Supporting Information

Chromium-Catalyzed Arylmagnesiation of Alkynes

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Instrumentation and Chemicals

^{1}H NMR (300 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian Mercury 300 and UNITY INOVA 500 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to $CHCl_3$ at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous $CrCl_2$ was purchased from Aldrich and was used under argon. Arylmagnesium bromide was prepared from magnesium metal and the corresponding bromoarene in diethyl ether. Diethyl ether was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Toluene was dried over slices of sodium and used after distillation. All reactions were carried out under argon atmosphere.

Characterization Data

The stereochemistry of the arylmagnesiation products was assigned by comparison with known compounds that have an analogous structure.[1]

The products shown in Table 2, entries 8[2], 9[3], and 10[2] are well known compounds.

(*E*)-6-Phenyl-6-dodecene (3): oil. IR (neat) 697, 758, 1444, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.24–1.50 (m, 12H), 2.18 (q, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 5.64 (t, *J* = 7.2 Hz, 1H), 7.18–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.25, 14.28, 22.70, 22.81, 28.62, 28.73, 29.79, 29.88, 31.85, 32.03, 126.50, 126.51, 128.29, 129.36, 140.25, 143.73; Found: C, 88.45; H, 11.55%. Calcd for $C_{18}H_{28}$: C, 88.27; H, 11.70%.

(*E*)-6-(2-Methylphenyl)-6-dodecene (Table 2, entry 1): oil. IR (neat) 729, 759, 1459, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.6 Hz, 3H), 0.90 (t, *J* = 6.6 Hz, 3H), 1.25–1.41 (m, 12H), 2.16 (q, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 2.31 (t, *J* = 7.2 Hz, 2H), 5.22 (t, *J* = 7.2 Hz, 1H), 7.02–7.15 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.27, 14.31, 20.14, 22.76, 22.82, 28.09 28.21, 29.77, 31.82, 31.94, 32.20, 125.37, 126.41, 129.24, 130.02, 130.10, 135.48, 140.78, 144.93; Found: C, 88.09; H, 11.89%. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70%.

(*E*)-6-(3-Methylphenyl)-6-dodecene (Table 2, entry 2): oil. IR (neat) 702, 782, 1460, 1602, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.27–1.53 (m, 12H), 2.17 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.46 (t, *J* = 7.5 Hz, 2H), 5.62 (t, *J* = 7.5 Hz, 1H), 7.01–7.04 (m, 1H) 7.11–7.21 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.27, 14.29,

21.75, 22.73, 22.85, 28.68, 28.76, 29.85, 29.98, 31.89, 32.10, 123.66, 127.33 (× 2C), 128.20, 129.17, 137.76, 140.42, 143.81; Found: C, 88.06; H, 11.56%. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70%.

(*E*)-6-(4-Methylphenyl)-6-dodecene (Table 2, entry 3): oil. IR (neat) 814, 1512, 2925 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.23–1.53 (m, 12H), 2.16 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.45 (t, *J* = 7.2 Hz, 2H), 5.61 (t, *J* = 7.2 Hz, 1H), 7.08–7.11 (m, 2H) 7.22–7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.28, 14.30, 21.23, 22.74, 22.85, 28.67, 28.74, 29.87, 29.91, 31.88, 32.10, 126.39, 128.64, 129.04, 136.13, 140.08, 140.85; Found: C, 88.23; H, 11.49%. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70%.

(*E*)-6-(4-Chlorophenyl)-6-dodecene (Table 2, entry 4): oil. IR (neat) 750, 829, 1092, 1490, 2928 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 6.6 Hz, 3H), 0.90 (t, *J* = 6.6 Hz, 3H), 1.26–1.43 (m, 12H), 2.17 (q, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 5.62 (t, *J* = 7.2 Hz, 1H), 7.04–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.24, 14.28, 22.72, 22.83, 28.52, 28.77, 29.75, 29.82, 31.87, 31.98, 127.84, 128.44, 129.96, 132.25, 139.31, 142.20; Found: C, 77.72; H, 10.04%. Calcd for $C_{18}H_{27}Cl$: C, 77.53; H, 9.76%.

(*E*)-6-(3-Methoxylphenyl)-6-dodecene (Table 2, entry 5): oil. IR (neat) 775, 1285, 1465, 1577, 2927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.24–1.46 (m, 12H), 2.17 (q, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 7.5 Hz, 2H), 3.81 (s, 3H), 5.65 (t, *J* = 7.2 Hz, 1H), 6.74–6.78 (m, 1H), 6.87–6.94 (m, 2H), 7.18–7.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.27, 14.29, 22.73, 22.84, 28.66, 28.74, 29.79, 30.00, 31.88, 32.08, 55.39,

111.69, 112.62, 119.17, 129.21, 129.49, 140.21, 145.40, 159.71; Found: C, 83.15; H, 11.28%. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02%.

(*E*)-2,2-Dimethyl-4-phenyl-3-decene (Table 2, entry 6): oil. IR (neat) 698, 747, 1465, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.0 Hz, 3H), 1.20 (s, 9H), 1.21–1.28 (m, 8H), 2.59 (t, *J* = 7.5 Hz, 2H), 5.55 (s, 1H), 7.18–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.21, 22.81, 29.06, 29.81, 30.65, 31.66, 31.87, 33.03, 126.45, 126.97, 128.18, 139.56, 140.69, 145.29; Found: C, 88.72; H, 11.76%. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55%.

(*E*)-1,2-Diphenyl-1-octene (Table 2, entry 7): oil. IR (neat) 697, 758, 1598, 2926 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (t, *J* = 6.9 Hz, 3H), 1.22–1.44 (m, 8H), 2.69 (t, *J* = 8.1 Hz, 2H), 6.69 (s, 1H), 7.16–7.58 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.23, 22.80, 28.90, 29.54, 30.43, 31.75, 126.69, 126.84, 127.32, 128.27, 128.44, 128.54, 128.99, 138.61, 143.41, 143.65; Found: C, 91.03; H, 9.06%. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15%.

(*E*)-6-Deuterio-7-phenyl-6-dodecene (5, 92%D): oil. ^1H NMR ($CDCl_3$) δ 0.85 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.24–1.50 (m, 12H), 2.17 (t, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 7.18–7.35 (m, 5H).

(*Z*)-4-Pentyl-5-phenyl-1,4-decadiene (6): oil. IR (neat) 702, 909, 1459, 1636, 2926 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H), 1.22–1.47 (m, 12H), 2.14 (t, *J* = 7.5 Hz, 2H), 2.29–2.36 (m, 2H), 2.57 (d, *J* = 6.3 Hz, 2H), 4.88–4.95 (m, 2H), 5.68 (ddt, *J* = 16.8, 10.2, 6.3 Hz, 1H), 7.06–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.27, 14.31, 22.77, 22.86, 28.28, 28.77, 30.99, 32.06, 32.37, 34.37, 37.80, 115.12, 126.10, 128.02,

128.97, 133.58, 137.90, 137.97, 144.03; Found: C, 88.66; H, 11.34%. Calcd for $C_{21}H_{32}$: C, 88.36; H, 11.37%.

(*Z*)-2-Pentyl-1,3-diphenyl-2-octene-1-ol (7): solid. IR (nujol) 703, 997, 1451, 2922, 3309 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (t, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 6.9 Hz, 3H), 1.16–1.30 (m, 12H), 1.57 (d, *J* = 3.6 Hz, 1H), 1.95 (dt, *J* = 5.1, 13.5 Hz, 1H), 2.13 (dt, *J* = 5.1, 13.5 Hz, 1H), 2.30–2.39 (m, 2H), 5.34 (d, *J* = 3.3 Hz, 1H), 7.18–7.36 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.21, 14.24, 22.51, 22.73, 27.68, 27.81, 30.90, 32.19, 32.81, 34.68, 74.05, 125.92, 126.66, 129.87, 128.15, 128.42, 128.94, 137.42, 141.44, 142.78, 143.31; Found: C, 85.47; H, 9.62%. Calcd for $C_{25}H_{34}O$: C, 85.66; H, 9.78%.

(*Z*)-6,7-Diphenyl-6-dodecene (8a): oil. IR (neat) 698, 2858 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (m, *J* = 6.9 Hz, 6H), 1.26–1.34 (m, 12H), 2.52 (t, *J* = 7.5 Hz, 4H), 6.90–7.07 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.26, 22.76, 28.34, 32.04, 34.49, 125.53, 127.49, 129.97, 138.51, 143.74; Found: C, 89.94; H, 10.06%. Calcd for $C_{25}H_{32}$: C, 90.23; H, 10.18%.

(*Z*)-6-(4-Methoxyphenyl)-7-phenyl-6-dodecene (8b): oil. IR (neat) 700, 831, 1245, 1509, 2955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83–0.88 (m, 6H), 1.22–1.29 (m, 12H), 2.47–2.51 (m, 4H), 3.69 (s, 3H), 6.57–6.60 (m, 2H), 6.82–7.08 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 14.27 (× 2C), 22.75, 22.77, 28.37, 28.39, 32.06 (× 2C), 34.56 (× 2C), 55.19, 112.95, 125.41, 127.55, 130.00, 130.93, 136.03, 137.90, 138.12, 143.98, 157.43; Found: C, 85.52; H, 9.81%. Calcd for $C_{25}H_{34}O$: C, 85.66; H, 9.78%.

(*Z*)-3-Pentyl-2,4-diphenyl-1,3-nonadiene (9): oil. IR (neat) 699, 897, 1491, 2927 cm^{-1};

^{1}H NMR ($CDCl_3$) δ 0.84–0.89 (m, 6H), 1.26–1.38 (m, 12H), 2.20 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 4.69 (d, *J* = 1.8 Hz, 1H), 5.26 (d, *J* = 1.8 Hz, 1H), 7.07–7.38 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.24, 14.29, 22.77 (× 2C), 28.24, 28.39, 31.87, 31.95, 32.10, 34.32, 115.83, 125.81, 126.93, 127.26, 127.59, 128.26, 128.69, 138.10, 139.78, 140.86, 143.95, 148.95; Found: C, 90.19; H, 9.96%. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89%. The stereochemical structure of **9** was determined tentatively by analogy with the stereochemistry of cross-coupling products **8a** and **8b**.

(*E*)-6-Methyl-7-phenyl-6-dodecene (10): oil. IR (neat) 701, 1440, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 6.9 Hz, 3H), 1.22–1.46 (m, 12H), 1.49 (s, 3H), 2.15 (t, *J* = 7.5 Hz, 2H), 2.28–2.32 (m, 2H), 7.05–7.09 (m, 2H) 7.16–7.32 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.24, 14.30, 20.05, 22.75, 22.90, 28.46 (× 2C), 32.05, 32.25, 34.14 (× 2C), 125.82, 127.99, 129.21, 131.59, 136.02, 144.62; Found: C, 88.05; H, 11.88%. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70%.

(*Z*)-6-Iodo-7-phenyl-6-dodecene (11): oil. IR (neat) 698, 1119, 1458, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 6.9 Hz, 3H), 1.23–1.39 (m, 10H), 1.60–1.65 (m, 2H), 2.45 (t, *J* = 8.1 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 7.05–7.07 (m, 2H) 7.24–7.37 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.16, 14.25, 22.61, 22.80, 28.03, 29.66, 31.01, 31.68, 34.83, 41.35, 106.52, 127.02, 128.22, 128.46, 147.39, 147.82; Found: C, 58.63; H, 7.32%. Calcd for $C_{18}H_{27}I$: C, 58.38; H, 7.35%.

References

(1) (a) Shirakawa, E.; Yamagami, T.; Kimura, T.; Yamaguchi, S.; Hayashi, T. *J. Am. Chem. Soc.* **2005**, *127*, 17164–17165. (b) Zhou, C.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 3765–3777. (b) Zhou, C.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 3765–3777.

(2) The products are commercially available from Aldrich.

(3) Chou, S. S. P.; Kuo, H. L.; Wang, C. J.; Tsai, C. Y.; Sun, C. M. *J. Org. Chem.* **1989**, *54*, 868–872.

Chart 1. ^{1}H NMR spectrum of product in Table 2, entry 8

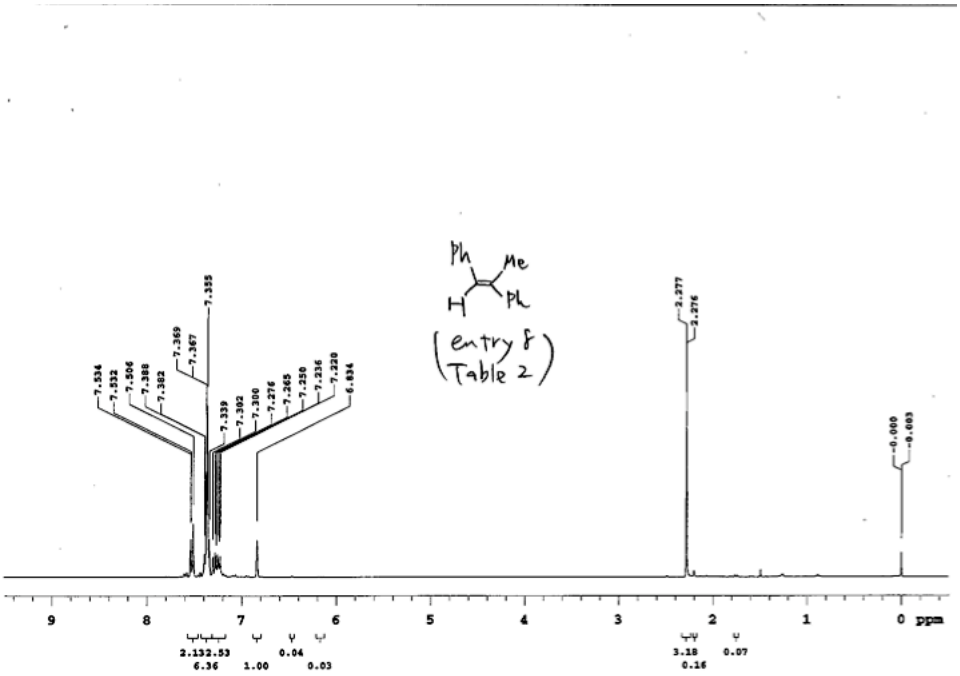

Chart 2. ^{13}C NMR spectrum of product in Table 2, entry 8

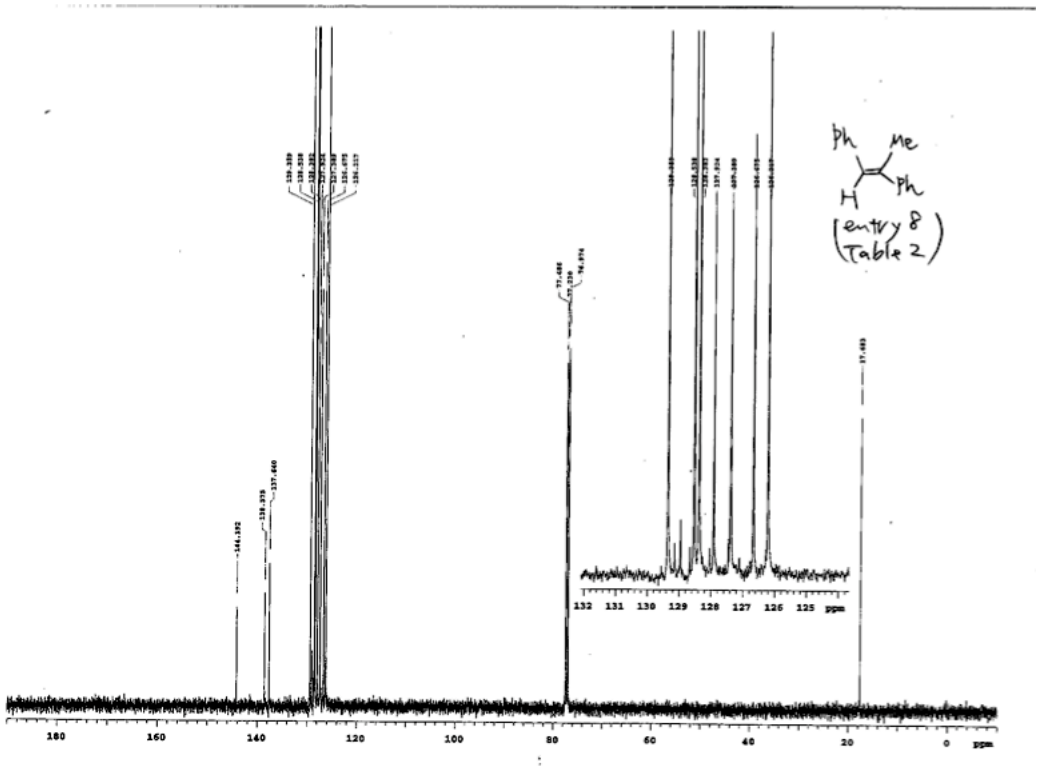

Chart 3. [1]H NMR spectrum of product in Table 2, entry 9

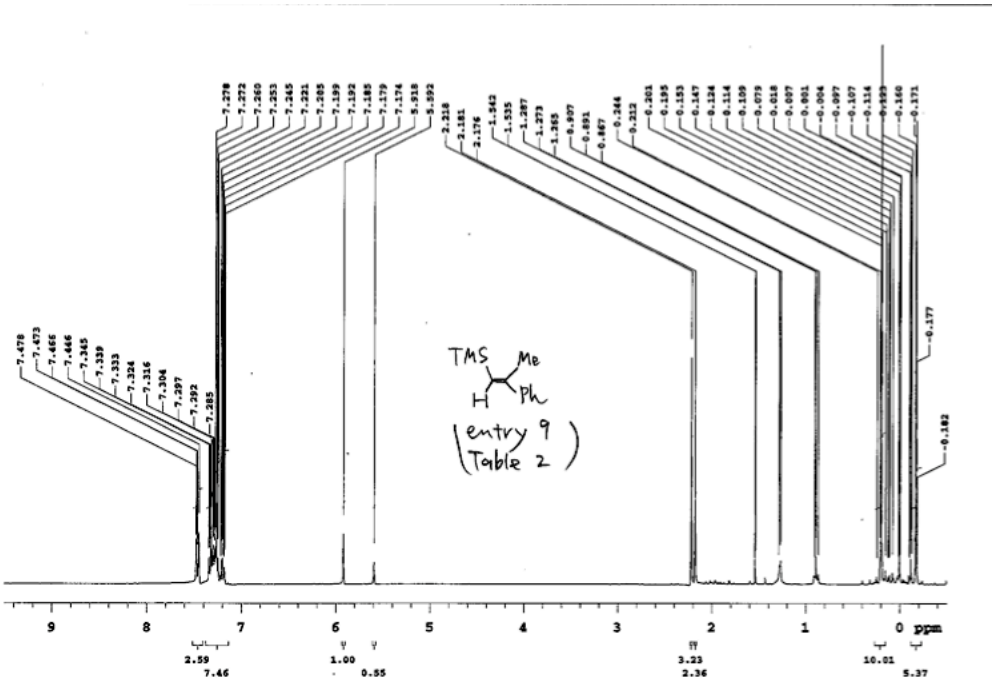

Chart 4. [13]C NMR spectrum of product in Table 2, entry 9

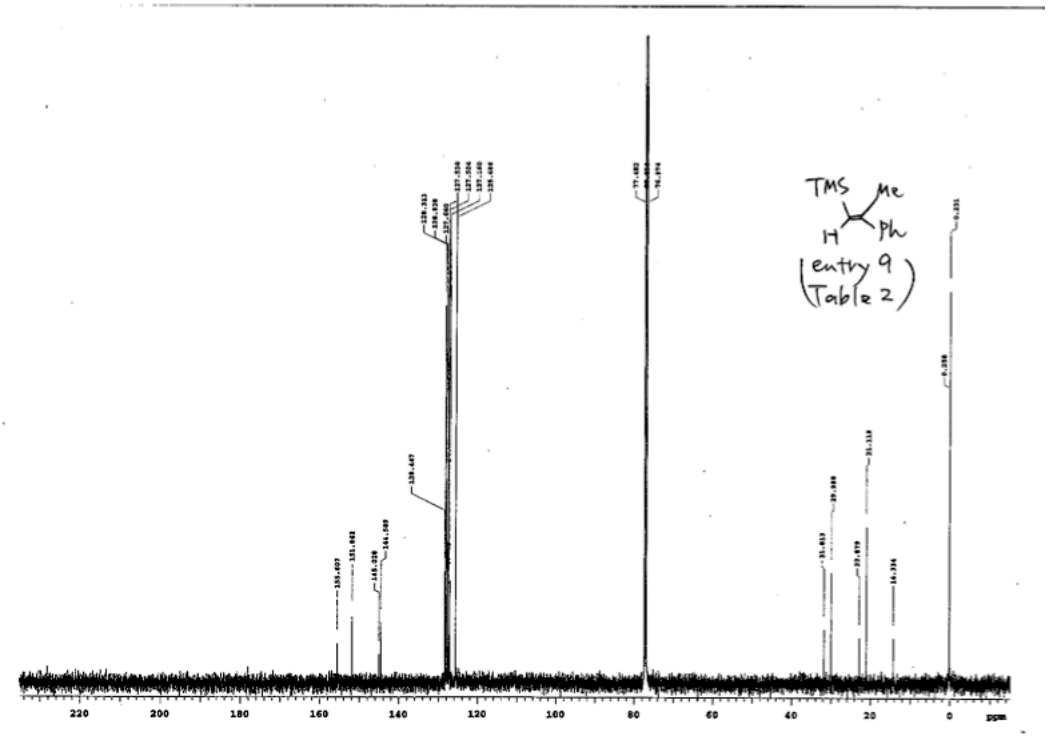

Chart 5. ^{1}H NMR spectrum of product in Table 2, entry 10

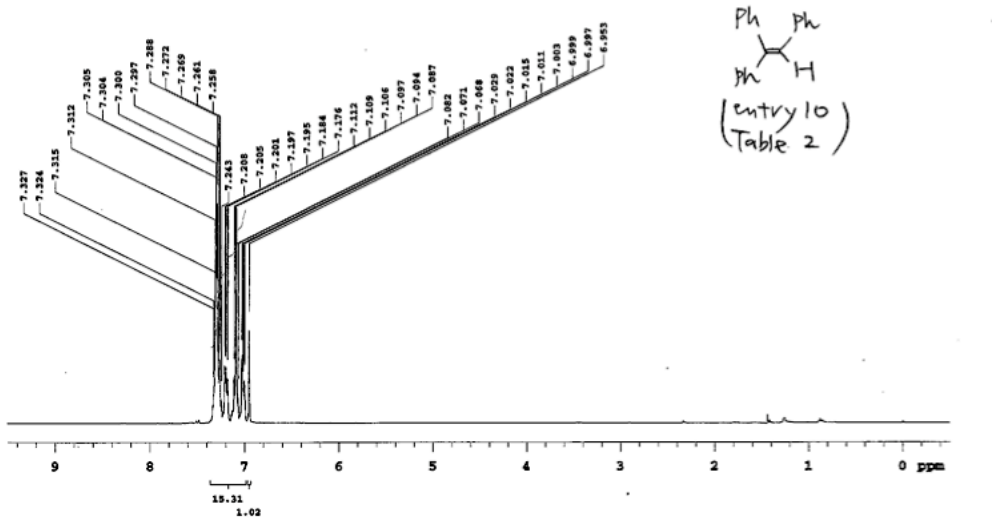

Chart 6. ^{13}C NMR spectrum of product in Table 2, entry 10