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Silver-Catalyzed Carbomagnesiation of Terminal Alkynes and Enynes in the Presence of 1,2-Dibromoethane

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General Comments

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. HPLC separations were performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted using Kanto Chemical Co., Inc. silica gel 60 (63-210 μm). Elemental analyses were performed on a Perkin Elmer 240C apparatus. GC yields were determined using octane as an internal standard. ^{t}Bu-MgCl, ^{s}Bu-MgCl, ^{n}Bu-MgCl, ^{c}Hex-MgCl, ^{n}Oct-MgCl, phenylacetylene, 2-ethynyltoluene, 3-ethynyltoluene 4-ethynyltoluene, 4-ethynylanisole, 4-ethynyltrifluorotoluene, 3-ethynylthiophene, dimethylphenylsilylacetylene, benzaldehyde and chlorophenylsilane (Aldrich Chemical Company), 1,2-dibromoethane and cyclopentanone (Tokyo Chemical Industry Company), AgOTs, D_2O (Wako Pure Chemical Industries) were purchased and used as received. (IMes)AgCl was prepared according to the literature (ref. [10]). Enynes **6a–c** were synthesized by Sonogashira coupling reactions of vinyl bromide with corresponding terminal alkynes.

Procedures and Characterization of Reaction Products

3,3-Dimethyl-1-phenyl-1-butene (2a)

To a mixture of phenyl acetylene (101.9 mg, 1.0 mmol), 1,2-dibromoethane (185 mg, 1.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 138 mg (88%) of **2a** as a mixture of stereoisomers (*E*/*Z* = 2/98). IR(NaCl): 3078, 3057, 2959, 2903, 2867, 1600, 1492, 1476, 1461, 1360, 1202, 1072, 1028, 918, 754, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.30-7.16 (m, 5H), 6.41 (d, *J* = 12.7 Hz, 1H), 5.60 (d, *J* = 12.7 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 142.6, 139.4, 128.9, 127.5, 127.1, 126.1, 34.2, 31.2; MS (EI) *m*/*z* (relative intensity, %): 160 (M, 28), 146 (11), 145 (100), 130 (11), 129 (8), 128 (8), 117 (19), 115 (8), 105 (9), 91 (21), 77 (6); HRMS (EI) calcd for $C_{12}H_{16}$: 160.1252, found 160.1255. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. found: C, 89.76; H, 10.27.

3,3-Dimethyl-1-(4-methylphenyl)-1-butene (2b)

To a mixture of 4-ethynyltoluene (114.5 mg, 0.99 mmol), 1,2-dibromoethane (187 mg, 1.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 138 mg (80%) of **2b** as a mixture of stereoisomers (*E*/*Z* = 2/98). IR(NaCl): 2958, 2866, 1510, 1475, 1462, 1360, 1200, 1108, 1022, 902, 849, 775, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.07 (s, 4H), 6.37 (d, *J* = 12.7 Hz, 1H), 5.57 (d, *J* = 12.7 Hz, 1H), 2.33 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 142.5, 136.3, 135.7, 128.8, 128.2, 127.1, 34.1, 31.2, 21.1; MS (EI) *m*/*z* (relative intensity, %): 174 (M, 30), 160 (12), 159 (100), 144 (13), 131 (11), 129 (9), 128 (8), 117 (8), 115 (8), 105 (16), 91 (6), 77 (3); HRMS (EI) calcd for $C_{13}H_{18}$: 174.1409, found 174.1413. Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. found: C, 89.30; H, 10.27.

3,3-Dimethyl-1-(3-methylphenyl)-1-butene (2c)

To a mixture of 3-ethynyltoluene (114.2 mg, 0.98 mmol), 1,2-dibromoethane (185 mg, 1.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and

evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 141 mg (83%) of **2c** as a mixture of stereoisomers (*E*/*Z* = 2/98). IR(NaCl): 2958, 2866, 1602, 1583, 1476, 1461, 1360, 1218, 812, 764, 738, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.15 (t, *J* = 7.4 Hz, 1H), 7.02-6.97 (m, 3H), 6.37 (d, *J* = 12.7 Hz, 1H), 5.57 (d, *J* = 12.7 Hz, 1H), 2.33 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 142.4, 139.3, 137.0, 129.6, 127.4, 127.2, 126.8, 126.0, 34.2, 31.2, 21.4; MS (EI) *m*/*z* (relative intensity, %): 174 (M, 31), 160 (14), 159 (100), 144 (12), 131 (12), 129 (9), 128 (9), 119 (4), 117 (7), 115 (7), 105 (15), 91 (6), 77 (4); HRMS (EI) calcd for $C_{13}H_{18}$: 170.1409, found 174.1398. Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. found: C, 89.40; H, 10.31.

3,3-Dimethyl-1-(2-methylphenyl)-1-butene (2d)

To a mixture of 2-ethynyltoluene (114.9 mg, 0.99 mmol), 1,2-dibromoethane (188 mg, 1.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 140 mg (81%) of **2d** as a mixture of stereoisomers (*E*/*Z* = 7/93). IR(NaCl): 2958, 2866, 1475, 1461, 1360, 1234, 1205, 901, 752, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.14-7.08 (m, 4H), 6.26 (d, *J* = 12.7 Hz, 1H), 5.61 (d, *J* = 12.7 Hz, 1H), 2.24 (s, 3H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 142.1, 138.9, 125.7, 129.5, 129.2, 126.6, 126.2, 124.8, 34.3, 30.8, 20.3; MS (EI) *m*/*z* (relative intensity, %): 174 (M, 36), 160 (14), 159 (100), 145 (5), 144 (13), 131 (14), 129 (10), 128 (9), 117 (11), 115 (10), 105 (16), 104 (7), 91 (7), 77 (4); HRMS (EI) calcd for $C_{13}H_{18}$: 174.1409, found 174.1405. Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. found: C, 89.50; H, 10.61.

3,3-Dimethyl-1-(4-methoxyphenyl)-1-butene (2e)

To a mixture of 4-ethynyanisole (132.2 mg, 1.0 mmol), 1,2-dibromoethane (187 mg, 1.00 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane/ether = 90/10) gave 133 mg (70%) of **2e** as a mixture of stereoisomers (*E*/*Z* = 2/98). IR(NaCl): 2994, 2957, 2904, 2865, 2835, 1607, 1509, 1464, 1441, 1410, 1360, 1284, 1247, 1201, 1171, 1106, 1039, 851, 816, 783, 745 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$) (*Z* isomer): δ 7.12-7.08 (m, 2H), 6.84-6.80 (m, 2H), 6.35 (d, *J* = 12.6 Hz, 1H), 5.56 (d, *J* = 12.6 Hz, 1H), 3.80 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 158.0, 142.5, 131.6, 130.0, 126.8, 113.0, 55.2, 34.0, 31.2 MS (EI) *m*/*z* (relative intensity, %): 190 (M, 30), 176 (12), 175 (100), 160 (11), 146 (4), 145 (4), 128 (4), 121 (12), 115 (5), 91 (6), 77 (4); HRMS (EI) calcd for $C_{13}H_{18}O$: 190.1358, found 190.1360. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. found: C, 81.77; H, 9.38.

3,3-Dimethyl-1-(4-trifluoromethylphenyl)-1-butene (2f)

To a mixture of 4-ethynytrifluoromethylbenzene (167.8 mg, 0.99 mmol), 1,2-dibromoethane (184.7 mg, 0.99 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 183 mg (81%) of **2f** as a mixture of stereoisomers (*E*/*Z* = 1/99). IR(NaCl): 2962, 2905, 2868, 1616, 1478, 1465, 1406, 1363, 1165, 1127, 1106, 1066, 1019, 903, 862, 814, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 12.9 Hz, 1H), 5.68 (d, *J* = 12.9 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 143.9, 143.3 (q, *J* = 1.4 Hz), 129.2, 128.5 (q, *J* = 32.5 Hz), 125.6, 124.5 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.4 Hz), 34.3, 31.2; MS (EI) *m*/*z* (relative intensity, %): 228 (M, 30), 214 (15), 213 (100), 209 (7), 185 (23), 173 (7), 165 (8), 159 (21), 144 (5), 129 (6), 128 (6); HRMS (EI) calcd for $C_{13}H_{15}F_3$: 228.1126, found 228.1140. Anal. Calcd for $C_{13}H_{15}F_3$: C, 68.41; H, 6.62. found: C, 68.70; H, 6.68.

3,3-Dimethyl-1-(3-thienyl)-1-butene (2g)

To a mixture of 3-ethynylthiophene (109.2 mg, 1.01 mmol), 1,2-dibromoethane (191 mg, 1.02 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 110 mg (65%) of **2g** as a mixture of stereoisomers (*E*/*Z* = 3/97). IR(NaCl): 2993, 2959, 2903, 2866, 1475, 1462, 1418, 1360, 1202, 1079, 890, 861, 836, 810, 758, 735, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 5.1, 2.8 Hz, 1H), 6.98 (ddd, *J* = 2.8, 1.4, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.21 (dd, *J* = 12.4, 1.4 Hz, 1H), 5.62 (d, *J* = 12.4 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 139.1, 129.3, 124.2, 122.1, 121.6, 33.8, 30.9; MS (EI) *m*/*z* (relative

intensity, %): 166 (M, 47), 153 (5), 152 (12), 151 (100), 136 (8), 135 (7), 134 (5), 123 (9), 118 (9), 117 (12), 111 (6), 105 (7), 97 (24), 91 (8), 77 (4), 67 (7), 65 (5), 59 (7); HRMS (EI) calcd for $C_{10}H_{14}S$: 166.0816, found 166.0812. Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49. found: C, 72.40; H, 8.44.

3-Methyl-1-phenyl-1-pentene (2h)

To a mixture of phenyl acetylene (99.5 mg, 0.98 mmol), 1,2-dibromoethane (373 mg, 2.0 mmol) and AgOTs (14.0 mg, 0.05 mmol), P(*p*-$C_6H_4Cl)_3$ (18.3 mg, 0.05 mmol) was added *sec*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 106 mg (68%) of **2h** as a mixture of stereoisomers (*E*/*Z* = 14/86). IR(NaCl): 2961, 2926, 2873, 1600, 1493, 1456, 1378, 1074, 1030, 965, 916, 798, 778, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.20 (m, 5H), 6.40-6.32 (m, 1H), 6.10 (dd, *J* = 15.9, 7.6 Hz, 0.14H), 5.43 (t, *J* = 11.1 Hz, 0.86H), 2.70-2.62 (m, 0.86H), 2.24-2.16 (m, 0.14H), 1.42-1.29 (m, 2H), 1.07 (d, *J* = 6.8 Hz, 0.42H), 1.03 (d, *J* = 6.6 Hz, 2.58 H), 0.92-0.84 (m, 3H);^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 139.4, 136.8, 128.6, 128.1, 127.5, 126.3, 33.8, 30.3, 20.7, 11.8; (*E* isomer): δ 138.0, 136.8, 128.5, 128.1, 126.7, 125.9, 38.9, 29.8, 20.2, 11.9; MS (EI) *m*/*z* (relative intensity, %) (*Z* isomer): 160 (M, 25), 145 (6), 132 (12), 131 (100), 129 (7), 128 (5), 117 (5), 116 (8), 115 (9), 104 (8), 91 (23), 77 (4); HRMS (EI) calcd for $C_{12}H_{16}$: 160.1252, found 160.1243. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. found: C, 89.54; H, 9.80.

1-Cyclohexyl-2-phenylethene (2i)

To a mixture of phenyl acetylene (102.4 mg, 1.0 mmol), 1,2-dibromoethane (374 mg, 2.0 mmol) and AgOTs (14.0 mg, 0.05 mmol), P(*p*-$C_6H_4Cl)_3$ (18.3 mg, 0.05 mmol) was added cyclohexyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 132 mg (71%) of **2i** as a mixture of stereoisomers (*E*/*Z* = 20/80). IR(NaCl): 3002, 2924, 2850, 1705, 1600, 1492, 1448, 1074, 1029, 957, 890, 788, 766, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.16 (m, 5H), 6.36-6.29 (m, 1H), 6.18 (dd, *J* = 16.0, 7.0 Hz, 0.2H), 5.48 (t, *J* = 10.9 Hz, 0.8H), 2.61-2.54 (m, 0.8H), 2.18-2.07 (m, 0.2H), 1.82-1.65 (m, 5H), 1.36-1.12 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 139.0, 137.9, 128.6, 128.2, 126.8, 126.4, 36.9, 33.2, 26.01, 25.7; (*E* isomer): δ 138.0, 136.9, 128.5, 127.1, 126.7, 125.9, 41.2, 32.9, 26.2, 26.04; MS (EI)

m/*z* (relative intensity, %) (*Z* isomer): 186 (M, 30), 143 (9), 130 (7), 129 (22), 128 (14), 117 (9), 115 (12), 105 (12), 104 (100), 95 (8), 91 (13); HRMS (EI) calcd for $C_{14}H_{18}$: 186.1409, found 186.1413. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. found: C, 89.98; H, 9.78.

1-Phenyl-1-hexene (2j)

To a mixture of phenyl acetylene (101.6 mg, 1.0 mmol), 1,2-dibromoethane (373 mg, 2.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *n*-butyl magnesium chloride (2.0 M in Et_2O, 1.0 mL, 2.0 mmol) at -10 °C. After stirring for 3 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 91 mg (58%) of **2j** as a mixture of stereoisomers (*E*/*Z* = 43/57). IR(NaCl): 3026, 2957, 2929, 2903, 2872, 2859, 1706, 1600, 1494, 1455, 1378, 1272, 1072, 1027, 965, 748, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.16 (m, 5H), 6.41-6.36 (m, 1H), 6.22 (dt, *J* = 15.6, 6.8 Hz, 0.43H), 5.66 (dt, *J* = 11.7, 7.4 Hz, 0.57H), 2.36-2.30 (m, 1.14H), 2.24-2.18 (m, 0.86H), 1.49-1.30 (m, 4H), 0.94-0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 137.8, 133.2, 128.7, 128.6, 128.1, 126.4, 32.1, 28.3, 22.4, 14.0; (*E* isomer): δ 137.9, 131.2, 129.7, 128.4, 126.7, 125.9, 32.7, 31.5, 22.3, 14.0; MS (EI) *m*/*z* (relative intensity, %) (*Z* isomer): 160 (M, 41), 131 (5), 118 (12), 117 (100), 116 (8), 115 (28), 105 (6), 104 (59), 92 (4), 91 (22), 77 (4); (*E* isomer): 160 (M, 40), 131 (5), 118 (11), 117 (100), 116 (8), 115 (26), 105 (6), 104 (54), 91 (21), 77 (4); HRMS (EI) calcd for $C_{12}H_{16}$: 160.1252, (*Z* isomer): found 160.1234; (*E* isomer): found 160.1235. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. found: C, 89.70; H, 9.77.

1-Phenyl-1-decene (2k)

To a mixture of phenyl acetylene (103.5 mg, 1.0 mmol), 1,2-dibromoethane (373 mg, 2.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *n*-octyl magnesium bromide (2.0 M in Et_2O, 1.0 mL, 2.0 mmol) at -10 °C. After stirring for 3 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) and HPLC with $CHCl_3$ as an eluent gave 158 mg (73%) of **2k** as a mixture of stereoisomers (*E*/*Z* = 42/58). IR(NaCl): 3025, 2924, 2854, 1600, 1494, 1466, 1448, 963, 768, 742, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.16 (m, 5H), 6.41-6.35 (m, 1H), 6.23 (dt, *J* = 15.6, 6.8 Hz, 0.42H), 5.66 (dt, *J* = 11.7, 7.3 Hz, 0.58H), 2.35-2.29 (m, 1.16H), 2.22-2.17 (m, 0.84H), 1.48-1.40 (m, 2H), 1.35-1.26 (m, 10H), 0.90-0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 137.8, 133.3, 128.7, 128.6, 128.1,

126.4, 31.9, 30.0, 29.5, 29.4, 29.3, 28.6, 22.7, 14.1; (*E* isomer): δ 137.9, 131.3, 129.6, 128.4, 126.7, 125.9, 33.1, 31.9, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1; MS (EI) *m*/*z* (relative intensity, %) (*Z* isomer): 216 (M, 23), 131 (5), 118 (12), 117 (74), 116 (5), 115 (16), 105 (11), 104 (100), 92 (6), 91 (23), 77 (3); (*E* isomer): 216 (M, 26), 131 (5), 118 (11), 117 (79), 116 (6), 115 (17), 105 (10), 104 (100), 92 (5), 91 (21), 77 (2); HRMS (EI) calcd for $C_{16}H_{24}$: 216.1878, (*Z* isomer): found 216.1866; (*E* isomer): found 216.1876. Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. found: C, 88.56; H, 10.98.

3,3-Dimethyl-1-dimethylphenylsilyl-1-butene (2l)

To a mixture of dimethylphenylsilyl acetylene (158.5 mg, 0.99 mmol), 1,2-dibromoethane (376 mg, 1.0 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 1.0 mL, 2.0 mmol) at -10 °C. After stirring for 3 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 142 mg (66%) of **2l** as a mixture of stereoisomers (*E*/*Z* = 8/92). IR(NaCl): 3051, 2956, 2905, 2867, 1596, 1476, 1464, 1428, 1360, 1248, 1112, 822, 786, 731, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.56-7.52 (m, 2H), 7.36-7.30 (m, 3H), 6.48 (d, *J* = 15.6 Hz, 1H), 5.51 (d, *J* = 15.6 Hz, 1H), 0.96 (s, 9H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 161.7, 140.9, 133.7, 128.6, 127.6, 122.6, 35.6, 30.0, 0.83; MS (EI) *m*/*z* (relative intensity, %): 218 (M, 5), 204 (8), 203 (40), 162 (9), 161 (60), 149 (6), 148 (10), 145 (6), 136 (13), 135 (100), 125 (10), 121 (31), 119 (5), 107 (6), 105 (12), 91 (4), 73 (30), 59 (9); HRMS (EI) calcd for $C_{14}H_{22}Si$: 218.1491, found 218.1501. Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. found: C, 76.72; H, 10.10.

1-Deuterio-3,3-dimethyl-1-phenyl-1-butene (3a)

To a mixture of phenyl acetylene (100 mg, 0.98 mmol), 1,2-dibromoethane (185.4 mg, 0.99 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, D_2O was added to the solution at -10 °C. After stirring for 3 h at 25 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 146 mg (94%) of **3a** as a mixture of stereoisomers (*E*/*Z* = 2/98). IR(NaCl): 3020, 2959, 2904, 2867, 1599, 1492, 1475, 1461, 1442, 1361, 1202, 1028, 918, 744, 721, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.29-7.17 (m, 5H), 5.60 (t, *J* = 1.8 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 142.6, 139.3, 129.0,

127.5, 126.8 (t, J = 23.6 Hz), 126.2, 34.1, 31.2; MS (EI) m/z (relative intensity, %): 161 (M, 27), 147 (12), 146 (100), 131 (10), 130 (7), 129 (7), 118 (13), 106 (6), 92 (15), 91 (7); HRMS (EI) calcd for $C_{12}H_{15}D$: 161.1314, found 161.1315. Anal. Calcd for $C_{12}H_{15}D$: C, 89.38; H and D, 10.62. found: C, 89.17; H and D, 10.83.

4,4-Dimethyl-2-phenyl-2-pentenoic acid (3b)

To a mixture of phenyl acetylene (100.7 mg, 0.99 mmol), 1,2-dibromoethane (187 mg, 1.00 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, dry Et_2O (0.8 mL) and CO_2 was added to the solution at -10 °C. Aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (hexane/ether = 1/2) gave 178 mg (88%) of **3b** as a mixture of stereoisomers (E/Z = 98/2). Mp: 129-133 °C; IR(KBr): 2965, 1674, 1423, 1268, 922, 784, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (Z isomer): δ 7.33-7.29 (m, 3H), 7.16-7.13 (m, 3H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (Z isomer): δ 173.2, 155.8, 135.6, 130.6, 130.1, 127.6, 127.5, 34.4, 30.2; MS (EI) m/z (relative intensity, %): 204 (M, 100), 189 (30), 186 (11), 171 (14), 161 (14), 159 (21), 146 (37), 145 (16), 144 (14), 143 (82), 129 (21), 128 (41), 127 (11), 118 (18), 117 (52), 116 (9), 115 (20), 103 (12), 102 (9), 91 (16), 77 (16), 59 (37); HRMS (EI) calcd for $C_{13}H_{16}O_2$: 204.1150, found 204.1154. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. found: C, 76.23; H, 7.65.

4,4-Dimethyl-1,2-diphenyl-2-pentene-1-ol (3c)

To a mixture of phenyl acetylene (105.5 mg, 1.03 mmol), 1,2-dibromoethane (189 mg, 1.01 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, dry Et_2O (0.8 mL) and benzaldehyde (212 mg, 2.0 mmol) was added to the solution at -10 °C. After stirring for 3 h at 25 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (hexane/ether = 90/10) gave 223 mg (81%) of **3c** as a mixture of stereoisomers (E/Z = 98/2). IR(NaCl): 3391, 3058, 3029, 2957, 2901, 2866, 1600, 1574, 1493, 1475, 1452, 1360, 1220, 1190, 1069, 1029, 1005, 916, 775, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (Z isomer): δ 7.29-7.12 (m, 8H), 6.80-6.77 (m, 2H), 5.90 (s, 1H), 5.26 (d, J = 4.9 Hz, 1H), 1.96 (d, J = 4.9 Hz, 1H), 0.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (Z isomer): δ 142.1, 140.1, 138.7, 137.7, 130.3, 128.0, 127.25, 127.21, 126.8, 126.5, 80.2, 33.4, 31.2; MS (EI) m/z (relative intensity,

%): 266 (M, 1), 209 (20), 208 (10), 161 (10), 160 (69), 146 (12), 145 (100), 131 (5), 129 (8), 128 (7), 117 (17), 107 (32), 105 (13), 103 (8), 91 (9), 79 (14), 77 (15), 57 (23); HRMS (EI) calcd for $C_{19}H_{22}O$: 266.1671, found 266.1674. Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. found: C, 85.38; H, 8.26.

3,3-Dimethyl-1-phenyl-1-phenylsilyl-1-butene (3d)

To a mixture of phenyl acetylene (101 mg, 0.99 mmol), 1,2-dibromoethane (188 mg, 1.01 mmol) and (IMes)AgCl (22.4 mg, 0.05 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.8 mL, 1.6 mmol) at -10 °C. After stirring for 30 min, dry THF (1.2 mL) and chlorophenylsilane (0.27 mL, 2.0 mmol) was added to the solution at -10 °C. After stirring for 1 h at 25 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give a crude product. Purification by column chromatography on silica gel (pentane) and HPLC with $CHCl_3$ as an eluent gave 194 mg (74%) of **3d** as a mixture of stereoisomers (*E*/*Z* = 98/2). IR(NaCl): 3053, 2958, 2901, 2867, 2134, 1608, 1592, 1490, 1494, 1462, 1429, 1360, 1205, 1115, 1071, 951, 924, 890, 839, 732, 712, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*Z* isomer): δ 7.47-7.45 (m, 2H), 7.38-7.29 (m, 3H), 7.21-7.10 (m, 3H), 6.96-6.94 (m, 2H), 6.18 (s, 1H), 4.59 (s, 2H), 0.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 154.9, 141.5, 135.6, 134.5, 132.0, 129.6, 128.2, 127.8, 127.6, 125.3, 36.6, 30.9; MS (EI) *m*/*z* (relative intensity, %): 266 (M, 44), 224 (21), 223 (53), 209 (32), 207 (12), 197 (19), 196 (68), 195 (15), 184 (18), 183 (100), 181 (14), 173 (15), 159 (54), 158 (14), 157 (20), 143 (13), 131 (37), 128 (10), 121 (15), 117 (24), 107 (32), 105 (58), 57 (15); HRMS (EI) calcd for $C_{18}H_{22}Si$: 266.1491, found 266.1493. Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. found: C, 80.99; H, 8.33.

2,2-Dimethyl-dodec-5-yne (7a) and 2,2-Dimethyl-dodeca-4,5-diene (7b)

To a mixture of dec-1-en-3-yne **6a** (66 mg, 0.49 mmol), 1,2-dibromoethane (93.2 mg, 0.50 mmol) and (IMes)AgCl (11.2 mg, 0.025 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.4 mL, 0.8 mmol) at -10 °C. After stirring for 30 min, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 60 mg (64%) of **7a** and 24 mg (26%) of **7b**. **7a**: IR(NaCl): 2955, 2932, 2859, 1467, 1365, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.15-2.08 (m, 4H), 1.49-1.26 (m, 10H), 0.90-0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 80.9, 79.8, 43.5, 31.4, 30.3, 29.1, 29.0, 28.6, 22.6, 18.8, 14.3, 14.1; MS (EI) *m*/*z* (relative intensity, %): 194 (M, 4), 179 (10), 165 (11), 151 (9), 123 (19), 110 (13), 109 (67), 97 (8), 96 (26), 95 (64), 83 (15), 82 (18), 81 (64), 71 (19), 70 (12), 69

(29), 68 (19), 67 (39), 57 (100), 55 (20), 43 (28), 41 (28); HRMS (EI) calcd for $C_{14}H_{26}$: 194.2035, found 194.2040. Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. found: C, 86.28; H, 13.60. **7b**: IR(NaCl): 2956, 2928, 2858, 1963, 1467, 1378, 1242, 1199, 883 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05-5.00 (m, 2H), 2.01-1.94 (m, 2H), 1.89-1.86 (m, 2H), 1.43-1.24 (m, 8H), 0.94-0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2, 89.5, 87.6, 44.0, 31.7, 31.2, 29.3, 29.04, 29.00, 28.8, 22.6, 14.1; MS (EI) *m*/*z* (relative intensity, %): 194 (M, 0.3), 124 (29), 109 (11), 96 (6), 95 (12), 81 (13), 69 (6), 68 (36), 67 (12), 57 (100), 54 (8), 41 (15); HRMS (EI) calcd for $C_{14}H_{26}$: 194.2035, found 194.2049. Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. found: C, 86.25; H, 13.45.

1-[1-(2,2-Dimethyl-propyl)-non-2-ynyl]-cyclopentanol (9a)

To a mixture of dec-1-en-3-yne **6a** (66 mg, 0.49 mmol), 1,2-dibromoethane (92.6 mg, 0.50 mmol) and (IMes)AgCl (11.2 mg, 0.025 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.4 mL, 0.8 mmol) at -10 °C. After stirring for 30 min, dry Et_2O (1.2 mL) and cyclopentanone (83.2 mg, 0.99 mmol) was added to the solution at -10 °C. After stirring for 1 h at -10 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give a crude product. Purification by column chromatography on silica gel (hexane/Et_2O = 95/5) gave 114 mg (85%) of **9a**. IR(NaCl): 3461, 2956, 2861, 1468, 1394, 1365, 1328, 1247, 1197, 999, 909, 884 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (tt, *J* = 4.9, 2.2 Hz, 1H), 2.15 (td, *J* = 6.8, 2.2 Hz, 2H), 1.86-1.58 (m, 11H), 1.52-1.24 (m, 8H), 0.96 (s, 9H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 84.5, 82.9, 82.8, 44.6, 38.8, 38.5, 37.2, 31.3, 30.6, 29.8, 29.0, 28.6, 24.4, 24.3, 22.6, 18.8, 14.0; MS (CI) *m*/*z* (relative intensity, %): 279 (M+1, 6), 262 (21), 261 (100), 205 (22), 191 (23), 177 (11), 165 (5), 151 (5), 124 (7), 109 (8); HRMS (CI) calcd for $C_{19}H_{35}O$: 279.2688, found 279.2687. Anal. Calcd for $C_{19}H_{34}O$: C, 81.95; H, 12.31. found: C, 81.62; H, 12.30.

1-[1-(2-Methyl-butyl)-non-2-ynyl]-cyclopentanol (9b)

To a mixture of dec-1-en-3-yne **6a** (67.5 mg, 0.50 mmol), 1,2-dibromoethane (91.3 mg, 0.49 mmol) and (IMes)AgCl (11.2 mg, 0.025 mmol) was added *sec*-butyl magnesium chloride (2.0 M in Et_2O, 0.4 mL, 0.8 mmol) at -10 °C. After stirring for 3 h, dry Et_2O (1.2 mL) and cyclopentanone (84.4 mg, 1.0 mmol) was added to the solution at -10 °C. After stirring for 1 h at -10 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give a crude product. Purification by column chromatography on silica gel (pentane/Et_2O = 95/5) gave 113 mg (81%) of **9b** as a mixture of diastereomers with ca. 1:1 ratio indicated by ^{1}H, ^{13}C

NMR and GC. A 1:1 mixture of diastereomers; IR(NaCl): 3454, 2958, 2872, 1463, 1378, 1328, 1272, 1196, 1066, 998, 906 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50-2.44 (m, 1H), 2.19-2.15 (m, 2H), 1.83-1.57 (m, 11H), 1.52-1.23 (m, 10H), 1.10-0.99 (m, 1H), 0.94-0.85 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 83.85, 83.81, 83.3, 83.2, 80.9, 80.7, 40.9, 40.8, 39.41, 39.35, 37.2, 37.10, 37.05, 37.0, 32.6, 32.3, 31.3, 30.7, 29.0, 28.49, 28.47, 27.3, 24.29, 24.28, 23.91, 23.90, 22.6 (2C), 20.1 (2C), 18.7, 18.3, 14.0 (2C), 11.5 (2C), 10.8 (2C); MS (CI) *m*/*z* (relative intensity, %): 279 (M+1, 13), 262 (22), 261 (100), 192 (6), 191 (54), 179 (8), 177 (8), 165 (8), 138 (9), 123 (8), 109 (14), 95 (7), 85 (5); HRMS (CI) calcd for $C_{19}H_{35}O$: 279.2688, found 279.2684. Anal. Calcd for $C_{19}H_{34}O$: C, 81.95; H, 12.31. found: C, 81.66; H, 12.42.

1-[1-(2,2-Dimethyl-propyl)-3-phenyl-prop-2-ynyl]-cyclopentanol (9d)

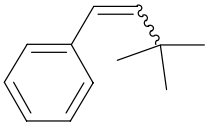
To a mixture of but-3-en-1-ynyl-benzene **6b** (63.1 mg, 0.49 mmol), 1,2-dibromoethane (91.6 mg, 0.50 mmol) and (IMes)AgCl (11.2 mg, 0.025 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.4 mL, 0.8 mmol) at -10 °C. After stirring for 30 min, dry Et_2O (1.2 mL) and cyclopentanone (84.4 mg, 1.0 mmol) was added to the solution at -10 °C. After stirring for 1 h at -10 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give a crude product. Purification by column chromatography on silica gel (hexane/Et_2O = 9/1) gave 115 mg (87%) of **9d**. IR(NaCl): 3452, 3055, 2955, 2868, 2228, 1699, 1634, 1598, 1489, 1472, 1442, 1365, 1245, 1197, 1070, 999, 911, 755, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.29-7.26 (m, 3H), 2.66 (dd, *J* = 8.8, 3.4 Hz, 1H), 1.90-1.61 (m, 11H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.4, 128.2, 127.7, 123.8, 92.9, 84.5, 82.9, 44.4, 39.2, 38.8, 37.7, 30.7, 29.8, 24.4, 24.3; MS (CI) *m*/*z* (relative intensity, %): 271 (M+1, 6), 254 (22), 253 (100), 197 (8), 186 (4), 130 (5); HRMS (CI) calcd for $C_{19}H_{27}O$: 271.2062, found 271.2067.

1-[1-(2,2-Dimethyl-propyl)-3-trimethylsilyl-prop-2-ynyl]-cyclopentanol (9e)

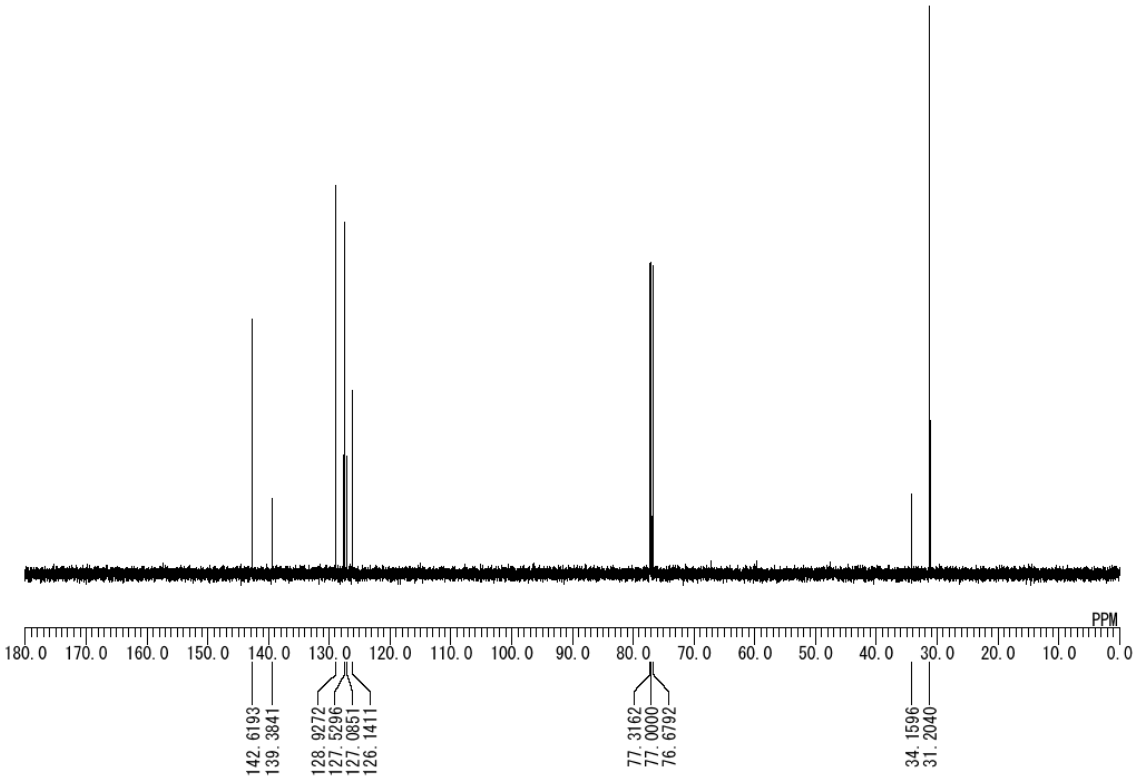
To a mixture of but-3-en-1-ynyl-trimethylsilane **6c** (63 mg, 0.51 mmol), 1,2-dibromoethane (91.3 mg, 0.49 mmol) and (IMes)AgCl (11.2 mg, 0.025 mmol) was added *tert*-butyl magnesium chloride (2.0 M in Et_2O, 0.4 mL, 0.8 mmol) at -10 °C. After stirring for 30 min, dry Et_2O (1.2 mL) and cyclopentanone (81.8 mg, 0.97 mmol) was added to the solution at -10 °C. After stirring for 1 h at -10 °C, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give a crude product. Purification by column chromatography on silica gel (pentane/Et_2O = 95/5) gave 115 mg (85%) of **9e**. IR(NaCl): 3458, 2956, 2869, 2165,

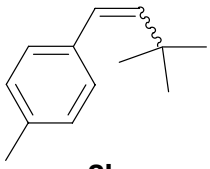
1475, 1394, 1366, 1250, 1197, 1066, 1000, 976, 874, 842, 759, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (dd, *J* = 9.6, 2.4 Hz, 1H), 1.86-1.45 (m, 11H), 0.96 (s, 9H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.2, 87.1, 84.1, 44.3, 39.5, 38.7, 37.3, 30.7, 29.8, 24.4, 24.3, 0.03; MS (CI) *m*/*z* (relative intensity, %): 267 (M+1, 2), 251 (6), 250 (23), 249 (100), 193 (9), 182 (5), 177 (7), 175 (7), 157 (7), 85 (5), 73 (7); HRMS (CI) calcd for $C_{16}H_{31}OSi$: 267.2144, found 267.2132. Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. found: C, 72.27; H, 11.28.

Copies of ^{1}H and ^{13}C NMR Spectra of 2a-l, 3a-d, 7a-b, 9a, 9b, 9d and 9e



2a





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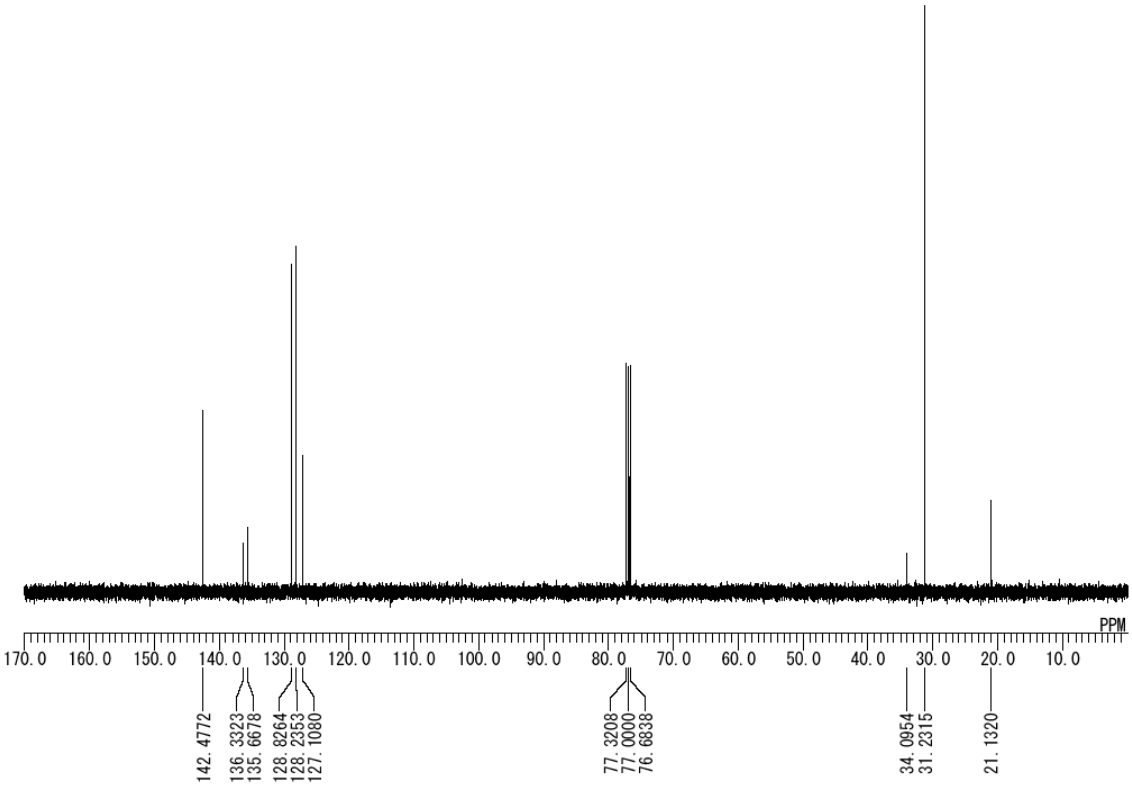
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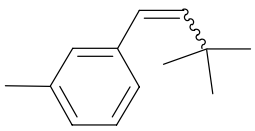

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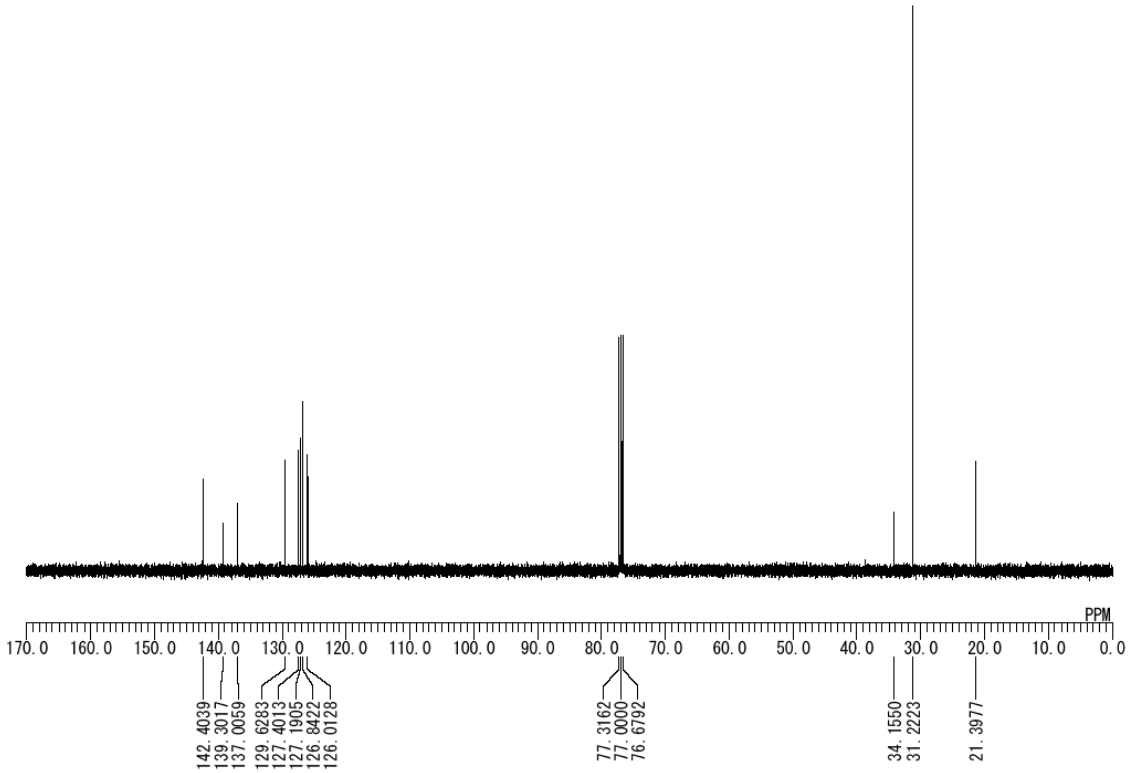
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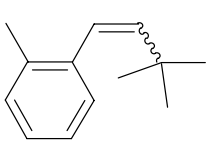

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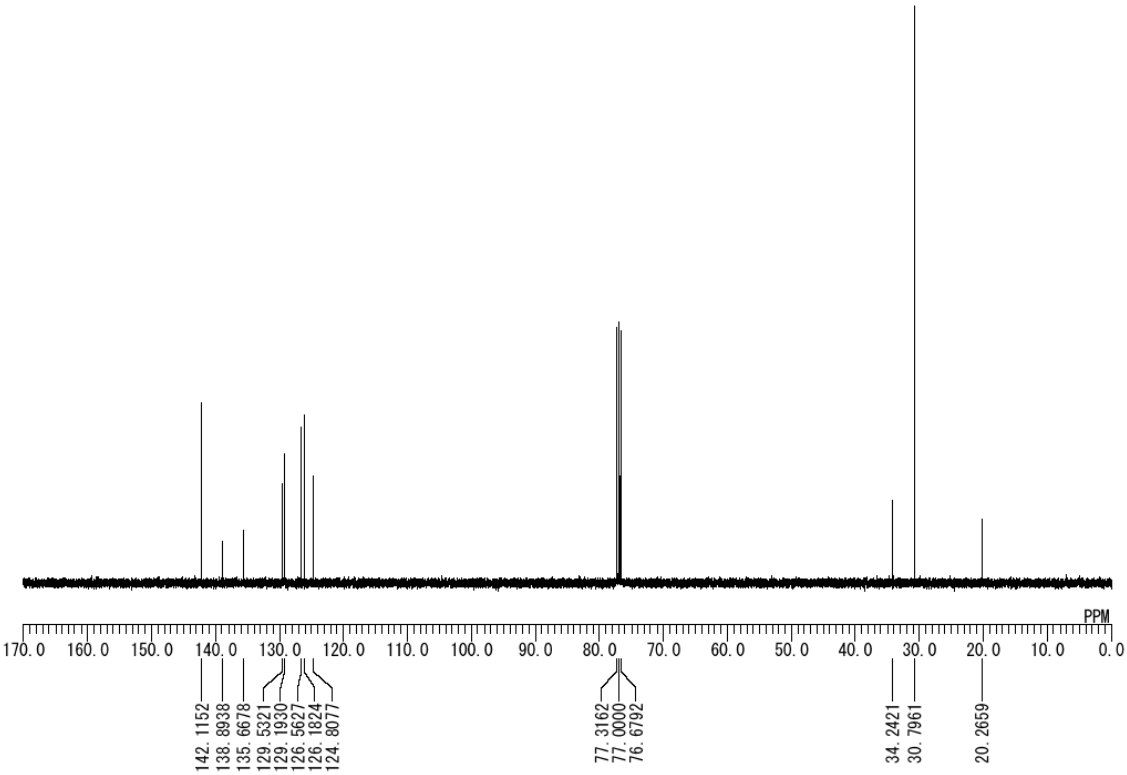
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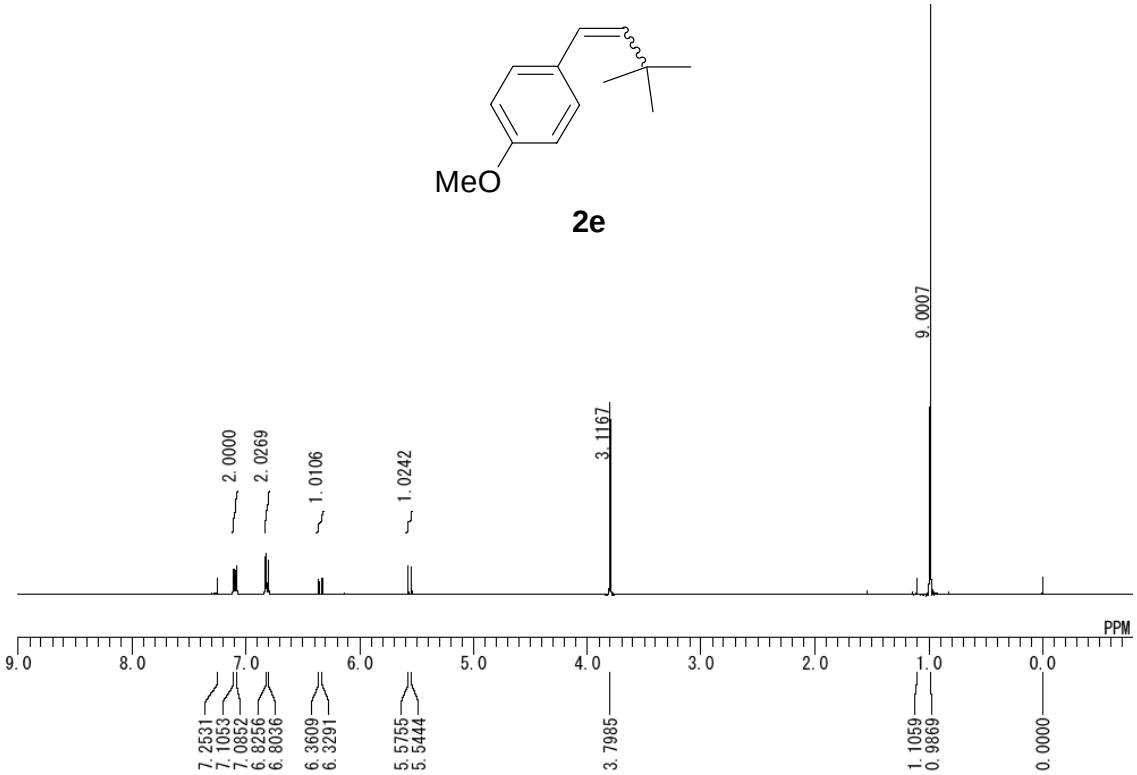
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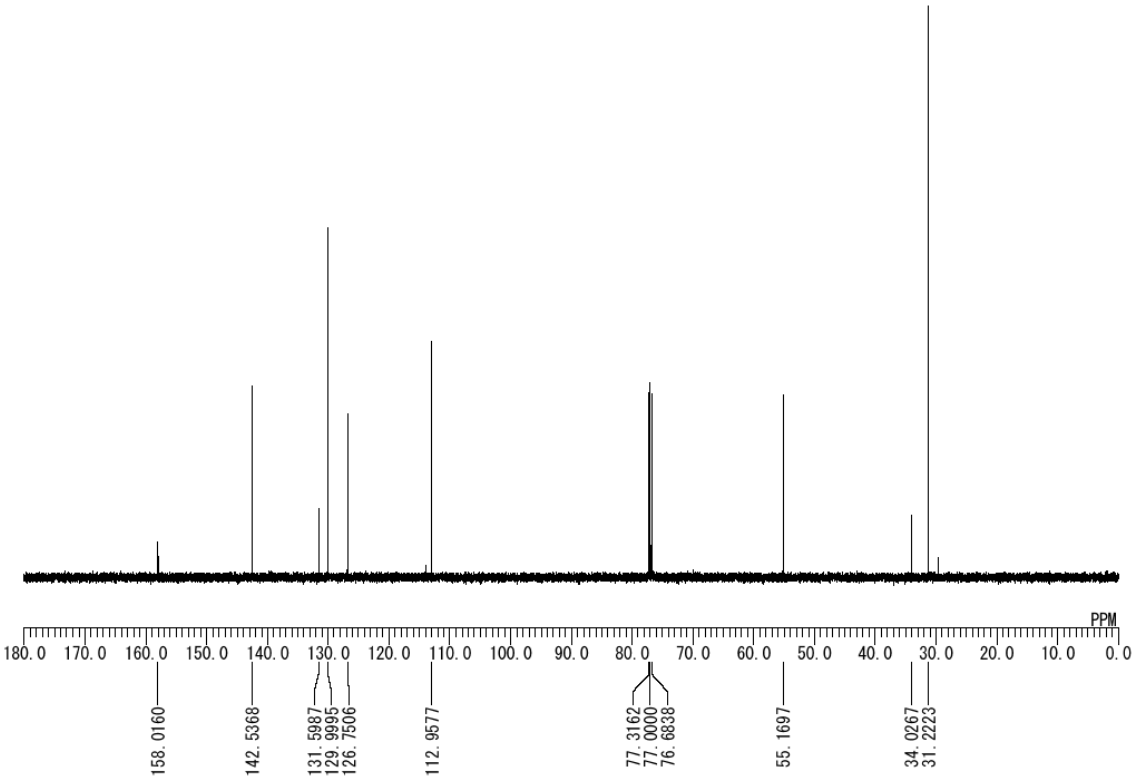
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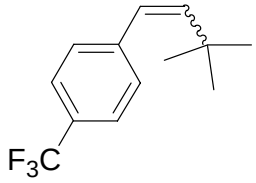
F3C

2f

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PPM
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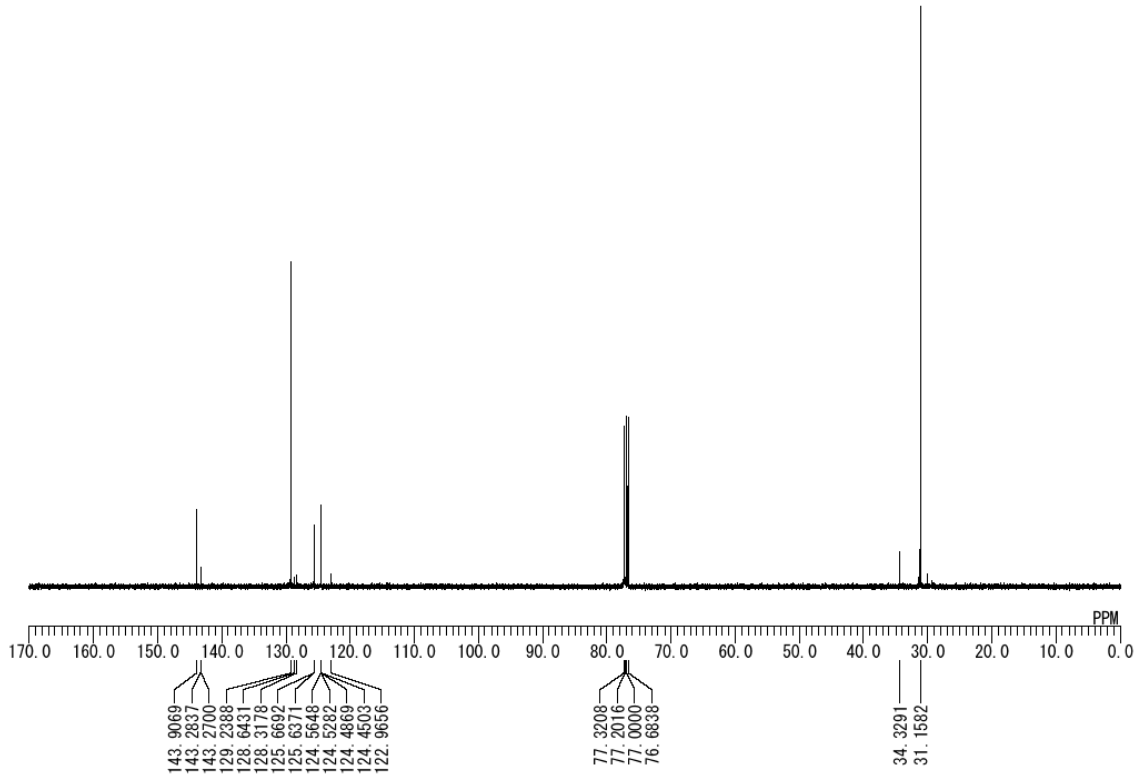
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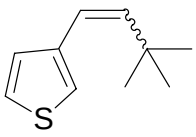
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2g

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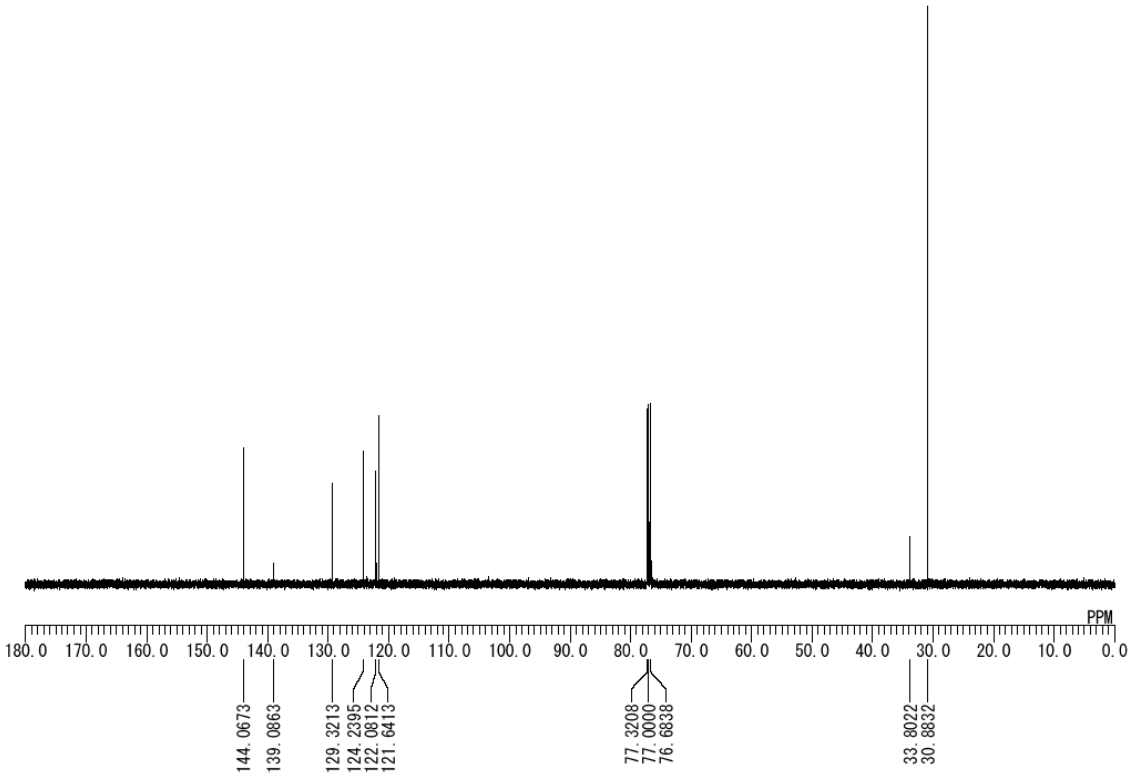
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40.0
30.0
20.0
10.0
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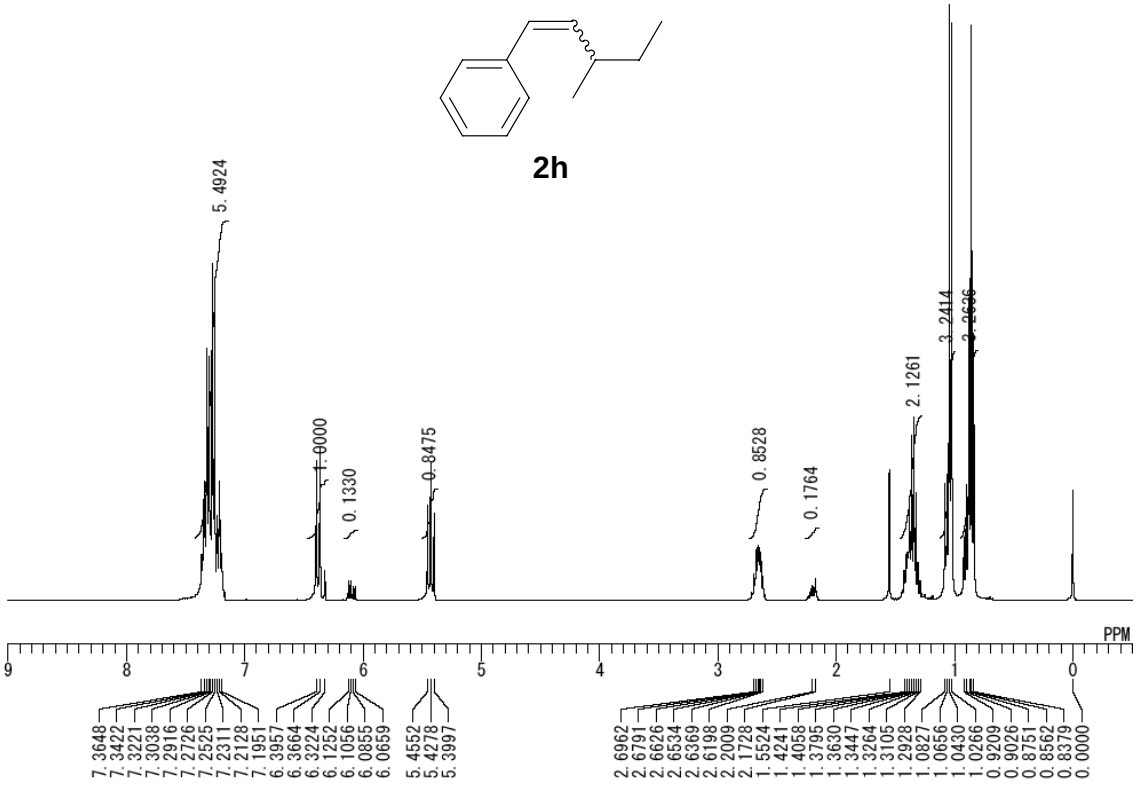
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0.8528
0.1764
2.1261
3.2414
3.2636
PPM
9
8
7
6
5
4
3
2
1
0
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7.3422
7.3221
7.3038
7.2916
7.2726
7.2525
7.2311
7.2128
7.1951
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6.3664
6.3224
6.1252
6.1056
6.0855
6.0659
5.4552
5.4278
5.3997
2.6962
2.6791
2.6626
2.6534
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2.2009
2.1728
1.5524
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1.3795
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1.3447
1.3264
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1.2928
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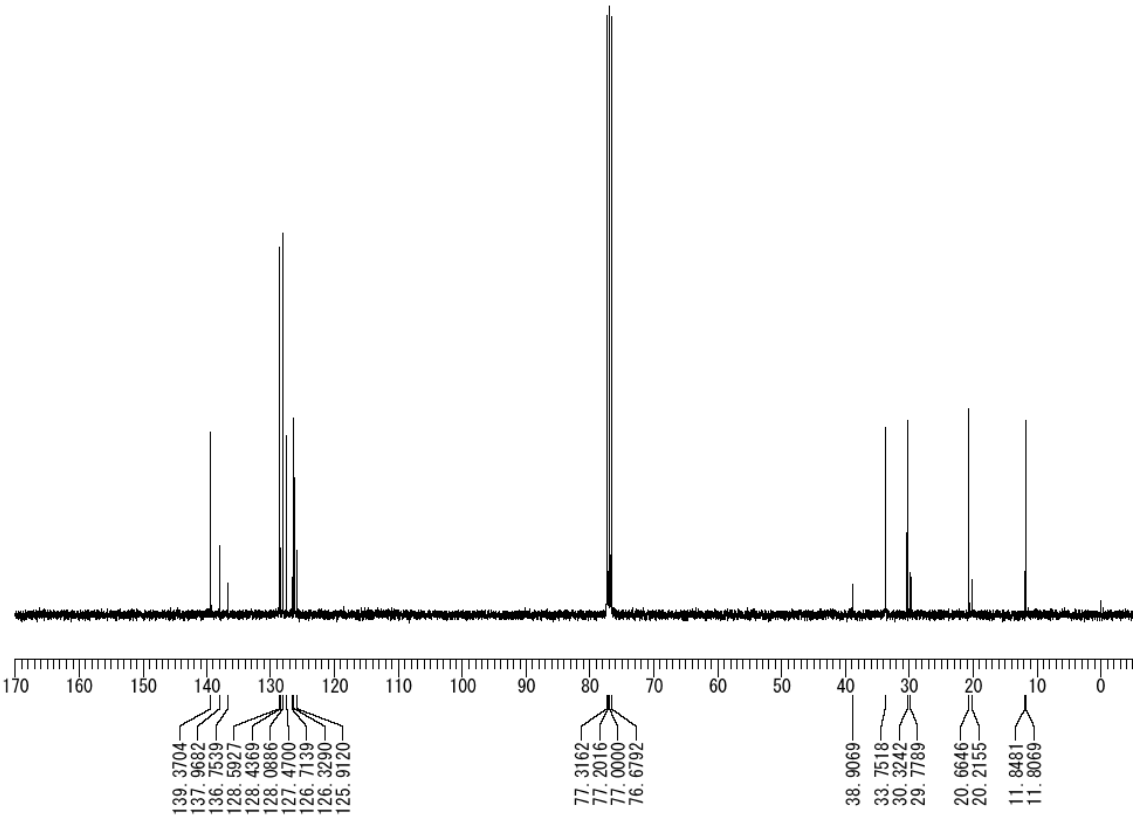
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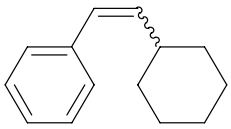

2i

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8
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3
2
1
0
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7.3343
7.3148
7.3044
7.2855
7.2702
7.2531
7.2427
7.2232
7.2036
7.1804
7.1627
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6.3242
6.2955
6.2064
6.1893
6.1667
6.1490
5.5126
5.4858
5.4583
2.6162
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2.1154
1.8162
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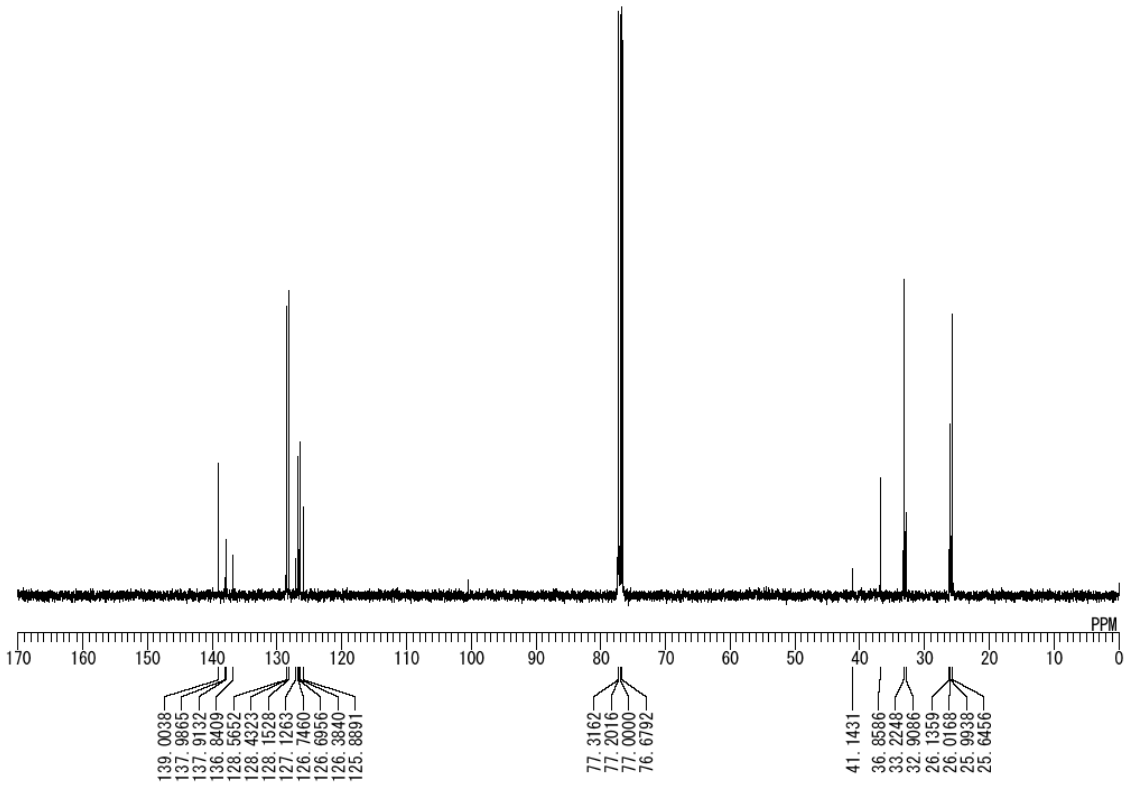
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140
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120
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20
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126.6956
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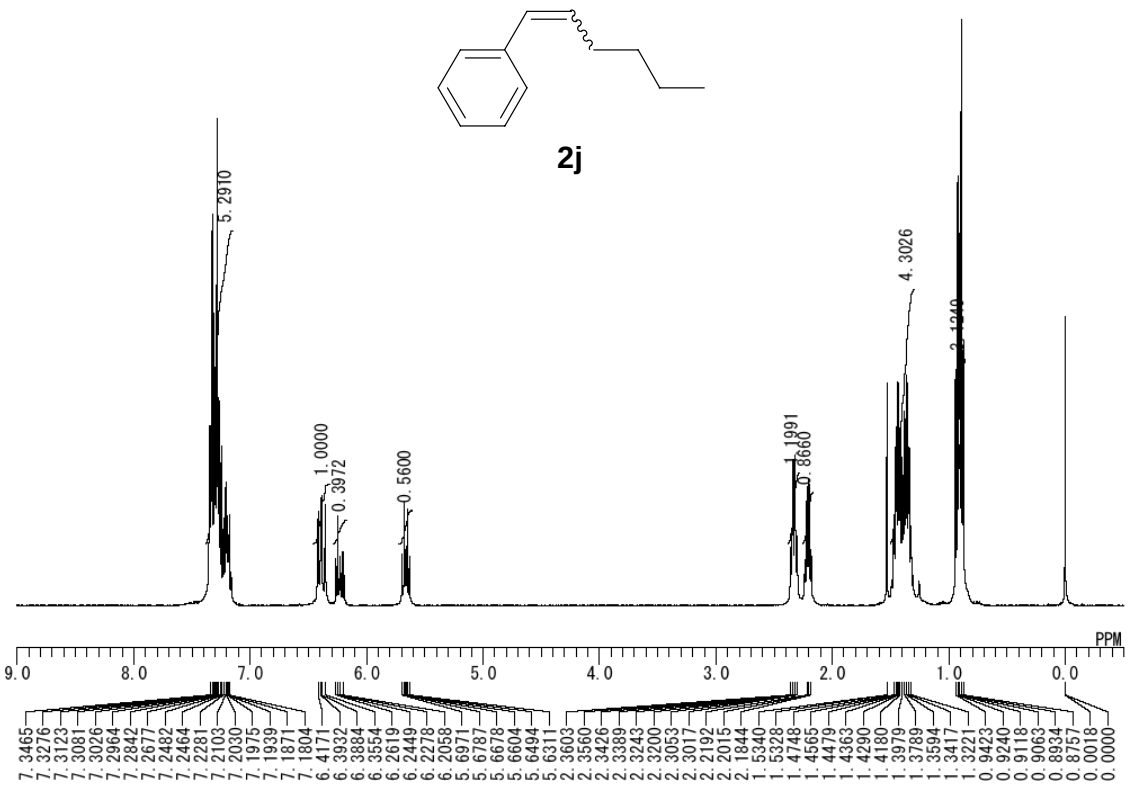
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5.0
4.0
3.0
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1.0
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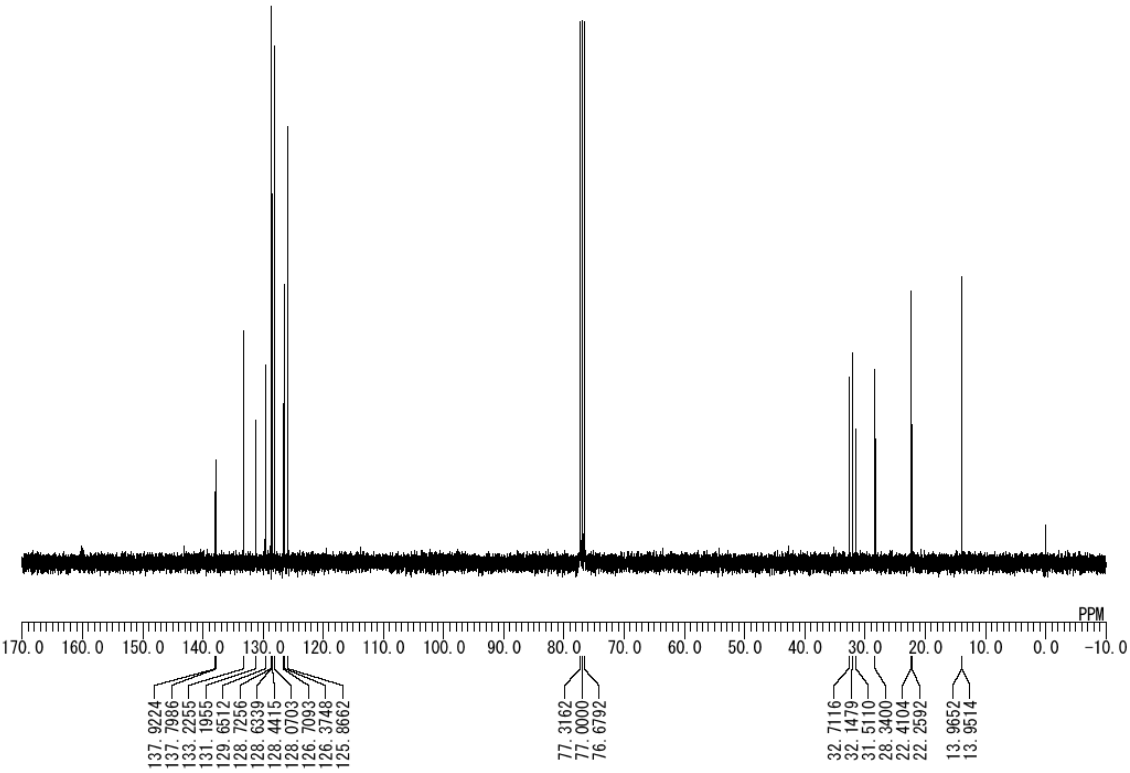
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110.0
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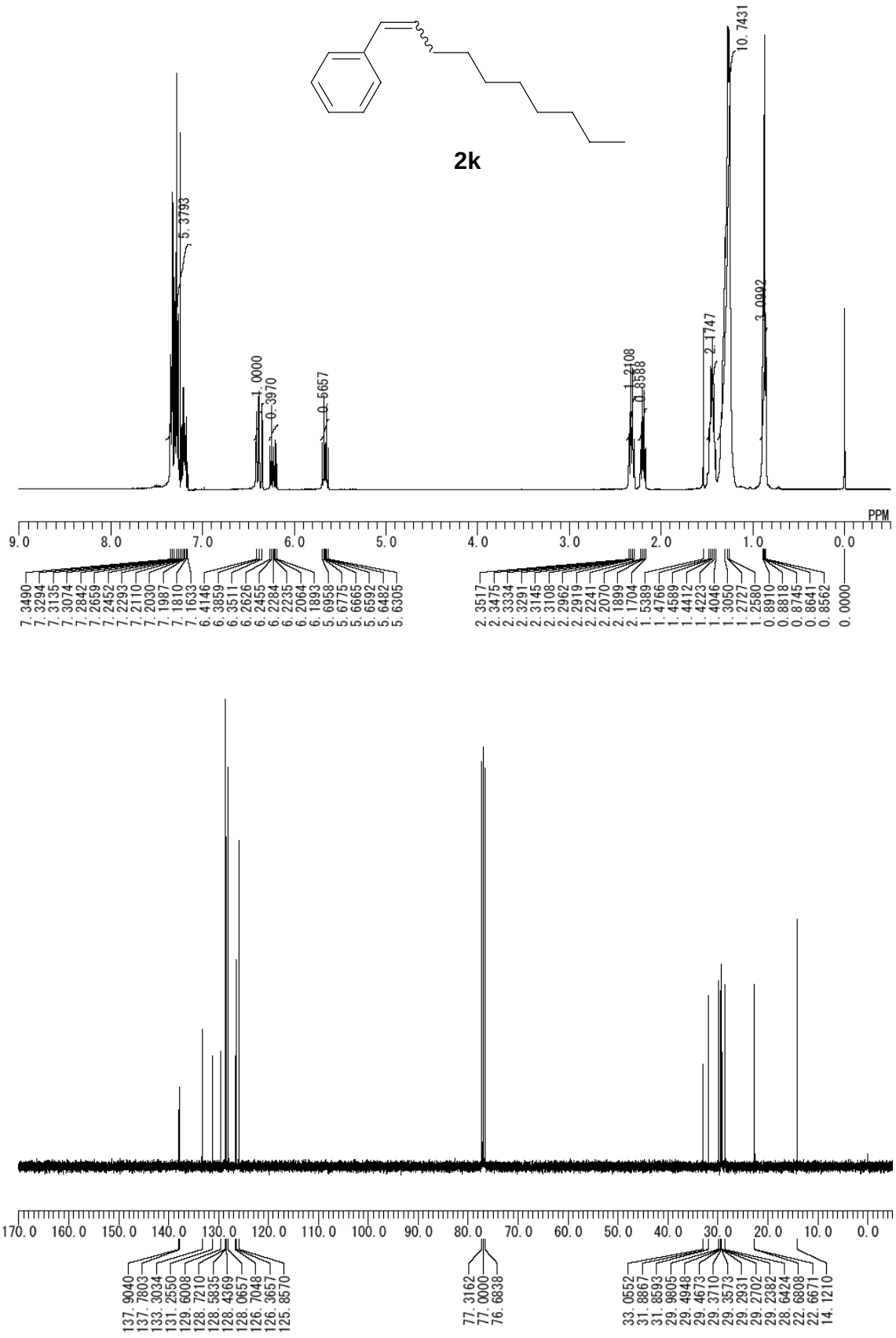
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PPM
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8.0
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6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.2110
7.2030
7.1987
7.1810
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6.3511
6.2626
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6.2284
6.2235
6.2064
6.1893
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5.6775
5.6665
5.6592
5.6482
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2.3475
2.3334
2.3291
2.3145
2.3108
2.2962
2.2919
2.2241
2.2070
2.1899
2.1704
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1.4766
1.4589
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1.4223
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1.3050
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1.2580
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0.8818
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0.8562
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140.0
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110.0
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80.0
70.0
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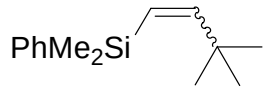
22.6808
22.6671
14.1210


PhMe2Si

2l

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PPM
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6
5
4
3
2
1
0
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7.3288
7.2464
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0.3139
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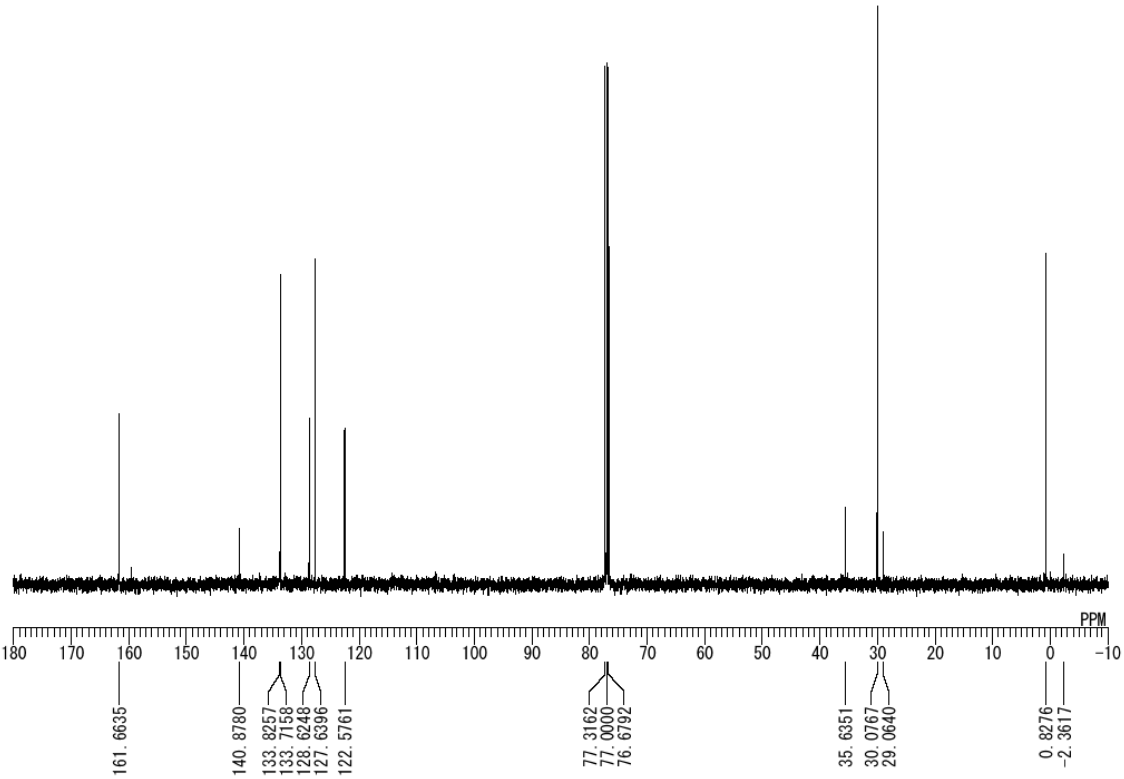
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110
100
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40
30
20
10
0
-10
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133.7158
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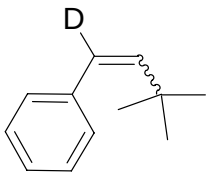
D

3a

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PPM
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.2848
7.2677
7.2525
7.2488
7.2134
7.2103
7.1951
7.1884
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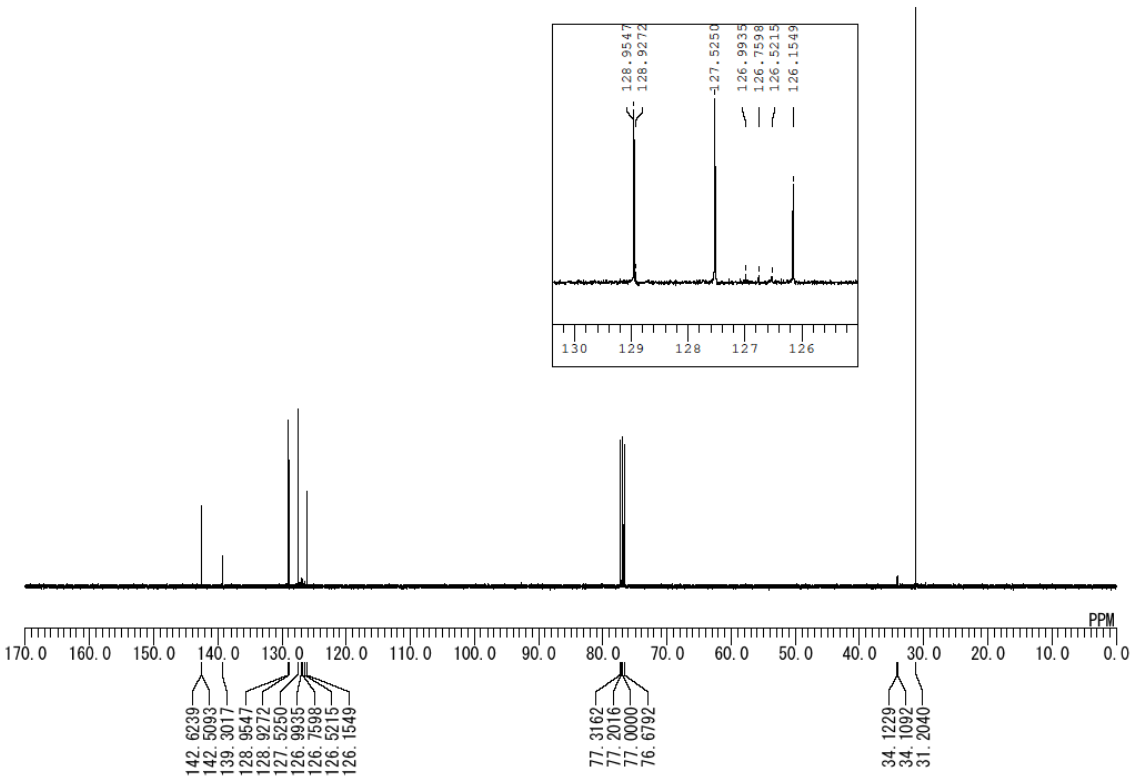
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126.7598
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126.1549
130
129
128
127
126
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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
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34.1229
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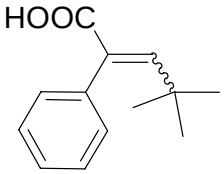
HOOC

3b

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3.0249
PPM
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8.0
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6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.2995
7.2580
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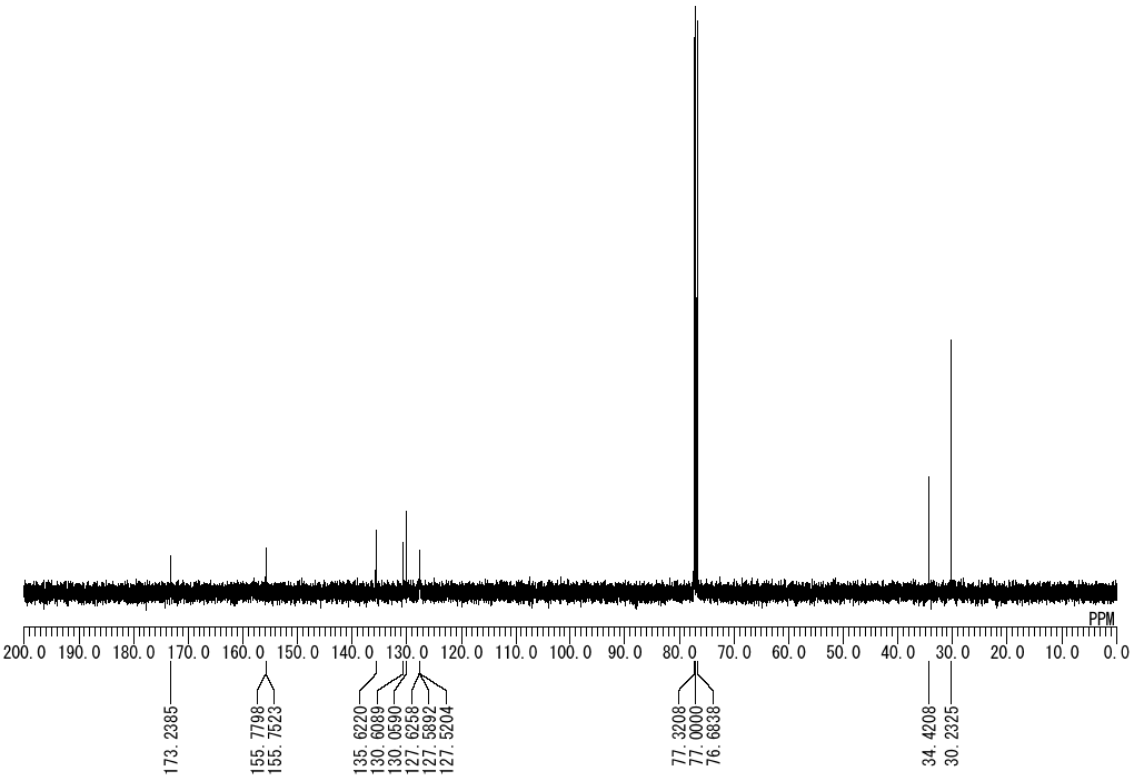
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173.2385
155.7798
155.7523
135.6220
130.6089
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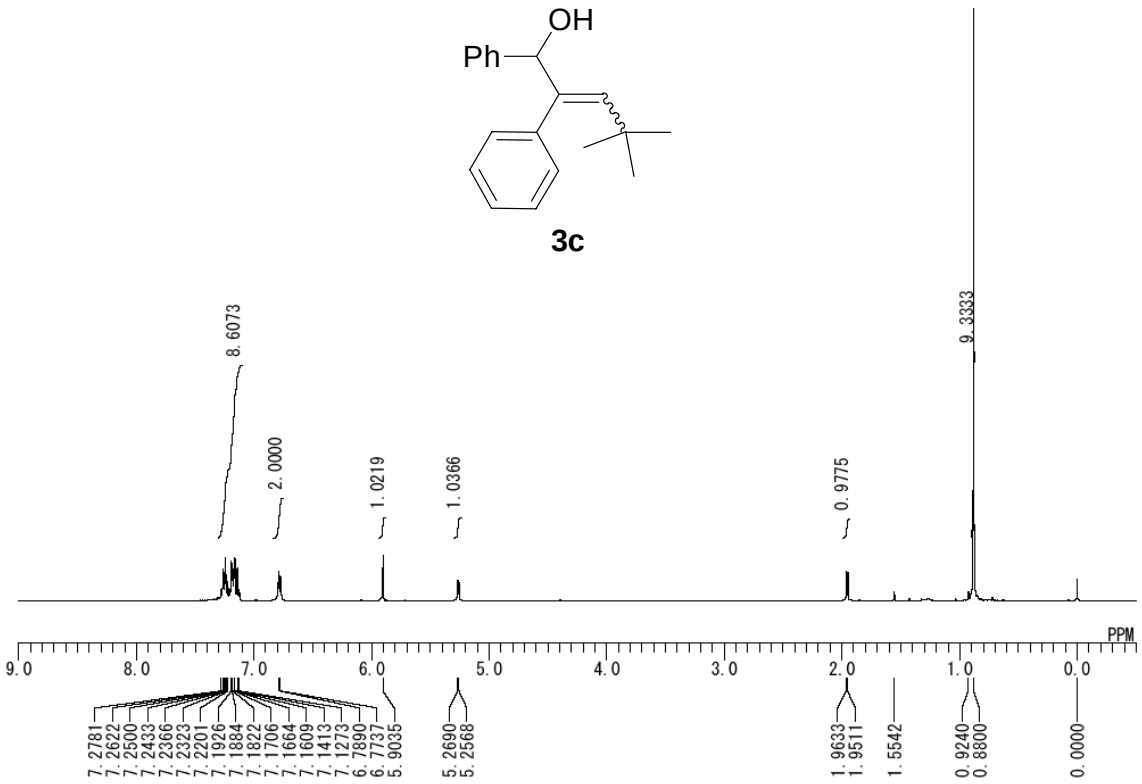
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Ph
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1.0219
1.0366
0.9775
9.3333
PPM
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.2781
7.2622
7.2500
7.2433
7.2366
7.2323
7.2201
7.1926
7.1884
7.1922
7.1706
7.1664
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7.1413
7.1273
6.7890
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1.5542
0.9240
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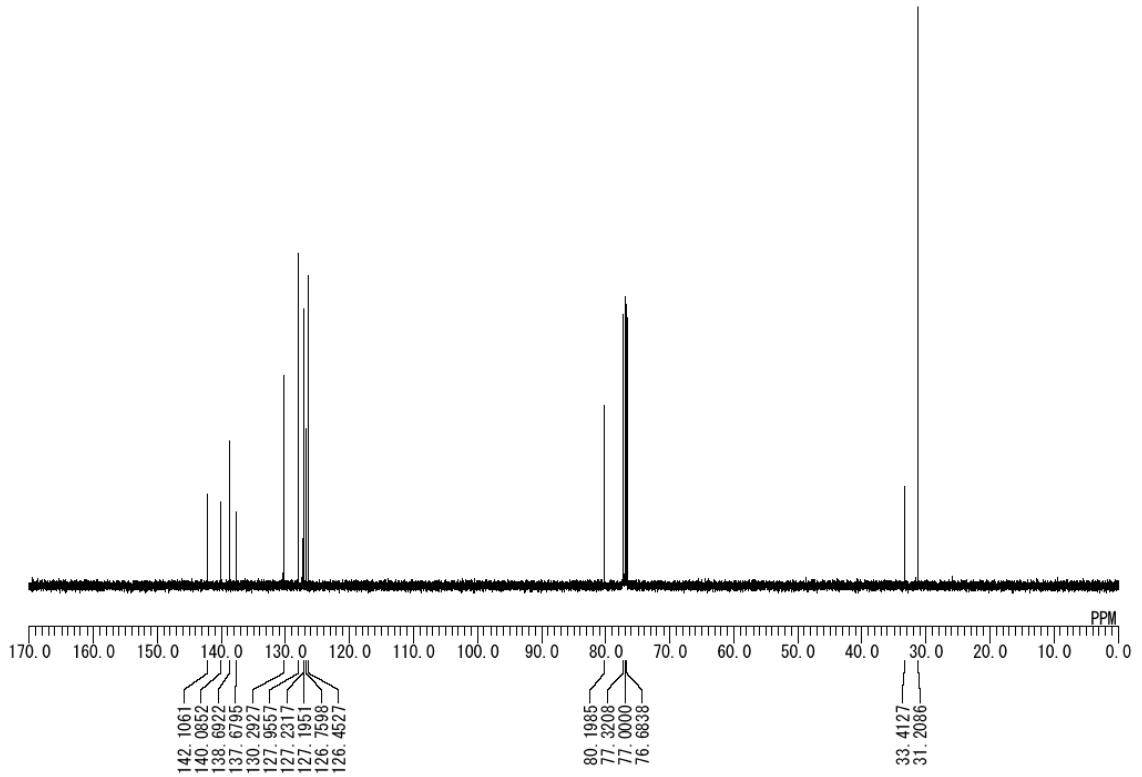
0.0000

3c


PPM
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
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138.6922
137.6795
130.2927
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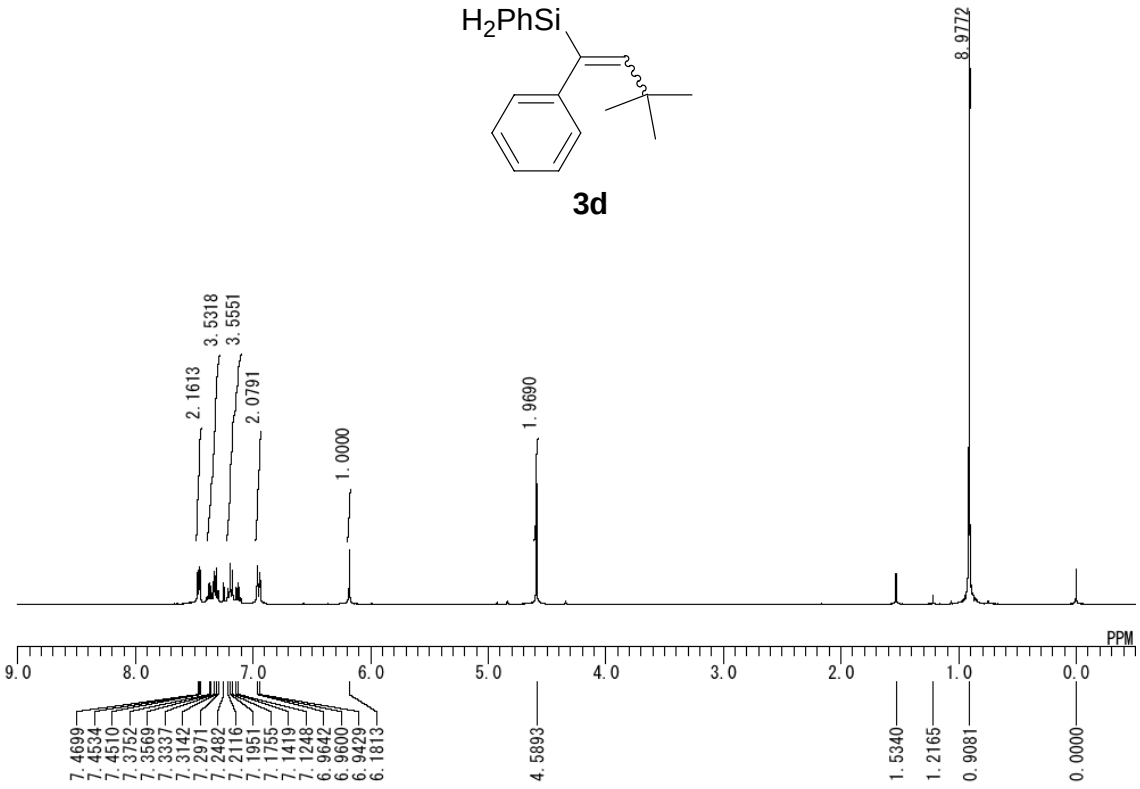
33.4127
31.2086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1.0000
1.9690
PPM
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.4534
7.4510
7.3752
7.3569
7.3337
7.3142
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7.2482
7.2116
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7.1755
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7.1248
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6.9600
6.9429
6.1813
4.5893
1.5340
1.2165
0.9081
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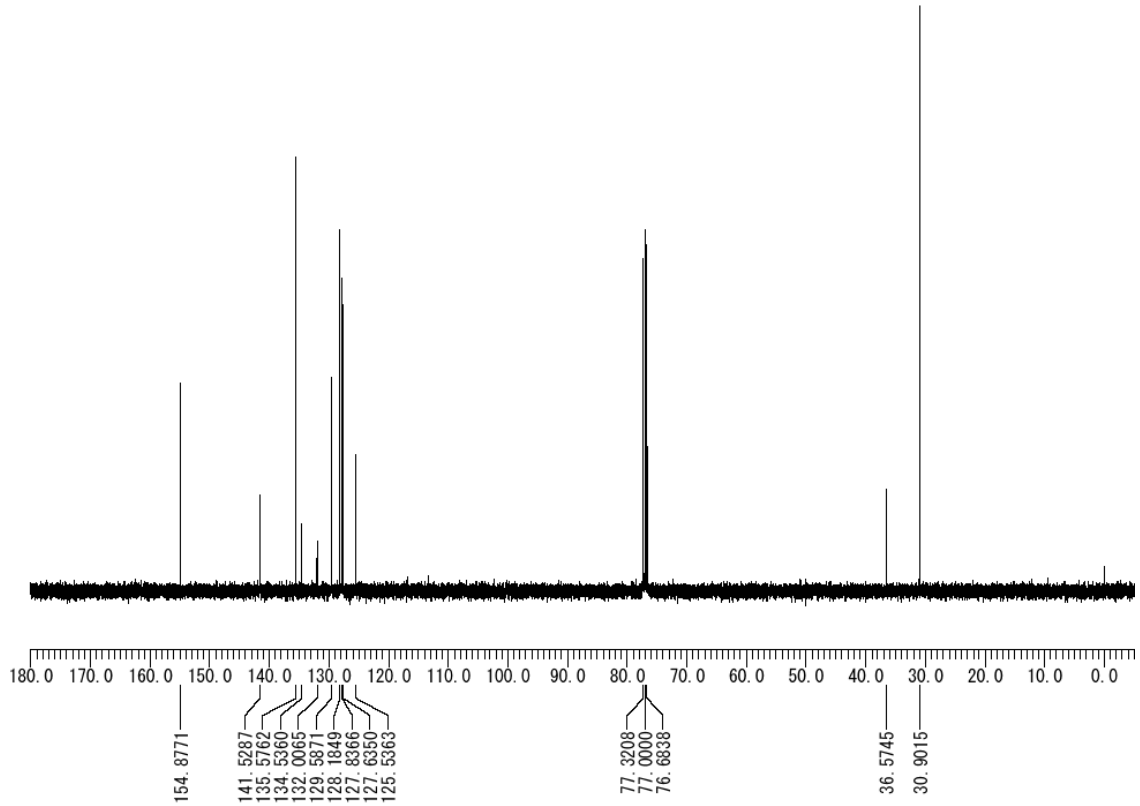
3d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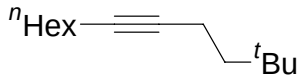
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2.0867
2.0812
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1.4284
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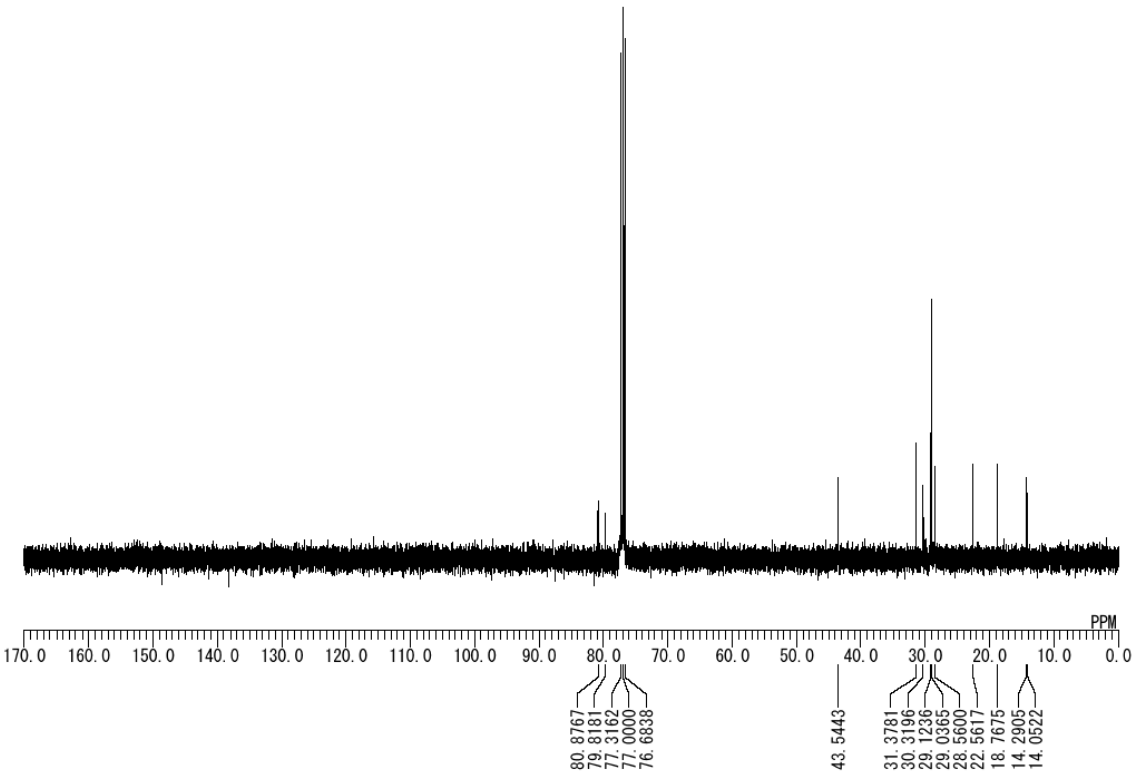
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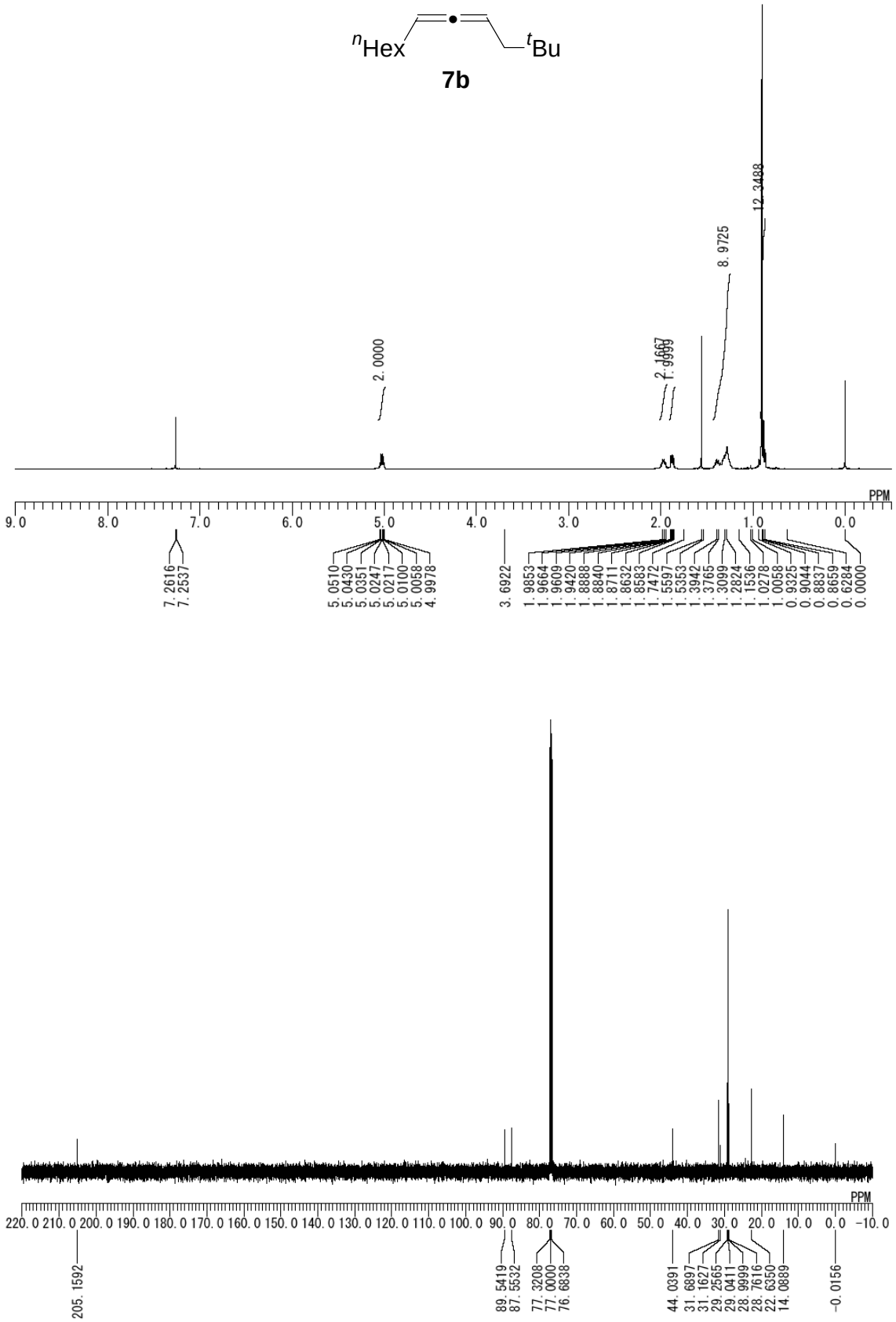
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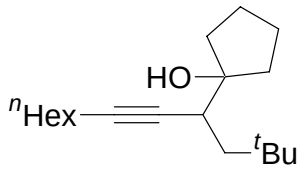
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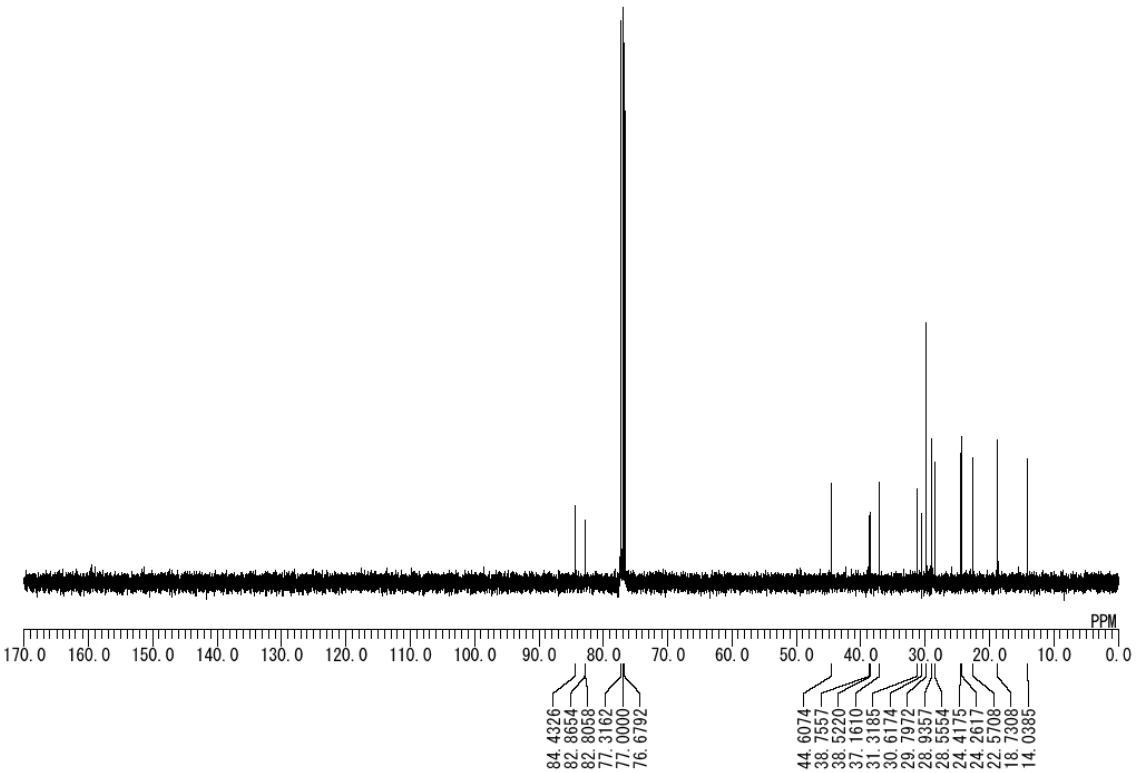
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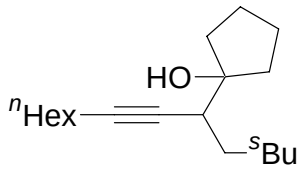
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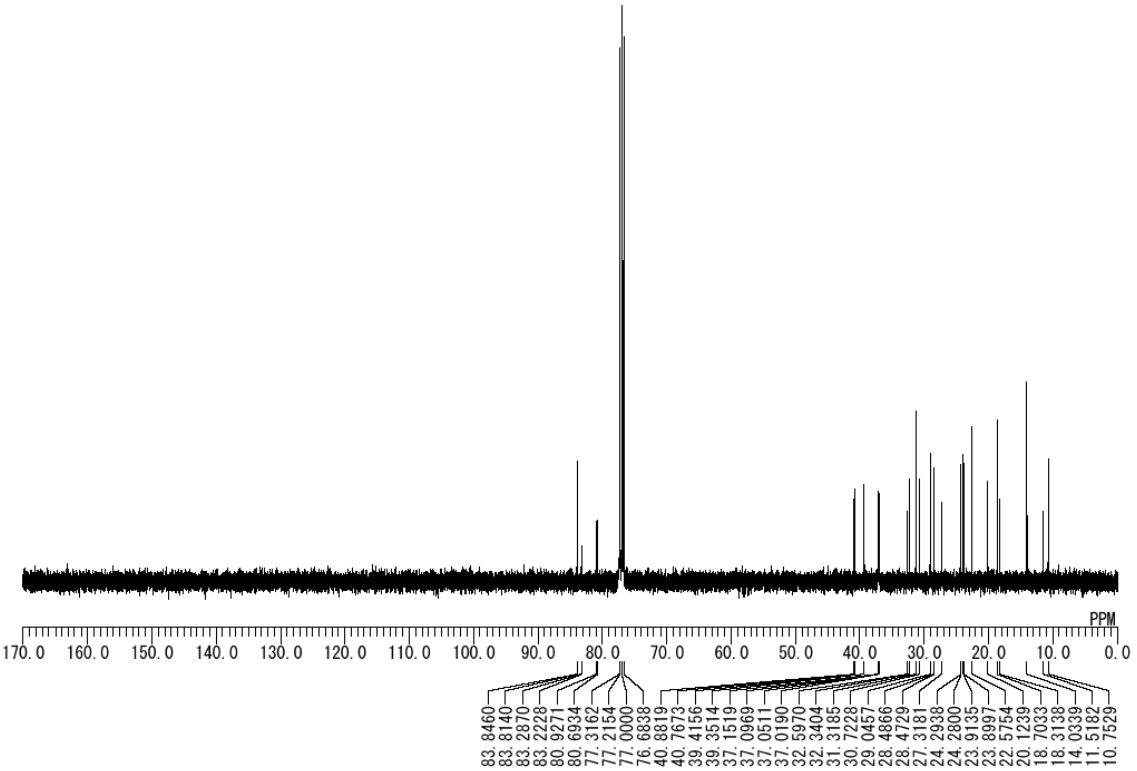
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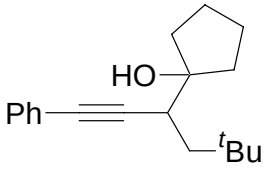
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Ph
tBu

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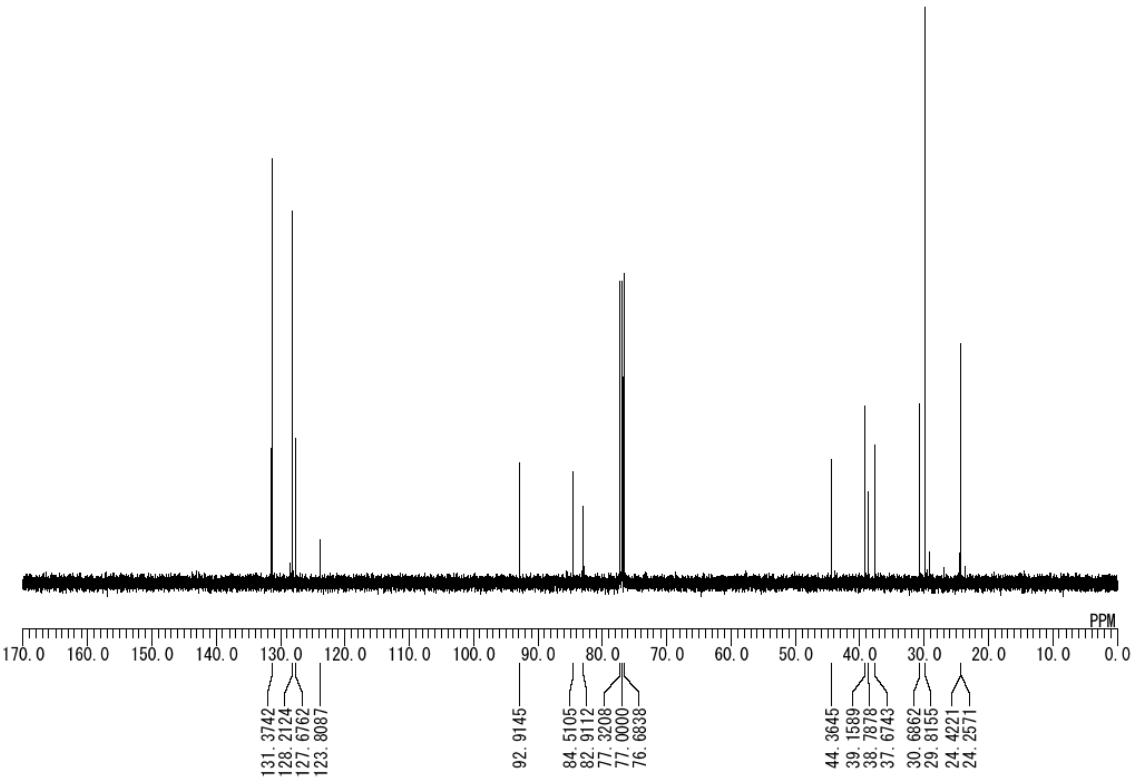
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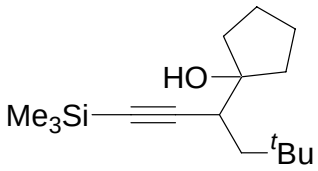
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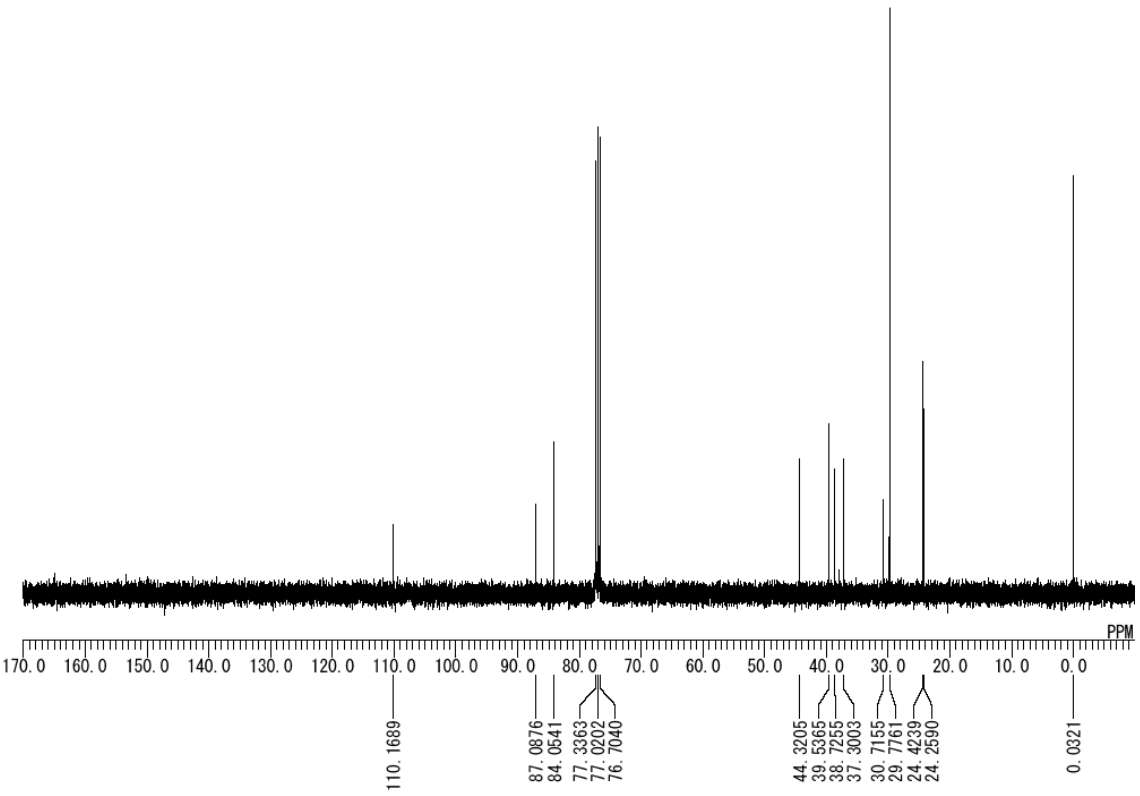
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