Direct and Practical Synthesis of 2-Arylbenzoxazoles Promoted by Activated Carbon

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Supporting Information

General methods. All melting points were measured on a Yanaco MP-500D and uncorrected. ^1H and ^{13}C NMR spectra (400 and 100.6 MHz, respectively) were recorded on a JEOL JNM-LA 400 using Me_4Si as the internal standard. IR spectra were measured with a PERKIN ELMER FT-IR Spectrometer SPECTRUM 1000. Elemental analyses were performed with a Yanaco CHN Corder MT-5. Mass spectra were taken on a Shimadzu GCMS-QP 2000A. Preparative column chromatography was carried out on Fuji Silysia BW-820MH. Thin-layer chromatography (TLC) was carried out on foil plates, Silica Gel 60 F₂₅₄ (E. Merck; layer thickness 0.2 mm).

Typical procedure is as follows (entry 1 in Table 2): A mixture of 2-aminophenol (873 mg, 8 mmol), benzaldehyde (849 mg, 8 mmol) and Darco[®] KB (1 g) in xylene (15 mL) was placed in a 100 mL three-necked flask under an oxygen atmosphere and stirred at 120 °C for 4 h. The reaction mixture was then filtered using Celite. After the filtrate was concentrated, the product was isolated by silica gel column chromatography to give a pale yellow crystalline solid 1.2 g (78%). When 0.2 g of activated carbon (Darco[®] KB) was used in the above reaction (in the same substrate scale), a longer reaction time was required (18 h, 85%).

2-phenylbenzoxazole (entry 1 in Table 2)

R_f 0.28 (30:1 hexane–ethyl acetate); mp 106–107 °C (lit.⁶ 102 °C); IR (KBr): ν_{max} (cm^{-1}) 3060, 1617, 1553, 1490, 1479, 1472, 1455, 1447, 1344, 1318, 1290, 1242, 1198, 1054, 924, 760, 745, 703, 689, 686; ^1H NMR (400 MHz, CDCl_3): δ 7.3–7.4 (m, 2H, H_6 , H_5), 7.5–7.6 (m, 3H, H_{12} , H_{13} , H_{14}), 7.5–7.6 (m, 1H, H_7), 7.7–7.8 (m, 1H, H_4), 8.2–8.3 (m, 2H, H_{11} , H_{15}); ^{13}C NMR (100.6 MHz, CDCl_3): δ 110.5 (C-7), 120.0 (C-4), 124.5 (C-6), 125.1 (C-5), 127.2 (C-13), 127.6 (C-11, C-15), 128.9 (C-12, C-14), 131.5 (C-10), 142.1 (C-9), 150.7 (C-8), 163.0 (C-2); MS m/z (relative intensity): 195 (100%), 167 (37.7%), 77 (32.9%), 64 (47.8%), 63 (76.1%), 51 (26.2%); Anal. Calcd for $\text{C}_{13}\text{H}_9\text{NO}$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.98; H, 4.66; N, 7.19.

2-(4'-methylphenyl)benzoxazole (entry 2 in Table 2)

R_f 0.26 (30:1 hexane–ethyl acetate); mp 118–119 °C (lit.⁶ 113–114 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3088, 3053, 3027, 2969, 2918, 2854, 2730, 1622, 1555, 1502, 1450, 1410, 1243, 1178, 1171, 1055, 821, 746, 728, 502; ¹H NMR (400 MHz, CDCl₃): δ 2.44 (s, 3H, H₁₆), 7.3–7.4 (m, 4H, H₆, H₅, H₁₂, H₁₄), 7.5–7.6 (m, 1H, H₇), 7.7–7.8 (m, 1H, H₄), 8.15 (d, 2H, $J_{\text{H11-H12}} = J_{\text{H15-H14}} = 8.0$ Hz, H₁₁, H₁₅); ¹³C NMR (100.6 MHz, CDCl₃): δ 21.6 (C-16), 110.5 (C-7), 119.8 (C-4), 124.4 (C-6), 124.5 (C-5), 124.8 (C-10), 127.6 (C-11, C-15), 129.6 (C-12, C-14), 142.0 (C-9), 142.2 (C-13), 150.7 (C-8), 163.3 (C-2); MS m/z (relative intensity): 210 (23.8%), 209 (100%), 208 (36.6%), 91 (30.9%), 64 (37.5%), 63 (63.7%); Anal. Calcd for C₁₄H₁₁NO: C, 80.36; H, 5.31; N, 6.67. Found: C, 80.39; H, 5.31; N, 6.67.

2-(4'-methoxyphenyl)benzoxazole (**2**)

R_f 0.28 (10:1 hexane–ethyl acetate); mp 101–103 °C (lit.⁶ 101 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3051, 3021, 2958, 2930, 2910, 2835, 1921, 1887, 1619, 1605, 1505, 1454, 1255, 1185, 1170, 1025, 786, 743, 730, 524; ¹H NMR (400 MHz, CDCl₃): δ 3.89 (s, 3H, H₁₆), 7.03 (ddd, 2H, $J_{\text{H12-H11}} = J_{\text{H14-H15}} = 9.5$ Hz, $J_{\text{H12-H14}} = 2.5$ Hz, $J_{\text{H12-H15}} = J_{\text{H14-H11}} = 2.5$ Hz, H₁₂, H₁₄), 7.3–7.4 (m, 2H, H₆, H₅), 7.5–7.6 (m, 1H, H₇), 7.7–7.8 (m, 1H, H₄), 8.20 (ddd, 2H, $J_{\text{H11-H12}} = J_{\text{H15-H14}} = 9.5$ Hz, $J_{\text{H11-H15}} = 2.5$ Hz, $J_{\text{H11-H14}} = J_{\text{H15-H12}} = 2.5$ Hz, H₁₁, H₁₅); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.4 (C-16), 110.4 (C-7), 114.4 (C-12, C-14), 119.6 (C-4), 119.7 (C-10), 124.4 (C-6), 124.6 (C-5), 129.4 (C-11, C-15), 142.3 (C-9), 150.7 (C-8), 162.3 (C-13), 163.2 (C-2); MS m/z (relative intensity): 226 (16.4%), 225 (100%), 210 (36.6%), 182 (35.3%), 64 (16.6%), 63 (26.7%); Anal. Calcd for C₁₄H₁₁NO₂: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.64; H, 4.85; N, 6.22.

2-(4'-chlorophenyl)benzoxazole (entry 4 in Table 2)

R_f 0.34 (30:1 hexane–ethyl acetate); mp 153–154 °C (lit.⁶ 147 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3088, 3074, 3058, 3022, 1617, 1484, 1477, 1472, 1452, 1405, 1343, 1245, 1092, 1057, 1052, 1012, 832, 758, 739, 498; ¹H NMR (400 MHz, CDCl₃): δ 7.3–7.4 (m, 2H, H₆, H₅), 7.51 (ddd, 2H, $J_{\text{H11-H12}} = J_{\text{H15-H14}} = 9.1$ Hz, $J_{\text{H11-H15}} = 2.2$ Hz, $J_{\text{H11-H14}} = J_{\text{H15-H12}} = 2.2$ Hz, H₁₁, H₁₅), 7.5–7.6 (m, 1H, H₇), 7.7–7.8 (m, 1H, H₄), 8.20 (ddd, 2H, $J_{\text{H12-H11}} = J_{\text{H14-H15}} = 9.1$ Hz, $J_{\text{H12-H14}} = 2.2$ Hz, $J_{\text{H12-H15}} = J_{\text{H14-H11}} = 2.2$ Hz, H₁₂, H₁₄); ¹³C NMR (100.6 MHz, CDCl₃): δ 110.6 (C-7), 120.1 (C-4), 124.7 (C-6), 125.3 (C-5), 125.7 (C-10), 128.8 (C-11, C-15), 129.2 (C-12, C-14), 137.7 (C-13), 142.0 (C-9), 150.8 (C-8), 162.0 (C-2); MS m/z (relative intensity): 231 (33.1%), 229 (100%), 92 (17.6%), 64 (49.7%), 63 (62.1%), 38 (19.2%); Anal. Calcd for C₁₃H₈ClNO: C, 67.99; H, 3.51; N, 6.10. Found: C, 68.15; H, 3.55; N, 6.05.

2-(4'-cyanophenyl)benzoxazole (entry 5 in Table 2)

R_f 0.27 (10:1 hexane–ethyl acetate); mp 207–209 °C (lit.⁹ 207–208 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3095, 3051, 3047, 2229, 1600, 1494, 1475, 1452, 1411, 1343, 1242, 1056, 1013, 843, 817, 761, 751, 693, 622, 548; ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.6 (m, 2H, H₆, H₅), 7.6–7.7 (m, 1H, H₇), 7.8–7.9 (m, 3H, H₄, H₁₂, H₁₄), 8.37 (ddd, 2H, $J_{\text{H11-H12}} = J_{\text{H15-H14}} = 8.6$ Hz, $J_{\text{H11-H15}} = 1.7$ Hz, $J_{\text{H11-H14}} = J_{\text{H15-H12}} = 1.7$ Hz, H₁₁, H₁₅); ¹³C NMR (100.6 MHz, CDCl₃): δ 110.8 (C-7), 114.8 (C-13), 118.1 (C-16), 120.6 (C-4), 125.1 (C-6), 126.1 (C-5), 127.9 (C-11, C-15), 131.1 (C-10), 132.7 (C-12, C-14), 141.9 (C-9), 150.9 (C-8), 160.9 (C-2); MS m/z (relative intensity): 221 (15.9%), 220 (100%), 192 (12.4%), 64 (31.1%), 63 (36.3%), 38 (10.2%); Anal. Calcd for C₁₄H₈N₂O: C, 76.35; H, 3.66; N, 12.72. Found: C, 76.45; H, 3.78; N, 12.55.

2-(4'-nitrophenyl)benzoxazole (entry 6 in Table 2)

R_f 0.29 (15:1 hexane–ethyl acetate); mp 269–270 °C (lit.⁶ 266–268 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3107, 3093, 3056, 3049, 2845, 1597, 1554, 1521, 1451, 1347, 1338, 1301, 1240, 1105, 1058, 857, 852, 766, 753, 707; ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.5 (m, 2H, H₆, H₅), 7.64 (dd, 1H, J_{H7-H6} = 6.5 Hz, J_{H7-H5} = 2.7 Hz, H₇), 7.83 (dd, 1H, J_{H4-H5} = 6.5 Hz, J_{H4-H6} = 2.7 Hz, H₄), 8.4–8.5 (m, 4H, H₁₁, H₁₂, H₁₄, H₁₅); ¹³C NMR (100.6 MHz, CDCl₃): δ 111.0 (C-7), 120.7 (C-4), 124.2 (C-11, C-15), 125.2 (C-6), 126.3 (C-5), 128.4 (C-12, C-14), 132.8 (C-10), 141.9 (C-9), 149.4 (C-13), 151.0 (C-8), 160.7 (C-2); MS m/z (relative intensity): 240 (100%), 210 (20.6%), 194 (31.6%), 182 (20.6%), 139 (20.9%), 64 (22.4%), 63 (38.1%); Anal. Calcd for C₁₃H₈N₂O₃: C, 65.00; H, 3.36; N, 11.66. Found: C, 64.94; H, 3.32; N, 11.53.

5-methyl-2-phenylbenzoxazole (entry 7 in Table 2)

R_f 0.26 (30:1 hexane–ethyl acetate); mp 108 °C (lit.⁶ 103 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3056, 2918, 2863, 1956, 1894, 1818, 1766, 1725, 1584, 1552, 1475, 1447, 1295, 1199, 1021, 927, 827, 797, 701, 597; ¹H NMR (400 MHz, CDCl₃): δ 2.48 (s, 3H, H₁₆), 7.15 (dd, 1H, J_{H6-H7} = 8.3 Hz, J_{H6-H4} = 1.2 Hz, H₆), 7.44 (d, 1H, J_{H7-H6} = 8.3 Hz, H₇), 7.4–7.5 (m, 3H, H₁₂, H₁₃, H₁₄), 7.55 (d, 1H, J_{H4-H6} = 1.2 Hz, H₄), 8.2–8.3 (m, 2H, H₁₁, H₁₅); ¹³C NMR (100.6 MHz, CDCl₃): δ 21.4 (C-16), 109.8 (C-7), 119.9 (C-4), 126.1 (C-6), 127.3 (C-10), 127.5 (C-11, C-15), 128.8 (C-12, C-14), 131.2 (C-13), 134.3 (C-5), 142.3 (C-9), 148.9 (C-8), 163.0 (C-2); MS m/z (relative intensity): 209 (100%), 208 (33.6%), 78 (48.0%), 77 (41.5%), 52 (25.7%), 51 (37.3%); Anal. Calcd for C₁₄H₁₁NO: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.34; H, 5.37; N, 6.73.

5-nitro-2-phenylbenzoxazole (entry 8 in Table 2)

R_f 0.26 (15:1 hexane–ethyl acetate); mp 177 °C (lit.⁹ 171.5–172.5 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3100, 3070, 3042, 2861, 1910, 1615, 1553, 1527, 1482, 1450, 1350, 1338, 1320, 1267, 1024, 821, 738, 705, 689, 489; ¹H NMR (400 MHz, CDCl₃): δ 7.5–7.6 (m, 3H, H₁₂, H₁₃, H₁₄), 7.69 (d, 1H, J_{H7-H6} = 9.2 Hz, H₇), 8.2–8.3 (m, 2H, H₁₁, H₁₅), 8.33 (dd, 1H, J_{H6-H7} = 9.2 Hz, J_{H6-H4} = 2.0 Hz, H₆), 8.66 (d, 1H, J_{H4-H6} = 2.0 Hz, H₄); ¹³C NMR (100.6 MHz, CDCl₃): δ 110.7 (C-7), 116.2 (C-4), 121.1 (C-6), 125.9 (C-10), 128.0 (C-11, C-15), 129.1 (C-12, C-14), 132.6 (C-13), 142.5 (C-9), 145.4 (C-5), 154.2 (C-8), 165.9 (C-2); MS m/z (relative intensity): 240 (100%), 194 (52.9%), 91 (100%), 63 (100%), 62 (41.1%), 51 (43.5%); Anal. Calcd for C₁₃H₈N₂O₃: C, 65.00; H, 3.36; N, 11.66. Found: C, 64.94; H, 3.42; N, 11.58.

2-(4'-methoxyphenyl)5-nitrobenzoxazole (entry 9 in Table 2)

R_f 0.21 (10:1 hexane–ethyl acetate); mp 188 °C (lit.⁹ 184–186 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3108, 3066, 3011, 2969, 2948, 2917, 2841, 1616, 1602, 1551, 1520, 1426, 1345, 1252, 1173, 1022, 839, 822, 745, 521; ¹H NMR (400 MHz, CDCl₃): δ 3.92 (s, 3H, H₁₆), 7.06 (ddd, 2H, $J_{H12-H11}$ = $J_{H14-H15}$ = 9.5 Hz, $J_{H12-H14}$ = 2.5 Hz, $J_{H12-H15}$ = $J_{H14-H11}$ = 2.5 Hz, H₁₂, H₁₄), 7.65 (d, 1H, J_{H7-H6} = 8.8

Hz, H₇), 8.23 (ddd, 2H, $J_{\text{H11-H12}} = J_{\text{H15-H14}} = 9.5$ Hz, $J_{\text{H11-H15}} = 2.5$ Hz, $J_{\text{H11-H14}} = J_{\text{H15-H12}} = 2.5$ Hz, H₁₁, H₁₅), 8.29 (dd, 1H, $J_{\text{H6-H8}} = 8.8$ Hz, $J_{\text{H6-H4}} = 2.1$ Hz, H₆), 8.60 (d, 1H, $J_{\text{H4-H6}} = 2.1$ Hz, H₄); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.5 (C-16), 110.4 (C-7), 114.6 (C-12, C-14), 115.7 (C-4), 118.3 (C-6), 120.6 (C-10), 129.9 (C-11, C-15), 142.8 (C-9), 145.3 (C-5), 154.3 (C-8), 163.2 (C-13), 166.1 (C-2); MS *m/z* (relative intensity): 271 (15.7%), 270 (100%), 224 (49.4%), 91 (58.6%), 79 (13.6%), 63 (59.3%); Anal. Calcd for C₁₄H₁₀N₂O₄: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.42; H, 3.77; N, 10.32.

2-(4'-chlorophenyl)5-nitrobenzoxazole (entry 10 in Table 2)

R_f 0.28 (15:1 hexane-ethyl acetate); mp 219 °C (lit.⁹ 218–219 °C); IR (KBr): ν_{max} (cm⁻¹) 3051, 3021, 2958, 2930, 2910, 2835, 1921, 1887, 1619, 1605, 1505, 1454, 1255, 1185, 1170, 1025, 786, 743, 730, 524; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (ddd, 2H, $J_{\text{H12-H11}} = J_{\text{H14-H15}} = 9.1$ Hz, $J_{\text{H12-H14}} = 2.3$ Hz, $J_{\text{H14-H11}} = J_{\text{H12-H15}} = 2.3$ Hz, H₁₂, H₁₄), 7.69 (d, 1H, $J_{\text{H7-H6}} = 9.1$ Hz, H₇), 8.22 (ddd, 2H, $J_{\text{H11-H12}} = J_{\text{H15-H14}} = 9.1$ Hz, $J_{\text{H11-H15}} = 2.3$ Hz, $J_{\text{H11-H14}} = J_{\text{H15-H12}} = 2.3$ Hz, H₁₁, H₁₅), 8.34 (dd, 1H, $J_{\text{H7-H6}} = 9.1$ Hz, $J_{\text{H6-H4}} = 2.1$ Hz, H₆), 8.65 (d, 1H, $J_{\text{H4-H6}} = 2.1$ Hz, H₄); ¹³C NMR (100.6 MHz, CDCl₃): δ 110.8 (C-7), 116.4 (C-4), 121.4 (C-6), 124.5 (C-10), 129.3 (C-11, C-15), 129.6 (C-12, C-14), 139.1 (C-13), 142.5 (C-9), 145.6 (C-5), 154.3 (C-8), 165.1 (C-2); MS *m/z* (relative intensity): 276 (28.1%), 274 (83.5%), 228 (30.4%), 91 (100%), 63 (78.5%), 62 (24.3%); Anal. Calcd for C₁₃H₇ClN₂O₃: C, 56.85; H, 2.57; N, 10.20. Found: C, 57.04; H, 2.57; N, 10.22.

2-pivalbenzoxazole (3)

R_f 0.31 (60:1 hexane-ethyl acetate); IR (KBr): ν_{max} (cm⁻¹) 3057, 2974, 2934, 2906, 2871, 1706, 1611, 1564, 1456, 1293, 1244, 1126, 1099, 1002, 929, 790, 765, 751, 736, 408; ¹H NMR (400 MHz, CDCl₃): δ 1.50 (s, 9H, H₁₁), 7.2–7.3 (m, 2H, H₆, H₅), 7.4–7.5 (m, 1H, H₇), 7.6–7.7 (m, 1H, H₄); ¹³C NMR (100.6 MHz, CDCl₃): δ 28.5 (C-11), 34.2 (C-10), 110.3 (C-7), 119.7 (C-4), 123.9 (C-6), 124.4 (C-5), 141.3 (C-9), 150.8 (C-8), 173.5 (C-2); MS *m/z* (relative intensity): 175 (32.8%), 160 (100%), 133 (36.9%), 119 (31.0%), 41 (53.5%), 39 (32.0%); Anal. Calcd for C₁₁H₁₃NO: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.46; H, 7.54; N, 7.96.

2-cyclohexylbenzoxazole (4)

R_f 0.22 (50:1 hexane-ethyl acetate); mp 35 °C; IR (KBr): ν_{max} (cm⁻¹) 3054, 3019, 2954, 2922, 2850, 1611, 1568, 1460, 1449, 1376, 1245, 1160, 1130, 1017, 944, 893, 837, 757, 742, 425; ¹H NMR (400 MHz, CDCl₃): δ 1.3–1.5 (m, 3H, H₁₂, H₁₃, H₁₄), 1.7–1.8 (m, 3H, H₁₁, H₁₃, H₁₅), 1.8–1.9 (m, 2H, H₁₂, H₁₄), 2.1–2.2 (m, 2H, H₁₁, H₁₅), 2.96 (tt, 1H, $J_{\text{H10-H11}} = J_{\text{H10-H15}} = 11.3$ Hz, $J_{\text{H10-H11}} = J_{\text{H10-H15}} = 3.7$ Hz, H₁₀), 7.2–7.3 (m, 2H, H₆, H₅), 7.4–7.5 (m, 1H, H₇), 7.6–7.7 (m, 1H, H₄); ¹³C NMR (100.6 MHz, CDCl₃): δ 25.6 (C-12, C-14), 25.8 (C-13), 30.5 (C-11, C-15), 37.9 (C-10), 110.2 (C-7), 119.6 (C-4), 123.9 (C-6), 124.3 (C-5), 141.3 (C-9), 150.6 (C-8), 170.4 (C-2); MS *m/z* (relative intensity): 201 (11.3%), 172 (13.0%), 160 (11.9%), 147 (14.9%), 146 (88.3%), 133 (100%), 65 (11.3%), 64 (13.6%), 63 (16.7%), 55 (17.6%), 41 (32.0%), 39 (21.2%); Anal. Calcd for C₁₃H₁₅NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.47; H, 7.59; N, 7.07.

2-phenylbenzimidazole (**5**)

R_f 0.36 (30:1 hexane–ethyl acetate); mp 299–301 °C (lit.⁸ 296–297.5 °C); IR (KBr): $\nu_{\max}$ (cm⁻¹) 3046, 2967, 2834, 2718, 2675, 2534, 1890, 1591, 1463, 1445, 1411, 1316, 1277, 1227, 1120, 745, 738, 704, 687, 561; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.1–7.2 (m, 2H, H₆, H₅), 7.5–7.6 (m, 4H, H₇, H₁₂, H₁₃, H₁₄), 7.67 (d, 1H, $J_{\text{H4-H5}}$ = 7.6 Hz, H₄), 8.1–8.2 (m, 2H, H₁₁, H₁₅), 12.9 (s, 1H, H₁); ¹³C NMR (100.6 MHz, DMSO-*d*₆): δ 111.5 (C-7), 119.0 (C-4), 121.8 (C-6), 122.7 (C-5), 126.6 (C-12, C-14), 129.1 (C-11, C-15), 130.0 (C-13), 130.3 (C-10), 135.2 (C-9), 144.0 (C-8), 151.4 (C-2); MS m/z (relative intensity): 195 (13.9%), 194 (100%), 193 (26.0%), 97 (13.5%), 64 (16.0%), 63 (18.2%); Anal. Calcd for C₁₃H₁₀N₂: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.25; H, 5.20; N, 14.35.

Analytical data of ICP-AES

Element	Darco [®] KB (ppm)	Darco [®] KB-B (ppm)	Darco [®] G-60 (ppm)
Li	34.5	41.5	0.32
B	6.61	20	4.93
Na	1750	1753	268
Mg	86.9	54.80	409
Al	831	1130	156
Si	200	130	302
P	3931	3710	197
K	517	575	43.1
Ca	605.5	423	544.0
Ti	38.05	30.52	73.2
Cr	6.9	5.80	— ^b
Mn	9.99	4.1	6.5
Fe	299	98.3	175
Cu	16.77	29.8	6.88
Zn	5.36	31.8	37
Sr	12.3	7.07	6.01
Y	0.67	— ^a	— ^b
Sn	12	13	— ^b
Ba	14.6	7.76	22.6
Eu	0.23	— ^a	— ^a
Ho	0.45	— ^b	0.6
Er	9.33	7.83	18.3
W	5.59	4.06	— ^b

^a Under the level of determination limit (10 σ method). ^b Under the level of detection limit (3 σ method).

Darco[®] KB: The following elements were not observed above the level of determination limit (10 σ method); V, Co, Ni, As, Rb, Mo, Ru, Pd, In, Nd, Tb, Dy. The following elements were not observed above the level of detection limit (3 σ method); Be, Ga, As, Se, Zr, Rh, Ag, Cd, Sb, La, Ce, Sm, Pr, Gd, Yb, Re, Os, Ir, Pt, Au, Pb, Bi.

Darco[®] KB-B: The following elements were not observed above the level of determination limit (10 σ method); Ni, Y, Zr, Mo, Ru, Pd, Ag, In, Sb, Pr, Nd, Eu, Tb, Pt, Pb. The following elements were not observed above the level of detection limit (3 σ method); Be, V, Co, Ga, As, Se, Rb, Rh, Cd, Sb, La, Ce, Sm, Gd, Dy, Ho, Yb, Re, Os, Ir, Au, Bi.

Darco[®] G-60: The following elements were not observed above the level of determination limit; Be, Co, Ni, Se, Zr, Ru, Pd, In, Nd, Eu, Tb, Pt (10 σ method). The following elements were not observed above the level of detection limit (3 σ method); V, Cr, Co, Ga, As, Rb, Y, Mo, Rh, Ag, Cd, Sn, Sb, La, Ce, Pr, Sm, Gd, Dy, Yb, W, Re, Os, Ir, Au, Pb, Bi.