Nickel-Catalyzed Regioselective Synthesis of Tetrasubstituted Alkene Using Alkylative Carboxylation of Disubstituted Alkyne

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Contents of Supporting Information

General. All manipulations were performed under an argon atmosphere unless otherwise mentioned. Solvents were distilled under an argon atmosphere from sodium-benzophenone (THF, Et_2O, toluene, and benzene), CaH_2 (CH_2Cl_2), or sodium (EtOH, MeOH). All other solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh) using the indicated solvent. $Ni(cod)_2$ was prepared by a literature

procedure.[1] Me_2Zn was purchased from Kanto Chemical Co., Inc. Bu_2Zn was prepared by treatment of $ZnCl_2$ with BuLi (molar ratio, 2/1). Alkyne **1a** is a commercially available.[2] Alkynes **1c**[3], and **5b**[4] were synthesized according to the literature.

(4-benzyloxy-1-butynyl)trimethylsilane (1b). IR (neat) 3030, 2959, 2178, 1249, 1103, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 2.54 (t, J = 7.2 Hz, 2 H), 3.58 (t, J = 7.2 Hz, 2 H), 4.54 (s, 2 H), 7.22-7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.13, 21.33, 68.30, 72.83, 85.64, 103.64, 127.49, 127.51, 128.26, 138.03; LR MS (EI) *m/z* 231 (M^+-H), 217, 159, 91; HR MS (EI) calcd for $C_{14}H_{19}OSi$ (M^+-H) 231.1205, found 231.1203.

(3-benzyloxy-1-propynyl)trimethylsilane (1d). IR (neat) 3031, 2959, 2173, 1250, 1089, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 4.17 (s, 2 H), 4.60 (s, 2 H), 7.28-7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.12, 57.81, 71.42, 91.45, 101.40, 127.67, 127.96, 128.24, 137.28; LR MS (EI) *m/z* 217 (M^+-H), 203, 145, 91, 73; HR MS (EI) calcd for $C_{13}H_{17}OSi$ (M^+-H) 217.1049, found 217.1054.

trimethyl(1-octynyl)silane (1e). IR (neat) 2959, 2933, 1249, 841, 759, 639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 0.89 (t, J = 7.2 Hz, 3 H), 1.27-1.41 (m, 6

H), 1.51 (tq, J = 7.2, 7.2 Hz, 2 H), 2.21 (t, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.27, 14.08, 19.93, 22.58, 28.53, 28.66, 31.34, 84.20, 101.72; LR MS (EI) *m/z* 182 (M^+), 167, 139, 125, 97, 73; HR MS (EI) calcd for $C_{10}H_{19}Si$ (M^+-Me) 167.1256, found 167.1260.

(3-methoxy-5-phenyl-1-pentynyl)trimethylsilane (1f). IR (neat) 2958, 2168, 1603, 1496, 1453, 1334, 1250, 1108, 843 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 9 H), 2.01 (dddd, J = 25.6, 12.8, 6.4, 6.4 Hz, 1 H), 2.03 (dddd, J = 25.6, 12.8, 6.4, 6.4 Hz, 1 H), 2.73-2.85 (m, 2 H), 3.42 (s, 3 H), 3.92 (dd, J = 6.4, 6.4 Hz, 1 H), 7.18 -7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) 0.04, 31.45, 37.15, 56.39, 70.71, 90.88, 104.26, 125.82, 128.30, 128.44, 141.38; LR MS (EI) *m/z* 246 (M^+), 231, 214, 173, 155, 141; HR MS (EI) calcd for $C_{15}H_{22}OSi$ 246.1440, found 246.1431.

(5,5-dimethyl-3-hexynyl)benzene (5a). IR (neat) 2967, 1603, 1454, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 9 H), 2.41 (t, J = 7.6 Hz, 2 H), 2.78 (t, J = 7.6 Hz, 2 H), 7.17-7.33 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.11, 27.36, 31.34, 35.76, 77.80, 89.74, 125.99, 128.11, 128.51, 140.99; LR MS (EI) *m/z* 186 (M^+), 171, 156, 129, 91, 77, 57; HR MS (EI) calcd for $C_{14}H_{18}$ 186.1408, found 186.1411.

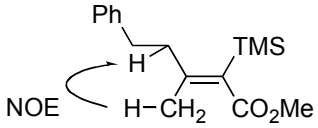
(4-(4-Methoxyphenyl)-3-butynyl)benzene (5c). IR (neat) 3027, 2931, 2835, 1606,

1509, 1245, 1033, 832, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.66 (t, *J* = 7.6 Hz, 2 H), 2.90 (t, *J* = 7.6 Hz, 2 H), 3.77 (s, 3 H), 6.78-6.81 (m, 2 H), 7.19-7.32 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.74, 35.35, 55.22, 80.99, 87.83, 113.74, 115.92, 126.17, 128.25, 128.44, 132.74, 140.69, 158.95; LR MS (EI) *m/z* 236 (M^+), 205, 145, 91; HR MS (EI) calcd for $C_{17}H_{16}O$ 236.1201, found 236.1202.

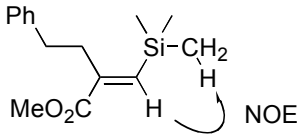
Methyl 4-(4-phenyl-1-butynyl)benzoate (5d). IR (neat) 3027, 2950, 2226, 1722, 1605, 1275, 1107, 769, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.72 (t, *J* = 7.6 Hz, 2 H), 2.93 (t, *J* = 7.6 Hz, 2 H), 3.90 (s, 3 H), 7.21-7.34 (m, 5 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.94 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.81, 35.00, 52.16, 80.88, 92.92, 126.33, 128.35, 128.42, 128.59, 128.91, 129.31, 131.36, 140.36, 166.48; LR MS (EI) *m/z* 264 (M^+), 249, 233, 205, 173, 91; HR MS (EI) calcd for $C_{18}H_{16}O_2$ 264.1150, found 264.1154.

Typical Procedure for Alkylative Carboxylation of 1a Using a Stoichiometric Amount of Ni(cod)$_2$. To a stirred suspension of $Ni(cod)_2$ (120.0 mg, 0.432 mmol) in degassed THF (2.9 mL) was added DBU (0.13 mL, 0.864 mmol) at 0 °C under an argon atmosphere. The solution was frozen in a liquid nitrogen bath and pumped up.

A balloon filled with CO_2 was attached to the reaction flask, and then the frozen mixture was allowed to stand until it thawed. To the resulting pale yellow suspension was added a solution of **1a** (73.0 mg, 0.36 mmol) in degassed THF (2.9 mL) at 0 °C and the solution was stirred at 0 °C for 18 hr. To this solution was added Me_2Zn (1.0 M in hexane, 1.1 mL, 1.1 mmol) at 0 °C and the solution was stirred at room temperature for 24 hr. To this solution was added 10 % HCl aq. at 0 °C. The aqueous layer was extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was treated with diazomethane in Et_2O at 0 °C according to standard procedures. The crude product was purified by column chromatography on silica gel (hexane/EtOAc=20/1) to afford ester **3a** as colorless oil (54.6 mg, 55%) along with **4a** as colorless oil (12.9 mg, 14%). **(*Z*)-methyl 3-methyl-2-(trimethylsilyl)-5-phenyl-2-pentenoate** (**3a**)**.** IR (neat) 3028, 2953, 1713, 1603, 1249, 1202, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 1.88 (s, 3 H), 2.43-2.47 (m, 2 H), 2.73-2.77 (m, 2 H), 3.72 (s, 3 H), 7.19-7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.05, 21.52, 34.75, 40.26, 51.23, 126.03, 128.11, 128.45, 132.90, 141.39, 152.45, 173.11; LR MS (EI) *m/z* 276 (M^+), 261, 245; HR MS (EI) calcd for $C_{16}H_{24}O_2Si$ 276.1546, found 276.1547.



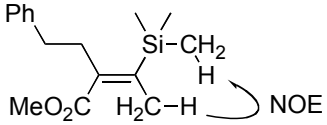
(*E*)-methyl 2-((trimethylsilyl)methylene)-4-phenylbutanoate (4a). IR (neat) 3027, 2952, 1714, 1603, 1225, 862, 838, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 2.66-2.77 (m, 4 H), 3.77 (s, 3 H), 6.90 (s, 1 H), 7.15-7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.34, 34.42, 36.26, 51.98, 125.92, 128.32, 128.36, 141.57, 142.09, 146.46, 167.51; LR MS (EI) *m/z* 262 (M^+), 247, 231, 171, 130, 89, 73, 59; HR MS (EI) calcd for $C_{15}H_{22}O_2Si$ 262.1389, found 262.1391.



Typical Procedure for Nickel-Catalyzed Methylative Carboxylation of 1a. To a stirred suspension of $Ni(cod)_2$ (20.0 mg, 0.072 mmol) in THF (1.2 mL) under an argon atmosphere was added DBU (0.54 mL, 3.6 mmol) at 0 °C. The mixture was frozen in a liquid nitrogen bath and pumped up. A balloon filled with CO_2 was attached to the reaction flask, and then the frozen mixture was allowed to stand until it thawed. To the resulting pale yellow suspension was slowly added a solution of **1a**

(73.0 mg, 0.36 mmol) in THF (1.2 mL) and dimethylzinc (1.0 M in hexane, 1.1 mL, 1.1 mmol) at 0 °C. After the solution was stirred at room temperature for 20 hr, the 10 % HCl aq. was added at 0 °C. The aqueous layer was extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was treated with diazomethane in Et_2O at 0 °C. The crude product was purified by column chromatography on silica gel (hexane/EtOAc=20/1) to afford the ester **3a** as colorless oil (67.7 mg, 68%) along with colorless oil of **2a** (22.6 mg, 23%).

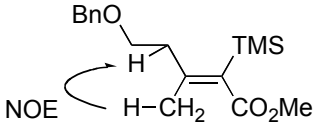
(*E*)-methyl 3-(trimethylsilyl)-2-phenethyl-2-butenoate (**2a**)**.** IR (neat) 2951, 1721, 1604, 1250, 1162, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 1.85 (s, 3 H), 2.68 (s, 4 H), 3.77 (s, 3 H), 7.16-7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.02, 20.39, 35.40, 35.82, 51.30, 125.93, 128.30 (CH x2), 140.16, 141.20, 142.04, 170.29; LR MS (EI) *m/z* 276 (M^+), 261, 245, 217, 185; HR MS (EI) calcd for $C_{16}H_{24}O_2Si$ 276.1546, found 276.1548.



Methylative Carboxylation of 1a using Ni(acac)$_2$. According to the typical procedure for nickel-catalyzed methylative carboxylation, $Ni(acac)_2$ was used instead

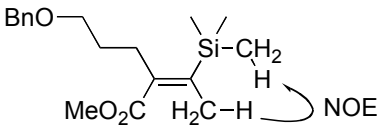
of $Ni(cod)_2$.

(*Z*)-methyl 5-(benzyloxy)-3-methyl-2-(trimethylsilyl)-2-pentenoate (3b). IR (neat) 3029, 2950, 1716, 1611, 1251, 1206, 1099, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 1.73 (s, 3 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 3.49 (t, *J* = 7.2 Hz, 2 H), 3.63 (s, 3 H), 4.44 (s, 2 H), 7.18-7.29 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.05, 21.96, 38.15, 51.20, 68.65, 73.04, 127.51, 127.53, 128.26, 134.21, 138.04, 149.77, 172.97; LR MS (EI) *m/z* 291 (M^+-Me), 275, 185, 91; HR MS (EI) calcd for $C_{16}H_{23}O_3Si$ (M^+-Me) 291.1416, found 291.1435.

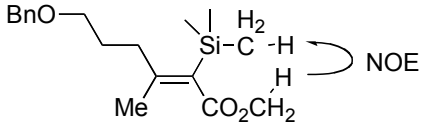


(*E*)-methyl 5-(benzyloxy)-2-(1-(trimethylsilyl)ethylidene)pentanoate (2c). IR (neat) 2950, 2856, 1722, 1607, 1454, 1432, 1250, 1192, 1151, 1104, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 1.69 (tt, *J* = 8.0, 6.4 Hz, 2 H), 1.81 (s, 3 H), 2.46 (t, *J* = 8.0 Hz, 2 H), 3.47 (t, *J* = 6.4 Hz, 2 H), 3.74 (s, 3 H), 4.49 (s, 2 H), 7.25-7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.01, 20.33, 29.24, 30.65, 51.28, 69.78, 72.29, 127.38, 127.45, 128.23, 138.48, 139.44, 142.42, 170.48; LR MS (EI) *m/z* 320 (M^+), 305, 261, 247; HR MS (EI) calcd for $C_{18}H_{28}O_3Si$ 320.1808, found

320.1816.

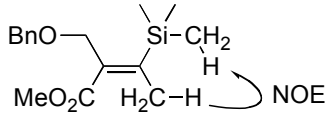


(*Z*)-methyl 6-(benzyloxy)-3-methyl-2-(trimethylsilyl)-2-hexenoate (3c). IR (neat) 2949, 1714, 1609, 1250, 1205, 1102, 841 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 1.66-1.73 (m, 2 H), 1.73 (s, 3 H), 2.17-2.21 (m, 2 H), 3.43 (t, *J* = 6.4 Hz, 2 H), 3.63 (s, 3 H), 4.44 (s, 2 H), 7.18-7.23 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.01, 21.27, 28.58, 34.85, 51.15, 69.99, 72.82, 127.40 (CH x2), 128.20, 132.45, 138.36, 152.95, 173.13; LR MS (EI) *m/z* 320 (M^+), 305, 229, 199, 107, 91; HR MS (EI) calcd for $C_{18}H_{28}O_3Si$ 320.1808, found 320.1797.

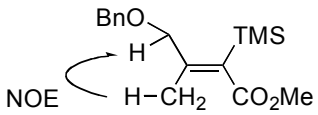


(*E*)-methyl 2-((benzyloxy)methyl)-3-(trimethylsilyl)-2-butenoate (2d). IR (neat) 2950, 1725, 1455, 1251, 1163, 1074, 839, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 1.90 (s, 3 H), 3.77 (s, 3 H), 4.24 (s, 2 H), 4.51 (s, 2 H), 7.27-7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.06, 20.47, 51.44, 69.56, 72.43,

127.55, 127.82, 128.21, 137.93, 139.62, 146.32, 169.24; LR MS (EI) *m/z* 277 (M^+-Me), 261, 185, 171, 91, 73; HR MS (EI) calcd for $C_{15}H_{21}O_3Si$ (M^+-Me) 277.1260, found 277.1255.

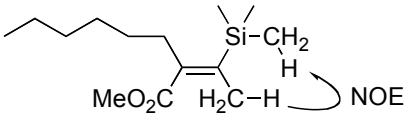


(*Z*)-methyl 4-(benzyloxy)-3-methyl-2-(trimethylsilyl)-2-butenoate (3d). IR (neat) 2950, 2856, 1718, 1617, 1454, 1431, 1251, 1208, 1072, 842, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 1.87 (s, 3 H), 3.72 (s, 3 H), 4.05 (s, 2 H), 4.50 (s, 2 H), 7.26-7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.06, 19.37, 51.24, 72.45, 72.55, 127.64, 127.67, 128.29, 135.56, 137.76, 149.10, 172.58; LR MS (EI) *m/z* 277 (M^+-Me), 261, 201, 185, 91, 73, 59; HR MS (EI) calcd for $C_{15}H_{21}O_3Si$ (M^+-Me) 277.1260, found 277.1258.

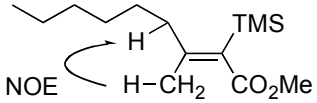


(*E*)-methyl 2-(1-(trimethylsilyl)ethylidene)octanoate (2e). IR (neat) 2955, 2928, 2857, 1724, 1609, 1249, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 0.88

(t, J = 6.8 Hz, 3 H), 1.27-1.32 (m, 8 H), 1.78 (s, 3 H), 2.31-2.35 (m, 2 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 0.19, 14.34, 20.53, 23.03, 29.72, 29.77, 32.17, 34.58, 50.73, 138.25, 144.32, 169.93; LR MS (EI) *m/z* 256 (M^+), 241, 225, 197, 73; HR MS (EI) calcd for $C_{14}H_{28}O_2Si$ 256.1859, found 256.1861.

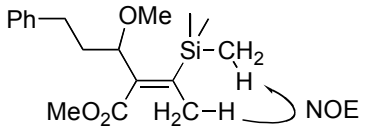


(*Z*)-methyl 3-methyl-2-(trimethylsilyl)-2-nonenoate (3e). IR (neat) 2955, 2929, 2858, 1718, 1610, 1249, 1203, 841 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.88 (t, J = 6.8 Hz, 3 H), 1.29-1.33 (m, 6 H), 1.40-1.43 (m, 2 H), 1.77 (s, 3 H), 2.10-2.14 (m, 2 H), 3.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.08, 14.10, 21.38, 22.62, 28.46, 29.62, 31.79, 38.27, 51.15, 131.76, 153.94, 173.28; LR MS (EI) *m/z* 256 (M^+), 241, 225, 197, 183, 171; HR MS (EI) calcd for $C_{14}H_{28}O_2Si$ 256.1859, found 256.1849.

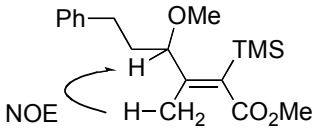


(*E*)-methyl 3-methoxy-2-(1-(trimethylsilyl)ethylidene)-5-phenylpentanoate (2f).

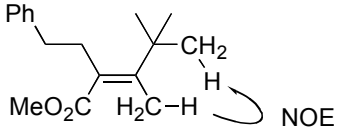
IR (neat) 2949, 1715, 1606, 1454, 1432, 1250, 1213, 1103, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 1.67-1.75 (m, 1 H), 1.76 (s, 3 H), 1.94 (dddd, *J* = 18.4, 9.2, 4.8, 4.4 Hz, 1 H), 2.53-2.63 (m, 1 H), 2.75 (ddd, *J* = 14.0, 9.6, 4.8 Hz, 1 H), 3.18 (s, 3 H), 3.53 (s, 3 H), 3.63 (dd, *J* = 9.2, 4.4 Hz, 1 H), 7.15-7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.53, 31.95, 35.47, 51.03, 56.49, 82.61, 85.42, 116.57, 125.66, 128.21, 128.48, 141.78, 151.02, 172.27; LR MS (EI) *m/z* 320 (M^+), 305, 289, 215, 184, 91, 73; HR MS (EI) calcd for $C_{18}H_{28}O_3Si$ 320.1808, found 320.1816.



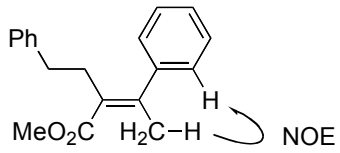
(*Z*)-methyl 4-methoxy-3-methyl-2-(trimethylsilyl)-6-phenyl-2-hexenoate (3f). IR (neat) 2950, 1719, 1605, 1251, 1203, 1103, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.56-1.64 (m, 1 H), 1.71 (s, 3 H), 1.95-2.05 (m, 1 H), 2.68 (ddd, *J* = 13.6, 8.4, 8.4 Hz, 1 H), 2.84 (ddd, *J* = 13.6, 9.2, 4.4 Hz, 1 H), 3.26 (s, 3 H), 3.69 (s, 3 H), 3.82 (dd, *J* = 10.0, 2.8 Hz, 1 H), 7.18-7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.19, 14.96, 32.16, 36.25, 51.25, 56.19, 81.07, 125.85, 128.31, 128.64, 135.84, 141.54, 152.49, 172.62; LR MS (EI) *m/z* 320 (M^+), 305, 289, 229; HR MS (EI) calcd for $C_{18}H_{28}O_3Si$ 320.1808, found 320.1808.



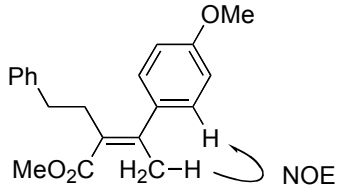
(*E*)-methyl 3,4,4-trimethyl-2-phenethyl-2-pentenoate (6a). IR (neat) 2950, 1721, 1236, 1203, 1163, 749, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9 H), 1.75 (s, 3 H), 2.64 -2.69 (m, 2 H), 2.72-2.77 (m, 2 H), 3.75 (s, 3 H), 7.17-7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.09, 30.43, 33.44, 34.99, 36.33, 51.50, 125.91, 128.24, 128.32, 130.33, 141.45, 145.23, 172.64; LR MS (EI) *m/z* 260 (M^+), 245, 229, 169, 91, 57; HR MS (EI) calcd for $C_{17}H_{24}O_2$ 260.1776, found 260.1772.



(*E*)-methyl 2-phenethyl-3-phenyl-2-butenoate (6b). IR (neat) 3025, 2948, 1715, 1600, 1165, 764, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 3 H), 2.40 -2.44 (m, 2 H), 2.58-2.62 (m, 2 H), 3.81 (s, 3 H), 6.96-6.99 (m, 4 H), 7.11-7.33 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.61, 33.20, 35.51, 51.42, 125.66, 126.70, 126.89, 128.06, 128.18, 128.35, 129.12, 141.28, 142.84, 146.05, 169.82; LR MS (EI) *m/z* 280 (M^+), 249, 189, 91,77; HR MS (EI) calcd for $C_{19}H_{20}O_2$ 280.1463, found 280.1467.

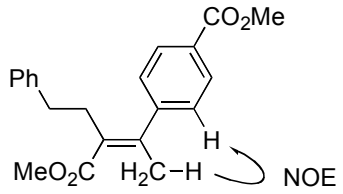


(*E*)-methyl 3-(4-methoxyphenyl)-2-phenethyl-2-butenoate (6c). IR (neat) 2949, 1715, 1608, 1509, 1245, 1165, 833, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3 H), 2.43-2.47 (m, 2 H), 2.59-2.63 (m, 2 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 7.00 (d, *J* = 7.2 Hz, 2 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 7.21(d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.70, 33.17, 35.47, 51.34, 55.11, 113.52, 125.62, 127.97, 128.02, 128.32, 129.08, 135.04, 141.30, 145.51, 158.37, 169.96; LR MS (EI) *m/z* 310 (M^+), 279, 219, 159, 91, 77; HR MS (EI) calcd for $C_{20}H_{22}O_3$ 310.1569, found 310.1574.

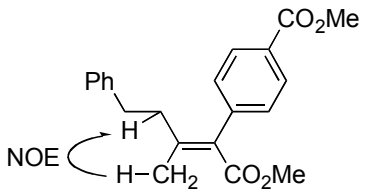


(*E*)-methyl 2-phenethyl-3-(4-methoxycarbonylphenyl)-2-butenoate (6d). IR (neat) 3026, 2950, 1722, 1606, 1275, 1112, 1103, 762, 710, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3 H), 2.39 (t, *J* = 8.0 Hz, 2 H), 2.60 (t, *J* = 8.0 Hz, 2 H), 3.83

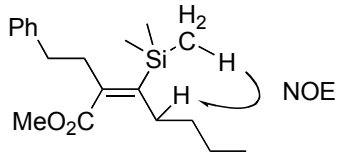
(s, 3 H), 3.92 (s, 3 H), 6.95-6.98 (m, 4 H), 7.13-7.26 (m, 3 H), 7.96 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.24, 33.19, 35.25, 51.58, 52.10, 125.80, 126.90, 128.14, 128.41, 128.71, 129.56, 129.66, 140.91, 144.65, 147.55, 166.59, 169.49; LR MS (EI) *m/z* 338 (M^+), 307, 247, 203, 91, 59; HR MS (EI) calcd for $C_{21}H_{22}O_4$ 338.1518, found 338.1520.



Methyl 4-((*E*)-1-(methoxycarbonyl)-2-methyl-4-phenyl-1-butenyl)benzoate (7d). IR (neat) 3025, 2950, 1722, 1715, 1605, 1285, 1273, 1217, 758, 700 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 2.05 (t, J = 8.0 Hz, 2 H), 2.18 (s, 3 H), 2.43 (t, J = 8.0 Hz, 2 H), 3.26 (s, 3 H), 3.45 (s, 3 H), 6.79 (d, J = 6.8 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 6.95-7.03 (m, 3 H), 8.07 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.42, 33.99, 38.78, 51.71, 52.12, 126.03, 128.19, 128.34, 128.76, 129.31, 129.46, 129.76, 140.74, 142.75, 149.84, 166.80, 167.84; LR MS (EI) *m/z* 338 (M^+), 323, 307, 278, 247, 203, 91; HR MS (EI) calcd for $C_{21}H_{22}O_4$ 338.1518, found 338.1524.

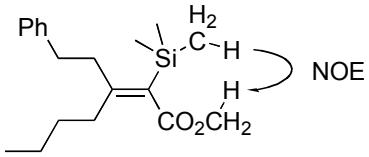


(*E*)-methyl 3-(trimethylsilyl)-2-phenethyl-2-heptenoate (Bu-2a, Table 2, run 7). IR (neat) 2955, 2871, 1722, 1603, 1250, 1161, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 1.29-1.31 (m, 4 H), 2.17 (t, *J* = 7.6 Hz, 2 H), 2.66 (s, 4 H), 3.76 (s, 3 H), 7.17-7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.52, 13.99, 23.02, 32.87, 34.14, 35.21, 36.12, 51.25, 125.94, 128.31, 128.33, 141.21, 142.28, 144.73, 170.35; LR MS (EI) *m/z* 318 (M^+), 303, 227; HR MS (EI) calcd for $C_{19}H_{30}O_2Si$ 318.2015, found 318.2012.



(*Z*)-methyl 2-(trimethylsilyl)-3-phenethyl-2-heptenoate (Bu-3a, Table **2, run 7).** IR (neat) 2956, 1715, 1603, 1217, 1031, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 0.92 (t, *J* = 7.2 Hz, 3 H), 1.32 (tq, *J* = 7.2, 7.2 Hz, 2 H), 1.47 (tt, *J* = 8.0, 7.2 Hz, 2 H), 2.19 (t, *J* = 8.0 Hz, 2 H), 2.44-2.48 (m, 2 H), 2.72-2.76 (m, 2 H), 3.71 (s,

3 H), 7.20-7.33 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.12, 13.99, 22.83, 30.82, 34.66, 35.01, 37.04, 51.10, 126.02, 128.07, 128.46, 132.68, 141.50, 156.55, 173.08; LR MS (EI) *m/z* 318 (M^+), 303, 287, 261, 245, 227; HR MS (EI) calcd for $C_{19}H_{30}O_2Si$ 318.2015, found 318.2018.



References

1) Schunn, R. A. *Inorg*. *Synth*. **1974**, *15*, 5.

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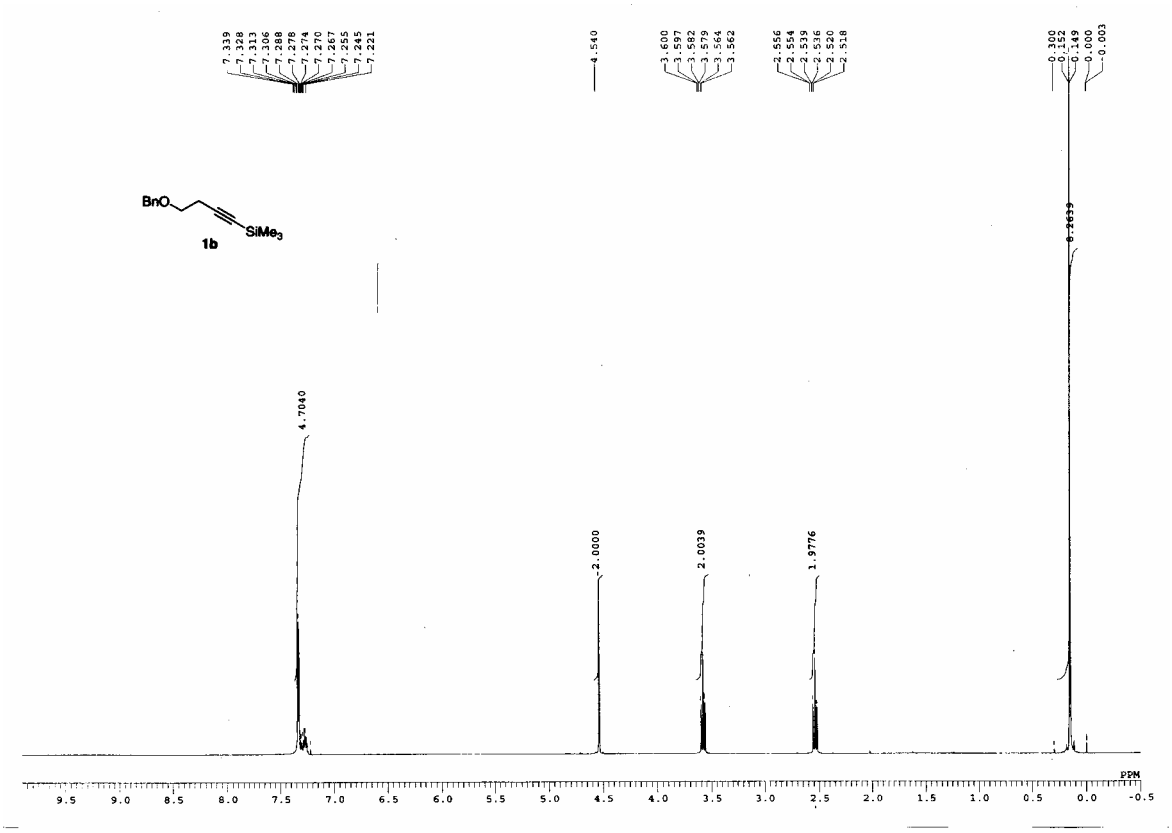
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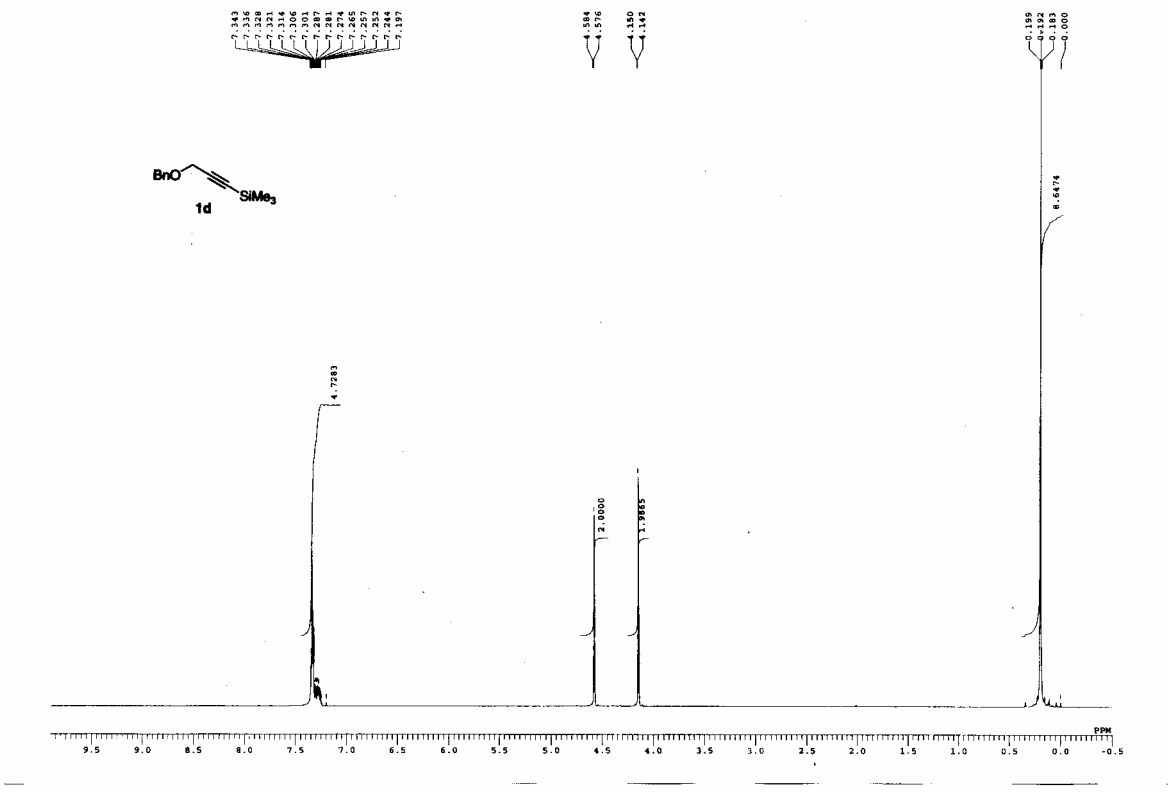
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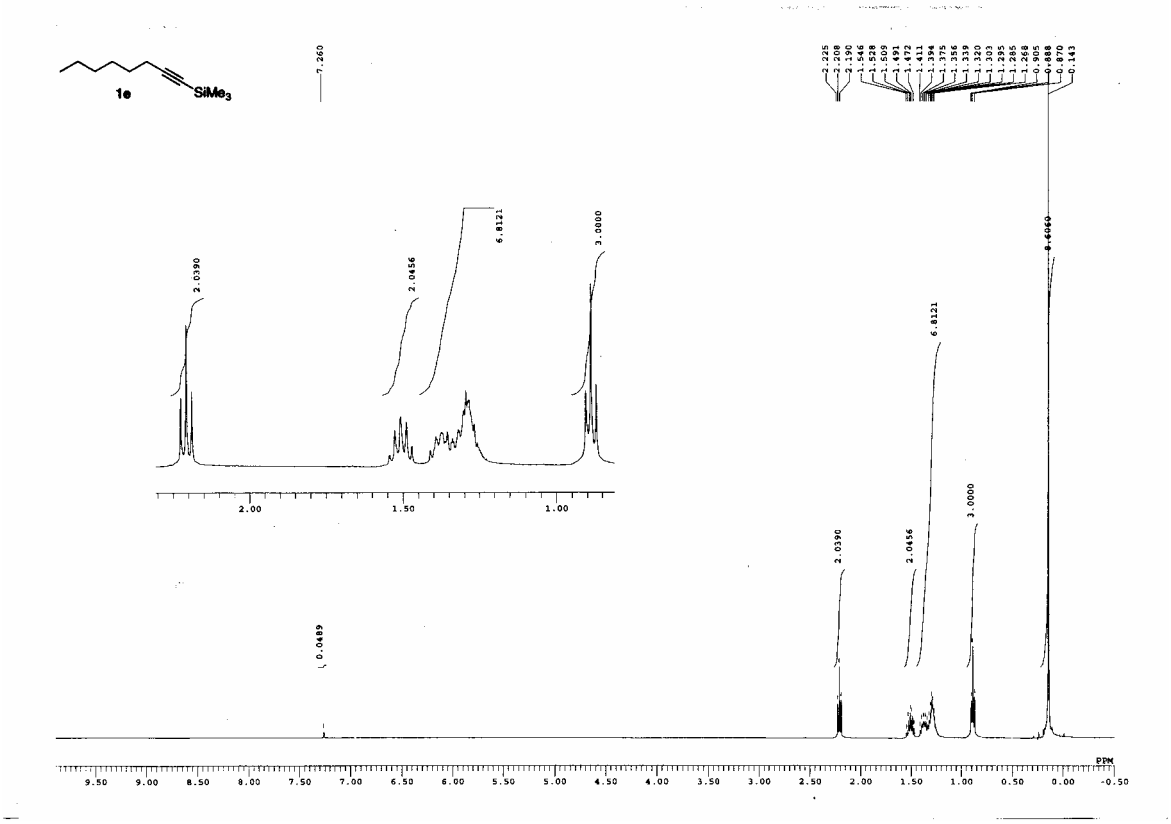
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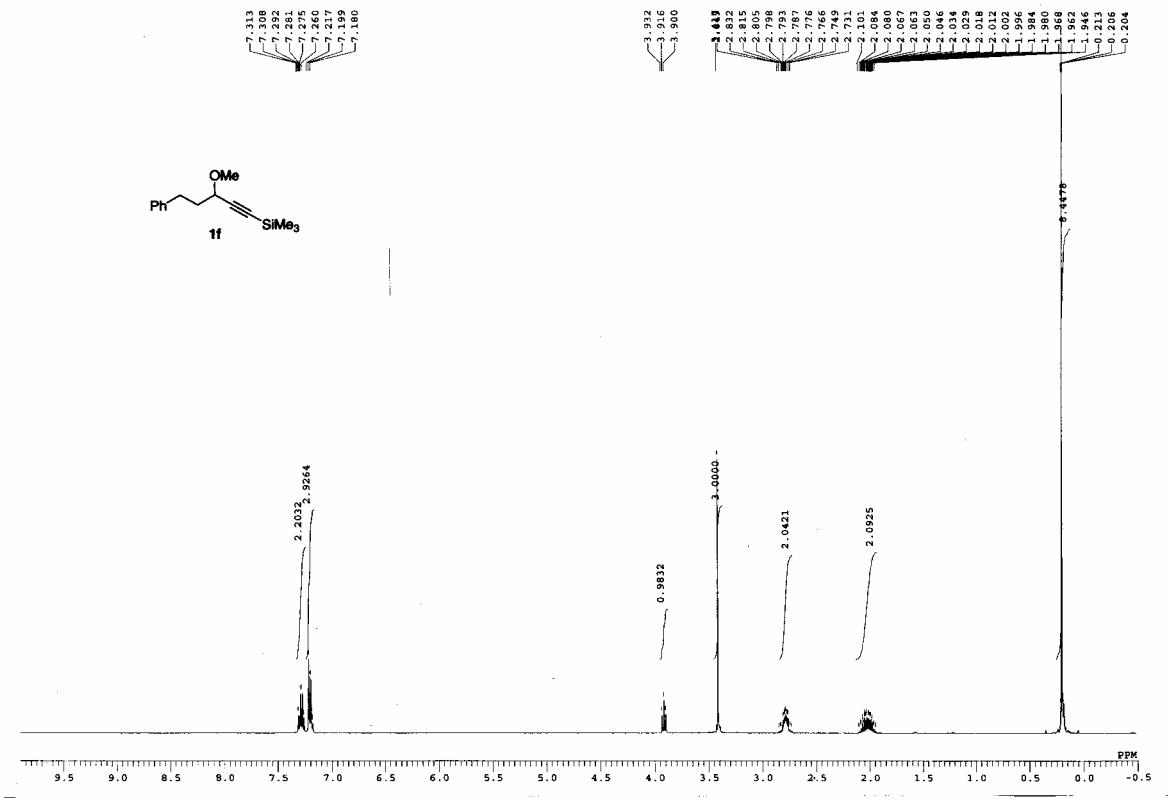
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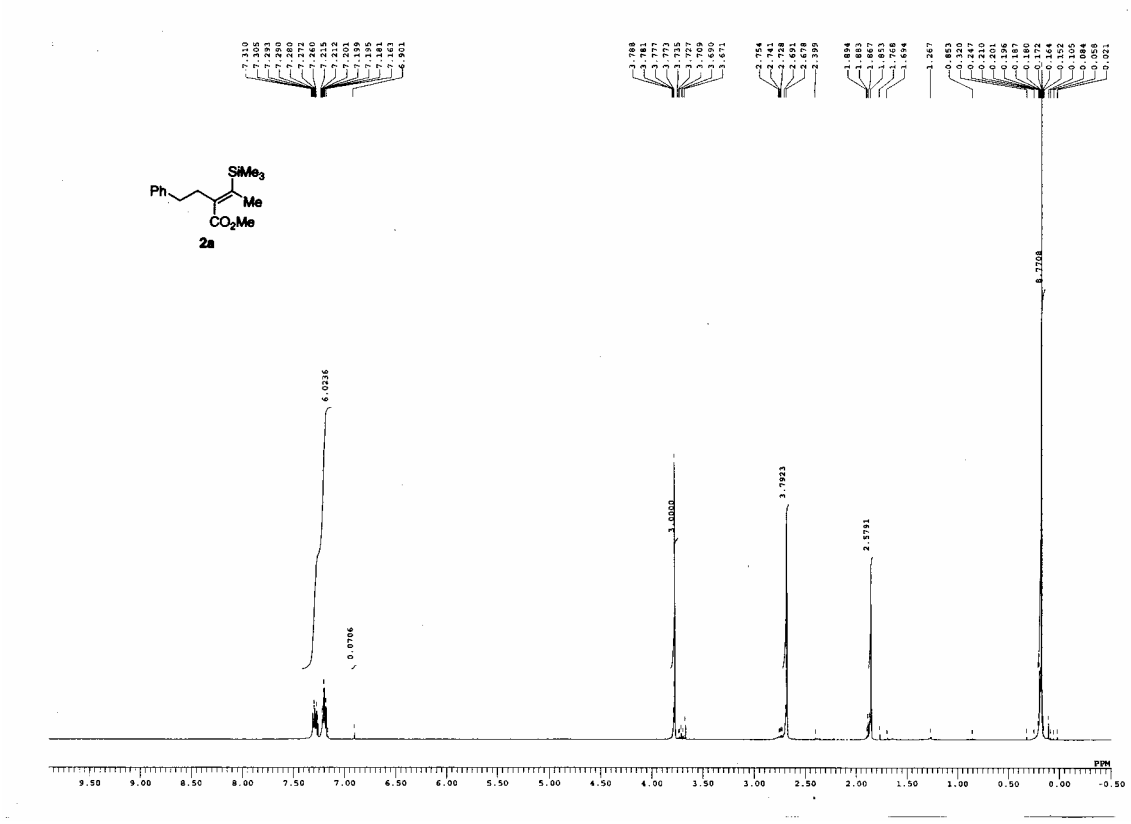
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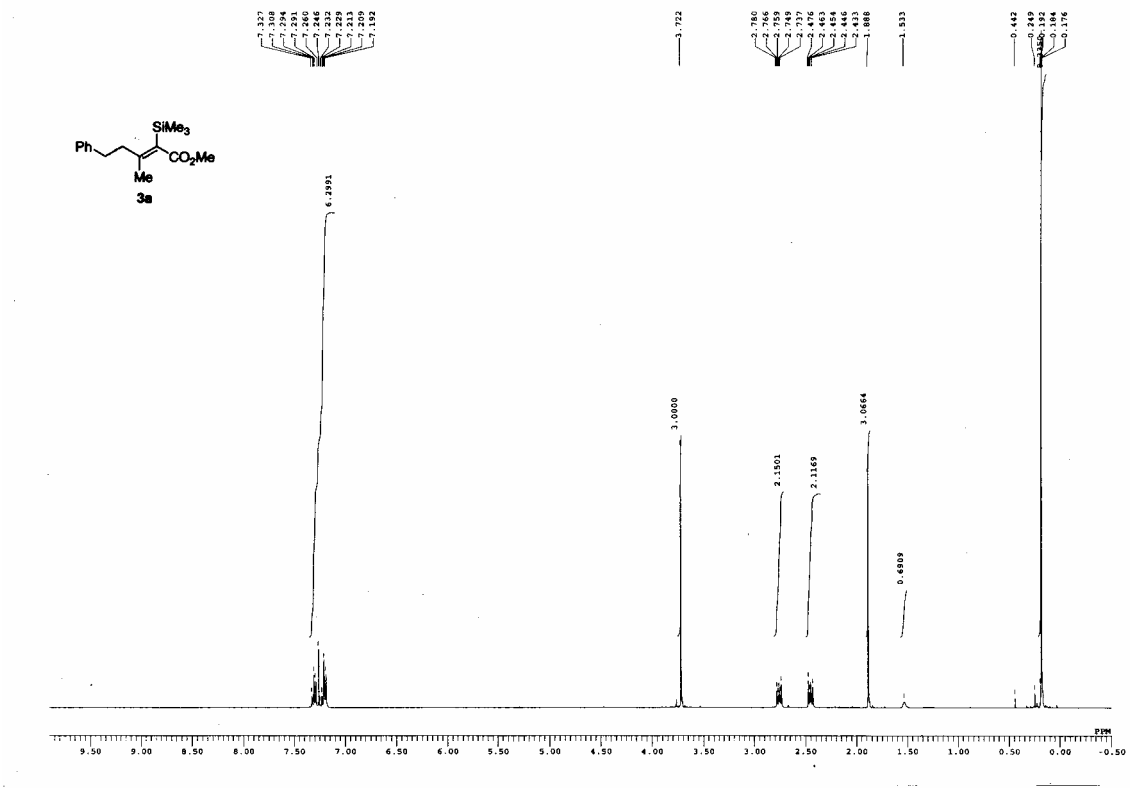
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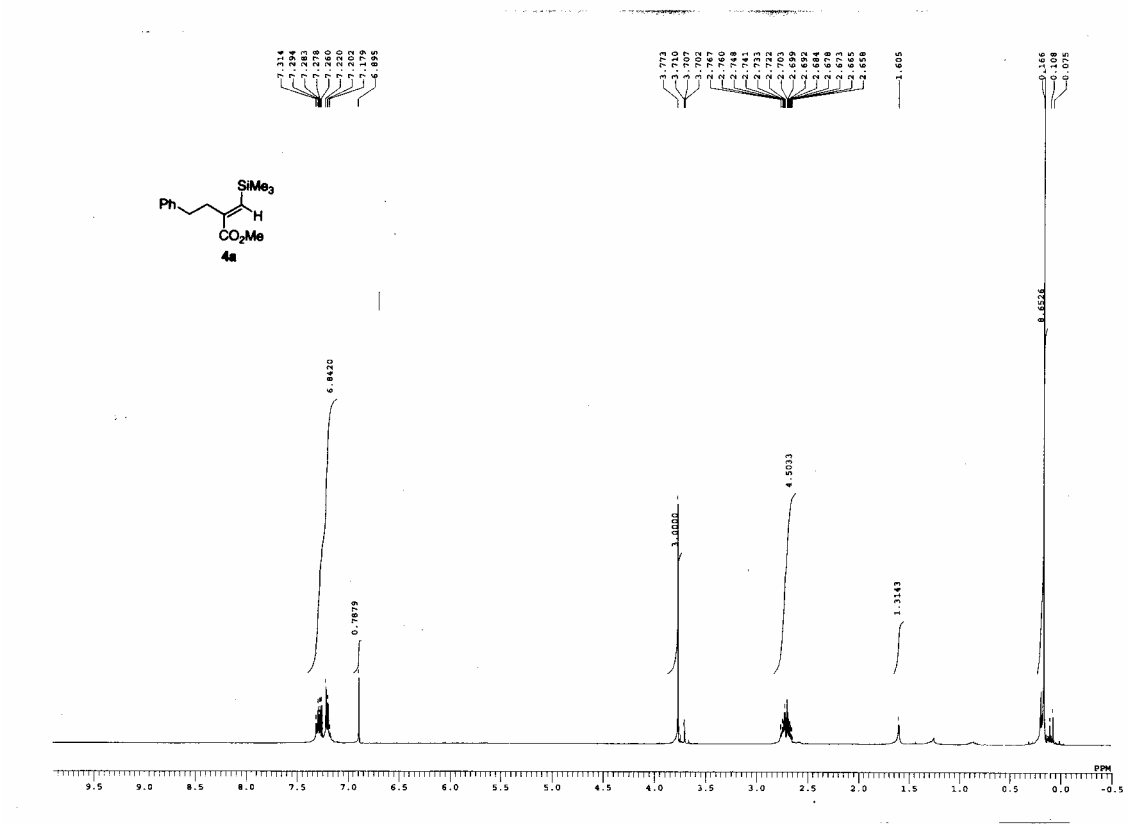
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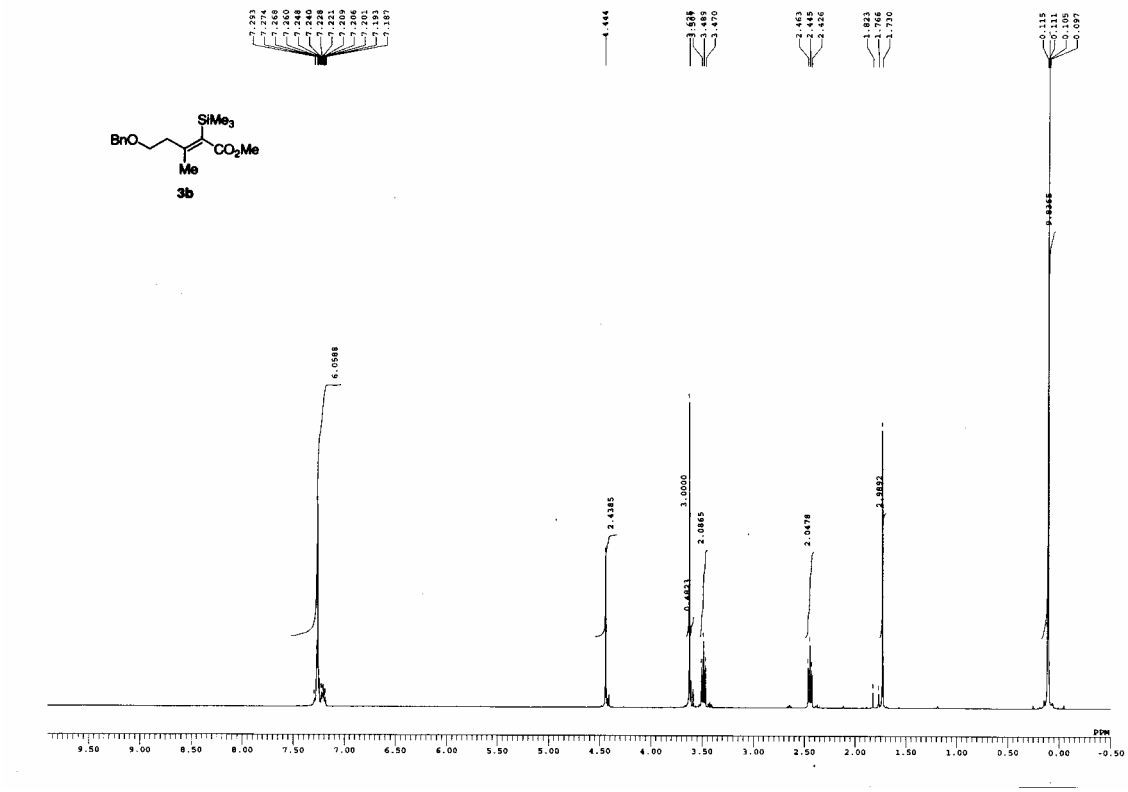
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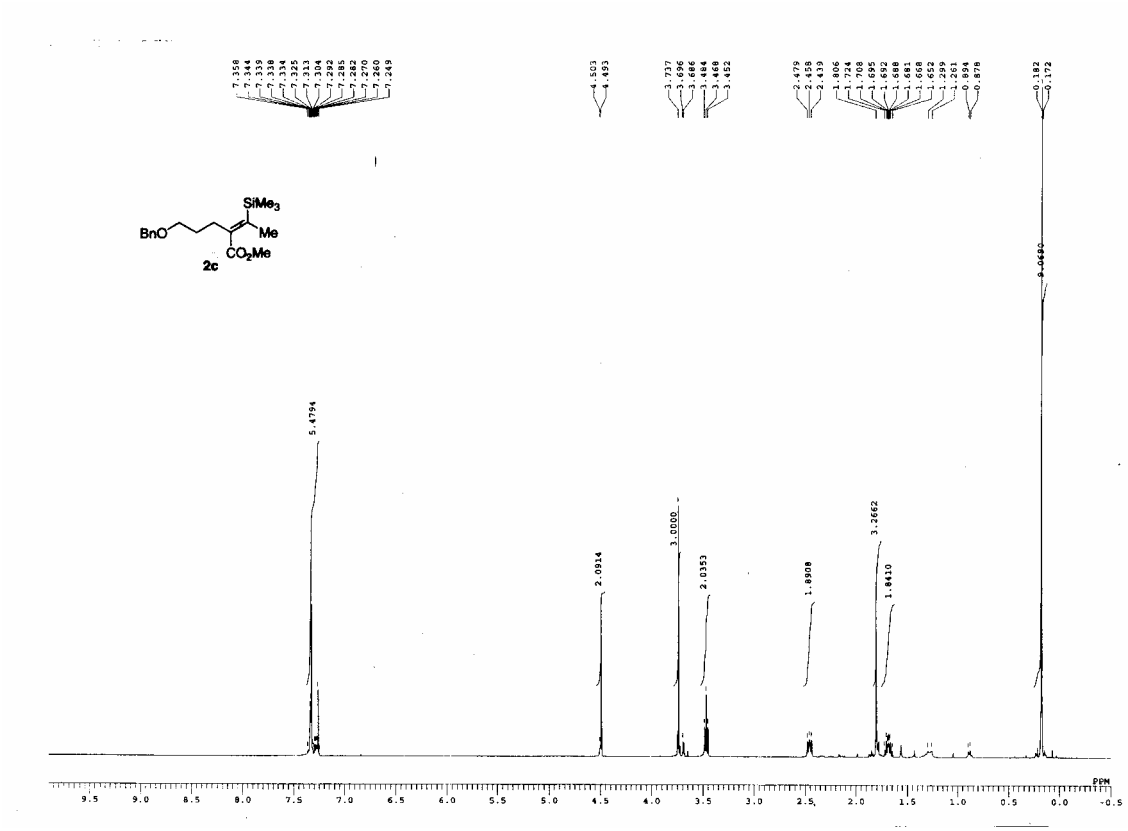
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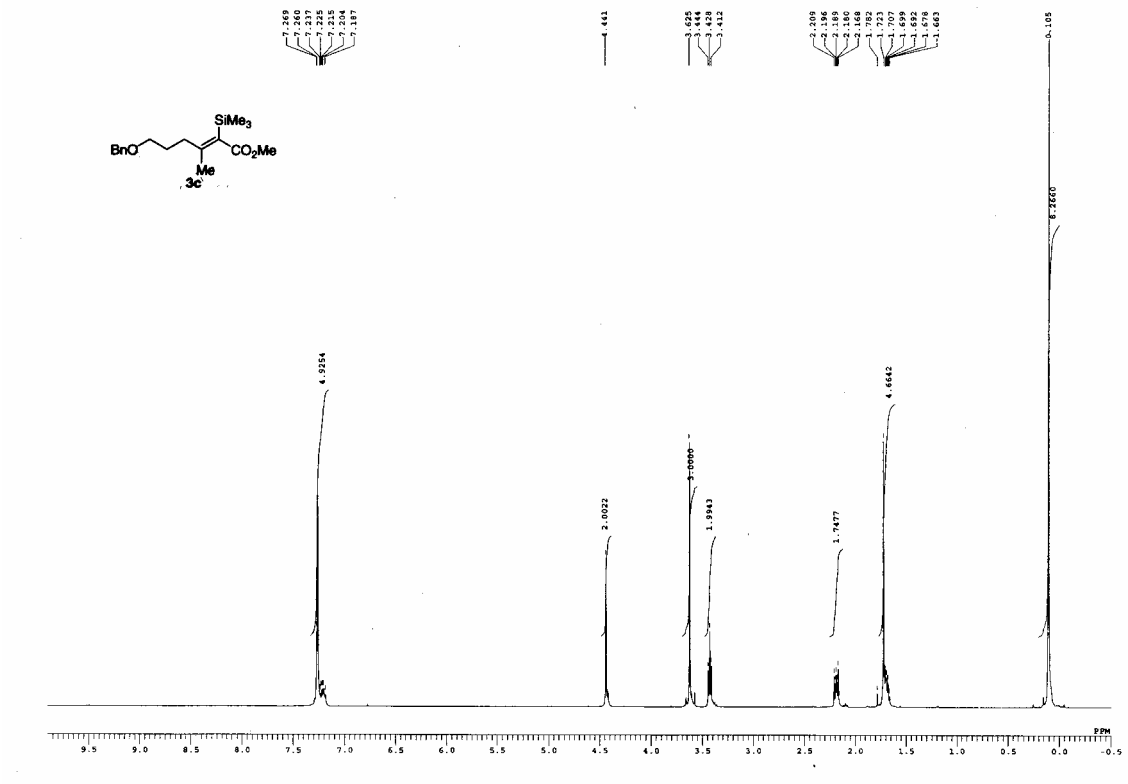
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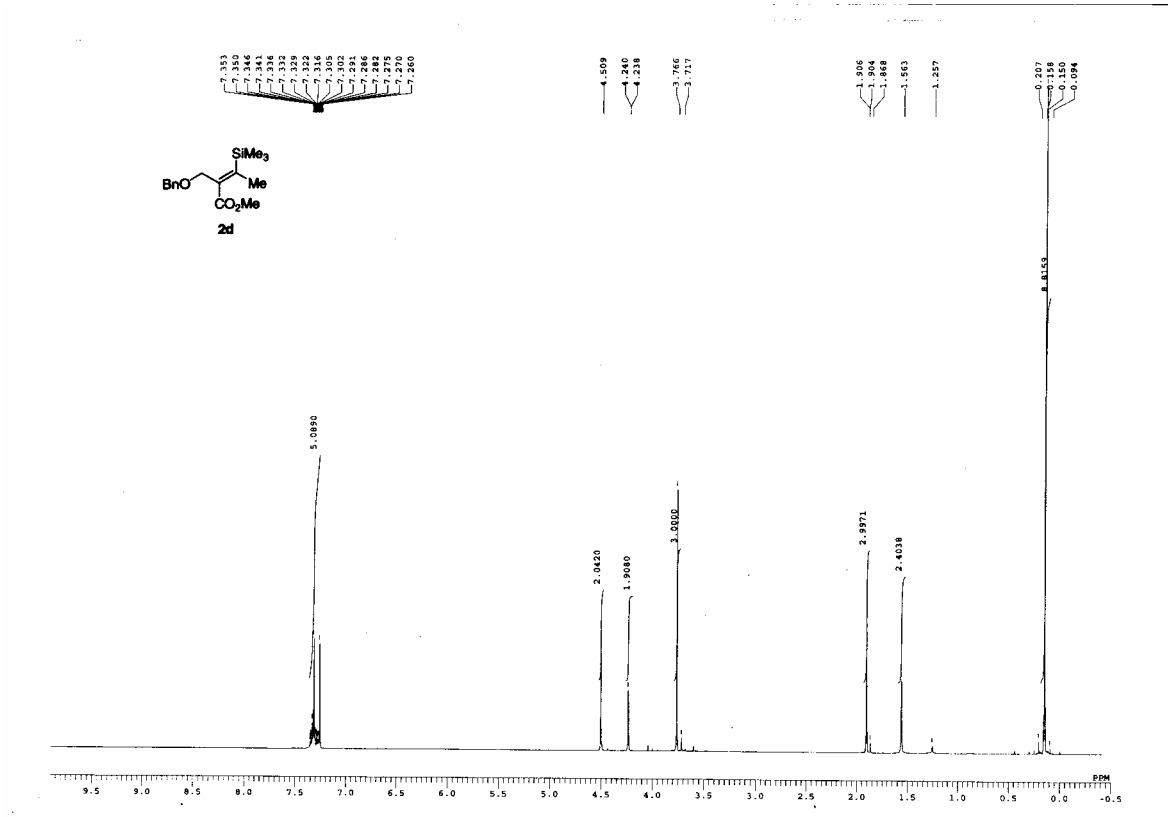
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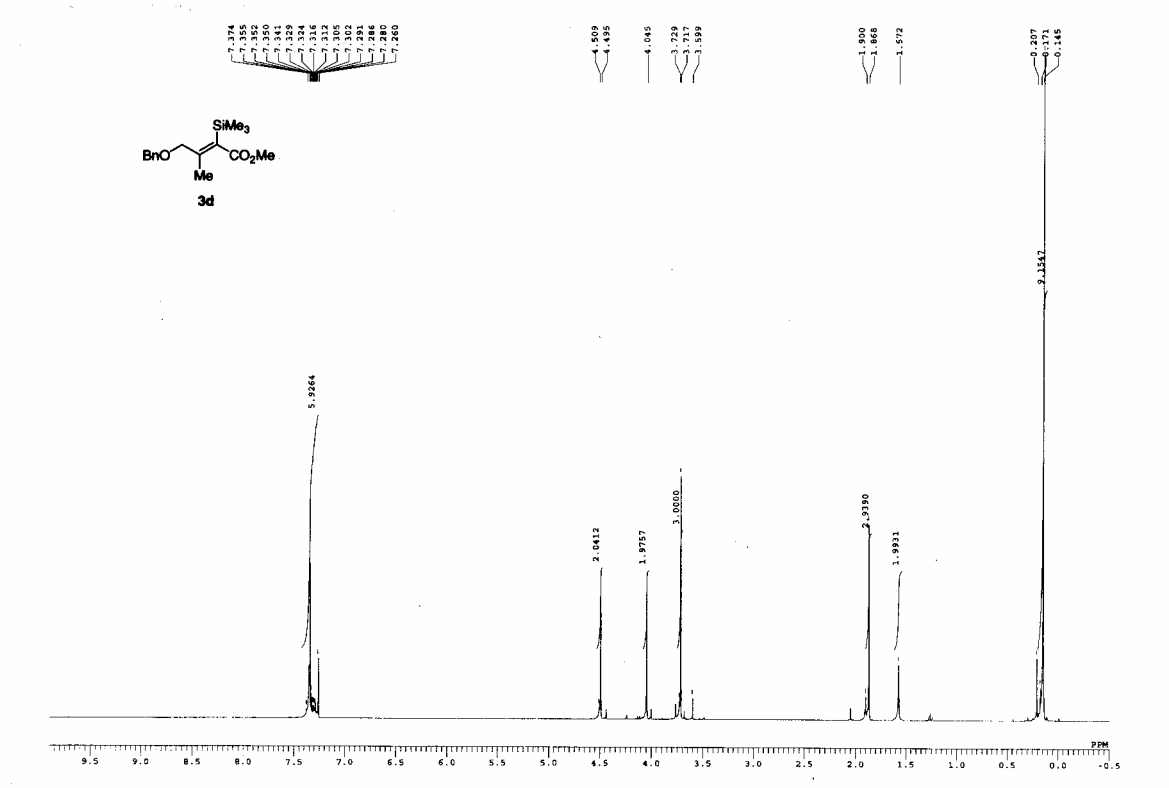
CO2Me
2d
PPM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CO2Me
Me
3d
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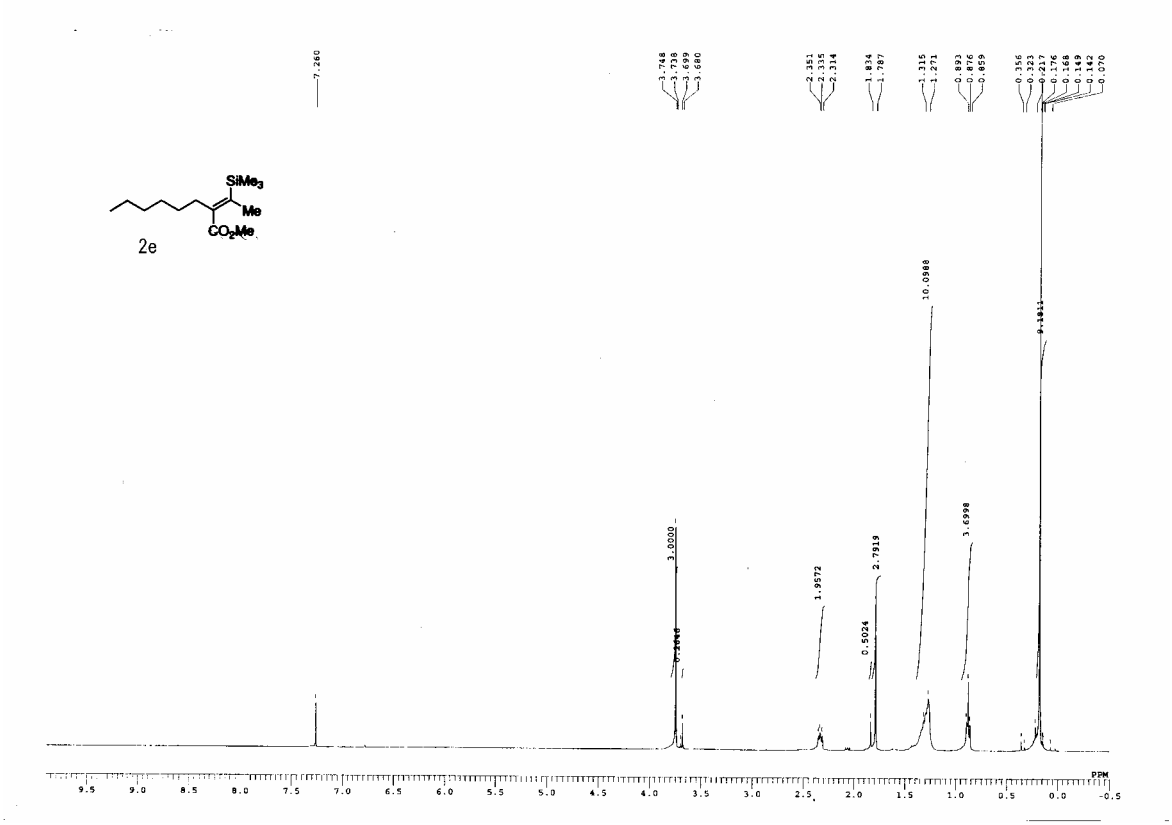
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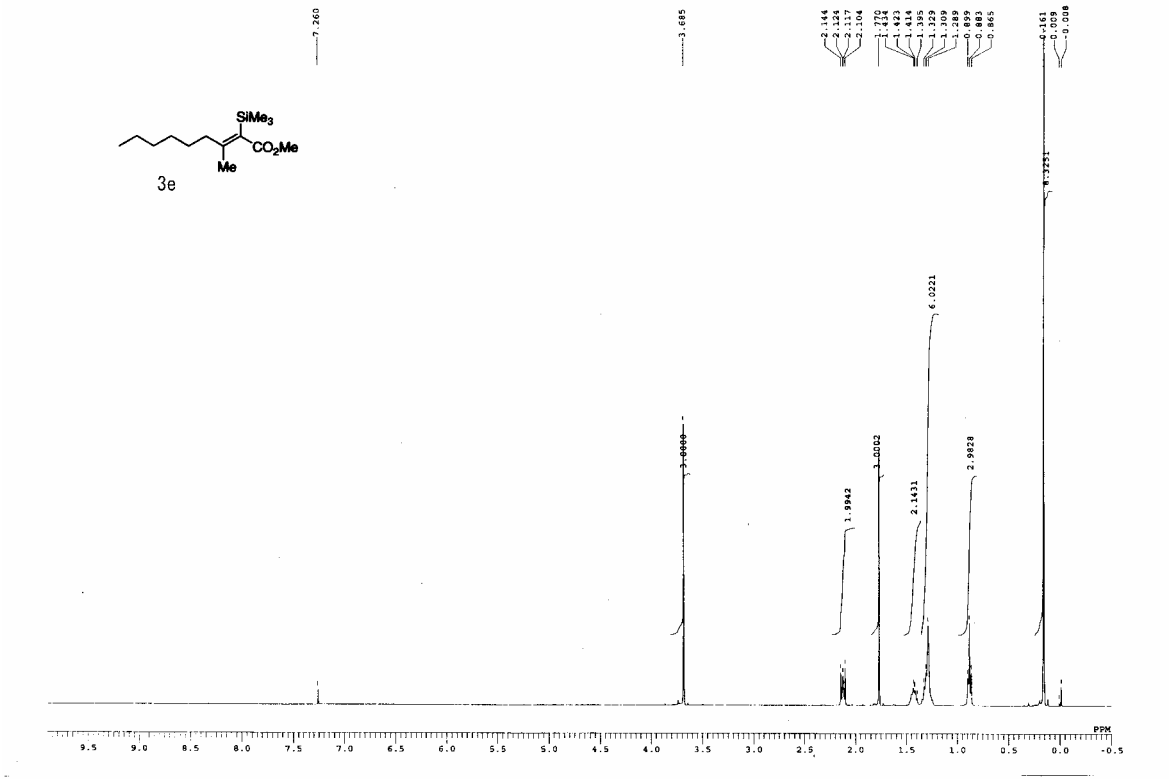
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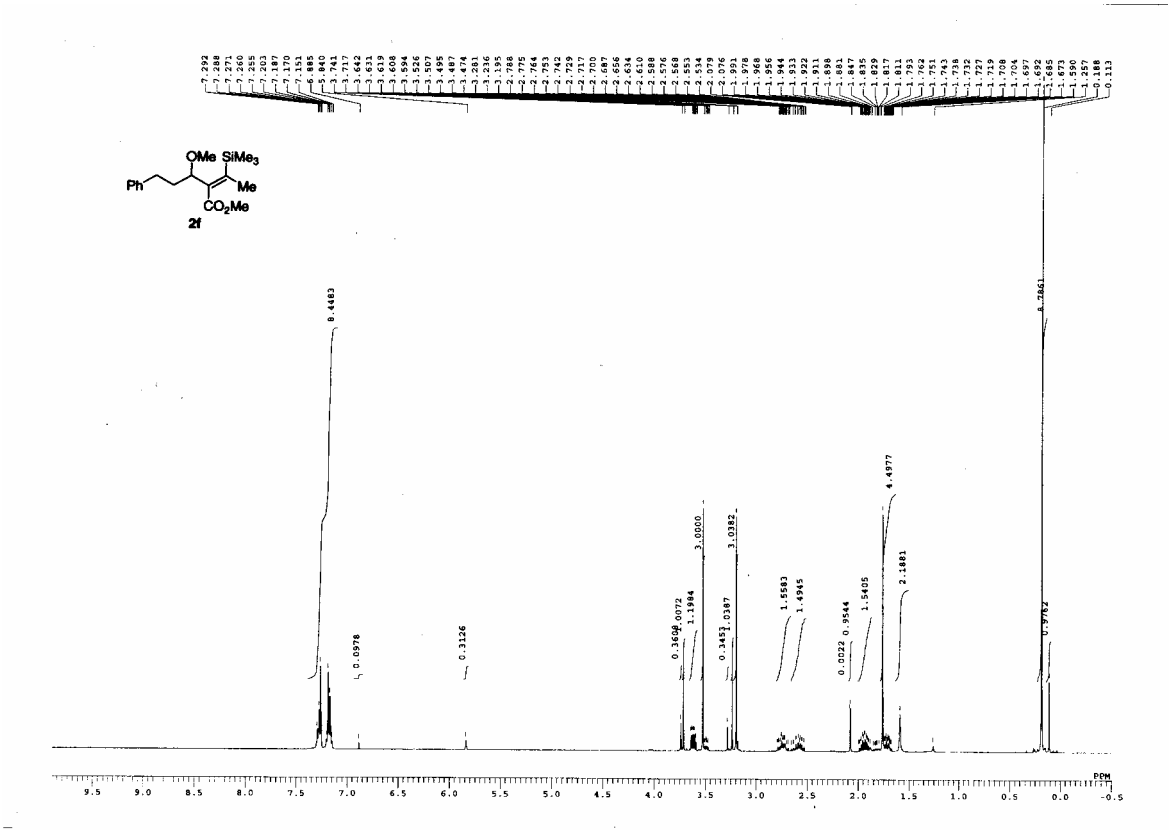
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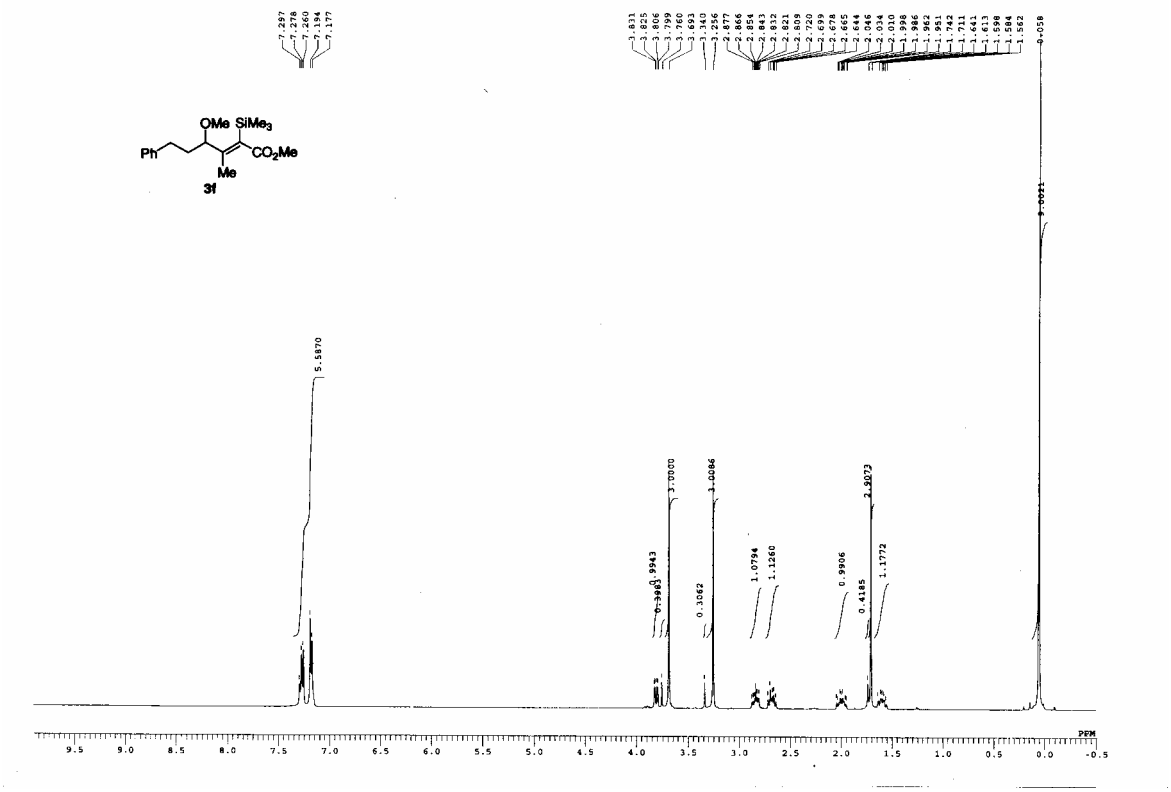
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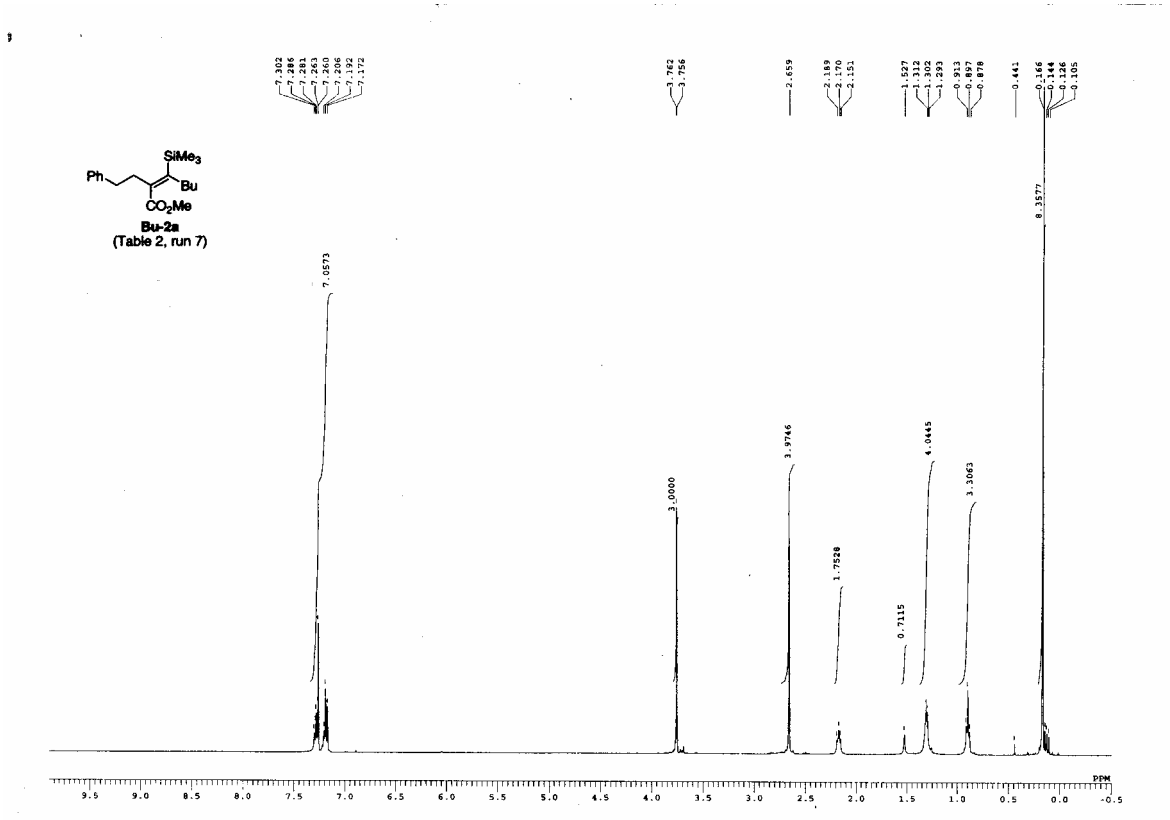
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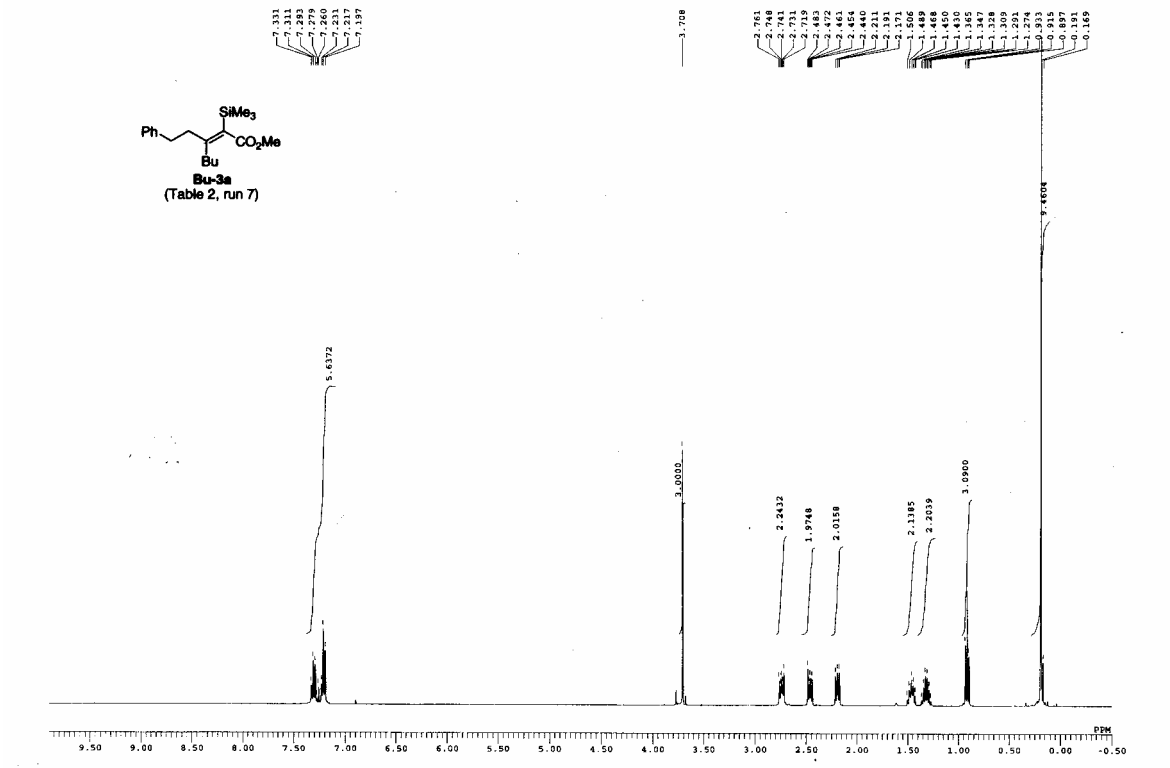
PPM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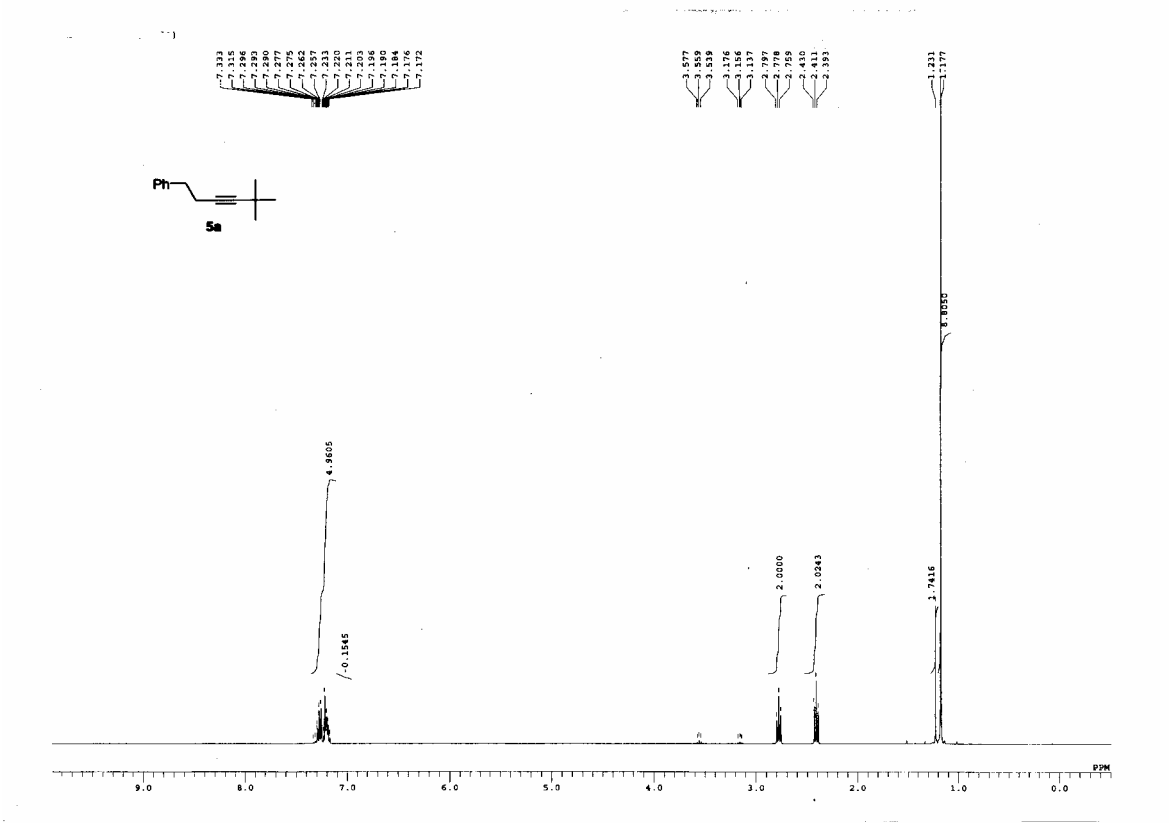
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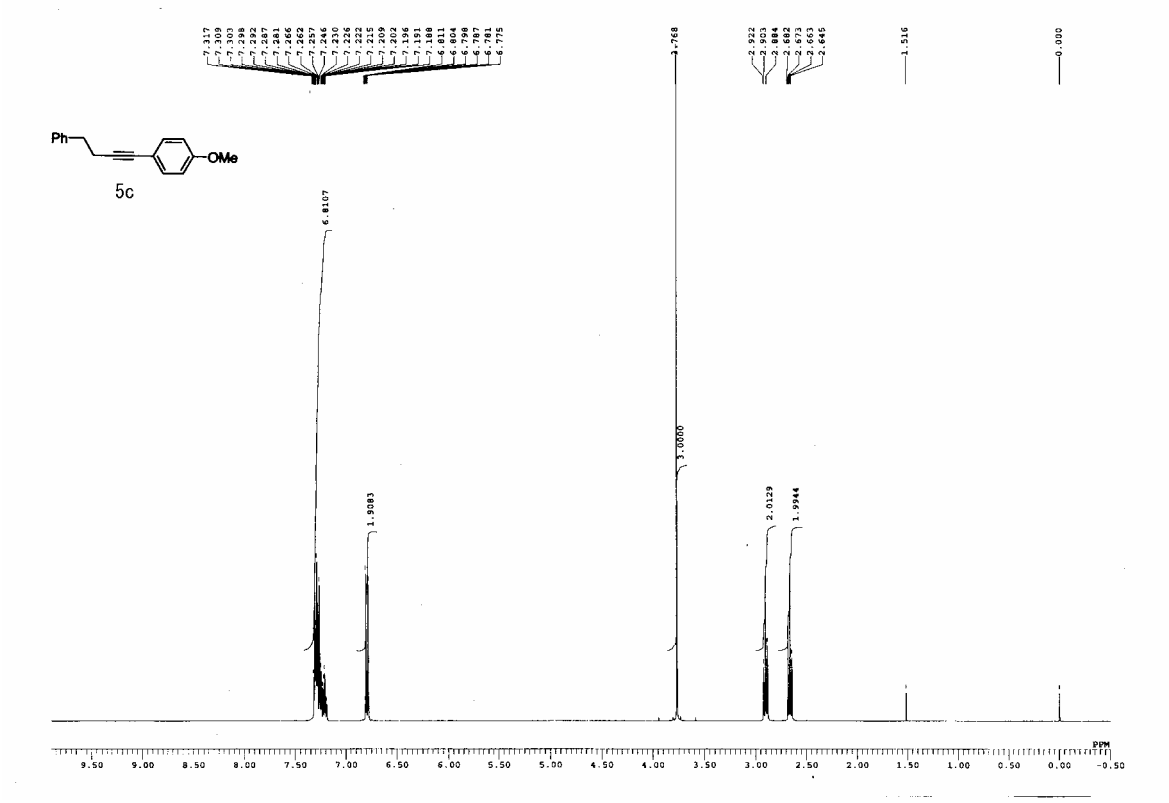
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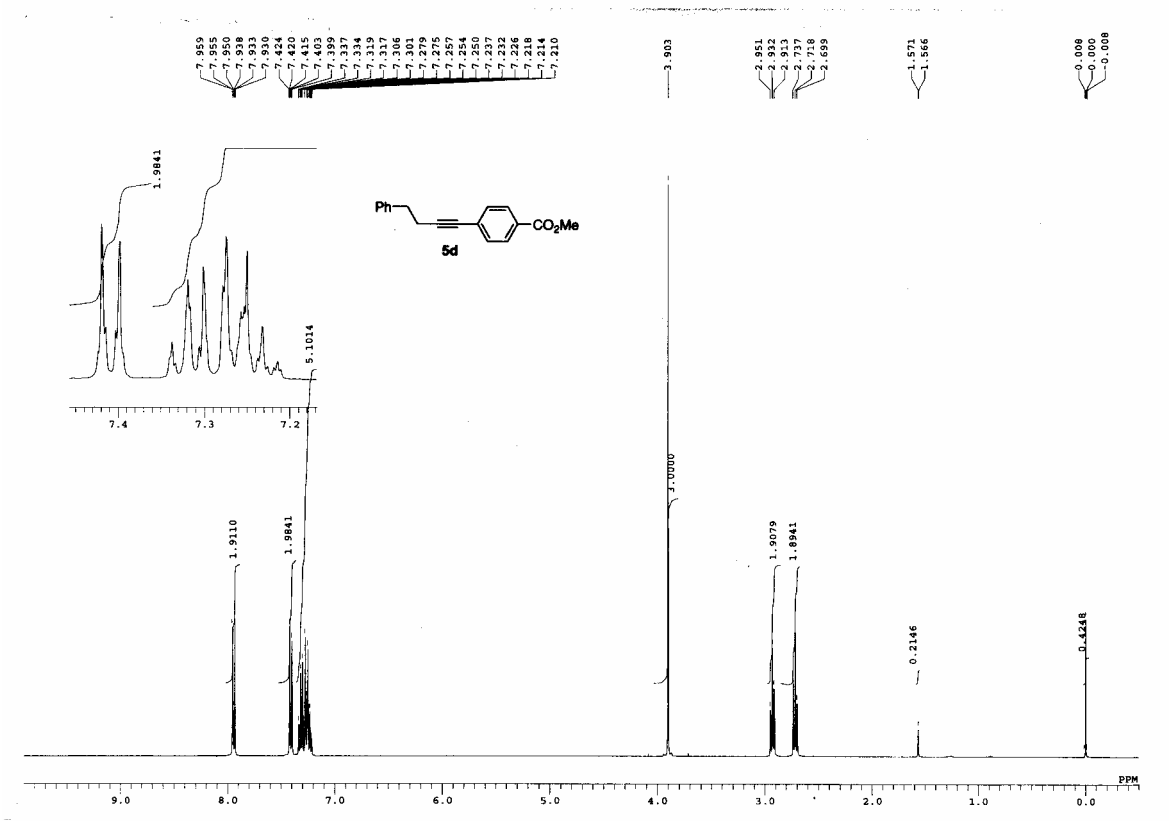
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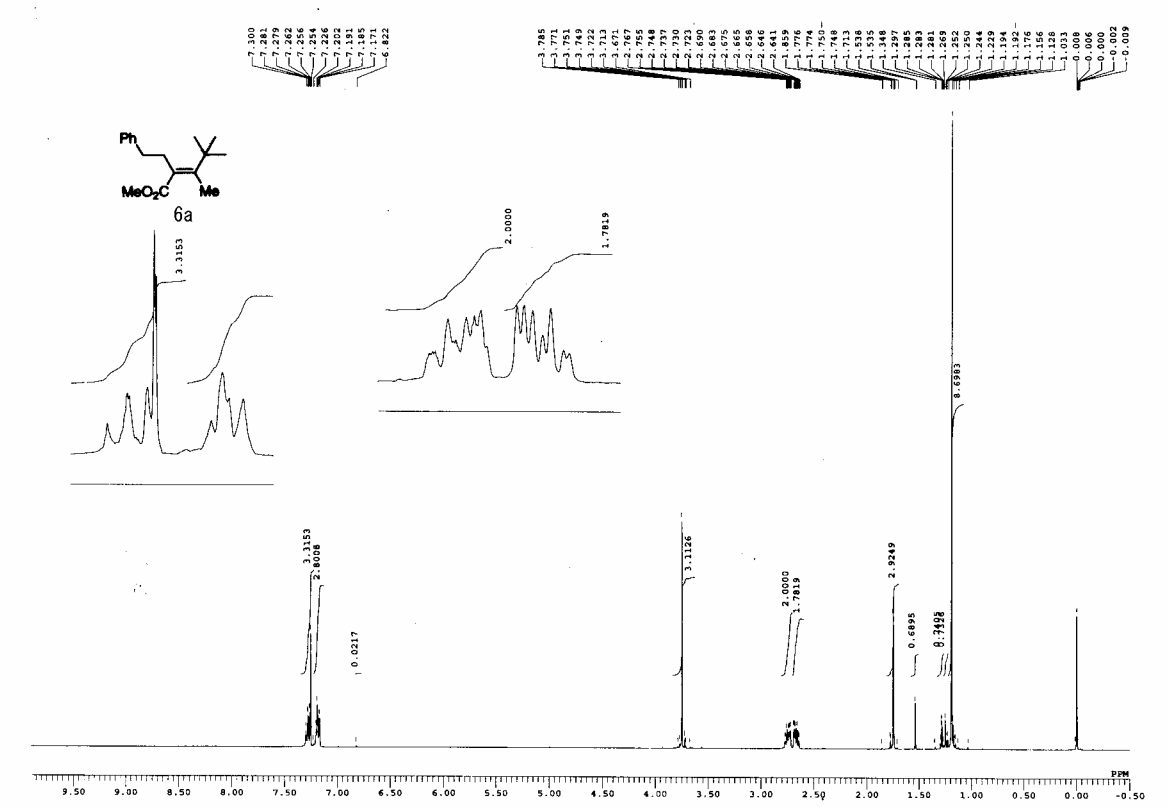
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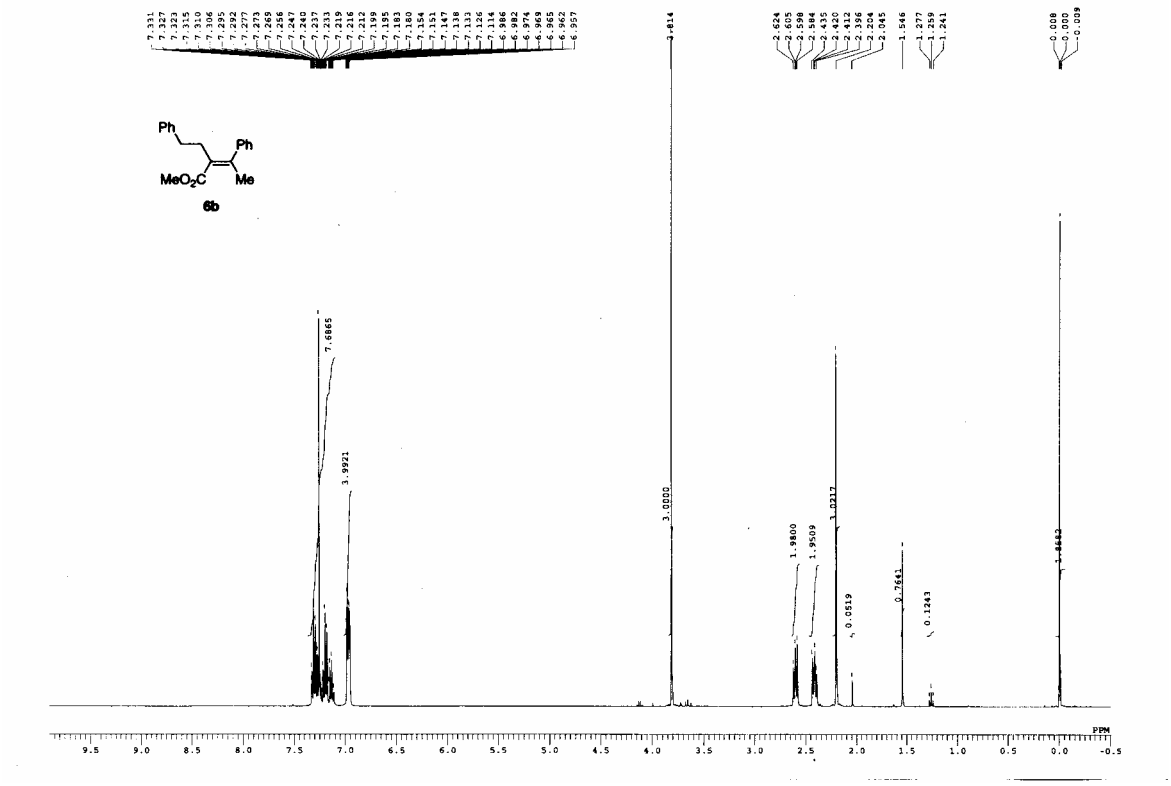
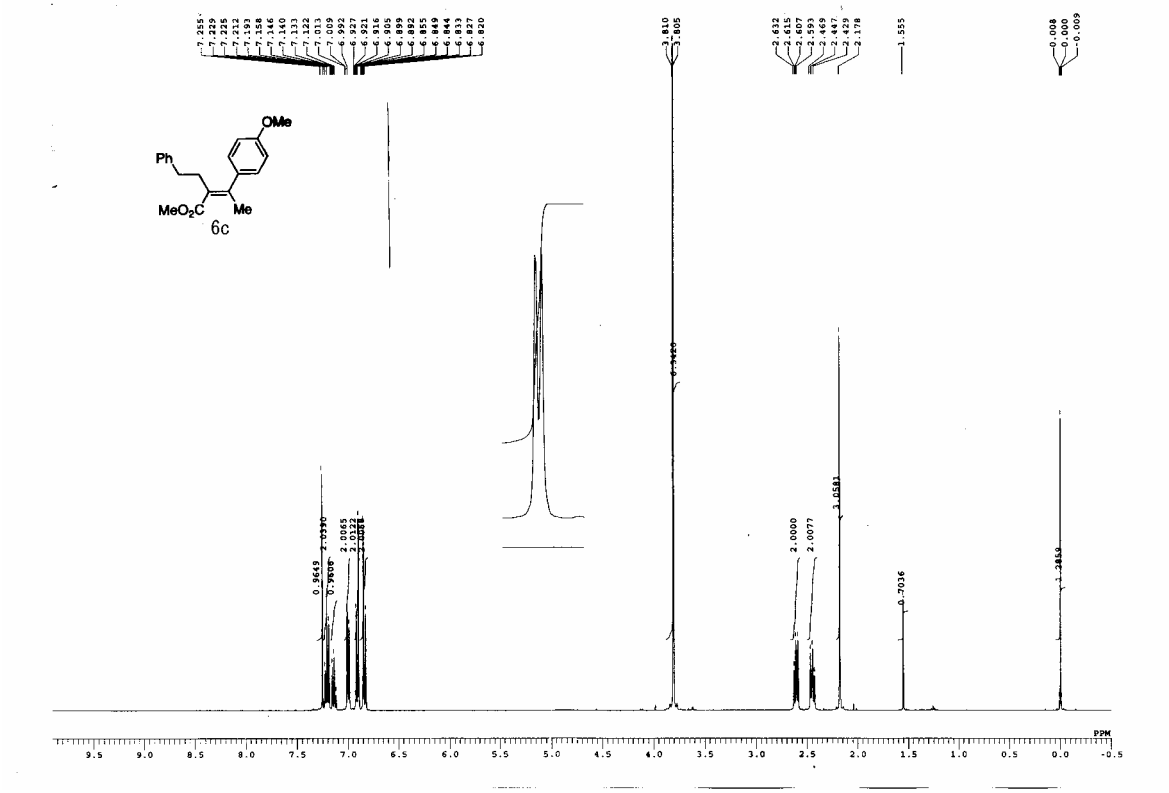
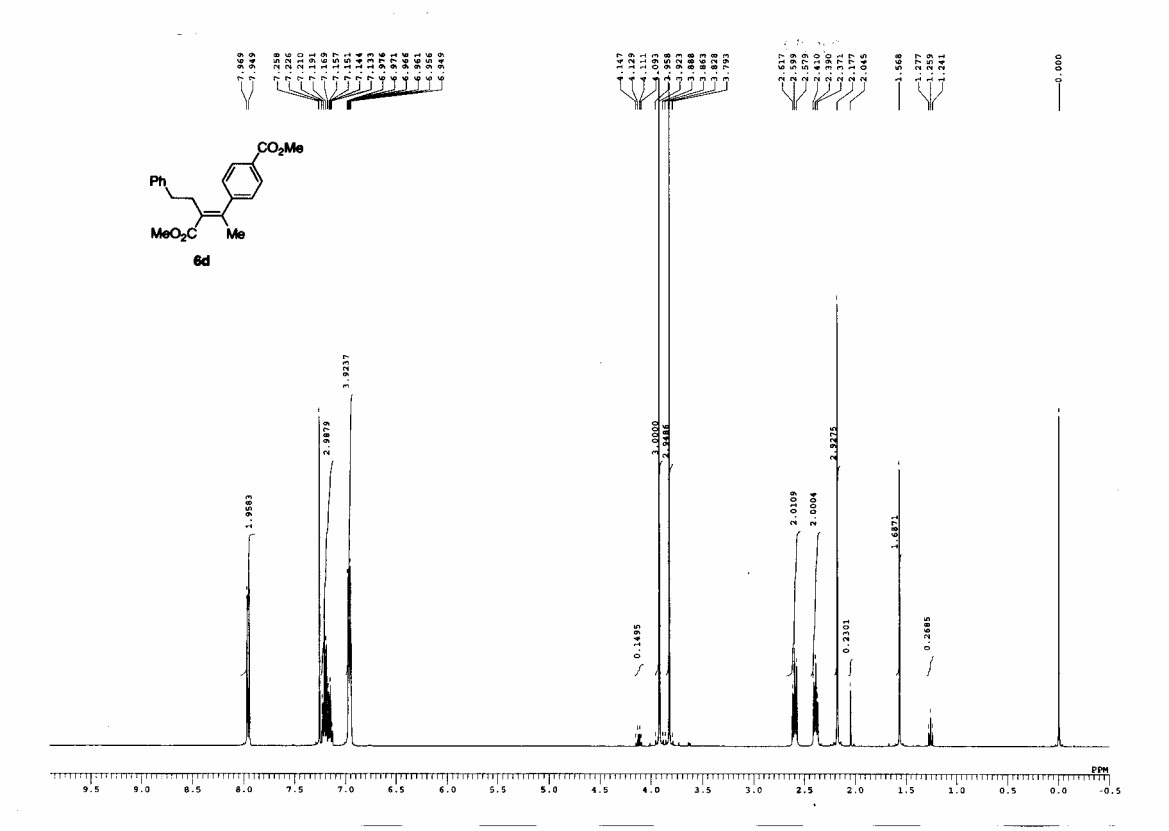
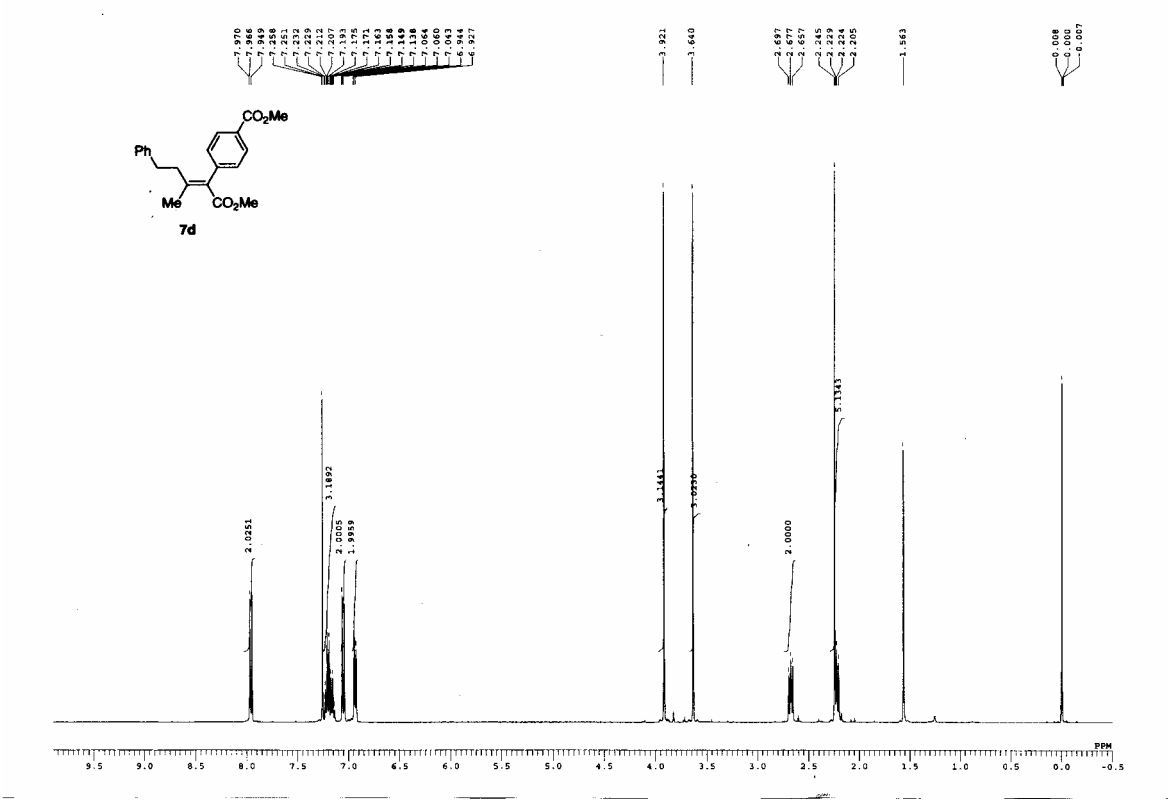
PPM


Ph
Ph
MeO2C
Me
6b
PPM


OMe
Ph
MeO2C
Me
6c
PPM


CO2Me
Ph
MeO2C
Me
6d
PPM


CO2Me
Ph
Me
CO2Me
7d
PPM