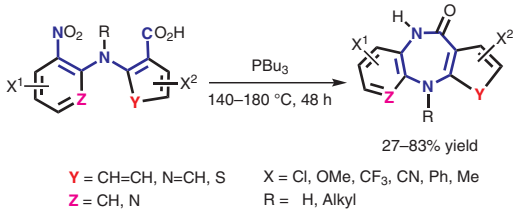
Synthesis M. Tryniszewski et al. Paper

Reductive Condensation of a Nitro Group with Carboxylic Acids Promoted by Phosphorus(III) Compounds: A Short Route to 5*H*-Dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-ones

Michał Tryniszewski[a,b]
Robert Bujok[b]
Roman Gańczarczyk[a]
Zbigniew Wróbel*[b]

[a] Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland
[b] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 00-266 Warsaw, Poland
zbigniew.wrobel@icho.edu.pl

Three Metal-Free Steps in One Operation in One Pot



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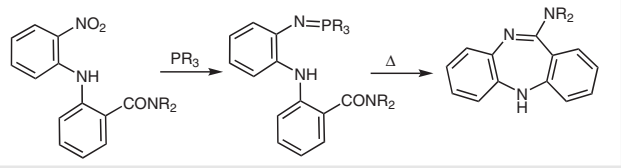
Abstract Tributyl- or triphenylphosphine promotes a one-pot, three-step method for the synthesis of differently substituted dibenzodiazepinones from *N*-aryl-2-nitroanilines. Pyridine analogues and the corresponding thiazepinones can also be formed using this method. The process involves deoxygenation of the nitro group, then formation of an iminophosphorane intermediate and its intramolecular condensation with a carboxyl group placed in the *N*-aryl group. The role of the carboxyl group in the formation of the iminophosphorane and the mode of cyclization are discussed.

Key words cyclocondensation, reduction, nitro compounds, dibenzodiazepines, regioselectivity

Recently, we described the intramolecular reductive cyclocondensation of a nitro group and an amido group leading to dibenzodiazepine systems.[1] The one-pot reaction, carried out in an excess of trivalent phosphorus compound, proceeds via formation of an iminophosphorane intermediate which subsequently undergoes an aza-Wittig reaction with the amido group (Scheme 1).



Scheme 1 Reductive cyclization of nitro amides to 11-aminodibenzodiazepines[1]

The method directly furnishes dibenzodiazepines such as clozapine, olanzapine and other 11-dialkylamino-substituted derivatives because the 11-amino group is introduced prior to the concluding cyclization. The alternative approach, more versatile regarding the assortment of final products and widely applied for the synthesis of various dibenzodiazepine derivatives, consists of the synthesis of the desired tricyclic system in the form of dibenzodiazepin-11-one. This can be easily transformed into 11-dialkylamino or other functionalized derivatives.[2–6] Moreover, dibenzodiazepin-11-ones themselves belong to the most prominent class of dibenzodiazepine derivatives amongst pharmaceutically important compounds (Figure 1). They exhibit various biological activities such as neuroleptic,[7] antimicrobial and antitumor,[8] anticancer,[6,9] antidepressant,[10] antimicrobial,[11] antiallergic[12] and antihistaminic[12] activity. Some of them have been revealed as muscarinic M_1-[13a,b] and M_2-selective[13c] antagonists or Chk1 kinase inhibitors.[14]

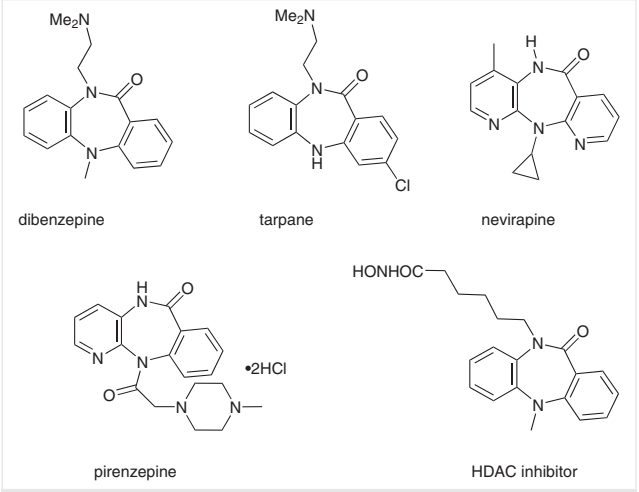


Figure 1 Examples of bioactive dibenzodiazepin-11-one derivatives

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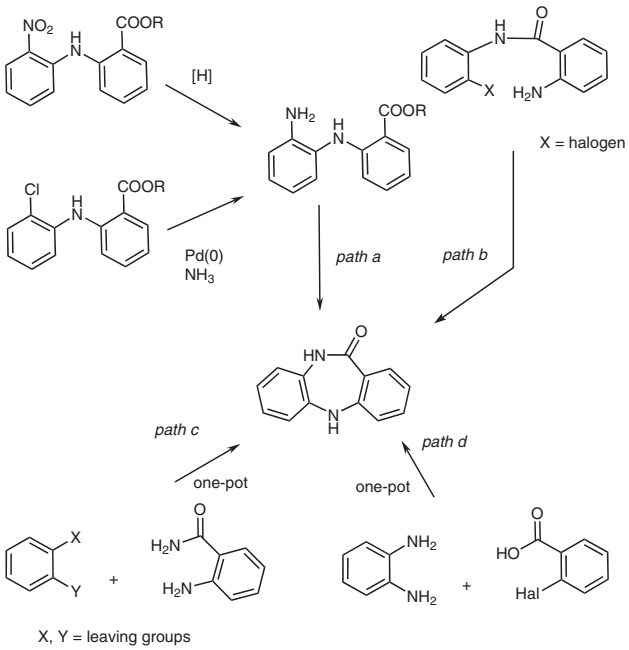
Considering the above, we decided to adapt our previously developed methodology to a simple, one-pot synthesis of dibenzodiazepin-11-ones from easily available nitrodiarylamine derivatives.

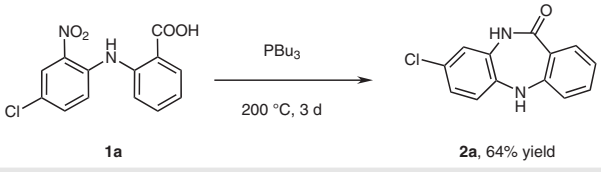
For the synthesis of 1,4-dibenzodiazepin-11-ones, dominating and most used are classical approaches. According to one of them (Scheme 2, path *a*), the central, seven-membered amide ring is formed by condensation of a suitable pair of functions, the amine from one side and a carboxyl-derived group from the other side of the appropriate diarylamine, by means of various condensing agents and protocols.[2–6,14,15] As a rule, the starting materials are prepared by reducing the nitro group of an appropriate 2-nitrodiarylamine. When catalytic amination of a suitable chlorodiarylamine is used for this purpose, the reaction leads to the cyclic product without isolation of the amine intermediate.[15] Another popular method for cyclization comprises formation of a new C–N bond between the arylamine nitrogen and the other arene ring of the amide by intramolecular Buchwald–Hartwig coupling (Scheme 2, path *b*).[8b,13b,16,17] This uses CuI or Pd(II) catalysts in the cyclization step and, as previously, synthesis of the starting amines requires a separate reduction of a nitro group. This narrows the set of compatible functional groups, and involves the use of metals or other environment-hostile reagents.



Scheme 2 The most popular methods for the synthesis of 1,4-dibenzodiazepin-11-ones

Another approach comprises creation of the amine and the amide linkages in one stage (Scheme 2, paths *c* and *d*). The domino reactions are promoted by Pd catalysts,[18a] Cs_2CO_3[18b] (path *c*) or Cu (path *d*).[9,19] It is not always clear which connection is formed first and, more importantly, both of these methods are principally nonselective and, in cases of substituted substrates, can lead to uncertain results or rather low yields.[19a] Perhaps the most promising regioselective procedure for path *c* is that reported lately by Laha et al.[18a] but the declared regioselectivity was actually demonstrated on the one example only.

The modification of our earlier approach to obtain cyclic 11-keto derivatives would require cyclocondensation of the initially formed iminophosphorane group with a carboxylic group. Iminophosphoranes, obtained in the Staudinger reaction of azides and phosphines, react with carboxylic acids with formation of carboxamides.[20] However, the reaction is known only for aliphatic reactants. Moreover, the synthesis of cyclic amides by this method was found to be limited to five-membered lactams.[20a] Our initial experiments showed that the proposed approach leading to fused, seven-membered rings of dibenzodiazepines was operational. When *N*-(4-chloro-2-nitrophenyl)anthranilic acid (**1a**) was heated at 200 °C for 3 days with an excess of PBu_3 (i.e., under the conditions previously used for cyclization of the amide analogues), dibenzodiazepin-11-one **2a** was obtained in 64% yield (Scheme 3).



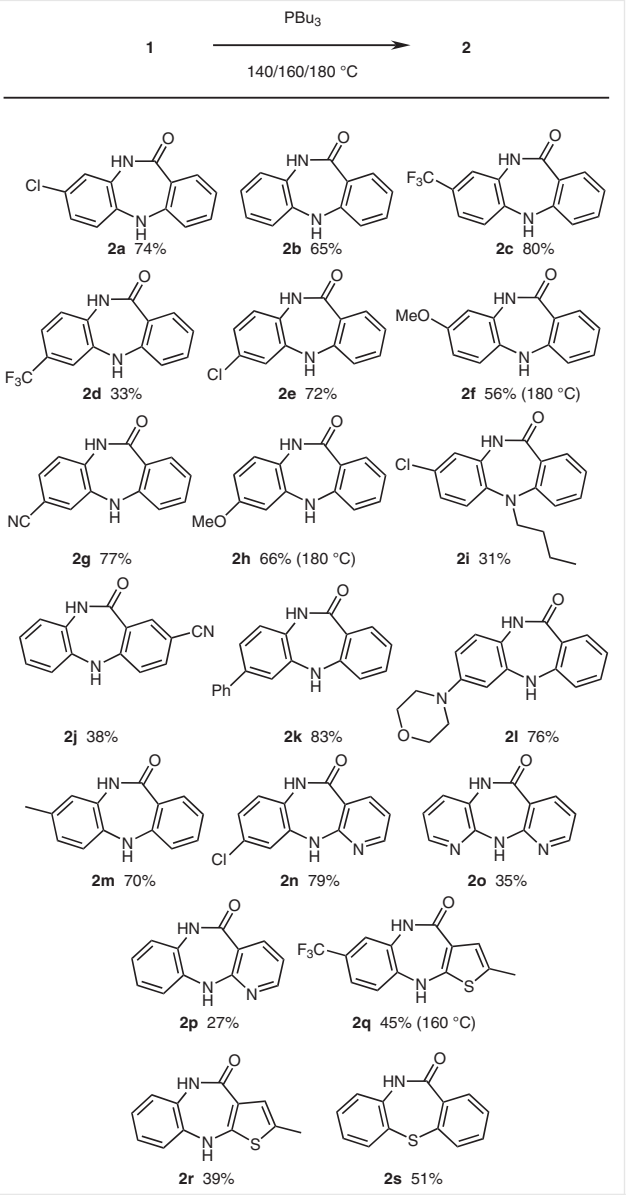
Scheme 3 Model reductive cyclocondensation of **1** to **2**

The reaction was then optimized to find the best reaction conditions. Similarly to previous findings,[21] the most efficient and convenient phosphorus reagent turned out to be PBu_3 used in an excess at 120–180 °C. Although reactions with PPh_3 achieved comparable yields, PBu_3 gave the product in high yield at lower temperature, and could be easily removed from the reaction mixture under reduced pressure during workup. Phosphorous acid derivatives such as $P(OMe)_3$ and $P(NMe_2)_3$ were found ineffective.

Under the chosen conditions, the cyclization of a series of nitrodiarylamines **1a–1r** carried out at 140 °C for 2 days yielded the expected 1,4-dibenzodiazepin-11-ones (Scheme 4).

When the yield was unsatisfactory, the reaction was repeated at higher temperature. In several instances this resulted in better yields. Scheme 4 shows the yields obtained at standard temperature 140 °C or at higher temperature, given in parentheses.

The reaction seems to be fairly general. It runs equally well with either electron-withdrawing or electron-donating substituents placed in either aromatic ring, as well as for some heterocyclic analogues. A very important feature

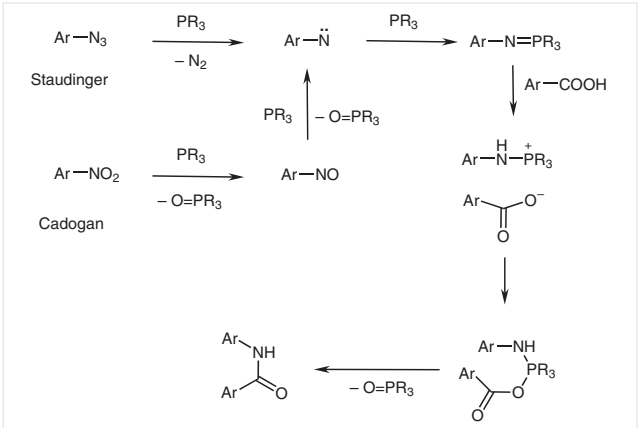


Scheme 4 1,4-Dibenzodiazepin-11-ones **2a–2m** and their analogues **2n–2s** obtained from the respective nitrodiarylamines **1a–1r** or from the corresponding sulfide **1s**

of the presented method is that it allows for unambiguous synthesis of the desired, differently substituted structures. This is a remarkable advantage over certain known methods, such as those shown in Scheme 2 as paths *c* and *d*, in which two C–N bonds are formed consecutively, and in most cases the intermediate is not recognized. For example, while the reductive cyclization of 2-{[2-nitro-4-(trifluoromethyl)phenyl]amino}benzoic acid (**1c**) leads definitely to 8-trifluoromethyl-substituted dibenzodiazepinone **2c** (Scheme 4), we found reported[18b] that the same structure was assigned to the compound obtained in the base-promoted reaction of 1,2-dichloro-4-(trifluoromethyl)benzene with 2-aminobenzamide, according to path *c* in Scheme 2, although the ^{1}H and ^{13}C NMR spectra of that compound and **2c** do not match. Similar discrepancy takes place in the case of **2a** and **2e** versus related compounds reported in the mentioned paper.[18b] Unfortunately, we could not reproduce the results presented in that paper. In our hands, the reaction did not provide any dibenzodiazepine derivative.

It is important to note that the reductive cyclization of nitro acids **1** gave positive results also with tertiary diarylamine derivatives (**1i**) as well as with their sulfur analogue (**1s**). This fact is interesting for mechanistic reasons and prompted us to take a closer look at this aspect.

Contrary to the cyclization of iminophosphoranes with amido groups,[1] the formation of amides from iminophosphoranes and carboxylic acids does not follow the aza-Wittig condensation scheme. The widely accepted mechanism of this process refers to the Staudinger method in which formation of the intermediate iminophosphorane from the corresponding azide is rather undoubted (Scheme 5).

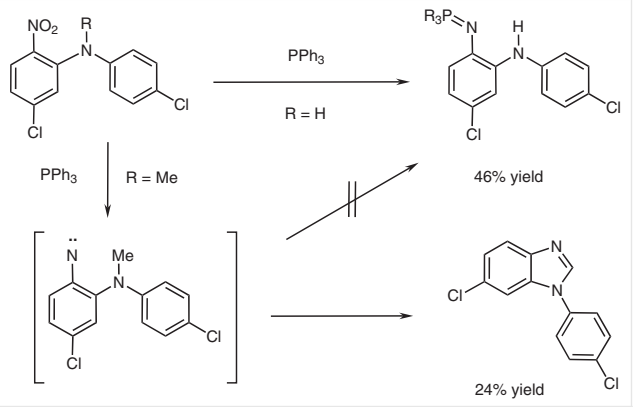


Scheme 5

Under the conditions of our reaction, Cadogan deoxygenation[22] of the nitro group is expected. This process leads initially to a nitroso group which, after the next deoxygenation, forms a nitrene intermediate. Finally, reaction of the phosphine with the nitrene gives iminophosphorane, and also further condensation with a carboxyl function can occur according to the above-mentioned Staudinger reaction (Scheme 5).

However, some reservations regarding the above mechanistic scheme can be raised. The first step of the deoxygenation is rather obvious, and we found previously that typical 2-nitrosodiarylamines easily form iminophosphoranes in the reaction with phosphines.[21a] Further investigations revealed that transformation of 2-nitrodiarylamines into the corresponding iminophosphoranes is possible only when there is a hydrogen atom at the amine nitrogen atom.[21b] This was shown in the reaction of *N*-methyl-substituted 2-nitrodiarylamine with triphenylphosphine in

which the iminophosphorane was not formed. Instead, *N*-arylbenzimidazole was obtained in low yield, apparently as a result of the insertion of the intermediate nitrene into a CH bond of the *N*-methyl group (Scheme 6).[21b]

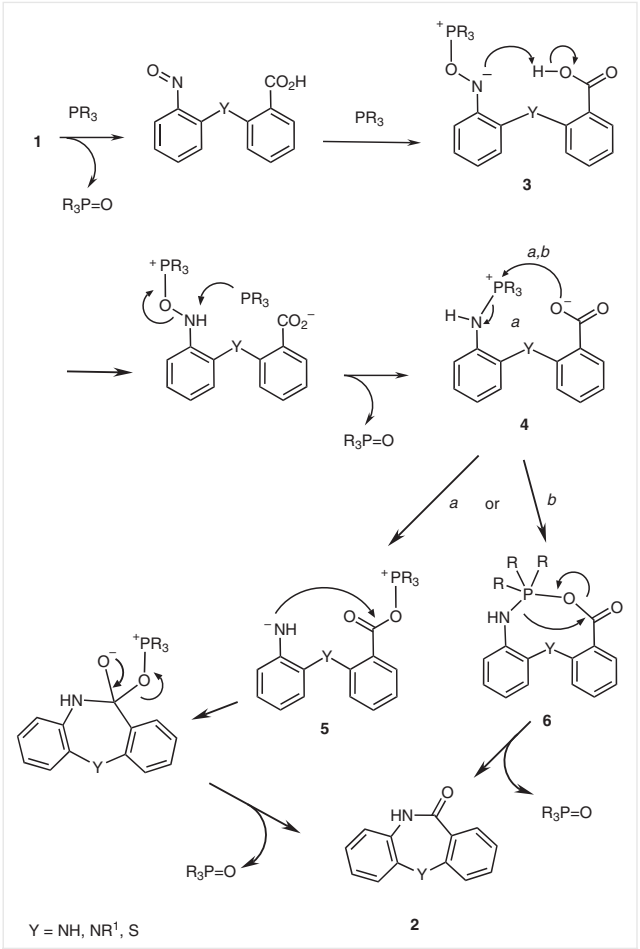


Scheme 6 Previously reported reaction of *N*-substituted and *N*-unsubstituted nitroanilines with triphenylphosphine[21b]

The evident difference in the behavior of *N*-substituted and *N*-unsubstituted nitroanilines in deoxygenation reactions under the action of trivalent phosphorus compounds has also been reported by others.[23] Although the reason for this phenomenon remains not well recognized, the role of the hydrogen atom at the amine nitrogen seems to be vital. For example, in the synthesis of benzimidazoles from nitroanilides and triphenylphosphine, a hydrogen bonding was acknowledged as responsible for stabilization of the nitrenoid intermediate that reacts with the phosphine. When the hydrogen atom is absent, undesired intramolecular reactions of the nitrene occur.[23a] In light of the above, positive results in the cyclization of **1i** and **1s**, affording **2i** and **2s** respectively, call for a reconsideration of the mechanism.

It is very likely that the carboxyl function can take the place of the *N*-hydrogen, playing the role of a proton source in the early step of the process. A supposed mechanistic scheme based on this suggestion is illustrated in Scheme 7. After partial deoxygenation of the nitro group, followed by addition of the phosphine to the nitroso group, protonation of the negative nitrogen in **3** occurs.[24] This prevents formation of a nitrene and allows the substitution of phosphine oxide by another phosphine molecule. Since iminophosphoranes are more basic than carboxylates,[20a] the intermediate iminophosphorane is formed and stays in zwitterionic form **4** that is not prone to a proton transfer. Instead, a transfer of the phosphonium group to the carboxylic oxygen takes place, followed by intramolecular acylation of the negatively charged nitrogen atom (Scheme 7, path *a*).

Alternatively, cyclic intermediate **6** is formed, followed by extrusion of phosphine oxide (Scheme 7, path *b*).[20] This

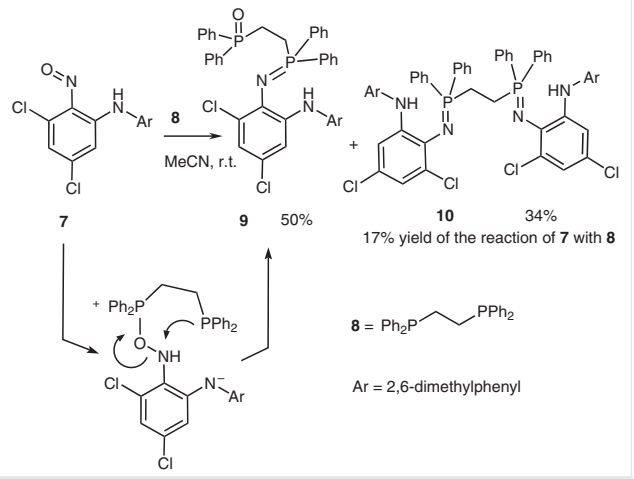


Scheme 7

mechanistic scheme should be also valid for the reactions of *N*-unsubstituted nitro acids **1** since carboxylic hydrogen is much more acidic than *N*-hydrogen of the diarylamine.

Looking for experimental support for the proposed mechanistic scheme, we attempted to isolate any intermediate products. For the reductive cyclization of nitro amides,[1] the corresponding iminophosphoranes could be isolated from reactions carried out at lower temperature, then transformed further into the final dibenzodiazepines. In the case of nitro acids **1**, that approach did not result in success. The reaction of nitro acid **1e** with an excess of PBu_3 or PPh_3 carried out at 120 or 100 °C led slowly to the cyclic product **2e**, and no iminophosphorane was obtained. Apparently, the last step of the reaction is the fastest one. Unfortunately, we were also unable to synthesize any corresponding nitroso acid by direct[25] or by multistep methods. Therefore, we tried to take a closer look at the crucial step of the supposed transformation leading to the iminophosphorane intermediate, by examining the reaction of nitrosodiarylamine **7**

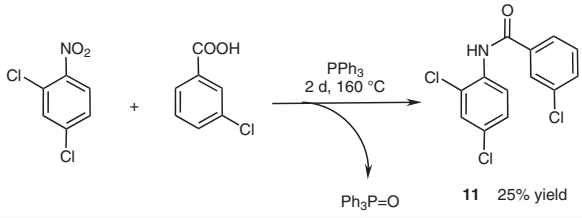
with tetraphenyldiphosphinoethane **8** (Scheme 8). In this case, as the carboxylic function is not present, the diarylamine NH group was expected to be a source of the crucial proton. Because of the two phosphine groups located in vicinity in **8**, the supposed intramolecular substitution of the phosphine oxide with the other phosphorus group placed in the same molecule, via a six-membered transition state, seemed to be the most convenient, thus, the most likely process.



Scheme 8

The reaction was carried out with a fivefold excess of **8** under the standard reaction conditions. As a result, the major compound **9** was obtained as major product in 50% yield, accompanied by **10** (formally 34% yield), apparently formed by initial intermolecular condensation of only 17% of **7** with **8**, without participation of the terminal PPh_2 group. The final formation of **10** was a result of subsequent condensation that excludes possibility of the intramolecular process. The alternative participation of a free nitrene intermediate would result in formation of the statistically preferred iminophosphorane bearing an unoxidized terminal phosphorus group. Thus, the reaction course via a nitrene intermediate seems to be marginal. The result supports the mechanism of iminophosphorane formation proposed for nitro acids **1** in which operation of the carboxylic hydrogen should be much more efficient.

One could expect that the intramolecular sequence of reactions presented here can also operate in the case of separated reactants, i.e. nitroarene and aromatic carboxylic acids in an intermolecular manner. Indeed, a prototype reaction of 2,4-dichloronitrobenzene with 3-chlorobenzoic acid and PPh_3, carried out under the typical reaction conditions, provided respective amide **11** (Scheme 9). However, the yield of this particular reaction was much lower than in most intramolecular instances.



Scheme 9 Intermolecular variant of the reductive amidation

In conclusion, a short, one-pot and regioselective method for the synthesis of differently substituted dibenzoazepinones and their analogues from *N*-aryl-2-nitroanilines or the corresponding sulfides has been presented. Deoxygenation of the nitro group initiates transformations that end in intramolecular condensation with the nearby carboxyl group, to form a fused seven-membered ring. The reaction tolerates various substituents in both aromatic rings, and proceeds well in the case of pyridine analogues.

Melting points were recorded in open capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra of all compounds studied were measured at temperature 298 K in $CDCl_3$ or DMSO-d_6 solutions with a VNMRS-500 spectrometer using TMS as internal standard. Mass spectra (EI, 70 eV) were obtained on an AutoSpec Premier (Waters) spectrometer. For ESI+ and ESI– measurements, a MALDI SYNAPT G2-S HDMS (Waters) system was used. Accurate mass measurements were obtained using a magnetic sector mass analyzer (EI) or TOF analyzer (ESI). IR spectra (KBr) were recorded on an FT/IR Jasco 6200 spectrophotometer. Merck silica gel 60 (230–400 mesh) was used for column chromatography. When required for melting point measurements, analytical samples of products were recrystallized from a suitable solvent. All commercial reagents were used without additional purification. The synthesis and characterization data of nitro acids **1** are provided in the Supporting Information.

Dibenzodiazepinones 2a–2s; General Procedure

In a Schlenk tube, equipped with a Teflon plug valve and a magnetic stirrer bar, were placed **1** (0.8 mmol) and PBu_3 (2.4 mL). The vessel was tightly closed, and partially immersed in an oil bath placed on a heating magnetic stirrer. The reaction mixture was stirred at 140 °C (at 160 °C or 180 °C in the specified cases) for 48 h then the excess PBu_3 was removed at reduced pressure (oil vacuum pump) at ca. 100 °C, and collected in a cold trap. The residue was then separated on a chromatography column (silica gel, DCM/MeOH, 50:1 to 10:1).

8-Chloro-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2a)

Yield: 144 mg (74%); yellow solid; mp 237–239 °C (Lit.[18b] 231.2–232.8 °C).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.89 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1 H), 6.95 (dd, *J* = 8.1, 1.1 Hz, 1 H), 6.97–6.99 (m, 3 H), 7.33 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1 H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 1 H), 7.95 (s, 1 H), 9.89 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 119.1, 120.4, 120.9, 121.0, 122.3, 123.9, 126.2, 131.2, 132.2, 133.5, 138.7, 149.7, 167.6.

MS (EI): *m*/*z* (%) = 246 (45), 244 (100, $[M]^+$), 209 (75), 181 (23), 154 (20).

HRMS (EI): *m*/*z* calcd for $C_{13}H_9{}^{35}ClN_2O$ [M]$^+$: 244.0403; found: 244.0398.

5*H*-Dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2b)

Yield: 109 mg (65%); yellow solid; mp 257–259 °C (Lit.[15] 255–257 °C).

IR (KBr): 3320, 3171, 3026, 1641, 1605, 1508, 1472, 1394 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.88–7.02 (m, 6 H), 7.34 (ddd, *J* = 8.1, 7.0, 1.6 Hz, 1 H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.84 (s, 1 H), 9.83 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 119.5, 120.2, 121.1, 121.7, 123.2, 123.4, 124.9, 130.3, 132.5, 133.6, 140.4, 150.9, 168.3.

MS (EI): *m*/*z* (%) = 210 (100, [M]$^+$), 181 (35), 154 (16).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{10}N_2O$ [M]$^+$: 210.0793; found: 210.0792.

8-(Trifluoromethyl)-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2c)

Obtained by following the general procedure, starting from **1c** (326 mg, 1.0 mmol).

Yield: 224 mg (80%); yellow solid; mp 177–180 °C (Lit.[12] 176–177 °C).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.91 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1 H), 6.98 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.13 (d, *J* = 8.2 Hz, 1 H), 7.25–7.29 (m, 2 H), 7.35 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1 H), 7.69 (dd, *J* = 7.9, 1.7 Hz, 1 H), 8.28 (s, 1 H), 9.97 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 117.8 (q, J_{FC} = 4 Hz), 119.2, 120.1, 121.1, 121.3 (q, J_{FC} = 4 Hz), 122.1, 123.0 (q, J_{FC} = 32 Hz), 124.1 (q, J_{FC} = 269 Hz), 129.9, 132.2, 133.6, 143.0, 148.7, 167.3.

MS (EI): *m*/*z* (%) = 278 (100, [M]$^+$), 249 (20), 209 (30).

HRMS (EI): *m*/*z* calcd for $C_{14}H_9F_3N_2O$ [M]$^+$: 278.0667; found: 278.0678.

7-(Trifluoromethyl)-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2d)

Yield: 74 mg (33%); creamy powder; mp 202–203 °C (hexane/EtOAc) (Lit.[15] 200–202 °C).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.94 (t, *J* = 7.4 Hz, 1 H), 6.99 (d, *J* = 7.7 Hz, 1 H), 7.13 (d, *J* = 8.2 Hz, 1 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 7.35–7.40 (m, 2 H), 7.71 (dd, *J* = 7.7, 1.4 Hz, 1 H), 8.14 (s, 1 H), 10.14 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 116.8 (q, J_{FC} = 4 Hz), 119.6, 120.1 (q, J_{FC} = 4 Hz), 121.6, 122.0, 122.7, 124.5 (q, J_{FC} = 271 Hz), 125.1 (q, J_{FC} = 32 Hz), 132.7, 133.9, 134.1, 140.2, 149.7, 167.9.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_9F_3N_2ONa$ [M + Na]$^+$: 301.0565; found: 301.0552.

7-Chloro-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2e)

Yield: 140 mg (72%); yellow crystals; mp 255–257 °C (Lit.[12] 253–254 °C).

IR (KBr): 3338, 3182, 3040, 1640, 1602, 1478, 1390, 1376 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.88–6.96 (m, 4 H), 7.05 (br s, 1 H), 7.34 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1 H), 7.66 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.95 (s, 1 H), 9.91 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 109.5, 119.09, 119.10, 121.2, 122.5, 122.6, 128.0, 128.9, 132.1, 133.4, 141.1, 149.4, 167.4.

MS (EI): *m*/*z* (%) = 244 (91, [M]$^+$), 209 (100), 181 (29), 154 (27).

HRMS (EI): *m*/*z* calcd for $C_{13}H_9{}^{35}ClN_2O$ [M]$^+$: 244.0403; found: 244.0400.

8-Methoxy-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2f)

Yield: 108 mg (56%); yellow solid; mp 176–179 °C (Lit.[12] 174–176 °C).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.64 (s, 3 H), 6.53–6.57 (m, 2 H), 6.82–6.86 (m, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 6.94 (dd, *J* = 8.1, 1.0 Hz, 1 H), 7.29 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1 H), 7.61 (s, 1 H), 7.64 (dd, *J* = 7.8, 1.7 Hz, 1 H), 9.75 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 55.2, 106.8, 109.4, 118.8, 120.36, 120.38, 122.6, 130.8, 132.0, 133.1, 133.1, 151.0, 155.3, 168.0.

MS (EI): *m*/*z* (%) = 240 (100, [M]$^+$), 211 (28), 197 (51), 169 (22), 77 (14).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{12}N_2O_2$ [M]$^+$: 240.0899; found: 240.0894.

11-Oxo-10,11-dihydro-5*H*-dibenzo[*b*,*e*][1,4]diazepine-7-carbonitrile (2g)

Yield: 145 mg (77%); yellow powder; mp >300 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.91 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1 H), 6.96 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.07 (d, *J* = 8.8 Hz, 1 H), 7.32–7.38 (m, 3 H), 7.68 (dd, *J* = 7.9, 1.6 Hz, 1 H), 8.14 (s, 1 H), 10.19 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 106.7, 119.1, 119.7, 121.7, 122.1, 122.6, 123.2, 127.4, 132.7, 134.3, 135.0, 140.2, 149.3, 167.8.

MS (EI): *m*/*z* (%) = 235 (100, [M]$^+$), 206 (27), 179 (21).

HRMS (EI): *m*/*z* calcd for $C_{14}H_9N_3O$ [M]$^+$: 235.0746; found: 235.0751.

7-Methoxy-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2h)

Yield: 127 mg (66%); yellow solid; mp 236–237 °C (Lit.[12] 239–240 °C).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.66 (s, 3 H), 6.48 (dd, *J* = 8.8, 2.7 Hz, 1 H), 6.59 (d, *J* = 2.7 Hz, 1 H), 6.85 (d, *J* = 8.8 Hz, 1 H), 6.86–6.89 (m, 1 H), 6.95 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.28–7.32 (m, 1 H), 7.64 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.77 (s, 1 H), 9.66 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 55.6, 105.6, 108.7, 119.5, 121.3, 122.6, 123.4, 123.4, 132.5, 133.4, 141.8, 150.6, 156.9, 168.1.

MS (EI): *m*/*z* (%) = 240 (100, [M]$^+$), 210 (23), 197 (39), 169 (14).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{12}N_2O_2$ [M]$^+$: 240.0899; found: 240.0901.

5-Butyl-8-chloro-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2i)

Yield: 75 mg (31%); colorless powder; mp 161–164 °C.

IR (KBr): 3185, 3057, 2956, 2868, 1666, 1584, 1496, 1379 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 0.84 (t, *J* = 7.3 Hz, 3 H), 1.34 (sext, *J* = 7.3 Hz, 2 H), 1.45–1.50 (m, 2 H), 3.63–3.78 (m, 2 H), 7.10–7.18 (m, 3 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 7.51 (ddd, *J* = 8.0, 7.2, 1.7 Hz, 1 H), 7.62 (dd, *J* = 7.8, 1.7 Hz, 1 H), 10.30 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.0, 19.8, 29.4, 48.5, 119.5, 121.1, 122.4, 123.6, 124.5, 127.9, 128.4, 131.2, 133.2, 135.4, 142.6, 152.1, 168.7.

MS (EI): *m*/*z* (%) = 302 (20), 300 (40, [M]$^+$), 259 (44), 257 (100), 221 (24).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}{}^{35}ClN_2O$ [M]$^+$: 300.1029; found: 300.1029.

11-Oxo-10,11-dihydro-5*H*-dibenzo[*b*,*e*][1,4]diazepine-2-carbonitrile (2j)

Yield: 71 mg (38%); yellow solid; mp >300 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.91–7.01 (m, 4 H), 7.07 (d, *J* = 8.3 Hz, 1 H), 7.69 (dd, *J* = 8.6, 2.0 Hz, 1 H), 8.03 (d, *J* = 2.0 Hz, 1 H), 8.65 (s, 1 H), 10.01 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 102.2, 119.2, 120.2, 120.6, 121.8, 121.9, 124.3, 125.2, 129.3, 136.4, 137.2, 137.8, 153.7, 166.3.

MS (EI): *m*/*z* (%) = 235 (100, [M]$^+$), 206 (33), 179 (22).

HRMS (EI): *m*/*z* calcd for $C_{14}H_9N_3O$ [M]$^+$: 235.0746; found: 235.0755.

7-Phenyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2k)

Yield: 190 mg (83%); colorless solid; mp 204–206 °C.

IR (KBr): 3322, 3174, 3025, 1645, 1599, 1469, 1377 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.89 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1 H), 6.99 (dd, *J* = 8.1, 1.0 Hz, 1 H), 7.02 (d, *J* = 8.2 Hz, 1 H), 7.18 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.29–7.35 (m, 3 H), 7.40–7.45 (m, 2 H), 7.53–7.56 (m, 2 H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.91 (s, 1 H), 9.91 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 118.3, 119.5, 121.2, 121.6, 122.1, 123.1, 126.6, 127.7, 129.4, 129.6, 132.6, 133.7, 136.9, 139.8, 140.6, 150.5, 168.2.

MS (EI): *m*/*z* (%) = 286 (100, [M]$^+$), 257 (21).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{14}N_2O$ [M]$^+$: 286.1106; found: 286.1103.

7-Morpholin-4-yl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2l)

Yield: 180 mg (76%); yellow crystals; mp 263–265 °C.

IR (KBr): 3319, 3160, 2958, 2867, 2808, 1641, 1600, 1471, 1395, 1236, 1117 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.95–2.99 (m, 4 H), 3.68–3.72 (m, 4 H), 6.51 (dd, *J* = 8.6, 2.6 Hz, 1 H), 6.57 (d, *J* = 2.6 Hz, 1 H), 6.80 (d, *J* = 8.6 Hz, 1 H), 6.86 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1 H), 6.93 (dd, *J* = 8.1, 0.9 Hz, 1 H), 7.29 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1 H), 7.63 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.66 (s, 1 H), 9.61 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.3, 66.5, 106.8, 110.7, 119.4, 121.1, 122.3, 122.4, 123.4, 132.4, 133.3, 141.2, 148.9, 150.7, 168.1.

MS (EI): *m*/*z* (%) = 295 (100, [M]$^+$), 237 (37), 209 (37), 181 (11).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}N_3O_2$ [M]$^+$: 295.1321; found: 295.1332.

8-Methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (2m)

Yield: 125 mg (70%); yellow solid; mp 200–204 °C (Lit.[12] 194–195 °C).

IR (KBr): 3380, 3174, 3028, 1656, 1602, 1518, 1466, 1390 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.17 (s, 3 H), 6.73–6.78 (m, 2 H), 6.84–6.89 (m, 2 H), 6.96 (dd, *J* = 8.1, 1.0 Hz, 1 H), 7.31 (ddd, *J* = 8.1, 7.3, 1.8 Hz, 1 H), 7.66 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.72 (s, 1 H), 9.76 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.1, 118.9, 119.6, 120.5, 121.5, 122.7, 124.9, 129.6, 131.9, 132.0, 133.1, 137.4, 150.7, 168.0.

MS (EI): *m*/*z* (%) = 224 (100, [M]$^+$), 209 (27), 195 (29), 181 (14).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{12}N_2O$ [M]$^+$: 224.0950; found: 224.0957.

9-Chloro-6,11-dihydro-5*H*-pyrido[2,3-*b*][1,5]benzodiazepin-5-one (2n)

Yield: 155 mg (79%); yellow powder; mp >300 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.95–7.00 (m, 3 H), 7.21 (d, *J* = 2.0 Hz, 1 H), 8.08 (dd, *J* = 7.8, 2.0 Hz, 1 H), 8.27 (dd, *J* = 4.6, 1.7 Hz, 1 H), 8.83 (s, 1 H), 10.05 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 116.0, 117.5, 120.1, 123.0, 123.3, 128.2, 128.7, 137.7, 142.2, 152.6, 158.7, 166.5.

MS (EI): *m*/*z* (%) = 247 (46), 245 (100, [M]$^+$), 217 (36), 210 (41), 182 (27).

HRMS (EI): *m*/*z* calcd for $C_{12}H_8{}^{35}ClN_3O$ [M]$^+$: 245.0356; found: 245.0358.

5,11-Dihydro-6*H*-dipyrido[2,3-*e*:3′,2′-*b*][1,4]diazepin-6-one (2o)

Yield: 59 mg (35%); yellow solid; mp 216 °C (dec. before melting).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.23 (s, 2 H), 6.86 (dd, *J* = 7.3, 1.2 Hz, 1 H), 7.00 (t, *J* = 7.3 Hz, 1 H), 7.49 (dd, *J* = 7.9, 4.4 Hz, 1 H), 8.18 (dd, *J* = 7.3, 1.2 Hz, 1 H), 8.66 (dd, *J* = 7.9, 2.1 Hz, 1 H), 9.05 (dd, *J* = 4.4, 2.1 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 109.0, 110.7, 113.6, 115.5, 120.8, 137.0, 141.9, 143.0, 156.2, 157.6, 159.9.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_9N_4O$ [M + H]$^+$: 213.0776; found: 213.0768.

6,11-Dihydro-5*H*-pyrido[2,3-*b*][1,5]benzodiazepin-5-one (2p)

Yield: 46 mg (27%); yellow solid; mp 293–295 °C (Lit.[26] 283–287 °C).

IR (KBr): 3235, 3195, 2958, 2925, 2855, 1649, 1518, 1442, 1296, 1138, 1090 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.91–6.99 (m, 4 H), 7.13 (d, *J* = 7.1 Hz, 1 H), 8.06 (dd, *J* = 7.7, 1.8 Hz, 1 H), 8.25 (dd, *J* = 4.6, 1.9 Hz, 1 H), 8.66 (s, 1 H), 9.96 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 116.1, 117.1, 120.9, 121.8, 123.8, 125.1, 129.2, 136.5, 142.1, 152.5, 159.6, 167.0.

MS (EI): *m*/*z* (%) = 211 (100, [M]$^+$), 183 (22).

HRMS (EI): *m*/*z* calcd for $C_{12}H_9N_3O$ [M]$^+$: 211.0746; found: 211.0745.

2-Methyl-7-(trifluoromethyl)-10*H*-thieno[2,3-*b*][1,5]benzodiazepin-4(5*H*)-one (2q)

Yield: 107 mg (45%); brown solid; mp 178–179 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.50 (d, *J* = 1.1 Hz, 3 H), 6.84–6.86 (m, 1 H), 7.09 (d, *J* = 3.6 Hz, 1 H), 7.24 (d, *J* = 8.3 Hz, 1 H), 7.32 (d, *J* = 1.7 Hz, 1 H), 7.41 (dd, *J* = 8.3, 1.7 Hz, 1 H), 11.60 (br s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 15.6, 106.2 (q, J_{FC} = 4 Hz), 109.2, 119.0 (q, J_{FC} = 4 Hz), 125.0 (q, J_{FC} = 122 Hz), 123.1 (q, J_{FC} = 32 Hz), 124.3, 124.4, 129.1, 131.6, 133.8, 138.4, 153.5.

MS (EI): *m*/*z* (%) = 298 (100, [M]$^+$), 237 (20), 97 (29).

HRMS (EI): *m*/*z* calcd for $C_{13}H_9F_3N_2OS$ [M]$^+$: 298.0388; found: 298.0389.

2-Methyl-10*H*-thieno[2,3-*b*][1,5]benzodiazepin-4(5*H*)-one (2r)

Yield: 72 mg (39%); brown solid; mp 161–163 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.53 (d, *J* = 1.3 Hz, 3 H), 6.74–6.77 (dq, *J* = 3.7, 1.3 Hz, 1 H), 6.99 (d, *J* = 3.7 Hz, 1 H), 7.05–7.15 (m, 4 H), 10.18 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 109.2, 110.0, 121.7, 122.6, 123.8, 124.5, 127.8, 131.2, 131.7, 138.9, 154.9.

MS (EI): *m*/*z* (%) = 230 (100, [M]$^+$), 201 (19), 169 (22).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{10}N_2OS$ [M]$^+$: 230.0514; found: 230.0517.

Dibenzo[*b*,*f*][1,4]thiazepin-11(10*H*)-one (2s)

Yield: 93 mg (51%); colorless solid; mp 257–258 °C (Lit.[27] 263–265 °C).

IR (KBr): 3171, 3040, 2955, 1647, 1581, 1477, 1376 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 7.12 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.21 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.32–7.36 (m, 1 H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.54 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.66 (dd, *J* = 7.5, 1.5 Hz, 1 H), 10.68 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 123.6, 125.9, 129.4, 129.4, 130.3, 131.7, 131.8, 132.5, 133.0, 136.7, 138.3, 140.4, 168.8.

MS (EI): *m*/*z* (%) = 227 (100, $[M]^+$), 195 (40), 167 (27).

HRMS (EI): *m*/*z* calcd for $C_{13}H_9NOS$ $[M]^+$: 227.0405; found: 227.0403.

Reaction of 2-Nitrosodiarylamine 7 with Excess Diphosphine 8

[2-(Diphenylphosphino)ethyl](diphenyl)phosphine (**8**) (1494 mg, 3.75 mmol) was suspended in MeCN (19 mL), and *N*-(3,5-dichloro-2-nitrosophenyl)-*N*-(2,6-dimethylphenyl)amine (**7**) (221 mg, 0.75 mmol) was added in a few portions. The mixture was stirred for 3 d at room temperature then the solvent was removed in vacuo. The residue was separated by column chromatography (silica gel, hexane/DCM, 1:1, then hexane/EtOAc, 2:1) to obtain **9** (262 mg, 50% yield) and **10** (122 mg, 34% yield).

***N*-(3,5-Dichloro-2-{[[2-(diphenylphosphoryl)ethyl](diphenyl)phosphoranylidene]amino}phenyl)-*N*-(2,6-dimethylphenyl)amine (9)**

Yield: 262 mg (50%); pale beige solid; mp 95–98 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, 6 H), 2.41–2.49 (m, 2 H), 2.75–2.84 (m, 2 H), 5.86 (t, *J* = 2.0 Hz, 1 H), 6.25 (s, 1 H), 6.64 (dd, *J* = 2.6, 0.5 Hz, 1 H), 7.03–7.07 (m, 3 H), 7.37–7.44 (m, 7 H), 7.46–7.51 (m, 4 H), 7.55–7.60 (m, 4 H), 7.74–7.78 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.2, 21.7 (dd, J_{PC} = 20.8, 3.3 Hz), 22.2 (dd, J_{PC} = 16.2, 3.5 Hz), 108.1, 117.3 (d, J_{PC} = 2.0 Hz), 124.1 (d, J_{PC} = 2.9 Hz), 125.7, 126.8 (d, J_{PC} = 7.5 Hz), 128.5, 128.8 (dd, J_{PC} = 12.0, 4.5 Hz), 130.6 (d, J_{PC} = 9.3 Hz), 131.1 (d, J_{PC} = 9.3 Hz), 131.4 (d, J_{PC} = 8.7 Hz), 131.9 (dd, J_{PC} = 21.9, 2.9 Hz), 132.2 (d, J_{PC} = 5.2 Hz), 132.5 (d, J_{PC} = 1.6 Hz), 135.3, 138.3, 143.6 (d, J_{PC} = 10.4 Hz).

MS (EI): *m*/*z* (%) = 694 (41), 692 (57, $[M]^+$), 493 (67), 491 (97), 207 (100).

HRMS (EI): *m*/*z* calcd for $C_{40}H_{36}{}^{35}Cl_2N_2OP_2$ $[M]^+$: 692.1680; found: 692.1671.

Compound 10

Yield: 122 mg (34%); colorless solid; mp 250–253 °C (dec.).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.99 (s, 12 H), 2.76–2.78 (m, 4 H), 5.81–5.83 (m, 2 H), 6.28 (s, 2 H), 6.53 (d, *J* = 2.5 Hz, 2 H), 7.03–7.08 (m, 6 H), 7.35–7.40 (m, 8 H), 7.44–7.49 (m, 4 H), 7.63–7.68 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): sample not pure enough.

MS (EI): *m*/*z* (%) = 956 (6), 954 (4, $[M]^+$), 493 (67), 491 (100).

HRMS (ESI): *m*/*z* calcd for $C_{54}H_{49}{}^{35}Cl_4N_4P_2$ $[M + H]^+$: 955.2187; found: 955.2177.

3-Chloro-*N*-(2,4-dichlorophenyl)benzamide (11)

Yield: 59 mg (25%); colorless solid; mp 140–142 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.32 (dd, *J* = 6.6, 2.4 Hz, 1 H), 7.44 (d, *J* = 2.4 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 1 H), 7.55–7.58 (m, 1 H), 7.76 (d, *J* = 7.8 Hz, 1 H), 7.88–7.90 (m, 1 H), 8.30 (br s, 1 H), 8.49 (d, *J* = 9.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 122.3, 123.6, 124.9, 127.6, 128.1, 128.8, 129.6, 130.3, 132.4, 133.1, 135.3, 136.0, 163.8.

MS (EI): *m*/*z* (%) = 301 (15), 299 (15, $[M]^+$), 266 (14), 264 (22), 141 (50), 139 (100), 111 (58).

HRMS (EI): *m*/*z* calcd for $C_{13}H_8{}^{35}Cl_3NO$ $[M]^+$: 298.9671; found: 298.9677.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707347.

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