

Supporting Information for

Visible-light-Induced Ligand to Metal Charge Transfer Excitation Enabled Phosphorylation of Aryl Halides

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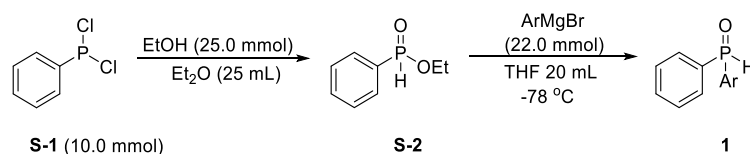
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1. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents used in reactions were p.A. grade and dried only if indicated. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063–0.2 mm). Melting points were measured on a Yanaco Micro Melting Point Apparatus. ^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR were recorded on a Varian VNMR 400 or Bruker AV-600 spectrometer in CDCl_3 . For ^1H NMR spectra, data are quoted in the following order: chemical shift (δ) in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard (CDCl_3 at 7.26 ppm). Multiplicities are indicated s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets); coupling constants (J) are in Hertz (Hz). For proton-decoupled ^{13}C NMR spectra, chemical shifts (J) are also quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard (CDCl_3 at 77.0 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR (KBr disc) and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained on AB 5800 MALDI-TOF/TOF and are recorded using electrospray ionization (ESI).

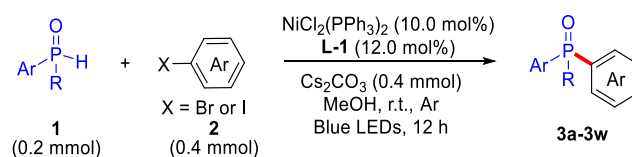
2. Secondary phosphine oxides preparation



A 100 mL flask was charged with dichlorophenylphosphine **S-1** (1.36 mL, 10.0 mmol, 1.0 equiv.) and Et_2O (25 mL). Absolute EtOH (1.46 mL, 25.0 mmol, 2.5 equiv.) was added over 5 min and the reaction mixture was stirred at r.t. for 2 h. The solvent was evaporated in vacuo and the crude ethyl phosphinate **S-2** was dissolved in dry THF (12 mL) under an argon atmosphere for next step.

A flame-dried flask was charged with commercially available Grignard reagent (22.0 mmol) under argon atmosphere and cooled to -78°C . The ethyl phosphinate **S-2** solution was added dropwise over 30 min and the resulting mixture stirred at r.t. for 2 h. The reaction was then quenched with sat. aq. NH_4Cl solution and subsequently extracted with CHCl_3 (3 x 50 mL) and the combined organic fractions dried over Na_2SO_4 , concentrated and flash column chromatography to give **1**, and all the characterization data of **1** are consistent with the previous reports.^[1]

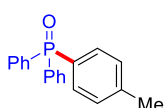
3. General procedure for the Phosphorylation of aryl halides



1 (0.2 mmol), **2** (0.4 mmol), NiCl₂(PPh₃)₂ (13.1 mg, 0.02 mmol), Cs₂CO₃ (130.3 mg, 0.4 mmol), 1,10-Phen **L-1** (4.76 mg, 0.024 mmol) and a stir bar were added to a sealed tube under an argon atmosphere, MeOH (2.0 mL) as solvent was then added. The mixture was stirred and irradiated by a 6 W blue LED trips for 12 hours. After **1** was completely consumed (monitored by TLC), the crude mixture was directly purified by flash column chromatography on silica gel (EtOAc/petroleum ether 1:2) to give the desired products **3a-3w**.

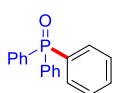
4. Characterization data of tertiary phosphine oxides

Diphenyl(p-tolyl)phosphine oxide (**3a**)^[2]



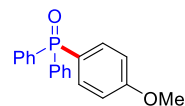
White gum (40.9 mg, 70% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.62 (m, 4H), 7.59–7.50 (m, 4H), 7.49–7.42 (m, 4H), 7.27 (dd, $J = 7.4, 3.0$ Hz, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 132.10 (d, $J = 10.1$ Hz, 1C), 132.07 (d, $J = 9.1$ Hz, 1C), 132.04 (d, $J = 10.1$ Hz, 1C), 131.9 (d, $J = 2.0$ Hz, 1C), 131.8 (d, $J = 2.0$ Hz, 1C), 129.2 (d, $J = 13.1$ Hz, 1C), 128.5 (d, $J = 12.1$ Hz, 1C), 128.4 (d, $J = 12.1$ Hz, 1C), 21.6 (d, $J = 2.0$ Hz, 1C). ³¹P NMR (162 MHz, CDCl₃) δ 29.4. IR (neat): $\nu = 2922, 2377, 1640, 1385, 1100, 874, 582, 486$ cm⁻¹; HRMS (ESI) Exact mass calculated for [C₁₉H₁₈OP]⁺ [M+H]⁺: 293.1086, found: 293.1086.

Triphenylphosphine oxide (**3b**)^[2]



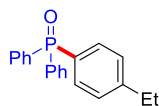
White gum (41.7 mg, 75% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.60 (m, 6H), 7.56–7.49 (m, 3H), 7.48–7.40 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 132.1 (d, $J = 10.1$ Hz, 1C), 131.9 (d, $J = 2.0$ Hz, 1C), 128.5, 128.4. ³¹P NMR (162 MHz, CDCl₃) δ 29.3. IR (neat): $\nu = 2976, 2339, 1622, 1439, 1185, 1048, 625, 544$ cm⁻¹; HRMS (ESI) Exact mass calculated for [C₁₈H₁₆OP]⁺ [M+H]⁺: 279.0933, found: 279.0929.

(4-methoxyphenyl)diphenylphosphine oxide (**3c**)^[2]



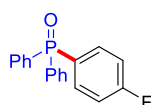
White gum (26.5 mg, 43% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.62 (m, 4H), 7.61–7.50 (m, 4H), 7.48–7.42 (m, 4H), 6.99–6.94 (m, 2H), 3.84 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 134.0 (d, $J = 11.1$ Hz, 1C), 133.5, 132.4, 132.1, 132.0, 131.8 (d, $J = 3.0$ Hz, 1C), 128.4 (d, $J = 12.1$ Hz, 1C), 114.1 (d, $J = 13.1$ Hz, 1C), 55.3. ³¹P NMR (162 MHz, CDCl₃) δ 29.3. IR (neat): $\nu = 3058, 2926, 2318, 1597, 1501, 1187, 1118, 700, 542$ cm⁻¹; HRMS (ESI) Exact mass calculated for [C₁₉H₁₈O₂P]⁺ [M+H]⁺: 309.1039, found: 309.1040.

(4-ethylphenyl)diphenylphosphine oxide (**3d**)



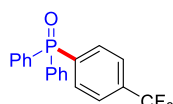
White gum (40.0 mg, 62% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.71–7.63 (m, 4H), 7.61–7.51 (m, 4H), 7.45 (m, 4H), 7.32–7.25 (m, 2H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 132.2 (d, $J = 10.1$ Hz, 1C), 132.1 (d, $J = 10.1$ Hz, 1C), 131.9 (d, $J = 2.0$ Hz, 1C), 131.8 (d, $J = 2.0$ Hz, 1C), 128.5 (d, $J = 12.1$ Hz, 1C), 128.4 (d, $J = 12.1$ Hz, 1C), 128.1 (d, $J = 12.1$ Hz, 1C), 28.9 (d, $J = 1.0$ Hz, 1C), 15.1. ^{31}P NMR (162 MHz, CDCl_3) δ 29.4. IR (neat): $\nu = 3055, 2965, 2317, 1436, 1191, 1117, 698, 631, 536$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{20}\text{OP}]^+$ $[\text{M}+\text{H}]^+$: 307.1246, found: 307.1253.

(4-fluorophenyl)diphenylphosphine oxide (3e)^[2]



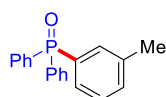
Yellow gum (26.1 mg, 44% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.71–7.60 (m, 6H), 7.58–7.51 (m, 2H), 7.49–7.43 (m, 4H), 7.14 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.5 (q, $J = 9.1$ Hz, 1H), 132.8, 132.1 (q, $J = 2.0$ Hz, 1C), 132.0 (d, $J = 9.1$ Hz, 1C), 131.8 (d, $J = 17.2$ Hz, 1c), 128.6 (d, $J = 12.1$ Hz, 1C), 128.5 (d, $J = 12.1$ Hz, 1C), 115.9 (q, $J = 13.1$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 28.6. ^{19}F NMR (376 MHz, CDCl_3) δ -106.6. IR (neat): $\nu = 3058, 2926, 2316, 1591, 1437, 1192, 1117, 699, 538$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{18}\text{H}_{15}\text{FOP}]^+$ $[\text{M}+\text{H}]^+$: 297.0839, found: 297.0831.

Diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (3f)^[5]



Yellow gum (42.2 mg, 61% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (dd, $J = 11.1, 8.3$ Hz, 2H), 7.75–7.70 (m, 2H), 7.69–7.63 (m, 4H), 7.58 (m, 2H), 7.49 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.1 (d, $J = 100.5$ Hz, 1C), 133.8 (d, $J = 3.0$ Hz, 1C), 133.5 (d, $J = 3.0$ Hz, 1C), 132.5 (d, $J = 10.1$ Hz, 1C), 132.3 (d, $J = 3.0$ Hz, 1H), 132.0 (d, $J = 10.1$ Hz, 1C), 131.61 (d, $J = 10.1$ Hz, 1C), 131.58 (d, $J = 106.1$ Hz, 1C), 128.7 (d, $J = 13.1$ Hz, 1H), 125.3 (q, $J = 4.0$ Hz, 1C), 125.2 (q, $J = 4.0$ Hz, 1C), 123.5 (q, $J = 274.7$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 28.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.1. IR (neat): $\nu = 3054, 2926, 2377, 1624, 1404, 1176, 1126, 710, 550$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{19}\text{H}_{15}\text{F}_3\text{OP}]^+$ $[\text{M}+\text{H}]^+$: 347.0807, found: 347.0804.

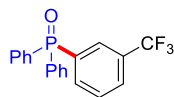
Diphenyl(m-tolyl)phosphine oxide (3g)^[6]



White gum (23.4 mg, 40% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.71–7.63 (m, 5H), 7.57–7.51 (m, 3H), 7.46 (m, 5H), 7.36–7.32 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.2, 132.7 (d, $J = 3.0$ Hz, 1C), 132.5 (d, $J = 10.1$ Hz, 1C), 132.1 (d, $J = 10.1$ Hz, 1C), 131.9 (d, $J = 3.0$ Hz, 1C), 131.85 (d, $J = 3.0$ Hz, 1C), 129.2 (d, $J = 10.1$ Hz, 1C), 128.5 (d, $J = 12.1$ Hz, 1C), 128.4 (d, $J = 12.1$ Hz, 1C), 128.3 (d, $J = 13.1$ Hz, 1C),

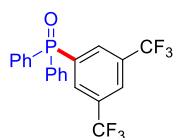
21.4. ^{31}P NMR (162 MHz, CDCl_3) δ 29.5. IR (neat): $\nu = 3054, 2923, 2337, 1436, 1189, 1116, 753, 698, 546\text{ cm}^{-1}$; HRMS (ESI) Exact mass calculated for $[\text{C}_{19}\text{H}_{18}\text{OP}]^+ [\text{M}+\text{H}]^+$: 293.1090, found: 293.1098.

Diphenyl(3-(trifluoromethyl)phenyl)phosphine oxide (3h)^[4]



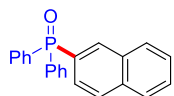
Yellow gum (36.0 mg, 52% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 11.9$ Hz, 1H), 7.87–7.77 (m, 2H), 7.70–7.60 (m, 4H), 7.60–7.54 (m, 3H), 7.48 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.3 (d, $J = 1.0$ Hz, 1C), 135.2 (d, $J = 1.0$ Hz, 1C), 134.3 (d, $J = 103.0$ Hz, 1C), 132.3 (d, $J = 3.0$ Hz, 1C), 132.2 (d, $J = 3.0$ Hz, 1C), 131.9 (d, $J = 10.1$ Hz, 1C), 131.6 (d, $J = 10.1$ Hz, 1C), 131.5 (d, $J = 106.1$ Hz, 1C), 131.2 (d, $J = 12.1$ Hz, 1C), 130.9 (d, $J = 13.1$ Hz, 1C), 129.0 (d, $J = 12.1$ Hz, 1C), 128.7 (d, $J = 12.1$ Hz, 1C), 128.6, 128.4, 123.51 (q, $J = 273.7$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 28.1. ^{19}F NMR (376 MHz, CDCl_3) δ -62.7. IR (neat): $\nu = 3061, 2930, 2317, 1600, 1433, 1194, 1125, 723, 695, 540\text{ cm}^{-1}$; HRMS (ESI) Exact mass calculated for $[\text{C}_{19}\text{H}_{15}\text{F}_3\text{OP}]^+ [\text{M}+\text{H}]^+$: 347.0807, found: 347.0806.

(3,5-bis(trifluoromethyl)phenyl)diphenylphosphine oxide (3i)^[3]



Yellow gum (27.7 mg, 40% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.5$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 11.3$ Hz, 2H), 8.04 (s, 1H), 7.71–7.59 (m, 6H), 7.56–7.49 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.7 (d, $J = 100.0$ Hz, 1C), 132.8 (d, $J = 3.0$ Hz, 1C), 132.2 (d, $J = 12.1$ Hz, 1C), 131.9 (d, $J = 10.1$ Hz, 1C), 131.2, 130.1, 129.0 (d, $J = 12.1$ Hz, 1C), 125.63 (q, $J = 3.0$ Hz, 1C), 122.8 (q, $J = 275.7$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 27.0. ^{19}F NMR (376 MHz, CDCl_3) δ -62.9. IR (neat): $\nu = 3052, 2925, 2320, 1617, 1438, 1281, 1189, 1132, 693, 540\text{ cm}^{-1}$; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{14}\text{F}_6\text{OP}]^+ [\text{M}+\text{H}]^+$: 415.0681, found: 415.0684.

Naphthalen-2-ylidiphenylphosphine oxide (3j)^[5]



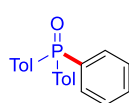
White gum (26.9 mg, 41% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 13.8$ Hz, 1H), 7.90–7.85 (m, 2H), 7.78–7.69 (m, 4H), 7.68–7.59 (m, 2H), 7.56 (dd, $J = 10.4, 4.3$ Hz, 3H), 7.47 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.7 (d, $J = 3.0$ Hz, 1C), 134.0 (d, $J = 9.1$ Hz, 1C), 133.0, 132.4 (d, $J = 14.1$ Hz, 1C), 132.11 (d, $J = 10.1$ Hz, 1C), 132.05 (d, $J = 10.1$ Hz, 1C), 132.0 (d, $J = 3.0$ Hz, 1C), 130.03, 128.94, 128.52 (d, $J = 12.1$ Hz, 1C), 128.46 (d, $J = 12.1$ Hz, 1C), 128.3, 128.2 (d, $J = 2.0$ Hz, 1C), 127.4 (d, $J = 88.9$ Hz, 1C), 126.8 (d, $J = 11.1$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 29.4. IR (neat): $\nu = 3054, 2924, 2317, 1626, 1435, 1189, 1112, 751, 537\text{ cm}^{-1}$; HRMS (ESI) Exact mass calculated for $[\text{C}_{22}\text{H}_{18}\text{OP}]^+ [\text{M}+\text{H}]^+$: 329.1090, found: 329.1097.

Diphenyl(thiophen-3-yl)phosphine oxide (3k)^[4]



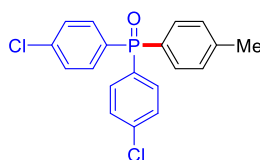
Yellow gum (23.9 mg, 42% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.74–7.62 (m, 5H), 7.54 (m, 2H), 7.50–7.43 (m, 5H), 7.25 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.4 (d, $J = 15.2$ Hz, 1C), 132.04 (d, $J = 14.1$ Hz, 1C), 132.0 (d, $J = 1.0$ Hz, 1C), 131.9 (d, $J = 3.0$ Hz, 1C), 131.7 (d, $J = 11.1$ Hz, 1C), 129.6 (d, $J = 15.2$ Hz, 1C), 128.50 (d, $J = 12.2$ Hz, 1C), 128.46 (d, $J = 12.1$ Hz, 1C), 127.6 (d, $J = 15.2$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 22.5. IR (neat): $\nu = 3064, 2924, 2315, 1435, 1187, 1116, 754, 695, 622, 542$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{16}\text{H}_{14}\text{OPS}]^+ [\text{M}+\text{H}]^+$: 285.0497, found: 285.0495.

Phenyldi-p-tolylphosphine oxide (3l)^[2]



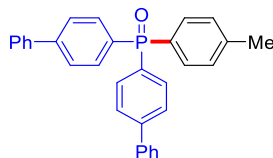
White gum (32.5 mg, 53% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.71–7.61 (m, 2H), 7.58–7.48 (m, 5H), 7.46–7.39 (m, 2H), 7.25 (dd, $J = 7.9, 2.5$ Hz, 4H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.3 (d, $J = 3.0$ Hz, 1C), 142.1 (d, $J = 3.0$ Hz, 1C), 132.04 (d, $J = 10.1$ Hz, 1C), 132.02 (d, $J = 11.1$ Hz, 1C), 131.98 (d, $J = 10.1$ Hz, 1C), 131.7 (d, $J = 3.0$ Hz, 1C), 129.9 (d, $J = 107.1$ Hz, 1C), 129.2 (d, $J = 13.1$ Hz, 1C), 129.1 (d, $J = 12.1$ Hz, 1C), 128.3 (d, $J = 12.1$ Hz, 1C), 21.5. ^{31}P NMR (162 MHz, CDCl_3) δ 29.5. IR (neat): $\nu = 3035, 2930, 2318, 1628, 1429, 1115, 808, 544$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{20}\text{OP}]^+ [\text{M}+\text{H}]^+$: 307.1247, found: 307.1243.

Bis(4-chlorophenyl)(p-tolyl)phosphine oxide (3m)



White gum (30.3 mg, 42% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.62–7.55 (m, 4H), 7.51 (dd, $J = 12.1, 8.1$ Hz, 2H), 7.46–7.41 (m, 4H), 7.28 (dd, $J = 8.0, 2.5$ Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.0 (d, $J = 3.0$ Hz, 1C), 138.7 (d, $J = 3.0$ Hz, 1C), 133.4 (d, $J = 10.1$ Hz, 1C), 132.0 (d, $J = 10.1$ Hz, 1C), 131.51, 130.46, 129.5 (d, $J = 13.1$ Hz, 1C), 129.0 (d, $J = 12.1$ Hz, 1C), 21.6 (d, $J = 1.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 27.9. IR (neat): $\nu = 3052, 2925, 2315, 1582, 1479, 1193, 1089, 751, 590$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{OP}]^+ [\text{M}+\text{H}]^+$: 361.0311, found: 361.0315.

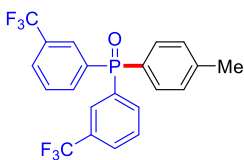
Di([1,1'-biphenyl]-4-yl)(p-tolyl)phosphine oxide (3n)



White gum (49.8 mg, 56% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (m, 4H), 7.73–7.67 (m, 5H), 7.65 (d, $J = 3.8$ Hz, 1H), 7.64–7.59 (m, 4H), 7.46 (t, $J = 6.6$ Hz, 4H), 7.39 (dd, $J = 8.3, 6.3$ Hz, 2H), 7.31 (dd, $J = 8.0, 2.2$ Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.5 (d, $J = 3.0$ Hz, 1C), 142.5 (d, $J = 3.0$ Hz, 1C), 139.8 (d, $J = 1.0$ Hz, 1C), 132.5 (d, $J = 10.1$ Hz, 1C), 132.1 (d, $J = 10.1$ Hz, 1C), 131.3 (d, $J = 106.1$ Hz, 1C), 129.3 (d, $J = 13.1$ Hz, 1C),

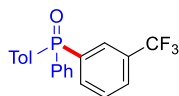
128.9, 128.1, 127.19, 127.16, 127.0, 21.6 (d, $J = 2.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 29.0. IR (neat): $\nu = 2922, 2854, 2317, 1460, 1181, 1117, 666, 514$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{31}\text{H}_{26}\text{OP}]^+ [\text{M}+\text{H}]^+$: 445.1716, found: 445.1714.

***p*-tolylbis(3-(trifluoromethyl)phenyl)phosphine oxide (3o)**



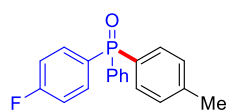
Yellow gum (40.3 mg, 47% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 12.1$ Hz, 2H), 7.82 (t, $J = 9.1$ Hz, 4H), 7.62 (td, $J = 7.8, 2.4$ Hz, 2H), 7.53 (dd, $J = 12.2, 8.0$ Hz, 2H), 7.32 (dd, $J = 7.9, 2.1$ Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.6 (d, $J = 1.0$ Hz, 1C), 135.2 (d, $J = 10.1$ Hz, 1C), 133.7 (d, $J = 104.0$ Hz, 1C), 132.0 (d, $J = 11.1$ Hz, 1C), 131.3 (q, $J = 13.1$ Hz, 1C), 129.7 (d, $J = 13.1$ Hz, 1C), 129.2 (d, $J = 12.1$ Hz, 1C), 129.0 (t, $J = 3.0$ Hz, 1C), 128.8 (q, $J = 4.0$ Hz, 1C), 128.7 (q, $J = 4.0$ Hz, 1C), 126.7, 126.3 (q, $J = 274.7$ Hz, 1C), 21.7 (d, $J = 1.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 27.1. ^{19}F NMR (376 MHz, CDCl_3) δ -62.8. IR (neat): $\nu = 3042, 2925, 2378, 1325, 1176, 1126, 650, 537$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{21}\text{H}_{16}\text{F}_6\text{OP}]^+ [\text{M}+\text{H}]^+$: 429.0838, found: 429.0830.

Phenyl(*p*-tolyl)(3-(trifluoromethyl)phenyl)phosphine oxide (3p)



Yellow gum (53.3 mg, 74% for 1-iodo-3-(trifluoromethyl)benzene; 32.4 mg, 45% for 1-bromo-3-(trifluoromethyl)benzene) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 11.9$ Hz, 1H), 7.87–7.76 (m, 2H), 7.70–7.44 (m, 8H), 7.30 (dd, $J = 8.1, 2.5$ Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.0 (d, $J = 3.0$ Hz, 1C), 135.3, 135.2 (d, $J = 1.0$ Hz, 1C), 135.1, 134.0, 132.3, 132.2 (d, $J = 3.0$ Hz, 1C), 132.0 (d, $J = 6.1$ Hz, 1C), 131.9 (d, $J = 6.1$ Hz, 1C), 131.3 (d, $J = 6.1$ Hz, 1C), 129.5 (d, $J = 13.1$ Hz, 1C), 129.0 (d, $J = 11.1$ Hz, 1C), 128.7 (d, $J = 12.1$ Hz, 1C), 128.6 (d, $J = 12.1$ Hz, 1C), 126.3 (q, $J = 272.7$ Hz, 1C), 21.6 (d, $J = 1.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 28.3. ^{19}F NMR (376 MHz, CDCl_3) δ -62.7. IR (neat): $\nu = 3026, 2967, 2326, 1427, 1123, 846, 625, 551$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{17}\text{F}_3\text{OP}]^+ [\text{M}+\text{H}]^+$: 361.0964, found: 361.0967.

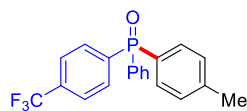
(4-fluorophenyl)(phenyl)(*p*-tolyl)phosphine oxide (3q)



Yellow gum (40.3 mg, 65% for 1-iodo-4-methylbenzene; 25.5 mg, 41% for 1-bromo-4-methylbenzene) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.60 (m, 4H), 7.57–7.40 (m, 5H), 7.30–7.22 (m, 2H), 7.18–7.08 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.2 (d, $J = 3.0$ Hz, 1C), 163.7 (d, $J = 3.0$ Hz, 1C), 142.6 (d, $J = 3.0$ Hz, 1C), 134.53 (d, $J = 8.1$ Hz, 1C), 134.42 (d, $J = 9.1$ Hz, 1C), 133.0, 132.0 (d, $J = 6.1$ Hz, 1C), 131.91, 131.90 (d, $J = 6.1$ Hz, 1C), 129.3 (d, $J = 12.1$ Hz, 1C), 128.5 (d, $J = 12.1$ Hz, 1C), 115.8 (q, $J = 13.1$

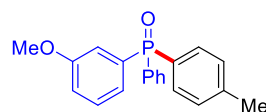
Hz, 1C), 21.6 (d, $J = 1.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 28.7. ^{19}F NMR (376 MHz, CDCl_3) δ -106.9. IR (neat): $\nu = 3051, 2923, 2313, 1630, 1193, 1116, 625, 536$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{19}\text{H}_{17}\text{FOP}]^+ [\text{M}+\text{H}]^+$: 311.0996, found: 311.0997.

Phenyl(p-tolyl)(4-(trifluoromethyl)phenyl)phosphine oxide (3r)



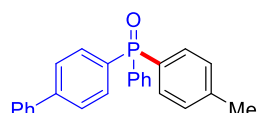
Yellow gum (44.0 mg, 61% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.78 (m, 2H), 7.65 (m, 4H), 7.56–7.41 (m, 5H), 7.27 (dd, $J = 7.9, 2.2$ Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.0 (d, $J = 3.0$ Hz, 1C), 137.4 (d, $J = 101.0$ Hz, 1C), 133.7 (d, $J = 3.0$ Hz, 1C), 133.3 (d, $J = 3.0$ Hz, 1C), 132.5 (d, $J = 10.1$ Hz, 1C), 132.2 (d, $J = 3.0$ Hz, 1C), 132.0 (q, $J = 6.1$ Hz, 1C), 131.8 (d, $J = 105.0$ Hz, 1C), 129.4 (d, $J = 13.1$ Hz, 1C), 128.6 (d, $J = 12.1$ Hz, 1C), 128.2 (d, $J = 108.1$ Hz, 1C), 125.3 (q, $J = 4.0$ Hz, 1C), 125.2 (q, $J = 4.0$ Hz, 1C), 123.5 (q, $J = 273.7$ Hz, 1C), 21.6 (d, $J = 1.3$ Hz, 1H). ^{31}P NMR (162 MHz, CDCl_3) δ 28.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.1. IR (neat): $\nu = 3054, 2923, 2351, 1605, 1439, 1175, 1125, 708, 556$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{17}\text{F}_3\text{OP}]^+ [\text{M}+\text{H}]^+$: 361.0964, found: 361.0967.

(3-methoxyphenyl)(phenyl)(p-tolyl)phosphine oxide (3s)



White gum (29.0 mg, 45% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.2$ (EtOAc/petroleum ether 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.66 (m, 2H), 7.59–7.50 (m, 3H), 7.44 (m, 2H), 7.40–7.32 (m, 1H), 7.28 (m, 3H), 7.17–7.10 (m, 1H), 7.08–7.03 (m, 1H), 3.79 (d, $J = 1.1$ Hz, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.4 (d, $J = 15.2$ Hz, 1C), 142.4 (d, $J = 3.0$ Hz, 1C), 134.3 (d, $J = 35.4$ Hz, 1C), 133.3 (d, $J = 36.4$ Hz, 1C), 132.0 (d, $J = 6.1$ Hz, 1C), 131.9 (d, $J = 6.1$ Hz, 1C), 131.8 (d, $J = 3.0$ Hz, 1C), 129.6 (d, $J = 14.1$ Hz, 1C), 129.5 (d, $J = 14.1$ Hz, 1C), 129.2 (d, $J = 12.1$ Hz, 1C), 128.4 (d, $J = 12.1$ Hz, 1C), 128.35 (d, $J = 12.1$ Hz, 1C), 124.2 (d, $J = 10.1$ Hz, 1C), 118.1 (d, $J = 2.0$ Hz, 1C), 118.0 (d, $J = 2.0$ Hz, 1C), 116.6 (d, $J = 11.1$ Hz, 1C), 55.3, 21.5 (d, $J = 1.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 29.6. IR (neat): $\nu = 3055, 2926, 2317, 1628, 1190, 1122, 699, 541$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{20}\text{O}_2\text{P}]^+ [\text{M}+\text{H}]^+$: 323.1196, found: 323.1191.

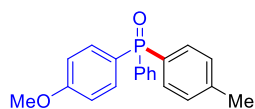
[1,1'-biphenyl]-4-yl(phenyl)(p-tolyl)phosphine oxide (3t)



White gum (37.6 mg, 51% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.3$ (EtOAc/petroleum ether 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (m, 6H), 7.62–7.50 (m, 5H), 7.48–7.41 (m, 4H), 7.40–7.34 (m, 1H), 7.27 (dd, $J = 8.0, 2.2$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.53 (d, $J = 2.0$ Hz, 1C), 142.46 (d, $J = 3.0$ Hz, 1C), 139.9 (d, $J = 3.0$ Hz, 1C), 133.2, 132.5 (d, $J = 10.1$ Hz, 1C), 132.1 (d, $J = 6.1$ Hz, 1C), 132.0 (d, $J = 6.1$ Hz, 1C), 131.8 (d, $J = 3.0$ Hz, 1C), 130.7, 129.6, 129.2 (d, $J = 13.1$ Hz, 1C), 128.9, 128.5, 128.4 (d, $J = 12.1$ Hz, 1C),

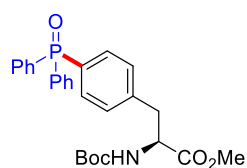
128.1, 127.2, 127.1 (d, $J = 12.1$ Hz, 1C), 21.6 (d, $J = 1.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 29.3. IR (neat): $\nu = 3055, 2924, 2317, 1441, 1187, 1119, 761, 554$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{25}\text{H}_{22}\text{OP}]^+ [\text{M}+\text{H}]^+$: 369.1403, found: 369.1396.

(4-methoxyphenyl)(phenyl)(p-tolyl)phosphine oxide (3u)



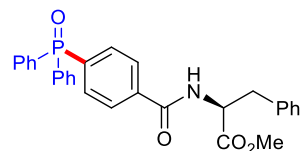
White gum (45.1 mg, 70% for 1-iodo-4-methylbenzene; 30.3 mg, 47% for 1-bromo-4-methylbenzene) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.2$ (EtOAc/petroleum ether 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.69–7.48 (m, 7H), 7.43 (m, 2H), 7.29–7.23 (m, 2H), 6.97–6.92 (m, 2H), 3.83 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.3, 142.2, 133.9 (d, $J = 11.1$ Hz, 1C), 133.2 (d, $J = 105.0$ Hz, 1C), 132.1 (d, $J = 6.1$ Hz, 1C), 132.0 (d, $J = 6.1$ Hz, 1C), 131.7 (d, $J = 3.0$ Hz, 1C), 130.1, 129.2 (d, $J = 13.1$ Hz, 1C), 128.3 (d, $J = 12.1$ Hz, 1C), 123.8 (d, $J = 11.1$ Hz, 1C), 114.0 (d, $J = 13.1$ Hz, 1C), 55.3, 21.6 (d, $J = 2.0$ Hz, 1C). ^{31}P NMR (162 MHz, CDCl_3) δ 29.3. IR (neat): $\nu = 3037, 2926, 2316, 1445, 1184, 1117, 661, 539$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{20}\text{H}_{20}\text{O}_2\text{P}]^+ [\text{M}+\text{H}]^+$: 323.1196, found: 323.1192.

Methyl (S)-2-((1-(tert-butoxy)vinyl)amino)-3-(4-(diphenylphosphoryl)phenyl)propanoate (3v)



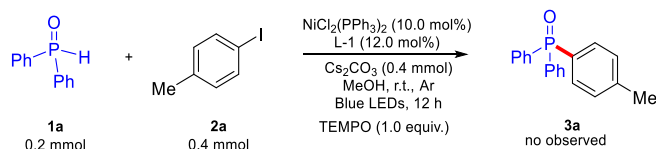
White gum (44.1 mg, 46% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 2:1). ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.50 (m, 8H), 7.44 (m, 4H), 7.22 (dd, $J = 8.0, 2.2$ Hz, 2H), 4.99 (d, $J = 7.9$ Hz, 1H), 4.60 (d, $J = 7.0$ Hz, 1H), 3.69 (s, 3H), 3.11 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.9, 154.9, 140.6 (d, $J = 2.0$ Hz, 1C), 133.0 (d, $J = 3.0$ Hz, 1C), 132.3 (d, $J = 10.1$ Hz, 1C), 132.04 (d, $J = 10.1$ Hz, 1C), 131.9 (d, $J = 3.0$ Hz, 1C), 129.5 (d, $J = 13.1$ Hz, 1C), 128.9 (d, $J = 11.1$ Hz, 1C), 128.5 (d, $J = 12.1$ Hz, 1C), 80.1, 54.1, 52.4, 38.4, 28.2. ^{31}P NMR (162 MHz, CDCl_3) δ 29.3. IR (neat): $\nu = 3024, 2936, 2322, 1709, 1517, 1280, 847, 547$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{27}\text{H}_{31}\text{NO}_5\text{P}]^+ [\text{M}+\text{H}]^+$: 480.1899, found: 480.1902.

Methyl (4-(diphenylphosphoryl)benzoyl)phenylalaninate (3w)

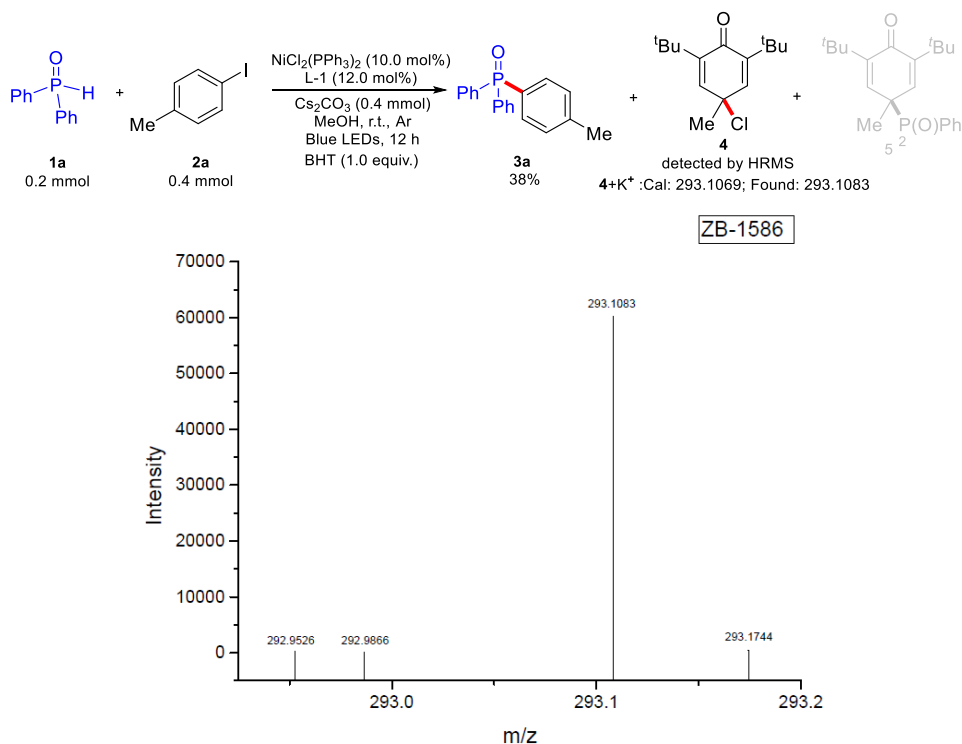


White gum (39.6 mg, 41% yield) were obtained by the purification with flash column chromatography on silica gel $R_f = 0.4$ (EtOAc/petroleum ether 2:1). ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.42 (m, 16H), 7.29 (t, $J = 5.4$ Hz, 1H), 7.12 (d, $J = 7.0$ Hz, 2H), 6.71 (d, $J = 7.5$ Hz, 1H), 5.07 (dd, $J = 12.9, 5.8$ Hz, 1H), 3.77 (s, 3H), 3.26 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.8, 166.0 (d, $J = 2.0$ Hz, 1C), 135.7, 132.5, 132.4, 132.2 (d, $J = 3.0$ Hz, 1C), 132.0 (d, $J = 10.1$ Hz, 1C), 130.7 (d, $J = 11.1$ Hz, 1C), 129.3, 128.7 (d, $J = 2.0$ Hz, 1C), 128.6, 127.3, 127.1, 126.9, 53.6, 52.5, 37.7. ^{31}P NMR (162 MHz, CDCl_3) δ 28.6. IR (neat): $\nu = 3058, 2953, 2317, 1744, 1656, 1542, 1439, 1184, 1119, 732, 565$ cm^{-1} ; HRMS (ESI) Exact mass calculated for $[\text{C}_{29}\text{H}_{27}\text{NO}_4\text{P}]^+ [\text{M}+\text{H}]^+$: 484.1672, found: 484.1666.

5. Mechanistic studies



When 1.0 equiv. of TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) as additive was subjected to the reaction mixture, the desired product **3a** was not observed even the reaction was taken after 24 hours.



When 1.0 equiv. of BHT (2,6-di-tert-butyl-4-methylphenol) was used as additive, **3a** was isolated in 38% yield, the cross-coupling product **4** by BHT with chlorine atom was detected, and possible product **5** by the cross-coupling reaction of **1a** with BHT was not detected. The above reaction indicated that the present transformation underwent a radical reaction pathway, and the chlorine atom radical was generated under the present reaction conditions.

6. References

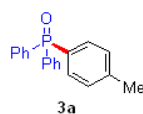
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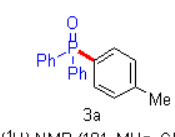
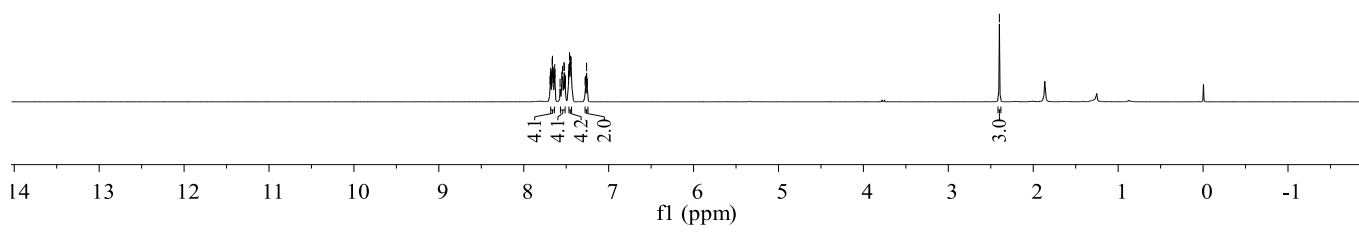
7.69 7.68 7.68 7.67 7.67 7.66 7.66 7.65 7.65 7.64 7.64 7.64 7.63 7.63 7.57 7.55 7.54 7.53 7.52 7.51 7.51 7.47 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.28 7.27 7.26 7.25

—2.40

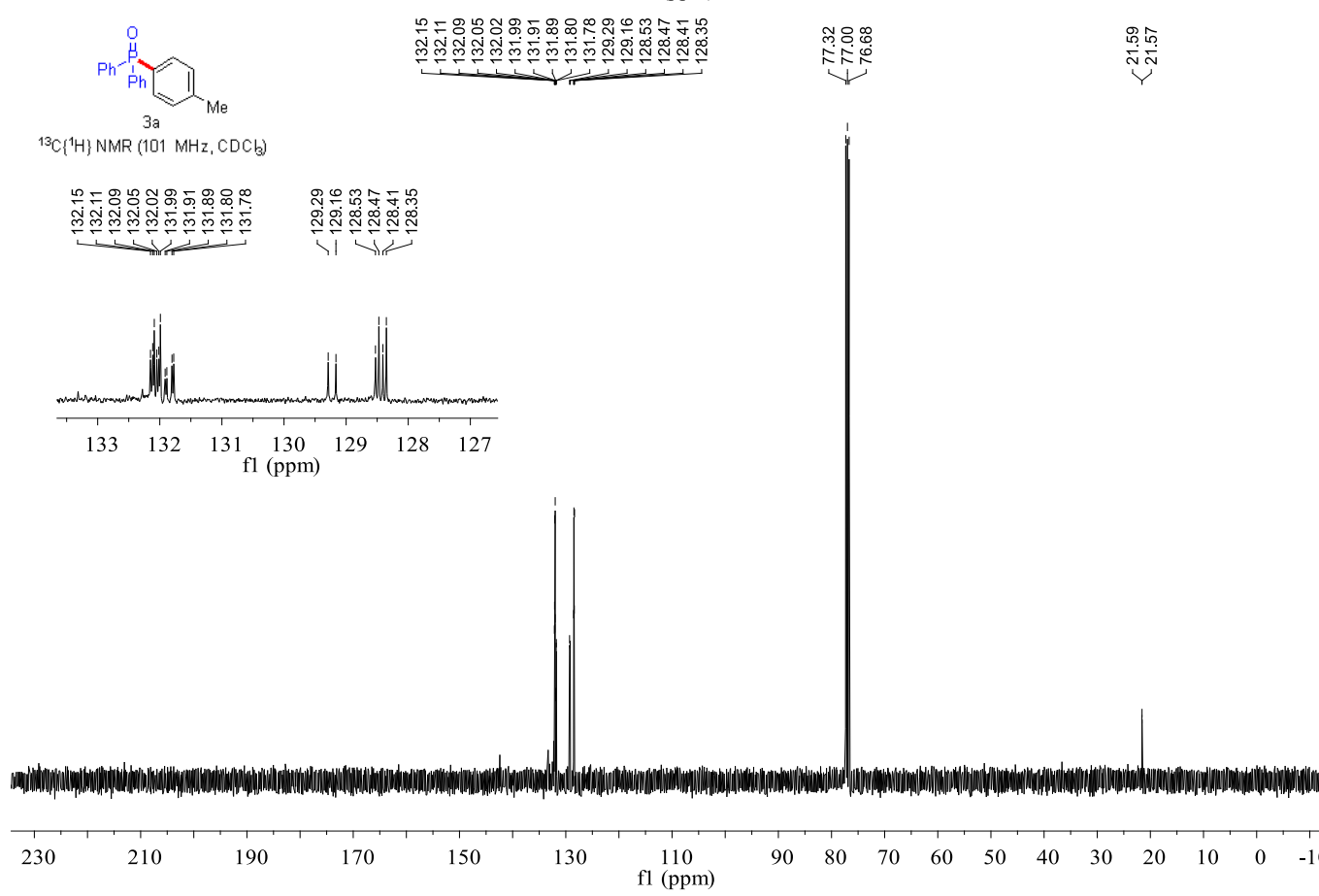
7. ¹H NMR, ¹³C NMR, ³¹P NMR and ¹⁹F NMR spectra of products

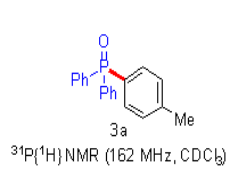


¹H NMR (400 MHz, CDCl₃)

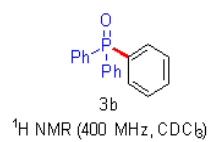
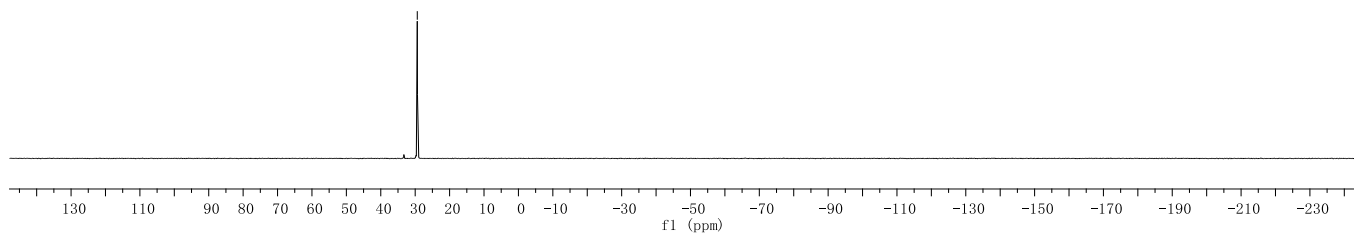


¹³C{¹H} NMR (101 MHz, CDCl₃)

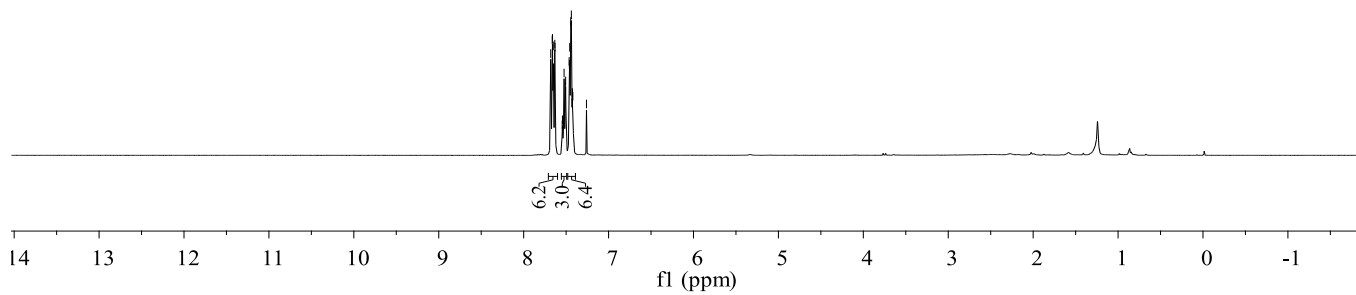


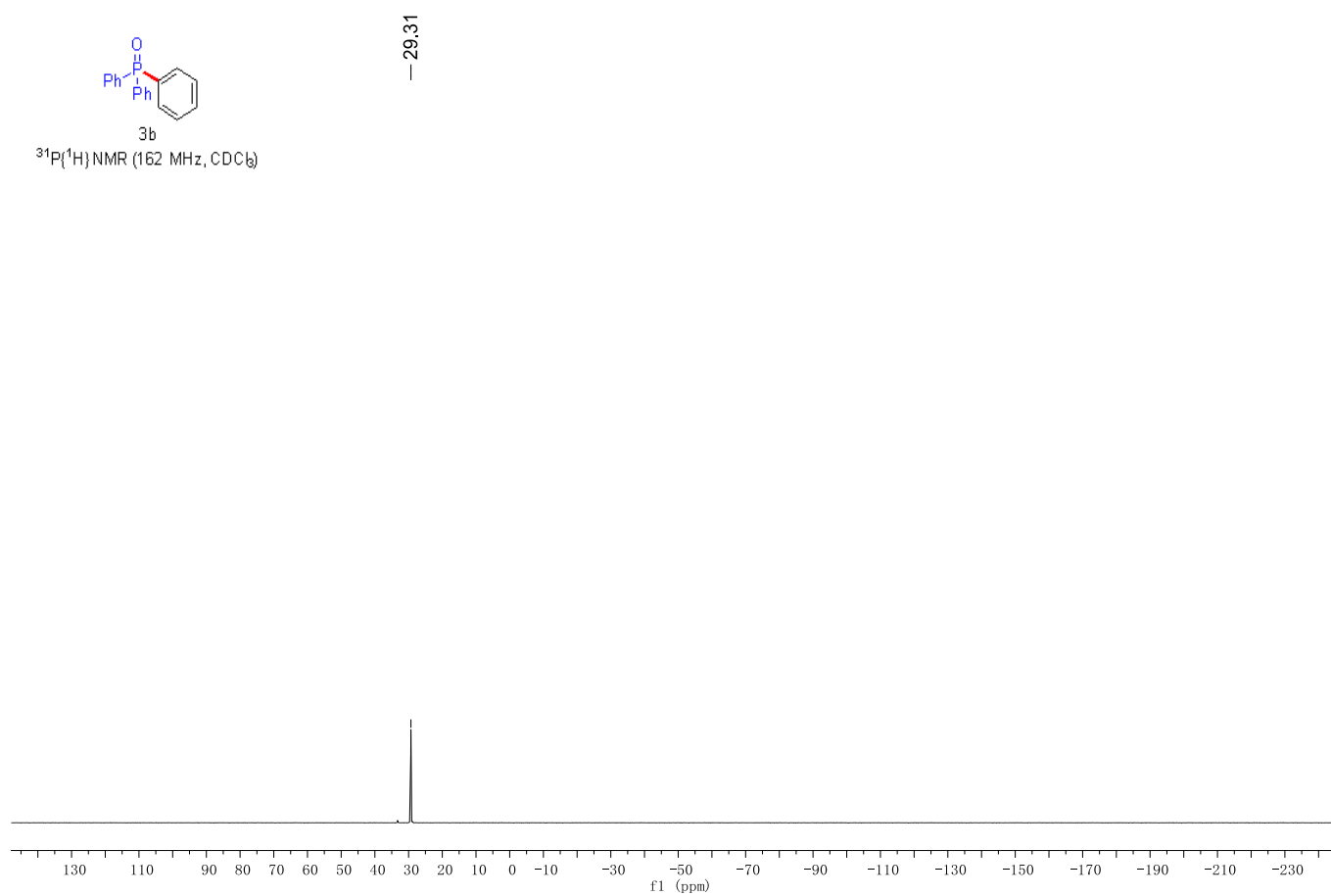
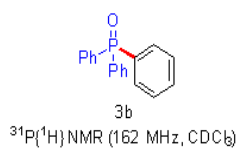
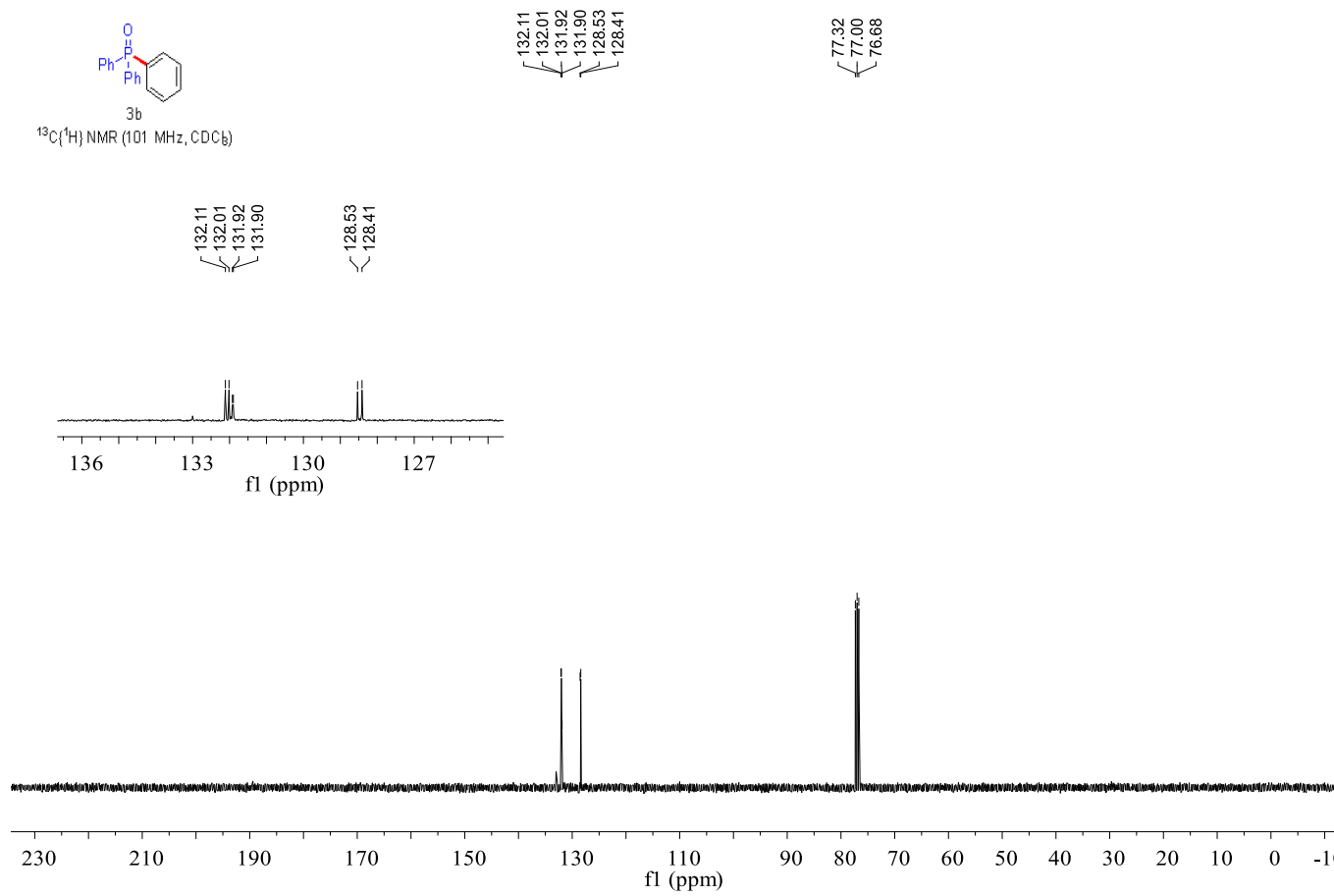
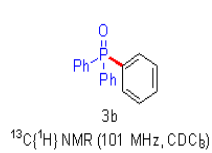


— 29.40



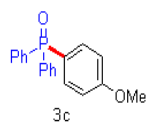
7.68
 7.66
 7.65
 7.63
 7.63
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 7.45
 7.44
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 7.43
 7.42
 7.42
 7.26



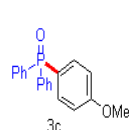
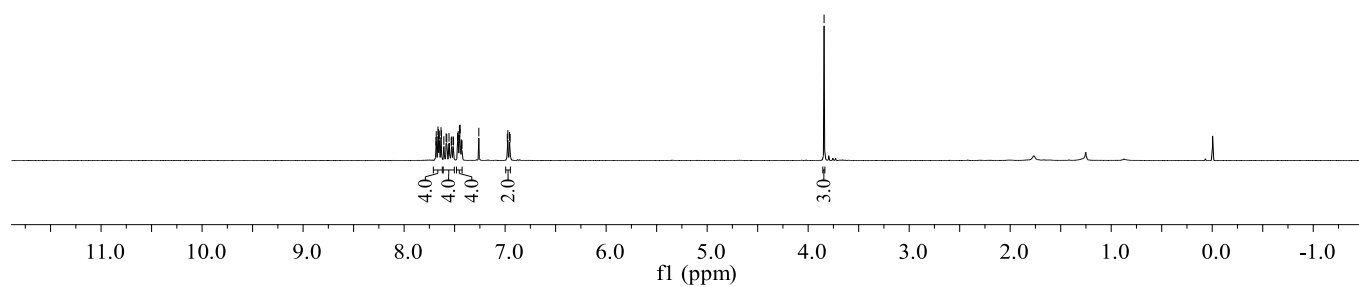


7.65
7.65
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7.61
7.58
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7.56
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7.51
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7.47
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7.46
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7.45
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7.43
7.26
6.98
6.97
6.96
6.95

3.84



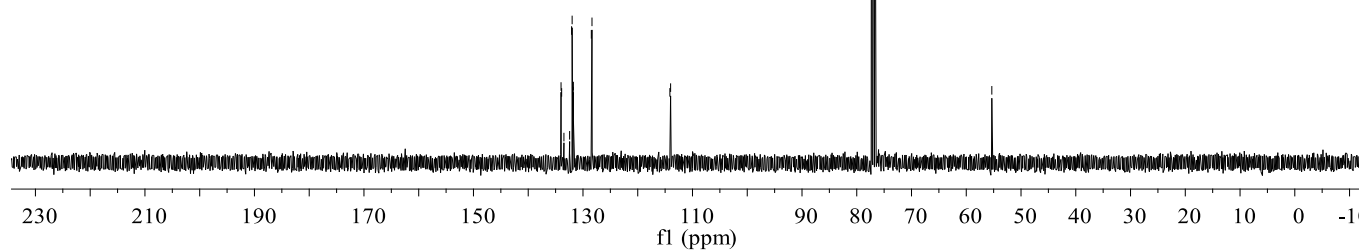
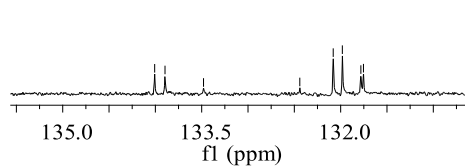
$^1\text{H NMR}$ (400 MHz, CDCl_3)

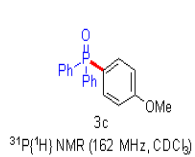


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)

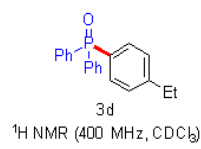
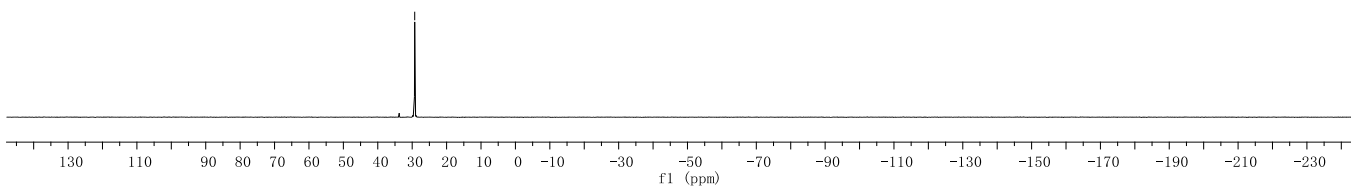
134.01
133.90
133.48
132.44
132.08
131.98
131.78
131.75
128.48
128.36
114.13
114.00
77.32
77.00
76.68
55.33

134.01
133.90
133.48
132.44
132.08
131.98
131.78
131.75

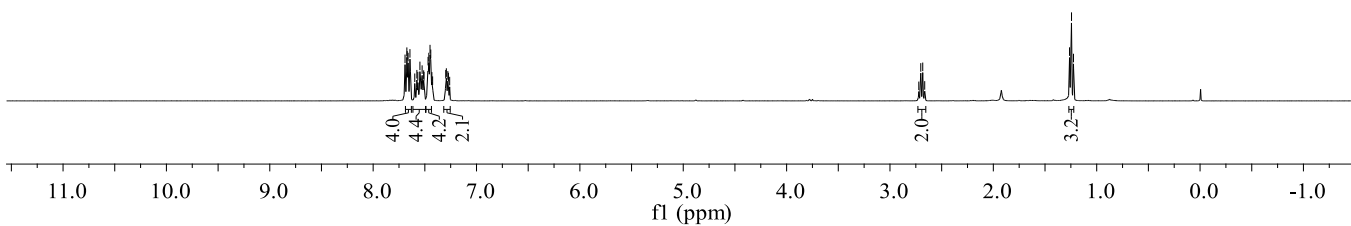


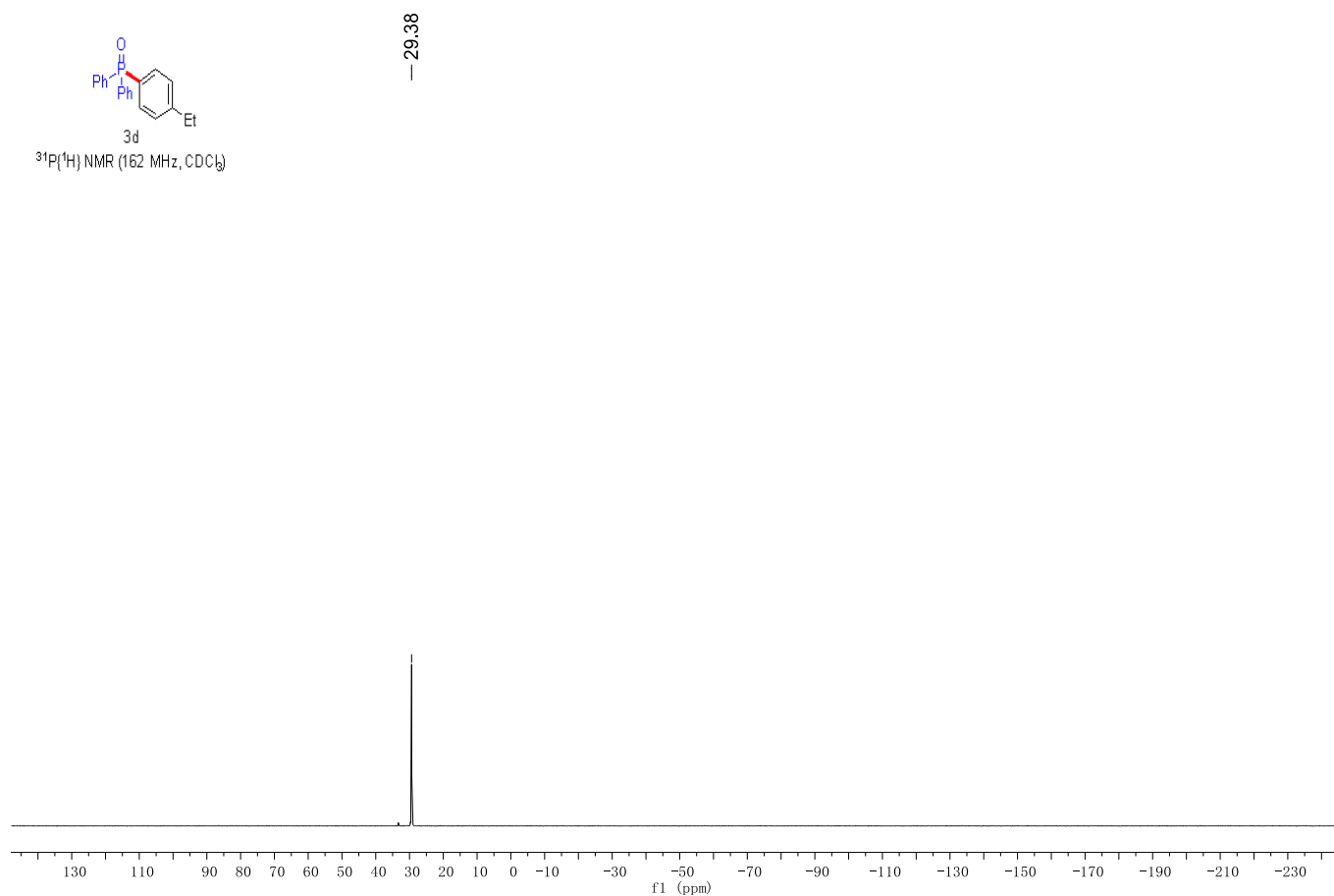
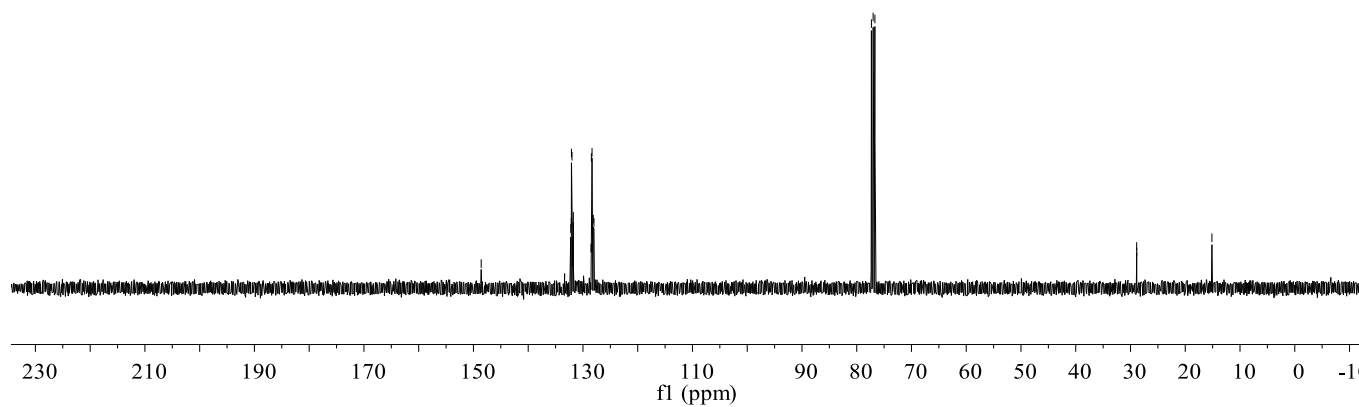
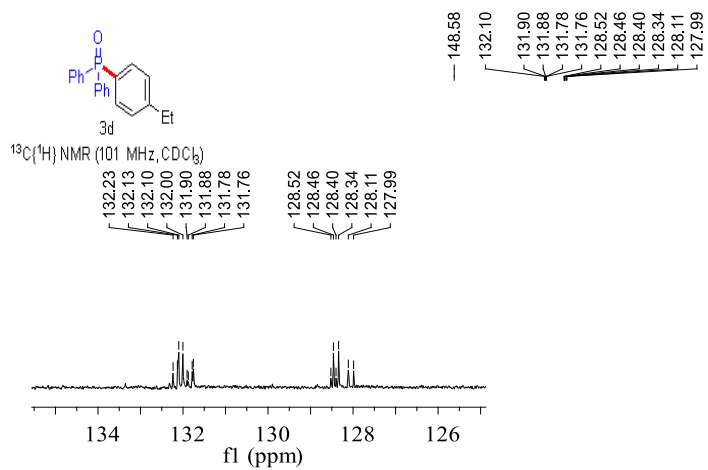


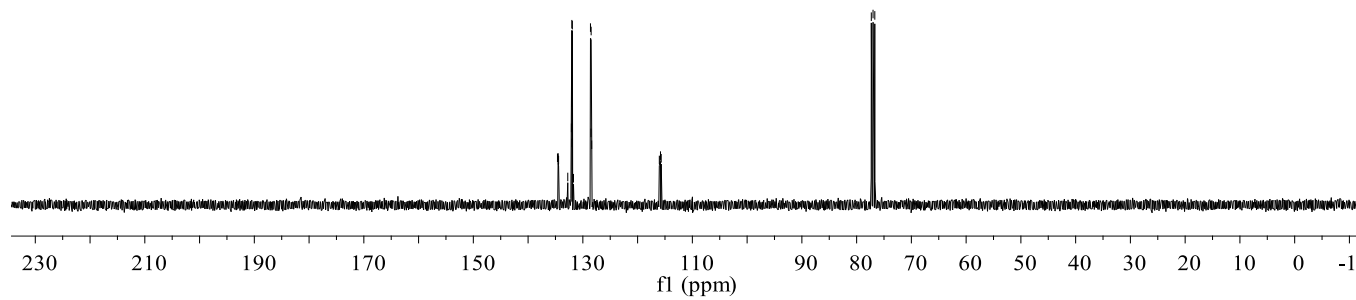
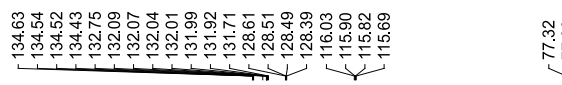
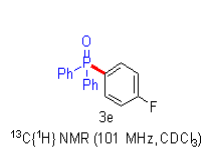
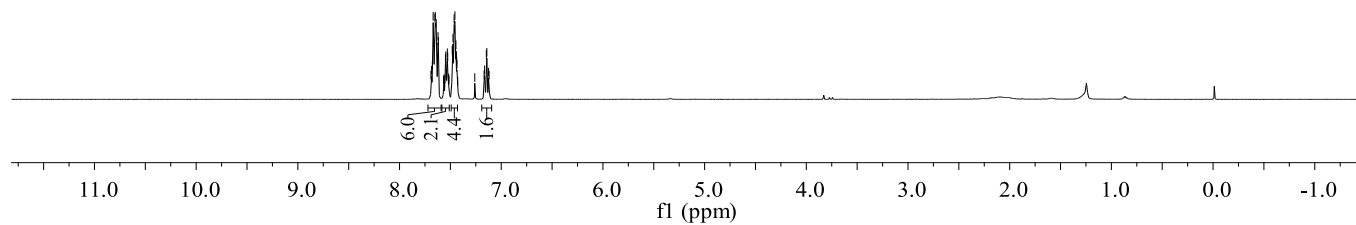
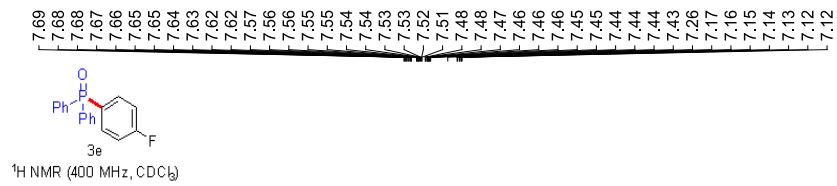
-29.27

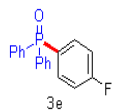


7.69 7.67 7.66 7.64 7.60 7.58 7.57 7.55 7.53 7.51 7.51 7.47 7.46 7.45 7.44 7.43 7.42 7.30 7.29 7.28 7.27 7.26
 2.72 2.70 2.68 2.66
 1.26 1.24 1.22



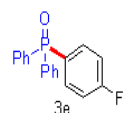
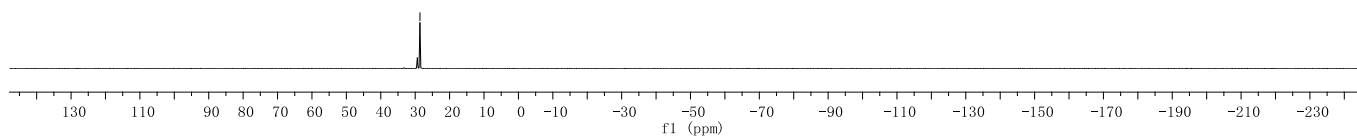






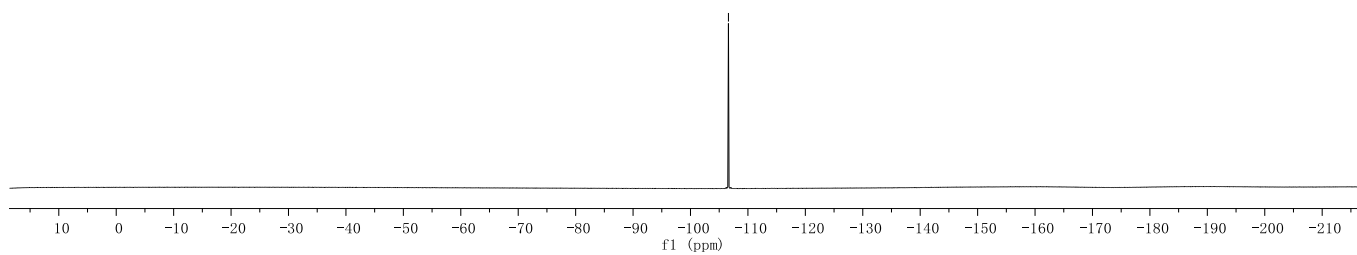
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3)

— 28.61

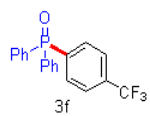


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

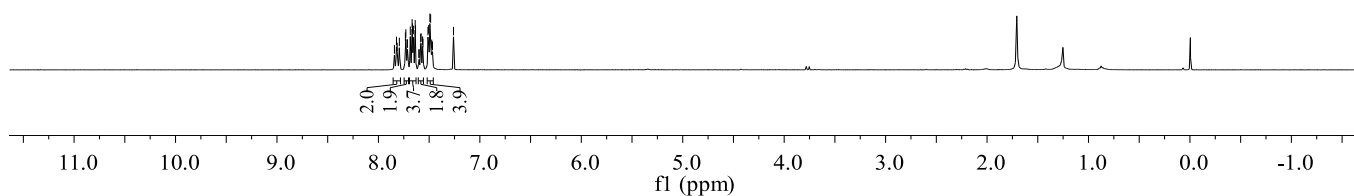
— -106.61



7.73
7.73
7.71
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7.66
7.66
7.64
7.63
7.60
7.60
7.58
7.58
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7.50
7.49
7.49
7.47
7.47
7.47
7.26

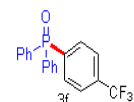


$^1\text{H NMR}$ (400 MHz, CDCl_3)

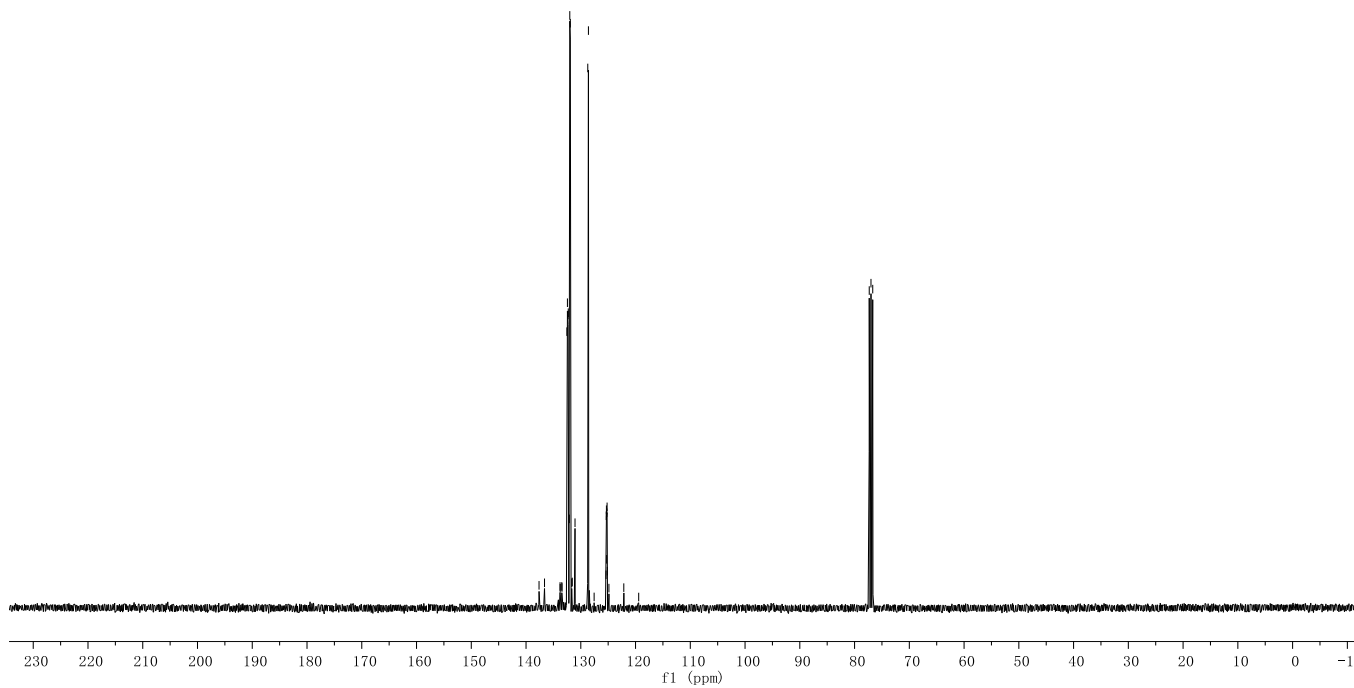


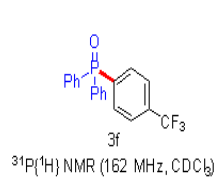
137.63
136.63
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133.76
133.46
133.43
132.54
132.44
132.31
132.28
132.10
132.01
131.91
131.66
131.56
131.05
128.73
128.60
127.57
125.39
125.36
125.32
125.28
125.24
125.20
125.16
124.86
122.15
119.43

77.32
77.00
76.68

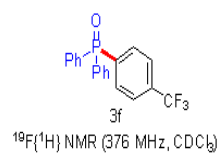
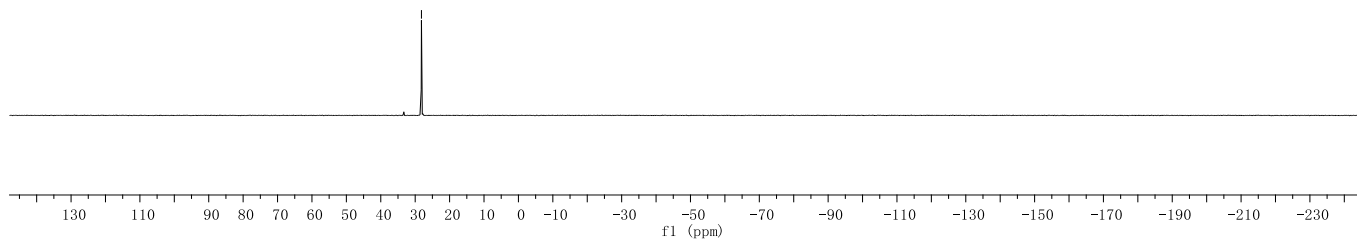


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)

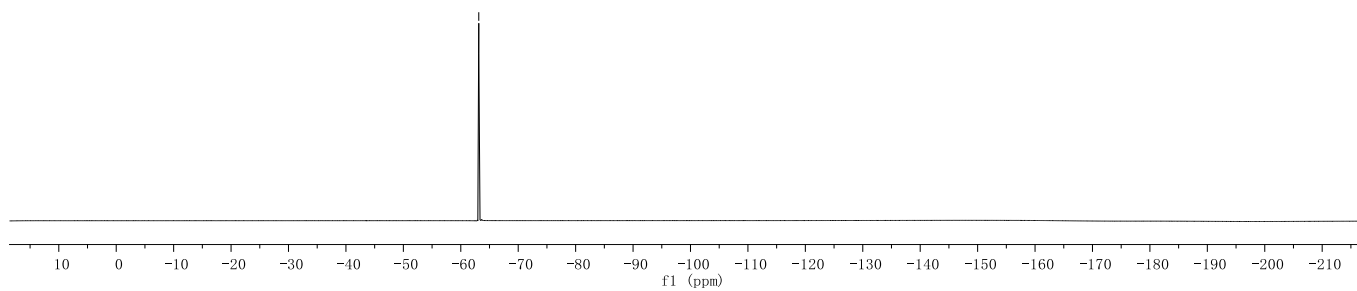




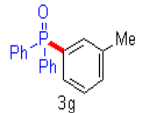
—28.18



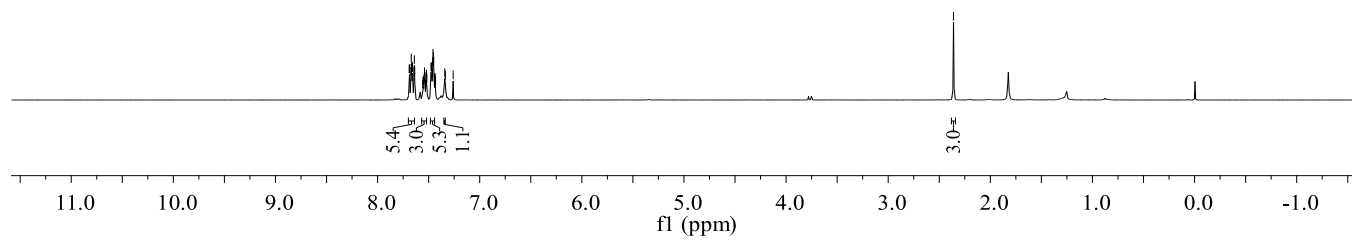
—63.13



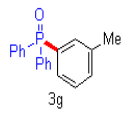
7.69
7.69
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7.67
7.66
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7.44
7.44
7.44
7.43
7.34
7.34
7.26



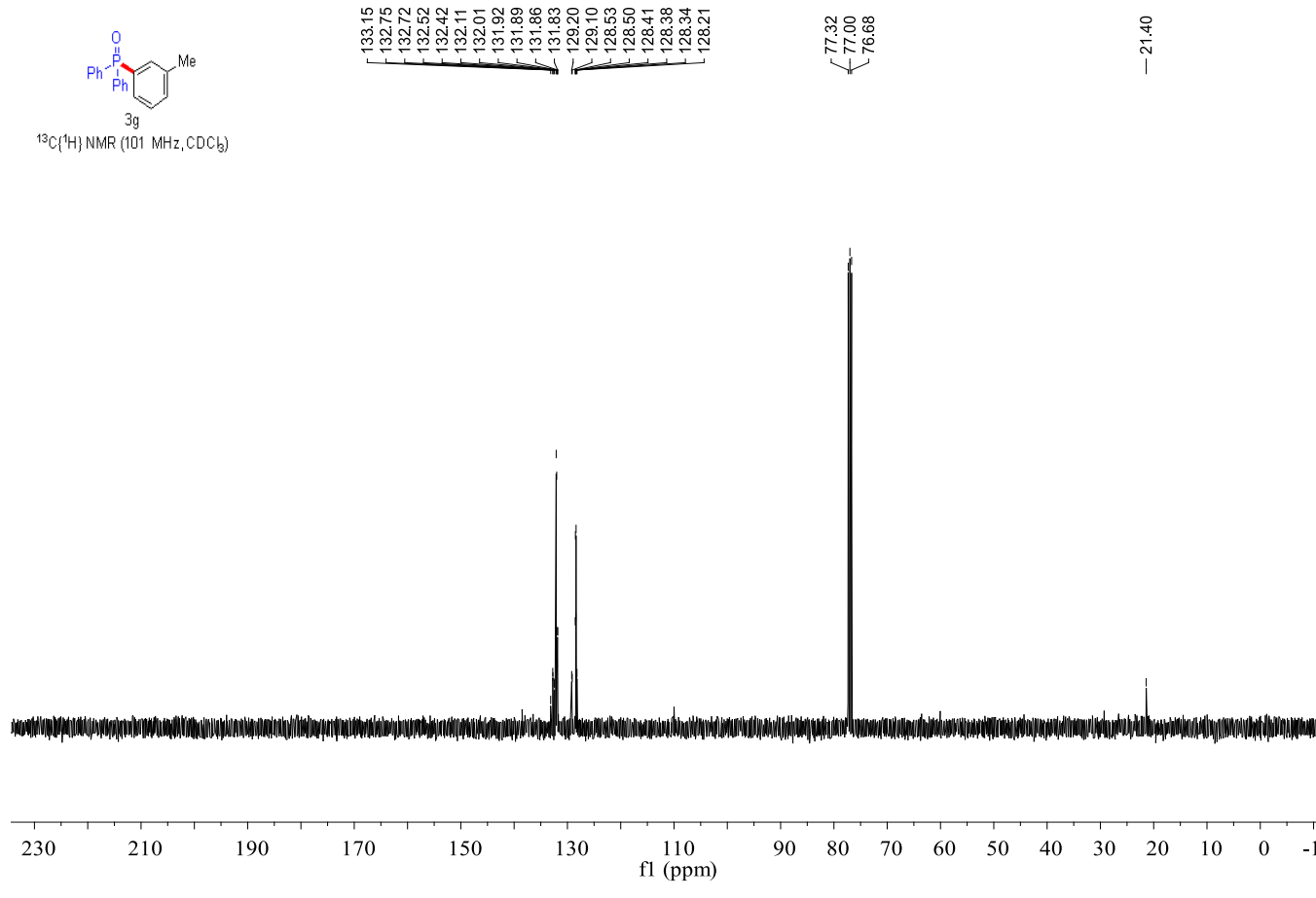
$^1\text{H NMR}$ (400 MHz, CDCl_3)

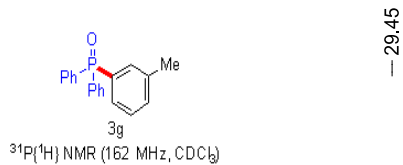


— 2.36

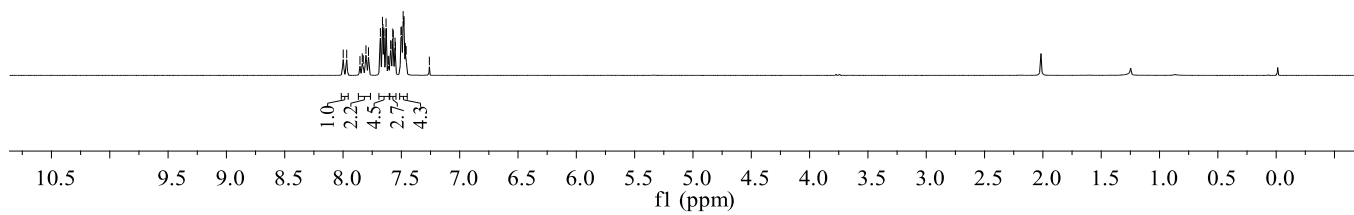
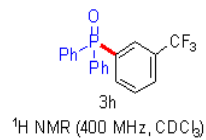
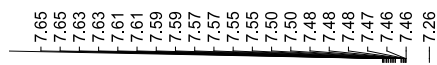
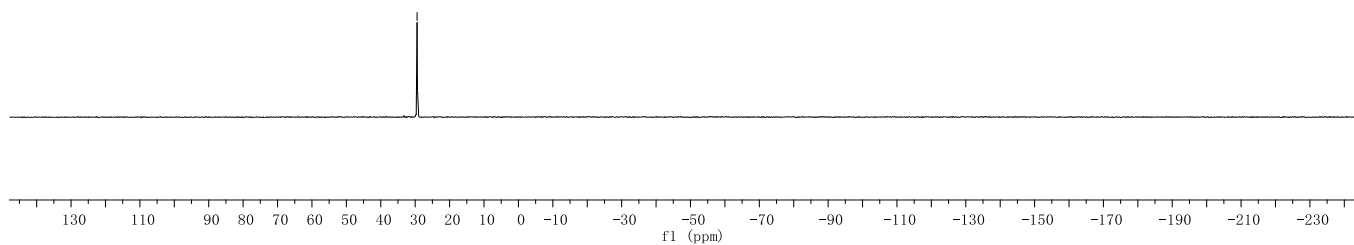


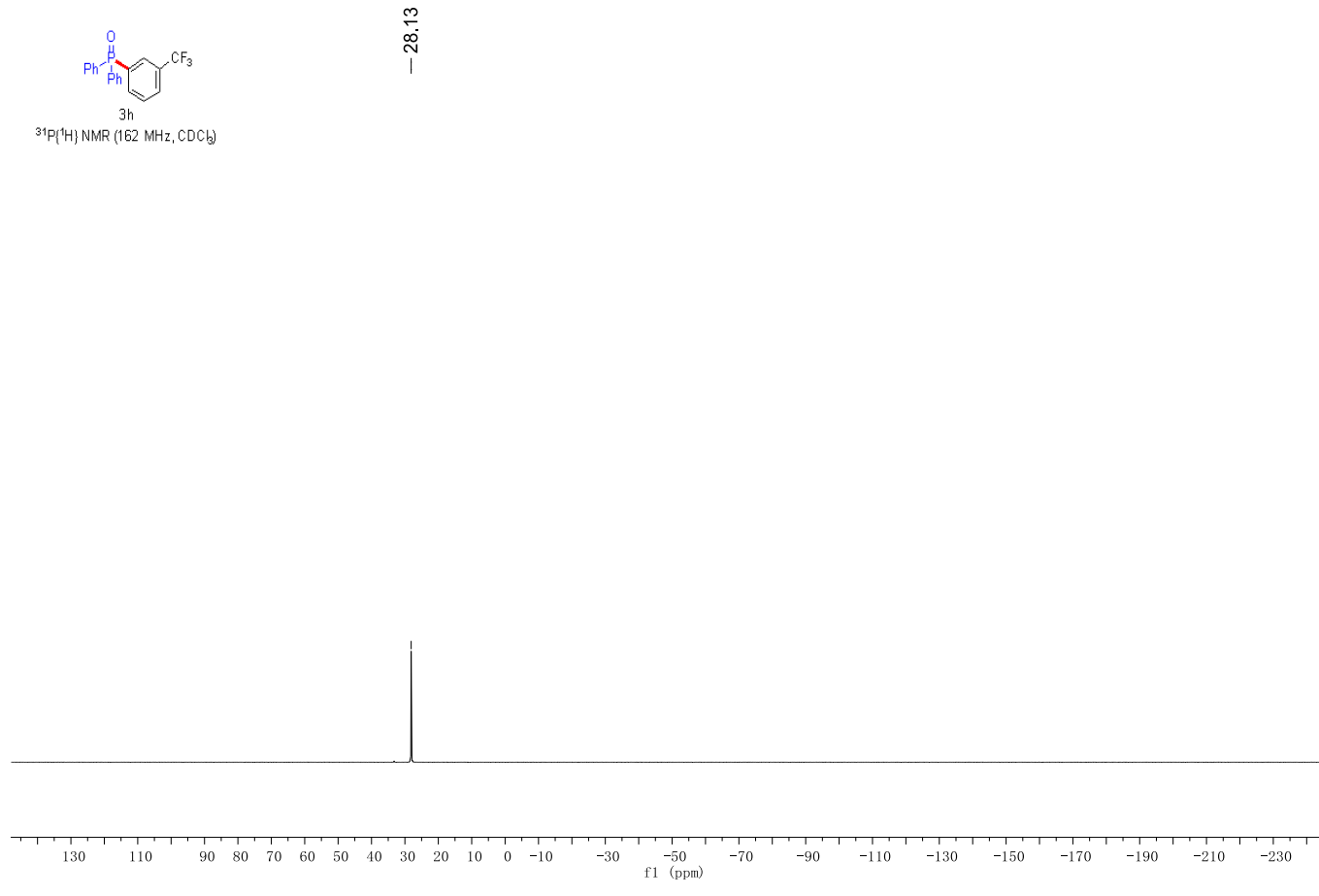
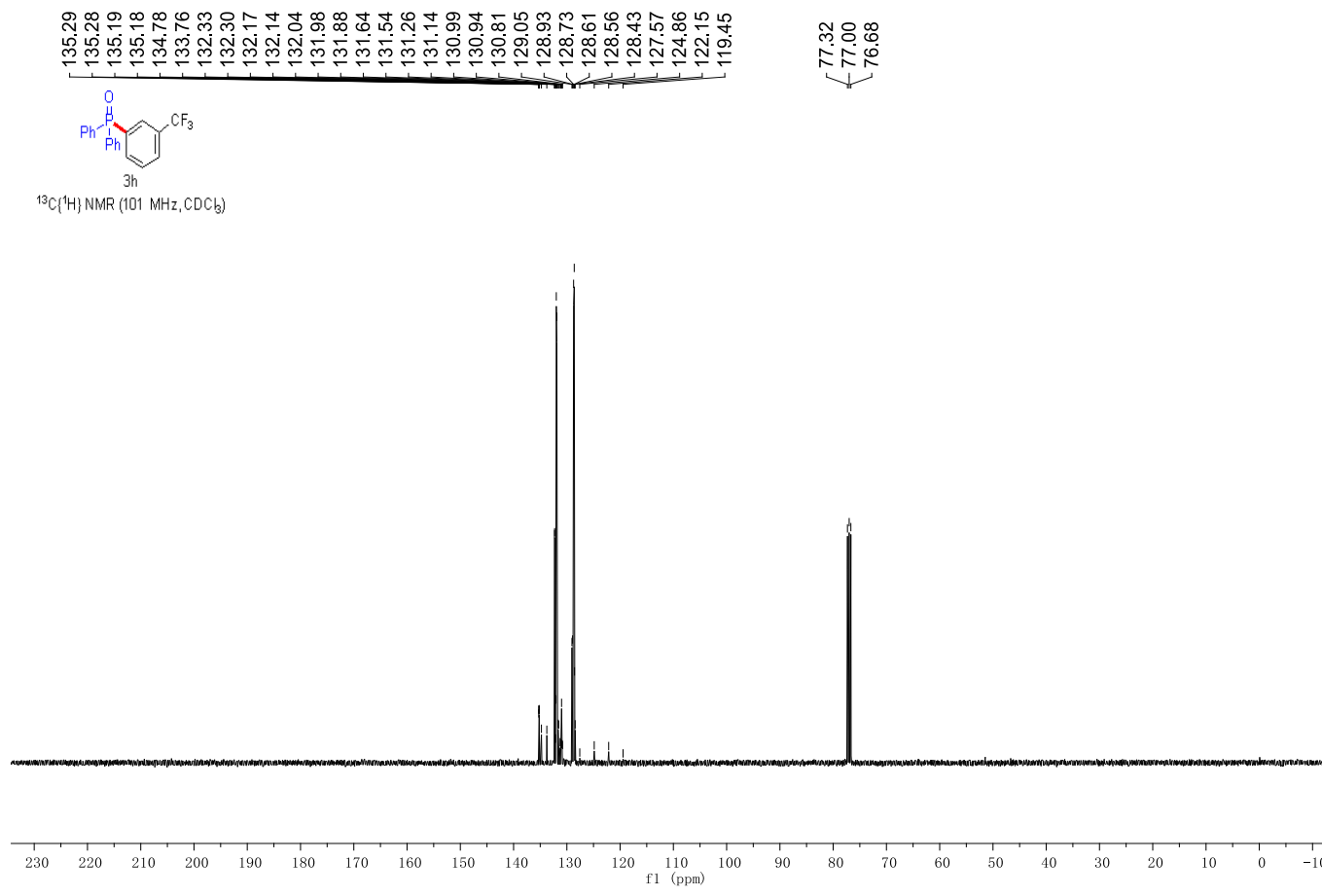
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)

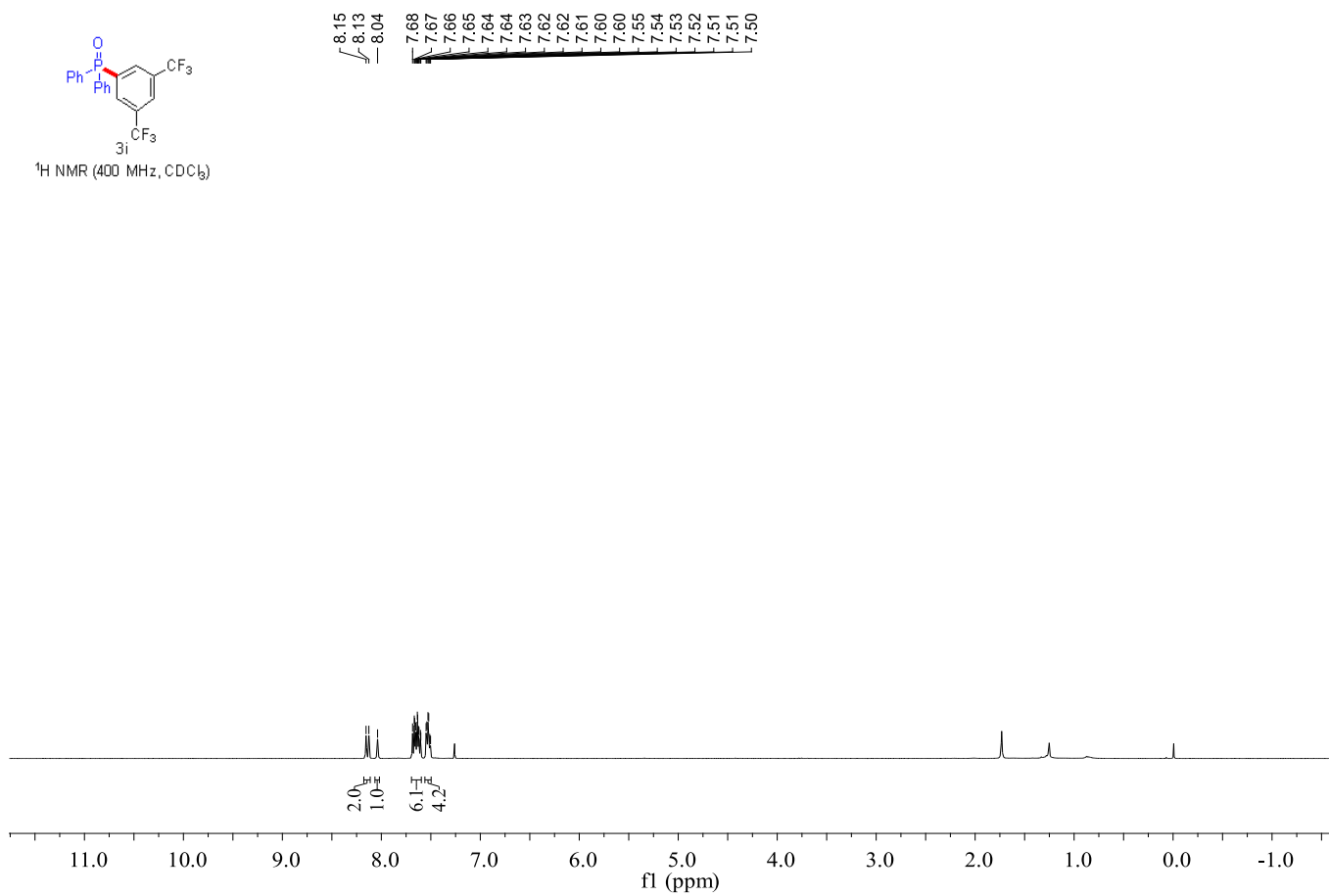
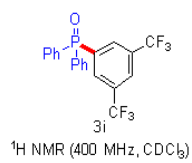
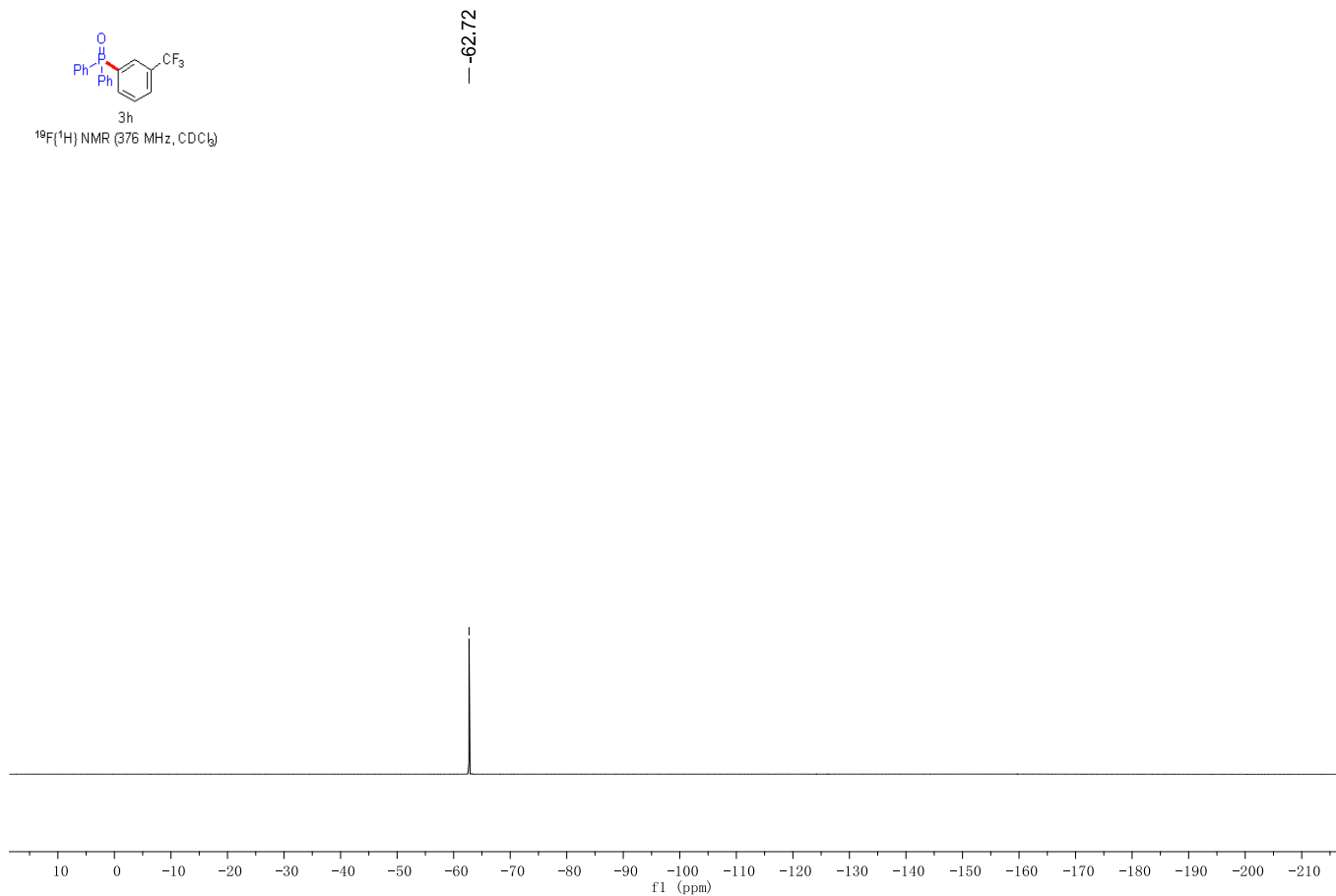
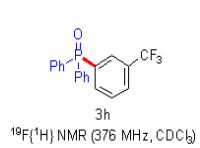


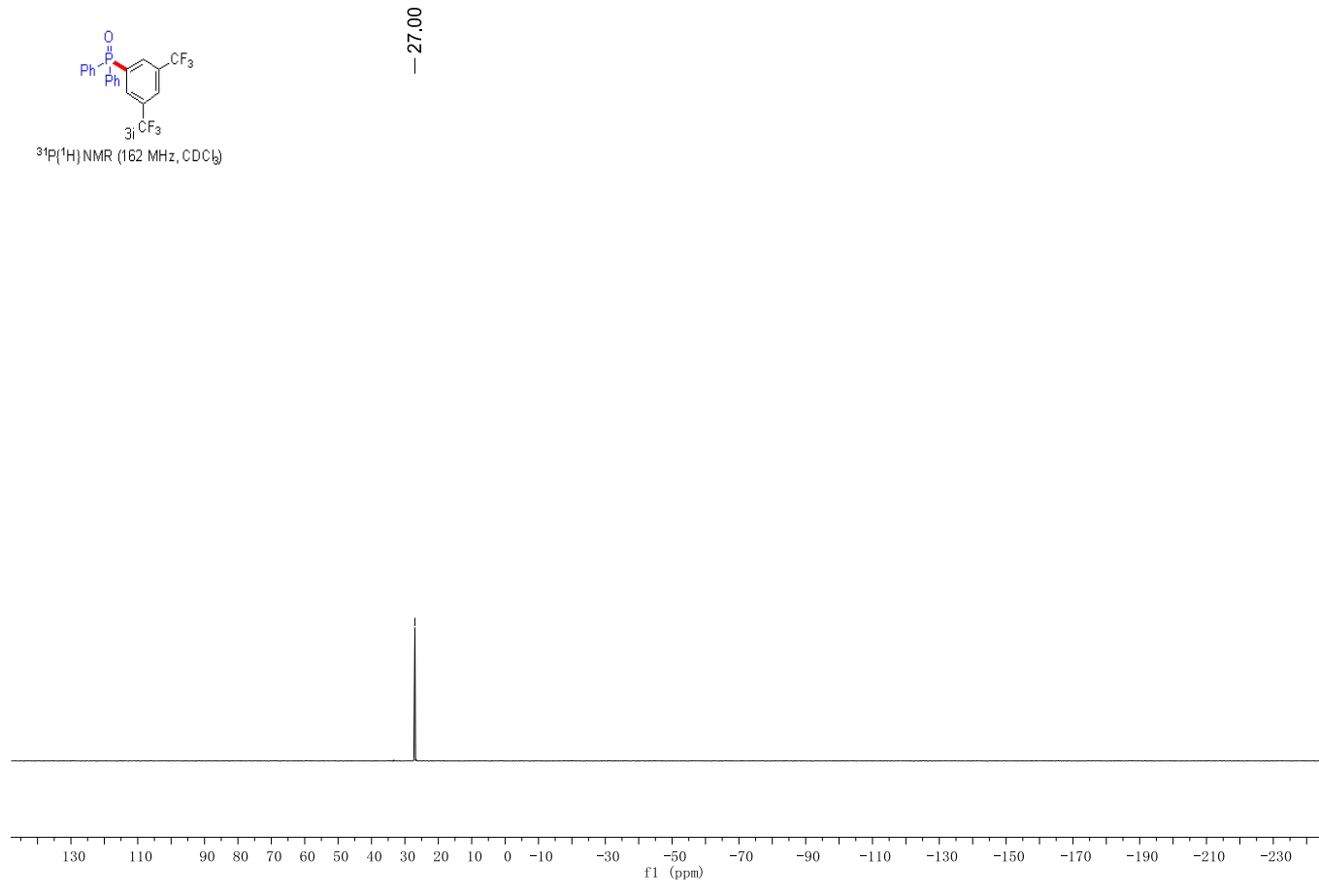
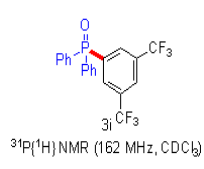
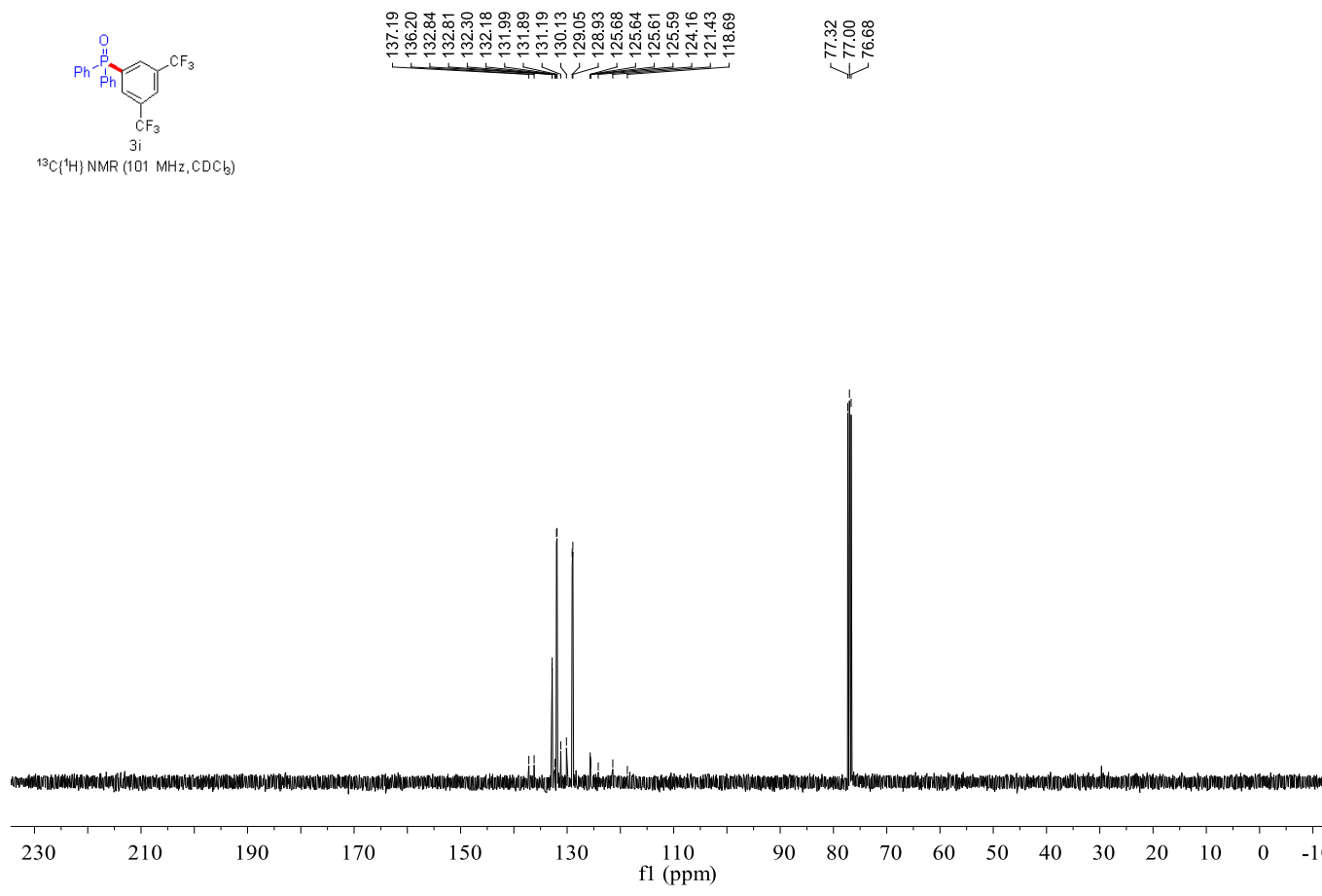
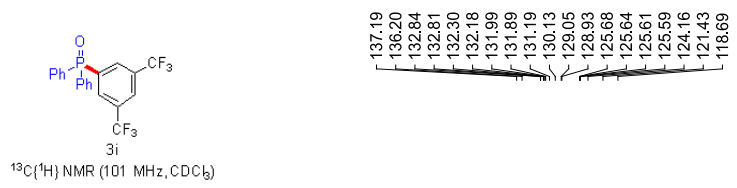


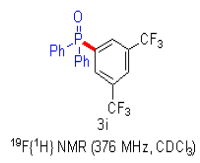
— 29.45



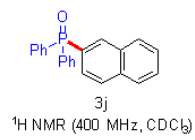
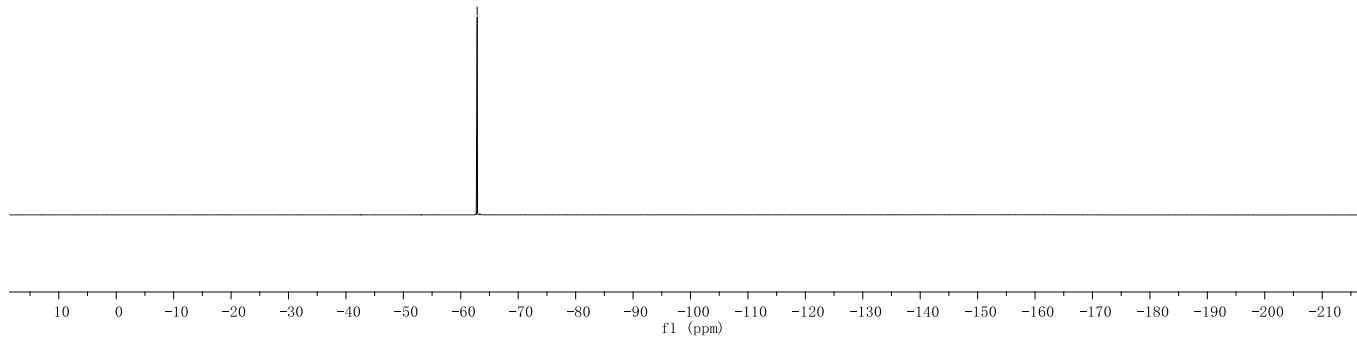




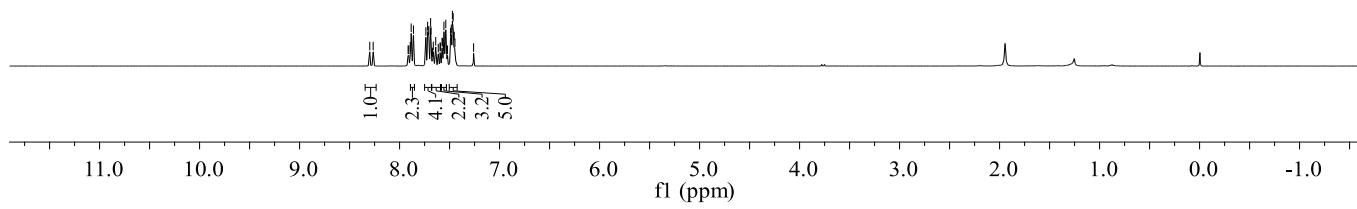


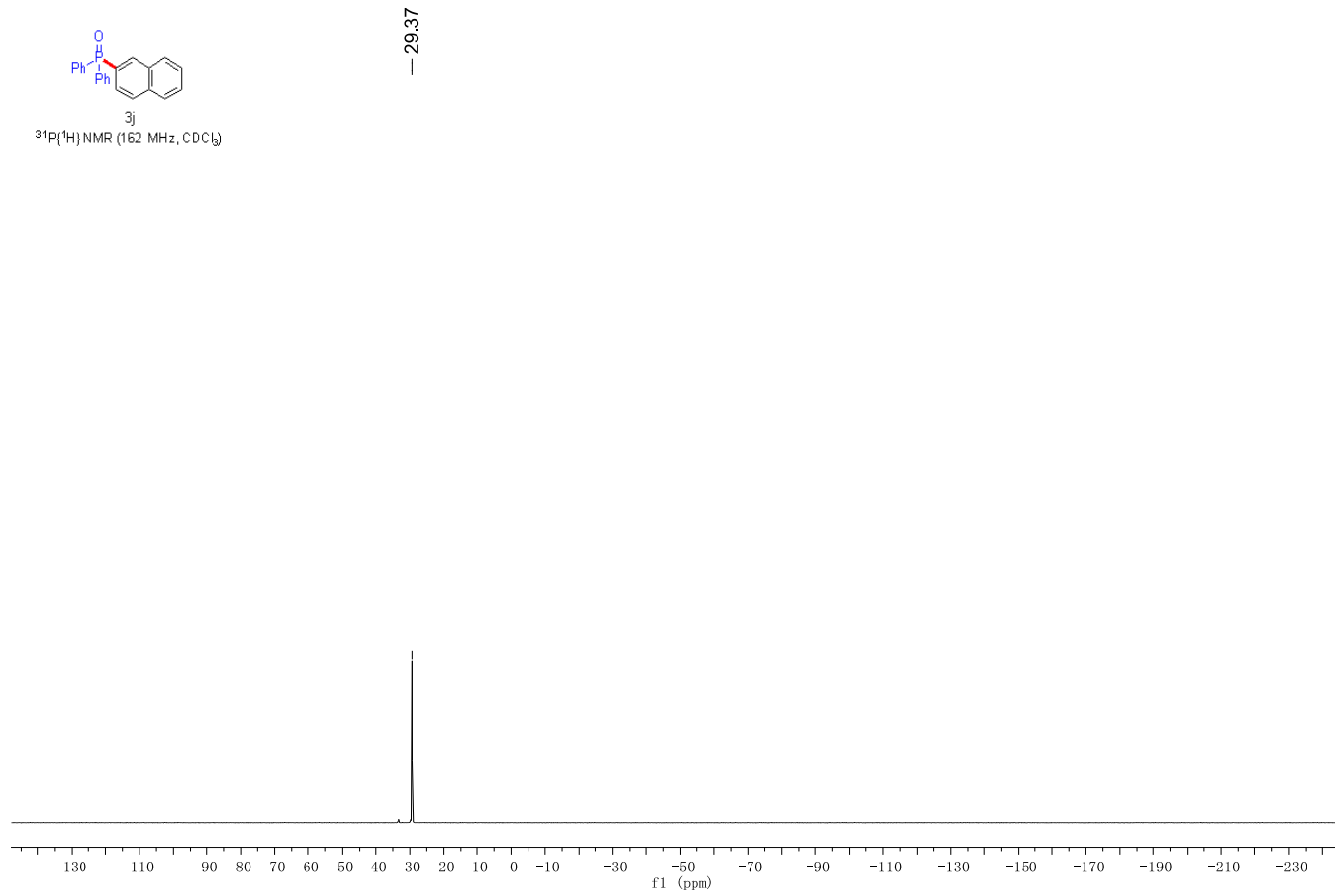
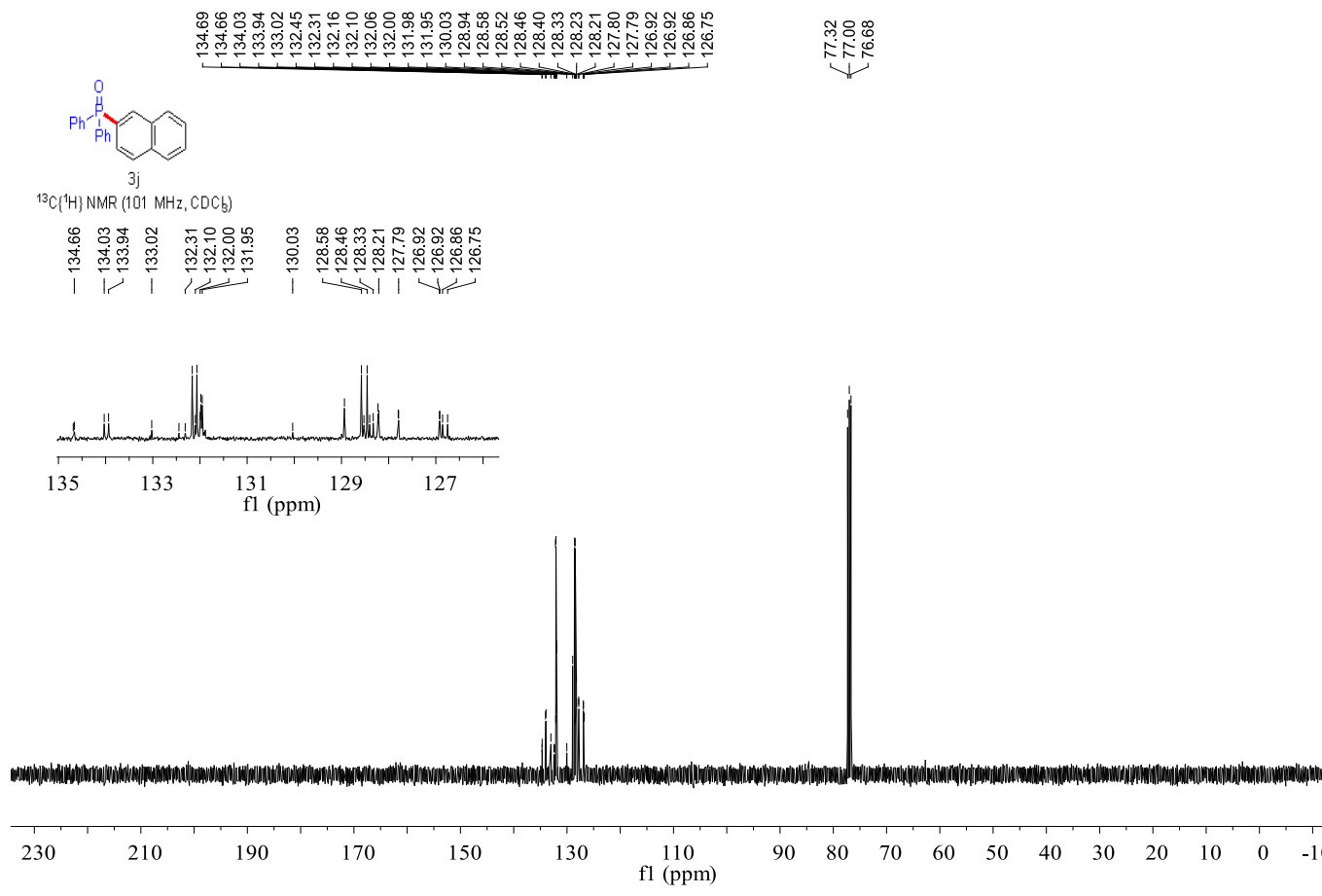


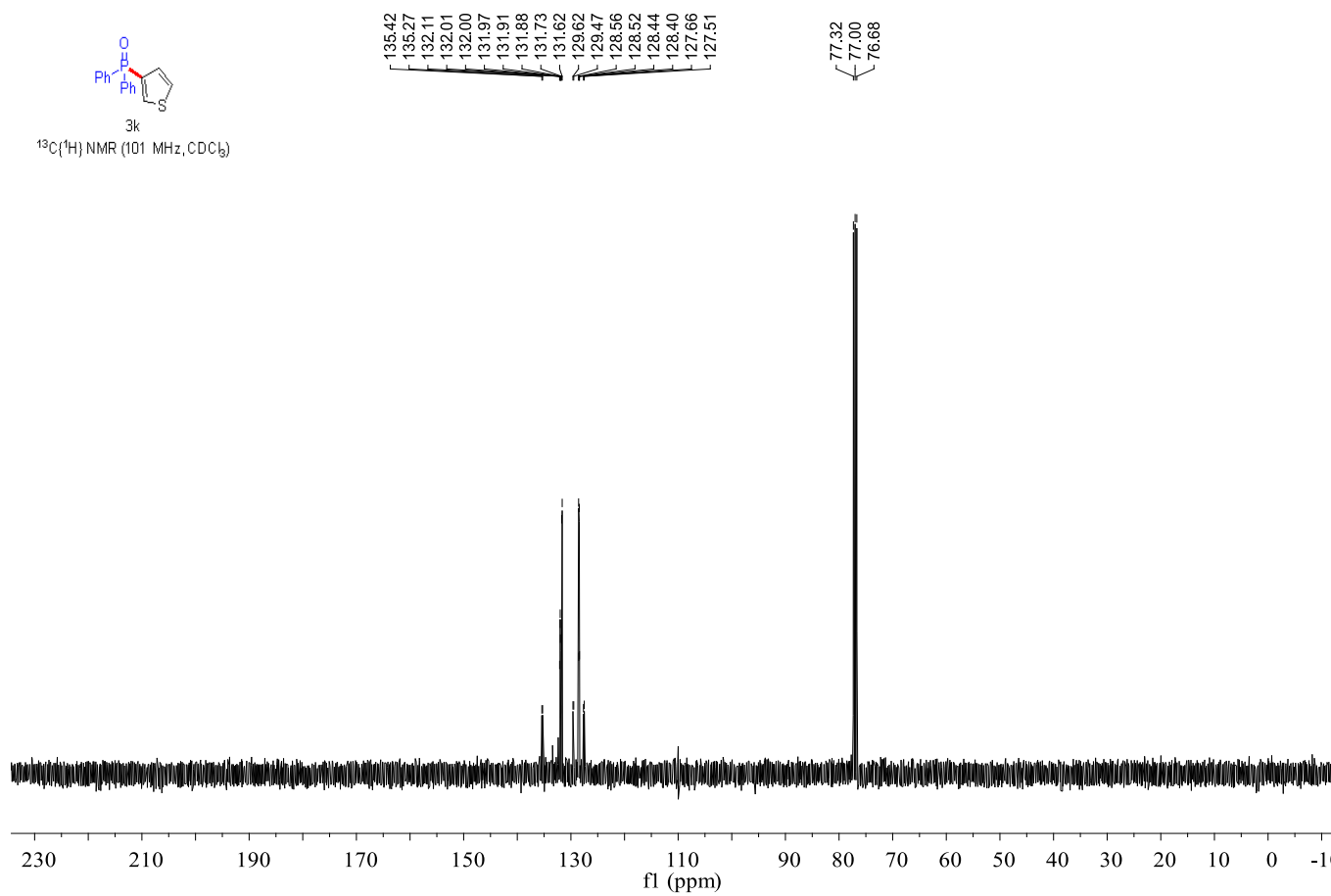
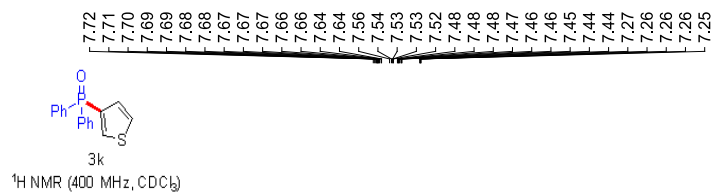
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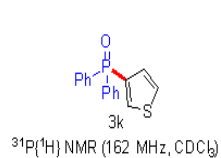


8.30
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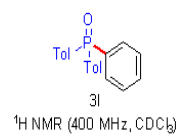
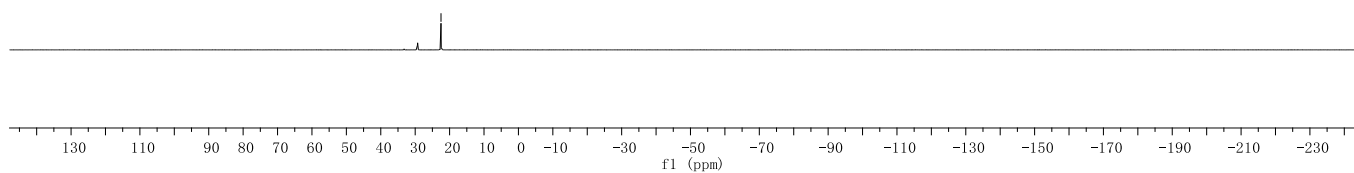






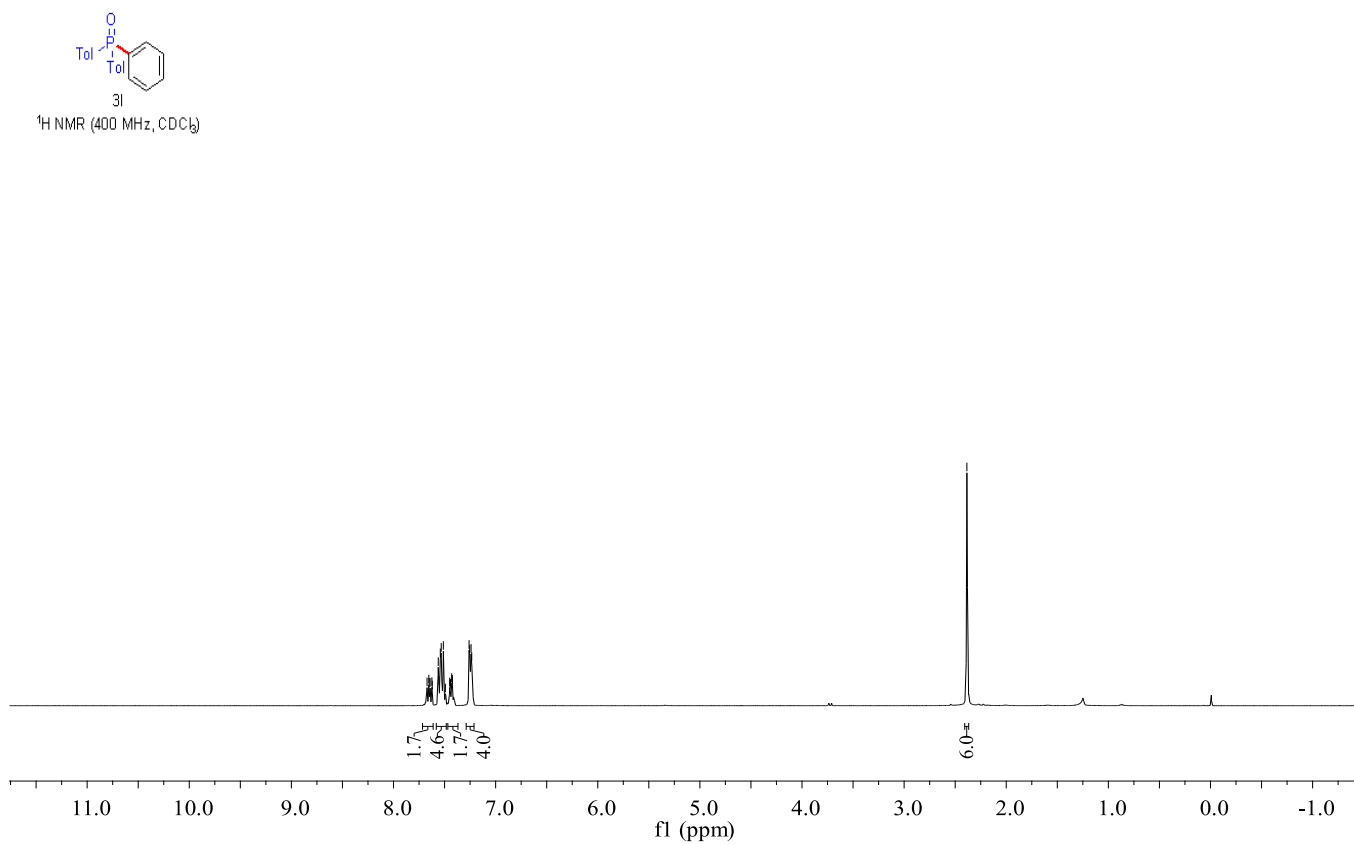


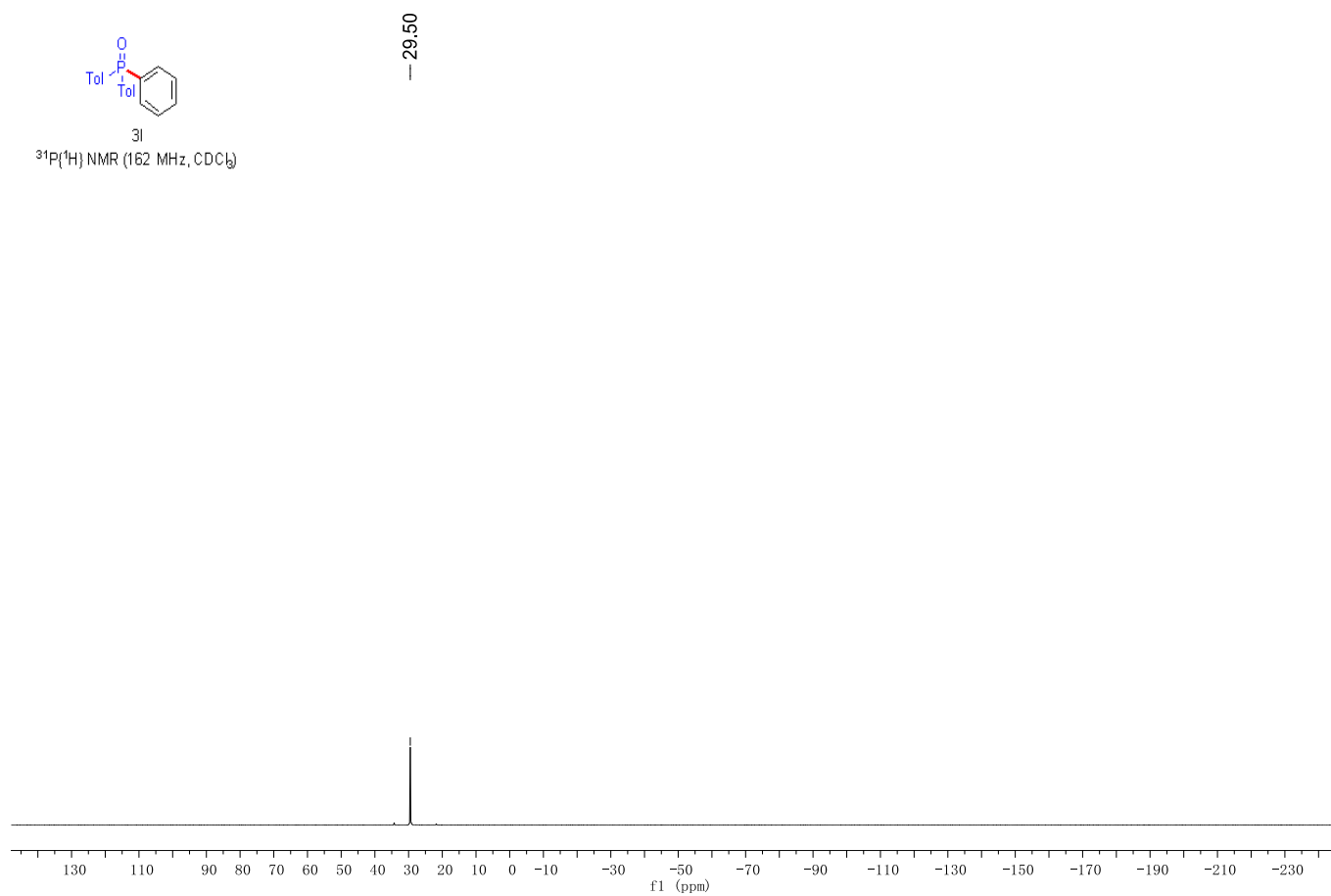
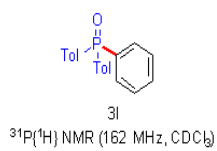
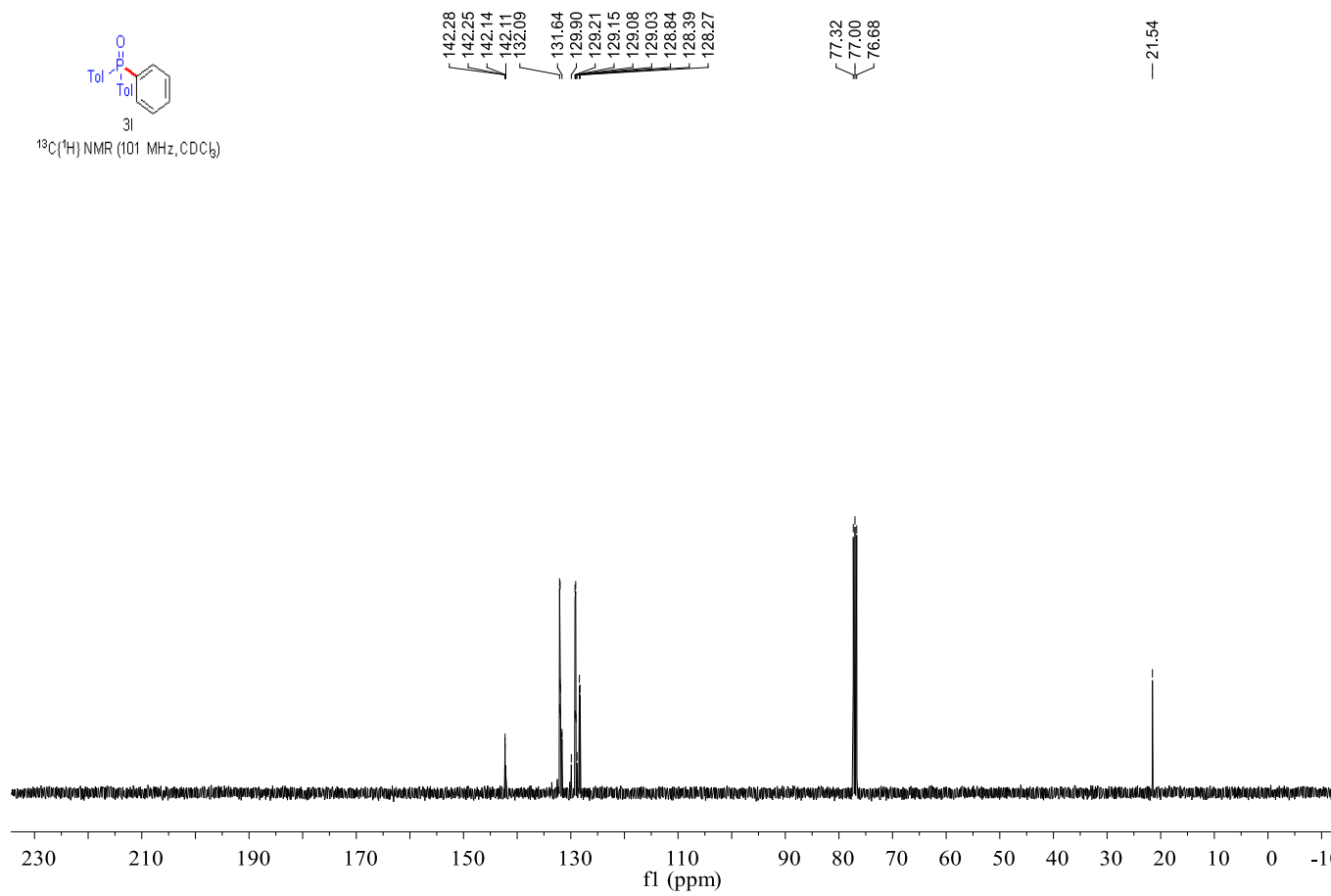
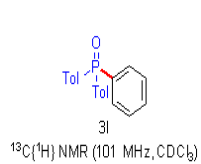
— 22.50

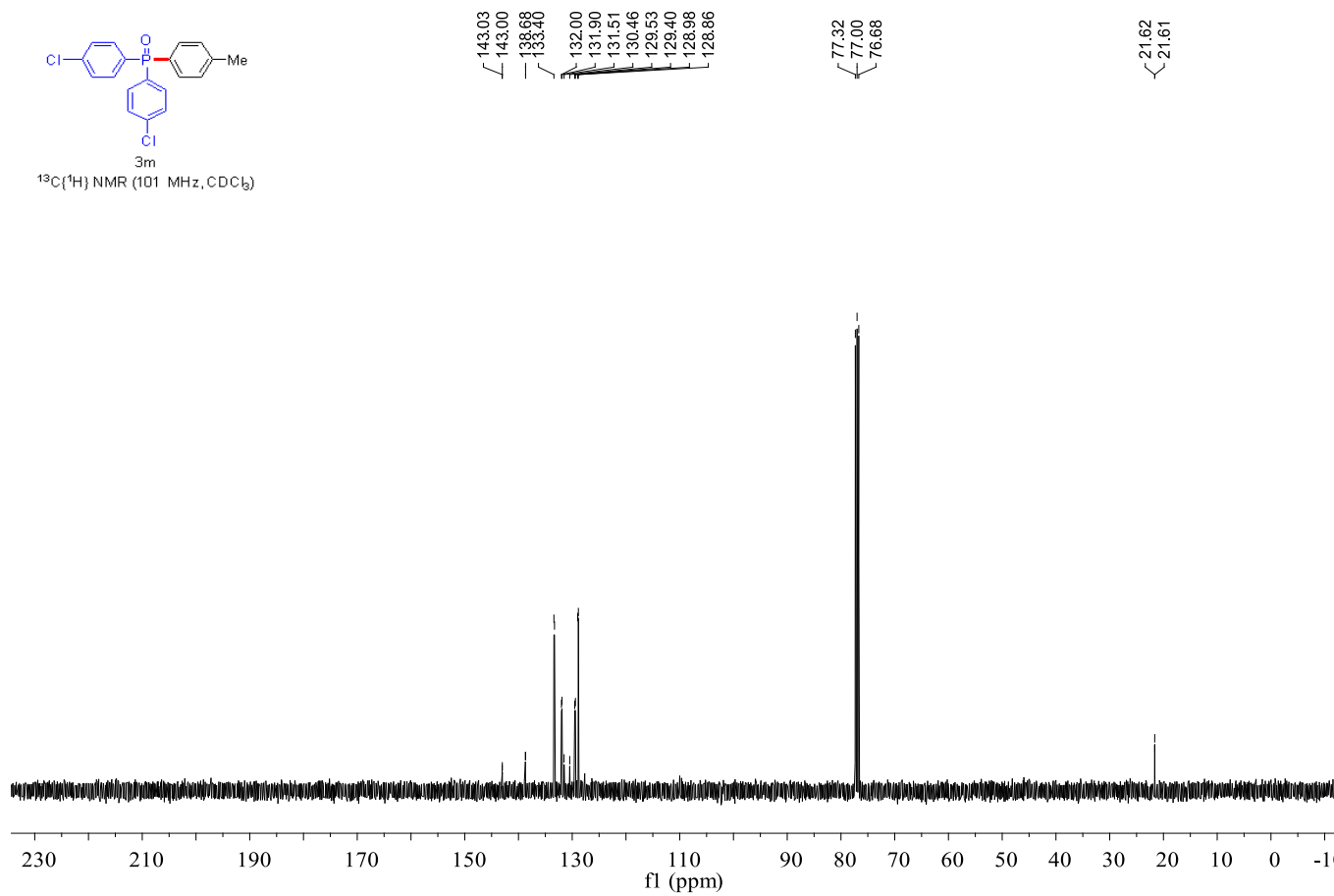
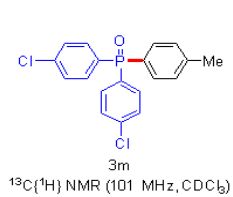
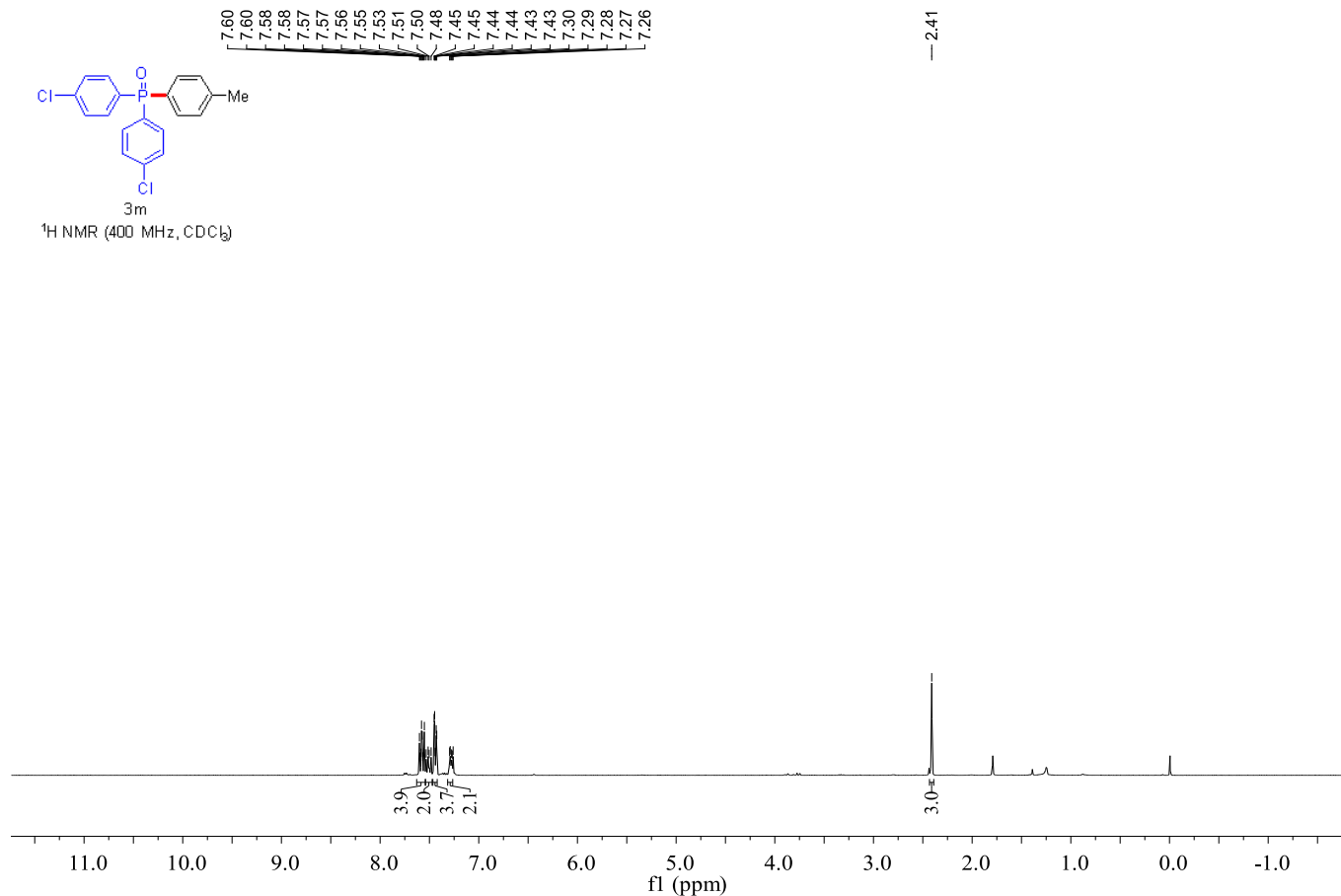
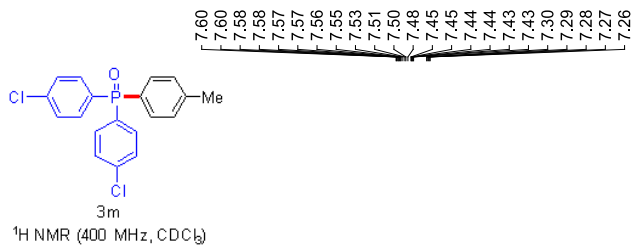


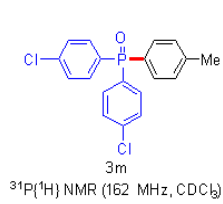
7.67
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 7.25
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 7.23

— 2.39

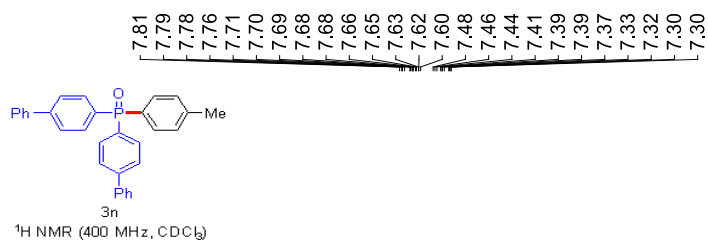
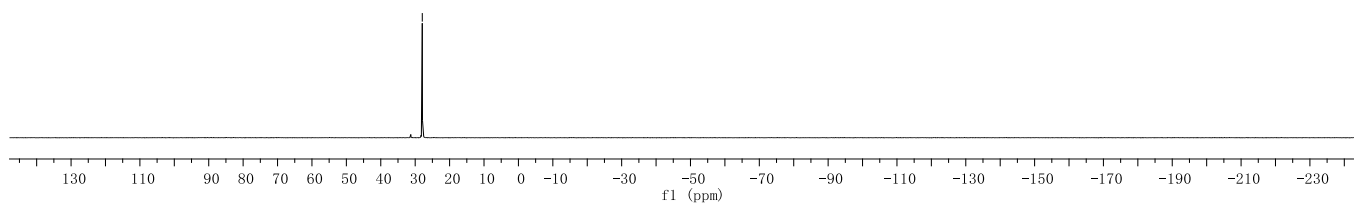




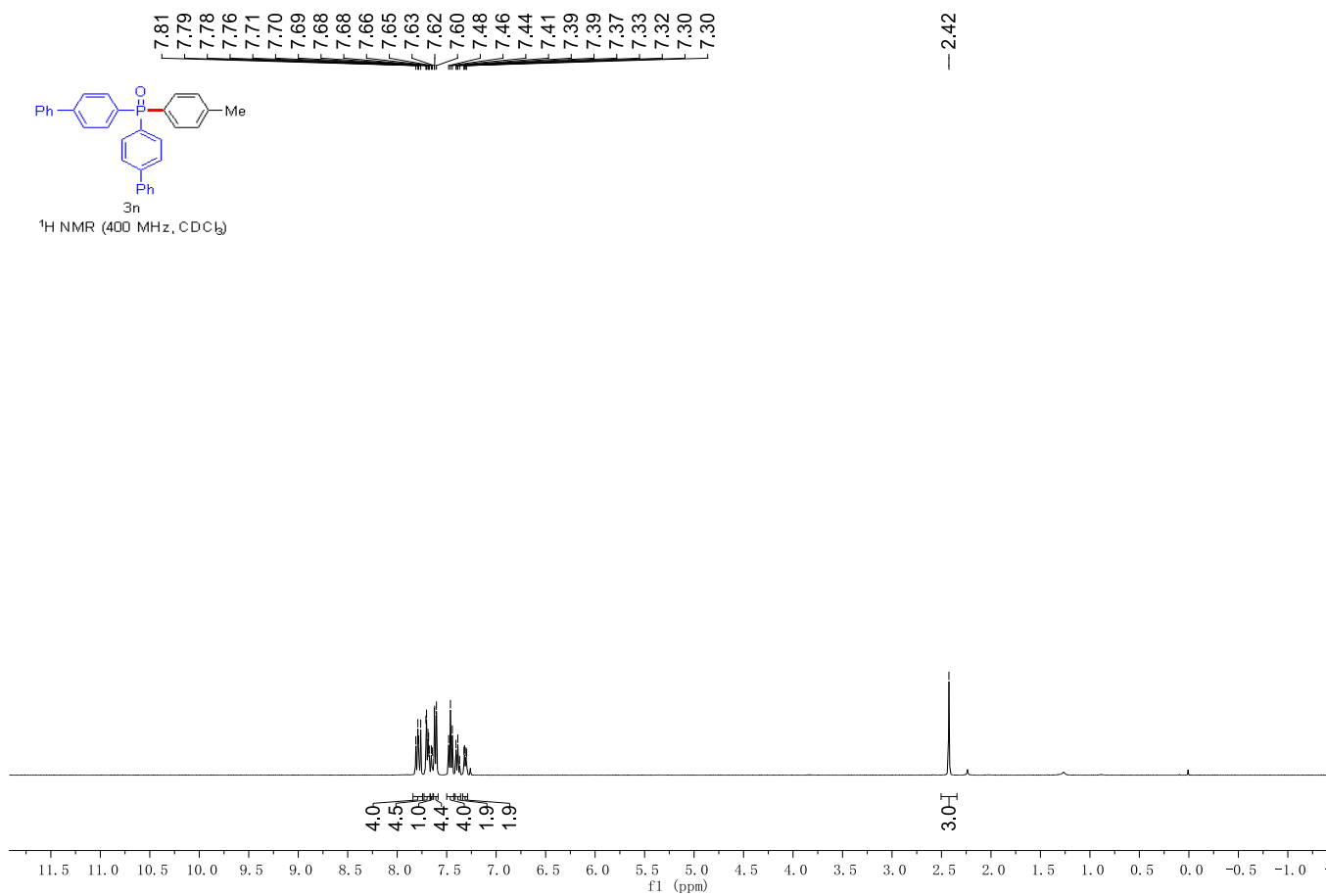


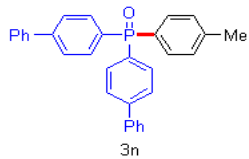


— 27.94



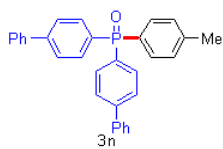
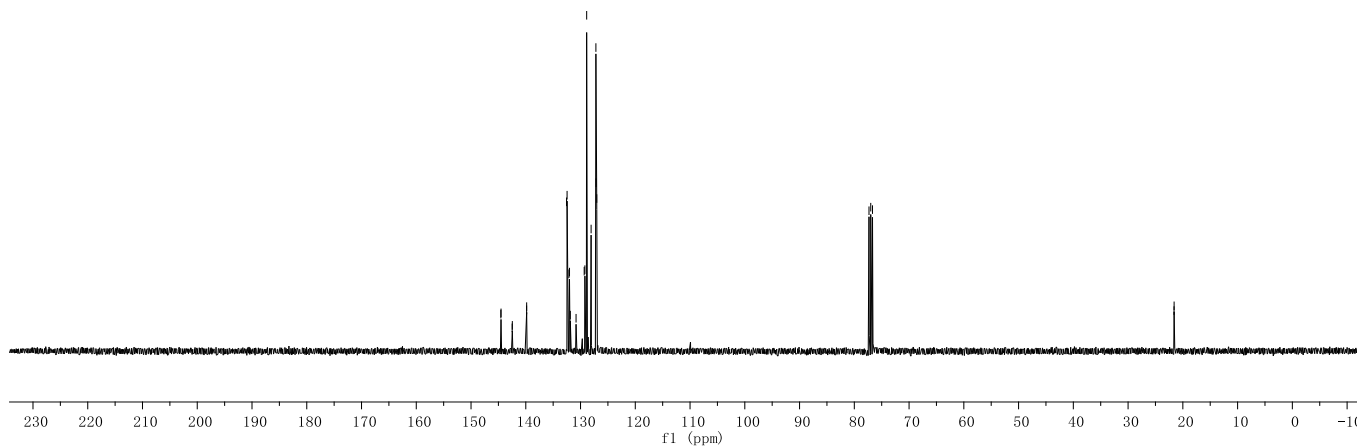
— 2.42





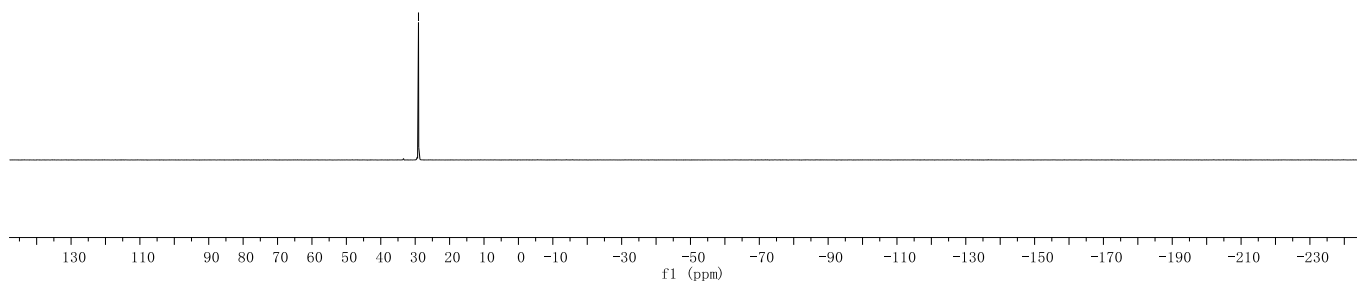
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)

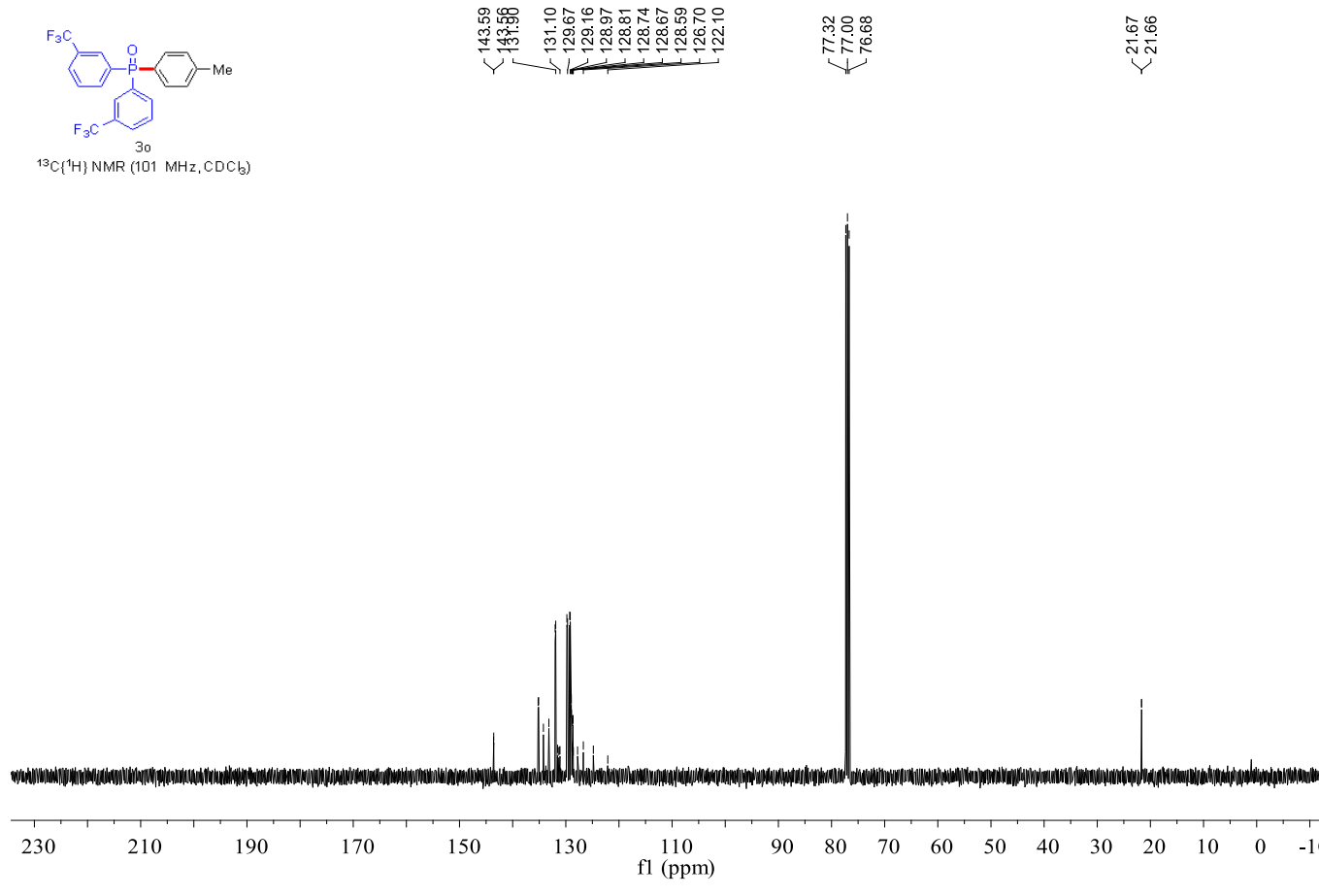
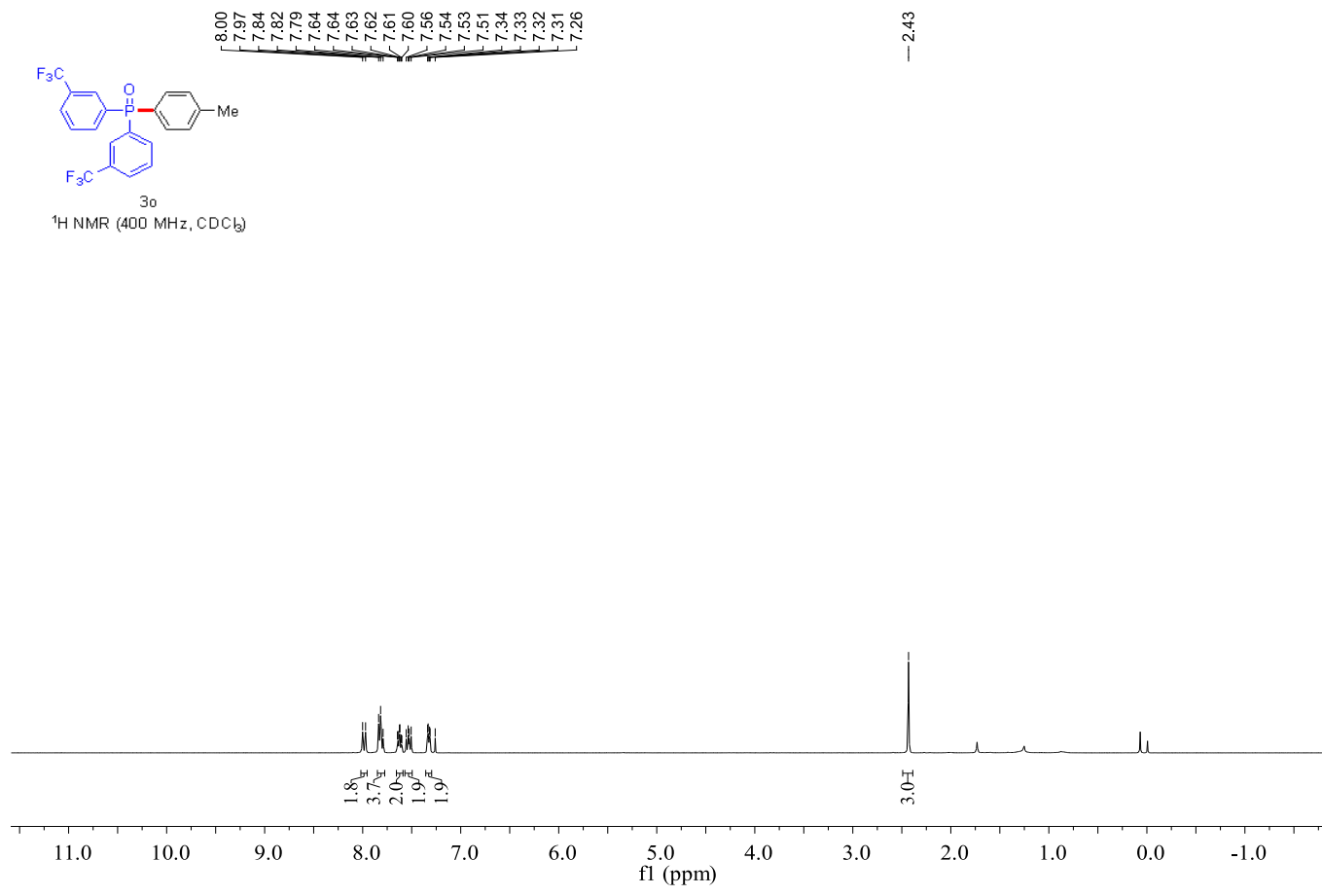
144.55
144.52
142.49
142.46
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139.84
132.46
129.20
128.88
128.07
127.19
127.16
127.04
77.32
77.00
76.68
21.61
21.59

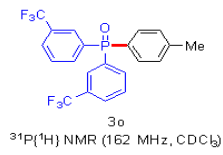


$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3)

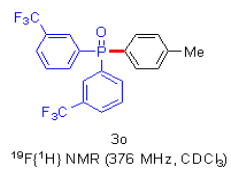
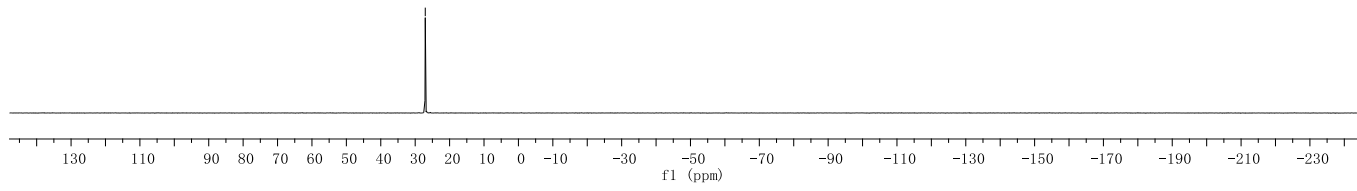
-29.04



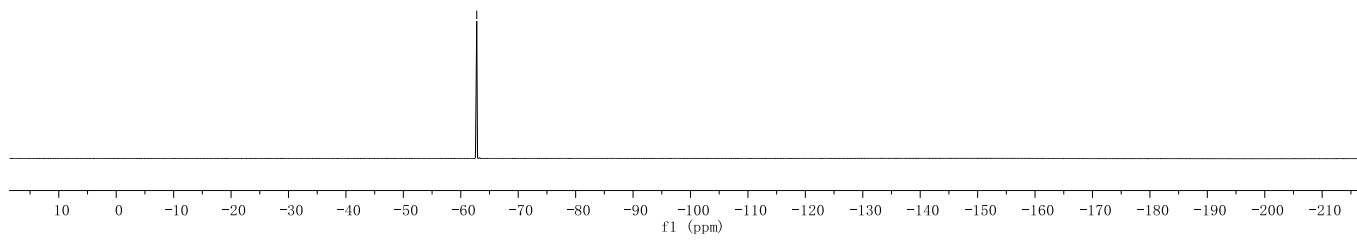




— 27.07

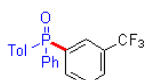


— -62.78



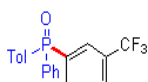
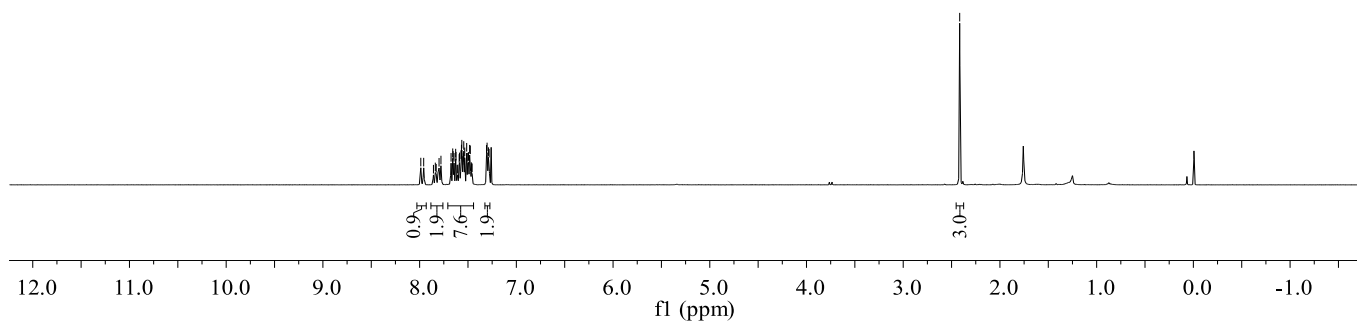
7.99
7.96
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7.80
7.78
7.67
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7.65
7.64
7.63
7.62
7.61
7.61
7.59
7.59
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.31
7.30
7.29
7.28

—2.42



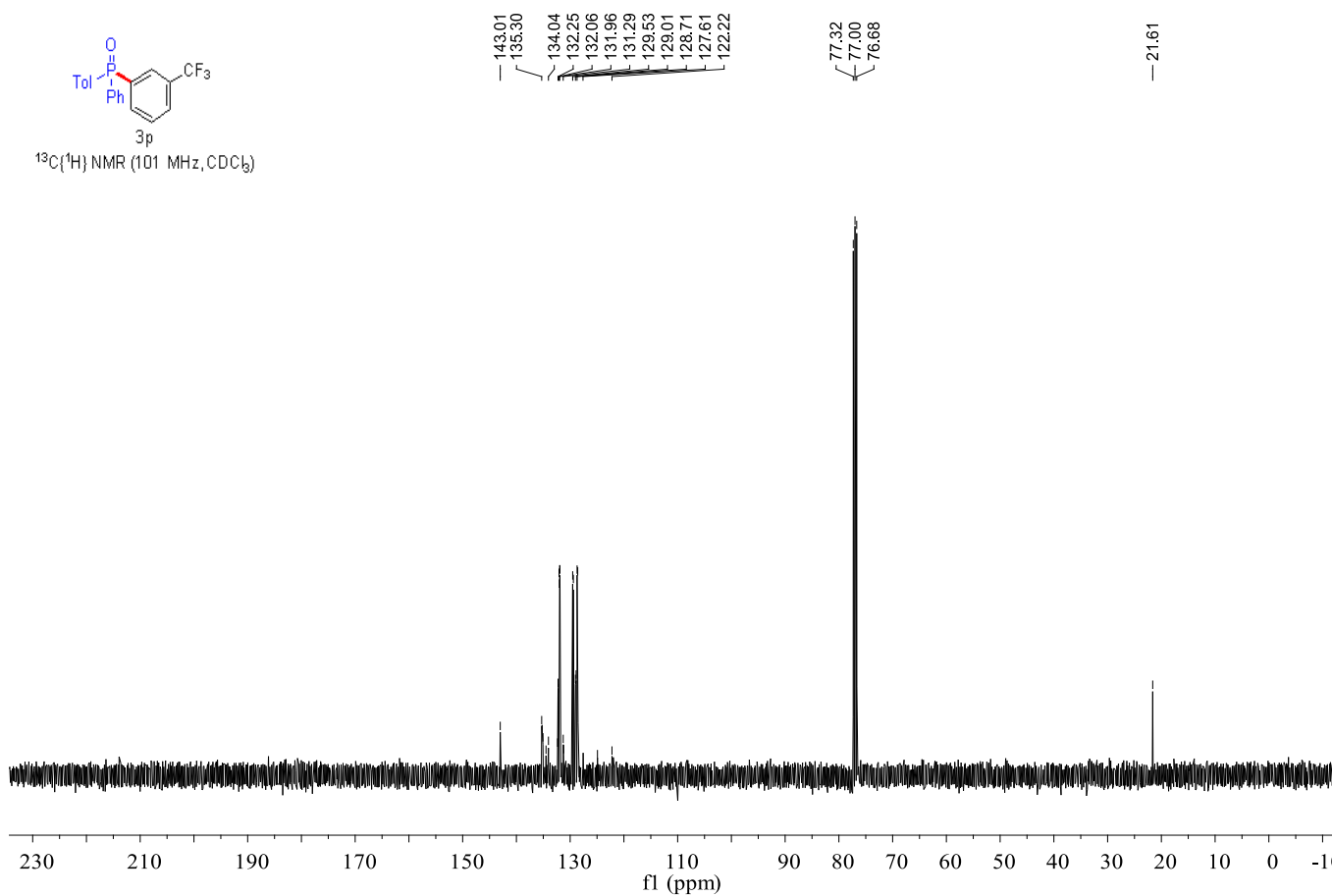
3p

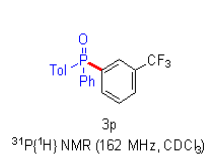
$^1\text{H NMR}$ (400 MHz, CDCl_3)



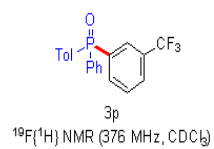
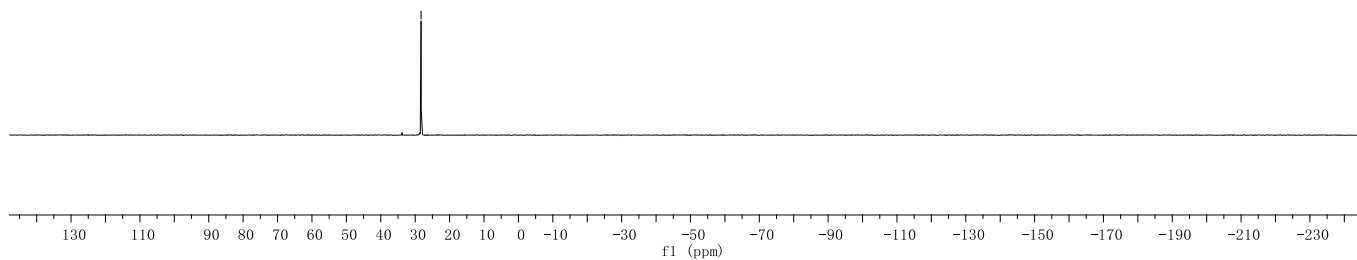
3p

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)

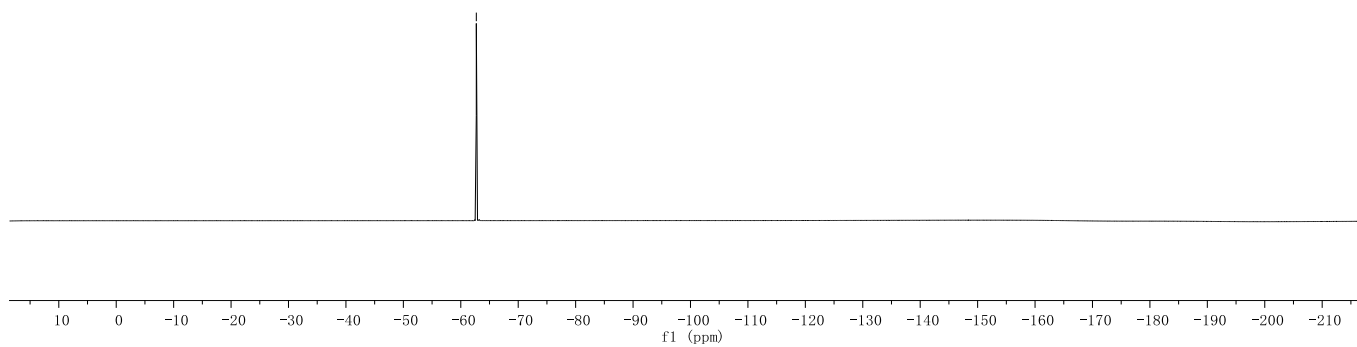




—28.29

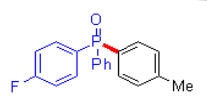


—62.71

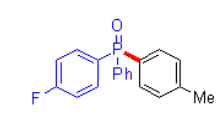
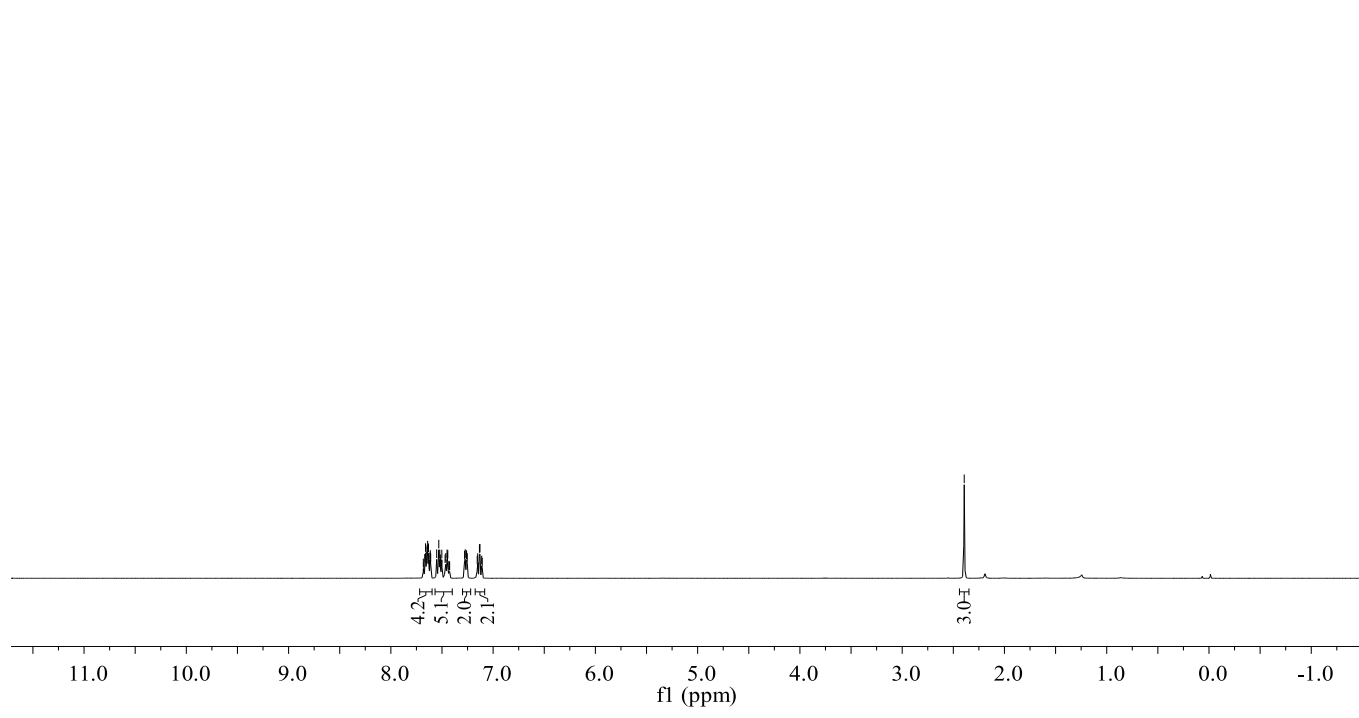


7.67
7.66
7.65
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7.64
7.63
7.62
7.62
7.61
7.61
7.55
7.53
7.52
7.52
7.51
7.50
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.28
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7.13
7.13
7.11
7.11

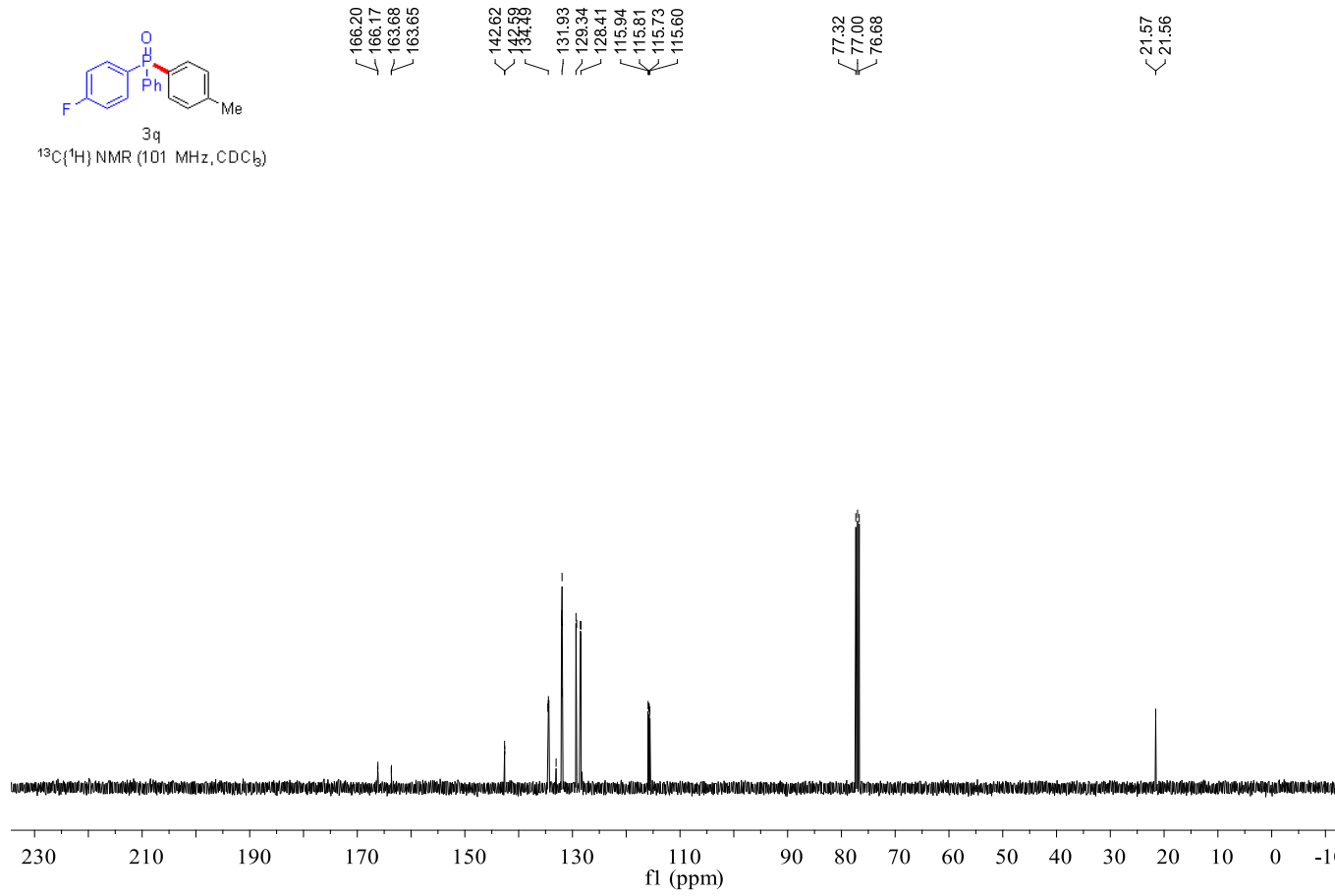
—2.39

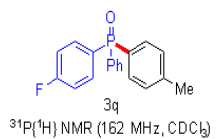


3q
¹H NMR (400 MHz, CDCl₃)

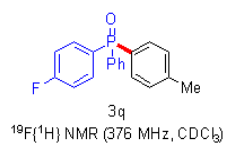
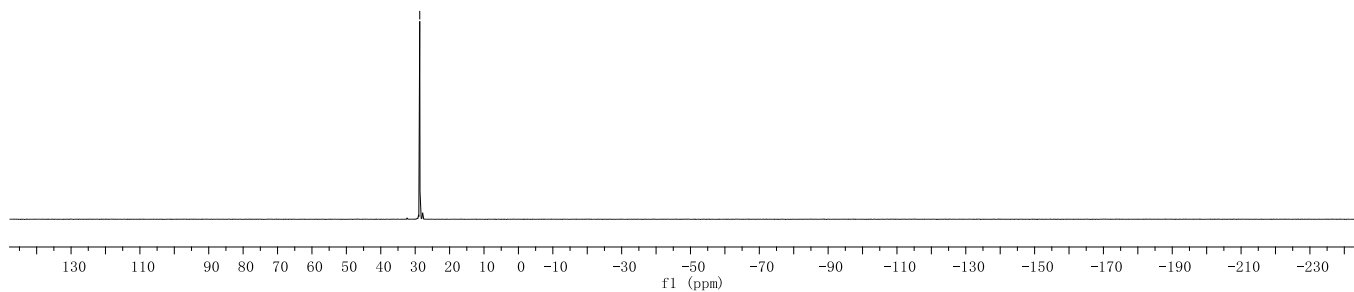


3q
¹³C{¹H} NMR (101 MHz, CDCl₃)

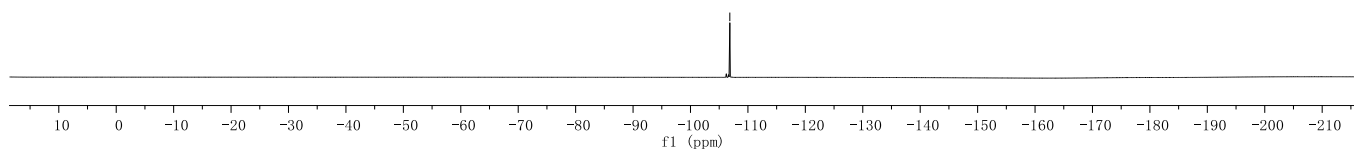


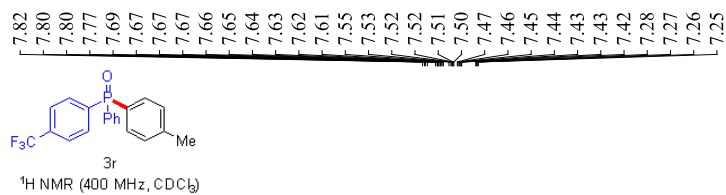


--28.67

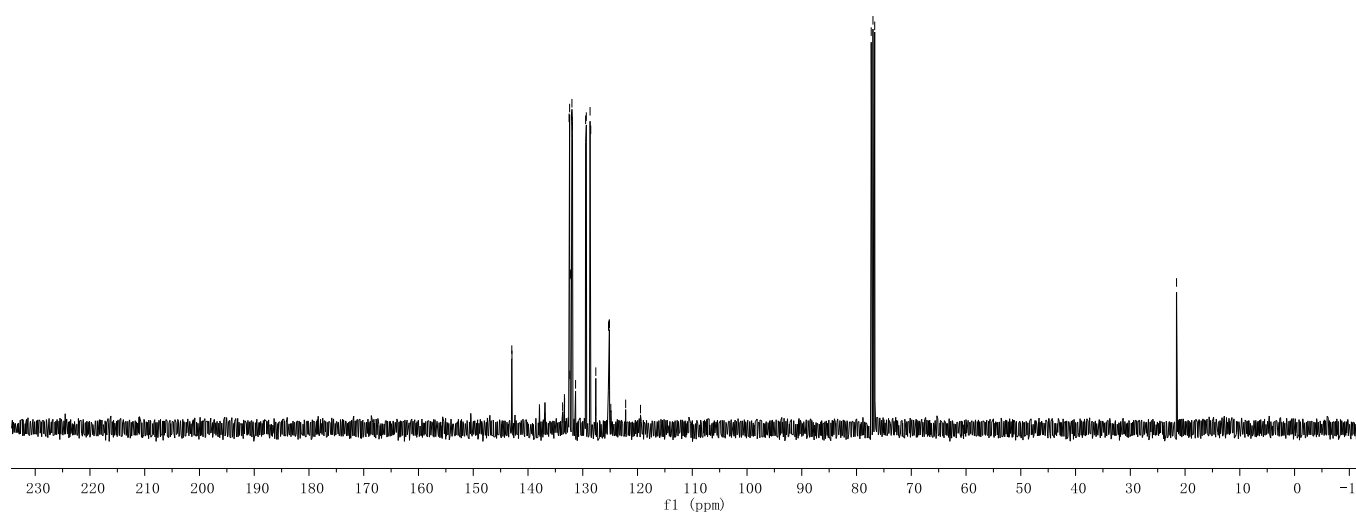
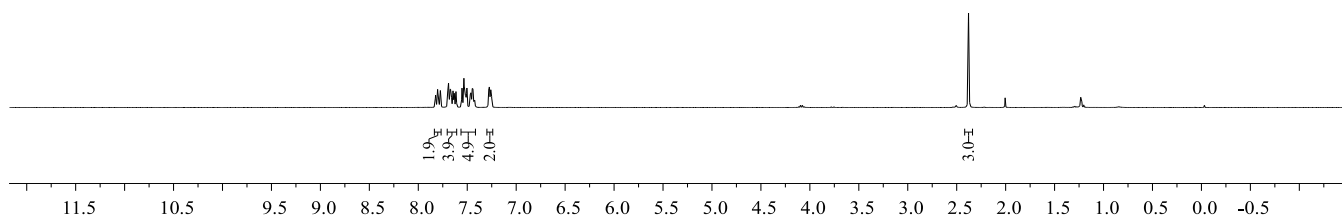


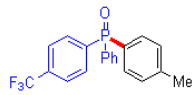
--106.85





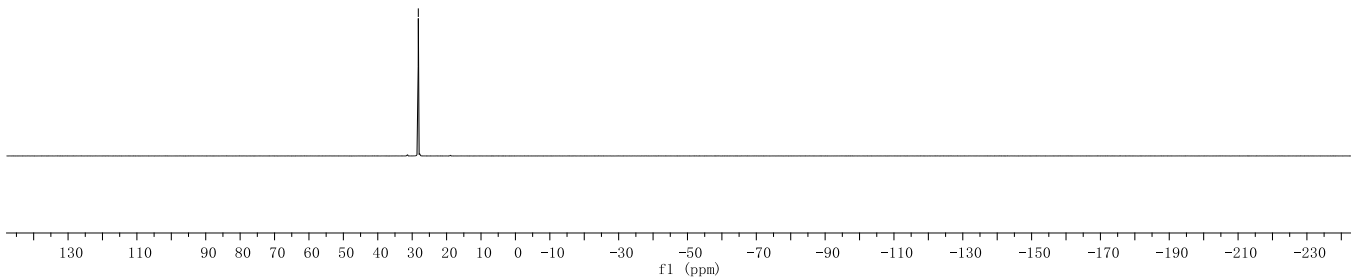
-2.38





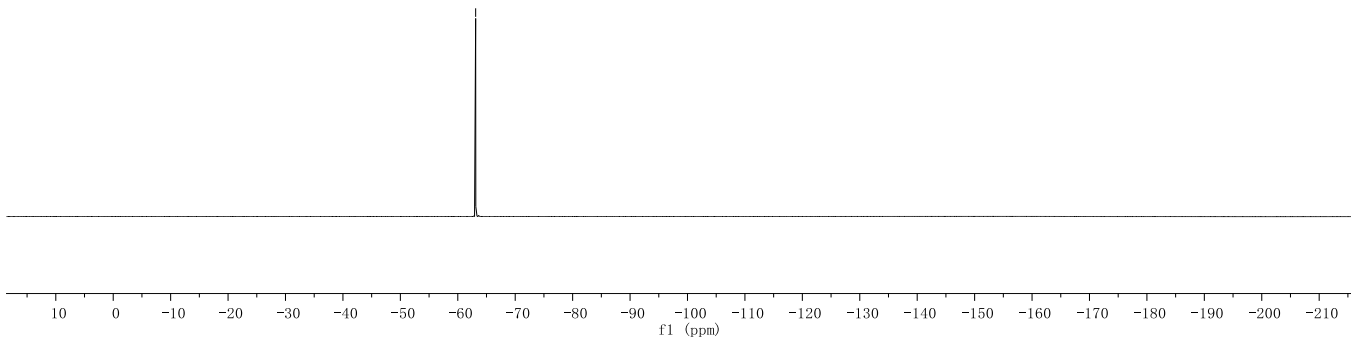
3r
³¹P{¹H} NMR (162 MHz, CDCl₃)

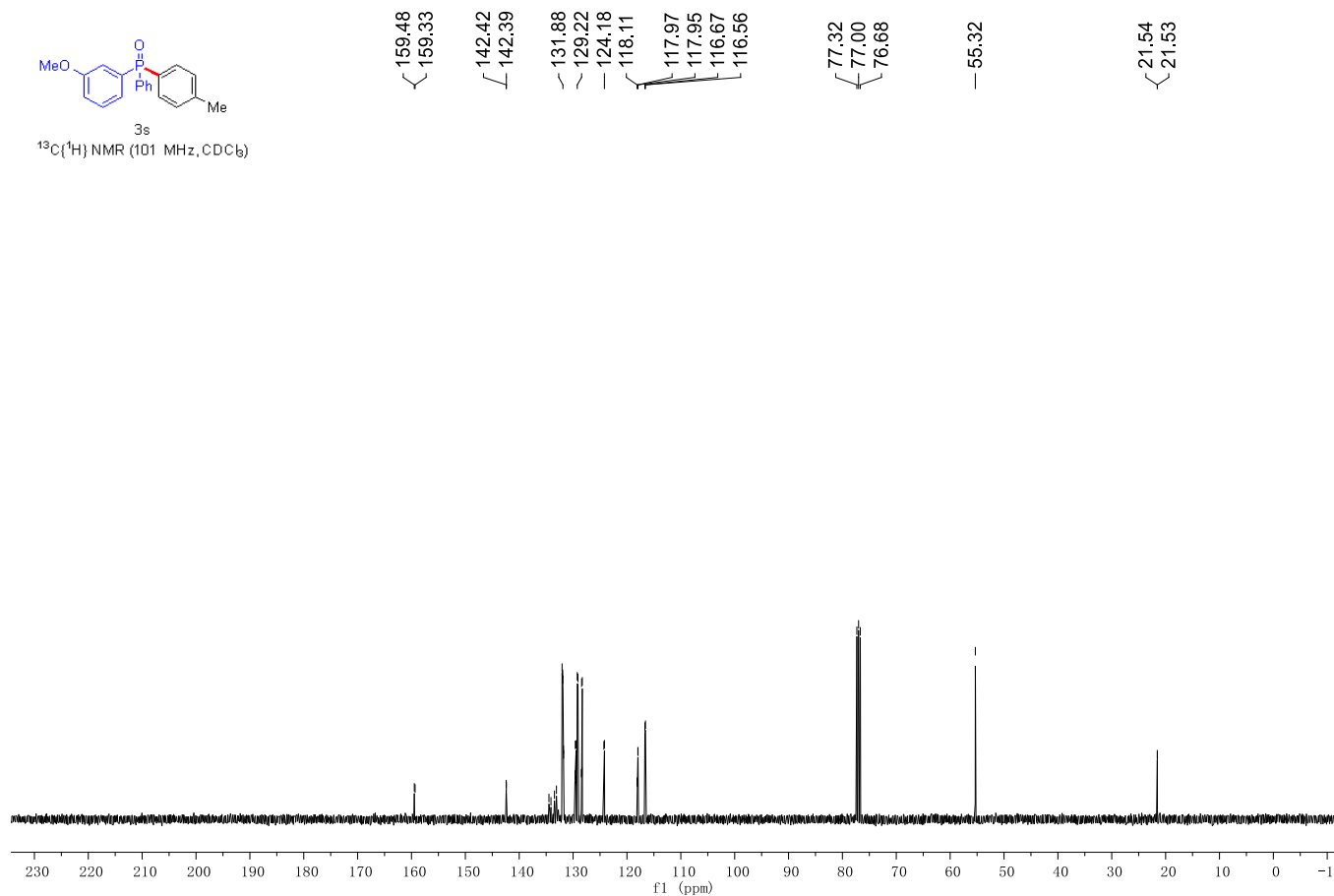
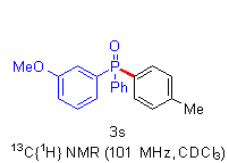
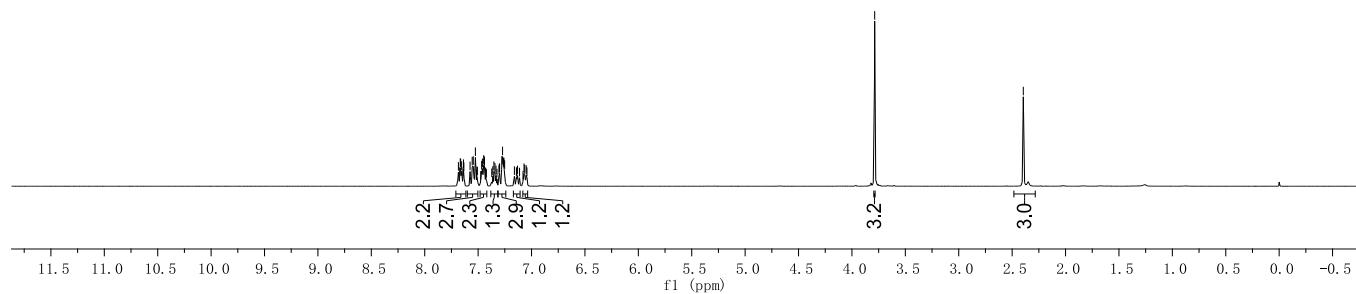
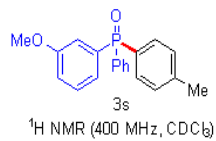
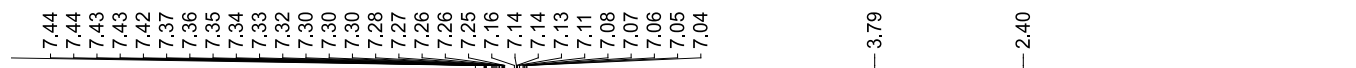
—28.22

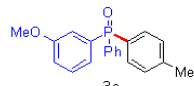


3r
¹⁹F{¹H} NMR (376 MHz, CDCl₃)

—-63.11



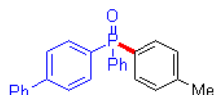
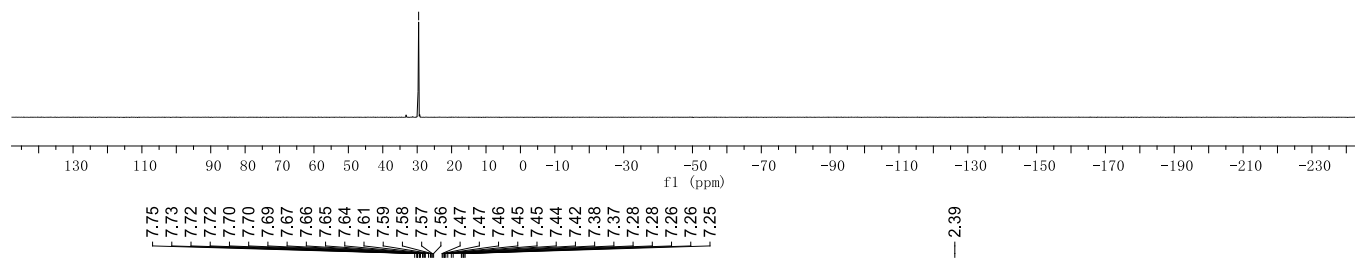




3s

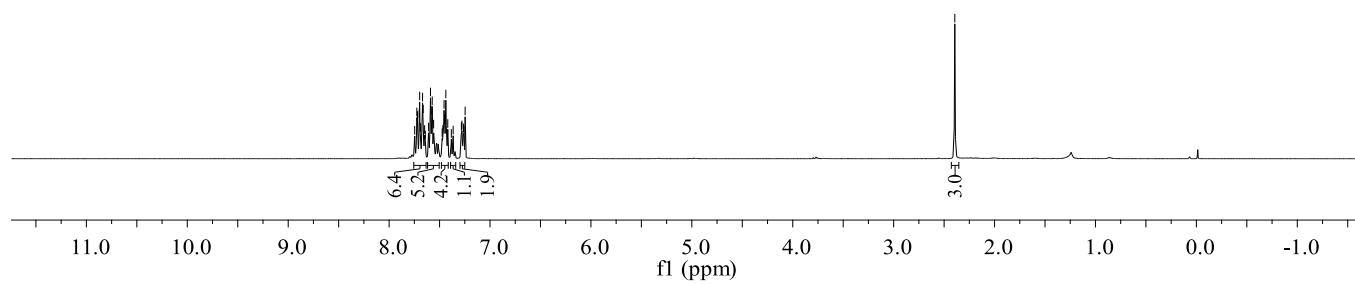
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3)

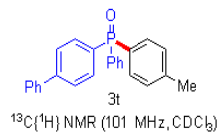
— 29.58



3t

^1H NMR (400 MHz, CDCl_3)

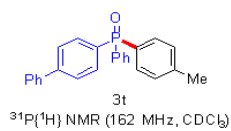
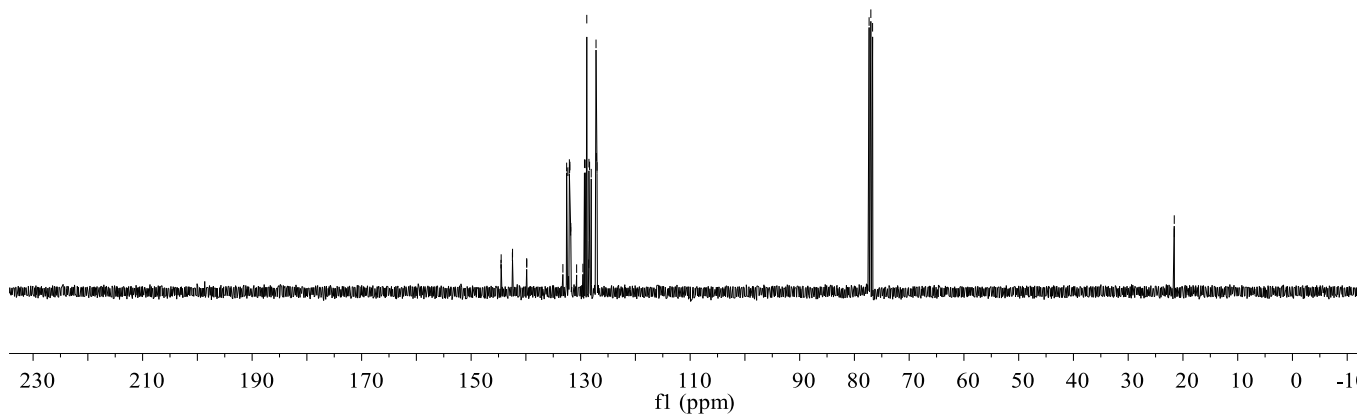




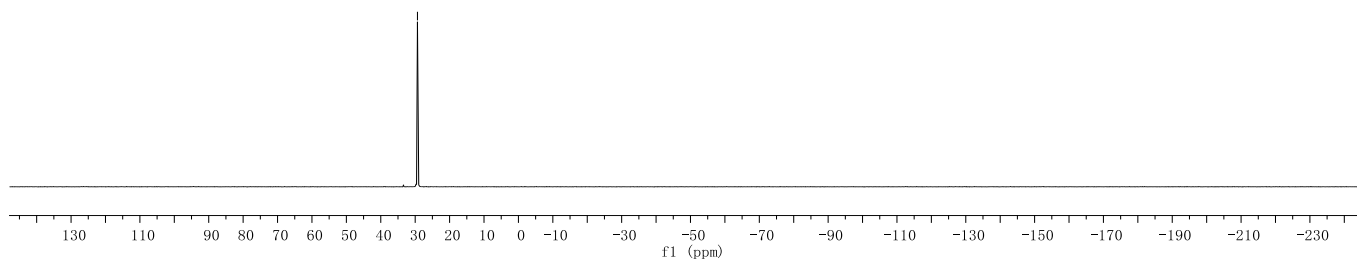
144.54
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 142.44
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 131.96
 131.80
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 129.17
 128.53
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 127.01

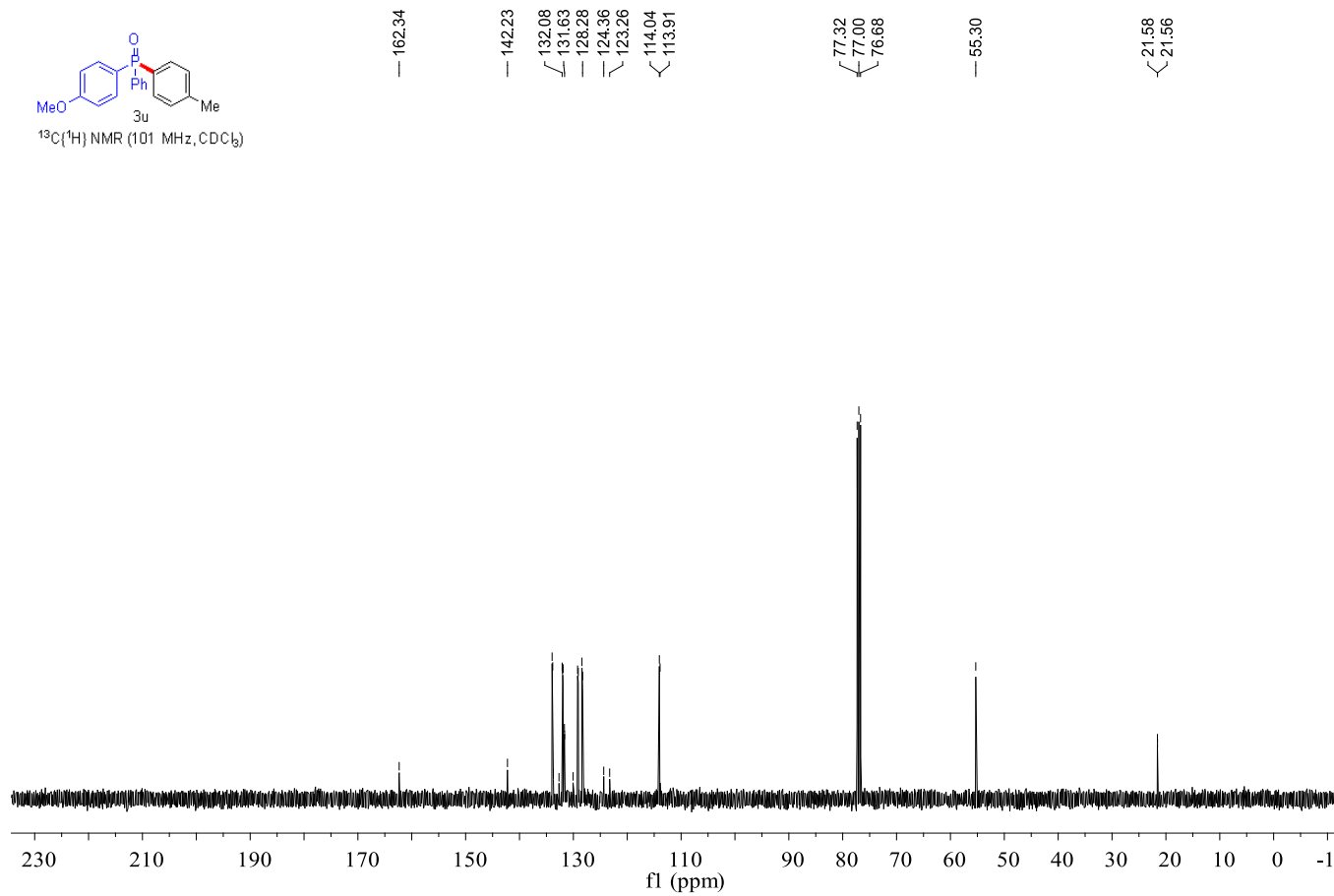
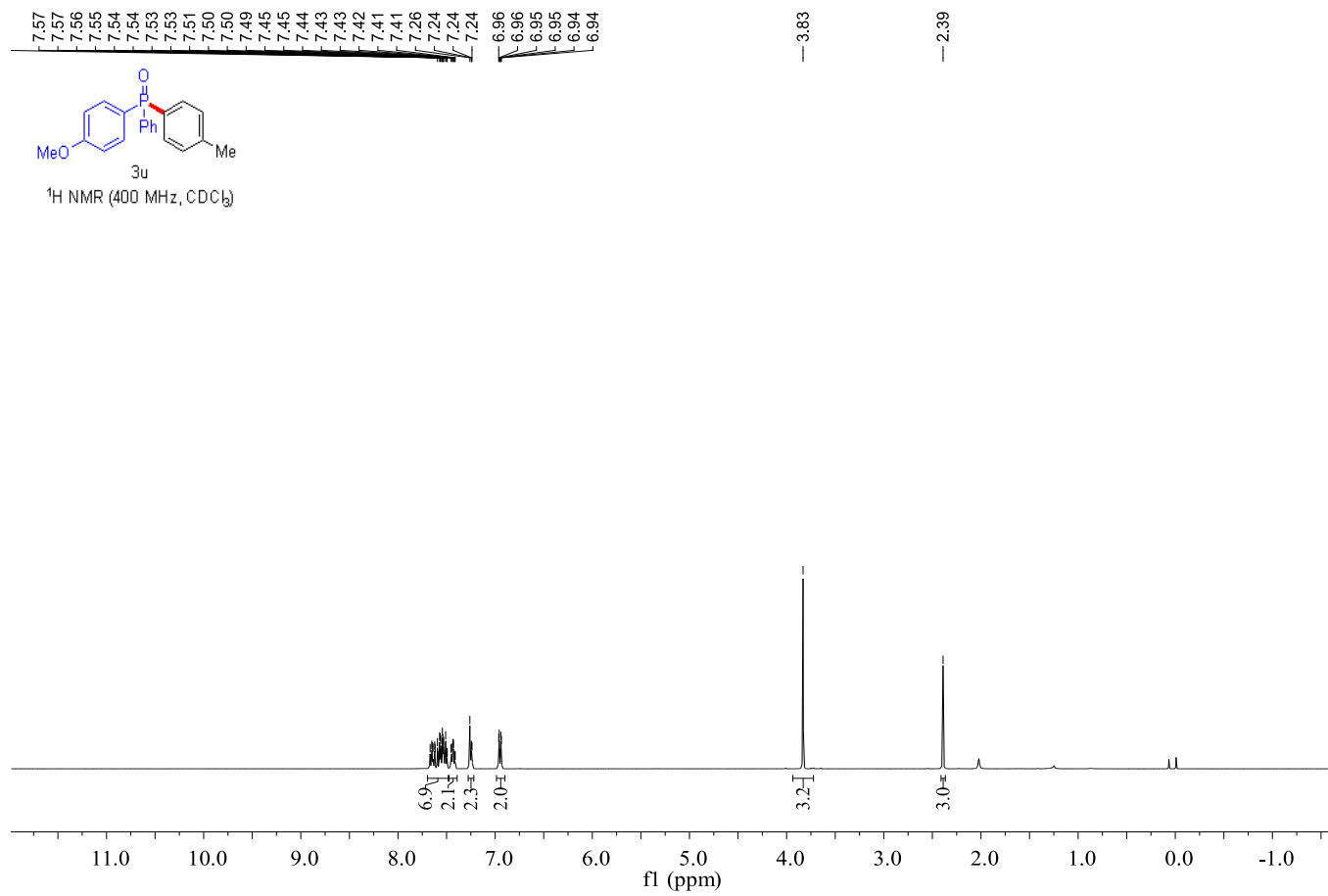
77.32
 77.00
 76.68

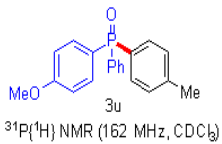
21.59
 21.58



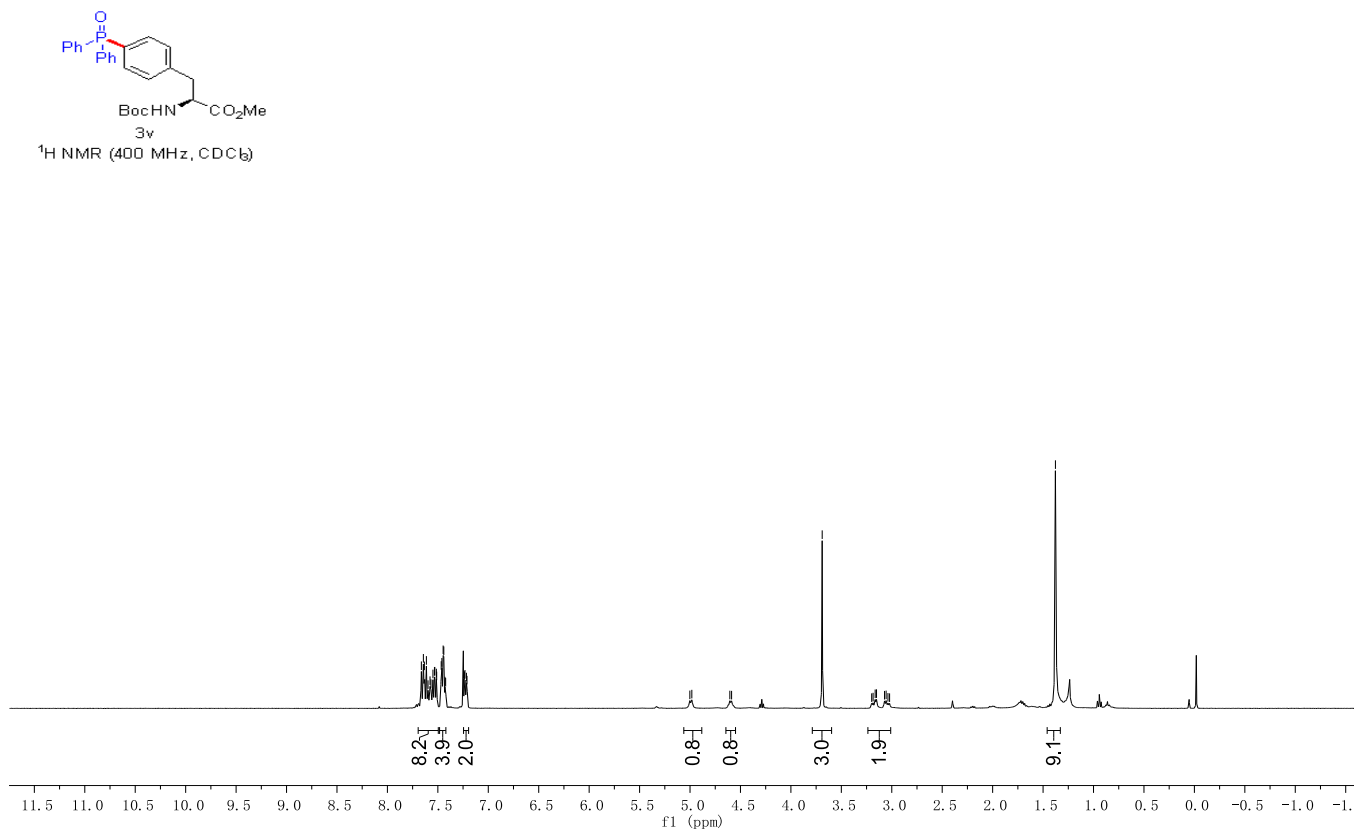
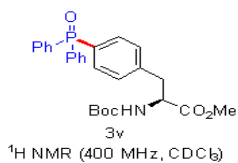
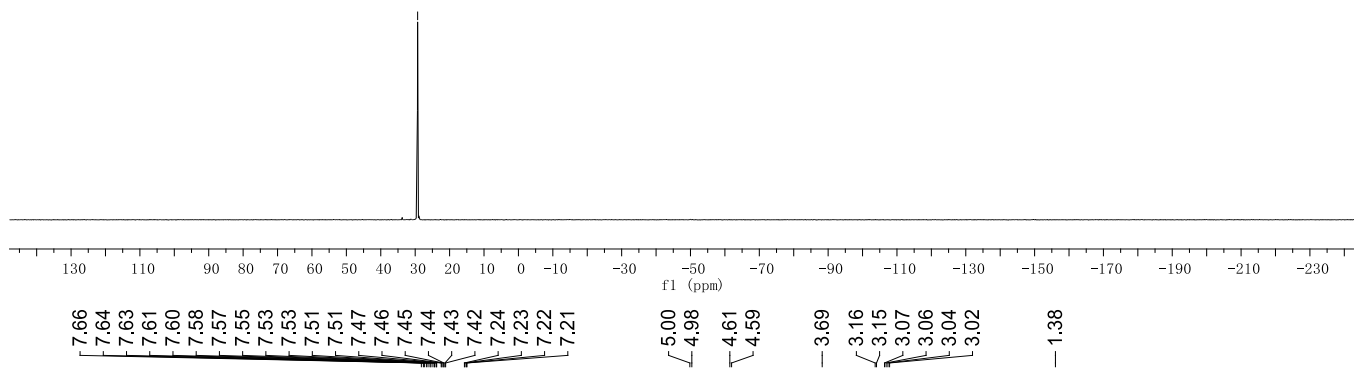
- 29.34

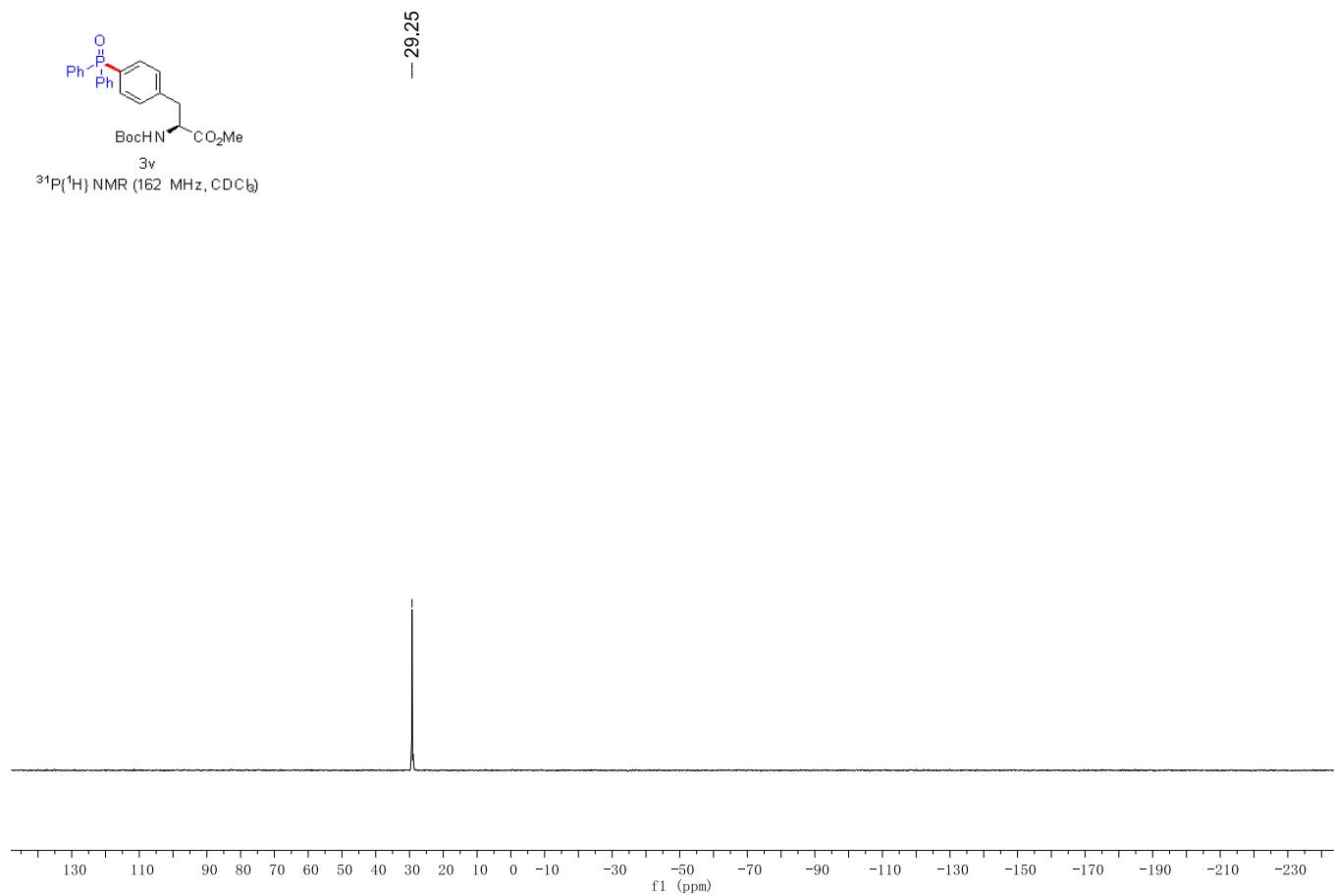
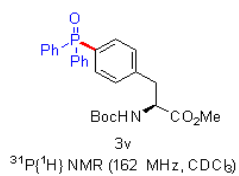
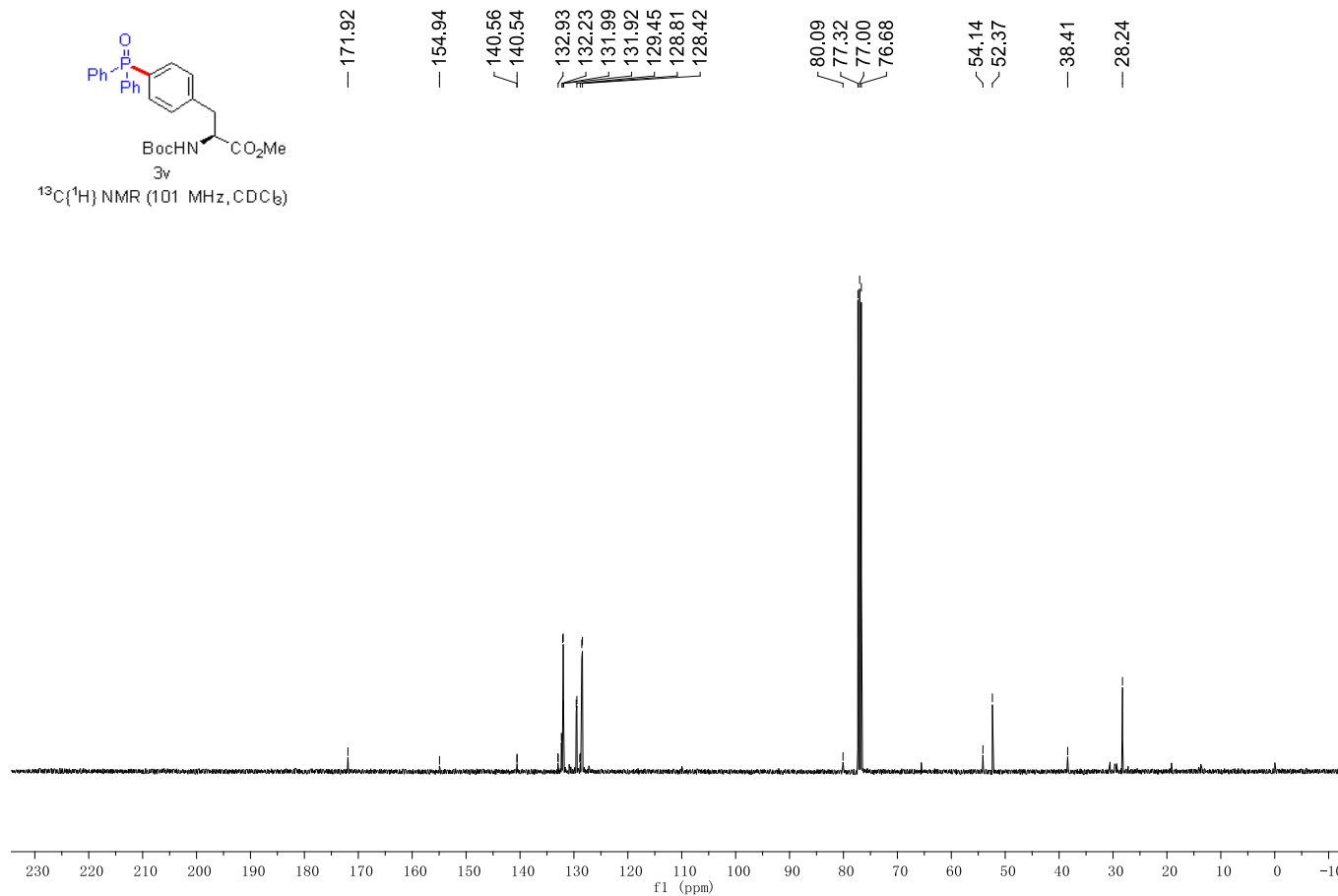
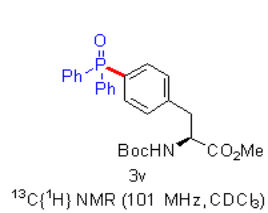


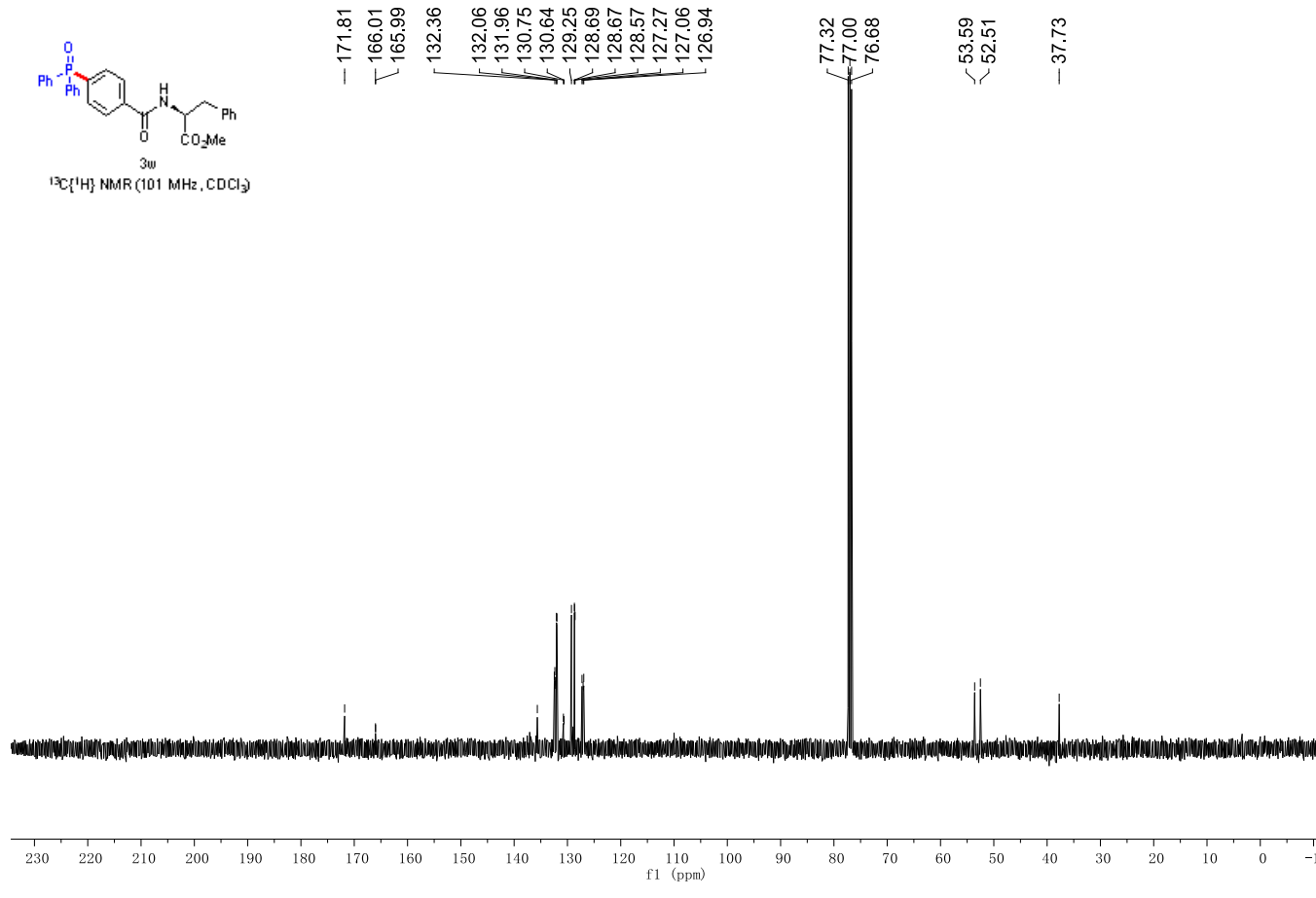
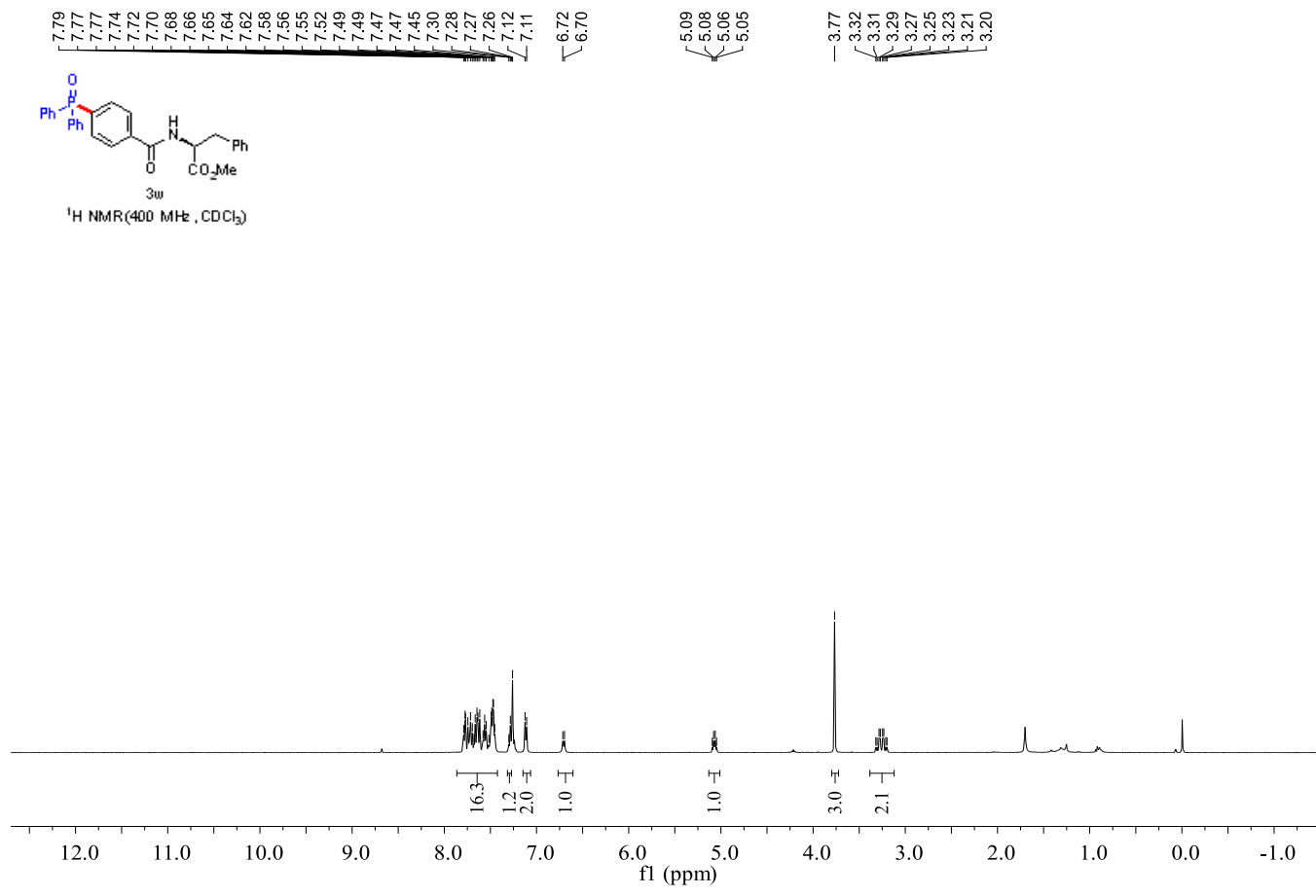


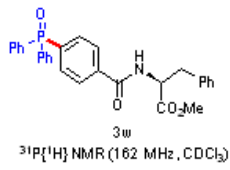


— 29.29









—28.56

