A new and a convenient route to enaminones and pyrazoles

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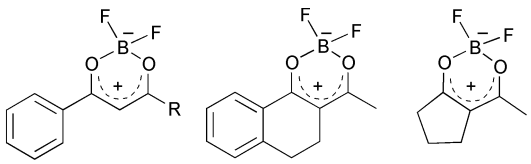
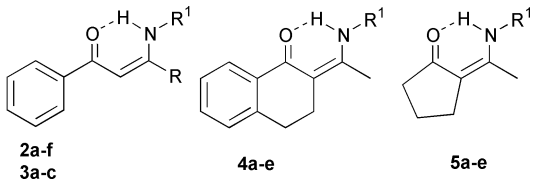
A new method has been developed for the regioselective preparation of enaminones and pyrazoles from 1,3-diketonatoboron difluorides. The reactions proceed smoothly under mild reaction conditions, producing enaminones and pyrazoles in high yields.

Enaminones and related compounds, possessing the structural unit N–C=C–Z (Z = COR, CO_2R, CN, etc.), are versatile synthetic intermediates in the construction of heterocycles.[1] Pyrroles, oxazoles, pyridinones, quinolines, dibenzodiazepines, tetrahydrobenzoxazines, tetronic acids, and aza steroids have been prepared from enaminones.[1,2] Enaminones are also valuable precursors for α-iodo enaminones,[3] 3-amino sugar derivatives,[4] azo compounds,[5] β-aminoketones,[6] as well as tetrahydropentalenes, tetrahydroindenes, and hexahydroazulenes.[7] In addition, some of these compounds are pharmaceuticals possessing anticonvulsant[8a–c] and analeptic[8d] activity, combined with low toxicity.

Enaminones are commonly prepared from amines and 1,3-diketones. The procedure leads to a single product if symmetrical 1,3-diketones[9] or compounds containing two carbonyl groups of substantially different reactivity are employed,[10] otherwise mixtures are obtained that are often difficult to separate. There is also a great variety of other methods for the preparation of unsymmetrical acyclic or cyclic enaminones.[11] These methods involve several reaction steps, but they also suffer from the availability of the starting materials and, when 1,3-diketones and primary or secondary amines are used, they require prolonged heating at high temperatures and the azeotropic removal of water. A few years ago we have described a new synthetic route to pyrimidine *N*-oxides, starting from 1,3-diketones and carboxamide oximes.[12] We found that reactions catalysed with $BF_3 \cdot OEt_2$ gave pyrimidine *N*-oxides in low yields. Later on we discovered that low yields were due to the formation of 1,3-diketonatoboron difluorides. 1,3-Diketonatoboron difluorides, first described by Morgan and Tunstall,[13] are known as valuable intermediates in organic synthesis.[14] They can also be considered as protected 1,3-diketones.[15]



Herein we wish to report our preliminary results on the use of 1,3-diketonatoboron difluorides as starting materials for the regioselective synthesis of unsymmetrical enaminones and substituted pyrazoles. Initially, 1,3-diketonatoboron difluorides **1a–d** were prepared in good yields by treatment of the corresponding 1,3-diketones with $BF_3 \cdot OEt_2$ at room temperature (Table 1). Reactions of **1a–d** with amino compounds afforded the products **2–5**. The processes are highly regioselective and the products are formed in high yields.



The reactions of 2,2-difluoro-4-methylnaphtho[1,2-*e*]-1,3,2-dioxaborin and its [2,1-*e*] isomer with aniline have been reported.[17] They give rise to the formation of the corresponding oxazaborines and not to the enaminones as described herein.

When we performed reactions with 1 or 2 equiv. of an amine, completion was not achieved within several hours. Under these conditions a small amount of the corresponding 1,3-diketones were detected in the reaction mixture. We found that at least 3 equiv. of the amine were required to avoid any side products. The above observation suggests that the coordination of boron in 1,3-diketonatoboron difluoride with an amine also plays a part in the successful termination of the reaction.

Benzoylacetonatoboron difluoride **1a** was treated with ammonia, methylamine, isopropylamine, cysteamine, 3-picolylamine, and 3-amino-2,2-dimethylethanol to afford enaminones **2a–f** (Table 2). It is worth mentioning that even cysteamine reacted with **1a** to yield only the enaminone **2d**. Comparable results were obtained employing difluorides **1b–c** and the appropriate amines.

The problems associated with the use of low boiling amines have been overcome by the utilisation of a Lewis acid–amine complex.[9] However, these reactions required prolonged heating in toluene and the removal of water. Furthermore, application of an excess of Lewis acid often resulted in the formation of a mixture of enaminones. In our procedure,

Table 1 Preparation of 1,3-diketonatoboron difluorides

Product	R	Reaction time/h	Yield (%)[a]	mp/°C
1a	Me	6	92	157–159[b,c]
1b	Ph	8	89	190–191[b,d]
1c	—	72	88	161–162[e,f]
1d	—	24	95	58–60[g]

[a] Isolated yields are given. [b] Ethyl acetate. [c] Lit.[16a] mp 158–160 °C. [d] Lit.[16b] mp 189–190 °C. [e] Toluene. [f] Lit.[16c] mp 163 °C. [g] Hexane.

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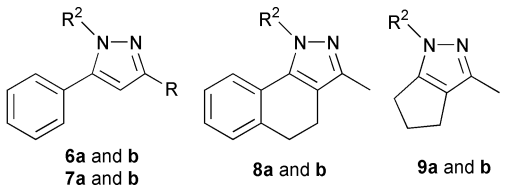
Table 2 Preparation of enaminones

Product	R	R^1	Reaction time/h	Yield (%)[a]	mp/°C
2a	Me	H	0.25	99	143–145[b,c]
2b	Me	Me	0.25	99	68–69[b,d]
2c	Me	*i*-Pr	0.5	98	57–58[b,e]
2d	Me	CH_2CH_2SH	0.5	98	Oil
2e	Me	3-$PyCH_2$	0.5	96	Oil
2f	Me	$C(Me)_2CH_2OH$	0.5	79	Oil
3a	Ph	*i*-Pr	0.5	91	Oil[18d]
3b	Ph	CH_2CH_2SH	0.5	88	Oil
3c	Ph	3-$PyCH_2$	1	95	85–86[f]
4a	—	H	0.25	98	117–118[g]
4b	—	Me	0.25	99	53–54[g]
4c	—	*i*-Pr	1.5	99	Oil
4d	—	CH_2CH_2SH	1.5	81	Oil
4e	—	3-$PyCH_2$	0.5	97	84–86[h]
5a	—	H	0.25	99	73–75[i]
5b	—	Me	0.25	99	Oil
5c	—	*i*-Pr	0.25	95	Oil
5d	—	CH_2CH_2SH	0.25	83	44–45[i]
5e	—	3-$PyCH_2$	0.25	97	Oil

[a] Isolated yields are given. [b] Toluene. [c] Lit.[18a] mp 144–145 °C. [d] Lit.[18b] mp 45–47 °C. [e] Lit.[18c] mp 56–58 °C. [f] Diethyl ether. [g] Hexane–ethyl acetate. [h] Hexane–diethyl ether. [i] Diethyl ether.

ammonia or methylamine was passed over the stirred solution of 1,3-diketonatoboron difluoride for 5 min and the reaction was completed after an additional 15 min, giving only one regioisomer in excellent yield.

Our attention was then directed towards hydrazino compounds as nitrogen nucleophiles. Reaction of unsymmetrical 1,3-diketones with monosubstituted hydrazines can yield isomeric pyrazoles. It is known that benzoylacetone gives both 1,3-dimethyl-5-phenylpyrazole and 1,5-dimethyl-3-phenylpyrazole on reaction with methylhydrazine.[19] There is also a report on pyrazole ring closure with methylhydrazine and phenylhydrazine, starting from benzoylacetone in heterogeneous media that resulted in a mixture of pyrazoles.[20] When we reacted **1a** with 3 equiv. of methylhydrazine we isolated only 1,3-dimethyl-5-phenylpyrazole (**6a**) in high yield. Similarly, phenylhydrazine furnished 1,5-diphenyl-3-methylpyrazole (**6b**). In addition, 1,3-diketonatoboron difluorides **1b–d** reacted smoothly with hydrazines to offer a single regioisomer of **7–9** Table 3.



The structure elucidation of the enaminones and pyrazoles obtained was established by spectroscopic analyses, ^1H, ^{13}C NMR, HMQC, HMBC and NOESY spectra. The ^1H-^{13}C HMBC correlation and 2D NOE cross peaks clearly confirm the assigned regioisomers. The structure of compound **8b** was also confirmed by an X-ray analysis (not reported).

In conclusion, we have described an efficient and regioselective approach to enaminones and pyrazoles. This methodology is of particular use, especially when one has to deal with a low boiling amine or an amine containing other nucleophilic functional groups (OH, SH). The reactions terminate under mild conditions in a short time with the formation of a single product that is easily isolable in high yields.

Table 3 Preparation of pyrazoles

Product	R	R^2	Reaction time/h	Yield (%)[a]	mp/°C
6a	Me	Me	0.5	95	Oil[b]
6b	Me	Ph	2	83	Oil[21b]
7a	Ph	Me	0.5	84	59–61[c,d]
7b	Ph	Ph	2	89	138–140[e,f]
8a	—	Me	0.5	88	165–167[g]
8b	—	Ph	0.5	91	87–89[h]
9a	—	Me	0.5	91	97–99[h]
9b	—	Ph	0.5	95	48–50[c]

[a] Isolated yields are given. [b] Lit.[21a] mp 22 °C. [c] Hexane–diethyl ether. [d] Lit.[21c] mp 59–60 °C. [e] Ethanol. [f] Lit.[21d] mp 138–139 °C. [g] Diethyl ether. [h] Toluene.

Experimental

General methods

Solvents and starting compounds were obtained from commercial sources (Fluka, Sigma and Aldrich). NMR spectra were recorded on a Bruker Avance 300 DPX spectrometer at 302 K. The HMBC spectra were obtained with 512 time increments and 32 scans per t_1 increment. NOESY studies were acquired using the noesytp program on the DPX spectrometer. The mixing time was 100 ms and 32 accumulations were collected. Chemical shifts are reported relative to internal standard Me_4Si. IR spectra were taken on BioRed FTS 3000MX instrument. Melting points were determined on a hot stage and are uncorrected. Microanalysis were performed on a Perkin-Elmer 2400 CHN Analyser. Mass spectra and high resolution mass measurements were acquired on a VG-Analytical Autospec EQ instrument.

General procedure for the preparation of 1,3-diketonatoboron difluorides 1a–d

To a solution of the corresponding 1,3-diketone (1 equiv.) in toluene or dichloromethane (3 mL), boron trifluoride etherate (3 equiv.) was added at room temperature. The reaction mixture was allowed to stand at room temperature for the time noted in Table 1. Afterwards the reaction mixture was evaporated and the residue suspended in water (10 mL). Solid material was filtered off and recrystallised from toluene.

2-Acetyl-3,4-dihydro-1(2*H*)-naphthalenolatoboron difluoride (1c). IR (KBr, ν cm^{-1}): 2943, 1608, 1506, 1347, 1274, 1216, 1033, 802, 745. ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.71 (t, 2H, J=7.4 Hz), 2.98 (t, 2H, J=7.4 Hz), 7.28 (d, 1H, J=7.5 Hz), 7.38 (dd, 1H, J_1=J_2=7.5 Hz), 7.56 (ddd, 1H, J_1=J_2=7.5 Hz, J_3=1.3 Hz), 8.11 (d, 1H, J=7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 22.3, 27.5, 107.2, 127.6, 128.0, 128.3, 135.4, 143.5, 177.9, 189.59, 189.61. MS (EI, 70 eV, m/z (%) 236 (M^+, 100), 221 (91), 215 (55), 193 (65), 127 (58). HRMS (EI) m/z calcd for $C_{12}H_{11}BF_2O_2$: 235.0857, found 235.0866. Anal. calcd. for $C_{12}H_{11}BF_2O_2$: C, 61.07; H, 4.70; found: C, 60.71; H, 4.50.

2-Acetylcyclopentanolatoboron difluoride (1d). IR (KBr, ν cm^{-1}): 2970, 1606, 1549, 1383, 1348, 1310, 1195, 1154, 1027, 968. ^1H NMR (300 MHz, $CDCl_3$): δ 2.10 (dd, 2H, J_1=J_2=7.8 Hz), 2.27 (s, 3H), 2.67–2.78 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ 20.1, 22.3, 25.2, 34.6, 113.0, 187.1, 199.3. MS (EI, 70 eV) m/z (%) 173 (M^+, 23), 159 (100), 118 (42), 79 (35). HRMS (EI) m/z calcd for $C_7H_9BF_2O_2$: 173.0700, found 173.0707. Anal. calcd. for $C_7H_9BF_2O_2$: C, 48.33; H, 5.21; found: C, 48.08; H, 5.26.

General procedure for the synthesis of enaminones

To a stirred solution of a boron complex (1 equiv.) in acetonitrile (8 mL), amine (3 equiv.) was added at room temperature. In the case of ammonia or methylamine, the amine was passed over the stirred solution of a boron complex for 5 min at room temperature. The reaction mixture was stirred at room temperature for 0.25–1.5 h (see Table 2) and then evaporated to dryness. The residue was dissolved in dichloromethane (30 mL), washed with water (2×10 mL), dried over magnesium sulfate and evaporated to dryness. Products were purified in some cases by flash chromatography.

(2*Z*)-1-Phenyl-3-[(2-sulfanylethyl)amino]-2-buten-1-one (2d). Colourless oil. IR (NaCl plates, ν cm^{-1}): 3058, 2930, 2554, 1598, 1545, 1438, 1373, 1321, 1291, 1177, 1087, 1065, 1027, 739. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60 (t, 1H, J=8.5 Hz), 2.07 (s, 3H), 2.67–2.74 (m, 2H), 3.46–3.52 (m, 2H), 5.69 (s, 1H), 7.34–7.42 (m, 3H), 7.83–7.86 (m, 2H), 11.55 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4, 25.0, 46.2, 92.6, 126.8, 128.1, 130.5, 140.1, 164.4, 187.9. MS (EI, 70 eV) m/z (%) 221 (M^+, 42), 188 (69), 174 (76), 105 (100), 91 (77), 77 (67). HRMS (EI) m/z calcd for $C_{12}H_{15}NOS$: 221.0874, found 221.0882.

(2*Z*)-1-Phenyl-3-[(3-pyridinylmethyl)amino]-2-buten-1-one (2e). The colourless oil obtained on work-up was subjected to flash chromatography (5 : 3 petroleum ether–ethyl acetate elution). IR (NaCl plates, ν cm^{-1}): 3058, 1601, 1543, 1435, 1319, 1295, 1065, 742. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (s, 3H), 4.54 (d, 2H, J=6.4 Hz), 5.69 (s, 1H), 7.04–7.32 (m, 5H), 7.50–7.56 (m, 1H), 7.80–7.84 (m, 2H), 8.48 (d, 1H, J=3.4 Hz), 11.80 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 48.6, 92.9, 121.1, 122.5, 127.0, 128.2, 130.6, 137.1, 140.3, 149.5, 157.2, 164.9, 188.1. MS (EI, 70 eV) m/z (%) 252 (M^+, 37), 147 (100), 133 (72), 105 (52), 92 (50), 77 (55).

(2*Z*)-3-[(2-Hydroxy-1,1-dimethylethyl)amino]-1-phenyl-2-buten-1-one (2f). Colourless oil. IR (NaCl plates, ν cm^{-1}): 3367, 2972, 2931, 1596, 1549, 1338, 1067, 740. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (s, 6H), 2.13 (s, 3H), 3.61 (s, 2H), 3.83 (br s, 1H), 5.57 (s, 1H), 7.35–7.40 (m, 3H), 7.80–7.84 (m, 2H), 11.90 (br s, 1H). MS (EI, 70 eV) m/z (%) 233 (M^+, 18), 202 (100), 184 (25), 162 (27), 105 (37). HRMS (EI) m/z calcd for $C_{14}H_{19}NO_2$: 233.1416, found 233.1424.

(2*Z*)-1,3-Diphenyl-3-[(2-sulfanylethyl)amino]-2-propen-1-one (3b). Colourless oil. IR (NaCl plates, ν cm^{-1}): 3058, 1594, 1566, 1480, 1331, 1058, 750. NMR (300 MHz, $CDCl_3$): δ 1.49 (t, 1H, J=8.5 Hz), 2.59–2.67 (m, 2H), 3.37–3.44 (m, 2H), 5.80 (s, 1H), 7.38–7.46 (m, 8H), 7.88–7.91 (m, 2H), 11.45 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 47.7, 94.2, 127.2, 127.8, 128.3, 128.7, 129.7, 130.9, 135.5, 140.2, 166.6, 188.9. MS (EI, 70 eV) m/z (%) 283 (M^+, 27), 250 (100), 236 (82), 105 (36). HRMS (EI) m/z calcd for $C_{17}H_{17}NOS$: 283.1031, found 283.1041.

(2*Z*)-1,3-Diphenyl-3-[(3-pyridinylmethyl)amino]-2-propen-1-one (3c). The colourless oil obtained on work-up was subjected to flash chromatography (5 : 3 petroleum ether–ethyl acetate elution). IR (NaCl plates, ν cm^{-1}): 3059, 2927, 1593, 1566, 1480, 1331, 1226, 1057, 1025, 752. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.38 (d, 2H, J=6.6 Hz), 5.87 (s, 1H), 7.18–7.22 (m, 1H), 7.33–7.53 (m, 8H), 7.53–7.57 (m, 1H), 7.87–7.90 (m, 2H), 8.36 (d, 1H, J=1.8 Hz), 8.46–8.49 (m, 1H), 11.68 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.9, 94.5, 123.6, 127.1, 127.7, 128.3, 128.7, 129.8, 131.0, 134.1, 134.7, 135.1, 139.9, 148.6, 148.8, 166.6, 189.0. MS (EI, 70 eV) m/z (%) 314 (M^+, 39), 223 (95), 149 (75), 105 (100), 77 (97). HRMS (EI) m/z: calcd for $C_{21}H_{18}N_2O$: 314.1419, found 314.1426.z

(2*Z*)-2-(1-Aminoethylidene)-3,4-dihydro-1(2*H*)-naphthalenone (4a). IR (KBr, ν cm^{-1}): 3289, 2888, 2831, 1591, 1487, 1359, 1308, 1146, 1032, 986, 901, 847, 777, 743. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 3H), 2.60 (t, 2H, J=7.2 Hz), 2.84 (t, 2H, J=7.2 Hz), 5.10 (br s, 1H), 7.15–7.37 (m, 3H), 7.99–8.02 (m, 1H), 10.88 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 25.0, 29.6, 101.3, 126.9 (2C), 127.6, 131.3, 136.2, 142.0, 160.7, 186.1. MS (EI, 70 eV) m/z (%) 187 (M^+, 100), 172 (14), 97 (13), 69 (15). HRMS (EI) m/z calcd for $C_{12}H_{13}NO$: 187.0997, found 187.1005.

(2*Z*)-2-[1-(Methylamino)ethylidene]-3,4-dihydro-1(2*H*)-naphthalenone (4b). IR (KBr, ν cm^{-1}): 2929, 2830, 1594, 1547, 1476, 1318, 1252, 1182, 1062, 899, 785, 743. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02, (s, 3H), 2.57 (t, 2H, J=6.4 Hz), 2.80 (t, 2H, J=6.4 Hz), 2.98 (d, 3H, J=5.1 Hz), 7.12–7.15 (m, 1H), 7.25–7.32 (m, 2H), 7.97–8.01 (m, 1H), 12.52 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.63, 25.0, 29.6, 30.2, 100.5, 126.3, 126.7, 127.2, 130.5, 136.5, 141.1, 164.7, 183.3. MS (EI, 70 eV) m/z (%) 201 (M^+, 100), 186 (52), 56 (97). HRMS (EI) m/z calcd for $C_{13}H_{15}NO$: 201.1154, found 201.1160.

(2*Z*)-2-[1-(Isopropylamino)ethylidene]-3,4-dihydro-1(2*H*)-naphthalenone (4c). Colourless oil. IR (NaCl plates, ν cm^{-1}): 2970, 2930, 1591, 1553, 1469, 1314, 1254, 1156, 1119, 743. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (d, 6H, J=6.1 Hz), 2.06 (s, 3H), 2.56 (t, 2H, J=7.6 Hz), 2.80 (t, 2H, J=7.6 Hz), 3.75–3.86 (m, 1H), 7.12–7.32 (m, 3H), 8.00–8.10 (m, 1H), 12.74 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.8, 24.1, 24.8, 29.5, 45.2, 100.1, 126.2, 126.6, 127.1, 130.4, 136.5, 140.9, 162.6, 183.0. MS (EI, 70 eV) m/z (%) 229 (M^+, 100), 212 (70), 186 (86), 145 (40), 69 (85). HRMS (EI) m/z calcd for $C_{15}H_{19}NO$: 229.1467, found 229.1475.

(2*Z*)-2-{1-[(2-Sulfanylethyl)amino]ethylidene}-3,4-dihydro-1(2*H*)-naphthalenone (4d). Yellow oil. IR (NaCl plates, ν cm^{-1}): 2930, 2834, 2556, 1589, 1466, 1319, 1252, 1173, 1065, 744. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60 (t, 1H, J=6.5 Hz), 2.02 (s, 3H), 2.56 (t, 2H, J=7.8 Hz), 2.67–2.81 (m, 4H), 3.49 (t, 2H, J=6.5 Hz), 7.11–7.14 (m, 1H), 7.26–7.30 (m, 2H), 7.97–8.00 (m, 1H), 12.70 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 24.4, 24.7, 28.9, 46.3, 100.5, 125.9, 126.1, 126.7, 130.2, 135.7, 140.6, 162.4, 183.5. MS (EI, 70 eV) m/z (%) 247 (M^+, 46), 214 (58), 200 (100), 102 (49). HRMS (EI) m/z calcd for $C_{14}H_{17}NOS$: 247.1031, found 247.1037.

(2*Z*)-2-{1-[(3-Pyridinylmethyl)amino]ethylidene}-3,4-dihydro-1(2*H*)-naphthalenone (4e). IR (KBr, ν cm^{-1}): 2989, 1586, 1545, 1466, 1423, 1366, 1310, 1287, 1248, 1173, 1063, 1016, 815, 733, 710. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.61 (t, 2H, J=6.3 Hz), 2.83 (t, 2H, J=6.3 Hz), 4.56 (d, 2H, J=6.0 Hz), 7.14–7.36 (m, 4H), 7.65–7.68 (m, 1H), 7.97–8.00 (m, 1H), 8.52–8.57 (m, 2H), 12.88 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.9, 24.8, 29.3, 44.9, 101.5, 123.8, 126.3, 126.6, 127.1, 130.8, 133.9, 134.7, 135.9, 144.1, 148.7, 149.0, 162.6, 184.5. MS (EI, 70 eV) m/z (%) 278 (M^+, 87), 261 (70), 186 (77), 92 (100), 65 (54). HRMS (EI) m/z calcd for $C_{18}H_{18}N_2O$: 278.1419, found 278.1420.

2-[(*Z*)-1-Aminoethylidene]-1-cyclopentanone (5a). IR (KBr, ν cm^{-1}): 3304, 3156, 2956, 2914, 1627, 1509, 1256, 1045, 913, 633. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85 (dd, 2H,

$J_1 = J_2 = 7.2$ Hz), 1.91 (s, 3H), 2.30 (d, 2H, $J = 7.2$ Hz), 2.51 (d, 2H, $J = 7.2$ Hz), 5.13 (br s, 1H), 9.23 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4, 20.6, 27.2, 39.0, 103.4, 155.8, 203.9. MS (EI, 70 eV) m/z (%) 125 (M^+, 92), 97 (33), 82 (40), 69 (100). HRMS (EI) m/z calcd for $C_7H_{11}NO$: 125.0841, found 125.0846.

(2*Z*)-2-[1-(Methylamino)ethylidene]cyclopentanone (5b). Colourless oil. IR (NaCl plates, ν cm^{-1}): 2949, 1628, 1584, 1487, 1341, 1258, 1065, 747. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78–1.88 (m, 2H), 1.93 (s, 3H), 2.31 (t, 2H, $J = 7.2$ Hz), 2.53 (t, 2H, $J = 7.2$ Hz), 2.93 (d, 3H, $J = 5.0$ Hz), 10.26 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.6, 20.4, 27.9, 29.5, 39.0, 102.3, 159.5, 201.4. MS (EI, 70 eV) m/z (%) 139 (M^+, 98), 124 (38), 82 (66), 61 (100). HRMS (EI) m/z calcd for $C_8H_{13}NO$: 139.0997, found 139.0997.

(2*Z*)-2-[1-(Isopropylamino)ethylidene]cyclopentanone (5c). Colourless oil. IR (NaCl plates, ν cm^{-1}): 2967, 2876, 1628, 1586, 1477, 1449, 1368, 1330, 1256, 1186, 1121. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (d, 6H, $J = 6.3$ Hz), 1.82 (tt, 2H, $J_1 = J_2 = 7.8$ Hz), 1.96 (s, 3H), 2.31 (t, 2H, $J = 7.8$ Hz), 2.51 (t, 2H, $J = 7.8$ Hz), 3.73 (sep, 1H, $J = 6.3$ Hz), 10.36 (br s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7, 20.3, 23.9, 28.0, 39.1, 44.5, 101.9, 157.6, 201.1. MS (EI, 70 eV) m/z (%) 167 (M^+, 24), 105 (37), 69 (100). HRMS (EI) m/z calcd for $C_{10}H_{17}NO$: 167.1310, found 167.1316.

(2*Z*)-2-{1-[(2-Sulfanylethyl)amino]ethylidene}cyclopentanone (5d). IR (KBr, ν cm^{-1}): 2943, 2840, 1630, 1583, 1474, 1335, 1248, 1128, 1067, 776. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (t, 1H, $J = 8.7$ Hz), 1.79–1.89 (m, 2H), 1.96 (s, 3H), 2.33 (t, 2H, $J = 7.8$ Hz), 2.53 (t, 2H, $J = 7.8$ Hz), 2.64–2.71 (m, 2H), 3.44 (dt, 2H, $J_1 = J_2 = 6.6$ Hz), 10.47 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.9, 20.4, 25.3, 27.9, 39.1, 46.0, 103.2, 157.7, 202.4. MS (EI, 70 eV) m/z (%) 185 (M^+, 25), 152 (45), 138 (100), 61 (32). HRMS (EI) m/z calcd for $C_9H_{15}NOS$: 185.0874, found 185.0875.

(2*Z*)-2-{1-[(3-Pyridinylmethyl)amino]ethylidene}cyclopentanone (5e). Colourless oil. IR (NaCl plates, ν cm^{-1}): 3259, 2951, 1623, 1574, 1477, 1427, 1249, 712. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.86 (tt, 2H, $J_1 = J_2 = 7.3$ Hz), 1.92 (s, 3H), 2.35 (t, 2H, $J = 7.3$ Hz), 2.55 (t, 2H, $J = 7.3$ Hz), 4.47 (d, 2H, $J = 6.6$ Hz), 7.27–7.31 (m, 1H), 7.61–7.64 (m, 1H), 8.52–8.55 (m, 2H), 10.67 (br s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 20.4, 27.9, 39.2, 44.3, 103.9, 123.8, 134.2, 134.6, 148.5, 148.9, 157.6, 203.0. MS (EI, 70 eV) m/z (%) 216 (M^+, 94), 159 (57), 124 (65), 107 (43), 92 (100). HRMS (EI) m/z calcd for $C_{13}H_{16}N_2O$: 216.1263, found 216.1271.

General procedure for the preparation of pyrazoles

To a stirred solution of a boron complex (1 mmol) in acetonitrile (5 mL), methylhydrazine or phenylhydrazine (3 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for the time mentioned in Table 3 and then evaporated to dryness. The residue was treated with ice-cold water (15 mL), then the solid material was filtered off and rinsed with water, yielding pure pyrazoles.

1,3-Dimethyl-4,5-dihydro-1*H*-benzo[*g*]indazole (8a). IR (KBr, ν cm^{-1}): 2529, 1594, 1485, 1314, 774, 725. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 2.66 (t, 2H, $J = 6.9$ Hz), 2.98 (t, 2H, $J = 6.9$ Hz), 4.40 (s, 3H), 7.28–7.40 (m, 2H), 7.60–7.63 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.2, 18.4, 30.2, 38.4, 117.6, 124.0, 124.2, 127.9, 130.0, 130.9, 139.3, 141.0, 141.7. MS (EI, 70 eV) m/z (%) 198 (M^+, 100), 183 (45), 115 (22). HRMS (EI) m/z calcd for $C_{13}H_{14}N_2O$: 198.1157, found 198.1162.

3-Methyl-1-phenyl-4,5-dihydro-1*H*-benzo[*g*]indazole (8b). IR (KBr, ν cm^{-1}): 3051, 2936, 1595, 1504, 1424, 1370, 1132, 1067, 965, 760, 731, 689. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.66 (t, 2H, $J = 6.9$ Hz), 2.97 (t, 2H, $J = 6.9$ Hz), 6.83 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz), 6.96 (ddd, 1H, $J_1 = J_2 = 7.8$ Hz, $J_3 = 1.2$ Hz), 7.08 (ddd, 1H, $J_1 = J_2 = 7.8$ Hz, $J_3 = 1.2$ Hz), 7.11–7.14 (m, 1H), 7.23–7.50 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.7, 19.3, 30.7, 118.6, 123.1, 125.6, 126.3, 127.1, 127.4, 127.9, 128.6, 129.3, 137.2, 138.2, 140.9, 146.0. MS (EI, 70 eV) m/z (%) 260 (M^+, 100), 245 (32), 218 (35), 115 (10). HRMS (EI) m/z calcd for $C_{18}H_{16}N_2$: 260.1314, found 260.1308.

1,3-Dimethyl-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole (9a). IR (KBr, ν cm^{-1}): 2925, 2862, 1543, 1475, 1429, 1367, 1281, 1182, 1113, 1046, 1000, 786, 677. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 3H), 2.50–2.65 (m, 6H), 3.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.7, 23.1, 23.8, 31.2, 36.7, 125.1, 141.7, 150.9. MS (EI, 70 eV) m/z (%) 136 (M^+, 100), 121 (42), 94 (31), 67 (43). HRMS (EI) m/z calcd for $C_8H_{12}N_2$: 136.1001, found 136.1007.

3-Methyl-1-phenyl-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole (9b). IR (KBr, ν cm^{-1}): 2913, 2853, 1597, 1514, 1439, 1378, 1294, 893, 758, 691. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.56–2.59 (m, 4H), 2.95 (t, 2H, $J = 1.8$ Hz), 7.15–7.20 (m, 1H), 7.35–7.41 (m, 2H), 7.57–7.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.7, 22.4, 26.9, 31.0, 118.9, 125.3, 128.4, 129.3, 140.3, 143.9, 149.2. MS (EI, 70 eV) m/z (%) 198 (M^+, 100), 156 (30), 77 (53). HRMS (EI) m/z calcd for $C_{13}H_{14}N_2$: 198.1157, found 198.1162.

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