

## Supporting Information

### Efficient Access to Alkynylated Quinalizinones via the Gold(I)-catalyzed Aminoalkynylation of Alkynes

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## 1. General information

### Practical Considerations:

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. The aminoalkynylation reactions were performed in 2.5 mL glass vials with a PTFE-lined cap and all other reactions for the preparation of starting materials were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by either staining in iodine chamber or potassium permanganate solution followed by charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet. ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

### Materials:

Unless otherwise noted, material obtained from commercial suppliers was used without further purification. Tetrahydrofuran was distilled from Na/benzophenone under an atmosphere of dry N<sub>2</sub>. Anhydrous methanol, dichloromethane, dimethylformamide, diethyl ether, acetonitrile and pet. ether were dried by using standard protocols under N<sub>2</sub>. The catalyst AuCl was purchased from Sigma–Aldrich. All deuterated solvents were used as supplied by Sigma–Aldrich.

### Instrumentation:

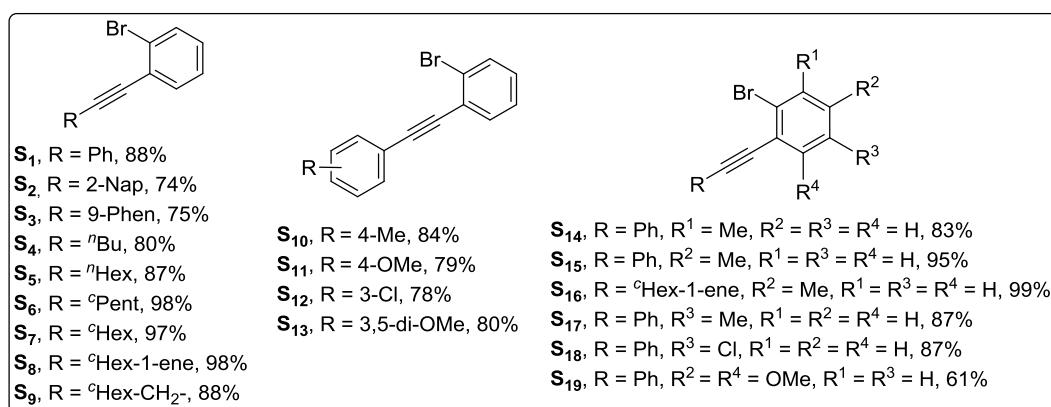
Melting points are uncorrected and recorded using digital Büchi melting point apparatus B-540. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on Bruker AV, 200/400/500, JEOL 400 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of <sup>1</sup>H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), br.s. (broad signal), m (multiplet)... etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Single-crystal data was collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK<sub>α</sub>= 0.71073Å) radiation.

## 2. All procedures

### 2.1 Sonogashira cross-coupling of aryl iodides with alkynes:

All bromoalkynes were prepared by literature known methods<sup>1</sup> except **S**<sub>1</sub>, **S**<sub>2</sub>, **S**<sub>9</sub>, **S**<sub>13</sub>, **S**<sub>14</sub> and **S**<sub>16</sub> which were synthesised by slightly modified procedure as described below.

*Representative procedure:* A suspension of 2-bromoiodobenzene (2 gm, 7.06 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (99.2 mg, 0.14 mmol, 2 mol%), CuI (40.2 mg, 0.21 mmol, 3 mol%) in 20 mL of Et<sub>3</sub>N was degassed. After 10 min, a solution of phenyl acetylene (0.84 mL, 7.77 mmol, 1.1 eq) in Et<sub>3</sub>N (3.6 mL) was added dropwise over a period of 5 min via syringe and the reaction mixture was left to stir for 12 h. After total consumption of the 2-bromoiodobenzene, the reaction mixture was filtered through celite and extracted with EtOAc (3 × 10 mL). The organic layer was washed with a saturated solution of NH<sub>4</sub>Cl (2 × 10 mL), water (2 × 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuo. The reaction mixture was purified by flash chromatography on silica gel, (eluent: pet. ether) to give the product 1-bromo-2-(phenylethynyl) benzene (**S**<sub>1</sub>) as a yellow oil (88% yield).



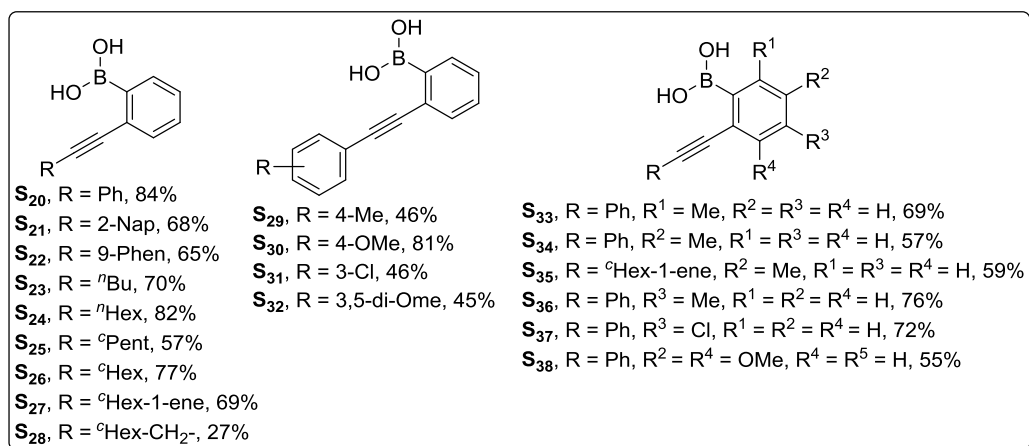
### 2.2 Synthesis of 2-alkynylphenylboronic acids:

The boronic acids **S**<sub>20</sub>, **S**<sub>23</sub>, **S**<sub>24</sub>, **S**<sub>27</sub> and **S**<sub>30</sub> were synthesised by literature known methods<sup>2</sup> and all others were synthesised by slightly modified procedure as described below.

<sup>1</sup> a) M. Kuhn, F. C. Falk, J. Paradies, *Org. Lett.* 2011, **13**, 4100; b) K. Hirano, Y. Inaba, K. Takasu, S. Oishi, Y. Takemoto, N. Fujii, H. Ohno, *J. Org. Chem.* 2011, **76**, 9068; c) T. Morishita, H. Yoshida, J. Ohshita, *Chem. Commun.* 2010, **46**, 640.

<sup>2</sup> a) R. Guo, K.-N. Li, B. Liu, H.-J. Zhu, Y.-M. Fan, L.-Z. Gong, *Chem. Commun.* 2014, **50**, 5451; b) W.-J. Yoo, T. V. Q. Nguyen, S. Kobayashi, *Angew. Chem., Int. Ed.* 2014, **53**, 10213; c) C. Körner, P. Starkov, T. D. Sheppard, *J. Am. Chem. Soc.* 2010, **132**, 5968.

*Representative procedure:* In a two-necked round bottom flask, 1.6 M solution of <sup>n</sup>BuLi in <sup>n</sup>hexane (5.5 mL, 8.78 mmol, 1.5 eq) was added dropwise to a solution of 2-phenylethynyl bromobenzene (**S**<sub>1</sub>) (1.5 g, 5.85 mmol) in 45 mL of diethyl ether under N<sub>2</sub> atmosphere at -78 °C. The mixture was stirred at -78 °C for 1 h and then at -40 °C for 1 h and then cooled back to -78 °C and B(O<sup>i</sup>Pr)<sub>3</sub> (1.65 g, 8.78 mmol, 1.5 eq) was added dropwise. The mixture was allowed to warm up gradually to room temperature, while maintaining vigorous stirring for 16 h. Then, the reaction was quenched with 40 mL of 1N HCl for 30 minutes and extracted with EtOAc (3 x 20 mL). The combined organic solution was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuo. The product was purified by flash chromatography on silica gel, (eluent: pet. ether/EtOAc) followed by recrystallization from pet. ether to give the product [2-(phenylethynyl)phenyl]boronic acid (**S**<sub>20</sub>) as a white solid (84% yield). **Note:** Boronic acids **S**<sub>22</sub> and **S**<sub>25</sub> are obtained in a slightly impure form and therefore used as such for next reactions.

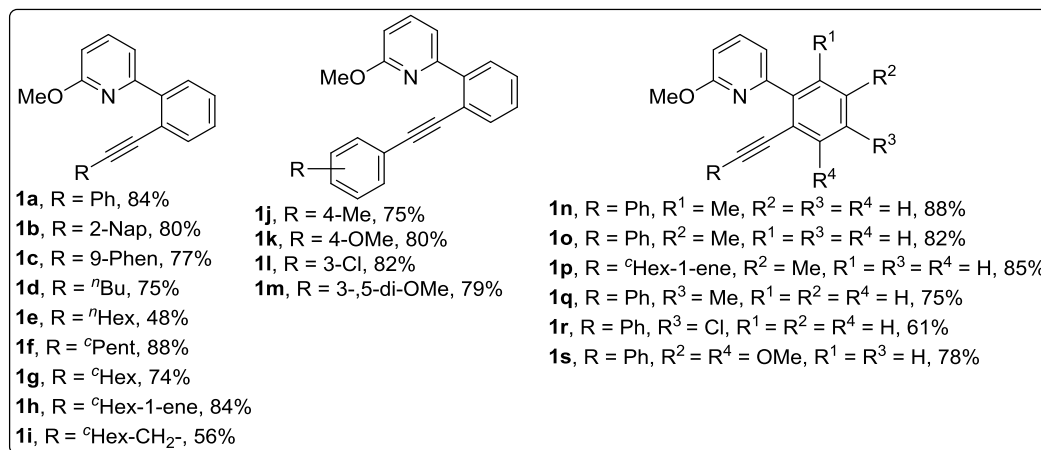


### 2.3 Synthesis of 2-methoxy-6-(2(alkynyl)-phenyl) pyridines:

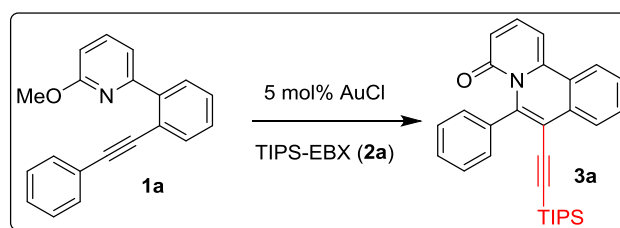
*Representative procedure:* In a sealed tube 2-bromo-6-methoxypyridine<sup>3</sup> (300 mg, 1.59 mmol) and [2-(phenylethynyl)phenyl]boronic acid (**S**<sub>20</sub>) (425 mg, 1.91 mmol, 1.2 eq) in DMF/H<sub>2</sub>O 1:1 (2 mL) was degassed with N<sub>2</sub> for 5 min followed by addition of Na<sub>2</sub>CO<sub>3</sub> (507 mg, 4.78 mmol, 3 eq) under continuous flow of N<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (55.8 mg, 0.079 mmol, 5 mol%) were added to the reaction mixture under a N<sub>2</sub> atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After total consumption of the starting materials, the reaction mixture was diluted with NaHCO<sub>3</sub> (5 mL) and then the product was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed

<sup>3</sup> P. K. Agarwal, M. Saifuddin, B. Kundu, *Tetrahedron* 2010, **66**, 862.

under vacuo. The crude product was purified on a silica gel column using pet. ether/EtOAc as eluent to afford 2-methoxy-6-[2-(phenylethynyl)-phenyl] pyridine (**1a**) as a yellow thick liquid (84% yield).



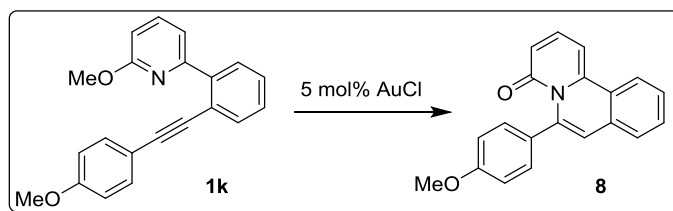
## 2.4 Gold-catalyzed aminoalkynylation reactions:



*Representative procedure:* To a screw-cap vial containing a stir bar were added 2-methoxy-6-[2-(phenylethynyl)-phenyl] pyridine (**1a**) (30 mg, 0.10 mmol), TIPS-EBX (**2a**) (64 mg, 0.15 mmol, 1.5 eq), AuCl (1.1 mg, 5 mol%) and CH<sub>3</sub>CN:MeOH (1.9:0.1 mL). The reaction vial was fitted with a cap, evacuated and back filled with N<sub>2</sub> and heated at 50 °C for 24 h. The reaction mixture was allowed to cool at ambient temperature. The reaction mixture was diluted with EtOAc and wash with NaHCO<sub>3</sub> followed by brine. The collective organic layer dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuo. The resulting residue was purified by flash column chromatography on silica gel (eluent: pet. ether/EtOAc) to give the product **3a** as yellow thick liquid (84% yield).

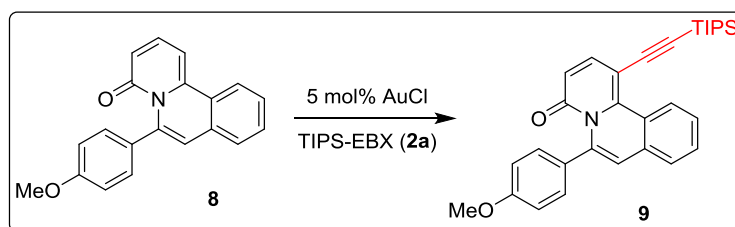
### 3. Control experiments

#### 3.1 Control experiment 1:



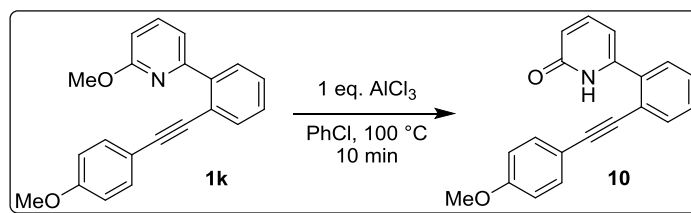
To a stirred solution of 2-methoxy-6-[2-(4-methoxyphenyl)ethynyl]phenylpyridine (**1k**) (40 mg, 0.126 mmol) in CH<sub>3</sub>CN:MeOH (1.9:0.1 ml) was added AuCl (1.47 mg, 0.0063 mmol, 5 mol%) at room temperature. The resulting mixture was stirred under temperature 80 °C for 24 h. The reaction mixture was warm to room temperature and evaporated in vacuo. The residue was purified by flash chromatography on silica gel, (eluent: pet. ether/EtOAc) to give the product 6-(4-methoxyphenyl)-4H-pyrido [2,1-a]isoquinolin-4-one (**8**) as a yellow thick liquid (68% yield).

#### 3.2 Control experiment 2:



To a screw-cap vial containing a stir bar were added 6-(4-methoxyphenyl)-4H-pyrido [2,1-a]isoquinolin-4-one (**8**) (30 mg, 0.10 mmol), TIPS-EBX (**2a**) (64 mg, 0.15 mmol, 1.5 eq), AuCl (1.1 mg, 5 mol%) and CH<sub>3</sub>CN:MeOH (1.9:0.1 mL). The reaction vial was fitted with a cap, evacuated and back filled with N<sub>2</sub> and heated at 50 °C for 24 h. The reaction mixture was allowed to cool at ambient temperature. The reaction mixture was diluted with EtOAc and wash with NaHCO<sub>3</sub> followed by brine. The collective organic layer dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuo. The resulting residue was purified by flash column chromatography on silica gel, (eluent: pet. ether/EtOAc) to give the product (**9**) as yellow solid (83% yield).

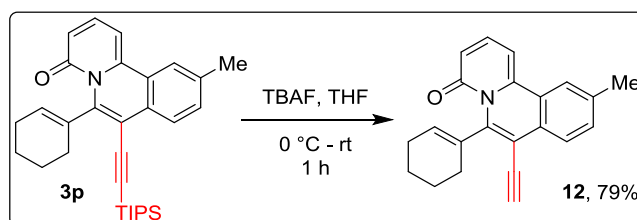
### 3.3 Control experiment 3:



To a stirred solution of 2-methoxy-6-[2-(4-methoxyphenyl)ethynyl]phenylpyridine (**1k**) (100 mg, 0.317 mmol) in chlorobenzene (2.5 ml) was added AlCl<sub>3</sub> (42 mg, 0.317 mmol, 1.1 eq) at room temperature. The resulting mixture was stirred under reflux for 10 min. The mixture was quenched with crushed ice at ice bath temperature and partitioned between EtOAc and aq. HCl. The organic layer was washed with water followed by brine and dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuo. The residue was triturated with pet. ether and dried under reduced pressure 6-(4-methoxyphenyl)-2(1H)-pyridinone (**10**) as a off white solid (47% yield).

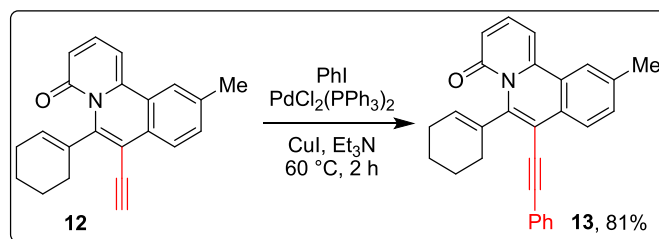
## 4. Product modifications

### a) Desilylation of **3p**:



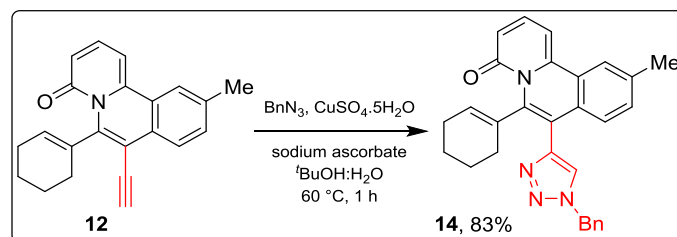
The substrate **3p** (50 mg, 0.10 mmol) was dissolved in THF (3 mL) and TBAF (1.0 M in THF, 0.15 mL, 0.15 mmol) was added slowly at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After complete conversion of starting material reaction mixture was quenched by addition of water. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined organic layers was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The crude product, thus obtained, was purified by column chromatography (eluent: pet. ether/EtOAc) to afford the terminal alkynes **12** as a yellow thick liquid (79% yield).

### b) Sonogashira reaction of **12** with Iodobenzene:



A suspension of iodobenzene (21 mg, 0.10 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (1.4 mg, 0.002 mmol, 2 mol%),  $\text{CuI}$  (0.57 mg, 0.003 mmol, 3 mol%) in 1.5 mL of  $\text{Et}_3\text{N}$  was degassed. After 10 min, a solution of **12** (36 mg, 0.11 mmol, 1.1 eq) in  $\text{Et}_3\text{N}$  (1.5 mL) was added dropwise over 5 min via syringe and the reaction mixture was heated at 60 °C for 2 h. After total consumption of the iodobenzene, the reaction mixture was filtered through celite and extracted with  $\text{EtOAc}$  ( $3 \times 5$  mL). The organic layer was washed with a saturated solution of  $\text{NH}_4\text{Cl}$  ( $2 \times 5$  mL), water ( $2 \times 5$  mL), dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under vacuo. The reaction mixture was purified by flash chromatography on silica gel, (eluent: pet. ether/  $\text{EtOAc}$ ) to give the desired product **13** as a yellow thick liquid (81% yield).

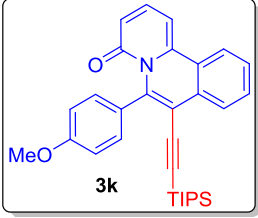
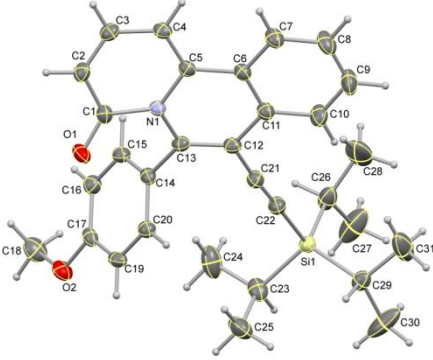
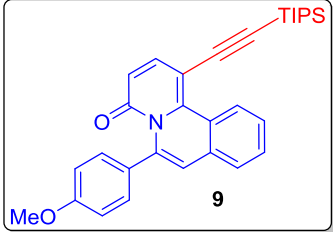
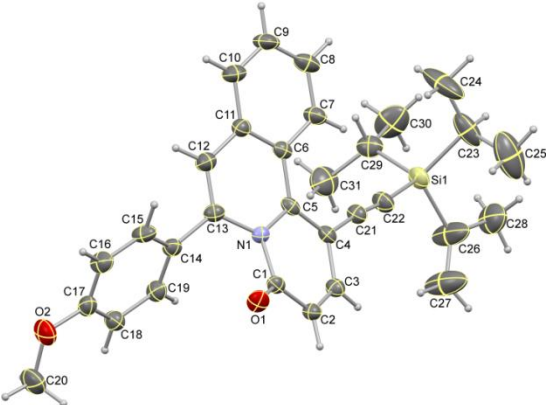
**c) Click reaction of 12 with benzyl azide:**



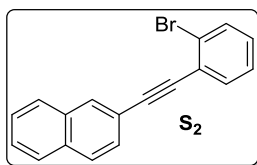
To a solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (5.5 mg, 0.02 mmol, 20 mol%), sodium ascorbate (8.8 mg, 0.04 mmol, 40 mol%) in  $^t\text{BuOH}/\text{H}_2\text{O}$  (1:2 v/v, 2.0 mL) was added a mixture of alkyne **12** (35 mg, 0.11 mmol) and benzyl azide (15 mg, 0.11 mmol, 1 eq) at room temperature. The resultant mixture was stirred at 60 °C for 1 h. After completion of the reaction, the reaction mixture was diluted with  $\text{EtOAc}$ . The organic layer was washed with  $\text{H}_2\text{O}$  followed by brine, dried over  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo. The crude product was purified by a column chromatography (eluent, pet. ether/ $\text{EtOAc}$ ) to give the desired product **14** as a yellow solid (83% yield).



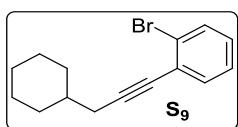
5. ORTEP diagram:

Sr. No	Compound Structure	ORTEP Diagram
1	 <p>3k TIPS</p> <p>CCDC No 1456690</p>	
2	 <p>9 TIPS</p> <p>CCDC No 1456691</p>	

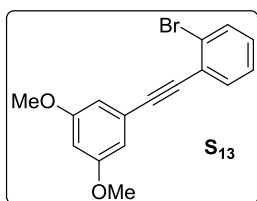
#### 4. Characterization data:



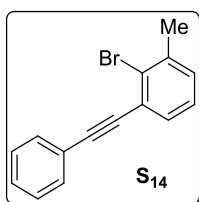
(**S**<sub>2</sub>): yellow solid, 74% yield; mp = 110-111 °C; *R*<sub>f</sub> = 0.80 (pet. ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.17 - 8.12 (m, 1 H), 7.88 - 7.82 (m, 3 H), 7.70 - 7.60 (m, 3 H), 7.57 - 7.49 (m, 2 H), 7.37 - 7.29 (m, 1 H), 7.24 - 7.16 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 133.2, 132.9, 132.4, 131.6, 129.4, 128.3, 128.0, 127.8, 127.8, 127.0, 126.8, 126.6, 125.7, 125.4, 120.2, 94.3, 88.4; HRMS (ESI) calcd for C<sub>18</sub>H<sub>12</sub>Br (M<sup>+</sup> + H) 307.0117, found 307.0114.



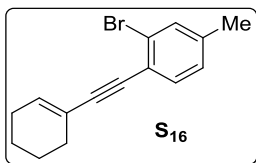
(**S**<sub>9</sub>): colourless liquid, 88% yield; *R*<sub>f</sub> = 0.80 (pet. ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.57 (d, *J* = 7.8 Hz, 1 H), 7.44 (d, *J* = 7.3 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 7.16 - 7.06 (m, 1 H), 2.38 (d, *J* = 6.8 Hz, 2 H), 1.92 (d, *J* = 12.2 Hz, 2 H), 1.76 (d, *J* = 12.7 Hz, 2 H), 1.69 (d, *J* = 12.2 Hz, 2 H), 1.28 (t, *J* = 12.5 Hz, 2 H), 1.22 - 1.11 (m, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 133.3, 132.2, 128.5, 126.8, 126.2, 125.4, 94.5, 80.2, 37.4, 32.7, 27.4, 26.3, 26.2; HRMS (ESI) calcd for C<sub>15</sub>H<sub>18</sub>Br (M<sup>+</sup> + H) 277.0519, found 277.0522.



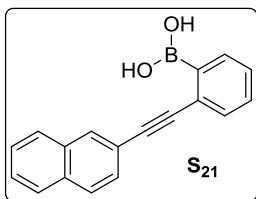
(**S**<sub>13</sub>): yellow liquid, 80% yield; *R*<sub>f</sub> = 0.20 (pet. ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.67 - 7.55 (m, 2 H), 7.45 - 7.30 (m, 3 H), 6.85 - 6.72 (m, 2 H), 6.52 (d, *J* = 2.3 Hz, 1 H), 3.83 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.5, 131.5, 128.3, 124.4, 123.0, 109.2, 101.7, 89.3, 88.9, 55.3; HRMS (ESI) calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>Br (M<sup>+</sup> + H) 317.0172, found 317.0168.



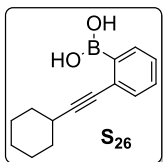
(S<sub>14</sub>): yellow liquid, 88% yield;  $R_f$  = 0.80 (pet. ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.66 - 7.61 (m, 2 H), 7.46 - 7.42 (m, 1 H), 7.41 - 7.38 (m, 3 H), 7.21 (d,  $J$  = 5.5 Hz, 2 H), 2.49 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.7, 132.5, 131.6, 130.7, 130.4, 128.5, 128.4, 128.3, 127.8, 126.7, 125.8, 123.1, 93.4, 88.8, 23.8; HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>Br (M<sup>+</sup>+ H) 271.0117, found 271.0116.



(S<sub>16</sub>): yellow liquid, 99% yield;  $R_f$  = 0.70 (pet. ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.40 (s, 1 H), 7.33 (d,  $J$  = 7.9 Hz, 1 H), 7.04 (d,  $J$  = 7.9 Hz, 1 H), 6.27 (t,  $J$  = 3.8 Hz, 1 H), 2.32 (s, 3 H), 2.29 - 2.25 (m, 2 H), 2.16 (dd,  $J$  = 2.7, 5.8 Hz, 2 H), 1.72 - 1.67 (m, 2 H), 1.66 - 1.62 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 139.4, 135.6, 132.8, 132.7, 127.8, 125.1, 122.8, 120.7, 95.1, 85.5, 29.0, 25.8, 22.3, 21.5, 21.0; HRMS (ESI) calcd for C<sub>15</sub>H<sub>16</sub>Br (M<sup>+</sup>+ H) 275.0326, found 275.0327.

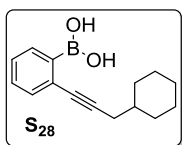


(S<sub>21</sub>): white solid, 68% yield; mp = 192-193 °C;  $R_f$  = 0.20 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.09 (d,  $J$  = 1.8 Hz, 1 H), 8.05 (dd,  $J$  = 1.4, 7.3 Hz, 1 H), 7.89 - 7.81 (m, 3 H), 7.68 - 7.63 (m, 1 H), 7.59 (dd,  $J$  = 1.8, 8.7 Hz, 1 H), 7.56 - 7.48 (m, 3 H), 7.46 - 7.41 (m, 1 H), 5.95 (s, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 135.7, 133.1, 132.9, 132.6, 131.7, 130.9, 128.4, 128.4, 127.9, 127.8, 127.1, 126.8, 126.7, 119.1, 93.9, 90.0; HRMS (ESI) calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>B (M<sup>+</sup>+ H) 273.1081, found 273.1082.

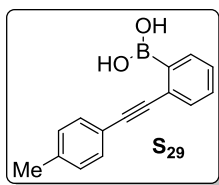


(S<sub>26</sub>): yellow solid, 77% yield; mp = 81-82 °C;  $R_f$  = 0.30 (pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.98 (d,  $J$  = 7.6 Hz, 1 H), 7.48 - 7.45 (m, 1 H), 7.40 (dt,  $J$  = 1.5, 7.5 Hz, 1 H), 7.37 - 7.33 (m, 1 H), 6.28 - 6.15 (m, 2 H), 2.74 - 2.60 (m, 1 H), 2.00 - 1.93

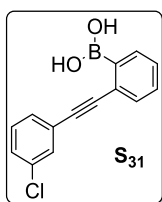
(m, 2 H), 1.82 - 1.74 (m, 2 H), 1.63 - 1.53 (m, 3 H), 1.44 - 1.35 (m, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 135.4, 132.5, 130.7, 127.6, 127.5, 99.0, 81.7, 32.5, 29.7, 25.7, 24.9; HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{B}$  ( $\text{M}^+ + \text{H}$ ) 229.1340, found 229.1344.



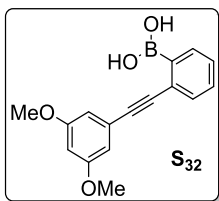
(**S<sub>28</sub>**): white solid, 27% yield; mp = 90-91 °C;  $R_f$  = 0.60 (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.00 (d,  $J$  = 7.3 Hz, 1 H), 7.52 - 7.45 (m, 1 H), 7.44 - 7.33 (m, 2 H), 6.54 (s, 2 H), 2.44 - 2.38 (m, 2 H), 1.89 (d,  $J$  = 11.9 Hz, 3 H), 1.77 (d,  $J$  = 12.8 Hz, 2 H), 1.73 - 1.52 (m, 3 H), 1.37 - 1.25 (m, 2 H), 1.22 - 1.05 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 135.4, 132.6, 130.7, 127.6, 127.5, 94.1, 82.6, 37.3, 32.7, 27.2, 26.1, 26.0; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{B}$  ( $\text{M}^+ + \text{H}$ ) 243.1551, found 243.15503.



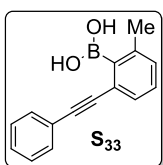
(**S<sub>29</sub>**): white solid, 46% yield; mp = 114-115 °C;  $R_f$  = 0.40 (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.06 - 7.99 (m, 1 H), 7.60 (d,  $J$  = 7.6 Hz, 1 H), 7.49 - 7.45 (m, 3 H), 7.43 - 7.39 (m, 1 H), 7.21 (d,  $J$  = 8.0 Hz, 2 H), 6.03 (s, 2 H), 2.40 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.4, 135.6, 132.5, 131.4, 130.8, 129.4, 128.1, 126.9, 118.8, 93.7, 89.2, 21.6; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{B}$  ( $\text{M}^+ + \text{H}$ ) 237.1081, found 237.1081.



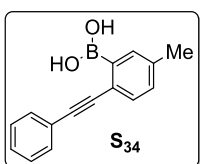
(**S<sub>31</sub>**): white solid, 46% yield; mp = 115-116 °C;  $R_f$  = 0.20 (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.03 (dd,  $J$  = 1.1, 7.5 Hz, 1 H), 7.62 - 7.58 (m, 1 H), 7.55 (t,  $J$  = 1.5 Hz, 1 H), 7.51 - 7.46 (m, 1 H), 7.46 - 7.41 (m, 2 H), 7.40 - 7.36 (m, 1 H), 7.34 (d,  $J$  = 7.6 Hz, 1 H), 5.84 (s, 2 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 135.7, 134.5, 132.7, 131.3, 130.9, 129.8, 129.7, 129.3, 128.7, 126.0, 123.6, 91.9, 90.8; HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{11}\text{O}_2\text{B}^{37}\text{Cl}$  ( $\text{M}^+ + \text{H}$ ) 259.0506, found 259.0504.



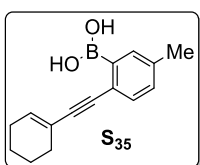
(**S**<sub>32</sub>): white solid, 45% yield; mp = 108-109 °C; *R*<sub>f</sub> = 0.20 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.06 - 7.95 (m, 1 H), 7.64 - 7.56 (m, 1 H), 7.47 (dt, *J* = 1.4, 7.6 Hz, 1 H), 7.42 (dt, *J* = 1.1, 7.4 Hz, 1 H), 6.70 (d, *J* = 2.3 Hz, 2 H), 6.52 (t, *J* = 2.3 Hz, 1 H), 5.92 (s, 2 H), 3.83 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 160.7, 135.6, 132.6, 130.8, 128.4, 126.5, 123.1, 109.3, 102.4, 93.4, 89.2, 55.5; HRMS (ESI) calcd for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>B (M<sup>+</sup>+ H) 283.1136, found 283.1135.



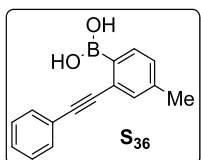
(**S**<sub>33</sub>): white solid, 69% yield; mp = 95-96 °C; *R*<sub>f</sub> = 0.30 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.60 - 7.49 (m, 2 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.39 - 7.33 (m, 3 H), 7.33 - 7.28 (m, 1 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 5.45 (s, 2 H), 2.52 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 142.3, 131.5, 130.1, 129.2, 128.5, 128.4, 125.8, 122.7, 91.8, 90.0, 22.7; HRMS (ESI) calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>B (M<sup>+</sup>+ H) 237.1081, found 237.1080.



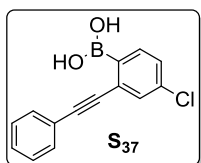
(**S**<sub>34</sub>): white solid, 57% yield; mp = 106-107 °C; *R*<sub>f</sub> = 0.20 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.85 (s, 1 H), 7.58 - 7.53 (m, 2 H), 7.51 (d, *J* = 7.8 Hz, 1 H), 7.42 - 7.36 (m, 3 H), 7.29 (dd, *J* = 1.6, 8.5 Hz, 1 H), 6.11 (s, 2 H), 2.41 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 138.4, 136.3, 132.5, 131.6, 131.5, 128.9, 128.6, 123.6, 122.1, 92.9, 89.9, 21.4; HRMS (ESI) calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>B (M<sup>+</sup>+ H) 237.1081, found 237.1080.



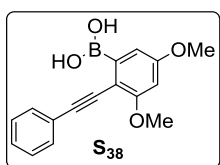
(S<sub>35</sub>): yellow solid, 59% yield; mp = 102-103 °C; *R<sub>f</sub>* = 0.30 (pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.80 (s, 1 H), 7.38 (d, *J* = 7.8 Hz, 1 H), 7.23 (d, *J* = 7.8 Hz, 1 H), 6.30 - 6.22 (m, 1 H), 6.14 (s, 2 H), 2.38 (s, 3 H), 2.28 - 2.23 (m, 2 H), 2.18 (dd, *J* = 2.6, 6.0 Hz, 2 H), 1.75 - 1.68 (m, 2 H), 1.67 - 1.61 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 137.8, 136.4, 136.2, 132.3, 131.6, 124.2, 119.8, 94.9, 87.3, 29.0, 25.8, 22.2, 21.3; HRMS (ESI) calcd for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>B (M<sup>+</sup>+ H) 241.1394, found 241.1393.



(S<sub>36</sub>): white solid, 76% yield; mp = 159-160 °C; *R<sub>f</sub>* = 0.20 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.92 (d, *J* = 7.6 Hz, 1 H), 7.56 (br. s., 2 H), 7.44 (s, 1 H), 7.42 - 7.37 (m, 3 H), 7.24 (d, *J* = 7.6 Hz, 1 H), 6.01 (br. s., 2 H), 2.40 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 141.3, 136.0, 133.4, 131.9, 131.8, 129.6, 129.3, 128.8, 126.8, 122.2, 93.3, 90.2, 21.6; HRMS (ESI) calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>B (M<sup>+</sup>+ H) 237.1081, found 237.1080.

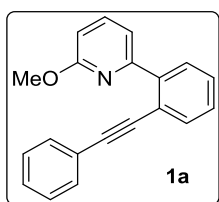


(S<sub>37</sub>): white solid, 72% yield; mp = 122-123 °C; *R<sub>f</sub>* = 0.20 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.96 (d, *J* = 8.3 Hz, 1 H), 7.63 - 7.51 (m, 3 H), 7.47 - 7.33 (m, 5 H), 6.04 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 137.3, 132.5, 131.9, 129.8, 129.0, 128.9, 128.6, 121.6, 94.8, 88.7; HRMS (ESI) calcd for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>BCl (M<sup>+</sup>+ H) 257.0535, found 257.0534.

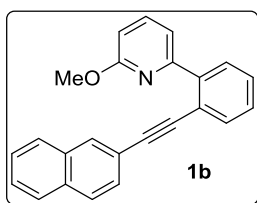


(S<sub>38</sub>): white solid, 55% yield; mp = 125-126 °C; *R<sub>f</sub>* = 0.20 (pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.56 (br. s., 2 H), 7.37 (br. s., 3 H), 7.15 (br. s., 1 H), 6.60 (br. s., 1 H), 6.12 (br. s., 2 H), 3.91 (br. s., 3 H), 3.89 (br. s., 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

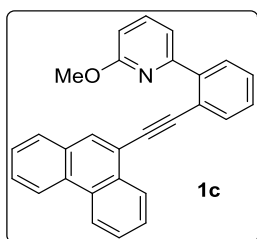
$\delta = 161.7, 160.7, 131.4, 128.6, 128.5, 122.5, 110.7, 108.4, 101.4, 96.6, 86.2, 56.0, 55.5$ ;  
**HRMS (ESI)** calcd for  $C_{16}H_{16}O_4B$  ( $M^+ + H$ ) 283.1136, found 283.1135.



**(1a)**: yellow thick liquid, 84% yield;  $R_f = 0.50$  (pet. ether/EtOAc = 98/02);  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta = 7.89$  (d,  $J = 7.8$  Hz, 1 H), 7.74 - 7.64 (m, 3 H), 7.51 - 7.38 (m, 4 H), 7.37 - 7.29 (m, 3 H), 6.83 - 6.71 (m, 1 H), 4.05 (s, 3 H);  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**  $\delta = 163.8, 155.1, 142.1, 138.5, 133.6, 131.6, 129.9, 128.7, 128.6, 128.4, 128.3, 123.7, 121.5, 117.3, 109.7, 92.8, 89.8, 53.6$ ; **HRMS (ESI)** calcd for  $C_{20}H_{16}NO$  ( $M^+ + H$ ) 286.1226, found 286.1224.

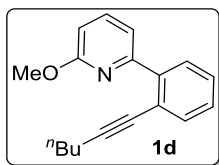


**(1b)**: yellow thick liquid, 80% yield;  $R_f = 0.60$  (pet. ether/EtOAc = 98/02);  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta = 7.94$  (s, 1 H), 7.89 (dd,  $J = 1.2, 7.6$  Hz, 1 H), 7.84 - 7.78 (m, 3 H), 7.75 - 7.70 (m, 2 H), 7.69 (d,  $J = 0.9$  Hz, 1 H), 7.53 - 7.49 (m, 2 H), 7.49 - 7.44 (m, 2 H), 7.41 (d,  $J = 1.2$  Hz, 1 H), 6.80 (dd,  $J = 1.1, 7.8$  Hz, 1 H), 4.04 (s, 3 H);  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**  $\delta = 163.6, 154.9, 141.9, 138.3, 133.4, 133.0, 132.7, 131.2, 129.7, 128.5, 128.1, 128.0, 128.0, 127.7, 126.6, 126.5, 121.2, 120.8, 117.0, 109.4, 92.9, 89.9, 53.4$ ; **HRMS (ESI)** calcd for  $C_{24}H_{18}NO$  ( $M^+ + H$ ) 336.1383, found 336.1383.

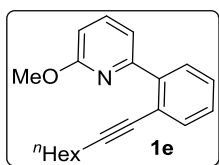


**(1c)**: yellow thick liquid, 77% yield;  $R_f = 0.60$  (pet. ether/EtOAc = 98/02);  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta = 8.67$  (t,  $J = 9.3$  Hz, 2 H), 8.21 (d,  $J = 8.3$  Hz, 1 H), 7.98 (s, 1 H), 7.89 - 7.80 (m, 3 H), 7.74 - 7.64 (m, 4 H), 7.64 - 7.54 (m, 2 H), 7.54 - 7.43 (m, 2 H), 6.83 (d,  $J = 7.8$

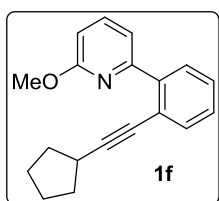
Hz, 1 H), 4.01 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.7, 155.3, 142.2, 138.6, 133.6, 131.7, 131.2, 131.1, 130.2, 130.0, 129.7, 128.6, 128.5, 128.1, 127.4, 127.0, 126.9, 126.9, 122.7, 122.6, 121.6, 119.9, 117.2, 109.5, 93.8, 91.0, 53.4; HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 386.1539, found 386.1540.



(1d): yellow thick liquid, 75% yield;  $R_f$  = 0.40 (pet. ether/EtOAc = 98/02);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.85 - 7.76 (m, 1 H), 7.65 - 7.59 (m, 2 H), 7.56 - 7.50 (m, 1 H), 7.42 - 7.34 (m, 1 H), 7.34 - 7.28 (m, 1 H), 6.76 - 6.66 (m, 1 H), 4.02 (s, 3 H), 2.42 - 2.33 (m, 2 H), 1.58 - 1.49 (m, 2 H), 1.45 - 1.36 (m, 2 H), 0.95 - 0.86 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.5, 155.0, 141.5, 138.1, 133.4, 129.5, 127.8, 127.6, 122.0, 117.0, 109.1, 93.8, 80.2, 53.2, 30.5, 21.9, 19.3, 13.6; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 266.1539, found 266.1539.



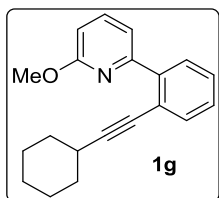
(1e): yellow thick liquid, 48% yield;  $R_f$  = 0.50 (pet. ether/EtOAc = 98/02);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.80 (dd,  $J$  = 1.2, 7.9 Hz, 1 H), 7.63 - 7.58 (m, 2 H), 7.53 (dd,  $J$  = 1.2, 7.6 Hz, 1 H), 7.38 (dt,  $J$  = 1.2, 7.6 Hz, 1 H), 7.33 - 7.28 (m, 1 H), 6.72 (dd,  $J$  = 2.4, 6.7 Hz, 1 H), 4.02 (s, 3 H), 2.37 (t,  $J$  = 7.0 Hz, 2 H), 1.57 - 1.48 (m, 2 H), 1.40 - 1.34 (m, 2 H), 1.32 - 1.26 (m, 4 H), 0.89 (t,  $J$  = 6.9 Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.5, 155.0, 141.5, 138.1, 133.5, 129.5, 127.8, 127.6, 122.0, 117.0, 109.1, 93.9, 80.2, 53.3, 31.4, 28.6, 28.4, 22.5, 19.6, 14.1; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{24}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 294.1852, found 294.1852.



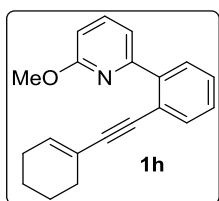
(1f): yellow thick liquid, 88% yield;  $R_f$  = 0.60 (pet. ether/EtOAc = 98/02);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.89 - 7.79 (m, 1 H), 7.68 - 7.56 (m, 2 H), 7.56 - 7.49 (m, 1 H), 7.38 (dt,  $J$  = 1.2, 7.6 Hz, 1 H), 7.33 - 7.28 (m, 1 H), 6.73 (dd,  $J$  = 2.0, 7.1 Hz, 1 H), 4.02 (s, 3 H), 2.81



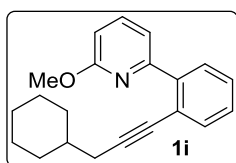
(quin,  $J = 7.2$  Hz, 1 H), 2.04 - 1.86 (m, 2 H), 1.76 - 1.55 (m, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.4, 154.9, 141.5, 138.0, 133.3, 129.5, 127.8, 127.6, 122.0, 117.0, 109.0, 98.0, 79.8, 53.2, 33.5, 31.0, 24.9$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 278.1539, found 278.1539.



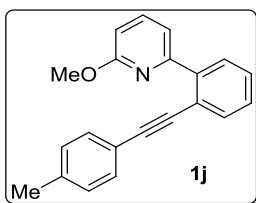
(1g): yellow thick liquid, 74% yield;  $R_f = 0.40$  (pet. ether/EtOAc = 98/02);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.83$  (d,  $J = 7.3$  Hz, 1 H), 7.68 - 7.58 (m, 2 H), 7.53 (d,  $J = 7.3$  Hz, 1 H), 7.38 (t,  $J = 7.6$  Hz, 1 H), 7.34 - 7.29 (m, 1 H), 6.72 (d,  $J = 7.8$  Hz, 1 H), 4.02 (s, 3 H), 2.65 - 2.50 (m, 1 H), 1.80 (d,  $J = 8.3$  Hz, 2 H), 1.69 (dd,  $J = 3.4, 5.9$  Hz, 2 H), 1.54 - 1.44 (m, 3 H), 1.37 - 1.30 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.5, 154.9, 141.5, 138.0, 133.4, 129.5, 127.8, 127.6, 122.0, 117.1, 109.1, 97.8, 80.3, 53.2, 32.3, 29.8, 25.9, 24.7$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 292.1696, found 292.1696.



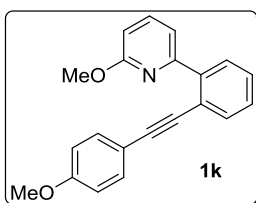
(1h): yellow solid, 84% yield; mp = 50-51 °C;  $R_f = 0.40$  (pet. ether/EtOAc = 98/02);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.88 - 7.78$  (m, 1 H), 7.68 - 7.59 (m, 2 H), 7.58 - 7.50 (m, 1 H), 7.39 (dt,  $J = 1.3, 7.5$  Hz, 1 H), 7.35 - 7.28 (m, 1 H), 6.73 (dd,  $J = 1.6, 7.2$  Hz, 1 H), 6.18 - 5.97 (m, 1 H), 4.02 (s, 3 H), 2.13 (dd,  $J = 3.7, 5.6$  Hz, 4 H), 1.69 - 1.56 (m, 4 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 163.5, 154.8, 141.4, 138.1, 135.0, 133.2, 129.5, 127.9, 127.9, 121.7, 120.9, 117.0, 109.2, 94.5, 86.8, 53.3, 28.8, 25.7, 22.2, 21.5$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 290.1539, found 290.1539.



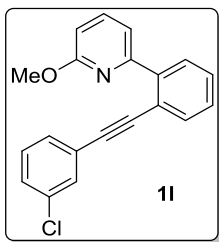
(**1i**): yellow thick liquid, 56% yield;  $R_f = 0.40$  (pet. ether/EtOAc = 98/02);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.81$  (dd,  $J = 1.2, 7.9$  Hz, 1 H), 7.67 - 7.58 (m, 2 H), 7.56 (dd,  $J = 1.2, 7.6$  Hz, 1 H), 7.39 (dt,  $J = 1.4, 7.6$  Hz, 1 H), 7.35 - 7.29 (m, 1 H), 6.74 (dd,  $J = 1.8, 7.0$  Hz, 1 H), 4.03 (s, 3 H), 2.28 (d,  $J = 6.7$  Hz, 2 H), 1.81 - 1.65 (m, 5 H), 1.55 - 1.46 (m, 1 H), 1.32 - 1.19 (m, 2 H), 1.15 (tt,  $J = 3.0, 12.3$  Hz, 1 H), 1.04 - 0.94 (m, 2 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta = 163.5, 155.0, 141.5, 138.0, 133.4, 129.4, 127.8, 127.6, 122.1, 117.0, 109.0, 92.8, 81.0, 53.2, 37.3, 32.7, 27.4, 26.2, 26.1$ ; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{24}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 306.1852, found 306.1851.



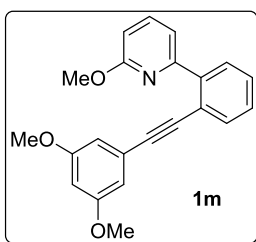
(**1j**): yellow thick liquid, 75% yield;  $R_f = 0.50$  (pet. ether/EtOAc = 98/02);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.84$  (dd,  $J = 1.5, 7.6$  Hz, 1 H), 7.68 - 7.59 (m, 3 H), 7.48 - 7.34 (m, 2 H), 7.31 (s, 1 H), 7.25 (s, 1 H), 7.16 - 7.07 (m, 2 H), 6.74 (dd,  $J = 2.4, 6.6$  Hz, 1 H), 4.00 (s, 3 H), 2.35 (s, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.6, 154.9, 141.7, 138.3, 138.2, 133.3, 131.2, 129.6, 129.1, 128.3, 128.0, 121.5, 120.4, 117.0, 109.3, 92.8, 88.8, 53.3, 21.5$ ; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 300.1383, found 300.1382.



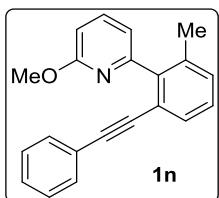
(**1k**): yellow thick liquid, 80% yield;  $R_f = 0.50$  (pet. ether/EtOAc = 98/02);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.87$  (d,  $J = 7.8$  Hz, 1 H), 7.73 - 7.59 (m, 3 H), 7.47 - 7.41 (m, 1 H), 7.41 - 7.32 (m, 3 H), 6.87 (d,  $J = 8.3$  Hz, 2 H), 6.77 (d,  $J = 7.3$  Hz, 1 H), 4.03 (s, 3 H), 3.82 (s, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.5, 159.5, 154.9, 141.5, 138.2, 133.1, 132.8, 129.6, 128.1, 128.0, 121.5, 117.0, 115.6, 114.0, 109.3, 92.6, 88.2, 55.2, 53.3$ ; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}_2$  ( $\text{M}^+ + \text{H}$ ) 316.1332, found 316.1331.



**(1l)**: yellow solid, 82% yield; mp = 52-53 °C;  $R_f$  = 0.50 (pet. ether/EtOAc = 98/02);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.94 - 7.85 (m, 1 H), 7.76 - 7.69 (m, 2 H), 7.61 (d,  $J$  = 7.3 Hz, 1 H), 7.51 (dt,  $J$  = 1.2, 7.6 Hz, 1 H), 7.47 - 7.40 (m, 2 H), 7.36 - 7.32 (m, 1 H), 7.32 - 7.28 (m, 2 H), 6.82 (d,  $J$  = 8.3 Hz, 1 H), 4.06 (s, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.6, 154.8, 142.1, 138.3, 134.2, 133.4, 131.1, 129.7, 129.5, 129.5, 128.8, 128.4, 128.0, 125.2, 120.8, 116.9, 109.5, 91.0, 90.7, 53.3; **HRMS (ESI)** calcd for  $\text{C}_{20}\text{H}_{15}\text{NOCl}$  ( $\text{M}^+$  + H) 320.0837, found 320.0837.

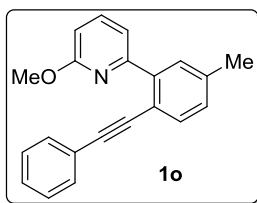


**(1m)**: yellow thick liquid, 79% yield;  $R_f$  = 0.20 (pet. ether/EtOAc = 95/05);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.86 (d,  $J$  = 7.7 Hz, 1 H), 7.73 - 7.65 (m, 2 H), 7.64 - 7.58 (m, 1 H), 7.51 - 7.42 (m, 1 H), 7.42 - 7.33 (m, 1 H), 6.77 (d,  $J$  = 8.2 Hz, 1 H), 6.58 (d,  $J$  = 2.2 Hz, 2 H), 6.47 (t,  $J$  = 2.2 Hz, 1 H), 4.03 (s, 3 H), 3.79 (s, 6 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.5, 160.5, 154.8, 142.0, 138.2, 133.2, 129.6, 128.5, 128.0, 124.7, 121.1, 116.9, 109.3, 109.1, 101.6, 92.5, 89.1, 55.3, 53.3; **HRMS (ESI)** calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}_3$  ( $\text{M}^+$  + H) 346.1438, found 346.1437.

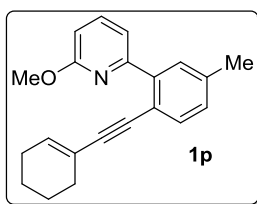


**(1n)**: yellow thick liquid, 88% yield;  $R_f$  = 0.50 (pet. ether/EtOAc = 98/02);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.74 - 7.64 (m, 1 H), 7.49 (br. s., 1 H), 7.31 - 7.23 (m, 5 H), 7.23 - 7.16 (m, 2 H), 7.07 (d,  $J$  = 7.0 Hz, 1 H), 6.77 (d,  $J$  = 8.2 Hz, 1 H), 3.95 (s, 3 H), 2.27 (s, 3 H);  $^{13}\text{C}$

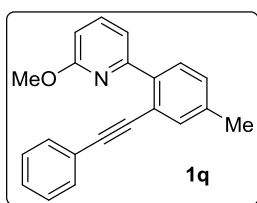
**NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  = 163.6, 156.2, 142.8, 138.4, 136.9, 131.5, 130.7, 129.9, 128.4, 128.2, 127.9, 123.7, 122.8, 118.4, 109.2, 92.3, 89.4, 53.7, 20.7; **HRMS (ESI)** calcd for C<sub>21</sub>H<sub>18</sub>NO (M<sup>+</sup>+ H) 300.1383, found 300.1384.



**(1o)**: yellow thick liquid, 82% yield;  $R_f$  = 0.50 (pet. ether/EtOAc = 98/02); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.71 - 7.65 (m, 2 H), 7.64 - 7.61 (m, 1 H), 7.58 (d,  $J$  = 7.9 Hz, 1 H), 7.44 - 7.38 (m, 2 H), 7.37 - 7.30 (m, 3 H), 7.24 - 7.15 (m, 1 H), 6.77 (d,  $J$  = 7.9 Hz, 1 H), 4.04 (s, 3 H), 2.46 (s, 3 H); **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  = 163.6, 155.1, 141.8, 138.7, 138.3, 133.3, 131.3, 130.3, 129.0, 128.3, 128.1, 123.7, 118.4, 117.2, 109.3, 91.9, 89.7, 53.4, 21.6; **HRMS (ESI)** calcd for C<sub>21</sub>H<sub>18</sub>NO (M<sup>+</sup>+ H) 300.1383, found 300.1384.

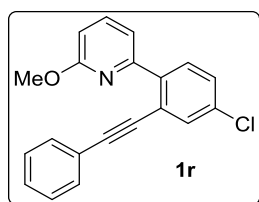


**(1p)**: orange thick liquid, 85% yield;  $R_f$  = 0.40 (pet. ether/EtOAc = 98/02); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.75 - 7.58 (m, 3 H), 7.45 (d,  $J$  = 7.9 Hz, 1 H), 7.14 (d,  $J$  = 7.9 Hz, 1 H), 6.72 (d,  $J$  = 7.9 Hz, 1 H), 6.08 (br. s., 1 H), 4.03 (s, 3 H), 2.42 (s, 3 H), 2.16 - 2.10 (m, 4 H), 1.68 - 1.63 (m, 2 H), 1.62 - 1.57 (m, 2 H); **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  = 163.5, 155.0, 141.3, 138.1, 138.0, 134.6, 133.1, 130.1, 128.8, 121.0, 118.8, 117.1, 109.0, 93.8, 86.9, 53.3, 28.9, 25.7, 22.3, 21.5; **HRMS (ESI)** calcd for C<sub>21</sub>H<sub>22</sub>NO (M<sup>+</sup>+ H) 304.1696, found 304.1695.

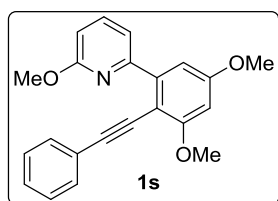


**(1q)**: yellow thick liquid, 75% yield;  $R_f$  = 0.20 (pet. ether/EtOAc = 98/02); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.79 (d,  $J$  = 7.9 Hz, 1 H), 7.70 - 7.64 (m, 2 H), 7.52 (s, 1 H), 7.46 - 7.41 (m, 2 H), 7.37 - 7.32 (m, 3 H), 7.29 (s, 1 H), 6.76 (d,  $J$  = 7.6 Hz, 1 H), 4.03 (s, 3 H), 2.43 (s, 3 H); **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  = 1163.5, 154.8, 139.1, 138.2, 137.9, 133.8, 131.3,

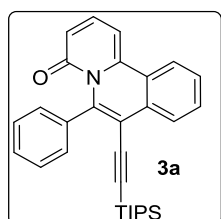
129.6, 129.5, 128.3, 128.1, 123.5, 120.9, 116.8, 109.1, 92.1, 89.7, 53.3, 20.9; **HRMS (ESI)** calcd for  $C_{21}H_{18}NO$  ( $M^+ + H$ ) 300.1383, found 300.1383.



(**1r**): yellow thick liquid, 61% yield;  $R_f = 0.50$  (pet. ether/EtOAc = 98/02);  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta = 7.82$  (d,  $J = 8.5$  Hz, 1 H), 7.70 - 7.61 (m, 3 H), 7.42 (dd,  $J = 2.0, 6.3$  Hz, 3 H), 7.37 - 7.32 (m, 3 H), 6.77 (d,  $J = 8.2$  Hz, 1 H), 4.00 (s, 3 H);  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**  $\delta = 163.6, 153.7, 140.1, 138.4, 133.8, 132.8, 131.4, 131.0, 128.7, 128.6, 128.4, 122.9, 122.7, 116.9, 109.7, 93.6, 88.2, 53.4$ ; **HRMS (ESI)** calcd for  $C_{20}H_{15}NOCl$  ( $M^+ + H$ ) 320.0837, found 320.0839.

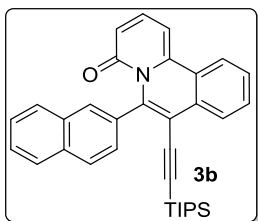


(**1s**): yellow thick liquid, 78% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 95/05);  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta = 7.69 - 7.63$  (m, 1 H), 7.60 (dd,  $J = 0.9, 7.3$  Hz, 1 H), 7.39 - 7.35 (m, 2 H), 7.31 - 7.25 (m, 3 H), 6.97 (d,  $J = 2.4$  Hz, 1 H), 6.76 (dd,  $J = 0.8, 8.1$  Hz, 1 H), 6.53 (d,  $J = 2.4$  Hz, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 3.89 (s, 3 H);  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**  $\delta = 163.7, 162.1, 160.7, 155.1, 145.0, 138.4, 131.4, 128.4, 127.9, 124.3, 117.6, 109.8, 106.4, 104.0, 98.6, 96.0, 85.7, 56.4, 55.7, 53.6$ ; **HRMS (ESI)** calcd for  $C_{22}H_{20}NO_3$  ( $M^+ + H$ ) 346.1438, found 346.1439.

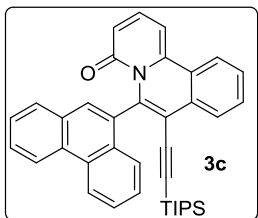


(**3a**): yellow thick liquid, 84% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  **$^1H$  NMR (500 MHz,  $DMSO-d_6$ )**  $\delta = 8.03$  (d,  $J = 7.3$  Hz, 1 H), 7.61 (br. s., 2 H), 7.58 - 7.50 (m, 4 H), 7.47 (t,  $J = 6.9$  Hz, 1 H), 7.21 (t,  $J = 7.2$  Hz, 1 H), 7.08 (d,  $J = 5.8$  Hz, 1 H), 6.60 (d,  $J = 7.9$  Hz, 1

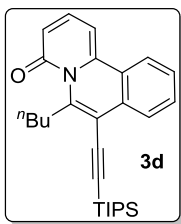
H), 6.43 (d,  $J = 8.9$  Hz, 1 H), 1.04 (br. s., 21 H);  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta = 158.3$ , 143.4, 138.7, 137.6, 136.8, 133.1, 130.7, 129.9, 129.7, 129.5, 129.0, 122.0, 121.3, 119.6, 114.7, 114.5, 106.0, 99.5, 18.4, 10.8; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{34}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 452.2404, found 452.2400.



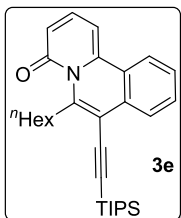
(**3b**): yellow thick liquid, 81% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta = 8.22$  (s, 1 H), 8.10 (d,  $J = 8.5$  Hz, 1 H), 8.05 (d,  $J = 7.9$  Hz, 2 H), 7.97 (d,  $J = 7.6$  Hz, 1 H), 7.74 (dd,  $J = 1.5, 8.5$  Hz, 1 H), 7.67 - 7.59 (m, 2 H), 7.56 (dd,  $J = 6.7, 9.2$  Hz, 1 H), 7.46 (t,  $J = 7.6$  Hz, 1 H), 7.19 - 7.06 (m, 2 H), 6.67 (d,  $J = 8.2$  Hz, 1 H), 6.46 (d,  $J = 8.9$  Hz, 1 H), 1.06 (s, 21 H);  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta = 158.4$ , 143.4, 138.9, 137.7, 134.1, 133.1, 133.1, 132.8, 130.8, 130.1, 129.8, 128.6, 128.3, 127.8, 127.3, 127.0, 121.9, 121.5, 119.6, 114.9, 114.4, 106.1, 99.7, 18.5, 10.8; HRMS (ESI) calcd for  $\text{C}_{34}\text{H}_{36}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 502.2561, found 502.2562.



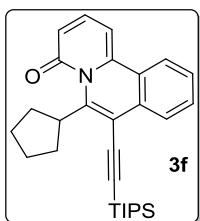
(**3c**): yellow thick liquid, 74% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta = 9.12$  (d,  $J = 8.1$  Hz, 1 H), 8.82 (t,  $J = 9.3$  Hz, 2 H), 8.18 (t,  $J = 9.0$  Hz, 2 H), 7.78 (d,  $J = 7.8$  Hz, 1 H), 7.74 - 7.68 (m, 2 H), 7.68 - 7.62 (m, 2 H), 7.60 - 7.54 (m, 2 H), 7.44 (s, 1 H), 7.40 (dd,  $J = 7.0, 8.9$  Hz, 1 H), 7.12 (d,  $J = 6.6$  Hz, 1 H), 5.91 (d,  $J = 9.0$  Hz, 1 H), 1.00 (d,  $J = 4.4$  Hz, 21 H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta = 158.7$ , 144.1, 140.6, 138.8, 137.7, 134.0, 132.1, 131.7, 131.0, 130.7, 130.4, 129.7, 129.2, 127.8, 127.5, 127.3, 126.8, 126.5, 125.3, 124.2, 123.3, 123.2, 122.0, 120.0, 111.4, 107.5, 105.5, 100.7, 18.8, 11.2; HRMS (ESI) calcd for  $\text{C}_{38}\text{H}_{38}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 552.2717, found 552.2719.



**(3d):** yellow thick liquid, 59% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 8.08$  (d,  $J = 8.2$  Hz, 1 H), 8.11 (d,  $J = 7.9$  Hz, 1 H), 7.61 (t,  $J = 7.5$  Hz, 1 H), 7.56 - 7.47 (m, 2 H), 7.20 (d,  $J = 7.3$  Hz, 1 H), 6.61 (d,  $J = 8.9$  Hz, 1 H), 3.67 - 3.58 (m, 2 H), 1.75 (quin,  $J = 7.7$  Hz, 2 H), 1.42 - 1.35 (m, 2 H), 1.23 - 1.14 (s, 21 H), 0.92 (t,  $J = 7.3$  Hz, 3 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta = 163.3, 147.3, 141.6, 137.3, 130.3, 129.7, 128.0, 125.8, 125.8, 123.3, 116.4, 111.2, 101.3, 101.0, 100.1, 33.2, 31.2, 22.9, 18.7, 13.9, 11.4$ ; **HRMS (ESI)** calcd for  $\text{C}_{28}\text{H}_{38}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 432.2717, found 432.2715.

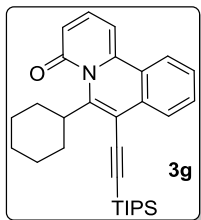


**(3e):** yellow thick liquid, 57% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 8.08$  (d,  $J = 8.2$  Hz, 1 H), 8.11 (d,  $J = 7.9$  Hz, 1 H), 7.61 (t,  $J = 7.5$  Hz, 1 H), 7.55 - 7.48 (m, 2 H), 7.20 (d,  $J = 6.7$  Hz, 1 H), 6.66 - 6.55 (m, 1 H), 3.68 - 3.60 (m, 2 H), 1.81 - 1.72 (m, 2 H), 1.41 - 1.33 (m, 2 H), 1.30 - 1.27 (m, 4 H), 1.22 - 1.17 (m, 21 H), 0.86 (t,  $J = 6.9$  Hz, 3 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta = 163.3, 147.3, 141.6, 137.3, 130.3, 129.7, 128.0, 125.9, 125.8, 123.3, 116.4, 111.2, 101.3, 101.0, 100.1, 33.4, 31.7, 29.5, 29.1, 22.7, 18.8, 14.0, 11.4$ ; **HRMS (ESI)** calcd for  $\text{C}_{30}\text{H}_{42}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 460.3030, found 460.3028.

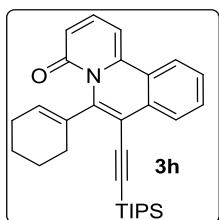


**(3f):** yellow thick liquid, 60% yield;  $R_f = 0.40$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 8.17$  (d,  $J = 7.9$  Hz, 1 H), 8.05 (d,  $J = 8.2$  Hz, 1 H), 7.58 (t,  $J = 7.5$  Hz, 1 H), 7.55 - 7.45 (m, 2 H), 7.16 (d,  $J = 7.3$  Hz, 1 H), 6.58 (d,  $J = 8.5$  Hz, 1 H), 3.74 (quin,  $J = 9.5$  Hz, 1 H), 2.68 - 2.53 (m, 2 H), 2.17 - 2.06 (m, 2 H), 1.98 - 1.86 (m, 2 H), 1.70 - 1.65 (s, 2

H), 1.25 - 1.16 (m, 21 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 164.3, 150.0, 141.8, 137.4, 130.6, 130.2, 128.0, 125.7, 125.5, 123.0, 116.1, 111.2, 105.6, 100.7, 99.5, 44.3, 31.6, 26.1, 18.7, 11.5; HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{38}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 444.2717, found 444.2716.

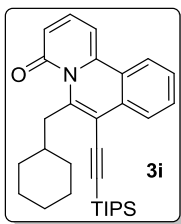


(**3g**): yellow thick liquid, 58% yield;  $R_f$  = 0.40 (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 8.19 (d,  $J$  = 7.8 Hz, 1 H), 8.04 (d,  $J$  = 8.1 Hz, 1 H), 7.58 (t,  $J$  = 7.6 Hz, 1 H), 7.53 - 7.46 (m, 2 H), 7.14 (d,  $J$  = 7.1 Hz, 1 H), 6.59 (d,  $J$  = 8.8 Hz, 1 H), 3.40 - 3.30 (m, 1 H), 2.73 - 2.62 (m, 2 H), 1.96 (d,  $J$  = 12.2 Hz, 2 H), 1.82 (br. s., 2 H), 1.73 - 1.68 (m, 1 H), 1.62 (br. s., 1 H), 1.39 - 1.36 (m, 2 H), 1.25 - 1.18 (m, 21 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 164.4, 151.2, 141.8, 137.3, 130.6, 130.2, 128.0, 125.7, 125.6, 123.0, 116.3, 111.2, 104.9, 101.4, 99.4, 43.4, 29.7, 27.1, 25.6, 18.7, 18.7, 18.3, 11.5; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{40}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 458.2874, found 458.2871.

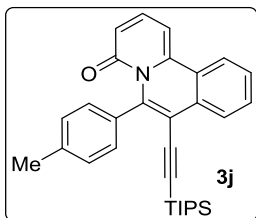


(**3h**): yellow thick liquid, 67% yield;  $R_f$  = 0.40 (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 8.20 (d,  $J$  = 8.0 Hz, 1 H), 8.15 (d,  $J$  = 8.0 Hz, 1 H), 8.06 (d,  $J$  = 8.0 Hz, 2 H), 8.04 - 7.95 (m, 2 H), 7.64 (t,  $J$  = 7.4 Hz, 1 H), 7.59 - 7.51 (m, 2 H), 7.45 (t,  $J$  = 7.4 Hz, 2 H), 7.25 (s, 1 H), 7.24 - 7.13 (m, 2 H), 6.67 (d,  $J$  = 8.8 Hz, 1 H), 5.59 (br. s., 1 H), 2.61 (br. s., 1 H), 2.50 (br. s., 1 H), 2.26 - 2.12 (m, 2 H), 1.87 (br. s., 2 H), 1.69 (br. s., 2 H), 1.19 (s, 21 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 162.1, 145.4, 141.9, 137.4, 133.3, 131.9, 130.4, 128.3, 128.0, 126.2, 125.5, 123.4, 116.2, 110.5, 101.3, 100.1, 94.6, 29.7, 25.4, 22.7, 21.8, 18.8, 11.4; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{38}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 456.2717, found 456.2720.

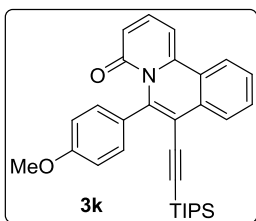




**(3i)**: yellow thick liquid, 62% yield;  $R_f$  = 0.40 (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.18 - 8.04 (m, 2 H), 7.65 - 7.60 (m, 1 H), 7.57 - 7.49 (m, 2 H), 7.23 - 7.20 (m, 1 H), 6.61 (dd,  $J$  = 1.4, 9.0 Hz, 1 H), 3.87 (br. s., 2 H), 1.42 (s, 1 H), 1.22 - 1.19 (s, 21 H), 1.07 (d,  $J$  = 8.2 Hz, 5 H), 1.01 - 0.95 (m, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.6, 145.8, 141.4, 137.4, 130.4, 129.5, 128.1, 126.3, 125.8, 123.3, 116.5, 112.3, 101.8, 101.2, 100.1, 39.1, 37.5, 32.8, 29.7, 26.4, 26.1, 18.8, 11.4; **HRMS (ESI)** calcd for  $\text{C}_{31}\text{H}_{42}\text{NOSi}$  ( $\text{M}^+$  + H) 472.3030, found 472.3026.

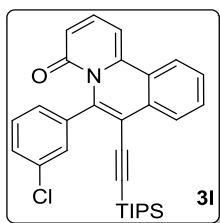


**(3j)**: yellow thick liquid, 80% yield;  $R_f$  = 0.30 (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 8.04 (d,  $J$  = 7.8 Hz, 1 H), 7.57 - 7.44 (m, 4 H), 7.37 (d,  $J$  = 7.3 Hz, 2 H), 7.23 (br. s., 1 H), 7.07 (d,  $J$  = 6.4 Hz, 1 H), 6.72 (d,  $J$  = 8.3 Hz, 1 H), 6.42 (d,  $J$  = 9.3 Hz, 1 H), 2.43 (s, 3 H), 1.04 (br. s., 21 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 158.3, 143.4, 139.3, 138.4, 137.6, 133.8, 133.2, 130.7, 130.1, 130.0, 129.6, 122.0, 121.4, 119.5, 114.7, 114.3, 106.1, 99.5, 21.0, 18.5, 10.8; **HRMS (ESI)** calcd for  $\text{C}_{31}\text{H}_{36}\text{NOSi}$  ( $\text{M}^+$  + H) 466.2561, found 466.2566.

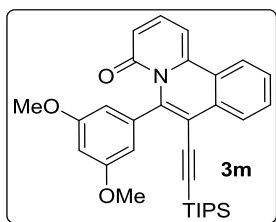


**(3k)**: yellow solid, 87% yield; mp = 53-54 °C;  $R_f$  = 0.20 (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 8.03 (d,  $J$  = 7.8 Hz, 1 H), 7.58 - 7.50 (m, 3 H), 7.47 (t,  $J$  = 7.6 Hz, 1 H), 7.26 (t,  $J$  = 7.7 Hz, 1 H), 7.12 (d,  $J$  = 8.6 Hz, 2 H), 7.07 (d,  $J$  = 6.6 Hz, 1 H), 6.78 (d,  $J$  = 8.1 Hz, 1 H), 6.41 (d,  $J$  = 9.0 Hz, 1 H), 3.87 (s, 3 H), 1.05 (s, 21 H);  $^{13}\text{C NMR}$

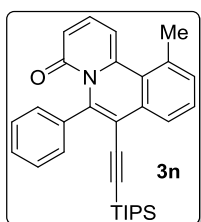
(100 MHz, DMSO- $d_6$ )  $\delta$  = 160.4, 158.3, 143.4, 137.9, 137.5, 133.3, 131.5, 130.6, 130.1, 129.5, 128.8, 121.8, 121.3, 119.4, 114.6, 114.5, 114.0, 106.2, 99.4, 55.4, 18.5, 10.8; HRMS (ESI) calcd for  $C_{31}H_{36}NO_2Si$  ( $M^+ + H$ ) 482.2510, found 482.2508.



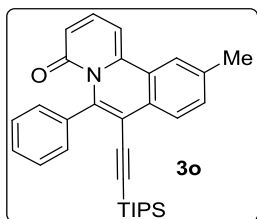
(3l): yellow thick liquid, 68% yield;  $R_f$  = 0.30 (pet. ether/EtOAc = 80/20);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  = 8.05 (d,  $J$  = 7.6 Hz, 1 H), 7.66 (d,  $J$  = 1.5 Hz, 1 H), 7.65 - 7.59 (m, 3 H), 7.55 (dd,  $J$  = 6.7, 9.2 Hz, 1 H), 7.51 (t,  $J$  = 7.3 Hz, 1 H), 7.31 - 7.24 (m, 1 H), 7.10 (dd,  $J$  = 0.6, 6.7 Hz, 1 H), 6.71 (d,  $J$  = 8.2 Hz, 1 H), 6.49 - 6.37 (m, 1 H), 1.07 - 1.02 (m, 21 H);  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  = 158.3, 143.3, 139.3, 138.9, 137.8, 133.6, 132.8, 130.9, 130.8, 130.2, 130.0, 129.5, 129.3, 128.9, 122.1, 121.5, 119.7, 115.3, 112.4, 105.7, 99.9, 18.4, 10.8; HRMS (ESI) calcd for  $C_{30}H_{33}NOCISi$  ( $M^+ + H$ ) 486.2014, found 486.2015.



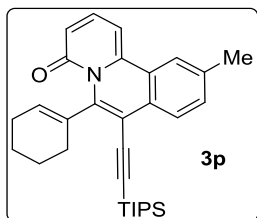
(3m): yellow thick liquid, 71% yield;  $R_f$  = 0.20 (pet. ether/EtOAc = 80/20);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  = 7.97 (br. s., 1 H), 7.53 - 7.39 (m, 2 H), 7.25 (br. s., 1 H), 7.02 (br. s., 1 H), 6.84 (d,  $J$  = 8.2 Hz, 1 H), 6.75 (s, 2 H), 6.64 (br. s., 1 H), 6.40 (d,  $J$  = 9.2 Hz, 1 H), 3.76 (s, 6 H), 1.04 (s, 21 H);  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  = 160.5, 158.3, 143.4, 139.0, 138.6, 137.4, 133.1, 130.7, 129.9, 129.5, 122.4, 121.1, 119.5, 114.6, 114.2, 107.6, 105.7, 101.6, 99.4, 79.1, 55.2, 18.4, 10.8; HRMS (ESI) calcd for  $C_{32}H_{38}NO_3Si$  ( $M^+ + H$ ) 512.2615, found 512.2609.



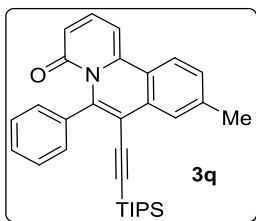
**(3n)**: yellow thick liquid, 72% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta = 7.59 - 7.53$  (m, 6 H), 7.28 (d,  $J = 7.3$  Hz, 1 H), 7.09 (t,  $J = 7.8$  Hz, 1 H), 6.94 (d,  $J = 6.8$  Hz, 1 H), 6.52 (d,  $J = 8.1$  Hz, 1 H), 6.44 (d,  $J = 9.3$  Hz, 1 H), 2.60 (s, 3 H), 1.04 (s, 21 H);  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta = 158.5, 143.7, 138.7, 137.7, 137.0, 134.0, 133.8, 131.8, 130.4, 129.9, 129.4, 129.1, 128.7, 119.7, 119.3, 114.5, 114.0, 106.3, 103.1, 20.4, 18.5, 10.8$ ; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{36}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 466.2561, found 466.2558.



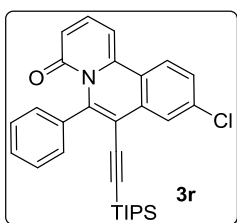
**(3o)**: yellow thick liquid, 70% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta = 7.83$  (s, 1 H), 7.60 - 7.57 (m, 2 H), 7.56 - 7.49 (m, 4 H), 7.04 - 6.99 (m, 2 H), 6.47 (d,  $J = 8.2$  Hz, 1 H), 6.41 (d,  $J = 9.2$  Hz, 1 H), 2.33 (s, 3 H), 1.03 (s, 21 H);  $^{13}\text{C NMR}$  (125 MHz, DMSO- $d_6$ )  $\delta = 177.4, 158.4, 143.5, 139.9, 138.9, 137.6, 136.9, 131.2, 131.0, 130.8, 130.0, 129.4, 129.0, 121.9, 121.3, 119.5, 114.1, 113.6, 106.1, 99.4, 72.7, 21.0, 18.5, 10.8$ ; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{36}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 466.2561, found 466.2559.



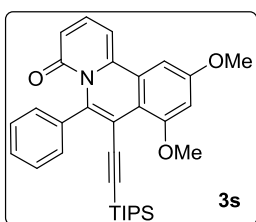
**(3p)**: yellow thick liquid, 77% yield;  $R_f = 0.40$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta = 8.07$  (d,  $J = 8.3$  Hz, 1 H), 7.91 (s, 1 H), 7.53 - 7.41 (m, 2 H), 7.19 (d,  $J = 7.3$  Hz, 1 H), 6.55 (d,  $J = 8.8$  Hz, 1 H), 5.57 (br. s., 1 H), 2.59 (br. s., 1 H), 2.51 (s, 3 H), 2.18 (br. s., 2 H), 1.86 (br. s., 2 H), 1.80 (br. s., 1 H), 1.69 (br. s., 1 H), 1.26 (s, 2 H), 1.19 (s, 21 H);  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta = 161.8, 144.6, 141.4, 138.2, 137.1, 136.2, 131.8, 127.7, 126.1, 125.8, 125.1, 123.2, 115.9, 110.2, 101.6, 99.5, 29.1, 25.3, 22.7, 21.8, 21.7, 18.7, 11.4$ ; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{40}\text{NOSi}$  ( $\text{M}^+ + \text{H}$ ) 470.2874, found 470.2870.



**(3q)**: yellow thick liquid, 74% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta = 7.91 - 7.81$  (m, 1 H), 7.62 - 7.50 (m, 5 H), 7.50 - 7.45 (m, 1 H), 7.27 (d,  $J = 8.3$  Hz, 1 H), 7.00 - 6.86 (m, 1 H), 6.44 - 6.30 (m, 2 H), 2.07 (s, 3 H), 1.04 (s, 21 H);  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta = 158.3, 143.5, 139.5, 138.7, 137.4, 136.9, 133.4, 130.6, 129.9, 129.3, 128.8, 128.5, 122.4, 121.0, 119.0, 114.5, 114.3, 105.9, 98.8, 21.6, 18.4, 10.8$ ; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{36}\text{ONSi}$  ( $\text{M}^+ + \text{H}$ ) 466.2561, found 466.2558.

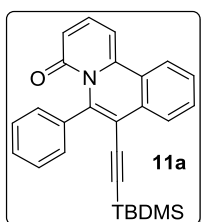


**(3r)**: yellow thick liquid, 71% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta = 8.08$  (d,  $J = 8.3$  Hz, 1 H), 7.60 (br. s., 5 H), 7.57 - 7.53 (m, 2 H), 7.12 (d,  $J = 6.4$  Hz, 1 H), 6.49 - 6.41 (m, 2 H), 1.04 (s, 21 H);  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta = 158.4, 142.7, 137.9, 136.8, 134.8, 134.4, 130.1, 129.9, 129.8, 129.4, 123.4, 122.0, 120.0, 116.3, 115.7, 106.0, 100.4, 18.7, 10.9$ ; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{33}\text{ONClSi}$  ( $\text{M}^+ + \text{H}$ ) 486.2014, found 486.2015.

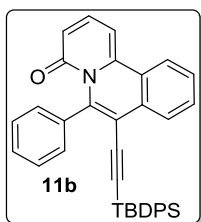


**(3s)**: yellow thick liquid, 75% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta = 7.52 - 7.47$  (m, 1 H), 7.38 - 7.32 (m, 5 H), 7.29 - 7.27 (m, 1 H), 7.11 (d,  $J = 6.7$  Hz, 1 H), 6.46 (s, 1 H), 6.39 (d,  $J = 9.2$  Hz, 1 H), 3.87 (s, 3 H), 3.07 (s, 3 H), 1.04 (s, 21 H);  $^{13}\text{C NMR}$  (125 MHz, DMSO- $d_6$ )  $\delta = 162.4, 158.7, 155.3, 143.7, 140.6, 138.8, 137.5, 136.9, 134.1, 129.4, 127.4, 127.2, 119.8, 114.6, 112.3, 111.8, 107.6, 100.7, 99.9, 96.8$ ,

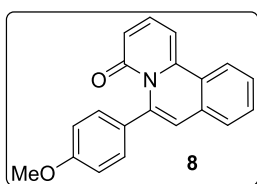
56.0, 55.2, 18.5, 10.9; **HRMS (ESI)** calcd for  $C_{32}H_{38}NO_3Si$  ( $M^+ + H$ ) 512.2615, found 512.2615.



**(11a):** yellow thick liquid, 74% yield;  $R_f = 0.40$  (pet. ether/EtOAc = 80/20);  **$^1H$  NMR (500 MHz, DMSO- $d_6$ )**  $\delta = 8.03$  (d,  $J = 7.6$  Hz, 1 H), 7.60 - 7.53 (m, 6 H), 7.47 (t,  $J = 7.3$  Hz, 1 H), 7.23 - 7.18 (m, 1 H), 7.09 (dd,  $J = 0.9, 6.7$  Hz, 1 H), 6.55 (d,  $J = 7.9$  Hz, 1 H), 6.46 (dd,  $J = 0.9, 9.2$  Hz, 1 H), 0.91 (s, 9 H), 0.12 (s, 6 H);  **$^{13}C$  NMR (125 MHz, DMSO- $d_6$ )**  $\delta = 158.4, 143.4, 139.1, 137.8, 136.6, 133.1, 130.8, 130.0, 130.0, 129.8, 129.6, 129.2, 122.1, 121.4, 119.6, 116.4, 114.2, 105.0, 99.7, 26.0, -4.6$ ; **HRMS (ESI)** calcd for  $C_{27}H_{28}NOSi$  ( $M^+ + H$ ) 410.1935, found 410.1934.

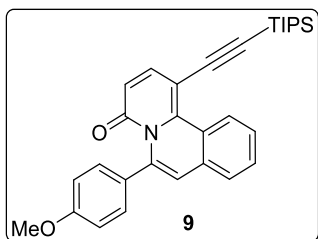


**(11b):** yellow thick liquid, 48% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  **$^1H$  NMR (500 MHz, DMSO- $d_6$ )**  $\delta = 8.06$  (d,  $J = 7.6$  Hz, 1 H), 7.83 - 7.77 (m, 4 H), 7.72 - 7.66 (m, 2 H), 7.63 - 7.58 (m, 4 H), 7.50 (t,  $J = 7.5$  Hz, 1 H), 7.46 - 7.38 (m, 6 H), 7.23 (t,  $J = 7.8$  Hz, 1 H), 7.13 (d,  $J = 6.7$  Hz, 1 H), 6.59 (d,  $J = 8.2$  Hz, 1 H), 6.53 (d,  $J = 9.2$  Hz, 1 H), 1.01 (s, 9 H);  **$^{13}C$  NMR (125 MHz, DMSO- $d_6$ )**  $\delta = 158.7, 143.5, 139.3, 138.1, 136.7, 135.3, 133.1, 132.6, 131.0, 130.1, 130.0, 129.7, 129.3, 127.9, 122.4, 121.5, 119.8, 113.9, 112.8, 107.7, 100.1, 26.8, 18.3$ ; **HRMS (ESI)** calcd for  $C_{37}H_{32}NOSi$  ( $M^+ + H$ ) 534.2248, found 534.2247.

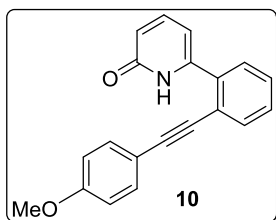


**(8):** yellow thick liquid, 68% yield;  $R_f = 0.20$  (pet. ether/EtOAc = 80/20);  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta = 8.22$  (d,  $J = 8.1$  Hz, 1 H), 7.65 - 7.58 (m, 3 H), 7.57 - 7.52 (m, 1 H), 7.36 -

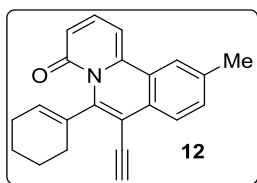
7.32 (m, 2 H), 7.31 - 7.30 (m, 1 H), 6.97 - 6.92 (m, 2 H), 6.87 (s, 1 H), 6.58 (dd,  $J = 1.0, 8.8$  Hz, 1 H), 3.86 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 162.2, 158.8, 142.6, 138.6, 137.4, 131.3, 130.4, 128.1, 127.1, 126.8, 126.6, 123.5, 119.2, 115.8, 113.2, 99.8, 55.3$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NO}_2$  ( $\text{M}^+ + \text{H}$ ) 302.1176, found 302.1174.



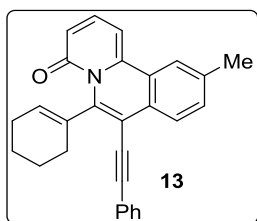
(**9**): yellow solid, 83% yield; mp = 61-62 °C;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta = 10.09$  (d,  $J = 8.4$  Hz, 1 H), 7.72 (d,  $J = 9.2$  Hz, 1 H), 7.62 (d,  $J = 6.9$  Hz, 1 H), 7.59 (s, 1 H), 7.49 - 7.46 (m, 1 H), 7.33 - 7.28 (m,  $J = 8.4$  Hz, 2 H), 6.97 - 6.91 (m,  $J = 8.8$  Hz, 2 H), 6.89 (s, 1 H), 6.51 (d,  $J = 9.2$  Hz, 1 H), 3.85 (s, 3 H), 1.23 - 1.18 (m, 21 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 161.7, 159.1, 144.5, 139.0, 134.2, 134.1, 131.5, 131.0, 130.9, 129.3, 129.2, 127.3, 126.9, 126.7, 126.5, 119.6, 115.5, 113.6, 106.6, 98.1, 97.4, 55.3, 18.8, 11.5$ ; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{36}\text{NO}_2\text{Si}$  ( $\text{M}^+ + \text{H}$ ) 482.2510, found 482.2509.



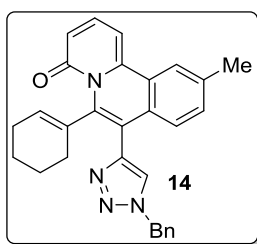
(**10**): off white solid, 47% yield; mp = 136-137 °C;  $R_f = 0.20$  (pet. ether/EtOAc = 40/60);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 11.01$  (br. s., 1 H), 7.68 - 7.60 (m, 1 H), 7.55 - 7.46 (m, 2 H), 7.43 (d,  $J = 5.9$  Hz, 4 H), 6.85 (d,  $J = 8.3$  Hz, 2 H), 6.57 (d,  $J = 9.3$  Hz, 1 H), 6.51 (d,  $J = 6.8$  Hz, 1 H), 3.80 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.7, 160.0, 145.6, 140.9, 134.6, 133.3, 133.2, 129.6, 128.7, 128.5, 121.4, 119.3, 114.4, 114.1, 106.7, 95.2, 85.8, 55.3$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NO}_2$  ( $\text{M}^+ + \text{H}$ ) 302.1176, found 302.1172.



**(12):** yellow thick liquid, 79% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.99$  (d,  $J = 8.3$  Hz, 1 H), 7.92 (s, 1 H), 7.51 (t,  $J = 8.3$  Hz, 1 H), 7.44 (d,  $J = 7.8$  Hz, 1 H), 7.20 (d,  $J = 7.3$  Hz, 1 H), 6.56 (d,  $J = 8.8$  Hz, 1 H), 5.51 (br. s., 1 H), 3.47 (s, 1 H), 2.64 (br. s., 1 H), 2.52 (s, 3 H), 2.19 (br. s., 2 H), 1.85 (br. s., 3 H), 1.69 (br. s., 2 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 161.7, 145.5, 141.4, 138.4, 137.2, 136.3, 131.8, 127.4, 125.8, 125.2, 123.3, 116.0, 108.9, 99.5, 85.0, 29.3, 25.4, 22.8, 21.9, 21.8$ ; **HRMS (ESI)** calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 314.1539, found 314.1539.



**(13):** yellow thick liquid, 81% yield;  $R_f = 0.30$  (pet. ether/EtOAc = 80/20);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.10$  (d,  $J = 8.3$  Hz, 1 H), 7.97 (s, 1 H), 7.63 - 7.57 (m, 2 H), 7.56 - 7.47 (m, 2 H), 7.45 - 7.35 (m, 3 H), 7.24 (d,  $J = 7.3$  Hz, 1 H), 6.58 (d,  $J = 9.3$  Hz, 1 H), 5.59 (br. s., 1 H), 2.69 (br. s., 2 H), 2.54 (s, 3 H), 2.25 (br. s., 2 H), 1.91 (br. s., 3 H), 1.75 (br. s., 1 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 161.8, 144.2, 141.4, 138.4, 137.1, 136.6, 131.8, 131.4, 128.5, 128.4, 127.5, 125.9, 125.9, 125.1, 123.4, 115.9, 110.0, 99.6, 97.1, 84.9, 29.5, 25.5, 22.9, 22.1, 21.8$ ; **HRMS (ESI)** calcd for  $\text{C}_{28}\text{H}_{24}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 390.1852, found 390.1852.



**(14):** yellow solid, 83% yield; mp = 120-121 °C;  $R_f = 0.30$  (pet. ether/EtOAc = 60/40);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.96$  (s, 1 H), 7.42 - 7.31 (m, 6 H), 7.26 - 7.19 (m, 3 H), 6.54 (d,  $J = 8.7$  Hz, 1 H), 5.63 (br. s., 1 H), 5.58 (br. s., 1 H), 5.19 (br. s., 1 H), 2.46 (s, 3 H), 2.02 (d,  $J = 7.8$  Hz, 1 H), 1.94 (br. s., 1 H), 1.66 - 1.45 (m, 4 H), 1.45 - 1.30 (m, 1 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta = 162.2, 142.8, 142.2, 140.6, 138.1, 137.1, 135.5, 134.6, 131.5, 129.2, 128.9, 128.8, 128.1, 126.1, 125.9, 125.8, 124.4, 123.4, 115.9, 115.7, 99.5, 54.3, 30.4, 24.9, 22.3, 21.7, 21.5$ ; **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{27}\text{N}_4\text{O}$  ( $\text{M}^+ + \text{H}$ ) 447.2178, found 447.2179.

## 5. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra:

