Supporting Information

Carbon-Carbon Bond Cleavage of Diynes through the Hydroamination with Transition Metal-Catalysts

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Experimental

General Information. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JNM GSX-270 (270 MHz), JEOL JNM LA-300 (300 MHz) and JEOL JNM α -500 (500 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CHCl_3 at 7.24 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. IR spectra were recorded on a SHIMADZU FTIR-8200A spectrometer; absorptions are reported in cm^{-1} . High-resolution mass spectra were obtained on a JEOL JMS-DX303, JEOL JMS-AX500 and BRUKER APEXIII spectrometers. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40–100 μm , KANTO Chemical Co. and Aluminum oxide 90 standardized (Merck). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254} (Merck). Gel permeation chromatography (GPC) was carried out employing JIAGEL-1H and JIAGEL-2H on JAILC-918.

Materials. Anhydrous methanol and $n\text{-BuOH}$ (WAKO), 2-aminophenol (**2a–2d**, **2f**, **2g**) (TCI), **2h** (WAKO) internal diynes (**1o** and **1p**) (Aldrich), $\text{Ru}_3(\text{CO})_{12}$ (Aldrich), $\text{Pd}(\text{NO}_3)_2$ (TCI) and NH_4PF_6 (WAKO) were purchased and used as received. Terminal diynes (**1a–1g**) and aminophenol **2e** were prepared according to the literature procedures.^{1,2} All other compounds used are commercially available.

Typical procedure for the ruthenium-catalyzed C-C bond cleavage of terminal diynes

To a methanol suspension (0.05 mL) of 2-aminophenol (81.8 mg, 0.75 mmol), $\text{Ru}_3(\text{CO})_{12}$ (3.2 mg, 0.005 mmol) and NH_4PF_6 (2.5 mg, 0.015 mmol), 1,3-decadiyne (**1a**) (67.1 mg, 0.50 mmol) was added under an argon atmosphere. The suspension was heated at 80 $^\circ\text{C}$ for 20 hour. The reaction mixture was cooled to room temperature and filtered through a short Al_2O_3 pad and the filtrate was concentrated. The residue was purified by column chromatography (silica gel, pentane-diethyl ether 10/1~5/1) to afford 2-hexylbenzoxazole **3a** in 75 % yield (76.0 mg) and 2-methylbenzoxazole **4a** in 23 % yield (14.2 mg).

Typical procedure for the palladium-catalyzed C-C bond cleavage of internal diynes

To a n -butanol suspension (0.05 mL) of 2-aminophenol (81.8 mg, 0.75 mmol) and $\text{Pd}(\text{NO}_3)_2$ (6.9 mg, 0.030 mmol), 5,7-dodecadiyne (**1o**) (81.1 mg, 0.50 mmol) was added under an argon atmosphere. The suspension was heated at 120 $^\circ\text{C}$ for 4 hour. The reaction mixture was cooled to room temperature and filtered through a short Al_2O_3 pad and the filtrate was concentrated. The residue was purified by column chromatography (silica gel, hexane-ethyl acetate 20/1) to afford a mixture of 2-pentylbenzoxazole **3o** and 2-butylbenzoxazole **4o**. Further purification using GPC afforded **3o** in 35 % yield (33.0 mg) and **4o** in 38 % yield (33.0 mg).

Analytical Data

1,3-Decadiyne (1a): colorless oil; ^1H NMR (270.20 MHz, CDCl_3) δ 0.89 (3H, t, J = 6.8 Hz), 1.30–1.40 (8H, m), 1.95 (1H, t, J = 1.1 Hz), 2.25 (2H, td, J = 7.0, 1.1 Hz); ^{13}C NMR (67.90 MHz, CDCl_3) δ 14.0, 19.0, 22.5, 28.0, 31.2, 64.4, 64.7, 68.5, 78.5; IR (neat) 3310, 2932, 2860, 2064, 1466, 1225 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{13}$ (M^+) 133.1024. Found 133.1018; Registry No. 55682-66-1.

1,3-Tetradecadiyne (1b): colorless oil; ^1H NMR (270.20 MHz, CDCl_3) δ 0.88 (3H, t, J = 6.6 Hz), 1.20-1.40 (14H, m), 1.50-1.60 (2H, m), 1.95 (1H, t, J = 1.3 Hz), 2.25 (2H, td, J = 7.0, 1.3 Hz); ^{13}C NMR (67.90 MHz, CDCl_3) δ 14.0, 19.0, 22.7, 28.0, 28.8, 29.1, 29.3, 29.5, 29.5, 31.9, 64.4, 64.6, 68.5, 78.5; IR (neat) 3584, 3312, 2926, 2855, 2297, 2226, 1466, 1211, 610 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{22}$ (M^+) 190.1760. Found 190.1721; Registry No. 66363-13-1.

1-Cyclohexyl-1,3-butadiyne (1c): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.53-1.20 (6H, m), 1.61-1.82 (4H, m), 1.78 (1H, s), 2.49-2.38 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 24.6, 25.7, 29.2, 31.9, 24.6, 25.0, 28.5, 82.2; IR (neat) 3306, 2939, 2856, 2226, 1448, 1234 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{22}$ (M^+) 132.0939. Found 132.0952; Registry No. 6248-06-2.

5,5-Dimethyl-1,3-pentadiyne (1d): colorless oil; ^1H NMR (270.20 MHz, CDCl_3) δ 1.23 (1H, s), 2.20 (s, 9H); ^{13}C NMR (67.90 MHz, CDCl_3) δ 27.8, 30.3, 63.4, 65.6, 68.3, 85.8; IR (neat) 3584, 3304, 2972, 2932, 2870, 2326, 2233, 1477, 1456, 1364, 1267, 1204, 1059, 918, 816, 617 cm^{-1} ; HRMS (EI) Calcd for C_8H_{10} (M^+) 106.0769. Found 106.0781; Registry No. 4911-56-2.

6-Phenyl-1,3-hexadiyne (1e): colorless oil; ^1H NMR (270.20 MHz, CDCl_3) δ 2.05 (1H, m), 2.64 (2H, t, J = 7.5 Hz), 2.95 (2H, t, J = 7.5 Hz), 7.4-7.3 (5H, m); ^{13}C NMR (67.90 MHz, CDCl_3) δ 21.0, 34.2, 64.9, 65.4, 68.3, 77.4, 126.4, 128.2, 128.4, 139.7; IR (neat) 3306, 3030, 2224, 1605, 1497, 1454, 1423, 1340, 1076, 1030, 789, 698, 621 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{10}$ (M^+) 154.0775. Found 154.0781; Registry No. 189317-64-4.

8-Triisopropylsilyloxy-1,3-octadiyne (1f): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.99-1.09 (21H, m), 1.58-1.67 (4H, m), 1.94 (1H, s), 2.24-2.33 (2H, m), 2.65-3.72 (2H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 12.0, 18.0, 18.9, 24.6, 30.3, 31.9, 62.6, 64.4, 68.5, 78.4; IR (neat) 3314, 2948, 2866, 2256, 1464, 1109, 883, 681 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{23}\text{SiO}$ ($\text{M}^+ - i\text{Pr}$) 235.1518. Found 235.1505.

7-Chloro-1,3-heptadiyne (1g): colorless oil; ^1H NMR (270.20 MHz, CDCl_3) δ 2.00 (1H, t, J = 0.9 Hz), 2.0 (5H, m), 2.48 (2H, td, J = 7.0, 1.1 Hz), 3.65 (2H, t, J = 6.2 Hz); ^{13}C NMR (67.90 MHz, CDCl_3) δ 16.4, 30.7, 43.3, 65.0, 65.6, 68.1, 76.3; IR (neat) 3290, 2962, 2922, 1441, 1425, 1290, 725 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_7\text{H}_7\text{Cl}$ (M^+) 126.0225. Found 126.0236; Registry No. 98550-64-2.

2-Hexylbenzoxazole (3a): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.82-0.91 (3H, m), 1.20-1.48 (6H, m), 1.86 (2H, tt, J = 7.5, 7.5 Hz), 2.91 (2H, t, J = 7.5 Hz), 7.24-7.31 (2H, m), 7.42-7.49 (1H, m), 7.60-7.68 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.00, 22.46, 26.73, 28.64, 28.83, 31.38, 110.22, 119.49, 124.00, 124.35, 141.37, 150.75, 167.38; IR (neat) 2957, 2930, 2858, 1728, 1614, 1574, 1456, 1242, 1151, 745 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ (M^+) 203.1310. Found 203.1292; Registry No.

6797-16-6.

2-Dodecylbenzoxazole (3b): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.86 (3H, t, $J = 7.0$ Hz), 1.17-1.47 (14H, m), 1.87 (2H, tt, $J = 7.9$, 7.9 Hz), 2.90 (2H, t, $J = 7.9$ Hz), 7.20-7.32 (2H, m), 7.40-7.50 (1H, m), 7.60-7.69 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.1, 22.7, 26.8, 28.6, 29.1, 29.2, 29.3, 29.4, 29.5, 31.9, 110.2, 119.5, 124.0, 124.3, 141.4, 150.8, 167.4; IR (neat) 3055, 2953, 2853, 1614, 1572, 1456, 1242, 1151, 748 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}$ (M^+) 259.1936. Found 259.1917.

2-Cyclohexylbenzoxazole (3c): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.20-1.50 (3H, m), 1.59-1.91 (5H, m), 2.06-2.21 (2H, m), 2.93 (1H, tt, $J = 11.3$, 3.8 Hz), 7.20-7.32 (2H, m), 7.39-7.49 (1H, m), 7.60-7.70 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 25.6, 25.8, 30.5, 37.9, 110.3, 119.6, 123.9, 124.3, 141.3, 150.6, 170.4; IR (neat) 2982, 2855, 1612, 1568, 1456, 1244, 1157, 743 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$ (M^+) 201.1153. Found 201.1162; Registry No. 104462-82-0.

2-(1,1-Dimethylethyl)benzoxazole (3d): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.48 (9H, s), 7.24-7.31 (2H, m), 7.43-7.50 (1H, m), 7.64-7.71 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 28.5, 34.2, 110.3, 119.7, 123.9, 124.4; IR (neat) 3057, 2974, 2932, 2870, 1612, 1566, 1456, 1244, 1126, 1099, 930, 791, 752, 737 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}$ (M^+) 175.0997. Found 175.1007; Registry No. 54696-03-6.

2-Phenethylbenzoxazole (3e): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 3.22 (4H, brs), 7.16-7.33 (7H, m), 7.42-7.51 (1H, m), 7.65-7.70 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 30.5, 32.8, 110.3, 119.6, 124.1, 124.6, 126.5, 128.3, 128.6, 140.1; IR (neat) 3028, 2934, 1614, 1570, 1456, 1242, 744, 702 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$ (M^+) 223.0997. Found 223.0991; Registry No. 83318-25-6.

2-(4-Triisopropylsiloxybutyl)benzoxazole (3f): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.98-1.10 (21H, m), 1.67 (2H, tt, $J = 7.4$, 6.3 Hz), 1.96 (2H, tt, $J = 7.4$, 7.4 Hz), 2.96 (2H, t, $J = 7.4$ Hz), 3.73 (2H, t, $J = 6.3$ Hz), 7.22-7.31 (2H, m), 7.41-7.48 (1H, m), 7.61-7.67 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 11.9, 18.0, 23.3, 28.4, 32.3, 62.8, 110.2, 119.5, 124.0, 124.4, 141.4, 150.8, 167.2; IR (neat) 2943, 2866, 1616, 1574, 1456, 1242, 1107, 883, 745 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{33}\text{NO}_2$ (M^+) 347.2280. Found 347.2292.

2-(3-Chloropropyl)benzoxazole (3g): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.37 (2H, tt, $J = 7.3$, 6.1 Hz), 3.12 (2H, t, $J = 7.3$ Hz), 3.69 (2H, t, $J = 6.1$ Hz), 7.25-7.35 (2H, m), 7.42-7.51 (1H, m), 7.61-7.70 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 25.7, 29.3, 43.8, 110.3, 119.6, 124.2, 124.7, 141.2, 150.8, 165.7; IR (neat) 2963, 2926, 1614, 1574, 1456, 1242, 746 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_9\text{NOCl}$ (M^+) 195.0451. Found 195.0438; Registry No. 51111-00-3.

2-Methylbenzoxazole (4a-4g, 14): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.61 (3H, s), 7.20-7.30 (2H, m), 7.39-7.47 (1H, m), 7.58-7.66 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.5, 110.1, 119.4, 124.0, 124.4, 141.5, 150.9, 163.7; IR (neat) 3061, 1618, 1578, 1456, 1267, 1242, 1169, 924, 831, 745 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_8\text{H}_7\text{NO}$ (M^+) 133.0528. Found 133.0539; Registry No. 95-21-6.

2-Hexyl-5-nitrobenzoxazole (3h): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.85 (3H, m), 1.23-1.50 (6H, m), 1.89 (2H, tt, $J = 7.5, 7.5$ Hz), 2.96 (2H, t, $J = 7.5$ Hz), 7.56 (1H, d, $J = 8.7$ Hz), 8.26 (1H, dd, $J = 8.7, 2.4$ Hz), 8.54 (1H, d, $J = 2.4$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.0, 22.4, 26.5, 28.7, 28.8, 31.3, 110.4, 116.0, 120.7, 141.9, 145.1, 154.4, 170.6; IR (neat) 3109, 3047, 2949, 2930, 2868, 2853, 1618, 1529, 1346, 1146, 955, 905, 839, 741, 692 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3$ (M^+) 248.1161. Found 248.1133.

2-Methyl-5-nitrobenzoxazole (4h): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.69 (3H, s), 7.56 (1H, d, $J = 8.7$ Hz), 8.26 (1H, dd, $J = 8.7, 2.3$ Hz), 8.53 (1H, d, $J = 2.3$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.7, 110.4, 115.9, 120.7, 142.0, 145.1, 154.5, 167.1; IR (neat) 3103, 3065, 1616, 1576, 1520, 1348, 1261, 1167, 1067, 912, 829, 739, 694 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_8\text{H}_6\text{N}_2\text{O}_3$ (M^+) 178.0378. Found 178.0368; Registry No. 32046-51-8.

2-Hexyl-5-chlorobenzoxazole (3i): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.87 (3H, m), 1.20-1.47 (6H, m), 1.85 (2H, tt, $J = 7.6, 7.6$ Hz), 2.90 (2H, t, $J = 7.6$ Hz), 7.24 (1H, dd, $J = 8.5, 2.0$ Hz), 7.37 (1H, d, $J = 8.5$ Hz), 7.62 (1H, d, $J = 2.0$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.99, 22.44, 26.63, 28.66, 28.80, 31.35, 110.94, 119.56, 124.65, 129.50, 142.55, 149.35, 168.87; IR (KBr) 2961, 2934, 2860, 1570, 1452, 1258, 1152, 818, 704 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}\text{NOCl}$ (M^+) 237.0915. Found 237.0907.

5-Chloro-2-methylbenzoxazole (4i): colorless solid; ^1H NMR (300.40 MHz, CDCl_3) δ 2.62 (3H, s), 7.24 (1H, dd, $J = 7.9, 2.2$ Hz), 7.36 (1H, d, $J = 7.9$ Hz), 7.61 (1H, d, $J = 2.2$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.58, 110.91, 119.48, 124.74, 129.57, 142.65, 149.54, 165.29; IR (KBr) 3055, 2924, 1609, 1574, 1458, 1435, 1256, 1167, 1049, 908, 802 cm^{-1} ; Registry No. 19219-99-9.

2-Hexyl-5-methylbenzoxazole (3j): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.81-0.92 (3H, m), 1.20-1.46 (6H, m), 1.85 (2H, tt, $J = 7.6, 7.6$ Hz), 2.43 (3H, s), 2.88 (2H, t, $J = 7.6$ Hz), 7.07 (1H, dd, $J = 8.4, 1.4$ Hz), 7.32 (1H, d, $J = 8.4$ Hz), 7.42 (1H, d, $J = 1.4$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.99, 21.40, 22.45, 26.75, 28.67, 28.82, 31.38, 109.55, 119.44, 125.34, 133.74, 141.58, 148.98, 167.44; IR (neat) 2957, 2930, 2858, 1574, 1261, 1159, 799 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ (M^+) 217.1461. Found 217.1456.

2,5-Dimethylbenzoxazole (4j): pale yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.44 (3H, s), 2.59 (3H, s), 7.07 (1H, d, $J = 8.5$ Hz), 7.31 (1H, d, $J = 8.5$ Hz), 7.40 (1H, s); Registry No. 5676-58-4.

2-Hexyl-5-methoxybenzoxazole (3k): pale yellow; ^1H NMR (300.40 MHz, CDCl_3) δ 0.82-0.92 (3H, m), 1.20-1.46 (6H, m), 1.85 (2H, tt, $J = 7.6, 7.6$ Hz), 2.87 (2H, t, $J = 7.6$ Hz), 3.83 (3H, s), 6.86 (1H, dd, $J = 9.0, 2.5$ Hz), 7.14 (1H, d, $J = 2.5$ Hz), 7.33 (1H, d, $J = 9.0$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.02, 22.47, 26.75, 28.74, 28.83, 31.40, 55.93, 102.78, 110.30, 112.61, 142.22, 145.38, 156.98, 168.25; IR (neat) 2955, 2932, 2858, 1574, 1483, 1441, 1196, 1151, 1030, 837, 804 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ (M^+) 233.1410. Found 233.1407.

2-Methyl-5-methoxybenzoxazole (4k): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.59 (3H, s), 2.82 (3H, s), 6.86 (1H, dd, $J = 8.9, 2.6$ Hz), 7.12 (1H, d, $J = 2.6$ Hz), 7.32 (1H, d, $J = 8.9$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.62, 55.93, 102.71, 110.26, 112.65, 142.35, 145.59, 157.02, 164.63; IR (neat) 2939, 2843, 1574, 1446, 1279, 1153, 1030, 935, 864, 812 cm^{-1} ; Registry No. 5676-57-3.

2-Hexyl-6-nitrobenzoxazole (3l): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.81-0.92 (3H, m), 1.20-1.50 (6H, m), 1.89 (2H, tt, $J = 7.6, 7.6$ Hz), 2.97 (2H, t, $J = 7.6$ Hz), 7.73 (1H, d, $J = 8.7$ Hz), 8.26 (1H, dd, $J = 8.7, 2.0$ Hz), 8.38 (1H, d, $J = 2.30$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.97, 22.41, 26.47, 28.75, 28.84, 31.29, 106.90, 119.39, 120.32, 144.85, 146.72, 149.89, 172.35; IR (neat) 3107, 2928, 2855, 1570, 1526, 1346, 1148, 937, 893, 827, 737 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3$ (M^+) 248.1155. Found 248.1149.

2-Methyl-6-nitrobenzoxazole (4l): colorless solid; ^1H NMR (300.40 MHz, CDCl_3) δ 2.71 (3H, s), 7.72 (1H, d, $J = 8.9$ Hz), 8.26 (1H, d, $J = 8.9, 2.3$ Hz), 8.37 (1H, d, $J = 2.3$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.87, 100.54, 106.88, 119.36, 120.38, 146.82, 150.09, 168.75; IR (KBr) 3074, 7061, 1578, 1522, 1352, 1269, 912, 827, 735 cm^{-1} ; Registry No. 5683-43-2.

2-Hexyl-6-methylbenzoxazole (3m): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.80-0.90 (3H, m), 1.20-1.46 (6H, m), 1.84 (2H, tt, $J = 7.5, 7.5$ Hz), 2.45 (3H, s), 2.88 (2H, t, $J = 7.5$ Hz), 7.08 (1H, d, $J = 8.0$ Hz), 7.25 (1H, s), 7.50 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.99, 21.62, 22.45, 26.73, 28.61, 31.38, 110.42, 118.79, 125.11, 134.62, 139.14, 151.04, 166.79; IR (neat) 2957, 2930, 2858, 1614, 1574, 1487, 1456, 1258, 1242, 1117, 941, 810 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ (M^+) 217.1461. Found 217.1457.

2,6-Dimethylbenzoxazole (4m): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.45 (3H, s), 2.59 (3H, s), 7.08 (1H, d, $J = 7.9$ Hz), 7.25 (1H, s), 7.48 (1H, d, $J = 7.9$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.49, 21.64, 110.38, 118.70, 125.19, 134.71, 139.27, 151.25, 163.21; IR (neat) 2926, 1616, 1580, 1489, 1435, 1244, 1119, 943, 912, 847, 812 cm^{-1} ; Registry No. 53612-61-6.

2-Hexyl-4-methylbenzoxazole (3n): pale yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.80-0.92 (3H, m), 1.20-1.47 (6H, m), 1.84 (2H, tt, $J = 7.6, 7.6$ Hz), 2.58 (3H, s), 2.92 (2H, t, $J = 7.6$ Hz), 7.07 (1H, d, $J = 8.0$ Hz), 7.16 (1H, dd, $J = 8.0, 8.0$ Hz), 7.28 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.98, 16.50, 22.45, 27.06, 28.80, 28.88, 31.38, 107.53, 123.97, 124.57, 129.85, 140.54, 150.52, 166.54; IR (neat) 2957, 2930, 2858, 1611, 1578, 1456, 1423, 1240, 1070, 750 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ (M^+) 217.1461. Found 217.1457.

2,4-Dimethylbenzoxazole (4n): pale yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.57 (3H, s), 2.62 (3H, s), 7.07 (1H, d, $J = 7.5$ Hz), 7.16 (1H, dd, $J = 7.5$ Hz), 7.27 (1H, d, $J = 7.5$ Hz); Registry No. 72692-90-1.

2-Butylbenzoxazole (3o): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.96 (3H, t, $J = 7.6$ Hz), 1.44 (2H, tq, $J = 7.6, 7.6$ Hz), 1.86 (2H, tt, $J = 7.6, 7.6$ Hz), 2.92 (2H, t, $J = 7.6$ Hz), 7.22-7.32 (2H, m), 7.42-7.50 (1H, m), 7.61-7.69 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.7, 22.3, 28.3, 28.8, 110.2, 119.5, 124.0, 124.3, 141.4, 150.8, 167.3; IR (neat) 2960, 2933, 2873, 1615, 1573, 1456, 1242, 1166, 1152, 745 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}$ (M^+) 175.0997. Found 175.0991.

2-Pentylbenzoxazole (4o): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.83-0.95 (3H, m), 1.27-1.46 (4H, m), 1.87 (2H, tt, $J = 7.8, 7.8$ Hz), 2.91 (2H, t, $J = 7.8$ Hz), 7.20-7.31 (2H, m), 7.40-7.50 (1H, m), 7.58-7.70 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.9, 22.3, 26.5, 28.6, 31.3, 110.2, 119.5, 124.0, 124.3, 141.4, 150.8, 167.4; IR (neat) 2959, 2932, 2860, 1614, 1572, 1456, 1242, 745, 665 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$ (M^+) 189.1154. Found 189.1162.

2-Phenylbenzoxazole (3p): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 7.31-7.38 (2H, m), 7.45-7.54 (3H, m), 7.54-7.61 (1H, m), 7.72-7.80 (1H, m), 8.21-8.29 (2H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 110.58, 120.01, 124.55, 125.09, 127.15, 127.60, 128.90, 131.50, 142.09, 150.74, 163.03; IR (KBr) 1616, 1553, 1456, 1242, 1053, 745, 704 cm^{-1} ; Registry No. 833-50-1.

2-Benzylbenzoxazole (4p): pale yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 4.20 (2H, s), 7.25-7.40 (7H, m), 7.40-7.50 (1H, m), 7.70-7.80 (1H, m); Registry No. 2008-07-3.

2-Ethylbenzoxazole (13): pale yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.45 (3H, t, $J = 7.6$ Hz), 2.93 (2H, q, $J = 7.6$ Hz), 7.20-7.30 (2H, m), 7.40-7.48 (1H, m), 7.60-7.68 (1H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 10.86, 22.12, 110.19, 119.49, 123.99, 124.37, 141.35, 150.79, 168.08; IR (KBr) 2984, 2941, 1614, 1573, 1456, 1244, 1153, 926, 822, 746 cm^{-1} ; Registry No. 6797-13-3.

2-Amino-4-methoxyphenol (2e)²: tan powder; ¹H NMR (300.40 MHz, CD₃CN) δ 3.63 (3H, s), 3.80-4.05 (2H, br s), 6.06 (1H, dd, J = 8.5, 3.0 Hz), 6.25 (1H, d, J = 3.0 Hz), 6.57 (1H, d, J = 8.5 Hz); ¹³C NMR (75.45 MHz, CD₃CN) δ 55.85, 102.50, 102.52, 115.98, 138.11, 138.77, 155.08; IR (neat) 3385, 3292, 1601, 1514, 1466, 1231, 1200, 1032, 839, 802, 710 cm⁻¹.

11: colorless oil; ¹H NMR (300.40 MHz, CDCl₃) δ 0.82-0.91 (3H, m), 1.20-1.48 (6H, m), 1.86 (2H, tt, J = 7.5, 7.5 Hz), 2.91 (2H, t, J = 7.5 Hz), 7.24-7.31 (2H, m), 7.42-7.49 (1H, m), 7.60-7.68 (1H, m); ¹³C NMR (75.45 MHz, CDCl₃) δ 14.00, 22.46, 26.73, 28.64, 28.83, 31.38, 110.22, 119.49, 124.00, 124.35, 141.37, 150.75, 167.38; IR (neat) 2957, 2930, 2858, 1728, 1614, 1574, 1456, 1242, 1151, 745 cm⁻¹; HRMS (EI) Calcd for C₁₃H₁₇NO (M⁺) 203.1310. Found 203.1292.

TIPSalkyl diyne

DPLE C:\WINNR95\COMMON\
COMPT TIPSalkyl diyne
DATIM Tue Jan 22 19:33:38
OBNUC 1H
EXMOD NON
OBREQ 300.40 MHz
OBSET 130.00 KHz
OBETN 1150.0 Hz
POINT 16384
PREQU 3300.3 Hz
SCANS 16
ACQTM 4.964 sec
PD 1.551 sec
PW1 5.3 us
IRNUC 1H
CTEMP 22.2 C
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.13 Hz
RGAIN 14

11

DFILE C:\WINNMR95\COMMON\
COMPT 2-Decylbenzoxazole
DATEIM Wed Jan 30 23:26:25
ORNUC 1H
EXMOD NON
OBFO 300.40 MHz
OBSET 130.00 KHz
OFFIN 1150.0 Hz
POINT 16384
FREOU 3300.3 Hz
SCANS 32
ACQTM 4.964 sec
PD 1.551 sec
FW 5.3 us
IRNUC 1H
CTEMP 21.0 C
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.13 Hz
RGAIN 15

2-TIPSoalkyl benzoxazole

DFILE C:\WINNR95\COMMON\
 COMNT 2-TIPSoalkyl benzoxa
 DATIM Tue Feb 05 02:16:06
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 16384
 FREQU 3300.3 Hz
 SCANS 32
 ACQTM 4.964 sec
 PD 1.551 sec
 FID 5.3 us
 IRNUC 1H 21.8 C
 CTMP CDCL3 7.24 ppm
 EXREF 0.13 Hz
 Bf 17
 RGAIN

5-Nitro-2-hexylbenzoxazole

DFILE C:\WINNMR95\COMMON\
 COMNT 5-Nitro-2-hexylbenz
 DATIM Fri Feb 01 23:52:25
 OBNUC 1H
 EXMOD NON
 OFFRQ 300.40 MHz
 ORSET 150.00 KHz
 OFFIN 1150.0 Hz
 POINT 16384
 FREQU 3300.3 Hz
 SCANS 32
 ACQTM 4.964 sec
 FID 1.551 sec
 FID 5.3 us
 TRUC 1H 21.0 C
 CTMP CDCL3
 SLANT 7.24 ppm
 EXREF 0.13 Hz
 BF 24
 RGAIN

2-Hexyl-5-methylbenzoxazole

DFILE C:\WINNR95\COMMON\
COMNT 2-Hexyl-5-methylbenz
DATIM Thu Dec 26 12:39:12
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 3300.3 Hz
SCANS 32
ACQTM 4.964 sec
PD 1.551 sec
FW 5.3 us
IRNUC 1H 21.3 C
CTEMP
SIVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 18

6-Methoxy-2-hexylbenzoxazole

DFILE C:\WINNR95\COMMON\
COMNT 6-Methoxy-2-hexylbenz
DATIM Thu Dec 26 01:30:45
OBNUC 1H
EXMOD NON
OBFREQ 300.40 MHz
OBSSET 130.00 KHz
OBSFID 1150.0 Hz
POINT 16384 Hz
FREQ 33001.2 Hz
SCANS 2
ACQTH 4.94 sec
PR 1.551 sec
PUL 5.3 us
TNUC 1H
CTEMP 22.4 C
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 22

DFILE C:\WINMR95\COMMON\
CONNT 5-Nitro-2-hexylbenz
DATIM Tue Dec 24 10:17:57
ORNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSEI 135.00 kHz
OBFTW 1150.0 Hz
PRENT 1638.0 Hz
FREQI 3300.3 Hz
SCANS 32
ACQTM 4.964 sec
PD 1.551 sec
PW1 5.3 us
IRNUC 1H
CTEMP 21.1 C
SLVNT CDCl3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 23

¹ Kende, A. S.; Smith, C. A. *J. Org. Chem.* **1988**, *53*, 2655-2657.

² Lok, R.; Leone, R. E.; Williams, A. J. *J. Org. Chem.* **1996**, *61*, 3289-3297.