Supporting Information:

The Rhodium-Catalysed Synthesis of Pyrrolidine-Substituted (Trialkylsilyloxy)Acrylic Esters

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General Experimental:

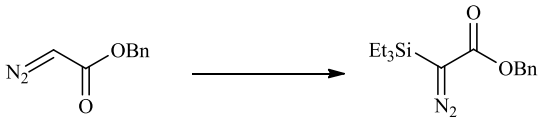
Drying and purification of solvents was performed by standard techniques. Toluene was dried by refluxing over Solvona/benzophenone and distillation. All reagents were purchased from Sigma-Aldrich, Acros or Alfa Aesar and were used without further purification. All product mixtures were analysed by thin layer chromatography using aluminum foil TLC plates with a fluorescent indicator from Merck. UV-active compounds were detected with a UV lamp (λ = 254 nm). For flash column chromatography basic alumina (Al_2O_3) was used as stationary phase. ^1H and ^{13}C NMR spectra were recorded either on a Varian V-NMRS 600 or a Varian V-NMRS 400 in deuterated chloroform at 25 °C. Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The IR-Spectra (KBr-pellet or neat liquids) were recorded with a Perkin Elmer 100 FT/IR spectrometer. The wave numbers of the absorption peaks are reported in cm^{-1}. Mass spectra were recorded on a Finnigan MAT 212 spectrometer (EI, 70 eV; CI, 100 eV). The atomic mass of the molecular ion and the fragments per elementary charge were reported in dimensionless quantities. The intensities were given in percent relative to the base peak. High resolution mass spectra (HRMS) were recorded on a Finnigan MAT 95 spectrometer. The elementary analysis measurements were performed by a machine *Vario El* from Elementar. The values were reported in weight percent. The compounds were considered to be pure in case of Δ(C, H, N) $\leq$ 0.4%. *N*-benzyl-2-pyrrolidinone[1] and *N*-TBDMS-2-pyrrolidinone[2] were prepared according to literature procedures. The α-diazoacetates were prepared in accordance with our previous publications.[3-5]

Specific Experimental:

General Procedure 1 for the synthesis of α-silyl α-diazoacetates:

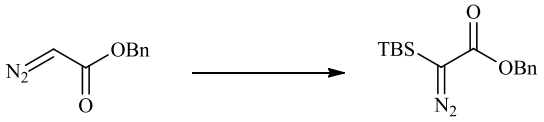
To a solution of diazoacetate (10 mmol) in THF at –78 °C was added DIPEA (10 mmol) followed by the (trialkylsilyl)trifluoromethanesulfonate (10 mmol) and the resulting solution allowed to warm to 0 °C over 1 hour and stirred at this temperature for 16 h. After this time the reaction mixture was filtered through a plug of celite, flushed with Et_2O and the solvent evaported. Column chromatography over basic alumina using 2% Et_2O/pentane afforded the corresponding α-silyl α-diazoacetates.

Benzyl 2-diazo-2-(triethylsilyl)acetate (1b)[3-5]



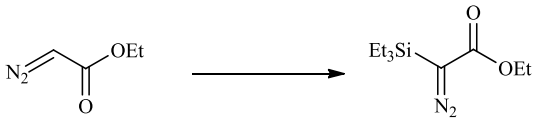
General procedure 1 afforded the title compound as a yellow oil (2.67 g, 92% yield); ^1H NMR ($CDCl_3$, 400 MHz,) δ = 7.29 – 7.39 (m, 5H), 5.19 (s, 2H), 0.97 (t, 9H, *J* = 8.0 Hz), 0.75 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5, 136.2, 128.5, 128.1, 128.0, 66.5, 7.2, 3.5; IR (neat, cm^{-1}) 2959, 2934, 2093, 1692, 1470, 1257, 1075, 840; MS (EI, 70 eV) *m/z* = 290 (M^+, 15), 261 (35), 199 (62), 175 (59), 115 (27), 91 (100); Anal. Calcd for $C_{15}H_{22}N_2O_2Si$: C, 62.03; H, 7.63; N, 9.64; Found: C, 61.99; H, 7.66; N, 9.57.

Benzyl 2-diazo-2-(*tert*-butyldimethylsilyl)acetate (1c)[3-5]



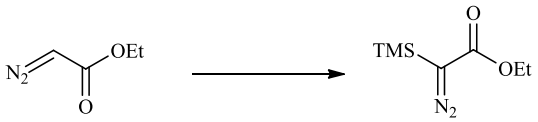
General procedure 1 afforded the title compound as a yellow oil (2.58 g, 89% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.30 – 7.37 (m, 5H), 5.17 (s, 2H), 0.94 (s, 9H), 0.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.8, 136.3, 128.6, 128.3, 128.26, 66.5, 26.5, 18.9, –6.1; IR (neat, cm^{-1}) 2946, 2861, 2090, 1690, 1463, 1259, 1074, 826; MS (EI, 70 eV) *m/z* = 290 (M^+, 28), 233 (56), 175 (72), 115 (32), 115 (27), 91 (100), 57 (45); Anal. Calcd for $C_{15}H_{22}N_2O_2Si$: C, 62.03; H, 7.63; N, 9.64; Found: C, 62.07; H, 7.64; N, 9.59.

Ethyl 2-diazo-2-(triethylsilyl)acetate (1a)[4,6]



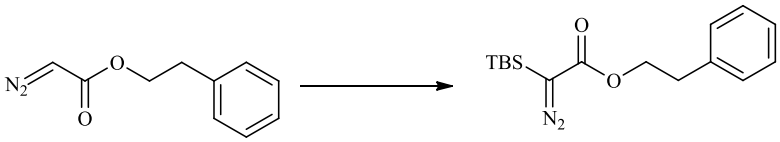
General procedure 1 afforded the title compound as a yellow oil (2.26 g, 99% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 4.15 (q, 2H, *J* = 7.1 Hz), 1.22 (t, 3H, *J* = 7.1 Hz), 0.95 (t, 9H, *J* = 8.0 Hz), 0.71 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 169.5, 60.5, 14.3, 6.9, 3.1.

Ethyl 2-diazo-2-(trimethylsilyl)acetate (1d)[4]



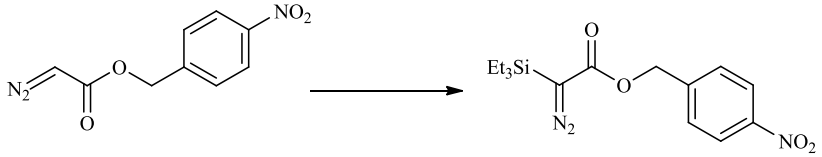
General procedure 1 afforded the title compound as a yellow oil (1.67 g, 89% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.15 (dq, 2H, *J* = 0.8 and 7.2 Hz), 1.24 (dt, 3H, *J* = 0.8 and 7.2 Hz), 0.23 (d, 9H, *J* = 0.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.2, 60.7, 60.5, 14.3, –1.6.

Phenethyl 2-(*tert*-butyldimethylsilyl)-2-diazoacetate (1e)



General procedure 1 afforded the title compound as a yellow oil (2.71 g, 89% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.09 – 7.13 (m, 5H), 4.17 (t, 2H, *J* = 7.2 Hz), 2.76 (t, 2H, *J* = 7.2 Hz), 0.74 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5, 138.0, 129.1, 128.7, 126.8, 65.4, 35.7, 26.7, 19.1, –5.9; IR (neat, cm^{-1}) 2954, 2929, 2858, 2088, 1691, 1261, 1199, 1075, 839, 825, 746, 699; MS (CI methane): *m/z* = 305 (M+H, 13), 277 (42), 274 (34), 247 (10), 157 (19), 121 (13); Anal. calcd. For $C_{16}H_{24}N_2O_2Si$: C, 63.12; H, 7.94: N, 9.20. Found: C, 62.81; H, 7.74; N, 9.29.

4-Nitrobenzyl 2-diazo-2-(triethylsilyl)acetate (1f)



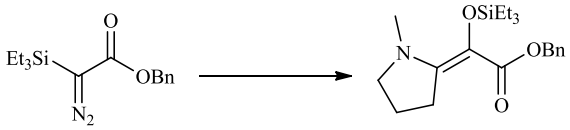
General procedure 1 afforded the title compound as a yellow oil that solidified on standing (2.75 g, 82% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 8.22 (d, 2H, *J* = 8.7 Hz), 7.50 (d, 2H, *J* = 8.7 Hz), 5.26 (s, 2H),

0.97 (t, 9H, J = 8.0 Hz), 0.75 (q, 6H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 168.9, 147.6, 143.5, 128.2, 123.8, 64.8, 60.4, 7.0, 3.1; IR (neat, cm^{-1}) 2949, 2879, 2086, 1677, 1520, 1344, 1256, 1199, 1070, 1003, 728; MS (CI methane): m/z = 335 (M^+, 12), 307 (20), 306 (100), 278 (15), 239 (16), 238 (96), 208 (31), 136 (34), 115 (60), 87 (73); HRMS (m/z) $C_{15}H_{21}O_4N_3Si$ Calcd. for 335.1296, found 335.1297.

General Procedure 2 for the synthesis of (Trialkylsilyloxy)Acrylic Esters:

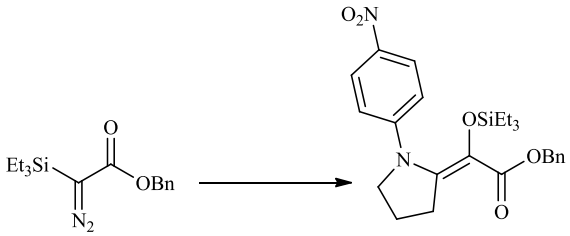
The trialkylsilyldiazoacetate **1** (0.55 mmol) was added dropwise to a solution of the pyrrolidinone **10** (1.00 mmol) and [$Rh_2(OAc)_4$] (0.5 mol %) in toluene (4 mL) at 70 °C. The reaction mixture was then stirred for 16 h. at 70 °C after which time the solvent was removed. Column chromatography over basic alumina using 100% pentane to 5% EtOAc/pentane afforded the (trialkylsilyloxy)acrylic esters **11**.

(*Z*)-Benzyl 2-(1-methylpyrrolidin-2-ylidene)-2-[(triethylsilyl)oxy]acetate (11a)



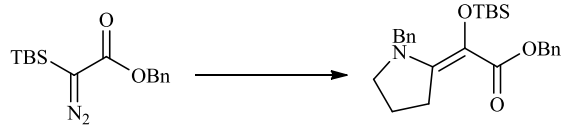
General procedure 2 afforded the title compound as a yellow oil (159 mg, 0.44 mmol, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.24 – 7.38 (m, 5H), 5.13 (s, 2H), 3.18 (t, 2H, J = 6.8 Hz), 3.11 (s, 3H), 2.95 (t, 3H, J = 7.6 Hz), 1.80 – 1.84 (m, 2H), 0.89 (t, 9H, J = 8.0 Hz), 0.62 (q, 6H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.5, 150.4, 137.1, 128.5, 128.2, 127.7, 114.5, 65.2, 56.5, 36.6, 33.3, 22.1, 6.9, 5.1; IR (neat, cm^{-1}) 3473, 2951, 2879, 1679, 1594, 1456, 1379, 1270, 1236, 1140, 1050, 815, 735; MS (EI, 70 eV) m/z = 361.1 (M^+, 22), 332.0 (21), 271.2 (17), 270.0 (100), 241.0 (37), 91.0 (24); HRMS (m/z) $C_{20}H_{32}O_3NSi$ Calcd. for 362.2146, found 362.2146.

(*Z*)-Benzyl 2-[1-(4-nitrophenyl)pyrrolidin-2-ylidene]-2-[(triethylsilyl)oxy]acetate (11b)



General procedure 2 afforded the title compound as a yellow oil (186 mg, 0.40 mmol, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.11 (d, 2H, J = 9.3 Hz), 7.32 – 7.41 (m, 5H), 6.77 (d, 2H, J = 9.3 Hz), 5.22 (s, 2H), 3.77 (t, 2H, J = 7.0 Hz), 3.10 (t, 2H, J = 7.5 Hz), 2.05 – 2.09 (m, 2H), 0.66 (t, 9H, J = 8.0 Hz), 0.20 (q, 6H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 148.3, 144.9, 139.9, 135.9, 131.5, 128.8, 128.5, 128.3, 123.8, 119.3, 66.4, 53.1, 30.5, 21.5, 6.5, 4.5; IR (neat, cm^{-1}) 3440, 2953, 2881, 1704, 1593, 1505, 1381, 1326, 1271, 1190, 1107, 1008, 842, 740, 698; MS (EI, 70 eV) m/z = 468.0 (M^+, 15), 438.9 (27), 393.0 (19), 376.9 (100), 347.9 (36), 91.0 (39); HRMS (m/z) [$C_{25}H_{32}O_5N_2Si$ – C_2H_5] Calcd. for 439.1684, found 439.1684.

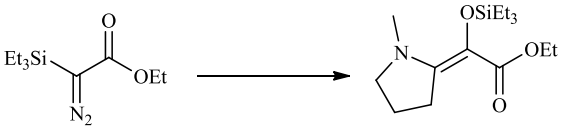
(*Z*)-Benzyl 2-(1-benzylpyrrolidin-2-ylidene)-2-[(*tert*-butyldimethylsilyl)oxy]acetate (11c)



General procedure 2 afforded the title compound as a yellow oil (156 mg, 0.36 mmol, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.20 – 7.42 (m, 10H), 5.16 (s, 2H), 4.83 (s, 3H), 3.12 (t, 2H, J = 6.9 Hz), 2.99 (t, 2H, J = 7.6 Hz), 1.80 – 1.84 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.6,

149.6, 138.1, 137.0, 128.6, 128.4, 128.3, 128.2, 127.7, 127.1, 114.4, 65.3, 52.3, 51.8, 33.8, 26.1, 22.2, 18.4, –4.0; IR (neat, cm^{-1}) 2941, 2859, 1683, 1588, 1457, 1257, 1070, 839, 740; MS (EI, 70 eV) *m/z* = 438.3 (M^+, 32), 437.2 (83), 381.2 (17), 380.1 (64), 347.2 (25), 346.1 (100), 289.1 (25), 91.1 (56); HRMS (*m/z*) $C_{26}H_{36}O_3NSi$ Calcd. for 438.2459, found 438.2459.

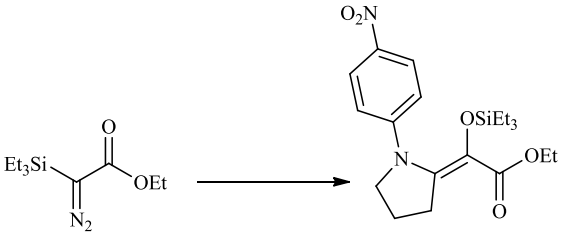
(*Z*)-Ethyl 2-(1-methylpyrrolidin-2-ylidene)-2-[(triethylsilyl)oxy]acetate (11d)



General procedure 2 afforded the title compound as a yellow oil (138 mg, 0.46 mmol, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.06 (q, 2H, *J* = 7.1 Hz), 3.14 (t, 2H, *J* = 6.8 Hz), 3.05 (s, 3H), 2.86 (t, 2H, *J* = 7.6 Hz), 1.75 – 1.81 (m, 2H), 1.20 (t, 3H, *J* = 7.1 Hz), 0.89 (t, 9H, *J* = 8.0 Hz), 0.62 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.7, 149.9, 114.6, 59.0, 56.4, 36.5, 33.1, 22.1, 14.5, 6.8, 5.1; IR (neat, cm^{-1}) 3472, 2951, 1681, 1598, 1269, 1057, 734; MS (CI, methane) *m/z* = 300.2 (M+H, 51), 299.0 (98), 271.2 (20), 270.0 (100), 254.0 (26); HRMS (*m/z*) $C_{15}H_{30}O_3NSi$ Calcd. for 300.1990, found 300.1993.

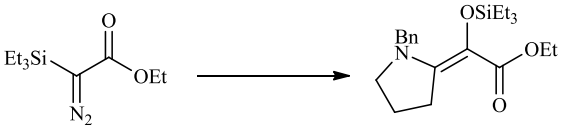
Microwave procedure: To a 10 mL microwave vial was added sequentially toluene (1 mL), *N*-methyl-2-pyrrolidinone (50 mg, 0.5 mmol), $[Rh_2(OAc)_4]$ (0.5 mol %) and ethyl 2-diazo-2-(triethylsilyl)acetate (125 mg, 0.55 mmol). The microwave vial was sealed and the reaction mixture heated to 100 °C for 30 minutes (CEM Discover, Maximum Power 200 W). After this time the solvent was removed and column chromatography over basic alumina using 100% pentane to 5% EtOAc/pentane afforded the title compound as a yellow oil (141 mg, 0.47 mmol, 94%).

(*Z*)-Ethyl 2-[1-(4-nitrophenyl)pyrrolidin-2-ylidene]-2-[(triethylsilyl)oxy]acetate (11e)



General procedure 2 afforded the title compound as a yellow oil (143 mg, 0.35 mmol, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.12 (d, 2H, *J* = 9.3 Hz), 6.77 (d, 2H, *J* = 9.3 Hz), 4.25 (q, 2H, *J* = 7.1 Hz), 3.77 (t, 2H, *J* = 7.1 Hz), 3.10 (t, 2H, *J* = 7.6 Hz), 2.05 – 2.12 (m, 2H), 1.35 (t, 3H, *J* = 7.1 Hz), 0.73 (t, 9H, *J* = 8.0 Hz), 0.30 (q, 6H, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.4, 148.4, 140.5, 139.5, 123.8, 123.2, 119.2, 60.5, 53.0, 30.4, 21.6, 14.3, 6.5, 4.6; IR (neat, cm^{-1}) 3392, 2953, 1708, 1595, 1378, 1323, 1107, 1016, 841, 738; MS (EI, 70 eV) *m/z* = 405.9 (M^+, 11), 378.1, (19), 376.9 (100), 347.9 (25); HRMS (*m/z*) $C_{20}H_{31}O_5N_2Si$ Calcd. for 407.1997, found 407.1997.

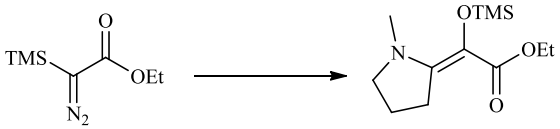
(*Z*)-Ethyl 2-(1-benzylpyrrolidin-2-ylidene)-2-[(triethylsilyl)oxy]acetate (11f)



General procedure 2 afforded the title compound as a yellow oil (190 mg, 0.51 mmol, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.21 – 7.33 (m, 5H), 4.86 (s, 2H), 4.17 (q, 2H, *J* = 7.1 Hz), 3.13 (t, 2H, *J* = 6.8 Hz), 3.00 (t, 2H, *J* = 7.6 Hz), 1.79 – 1.87 (m, 2H), 1.33 (t, 3H, *J* = 7.1 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 0.67 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.8, 148.2, 138.5, 128.4, 127.8, 126.9, 115.0, 59.2, 52.7, 51.7, 33.5, 22.1, 14.7, 6.9, 5.3; IR (neat, cm^{-1}) 2953, 2878, 1735, 1680, 1594, 1456, 1264,

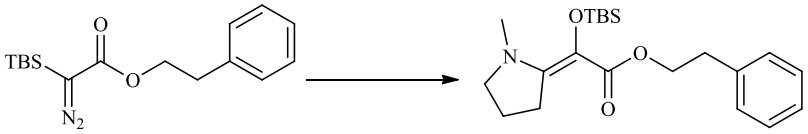
1167, 1084, 1015, 809, 734; MS (EI, 70 eV) *m/z* = 376.2 (M^+, 13), 375.2 (38), 347.2 (24), 346.1 (100), 317.1 (16), 91.1 (15); HRMS (*m/z*) $C_{21}H_{34}O_3NSi$ Calcd. for 376.2303, found 376.2304.

(*Z*)-Ethyl 2-(1-methylpyrrolidin-2-ylidene)-2-[(trimethylsilyl)oxy]acetate (11g)



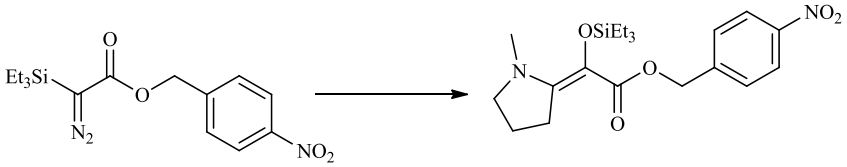
General procedure 2 afforded the title compound as a yellow oil (37 mg, 0.14 mmol, 26%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.11 (q, 2H, *J* = 7.2 Hz), 3.18 (t, 2H, *J* = 6.8 Hz), 3.08 (s, 3H), 2.94 (t, 2H, *J* = 7.6 Hz), 1.79 – 1.87 (m, 2H), 1.25 (t, 3H, *J* = 7.2 Hz), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.7, 150.2, 113.9, 59.0, 56.5, 36.6, 33.0, 22.0, 14.6, 0.4; IR (neat, cm^{-1}) 2975, 1734, 1662, 1455, 1205, 1095, 1026; HRMS (*m/z*) $C_{12}H_{24}O_3NSi$ Calcd. for 258.1520, found 258.1518.

(*Z*)-Phenethyl 2-[(*tert*-butyldimethylsilyl)oxy]-2-(1-methylpyrrolidin-2-ylidene)acetate (11h)



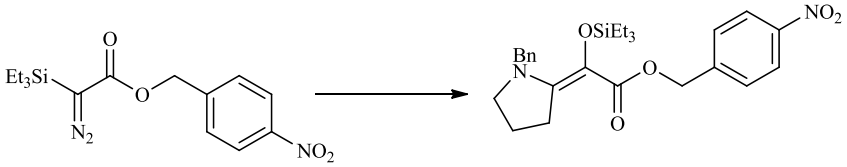
General procedure 2 afforded the title compound as a yellow oil (128 mg, 0.34 mmol, 62%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 7.19 – 7.29 (m, 5H), 4.28 (t, 2H, *J* = 7.6 Hz), 3.18 (t, 2H, *J* = 6.8 Hz), 3.11 (s, 3H), 2.98 (t, 2H, *J* = 7.7 Hz), 2.91 (t, 2H, *J* = 7.6 Hz), 1.84 – 1.87 (m, 2H), 0.96 (s, 9H), 0.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 166.8, 151.2, 138.2, 128.9, 128.5, 128.4, 126.3, 114.0, 63.9, 56.4, 36.9, 35.5, 33.4, 26.1, 22.2, 18.3, –4.3; IR (neat, cm^{-1}) 3471, 2942, 2857, 1682, 1594, 1264, 1123, 1054, 841; MS (CI, methane) *m/z* = 376.2 (M+H, 100), 375.1 (75), 360.0 (46), 318.0 (54) 254.0 (37), 105.0 (37); HRMS (*m/z*) $C_{21}H_{33}O_3NSi$ Calcd. for 375.2224, found 375.2228.

(*Z*)-4-Nitrobenzyl 2-(1-methylpyrrolidin-2-ylidene)-2-[(triethylsilyl)oxy]acetate (11i)



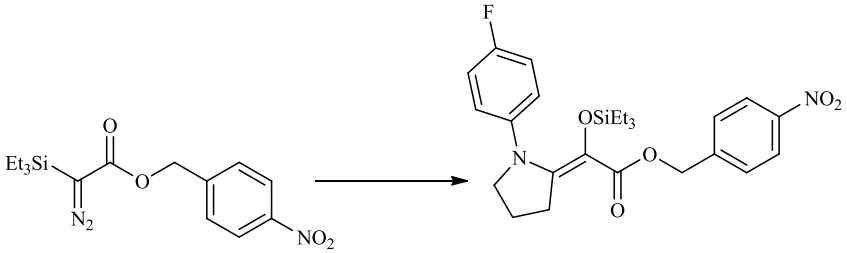
General procedure 2 afforded the title compound as a yellow oil (177 mg, 0.43 mmol, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 8.19 (d, 2H, *J* = 8.6 Hz), 7.53 (d, 2H, *J* = 8.6 Hz), 5.22 (s, 2H), 3.25 (t, 2H, *J* = 7.0 Hz), 3.16 (s, 3H), 2.95 (t, 2H, *J* = 7.7 Hz), 1.86 – 1.88 (m, 2H), 0.93 (t, 9H, *J* = 8.0 Hz), 0.64 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.1, 151.4, 147.4, 144.8, 128.5, 123.6, 113.7, 63.6, 56.6, 36.5, 33.5, 22.0, 6.8, 5.1; IR (neat, cm^{-1}) 3473, 2951, 2879, 1679, 1590, 1523, 1347, 1317, 1271, 1236, 1115, 1054, 1011, 737; MS (CI, methane) *m/z* = 407.1 (M+H, 59), 406.3 (29), 390.1 (17), 377.0 (21), 271.2 (34), 270.1 (100), 241.1 (19), 154.0 (11); HRMS (*m/z*) [$C_{20}H_{30}O_5N_2Si$ – C_2H_5] Calcd. for 377.1527, found 377.1527.

(*Z*)-4-Nitrobenzyl 2-(1-benzylpyrrolidin-2-ylidene)-2-[(triethylsilyl)oxy]acetate (11j)



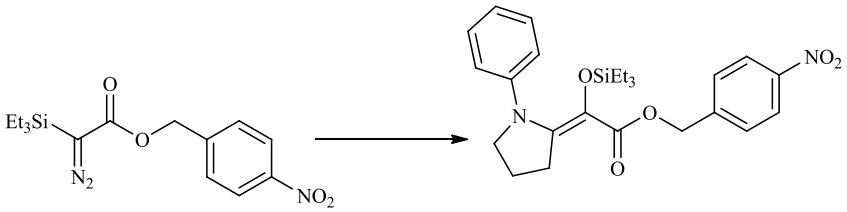
General procedure 2 afforded the title compound as a yellow oil (234 mg, 0.48 mmol, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.20 (d, 2H, *J* = 8.9 Hz), 7.54 (d, 2H, *J* = 8.9 Hz), 7.19 – 7.31 (m, 5H), 5.25 (s, 2H), 4.87 (s, 2H), 3.17 (t, 2H, *J* = 6.9 Hz), 2.99 (t, 2H, *J* = 7.6 Hz), 1.82 – 1.85 (m, 2H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.61 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.0, 149.6, 147.4, 144.8, 138.1, 128.5, 128.4, 127.8, 127.1, 123.6, 114.1, 63.7, 52.9, 51.7, 33.8, 22.0, 6.9, 5.3; IR (neat, cm^{-1}) 2952, 2877, 1679, 1584, 1523, 1347, 1261, 1072, 734; MS (CI, methane) *m/z* = 482.1 (M^+, 44), 453.1 (31), 247.2 (25), 346.1 (100), 318.1 (22), 317.1 (88) 91.1 (62); HRMS (*m/z*) [$C_{26}H_{34}O_5N_2Si$] Calcd. for 482.2231, found 482.2230.

(*Z*)-4-Nitrobenzyl 2-[1-(4-fluorophenyl)pyrrolidin-2-ylidene]-2-[(triethylsilyl)oxy]acetate (11k)



General procedure 2 afforded the title compound as a yellow oil (155 mg, 0.32 mmol, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.22 (d, 2H, *J* = 8.8 Hz), 7.56 (d, 2H, *J* = 8.8 Hz), 6.92 – 6.96 (m, 2H), 6.84 – 6.88 (m, 2H), 5.27 (s, 2H), 3.73 (t, 2H, *J* = 7.0 Hz), 3.13 (t, 2H, *J* = 7.6 Hz), 2.02 – 2.06 (m, 2H), 0.70 (t, 9H, *J* = 8.0 Hz), 0.24 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.6, 159.7, 157.3, 147.5, 144.4, 144.2, 139.23, 139.21, 128.7, 123.6, 123.34, 123.26, 117.6, 114.3, 114.1, 64.2, 55.7, 32.2, 21.9, 6.6, 4.4; IR (neat, cm^{-1}) 2952, 2880, 1693, 1596, 1515, 1343, 1269, 1225, 1103, 1011, 824, 736; MS (CI, methane) *m/z* = 486.1 (M^+, 33), 457.1 (30), 350.1 (46), 322.1 (29), 321.1 (100), 87.1 (19), 29.1 (19); HRMS (*m/z*) [$C_{25}H_{31}O_5N_2FSi$] Calcd. for 486.1981, found 486.1991.

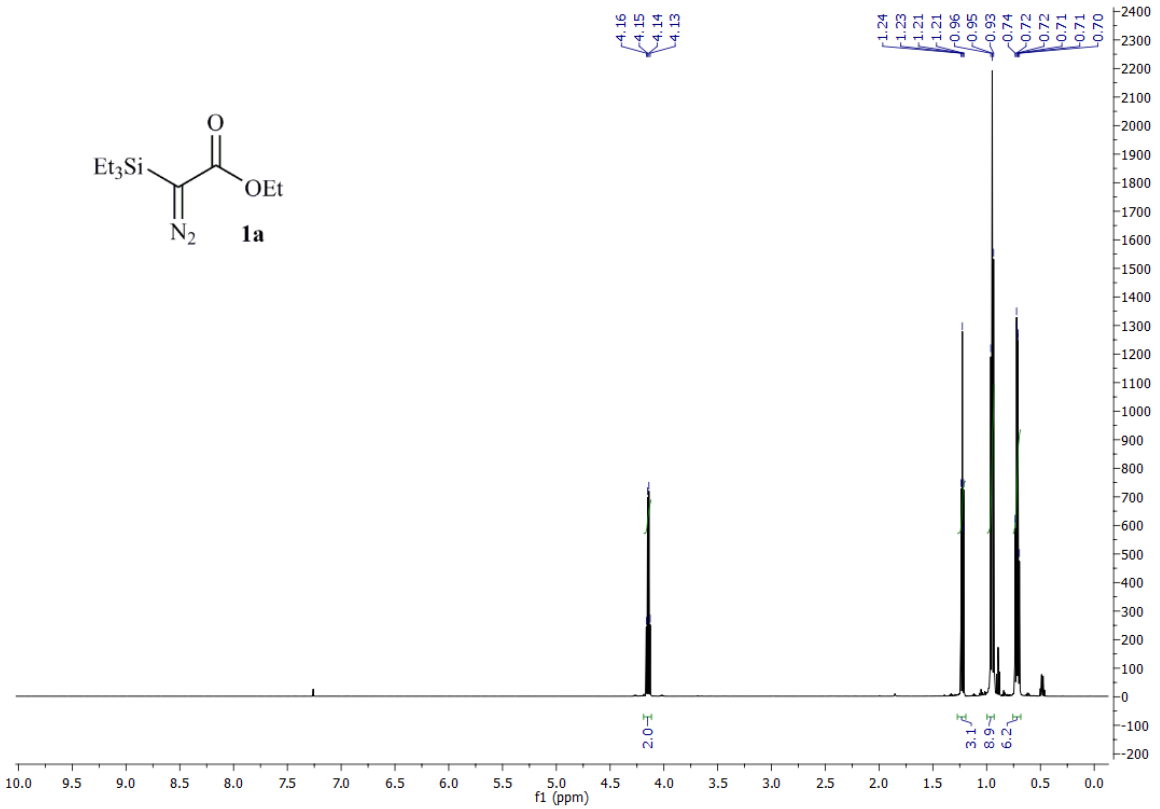
(*Z*)-4-Nitrobenzyl 2-(1-phenylpyrrolidin-2-ylidene)-2-[(triethylsilyl)oxy]acetate (11l)



General procedure 2 afforded the title compound as a yellow oil (186 mg, 0.40 mmol, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.21 (d, 2H, *J* = 8.8 Hz), 7.56 (d, 2H, *J* = 8.8 Hz), 7.22 (dd, 2H, *J* = 7.4 and 8.5 Hz), 6.95 (dt, 1H, *J* = 1.1 and 7.4 Hz), 6.89 (dd, 2H, *J* = 1.1 and 8.6 Hz), 5.26 (s, 2H), 3.75 (t, 2H, *J* = 7.0 Hz), 3.12 (t, 2H, *J* = 7.6 Hz), 2.00 – 2.04 (m, 2H), 0.66 (t, 9H, *J* = 8.0 Hz), 0.20 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.7, 147.5, 144.3, 144.1, 143.0, 128.7, 127.6, 123.6, 122.4, 121.9, 117.9, 64.2, 55.2, 32.1, 21.8, 6.6, 4.4; IR (neat, cm^{-1}) 2949, 2878, 1682, 1585, 1518, 1257, 1098, 1009, 731; MS (CI, methane) *m/z* = 468.1 (M^+, 26), 439.1 (25), 332.1 (47), 303.1 (100), 87.1 (19), 59.1 (16); HRMS (*m/z*) [$C_{25}H_{32}O_5N_2Si$] Calcd. for 468.2075, found 468.2075.

References:

(1) C. Curti, B. Ranieri, L. Battistini, G. Rassu, V. Zambrano, G. Pelosi, G. Casiraghi and F. Zanardi, *Adv. Synth. Catal.*, 2010, **352**, 2011.
(2) A. Padwa, S. J. Coats, S. R. Harring, L. Hadjiarapoglou and M. A. Semones, *Synthesis*, 1995, **27**, 973.
(3) C. Bolm, S. Saladin and A. Kasyan, *Org. Lett.*, 2002, **4**, 4631.
(4) C. Bolm, A. Kasyan, K. Drauz, K. Günther and G. Raabe, *Angew. Chem. Int. Ed.*, 2000, **39**, 2288.
(5) C. Bolm, S. Saladin, A. Classen, A. Kasyan, E. Veri and G. Raabe, *Synlett*, 2005, **16**, 461.
(6) G. S. Nandra, P. S. Pang, M. J. Porter and J. M. Elliott, *Org. Lett.*, 2005, **7**, 3453.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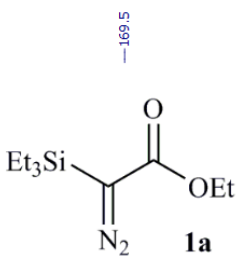
4.15
4.14
4.13
1.24
1.23
1.21
1.21
0.96
0.95
0.93
0.74
0.72
0.72
0.71
0.71
0.70
2.0
3.1
8.9
6.2
f1 (ppm)

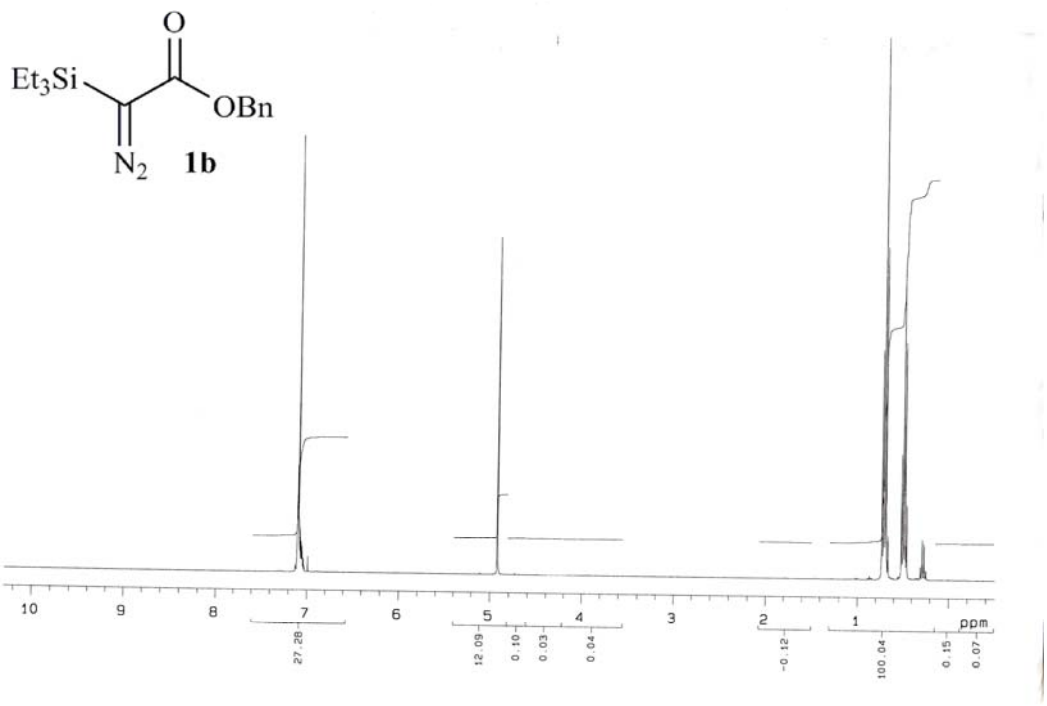

Et3Si
O
OEt
N2

1a

169.5
77.2
77.0
76.8
60.5
14.3
6.9
3.1
f1 (ppm)

Et3Si
O
OEt
N2

1a


Et3Si
O
OBn
N2
1b
10
9
8
7
6
5
4
3
2
1
ppm
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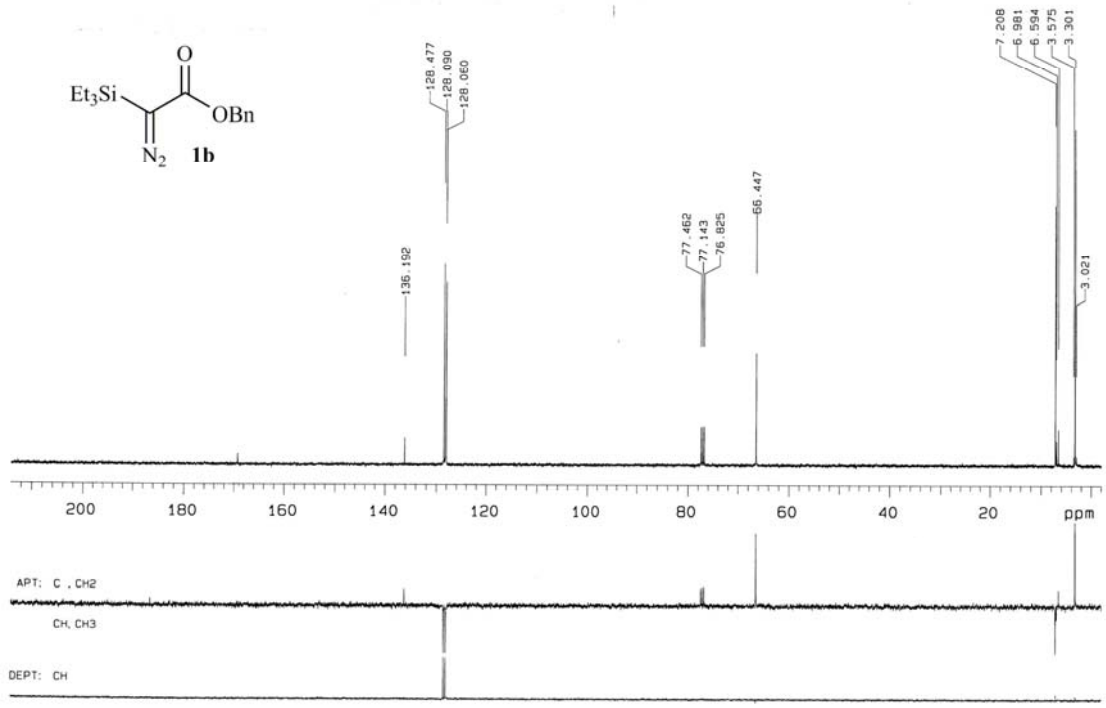
12.09
0.10
0.03
0.04
-0.12
100.04
0.15
0.07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O
OBn
N2
1b
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128.090
128.060
136.192
77.462
77.143
76.825
66.447
7.208
6.981
6.594
3.575
3.301
3.021
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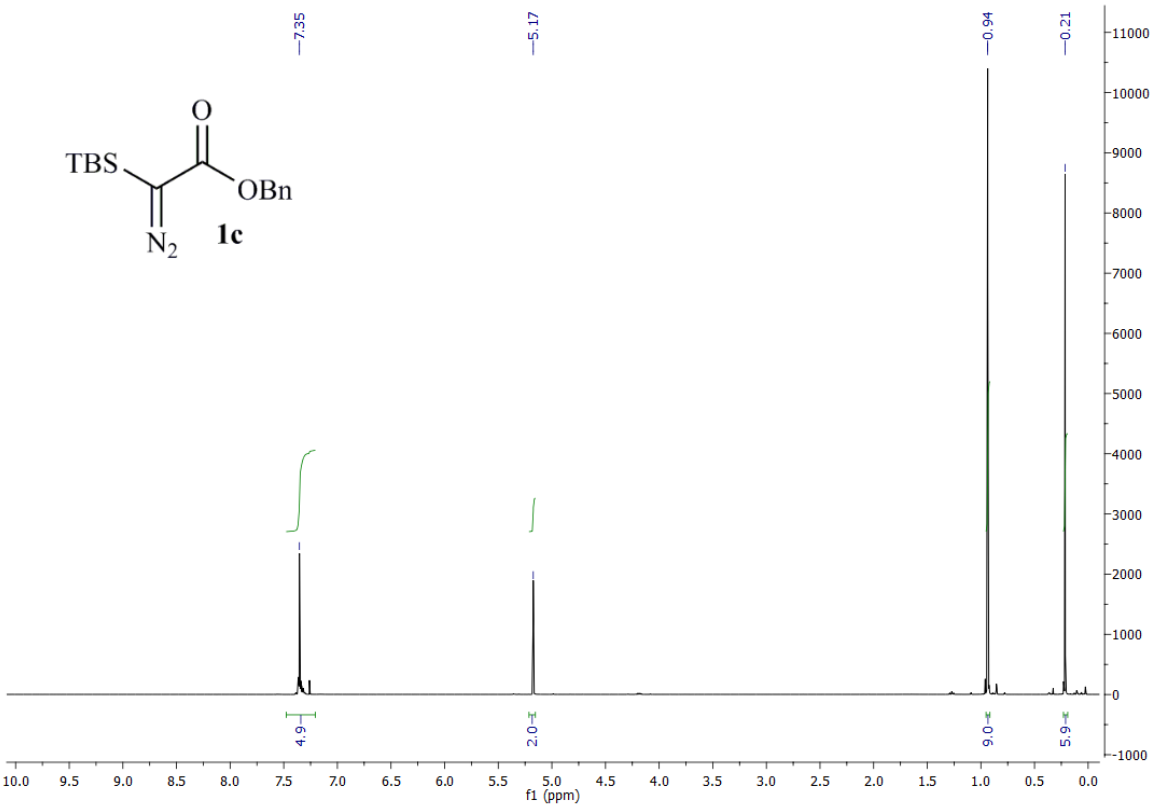
180
160
140
120
100
80
60
40
20
ppm
APT: C , CH2
CH, CH3
DEPT: CH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OBn
N2
1c
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5.17
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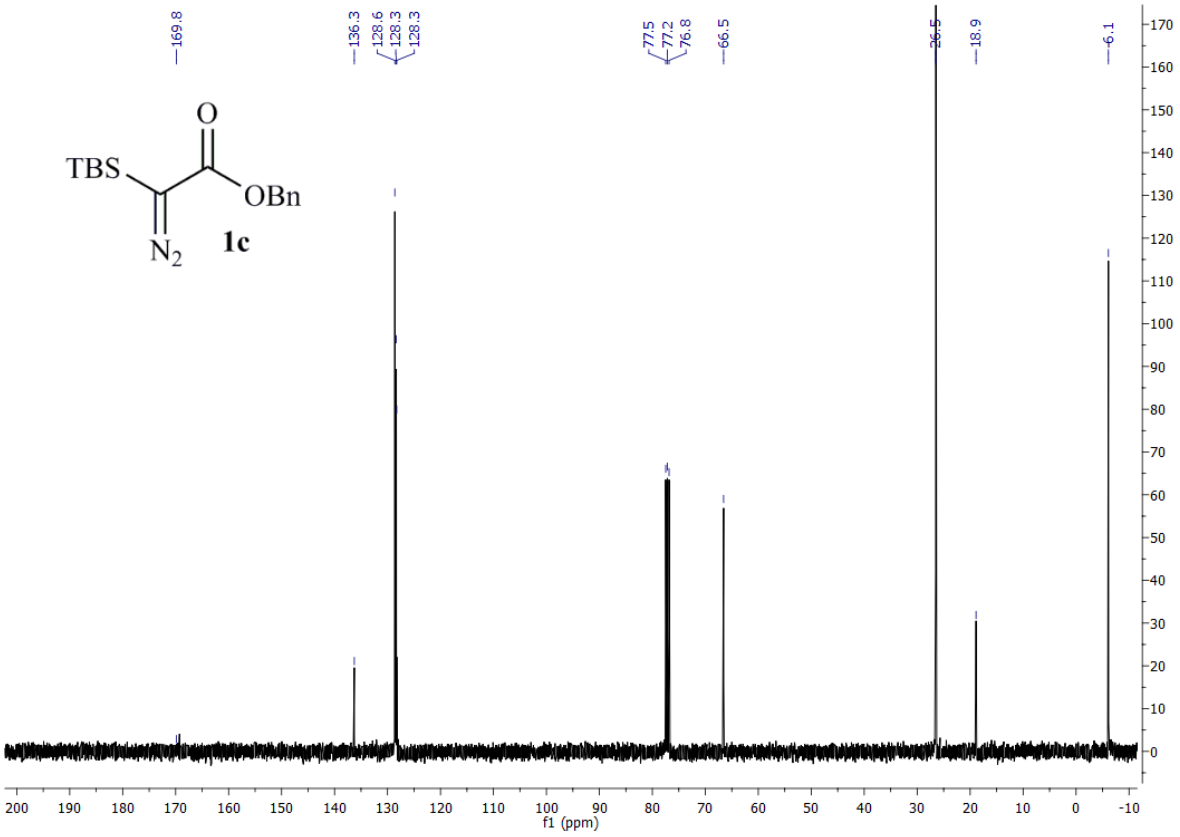
2.0
9.0
5.9
f1 (ppm)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OBn
N2
1c
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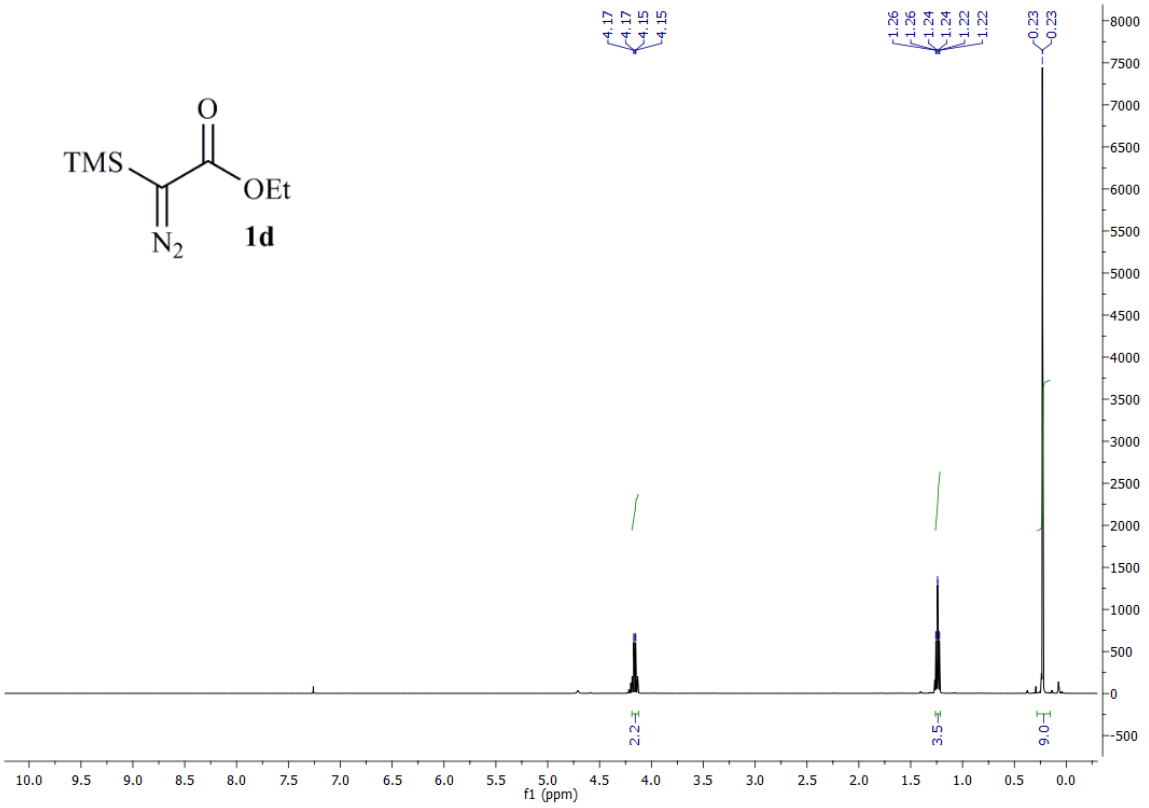
77.2
76.8
66.5
26.5
18.9
-6.1
f1 (ppm)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N2
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4.17
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4.15
1.26
1.26
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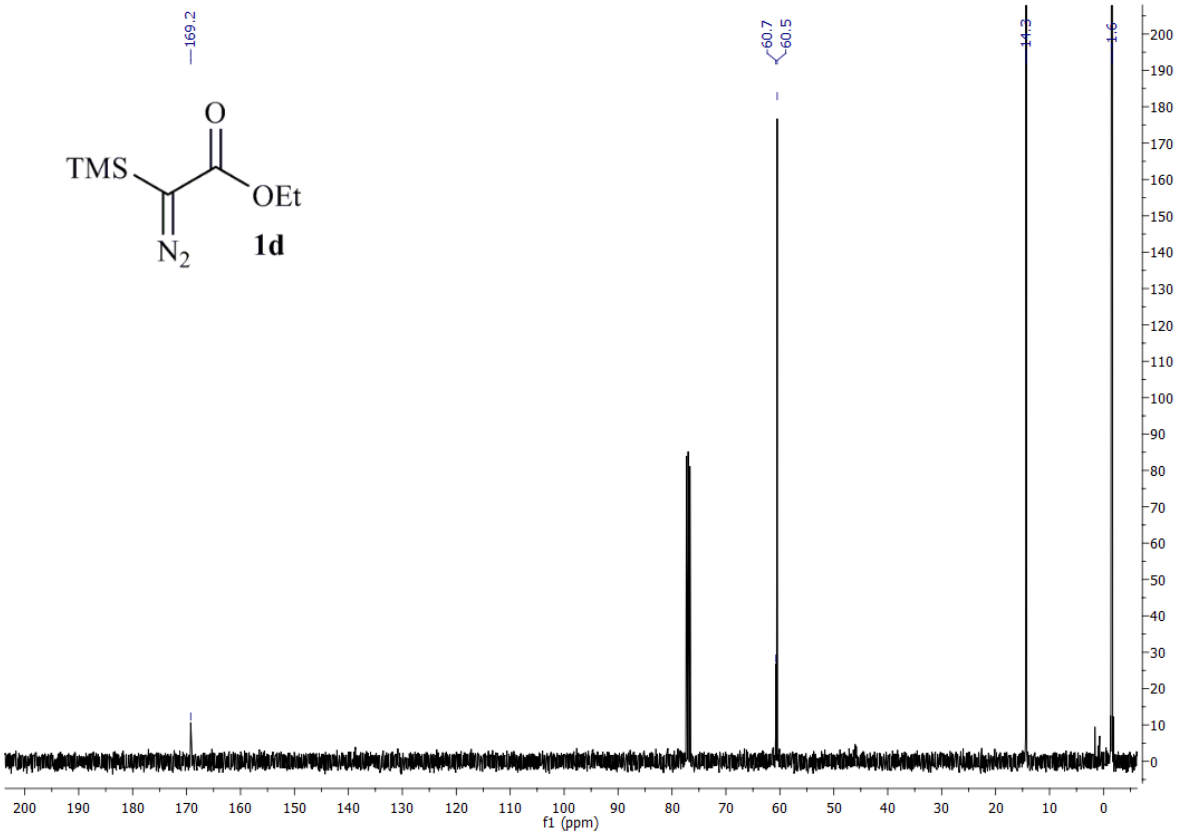
1.24
1.22
1.22
0.23
0.23
2.2
3.5
9.0
f1 (ppm)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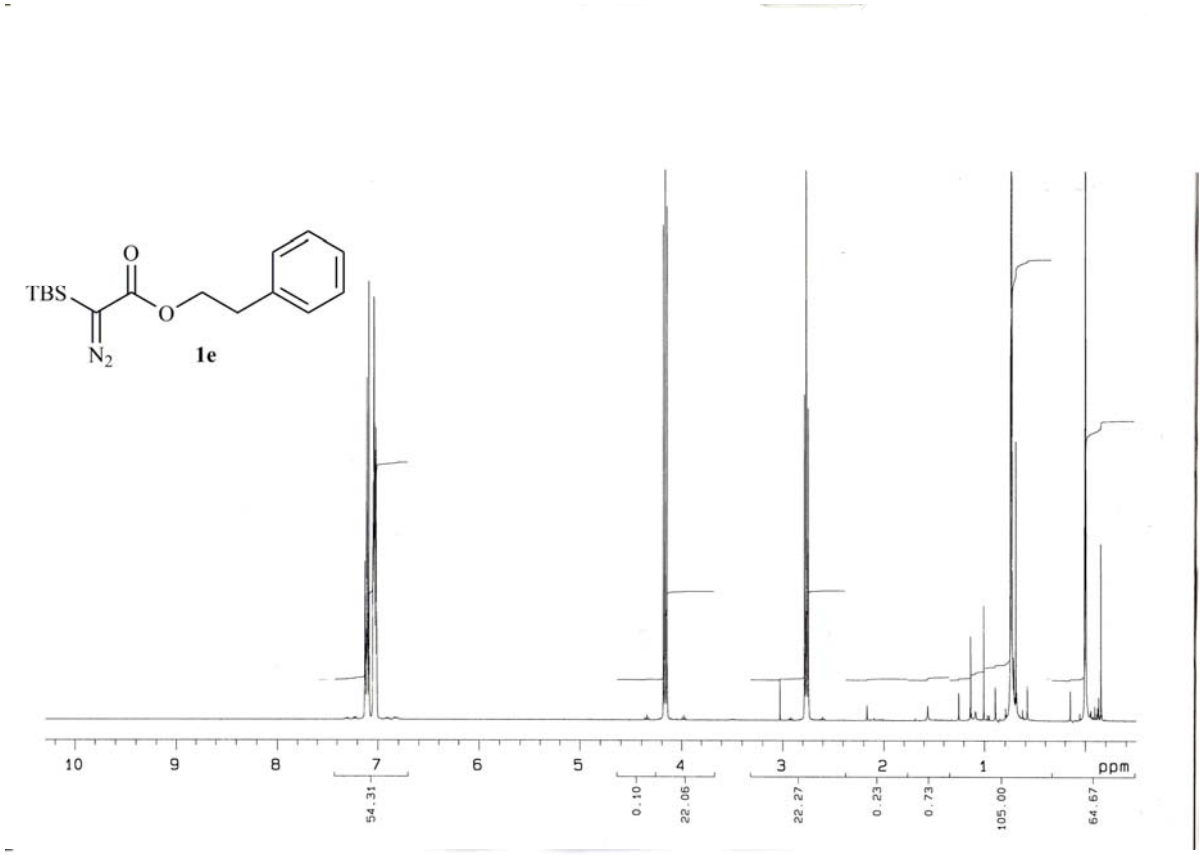
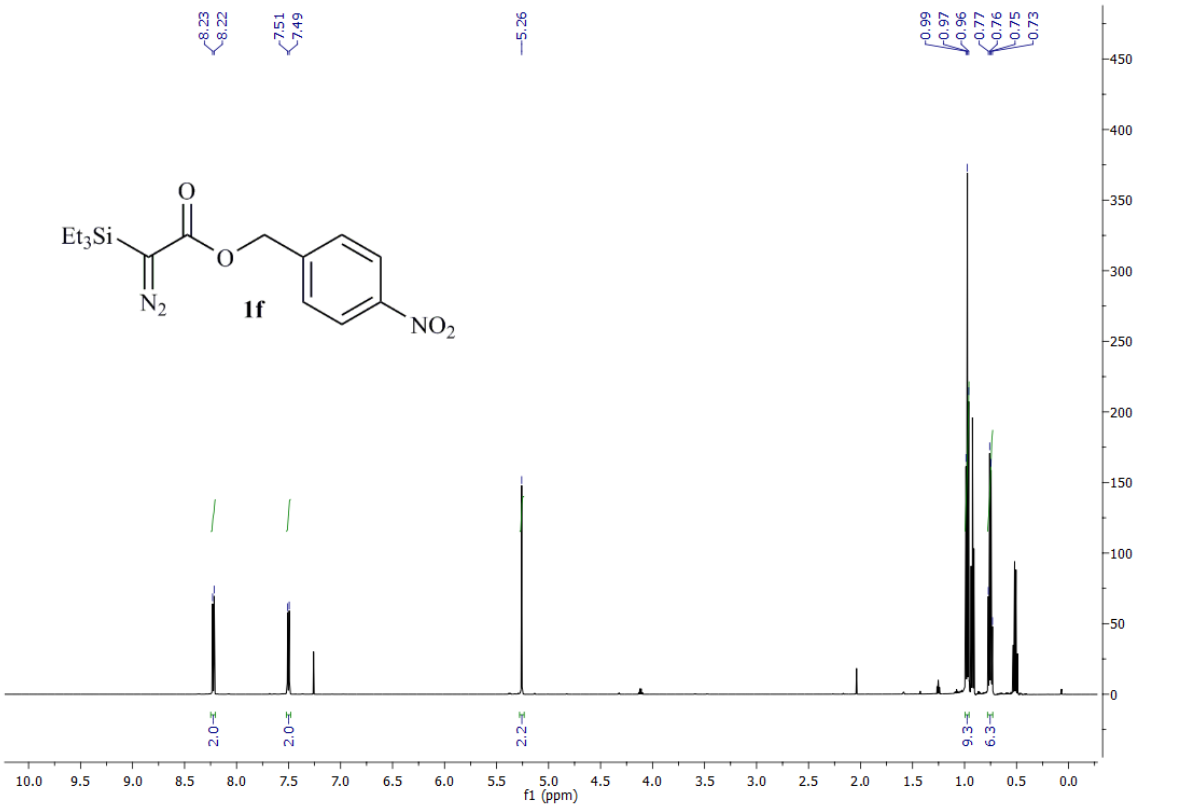
OEt
N2
1d
169.2
60.7
60.5
14.3
14.1
f1 (ppm)

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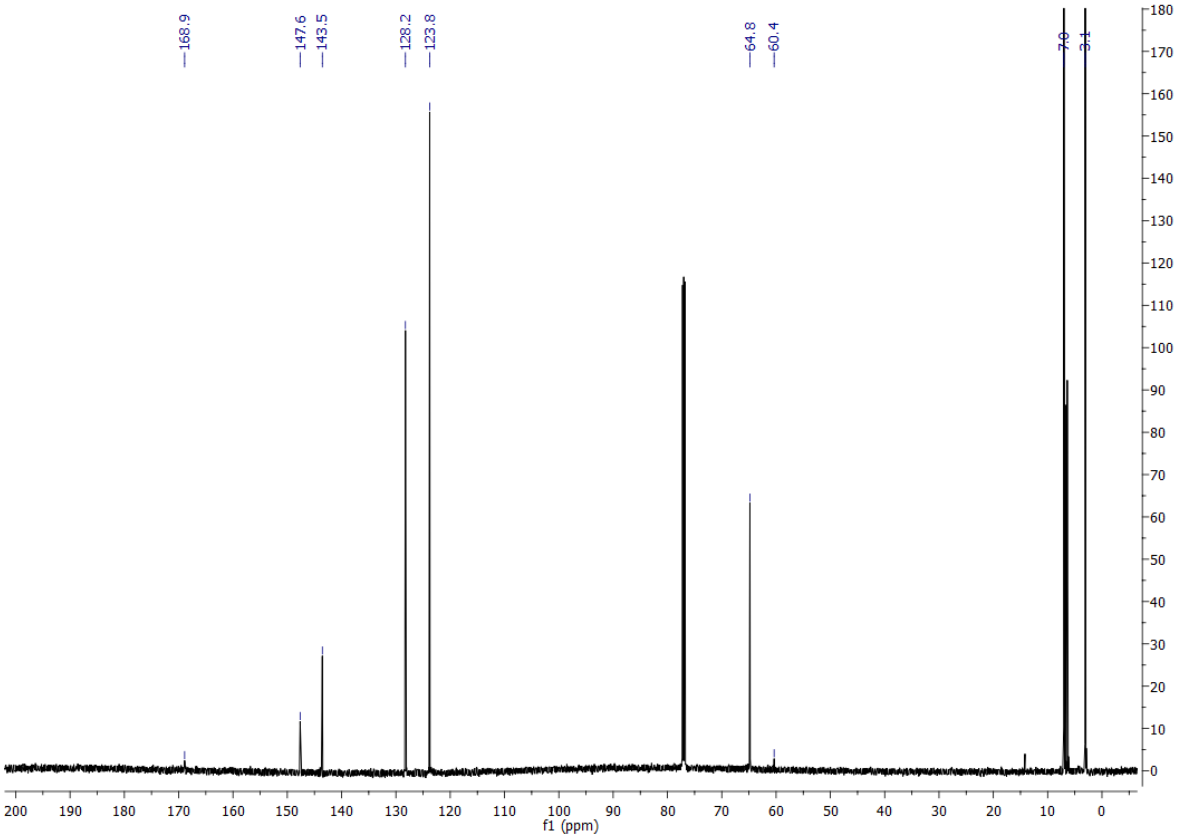
8.22
7.51
7.49
5.26
0.99
0.97
0.96
0.77
0.76
0.75
0.73
O
Et3Si
O
N2
1f
NO2
2.0
2.0
2.2
9.3
6.3
f1 (ppm)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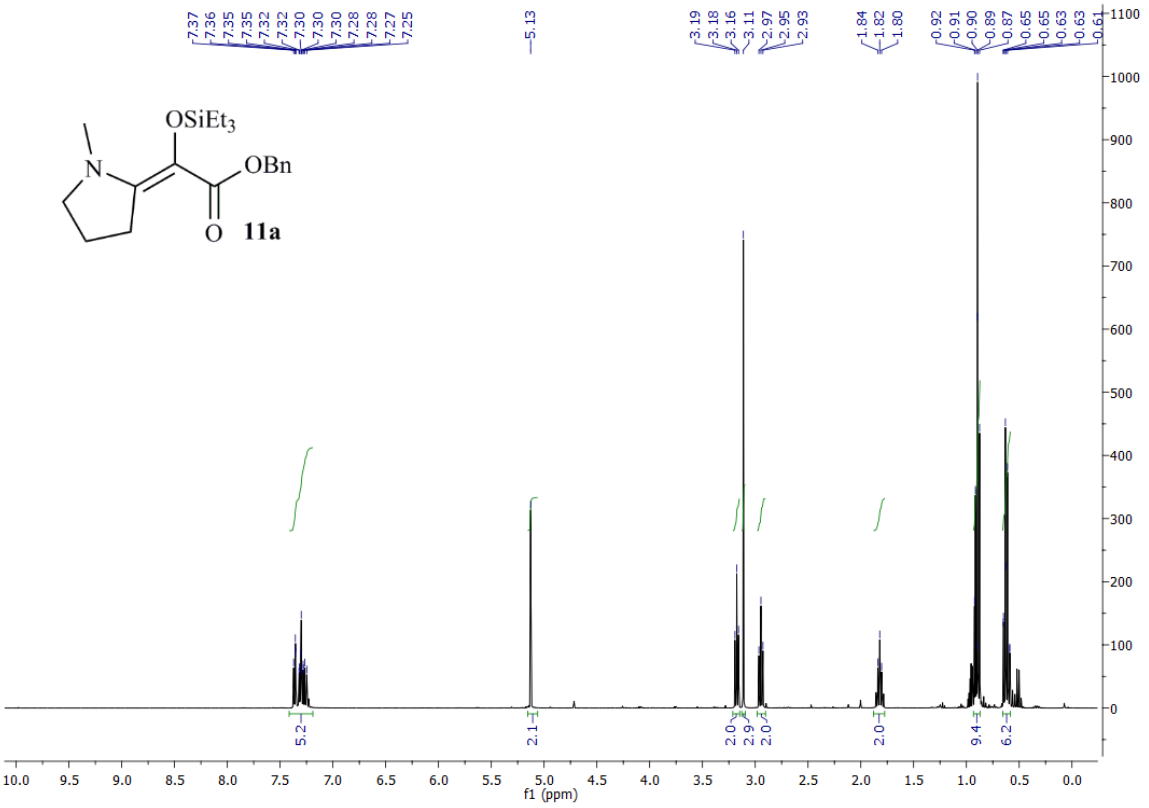
143.5
128.2
123.8
64.8
60.4
7.0
3.1
f1 (ppm)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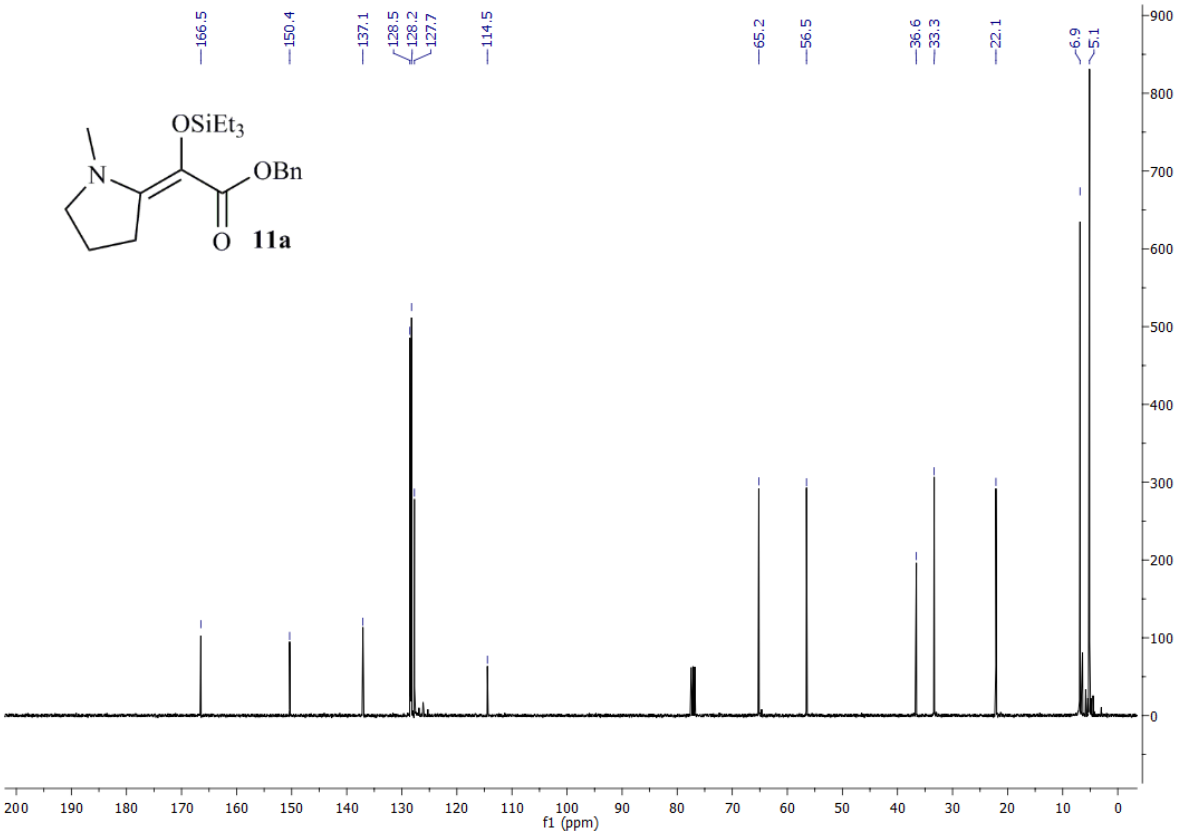
7.35
7.35
7.32
7.32
7.30
7.30
7.28
7.28
7.27
7.25
5.13
3.19
3.18
3.16
3.11
2.97
2.95
2.93
1.84
1.82
1.80
0.92
0.91
0.90
0.89
0.87
0.65
0.65
0.63
0.63
0.61
OSiEt3
N
OBn
O
11a
5.2
2.1
2.0
2.9
2.0
2.0
9.4
6.2
f1 (ppm)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150.4
137.1
128.5
128.2
127.7
114.5
65.2
56.5
36.6
33.3
22.1
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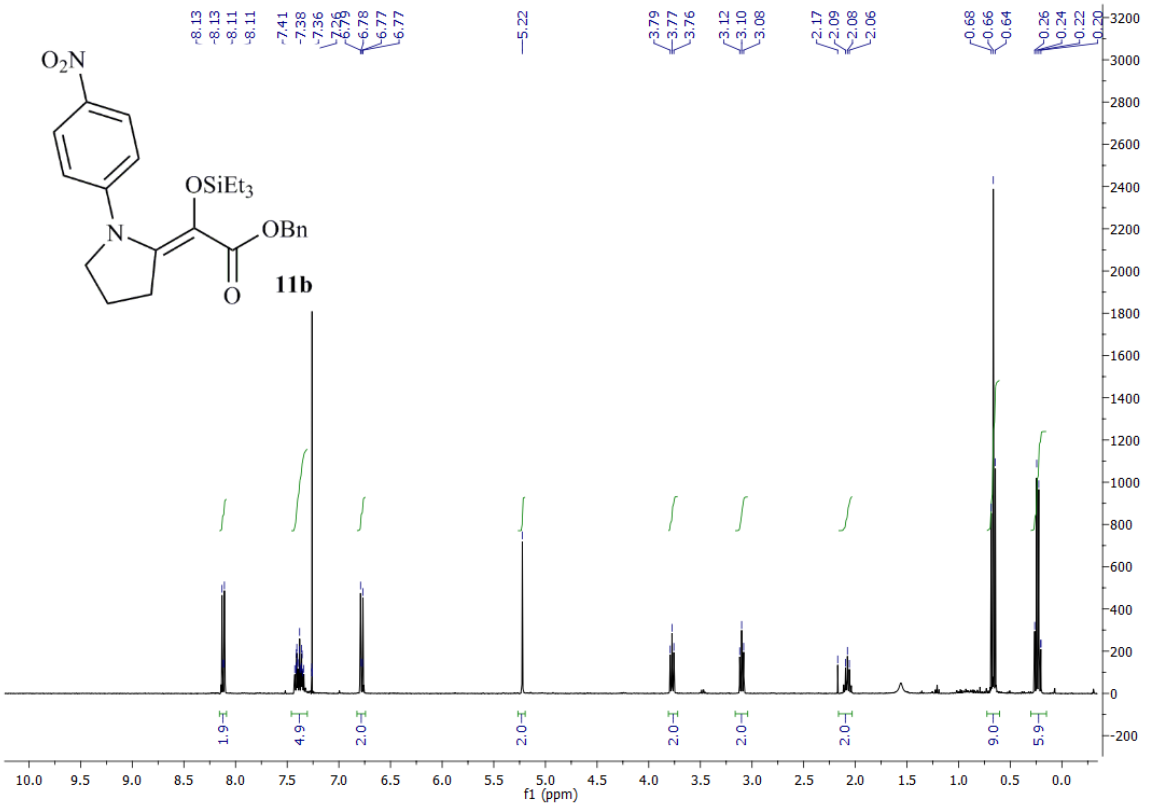
5.1
OSiEt3
N
OBn
O
11a
f1 (ppm)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OSiEt3
N
OBn
O
11b
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8.13
8.11
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7.38
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3.10
3.08
2.17
2.09
2.08
2.06
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0.64
0.26
0.24
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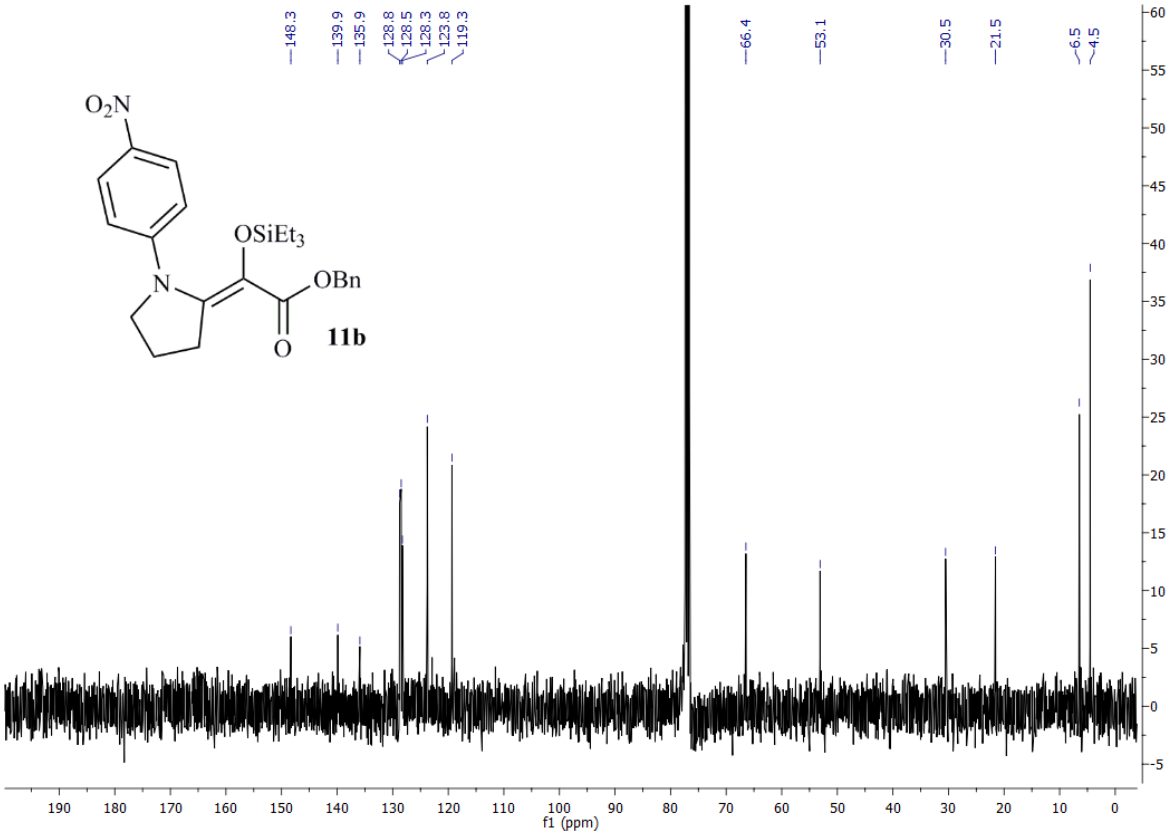
5.9
f1 (ppm)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N
OBn
O
11b
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135.9
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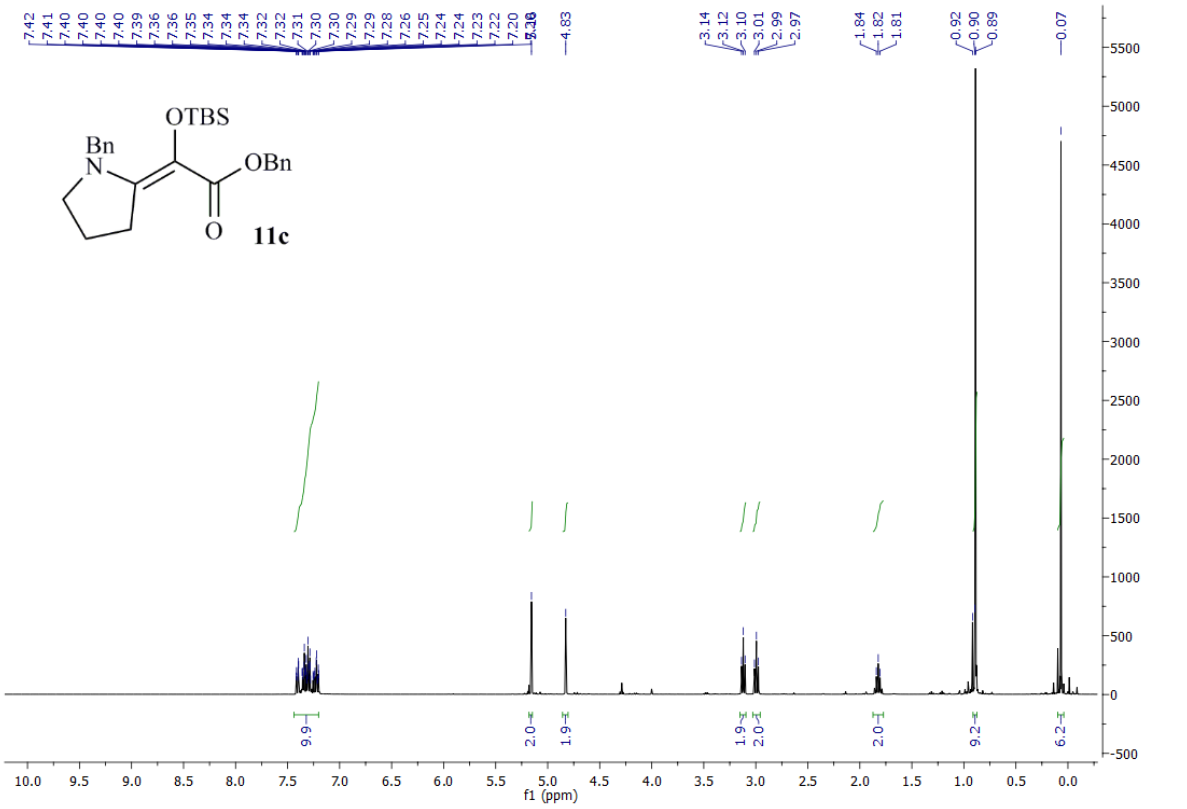
30.5
21.5
6.5
4.5
f1 (ppm)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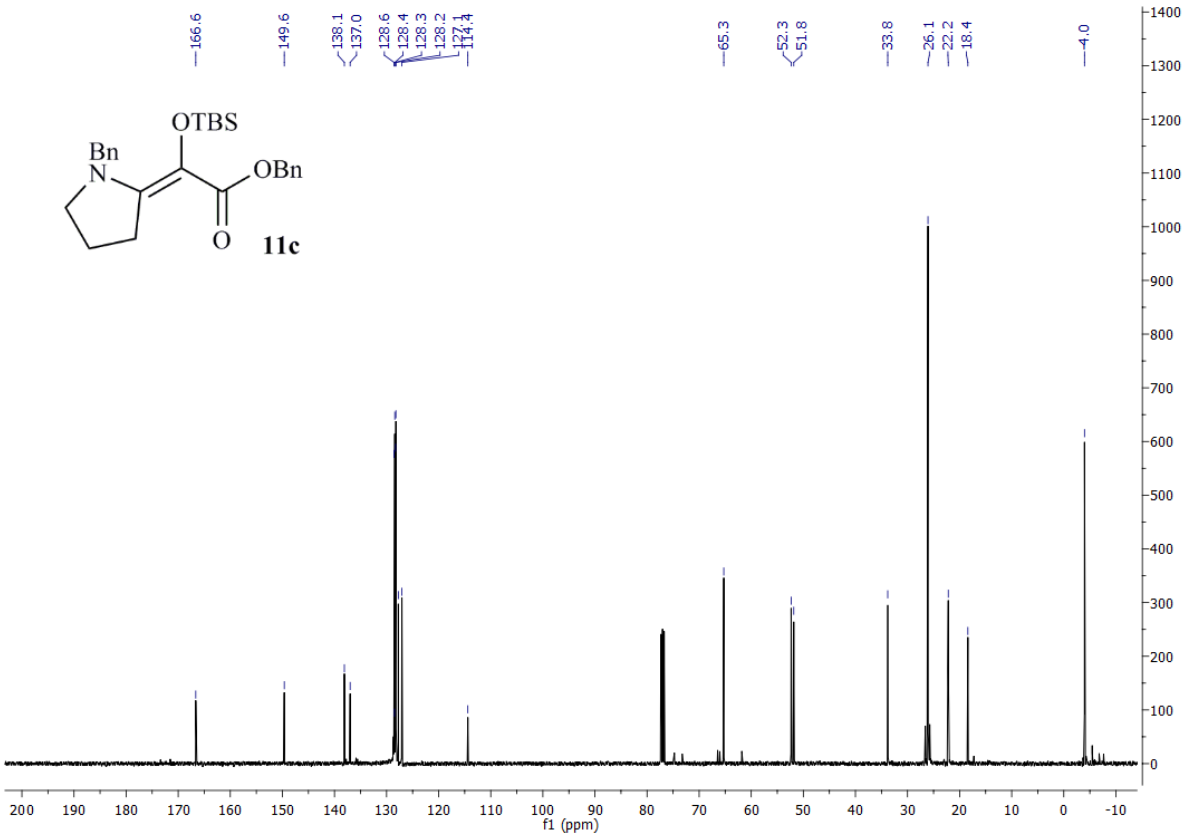
11c
f1 (ppm)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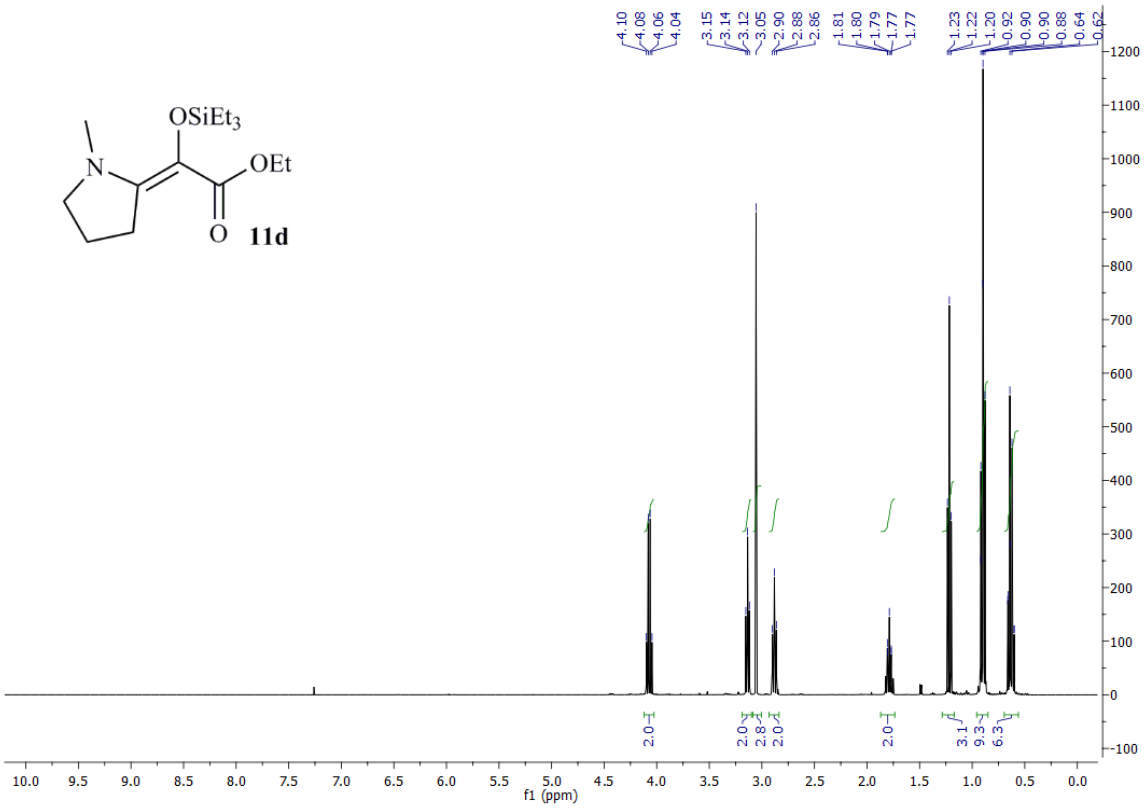
O
11c
f1 (ppm)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OEt
O
11d
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4.08
4.06
4.04
3.15
3.14
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2.90
2.88
2.86
1.81
1.80
1.79
1.77
1.77
1.23
1.22
1.20
0.92
0.90
0.90
0.88
0.64
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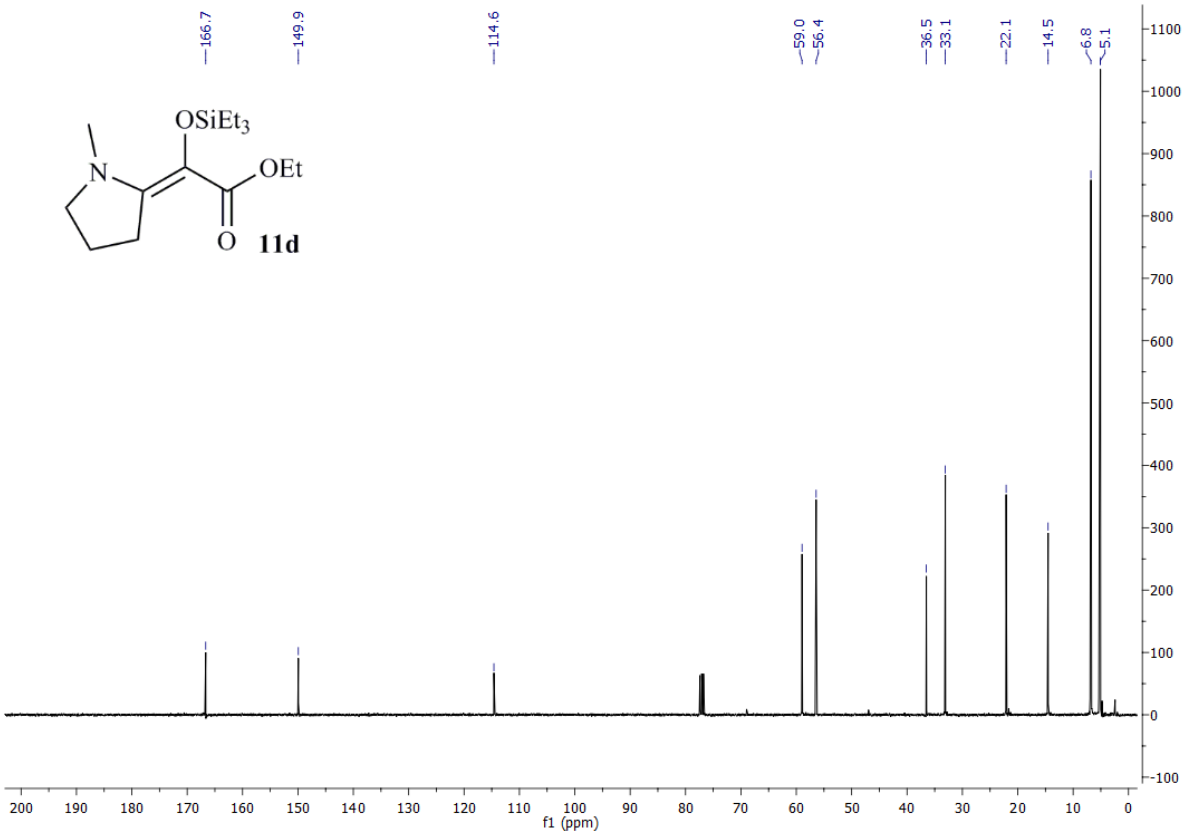
2.0
2.8
2.0
2.0
3.1
9.3
6.3
f1 (ppm)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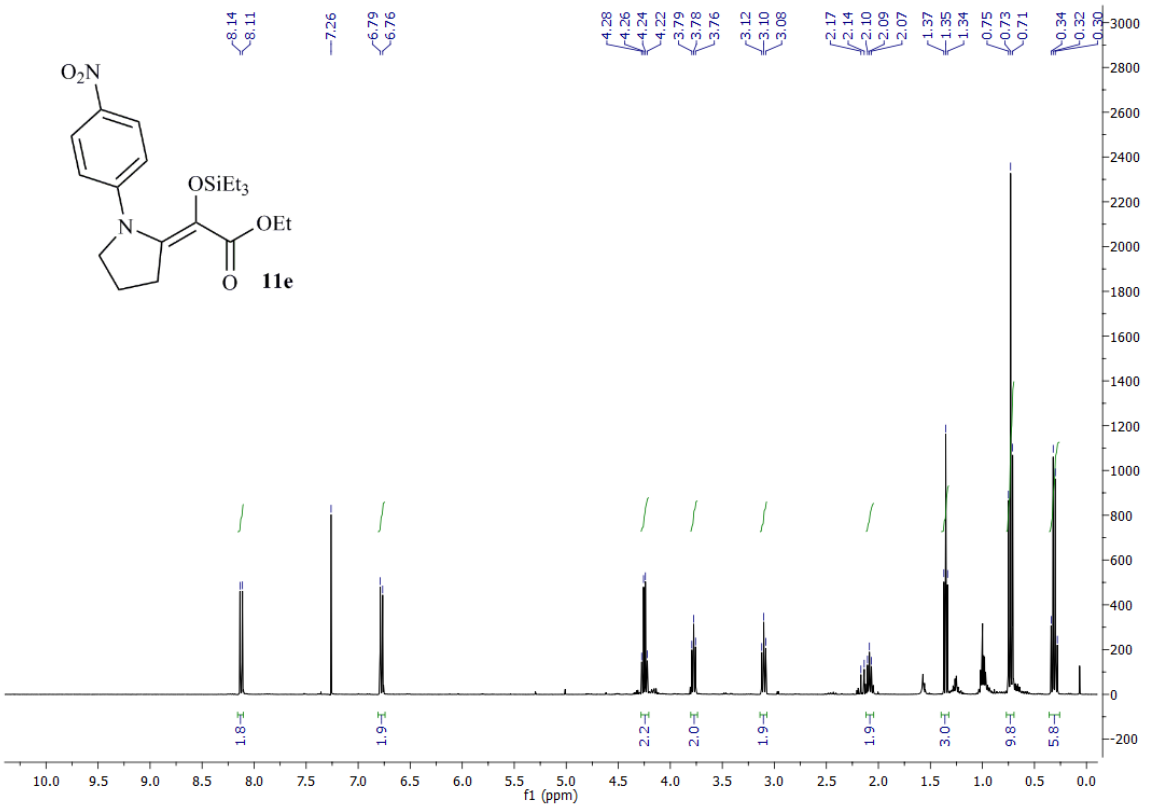
6.8
5.1
OSiEt3
N
OEt
O
11d
f1 (ppm)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3.76
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3.08
2.17
2.14
2.10
2.09
2.07
1.37
1.35
1.34
0.75
0.73
0.71
0.34
0.32
0.30
O2N
OSiEt3
OEt
O
11e
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1.9
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2.0
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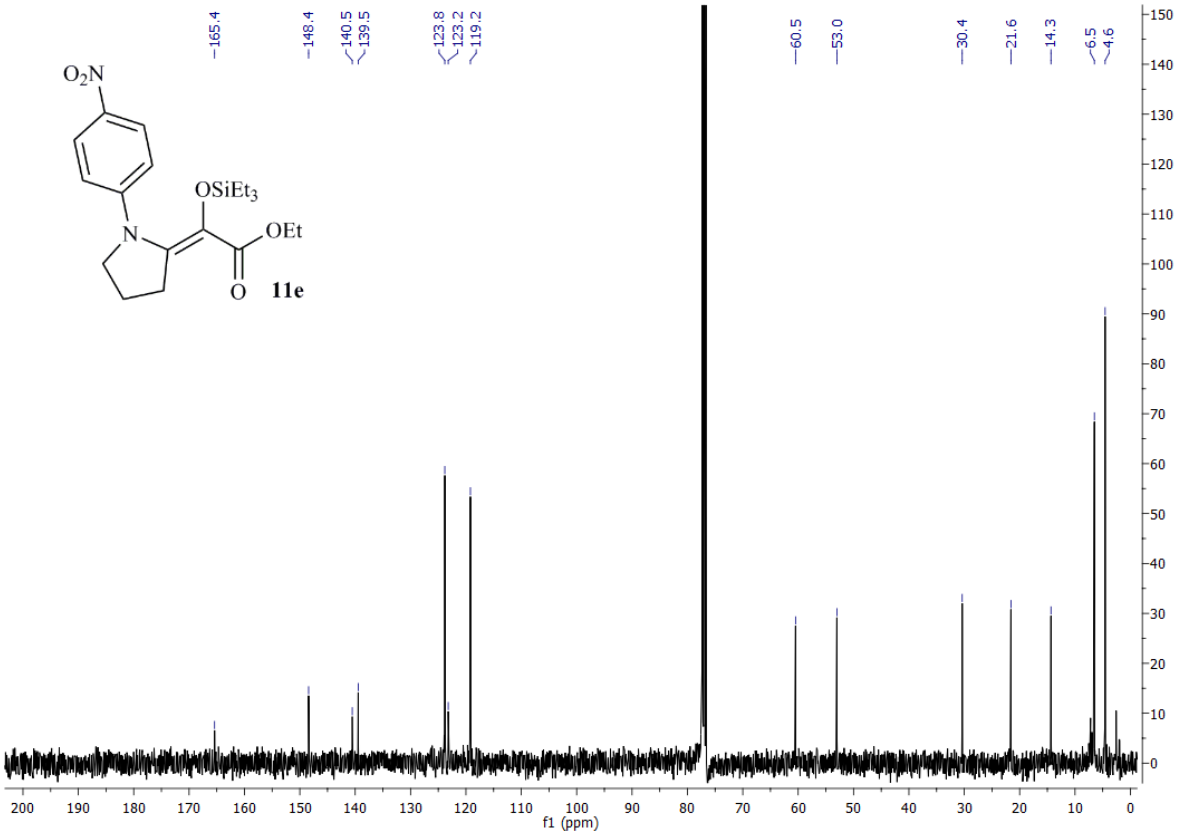
9.8
5.8
f1 (ppm)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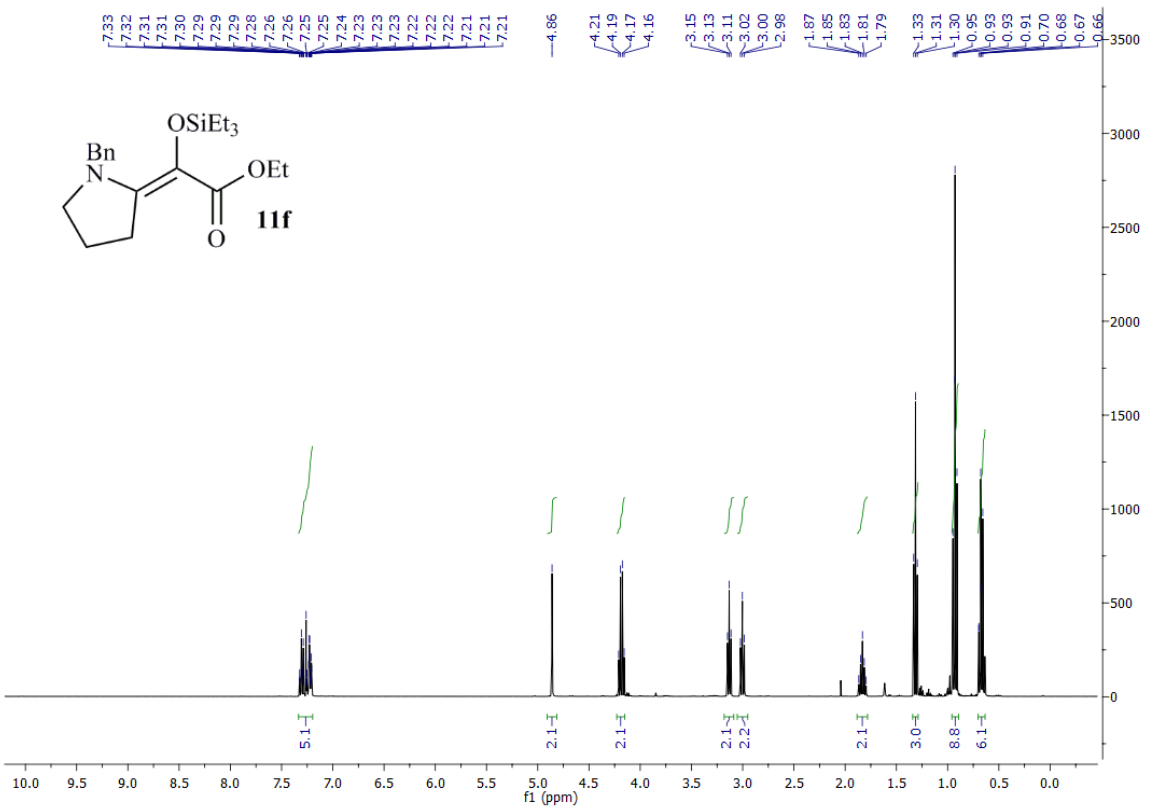
O2N
OSiEt3
OEt
O
11e
f1 (ppm)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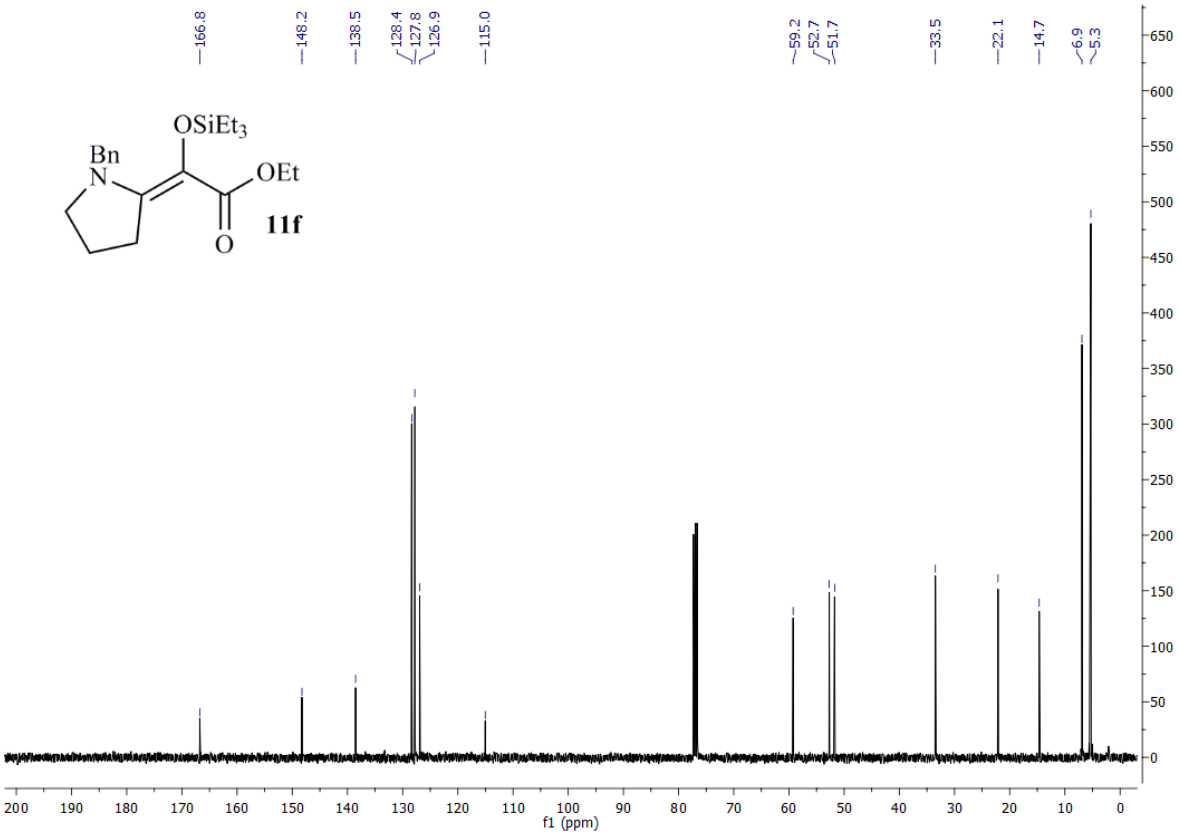
Bn
N
OEt
O
11f
f1 (ppm)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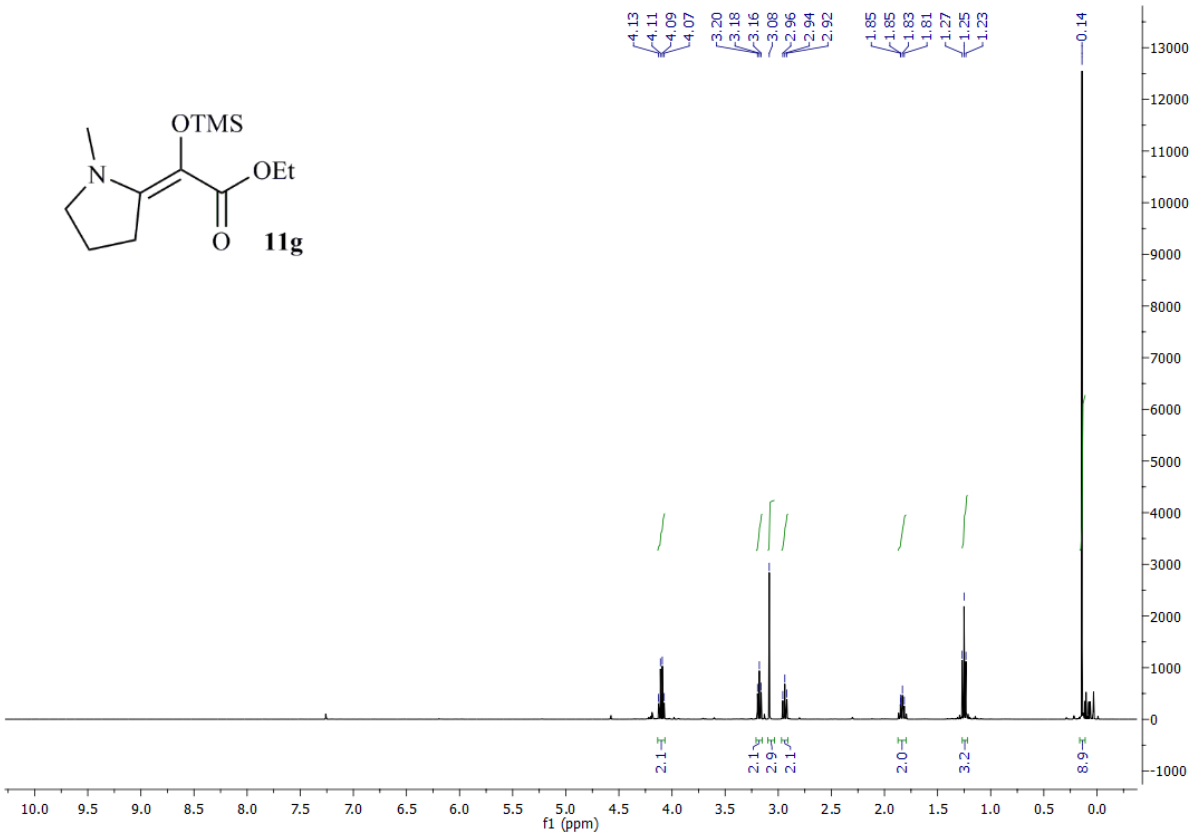
OEt
O
11f
f1 (ppm)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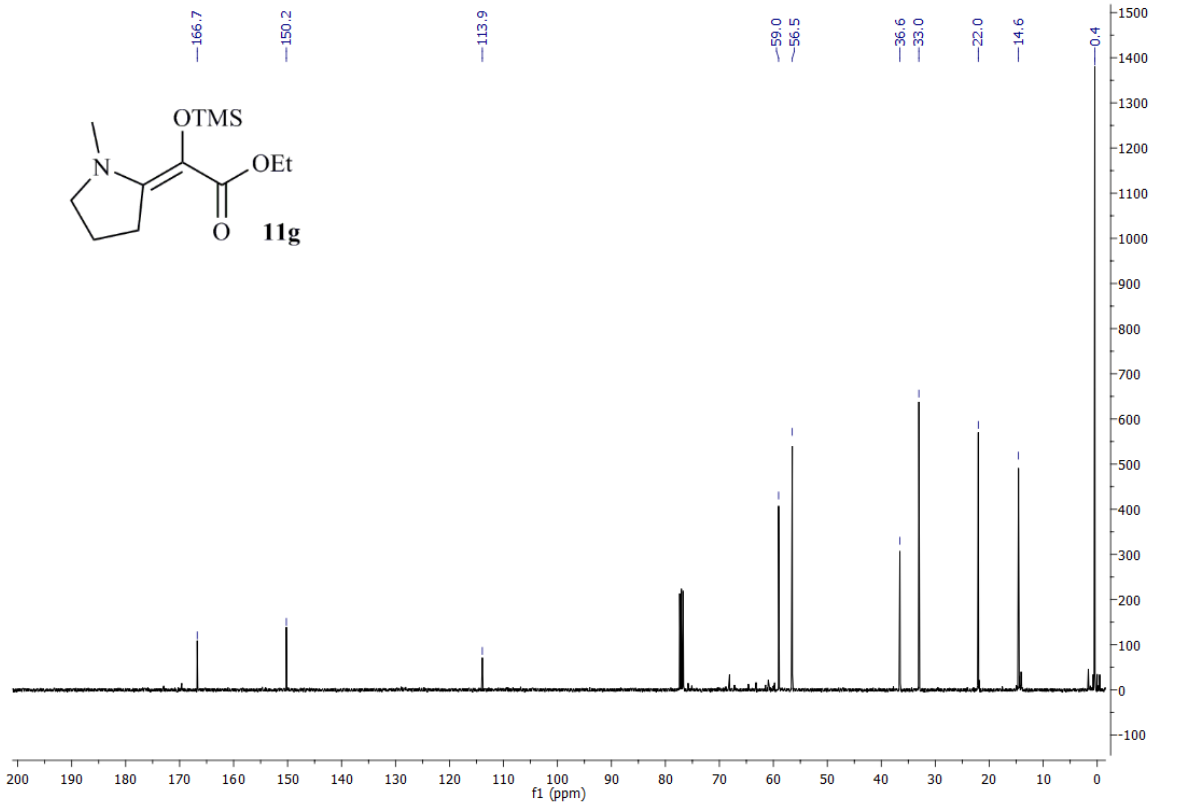
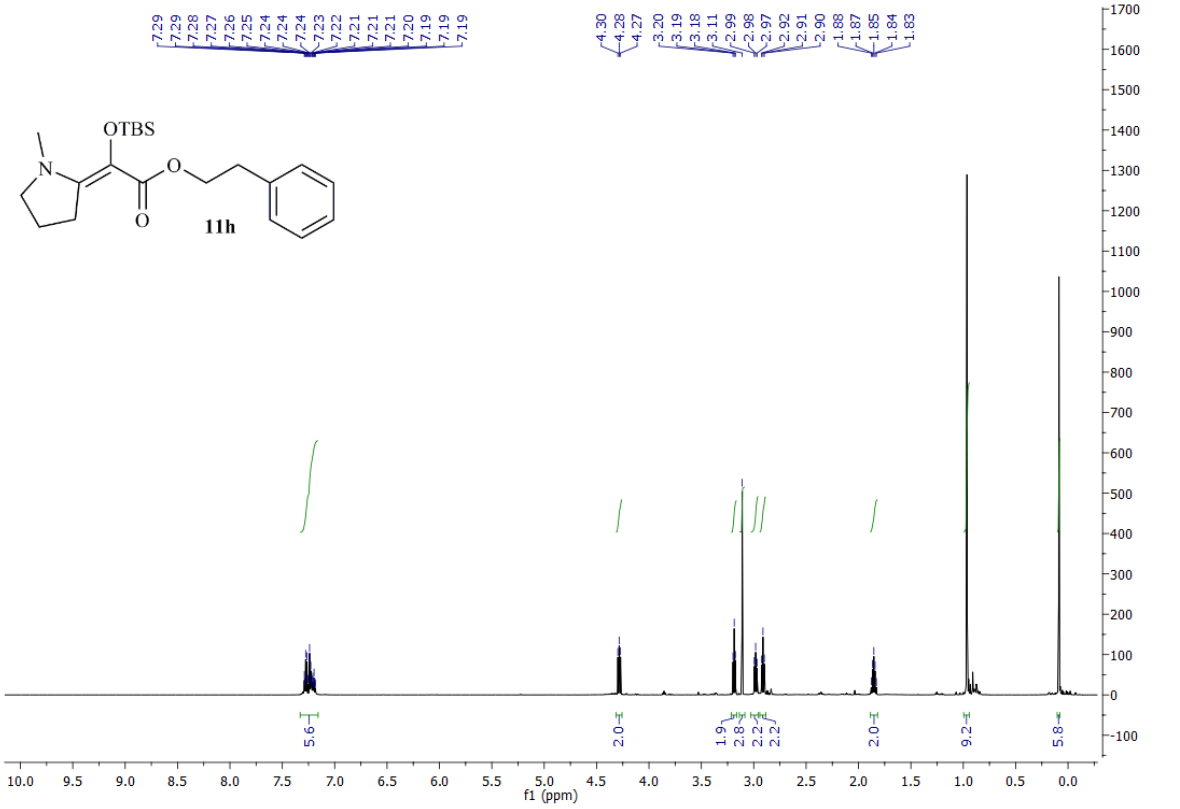
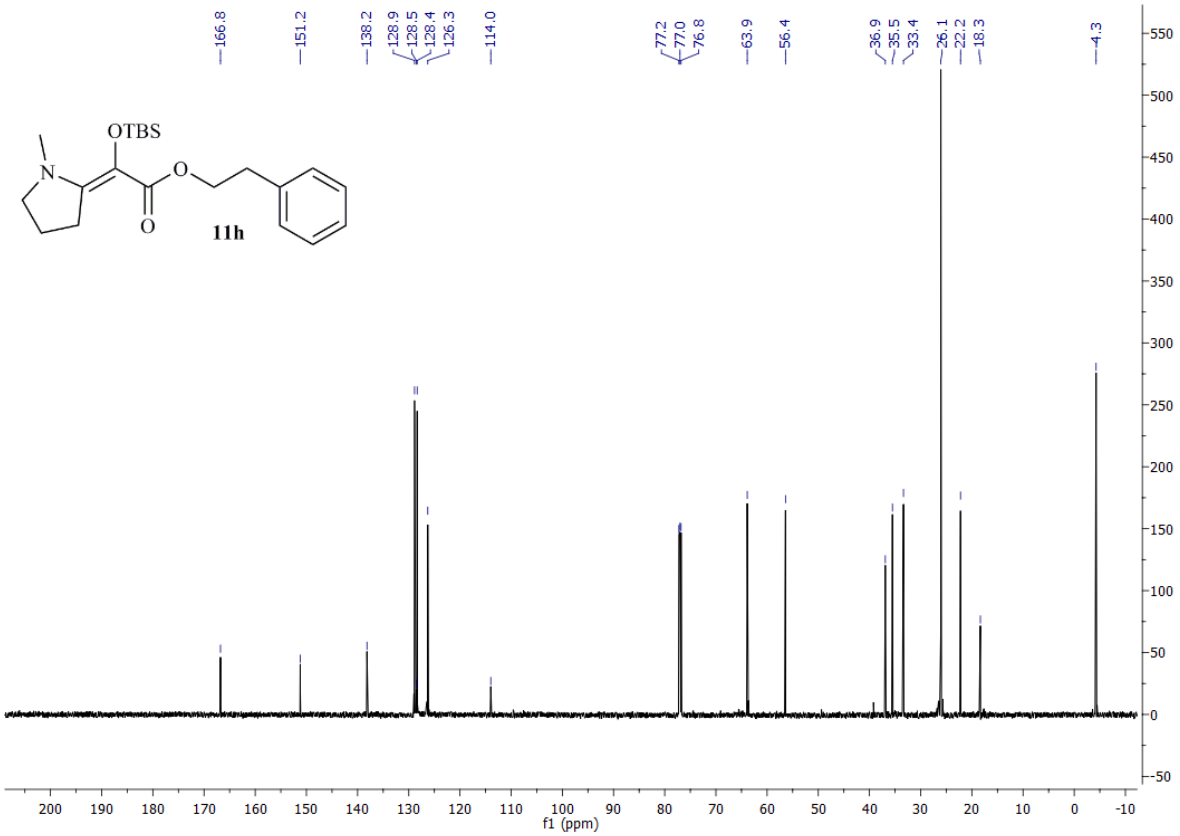
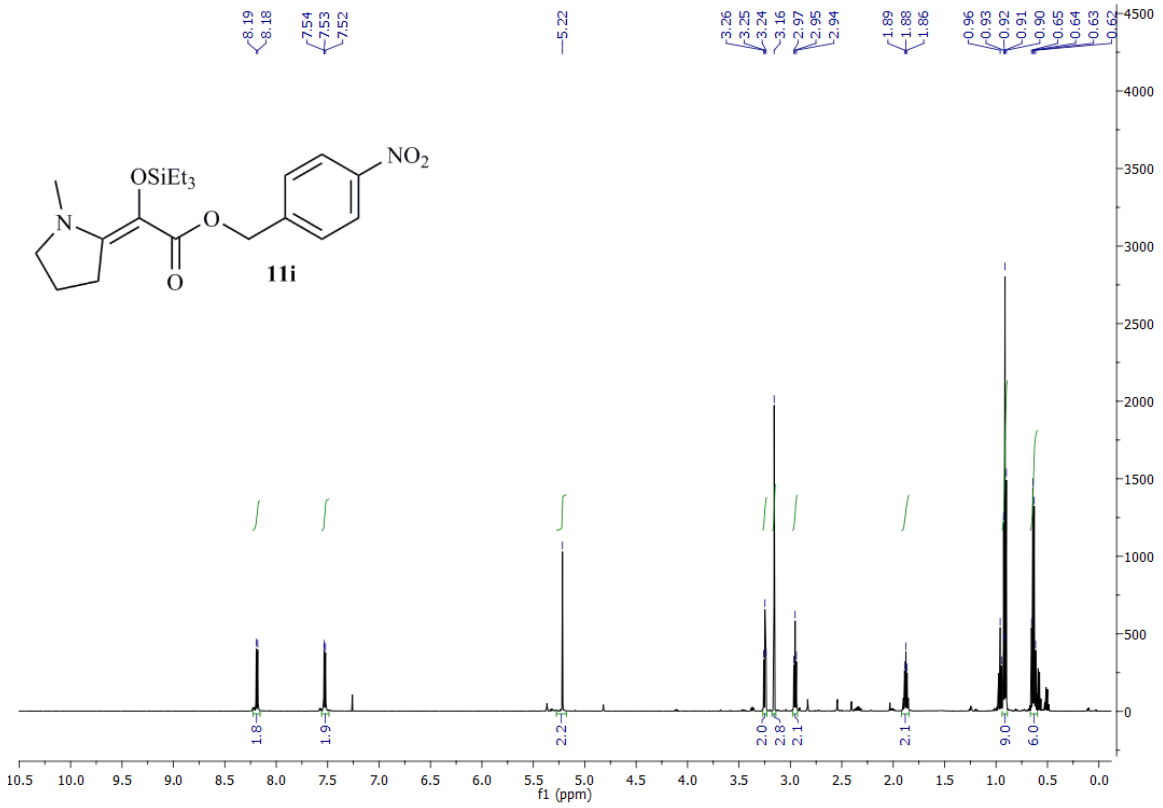
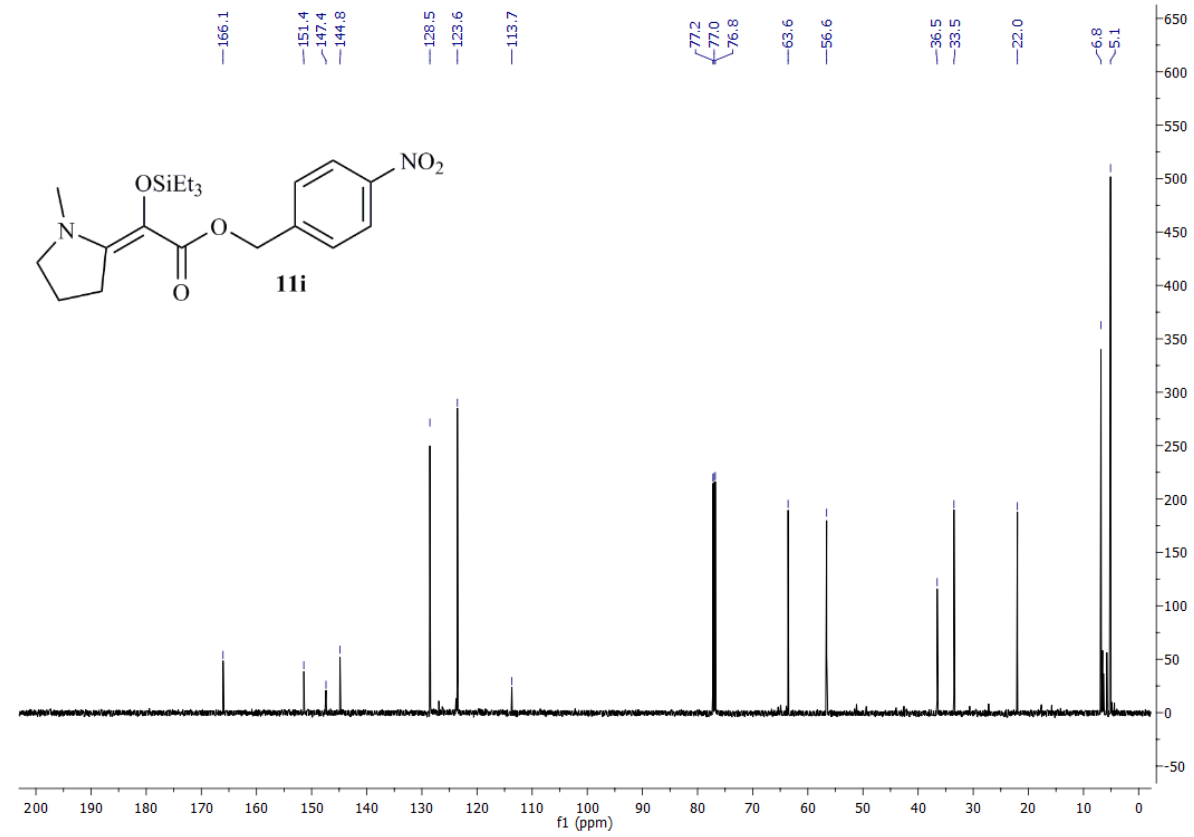
4.11
4.09
4.07
3.20
3.18
3.16
3.08
2.96
2.94
2.92
1.85
1.85
1.83
1.81
1.27
1.25
1.23
0.14
2.1
2.9
2.1
2.0
3.2
8.9
f1 (ppm)

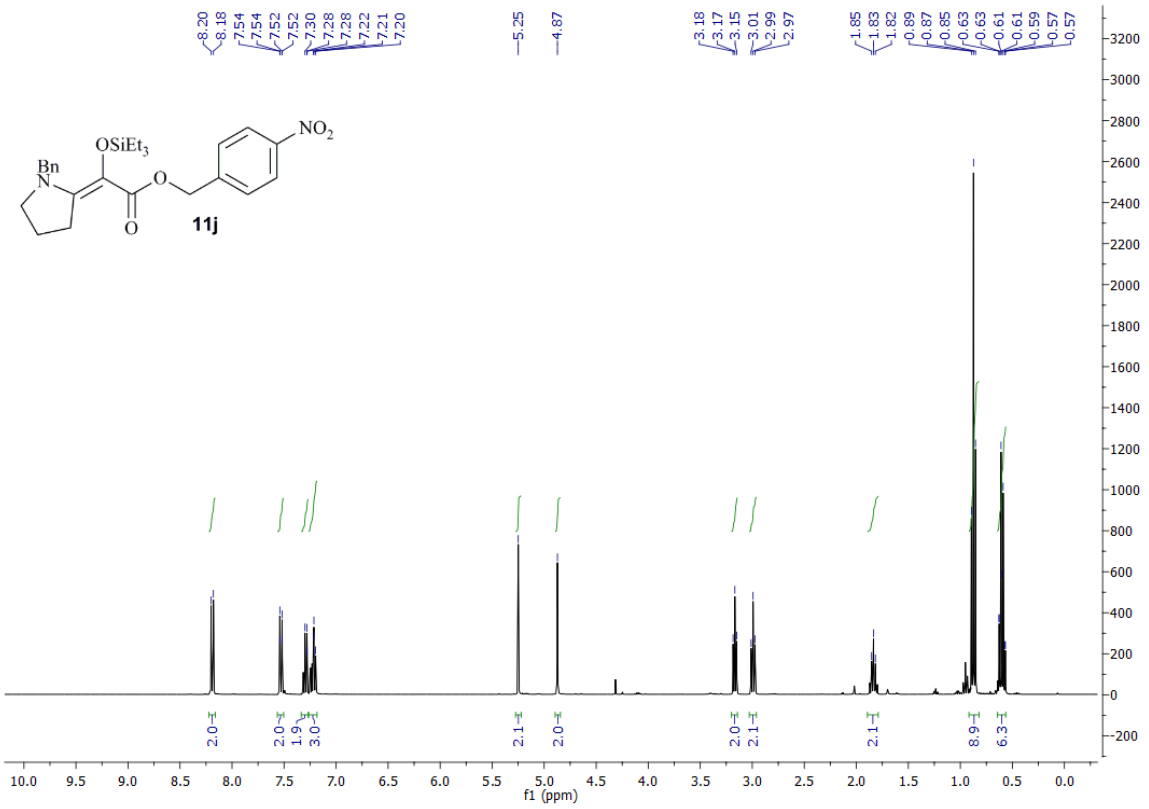

OTMS
N
OEt
O
11g
166.7
150.2
113.9
59.0
56.5
36.6
33.0
22.0
14.6
0.4
f1 (ppm)

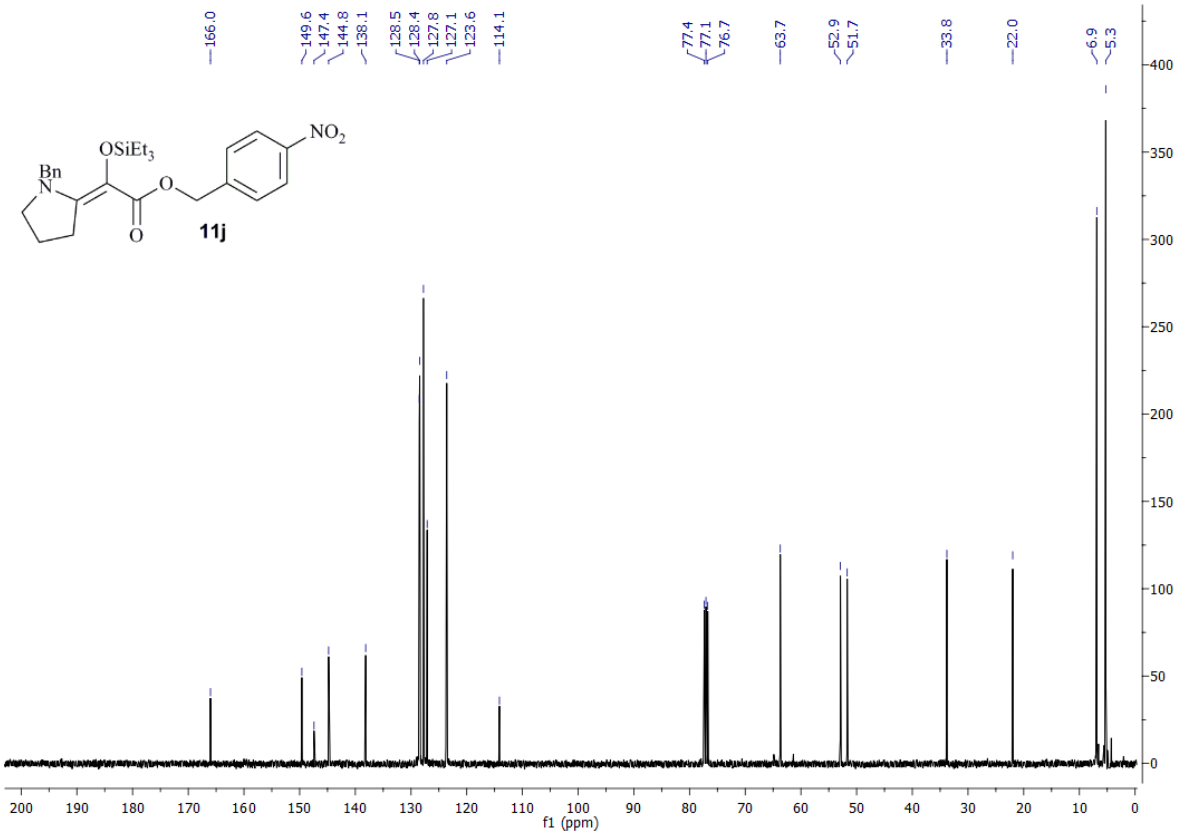

OTBS
N
O
O
11h
7.29 7.29 7.28 7.27 7.26 7.25 7.24 7.24 7.24 7.23 7.22 7.21 7.21 7.21 7.20 7.19 7.19 7.19
4.30 4.28 4.27
3.20 3.19 3.18 3.11 2.99 2.98 2.97 2.92 2.91 2.90
1.88 1.87 1.85 1.84 1.83
5.6 2.0 1.9 2.8 2.2 2.2 2.0 9.2 5.8
f1 (ppm)

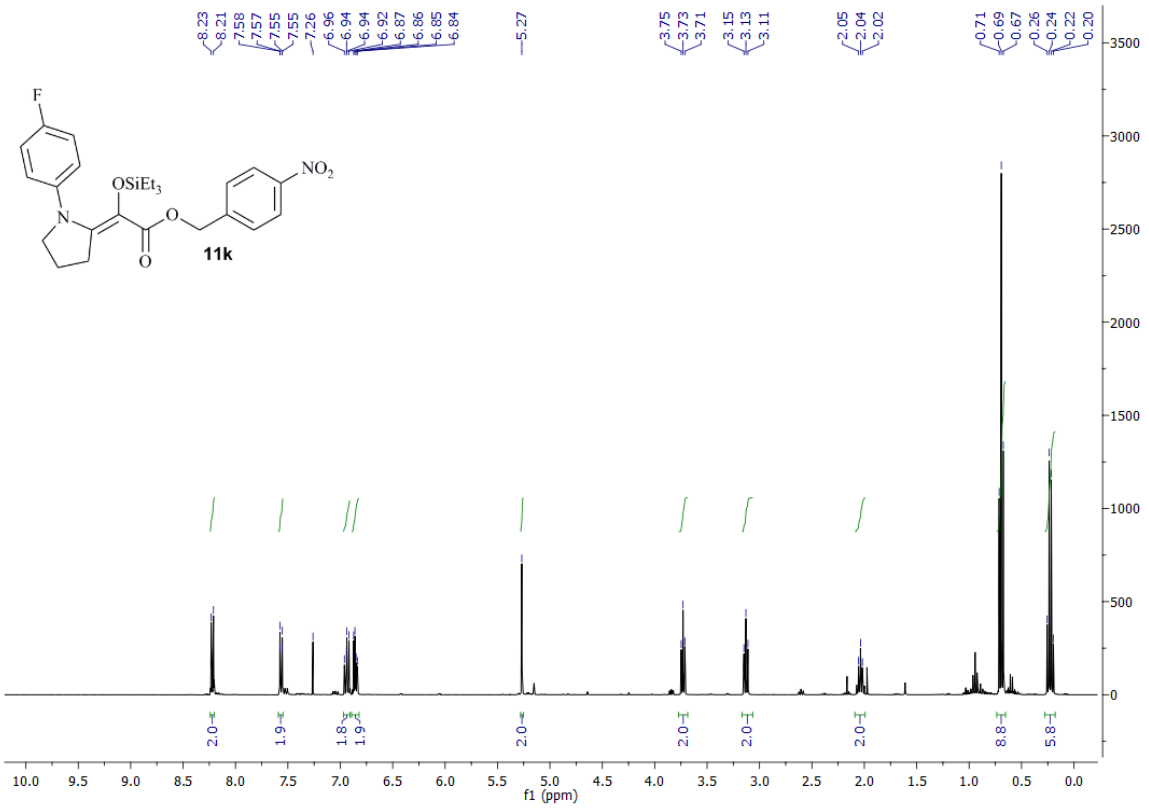

OTBS
N
O
O
11h
166.8 151.2 138.2 128.9 128.5 128.4 126.3 114.0
77.2 77.0 76.8 63.9 56.4 36.9 35.5 33.4 26.1 22.2 18.3 -4.3
f1 (ppm)

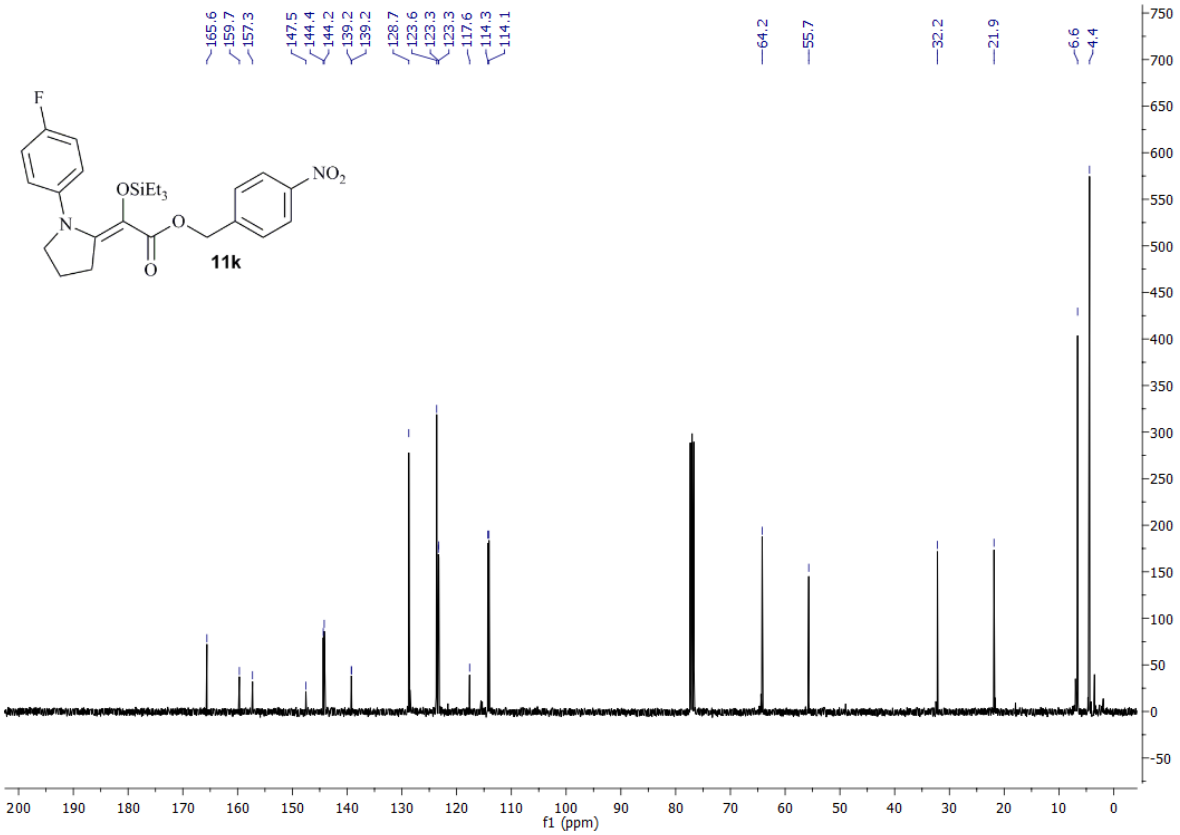

8.19
8.18
7.54
7.53
7.52
5.22
3.26
3.25
3.24
3.16
2.97
2.95
2.94
1.89
1.88
1.86
0.96
0.93
0.92
0.91
0.90
0.65
0.64
0.63
0.62
OSiEt3
NO2
N
O
O
11i
1.8
1.9
2.2
2.0
2.8
2.1
2.1
9.0
6.0
f1 (ppm)

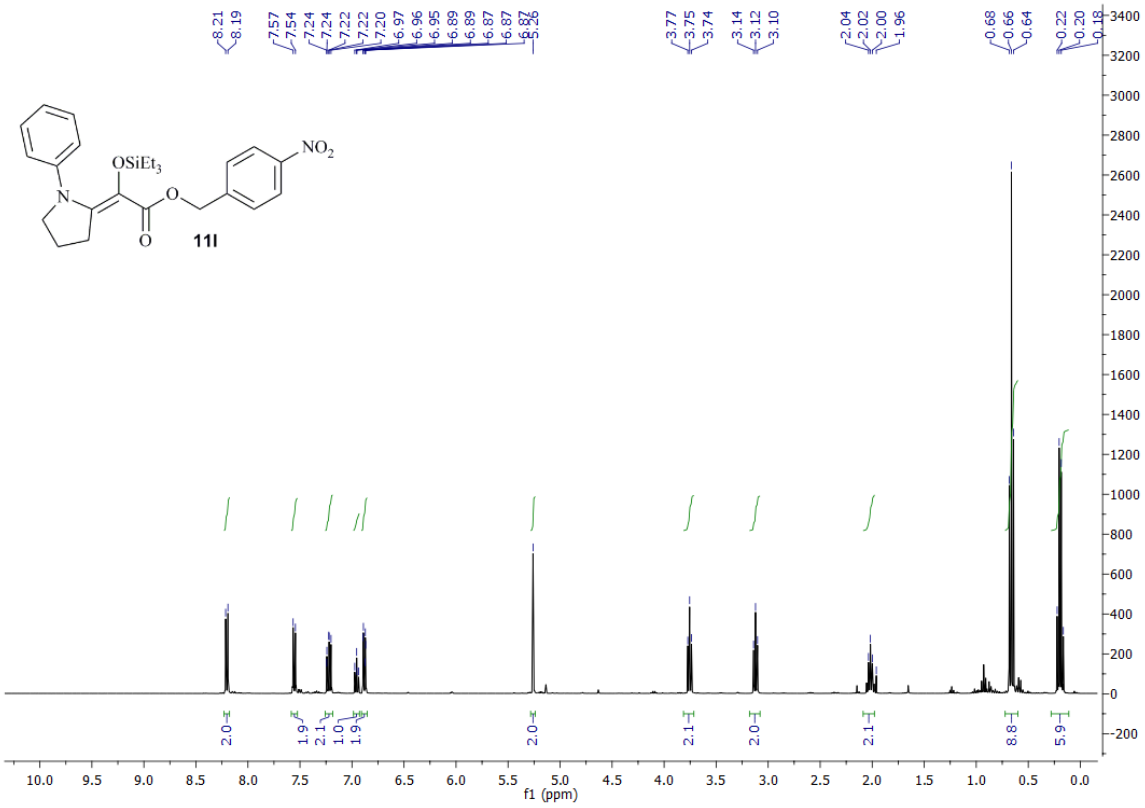

166.1
151.4
147.4
144.8
128.5
123.6
113.7
77.2
77.0
76.8
63.6
56.6
36.5
33.5
22.0
6.8
5.1
OSiEt3
NO2
N
O
O
11i
f1 (ppm)

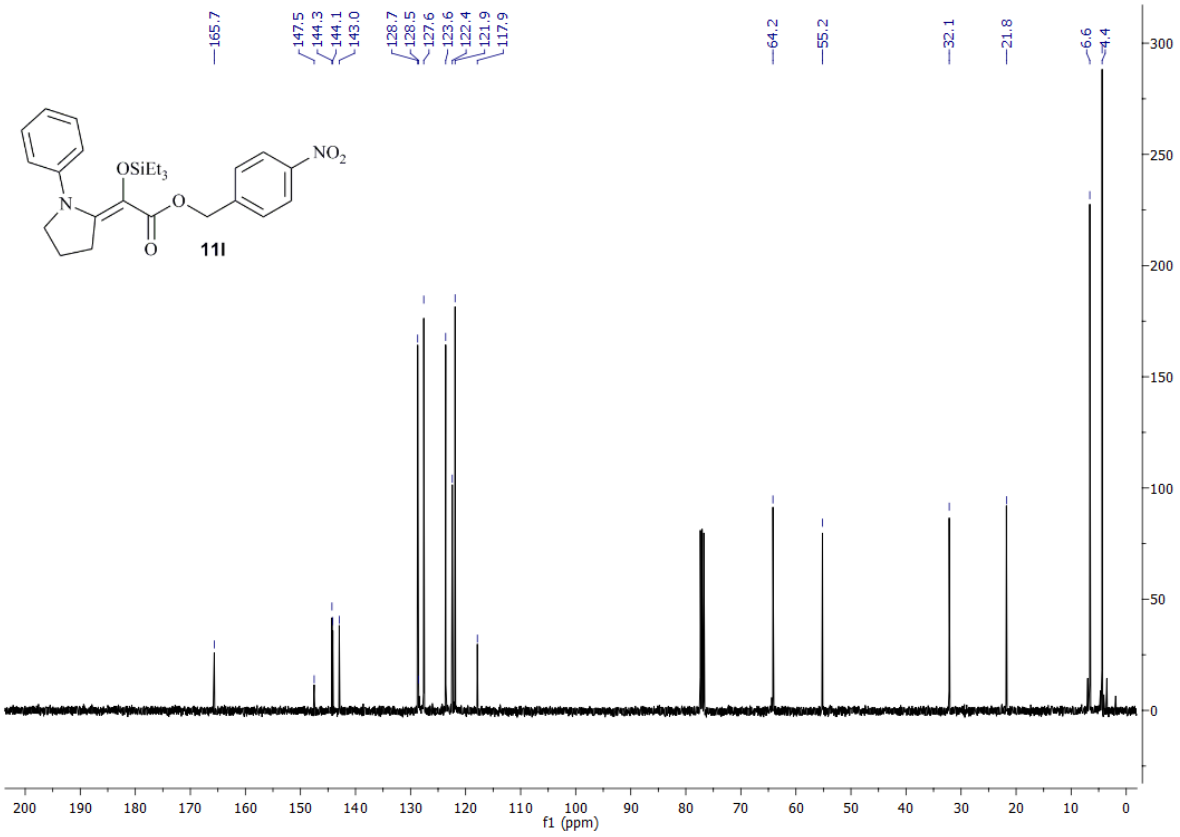

8.20
8.18
7.54
7.54
7.52
7.52
7.30
7.28
7.28
7.22
7.21
7.20
5.25
4.87
3.18
3.17
3.15
3.01
2.99
2.97
1.85
1.83
1.82
0.89
0.87
0.85
0.63
0.61
0.61
0.59
0.57
0.57
OSiEt3
Bn
N
O
O
NO2
11j
2.0
2.0
1.9
3.0
2.1
2.0
2.0
2.1
2.1
8.9
6.3
f1 (ppm)


166.0
149.6
147.4
144.8
138.1
128.5
128.4
127.8
127.1
123.6
114.1
77.4
77.1
76.7
63.7
52.9
51.7
33.8
22.0
6.9
5.3
OSiEt3
Bn
N
O
O
NO2
11j
f1 (ppm)


8.23
8.21
7.58
7.57
7.55
7.55
7.26
6.96
6.94
6.94
6.92
6.87
6.86
6.85
6.84
5.27
3.75
3.73
3.71
3.15
3.13
3.11
2.05
2.04
2.02
0.71
0.69
0.67
0.26
0.24
0.22
0.20
F
OSiEt3
N
O
O
NO2
11k
2.0
1.9
1.8
1.9
2.0
2.0
2.0
2.0
8.8
5.8
f1 (ppm)


165.6
159.7
157.3
147.5
144.4
144.2
139.2
139.2
128.7
123.6
123.3
123.3
117.6
114.3
114.1
64.2
55.7
32.2
21.9
6.6
4.4
F
OSiEt3
N
O
O
NO2
11k
f1 (ppm)


8.21
8.19
7.57
7.54
7.24
7.24
7.22
7.22
7.20
6.97
6.96
6.95
6.89
6.89
6.87
6.87
5.26
3.77
3.75
3.74
3.14
3.12
3.10
2.04
2.02
2.00
1.96
0.68
0.66
0.64
0.22
0.20
0.18
OSiEt3
NO2
N
O
O
11l
2.0
1.9
2.1
1.0
1.9
2.0
2.1
2.0
2.1
8.8
5.9
f1 (ppm)


165.7
147.5
144.3
144.1
143.0
128.7
128.5
127.6
123.6
122.4
121.9
117.9
64.2
55.2
32.1
21.8
6.6
4.4
OSiEt3
NO2
N
O
O
11l
f1 (ppm)