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Facile One-Pot Synthesis of Novel Tricyclic Dibenzoheterocycles via the Dianion Protocol of Ditopic Ligands

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Abstract: In our ongoing studies on the synthesis of new heterocyclic ring systems via a dianion intermediate, we herein describe the preparation of novel dibenzoazadioxoninone, dibenzoazadioxoninethione, dibenzoazadioxocine, dibenzoazadioxacycloundecine, dibenzoazadioxacyclododecine, dibenzoaza-2-oxodioxaphosphonine, and dibenzoaza-2-oxo-1,3-thioxaphosphonine in good yields.

Keywords: Dianion, dielectrophiles, ditopic Schiff base ligand, nucleophilic substitution, tricyclic dibenzoheterocycles

INTRODUCTION

Medium-size polyheterocyclic rings containing nitrogen, phosphorus, oxygen, and sulfur are rare in the literature. Benzodiazepines have been synthesized under solvent-free conditions.[1] Dibenzoxazocine and dibenzothiazocine[2] have been synthesized. Monocyclic medium-ring nitrogen heterocycles are an extremely important class of compounds, which occur in a range of natural and synthetic products.[3] Medium-sized rings are generally the most difficult to prepare using conventional cyclization methods.[4] To the best of our knowledge, there are no reports of the

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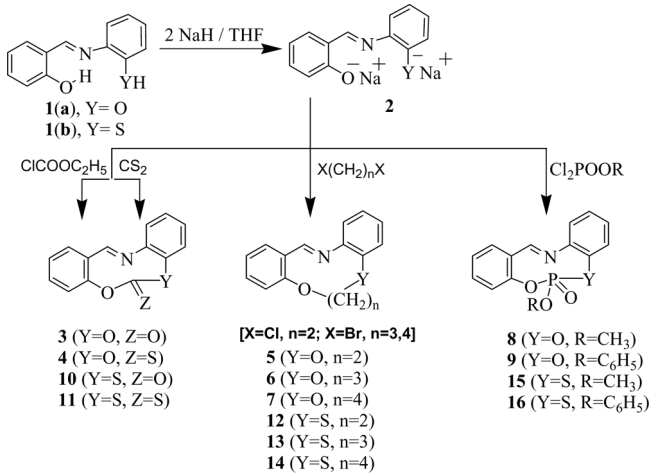

Scheme 1. Synthesis of tricyclic dibenzoheterocycles.

synthesis of heterocycles (Scheme 1). With this background, the goal of the present article is to provide cyclization reactions of dianions. For this purpose, we have focused our efforts on selected examples of cyclization reactions that follow 1:1 stoichiometry of dianion and electrophile.

RESULTS AND DISCUSSION

It is known that the Schiff bases prepared from salicylaldehyde and aromatic amines possess the E-configuration as a result of H-bonding between the hydroxyl and the nitrogen of the imine group.[5] Our synthesis involves the initial formation of dianion **2** from sequential deprotonations of the acidic protons of salicylidene-*o*-aminophenol **1a** and salicylidene-*o*-aminothiophenol **1b** by sodium hydride. The remote 1,8-dianion thus generated attacks to a variety of dielectrophilic reagents, leading to the formation of tricyclic compounds **3–16** (Scheme 1).

The spectral analysis showed infrared (IR) bands for C=N, C=O, and C=S groups in their respective regions, which are listed in the experimental part. The stretching frequency for P=O in compounds **8**, **9** and **15**, **16** appears at 1274 and 1272 cm^{-1}, respectively.

The NMR (^{1}H, ^{13}C, and ^{31}P) spectra of the compounds **3–16** were consistent with the suggested structures. The two phenyl rings display signals in the NMR spectra in the expected region. Ethylene protons attached to oxygen resonate as triplet ($J = 8.2$ Hz) centered on 3.87 ppm integrating for four protons. As anticipated, the ^{13}C NMR spectra

support the structures by having the signals for the carbon atoms present in the appropriate regions. Comparison of the ^{13}C NMR spectra for the parent benzaldehyde and those of the Schiff base **1** allows rather simple assignment of the observable signals of the carbon atoms to corresponding groups. Thus, the carbon signals in the region of sp^2-hybridized atoms evidently correspond to the imino group (CH=N). In all cases, the mass spectra showed peaks for the molecular ion corresponding to their molecular weight.

EXPERIMENTAL

Ethyl chloroformate, carbon disulfide, 1,2-dichloroethane, 1,3-dibromopropane, 1,4-dibromobutane, methyldichlorophosphate, and phenyldichlorophosphate were used as obtained from commercial sources. Salicylidene-*o*-aminophenol and salicylidene-*o*-aminothiophenol were prepared by the literature method. All reactions were carried out under a dry, oxygen-free nitrogen or argon atmosphere. All solvents (analytical reagent or extra pure grade) used for spectroscopic and other physical studies were further purified by literature methods. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Thin-layer chromatography (TLC) was used to monitor the progress of the reactions. Infrared (IR) spectra were recorded as KBr discs on a Fourier transform (FT)–IR Perkin-Elmer model RX-I spectrophotometer. Melting points were determined using a calibrated thermometer on a Remi melting-point apparatus and are uncorrected. Elemental analyses were performed by Central Drug Research Institute, Lucknow. NMR (^1H, ^{13}C, and ^{31}P) spectra were recorded on a Jeol AL 300 instrument. The chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and referenced to residual protons of dimethyl sulfoxide (DMSO-d_6) (δ 2.49). Mass spectra (MS) were recorded at 70 eV ionizing voltage on a Jeol-D300 MS instrument.

Typical Procedure for the Synthesis of Diatopic Ligands

Salicylaldehyde (6.10 g, 50 mmol) was added to a methanolic solution of *o*-aminophenol (5.45 g, 50 mmol). The reaction mixture was shaken on a shaker for half an hour. The resulting orange-colored precipitate was filtered and washed with methanol. The Schiff base was recrystallized from a mixture of chloroform and petroleum ether. The yield of pure salicylidene-*o*-aminophenol (**1a**) was 8.52 g (80%), mp 136 °C (mp 137 °C). Similarly, salicylidene-*o*-aminothiophenol (**1b**) was synthesized from

salicylaldehyde (6.10 g, 50 mmol) and *o*-aminothiophenol (6.25 g, 50 mmol) in 76% yield, mp 154 °C (mp 155 °C). The ^{1}H NMR and ^{13}C NMR data are consistent with the literature[6] values.

11,13-Dioxa-5-aza-dibenzo[*a,e*]cyclononen-12-one (3)

A solution of salicylidene-*o*-aminophenol (426 mg, 2 mmol) in dry THF (25 mL) was added to a suspension of sodium hydride (96 mg, 4 mmol) in dry THF (10 mL). After completion of the addition, the solution was stirred at reflux for 5 h. The mixture was allowed to attain room temperature. Ethylchloroformate (217 mg, 2 mmol) was added dropwise to the reaction vessel, and the contents were further stirred at reflux for 30 minutes. TLC confirmed the completion of the reaction. The reaction mixture was concentrated using a rotary evaporator, and the residue was purified by column chromatography on silica gel (ethylacetate/hexane, 1:8) to afford 325 mg (60%); mp 118–119 °C; IR (KBr, cm^{-1}) 1752, 1645, 1533, 1482, 1390, 1247, 1086; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.32 (s, 1H, CH=N), 8.12–7.26 (m, 8H, H-Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.85, 164.97, 158.93, 147.84, 143.42, 133.66, 132.58, 127.63, 127.56, 118.62, 118.44, 116.60, 115.27; MS (EI, 70 eV): m/z 239 (M^+, 24). Anal. calcd. for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86. Found: C, 70.64; H, 4.22; N, 5.71.

11,13-Dioxa-5-aza-dibenzo[*a,e*]cyclononen-12-thione (4)

The same procedure as for **3** with 426 mg (2 mmol) of salicylidene-*o*-aminophenol, 96 mg (4 mmol) of sodium hydride, and 152 mg (2 mmol) of carbon disulphide yielded **4** (352 mg, 69%); mp 93–95 °C; IR (KBr, cm^{-1}) 1654, 1490, 1395, 1262, 1235, 914; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.26 (s, 1H, CH=N), 8.06–7.18 (m, 8H, H-Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 180.36, 164.53, 158.48, 148.52, 146.51, 133.62, 132.41, 127.65, 127.68, 118.61, 118.43, 116.95, 115.68; MS (EI, 70 eV): m/z 255 (M^+, 21). Anal. calcd. for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 66.26; H, 3.89; N, 5.69.

6,7-Dihydro-5,8-dioxa-13-aza-dibenzo[*a,f*]cyclodecene (5)

The same procedure as for **3** with 426 mg (2 mmol) of salicylidene-*o*-aminophenol, 96 mg (4 mmol) of sodium hydride, and 198 mg (2 mmol) of 1,2-dichloroethane afforded **5** (330 mg, 69%); mp 178–180 °C; IR (KBr, cm^{-1}) 1634, 1630, 1522, 1493, 1460, 1431, 1391, 1321, 1249,

1238, 1172, 1148, 1093; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.34 (s, 1H, CH=N), 7.96–7.12 (m, 8H, H-Ar), 3.87 (t, $J = 8.2$ Hz, 4H, OCH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.43, 159.16, 148.58, 146.23, 133.51, 132.46, 127.54, 123.87, 119.04, 117.47, 114.87, 111.71, 110.41, 58.84, 58.62; MS (EI, 70 eV): m/z 239 (M^+, 18). Anal. calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.71; H, 5.85; N, 6.00.

7,8-Dihydro-6*H*-5,9-dioxa-14-aza-dibenzo[*a,e*]cycloundecene (6)

The same procedure as for **3** with salicylidene-*o*-aminophenol (426 mg, 2 mmol), NaH (96 mg, 4 mmol), and 1,3-dibromopropane (404 mg, 2 mmol) afforded **6** (360 mg, 71%); mp 195–197 °C; IR (KBr, cm^{-1}) 1647, 1627, 1593, 1483, 1449, 1326, 1241, 1211, 1173, 1098; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.36 (s, 1H, CH=N), 7.88–6.85 (m, 8H, H-Ar), 3.89 (t, 4H, $J = 8.2$ Hz, OCH_2), 1.35 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.86, 158.75, 148.67, 144.10, 132.96, 132.45, 127.52, 123.73, 119.31, 117.42, 114.78, 110.86, 109.82, 59.74, 59.62, 20.68; MS (EI, 70 eV): m/z 253 (M^+, 24). Anal. calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.16; H, 6.31; N, 5.67.

6,7,8,9-Tetrahydro-5,10-dioxa-15-aza-dibenzo[*a,e*]cyclododecene (7)

The same procedure as for **3** with salicylidene-*o*-aminophenol (426 mg, 2 mmol), NaH (96 mg, 4 mmol), and 1,4-dibromobutane (432 mg, 2 mmol) yielded **7** (360 mg, 67%); mp 180–182 °C; IR (KBr, cm^{-1}) 1632, 1462, 1377, 1247, 1169, 1079, 1054; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.33 (s, 1H, CH=N), 7.96–6.80 (m, 8H, H-Ar), 3.85 (t, $J = 8.2$ Hz, 4H, OCH_2), 1.36–1.30 (m, 4H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.81, 160.27, 148.61, 145.20, 133.25, 132.98, 127.61, 124.29, 118.86, 118.25, 115.95, 111.23, 108.94, 59.84, 59.57, 20.98, 20.65; MS (EI, 70 eV): m/z 267 (M^+, 19). Anal. calcd. for $C_{17}H_{17}NO_2$: C, 76.39; H, 6.41; N, 5.24. Found: C, 76.67; H, 6.18; N, 5.44.

12-Methoxy-11,13-dioxa-5-aza-12-phospha-dibenzo [*a,e*]cyclononen-12-oxide (8)

Methyldichlorophosphate (298 mg, 2 mmol) was added to a solution of dianion **2** prepared as before from salicylidene-*o*-aminophenol (426 mg, 2 mmol) and NaH (96 mg, 4 mmol) in dry THF, and the reaction mixture was refluxed for 1 h. The salt was filtered off, and the solvent was removed using a rotary evaporator. The crude mixture was purified by

column chromatography using ethylacetate/hexane (1:4) to afford **8** (400 mg, 70%); mp 221–223 °C; IR (KBr, cm^{-1}) 1644, 1578, 1521, 1435, 1301, 1274, 1205, 1071, 1048; ^1H NMR (300 MHz, DMSO-d_6): δ 8.36 (s, 1H, CH=N), 8.07–6.85 (m, 8H, H-Ar), 3.20 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.54, 160.22, 149.21, 147.20, 132.16, 131.95, 128.06, 127.91, 126.29, 125.17, 119.66, 119.53, 117.45, 56.34; ^{31}P NMR (121 MHz, DMSO-d_6): δ −11.91; MS (EI, 70 eV): m/z 289 (M^+, 15). Anal. calcd. for $C_{14}H_{12}NO_4P$: C, 58.14; H, 4.18; N, 4.84. Found: C, 58.54; H, 4.58; N, 5.01.

12-Phenoxy-11,13-dioxa-5-aza-12-phospha-dibenzo [*a,e*]cyclononen-12-oxide (9)

Same procedure as for **7** with salicylidene-*o*-aminophenol (426 mg, 2 mmol), NaH (96 mg, 4 mmol), and phenyldichlorophosphate (422 mg, 2 mmol) yielded **9** (456 mg, 65%); mp 242 °C (d), IR (KBr, cm^{-1}) 1642, 1609, 1498, 1472, 1362, 1274, 1230, 1164, 1021; ^1H NMR (300 MHz, DMSO-d_6): δ 8.13 (s, 1H, CH=N), 7.86–6.92 (m, 13H, H-Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.74, 160.42, 148.21, 146.26, 133.63, 132.58, 131.55, 131.10, 127.64, 127.22, 119.26, 119.05, 118.16, 117.61, 117.45, 117.32; ^{31}P NMR (121 MHz, DMSO-d_6): δ −18.91; MS (EI, 70 eV): m/z 351 (M^+, 17). Anal. calcd. for $C_{19}H_{14}NO_4P$: C, 64.96; H, 4.02; N, 3.99. Found: C, 65.44; H, 4.43; N, 4.09.

11-Oxa-13-thia-5-aza-dibenzo[*a,e*]cyclononen-12-one (10)

A solution of salicylidene-*o*-aminothiophenol (458 mg, 2 mmol) in dry THF (25 mL) was added to a suspension of sodium hydride (96 mg, 4 mmol) in dry THF (10 mL). After completion of the addition, the solution was stirred at reflux for 6 h. The mixture was allowed to attain room temperature. Ethylchloroformate (217 mg, 2 mmol) was added dropwise to the reaction vessel, and the contents were further stirred at reflux for 1 h. TLC confirmed the completion of the reaction. The reaction mixture was concentrated using a rotary evaporator, and the residue was chromatographed on silica gel using ethylacetate/hexane (1:10) to give **10** (332 mg, 65%); mp 125–127 °C; IR (KBr, cm^{-1}) 1747, 1625, 1503, 1452, 1380, 1263, 1115, 1046; ^1H NMR (300 MHz, DMSO-d_6): δ 8.22 (s, 1H, CH=N), 7.88–6.96 (m, 8H, H-Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.65, 164.87, 158.93, 147.73, 143.22, 133.66, 132.88, 130.57, 127.73, 127.61, 127.52, 119.19, 119.07, 116.95, 115.65; MS (EI, 70 eV): m/z 255 (M^+, 21). Anal. calcd. for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 66.30; H, 3.96; N, 5.65.

11-Oxa-13-thia-5-aza-dibenzo[*a,e*]cyclononen-12-thione (11)

A solution of salicylidene-*o*-aminothiophenol (458 mg, 2 mmol) in dry THF (25 mL) was added to a suspension of sodium hydride (96 mg, 4 mmol) in dry THF (10 mL). After completion of the addition, the solution was stirred at reflux for 6 h. The mixture was allowed to attain room temperature. Carbon disulphide (152 mg, 2 mmol) was added dropwise to the reaction vessel, and the contents were further stirred at reflux for 1 h. TLC confirmed the completion of the reaction. The reaction mixture was concentrated using a rotary evaporator, and the residue was chromatographed on silica gel using ethylacetate/hexane (1:10) to give **11** (370 mg, 68%); mp 102–104 °C; IR (KBr, cm^{-1}) 1631, 1529, 1463, 1377, 1276, 1223, 1139, 1116; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.29 (s, 1H, CH=N), 7.94–6.84 (m, 8H, H-Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.76, 164.73, 158.28, 147.62, 145.51, 133.76, 132.83, 130.99, 127.85, 127.48, 126.94, 118.85, 118.63, 116.25, 115.63; MS (EI, 70 eV): m/z 271 (M^+, 14). Anal. calcd. for $C_{14}H_9NOS_2$: C, 61.97; H, 3.34; N, 5.16. Found: C, 62.24; H, 3.76; N, 5.27.

6,7-Dihydro-5-oxa-8-thia-13-aza-dibenzo[*a,f*]cyclodecene (12)

The same procedure as for **10** with 458 mg (2 mmol) of salicylidene-*o*-aminothiophenol, 96 mg (4 mmol) of NaH, and 198 mg (2 mmol) of 1,2-dichloroethane yielded **12** (357 mg, 70%); mp 165–167 °C; IR (KBr, cm^{-1}) 1630, 1590, 1490, 1420, 1319, 1261; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.29 (s, 1H, CH=N), 8.06–6.64 (m, 8H, H-Ar), 3.86 (t, $J = 8.2$ Hz, 2H, OCH_2), 3.12 (t, $J = 7.8$ Hz, 2H, SCH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.57, 159.61, 148.58, 133.81, 132.86, 132.07, 127.84, 127.67, 126.87, 119.34, 117.47, 114.47, 111.21, 110.01, 56.84, 56.22; MS (EI, 70 eV): m/z 255 (M^+, 16). Anal. calcd. for $C_{15}H_{13}NOS$: C, 70.56; H, 5.13; N, 5.49. Found: C, 70.83; H, 4.85; N, 5.61.

7,8-Dihydro-6*H*-5-oxa-9-thia-14-aza-dibenzo[*a,e*]cycloundecene (13)

Same procedure as for **10** with salicylidene-*o*-aminothiophenol (456 mg, 2 mmol), NaH (96 mg, 4 mmol), and 1,3-dibromopropane (404 mg, 2 mmol) gave **13** (377 mg, 70%); mp 188–190 °C; IR (KBr, cm^{-1}) 1627, 1587, 1493, 1442, 1346, 1231, 1205, 1170, 1088; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.30 (s, 1H, CH=N), 7.97–6.72 (m, 8H, H-Ar), 3.92 (t, 2H, $J = 8.2$ Hz, OCH_2), 3.17 (t, $J = 7.8$ Hz, 2H, SCH_2), 1.42 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.16, 159.05, 148.97,

145.64, 133.96, 128.45, 128.22, 123.70, 119.61, 117.62, 116.78, 115.86, 58.72, 58.62, 20.28; MS (EI, 70 eV): m/z 269 (M^+, 27). Anal. calcd. for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20. Found: C, 71.71; H, 5.93; N, 5.45.

6,7,8,9-Tetrahydro-5-oxa-10-thia-15-aza-dibenzo [*a,e*]-cyclododecane (14)

A solution of salicylidene-*o*-aminothiophenol (458 mg, 2 mmol) in dry THF (25 mL) was added to a suspension of sodium hydride (96 mg, 4 mmol) in dry THF (10 mL). After completion of the addition, the solution was stirred at reflux for 6 h. The mixture was allowed to attain room temperature. 1,4-Dibromobutane (432 mg, 2 mmol) was added dropwise to the reaction vessel, and the contents were further stirred at reflux for 1 h. TLC confirmed the completion of the reaction. The reaction mixture was concentrated using a rotary evaporator, and the residue was chromatographed on silica gel using ethylacetate/hexane (1:10) to give **14** (380 mg, 67%); mp 176–178 °C; IR (KBr, cm^{-1}) 1632, 1492, 1420, 1396, 1262, 1249; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.27 (s, 1H, CH=N), 7.95–6.73 (m, 8H, H-Ar), 3.84 (t, $J = 8.2$ Hz, 2H, OCH_2), 3.15 (t, $J = 7.8$ Hz, 2H, SCH_2), 1.23 (m, 4H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.87, 160.21, 147.90, 133.75, 133.18, 132.88, 127.83, 126.92, 119.26, 118.95, 116.95, 111.53, 108.74, 57.84, 57.57, 20.88, 20.69; MS (EI, 70 eV): m/z 283 (M^+, 18). Anal. calcd. for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94. Found: C, 72.47; H, 6.38; N, 5.10.

12-Methoxy-11-oxa-13-thia-5-aza-12-phospha-dibenzo [*a,e*]-cyclononene-12-oxide (15)

Methyldichlorophosphate (298 mg, 2 mmol) was added to a solution of dianion **2** prepared as before from salicylidene-*o*-aminothiophenol (426 mg, 2 mmol) and NaH (96 mg, 4 mmol) in dry THF, and the reaction mixture was refluxed for 1.5 h. The salt was filtered off, and the solvent was removed using a rotary evaporator. The crude mixture was purified by column chromatography using ethylacetate/hexane (1:4) to afford **15** (434 mg, 71%); mp 253 °C (d); IR (KBr, cm^{-1}) 1624, 1573, 1481, 1445, 1381, 1272, 1232, 1208, 1071, 1032; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.27 (s, 1H, CH=N), 7.87–6.72 (m, 8H, H-Ar), 3.27 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.64, 160.28, 149.21, 147.18, 133.46, 133.25, 132.73, 127.86, 127.41, 126.36, 119.26, 118.33, 117.95, 117.43, 55.34; ^{31}P NMR (121 MHz, DMSO-d_6): δ −12.01; MS (EI, 70 eV): m/z 305 (M^+, 15). Anal. calcd. for $C_{14}H_{12}NO_3SP$: C, 55.08; H, 3.96; N, 4.59. Found: C, 55.42; H, 4.33; N, 4.71.

12-Phenoxy-11-oxa-13-thia-5-aza-12-phospha-dibenzo [*a,e*]cyclononen-12-oxide (16)

The same procedure as for **15** with salicylidene-*o*-aminothiophenol (426 mg, 2 mmol), NaH (96 mg, 4 mmol), and phenyldichlorophosphate (422 mg, 2 mmol) yielded **16** (514 mg, 70%); mp 228–230 °C; IR (KBr, cm^{-1}) 1638, 1587, 1488, 1372, 1315, 1272, 1220, 1134, 1031; ^1H NMR (300 MHz, DMSO-d_6): δ 8.18 (s, 1H, CH=N), 7.98–6.84 (m, 13H, H-Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.78, 160.54, 148.56, 133.43, 132.38, 131.62, 131.23, 127.86, 127.42, 119.74, 119.52, 119.21, 118.36, 117.41, 117.25, 117.02; ^{31}P NMR (121 MHz, DMSO-d_6): δ −18.51; MS (EI, 70 eV): m/z 367 (M^+, 17). Anal. calcd. for $C_{19}H_{14}NO_3SP$: C, 62.12; H, 3.84; N, 3.81. Found: C, 62.34; H, 4.23; N, 4.01.

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