127.07, 126.29, 125.15, 122.59, 121.24, 121.08, 115.19, 111.46, 77.37, 77.16, 76.95, 55.67, 26.07, 18.60, -4.13; IR (thin film, cm^{-1}): 3400, 3088, 2901, 2833, 1465, 1401, 1379, 1256, 1031, 931; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{29}O_2Si$ $[M+H]^+$ 365.1932, Found 365.1935.

((3-(2-(Benzyloxy)phenyl)naphthalen-1-yl)oxy)(tert-butyl)dimethylsilane (11h) Yellow oily liquid (317 mg, 0.72 mmol, 72%) (EtOAc/petroleum ether = 1:5); ^1H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 1H), 7.84 – 7.79 (m, 1H), 7.63 (s, 1H), 7.52 – 7.42 (m, 3H), 7.34 – 7.23 (m, 7H), 7.19 (d, *J* = 1.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 5.11 (s, 2H), 1.08 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.91, 150.98, 137.31, 136.70, 134.92, 131.61, 131.38, 128.76, 128.59, 127.99, 127.74, 127.09, 126.31, 125.14, 122.62, 121.56, 121.55, 115.19, 113.72, 70.71, 26.04, 18.56, -4.17; IR (thin film, cm^{-1}): 2930, 2708, 2318, 1446, 1362, 935, 833, 524, 480; HRMS (ESI): *m/z* Calcd. for $C_{29}H_{33}O_2Si$ $[M+H]^+$ 441.2245, Found 441.2241.

tert-Butyl(2-(4-((tert-butyldimethylsilyl)oxy)naphthalen-2yl)phenoxy)dimethylsilane (11i) Yellow oily liquid (325 mg, 0.70 mmol, 70%) (EtOAc/petroleum ether = 1:15); ^1H NMR (600 MHz, DMSO-d_6) δ 8.10 – 8.05 (m, 1H), 7.87 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.62 (s, 1H), 7.52 – 7.48 (m, 2H), 7.38 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.29 (m, *J* = 8.0, 1.8 Hz, 1H), 7.09 (m, *J* = 7.5, 1.0 Hz, 1H), 6.99 (dd, *J* = 8.1, 1.0 Hz, 2H), 1.05 (s, 9H), 0.72 (s, 9H), 0.23 (s, 6H), -0.10 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.12, 150.42, 136.29, 134.21, 132.61, 131.01, 130.81, 128.75, 127.87, 126.49, 126.11, 125.37, 122.03, 121.70, 121.65, 120.50, 114.93, 25.68, 25.51, 25.39, 18.11, 17.72, -4.35, -4.47, -4.65; IR (thin film, cm^{-1}): 3028, 2930, 2373, 2345, 1445, 1382, 918, 842, 596, 472; HRMS (ESI): *m/z* Calcd. for $C_{28}H_{41}O_2Si_2$ $[M+H]^+$ 465.2640, Found 465.2644.

tert-Butyl((3-(4-methoxyphenyl)naphthalen-1-yl)oxy) dimethylsilane (11j) Brown oily liquid (266 mg, 0.73 mmol, 73%) (EtOAc/petroleum ether = 1:5); ^1H NMR (600 MHz, DMSO-d_6) δ 8.06 (d, *J*

= 7.9 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.75 (s, 1H), 7.70 – 7.66 (m, 2H), 7.53 – 7.46 (m, 2H), 7.13 (d, *J* = 1.5 Hz, 1H), 7.09 – 7.04 (m, 2H), 3.80 (s, 3H), 1.06 (s, 9H), 0.30 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.08, 151.43, 137.65, 134.88, 132.28, 128.02, 127.96, 126.76, 126.07, 125.26, 121.75, 117.89, 114.51, 111.67, 55.20, 25.73, 18.19, -4.32; IR (thin film, cm^{-1}): 3421, 3057, 1580, 1254, 1178, 931, 823, 534, 431; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{29}O_2Si$ $[M+H]^+$ 365.1932, Found 365.1934.

2-(4-((tert-Butyldimethylsilyl)oxy)-3-methylnaphthalen-2-yl)aniline (11k) Yellow oily liquid (291 mg, 0.80 mmol, 80%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.20 (m, *J* = 7.9, 1.3 Hz, 1H), 7.08 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.50 (d, *J* = 7.3 Hz, 2H), 2.17 (s, 3H), 1.14 (s, 9H), 0.21 (d, *J* = 4.7 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.21, 143.96, 138.86, 133.25, 130.26, 128.57, 127.87, 127.64, 125.56, 125.04, 123.44, 122.99, 122.65, 118.35, 115.16, 26.28, 18.91, 14.85, -2.86, -3.01; IR (thin film, cm^{-1}): 3012, 2983, 2903, 1300, 1258, 862, 833, 542, 470; HRMS (ESI): *m/z* Calcd. for $C_{23}H_{29}O_2Si$ $[M+H]^+$ 364.2091, Found 364.2090.

2-(4-((tert-Butyldimethylsilyl)oxy)-3-propylnaphthalen-2-yl)aniline (11l) Brown oily liquid (313 mg, 0.80 mmol, 80%) (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.23 (m, *J* = 7.8, 1.5 Hz, 1H), 7.15 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.81 (dd, *J* = 8.0, 0.6 Hz, 1H), 3.56 (s, 2H), 2.83 (m, *J* = 13.0, 10.0, 5.7 Hz, 1H), 2.51 (m, *J* = 13.0, 10.0, 5.8 Hz, 1H), 1.46 – 1.33 (m, 2H), 1.17 (s, 9H), 0.76 (t, *J* = 7.3 Hz, 3H), 0.27 (d, *J* = 11.3 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.31, 143.89, 138.48, 133.36, 130.70, 128.48, 128.36, 127.71, 127.67, 127.59, 125.56, 124.88, 123.28, 123.16, 118.17, 115.13, 77.37, 77.16, 76.95, 30.32, 26.24, 23.30, 18.85, 14.26, -2.60, -3.16; IR (thin film, cm^{-1}):

3458, 2954, 2856, 1612, 1455, 1255, 1064, 964, 632, 504; HRMS (ESI): *m/z* Calcd. for $C_{25}H_{34}NOSi$ $[M+H]^+$ 392.2404, Found 392.2407.

6. Procedures for the Syntheses of Compounds 12-15 and Characterization Data

A magnetically stirred solution of substrate **8b** (283 mg, 1 mmol) and $MgSO_4$ (1.2 g, 10 mmol) in dry DCM (20 mL) at room temperature under an atmosphere of nitrogen was treated with benzaldehyde (530 mg, 5 mmol) in dry DCM (5 mL). The resulted mixture was stirred at room temperature overnight then filtered, and concentrated *in vacuo*. The residue was used directly for the next step without further purification.

A magnetically stirred solution of imine in dry DCM (20 mL) at room temperature under an atmosphere of oxygen was treated with trifluoroacetic acid (60 mg, 0.5 mmol) in dry DCM (10 mL). The resulted mixture was stirred at room temperature overnight then concentrated under reduced pressure. The residue was purified by a flash column chromatography (EtOAc/petroleum ether = 1:5) on silica gel to afford the cyclized product **12** (192 mg, 0.52 mmol, 52%) as a brown oily liquid. ***9-Chloro-12-methoxy-5-phenylbenzo[i]phenanthridine (12)*** ^{1}H NMR (600 MHz, D_2O) δ 8.13 (d, *J* = 2.3 Hz, 1H), 8.00 (d, *J* = 2.3 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.52 (d, *J* = 5.2 Hz, 1H), 7.50 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.15 – 7.12 (m, 2H), 7.05 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.24 (s, 1H), 4.14 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 133.07, 132.02, 130.64, 129.82, 129.45, 129.14, 128.13, 124.89, 124.26, 121.95, 116.52, 99.90, 65.50, 57.99, 56.49, 30.46; IR (thin film, cm^{-1}): 3009, 2996, 2900, 2839, 2781, 2603, 2315, 1269, 1207, 1066; HRMS (ESI): *m/z* Calcd. for $C_{24}H_{17}ClNO$ $[M+H]^+$ 370.0993, Found 370.0995.

A magnetically stirred solution of substrate **8b** (283 mg, 1 mmol), triphosgene (79 mg, 0.8 mmol) and $AlCl_3$ (270 mg, 2 mmol) in dry DCE at room temperature under an atmosphere of nitrogen was

treated with TEA (20 mg, 0.2 mmol). The resulted mixture was stirred at room temperature overnight then concentrated under reduced pressure. The residue was purified by a flash column chromatography (EtOAc/petroleum ether = 1:2) on silica gel to afford the cyclized product **13** as a brown oily liquid (207 mg, 0.67 mmol, 67%).

9-Chloro-12-methoxybenzo[i]phenanthridin-5-ol (13) ^{1}H NMR (600 MHz, Pyr-d_5) δ 8.15 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.15 – 7.09 (m, 2H), 6.98 (d, J = 0.9 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 5.13 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (150 MHz, Pyr-d_5) δ 154.36, 154.04, 137.21, 137.18, 132.54, 132.49, 130.75, 130.36, 129.43, 128.41, 127.29, 124.90, 122.25, 121.07, 120.24, 106.78, 55.17; IR (thin film, cm^{-1}): 3312, 3146, 2901, 2650, 1370, 1199, 1021, 973; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{13}ClNO_2$ $[M+H]^+$ 310.0630, Found 310.0633.

A magnetically stirred solution of substrate **8j** (317 mg, 1 mmol) in dry DCM (20 mL) at room temperature under an atmosphere of nitrogen was treated with pyridine (1.2 mL, 1.5 mmol) and a solution of TsCl (292 mg, 1.5 mmol) in dry DCM (5 mL). The resulted mixture was stirred at room temperature overnight then quenched with water (5 mL) and extracted with EtOAc (15 mL x 3). The combined organic layers were washed with brine (15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was used directly for the next step without further purification.

To a stirred solution of sulfonyl compound (390 mg, 0.9 mmol) in DMF/*t*-butanol (1:3, v/v) (20 mL) were added $Pd(OAc)_2$ (20 mg, 0.1 mmol) and oxone (310 mg, 0.5 mmol) at room temperature under an atmosphere of nitrogen. The resulted mixture was stirred at room temperature overnight. The residue was purified by a flash column chromatography (EtOAc/petroleum ether = 1:1) on silica gel to afford the cyclized product **14** as a brown oily liquid (208 mg, 0.66 mmol, 66%).

3,8-Dichloro-5-methoxy-11H-benzo[a]carbazole (14) ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.84 – 7.71 (m, 2H), 7.64 – 7.55 (m, 3H), 7.45 – 7.38 (m, 1H), 7.17 – 7.08 (m, 1H), 6.90 – 6.78 (m, 3H), 6.36 (d, J = 7.4 Hz, 2H), 6.29 (s, 1H), 5.29 (s, 1H), 3.94 – 3.86 (m, 3H), 1.65 (dd, J = 55.4, 12.9 Hz, 3H), 1.47 – 1.36 (m, 2H), 1.31 – 1.14 (m, 3H), 1.05 (dd, J = 13.7, 6.8 Hz, 3H), 0.89 – 0.80 (m, 1H), 0.80 – 0.69 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 158.23, 145.77, 141.98, 138.70, 132.46, 131.89, 130.22, 129.59, 128.91, 126.66, 123.98, 122.57, 121.90, 121.36, 95.93, 57.27; IR (thin film, cm^{-1}): 3362, 2937, 2884, 2823, 2793, 2669, 2430, 1277, 1064, 1019; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{12}Cl_2NO$ $[M+H]^+$ 316.0291, Found 316.0292.

A magnetically stirred solution of substrate **8b** (283 mg, 1 mmol) and $NaNO_2$ (90 mg, 1.2 mmol) in a mixed solvent of water and ethanol (10:1, v/v) (20 mL) at room temperature was treated with HCl (2 M). The resulted mixture was stirred at room temperature for 2 h then filtered, the cake was collected and dried to give the diazonium salt. The residue was used directly for the next step without further purification.

The solution of diazonium salt in DCM (20 mL) was heated to reflux for 3 h. After the reaction was completed, the reaction mixture was concentrated and purified by a flash column chromatography (EtOAc/petroleum ether = 1:2) on silica gel to afford the cyclized product **15** as a yellow oily liquid (212 mg, 0.72 mmol, 72%).

9-Chloro-12-methoxydibenzo[c,h]cinnoline (15) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.50 (d, J = 7.8 Hz, 1H), 9.14 (s, 1H), 8.60 (d, J = 8.6 Hz, 1H), 8.34 (d, J = 7.7 Hz, 1H), 8.05 – 7.92 (m, 3H), 7.87 (t, J = 7.0 Hz, 1H), 4.27 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.27, 144.41, 138.83, 136.56, 131.77, 131.48, 131.32, 129.90, 129.38, 126.82, 123.99, 123.32, 122.72, 122.14, 96.24, 57.64; IR

(thin film, cm^{-1}): 3124, 2951, 2827, 2893, 2664, 2500, 2309, 2227, 1062, 1046; HRMS (ESI): *m/z* Calcd. for $C_{17}H_{12}ClN_2O$ $[M+H]^+$ 296.0633, Found 296.0631.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

^1H and ^{13}C NMR spectra for all compounds (PDF)

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