Carbamoyl anion-initiated cascade reaction for stereoselective synthesis of substituted α-hydroxy-β-amino amides

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Supporting Information

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General experimental information

All commercially available reagents were used without further purification unless otherwise stated. THF was freshly distilled from sodium benzophenone under argon atmosphere. All reactions were carried out under an argon atmosphere in flame-dried glassware under positive pressure of argon with magnetic stirring using standard Schlenk techniques. Column chromatography was performed on silica gel (200−300 mesh). Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with aqueous ceric ammonium molybdate followed by heating. ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm; ^{13}C NMR, $CDCl_3$ at 77.2 ppm, C_6D_6 at 128.1 ppm). NMR data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in (Hz), and integration. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) with a time-of-flight mass analyzer.

Diphenylphosphinyl aldimines were synthesized using the procedure of Jennings and co-workers.[1] Acylsilanes were synthesized from the method involving silyldithianes.[2]

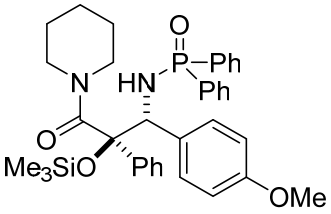
References

(1) W. B. Jenning and C. J. Lovely, *Tetrahedron*, 1991, **47**, 5561.

(2) X. Linghu, D. A. Nicewicz and J. S. Johnson, *Org. Lett*., 2002, **4**, 2957.

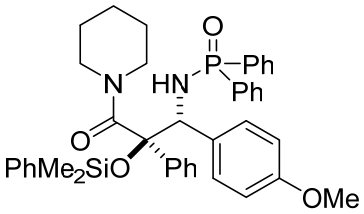
General procedure for the preparation of α-hydroxy-β-amino amides 4, 6 and 13

Formamide (0.40 mmol, 2.0 equiv) and acylsilane (0.40 mmol, 2.0 equiv) in THF (1.0 mL) were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to –78 °C, and LDA (0.50 M in THF, 0.96 mL, 2.4 equiv) was added to the reaction mixture by syringe. After the reaction mixture was stirred at this temperature for 20 min, a solution of *N*,*N*-diphenylphosphinyl aldimine (0.20 mmol) in THF (1.0 mL) was added to the reaction mixture via syringe. After the imine addition, the reaction mixture was stirred at –78 °C for an additional 30 min, at which point the reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

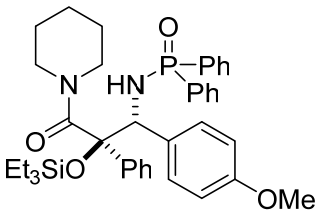


***N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((trimethyl silyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphos phinyl)-amido)-propionamide (4a):** Pale yellow oil (112.8 mg, 90%, two isomers, inseparable by column chromatography); R_f = 0.45 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.12−8.06 (m, 4H), 8.01−7.96 (m, 2H), 7.69 (dd, J = 12.0, 7.6 Hz, 2H), 7.58 (s, 2H), 7.36 (s, 2H), 7.08−6.93 (m, 18H), 6.91−6.83 (m, 5H), 6.55 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 8.4 Hz, 2H), 6.04 (s, 1H), 5.58 (s, 1H), 5.31 (s, 1H), 5.24 (t, J = 8.0 Hz, 1H), 3.54 (s, 2H), 3.22 (s, 3H), 3.20 (s, 3H), 3.10−2.92 (m, 4H), 1.39−0.95 (m, 12H), 0.61−0.58 (s, 2H), 0.46 (s, 9H), 0.37 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.8, 171.1, 159.2, 158.8, 142.6, 142.2, 132.4, 132.2, 132.1, 132.0, 131.5, 131.4, 131.3, 131.1, 131.1, 130.3, 130,3, 128.6, 128.6, 128.5, 128.4, 127.7, 127.6, 127.5, 127.0, 126.9, 112.7, 112.6, 86.7 (d, J_{C-P}= 7.9 Hz), 85.8 (d,

J_{C-P} = 7.8 Hz), 64.5, 64.2, 54.6, 54.5, 47.9, 43.8, 25.3, 24.4, 24.3, 3.3, 2.9; HRMS (ESI-TOF) calcd for $C_{36}H_{43}N_2NaO_4PSi$ $[M+Na]^+$ m/z = 649.2622, found 649.2597.

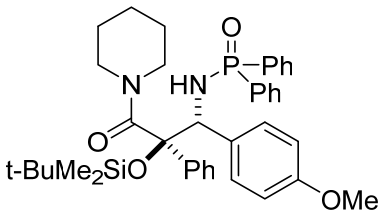


***N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((phenyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (4b):** White solid (113.7 mg, 83%, major isomer); mp 72−73 °C; R_f = 0.40 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.00−7.94 (m, 4H), 7.70−7.65 (m, 4H), 7.19−7.15 (m, 4H), 7.10−6.98 (m, 7H), 6.93−6.82 (m, 3H), 6.45 (d, J = 8.7 Hz, 2H), 5.66−5.62 (m, 1H), 5.51 (t, J = 8.0 Hz, 1H), 3.53 (s, 1H), 3.23 (s, 3H), 2.94 (s, 2H), 2.63 (s, 1H), 0.99 (s, 2H), 0.91 (s, 3H), 0.85 (s, 2H), 0.73 (s, 3H), 0.54 (s, 1H), 0.32 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 159.1, 143.1, 142.3, 135.9, 135.3, 134.7, 134.1, 134.0, 133.8, 132.5 (d, J_{C-P} = 9.9 Hz), 132.2, 131.5 (d, J_{C-P} = 2.5 Hz), 131.4 (d, J_{C-P} = 9.5 Hz), 130.9, 130.5 (d, J_{C-P}= 2.7 Hz), 128.9, 128.7, 128.6, 128.5, 128.0, 127.7, 127.6, 112.8, 86.1 (d, J_{C-P} = 7.0 Hz), 60.9, 54.6, 47.8, 44.0, 25.4, 24.4, 24.1, 3.4, 2.5; HRMS (ESI-TOF) calcd for $C_{41}H_{46}N_2O_4PSi$ $[M+H]^+$ m/z = 689.2959, found 689.2943.

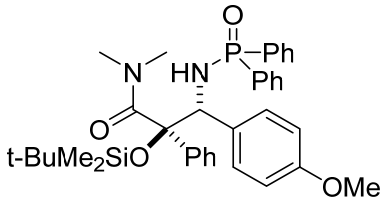


***N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((triethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (4c):** White solid (113.7 mg, 85%, major isomer); mp 118 − 119 °C; R_f = 0.43 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.10−8.05 (m, 2H), 7.69−7.64 (m, 4H), 7.12 (s, 2H), 7.09−7.05 (m, 5H), 6.95 (t, J = 7.2 Hz, 1H), 6.89−6.81 (m, 3H), 6.38 (d, J = 8.4 Hz, 2H), 6.06 (s, 1H), 5.23 (t, J = 8.0 Hz, 1H), 3.31 (s, 2H), 3.20 (s, 3H), 2.95 (s, 2H), 1.14−1.11 (m, 2H), 1.10 (s, 9H), 1.08−1.02 (m, 2H), 1.00−0.91 (m, 6H), 0.62 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.0, 158.8, 143.0, 136.3, 136.1, 135.1, 134.9, 132.6, 132.1 (d, J_{C-P} = 9.8 Hz), 131.3 (d, J_{C-P} = 2.4 Hz), 131.3, 131.2 (d, J_{C-P} = 3.2 Hz), 130.2 (d, J_{C-P} = 2.6 Hz), 128.6, 128.5, 128.2, 127.7, 127.0, 112.7, 85.7 (d, J_{C-P} = 7.4 Hz), 64.4, 54.6, 47.7, 43.7, 25.6, 24.6, 24.3, 8.0, 7.6; HRMS (ESI-TOF) calcd for $C_{39}H_{49}N_2NaO_4PSi$ $[M+Na]^+$ m/z = 691.3091, found

691.3080.

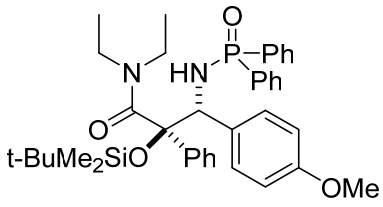


***N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (4d):** White solid (132.0 mg, 99%); mp 60−61 °C; R_f = 0.45 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.33 (d, J = 7.6 Hz, 2H), 8.04−7.99 (m, 2H), 7.79 (dd, J = 12.4, 6.8 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 2.4 Hz, 3H), 6.98−6.90 (m, 3H), 6.59 (d, J = 8.4 Hz, 2H), 5.59 (t, J = 8.4 Hz, 1H), 5.29 (dd, J = 14.4, 8.4 Hz, 1H), 3.84 (s, 1H), 3.27 (s, 3H), 3.13 (s, 1H), 2.40 (s, 1H), 2.25 (s, 1H), 1.03 (s, 3H), 0.88 (s, 9H), 0.82 (s, 1H), 0.71 (s, 3H), 0.63 (s, 1H), 0.45 (s, 1H), 0.32 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 169.8, 159.3, 142.5, 135.9, 134.7, 134.5, 133.3, 133.2, 133.0 (d, J_{C-P} = 9.9 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 9.8 Hz), 130.9 (d, J_{C-P} = 2.6 Hz), 130.1, 128.8, 128.7, 128.6, 128.4, 128.0, 113.0, 85.9 (d, J_{C-P} = 6.1 Hz), 58.3, 54.7, 47.5, 43.9, 26.9, 25.4, 24.4, 24.3, 19.9, −0.8, −1.5; HRMS (ESI-TOF) calcd for $C_{39}H_{50}N_2O_4PSi$ $[M+H]^+$ m/z = 669.3272, found 669.3269.

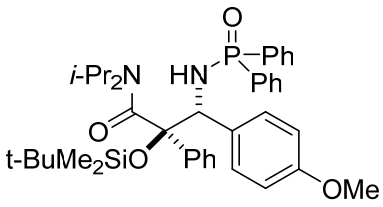


***N*,*N*-dimethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (4e):** Yellow oil (119.1 mg, 93%); R_f = 0.30 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.09 (d, J = 7.6 Hz, 2H), 8.05−8.00 (m, 2H), 7.79 (dd, J = 12, 7.6 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 8.8 Hz, 3H), 7.06−7.04 (m, 3H), 6.98−6.91 (m, 3H), 6.54 (d, J = 8.8 Hz, 2H), 5.47 (t, J = 8.4 Hz, 1H), 5.30 (dd, J =12.8, 8.4 Hz, 1H), 3.26 (s, 3H), 2.31 (s, 3H), 2.03 (s, 3H), 0.86 (s, 9H), 0.66 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.5, 159.3, 142.2, 137.8, 136.0, 134.7 (d, J_{C-P}= 4.7 Hz), 133.5, 132.9 (d, J_{C-P} = 9.9 Hz), 132.4, 132.1 (d, J_{C-P} = 8.9 Hz), 131.6 (d, J_{C-P} = 2.8 Hz), 131.6, 131.5, 130.8, 130.8, 130.2, 128.8, 128.6, 128.6, 128.5, 128.0, 127.9, 113.0, 85.7 (d, J_{C-P} = 5.6 Hz), 59.4, 54.7, 38.0, 36.5, 26.8, 19.7, −1.0, −2.1; HRMS (ESI-TOF) calcd for $C_{36}H_{46}N_2O_4PSi$ $[M+H]^+$

m/z = 629.2959, found 629.2951.

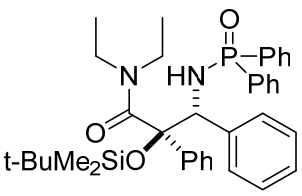


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (4f):** White solid (131.3 mg, 100%); mp 89−90 °C; R_f = 0.45 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.30 (d, J = 7.7 Hz, 2H), 7.98−7.93 (m, 2H), 7.76 (dd, J = 12.0, 6.4 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.03−7.02 (m, 3H), 6.98−6.89 (m, 3H), 6.57 (d, J = 8.5 Hz, 2H), 5.68 (t, J = 8.4 Hz, 1H), 5.22 (dd, J = 14.7, 8.4 Hz, 1H), 3.29 (s, 3H), 3.26−3.17 (m, 1H), 3.15−3.05 (m, 1H), 2.47−2.37 (m, 1H), 2.32−2.26 (m, 1H), 0.85 (s, 9H), 0.69 (s, 3H), 0.45 (t, J = 6.9 Hz, 3H), 0.34 (s, 3H), 0.05 (t, J = 6.8 Hz, 3H); ^{3}C NMR (100 MHz, C_6D_6) δ 170.6, 159.6, 142.5, 135.9, 134.7, 134.5, 133.2, 133.0 (d, J_{C-P} = 10.0 Hz), 131.7 (d, J_{C-P} = 2.4 Hz), 131.5 (d, J_{C-P} = 9.8 Hz), 130.8 (d, J_{C-P} = 2.6 Hz), 130.3, 128.8, 128.7, 128.5, 128.4, 127.9, 113.1, 86.0 (d, J_{C-P} = 6.2 Hz), 57.9, 54.8, 42.2, 40.3, 27.0, 19.9, 11.7, 11.5, −0.7, −1.2; HRMS (ESI-TOF) calcd for $C_{38}H_{49}N_2NaO_4PSi$ $[M+H]^+$ m/z = 679.3091, found 679.3088.

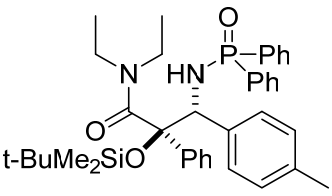


***N*,*N*-diisopropyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (4g):** White solid (56.8 mg, 42%); mp 57−58 °C, R_f = 0.60 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.41 (d, J = 8.0 Hz, 2H), 7.89−7.84 (m, 2H), 7.72−7.67 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 7.01−6.89 (m, 6H), 6.57 (d, J = 8.8 Hz, 2H), 5.83 (t, J = 8.4 Hz, 1H), 4.97 (dd, J = 16.4, 8.8 Hz, 1H), 3.84−3.74 (m, 1H), 3.26 (s, 3H), 2.73−2.63 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H), 0.88−0.79 (m, 12H), 0.72 (s, 3H), 0.58 (d, J = 6.5 Hz, 3H), 0.38 (s, 3H), 0.08 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 169.8, 159.5, 142.8, 136.2, 135.0, 134.5, 133.3, 133.0, 132.9 (d, J_{C-P} = 10.0 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.4 (d, J_{C-P} = 10.1 Hz), 131.2, 130.7 (d, J_{C-P} = 2.7 Hz), 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 112.9, 86.4 (d, J_{C-P} = 6.2 Hz), 57.2, 54.8, 48.9, 46.6, 27.0,

20.2, 20.1, 19.8, 19.3, 18.9, −0.5, −0.7. HRMS (ESI-TOF) calcd for $C_{40}H_{54}N_2O_4PSi$ $[M+H]^+$ m/z = 685.3585, found 685.3579.

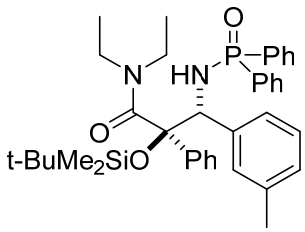


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-phenyl-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6b):** White solid (124.3 mg, 99%); mp 181−182 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.32 (d, J = 8.0 Hz, 2H), 7.98−7.92 (m, 2H), 7.76−7.71 (m, 2H), 7.30 (t, J = 8.0 Hz, 4H), 7.08 (t, J = 7.2 Hz, 1H), 7.03−7.00 (m, 3H), 6.98−6.93 (m, 4H), 6.90 −6.87 (m, 2H), 5.70 (t, J = 8.8 Hz, 1H), 5.23 (dd, J = 14.8, 8.4 Hz, 1H), 3.26−3.08 (m, 2H), 2.38−2.19 (m, 2H), 0.84 (s, 9H), 0.68 (s, 3H), 0.38−0.34 (m, 6H), 0.02 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.4, 142.4, 141.0, 135.9, 134.7, 134.3, 133.0 (d, J_{C-P} = 9.9 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 9.9 Hz), 130.9 (d, J_{C-P} = 2.7 Hz), 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.7, 127.5, 85.8 (d, J_{C-P} = 5.8 Hz), 58.2, 42.2, 40.2, 27.0, 19.9, 11.5, 11.5, −0.7, −1.2; HRMS (ESI-TOF) calcd for $C_{37}H_{48}N_2O_3PSi$ $[M+H]^+$ m/z = 627.3166, found 627.3165.

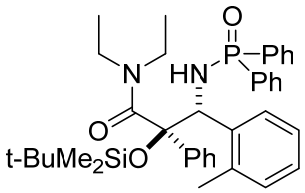


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methylphenyl)-3-((*N'*-diphenylphosphinyl)-amido) -propionamide (6c):** White solid (119.2 mg, 93%); mp 133−134 °C, R_f = 0.55 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.31 (d, J = 8.0 Hz, 2H), 7.98 - 7.90 (m, 2H), 7.77−7.71 (m, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 7.03−7.01 (m, 3H), 6.98−6.94 (m, 1H), 6.91−6.86 (m, 2H), 6.75 (d, J = 7.6 Hz, 2H), 5.69 (t, J = 8.6 Hz, 1H), 5.20 (dd, J = 14.8, 8.4 Hz, 1H), 3.25−3.08 (m, 2H), 2.44 −2.36 (m, 1H), 2.31−2.21 (m, 1H), 2.06 (s, 3H), 0.86 (s, 9H), 0.70 (s, 3H), 0.42 (t, J = 7.0 Hz, 3H), 0.35 (s, 3H), 0.03 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 142.5, 138.1, 136.8, 136.0, 134.7, 134.4, 133.2, 133.0 (d, J_{C-P} = 10 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.5 (d, J_{C-P}= 9.9 Hz), 130.7 (d, J_{C-P} = 2.7 Hz), 129.1, 128.8, 128.6, 128.6, 128.5, 128.4, 128.3, 127.9, 127.7, 85.9 (d, J_{C-P} = 6.0 Hz), 58.0, 42.2, 40.3, 27.0, 21.1, 20.0, 11.5, −0.7, −1.2; HRMS (ESI-TOF) calcd for $C_{38}H_{50}N_2O_3PSi$

$[M+H]^+$ m/z = 641.3323, found 641.3335.

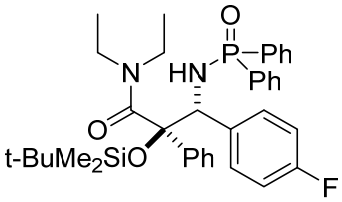


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(3-methylphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6d):** White solid (120.3 mg, 94%); mp 144−145 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.32 (d, J = 7.6 Hz, 2H), 7.97−7.91 (m, 2H), 7.76−7.71 (m, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.13−7.06 (m, 3H), 7.02−7.00 (m, 3H), 6.95−6.93 (m, 1H), 6.93−6.87 (m, 3H), 6.77 (d, J = 7.6 Hz, 1H), 5.70 (t, J = 8.6 Hz, 1H), 5.18 (dd, J = 15.2, 8.6 Hz, 1H), 3.30−3.22 (m, 1H), 3.19−3.10 (m, 1H), 2.38−2.30 (m, 1H), 2.27−2.20 (m, 1H), 2.08 (s, 3H), 0.86 (s, 9H), 0.67 (s, 3H), 0.39−0.36 (m, 6H), 0.02 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.4, 142.5, 140.7, 136.7, 135.9, 134.6, 134.4, 133.1, 133.0 (d, J_{C-P} = 10.0 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 10.0 Hz), 130.8 (d, J_{C-P} = 2.8 Hz), 130.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.7, 127.6, 126.3, 85.8 (d, J_{C-P} = 5.9 Hz), 58.1, 42.1, 40.2, 27.0, 21.3, 20.0, 11.5, 11.4, −0.7, −1.1; HRMS (ESI-TOF) calcd for $C_{38}H_{50}N_2O_3PSi$ $[M+H]^+$ m/z = 641.3323, found 641.3312.

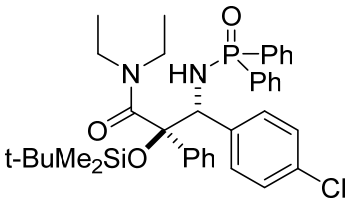


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(2-methylphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6e):** White solid (115.4 mg, 89%); mp 91−92 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.27 (d, J = 7.6 Hz, 2H), 8.15 (d, J = 7.2 Hz, 1H), 7.92−7.86 (m, 2H), 7.63−7.58 (m, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.10−7.04 (m, 2H), 7.01−6.98 (m, 3H), 6.95 (dd, J = 7.6, 1.2 Hz, 1H), 6.89−6.82 (m, 3H), 6.48 (d, J = 7.6 Hz, 1H), 6.02 (t, J = 8.4 Hz, 1H), 5.41 (dd, J = 15.3, 8.6 Hz, 1H), 3.47−3.38 (m, 1H), 3.14−3.05 (m, 1H), 2.45−2.32 (m, 2H), 2.08 (s, 3H), 0.80 (s, 9H), 0.78 (s, 3H), 0.32 (t, J = 6.8 Hz, 3H), 0.23 (s, 3H), 0.07 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.7, 142.8, 140.4, 136.2, 136.0, 135.0, 134.3, 133.0, 132.9 (d, J_{C-P} = 10.0 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 9.9 Hz), 130.8 (d, J_{C-P} = 2.8 Hz), 129.9, 129.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 127.7, 127.3, 126.1, 85.9 (d, J_{C-P} =

6.3 Hz), 53.9, 42.1, 39.8, 26.8, 19.8, 19.7, 11.6, 11.0, −1.0, −1.7; HRMS (ESI-TOF) calcd for $C_{38}H_{50}N_2O_3PSi$ $[M+H]^+$ m/z = 641.3323, found 641.3323.

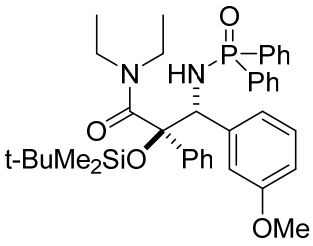


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl) -3-(4-fluorophenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6f):** White solid (116.0 mg, 90%); mp 187−188 °C, R_f = 0.40 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.21 (d, J = 7.6 Hz, 2H), 7.95−7.90 (m 2H), 7.69 (dd, J = 12.4, 7.2 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.13 (s, 2H), 7.06 (t, J = 7.2 Hz, 4H), 7.02−7.01 (m, 3H), 6.95 (t, J = 8Hz, 1H), 6.91−6.87 (m, 2H), 6.61 (t, J = 8.6 Hz, 2H), 5.63 (t, J = 8.3 Hz, 1H), 5.22 (dd, J = 14.0, 8.4 Hz, 1H), 3.20−3.12 (m, 1H), 3.09 −3.00 (m, 1H), 2.40−2.31 (m, 1H), 2.24−2.19 (m, 1H), 0.82 (s, 9H), 0.63 (s, 3H), 0.40 (t, J = 6.8 Hz, 3H), 0.31 (s, 3H), 0.02 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.4, 162.6 (d, J_{C-P} = 244.2 Hz), 142.2, 136.8 (d, J_{C-P} = 2.9 Hz), 135.6, 134.4, 134.2, 132.9, 132.8 (d, J_{C-P} = 9.9 Hz), 132.2 (d, J_{C-P} = 9.5 Hz), 131.8 (d, J_{C-P} = 2.5 Hz), 131.5 (d, J_{C-P} = 9.8 Hz), 131.0 (d, J_{C-P} = 2.7 Hz), 130.9 (d, J_{C-P} = 7.9 Hz), 128.8, 128.7, 128.6, 128.4, 128.2, 128.0, 127.9, 127.82, 114.3 (d, J_{C-P} = 21 Hz), 85.8 (d, J_{C-P} = 6.1 Hz), 57.8, 42.2, 40.3, 26.9, 19.9, 11.6, 11.5, −0.8, −1.3; HRMS (ESI-TOF) calcd for $C_{37}H_{47}FN_2O_3PSi$ $[M+H]^+$ m/z = 645.3072, found 645.3077.

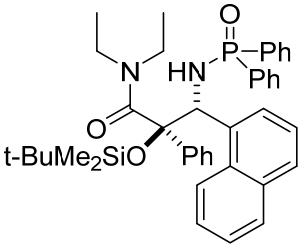


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-ox yl)-3-(4-chlorophenyl)-3-((*N'*-diphenylphosphinyl)-a mido)-propionamide (6g):** White solid (124.3 mg, 94%); mp 161−162 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.18 (d, J = 7.6 Hz, 2H), 7.95 - 7.89 (m, 2H), 7.69 - 7.64 (m, 2H), 7.26 (t, J = 7.8 Hz, 2H), 7.11−7.08 (m, 2H), 7.06−6.96 (m, 5H), 6.90 (d, J = 8.4 Hz, 4H), 5.58 (t, J = 8.4 Hz, 1H), 5.22 (dd, J = 14.4, 8.4 Hz, 1H), 3.18−3.10 (m, 1H), 3.05−2.96 (m, 1H), 2.40−2.31 (m, 1H), 2.24−2.19 (m, 1H), 0.82 (s, 9H), 0.62 (s, 3H), 0.40 (t, J = 6.8 Hz, 3H), 0.29 (s, 3H), 0.02 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.3, 142.1, 139.5, 135.5, 134.2, 134.0, 133.4, 133.3 (d, J_{C-P} = 8.7 Hz)), 132.8 (d, J_{C-P} = 9.9 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 9.4

Hz), 131.4 (d, J_{C-P} = 10 Hz), 131.0 (d, J_{C-P} = 2.8 Hz), 130.8 (d, J_{C-P} = 2.0 Hz), 130.6, 128.8, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.7, 126.4, 85.6(d, J_{C-P} = 6.1 Hz) , 58.1, 42.2, 40.3, 26.9, 19.8, 11.5, 11.5, −0.8, −1.4; HRMS (ESI-TOF) calcd for $C_{37}H_{47}ClN_2O_3PSi$ $[M+H]^+$ m/z = 661.2777, found 661.2751.

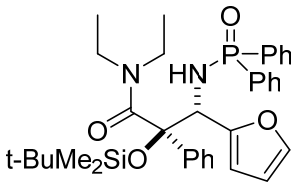


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(3-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6h):** White solid (123.1 mg, 93%); mp 138−139 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.30 (d, J = 7.7 Hz, 2H), 7.97−7.92 (m, 2H), 7.77 (dd, J = 12.4, 6.8 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 7.02−7.01 (m, 3H), 6.98−6.89 (m, 6H), 6.57 (d, J = 8.0 Hz, 1H), 5.71 (t, J = 8.4 Hz, 1H), 5.22 (dd, J = 15.2, 8.8 Hz, 1H), 3.39 (s, 3H), 3.32−3.21 (m, 1H), 3.16−3.04 (m, 1H), 2.46−2.37 (m, 1H), 2.35−2.27 (m, 1H), 0.85 (s, 9H), 0.68 (s, 3H), 0.44 (t, J = 6.8 Hz, 3H), 0.30 (s, 3H), 0.02 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 153.0, 141.7, 141.2, 135.6, 135.1, 134.4, 133.8, 132.6 (d, J_{C-P} = 9.9 Hz), 131.8, 131.7 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 2.7 Hz), 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 110.1, 109.4, 84.7 (d, J_{C-P} = 6.1 Hz), 53.5, 42.6, 41.2, 27.0, 19.9, 12.5, 11.7, −1.1, −1.5; HRMS (ESI-TOF) calcd for $C_{38}H_{50}N_2O_4PSi$ $[M+H]^+$ m/z = 657.3272, found 657.3250.

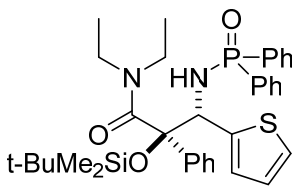


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(1-naphthyl)-3-((*N'*-diphenylphosphinyl)-amido)-propion amide (6i):** White solid (98.3 mg, 73%); mp 202−203 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.51 (d, J = 7.6 Hz, 2H), 8.37−8.32 (m, 2H), 7.96−7.90 (m, 2H), 7.49−7.43 (m, 3H), 7.37 (dd, J = 12.0, 8.4 Hz, 4H), 7.11−7.00 (m, 6H), 6.77 (t, J = 8.4 Hz, 1H), 6.63−6.59 (m, 1H), 6.55−6.51 (m, 2H), 5.29 (dd, J = 15.6, 8.8 Hz, 1H), 3.29−3.18 (m, 2H), 2.09−2.01 (m, 1H), 1.99−1.91 (m, 1H), 0.87 (s, 9H), 0.83 (s, 3H), 0.28 (s, 3H), −0.04 (t, J = 6.8 Hz, 3H), −0.29 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.2, 143.0, 138.4, 135.9, 134.7, 133.4, 132.6 (d, J_{C-P}

= 10 Hz), 132.1, 131.8 (d, J_{C-P} = 2.6 Hz), 131.6, 131.4 (d, J_{C-P} = 10.1 Hz), 130.6 (d, J_{C-P} = 2.8 Hz), 129.0, 128.65, 128.59, 128.5, 128.40, 128.35, 127.1 (d, J_{C-P} = 3.8 Hz), 127.0, 125.5 (d, J_{C-P} = 10.6 Hz), 124.9, 123.8, 86.3 (d, J_{C-P} = 6.2 Hz), 50.9, 42.2, 39.3, 26.9, 19.9, 11.5, 10.4, −0.9, −1.5; HRMS (ESI-TOF) calcd for $C_{41}H_{50}N_2O_3PSi$ $[M+H]^+$ m/z = 677.3323, found 677.3302.

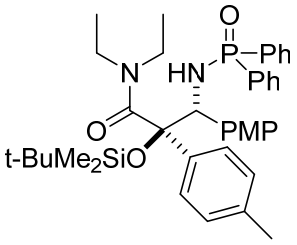


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(2-furyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6j):** White solid (106.9 mg, 87%); mp 102−103 °C, R_f = 0.45 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.08 (d, J = 7.6 Hz, 2H), 7.97−7.89 (m, 4H), 7.24 (t, J = 7.8 Hz, 2H), 7.08−7.04 (m, 4H), 7.01−6.98 (m, 3H), 6.88 (d, J = 0.4 Hz, 1H), 5.87−5.81 (m, 3H), 4.97 (dd, J = 13.6, 8.8 Hz, 1H), 3.78 (s, 1H), 2.90 (s, 1H), 2.62 (s, 2H), 0.90 (s, 9H), 0.79 (s, 3H), 0.56 (s, 3H), 0.39 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 153.0, 141.7, 135.6, 135.1, 134.4, 133.8, 132.6 (d, J_{C-P} = 9.9 Hz), 131.7, 131.6 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 2.7 Hz), 128.6, 128.47, 128.45, 128.2, 128.1, 110.1, 109.4, 84.6 (d, J_{C-P} = 6.0 Hz), 53.4, 42.6, 41.2, 27.0, 19.9, 12.5, 11.7, −1.1, −1.5; HRMS (ESI-TOF) calcd for $C_{35}H_{46}N_2O_4PSi$ $[M+H]^+$ m/z = 617.2959, found 617.2962.

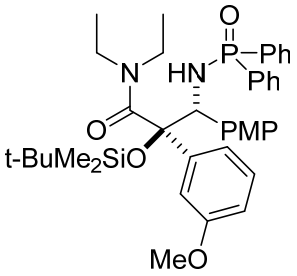


***N*,*N*-diethyl-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(2-thienyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6k):** White solid (114.1 mg, 90%); mp 174−175 °C, R_f = 0.45 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.21 (d, J = 7.6 Hz, 2H), 7.98−7.93 (m, 2H), 7.85−7.80 (m, 2H), 7.24 (t, J = 8.0 Hz, 2H), 7.08−6.95 (m, 7H), 6.67 (m, 2H), 6.37 (dd, J = 4.8, 3.6 Hz, 1H), 6.02 (t, J = 8.4 Hz, 1H), 5.19 (dd, J = 14.4, 9.2 Hz, 1H), 3.35−3.27 (m, 1H), 3.01−2.93 (m, 1H), 2.56−2.51 (m, 2H), 0.88 (s, 9H), 0.72 (s, 3H), 0.58 (t, J = 6.4 Hz, 3H), 0.27 (s, 3H), 0.07 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.4, 143.7, 141.7, 135.9, 134.7, 134.6, 133.4, 132.6 (d, J_{C-P} = 10.0 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 9.7 Hz), 130.9 , (d, J_{C-P} = 2.7 Hz), 128.65, 128.61, 128.5, 128.4,

127.9, 127.1, 125.3, 125.2, 85.6 (d, J_{C-P} = 6.0 Hz), 55.5, 42.3, 40.4, 26.9, 19.9, 11.7, 11.6, −0.6, −1.6; HRMS (ESI-TOF) calcd for $C_{35}H_{46}N_2O_3PSSi$ $[M+H]^+$ m/z = 633.2731, found 633.2727.

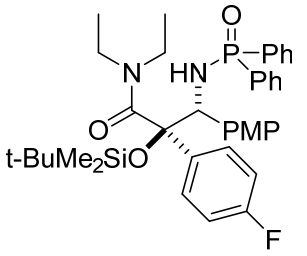


***N*,*N*-diethyl-2-(4-methylphenyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6l):** White solid (120.3 mg, 90%); mp 155−156 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.23 (d, J = 8.0 Hz, 2H), 8.01−7.95 (m, 2H), 7.78 (dd, J = 12.0, 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 2.4 Hz, 3H), 6.98−6.89 (m, 3H), 6.58 (d, J = 8.4 Hz, 2H), 5.69 (t, J = 8.4 Hz, 1H), 5.21 (dd, J = 14.8, 8.4 Hz, 1H), 3.29 (s, 3H), 3.27−3.13 (m, 2H), 2.47−2.39 (m, 1H), 2.34−2.25 (m, 1H), 2.07 (s, 3H), 0.88 (s, 9H), 0.71 (s, 3H), 0.45 (t, J = 6.8 Hz, 3H), 0.36 (s, 3H), 0.10 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.7, 159.6, 139.7, 137.9, 136.1, 134.9, 134.5, 133.4, 133.3, 133.1 (d, J_{C-P} = 9.8 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.5 (d, J_{C-P} = 9.9 Hz), 130.8 (d, J_{C-P} = 2.8 Hz), 130.3, 129.5, 128.64, 128.59, 128.5, 128.4, 127.9, 126.4, 113.1, 85.9 (d, J_{C-P} = 6.11 Hz), 57.8, 54.8, 42.2, 40.3, 26.9, 21.1, 20.0, 11.72, 11.68, −0.7, −1.2; HRMS (ESI-TOF) calcd for $C_{39}H_{52}N_2O_4PSi$ $[M+H]^+$ m/z = 671.3428, found 671.3431.

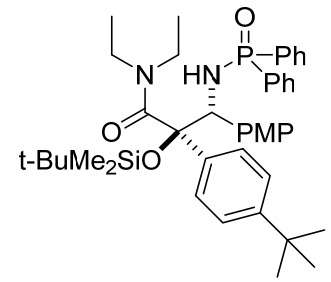


***N*,*N*-diethyl-2-(3-methoxyphenyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6m):** White solid (126.4 mg, 92%); mp 134−135 °C, R_f = 0.45 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.24 (s, 1H), 7.97−7.92 (m, 2H), 7.75 (dd, J = 12.0, 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 8.4 Hz, 3H), 7.02 (s, 3H), 6.95−6.86 (m, 4H), 6.55 (d, J = 8.4 Hz, 2H), 5.67 (t, J = 8.4 Hz, 1H), 5.27 (dd, J = 14.8, 8.4 Hz, 1H), 3.86 (s, 3H), 3.28 (s, 3H), 3.22−3.13 (m, 2H), 2.45−2.37 (m, 1H), 2.30−2.25 (m, 1H), 0.89 (s, 9H), 0.72 (s, 3H), 0.43 (t, J = 6.8 Hz, 3H), 0.38 (s, 3H), 0.13 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 160.8, 159.5, 144.0, 135.8, 134.6, 134.3, 133.3, 133.0 (d, J_{C-P} = 9.9 Hz), 131.8 (d,

J_{C-P} = 2.5 Hz), 131.4 (d, J_{C-P} = 9.8 Hz), 130.8 (d, J_{C-P} = 2.7 Hz), 130.2, 129.6, 128.7, 128.6, 127.9, 121.0, 115.4, 113.1, 112.8, 86.0 (d, J_{C-P} = 6.3 Hz), 57.7, 56.1, 54.8, 42.2, 40.3, 27.0, 20.0, 11.7, 11.6, −0.7, −1.2; HRMS (ESI-TOF) calcd for $C_{39}H_{52}N_2O_5PSi$ $[M+H]^+$ m/z = 687.3378, found 687.3358.

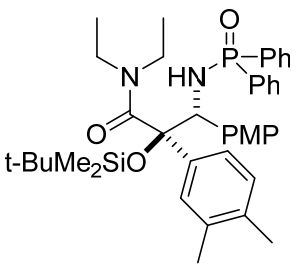


***N*,*N*-diethyl-2-(4-fluorophenyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6n):** White solid (135.0 mg, 100%); mp 87−88 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.21 (s, 2H), 7.95−7.90 (m, 2H), 7.74 (dd, J = 12.0, 7.6 Hz, 2H), 7.18 (s, 2H), 7.03 (s, 3H), 7.00−6.89 (m, 5H), 6.57 (d, J = 8.4 Hz, 2H), 5.59 (t, J = 8.4 Hz, 1H), 5.17 (dd, J = 14.4, 8.4 Hz, 1H), 3.28 (s, 3H), 3.23 - 3.15 (m, 1H), 3.08−2.99 (m, 1H), 2.43−2.37 (m, 1H), 2.35−2.22 (m, 1H), 0.83 (s, 9H), 0.67 (s, 3H), 0.42 (t, J = 6.8 Hz, 3H), 0.30 (s, 3H), 0.01 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.3, 162.8 (d, J_{C-P} = 246.3 Hz), 159.6, 138.6 (d, J_{C-P} = 3.2 Hz), 135.6, 134.4, 134.1, 133.0 (d, J_{C-P} = 9.9 Hz), 131.9 (d, J_{C-P} = 2.6 Hz), 131.4 (d, J_{C-P} = 10.0 Hz), 130.9 (d, J_{C-P} = 2.6 Hz), 130.4 (d, J_{C-P} = 7.7 Hz), 130.2, 128.7, 128.6, 128.0, 115.6 (d, J_{C-P} = 20.9 Hz), 113.1, 85.4 (d, J_{C-P} = 6.1 Hz), 57.9, 54.8, 42.1, 40.3, 26.9, 19.8, 11.63, 11.59, −0.8, −1.3; HRMS (ESI-TOF) calcd for $C_{38}H_{49}FN_2O_4PSi$ $[M+H]^+$ m/z = 675.3178, found 675.3178.

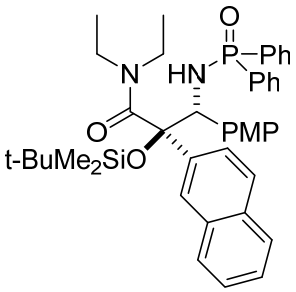


(*N*,*N*-diethyl-2-(4-*tert*-butylphenyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide 6o): White solid (142.6 mg, 100%); mp 154−155 °C, R_f = 0.55 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.26 (d, J = 8.4 Hz, 2H), 8.01−7.96 (m, 2H), 7.80−7.75 (m, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.02−7.01 (m, 3H), 6.96−6.88 (m, 3H), 6.57 (d, J = 8.4 Hz, 2H), 5.68 (t, J = 8.4 Hz, 1H), 5.25 (dd, J = 14.8, 8.0 Hz, 1H), 3.30 (s, 3H), 3.27−3.20 (m, 1H), 3.19−3.10 (m, 1H), 2.47−2.38 (m, 1H), 2.32−2.25 (m, 1H), 1.20 (s, 9H), 0.88 (s, 9H), 0.70 (s, 3H), 0.47 (t, J = 6.8 Hz, 3H), 0.36 (s, 3H), 0.05 (t, J =

6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.7, 159.5, 151.2, 139.5, 135.9, 134.7, 134.5, 133.4, 133.2, 133.1 (d, J_{C-P} = 9.8 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 9.8 Hz), 130.7 (d, J_{C-P} = 2.6 Hz), 130.3, 128.7, 128.5, 128.2, 127.9, 125.7, 113.1, 85.8 (d, J_{C-P} = 6.1 Hz), 57.9, 54.9, 42.3, 40.3, 34.6, 31.3, 27.0, 19.9, 11.8, 11.5, −0.7, −1.3; HRMS (ESI-TOF) calcd for $C_{42}H_{58}N_2O_4PSi$ $[M+H]^+$ m/z = 713.3898, found 713.3893.

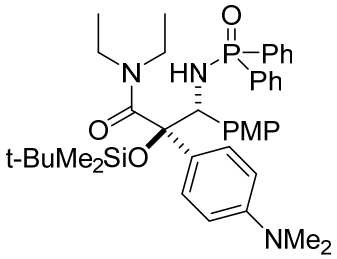


***N*,*N*-diethyl-2-(3,4-dimethylphenyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6p):** White solid (137.1 mg, 100%); mp 132−133 °C, R_f = 0.45 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.28 (s, 1H), 8.00−7.95 (m, 3H), 7.79−7.74 (m, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.0 Hz, 1H), 7.05−7.03 (m, 3H), 6.97−6.90 (m, 3H), 6.58 (d, J = 8.8 Hz, 2H), 5.69 (t, J = 8.4 Hz, 1H), 5.21 (dd, J = 14.8, 8.4 Hz, 1H), 3.30 (s, 3H), 3.26−3.18 (m, 2H), 2.48−2.40 (m, 1H), 2.32−2.28 (m, 4H), 2.01 (s, 3H), 0.87 (s, 9H), 0.71 (s, 3H), 0.44 (t, J = 6.8 Hz, 3H), 0.36 (s, 3H), 0.14 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.7, 159.5, 140.0, 136.9, 136.4, 136.1, 134.9, 134.4, 133.5, 133.1 (d, J_{C-P} = 9.9 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.5 (d, J_{C-P} = 9.9 Hz), 130.8 (d, J_{C-P} = 2.6 Hz), 130.2, 130.0, 129.5, 128.7, 128.6, 128.5, 127.9, 126.0, 113.1, 85.94, 85.9 (d, J_{C-P} = 5.9 Hz), 57.7, 54.8, 42.1, 40.3, 27.0, 20.0, 19.7, 19.4, 11.7, −0.7, −1.2; HRMS (ESI-TOF) calcd for $C_{40}H_{54}N_2O_4PSi$ $[M+H]^+$ m/z = 685.3585, found 685.3560.

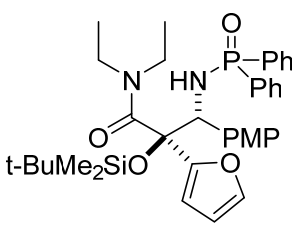


***N*,*N*-diethyl-2-(2-naphthyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6q):** White solid (134.0 mg, 95%); mp 96−97 °C, R_f = 0.50 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 9.46 (s, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.00−7.95 (m, 2H), 7.85−7.80 (m, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.33−7.25 (m, 4H), 6.98−6.94 (m, 6H), 6.61 (d, J = 8.0 Hz, 2H), 5.85 (t, J = 8.4 Hz, 1H), 5.27 (dd, J =

14.4, 8.4 Hz, 1H), 3.30 (s, 3H), 3.24−3.19 (m, 2H), 2.44−2.40 (m, 1H), 2.24−2.19 (m, 1H), 0.80 (s, 9H), 0.73 (s, 3H), 0.46 (t, J = 6.4 Hz, 3H), 0.42 (s, 3H), −0.13 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.4, 159.6, 139.6, 135.9, 134.7, 134.3, 134.2, 133.4, 133.2 (d, J_{C-P} = 9.6 Hz), 132.9, 131.7 (d, J_{C-P} = 2.5 Hz), 131.4 (d, J_{C-P} = 9.9 Hz), 131.0 (d, J_{C-P} = 2.5 Hz), 130.3, 129.3, 128.7, 128.6, 128.2, 128.0, 127.4, 126.8, 126.73, 126.67, 113.2, 86.2 (d, J_{C-P} = 5.9 Hz), 57.7, 54.8, 42.2, 40.4, 26.9, 20.0, 11.7, 11.6, −0.6, −0.9; HRMS (ESI-TOF) calcd for $C_{42}H_{52}N_2O_4PSi$ $[M+H]^+$ m/z = 707.3428, found 707.3406.

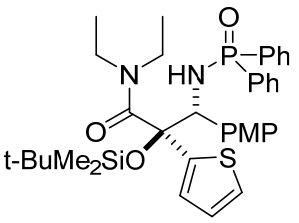


N,N-diethyl-2-((4-dimethylamino)-phenyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (6r): White solid (105.9 mg, 76%); mp 70−71 °C, R_f = 0.45 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, C_6D_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.05−8.00 (m, 2H), 7.80 (dd, J = 12.0, 7.6 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 2.0 Hz, 3H), 6.96−6.91 (m, 3H), 6.71 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 5.71 (t, J = 8.4 Hz, 1H), 5.29 (dd, J = 15.2, 8.4 Hz, 1H), 3.29 (s, 5H), 2.46 (s, 7H), 2.33−2.29 (m, 1H), 0.93 (s, 9H), 0.74 (s, 3H), 0.46 (t, J = 6.8 Hz, 3H), 0.41 (s, 3H), 0.21 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.0, 159.5, 150.2, 136.2, 134.9, 134.4, 133.7, 133.2 (d, J_{C-P} = 9.8 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.6 (d, J_{C-P} = 9.8 Hz), 130.8 (d, J_{C-PP} = 2.6 Hz), 130.2, 129.9, 129.4, 128.7, 128.6, 128.5, 127.9, 113.1, 112.2, 85.9 (d, J_{C-P} = 6.0 Hz), 57.9, 54.8, 42.3, 40.3, 39.9, 27.1, 20.0, 12.1, 11.8, −0.7, −1.1; HRMS (ESI-TOF) calcd for $C_{40}H_{54}N_3NaO_4PSi$ $[M+Na]^+$ m/z = 722.3513, found 722.3511.

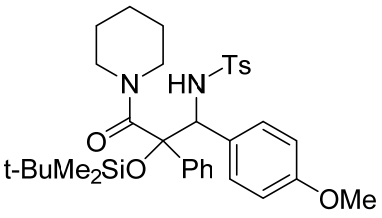


N,N-diethyl-2-(2-furyl)-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amino)-propionamide (6s): White solid (108.2 mg, 84%); mp 113−114 °C, R_f = 0.65 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.45 (d, J = 3.2 Hz, 1H), 7.98−7.93 (m, 2H), 7.79−7.74 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 2.0 Hz, 3H), 6.97−6.87 (m, 4H), 6.64 (d,

J = 8.8 Hz, 2H), 6.25 (dd, J = 3.2, 1.6 Hz, 1H), 5.46 (t, J = 9.6 Hz, 1H), 5.11 (dd, J = 14.4, 8.8 Hz, 1H), 3.49−3.39 (m, 1H), 3.29 (s, 3H), 3.26−3.20 (m, 1H), 2.44−2.35 (m, 1H), 2.32−2.24 (m, 1H), 0.91 (s, 9H), 0.73 (s, 3H), 0.46−0.43 (m, 6H), 0.27 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 167.3, 159.7, 154.9, 141.0, 135.8, 134.6, 134.0, 133.4 (d, J_{C-P} = 10.0 Hz), 133.1, 132.7, 131.8 (d, J_{C-P} = 2.5 Hz), 131.4 (d, J_{C-P} = 9.9 Hz), 131.1 (d, J_{C-P} = 2.7 Hz), 130.0, 128.7, 128.6, 128.0, 113.2, 112.0, 109.1, 81.7 (d, J_{C-P} = 5.0 Hz), 57.2, 54.8, 42.3, 41.0, 20.0, 13.1, 11.9, −1.6, −2.7; HRMS (ESI-TOF) calcd for $C_{36}H_{47}N_2NaO_5PSi$ $[M+Na]^+$ m/z = 669.2884, found 669.2875.

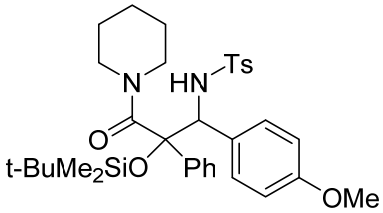


***N*,*N*-diethyl-2-(2-thienyl)-2-((*tert*-butyldimethylsilyl)-oxy l)-3-(4-methoxyphenyl)-3-((*N*'-diphenylphosphinyl)-ami no)-propionamide (6t):** White solid (83.6 mg, 63%); mp 147−148 °C, R_f = 0.60 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ 8.07−8.01 (m, 2H), 7.84 (d, J = 2.8 Hz, 1H), 7.77−7.72 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.05 (s, 3H), 6.92−6.90 (m, 3H), 6.86 (d, J = 4.8 Hz, 1H), 6.75 (dd, J = 4.8, 3.6 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 5.62 (t, J = 8.4 Hz, 1H), 5.05 (dd, J = 14.8, 9.2 Hz, 1H), 3.33 (dd, J = 14.0, 7.2 Hz, 1H), 3.26 (s, 3H), 3.18−3.10 (m, 1H), 2.55−2.39 (m, 2H), 0.97 (s, 9H), 0.68 (s, 3H), 0.49 (t, J = 6.8 Hz, 3H), 0.40 (s, 3H), 0.28 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 169.4, 159.6, 145.0, 135.8, 134.8, 134.6, 133.5, 132.8 (d, J_{C-P} = 9.9 Hz), 132.5, 131.8 (d, J_{C-P} = 2.5 Hz), 131.6 (d, J_{C-P} = 10.0 Hz), 130.8 (d, J_{C-P} = 2.8 Hz), 130.2, 128.7, 128.6, 128.0, 127.9, 126.2, 126.1, 113.2, 83.6 (d, J_{C-P} = 6.4 Hz), 59.4, 54.8, 42.7, 40.6, 30.2, 27.0, 12.1, 11.8, −0.8, −1.8; HRMS (ESI-TOF) calcd for $C_{36}H_{48}N_2O_4PSSi$ $[M+H]^+$ m/z = 663.2836, found 663.2835.



***N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((*tert*-b utyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N*'-paratoluensulfonyl)-amido)-propionamide (13**, minor isomer**):** Colorless oil (49.3 mg, 39%); R_f = 0.35 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.87 (d, J = 7.6 Hz, 1H), 7.29 (dd, J = 8.4, 2.0 Hz, 3H), 6.90 (s, 3H), 6.71 (s, 2H), 6.45 (d, J = 8.0

Hz, 2H), 6.11 (d, *J* = 8.8 Hz, 2H), 4.92 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.06 (s, 1H), 3.28 (d, *J* = 12.8 Hz, 1H), 3.16 (s, 3H), 2.75−2.65 (m, 2H), 1.83 (s, 3H), 1.14 (s, 1H), 1.10 (s, 9H), 1.06−1.03 (m, 2H), 0.98 (d, *J* = 3.6 Hz, 3H), 0.93−0.85 (m, 1H), 0.57 (s, 2H), 0.50 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.6, 158.8, 142.3, 141.2, 140.1, 131.4, 128.82, 128.78, 128.74, 127.9, 127.7, 126.5, 112.6, 85.7, 70.0, 54.6, 48.5, 43.8, 27.1, 25.6, 24.2, 21.0, 20.0, −0.5, −2.8. HRMS (ESI-TOF) calcd for $C_{34}H_{47}N_2O_5SSi$ $[M+H]^+$ m/z =623.2975, found 623.2964.

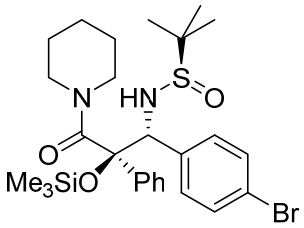


***N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-methoxyphenyl)-3-((*N'*-paratoluensulfonyl)-amido)-propionamide (13**, major isomer**):** White solid (74.2 mg, 59%); mp 73−75 °C, R_f = 0.30 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.39 (dd, *J* = 8.0, 2.8 Hz, 2H), 7.07 (s, 2H), 6.91−6.76 (m, 5H), 6.49−6.47 (m, 2H), 6.31 (d, *J* = 7.6 Hz, 1H), 6.20 (s, 1H), 5.69 (s, 1H), 3.96−3.87 (m, 1H), 3.22−3.16 (m, 4H), 3.04−2.91 (m, 2H), 1.79 (d, *J* = 4.4 Hz, 3H), 1.13 (d, *J* = 2.0 Hz, 9H), 0.97−0.91 (m, 6H), 0.77−0.69 (m, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 169.6, 159.3, 141.85, 141.83, 140.4, 139.22, 139.21, 133.3, 128.9, 127.6, 127.5, 127.0, 112.0, 84.5, 65.1, 60.1, 54.6, 46.1, 26.8, 24.7, 24.3, 21.0, 19.5, −0.9, −3.5. HRMS (ESI-TOF) calcd for $C_{34}H_{47}N_2O_5SSi$ $[M+H]^+$ m/z =623.2975, found 623.2958.

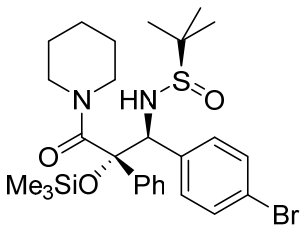
General procedure for the preparation of product 8/8'

Formamide (0.60 mmol, 3.0 equiv) and acylsilane (0.60 mmol, 3.0 equiv) in THF (1.0 mL) were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to −78 °C, and LDA (0.50 M in THF, 1.8 mL, 4.5 equiv) was added to the reaction mixture by syringe. After the reaction mixture was stirred at this temperature for 30 min, a solution of *N-tert*-butanesulfinyl imine **7** (0.20 mmol) in THF (1.0 mL) was added to the reaction mixture via syringe. After the imine addition, the reaction mixture was stirred at −78 °C for an additional 30 min, at which point the reaction was quenched with

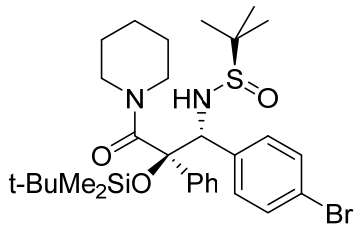
saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.



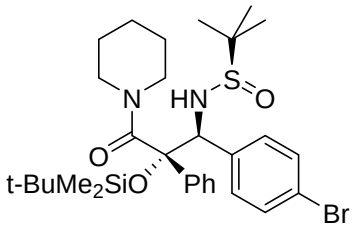
(2*R*,3*R*,*R*$_S$)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((trimethylsilyl)-oxyl)-3-(4-bromophenyl)-3-((*N*'-(*R*$_S$-*tert*-butanesulfinyl))-amido)-propionamide (8a): White solid (98.6 mg, 86%); mp. 70−71 °C; R_f = 0.75 (petroleum ether/ethyl acetate = 1/1); $[\alpha]_D^{25}$ = −133.5º (c = 0.2, MeOH); ^{1}H NMR (400 MHz, C_6D_6) δ 7.22 (d, *J* = 6.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.08−7.01 (m, 3H), 6.68 (d, *J* = 2.8 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 5.28 (d, *J* = 3.2 Hz, 1H), 4.51 (d, *J* = 7.6 Hz, 1H), 3.44 (d, *J* = 10.4 Hz, 1H), 2.37 (s, 1H), 2.26 (s, 1H), 1.18 (s, 3H), 1.11 (s, 9H), 0.83 (s, 1H), 0.52 (s, 1H), 0.31 (s, 1H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) *δ* 171.1, 139.9, 135.4, 134.0, 130.2, 128.6, 128.0, 127.5, 127.2, 122.5, 84.2, 65.8, 55.0, 48.5, 44.2, 25.6, 24.3, 24.0, 22.9, 2.6; HRMS (ESI-TOF) calcd for $C_{27}H_{39}BrN_2NaO_3SSi$ $[M+Na]^+$ m/z = 601.1526, found 601.1524.



(2*S*,3*S*,*R*$_S$)*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((trimethylsilyl)-oxyl)-3-(4-bromophenyl)-3-((*N*'-(*R*$_S$-*tert*-butanesulfinyl))-amido)-propionamide (8'a): Yellow oil (12.3 mg, 10%); R_f = 0.70 (petroleum ether/ethyl acetate = 1/1); $[\alpha]_D^{25}$ = +16.0º (c = 0.2, MeOH); ^{1}H NMR (400 MHz, C_6D_6) *δ* 7.33−7.31 (m, 2H), 7.10−7.08 (m, 2H), 7.05−6.99 (m, 3H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.68 (d, *J* = 3.2 Hz, 1H), 5.41 (d, *J* = 3.2 Hz, 1H), 4.51 (s, 1H), 3.48 (s, 1H), 2.41 (s, 2H), 2.31 (s, 1H), 1.35−1.28 (m, 3H), 1.12 (s, 9H), 0.83 (s, 1H), 0.35 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.0, 141.2, 138.5, 132.4, 130.4, 129.0, 128.2, 127.9, 127.7, 126.8, 121.7, 85.2, 70.1, 56.8, 45.4, 43.8, 25.4, 24.3, 24.2, 22.9, 2.6; HRMS (ESI-TOF) calcd for $C_{27}H_{39}BrN_2NaO_3SSi$ $[M+Na]^+$ m/z = 601.1526, found 601.1501.



(2*R*,3*R*,*R*$_S$)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-bromophenyl)-3-((*N'*-(*R*$_S$-*tert*-butanesulfinyl))-amido)-propionamide (8d): Colorless oil (27.6 mg, 22%); R_f = 0.25 (petroleum ether/ethyl acetate = 2/1), $[\alpha]_D^{25}$ = −118º (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.32 (d, *J* = 4.4 Hz, 2H), 7.14 (s, 2H), 7.02−7.00 (m, 3H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.35 (s, 1H), 5.43 (d, *J* = 2.0 Hz, 1H), 4.31 (s, 1H), 3.36 (d, *J* = 9.2 Hz, 1H), 2.37 (s, 2H), 1.36−1.28 (m, 1H), 1.20−1.15 (m, 3H), 1.12 (s, 9H), 1.10−1.04 (m, 1H), 0.86 (s, 9H), 0.47 (s, 1H), 0.44 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 140.7, 137.7, 135.2, 133.7, 130.1, 128.5, 127.9, 127.3, 127.3, 122.5, 84.1, 64.1, 55.0, 48.3, 44.1, 26.4, 25.5, 24.2, 23.6, 22.8, 19.2, −0.1, −3.1. HRMS (ESI-TOF) calcd for $C_{30}H_{46}BrN_2O_3SSi$ $[M+H]^+$ m/z = 621.2176, found 621.2169.

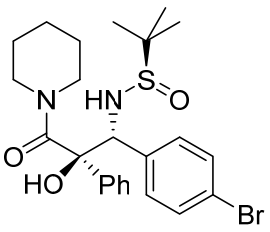


(2*S*,3*S*,*R*$_S$)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((*tert*-butyldimethylsilyl)-oxyl)-3-(4-bromophenyl)-3-((*N'*-(*R*$_S$-*tert*-butanesulfinyl))-amido)-propionamide (8'd): Colorless oil: (71.8 mg, 58%); R_f = 0.3 (petroleum ether/ethyl acetate = 2/1), $[\alpha]_D^{25}$ = +31º (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.39 (d, *J* = 5.2 Hz, 2H), 7.15 (s, 2H), 7.01−6.98 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.44 (d, *J* = 6.0 Hz, 1H), 5.16 (d, *J* = 6.4 Hz, 1H), 3.96 (s, 1H), 3.14 (s, 1H), 2.63 (s, 1H), 2.42 (s, 1H), 1.39−1.32 (m, 1H), 1.23 (s, 9H), 1.11−0.97 (m, 4H), 0.90 (s, 9H), 0.56 (s, 1H), 0.47 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.3, 140.5, 137.4, 132.1, 130.56, 128.5, 127.9, 127.7, 127.2, 126.4, 122.2, 84.6, 67.1, 56.9, 48.1, 44.3, 26.5, 25.5, 24.2, 22.7, 20.2, 19.3, −0.7, −3.0. HRMS (ESI-TOF) calcd for $C_{30}H_{46}BrN_2O_3SSi$ $[M+H]^+$ m/z = 621.2176, found 621.2160.

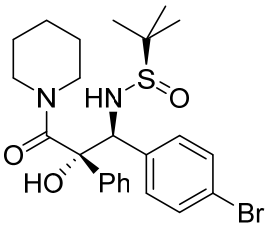
Procedure for desilylation of 8 and 8'

To a solution of **8** (or **8**') in THF was added Bu_4NF (0.50 M in THF, 2.0 equiv). The reaction mixture was stirred at ambient temperature until no starting material was present determined by TLC. Then, the reaction mixture was transferred to a separating

funnel, washed with water, dried with anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel to give **9** (or **9**').



(2*R*,3*R*,R_S)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-hydroxyl-3-(4-bromophenyl)-3-((*N'*-(R_S-*tert*-butanesulfinyl))-amido)-propionamide (9): White solid (98.4 mg, 97%; 0.20 mmol **8a** was used); mp 188−190 °C, R_f = 0.4 (petroleum ether/ethyl acetate = 4/1), $[\alpha]_D^{25}$ = −51.7º (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 7.12 (d, *J* = 8.4 Hz, 3H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.31 (d, *J* = 9.2 Hz, 1H), 3.46 (s, 2H), 3.36 (s, 1H), 3.12 (s, 1H), 1.45 (s, 4H), 1.27 (s, 9H), 1.19 (s, 1H), 0.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 139.0, 137.3, 130.1, 129.1, 127.1, 127.0, 119.75, 81.1, 76.4, 55.1, 46.5, 43.0, 30.1, 24.8, 24.3, 23.4, 22.0, 17.0. HRMS (ESI-TOF) calcd for $C_{24}H_{31}BrN_2NaO_3S$ $[M+Na]^+$ m/z = 529.1131, found 529.1120.

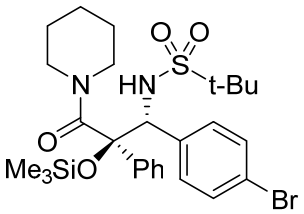


(2*S*,3*S*,R_S)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-hydroxyl-3-(4-bromophenyl)-3-((*N'*-(R_S-*tert*-butanesulfinyl))-amido)-propionamide (9'): Colorless oil (41.1 mg, 81%; 0.10 mmol **8'a** was used); R_f = 0.6 (petroleum ether/ethyl acetate = 4/1); $[\alpha]_D^{25}$ = +44.3º (c = 0.4, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.32 (m, 2H), 7.24 (d, *J* = 4.8 Hz, 5H), 7.01 (s, 2H), 6.11 (s, 1H), 4.75 (s, 1H), 3.38 (s, 4H), 1.45−1.41 (m, 4H), 1.27−1.24 (m, 1H), 1.06 (s, 9H), 0.93−0.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 140.9, 137.4, 131.6, 130.6, 128.3, 128.0, 126.3, 121.5, 81.7, 77.4, 66.2, 57.1, 45.6, 29.8, 25.4, 24.4, 24.3, 23.2, 22.6. HRMS (ESI-TOF) calcd for $C_{24}H_{32}BrN_2O_3S$ $[M+H]^+$ m/z = 507.1312, found 507.1289.

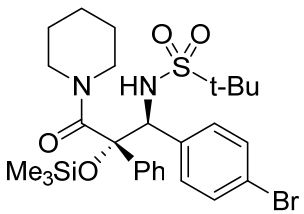
Procedure for oxidation of 8a and 8'a

To a solution of **8a** (0.20 mmol)in CH_2Cl_2 (5.0 mL) was added m-CPBA(85%, 61.0 mg, 1.5 equiv). The reaction mixture was stirred at ambient temperature until the starting material was consumed (TLC analysis). Then the reaction mixture was

quenched with aqueous sodium thiosulfate and extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.



(2*R*,3*R*)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((trimethylsilyl)-oxyl)-3-(4-bromophenyl)-3-((*N'*-(*tert*-butanesulfonyl))-amido)-propionamide (10): White solid (98.8 mg, 83%); mp 173−175 °C, R_f = 0.25 (petroleum ether/ethyl acetate =10/1), $[\alpha]_D^{25}$ = −2.0º (c = 0.2, MeOH); ^{1}H NMR (400 MHz, C_6D_6) δ 7.30 (d, *J* = 9.2 Hz, 1H), 7.03−6.98 (m, 5H), 6.86−6.79 (m, 3H), 4.79 (d, *J* = 9.6 Hz, 1H), 4.11 (s, 1H), 3.18 (s, 1H), 2.65 (s, 2H), 1.35−1.04 (m, 4H), 0.93 (s, 9H), 0.87−0.85 (m, 1H), 0.61 (s, 9H), 0.54−0.45 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 142.3, 140.4, 132.4, 130.9, 128.0, 126.1, 121.4, 86.4, 70.6, 59.7, 48.2, 43.7, 25.6, 24.5, 24.3, 24.1, 3.0. HRMS (ESI-TOF) calcd for $C_{27}H_{40}BrN_2O_4SSi$ $[M+H]^+$ m/z = 595.1656, found 595.1638.



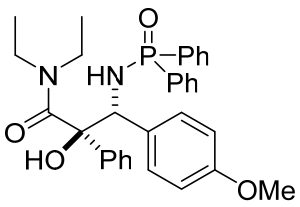
(2*S*,3*S*)-*N*,*N*-((1,5-pentamethylene)-yl)-2-phenyl-2-((trimethylsilyl)-oxyl)-3-(4-bromophenyl)-3-((*N'*-(*tert*-butanesulfonyl))-amido)-propionamide (10'): White solid (50.0 mg, 84%; 0.10 mmol **8'a** was used); mp 172−174 °C, R_f = 0.25 (petroleum ether/ethyl acetate = 10/1), $[\alpha]_D^{25}$ = +0.5º (c = 0.2, MeOH) ; ^{1}H NMR (400 MHz,C_6D_6) δ 7.36 - 7.31 (m, 1H), 7.03−6.96 (m, 5H), 6.85−6.79 (m, 3H), 4.80 (d, *J* = 9.6 Hz, 1H), 4.11 (s, 1H), 3.18 (s, 1H), 2.65 (s, 2H), 1.19−1.03 (m, 4H), 0.94 (s, 9H), 0.89−0.86 (m, 1H), 0.62 (s, 9H), 0.57−0.52 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.5, 142.3, 140.4, 132.4, 130.9, 128.0, 126.1, 121.4, 86.4, 70.6, 59.7, 48.2, 43.7, 25.6, 24.5, 24.3, 24.1, 3.0. HRMS (ESI-TOF) calcd for $C_{27}H_{40}BrN_2O_4SSi$ $[M+H]^+$ m/z = 595.1656, found 595.1647.

Deprotection of product 4f

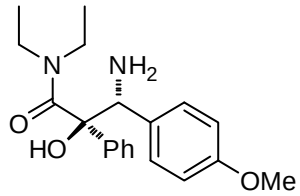
To a solution of **4f** (131.4 mg, 0.20 mmol) in THF (6.0 mL) was added Bu_4NF

(0.50 M in THF, 0.80 mL, 2.0 equiv). The reaction mixture was stirred at ambient temperature until no starting material was present determined by TLC. Then, the reaction mixture was transferred to a separating funnel, washed with water, dried with anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel to give **11** (101.2 mg, 93%).

A solution of **11** (108.5mg, 0.20 mmol) in a mixture of MeOH (3.0 mL) and conc. HCl (1.0 mL) was stirred at ambient temperature until the starting material was consumed (TLC analysis). Then, volatiles was evaporated under reduced pressure and the resulting residue was diluted with water, and the resulted aqueous was washed with ether and ethyl acetate successively. Then, the aqueous phase was neutralized with 1.0 *N* aqueous sodium hydroxide, and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel to give **12** (67.8 mg, 99%).



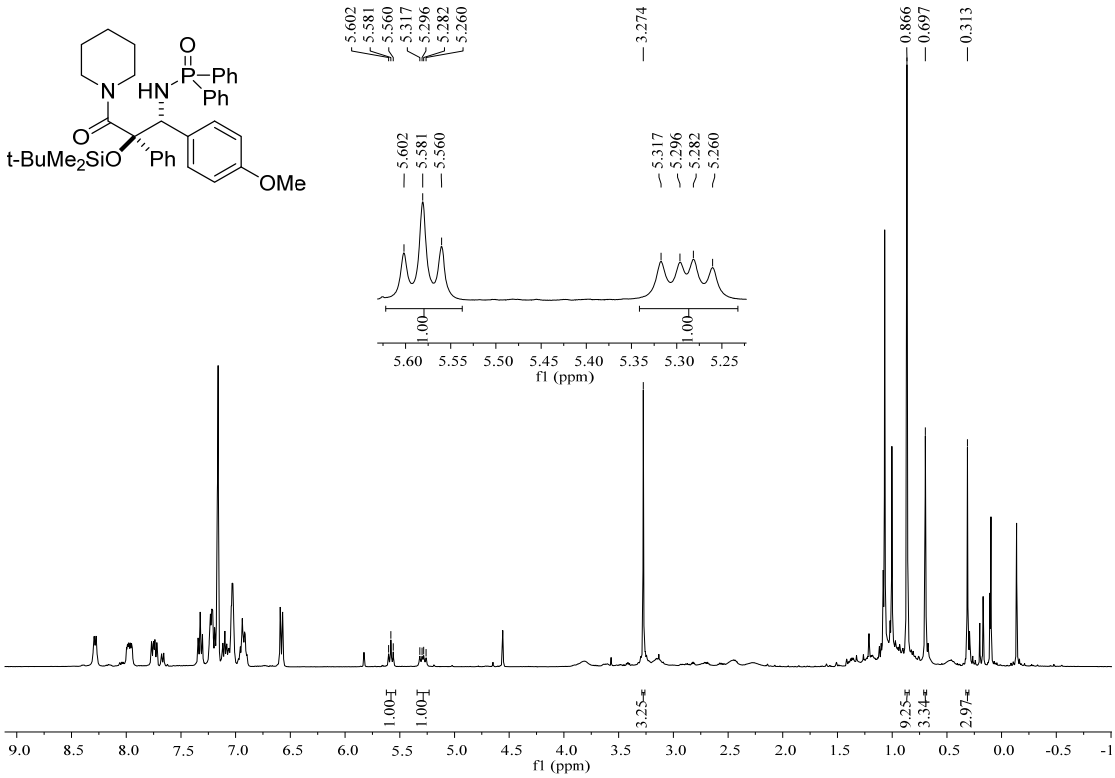
***N*,*N*-diethyl-2-phenyl-2-hydroxyl-3-(4-methoxyphenyl)-3-((*N'*-diphenylphosphinyl)-amido)-propionamide (11):** Colorless oil; R_f = 0.35 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 12.0, 7.6 Hz, 2H), 7.67 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.50−7.46 (m, 1H), 7.42−7.38 (m, 3H), 7.29−7.25 (m, 3H), 7.10 (s, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 5.69 (s, 1H), 4.20 (s, 1H), 3.72 (s, 3H), 3.46−3.32 (m, 2H), 3.05 (d, *J* = 6.0 Hz, 1H), 2.94−2.89 (m, 1H), 1.01 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 158.2, 140.8, 132.9 (d, J_{C-P} = 9.8 Hz), 132.2, 132.0, 131.7, 131.6 (d, J_{C-P} = 9.8 Hz), 131.3, 130.3, 130.0, 128.7 (d, J_{C-P} = 12.9 Hz), 128.5(d, J_{C-P} = 12.9 Hz), 127.8, 127.4, 126.2, 112.4, 82.4, 68.3, 55.2, 42.3, 40.7, 13.1, 12.3. HRMS (ESI-TOF) calcd for $C_{32}H_{35}N_2NaO_4P$ $[M+Na]^+$ m/z = 565.2227, found 565.2207.



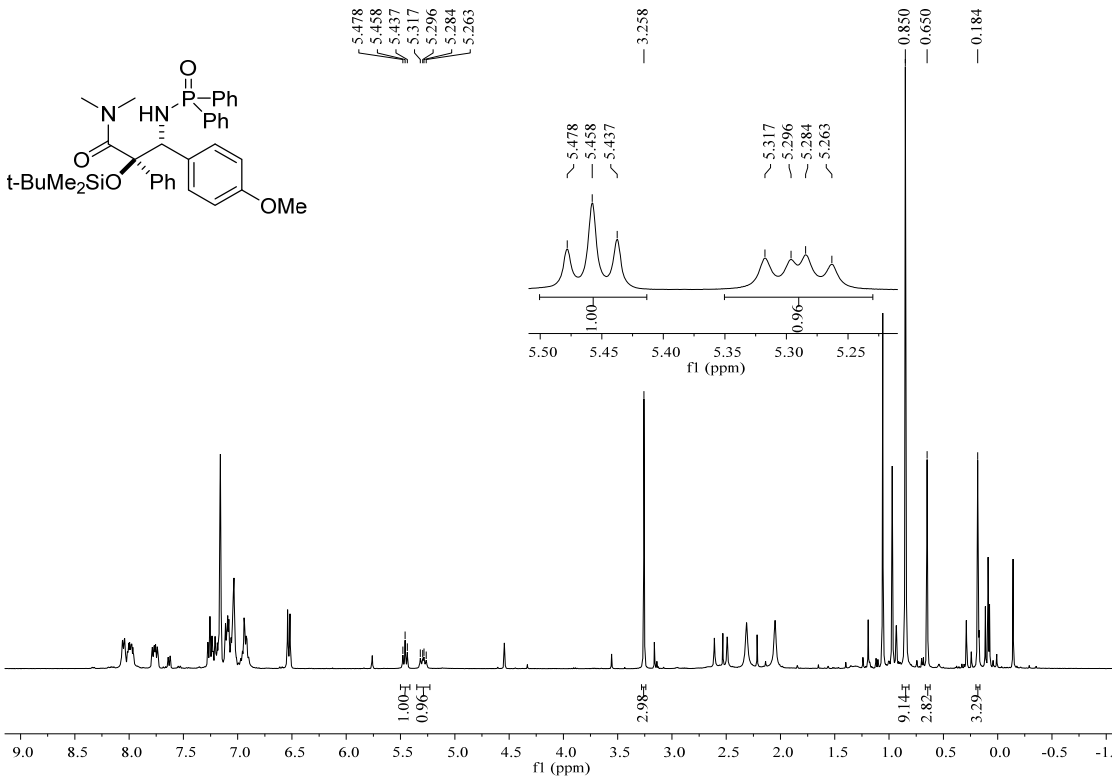
***N*,*N*-diethyl-2-phenyl-2-hydroxyl-3-(4-methoxyphenyl)-3-amido-propionamide (12):** Colorless oil; R_f = 0.4 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.27−7.23 (m, 3H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.59 (s, 1H), 3.77 (s, 3H), 3.46 (s, 1H), 3.28 (s, 1H), 3.03−2.94 (m, 2H), 0.84 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 158.9, 141.5, 133.2, 129.8, 128.3, 127.6, 126.5, 113.2, 81.2, 62.3, 55.3, 42.0, 41.2, 13.2, 12.3; HRMS (ESI-TOF) calcd for $C_{20}H_{27}N_2O_3$ $[M+H]^+$ m/z = 343. 2016, found 343.2026.

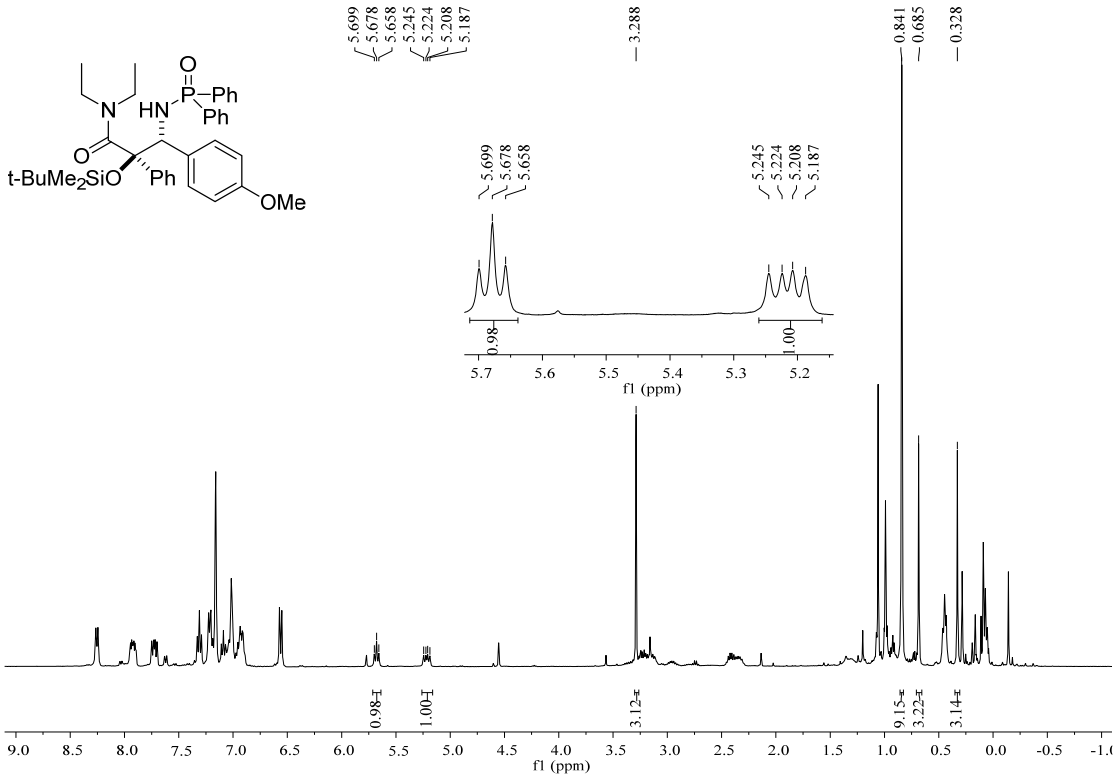
^{1}H NMR spectrum of the crude product 4d, 4e, 4f, and 4g



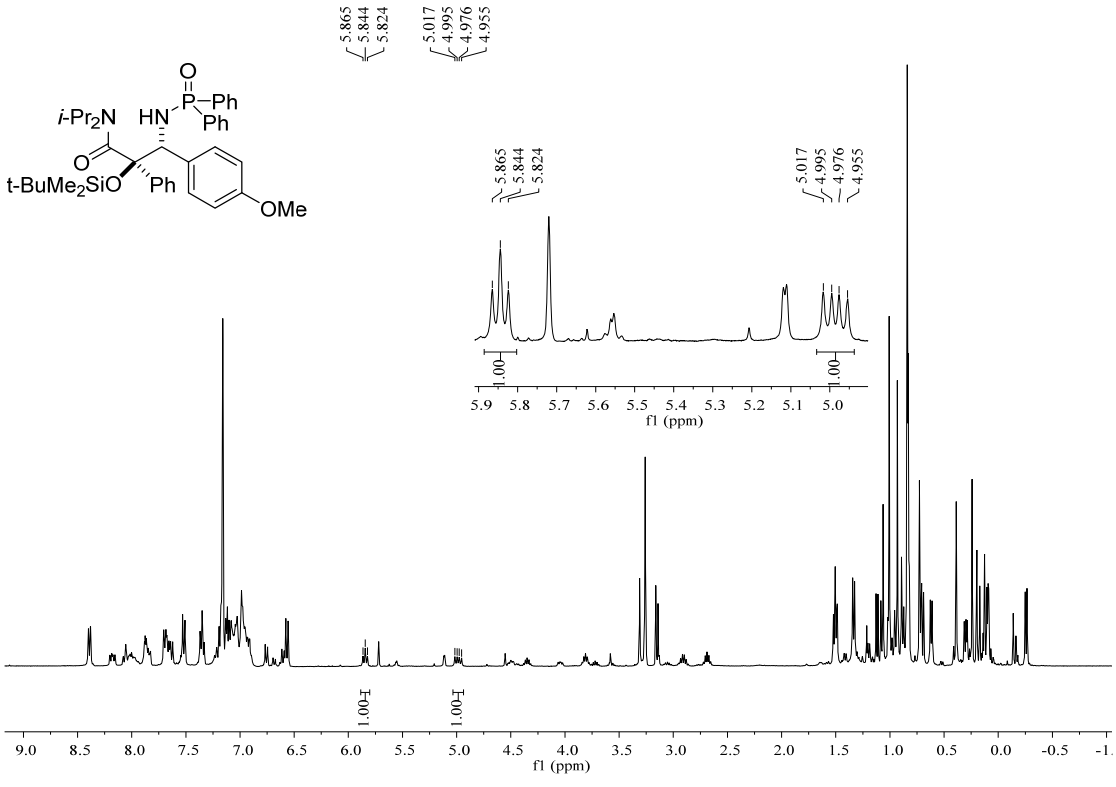
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture **4d**



^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture **4e**

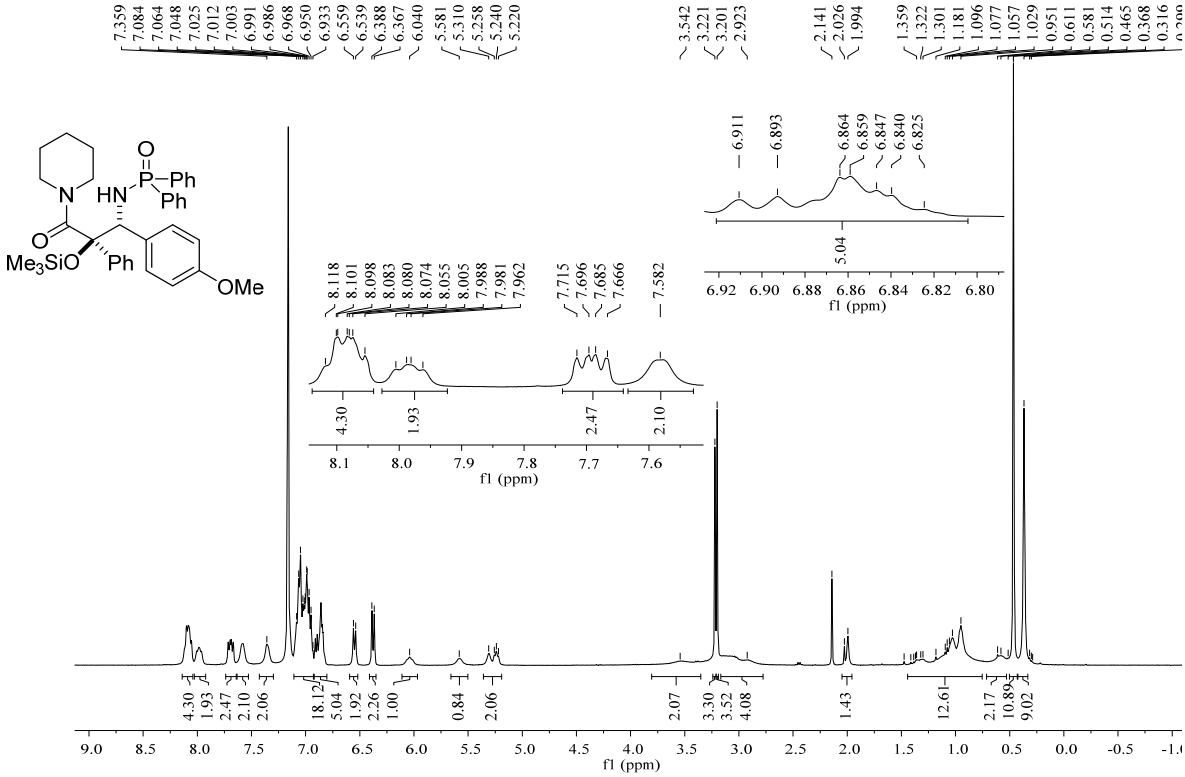


^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture **4f**

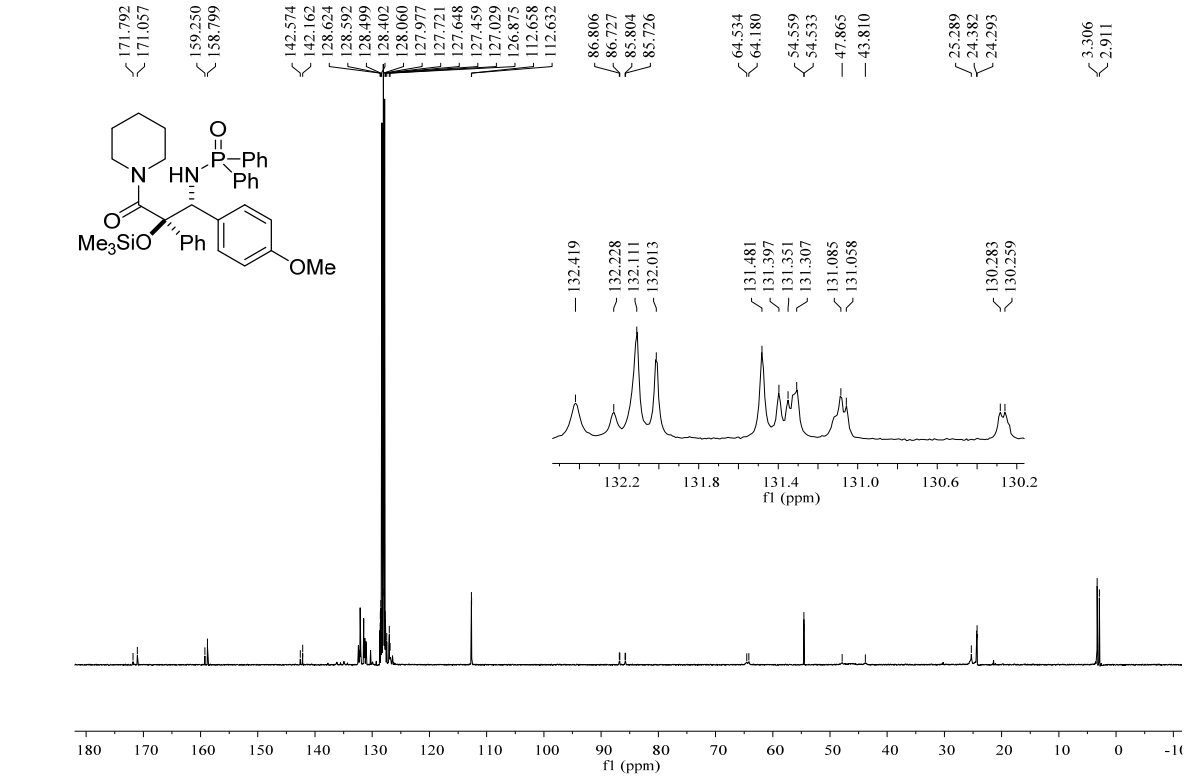


^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture **4g**

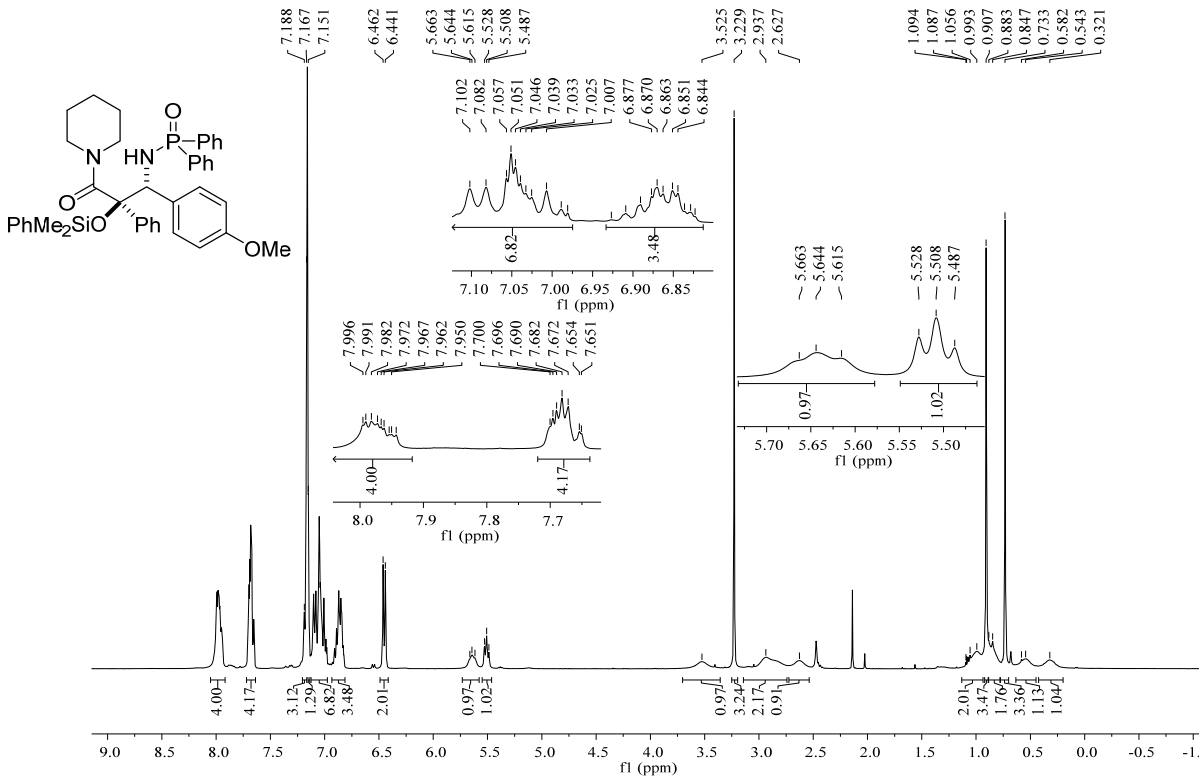
^{1}H NMR and ^{13}C NMR spectra for new compounds



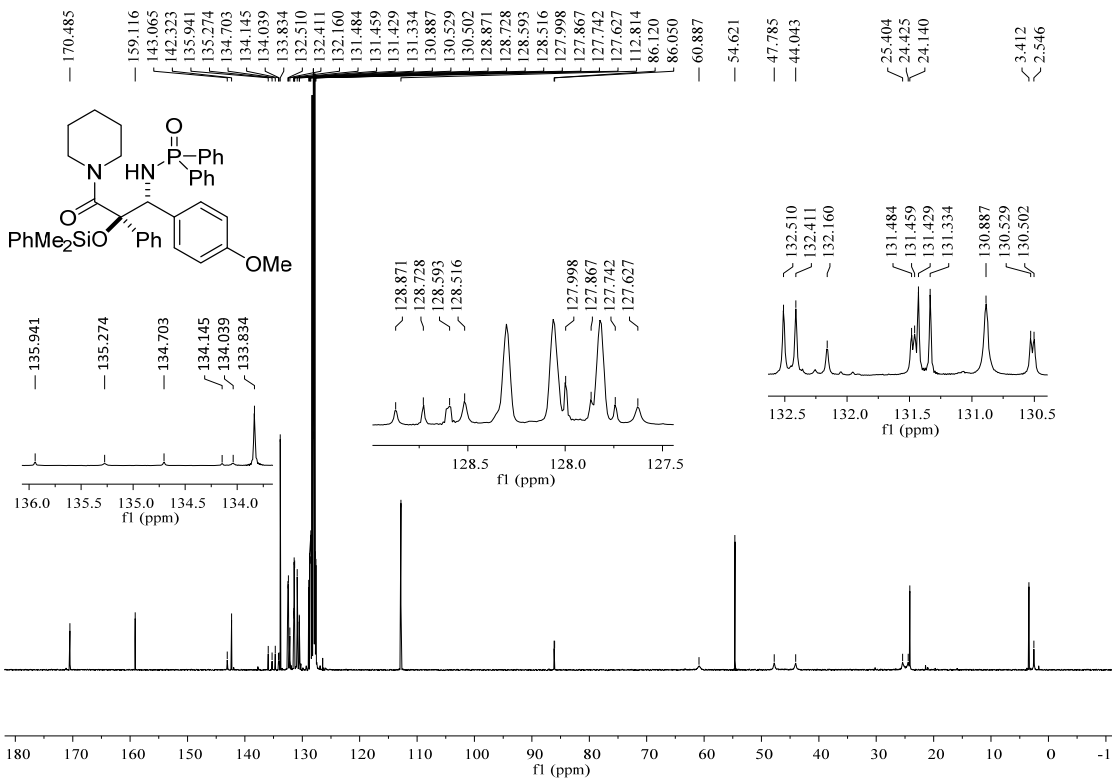
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4a** (mixture of two isomers)



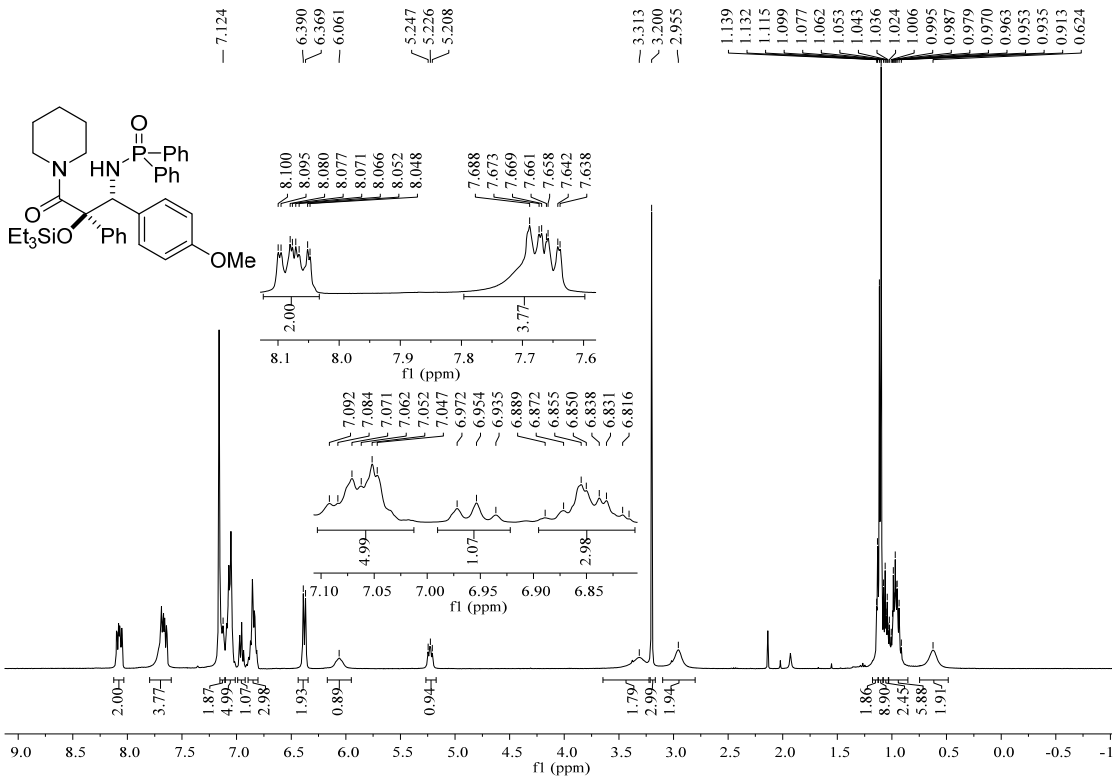
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4a** (mixture of two isomers)



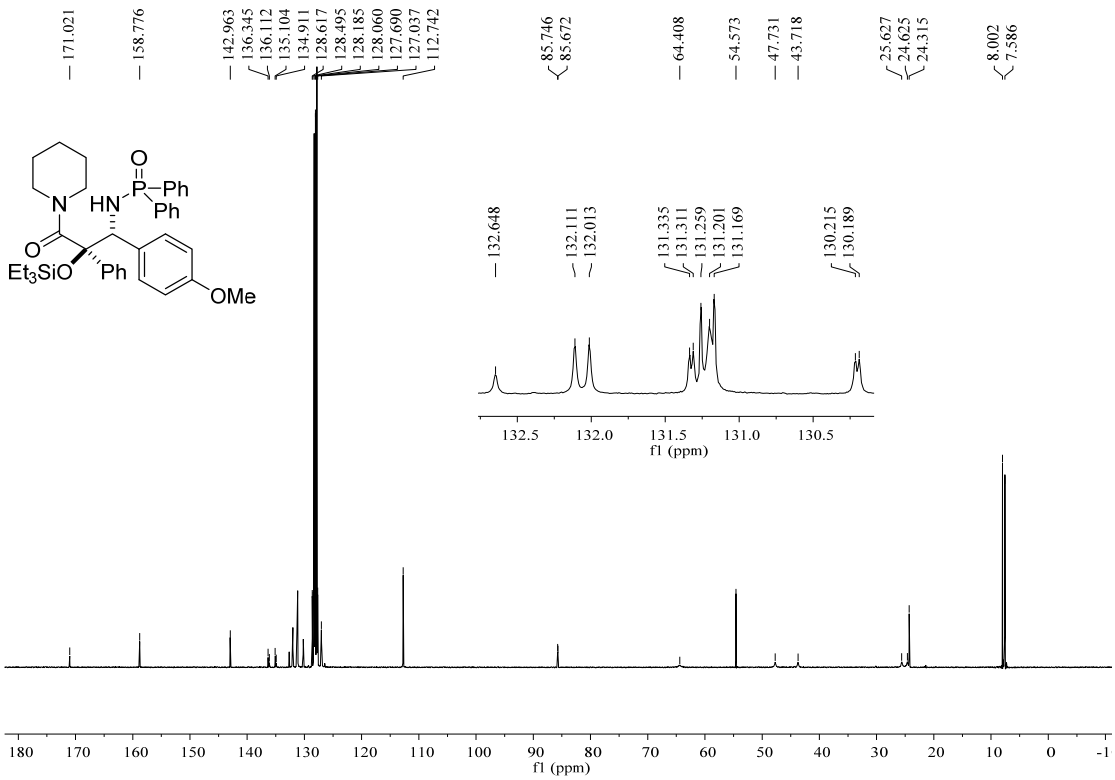
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4b** (major isomer)



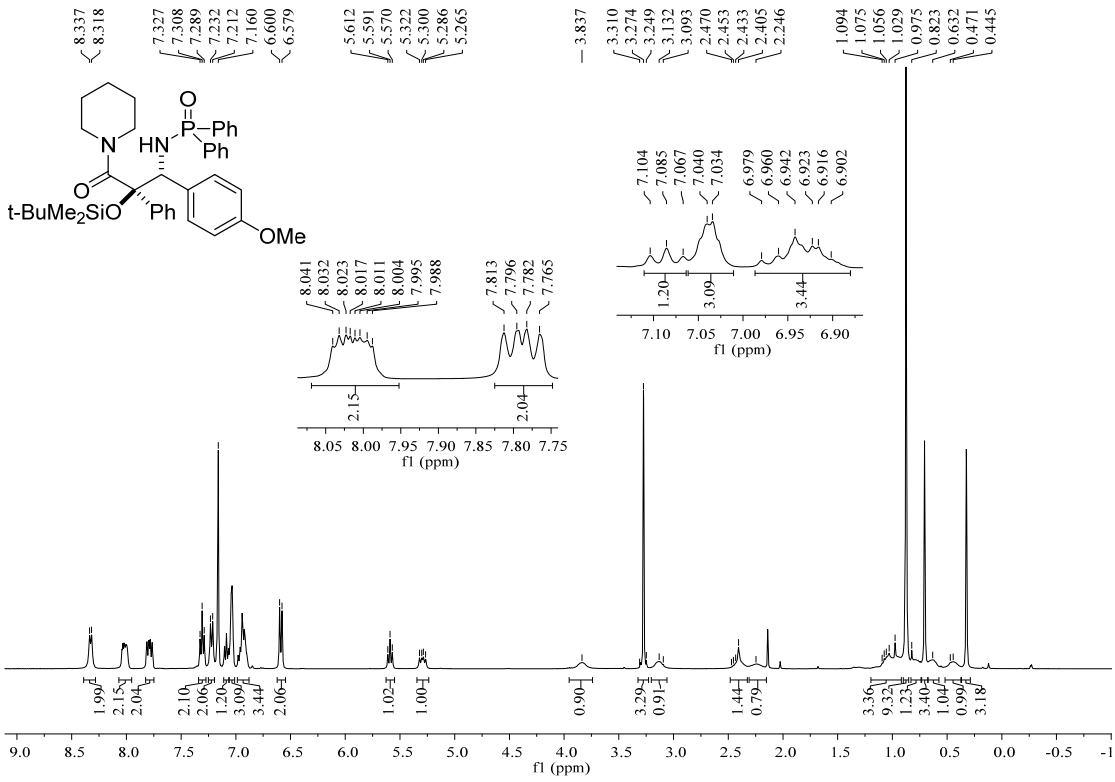
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4b** (major isomer)



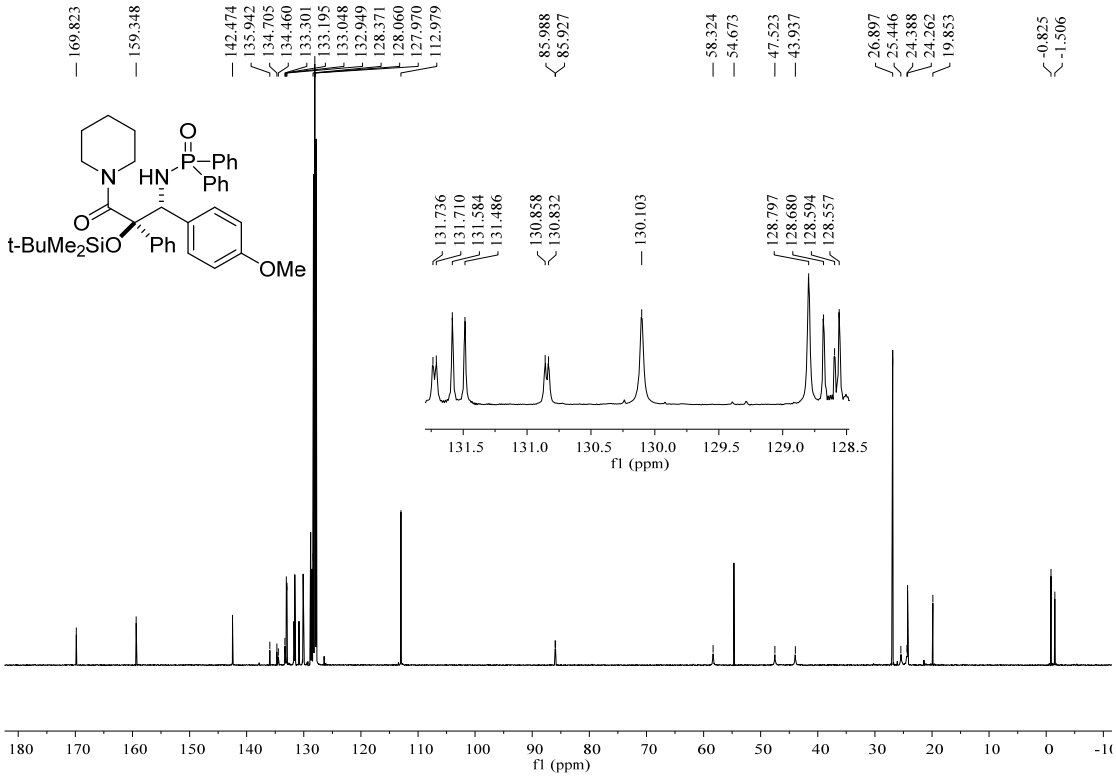
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4c** (major isomer)



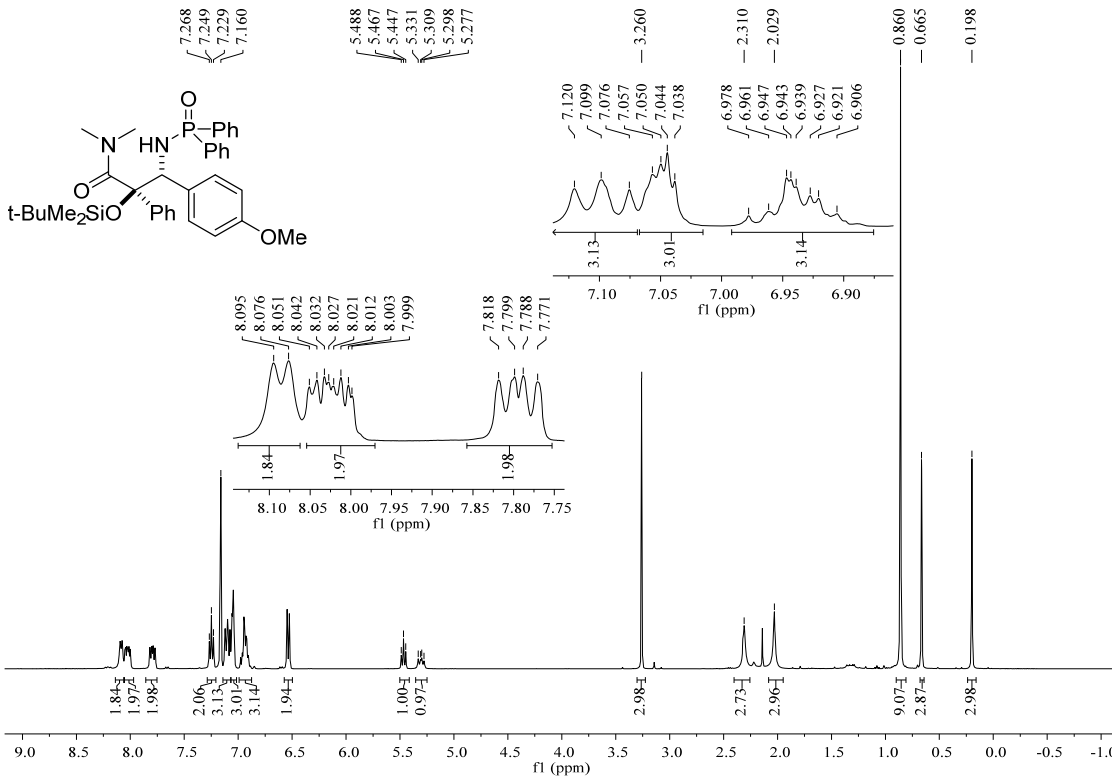
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4c** (major isomer)



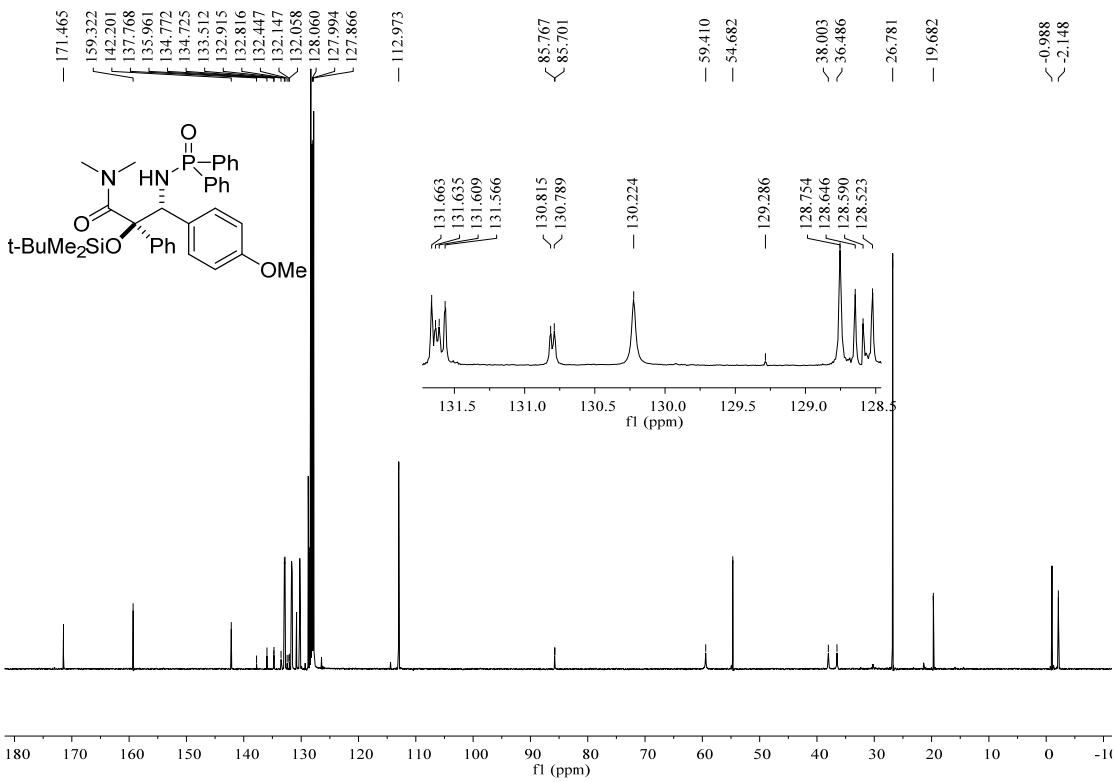
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4d**



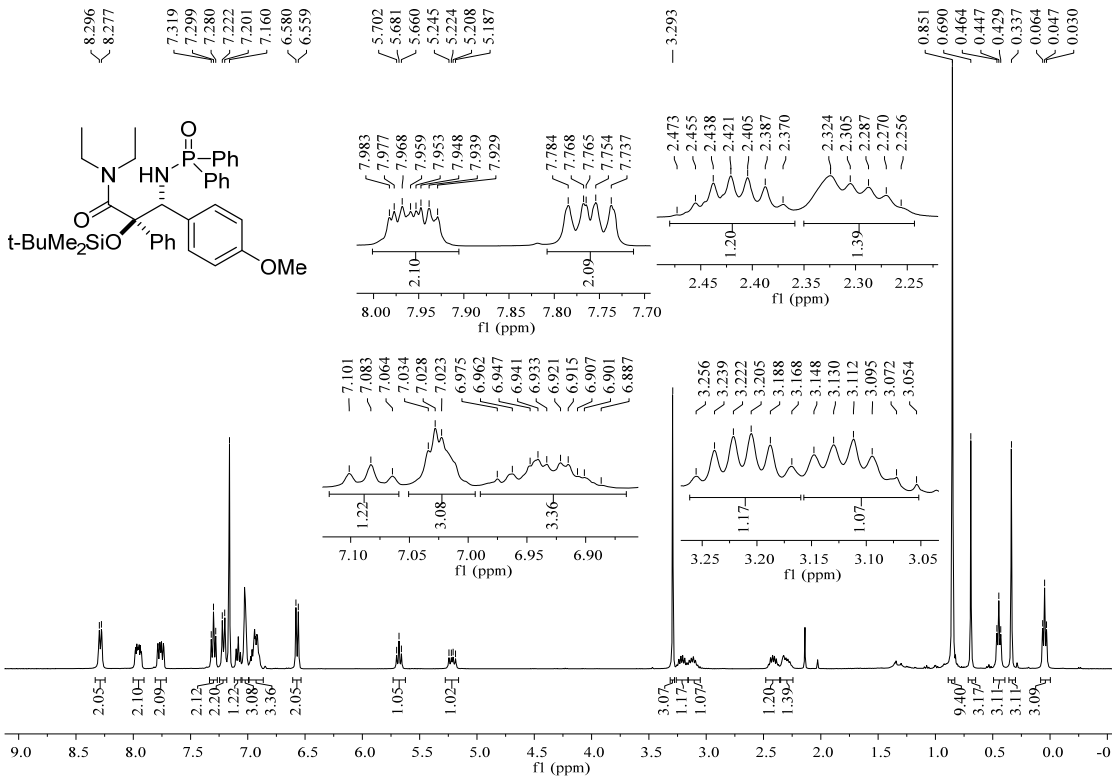
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4d**



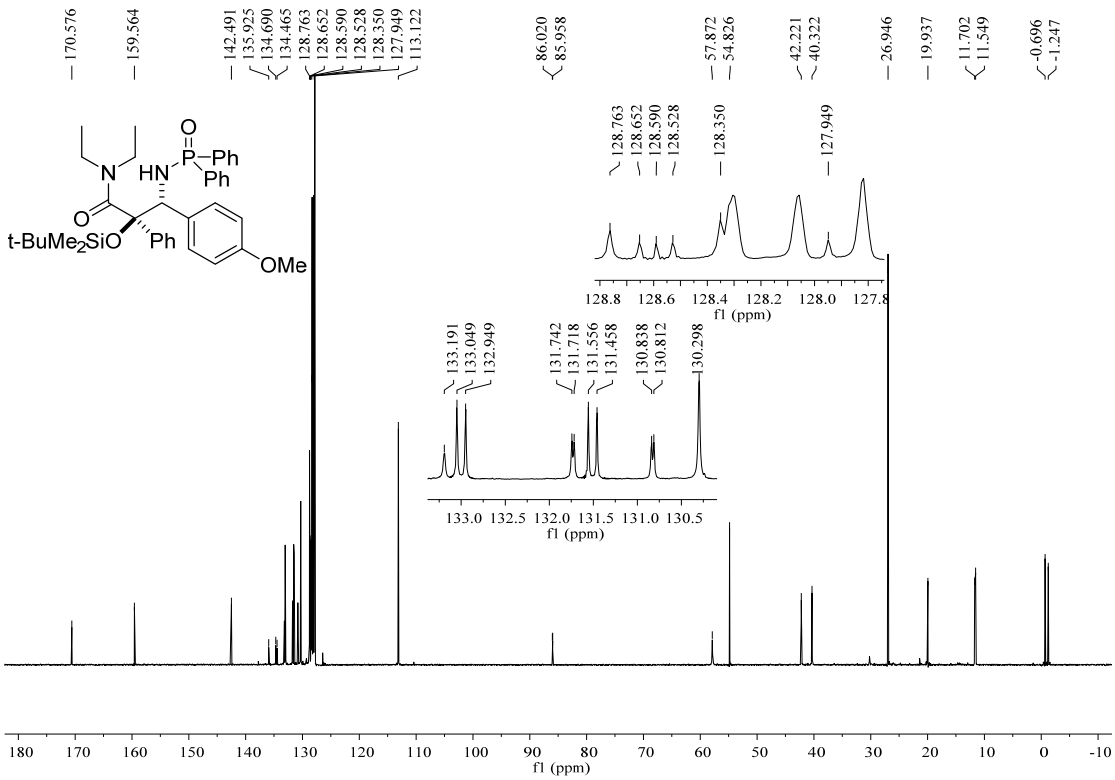
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4e**



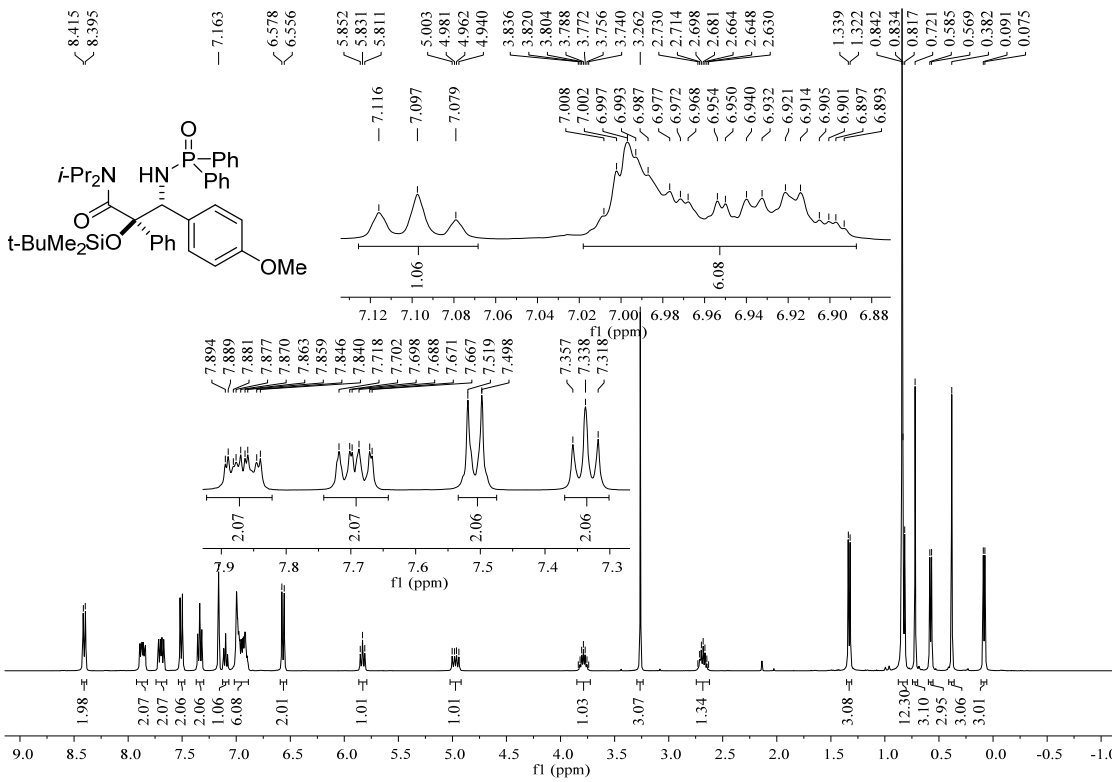
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4e**



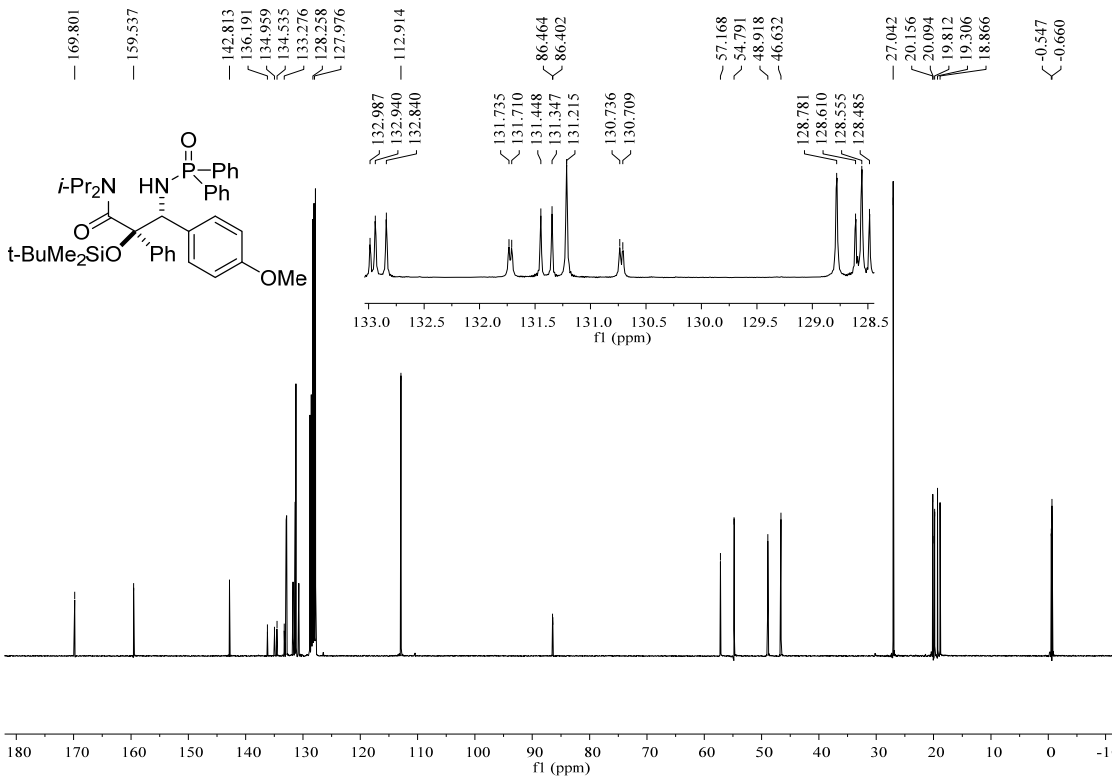
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4f**



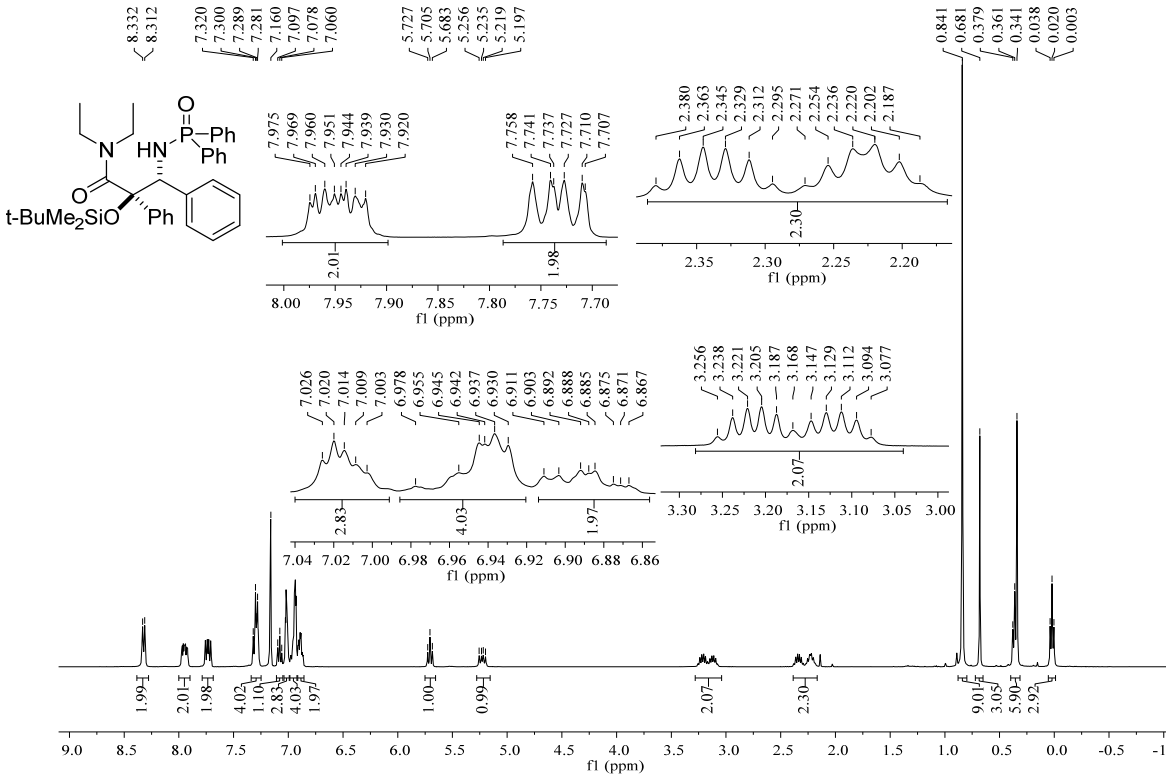
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4f**



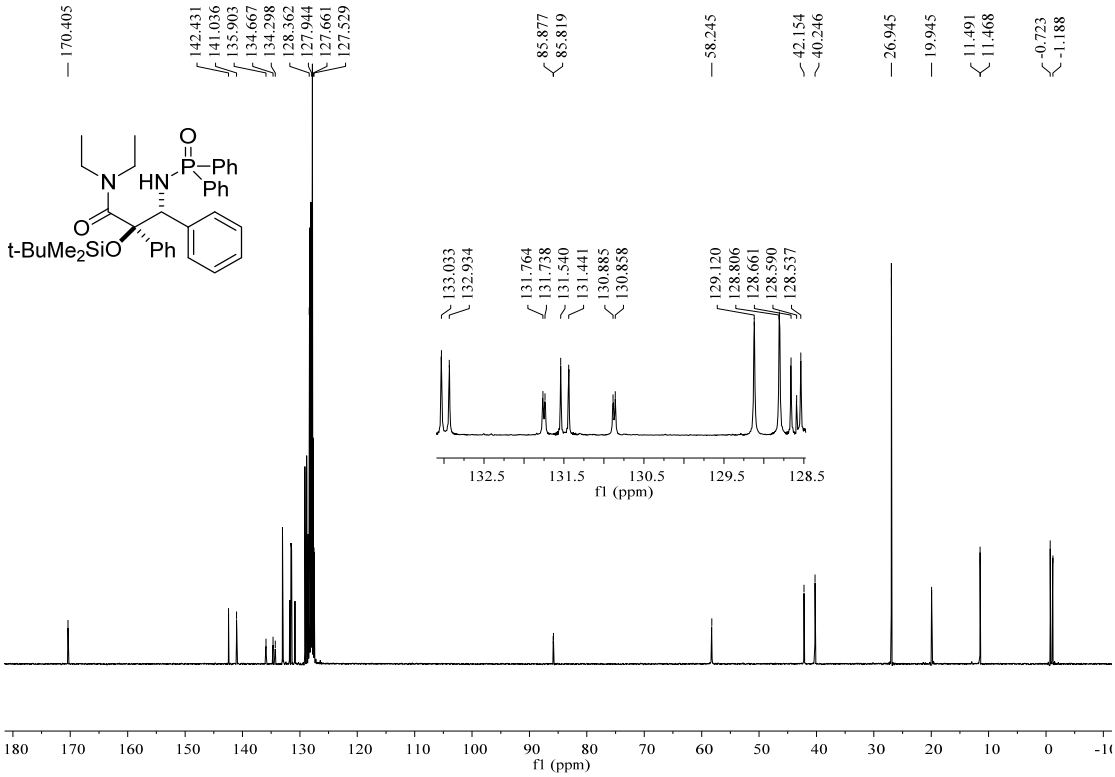
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **4g**



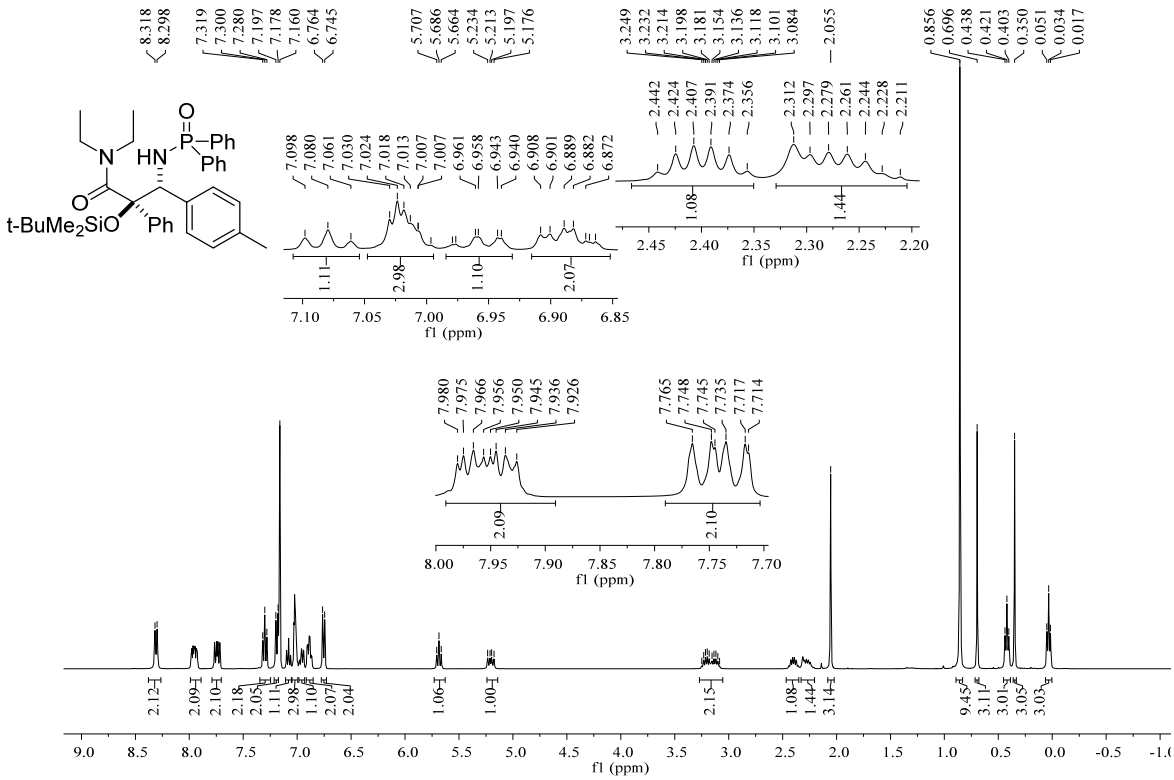
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **4g**



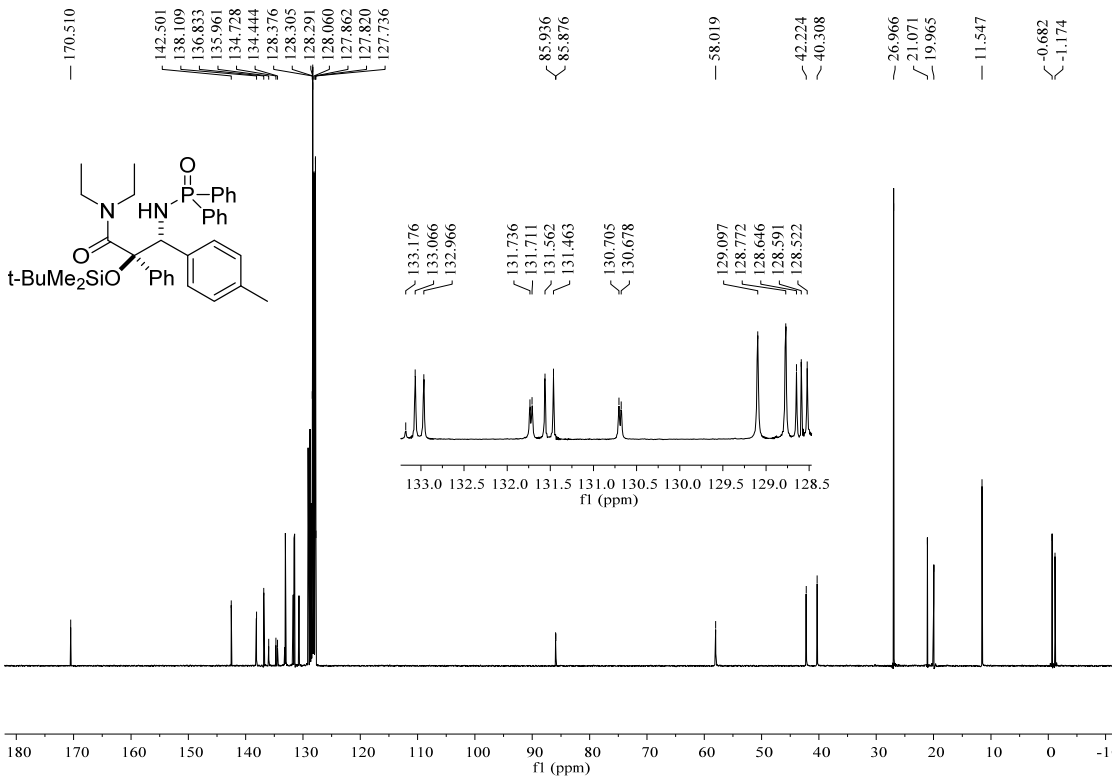
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6b**



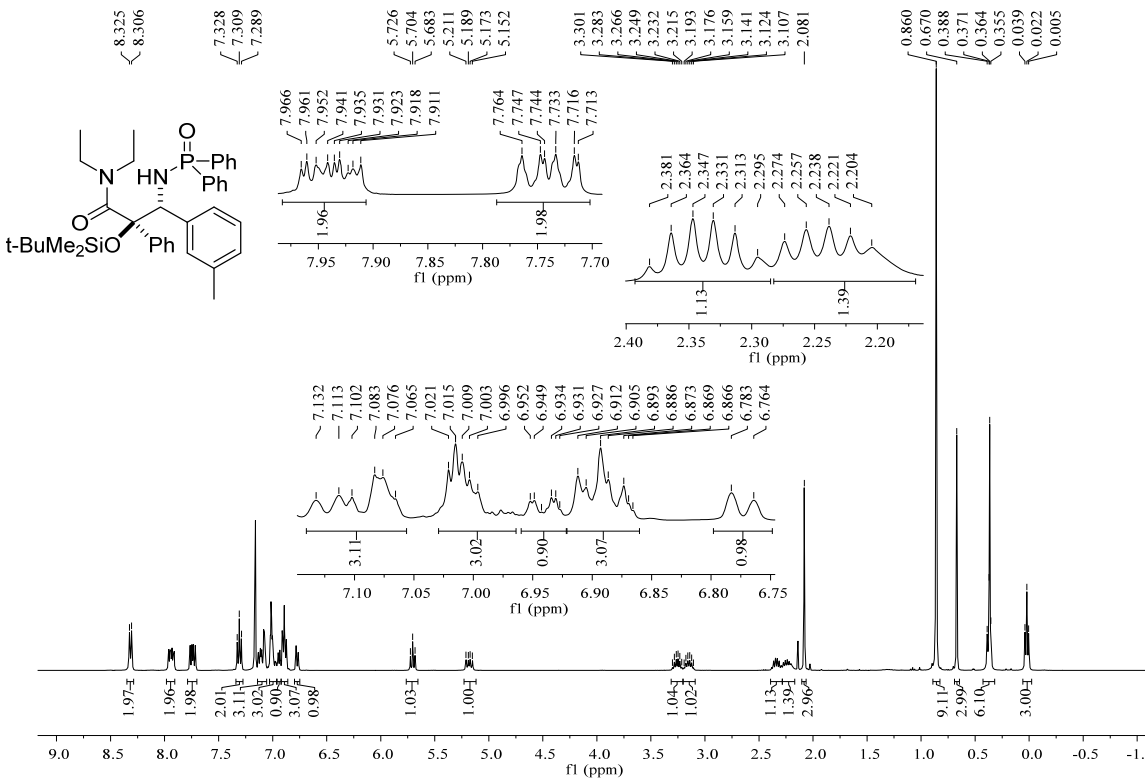
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6b**



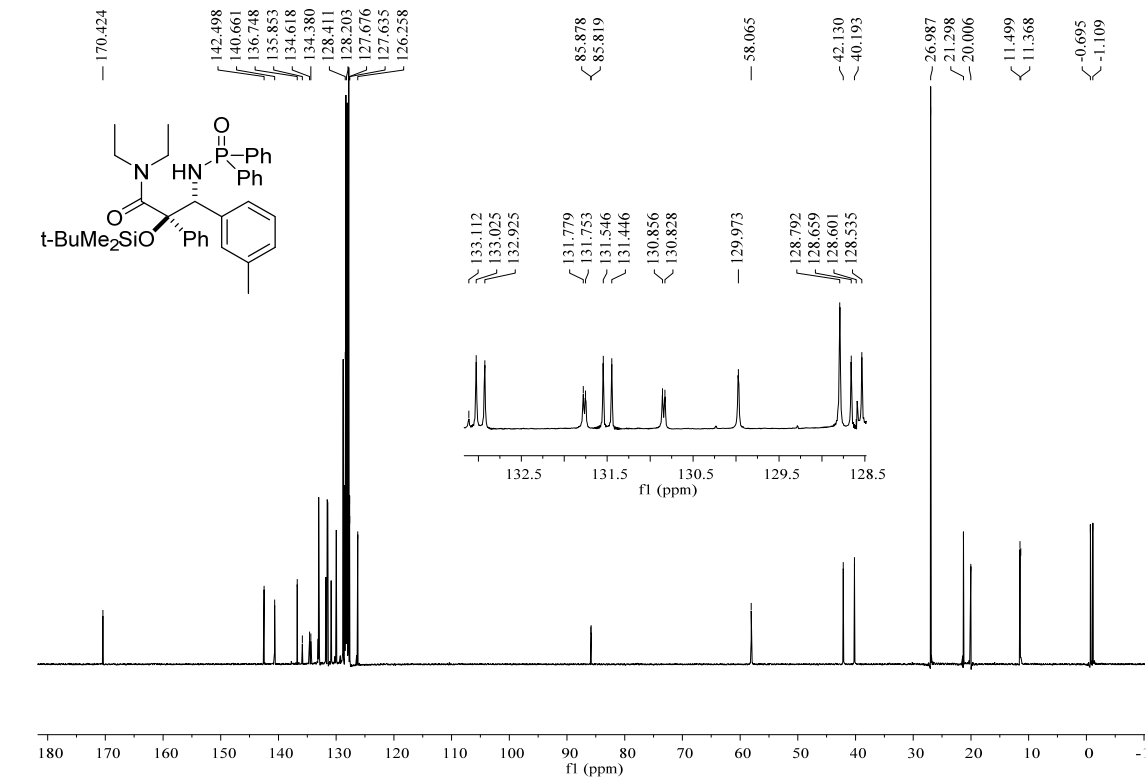
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6c**



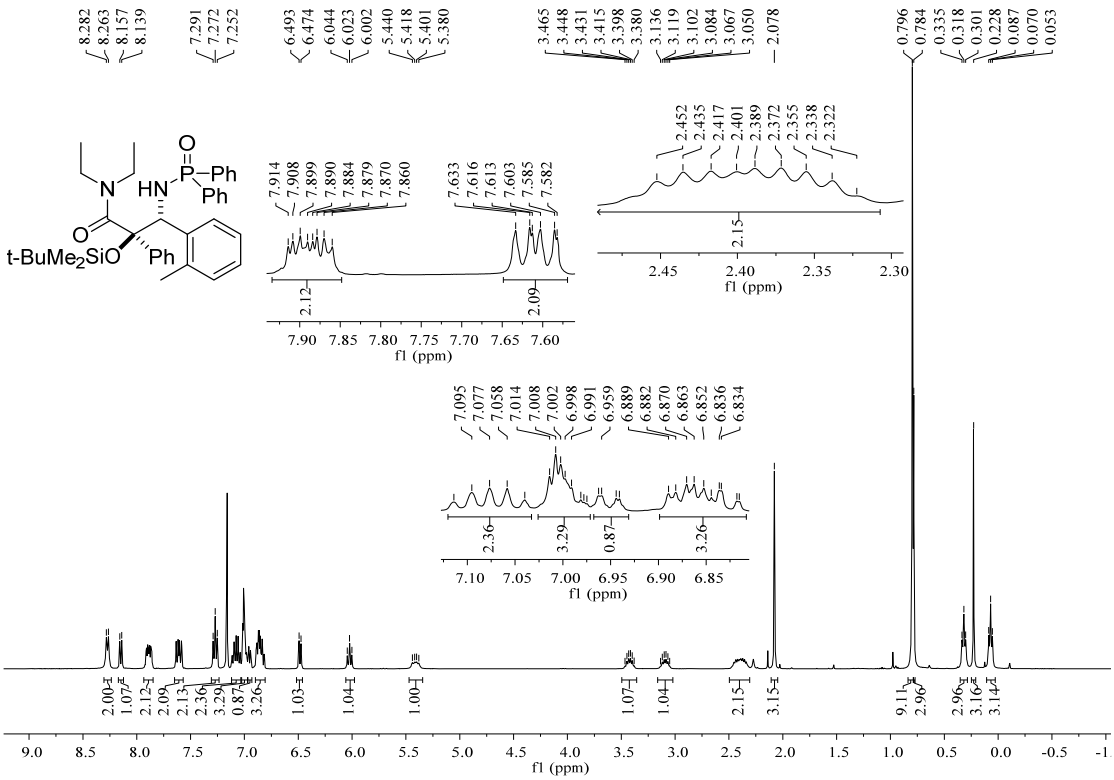
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6c**



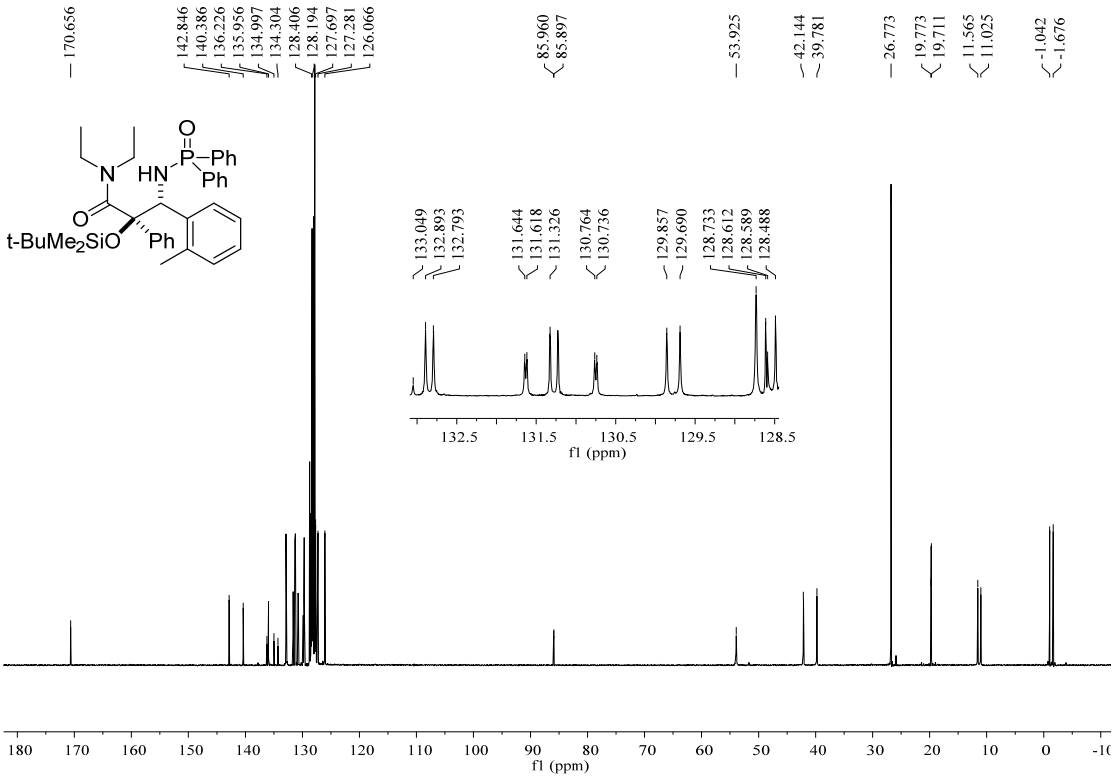
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6d**



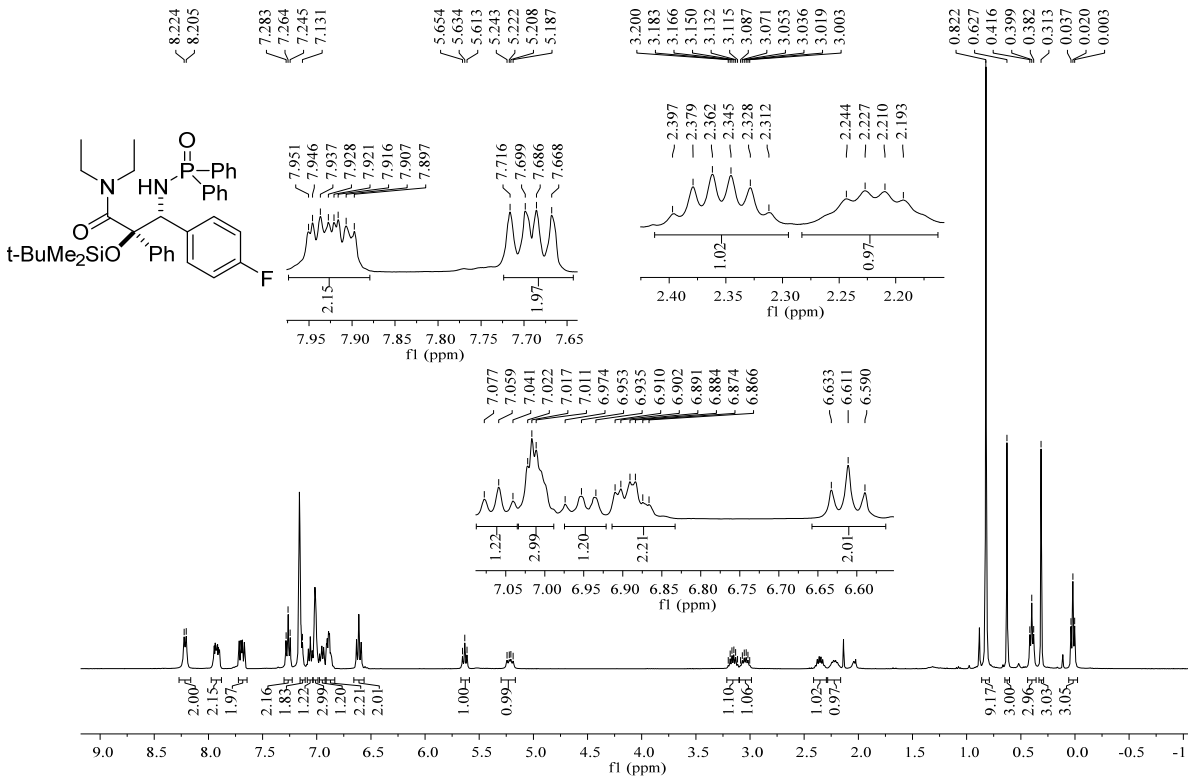
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6d**



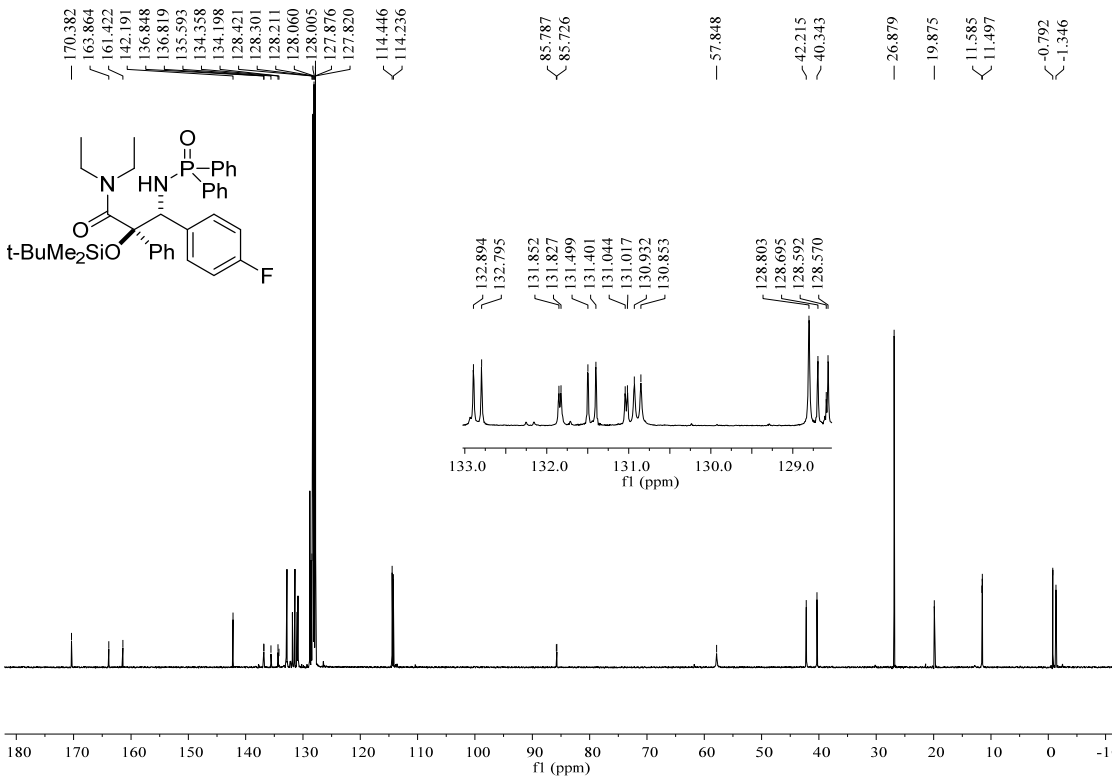
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6e**



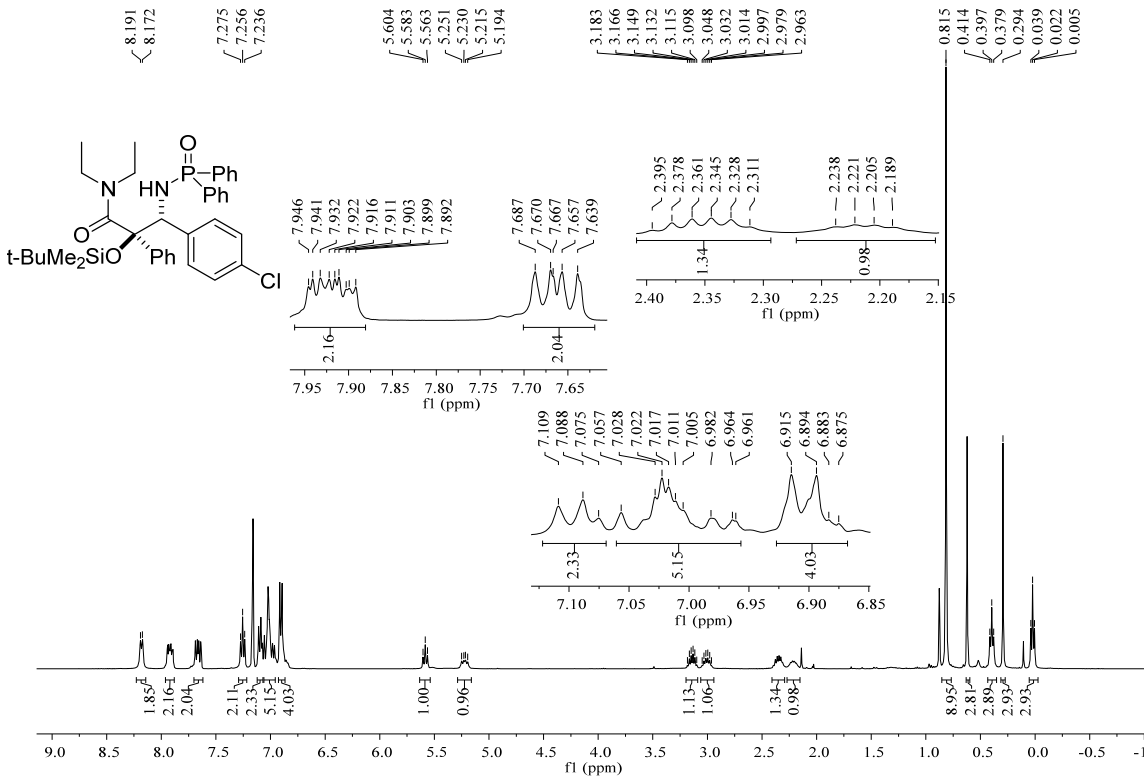
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6e**



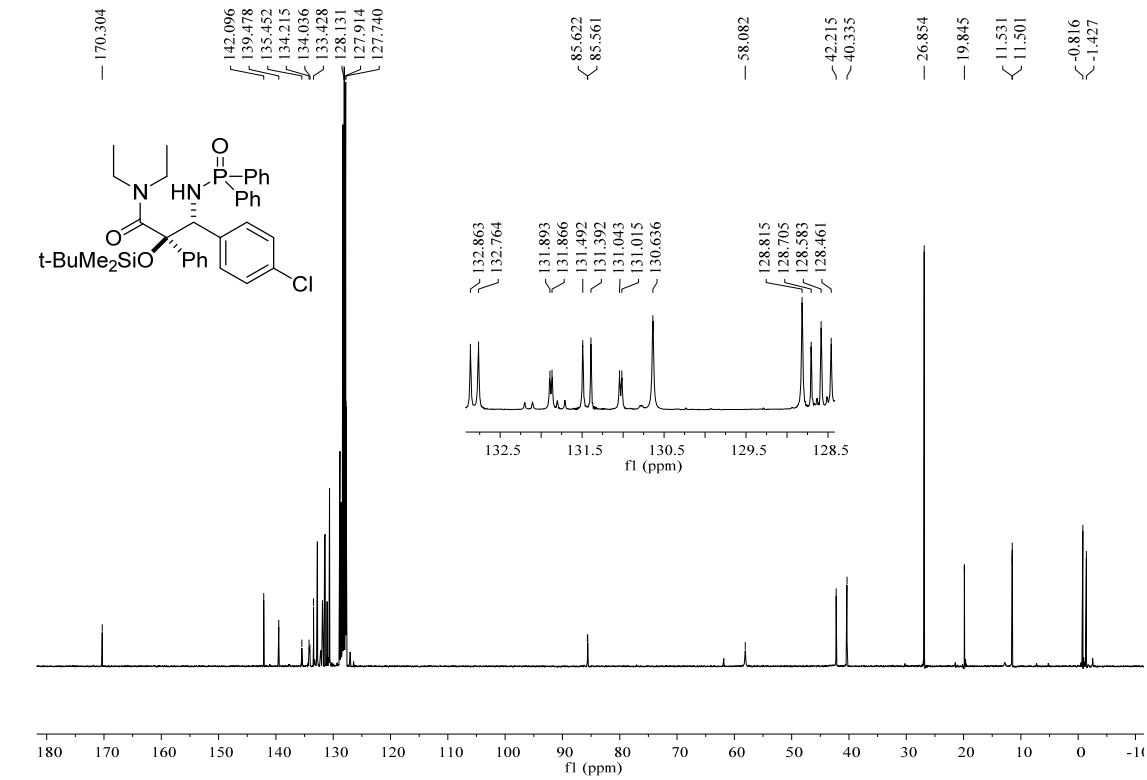
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6f**



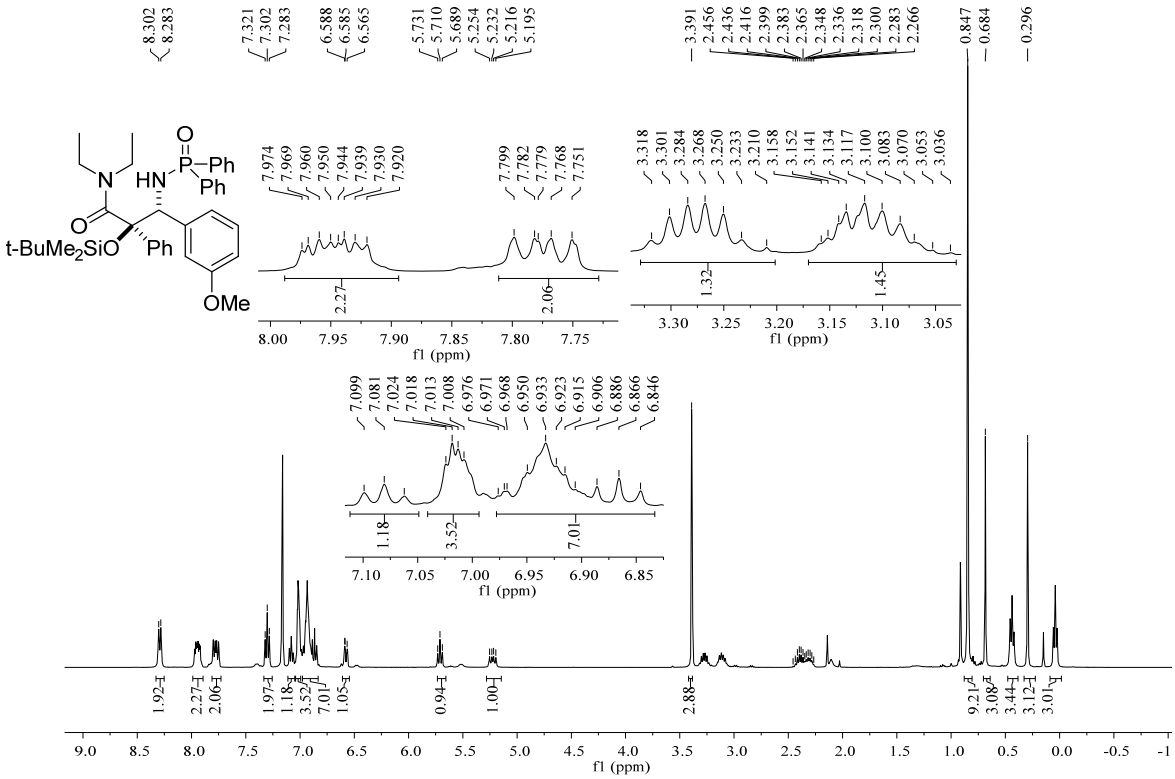
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6f**



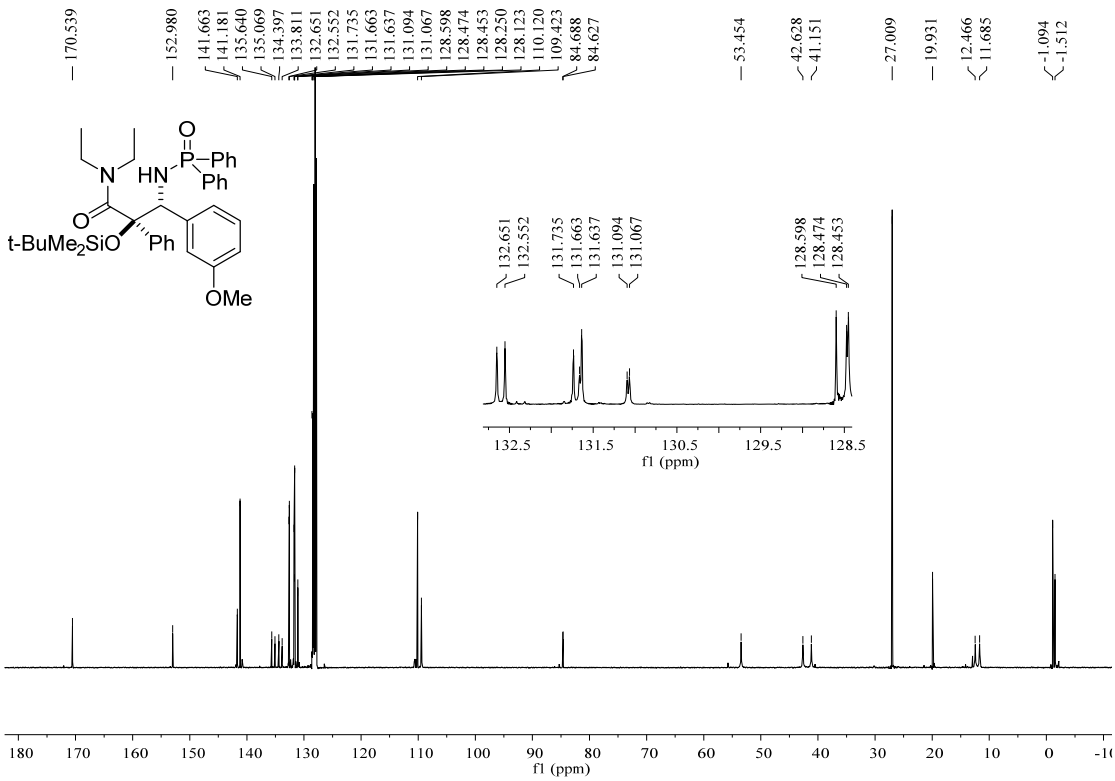
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6g**



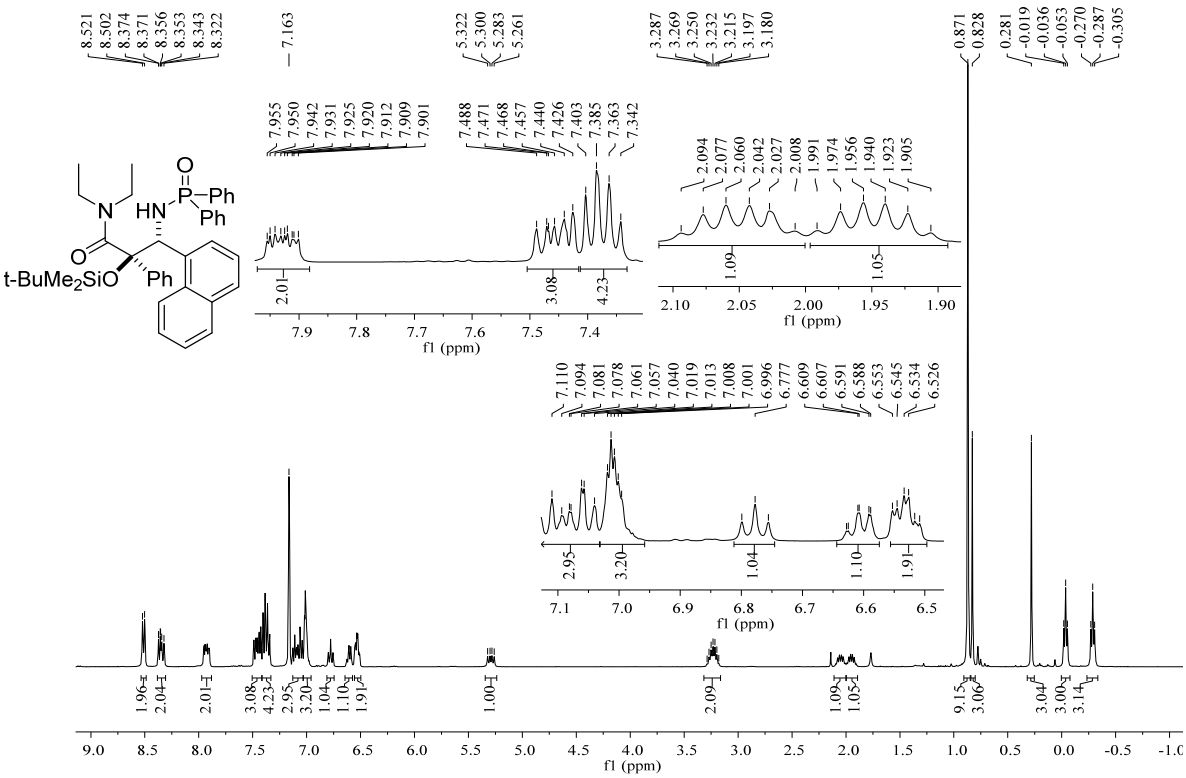
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6g**



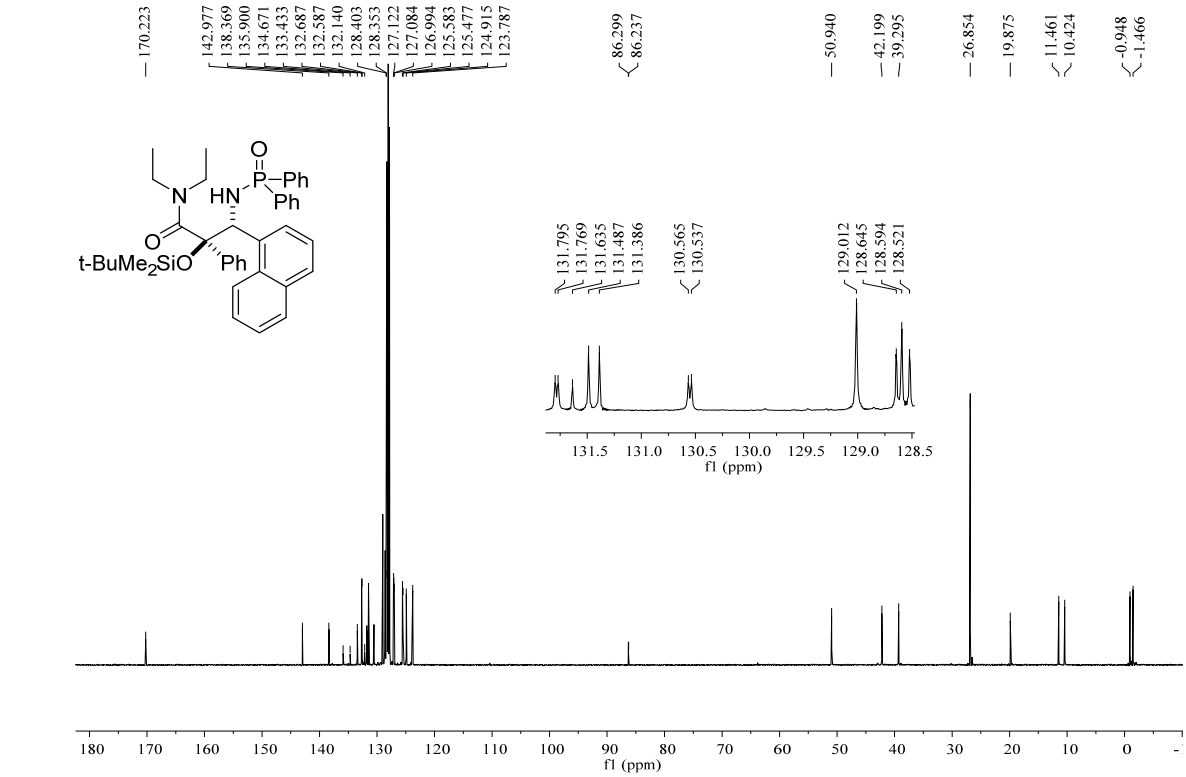
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6h**



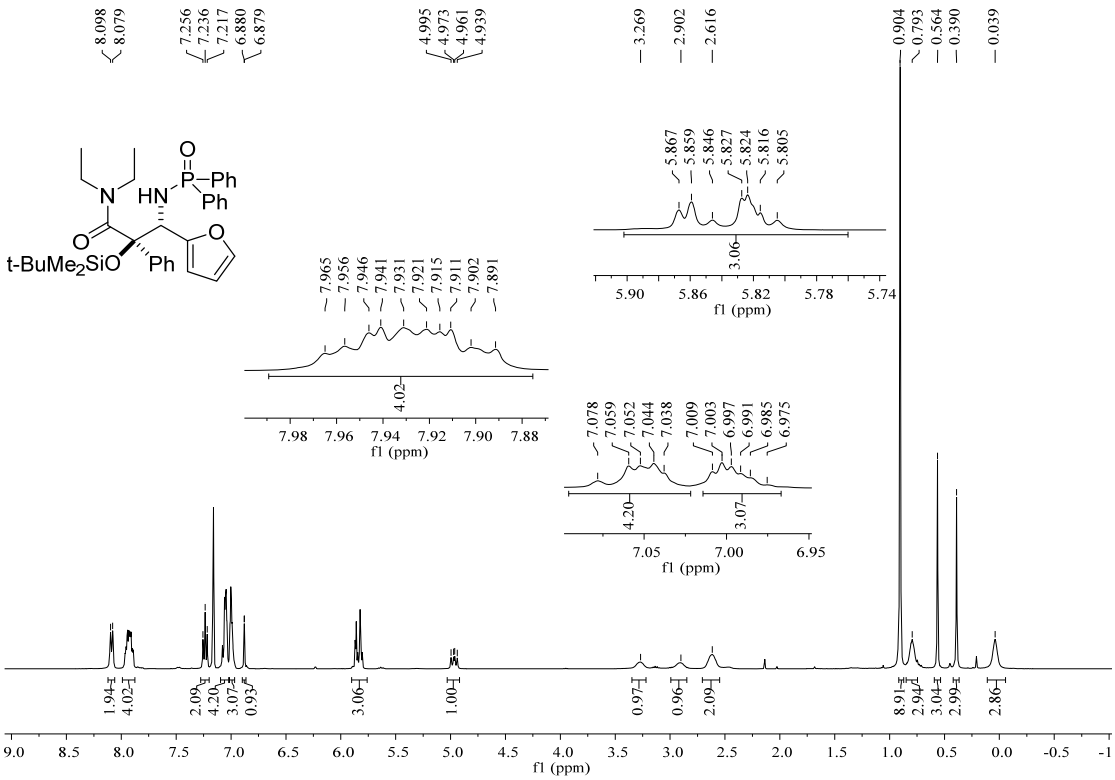
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6h**



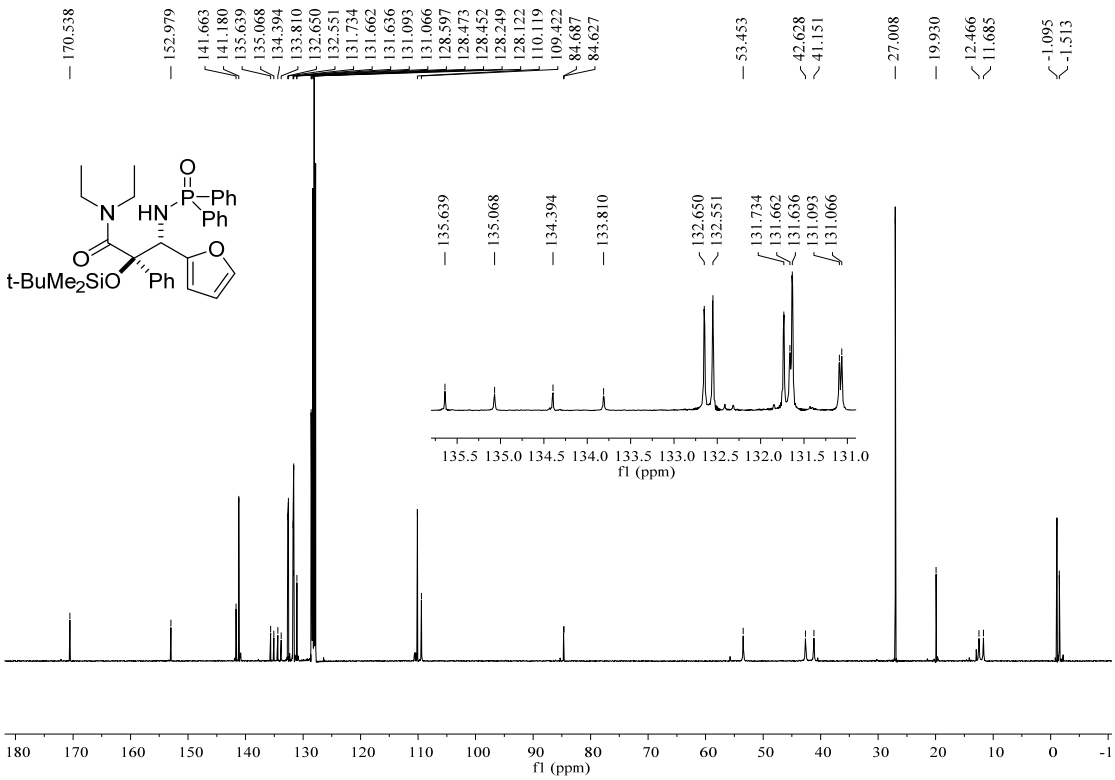
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6i**



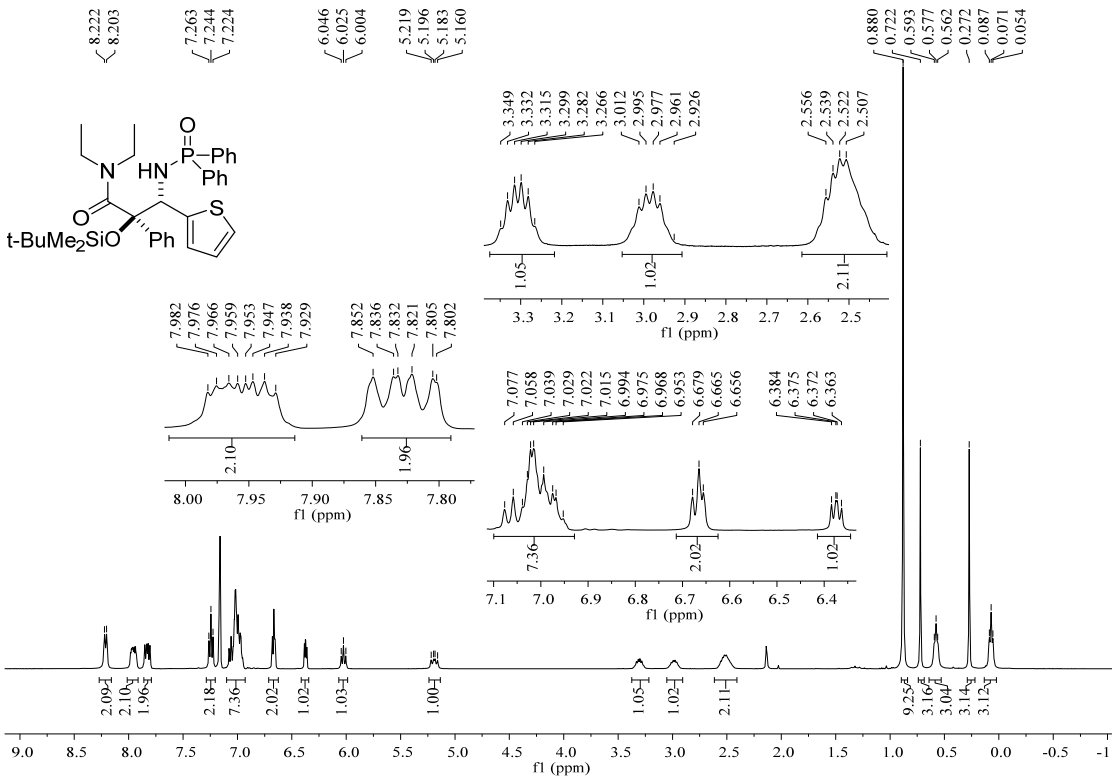
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6i**



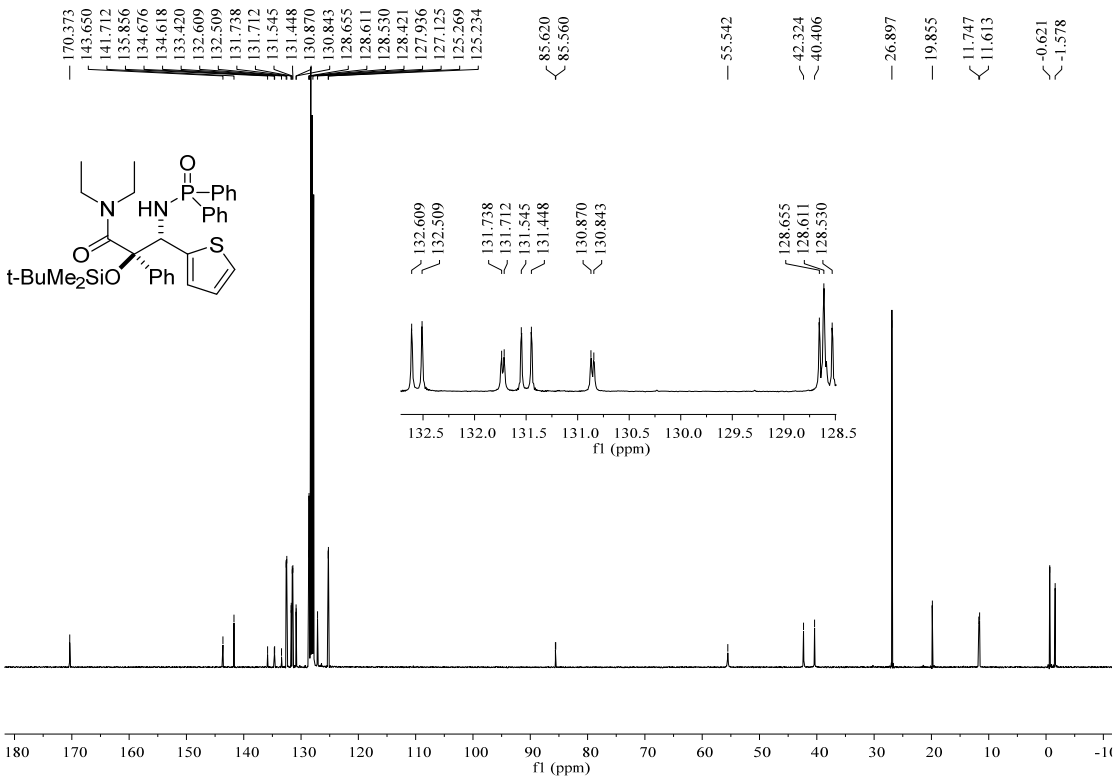
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6j**



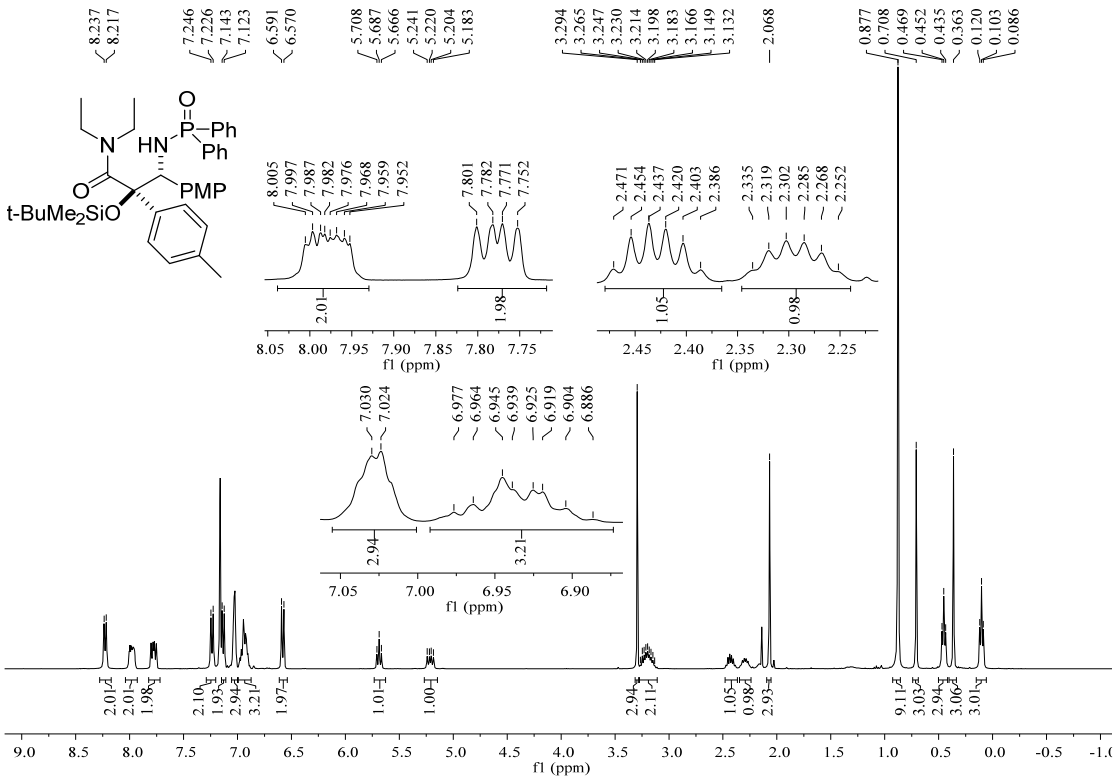
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6j**



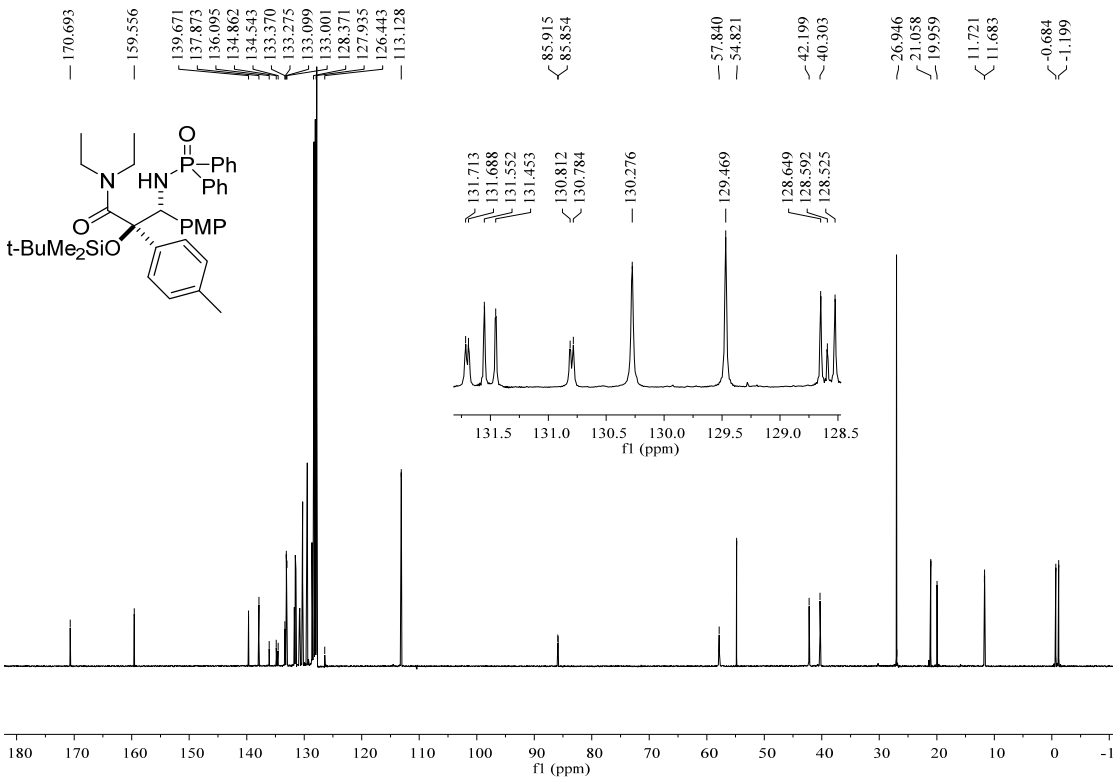
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6k**



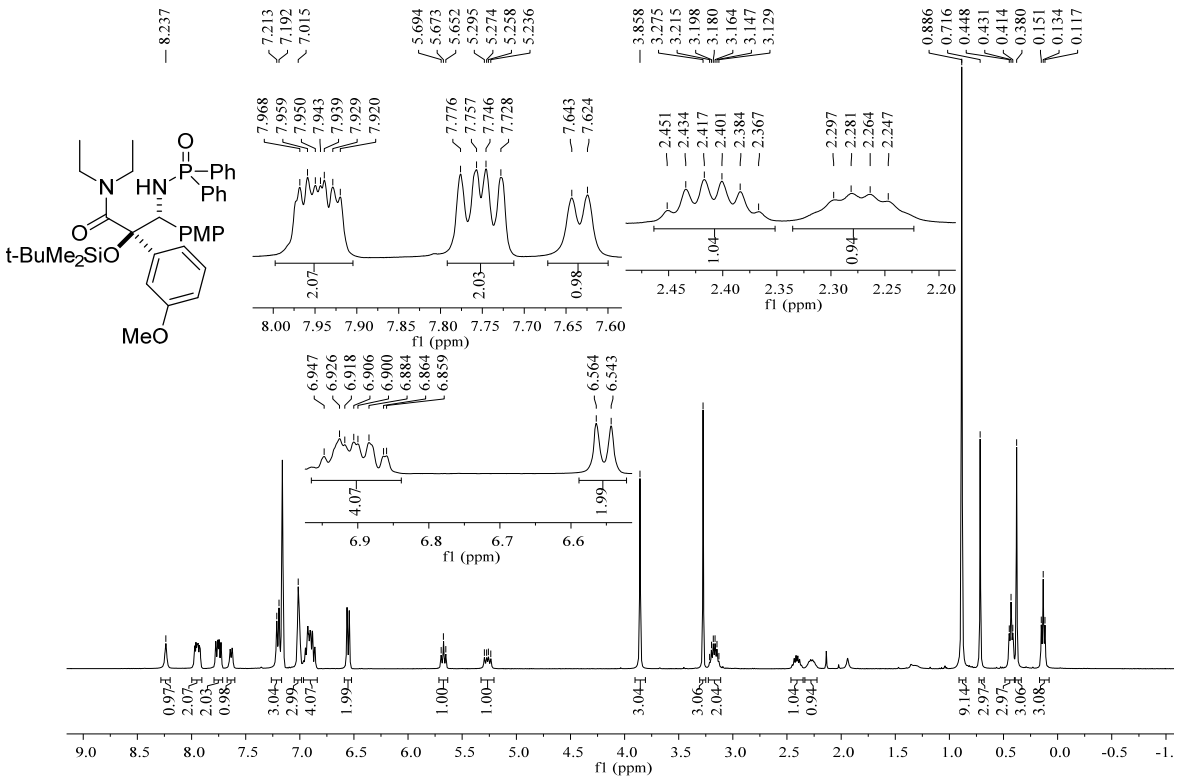
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6k**



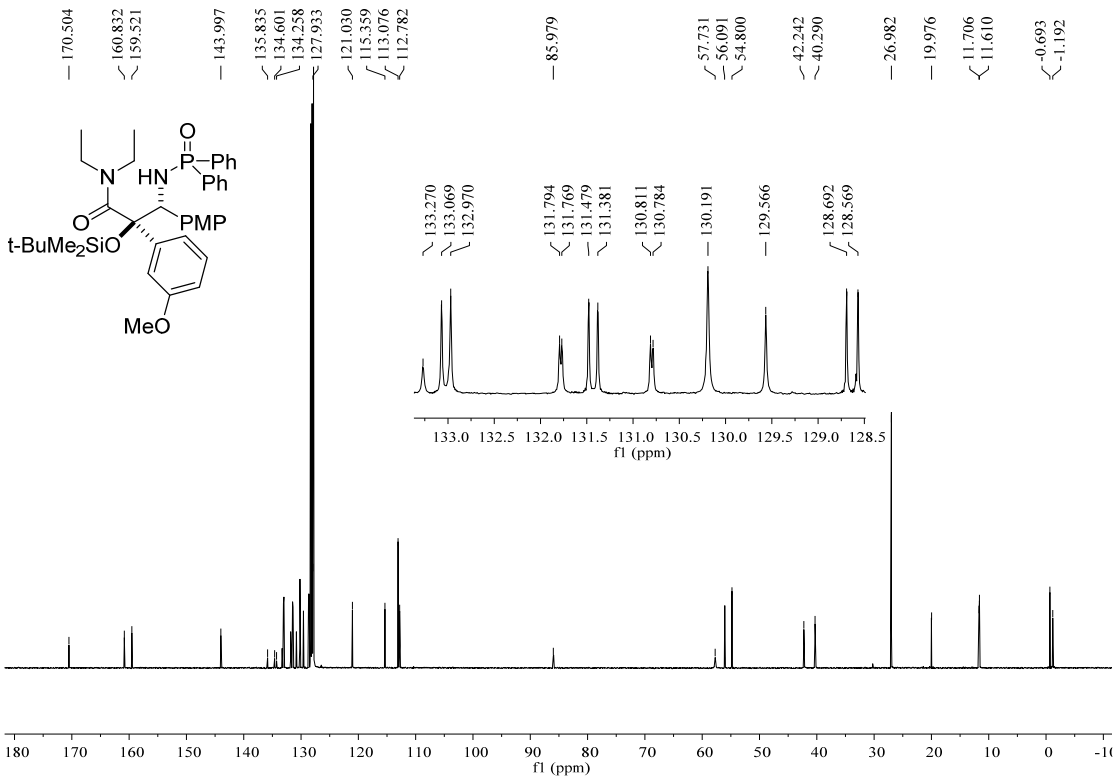
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6l**



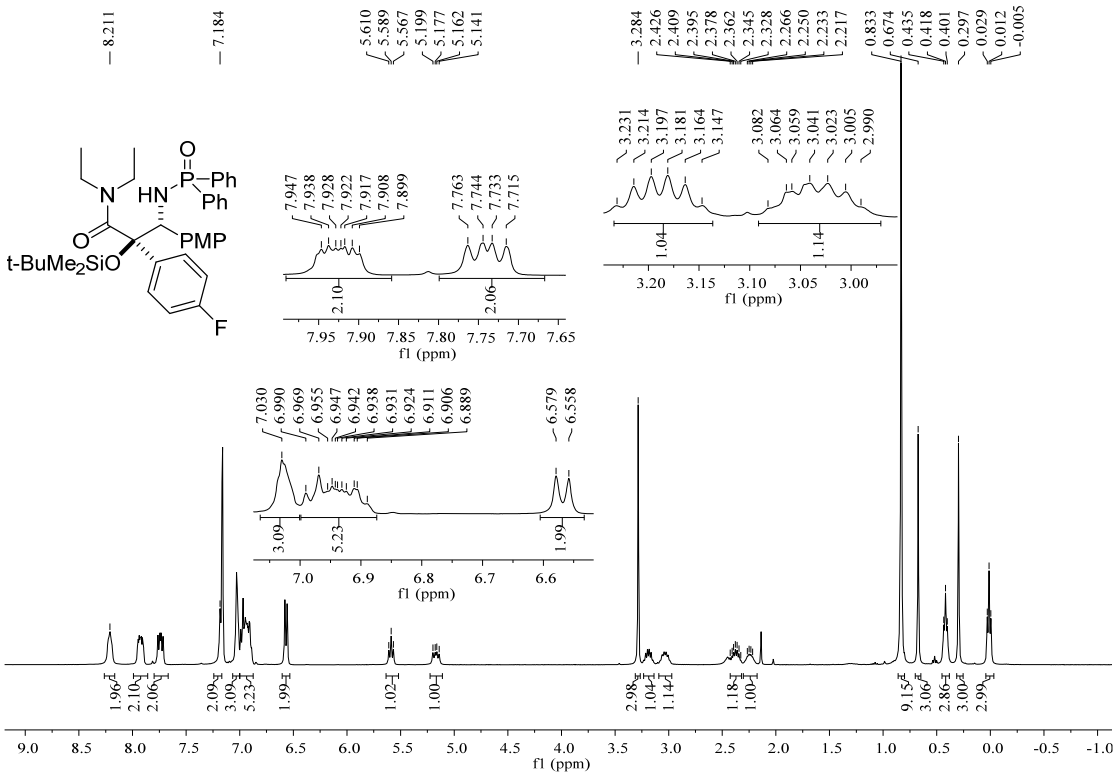
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6l**



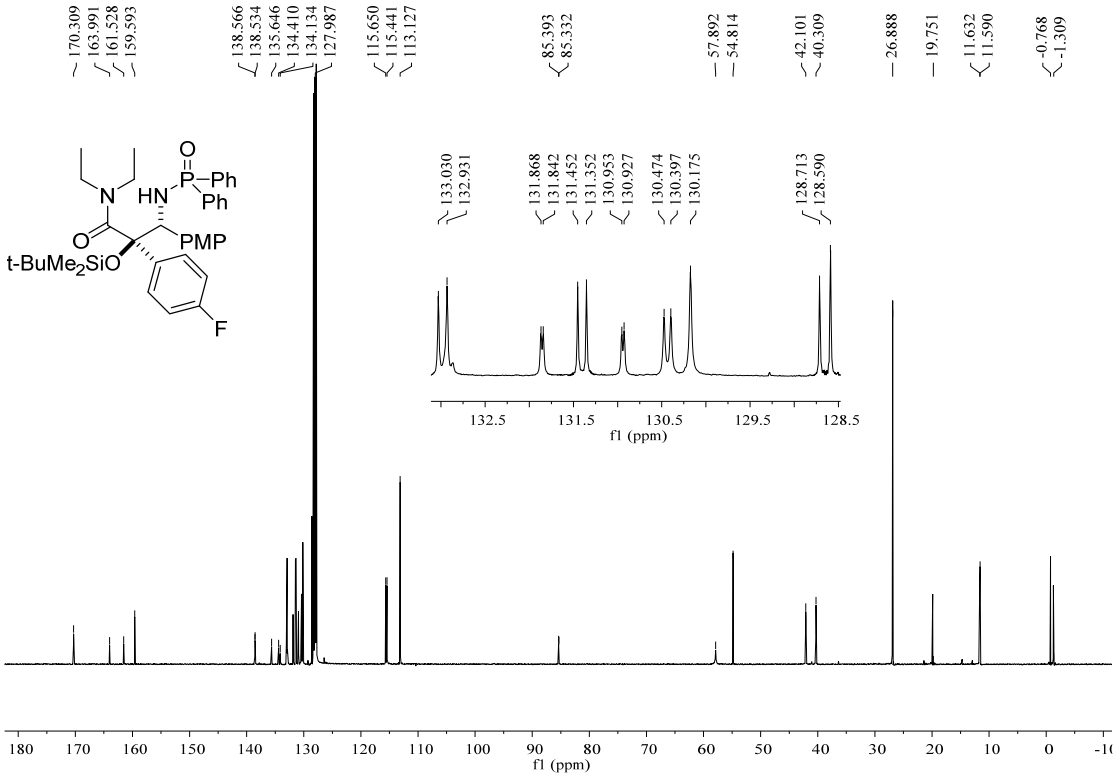
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6m**



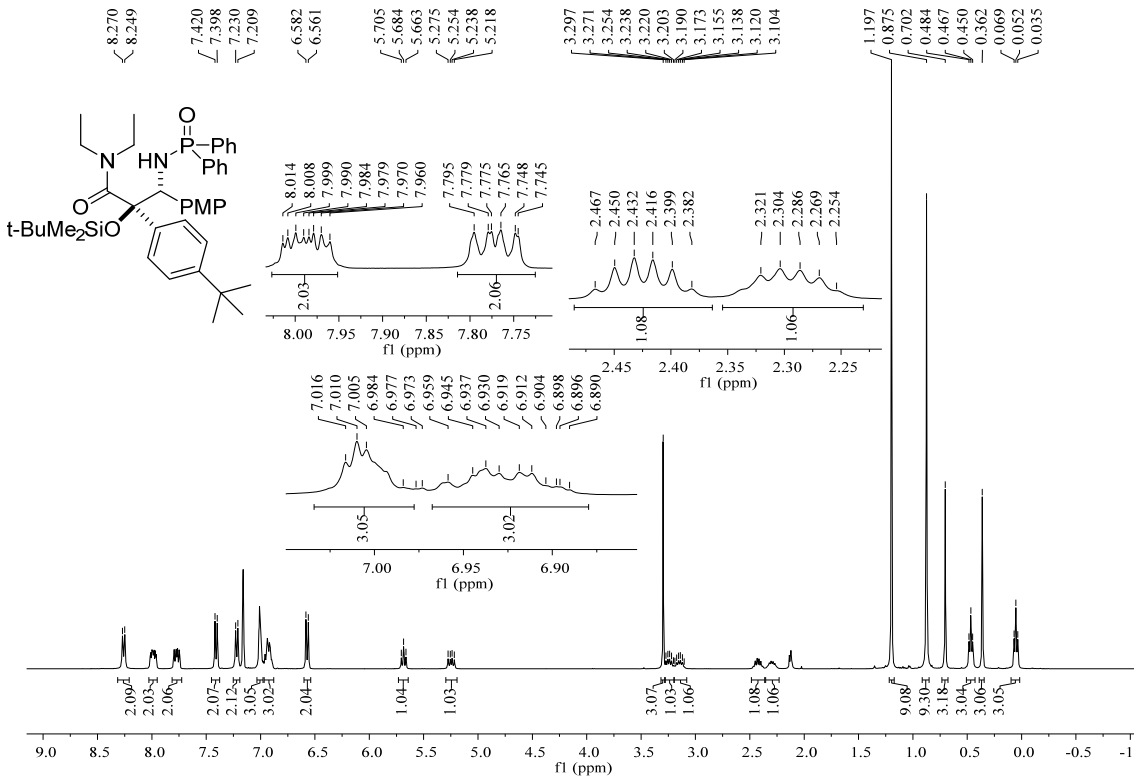
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6m**



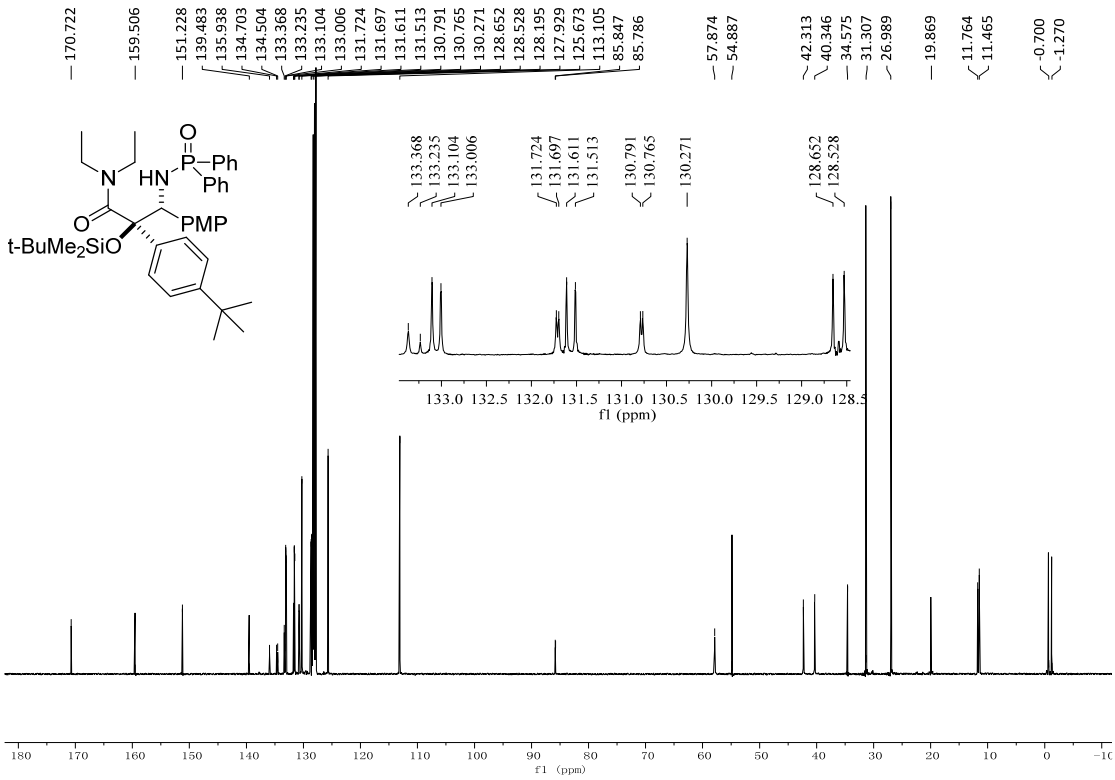
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6n**



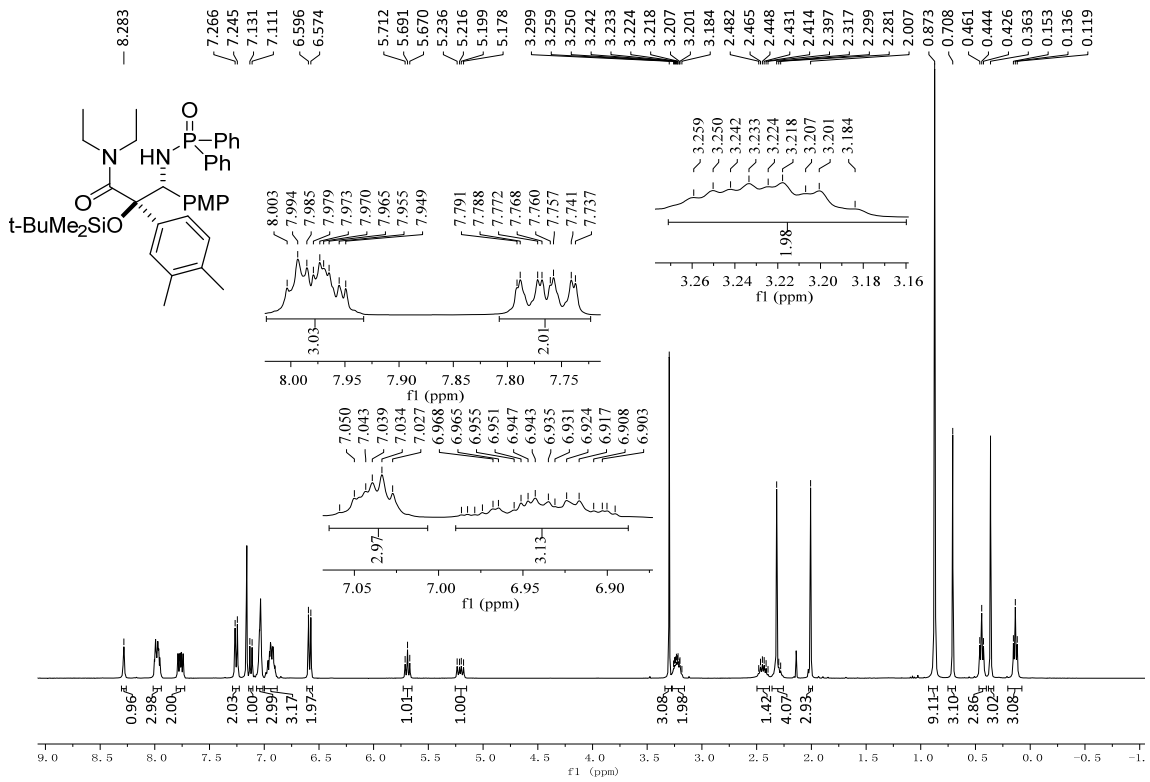
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6n**



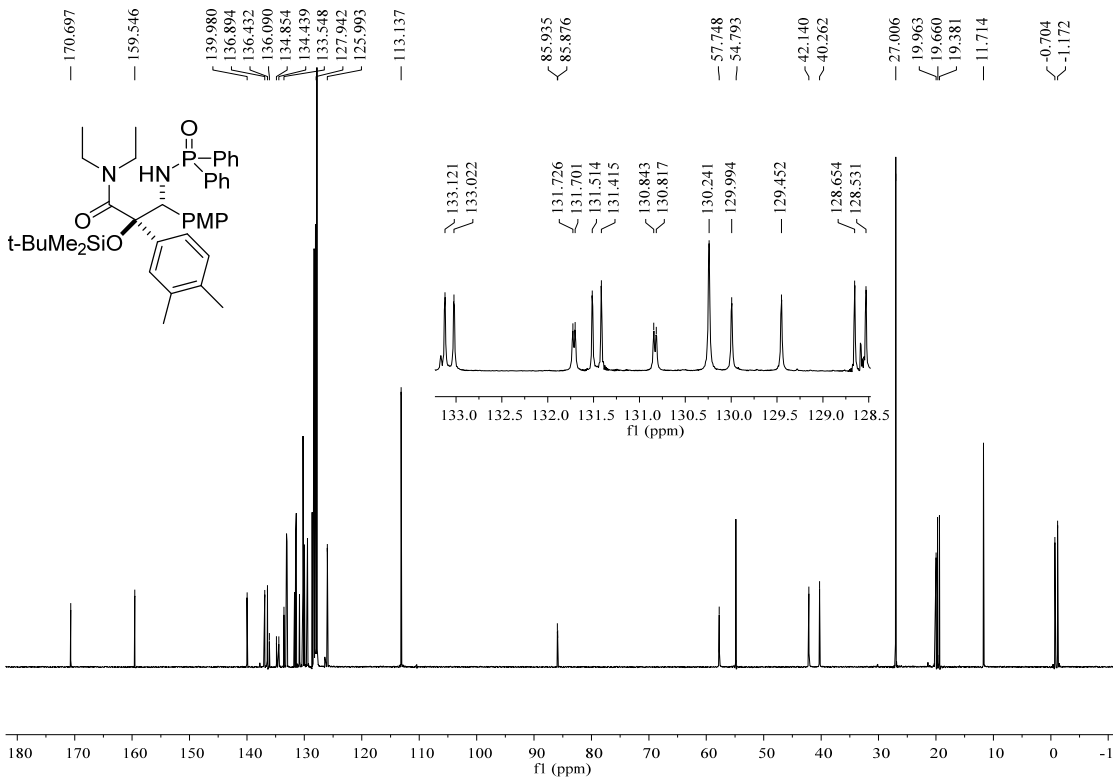
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6o**



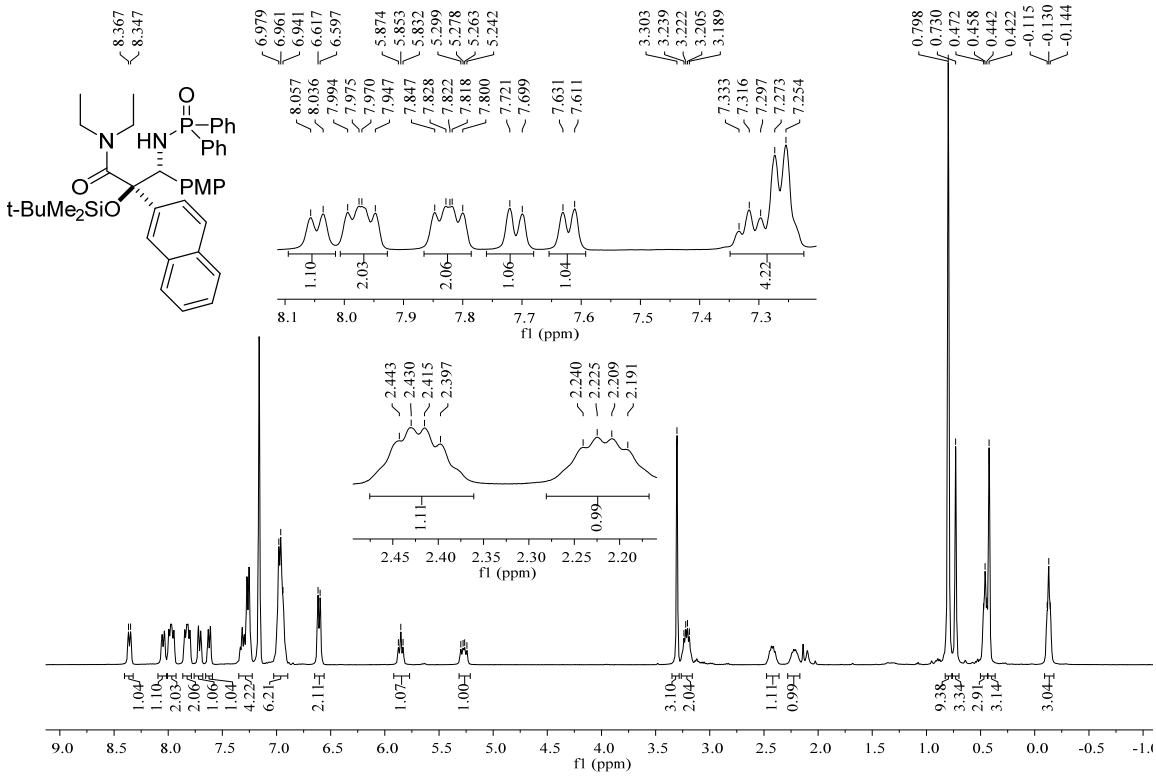
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6o**



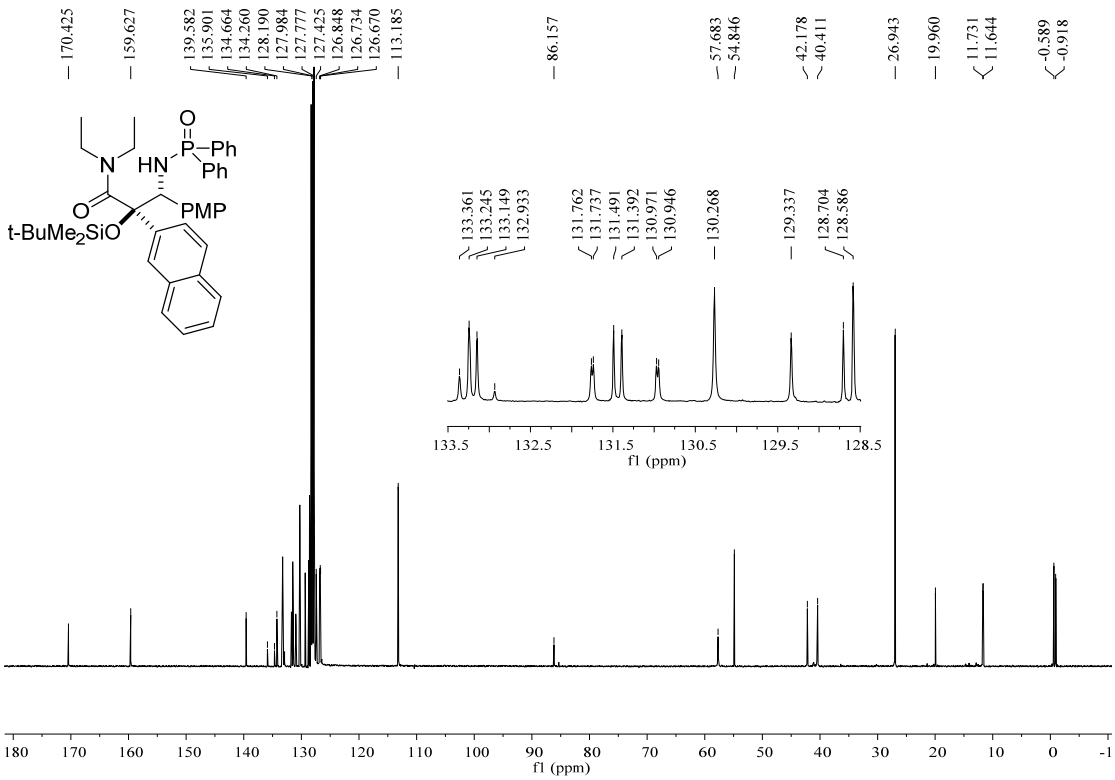
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6p**



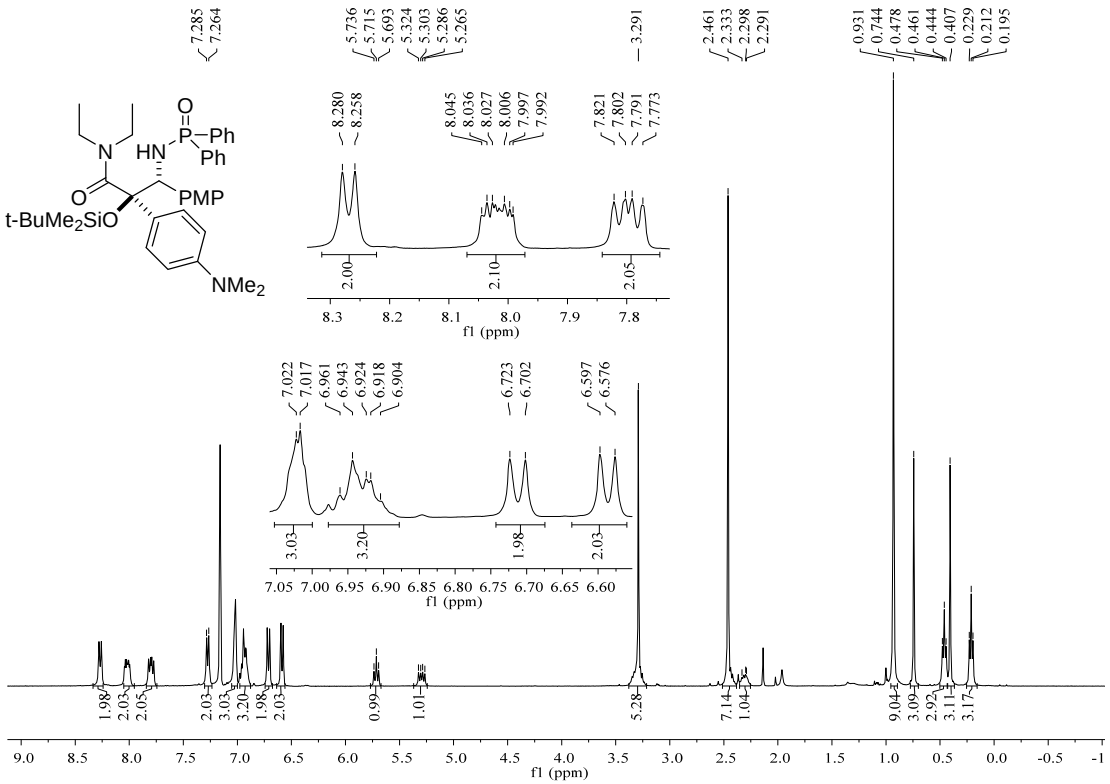
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6p**



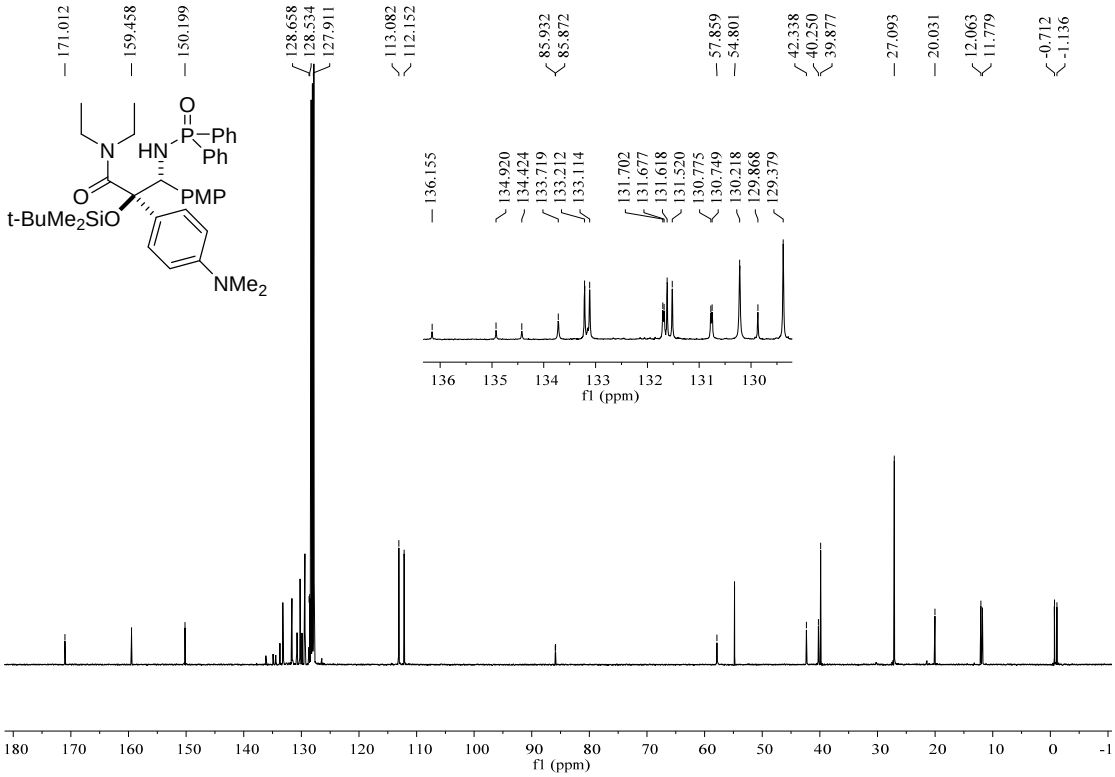
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6q**



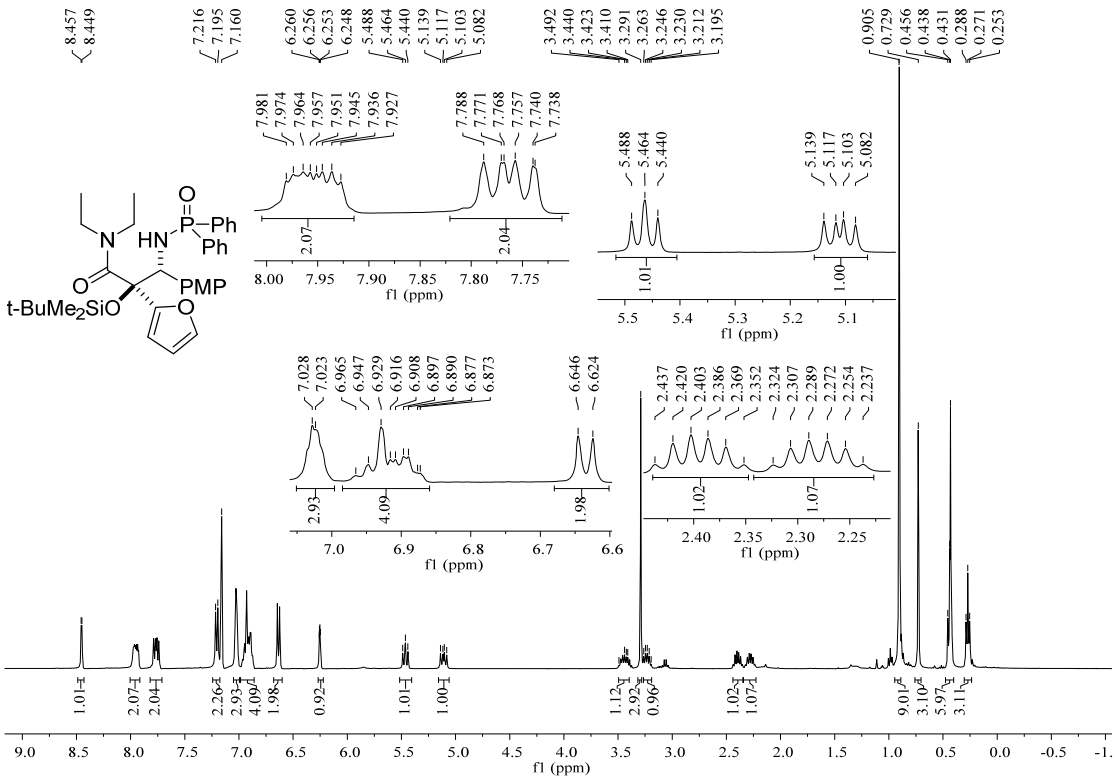
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6q**



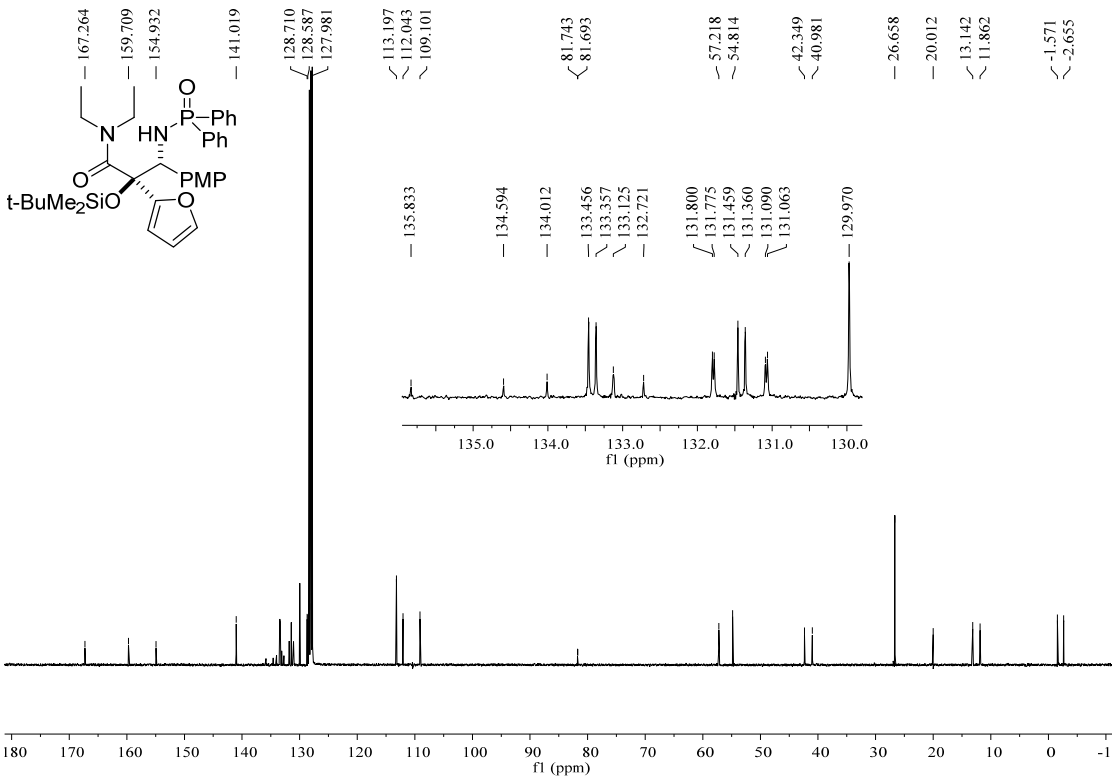
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6r**



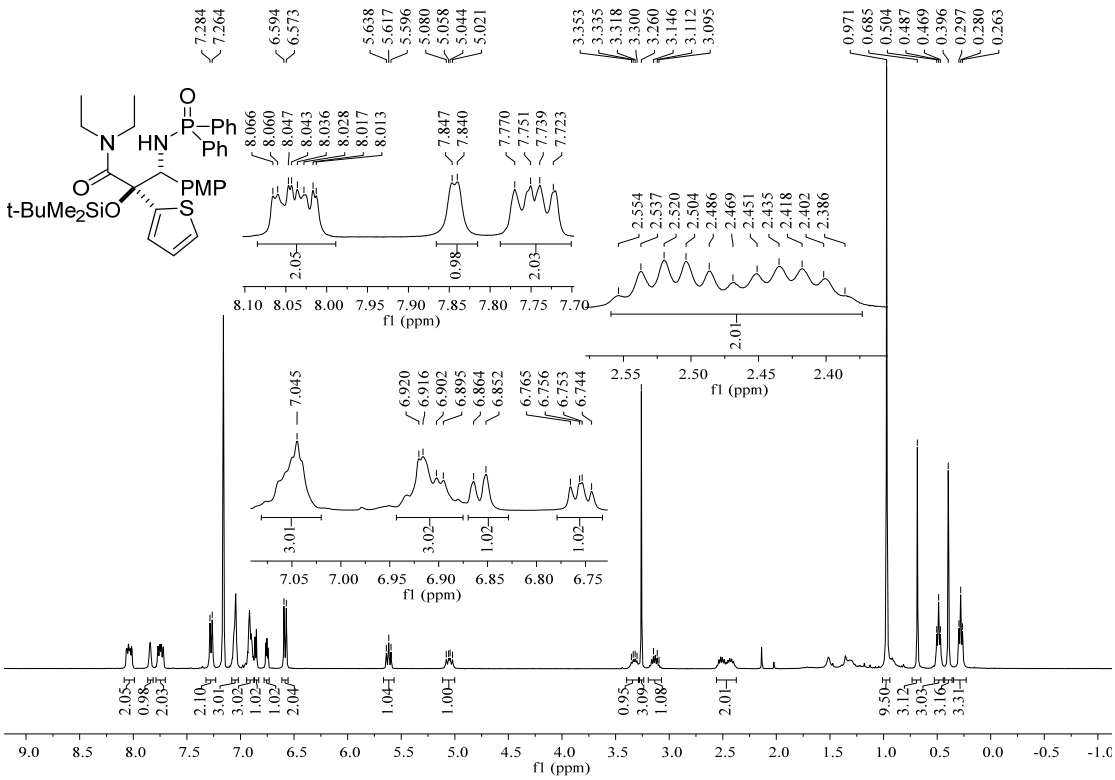
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6r**



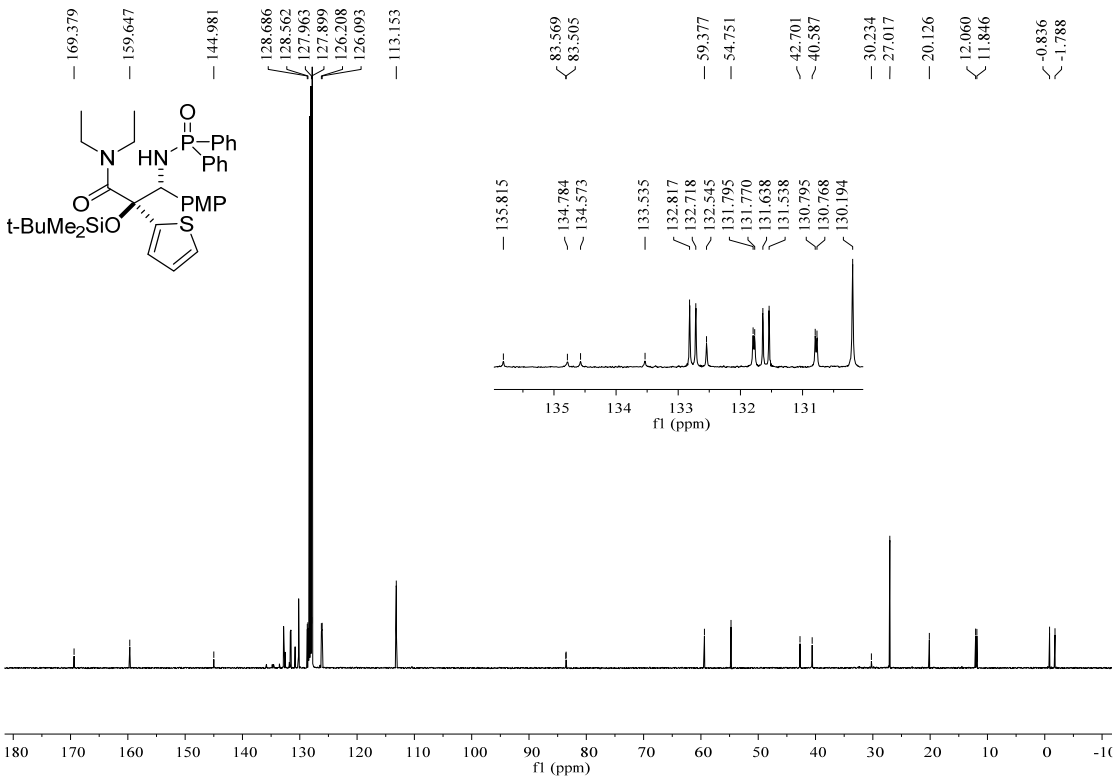
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6s**



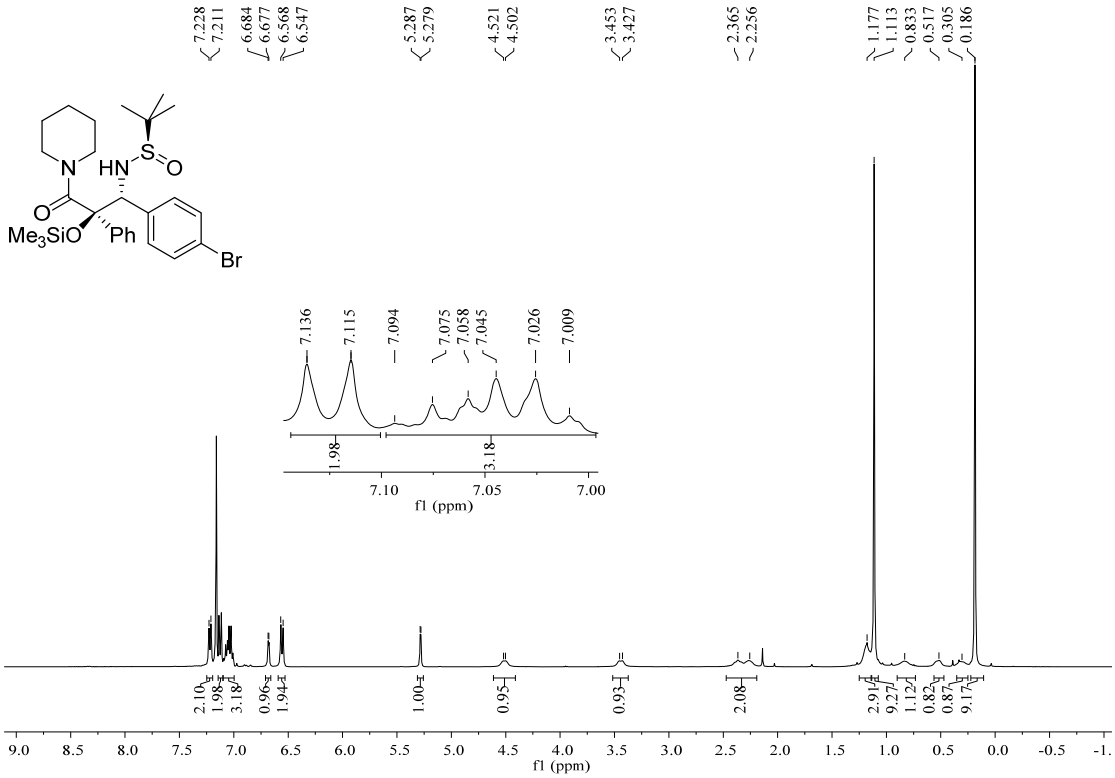
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6s**



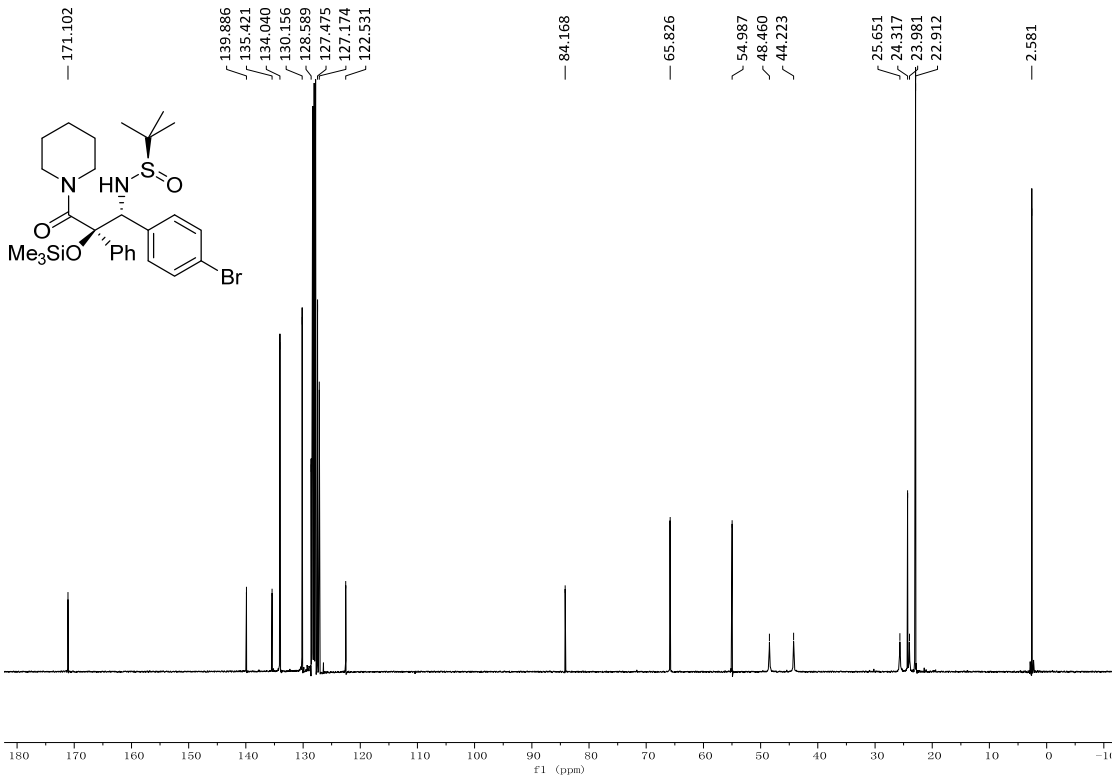
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6t**



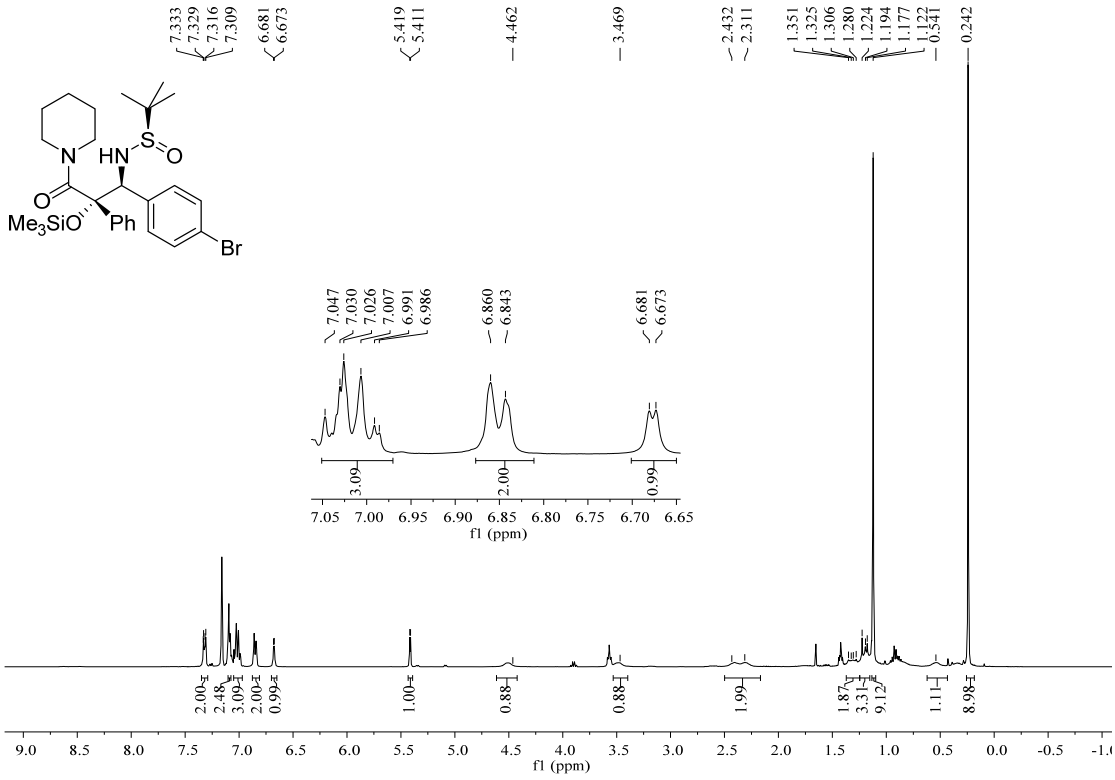
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **6t**



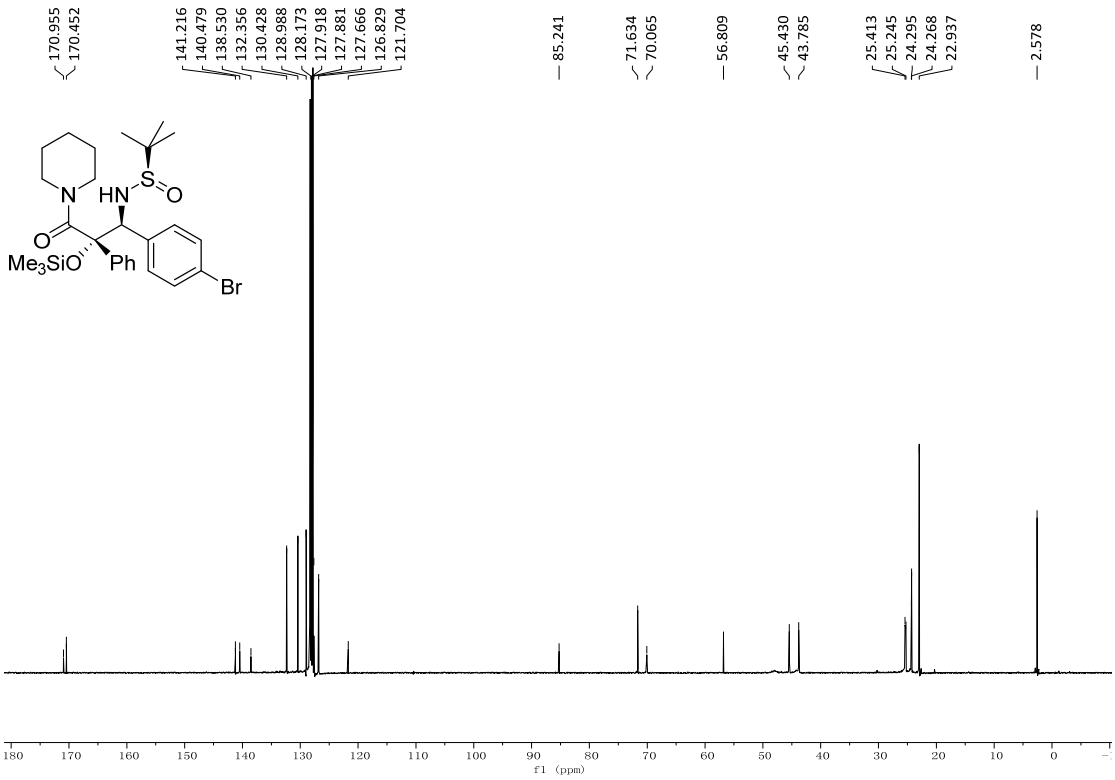
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **8a** (major isomer)



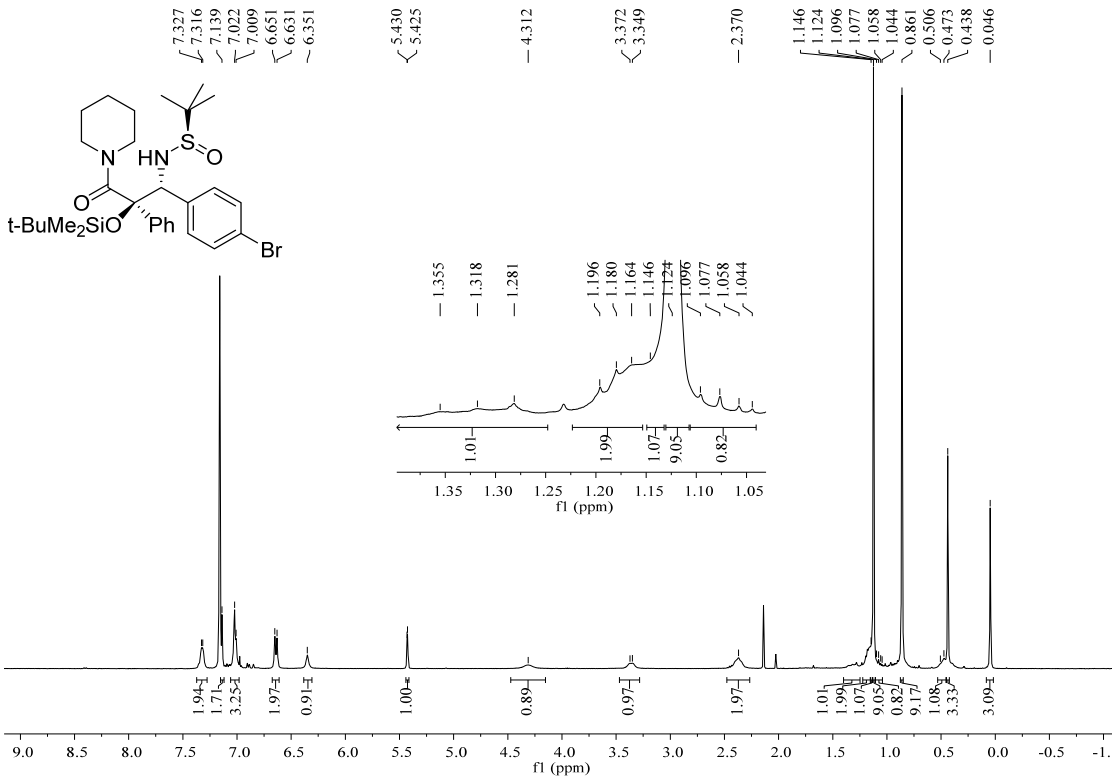
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **8a** (major isomer)



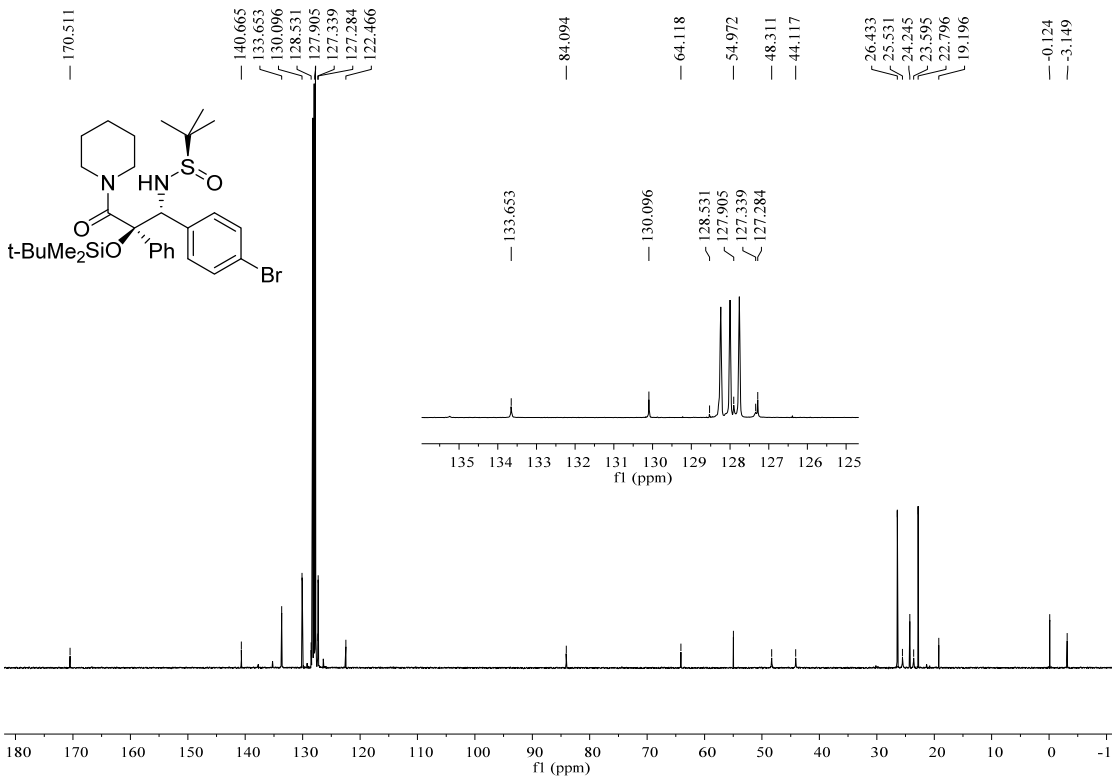
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **8'a** (minor isomer)



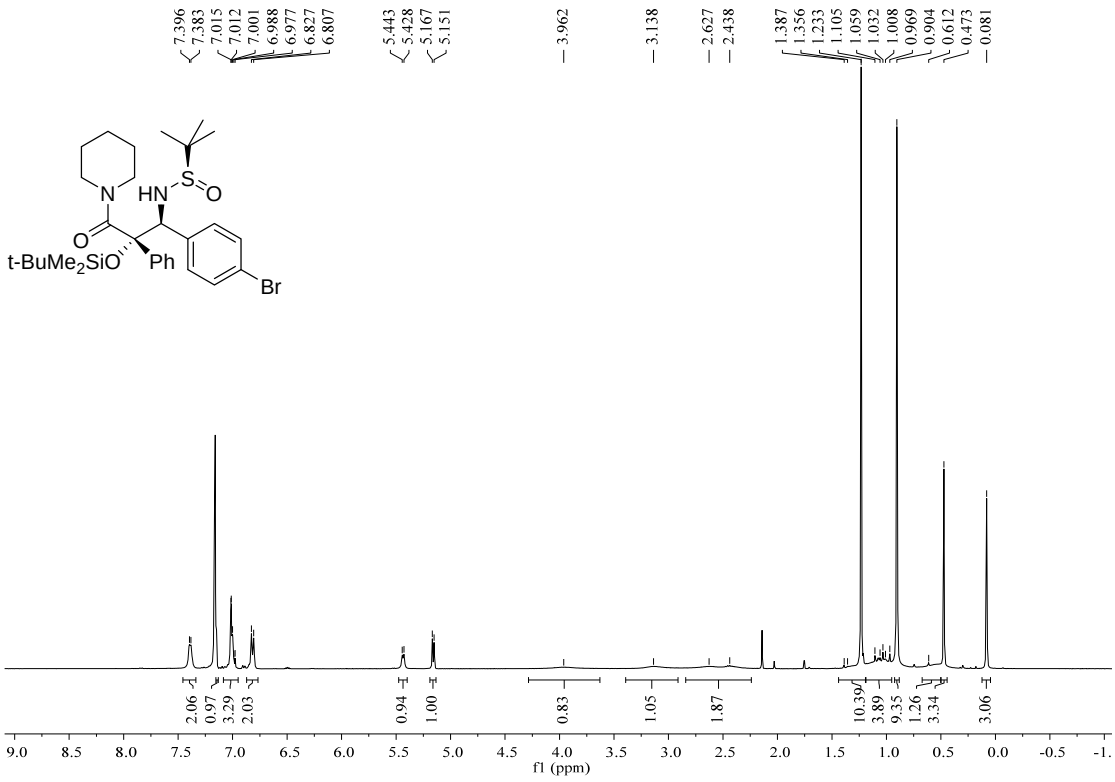
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **8'a** (minor isomer)



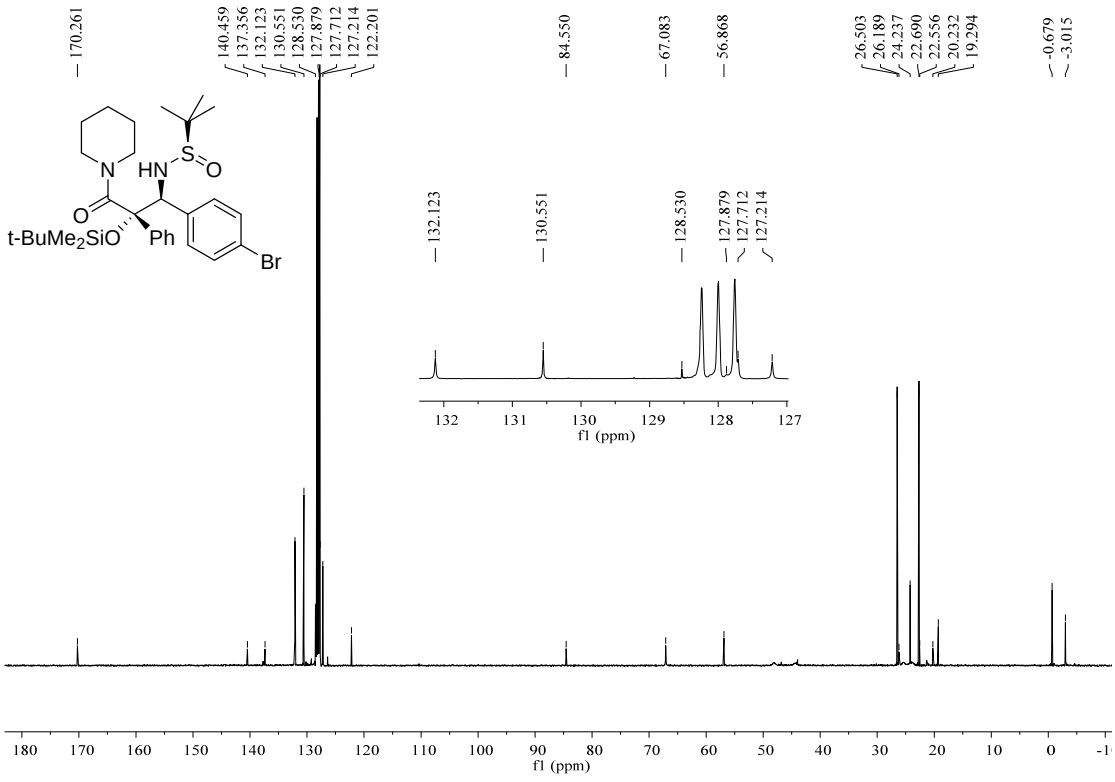
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **8d** (minor isomer)



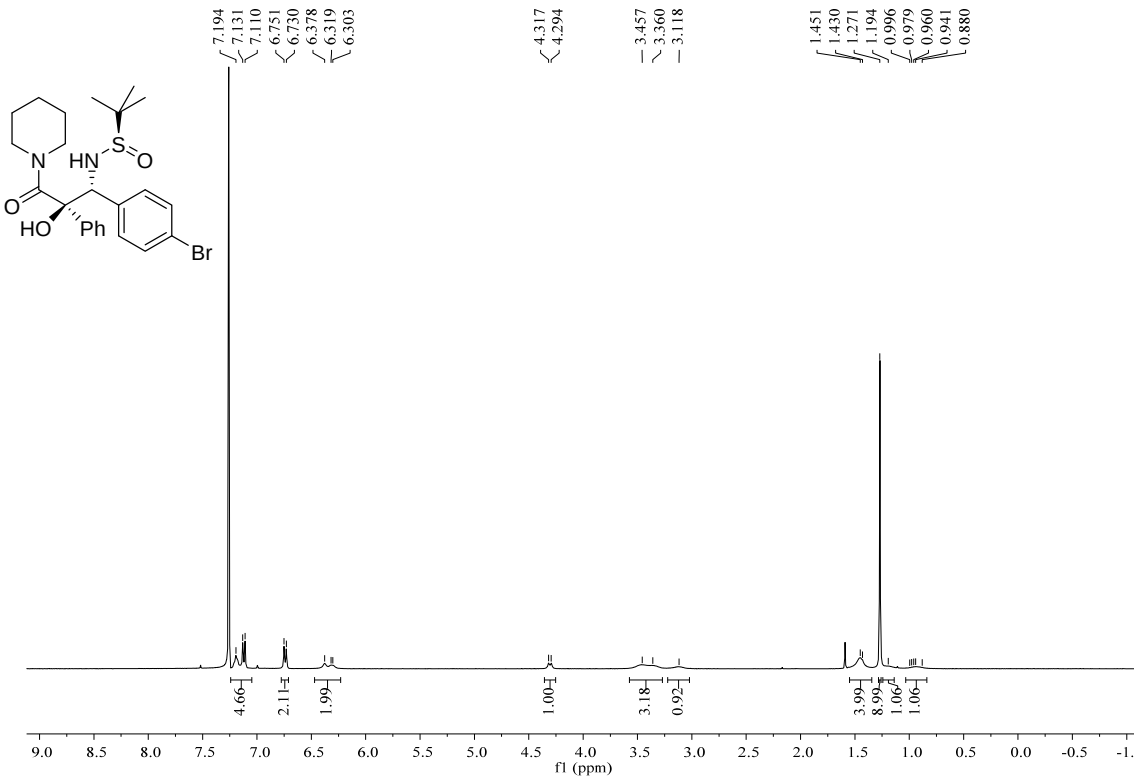
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **8d** (minor isomer)



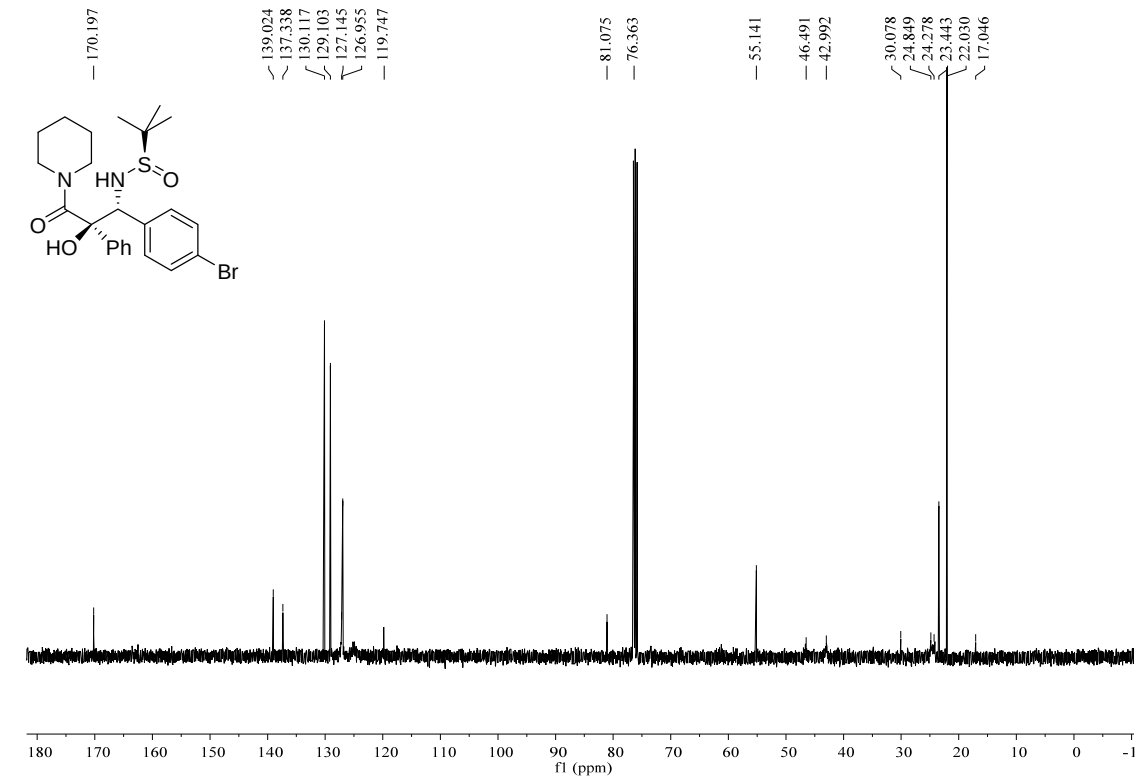
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **8'd** (major isomer)



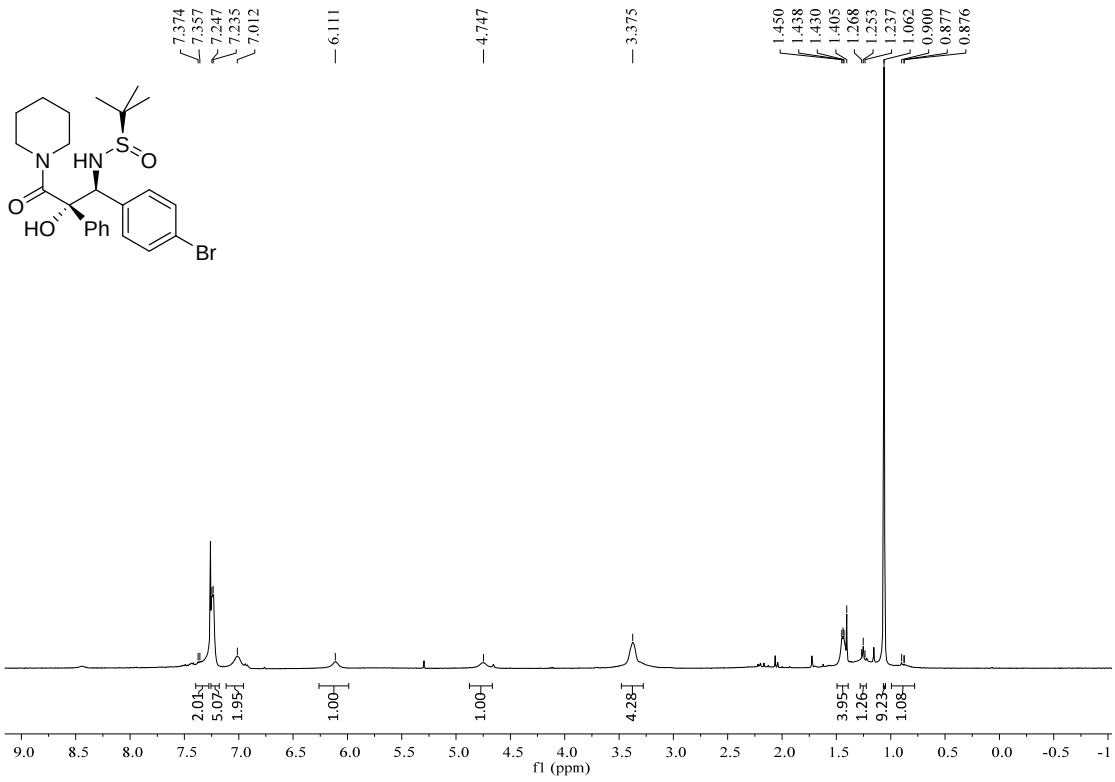
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **8'd** (major isomer)



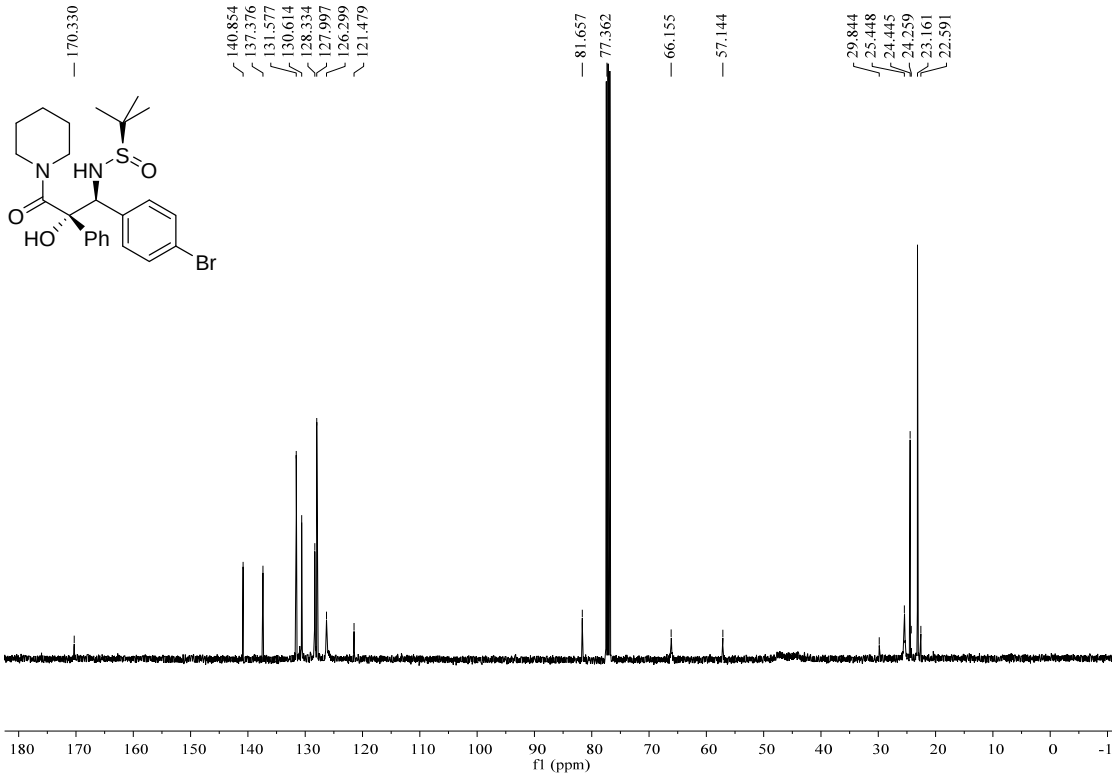
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **9**



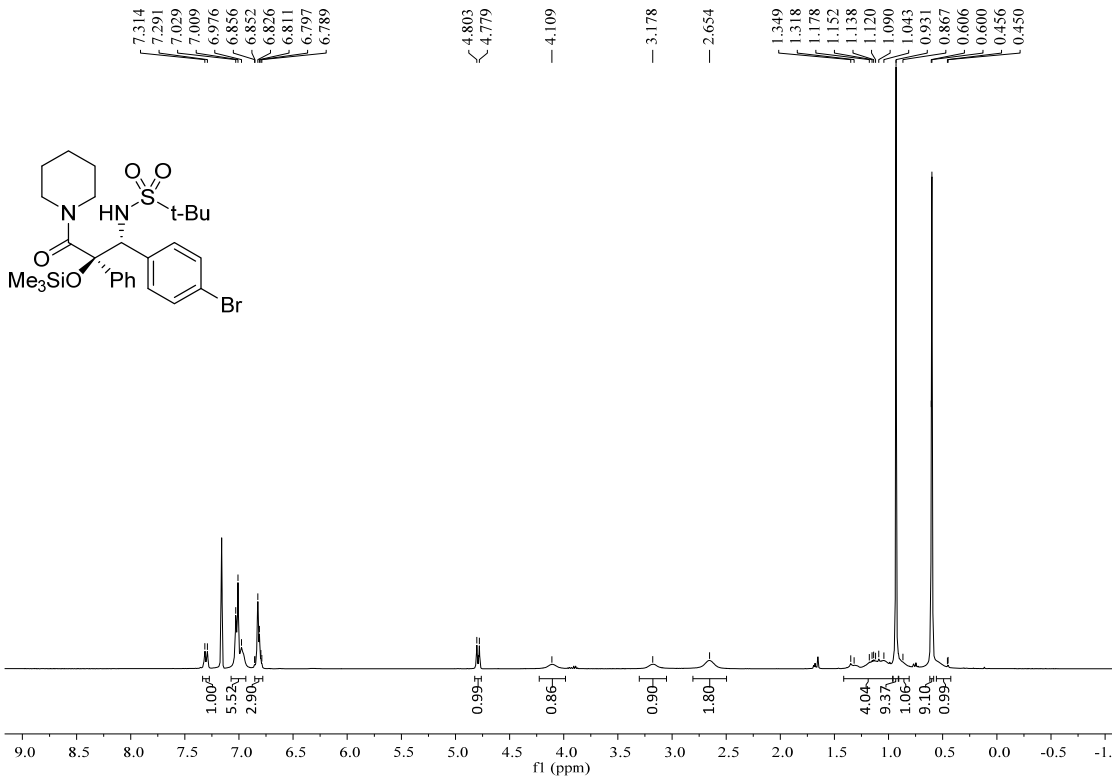
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **9**



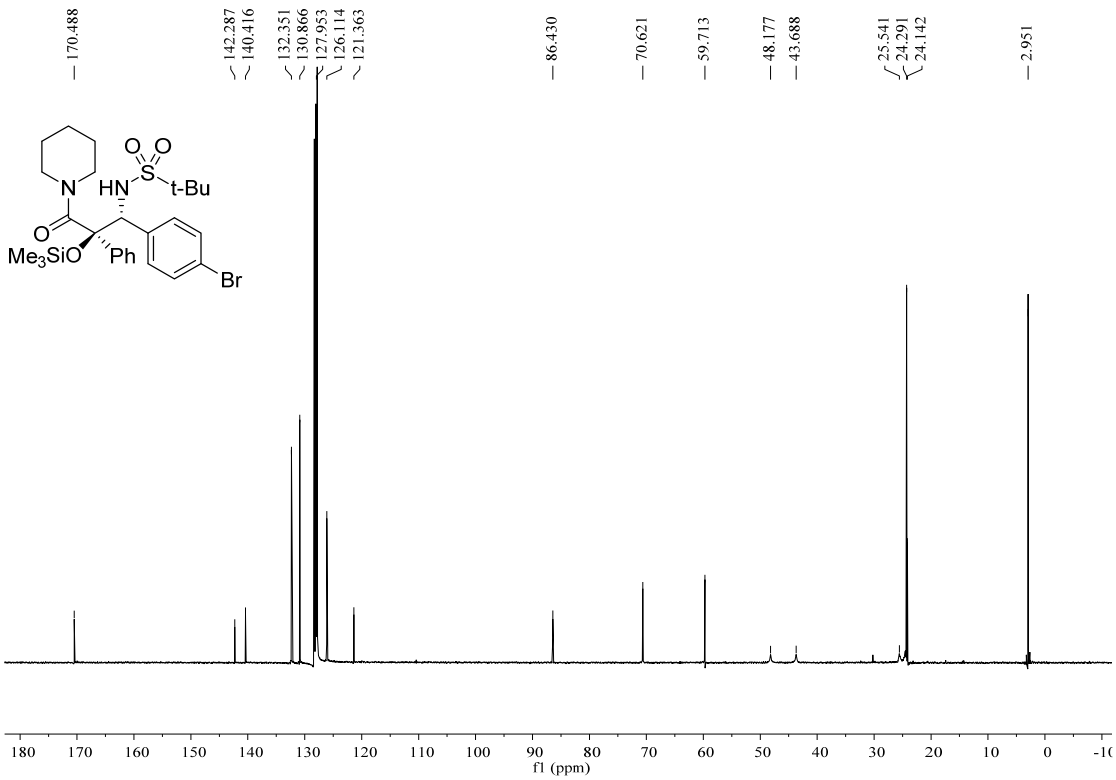
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **9'**



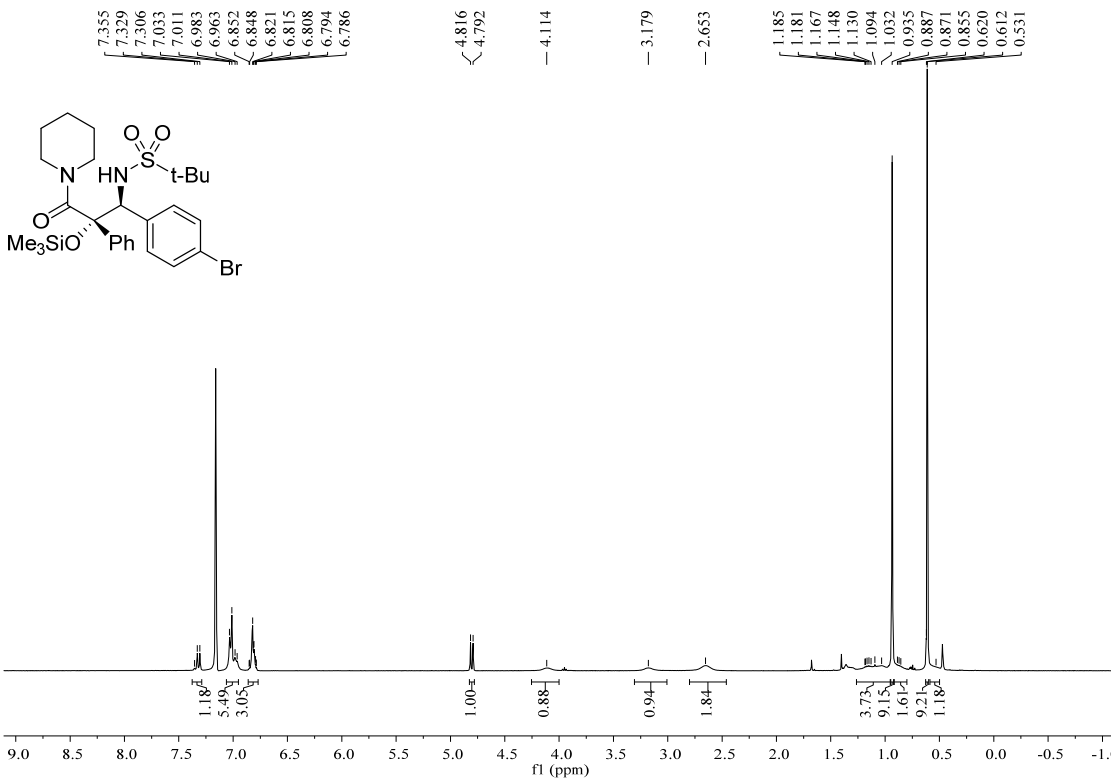
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **9'**



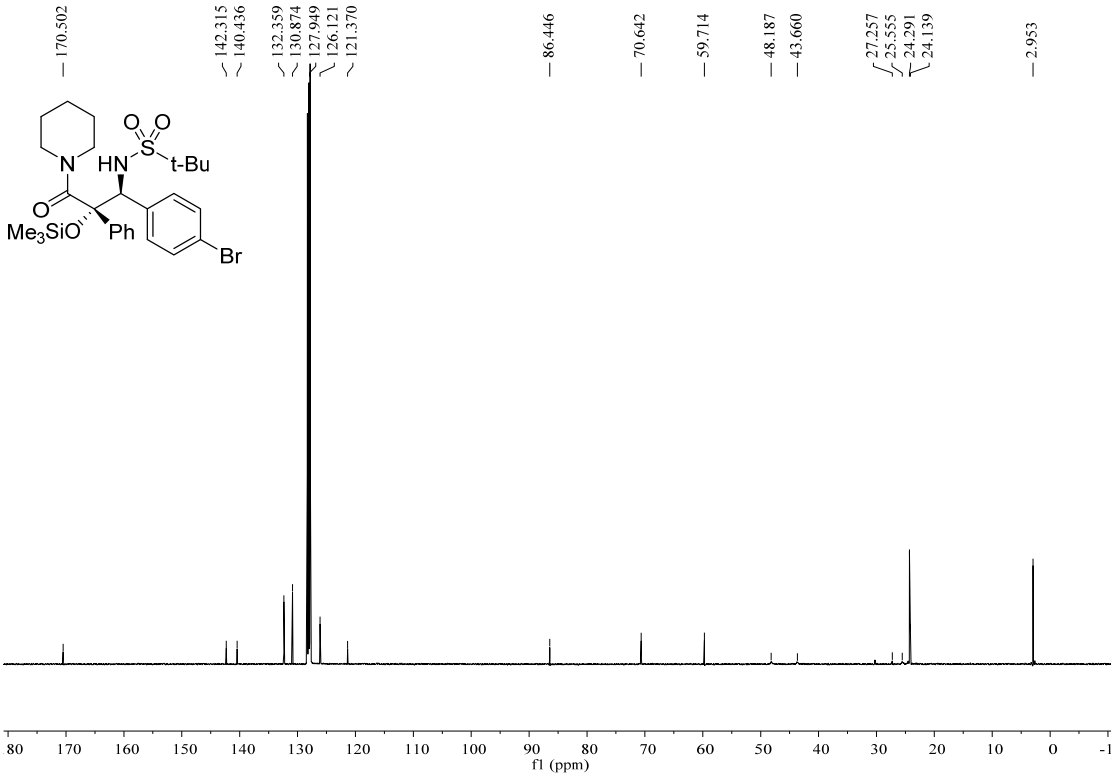
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **10**



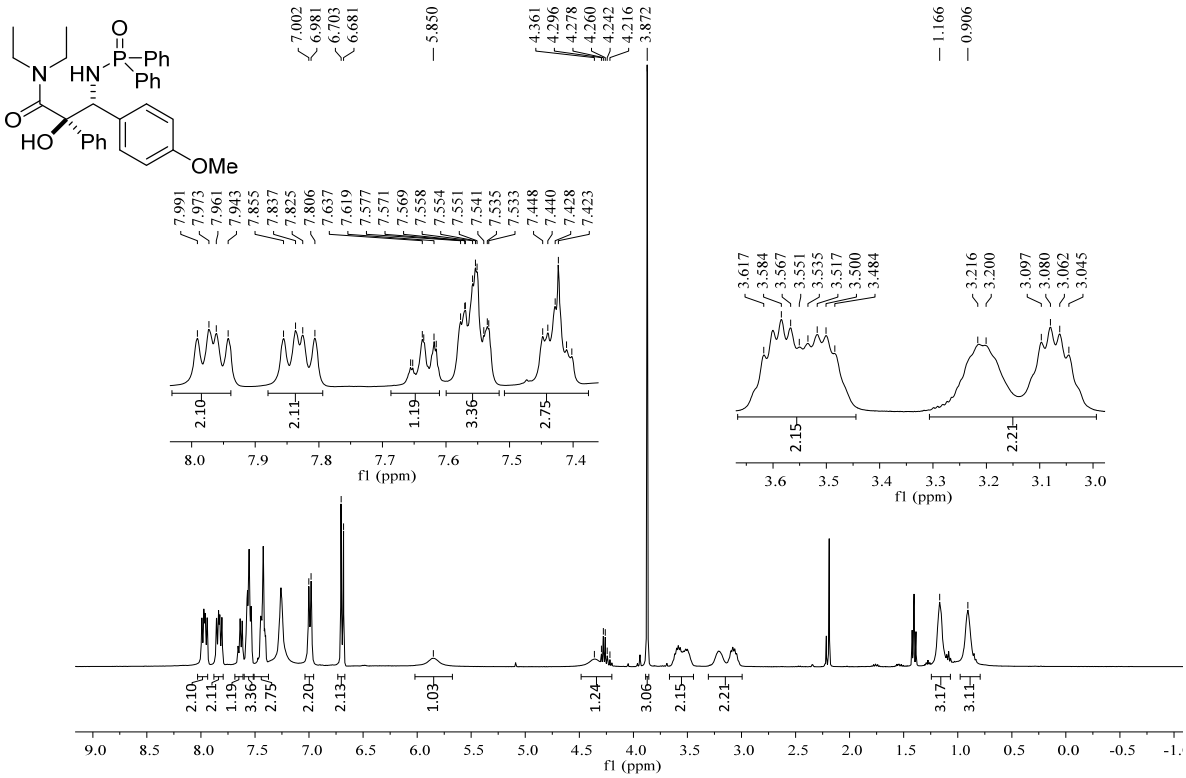
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **10**



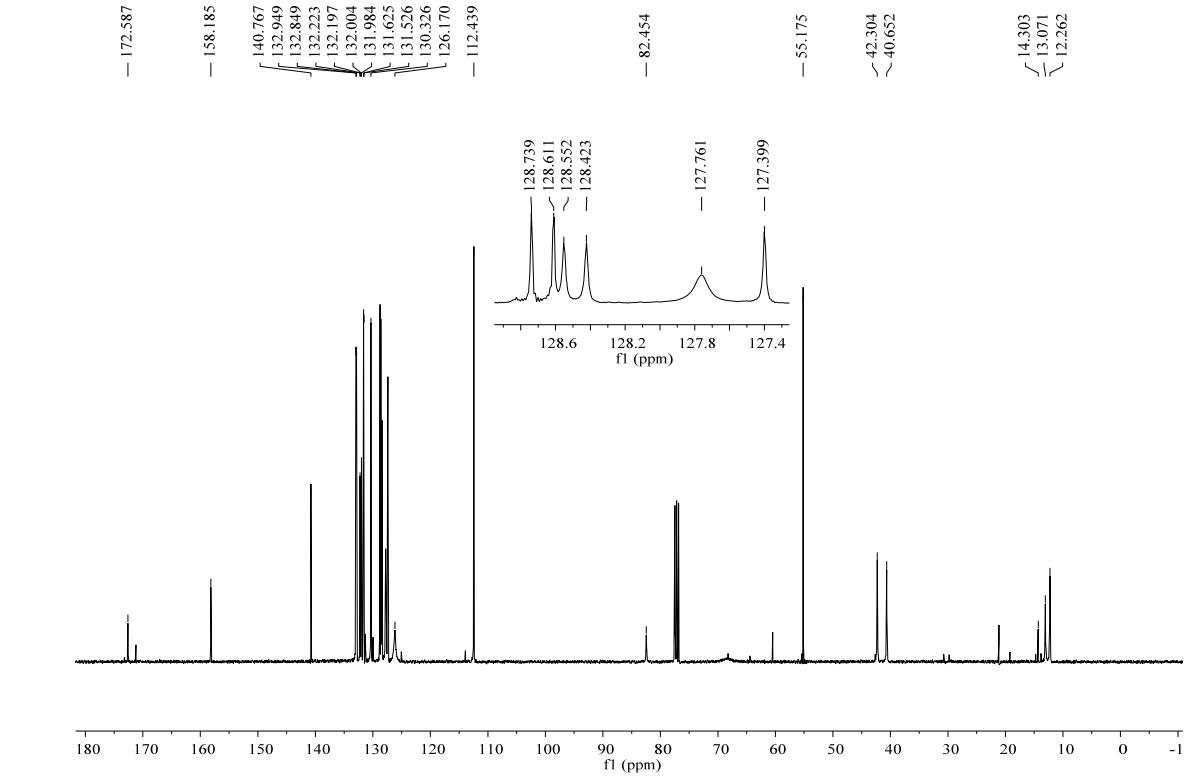
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **10'**



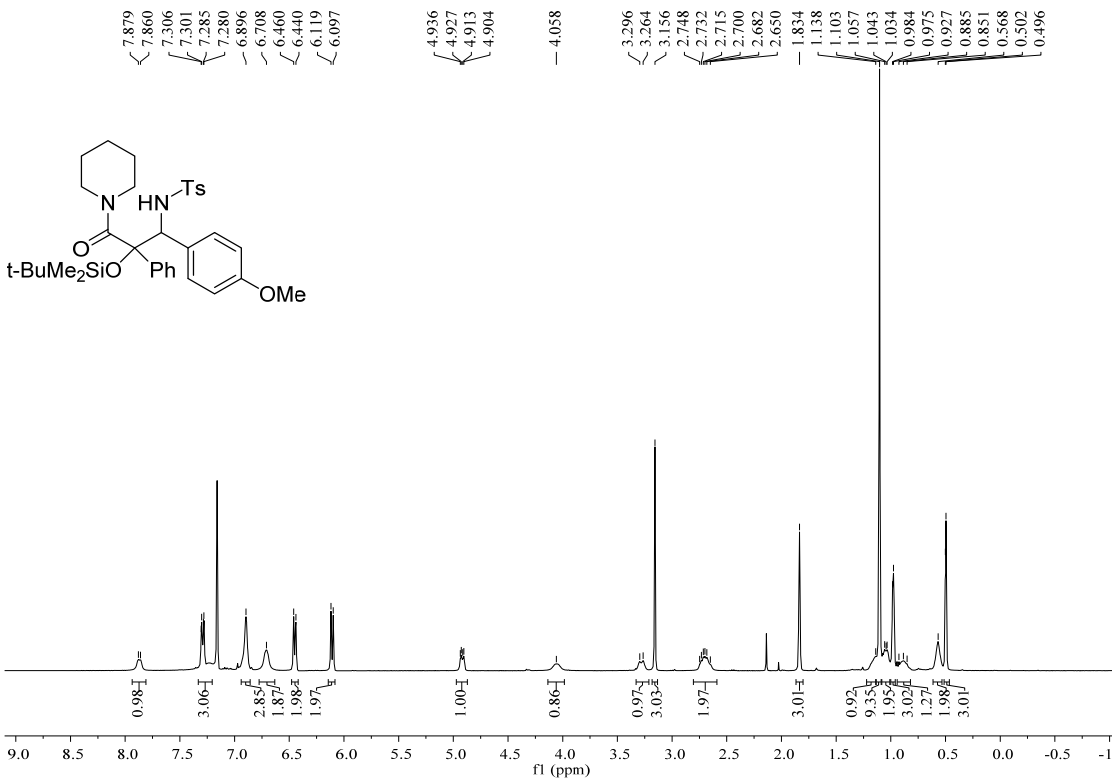
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **10'**



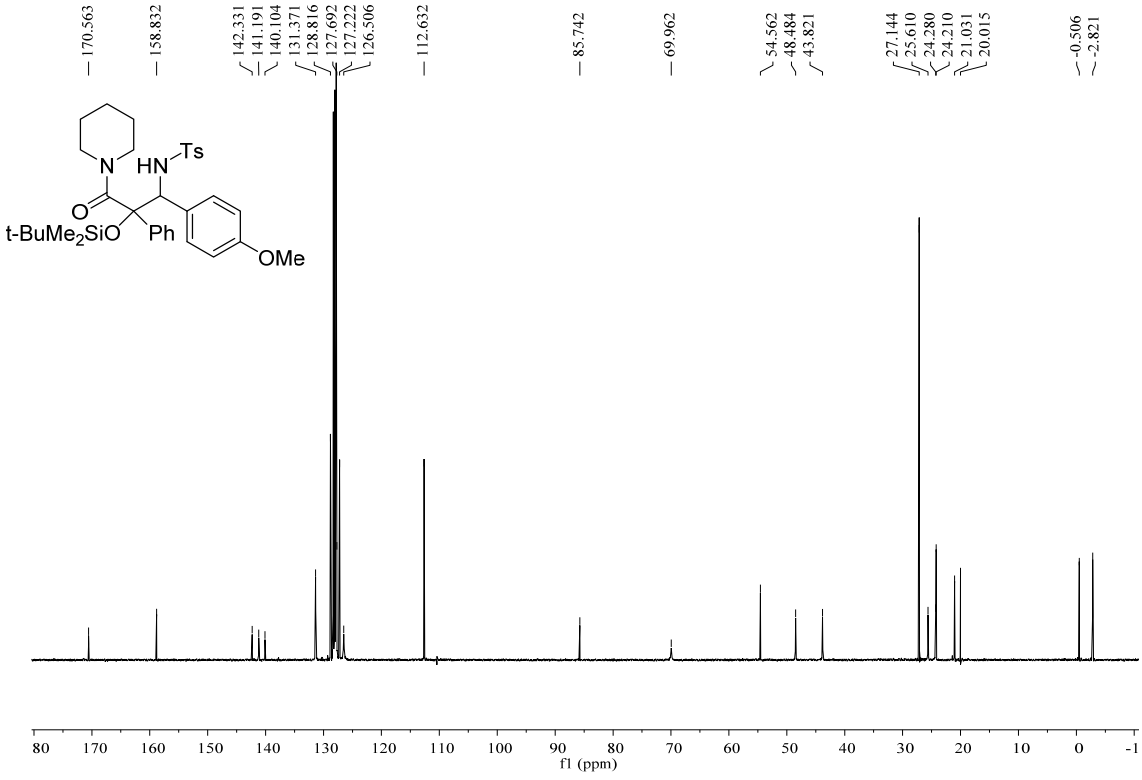
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **11**



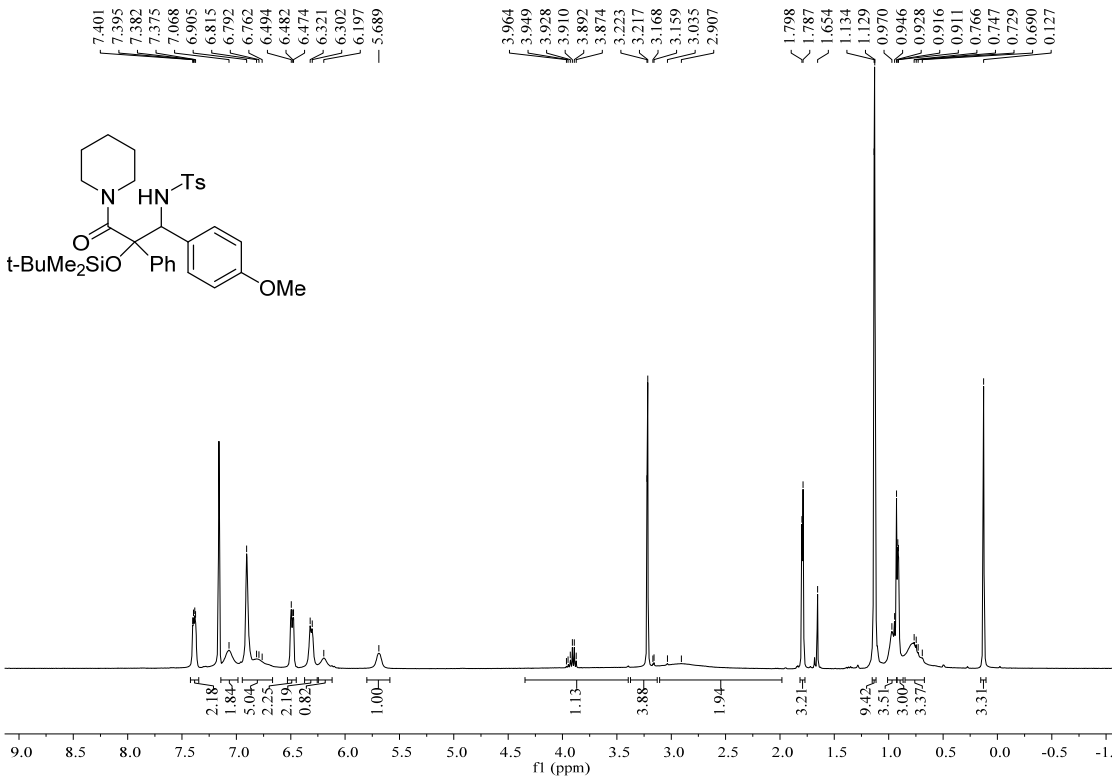
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **11**



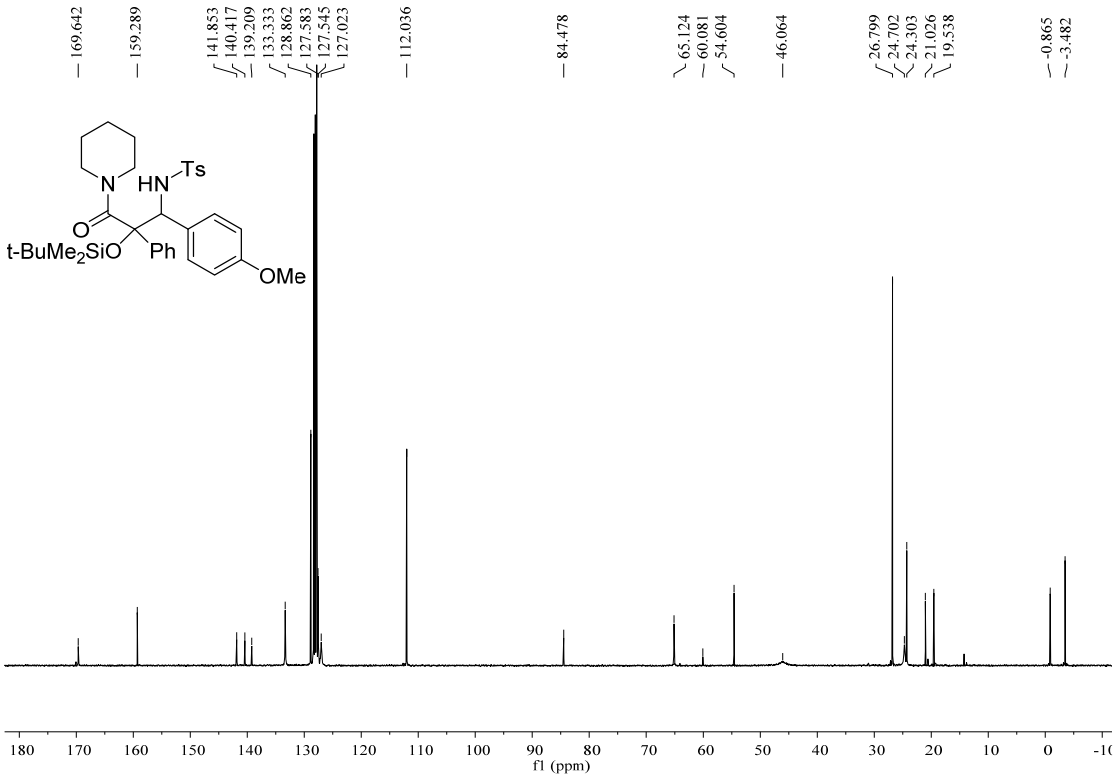
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **13a** (minor isomer)



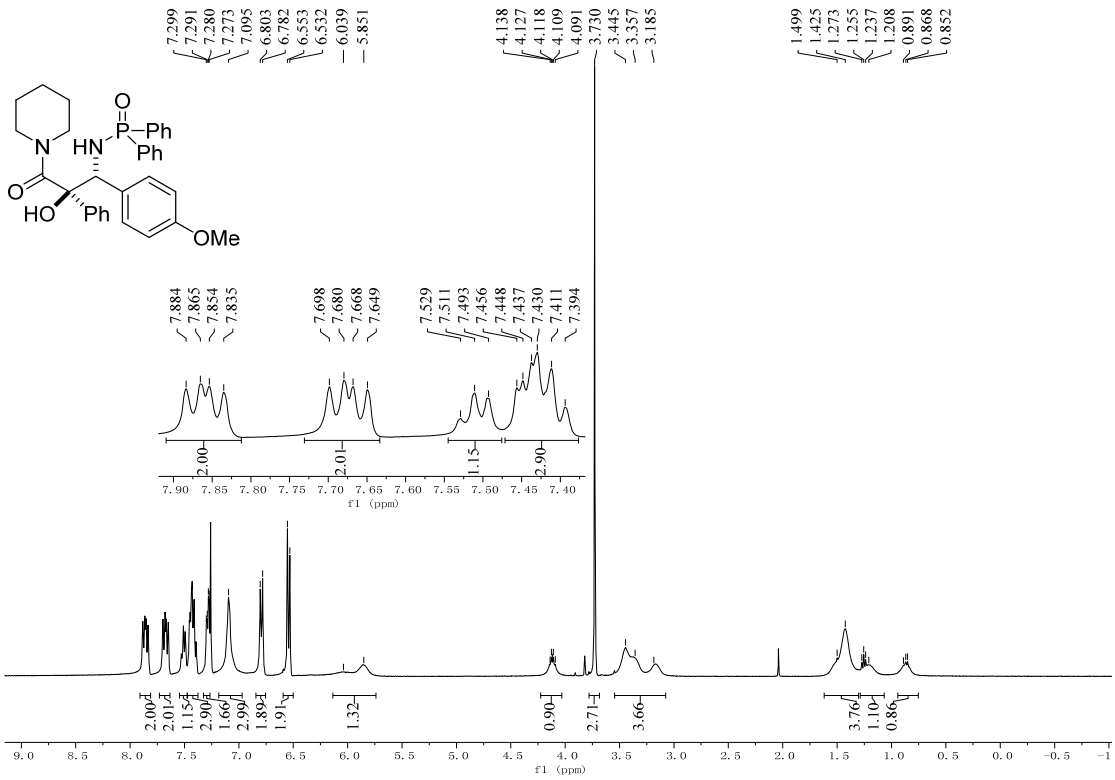
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **13a** (minor isomer)



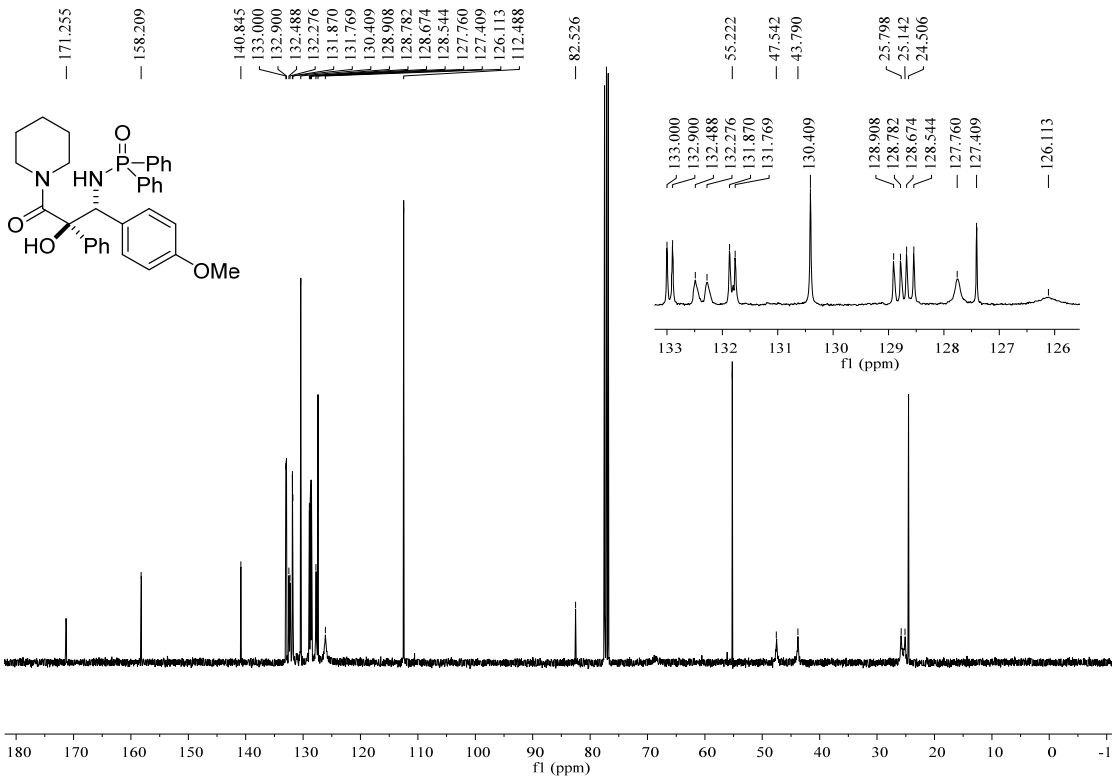
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **13b** (major isomer)



^{13}C NMR spectrum (C_6D_6, 100 MHz) of **13b** (major isomer)



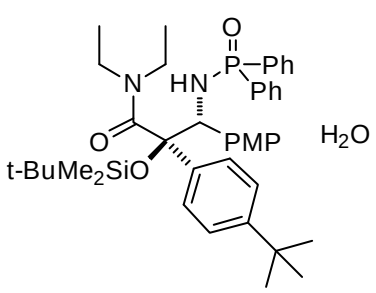
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **14**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **14**

X-Ray crystal structure of the compound 6o

X-Ray crystal structure (ORTEP) of the compound **6o**, with the thermal ellipsoids shown at a 50% probability level.



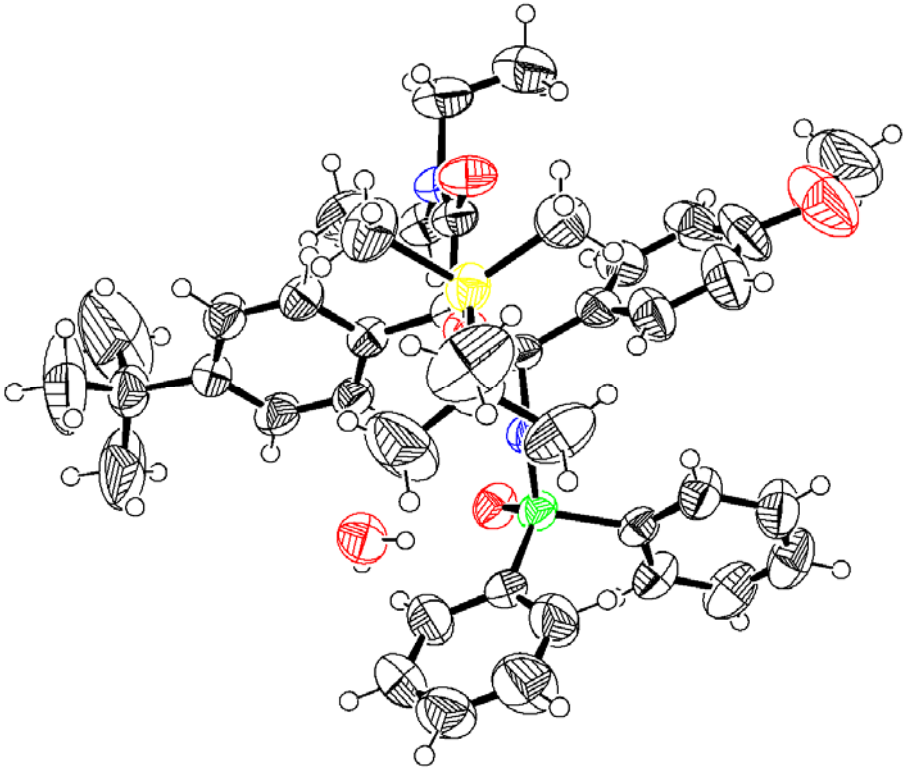


Table 1 Crystal data and structure refinement for 6o.

Identification code	**6o**
Empirical formula	$C_{42}H_{57}N_2O_4PSi$
Formula weight	721.96
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	11.473(4)
b/Å	13.299(5)
c/Å	13.766(5)
α/°	85.201(5)
β/°	86.909(5)
γ/°	86.437(5)
Volume/Å^3	2086.5(12)
Z	2
ρ_{calc}g/cm^3	1.149
μ/mm^{-1}	0.137
F(000)	778.0
Crystal size/mm^3	0.275 × 0.224 × 0.189
Radiation	MoKα (λ = 0.71073)
Theta range for data collection/°	4.104 to 54.434
Index ranges	$-9 \le h \le 14$, $-16 \le k \le 16$, $-17 \le l \le 17$
Reflections collected	12527
Independent reflections	8916 [R_{int}= 0.0449, R_{sigma}= 0.1281]
Data/restraints/parameters	8916/18/475
Goodness-of-fit on F^2	0.911
Final R indexes [I>=2σ (I)]	R_1= 0.0750, wR_2= 0.1911
Final R indexes [all data]	R_1= 0.1755, wR_2= 0.2528
Largest diff. peak/hole / e Å^{-3}	0.34/-0.36

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6o. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
P1	8084.4(9)	2891.9(8)	4569.8(7)	48.8(3)
Si1	5631.2(11)	2059.6(9)	1310.4(8)	53.7(4)
O1	8297(3)	3933(2)	4755(2)	60.7(8)
O2	2191(5)	1554(5)	5636(3)	162(2)
O3	4103(2)	3608(2)	1791(2)	65.7(9)
O4	6138(2)	2764(2)	2109.5(17)	49.4(7)

N1	7102(3)	2800(2)	3769(2)	49.9(9)
N2	4245(3)	5022(3)	2508(2)	59.1(9)
C1	7163(6)	1152(4)	7475(4)	87.1(17)
C2	6581(5)	971(4)	6672(4)	88.0(17)
C3	6852(4)	1503(4)	5788(3)	71.6(13)
C4	7680(4)	2208(3)	5702(3)	48.4(10)
C5	8249(4)	2380(3)	6519(3)	64.8(12)
C6	7984(6)	1855(4)	7405(4)	87.7(17)
C7	9305(3)	2216(3)	4039(3)	51.7(10)
C8	10174(4)	2749(4)	3549(4)	77.5(15)
C9	11105(5)	2234(5)	3083(4)	92.6(17)
C10	11185(5)	1207(5)	3104(4)	87.5(16)
C11	10343(6)	667(5)	3609(5)	111(2)
C12	9393(5)	1162(4)	4068(4)	85.3(16)
C13	6042(3)	3454(3)	3642(3)	48.1(10)
C14	4967(4)	2995(4)	4145(3)	56.3(11)
C15	4790(4)	1955(4)	4114(3)	75.5(15)
C16	3861(5)	1513(5)	4602(4)	99(2)
C17	3067(5)	2122(8)	5136(4)	113(3)
C18	3211(5)	3126(6)	5171(4)	93.9(19)
C19	4164(4)	3546(4)	4666(3)	73.5(14)
C20	1436(7)	2080(8)	6203(6)	191(5)
C21	5924(3)	3702(3)	2515(3)	44.0(9)
C22	6779(3)	4444(3)	2028(3)	46.8(10)
C23	6666(4)	4770(3)	1053(3)	54.7(11)
C24	7367(4)	5453(3)	575(3)	60.8(12)
C25	8246(4)	5864(3)	1039(3)	57.2(11)
C26	8383(4)	5517(3)	2010(3)	63.4(12)
C27	7667(4)	4816(3)	2492(3)	55.2(11)
C28	8981(5)	6698(4)	520(4)	74.5(14)
C29	9216(9)	6550(8)	-526(5)	204(5)
C30	8342(9)	7694(5)	633(9)	255(7)
C31	10101(8)	6746(8)	958(6)	224(6)
C32	4667(4)	4117(3)	2267(3)	50.8(10)
C33	4809(4)	5735(3)	3074(3)	64.9(12)
C34	5179(5)	6684(4)	2498(4)	80.0(15)
C35	3051(4)	5354(4)	2218(4)	78.1(15)
C36	2150(5)	4935(5)	2927(5)	103.1(19)
C37	5497(5)	2675(4)	62(3)	83.3(16)
C38	4288(4)	1403(4)	1683(4)	76.8(14)

C39	6865(5)	1063(4)	1250(4)	70.8(13)
C40	6960(6)	440(4)	2223(4)	100.0(19)
C41	8010(5)	1540(5)	985(5)	135(3)
C42	6628(7)	366(5)	462(4)	129(3)
O5	9630(6)	5617(6)	4251(5)	89(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 60. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	51.4(7)	50.8(7)	44.5(6)	0.2(5)	-9.2(5)	-4.5(5)
Si1	64.3(8)	56.0(8)	42.0(7)	-4.6(5)	-5.8(6)	-9.7(6)
O1	73(2)	48.3(18)	62.4(18)	-2.6(14)	-14.2(15)	-12.2(15)
O2	104(4)	307(8)	83(3)	-20(4)	13(3)	-77(5)
O3	57.6(18)	76(2)	67(2)	-20.0(17)	-23.0(16)	4.4(16)
O4	50.3(16)	57.5(18)	41.7(14)	-9.0(13)	-6.1(12)	-4.0(13)
N1	51(2)	49(2)	50.3(19)	2.4(16)	-13.0(16)	-8.1(16)
N2	53(2)	70(3)	55(2)	-13.7(19)	-14.9(17)	9.8(19)
C1	131(5)	75(4)	50(3)	3(3)	10(3)	9(4)
C2	103(4)	89(4)	70(4)	14(3)	0(3)	-25(3)
C3	88(4)	68(3)	58(3)	7(2)	-9(3)	-12(3)
C4	57(3)	40(2)	48(2)	-2.2(18)	-5(2)	7(2)
C5	87(3)	54(3)	53(3)	0(2)	-16(2)	1(2)
C6	129(5)	83(4)	52(3)	-8(3)	-23(3)	3(4)
C7	47(2)	57(3)	50(2)	2(2)	-10.0(19)	0(2)
C8	65(3)	70(3)	93(4)	3(3)	15(3)	-5(3)
C9	64(4)	113(5)	97(4)	0(4)	22(3)	-4(3)
C10	70(4)	88(4)	102(4)	-15(4)	7(3)	10(3)
C11	93(5)	71(4)	166(6)	-16(4)	20(5)	10(4)
C12	72(3)	70(4)	109(4)	6(3)	19(3)	4(3)
C13	47(2)	56(3)	41(2)	-6.2(19)	-8.3(18)	6(2)
C14	51(3)	81(3)	39(2)	-7(2)	-12(2)	-7(2)
C15	66(3)	110(4)	53(3)	-9(3)	2(2)	-31(3)
C16	98(5)	137(5)	66(3)	-7(3)	7(3)	-58(4)
C17	66(4)	231(9)	49(3)	4(4)	-4(3)	-75(5)
C18	60(4)	166(7)	58(3)	-23(4)	7(3)	-12(4)
C19	62(3)	105(4)	54(3)	-14(3)	-3(2)	-1(3)
C20	98(6)	321(14)	146(8)	12(8)	35(6)	-11(7)
C21	49(2)	43(2)	41(2)	-10.9(18)	-4.2(18)	0.4(18)
C22	53(2)	43(2)	45(2)	-5.3(18)	-8.1(19)	-3.4(19)

C23	66(3)	52(3)	47(2)	-6(2)	-10(2)	-4(2)
C24	69(3)	64(3)	49(2)	1(2)	-9(2)	-9(2)
C25	59(3)	57(3)	54(3)	4(2)	-1(2)	-4(2)
C26	64(3)	71(3)	57(3)	2(2)	-19(2)	-10(2)
C27	59(3)	56(3)	51(2)	5(2)	-14(2)	-6(2)
C28	84(4)	62(3)	75(3)	12(3)	2(3)	-18(3)
C29	264(11)	288(12)	73(4)	22(6)	15(6)	-185(10)
C30	231(11)	63(5)	444(18)	47(7)	138(12)	-8(6)
C31	173(8)	342(14)	161(7)	137(8)	-74(6)	-192(10)
C32	48(2)	57(3)	46(2)	-8(2)	-7(2)	9(2)
C33	74(3)	66(3)	55(3)	-16(2)	-11(2)	11(3)
C34	99(4)	64(3)	79(3)	-11(3)	-25(3)	7(3)
C35	67(3)	92(4)	76(3)	-19(3)	-20(3)	23(3)
C36	67(4)	121(5)	121(5)	-13(4)	-11(4)	11(3)
C37	119(4)	89(4)	45(3)	-12(3)	-20(3)	-16(3)
C38	80(3)	68(3)	85(3)	-9(3)	-16(3)	-18(3)
C39	84(4)	63(3)	67(3)	-22(3)	-2(3)	5(3)
C40	130(5)	61(3)	108(5)	-9(3)	-31(4)	30(3)
C41	85(5)	130(6)	184(7)	-27(5)	45(5)	9(4)
C42	188(7)	99(5)	102(5)	-40(4)	-29(5)	45(5)
O5	79(5)	102(6)	90(5)	0(4)	-24(4)	-37(4)

Table 4 Bond Lengths for 6o.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.465(3)	C11	C12	1.387(7)
P1	N1	1.636(3)	C13	C14	1.517(6)
P1	C4	1.792(4)	C13	C21	1.571(5)
P1	C7	1.774(4)	C14	C15	1.416(6)
Si1	O4	1.654(3)	C14	C19	1.354(6)
Si1	C37	1.850(5)	C15	C16	1.367(6)
Si1	C38	1.846(5)	C16	C17	1.401(9)
Si1	C39	1.881(5)	C17	C18	1.360(9)
O2	C17	1.410(7)	C18	C19	1.386(7)
O2	C20	1.338(9)	C21	C22	1.524(5)
O3	C32	1.217(4)	C21	C32	1.557(5)
O4	C21	1.411(4)	C22	C23	1.386(5)
N1	C13	1.460(5)	C22	C27	1.370(5)
N2	C32	1.330(5)	C23	C24	1.357(5)
N2	C33	1.476(5)	C24	C25	1.385(6)
N2	C35	1.479(6)	C25	C26	1.391(6)

C1	C2	1.368(7)	C25	C28	1.540(6)
C1	C6	1.363(7)	C26	C27	1.384(6)
C2	C3	1.385(6)	C28	C29	1.478(8)
C3	C4	1.369(6)	C28	C30	1.489(9)
C4	C5	1.372(5)	C28	C31	1.455(8)
C5	C6	1.382(7)	C33	C34	1.505(6)
C7	C8	1.374(6)	C35	C36	1.484(7)
C7	C12	1.396(6)	C39	C40	1.521(7)
C8	C9	1.389(7)	C39	C41	1.508(7)
C9	C10	1.362(7)	C39	C42	1.530(7)
C10	C11	1.365(7)			

Table 5 Bond Angles for 6o.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	N1	114.22(17)	C16	C15	C14	121.8(5)
O1	P1	C4	109.00(17)	C15	C16	C17	118.1(6)
O1	P1	C7	114.48(19)	C16	C17	O2	111.6(8)
N1	P1	C4	110.28(18)	C18	C17	O2	127.0(8)
N1	P1	C7	101.11(17)	C18	C17	C16	121.3(5)
C7	P1	C4	107.37(19)	C17	C18	C19	118.9(6)
O4	Si1	C37	115.44(19)	C14	C19	C18	122.6(6)
O4	Si1	C38	117.01(18)	O4	C21	C13	104.8(3)
O4	Si1	C39	99.70(18)	O4	C21	C22	108.8(3)
C37	Si1	C39	107.0(2)	O4	C21	C32	108.1(3)
C38	Si1	C37	109.3(2)	C22	C21	C13	115.2(3)
C38	Si1	C39	107.1(2)	C22	C21	C32	107.7(3)
C20	O2	C17	114.8(8)	C32	C21	C13	112.0(3)
C21	O4	Si1	141.8(2)	C23	C22	C21	118.8(3)
C13	N1	P1	126.1(3)	C27	C22	C21	124.2(3)
C32	N2	C33	127.8(4)	C27	C22	C23	117.0(4)
C32	N2	C35	117.4(4)	C24	C23	C22	122.4(4)
C33	N2	C35	114.8(4)	C23	C24	C25	121.5(4)
C6	C1	C2	120.2(5)	C24	C25	C26	116.2(4)
C1	C2	C3	118.9(5)	C24	C25	C28	121.5(4)
C4	C3	C2	121.7(5)	C26	C25	C28	122.2(4)
C3	C4	P1	123.2(3)	C27	C26	C25	122.0(4)
C3	C4	C5	118.4(4)	C22	C27	C26	120.9(4)
C5	C4	P1	118.4(3)	C29	C28	C25	111.9(5)
C4	C5	C6	120.5(5)	C29	C28	C30	110.0(7)

C1	C6	C5	120.3(5)	C30	C28	C25	108.5(5)
C8	C7	P1	118.8(4)	C31	C28	C25	112.2(5)
C8	C7	C12	118.8(4)	C31	C28	C29	107.8(7)
C12	C7	P1	122.4(3)	C31	C28	C30	106.3(7)
C7	C8	C9	119.6(5)	O3	C32	N2	120.7(4)
C10	C9	C8	121.6(5)	O3	C32	C21	117.5(4)
C9	C10	C11	119.3(5)	N2	C32	C21	121.7(4)
C10	C11	C12	120.3(6)	N2	C33	C34	115.0(4)
C11	C12	C7	120.4(5)	N2	C35	C36	111.5(4)
N1	C13	C14	112.7(3)	C40	C39	Si1	110.8(3)
N1	C13	C21	107.1(3)	C40	C39	C42	109.1(4)
C14	C13	C21	113.0(3)	C41	C39	Si1	110.6(4)
C15	C14	C13	120.7(4)	C41	C39	C40	109.0(5)
C19	C14	C13	122.0(4)	C41	C39	C42	108.6(5)
C19	C14	C15	117.3(4)	C42	C39	Si1	108.6(4)

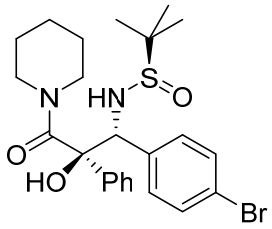
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6o.

Atom	*x*	*y*	*z*	U(eq)
H1	6902	2185	3807	60
H1A	6998	793	8071	105
H2	6012	498	6718	106
H3	6462	1378	5240	86
H5	8816	2854	6476	78
H6	8369	1982	7956	105
H8	10139	3451	3529	93
H9	11688	2600	2750	111
H10	11808	876	2778	105
H11	10405	-36	3646	134
H12	8811	790	4396	102
H13	6153	4088	3932	58
H15	5320	1561	3751	91
H16	3759	827	4581	119
H18	2678	3523	5528	113
H19	4255	4234	4686	88
H20A	1178	2699	5847	287
H20B	1814	2232	6774	287
H20C	775	1688	6393	287
H23	6088	4510	714	66

H24	7255	5650	-79	73
H26	8973	5762	2345	76
H27	7791	4595	3139	66
H29A	9636	5911	-591	306
H29B	9676	7083	-823	306
H29C	8489	6562	-842	306
H30A	7706	7777	202	383
H30B	8866	8226	475	383
H30C	8041	7722	1295	383
H31A	9972	6923	1618	336
H31B	10548	7247	591	336
H31C	10521	6099	953	336
H33A	5493	5389	3360	78
H33B	4270	5922	3605	78
H34A	5770	6514	2009	120
H34B	5486	7123	2929	120
H34C	4515	7022	2189	120
H35A	2933	5135	1578	94
H35B	2965	6086	2176	94
H36A	1390	5082	2674	155
H36B	2185	5236	3534	155
H36C	2294	4216	3032	155
H37A	4884	3200	67	125
H37B	5315	2183	-370	125
H37C	6222	2961	-158	125
H38A	4375	1047	2313	115
H38B	4155	932	1215	115
H38C	3635	1889	1714	115
H40A	7222	852	2699	150
H40B	7509	-126	2149	150
H40C	6208	201	2435	150
H41A	7999	1848	329	202
H41B	8639	1030	1031	202
H41C	8120	2045	1425	202
H42A	5838	163	550	194
H42B	7158	-222	514	194
H42C	6738	718	-170	194
H5A	10029	5887	4651	133
H5B	9373	5071	4520	133

X-Ray crystal structure of the compound 9

X-Ray crystal structure (ORTEP) of this compound, with the thermal ellipsoids shown at a 50% probability level.



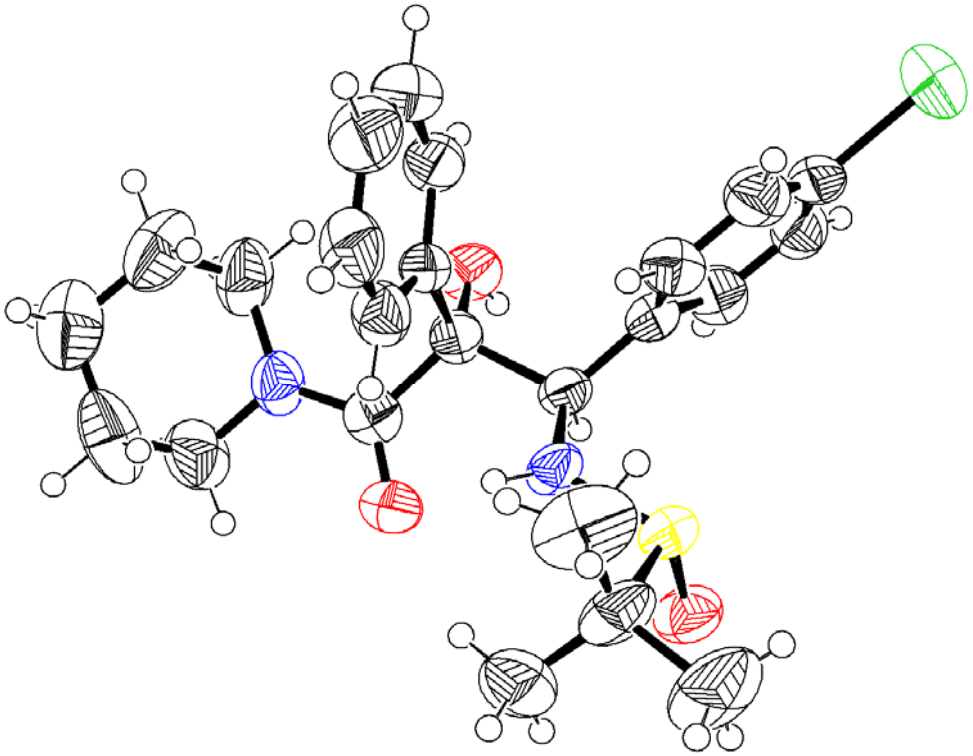


Table 1 Crystal data and structure refinement for 9.

Identification code	**9**
Empirical formula	$C_{24}H_{31}BrN_2O_3S$
Formula weight	507.48
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.891(13)
b/Å	16.14(2)
c/Å	16.21(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2588(6)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	1.695
F(000)	1056.0
Crystal size/mm^3	0.34 × 0.158 × 0.136
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.824 to 54.358
Index ranges	$-8 \le h \le 12$, $-18 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	15227
Independent reflections	5656 [R_{int} = 0.0964, R_{sigma} = 0.1660]
Data/restraints/parameters	5656/3/286
Goodness-of-fit on F^2	0.906
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.1683
Final R indexes [all data]	R_1 = 0.1860, wR_2 = 0.2260
Largest diff. peak/hole / e Å^{-3}	0.67/-0.35
Flack parameter	0.01(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 9. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Br1	-1417.6(17)	8977.8(10)	-3448.1(10)	112.8(8)
S1	-6544(3)	7378.2(16)	-1351.2(16)	56.5(7)
O1	-6914(7)	7786(5)	-565(5)	71(2)

O2	-5187(8)	5547(5)	157(5)	78(2)
O3	-2096(6)	5999(5)	-606(4)	61.2(19)
N1	-5633(7)	6533(5)	-1156(5)	55(2)
N2	-3631(10)	4556(5)	39(5)	65(2)
C1	-9097(13)	7531(10)	-1808(11)	120(6)
C2	-8604(13)	6275(8)	-985(8)	87(4)
C3	-8096(10)	6843(7)	-1671(8)	73(3)
C4	-7772(14)	6358(10)	-2464(8)	106(5)
C5	-3706(11)	7133(7)	-2406(7)	61(3)
C6	-3100(11)	7641(8)	-2960(7)	67(3)
C7	-2281(11)	8268(8)	-2665(9)	69(3)
C8	-2083(11)	8417(7)	-1863(8)	63(3)
C9	-2688(10)	7890(7)	-1305(7)	64(3)
C10	-3519(9)	7243(6)	-1564(6)	51(2)
C11	-4184(9)	6697(6)	-941(6)	48(2)
C12	-3461(9)	5821(6)	-849(6)	50(2)
C13	-3407(10)	5357(5)	-1656(6)	48(2)
C14	-2284(11)	5308(7)	-2102(8)	66(3)
C15	-2239(13)	4905(8)	-2853(8)	77(4)
C16	-3361(16)	4533(8)	-3131(8)	86(4)
C17	-4514(13)	4551(7)	-2680(8)	74(3)
C18	-4552(11)	4950(6)	-1943(7)	62(3)
C19	-4153(11)	5305(7)	-164(6)	55(3)
C20	-4383(13)	4009(8)	563(8)	85(4)
C21	-4808(17)	3236(9)	63(9)	102(5)
C22	-3572(19)	2797(9)	-309(10)	109(5)
C23	-2752(16)	3398(9)	-794(9)	98(4)
C24	-2385(13)	4177(7)	-301(8)	84(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 9. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	117.0(13)	90.7(11)	130.8(14)	42.4(9)	41.1(10)	-3.4(9)
S1	46.4(14)	56.8(15)	66.2(17)	-0.8(13)	3.2(13)	11.0(13)
O1	70(5)	70(5)	72(5)	-18(4)	12(4)	8(4)
O2	66(5)	79(6)	89(6)	19(4)	27(4)	10(4)
O3	39(4)	69(5)	76(5)	-11(4)	-10(3)	-5(3)
N1	30(4)	45(5)	89(6)	-7(4)	-2(4)	2(4)
N2	63(6)	56(5)	74(6)	16(5)	-11(5)	2(5)

C1	62(8)	127(13)	169(15)	-3(12)	-36(9)	36(9)
C2	61(7)	91(9)	108(10)	-2(8)	5(7)	-17(8)
C3	40(6)	77(8)	103(9)	-18(8)	-18(6)	16(5)
C4	85(9)	133(13)	99(11)	-48(10)	-23(8)	6(9)
C5	55(7)	69(7)	60(7)	0(6)	2(6)	0(6)
C6	55(7)	79(8)	65(7)	9(7)	0(5)	8(6)
C7	43(6)	73(8)	92(10)	25(7)	22(6)	18(6)
C8	56(6)	56(7)	77(9)	1(6)	-1(6)	-1(5)
C9	47(6)	72(7)	73(8)	6(6)	-9(6)	-1(6)
C10	42(5)	51(6)	60(7)	1(5)	4(5)	9(5)
C11	42(5)	47(6)	55(6)	-4(5)	2(4)	3(4)
C12	45(5)	51(6)	55(6)	3(5)	-3(5)	0(5)
C13	48(6)	42(5)	53(6)	-3(4)	10(5)	-2(5)
C14	46(6)	59(7)	93(9)	-3(7)	5(6)	-5(5)
C15	71(8)	80(9)	80(9)	-2(8)	22(7)	-1(7)
C16	119(12)	72(8)	67(8)	-22(6)	9(9)	-4(9)
C17	90(9)	55(7)	78(9)	-14(7)	-8(7)	-20(6)
C18	58(7)	54(7)	76(8)	1(6)	-4(6)	-8(5)
C19	46(6)	62(7)	56(7)	0(6)	-11(5)	-4(5)
C20	91(9)	88(9)	75(8)	28(8)	0(7)	2(8)
C21	115(13)	87(10)	104(11)	24(9)	-33(9)	-47(10)
C22	143(14)	76(10)	107(11)	8(9)	-12(11)	3(11)
C23	122(12)	81(10)	91(10)	-3(9)	-16(9)	36(9)
C24	85(9)	63(9)	103(10)	19(8)	-21(7)	10(7)

Table 4 Bond Lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C7	1.911(11)	C8	C9	1.378(15)
S1	O1	1.480(7)	C9	C10	1.393(14)
S1	N1	1.665(8)	C10	C11	1.494(13)
S1	C3	1.836(11)	C11	C12	1.591(13)
O2	C19	1.212(12)	C12	C13	1.509(13)
O3	C12	1.436(11)	C12	C19	1.548(14)
N1	C11	1.498(12)	C13	C14	1.327(13)
N2	C19	1.355(13)	C13	C18	1.389(12)
N2	C20	1.434(14)	C14	C15	1.381(14)
N2	C24	1.482(15)	C15	C16	1.340(17)
C1	C3	1.504(16)	C16	C17	1.355(14)
C2	C3	1.526(18)	C17	C18	1.359(15)

C3	C4	1.538(17)	C20	C21	1.547(18)
C5	C6	1.355(15)	C21	C22	1.54(2)
C5	C10	1.388(14)	C22	C23	1.49(2)
C6	C7	1.382(16)	C23	C24	1.533(17)
C7	C8	1.337(16)			

Table 5 Bond Angles for 9.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	109.6(4)	C10	C11	N1	111.6(8)
O1	S1	C3	104.2(5)	C10	C11	C12	112.9(8)
N1	S1	C3	97.0(4)	O3	C12	C11	105.7(7)
C11	N1	S1	114.7(6)	O3	C12	C13	107.6(7)
C19	N2	C20	119.7(10)	O3	C12	C19	109.1(7)
C19	N2	C24	126.5(9)	C13	C12	C11	112.0(7)
C20	N2	C24	113.4(9)	C13	C12	C19	111.8(8)
C1	C3	S1	104.2(9)	C19	C12	C11	110.3(8)
C1	C3	C2	109.5(11)	C14	C13	C12	122.1(9)
C1	C3	C4	112.9(12)	C14	C13	C18	118.2(10)
C2	C3	S1	110.6(8)	C18	C13	C12	119.7(9)
C2	C3	C4	111.8(11)	C13	C14	C15	122.3(11)
C4	C3	S1	107.5(8)	C16	C15	C14	118.8(11)
C6	C5	C10	121.0(11)	C15	C16	C17	120.4(11)
C5	C6	C7	118.2(11)	C16	C17	C18	120.5(12)
C6	C7	Br1	118.1(11)	C17	C18	C13	119.7(11)
C8	C7	Br1	118.2(11)	O2	C19	N2	120.3(10)
C8	C7	C6	123.7(11)	O2	C19	C12	120.5(9)
C7	C8	C9	117.6(11)	N2	C19	C12	119.1(9)
C8	C9	C10	121.4(11)	N2	C20	C21	109.1(10)
C5	C10	C9	118.1(10)	C22	C21	C20	111.2(11)
C5	C10	C11	122.1(9)	C23	C22	C21	109.9(11)
C9	C10	C11	119.9(9)	C22	C23	C24	112.9(12)
N1	C11	C12	107.2(7)	N2	C24	C23	109.6(10)

Table 6 Torsion Angles for 9.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C7	C8	C9	-178.7(7)	C10	C5	C6	C7	0.5(15)
S1	N1	C11	C10	-51.4(9)	C10	C11	C12	O3	59.3(10)

S1	N1	C11	C12	-175.5(6)	C10	C11	C12	C13	-57.7(10)
O1	S1	N1	C11	-77.8(7)	C10	C11	C12	C19	177.1(8)
O1	S1	C3	C1	63.2(11)	C11	C12	C13	C14	103.1(11)
O1	S1	C3	C2	-54.4(9)	C11	C12	C13	C18	-78.3(11)
O1	S1	C3	C4	-176.8(9)	C11	C12	C19	O2	7.5(13)
O3	C12	C13	C14	-12.7(12)	C11	C12	C19	N2	-176.3(8)
O3	C12	C13	C18	165.9(9)	C12	C13	C14	C15	-178.1(10)
O3	C12	C19	O2	123.3(10)	C12	C13	C18	C17	178.3(9)
O3	C12	C19	N2	-60.6(11)	C13	C12	C19	O2	-117.8(10)
N1	S1	C3	C1	175.4(10)	C13	C12	C19	N2	58.3(11)
N1	S1	C3	C2	57.8(9)	C13	C14	C15	C16	-1.6(19)
N1	S1	C3	C4	-64.5(9)	C14	C13	C18	C17	-3.1(16)
N1	C11	C12	O3	-177.4(7)	C14	C15	C16	C17	0(2)
N1	C11	C12	C13	65.6(10)	C15	C16	C17	C18	0(2)
N1	C11	C12	C19	-59.6(9)	C16	C17	C18	C13	1.3(18)
N2	C20	C21	C22	57.0(14)	C18	C13	C14	C15	3.3(17)
C3	S1	N1	C11	174.5(7)	C19	N2	C20	C21	113.4(12)
C5	C6	C7	Br1	179.6(8)	C19	N2	C24	C23	-114.6(12)
C5	C6	C7	C8	-2.0(16)	C19	C12	C13	C14	-132.5(10)
C5	C10	C11	N1	-43.2(12)	C19	C12	C13	C18	46.1(12)
C5	C10	C11	C12	77.6(11)	C20	N2	C19	O2	7.1(15)
C6	C5	C10	C9	0.0(15)	C20	N2	C19	C12	-169.1(9)
C6	C5	C10	C11	179.5(9)	C20	N2	C24	C23	58.3(12)
C6	C7	C8	C9	2.9(16)	C20	C21	C22	C23	-53.6(16)
C7	C8	C9	C10	-2.4(15)	C21	C22	C23	C24	52.6(16)
C8	C9	C10	C5	1.0(15)	C22	C23	C24	N2	-53.9(14)
C8	C9	C10	C11	-178.5(9)	C24	N2	C19	O2	179.7(10)
C9	C10	C11	N1	136.3(9)	C24	N2	C19	C12	3.5(14)
C9	C10	C11	C12	-102.9(10)	C24	N2	C20	C21	-60.0(13)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 9.

Atom	x	y	z	U(eq)
H3	-2099	6336	-228	92
H1	-5967	6042	-1177	66
H1A	-9253	7817	-1297	179
H1B	-9933	7303	-2005	179
H1C	-8744	7912	-2208	179
H2A	-7926	5869	-861	130

H2B	-9416	6002	-1162	130
H2C	-8790	6598	-501	130
H4A	-7119	6660	-2783	158
H4B	-8583	6288	-2781	158
H4C	-7411	5825	-2321	158
H5	-4256	6705	-2593	74
H6	-3232	7569	-3524	80
H8	-1555	8860	-1687	76
H9	-2540	7967	-744	77
H11	-4156	6978	-405	58
H14	-1500	5555	-1902	79
H15	-1445	4891	-3160	92
H16	-3348	4261	-3636	103
H17	-5286	4288	-2877	89
H18	-5341	4951	-1631	75
H20A	-5179	4290	772	102
H20B	-3831	3844	1030	102
H21A	-5289	2854	420	122
H21B	-5417	3401	-377	122
H22A	-3024	2562	129	130
H22B	-3867	2349	-665	130
H23A	-3255	3559	-1282	118
H23B	-1927	3129	-975	118
H24A	-1776	4032	145	100
H24B	-1929	4571	-657	100