4-Nitro-2-(*p*-toluenesulfonamido)-1-[2′-(*p*-toluenesulfonamido)ethoxy]benzene (4). Sulfonamide **3** (5.15 g, 14.7 mmol) was suspended in CH_2Cl_2 (250 mL) and pyridine (14 mL). *p*-Toluenesulfonyl chloride (4.19 g, 22.0 mmol) was added in one portion, and the mixture was stirred at rt for 2 h. The reaction mixture was washed with 5% HCl and then water. The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated in vacuo to give a yellow solid which was washed with cold CH_2Cl_2 to give **4** (5.14 g, 69%) as a white solid: mp 188.5–189.5 °C; IR (KBr) 3327, 3223 (NH), 1528 (NO_2), 1343, 1162 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 2.31 (s, 3 H), 2.36 (s, 3 H), 3.13 (q, J = 5.0 Hz, 2 H), 3.67 (t, J = 4.8 Hz, 2 H), 6.55 (d, J = 9.1 Hz, 1 H), 7.03 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.59 (d, J = 8.3 Hz, 2 H), 7.75 (d, J = 8.3 Hz, 2 H), 7.85–8.05 (m, 2 H), 8.41 (d, J = 2.7 Hz, 1 H), 9.50 (s, 1 H); ^{13}C NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 21.04, 41.39, 66.94, 109.99, 119.42, 121.40, 126.31, 126.66, 128.91, 129.26, 136.53, 137.81, 141.05, 142.80, 143.19, 154.38. Anal. Calcd for $C_{22}H_{23}N_3O_7S_2$: C, 52.27; H, 4.59. Found: C, 52.29; H, 4.52.

4,10-Bis(*p*-toluenesulfonamido)-5′-nitro-2,3-dibenzo-12-crown-4 (5). Disulfonamide **4** (3.15 g, 6.23 mmol) and the dimesylate of diethylene glycol (1.63 g, 6.23 mmol) were dissolved in DMF (30 mL), and the solution was added with a syringe pump to a stirred suspension of K_2CO_3 (4.31 g, 31.2 mmol) in DMF (20 mL) during a 7-h period. The reaction mixture was stirred for an additional 17 h at rt, and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2–Et_2O (30:1) as eluent to give **5** (2.40 g, 67%) as a tan solid: mp 92–93 °C; IR (KBr) 1518 (NO_2), 1343, 1162 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 2.43 (s, 3 H), 3.20–4.00 (m, 10 H), 4.25 (t, J = 4.2 Hz, 2 H), 6.71 (dd, J = 1.7, 7.9 Hz, 1 H), 6.80–7.00 (m, 2 H), 7.15–7.40 (m, 4 H), 7.61 (d, J = 8.2 Hz, 2 H), 7.69 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.47, 50.98, 52.50, 68.83, 70.14, 71.53, 112.63, 128.86, 125.96, 127.24, 127.71, 129.30, 129.61, 129.84, 134.77, 135.64, 140.63, 143.85, 144.00, 162.82. Anal. Calcd for $C_{26}H_{29}N_3O_8S_2$: C, 54.25; H, 5.08. Found: C, 54.20; H, 5.04.

4,10-Diaza-5′-nitro-2,3-dibenzo-12-crown-4 (1). Macrocycle **5** (2.87 g, 4.99 mmol) was dissolved in concentrated H_2SO_4 (10 mL) and heated at 100 °C for 12 h under N_2. The reaction mixture was cooled in an ice bath, and Et_2O (200 mL) was added dropwise; a light gray precipitate formed. The solid was filtered and dissolved in a minimum amount of water. Solid KOH was added to pH >10, and an orange precipitate formed which was filtered. The filtrate was extracted several times with CH_2Cl_2, and the orange solid and organic extracts were combined. The solution was dried (Na_2SO_4) and evaporated in vacuo. The residue was passed through a short bed of alumina with CH_2Cl_2–MeOH (49:1) as eluent to provide **1** (0.80 g, 60%) as a yellow solid: mp 138–139 °C; IR (KBr) 3346 (NH), 1518, 1338 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$)[8] δ 1.86 (br s, 1 H), 2.75 (t, J = 4.7 Hz, 2 H), 2.87 (t, J = 4.7 Hz, 2 H), 3.39 (t, J = 4.7 Hz, 2 H), 3.56 (t, J = 4.8 Hz, 2 H), 3.65 (t, J = 4.7 Hz, 2 H), 4.22 (t, J = 4.5 Hz, 2 H), 6.15 (br s, 1 H), 7.00 (d, J = 8.6 Hz, 1 H), 7.45–7.65 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 44.29, 47.24, 47.58, 67.89, 68.86, 71.49, 107.01, 113.03, 117.75, 141.84, 144.22, 151.54. Anal. Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.41. Found: C, 53.74; H, 6.33.

4-Nitro-2-(*p*-toluenesulfonamido)phenol (6). A stirred solution of 2-amino-4-nitrophenol (2.00 g, 13.0 mmol) and pyridine (1.13 g, 143 mmol) in CH_2Cl_2 (20 mL) was cooled to −3 °C in an ice–salt bath, and *p*-toluenesulfonyl chloride (2.47 g, 12.98 mmol) was added in one portion. The reaction mixture was allowed to warm to rt during a 5-h period. The mixture was washed with 6 N HCl which produced a precipitate. The solid was filtered and washed with water and then CH_2Cl_2 to give **6** (3.09 g, 77%) as a light brown solid: mp 206.5–208 °C; IR (KBr) 3395 (OH), 1529 (NO_2) 1345, 1159 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 2.36 (s, 3 H), 6.86 (d, J = 9.0 Hz, 1 H), 7.23 (d, J = 5.9 Hz, 2 H), 7.71 (d, J = 6.5 Hz, 2 H), 7.78–7.84 (dd, J = 2.9, 8.7 Hz, 2 H), 8.28 (d, J = 2.8 Hz, 1 H), 10.66 (br s, 1 H); ^{13}C NMR (CD_3Cl_3 + $CD_3S(O)CD_3$) δ 21.21, 114.74, 116.15, 121.08, 124.96, 126.92, 129.40, 135.66, 140.07, 143.85, 153.59. Anal. Calcd for $C_{13}H_{12}N_2O_5S$: C, 50.65; H, 3.92. Found: C, 50.34; H, 3.89.

***N*-Methyl-4-nitro-2-(*p*-toluenesulfonamido)anisole (7).** A mixture of tosylamide **6** (3.18 g, 10.0 mmol) K_2CO_3 (5.68 g, 22.0 mmol), and iodomethane (5.68 g, 40.0 mmol) in DMF (30 mL) was vigorously stirred and heated at 80 °C for 16 h. The mixture was evaporated in vacuo, and 100 mL of CH_2Cl_2 and 100 mL of water were added to the residue. The organic layer was separated, washed with water (2 × 50 mL), and dried ($CaCl_2$). Evaporation of the solvent in vacuo gave **7** (3.15 g, 91%): mp 119–121 °C; IR (KBr) 1589 (NO_2), 1344, 1157 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 3.19 (s, 3 H), 3.60 (s, 3 H), 6.92 (d, J = 9.0 Hz, 1 H), 7.30 (d, J = 8.5 Hz, 2 H), 7.57 (d, J = 8.3 Hz, 2 H), 8.13–8.20 (m, 2 H). Anal. Calcd for $C_{15}H_{16}N_2O_5S$: C, 53.56; H, 4.80. Found: C, 53.35; H, 4.75.

***N*-Methyl-2-methoxy-5-nitroaniline (2).** A solution of **7** (0.80 g, 2.3 mmol) in 15 mL of concentrated H_2SO_4 was heated at 100 °C for 16 h under N_2. The mixture was cooled to 0 °C in an ice bath, and 30 mL of 30% aqueous NaOH was added. The mixture was filtered and washed with 5 mL of water. The combined filtrate and washing were extracted with CH_2Cl_2 (3 × 40 mL). The organic layer was dried (K_2CO_3) and evaporated in vacuo to give **2** (0.38 g, 91%) as an orange solid: mp 85–87 °C (lit.[7] mp 87 °C); IR (KBr) 3448 (NH); 1529, 1336 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$)[8] δ 2.85 (d, J = 5.2 Hz, 3 H), 3.87 (s, 3 H), 4.40 (br s, 1 H), 6.67 (d, J = 8.8 Hz, 1 H), 7.28 (s, 1 H), 7.55 (dd, J = 2.7, 8.7 Hz, 2 H).

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Supplementary Material Available: A description of the crystal determination for **1** and tables (1S–3S) which contain a summary of crystal and experimental data, structure solution details, atom postional and thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

On the Mechanism of the Reaction between Ketones and Trifluoromethanesulfonic Anhydride. An Improved and Convenient Method for the Preparation of Pyrimidines and Condensed Pyrimidines

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Introduction

Carbonyl compounds react with trifluoromethanesulfonic (triflic) anhydride to give products of different structure and stereochemistry. Ketones afford vinyl trifluoromethanesulfonates (triflates), while *gem*-ditriflates have been isolated from aldehydes and nonenolizable ketones.[1] Triflates have been found to be valuable starting

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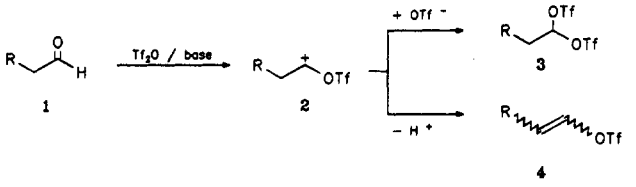
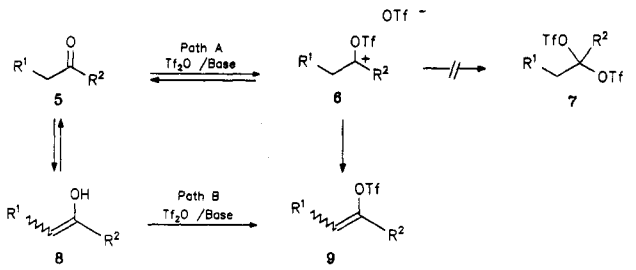
Scheme I



Scheme II



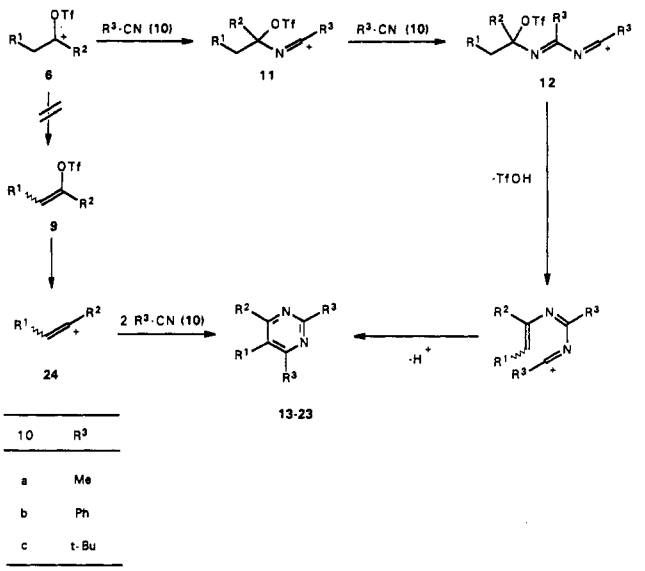
materials for carbon–carbon bond formation,[2] and applications of vinyl triflates in organic synthesis are rapidly increasing.[3] However, only limited attention has been focused on the mechanism of the formation of triflates from carbonyl compounds and triflic anhydride. We and others have shown earlier[4,5] that the reaction of aliphatic aldehydes **1** with triflic anhydride in the presence of a base involves an electrophilic attack at the carbonyl group with formation of (trifluoromethanesulfonyl)carbenium ion **2** as the intermediate. When the reaction is carried out at 0–25 °C in dichloromethane, these intermediate cations **2** are trapped by the triflate anion to give geminal ditriflates **3**. However, when the reaction is carried out in refluxing 1,2-dichloroethane elimination of a proton from the carbenium ion intermediate **2** takes place to afford the corresponding vinyl triflate **4** (Scheme I). *gem*-Ditriflates were also obtained from strained bicyclic ketones, e.g., camphor, which are not capable of accommodating double bonds at the bridgehead.[6]

The reaction of ketones with triflic anhydride in the presence of a base affords vinyl triflates in good yields. The formation of *gem*-triflates in these cases was not observed or detected.[5,7] Accordingly, it was concluded[1,5] that the formation of vinyl triflates proceeds mainly by the reaction of an enol tautomer **8** with triflic anhydride (Scheme II, path B).

Results and Discussion

In order to clarify this latter mechanistic aspect, we have now carried out the reaction of ketones **5** with triflic anhydride under mild conditions (room temperature in dichloromethane)[1,9] in the presence of a nucleophile such as a nitrile **10** (Scheme III). Nitriles have shown their efficiency in trapping the reactive intermediate vinyl cations[8] by nucleophilic attack to give pyrimidines.

Scheme III



The formation of pyrimidines in good yields (Table I) proves unambiguously that the reaction between ketones **5** and triflic anhydride proceeds via the (triflyloxy)carbenium ion **6** (Scheme II, path A). (Triflyloxy)carbenium ions **6** are stable enough to be generated in nonpolar solvents. Thus, the reaction of *tert*-butyl methyl ketone and *tert*-butyronitrile with triflic anhydride in *n*-pentane as well as in carbon tetrachloride, carried out under the same conditions as that for dichloromethane (see Experimental Section) gave the pyrimidine **18** in good yield (85% and 86%, respectively).[10] This result is comparable with that obtained for the same reaction in dichloromethane as the solvent (see Table I). As expected, the secondary cations **6** (R^2 = H) formed from aldehydes are less stable and can be easily formed[3b] in polar solvents (such as dichloromethane). The intermediate formation of cations **6** supports the satisfactory explanation of the experimentally proved solvent dependability of the reaction between aldehydes and ketones with triflic anhydride.[3b,10]

In the presence of nitriles **10**, the cation **6** is trapped by the nucleophile, whereby a resonance-stabilized nitrilium species **11** is formed. A second molecule of nitrile **10** reacts with the intermediate **11** to give products **13–23**, after elimination of triflic acid, cyclization, and loss of a proton (Scheme III).

Although the reaction of aliphatic and alicyclic ketones with triflic anhydride proceeds, analogous to the reaction of aliphatic aldehydes and strained bicyclic ketones, by the same route, *gem*-bistriflates **3** are not obtained. The reason for this fact seems to be the steric hindrance that may preclude the reaction of **2** with the triflate anion. Thus, in these cases the elimination of a proton to give the vinyl triflates **9**, as well as trapping by the nitrile **10** to yield the corresponding pyrimidines are preferred. The formation of pyrimidines is accompanied by a minimum amount of vinyl triflates **9**. This result demonstrates that the trapping of the cationic species **6** by means of the nitrile **10** occurs faster than the loss of a proton. This observation does not support the intermediacy of vinyl cations **24** in the formation of pyrimidines **13–23** from ketones **5** and proves that this reaction occurs through a (triflyloxy)carbenium ion **6** as intermediate. In the case of cyclo-

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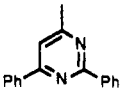
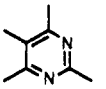
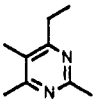
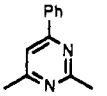
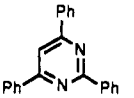
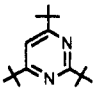
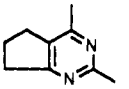
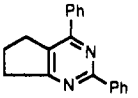
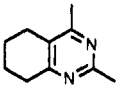
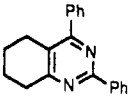
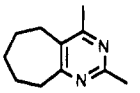
(10) We thank the reviewer, who suggested to carry out the reaction.

Table I. Pyrimidines and Condensed Pyrimidines Obtained from Ketones, Nitriles, and Triflic Anhydride

entry	ketone (5)	nitrile (10)	reaction time (h)	product	yield (%)
1	acetone	benzonitrile	18	 **13**	17
2	methyl ethyl ketone	acetonitrile	24	 **14**	70
3	diethyl ketone	acetonitrile	24	 **15**	90
4	acetophenone	acetonitrile	24	 **16**	90
5	acetophenone	benzonitrile	22	 **17**	90
6	*tert*-butyl methyl ketone	*tert*-butyronitrile	18	 **18**	92
7	cyclopentanone	acetonitrile	24	 **19**	85
8	cyclopentanone	benzonitrile	24	 **20**	85
9	cyclohexanone	acetonitrile	24	 **21**	80
10	cyclohexanone	benzonitrile	24	 **22**	87
11	cycloheptanone	acetonitrile	24	 **23**	85

[a] All reactions were carried out in CH_2Cl_2 at room temperature, except entry 4 which was done in refluxing 1,2-dichloroethane (81 °C). [b] Yield of isolated product.

pentenyl triflate (**8d**), it is known that its solvolysis in 100% trifluoroethanol requires 10 days at 100 °C and proceeds via a sulfur–oxygen cleavage,[9] since the formation of a highly strained non-linear cyclopentenyl vinyl cation is avoided.

Conclusion

Our results on the reaction of triflic anhydride with ketones in the presence of nitriles are not only of theoretical interest, but also offer an improved method for the preparation of pyrimidines and condensed pyrimidines.[11-15] Some derivatives of these compounds are also of interest, since they show hypoglycemic,[11] bacteriological,[12] and antitumor[13,14] activities.

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Experimental Section

All melting and boiling points are uncorrected. Melting points were obtained using a Mel-Temp capillary melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer, and the chemical shifts are reported in δ from internal standard TMS and with reference to $CDCl_3$ resonance at δ = 7.28 and 76.89, respectively. The IR spectra were recorded using a Perkin-Elmer spectrophotometer. Mass spectra were obtained on a Varian Mat-711 spectrometer at 100 eV.

All ketones and nitriles used are commercial samples. They were dried over molecular sieves (4 Å) and distilled. Triflic anhydride was prepared from triflic acid and P_2O_5 as reported in the literature[1] and freshly distilled from P_2O_5[21] before use. Solvents were purified by distillation from standard drying agents.

General Procedure for the Reaction of Ketones with Nitriles and Triflic Anhydride. To a well-stirred solution of triflic anhydride (6.4 g, 22.8 mmol) and the nitrile **10** (42 mmol) in anhydrous CH_2Cl_2 (20 mL) was added slowly a solution of the ketone **5** (20 mmol) in anhydrous CH_2Cl_2 (10 mL) or 1,2-dichloroethane (10 mL). The red-brown mixture was magnetically stirred for the appropriate time at room temperature or refluxed depending upon the ketone (Table I). Saturated $NaHCO_3$ solution (50 mL) was carefully added, and the organic phase was washed with brine (2 × 50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by distillation, crystallization, or column chromatography over silica gel 60 (Merck) using CH_2Cl_2/Et_2O (2:1) as the eluent (Table I).

4-Methyl-2,6-diphenylpyrimidine (13): mp 91–92 °C (lit.[16] mp 92–94 °C); IR (KBr) 1575, 1535, 1445, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.58 (s, 3 H), 7.46 (m, 7 H), 8.16 (m, 2 H), 8.59 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.39, 113.72, 126.95, 128.14, 128.22, 128.59, 130.23, 130.42, 136.99, 137.92, 163.36, 164.02, 167.50; MS *m/z* (relative intensity) 246 (M^+, 20), 245 (100), 142 (17), 126 (7).

2,4,5,6-Tetramethylpyrimidine (14): bp 29–30 °C (0.15 Torr) (lit.[15] bp 196–197 (760 Torr)); IR (film), 1570, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.57 (s, 3 H), 2.83 (s, 6 H), 3.02 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 11.76, 20.46, 23.73, 121.56, 162.04, 162.25; MS *m/z* (relative intensity) 136 (M^+, 100) 135 (28).

4-Ethyl-2,5,6-trimethylpyrimidine (15): bp 52–54 °C (2.5 Torr) (lit.[8] bp reported as a mixture of 4- and 5-ethyl isomers); IR (CCl_4) 1560, 1415 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, *J* = 8 Hz), 2.20 (s, 3 H), 2.43 (s, 3 H), 2.61 (s, 3 H), 2.74 (q, 2 H, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 11.22, 11.81, 20.96, 24.04, 27.06, 121.73, 162.46, 163.27, 167.41; MS *m/z* (relatively intensity) 150 (M^+, 61), 149 (100), 135 (10), 122 (15).

2,6-Dimethyl-4-phenylpyrimidine (16): bp 95–96 °C (0.7 Torr) (lit.[8] bp 95–96 °C (0.7 Torr)). Spectral data identical with the values, which we have reported in ref 8.

2,4,6-Triphenylpyrimidine (17): mp 184–185 °C (EtOH) (lit.[17] mp 184–185 °C). Spectral data identical with the values reported by us earlier.[8]

2,4,6-Tri-*tert*-butylpyrimidine (18): mp 76–77 °C (MeOH) (lit.[18] mp 78–80 °C). Spectral data identical with the values reported by us earlier.[8]

2,4-Dimethyl-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidine (19): bp 61–63 °C (1.5 Torr) (lit.[19] bp not reported); IR (film) 1585, 1430, 1405 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (q, 2 H, *J* = 7.5 Hz), 2.42 (s, 3 H), 2.66 (s, 3 H), 2.92 (t, 2 H, *J* = 7.5 Hz), 2.95 (t, 2 H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.57, 20.81, 24.49, 27.13, 33.07, 128.67, 160.48, 164.71, 172.88; MS *m/z* (relative intensity) 148 (M^+, 100), 147 (37), 133 (6), 120 (7), 106 (33).

2,4-Diphenyl-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidine (20): mp 126–127 °C (EtOH); IR (KBr) 1570, 1400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15 (q, 2 H, *J* = 7.3 Hz), 3.11 (t, 2 H, *J* = 7.3 Hz), 318 (t, 2 H, *J* = 7.3 Hz), 7.47–7.59 (m, 6 H), 8.07–8.10 (m, 2 H), 8.60–8.65 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.51, 30.62, 34.10, 127.91, 128.15, 128.19, 128.42, 128.70, 129.55, 129.85, 137.78, 138.03, 158.88, 162.75, 176.22; MS *m/z* (relative intensity) 286 (M^+, 23), 285 (100), 284 (94), 182 (5). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.78; H, 5.92; N, 10.28. Found: C, 83.78; H, 6.03; N, 10.42.

2,4-Dimethyl-5,6,7,8-tetrahydrobenzo[*d*]pyrimidine (21): bp 82–83 °C (1.5 Torr) (lit.[19] bp not reported); IR (film) 1560, 1425 cm^{-1}; ^1H NMR (reported by us earlier);[8] ^{13}C NMR ($CDCl_3$) δ 21.37, 22.28, 22.59, 24.72, 25.54, 32.28, 124.66, 163.84, 164.50, 164.98; MS *m/z* (relative intensity) 162 (M^+, 100), 161 (20), 121 (31), 108 (37), 79 (22).

2,4-Diphenyl-5,6,7,8-tetrahydrobenzo[*d*]pyrimidine (22): mp 124–126 °C (EtOH) (lit.[20] mp 122–123 °C); IR (KBr) 1550, 1405 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69–1.78 (m, 2 H), 1.87–1.97 (m, 2 H), 2.75 (t, 2 H, *J* = 6 Hz), 3.01 (t, 2 H, *J* = 6.6 Hz), 7.40–7.50 (m, 6 H), 7.60–7.65 (m, 2 H), 8.40–8.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.26, 22.70, 26.76, 32.57, 125.20, 127.84, 127.97, 128.15, 128.74, 128.83, 129.78, 138.00, 138.49, 161.21, 164.85, 166.53; MS *m/z* (relative intensity) 272 (M^+, 20), 271 (94), 270 (100), 168 (6).

2,4-Dimethyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*d*]pyrimidine (23): bp 83–84 °C (0.1 Torr); IR (film) 1580, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19–1.30 (m, 4 H), 1.42–1.48 (m, 2 H), 2.07 (s, 3 H), 2.21 (s, 3 H), 2.34–2.40 (m, 2 H), 2.50–2.56 (m, 2 H); ^{13}C NMR 21.89, 25.16, 25.49, 26.40, 27.57, 31.83, 38.11, 129.66, 162.51, 163.48, 170.28; MS *m/z* (relative intensity) 176 (M^+, 29), 161 (6), 123 (70), 43 (100). Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.94; H, 9.15; N, 15.96. Found: C, 75.09; H, 8.92; N, 16.06.

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