Supporting Information

Palladium-Catalyzed $R_2(O)P$ Directed $C(sp^2)$-H Acetoxylation

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Supporting Information

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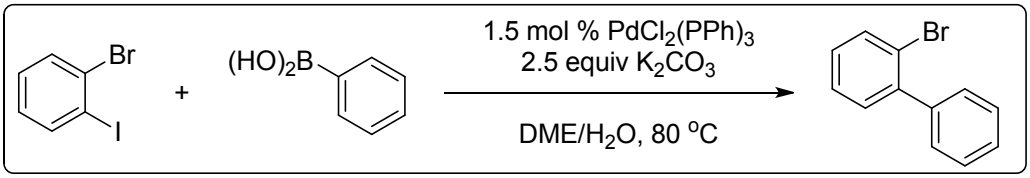
I. General Methods and Materials

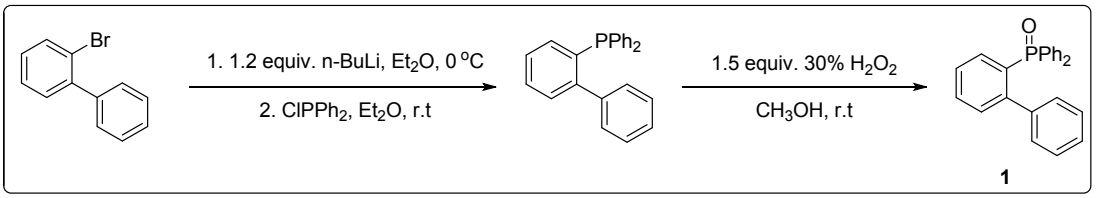
^1H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^1H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{31}P NMR spectra and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = double, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis employing a Darcel Chiracel AD-H column. Substrates [1,1'-biphenyl]-2-yldiphenylphosphine oxide were prepared according to literature methods A[1] and methods B[2].

II. Typical Procedures for the Synthesis of Substrates

Method A



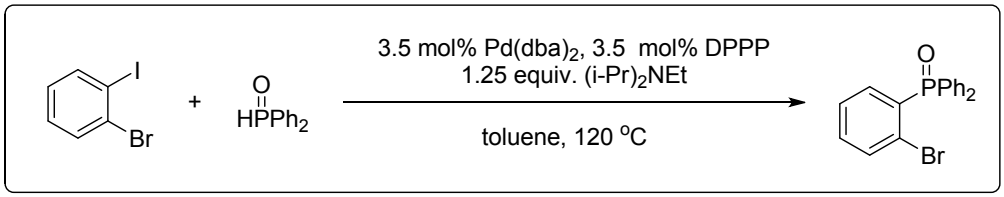
Water (4.0 mL) and DME (30.0 mL) were poured into a round-bottomed flask, fitted with a condenser and argon flow, and bubbled through with argon. Potassium carbonate (3.45 g, 25 mmol), 1-bromo-2-iodobenzene (2.8 g, 10.0 mmol), substituted phenylboronic acid (10.5 mmol), and bis(triphenylphosphine)palladium(II) chloride (105 mg, 0.15 mmol) were added to the mixture, which was stirred at 80 °C for 5 h in an oil bath until substrate disappeared as judged by TLC. The reaction mixture was allowed to cool to r.t., DME was evaporated, and water (40.0 mL) and ether (20.0 mL) were added. The layers were separated and the aqueous layer was extracted with diethylether (3 x 20.0 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and evaporated in vacuo to obtain a yellow oil, which was purified further using column chromatography on silica gel (eluent: heptane 30% EtOAc in heptane). The title compound was isolated as a white amorphous solid (2.10 g, 90%).

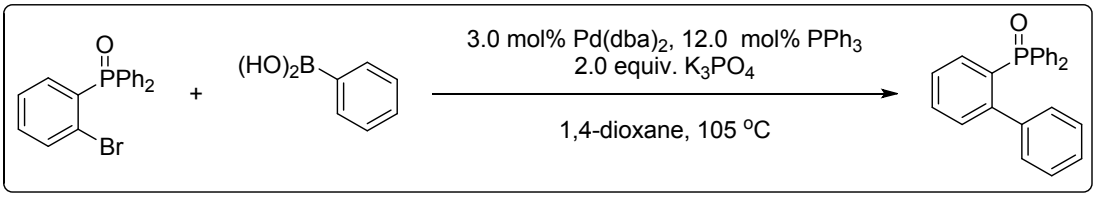


4.0 mL (9.60 mmol) of *n*-BuLi in *n*-hexane (2.40 M) were added dropwise to a suspension of (8.0 mmol) of 2-bromo-1, 1'-biphenyl in 24 mL of diethyl ether at 0 °C. The resulting beige-colored suspension was stirred for an additional 2 h at 0 °C. Then, freshly distilled Ph_2PCl (1.77 g, 8.0 mmol) was added dropwise in diethyl ether (16.0 ml). The mixture was then stirred at r.t. for 1 h, filtered and solvent was removed in vacuo to yield a residue, which was used without futher purification. To the residue in MeOH (36.0 ml) was added dropwise at < 40℃ 30 % aq. H_2O_2, solution (1.63 ml, 16.0 mol). The resulting clear solution was stirred at r.t. for 1 h, treated for 1 h with sat. Na_2SO_3, solution (8.0 ml) and 1N HCl solution (5.0 ml), and the mixture was concentrated at the rotavapor to remove the

MeOH. The aqueous layer was extracted with CH_2C1_2 (3 × 20 ml). The extract was washed with brine and dried over $MgSO_4$, then concentrated under reduced pressure and purified by silica gel flash chromatography to afford the product as white powder.

Method B:





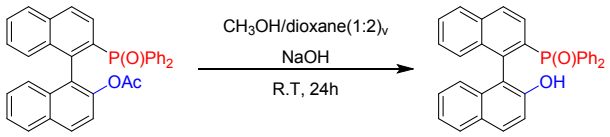
An oven-dried, 100 mL Schlenk tube equipped with a magnetic stir bar, a rubber septum and a reflux condenser was charged with diphenylphosphine oxide (6.86 g, 34.0 mmol), $Pd(dba)_2$ (0.56 g, 1.2 mmol) and DPPP (0.42 g, 1.2 mmol) in 50.0 mL toluene. 1,2-Bromo-iodobenzene (5.2 mL, 41 mmol), and $(i\text{-}Pr)_2NEt$ (7.4 mL, 43 mmol) was added via syringe and the mixture refluxed at 120℃ for 4 days. After cooling to room temperature, the product was partitioned between 100.0 mL $CHCl_3$ and 50.0 mL H_2O. The phases were separated and the organic layer was washed with brine (50.0 mL), dried over $MgSO_4$ and evaporated in vacuo to give a pale orange precipitate. Purification by flash chromatography (2:1 EtOAc/hexane) gave the title compound as a white solid (7.90 g, 65% yield)

To a Schlenk tube were charged (2-bromophenyl)diphenylphosphine oxide (0.50 g, 1.4 mmol) and arylboronic acid (1.4 mmol) together with $Pd(dba)_2$ (24 mg, 0.04 mmol), PPh_3 (44 mg, 0.17 mmol) and K_3PO_4 (0.59 g, 2.8 mmol) in 5.0 mL of dioxane under an atmosphere of argon. The Schlenk tube was stirred at 105℃ for 12 h and cooled to room temperature. The mixture was diluted with water (10 mL) and extracted with $CHCl_3$ (3×20.0 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by flash chromatography (2:1 EtOAc/hexane).

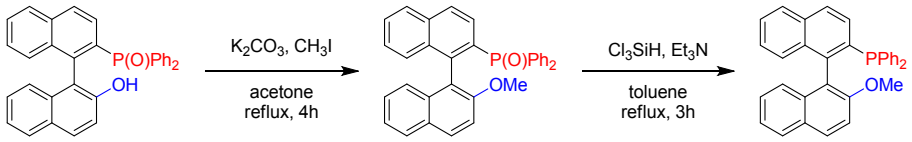
III. General procedures for the preparation of the acetoxylated compounds:

Under air atmosphere, 2-diphenylphosphino-2'-methylbiphenyl (**1a)** (73.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 10.0 mol %) and $PhI(OAc)_2$ (193.2 mg, 0.60 mmol, 3.0 equiv) were added to tube containing a magnetic stir bar. After sealed tube, 2.0 mL CF_3CH_2OH was added using a syringe. The mixture was stirred at 100 ℃ in an oil bath until substrate disappeared as judged by TLC. After cooling to room temperature, the solution was removed in vacuo to yield a residue, which was purified by silica gel using (1:1 EtOAc/hexane) to afford pure **2a** as oil (73 mg, 86%).

IV. Typical procedure for the preparation of (*R*)-MeO-MOP

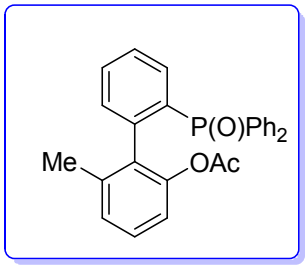


To a mixture of (*R*)-2'-(diphenylphosphoryl)-[1,1'-binaphthalen]-2-yl acetate (**2v**) (102.4 mg, 0.2 mmol) in CH_3OH (1 mL) and dioxane (2 mL) was added NaOH (12.0 mg, 0.3 mmol). The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the crude product was purified by chromatography on silica gel with EtOAc/hexane (1:2) to yield (*R*)-(2'-hydroxy-[1, 1'-binaphthalen]-2-yl)diphenylphosphine oxide (**2va**) as a white solid (68.8 mg, 73%)[3].

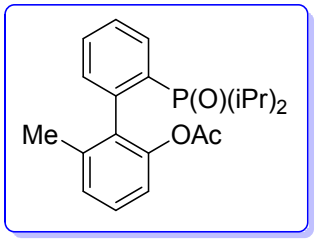


To a mixture of (*R*)-(2'-hydroxy-[1, 1'-binaphthalen]-2-yl)diphenylphosphine oxide (**2va**) (92.3 mg, 0.2 mmol) and K_2CO_3 (170 mg, 1.23 mmol) in acetone (3 mL) was added CH_3I (85.0 mg, 0.60 mmol). The mixture was stirred and heated under reflux for 4 h and cooled to room temperature. The solvent was removed and the residue was dissolved in a saturated solution of Na_2CO_3. The aqueous solution was extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with EtOAc/hexane (1:4) to yield (*R*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphine oxide (*R*-**2ub**) as a white solid (91.9 mg, 95%). To a mixture of (*R*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphine oxide (**2vb**) (96.8 mg, 0.2 mmol) and triethylamine (0.56 mL, 4.0 mmol) in xylene (3.3 mL) was added trichlorosilane (0.10 mL, 1.00 mmol) at 0 °C, the mixture was refluxed under Ar for 3 h. After being cooled to room temperature, the mixture was concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with EtOAc/hexane (1:6) to yield (*R*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphine ((*R*)-MeO-MOP) as a white solid (72.1 mg, 77%)[4].

V. Characterization of the Products

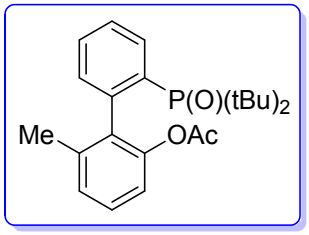


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.78 (s, 3.0 H), 1.95 (s, 3.0 H), 6.59 (d, *J* = 8.0 Hz, 1.0 H), 6.93 (d, *J* = 4.0 Hz, 1.0 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 7.13-7.16 (m, 1 H), 7.26-7.32 (m, 2 H), 7.36-7.40 (m, 4 H), 7.42-7.56 (m, 6 H), 7.61-7.66 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.55, 20.65, 118.86, 127.06, 127.14, 127.18, 127.81, 127.93, 128.14, 128.26, 128.54, 131.21, 131.24, 131.30, 131.46, 131.48, 131.55, 131.65, 131.68, 131.72, 131.81, 131.97, 132.06, 132.31, 132.62, 132.66, 132.72, 132.99, 133.71, 133.75, 133.83, 139.13, 141.30, 141.38, 148.04, 169.38; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 26.65; **MS (ESI):** found $[M+H]^+$427.14.

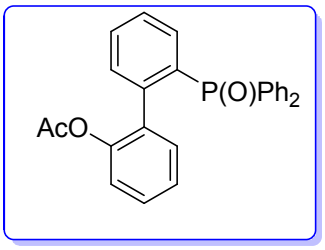


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.05-1.21 (m,12.0 H), 1.82 (s, 3.0 H), 2.06 (s, 3.0 H), 2.06-2.13 (m,1H), 2.19-2.28(m,1H),6.91(d, *J* = 8.0 Hz, 1.0 H), 7.13-7.17 (m, 2.0H), 7.27 (t, *J* = 12.0 Hz 1H), 7.42-7.52(m, 2H), 7.62 (t, *J* = 20.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 15.69 (d *J* = 4.0 Hz), 16.98 (d *J* = 12.0 Hz), 20.47, 20.57, 26.33, 26.99, 27.48, 28.14, 119.12, 124.66, 126.76, 126.86, 127.21, 127.83, 128.19, 128.82, 129.80, 130.61, 130.73, 130.76,

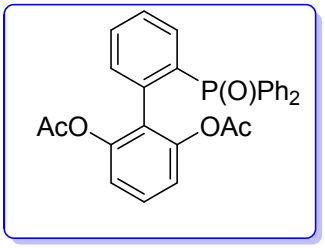
131.47, 131.57, 132.00, 132.09, 133.88, 133.91, 138.51, 141.75, 141.80, 148.03, 169.42; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 51.02; **MS (ESI):** found $[M+H]^+$359.17.



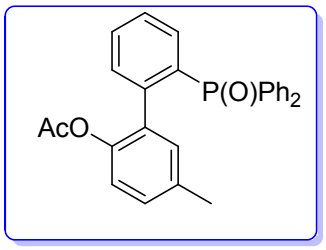
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.80 (s, 3.0 H),2.10 (s, 3.0 H), 6.85 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 7.15-7.18 (q, ,1 H), 7.22-7.27 (q, 1 H), 7.37-7.41 (m, 1 H), 7.45-7.49 (t, *J* = 16.0 Hz, 1.0 H),7.65-7.70 (t, *J* = 20.0 Hz, 1.0 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.59, 20.85, 27.53, 27.97, 37027, 37.55, 37.86, 38.13, 118.70, 125.59, 125.70, 126.95, 127.74, 130.26, 131.02, 131.49, 131.61, 132.83, 132.92, 134.49, 134.51, 137.71, 143.48, 143.51, 147.51, 169.63; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 53.30; **MS (ESI):** found $[M+H]^+$387.20.



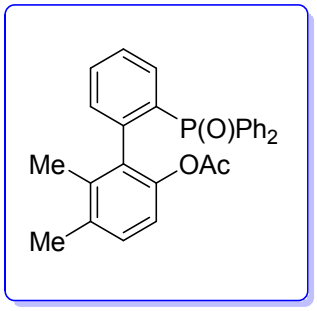
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.95 (s, 3 H), 6.68-6.70 (t, 1 H), 7.00-7.04 (m, 1 H), 7.11-7.15 (m, 1 H), 7.22-7.31 (m, 4 H), 7.35-7.41 (m, 4 H), 7.45-7.51 (m, 5 H), 7.63-7.68 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.74, 121.77, 124.80, 127.15, 127.27, 127.87, 127.99, 128.19, 128.31, 128.96, 131.11, 131.14, 131.23, 131.33, 131.41, 131.55, 131.65, 131.96, 132.06, 132.14, 132.45, 132.6, 133.17, 133.44, 133.82, 133.93, 142.09, 142.17, 147.60; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.31; **MS (ESI):** found $[M+H]^+$413.14.



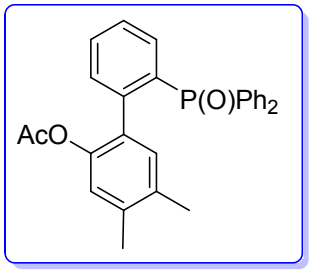
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.84 (s, 6 H), 6.82-6.84 (d, *J* = 8.0 Hz), 7.16-7.20 (m, 2 H), 7.22-7.27 (m, 1 H), 7.33-7.37 (m, 4 H), 7.41-7.47 (m, 3 H), 7.49-7.53 (m, 1 H), 7.55-7.60 (m, 5 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.50, 119.43, 126.73, 126.77, 127.49, 127.61, 127.93, 128.05, 128.89, 131.24, 131.26, 131.34, 131.37, 131.88, 131.91, 131.97, 132.01, 132.40, 132.45, 133.46, 133.49, 133.57, 136.80, 136.87, 148.95, 168.71; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.33; **MS (ESI):** found $[M+H]^+$471.14.



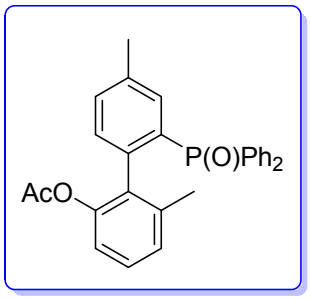
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.95 (s, 3 H), 2.15 (s, 3 H),6.62 (d, *J* = 8.0 Hz, 1 H), 6.90 (d, *J* = 4.0 Hz, 1 H), 6.93 (s, 1 H), 7.23 (q, J_1 = 4.0 Hz J_2 = 8.0 Hz), 7.27-7.31 (m, 2 H), 7.36-7.39 (m, 2 H), 7.45-7.56 (m, 5 H), 7.61-7.66 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.67, 20.74, 121.51, 127.07, 127.19, 127.88, 128.00, 128.14, 128.26, 129.50, 131.15, 131.29, 131.32, 131.29, 131.32, 131.39, 131.48, 131.58, 131.61, 131.88, 131.98, 132.04, 132.19, 132.63, 132.91, 133.23, 133.68, 133.80, 133.92, 134.31, 142.19, 142.27, 145.54, 169.86; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.39; **MS (ESI):** found $[M+H]^+$427.14.



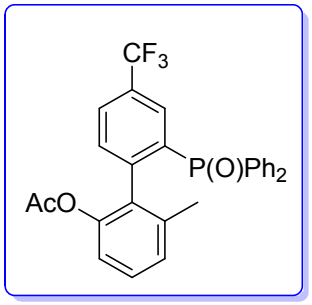
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.69 (s, 3 H), 1.80 (s, 3 H), 2.09 (s, 3 H),6.54 (d, *J* = 8.0 Hz, 1 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 7.12 (q, *J* = 4.0 Hz, 1 H), 7.26-7.30 (m, 2 H), 7.34-7.41 (m, 4 H), 7.44(t, *J* = 4.0 Hz,1 H), 7.48 (t, *J* = 4.0 Hz,1 H), 7.50-7.53 (m, 3 H), 7.57-7.66(m,3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:17.52, 19.82, 20.44, 118.40, 126.92, 127.05, 127.59, 127.71, 127.91, 128.02, 129.91, 131.08, 131.11, 131.31, 131.33, 131.46, 131.56, 131.63, 131.72, 131.81, 131.91, 132.19, 132.22, 132.48, 132.60, 133.51, 133.68, 133.79, 133.91, 136.99, 141.63, 141.71, 146.24, 169.57; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.33; **MS (ESI):** found $[M+H]^+$441.16.



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.96 (s, 3 H), 2.03 (s, 3 H), 2.11 (s, 3 H), 6.48 (s, 1 H), 6.87(s, 1 H), 7.22-7.29 (m, 3 H), 7.36-7.39 (m, 4 H), 7.45-7.55 (m, 5 H), 7.60-7.65 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:18.87, 19.41, 20.66, 122.60, 126.92, 127.04, 127.65, 127.77, 127.98, 128.10, 129.49, 129.53, 130.89, 131.23, 131.32, 131.48, 131.58, 131.79, 131.88, 132.20, 132.61, 132.66, 132.91, 133.10, 133.24, 133.70, 133.76, 133.87, 137.40, 142.02, 142.10, 145.41, 169.97; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.60; **MS (ESI):** found $[M+Na]^+$463.14.

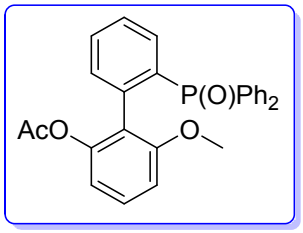


Dark oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.84 (s, 3 H), 1.91 (s, 3 H), 2.35 (s, 3 H), 6.56 (d, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 7.00-7.07 (m, 2 H), 7.26-7.29 (m, 2 H), 7.33-7.40 (m, 3 H), 7.43 (s, 1 H), 7.45-7.51 (m, 4 H), 7.60-7.65 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.51， 21.05， 21.19， 118.84， 127.03， 127.72， 127.84， 128.01， 128.13， 128.32， 130.49， 131.14， 131.17， 131.40， 131.51， 131.66， 131.76， 131.8， 131.98， 132.51， 132.54， 132.77， 133.57， 134.16， 134.28， 136.80， 136.92， 137.38， 138.01， 138.09， 139.12， 148.08， 169.28; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 23.00; **MS (ESI):** found $[M+H]^+$441.16.

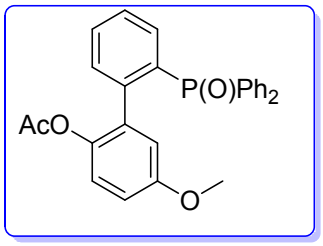


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.80 (s, 3 H), 1.92 (s, 3 H), 6.61 (d, *J* = 8.0 Hz, 1 H), 6.95 (d, *J* = 8.0 Hz, 1 H),7.13 (t, J_1 = 8.0 Hz 1 H), 7.29-7.35 (m, 3 H), 7.35-7.43 (m, 3 H), 7.44-7.53 (m, 3 H), 7.60-7.65 (m, 2 H), 7.78-

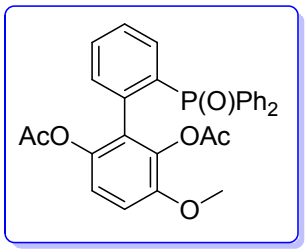
7.82 (m,2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.54, 20.57, 119.01, 122.23, 124.95, 127.28, 128.02, 128.14, 128.23, 128.26, 128.38, 128.51, 129.10, 129.37, 129.49, 129.70, 129.82, 130.24, 130.28, 130.32, 130.37, 130.40, 130.89, 131.37, 131.40, 131.58, 131.63, 131.66, 131.76, 131.88, 131.94, 131.97, 132.31, 132.41, 132.62, 133.29, 134.28, 138.86, 145.30, 145.37, 147.78, 169.14; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 25.71; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.74; **MS (ESI):** found $[M+H]^+$495.13.



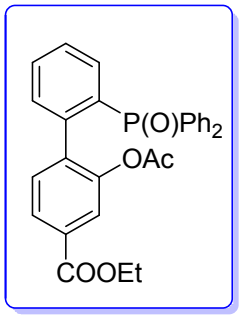
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.88 (s, 3 H), 3.37 (s, 3 H), 6.42 (d, J = 8.0 Hz, 1 H), 6.53(q, J_1 = 0.4 Hz, J_2 = 8.0 Hz), 7.12 (t, J = 8.0 Hz), 7.17-7.20 (m, 1 H), 7.27-7.35 (m, 4 H), 7.38-7.43 (m, 2 H), 7.49-7.55 (m, 4 H), 7.57-7.59 (m, 1 H), 7.63-7.66(m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.65， 55.07， 107.48， 114.22， 122.30， 122.33， 127.11， 127.23， 127.75， 127.84， 127.87， 127.96， 129.30， 131.10， 131.13， 131.21， 131.24， 131.45， 131.47， 131.53， 131.81， 131.91， 131.97， 132.04， 132.13， 132.22， 132.55， 132.72， 132.88， 133.76， 133.83， 133.91， 133.94， 138.12， 138.20， 149.08， 157.52， 169.43; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 27.84; **MS (ESI):** found $[M+H]^+$443.14.



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.98 (s, 3 H), 3.71 (s, 3 H), 6.56-6.65 (m, 2 H), 6.92 (d, J = 4.0 Hz, 1 H), 7.24-7.29 (m, 3H), 7.33-7.43 (M, 4H), 7.46-7.54 (m, 5 H), 7.67-7.72 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.73, 55.57, 115.82, 116.38, 122.69, 127.26, 127.39, 127.88, 128.00, 128.23, 128.35, 131.06, 131.16, 131.31, 131.40, 131.46, 131.56, 131.94, 132.03, 132.35, 132.57, 132.87, 132.91, 133.01, 133.38, 134.07, 134.18, 141.04, 142.00, 142.08, 155.98, 170.07; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.79; **MS (ESI):** found $[M+H]^+$443.14.

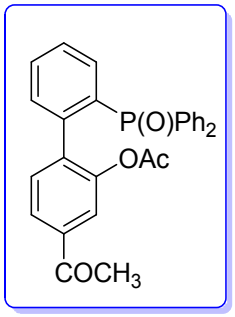


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.98 (s, 3 H), 1.90 (s, 3 H),) δ: 1.98 (s, 3 H), 3.72 (s, 3 H), 7.15-7.18（m, 1 H）, 7.28-7.44 (M, 7 H), 7.46-7.62 (m, 5H), 7.64-7.70(m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.14, 20.54, 56.03, 111.71, 119.44, 127.66, 127.78, 127.81, 127.94, 128.06, 128.14, 128.18, 131.26, 131.29, 131.33, 131.74, 131.83, 131.93, 132.03, 132.13, 132.33, 132.69, 132.81, 133.66, 133.73, 133.77, 133.85, 136.53, 136.60, 137.64, 141.97, 148.71, 168.21, 169.13; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.58; **MS (ESI):** found $[M+H]^+$501.14.

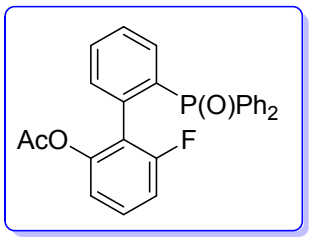


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.36-1.39 (t, J = 8.0 Hz, 3 H), 1.95 (s 3 H), 4.32-4.38 (m, 2 H), 7.20-

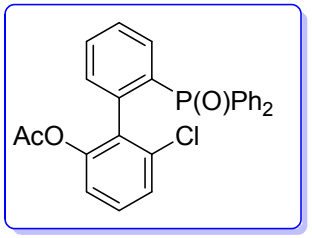
7.23 (m, 1 H), 7.27-7.33 (m, 3 H), 7.37-7.42 (m, 5 H), 7.45-7.55 (m, 5 H), 7.60-7.65 (m, 2 H), 7.69-7.72 (m,1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 14.27, 20.56, 61.05, 123.05, 125.84, 127.50, 127.62, 127.95, 128.07, 128.23, 128.35, 131.11, 131.22, 131.35, 131.45, 131.57, 131.89, 131.99, 132.26, 132.58, 132.92, 133.27, 133.71, 133.82, 137.31, 137.35, 141.18, 141.26, 147.64, 165.43, 169.32; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.36; **MS (ESI):** found $[M+H]^+$485.15.



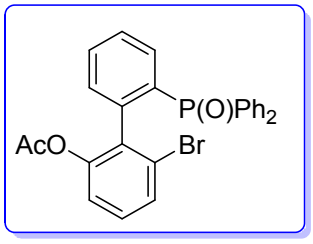
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.97 (s 3 H), 2.55 (s 3 H), 7.21-7.24 (q, J = 4.0 Hz, 1 H), 7.27-7.32 (m, 3 H), 7.38-7.43 (m, 5 H), 7.47-7.57 (m, 5 H), 7.62-7.68 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.59 26.60 119.51 121.63 124.71 127.57 127.70 127.95 128.07 128.21 128.27 128.39 131.02 131.12 131.29 131.34 131.39 131.52 131.61 131.63 131.77 131.90 131.99 132.10 132.53 132.65 132.80 133.14 133.75 133.86 137.57 137.63 141.09 141.16 147.96 169.36; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.44; **MS (ESI):** found $[M+H]^+$455.14.



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.85 (s, 3 H), 6.69-6.74 (m, 2 H), 7.14-7.19 (m, 1 H), 7.24-7.26 (m, 1 H), 7.30-7.36(m, 2 H), 7.36-7.49(m, 5 H), 7.51-7.64 (m,6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.54, 112.39, 112.61, 117.55, 117.58, 121.79, 122.03, 127.81, 127.93, 128.06, 128.08, 128.18, 128.20, 129.42, 129.51, 131.46, 131.48, 131.50, 131.53, 131.56, 131.59, 131.77, 131.87, 131.96, 132.06, 132.12, 132.24, 132.34, 133.04, 133.16, 133.69, 133.80, 135.45, 135.53, 149.23, 149.29, 158383, 161.29, 169.06; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.29; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.9(d, J = 5.2 Hz, 1 F); **MS (ESI):** found $[M+H]^+$431.12.

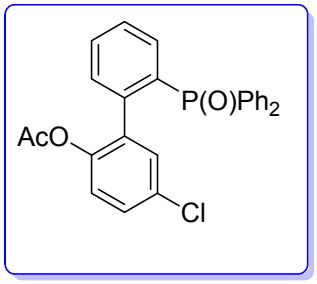


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ:1.79 (s, 3 H), 6.87-6.89 (m, 1 H), 7.10-7.16 (m,1 H), 7.18-7.21 (m, 1 H), 7.30-7.34 (m, 2 H), 7.36-7.42 (m, 4 H), 7.45-7.49 (m, 1 H), 7.51-7.59 (m, 4 H), 7.61-7.66 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.48, 120.43, 126.53, 127.64, 127.76, 128.05, 128.07, 128.17, 128.19, 129.29, 131.06, 131.45, 131.49, 131.52, 131.55, 131.90, 132.00, 132.04, 132.13, 132.43, 132.64, 132.73, 132.76, 133.46, 133.65, 133.68, 133.76, 134.67, 139.10, 139.17, 149.32, 168.97; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.33; **MS (ESI):** found $[M+Na]^+$469.07.

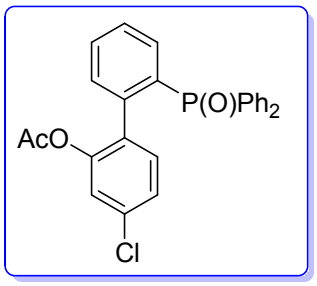


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ:1.77 (s, 3 H), 6.92-6.94 (m. 1 H), 7.08-7.12 (t, J = 8.0 Hz, 1 H), 7.18-7.21 (q, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 1 H), 7.31-7.35 (m, 3 H), 7.36-7.42 (m, 4 H), 7.44-7.50 (m, 2 H), 7.52-7.67 (m, 6 H);

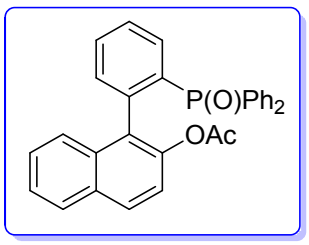
^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.45, 121.03, 124.84, 127.61, 127.73, 128.06, 128.19, 129.65, 129.68, 130.72, 131.48, 131.50, 131.73, 131.99, 132.05, 132.09, 132.15, 132.23, 132.51, 132.78, 133.55, 133.60, 133.72, 133.81, 134.61, 134.64, 140.94, 141.01, 149.12, 168.94; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.35; **MS (ESI):** found $[M+H]^+$493.03.



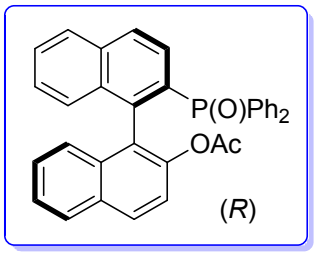
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.95 (s, 3 H), 6.73-6.75 (d, *J* = 8.0 Hz, 1 H), 7.08-7.12 (m, 2 H), 7.19-7.22 (m, 1 H), 7.31-7.34 (m, 1 H), 7.35-7.43 (m, 4 H), 7.44-7.54 (m, 4 H), 7.56-7.64 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.62, 123.01, 127.51, 127.63, 127.76, 127.88, 128.04, 128.14, 128.21, 128.34, 128.79, 129.76, 130.05, 130.93, 131.03, 131.30, 131.36, 131.39, 131.45, 131.56, 131.59, 131.72, 131.81, 131.88, 131.92, 132.01, 132.22, 132.80, 132.96, 133.26, 133.62, 133.73, 133.97, 134.01, 140.57, 140.65, 146.44, 169.31; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.24; **MS (ESI):** found $[M+H]^+$447.09.



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.95 (s, 3 H), 6.72 (d, *J* = 4.0 Hz, 1 H), 6.99-7.02 (m, 1 H), 7.19-7.24 (m, 2 H), 7.29-7.33 (m, 2 H), 7.38-7.45 (m, 4 H), 7.49-7.54 (m, 5 H),7.63-7.68 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.64, 122.27, 125.04, 127.47, 127.59, 127.95, 128.07, 128.27, 128.39, 131.09, 131.13, 131.23, 131.32, 131.45, 131.55, 131.58, 131.92, 131.97, 132.02, 132.14, 132.95, 132.98, 133.12, 133.18, 133.81, 133.93, 134.07, 140.99, 141.07, 147.99, 169.08; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 26.97; **MS (ESI):** found $[M+H]^+$447.09.

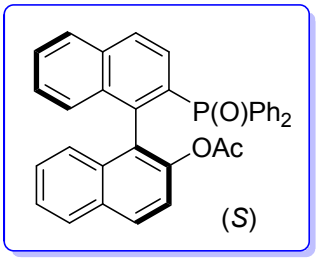


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.97 (s, 3 H), 7.01-7.03 (d, *J*=8.0 Hz, 1 H), 7.08-7.16 (m, 5 H), 7.18-7.28 (m, 4 H), 7.29-7.33 (m, 1 H), 7.38-7.44 (m, 4 H), 7.52-7.55 (m, 1 H), 7.58-7.64 (m, 3 H), 7.83-7.89 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:20.75, 120.93, 125.21, 126.09, 126.34, 127.45, 127.57, 127.60, 127.72, 127.79, 127.83, 128.59, 128.63, 129.62, 131.03, 131.06, 131.09, 131.18, 131.57, 131.59, 131.66, 131.69, 131.84, 132.34, 132.45, 132.53, 132.8, 133.30, 133.37, 133.54, 134.18, 134.28, 139.31, 139.39, 145.90, 169.50; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 27.45; **MS (ESI):** found $[M+H]^+$463.14.

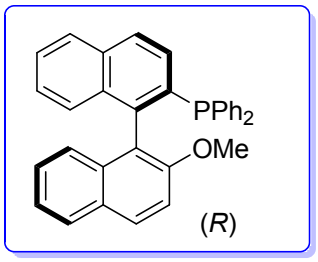


Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ:1.95 (s, 3 H), 6.91 (d, *J* = 4.0 Hz, 1 H), 7.08-7.17 (m, 6 H), 7.19-7.32 (m,

5 H), 7.39-7.46 (m, 4 H), 7.50-7.54 (t, *J* = 4.0 Hz, 1 H), 7.84-7.91(m, 2 H), 7.98- 8.00 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.75, 121.31, 125.23, 125.51, 125.55, 126.27, 127.01, 127.30, 127.41, 127.53, 127.61, 127.73, 127.98, 128.10, 128.19, 128.71, 128.82, 129.44, 129.80, 130.45, 130.89, 130.89, 130.96, 131.00, 131.51, 131.55, 131.60, 131.64, 132.10, 132.45, 132.66, 132.77, 133.14, 133.48, 133.66, 134.48, 138.68, 138.76, 146.93; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 28.44; **MS (ESI):** found $[M+H]^+$513.16; $[\alpha]^{22}_D$ = +4° (c = 1.0, $CHCl_3$). Enantiomeric excess is 99% determined by HPLC (Chiralcel AD-H, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min, 230 nm): major isomer: t_R = 54.90 min.



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ:1.78 (s, 3 H), 6.90-6.93 (d, *J* = 12.0 Hz,1 H), 7.09-7.25 (m, 9 H), 7.27-7.33 (m, 2 H), 7.39-7.45 (m, 4 H), 7.52-7.56 (t, *J* =8.0 Hz, 1 H), 7.66-7.71 (m, 2 H), 7.87-7.93 (m, 2 H), 8.00-8.02 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 20.76, 121.32, 125.24, 125.51, 126.28, 127.01, 127.30, 127.41, 127.53, 127.62, 127.73, 127.99, 128.11, 128.20, 128.71, 128.82, 129.81, 130.45, 130.89, 130.94, 130.97, 131.51, 131.55, 131.61, 131.65, 132.10, 132.45, 132.66, 133.14, 133.48, 133.66, 134.48, 138.68, 138.76, 146.93, 168.86; **^{31}P NMR** (162 MHz,$CDCl_3$) δ: 28.45; **MS (ESI):** found $[M+H]^+$513.16. $[\alpha]^{22}_D$ = -6° (c = 1.0, $CHCl_3$). Enantiomeric excess is 99% determined by HPLC (Chiralcel AD-H, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min, 230 nm): major isomer: t_R = 38.72 min.

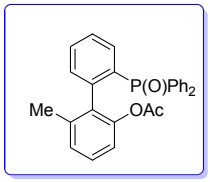


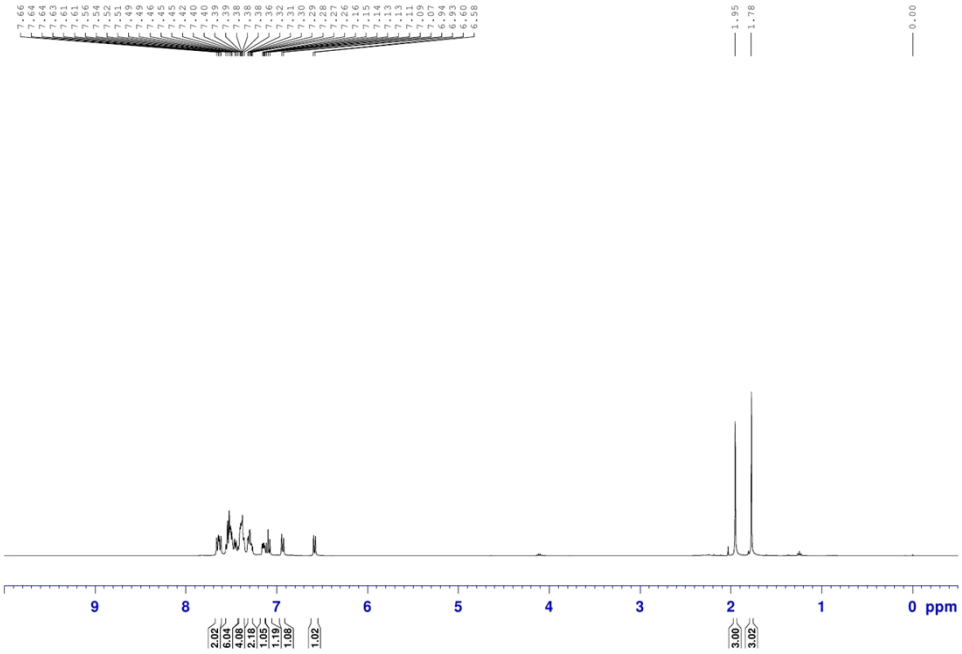
White power. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.32-3.33 (d, 3 H), 6.94 (d, *J* = 8.0 Hz, 1 H), 7.04-7.19 (m, 7 H), 7.20 (s, 1 H), 7.23-7.28 (m, 9 H), 7.37-7.45 (m, 2 H), 7.84-7.85 (d, 3 H), 7.96-7.99 (d, *J* = 12.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 55.44, 112.57, 121.71, 121.80, 123.34, 125.24, 126.32, 126.40, 126.66, 126.70, 126.73, 127.79, 127.89, 127.95, 128.00, 128.06, 128.07, 128.13, 128.57, 129.85, 130.46, 132.98, 133.05, 133.16, 133.36, 133.45, 133.64, 133.68, 134.05, 135.37, 135.46, 137.58, 137.71, 138.38, 138.52, 142.11, 142.46, 155.03, 155.05; **^{31}P NMR** (162 MHz,$CDCl_3$) δ:-13.95; **MS (ESI):** found $[M+H]^+$469.16. Enantiomeric excess is 99% determined by HPLC (Chiralcel AD-H, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): major isomer: t_R = 5.23 min.

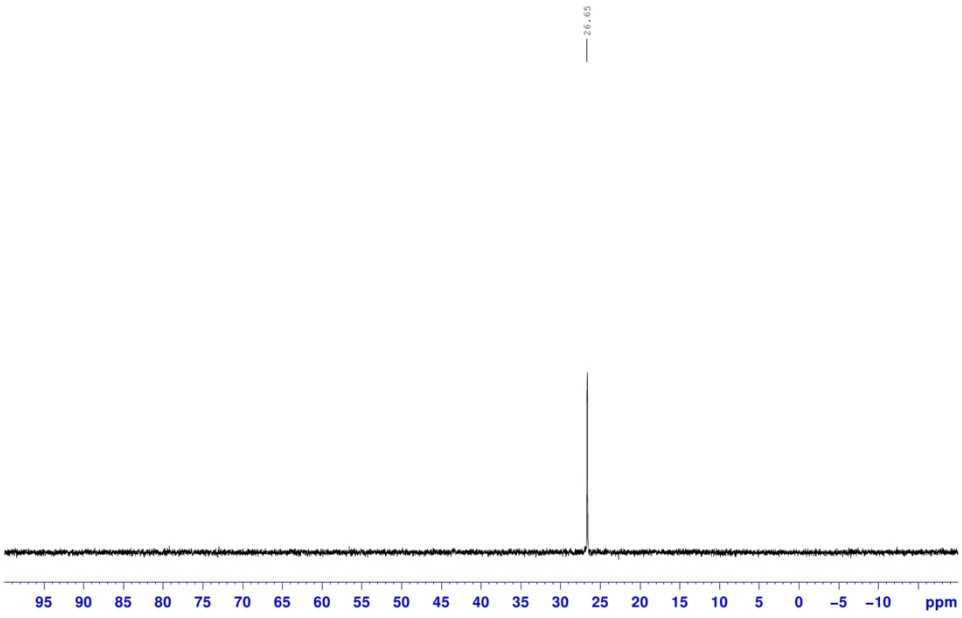
VI. References:

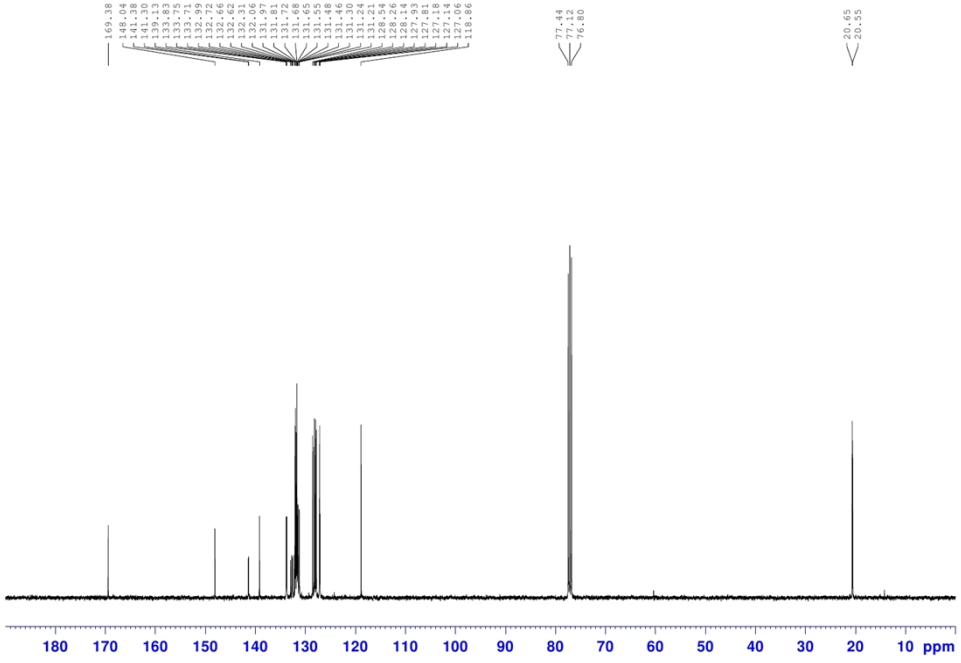
1. a) T. H. Jepsen, M. Larsen, M. Jørgensen, K. A. Solanko, A. D. Bond, A. Kadziola, M. B. Nielsen, *Eur. J. Org. Chem.* **2011**, 53–57; b) A. Port, A. Virgili, A. Alvarez-Larena, J. F. Piniella, *Tetraledron: Asymmetry*, **2000**, *11*, 3747-3757; c) B. E. Mann, B. L. Shaw, R. M. Slade, *J. Chem. Soc. (A),* **1971**, 2976-2980; d) R. Schmid, J. Foricher, M. Cereghetti, *Helv. Chim. Acta.,***1991**, *74*, 370-389.
2. C. Baillie, J.-L.Xiao, *Tetrahedron,* **2004**, *60*, 4159-4168.
3. M. Shi, L.-H. Chen, C.-Q. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3790;
4. N. Obara, I. Yoshida, K. Tanaka ,T Kan, T. Morimoto, *Tetrahedron Letters* **2007** *48* 3093–3095.

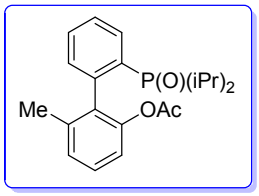
VII. NMR Charts

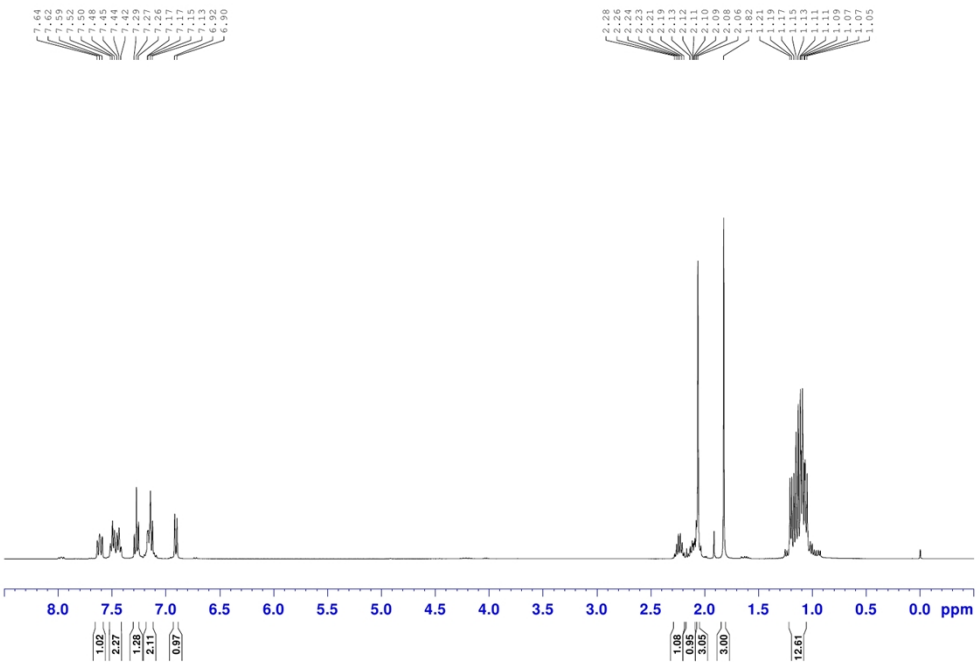


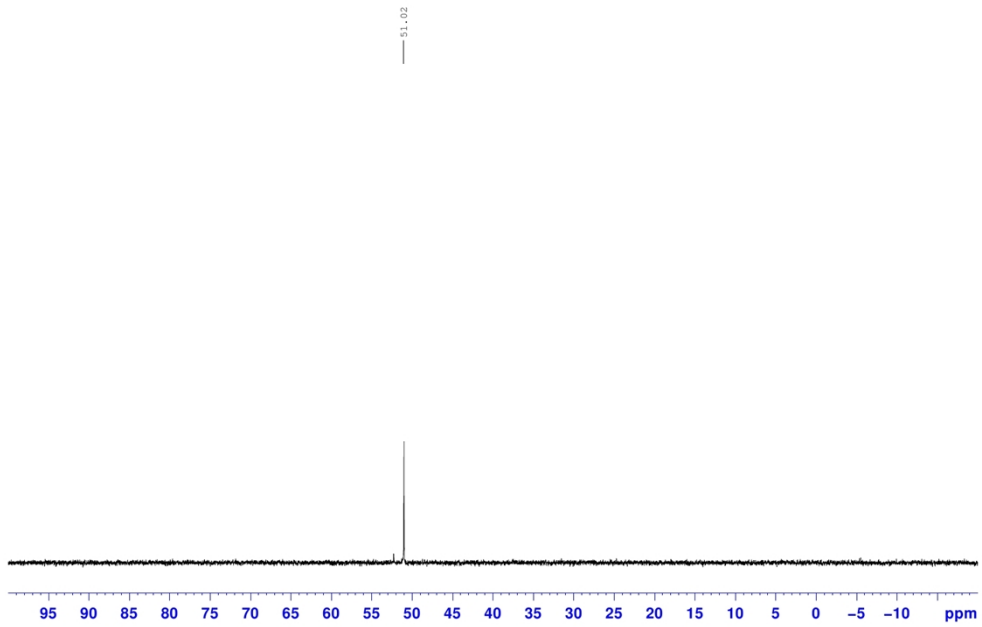


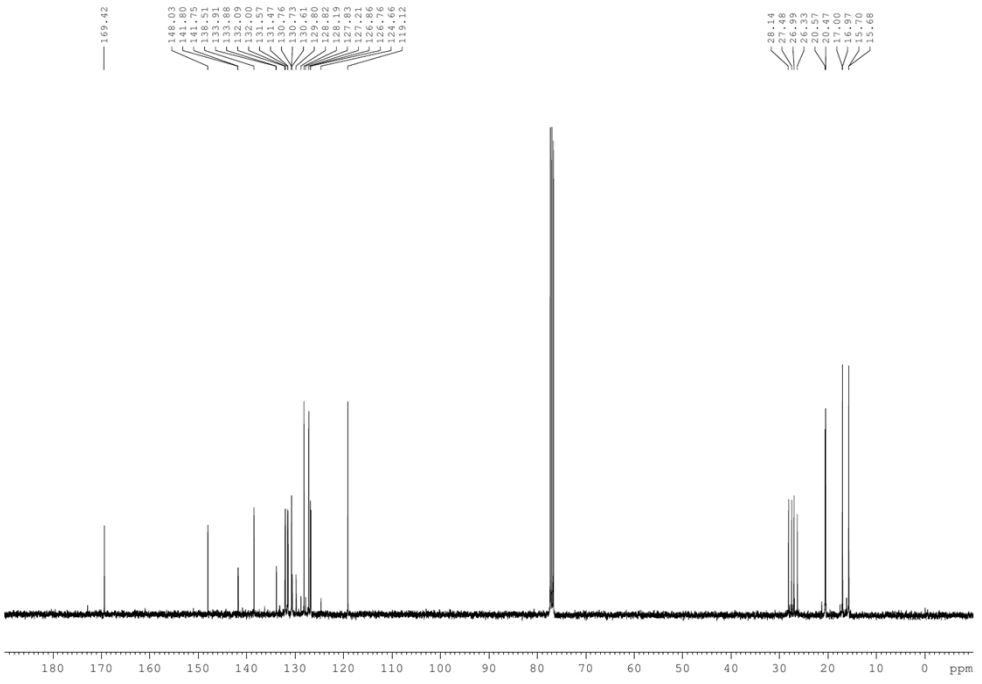


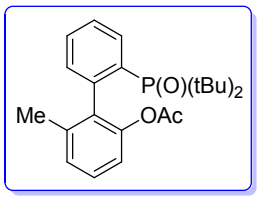


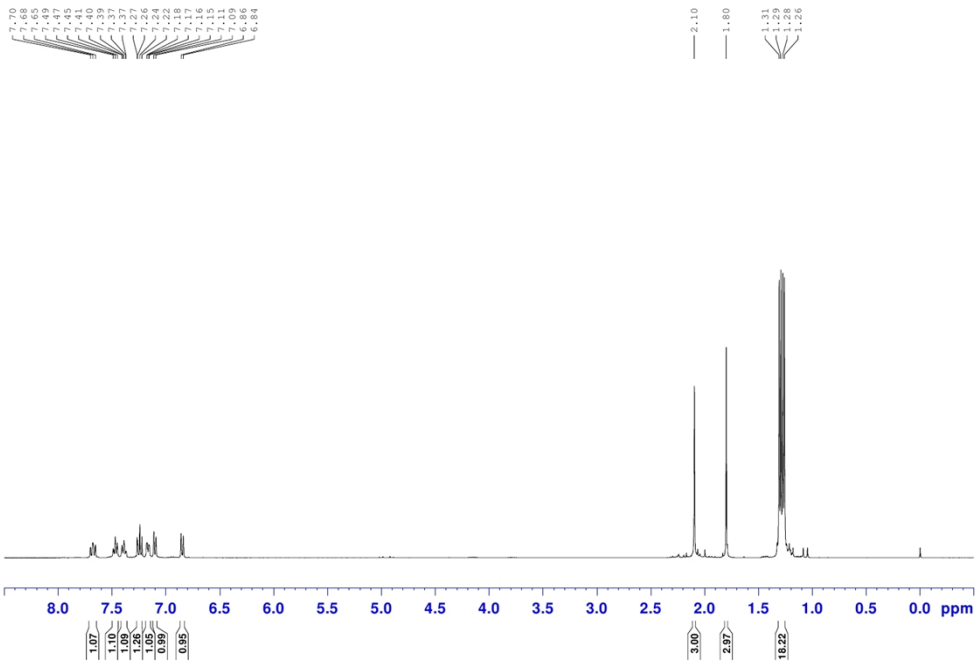

P(O)(iPr)2
Me
OAc

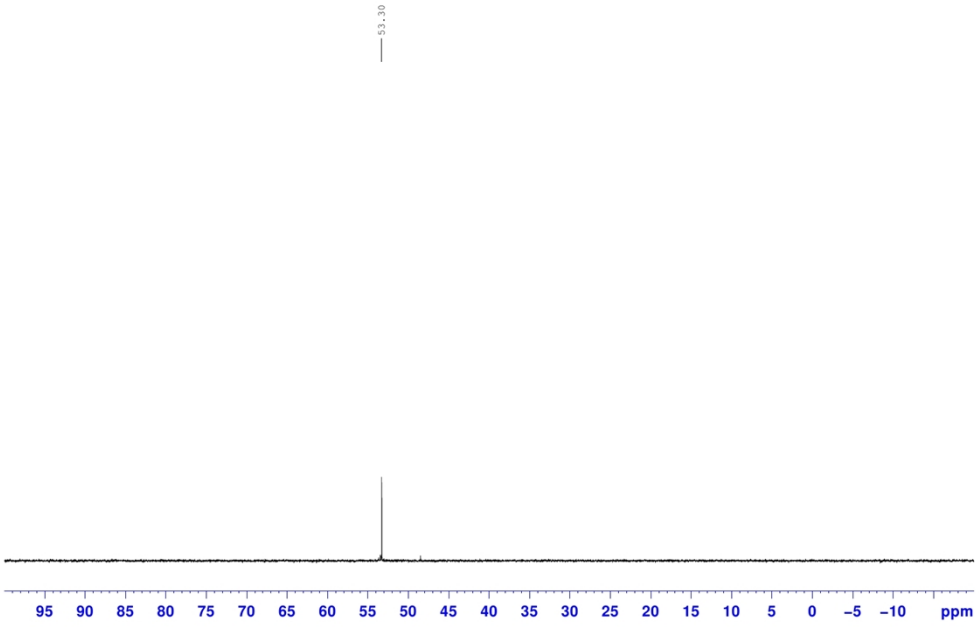


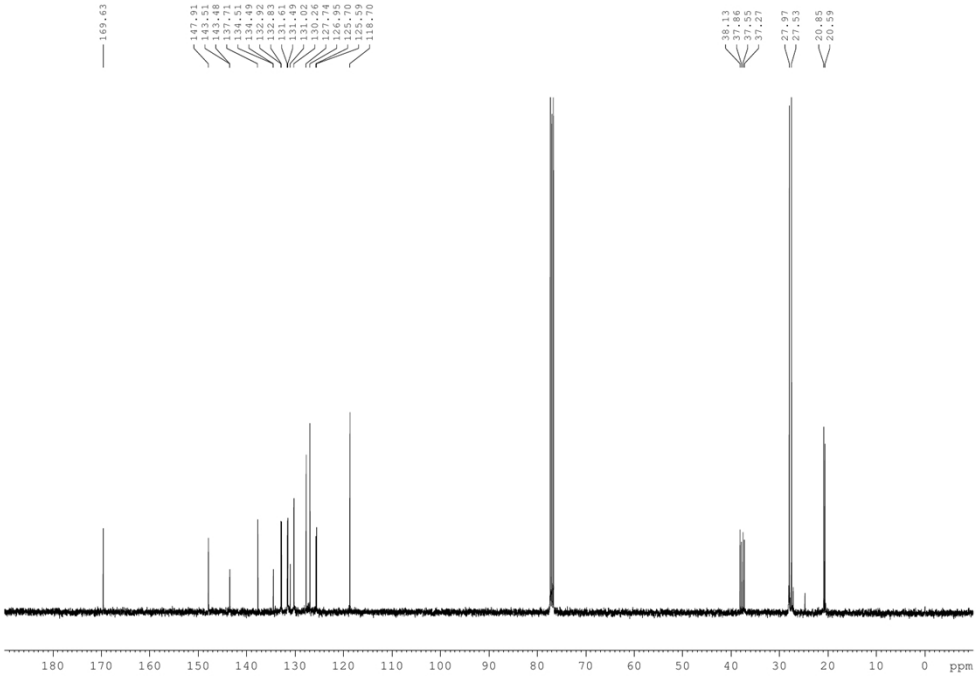

51.02
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

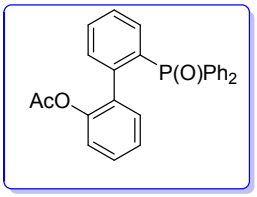

169.42
148.03
141.60
141.75
138.51
133.01
132.88
132.09
132.00
131.57
131.47
130.76
130.73
130.61
129.80
128.82
128.19
127.83
127.21
126.86
126.76
124.66
119.12
28.14
27.48
26.99
26.33
20.57
20.47
17.00
16.97
15.70
15.68
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

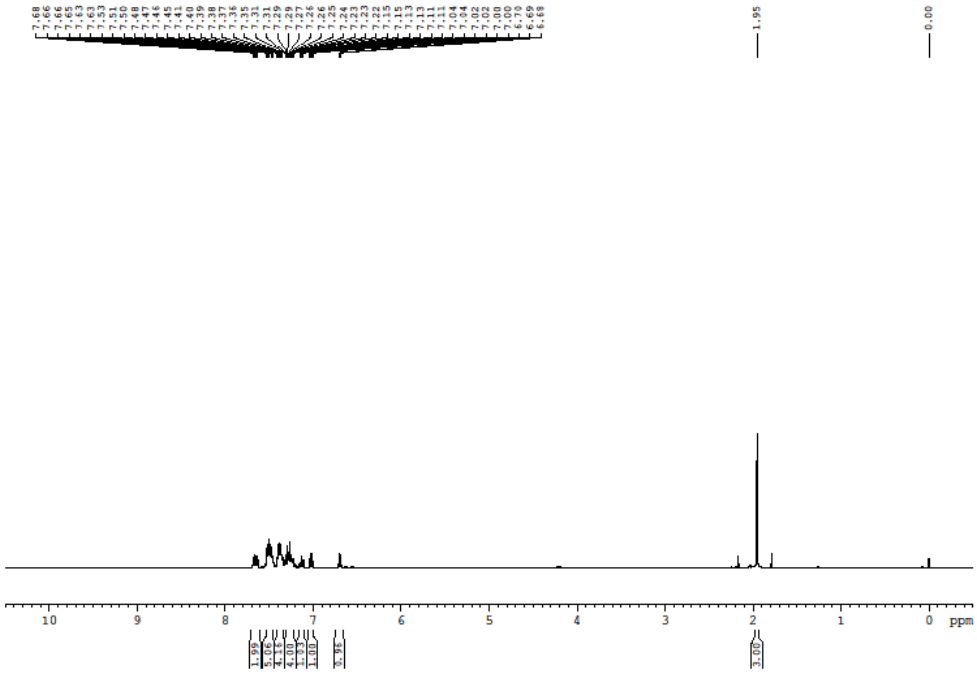

P(O)(tBu)2
Me
OAc

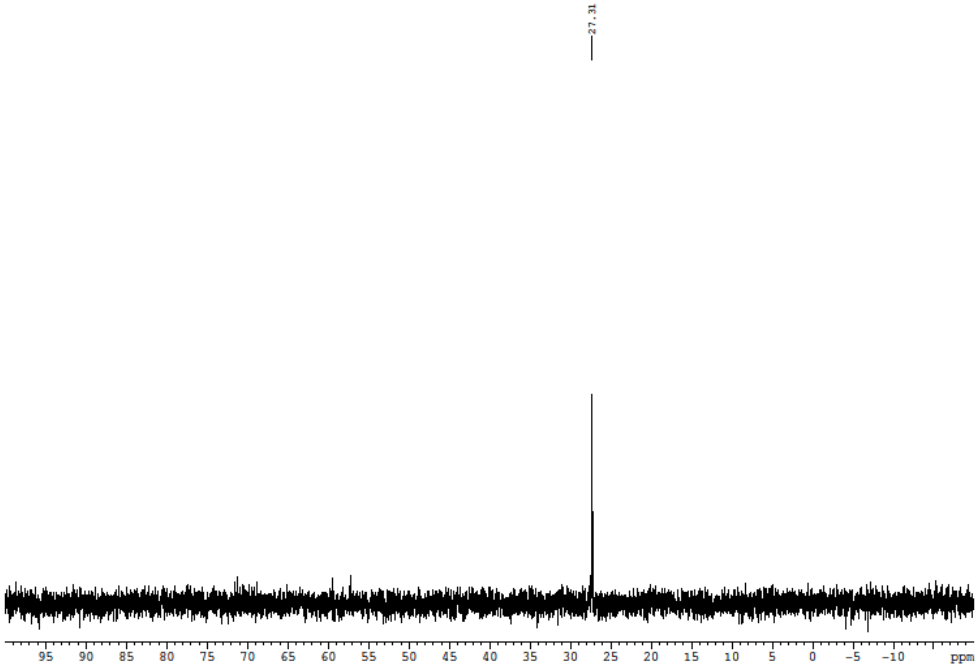

7.70
7.68
7.65
7.49
7.47
7.45
7.41
7.40
7.39
7.37
7.27
7.26
7.24
7.22
7.18
7.17
7.16
7.15
7.11
7.09
6.86
6.84
2.10
1.80
1.31
1.29
1.28
1.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.07
1.10
1.09
1.26
1.05
0.99
0.95
3.00
2.97
18.22

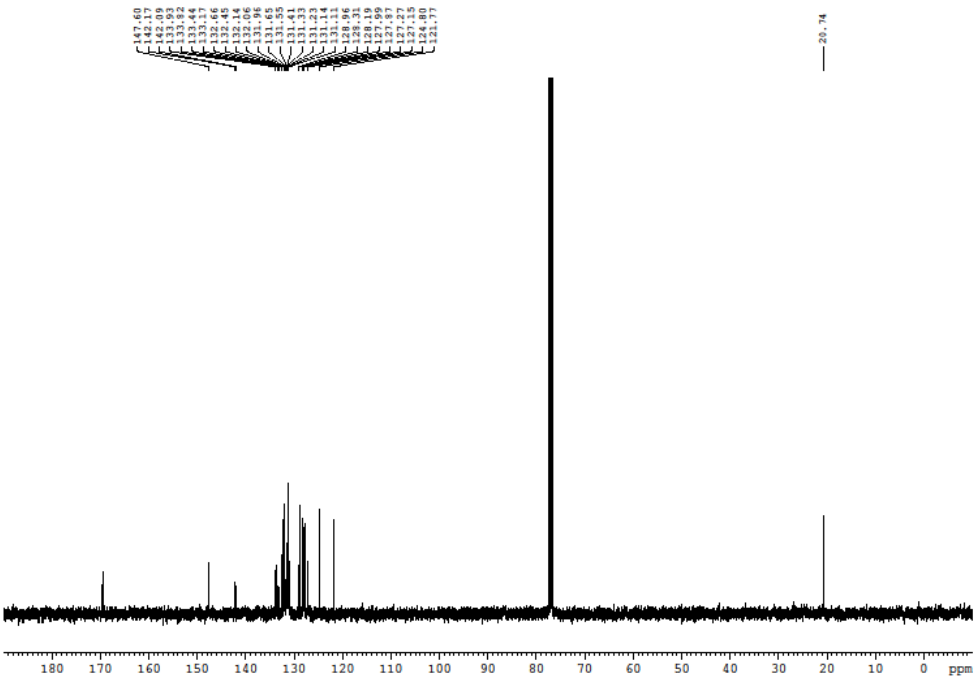

53.30
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
ppm

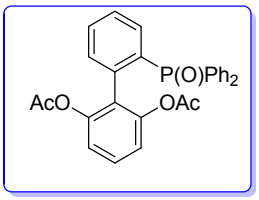

169.63
147.91
143.51
143.48
137.71
134.71
134.49
132.92
132.83
131.61
131.49
131.02
130.26
127.74
126.95
125.70
125.59
118.70
38.13
37.86
37.55
37.27
27.97
27.53
20.85
20.59
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

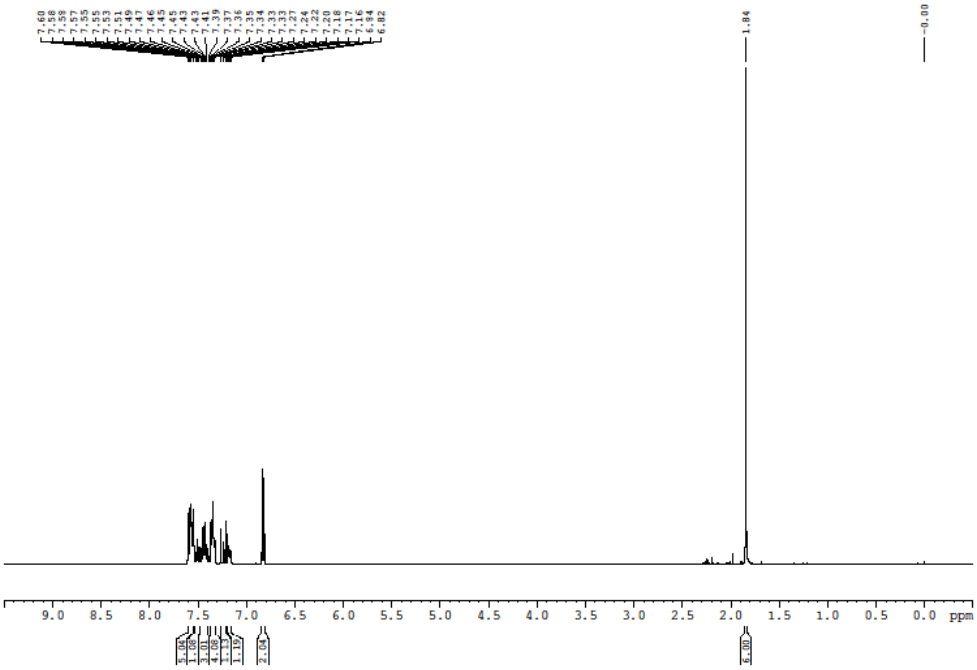

P(O)Ph2
AcO

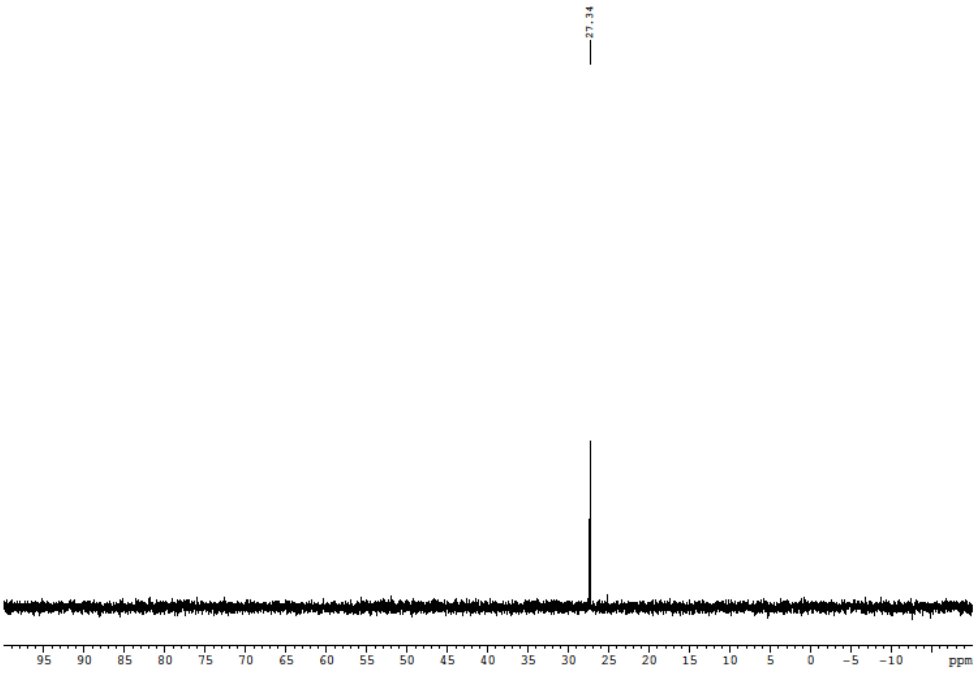

7.68
7.66
7.66
7.65
7.63
7.53
7.51
7.50
7.48
7.47
7.46
7.45
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.31
7.31
7.29
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.15
7.13
7.13
7.11
7.11
7.04
7.04
7.02
7.02
7.00
7.00
6.70
6.69
6.68
1.95
0.00
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.06
1.16
4.00
3.03
1.00
5.96
3.00

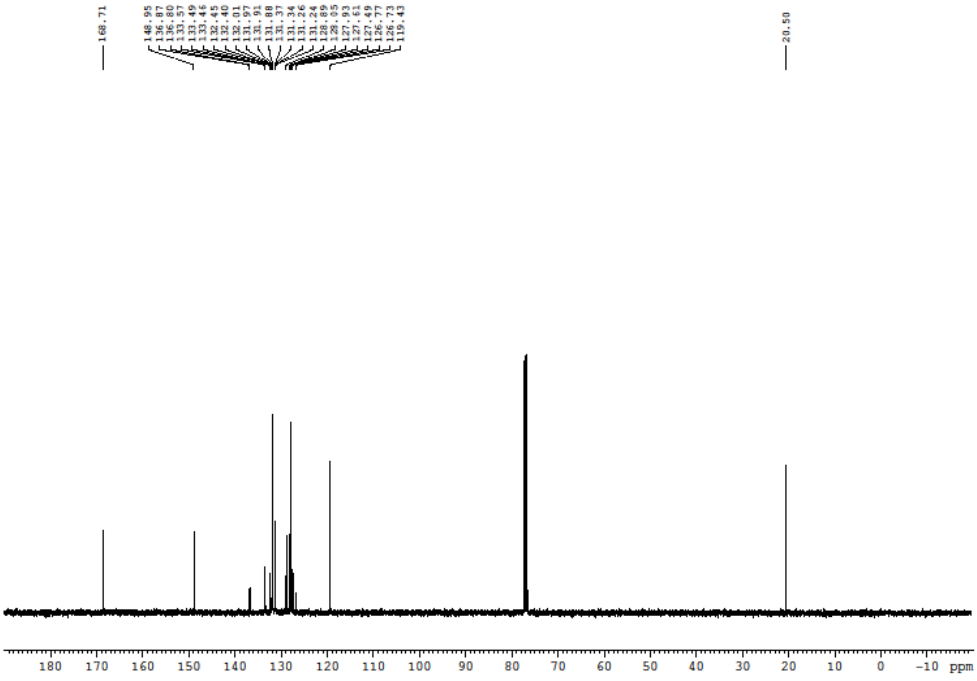

27.31
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 ppm

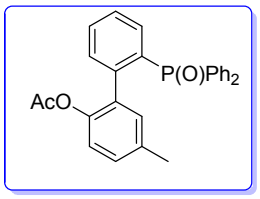

147.60
142.17
142.09
141.83
133.92
133.44
133.17
132.66
132.46
132.14
132.06
131.96
131.65
131.55
131.41
131.33
131.23
131.14
131.11
128.96
128.31
128.19
127.99
127.87
127.27
127.15
124.80
121.77
20.74
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

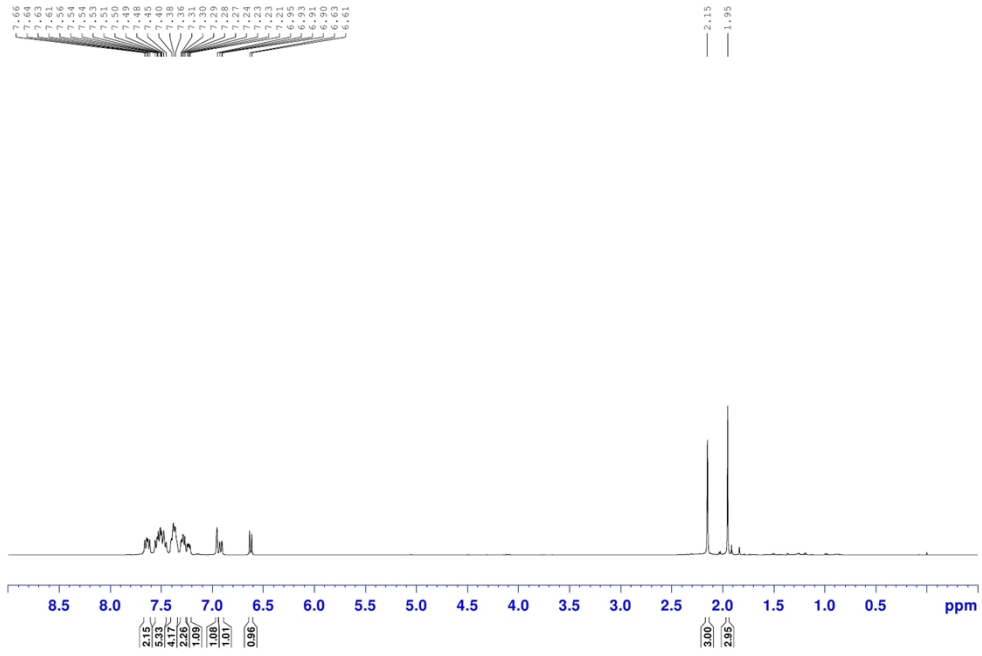

P(O)Ph2
AcO
OAc

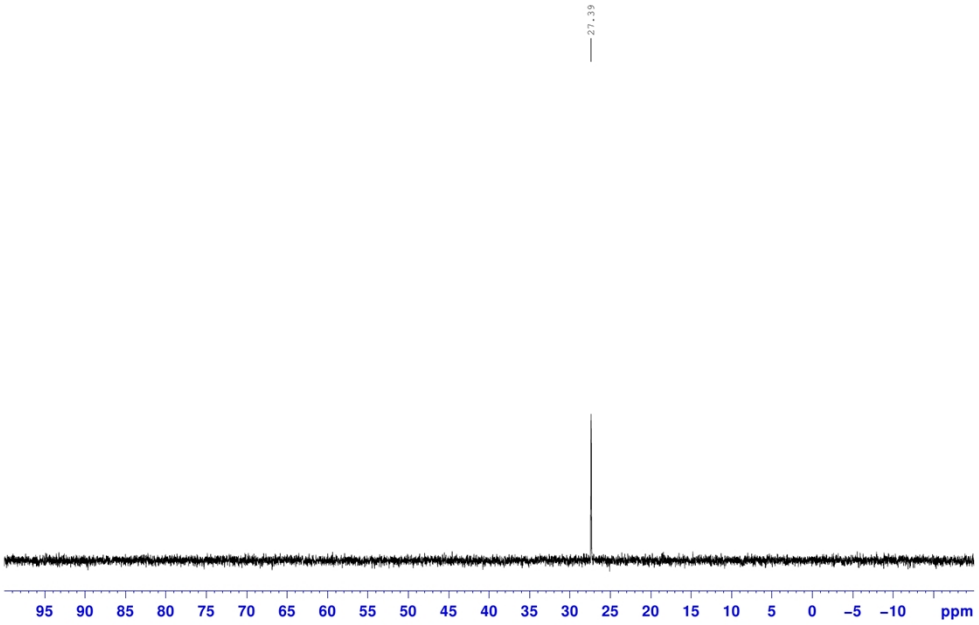

7.60
7.58
7.58
7.57
7.55
7.55
7.53
7.51
7.49
7.47
7.46
7.45
7.45
7.43
7.43
7.41
7.39
7.37
7.36
7.35
7.34
7.33
7.33
7.27
7.24
7.22
7.20
7.18
7.17
7.16
6.84
6.82
1.84
0.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.04
1.09
3.01
4.08
1.33
1.16
2.04
6.00

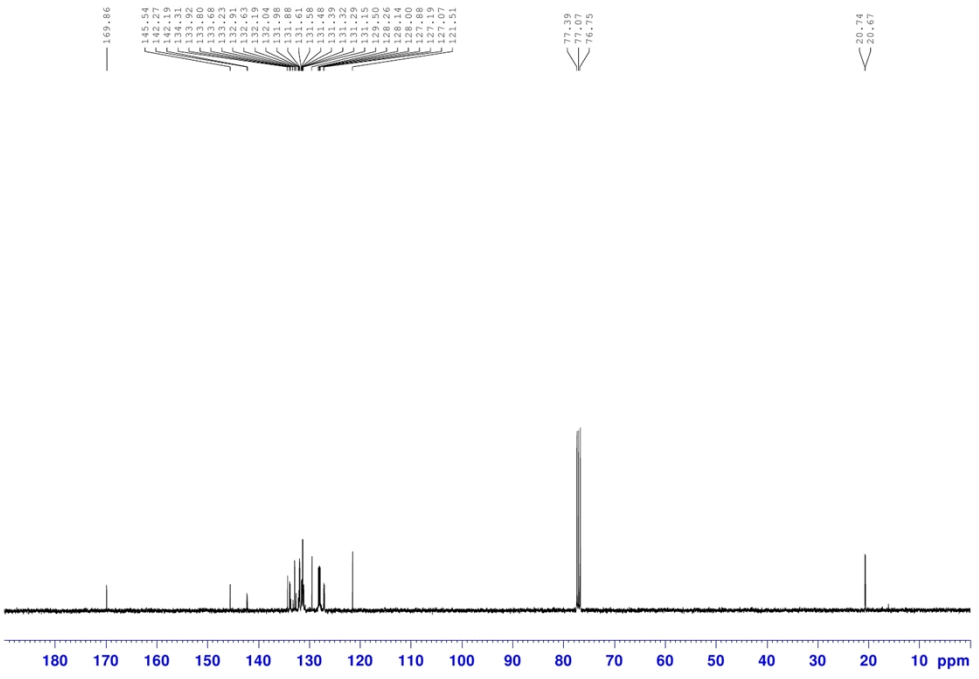

27.34
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 ppm

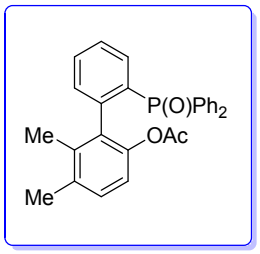

168.71
148.95
136.87
136.60
133.57
133.49
133.46
132.45
132.40
132.01
131.97
131.91
131.88
131.37
131.34
131.26
131.24
130.89
128.05
127.93
127.61
127.49
126.77
126.73
119.43
20.50
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

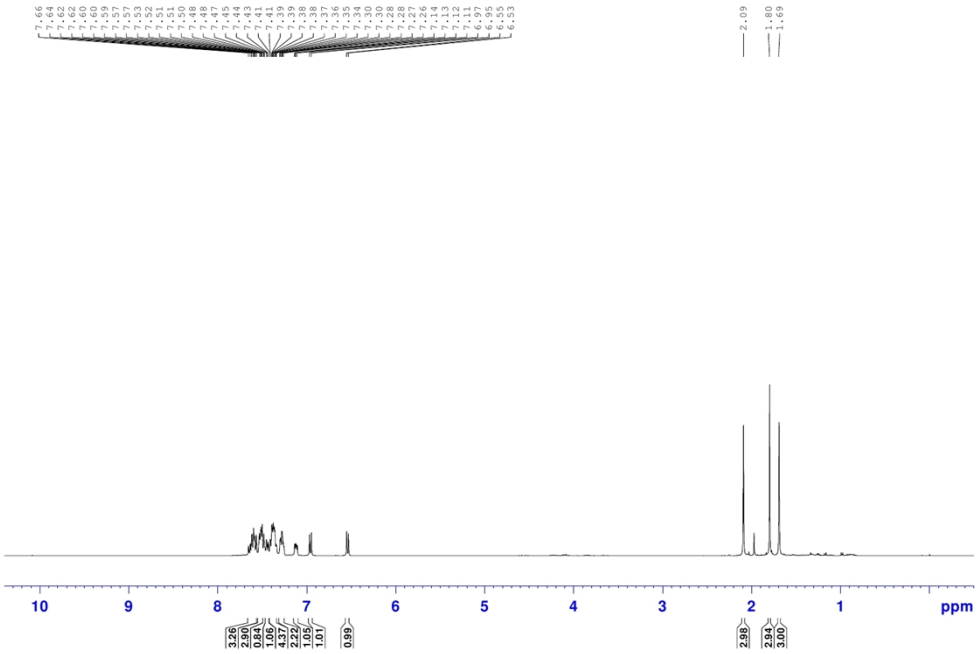

P(O)Ph2
AcO

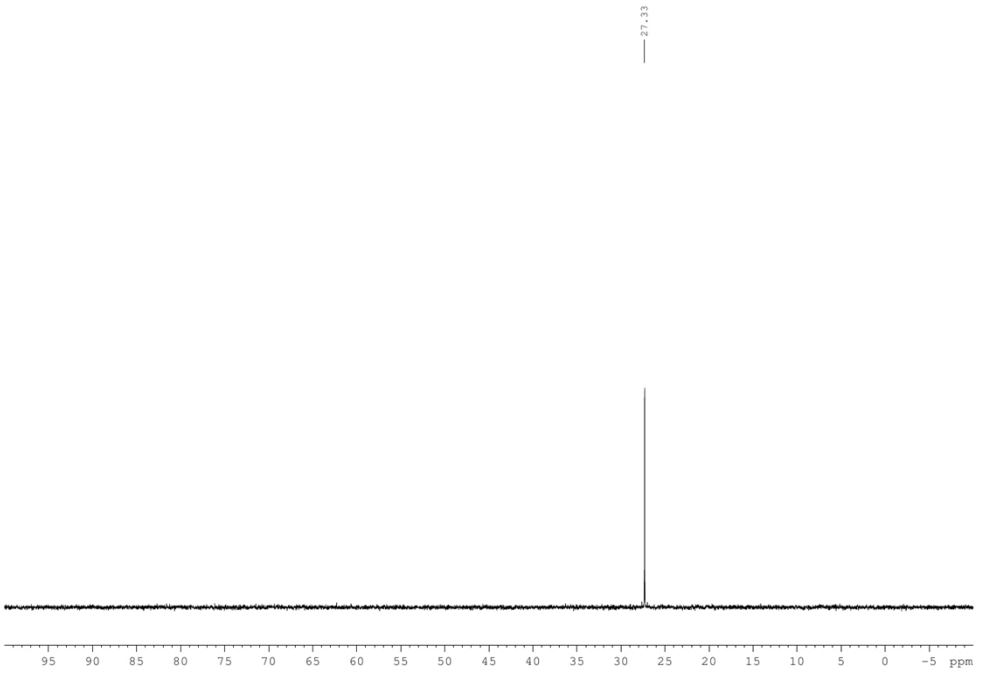

7.66
7.64
7.63
7.61
7.56
7.54
7.54
7.53
7.51
7.50
7.49
7.48
7.45
7.40
7.38
7.36
7.31
7.30
7.29
7.28
7.27
7.24
7.23
7.21
6.95
6.93
6.91
6.89
6.63
6.61
2.15
1.95
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.15
5.33
4.17
2.26
1.09
1.08
1.01
0.96
3.00
2.95

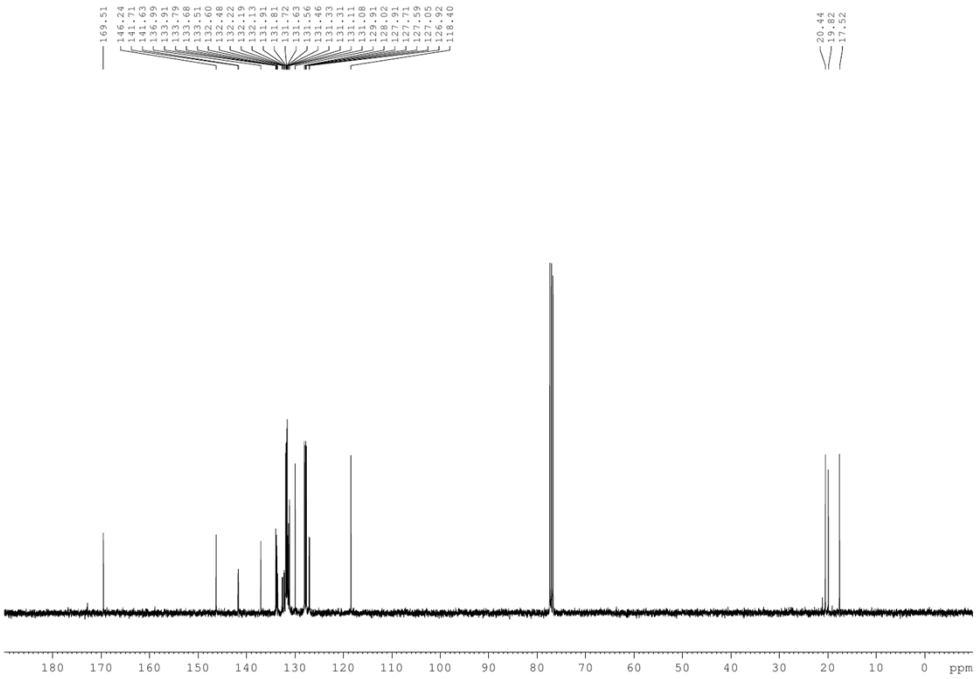

27.39
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

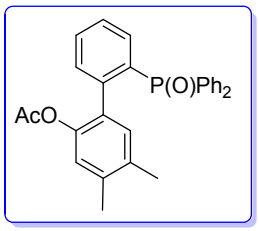

169.86
145.54
142.27
142.09
134.31
133.92
133.80
133.68
133.21
132.91
132.63
132.19
132.04
131.98
131.88
131.61
131.58
131.48
131.39
131.32
131.29
131.15
131.00
128.26
128.14
128.00
127.88
127.19
127.07
121.51
77.39
77.07
76.75
20.74
20.67
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

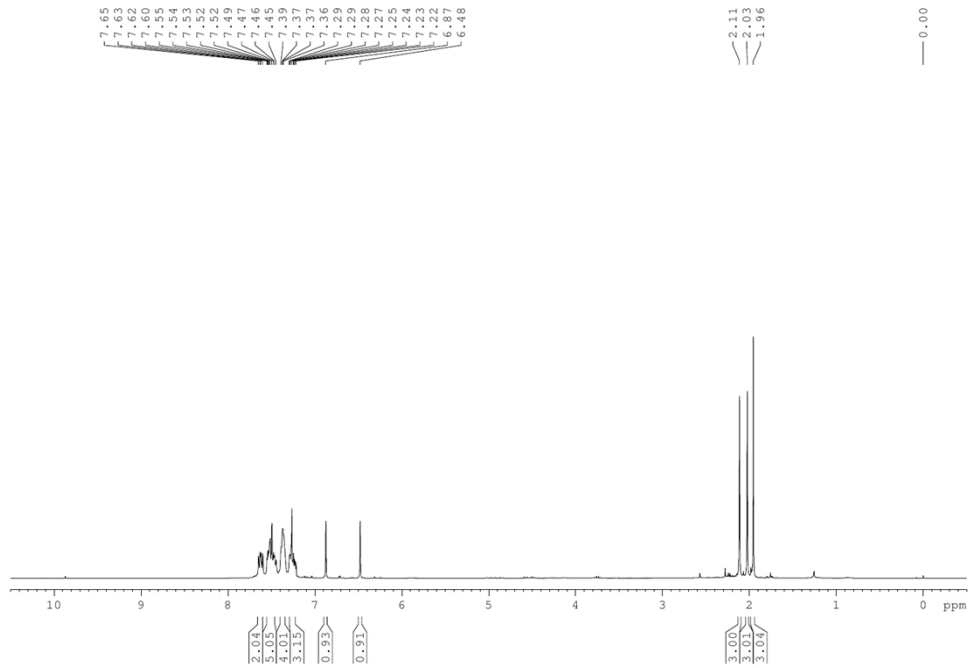

P(O)Ph2
Me
OAc
Me

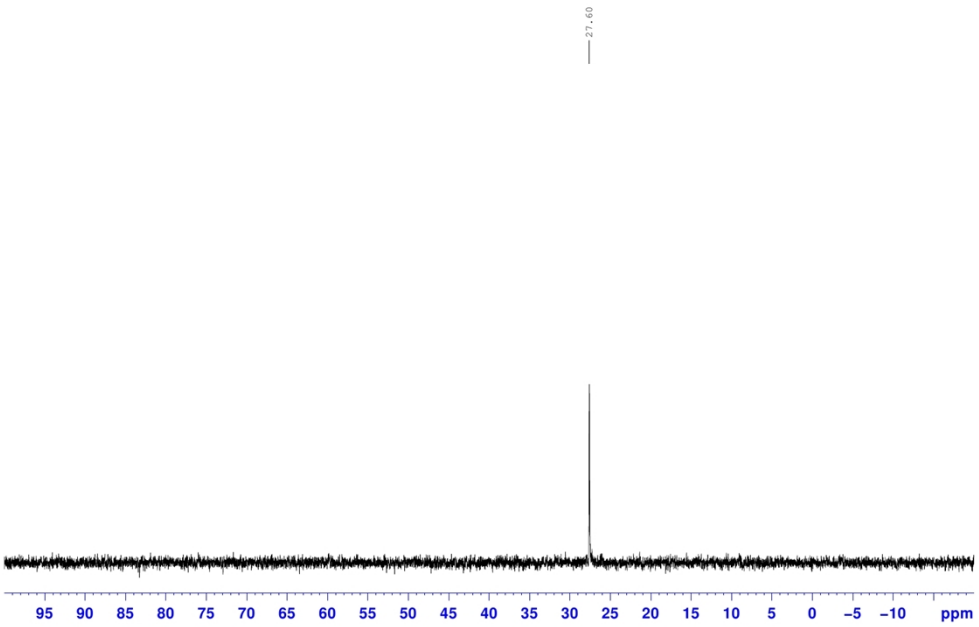

7.66
7.64
7.62
7.62
7.60
7.60
7.59
7.57
7.53
7.52
7.51
7.50
7.48
7.48
7.47
7.45
7.44
7.43
7.41
7.41
7.39
7.39
7.38
7.37
7.36
7.35
7.34
7.30
7.30
7.28
7.28
7.27
7.26
7.14
7.13
7.12
7.11
6.97
6.95
6.55
6.53
2.09
1.80
1.69
10
9
8
7
6
5
4
3
2
1
ppm
3.26
2.90
0.84
1.06
4.37
2.29
1.15
1.01
0.99
2.98
2.94
3.00

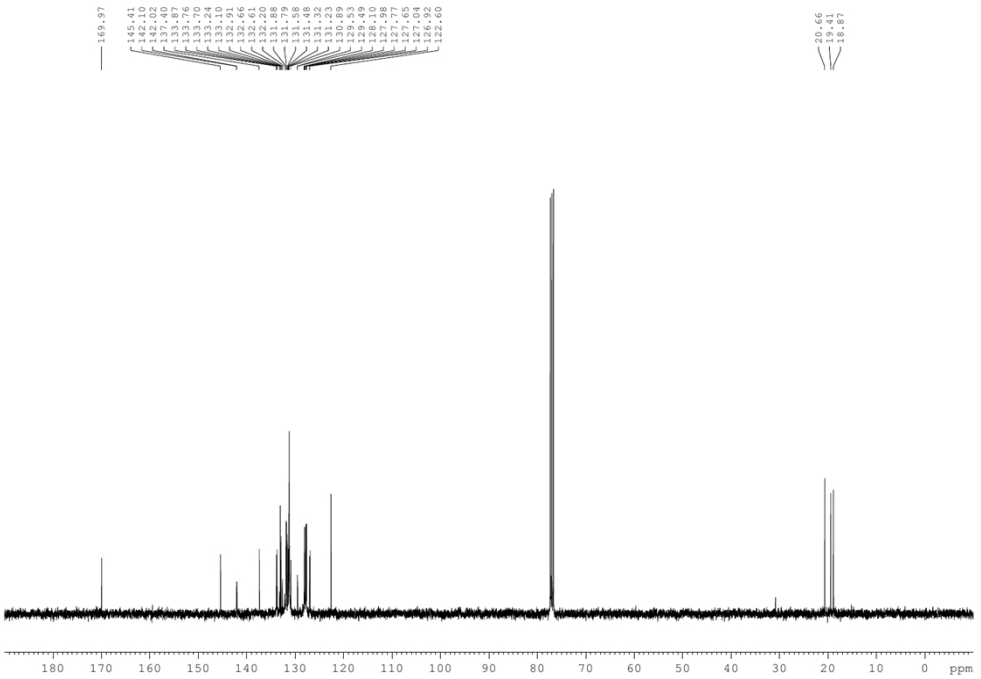

27.33
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
ppm

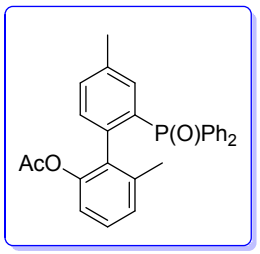

169.51
146.24
141.71
141.63
136.89
133.91
133.79
133.68
133.51
132.60
132.48
132.22
132.19
132.13
131.91
131.81
131.72
131.63
131.56
131.46
131.33
131.31
131.11
131.08
129.91
128.02
127.91
127.71
127.59
127.05
126.92
118.40
20.44
19.82
17.52
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

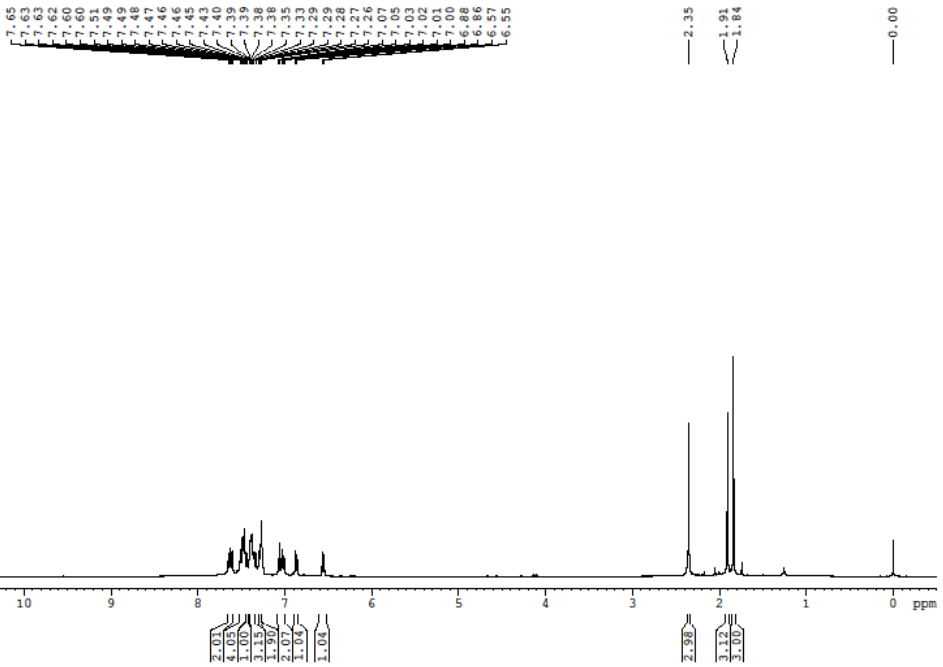

P(O)Ph2
AcO

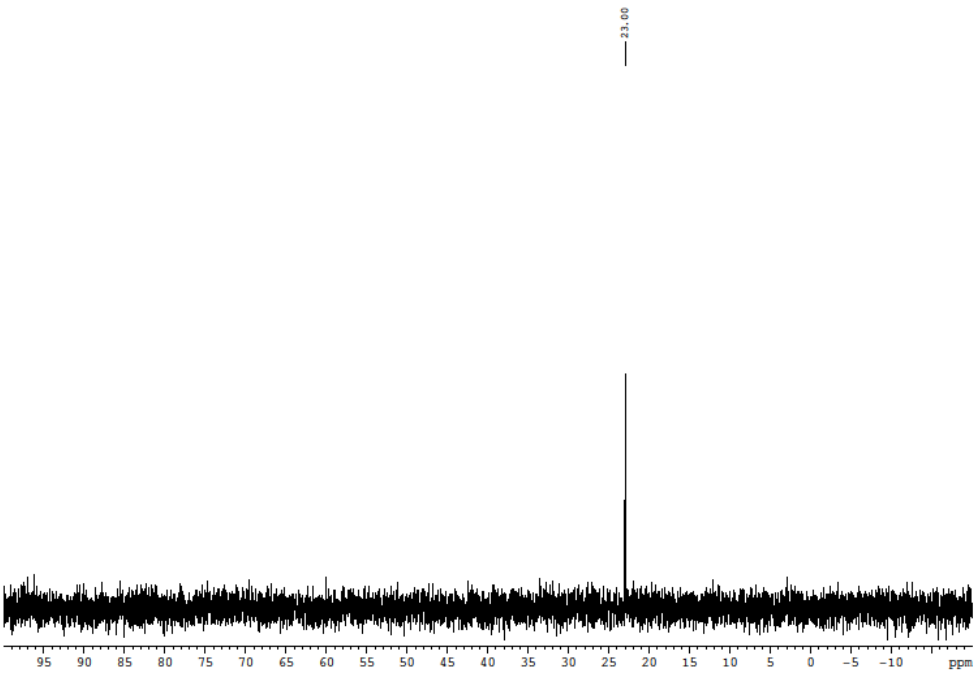

7.65
7.63
7.62
7.60
7.55
7.54
7.53
7.52
7.52
7.49
7.47
7.46
7.45
7.39
7.37
7.37
7.36
7.29
7.29
7.28
7.27
7.25
7.24
7.23
7.22
6.87
6.48
2.11
2.03
1.96
0.00
10 9 8 7 6 5 4 3 2 1 0 ppm
2.04
5.05
4.01
3.15
0.93
0.91
3.00
3.01
3.04

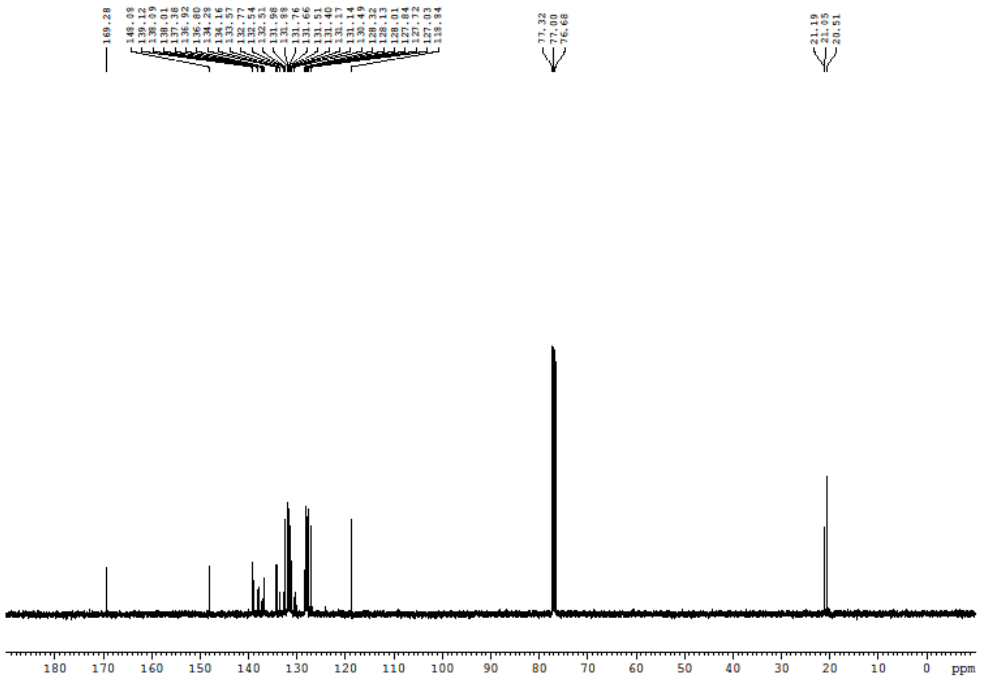

27.60
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

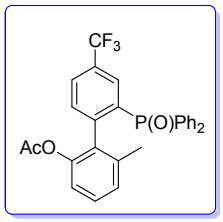

169.97
145.41
142.10
142.02
137.40
133.87
133.76
133.70
133.24
133.10
132.91
132.66
132.41
132.20
131.88
131.79
131.58
131.48
131.32
131.23
130.89
129.53
129.49
128.10
127.98
127.77
127.65
127.04
126.92
122.60
20.66
19.41
18.87
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

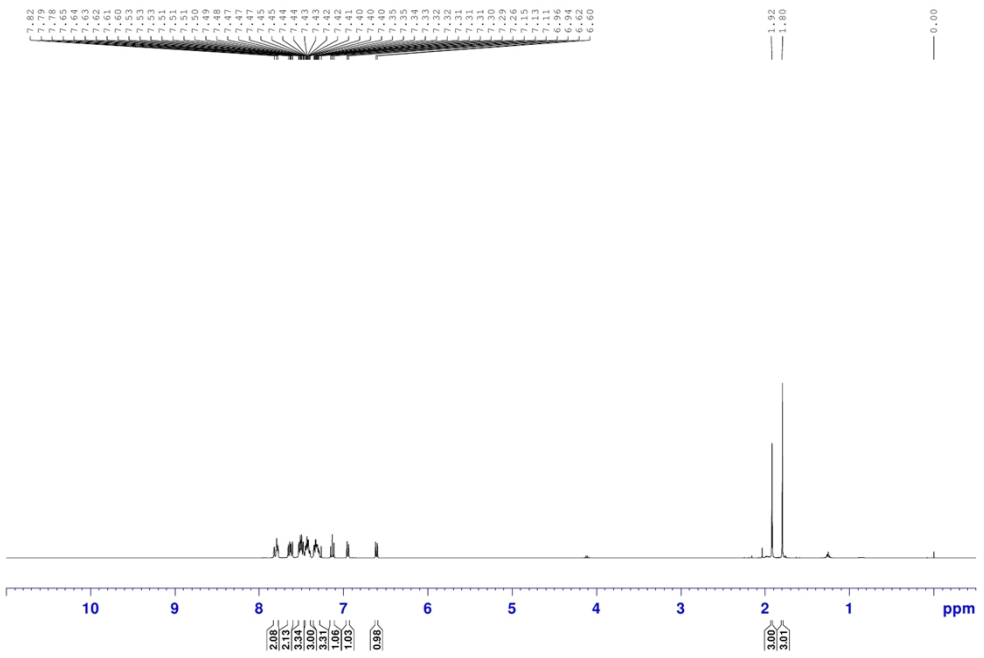

P(O)Ph2
AcO

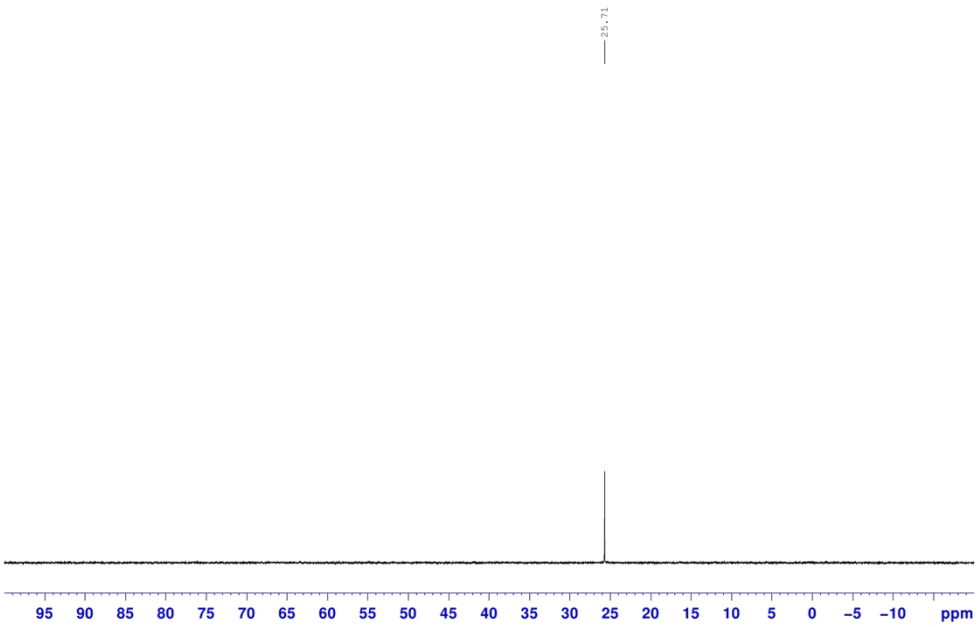

7.65
7.63
7.63
7.62
7.60
7.60
7.51
7.49
7.49
7.48
7.47
7.46
7.46
7.45
7.43
7.40
7.39
7.39
7.38
7.38
7.35
7.33
7.29
7.29
7.28
7.27
7.26
7.07
7.05
7.03
7.02
7.01
7.00
6.88
6.86
6.57
6.55
2.35
1.91
1.84
0.00
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
4.05
1.00
3.15
1.90
2.07
1.04
1.04
2.98
3.12
3.00

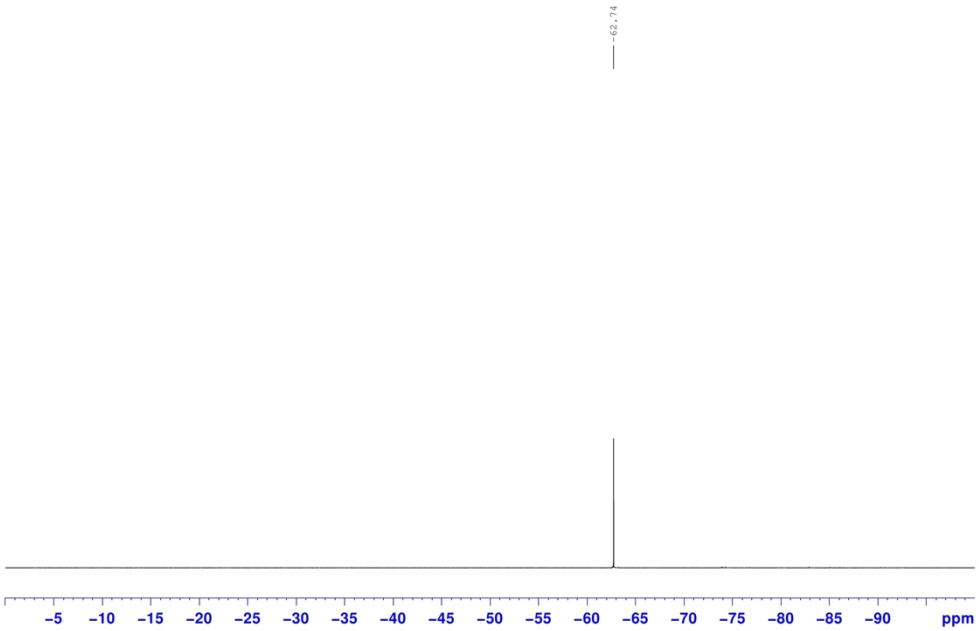

23.00
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
ppm

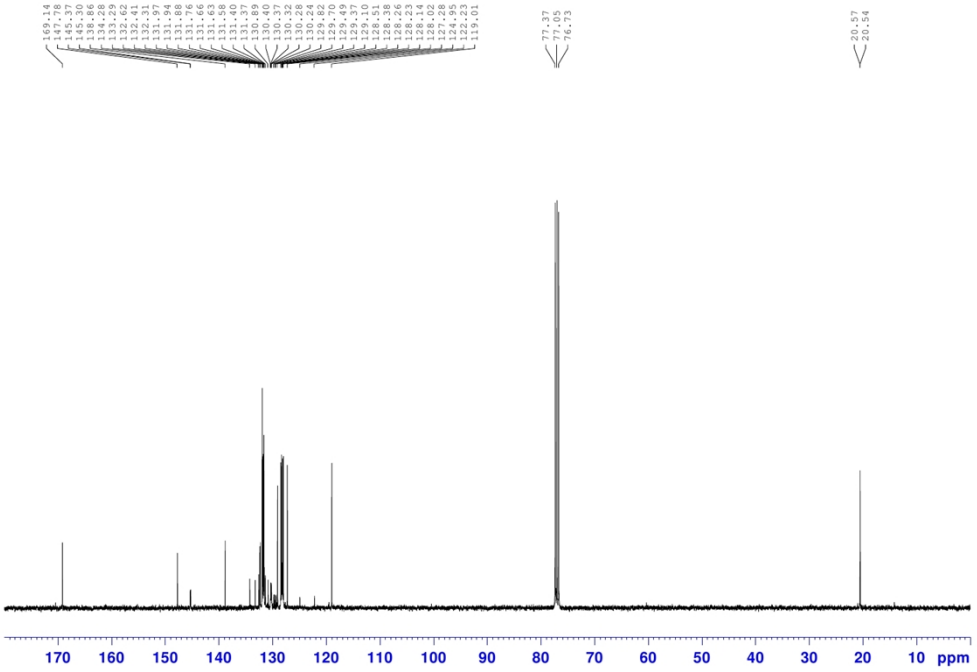


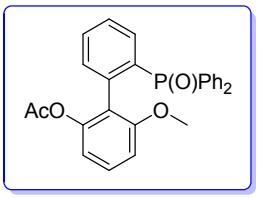

CF3
P(O)Ph2
AcO

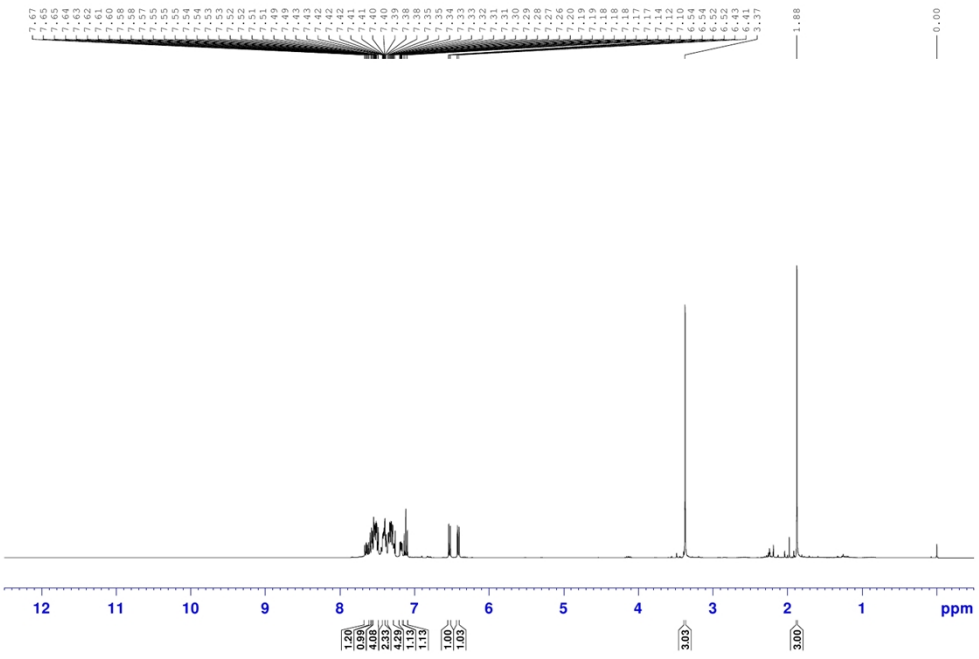


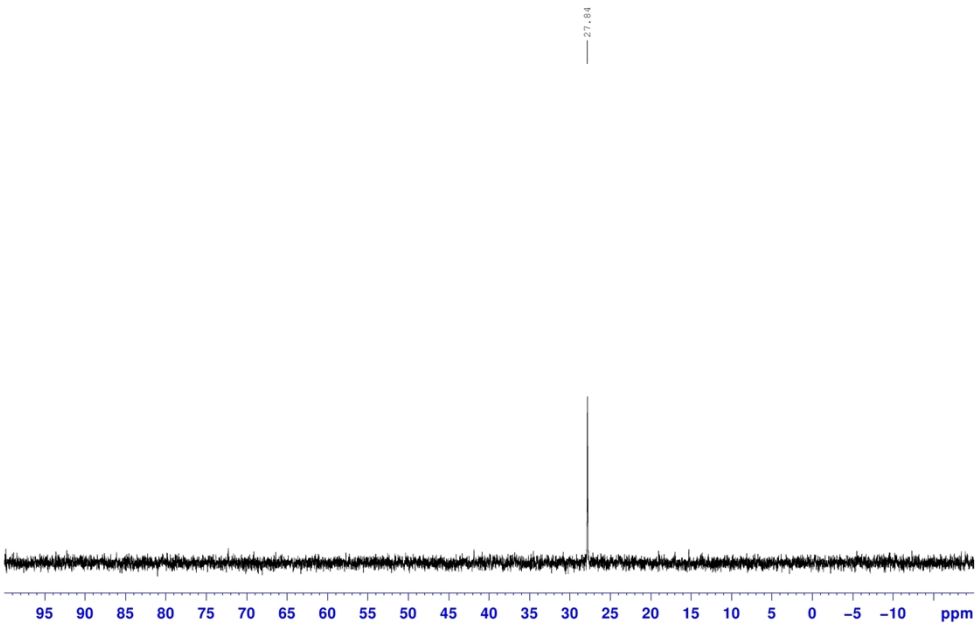

25.71
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

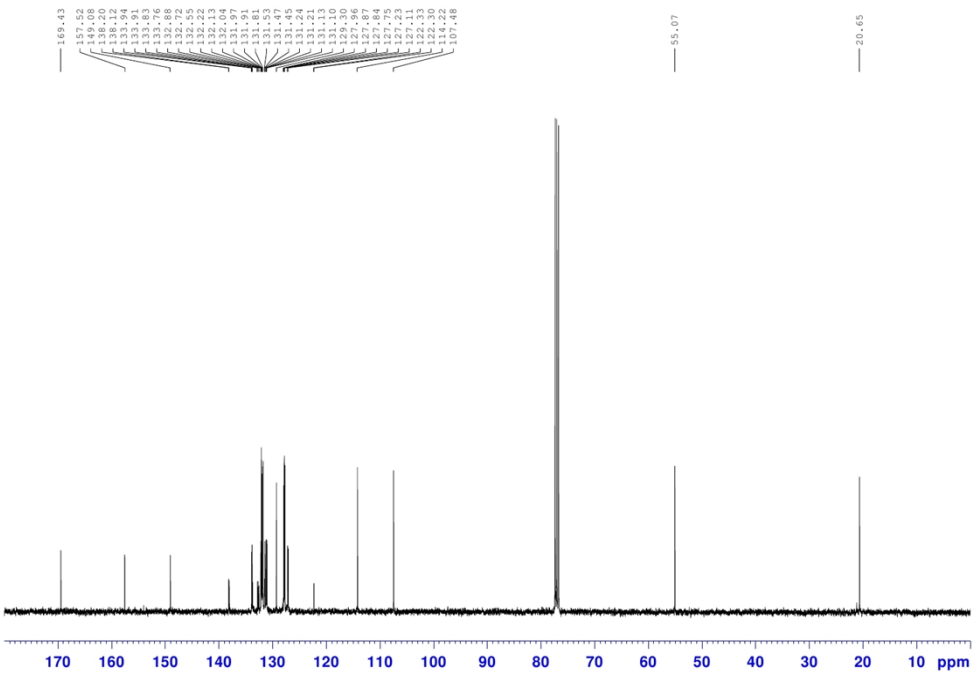

-62.74
−5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 ppm

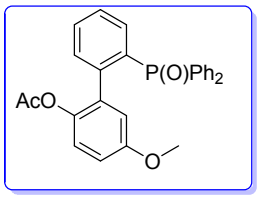


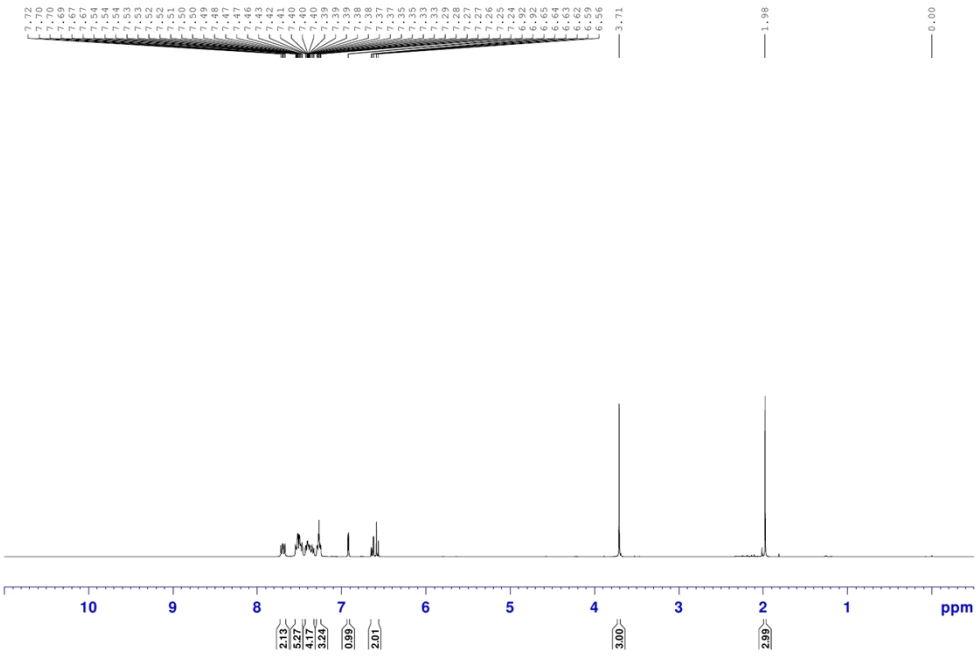

P(O)Ph2
AcO
O

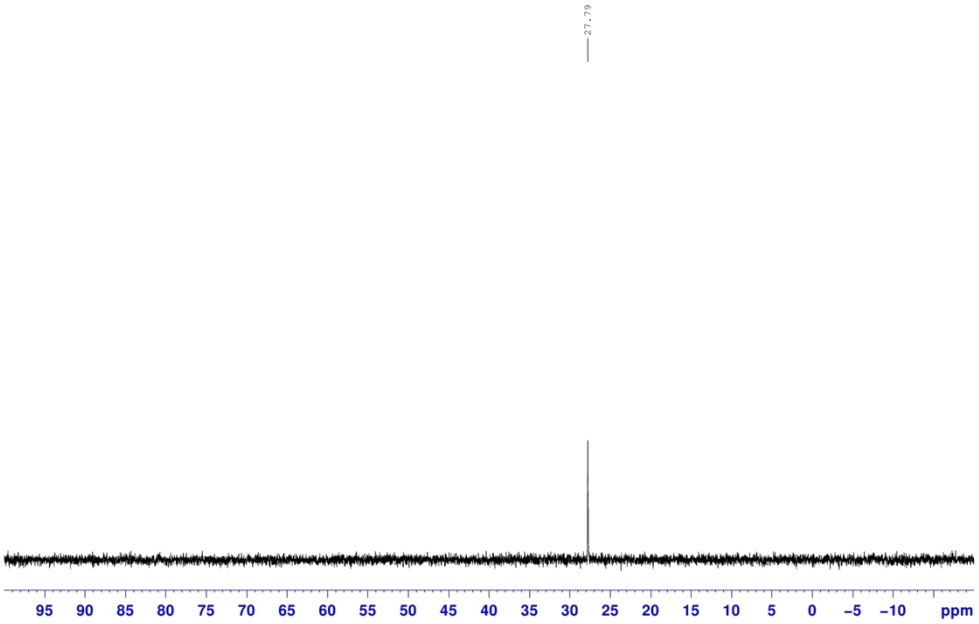


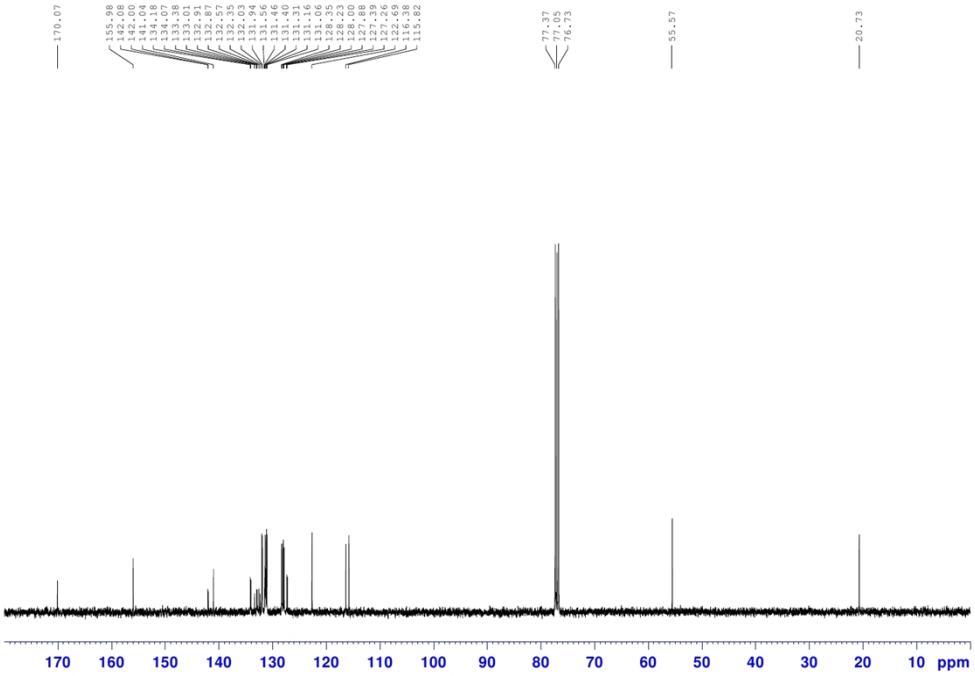

27.84
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

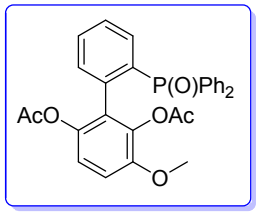

169.43
157.52
149.08
138.20
138.12
135.94
133.91
133.83
133.76
132.88
132.72
132.55
132.22
132.13
132.04
131.97
131.91
131.81
131.53
131.47
131.45
131.24
131.21
131.13
131.10
129.30
127.96
127.87
127.84
127.75
127.23
127.11
122.33
122.30
114.22
107.48
55.07
20.65
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

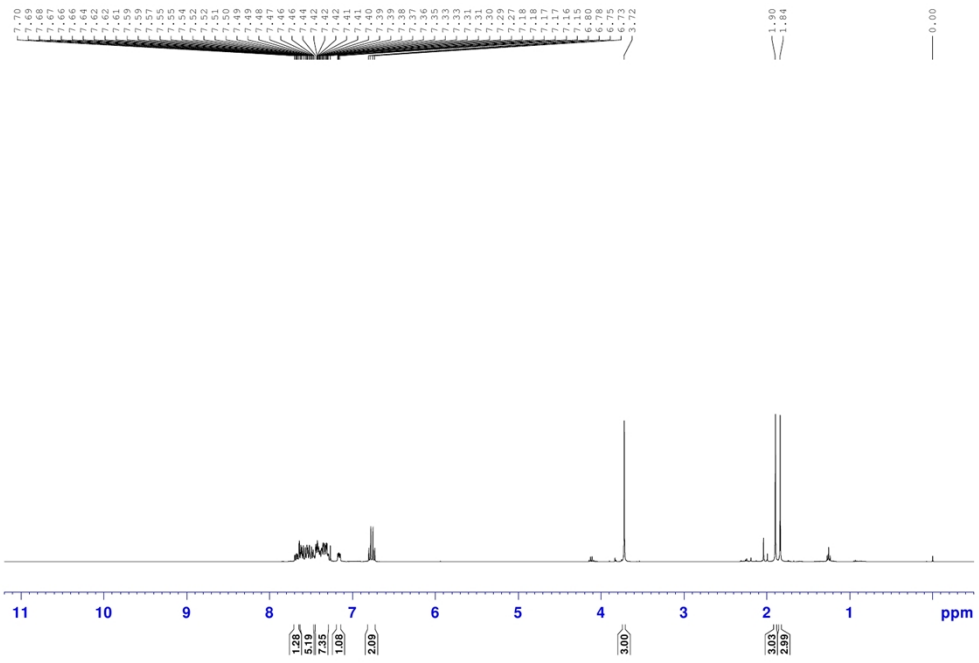

P(O)Ph2
AcO
O

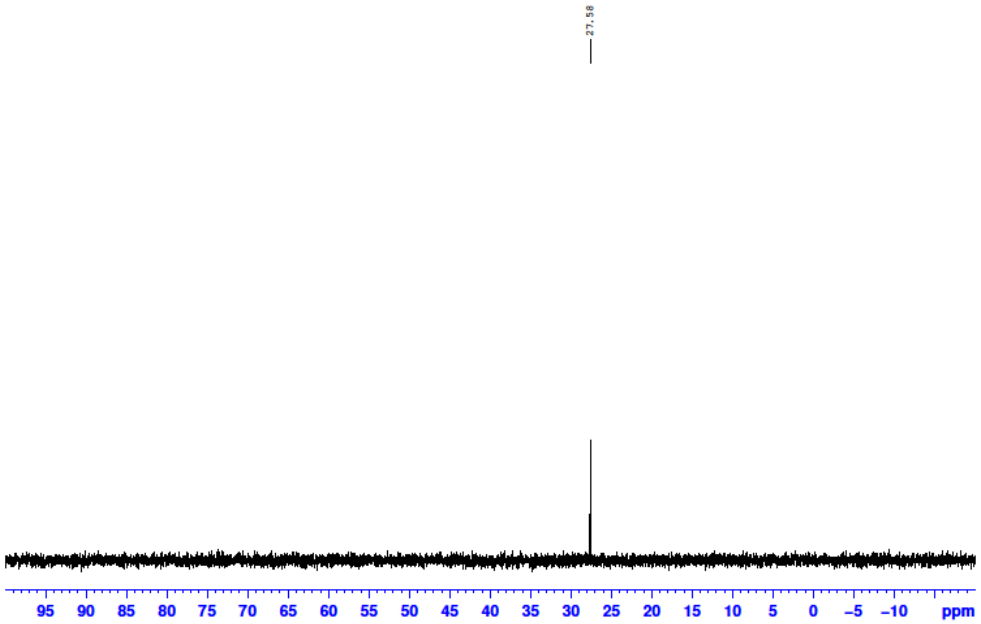

10
9
8
7
6
5
4
3
2
1
ppm

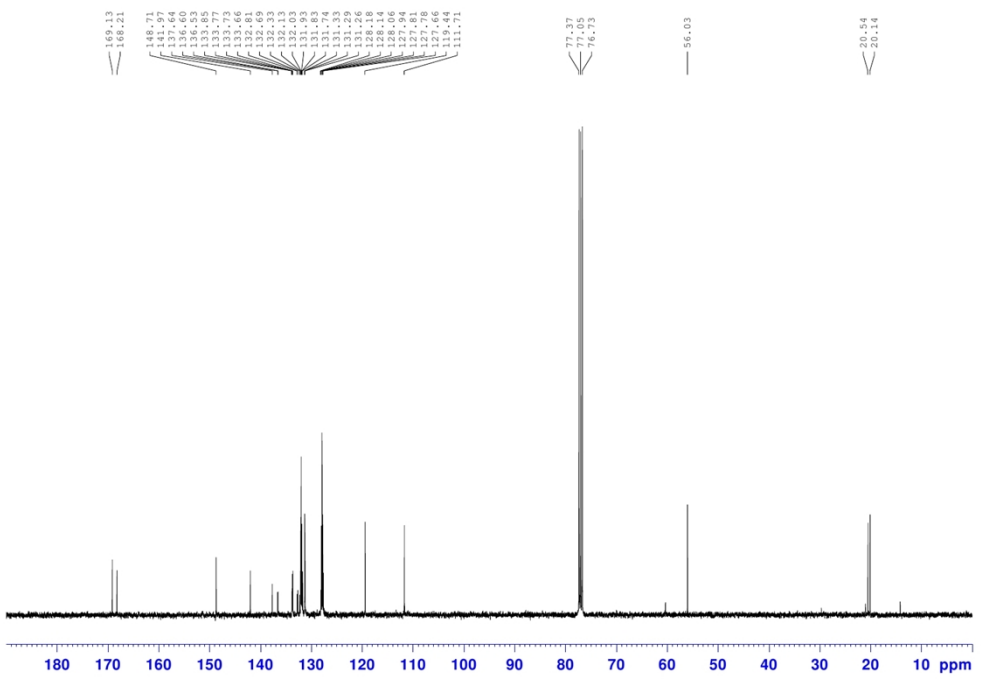

95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
ppm

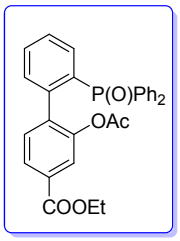

170.07
155.98
142.08
142.00
141.04
134.88
134.07
133.38
133.01
132.91
132.87
132.57
132.35
132.03
131.64
131.56
131.46
131.40
131.31
131.16
131.06
128.35
128.23
128.00
127.88
127.39
127.26
122.69
116.88
116.82
77.37
77.05
76.73
55.57
20.73
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

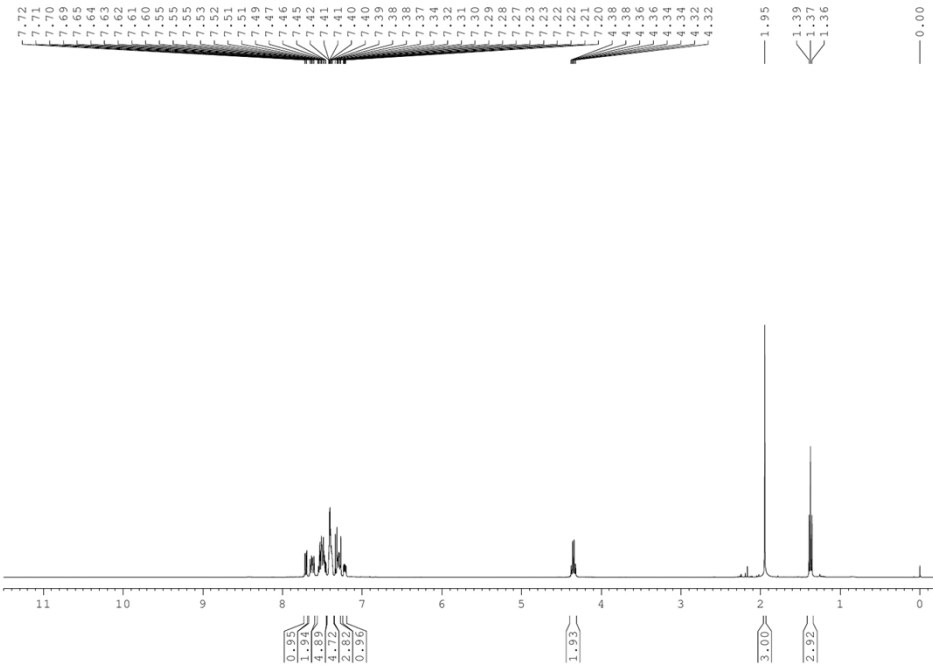

P(O)Ph2
AcO
OAc
O

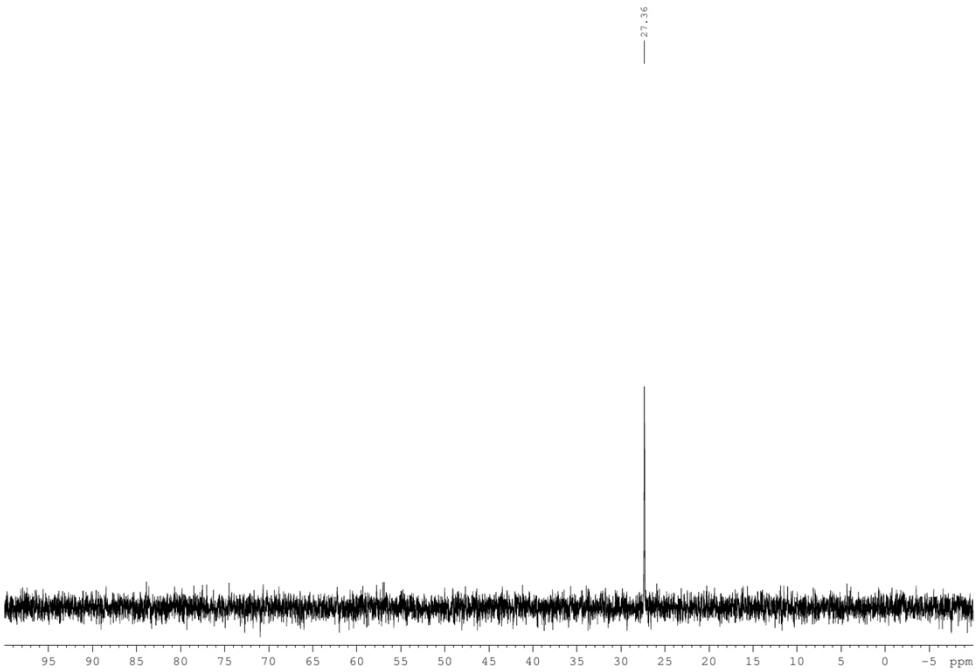

7.70
7.69
7.68
7.67
7.66
7.64
7.62
7.61
7.59
7.58
7.57
7.55
7.54
7.54
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.46
7.44
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.35
7.33
7.31
7.30
7.29
7.27
7.18
7.18
7.17
7.16
7.15
6.80
6.78
6.75
6.73
3.72
1.90
1.84
0.00
11 10 9 8 7 6 5 4 3 2 1 ppm
1.28
5.19
7.35
1.08
2.09
3.00
3.03
2.99

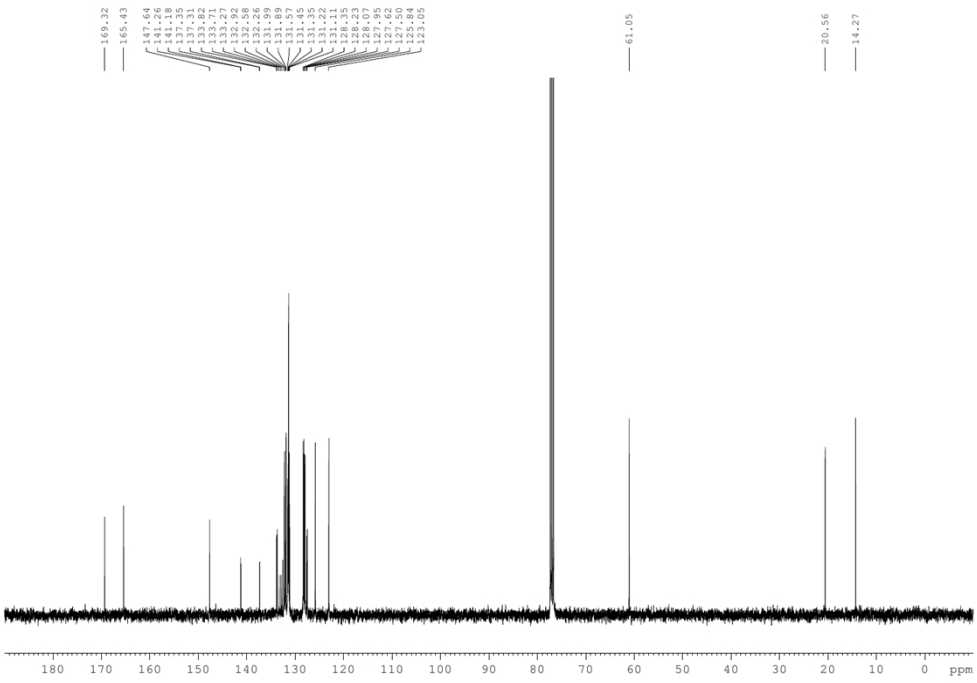

27.58
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

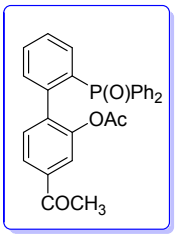

169.13
168.21
148.71
141.97
137.64
136.60
136.53
133.85
133.77
133.73
133.26
132.81
132.69
132.33
132.13
132.03
131.93
131.83
131.74
131.35
131.29
131.26
128.18
128.14
128.06
127.94
127.81
127.78
127.66
119.44
111.71
77.37
77.05
76.73
56.03
20.54
20.14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

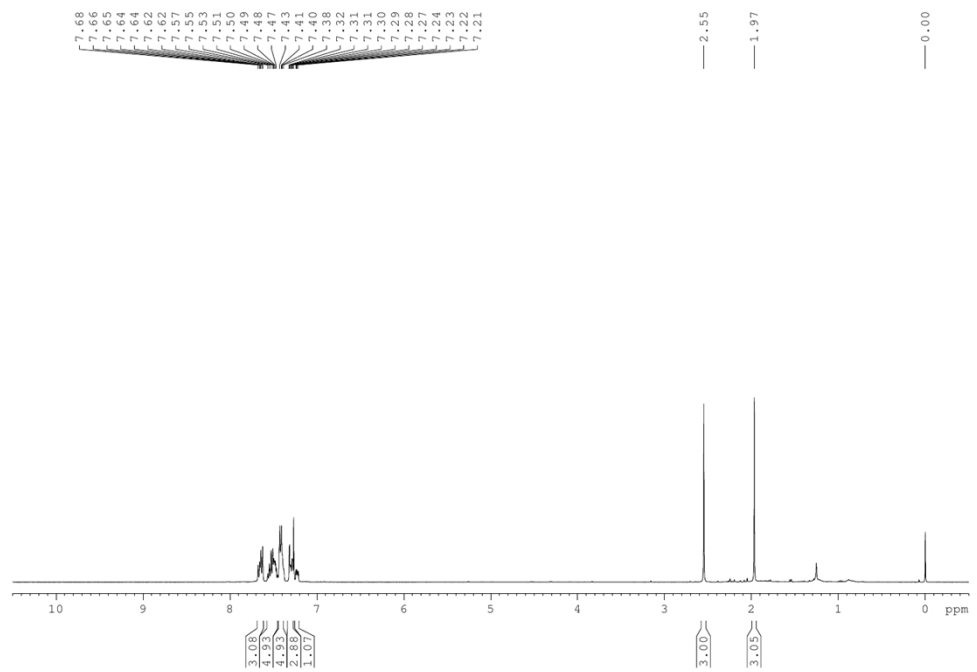

P(O)Ph2
OAc
COOEt

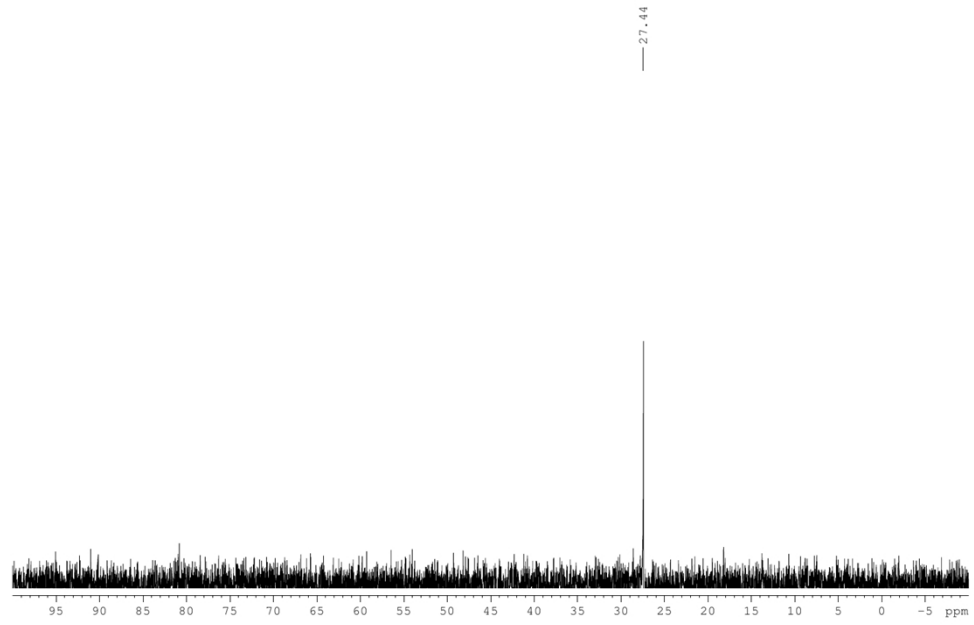

7.72
7.71
7.70
7.69
7.65
7.64
7.63
7.62
7.61
7.60
7.55
7.55
7.55
7.53
7.52
7.51
7.51
7.49
7.47
7.46
7.45
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.34
7.32
7.31
7.30
7.29
7.28
7.27
7.23
7.23
7.22
7.22
7.21
7.20
4.38
4.38
4.36
4.36
4.34
4.34
4.32
4.32
1.95
1.39
1.37
1.36
0.00
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.95
1.94
4.89
4.72
2.82
0.96
1.93
3.00
2.92

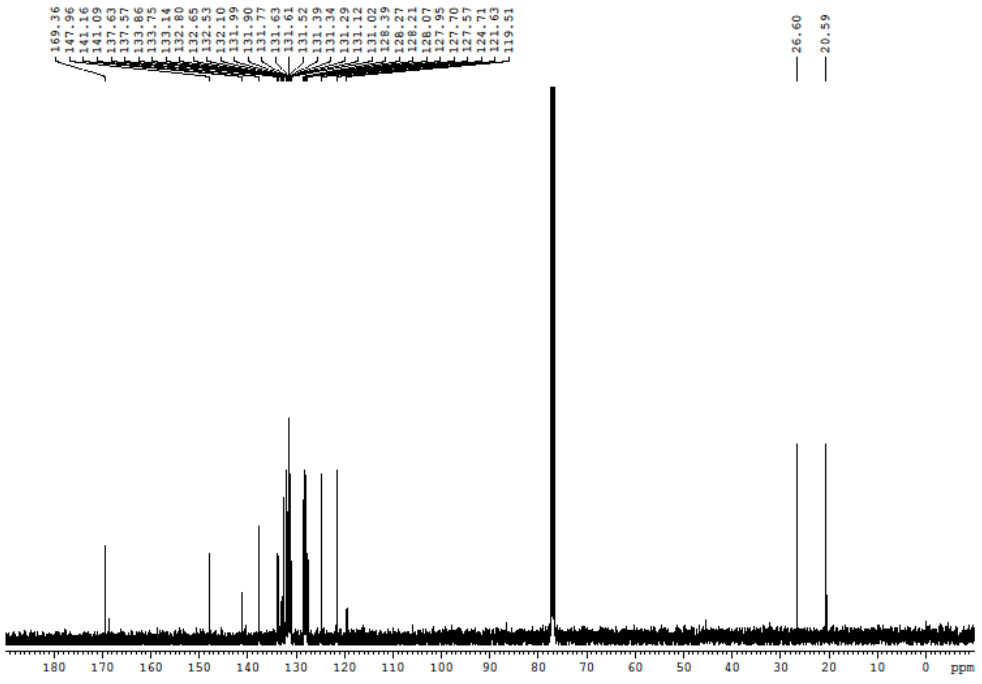

27.36
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
ppm

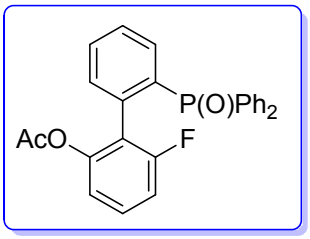

169.32
165.43
147.64
141.26
141.18
137.35
137.31
133.82
133.71
133.27
132.92
132.58
132.26
131.99
131.89
131.57
131.45
131.35
131.22
131.11
128.35
128.23
128.07
127.95
127.62
127.50
125.84
123.05
61.05
20.56
14.27
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

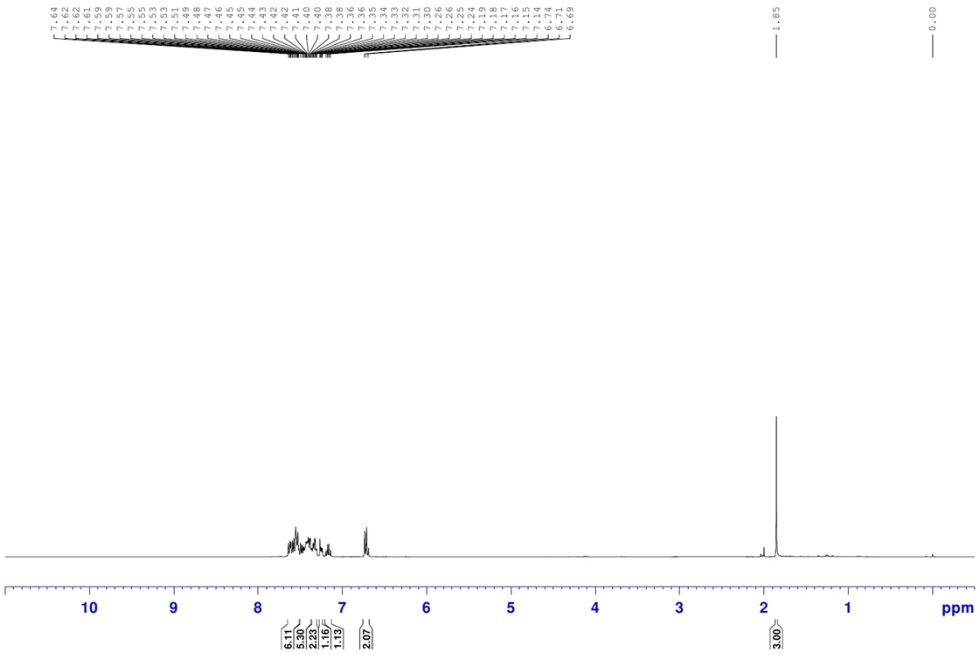

P(O)Ph2
OAc
COCH3


7.68
7.66
7.65
7.64
7.64
7.62
7.62
7.57
7.55
7.53
7.51
7.50
7.49
7.48
7.47
7.43
7.41
7.40
7.38
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.24
7.23
7.22
7.21
2.55
1.97
0.00
10 9 8 7 6 5 4 3 2 1 0 ppm
3.08
4.93
4.93
2.88
1.07
3.00
3.05


27.44
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 ppm


169.36
147.96
141.16
141.09
137.63
137.57
133.86
133.75
133.14
132.80
132.65
132.53
132.10
131.99
131.90
131.77
131.63
131.61
131.52
131.39
131.34
131.29
131.12
131.02
128.39
128.27
128.21
128.07
127.95
127.70
127.57
124.71
124.63
119.51
26.60
20.59
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


P(O)Ph2
AcO
F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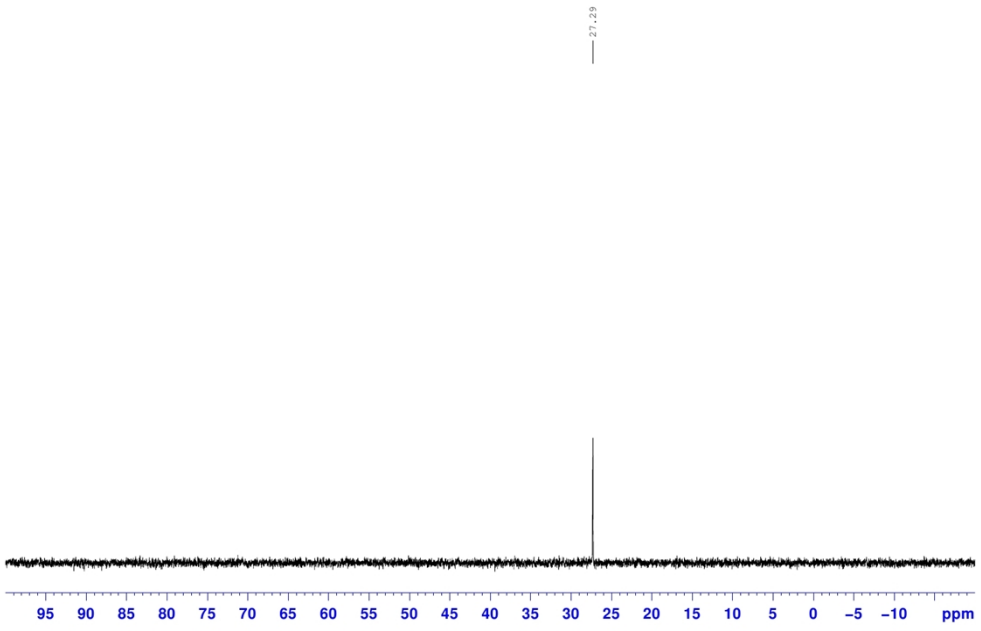
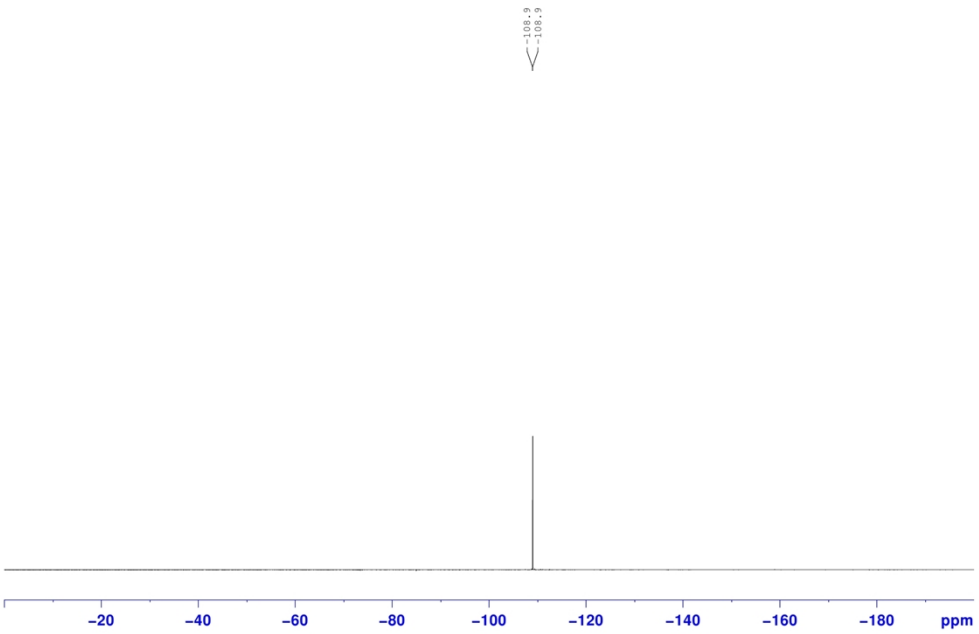
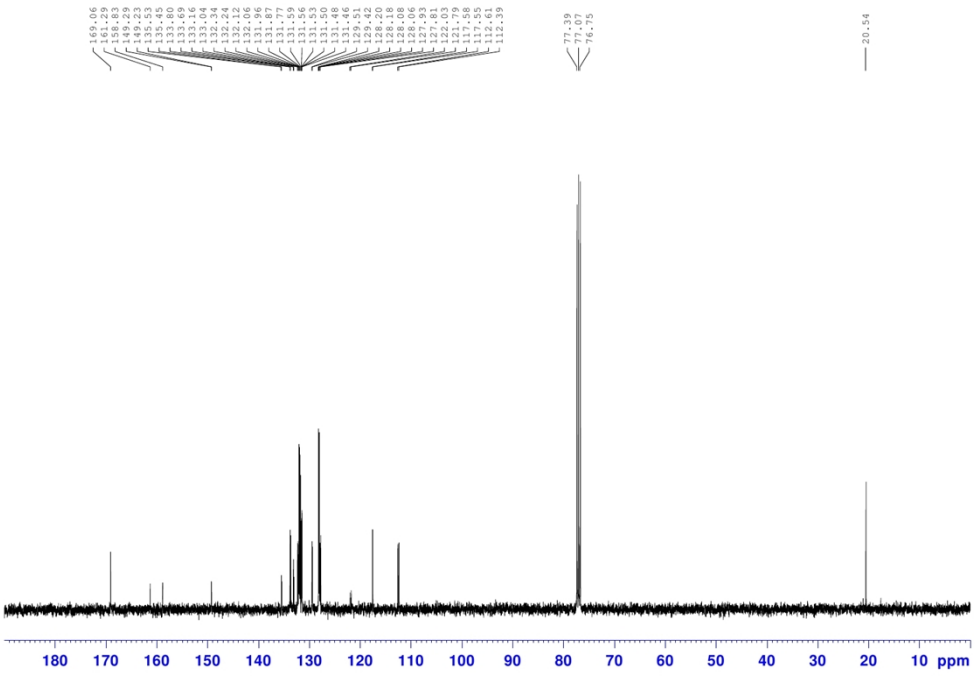
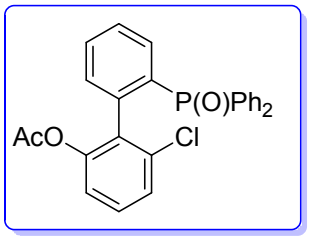
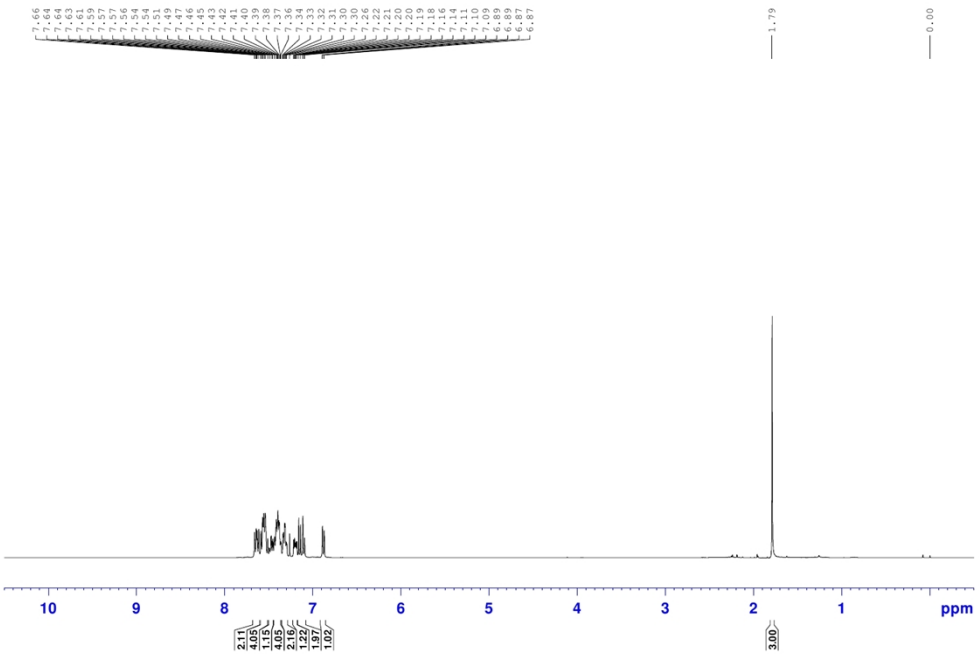
7.62
7.61
7.59
7.58
7.57
7.55
7.53
7.51
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.26
7.25
7.24
7.19
7.18
7.17
7.16
7.15
7.14
6.74
6.71
6.69
1.85
0.00
10
9
8
7
6
5
4
3
2
1
ppm
6.11
5.30
2.23
1.16
1.13
2.07
3.00

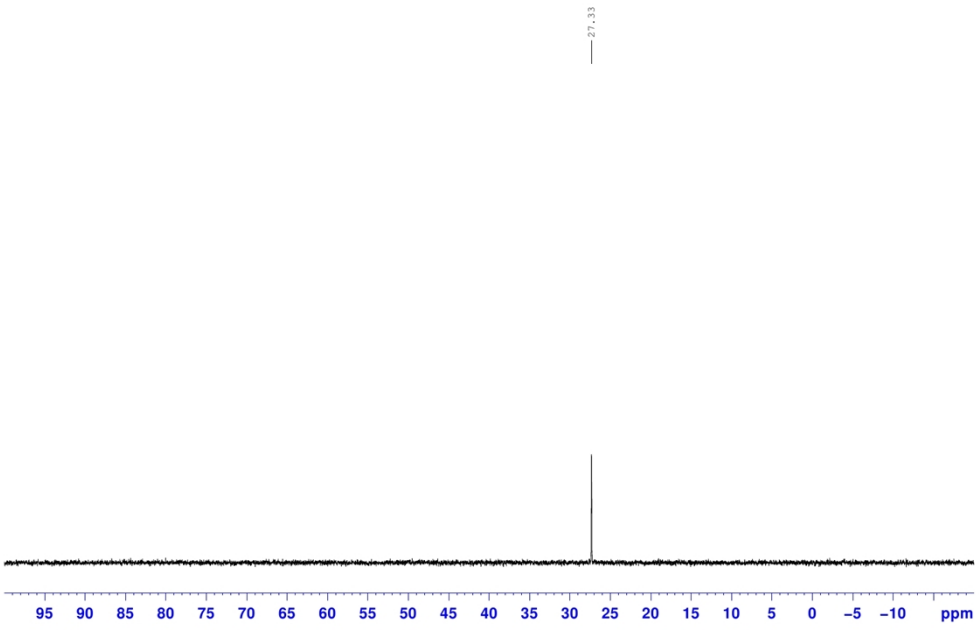

27.29
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
ppm

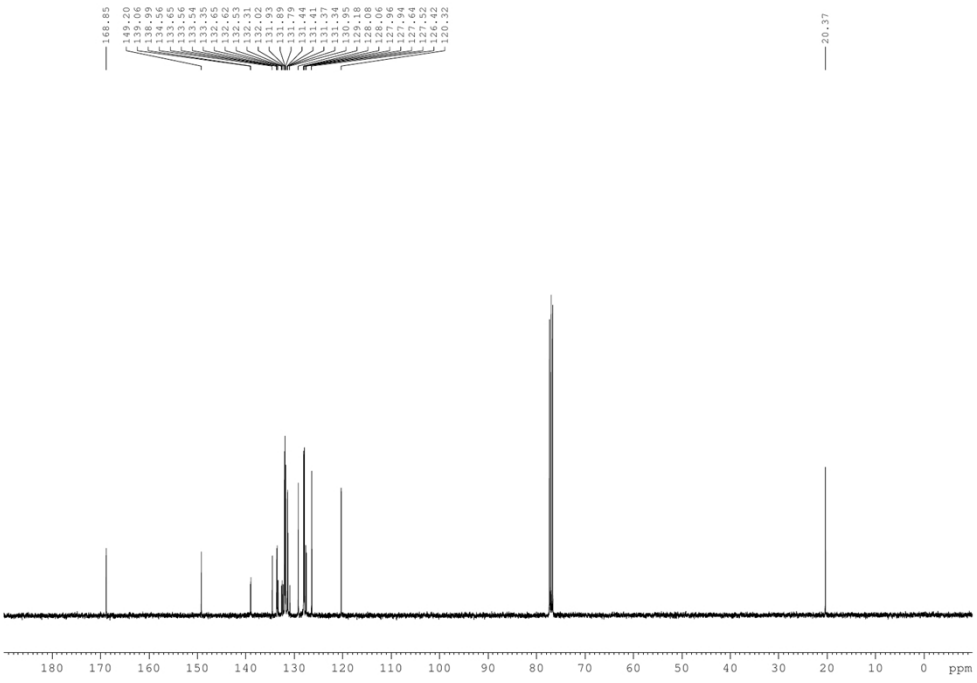

-108.9
-108.9
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

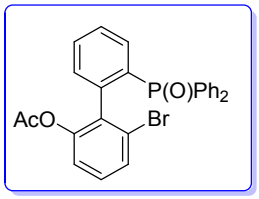

169.06
161.29
158.83
148.89
140.23
135.53
135.45
133.60
133.09
133.16
133.04
132.34
132.24
132.12
132.06
131.96
131.87
131.77
131.59
131.56
131.53
131.50
131.48
131.46
129.51
129.42
128.28
128.18
128.08
128.06
127.93
127.81
122.03
121.79
117.58
117.55
117.41
112.39
77.39
77.07
76.75
20.54
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

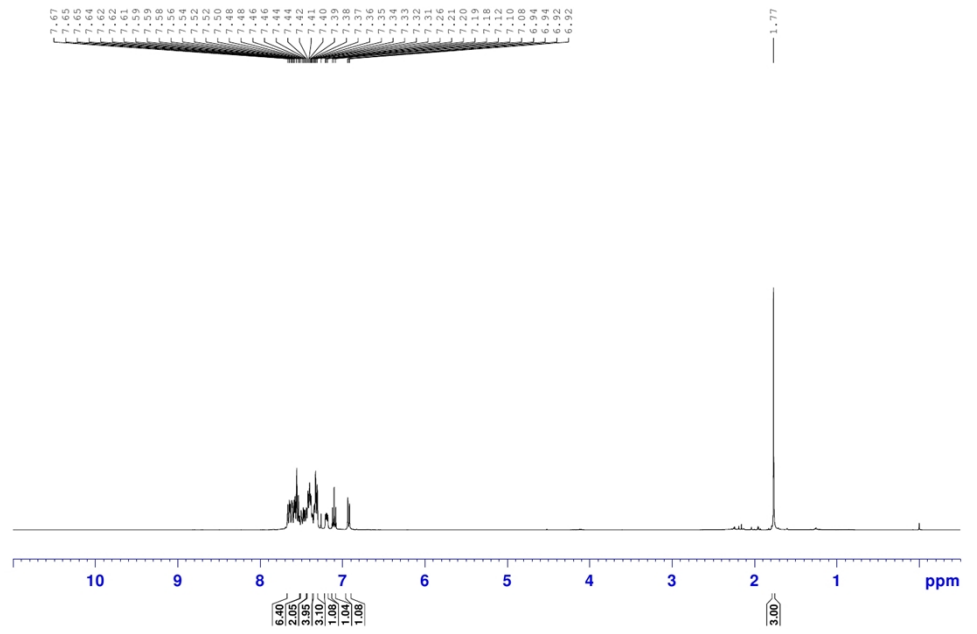

P(O)Ph2
AcO
Cl

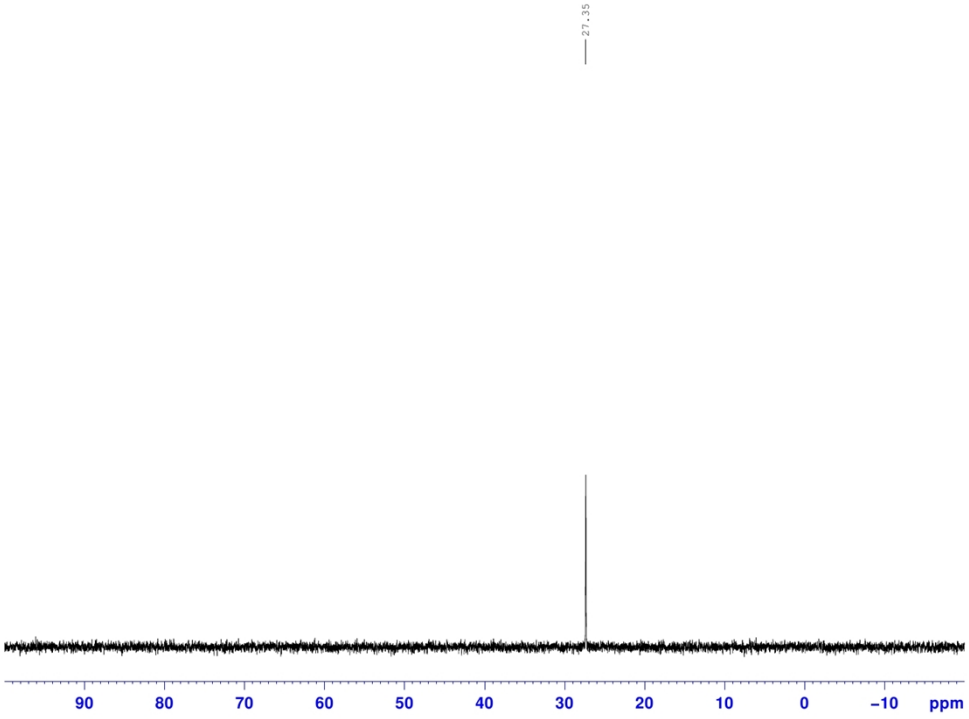

7.66
7.64
7.64
7.63
7.61
7.59
7.57
7.57
7.56
7.54
7.51
7.49
7.47
7.46
7.45
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.34
7.33
7.32
7.31
7.30
7.26
7.22
7.21
7.20
7.20
7.18
7.18
7.16
7.14
7.11
7.10
7.09
6.89
6.89
6.87
6.87
1.79
0.00
10
9
8
7
6
5
4
3
2
1
ppm
2.11
4.05
1.15
4.05
2.16
1.22
1.97
1.02
3.00


27.33
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
ppm


168.85
149.20
139.06
138.99
134.56
134.45
133.56
133.54
133.35
132.65
132.62
132.53
132.31
132.02
131.93
131.89
131.79
131.44
131.41
131.37
131.34
130.95
129.18
128.08
128.06
127.96
127.94
127.64
127.52
126.42
120.32
20.37
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


P(O)Ph2
AcO
Br


7.67
7.65
7.64
7.62
7.61
7.59
7.58
7.56
7.54
7.52
7.50
7.48
7.46
7.44
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.26
7.21
7.20
7.19
7.18
7.12
7.10
7.08
6.94
6.92
1.77
10 9 8 7 6 5 4 3 2 1 ppm
6.40
2.05
3.95
3.10
1.08
1.04
1.08
3.00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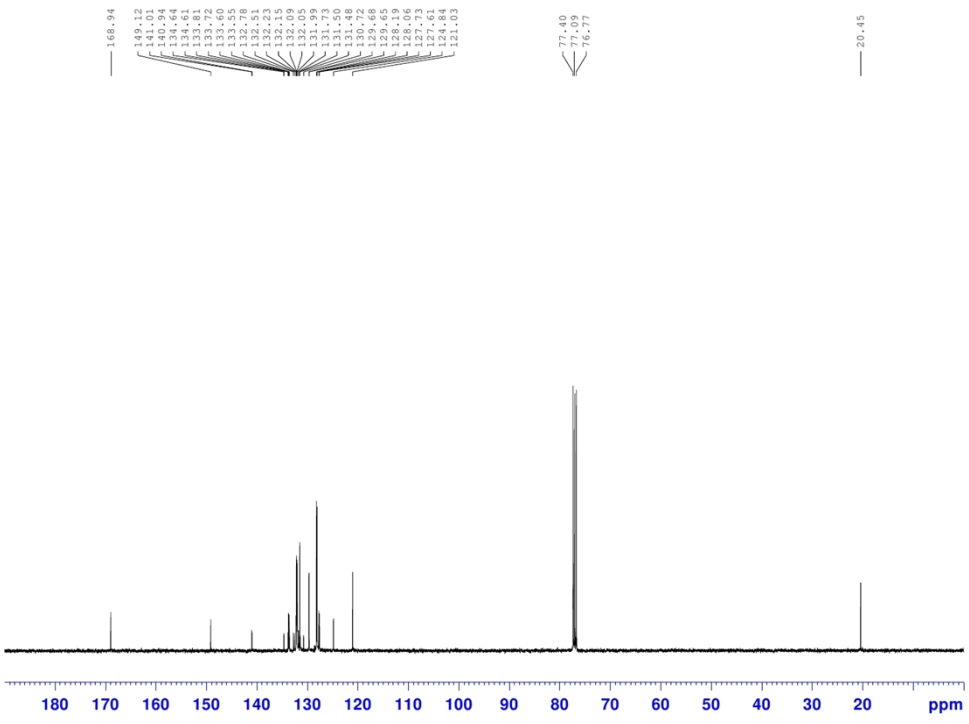
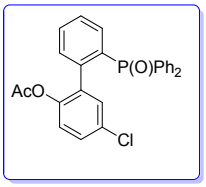
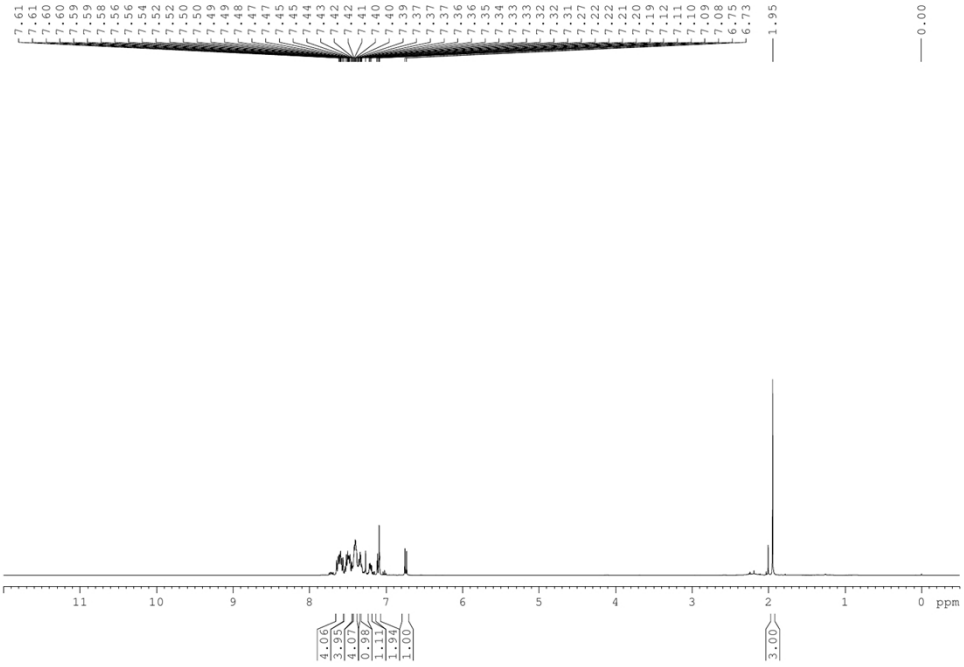
90
80
70
60
50
40
30
20
10
0
−10
ppm


168.94
149.12
141.01
140.94
134.64
134.61
133.81
133.72
133.60
133.55
132.78
132.51
132.23
132.15
132.09
132.05
131.99
131.73
131.50
131.48
130.72
129.68
129.65
128.19
128.06
127.73
127.61
124.84
121.03
77.40
77.09
76.77
20.45
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


P(O)Ph2
AcO
Cl


7.61
7.61
7.60
7.60
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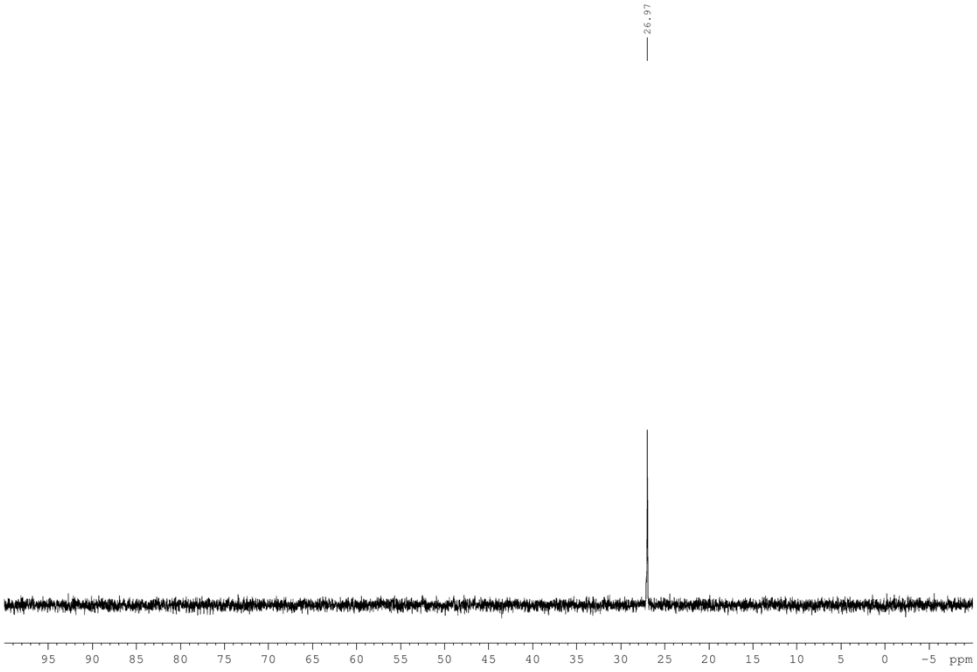
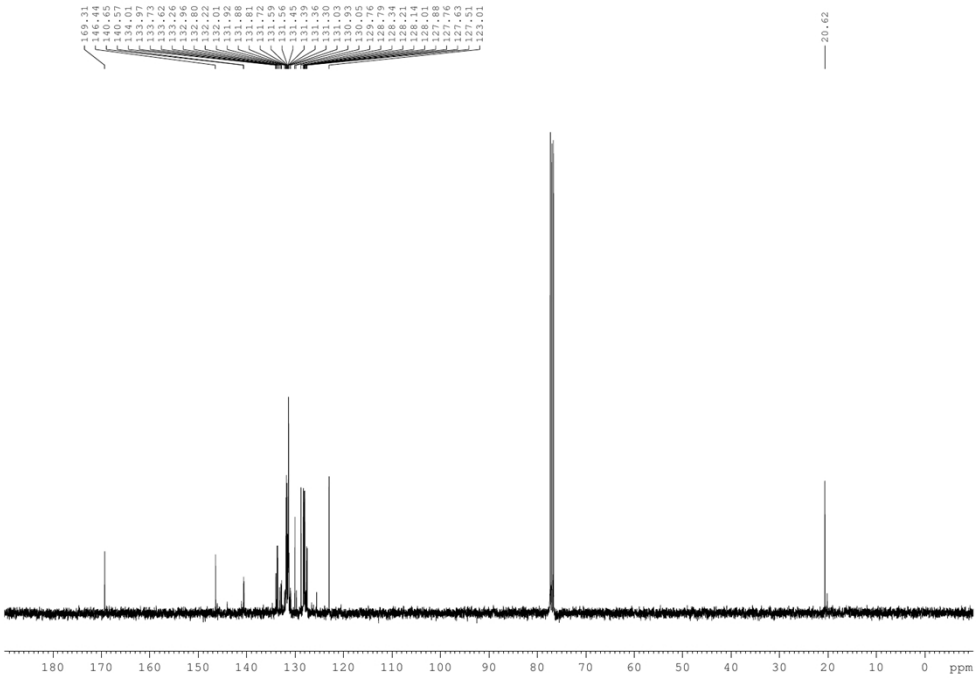
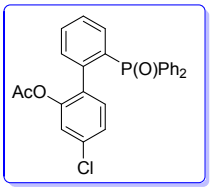
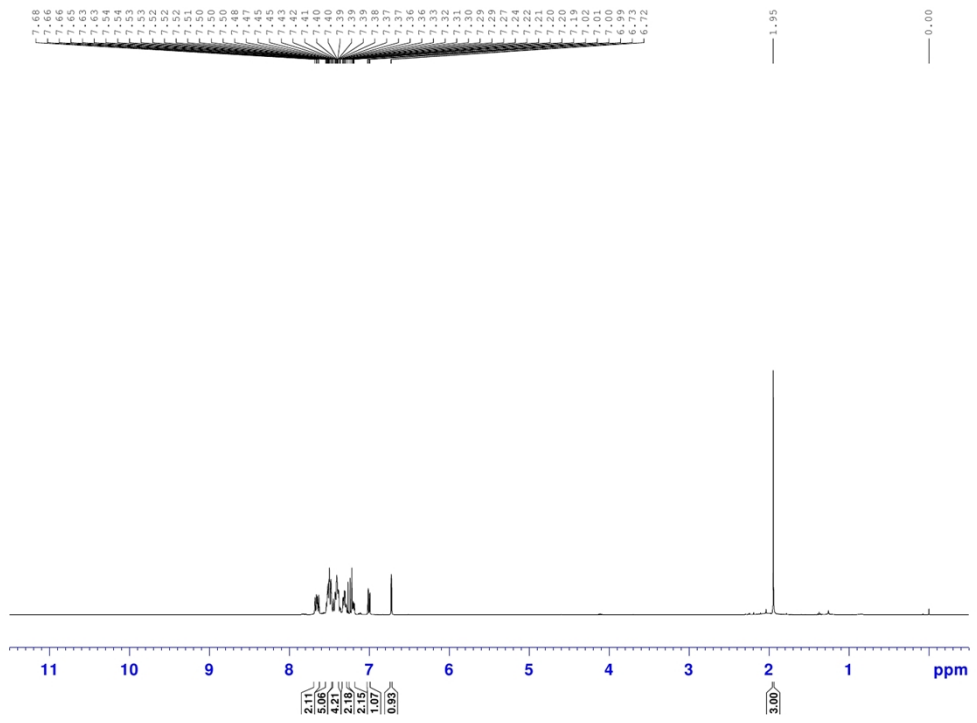
7.59
7.58
7.56
7.54
7.52
7.52
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.27
7.22
7.22
7.21
7.20
7.19
7.12
7.11
7.10
7.09
7.08
6.75
6.73
1.95
0.00
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.06
3.95
4.07
0.98
1.11
1.94
1.00
3.00


26.97
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
ppm


169.31
146.44
140.65
140.57
134.01
133.73
133.62
133.26
132.96
132.80
132.22
132.01
131.92
131.88
131.81
131.72
131.59
131.56
131.45
131.39
131.36
131.30
131.03
130.93
130.05
129.76
128.79
128.34
128.21
128.14
128.01
127.88
127.76
127.63
127.51
123.01
20.62
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


P(O)Ph2
AcO
Cl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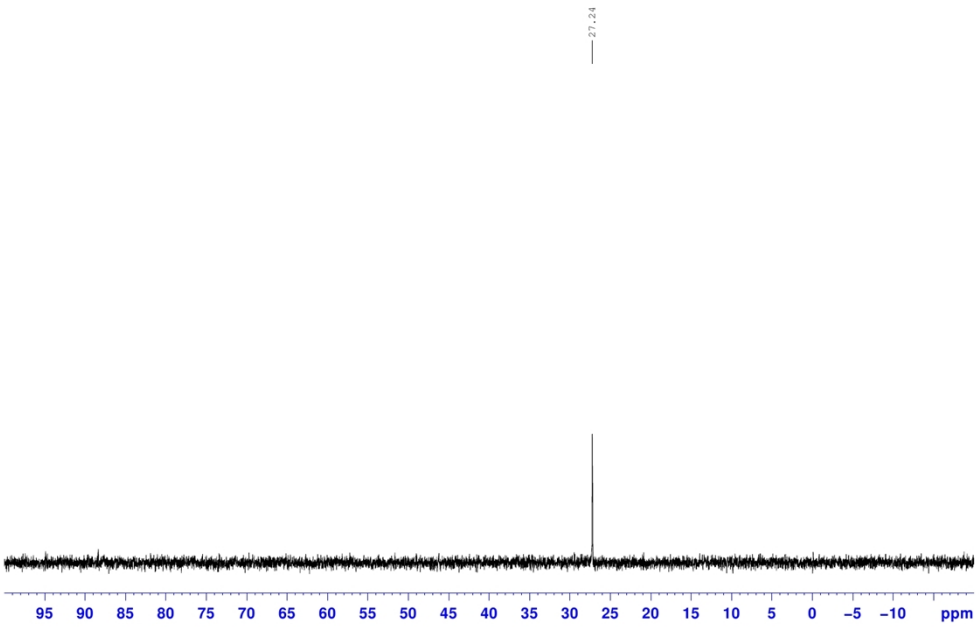
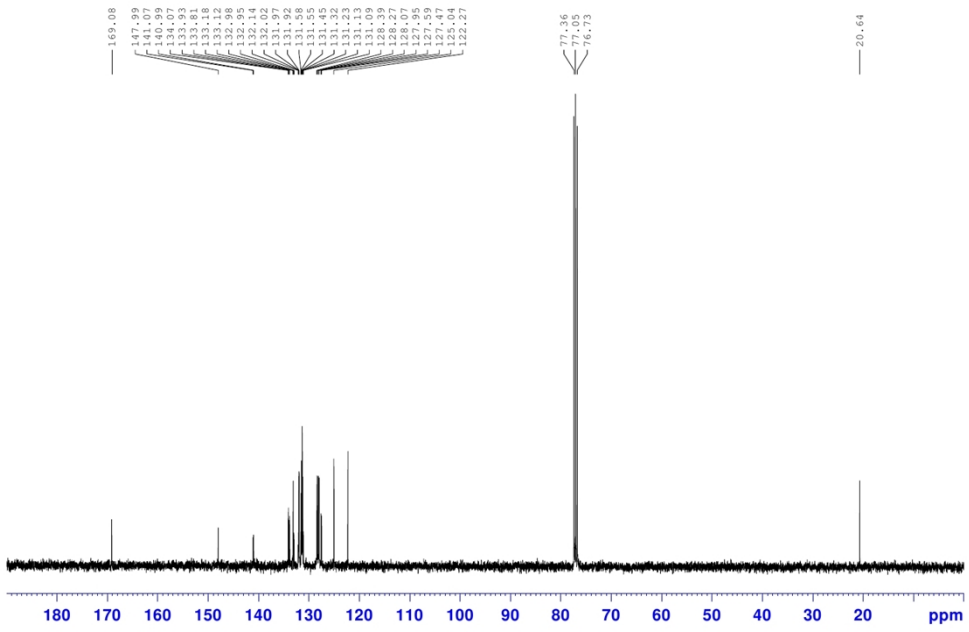
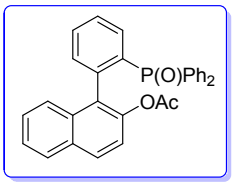
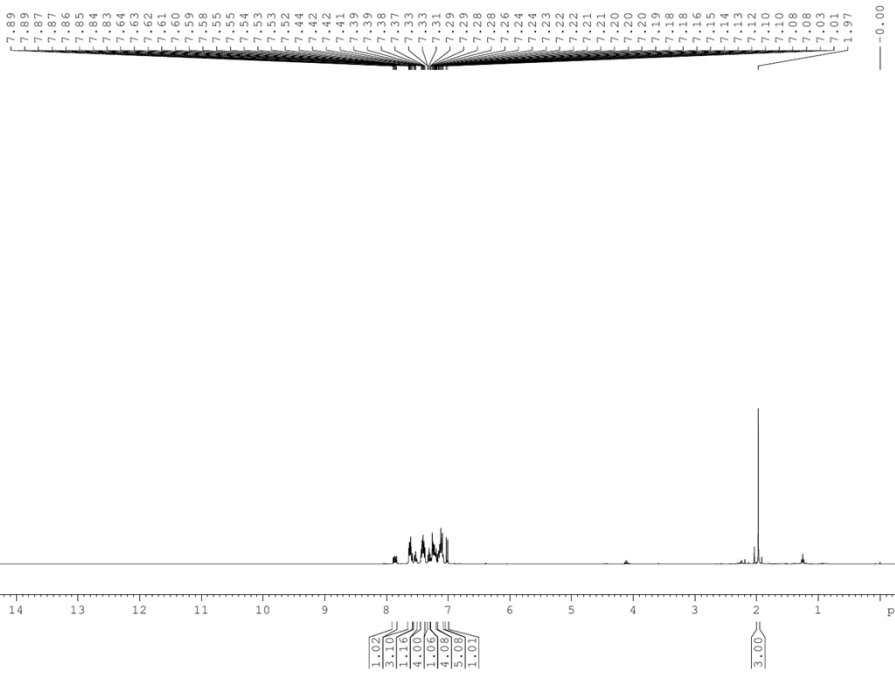
7.66
7.66
7.65
7.63
7.63
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.48
7.47
7.45
7.45
7.43
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.32
7.31
7.30
7.29
7.29
7.27
7.24
7.22
7.21
7.20
7.20
7.19
7.02
7.01
7.00
6.99
6.73
6.72
1.95
0.00
11 10 9 8 7 6 5 4 3 2 1 ppm
2.11
5.06
4.21
2.18
2.15
1.07
0.93
3.00


27.24
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm


169.08
147.99
141.07
140.99
134.07
133.93
133.81
133.18
133.12
132.98
132.95
132.14
132.02
131.97
131.92
131.58
131.55
131.45
131.32
131.23
131.13
131.09
128.39
128.27
128.07
127.95
127.59
127.47
125.04
122.27
77.36
77.05
76.73
20.64
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


P(O)Ph2
OAc


7.89
7.89
7.87
7.87
7.86
7.85
7.84
7.83
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.55
7.55
7.54
7.53
7.53
7.52
7.44
7.42
7.42
7.41
7.39
7.39
7.38
7.37
7.33
7.31
7.29
7.29
7.28
7.28
7.26
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.16
7.15
7.14
7.13
7.12
7.10
7.10
7.08
7.08
7.03
7.01
1.97
0.00
14
13
12
11
10
9
8
7
6
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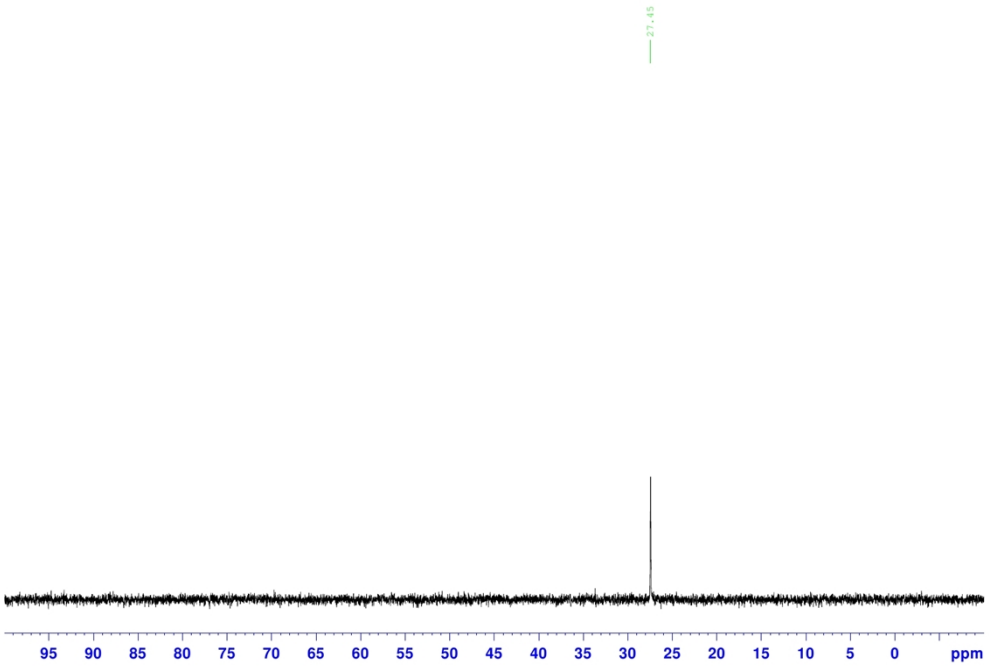
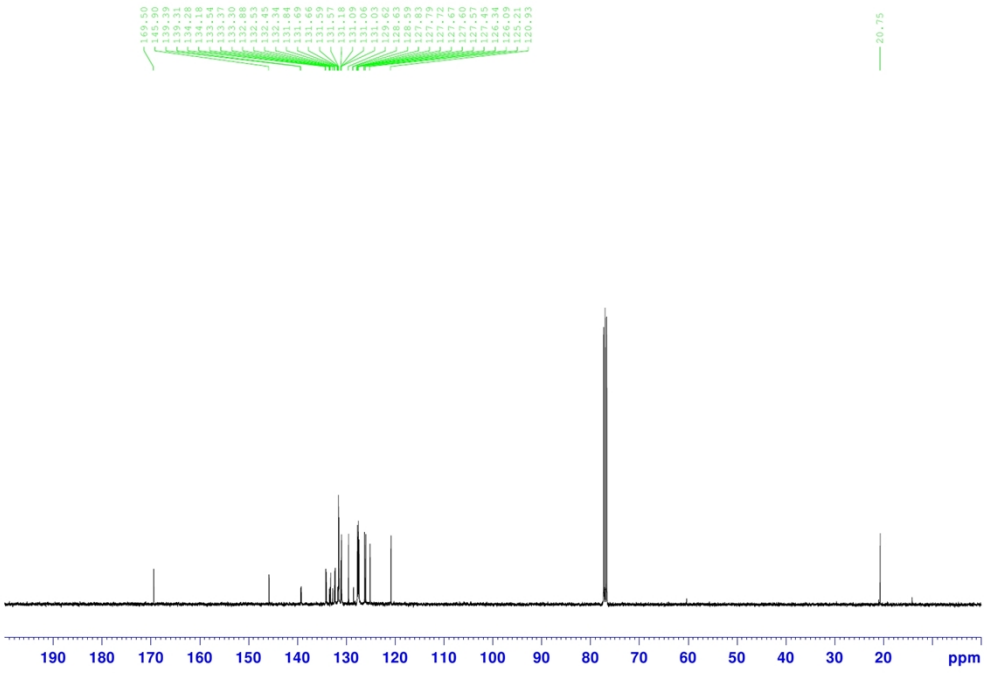
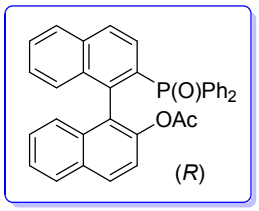
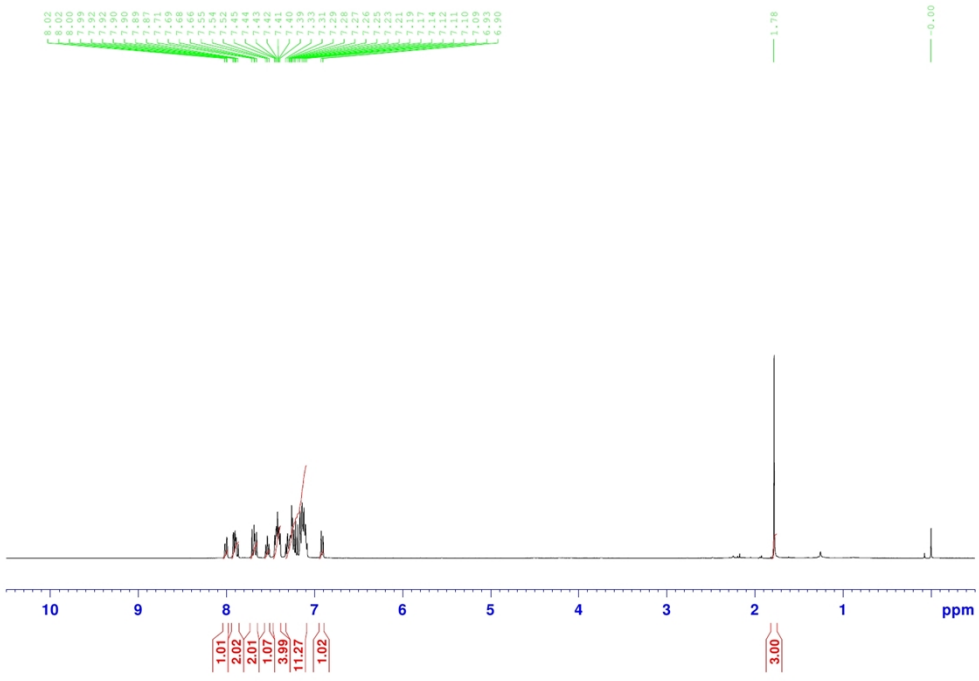
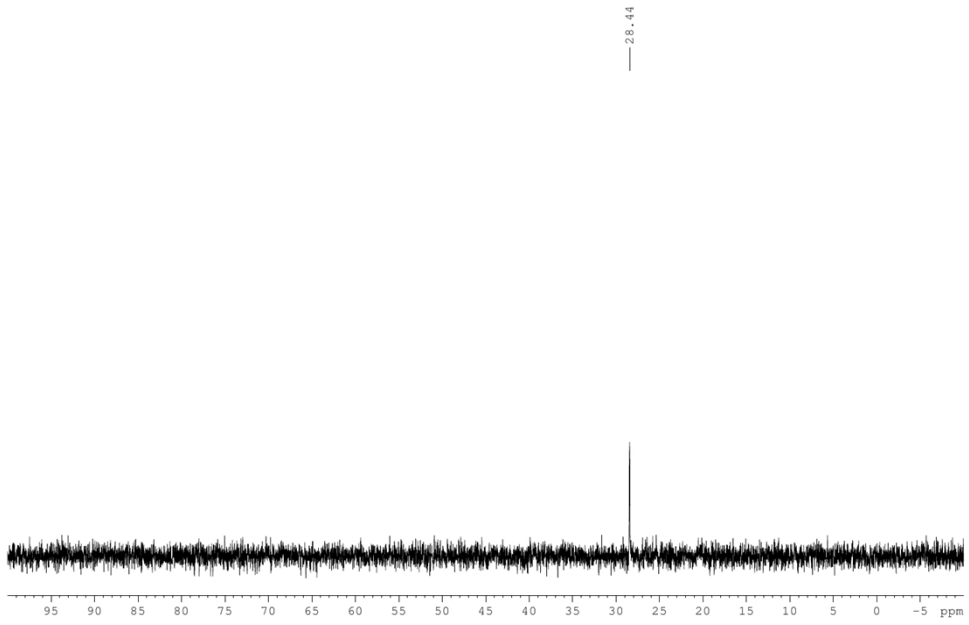
4.00
1.06
4.08
5.08
1.01
3.00

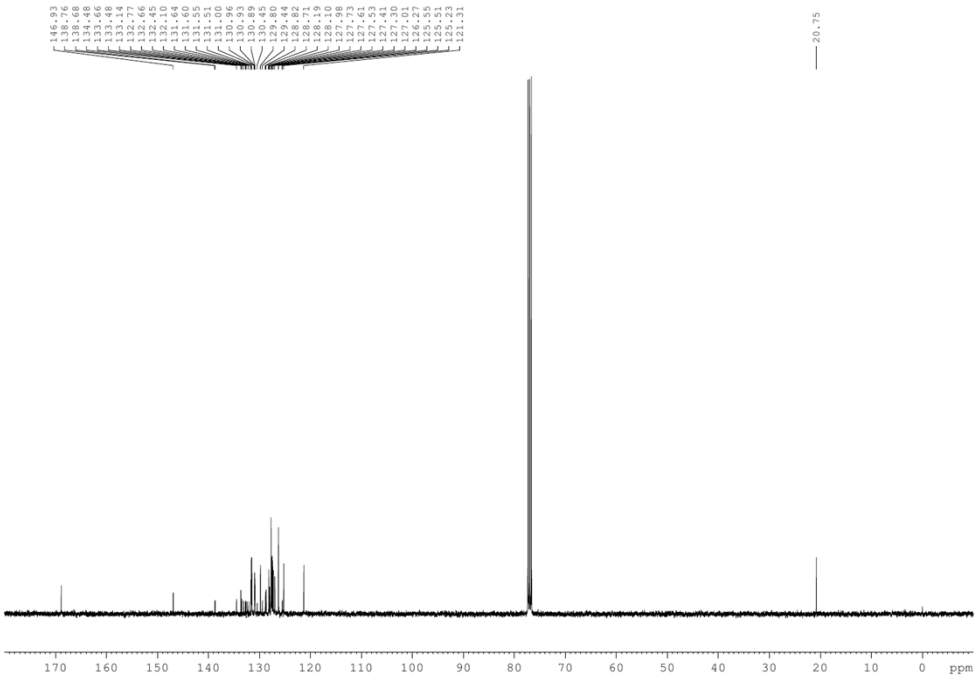

27.45
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

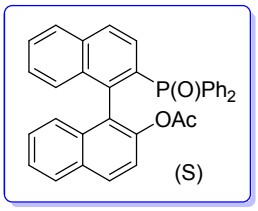


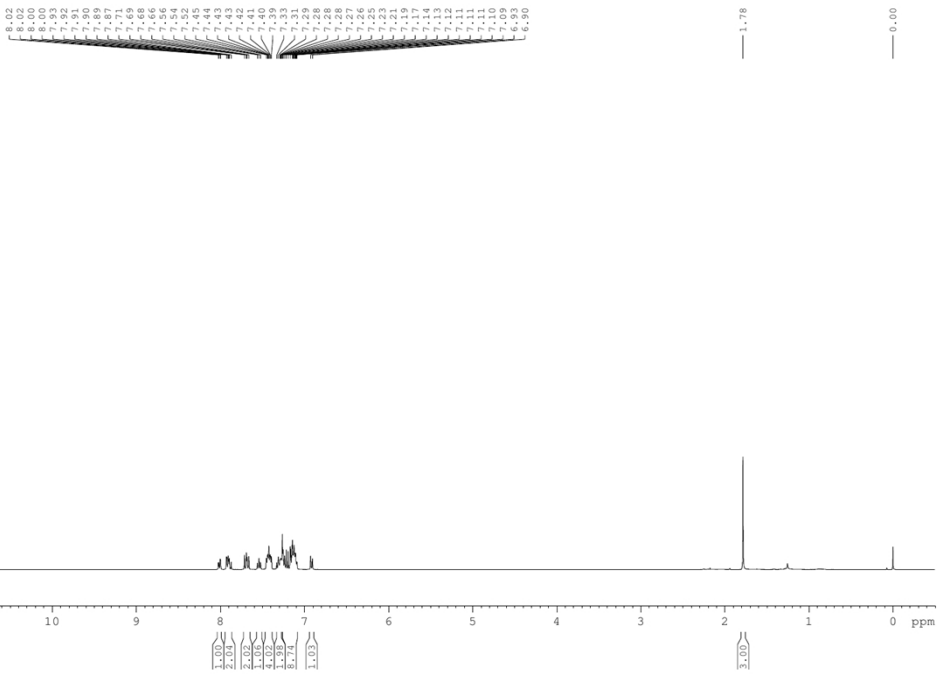

P(O)Ph2
OAc
(R)

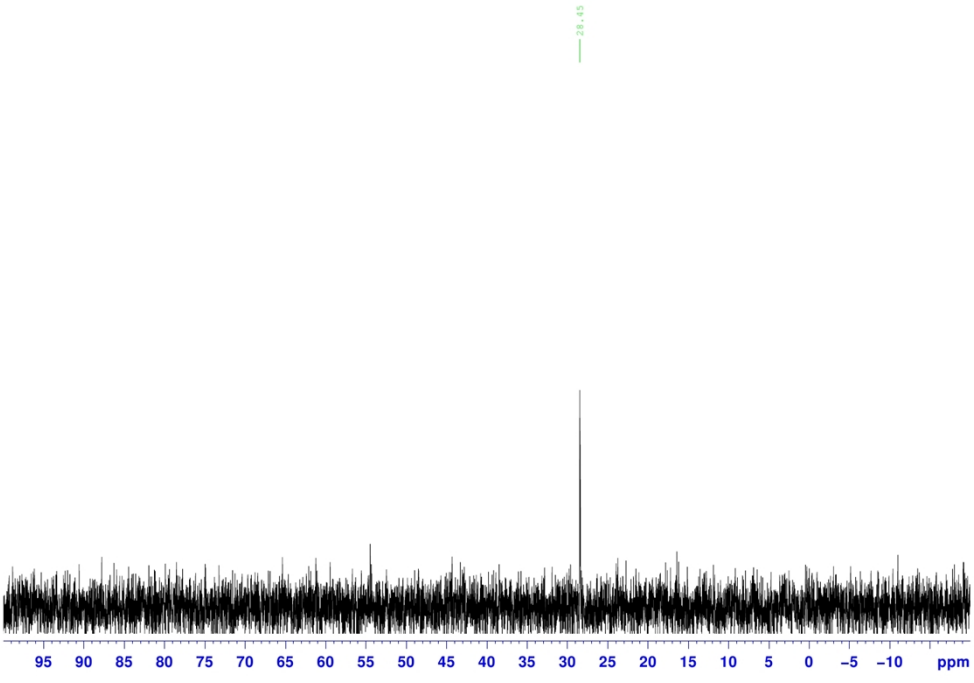


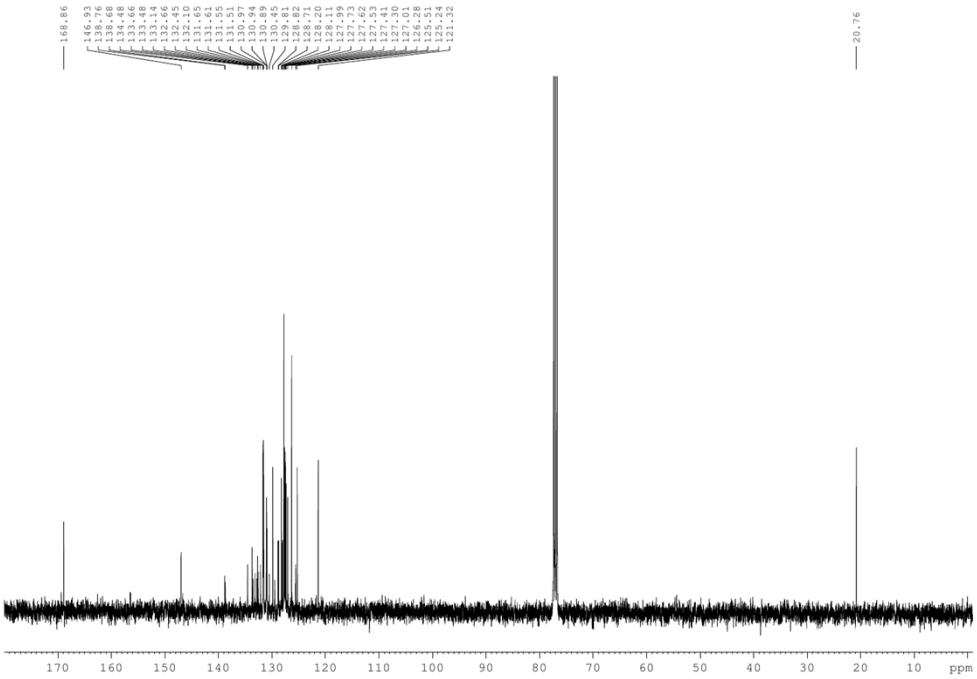

28.44
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 ppm

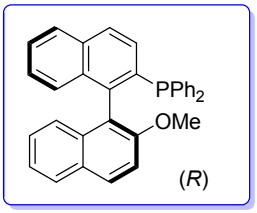

146.93
138.76
138.68
134.48
134.46
133.48
133.14
132.77
132.66
132.45
132.10
131.64
131.60
131.55
131.51
131.00
130.96
130.93
130.89
130.45
129.80
129.44
128.92
128.71
128.19
128.10
127.98
127.93
127.61
127.53
127.41
127.30
127.01
126.27
125.55
125.51
125.33
121.31
20.75
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

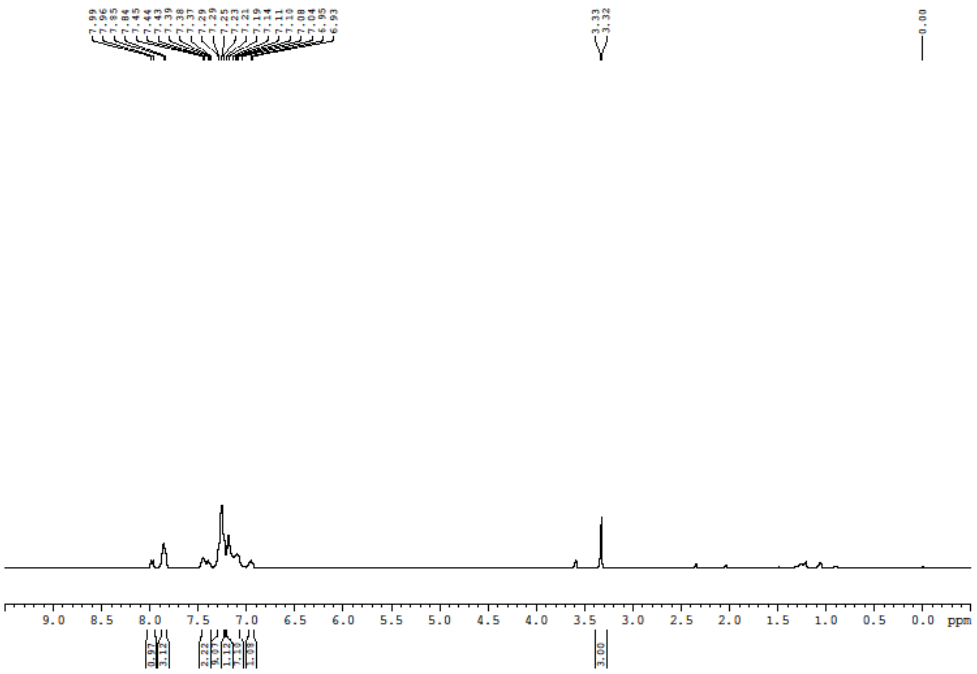

P(O)Ph2
OAc
(S)

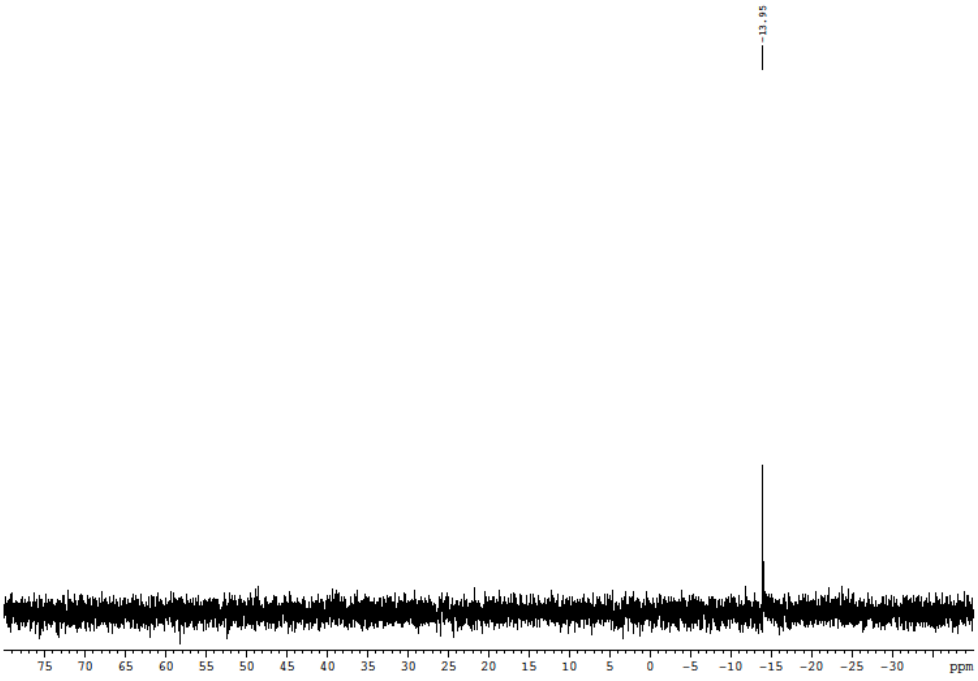

8.02
8.02
8.00
8.00
7.93
7.92
7.91
7.90
7.89
7.87
7.71
7.69
7.68
7.66
7.56
7.54
7.52
7.45
7.44
7.43
7.43
7.42
7.41
7.40
7.39
7.33
7.31
7.29
7.28
7.28
7.28
7.27
7.26
7.25
7.23
7.21
7.19
7.17
7.14
7.13
7.12
7.11
7.11
7.11
7.10
7.09
6.93
6.90
1.78
0.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.04
2.02
4.06
4.00
3.98
8.74
1.03
3.00

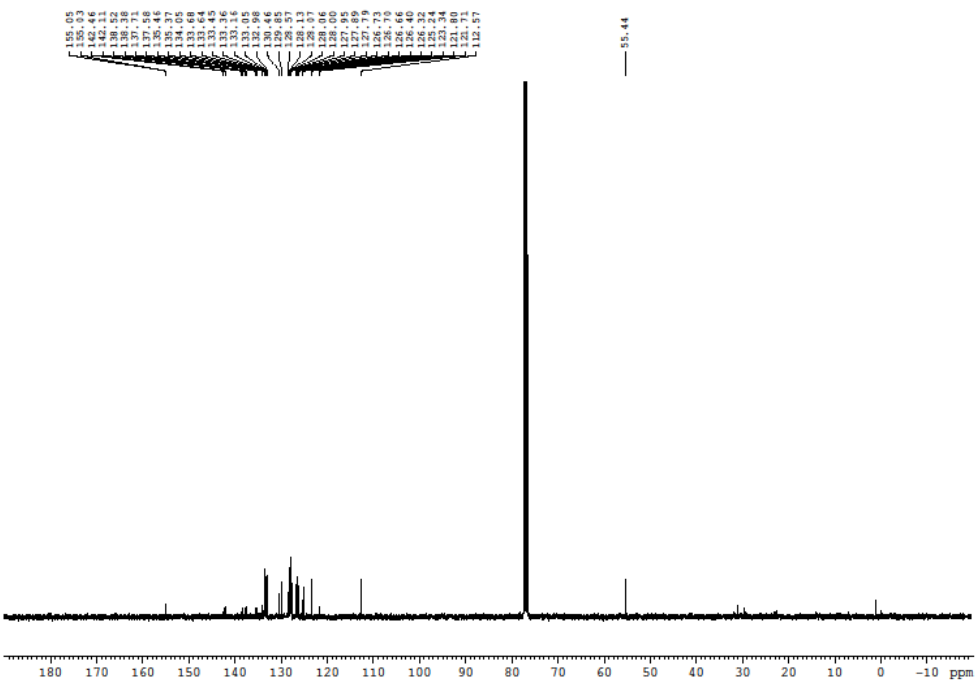

28.45
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
ppm



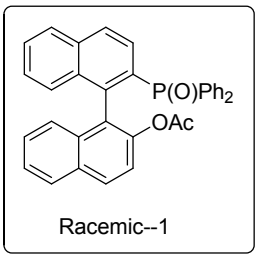

PPh2
OMe
(R)




-13.95
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


155.05
155.03
142.46
142.11
139.52
138.38
137.71
137.58
135.44
135.37
134.05
133.68
133.64
133.45
133.36
133.16
133.05
132.98
132.66
129.85
128.57
128.13
128.07
128.06
128.00
127.95
127.89
127.79
126.73
126.70
126.66
126.40
126.32
125.24
123.34
121.80
121.71
112.57
55.44
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

VIII Copies of HPLC spectra



Racemic--1

User name: System Project name: A2014

Sample Information	
Sample name: zhangheng140110-5rs	Collector: System
Sample type: unknow	Collect time: 2014-1-210 16:31:17
Number: 1	Group of collection: zhangheng20140103
Times of injection: 5	Processing time: 2014-1-10 19:20:07
Volume of injection: 5.00 μL	Processing method: zhangheng2014011005rs
Runtime: 120.0 Miuntes	Channel name: Wvln Ch1
Sample group's name:	Processing channel notes: PDA 230.0 nm

Empower software

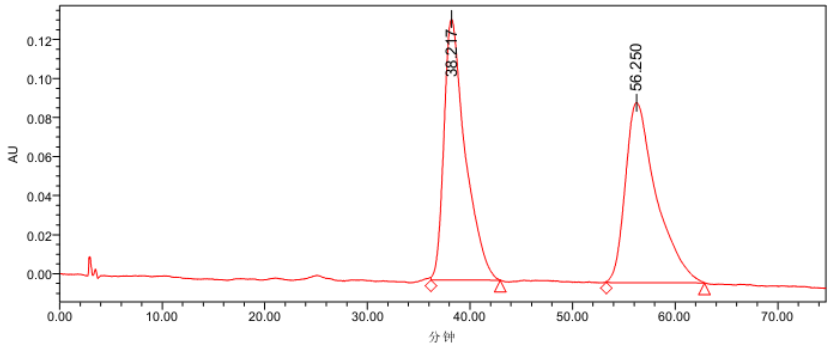
进样综合报告 报告

用户名称: System 项目名称: A2014

样品信息

样品名称:	zhangheng 140110-5rs	采集者:	System
样品类型:	未知	采集时间:	2014-1-10 16:31:17
瓶号:	1	采集方法组:	zhangheng20140103
进样次数:	5	处理日期:	2014-1-10 19:20:07
进样体积:	5.00 ul	处理方法:	zhangheng2014011005rs
运行时间:	120.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 230.0 纳米

自动标尺色谱图



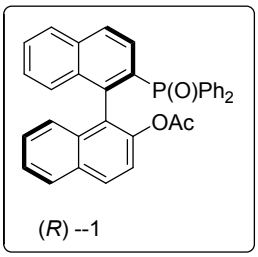
SampleName zhangheng 140110-5rs; Vial 1; Injection 5; Channel W2996 ; Date Acquired 2014-1-10 16:31:17

处理通道: **PDA 230.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 230.0 纳米	38.217	19297959	49.95	133673
2	PDA 230.0 纳米	56.250	19338567	50.05	92188

Processing channel: PDA 230.00 nm

	Processing channel	Retention time (minute)	Area	Area %	Peak height
1	PDA 230.0 nm	38.217	19297959	49.95	133673
2	PDA 230.0 nm	56.250	19338567	50.05	92188



(*R*) --1

User name: System Project name: A2014

Sample Information	
Sample name: zhangheng140110-4r	Collector: System
Sample type: unknow	Collect time: 2014-1-210 15:14:12
Number: 1	Group of collection: zhangheng20140103
Times of injection: 4	Processing time: 2014-1-10 19:14:16
Volume of injection: 5.00 μL	Processing method: zhangheng2014011004r
Runtime: 120.0 Miuntes	Channel name: Wvln Ch1
Sample group's name:	Processing channel notes: PDA 230.0 nm

Empower software

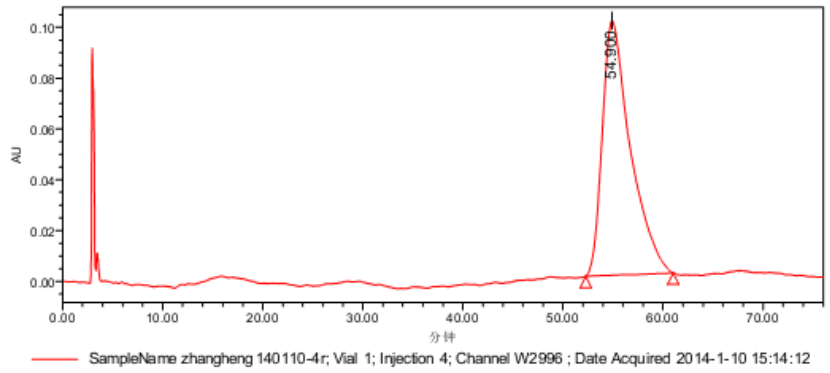
进样综合报告 报告

用户名称: System 项目名称: A2014

样品信息

样品名称:	zhangheng140110-4r	采集者:	System
样品类型:	未知	采集时间:	2014-1-10 15:14:12
瓶号:	1	采集方法组:	zhangheng20140103
进样次数:	4	处理日期:	2014-1-10 19:14:16
进样体积:	5.00 ul	处理方法:	zhangheng2014011004r
运行时间:	120.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 230.0 纳米

自动标尺色谱图



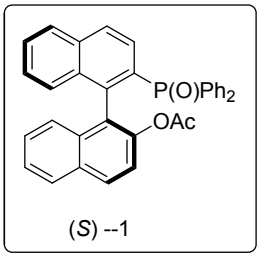
SampleName zhangheng140110-4r; Vial 1; Injection 4; Channel W2996 ; Date Acquired 2014-1-10 15:14:12

处理通道: **PDA 230.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 230.0 纳米	54.900	19557067	100.00	100272

Processing channel: PDA 230.0 nm

	Processing channel	Retention time (minute)	Area	Area %	Peak height
1	PDA 230.0 nm	54.900	19557067	100.00	100272



(*S*) --1

User name: System Project name: A2014

Sample Information	
Sample name: zhangheng140110-6s	Collector: System
Sample type: unknow	Collect time: 2014-1-210 17:47:08
Number: 1	Group of collection: zhangheng20140103
Times of injection: 6	Processing time: 2014-1-10 19:17:49
Volume of injection: 5.00 μL	Processing method: zhangheng2014011006s
Runtime: 120.0 Miuntes	Channel name: Wvln Ch1
Sample group's name:	Processing channel notes: PDA 230.0 nm

Empower software

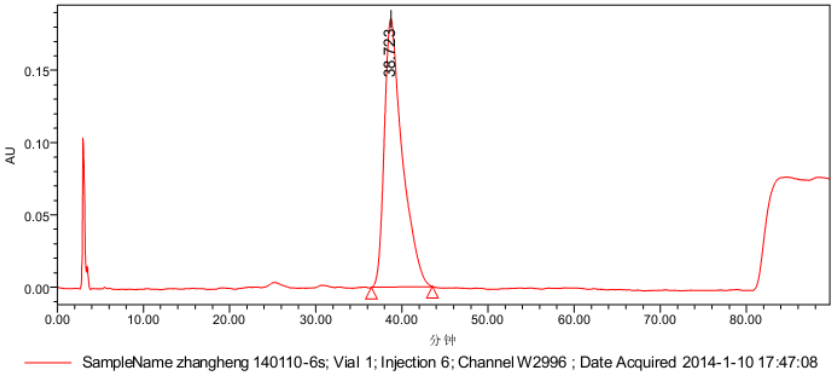
进样综合报告 报告

用户名称： System 项目名称： A2014

样品信息

样品名称:	zhangheng 140110-6s	采集者:	System
样品类型:	未知	采集时间:	2014-1-10 17:47:08
瓶号:	1	采集方法组:	zhangheng20140103
进样次数:	6	处理日期:	2014-1-10 19:17:49
进样体积:	5.00 ul	处理方法:	zhangheng2014011006s
运行时间:	120.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 230.0 纳米

自动标尺色谱图



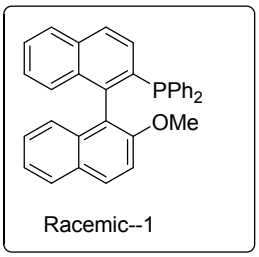
SampleName zhangheng 140110-6s; Vial 1; Injection 6; Channel W2996 ; Date Acquired 2014-1-10 17:47:08

处理通道: **PDA 230.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 230.0 纳米	38.723	26944821	100.00	185606

Processing channel: PDA 230.0 nm

	Processing channel	Retention time (minute)	Area	Area %	Peak height
1	PDA 230.0 nm	38.723	26944821	100.00	185606



Racemic--1

User name: System Project name: A2014

Sample Information	
Sample name: zhangheng14011608	Collector: System
Sample type: unknow	Collect time: 2014-1-16 14:11:11
Number: 1	Group of collection: zhangheng20140103
Times of injection: 1	Processing time: 2014-1-16 14:49:17
Volume of injection: 5.00 μL	Processing method: zhhP3OMers
Runtime: 120.0 Miuntes	Channel name: Wvln Ch1
Sample group's name:	Processing channel notes: PDA 254.0 nm

Empower software

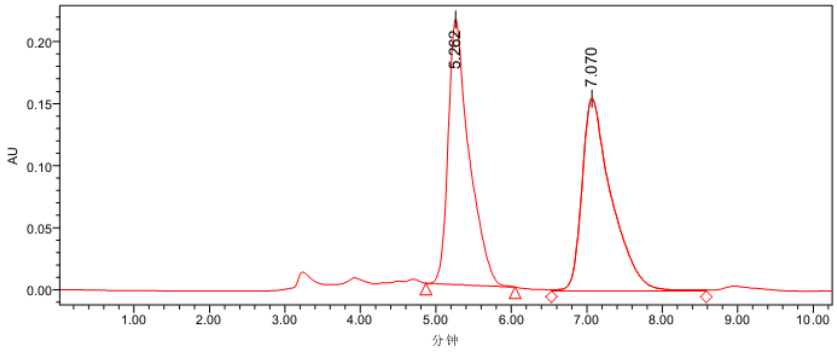
进样综合报告 报告

用户名称: System 项目名称: A2014

样品信息

样品名称:	zhangheng14011608	采集者:	System
样品类型:	未知	采集时间:	2014-1-16 14:11:11
瓶号:	1	采集方法组:	zhangheng20140103
进样次数:	1	处理日期:	2014-1-16 14:49:17
进样体积:	5.00 ul	处理方法:	zhhP3OMers
运行时间:	120.0 Minutes	通道名称:	Wvln Ch4
样品组名称:		处理通道注释:	PDA 254.0 纳米

自动标尺色谱图



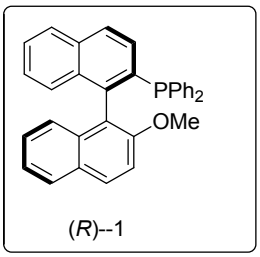
SampleName zhangheng14011608; Vial 1; Injection 1; Channel W2996 ; Date Acquired 2014-1-16 14:11:11

处理通道: **PDA 254.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	5.262	4138398	49.49	214263
2	PDA 254.0 纳米	7.070	4222996	50.51	155545

Processing channel: PDA 254.00 nm

	Processing channel	Retention time (minute)	Area	Area %	Peak height
1	PDA 254.0 nm	5.262	4138398	49.49	214263
2	PDA 254.0 nm	7.070	422996	50.51	155545



(*R*)--1

User name: System Project name: A2014

Sample Information	
Sample name: zhangheng14011610	Collector: System
Sample type: unknow	Collect time: 2014-1-16 14:36:28
Number: 1	Group of collection: zhangheng20140103
Times of injection: 3	Processing time: 2014-1-16 14:55:51
Volume of injection: 5.00 μL	Processing method: zhhP3OMer2
Runtime: 120.0 Miuntes	Channel name: Wvln Ch1
Sample group's name:	Processing channel notes: PDA 254.0 nm

Empower software

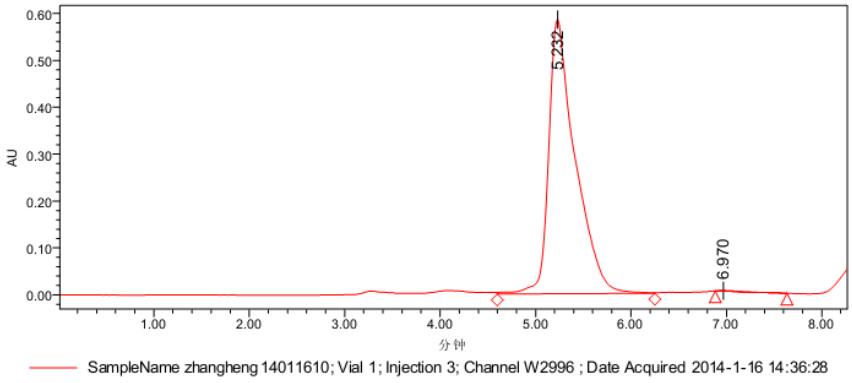
进样综合报告 报告

用户名称: System 项目名称: A2014

样品信息

样品名称:	zhangheng14011610	采集者:	System
样品类型:	未知	采集时间:	2014-1-16 14:36:28
瓶号:	1	采集方法组:	zhangheng20140103
进样次数:	3	处理日期:	2014-1-16 14:55:51
进样体积:	5.00 ul	处理方法:	zhhP3OMer2
运行时间:	120.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 254.0 纳米

自动标尺色谱图



SampleName zhangheng14011610; Vial 1; Injection 3; Channel W2996 ; Date Acquired 2014-1-16 14:36:28

处理通道: **PDA 254.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	5.232	11330312	99.82	585201
2	PDA 254.0 纳米	6.970	20160	0.18	1302

Processing channel: PDA 254.00 nm

	Processing channel	Retention time (minute)	Area	Area %	Peak height
1	PDA 254.0 nm	5.232	11330312	99.82	585201
2	PDA 254.0 nm	6.970	20160	0.18	1302