

Catalyst Free Approach to Benzimidazoles Using Air as the Oxidant at Room Temperature

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Supporting Information

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Experimental section:

General Remarks.

All manipulations were conducted with test tube. $^1\text{H-NMR}$ spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to dimethyl sulfoxide ($\delta = 2.49$ ppm) or tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 as an internal standard. $^{13}\text{C-NMR}$ spectra were obtained by using the same NMR spectrometers and were calibrated with dimethyl sulfoxide ($\delta = 39.5$ ppm) or CDCl_3 ($\delta = 77.00$ ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The tautomerism of benzimidazoles is serious in DMSO-d_6 , so the signal of ^{13}C NMR of some products is not good.

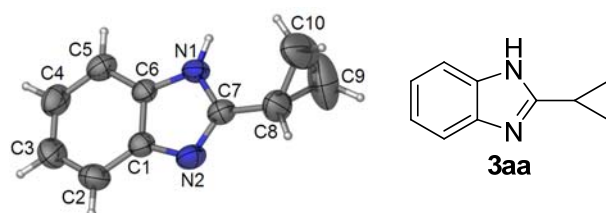
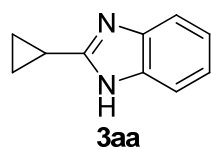


Figure S1. The crystal structure of **3aa**.

CCDC-899934 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

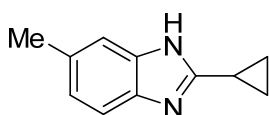
Analytical data for compounds **3**



1):

2-Cyclopropyl-1H-benzo[d]imidazole.¹ Typical procedure: Mix benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL) under air (1 atm). The reaction mixture was stirred at 25 °C for 12 h. After concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 1:1) to afford 38 mg (96 %) of **3aa**. **3aa**: yellow solid; ^1H NMR (DMSO-d_6 , 400 MHz): $\delta = 7.41\text{--}7.39$ (m, 2H), 7.08–7.05 (m, 2H), 3.55 (brs, 1H), 2.13–2.06 (m, 1H), 1.03 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR (DMSO-d_6 , 100 MHz): $\delta = 156.9, 138.9, 121.0, 114.2, 113.7, 113.6, 9.4, 8.7$ ppm; IR (neat): $\nu = 3735.6, 2922.5, 1425.7, 1266.3, 744.5$ cm^{-1} ; Ms (70 ev): m/z (%): 158.2 [M] (63),

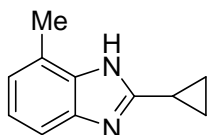
157.2[M-H] (100).



2):

3ba

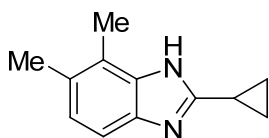
2-Cyclopropyl-6-methyl-1H-benzo[d]imidazole.¹ The reaction of 4-methylbenzene-1,2-diamine **1b** (30.5 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 37 mg (86 %) of **3ba**. **3ba**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.26 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.36 (brs, 1H), 2.35 (s, 3H), 2.07-2.03 (m, 1H), 1.02-0.97 (m, 4H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 156.4, 129.9, 122.3, 21.2, 9.4, 8.5 ppm; IR (neat): ν = 3442.9, 1641.3, 1025.1, 991.7, 766.2 cm⁻¹; Ms (70 ev): m/z (%): 172.3 [M] (58), 171.2 [M-H] (100).



3):

3ca

2-Cyclopropyl-7-methyl-1H-benzo[d]imidazole.² The reaction of 3-methylbenzene-1,2-diamine **1c** (30.5 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 39 mg (91 %) of **3ca**. **3ca**: yellow solid; ¹H NMR (CDCl₃, 400 MHz): δ = 10.80 (brs, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 6.8 Hz, 1H), 2.51 (s, 3H), 2.19-2.12 (m, 1H), 1.20-1.19 (m, 2H), 1.03-1.01 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 156.7, 138.8, 137.5, 123.9, 122.6, 122.0, 112.3, 17.2, 9.8, 8.5 ppm; IR (neat): ν = 2921.7, 1545.5, 1429.4, 1242.2, 749.1 cm⁻¹; Ms (70 ev): m/z (%): 172.3 [M] (75), 171.3 [M-H] (100).

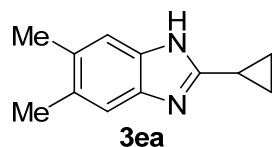


4):

3da

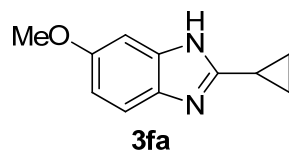
2-Cyclopropyl-6,7-dimethyl-1H-benzo[d]imidazole. The reaction of 3,4-dimethylbenzene-1,2-diamine **1d** (34.1 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 41 mg (88 %) of **3da**. **3da**: yellow solid; ¹H NMR (CDCl₃, 400 MHz): δ = 11.22 (brs, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0

Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 2.16-2.09 (m, 1H), 1.18-1.16 (m, 2H), 0.99-0.96 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 156.6, 137.8, 137.6, 129.5, 124.1, 121.4, 112.0, 19.2, 14.0, 9.8, 8.4 ppm; IR (neat): = 2995.9, 1375.4, 1056.5, 711.4, 629.0 cm^{-1} ; Ms (70 ev): m/z (%): 186.3 [M] (63), 185.2 [M-H] (100). HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2$ (M + H) $^+$ 187.1230, found 187.1227.



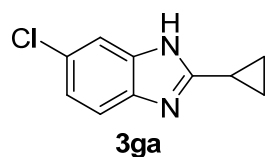
5):

2-Cyclopropyl-5,6-dimethyl-1H-benzo[d]imidazole.³ The reaction of 4,5-dimethylbenzene-1,2-diamine **1e** (34.1 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 36 mg (77 %) of **3ea**. **3ea**: yellow solid; ^1H NMR (DMSO-d_6 , 400 MHz): δ = 7.15 (s, 2H), 3.38 (brs, 1H), 2.24 (s, 6H), 2.10-2.02 (m, 1H), 1.00-0.96 (m, 4H); ^{13}C NMR (DMSO-d_6 , 100 MHz): δ = 155.8, 129.0, 19.9, 9.4, 8.4 ppm; IR (neat): = 3430.0, 1650.5, 1025.3, 997.8, 826.3 cm^{-1} ; Ms (70 ev): m/z (%): 186.3 [M] (63), 185.2 [M-H] (100).



6):

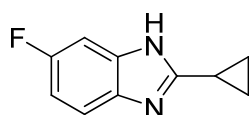
2-Cyclopropyl-6-methoxy-1H-benzo[d]imidazole.⁴ The reaction of 4-methoxybenzene-1,2-diamine **1f** (34.6 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 43 mg (90 %) of **3fa**. **3fa**: yellow solid; ^1H NMR (CDCl_3 , 400 MHz): δ = 10.43 (brs, 1H), 7.36 (d, J = 8.8 Hz, 1H), 6.98 (s, 1H), 6.81 (d, J = 8.8 Hz, 1H), 3.77 (s, 3H), 2.13-2.09 (m, 1H), 1.19-1.17 (m, 2H), 1.04-1.02 (m, 2H); ^{13}C NMR (DMSO-d_6 , 100 MHz): δ = 156.9, 156.1, 138.5, 132.8, 114.7, 111.2, 97.6, 55.8, 9.6, 8.7 ppm; IR (neat): = 3448.6, 2922.2, 1452.7, 1154.9, 444.6 cm^{-1} ; Ms (70 ev): m/z (%): 188.3 [M] (100).



7):

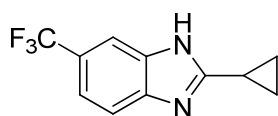
6-Chloro-2-cyclopropyl-1H-benzo[d]imidazole. The reaction of 4-chlorobenzene-1,2-diamine

1g (35.7 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 35.2 mg (73 %) of **3ga**. **3ga**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.44 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.35 (s, 1H), 2.1-2.07 (m, 1H), 1.06-1.00 (m, 4H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 158.5, 125.4, 121.1, 9.3, 8.9 ppm; IR (neat): = 3422.5, 1461.4, 1242.5, 994.8, 745.5 cm⁻¹; Ms (70 ev): *m/z* (%): 192.3 [M] (63), 191.1 [M-H] (100). HRMS *m/z* (ESI) calcd for C₁₀H₁₀ClN₂ (M + H)⁺ 193.0527, found 193.0524.



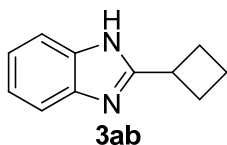
8):

2-Cyclopropyl-6-fluoro-1H-benzo[d]imidazole. The reaction of 4-fluorobenzene-1, 2-diamine **1h** (32 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 41 mg (93 %) of **3ha**. **3ha**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.37 (brs, 1H), 7.21-7.18 (m, 1H), 6.93-6.88 (m, 1H), 3.41 (brs, 1H), 2.08-2.06 (m, 1H), 1.04-1.01 (m, 4H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 158.4, 158.2 (d, *J* = 232.9 Hz), 108.8, 108.6, 9.4, 8.7 ppm; IR (neat): = 3401.6, 2926.0, 1450.7, 1244.7, 1026.3 cm⁻¹; Ms (70 ev): *m/z* (%): 176.3 [M] (64), 175.3 [M-H] (100). HRMS *m/z* (ESI) calcd for C₁₀H₁₀FN₂ (M + H)⁺ 177.0823, found 177.0820.



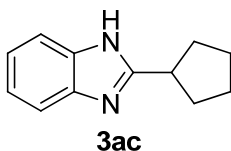
9):

2-Cyclopropyl-6-(trifluoromethyl)-1H-benzo[d]imidazole. The reaction of 4-(trifluoromethyl)benzene-1, 2-diamine **1i** (44 mg, 0.25 mmol) and cyclopropanecarbaldehyde **2a** (26.28 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 30 mg (53 %) of **3ia**. **3ia**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.75-7.74 (m, 1H), 7.58-7.56 (m, 1H), 7.41-7.39 (m, 1H), 3.36 (s, 1H), 2.18-2.11 (m, 1H), 1.12-1.02 (m, 4H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 160.0, 142.7, 136.6, 129.2, 126.5, 123.8, 121.9, 121.5, 121.2, 118.3, 117.83, 117.80, 114.78, 111.3, 107.9, 9.4, 9.1 ppm; IR (neat): = 3423.6, 1332.7, 1025.3, 996.9, 826.2 cm⁻¹; Ms (70 ev): *m/z* (%): 226.3 [M] (69), 225.3 [M-H] (100). HRMS *m/z* (ESI) calcd for C₁₁H₁₀F₃N₂ (M + H)⁺ 227.0791, found 227.0788.



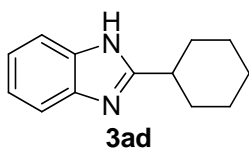
10):

2-Cyclobutyl-1H-benzo[d]imidazole.⁵ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and cyclobutanecarbaldehyde **2b** (31.5 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 23.1 mg (53 %) of **3ab**. The above reaction under O₂ (1 atm), for 12 h, afforded 33 mg (77 %) of **3ab**. **3ab**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.47-7.44 (m, 2H), 7.12-7.07 (m, 2H), 3.73-3.64 (m, 1H), 3.41 (brs, 1H), 2.43-2.31 (m, 4H), 2.08-1.85 (m, 2H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 157.7, 121.2, 114.4, 33.6, 27.5, 18.2; IR (neat): = 2971.0, 1454.4, 1416.1, 1326.5, 1058.1 cm⁻¹; Ms (70 ev): m/z (%): 172.3 [M] (45), 144.2 (100).



11):

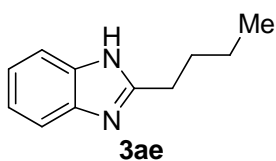
2-Cyclopentyl-1H-benzo[d]imidazole.⁵ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and cyclopentanecarbaldehyde **2c** (36.8 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 25 mg (54 %) of **3ac**. The above reaction under O₂ (1 atm), for 12 h, afforded 35 mg (75 %) of **3ac**. **3ac**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.45-7.43 (m, 2H), 7.10-7.07 (m, 2H), 3.40 (brs, 1H), 3.29-3.21 (m, 1H), 2.05-2.04 (m, 2H), 1.92-1.83 (m, 2H), 1.74-1.69 (m, 2H), 1.67-1.61 (m, 2H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 158.5, 121.1, 39.0, 31.8, 25.2; IR (neat): = 3713.9, 2924.7, 1419.4, 1243.1, 1052.2 cm⁻¹; Ms (70 ev): m/z (%): 186.3 [M] (22), 145.2 (100).



12):

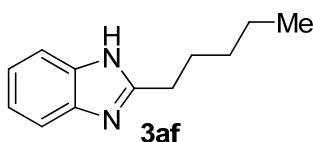
2-Cyclohexyl-1H-benzo[d]imidazole.⁵ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and cyclohexanecarbaldehyde **2d** (42.1 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 38 mg (76 %) of **3ad**. **3ad**: yellow solid; ¹H NMR (DMSO-d⁶, 400 MHz): δ = 7.44-7.43 (m, 2H), 7.10-7.08 (m, 2H), 3.36 (brs, 1H), 2.85-2.79(m, 1H), 2.00 (d, *J* = 12.8, 2H), 1.78 (d, *J* = 11.6 Hz, 2H), 1.70-1.54 (m, 3H), 1.42-1.23 (m, 3H); ¹³C NMR (DMSO-d⁶, 100 MHz): δ = 158.8, 121.03, 120.95, 37.7, 31.2, 25.6, 25.5; IR (neat): = 3418.1,

1025.2, 994.6, 827.4, 766.1 cm^{-1} ; Ms (70 ev): m/z (%): 200.3 [M] (22), 145.2 (100).



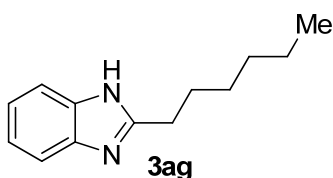
13):

2-Butyl-1H-benzo[d]imidazole.⁶ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and pentanal **2e** (32.3 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 20 mg (46 %) of **3ae**. The above reaction under O₂ (1 atm), for 12 h, afforded 23 mg (53 %) of **3ae**. **3ae**: yellow solid; ¹H NMR (CDCl₃, 400 MHz): δ = 10.43 (brs, 1H), 7.54 (s, 2H), 7.20 (s, 2H), 2.94 (t, J = 7.6 Hz, 2H), 1.83 (d, J = 7.2 Hz, 2H), 1.38 (q, J = 7.2 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 155.4, 138.3, 122.2, 114.5, 30.3, 28.9, 22.4, 13.6; IR (neat): = 3735.6, 2926.5, 1452.0, 1243.9, 743.2 cm^{-1} ; Ms (70 ev): m/z (%): 174.3 [M] (10), 132.2 (100).



14):

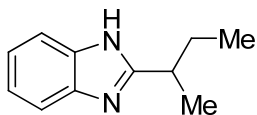
2-Pentyl-1H-benzo[d]imidazole.⁷ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and hexanal **2f** (37.5 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 20 mg (43 %) of **3af**. The above reaction under O₂ (1 atm), for 12 h, afforded 23.4 mg (50 %) of **3af**. **3af**: yellow solid; ¹H NMR (CDCl₃, 400 MHz): δ = 9.99 (brs, 1H), 7.55-7.53 (m, 2H), 7.22-7.19 (m, 2H), 2.93 (t, J = 7.6 Hz, 2H), 1.85 (t, J = 7.2 Hz, 2H), 1.32-1.26 (m, 4H), 0.83 (t, J = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 155.4, 138.4, 122.1, 114.6, 31.4, 29.2, 28.0, 22.3, 13.8; IR (neat): = 2995.6, 1373.8, 1057.5, 913.9, 744.4 cm^{-1} ; Ms (70 ev): m/z (%): 188.1 [M] (13), 132.2 (100).



15):

2-Hexyl-1H-benzo[d]imidazole.⁸ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and heptanal **2g** (42.8 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 21 mg (41 %) of **3ag**. The above reaction under O₂ (1 atm), for 12 h, afforded 27 mg (53 %) of **3ag**. **3ag**: yellow solid; ¹H NMR (CDCl₃, 400 MHz): δ = 9.99 (brs, 1H), 7.55-7.52 (m,

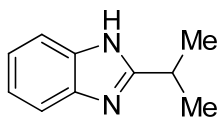
2H), 7.22-7.19 (m, 2H), 2.92 (t, $J = 7.6$ Hz, 2H), 1.88-1.79 (m, 2H), 1.37-1.33 (m, 2H), 1.25-1.23 (m, 4H), 0.83-0.81 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 155.4, 138.3, 122.2, 114.5, 31.4, 29.2, 29.0, 28.2, 22.4, 13.9$; IR (neat): = 2926.1, 2857.0, 1452.0, 1273.4, 741.7 cm^{-1} ; Ms (70 ev): m/z (%): 202.3 [M] (15), 132.2 (100).



16):

3ah

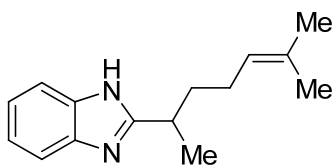
2-sec-butyl-1H-benzo[d]imidazole.⁹ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and 2-methylbutanal **2h** (32.3 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 27 mg (62 %) of **3ah**. **3ah**: yellow solid; ^1H NMR (CDCl_3 , 400 MHz): $\delta = 10.51$ (brs, 1H), 7.55-7.53 (m, 2H), 7.26-7.19 (m, 2H), 3.11-3.05 (m, 1H), 1.98-1.74 (m, 2H), 1.46 (d, $J = 6.8$ Hz, 3H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 159.5, 122.0, 114.7, 36.3, 29.3, 19.4, 11.9$; IR (neat): = 2958.1, 2925.9, 1454.6, 1427.1, 744.8 cm^{-1} ; Ms (70 ev): m/z (%): 174.3 [M] (28), 145.2 (100).



17):

3ai

2-Isopropyl-1H-benzo[d]imidazole.⁵ The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and isobutyraldehyde **2i** (27 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 28 mg (70 %) of **3ai**. **3ai**: yellow solid; ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.55-7.53$ (m, 2H), 7.21-7.19 (m, 2H), 3.28 (t, $J = 7.0$ Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 159.9, 122.1, 29.0, 21.5$; IR (neat): = 2974.7, 1415.2, 1243.2, 1056.6, 746.0 cm^{-1} ; Ms (70 ev): m/z (%): 160.3 [M] (30), 145.2 (100).



18):

3aj

2-(6-Methylhept-5-en-2-yl)-1H-benzo[d]imidazole. The reaction of benzene-1, 2-diamine **1a** (27 mg, 0.25 mmol) and 2,6-dimethylhept-5-enal **2j** (52.6 mg, 0.375 mmol) in toluene (2.5 mL), at 25 °C, under air (1 atm), for 12 h, afforded 32 mg (56 %) of **3aj**. **3aj**: yellow solid; ^1H NMR (CDCl_3 ,

400 MHz): δ = 10.8 (brs, 1H), 7.54-7.53 (m, 2H), 7.21-7.18 (m, 2H), 5.03 (s, 1H), 3.19 (t, J = 6.8 Hz, 1H), 2.01 (d, J = 4.8 Hz, 3H), 1.78-1.67 (m, 4H), 1.59-1.45 (m, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 159.6, 132.2, 123.5, 122.0, 114.7, 36.4, 34.1, 25.8, 25.5, 19.7, 17.6; IR (neat): = 3720.3, 2921.9, 1452.3, 1425.2, 1243.4 cm^{-1} ; Ms (70 ev): m/z (%): 228.4 [M] (30), 145.2 (100). HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2$ (M + H) $^+$ 229.1699, found 229.1696.

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