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Syntheses in the Nitrogen π-Deficient Heterocycles Series Using a Barbier Type Reaction Under Sonication. Diazines. Part 29

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Abstract—Barbier type reaction with lithium metal has been tested under sonication on pyridines, a cinnoline and on various diazines. This very convenient method allows a very fast and smooth functionalization of these heterocycles.

Introduction

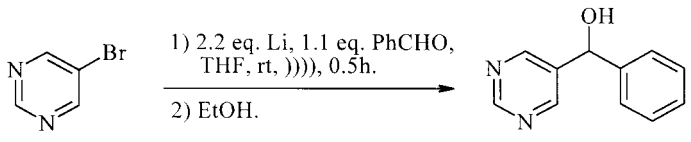
The lithiation reaction is a well-known and powerful tool to functionalize the nitrogen π-deficient heterocyclic compounds. The metalation reaction[1] has been extensively studied in the pyridine series and more recently in the diazine series. Lithiated derivatives can also be prepared by the halogen–metal exchange reaction on pyridines[1a,2] and on diazines.[3] This less developed way can be performed with lithium alkyls or exceptionally with lithium alkylamides.[4] A problem often encountered with these reactions is that they must be performed at very low temperature (−75°C) because these organolithium compounds are excessively reactive. However, this problem can be solved by the use of the Barbier reaction[5] which allows the lithio derivatives formed in situ to react immediately with the electrophile. The slow attack of the metal by the halogen derivatives can be a problem, but this can be solved by the use of sonication. Indeed, sonication is known to afford an enhancement in the preparation of lithium or magnesium derivatives from metal powder. Luche[6] has described easy syntheses using this technique and has obtained very good yields under mild conditions. However, to our knowledge, this very useful method has not been described in the π-deficient heterocyclic series. So we decided to study this method in these series using a simple ultrasonic cleaning device.

In a first step, we have tested different experimental conditions with 5-bromopyrimidine **1**, then we have extended this reaction to the three diazines, two pyridines and a benzodiazine.

Results and Discussion

Experimental conditions were determined with the commercially available 5-bromopyrimidine **1**, using benzaldehyde as the electrophile (Scheme 1).

The reaction was tested with various solvents: THF, ether, cyclohexane, toluene and gave only results with THF. The relative proportion of the reactants and the reaction time were tested and the best result (55%) was obtained with 2.2 equiv. of lithium powder for 1 equiv. of 5-bromopyrimidine, a larger excess of lithium powder decreased the yield. The reaction time was 0.5 h, increasing this time did not enhance the yield.



1 **2**

Yield : 55%

Scheme 1. Tests on 5-bromopyrimidine.

Keywords: Barbier reaction; lithium; diazines; sonochemistry.

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Table 1. Variation of the yield as a function of the temperature

Entry	*T* (°C)	Yield (%)
1	10	21
2	20	55[a]
3	30	43
4	40	40
5	60	38

[a] Without sonication: 27%.

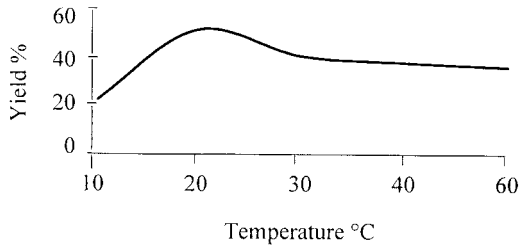


Figure 1. Influence of the temperature on the yield.

The temperature was varied using the experimental conditions determined above (2.2 equiv. Li, 0.5 h). The results are listed in the following table and a curve has been pictured (Table 1, Fig. 1).

It can be noticed that the best yield occurred at room temperature. Lowering or increasing the reaction temperature decreased the yield. This is a well-known result for the reactions under sonication for which an optimum range of temperature exists.[6c] At low temperature, the ultrasonic irradiation is not totally efficient, whereas at higher temperature, the cavitation is less efficient. Indeed, in this case, the presence of relatively large amounts of vaporized liquid in the bubbles of cavitation makes the collapse less energetic.

In order to check the usefulness of the sonication, a silent reaction was performed: the reaction rate was reduced and the yield was only 27% instead of 55%. When a very long time (one night) was used, the yield of the silent reaction was limited to 43%. These results proved the efficiency of sonication for this reaction.

Once suitable experimental conditions have been determined, we have extended this reaction to other nitrogen π-deficient heterocycles. Three electrophiles have been used: benzaldehyde, hexanal and diphenyl disulfide.

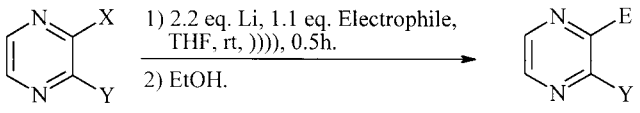
In the pyrazine series (Scheme 2, Table 2):

The good results observed with the chloro substituted derivative **7** reveals a good compatibility of this method with halogen substituents.

In the pyrimidine series:

The 5-bromopyrimidine and two iodopyrimidines were tested too, as shown in the following scheme (Scheme 3, Table 3).

Benzaldehyde was not used as an electrophile with the 2-iodo-4-methoxypyrimidine **13** because the alcohol so obtained was previously found to be unstable.[7] It can be noticed that the presence of a methoxy or a methylsulfanyl group does not interfere with the reaction; although, it has been demonstrated that these groups could be cleaved in the presence of lithium powder.[8]



X=I, Y=H, **3** **4-6**

X=I, Y=Cl, **7** **8-10**

Scheme 2. Tests on pyrazines.

Table 2. Yields with pyrazines

Entry	Compound	Electrophile	Product	Yield (%)
1	**3**	PhCHO	**4**	70
2	**3**	$C_5H_{11}CHO$	**5**	64
3	**3**	PhSSPh	**6**	44
4	**7**	PhCHO	**8**	70
5	**7**	$C_5H_{11}CHO$	**9**	60
6	**7**	PhSSPh	**10**	33

In the pyridazine series and with a cinnoline (Scheme 4, Table 4):

The cinnoline **28** gave no reaction when hexanal was used as the electrophile and the starting material was recovered.

In the pyridine series:

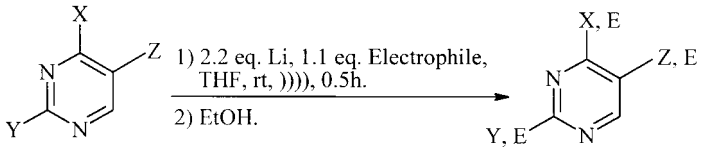
Thanks to the easy availability of bromo and iodo derivatives of pyridine, we could test the influence of the nature of the halogen, thus we used 2-bromopyridine **31**, 2-iodopyridine **32** and the benzaldehyde as an electrophile. The yields of alcohol **33** were 58 and 60%, respectively. As the reactivity of these two compounds was similar, we decided to use the commercially available 2-bromopyridine **31** and 3-bromopyridine **36** (Scheme 5, Table 5).

A comparison of all these results (Tables 1–5) indicates that the yields often followed the sequence: benzaldehyde> hexanal>diphenyl disulfide. These results could be explained by the fact that benzaldehyde is not enolizable contrary to hexanal and that diphenyl disulfide is a weaker electrophile than the aldehydes.

It must also be emphasized that the purity and the particle size of the lithium powder play a great role. The best results were obtained with a 0.5% amount of sodium in the lithium powder and a 50–200 μ particle size. In some cases, Luche[6] found that a small amount of water in THF did not hinder the Barbier reaction under sonication but our tests with wet THF gave no reaction products, so it was necessary to avoid cautiously the presence of water with azines.

Conclusion

To our knowledge, it is the first time that the Barbier reaction has been studied in these heterocyclic series. This

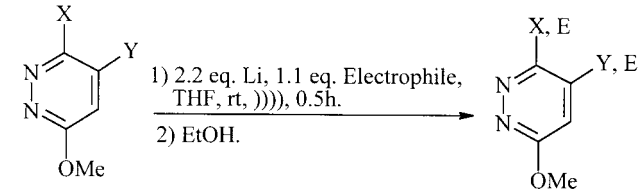


X=Y=H, Z=Br	**1**	**11-12**
X=OMe, Y=I, Z=H	**13**	**14-15**
X=I, Y=SMe, Z=H	**16**	**17-19**

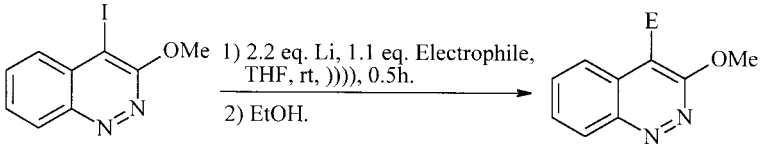
Scheme 3. Tests on pyrimidines.

Table 3. Yields with pyrimidines

Entry	Compound	Electrophile	Product	Yield (%)
1	**1**	PhCHO	**2**	55
2	**1**	$C_5H_{11}CHO$	**11**	22
3	**1**	PhSSPh	**12**	25
4	**13**	$C_5H_{11}CHO$	**14**	48
5	**13**	PhSSPh	**15**	30
6	**16**	PhCHO	**17**	52
7	**16**	$C_5H_{11}CHO$	**18**	48
8	**16**	PhSSPh	**19**	39



X=OMe, Y=I,	**20**	**21-23**
X=I, Y=H,	**24**	**25-27**

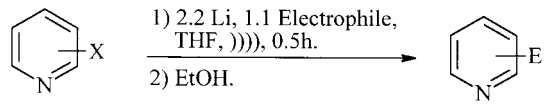


28 **29-30**

Scheme 4. Tests on pyridazines and a cinnoline.

Table 4. Yields with pyridazines and a cinnoline

Entry	Compound	Electrophile	Product	Yield (%)
1	**20**	PhCHO	**21**	72
2	**20**	$C_5H_{11}CHO$	**22**	58
3	**20**	PhSSPh	**23**	49
4	**24**	PhCHO	**25**	65
5	**24**	$C_5H_{11}CHO$	**26**	50
6	**24**	PhSSPh	**27**	38
7	**28**	PhCHO	**29**	64
8	**28**	$C_5H_{11}CHO$	–	–
9	**28**	PhSSPh	**30**	35



X= 2-Bromo, **31** **33-35**

X= 2-Iodo, **32** **33**

X= 3-Bromo, **36** **37-38**

Scheme 5. Tests on pyridines.

Table 5. Yields with bromopyridines

Entry	Compound	Electrophile	Product	Yield %
1	**31**	PhCHO	**33**	58
2	**31**	$C_5H_{11}CHO$	**34**	51
3	**31**	PhSSPh	**35**	21
4	**36**	PhCHO	**37**	54
5	**36**	$C_5H_{11}CHO$	–	–
6	**36**	PhSSPh	**38**	24

allowed a convenient functionalization of these rings at room temperature with a short reaction time. Furthermore, it has been demonstrated that the use of sonication is an essential factor.

These results may be compared with the ones obtained by the halogen lithium exchange reaction. In the diazine series, very few exchange reactions have been performed[3] because the use of lithium alkyls can lead to addition reactions. The main results in these series dealt with 5-bromopyrimidine or its derivatives. The best yield obtained by Van Der Plas[3g] was 80% at −100°C. In the pyridazine series, the sole paper by Rosseels[3a] described an exchange reaction with 3,6-dichloropyridazine affording a 23% yield at −15°C. In the pyrazine series, the best yield (57%) was obtained by Spoerri[3l] with 2-iodo-3,6-dimethylpyrazine at −50°C.

In the pyridine series, the halogen lithium exchange reaction has been largely developed[1a,2] and the yields are often very good but as for diazines, these reactions must ever be carried out at low temperature.

In conclusion, we have highlighted that the Barbier reaction known for many decades could be efficient in present day organometallic diazine and pyridine syntheses when allied with an ultrasonic irradiation. We have also shown that this reaction could afford good results even in the presence of substituents on the ring such as methylsulfanyl, methoxy or chloro group.

Experimental

Melting points were determined on a Kofler hot stage. The ^{1}H- and ^{13}C NMR spectra were recorded in deuteriochloroform on a Bruker AC 200 instrument. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus. The IR spectra were obtained as a potassium bromide pellets with a Perkin Elmer FTIR 1650 spectrophotometer. Mass spectra were recorded at 70 eV (EI) on a JEOL JMS-AX 500 spectrometer.

Tetrahydrofuran was distilled from benzophenone/sodium solution and used immediately. Water content of the solvent was estimated by the modified Karl Fischer method (THF less than 50 ppm water). Reactions were performed under an argon atmosphere. Reagents were handled with syringes through septa.

Lithium powder was purchased from Fluka Chemika: lithium powder containing 0.5% of sodium (50–200 μ). The reactions were performed in an ultrasound cleaning device (Transsonic 950/H, Prolabo).

Some compounds are commercially available: 5-bromopyrimidine **1**, 2-bromopyridine **31** and 3-bromopyridine **36**.

The following compounds were synthesized according to the literature: 2-iodopyrazine[9] **3**, 2-chloro-3-iodopyrazine[10] **7**, 4-iodo-2-methylsulfanylpyrimidine[11] **16**, 4-iodo-3,6-dimethoxypyridazine[12] **20**, 3-iodo-6-methoxypyridazine[13] **24**, 2-iodo-4-methoxypyrimidine[7] **13**, 4-iodo-2-methoxycinnoline[14] **28**, 2-iodopyridine[15] **32**.

General procedure for Barbier reaction

The diazine derivative (1.0 mmol), the lithium powder (2.2 mmol, 16 mg) and the electrophile (1.1 mmol), were introduced in 3 mL of THF under an atmosphere of dry argon. The reaction medium was placed in the ultrasound cleaning bath during 30 min. Elimination of the remaining lithium powder was then carried out using 3 mL of ethanol. The reaction medium was then diluted with 3 mL of water and evaporated. The aqueous layer was extracted with ethyl acetate (4×10 mL). The organic layer was dried over magnesium sulphate and evaporated. The crude product was purified by column chromatography on silica gel.

(Pyrimidin-5-yl)phenylmethanol (2). Barbier reaction with **1** (1.0 mmol, 159 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 102 mg (55%) of **2** as a yellow oil. Product previously described in reference.[3g]

(Pyrazin-2-yl)phenylmethanol (4). Barbier reaction with **3** (1.0 mmol, 206 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 129 mg (70%) of **4** as a white solid. Product previously described in reference.[7]

1-(Pyrazin-2-yl)hexan-1-ol (5). Barbier reaction with **3** (1.0 mmol, 206 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 116 mg (64%) of **5** as colorless oil. Product previously described in reference.[7]

2-(Phenylsulfanyl)pyrazine (6). Barbier reaction with **3** (1.0 mmol, 206 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 83 mg (44%) of **6** as a colorless oil. Product previously described in reference.[16]

(3-Chloropyrazin-2-yl)phenylmethanol (8). Barbier reaction with **7** (1.0 mmol, 240.5 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 154 mg (70%) of **8** as a white solid. Product previously described in reference.[7]

1-(3-Chloropyrazin-2-yl)hexan-1-ol (9). Barbier reaction with **7** (1.0 mmol, 240.5 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 126 mg (60%) of **9** as a colorless oil. Product previously described in reference.[7]

2-(Phenylsulfanyl)-3-chloropyrazine (10). Barbier reaction with **7** (1.0 mmol, 240.5 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 74 mg (33%) of **10** as a beige solid. Product previously described in reference[17] (patent); mp 102°C; ^{1}H NMR ($CDCl_3$): δ 8.08 (d, J=2.6 Hz, 1H), 7.95 (d, J=2.6 Hz, 1H), 7.49 (m, 2H, H_{Ph}), 7.40 (m, 3H, H_{Ph}); ir: ν 3470, 3060, 2928, 1477, 1440, 1337, 1322, 1136, 1123, 1050, 1023, 860, 747, 689 cm^{-1}. Anal. Calcd for $C_{10}H_7ClN_2S$ (222.70): C, 53.93; H, 3.17; N, 12.58. Found: C, 54.08; H, 3.12; N, 12.69.

1-(Pyrimidin-5-yl)hexan-1-ol (11). Barbier reaction with **1** (1.0 mmol, 159 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 40 mg (22%) of **11** as a yellow oil; ^{1}H NMR ($CDCl_3$): δ 9.00 (s, 1H, H_2); 8.46 (s, 2H, H_4, H_6); 3.95 (m, 1H, CH); 3.00 (s, 1H, OH); 1.25 (m, 6H, 4×CH_2); 0.90 (m, 3H, CH_3); ir: ν 3058, 2925, 2855, 1727, 1582, 1540, 1476, 1440, 1399, 1025, 744, 720, 691 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2O$ (180.25): C, 66.64; H, 8.95; N, 15.54. Found: C, 66.67; H, 8.81; N, 15.63.

5-(Phenylsulfanyl)pyrimidine (12). Barbier reaction with **1** (1.0 mmol, 159 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 47 mg (25%) of **12** as a yellow oil. Product previously described in reference.[18]

1-(4-Methoxypyrimidin-2-yl)hexan-1-ol (14). Barbier reaction with **13** (1.0 mmol, 236 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 100 mg (48%) of **14** as a white oil. Product previously described in reference.[7]

4-Methoxy-2-(phenylsulfanyl)pyrimidine (15). Barbier reaction with **13** (1.0 mmol, 236 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 65 mg (30%) of **15** as a yellow oil; ^{1}H NMR ($CDCl_3$): δ 8.10 (d, J=5.5 Hz, 1H, H_6), 7.54 (m, 2H, H_{Ph}), 7.32 (m, 3H, H_{Ph}), 6.30 (d, J=5.5 Hz, 1H, H_5), 3.66 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$): δ 172.2; 169.4; 157.8; 135.5; 130.1; 129.5; 129.3; 108.3; 54.0; ir: ν 3440, 3060, 2994, 2927, 2854, 1726, 1555, 1470, 1441, 1407, 1322, 1237, 1178, 1022, 903, 822, 748, 690 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2OS$ (218.28): C, 60.53; H, 4.62; N, 12.83. Found: C, 60.40; H, 4.48; N, 12.79.

[2-(Methylsulfanylpyrimidin-4-yl)]phenylmethanol (17). Barbier reaction with **16** (1.0 mmol, 252 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 121 mg (52%) of **17** as a yellow solid. Product previously described in reference.[7]

1-[2-(Methylsulfanyl)pyrimidin-4-yl)]hexan-1-ol (18). Barbier reaction with **16** (1.0 mmol, 252 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 108 mg (48%) of **18** as colorless oil. Product previously described in reference.[7]

2-(Methylsulfanyl)-4-(phenylsulfanyl)pyrimidine (19). Barbier reaction with **16** (1.0 mmol, 252 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 79 mg (39%) of **19** as a yellow oil; ^{1}H NMR ($CDCl_3$): δ 8.01 (d, J=4.8 Hz, 1H, H_6), 7.49 (m, 2H, H_{Ph}), 7.38 (m, 3H, H_{Ph}), 6.36 (d, J=4.8 Hz, 1H, H_5), 2.30 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$): δ 171.6; 171.0; 154.5; 134.9; 129.0; 128.7; 127.8; 111.1; 12.9; ir: ν 3057, 3020, 2962, 2925, 1539, 1521, 1476, 1440, 1402, 1337, 1213, 1166, 1023, 812, 749, 691 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2S$ (202.28): C, 65.32; H, 4.98; N, 13.85. Found: C, 65.69; H, 5.29; N, 14.17.

(3,6-Dimethoxypyridazin-4-yl)phenylmethanol (21). Barbier reaction with **20** (1.0 mmol, 266 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 178 mg (72%) of **21** as a white solid. Product previously described in reference.[7]

1-(3,6-Dimethoxypyridazin-4-yl)hexan-1-ol (22). Barbier reaction with **20** (1.0 mmol, 266 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 139 mg (58%) of **22** as a yellow oil. Product previously described in reference.[7]

3,6-Dimethoxy-4-(phenylsulfanyl)pyridazine (23). Barbier reaction with **20** (1.0 mmol, 266 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 121 mg (49%) of **23** as an orange oil. Product previously described in reference.[7]

(6-Methoxypyridazin-3-yl)phenylmethanol (25). Barbier reaction with **24** (1.0 mmol, 236 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 140 mg (65%) of **25** as a white solid. Product previously described in reference.[19]

1-(6-Methoxypyridazin-3-yl)hexan-1-ol (26). Barbier reaction with **24** (1.0 mmol, 236 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL),

gave after purification by column chromatography (eluent: dichloromethane) 105 mg (50%) of **26** as a yellow oil; ^{1}H NMR ($CDCl_3$): δ 7.59 (d, J=9.1 Hz, 1H, H_6), 6.63 (d, J=9.1 Hz, 1H, H_5); 5.05 (m, 1H, CH); 4.01 (s, 3H, OCH_3); 3.55 (br, 1H, OH); 2.24 (m, 2H, CH_2); 1.30 (m, 6H, 3×CH_2); 0.80 (m, 3H, CH_3); ir: ν 3418, 2931, 2860, 1732, 1463, 1394, 1316, 1249, 1176, 1116, 1006 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_2O_2$ (210.28): C, 62.83; H, 8.63; N, 13.32. Found: C, 62.97; H, 8.55; N, 13.40.

6-Methoxy-3-(phenylsulfanyl)pyridazine (27). Barbier reaction with **24** (1.0 mmol, 236 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 83 mg (38%) of **27** as a yellow solid. Product previously described in reference.[20]

(3-Methoxycinnolin-4-yl)phenylmethanol (29). Barbier reaction with **28** (1.0 mmol, 286 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 170 mg (64%) of **29** as a beige solid. Product previously described in reference.[14]

3-Methoxy-4-(phenylsulfanyl)cinnoline (30). Barbier reaction with **28** (1.0 mmol, 286 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 68 mg (24%) of **30** as a red solid, mp 98°C; ^{1}H NMR ($CDCl_3$): δ 8.29 (m, 1H); 8.14 (m, 1H); 7.52 (m, 2H); 7.09 (s, 5H, H_{Ph}); 4.15 (s, 3H, OCH_3); ir: ν 3054, 2991, 2952, 2895, 1580, 1550, 1524, 1460, 1324, 1239, 1110, 751, 691 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2OS$ (284.38): C, 67.58; H, 5.67; N, 9.85. Found: C, 67.79; H, 5.81; N, 9.89.

(Pyridin-2-yl)phenylmethanol (33). Barbier reaction with **31** (1.0 mmol, 158 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 107 mg (58%) of **33** as a yellow solid. Product previously described in reference.[21]

1-(Pyridin-2-yl)hexan-1-ol (34). Barbier reaction with **31** (1.0 mmol, 158 mg) according to the general procedure with hexanal (1.1 mmol, 0.13 mL), gave after purification by column chromatography (eluent: dichloromethane) 92 mg (51%) of **34** as a yellow oil. Product previously described in reference.[21]

2-(Phenylsulfanyl)pyridine (35). Barbier reaction with **31** (1.0 mmol, 158 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 39 mg (21%) of **35** as a yellow oil. Product previously described in reference.[18]

(Pyridin-3-yl)phenylmethanol (37). Barbier reaction with **36** (1.0 mmol, 158 mg) according to the general procedure with benzaldehyde (1.1 mmol, 0.11 mL), gave after purification by column chromatography (eluent: dichloromethane) 100 mg (54%) of **37** as a yellow solid. Product previously described in reference.[15]

3-(Phenylsulfanyl)pyridine (38). Barbier reaction with **36** (1.0 mmol, 158 mg) according to the general procedure with diphenyl disulfide (1.1 mmol, 242 mg), gave after purification by column chromatography (eluent: dichloromethane) 45 mg (24%) of **38** as a yellow oil. Product previously described in reference.[15]

All mentioned products had satisfactory analyses.

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