

Supporting Information for:

Additive-free Nucleophilic Addition of Imidazolines and Imidazoles to Haloacetylenes.

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General. ¹H and ¹³C NMR spectra were taken on a Varian Gemini-300 spectrometer at 300 and 75 MHz or Agilent 400-MR spectrometer at 400 and 100 MHz, respectively. CDCl₃ was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me₄Si (δ 0 ppm for ¹H) or based on the middle peak of the solvent (CDCl₃) (δ 77.00 ppm for ¹³C) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in Hertz. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer and are reported in wave numbers (cm⁻¹). Dry solvents (THF, CH₂Cl₂, and DMF) were purchased from Kanto Chemicals Co. (Japan). Imidazolines **4**, **15**, and imidazoles **37-42** are commercially available from Tokyo Chemical Industry Co. (Japan) or Sigma-Aldrich Co. Chemicals were purified or dried in a standard manner, if necessary.

1-Chloro-1-octyne (1). This is a known compound [Salvi, L.; Jeon, S.-J.; Fisher, E. L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 16119-16125].

¹H NMR (400 MHz) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.18-1.41 (m, 6H), 1.50 (quintet, *J* = 7.2 Hz, 2H), 2.17 (t, *J* = 7.2 Hz, 2H).

¹³C NMR (75 MHz) δ 14.14, 18.83, 22.63, 28.41, 28.56, 31.37, 56.90 (C \equiv CCl), 69.74 (C \equiv CCl).

The ¹³C NMR shifts assigned to acetylenic carbons were in good agreement with those reported in the following literature [Stothers, J. B. In *Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1972; Vol. 24, p 195].

IR (neat) 2959, 2928, 2857, 2240 (C \equiv C), 1460, 1377, 1089, 728 cm⁻¹.

These spectral properties were in good agreement with those reported in the above literature.

1-Bromo-1-octyne (2). This is a known compound [Correia, J. *J. Org. Chem.* **1992**, *57*, 4555-4557] and was prepared according to a literature method [Tobe, Y.; Utsumi, N.; Kawabata, K.; Nagano, A.; Adachi, K.; Araki, S.; Sonoda, M.; Hirose, K.; Naemura, K. *J. Am. Chem. Soc.* **2002**, *124*, 5350-5363].

^1H NMR (300 MHz) δ 0.89 (t, J = 6.9 Hz, 3H), 1.28-1.42 (m, 6H), 1.51 (quintet, J = 7.2 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H).

^{13}C NMR (75 MHz) δ 13.90, 19.57, 22.42, 28.18, 28.38, 31.20, 37.33 ($\text{C}\equiv\text{CBr}$), 80.48 ($\text{C}\equiv\text{CBr}$).

The ^{13}C NMR shifts assigned to acetylenic carbons were in good agreement with those reported in the following literature [Stothers, J. B. In *Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1972; Vol. 24, p 195].

IR (neat) 2930, 2903, 2859, 2209 ($\text{C}\equiv\text{C}$), 1466, 1378, 1327, 1111, 725 cm^{-1} .

These spectral properties were in good agreement with those reported in the above literature.

1-Iodo-1-octyne (3). This is a known compound [Reddy, K. R.; Venkateshwar, M.; Maheswari, C. U.; Kumar, P. S. *Tetrahedron Lett.* **2010**, *51*, 2170-2173].

^1H NMR (300 MHz) δ 0.89 (t, J = 6.9 Hz, 3H), 1.20-1.43 (m, 6H), 1.50 (m, 2H), 2.35 (t, J = 7.1 Hz, 2H).

^{13}C NMR (75 MHz) δ -7.44 ($\text{C}\equiv\text{CI}$), 14.17, 20.90, 22.61, 28.52, 28.53, 31.34, 94.78 ($\text{C}\equiv\text{CI}$).

The ^{13}C NMR shifts assigned to acetylenic carbons were in good agreement with those reported in the following literature [Stothers, J. B. In *Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1972; Vol. 24, p 195].

IR (neat) 2952, 2926, 2857, 2188 ($\text{C}\equiv\text{C}$), 1468, 1379, 1101, 722 cm^{-1} .

The ^1H NMR data were in good agreement with those reported in the above literature.

(Z)-1-(1-Chloro-1-octen-2-yl)-2-methylimidazoline (5).

A mixture of chloroacetylene **1** (28.3 mg, 0.196 mmol) and 2-methylimidazoline (**4**) (34.8 mg, 0.414 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (33.6 mg, 75%) as an oil and as a single isomer.

^1H NMR (400 MHz) δ 0.89 (t, J = 6.8 Hz, 3H), 1.20-1.36 (m, 6H), 1.40 (m, 2H), 1.93 (s, 3H), 2.18

(t, $J = 7.6$ Hz, 2H), 3.53 (t, $J = 9.8$ Hz, 2H), 3.81 (t, $J = 9.8$ Hz, 2H), 5.90 (s, 1H).

NOESY (400 MHz) experiment showed correlation between the peaks at δ 2.18 (t, $J = 7.6$ Hz, 2H, $\text{CH}_2\text{C}=\text{CCl}$) and at δ 5.90 (s, 1H, CHCl). Thus, the stereochemistry of the olefinic bond has been confirmed.

^{13}C NMR (100 MHz) δ 13.96, 14.23, 22.47, 26.79, 28.74, 31.46, 33.58, 49.24, 52.38, 112.06, 141.18, 162.29 (C=N).

IR (neat) 2932, 2857, 1659, 1623 (C=N), 1401, 1262, 938, 831 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{ClN}_2$: C, 63.00; H, 9.25. Found: C, 63.08; H, 9.36.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-methylimidazoline (6).

A mixture of bromoacetylene **2** (47.3 mg, 0.250 mmol) and 2-methylimidazoline (**4**) (42.8 mg, 0.509 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (58.4 mg, 84%) as an oil and as a single isomer.

^1H NMR (400 MHz) δ 0.89 (t, $J = 6.8$ Hz, 3H), 1.22-1.46 (m, 8H), 1.95 (s, 3H), 2.20 (t, $J = 7.5$ Hz, 2H), 3.55 (t, $J = 9.6$ Hz, 2H), 3.82 (t, $J = 9.6$ Hz, 2H), 6.04 (s, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 2.19 (t, $J = 7.5$ Hz, 2H, $\text{CH}_2\text{C}=\text{CBr}$) and at δ 6.02 (s, 1H, CHBr). Thus, the stereochemistry of the olefinic bond has been confirmed.

^{13}C NMR (100 MHz) δ 13.96, 14.41, 22.48, 26.79, 28.74, 31.46, 34.75, 49.16, 52.22, 101.80, 143.70, 162.10 (C=N).

IR (neat) 2929, 2857, 1650, 1625 (C=N), 1400, 1263, 1184, 1033, 935, 752 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{BrN}_2$: C, 52.75; H, 7.75. Found: C, 52.67; H, 7.89.

Control experiment with 5 mol % of butylated hydroxytoluene (BHT).

A mixture of bromoacetylene **2** (75.1 mg, 0.397 mmol), 2-methylimidazoline (**4**) (68.1 mg, 0.810 mmol), and BHT (4.3 mg, 0.020 mmol) in DMF (1.6 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a

crude oil, ^1H NMR analysis of which with trichloroethylene as an internal standard showed the presence of the compound **6** in 56% yield.

Control experiment with 5 mol % of galvinoxyl.

A mixture of bromoacetylene **2** (38.9 mg, 0.206 mmol), 2-methylimidazoline (**4**) (34.7 mg, 0.413 mmol), and galvinoxyl (4.2 mg, 0.010 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which with trichloroethylene as an internal standard showed the presence of the compound **6** as a single isomer in 81% yield.

(Z)-1-(1-Iodo-1-octen-2-yl)-2-methylimidazoline (7).

A mixture of iodoacetylene **3** (96.6 mg, 0.409 mmol) and 2-methylimidazoline (**4**) (68.3 mg, 0.812 mmol) in DMF (1.6 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water, aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (54.2 mg, 41%) as an oil and as a single isomer.

^1H NMR (400 MHz) δ 0.89 (t, J = 6.6 Hz, 3H), 1.19-1.38 (m, 6H), 1.42 (m, 2H), 1.96 (s, 3H), 2.25 (t, J = 7.6 Hz, 2H), 3.55 (t, J = 9.6 Hz, 2H), 3.83 (t, J = 9.6 Hz, 2H), 6.14 (s, 1H).

^{13}C NMR (100 MHz) δ 13.99, 14.74, 22.49, 27.03, 28.77, 31.47, 35.67, 49.02, 52.08, 76.26, 149.02, 161.77 (C=N).

IR (neat) 2928, 2857, 1631 (C=N and C=C), 1401, 1258, 1164, 1029, 931, 760 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{IN}_2$: C, 45.01; H, 6.61. Found: C, 44.95; H, 6.82.

1-Bromo-5,9-dimethyl-1-decyne (8). This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

^1H NMR (300 MHz) δ 0.86 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 6H), 1.00-1.40 (m, 7H), 1.42-1.62 (m, 3H), 2.20 (m, 2H).

^{13}C NMR (75 MHz) δ 17.42, 19.13, 22.60, 22.70, 24.57, 27.94, 31.86, 35.32, 36.72, 37.27 (C=C), 39.20, 80.55 (C \equiv C).

IR (neat) 2954, 2927, 2868, 2218 (C≡C), 1466, 1383, 1169, 1061 cm⁻¹.

Anal. Calcd for C₁₂H₂₁Br: C, 58.78; H, 8.63. Found: C, 58.42; H, 8.30.

1-Bromo-11-dodecen-1-yne (9). This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR (300 MHz) δ 1.18-1.46 (m, 10H), 1.51 (quintet, *J* = 6.9 Hz, 2H), 2.04 (q, *J* = 6.9 Hz, 2H), 2.20 (t, *J* = 6.9 Hz, 2H), 4.94 (dd, *J* = 2.1, 10.2 Hz, 1H), 4.99 (dd, *J* = 2.1, 17.1 Hz, 1H), 5.82 (tdd, *J* = 6.9, 10.2, 17.1 Hz, 1H).

¹³C NMR (75 MHz) δ 19.65, 28.25, 28.74, 28.87, 29.00, 29.05, 29.30, 37.79, 37.42 (C≡C), 80.44 (C≡C), 114.14, 139.19.

IR (neat) 2917, 2854, 2210 (C≡C), 1639, 1464, 993, 910, 723 cm⁻¹.

Anal. Calcd for C₁₂H₁₉Br: C, 59.27; H, 7.88. Found: C, 59.01; H, 7.67.

5-(Benzyloxy)-1-bromo-1-pentyne (10). This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR (300 MHz) δ 1.82 (quintet, *J* = 6.4 Hz, 2H), 2.34 (t, *J* = 6.4 Hz, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 4.51 (s, 2H), 7.28-7.35 (m, 5H).

¹³C NMR (75 MHz) δ 16.50, 28.40, 37.93 (C≡C), 68.49, 72.89 79.66 (C≡C), 127.50 (2 carbons), 127.53, 128.31 (2 carbons), 138.33.

IR (neat) 3063, 3030, 2927, 2857, 2209 (C≡C), 1453, 1364, 1105, 736, 697 cm⁻¹.

Anal. Calcd for C₁₂H₁₃BrO: C, 56.94; H, 5.18. Found: C, 56.71; H, 5.21.

11-Bromo-10-undecyn-1-ol (11). This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR (300 MHz) δ 1.08-1.58 (m, 15H), 2.12 (t, *J* = 6.9 Hz, 2H), 3.56 (t, *J* = 6.6 Hz, 2H).

¹³C NMR (75 MHz) δ 19.72, 25.75, 28.30, 28.78, 29.04, 29.40, 29.47, 32.79, 37.50 (C≡C), 63.03, 80.40 (C≡C).

IR (neat) 3344 (OH), 2929, 2856, 2218 (C≡C), 1464, 1214, 1057, 758 cm⁻¹.

Anal. Calcd for C₁₁H₁₉BrO: C, 53.45; H, 7.75. Found: C, 53.62; H, 7.63.

1-Bromo-3-methoxy-1-octyne (12). This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.21-1.50 (m, 6H), 1.64-1.75 (m, 2H), 3.40 (s, 3H), 3.95 (t, *J* = 6.6 Hz, 1H).

¹³C NMR (75 MHz) δ 13.88, 22.43, 24.72, 31.38, 35.34, 45.01 (C≡C), 56.43, 72.11 (C≡C), 79.17.

IR (neat) 2931, 2861, 2200 (C≡C), 1466, 1341, 1098, 898 cm⁻¹.

Anal. Calcd for C₉H₁₅BrO: C, 49.33; H, 6.90. Found: C, 49.48; H, 6.57.

2-Ethylimidazoline (13). This is a known compound [Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* **1987**, *52*, 1017-1021] and was prepared according to a literature method [Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824-2826].

¹H NMR (300 MHz) δ 1.18 (t, *J* = 7.5 Hz, 3H), 2.27 (q, *J* = 7.5 Hz, 2H), 3.59 (br s, 5H).

¹³C NMR (75 MHz) δ 10.73, 22.52, 49.77 (2 carbons), 168.84 (C=N).

IR (neat) 3276 (N-H), 2975, 2938, 2869, 1617 (C=N), 1496, 1282, 1232, 979 cm⁻¹.

The ¹H NMR data were in good agreement with those reported in the above literature.

2-Cyclohexylimidazoline (14). This was prepared according to a literature method [Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824-2826].

¹H NMR (300 MHz) δ 1.16-1.96 (m, 10H), 2.22 (m, 1H), 3.56 (br s, 4H), 4.57 (br s, 1H).

¹³C NMR (75 MHz) δ 25.67, 25.73 (2 carbons), 30.40 (2 carbons), 38.40, 49.26 (2 carbons), 171.58 (C=N).

IR (KBr) 3131 (N-H), 2931, 2852, 1606 (C=N), 1500, 1446, 1290, 983 cm⁻¹.

Anal. Calcd for C₉H₁₆N₂: C, 71.01; H, 10.59. Found: C, 70.84; H, 10.63.

M.p. 124-127 °C.

2-(*o*-Bromophenyl)imidazoline (16). This was prepared by a literature method [Mizuhara, T.; Oishi, S.; Fujii, N.; Ohno, H. *J. Org. Chem.* **2010**, *75*, 265-268].

¹H NMR (300 MHz) δ 3.71 (s, 4H), 5.37 (br s, 1H), 7.23 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.30 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.52-7.58 (m, 2H).

¹³C NMR (75 MHz) δ 50.09 (2 carbons), 120.60, 127.12, 130.78, 130.83, 132.62, 132.95, 164.32 (C=N).

IR (KBr) 3101 (N-H), 3031, 2913, 1610 (C=N), 1508, 1257, 985, 728 cm⁻¹.

Anal. Calcd for C₉H₉BrN₂: C, 48.02; H, 4.03. Found: C, 48.13; H, 4.04.

M.p. 98-100 °C.

These spectral properties were in good agreement with those reported in the above literature.

2-Ethyl-4-methylimidazoline (17). This is a known compound [Zimmerman, S. C.; Cramer, K. D.; Galan, A. A. *J. Org. Chem.* **1989**, *54*, 1256-1264] and was prepared according to a literature method [Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824-2826].

¹H NMR (300 MHz) δ 1.17 (t, *J* = 7.6 Hz, 3H), 1.19 (d, *J* = 6.6 Hz, 3H), 2.24 (q, *J* = 7.6 Hz, 2H), 3.15 (dd, *J* = 7.4 Hz, 10.7 Hz, 1H), 3.42 (br s, 1H), 3.70 (dd, *J* = 10.4 Hz, 10.7 Hz, 1H), 3.97 (m, 1H).

¹³C NMR (75 MHz) δ 10.73, 21.67, 22.58, 56.42, 57.44, 167.43 (C=N).

IR (neat) 3220 (N-H), 2923, 2867, 1612 (C=N), 1465, 1375, 1274, 1232, 981 cm⁻¹.

These spectral properties were in good agreement with those reported in the above literature. However, the reported assignments in ¹H NMR for the following two peaks, 1.17 (d, 3H, *J* = 6.0 Hz, NCHCH₃) and 1.20 (t, 3H, *J* = 7.6 Hz, N=CCH₂CH₃), should be reversed.

2-Ethyl-4,4-dimethylimidazoline (18). This was prepared according to a literature method [Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824-2826].

¹H NMR (300 MHz) δ 1.11 (s, 6H), 1.18 (t, *J* = 7.5 Hz, 3H), 2.25 (q, *J* = 7.5 Hz, 2H), 3.14 (d, *J* = 5.7 Hz, 2H), 6.06 (br s, 1H).

¹³C NMR (75 MHz) δ 9.98, 28.46 (2 carbons), 29.73, 49.94, 50.18, 174.21 (C=N).

IR (neat) 3320 (N-H), 2965, 2863, 1617 (C=N), 1459, 1307, 1203, 987, 798 cm⁻¹.

(4*RS*,5*RS*)-4,5-(1,4-Butylidene)-2-ethylimidazoline (19). This was prepared according to a literature method [Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824-2826].

¹H NMR (300 MHz) δ 1.18 (t, *J* = 7.5 Hz, 3H), 1.23-1.52 (m, 5H), 1.78 (br m, 2H), 2.16 (br m, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 2.94 (m, 2H).

¹³C NMR (75 MHz) δ 10.35, 23.07, 24.62 (2 carbons), 30.41 (2 carbons), 68.94 (2 carbons), 169.77 (C=N).

IR (KBr) 3276 (N-H), 2931, 2861, 1601 (C=N), 1450, 1369, 1216, 1058, 827 cm⁻¹.

Anal. Calcd for C₉H₁₆N₂: C, 59.82; H, 8.56. Found: C, 59.93; H, 8.70.

M.p. 105-108 °C.

2-Ethyl-1,4,5,6-tetrahydropyrimidine (20). This is a known compound [Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* **1987**, *52*, 1017-1021] and was prepared according to a literature method [Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824-2826].

¹H NMR (400 MHz) δ 1.31 (t, *J* = 7.4 Hz, 3H), 1.76 (m, 2H), 2.13 (q, *J* = 7.4 Hz, 2H), 3.31 (br t, *J* = 5.0 Hz, 4H), 4.53 (br s, 1H).

¹³C NMR (100 MHz) δ 11.38, 20.53, 29.43, 41.40 (2 carbons), 158.87 (C=N).

IR (neat) 3304 (N-H), 2936, 2857, 1627 (C=N), 1539, 1440, 1314, 1045, 938 cm⁻¹.

(Z)-1-(1-Bromo-5,9-dimethyl-1-decen-2-yl)-2-methylimidazoline (21).

A mixture of bromoacetylene **8** (49.1 mg, 0.200 mmol) and 2-methylimidazoline (**4**) (33.8 mg, 0.402 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (48.7 mg, 74%) as an oil and as a single isomer.

¹H NMR (400 MHz) δ 0.87 (d, *J* = 6.4 Hz, 6H), 0.88 (d, *J* = 6.4 Hz, 3H), 1.06-1.36 (m, 7H), 1.41 (m, 2H), 1.51 (nonet, *J* = 6.4 Hz, 1H), 1.96 (s, 3H), 2.17 (ddd, *J* = 5.6, 10.8, 14.8 Hz, 1H), 2.24 (ddd, *J* = 5.4, 10.2, 14.8 Hz, 1H), 3.55 (m, 2H), 3.82 (m, 2H), 6.04 (s, 1H).

¹³C NMR (100 MHz) δ 14.37, 19.34, 22.51, 22.61, 24.60, 27.86, 32.30, 32.36, 34.09, 36.87, 39.15, 49.15, 51.94, 101.86, 143.80, 162.28 (C=N).

IR (neat) 2952, 2869, 1659, 1623 (C=N), 1393, 1262, 1183, 934, 783 cm⁻¹.

Anal. Calcd for C₁₆H₂₉BrN₂: C, 58.35; H, 8.88. Found: C, 58.15; H, 9.01.

(Z)-1-(1-Bromo-1,11-dodecadien-2-yl)-2-methylimidazoline (22).

A mixture of bromoacetylene **9** (48.9 mg, 0.201 mmol) and 2-methylimidazoline (**4**) (33.9 mg, 0.404 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (51.5 mg, 78%) as an oil and as a single isomer.

¹H NMR (400 MHz) δ 1.24-1.46 (m, 12H), 1.95 (s, 3H), 2.04 (q, *J* = 6.8 Hz, 2H), 2.20 (dt, *J* = 1.2, 7.4 Hz, 2H), 3.55 (t, *J* = 9.6 Hz, 2H), 3.82 (t, *J* = 9.6 Hz, 2H), 4.93 (dd, *J* = 2.4, 10.2 Hz, 1H), 4.99 (dd, *J* = 2.4, 17.2 Hz, 1H), 5.81 (tdd, *J* = 6.8, 10.2, 17.2 Hz, 1H), 6.03 (t, *J* = 1.2 Hz, 1H).

¹³C NMR (75 MHz) δ 14.32, 26.91, 28.88, 29.05, 29.13, 29.29, 29.36, 33.77, 34.77, 49.21, 51.43, 102.38, 114.08, 138.91, 143.19, 162.45 (C=N).

IR (neat) 2924, 2853, 1662, 1623 (C=N), 1401, 1266, 906, 728 cm⁻¹.

Anal. Calcd for C₁₆H₂₇BrN₂: C, 58.71; H, 8.31. Found: C, 58.40; H, 8.56.

(Z)-1-[5-(Benzyloxy)-1-bromo-1-octen-2-yl]-2-methylimidazoline (23).

A mixture of bromoacetylene **10** (50.7 mg, 0.200 mmol) and 2-methylimidazoline (**4**) (34.1 mg, 0.405 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (50.5 mg, 75%) as an oil and as a single isomer.

¹H NMR (400 MHz) δ 1.73 (m, 2H), 1.94 (s, 3H), 2.33 (t, *J* = 7.6 Hz, 2H), 3.48 (t, *J* = 6.0 Hz, 2H), 3.55 (t, *J* = 9.8 Hz, 2H), 3.81 (t, *J* = 9.8 Hz, 2H), 4.50 (s, 2H), 6.04 (s, 1H), 7.25-7.39 (m, 5H).

¹³C NMR (75 MHz) δ 14.34, 27.18, 31.59, 49.18, 51.56, 68.77, 73.04, 102.59, 127.55 (2 carbons), 127.59, 128.29 (2 carbons), 137.98, 142.74, 162.20 (C=N).

IR (neat) 3031, 2936, 2865, 1659, 1623 (C=N), 1401, 1266, 1100, 927, 732 cm⁻¹.

Anal. Calcd for C₁₆H₂₁BrN₂O: C, 56.98; H, 6.28. Found: C, 56.74; H, 6.60.

(Z)-1-(11-Bromo-1-hydroxy-10-undecen-10-yl)-2-methylimidazoline (24).

A mixture of bromoacetylene **11** (49.6 mg, 0.201 mmol) and 2-methylimidazoline (**4**) (35.0 mg, 0.416 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (53.7 mg, 81%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 1.22-1.48 (m, 12H), 1.56 (m, 2H), 1.94 (br s, 4H), 2.19 (t, *J* = 6.9 Hz, 2H), 3.53 (m, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 3.80 (m, 2H), 6.02 (s, 1H).

¹³C NMR (75 MHz) δ 14.38, 25.77, 26.86, 29.06, 29.19, 29.33, 29.40, 32.79, 34.75, 49.17, 51.89, 62.54, 102.00, 143.38, 162.16 (C=N).

IR (neat) 3414 (OH), 2928, 2857, 1659, 1623 (C=N), 1404, 1262, 1053, 934, 728 cm⁻¹.

Anal. Calcd for C₁₅H₂₇BrN₂O: C, 54.38; H, 8.21. Found: C, 54.36; H, 8.56.

(Z)-1-(1-Bromo-3-methoxy-1-octen-2-yl)-2-methylimidazoline (25).

A mixture of bromoacetylene **12** (55.9 mg, 0.255 mmol) and 2-methylimidazoline (**4**) (42.7 mg, 0.508 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (53.7 mg, 69%) as an oil and as a single isomer.

¹H NMR (400 MHz) δ 0.89 (t, *J* = 6.4 Hz, 3H), 1.20-1.52 (m, 6H), 1.57 (m, 2H), 1.93 (s, 3H), 3.34 (s, 3H), 3.58 (t, *J* = 6.4 Hz, 1H), 3.61 (t, *J* = 9.6 Hz, 2H), 3.82 (t, *J* = 9.6 Hz, 2H), 6.37 (s, 1H).

¹³C NMR (75 MHz) δ 13.96, 14.54, 22.52, 25.11, 31.63, 33.48, 50.46, 52.97, 57.12, 83.87, 105.90, 143.67, 161.94 (C=N).

IR (neat) 2932, 2865, 1659, 1623 (C=N), 1397, 1258, 1093, 934 cm⁻¹.

Anal. Calcd for C₁₃H₂₃BrN₂O: C, 51.49; H, 7.65. Found: C, 51.56; H, 7.75.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-ethylimidazoline (26).

A mixture of bromoacetylene **2** (38.6 mg, 0.204 mmol) and 2-ethylimidazoline (**13**) (39.9 mg, 0.407 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (45.4 mg, 77%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.05-1.50 (m, 8H), 1.22 (t, *J* = 7.5 Hz, 3H), 2.20 (t, *J* = 7.5 Hz, 2H), 2.21 (q, *J* = 7.5 Hz, 2H), 3.55 (t, *J* = 9.7 Hz, 2H), 3.84 (t, *J* = 9.7 Hz, 2H), 6.04 (s, 1H).

¹³C NMR (75 MHz) δ 10.79, 13.99, 21.12, 22.50, 26.98, 28.79, 31.51, 35.05, 49.41, 52.86, 101.64, 144.15, 166.05 (C=N).

IR (neat) 2929, 2858, 1654, 1620 (C=N), 1400, 1234, 1066, 989, 795, 725 cm⁻¹.

Anal. Calcd for C₁₃H₂₃BrN₂: C, 54.36; H, 8.07. Found: C, 54.43; H, 8.15.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-cyclohexylimidazoline (27).

A mixture of bromoacetylene **2** (39.2 mg, 0.207 mmol) and 2-cyclohexylimidazoline (**14**) (60.9 mg, 0.400 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (52.4 mg, 74%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.05-1.91 (m, 18H), 2.07 (m, 1H), 2.20 (t, *J* = 7.5 Hz, 2H), 3.50 (t, *J* = 9.6 Hz, 2H), 3.82 (t, *J* = 9.6 Hz, 2H), 6.02 (s, 1H).

¹³C NMR (75 MHz) δ 13.96, 22.48, 25.82, 26.17 (2 carbons), 27.05, 28.72, 31.36 (2 carbons), 31.46, 35.45, 36.95, 49.41, 52.61, 101.69, 144.23, 169.32 (C=N).

IR (neat) 2929, 2856, 1654, 1617 (C=N), 1448, 1405, 1253, 1214, 1006, 723 cm⁻¹.

Anal. Calcd for C₁₇H₂₉BrN₂: C, 59.82; H, 8.56. Found: C, 59.57; H, 8.53.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-phenylimidazoline (28).

A mixture of bromoacetylene **2** (47.8 mg, 0.253 mmol) and 2-phenylimidazoline (**15**) (40.9 mg, 0.278 mmol) in DMF (2.5 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (20%-100% ethyl acetate in hexane) to afford the title compound (42.3 mg, 50%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.84 (t, *J* = 6.9 Hz, 3H), 1.01-1.40 (m, 8H), 1.86 (t, *J* = 7.5 Hz, 2H), 3.85 (t, *J* = 9.3 Hz, 2H), 4.03 (t, *J* = 9.3 Hz, 2H), 5.77 (s, 1H), 7.30-7.45 (m, 3H), 7.62 (d, *J* = 6.6 Hz, 2H).

¹³C NMR (75 MHz) δ 13.94, 22.40, 26.68, 28.62, 31.33, 35.99, 51.76, 53.88, 98.49, 127.67 (2 carbons), 128.34 (2 carbons), 130.36, 131.54, 146.44, 163.21 (C=N).

IR (neat) 3062, 2929, 2857, 1655, 1610 (C=N), 1375, 1272, 1130, 1004, 775, 698 cm⁻¹.

Anal. Calcd for C₁₇H₂₃BrN₂: C, 60.90; H, 6.91. Found: C, 61.19; H, 7.08.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-(*o*-bromophenyl)imidazoline (29).

A mixture of bromoacetylene **2** (163 mg, 0.864 mmol) and 2-(*o*-bromophenyl)imidazoline (**16**)

(219 mg, 0.973 mmol) in DMF (2.5 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (20%-100% ethyl acetate in hexane) to afford the title compound (210 mg, 59%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.86 (t, *J* = 6.9 Hz, 3H), 1.08-1.43 (m, 8H), 1.80 (t, *J* = 7.5 Hz, 2H), 3.93 (m, 2H), 4.10 (m, 2H), 5.71 (s, 1H), 7.20-7.34 (m, 2H), 7.41 (dd, *J* = 2.1, 7.5 Hz, 1H), 7.61 (dd, *J* = 1.5, 7.8 Hz, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 1.80 (t, *J* = 7.5 Hz, 2H, CH₂C=CB_r) and at δ 5.71 (s, 1H, CHBr). Thus, the stereochemistry of the olefinic bond has been confirmed.

¹³C NMR (75 MHz) δ 13.85, 22.29, 26.77, 28.43, 31.27, 36.19, 50.60, 54.17, 98.27, 121.72, 126.92, 130.26, 130.70, 132.87, 133.30, 144.41, 160.93 (C=N).

IR (neat) 3058, 2927, 2856, 1653, 1610 (C=N), 1375, 1263, 1141, 1000, 761, 729 cm⁻¹.

Anal. Calcd for C₁₇H₂₂Br₂N₂: C, 49.30; H, 5.35. Found: C, 49.28; H, 5.47.

A 66:34 mixture of (Z)-1-(1-bromo-1-octen-2-yl)-2-ethyl-4-methylimidazoline and (Z)-1-(1-bromo-1-octen-2-yl)-2-ethyl-5-methylimidazoline (30).

A mixture of bromoacetylene **2** (39.8 mg, 0.210 mmol) and 2-ethyl-4-methylimidazoline (**17**) (44.8 mg, 0.411 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which revealed the presence of regioisomers in a 65:35 ratio and in quantitative yield. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compounds (56.9 mg, 90%) as an oil and as a 66:34 mixture of regioisomers.

Major isomer

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.02-1.50 (m, 8H), 1.18 (t, *J* = 7.5 Hz, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 2.01-2.34 (m, 4H), 3.08 (dd, *J* = 7.8, 8.2 Hz, 1H), 3.66 (dd, *J* = 8.2, 9.9 Hz, 1H), 4.08 (m, 1H), 6.00 (s, 1H).

¹³C NMR (75 MHz) δ 10.99, 13.94, 21.05, 21.96, 22.44, 26.91, 28.72, 31.45, 34.97, 56.18, 59.28, 101.46, 143.80, 164.55 (C=N).

Minor isomer

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.02-1.50 (m, 8H), 1.18 (t, *J* = 7.5 Hz, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 2.01-2.34 (m, 4H), 3.37 (m, 1H), 3.90-4.02 (m, 2H), 6.12 (s, 1H).

¹³C NMR (75 MHz) δ 10.51, 13.94, 19.46, 21.27, 22.44, 26.85, 28.83, 31.45, 34.11, 56.30, 60.95, 103.38, 142.59, 165.59 (C=N).

IR (neat) 2927, 2857, 1655, 1617 (C=N), 1459, 1402, 1236, 1074, 796, 723 cm⁻¹ for a 66:34 mixture of regioisomers.

Anal. Calcd for C₁₄H₂₅BrN₂: C, 55.81; H, 8.36. Found: C, 55.68; H, 8.35 for a 66:34 mixture of regioisomers.

An 83:17 mixture of (Z)-1-(1-bromo-1-octen-2-yl)-2-ethyl-4,4-dimethylimidazoline and (Z)-1-(1-bromo-1-octen-2-yl)-2-ethyl-5,5-dimethylimidazoline (31).

A mixture of bromoacetylene **2** (39.8 mg, 0.210 mmol) and 2-ethyl-4,4-dimethylimidazoline (**18**) (54.1 mg, 0.428 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which revealed the presence of regioisomers in an 83:17 ratio and in 92% yield. The crude sample was chromatographed on silica gel (20%-100% ethyl acetate in hexane) to afford the title compounds (55.3 mg, 83%) as an oil and as an 83:17 mixture of regioisomers.

Major isomer

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.0 Hz, 3H), 1.05-1.54 (m, 8H), 1.17 (t, *J* = 7.5 Hz, 3H), 1.28 (s, 6H), 1.94-2.40 (m, 4H), 3.24 (s, 2H), 5.98 (s, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 1.94-2.40 (m, 4H, CH₂C=CBr and N=CCH₂CH₃) and at δ 3.24 (s, 2H, C=NCCH₂). Thus, the major isomer proved to be (Z)-1-(1-bromo-1-octen-2-yl)-2-ethyl-4,4-dimethylimidazoline.

¹³C NMR (75 MHz) δ 11.24, 13.94, 21.09, 22.45, 26.92, 28.73, 28.77 (2 carbons), 31.46, 34.97, 61.59, 64.22, 101.16, 143.71, 162.65 (C=N).

Minor isomer

¹H NMR (300 MHz) δ 0.89 (t, *J* = 6.0 Hz, 3H), 1.05-1.54 (m, 14H), 1.17 (t, *J* = 7.5 Hz, 3H), 1.94-2.40 (m, 4H), 3.54 (d, *J* = 13.5 Hz, 1H), 3.66 (d, *J* = 13.5 Hz, 1H), 6.14 (s, 1H).

¹³C NMR (75 MHz) δ 10.66, 13.94, 22.03, 25.15, 27.17, 28.86 (2 carbons), 29.02, 31.46, 37.18, 63.43, 69.19, 103.68, 142.87, 164.70 (C=N).

IR (neat) 2960, 2929, 2857, 1653, 1617 (C=N), 1461, 1402, 1272, 1193, 1068, 894, 752 cm⁻¹ for an 83:17 mixture of regioisomers.

Anal. Calcd for $C_{15}H_{27}BrN_2$: C, 57.14; H, 8.63. Found: C, 57.06; H, 8.58 for an 83:17 mixture of regioisomers.

(Z)-(4*RS*,5*RS*)-4,5-(1,4-Butylidene)-1-(1-bromo-1-octen-2-yl)-2-ethylimidazoline (32).

A mixture of bromoacetylene **2** (38.5 mg, 0.203 mmol) and (4*RS*,5*RS*)-4,5-(1,4-butylidene)-2-ethylimidazoline (**19**) (61.0 mg, 0.401 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (remaining DMF was eluted with 50% ethyl acetate in hexane and then the product with 30% methanol in ethyl acetate) to afford the title compound (48.2 mg, 69%) as an oil and as a single isomer.

As this compound appears to suffer the inhibition of free rotation around the bromoolefin-imidazoline axis in the NMR time scale, its 1H and ^{13}C NMR spectra show peaks broadening and increased number of peaks, respectively.

1H NMR (300 MHz) δ 0.89 (t, J = 6.6 Hz, 3H), 1.01-1.60 (m, 12H), 1.19 (t, J = 7.4 Hz, 3H), 1.80 (br m, 2H), 1.93 (m, 1H), 2.02-2.23 (m, 3H), 2.33 (m, 2H), 2.95 (m, 1H), 3.07 (br m, 1H), 6.05 (s, 1H).

^{13}C NMR (75 MHz) δ (10.45, 10.71), (13.97, 14.01), (21.06, 21.88), (22.47, 22.52), 24.39, (25.43, 25.51), (26.87, 27.19), (28.77, 28.92), (29.37, 29.59), 30.93, (31.45, 31.52), (32.68, 38.78), (68.40, 69.26), (70.53, 70.98), (100.95, 102.81), (142.76, 144.45), 167.28 (C=N). Each pair of isomeric peaks is in parentheses.

IR (neat) 2933, 2857, 1649, 1593 (C=N), 1459, 1365, 1214, 1133, 798, 728 cm^{-1} .

Anal. Calcd for $C_{17}H_{29}BrN_2$: C, 59.82; H, 8.56. Found: C, 59.93; H, 8.70.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-ethyl-1,4,5,6-tetrahydropyrimidine (33).

A mixture of bromoacetylene **2** (36.5 mg, 0.193 mmol) and 2-ethyl-1,4,5,6-tetrahydropyrimidine (**20**) (43.1 mg, 0.384 mmol) in DMF (0.8 mL) was stirred in an oil bath maintained at 150 °C for 2 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on Chromatorex^R NH (Cat. No. DM1012, size 100-200 mesh, Fuji Silysia Chemical Ltd., Japan) (hexane-ethyl acetate) to afford the title compound (43.7 mg, 75%) as an oil

and as a single isomer.

^1H NMR (400 MHz) δ 0.90 (t, J = 6.6 Hz, 3H), 1.10 (t, J = 7.4 Hz, 3H), 1.21-1.40 (m, 6H), 1.48 (m, 2H), 1.86 (m, 1H), 1.91 (m, 1H), 2.05 (m, 1H), 2.17 (m, 1H), 2.21 (t, J = 7.4 Hz, 2H), 3.26 (t, J = 5.6 Hz, 1H), 3.29 (t, J = 5.6 Hz, 1H), 3.43 (m, 2H), 6.04 (s, 1H).

^{13}C NMR (100 MHz) δ 11.25, 13.96, 21.68, 22.47, 26.81, 27.03, 28.91, 31.51, 35.76, 44.32, 46.18, 103.40, 143.43, 156.58 (C=N).

IR (neat) 2928, 2857, 1631 (C=N and C=C), 1464, 1393, 1275, 1191, 1116, 954 cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{BrN}_2$: C, 55.81; H, 8.36. Found: C, 55.63; H, 8.45.

1-Bromo-12-tridecen-1-yne (34).

^1H NMR (300 MHz) δ 1.24-1.42 (m, 12H), 1.51 (quintet, J = 7.2 Hz, 2H), 2.04 (q, J = 6.6 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 4.93 (d, J = 10.2 Hz, 1H), 4.99 (d, J = 17.0 Hz, 1H), 5.81 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H).

^{13}C NMR (75 MHz) δ 19.69, 28.32, 28.77, 28.95, 29.04, 29.10, 29.41 (2 carbons), 33.77, 37.42 (C=C), 80.48 (C=C), 114.09, 139.16.

IR (neat) 2926, 2854, 2218 (C=C), 1640, 1466, 992, 909, 722 cm^{-1} .

Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{Br}$: C, 60.70; H, 8.23. Found: C, 60.30; H, 7.85.

1-Bromo-1-octyn-3-ol (35). This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

^1H NMR (300 MHz) δ 0.90 (t, J = 6.8 Hz, 3H), 1.23-1.51 (m, 6H), 1.65-1.75 (m, 3H), 4.39 (t, J = 6.6 Hz, 1H).

^{13}C NMR (75 MHz) δ 13.93, 22.48, 24.66, 31.34, 37.52, 44.78 (C=C), 63.35, 81.19 (C=C).

IR (neat) 3340 (OH), 2951, 2934, 2861, 2219 (C=C), 1477, 1341, 1133, 1034, 735 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{13}\text{BrO}$: C, 46.85; H, 6.39. Found: C, 46.84; H, 6.16.

13-Bromo-12-tridecyn-2-one (36).

^1H NMR (300 MHz) δ 1.24-1.40 (m, 10H), 1.45-1.59 (m, 4H), 2.13 (s, 3H), 2.19 (t, J = 7.2 Hz, 2H), 2.42 (t, J = 7.5 Hz, 2H).

^{13}C NMR (75 MHz) δ 19.48, 23.66, 28.10, 28.56, 28.82, 28.97, 29.11, 29.16, 29.65, 37.32 (C=C), 43.58, 80.25 (C=C), 209.01 (C=O).

IR (neat) 2928, 2855, 2223 (C=C), 1717 (C=O), 1458, 1358, 1167, 720 cm^{-1} .

Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{BrO}$: C, 57.15; H, 7.75. Found: C, 57.21; H, 7.72.

(Z)-1-(1-Bromo-1-octen-2-yl)imidazole (43).

A mixture of bromoacetylene **2** (37.6 mg, 0.199 mmol) and imidazole (**37**) (27.2 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (36.7 mg, 72%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.21-1.40 (m, 8H), 2.48 (t, *J* = 6.9 Hz, 2H), 6.22 (br s, 1H), 7.02 (br s, 1H), 7.16 (br s, 1H), 7.65 (br s, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 2.48 (t, *J* = 6.9 Hz, 2H, CH₂C=CHBr) and at δ 6.22 (br s, 1H, C=CHBr). Thus, the stereochemistry of the olefinic bond has been confirmed.

¹³C NMR (75 MHz) δ 13.82, 22.28, 26.36, 28.15, 31.15, 36.79, 99.74, 117.94, 129.02, 136.78, 140.59.

IR (neat) 3114, 3078, 2951, 2924, 2861, 1649, 1468, 1314, 1224, 1069, 825, 744, 672 cm⁻¹.

MS (FAB, NBA) *m/z* (rel intensity): 257 [M⁺ (⁷⁹Br)] (100), 259 [M⁺ (⁸¹Br)] (91).

Anal. Calcd for C₁₁H₁₇BrN₂: C, 51.37; H, 6.66. Found: C, 51.76; H, 6.90.

(Z)-1-(1-Bromo-1,12-tridecadien-2-yl)imidazole (44).

A mixture of bromoacetylene **34** (51.4 mg, 0.200 mmol) and imidazole (**37**) (27.2 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (50.8 mg, 78%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 1.18-1.42 (m, 14H), 2.03 (q, *J* = 6.8 Hz, 2H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.93 (d, *J* = 10.3 Hz, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 5.81 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 6.21 (br s, 1H), 7.02 (br s, 1H), 7.15 (br s, 1H), 7.63 (br s, 1H).

¹³C NMR (75 MHz) δ 26.49, 28.57, 28.80, 28.96, 29.04, 29.27 (2 carbons), 33.70, 36.90, 99.74, 114.09, 117.97, 129.25, 136.48, 139.08, 140.67.

IR (neat) 3114, 3068, 2933, 2851, 1649, 1640, 1468, 1323, 1224, 1069, 916, 763, 672 cm⁻¹.

Anal. Calcd for C₁₆H₂₅BrN₂: C, 59.08; H, 7.75. Found: C, 58.70; H, 7.66.

(Z)-1-(1-Bromo-3-hydroxy-1-octen-2-yl)imidazole (45).

A mixture of bromoacetylene **35** (41.0 mg, 0.200 mmol) and imidazole (**37**) (27.2 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (39.8 mg, 73%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.87 (t, *J* = 6.3 Hz, 3H), 1.19-1.35 (m, 6H), 1.43 (m, 3H), 4.42 (t, *J* = 6.0 Hz, 1H), 6.64 (br s, 1H), 7.04 (br s, 1H), 7.15 (br s, 1H), 7.60 (br s, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 4.42 (t, *J* = 6.0 Hz, 1H, CHOH) and at δ 6.64 (br s, 1H, C=CHBr). Thus, the stereochemistry of olefinic bond has been confirmed.

¹³C NMR (75 MHz) δ 13.93, 22.45, 25.06, 31.40, 34.21, 73.71, 105.25, 119.31, 128.55, 136.80, 143.27.

IR (neat) 3313 (OH), 3114, 2951, 2924, 2851, 1639, 1495, 1314, 1069, 925, 817, 754 cm⁻¹.

Anal. Calcd for C₁₁H₁₇BrN₂O : C, 48.36; H, 6.27. Found: C, 48.68; H, 6.40.

(Z)-1-(1-Bromo-12-oxo-1-tridecen-2-yl)imidazole (46).

A mixture of bromoacetylene **36** (54.3 mg, 0.199 mmol) and imidazole (**37**) (27.2 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (37.9 mg, 56%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 1.16-1.38 (m, 12H), 1.55 (quintet, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 6.22 (br s, 1H), 7.02 (br s, 1H), 7.15 (br s, 1H), 7.64 (br s, 1H).

¹³C NMR (75 MHz) δ 23.71, 26.50, 28.57, 29.01 (2 carbons), 29.14, 29.22, 29.84, 36.91, 43.70, 99.78, 118.01, 129.31, 136.51, 140.68, 209.28 (C=O).

IR (neat) 3123, 3087, 2933, 2851, 1712 (C=O), 1649, 1486, 1368, 1224, 1079, 916, 825, 753 cm⁻¹.

Anal. Calcd for C₁₆H₂₅BrN₂O: C, 56.31; H, 7.38. Found: C, 56.70; H, 7.54.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-methylimidazole (47).

A mixture of bromoacetylene **2** (37.5 mg, 0.198 mmol) and 2-methylimidazole (**38**) (32.8 mg, 0.400

mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (43.5 mg, 81%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.20-1.44 (m, 8H), 2.34 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 6.38 (br s, 1H), 6.74 (br s, 1H), 7.02 (br s, 1H).

¹³C NMR (75 MHz) δ 13.12, 13.88, 22.40, 26.46, 28.49, 31.34, 36.97, 104.89, 118.04, 128.01, 142.01, 143.99.

IR (neat) 3114, 3068, 2951, 2924, 2861, 1640, 1414, 1305, 1224, 735, 672 cm⁻¹.

Anal. Calcd for C₁₂H₁₉BrN₂ : C, 53.15; H, 7.06. Found: C, 53.54; H, 7.20.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-ethylimidazole (48).

A mixture of bromoacetylene **2** (37.8 mg, 0.200 mmol) and 2-ethylimidazole (**39**) (38.5 mg, 0.401 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (50.2 mg, 88%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.20-1.44 (m, 11H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.60 (q, *J* = 7.5 Hz, 2H), 6.39 (br s, 1H), 6.73 (br s, 1H), 7.06 (br s, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 2.40 (t, *J* = 7.4 Hz, 2H, CH₂C=CHBr) and at δ 6.39 (br s, 1H, C=CHBr). Thus, the stereochemistry of the olefinic bond has been confirmed.

¹³C NMR (75 MHz) δ 12.04, 13.93, 20.36, 22.46, 26.64, 28.56, 31.40, 37.12, 105.04, 118.00, 128.26, 142.18, 148.68.

IR (neat) 3080, 3051, 2969, 2929, 2851, 1634, 1489, 1422, 1314, 1049, 804, 723 cm⁻¹.

Anal. Calcd for C₁₃H₂₁BrN₂ : C, 54.74; H, 7.42. Found: C, 54.43; H, 7.55.

A 57:43 (or vice versa) mixture of (Z)-1-(1-bromo-1-octen-2-yl)-5-(hydroxymethyl)imidazole and (Z)-1-(1-bromo-1-octen-2-yl)-4-(hydroxymethyl)imidazole (49).

A mixture of bromoacetylene **2** (37.4 mg, 0.198 mmol) and 4(and/or 5)-(hydroxymethyl)imidazole (**40**) (39.2 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which revealed the presence of regioisomers in a 57:43 ratio in 78% yield. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32.9 mg, 58%) as an oil and as a 57:43 mixture of regioisomers.

Major isomer

¹H NMR (300 MHz) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.17-1.49 (m, 9H), 2.46 (t, *J* = 6.0 Hz, 2H), 4.66 (s, 2H), 6.21 (br s, 1H), 6.98 (br s, 1H), 7.61 (br s, 1H).

¹³C NMR (75 MHz) δ 13.87, 22.40, 26.62, 28.31, 31.28, 36.89, 58.49, 99.78, 128.73, 136.52, 140.66, 142.41.

Minor isomer

¹H NMR (300 MHz) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.17-1.49 (m, 9H), 2.52 (t, *J* = 6.0 Hz, 2H), 4.57 (s, 2H), 6.46 (br s, 1H), 7.13 (br s, 1H), 7.39 (br s, 1H).

¹³C NMR (75 MHz) δ 13.90, 22.42, 26.57, 28.45, 31.37, 36.89, 54.33, 105.50, 115.11, 130.68, 137.27, 141.46.

IR (neat) 3223 (OH), 3078, 2951, 2915, 2861, 1649, 1486, 1377, 1178, 1025, 835 cm⁻¹ for a 57:43 mixture of regioisomers.

Anal. Calcd for C₁₂H₁₉BrN₂O : C, 50.18; H, 6.67. Found: C, 50.46; H, 6.80 for a 57:43 mixture of regioisomers.

The structural assignment to the major and minor isomers has not been done.

(Z)-1-(1-Bromo-1-octen-2-yl)benzimidazole (50). This is a known compound [Xu, H.; Gu, S.; Chen, W.; Li, D.; Dou, J. *J. Org. Chem.* **2011**, 76, 2448-2458].

A mixture of bromoacetylene **2** (37.7 mg, 0.199 mmol) and benzimidazole (**41**) (47.3 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (43.3 mg, 71%) as an oil and as a single isomer.

¹H NMR (300 MHz) δ 0.84 (t, *J* = 6.6 Hz, 3H), 1.13-1.40 (m, 8H), 2.60 (t, *J* = 6.5 Hz, 2H), 6.52 (br

s, 1H), 7.28-7.37 (m, 3H), 7.85 (m, 1H), 7.89 (br s, 1H).

NOESY (300 MHz) experiment showed correlation between the peaks at δ 2.60 (t, J = 6.5 Hz, 2H, $\text{CH}_2\text{C}=\text{CHBr}$) and at δ 6.52 (br s, 1H, $\text{C}=\text{CHBr}$). Thus, the stereochemistry of the olefinic bond has been confirmed.

^{13}C NMR (75 MHz) δ 13.88, 22.35, 26.66, 28.30, 31.21, 36.11, 104.08, 110.81, 120.46, 122.57, 123.47, 132.36, 140.20, 141.77, 143.21.

IR (neat) 3078, 2951, 2924, 2861, 1649, 1612, 1486, 1305, 1215, 744 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{BrN}_2$: C, 58.64; H, 6.23. Found: C, 59.01; H, 6.50.

These spectral properties were in good agreement with those reported in the above literature.

(Z)-1-(1-Bromo-1-octen-2-yl)-2-methylbenzimidazole (51).

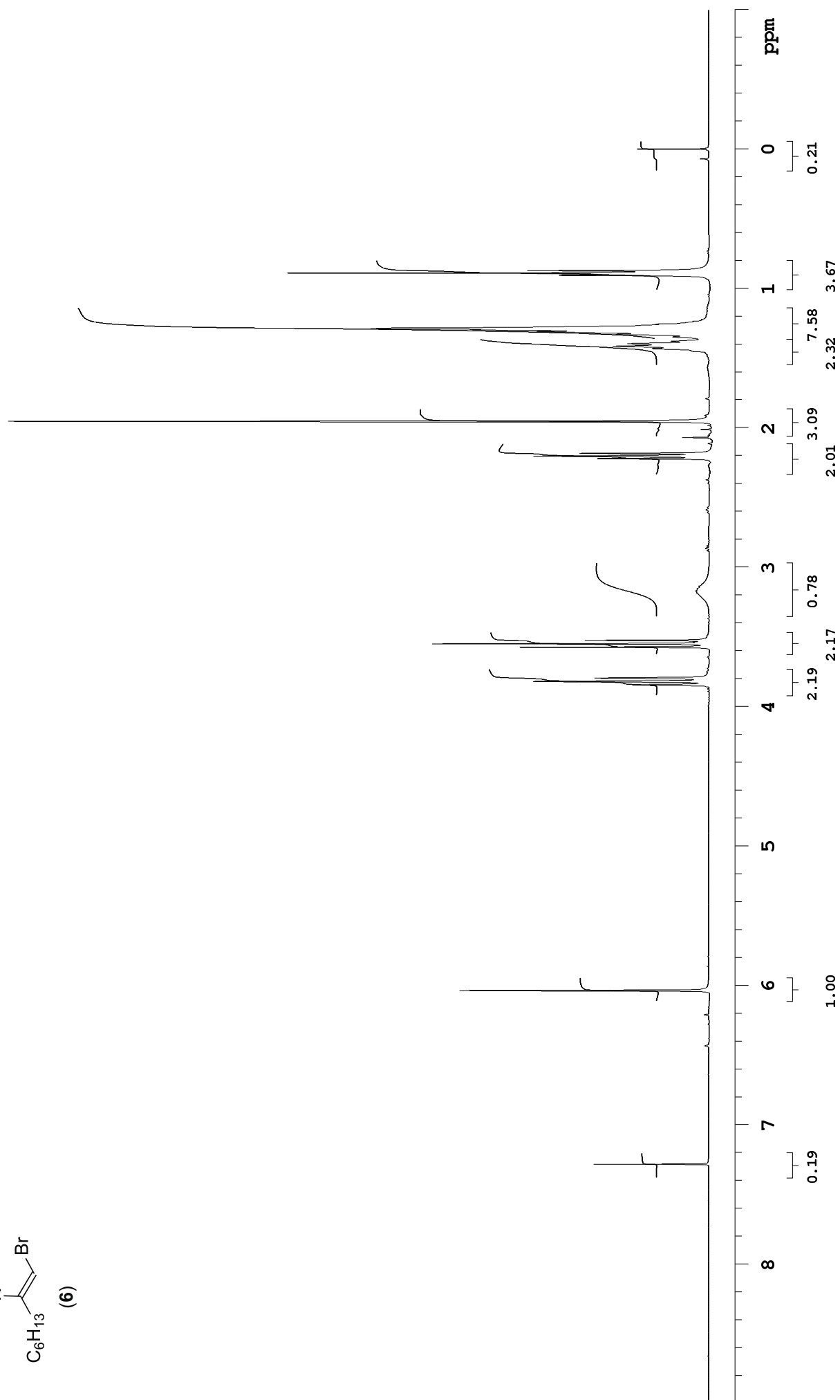
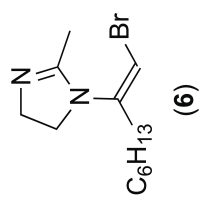
A mixture of bromoacetylene **2** (37.8 mg, 0.200 mmol) and 2-methylbenzimidazole (**42**) (52.9 mg, 0.400 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with 1 N NaOH (4 mL) and extracted with ethyl acetate (3 mL x 4). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (51.3 mg, 80%) as an oil and as a single isomer.

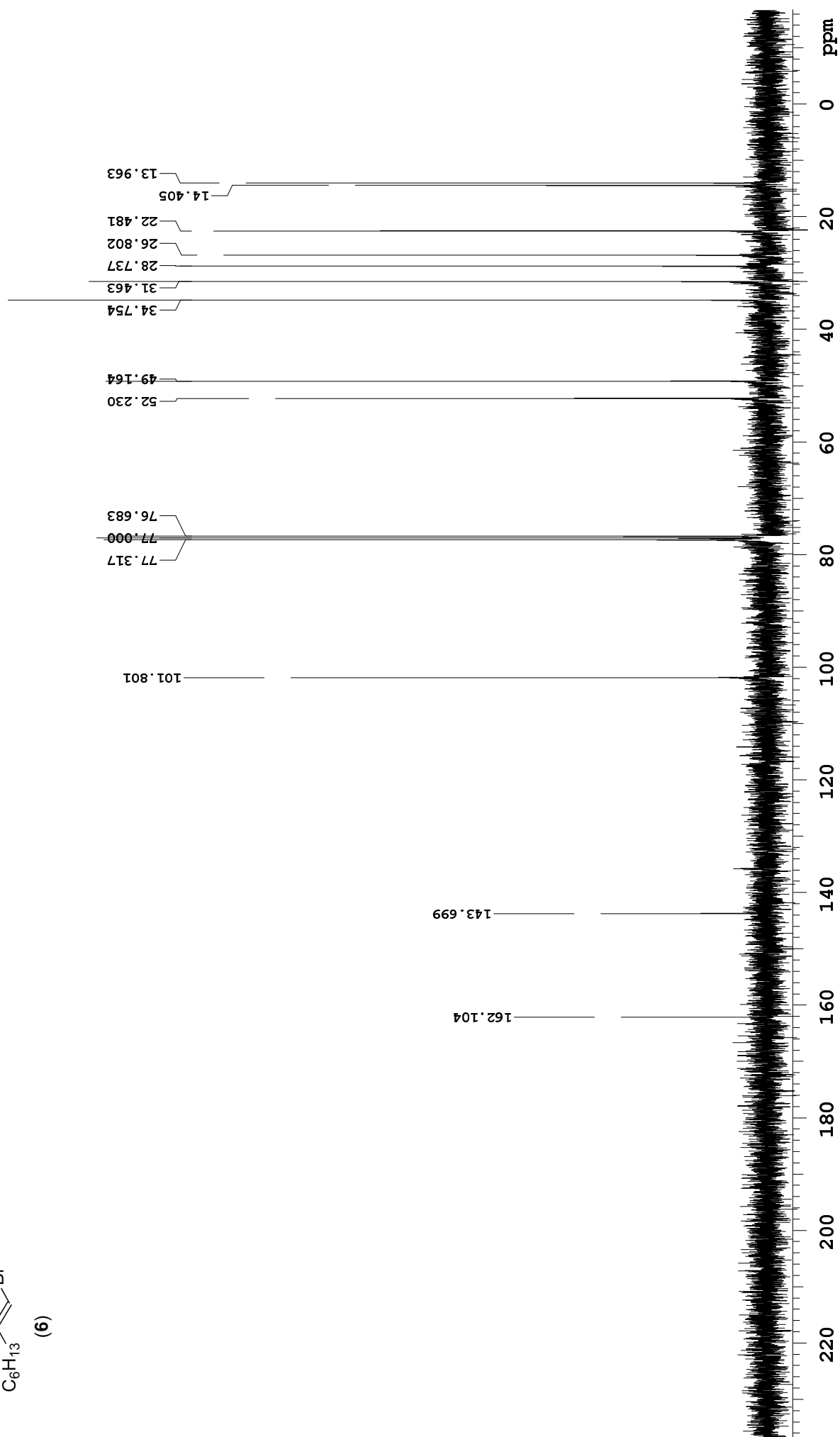
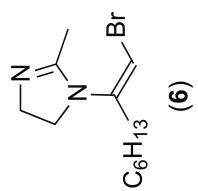
^1H NMR (300 MHz) δ 0.86 (t, J = 6.6 Hz, 3H), 1.16-1.48 (m, 8H), 2.50 (t, J = 6.3 Hz, 2H), 2.54 (s, 3H), 6.63 (br s, 1H), 7.16 (m, 1H), 7.20-7.29 (m, 2H), 7.72 (m, 1H).

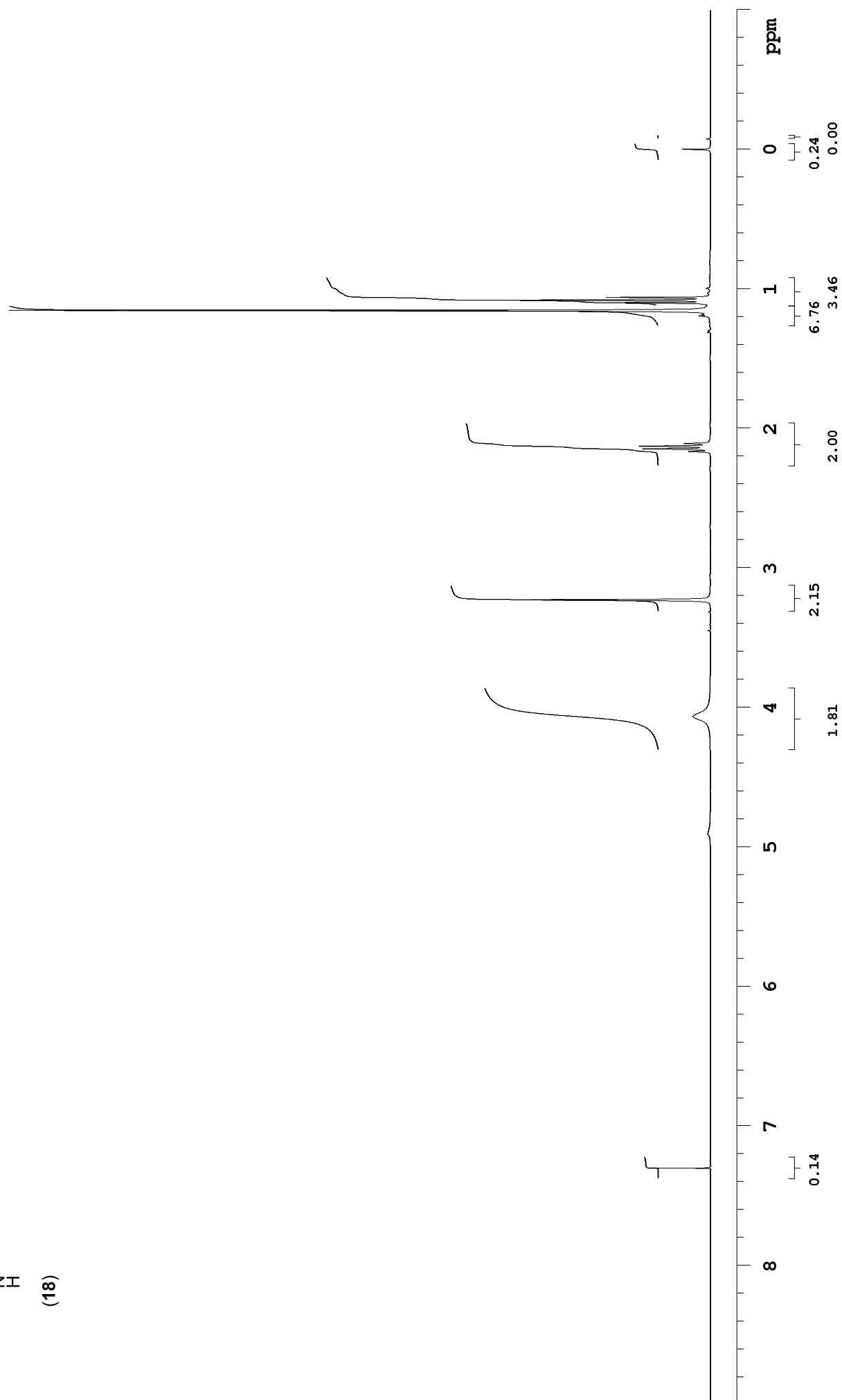
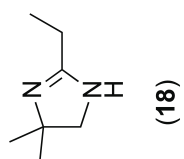
^{13}C NMR (75 MHz) δ 13.90, 13.98, 22.40, 26.75, 28.67, 31.31, 35.98, 107.08, 109.71, 119.11, 122.22, 122.50, 133.99, 140.57, 142.77, 150.45.

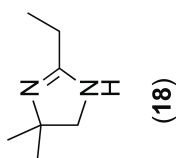
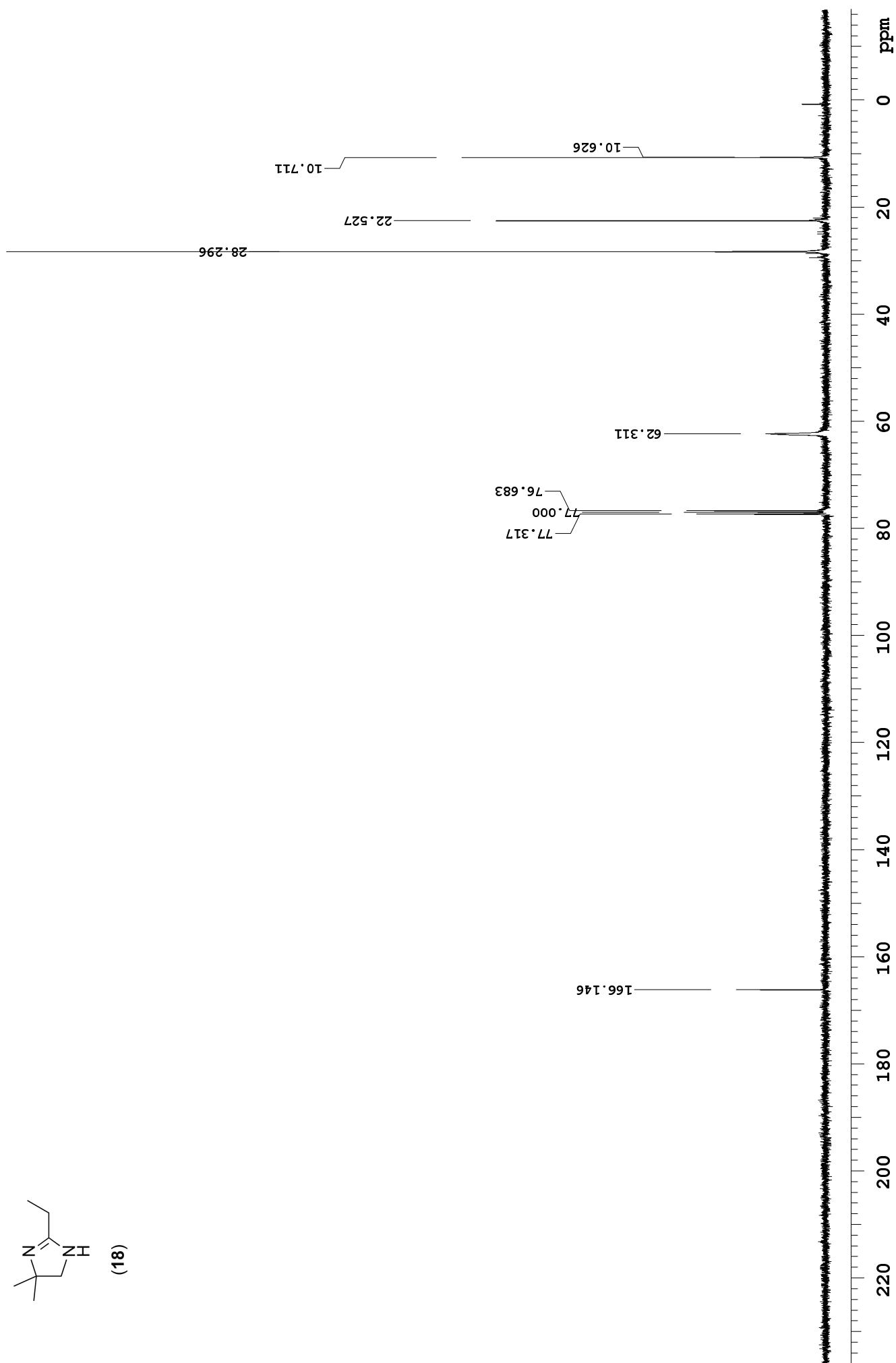
IR (neat) 3079, 3051, 2951, 2924, 2851, 1639, 1540, 1468, 1395, 1224, 753 cm^{-1} .

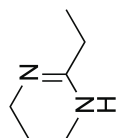
Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{BrN}_2$: C, 59.82; H, 6.59. Found: C, 59.52; H, 6.85.











(20)

