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Mechanistic Study on Rearrangement Cascades Starting from Annulated 2-Aza-hepta-2,4-dienyl-6-ynyl Anions: Formation of Aniline and Azepine Derivatives

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Dedicated to Professor Dr. Herbert Mayr on the occasion of his 60th birthday

Abstract: Deprotonation of benzothiophene-derived alkynyl imine **11** with lithium diisopropylamide (LDA) and subsequent transmetalation with $ZnCl_2$ etherate furnished azepine **12** upon aqueous workup. Similarly, alkynyl benzaldimine **1a** gave a mixture of benzazepine **13** and naphthylamine **14**. Allylic benzonitriles **15a**,**b** reacted to produce naphthylamine **16** upon deprotonation with LDA at room temperature. In an analogous manner, imino benzonitrile **17** may be converted into 4-amino isoquinoline **18** by means of an intramolecular nucleophilic attack on the nitrile function upon treatment with LDA. The allylic benzonitriles **19a**,**b** were prepared by LDA treatment of alkynyl imine **11**. They were further converted to amino dibenzothiophene **20** by LDA deprotonation and aqueous workup. These various transformations represent the key steps of a multistep reaction cascade, which was previously postulated on the basis of quantum chemical calculations. Thus, all features of this complex rearrangement mechanism could now be confirmed experimentally. DFT calculations support the lower reactivity of zinc species in the ring-opening step compared to the lithium intermediates. All new compounds were completely characterized by spectroscopic data, including X-ray diffraction studies for the key compounds **12**, **19a**, and **20**.

Keywords: azepines · density functional calculations · lithium · organic chemistry · ring closure · zinc compounds

Introduction

Recently, we have reported a new and unexpected rearrangement of annulated 2-aza-hepta-2,4-dien-6-ynyl anions to give various aniline systems.[1] We proposed a multistep cascade mechanism to explain the formation of the final products.[1] This mechanistic proposal was supported by high-level quantum chemical calculations for a simplified model system (**1**, R = Me; Scheme 1). Thus, the deprotonation of imine **1** with lithium diisopropylamide (LDA) leads to the 2-aza-4,5-benzohepta-2,4-dienyl-6-ynyl anion **2**. An electrocyclic ring-closure reaction of **2**, forming a seven-membered intermediate **3** with a vinyl anion moiety, is postulated as a second step (calculated activation barrier approximately 2 kcal mol^{-1}). The proposed third step consists of an intermolecular proton shift combined with a ring-opening reaction leading to nitrile **5**, which is calculated to be 46.7 kcal mol^{-1} lower in energy than **2**. Interestingly, the more acidic benzylic proton is not involved in the proton shift, as a transfer of this proton to the vinyl anion would result in an energetically unfavorable conjugated eight π-electron seven-membered intermediate **4** with Hückel-antiaromatic character. After nucleophilic addition of the allyl anion moiety to the nitrile function (six π-electrocyclization) a tautomerism follows, leading to the aromatic 1-aminonaphthalene anion **7**. Trapping of this final intermediate with various electrophiles yielded the observed N-substituted products **8**. The simple general procedure (deprotonation of the imine with LDA by −78 °C and following warming to room temperature for 16 h), wide applicability (different carbo- and heterocyclic imines can be used, R = *n*Bu, Ph) and good yields of the final products (60–90 %)[1] render this reaction synthetically very attractive.[2]

Certainly, such a complex multistep mechanistic proposal requires not only theoretical, but also experimental evidence. In this report, we will present several experimental observations supporting the proposed mechanism.

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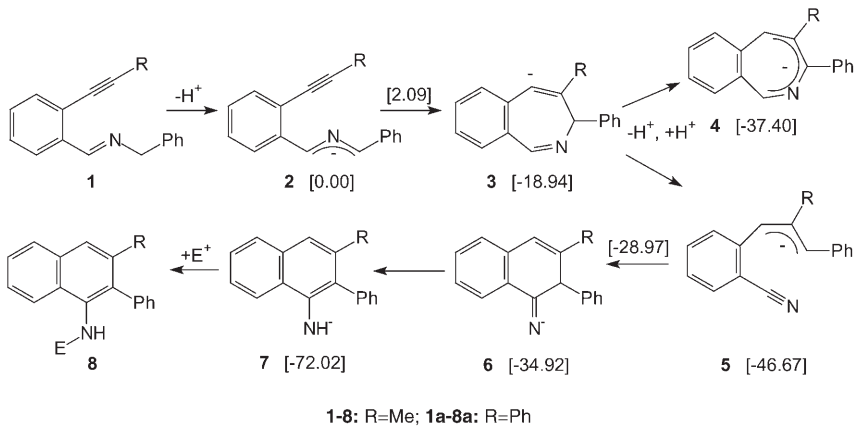
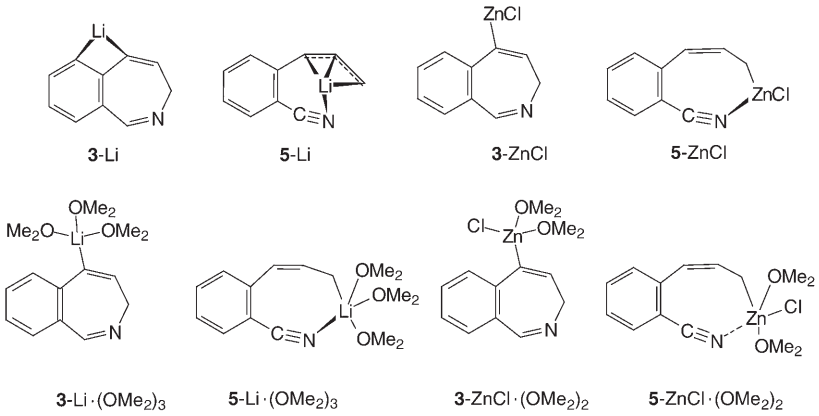


Scheme 1. Proposed mechanism of the rearrangement of **1** to give **8** (for **2**–**8** (R = Me). Relative energies[1] of the minima are given below the formulas and the relative energies of the transition states are given above the arrows (G3MP2 theory [kcal mol^{-1}]).

Results and Discussion

Evidence for the formation of seven-membered intermediates of type 3: The best indication for the validity of the proposed reaction mechanism would be the isolation or trapping of an azepine anion intermediate of type **3** and the subsequent conversion to an aniline of type **8**. However, all attempts to isolate such an intermediate by reducing the reaction time or by lowering the temperature were unsuccessful. Obviously, as suggested by the quantum chemical calculations, the considered lithiated intermediate **3** is too reactive and additional stabilization is necessary for its characterization. To solve this problem, transmetalation by using zinc chloride was considered for this purpose with respect to the well-known reduced reactivity of organozinc compounds in comparison to organolithium species.[3,4]

To estimate the relative stability of the corresponding cyclic (**3**) and allylic (**5**) lithium and zinc intermediates quantum chemical calculations using the B3LYP/6-31+G-(d,p) DFT method[5] (including zero-point correction) were carried out. We performed these calculations both for the Li and ZnCl substances **3**-Li, **3**-ZnCl, **5**-Li, and **5**-ZnCl, and for solvated species with Li·$(OMe_2)_3^+$ and ZnCl·$(OMe_2)_2^+$ as counterions (**3**-Li·$(OMe_2)_3$, **3**-ZnCl·$(OMe_2)_2$, **5**-Li·$(OMe_2)_3$, and **5**-ZnCl·$(OMe_2)_2$; Scheme 2). The relative energies (E_{rel}) of the seven-membered intermediates **3**-Li and **3**-ZnCl with metalated sp^2 carbon atoms (bridging for Li, monohapto with respect to ZnCl) compared to the metalated allylic nitriles **5**-Li and **5**-ZnCl (with Li in the bridging position and coordination to the nitrile nitrogen atom and ZnCl with contact to CN, respectively) were used to estimate the relative preference of zinc and lithium species, respectively. As Table 1 clearly indicates for the lithium species, the structure type **5** is significantly preferred over the type **3** (approximately 33 kcal mol^{-1}). For the ZnCl species, however, the preference for type **5** is much smaller (approximately 12 kcal mol^{-1}). This implies a strong thermodynamic gradient in favor of the transformation giving **5** for the Li compounds, but a much smaller one for the corresponding ZnCl derivatives. The solvated species show similar tendencies, with a preference for the ZnCl compound type **5**-ZnCl·$(OMe_2)_2$ of only approximately 5 kcal mol^{-1} over **3**-ZnCl·$(OMe_2)_2$.

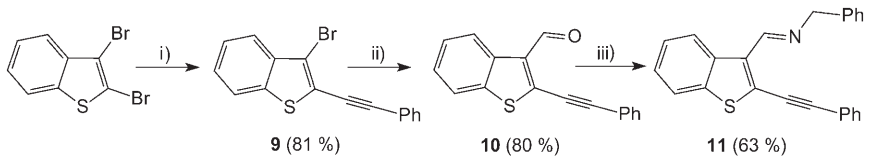


Scheme 2.

Table 1. Relative energies of the lithium and zinc chloride compounds **3** and **5** with and without additional dimethyl ether solvation (quantum-chemical DFT calculations B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) including zero-point correction (ZPE) [kcal mol^{-1}]).

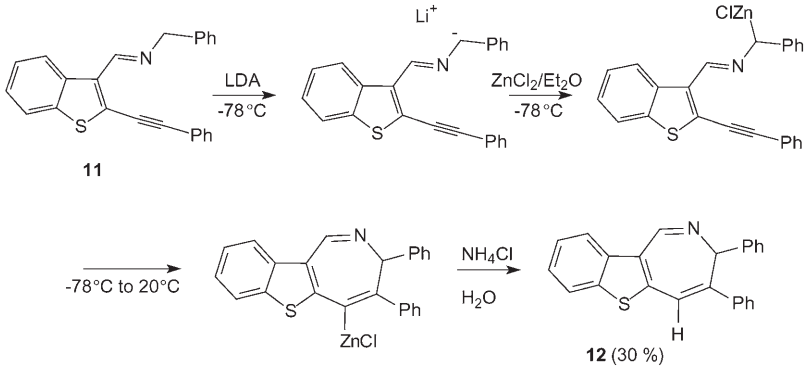
Compound	E_{rel}	Compound	E_{rel}
3-Li	33.23	**3**-Li·$(OMe_2)_3$,	17.48
5-Li	0.00	**5**-Li·$(OMe_2)_3$,	0.00
3-ZnCl	11.86	**3**-ZnCl·$(OMe_2)_2$	4.90
5-ZnCl	0.00	**5**-ZnCl·$(OMe_2)_2$	0.00

Lithium–zinc transmetalation was carried out experimentally by using the imine **11**, which was synthesized according to Scheme 3. The literature-known 2,3-dibromobenzo[*b*]-thiophene[6] underwent Sonogashira coupling with phenyl acetylene to give bromide **9**, which was transformed into aldehyde **10** by base-induced formylation using DMF. The condensation reaction of compound **10** with benzyl amine led to the target imine **11**.



Scheme 3. Reagents and conditions: i) PhCCH, $[Pd(Ph_3P)_2Cl_2]$, CuI, Et_3N, 20°C; ii) 1. *n*BuLi, 2. DMF; iii) $PhCH_2NH_2$, CH_2Cl_2, molecular sieves.

Compound **11** was deprotonated with LDA at −78°C. The resulting lithium species was then transmetalated by using zinc chloride etherate at −78°C, followed by warming to 0°C with stirring for 1.5 h, and aqueous workup leading to azepine **12** in 30% yield (Scheme 4). The structure of azepine **12** was confirmed by X-ray structure analysis (Figure 1). The formation of **12** may be understood as the



Scheme 4.

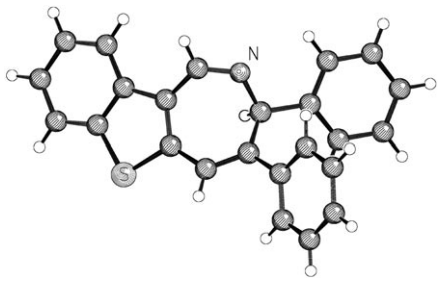
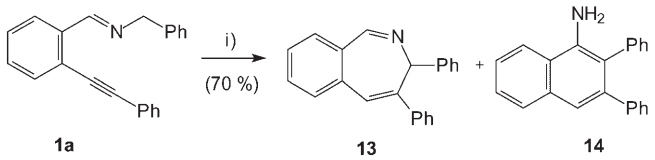


Figure 1. Molecular structure of **12** as obtained by X-ray diffraction (SCHAKAL plot).[7]

result of proton addition to an intermediate anion such as **3** during the aqueous workup. There are no indications for an anion with antiaromatic character such as **4** (Scheme 1). In contrast, the reaction of the lithiated imine **11** (without transmetalation) under the same reaction conditions led to a complex mixture of different compounds (GC analysis), in which **12** could not be detected by spectroscopic methods (see below).

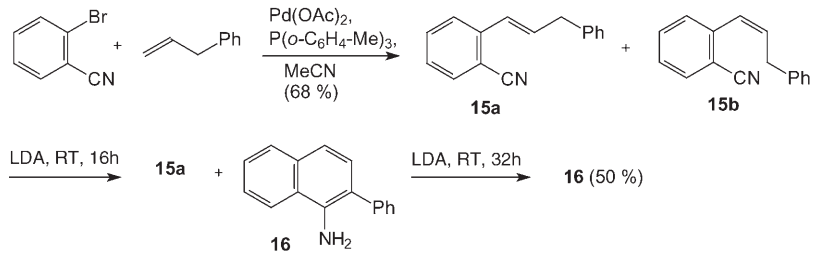
The same transmetalation procedure applied for imine **1a** (Scheme 1, R = Ph) gave a (inseparable) mixture of two substances (ratio 67:33 as determined by GC analysis), which were identified by ^1H and ^{13}C NMR spectra as benzazepine **13** and naphthylamine **14** (Scheme 5). The formation of such reaction mixtures was also observed in cases of longer reaction times (16 and 32 h). This might be explained by the higher reactivity of the respective seven-membered zinc intermediate in comparison to the corresponding one attached to a benzothiophene system. Apparently, the presence of the benzazepine **13** in the mixture is a result of the reaction of the seven-membered zinc intermediate with some proton sources (such as diisopropylamine, before the aqueous workup) in the reaction mixture. Hence in this case, the more reactive (in comparison to the benzothiophene compound) seven-membered zinc intermediate not only reacts with proton sources (giving benzazepine **13**), but also rearranges to naphthylamine **14** (see Scheme 1) as is known for the lithium compound.[1]



Scheme 5. i) 1. LDA, −78°C, 2. $ZnCl_2 \cdot 2Et_2O$, 3. −78–20°C, NH_4Cl/H_2O.

This pathway, used here for the synthesis of azepines **12** and **13**, is new and is expected to offer a quick and versatile method for the preparation other annulated azepine derivatives.[8,9] It adds nicely to our previous electrocyclization studies on the formation of 2,3- and 4,5-dihydroazepins[10,11] and 4,5-dihydro-3*H*-benzo[*c*]azepines.[12]

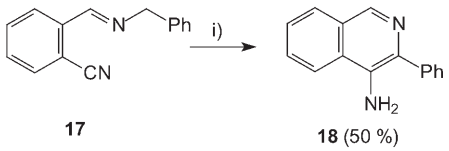
Evidence for the formation of nitrile intermediates of type 5 and their electrocyclization: The intramolecular addition of a carbanion to a nitrile function was observed first by Kobayashi et al.[13–15] DMF was used as solvent (instead of THF as we used it) and CO_2Et and CN groups (instead of Ph) were present in their work. To investigate the cyclization under typical conditions for concerted reactions, we synthesized model compound **15**. Compound **15** was obtained as a mixture of (*E*)-(**15a**) and (*Z*)-(**15b**) isomers (ratio 70:30) by the Heck reaction of 2-bromobenzonitrile and allylbenzene in 68% total yield (Scheme 6). Deprotonation under standard conditions (16 h, −78°C to room temperature) gave a mixture of naphthylamine **16** and the *E* isomer of the initial nitrile **15a** in a 35:65 ratio. The mixture obtained was again subjected to deprotonation conditions and stirred at room temperature for an additional 32 h (not optimized reaction time) to give the pure amine **16** (50% yield). Apparently,



Scheme 6.

the longer reaction time required in the case of model compound **15** in comparison to the cyclization of imine **1a** is dependent on the *Z* or *E* configuration of the nitrile **15**, as only the (*Z*)-(**15b**)-, but not the (*E*)-(**15a**)-derived allyl anion of type **5** will be involved in the cyclization. As the formation of the nitrile species from the seven-membered intermediate **3** leads to the pure (*Z*)-allyl-anion, the fast cyclization to give the six-membered intermediate **6** is well understandable. In contrast, the presence of the less reactive *E* isomer **15a** in the mixture led to an increase of the reaction time, as in this case obviously the comparably slow rate of the *E*–*Z* isomerization determined the reaction time.

For comparison, we included the imino nitrile **17** (Scheme 7) into this study. Its cyclization after lithiation may be considered as further, indirect evidence for the dependence of the reaction rate on the rate of the *trans–cis* isomerization of the allyl-anion. In the lithium compound of imino nitrile **17**, the nitrogen atom of the C=N double bond is expected to reduce the rotational barrier about this bond and consequently to decrease the reaction time in comparison to the one of model compounds **15a**,**b**. Indeed, the cyclization of imine **17** was completed in 16 h (not optimized period of time), comparably fast as in the case of imine **1a**. Transmetalation by using $ZnCl_2$ after the lithiation also gives **18**, although in a slower reaction. This reaction is also of interest from the preparative point of view as a new and



Scheme 7. i) LDA, −78–20 °C, 16 h, then NH_4Cl/H_2O.

simple method for the synthesis of 4-aminoisoquinoline derivatives **18**.[16]

Of course, the best evidence for the occurrence of the nitrile intermediate during the reaction is its isolation in the case of slowly reacting substances. As we found, imine **11** is a precursor for such a slowly reacting intermediate (Scheme 8). Thus, reaction of imine **11** under standard lithiation conditions (addition of LDA at −78 °C, warming to room temperature for 16 h) and aqueous workup gave a mixture of the two isomeric nitriles **19a**,**b**. A X-ray diffraction study of **19a** confirms the postulated structure (Figure 2). The configuration of the C=C double bond in nitrile **19b** could not be determined from the spectra of the mixture. Shorter reaction times gave a complex mixture of compounds (see above).

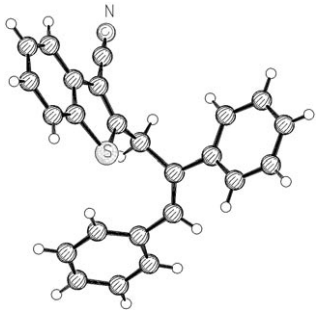


Figure 2. Molecular structure of **19a** as obtained by X-ray diffraction (SCHAKAL plot).[7]

Finally, deprotonation of nitriles **19a**,**b** with LDA, stirring of the resulting lithium species for 36 h at room temperature, and aqueous workup led to amine **20** in 90 % yield (for X-ray structure see Figure 3). We take this experiment as additional evidence for the nitrile cyclization upon deprotonation.

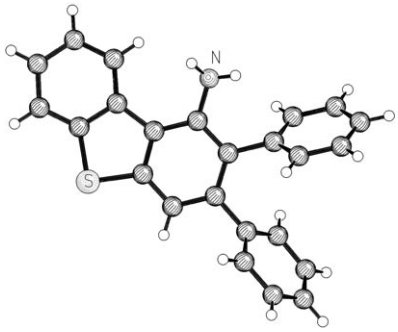
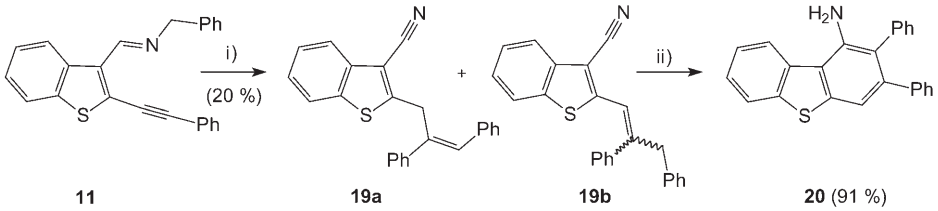


Figure 3. Molecular structure of **20** as obtained by X-ray diffraction (SCHAKAL plot).[7]



Scheme 8. i) LDA, −78–20 °C, 16 h, then NH_4Cl/H_2O; ii) LDA, 20 °C, 32 h, then NH_4Cl/H_2O.

Conclusion

The previously discovered novel rearrangement cascade of lithiated 2-(1-alkynyl)-benzaldimines of type **2** had been elucidated mechanistically on the basis of quantum chemical calculations, postulating the formation of a seven-membered heterocyclic intermediate and an open-chain nitrile compound as reaction intermediates. In this report, we present experimental proof for the postulated mechanism. Thus, we were able to prepare 3,4-diphenyl-3*H*-benzo[4,5]thieno[3,2-*c*]azepine (**12**) by low-temperature transmetalation of the highly reactive lithium intermediate to the less reactive ZnCl compound. Similarly, imine **1a** gave a mixture of the corresponding benzazepine derivate **13** together with the rearranged naphthylamine **14** after transmetalation. The ratio of the two compounds formed was found to depend on the reaction time applied.

Allyl nitriles **15** were successfully converted to the corresponding aminobenzannulated compound **16**. The anion derived from the *Z* isomer of **15** was found to cyclize much faster compared to one from the *E* isomer. The analogous imino nitrile **17** gave a similar cyclization providing a new synthetic pathway to amino-isoquinolines, such as **18**. The postulated interconversion of alkynyl imino compounds into allyl nitriles could be confirmed in the case of **11**, which gives the nitriles **19** under mild conditions. They may be transformed into the respective dibenzothiophene amine **20** by prolonged treatment with LDA as base.

In summary, we are able to present experimental proof for the involvement of intermediates of type **3** (azepine anions) and **5** (allyl anions; Scheme 1) in the cascade reaction mechanism, previously postulated on the basis of quantum chemical calculations. This study also leads to a deeper understanding of this mechanism and additionally offers the possibility to enter the reaction cascade from new precursor compounds, thus widening the scope of the reaction, for example, also for the synthesis of new types of compounds including new azepines and 4-amino-isoquinolines.

Experimental Section

Materials and methods: Solvents were dried by distillation from a drying agent: THF from K/benzophenone; CH_2Cl_2 from P_2O_5. Melting points: Büchi melting point B-540, uncorrected. IR: Nicolet FTIR 5DXC spectrometer. ^{1}H NMR: Bruker WM 300 (300 MHz), Bruker AMX 400 (400 MHz), Varian 500 MHz INOVA (500 MHz), Varian 600 Unity plus (600 MHz) spectrometers. ^{13}C NMR: Bruker WM 300 (75 MHz), Bruker AMX 400 (100 MHz), Varian 500 MHz INOVA (125 MHz), Varian 600 Unity plus (150 MHz) spectrometers. TMS as internal standard. GC analysis: Hewlett Packard 6890 Series, column HP5 (30 m), temperature program: 40 °C, 10 °C min^{-1}, 280 °C, 5 min. Electron ionization mass spectra (EIMS): Finnigan MAT C 312 spectrometer (70 eV). Electrospray mass spectra (ESIMS): Micromass Quartto LC-Z quadrupole mass spectrometer. GCMS: Varian MAT 8230 spectrometer with GC Varian 3400 plus datasystem Mass II by using Quartz capillary column HP5. Exact mass determination (HRMS): Micromass MAT 8200 spectrometer. Elemental analysis: Elementar Vario EL III analyze automate. Flash chromatography: silica gel Merck 60 (0.040–0.063 mm) with excess pressure of about 1.2 bar. TLC: Merck silica gel plates (silica gel 60 F_{254}).

1-(3-Bromobenzo[*b*]thiophen-2-yl)-2-phenylacetylene (9): A suspension of 2,3-dibromobenzo[*b*]thiophene[6] (2.00 g, 6.84 mmol), triethylamine (30 mL), phenyl acetylene (0.82 g, 8.04 mmol), $[Pd(PPh_3)_2Cl_2]$ (96 mg), and CuI (13 mg) was stirred for 19 h at RT. The precipitate was filtered off. The filtrate was freed from the solvent under reduced pressure. Purification by flash chromatography (heptane) gave **9** (1.73 g, 5.53 mmol, 81 %) as a colorless solid. M.p. 77–79 °C; IR (KBr): $\tilde{\nu}$ = 3049 (w), 2954 (m), 2923 (s), 2852 (s), 2206 (w), 1593 (m), 1568 (w), 1556 (w), 1521 (w), 1481 (s), 1454 (m), 1438 (m), 1431 (m), 1377 (w), 1319 (m), 1307 (m), 1290 (w), 1276 (w), 1244 (m), 1157 (w), 1097 (w), 1066 (w), 914 (m), 844 (w), 817 (m), 750 (s), 721 (s), 709 (s), 684 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.32–7.53 (m, 5H), 7.59–7.62 (m, 2H), 7.72–7.80 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 80.85 (*C*≡C), 98.30 (C≡*C*), 112.86, 119.58, 121.39, 122.80, 124.63, 125.64, 127.60, 128.25, 138.90, 131.64, 136.62, 137.45 ppm; MS (EI): *m*/*z* (%): 314 $[M]^+$ (100), 312 $[M]^+$ (100), 232 (42), 202 (71), 189 (52), 163 (9), 127 (39), 98 (6), 57 (22); elemental analysis calcd (%) for $C_{16}H_9BrS$ (313.22): C 61.36, H 2.90; found: C 61.77, H 2.95.

2-(2-Phenyl-1-ethynyl)benzo[*b*]thiophene-3-carbaldehyde (10): *n*BuLi (1.51 mL of 1.6 M solution in hexane, 2.42 mmol) was added to a solution of **9** (0.74 g, 2.37 mmol) in dry THF (50 mL) at −78 °C under an argon atmosphere. The reaction mixture was stirred for 1 h at this temperature. Then DMF (0.28 mg, 3.83 mmol) was added and the mixture was stirred for an additional 3 h while warming to room temperature. After the addition of diluted ammonium chloride solution (60 mL) and extraction of the water layer with diethyl ether (3×30 mL), the combined organic extracts were dried over magnesium sulfate. Purification by flash chromatography (Et_2O/pentane 0.3:10) gave **10** (0.50 g, 1.90 mmol, 80 %) as a colorless solid. M.p. 101–101.5 °C; IR (KBr): $\tilde{\nu}$ = 3057 (w), 2924 (w), 2831 (w), 2202 (m), 1666 (s), 1505 (m), 1481 (m), 1458 (m), 1429 (m), 1394 (w), 1360 (m), 1315 (m), 1291 (w), 1250 (m), 1161 (m), 1140 (m), 1119 (m), 1061 (w), 1041 (w), 1015 (w), 916 (w), 868 (m), 758 (s), 687 (s), 588 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.38–7.51 (m, 5H), 7.58–7.60 (m, 2H), 7.76–7.78 (m, 1H), 8.68–8.70 (m, 1H), 10.47 ppm (s, 1H; C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.18 (*C*≡C), 102.03 (C≡*C*), 120.56, 120.81, 124.32, 125.68, 126.00, 127.78, 129.00, 130.99, 134.38, 135.11, 137.76, 138.01, 184.11 ppm (*C*HO); MS (GCMS): *m*/*z*: 262 $[M]^+$, 234, 221, 202, 189, 163, 150, 117, 104, 95, 69, 63, 51; HRMS: *m*/*z*: calcd for $C_{17}H_{10}OS$: 262.0452; found: 262.0452; elemental analysis calcd (%) for $C_{17}H_{10}OS$: 262.33: C 77.84, H 3.84; found: C 77.73, H 3.63.

***N*-Benzyl-2-(2-phenyl-1-ethynyl)benzo[*b*]thiophen-3-ylmethanimine (11)**: Aldehyde **10** (1.31 g, 5.00 mmol) and benzyl amine (0.53 g, 5.00 mmol) were mixed together in dry dichloromethane (20 mL) and stirred in the presence of molecular sieves (4 Å) at RT for 16 h. The molecular sieves were then removed by filtration and washed with dichloromethane (20 mL). The solvent was removed in vacuo to afford **11** (1.11 g, 3.15 mmol, 63 %) as a brown oil. IR (KBr): $\tilde{\nu}$ = 3084 (w), 3060 (m), 3028 (m), 3003 (w), 2856 (m), 2202 (w), 1631 (s), 1595 (m), 1585 (m), 1571 (w), 1556 (w), 1517 (w), 1494 (m), 1483 (m), 1460 (m), 1452 (m), 1442 (m), 1431 (m), 1382 (w), 1359 (m), 1342 (w), 1315 (m), 1296 (w), 1265 (w), 1249 (w), 1176 (w), 1159 (w), 1143 (m), 1120 (m), 1068 (w), 1026 (m), 999 (w), 947 (w), 914 (w), 858 (w), 756 (s), 732 (s), 690 (s), 669 (w), 642 (w), 592 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.86 (s, 2H; CH_2), 7.20–7.36 (m, 10H), 7.78–7.50 (m, 2H), 7.67–7.69 (m, 1H), 8.88–8.93 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.07 (N−*C*H_2), 97.82 (*C*≡C), 102.83 (C≡*C*), 121.76, 125.76, 126.25, 126.39, 127.03, 127.17, 127.46, 127.75, 128.04, 128.27, 128.43, 128.65, 128.87, 129.14, 129.34, 131.78, 156.92 ppm; HRMS: *m*/*z*: calcd for $C_{24}H_{17}NSH$: 352.1159; found: 352.1154; elemental analysis calcd (%) for $C_{24}H_{17}NS$ (351.47): C 82.02, H 4.88, N 3.99; found: C 81.93, H 4.75, N 3.88.

3,4-Diphenyl-3*H*-benzo[4,5]thieno[3,2-*c*]azepine (12): A solution of LDA was prepared by adding *n*BuLi (0.70 mL, 1.12 mmol, 1.6 M solution in hexane) to diisopropylamine (0.12 g, 1.12 mmol) in dry THF (25 mL) at −78 °C. Imine **11** (1.00 mmol, 0.35 g) dissolved in THF (10 mL) was then added dropwise over a period of 30 min. Zinc chloride solution (3 mL, 3 mmol, 1 M solution in diethyl ether, ACROS) was added after 1 h of stirring at −78 °C. Then, the reaction mixture was stirred for an additional 1 h and was warmed to −20 °C over 20 min and stirred at −20–0 °C for

1 h. Diluted ammonium chloride solution (30 mL) was added and the mixture was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was evaporated in vacuo. Purification by flash chromatography (EtOAc/pentane/Et_3N 0.4:10:0.2, 15 cm length column) gave **12** (0.10 g, 0.3 mmol, 30%) as a colorless solid. M.p. 173–175°C; IR (KBr): $\tilde{\nu}$=3060 (m), 3022 (m), 2814 (m), 1643 (m), 1598 (s), 1577 (s), 1571 (m), 1552 (m), 1490 (s), 1444 (s), 1431 (s), 1365 (w), 1342 (m), 1313 (m), 1305 (m), 1259 (m), 1211 (s), 1182 (m), 1157 (w), 1132 (w), 1072 (m), 1031 (w), 1008 (s), 977 (m), 939 (w), 910 (w), 898 (w), 858 (s), 829 (w), 765 (s), 740 (s), 696 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=4.94 (brs, 1H; N−C*H*), 7.12–7.23 (m, 9H), 7.41–7.51 (m, 4H), 7.84–7.88 (m, 1H), 7.95–7.98 (m, 1H), 8.86 ppm (d, $^4J_{H,H}$=1.7 Hz, 1H; C*H*=N); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=67.53 (N−*C*H), 121.71, 122.53, 122.72, 125.33, 125.96, 126.74, 127.31, 127.80, 127.94, 127.99, 129.13, 132.78, 137.93, 138.35, 139.13, 140.84, 143.19, 145.70, 153.20 ppm; MS (GC-EI): *m*/*z* (%): 350 $[M-H]^+$, 336, 321, 273, 247, 215, 202, 175, 165, 137, 102, 91, 89, 77; elemental analysis calcd (%) for $C_{24}H_{17}NS$ (351.47): C 82.02, H 4.88, N 3.99; found: C 81.80, H 4.82, N 3.85.

X-ray crystal-structure analysis of ***12***:[17] Formula: $C_{24}H_{17}NS$; M=351.45; colorless crystal; crystal size: 0.30×0.15×0.05 mm; a=17.559(1), b=6.045(1), c=17.831(1) Å; β=112.14(1)°; V=1753.1(3) $Å^3$; ρ_{calcd}=1.332 $g\,cm^{-3}$; μ=0.191 mm^{-1}; empirical absorption correction ($0.945 \le T \le 0.991$); Z=4; crystal system: monoclinic; space group: $P2_1/c$ (no. 14); λ=0.71073 Å; T=198 K; ω and ϕ scans; 11311 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$=0.67 $Å^{-1}$; 4212 independent (R_{int}=0.058) and 2626 observed reflections [$I \ge 2\sigma I$]; 235 refined parameters; R=0.051; $wR2$=0.108; max. residual electron density 0.25 $e\,Å^{-3}$ (−0.31); hydrogen atoms calculated and refined riding.

3,4-Diphenyl-3*H*-2-benzazepine (13): 3,4-Diphenyl-3*H*-2-benzazepine (**13**) was obtained as a mixture with aminonaphthalene **14**[1] from imine **1a**[1] in a similar manner as described for the synthesis of **12** from **11** (overall yield 70%). Separation of the mixture (chromatography, silica gel, Et_2O/Et_3N/pentane 0.5:0.2:10) was not possible. Spectroscopic data for **13** and **14** were taken from the spectra of the reaction mixture. ^1H NMR (500 MHz, $CDCl_3$): δ=4.21 (brs; NH_2, **14**), 5.14 (s; Ph−C*H*−N, **13**), 6.97 (s; =C*H*, **13**), 7.07–7.10 (m), 7.14–7.24 (m), 7.28–7.31 (m), 7.33–7.39 (m), 7.45–7.51 (m), 7.56 (d, ^3J=7–9 Hz), 7.83–7.87 (m), 8.62 ppm (d, ^4J=1.7 Hz, C*H*=N, **13**); ^{13}C NMR (125 MHz, $CDCl_3$): δ=65.26 (Ph−C*H*−N, **13**), 119.55 (**14**), 121.11 (**14**), 121.68 (**14**), 125.21 (**14**), 126.12 (**14**), 126.22 (**14**), 126.46 (**14**), 126.53 (**13**), 126.89 (**13**), 127.06 (**13**), 127.42 (**14**), 122.77 (**14**), 127.79 (**14**), 127.82 (**13**), 127.85 (**13**), 128.42 (**13**), 128.55 (**13**), 128.55 (**14**), 128.59 (**14**), 128.64 (**13**), 129.61 (**13**), 129.84 (**14**), 129.96 (**13**), 131.27 (**13**), 133.34 (**14**), 134.60 (**13**), 137.24 (**13**), 138.21 (**14**), 139.31 (**14**), 140.36 (**14**), 140.40 (**13**), 140.68 (**13**), 142.07 (**14**), 145.76 (**13**), 160.98 ppm (*C*H=N, **13**).

2-[(*E*)-3-Phenyl-1-propenyl]benzonitrile (15a) and 2-[(*Z*)-3-phenyl-1-propenyl]benzonitrile (15b): Compounds **15a** and **15b** were prepared in analogy to a published procedure.[18] 2-Bromobenzonitrile (0.18 g, 1.00 mmol), 1-allylbenzene (0.12 g, 1 mmol, 0.13 mL), triethylamine (0.20 g, 2.00 mmol, 0.28 mL), palladium acetate (5 mg), tri-*o*-tolylphosphine (12 mg), and acetonitrile (8 mL) were combined in a dried Schlenk flask under an argon atmosphere and warmed to 80–85°C. Water (20 mL) was added after disappearance of the initial compounds (checked by TLC, approximately 40 h) and the mixture was extracted with diethyl ether (3×20 mL). The combined organic extracts were dried over magnesium sulfate and the solvent was removed in vacuo. Purification of the residue by flash chromatography (EtOAc/pentane 1:10) gave a mixture of **15a** and **15b** (0.15 g, 0.68 mmol, 68%, **15a**/**15b** 68:32 (as determined by ^1H NMR spectroscopy) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=3.56 (d, $^3J_{H,H}$=7.1 Hz), 3.70 (d, $^3J_{H,H}$=6.80 Hz), 6.19–6.20 (m), 6.43–6.53 (m), 6.76–6.81 (m), 7.12–7.34 (m), 7.40–7.59 ppm (m); MS (ESI): *m*/*z*: 242 $[M+Na]^+$, 237, 217, 191, 157, 115, 113, 83, 55, 41, 23.

2-Phenyl-1-naphthalenamine (16): A solution of LDA was prepared by adding *n*BuLi (0.70 mL, 1.12 mmol, 1.6 M in hexane) to diisopropylamine (0.12 g, 1.12 mmol) in dry THF (25 mL) at −78°C. Then, the mixture of **15a** and **15b** (1.00 mmol, 0.22 g) dissolved in THF (10 mL) was added dropwise over a period of 30 min. The reaction mixture was warmed to RT for 48 h and was then quenched by addition of diluted ammonium chloride solution (5 mL). Water (20 mL) was added and the mixture was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was evaporated. Purification by flash chromatography (EtOAc/pentane 1:10) gave **16** (0.11 g, 0.50 mmol, 50%) as a brown solid. M.p. 98–100°C; IR (film): $\tilde{\nu}$=3363 (s, br), 3224 (s, br), 3055 (s), 3030 (s), 2958 (m), 2925 (m), 2869 (m), 2854 (m), 1955 (m), 1894 (m), 1811 (m), 1643 (s), 1633 (s), 1575 (s), 1548 (s), 1506 (s), 1494 (s), 1463 (s), 1446 (s), 1427 (s), 1394 (s), 1332 (m), 1311 (m), 1280 (m), 1255 (s), 1228 (m), 1180 (m), 1157 (m), 1132 (m), 1099 (m), 1072 (m), 1026 (s), 983 (w), 952 (w), 920 (w), 894 (m), 856 (m), 806 (s), 758 (s), 744 (s), 696 cm^{-1} (s); ^1H NMR (100 MHz, [D_6]DMSO, 25°C): δ=5.39 (brs, 2H; NH_2), 7.19–7.27 (m, 2H), 7.36–7.52 (m, 7H), 7.78–7.81 (m, 1H), 8.20–8.24 ppm (m, 1H); ^{13}C NMR (75 MHz, [D_6]DMSO): δ=116.56, 119.78, 122.80, 123.07, 124.51, 125.75, 126.79, 127.84, 128.64, 128.97, 129.26, 133.47, 139.84, 140.14 ppm; HRMS: *m*/*z*: calcd for $C_{16}H_{13}NH$: 220.1126; found: 220.1121; elemental analysis calcd (%) for $C_{16}H_{13}N$ (219.29): C 87.64, H 5.98, N 6.39; found: C 87.22, H 5.91, N 6.06.

2-Benzyliminomethylbenzonitrile (17): Treatment of 2-formylbenzonitrile (0.65 g, 5.00 mmol) according to the general procedure described for imine **11** gave **17** (0.63 g, 2.85 mmol, 57%) as a colorless solid. M.p. 63–65°C; IR (film): $\tilde{\nu}$=3085 (w), 3062 (w), 3030 (w), 2858 (w), 2844 (w), 2231 (s), 1708 (w), 1647 (s), 1602 (w), 1581 (w), 1496 (m), 1475 (m), 1454 (m), 1434 (m), 1371 (m), 1342 (m), 1315 (w), 1288 (m), 1244 (w), 1168 (w), 1155 (w), 1141 (w), 1095 (w), 1080 (w), 1028 (m), 999 (w), 964 (w), 908 (w), 798 (m), 756 (m), 736 (m), 700 (s), 686 (s), 613 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ=4.90 (d, $^4J_{H,H}$=1.4 Hz, 2H; N−CH_2), 7.25–7.38 (m, 5H), 7.49 (td, $^3J_{H,H}$=7.6, $^4J_{H,H}$=1.4 Hz, 1H), 7.61 (tm, $^3J_{H,H}$=7.7 Hz, 1H), 7.67 (dm, $^3J_{H,H}$=7.7 Hz, 1H), 8.18 (dm, $^3J_{H,H}$=8.0 Hz, 1H), 8.78 ppm (t, $^4J_{H,H}$=1.4 Hz, 1H; N=C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ=65.35 (N−CH_2−Ph), 112.93, 117.08, 127.31, 127.70, 128.11, 128.69, 130.78, 132.94, 133.08, 138.39, 138.70, 157.78 ppm. HRMS: *m*/*z*: calcd for $C_{15}H_{12}N_2Na$: 243.0898; found: 243.0893; elemental analysis calcd (%) for $C_{15}H_{12}N_2$ (220.28): C 81.79, H 5.49, N 12.72; found: C 81.52, H 5.35, N 12.62.

3-Phenyl-4-isoquinolinamine (18): Isoquinoline **18** was synthesized from imine **17** (0.22 g, 1 mmol) by following the method described for the synthesis of **16** (16 h of stirring before workup). Purification by flash chromatography (*tert*-butyl methyl ether) gave **18** (0.11 g, 0.50 mmol, 50%) as a colorless solid. M.p. 89–92°C; IR (KBr): $\tilde{\nu}$=3321 (s, br), 3222 (s, br), 3047 (m), 2962 (m), 2925 (m), 2856 (m), 1629 (s), 1571 (s), 1560 (s), 1543 (s), 1490 (s), 1448 (m), 1425 (m), 1396 (s), 1340 (m), 1311 (m), 1261 (s), 1164 (m), 1105 (m), 1072 (s), 1018 (m), 956 (w), 906 (m), 896 (m), 856 (m), 804 (m), 763 (s), 723 (m), 709 (s), 594 (m), 576 (m), 545 (m), 484 (m), 470 (w), 447 (w), 432 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ=4.33 (brs, 2H; NH_2), 7.34–7.38 (tt, $^3J_{H,H}$=7.4, $^4J_{H,H}$=1.3 Hz, 1H), 7.45–7.55 (m, 3H), 7.59–7.63 (m, 1H), 7.70–7.73 (m, 2H), 7.80 (dd, $^3J_{H,H}$=8.5, $^4J_{H,H}$=0.9 Hz, 1H), 7.88 (d, $^3J_{H,H}$=7.9 Hz, 1H), 8.80 ppm (d, $^4J_{H,H}$=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ=120.42, 126.58, 126.85, 127.79, 127.90, 128.20, 128.89, 129.18, 129.26, 133.68, 136.25, 139.37, 142.52 ppm; HRMS: *m*/*z*: calcd for $C_{15}H_{12}N_2H$: 221.1079; found: 221.1073; elemental analysis calcd (%) for $C_{15}H_{12}N_2$ (220.28): C 81.79, H 5.49, N 12.72; found: C 81.53, H 5.28, N 12.66.

2-[(*E*)-2,3-Diphenyl-2-propenyl]benzo[*b*]thiophen-3-yl cyanide (19a) and 2-[(*E*,*Z*)-2,3-diphenyl-1-propenyl]benzo[*b*]thiophen-3-yl cyanide (19b): Compounds **19a**,**b** were synthesized from imine **11** (0.35 g, 1 mmol) by following the method described for the synthesis of amine **16** (16 h of stirring before workup). Purification by flash chromatography (EtOAc/pentane 1:10) gave **19a** and **19b** (70 mg, 0.20 mmol, 20%) as colorless solids. IR (KBr): $\tilde{\nu}$=3051 (w), 3024 (w), 2947 (w), 2912 (w), 2218 (m), 1597 (w), 1519 (w), 1492 (w), 1460 (w), 1434 (m), 1359 (w), 1315 (w), 1296 (w), 1263 (w), 1245 (w), 1199 (w), 1176 (w), 1155 (w), 1128 (w), 1078 (w), 1068 (w), 1022 (w), 999 (w), 987 (w), 950 (w), 923 (m), 877 (m), 850 (w), 813 (w), 802 (w), 758 (s), 748 (m), 729 (m), 700 (s), 646 (m), 617 (w), 547 (w), 511 (w), 503 (w), 480 (w), 443 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ=4.26 (s), 4.54 (s), 6.70 (s), 6.98–7.00 (m), 7.08–7.10 (m), 7.6–

7.17 (m), 7.19–7.41 (m), 7.52–7.53 (m), 7.62 (dd, $^3J_{H,H}=8.0$, $^4J=0.5$ Hz), 7.67 (dd, $^3J_{H,H}=8.2$, $^4J_{H,H}=0.6$ Hz), 7.78 ppm (td, $^3J_{H,H}=7.3$, $^4J_{H,H}=0.7$ Hz); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=31.47$, 41.06, 114.23, 121.95, 122.13, 122.45, 122.49, 125.55, 125.68, 125.78, 126.65, 127.13, 127.69, 127.81, 128.07, 128.10, 128.67, 128.78, 128.79, 128.87, 129.29, 130.17, 132.09, 136.35, 137.00, 137.29, 137.54, 137.75, 138.44, 138.95, 140.62, 158.07 ppm; MS (GCMS): two GC peaks were observed (25.20 and 25.68 min, relative intensity: 39 and 61%, correspondingly); peak 25.20 min: *m/z*: 351 $[M]^+$, 332, 324, 274, 259, 240, 227, 214, 202, 191, 178, 172, 165, 152, 128, 115, 102, 89, 77, 63, 51; peak 25.68 min: *m/z*: 351 $[M]^+$, 351, 334, 324, 274, 259, 240, 227, 178, 172, 165, 152, 145, 128, 115, 102, 91, 77, 63, 51.

X-ray crystal-structure analysis of ***19a***: Crystals obtained by crystallization from $CHCl_3$/pentane of the mixture of compounds.[17] Formula $C_{23}H_{17}NS$; $M=353.45$; colorless crystal; crystal size: $0.40\times0.30\times0.20$ mm; $a=9.619(1)$, $b=11.441(1)$, $c=18.196(1)$ Å; $\alpha=77.11(1)$, $\beta=81.52(1)$, $\gamma=72.93(1)°$; $V=1858.8(3)$ Å^3; $\rho_{calcd}=1.263$ g cm^{-3}; $\mu=1.591$ mm^{-1}; empirical absorption correction ($0.569\le T\le0.741$); $Z=4$; crystal system: triclinic; space group $P\bar{1}$ (no. 2); $\lambda=1.54178$ Å; $T=223$ K; ω and ϕ scans; 21392 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.60$ Å^{-1}; 6430 independent ($R_{int}=0.034$) and 6166 observed reflections [$I\ge2\sigma I$]; 469 refined parameters; $R=0.045$; $wR2=0.128$; max. residual electron density 0.32 e Å^{-3} (−0.52); two almost identical molecules in the asymmetric unit; hydrogen atoms calculated and refined riding.

2,3-Diphenyldibenzo[*b*,*d*]thiophen-1-amine (20): Compound **20** was synthesized from the mixture of nitriles **19a**,**b** (0.35 g, 1 mmol) by following the method described for the synthesis of amine **16**. Purification by flash chromatography (EtOAc/pentane 1:10) gave **20** (0.32 g, 0.91 mmol, 91%) as a colorless solid. M.p. 172–173.5 °C; IR (KBr): $\tilde{\nu}=3479$ (w), 3429 (w), 3350 (m), 3047 (w), 3030 (w), 3018 (w), 2995 (w), 2922 (w), 2852 (w), 1606 (m), 1598 (m), 1583 (m), 1556 (w), 1537 (m), 1504 (m), 1492 (m), 1471 (w), 1454 (m), 1438 (m), 1425 (m), 1402 (s), 1313 (m), 1299 (m), 1288 (m), 1228 (m), 1190 (w), 1174 (m), 1157 (w), 1143 (w), 1072 (m), 1051 (w), 1026 (m), 1006 (w), 989 (w), 968 (w), 954 (w), 914 (w), 848 (w), 837 (w), 788 (w), 767 (m), 738 (m), 727 (m), 702 (s), 667 (w), 636 (m), 626 (w), 609 (w), 574 (m), 536 (m), 511 (w), 480 (w), 457 (w), 430 cm^{-1} (w); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=4.35$ (br s, 2H; NH_2), 7.14–7.50 (m, 12H), 7.87–7.90 (m, 1H), 8.23–8.26 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=114.71$, 121.34, 123.01, 123.36, 124.11, 124.60, 125.42, 126.46, 127.29, 127.66, 128.81, 129.89, 131.75, 135.81, 137.38, 139.56, 139.97, 141.12, 141.76, 141.80 ppm; MS (GCMS): *m/z*: 351 $[M]^+$, 334, 273, 245, 213, 175, 167, 159, 89, 69, 63; HRMS: *m/z*: calcd for $C_{24}H_{17}NS$: 351.1082; found: 351.1082; elemental analysis calcd (%) for $C_{24}H_{17}NS$ (351.47): C 82.02, H 4.88, N 3.99; found: C 81.85, H 4.75, N 3.88.

X-ray crystal-structure analysis of ***20***:[17] Formula: $C_{24}H_{17}NS$; $M=351.45$; colorless crystal; crystal size: $0.50\times0.30\times0.15$ mm; $a=24.915(1)$, $b=8.374(1)$, $c=20.748(1)$ Å; $\beta=125.39(1)°$; $V=3529.0(5)$ Å^3; $\rho_{calcd}=1.323$ g cm^{-3}; $\mu=1.658$ mm^{-1}; empirical absorption correction ($0.491\le T\le0.789$); $Z=8$; crystal system: monoclinic; space group: *C*2/*c* (no. 15); $\lambda=1.54178$ Å; $T=223$ K; ω and ϕ scans; 14069 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.60$ Å^{-1}, 3110 independent ($R_{int}=0.037$) and 2996 observed reflections [$I\ge2\sigma I$], 243 refined parameters; $R=0.035$; $wR2=0.093$; max. residual electron density 0.21 e Å^{-3} (−0.25); hydrogen atoms at N1 from Fourier map; other calculated and refined riding.

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