

Supporting information for

Silver-catalyzed carbonphosphonation of α,α -diaryl allylic alcohols: synthesis of β -aryl- γ -ketophosphonates

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General Information:

All reactions were performed under N₂ atmosphere. Solvents were dried and degassed by standard methods before use. All allylic alcohols were synthesized according to the method in the literature.¹ Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. ¹H NMR spectra were recorded on a **Bruker DPX-400** (400 MHz) spectrometer with deuterated chloroform as solutions. The chemical shifts δ are reported in ppm relative to tetramethylsilane. ¹³C NMR spectra were recorded at 100 MHz on **Bruker DPX-400**. The chemical shifts δ are reported relative to residual CHCl₃ ($\delta_c = 77.00$ ppm). ³¹P NMR spectra were recorded at 160 MHz on **Bruker DPX-400**. The chemical shifts δ are reported relative to H₃PO₄ ($\delta = 0$ ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants *J* are reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an **Agilent LC-MSD-Trap-XCT** spectrometer with micromass MS software using electrospray ionisation (ESI). Infrared spectra (IR) were measured with a **Bruker ALPHA** spectrometer.

General Procedure for Carbonphosphonation of Allylic Alcohols

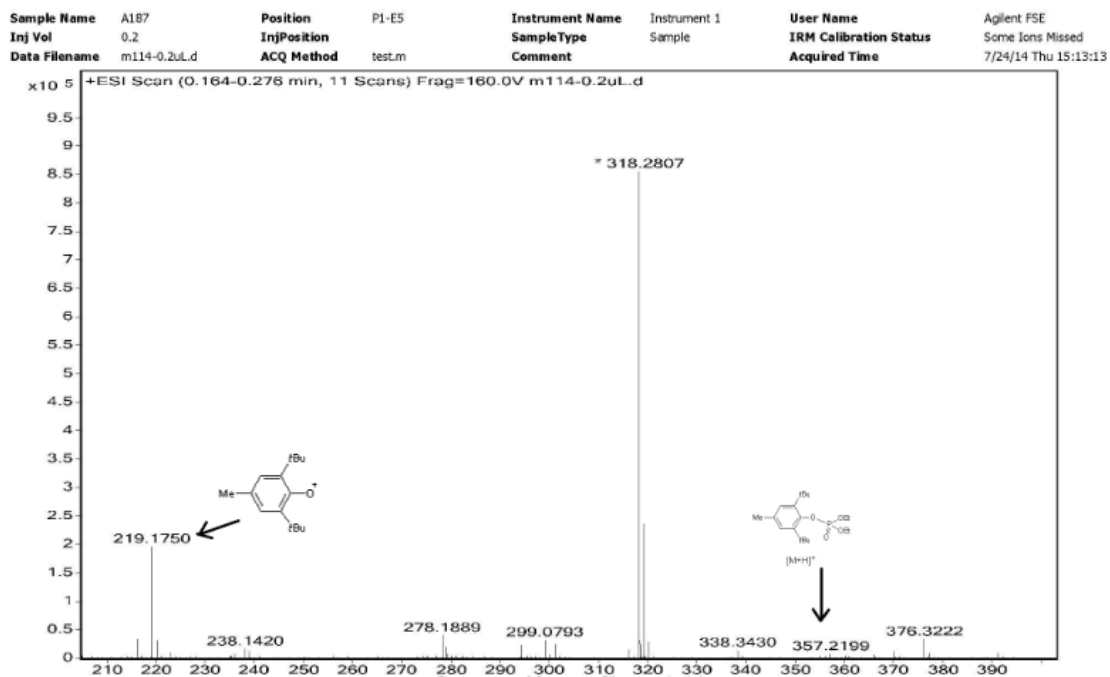
1.5 mmol diethyl phosphate **2** in 3.0 mL CH₃CN was added into the 10 mL flask charged with 0.5 mmol **1**, 5 mol % AgNO₃, 30 mol % Mg(NO₃)₂, 100 mg 4Å MS. The mixture was stirred at 100 °C (oil bath) for 18 h, then cooled down to room temperature. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue

¹ Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653-2656.

was purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/1 - 5/1, v/v) to give the desired product.

Radical trapping Experiment

One equivalent of radical scavenger (TEMPO or BHT) was added to the reaction of **1a** and **2a** in the standard conditions and stirred for two hours. The reaction mixture was cooled to room temperature. Injection of the crude reaction mixture to ESI-MS showed no peak of the desired product. An adduct of diethyl *H*-phosphonate and BHT was detected shown in Figure S1.



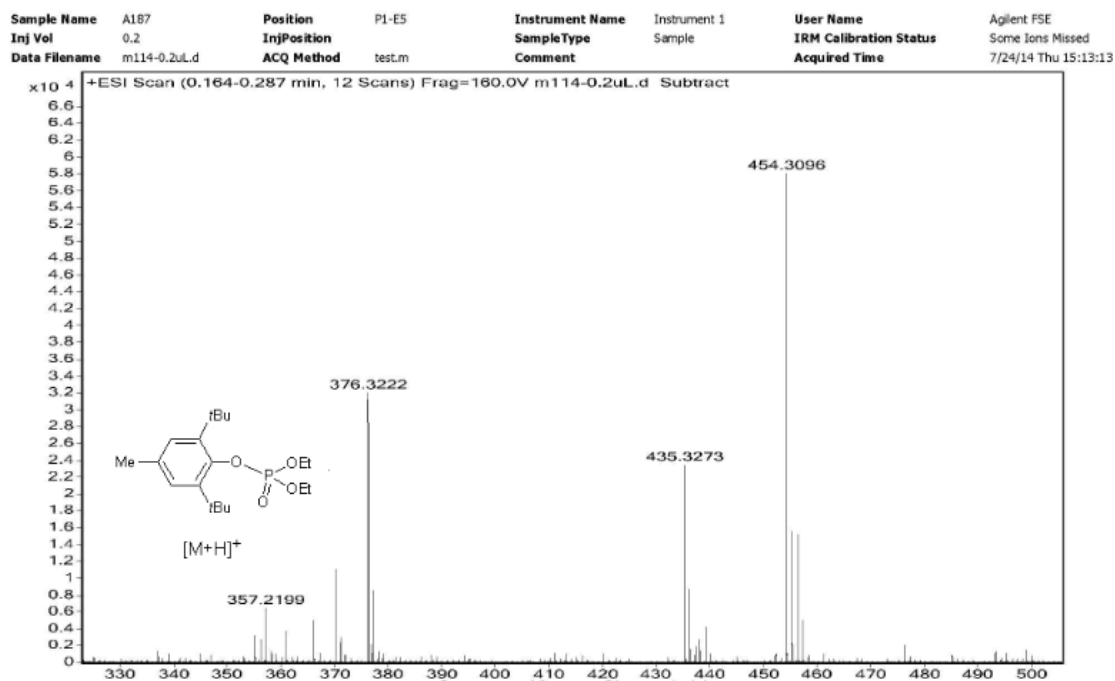
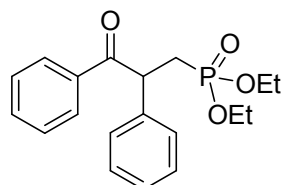


Figure S1. ESI-MS spectra of the mixture with BHT.

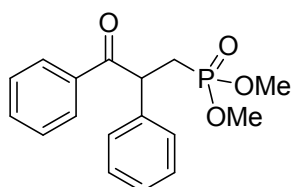
Characterization of Products

Diethyl (3-oxo-2,3-diphenylpropyl)phosphonate (3a)



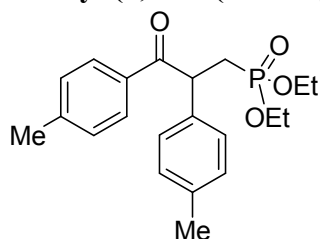
Yellow oil (62 %). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41-7.36 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.29-7.25 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.07-5.00 (m, 1H), 4.02-3.81 (m, 4H), 2.95-2.84 (m, 1H), 2.28-2.18 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.90 (d, *J* = 8.1 Hz), 138.73 (d, *J* = 10.9 Hz), 136.04, 133.13, 129.11, 128.88, 128.58, 128.23, 127.54, 61.70, 61.65, 61.60, 47.62 (d, *J* = 2.0 Hz), 29.75 (d, *J* = 139.2 Hz), 16.30 (d, *J* = 6.3 Hz), 16.17 (d, *J* = 6.5 Hz). ³¹P NMR (162 MHz, CDCl₃): δ. 29.66. IR (KBr, cm⁻¹): 2986, 1684, 1596, 1491, 1449, 1398, 1242, 1027, 965, 781, 700, 518. HRMS (ESI): calculated for C₁₉H₂₄O₄P⁺ [M+H]⁺ m/z 347.1407, found 347.1409.

Dimethyl (3-oxo-2,3-diphenylpropyl)phosphonate (3b)



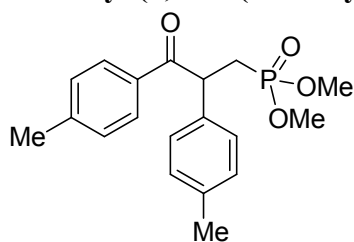
Yellow oil (44 %). ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.3$ Hz, 1H), 7.41-7.36 (m, 2H), 7.33 (d, $J = 7.2$ Hz, 2H), 7.31-7.26 (m, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 5.06-4.99 (m, 1H), 3.63 (d, $J = 10.9$ Hz, 3H), 3.51 (d, $J = 10.8$ Hz, 3H), 2.97-2.86 (m, 1H), 2.29-2.19 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.65 (d, $J = 8.3$ Hz), 138.46 (d, $J = 10.7$ Hz), 135.76, 133.06, 129.03, 128.72, 128.48, 128.02, 127.49, 52.21 (d, $J = 6.3$ Hz), 52.10 (d, $J = 6.6$ Hz), 47.46, 28.69 (d, $J = 138.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 32.46. IR (KBr, cm^{-1}): 2954, 1684, 1451, 1401, 1250, 1031, 899, 819, 699, 518. HRMS (ESI): calculated for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 319.1094, found 319.1104.

Diethyl (2,3-bis(4-methylphenyl)-3-oxopropyl)phosphonate (3d)



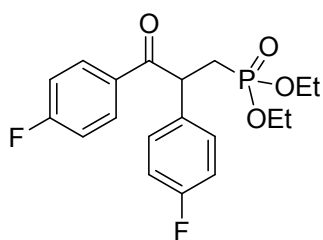
Yellow oil (55 %). ^1H NMR (400 MHz, CDCl_3): δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.21-7.16 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H), 5.01-4.94 (m, 1H), 4.03-3.82 (m, 4H), 2.93-2.83 (m, 1H), 2.34 (s, 2H), 2.25 (s, 2H), 1.20 (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.45 (d, $J = 8.1$ Hz), 143.82, 137.06, 135.88 (d, $J = 11.0$ Hz), 133.42, 129.66, 129.18, 128.93, 127.95, 61.57 (d, $J = 6.5$ Hz), 61.48 (d, $J = 6.4$ Hz), 46.94 (d, $J = 2.0$ Hz), 29.58 (d, $J = 138.6$ Hz), 21.55, 20.95, 16.23 (d, $J = 6.1$ Hz), 16.09 (d, $J = 6.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 29.98. IR (KBr, cm^{-1}): 2984, 1680, 1400, 1239, 1054, 1026, 963, 815, 782, 558. HRMS (ESI): calculated for $\text{C}_{21}\text{H}_{28}\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 375.1720, found 375.1725.

Dimethyl (2,3-bis(4-methylphenyl)-3-oxopropyl)phosphonate (3e)



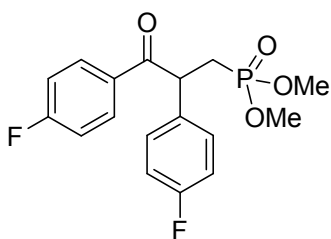
Yellow oil (49%). ^1H NMR (400 MHz, CDCl_3): δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 5.00-4.94 (m, 1H), 3.61 (d, $J = 10.8$ Hz, 3H), 3.51 (d, $J = 10.9$ Hz, 3H), 2.95-2.84 (m, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 2.21-2.15 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.28 (d, $J = 7.8$ Hz), 143.77, 137.04, 135.71 (d, $J = 11.1$ Hz), 133.30, 129.63, 129.11, 128.82, 127.81, 52.14 (d, $J = 6.4$ Hz), 51.92 (d, $J = 6.4$ Hz), 46.87 (d, $J = 2.0$ Hz), 28.65 (d, $J = 138.6$ Hz), 21.42, 20.84. ^{31}P NMR (162 MHz, CDCl_3): δ 32.71. IR (KBr, cm^{-1}): 2954, 1680, 1607, 1403, 1250, 1181, 1031, 902, 819, 558. HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{24}\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 347.1407, found 347.1409.

Diethyl (2,3-bis(4-fluorophenyl)-3-oxopropyl)phosphonate (3f)



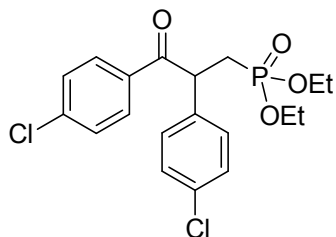
Yellow oil (66%). ^1H NMR (400 MHz, CDCl_3): δ 8.01-7.97 (m, 2H), 7.32-7.28 (m, 2H), 7.08 (t, $J = 8.6$ Hz, 2H), 6.98 (t, $J = 8.6$ Hz, 2H), 5.03-4.96 (m, 1H), 4.07-3.84 (m, 1H), 3.93-3.83 (m, 4H), 2.88-2.77 (m, 1H), 2.26-2.15 (m, 1H), 1.22 (t, $J = 7.0$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.20 (d, $J = 8.6$ Hz), 166.63 (d, $J_{\text{C-F}} = 254.0$ Hz), 162.06 (d, $J_{\text{C-F}} = 245.4$ Hz), 134.18 (dd, $J_{\text{C-P}} = 10.5$ Hz, $J_{\text{C-F}} = 2.7$ Hz), 131.39 (d, $J_{\text{C-F}} = 9.3$ Hz), 129.71 (d, $J_{\text{C-F}} = 8.1$ Hz), 127.73 (d, $J_{\text{C-F}} = 7.9$ Hz), 115.97 (d, $J_{\text{C-F}} = 21.5$ Hz), 114.72 (d, $J_{\text{C-F}} = 21.8$ Hz), 114.89 (d, $J_{\text{C-F}} = 21.2$ Hz), 61.63 (d, $J = 3.7$ Hz), 61.57 (d, $J = 3.9$ Hz), 47.67, 29.70 (d, $J = 139.5$ Hz), 16.18 (d, $J = 6.1$ Hz), 16.06 (d, $J = 6.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 29.33. IR (KBr, cm^{-1}): 2986, 1686, 1597, 1509, 1402, 1232, 1160, 1028, 965, 839, 525. HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{22}\text{F}_2\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 383.1218, found 383.1202.

Dimethyl (2,3-bis(4-fluorophenyl)-3-oxopropyl)phosphonate (3g)



Yellow oil (47%). ^1H NMR (400 MHz, CDCl_3): δ 8.00-7.96 (m, 2H), 7.31-7.27 (m, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 7.01-6.96 (m, 2H), 5.02-4.95 (m, 1H), 3.63 (d, $J = 10.8$ Hz, 3H), 3.53 (d, $J = 10.9$ Hz, 3H), 2.26-2.16 (m, 1H), 2.90-2.79 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.22 (d, $J = 8.7$ Hz), 165.76 (d, $J_{\text{C-F}} = 254.1$ Hz), 162.19 (d, $J_{\text{C-F}} = 245.6$ Hz), 134.18 (dd, $J_{\text{C-P}} = 10.8$ Hz, $J_{\text{C-F}} = 3.2$ Hz), 131.50 (d, $J_{\text{C-F}} = 9.3$ Hz), 129.77 (d, $J_{\text{C-F}} = 8.1$ Hz), 127.83 (d, $J_{\text{C-F}} = 7.9$ Hz), 116.15 (d, $J_{\text{C-F}} = 21.5$ Hz), 115.84 (d, $J_{\text{C-F}} = 21.8$ Hz), 114.99 (d, $J_{\text{C-F}} = 21.2$ Hz), 52.34, 52.27, 46.79, 28.89 (d, $J = 139.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 32.00. IR (KBr, cm^{-1}): 2957, 1685, 1597, 1508, 1406, 1231, 1160, 1033, 902, 836, 804, 599, 559, 522. HRMS (ESI): calculated for $\text{C}_{17}\text{H}_{18}\text{F}_2\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 355.0905, found 393.0909.

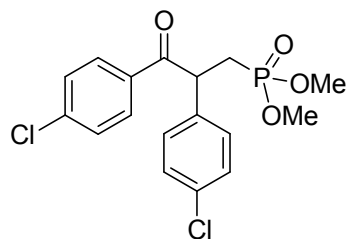
Diethyl (2,3-bis(4-chlorophenyl)-3-oxopropyl)phosphonate (3h)



Yellow oil (65%). ^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.26 (s, 4H), 5.01-4.94 (m, 1H), 4.05-3.85 (m, 4H), 2.89-2.78 (m, 1H), 2.25-2.15 (m, 1H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.26 (d, $J = 8.9$ Hz), 139.35, 136.68 (d, $J = 10.6$ Hz), 133.89, 133.52, 130.04, 129.37, 129.16, 128.85, 61.63 (d, $J = 3.5$ Hz), 61.57 (d, $J = 3.5$ Hz), 46.84, 29.44 (d, $J = 140.0$ Hz), 16.13 (d, $J = 6.1$ Hz), 16.00 (d, $J = 6.3$ Hz).

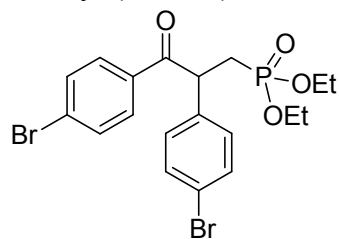
= 6.2 Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 29.12. IR (KBr, cm^{-1}): 2984, 1691, 1488, 1234, 1024, 960, 550, 492. HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 415.0627, found 415.0636.

Dimethyl (2,3-bis(4-chlorophenyl)-3-oxopropyl)phosphonate (3i)



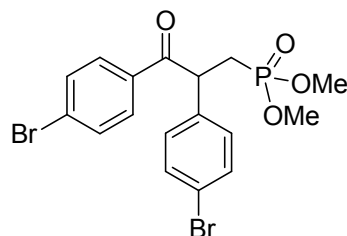
Yellow oil (50%). ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.51 (m, 3H), 7.33-7.27 (m, 3H), 6.91 (d, $J = 8.6$ Hz, 1H), 4.08-3.87 (m, 4H), 1.12 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.23 (d, $J = 8.4$ Hz), 139.74, 136.62 (d, $J = 10.8$ Hz), 133.87, 133.65, 130.07, 129.33, 129.28, 128.91, 52.21 (d, $J = 6.4$ Hz), 46.88 (d, $J = 2.0$ Hz), 28.58 (d, $J = 139.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 31.76. IR (KBr, cm^{-1}): 2955, 1685, 1590, 1489, 1403, 1248, 1093, 1034, 972, 902, 819, 536. HRMS (ESI): calculated for $\text{C}_{17}\text{H}_{18}\text{Cl}_2\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 387.0314, found 387.0316.

Diethyl (2,3-bis(4-bromophenyl)-3-oxopropyl)phosphonate (3j)



Yellow oil (57%). ^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 4.99-4.92 (m, 1H), 4.04-3.85 (m, 1H), 2.88-2.78 (m, 1H), 2.24-2.14 (m, 1H), 1.22 (t, $J = 7.0$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.39 (d, $J = 8.5$ Hz), 137.18 (d, $J = 10.6$ Hz), 134.31, 132.13, 131.85, 130.12, 129.71, 128.44, 121.65, 61.63 (d, $J = 4.0$ Hz), 61.57 (d, $J = 4.1$ Hz), 46.92 (d, $J = 1.9$ Hz), 29.40 (d, $J = 139.8$ Hz), 16.14 (d, $J = 6.1$ Hz), 16.00 (d, $J = 6.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 29.06. IR (KBr, cm^{-1}): 2983, 1686, 1585, 1485, 1399, 1245, 1063, 1029, 964, 820, 796, 529. HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{22}\text{Br}_2\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 502.9617, found 502.9626.

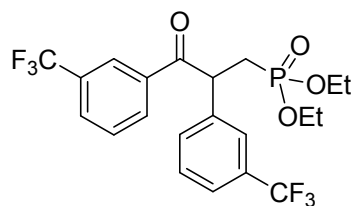
Dimethyl (2,3-bis(4-bromophenyl)-3-oxopropyl)phosphonate (3k)



Yellow oil (32%). ^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.19-7.16 (m, 2H), 4.96-4.89 (m, 1H), 3.65 (d, $J = 10.9$ Hz, 3H), 3.54 (d, $J = 10.9$ Hz, 3H), 2.90-2.79 (m, 1H), 2.24-2.14 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.52 (d, $J = 8.3$ Hz), 137.27 (d, $J = 10.8$ Hz), 134.44, 132.41, 132.08, 130.30, 129.81, 128.70, 121.95, 52.38 (d, $J = 6.5$ Hz), 47.12 (d, $J = 1.9$ Hz), 28.68 (d, $J = 139.7$ Hz). ^{31}P NMR (162

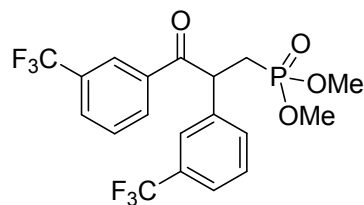
MHz, CDCl₃): δ . 31.71. IR (KBr, cm⁻¹): 2954, 1684, 1585, 1486, 1397, 1250, 1058, 1032, 902, 823, 527. HRMS (ESI): calculated for C₁₇H₁₈Br₂O₄P⁺ [M+H]⁺ m/z 474.9304, found 474.9305.

Diethyl (3-oxo-2,3-bis(3-trifluoromethylphenyl)propyl)phosphonate (3l)



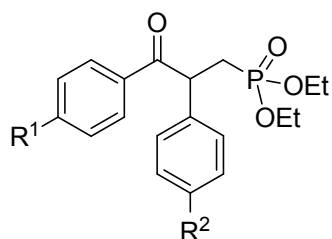
Yellow oil (63%). ¹H NMR (400 MHz, CDCl₃): δ 8.24 (s, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.63 (s, 1H), 7.60-7.50 (m, 3H), 7.45 (t, J = 7.7 Hz, 1H), 5.16-5.09 (m, 1H), 4.07-3.86 (m, 4H), 2.93-2.83 (m, 1H), 2.33-2.24 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 196.13 (d, J_{C-P} = 8.8 Hz), 138.88 (d, J_{C-P} = 10.5 Hz), 136.07, 131.77, 131.52, 131.49 (q, J_{C-F} = 32.3 Hz), 131.31 (q, J_{C-F} = 32.5 Hz), 129.7 (q, J_{C-F} = 3.3 Hz), 129.67, 129.37, 125.55 (q, J_{C-F} = 3.3 Hz), 124.91 (q, J_{C-F} = 3.2 Hz), 124.66 (q, J_{C-F} = 3.8 Hz), 123.62 (q, J_{C-F} = 271.0 Hz), 123.40 (q, J_{C-F} = 271.2 Hz), 61.81 (d, J_{C-P} = 6.5 Hz), 61.67 (d, J_{C-P} = 6.9 Hz), 47.49, 29.71 (d, J_{C-P} = 140.3 Hz), 16.09 (d, J_{C-P} = 6.1 Hz), 15.94 (d, J_{C-P} = 6.3 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 32.46. IR (KBr, cm⁻¹): 2989, 1694, 1331, 1128, 1074, 968, 820, 696. HRMS (ESI): calculated for C₂₁H₂₂F₆O₄P⁺ [M+H]⁺ m/z 483.1154, found 483.1166.

Dimethyl (3-oxo-2,3-bis(3-trifluoromethylphenyl)propyl)phosphonate (3m)



Yellow oil (53%). ¹H NMR (400 MHz, CDCl₃): δ 8.22 (s, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.61 (s, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.8 Hz, 1H), 5.13-5.06 (m, 1H), 3.66 (d, J = 10.9 Hz, 3H), 3.55 (d, J = 10.9 Hz, 3H), 2.96-2.85 (m, 1H), 2.31-2.22 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 196.08 (d, J = 8.3 Hz), 138.91 (d, J = 10.9 Hz), 136.12, 131.79, 131.67 (q, J = 32.5 Hz), 131.44 (q, J = 32.8 Hz), 129.88, 129.84, 129.80, 129.43, 125.61 (q, J = 3.8 Hz), 124.94 (q, J = 3.7 Hz), 124.79 (q, J = 3.7 Hz), 123.66 (q, J = 270.5 Hz), 123.46 (q, J = 271.0 Hz), 52.36 (d, J = 6.5 Hz), 52.26 (d, J = 6.5 Hz), 47.58 (d, J = 2.0 Hz), 28.91 (d, J = 140.2 Hz). ³¹P NMR (162 MHz, CDCl₃): δ . 31.18. IR (KBr, cm⁻¹): 2960, 1693, 1401, 1330, 1245, 1172, 1128, 1068, 1035, 905, 828, 701, 522. HRMS (ESI): calculated for C₁₉H₁₈F₆O₄P⁺ [M+H]⁺ m/z 455.0841, found 455.0845.

Diethyl (3-(*p*-methoxyphenyl)-3-oxo-2-phenylpropyl)phosphonate (3n) and Diethyl (2-(*p*-methoxyphenyl)-3-oxo-3-phenylpropyl)phosphonate (3n')

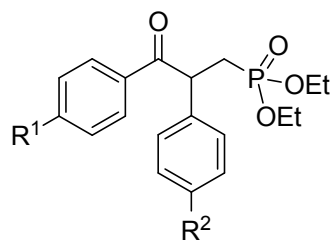


R¹ = OMe, R² = H, **3n**

R¹ = H, R² = OMe, **3n'**

Yellow oil (67%, **3n:3n'** = 2.5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.48-7.16 (m, 7H), 6.87-6.79 (m, 2.7H), 5.02-4.96 (m, 1H), 4.00-3.93 (m, 2.1H), 3.90-3.82 (m, 2H), 3.80 (s, 3H), 3.73 (s, 1.2H), 2.92-2.81 (m, 1.1H), 2.27-2.14 (m, 1H), 1.3-1.24 (m, 1.2H), 1.21-1.17 (m, 3H), 1.12-1.08 (m, 4.4H). ¹³C NMR (100 MHz, CDCl₃): δ 196.25 (d, *J* = 8.2 Hz), 163.42, 139.15 (d, *J* = 10.5 Hz), 132.94, 131.13, 129.24, 128.95, 128.90, 128.77, 128.48, 128.15, 128.09, 127.32, 127.27, 125.96, 114.41, 113.70, 113.50, 61.54 (d, *J* = 3.1 Hz), 61.48 (d, *J* = 3.1 Hz), 55.27 (d, *J* = 2.0 Hz), 47.15, 47.13, 46.68, 29.67 (d, *J* = 139.1 Hz), 16.22 (d, *J* = 6.1 Hz), 16.09 (d, *J* = 6.3 Hz). ³¹P NMR (162 MHz, CDCl₃): δ. 29.89, 29.83. IR (KBr, cm⁻¹): 2986, 1684, 1596, 1491, 1449, 1398, 1242, 1027, 965, 781, 700, 518. HRMS (ESI): calculated for C₂₀H₂₆O₅P⁺ [M+H]⁺ *m/z* 377.1512, found 377.1514.

Diethyl (3-oxo-2-phenyl-2-(*p*-trifluoromethylphenyl)propyl)phosphonate (3o)
and Diethyl (3-oxo-2-phenyl-3-(*p*-trifluoromethylphenyl)propyl)phosphonate (3o')

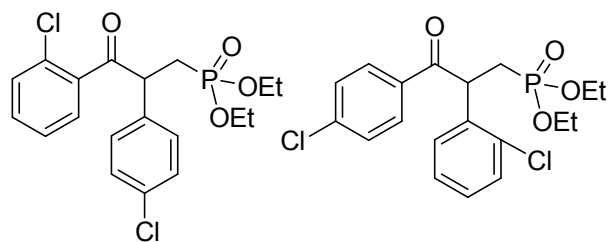


R¹ = H, R² = CF₃, **3o**

R¹ = CF₃, R² = H, **3o'**

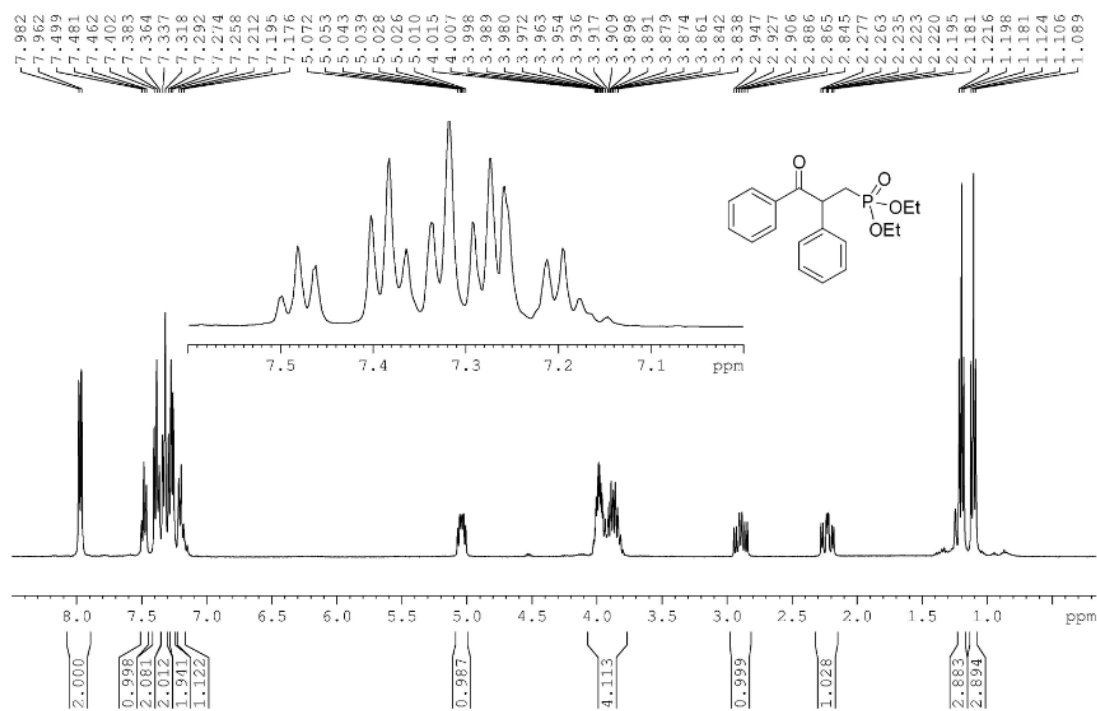
Yellow oil (77%, **3o:3o'** = 11.4:1). ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.57-7.40 (m, 7.4H), 7.32-7.29 (m, 0.4H), 5.17-5.10 (m, 1H), 5.07-5.00 (m, 0.08H), 4.07-3.82 (m, 4.6H), (m, 4H), 2.92-2.82 (m, 1H), 2.31-2.21 (m, 1.5H), 1.23-1.18 (m, 3.2H), 1.12-1.08 (m, 3.2H). ¹³C NMR (100 MHz, CDCl₃): δ 197.26 (d, *J* = 8.7 Hz), 142.60 (d, *J* = 9.5 Hz), 135.61, 133.42, 129.94, 129.61, 129.22, 129.05, 128.75, 128.67, 128.61, 128.11, 127.90, 127.76, 126.37, 125.96, 125.92, 125.89, 125.85, 125.58, 125.54, 125.19, 122.49, 61.75, 61.67, 61.60, 47.25 (d, *J* = 2.0 Hz), 29.65 (d, *J* = 140.3 Hz), 16.16 (d, *J* = 6.1 Hz), 15.99 (d, *J* = 6.4 Hz). ³¹P NMR (162 MHz, CDCl₃): δ. 29.29, 28.93. IR (KBr, cm⁻¹): 2986, 1684, 1596, 1491, 1449, 1398, 1242, 1027, 965, 781, 700, 518. HRMS (ESI): calculated for C₂₀H₂₃F₃O₄P⁺ [M+H]⁺ *m/z* 415.1281, found 415.1284.

Diethyl (2-(*p*-chlorophenyl)-3-oxo-3-(*o*-chlorophenyl)propyl)phosphonate (3p)
and Diethyl (3-oxo-2-(*o*-chlorophenyl)-3-(*p*-chlorophenyl)propyl)phosphonate (3p')

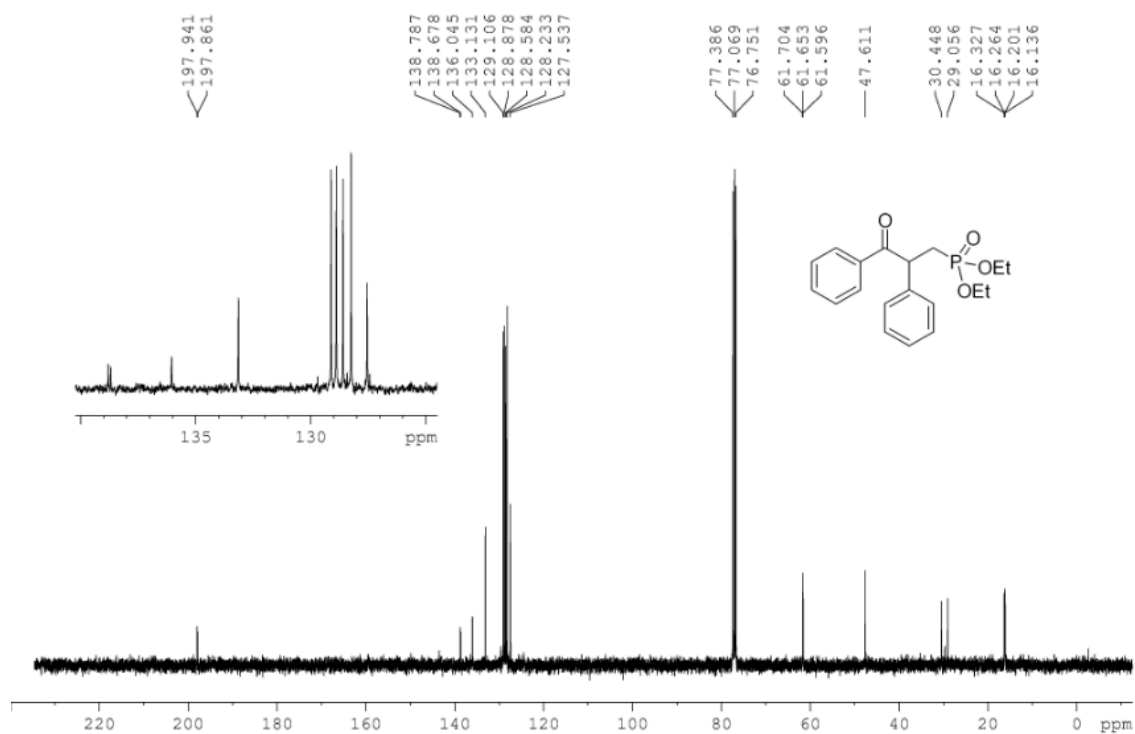


Yellow oil (69%, **3p:3p'** = 2.5:1). ^1H NMR (400 MHz, CDCl_3): δ 8.79 (s, 0.4H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.38-7.28 (m, 5.6H), 7.24-7.21 (m, 3H), 7.14 (d, $J = 8.4$ Hz, 2H), 6.03-5.97 (m, 0.4H), 4.88-4.81 (m, 1H), 4.33-4.22 (m, 1H), 4.18-4.09 (m, 1.3H), 4.07-3.97 (m, 2H), 3.95-3.84 (m, 1H), 2.91-2.80 (m, 1H), 2.68-2.57 (m, 0.4H), 2.42-2.19 (m, 0.5H), 2.29-2.19 (m, 1H), 1.43 (t, $J = 7.0$ Hz, 1.3H), 1.34 (t, $J = 7.0$ Hz, 1.5H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.15 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 199.62 (d, $J = 10.9$ Hz), 167.98, 138.11, 138.02, 137.94, 135.22, 135.13, 133.68, 131.66, 131.01, 130.73, 130.41, 130.06, 129.96, 129.41, 128.96, 128.84, 128.75, 127.99, 127.81, 126.56, 126.41, 63.11 (d, $J = 6.7$ Hz), 62.59 (d, $J = 6.8$ Hz), 61.70, 61.64, 61.58, 53.74 (d, $J = 6.6$ Hz), 51.21 (d, $J = 1.9$ Hz), 29.59 (d, $J = 137.1$ Hz), 28.20 (d, $J = 140.8$ Hz), 16.40 (d, $J = 5.5$ Hz), 16.31 (d, $J = 5.7$ Hz), 16.30 (d, $J = 6.3$ Hz), 16.21 (d, $J = 6.2$ Hz), 16.10 (d, $J = 6.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ . 29.09, 28.99. IR (KBr, cm^{-1}): 2986, 1684, 1596, 1491, 1449, 1398, 1242, 1027, 965, 781, 700, 518. HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{O}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ m/z 415.0627, found 415.0629.

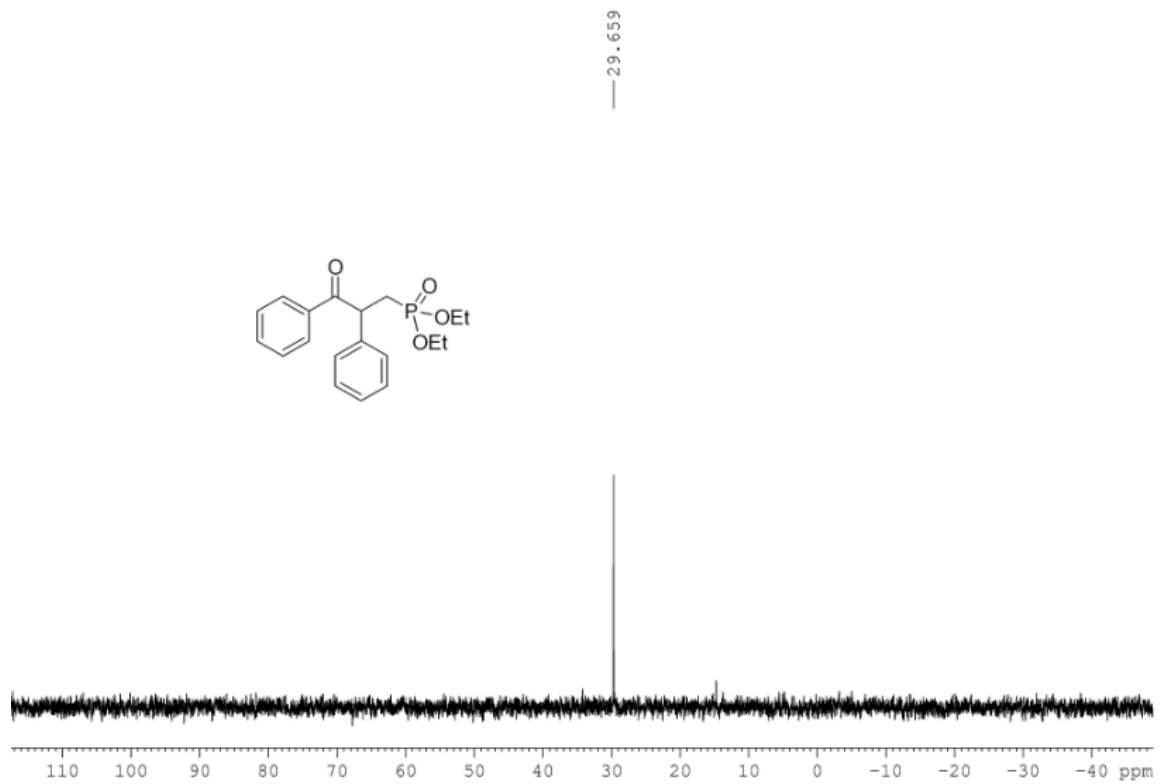
NMR and HRMS Spectra



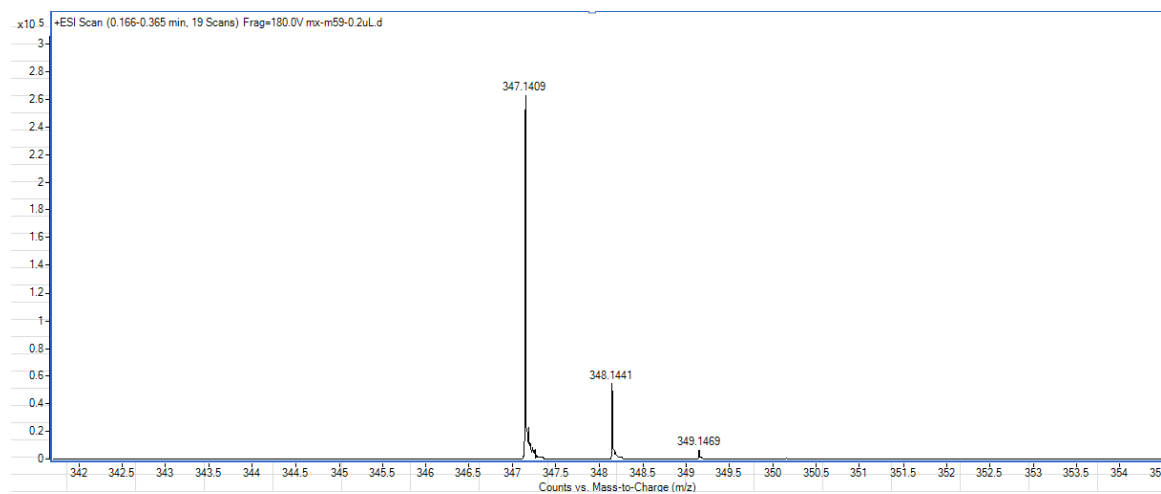
¹H NMR spectrum of compound **3a**



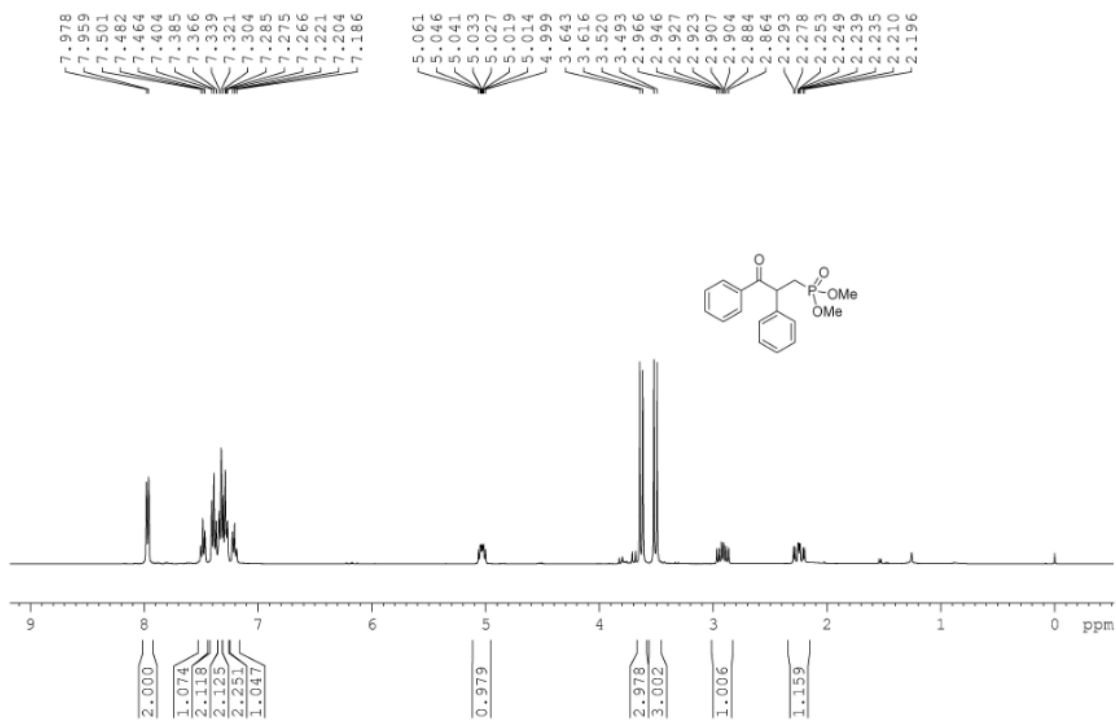
¹³C NMR spectrum of compound **3a**



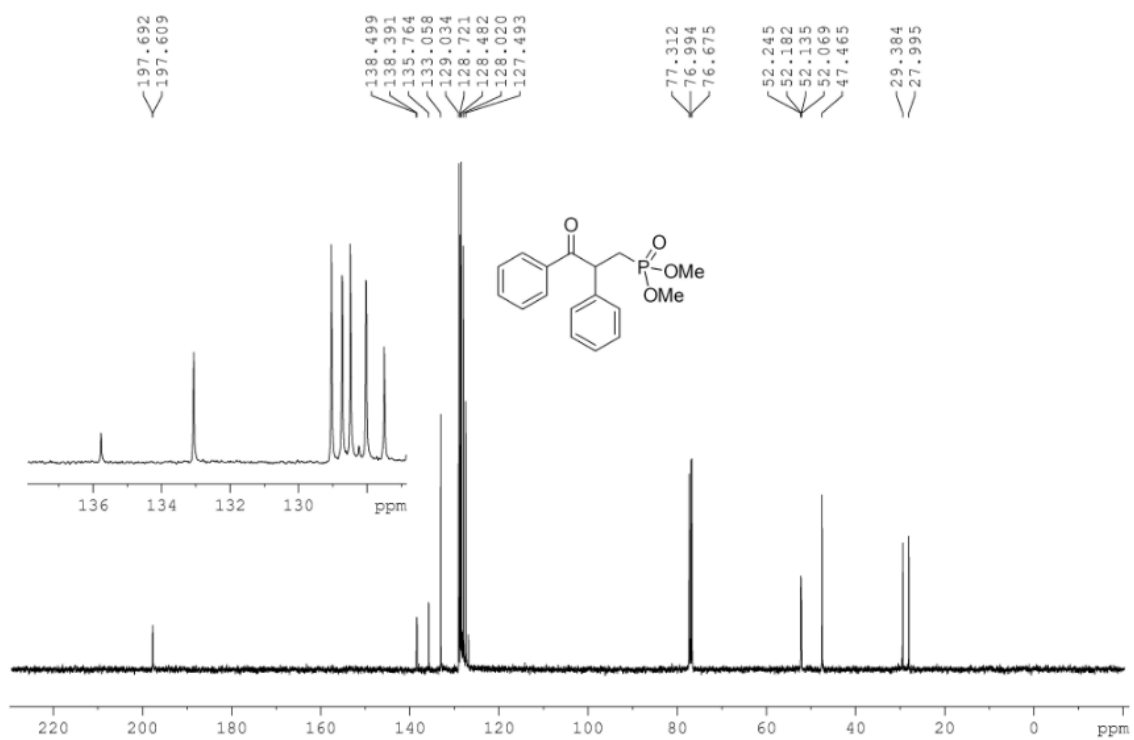
^{31}P NMR spectrum of compound **3a**



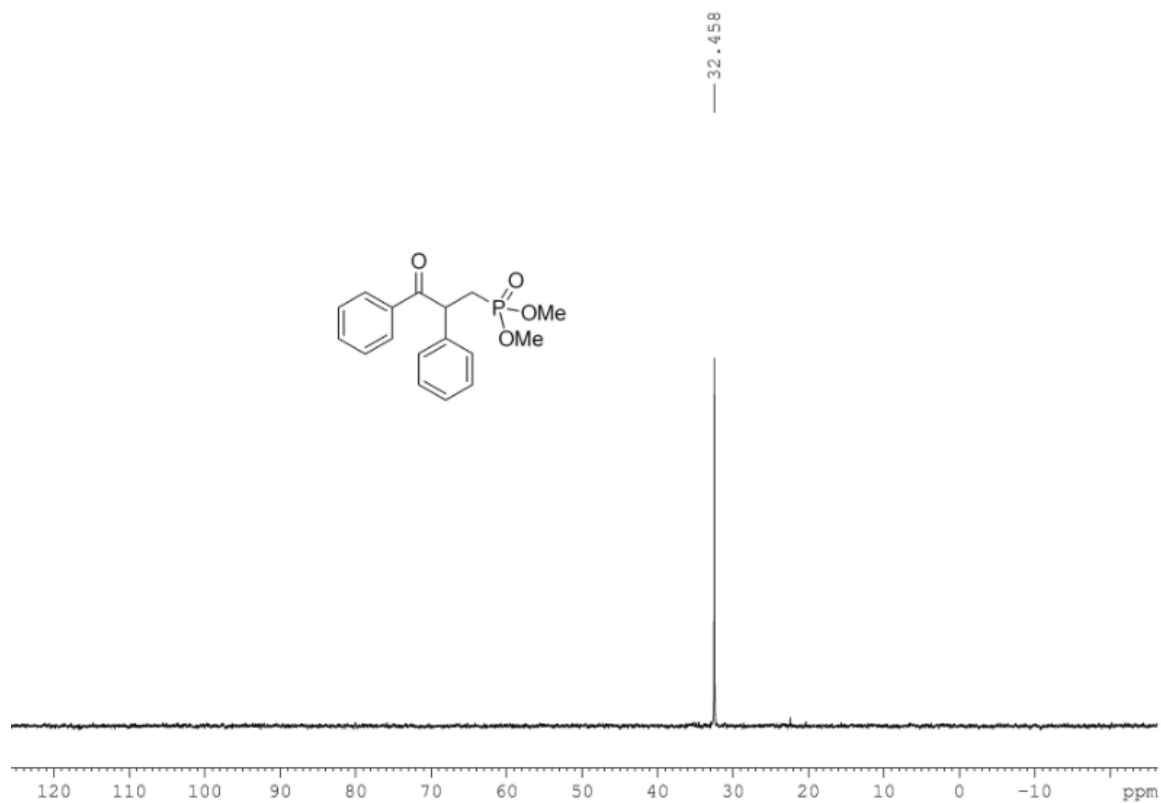
HRMS spectrum of compound **3a**



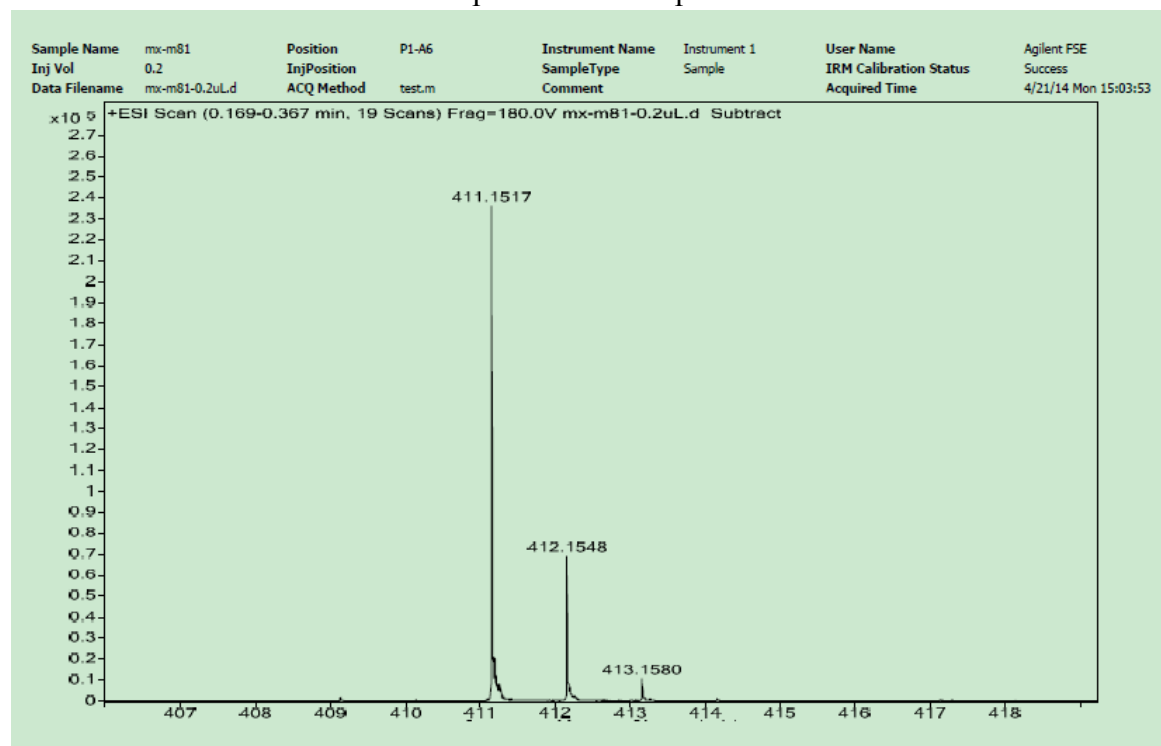
¹H NMR spectrum of compound **3b**



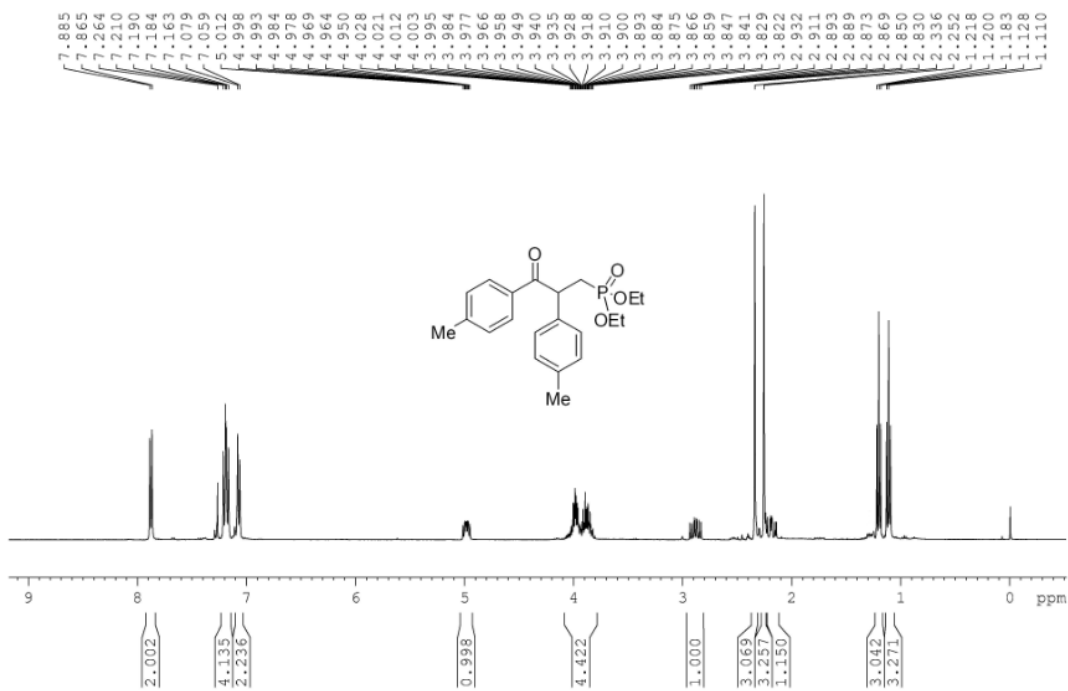
¹³C NMR spectrum of compound **3b**



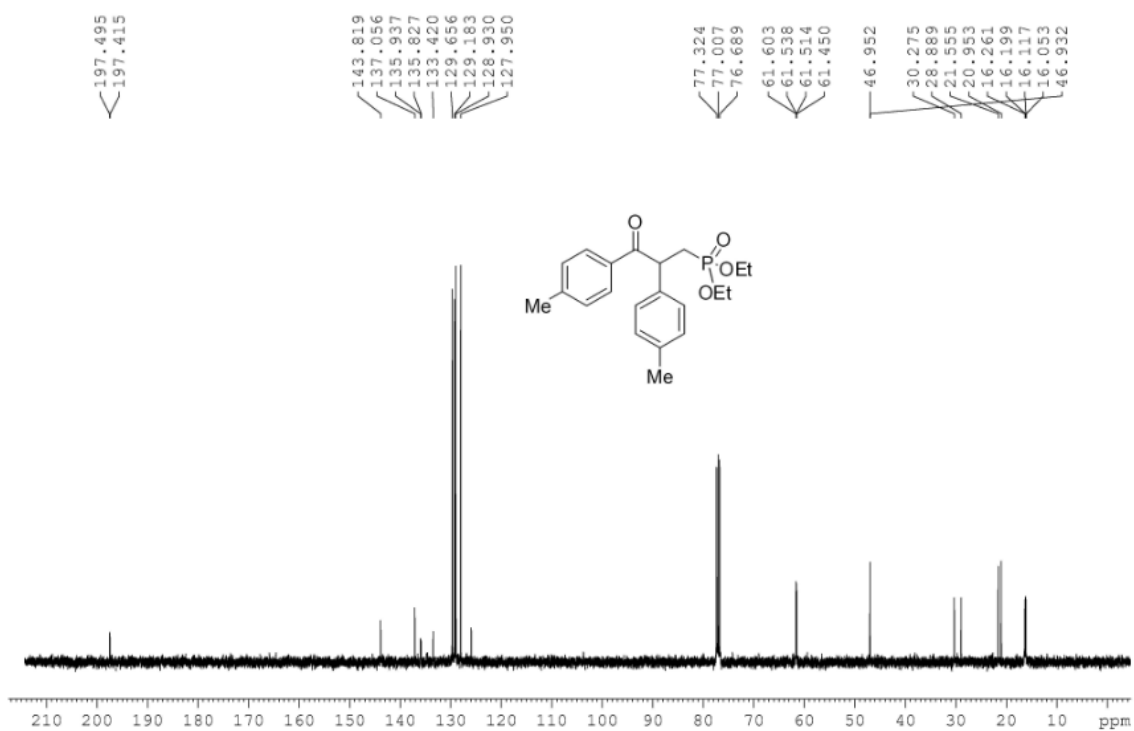
³¹P NMR spectrum of compound **3b**



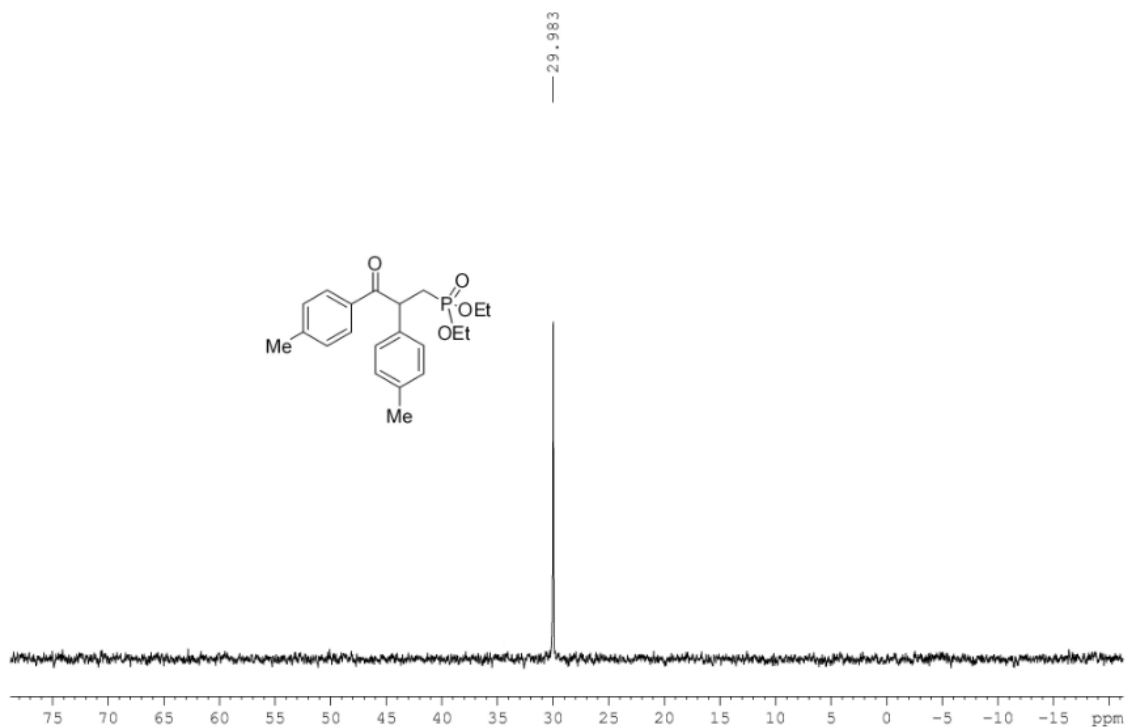
HRMS spectrum of compound **3b**



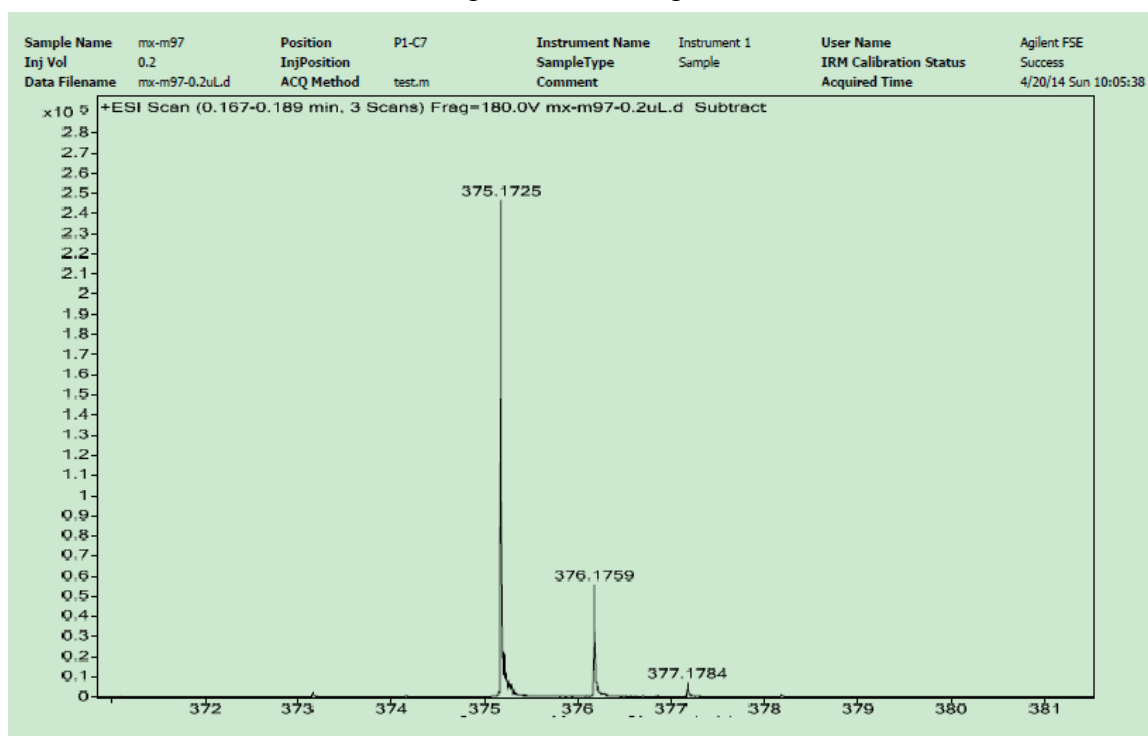
¹H NMR spectrum of compound 3d



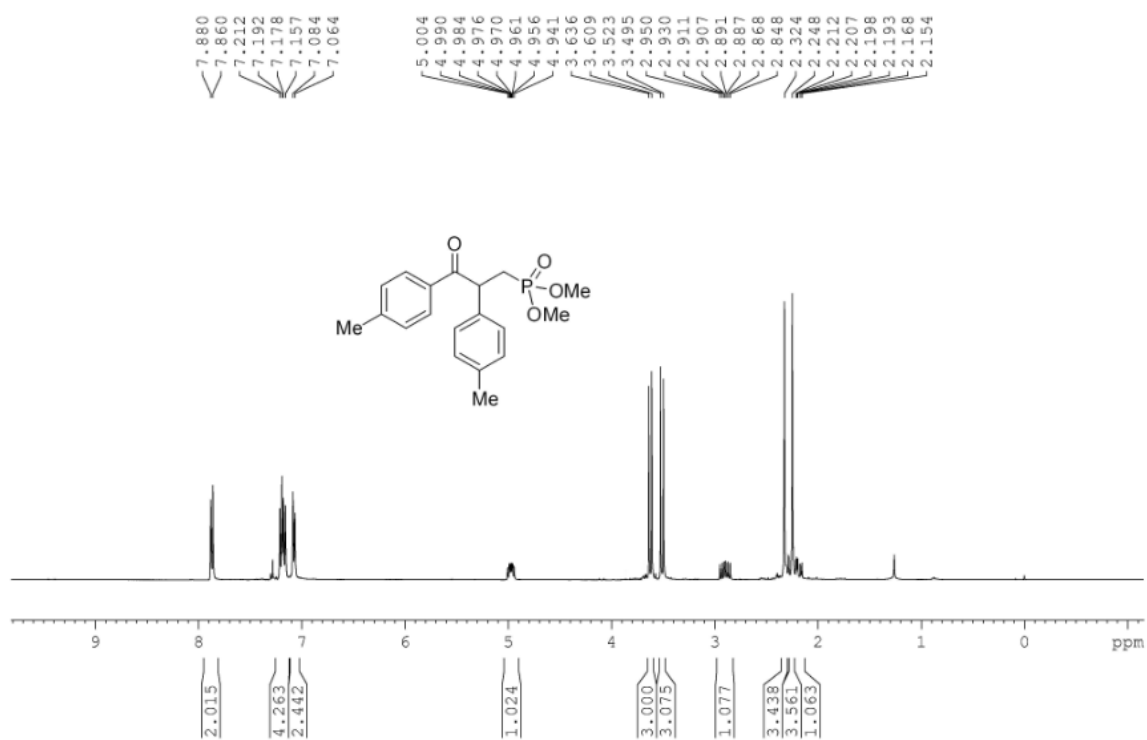
¹³C NMR spectrum of compound 3d



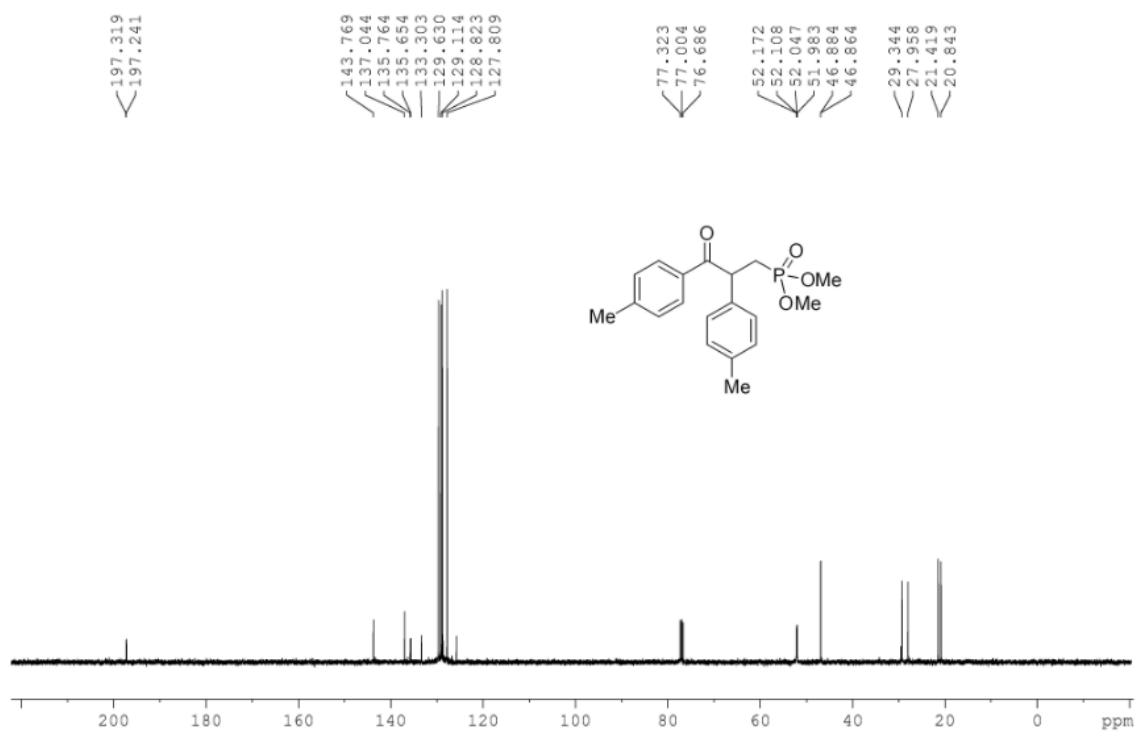
³¹P NMR spectrum of compound **3d**



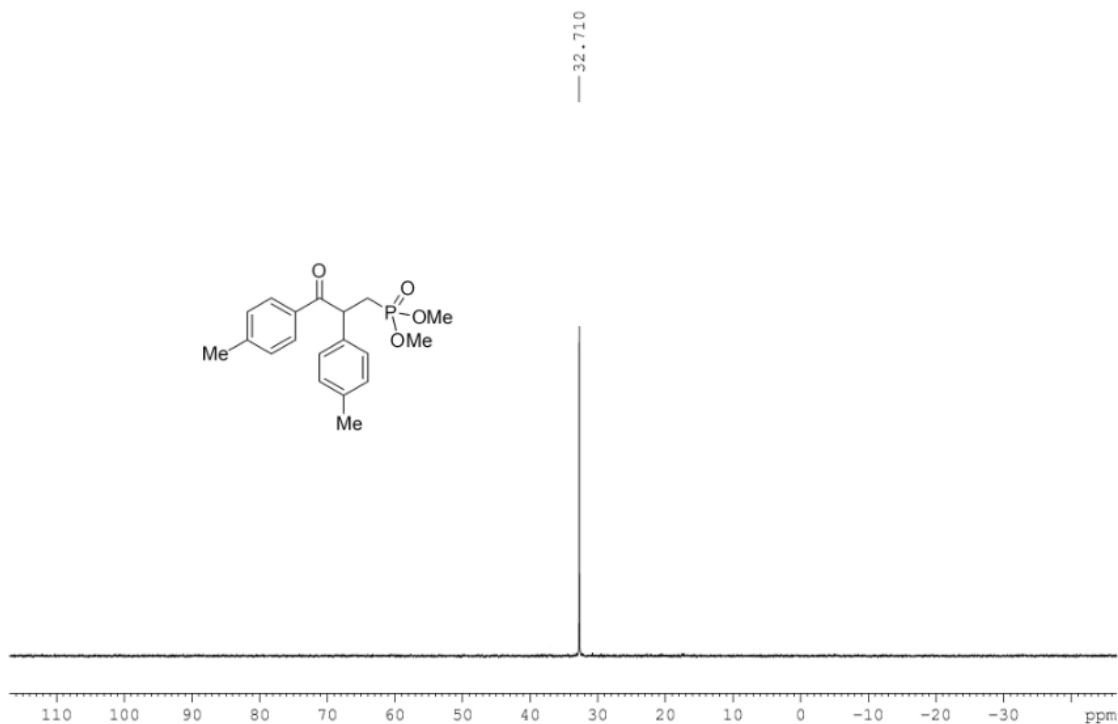
HRMS spectrum of compound **3d**



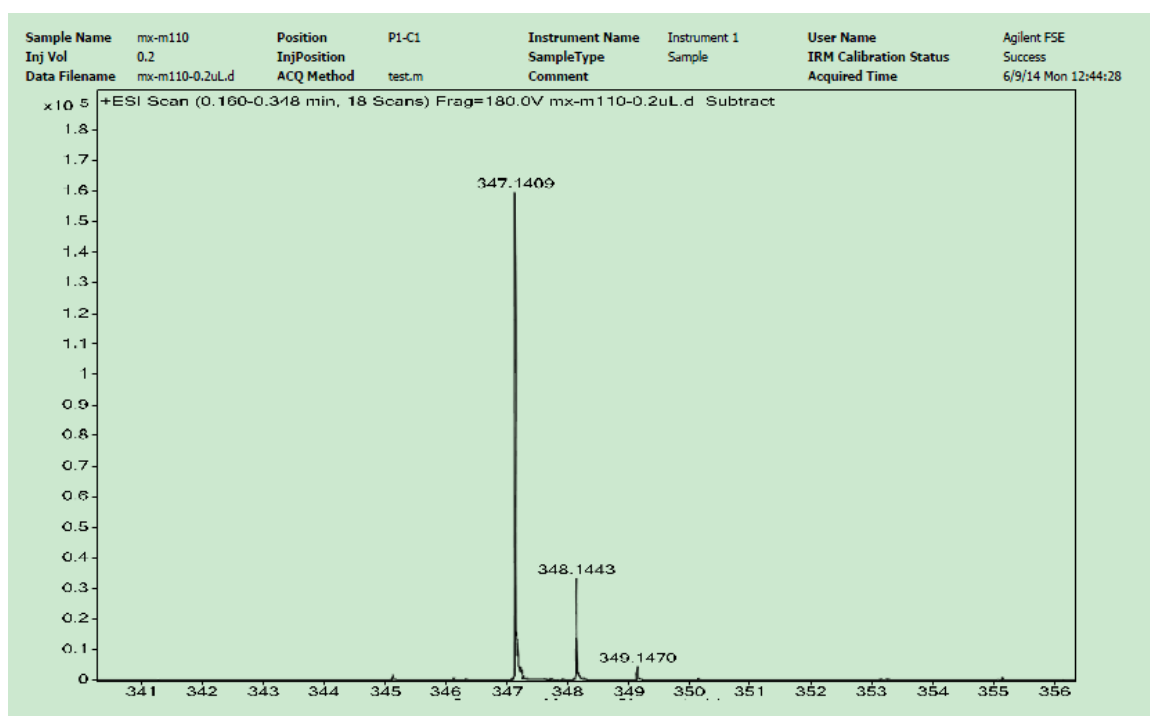
¹H NMR spectrum of compound **3e**



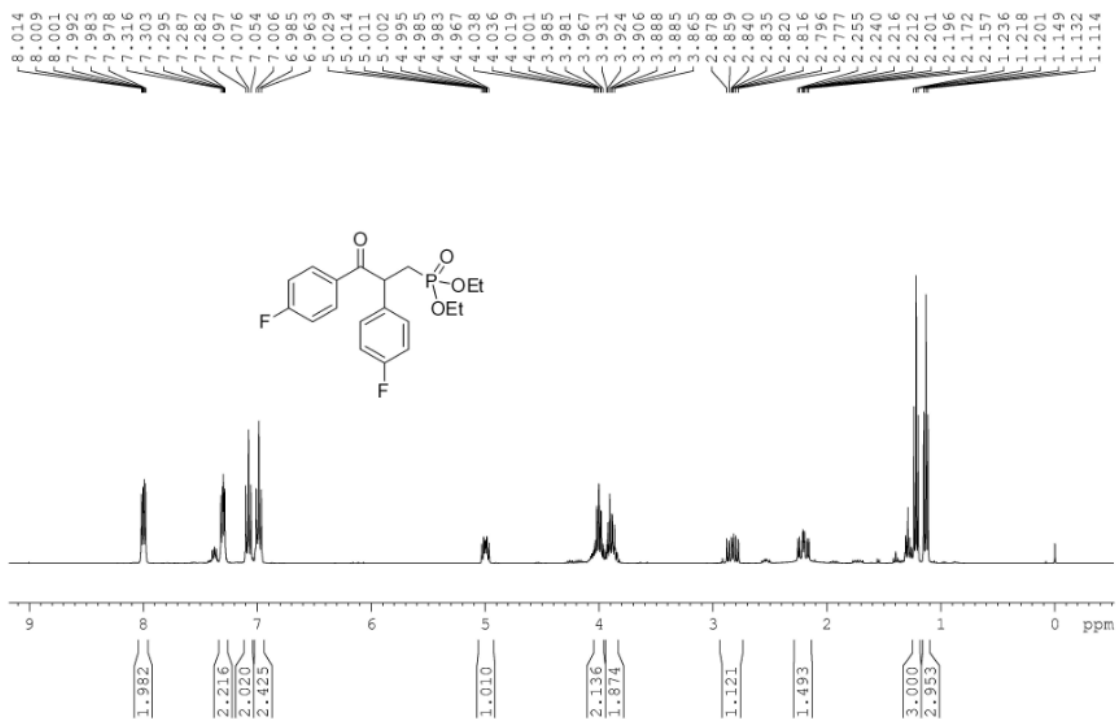
¹³C NMR spectrum of compound **3e**



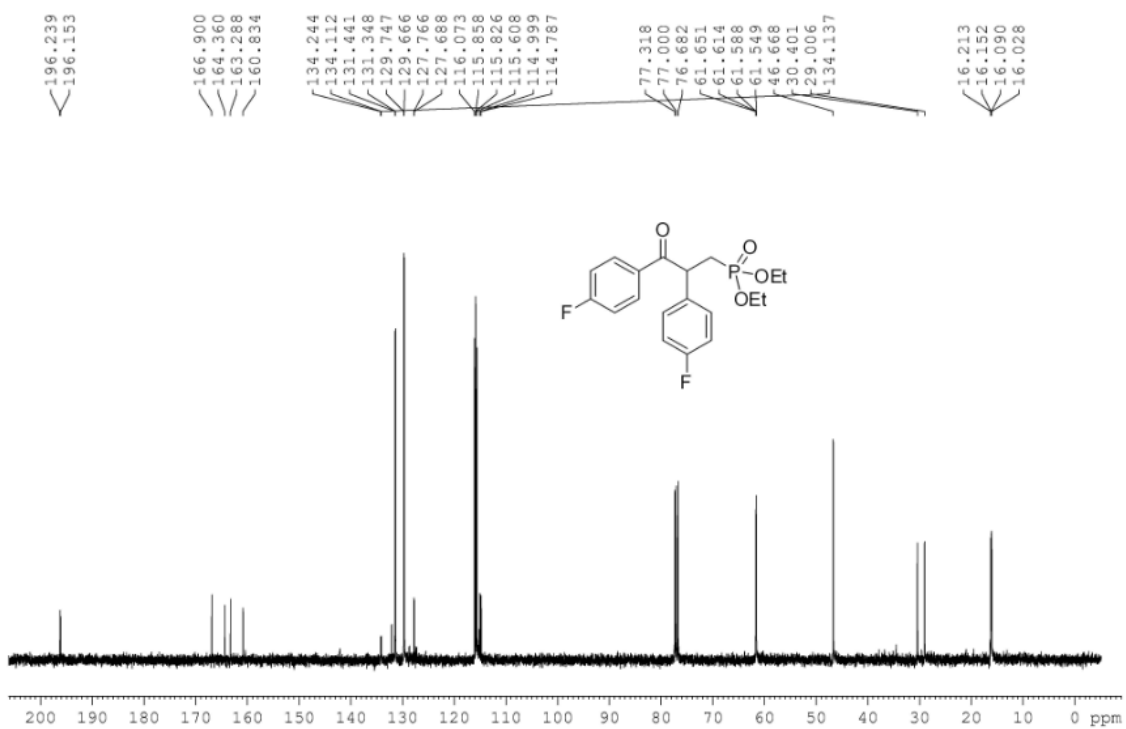
³¹P NMR spectrum of compound **3e**



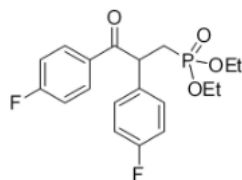
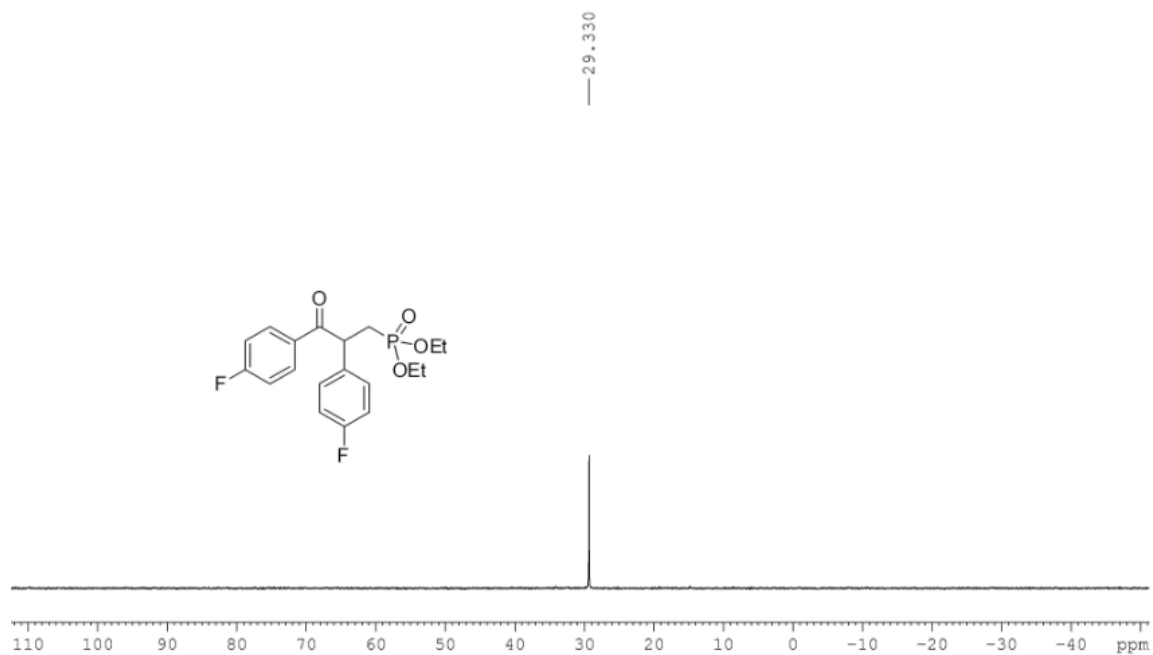
HRMS spectrum of compound **3e**



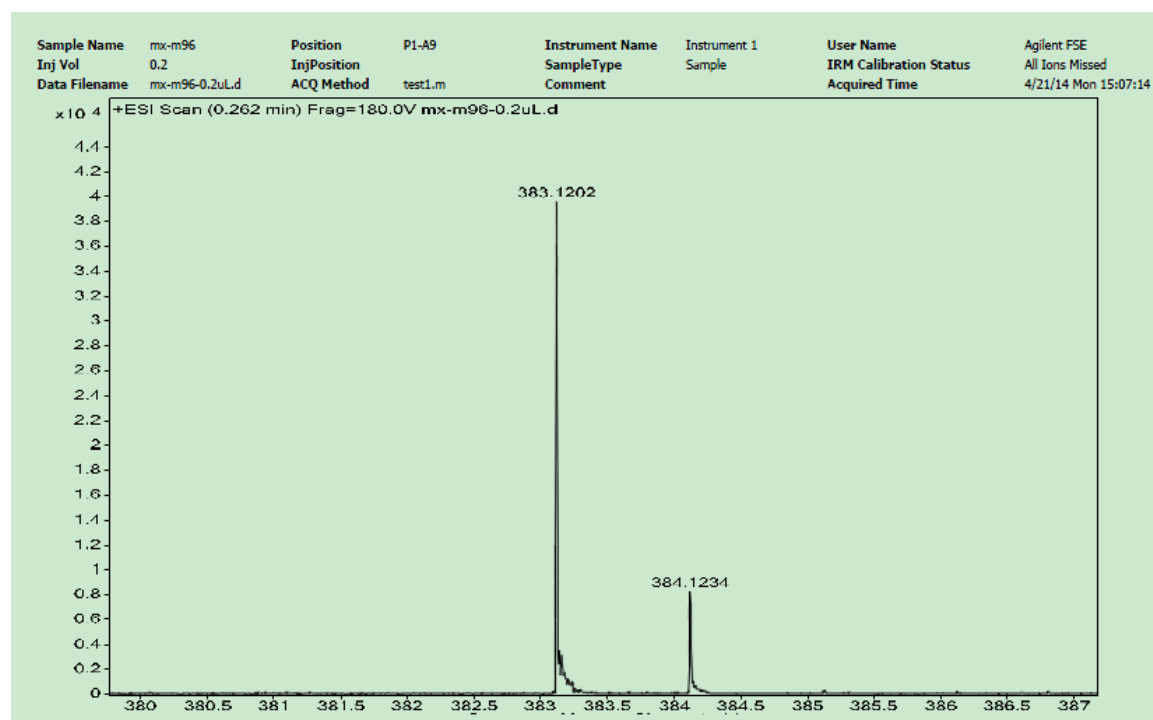
¹H NMR spectrum of compound 3f



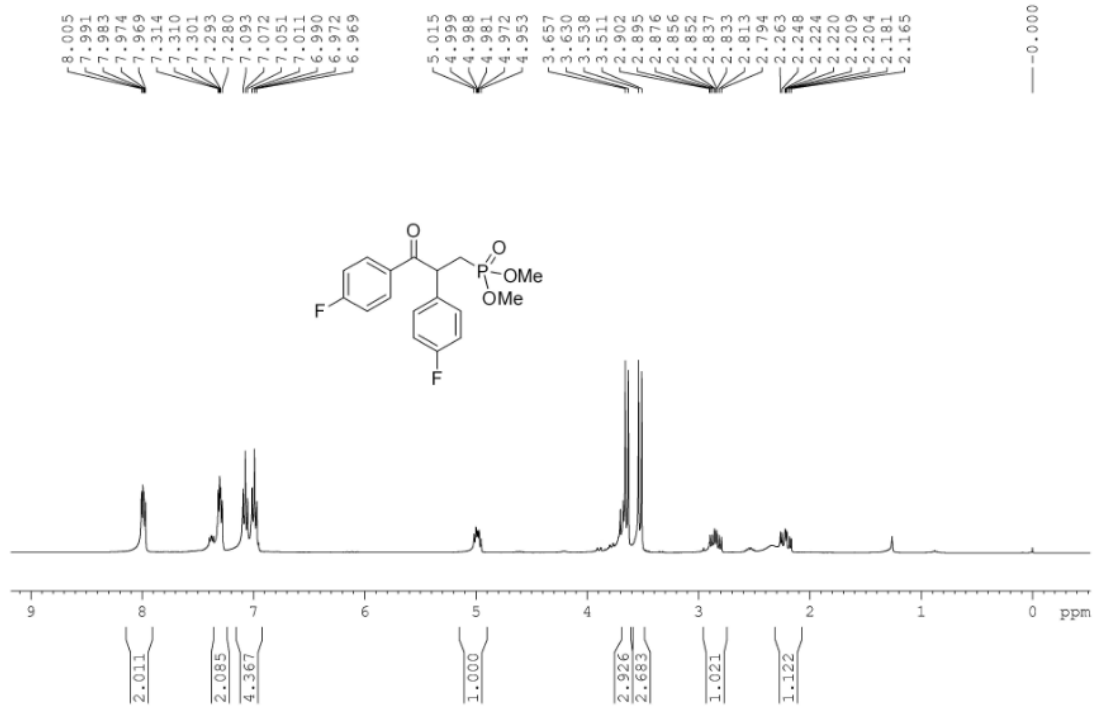
¹³C NMR spectrum of compound 3f



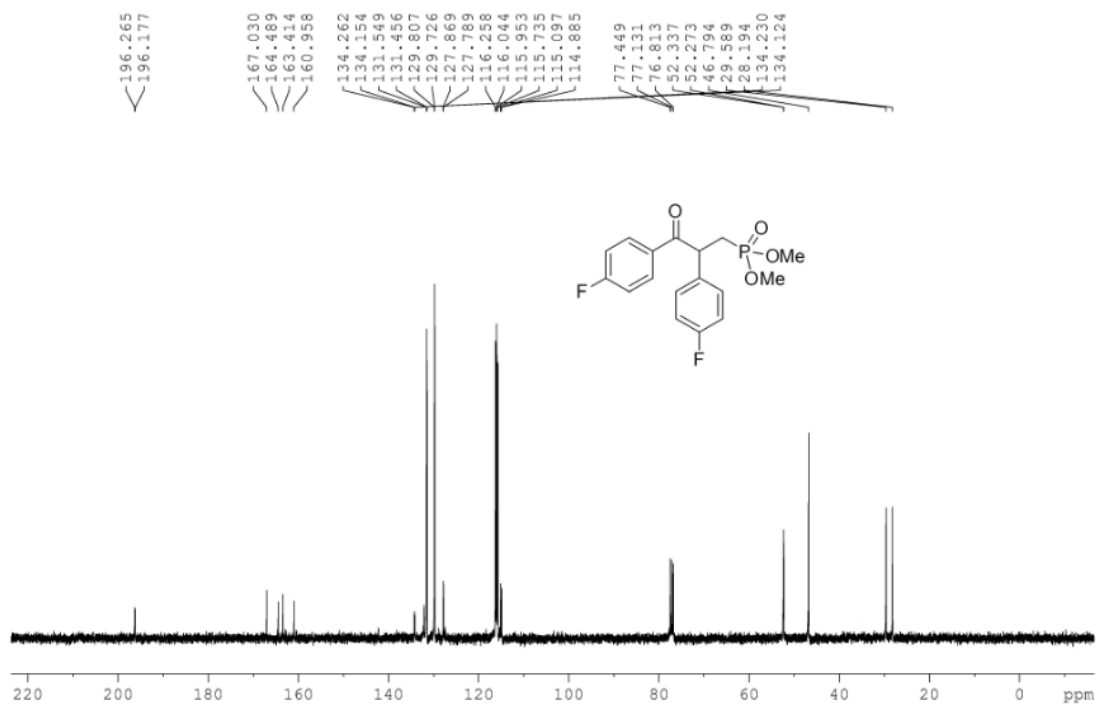
³¹P NMR spectrum of compound **3f**



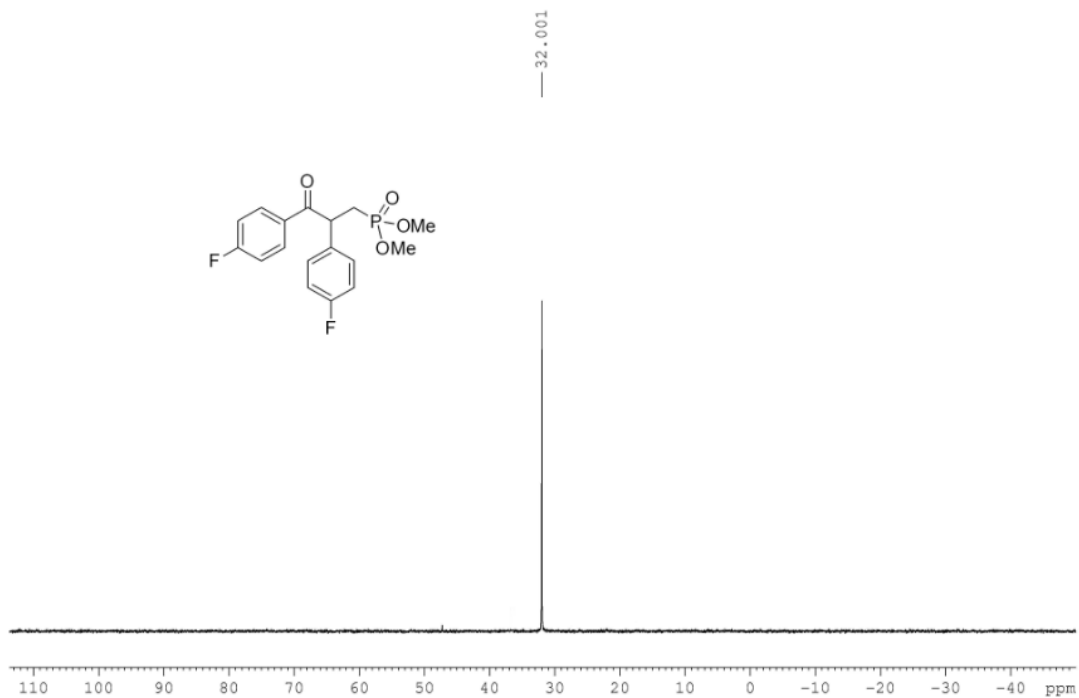
HRMS spectrum of compound **3f**



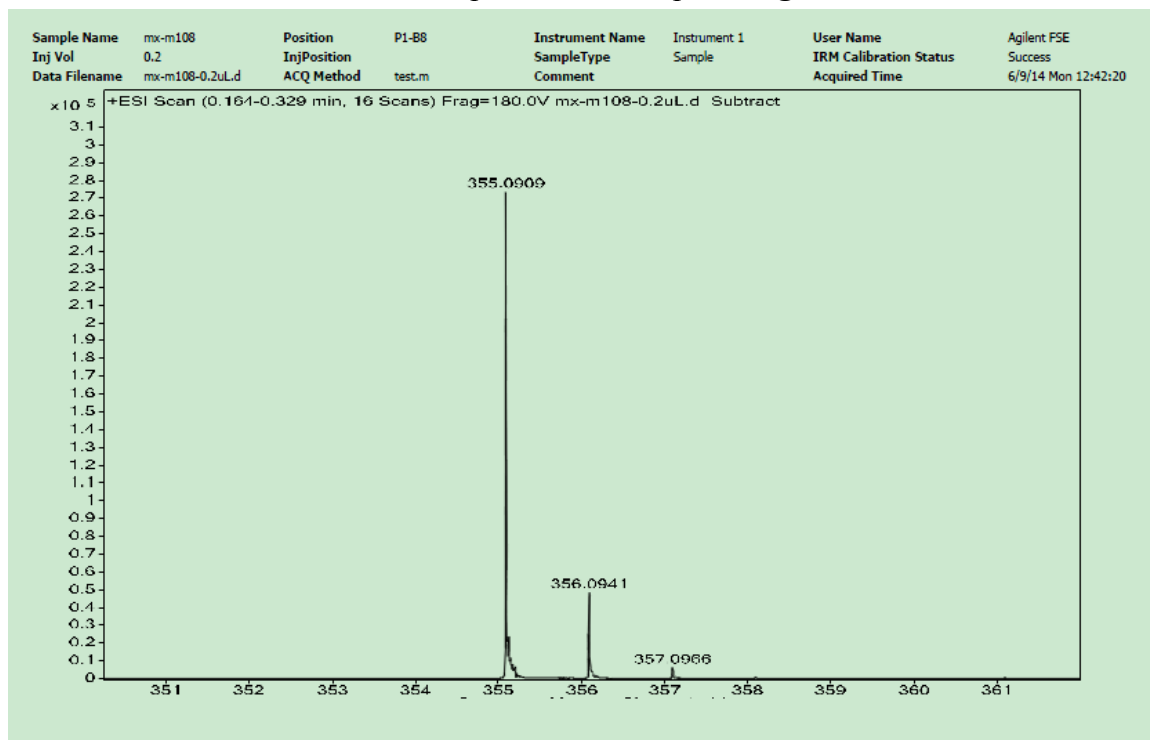
¹H NMR spectrum of compound **3g**



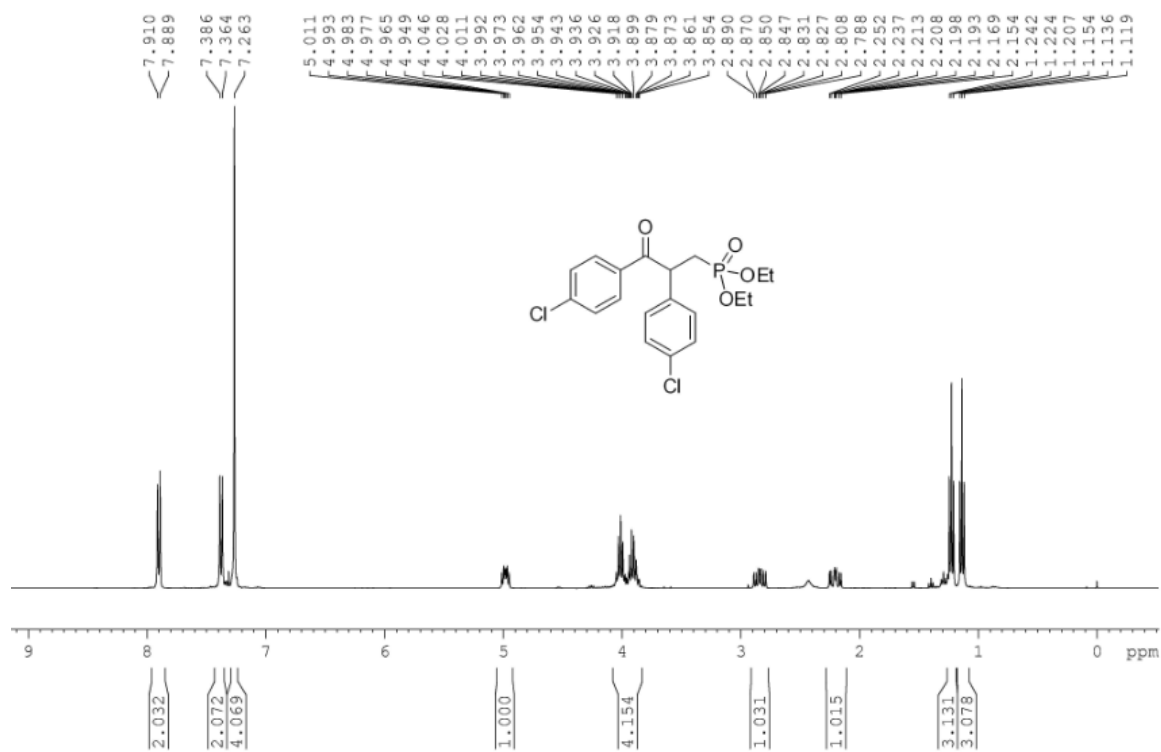
¹³C NMR spectrum of compound **3g**



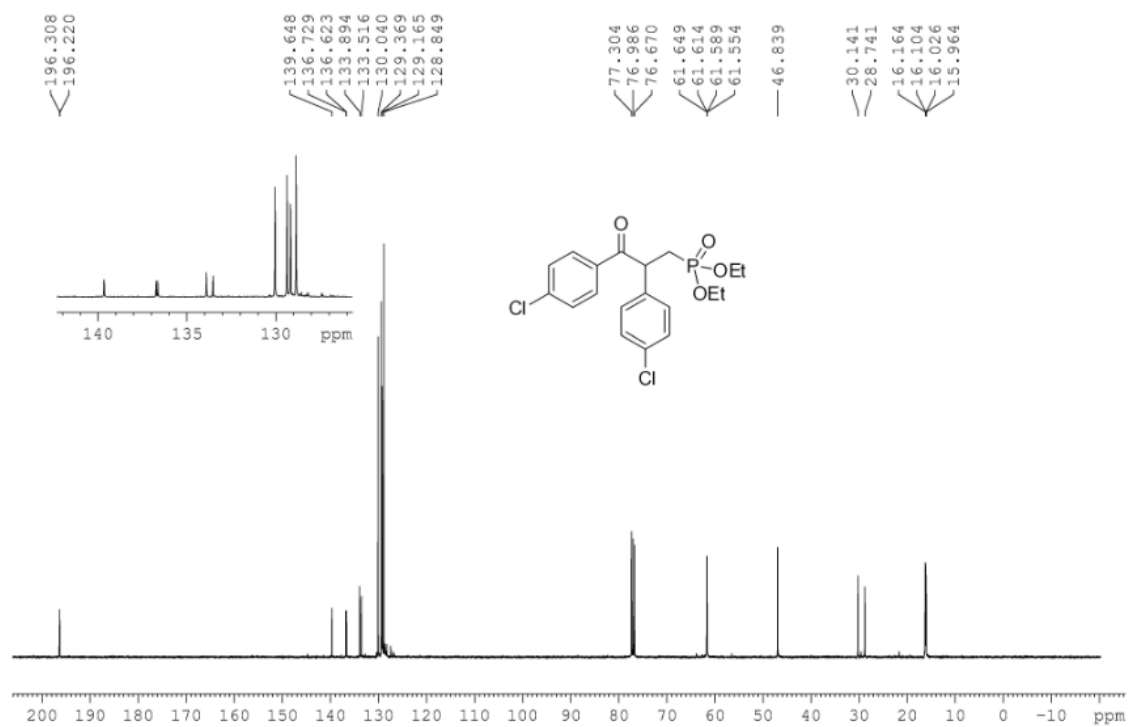
³¹P NMR spectrum of compound **3g**



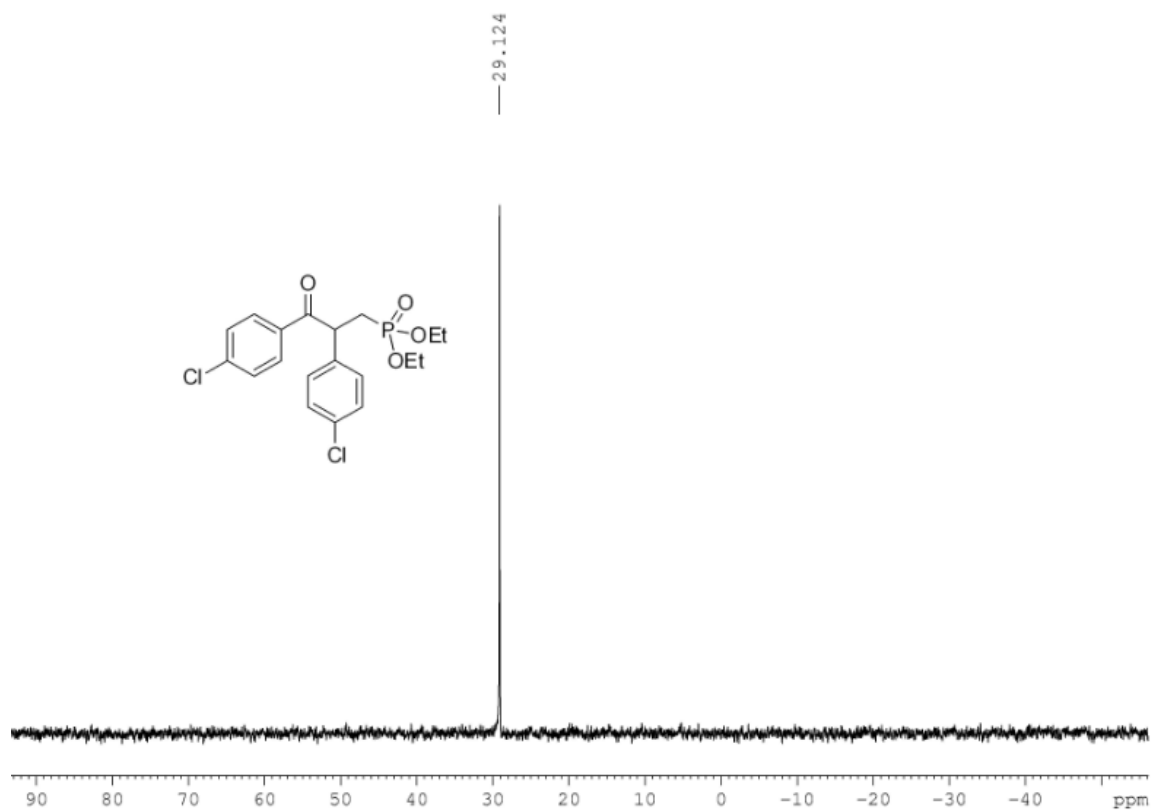
HRMS spectrum of compound **3g**



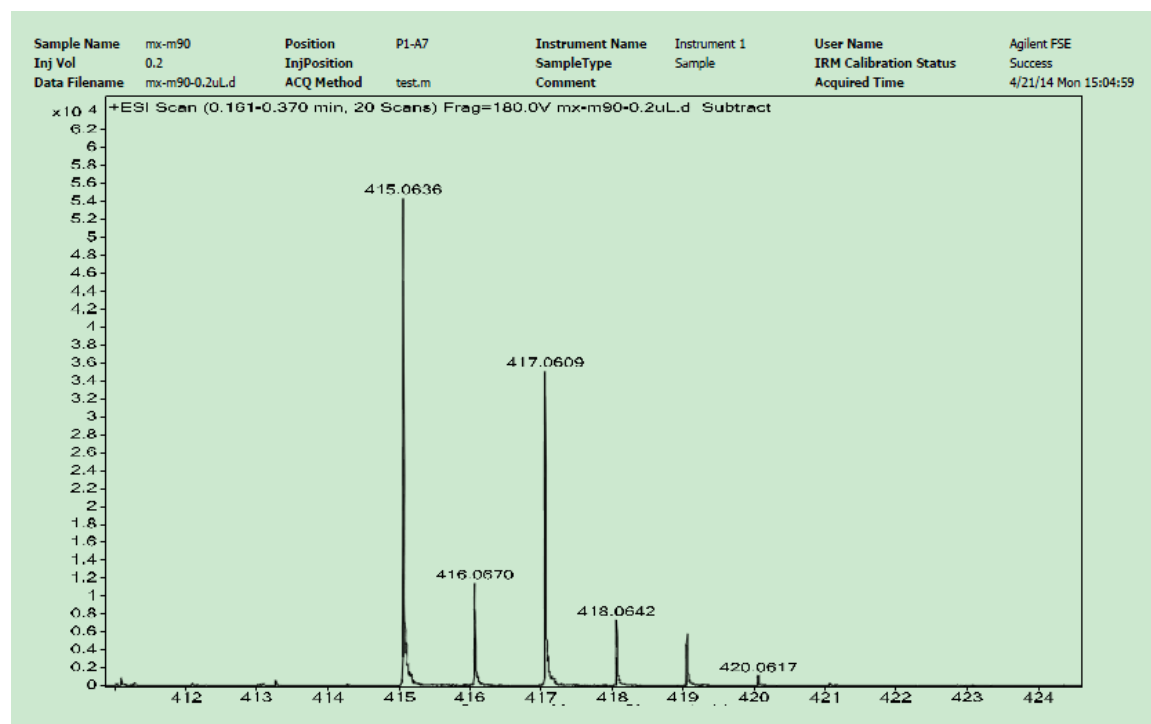
¹H NMR spectrum of compound 3h



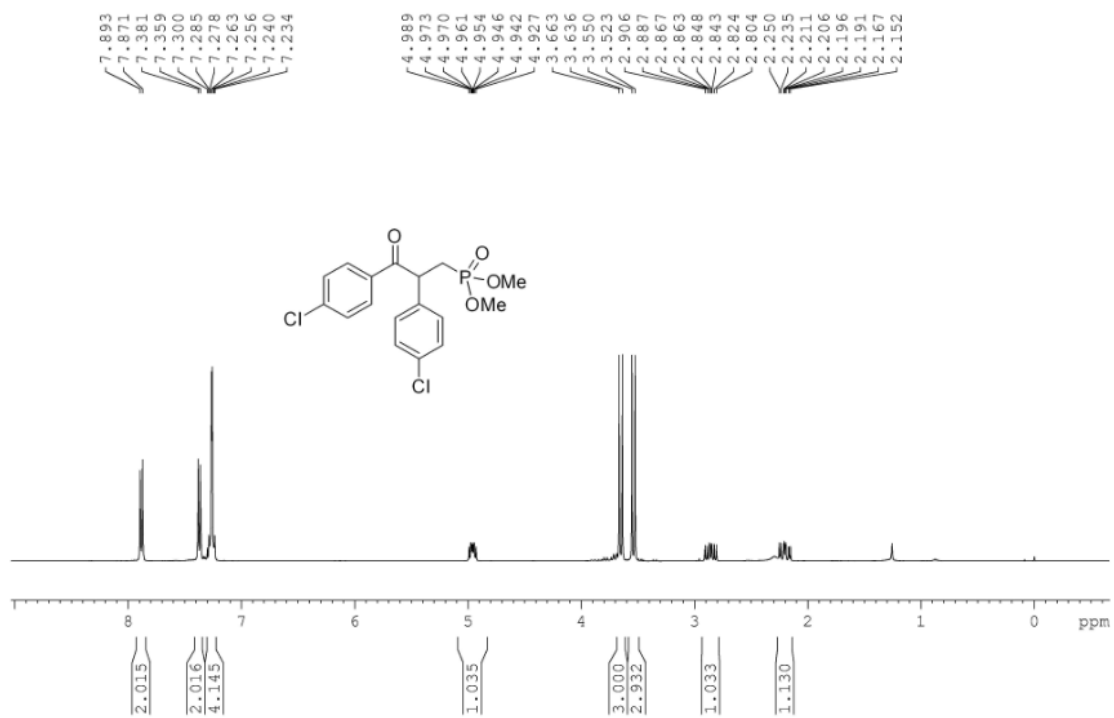
¹³C NMR spectrum of compound 3h



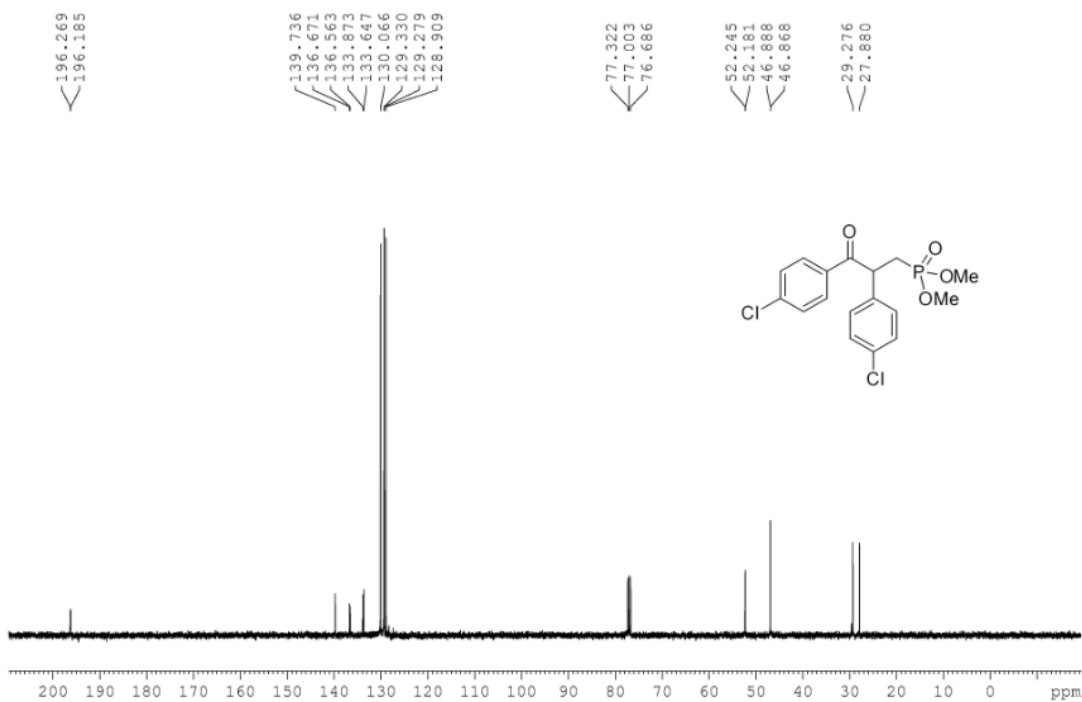
^{31}P NMR spectrum of compound **3h**



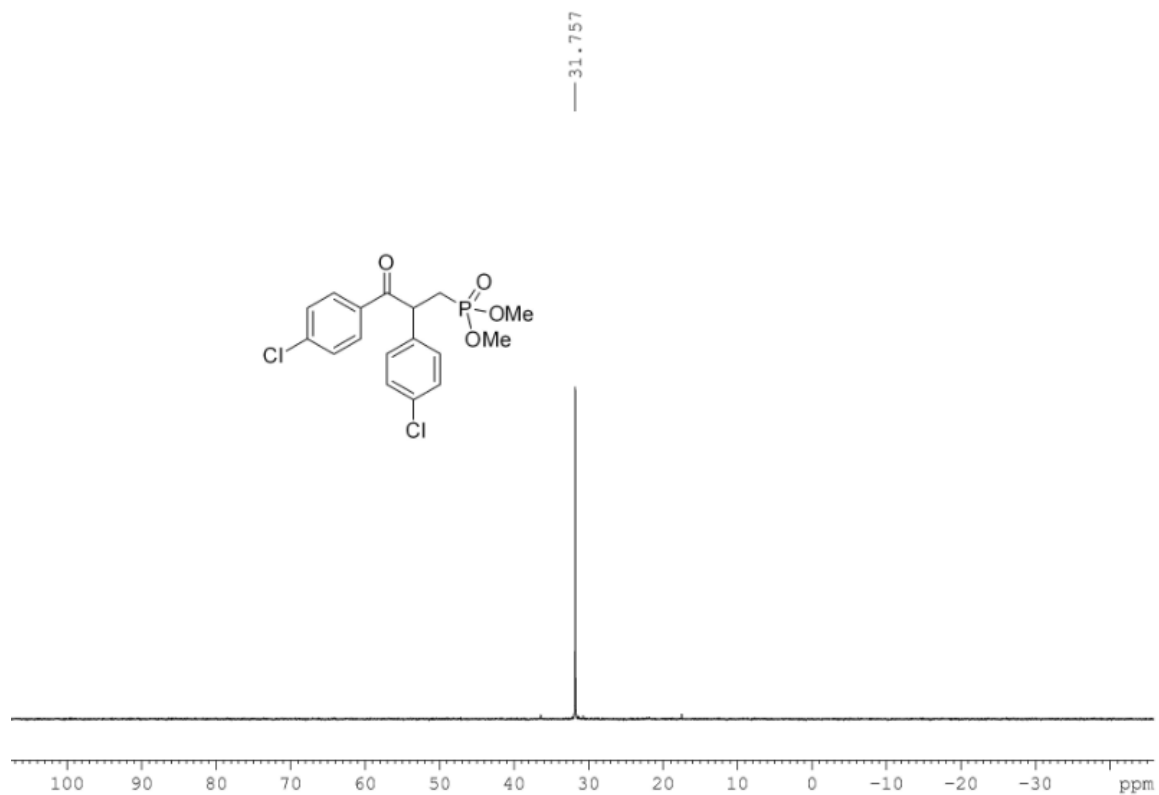
HRMS spectrum of compound **3h**



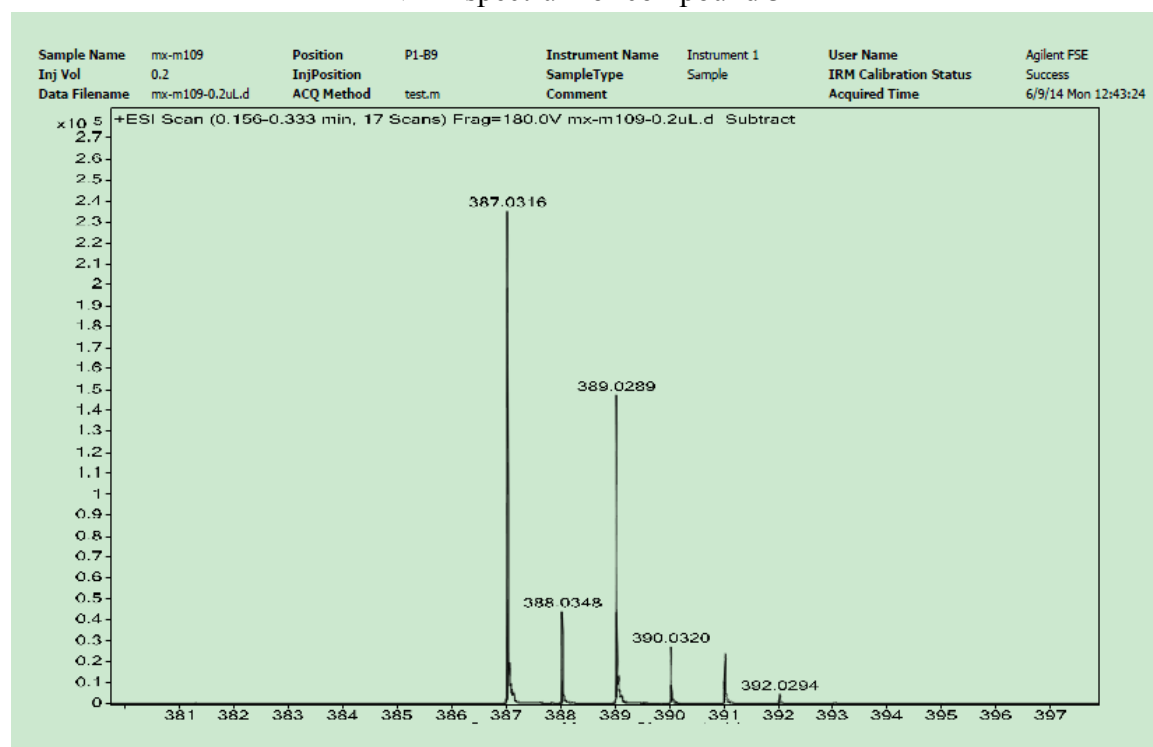
¹H NMR spectrum of compound **3i**



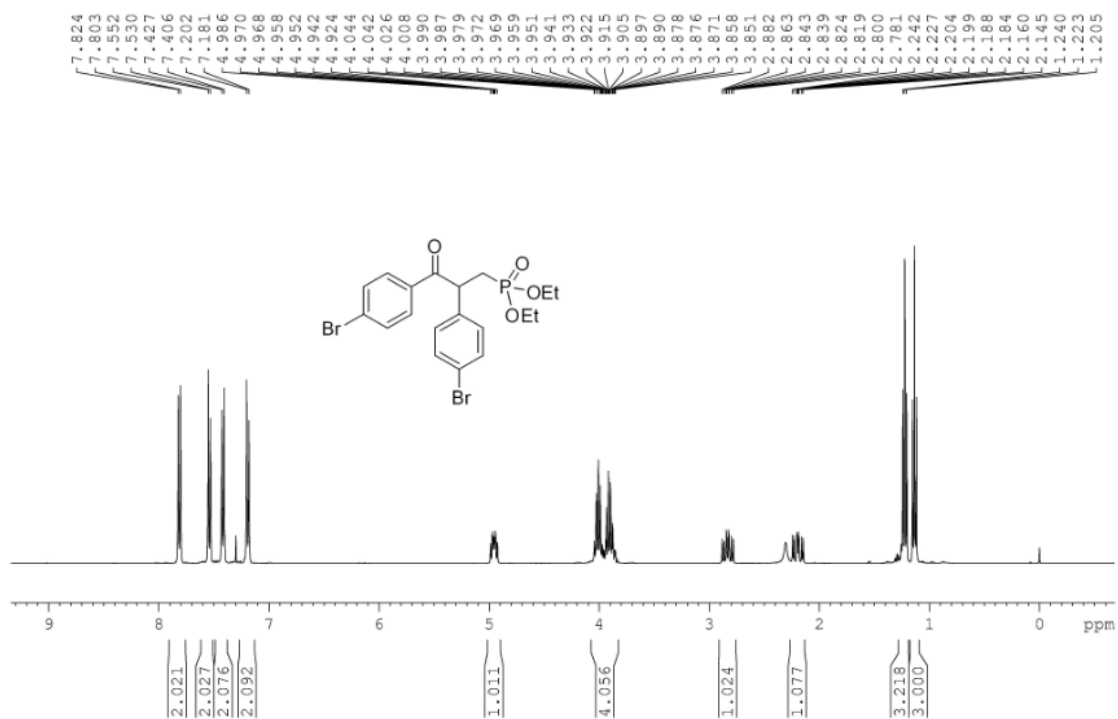
¹³C NMR spectrum of compound **3i**



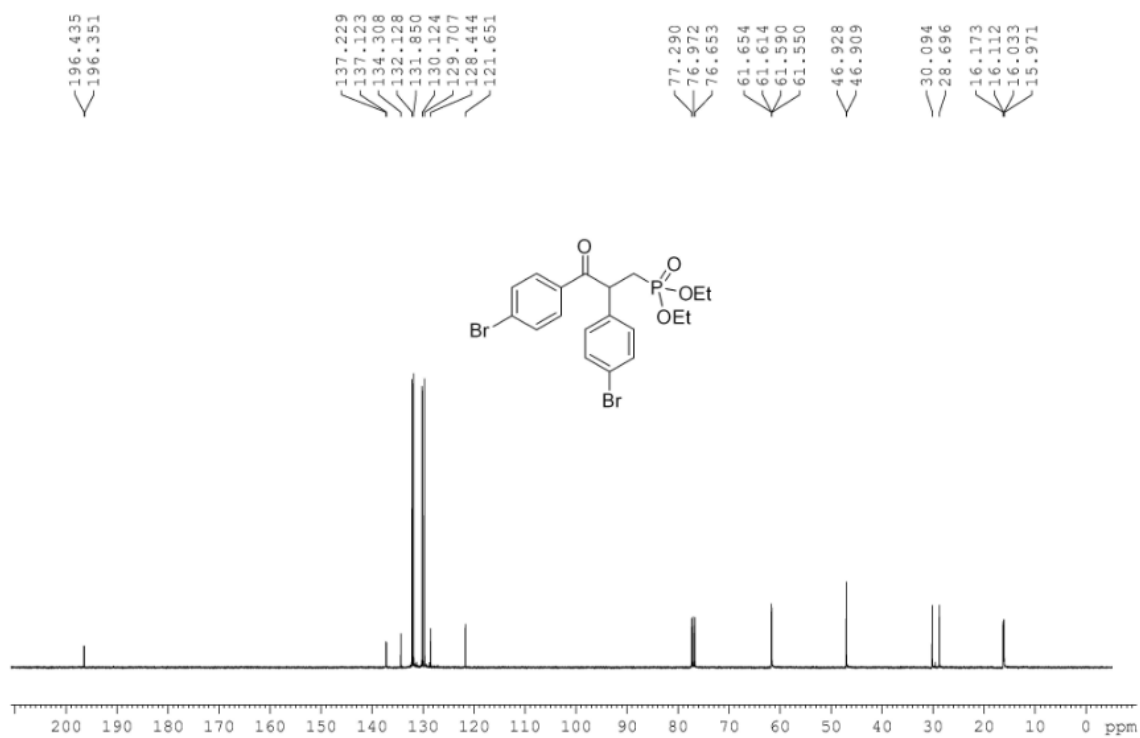
³¹P NMR spectrum of compound **3i**



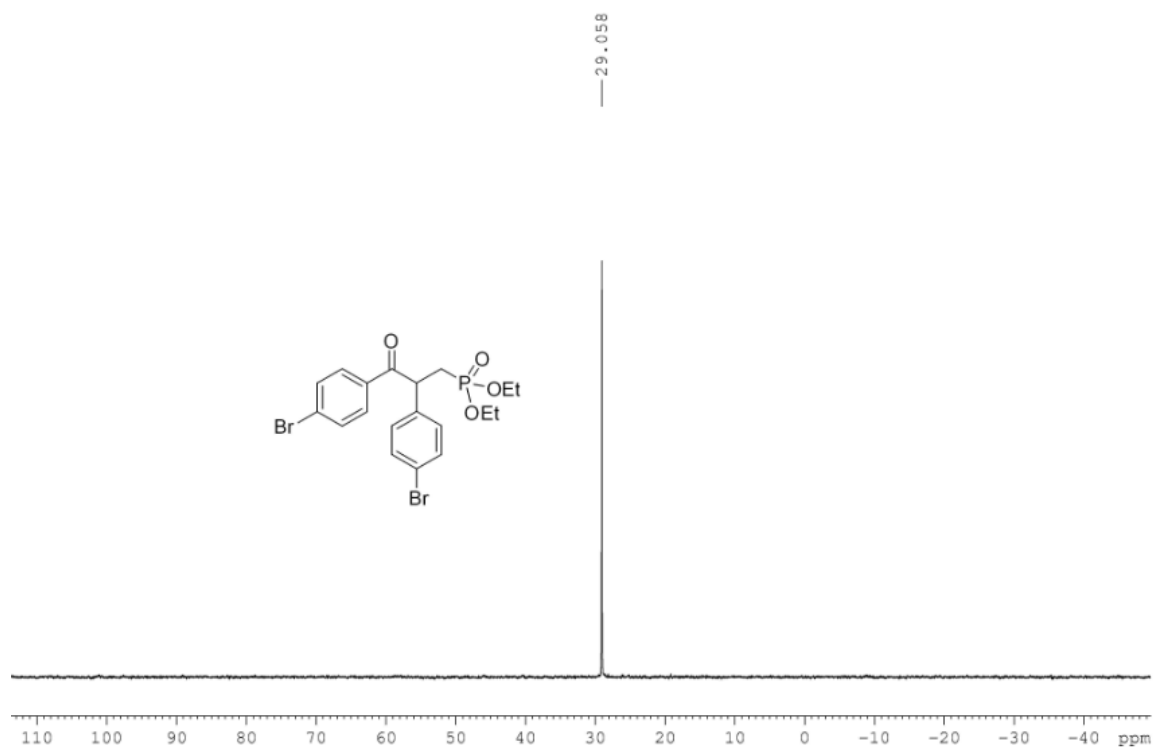
HRMS spectrum of compound **3i**



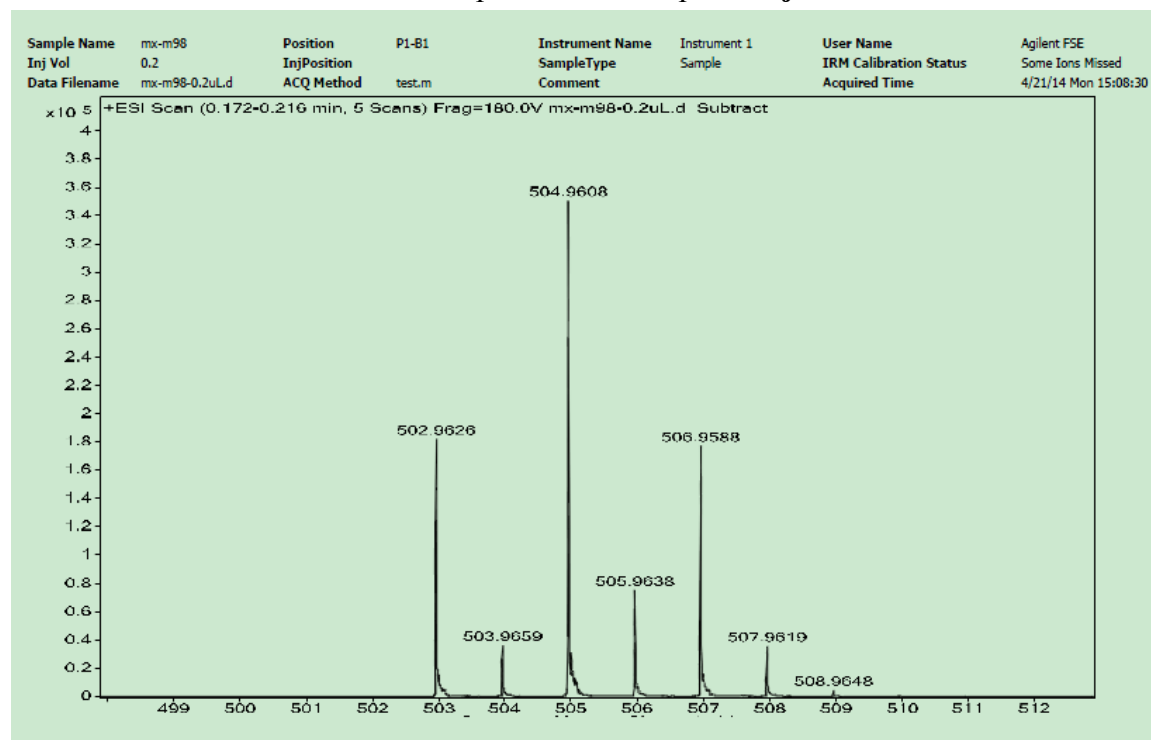
¹H NMR spectrum of compound 3j



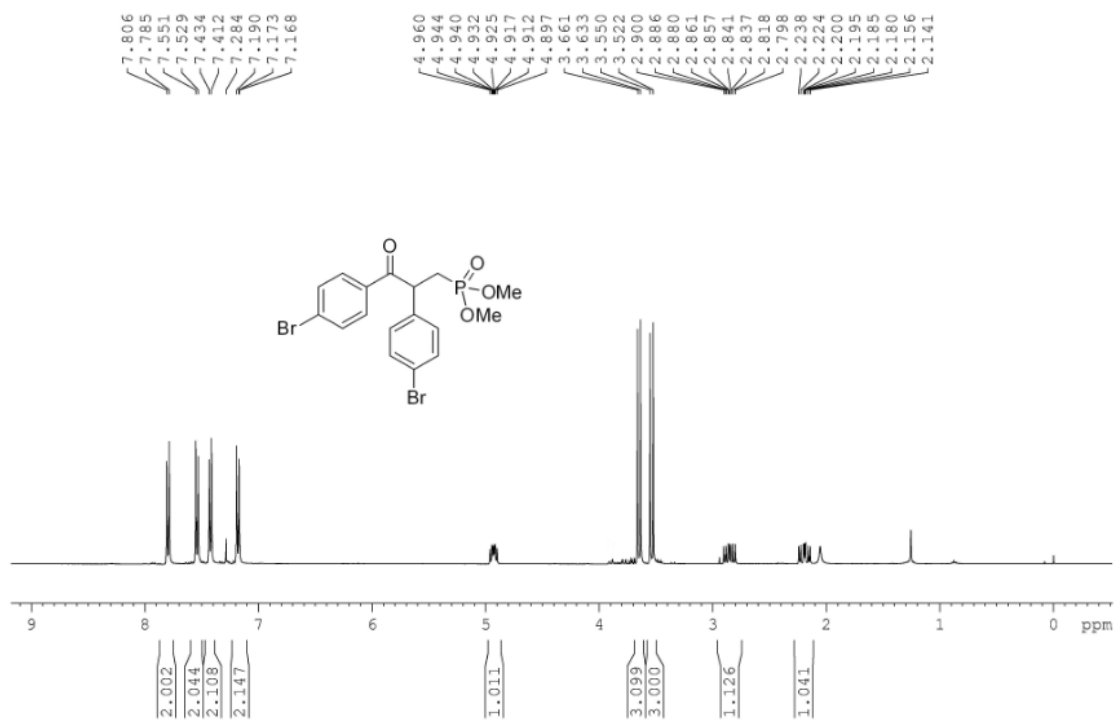
¹³C NMR spectrum of compound 3j



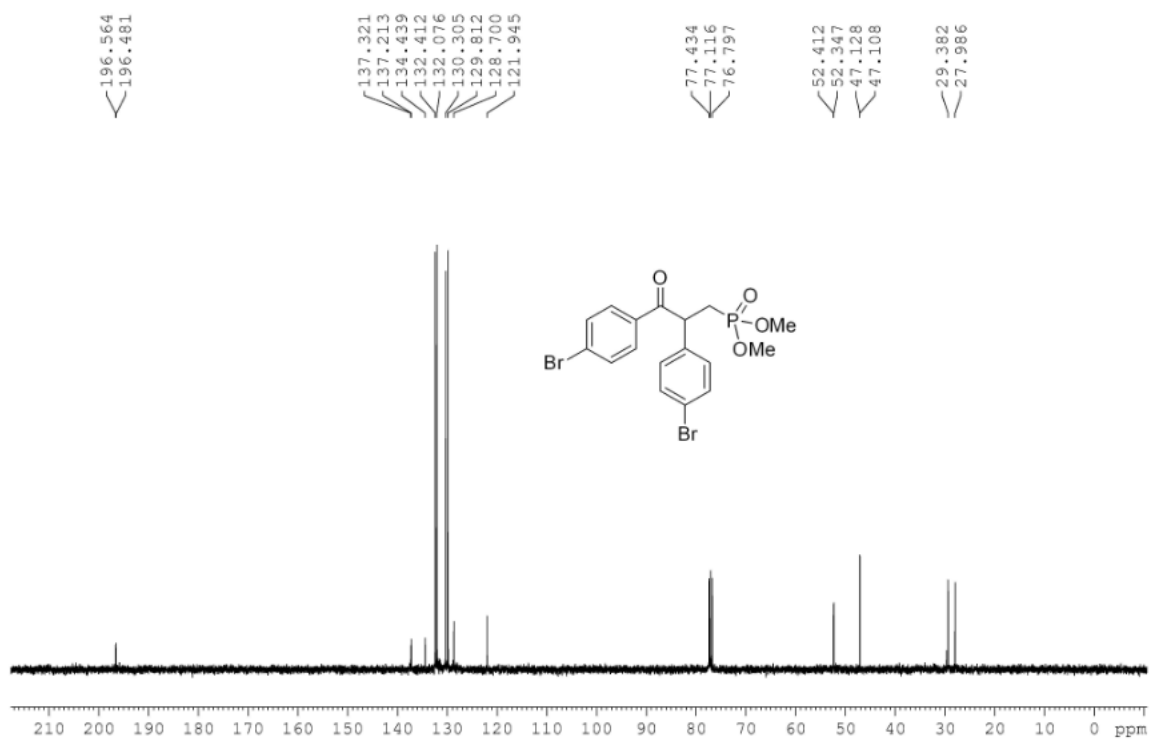
³¹P NMR spectrum of compound **3j**



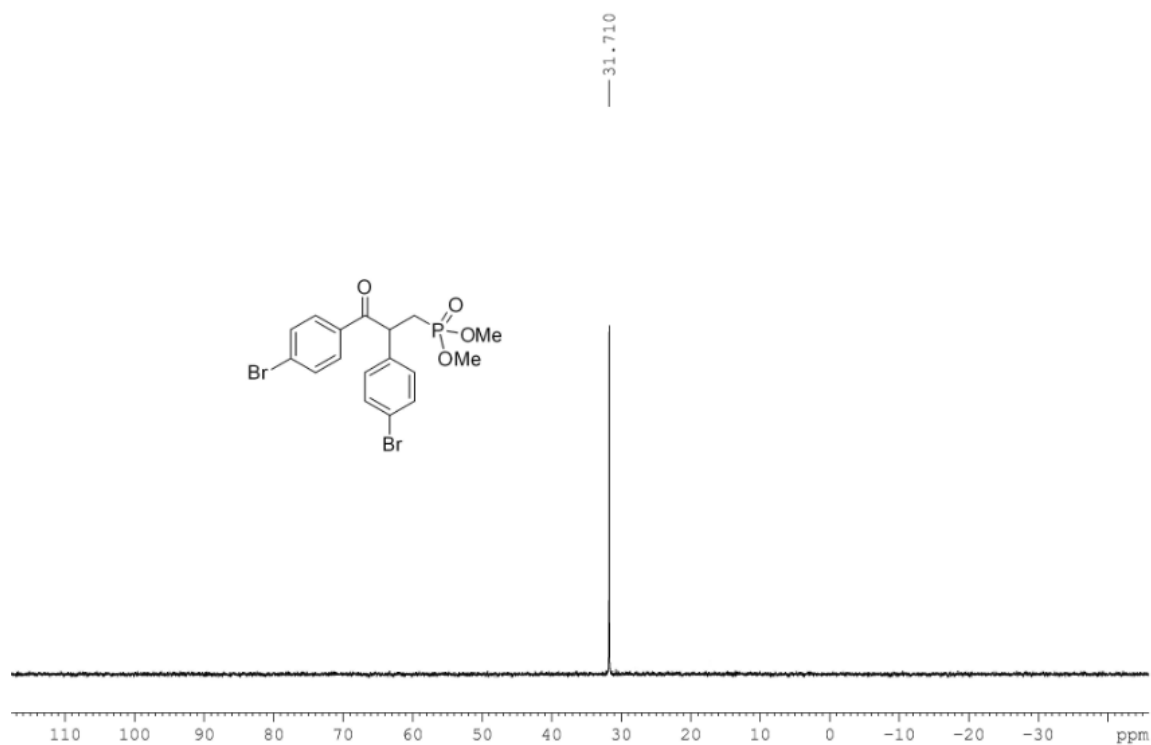
HRMS spectrum of compound **3j**



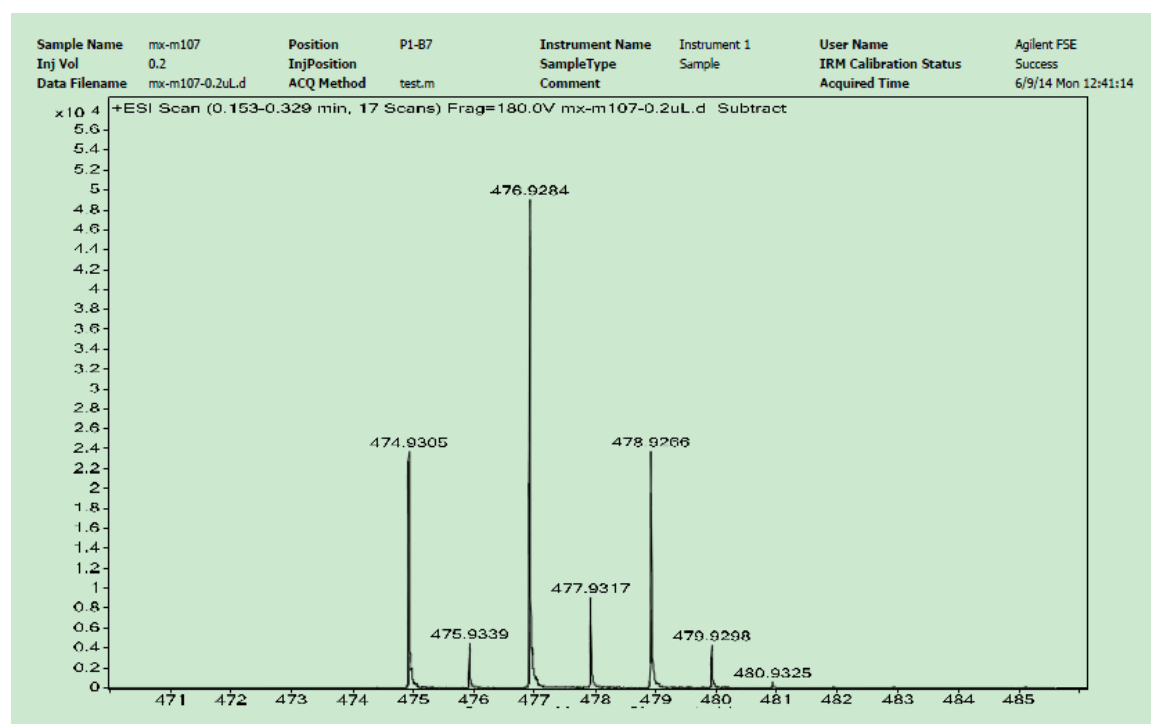
¹H NMR spectrum of compound **3k**



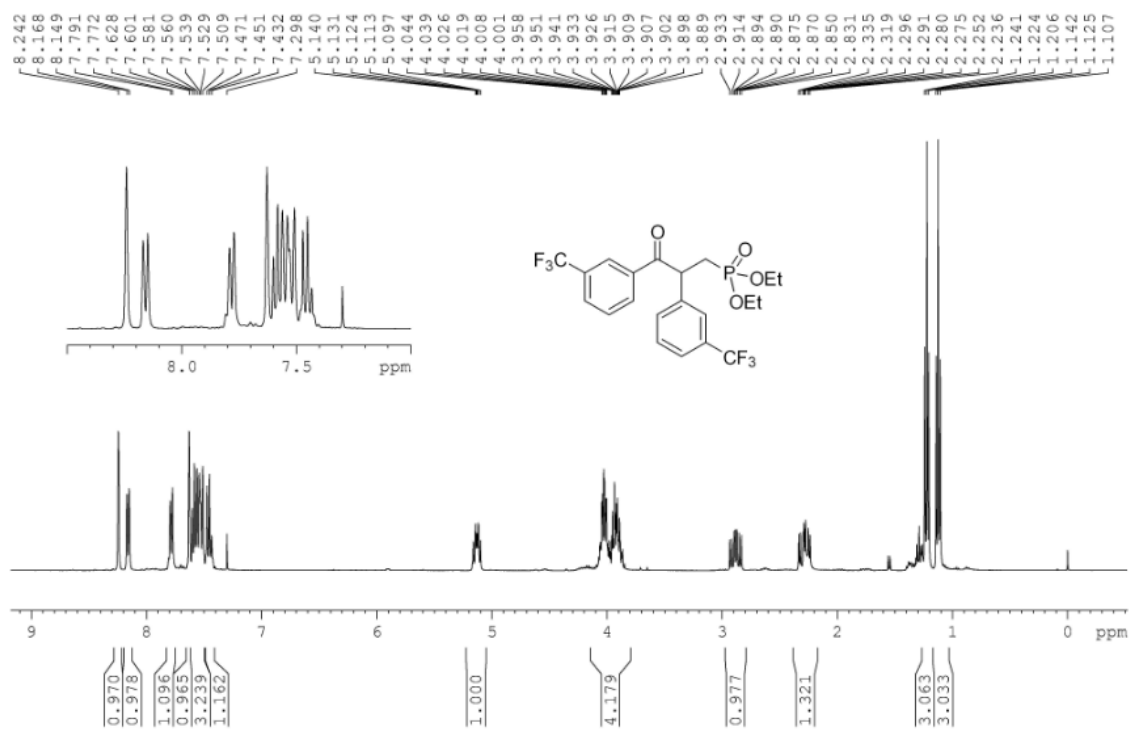
¹³C NMR spectrum of compound **3k**



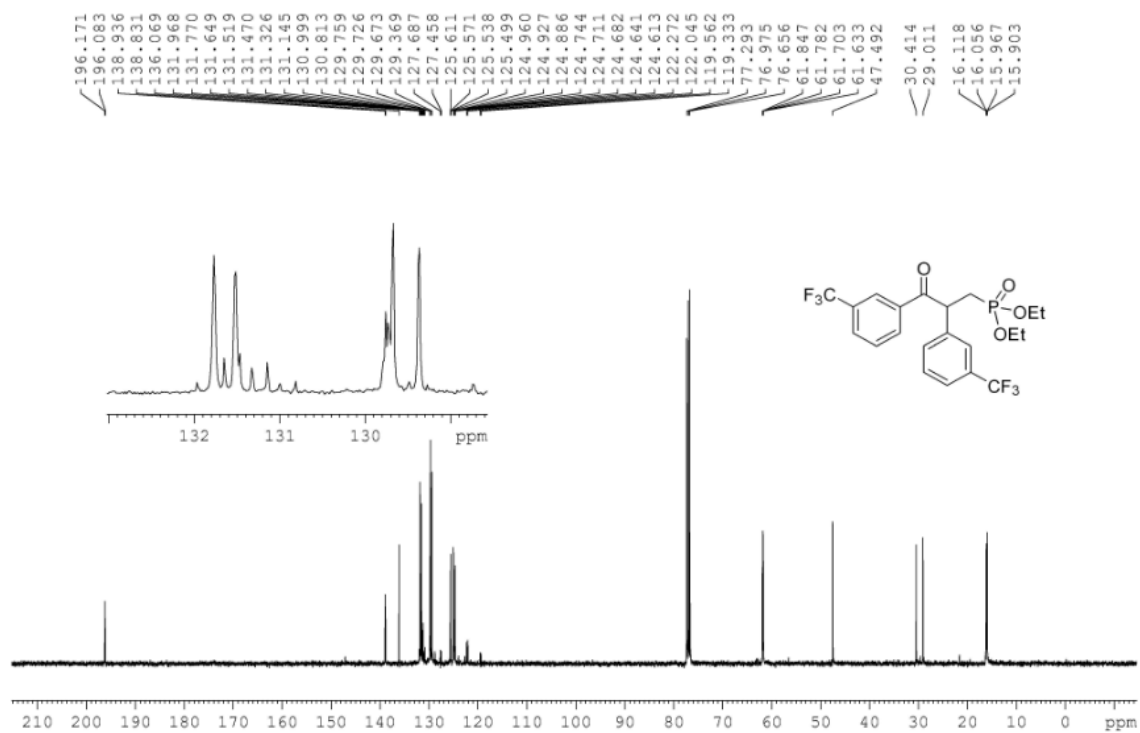
^{31}P NMR spectrum of compound 3k



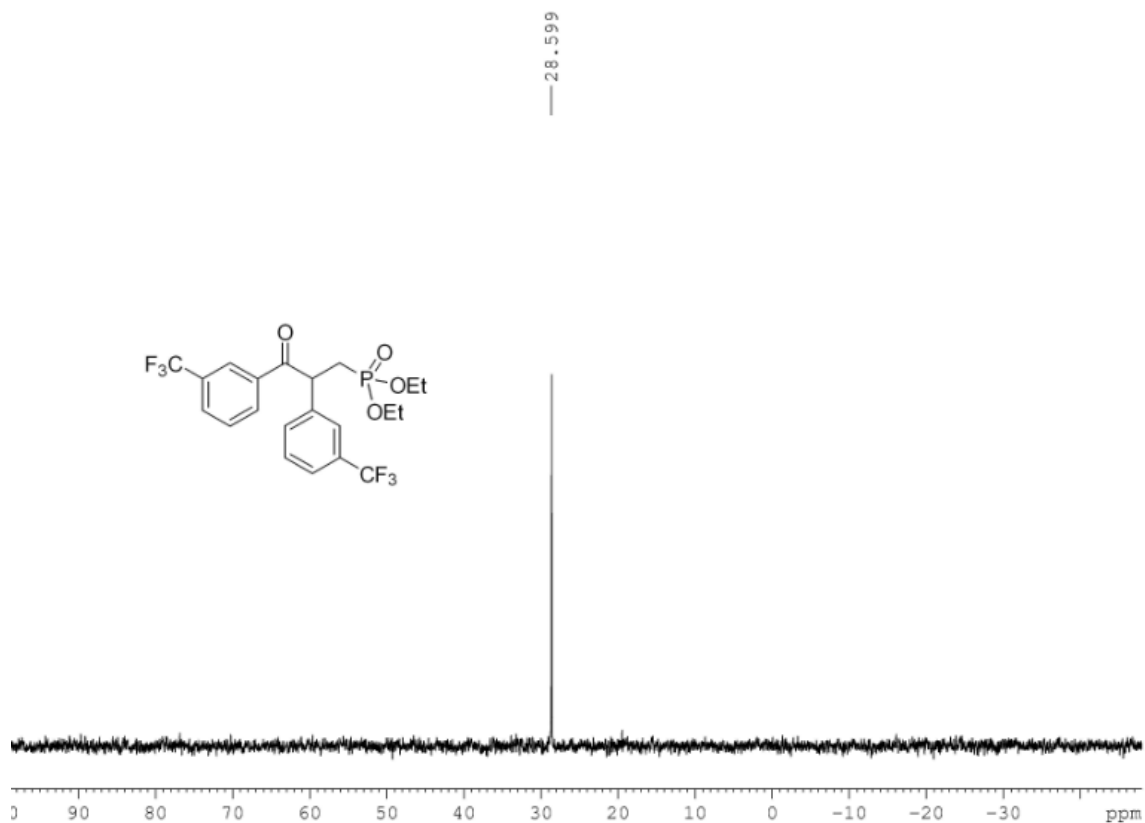
HRMS spectrum of compound 3k



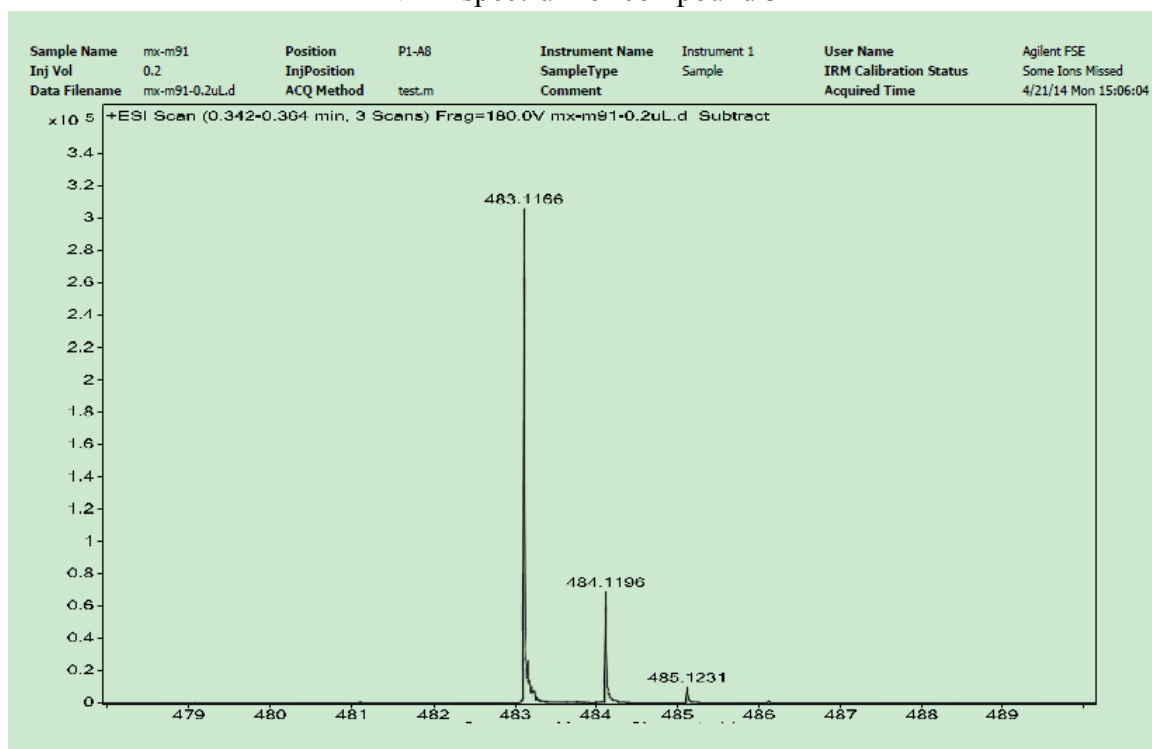
¹H NMR spectrum of compound 31



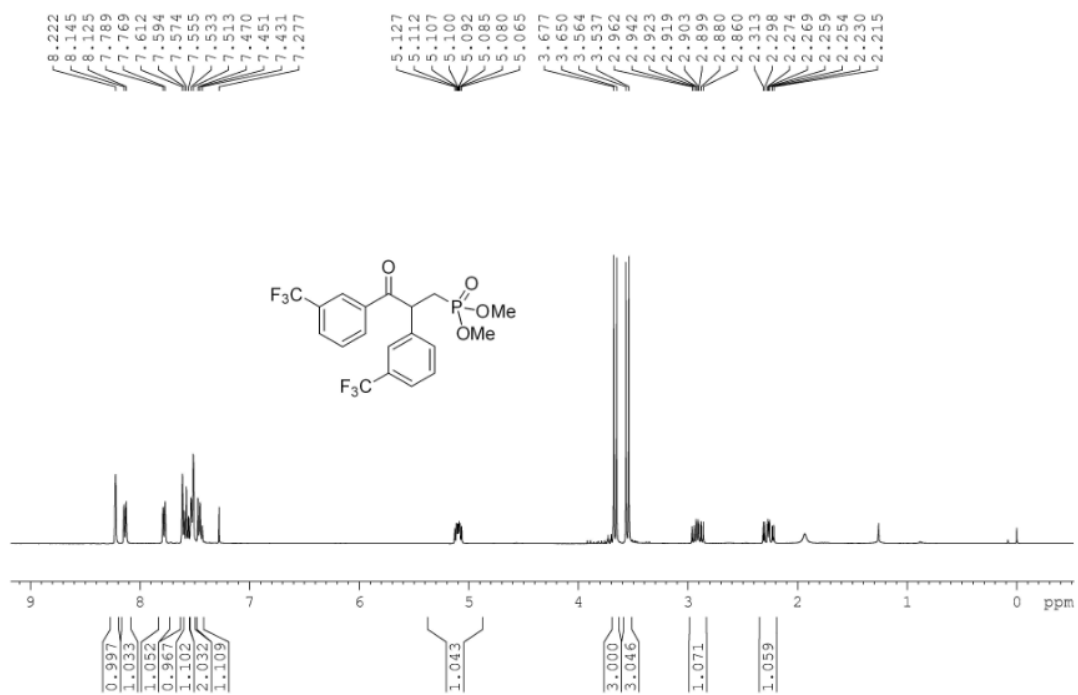
¹³C NMR spectrum of compound 31



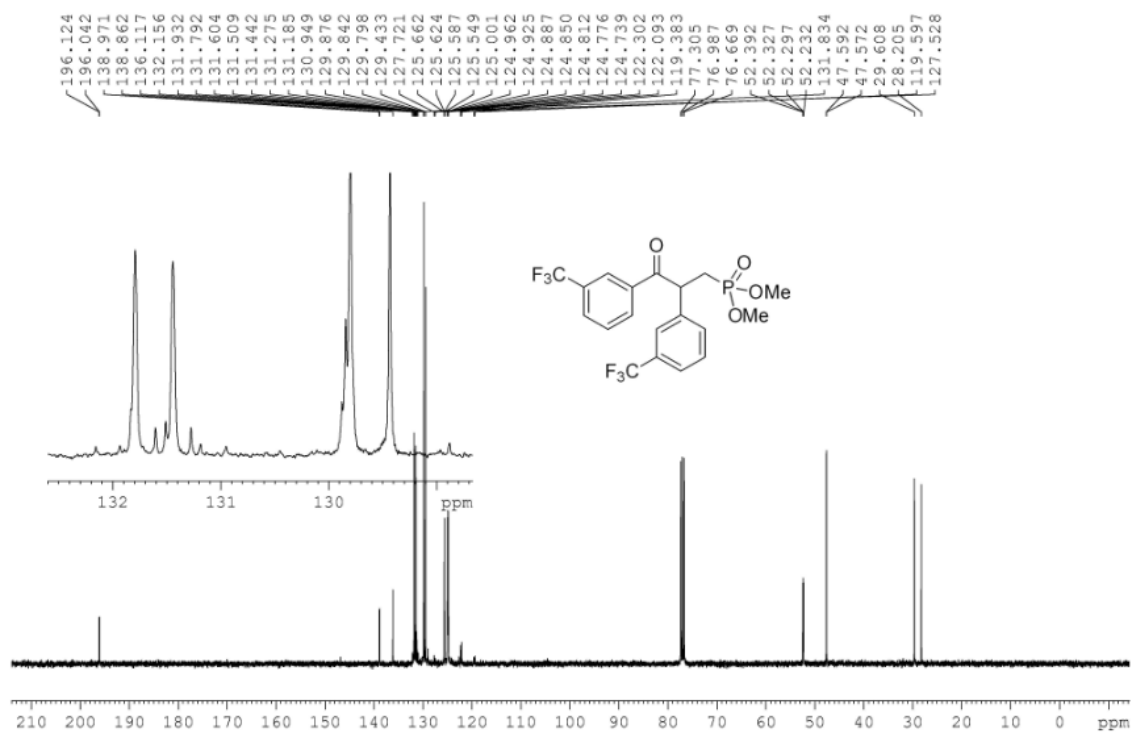
³¹P NMR spectrum of compound **31**



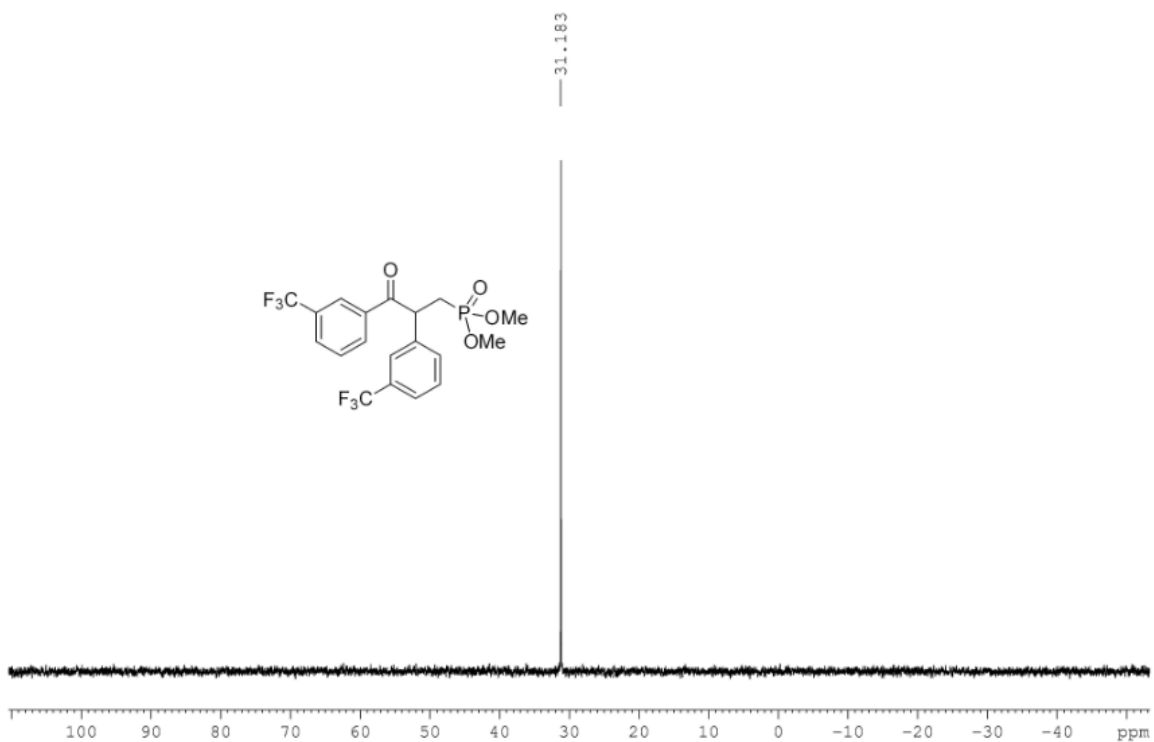
HRMS spectrum of compound **31**



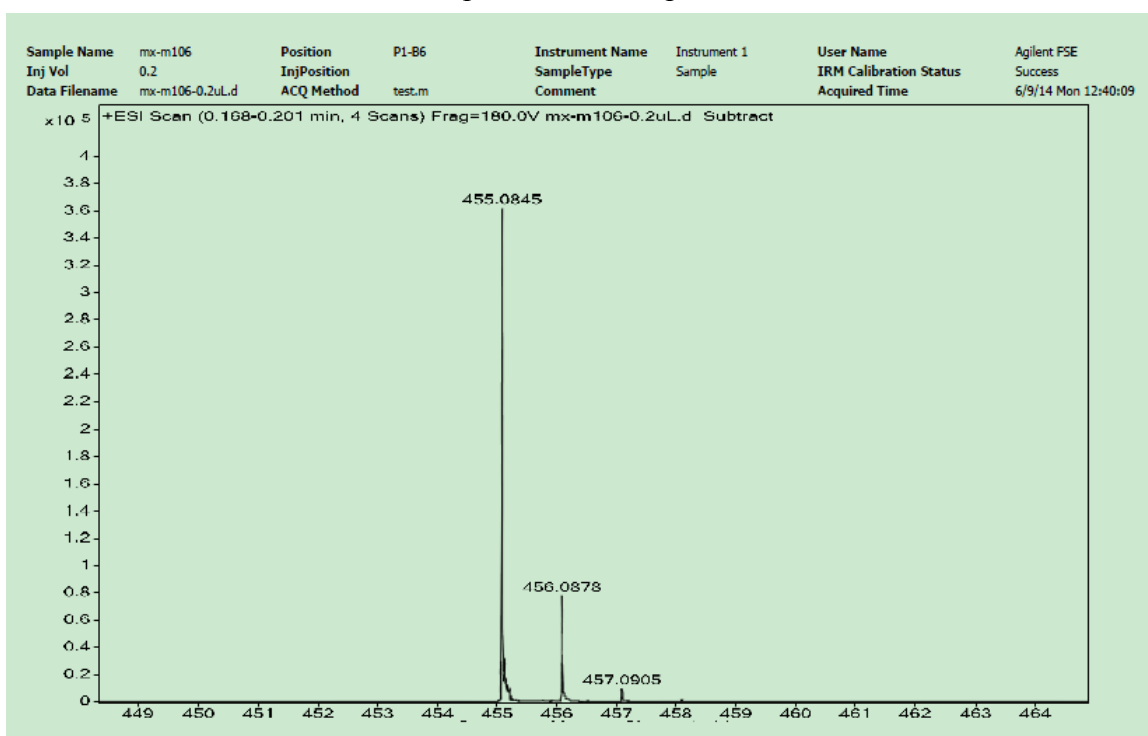
¹H NMR spectrum of compound **3m**



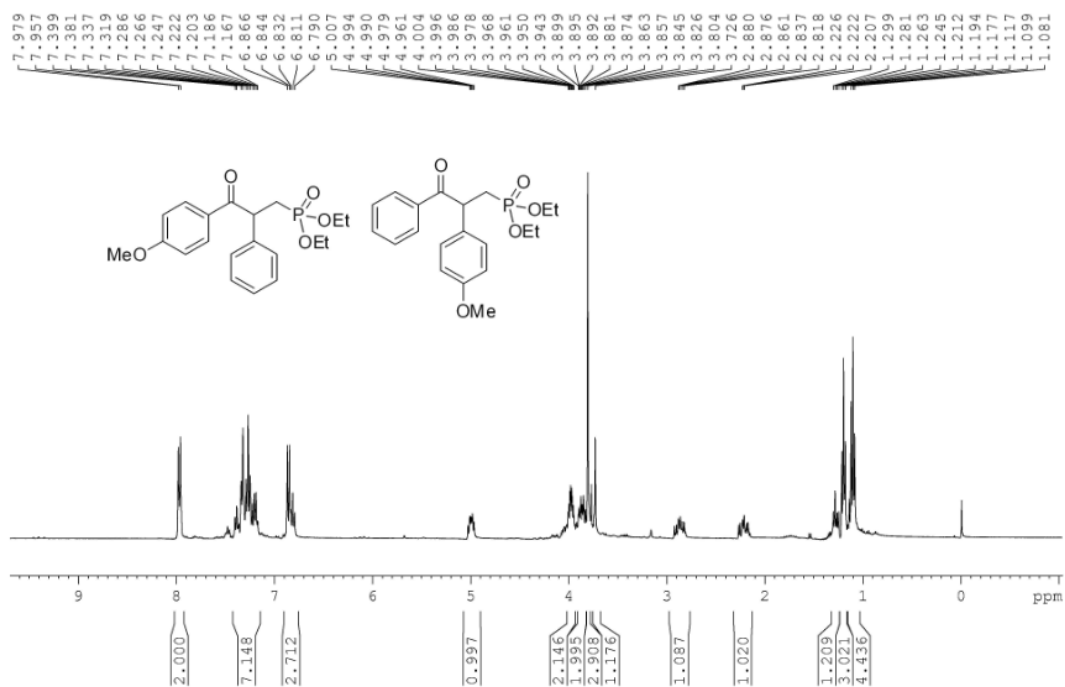
¹³C NMR spectrum of compound **3m**



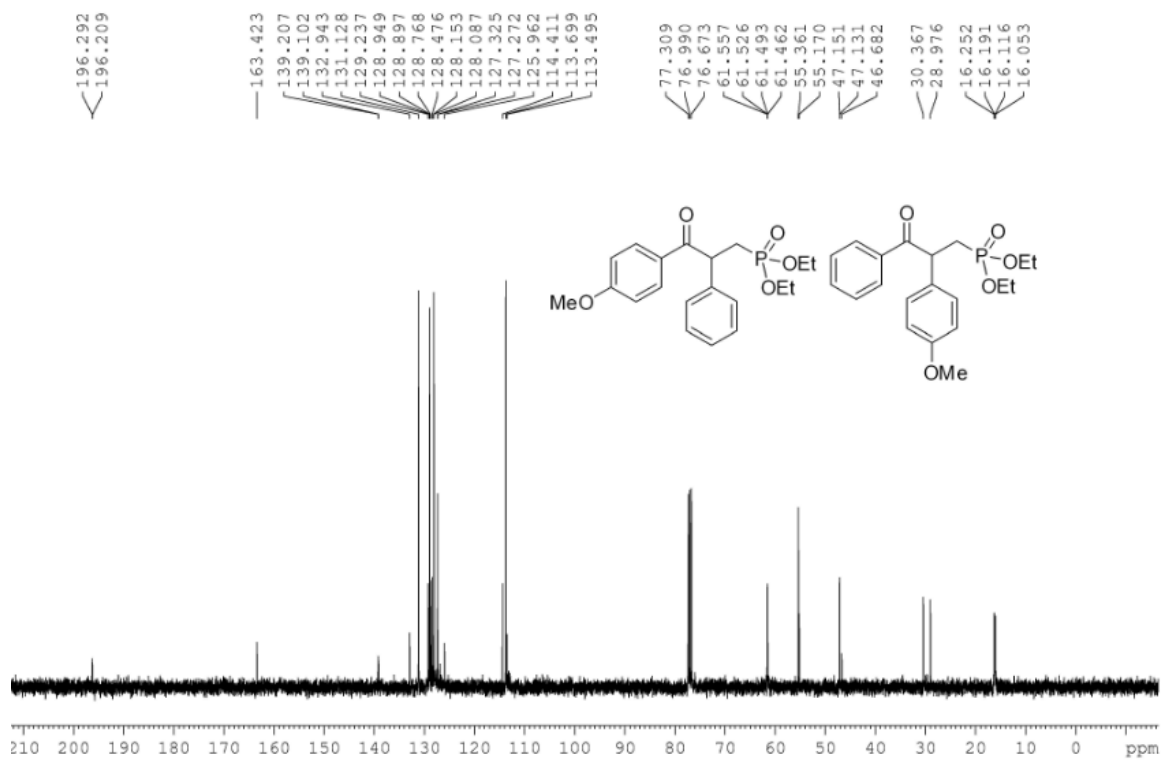
³¹P NMR spectrum of compound **3m**



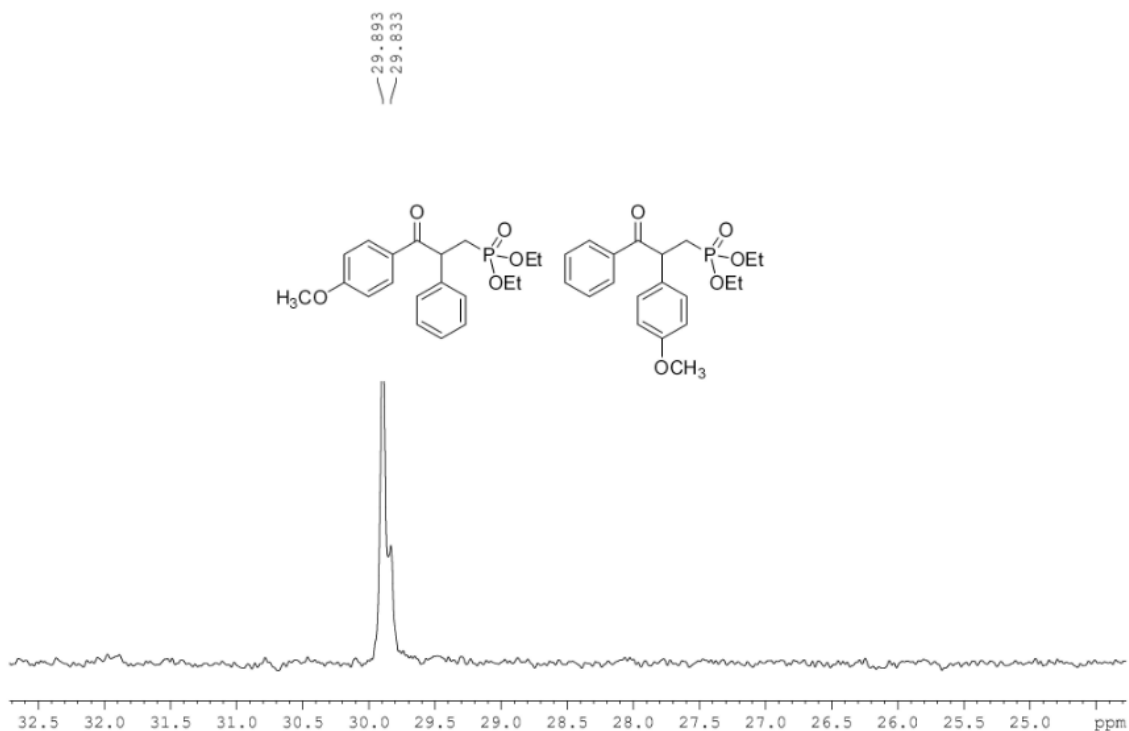
HRMS spectrum of compound **3m**



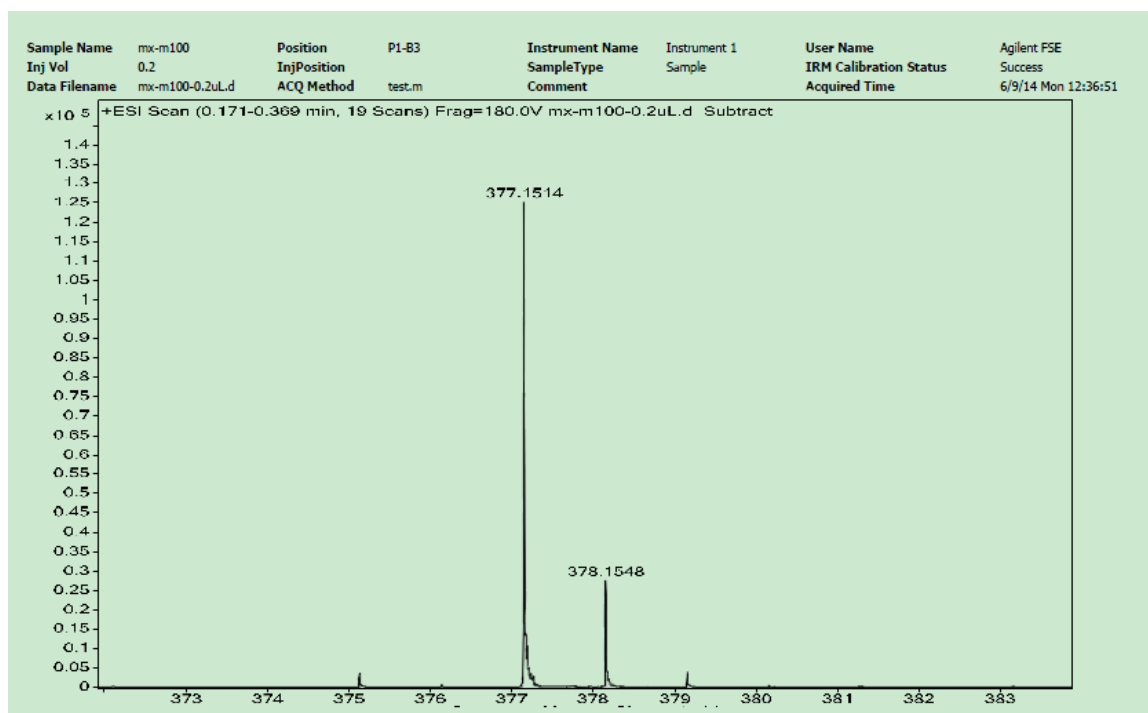
¹H NMR spectrum of compound **3n** and **3n'**



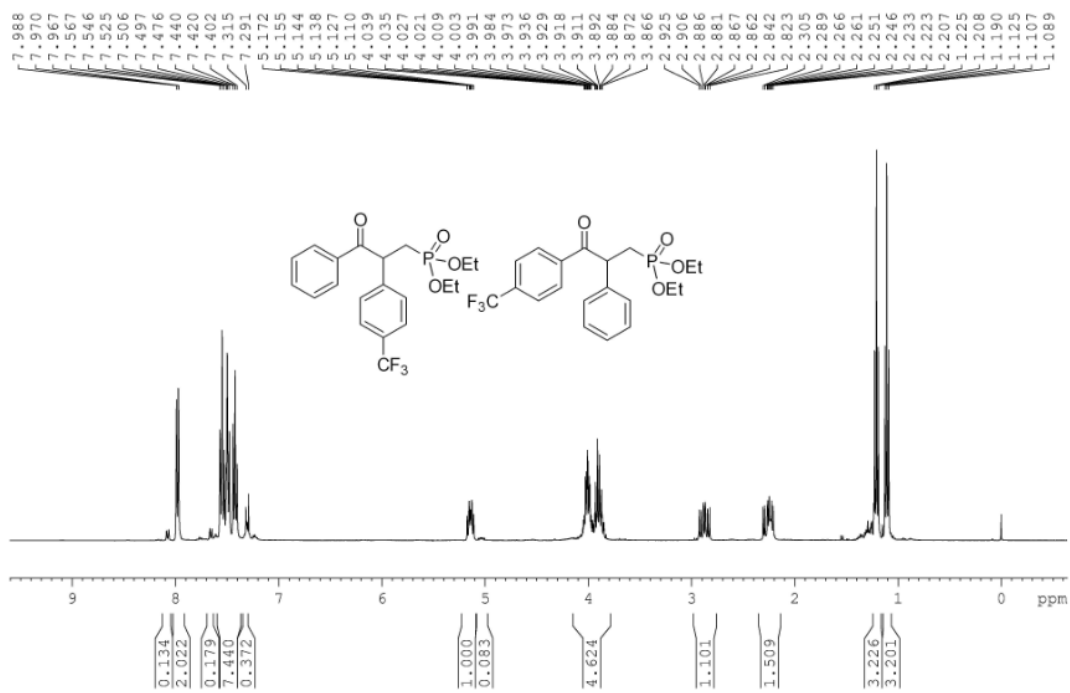
¹³C NMR spectrum of compound **3n** and **3n'**



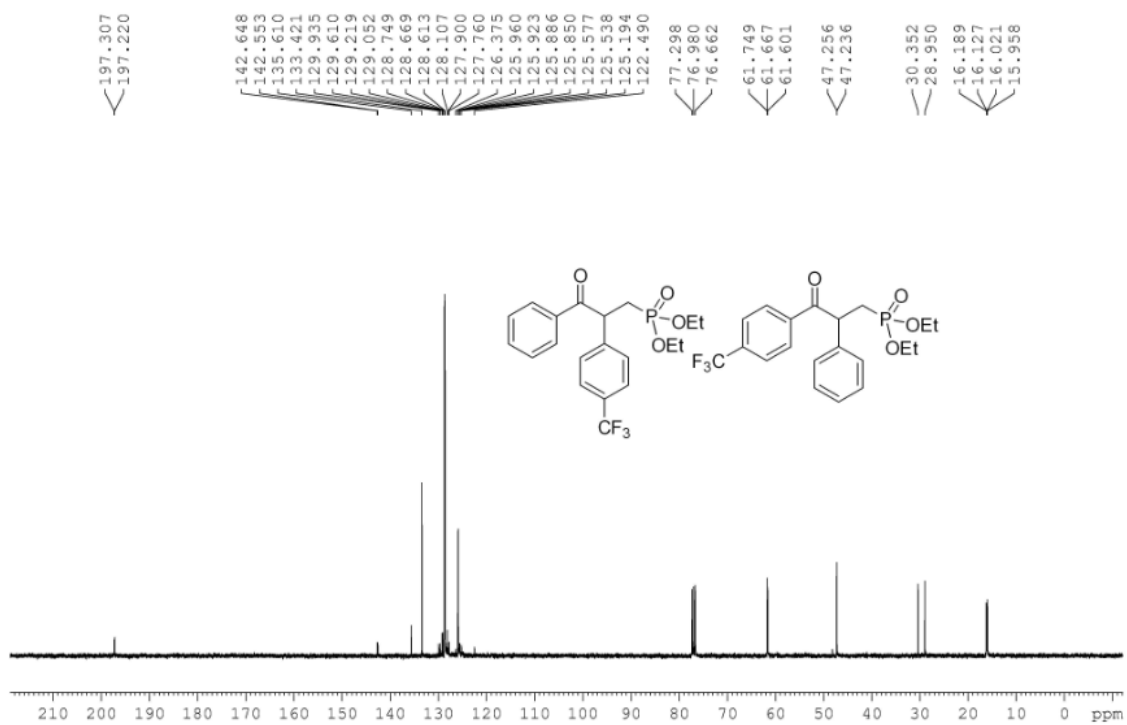
^{31}P NMR spectrum of compound **3n** and **3n'**



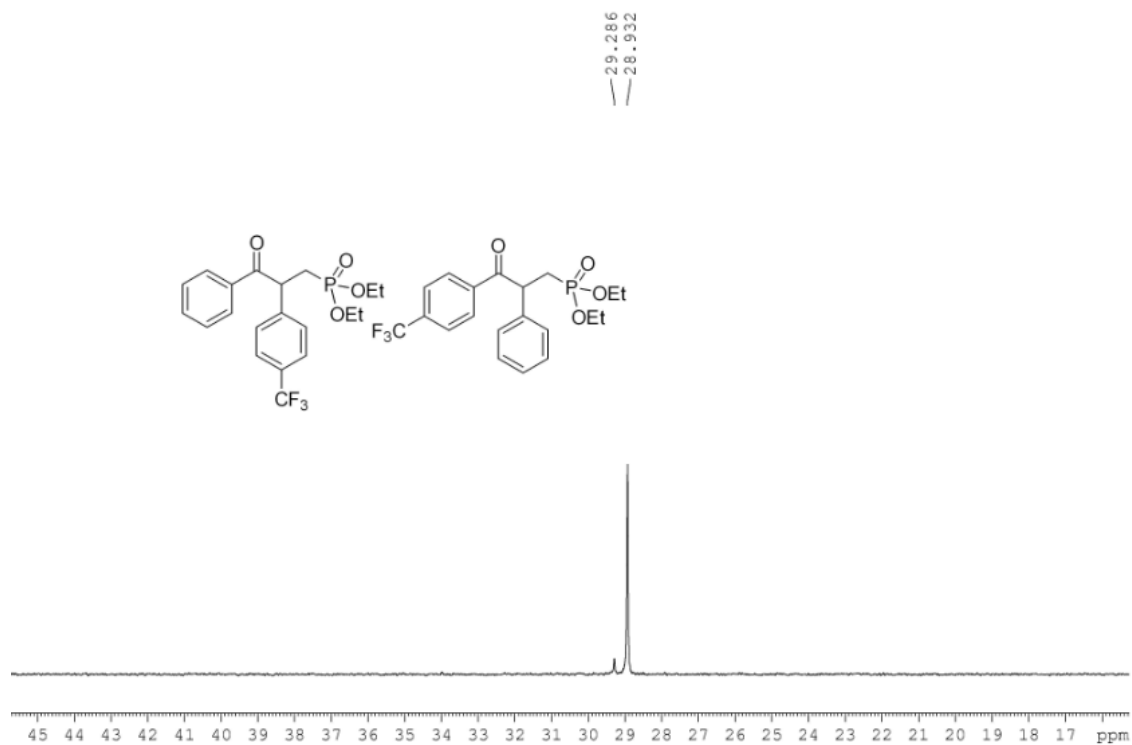
HRMS spectrum of compound **3n** and **3n'**



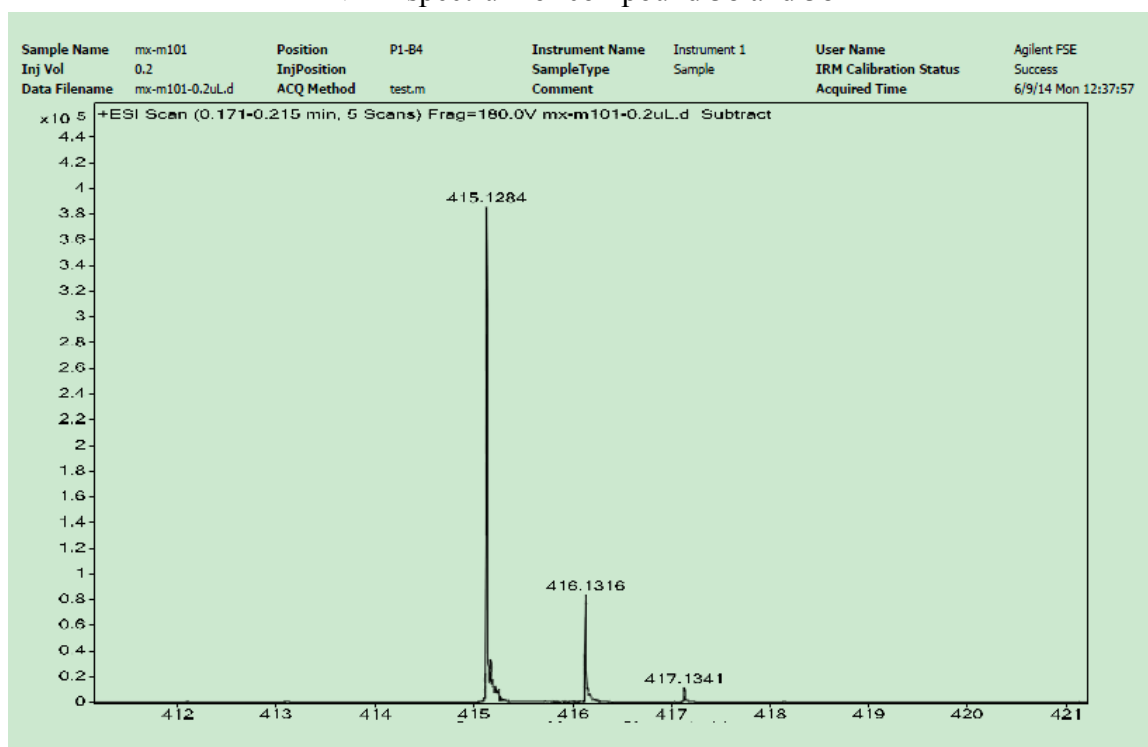
¹H NMR spectrum of compound **3o** and **3o'**



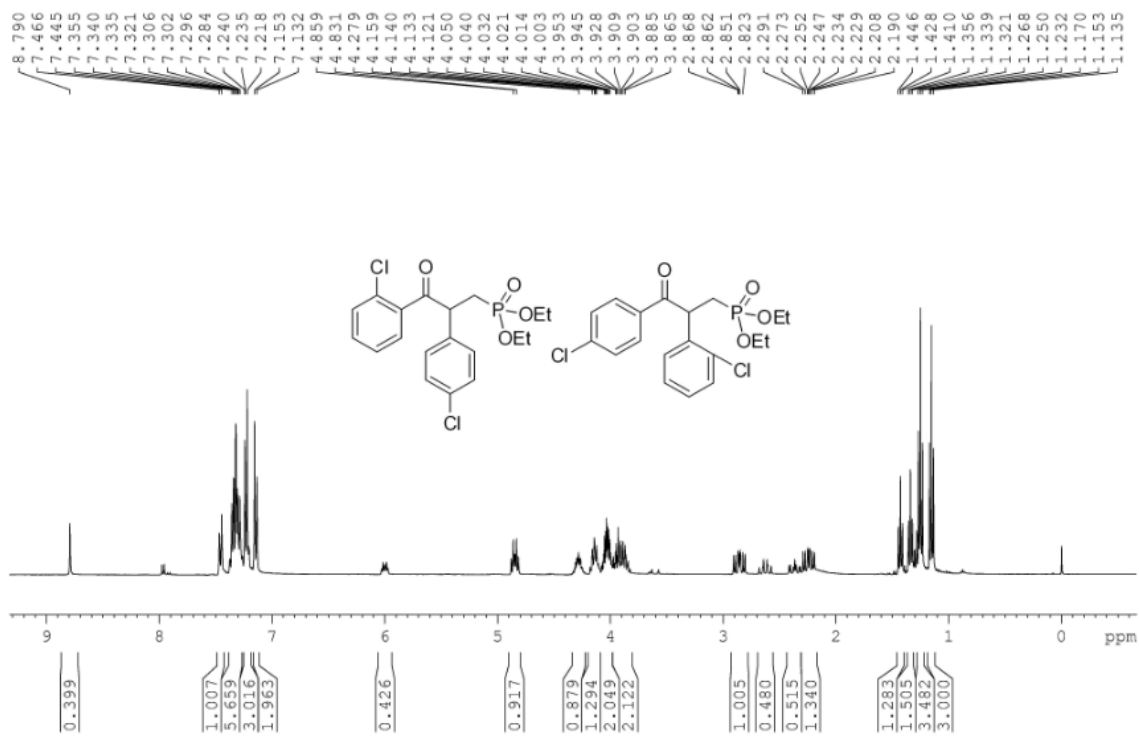
¹³C NMR spectrum of compound **3o** and **3o'**



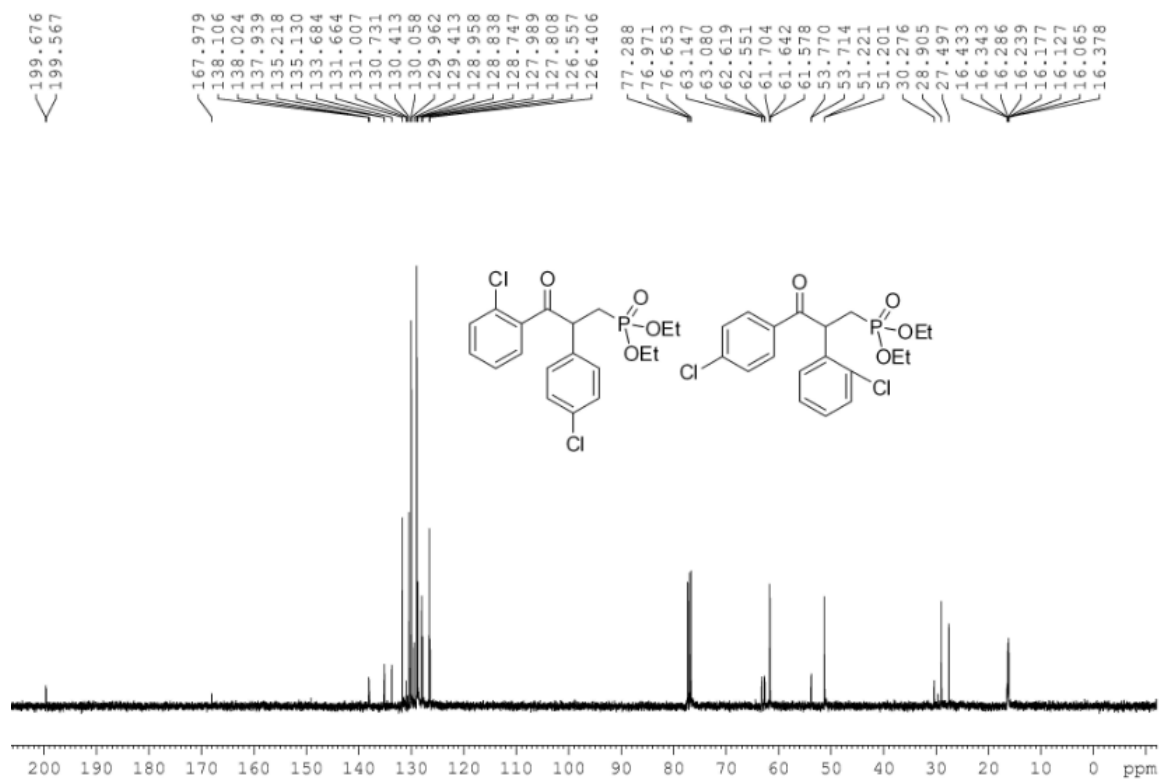
³¹P NMR spectrum of compound **3o** and **3o'**



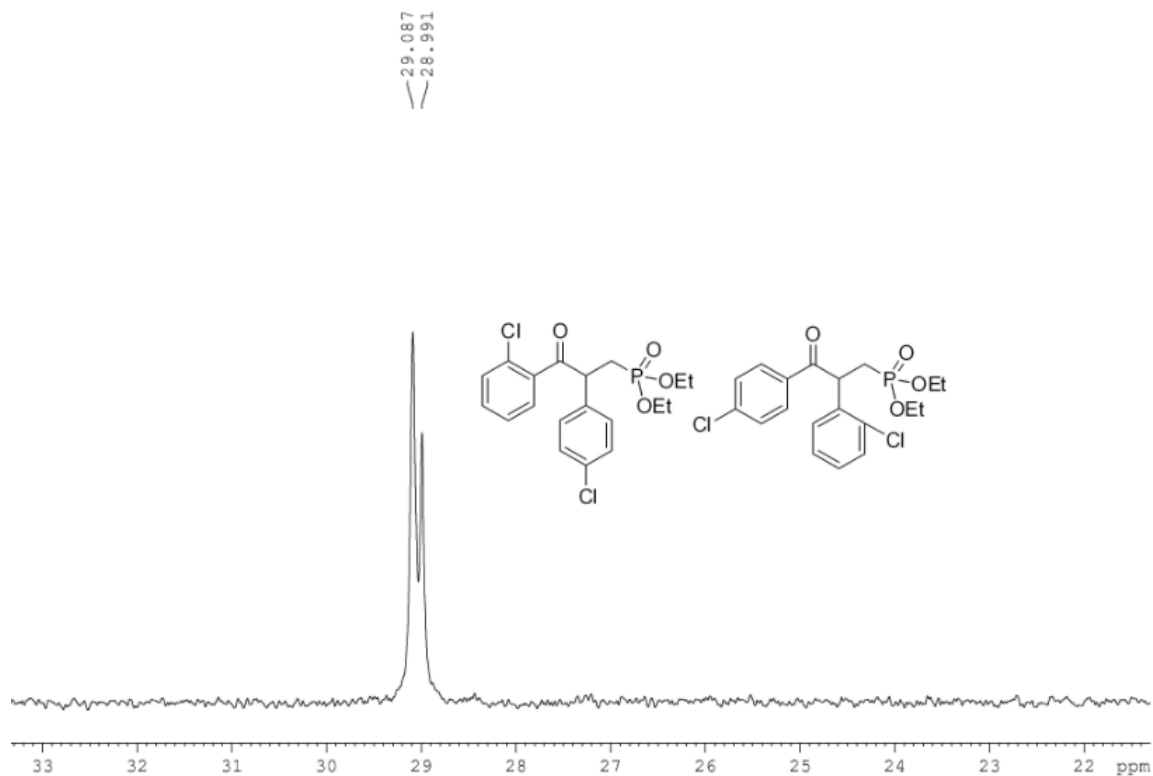
HRMS spectrum of compound **3o** and **3o'**



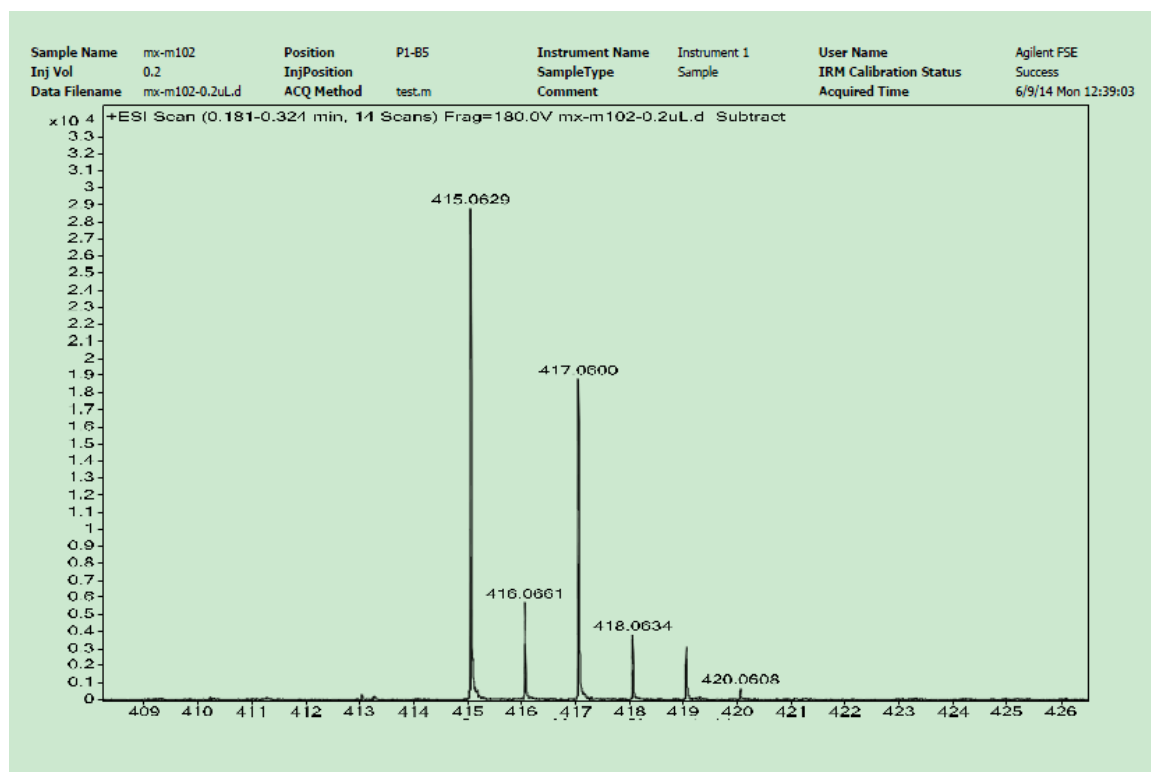
¹H NMR spectrum of compound 3p and 3p'



¹³C NMR spectrum of compound 3p and 3p'



^{31}P NMR spectrum of compound **3p** and **3p'**



HRMS spectrum of compound **3p** and **3p'**