Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper(II)-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Unactivated Internal Alkynes with Silylborate in Water

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Supplementary Information

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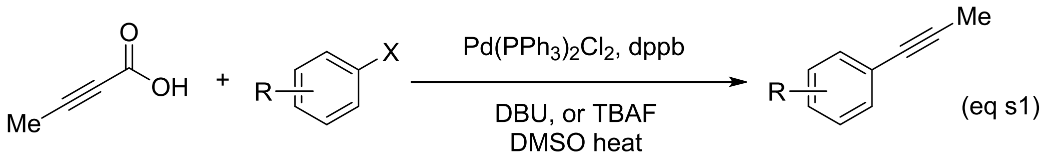
1. General methods

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. Internal alkynes were prepared according to original or modified literature procedures. All reactions were carried out under N_2 atomosphere, unless otherwise noted. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, h= heptet, m= multiplet,. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). IR spectra were recorded on a Bruker tensor 27 infrared spectrometer. Melting points were measured on Beijing Tech X-4 apparatus without correction. Mass spectra were obtained using electrospray ionization (APCI) mass spectrometer. Column chromatography was performed using silica gel (200-300 mesh). TLC was performed on glass-backed silica plates.

2. Experimental section

2.1 The Preparation of Internal Alkynes

The internal alkynes were synthesized from methyl propiolate acid and an aryl halide following the literature procedure (eq s1).[1]



General procedure:

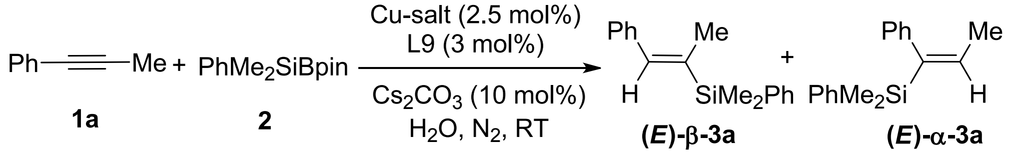
A mixture of $Pd(PPh_3)_2Cl_2$ (0.0343 mmol), 1,4-bis(diphenylphosphanyl)butane (0.0701 mmol), 4-halosubstituted benzene (3.04 mmol), 2-butynoic acid (3.00 mmol), base (6.0 mmol), and DMSO (6.0 mL) was stirred at 80-110 °C. After 2 -24 h, the reaction mixture was poured into a saturate aqueous solution of NH_4Cl and was extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with H_2O, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo*, and the resulting residue was purified using silicagel column chromatography.

1. Y. Okuno, M. Yamashita, K. Nozaki, *Eur. J. Org. Chem.* **2011**, 3951.

2.2 General Procedure for the Reaction of Internal Alkynes 1 with $Me_2PhSiBpin$ 2.

Ligand **L9** (0.003mmol, 0.5mg), and Cs_2CO_3 were added to a Schlenk tube, which was evacuated and backfilled with N_2. Then 1ml solution of $Cu(OTf)_2$ (0.9mg/ml), $Me_2PhSiBpin$ (0.15mmol, 40μl) and internal alkyne **1a** (0.1mmol,12.6μl) were added via syringe, and the reaction mixture was stirred for 20h at room temperature. Then the reaction solution was extracted with ether for 3 times, the organic layer was combined and dried over Na_2SO_4. Next, the organic solvent was evaporated and the residue was subjected to flash column chromatography on silica gel with petroleum ether as eluent to afford the desired product **3a**.

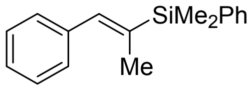
2.3 The screening of copper source.



Entry[a]	Cu-salt	Yield(%)[b]	β/α[c]
1	CuOTf	65	88/12
2	CuOAc	22	83/17
3[d]	$Cu(OTf)_2$	75	92/8

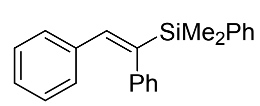
[a] General procedure: A mixture of 1a (1.0 equiv), 2 (1.5 equiv), ligand (3~6 mol%), base (10 mol%) and $Cu(OTf)_2$ (2.5 mol%) in water (1 mL) was stirred under N_2 at room temperature. [b] The yields of 3a were determined by ^1H NMR analysis. [c] The ratio (β/α) was determined by ^1H NMR analysis. [d] The reaction was carried out under air.

(*E*)-(1-(4-fluorophenyl)prop-1-en-2-yl)dimethyl(phenyl)silane (*β*-3a)[1]



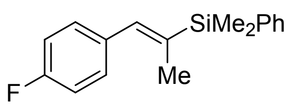
colourless oil.yield 95%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.56(d, *J*=4Hz, 2H), 7.36-7.26(m, 7H), 7.24-7.20(t, *J*=8Hz, 1H), 6.80(s, 1H), 1.94(s, 3H), 0.43(s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 137.99, 137.41, 137.4, 137.3, 133.2, 128.2, 128.1, 127.2, 126.9, 125.7, 15.8, -4.3. IR ν_{max} (KBr, film, cm^{-1}): 1594, 1427, 1243, 1029, 823. HRMS (APCI): calcd for $C_{17}H_{20}Si$ $[M+H]^+$ 253.14070, found: 253.14055.

(*E*)-(1,2-diphenylvinyl)dimethyl(phenyl)silane (*β*-3b)



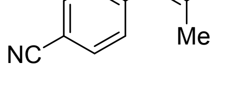
colourless oil. yield 93% ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53(t, *J*=4Hz, 2H), 7.36-7.35(d, *J*=4Hz, 3H), 7.36-7.14(m, 3H), 7.08-7.06(t, *J*=4Hz, 3H), 6.94-6.88(m, 4H), 6.82(s, 1H), 0.39(s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 144.1, 141.4, 138.3, 136.8, 136.3, 133.4, 128.6, 128.2, 127.6, 127.0, 126.8, 127.7, 126.3, 124.8, -3.9. IR ν_{max} (KBr, film, cm^{-1}): 1593, 1426, 1246, 968, 823. HRMS (APCI): calcd for $C_{22}H_{22}Si$ $[M]^+$ 314.14853, found: 314.14835.

(*E*)-(1-(4-fluorophenyl)prop-1-en-2-yl)dimethyl(phenyl)silane (*β*-3c)



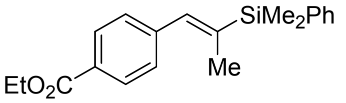
colourless oil. yield 85%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.54(m, 2H), 7.38-7.36(m,3H), 7.28-7.25(m, 3H), 7.04-7.69(t, *J*=10Hz, 2H), 1.92-1.91(d, *J*=4Hz, 3H), 0.43(s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 140.6, 137.3, 137.1, 136.8, 133.4, 133.2, 129.8(d, $^1J_{CF}$=160Hz), 129.7, 126.93, 114(d, $^2J_{CF}$=21.2Hz), 15.7, -4.3. IR ν_{max} (KBr, film, cm^{-1}): 1596, 1422, 1360, 1263, 908. HRMS (APCI): calcd for $C_{17}H_{19}FSi$ $[M+H]^+$ 271.13128, found: 271.13103.

(*E*)-4-(2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)benzonitrile (*β*-3d)



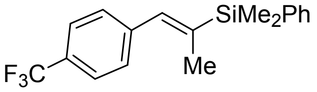
colourless oil. yield 95%. ^1H NMR (400 MHz, $CDCl_3$) δ:7.62-7.60(d, J=8Hz, 2H), 7.56-7.53(m, 2H), 7.39-7.38(t, *J*=2Hz, 4H), 7.36(s, 1H), 6.760-6.757(d, *J*=1.2Hz, 1H), 1.934-1.929(d, *J*=1.5Hz, 3H), 0.45(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ:142.0, 141.9, 136.8, 136.0, 133.1, 130.9, 128.7, 128.4, 127.0, 118.2, 109.1, 15.9, -4.5. IR ν_{max} (KBr, film, cm^{-1}): 2242, 1591, 1422, 1202, 1029, 834. HRMS (APCI): calcd for $C_{18}H_{19}NSi$ [M+H]$^+$ 278.13595, found: 278.13571.

(*E*)-4-(2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)benzonitrile (*β*-3e)



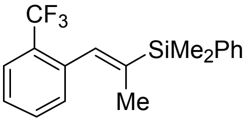
colourless oil. yield 90%. ^{1}H NMR (400 MHz, CDCl3) δ: 8.02-8.00(d, *J*=8Hz, 2H), 7.57-7.55(m, 2H), 7.39-7.34(m, 5H), 6.819-6.816(d, *J*=1.2Hz, 1H), 4.40-4.35(q, *J*=7.2Hz, 2H), 1.952-1.948(d, *J*=1.6Hz, 3H), 1.41-1.38(t, *J*=7.2Hz, 3H), 0.45(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 165.6, 141.9, 140.3, 137.0, 133.2, 130.5, 128.5, 128.0, 127.6, 126.9, 59.9, 15.9, 13.5, -4.4. IR ν_{max} (KBr, film, cm^{-1}): 1597, 1716, 1437, 1263, 1029, 829. HRMS (APCI): calcd for $C_{20}H_{24}O_2Si$ [M+H]$^+$325.16183, found: 325.16150.

(*E*)-dimethyl(phenyl)(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)silane (*β*-3f)



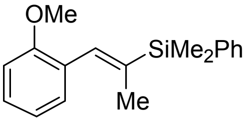
colourless oil. yield 76%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.59-7.55(dd, *J*=8Hz, *J*=4Hz, 3H), 7.39-7.38(t, *J*=3.6Hz, 5H), 6.80(s, 1H), 1.939-1.936(d, *J*=1.6Hz, 3H), 0.46(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 140.9, 140.4, 137.6, 136.7, 136.5, 133.2, 128.3, 127.4 (q, $^2J_{CF}$=32.2Hz), 126.9, 124.7 (q, $^1J_{CF}$=255), 124.1(q, $^3J_{CF}$=3.8), 15.8, -4.4. IR ν_{max} (KBr, film, cm^{-1}): 1595, 1332, 1426, 1223, 827. HRMS (APCI): calcd for $C_{18}H_{19}F_3Si$ [M+H]$^+$ 321.12809, found: 321.12750.

(*E*)-dimethyl(phenyl)(1-(2-(trifluoromethyl)phenyl)prop-1-en-2-yl)silane (*β*-3g)



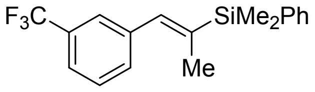
colourless oil. yield 78%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.66-7.64(d, *J*=8Hz, 1H), 7.58-7.55(dd, *J*=2.5Hz, *J*=3.6Hz, 2H), 7.49-7.46(t, *J*=7.6Hz, 1H), 7.38-7.36(t, *J*=3.2Hz, 3H), 7.34-7.32(d, *J*=8Hz, 1H), 7.30-7.26(t, J=5.2Hz, 1H), 6.99(s, 1H), 1.698-1.695(d, *J*=1.2Hz, 3H), 0.44(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 139.7, 136.8, 136.7, 135.0, 132.2, 133.1, 130.2, 129.9, 128.7, 127.6(d, $^2J_{CF}$=77.8Hz,), 126.9, 125.7(d, $^1J_{CF}$=250), 124.8 (d, $^3J_{CF}$=5Hz), 15.4, -4.5. IR ν_{max} (KBr, film, cm^{-1}): 1594, 1334, 1428, 1243, 1029. HRMS (APCI): calcd for $C_{18}H_{19}F_3Si$ [M+H]$^+$ 321.12809, found: 321.12757.

(*E*)-(1-(2-methoxyphenyl)prop-1-en-2-yl)dimethyl(phenyl)silane (*β*-3h)



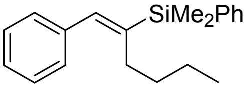
colourless oil. yield 85%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.63-7.60(m, 2H), 7.39-7.38(t, *J*=2.4Hz, 3H), 7.27-7.22(m, 2H), 6.97(s, 1H), 6.95-6.89(dd, *J*=7.6Hz, *J*=8.4Hz, 2H), 3.84(s, 3H), 1.899-1.895(d, *J*=1.2Hz, 3H), 0.47(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 156.3, 137.7, 136.8, 133.8, 133.2, 129.4, 128.0, 127.2, 126.8, 126.3, 118.9, 109.7, 54.6, 15.9, -4.2. IR ν_{max} (KBr, film, cm^{-1}): 1592, 1425, 1247, 1210, 1029. HRMS (APCI): calcd for $C_{18}H_{22}OSi$ [M+H]$^+$ 283.15127, found: 283.15097.

(*E*)-dimethyl(phenyl)(1-(3-(trifluoromethyl)phenyl)prop-1-en-2-yl)silane (*β*-3i)



colourless oil. yield 87%. ^{1}H NMR (400 MHz, CDCl3) δ:7.57-7.55(dd, *J*=2.4Hz, *J*=3.6Hz, 2H), 7.53(s, 1H), 7.48-7.44(m, 3H), 7.39-7.38(m, 3H), 6.97(s, 1H), 1.933-1.929(d, *J*=1.2Hz, 3H), 0.45(s, 6H).^{13}C NMR (100MHz, CDCl$_3$) δ: 139.8, 138.0, 136.7, 136.4, 136.2, 131.3, 127.9 (q, $^2J_{CF}$=31.8Hz), 128.3, 127.5, 126.9, 124.8 (q, $^3J_{CF}$=5.3Hz), 124.7(d, $^1J_{CF}$=270Hz), 122,3 (t, $^3J_{CF}$=3.7Hz), 15.7, -4.4. IR ν_{max} (KBr, film, cm^{-1}): 1594, 1427, 1334, 1246, 1129. HRMS (APCI): calcd for $C_{18}H_{19}F_3Si$ [M+H]$^+$ 321.12809, found: 321.12769.

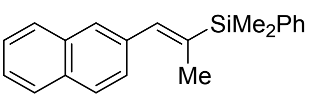
(*E*)-dimethyl(phenyl)(1-phenylhex-1-en-2-yl)silane (*β*-3j)



colourless oil. yield 65%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.60-7.58(dd, J=2.8 Hz, *J*=3.6 Hz, 2H), 7.38-7.36(dd, *J*=2.8 Hz, *J*=2.8 Hz, 4H), 7.34-

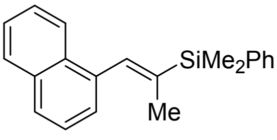
7.32(d, *J*=8Hz, 2H), 7.29-7.21(m, 2H), 6.82(s, 1H), 2.38-2.34(t, *J*=8.2Hz, 2H), 1.35-1.23(m, 4H), 0.82-0.78(t, *J*=8Hz, 3H), 0.46(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 142.7, 138.7, 137.9, 137.5, 133.2, 128.0, 127.8, 127.2, 126.8, 125.7, 31.1, 29.6, 22.1, 12.9, -3.3. IR ν_{max} (KBr, film, cm^{-1}): 1594, 1485, 1288, 1110, 923. HRMS (APCI): calcd for $C_{20}H_{26}Si$ [M+H]$^+$ 295.18765, found: 295.18710.

(*E*)-dimethyl(1-(naphthalen-2-yl)prop-1-en-2-yl)(phenyl)silane (*β*-3k)



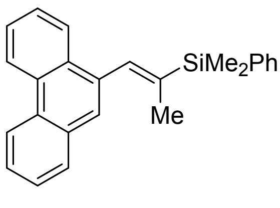
white solide. yield 92%. m.p. 56-58°C. ^{1}H NMR (400 MHz, CDCl3) δ:7.81-7.78(m, 3H), 7.75(s, 1H), 7.61-7.58(dd, *J*=2.8Hz, *J*=3.2Hz, 2H), 7.45-7.43(m, 3H), 7.39-7.37(t, *J*=4Hz, 3H), 6.95(s, 1H), 2.023-2.019(d, *J*=1.6Hz, 3H), 0.47(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 138.0, 137.9, 137.2, 134.9, 133.2, 132.4, 131.3, 128.2, 127.8, 127.1, 126.9, 126.9, 126.7, 126.6, 125.1, 124.8, 15.9, -4.3. IR ν_{max} (KBr, film, cm^{-1}): 1633, 1427, 1243, 894, 753. HRMS (APCI): calcd for $C_{21}H_{22}Si$ [M]$^+$ 302.14853, found: 302.14819.

(*E*)-dimethyl(1-(naphthalen-1-yl)prop-1-en-2-yl)(phenyl)silane (*β*-3l)



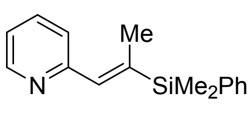
colourless oil. yield 89%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.92-7.89(t, *J*=6Hz, 1H), 7.86-7.83(t, *J*=6Hz, 1H), 7.76-7.74(d, *J*=8Hz, 1H), 7.65-7.64(t, J=2Hz, 2H), 7.49-7.46(m, 2H), 7.44-7.42(d, *J*=8Hz, 1H), 7.40-7.39(t, *J*=2Hz, 3H), 7.33-7.31(t, *J*=4Hz, 1H), 7.24(s, 1H), 1.78(s, 3H), 0.52(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 139.4, 137.3, 136.6, 134.7, 133.2, 132.7, 130.8, 128.2, 127.5, 126.9, 126.2, 125.4, 124.9, 127.77, 124.3, 124.1, 15.9, -4.2. IR ν_{max} (KBr, film, cm^{-1}): 1634, 1423, 1247, 1129, 843. HRMS (APCI): calcd for $C_{21}H_{22}Si$ [M]$^+$ 320.14853, found:302.14818.

(*E*)-dimethyl(1-(phenanthren-9-yl)prop-1-en-2-yl)(phenyl)silane (*β*-3m)



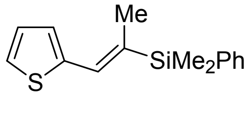
white soilde. yield 91%. M.p. 80-82°C. ^{1}H NMR (400 MHz, CDCl3) δ: 8.77-8.75(d, *J*=8Hz, 1H), 8.72-8.70(d, *J*=8Hz, 1H), 8.05-8.03(m, 1H), 7.90-7.88(m, 1H), 7.74-7.71(m, 2H), 7.70-7.66(m, 2H), 7.64-7.61(m, 3H), 7.30(s, 1H), 1.894-1.890(d, *J*=1.6Hz, 3H), 0.597(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 139.8, 137.3, 136.8, 133.3, 133.2, 130.7, 130.3, 129.6, 128.9, 128.3, 127.6, 127.1, 126.0, 125.8, 125.6, 125.5, 125.5, 124.8, 122.1, 121.7, 16.0, -4.1. IR ν_{max} (KBr, film, cm^{-1}): 1698, 1574, 1457, 1029, 893. HRMS (APCI): calcd for $C_{25}H_{24}Si$ [M]$^+$ 352.16418, found: 352.16388.

(*E*)-2-(2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)pyridine (*β*-3n)



yellow oil. yield 87%. ^{1}H NMR (400 MHz, CDCl3) δ: 8.62-8.61(d, *J*=4Hz, 1H), 7.66-7.62(td, *J*=1.6 Hz, *J*=1.2 Hz, *J*=1.2 Hz, 1H), 7.58-7.56(dd, *J*=2 Hz, *J*=3.4 Hz, 2H), 7.37-7.36(m, 3H), 7.30-7.28(d, *J*=8Hz, 1H), 7.11-7.09(q, *J*=4.4Hz, 1H), 6.87(s, 1H), 2.092-2.089(d, *J*=1.2Hz, 3H), 0.461(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 156.91, 149.29, 143.23, 138.14, 137.64, 135.85, 134.13, 129.12, 127.85, 124.22, 121.27, 16.95, -3.45. IR ν_{max} (KBr, film, cm^{-1}): 1598, 1432, 1193, 1009, 873. HRMS (APCI): calcd for $C_{16}H_{19}NSi$ [M+H]$^+$ 254.13595, found: 254.13580.

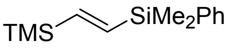
(*E*)-dimethyl(phenyl)(1-(thiophen-2-yl)prop-1-en-2-yl)silane (*β*-3o)



yellow oil. yield 94%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.55-7.53(m, 2H), 7.37-7.35(dd, *J*=2Hz, *J*=1.6Hz, 3H), 7.299-7.287(d, *J*=5.2Hz, 1H), 7.06-7.02(m, 2H), 6.936-6.933(d, *J*=1.2Hz. 3H), 0.42(s, 6H). ^{13}C NMR (100MHz, CDCl$_3$) δ: 140.9, 137.1, 135.0, 133.2,132.1, 130.4, 128.2, 126.9, 125.8, 124.9, 16.2, -

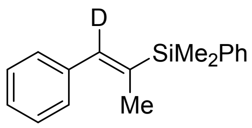
4.3. IR ν_{max} (KBr, film, cm^{-1}): 1592, 1426, 1126, 1111, 868. HRMS (APCI): calcd for $C_{15}H_{18}SSi$ $[M+H]^+$ 259.09712, found:259.09690.

(*E*)-(2-(dimethyl(phenyl)silyl)vinyl)trimethylsilane (*β*-3p)



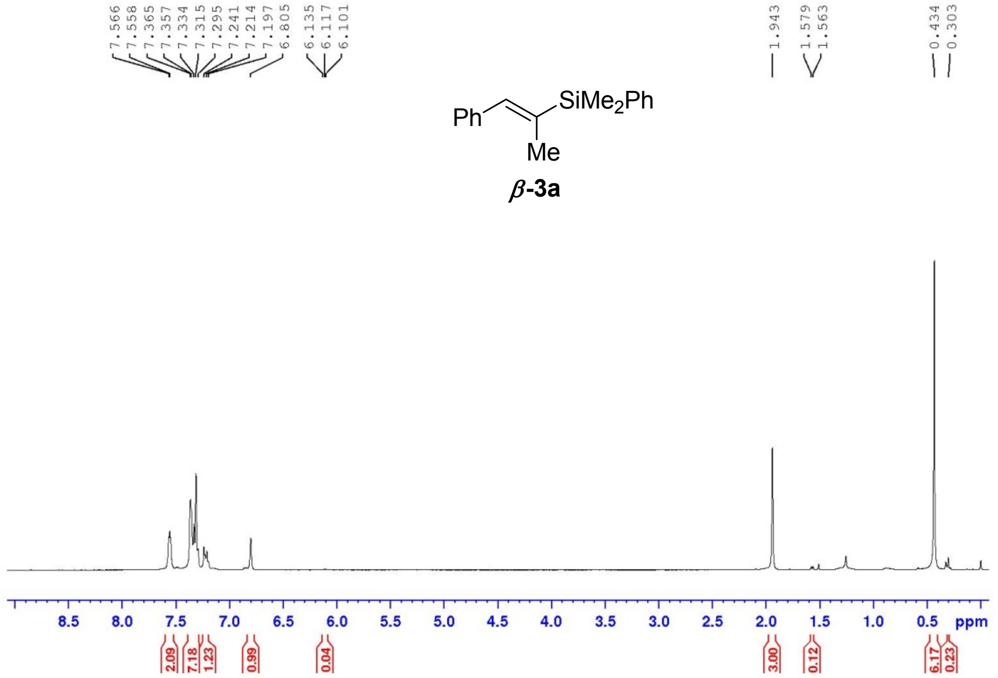
colourless oil. yield 95%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.56-7.53(dd, *J*=2.8Hz, *J*=3.6Hz, 2H), 7.39-7.38(t, *J*=2Hz, 3H), 6.73(s, 2H), 0.37(s, 6H), 0.1(s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 152.1, 147.1, 137.9, 132.9, 127.9, 126.8, -2.5, -3.8. IR ν_{max} (KBr, film, cm^{-1}): 1594, 14527, 1243, 867, 823. HRMS (APCI): calcd for $C_{13}H_{22}Si$ $[M+H]^+$ 235.13328, found:235.13307.

(*E*)-dimethyl(phenyl)(1-phenylprop-1-en-2-yl-1-d)silane (*β*-4a)



colourless oil. yield 96%. ^{1}H NMR (400 MHz, CDCl3) δ: 7.56-7.55(t, *J*=2Hz, 2H), 7.37-7.35(t, *J*=4Hz, 3H), 7.33-7.30(t, *J*=6Hz, 4H), 7.22-7.19(m, 1H), 1.94(s, 3H), 0.43(s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 137.3, 137.3, 137.2, 133.2, 128.2, 128.1, 127.2, 126.9, 125.8, 124.5, 15.8, -4.3. IR ν_{max} (KBr, film, cm^{-1}): 2596, 1584, 1426, 1019, 833. HRMS (APCI): calcd for $C_{17}H_{19}DSi$ $[M+H]^+$ 254.14705, found:254.14698.

1. Hazra, C. K.; Fopp, C.; Oestreich, M. *Chem. Asian J.,* 2014, **9**, 3005.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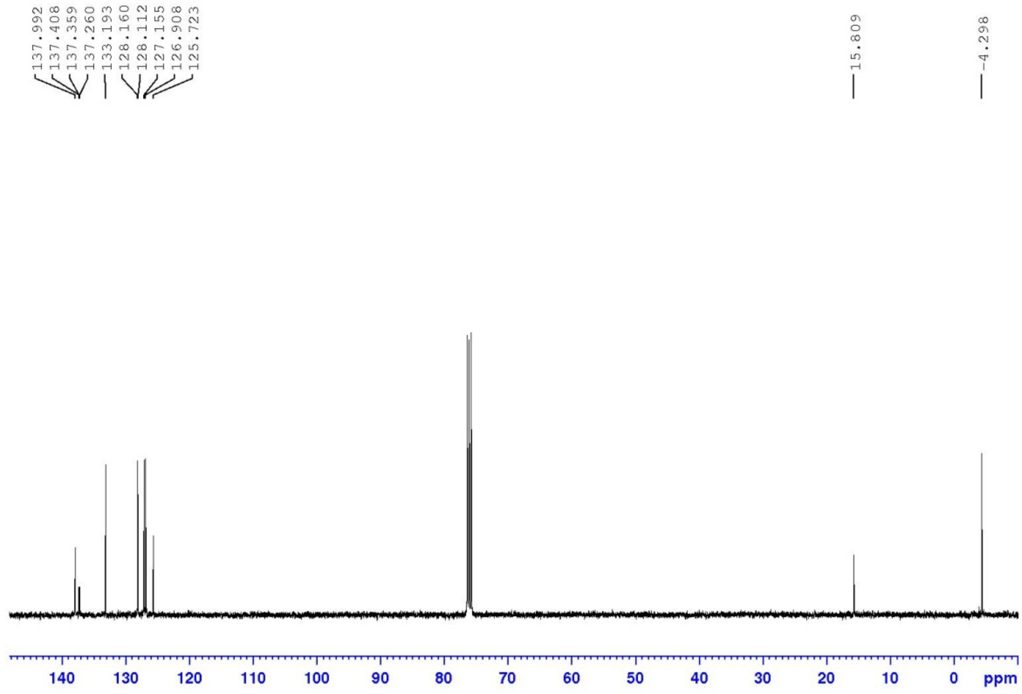
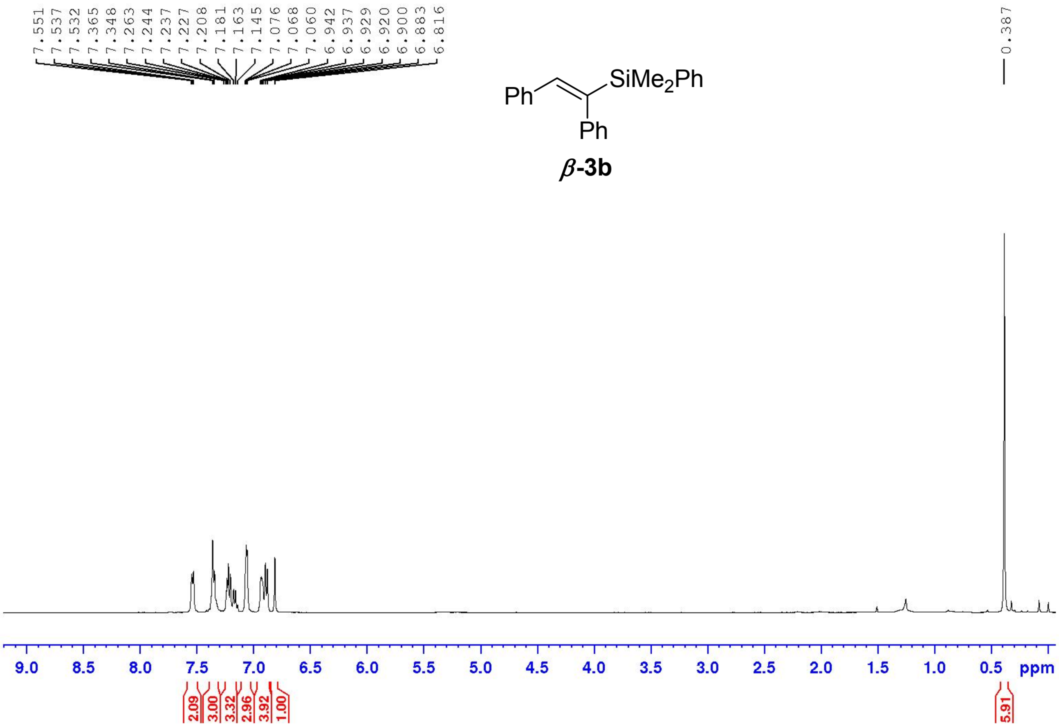
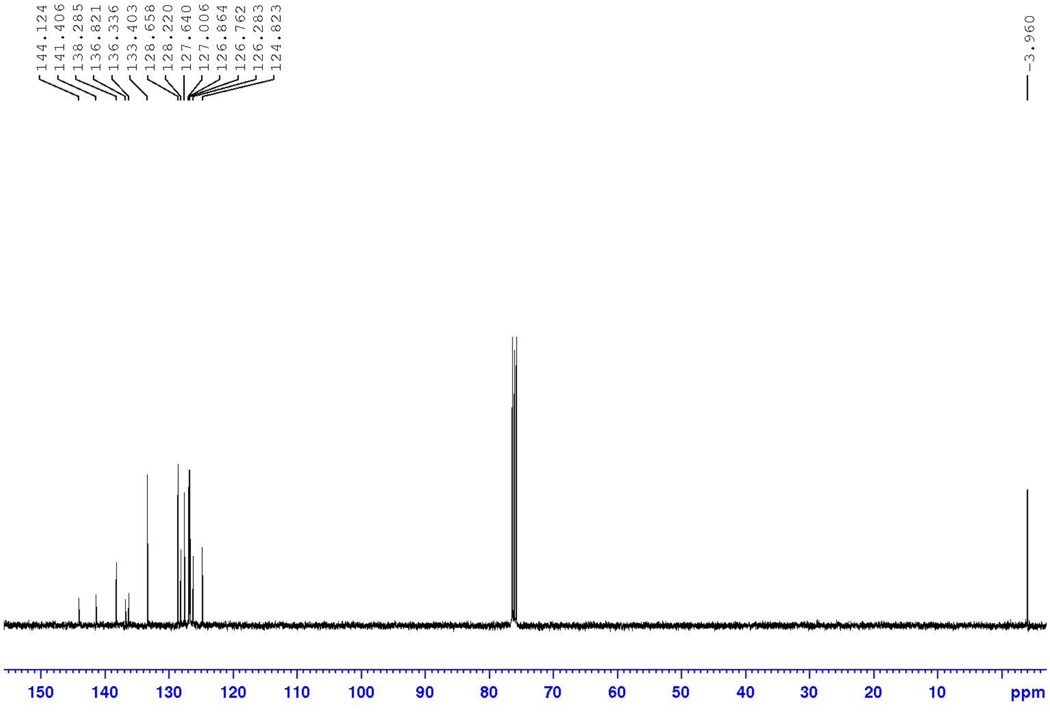
7.558
7.365
7.357
7.334
7.315
7.295
7.241
7.214
7.197
6.805
6.135
6.117
6.101
1.943
1.579
1.563
0.434
0.303
Ph
SiMe2Ph
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.09
7.18
1.23
0.99
0.04
3.00
0.12
6.17
0.23

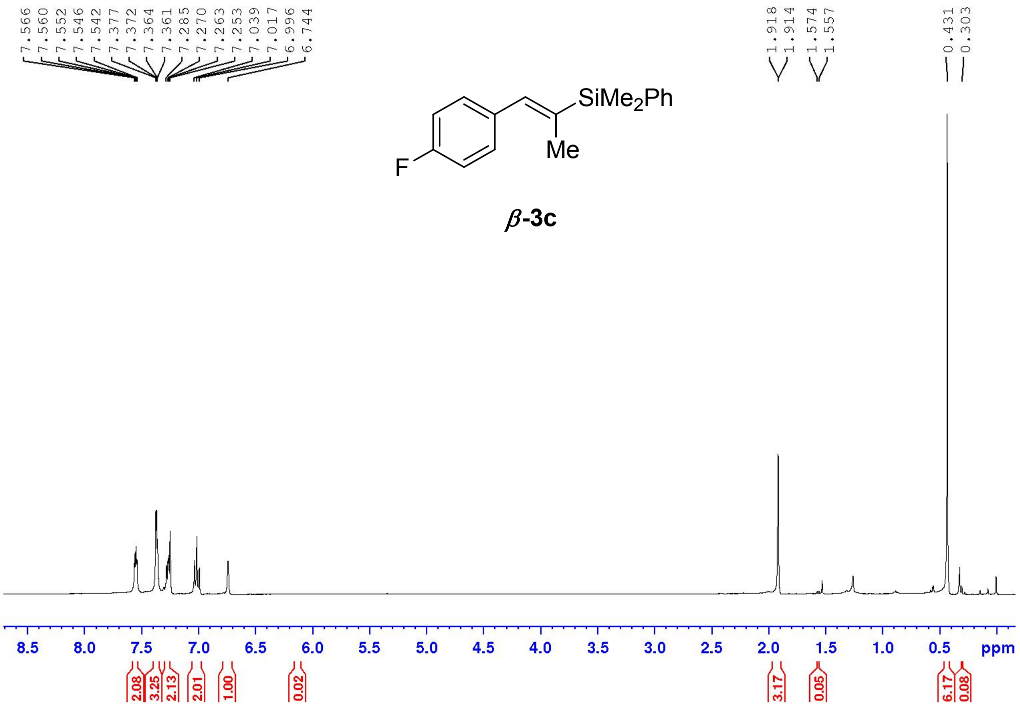
***β*-3a**

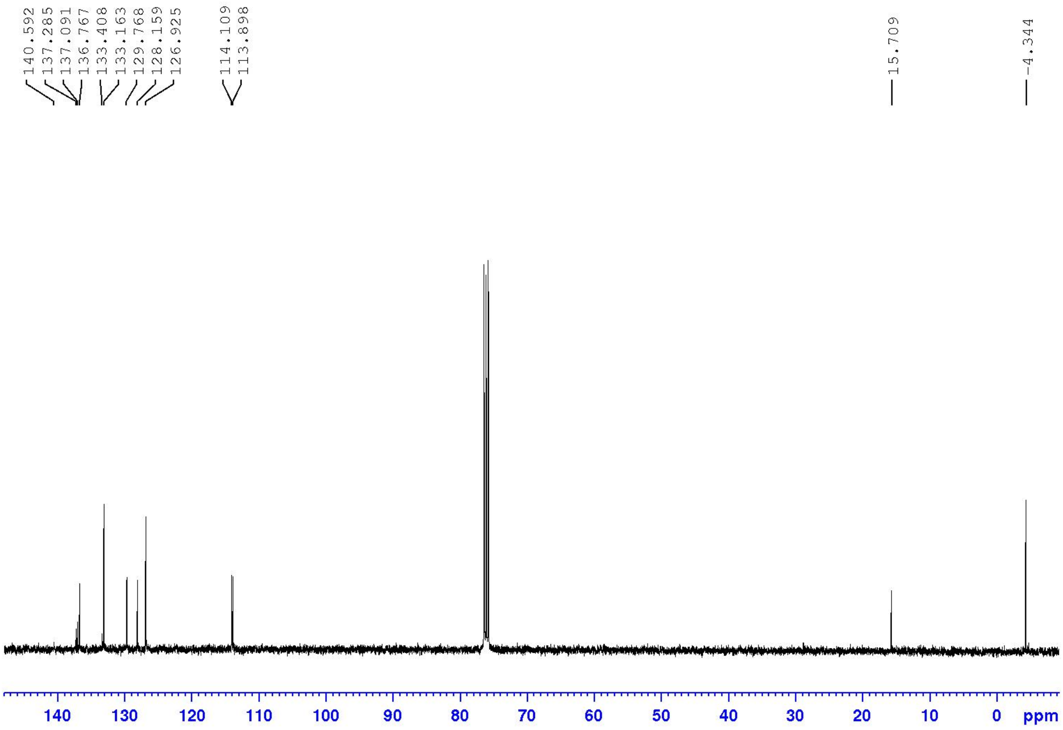

137.992
137.408
137.359
137.260
133.193
128.160
128.112
127.155
126.908
125.723
15.809
-4.298
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

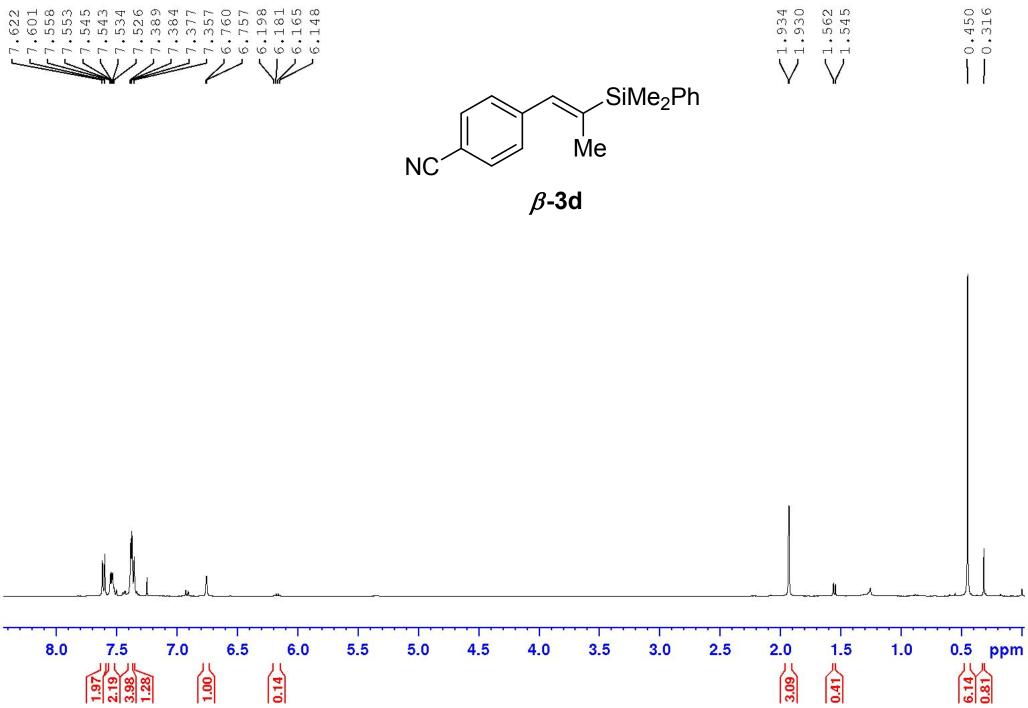

7.551
7.537
7.532
7.365
7.348
7.263
7.244
7.237
7.227
7.208
7.181
7.163
7.145
7.076
7.068
7.060
6.942
6.937
6.929
6.920
6.900
6.883
6.816
0.387
Ph
SiMe2Ph
Ph
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.09
3.00
3.32
2.96
3.92
1.00
5.91

***β*-3b**

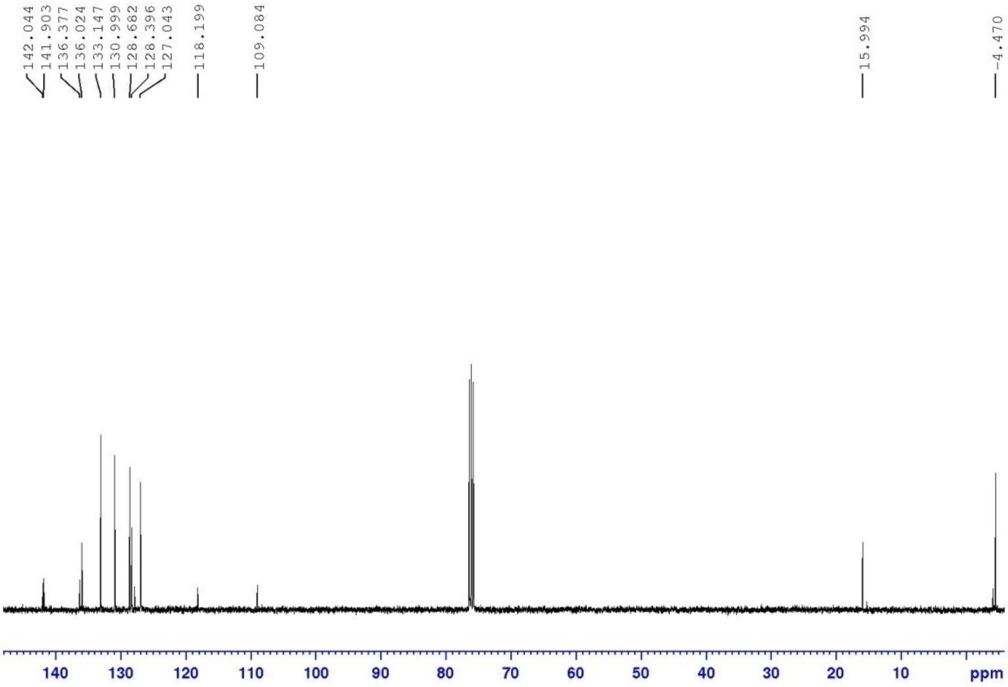

144.124
141.406
138.285
136.821
136.336
133.403
128.658
128.220
127.640
127.006
126.864
126.762
126.283
124.823
-3.960
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

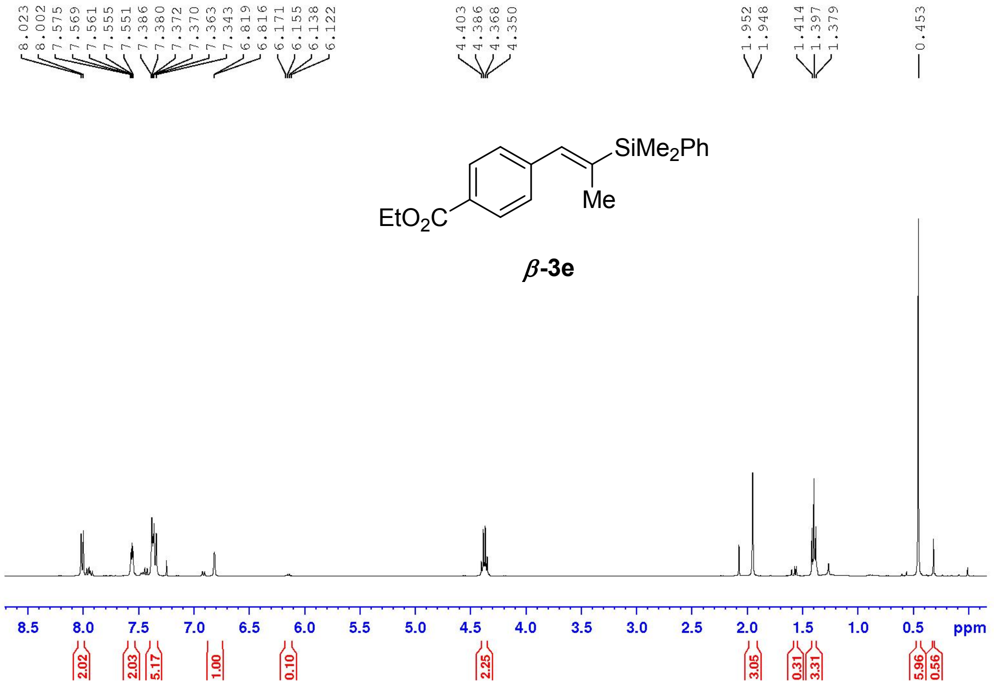

7.566
7.560
7.552
7.546
7.542
7.377
7.372
7.364
7.361
7.285
7.270
7.263
7.253
7.039
7.017
6.996
6.744
1.918
1.914
1.574
1.557
0.431
0.303
SiMe$_2$Ph
Me
F
β-**3c**
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
3.25
2.13
2.01
1.00
0.02
3.17
0.05
6.17
0.08


140.592
137.285
137.091
136.767
133.408
133.163
129.768
128.159
126.925
114.109
113.898
15.709
-4.344
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

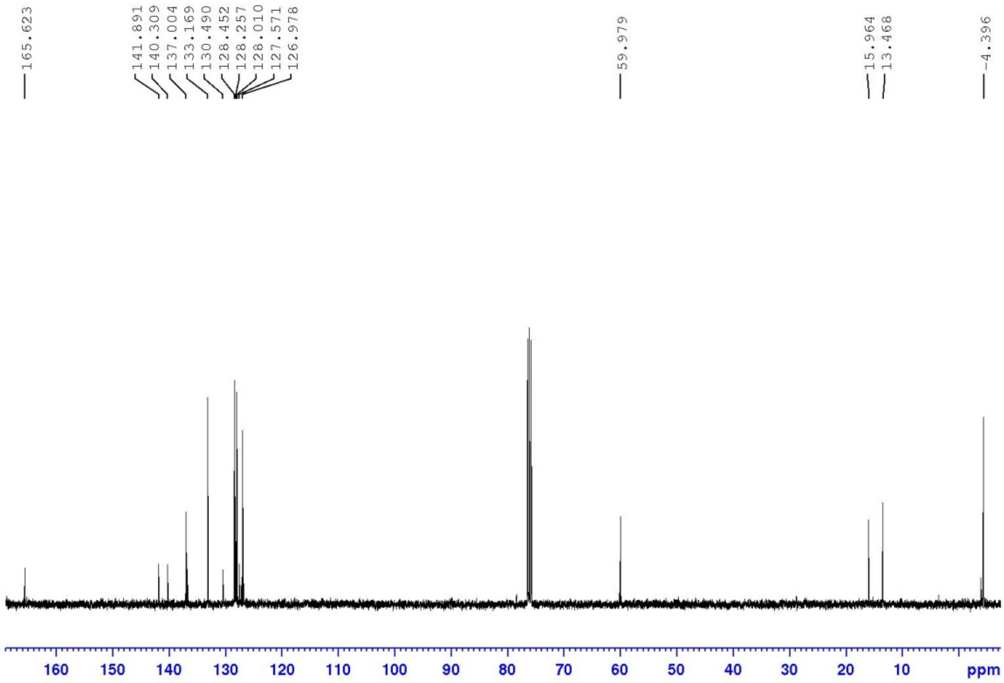

7.622
7.601
7.558
7.553
7.545
7.543
7.534
7.526
7.389
7.384
7.377
7.357
6.760
6.757
6.198
6.181
6.165
6.148
1.934
1.930
1.562
1.545
0.450
0.316
SiMe2Ph
NC
Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
2.19
3.98
1.28
1.00
0.14
3.09
0.41
6.14
0.81

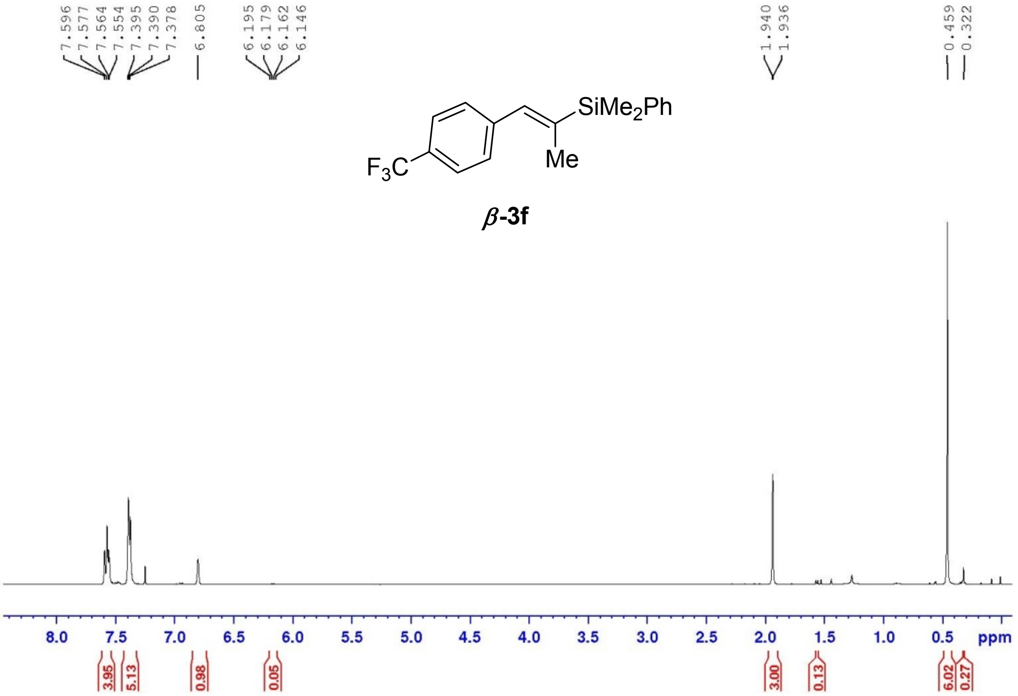
***β*-3d**


142.044
141.903
136.377
136.024
133.147
130.999
128.682
128.396
127.043
118.199
109.084
15.994
-4.470
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

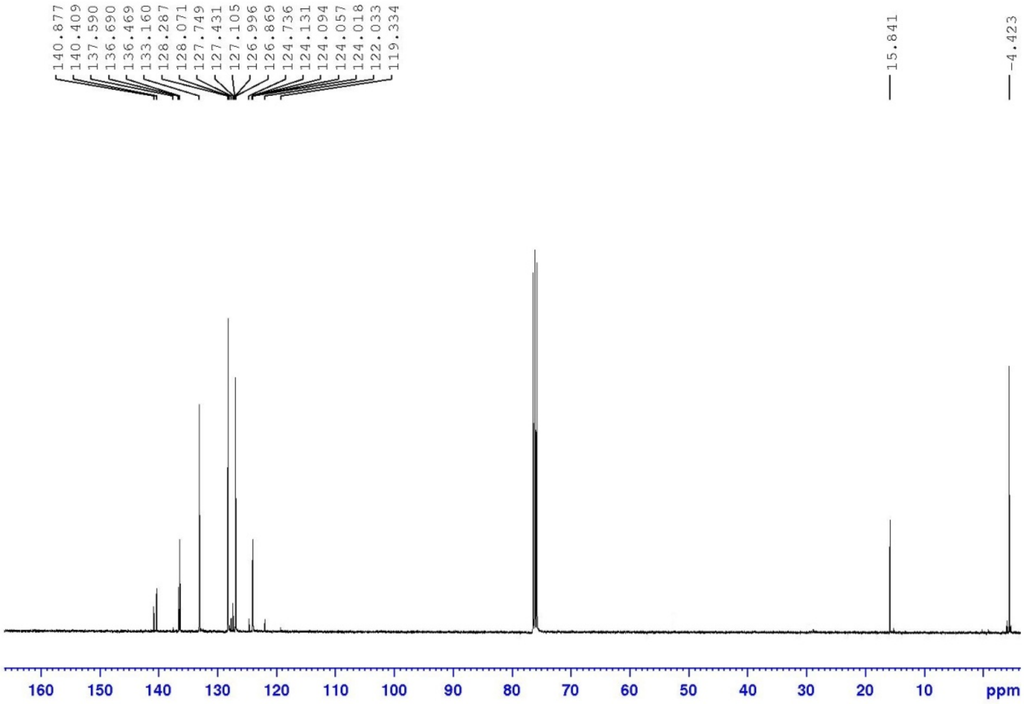

8.023
8.002
7.575
7.569
7.561
7.555
7.551
7.386
7.380
7.372
7.370
7.363
7.343
6.819
6.816
6.171
6.155
6.138
6.122
4.403
4.386
4.368
4.350
1.952
1.948
1.414
1.397
1.379
0.453
SiMe2Ph
Me
EtO2C
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
2.03
5.17
1.00
0.10
2.25
3.05
0.31
3.31
5.96
0.56

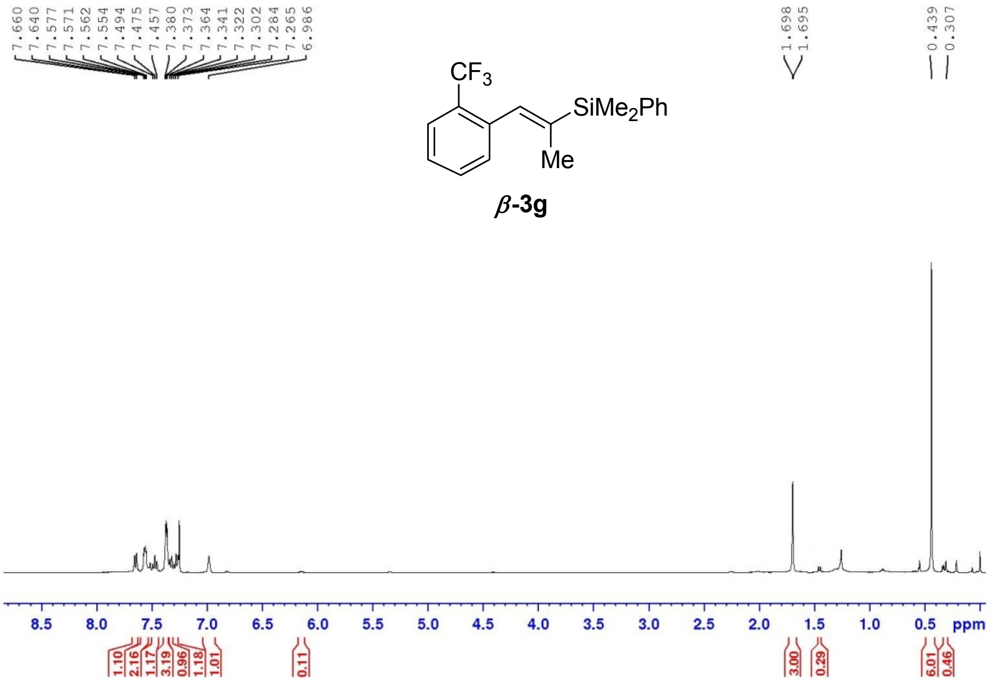
β-**3e**


165.623
141.891
140.309
137.004
133.169
130.490
128.452
128.257
128.010
127.571
126.978
59.979
15.964
13.468
-4.396
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

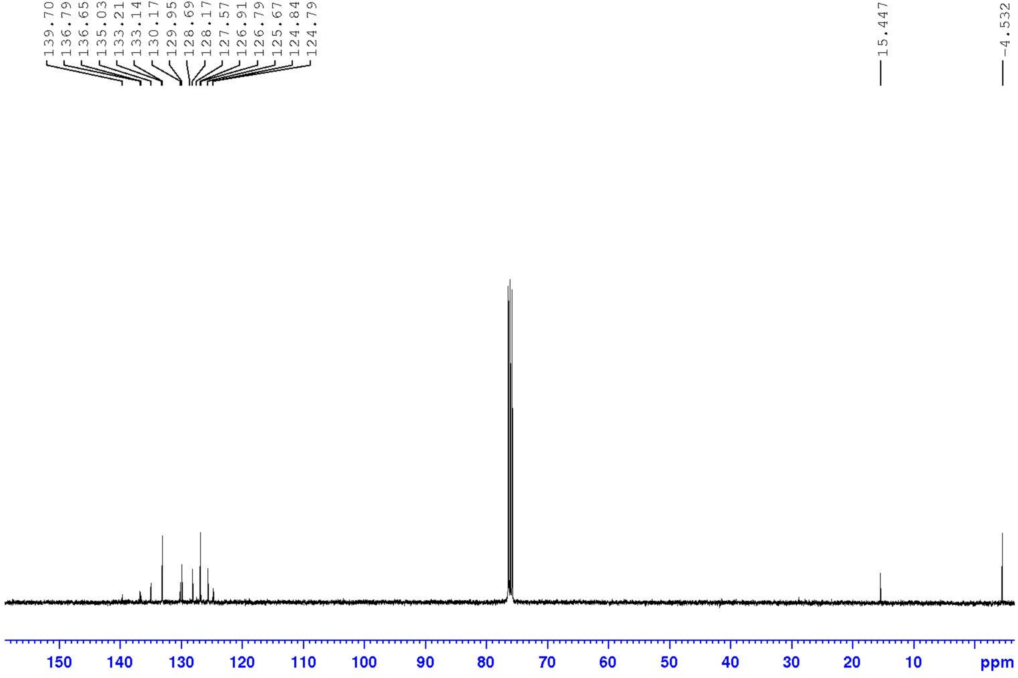

β-3f

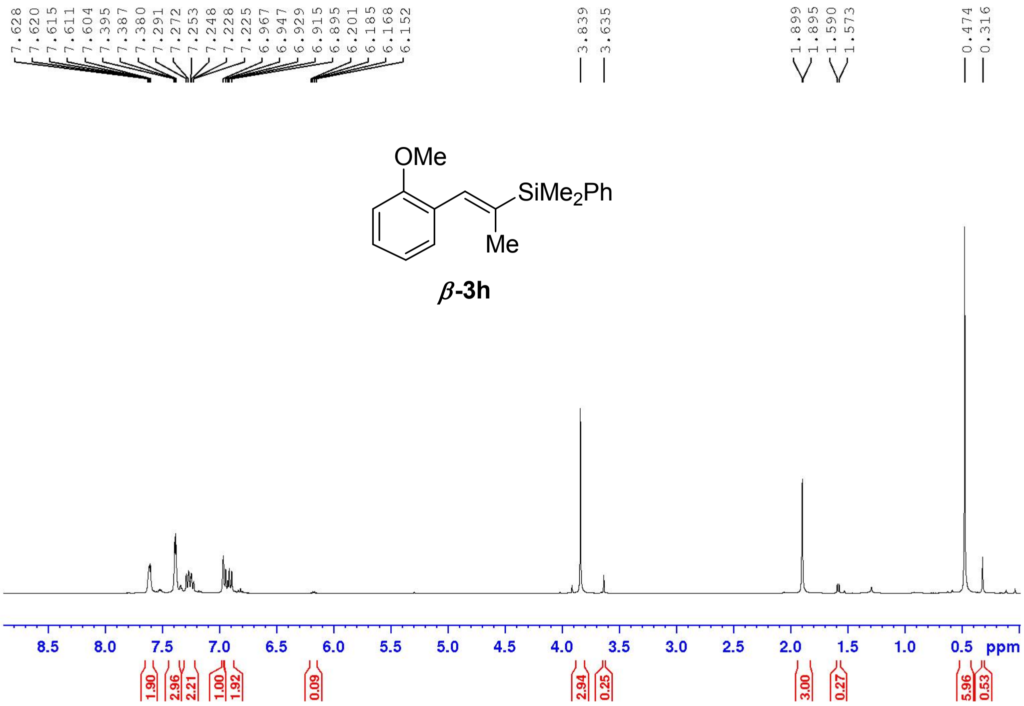
7.596
7.577
7.564
7.554
7.395
7.390
7.378
6.805
6.195
6.179
6.162
6.146
1.940
1.936
0.459
0.322
SiMe$_2$Ph
F$_3$C
Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.95
5.13
0.98
0.05
3.00
0.13
6.02
0.27


140.877
140.409
137.590
136.690
136.469
133.160
128.287
128.071
127.749
127.431
127.105
126.996
126.869
124.736
124.131
124.094
124.057
124.018
122.033
119.334
15.841
-4.423
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

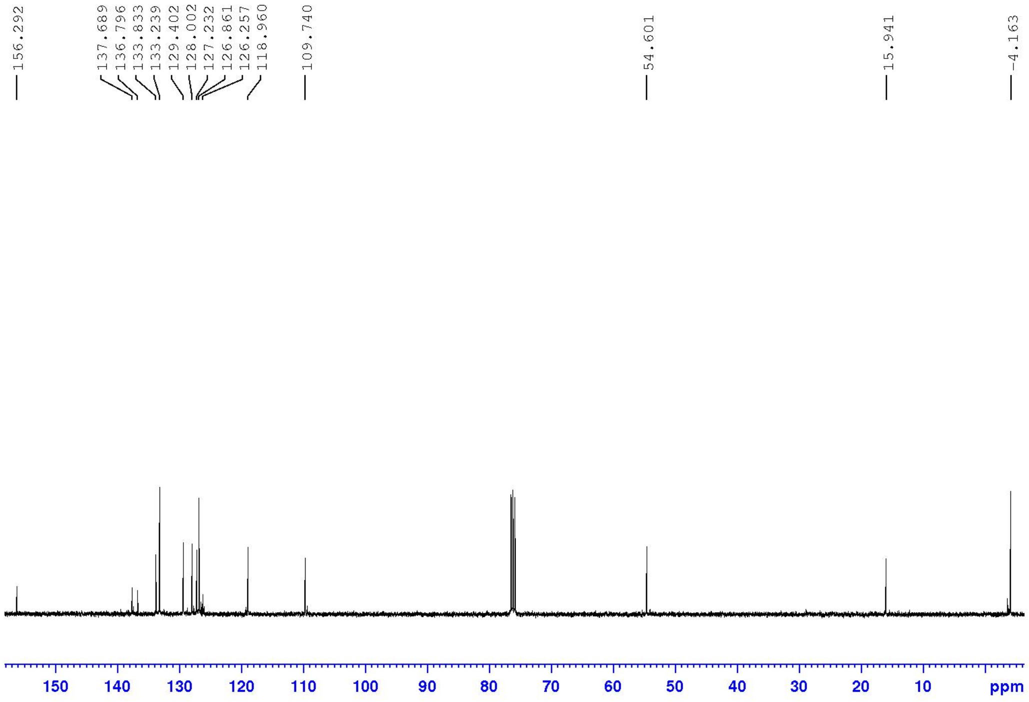

7.660
7.640
7.577
7.571
7.562
7.554
7.494
7.475
7.457
7.380
7.373
7.364
7.341
7.322
7.302
7.284
7.265
6.986
1.698
1.695
0.439
0.307
CF3
SiMe2Ph
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.10
2.16
1.17
3.19
0.96
1.18
1.01
0.11
3.00
0.29
6.01
0.46

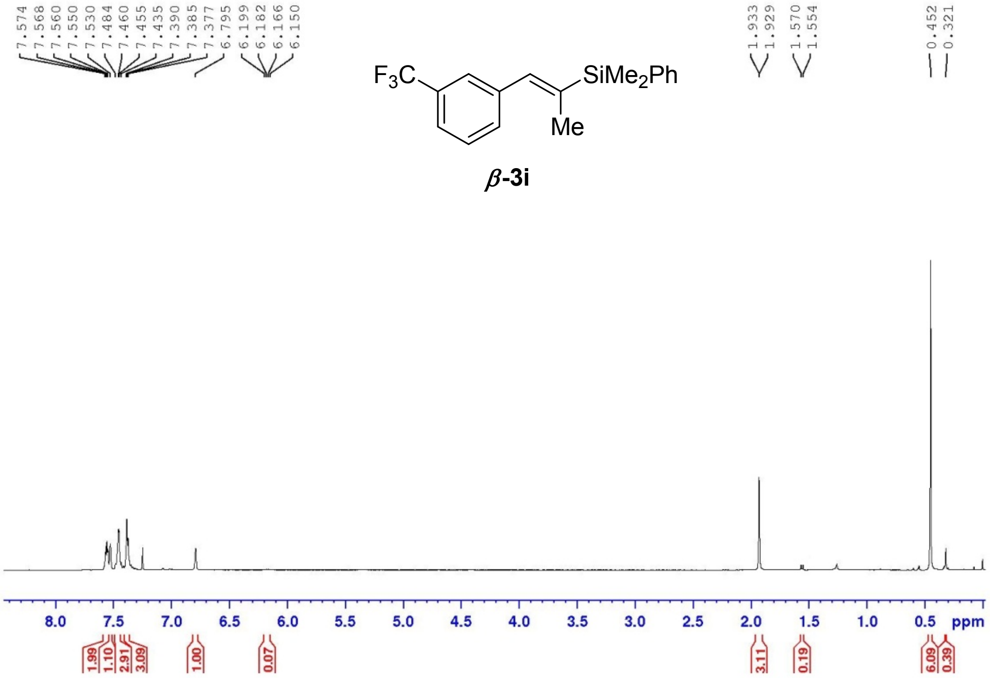
***β*-3g**


139.703
136.799
136.656
135.037
133.215
133.140
130.175
129.955
128.694
128.178
127.571
126.915
126.794
125.674
124.846
124.794
15.447
-4.532
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

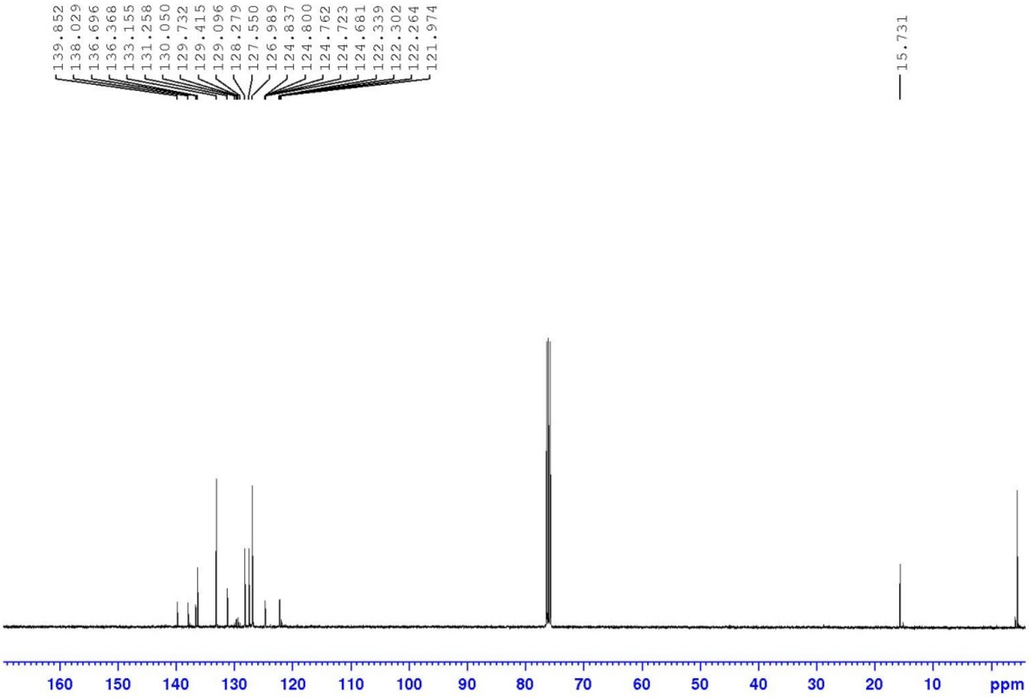

7.628
7.620
7.615
7.611
7.604
7.395
7.387
7.380
7.291
7.272
7.253
7.248
7.228
7.225
6.967
6.947
6.929
6.915
6.895
6.201
6.185
6.168
6.152
3.839
3.635
1.899
1.895
1.590
1.573
0.474
0.316
OMe
SiMe2Ph
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.90
2.96
2.21
1.00
1.92
0.09
2.94
0.25
3.00
0.27
5.96
0.53

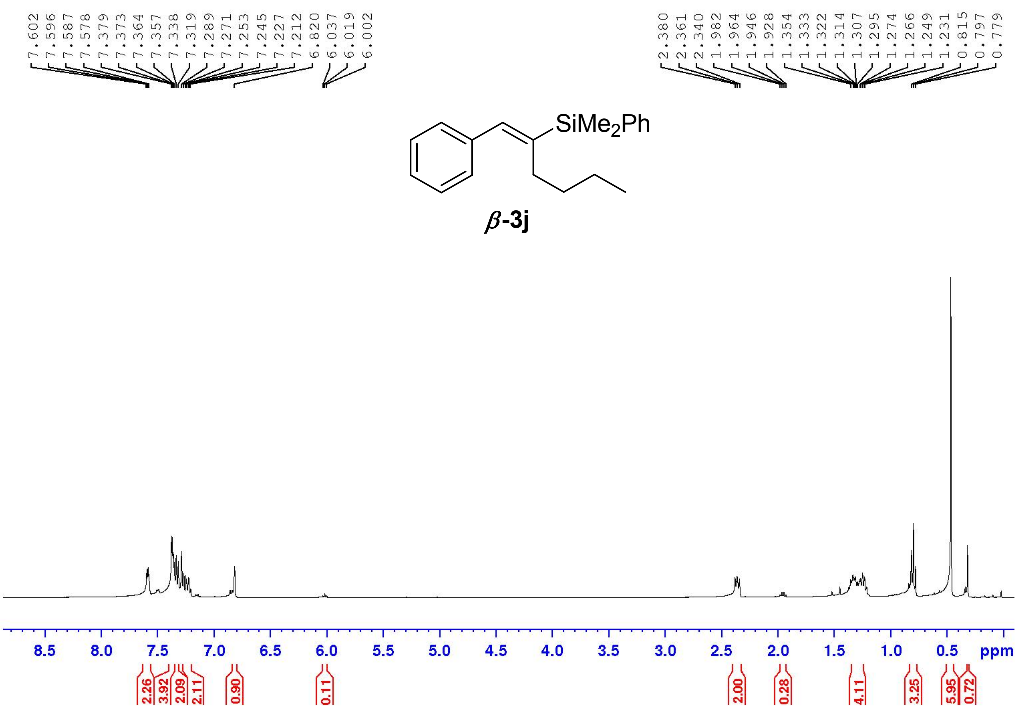
***β*-3h**


156.292
137.689
136.796
133.833
133.239
129.402
128.002
127.232
126.861
126.257
118.960
109.740
54.601
15.941
-4.163
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

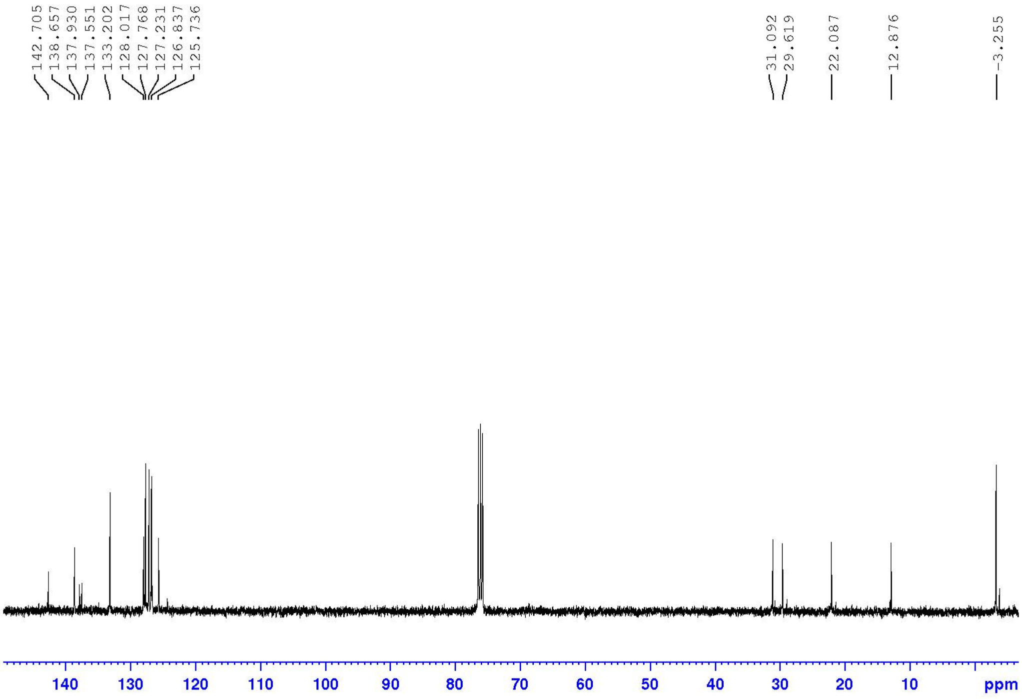

7.574
7.568
7.560
7.550
7.530
7.484
7.460
7.455
7.435
7.390
7.385
7.377
6.795
6.199
6.182
6.166
6.150
1.933
1.929
1.570
1.554
0.452
0.321
F3C
SiMe2Ph
Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
1.10
2.91
3.09
1.00
0.07
3.11
0.19
6.09
0.39

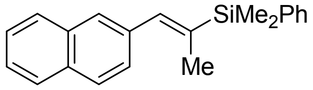
β-3i


139.852
138.029
136.696
136.368
133.155
131.258
130.050
129.732
129.415
129.096
128.279
127.550
126.989
124.837
124.800
124.762
124.723
124.681
122.339
122.302
122.264
121.974
15.731
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

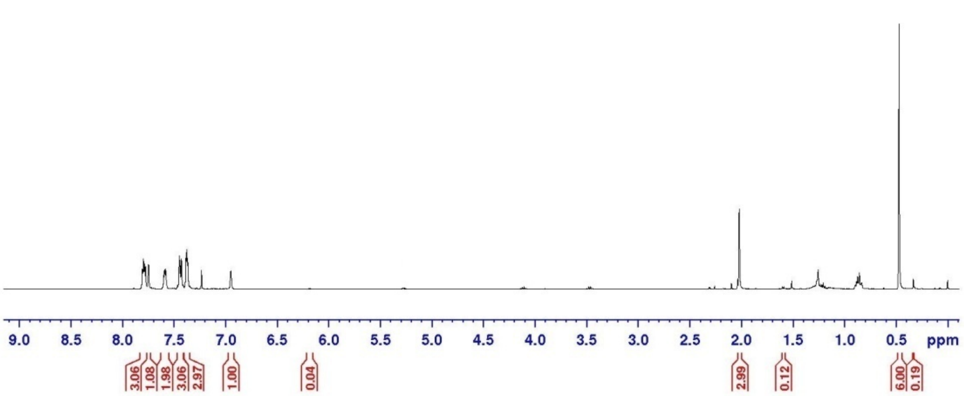

7.602
7.596
7.587
7.578
7.379
7.373
7.364
7.357
7.338
7.319
7.289
7.271
7.253
7.245
7.227
7.212
6.820
6.037
6.019
6.002
2.380
2.361
2.340
1.982
1.964
1.946
1.928
1.354
1.333
1.322
1.314
1.307
1.295
1.274
1.266
1.249
1.231
0.815
0.797
0.779
SiMe2Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.26
3.92
2.09
2.11
0.90
0.11
2.00
0.28
4.11
3.25
5.95
0.72

β-**3j**


142.705
138.657
137.930
137.551
133.202
128.017
127.768
127.231
126.837
125.736
31.092
29.619
22.087
12.876
-3.255
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



β-**3k**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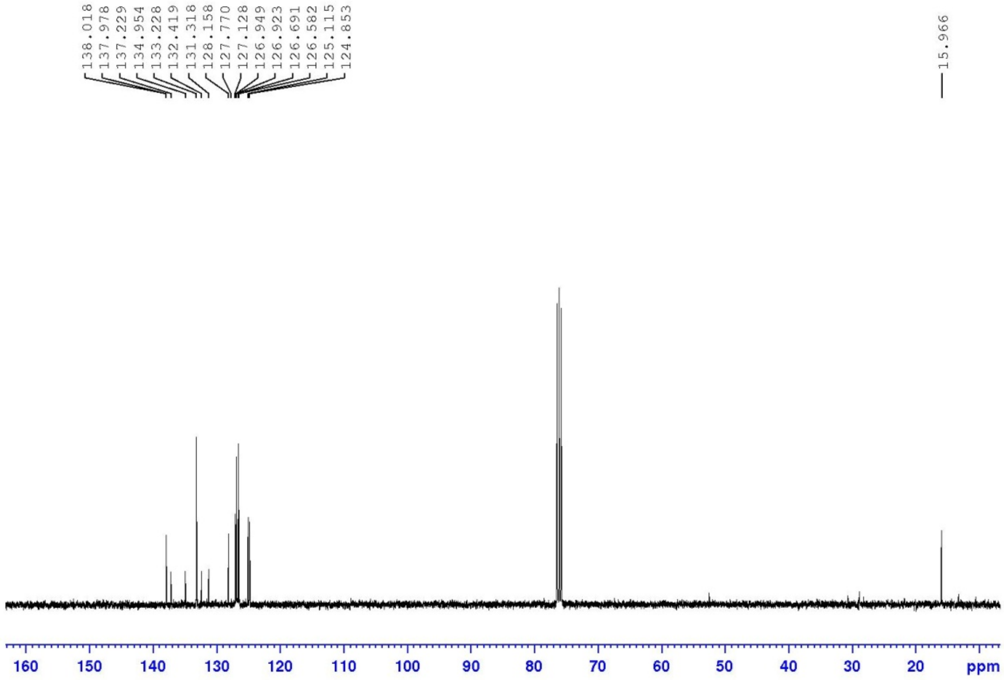
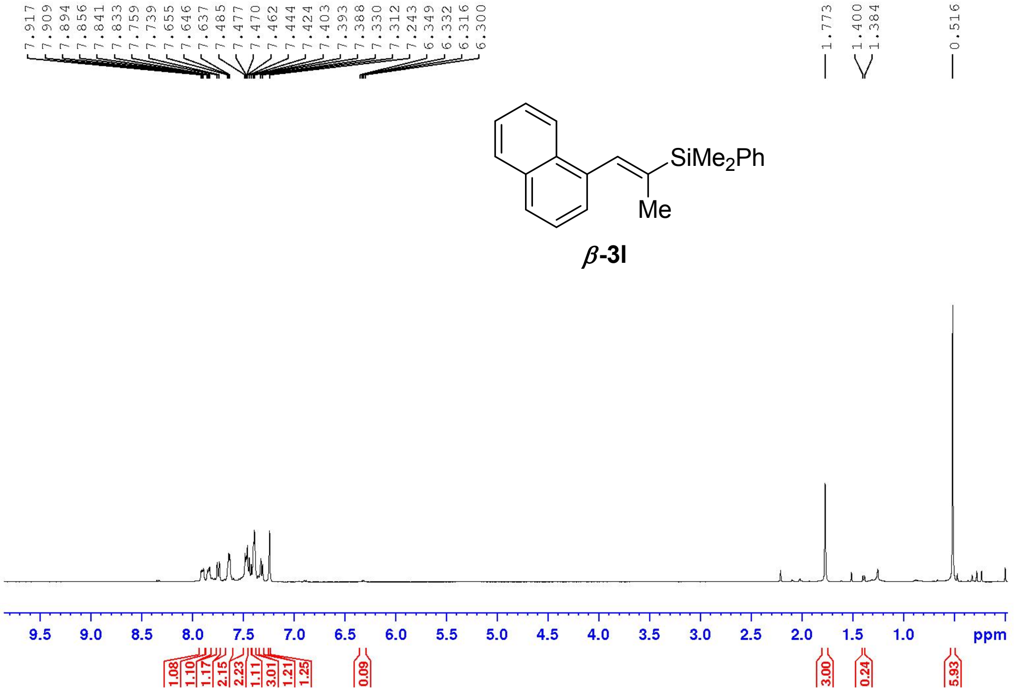
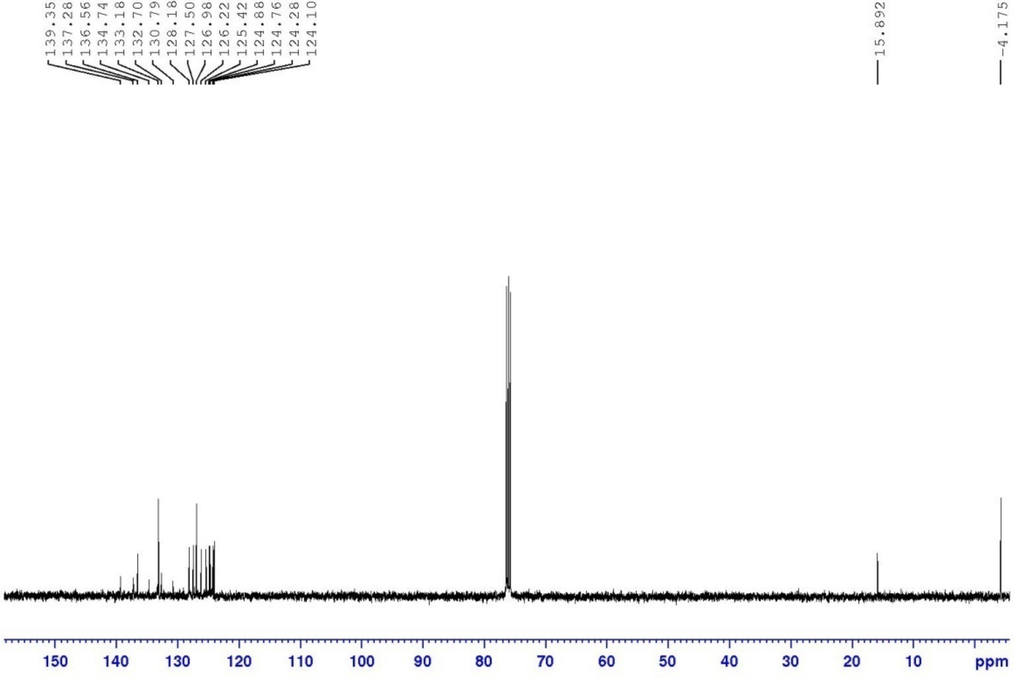
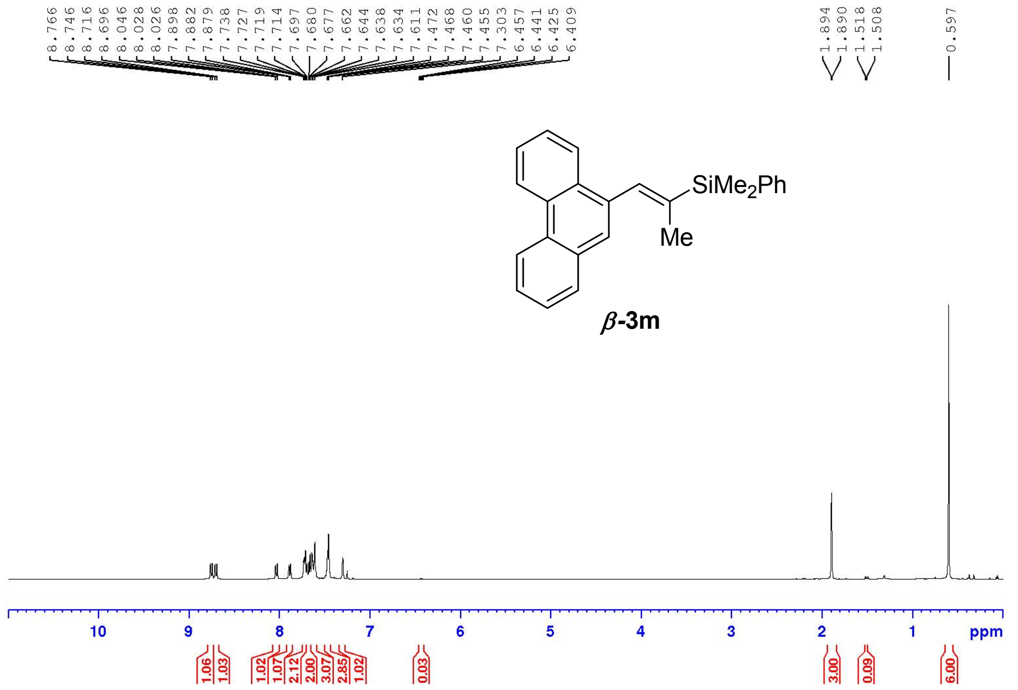
7.800
7.788
7.780
7.751
7.605
7.599
7.590
7.582
7.452
7.443
7.433
7.429
7.387
7.380
7.371
7.238
6.952
2.023
2.019
0.470
0.333
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.06
1.08
1.98
3.06
2.97
1.00
0.04
2.99
0.12
6.00
0.19

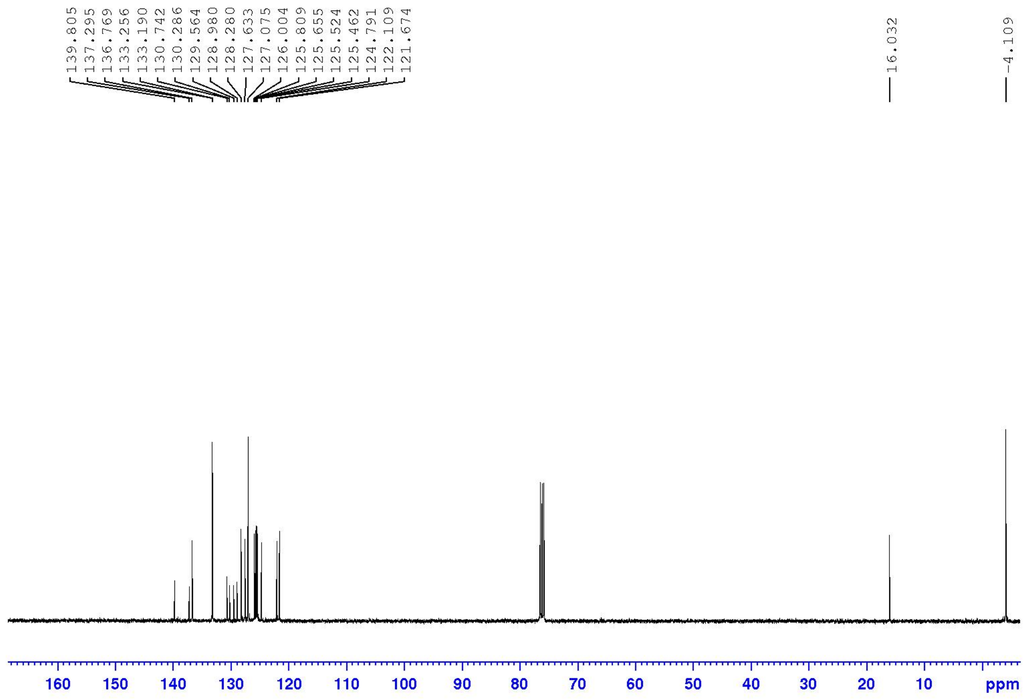

138.018
137.978
137.229
134.954
133.228
132.419
131.318
128.158
127.770
127.128
126.949
126.923
126.691
126.582
125.115
124.853
15.966
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

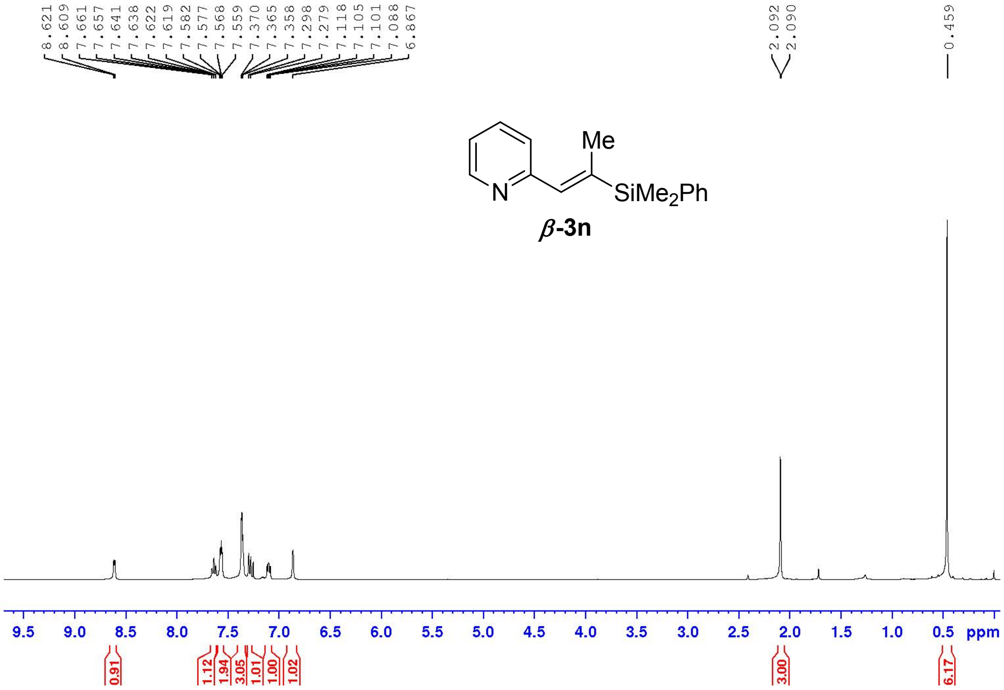

7.917
7.909
7.894
7.856
7.841
7.833
7.759
7.739
7.655
7.646
7.637
7.485
7.477
7.470
7.462
7.444
7.424
7.403
7.393
7.388
7.330
7.312
7.243
6.349
6.332
6.316
6.300
1.773
1.400
1.384
0.516
SiMe$_2$Ph
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.08
1.10
1.17
2.15
2.23
1.11
3.01
1.21
1.25
0.09
3.00
0.24
5.93

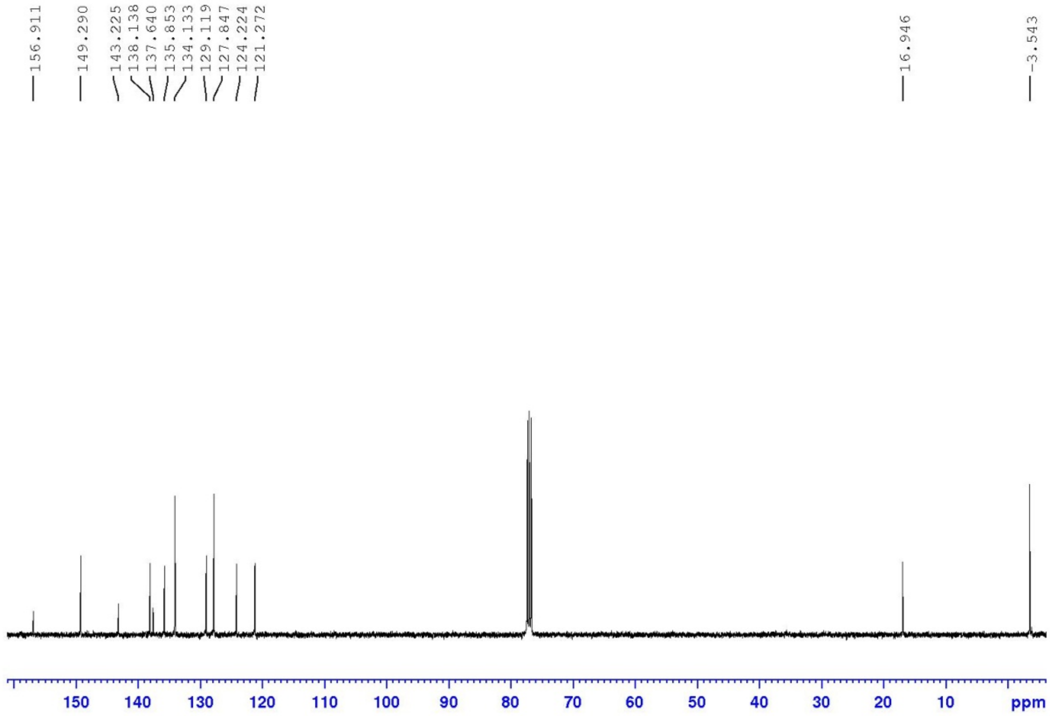
β-**3l**

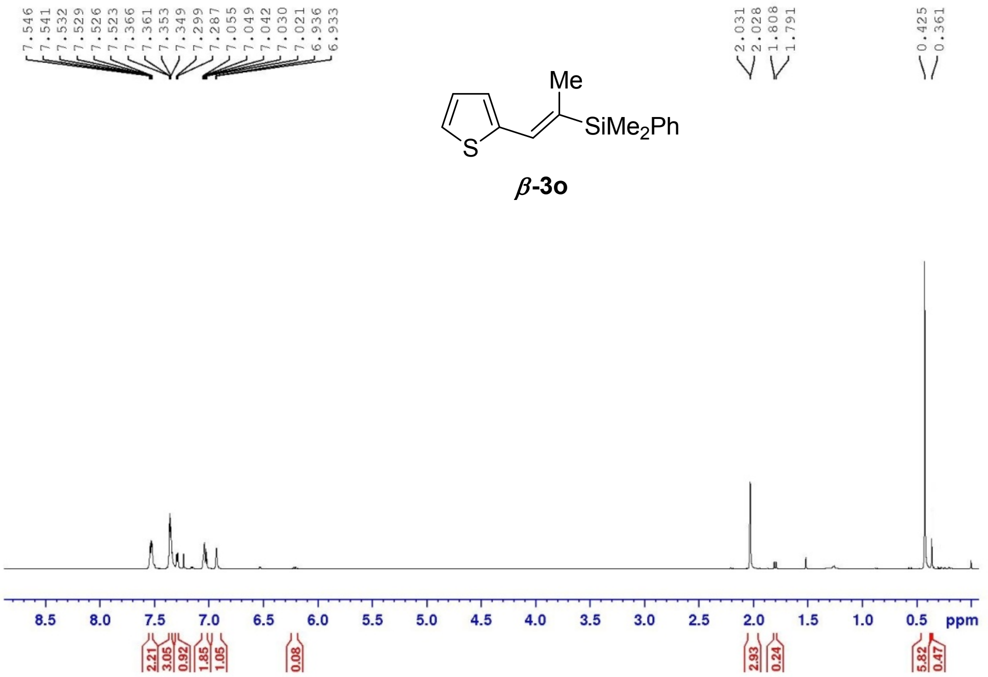

139.357
137.289
136.565
134.743
133.186
132.704
130.797
128.185
127.505
126.987
126.220
125.427
124.888
124.766
124.284
124.103
15.892
-4.175
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.766
8.746
8.716
8.696
8.046
8.028
8.026
7.898
7.882
7.879
7.738
7.727
7.719
7.714
7.697
7.680
7.677
7.662
7.644
7.638
7.634
7.611
7.472
7.468
7.460
7.455
7.303
6.457
6.441
6.425
6.409
1.894
1.890
1.518
1.508
0.597
SiMe$_2$Ph
Me
β-**3m**
10
9
8
7
6
5
4
3
2
1
ppm
1.06
1.03
1.02
1.07
2.12
2.00
3.07
2.85
1.02
0.03
3.00
0.09
6.00

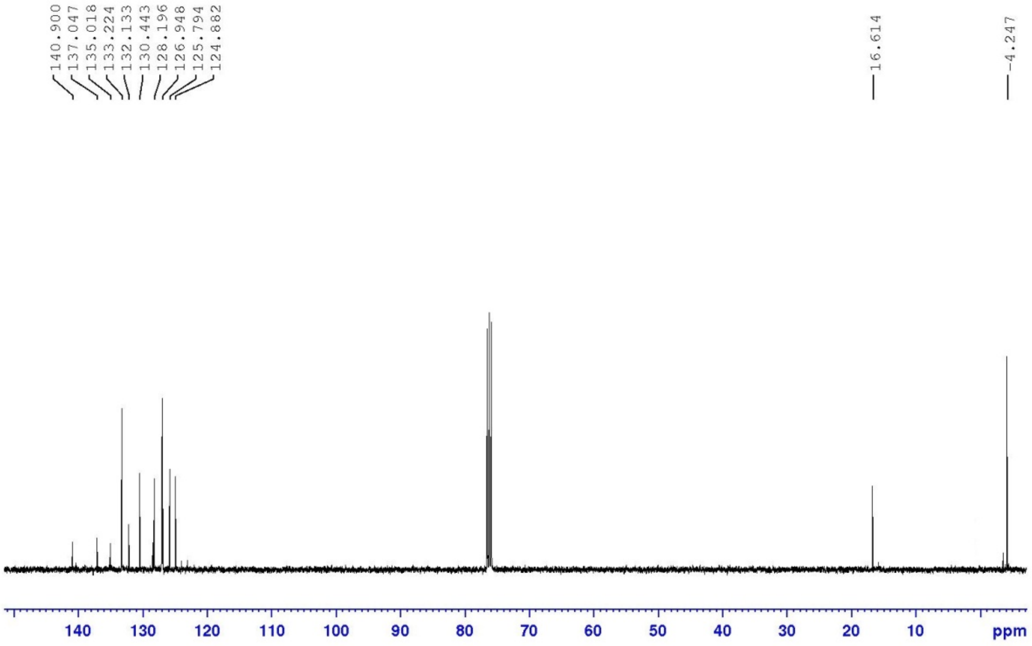

139.805
137.295
136.769
133.256
133.190
130.742
130.286
129.564
128.980
128.280
127.633
127.075
126.004
125.809
125.655
125.524
125.462
124.791
122.109
121.674
16.032
-4.109
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

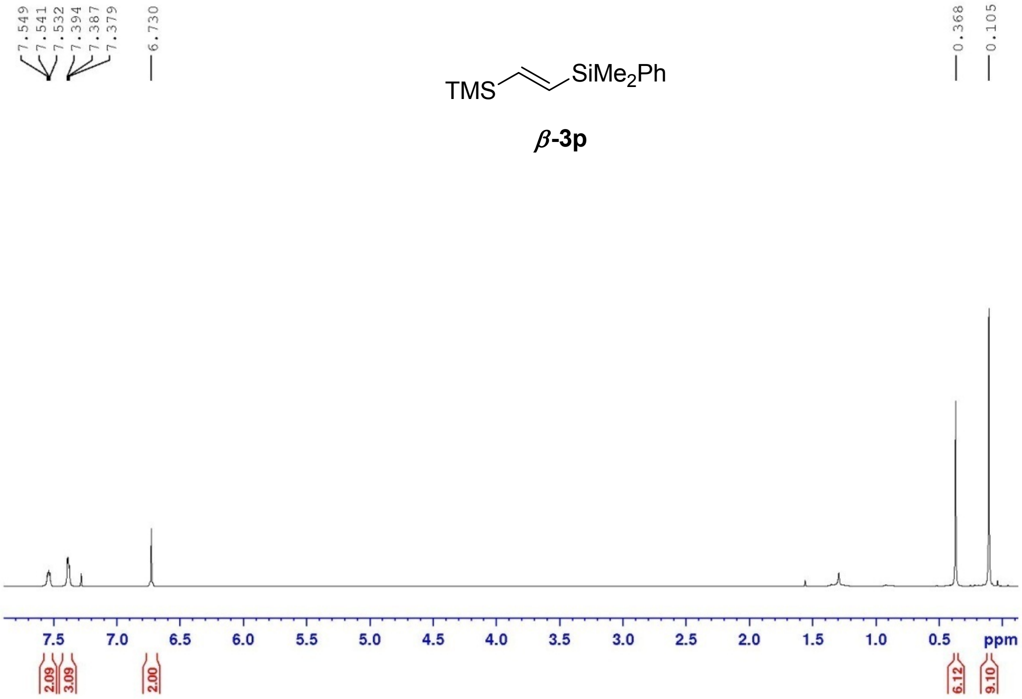

8.621
8.609
7.661
7.657
7.641
7.638
7.622
7.619
7.582
7.577
7.568
7.559
7.370
7.365
7.358
7.298
7.279
7.118
7.105
7.101
7.088
6.867
2.092
2.090
0.459
Me
N
SiMe2Ph
β-3n
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.91
1.12
1.94
3.05
1.01
1.00
1.02
3.00
6.17


156.911
149.290
143.225
138.138
137.640
135.853
134.133
129.119
127.847
124.224
121.272
16.946
-3.543
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.546
7.541
7.532
7.529
7.526
7.523
7.366
7.361
7.353
7.349
7.299
7.287
7.055
7.049
7.042
7.030
7.021
6.936
6.933
2.031
2.028
1.808
1.791
0.425
0.361
Me
S
SiMe2Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.21
3.05
0.92
1.85
1.05
0.08
2.93
0.24
5.82
0.47

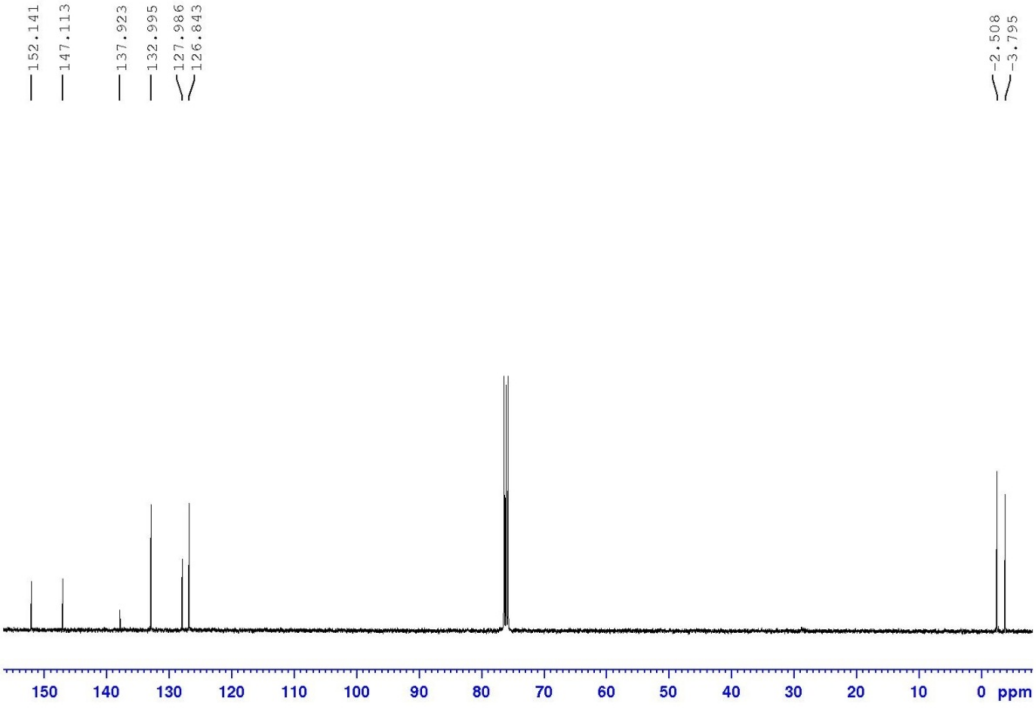
***β*-3o**


140.900
137.047
135.018
133.224
132.133
130.443
128.196
126.948
125.794
124.882
16.614
-4.247
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

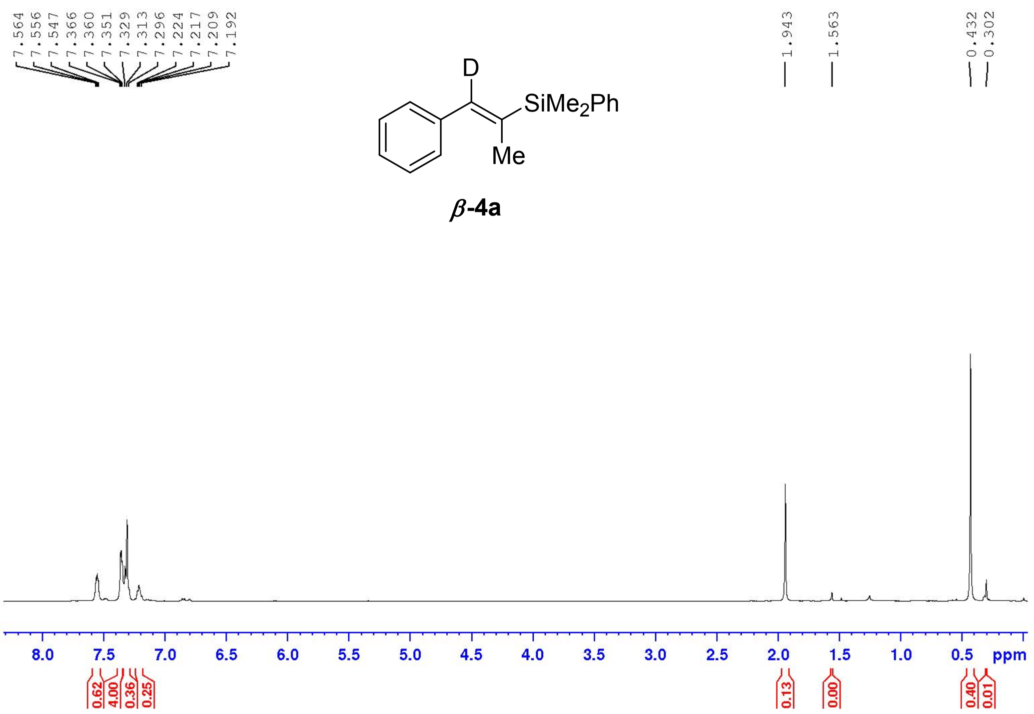


***β*-3p**

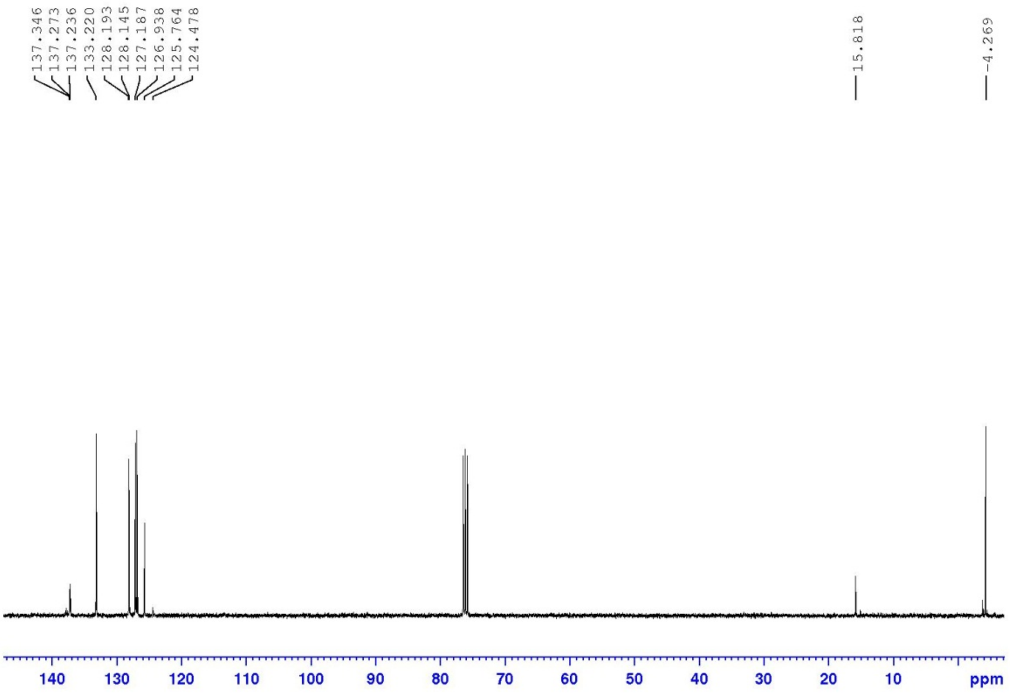
7.549
7.541
7.532
7.394
7.387
7.379
6.730
0.368
0.105
TMS
SiMe2Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.09
3.09
2.00
6.12
9.10



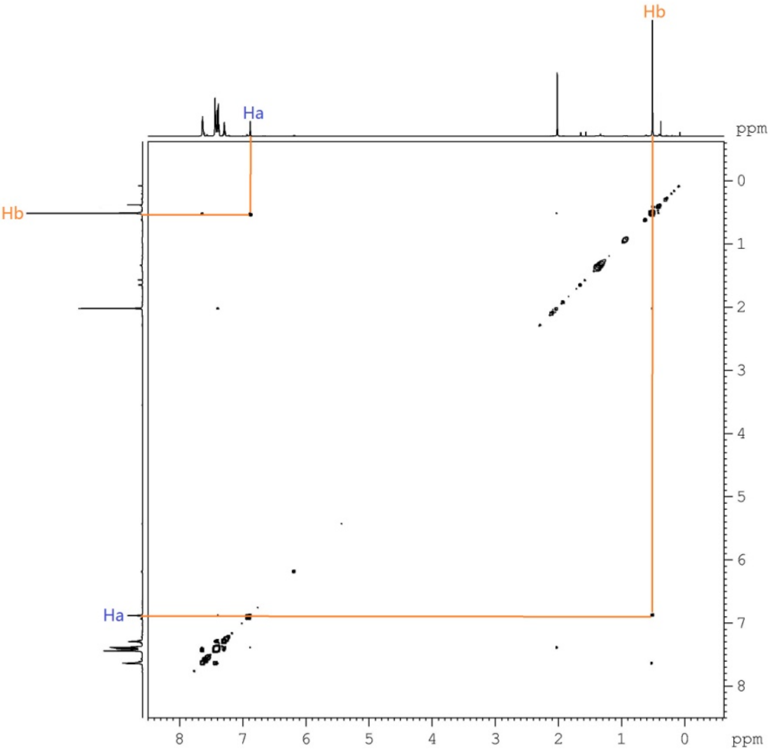
152.141
147.113
137.923
132.995
127.986
126.843
-2.508
-3.795
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

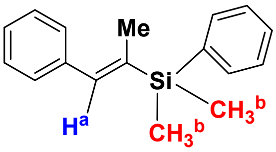

7.564
7.556
7.547
7.366
7.360
7.351
7.329
7.313
7.296
7.224
7.217
7.209
7.192
1.943
1.563
0.432
0.302
D
SiMe2Ph
Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.62
4.00
0.36
0.25
0.13
0.00
0.40
0.01

***β*-4a**


137.346
137.273
137.236
133.220
128.193
128.145
127.187
126.938
125.764
124.478
15.818
-4.269
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

NOESY spectrum of *β*-3a





NOESY spectrum of *β*-3n