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Supporting Information

Air-induced Double Addition of P(O)-H to Bond to Alkynes: A Clean and Practical Method for the Preparation of 1,2-Bisphosphorylethanes

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General Comments

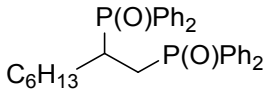
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All solvents were dried by standard methods. Diphenylphosphine oxide from *Katayama Chemical Industries Company* was purified by sublimation and stored in the glove box. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL (Tokyo, Japan) JNM-ECX400 FT NMR (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 162 MHz for ^{31}P) using $CDCl_3$. The coupling constants *J* are given in Hz. Melting points were determined on Opti Melt MPA100 apparatus (TOKYO INSTRUMENT, INC.).

Experimental procedures:

A typical procedure at 0.1 mmol scale: In a 1 mL closed vial were placed diphenylphosphine oxide (0.2 mmol), 1-octyne (0.1 mmol), dioxane (25μL), and air (1 mL) under nitrogen. The mixture was stirred at 100 °C for 22 h. The NMR yield of the product **1a** was obtained in 80% based on ^{31}P NMR spectroscopy. The product was isolated using a preparative GPC (Japan Analytical Industry Co., Ltd., LC-908) using chloroform as an eluent.

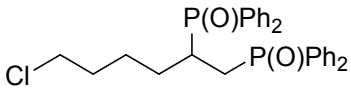
A typical procedure under solvent-free conditions at 1 mmol scale: In a 10 mL Schlenk flask were placed diphenylphosphine oxide (1.0 mmol), 1-octyne (1.5 mmol), and air (1 mL) under nitrogen. The mixture was stirred at 150 °C for 43 h. The mixture was washed with hexane (8 mL, 60 °C) to remove the remained starting materials to give NMR spectroscopically pure **1a**.

1a [1]



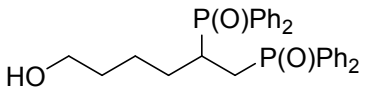
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78–7.67 (m, 6H), 7.48–7.30 (m, 14H), 3.03–2.93 (m, 1H), 2.66–2.45 (m, 3H), 1.77–1.62 (m, 1H), 1.48–1.36 (m, 1H), 1.27–1.16 (m, 1H), 1.04–0.94 (m, 1H), 0.92–0.78 (m, 3H), 0.76–0.68 (m, 4H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 37.9 (d, J = 48.6 Hz), 30.9 (d, J = 48.6 Hz).

1b



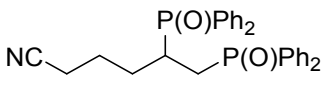
White solid; m.p. 146-148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71–7.62 (m, 6H), 7.45–7.28 (m, 14H), 3.09 (t, J = 6.6 Hz, 2H), 2.95–2.85 (m, 1H), 2.61–2.40 (m, 2H), 1.79–1.64 (m, 1H), 1.50–1.29 (m, 2H), 1.27–1.13 (m, 2H), 1.09–0.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.2 (d, $J_{C–P}$ = 97.7 Hz), 132.8 (d, $J_{C–P}$ = 99.6 Hz), 132.2, 132.0, 131.9, 131.8, 131.0 (d, $J_{C–P}$ = 8.6 Hz), 130.8 (d, $J_{C–P}$ = 8.6 Hz), 130.6 (d, $J_{C–P}$ = 9.6 Hz), 130.6 (d, $J_{C–P}$ = 9.6 Hz), 128.8 (d, $J_{C–P}$ = 10.5 Hz), 128.7 (d, $J_{C–P}$ = 11.5 Hz), 128.7 (d, $J_{C–P}$ = 11.5 Hz), 128.7 (d, $J_{C–P}$ = 11.5 Hz), 128.6 (d, $J_{C–P}$ = 11.5 Hz), 44.3, 32.5, 31.3 (dd, $J_{C–P}$ = 69.0 Hz, J = 3.8 Hz), 27.5, 27.3 , $J_{C–P}$ = 69.0 Hz), 24.4 (d, J = 3.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 37.5 (d, J = 44.9 Hz), 30.9 (d, J = 44.9 Hz).

1c



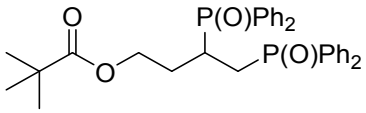
Colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68–7.56 (m, 6H), 7.45–7.25 (m, 14H), 3.37 (br, 2H), 2.83–2.56 (m, 3H), 2.44–2.35 (m, 1H), 1.89–1.72 (m, 1H), 1.63–1.40 (m, 1H), 1.15 (br, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.1 (d, $J_{C–P}$ = 100.6 Hz), 132.1, 131.8, 131.6 (d, $J_{C–P}$ = 99.6 Hz), 130.9 (d, $J_{C–P}$ = 8.6 Hz), 130.9 (d, $J_{C–P}$ = 8.6 Hz), 130.9 (d, $J_{C–P}$ = 8.6 Hz), 130.8 (d, $J_{C–P}$ = 8.6 Hz), 128.8 (d, $J_{C–P}$ = 10.5 Hz), 128.8 (d, $J_{C–P}$ = 10.5 Hz), 128.6 (d, $J_{C–P}$ = 10.5 Hz), 128.8 (d, $J_{C–P}$ = 11.5 Hz), 60.6, 31.8 (dd, $J_{C–P}$ = 68.0 Hz, J = 3.8 Hz), 31.7, 27.3 (d, $J_{C–P}$ = 68.0 Hz), 26.8, 22.9 (d, J = 3.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 38.0 (d, J = 52.3 Hz), 32.6 (d, J = 52.3 Hz).

1d [1(c)]



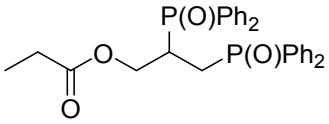
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76–7.62 (m, 6H), 7.53–7.33 (m, 14H), 2.88 (brs, 1H), 2.64–2.43 (m, 2H), 2.02–1.85 (m, 3H), 1.79–1.57 (m, 2H), 1.41–1.30 (m, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 37.2 (d, J = 44.9 Hz), 31.1 (d, J = 44.9 Hz).

1e [1(c)]



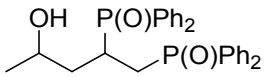
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71–7.60 (m, 6H), 7.44–7.28 (m, 14H), 3.84–3.74 (m, 2H), 3.06–2.91 (m, 1H), 2.61–2.43 (m, 2H), 2.13–2.00 (m, 1H), 1.97–1.85 (m, 1H), 1.00 (s, 9H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 37.3 (d, J = 44.9 Hz), 31.0 (d, J = 44.9 Hz).

1f



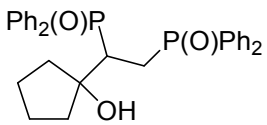
White solid; m.p. 155-156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70–7.61 (m, 6H), 7.46–7.26 (m, 14H), 4.25 (dd, J = 16.5, 5.5 Hz, 2H), 3.37–3.25 (m, 1H), 2.66–2.47 (m, 2H), 1.75 (q, J = 7.5 Hz, 2H), 0.82 (t, J = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 132.9 (d, $J_{C–P}$ = 99.6 Hz), 132.1 (d, $J_{C–P}$ = 2.9 Hz), 132.0 (d, $J_{C–P}$ = 2.9 Hz), 131.9 (d, $J_{C–P}$ = 2.9 Hz), 131.9 (d, $J_{C–P}$ = 2.9 Hz), 131.6 (d, $J_{C–P}$ = 97.7 Hz), 131.0 (d, $J_{C–P}$ = 8.6 Hz), 131.0 (d, $J_{C–P}$ = 9.6 Hz), 131.0 (d, $J_{C–P}$ = 9.6 Hz), 130.6 (d, $J_{C–P}$ = 9.6 Hz), 128.9 (d, $J_{C–P}$ = 11.5 Hz), 128.7 (d, $J_{C–P}$ = 11.5 Hz), 128.7 (d, $J_{C–P}$ = 11.5 Hz), 128.6 (d, $J_{C–P}$ = 10.5 Hz), 64.6, 32.1 (dd, $J_{C–P}$ = 68.0 Hz, J = 3.8 Hz), 26.8, 25.3 (d, $J_{C–P}$ = 68.0 Hz), 8.7; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 34.7 (d, J = 41.1 Hz), 31.1 (d, J = 41.1 Hz).

1g



White solid; m.p. 117-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75–7.15 (m, 20H), 3.90–3.76 (m, 0.5H), 3.24–2.93 (m, 1.5H), 2.88–2.75 (m, 0.5H), 2.70–2.59 (m, 0.5H), 2.50–2.28 (m, 1H), 2.16–2.02 (m, 0.5H), 1.86–1.73 (m, 0.5H), 1.69–1.55 (m, 1H), 0.98 (d, J = 5.9 Hz, 1.5H), 0.79 (d, J = 5.9 Hz, 1.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.0 (d, $J_{C–P}$ = 101.6 Hz), 132.1 (dd, $J_{C–P}$ = 2.9, 2.9 Hz), 132.0 (dd, $J_{C–P}$ = 2.9, 2.9 Hz), 131.8 (dd, $J_{C–P}$ = 2.9, 2.9 Hz), 131.6 (dd, $J_{C–P}$ = 2.9, 2.9 Hz), 131.6 (d, $J_{C–P}$ = 99.6 Hz), 131.1-130.8 (m), 130.7 (dd, $J_{C–P}$ = 8.6, 9.6 Hz), 130.3 (dd, $J_{C–P}$ = 9.6, 9.6 Hz), 128.9-128.5 (m), 65.4 (d, $J_{C–P}$ = 2.9 Hz), 63.2 (d, $J_{C–P}$ = 12.5 Hz), 38.4 (d, $J_{C–P}$ = 193.5 Hz), 29.6-26.9 (m), 23.7 (d, $J_{C–P}$ = 107.3 Hz), ^{31}P NMR ($CDCl_3$, 162 MHz) δ 39.4 (dd, J = 48.6, 41.1 Hz), 33.8 (dd, J = 48.6, 41.1 Hz).

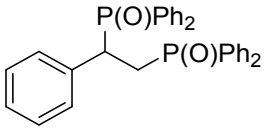
1h



White solid; m.p. 182-183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95–7.90 (m, 2H), 7.71–7.66 (m, 2H), 7.63–7.28 (m, 2H), 7.45–7.30 (m, 7H), 7.21–7.11 (m, 7H), 4.87 (br, s, 1H), 3.42–3.33 (m, 1H), 2.98–

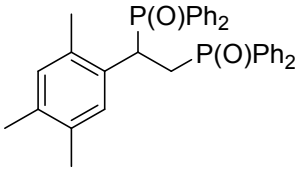
2.89 (m, 1H), 2.62–2.48 (m, 1H), 1.71–1.59 (m, 1H), 1.54–1.44 (m, 1H), 1.41–1.33 (m, 1H), 1.28–1.12 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.1 (d, $J_{C–P}$ = 94.9 Hz), 133.5 (d, $J_{C–P}$ = 99.6 Hz), 133.3 (d, $J_{C–P}$ = 99.6 Hz), 131.9 (d, $J_{C–P}$ = 98.7 Hz), 131.9 (br), 131.4 (br), 131.2 (d, $J_{C–P}$ = 8.6 Hz), 130.6 (d, $J_{C–P}$ = 9.6 Hz), 130.5 (d, $J_{C–P}$ = 9.6 Hz), 130.2 (d, $J_{C–P}$ = 9.6 Hz), 128.7 (d, $J_{C–P}$ = 12.5 Hz), 128.6 (d, $J_{C–P}$ = 11.5 Hz), 128.5 (d, $J_{C–P}$ = 11.5 Hz), 128.4 (d, $J_{C–P}$ = 12.5 Hz), 83.4 (dd, $J_{C–P}$ = 2.9, 2.9 Hz), 40.3 (d, $J_{C–P}$ = 9.6 Hz), 40.1, 39.7 (dd, $J_{C–P}$ = 66.1 Hz, J = 3.8 Hz), 26.3 ($J_{C–P}$ = 68.0 Hz), 23.6, 22.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 40.6 (d, J = 22.4 Hz), 30.7 (d, J = 22.4 Hz).

1i [1(a,c), 2]



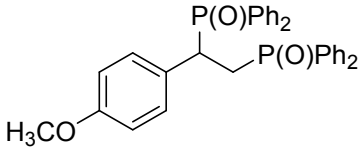
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14–7.95 (m, 2H), 7.66–7.48 (m, 5H), 7.46–6.95 (m, 15H), 6.93–6.73 (m, 3H), 4.42–4.12 (m, 1H), 3.36–3.00 (m, 1H), 3.00–2.73 (m, 1H),; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 36.0 (d, J = 48.6 Hz), 30.8 (d, J = 48.6 Hz).

1j [1(c)]



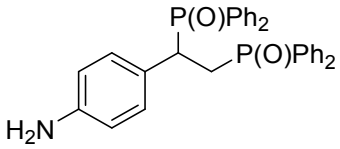
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04–7.99 (m, 2H), 7.58–7.53 (m, 5H), 7.44–7.37 (m, 1H), 7.35–7.31 (m, 2H), 7.28–7.24 (m, 1H), 7.21–7.07 (m, 8H), 6.99 (ddd, J = 7.8, 7.8, 2.7 Hz, 2H), 6.32 (s, 1H), 4.42–4.35 (m, 1H), 3.21–3.12 (m, 1H), 2.80–2.70 (m, 1H), 1.95 (s, 3H), 1.94 (s, 3H), 1.77 (s, 3H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.7 (d, J = 48.6 Hz), 30.3 (d, J = 48.6 Hz).

1k[1(c), 3]



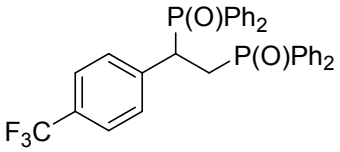
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98–7.91 (m, 2H), 7.51–7.44 (m, 5H), 7.39–7.34 (m, 1H), 7.30–7.24 (m, 4H), 7.22–7.28 (m, 3H), 7.16–7.08 (m, 3H), 7.02 (ddd, J = 7.8, 7.8, 2.7 Hz, 2H), 6.93 (dd, J = 8.7, 1.8 Hz, 2H), 6.28 (d, J = 8.7 Hz, 2H), 4.17 (dddd, J = 12.4, 12.4, 12.4, 1.4 Hz, 1H), 3.55 (s, 3H), 3.03 (dddd, J = 11.9, 11.4, 4.6, 4.6 Hz, 1H), 2.72 (dddd, J = 15.1, 15.4, 15.1, 1.4 Hz, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.8 (d, J = 48.6 Hz), 30.6 (d, J = 48.6 Hz).

1l [1(c)]



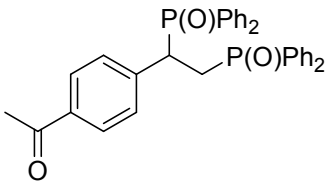
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96–7.91 (m, 1H), 7.49–7.44 (m, 5H), 7.36 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.31–7.26 (m, 4H), 7.24–7.16 (m, 4H), 7.10 (ddd, *J* = 7.8, 7.8, 3.2 Hz, 2H), 7.05 (ddd, *J* = 7.8, 7.8, 3.2 Hz, 2H), 6.78 (dd, *J* = 8.2, 1.8 Hz, 2H), 6.07 (d, *J* = 8.2 Hz, 2H), 4.10 (dddd, *J* = 12.8, 11.9, 6.9, 1.8 Hz, 1H), 3.01 (dddd, *J* = 11.9, 11.4, 4.6, 4.6 Hz, 1H), 2.71 (dddd, *J* = 15.1, 15.1, 11.4, 1.8 Hz, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.8 (d, *J* = 48.6 Hz), 30.9 (d, *J* = 48.6 Hz).

1m [1(c)]



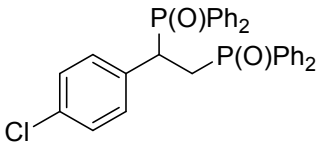
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01–7.94 (m, 2H), 7.52–7.45 (m, 5H), 7.38 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1H), 7.32–7.25 (m, 4H), 7.24–7.17 (m, 3H), 7.16–7.08 (m, 5H), 7.00–6.95 (m, 4H), 4.30 (dddd, *J* = 12.1, 12.1, 6.9, 1.8 Hz, 1H), 3.06 (dddd, *J* = 11.9, 11.9, 4.1, 4.1 Hz, 1H), 2.76 (dddd, *J* = 15.3, 15.3, 11.4, 1.8 Hz, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.3 (d, *J* = 44.9 Hz), 30.2 (d, *J* = 44.9 Hz).

1n [1(c)]



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99–7.93 (m, 2H), 7.52–7.43 (m, 5H), 7.39 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1H), 7.34–7.26 (m, 6H), 7.24–7.18 (m, 3H), 7.14–7.08 (m, 5H), 6.97 (ddd, *J* = 7.8, 7.8, 3.2 Hz, 1H), 4.28 (dddd, *J* = 11.9, 11.9, 6.9, 1.4 Hz, 1H), 3.08 (dddd, *J* = 11.4, 11.4, 4.1, 4.1 Hz, 1H), 2.77 (dddd, *J* = 15.1, 15.1, 11.4, 1.8 Hz, 1H), 2.36 (s, 3H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.2 (d, *J* = 44.9 Hz), 30.2 (d, *J* = 44.9 Hz).

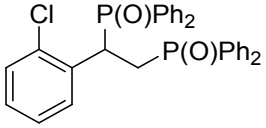
1o [1(c), 3]



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98–7.93 (m, 2H), 7.53–7.44 (m, 5H), 7.38 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1H), 7.32–7.26 (m, 4H), 7.24–7.17 (m, 4H), 7.12 (ddd, *J* = 7.3, 7.3, 2.7 Hz, 2H), 7.04 (ddd, *J* = 7.8, 7.8, 3.2 Hz, 2H), 6.95 (dd, *J* = 8.7, 1.8 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 4.20 (dddd, *J* = 12.4, 12.4,

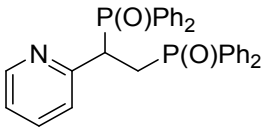
6.4, 1.8 Hz, 1H), 3.02 (dddd, J = 11.9, 11.9, 4.6, 4.6 Hz, 1H), 2.73 (dddd, J = 15.1, 15.1, 11.0, 1.8 Hz, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.4 (d, J = 48.6 Hz), 30.3 (d, J = 48.6 Hz).

1p [1(c)]



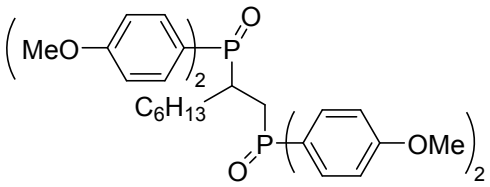
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08–7.98 (m, 2H), 7.74–7.67 (m, 1H), 7.63–7.53 (m, 5H), 7.50–7.33 (m, 5H), 7.32–7.18 (m, 4H), 7.16–7.07 (m, 4H), 7.01 (dd, J = 7.3, 7.3 Hz, 1H), 6.85 (dd, J = 7.8, 7.3 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.92 (ddd, J = 11.9, 11.9, 7.3 Hz, 1H), 3.22-3.08 (m, 1H), 2.85 (dd, J = 14.2, 13.7 Hz, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 36.2 (d, J = 44.9 Hz), 30.0 (d, J = 44.9 Hz).

1q [1(c), 4]



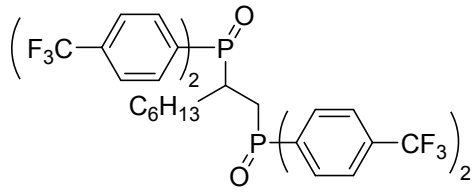
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79-6.06 (br, 29H), 4.49 (br, 29H), 3.57 (br, 1H), 2.81 (m, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.2 (d, J = 41.1 Hz), 31.0 (d, J = 41.1 Hz).

1r



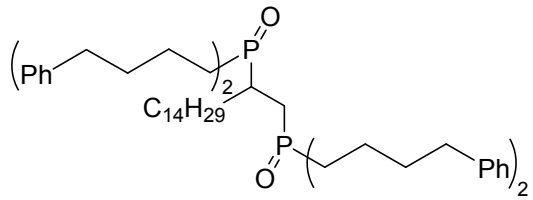
Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68–7.48 (m, 6H), 7.35–7.30 (m, 2H), 6.90–6.80 (m, 6H), 6.78 (d, J = 7.3 Hz, 2H), 3.75–3.37 (m, 12H), 2.90–2.71 (m, 1H), 2.53–2.33 (m, 2H), 1.73–1.54 (m, 1H), 1.43–1.27 (m, 1H), 1.26–1.09 (m, 2H), 1.03–0.94 (m, 2H), 0.91–0.78 (m, 2H), 0.78–0.71 (m, 2H), 0.68 (t, J = 7.3, 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2, 162.1, 132.8 (d, $J_{C–P}$ = 8.6 Hz), 132.7 (d, $J_{C–P}$ = 9.6 Hz), 132.5 (d, $J_{C–P}$ = 8.6 Hz), 132.4 (d, $J_{C–P}$ = 9.6 Hz), 124.8 (d, $J_{C–P}$ = 108.3 Hz), 123.2 (d, $J_{C–P}$ = 101.6 Hz), 114.3 (d, $J_{C–P}$ = 12.5 Hz), 114.1 (d, $J_{C–P}$ = 11.5 Hz), 55.3 (d, $J_{C–P}$ = 2.9 Hz), 31.2, 30.8 (d, $J_{C–P}$ = 228.0 Hz), 29.3, 28.4, 27.8 (dd, $J_{C–P}$ = 69.9 Hz, J = 3.8 Hz), 27.1, 22.4, 14.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 38.5 (d, J = 44.9 Hz), 31.2 (d, J = 44.9 Hz).

1s



White solid; m.p. 52-53 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99–7.75 (m, 6H), 7.69–7.66 (m, 4H), 7.63–7.40 (m, 6H), 3.35–2.98 (m, 1H), 2.81–2.42 (m, 2H), 1.74–1.49 (m, 1H), 1.49–1.29 (m, 1H), 1.18–1.05 (m, 1H), 1.00–0.87 (m, 3H), 0.83–0.71 (m, 4H), 0.66 (t, J = 7.3, 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.4 (d, $J_{C–P}$ = 15.3 Hz), 134.2 (d, $J_{C–P}$ = 14.4 Hz), 134.2 (d, $J_{C–P}$ = 99.6 Hz), 134.1 (d, $J_{C–P}$ = 13.4 Hz), 133.9 (d, $J_{C–P}$ = 12.5 Hz), 131.6, 131.4, 131.1 (d, $J_{C–P}$ = 3.8 Hz), 130.8 (d, $J_{C–P}$ = 3.8 Hz), 130.0 (d, $J_{C–P}$ = 98.7 Hz), 126.1-125.6 (m), 123.4 (q, $J_{C–P}$ = 273.1 Hz), 123.3 (q, $J_{C–P}$ = 274.0 Hz), 123.3 (q, $J_{C–P}$ = 273.1 Hz), 123.2 (q, $J_{C–P}$ = 273.1 Hz), 31.1, 30.9 (dd, $J_{C–P}$ = 68.0 Hz, J = 3.8 Hz), 29.4 (d, $J_{C–P}$ = 64.2 Hz), 29.0, 28.7, 26.9, 22.3, 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.6 (d, J = 22.4 Hz), 28.1 (d, J = 22.4 Hz).

1t



White solid; m.p. 190-192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31–7.23 (m, 8H), 7.21–7.12 (m, 12H), 2.67–2.59 (m, 8H), 2.23–2.09 (m, 2H), 1.85–1.46 (m, 29H), 1.26 (br, s, 22H), 0.89 (t, J = 6.9, 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.8 (d, $J_{C–P}$ = 3.8 Hz), 141.7, 128.4 (d, $J_{C–P}$ = 2.9 Hz), 128.3, 125.9 (d, $J_{C–P}$ = 3.8 Hz), 125.9 (d, $J_{C–P}$ = 2.9 Hz), 35.4, 33.0, 32.9, 32.9, 32.8, 32.8, 32.7, 31.9, 31.1 (dd, $J_{C–P}$ = 69.0 Hz, J = 3.8 Hz), 30.5, 30.0, 29.7, 29.4, 29.4, 28.0, 28.0, 26.9 (d, $J_{C–P}$ = 63.2 Hz), 26.5 (d, $J_{C–P}$ = 63.2 Hz), 25.7 (d, $J_{C–P}$ = 62.3 Hz), 22.7, 21.5 (d, $J_{C–P}$ = 2.9 Hz), 21.4 (d, $J_{C–P}$ = 3.89 Hz), 21.3 (d, $J_{C–P}$ = 3.8 Hz), 14.1; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 53.8 (d, J = 22.4 Hz), 48.9 (d, J = 22.4 Hz).

References

[1] (a) R. A. Khachatryan, N. Yu. Grigoryan, M. G. Indzhikyan, *Russ. J. Gen. Chem.* 1994, **64**, 1134–1138; (b) A. V. Kharitonov, A. E. Antoshin, A. N. Pushin, E. N. Tsvetkov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1988, **58**, 1021–1024, 905–908; (c) A. Yoshimura, Y. Saga, Y. Sato, A. Ogawa, T. Chen, L.-B. Han, *Tetrahedron Lett*., 2016, **57**, 3382.

[2] (a) L. Liu, Y. Wang, A. Zeng, P. Xu, Y. Gao, Y. Yin, Z. Zhao, *Adv. Synth. Catal.* 2016, **355**, 659–666; (b) A. M. Gonzalez-Nogal, P. Cuadrado, M. A. Sarmentero, *Tetrahedron*, 2010, **66**, 9610–9619; (c) A. E. Antoshin, Y. N. Reikhov, K. V. Tugushov, I. V. Rybal'Cchenko, V. F. Taranchenko, S. A. Lermontov, A. N. Malkovac, *Russ. J. Gen. Chem.* 2009, **79**, 2113–2115; (d) P. J. Stang, A. M. Arif, V. V. Zhdankin, *Tetrahedron*, 1991, **47**, 4539–4546; (e) R. J. Cross, L. J. Farrugia, P. D. Newman, R. D. Peacock, D. Stirling, *J. Chem. Soc. Dalton. Trans.* 1996, 1637–1644; (f) D. Semenzin, G. Etemad-Moghadam, D. Albouy, O. Diallo, M. Koeing, *J. Org. Chem.* 1997, **62**, 2414–2422.

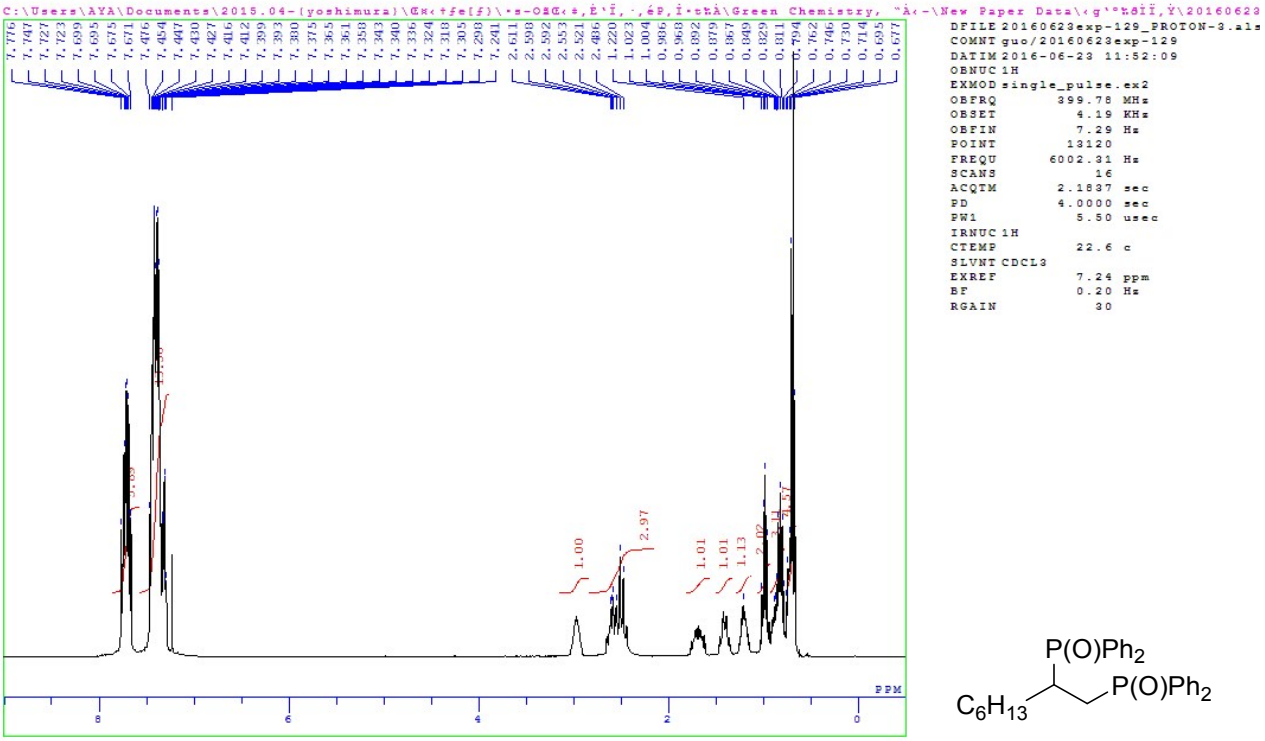
[3] H. Teichmann, W. Thierfelder, E. Schafer, A. Weigt, *Tetrahedron Lett.* 1997, **18**, 2889–2892.

[4] A. Allen, Jr. L. Ma, W. Lin, *Tetrahedron Lett.* 2002, **43**, 3707–3710.

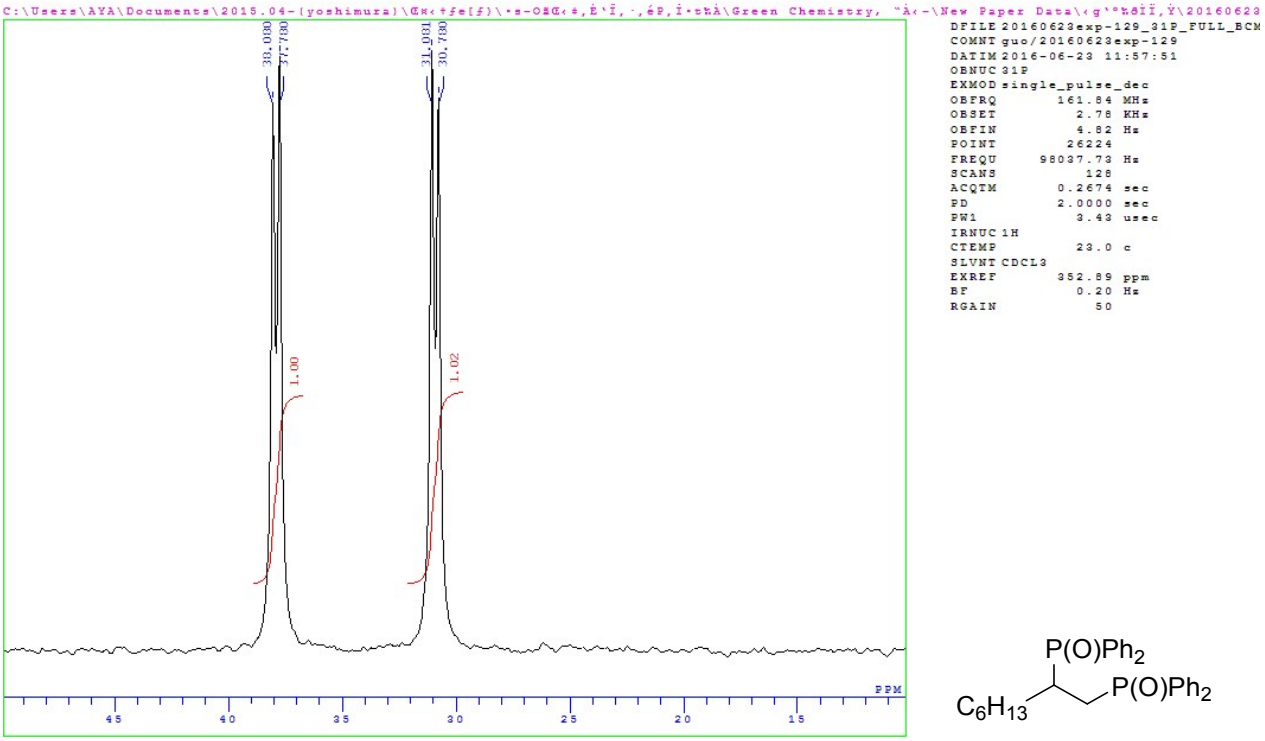
NMR Spectra

1a

^{1}H NMR

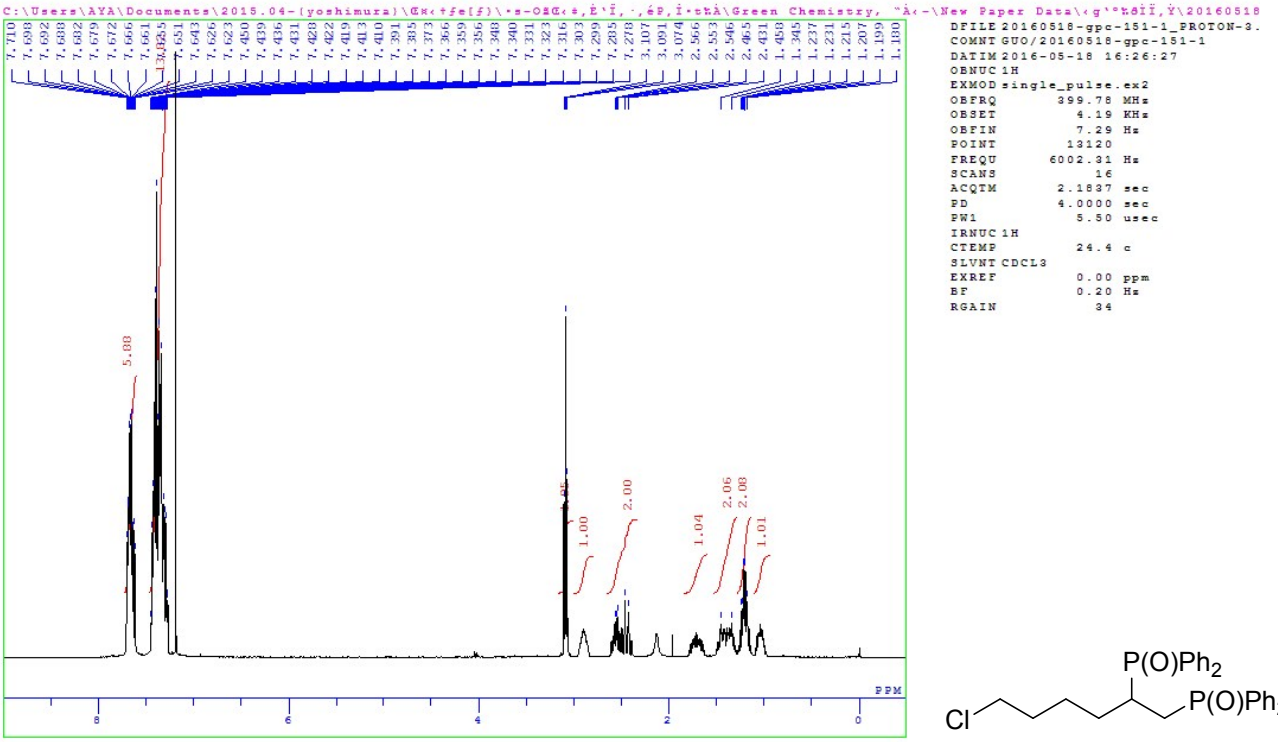


^{31}P NMR

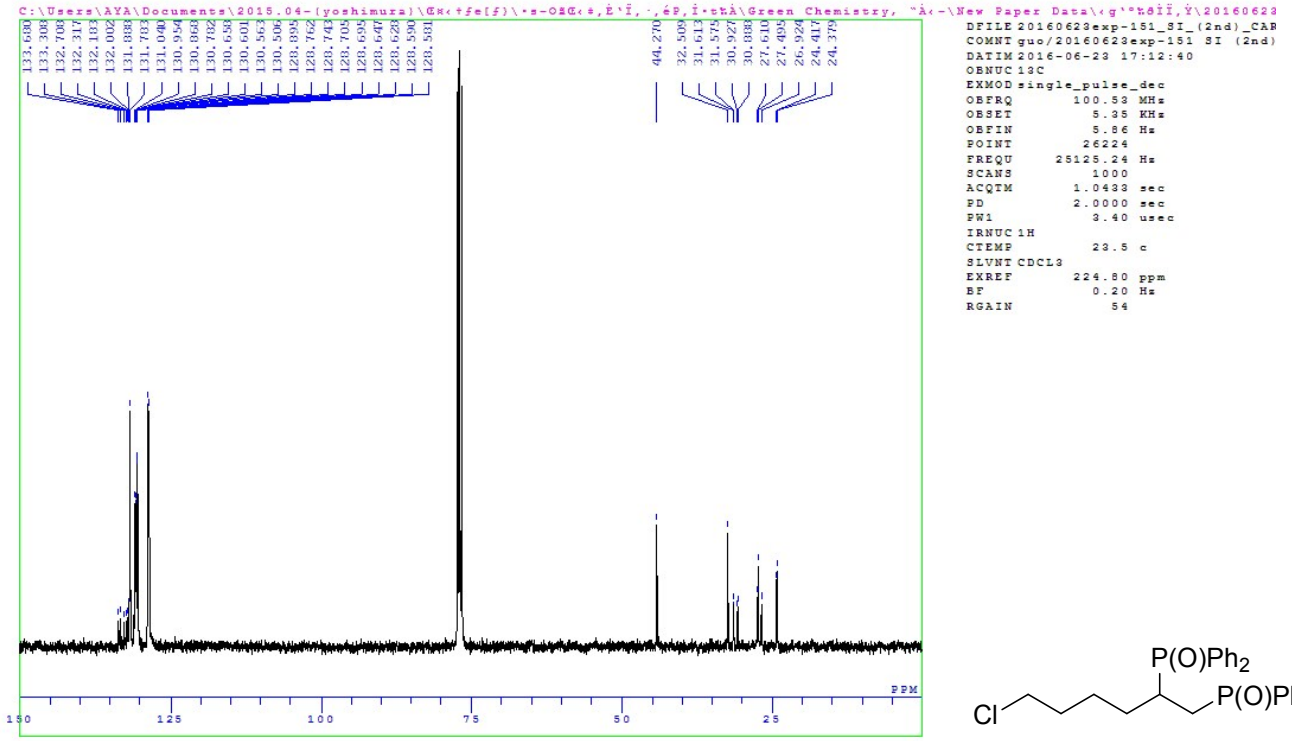


1b

^{1}H NMR



^{13}C NMR



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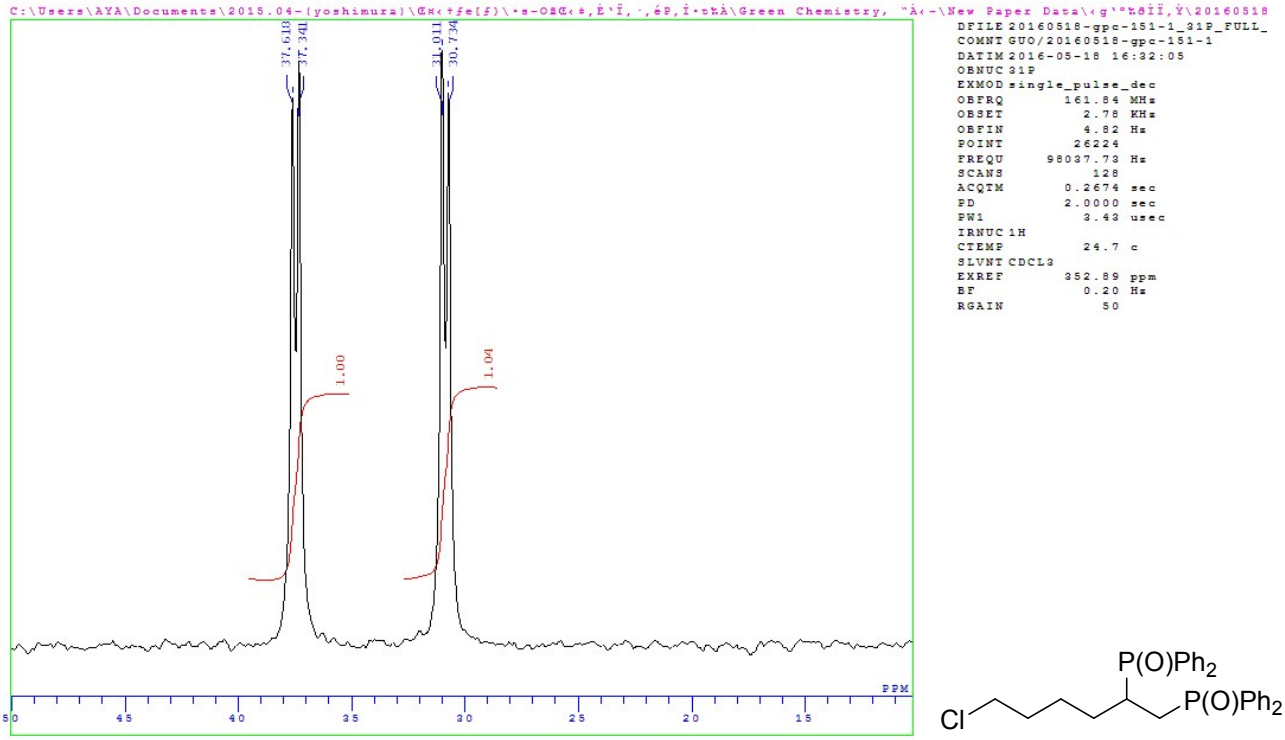

1c

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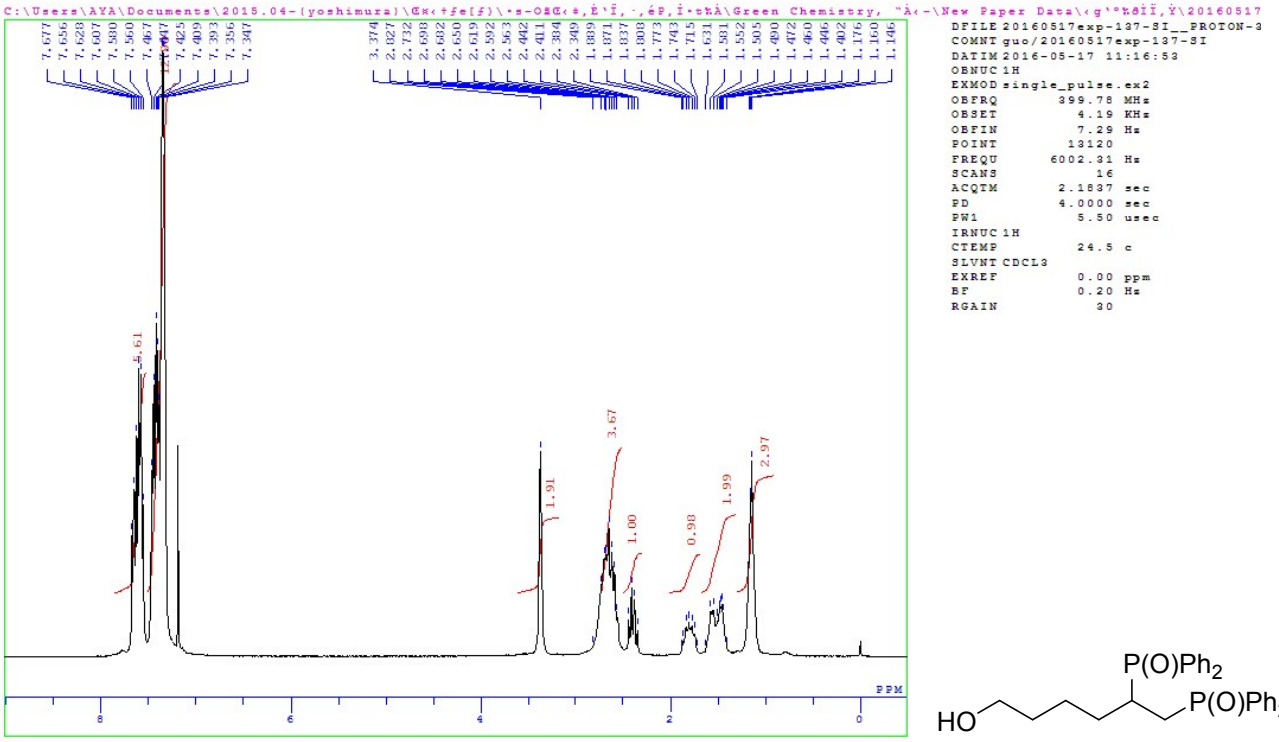
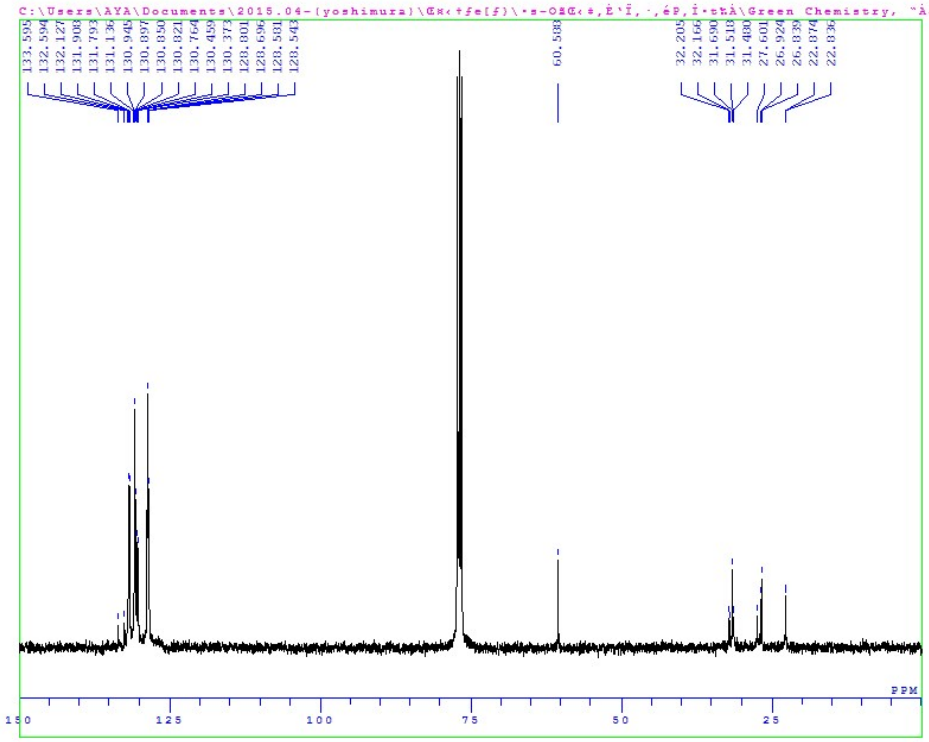


^{13}C NMR



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OBFIN 5.86 Hz
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CTEMP 23.3 c
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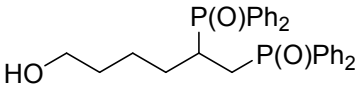
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 50



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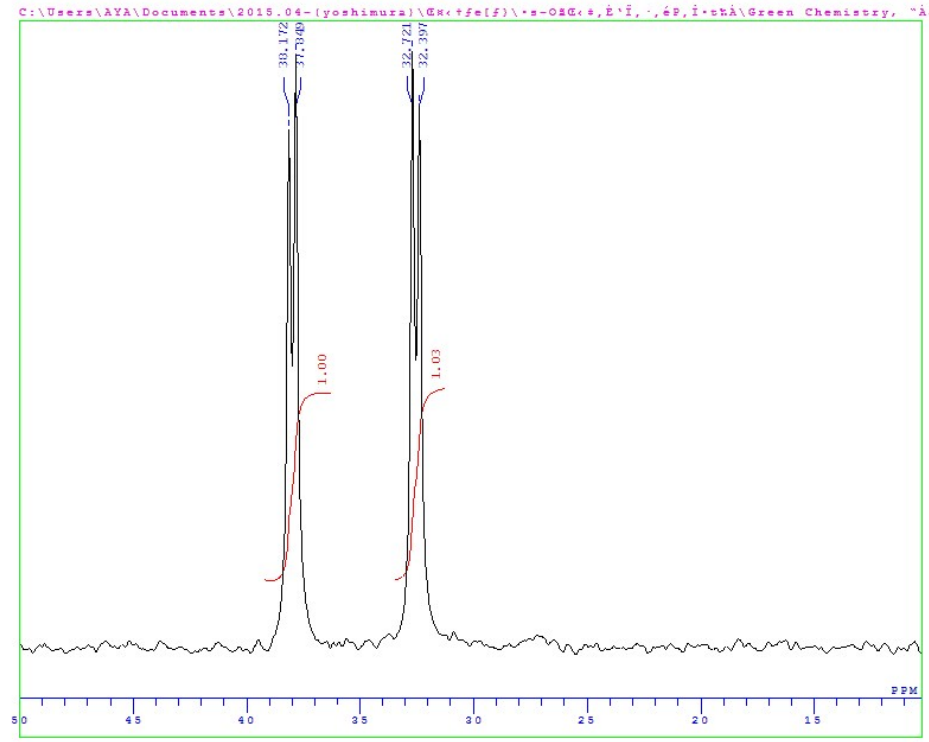

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OBFIN 4.82 Hz
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SCANS 128
ACQTM 0.2674 sec
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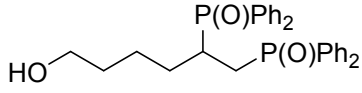
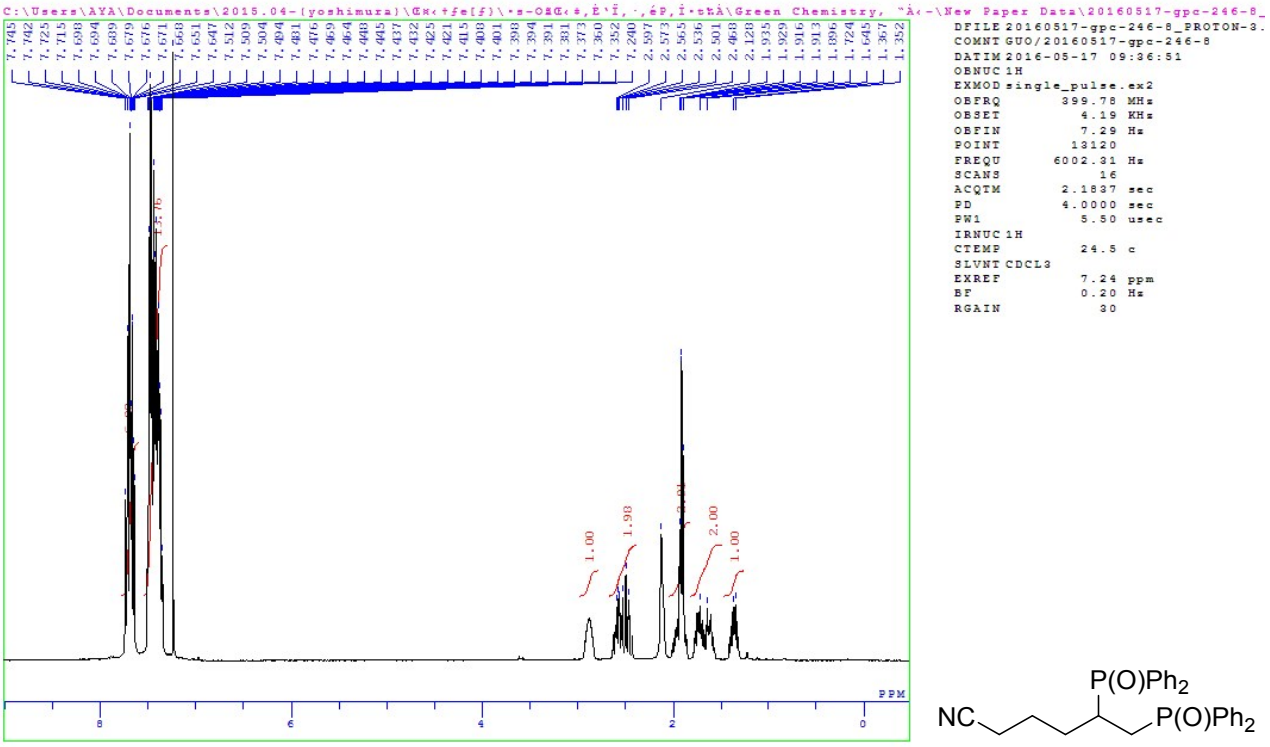
RGAIN 50



1d

^{1}H NMR



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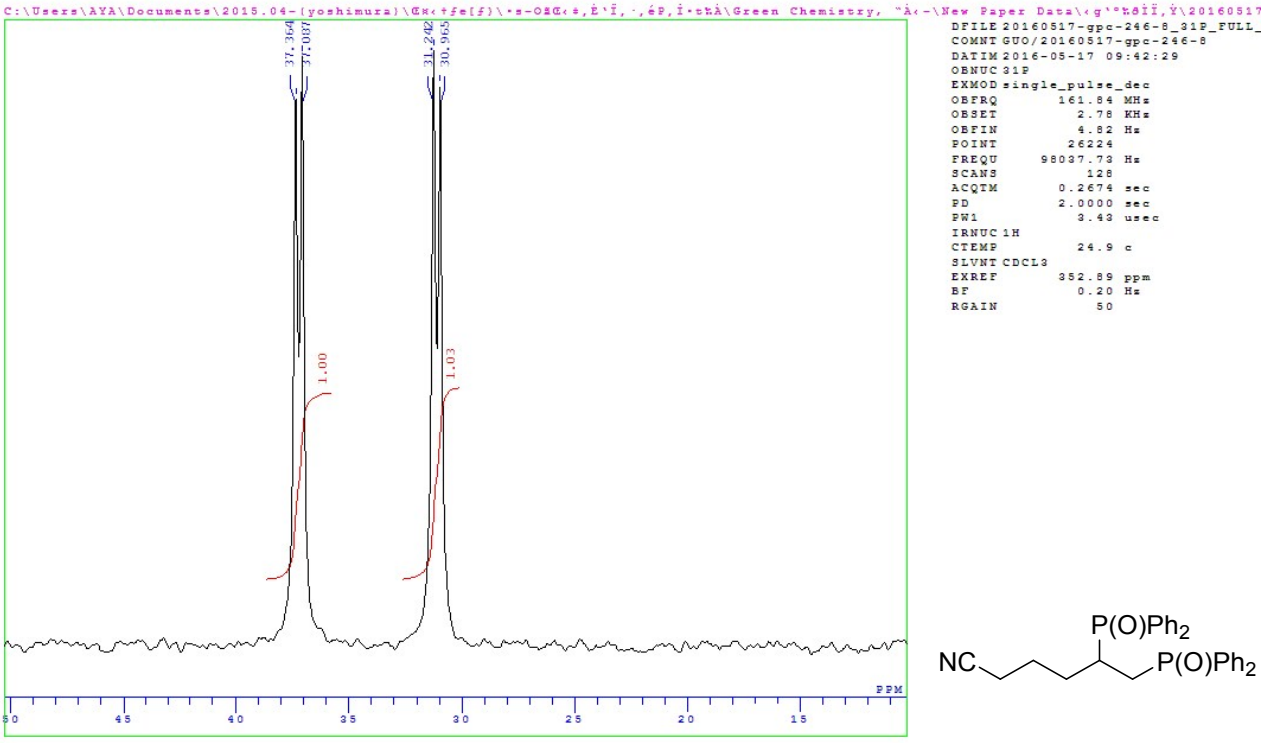

1e

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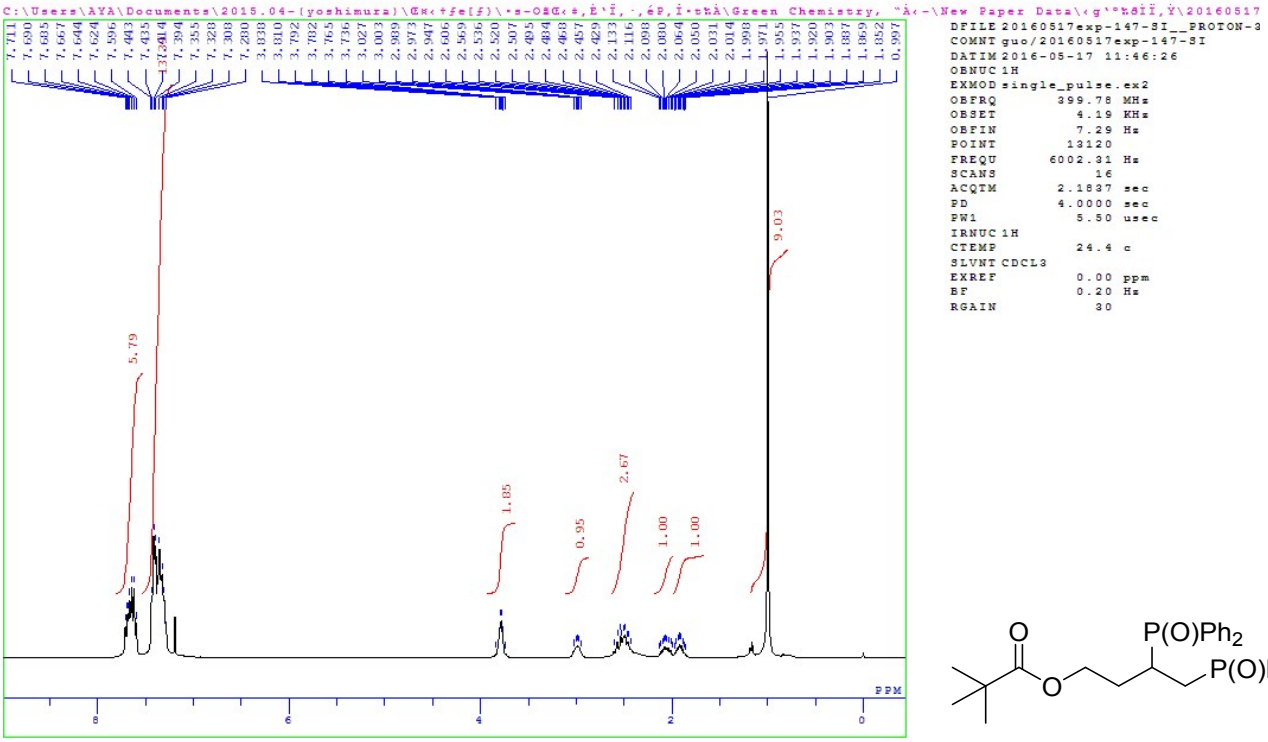

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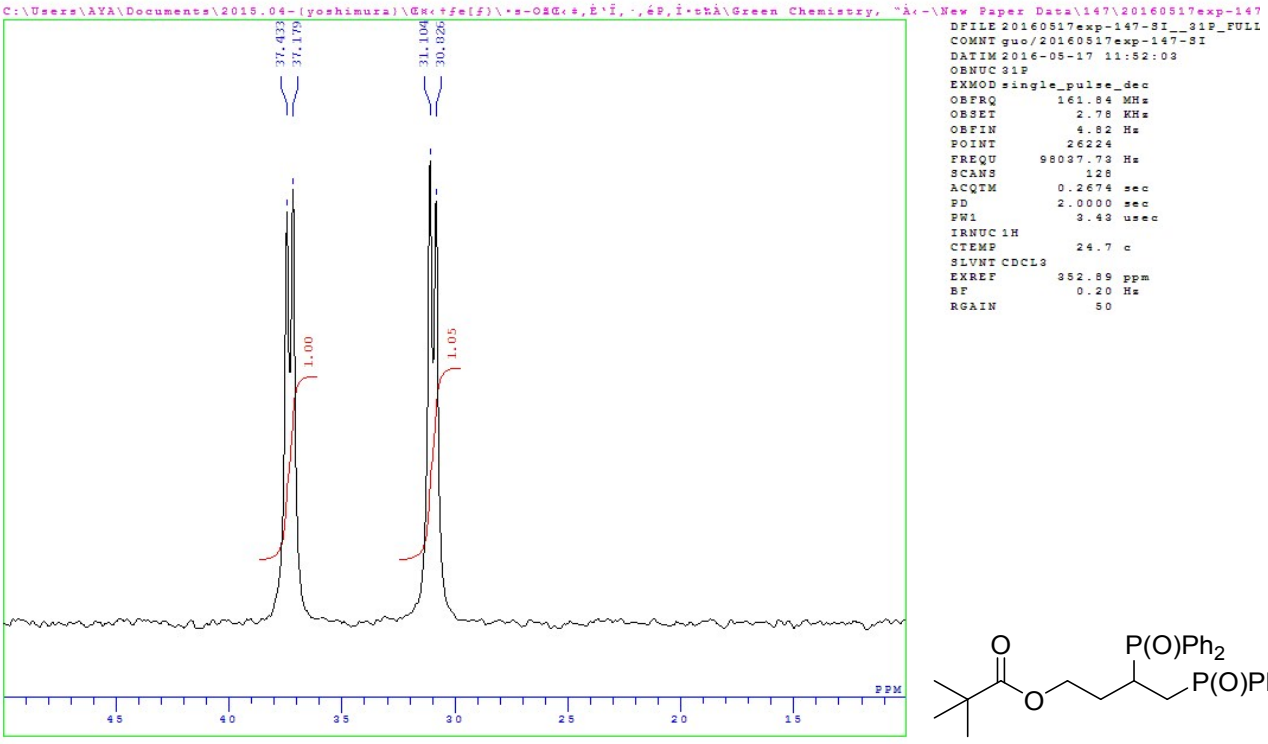
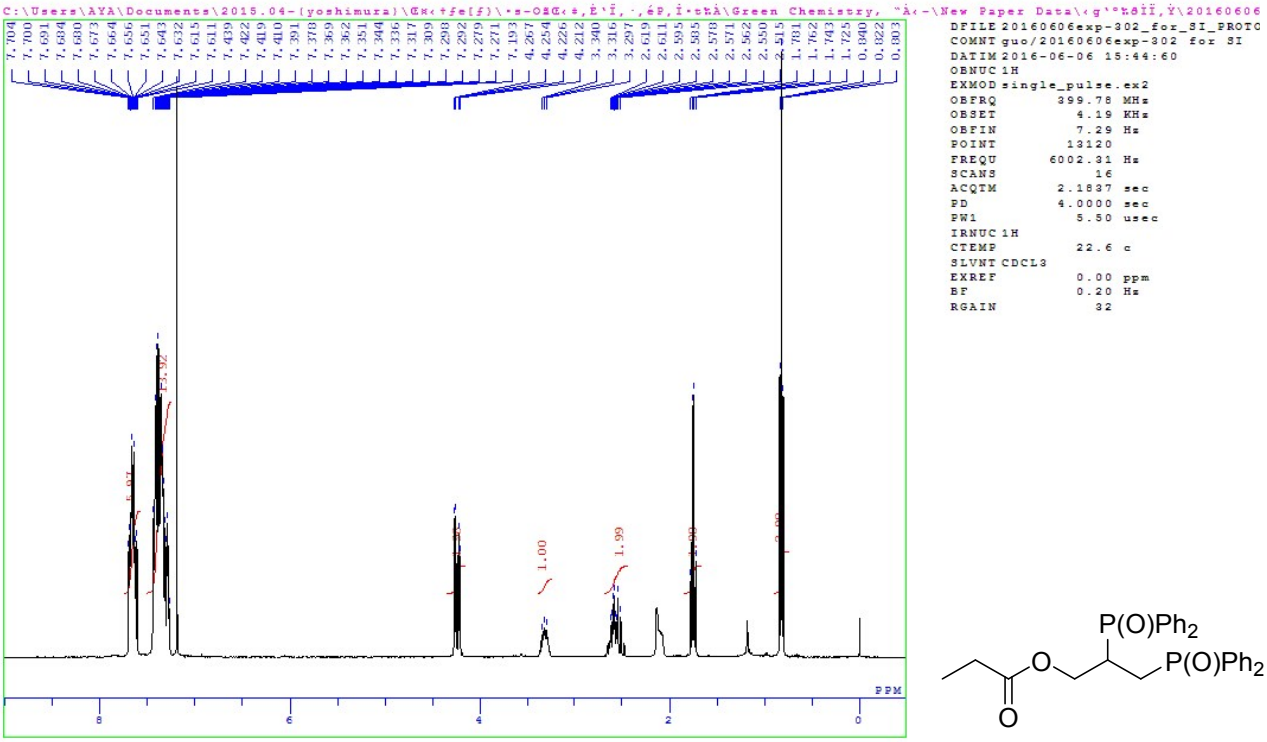
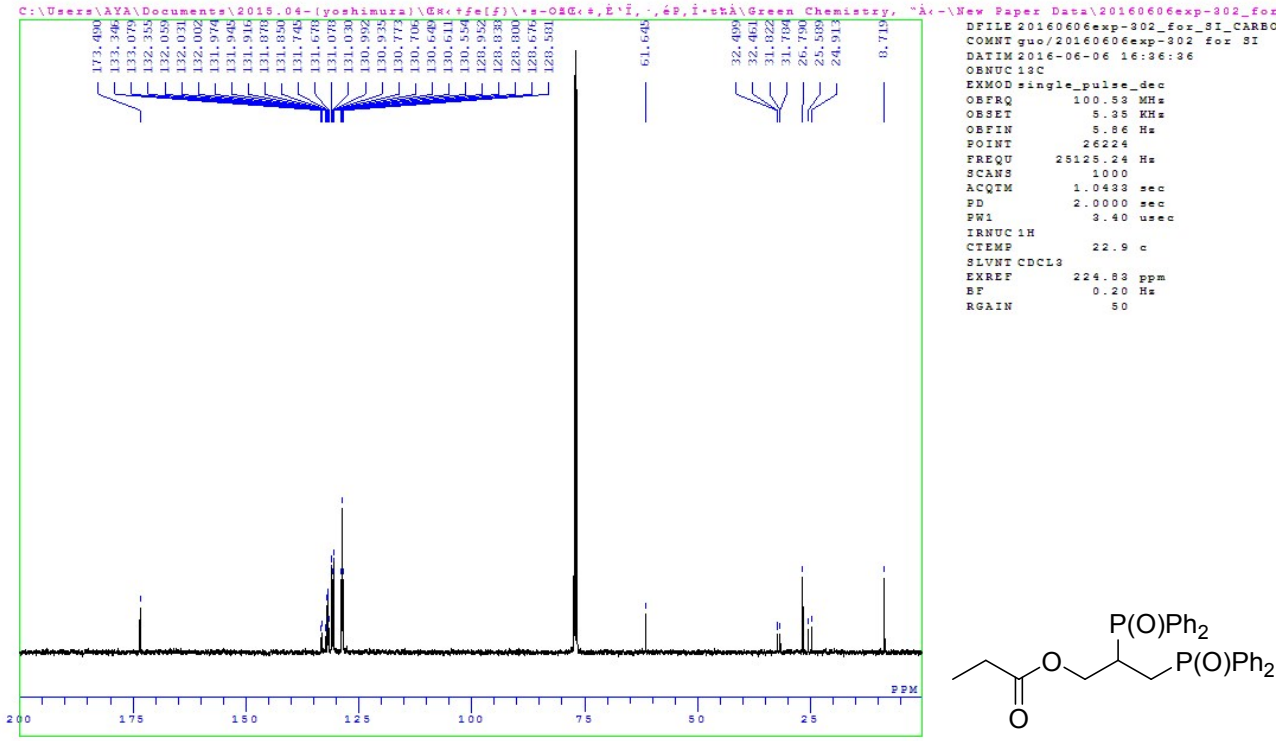


1f

^{1}H NMR



^{13}C NMR



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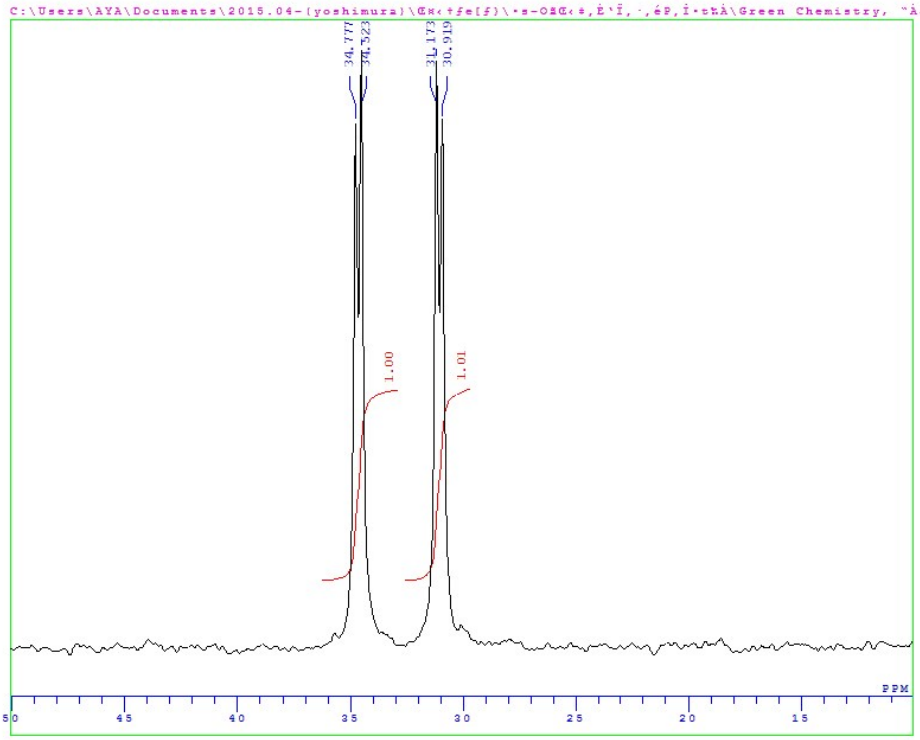

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CTEMP 22.7 c
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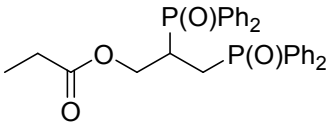
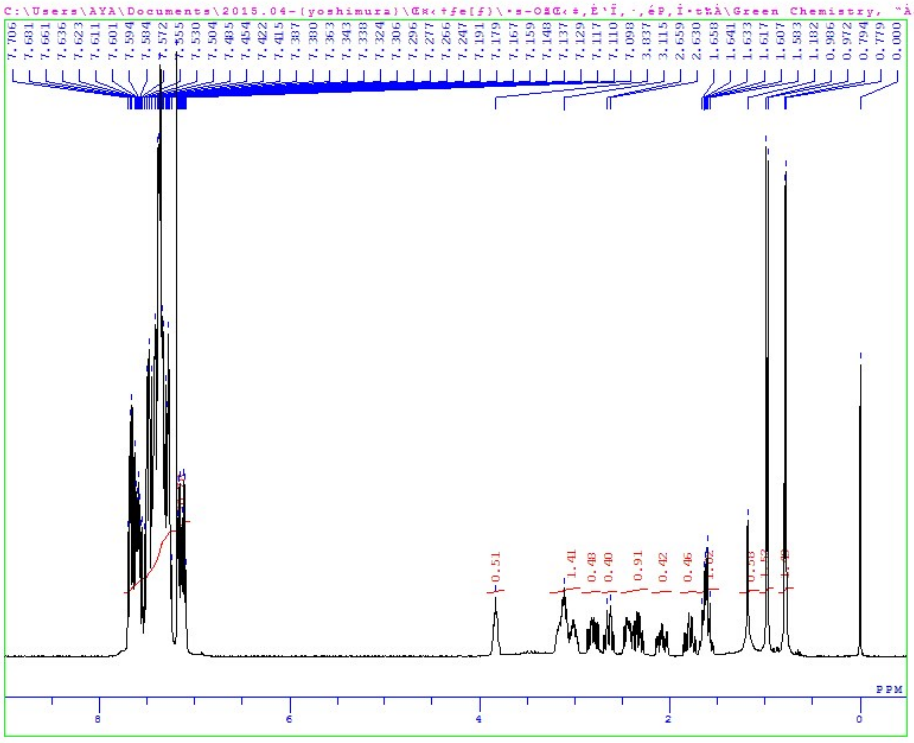
BF 0.20 Hz
RGAIN 50



1g

^{1}H NMR



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BF 0.30 Hz
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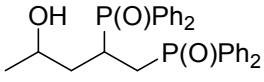
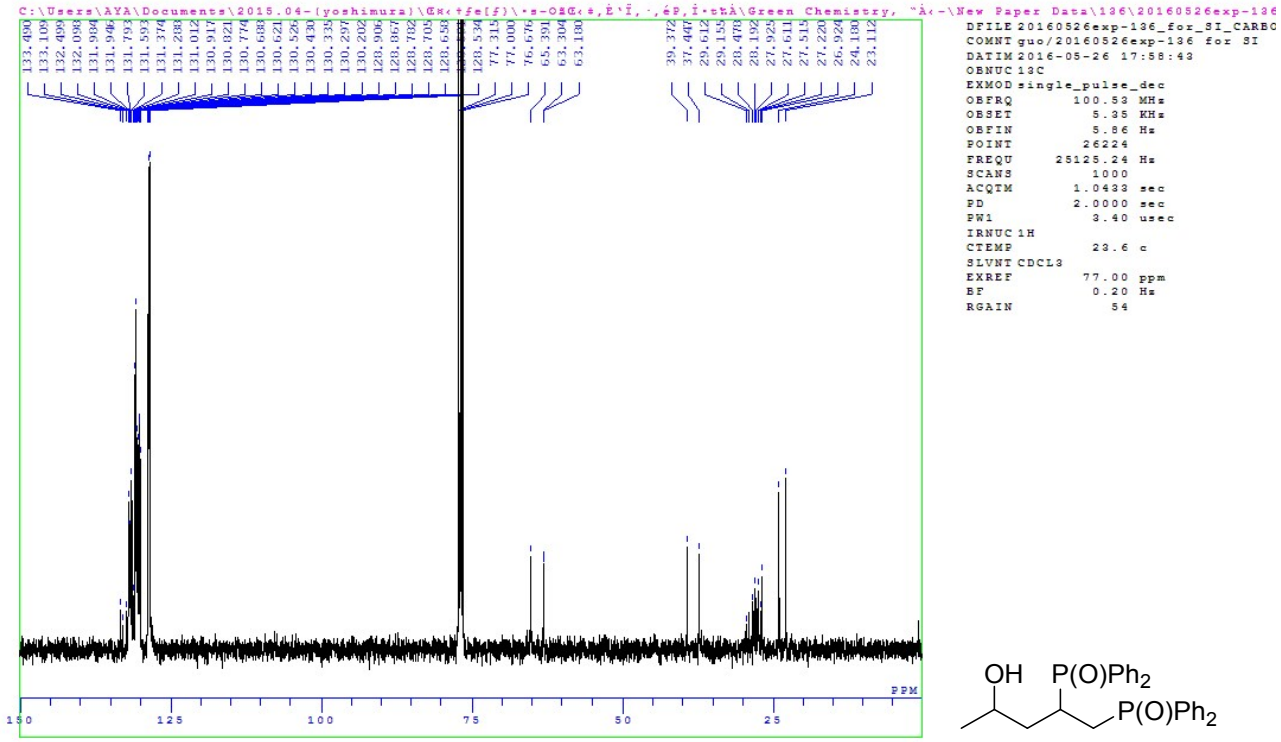


^{13}C NMR



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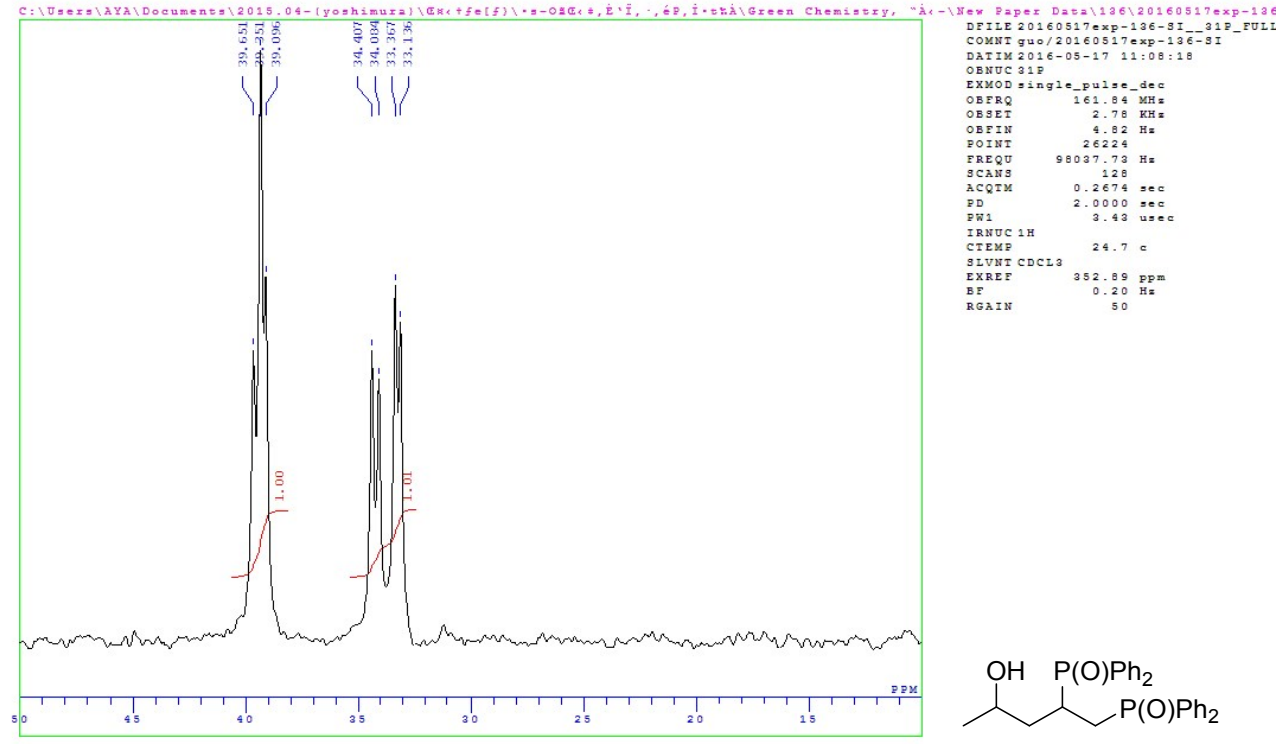
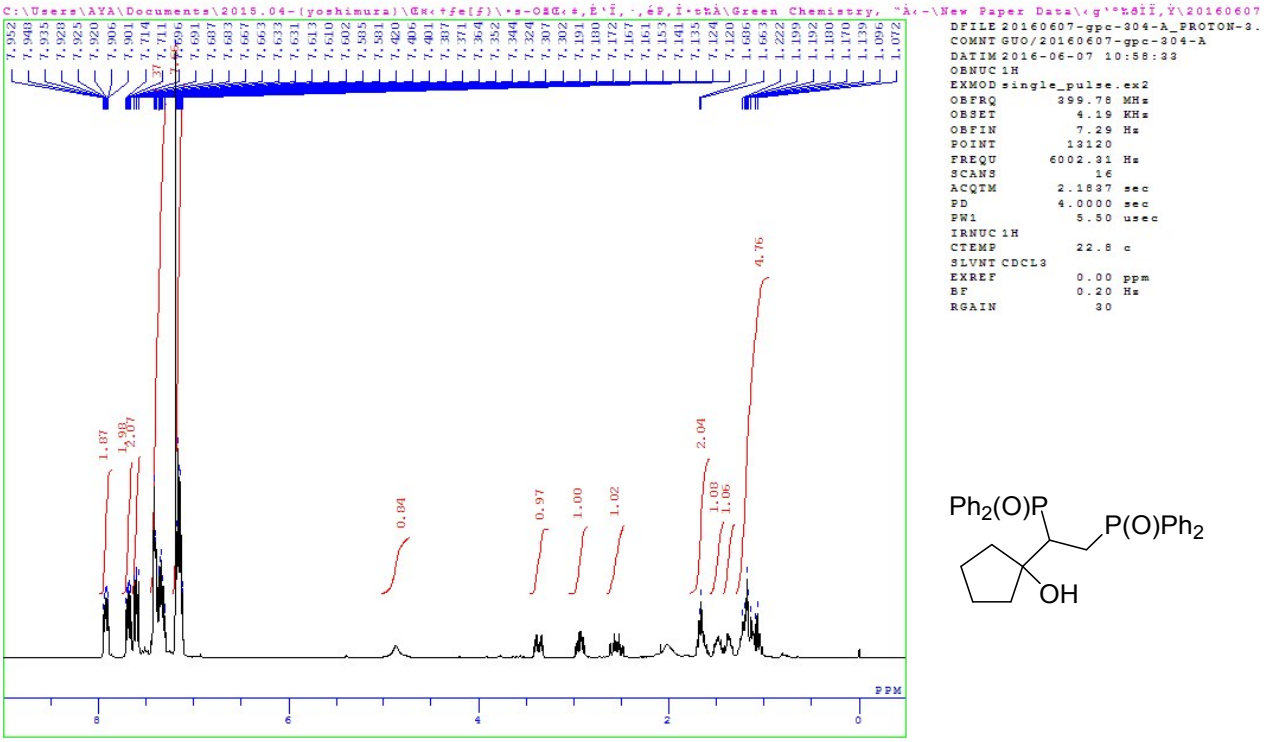


1h

^{1}H NMR



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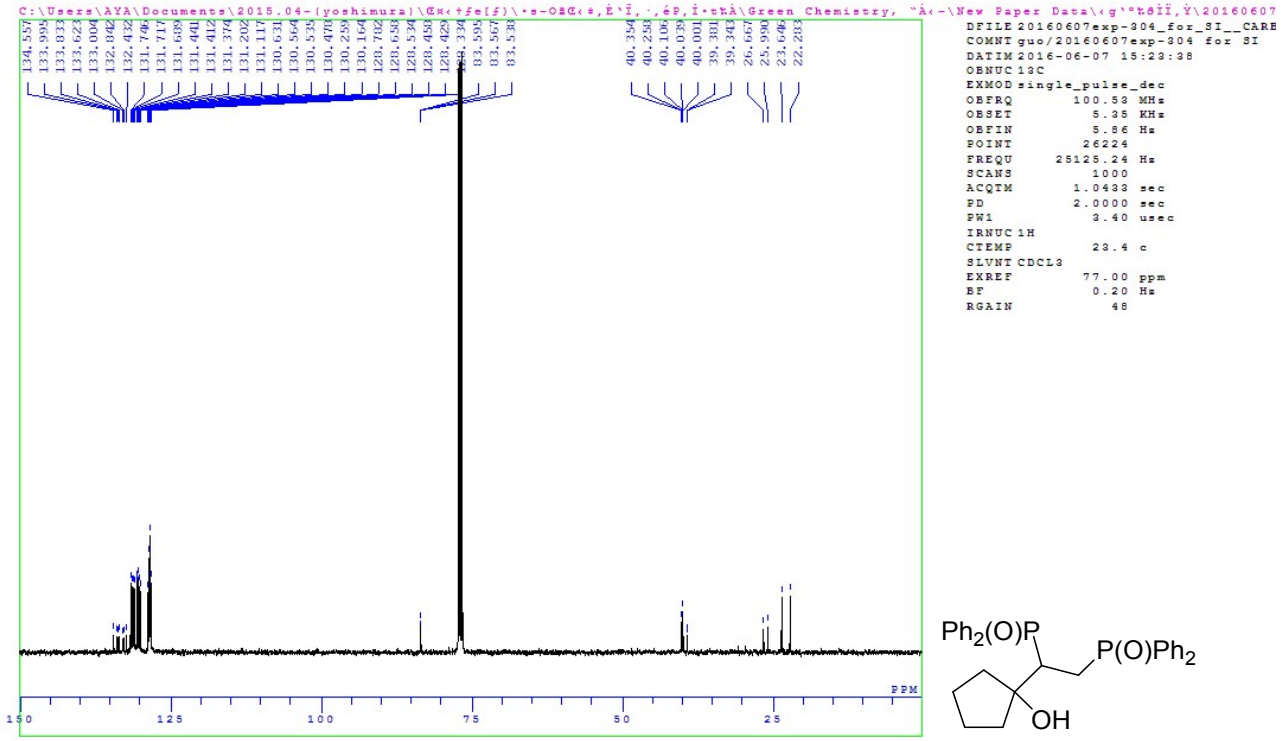

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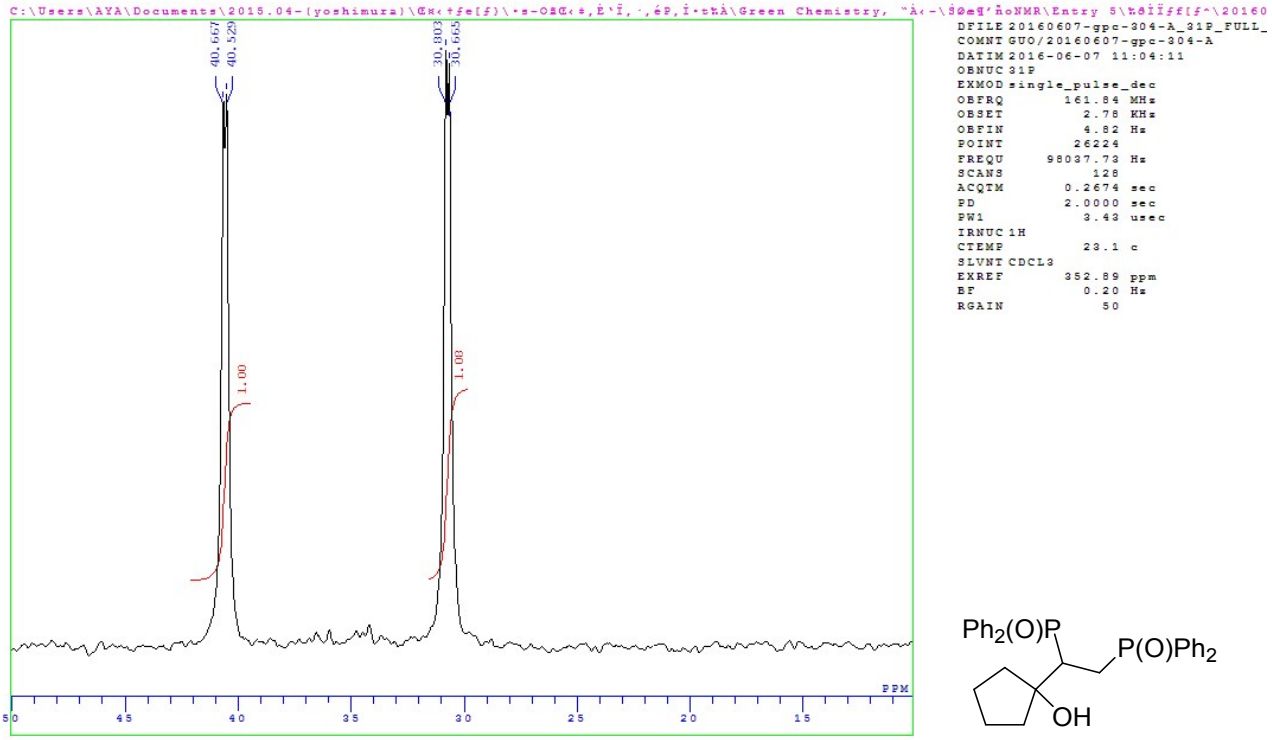

1i

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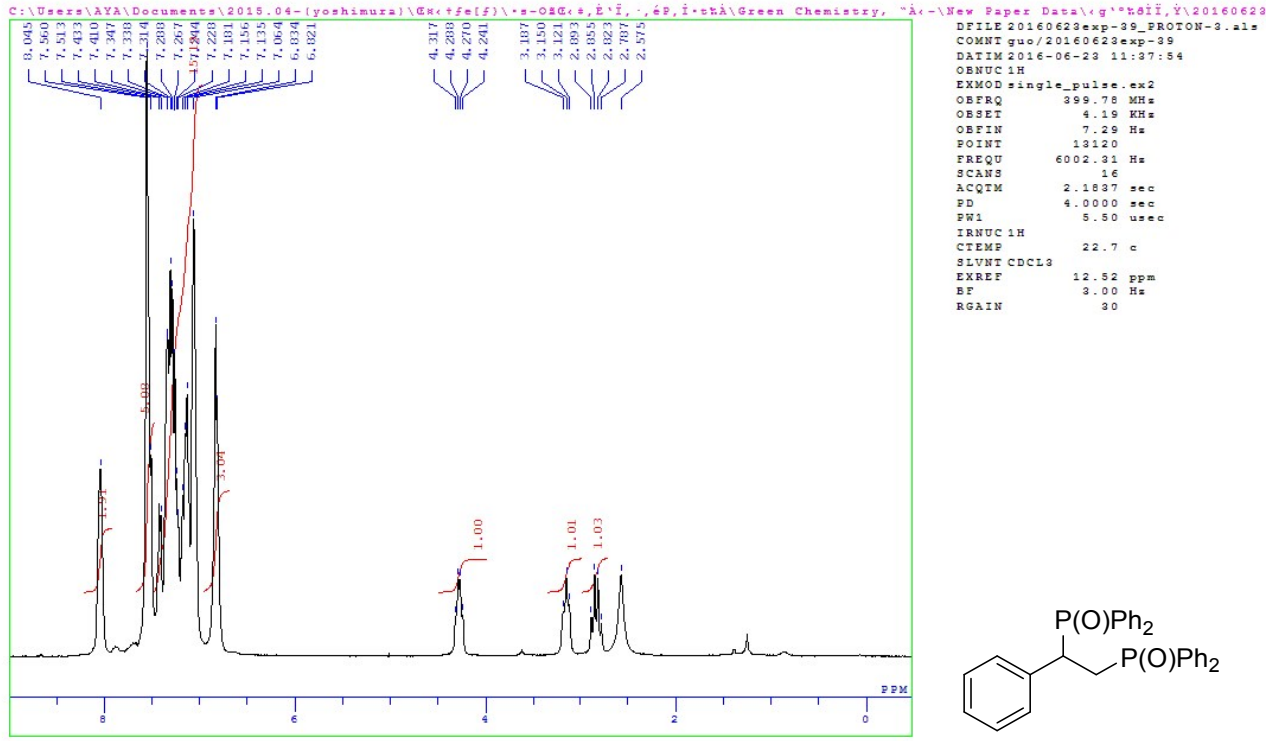

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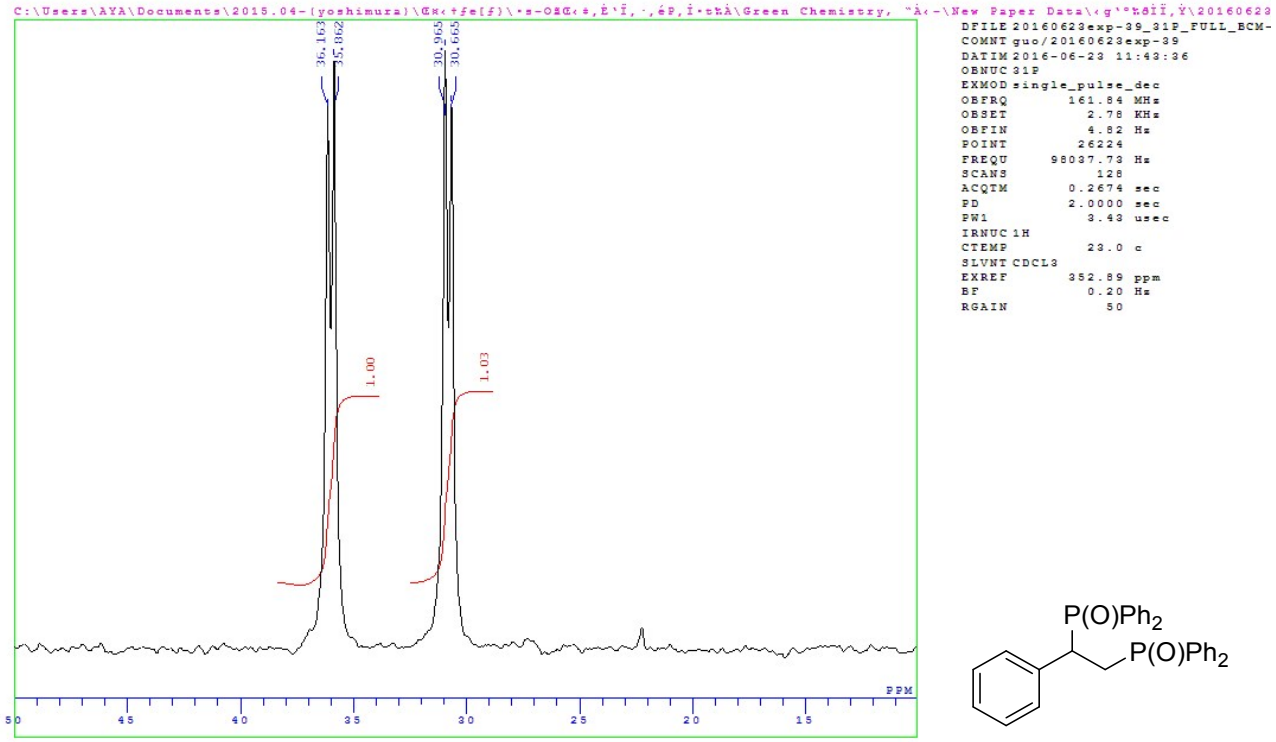
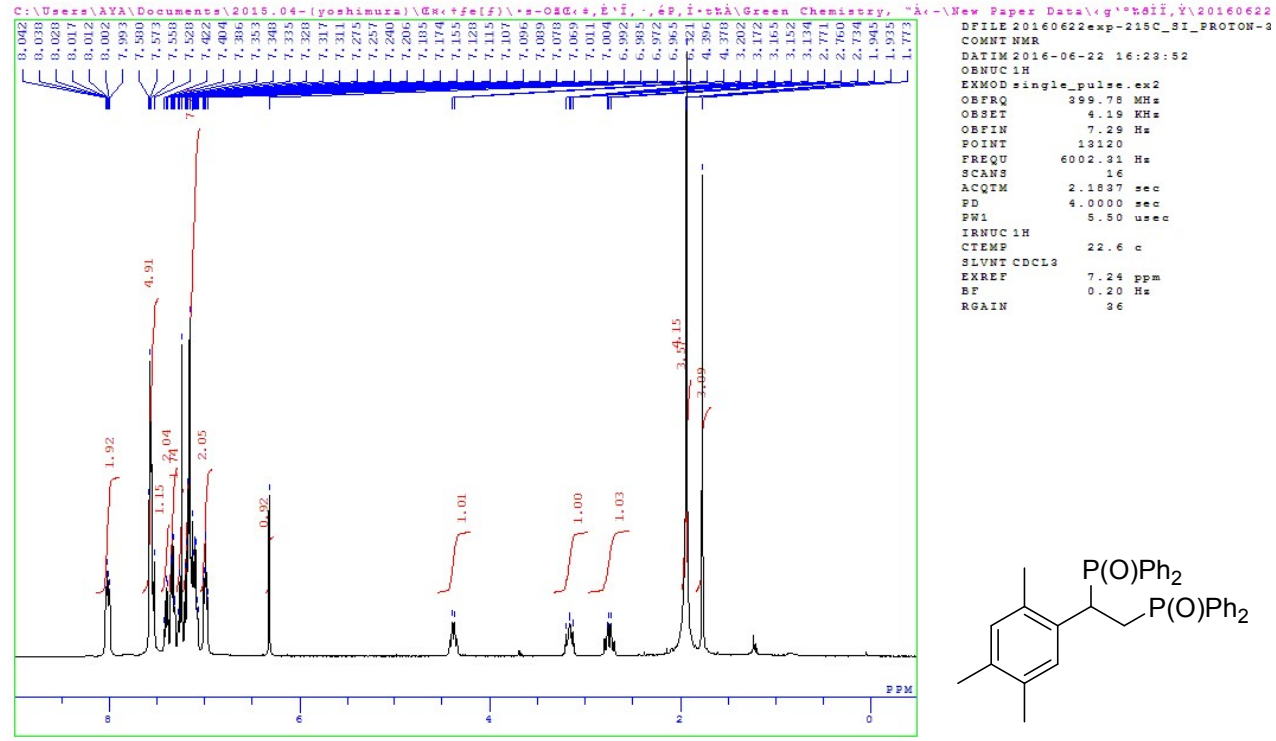


1j

^{1}H NMR



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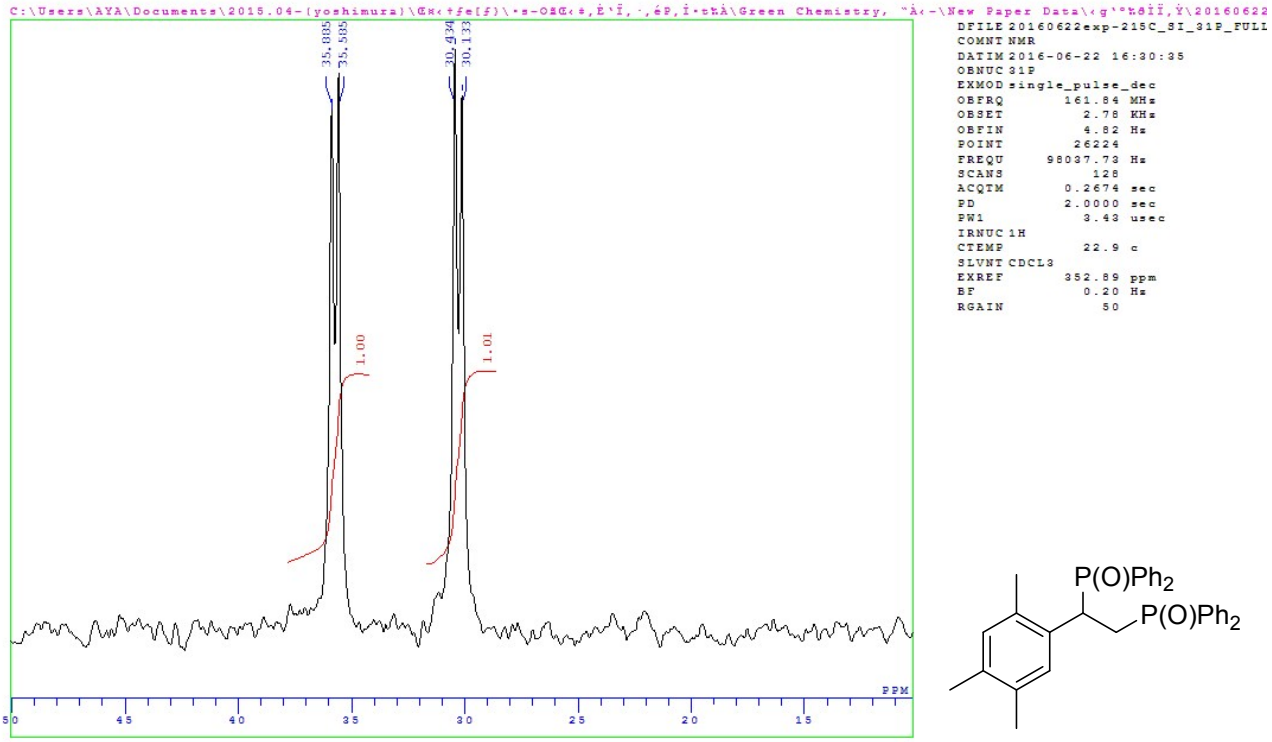
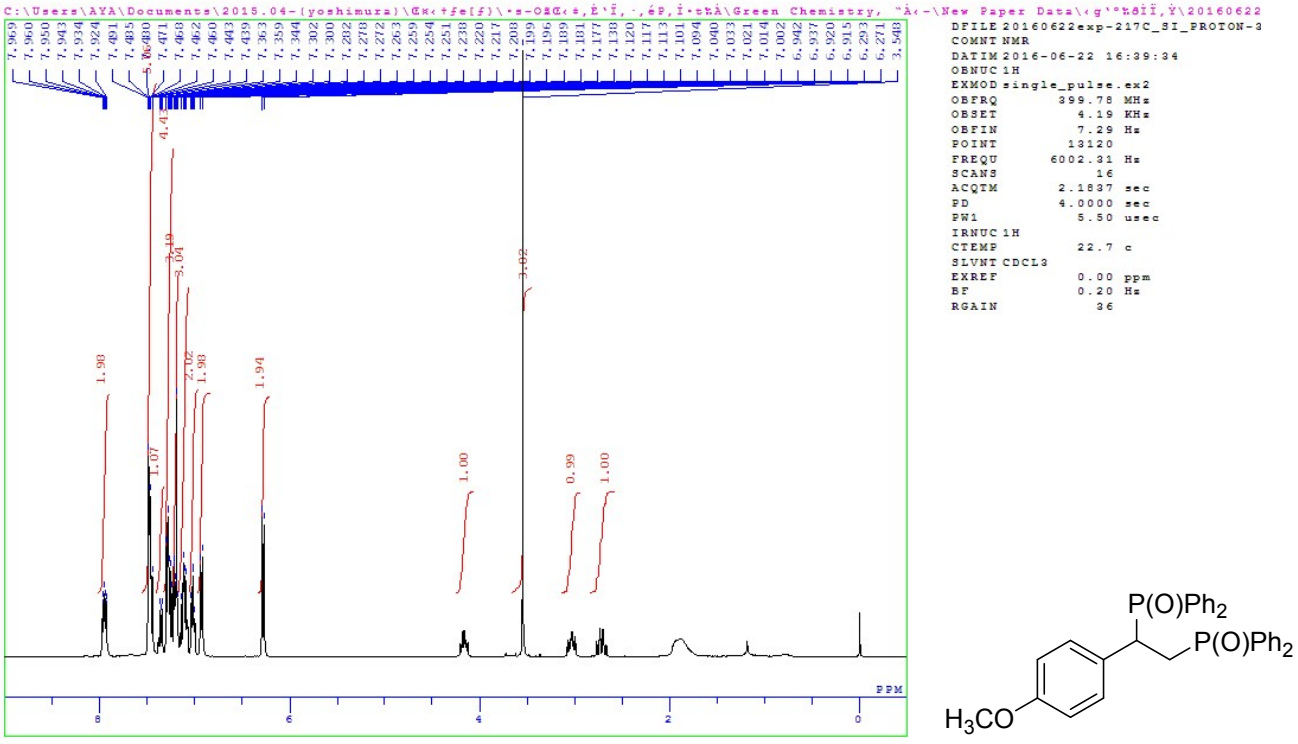
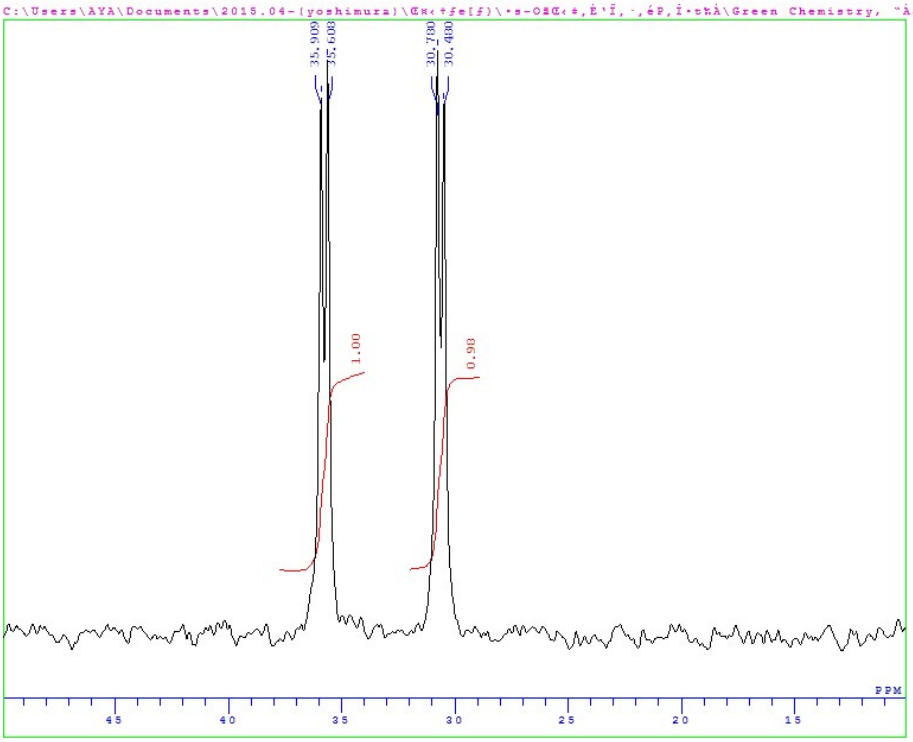


1k

^{1}H NMR



^{13}P NMR



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SCANS 128
ACQTM 0.2674 sec
PD 2.0000 sec
PW1 3.43 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
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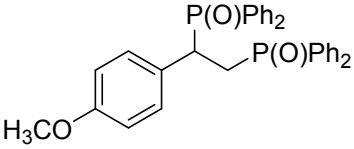
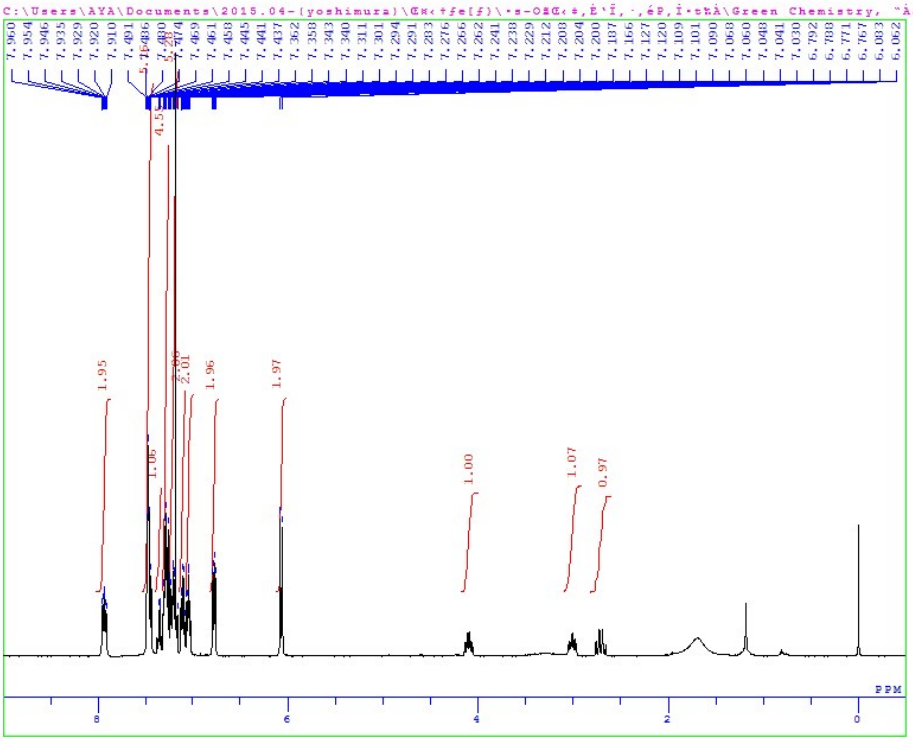
RGAIN 48



1l

^{1}H NMR



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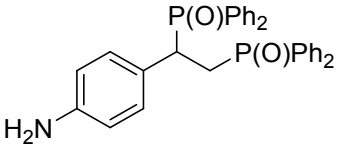
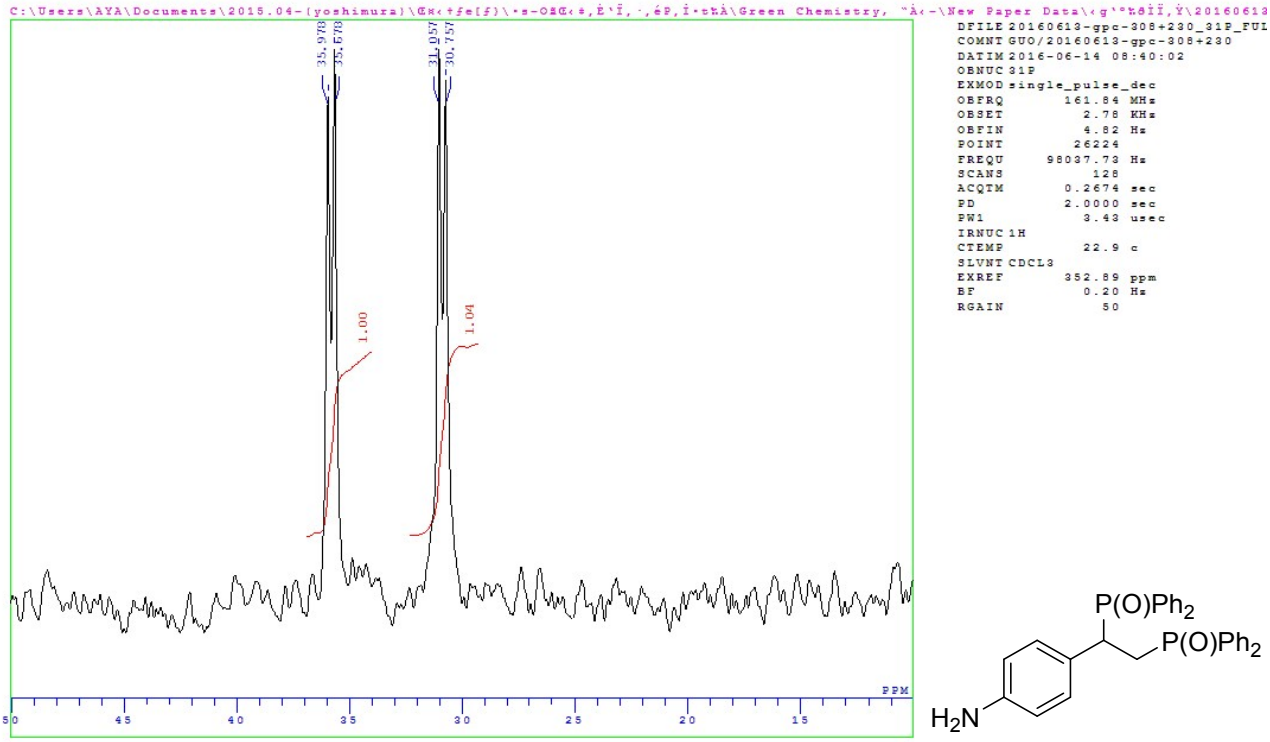
COMNT GUO/20160613-gpc-308+230
DATIM 2016-06-14 08:34:23
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.31 Hz
SCANS 16
ACQTM 2.1837 sec
PD 4.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 38

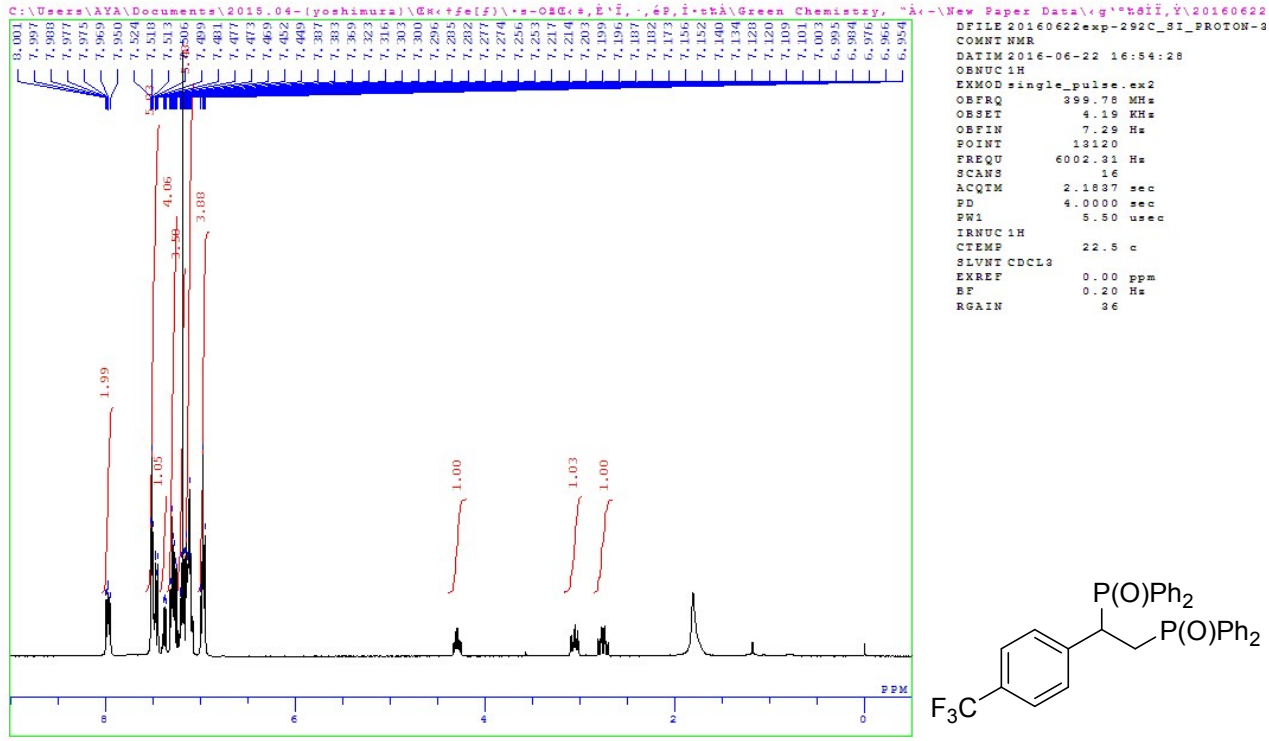


^{13}P NMR



1m

^{1}H NMR



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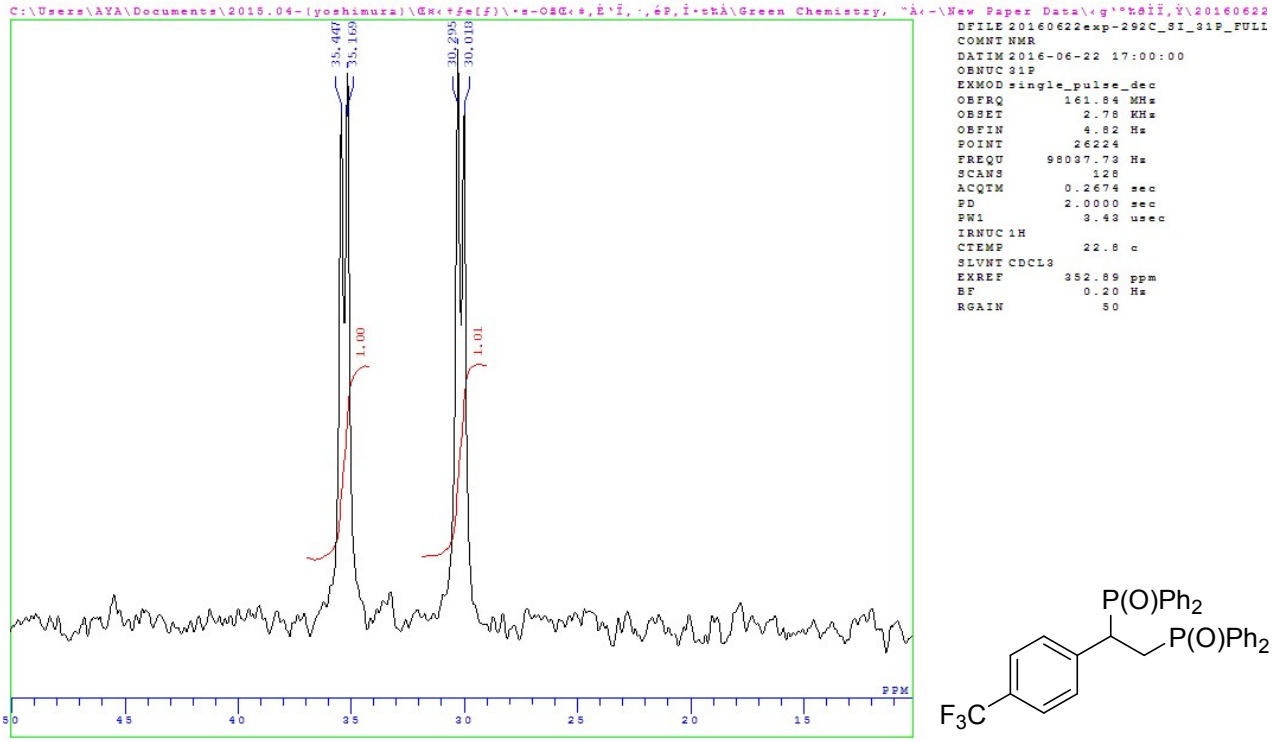
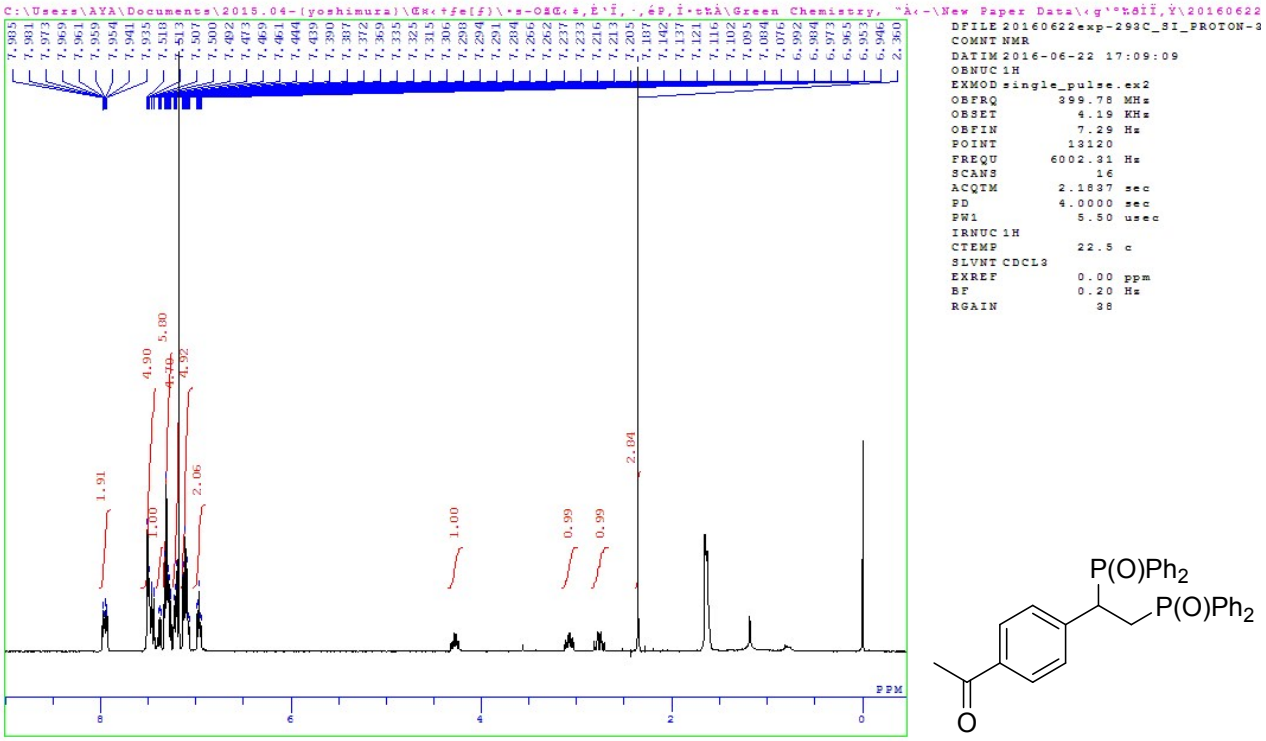
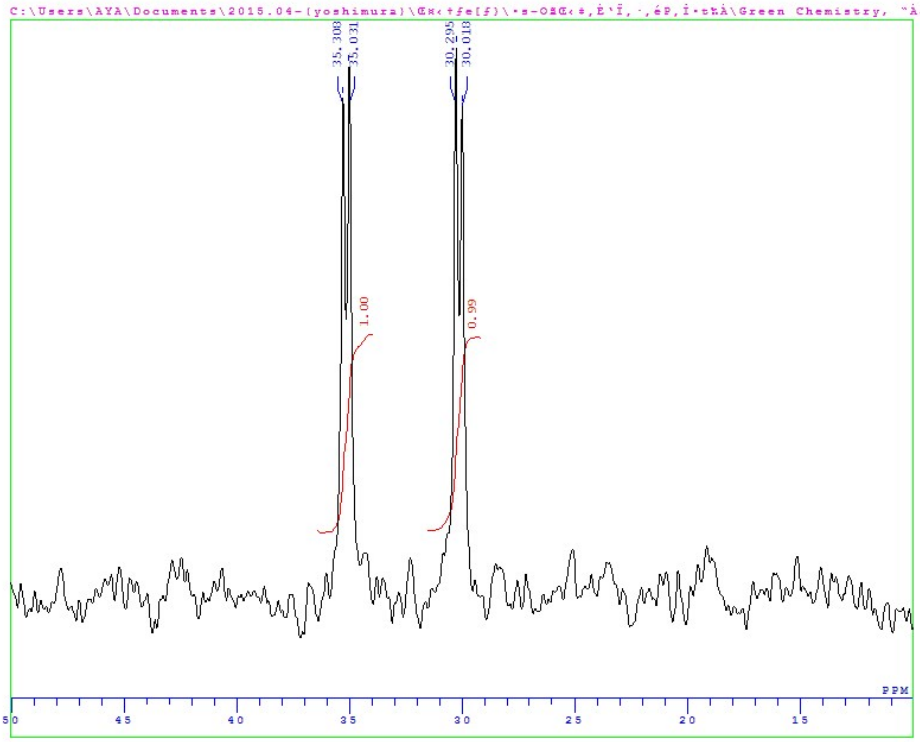


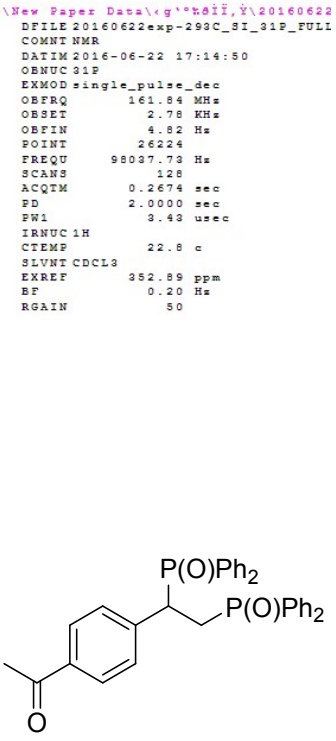
1n

^{1}H NMR



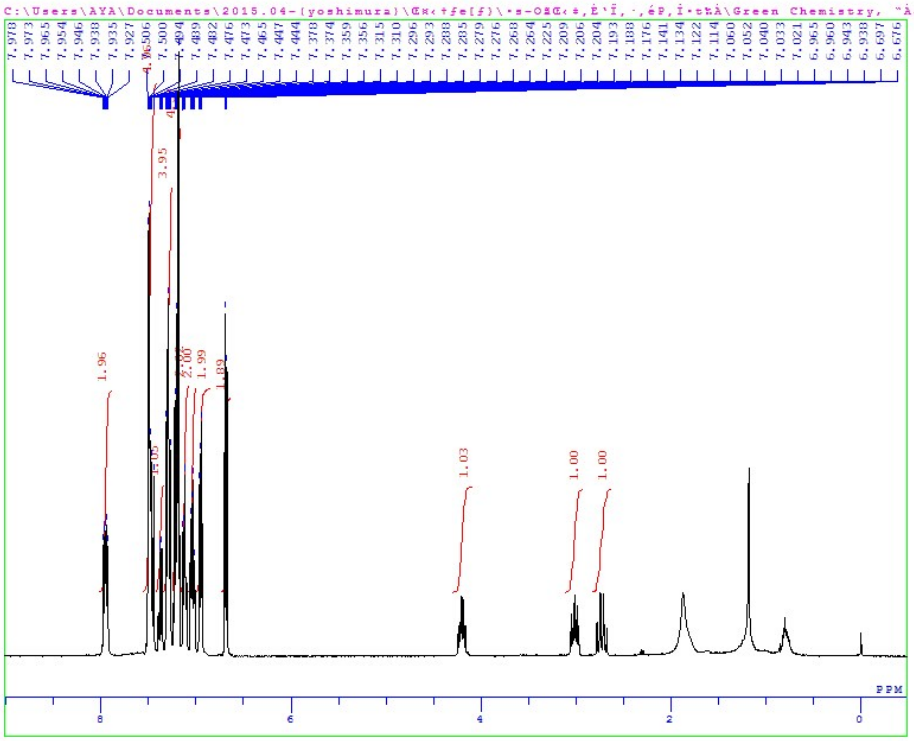
^{13}P NMR

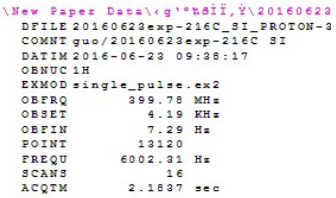


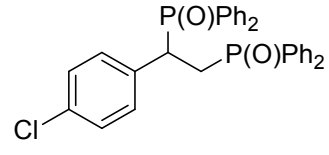


1o

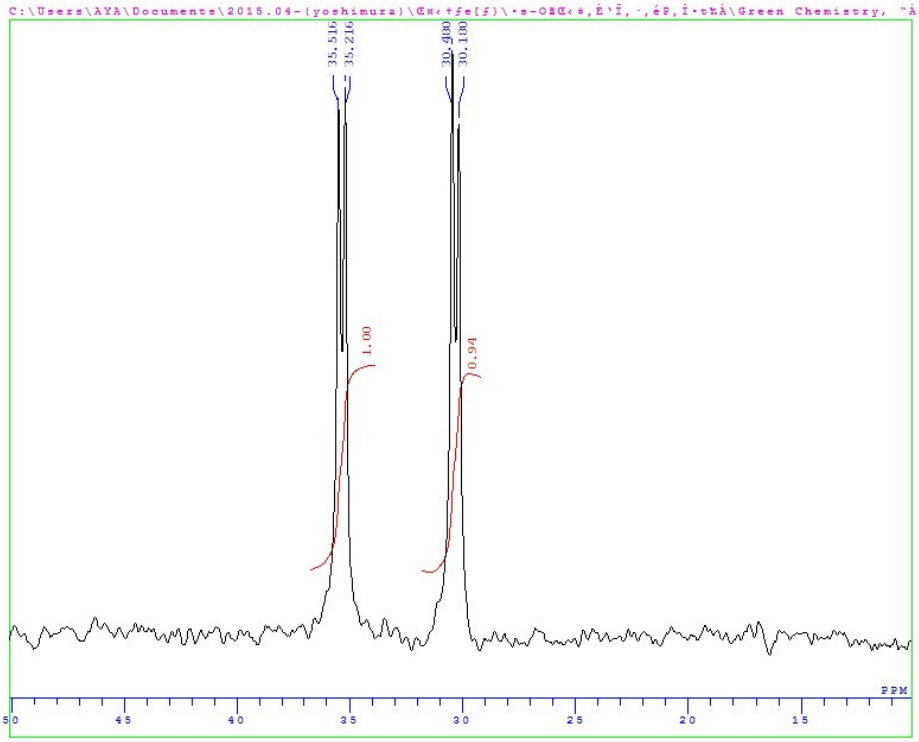
^{1}H NMR





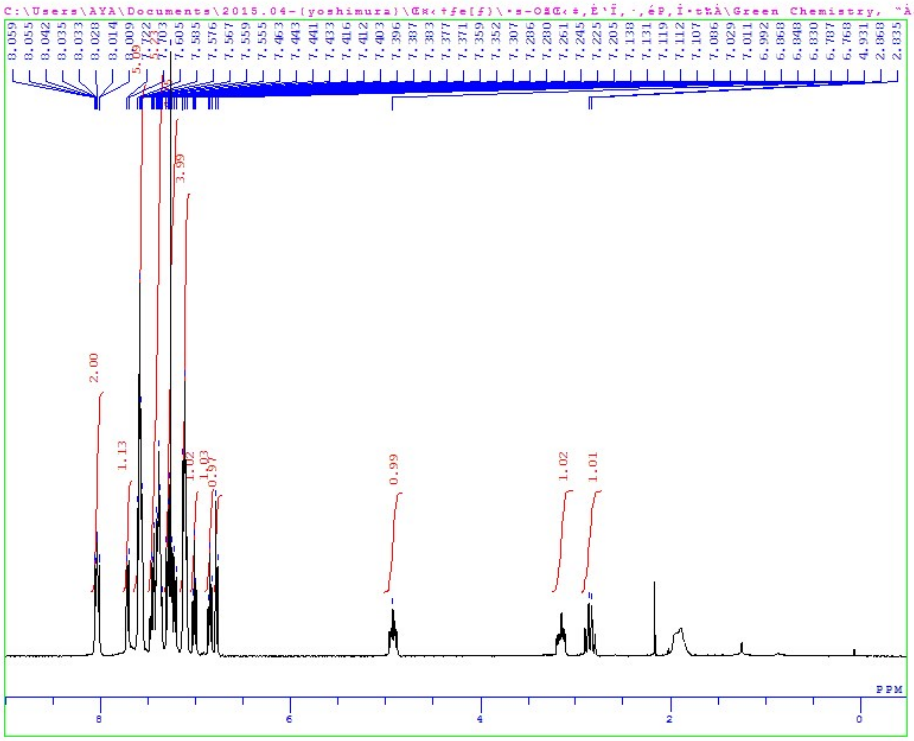


^{13}P NMR

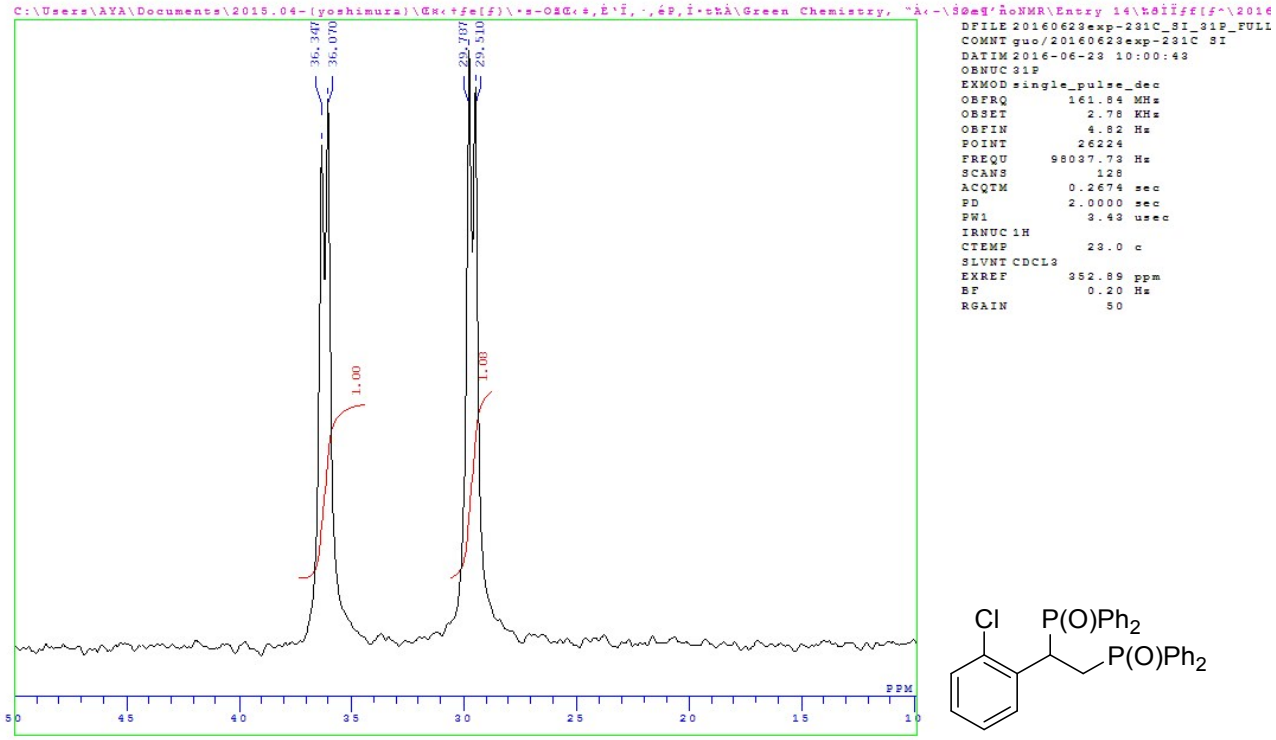


1p

^{1}H NMR

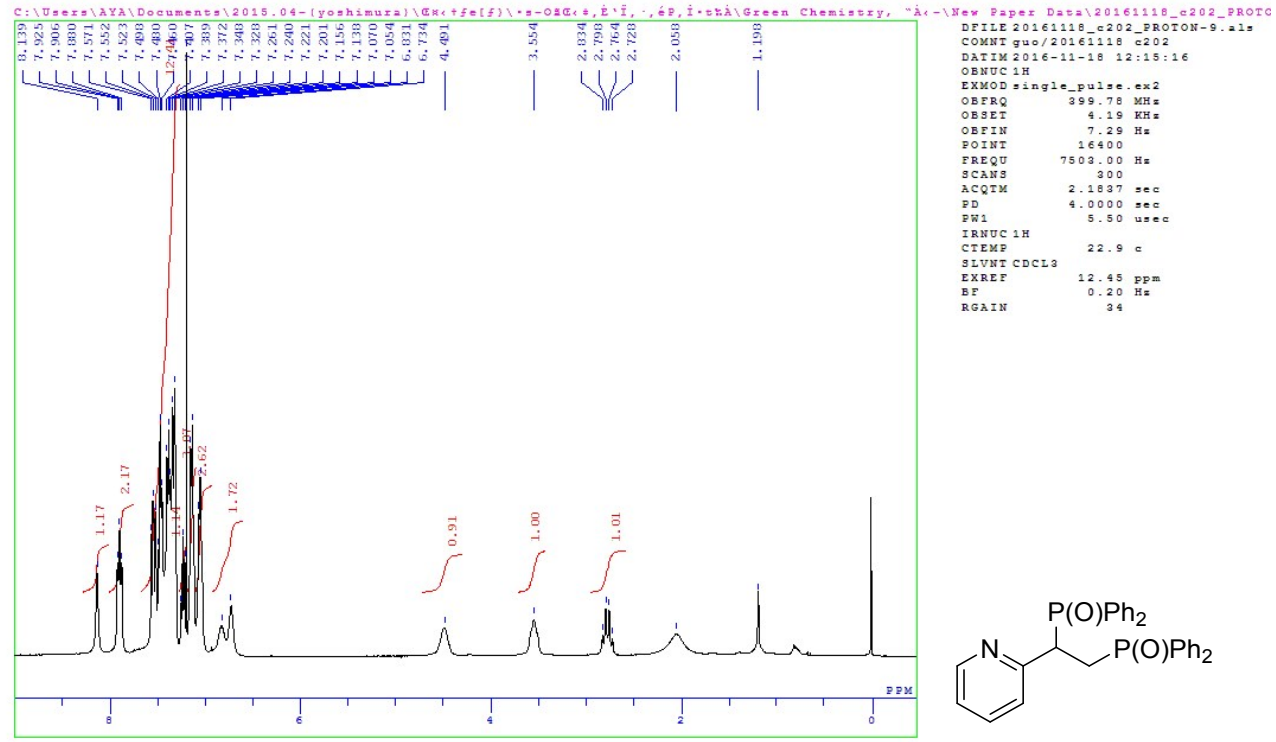


^{31}P NMR

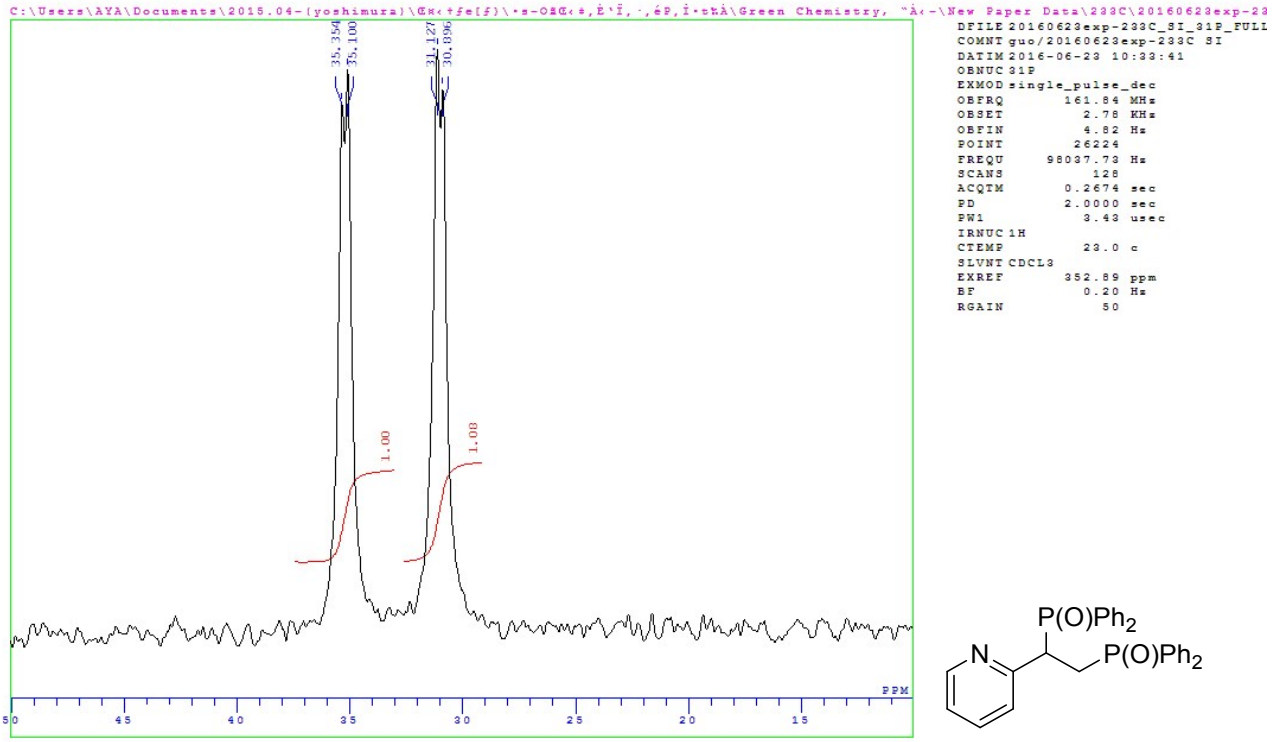


1q

^{1}H NMR

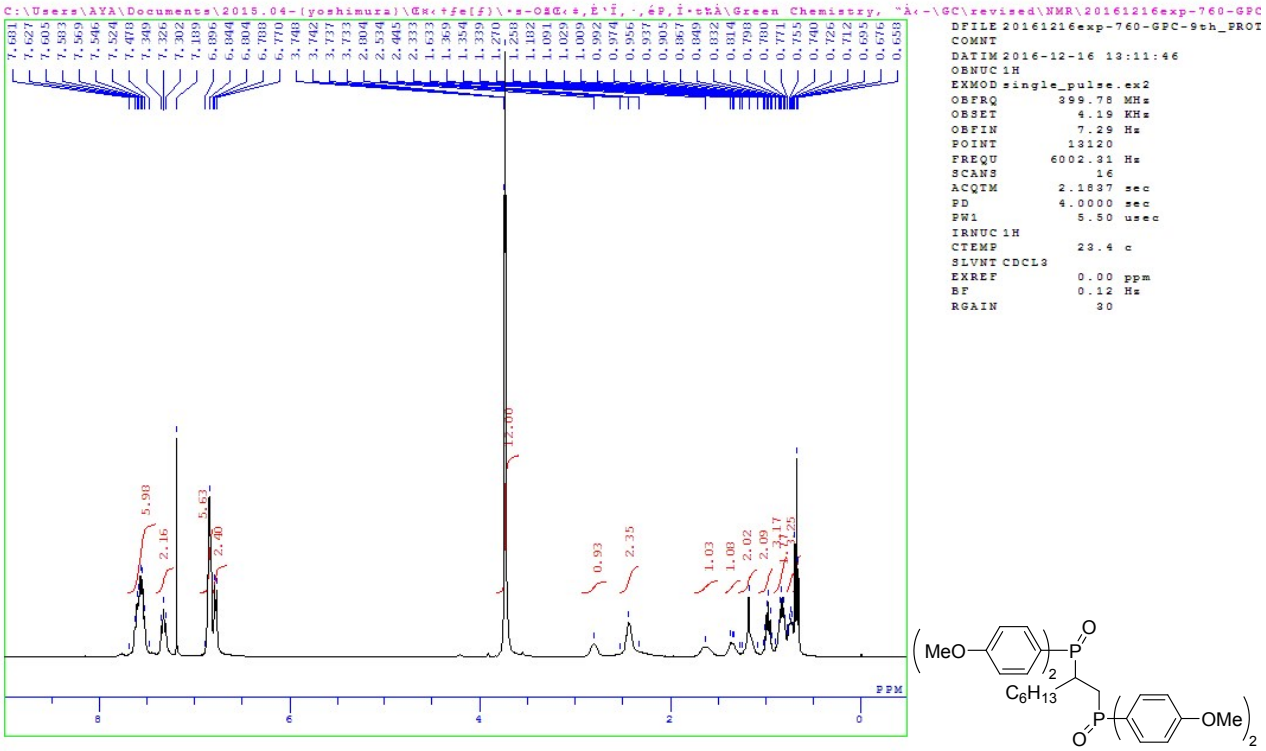


^{31}P NMR

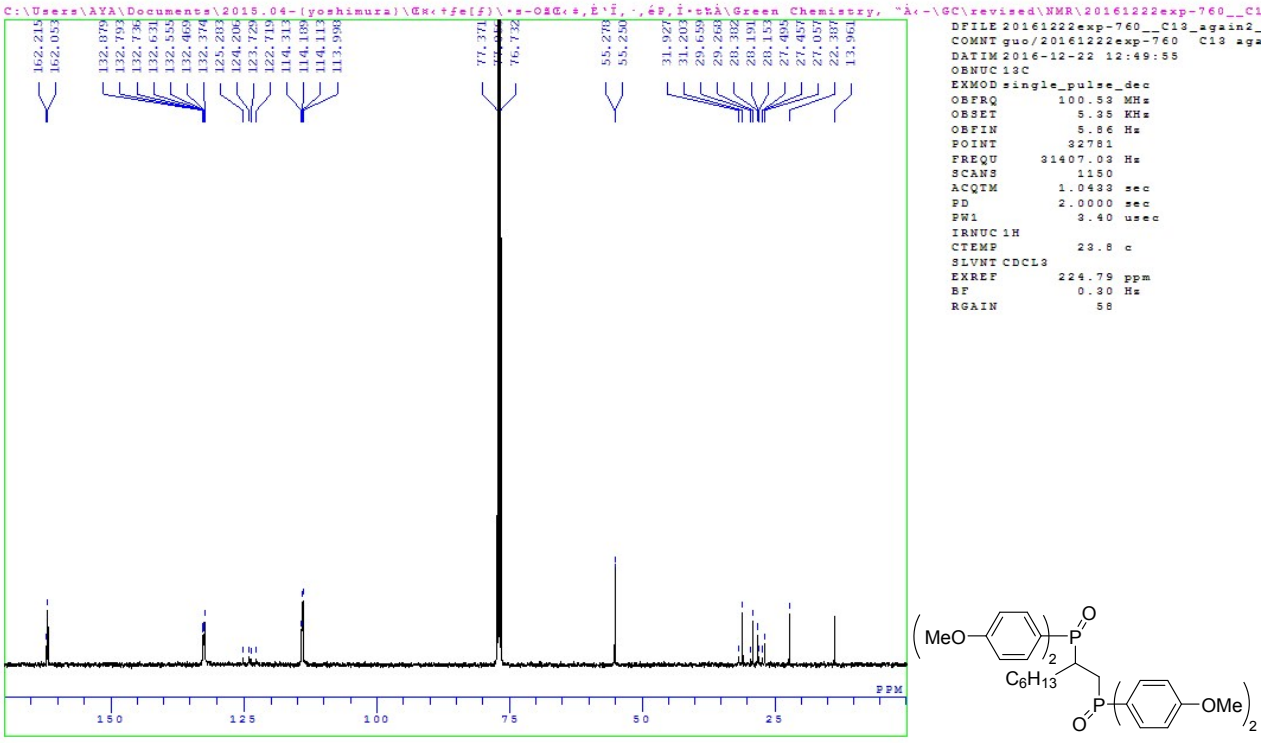


1r

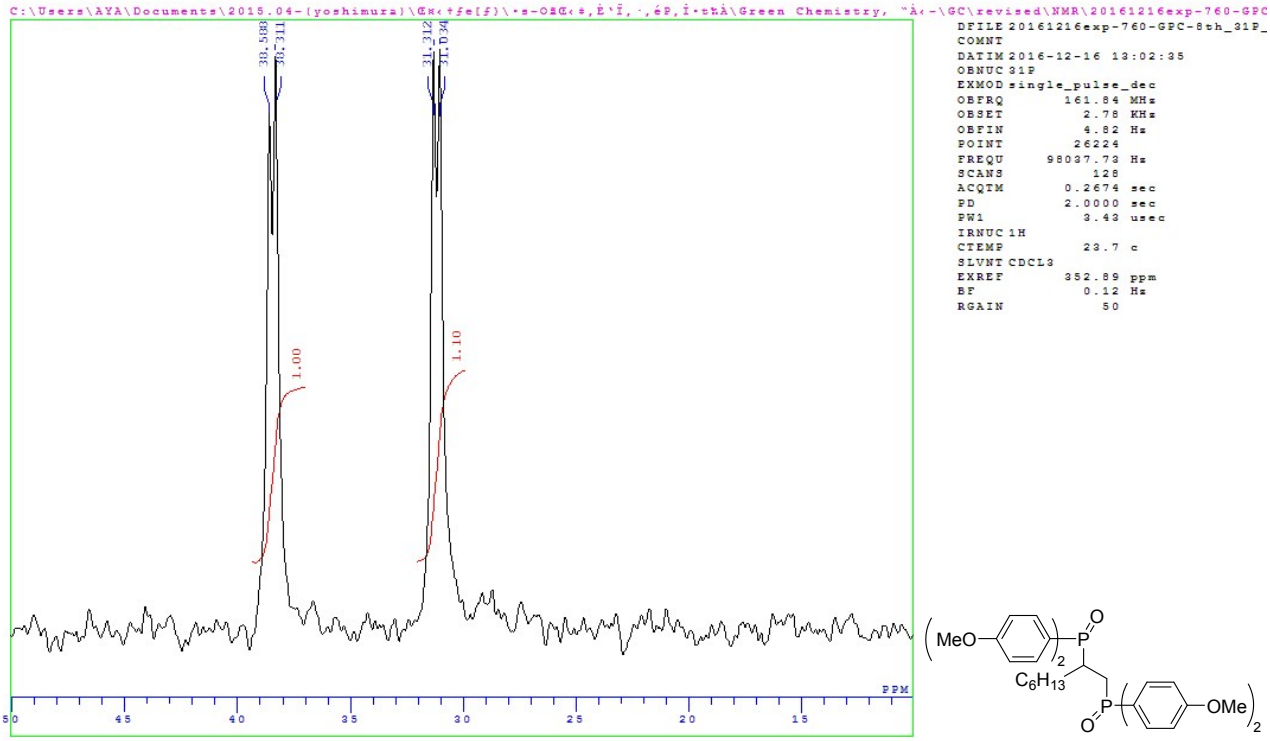
^{1}H NMR



^{13}C NMR

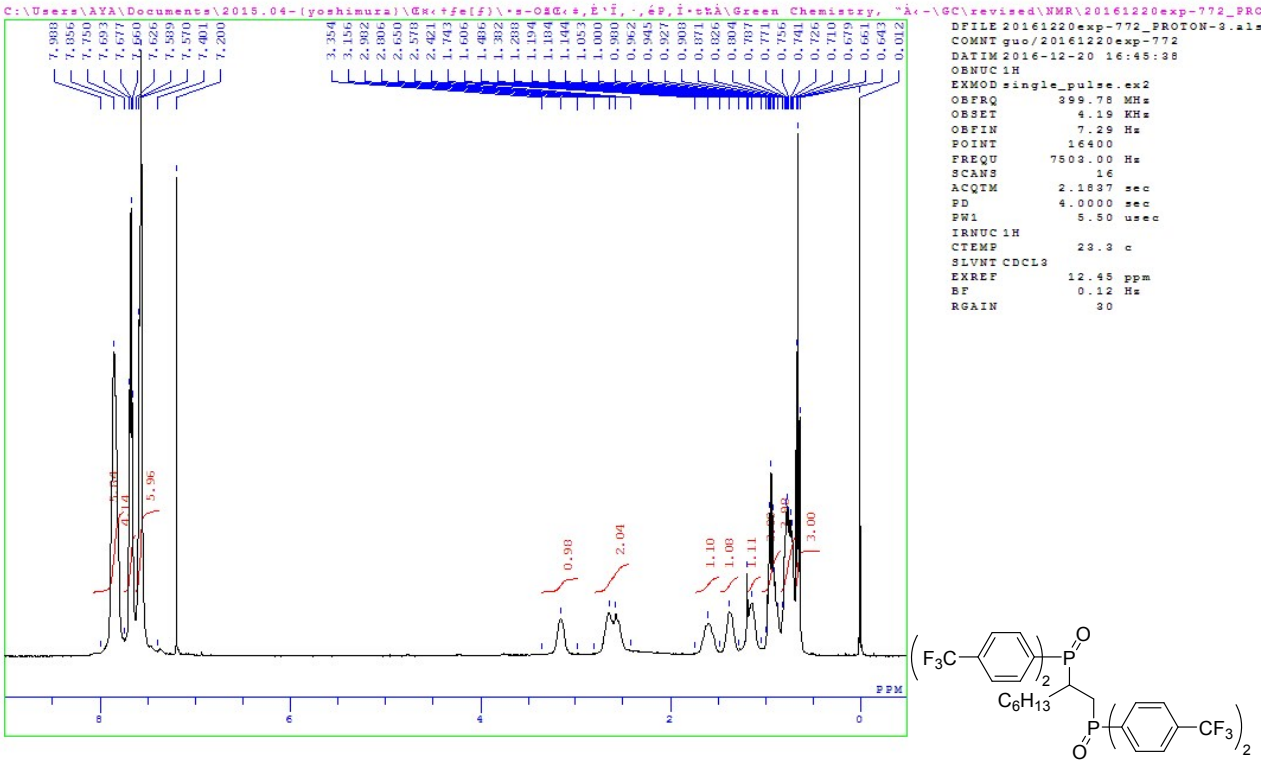


^{31}P NMR

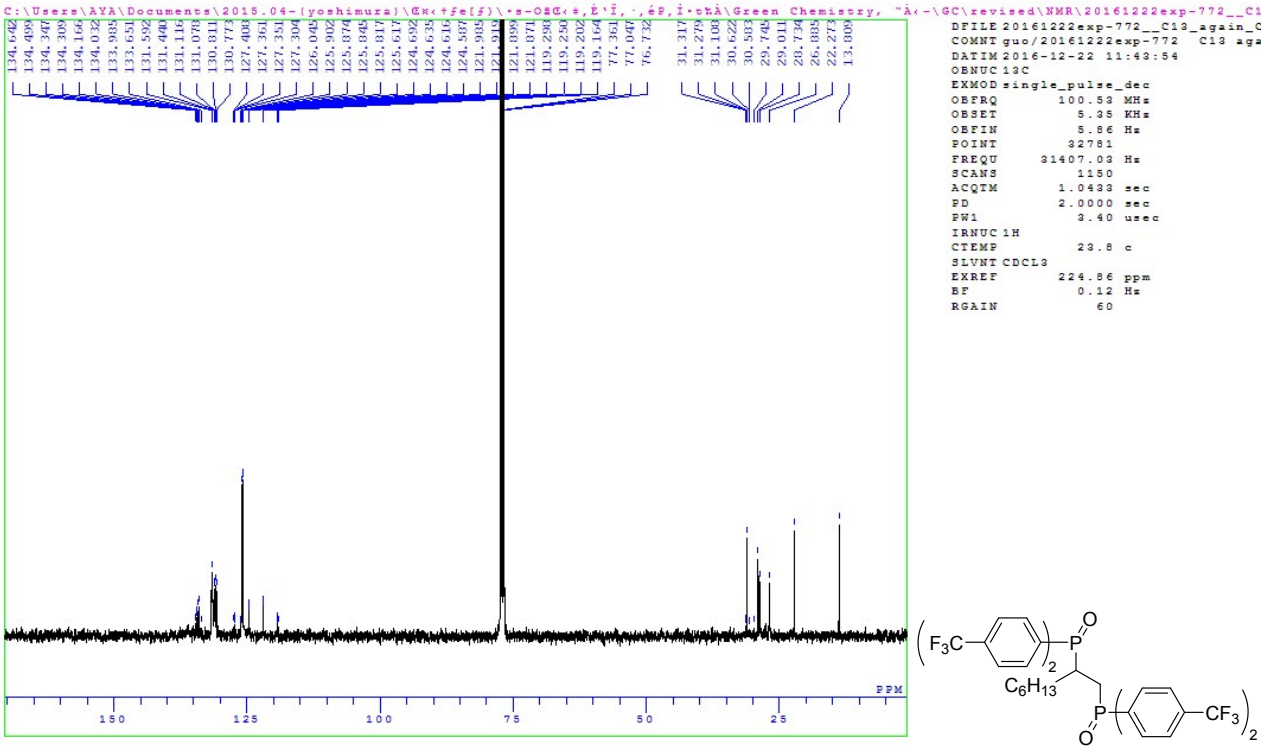


1s

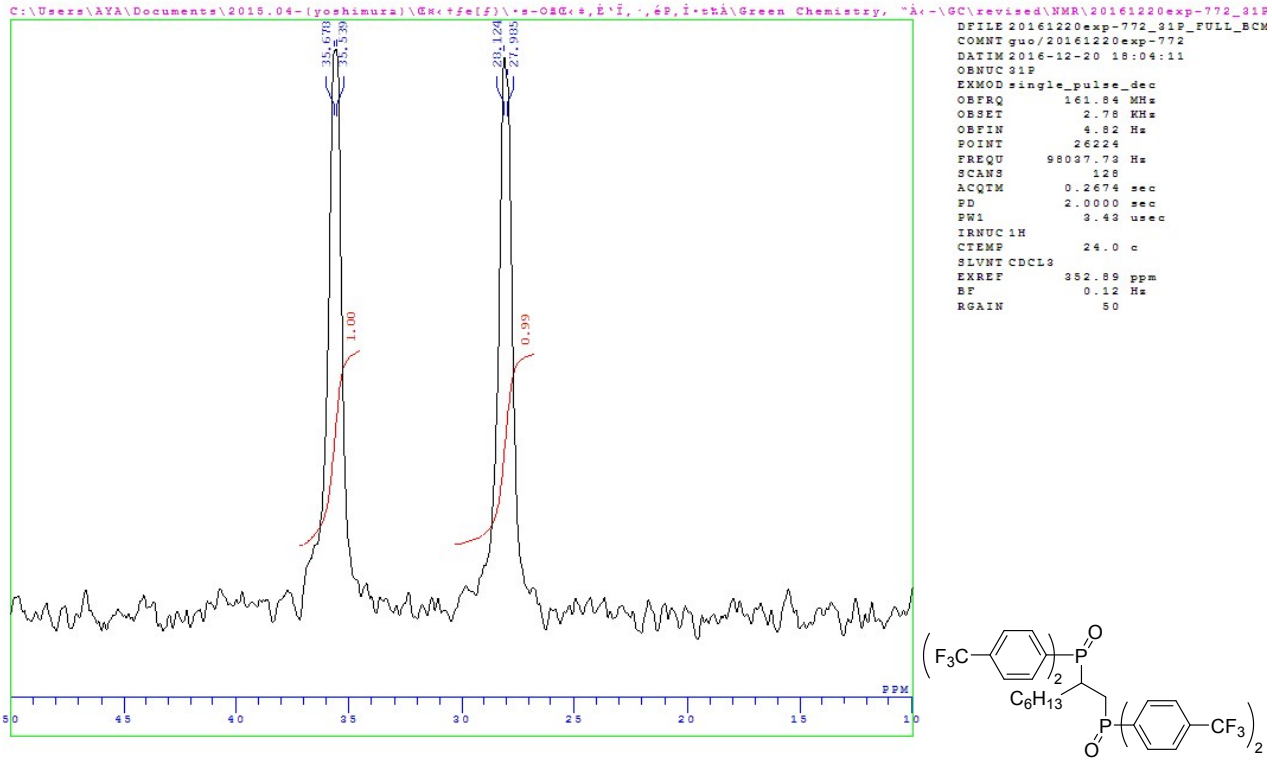
^{1}H NMR



^{13}C NMR

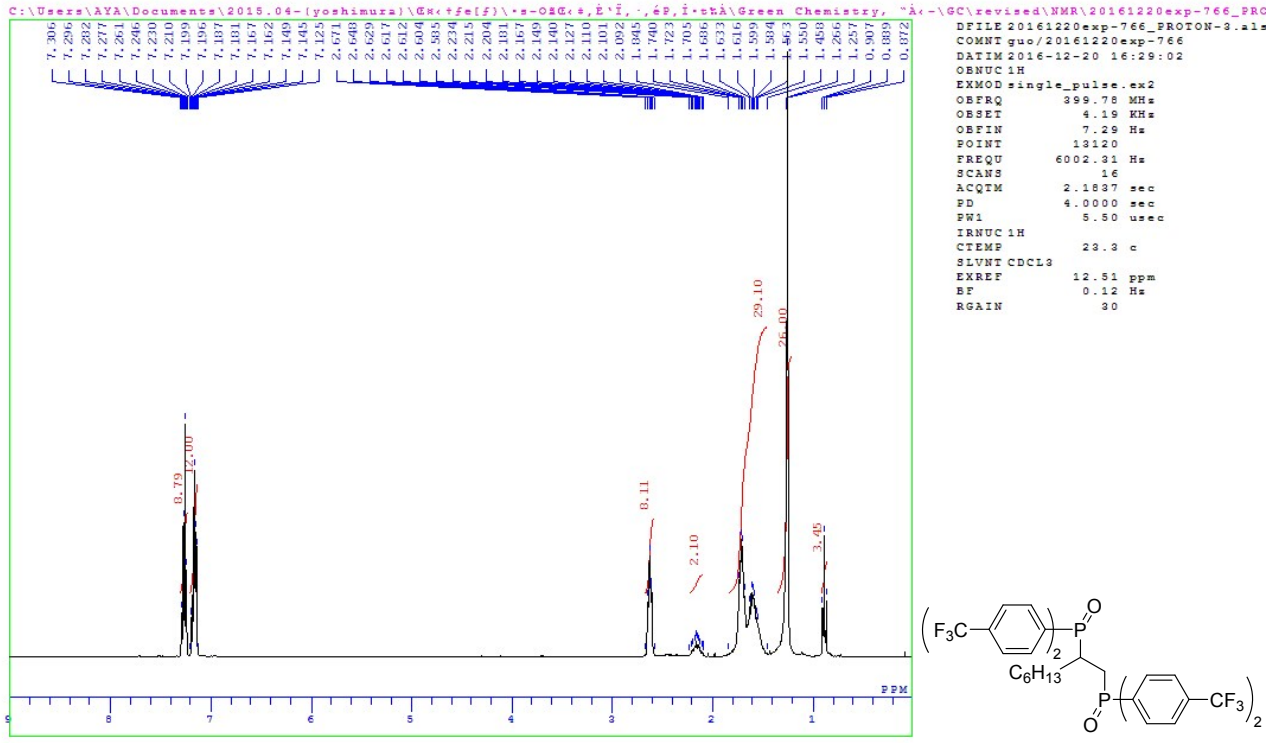


^{31}P NMR

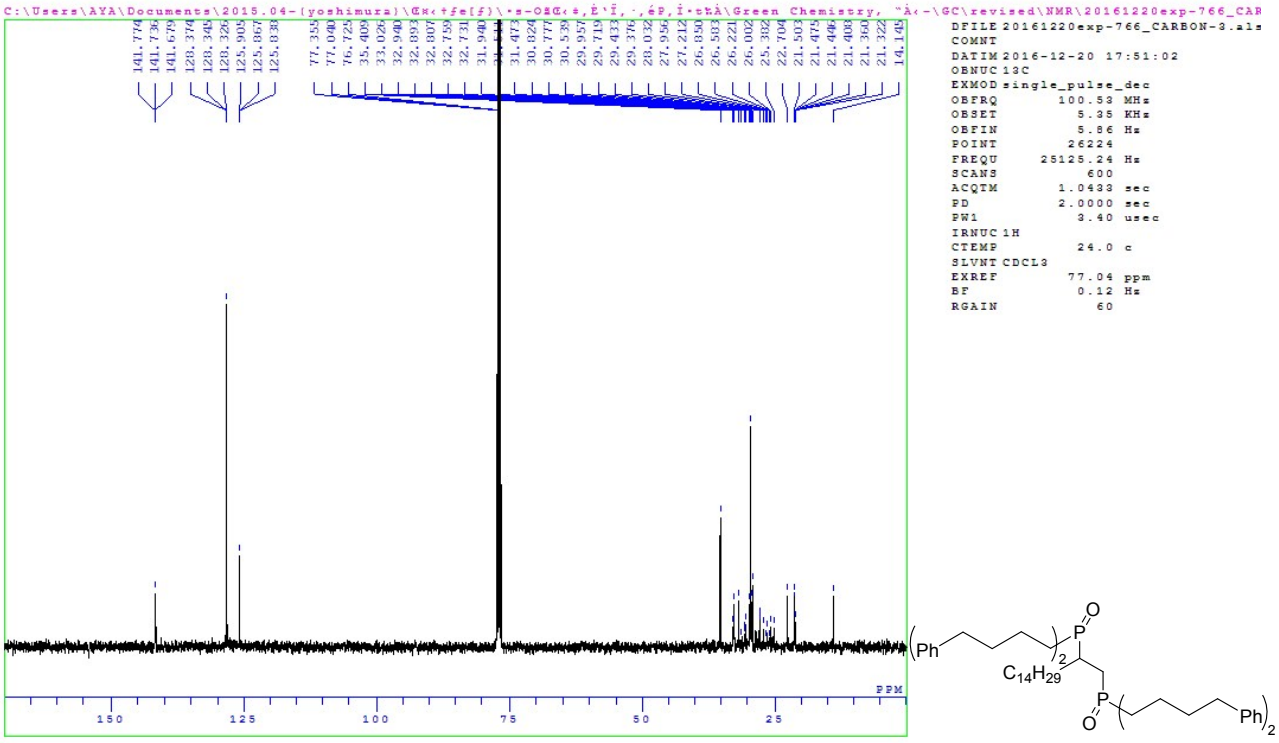


1t

^{1}H NMR



^{13}C NMR



^{31}P NMR