Supporting Information

Development of 5-silylethynyl-1,3-dioxolan-4-one as a new prochiral template for asymmetric phase-transfer catalysis

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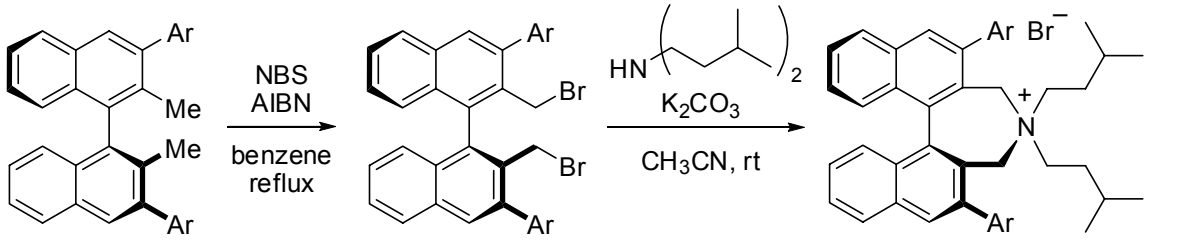
General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad, app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments at 220 nm using 4.6 mm x 25 cm Daicel Chiralpak AD-H, IC and Chiralcel OD-H. High-resolution mass spectra (HRMS) were performed on Brucker microTOF. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography silica gel 60 (Merck, 230-400 mesh).

In experiments requiring dry solvent, CH_2Cl_2 and THF were purchased from Kanto Chemical Co. Inc. as “Dehydrated”, and further purified by passing through neutral alumina under nitrogen atmosphere. Commercially obtained reagents were used as received.

Preparation of Chiral Quaternary Ammonium Bromide (*S*)-1e.



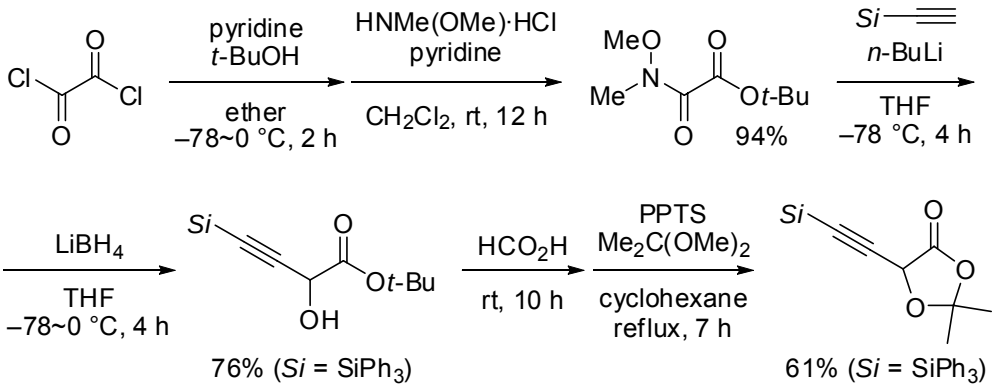
Ar = 3,5-(3,5-$(CF_3)_2C_6H_3)_2C_6H_3$

(*S*)-**1e** : 71% (2 steps)

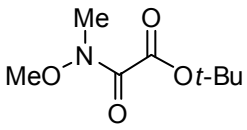
To a stirred solution of (*S*)-3,3'-bis(3,5-bis(trifluoromethylphenyl)phenyl)-2,2'-bisdimethyl-1,1'-binaphthalene[1] (641 mg, 0.50 mmol) and *N*-bromosuccinimide (187 mg, 1.05 mmol) in benzene (5.0 mL) was added 2,2'-azobis(isobutyronitrile) (8.2 mg, 0.05 mmol) at room temperature. The reaction mixture was then refluxed for 4 h, poured into water and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. To this residue were added acetonitrile (3.0 mL), diisopentylamine (113 μL, 0.50 mmol), and K_2CO_3 (104 mg, 0.75 mmol) at room temperature. After stirring for 12 h, the resulting mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with CH_2Cl_2/MeOH = 20:1) to give (*S*)-**1e** (536 mg, 0.36 mmol, 71%).

$[\alpha]_D^{18}$ −13.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (4H, s, ArH), 8.20 (6H, br, ArH), 8.13 (2H, d, *J* = 8.4 Hz, ArH), 8.07 (2H, s, ArH), 7.99 (2H, s, ArH), 7.94 (2H, s, ArH), 7.89 (2H, s, ArH), 7.81 (2H, s, ArH), 7.71 (2H, m, ArH), 7.47 (4H, app d, *J* = 3.6 Hz, ArH), 5.23 (2H, d, *J* = 14.0 Hz, ArCH), 4.04 (2H, d, *J* = 13.6 Hz, ArCH), 3.56 (2H, t, *J* = 12.4 Hz, NCH), 2.83 (2H, dt, *J* = 13.2, 4.8 Hz, NCH), 2.18 (2H, br, $CH(CH_3)_2$), 1.18-0.95 (4H, m, CH_2), 0.71 (6H, d, *J* = 6.4 Hz, CH_3), 0.45 (6H, d, *J* = 6.4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.70, 141.67, 140.9, 140.7, 138.81, 138.76, 134.0, 132.4 (q, $^2J_{C\text{-}F}$ = 33 Hz), 132.4, 131.2, 130.0, 128.8, 128.1, 127.8, 127.5, 126.3, 123.5, 123.2 (q, $^1J_{C\text{-}F}$ = 272 Hz), 122.1, 58.4, 57.0, 30.9, 26.2, 23.0, 21.6; IR (neat) 1368, 1279, 1175, 1132, 901, 885, 845, 752, 706, 685, 638 cm^{-1}; HRMS (ESI) Calcd for $C_{76}H_{54}F_{24}N$ (M^+): 1436.3868, Found: 1436.3872.

General Procedure for the Preparation of 2,2-Dimethyl-5-silylethynyl-1,3-dioxolan-4-one (Scheme 1).



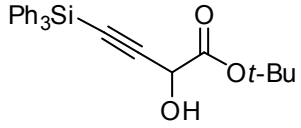
***tert*-Butyl 2-(*N*-Methoxy-*N*-methylamino)-2-oxoacetate.**



To a stirred solution of oxalyl chloride (3.87 mL, 45 mmol) in Et_2O (60 mL) was added *t*-BuOH (2.87 mL, 30 mmol) at –78 °C, and the solution was then allowed to warm to room temperature and stirred for 1 h. After cooling to –78 °C, pyridine (3.64 mL, 45 mmol) was added to this reaction mixture, and the reaction solution was then allowed to warm to room temperature and stirred for 1 h. The reaction mixture was then concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (30 mL). Pyridine (3.64 mL, 45 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (2.93 g, 30 mmol) were added dropwise to this solution at 0 °C. After stirring for 6 h at room temperature, the resulting mixture was poured into 1N HCl and then extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by column chromatography on silica gel (eluting with hexane/AcOEt = 3:1) to give the title compound as colorless oil (5.34 g, 28.2 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (3H, s, OCH_3), 3.21 (3H, s, NCH_3), 1.56 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 161.8, 84.1, 62.0, 31.1, 27.8; IR (neat) 2980, 1736, 1676, 1458, 1369, 1261, 1152, 1092, 993, 845 cm^{-1}; HRMS (ESI) Calcd for $C_8H_{15}NNaO_4$ ([M+Na]$^+$): 212.0893, Found: 212.0884.

***tert*-Butyl 2-hydroxy-4-(triphenylsilyl)but-3-ynoate.**

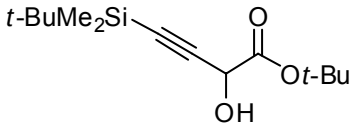


To a stirred solution of triphenylsilylacetylene (5.68 g, 20 mmol) in THF (20 mL) was added *n*-BuLi (1.6 M in hexane, 12.5 mL, 20 mmol) at

–78 °C. After stirring for 1 h at the same temperature, a THF solution (20 mL) of *tert*-butyl 2-(*N*-methoxy-*N*-methylamino)-2-oxoacetate (3.78 g, 20 mmol) was added to the reaction mixture, and the solution was stirred for 6 h at –78 °C. The reaction mixture was then poured into 1N HCl and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was then dissolved in THF (20 mL) and treated with $LiBH_4$ (145 mg, 6.0 mmol) at –78 °C. After gradually warming to 0 °C within 4 h, the solution was poured into 1 N HCl and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/AcOEt = 10:1) to give the title compound as a white solid (15.2 mmol, 6.30 g, 76%).

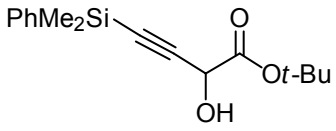
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (6H, m, ArH), 7.43 (3H, m, ArH), 7.37 (6H, m, ArH), 4.86 (1H, d, *J* = 7.2 Hz, CH), 3.17 (1H, d, *J* = 7.2 Hz, OH), 1.50 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 135.5, 132.9, 130.0, 128.0, 105.5, 85.2, 84.2, 62.4, 27.8; IR (neat) 3485, 2980, 2180, 1732, 1429, 1153, 1113, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{26}NaO_3Si$ ($[M+Na]^+$): 437.1543, Found: 437.1550.

***tert*-Butyl 4-(*tert*-butyldimethylsilyl)-2-hydroxybut-3-ynoate:** ^{1}H NMR (400 MHz, $CDCl_3$)



δ 4.70 (1H, d, *J* = 6.4 Hz, CH), 3.05 (1H, d, *J* = 6.4 Hz, OH), 1.51 (9H, s, O*t*Bu), 0.94 (9H, s, Si*t*Bu), 0.11 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 101.5, 88.1, 83.5, 62.1, 27.7, 25.9, 16.4, –5.0; IR (neat) 3491, 2930, 2859, 1736, 1369, 1281, 1250, 1157, 1092, 1018, 826, 777 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{26}NaO_3Si$ ($[M+Na]^+$): 293.1543, Found: 293.1541.

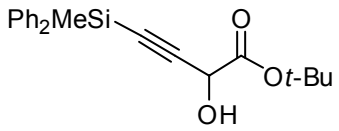
***tert*-Butyl 2-hydroxy-4-(dimethylphenylsilyl)but-3-ynoate:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61



(2H, dd, *J* = 7.4, 2.1 Hz, ArH), 7.38-7.36 (3H, m, ArH), 4.74 (1H, d, *J* = 7.2 Hz, CH), 3.08 (1H, d, *J* = 7.2 Hz, OH), 1.51 (9H, s,*t*Bu), 0.42 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 136.3, 133.6, 129.5, 127.8, 102.6, 88.0, 83.8, 62.2, 27.7, –1.2; IR (neat) 3480, 2978, 2180, 1734, 1250, 1155, 1090, 818, 781, 731, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{22}NaO_3Si$ ($[M+Na]^+$): 313.1230,

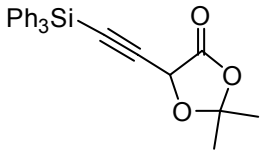
Found: 313.1230.

***tert*-Butyl 2-hydroxy-4-(methyldiphenylsilyl)but-3-ynoate:** ^{1}H NMR (400 MHz, $CDCl_3$)



δ 7.64-7.61 (4H, m, ArH), 7.40-7.34 (6H, m, ArH), 4.80 (1H, d, J = 7.2 Hz, CH), 3.13 (1H, d, J = 7.2 Hz, OH), 1.51 (9H, s,*t*Bu), 0.69 (3H, s, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 134.5, 133.9, 129.8, 127.9, 104.2, 86.5, 84.1, 62.3, 27.8, –2.3; IR (neat) 3478, 2980, 2180, 1734, 1254, 1153, 1111, 1018, 793, 729, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{24}NaO_3Si$ ($[M+Na]^+$): 375.1387, Found: 375.1398.

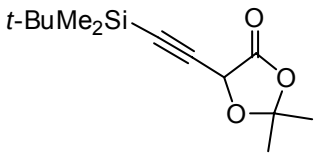
2,2-Dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (2a).



To a stirred solution of *tert*-butyl 2-hydroxy-4-(triphenylsilyl)but-3-ynoate (4.15 g, 10 mmol) in CH_2Cl_2 (5.0 mL) was added formic acid (10 mL) at room temperature. After stirring for 10 h, the reaction mixture was concentrated in vacuo. To the residue were added cyclohexane (15 mL), 2,2-dimethoxypropane (15 mL), and PPTS (254 mg, 1.0 mmol) at room temperature. The reaction mixture was then refluxed at 90 °C for 7 h and poured into water and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/AcOEt = 15:1) to give the title compound as a white solid (2.43 g, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (6H, m, ArH), 7.44 (3H, m, ArH), 7.38 (6H, m, ArH), 5.21 (1H, s, CH), 1.72 (3H, s, CH_3), 1.61 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 135.5, 132.3, 130.2, 128.1, 113.0, 101.2, 89.6, 65.7, 26.9, 26.4; IR (neat) 1800, 1429, 1381, 1267, 1244, 1113, 914, 885, 731, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{22}KO_3Si$ ($[M+K]^+$): 437.0970, Found: 437.0962.

5-((*tert*-Butyldimethylsilyl)ethynyl)-2,2-dimethyl-1,3-dioxolan-4-one (2b): ^{1}H NMR (400 MHz,



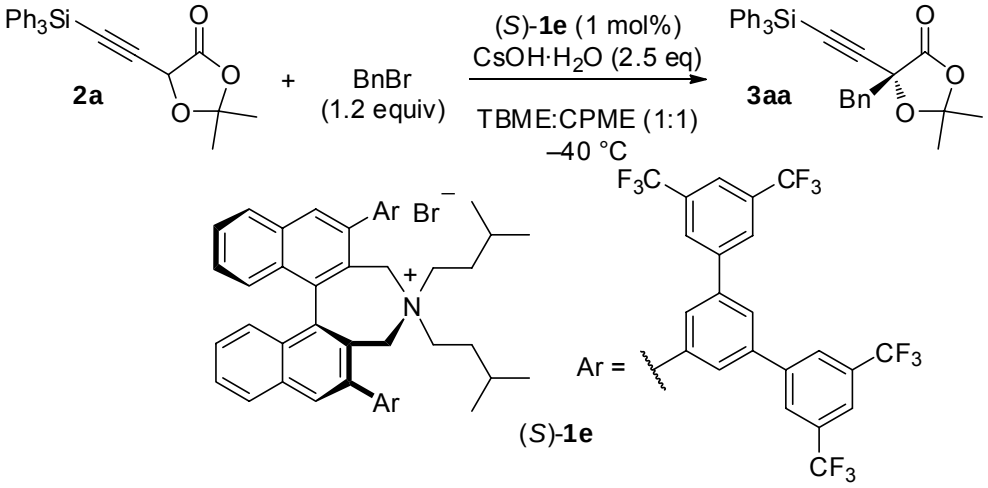
$CDCl_3$) δ 5.06 (1H, s, CH), 1.72 (3H, s, CCH_3), 1.59 (3H, s, CCH_3), 0.94 (9H, s, Si*t*Bu), 0.13 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 112.7, 97.5, 92.7, 65.5, 26.8, 26.4, 25.9, 16.5, –5.1; IR

(neat) 2930, 1805, 1267, 1117, 1074, 887, 826, 777 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{22}NaO_3Si$ ($[M+Na]^+$): 277.1230, Found: 277.1236.

5-((Dimethylphenylsilyl)ethynyl)-2,2-dimethyl-1,3-dioxolan-4-one (2c): ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (2H, m, ArH), 7.39-7.35 (3H, m, ArH), 5.09 (1H, s, CH), 1.70 (3H, s, CCH_3), 1.57 (3H, s, CCH_3), 0.44 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 135.5, 133.6, 129.6, 127.9, 112.7, 98.3, 92.3, 65.5, 26.7, 26.3, –1.4; IR (neat) 2995, 1798, 1381, 1250, 1115. 1074, 914, 885, 839, 816, 783, 731, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{18}NaO_3Si$ ($[M+Na]^+$): 297.0917, Found: 297.0911.

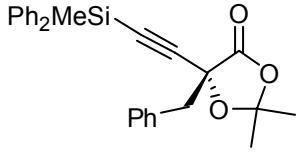
2,2-Dimethyl-5-((methyldiphenylsilyl)ethynyl)-1,3-dioxolan-4-one (2d): ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (4H, d, J = 7.2 Hz, ArH), 7.41-7.35 (6H, m, ArH), 5.15 (1H, s, CH), 1.71 (3H, s, CCH_3), 1.59 (3H, s, CCH_3), 0.71 (3H, s, $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 134.5, 134.0, 130.0, 128.1, 112.9, 99.9, 90.8, 65.7, 26.9, 26.4, –2.5; IR (neat) 2997, 1798, 1429, 1381, 1267, 1115, 1074, 914, 885, 791, 733, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{20}NaO_3Si$ ($[M+Na]^+$): 359.1074, Found: 359.1074.

Representative Procedure for the Phase-transfer Catalyzed Enantioselective Alkylation of 5-(Triphenylsilyl)ethynyl-1,3-dioxolan-4-one.

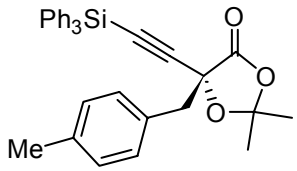


To a mixture of 2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (0.1 mmol, 39.9 mg) and chiral quaternary ammonium bromide (*S*)-**1e** (0.001 mmol, 1.5 mg) in *tert*-butyl methyl ether (TBME) (0.5 mL) and cyclopentyl methyl ether (CPME) (0.5 mL) were added benzyl bromide (0.12 mmol, 14.3 μL) and $CsOH{\cdot}H_2O$ (0.25 mmol, 46.6 mg) at –40 °C under argon atmosphere. After stirring vigorously for 11 h at –40 °C, the resulting mixture was then poured into saturated NH_4Cl aq and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 30:1) to give the title compound as colorless oil (0.071 mmol, 34.7 mg, 71% yield).

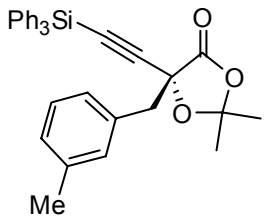
(*R*)-5-Benzyl-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 1, 3aa): $[\alpha]_D^{22}$ +23.2 [*c* 1.0, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (6H, dd, *J* = 8.0, 1.2 Hz, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.37 (6H, app t, *J* = 7.2 Hz, ArH), 7.26 (5H, br, ArH), 3.40 (1H, d, *J* = 14.0 Hz, ArCH), 3.34 (1H, d, *J* = 14.0 Hz, ArCH), 1.64 (3H, s, CH_3), 1.19 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 135.5, 133.6, 132.4, 131.1, 130.1, 128.2, 128.0, 127.5, 111.5, 105.3, 89.1, 76.3, 44.4, 26.9, 26.7; IR (neat) 3069, 1796, 1429, 1273, 1233, 1115, 918, 741, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{28}NaO_3Si([M+Na]^+)$: 511.1700, Found: 511.1681; HPLC analysis: Daicel Chiralpak AD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 21.9 min (minor) and 23.4 min (major).

(*R*)-5-Benzyl-2,2-dimethyl-5-((methyldiphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 1, entry 11, 3da): 

$[\alpha]_D^{19}$ +6.9 [*c* 1.0, $CHCl_3$ (68% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (4H, dd, *J* = 7.6, 1.6 Hz, ArH), 7.41-7.35 (6H, m, ArH), 7.26 (5H, br, ArH), 3.37 (1H, d, *J* = 14.0 Hz, ArCH), 3.31 (1H, d, *J* = 14.0 Hz, ArCH), 1.64 (3H, s, CH_3), 1.18 (3H, s, CH_3), 0.69 (3H, s, $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 134.5, 134.2, 133.7, 131.1, 129.9, 128.1, 128.0, 127.5, 111.5, 104.1, 90.2, 76.3, 44.4, 26.9, 26.7, –2.4; IR (neat) 2924, 1798, 1429, 1273, 1117, 795, 773, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{26}NaO_3Si([M+Na]^+)$: 449.1543, Found: 449.1556; HPLC analysis: Daicel Chiralcel OD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 18.5 min (minor) and 20.5 min (major).

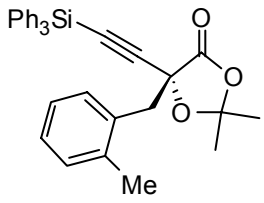
(*R*)-2,2-Dimethyl-5-(4-methylbenzyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 2, 3ab): 

$[\alpha]_D^{18}$ +14.1 [*c* 1.0, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (6H, m, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.38-7.35 (6H, m, ArH), 7.15 (2H, d, *J* = 8.0 Hz, ArH), 7.07 (2H, d, *J* = 8.0 Hz, ArH), 3.34 (1H, d, *J* = 14.0 Hz, ArCH), 3.30 (1H, d, *J* = 14.0 Hz, ArCH), 2.32 (3H, s, $ArCH_3$), 1.64 (3H, s, CH_3), 1.23 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 135.5, 132.5, 130.9, 130.5, 130.1, 128.9, 128.2, 128.0, 111.5, 105.4, 89.0, 76.4, 44.0, 26.9, 26.8, 21.1; IR (neat) 2922, 1798, 1429, 1273, 1115, 914, 745, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}KO_3Si([M+K]^+)$: 541.1596, Found: 541.1618; HPLC analysis: Daicel Chiralpak AD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 18.3 min (minor) and 22.1 min (major).

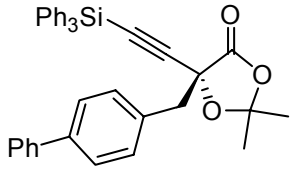
(*R*)-2,2-Dimethyl-5-(3-methylbenzyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 3, 3ac): 

$[\alpha]_D^{23}$ +6.1 [*c* 1.0, $CHCl_3$ (87% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (6H, m, ArH), 7.43 (3H, tt, *J* = 7.6, 1.6 Hz, ArH), 7.37 (6H, t, *J* = 7.6 Hz, ArH), 7.16 (1H, m, ArH), 7.08-7.06 (3H, m, ArH), 3.35 (1H, d, *J* = 14.0 Hz, ArCH), 3.31 (1H, d, *J* = 14.0 Hz, ArCH), 2.27 (3H, s, $ArCH_3$), 1.64 (3H, s, CH_3), 1.21 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 137.7, 135.5, 133.5,

132.5, 131.8, 130.1, 128.2, 128.1, 111.5, 105.4, 89.0, 76.3, 44.4, 26.9, 26.8, 21.3 (two peaks overlap); IR (neat) 1796, 1429, 1273, 1231, 1115, 914, 772, 743, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}NaO_3Si([M+Na]^+)$: 525.1856, Found: 525.1850; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 14.2 min (major) and 17.1 min (minor).

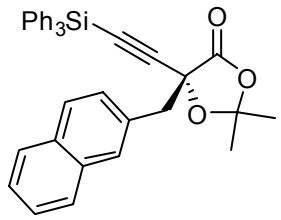
(*R*)-2,2-Dimethyl-5-(2-methylbenzyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 4, 3ad): 

$[\alpha]_D^{20}$ +5.6 [*c* 1.0, $CHCl_3$ (95% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (6H, d, *J* = 8.0 Hz, ArH), 7.44 (3H, t, *J* = 7.2 Hz, ArH), 7.37 (6H, app t, *J* = 7.2 Hz, ArH), 7.26 (1H, d, *J* = 8.0 Hz, ArH), 7.18-7.07 (3H, m, ArH), 3.50 (1H, d, *J* = 14.8 Hz, ArCH), 3.35 (1H, d, *J* = 14.8 Hz, ArCH), 2.35 (3H, s, $ArCH_3$), 1.63 (3H, s, CH_3), 1.18 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 138.4, 135.5, 132.4, 132.4, 131.3, 130.3, 130.1, 128.0, 127.5, 125.8, 111.5, 105.4, 88.9, 76.9, 40.8, 26.9, 26.7, 20.2; IR (neat) 3069, 1796, 1429, 1269, 1234, 1115, 920, 737, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}NaO_3Si([M+Na]^+)$: 525.1856, Found: 525.1866; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 13.5 min (major) and 17.5 min (minor).

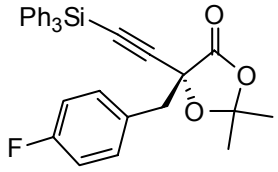
(*R*)-2,2-dimethyl-5-(4-phenylbenzyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 5, 3ae): 

$[\alpha]_D^{22}$ +16.1 [*c* 1.0, $CHCl_3$ (88% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (8H, m, ArH), 7.50 (2H, d, *J* = 8.0 Hz, ArH), 7.44-7.40 (5H, m, ArH), 7.38-7.31 (9H, m, ArH), 3.41 (2H, s, $ArCH_2$), 1.66 (3H, s, CH_3), 1.26 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 140.7, 140.3, 135.5, 132.7, 132.4, 131.5, 130.2, 128.7, 128.1, 127.3, 127.0, 126.8, 111.6, 105.2, 89.3, 76.3, 44.1, 26.9 (one peak overlaps); IR (neat) 1794, 1429, 1269, 1229, 1113, 912, 762, 733, 710, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{32}NaO_3Si([M+Na]^+)$: 587.2013, Found: 587.1986; HPLC analysis: Daicel Chiralpak AD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 27.3 min (major) and 33.3 min (minor).

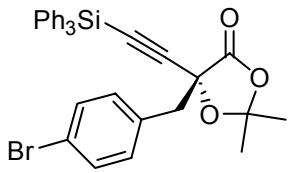
(*R*)-2,2-Dimethyl-5-(naphthalen-2-ylmethyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 6, 3af): $[\alpha]_D^{26}$ +8.5 [*c* 1.0, $CHCl_3$ (87% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, m, ArH), 7.75-7.72 (3H, m, ArH), 7.56-7.54 (6H, m, ArH), 7.46-7.40 (6H, m, ArH), 7.33 (6H, t, *J* = 6.8 Hz, ArH), 3.53 (2H, s, $ArCH_2$), 1.64 (3H, s, CH_3), 1.21 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 135.5, 133.2, 132.7, 132.4, 131.2, 130.1, 130.0, 129.0, 128.03, 127.95, 127.62, 127.57, 126.0, 125.9, 111.6, 105.2, 89.4, 76.4, 44.6, 26.9, 26.8; IR (neat) 3051, 1796, 1429, 1275, 1236, 1115, 912, 743, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{30}NaO_3Si([M+Na]^+)$: 561.1856, Found: 561.1877; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 300:1, flow rate = 0.5 mL/min, retention time; 33.8 min (major) and 38.9 min (minor).



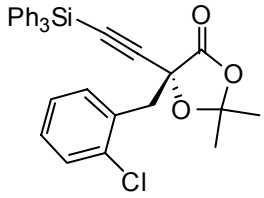
(*R*)-5-(4-Fluorobenzyl)-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 7, 3ag): $[\alpha]_D^{19}$ +12.8 [*c* 1.0, $CHCl_3$ (84% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (6H, dd, *J* = 8.0, 1.6 Hz, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.37 (6H, app t, *J* = 7.2 Hz, ArH), 7.22 (2H, dd, *J* = 8.8, 5.6 Hz, ArH), 6.94 (2H, t, *J* = 8.8 Hz, ArH), 3.33 (2H, s, $ArCH_2$), 1.65 (3H, s, CH_3), 1.26 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 162.4 (d, $^1J_{C\text{-}F}$ = 247 Hz), 135.5, 132.6 (d, $^3J_{C\text{-}F}$ = 8 Hz), 132.3, 130.2, 129.4 (d, $^4J_{C\text{-}F}$ = 3 Hz), 128.1, 115.0 (d, $^2J_{C\text{-}F}$ = 21 Hz), 111.6, 105.0, 89.5, 76.2, 43.6, 26.9, 26.8; IR (neat) 3071, 1798, 1510, 1429, 1275, 1225, 1115, 916, 737, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{27}FNaO_3Si([M+Na]^+)$: 529.1606, Found: 529.1602; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 13.4 min (major) and 17.4 min (minor).



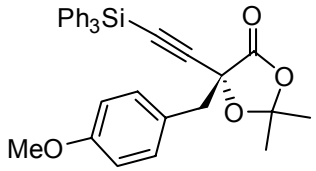
(*R*)-5-(4-Bromobenzyl)-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 8, 3ah): $[\alpha]_D^{23}$ +27.3 [*c* 1.0, $CHCl_3$ (86% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (6H, app dt, *J* = 7.2, 1.6 Hz, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.40-7.36 (8H, m, ArH), 7.13 (2H, d, *J* = 8.4 Hz, ArH), 3.30 (2H, s, $ArCH_2$), 1.65 (3H, s, CH_3), 1.30 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 135.5, 132.7, 132.6, 132.3, 131.3, 130.2, 128.1, 121.7, 111.6, 104.7, 89.7, 75.9, 43.8, 27.0, 26.7; IR (neat) 2924,



1796, 1429, 1271, 1115, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{27}BrNaO_3Si([M+Na]^+)$: 589.0805, Found: 589.0820; HPLC analysis: Daicel Chiralpak AD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 23.4 min (minor) and 26.8 min (major).

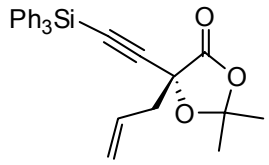
(*R*)-5-(2-Chlorobenzyl)-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 9, 3ai): 

$[\alpha]_D^{23}$ +13.5 [*c* 1.0, $CHCl_3$ (85% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (6H, app dt, *J* = 6.8, 1.6 Hz, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.40-7.34 (8H, m, ArH), 7.20 (1H, m, ArH), 7.13 (1H, m, ArH), 3.73 (1H, d, *J* = 14.4 Hz, ArCH), 3.45 (1H, d, *J* = 14.4 Hz, ArCH), 1.65 (3H, s, CH_3), 1.27 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 135.9, 135.5, 132.3, 132.2, 132.0, 130.1, 129.6, 128.8, 128.0, 126.7, 111.7, 104.8, 89.5, 76.3, 40.8, 26.82, 26.79; IR (neat) 3069, 2997, 1796, 1429, 1271, 1113, 1082, 914, 739, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{27}ClKO_3Si([M+K]^+)$: 561.1050, Found: 561.1040; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 14.5 min (major) and 19.2 min (minor).

(*R*)-5-(4-Methoxybenzyl)-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 10, 3aj): 

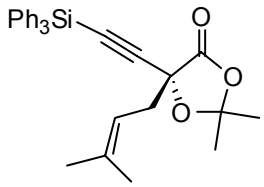
$[\alpha]_D^{25}$ +4.8 [*c* 1.0, $CHCl_3$ (83% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (6H, app dt, *J* = 6.8, 1.6 Hz, ArH), 7.44 (3H, tt, *J* = 7.6, 1.6 Hz, ArH), 7.39-7.35 (6H, m, ArH), 7.18 (2H, d, *J* = 8.8 Hz, ArH), 6.79 (2H, d, *J* = 8.8 Hz, ArH), 3.77 (3H, s, OCH_3), 3.33 (1H, d, *J* = 14.4 Hz, $ArCH_2$), 3.29 (1H, d, *J* = 14.4 Hz, $ArCH_2$), 1.64 (3H, s, CH_3), 1.24 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 159.0, 135.5, 132.5, 132.1, 130.1, 128.0, 125.7, 113.5, 111.5, 105.4, 89.0, 76.4, 55.2, 43.6, 26.87, 26.85; IR (neat) 1796, 1514, 1429, 1273, 1252, 1115, 735, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}NaO_4Si([M+Na]^+)$: 541.1806, Found: 541.1805; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 21.7 min (major) and 27.4 min (minor).

(*R*)-5-Allyl-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 11, 3ak):



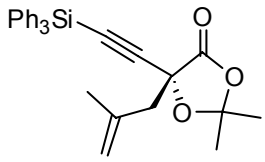
$[\alpha]_D^{22}$ +3.2 [*c* 1.0, $CHCl_3$ (76% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (6H, dd, *J* = 8.0, 1.6 Hz, ArH), 7.43 (3H, tt, *J* = 7.6, 1.6 Hz, ArH), 7.37 (6H, app t, *J* = 7.6 Hz, ArH), 5.84 (1H, m, $CH_2CH{=}CH_2$), 5.27-5.23 (2H, m, $C{=}CH_2$), 2.86 (1H, dd, *J* = 14.4, 7.2 Hz, C=CCH), 2.76 (1H, dd, *J* = 14.4, 7.2 Hz, C=CCH), 1.70 (3H, s, CH_3), 1.59 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 135.5, 132.4, 130.2, 130.0, 128.0, 121.1, 111.4, 105.1, 89.0, 75.4, 42.8, 27.2, 26.7; IR (neat) 3069, 2997, 1798, 1429, 1275, 1115, 914, 743, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{26}NaO_3Si([M+Na]^+)$: 461.1543, Found: 461.1540; HPLC analysis: Daicel Chiralpak AD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 13.8 min (major) and 17.2 min (minor).

(*R*)-2,2-Dimethyl-5-((triphenylsilyl)ethynyl)-5-prenyl-1,3-dioxolan-4-one (Table 2, entry 12, 3al):



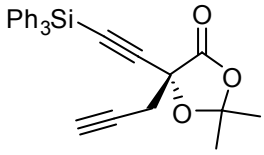
$[\alpha]_D^{22}$ +5.2 [*c* 1.0, $CHCl_3$ (80% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (6H, dd, *J* = 6.4, 1.6 Hz, ArH), 7.43 (3H, tt, *J* = 6.8, 1.6 Hz, ArH), 7.37 (6H, app t, *J* = 6.8 Hz, ArH), 5.23 (1H, t, *J* = 7.6 Hz, C=CH), 2.82 (1H, dd, *J* = 15.2, 7.6 Hz, $C{=}CCH_2$), 2.72 (1H, dd, *J* = 15.2, 7.6 Hz, $C{=}CCH_2$), 1.73 (3H, s, $C{=}CCH_3$), 1.69 (3H, s, CH_3), 1.63 (3H, s, $C{=}CCH_3$), 1.56 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 138.1, 135.5, 132.5, 130.1, 128.0, 115.8, 111.2, 105.6, 88.3, 76.0, 37.4, 27.1, 26.8, 26.0, 18.2; IR (neat) 2995, 1796, 1429, 1273, 1240, 1113, 1086, 920, 739, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{30}KO_3Si([M+K]^+)$: 505.1596, Found: 505.1590; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 11.6 min (major) and 14.4 min (minor).

(*R*)-5-methallyl-2,2-Dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 13, 3am):



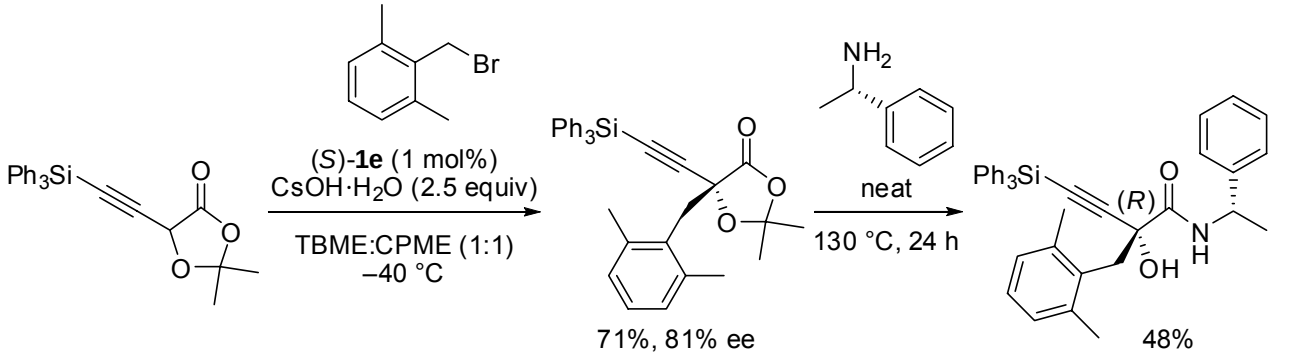
$[\alpha]_D^{20}$ +10.1 [*c* 1.0, $CHCl_3$ (86% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (6H, dd, *J* = 6.4, 1.6 Hz, ArH), 7.43 (3H, tt, *J* = 6.8, 1.6 Hz, ArH), 7.38-7.34 (6H, m, ArH), 4.97 (1H, app t, *J* = 1.2 Hz, $C{=}CH_2$), 4.92 (1H, d, *J* = 1.2 Hz, $C{=}CH_2$), 2.81 (1H, d, *J* = 14 Hz, ArCH), 2.75 (1H, d, *J* = 14 Hz, ArCH), 1.83 (3H, s, $CH_2{=}CCH_3$), 1.70 (3H, s, CH_3), 1.58 (3H, s, CH_3); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 169.4, 138.9, 135.5, 132.5, 130.1, 128.0, 116.9, 111.3, 105.4, 88.9, 76.0, 45.8, 27.2, 26.7, 24.1; IR (neat) 2922, 1798, 1429, 1275, 1234, 1115, 914, 743, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{28}NaO_3Si([M+Na]^+)$: 475.1700, Found: 475.1704; HPLC analysis: Daicel Chiralpak AD-H, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 12.4 min (major) and 15.9 min (minor).

(*R*)-2,2-Dimethyl-5-(prop-2-ynyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (Table 2, entry 14, 3an): 

$[\alpha]_D^{21}$ +17.5 [*c* 1.0, $CHCl_3$ (86% ee)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (6H, dd, *J* = 8.0, 1.6 Hz, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.39-7.35 (6H, m, ArH), 3.01 (2H, d, *J* = 2.4 Hz, C≡CCH_2), 2.14 (1H, t, *J* = 2.4 Hz, C≡CH), 1.72 (3H, s, CH_3), 1.67 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 135.5, 132.2, 130.2, 128.1, 111.9, 103.8, 89.8, 77.1, 74.7, 72.4, 29.8, 26.9, 26.8; IR (neat) 3291, 2999, 1798, 1429, 1275, 1240, 1113, 920, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{24}KO_3Si([M+K]^+)$: 475.1126, Found: 475.1136; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 18.4 min (major) and 27.6 min (minor).

Determination of the Absolute Configuration by X-ray Crystallographic Analysis.



(*R*)-5-(2,6-Dimethylbenzyl)-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one: $[\alpha]_D^{25}$ +12.1 [*c* 1.0, $CHCl_3$ (81% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (6H, app dt, *J* = 6.8, 1.6 Hz, ArH), 7.42 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.40-7.32 (6H, m, ArH), 7.06 (1H, dd, *J* = 8.4, 6.8 Hz, ArH), 6.97 (2H, d, *J* = 7.6 Hz, ArH), 3.63 (1H, d, *J* = 14.8 Hz, ArCH), 3.41 (1H, d, *J* = 14.8 Hz, ArCH), 2.35 (6H, s, $ArCH_3$), 1.63 (3H, s, CH_3), 1.39 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 138.7, 135.5, 132.3, 131.6, 130.1, 128.3, 128.0, 127.1, 111.5, 105.2, 89.4, 76.9, 38.1, 27.2, 26.7, 21.2; IR (neat) 1796, 1429, 1267, 1231, 1113, 1086, 903, 773, 739, 710, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{32}NaO_3Si$([M+Na]$^+$): 539.2013, Found: 539.2001; HPLC analysis: Daicel Chiralpak IC, hexane/isopropyl alcohol = 200:1, flow rate = 0.5 mL/min, retention time; 12.0 min (major) and 13.7 min (minor).

To a stirred solution of (*R*)-5-(2,6-dimethylbenzyl)-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (0.1 mmol, 51.7 mg) in (*S*)-1-phenylethylamine (1.0 mmol, 110 μL) was stirred at 130 °C for 24 h. The reaction mixture was then poured into 1N HCl and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 3:1) to give the title compound as a white solid (0.048 mmol, 27.8 mg, 48% yield).

***N*-(*S*)-1-Phenylethyl (*R*)-2-(2,6-dimethylbenzyl)-2-hydroxy-4-(triphenylsilyl)but-3-ynamide:** $[\alpha]_D^{26}$ +5.3 [*c* 1.0, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (6H, app dt, *J* = 6.4, 1.6 Hz, ArH), 7.42 (3H, tt, *J* = 7.6, 1.6 Hz, ArH), 7.35-7.31 (6H, m, ArH), 7.23-7.20 (3H, m, ArH), 7.13-7.10 (2H, m, ArH), 7.01 (1H, t, *J* = 7.6 Hz, ArH), 6.86 (2H, d, *J* = 7.6 Hz, ArH), 6.71 (1H, d, *J* = 8.0 Hz, NH), 5.05 (1H, app quint, *J* = 7.6 Hz, ArCHN), 3.59 (1H, s, OH), 3.46 (1H, d, *J* = 14.4 Hz, ArCH), 3.31

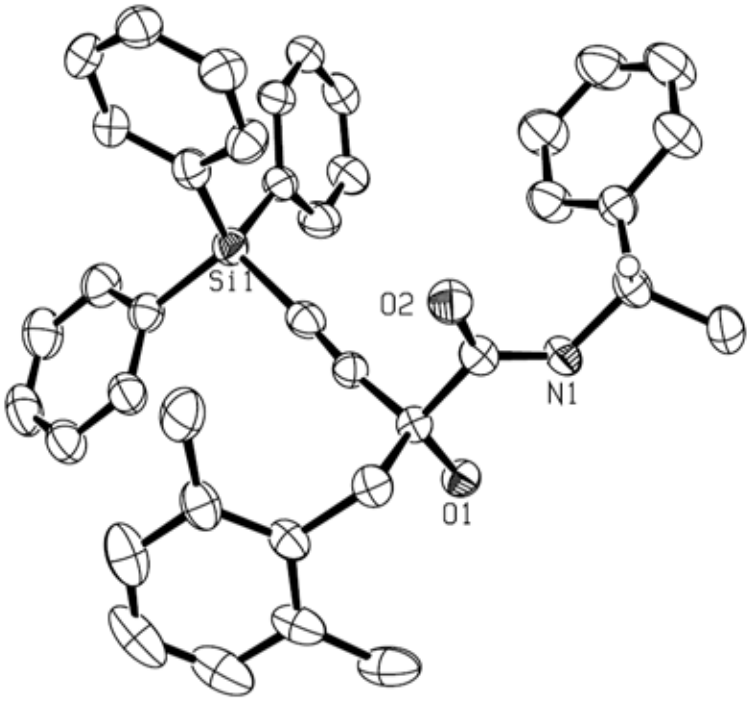
(1H, d, J = 14.4 Hz, ArCH), 2.21 (6H, s, $ArCH_3$), 1.36 (3H, d, J = 7.2 Hz, $NCHCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 142.1, 138.7, 135.5, 132.4, 132.0, 130.1, 128.7, 128.4, 128.0, 127.4, 126.8, 125.9, 108.9, 88.0, 73.5, 49.7, 39.7, 21.9, 21.2; IR (neat) 1657, 1516, 1427, 1111, 1080, 907, 733, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{39}H_{37}NNaO_2Si$($[M+Na]^+$): 602.2486, Found: 602.2488.

The product was recrystallized from hexane/dichloromethane. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The crystallographic data were summarized in the following table.

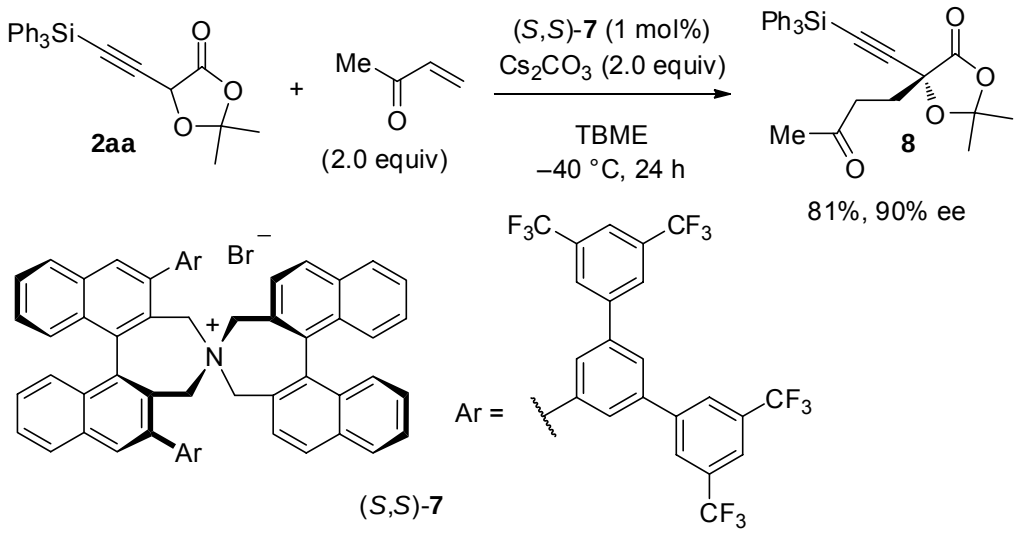
The absolute configuration was determined by reference to the Flack parameter[4] –0.01(3). The crystallographic data were summarized in the following table.

empirical formula	$C_{39}H_{37}NO_2Si$
formula weight	579.81
crystal system	orthorhombic
space group	$P2_12_12_1$ (#19)
a, Å	10.22255(18)
b, Å	13.9241(3)
c, Å	22.6976(4)
V, $Å^3$	3230.77(10)
Z	4
D_{calc}, g/cm^3	1.192
T, °C	–150
μ (CuKα), cm^{-1}	9.022
no. of reflns meased	32834
no. of reflns obsd	5875
no. of reflns variable	397
R (All reflections)	0.0808
R_w (All reflections)	0.1222
Goodness of Fit	1.174
Flack Parameter (Friedel pairs = 2555)	–0.01(3)

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 733521). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.


Si1
O2
N1
O1

Phase-transfer Catalyzed Enantioselective Michael Addition of 5-(Triphenylsilyl)ethynyl-1,3-dioxolan-4-one with Methyl Vinyl Ketone (Scheme 3).



To a mixture of 2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (39.9 mg, 0.1 mmol) and chiral quaternary ammonium bromide (*S*,*S*)-**7** (1.7 mg, 0.001 mmol) in *tert*-butyl methyl ether (TBME) (1.0 mL) was added 3-buten-2-one (16.2 μL, 0.20 mmol) and Cs_2CO_3 (65.2 mg, 0.20 mmol) at –40 °C. After stirring for 24 h at –40 °C, the resulting mixture was then poured into saturated NH_4Cl aq and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 6:1) to give the title compound as a white solid (38.0 mg, 0.081 mmol, 81% yield).

(*R*)-2,2-Dimethyl-5-(3-oxobutyl)-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one (8): $[\alpha]_D^{23}$ +39.1 [*c* 1.0, $CHCl_3$ (90% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (6H, m, ArH), 7.44 (3H, tt, *J* = 7.2, 1.6 Hz, ArH), 7.38 (6H, m, ArH), 2.79 (1H, dq, *J* = 18.0, 5.2 Hz, COCH), 2.63 (1H, dq, *J* = 18.0, 5.2 Hz, COCH), 2.39 (1H, dq, *J* = 14.4, 5.2 Hz, $COCH_2CH$), 2.27 (1H, dq, *J* = 14.4, 5.2 Hz, $COCH_2CH$), 2.12 (3H, s, $COCH_3$), 1.70 (3H, s, CH_3), 1.59 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 169.2, 135.4, 132.3, 130.2, 128.1, 111.4, 104.7, 89.5, 74.7, 37.9, 32.7, 29.9, 27.4, 26.5; IR (neat) 1796, 1719, 1429, 1385, 1267, 1244, 1213, 1113, 916, 741, 708, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{28}NaO_4Si$([M+Na]$^+$): 491.1649, Found: 491.1633; HPLC analysis: Daicel Chiralcel OD-H, hexane/isopropyl alcohol = 60:1, flow rate = 0.5 mL/min, retention time; 16.3 min (major) and 18.7 min (minor).

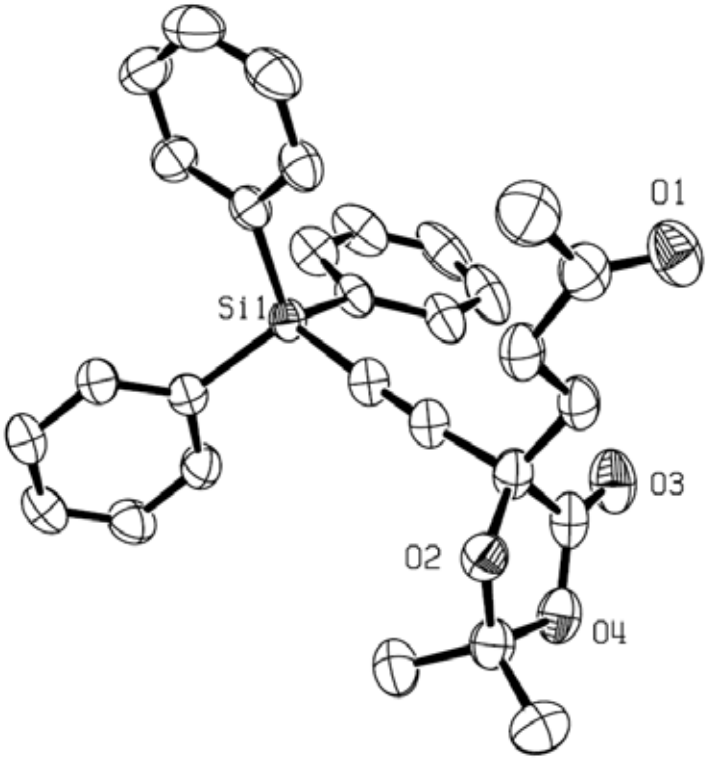
Determination of the Absolute Configuration by X-ray Crystallographic Analysis.

The product was recrystallized from methanol. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The crystallographic data were summarized in the following table.

The absolute configuration was determined by reference to the Flack parameter[4] 0.00(2). The crystallographic data were summarized in the following table.

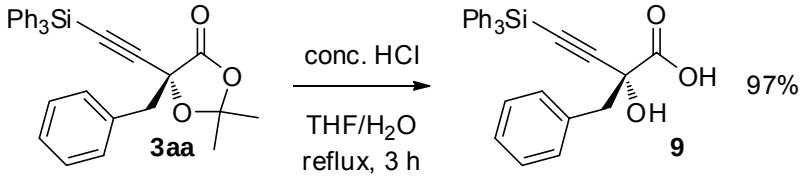
empirical formula	$C_{29}H_{28}O_4Si$
formula weight	468.62
crystal system	orthorhombic
space group	$P2_12_12_1$ (#19)
a, Å	11.1919(2)
b, Å	14.0119(3)
c, Å	16.5141(3)
V, Å^3	2589.72(8)
Z	4
D_{calc}, g/cm^3	1.202
T, °C	–150
μ (CuKα), cm^{-1}	10.533
no. of reflns meased	26668
no. of reflns obsd	4720
no. of reflns variable	309
R (All reflections)	0.0370
R_w (All reflections)	0.0830
Goodness of Fit	1.043
Flack Parameter (Friedel pairs = 2043)	0.00(2)

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 719866). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.


O1
Si1
O3
O2
O4

Selective Transformation of the Protecting Groups of 3aa (Scheme 4).

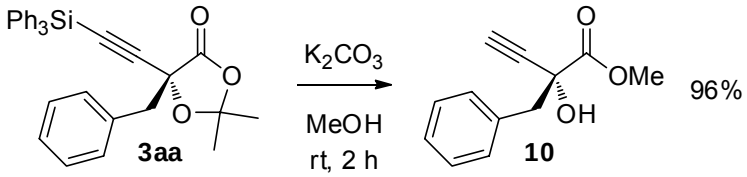
(*R*)-2-Benzyl-2-hydroxy-4-(triphenylsilyl)but-3-ynoic acid (9).



To a stirred solution of 5-benzyl-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one **3aa** (0.1 mmol, 48.9 mg) in dioxane (2.0 mL) and H_2O (0.5 mL) was added conc. HCl (0.5 mL) at room temperature. The reaction mixture was refluxed at 90 °C for 3 h, and then poured into water and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate/acetic acid = 1:1:0.05) to give the title compound as colorless oil (0.097 mmol, 43.5 mg, 97% yield).

$[\alpha]_D^{26}$–21.8 [*c* 1.0, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (6H, dd, *J* = 8.0, 1.6 Hz, ArH), 7.42-7.33 (9H, m, ArH), 7.29-7.20 (5H, m, ArH), 3.38 (1H, d, *J* = 13.6 Hz, ArCH), 3.29 (1H, d, *J* = 13.6 Hz, ArCH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 135.5, 133.9, 132.6, 130.7, 130.1, 128.2, 128.0, 127.5, 106.4, 87.3, 72.0, 45.9; IR (neat) 1724, 1429, 1113, 907, 735, 708, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{24}NaO_3Si([M+Na]^+)$: 471.1387, Found: 471.1391.

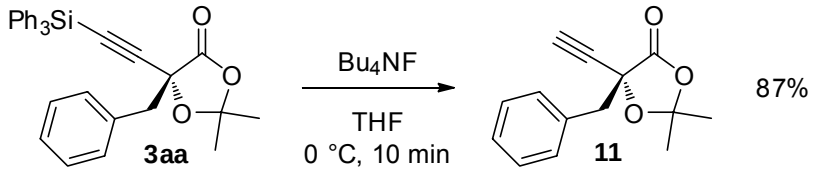
(*R*)-Methyl 2-benzyl-2-hydroxybut-3-ynoate (10).



To a stirred solution of 5-benzyl-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one **3aa** (0.1 mmol, 48.9 mg) in methanol (1.0 mL) was added K_2CO_3 (0.5 mL) at 0 °C. After stirring for 2 h, the reaction mixture was poured into 1N HCl and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent with hexane/ethyl acetate = 5:1) to give the title compound as colorless oil (0.096 mmol, 19.6 mg, 96% yield).

$[\alpha]_D^{24}$ −2.5 [*c* 1.0, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (5H, m, ArH), 3.83 (3H, s, CO_2CH_3), 3.42 (1H, s, OH), 3.29 (1H, d, *J* = 13.6 Hz, ArCH), 3.25 (1H, d, *J* = 13.6 Hz, ArCH), 2.59 (1H, s, C≡CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 134.2, 130.4, 128.2, 127.4, 82.0, 73.8, 71.3, 53.7, 46.1; IR (neat) 1742, 1456, 1437, 1263, 1209, 1098, 1032, 743, 700, 667 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{12}NaO_3$([M+Na]$^+$): 227.0679, Found: 227.0674.

(*R*)-5-Benzyl-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-one (11).



To a stirred solution of 5-benzyl-2,2-dimethyl-5-((triphenylsilyl)ethynyl)-1,3-dioxolan-4-one **3aa** (0.1 mmol, 48.9 mg) in THF (1.0 mL) was added tetrabutylammonium fluoride (1.0 M in THF, 0.1 mL) at 0 °C. After stirring for 10 min, the reaction mixture was poured into saturated NH_4Cl aq and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1) to give the title compound as colorless oil (0.087 mmol, 20.0 mg, 87% yield).

$[\alpha]_D^{19}$ +8.8 [*c* 1.0, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (5H, m, ArH), 3.34 (1H, d, *J* = 14.4 Hz, ArCH), 3.27 (1H, d, *J* = 14.0 Hz, ArCH), 2.73 (1H, s, C≡CH), 1.65 (3H, s, CH_3), 1.12 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 133.5, 131.1, 128.2, 127.6, 111.6, 80.3, 76.2, 75.7, 44.3, 26.9, 26.6; IR (neat) 3289, 1794, 1389, 1379, 1275, 1233, 1121, 920, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{14}NaO_3$([M+Na]$^+$): 253.0835, Found: 253.0829.

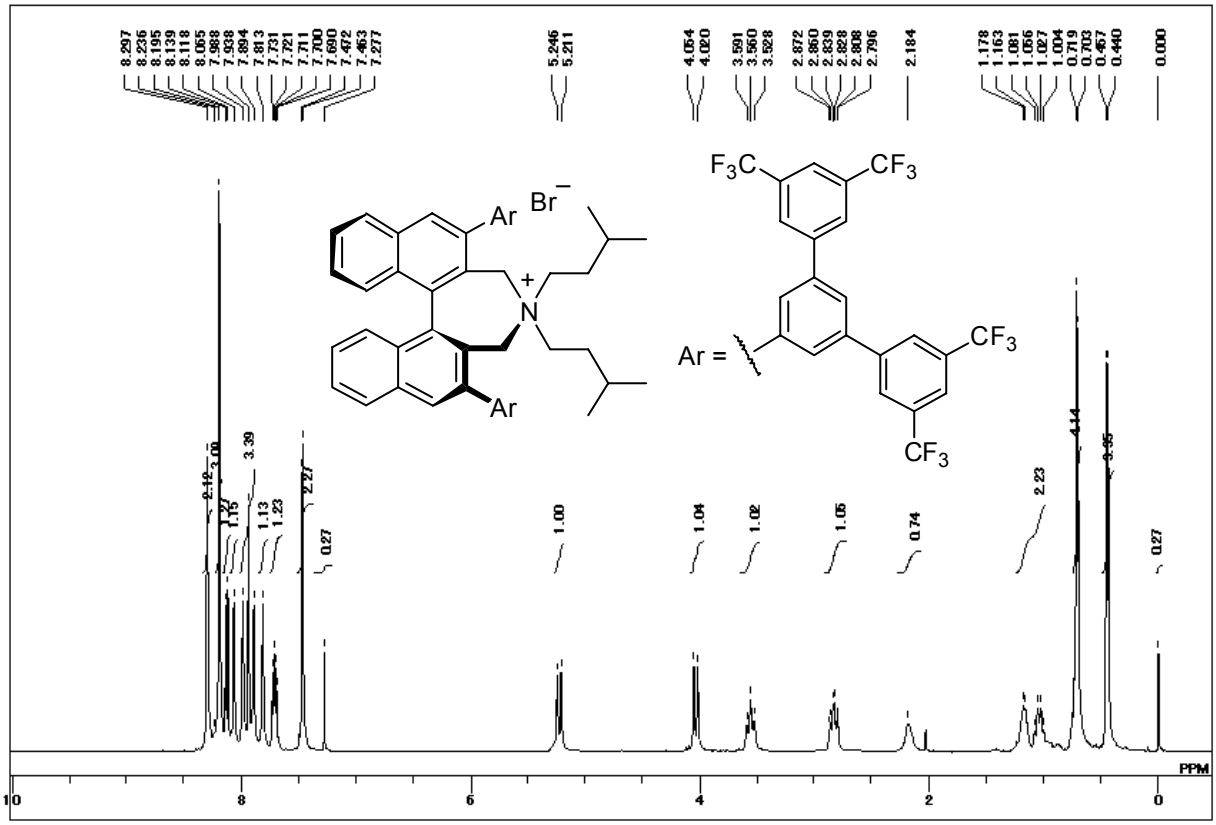
References

(1) T. Ooi, M. Kameda, M. Taniguchi, K. Maruoka, *J. Am. Chem. Soc.* **2005**, *127*, 9685.

(2) L. G. Mueller, R. G. Lawton, *J. Org. Chem.* **1979**, *44*, 4741.

(3) G. M. Sheldrick, SHELX-97: Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.

(4) H. D. Flack, *Acta Cryst.* **1983**, *A39*, 876.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+
N
Ar
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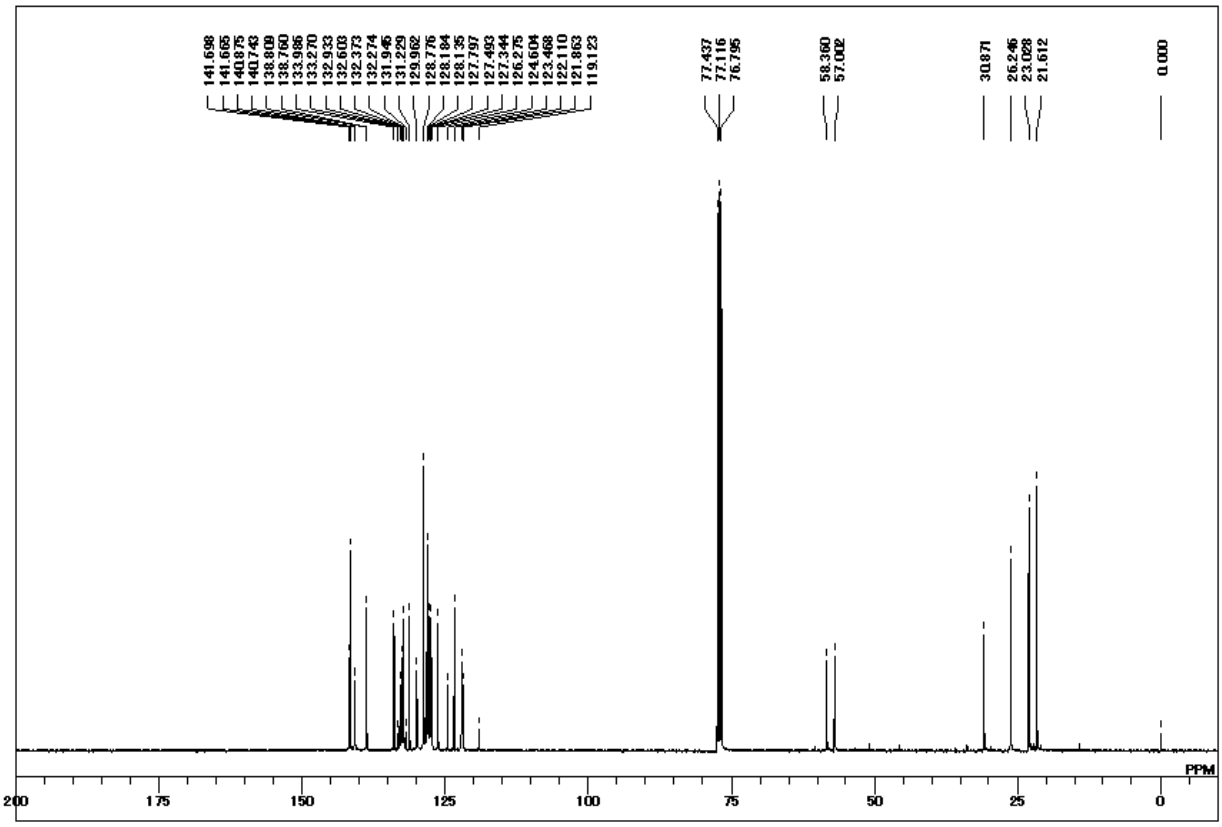
F3C
CF3
CF3
CF3
PPM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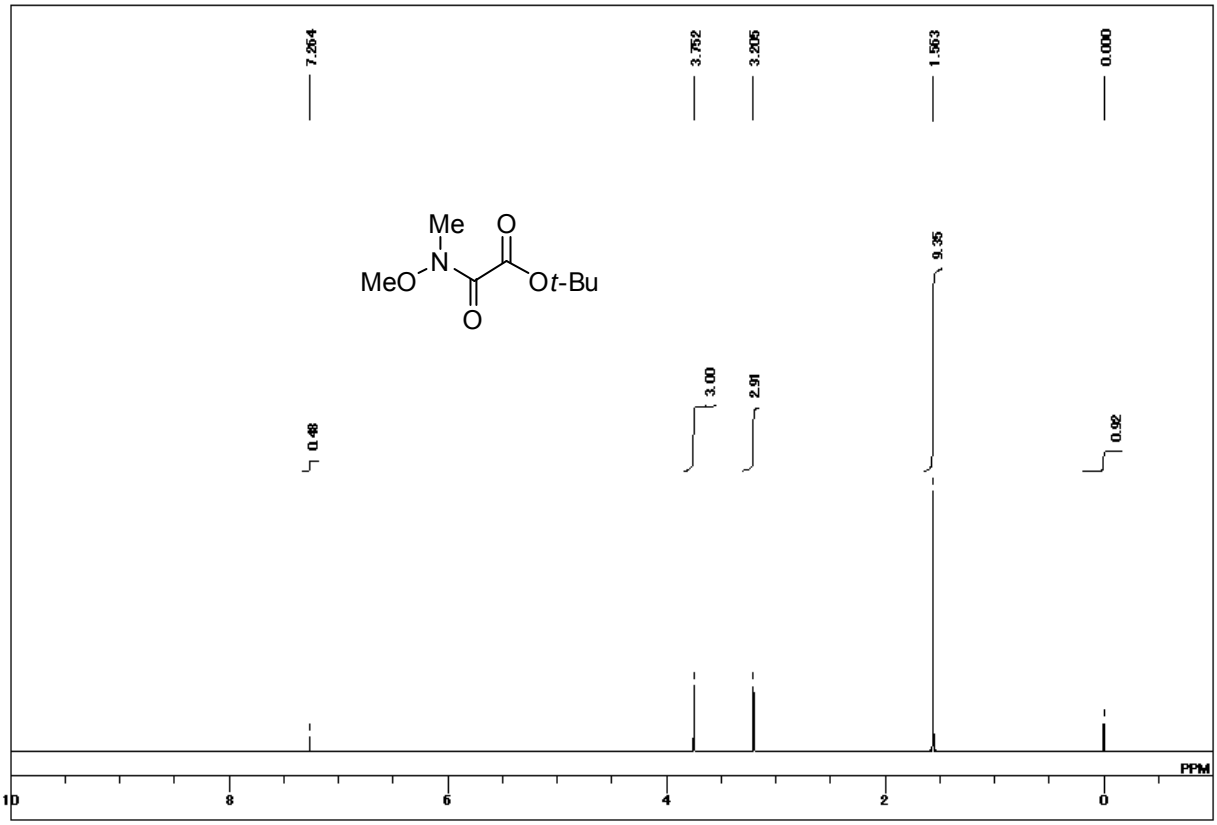
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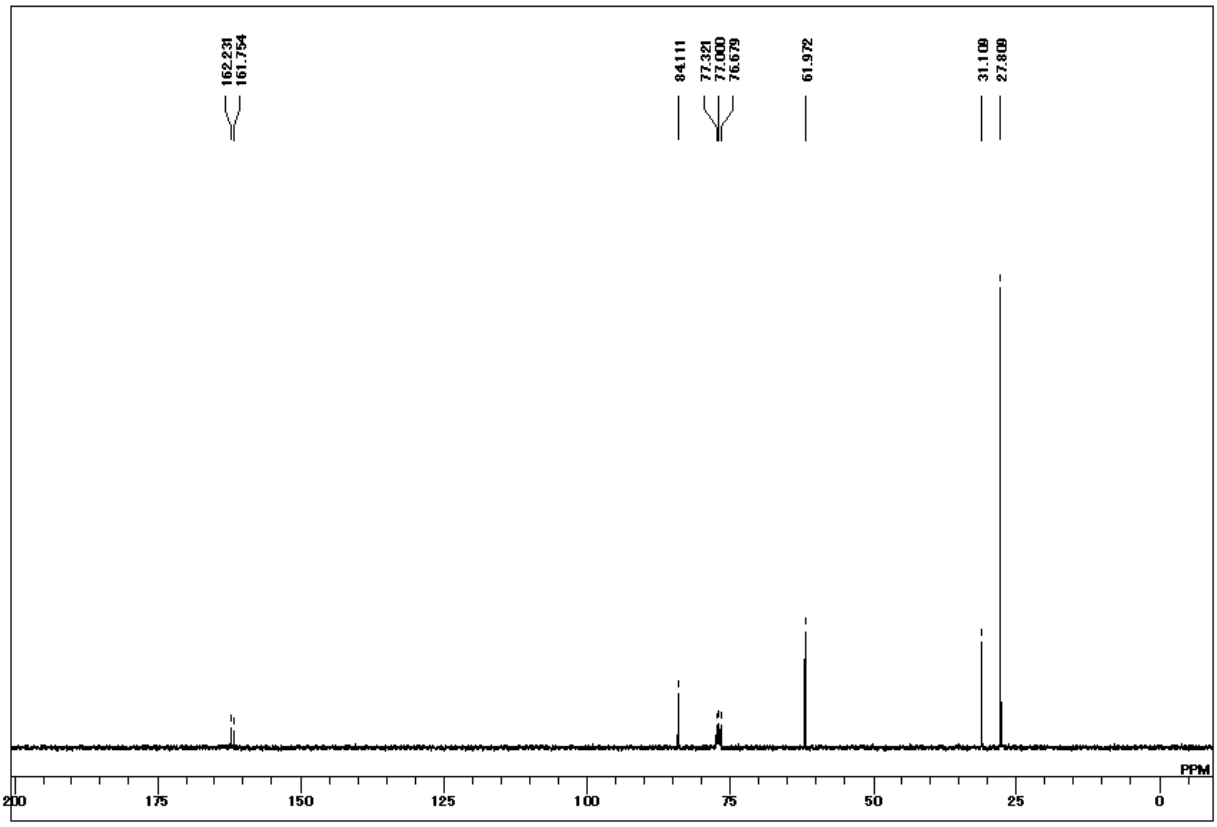
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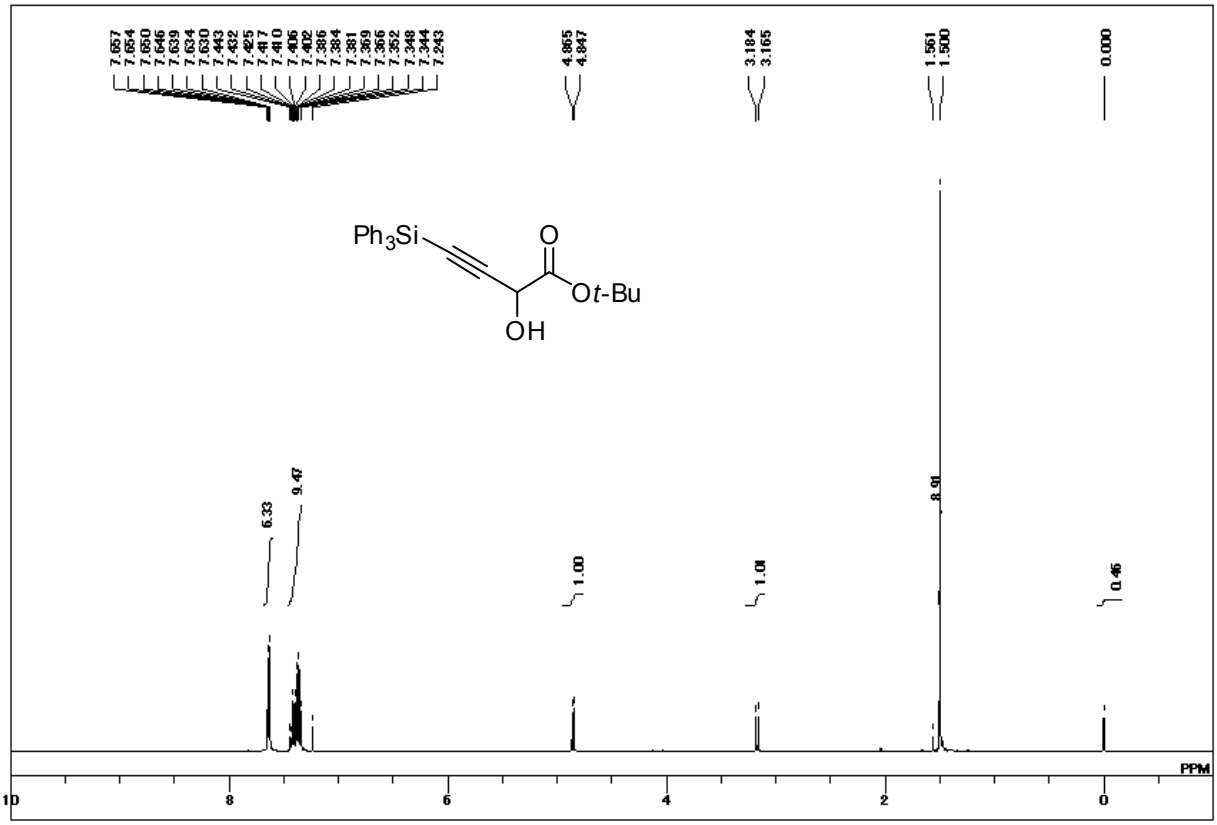
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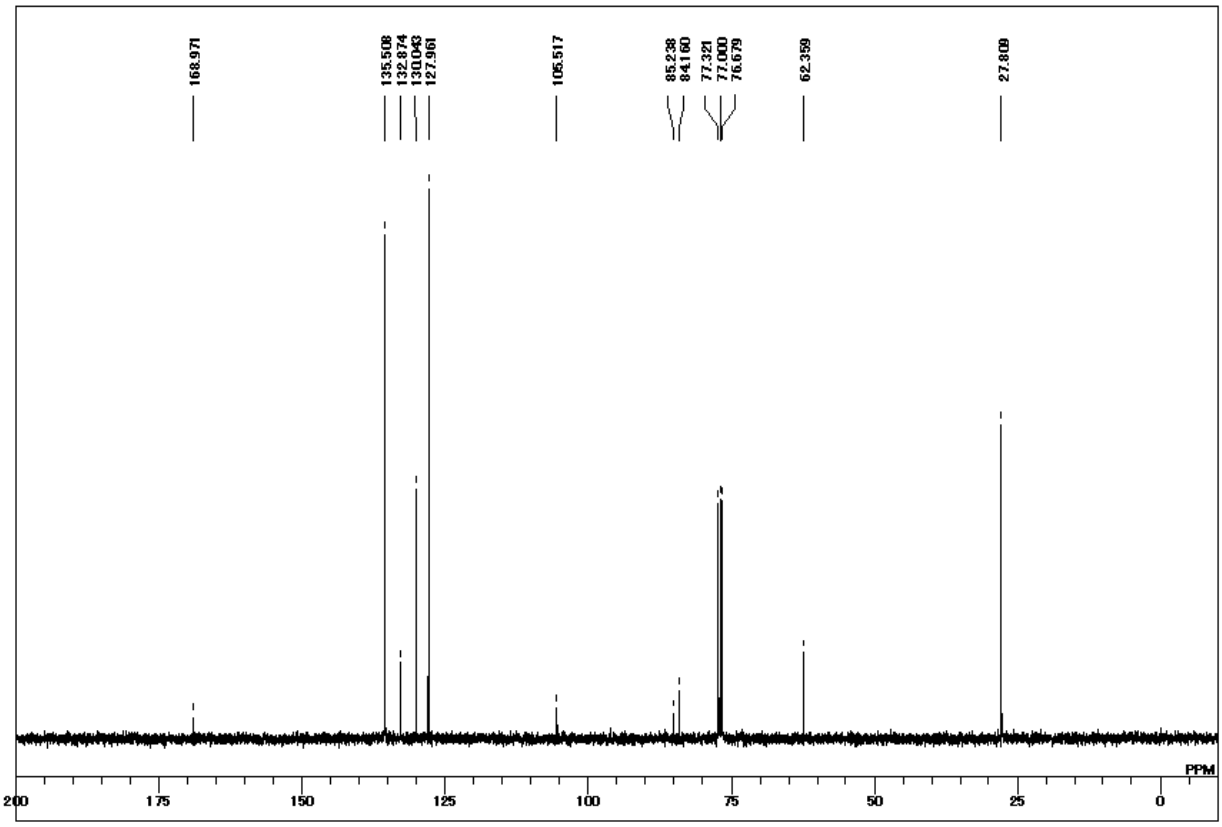
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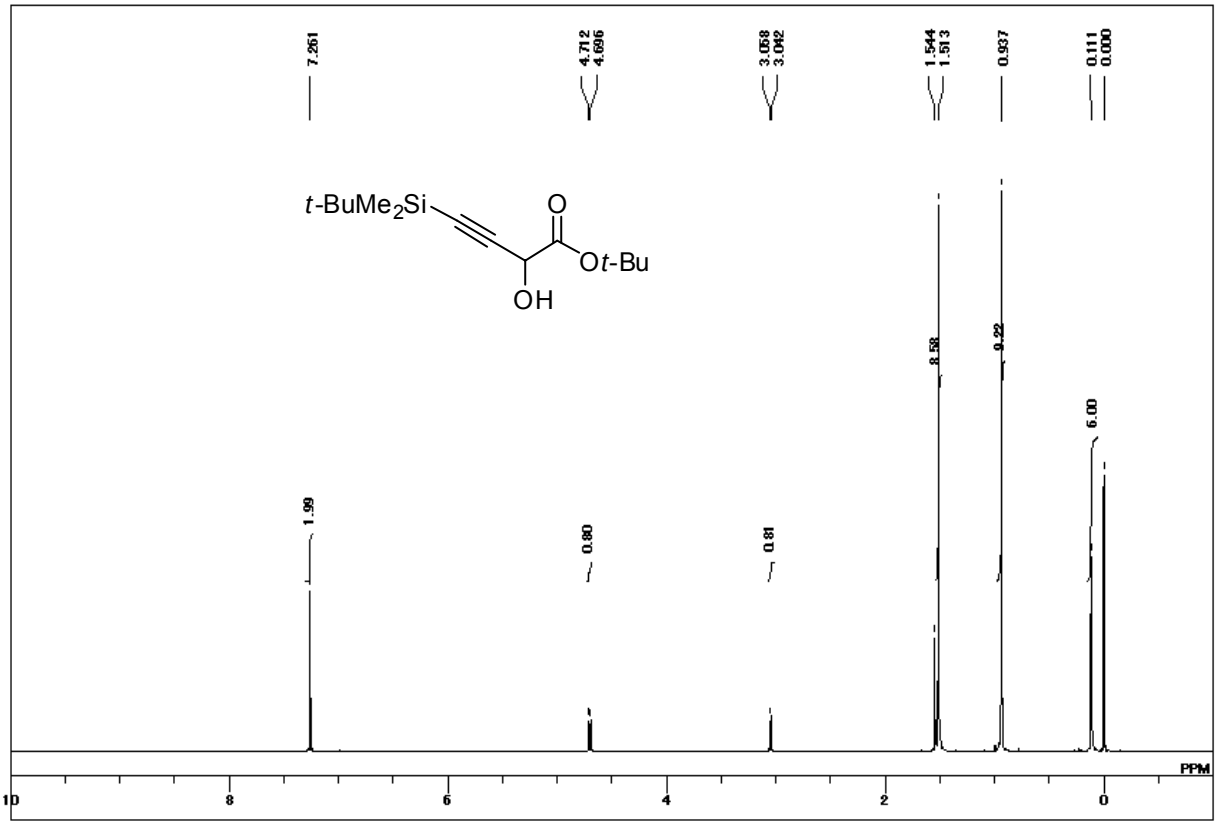
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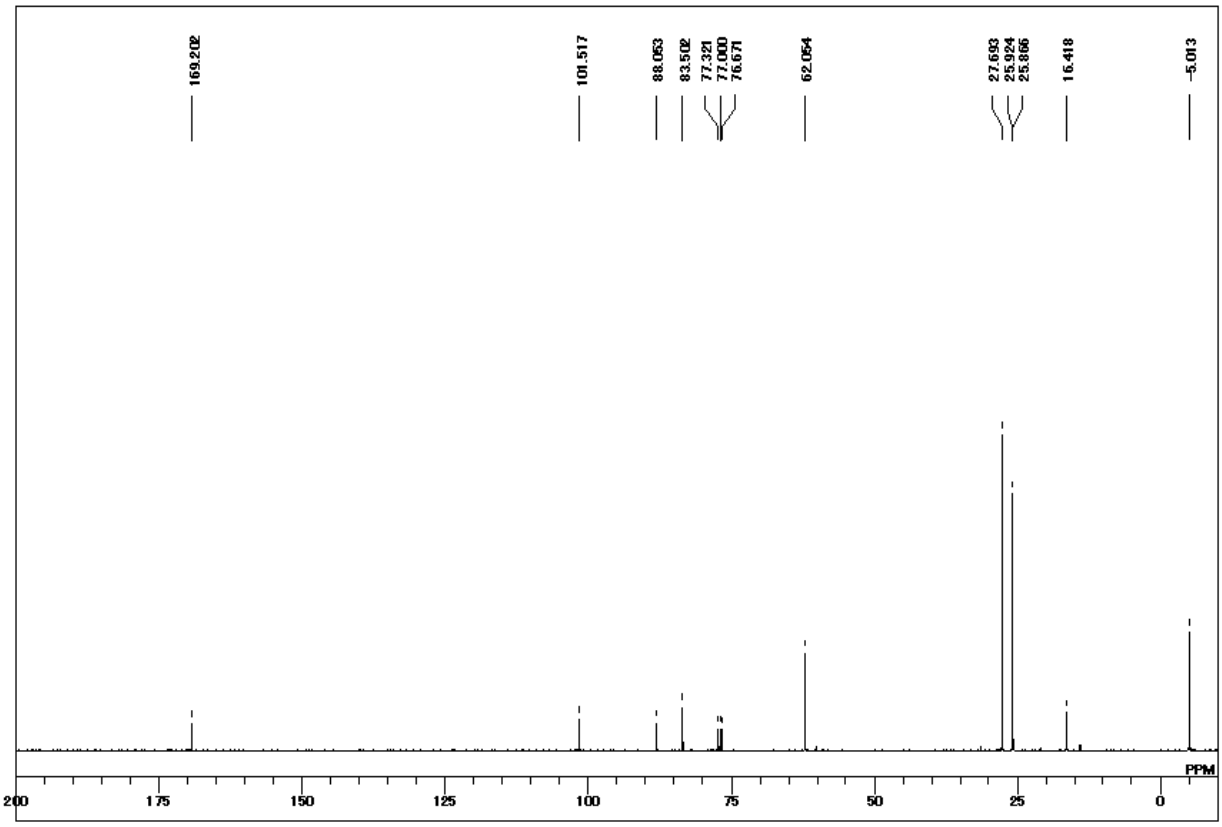
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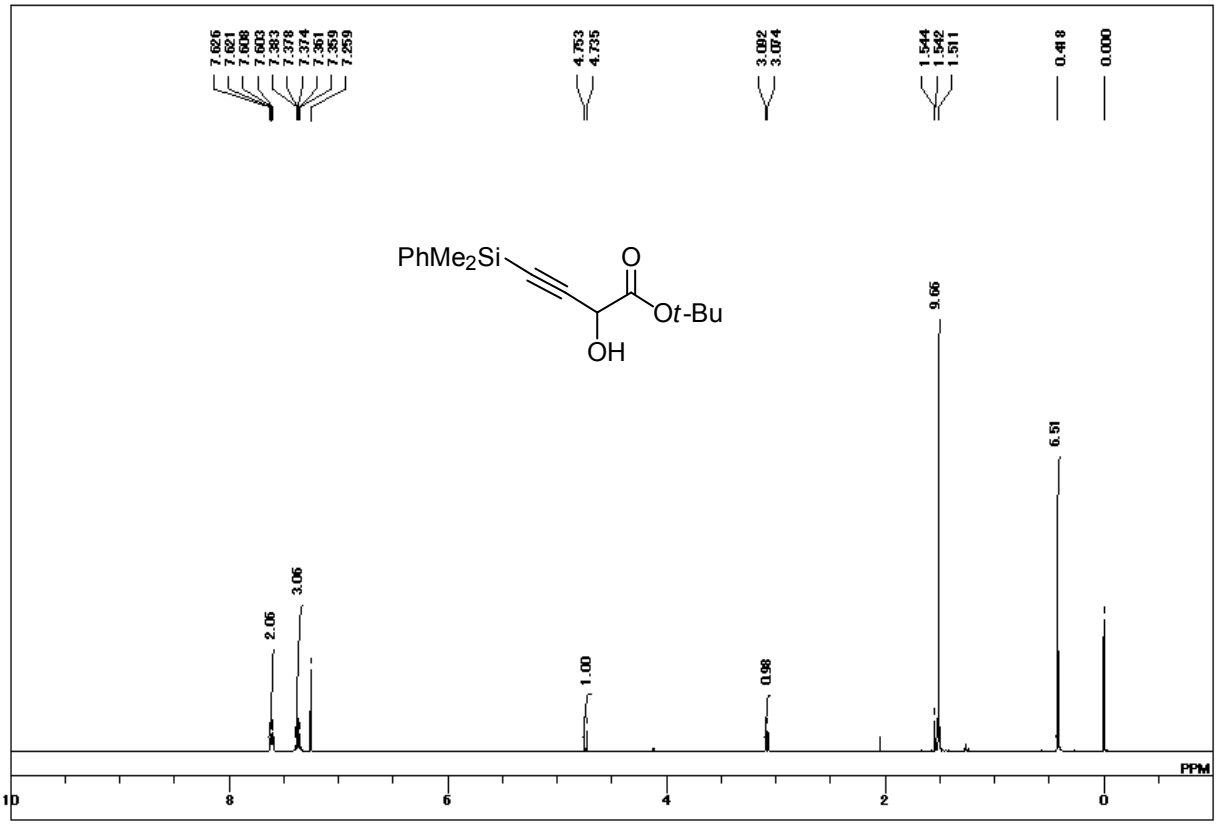
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0.000
PhMe2Si
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Ot-Bu
OH
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3.06
2.06
1.00
0.98
PPM
10
8
6
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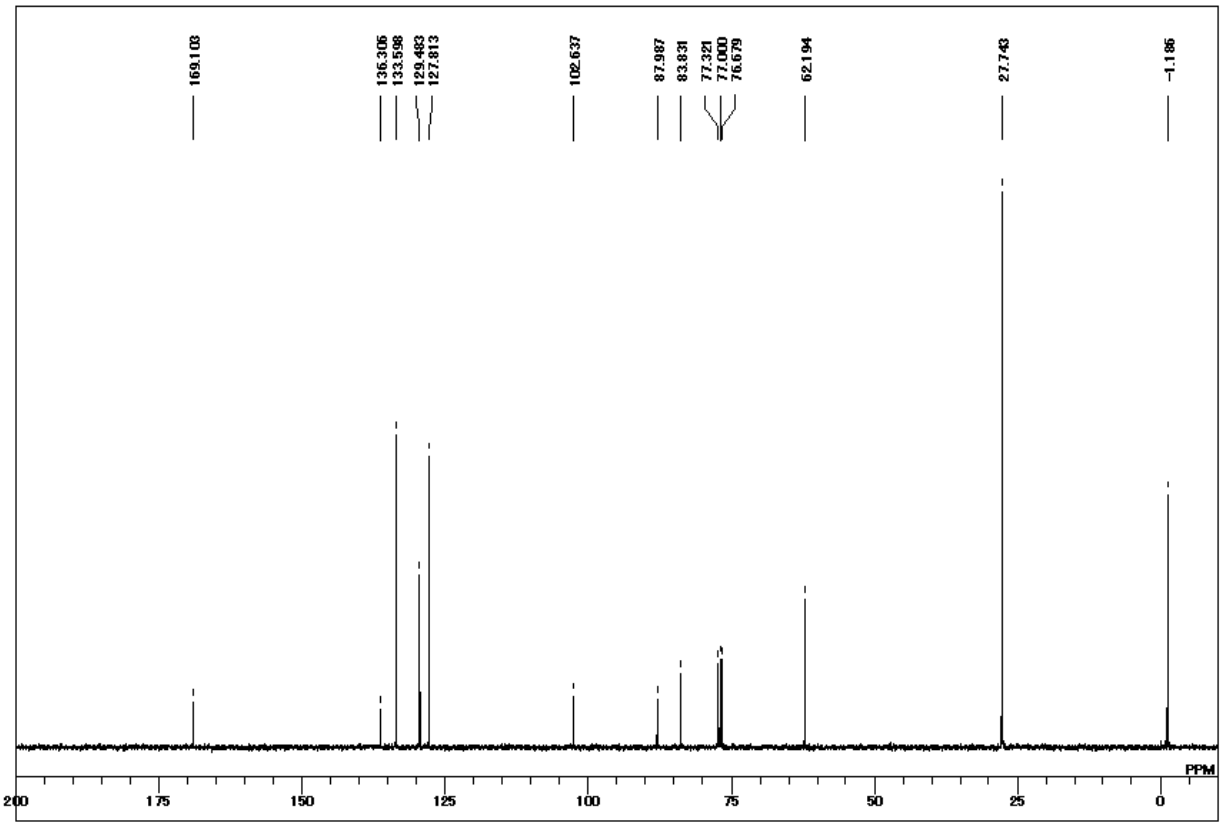
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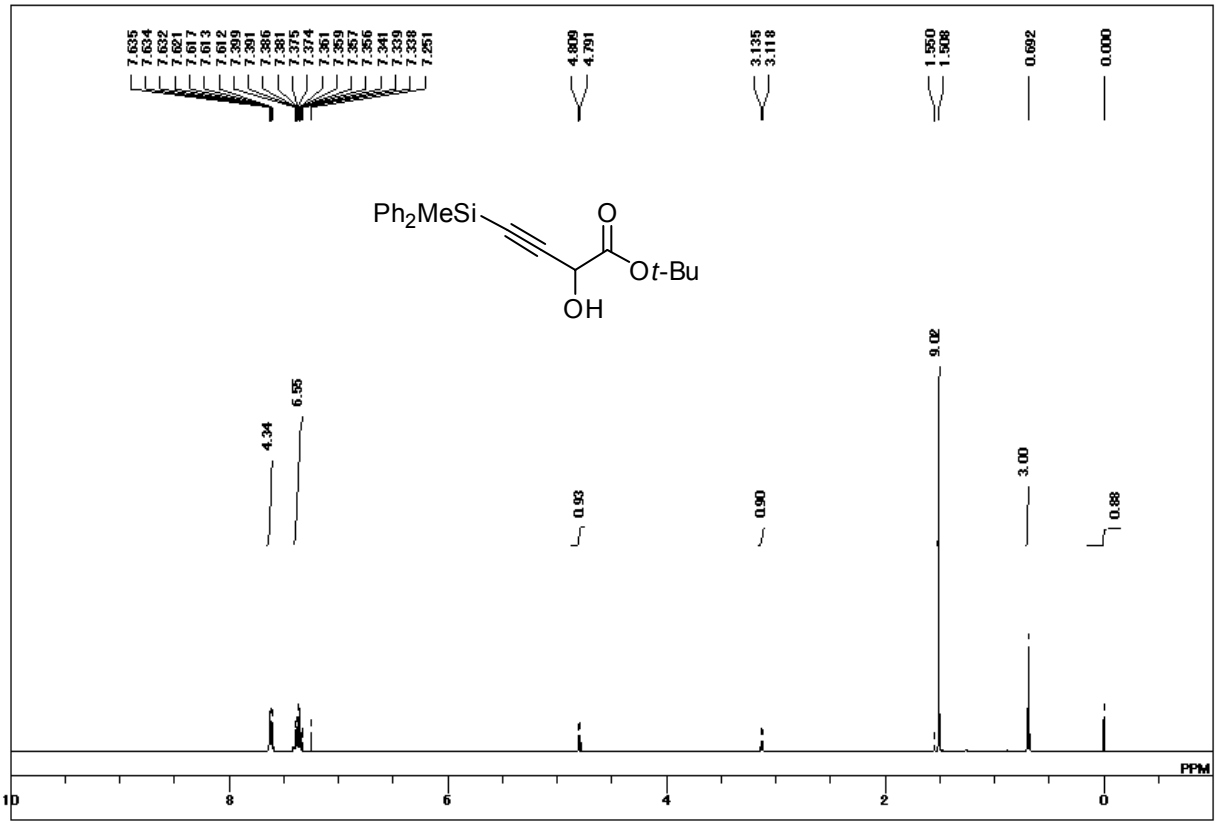
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Ot-Bu
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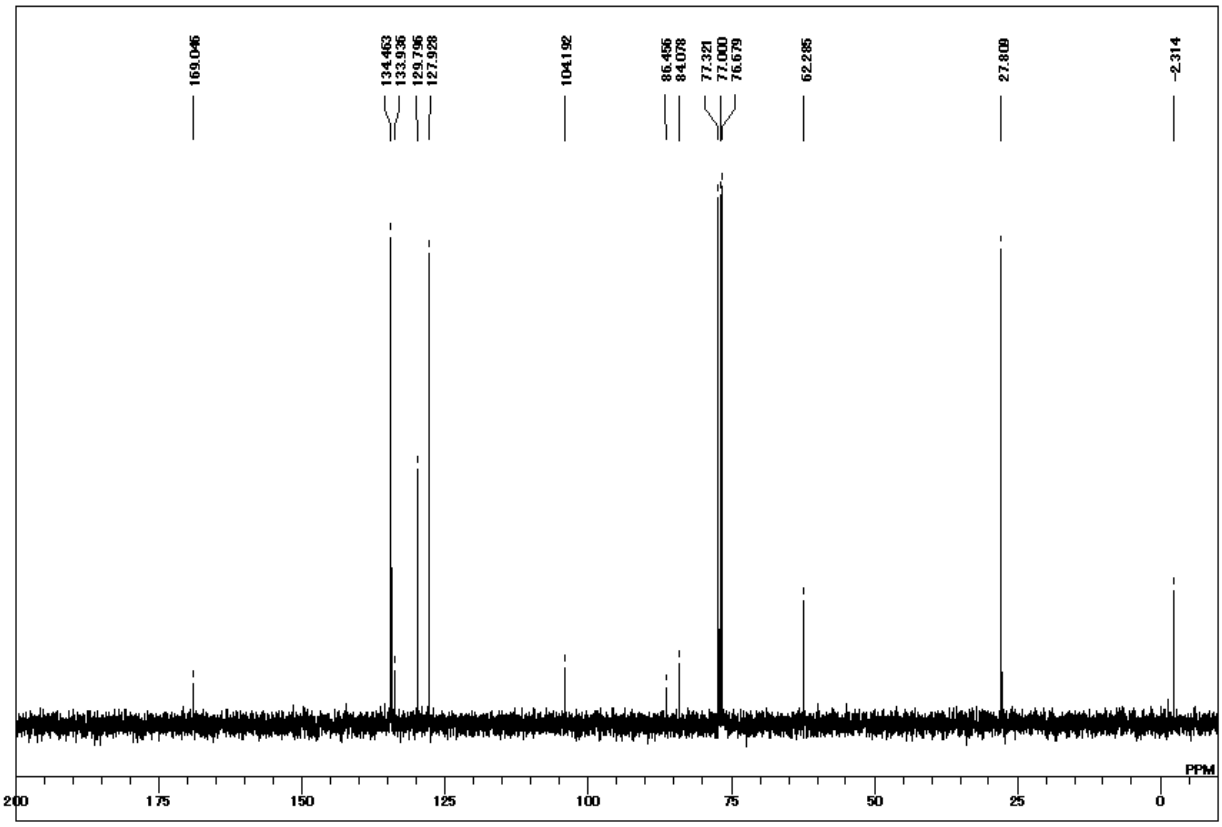
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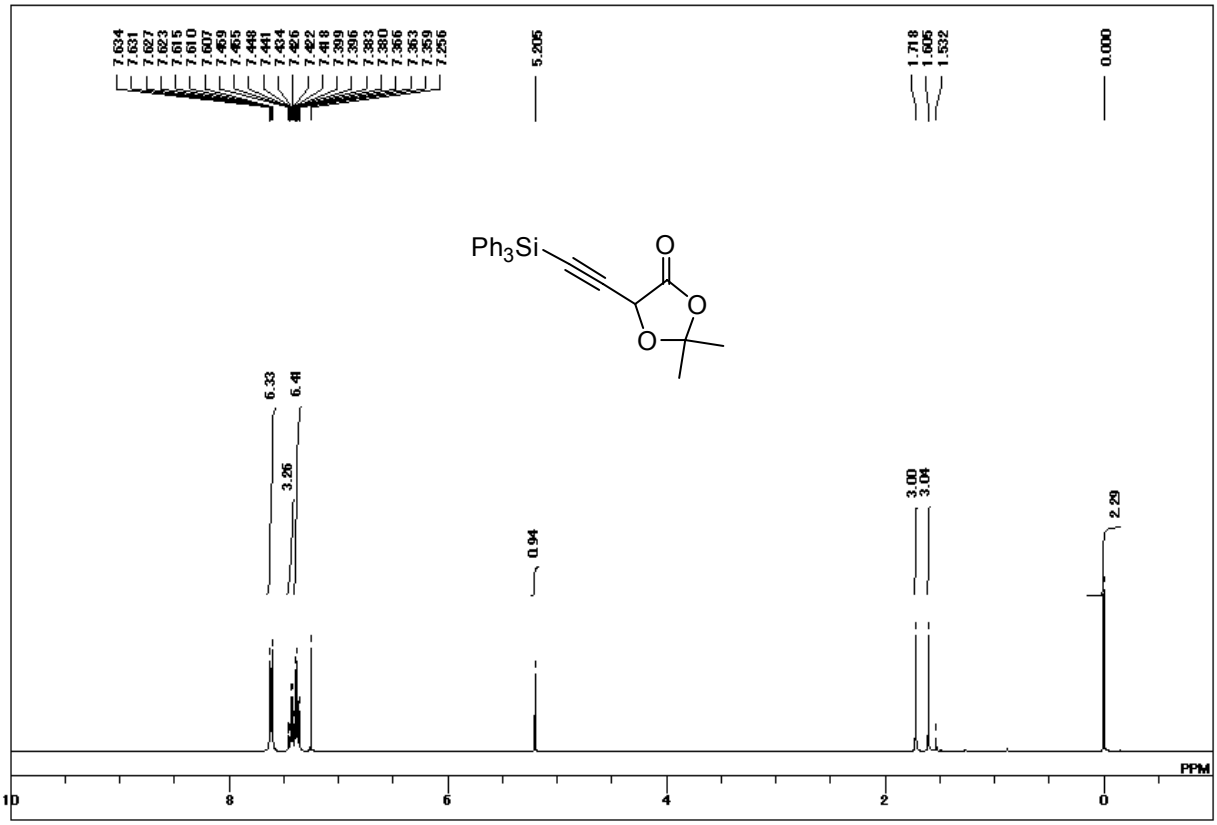
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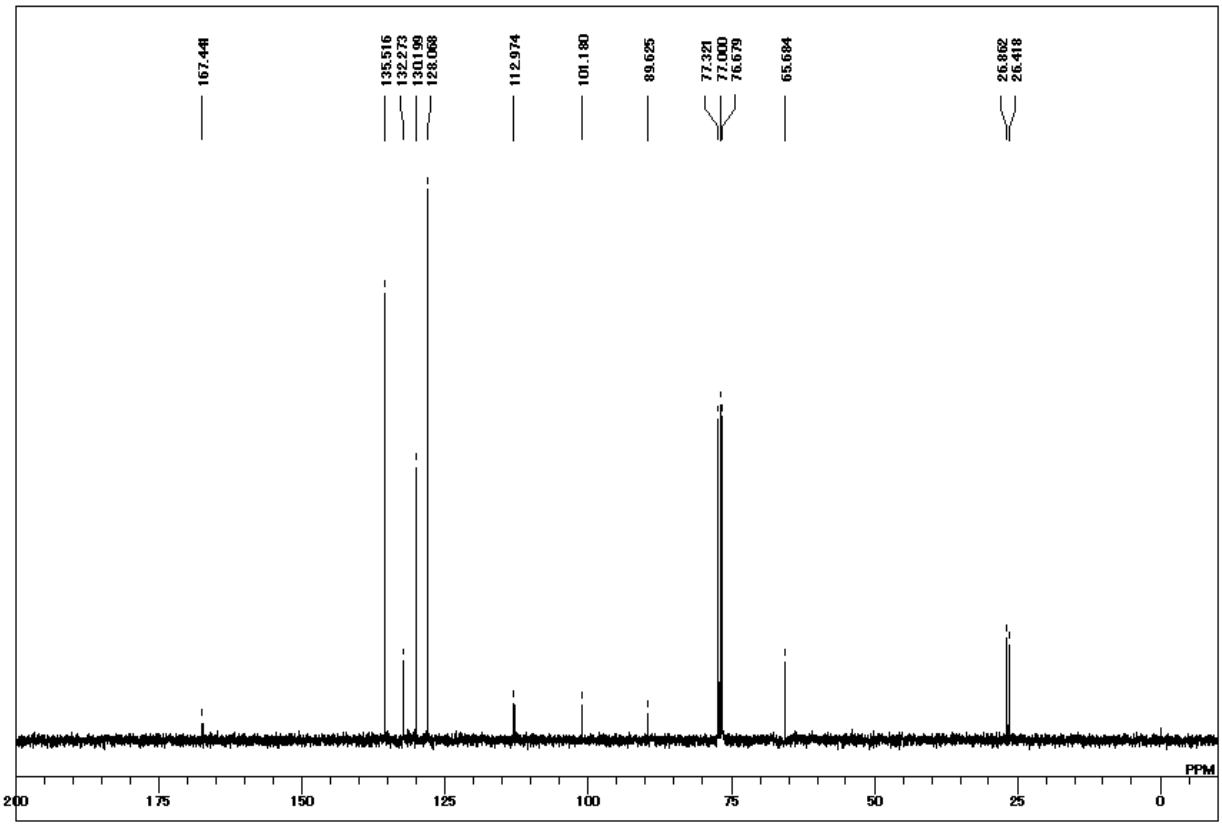
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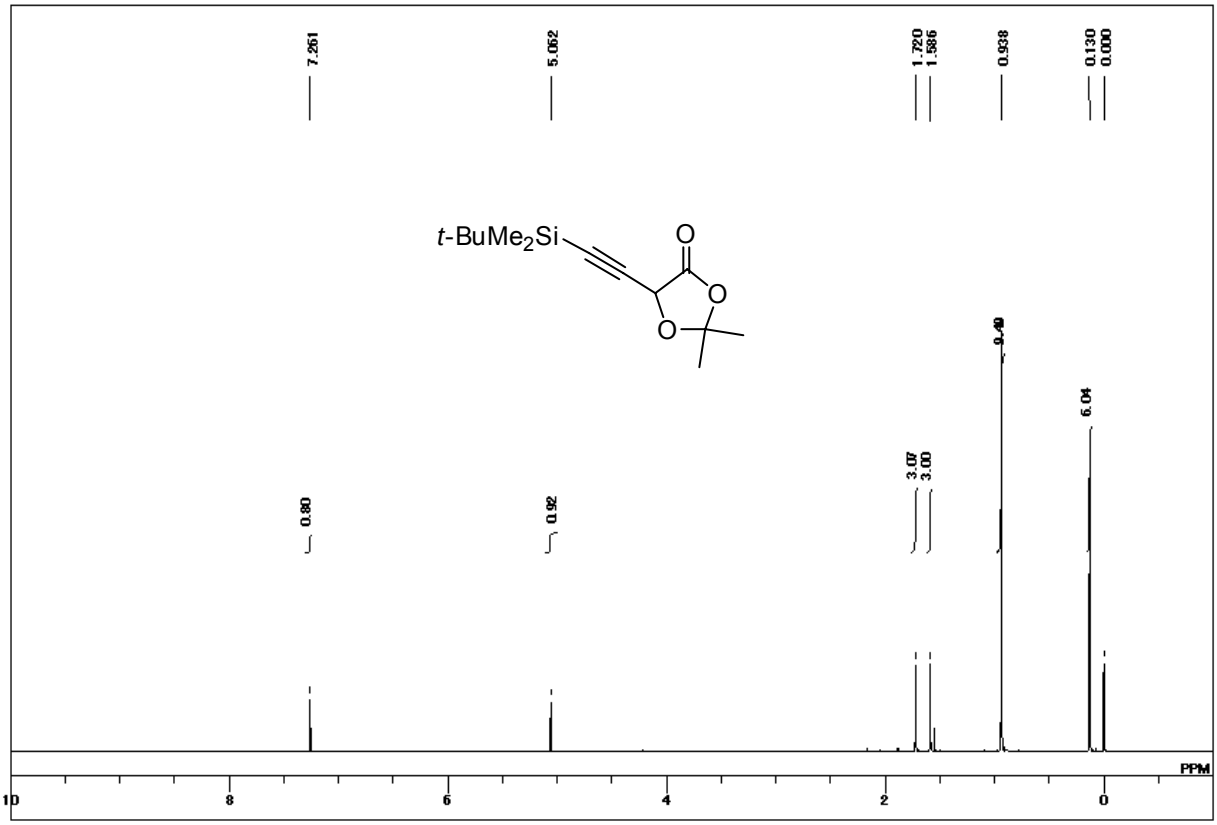
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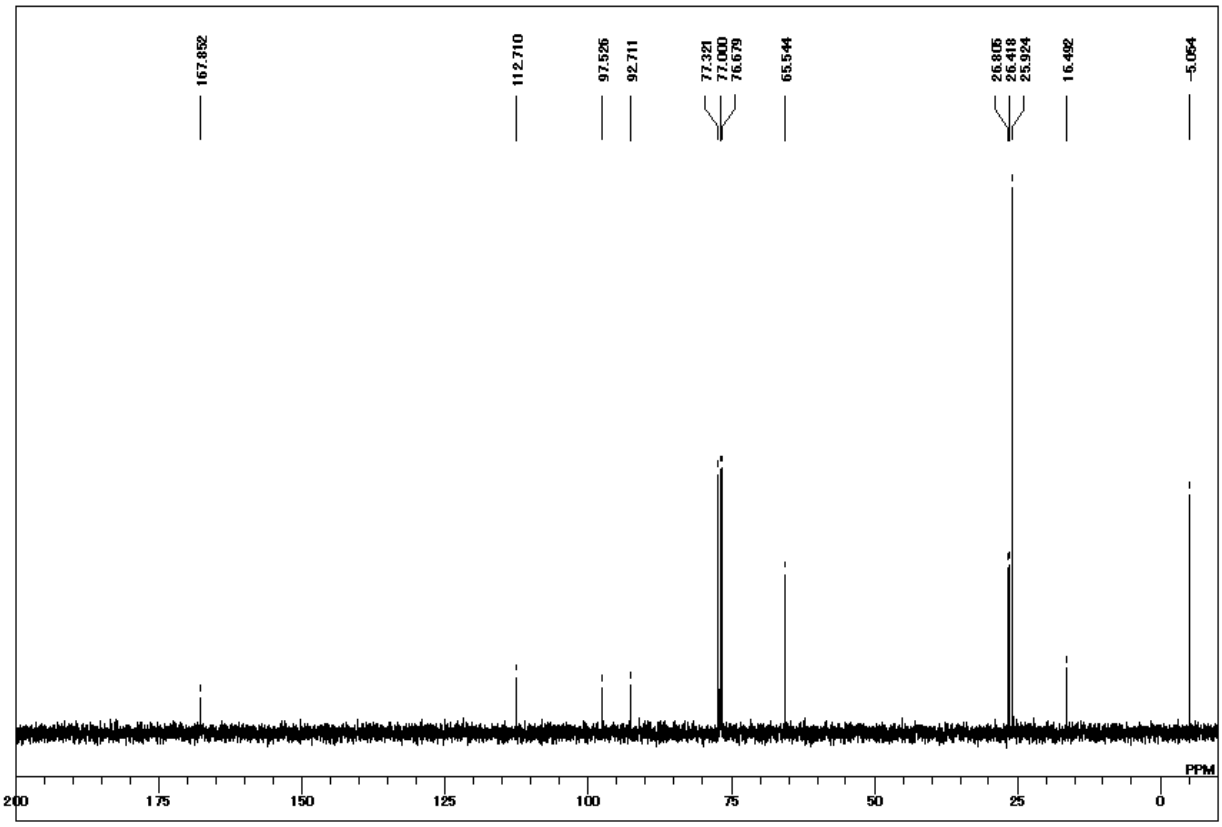
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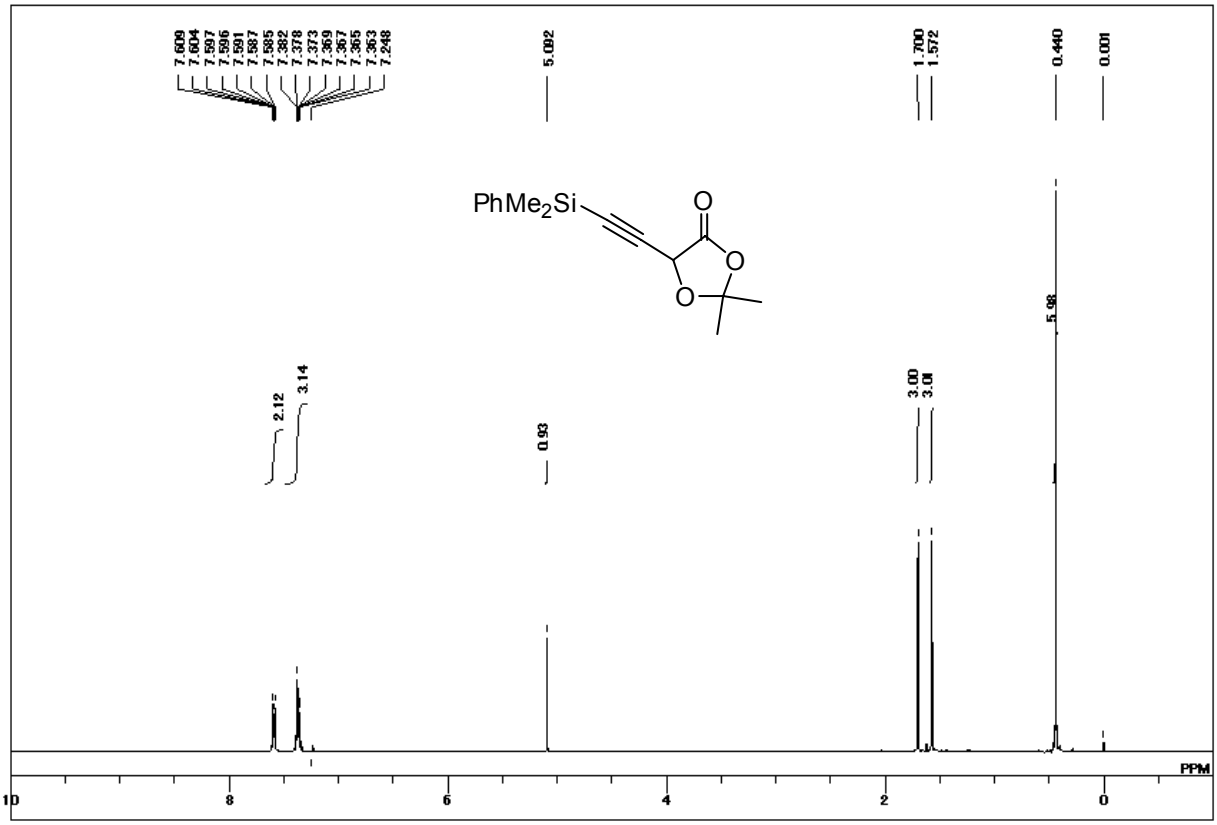
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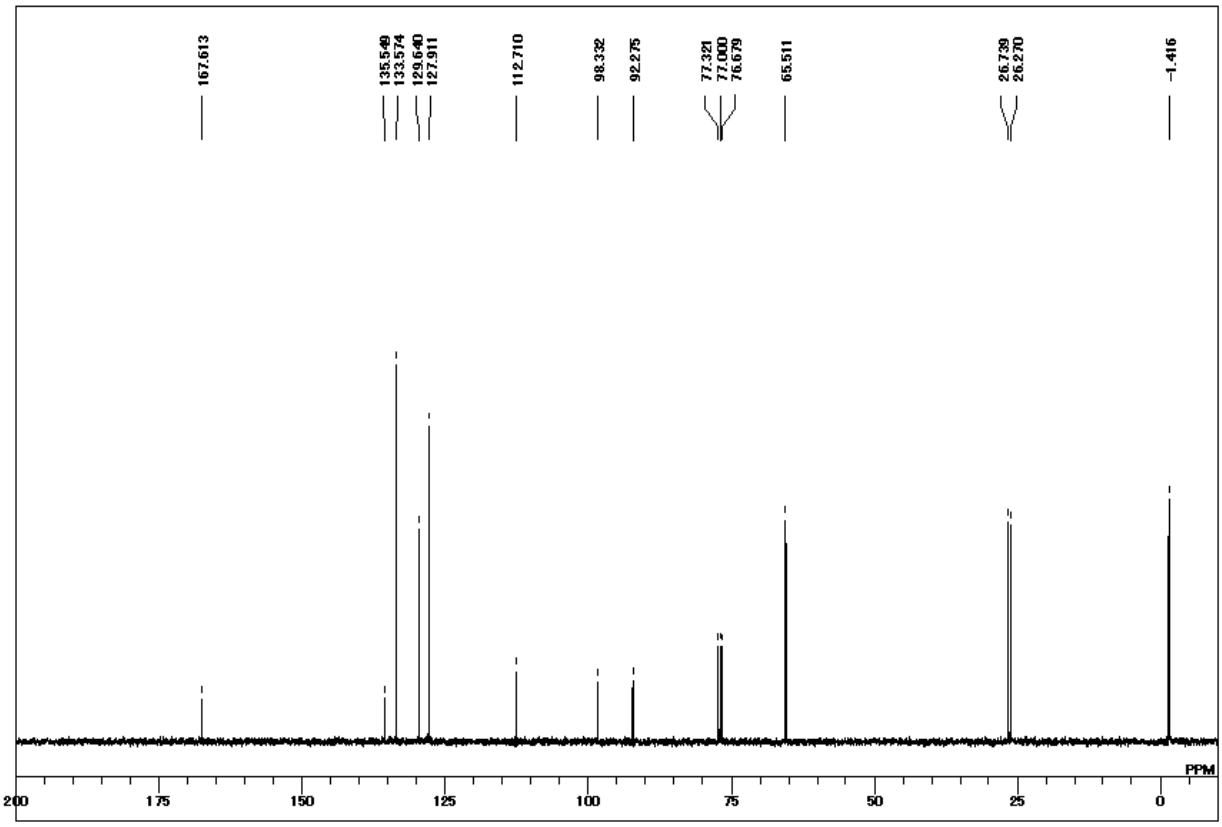
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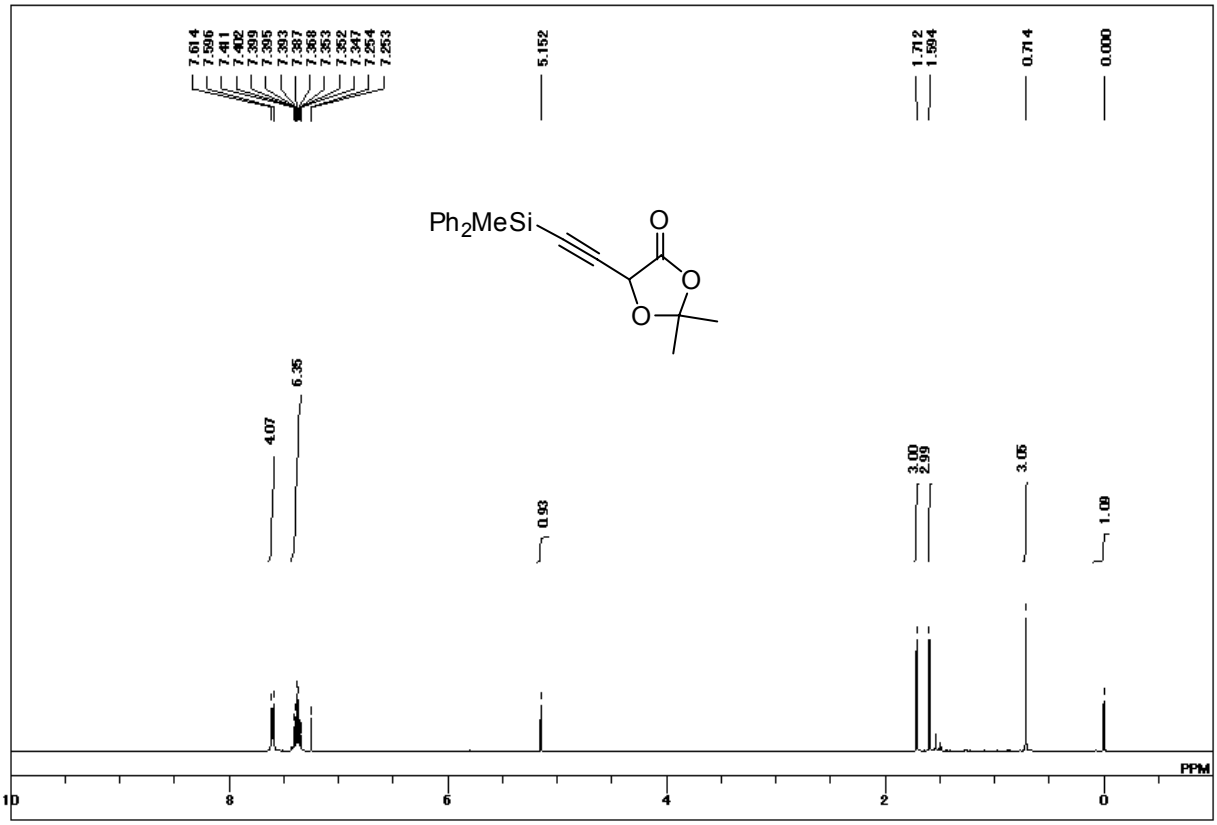
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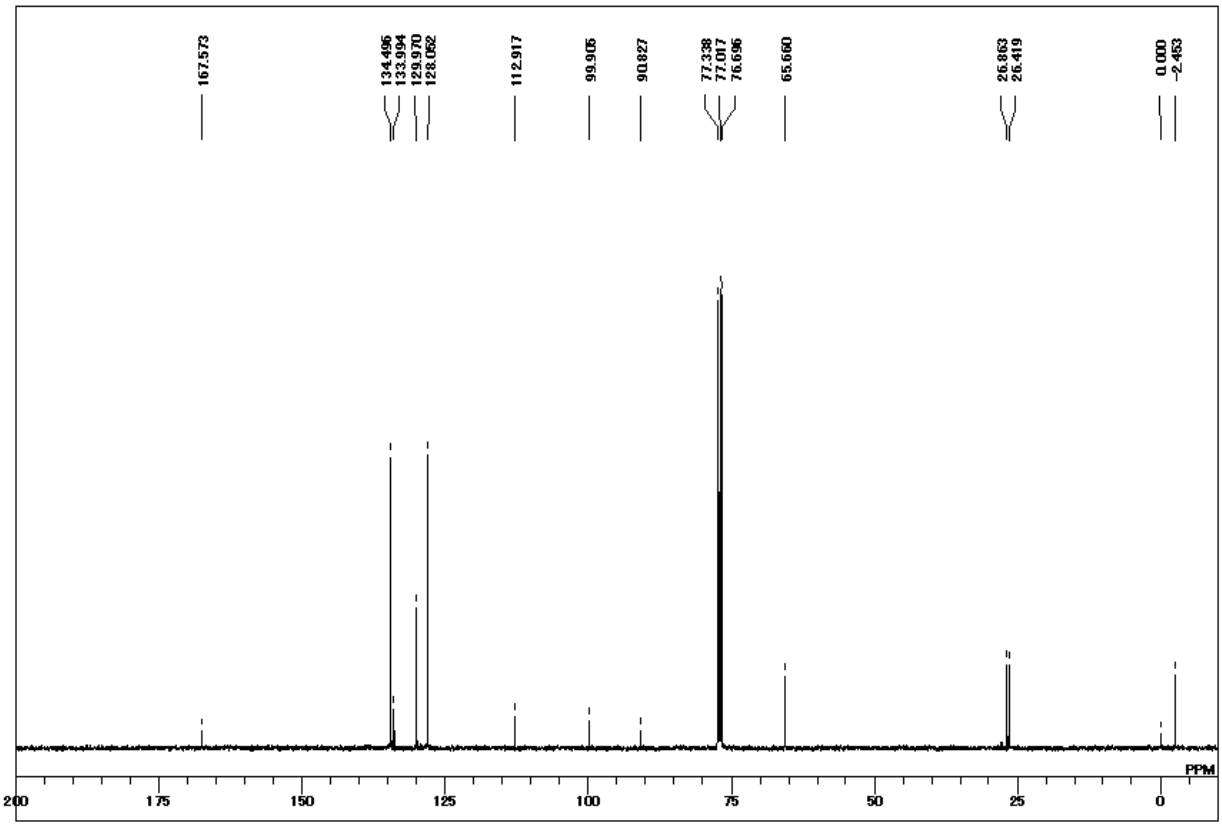
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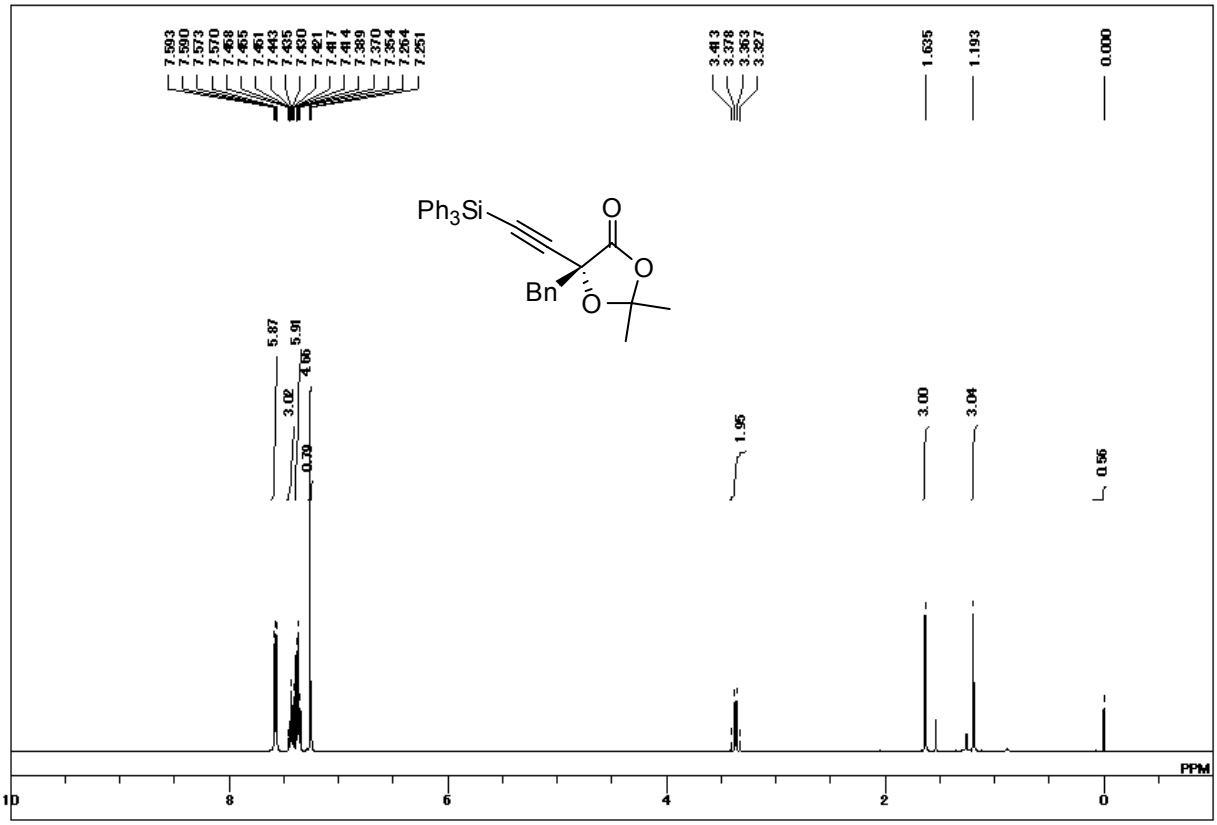
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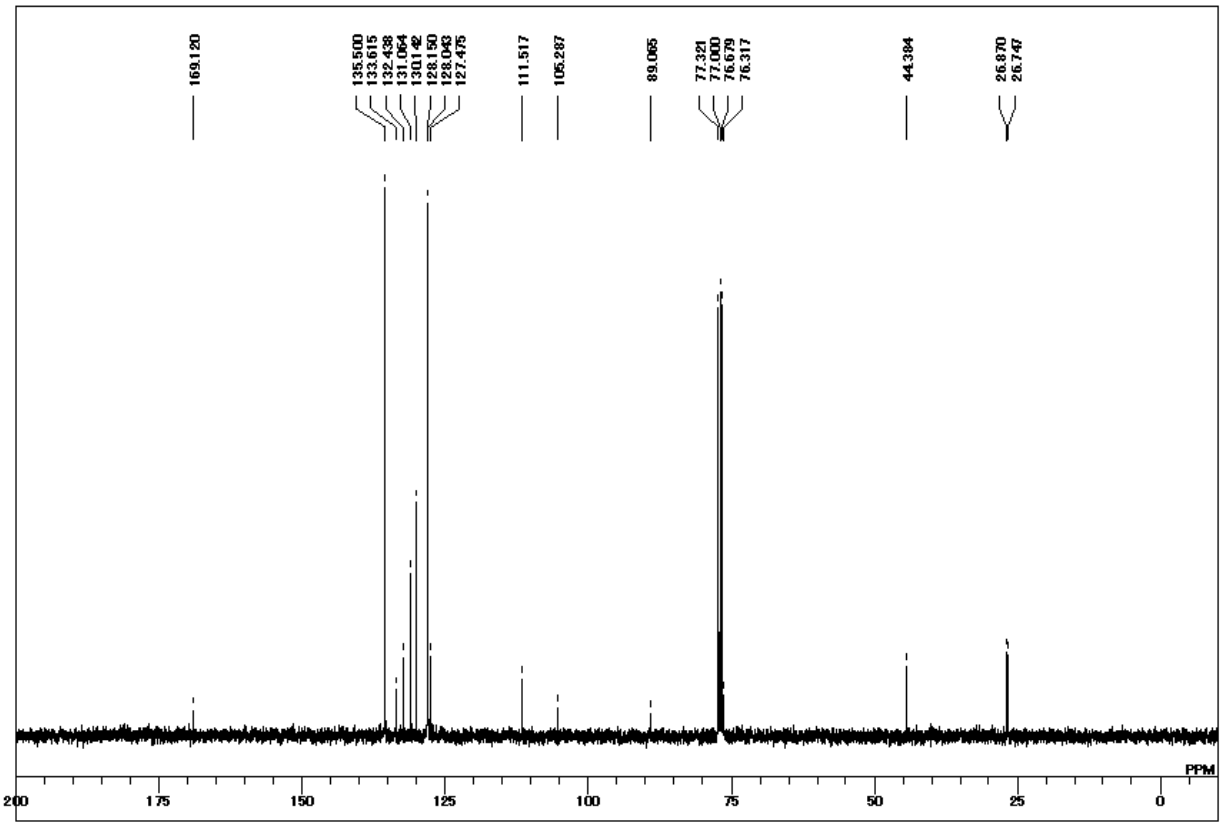
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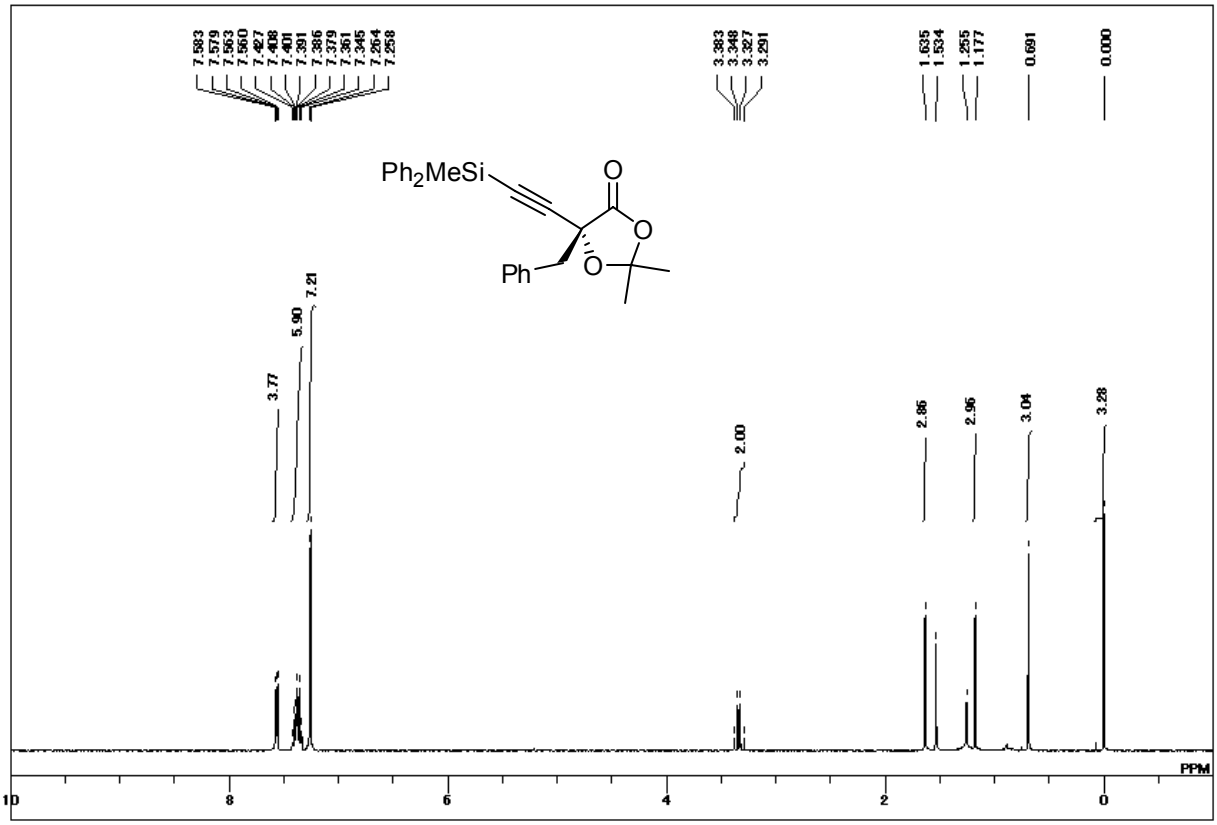
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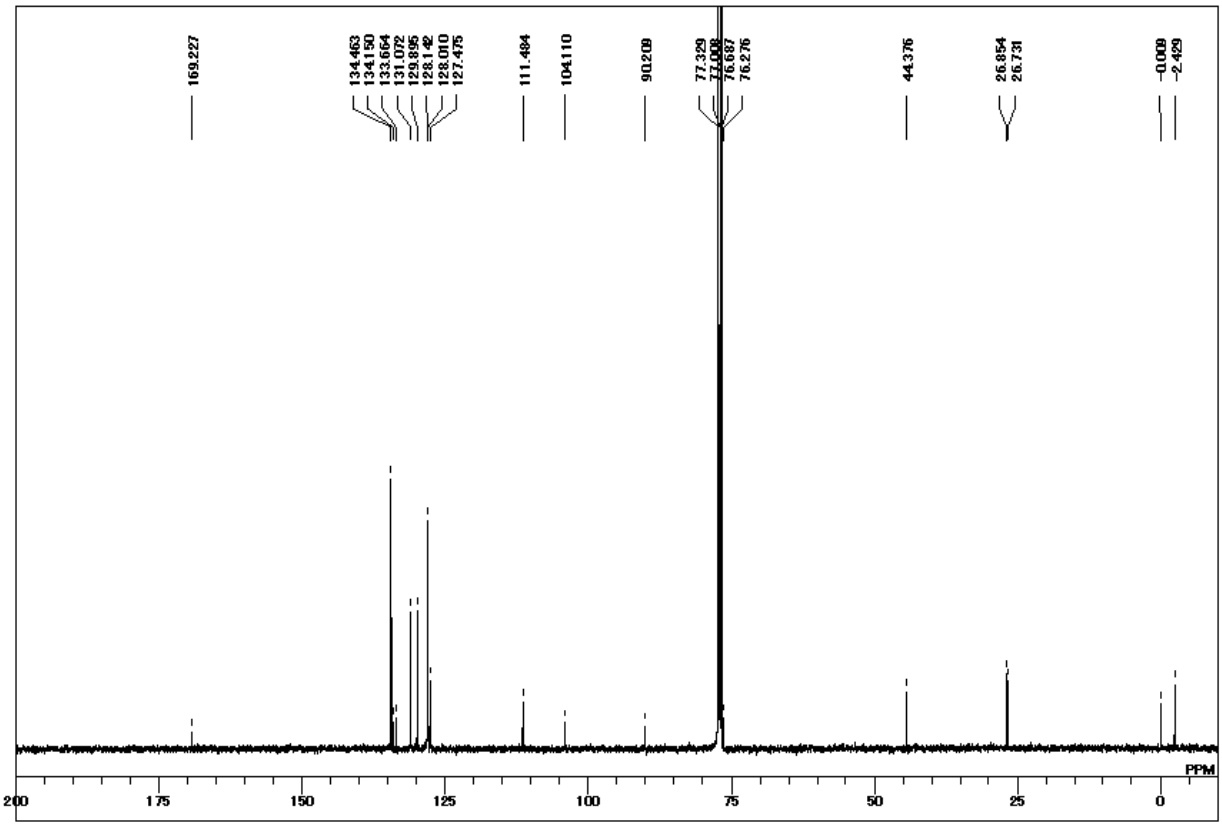
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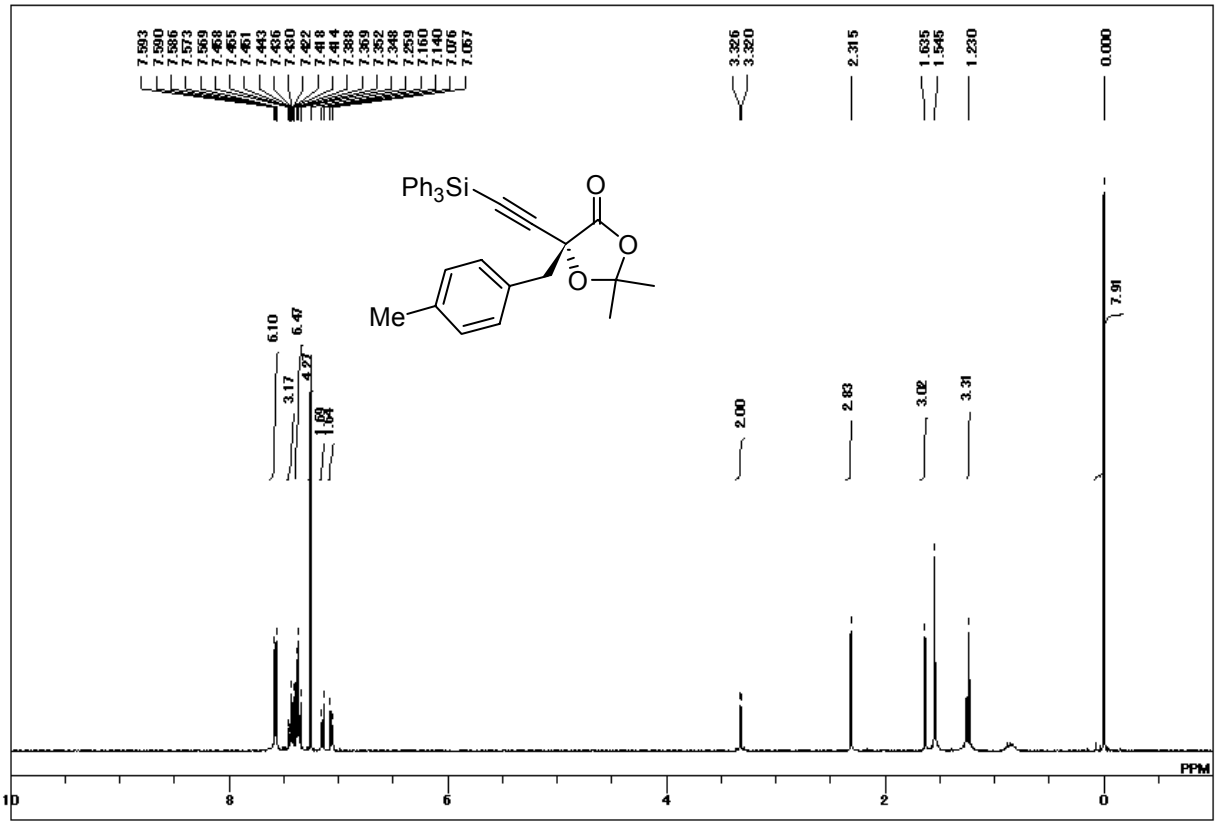
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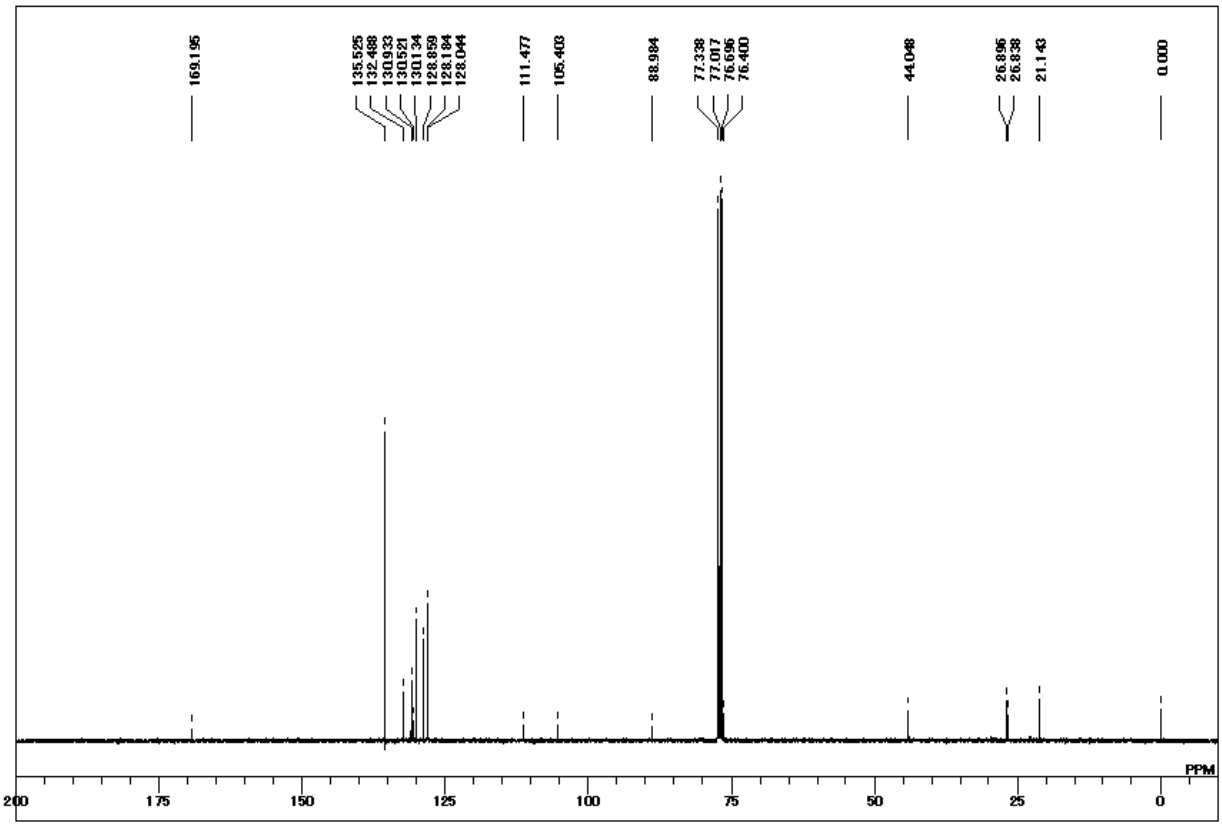
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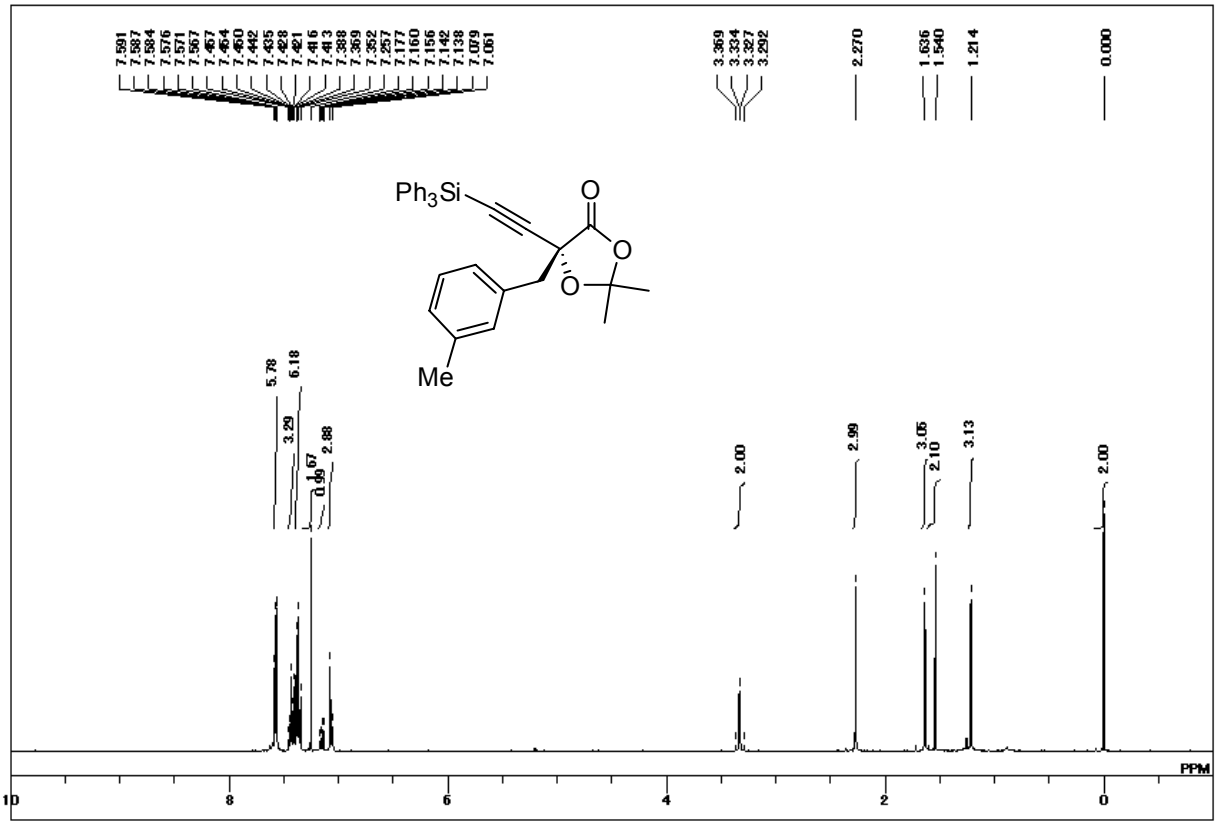
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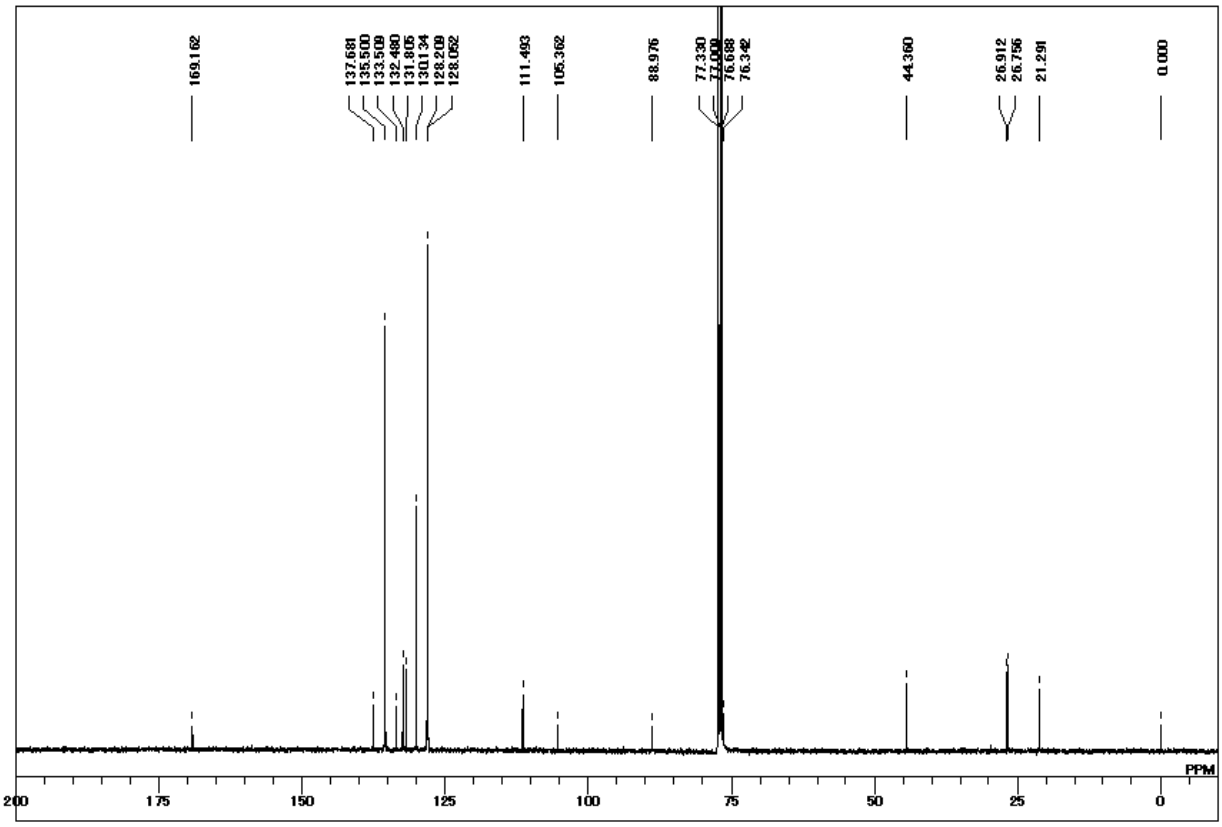
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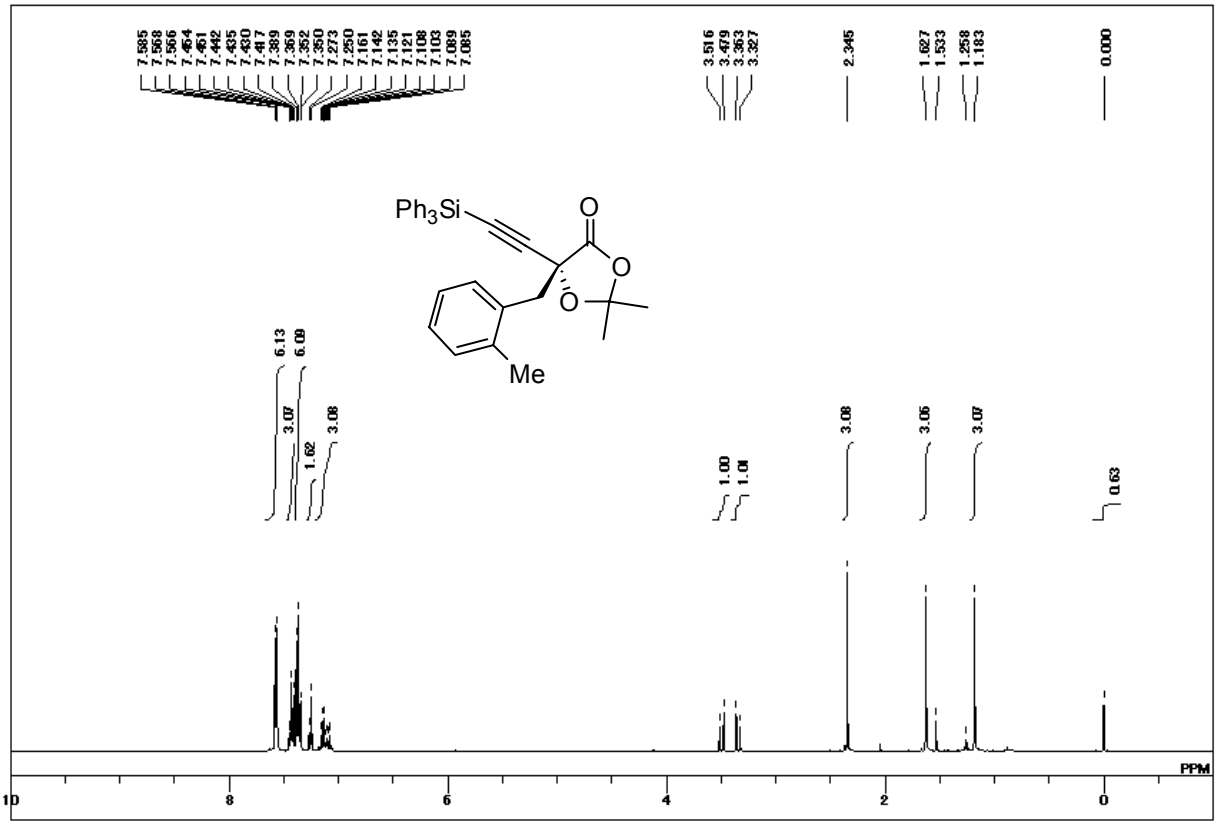
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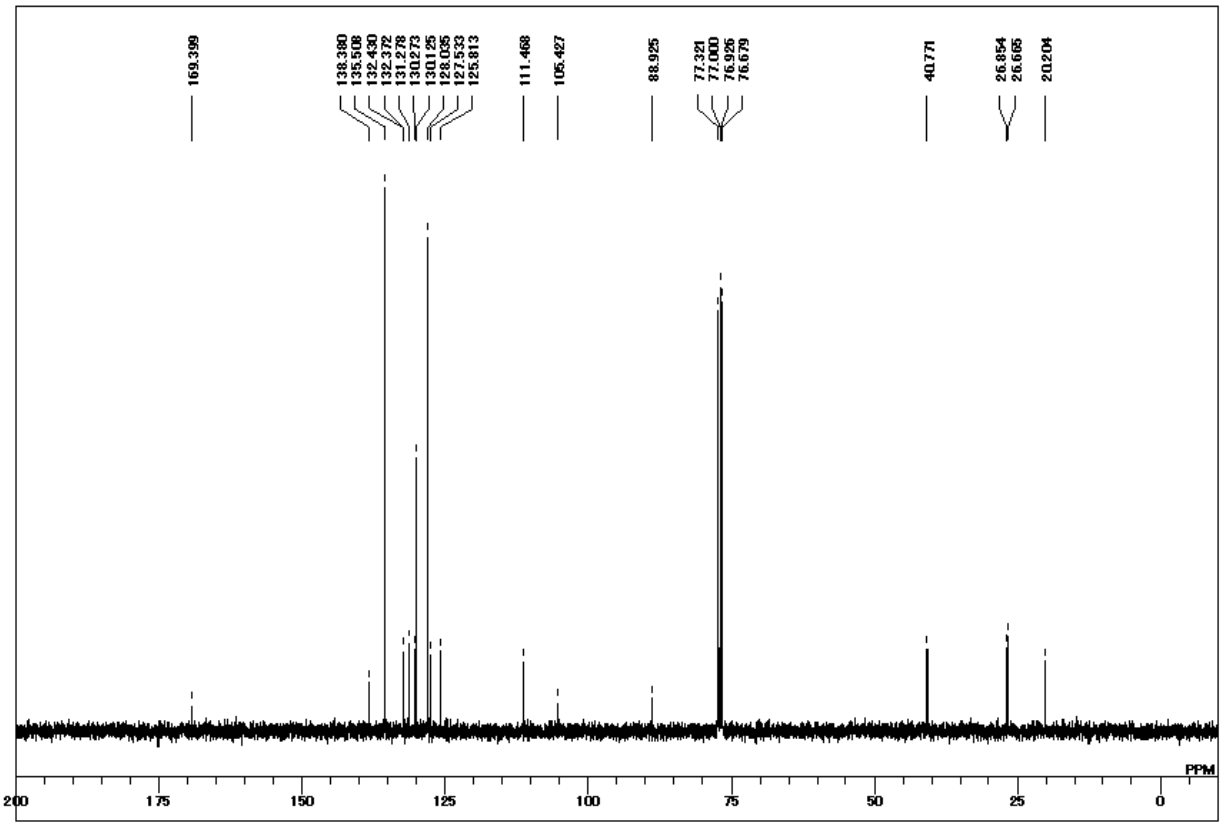
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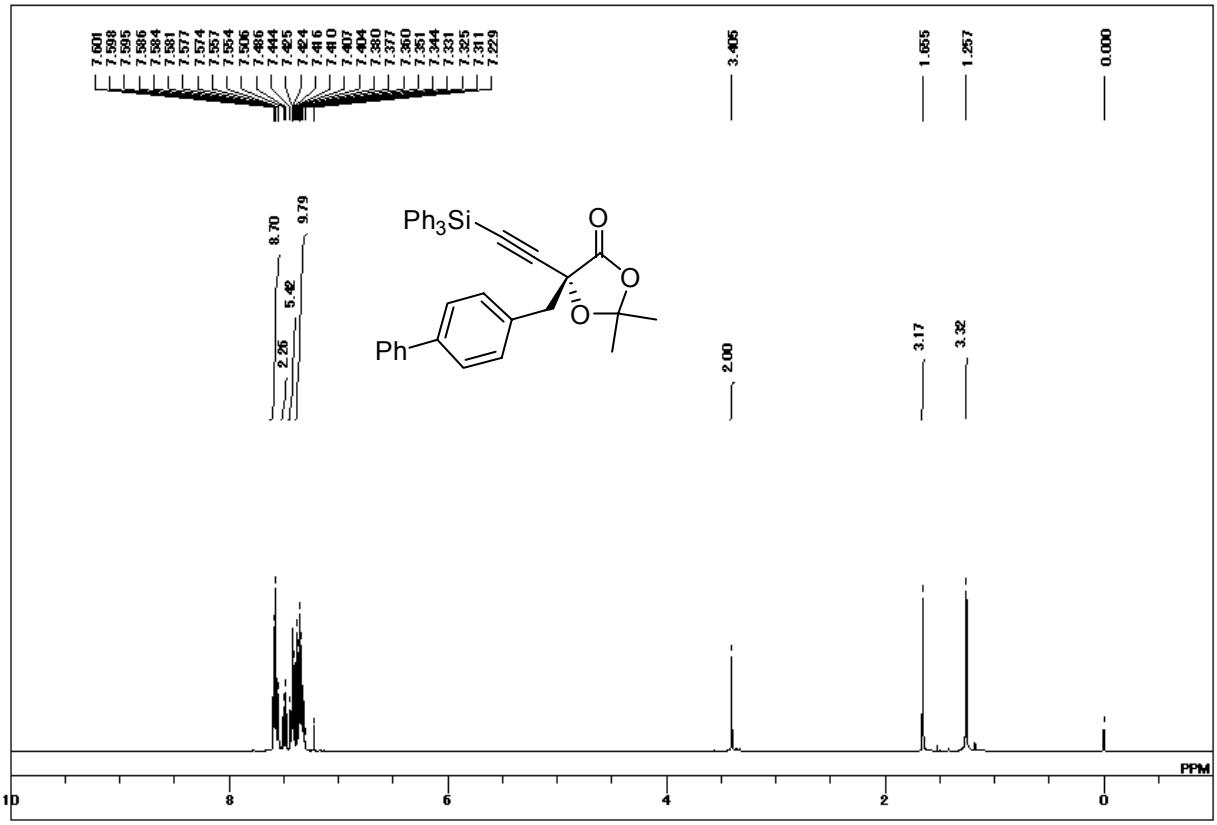
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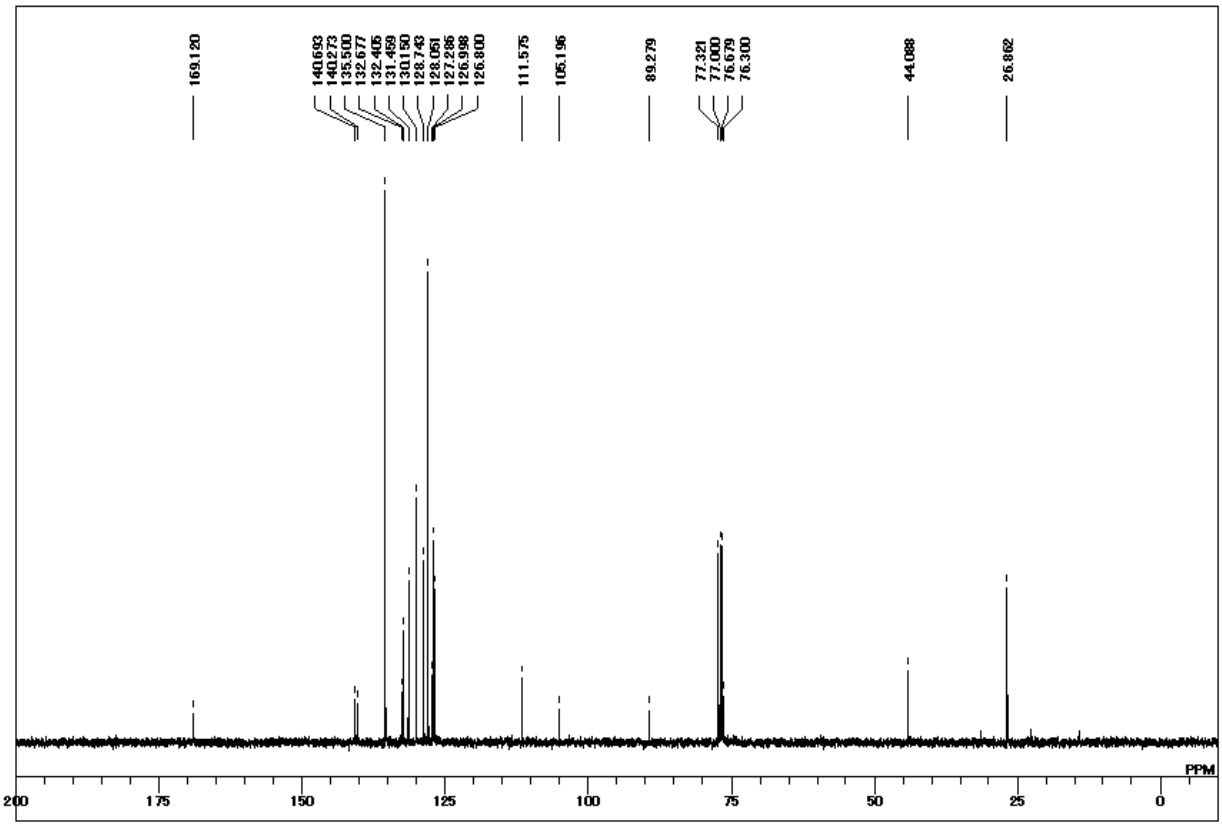
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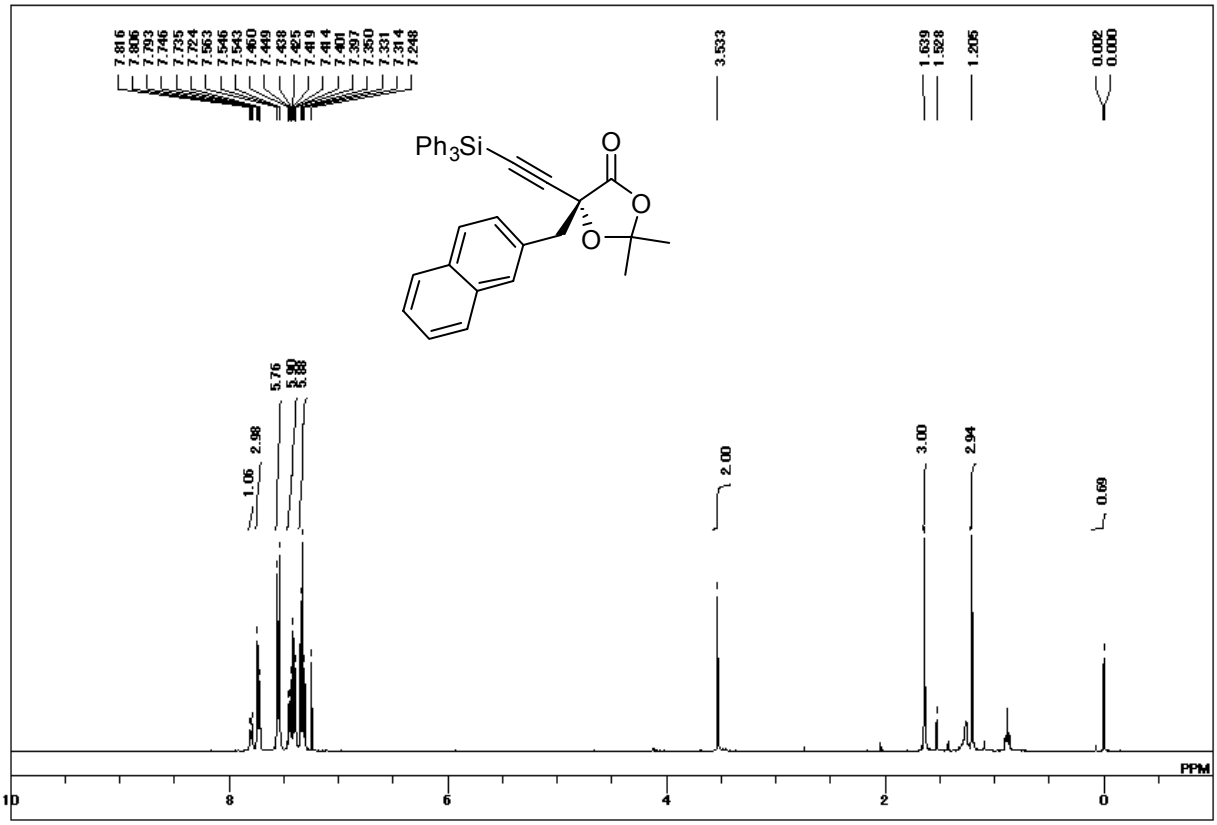
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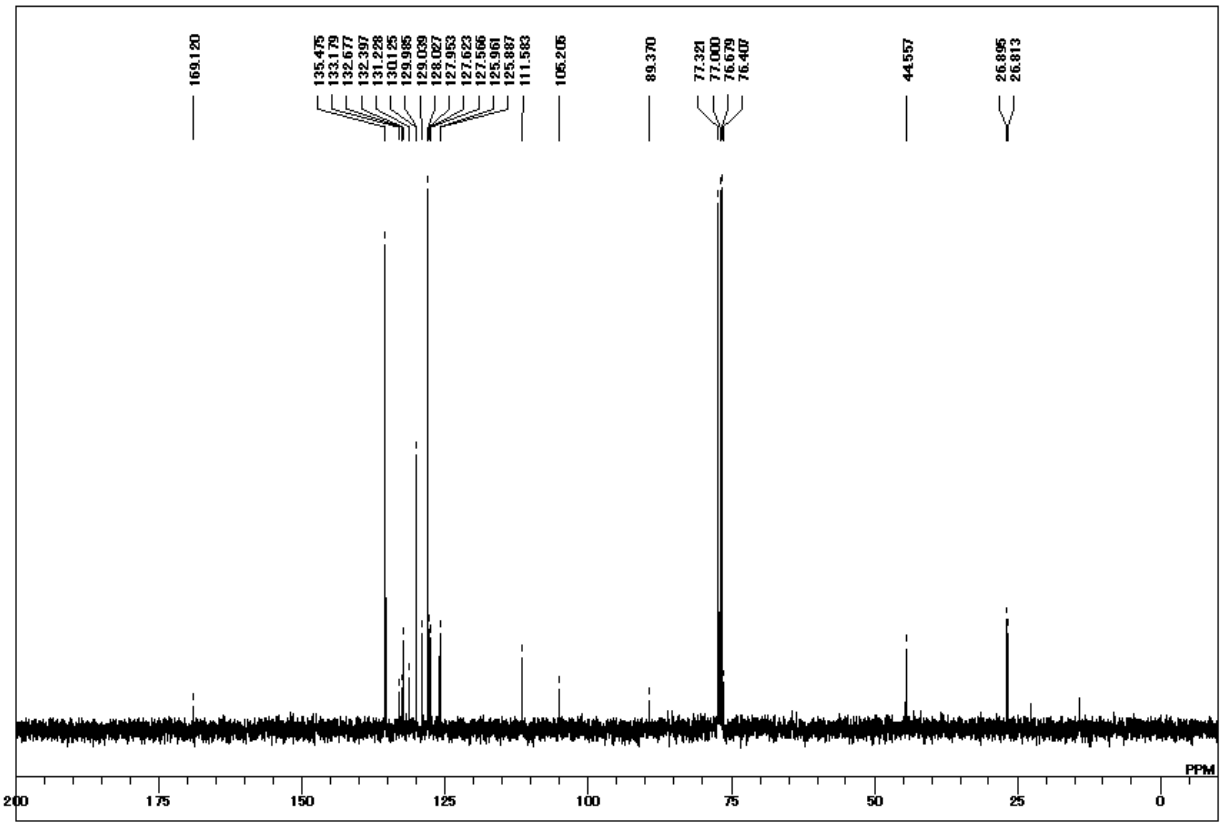
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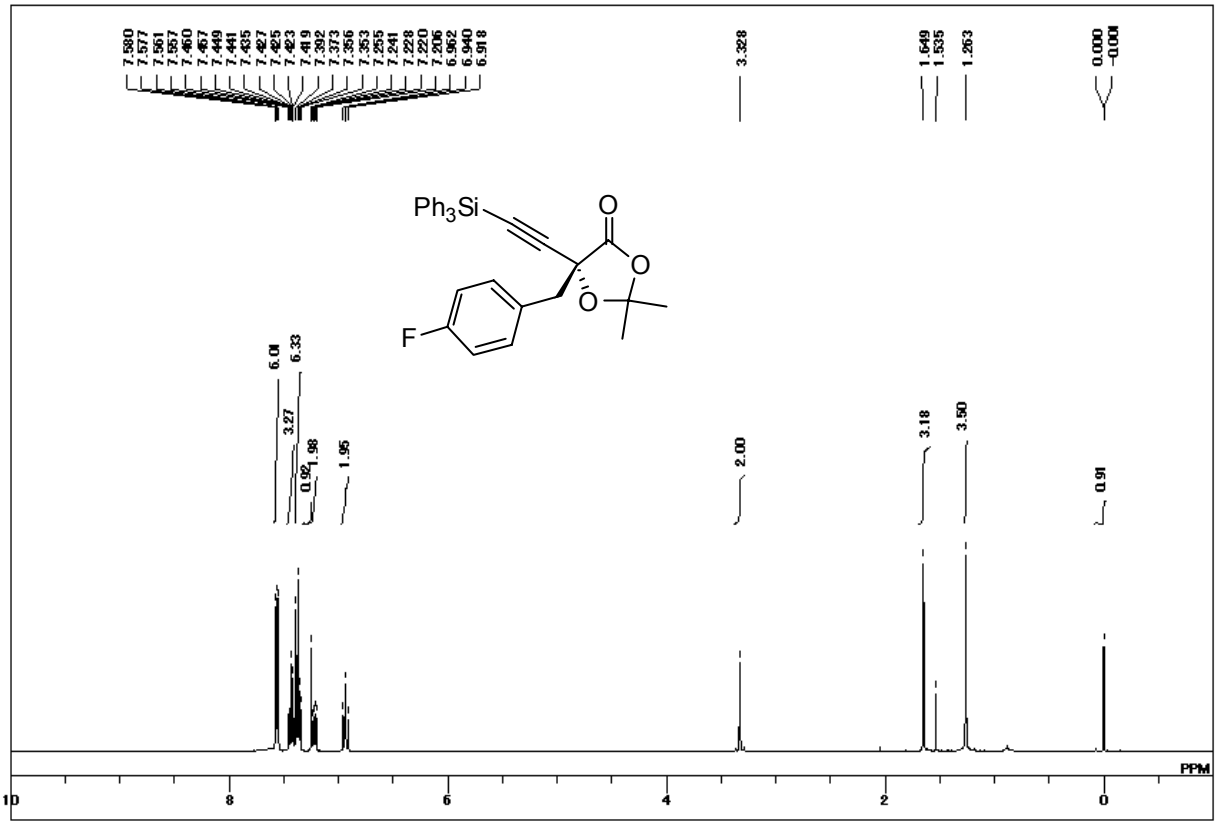
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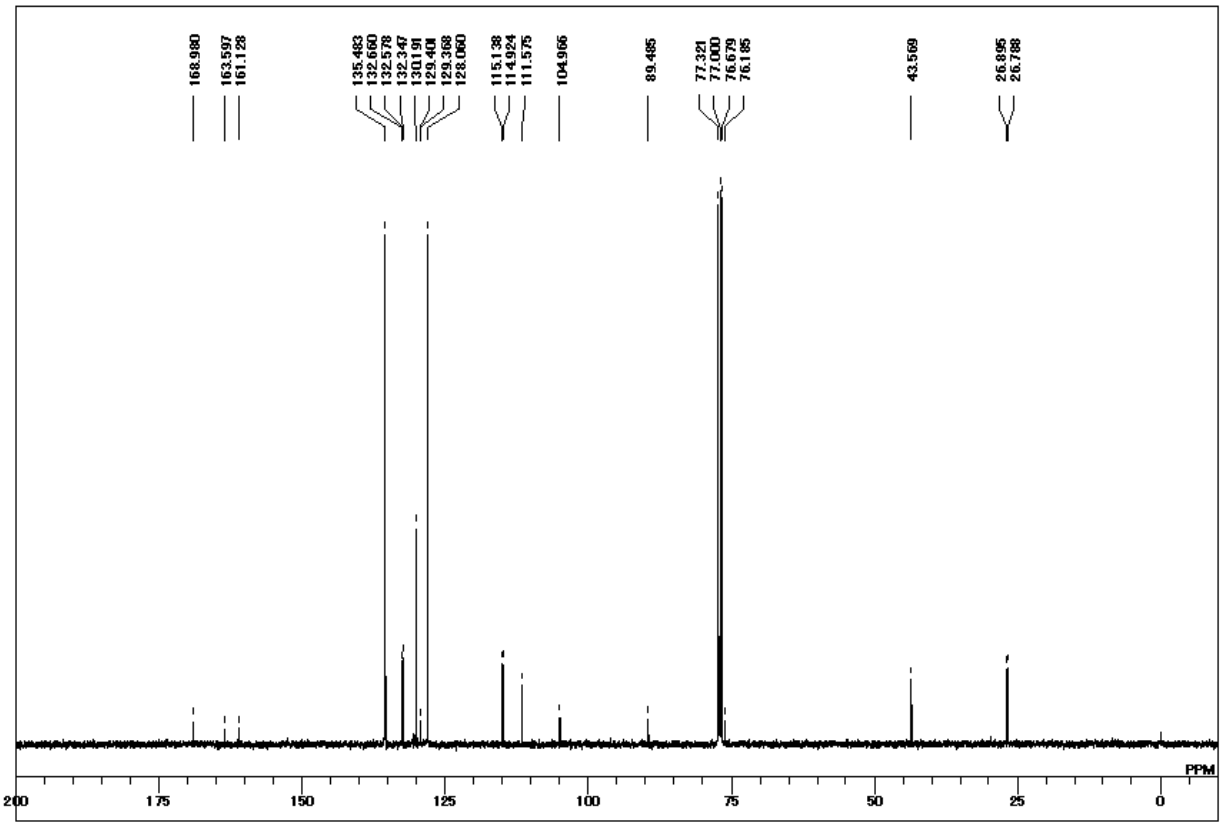
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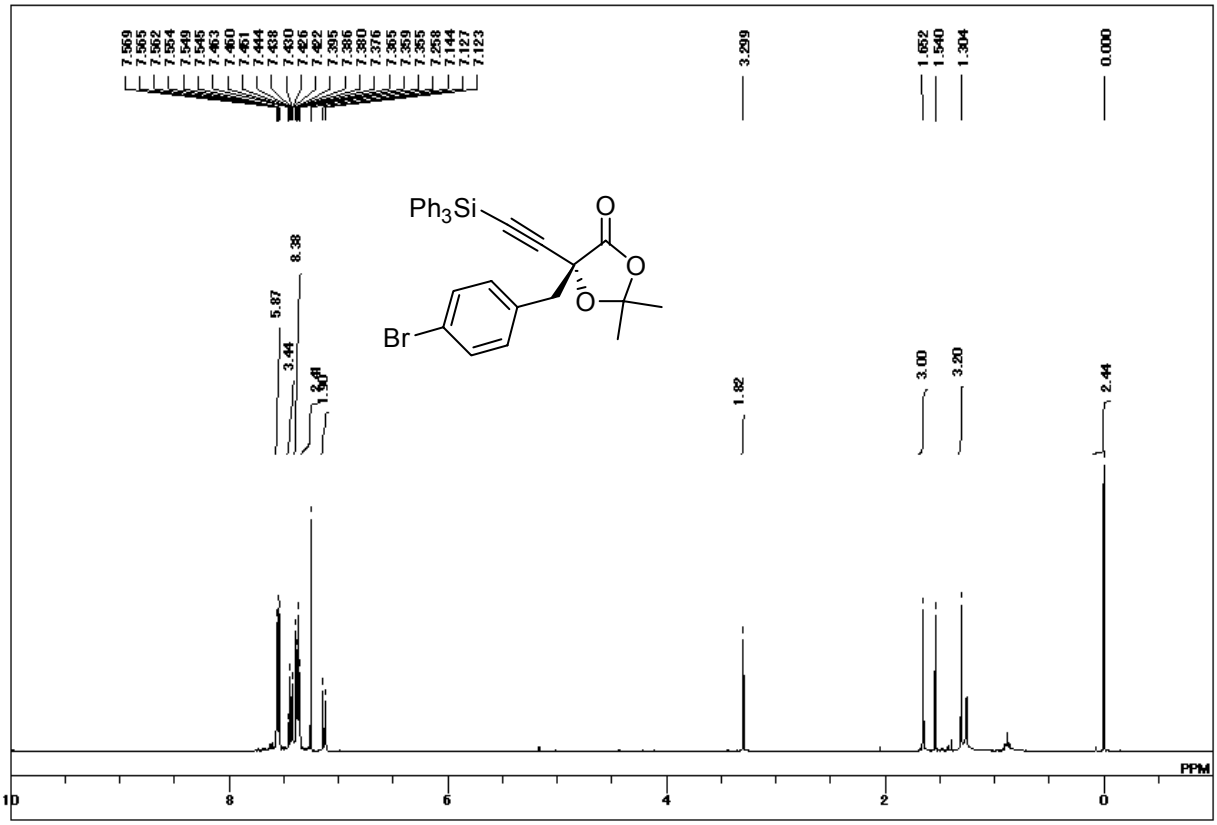
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7.426
7.422
7.395
7.386
7.380
7.376
7.365
7.359
7.355
7.258
7.144
7.127
7.123
3.299
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1.540
1.304
0.000
Ph3Si
O
O
O
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PPM
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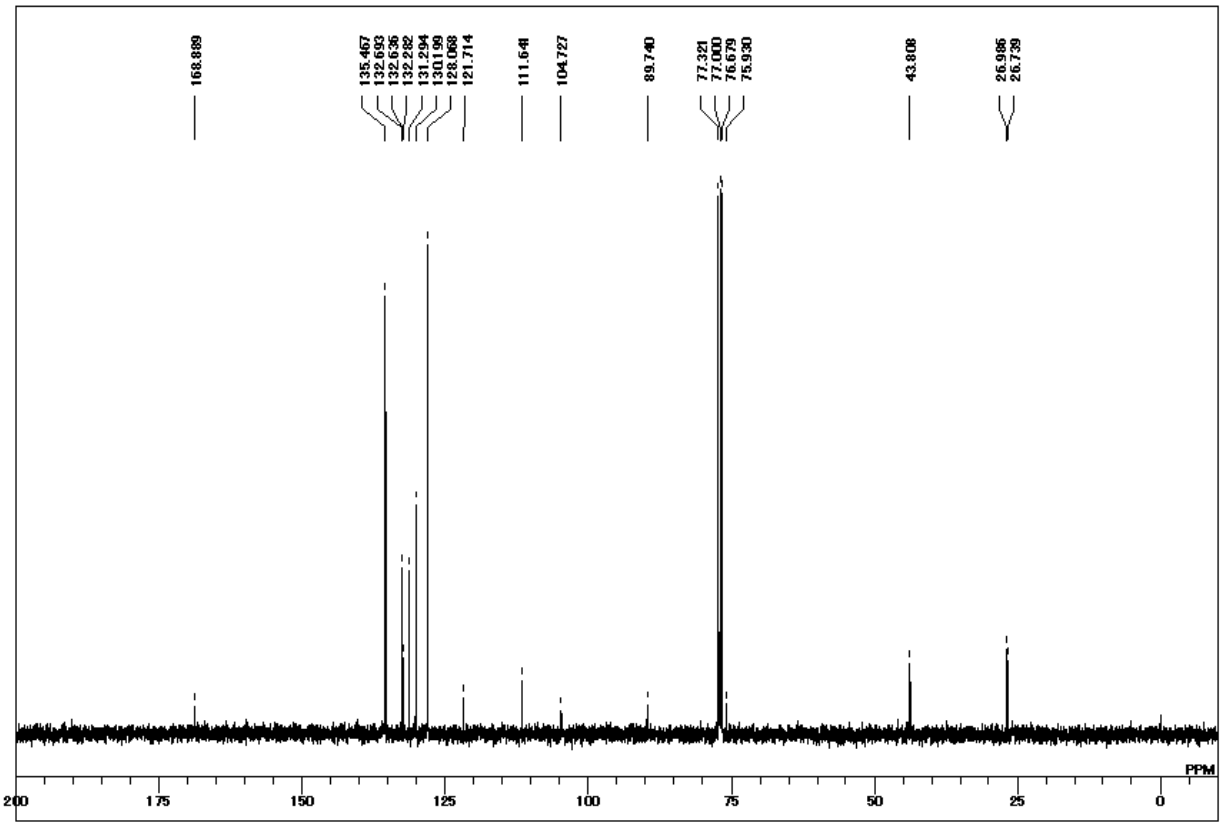
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77.321
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43.808
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26.739
PPM
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175
150
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75
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25
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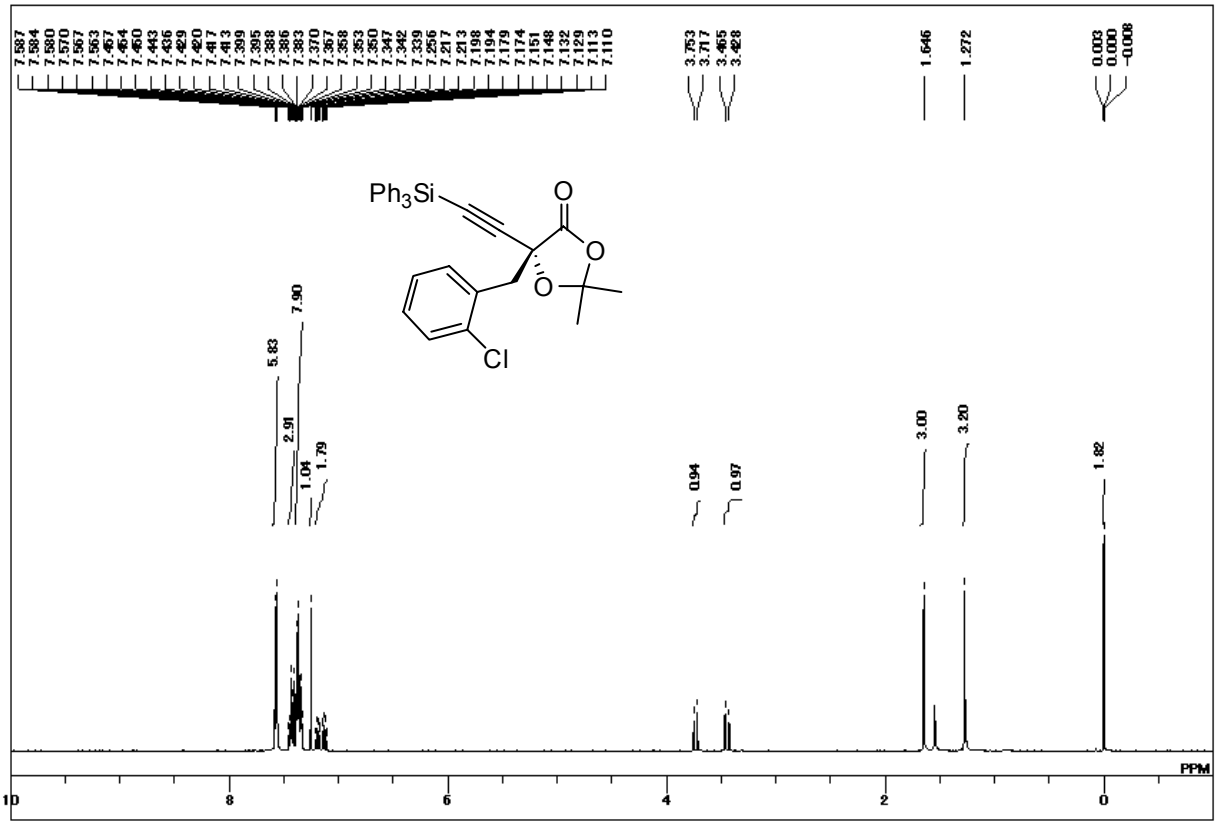
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7.420
7.417
7.413
7.399
7.395
7.388
7.386
7.383
7.370
7.367
7.358
7.353
7.350
7.347
7.342
7.339
7.256
7.217
7.213
7.198
7.194
7.179
7.174
7.151
7.148
7.132
7.129
7.113
7.110
3.753
3.717
3.465
3.428
1.646
1.272
0.003
0.000
-0.008
Ph3Si
O
O
O
Cl
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2.91
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0.94
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PPM
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2
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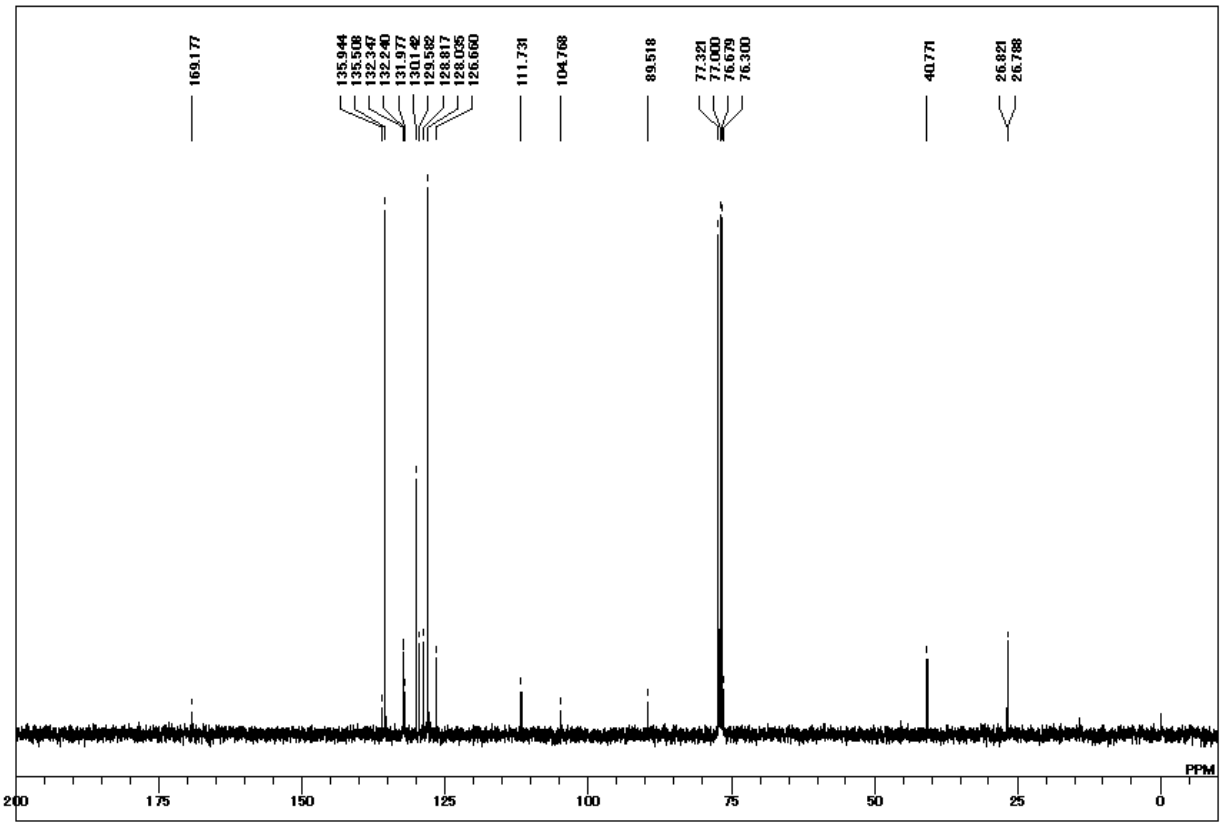
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129.582
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89.518
77.321
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175
150
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75
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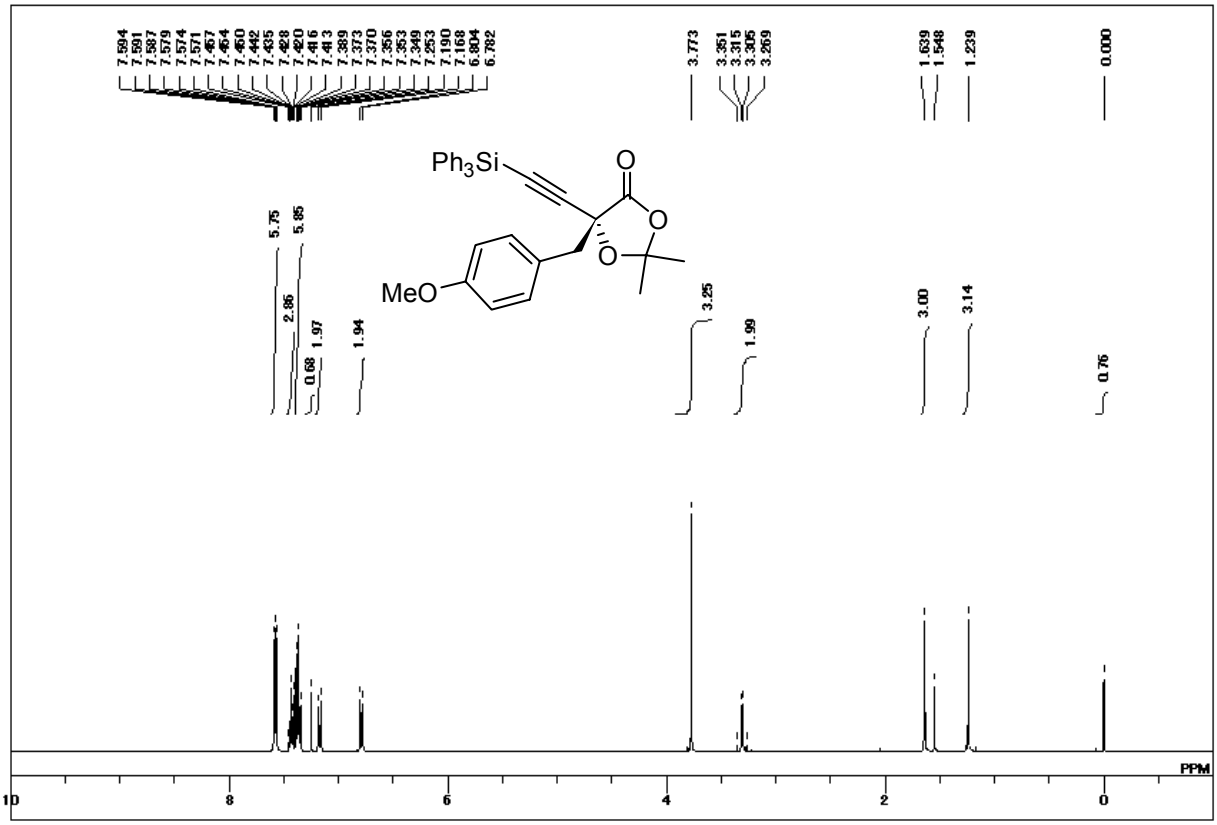
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7.416
7.413
7.389
7.373
7.370
7.356
7.353
7.349
7.253
7.190
7.168
6.804
6.782
3.773
3.351
3.315
3.305
3.269
1.639
1.548
1.239
0.000
Ph3Si
O
O
O
O
MeO
5.75
5.85
2.86
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3.25
1.99
3.00
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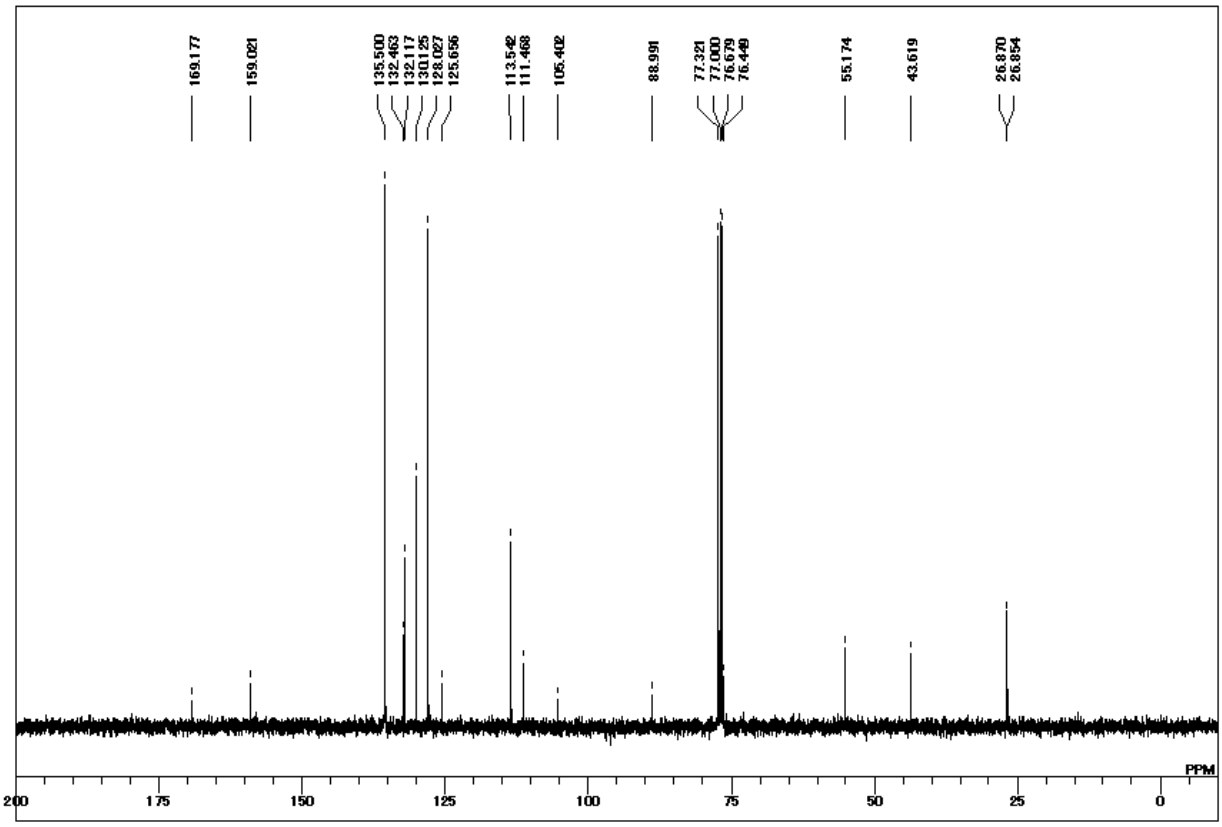
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125.656
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77.321
77.000
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26.854
PPM
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175
150
125
100
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50
25
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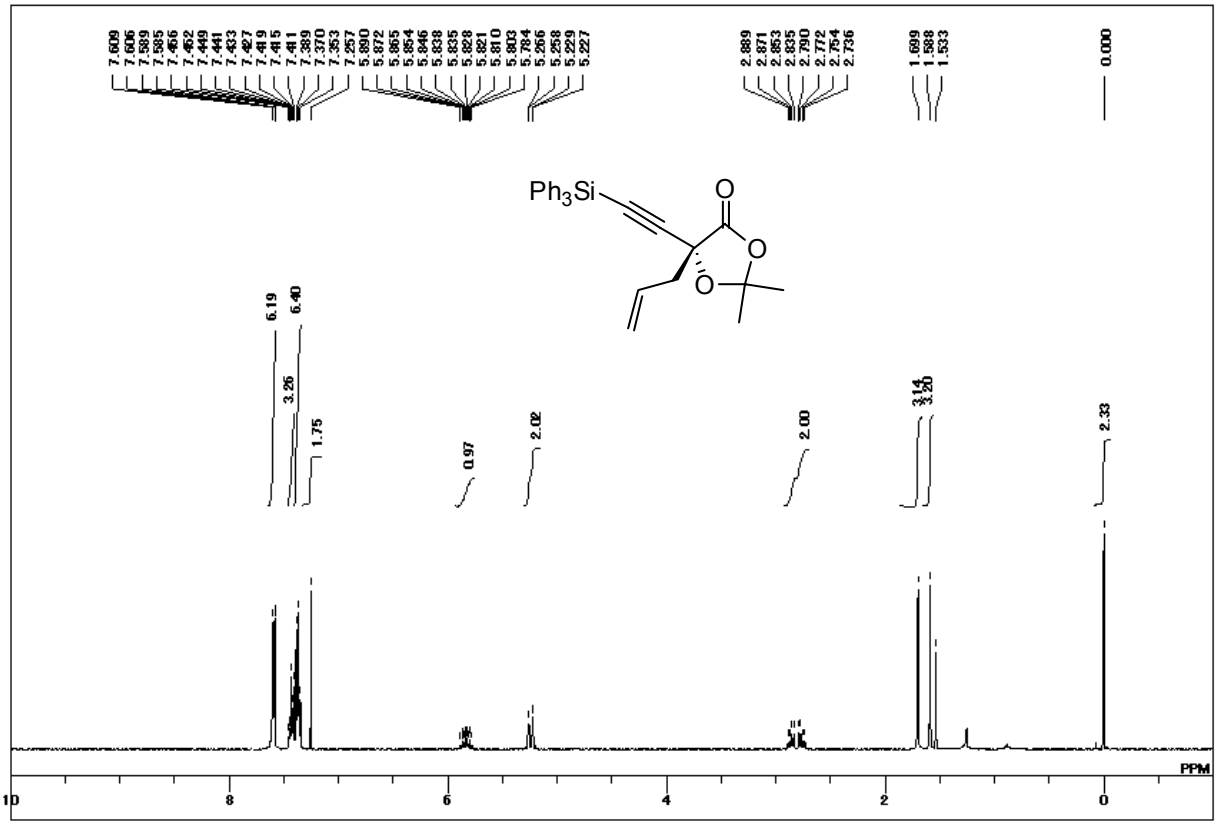
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7.585
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7.462
7.449
7.441
7.433
7.427
7.419
7.415
7.411
7.389
7.370
7.353
7.257
5.890
5.872
5.865
5.854
5.846
5.838
5.835
5.828
5.821
5.810
5.803
5.784
5.266
5.258
5.229
5.227
2.889
2.871
2.853
2.835
2.790
2.772
2.754
2.736
1.699
1.588
1.533
0.000
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O
O
O
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6.40
3.26
1.75
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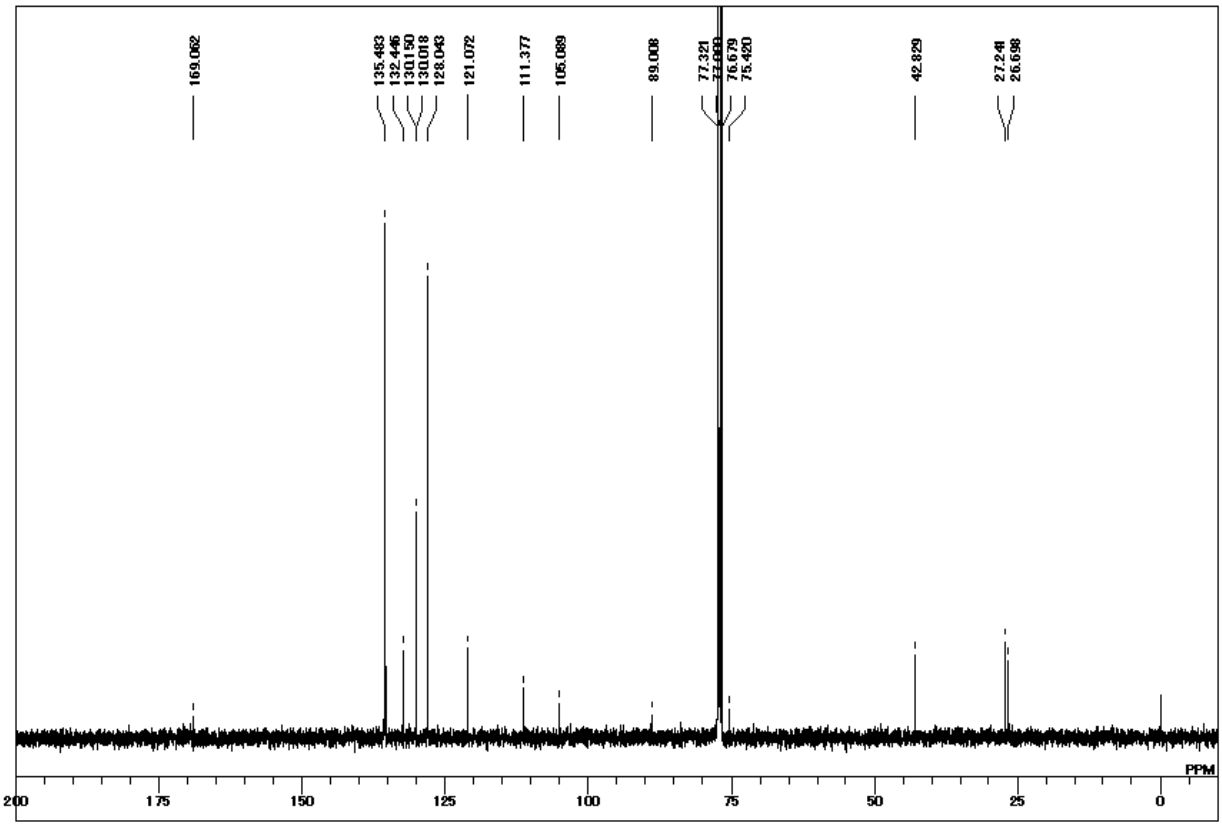
2.00
3.14
3.20
2.33
PPM
10
8
6
4
2
0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128.043
121.072
111.377
105.089
89.008
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42.829
27.241
26.698
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175
150
125
100
75
50
25
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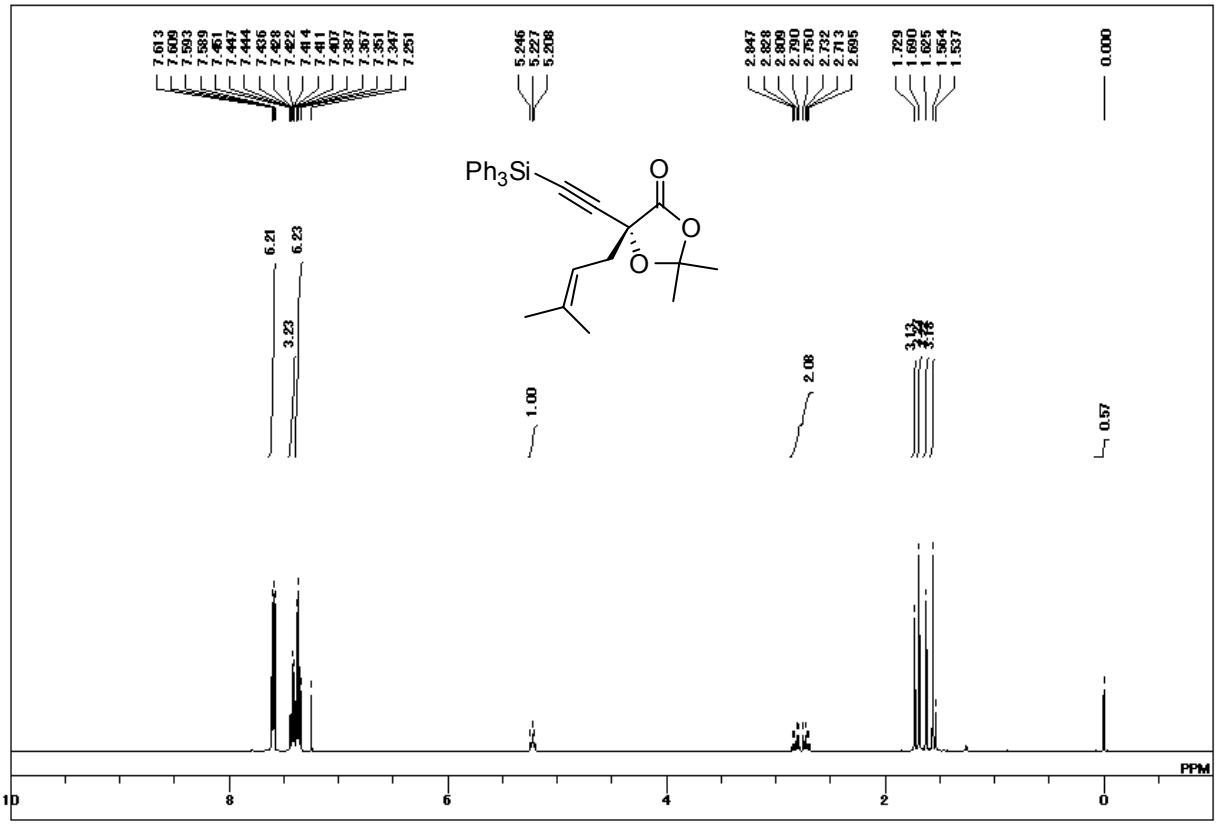
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7.447
7.444
7.436
7.428
7.422
7.414
7.411
7.407
7.387
7.367
7.351
7.347
7.251
5.246
5.227
5.208
2.847
2.828
2.809
2.790
2.750
2.732
2.713
2.695
1.729
1.690
1.625
1.564
1.537
0.000
Ph3Si
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6.23
3.23
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2.08
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4
2
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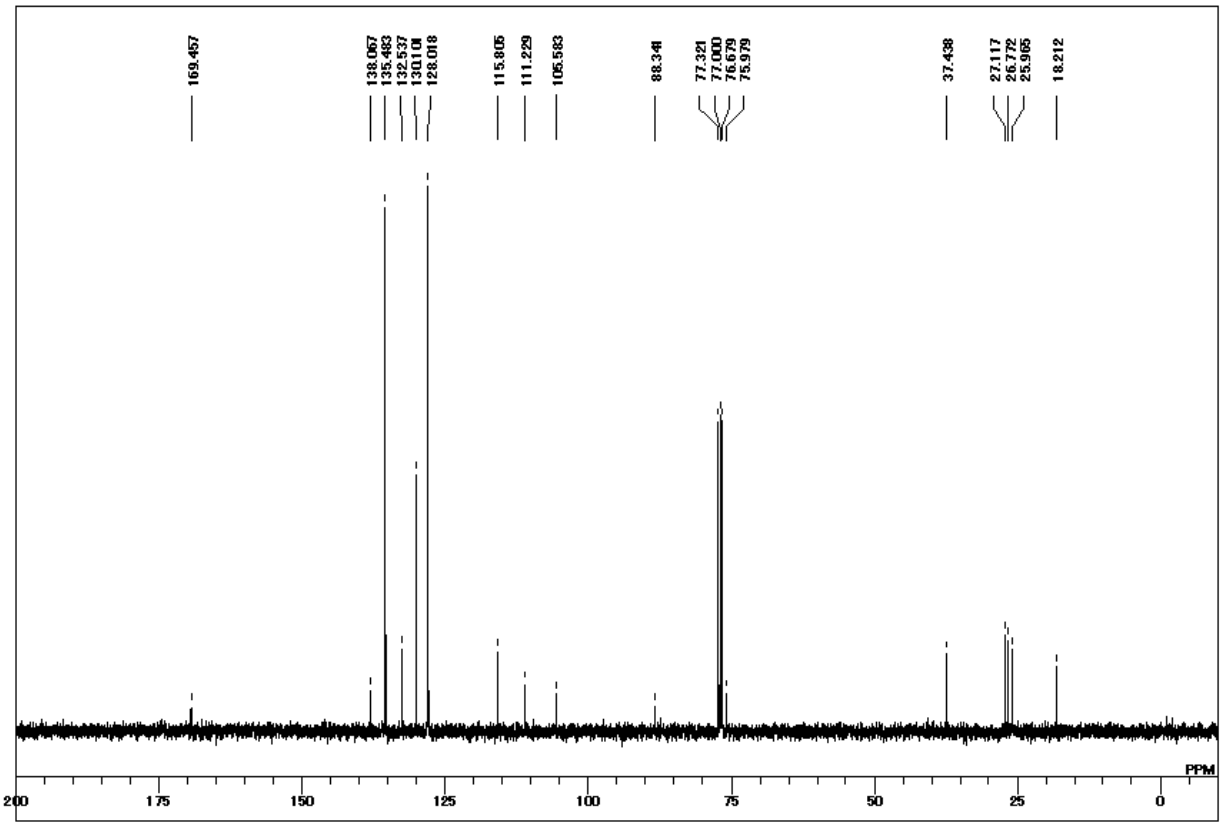
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115.805
111.229
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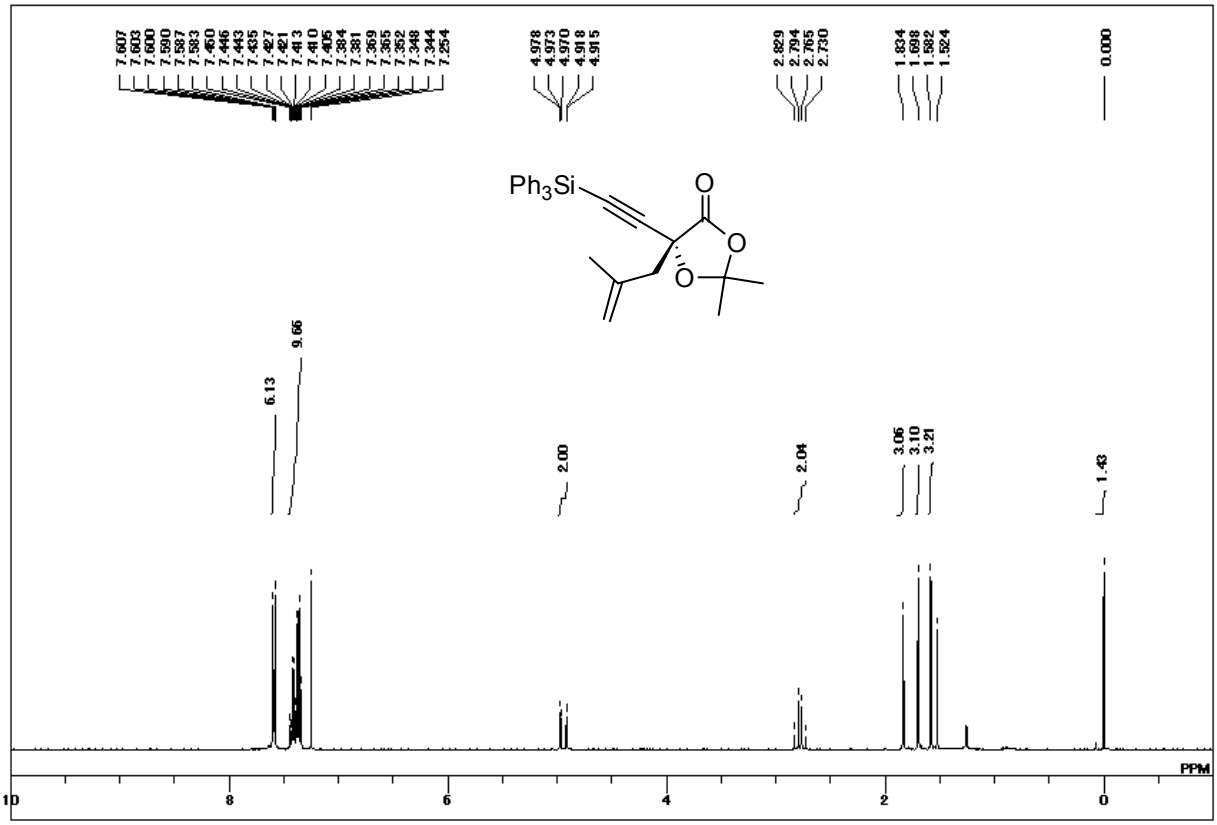
88.341
77.321
77.000
76.679
75.979
37.438
27.117
26.772
25.965
18.212
PPM
200
175
150
125
100
75
50
25
0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7.600
7.590
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7.583
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7.446
7.443
7.435
7.427
7.421
7.413
7.410
7.405
7.384
7.381
7.369
7.365
7.352
7.348
7.344
7.254
4.978
4.973
4.970
4.918
4.915
2.829
2.794
2.765
2.730
1.834
1.698
1.582
1.524
0.000
Ph3Si
O
O
O
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2.04
3.06
3.10
3.21
1.43
PPM
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6
4
2
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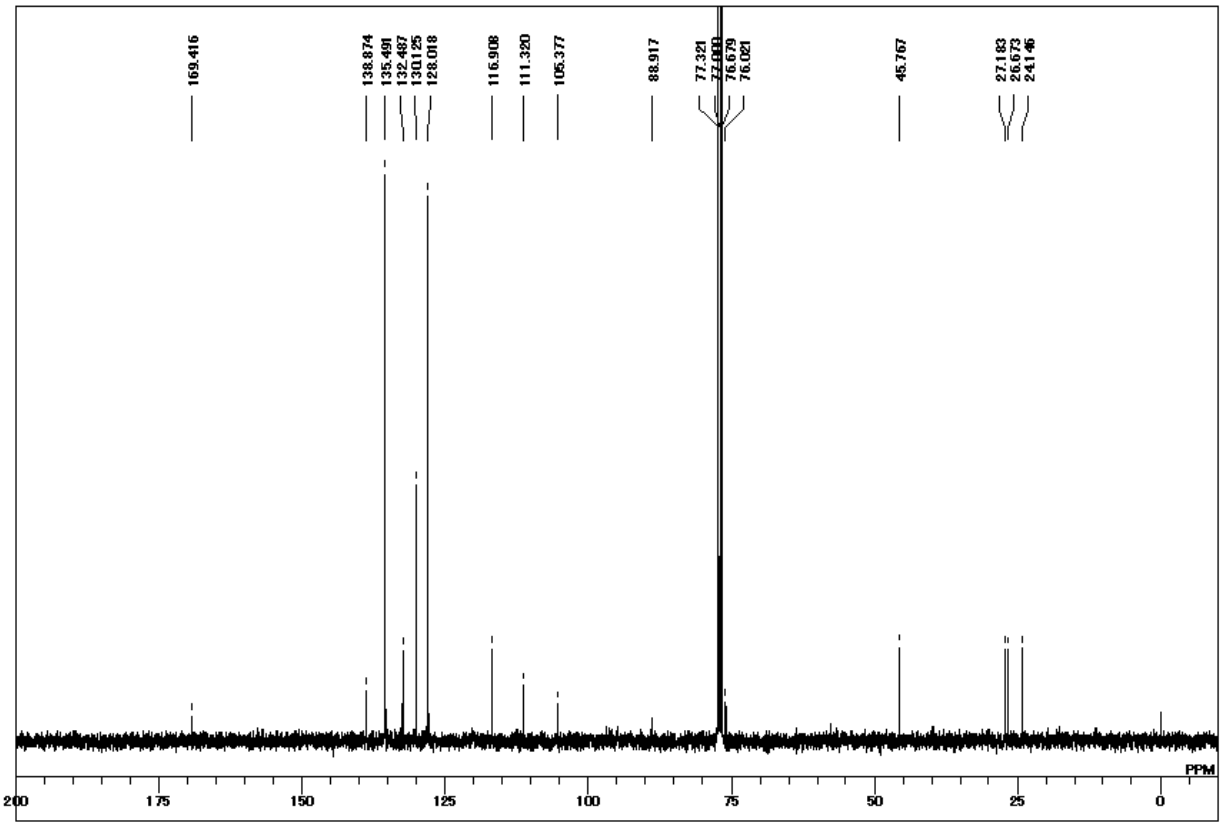
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27.183
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175
150
125
100
75
50
25
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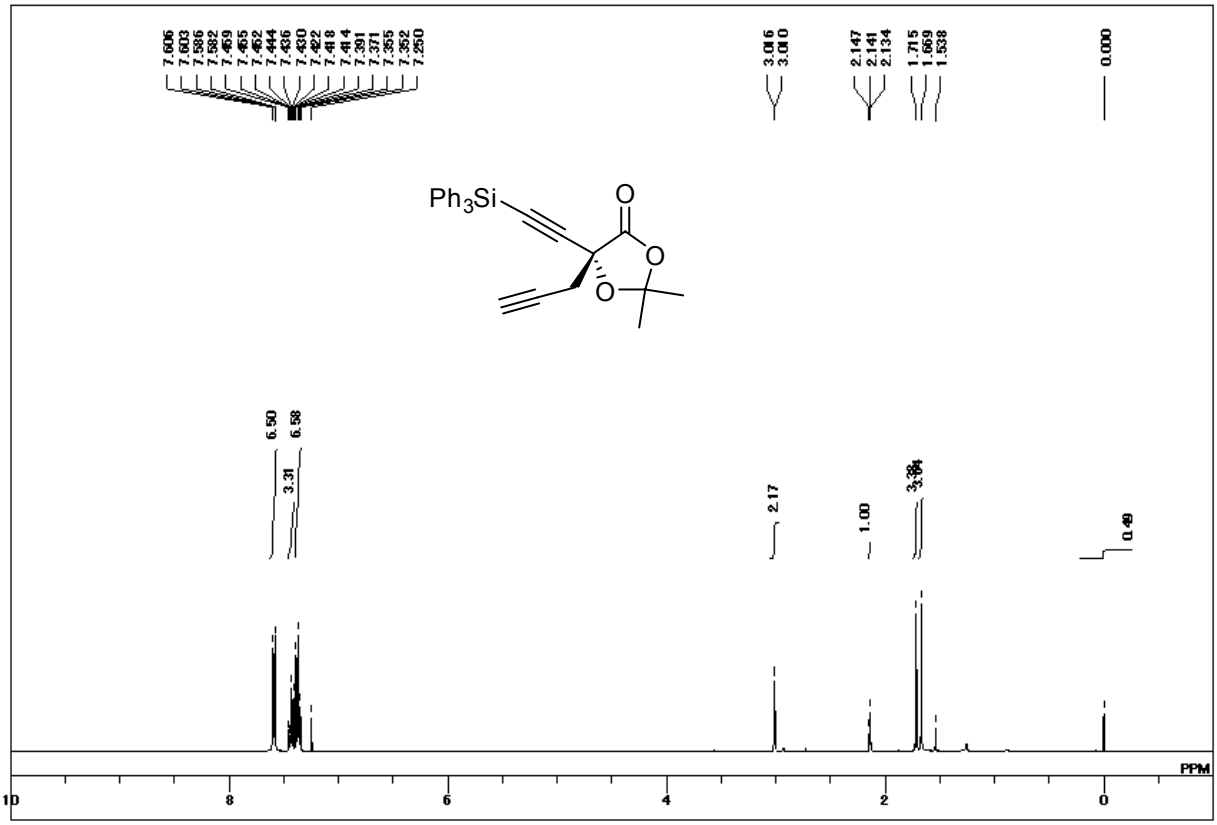
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7.603
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7.582
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7.462
7.444
7.436
7.430
7.422
7.418
7.414
7.391
7.371
7.365
7.352
7.250
3.016
3.010
2.147
2.141
2.134
1.715
1.669
1.538
0.000
Ph3Si
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O
O
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6.58
3.31
2.17
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PPM
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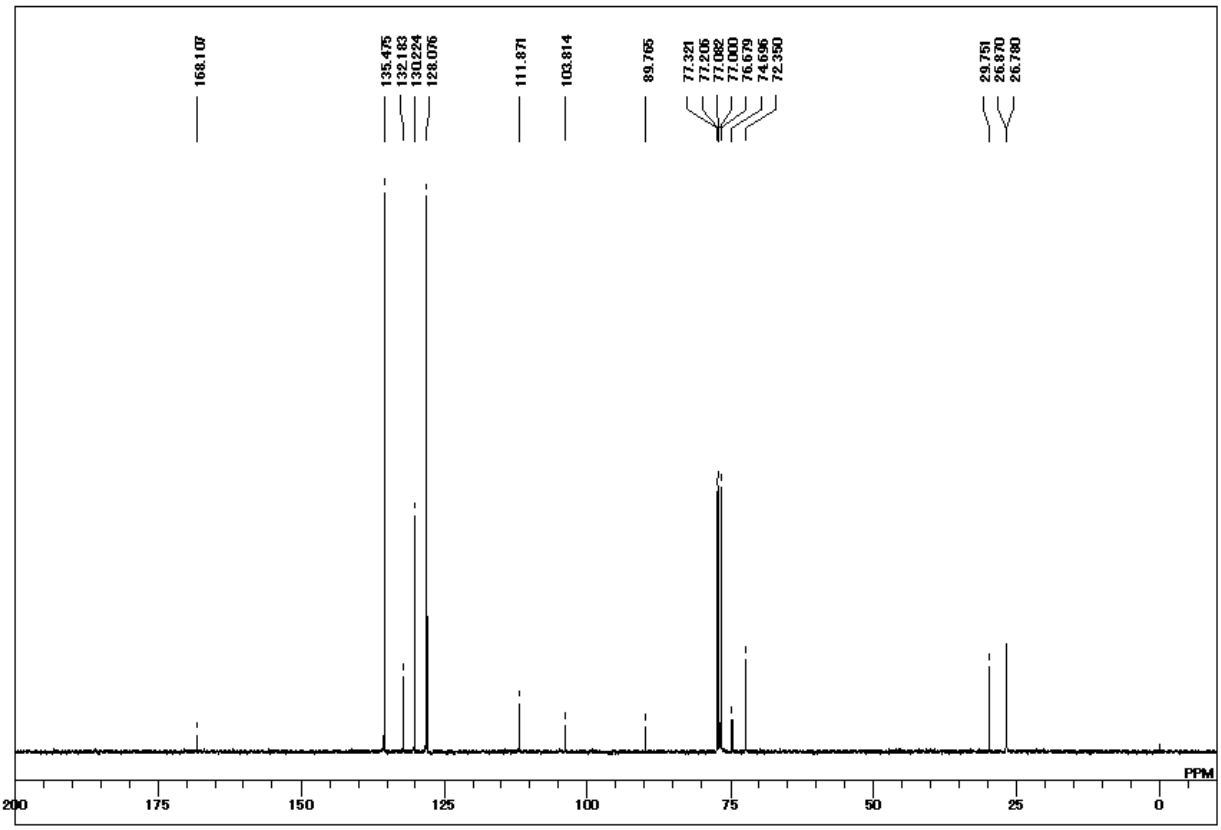
8
6
4
2
0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77.321
77.206
77.082
77.000
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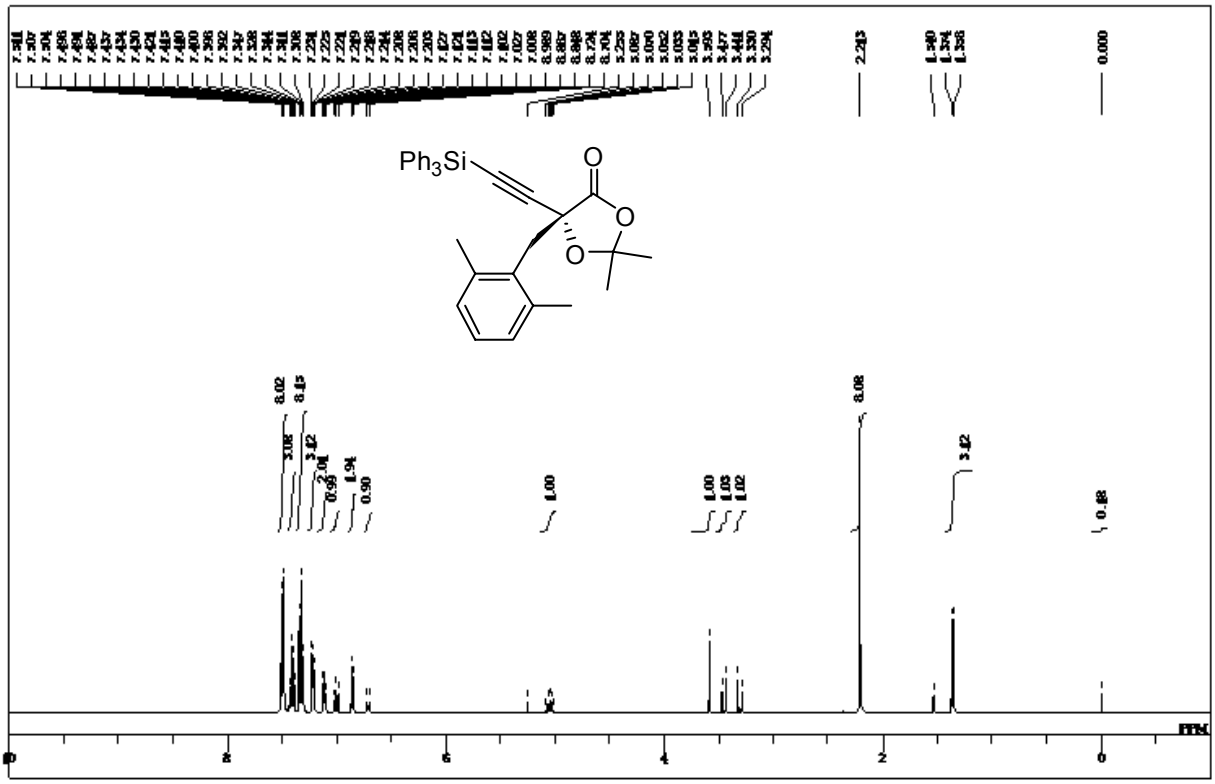
74.696
72.350
29.751
26.870
26.780
PPM
200
175
150
125
100
75
50
25
0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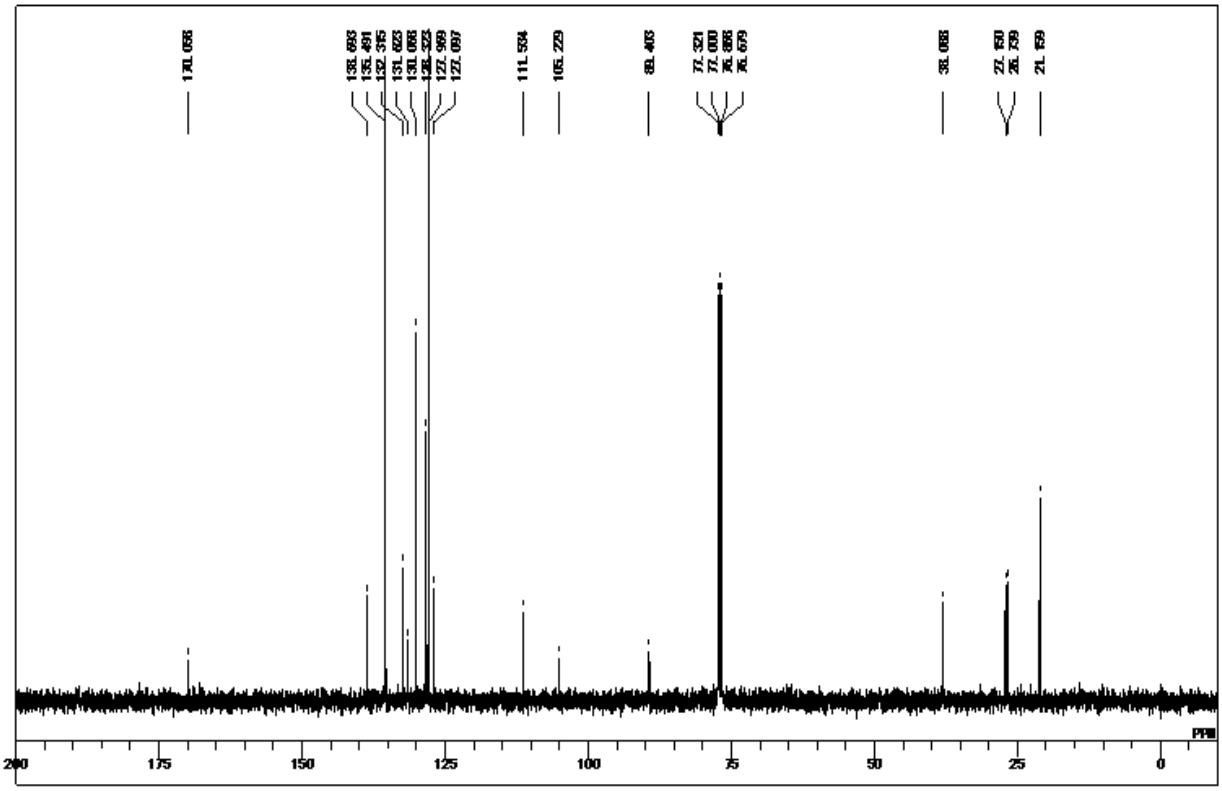
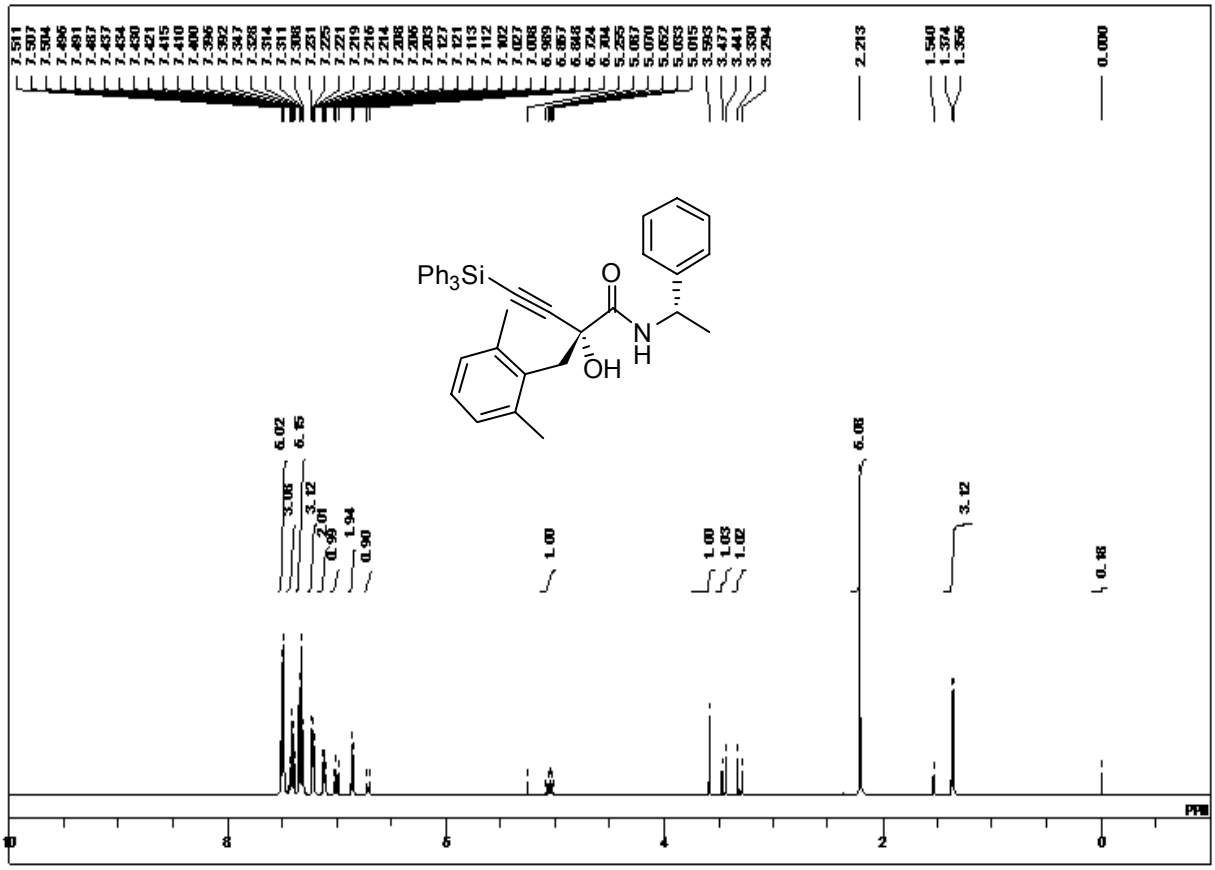
O
O
O

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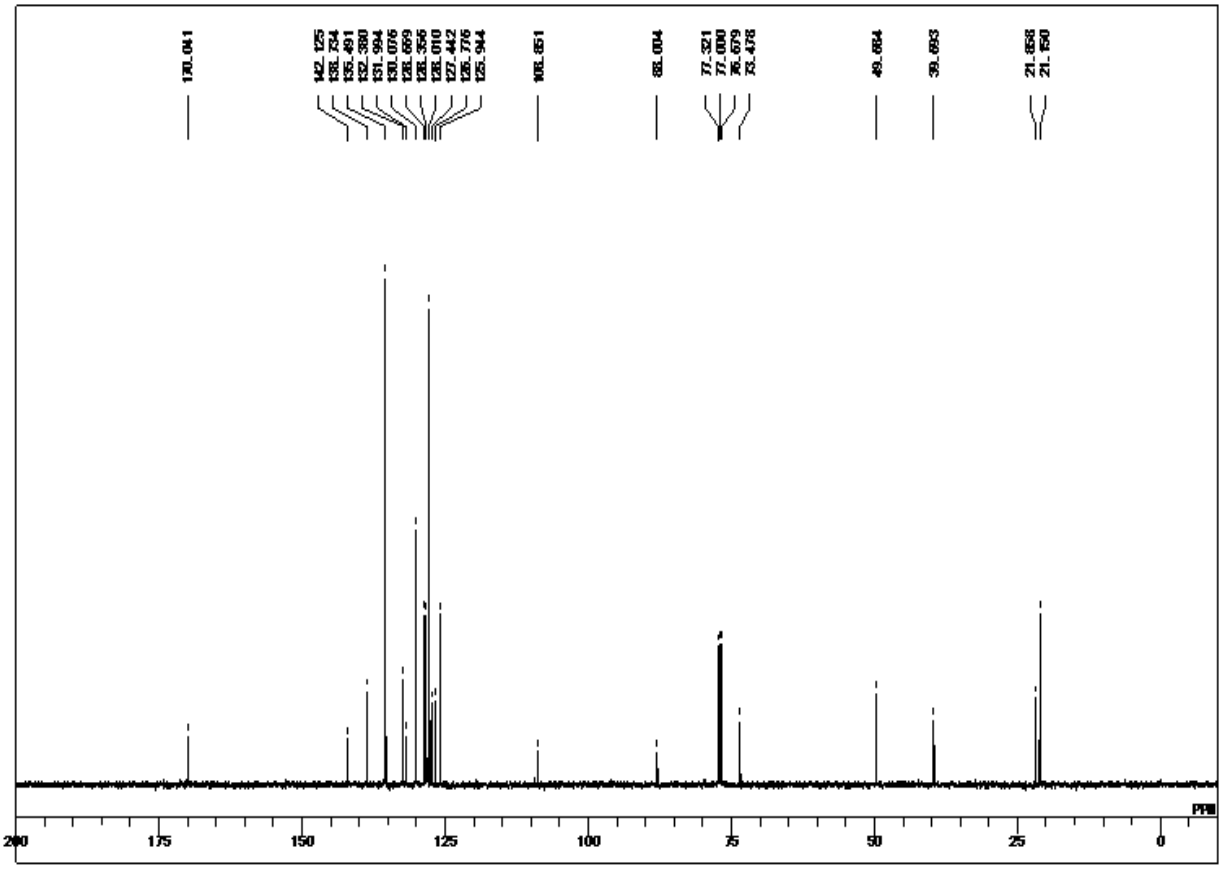
N
H
OH
PPM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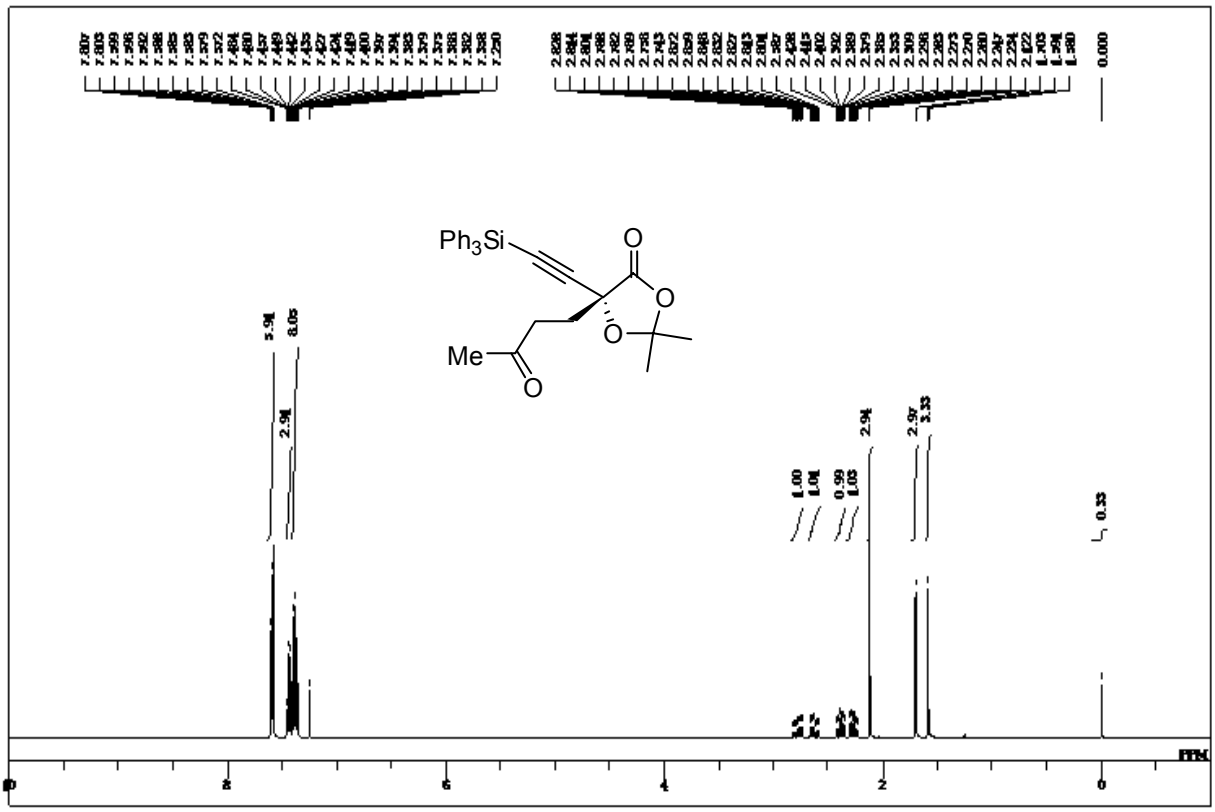
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O
O
O
O
Me
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1.00
1.01
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1.03
2.94
2.97
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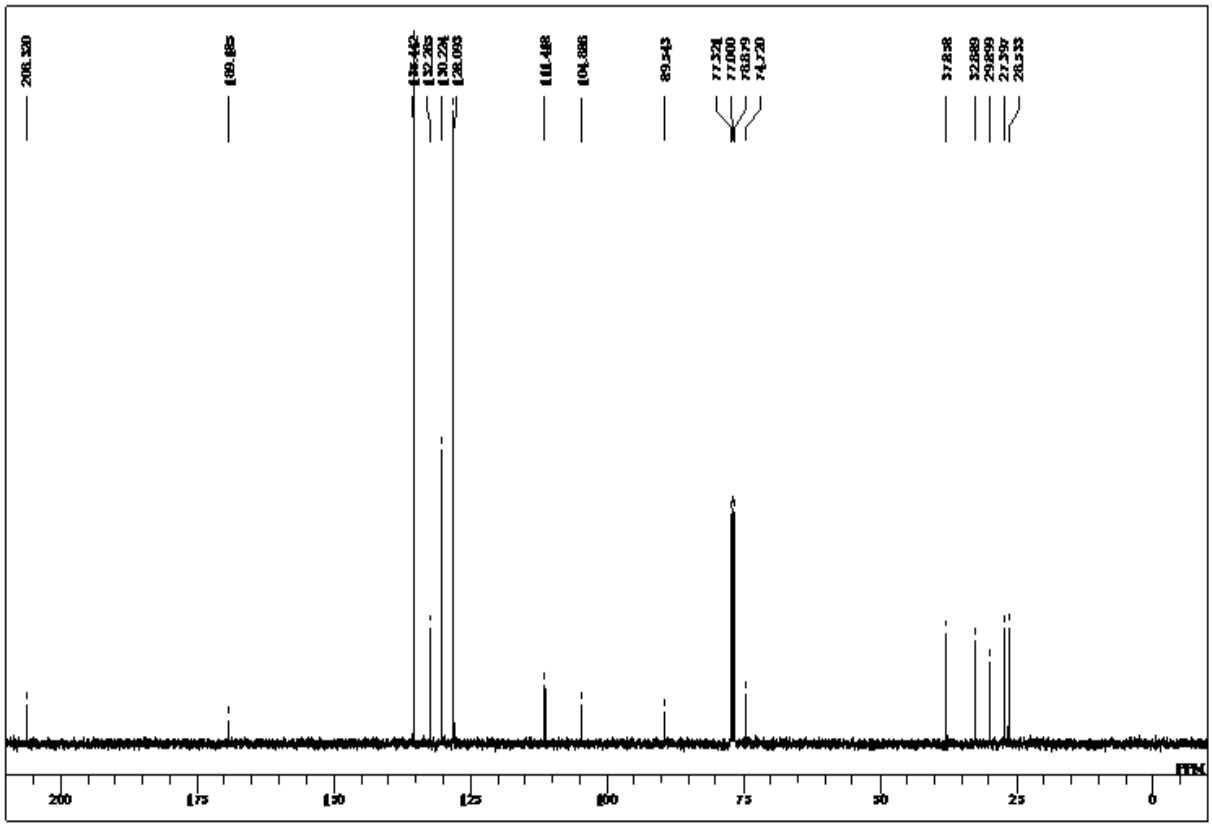
0.000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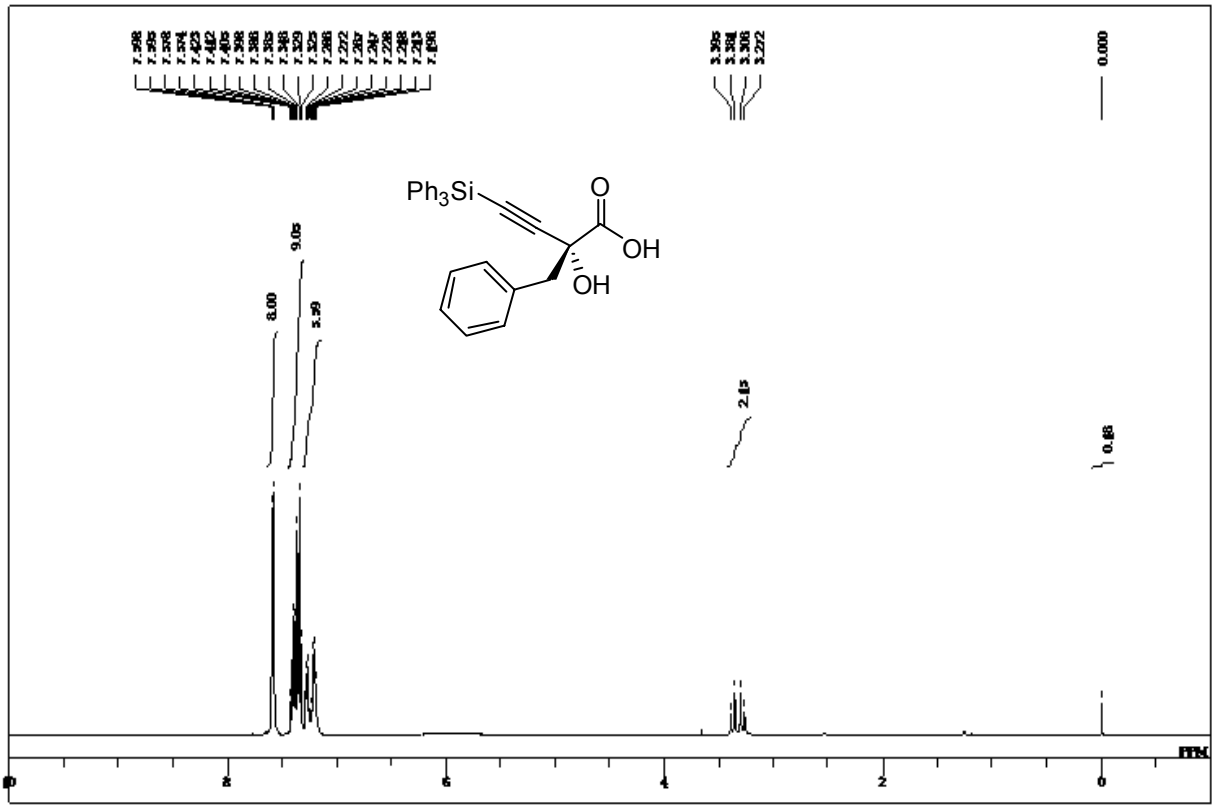
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OH
OH
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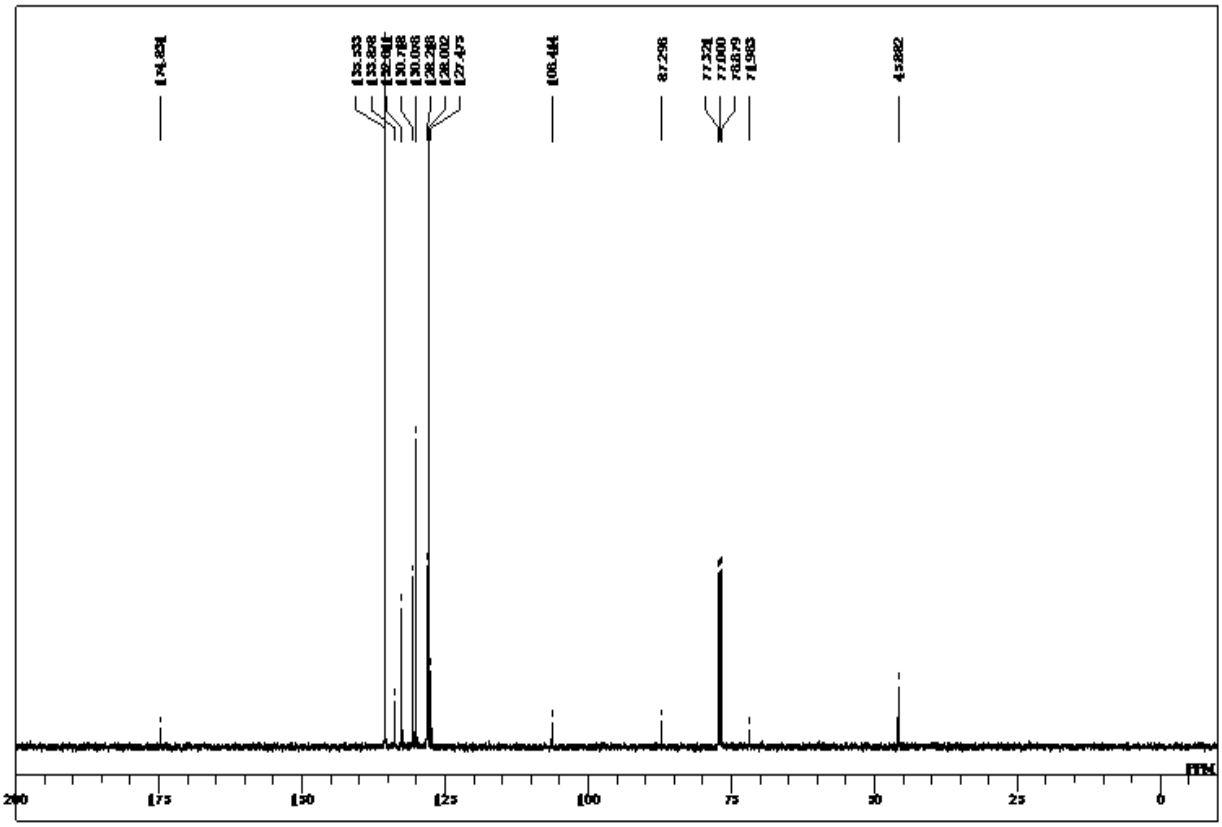
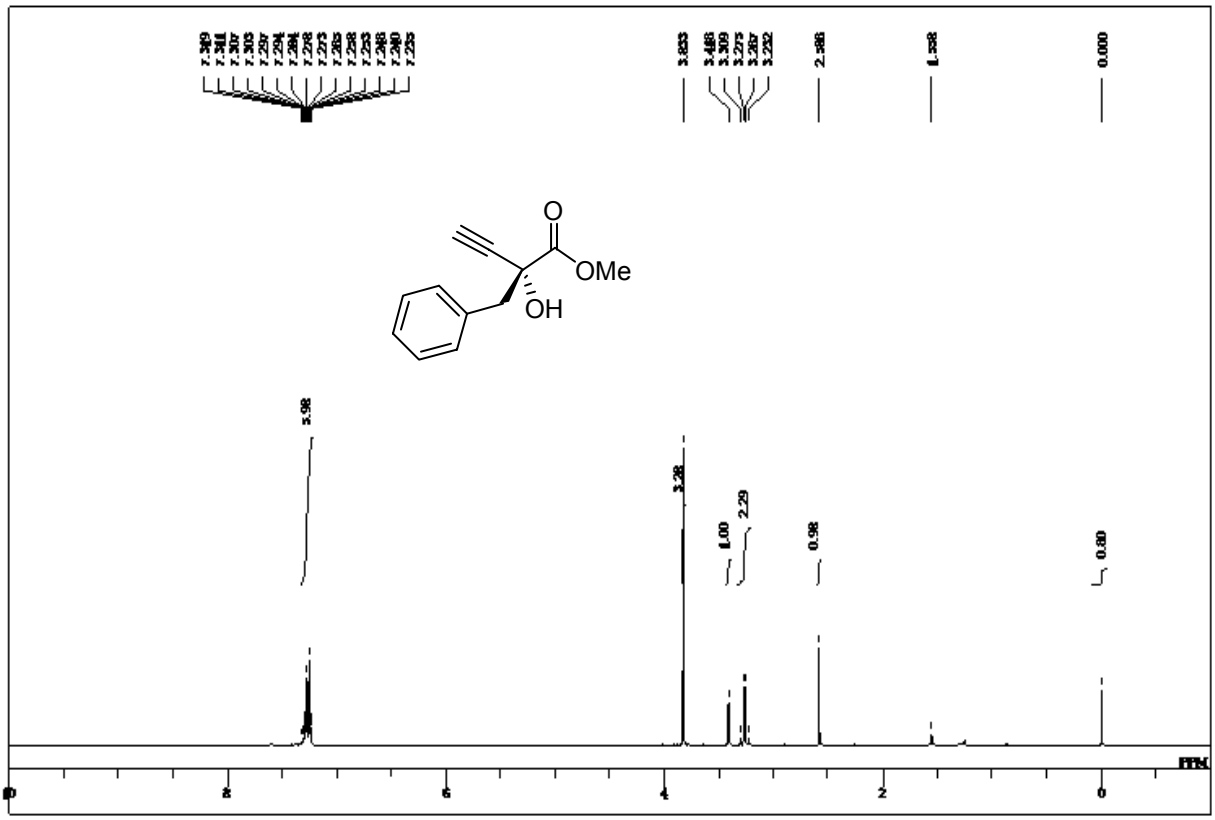
0.000

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OMe
OH
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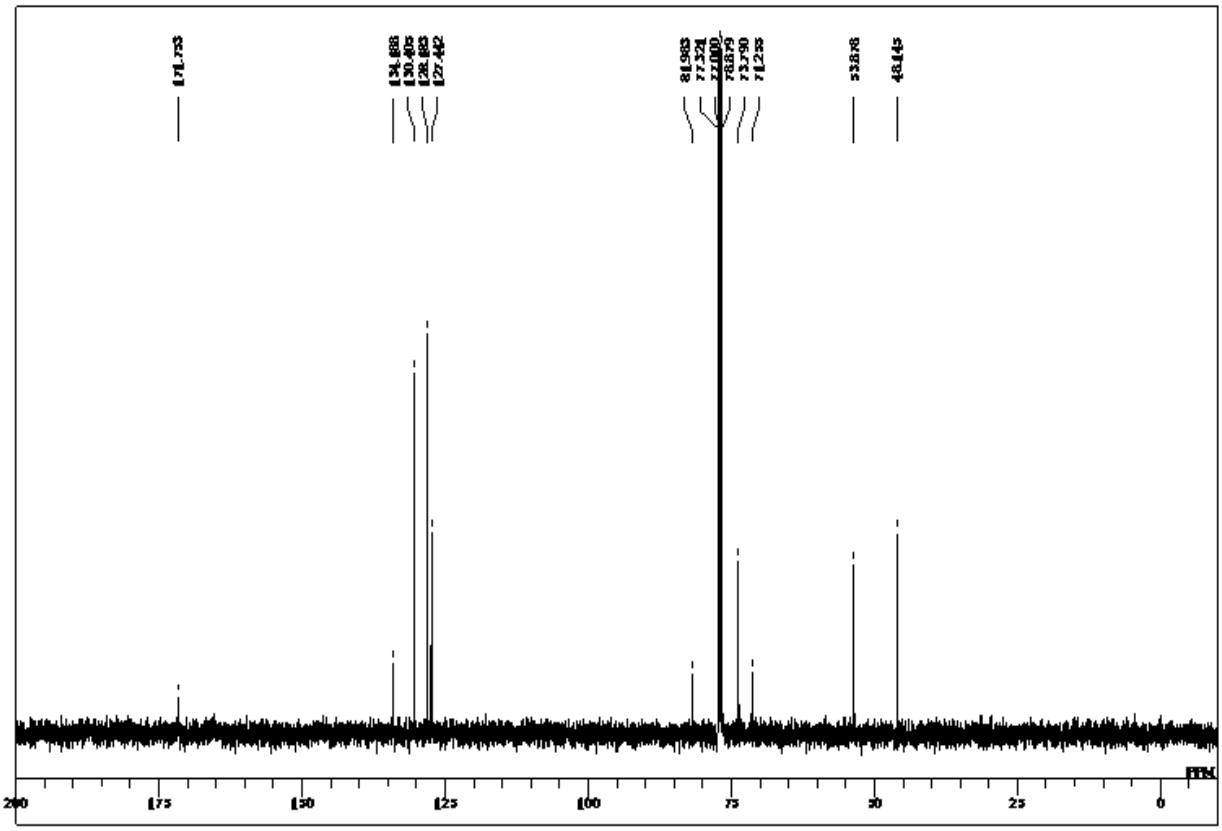

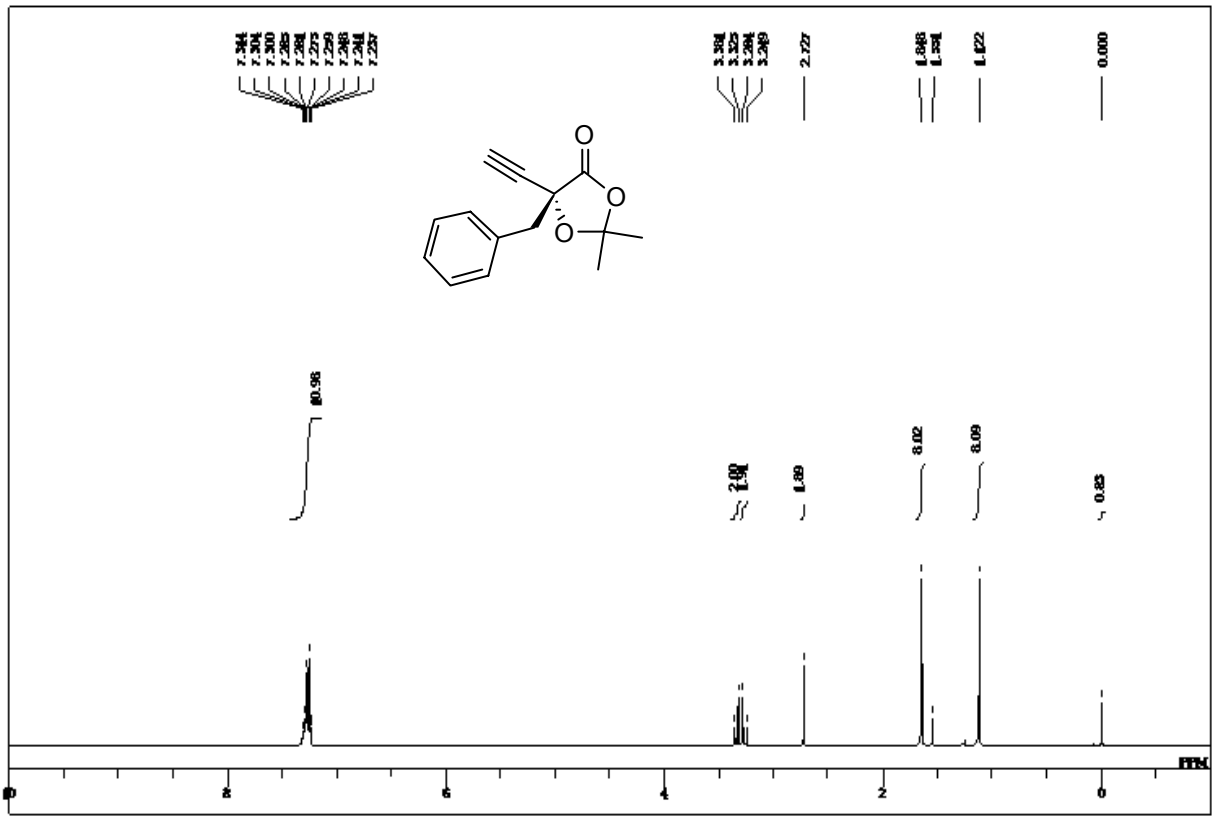
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O
O
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1.89
8.02
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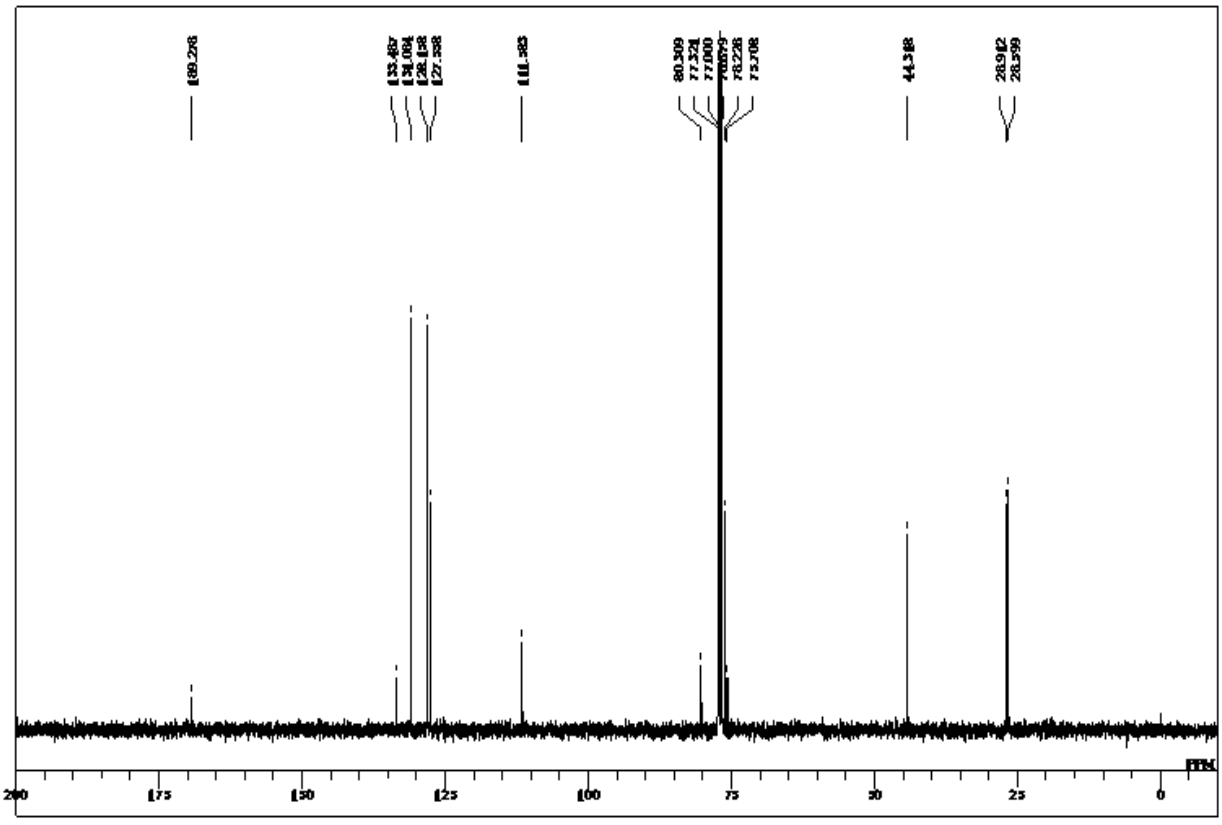
PPM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28.599
PPM