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Synthesis of new polyaza heterocycles. Part 42: Diazines

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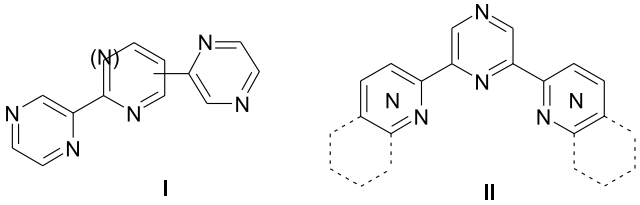
Abstract—Using Pd-catalyzed Stille cross-coupling reactions, we report here the synthesis of various mono- or bis(tri-*n*-butylstannyl)diazines which were reacted with various halogenated diazines to access to various polyaza heterocyclic derivatives.

Polyaromatic compounds containing N-heterocyclic subunits have received considerable attention due to their wide use in various fields such as molecular recognition, metal cryptates, supramolecular devices and self-assembly. Among them, oligopyridines have been extensively studied during the last two decades and many well-defined supramolecular architectures with 2,2′-bipyridines (bpy) and 2,2′6′,2″-terpyridines (tpy) units as building blocks have found applications in catalysis,[1] electrochemistry,[2] photochemistry[3] or new materials.[4]

More recently, synthesis of polydentate nitrogen ligands based on pyridine and 1,3-pyrimidine[5] or 3,6 pyridazine[6] units have been reported. Interest in this class of molecules incorporating several coordination sites is mostly due to their use in supramolecular chemistry, and as building blocks for self-assembled polynuclear coordination arrays.[7]

We report here the synthesis of a new family of polyaromatic compounds containing a pyridine or pyrimidine ring as central unit substituted by two pyrazinyl groups (type I) and symmetrical structures with a pyrazine central unit substituted at the 2 and 6 positions by π-deficient heterocycles such as pyridine, quinoline, diazine or benzodiazine (type II) (Scheme 1).

Synthetic approaches to such polyaza heterocyclic compounds are based either on palladium-catalyzed cross-coupling procedures: Suzuki,[8] Negishi[9] and Stille[10] coupling reactions or by generation of the aza-heterocyclic rings with the help of ring-closure reactions.



Scheme 1.

The Suzuki reaction involves the palladium-catalyzed cross-coupling of heteroarylboronic acids with heteroaryl halides (or triflates). It is remarkable that whereas halopyridines have often been employed in Suzuki reactions there are only few examples in the literature of use of pyridylboronic acids or esters.[11] In diazine series only the 5-pyrimidylboronic acids or esters have been described[12] while to our knowledge, they are unknown with pyrazine or pyridazine rings probably because of their unstability.

Some Negishi reactions have been achieved with organozinc derivatives of diazines to give cross-coupling reactions with iodo or bromo aromatics leading to diazine-aryl or (heteroaryl) bound.[13]

Stille-type coupling provides another efficient way for the formation of aryl–aryl bonds in particular between π-deficient N-heterocycles. This process has been used to prepare a wide variety of functionalized 2,2′-bipyridines and 2,2′6′,2″-terpyridines.[14]

Using a synthetic strategy based on Stille coupling reaction, we report here the synthesis of mono- or bis(tri-*n*-butylstannyl) diazines which were reacted with various halogenated diazines to obtain polyaza heterocyclic derivatives.

Keywords: Stille cross-coupling reaction; Diazines; Polyaza heterocycles.
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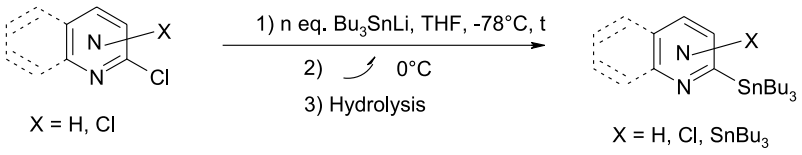
1. Results

The synthesis of diazinylstannanes could be performed either using the lithiation reaction of diazine followed by a transmetalation step with tributyltin chloride[15] or by use of the nucleophilic substitution of a chlorine atom by the stannyl anion.[16]

We have investigated this last procedure to synthesize the tri-(*n*-butyl)organostannanes (**1**–**9**) with a diazine moiety (Scheme 2) the results of which are given in Table 1.

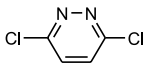
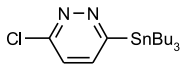
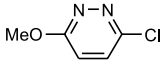
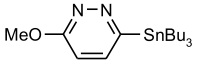
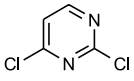
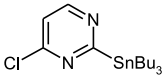
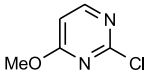
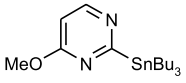
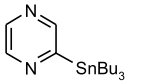
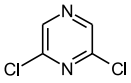
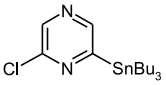
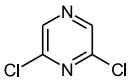
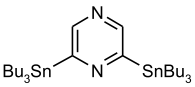
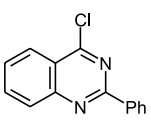
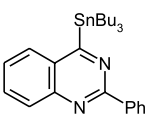
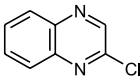
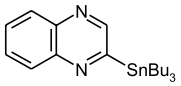
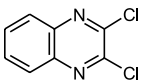
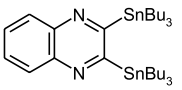
One can observe a monosubstitution with very low yields for dichloro-pyridazine and pyrimidine (entries 1 and 3). These low yields could be explained by competitive radical reactions, since some dimers and bistributyltin were observed besides the expected compounds. Good results were obtained for chloropyrazine (entry 5) and 2,6-dichloropyrazine (entry 6). For this last compound, mono or distannylation has been achieved in good and moderate yield (entries 6 and 7). The nucleophilic substitution was performed successfully with good yield with 2-chloro-4-methoxypyrimidine (entry 4) whereas the yield was low with 2,4-dichloropyrimidine (entry 3). Such a result could suggest that the presence of a methoxy group makes the substitution reaction more easy, however, it can be noticed that stannylation failed with 3-chloro-6-methoxypyridazine (entry 2). In benzodiazine series good yields with mono-chloro-quinazoline (entry 8) or quinoxaline (entry 9) were observed. With 2,3-dichloroquinoxaline, a disubstitution can be obtained with a very good yield (entry 10) despite the steric hindrance of the tri-*n*-butylstannyl group.

Coupling reactions of the stannyl derivatives **3**, **7**–**9** were

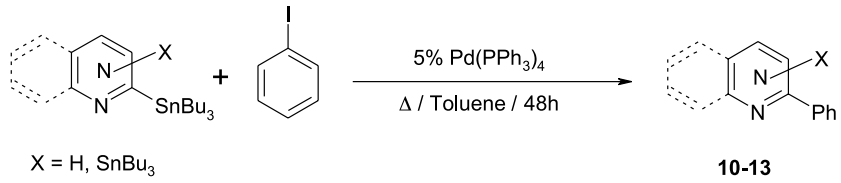


Scheme 2.

Table 1. Synthesis of tri-*n*-butyl-*N*-heteroarylstannanes

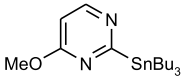
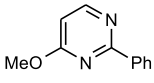
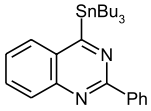
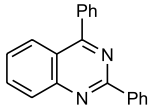
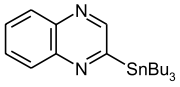
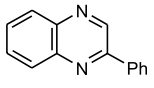
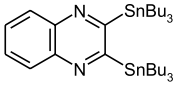
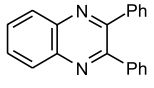
Entry	Het-Cl	Product	*n* (equiv)	*t* (h)	Compound	Yield (%)
1			1.1	5	**1**	9
2			1.1	5	—	—
3			1.1	6	**2**	4
4			1.1	1	**3**	70
5			1.1	8	**4**	85[a]
6			1.1	21	**5**	95
7			2.1	24	**6**	56
8			1.1	1	**7**	97
9			1.1	1	**8**	54
10			2.1	1	**9**	98

[a] Hydrolysis was performed at −40 °C.

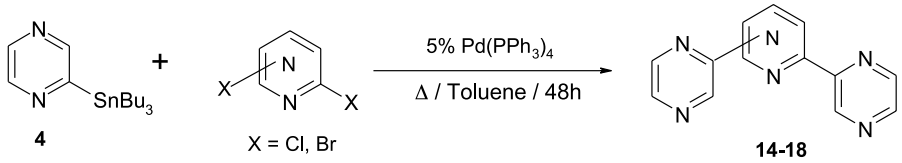


Scheme 3.

Table 2. Cross-coupling reaction of $HetSnBu_3$ with iodobenzene

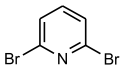
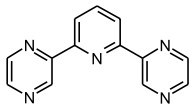
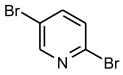
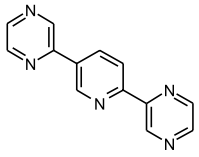
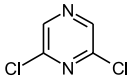
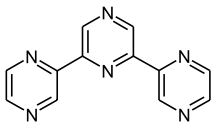
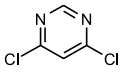
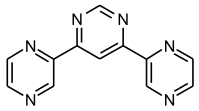
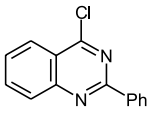
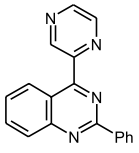
Entry	$HetSnBu_3$	Product	Compound[a]	Yield (%)
1			**10**[17]	78
2			**11**[18]	67
3			**12**[18]	64
4			**13**[19]	39

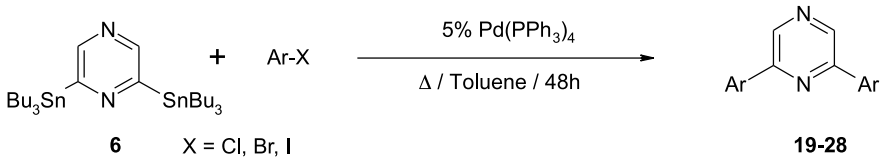
[a] All products **10–13** have been characterized and comparison with already published data are in agreement.



Scheme 4.

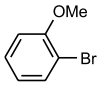
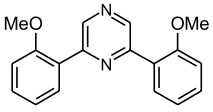
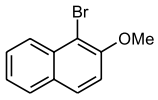
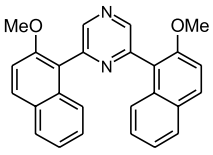
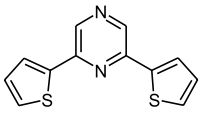
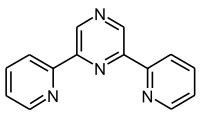
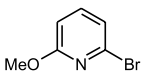
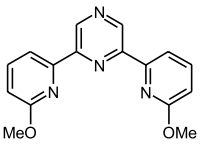
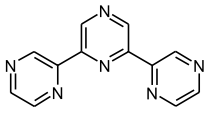
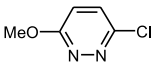
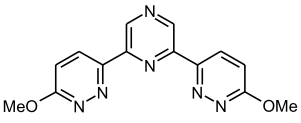
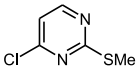
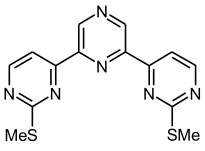
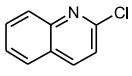
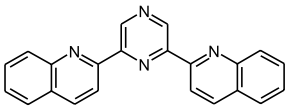
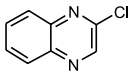
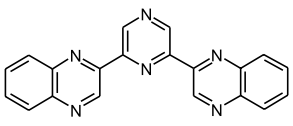
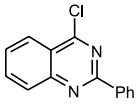
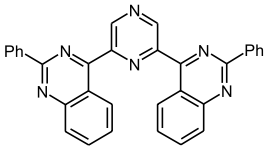
Table 3. Cross-coupling reaction of tri-(*n*-butyl)stannylpyrazine **4** with halogeno-N-heteroaryl compounds

Entry	N-$HetX_2$	Product	*t* (h)	Compound	Yield (%)
1			15	**14**	66
2			27	**15**	64
3			26	**16**	75
4			27	**17**	61
5			48	**18**	70



Scheme 5.

Table 4. Cross-coupling reaction of the 2,6-distannylpyrazine **6** with halogenoaromatics

Entry	ArX	Product	Compound	Yield (%)
1			**19**	82
2			**20**	51
3			**21**	76
4			**22**	30
5			**23**	60
6			**16**	65
7			**24**	21
8			**25**	59
9			**26**	91
10			**27**	65
11			**28**	71

tested with iodobenzene according to the general procedure for Stille reaction in toluene with $Pd(PPh_3)_4$ as catalyst. Under these conditions, the expected phenyl or diphenyl compounds **10–13** were obtained in moderate yields (Scheme 3, Table 2).

We then extended this procedure to the coupling reaction of 2-tri-*n*-butylstannylpyrazine **4** with various mono or dihalogeno N-heteroaryl compounds leading to various π-deficient heterocycles appended to a pyrazinyl group (Scheme 4, Table 3).

Compounds **14–18** were obtained in fairly good yields and present a bi- or tridentate binding system which make them potential metal cryptands. Compounds **15** and **18** may be viewed as aza-analogues of bipyridine (bpy), **17** as aza-analogue of two bpys and **14** and **16** as aza-analogues of terpyridine (tpy). Compounds **16** and **17** belong to a family of symmetrical tridiazines, whereas **14** and **15** are di-pyrazinylpyridines.

In the aim to synthesize symmetrical polydentates with a pyrazine moiety as central unit, the cross-coupling reaction of the 2,6-bis-tri-*n*-butylstannylpyrazine **6** was performed with various monohalogenoaryl compounds. Pyrazine linked to various aromatic rings (benzene, naphthalene, thiophene or π-deficient N-heterocycles) were obtained (Scheme 5, Table 4).

This general methodology allowed us to access to a wide range of compounds which constitute a new family of triaromatic strands with a diazine as central unit, most of them (**16**, **22–28**) are tri-π-deficient N-heterocycles linked by direct aryl–aryl bounds and could be seen as aza-analogues of terpyridines. These structures are potential trinucleating ligands due to the presence of coordinating atoms such as nitrogen, oxygene or sulfur.

Compounds **19** and **20** have two phenyl or naphthyl ring, *ortho* substituted by a methoxy group which could allow complexation, whereas for the compound **21**, the sulfur of the thiophene ring could play this role. All the other compounds **16**, **22–28** are obtained in moderate to good yields. One can notice an exception observed with a pyridazine unit as lateral rings (**24**).

2. Conclusion

In conclusion, a simple general procedure for the synthesis of new polyaza heterocycles has been developed on the basis of palladium-mediated coupling of mono- or bis-tribuylstannanes of diazines. Among the compounds prepared here some are aza-analogues of terpyridines (tpy) and will be new potential ligands for metal chelation and new building blocks for synthesis of supramolecular arrays. Further studies on this new family of polyaza heterocycles are underway and will include a careful assessment of metal coordination, photo- and electrochemical properties. Variation of functionalization of lateral units will be performed to access new ligand-bridged supramolecular structures.

3. Experimental

Melting points were determined on a Kofler hot-stage. The ^1H, and ^{13}C spectra were recorded on a Bruker AC 300 (300 MHz ^1H, 75 MHz ^{13}C) instrument. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus. The IR spectra were obtained as potassium bromide pellets with a Perkin–Elmer Paragon 500 spectrophotometer. Mass spectra were recorded on an ATI-Unicam Automass® apparatus.

3.1. General procedure A for the nucleophilic substitution of a chlorine atom by the tributylstannyl anion

A solution of *n*-butyllithium (1.6 or 2.5 M in hexane) was added to cold (0 °C), stirred and anhydrous mixture of THF (50 mL) and diisopropylamine (DIPAH) under an atmosphere of dry nitrogen. After 15 min, tributyltinhydride was introduced, the yellow pale solution was stirred at 0 °C for 15 min and the temperature was decreased to at −78 °C. Then a solution of chloro- or dichlorodiazine in THF at −78 °C was added, after *t* hours of stirring, mixture was warmed to 0 °C. Hydrolysis was then carried out at this temperature, using a saturated aqueous solution of potassium fluoride. The aqueous layer was extracted with dichoromethane or ethylacetate (3×20 mL), the combined organic extracts were then dried over magnesium sulfate, filtered and evaporated in vacuo. The crude product was purified by column chromatography on silica gel.

3.2. Procedure B for cross-coupling of heteroaryl halides with tributylstannylheteroarene under Stille conditions

A solution of tributylstannylheteroarene, arylhalide and $Pd(PPh_3)_4$ (0.05 equiv) in degassed toluene (15 mL) was heated under reflux under nitrogen atmosphere for a time *t*. After cooling, water (20 mL) was added. The aqueous phase was extracted with dichloromethane (3×20 mL). The combined organic extracts were then dried over magnesium sulfate, filtered and evaporated in vacuo. The crude product was purified by column chromatography on silica gel.

3.3. Procedure C for cross-coupling of heteroaryl halides with 2,6-bis(tributylstannyl)pyrazine under Stille conditions

A mixture of 2,6-bis(tributylstannyl)pyrazine used as crude product (constituted with 77% of **6** and 21% of hexabutylditin) (1.010 g, 1.17 mmol of **6**), heteroaryl halide (2–3 mmol), and $Pd(PPh_3)_4$ (0.10 equiv) in degassed toluene (25 mL) was heated under reflux under nitrogen atmosphere for a time *t*. After cooling, dichloromethane (150 mL) was added and the mixture was filtered. The organic phase was washed with aqueous ammonia (2×25 mL). The combined organic extracts were then dried over magnesium sulfate, filtered and evaporated in vacuo. The crude product was purified by column chromatography on silica gel.

3.3.1. 3-Chloro-6-tri-*n*-butylstannylpyridazine (1). Substitution of 3,6-dichloropyridazine (2.0 g, 13.02 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 2.5 M (14.7 mmol, 5.88 mL), DIPAH (14.1 mmol, 2.00 mL), tributyltinhydride (14.4 mmol, 4.00 mL), $t=5$ h,

gave after purification by column chromatography (silica, eluent petroleum ether/ethyl acetate (9/1)) 480 mg of **1** (9.2%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.63 (m, 9H), 0.93 (m, 6H), 1.04 (m, 6H), 133 (m, 6H), 7.07 (dd, J= 8.67, 2.64 Hz, 1H), 7.22 (dd, J=8.67, 2.64 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 10.63, 13.70, 27.60, 29.24, 126.0, 136.6, 156.7, 174.4. MS (CI) m/z 403 (M^+, 40), 347 (M−Bu, 10), 269 (M−2Bu, 10), 235 (M−3Bu, 5).

3.3.2. 4-Chloro-2-tri-*n*-butylstannylpyrimidine (2). Substitution of 2,4-dichloropyrimidine (1.0 g, 6.7 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (14.1 mmol, 8.80 mL), DIPAH (14.1 mmol, 1.99 mL), tributyltinhydride (14.1 mmol, 3.91 mL), t=6 h, gave after purification by column chromatography (silica, eluent petroleum ether/ethyl acetate (25/1)) 120 mg of **2** (4%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.80 (t, J= 7.1 Hz, 9H), 1.11 (m, 6H), 1.26 (m, 6H), 1.51 (m, 6H), 7.09 (d, J=5.65 Hz, 1H), 8.46 (d, J=5.65 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 10.8, 14.0, 27.6, 29.2, 120.1, 155.9, 159.9, 191.3.

3.3.3. 4-Methoxy-2-tri-*n*-butylstannylpyrimidine (3). Substitution of 2-chloro,4-methoxypyrimidine (0.650 g, 4.5 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (5 mmol, 3.12 mL), DIPAH (5 mmol, 0.71 mL), tributyltinhydride (5 mmol, 1.35 mL), t=1 h, gave after purification by column chromatography (silica, eluent petroleum ether/ethyl acetate (25/1)) 1.20 g of **3** (70%) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 0.80 (t, J= 7.1 Hz, 9H), 1.11 (m, 6H), 1.26 (m, 6H), 1.51 (m, 6H), 3.73 (s, 3H), 6.32 (d, J=6.0 Hz, 1H), 8.15 (d, J=6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 10.3, 14.0, 27.8, 31.0, 54.8, 117.1, 153.9, 158.9, 188.6. MS (EI) m/z 343 (M−Bu, 100).

3.3.4. Tri-*n*-butylstannylpyrazine (4). Substitution of chloropyrazine (1.50 g, 12.8 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (13.5 mmol, 8.5 mL), DIPAH (13.47 mmol, 1.90 mL), tributyltinhydride (13.5 mmol, 3.75 mL), t=8 h. Hydrolysis was carried out at −40 °C. Purification by column chromatography (silica, eluent petroleum ether/ethyl acetate (10/1)) gave 4.05 g of **4** (85%) as a yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.80 (t, J= 7.5 Hz, 9H), 1.10 (m, 6H), 1.25 (m, 6H), 1.48 (m, 6H), 8.29 (d, J=2.64 Hz, 1H), 8.48 (d, J=1.86 Hz, 1H), 8.63 (dd, J= 2.64, 1.88 Hz); ^{13}C NMR ($CDCl_3$): δ 10.2, 14.0, 27.6, 29.3, 143.3, 147.1, 151.7, 170.2. MS (CI) m/z 371 (M^+, 100).

3.3.5. 6-Chloro-2-tri-*n*-butylstannylpyrazine (5). Substitution of 2,6-dichloropyrazine (0.75 g, 5.0 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (5.30 mmol, 3.30 mL), DIPAH (5.30 mmol, 0.75 mL), tributyltinhydride (5.30 mmol, 1.47 mL), t= 21 h, gave after purification by column chromatography (silica, eluent petroleum ether/ethyl acetate (30/1)) 456 mg of **5** (56%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.85 (t, J=7.1 Hz, 9H), 1.16 (m, 6H), 1.31 (m, 6H), 1.54 (m, 6H), 8.34 (s, 1H), 8.41 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 10.5, 14.0, 27.6, 29.3, 143.2, 149.2, 151.6, 170.7. HRMS (FAB) calcd for $C_{16}H_{29}ClN_2Sn$ 403.58394; found 403.57764).

3.3.6. 2,6-Bis(tri-*n*-butylstannyl)pyrazine (6). Substitution of 2,6-dichloropyrazine (0.75 g, 5.0 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (10.60 mmol, 6.60 mL), DIPAH (10.60 mmol, 1.50 mL), tributyltinhydride (10.60 mmol, 2.95 mL), t= 4 h. gave 2.7 g as a yellow oil which contains 77% of **6** and 21% of hexabutylditin. The product was not purified by column chromatography because its unstability on silica gel. It will be used as crude product for further reactions; ^{1}H NMR ($CDCl_3$): δ 0.85–1.70 (m 76H, (H_{Bu} of **6** and $(SnBu_3)_2$), 8.07 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 10.3, 14.1, 27.7, 29.4, 149.0, 171.7. MS (CI) m/z 658 (M^+, 100).

3.3.7. 2-Phenyl-4-tri-*n*-butylquinazoline (7). Substitution of 2-phenyl-4-chloroquinazoline (1.08 g, 4.5 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (4.5 mmol, 2.81 mL), DIPAH (4.5 mmol, 0.64 mL), tributyltinhydride (4.5 mmol, 1.25 mL), t=1 h, gave after purification by column chromatography (silica, eluent cyclohexane) 2.15 g of **7** (97%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.91 (m, 9H), 1.16 (m 6H), 1.32 (m, 6H), 1.47 (m, 6H), 7.77 (m, 3H), 7.92 (t, J=8.3 Hz, 1H), 8.19 (t, J=8.3 Hz, 1H), 8.35 (d, J=8.3 Hz, 1H), 8.51 (d, J=8.3 Hz, 1H), 8.85 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 11.7, 14.1, 27.8, 29.6, 127.0, 128.9, 129.1, 129.6, 130.0, 130.6, 131.4, 133.4, 139.1, 148.6, 159.0, 193.0. MS (EI) m/z 455 (90, M−Bu).

3.3.8. 2-Tri-*n*-butylquinoxaline (8). Substitution of 2-chloroquinoxaline (0.740 g, 4.5 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (4.5 mmol, 2.81 mL), DIPAH (4.5 mmol, 0.64 mL), tributyltinhydride (4.5 mmol, 1.25 mL), t=1 h, gave after purification by column chromatography (silica, eluent cyclohexane) 1.01 g of **8** (54%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.82 (m, 9H), 1.17 (m 6H), 1.30 (m, 6H), 1.55 (m, 6H), 7.63 (m, 2H), 7.96 (m, 1H), 8.06 (m, 1H), 8.52 (s, 1H). MS (EI) m/z 363 (10, M−Bu).

3.3.9. 2,6-Bis(tri-*n*-butylstannyl)quinoxaline (9). Substitution of 2,3-dichloroquinoxaline (0.445 g, 4.5 mmol) by Bu_3SnLi according to the general procedure A with *n*-BuLi 1.6 M (4.5 mmol, 2.81 mL), DIPAH (4.5 mmol, 0.64 mL), tributyltinhydride (4.5 mmol, 1.25 mL), t=1 h, gave after purification by column chromatography (silica, eluent cyclohexane) 3.12 g of **9** (98%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.86 (m, 18H), 1.10 (m 12H), 1.27 (m, 12H), 1.55 (m, 12H), 7.59 (dd, J=6.4 Hz, 3.3 Hz, 2H), 7.82 (dd, J=6.4 Hz, 3.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 11.2, 13.7, 27.4, 29.2, 128.4, 129.7, 142.0, 179.2. MS (EI) m/z 708 (M^+, 1), 651 (M−Bu, 5), 413 (M−$SnBu_3$, 90).

3.3.10. 2-Phenyl-4-methoxypyrimidine (10). Cross-coupling reaction of iodobenzenze (408 mg, 225 μL, 2 mmol) with **3** (400 mg, 1 mmol) according to the general procedure B (t=48 h) gave after purification by column chromatography (silica, eluent: dichloromethane) 145 mg (76%) of **10** as a colorless solid, mp 44–45 °C (lit.[16] 45 °C); ^{1}H NMR ($CDCl_3$): δ 4.05 (s, 3H, H_{OMe}); 6.80 (d, J=6.0 Hz, 1H, H_5') 7.51 (m, 3H, H_{Ph}'); 8.40 (m, 2H, H_{Ph}); 8.60 (d, J= 6.0 Hz, 1H, H_6')). Anal. Calcd for $C_{11}H_{10}N_2O$ (186.21): C, 70.95; N, 15.04; H, 5.41. Found: C, 71.02; N, 15.15; H, 5.35. MS (EI) m/z 186 (M^+, 100).

3.3.11. 2,4-Diphenylquinazoline (11). Cross-coupling reaction of iodobenzenze (408 mg, 225 μL, 2 mmol) with

7 (500 mg, 1 mmol) according to the general procedure B ($t=48$ h) gave after purification by column chromatography (silica, eluent: dichloromethane) 189 mg (67%) of **11** as a colorless solid, mp 115–116 °C (lit.[17] 118 °C); ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 7H), 7.90 (m, 3H), 8.15 (d, $J=8.3$ Hz, 1H), 8.17 (d, $J=8.3$ Hz, 1H), 8.73 (m, 2H). NMR ^{13}C ($CDCl_3$) δ 121.7, 127.0, 128.5, 128.7, 129.2, 129.9, 130.2, 130.5, 133.5, 137.8, 138.2, 152.0, 160.2, 168.3. Anal. Calcd for $C_{20}H_{14}N_2$ (282.12): C, 85.08; N, 9.92; H, 5.00. Found: C, 85.46; N, 9.75; H, 4.78. MS (EI) *m/z* 282 (M^+, 100).

3.3.12. 2-Phenylquinoxaline (12). Cross-coupling reaction of iodobenzenze (408 mg, 225 μL, 2 mmol) with **8** (420 mg, 1 mmol) according to the general procedure B ($t=48$ h) gave after purification by column chromatography (silica, eluent: dichloromethane) 131 mg (64%) of **12** as a yellow solid, mp 74–75 °C (lit.[17] 73–75 °C); ^{1}H NMR ($CDCl_3$): δ 7.54 (m, 3H), 7.75 (m, 2H), 8.15 (m, 4H), 9.32 (s, 1H). NMR ^{13}C ($CDCl_3$) δ 127.5, 129.1, 129.5, 129.6, 130.1, 130.2, 136.8, 141.5, 142.3, 143.3, 151.8. Anal. Calcd for $C_{14}H_{10}N_2$ (206.24): C, 81.53; N, 13.58; H, 4.89. Found: C, 81.46; N, 13.75; H, 4.78. MS (EI) *m/z* 206 (M^+, 100).

3.3.13. 2,3-Diphenylquinoxaline (13). Cross-coupling reaction of iodobenzenze (612 mg, 340 μL, 3 mmol) with **9** (708 mg, 1 mmol) according to the general procedure B ($t=48$ h) gave after purification by column chromatography (silica, eluent: dichloromethane) 110 mg (39%) of **13** as a yellow solid, mp 123–124 °C (lit.[18] 124.5 °C); ^{1}H NMR ($CDCl_3$): δ 7.44 (m, 2H), 7.48 (m, 4H), 7.64 (dd, $J=7.2$, 1.5 Hz, 4H), 7.88 (d, $J=6.4$ Hz, 2H), 8.31 (d, $J=6.4$ Hz, 2H). NMR ^{13}C ($CDCl_3$) δ 128.7, 129.2, 129.6, 130.2, 130.4, 139.4, 141.6. Anal. Calcd for $C_{20}H_{14}N_2$ (282.34): C, 85.08; N, 9.92; H, 5.00. Found: C, 85.52; N, 9.65; H, 5.38. MS (EI) *m/z* 235 (M^+, 100).

3.3.14. 2,6-Bispyrazinylpyridine (14). Cross-coupling reaction of 2,6-dibromopyridine (237 mg, 1 mmol) with **4** (738 mg, 2 mmol) according to the general procedure B ($t=$ 15 h) gave after purification by column chromatography (silica, eluent: ethyl acetate) 155 mg (66%) of **14** as a colorless solid, mp 215–216 °C; ^{1}H NMR ($CDCl_3$): δ 7.90 (t, $J=7.9$ Hz, 1H), 8.35 (d, $J=7.9$ Hz, 2H), 8.55 (m, 4H), 9.72 (d, $J=0.75$ Hz, 2H). NMR ^{13}C ($CDCl_3$) δ 122.4, 138.7, 143.8, 143.9, 145.1, 151.0, 154.1. MS (EI) *m/z* 235 (M^+, 100). Anal. Calcd for $C_{13}H_9N_5$ (235.25): C, 66.37; N, 29.77; H, 3.86. Found: C, 66.36; N, 29.77; H, 3.85.

3.3.15. 2,5-Bispyrazinylpyridine (15). Cross-coupling reaction of 2,5-dibromopyridine (237 mg, 1 mmol) with **4** (1.107 g, 3 mmol) according to the general procedure B ($t=$ 27 h) gave after purification by recrystallization in ethyl acetate 150 mg (64%) of **15** as a colorless solid, mp 265–266 °C; ^{1}H NMR ($CDCl_3$): δ 8.39 (d, $J=8.0$ Hz, 1H), 8.53 (dd, $J=8.4$, 2.0 Hz, 1H), 8.56 (d, $J=2.4$ Hz, 1H), 8.58 (d, $J=2.8$ Hz, 1H), 8.75 (d, $J=2.4$ Hz, 1H), 8.76 (d, $J=$ 2.4 Hz, 1H), 9.03 (d, $J=1.6$ Hz, 1H), 9.27 (d, $J=1.6$ Hz, 1H), 9.37 (d, $J=0.8$ Hz, 1H). NMR ^{13}C ($CDCl_3$) δ 124.2, 135.0, 138.7, 143.6, 144.3, 145.1, 145.8, 146.7, 147.1, 149.9, 152.7, 153.2, 156.3. MS (EI) *m/z* 235 (M^+, 100). Anal. Calcd for $C_{13}H_9N_5$ ($M_w=235.25$): C, 66.37; H, 3.86; N, 29.77. Found: C, 66.55; H, 3.67; N, 29.82.

3.3.16. 2,2′,6′,2″-Terpyrazine (16). Method 1—cross-coupling reaction of 2,6-dichloropyrazine (282 mg, 1.89 mmol) with **4** (1.400 g, 3.79 mmol) according to the general procedure B ($t=24$ h) gave after purification by recrystallization in methanol 333 mg (74%) of **16** as a grey solid, mp >265 °C; compound **16** has a very low solubility in the usual organic solvents; ^{1}H NMR (CF_3CD_2OD): δ 8.61 (d, $J=2.8$ Hz, 1H), 8.76 (dd, $J=2.4$, 1.6 Hz, 1H), 9.56 (s, 1H), 9.64 (d, $J=1.2$ Hz, 1H); ^{13}C NMR (CF_3CD_2OD): δ 129.0, 129.2, 131.8, 131.9, 132.4, 133.7. IR (KBr) ν (cm^{-1}) 3053.8, 3012.9, 1530.2, 1473.7, 1431.0, 1382.9, 1108.4, 1030.0, 1015.9, 858.9. MS (EI) *m/z* 236 (M^+, 100).

Method 2—cross-coupling reaction of 2,6-bis(tributyltin)-pyrazine **6** (1.17 mmol) with chloropyrazine (0.446 g, 3 mmol) according to the general procedure C (t = 48 h) gave after purification by recrystallization in methanol 179 mg (65%) of **16**. Anal. Calcd for $C_{12}H_8N_6$ (236.24): C, 61.01; H, 3.41; N, 35.57. Found: C, 61.20; H, 3.42; N, 35.77.

3.3.17. 4,6-Bispyrazinylpyrimidine (17). Cross-coupling reaction of 2,6-dichloropyrimidine (262 mg, 1.76 mmol) with **4** (1.400 g, 3.79 mmol) according to the general procedure B ($t=27$ h) gave after purification by recrystallization in ethanol then in ethyl acetate 254 mg (61%) of **17** as a pale yellow solid, mp 217–218 °C; ^{1}H NMR ($CDCl_3$): δ 8.75 (s, 4H), 9.35 (d, $J=1.2$ Hz, 1H), 9.45 (d, $J=1.2$ Hz, 1H), 9.77 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 114.7, 144.1, 144.5, 146.8, 149.3, 160.0, 163.0. MS (EI) *m/z* 236 (100, M^+). Anal. Calcd for $C_{12}H_8N_6$ (236.24): C, 61.01; H, 3.41; N, 35.57. Found: C, 60.18; H, 3.23; N, 35.61.

3.3.18. 2-Phenyl-4-(pyrazinyl)quinazoline (18). Cross-coupling reaction of 4-chloro-2-phenylquinazoline (240 mg, 1.0 mmol) with **4** (738 mg, 2 mmol) according to the general procedure B ($t=28$ h) gave after purification by column chromatography (silica, eluent: ethyl acetate/dichloromethane (5/5)) 198 mg (70%) of **18** as a colorless solid, mp 206–207 °C; ^{1}H NMR ($CDCl_3$): δ 7.46–7.52 (m, 5H), 7.58 (td, $J=8.29$, 1.13 Hz, 1H), 7.86 (td, $J=8.3$, 1.13 Hz, 1H), 8.12 (d, $J=8.3$ Hz, 1H), 8.65 (dd, $J=7.5$, 1.88 Hz, 2H), 8.86 (dd, $J=8.3$, 1.13 Hz, 1H), 9.62 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 121.9, 127.6, 128.2, 129.0, 129.1, 131.2, 134.4, 138.1, 143.2, 145.5, 147.2, 152.7, 153.1, 160.2, 161.7. IR (KBr) ν (cm^{-1}) 3036.2, 2924.8, 2849.8, 1612.1, 1560.5, 1542.8, 1471.2, 1338.9, 1017.8, 853.8, 767.7, 705.0, 688.8, 649.2. MS (EI) *m/z* 284 (M^+, 100), 205 (M − pyrazine, 24). Anal. Calcd for $C_{18}H_{12}N_4$ ($M_w=$ 284.11): C, 76.04; H, 4.25; N, 19.71. Found: C, 76.01; H, 4.24; N, 19.70.

3.3.19. 2,6-Bis[3′-(6′-methoxypyridazinyl)pyrazine] (19). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 3-chloro-6-methoxypyridazine (0.338 g, 2.34 mmol) according to the general procedure C ($t=48$ h) gave after purification by column chromatography (silica, eluent: petroleum ether/ethyl acetate (5/5)) 280 mg (82%) of **19** as a colorless solid, mp 116–117 °C; ^{1}H NMR ($CDCl_3$): δ 3.90 (s, 6H), 6.94 (d, $J=8.7$ Hz, 2H), 7.02 (t, $J=$ 7.9 Hz, 2H), 7.42 (td, $J=8.7$, 1.5 Hz, 2H), 8.04 (dd, $J=7.9$, 1.5 Hz, 2H), 9.0 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 56.1, 111.9, 120.3, 121.8, 131.9, 133.8, 158.8, 162.5, 166.7. MS (EI) *m/z*

292 (M^+, 100). Anal. Calcd for $C_{18}H_{16}N_2O_2$ (292.12) C, 73.96; H, 5.52; N, 9.58. Found: C, 73.97; H, 5.50; N, 9.57.

3.3.20. 2,6-Bis[1′-(2′-methoxynaphtyl)]pyrazine (20). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 1-bromo-2-methoxynaphthalene (0.702 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by column chromatography (silica, eluent: dichloromethane) 233 mg (51%) of **20** as a colorless solid, mp 190–191 °C; ^{1}H NMR ($CDCl_3$): δ 3.95 (s, 6H), 7.45–7.33 (m, 6H), 7.71 (d, J=8.3 Hz, 2H), 7.83 (d, J=7.9 Hz, 2H), 7.95 (d, J=9.0 Hz, 2H), 8.77 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 55.5, 112.1, 119.4, 122.7, 123.4, 126.1, 127.1, 128.0, 130.0, 132.3, 144.2, 150.3, 153.8. MS (EI) m/z 392 (M^+, 100). Anal. Calcd for $C_{26}H_{20}N_2O_2$ (392.15) C, 79.57; H, 5.14; N, 7.14. Found: C, 79.56; H, 5.14; N, 7.17.

3.3.21. 2,6-Di(2′-thienyl)pyrazine (21). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 2-iodothiophene (0.636 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by column chromatography (silica, eluent: dichloromethane/ethyl acetate (5/5)) 217 mg (76%) of **21** as a yellow solid, mp 187–188 °C; ^{1}H NMR ($CDCl_3$): δ 7.07–7.11 (m, 2H), 7.42 (dd, J=4.89, 1.51 Hz, 2H), 7.66 (dd, J=4.9, 1.51 Hz, 2H), 8.68 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 126.4, 128.7, 129.5, 138.1, 141.7, 147.8. MS (EI) m/z 244 (100, M^+). Anal. Calcd for $C_{12}H_8N_2S_2$ (244.34) C, 58.99; H, 3.30; N, 11.46. Found: C, 59.06; H, 3.29; N, 11.44.

3.3.22. 2,6-Di(2′-pyridyl)pyrazine (22). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 2-bromopyridine (0.294 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by column chromatography (silica, eluent: ethylacetate) 82 mg (30%) of **22** as a colorless solid, mp 167–168 °C; ^{1}H NMR ($CDCl_3$): δ 7.33–7.38 (m, 2H), 7.85 (td, J=7.91, 1.88 Hz, 2H), 8.51 (d, J=7.92 Hz, 2H), 8.72 (dd, J=3.76, 0.75 Hz, 2H), 9.64 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 121.8, 124.8, 137.4, 143.1, 149.8, 154.7. MS (EI) m/z 234 (100, M^+). Anal. Calcd for $C_{14}H_{10}N_4$ (234): C, 71.78; H, 4.30; N, 23.92. Found: C, 71.64; H, 4.42; N, 23.84.

3.3.23. 2,6-Bis[2′-(6′-methoxypyridyl)]pyrazine (23). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 2-chloro-6-methoxypyridine (0.430 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by column chromatography (silica, eluent: dichloromethane/ethanol: (98/2)) 206 mg (60%) of **23** as a colorless solid, mp 178–179 °C; ^{1}H NMR ($CDCl_3$): δ 4.07 (s, 6H), 6.84 (d, J=8.3 Hz, 2H), 7.75 (dd, J=8.3, 7.5 Hz, 2H), 8.14 (d, J=7.5 Hz, 2H), 9.61 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 53.8, 112.5, 114.6, 139.8, 142.8, 149.8, 152.0, 164.0. MS (EI) m/z 294 (M^+, 100), 263 (M−OCH_3, 34). Anal. Calcd for $C_{16}H_{14}N_4O_2$ (M_w=294.31) C, 65.30; H, 4.79; N, 19.04. Found: C, 65.35; H, 4.74; N, 19.01.

3.3.24. 2,6-Bis[3′-(6′-methoxypyridazinyl)]pyrazine (24). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 3-chloro-6-methoxypyridazine (0.433 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by column chromatography (silica, eluent: petroleum ether/ethyl acetate (1/1)) 73 mg (21%) of **24** as a colorless solid, mp 238–239 °C; ^{1}H NMR ($CDCl_3$): δ 4.20 (s, 3H), 7.12 (d, J=9.05 Hz, 1H), 8.44 (d, J=9.05 Hz, 1H), 9.80 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 55.6, 118.4, 128.0, 143.0, 147.8, 153.4, 165.8. MS (EI) m/z 296 (M^+, 100). Anal. Calcd for $C_{14}H_{12}N_6O_2$ (296.10) C, 56.75; H, 4.08; N, 28.36. Found: C, 56.73; H, 4.05; N, 28.19.

3.3.25. 2,6-Bis[4′-(2′-methylsulfanylpyrimidinyl)]pyrazine (25). Cross-coupling reaction of 2,6-bis(tributyltin)-pyrazine **6** (770 mg, 1.17 mmol) with 4-chloro-2-methylsulfanylpyrazine (0.481 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by column chromatography (silica, eluent: n-hexane/dichloromethane/ethyl acetate (4/2/4)) 226 mg (59%) of **25** as a yellow solid, mp 208–209 °C; ^{1}H NMR ($CDCl_3$): δ 2.61 (s, 6H), 8.00 (d, J=4.9 Hz, 2H), 8.66 (d, J=4.9 Hz, 2H), 9.72 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 14.7, 112.9, 134.6, 135.7, 145.3, 148.1, 159.0, 161.2, 173.6. MS (EI) m/z 328 (M^+, 100), 313 (M−CH_3, 10), 299 (M−$2CH_3$, 45), 282 (M−SCH_3, 15), 264 (M−$2SCH_3$, 25). Anal. Calcd for $C_{14}H_{12}N_6S_2$ (328.42): C, 51.20; H, 3.68; N, 25.59; S, 19.53. Found: C, 51.25; H, 3.67; N, 25.82; S, 19.19.

3.3.26. 2,6-Bis(2′-quinolyl)pyrazine (26). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 2-chloro-quinoline (0.490 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by washing with petroleum ether (3×5 mL) 356 mg (95%) of **26** as a colorless solid, mp>260 °C; ^{1}H NMR ($CDCl_3$): δ 7.61 (m, 2H), 7.80 (m, 2H), 7.91 (dd, J=8.3, 1.1 Hz, 2H), 8.25 (d, J=8.3 Hz, 2H), 8.37 (d, J=8.7 Hz, 2H), 8.75 (d, J=8.7 Hz, 2H), 9.97 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 119.3, 127.7, 128.1, 128.8, 130.4, 137.3, 143.9, 144.2, 148.3, 150.0, 154.7. MS (FAB) m/z 335 (10), 154 (100), 136 (70). Anal. Calcd for $C_{22}H_{14}N_4$ (334.38): C, 79.02; H, 4.22; N, 16.76. Found: C, 79.00; H, 4.21; N, 16.79.

3.3.27. 2,6-Bis(2′-quinoxalyl)pyrazine (27). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 2-chloro-quinoxaline (0.494 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by washing with petroleum ether (3×5 mL) 255 mg (65%) of **27** as a colorless solid, mp>260 °C; ^{1}H NMR ($CDCl_3$): δ 8.08–8.11 (m, 4H), 8.43–8.49 (m, 4H), 10.17 (s, 2H), 10.33 (s, 2H). MS (EI) m/z 336 (M^+, 100). Anal. Calcd for $C_{20}H_{12}N_6$ (336.36): C, 71.42; H, 3.60; N, 24.99. Found: C, 71.42; H, 3.59; N, 25.04.

3.3.28. 2,6-Bis[4′-(2′-phenylquinazolyl)]pyrazine (28). Cross-coupling reaction of 2,6-bis(tributyltin)pyrazine **6** (770 mg, 1.17 mmol) with 2-phenyl-4-chloro-quinazoline (0.490 g, 3 mmol) according to the general procedure C (t=48 h) gave after purification by washing with petroleum ether (3×5 mL) 405 mg (71%) of **28** as a colorless solid, mp>260 °C; ^{1}H NMR ($CDCl_3$): δ 7.59 (m, 8H), 7.93 (td, J=7.7 Hz, 1.15 Hz, 4H), 8.22 (d, J=8.3 Hz, 2H), 8.78 (dd, J=7.7 Hz, 1.15 Hz, 4H), 9.01 (d, J=8.3 Hz, 2H), 9.92 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 112.0, 127.5, 128.3, 129.0, 129.1, 129.8, 131.3, 134.4, 138.1, 147.2, 150.7, 153.2, 160.4, 161.3. MS (EI) m/z 488 (100, M^+). Anal. Calcd for $C_{32}H_{20}N_6$ (488.54) C, 78.61; H, 4.13; N, 17.20. Found: C, 78.60; H, 4.20; N, 17.17.

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