Electronic Supplementary Information

for

Copper-Catalyzed Tandem Phosphination-Decarboxylation-Oxidation of Alkynyl Acids with H-Phosphine Oxides: A Facile Synthesis of β-Ketophosphine Oxides

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General and Experimental Section

General

All reactions were carried out under Air. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker AVⅢ 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz). Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.23 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300-400 mesh. The CAS number of the known compound was listed. The unknown products were further characterized by HRMS(FT-ICR-MS).

Typical procedure for the synthesis of β-ketophosphine oxides:

An tube was charged with a magnetic stir-bar, P(O)H (0.8 mmol), alkynyl acids (0.2 mmol) $CuSO_4 \cdot 5H_2O$ (10 mmol %), TBHP (2 equiv), and MeCN (1.5 mL). Then, $NH_3 \cdot H_2O$ (0.25 mL, 25%) was added and the tube was stirred vigorously under air at 60 ^{o}C for 2 h. The resulting mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography using petroleum ether–AcOEt (3:1-1:1, v/v) as the eluent to give the corresponding products.

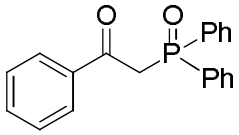
Synthesis of 2-(diphenylphosphoryl)-1-phenylethanone 4:

An tube was charged with a magnetic stir-bar, **3a** (0.20 mmol), sodium methoxide (0.22 mmol), and anhydrous THF (3.0 mL). The tube was stirred vigorously under air at 70 ^{o}C. After 1 h benzyl bromide (0.22 mmol) was added and stirring was continued at 70 ^{o}C for 12 h. The reaction mixture was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel (3.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dryloaded onto a silica gel column and purified by flash chromatography using petroleum ether:AcOEt (2:1, v/v) as the eluent to give the corresponding product **4**.

Synthesis of 1,3-diphenylpropan-1-one 5:

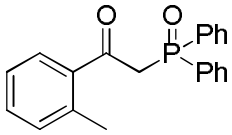
An tube was charged with a magnetic stir-bar, 2-(diphenylphosphoryl)-1-phenylethanone (0.15 mmol), 4 M aqueous NaOH (2 mL), ethanol (2 mL). The reaction mixture was heated with stirring at 80 ^{o}C for 1 h. The reaction mixture was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel (3.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dryloaded onto a silica gel column and purified by flash chromatography using petroleum ether as the eluent to give the corresponding product **5**.

2-(Diphenylphosphoryl)-1-phenylethanone (**3a**) (CAS number: 1733-58-0)



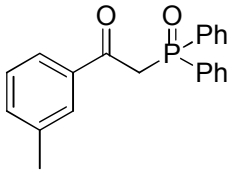
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 8.0 Hz, 2H), 7.82-7.77 (m, 4H), 7.54-7.49 (m, 3H), 7.47-7.38 (m, 6H), 4.14 (d, J = 15.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.0 (d, $J_{C\text{-}P}$ = 5.7 Hz), 137.1, 133.8, 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 103.3 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.4, 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.7, 43.4 (d, $J_{C\text{-}P}$ = 58.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.05. MS-ESI: *m/z* 342.5, $[M+Na]^+$.

2-(Diphenylphosphoryl)-1-(o-tolyl)ethanone (**3b**) (CAS number: 311317-27-8)



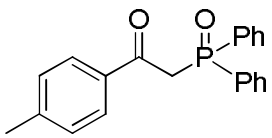
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, J = 8.0 Hz, 1H), 7.80-7.75 (m, 4H), 7.51-7.48 (m, 2H), 7.46-7.41 (m, 4H), 7.32 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 4.10 (d, J = 15.1 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 139.1, 137.6, 132.3 (d, $J_{C\text{-}P}$ = 103.2 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1, 132.0, 131.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.4, 128.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 125.9, 45.7 (d, $J_{C\text{-}P}$ = 58.7 Hz), 21.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1. MS-ESI: *m/z* 356.5, $[M+Na]^+$.

2-(Diphenylphosphoryl)-1-(m-tolyl)ethanone (**3c**)



White solid; m.p. 82.6-83.6 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, J = 8.0 Hz, 1H), 7.80-7.75 (m, 4H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 4H), 7.34-7.30 (m, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 4.11 (d, J = 15.1 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 139.1, 137.6, 132.3 (d, $J_{C\text{-}P}$ = 103.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1, 132.0, 131.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.4, 128.8 (d, $J_{C\text{-}P}$ = 12.3 Hz), 125.9, 45.8 (d, $J_{C\text{-}P}$ = 58.4 Hz), 21.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1. MS-ESI: *m/z* 356.5, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{21}H_{20}NaO_2P^+$: 357.1020, found: 357.1021.

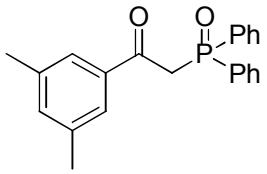
2-(Diphenylphosphoryl)-1-(p-tolyl)ethanone (**3d**) (CAS number: 41069-03-8)



White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.0 Hz, 2H), 7.81-7.76 (m, 4H), 7.51-7.48 (m, 2H), 7.45-7.41 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 4.10 (d, J = 15.4 Hz, 2H), 2.35 (s, 3H); ^{13}C

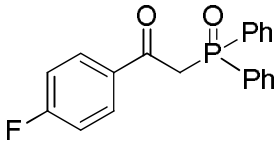
NMR ($CDCl_3$, 100 MHz): δ 192.4 (d, J_{C-P} = 5.7 Hz), 144.7, 134.7, 132.2 (d, J_{C-P} = 2.6 Hz), 132.1 (d, J_{C-P} = 103.3 Hz), 131.2 (d, J_{C-P} = 9.9 Hz), 129.5, 129.3, 128.7 (d, J_{C-P} = 12.4 Hz), 43.3 (d, J_{C-P} = 58.4 Hz), 21.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1. MS-ESI: *m/z* 356.5, $[M+Na]^+$.

1-(3,5-Dimethylphenyl)-2-(diphenylphosphoryl)ethanone (**3e**)



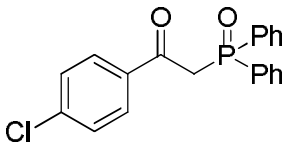
White solid; m.p. 157.4-160.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.76 (m, 4H), 7.51-7.47 (m, 4H), 7.46-7.38 (m, 4H), 7.13 (s, 1H), 4.10 (d, *J* = 15.5 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3 (d, J_{C-P} = 5.5 Hz), 138.3, 137.2, 135.4, 132.2 (d, J_{C-P} = 103.0 Hz), 132.2 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 9.8 Hz), 128.7 (d, J_{C-P} = 12.5 Hz),127.1, 43.3 (d, J_{C-P} = 58.8 Hz), 21.3; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1. MS-ESI: *m/z* 370.6, $[M + Na]^+$. HRMS: $[M + Na]^+$ *m/z* calcd for $C_{22}H_{22}FNaO_2P^+$: 371.1177, found: 371.1175.

2-(Diphenylphosphoryl)-1-(4-fluorophenyl)ethanone (**3f**)



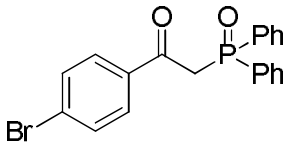
White solid; m.p. 164.0-164.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04-8.01 (m, 2H), 7.80-7.76 (m, 4H), 7.52-7.49 (m, 2H), 7.46-7.42 (m, 4H), 7.09-7.04 (m, 2H), 4.09 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.3 (d, J_{C-P} = 5.5 Hz), 166.2 (d, J_{C-F} = 255.9 Hz), 133.6 (d, J_{C-F} = 2.7 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 132.3 (d, J_{C-F} = 9.9 Hz), 131.9 (d, J_{C-P} = 103.1 Hz), 131.2 (d, J_{C-P} = 9.8 Hz), 128.8 (J_{C-P} = 12.5 Hz), 115.8 (d, J_{C-F} = 22.1 Hz), 43.6 (d, J_{C-P} = 57.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7. MS-ESI: *m/z* 361.1, $[M+ Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{20}H_{16}FO_2PNa^+$: 361.0770, found: 361.0769.

1-(4-Chlorophenyl)-2-(diphenylphosphoryl)ethanone (**3g**) (CAS number: 41069-05-0)



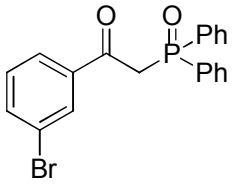
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.81-7.76 (m, 4H), 7.55-7.51 (m, 2H), 7.48-7.44 (m, 4H), 7.38 (d, *J* = 8.5 Hz, 2H), 4.09 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.8 (d, J_{C-P} = 5.8 Hz), 140.3, 135.4, 132.4 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 103.4 Hz), 131.7 (d, J_{C-P} = 9.9 Hz), 130.9, 129.0, 128.8 (d, J_{C-P} = 12.1 Hz), 43.7 (d, J_{C-P} = 56.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.8. MS-ESI: *m/z* 376.6, $[M+Na]^+$.

1-(4-Bromophenyl)-2-(diphenylphosphoryl)ethanone (**3h**) (CAS number: 19797-85-4)



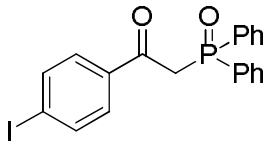
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 8.5 Hz, 2H), 7.80-7.72 (m, 4H), 7.55-7.50 (m, 4H), 7.47-7.43 (m, 4H), 4.09 (d, J = 15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 135.8, 132.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.0, 131.8 (d, $J_{C\text{-}P}$ = 103.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.0, 129.3, 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 43.7 (d, $J_{C\text{-}P}$ = 56.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7. MS-ESI: *m/z* 422.6, $[M+Na]^+$.

1-(3-Bromophenyl)-2-(diphenylphosphoryl)ethanone (**3i**) (CAS number: 41069-07-2)



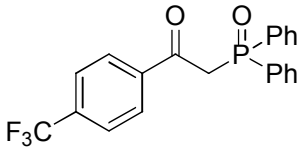
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (t, J = 1.8 Hz, 1H), 7.97-7.94 (m, 1H), 7.82-7.75 (m, 4H), 7.66-7.62 (m, 1H), 7.56-7.50 (m, 2H), 7.49-7.43 (m, 4H), 7.29 (t, J = 8.0 Hz, 1H), 4.11 (d, J = 15.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 138.8, 136.6, 132.5 (d, $J_{C\text{-}P}$ = 2.9 Hz),132.3, 131.9 (d, $J_{C\text{-}P}$ = 103.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.3, 128.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3, 123.0, 43.7 (d, $J_{C\text{-}P}$ = 57.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.6. MS-ESI: *m/z* 422.6, $[M+Na]^+$.

2-(Diphenylphosphoryl)-1-(4-iodophenyl)ethanone (**3j**)



White solid; m.p. 154.0-156.0 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.75 (m, 6H), 7.72-7.68 (m, 2H), 7.55-7.50 (m, 2H), 7.48-7.43 (m, 4H), 4.08 (d, J = 15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.4 (d, $J_{C\text{-}P}$ = 5.6 Hz), 138.0, 136.4, 132.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 103.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.8, 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 102.3, 43.7 (d, $J_{C\text{-}P}$ = 56.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7. MS-ESI: *m/z* 468.7, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{20}H_{17}INaO_2P^+$:468.9830, found: 468.9831.

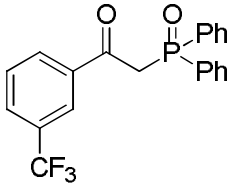
2-(diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)ethanone(**3k**)



White solid; m.p. 144.4-146.8 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J = 8.1 Hz, 2H), 7.81-7.76 (m, 4H), 7.66 (d, J = 8.3 Hz, 2H), 7.55-7.51 (m, 2H), 7.49-7.44 (m, 4H), 4.16 (d, J = 15.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 139.7, 134.8 (q, $J_{C\text{-}F}$ = 32.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 103.3 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.8, 128.9 (d,

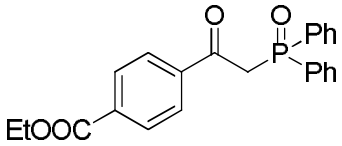
$J_{C\text{-}P}$ = 12.4 Hz), 123.7 (q, $J_{C\text{-}F}$ = 272.9 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 44.0 (d, $J_{C\text{-}P}$ = 56.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.8. MS-ESI: *m/z*410.6, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{21}H_{17}F_3NaO_2P^+$: 411.0738, found: 411.0736

2-(Diphenylphosphoryl)-1-(3-(trifluoromethyl)phenyl)ethanone (**3l**) (CAS number: 1642853-05-1)



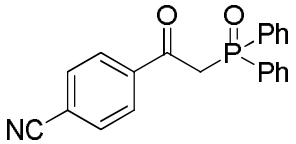
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, *J* = 7.8, 1H), 8.15 (s, 1H), 7.81-7.74 (m, 5H), 7.57-7.50 (m, 3H), 7.47-7.43 (m, 4H), 4.16 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.9 (d, $J_{C\text{-}P}$ = 5.6 Hz), 137.6, 132.9, 132.5 (q, $J_{C\text{-}F}$ = 2.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 103.3 Hz), 131.3 (d, $J_{C\text{-}F}$ = 32.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.0 (q, $J_{C\text{-}F}$ = 3.5 Hz), 129.4, 128.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 125.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.7 (q, $J_{C\text{-}F}$ = 273.6 Hz), 43.7 (d, $J_{C\text{-}P}$ = 56.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.6. MS-ESI: *m/z* 410.6, $[M+Na]^+$.

Ethyl 4-(2-(diphenylphosphoryl)acetyl)benzoate (**3m**)



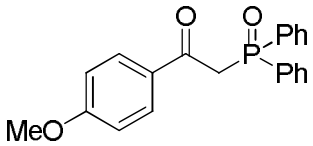
White solid; m.p. 135.4-137.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06-7.99 (m, 4H), 7.80-7.75 (m, 4H), 7.52-7.48 (m, 2H), 7.46-7.42 (m, 4H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 15.5 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 165.7, 140.1, 134.6, 132.4 (d, $J_{C\text{-}P}$ = 2.6 Hz),131.8 (d, $J_{C\text{-}P}$ = 103.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.8, 129.2, 128.8 (d, $J_{C\text{-}P}$ = 12.1 Hz), 61.6, 43.8 (d, $J_{C\text{-}P}$ = 58.2 Hz), 14.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7. MS-ESI: *m/z* 414.7, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{23}H_{22}NaO_4P^+$: 415.1075, found: 415.1075.

4-(2-(Diphenylphosphoryl)acetyl)benzonitrile (**3n**) (CAS number: 58971-81-6)



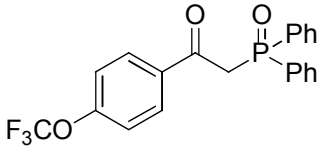
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.80-7.74 (m, 4H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.56-7.51 (m, 2H), 7.49-7.44 (m, 4H), 4.13 (d, *J* = 15.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 139.9, 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5, 131.5 (d, $J_{C\text{-}P}$ = 103.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.9, 128.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 118.0, 116.8, 44.1 (d, $J_{C\text{-}P}$ = 55.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.6. MS-ESI: *m/z* 367.5, $[M+Na]^+$.

2-(Diphenylphosphoryl)-1-(4-methoxyphenyl)ethanone (**3o**) (CAS number: 19797-86-5)



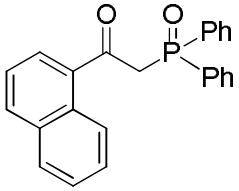
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99-7.95 (m, 2H), 7.82-7.77 (m, 4H), 7.53-7.48 (m, 2H), 7.47-7.42 (m, 4H), 6.89-6.85(m, 2H), 4.08 (d, J = 15.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.2 (d, $J_{C\text{-}P}$ = 5.5 Hz), 164.1, 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.2 (d, $J_{C\text{-}P}$ = 103.0 Hz), 131.9, 131.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.3, 128.8 (d, $J_{C\text{-}P}$ = 12.3 Hz), 113.9, 55.7, 43.3 (d, $J_{C\text{-}P}$ = 58.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.2. MS-ESI: *m/z* 373.5, $[M+Na]^+$.

2-(Diphenylphosphoryl)-1-(4-(trifluoromethoxy)phenyl)ethanone (**3p**)



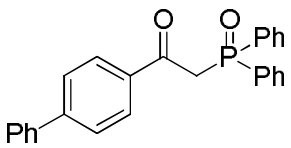
White solid; m.p. 113.4-115.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07-8.04 (m, 2H), 7.81-7.75 (m, 4H), 7.54-7.49 (m, 2H), 7.47-7.43 (m, 4H), 7.24-7.19 (m, 2H), 4.11 (d, J = 15.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5 (d, $J_{C\text{-}P}$ = 5.7 Hz), 153.1 (q, $J_{C\text{-}F}$ = 1.4 Hz), 135.3, 132.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 103.3 Hz), 131.6, 131.2 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.6 Hz), 120.4 (q, $J_{C\text{-}F}$ = 258.9 Hz), 120.3, 43.8 (d, $J_{C\text{-}P}$ = 56.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.8. MS-ESI: *m/z* 426.6, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{21}H_{17}F_3NaO_3P^+$: 427.0687, found: 427.0682.

2-(Diphenylphosphoryl)-1-(naphthalen-1-yl)ethanone (**3q**)



White solid; m.p. 153.4-155.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45-8.40 (m, 1H), 8.15 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.82-7.77 (m, 5H), 7.51-7.45 (m, 5H), 7.44-7.39 (m, 4H), 4.27 (d, J = 15.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.7 (d, $J_{C\text{-}P}$ = 5.5 Hz), 135.3, 133.9, 133.8, 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 103.2 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.4, 130.2, 128.8 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.5, 128.3, 126.6, 125.8, 124.6, 46.6 (d, $J_{C\text{-}P}$ = 58.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3. MS-ESI: *m/z* 392.6, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{20}NaO_2P^+$: 393.1020, found: 393.1020.

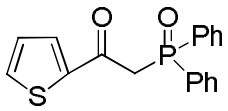
1-([1,1'-Biphenyl]-4-yl)-2-(diphenylphosphoryl)ethanone (**3r**)



White solid; m.p. 117.0-119.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10-8.05 (m, 2H), 7.85-7.80 (m, 4H), 7.64-7.57 (m, 4H), 7.53-7.49 (m, 2H), 7.47-7.42 (m, 6H), 7.38-7.35 (m, 1H), 4.16 (d, J =

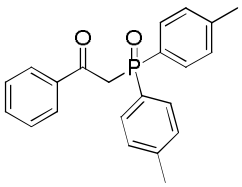
15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.4 (d, J_{C-P} = 5.5 Hz), 146.3, 139.8, 135.8, 132.3 (d, J_{C-P} = 2.7 Hz), 132.1 (d, J_{C-P} = 103.0 Hz), 131.2 (d, J_{C-P} = 9.9 Hz), 130.0, 129.0, 128.8 (d, J_{C-P} = 12.3 Hz), 128.4, 127.4, 127.2, 43.5 (d, J_{C-P} = 57.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.0. MS-ESI: *m/z* 418.7, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{22}NaO_2P^+$: 419.1177, found: 419.1174.

2-(Diphenylphosphoryl)-1-(thiophen-2-yl)ethanone (**3s**) (CAS number: 58971-83-8)



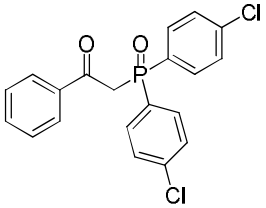
yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, *J* = 3.8 Hz, 1H), 7.82-7.77 (m, 4H), 7.61 (d, *J* = 4.9 Hz, 1H), 7.60-7.49 (m, 2H), 7.47-7.42 (m, 4H), 7.07 (t, *J* = 4.6 Hz, 1H), 4.04 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.1 (d, J_{C-P} = 5.1 Hz), 144.6, 135.4, 135.2, 132.4 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 103.6 Hz), 131.3 (d, J_{C-P} = 9.7 Hz), 128.8 (d, J_{C-P} = 12.5 Hz), 128.6, 44.5 (d, J_{C-P} = 57.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.89. MS-ESI: *m/z* 327.1, $[M+H]^+$.

2-(Di-p-tolylphosphoryl)-1-phenylethanone (**3t**) (CAS number: 1229530-93-1)



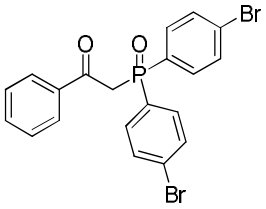
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.95 (m, 2H), 7.70-7.62 (m, 4H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.39 (t, J_{C-P} = 7.8 Hz, 2H), 7.27-7.21 (m, 4H), 4.08 (d, *J* = 15.3 Hz, 2H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.2 (d, J_{C-P} = 5.7 Hz), 142.7 (d, J_{C-P} = 2.7 Hz), 137.2, 133.6, 131.2 (d, J_{C-P} = 10.2 Hz), 129.5 (d, J_{C-P} = 12.5 Hz), 129.4, 129.0 (d, J_{C-P} = 105.7 Hz), 128.6, 43.7 (d, J_{C-P} = 57.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3. MS-ESI: *m/z* 371.2, $[M+Na]^+$.

2-(Bis(4-chlorophenyl)phosphoryl)-1-phenylethanone (**3u**)



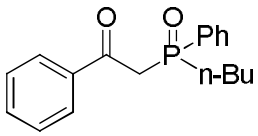
White solid; m.p. 116.4-118.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98-7.93 (m, 2H), 7.76-7.68 (m, 4H), 7.58-7.53 (m, 1H), 7.48-7.40 (m, 6H), 4.11 (d, *J* = 15.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.7 (d, J_{C-P} = 5.8 Hz), 139.3 (d, J_{C-P} = 3.5 Hz), 136.9, 134.1, 132.7 (d, J_{C-P} = 10.8 Hz), 130.3 (d, J_{C-P} = 104.8 Hz), 129.4, 129.3 (d, J_{C-P} = 12.9 Hz), 128.8, 43.2 (d, J_{C-P} = 59.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.9. MS-ESI: *m/z* 410.6, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{20}H_{16}Cl_2NaO_2P^+$: 411.0084, found: 411.0081.

2-(Bis(4-bromophenyl)phosphoryl)-1-phenylethanone (**3v**)



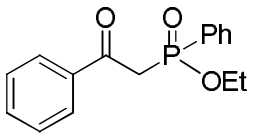
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96-7.93 (m, 2H), 7.68-7.61 (m, 5H), 7.61-7.58 (m, 3H), 7.56-7.4 (m, 1H), 7.44-7.40 (m, 2H), 4.11 (d, J = 15.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 136.9, 134.1, 132.7 (d, $J_{C\text{-}P}$ = 10.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 12.9 Hz),130.7 (d, $J_{C\text{-}P}$ = 104.8 Hz), 129.4, 128.9, 127.9 (d, $J_{C\text{-}P}$ = 3.5 Hz), 43.1 (d, $J_{C\text{-}P}$ = 59.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.3. MS-ESI: *m/z* 500.7, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{20}H_{16}Br_2NaO_2P^+$: 500.9054, found: 500.9053.

2-(Butyl(phenyl)phosphoryl)-1-phenylethanone (**3w**)



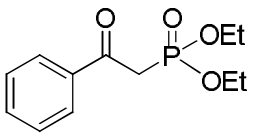
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.89 (m, 2H), 7.74-7.69 (m, 2H), 7.54-7.47 (m, 2H), 7.45-7.38 (m, 4H), 3.84-3.71 (m, 2H), 2.28-2.18 (m, 1H), 2.14-2.05 (m, 1H), 1.68-1.58 (m, 1H), 1.49-1.42 (m, 1H), 1.41-1.33 (m, 2H), 0.85 (t, J = 7.26 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.0 (d, $J_{C\text{-}P}$ = 4.8 Hz), 137.1, 133.9, 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 70.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 129.2, 128.8 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.7, 43.7 (d, $J_{C\text{-}P}$ = 53.7 Hz), 29.4 (d, $J_{C\text{-}P}$ = 70.6 Hz), 24.1 (d, $J_{C\text{-}P}$ = 15.5 Hz), 23.4 (d, $J_{C\text{-}P}$ = 4.3 Hz), 13.7; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.5. MS-ESI: *m/z* 323.1, $[M+Na]^+$. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{18}H_{22}NaO_2P^+$: 323.1177, found: : 323.1177.

Ethyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (**3x**) (CAS number: 51104-34-8)



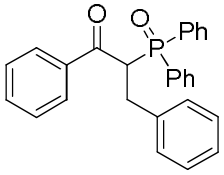
Oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 7.8 Hz, 2H), 7.78-7.74 (m, 2H), 7.55-7.51 (m, 2H), 7.46-7.39 (m, 4H), 4.14-3.88 (m, 2H), 3.83-3.72 (m, 2H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.3 (d, $J_{C\text{-}P}$ = 5.7 Hz), 136.9, 133.7, 132.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.2 (d, $J_{C\text{-}P}$ = 132.8 Hz), 129.7, 128.8 (d, $J_{C\text{-}P}$ = 13.3 Hz), 128.7, 61.6 (d, $J_{C\text{-}P}$ = 6.3 Hz), 43.1 (d, $J_{C\text{-}P}$ = 86.5 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.50. MS-ESI: *m/z* 311.1, $[M+Na]^+$.

Diethyl (2-oxo-2-phenylethyl)phosphonate (**3y**) (CAS Number: 3453-00-7).

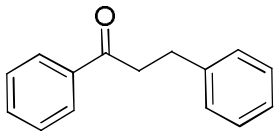


Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04-7.96 (m, 2H), 7.60-7.51 (m, 1H), 7.47-7.39

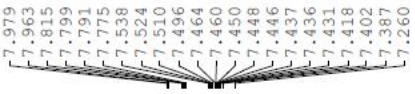
(m, 2H), 4.14-4.08 (m, 4H), 3.60 (d, J = 22.7 Hz, 2H), 1.24 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.1 (d, $J_{C\text{-}P}$ = 6.5 Hz), 136.7, 133.8, 129.2, 128.8, 62.8 (d, $J_{C\text{-}P}$ = 6.5 Hz), 38.6 (d, $J_{C\text{-}P}$ = 130.0 Hz), 16.3 (d, J = 6.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.92. MS-ESI: *m/z* 257.1, $[M + H]^+$.



White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96-7.91 (m, 2H), 7.79-7.74 (m, 2H), 7.50-7.42 (m, 6H), 7.38-7.32 (m, 3H), 7.19-7.12 (m, 4H), 7.10-7.06 (m, 3H), 4.86-4.80 (m, 1H), 3.58-3.51 (m, 1H), 3.28-3.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.9, 139.3 (d, $J_{C\text{-}P}$ = 13.5 Hz), 138.6, 132.9, 132.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (×2) (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.1 (d, $J_{C\text{-}P}$ = 99.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 99.9 Hz), 128.8 (×2) (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.7 (×2), 128.4, 128.3, 126.8, 54.6 (d, $J_{C\text{-}P}$ = 54.5 Hz), 34.3; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.99. MS-ESI: *m/z* 433.1, $[M+Na]^+$.



White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92-7.89 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.41-7.37 (m, 2H), 7.27-7.19 (m, 4H), 7.15 (t, J = 7.2 Hz, 1H), 3.25 (t, J = 8.0 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.4, 141.5, 137.1, 133.3, 128.8, 128.7, 128.6, 128.2, 126.3, 40.6, 30.3;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7.963
7.815
7.799
7.791
7.775
7.538
7.524
7.510
7.496
7.464
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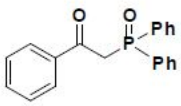
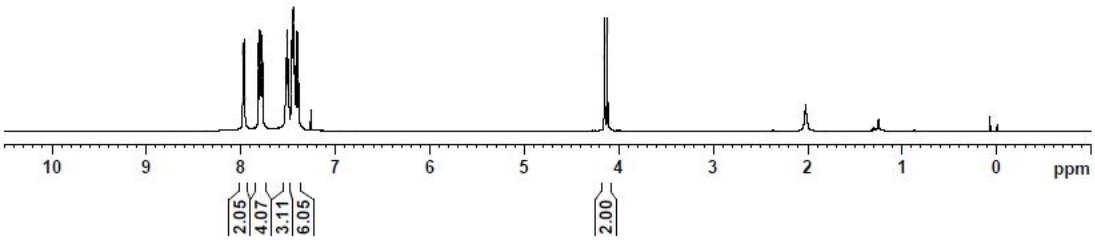
7.418
7.402
7.387
7.260


4.151
4.120


O
O
P
Ph
Ph


10
9
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6
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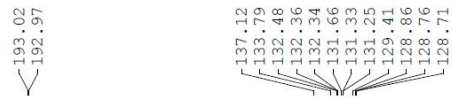
6.05
2.00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133.79
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128.71
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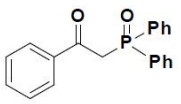
43.68
43.21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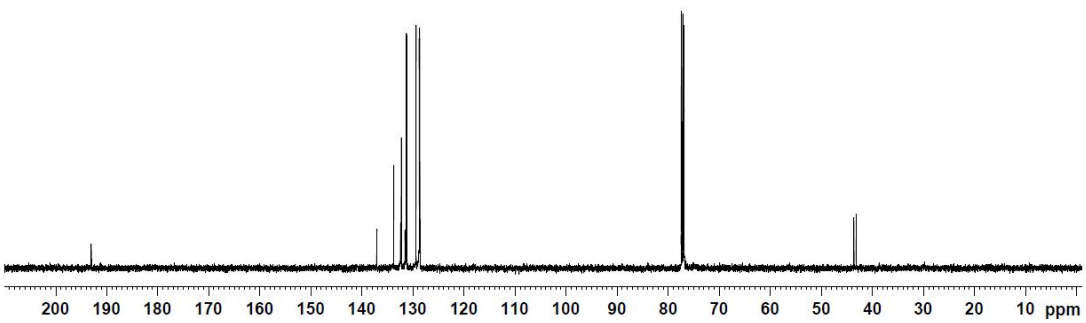
Ph
Ph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90
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30
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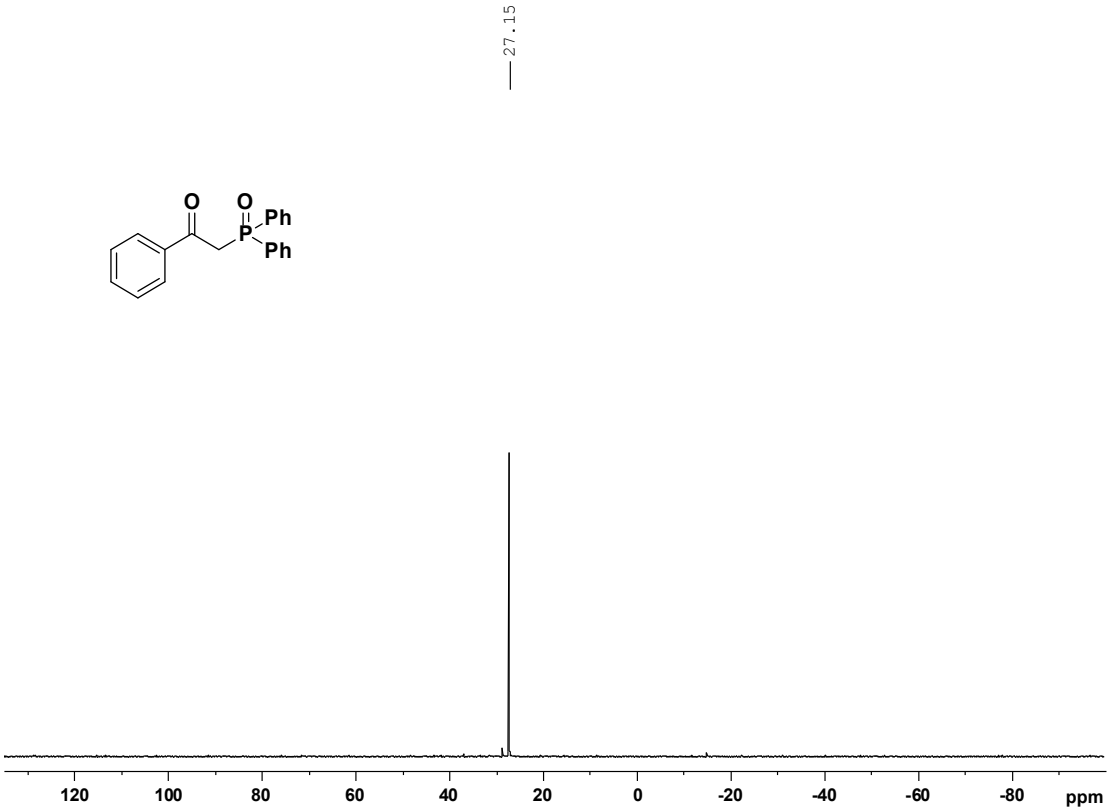
10
ppm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Ph
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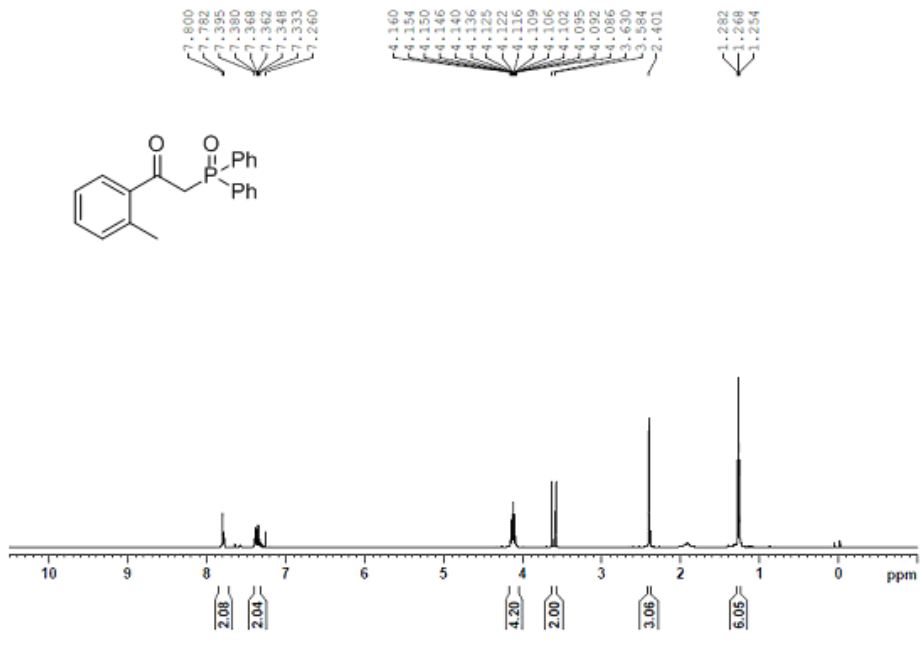
ppm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1.282
1.268
1.254
O
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Ph
P
Ph
10
9
8
7
6
5
4
3
2
1
0
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2.04
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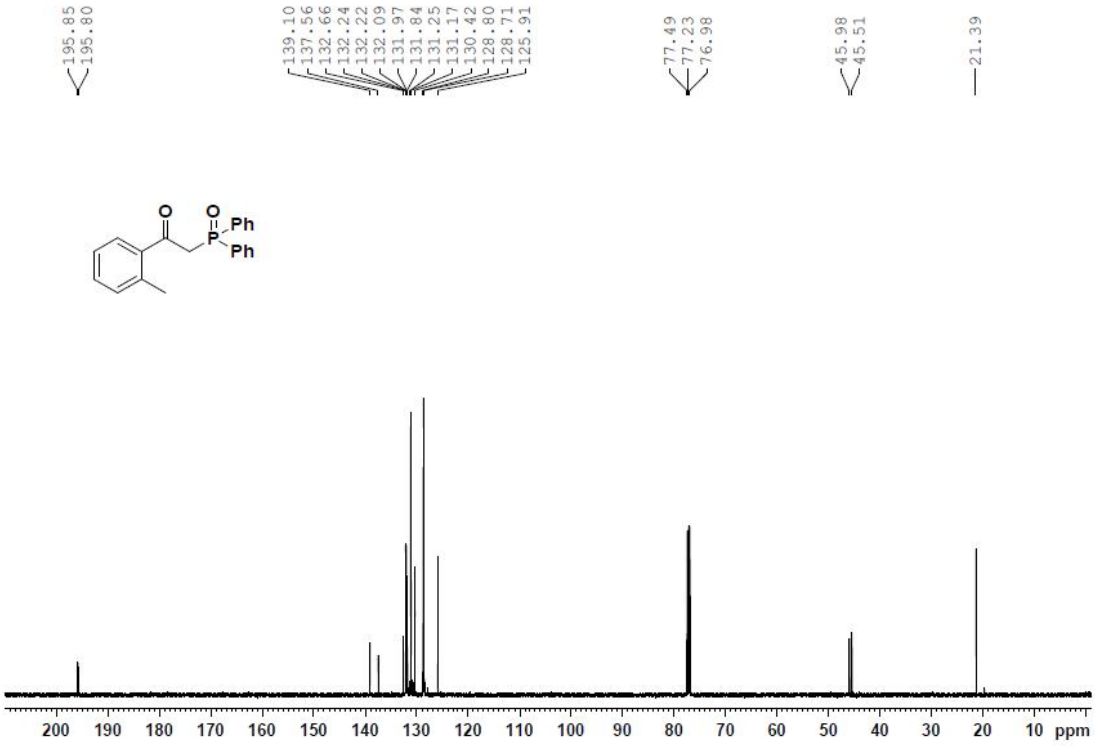
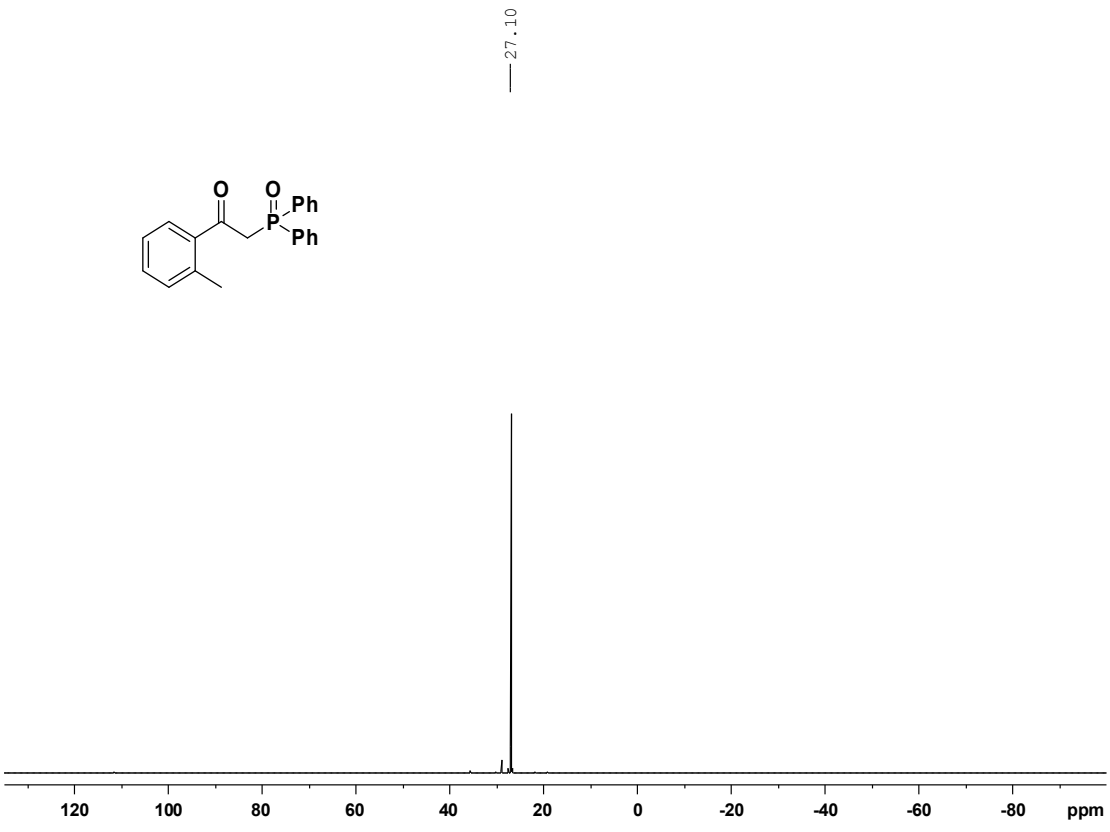
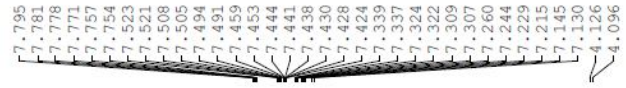
3.06
6.05


195.85
195.80
139.10
137.56
132.66
132.24
132.22
132.09
131.97
131.84
131.25
131.17
130.42
128.80
128.71
125.91
77.49
77.23
76.98
45.98
45.51
21.39
O
O
Ph
P
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


27.10
O
O
Ph
P
Ph
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm


7.795
7.781
7.778
7.771
7.757
7.754
7.523
7.521
7.508
7.505
7.494
7.491
7.459
7.453
7.444
7.441
7.438
7.430
7.428
7.424
7.339
7.337
7.324
7.322
7.309
7.307
7.260
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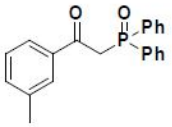
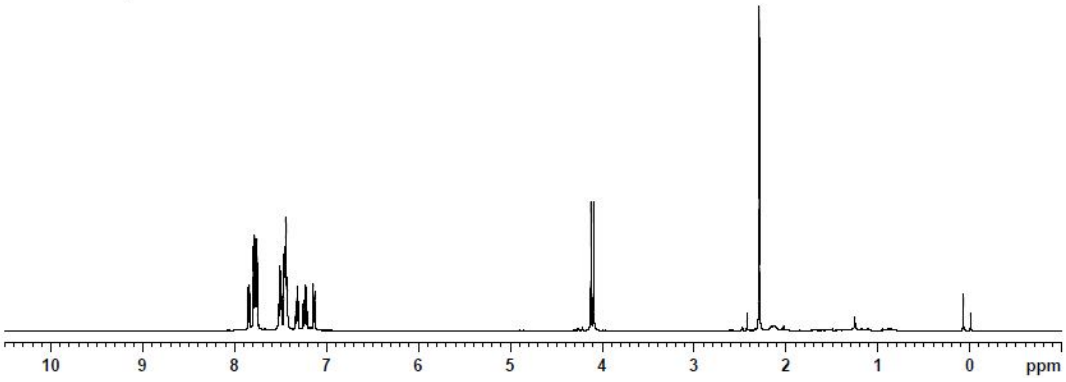
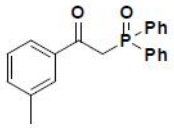
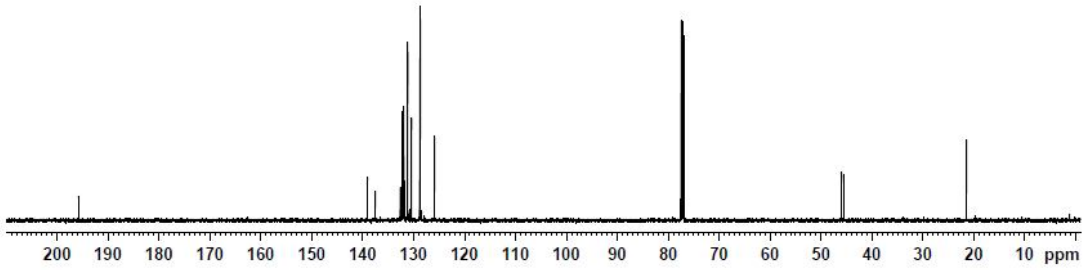
7.215
7.145
7.130
4.126
4.096
2.294

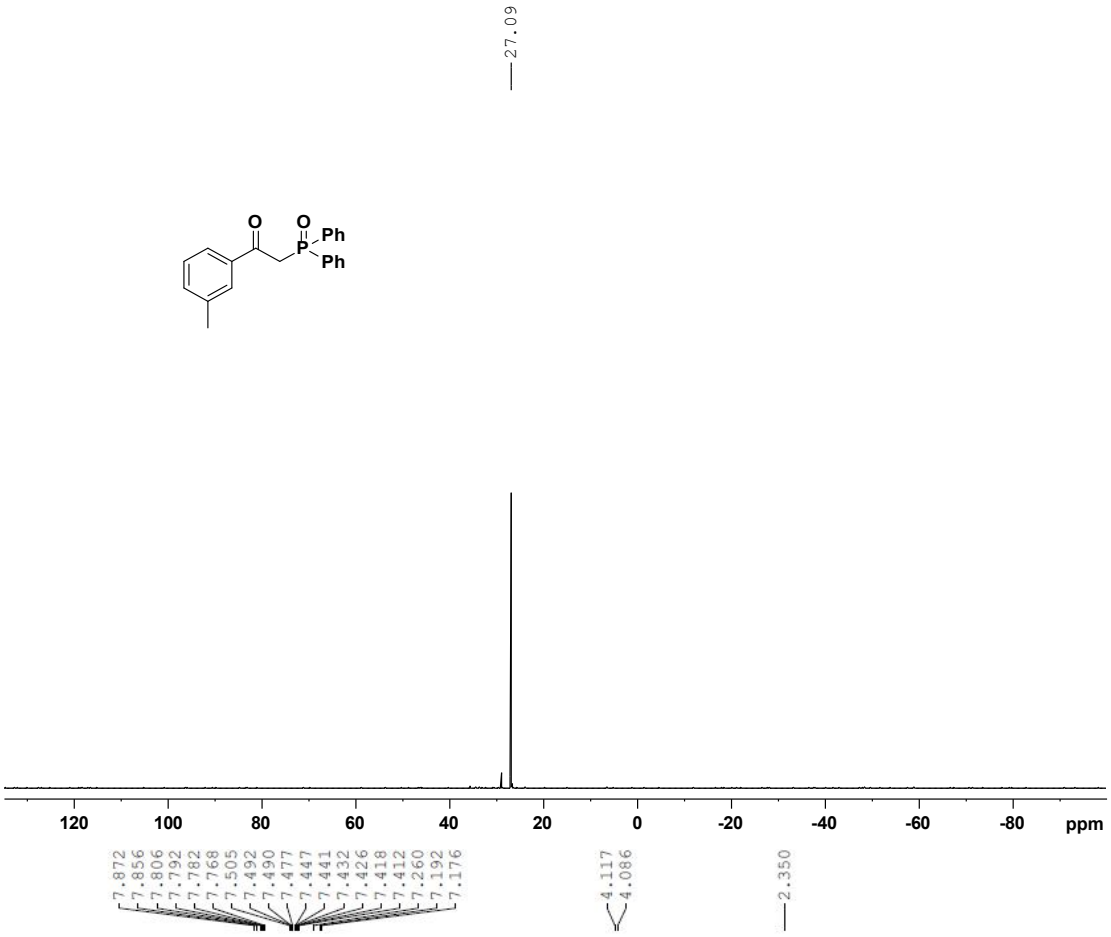

O
O
P
Ph
Ph

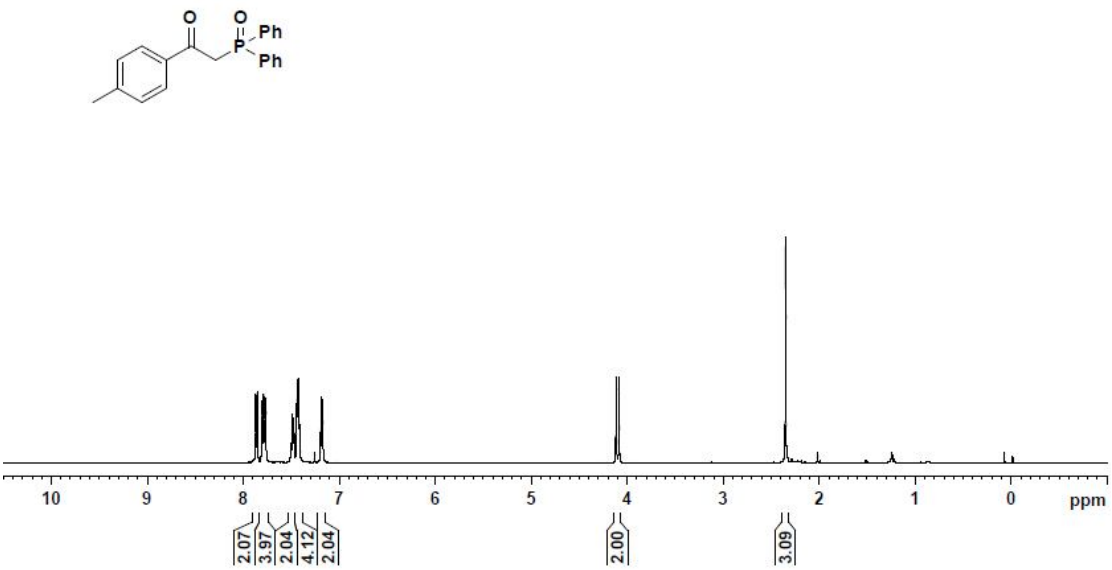

10
9
8
7
6
5
4
3
2
1
0
ppm

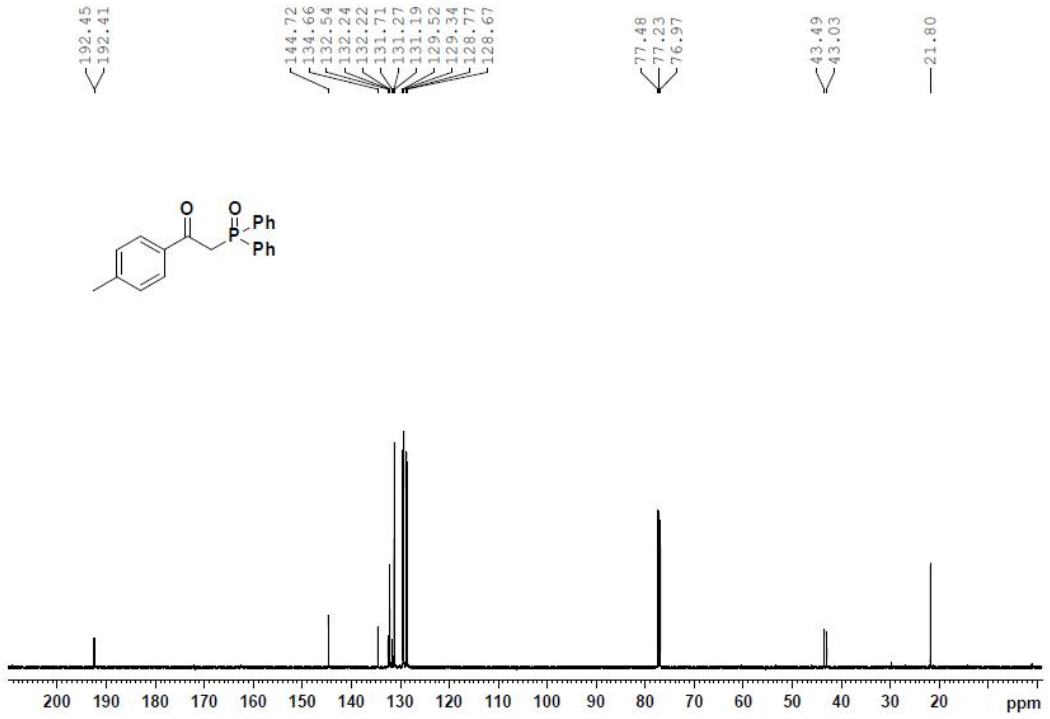

195.86
195.81
139.13
137.57
132.68
132.25
132.23
132.11
131.99
131.86
131.27
131.19
130.45
128.82
128.72
125.92
77.48
77.23
76.97
46.01
45.54
21.41

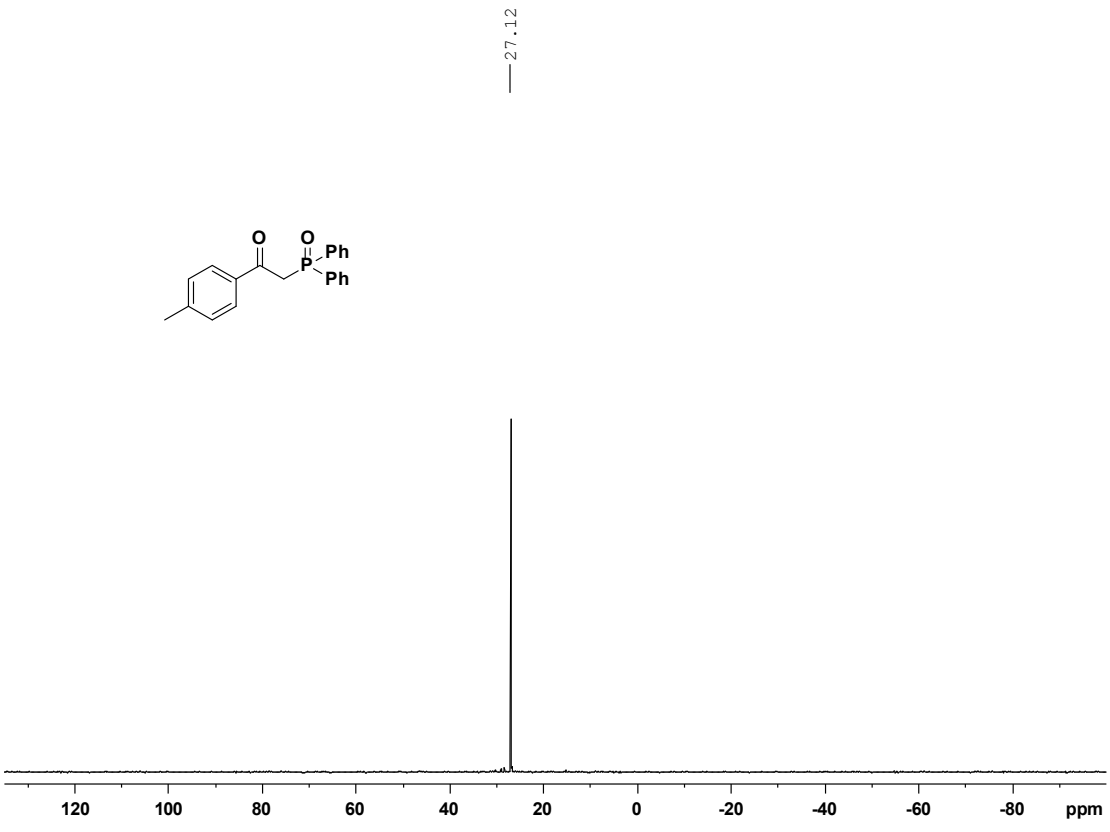

O
O
P
Ph
Ph

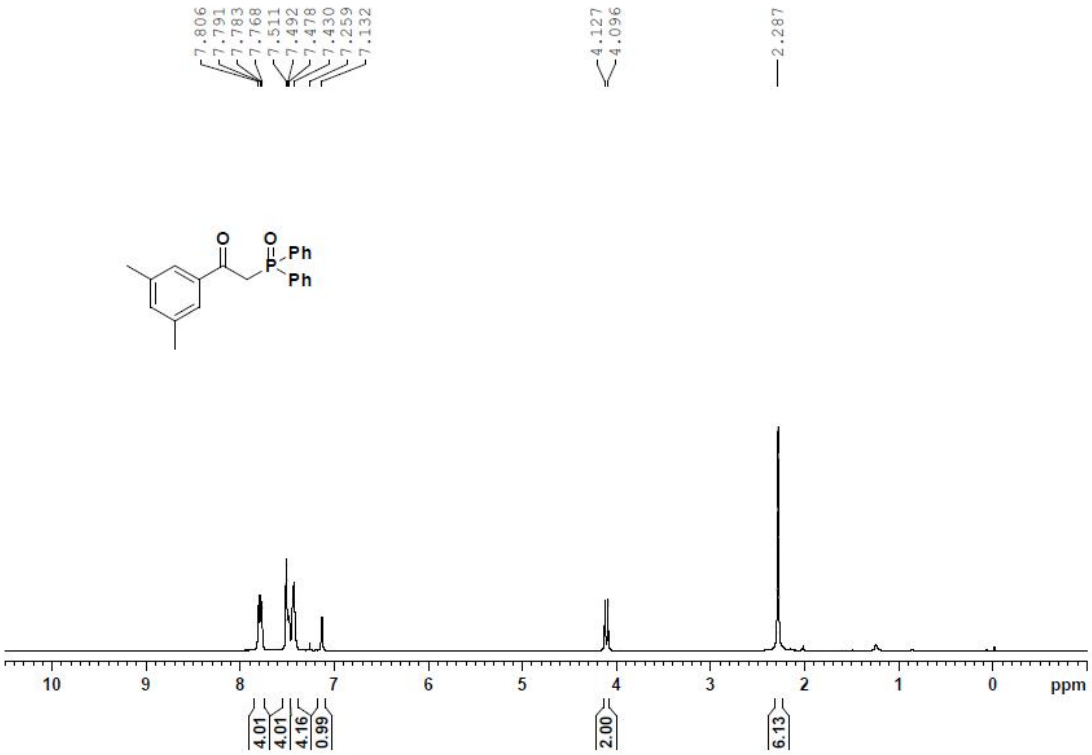

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

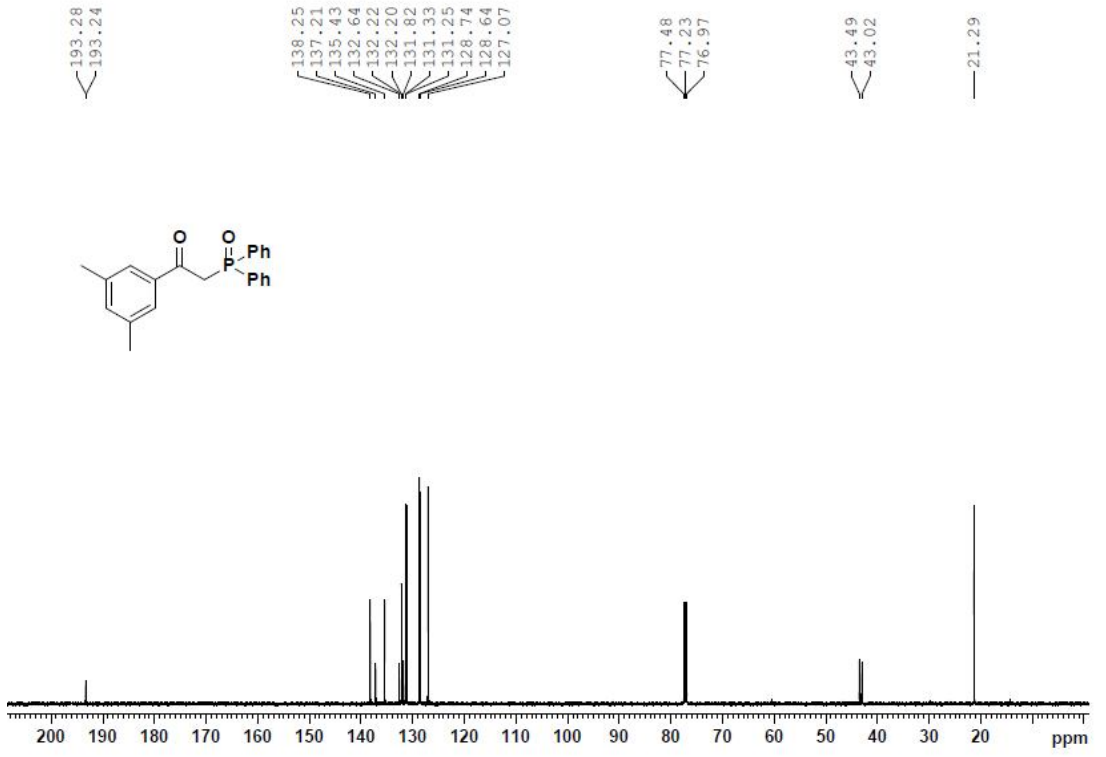

27.09
O
O
P
Ph
Ph
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm
7.872
7.856
7.806
7.792
7.782
7.768
7.505
7.492
7.490
7.477
7.447
7.441
7.432
7.426
7.418
7.412
7.260
7.192
7.176
4.117
4.086
2.350

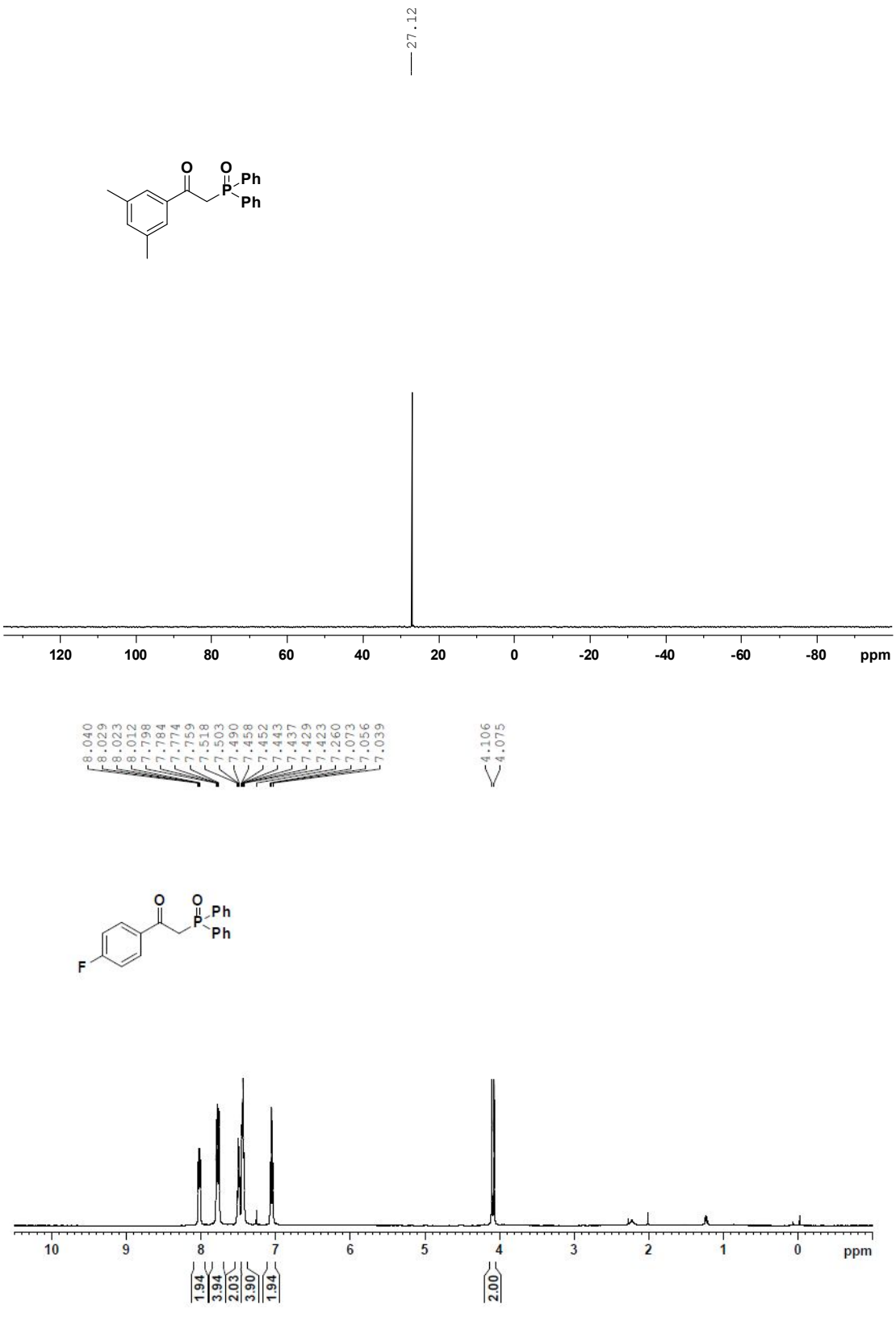

O
O
P
Ph
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
2.07
3.97
2.04
4.12
2.04
2.00
3.09

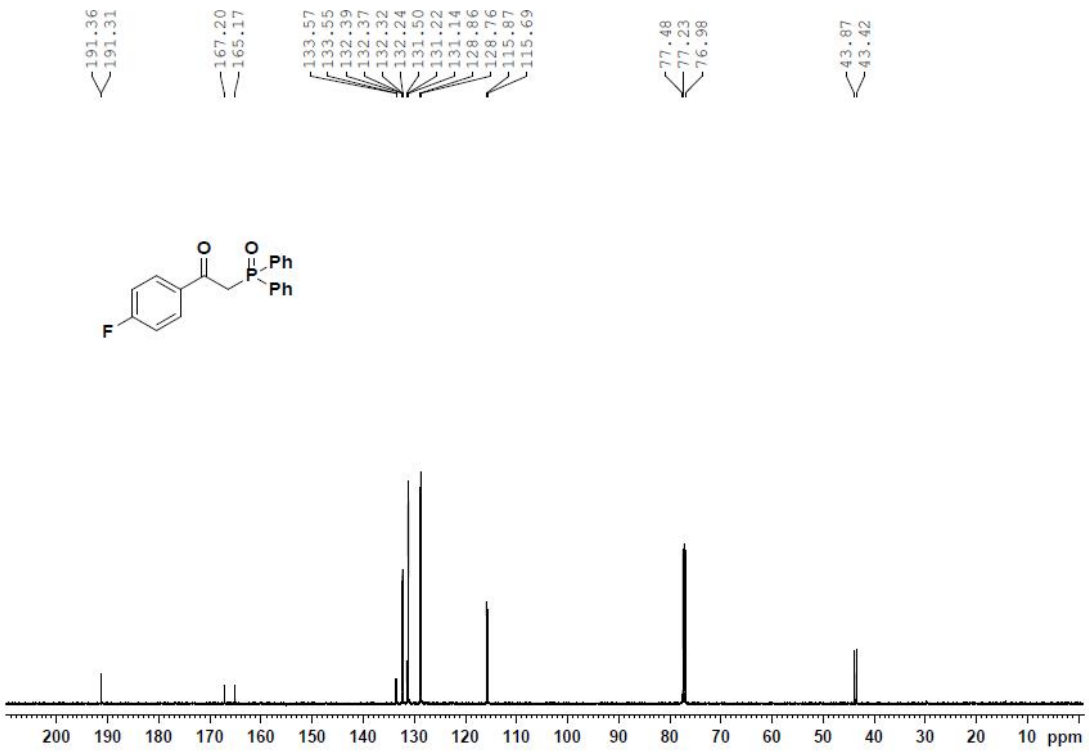

192.45
192.41
144.72
134.66
132.54
132.24
132.22
131.71
131.27
131.19
129.52
129.34
128.77
128.67
77.48
77.23
76.97
43.49
43.03
21.80
O
O
P
Ph
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

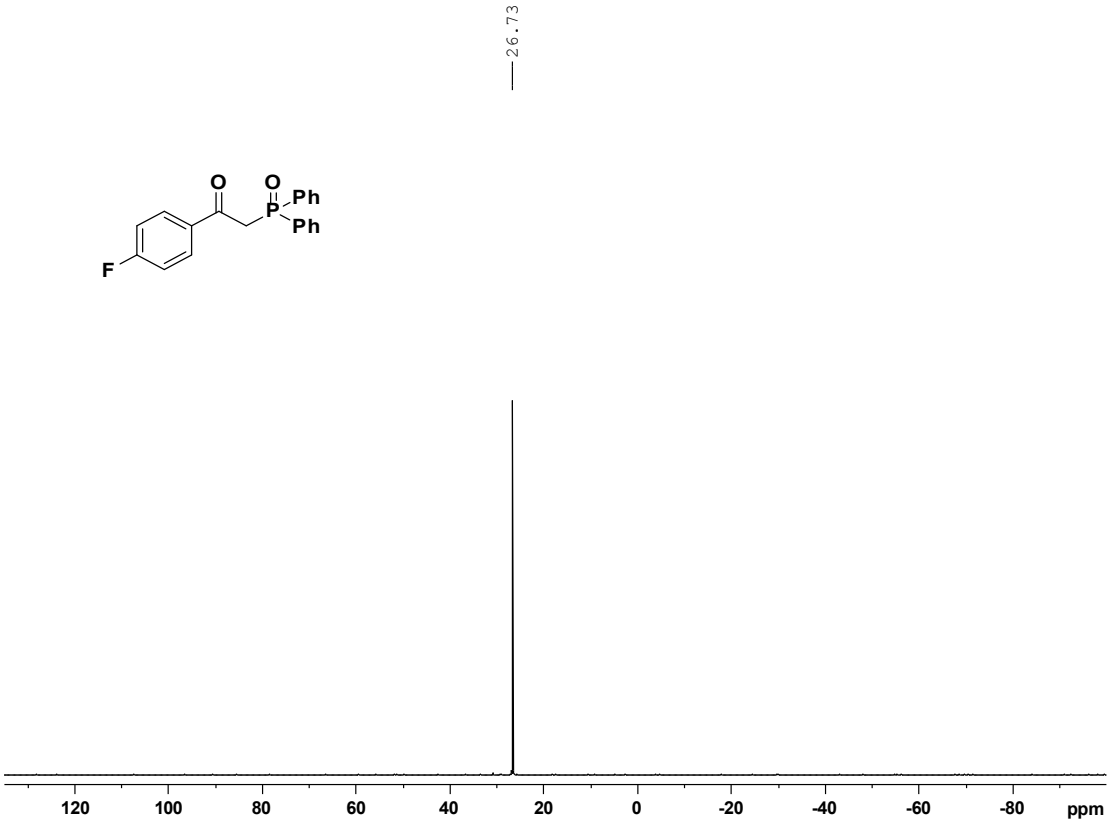

27.12
O
O
P
Ph
Ph
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm


7.806
7.791
7.783
7.768
7.511
7.492
7.478
7.430
7.259
7.132
4.127
4.096
2.287
O
O
P
Ph
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
4.01
4.01
4.16
0.99
2.00
6.13

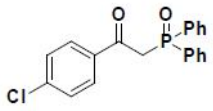

193.28
193.24
138.25
137.21
135.43
132.64
132.22
132.20
131.82
131.33
131.25
128.74
128.64
127.07
77.48
77.23
76.97
43.49
43.02
21.29
O
O
P
Ph
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

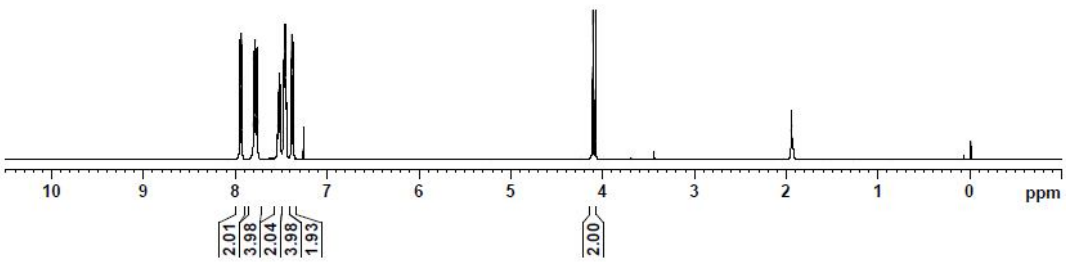

27.12
O
O
P
Ph
Ph
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm
8.040
8.029
8.023
8.012
7.798
7.784
7.774
7.759
7.518
7.503
7.490
7.458
7.452
7.443
7.437
7.429
7.423
7.260
7.073
7.056
7.039
4.106
4.075
F
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
3.94
2.03
3.90
1.94
2.00


191.36
191.31
167.20
165.17
133.57
133.55
132.39
132.37
132.32
132.24
131.50
131.22
131.14
128.86
128.76
115.87
115.69
77.48
77.23
76.98
43.87
43.42
O
O
Ph
P
Ph
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

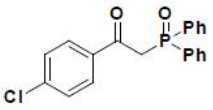

26.73
O
O
Ph
P
Ph
F
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm

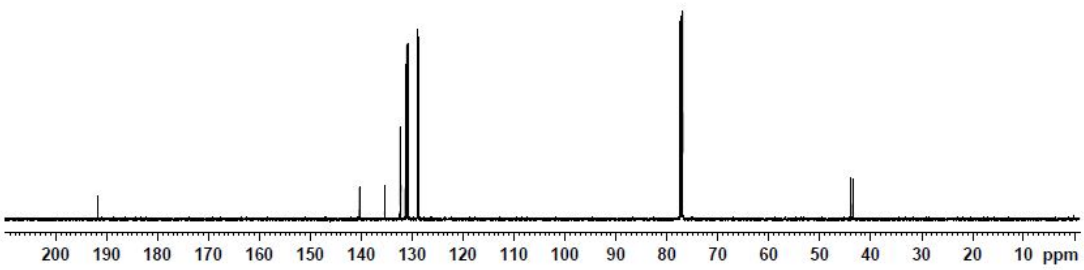

7.952
7.935
7.802
7.787
7.778
7.763
7.541
7.526
7.512
7.478
7.473
7.463
7.458
7.448
7.443
7.389
7.372
7.260
4.110
4.079

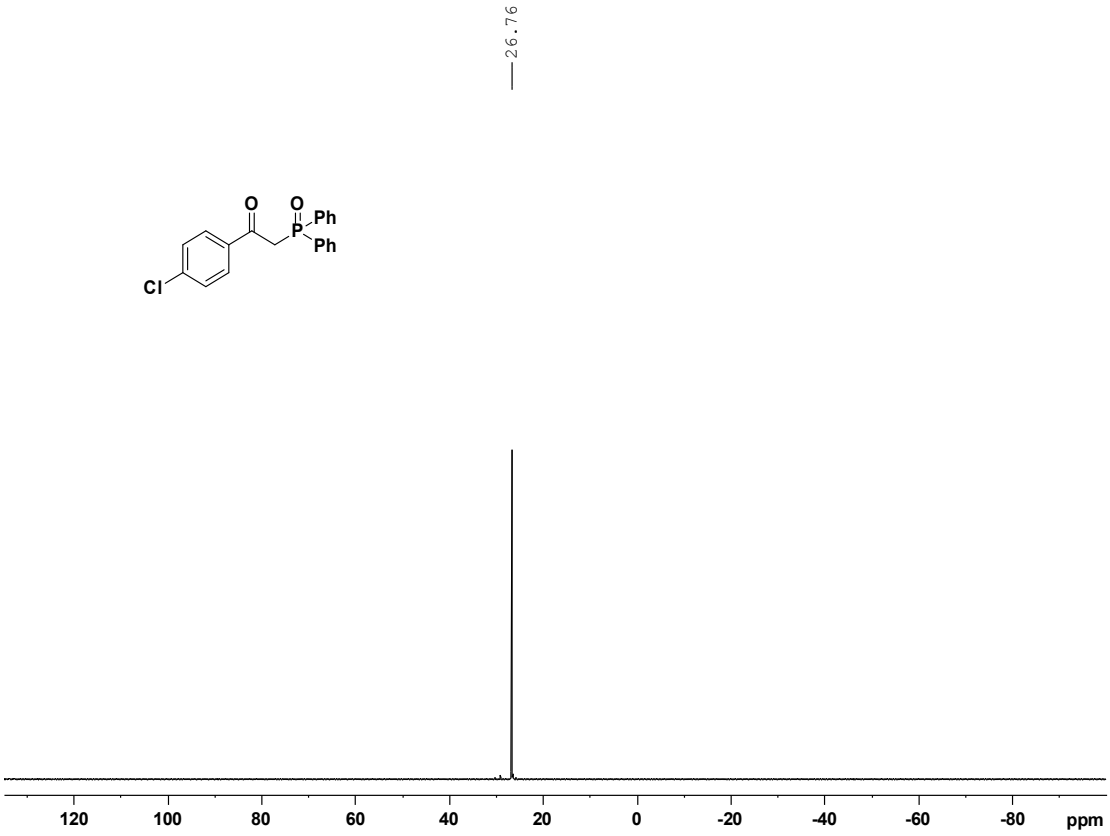

O
O
P
Ph
Ph
Cl

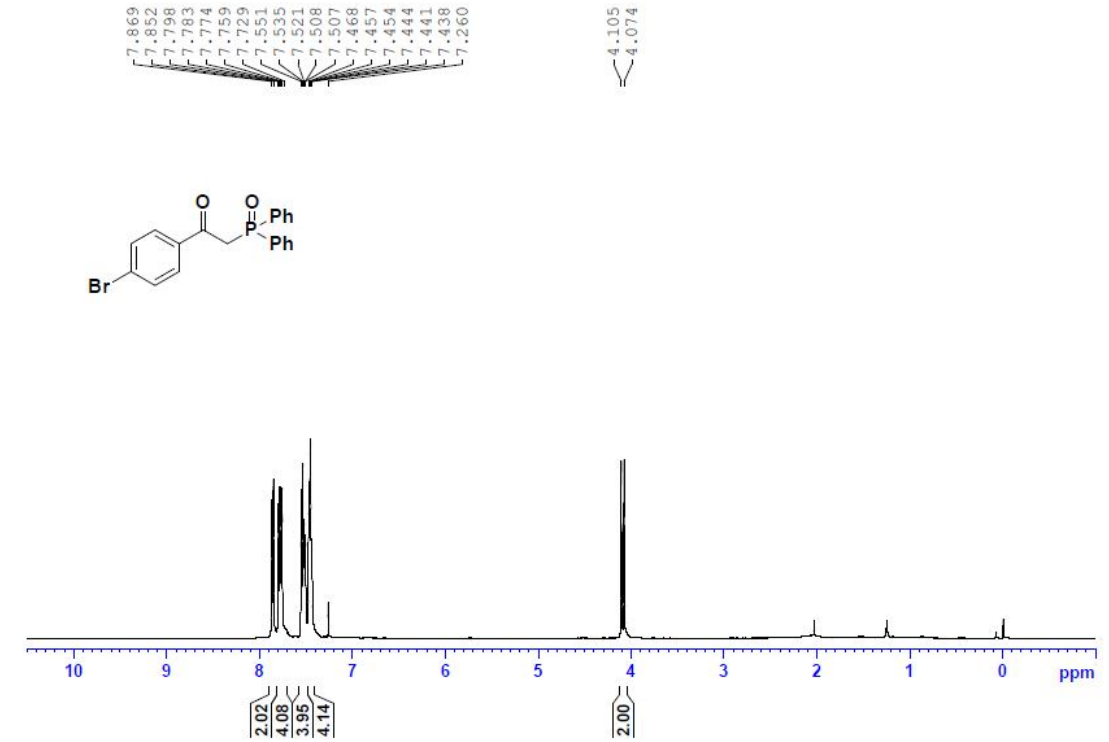

10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
3.98
2.04
3.98
1.93
2.00


191.85
191.81
140.44
135.45
132.49
132.47
132.28
131.46
131.28
131.20
130.95
129.03
128.94
128.84
77.49
77.23
76.98
44.00
43.55

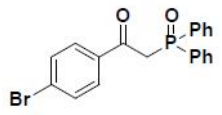

O
O
P
Ph
Ph
Cl

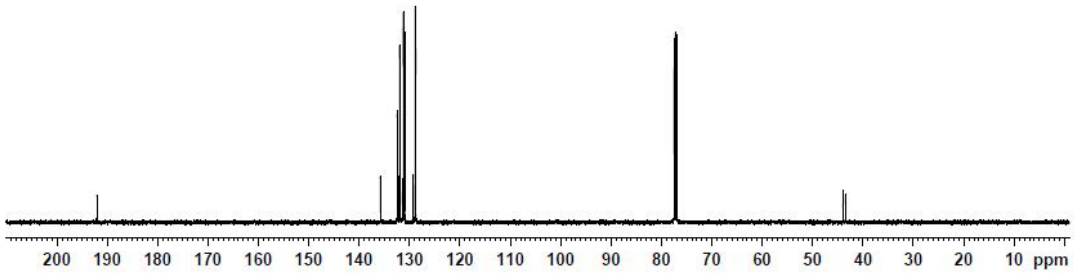

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


26.76
O
O
Ph
P
Ph
Cl
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

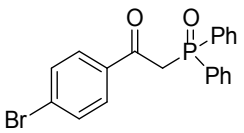

7.869
7.852
7.798
7.783
7.774
7.759
7.729
7.551
7.535
7.521
7.508
7.507
7.468
7.457
7.454
7.444
7.441
7.438
7.260
4.105
4.074
O
O
Ph
P
Ph
Br
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
4.08
3.95
4.14
2.00

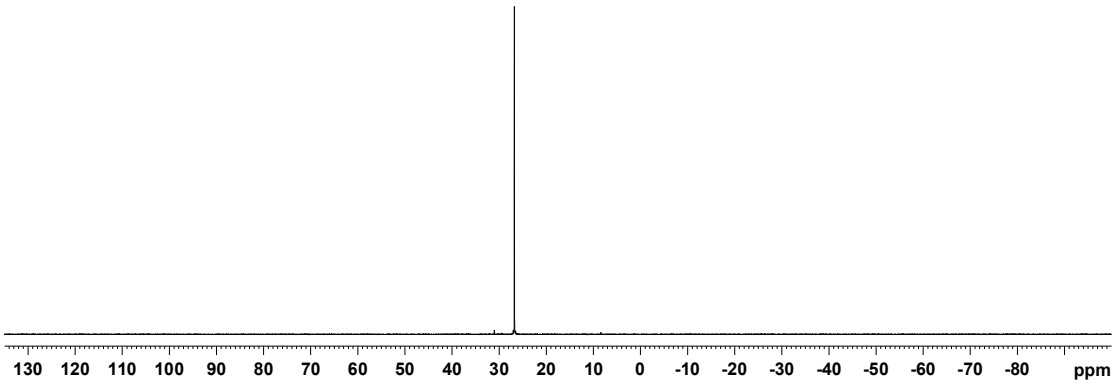

192.05
192.00
135.83
132.48
132.45
132.25
132.01
131.43
131.26
131.18
131.00
129.28
128.92
128.82
77.48
77.23
76.98
43.95
43.50

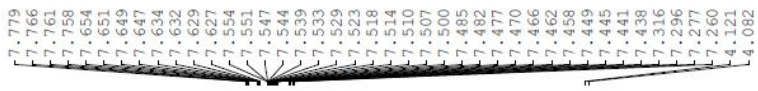

O
O
Ph
P
Ph
Br

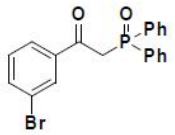

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

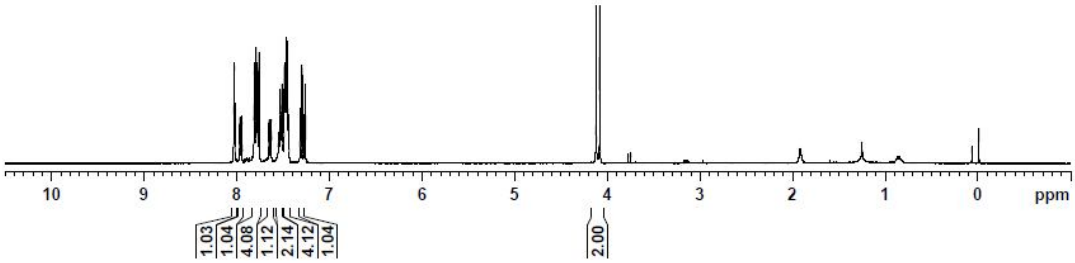

26.73


O
O
Ph
P
Ph
Br

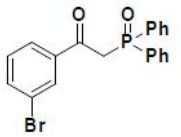

130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

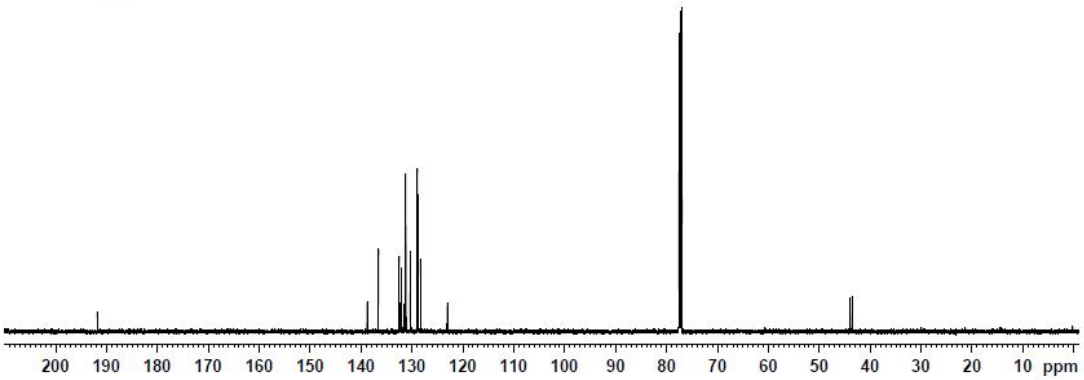

7.779
7.766
7.761
7.758
7.654
7.651
7.649
7.647
7.634
7.632
7.629
7.627
7.554
7.551
7.547
7.544
7.539
7.533
7.529
7.523
7.518
7.514
7.510
7.507
7.500
7.485
7.482
7.477
7.470
7.466
7.462
7.458
7.449
7.445
7.441
7.438
7.316
7.296
7.277
7.260
4.121
4.082

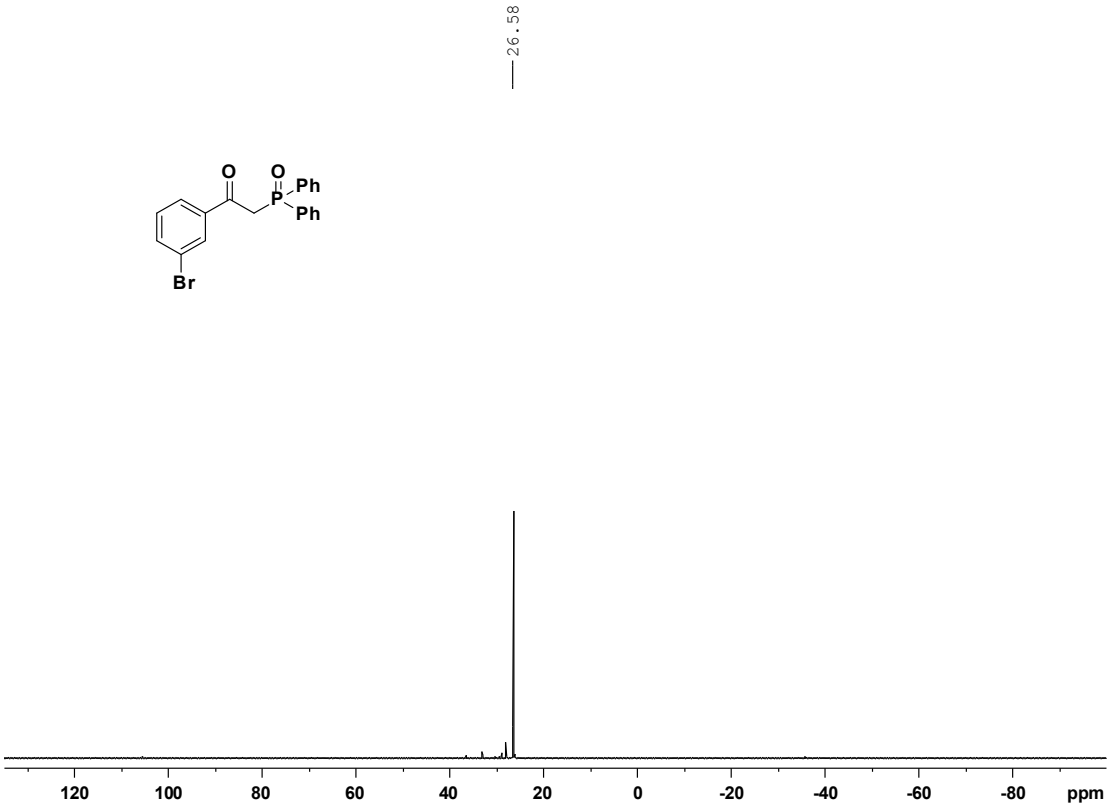

O
O
P
Ph
Ph
Br

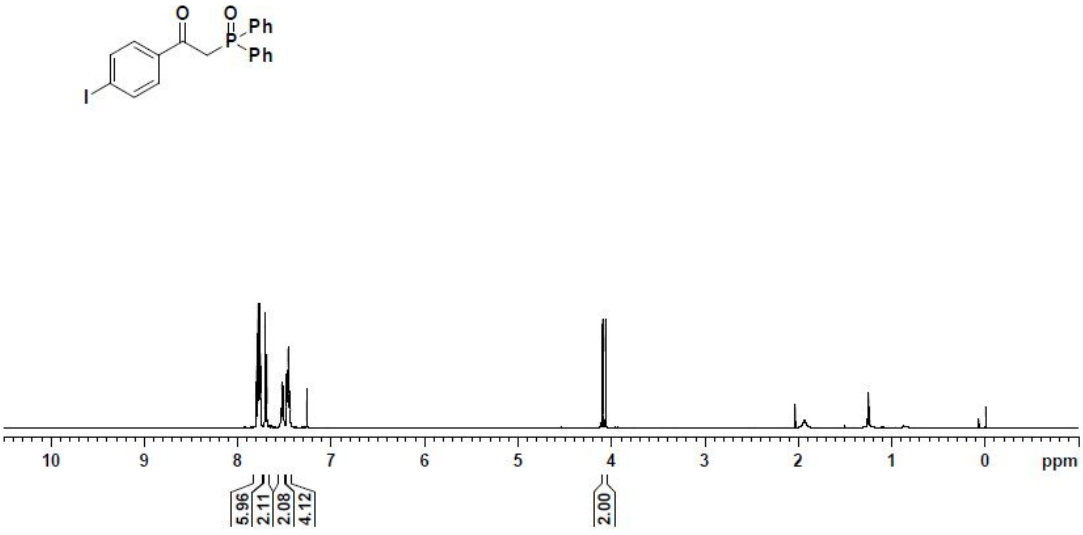

10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.04
4.08
1.12
2.14
4.12
1.04
2.00

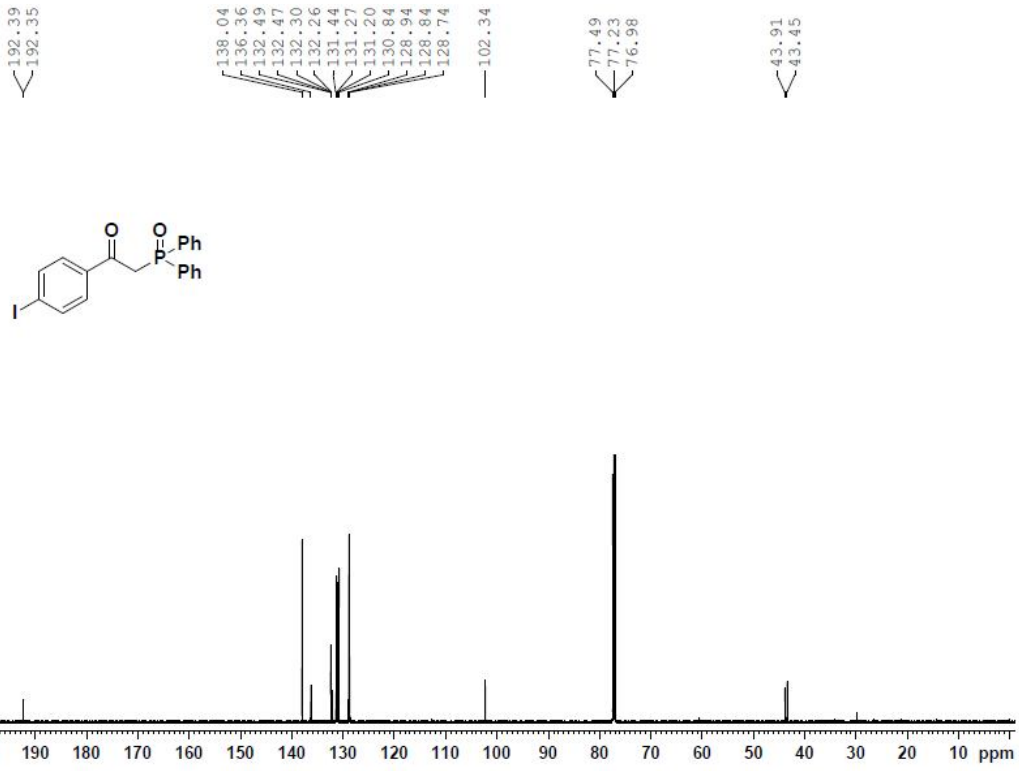

191.83
191.78
138.81
136.59
132.52
132.50
132.28
132.08
131.91
131.46
131.31
131.23
130.32
128.95
128.85
128.30
123.05
77.49
77.23
76.98
43.94
43.49

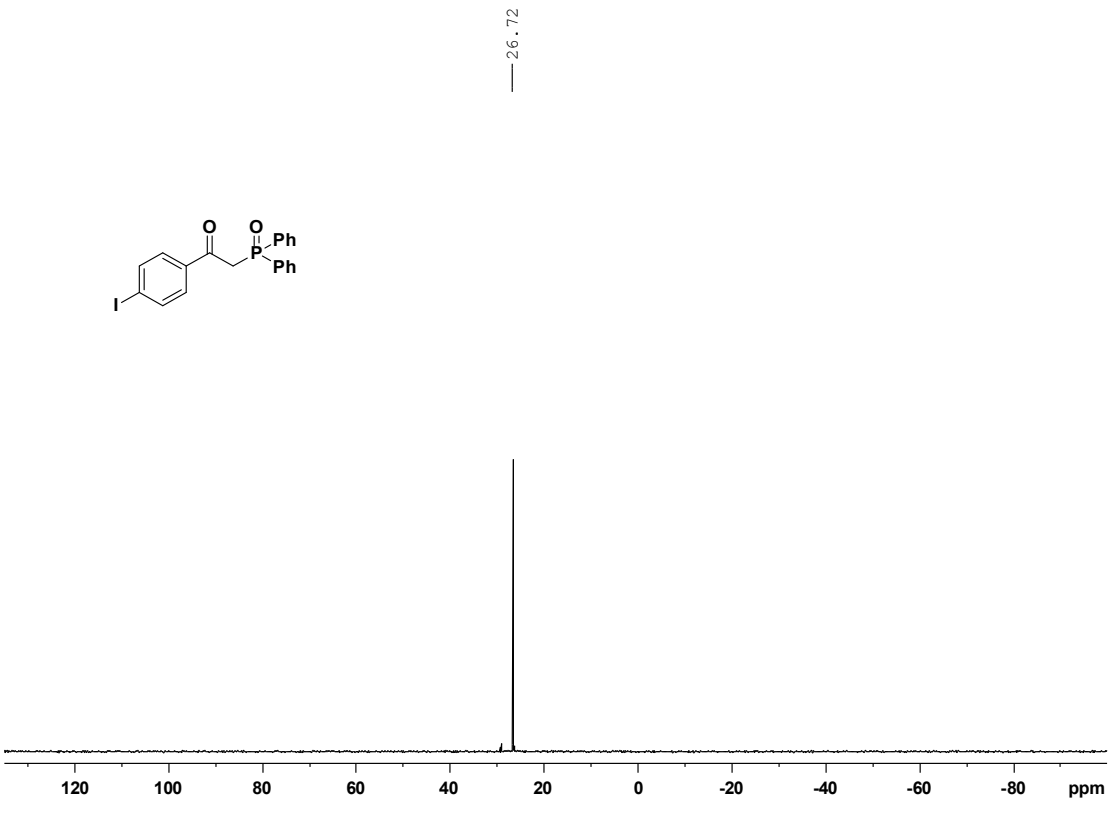

O
O
P
Ph
Ph
Br

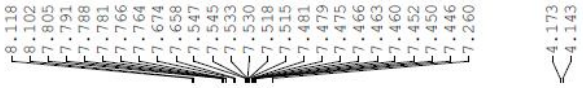

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.58
O
O
P
Ph
Ph
Br
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm
7.762
7.758
7.755
7.712
7.708
7.705
7.695
7.691
7.687
7.546
7.543
7.540
7.537
7.533
7.528
7.525
7.521
7.516
7.513
7.510
7.508
7.477
7.474
7.471
7.468
7.464
7.462
7.458
7.455
7.447
7.445
7.441
7.439
7.260
4.094
4.064


O
O
P
Ph
Ph
I
10
9
8
7
6
5
4
3
2
1
0
ppm
5.96
2.11
2.08
4.12
2.00


192.39
192.35
138.04
136.36
132.49
132.47
132.30
132.26
131.44
131.27
131.20
130.84
128.94
128.84
128.74
102.34
77.49
77.23
76.98
43.91
43.45
O
O
Ph
P
Ph
I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


26.72
O
O
Ph
P
Ph
I
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm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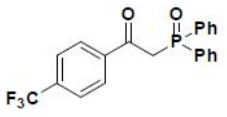
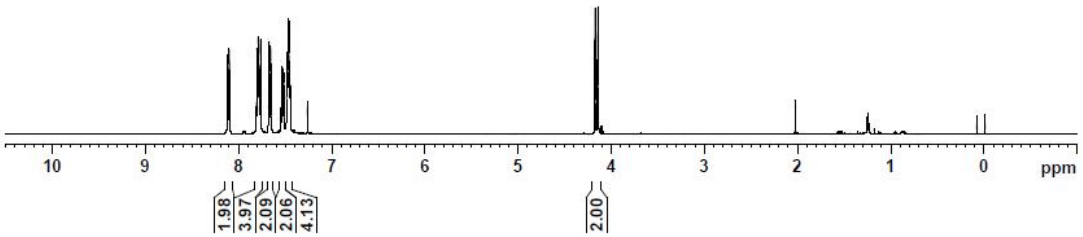
8.102
7.805
7.791
7.788
7.781
7.766
7.764
7.674
7.658
7.547
7.545
7.533
7.530
7.518
7.515
7.481
7.479
7.475
7.466
7.463
7.460
7.452
7.450
7.446
7.260
4.173
4.143


O
O
Ph
P
Ph
F3C


10
9
8
7
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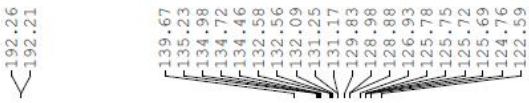
5
4
3
2
1
0
ppm
1.98
3.97
2.09
2.06
4.13
2.00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135.23
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134.72
134.46
132.58
132.56
132.09
131.25
131.17
129.83
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128.88
126.93
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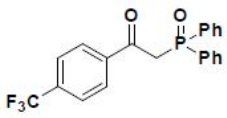
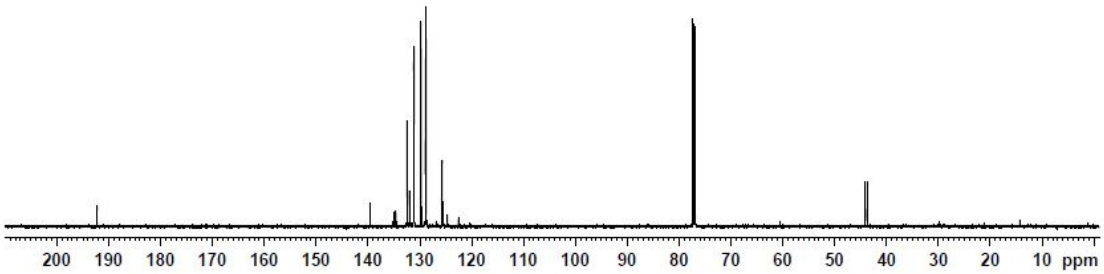
125.75
125.72
125.69
124.76
122.59
44.21
43.77


O
O
Ph
P
Ph
F3C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180
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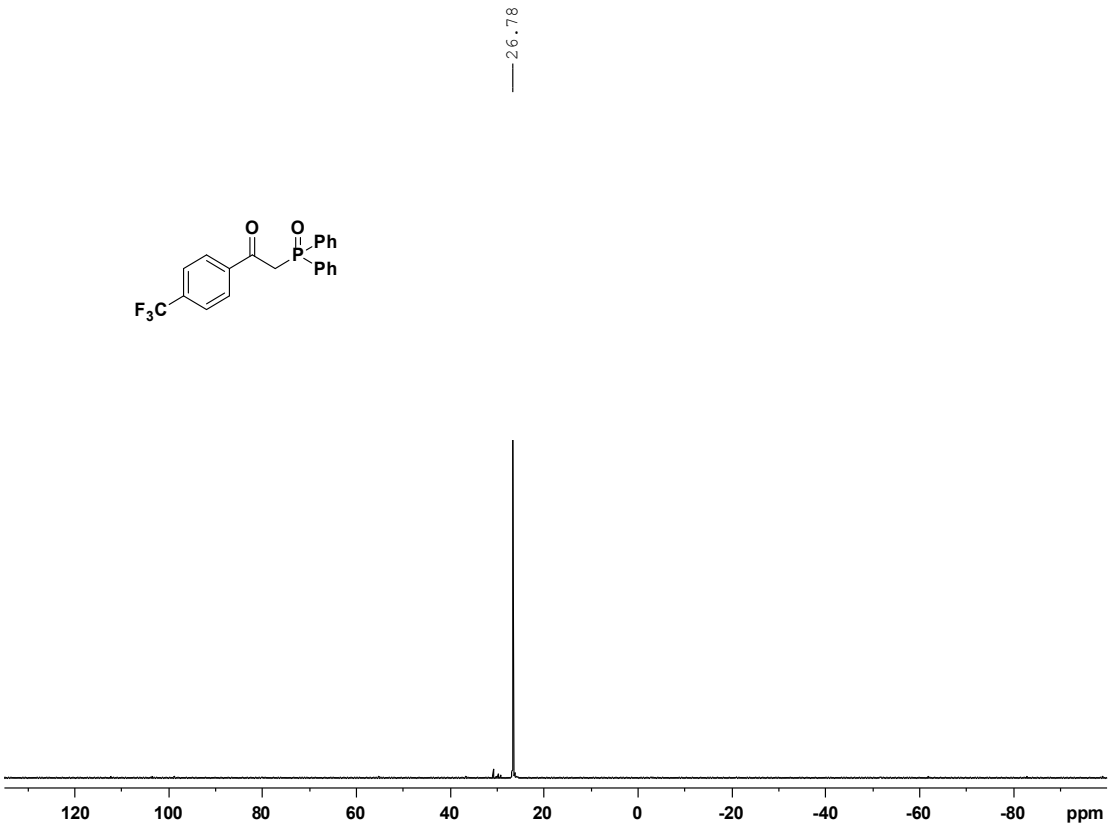
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.78
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O
Ph
P
Ph
F3C
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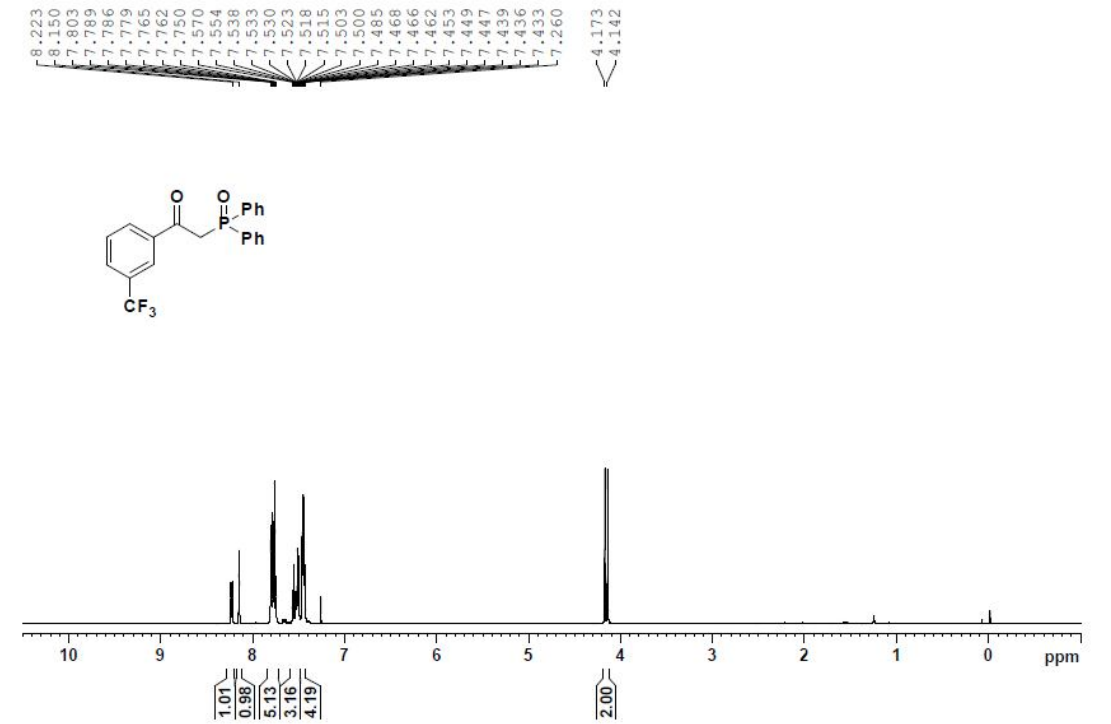
-60
-80
ppm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8.150
7.803
7.789
7.786
7.779
7.765
7.762
7.750
7.570
7.554
7.538
7.533
7.530
7.523
7.518
7.515
7.503
7.500
7.485
7.468
7.466
7.462
7.453
7.449
7.447
7.439
7.436
7.433
7.260
4.173
4.142
O
O
Ph
P
Ph
CF3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.98
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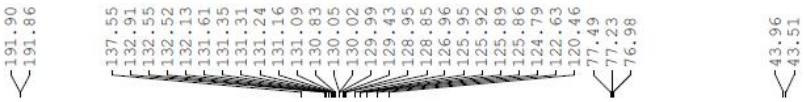
3.16
4.19
2.00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191.86
137.55
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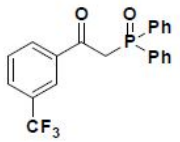
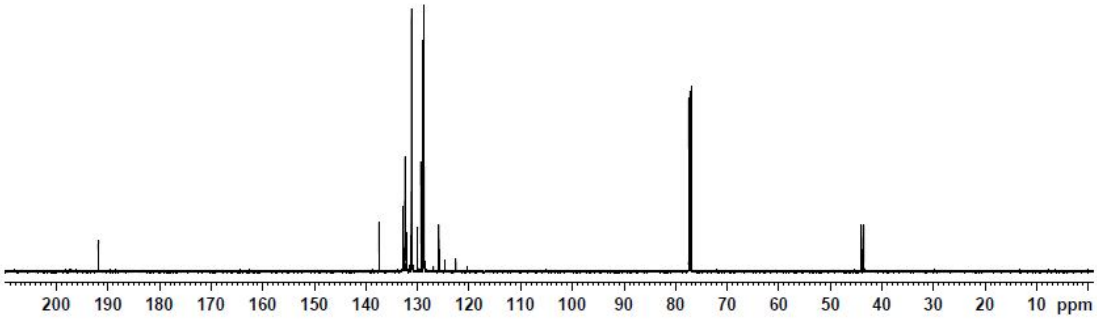
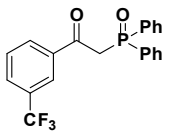
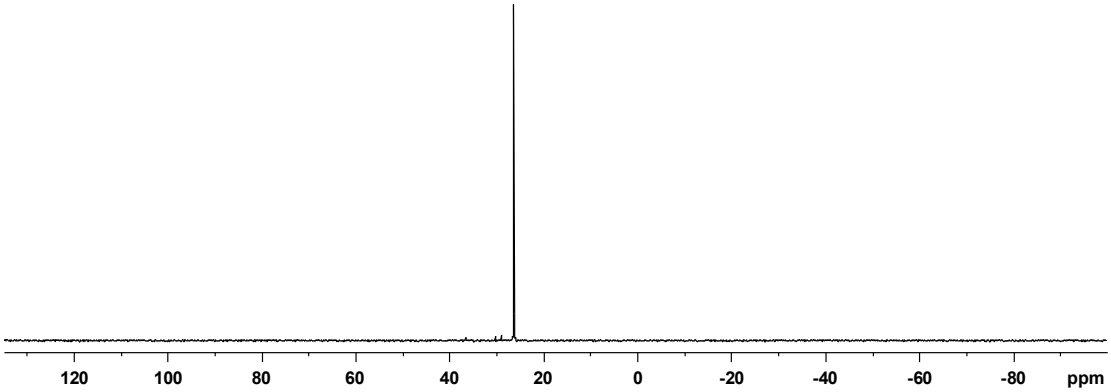
132.13
131.61
131.35
131.31
131.24
131.16
131.09
130.83
130.05
130.02
129.99
129.43
128.95
128.85
126.96
125.95
125.92
125.89
125.86
124.79
122.63
120.46
77.49
77.23
76.98
43.96
43.51


O
O
P
Ph
Ph
CF3


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.62


O
O
P
Ph
Ph
CF3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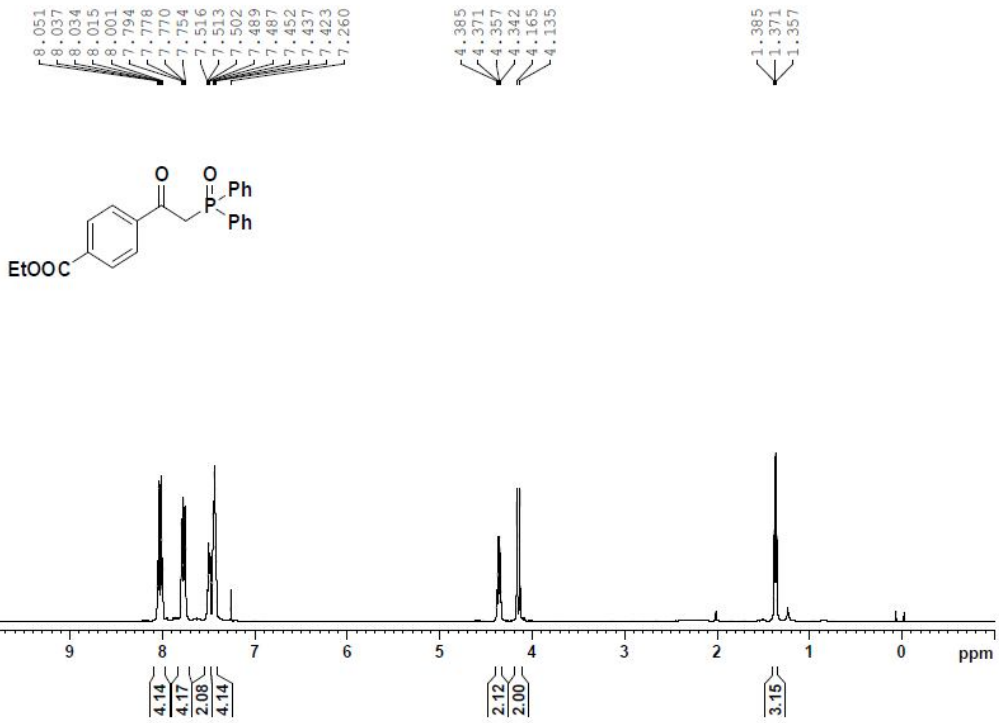
100
80
60
40
20
0
-20
-40
-60
-80
ppm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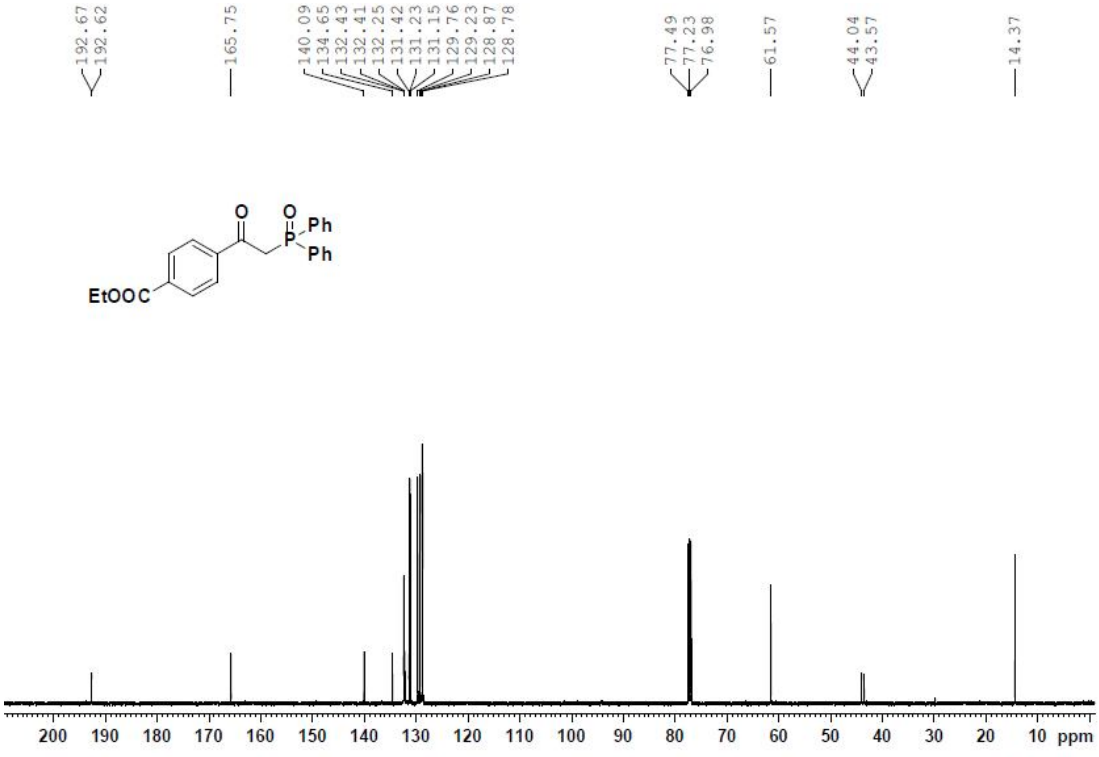
8.037
8.034
8.015
8.001
7.794
7.778
7.770
7.754
7.516
7.513
7.502
7.489
7.487
7.452
7.437
7.423
7.260
4.385
4.371
4.357
4.342
4.165
4.135
1.385
1.371
1.357
O
O
Ph
P
Ph
EtOOC
10
9
8
7
6
5
4
3
2
1
0
ppm
4.14
4.17
2.08
4.14
2.12
2.00
3.15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192.62
165.75
140.09
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132.43
132.41
132.25
131.42
131.23
131.15
129.76
129.23
128.87
128.78
77.49
77.23
76.98
61.57
44.04
43.57
14.37
O
O
Ph
P
Ph
EtOOC
200
190
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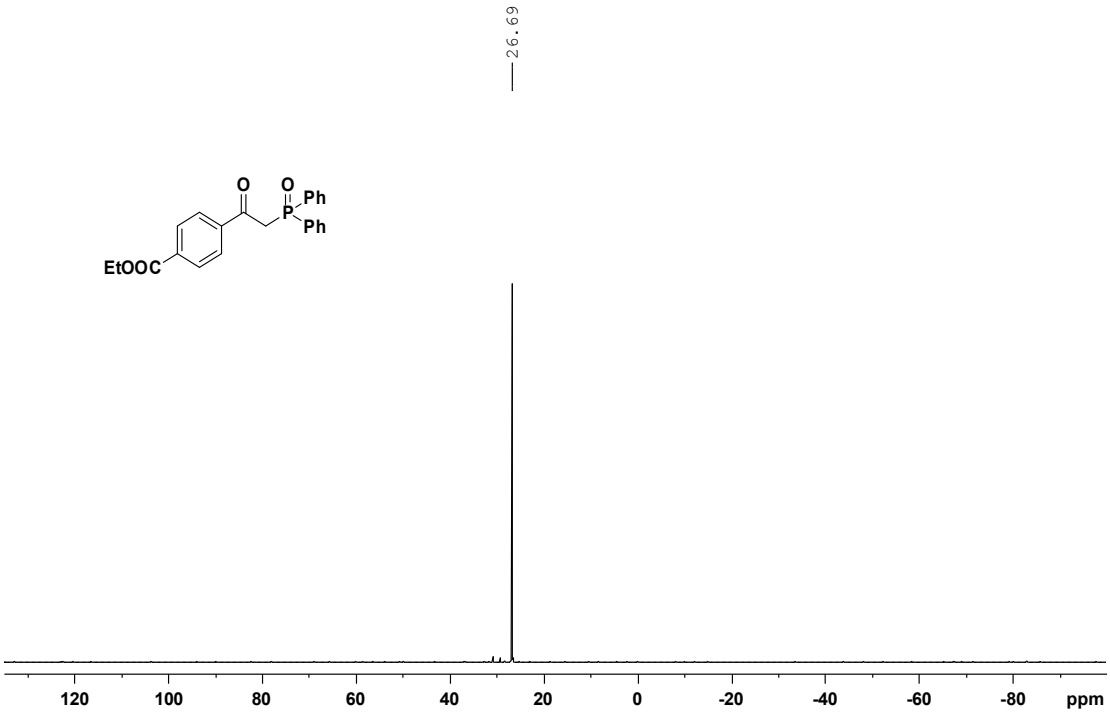
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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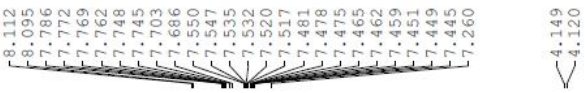
EtOOC
Ph
Ph
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm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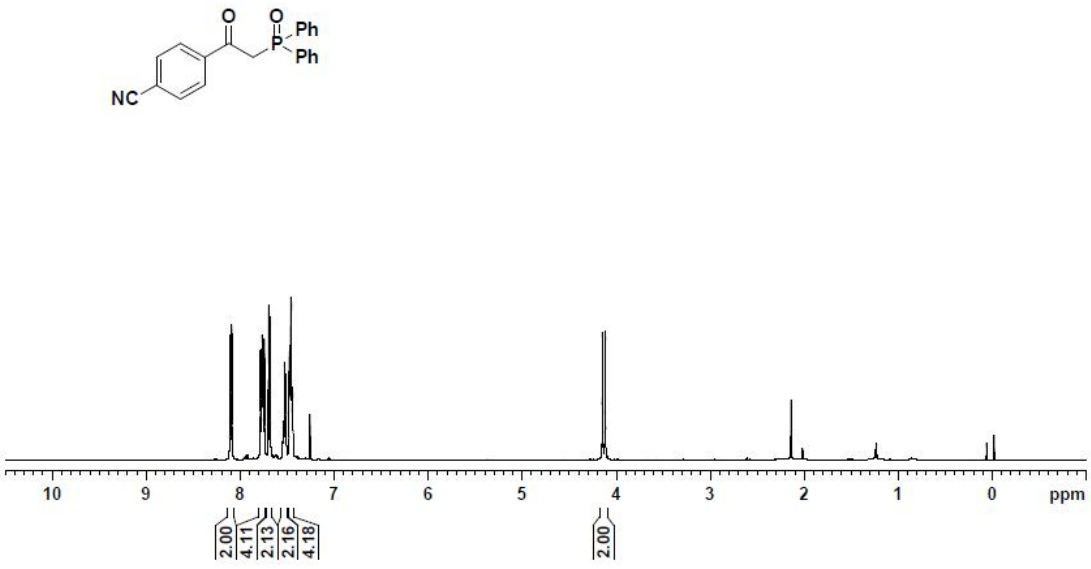
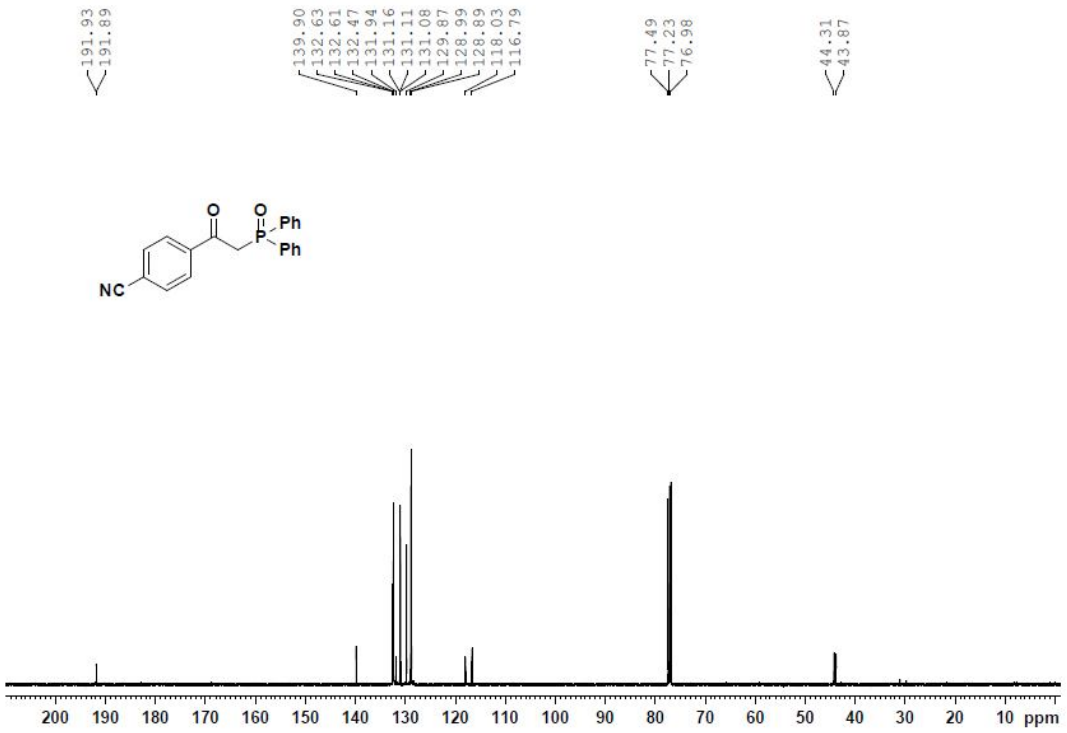
8.095
7.786
7.772
7.769
7.762
7.748
7.745
7.703
7.686
7.550
7.547
7.535
7.532
7.520
7.517
7.481
7.478
7.475
7.465
7.462
7.459
7.451
7.449
7.445
7.260
4.149
4.120


NC
Ph
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.11
2.13
2.16
4.18
2.00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191.89
139.90
132.63
132.61
132.47
131.94
131.16
131.11
131.08
129.87
128.99
128.89
118.03
116.79
77.49
77.23
76.98
44.31
43.87
O
O
P
Ph
Ph
NC
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190
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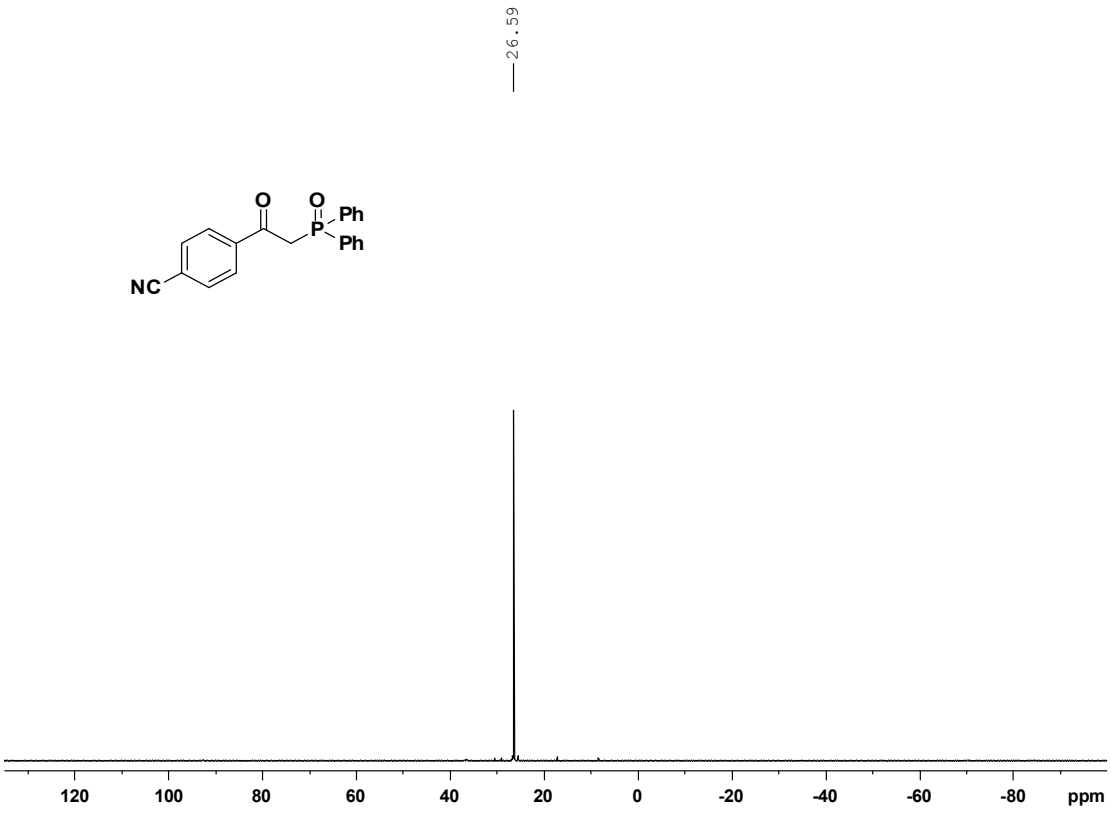
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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O
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Ph
Ph
NC
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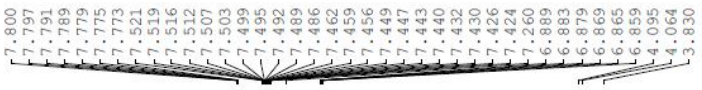
100
80
60
40
20
0
-20
-40
-60
-80
ppm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7.791
7.789
7.779
7.775
7.773
7.521
7.519
7.516
7.512
7.507
7.503
7.499
7.495
7.492
7.489
7.486
7.462
7.459
7.456
7.449
7.447
7.443
7.440
7.432
7.430
7.426
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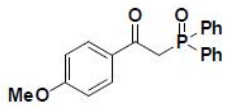
6.869
6.865
6.859
4.095
4.064
3.830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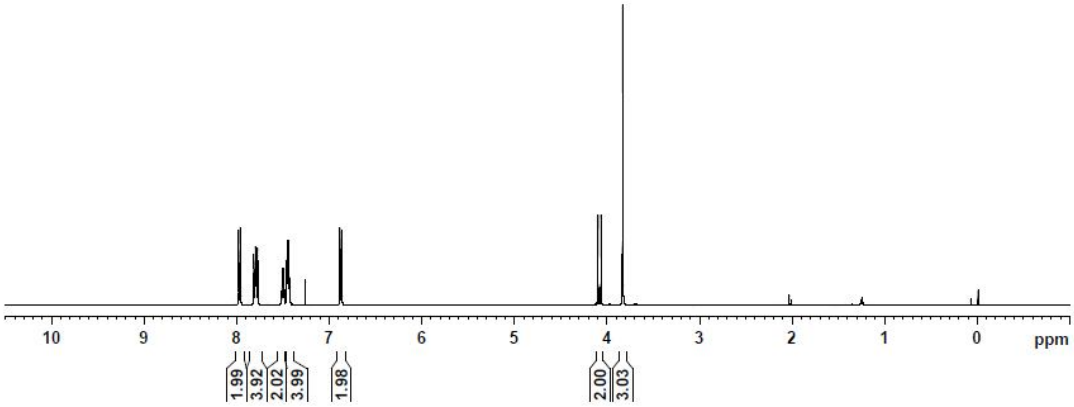
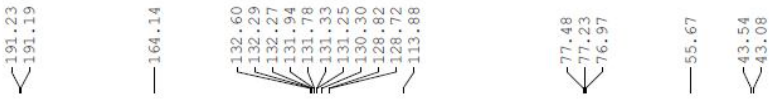
O
P
Ph
Ph
MeO


10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
3.92
2.02
3.99
1.98
2.00
3.03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191.19
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132.27
131.94
131.78
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130.30
128.82
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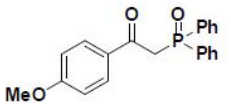
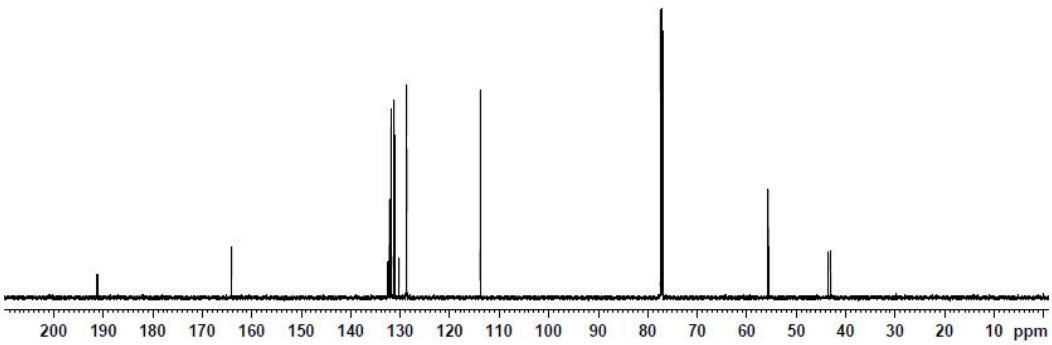
77.48
77.23
76.97
55.67
43.54
43.08


O
O
P
Ph
Ph
MeO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150
140
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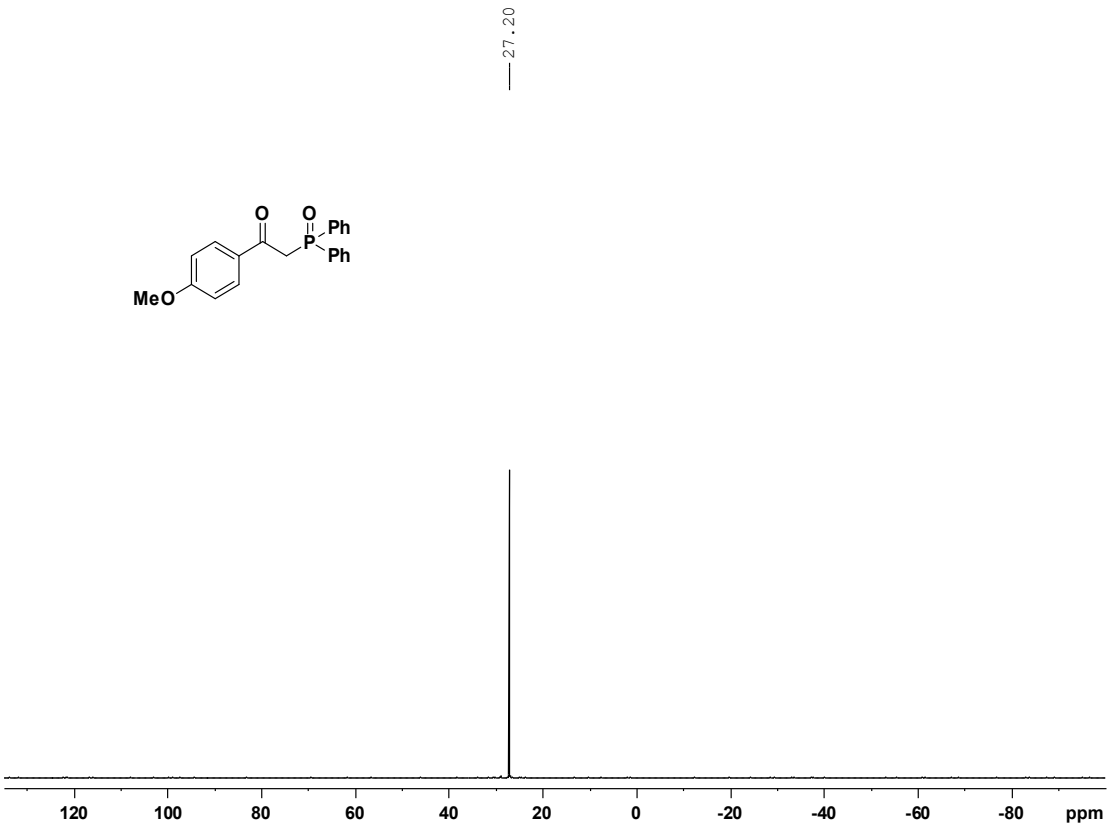
120
110
100
90
80
70
60
50
40
30
20
10
ppm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Ph
Ph
MeO
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60
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20
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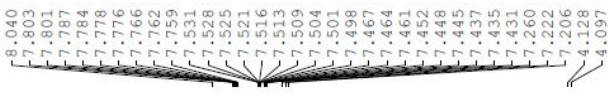
-60
-80
ppm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7.787
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7.778
7.776
7.766
7.762
7.759
7.531
7.528
7.525
7.521
7.516
7.513
7.509
7.504
7.501
7.498
7.467
7.464
7.461
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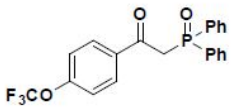
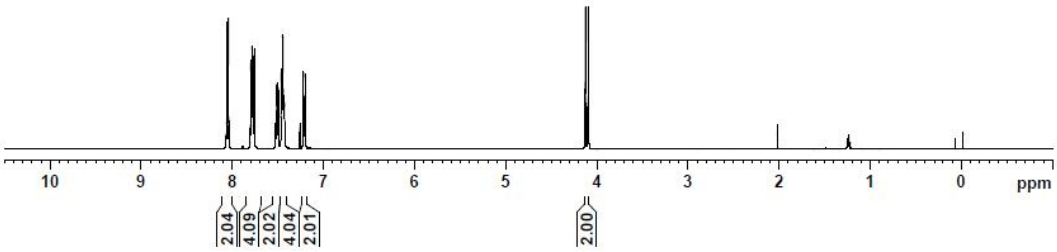
7.448
7.445
7.437
7.435
7.431
7.260
7.222
7.206
4.128
4.097


O
O
P
Ph
Ph
F3CO


10
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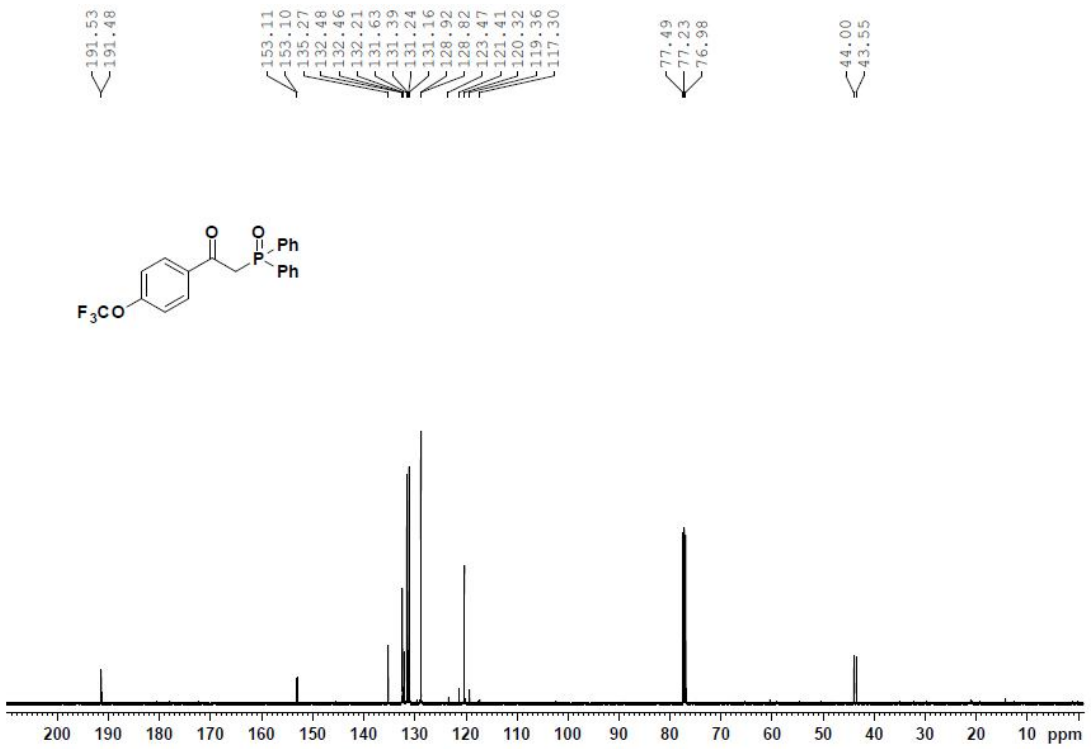
8
7
6
5
4
3
2
1
0
ppm
2.04
4.09
2.02
4.04
2.01
2.00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153.10
135.27
132.48
132.46
132.21
131.63
131.39
131.24
131.16
128.92
128.82
123.47
121.41
120.32
119.36
117.30
77.49
77.23
76.98
44.00
43.55
O
O
P
Ph
Ph
F3CO
200
190
180
170
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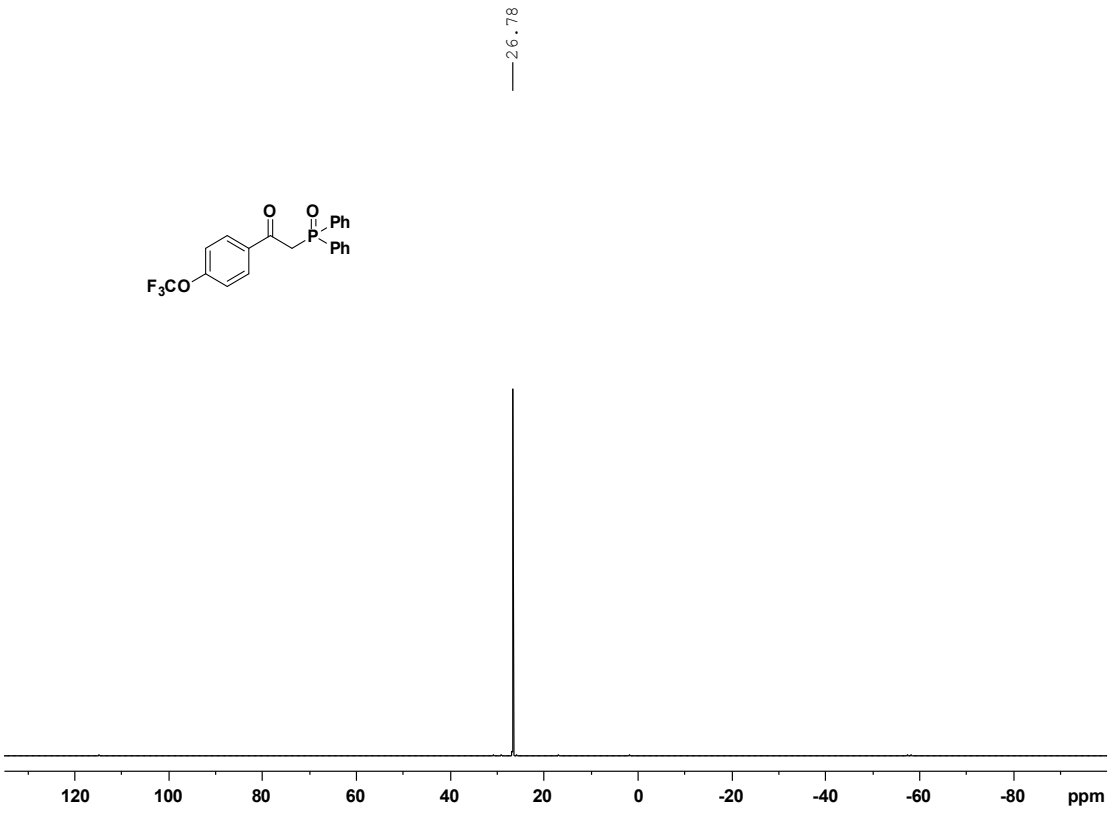
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.78
O
O
P
Ph
Ph
F3CO
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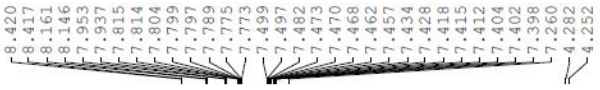
100
80
60
40
20
0
-20
-40
-60
-80
ppm


8.420
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8.161
8.146
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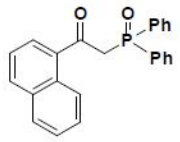
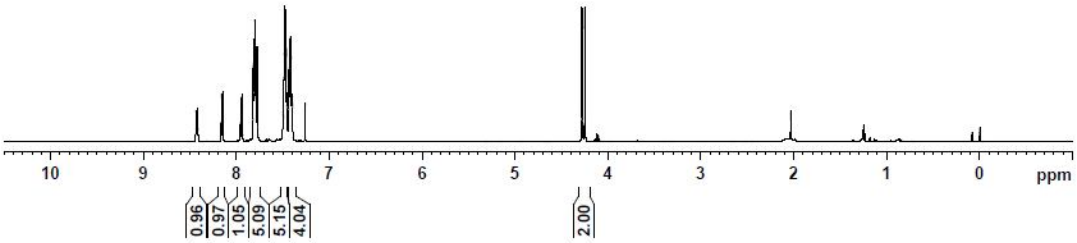
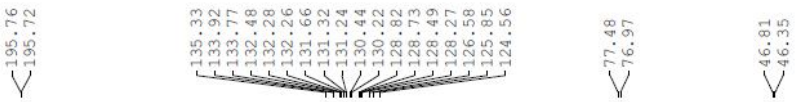
7.937
7.815
7.814
7.804
7.799
7.797
7.789
7.775
7.773
7.499
7.497
7.482
7.473
7.470
7.468
7.462
7.457
7.434
7.428
7.418
7.415
7.412
7.404
7.402
7.398
7.260
4.282
4.252


O
O
Ph
P
Ph


10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
0.97
1.05
5.09
5.15
4.04
2.00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195.72
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133.92
133.77
132.48
132.28
132.26
131.66
131.32
131.24
130.44
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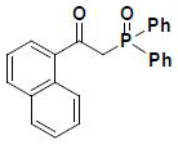
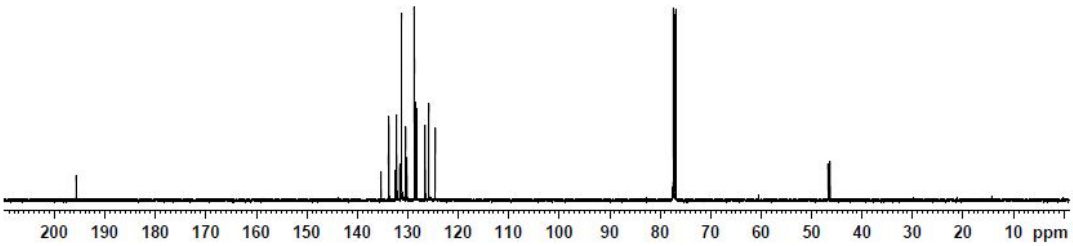
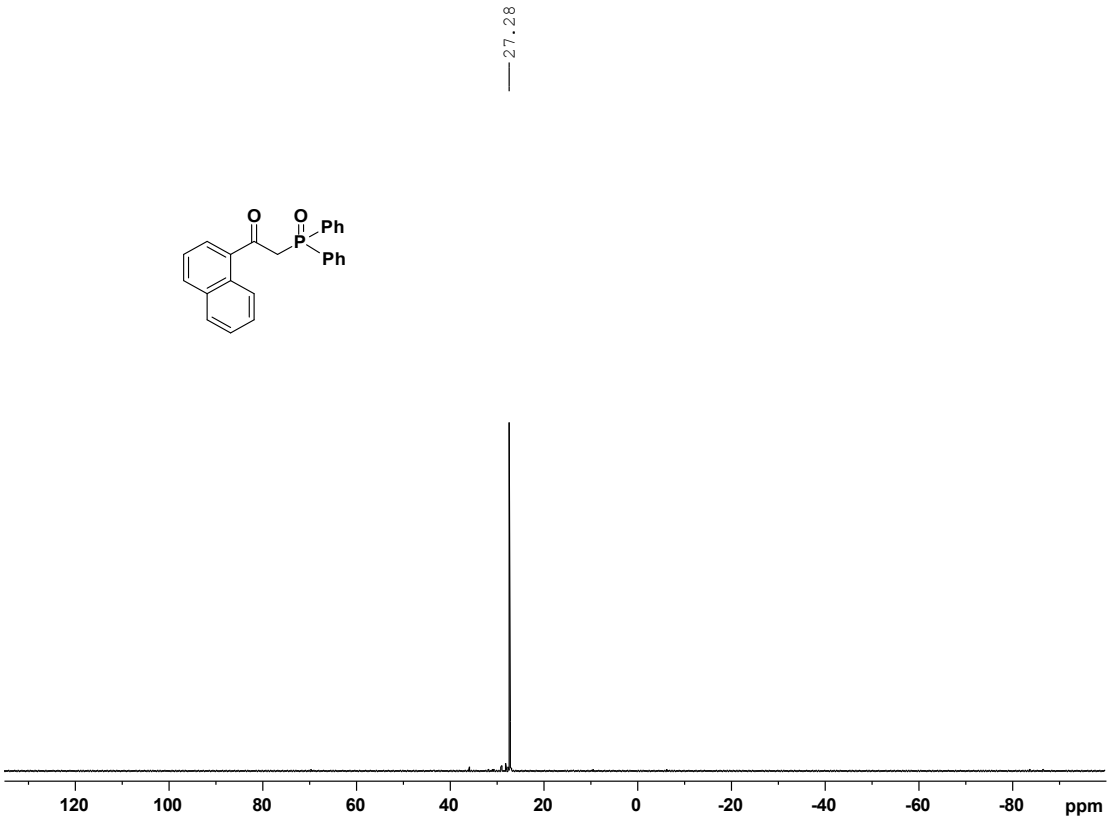
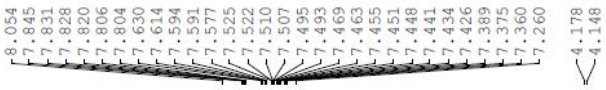
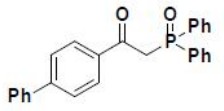
128.49
128.27
126.58
125.85
124.56
77.48
76.97
46.81
46.35

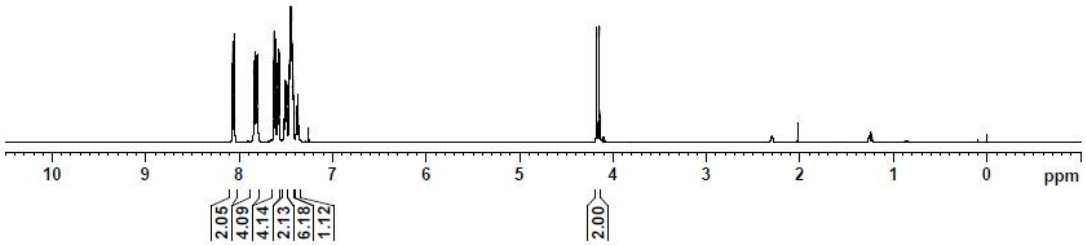

O
O
Ph
P
Ph

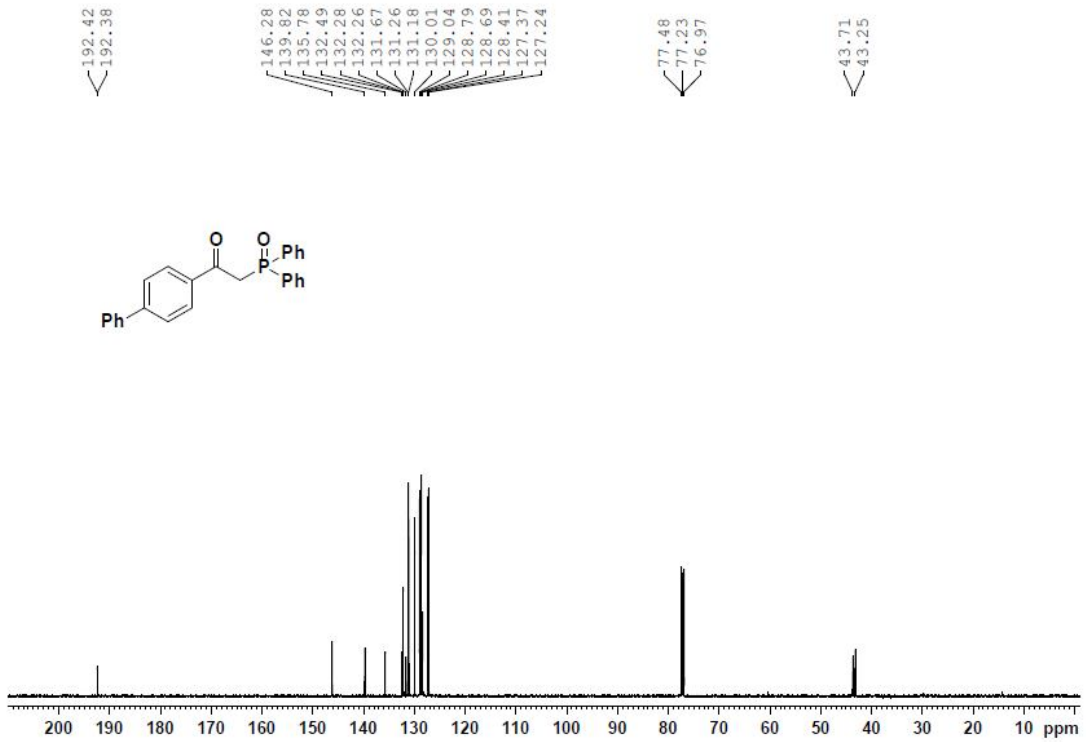

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

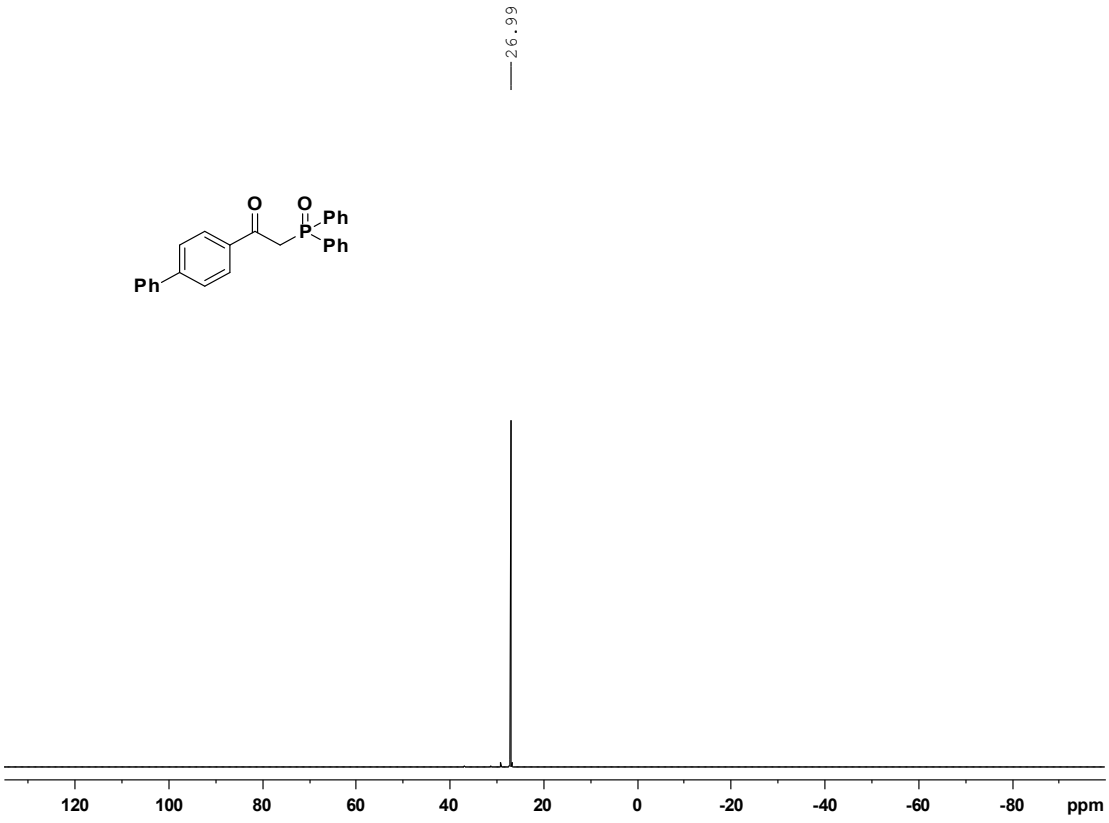

27.28
O
O
Ph
P
Ph
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

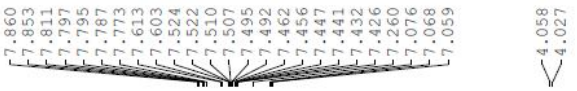

8.054
7.845
7.831
7.828
7.820
7.806
7.804
7.630
7.614
7.594
7.591
7.577
7.525
7.522
7.510
7.507
7.495
7.493
7.469
7.463
7.455
7.451
7.448
7.441
7.434
7.426
7.389
7.375
7.360
7.260
4.178
4.148

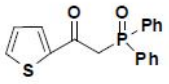

O
O
Ph
P
Ph
Ph

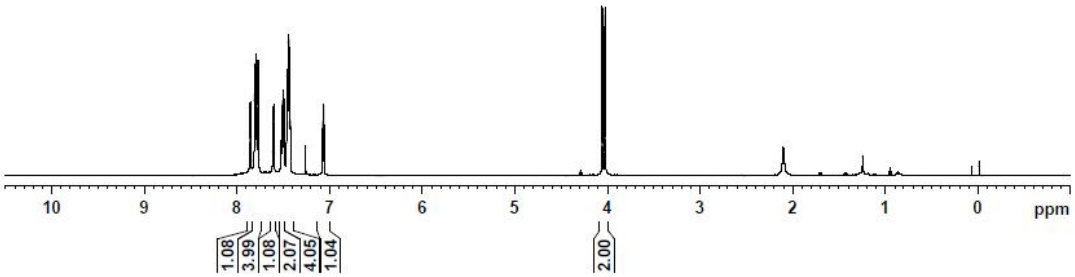

10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
4.09
4.14
2.13
6.18
1.12
2.00


192.42
192.38
146.28
139.82
135.78
132.49
132.28
132.26
131.67
131.26
131.18
130.01
129.04
128.79
128.69
128.41
127.37
127.24
77.48
77.23
76.97
43.71
43.25
O
O
P
Ph
Ph
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

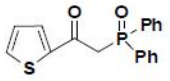

26.99
O
O
P
Ph
Ph
Ph
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm

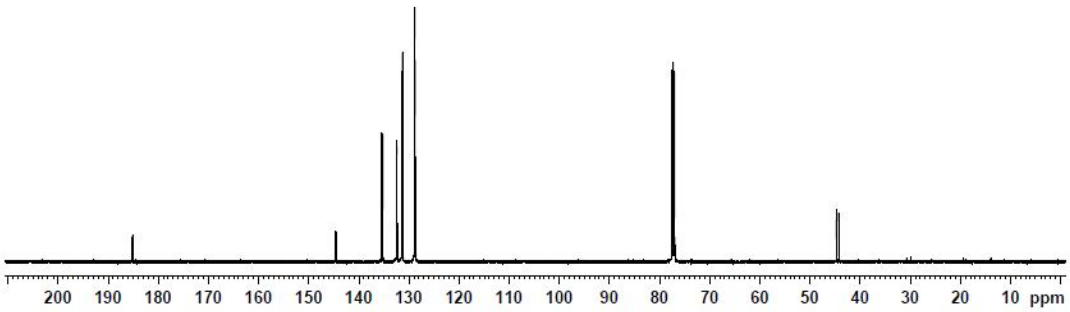

7.860
7.853
7.811
7.797
7.795
7.787
7.773
7.613
7.603
7.524
7.522
7.510
7.507
7.495
7.492
7.462
7.456
7.447
7.441
7.432
7.426
7.260
7.076
7.068
7.059
4.058
4.027

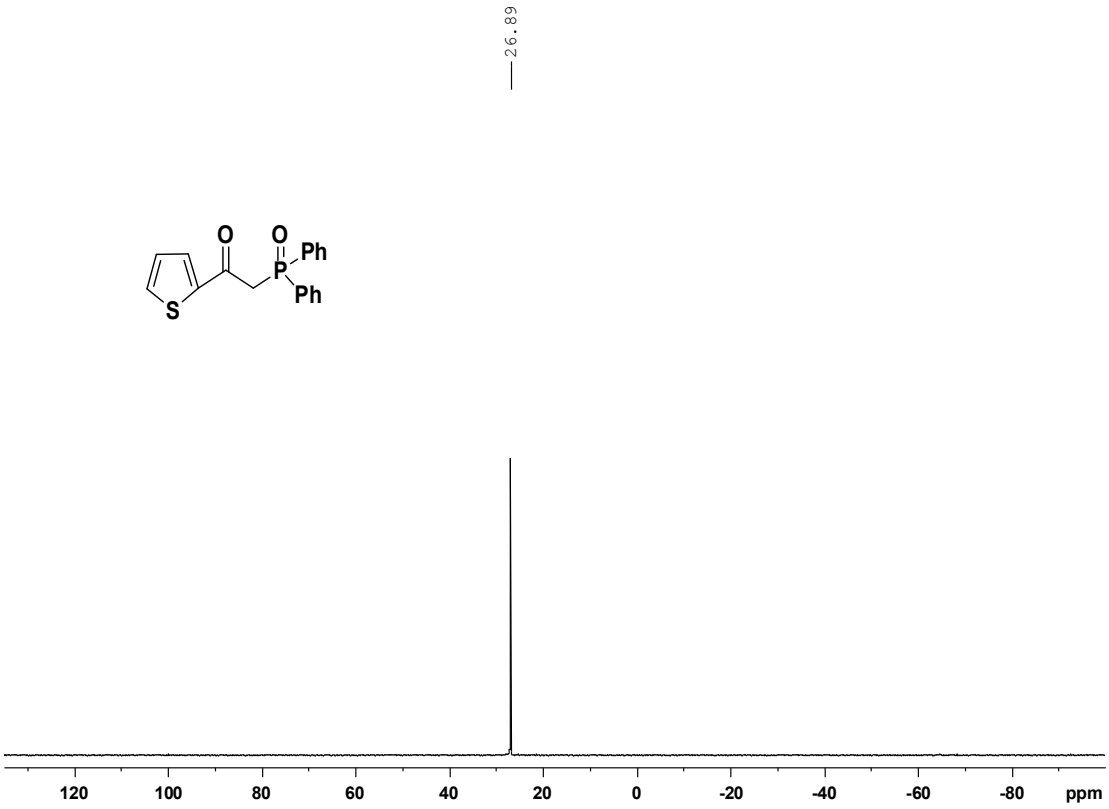

O
O
Ph
P
Ph
S

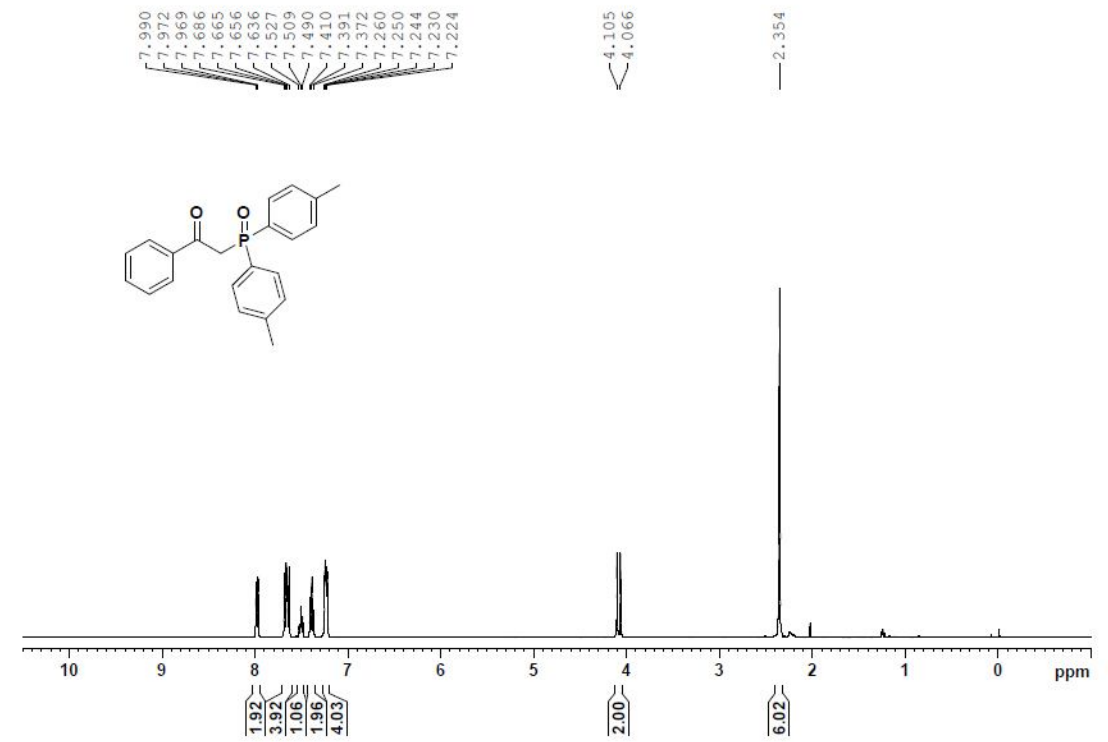

10
9
8
7
6
5
4
3
2
1
0
ppm
1.08
3.99
1.08
2.07
4.05
1.04
2.00

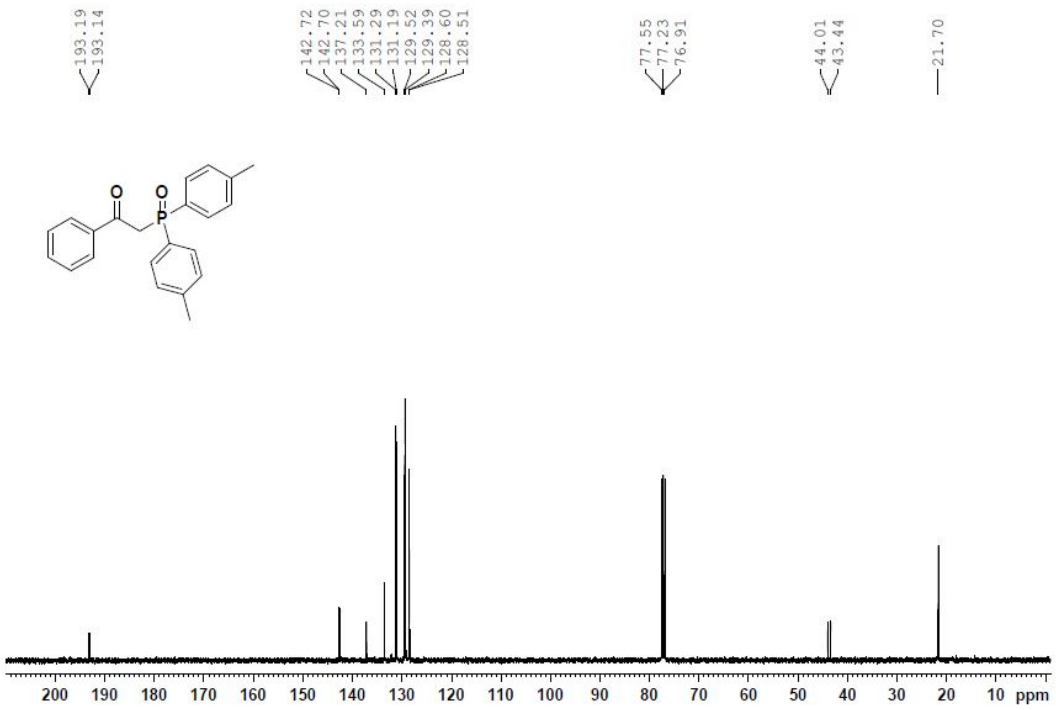

185.13
185.09
144.58
135.40
135.18
132.42
132.39
132.23
131.41
131.34
131.26
128.86
128.76
128.62
77.48
77.23
76.98
44.69
44.24

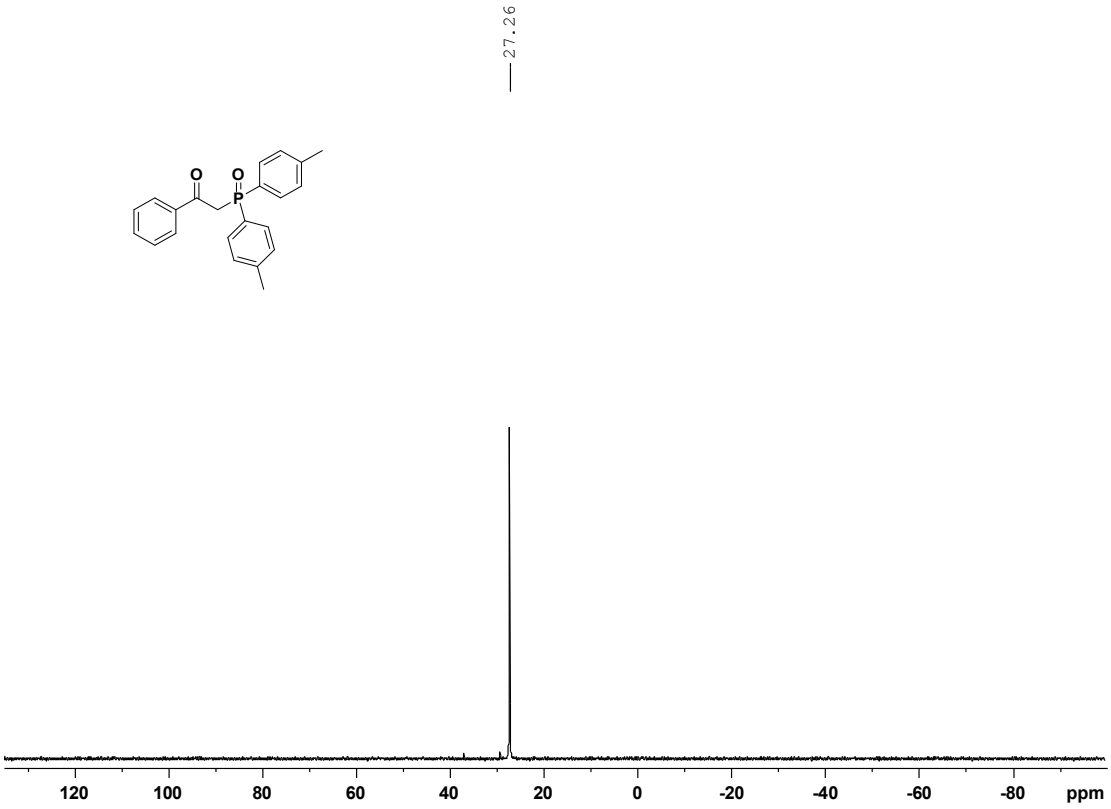

O
O
Ph
P
Ph
S

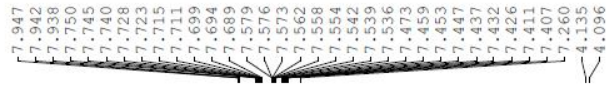

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

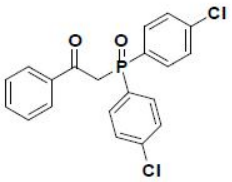

26.89
O
O
Ph
P
Ph
S
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

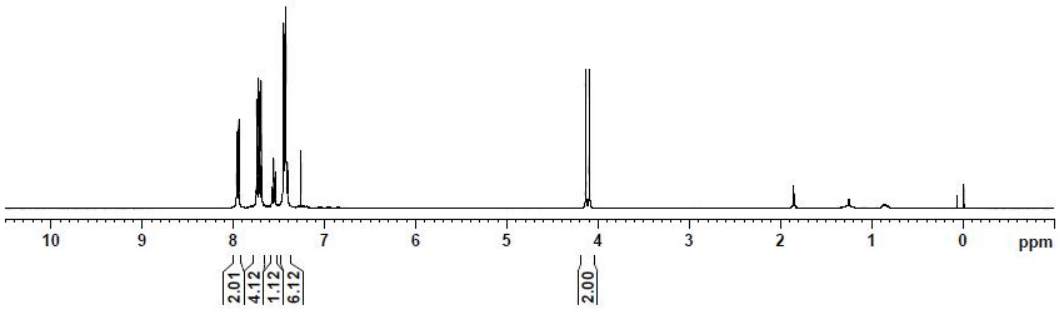

7.990
7.972
7.969
7.686
7.665
7.656
7.636
7.527
7.509
7.490
7.410
7.391
7.372
7.260
7.250
7.244
7.230
7.224
4.105
4.066
2.354
O
O
P
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
3.92
1.06
1.96
4.03
2.00
6.02

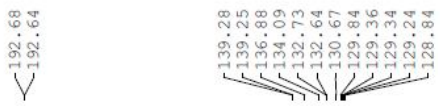

193.19
193.14
142.72
142.70
137.21
133.59
131.29
131.19
129.52
129.39
128.60
128.51
77.55
77.23
76.91
44.01
43.44
21.70
O
O
P
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


27.26
O
O
P
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm


7.947
7.942
7.938
7.750
7.745
7.740
7.728
7.723
7.715
7.711
7.699
7.694
7.689
7.579
7.576
7.573
7.562
7.558
7.554
7.542
7.539
7.536
7.473
7.459
7.453
7.447
7.437
7.432
7.426
7.411
7.407
7.260
4.135
4.096


O
O
P
Cl
Cl

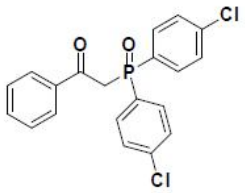

10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
4.12
1.12
6.12
2.00

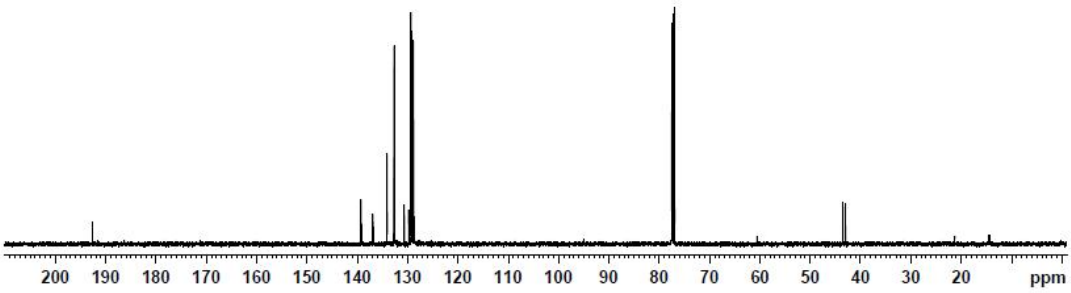

192.68
192.64

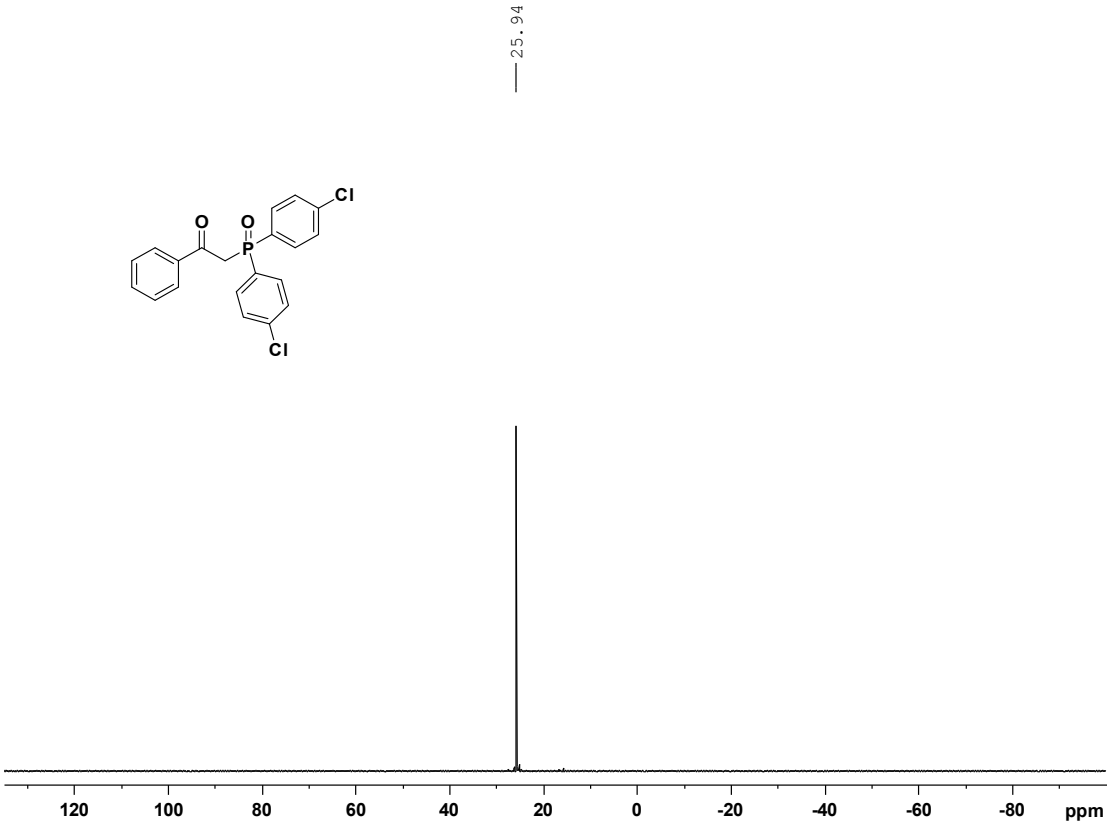
139.28
139.25
136.88
134.09
132.73
132.64
130.67
129.84
129.36
129.34
129.24
128.84

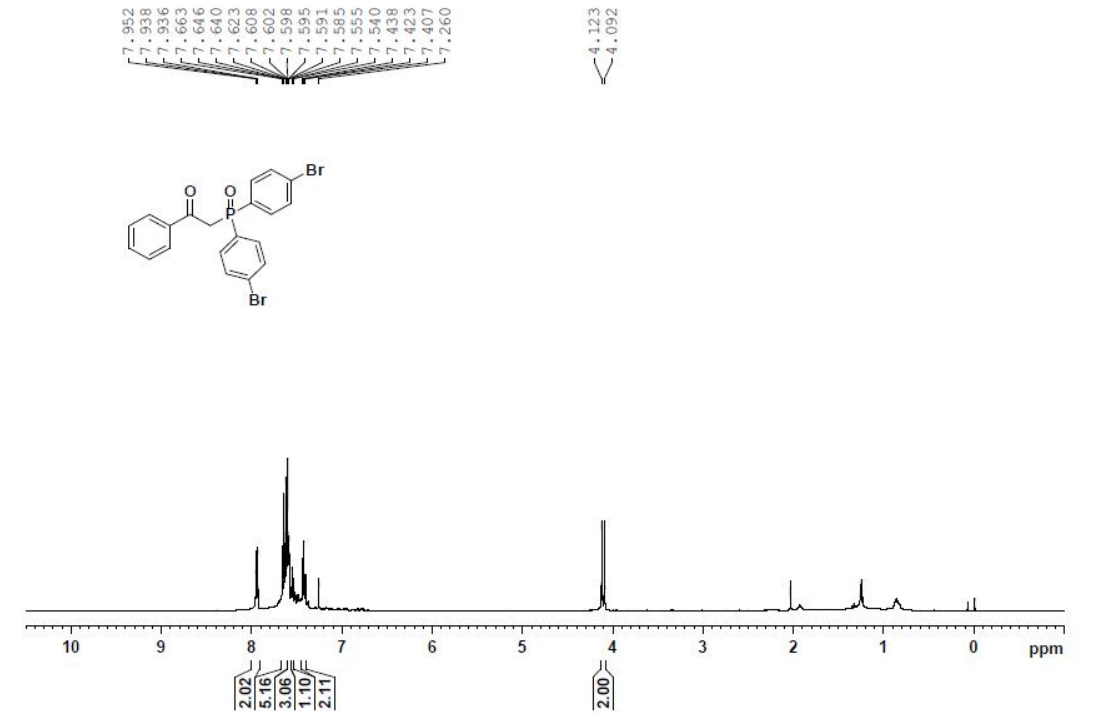

77.49
77.23
76.98

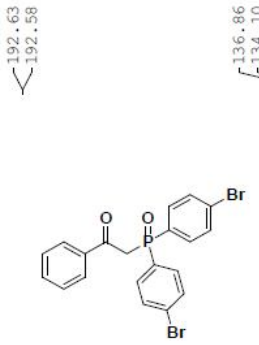

43.47
42.99

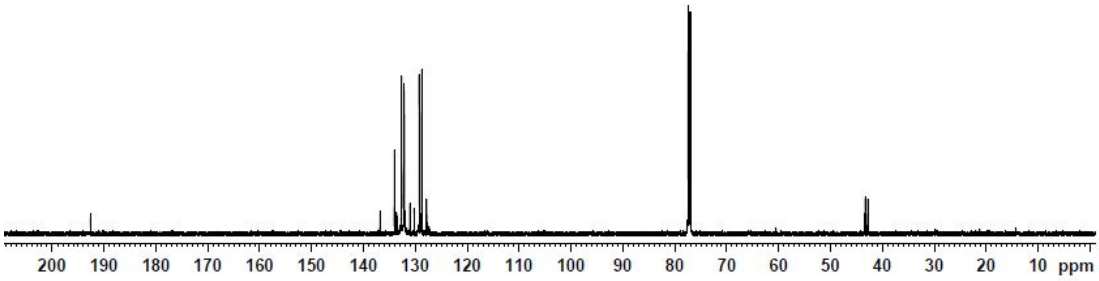

O
O
P
Cl
Cl

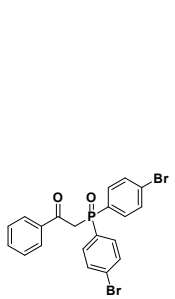

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

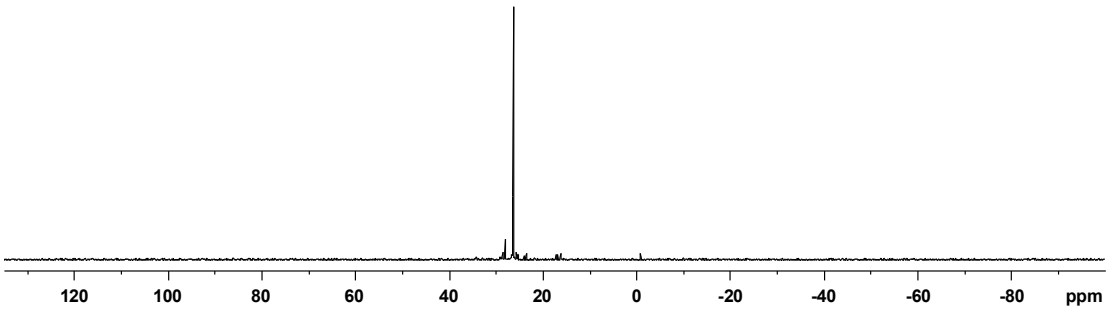

25.94
Cl
O
O
P
Cl
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

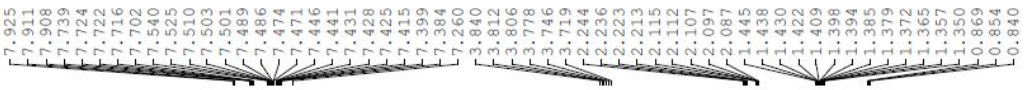

7.952
7.938
7.936
7.663
7.646
7.640
7.623
7.608
7.602
7.598
7.595
7.591
7.585
7.555
7.540
7.438
7.423
7.407
7.260
4.123
4.092
Br
O
O
P
Br
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
5.16
3.06
1.10
2.11
2.00


192.63
192.58
136.86
134.10
132.81
132.72
132.29
132.19
131.13
130.29
129.36
128.85
127.90
127.87
77.48
77.23
76.97
43.36
42.88
Br
Br
O
O
P


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.26
Br
Br
O
O
P


120
100
80
60
40
20
0
-20
-40
-60
-80
ppm


7.925
7.911
7.908
7.739
7.724
7.722
7.716
7.702
7.540
7.525
7.510
7.503
7.501
7.489
7.486
7.474
7.471
7.446
7.441
7.431
7.428
7.425
7.415
7.399
7.384
7.260
3.840
3.812
3.806
3.778
3.746
3.719
2.244
2.236
2.223
2.213
2.115
2.112
2.107
2.097
2.087
1.445
1.438
1.430
1.422
1.409
1.398
1.394
1.385
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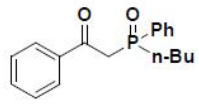
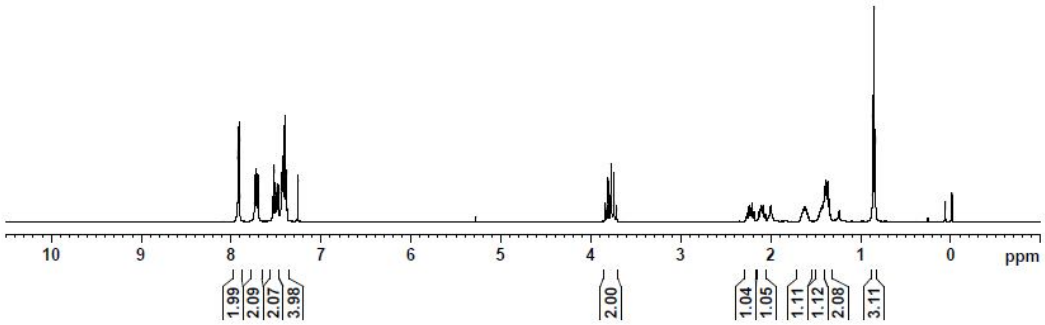
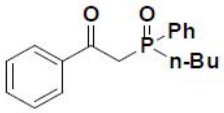
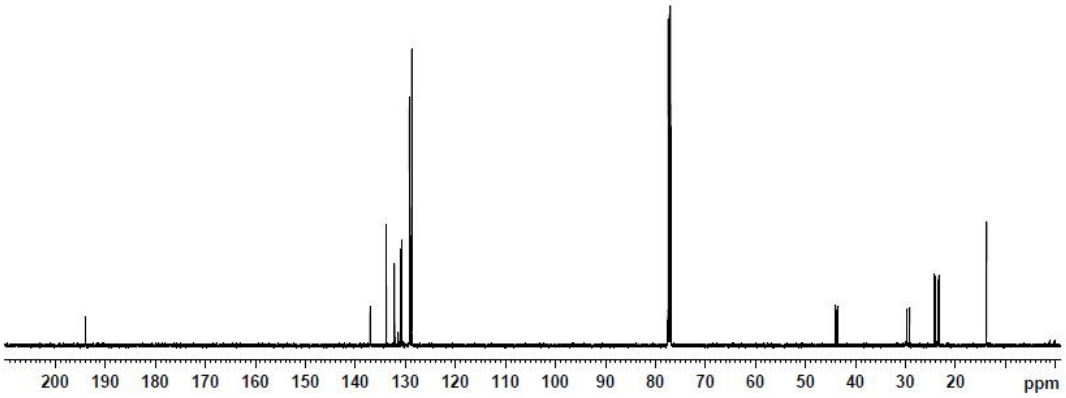
1.357
1.350
0.869
0.854
0.840

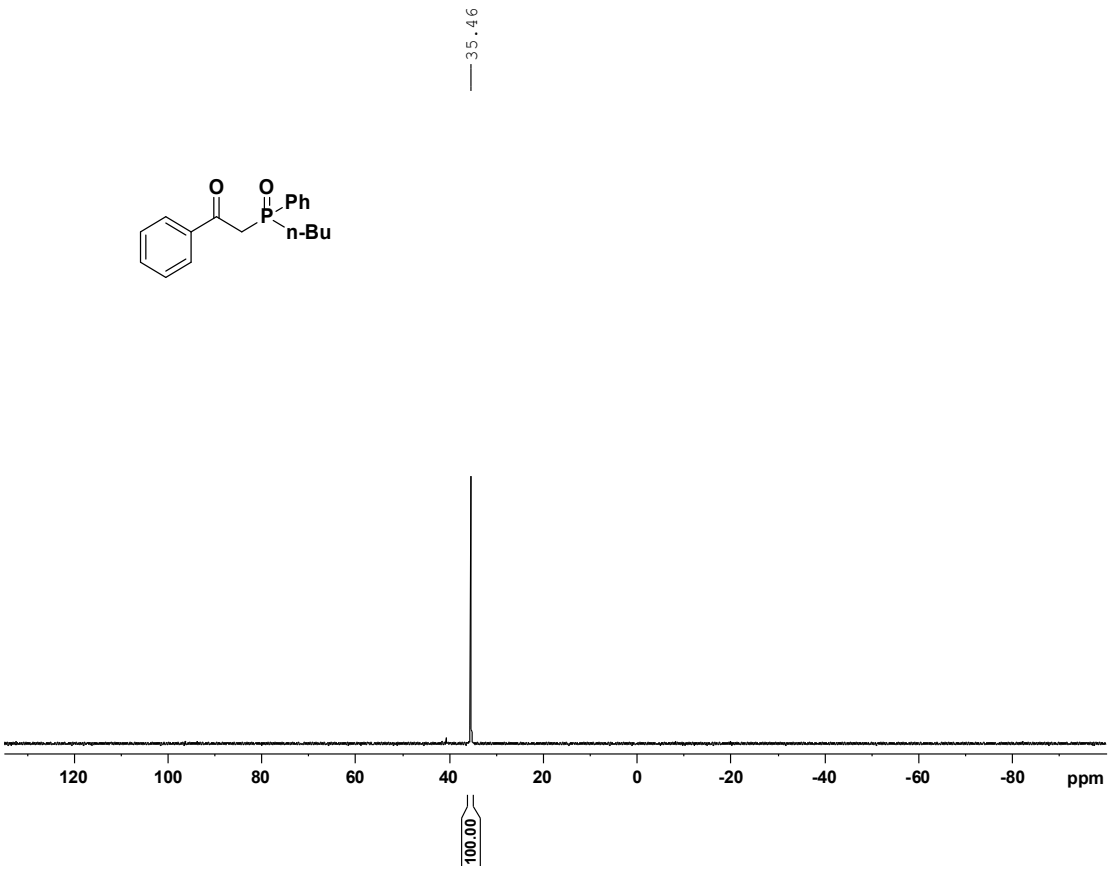

O
O
Ph
P
n-Bu


10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
2.09
2.07
3.98
2.00
1.04
1.05
1.11
1.12
2.08
3.11

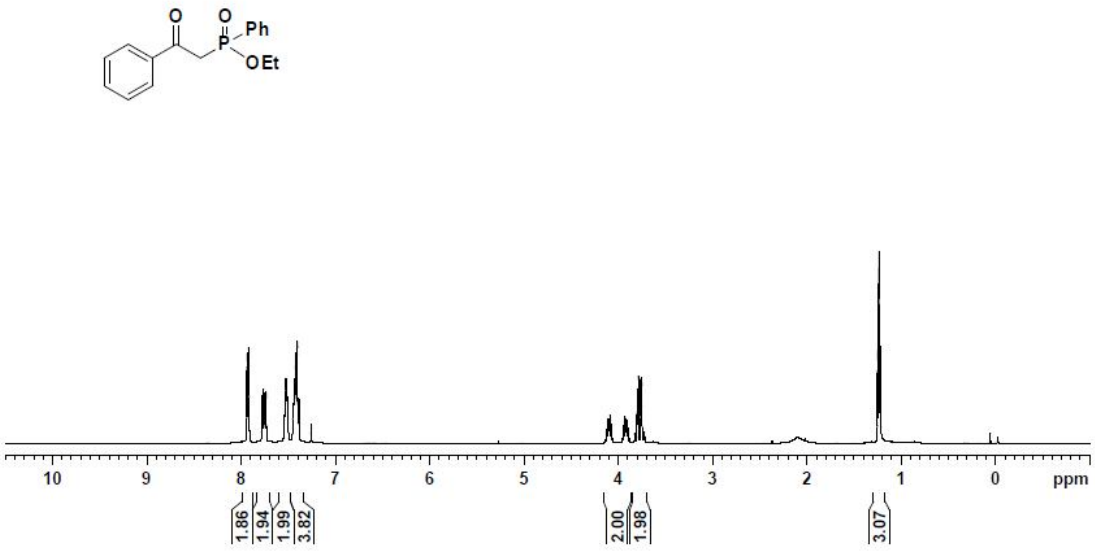

194.00
193.96
137.08
133.86
132.20
132.18
131.42
130.84
130.77
129.24
128.88
128.79
77.49
77.23
76.98
43.94
43.52
29.87
29.71
29.15
24.18
24.06
23.40
23.36
13.74

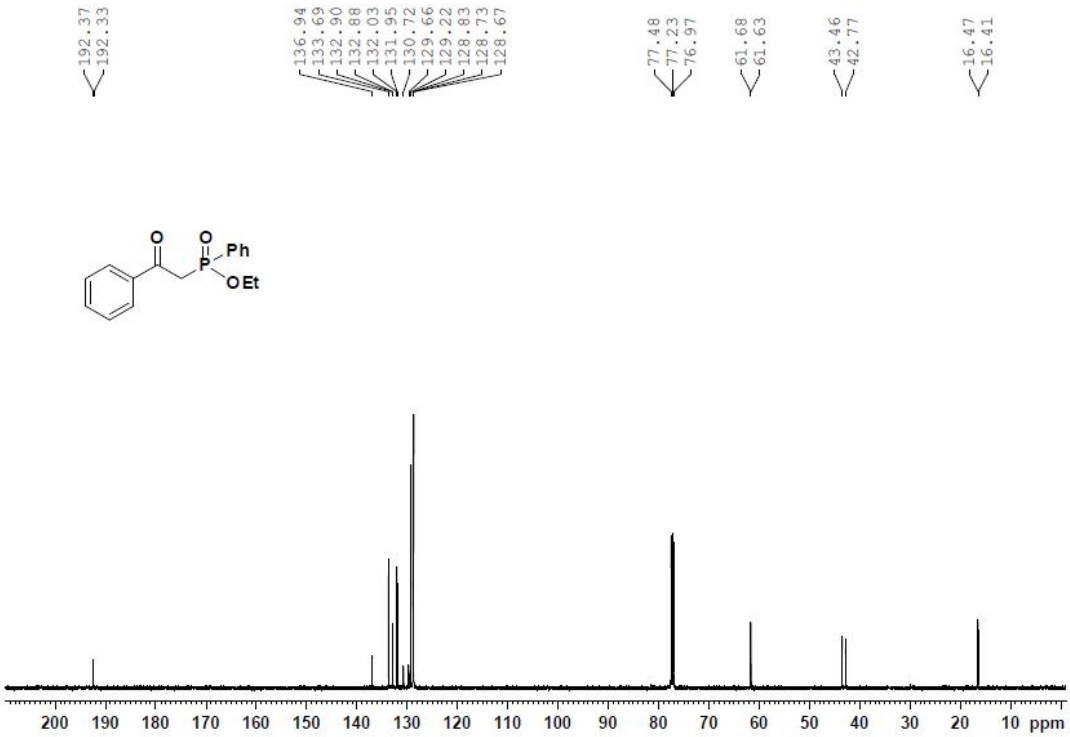

O
O
Ph
P
n-Bu

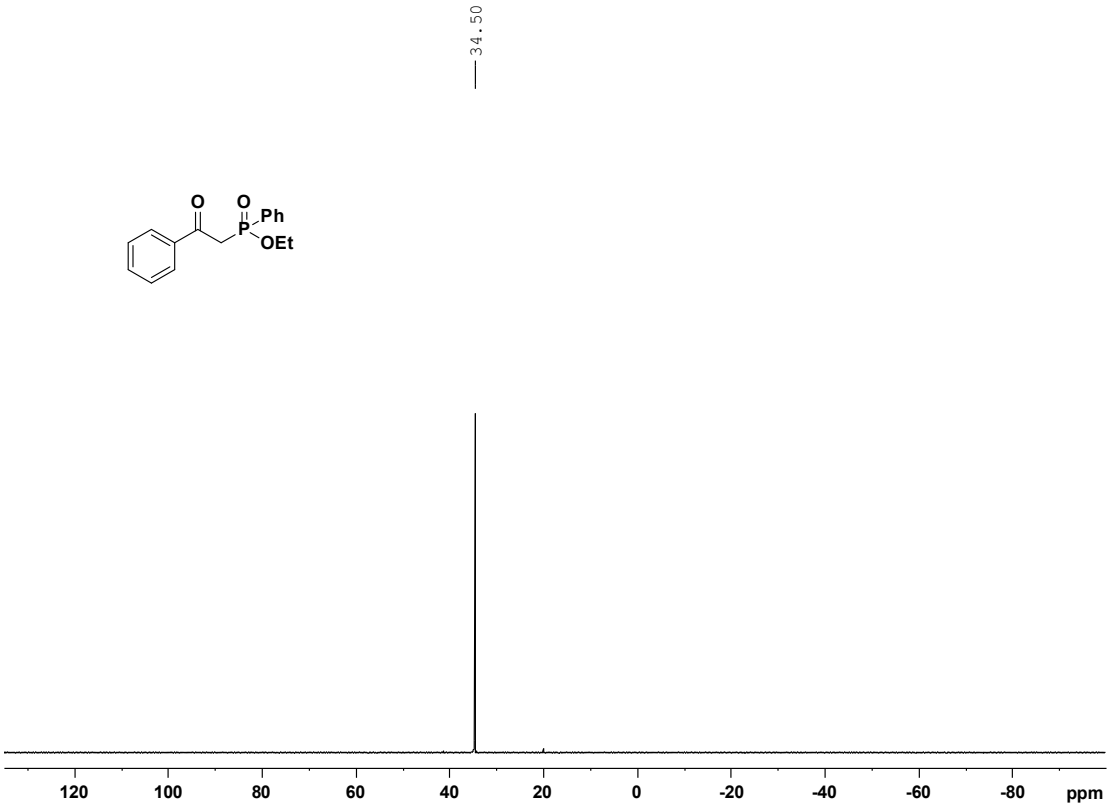

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

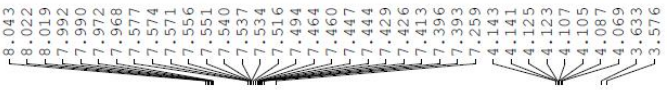

35.46
O
O
Ph
P
n-Bu
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm
100.00


7.939
7.924
7.780
7.765
7.756
7.740
7.543
7.540
7.529
7.515
7.450
7.443
7.435
7.423
7.408
7.392
7.260
4.139
4.125
4.119
4.110
4.105
4.090
4.076
4.061
3.963
3.949
3.934
3.918
3.915
3.900
3.885
3.827
3.800
3.789
3.762
3.752
3.724
3.637
3.592
1.250
1.236
1.222


O
O
Ph
P
OEt
10
9
8
7
6
5
4
3
2
1
0
ppm
1.86
1.94
1.99
3.82
2.00
1.98
3.07


192.37
192.33
136.94
133.69
132.90
132.88
132.03
131.95
130.72
129.66
129.22
128.83
128.73
128.67
77.48
77.23
76.97
61.68
61.63
43.46
42.77
16.47
16.41
O
O
Ph
P
OEt
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


34.50
O
O
Ph
P
OEt
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm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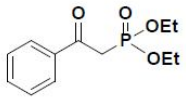
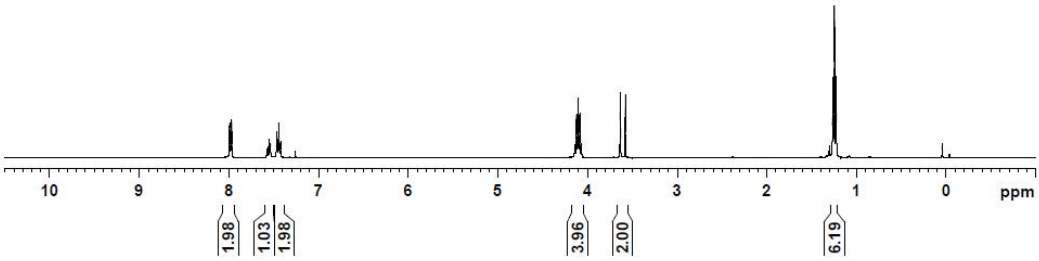
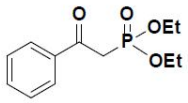
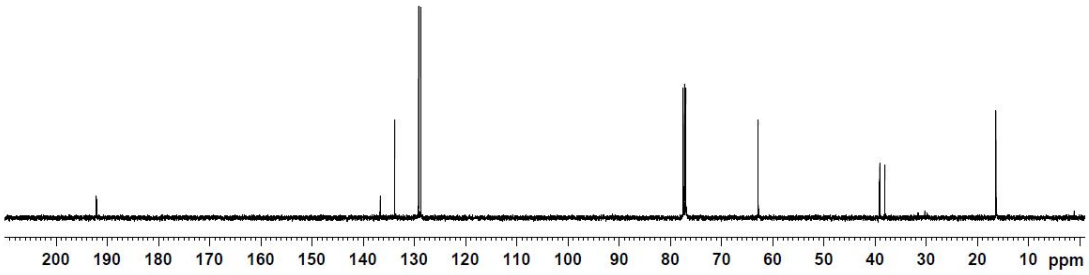
8.022
8.019
7.992
7.990
7.972
7.968
7.577
7.574
7.571
7.556
7.551
7.540
7.537
7.534
7.516
7.494
7.464
7.460
7.447
7.444
7.429
7.426
7.413
7.396
7.393
7.259
4.143
4.141
4.125
4.123
4.107
4.105
4.087
4.069
3.633
3.576
1.264
1.246
1.228

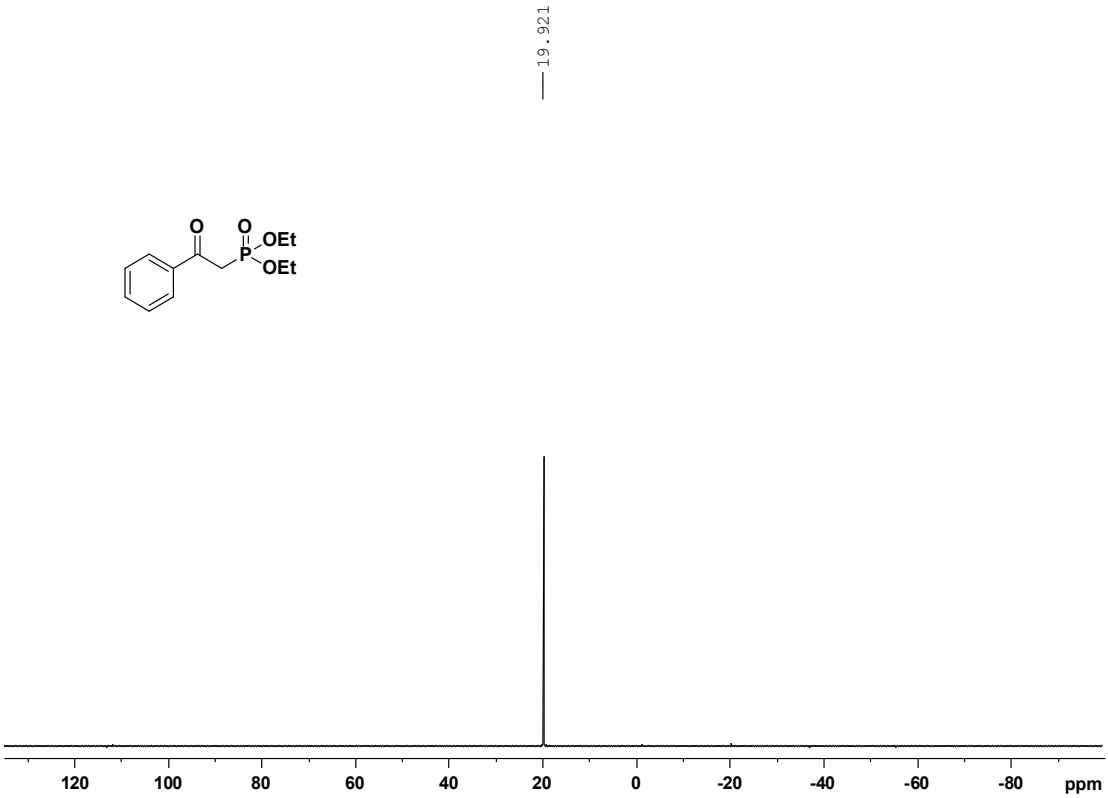

O
O
P
OEt
OEt

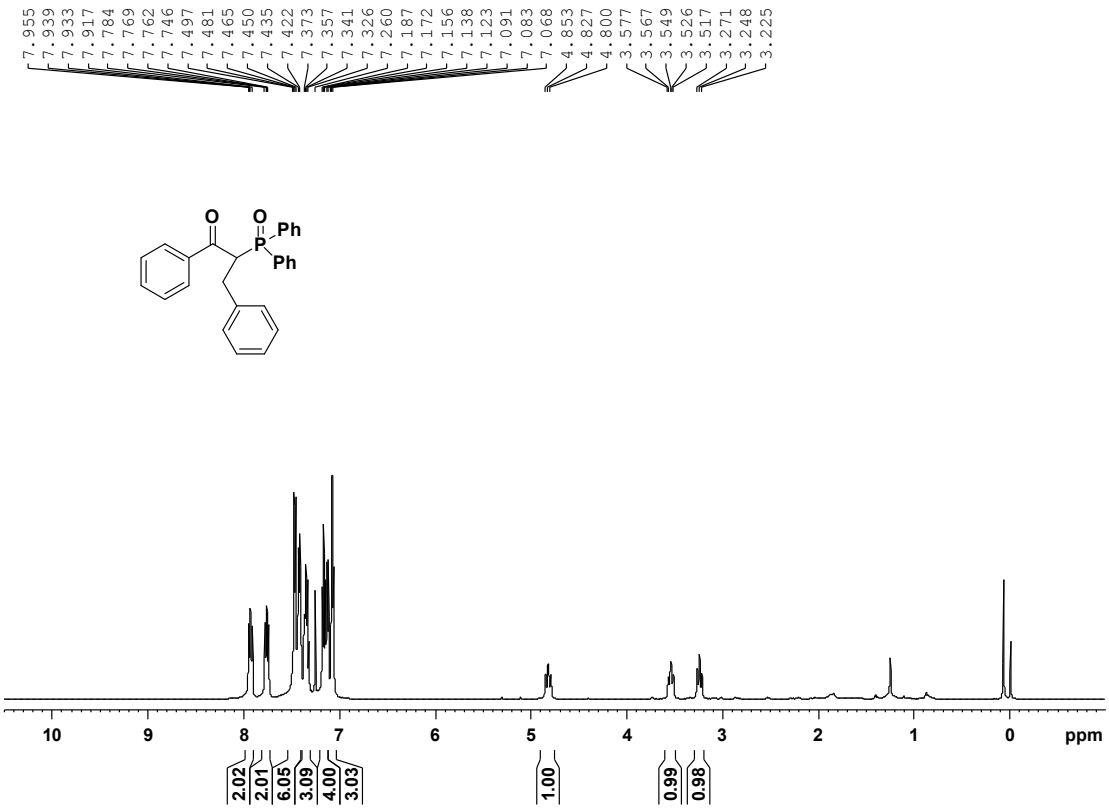

10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
1.03
1.98
3.96
2.00
6.19

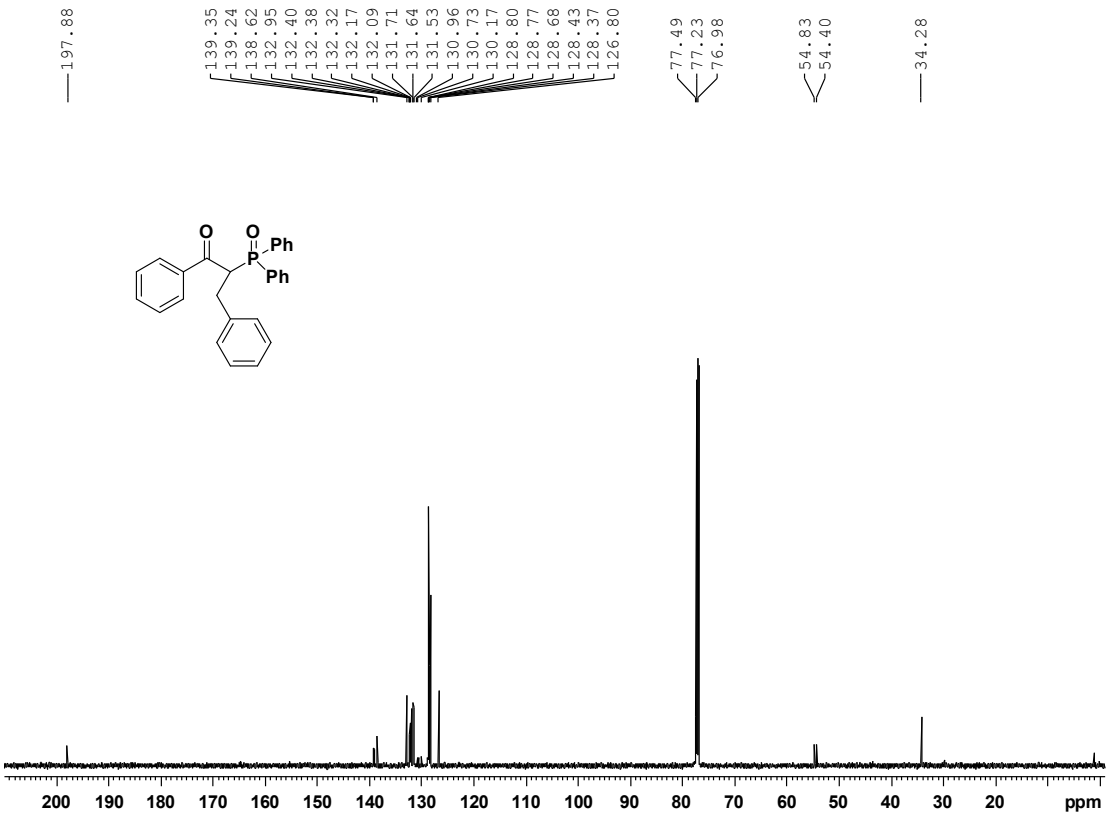

192.14
192.09
136.68
133.82
129.19
128.75
77.49
77.23
76.98
62.85
62.80
39.11
38.08
16.40
16.35


O
O
P
OEt
OEt


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


19.921
O
O
OEt
P
OEt
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm


7.955
7.939
7.933
7.917
7.784
7.769
7.762
7.746
7.497
7.481
7.465
7.450
7.435
7.422
7.373
7.357
7.341
7.326
7.260
7.187
7.172
7.156
7.138
7.123
7.091
7.083
7.068
4.853
4.827
4.800
3.577
3.567
3.549
3.526
3.517
3.271
3.248
3.225
O
O
Ph
P
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.01
6.05
3.09
4.00
3.03
1.00
0.99
0.98


197.88
139.35
139.24
138.62
132.95
132.40
132.38
132.32
132.17
132.09
131.71
131.64
131.53
130.96
130.73
130.17
128.80
128.77
128.68
128.43
128.37
126.80
77.49
77.23
76.98
54.83
54.40
34.28
O
O
Ph
P
Ph
200
190
180
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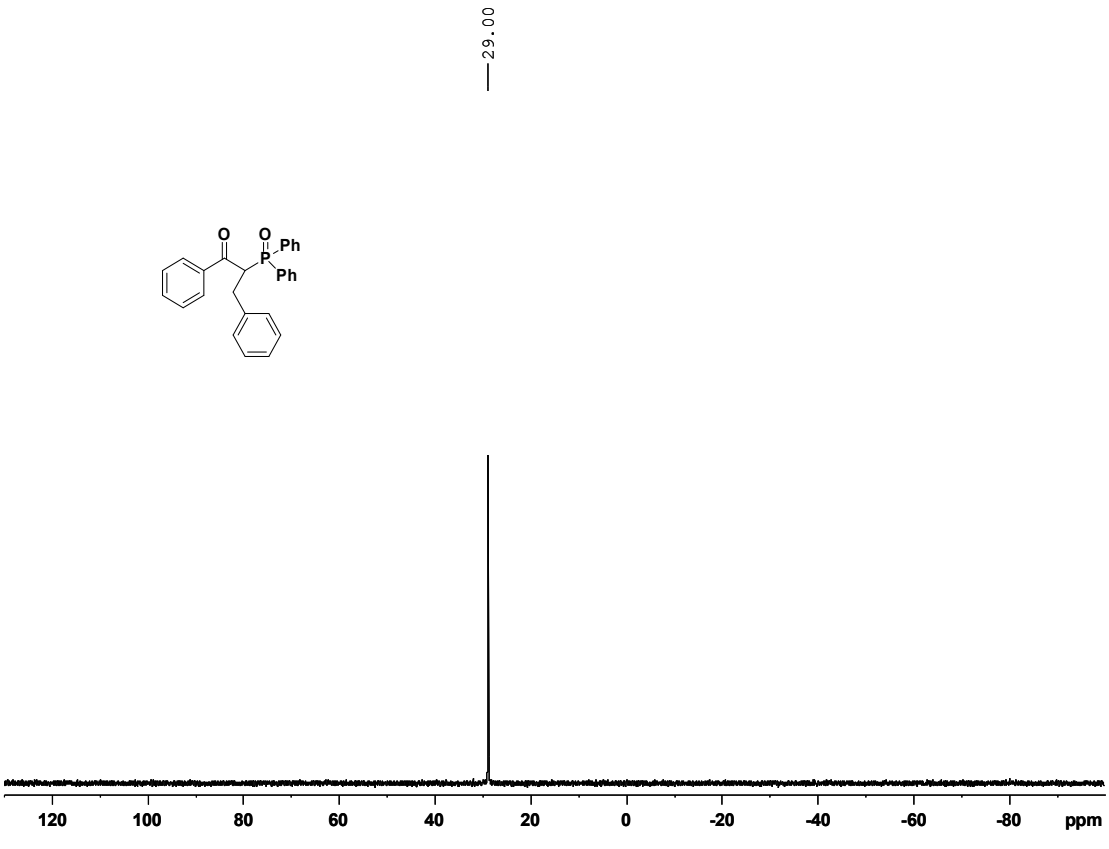
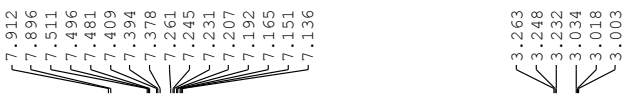
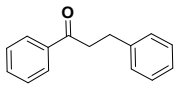
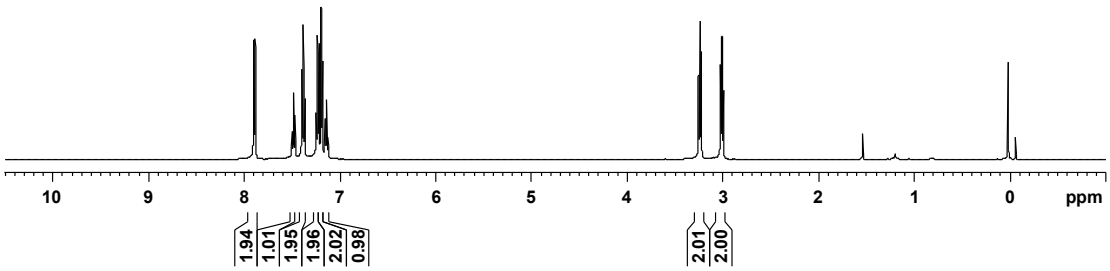
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

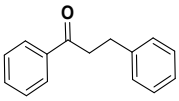

29.00
O
O
Ph
P
Ph
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

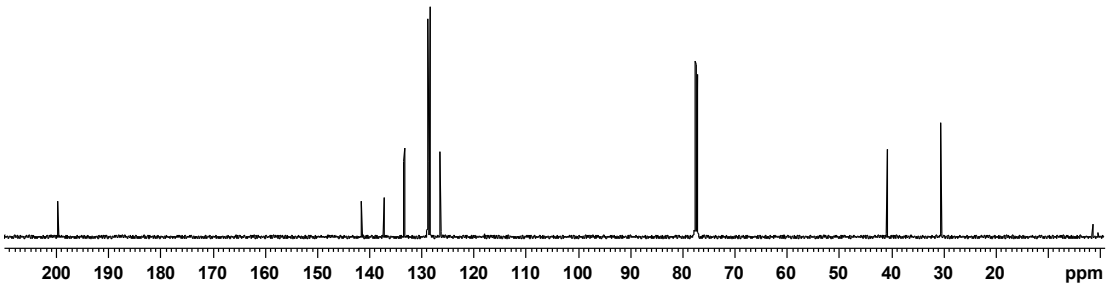

7.912
7.896
7.511
7.496
7.481
7.409
7.394
7.378
7.261
7.245
7.231
7.207
7.192
7.165
7.151
7.136
3.263
3.248
3.232
3.034
3.018
3.003


O


10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.01
1.95
1.96
2.02
0.98
2.01
2.00


199.41
141.49
137.05
133.25
128.80
128.72
128.62
128.23
126.33
77.48
77.23
76.97
40.64
30.32


O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm