

Supplementary information

Reusable zinc oxide nanoflowers for the synthesis of α -aminophosphonates under solvent-free ultrasonication

Sarika Rasal^a, Shilpa Jain^a and Navinchandra G Shimpi^{a*}

^a *Department of Chemistry, University of Mumbai, Santacruz (E), Mumbai 400098(India)*

***Corresponding author:** Dr. Navinchandra G. Shimpi (navin_shimpi@rediffmail.com), Phone no.: +91-22-26543575

Supporting information

Sr. no.	Contents	Page No.
1.	Catalytic activity of ZnO NFs in Kabachnik–Fields reaction	2
2.	TGA spectra	2
3.	Spectroscopic data of compounds (1p-30p)	3
4.	¹H NMR, ¹³C NMR and GC-MS spectra of some selected products	10
5.	References	47

1. Catalytic activity of ZnO NFs in Kabachnik–Fields reaction

In a round bottom flask, ZnO NFs (10 mol%) was added to a mixture of aldehyde, amine and diethyl phosphite (1:1:1) at room temperature. The reaction mixture was then subjected to ultrasonication with 5s/2s on/off time. The progress of reaction was monitored by TLC. Once the reaction was completed, ethyl acetate (10ml) was added to the reaction mixture and mixture was centrifuged at 4000 rpm for 10 min so as to separate catalyst. Organic layer was washed with excess of brine and dried over anhydrous Na_2SO_4 . Solvent was removed under vacuum. Subsequently, the reaction mixture was crystallized using ethyl acetate and n-hexane (1:4) so as to obtain the pure α -aminophosphonate.

2. TGA spectra

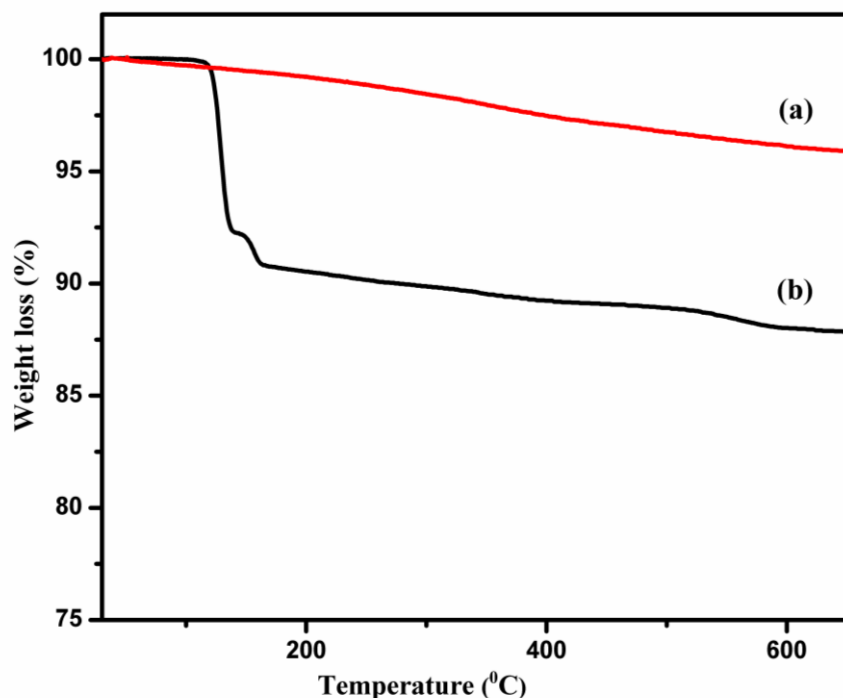


Figure S1: TGA spectra of ZnO NFs (a) fresh (b) after fourth cycle

This study shows decomposition temperature of pure catalyst was more than 800 °C, while the used materials shows decomposition temperature at 580 °C. This major loss was due to loss of thermal stability of the material as its surface becomes rough.

3. Spectroscopic data of compounds (1p-30p)

1p: Diethyl[(phenyl)(phenylamino)-methyl]-phosphonate^[1]

Yield 98% (White crystalline solid); Mp=97-99°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3295(N-H), 1236(P=O), 1058,1018(P-O-C), ¹H NMR(300MHz, CDCl₃): δ = 1.11-1.14 (t, 3H, -OCH₂-CH₃), 1.29-1.31 (t, 3H, -OCH₂-CH₃), 3.65-3.74 (m, 1H, -OCH₂-Me), 3.92-4.00 (m, 1H, -OCH₂-Me), 4.11-4.18 (m, 2H, OCH₂-Me), 4.76-4.84 (d, 2H, CHP+NH), 6.61 (dd, 2H, Ar), 6.72 (dd, 1H, Ar), 7.13 (dd, 2H, Ar), 7.31-7.38 (m, 3H, Ar), 7.49 (d, 2H, Ar). GC-MS (EI) m/z (%) calcd. for C₁₇H₂₂NO₃P: 319.34; found: 319 [M]⁺. Anal. calcd. for C₁₇H₂₂NO₃P: C, 63.94; H, 6.94; N, 4.39; found: C, 63.85; H, 6.81; N, 4.24.

2p: Diethyl[(4-chlorophenyl)(phenylamino)-methyl]-phosphonate^[1]

Yield 95% (White crystalline solid); Mp=86-88°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3304(N-H), 1237(P=O), 1040,1009(P-O-C), ¹H NMR (300MHz, CDCl₃): δ = 1.11-1.14 (t, 3H, -OCH₂-CH₃), 1.29-1.31 (t, 3H, -OCH₂-CH₃), 3.65-3.74 (m, 1H, -OCH₂-Me), 3.92-4.00 (m, 1H, -OCH₂-CH₃), 4.11-4.18 (m, 2H, OCH₂-CH₃), 4.76-4.84 (d, 2H, CHP+NH), 6.61 (dd, 2H, Ar), 6.69 (t, 1H, Ar), 7.10 (dd, 2H, Ar), 7.31-7.38 (m, 3H, Ar), 7.49 (dd, 2H, Ar). GC-MS (EI) m/z (%) calcd. for C₁₇H₂₁ClNO₃P: 353.78; found: 353 [M]⁺. Anal. calcd. for C₁₇H₂₁ClNO₃P: C, 57.71; H, 5.98; N, 3.96; found: C, 57.64; H, 5.81; N, 3.84.

3p: Diethyl[(4-methoxyphenyl)(phenylamino)-methyl]-phosphonate^[3]

Yield 91% (White crystalline solid); Mp=104-108°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3296(N-H), 1229(P=O), 1057,1025(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.13-1.15 (t, 3H, -OCH₂-CH₃), 1.30 (t, 3H, -OCH₂-CH₃), 3.67-3.76 (m, 1H, -OCH₂-CH₃), 3.79 (s, 3H, -OCH₃), 3.92-4.00 (m, 1H, -OCH₂-CH₃), 4.09-4.16 (m, 2H, OCH₂-CH₃), 4.70-4.76 (m, 2H, CHP+NH), 6.59 (d, 2H, Ar), 6.70 (t, 1H, Ar), 6.87 (d, 2H, Ar), 7.09-7.14 (m, 2H, Ar), 7.39 (d, 2H, Ar). Anal. calcd. for C₁₈H₂₄NO₄P: C, 61.88; H, 6.92; N, 4.01; found: C, 61.75; H, 6.76; N, 3.94.

4p: Diethyl[(4-nitro-phenyl)(phenylamino)-methyl]-phosphonate^[1]

Yield 96% (Yellow crystalline solid); Mp =149-150°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3288(N-H), 1275(P=O), 1053,1034(P-O-C), ¹H NMR (300MHz, CDCl₃): δ = 1.09-1.11 (t, 3H, -OCH₂-CH₃), 1.26-1.28 (t, 3H, -OCH₂-CH₃), 3.63-3.72 (m, 1H, -OCH₂-Me), 3.90-3.98 (m, 1H, -OCH₂-Me), 4.08-4.15 (m, 2H, OCH₂-Me), 4.74-4.81 (m, 2H, CHP+NH), 6.58 (dd, 2H, Ar), 6.69 (t, 1H, Ar), 7.10 (dd, 2H, Ar), 7.28-7.35 (m, 3H, Ar), 7.49 (dd, 2H, Ar). GC-MS (EI) m/z (%) calcd. for C₁₇H₂₁N₂O₅P: 364.33; found: 364 [M]⁺, Anal. calcd. for C₁₇H₂₁N₂O₅P: C, 56.04; H, 5.81; N, 7.69; found: C, 55.94; H, 5.73; N, 7.54.

5p: Diethyl[(2-Hydroxy-3-methoxy-phenyl)(phenylamino)-methyl]-phosphonate

Yield 95% (White solid); Mp = 122-125°C; IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3295(N-H), 1236(P=O), 1058,1018(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.11-1.15 (t, 3H, -OCH₂-CH₃), 1.29-1.34 (t, 3H, -OCH₂-CH₃), 3.74-3.82 (m, 1H, -OCH₂-CH₃), 3.89 (s, 3H, -OCH₃), 3.96-4.04 (m, 1H, -OCH₂-CH₃), 4.15-4.22 (m, 2H, OCH₂-CH₃), 4.84 (d, 1H, NH), 5.22 (d, 1H, CHP), 6.66-6.86 (m, 6H, Ar), 7.04 (d, 1H, Ar), 7.15 (t, 2H, Ar). Anal. calcd. for C₁₈H₂₄NO₅P: C, 59.17; H, 6.62; N, 3.83; found: C, 59.09; H, 6.58; N, 3.71.

6p: Diethyl[(2-thiophenyl)(Phenylamino) -methyl]-phosphonate^[3]

Yield 84% (White crystalline solid); Mp=69-70°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3295(N-H), 1236(P=O), 1058,1018(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.20-1.25(t, 3H, -OCH₂-CH₃), 1.28-1.33 (t, 3H, -OCH₂-CH₃), 3.88-4.04(m, 1H, -OCH₂-CH₃), 4.07-4.20 (m, 3H, -OCH₂-CH₃), 4.67 (t, 1H, NH), 5.12 (d, 1H, CHP), 6.68 (d, 2H, Ar), 6.74-6.79 (t, 1H, Ar), 6.99-7.00 (d, 1H, Ar), 7.15-7.28 (m, 4H Ar). Anal. calcd. for C₁₅H₂₀NO₃PS: C, 55.37; H, 6.20; N, 4.30; S, 9.86; found: C, 55.28; H, 6.13; N, 4.11; S, 9.74.

8p: Diethyl[(4-Methoxy-phenylamino)(4-nitro-phenyl)-methyl]-phosphonate

Yield 98% (Yellow crystalline solid); Mp= 126-128°C, IR (KBr, $\nu_{\max}/\text{cm}^{-1}$):3350(N-H), 1237(P=O), 1040,1005(P-O-C) ^1H NMR (300 MHz, CDCl_3): δ = 1.10-1.15 (t, 3H, -OCH₂-CH₃), 1.26-1.31 (t, 3H, -OCH₂-CH₃), 3.60-3.69 (m, 1H, -OCH₂-CH₃), 3.76 (s, 3H, -OCH₃), 3.88-3.96 (m, 1H, -OCH₂-CH₃), 4.09-4.16 (m, 2H, -OCH₂-CH₃), 4.71-4.81 (d, 1H, CHP), 6.57 (dd, 2H, Ar), 6.85 (dd, 2H, Ar), 7.36 (dd, 2H, Ar), 7.97 (dd, 2H, Ar). Anal. calcd. for C₁₈H₂₃N₂O₆P: C, 54.82; H, 5.88; N, 7.10; found: C, 54.75; H, 5.65; N, 7.01.

10p:Diethyl[(2-Hydroxy-3-methoxy-phenyl)-(4-methoxy-phenylamino)-methyl]-phosphonate

Yield 97% (Grey crystalline solid); Mp= 149-151°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$):3541(O-H), 3327(N-H), 1239(P=O), 1034,1018(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.12-1.16 (t, 3H, -OCH₂-CH₃), 1.29-1.34 (t, 3H, -OCH₂-CH₃),3.69 (s, 3H, -OCH₃), 3.77-3.88 (m, 1H, -OCH₂-CH₃), 3.97(s, 3H,-OCH₃), 4.00-4.05 (m, 1H, -OCH₂-CH₃), 4.16-4.23 (m, 2H, -OCH₂-CH₃), 4.58 (s, 1H, NH), 5.18 (s, 1H, CHP) 6.62-6.85 (m, 6H, Ar), 6.94-7.01 (m, 2H, Ar). ^{13}C NMR (75 MHz, CDCl_3): 16.21(d, -OCH₂CH₃), 16.47(d, -OCH₂CH₃), 20.37(-CH₃), 49.21-51.26(d, -CH), 55.98(-OCH₃), 63.34(d, -OCH₂CH₃), 63.48(d, -OCH₂CH₃), 110.31, 114.04, 120.08, 120.51, 122.17, 127.76, 129.66, 144.05, 144.19, 147.10(Ar). Anal. calcd. for C₁₉H₂₆NO₆P: C, 57.72; H, 6.63; N, 3.54; found: C, 57.66; H, 6.59; N, 3.49.

11p: Diethyl[(2-Fluoro-phenyl)-(4-methoxy-phenylamino)-methyl]-phosphonate

Yield 96% (Grey crystalline solid); Mp=84-85°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$):3342(N-H), 1231(P=O), 1048,1005(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.06-1.11 (t, 3H, -OCH₂-CH₃), 1.30-1.34 (t, 3H, -OCH₂-CH₃), 3.68-3.78 (m, 4H, -OCH₂-CH₃, -OCH₃), 3.91-3.99 (m, 1H, -OCH₂-CH₃), 4.16-4.25 (m, 2H, -OCH₂-CH₃), 4.55 (s, 1H, NH), 5.08 (s, 1H, CHP), 6.56-6.68 (dd, 4H, Ar), 7.02-7.26 (m, 3H, Ar), 7.48-7.52 (m, 1H, Ar). ^{13}C NMR (75 MHz, CDCl_3): 16.21(d, -OCH₂CH₃), 16.47(d, -OCH₂CH₃), 20.37(-CH₃), 49.21-51.26(d, -CH), 55.98(-OCH₃), 63.34(d, -

OCH₂CH₃), 63.48(d, -OCH₂CH₃), 110.31, 114.04, 120.08, 120.51, 122.17, 127.76, 129.66, 144.05, 144.19, 147.10(Ar). GC-MS (EI) m/z (%) calcd. for C₁₈H₂₃FNO₄P: 367.35; found: 367 [M]⁺. Anal. calcd. for C₁₈H₂₃FNO₄P: C, 58.85; H, 6.31; N, 3.81; found: C, 58.73; H, 6.16; N, 3.65.

12p: Diethyl[(phenyl)(p-tolylamino)-methyl]-phosphonate

Yield 97% (White crystalline solid); Mp= 114-115°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3323(N-H), 1230(P=O), 1050,1013(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.109-1.14 (t, 3H, -OCH₂-CH₃), 1.26-1.31 (t, 3H, -OCH₂-CH₃), 2.18 (s, 3H, CH₃-Ph), 3.63-3.72 (m, 1H, -OCH₂-CH₃), 3.90-3.98 (m, 1H, -OCH₂-CH₃), 4.08-4.15 (m, 2H, OCH₂-CH₃), 4.70-4.77 (d, 2H, CHP+NH), 6.53 (d, 2H, Ar), 6.92 (d, 2H, Ar), 7.25-7.35 (m, 3H, Ar), 7.45-7.48 (d, 2H, Ar). GC-MS (EI) m/z (%) calcd. for C₁₈H₂₄NO₃P: 333.36; found: 333[M]⁺. Anal. calcd. for C₁₈H₂₄NO₃P: C, 64.85; H, 7.26; N, 4.20; found: C, 64.63; H, 7.13; N, 4.11.

13p: Diethyl[(4-methoxyphenyl)(p-tolylamino)-methyl]-phosphonate^[2]

Yield 98% (White crystalline solid); Mp= 98-99°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3296(N-H), 1237(P=O), 1050,1023(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.13-1.18 (t, 3H, -OCH₂-CH₃), 1.28-1.33 (t, 3H, -OCH₂-CH₃), 2.20 (s, 3H, CH₃-Ph), 3.68-3.76 (m, 1H, -OCH₂-CH₃), 3.79 (s, 3H, -OCH₃), 3.93-4.01 (m, 1H, -OCH₂-CH₃), 4.09-4.16 (m, 2H, OCH₂-CH₃), 4.66 (d, 1H, NH), 4.76 (d, 1H, CHP), 6.54 (d, 2H, Ar), 6.94 (dd, 4H, Ar), 7.38-7.41 (m, 2H, Ar). GC-MS (EI) m/z (%) calcd. for C₁₉H₂₆NO₄P: 363.39; found: 363 [M]⁺, Anal. calcd. for C₁₉H₂₆NO₄P: C, 62.80; H, 7.21; N, 3.85; found: C, 62.14; H, 7.13; N, 3.69.

14p: Diethyl[(4-chlorophenyl)(p-tolylamino)-methyl]-phosphonate

Yield 95% (White crystalline solid); Mp=118-120°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3291(N-H), 1237(P=O), 1050,1018(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.18-1.20 (t, 3H, -OCH₂-CH₃), 1.31-1.33 (t, 3H, -OCH₂-CH₃), 2.21 (s, 3H, CH₃-Ph), 3.76-3.84 (m, 1H, -OCH₂-CH₃), 3.97-4.02 (m, 1H, -OCH₂-CH₃), 4.10-4.17 (m, 2H, -OCH₂-CH₃), 4.68-4.76 (d, 2H, CH+NH), 6.51 (d, 2H, Ar), 6.95 (d, 2H, Ar), 7.30 (m, 2H, Ar), 7.43 (dd, 4.0 Hz, 2H, Ar). GC-MS (EI) m/z (%) calcd. for C₁₈H₂₃ClNO₃P: 367.81; found: 367[M]⁺ Anal. calcd. for C₁₈H₂₃ClNO₃P: C, 58.78; H, 6.30; N, 3.81; found: C, 58.66; H, 6.14; N, 3.72.

15p: Diethyl[(2-Methoxy-phenyl)-p-tolylamino-methyl]-phosphonate

Yield 99% (White crystalline solid); Mp= 117-118°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3297(N-H), 1227(P=O), 1051, 1022 (P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.00-1.05 (t, 3H, -OCH₂-CH₃), 1.27-1.32 (t, 3H, -OCH₂-CH₃), 2.16 (s, 3H, -CH₃), 3.57-3.65 (m, 1H, -OCH₂-CH₃), 3.85-3.90 (m, 1H, -OCH₂-CH₃), 3.91 (s, 3H, -OCH₃), 4.12-4.22 (m, 2H, -OCH₂-CH₃), 4.71 (s, 1H, NH), 5.32- 5.40(s, 1H, CHP), 6.51-6.53 (dd, 2H, Ar), 6.85-6.92 (m, 4H, Ar), 7.17-7.25 (m, 1H, Ar), 7.42-7.46 (m, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃) δ =16.06(d, -OCH₂CH₃), 16.40(d, -OCH₂CH₃), 47.20 -49.25(d, -CH), 20.34(-CH₃), 55.70(-OCH₃), 63.03(d, -OCH₂CH₃), 110.45, 113.67, 121.01, 124.67, 127.23, 128.18, 128.85, 129.61, 143.98, 157.30. GC-MS (EI) m/z (%)

calcd. for $C_{18}H_{24}NO_3P$: 363.36; found: 363[M]⁺. Anal. calcd. for $C_{19}H_{26}NO_4P$: C, 62.80; H, 7.21; N, 3.85; found: C, 62.74; H, 7.09; N, 3.71.

16p: Diethyl[(4-Hydroxy-3,5-dimethoxy-phenyl)-p-tolylamino-methyl]-phosphonate

Yield 99% (White crystalline solid); Mp= 143-145°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3327(O-H), 3378(N-H), 1228(P=O), 1043,1017(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.13-1.18 (t, 3H, -OCH₂-CH₃), 1.26-1.31 (t, 3H, -OCH₂-CH₃), 2.19 (s, 3H, -CH₃), 3.67-3.86 (m, 1H, -OCH₂-CH₃), 3.92 (s, 6H, -OCH₃), 3.96-3.99 (m, 1H, -OCH₂-CH₃), 4.07-4.14 (m, 2H, -OCH₂-CH₃), 4.58-4.66 (s, 2H, CHP+NH), 6.51 (dd, 2H, Ar), 6.70 (s, 2H, Ar), 6.91(dd, 2H, Ar), 7.26 (s,1H, Ar). ¹³C NMR (75 MHz, CDCl₃) δ =16.28 (d, -OCH₂CH₃), 16.42(d, -OCH₂CH₃), 56.35 (-OCH₃), 20.36 (-CH₃), 55.59-57.61(d, -CH), 63.24(d, -OCH₂CH₃), 104.66, 114.07, 126.95, 127.73, 129.66, 134.45, 144.18, 147.23. Anal. calcd. for $C_{20}H_{28}NO_6P$: C, 58.67; H, 6.89; N, 3.42; found: C, 58.51; H, 6.80; N, 3.29.

17p: Diethyl[p-Tolylamino-(3,4,5-trimethoxy-phenyl)-methyl]-phosphonate

Yield 99% (White crystalline solid); Mp= 120-122°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3305(N-H), 1230(P=O), 1050, 1021(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.13-1.17 (t, 3H, -OCH₂-CH₃), 1.26-1.31 (t, 3H, -OCH₂-CH₃), 2.20 (s, 3H, -CH₃), 3.69-3.81 (m, 1H, -OCH₂-CH₃), 3.83 (s, 9H, -OCH₃), 4.02-4.15 (m, 3H, -OCH₂-CH₃), 4.59 (s, 1H, CHP), 6.52 (dd, 2H, Ar), 6.69 (s, 2H, Ar), 6.92 (dd, 2H, Ar). ¹³C NMR (75 MHz, CDCl₃) δ =16.25(d, -OCH₂CH₃), 16.48(d, -OCH₂CH₃), 55.78-56.19 (d, -CH), 20.37(-CH₃), 57.78 (-OCH₃), 60.80(-OCH₃), 63.18(d, -OCH₂CH₃), 63.27 (d, -OCH₂CH₃), 104.98, 114.02, 127.81, 129.71, 131.75, 137.76, 144.21, 153.37. Anal. calcd. for $C_{21}H_{30}NO_6P$: C, 59.57; H, 7.14; N, 3.31; found: C, 59.49; H, 7.09; N, 3.18.

18p: Diethyl[(ferrocenyl)-p-tolylamino-methyl]-phosphonate

Yield 98% (Yellow solid); Mp= 168-172°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3332(N-H), 1226(P=O), 1041, 1016(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.15-1.19 (t, 3H, -OCH₂-CH₃), 1.20-1.23 (t, 3H, -OCH₂-CH₃), 2.25 (s, 3H, -CH₃), 3.90-4.10 (m, 5H, Ferrocenyl, 4H, -OCH₂-CH₃), 4.29 (s, 2H, Ferrocenyl),4.15-4.18 (dd, 2H, Ferrocenyl), 4.40-4.49 (d, 1H, CHP), 6.72 (dd, 2H, Ar), 7.03 (dd, 2H, Ar). ¹³C NMR (75 MHz, CDCl₃) δ = 16.35 (d, -OCH₂CH₃), 16.48(d, -OCH₂CH₃), 20.42(-CH₃), 51.24-53.38 (d, -CH), 62.55(d, -OCH₂CH₃), 63.21(d, -OCH₂CH₃), 65.95(Ferrocenyl), 67.71(Ferrocenyl), 68.74 (5C, Ferrocenyl), 85.69 (Ferrocenyl), 113.80, 127.6, 129.86, 145.07. Anal. calcd. for $C_{24}H_{34}FeNO_3P$: C, 61.16; H, 7.27; N, 2.97; found: C, 61.03; H, 7.19; N, 2.90.

19p: Diethyl[p-Tolylamino-(3,4-dimethoxy-phenyl)-methyl]-phosphonate

Yield 98% (Yellow viscous oil); IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3301(N-H), 1230(P=O), 1051, 1019(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.12-1.16 (t, 3H, -OCH₂-CH₃), 1.26-1.30 (t, 3H, -OCH₂-CH₃), 2.18 (s, 3H, -CH₃), 3.75-3.66 (m, 1H, -OCH₂-CH₃), 3.86 (s, 6H, -OCH₃), 3.97-3.94 (m, 1H, -OCH₂-CH₃), 4.07-4.15 (m, 2H, -OCH₂-CH₃), 4.62 (s, 2H, CHP+NH), 6.50 (dd, 2H, Ar),

6.80–7.26 (m, 7H, Ar). ^{13}C NMR (75 MHz, CDCl_3) δ = 16.11(d, $-\text{OCH}_2\text{CH}_3$), 16.41(d, $-\text{OCH}_2\text{CH}_3$), 47.38–49.42(d, $-\text{CH}$), 20.34($-\text{CH}_3$), 55.60 ($-\text{OCH}_3$), 56.32 ($-\text{OCH}_3$), 63.05 (d, $-\text{OCH}_2\text{CH}_3$), 111.68, 113.55, 113.78, 113.82, 125.83, 127.33, 129.62, 143.97, 151.60, 153.89. Anal. calcd. for $\text{C}_{20}\text{H}_{28}\text{NO}_5\text{P}$: C, 61.06; H, 7.17; N, 3.56; found: C, 60.92; H, 7.04; N, 3.49.

20p: Diethyl[(4-Hydroxy-3-methoxy-phenyl)-p-tolylamino-methyl]-phosphonate

Yield 98% (Buff solid); Mp=88–90°C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3524(O-H), 3385(N-H), 1226(P=O), 1048, 1016(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.12–1.16 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 1.26–1.30 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 2.18 (s, 3H, $-\text{CH}_3$), 3.75–3.66 (m, 1H, $-\text{OCH}_2\text{CH}_3$), 3.86 (s, 6H, $-\text{OCH}_3$), 3.97–3.94 (m, 1H, $-\text{OCH}_2\text{CH}_3$), 4.07–4.15 (m, 2H, $-\text{OCH}_2\text{CH}_3$), 4.62 (s, 2H, $\text{CHP}+\text{NH}$), 6.50 (dd, 2H, Ar), 6.80–7.26 (m, 7H, Ar). Anal. calcd. for $\text{C}_{19}\text{H}_{26}\text{NO}_5\text{P}$: C, 60.15; H, 6.91; N, 3.69; found: C, 60.09; H, 6.88; N, 3.51.

21p: Diethyl[(Thiophen-2-yl-p-tolylamino-methyl)-phosphonate

Yield 84% (buff colour solid); Mp= 110–112°C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3379(N-H), 1233(P=O), 1048, 1019(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.20–1.22(t, 3H, $-\text{OCH}_2\text{CH}_3$), 1.28–1.30 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 3.68 (s, 3H, $-\text{OCH}_3$), 3.85–3.93(m, 1H, $-\text{OCH}_2\text{CH}_3$), 4.04–4.20 (m, 3H, $-\text{OCH}_2\text{CH}_3$), 4.39 (t, 1H, NH), 4.99 (d, 1H, CHP), 6.60–6.62(m, 2H, Ar), 6.96–6.99 (m, 3H, Ar), 7.16–7.24 (m, 2H, Ar). ^{13}C NMR (75 MHz, CDCl_3): 16.31(d, $-\text{OCH}_2\text{CH}_3$), 16.48(d, $-\text{OCH}_2\text{CH}_3$), 52.13–54.22(d, $-\text{CH}$), 55.59($-\text{OCH}_3$), 63.38(d, $-\text{OCH}_2\text{CH}_3$), 63.63 (d, $-\text{OCH}_2\text{CH}_3$), 114.73, 115.53, 125.23, 126.12, 127.05, 140.13, 140.22, 153.08(Ar). GC-MS (EI) m/z (%) calcd. for $\text{C}_{19}\text{H}_{26}\text{NO}_5\text{P}$: 339.39; found: 339[M] $^+$; Anal. calcd. for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{PS}$: C, 56.62; H, 6.53; N, 4.13; S, 9.45; found: C, 56.59; H, 6.48; N, 4.09; S, 9.37.

22p: Diethyl[(2-Hydroxy-3-methoxy-phenyl)-o-tolylamino-methyl]-phosphonate

Yield 96% (buff colour solid); Mp= 118–120 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3520(O-H), 3379(N-H), 1226(P=O), 1051, 1013(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.12–1.17 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 1.29–1.34 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 2.27 (s, 3H, $-\text{CH}_3$), 3.78–3.85 (m, 1H, $-\text{OCH}_2\text{CH}_3$), 3.90 (s, 3H, $-\text{OCH}_3$), 3.98–4.06 (m, 1H, $-\text{OCH}_2\text{CH}_3$), 4.15–4.22 (m, 2H, $-\text{OCH}_2\text{CH}_3$), 5.22 (s, 1H, CHP), 6.57–6.69 (m, 2H, Ar), 6.77–6.85 (m, 2H, Ar), 6.98–7.06 (m, 3H, Ar). ^{13}C NMR (75 MHz, CDCl_3): 16.22(d, $-\text{OCH}_2\text{CH}_3$), 16.47(d, $-\text{OCH}_2\text{CH}_3$), 17.54($-\text{CH}_3$), 48.92–50.09(d, $-\text{CH}$), 55.99($-\text{OCH}_3$), 63.38(d, $-\text{OCH}_2\text{CH}_3$), 63.49 (d, $-\text{OCH}_2\text{CH}_3$), 110.33, 111.16, 118.14, 120.14, 120.37, 122.20, 123.05, 127.03, 130.11, 144.11, 144.39, 147.13(Ar). GC-MS (EI) m/z (%) calcd. for $\text{C}_{19}\text{H}_{26}\text{NO}_5\text{P}$: 379.39; found: 379[M] $^+$; Anal. calcd. for $\text{C}_{19}\text{H}_{26}\text{NO}_5\text{P}$: C, 60.15; H, 6.91; N, 3.69; found: C, 60.09; H, 6.86; N, 3.52.

23p: Diethyl[(4-Bromo-phenylamino)-thiophen-2-yl-methyl]-phosphonate

Yield 87% (White crystalline solid); Mp= 161–164°C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3329(N-H), 1230(P=O), 1054, 1012(P-O-C), ^1H NMR (300 MHz, CDCl_3): δ = 1.19–1.24 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 1.29–1.34 (t, 3H, $-\text{OCH}_2\text{CH}_3$), 3.83–3.91 (m, 1H, $-\text{OCH}_2\text{CH}_3$), 4.03–4.20 (m, 3H, $-\text{OCH}_2\text{CH}_3$), 7.16–7.24 (m, 2H, Ar), 7.38–7.42 (m, 2H, Ar).

OCH₂-CH₃), 4.95 (d, 1H, CH), 6.55–6.58 (d, 2H, Ar), 6.98–7.01 (m, 1H, Ar), 7.15–7.16 (m, 1H, Ar) 7.234–7.284 (m, 4H, Ar). ¹³C NMR (75 MHz, CDCl₃): 16.30 (d, -OCH₂CH₃), 16.47 (d, -OCH₂CH₃), 51.16–53.25 (d, -CH), 63.55 (d, -OCH₂CH₃), 63.65 (d, -OCH₂CH₃), 115.13, 123.60, 125.44, 126.34, 127.15, 129.07, 139.39, 144.83 (Ar). Anal. calcd. for C₁₅H₁₉BrNO₃PS: C, 44.57; H, 4.74; N, 3.46; S, 7.93; found: C, 44.48; H, 4.68; N, 3.31; S, 7.89.

24p: Diethyl[(4-Bromo-phenylamino)-(2-hydroxy-3-methoxy-phenyl)-methyl]-phosphonate
Yield 94% (White crystalline solid); Mp= 174–177°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3558 (O-H), 3318 (N-H), 1214 (P=O), 1047, 1009 (P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.09 (t, 3H, -OCH₂-CH₃), 1.30 (t, 3H, -OCH₂-CH₃), 3.71–3.80 (m, 1H, -OCH₂-CH₃), 3.90 (s, 3H, -OCH₃), 3.95–4.03 (m, 1H, -OCH₂-CH₃), 4.16–4.22 (m, 2H, -OCH₂-CH₃), 5.16 (s, 1H, CHP), 6.53–6.56 (dd, 2H, Ar), 6.78–6.81 (m, 2H, Ar), 6.85–6.86 (m, 1H, Ar), 7.18–7.20 (dd, 2H, Ar). ¹³C NMR (75 MHz, CDCl₃): 15.98 (d, -OCH₂CH₃), 16.39 (d, -OCH₂CH₃), 48.32–50.37 (d, -CH), 56.00 (-OCH₃), 63.16 (d, -OCH₂CH₃), 63.46 (d, -OCH₂CH₃), 110.32, 114.90, 120.15, 120.27, 121.81, 122.99, 128.98, 143.84, 145.03, 146.79 (Ar). Anal. calcd. for C₁₈H₂₃BrNO₅P: C, 48.66; H, 5.22; N, 3.15; found: C, 48.62; H, 5.09; N, 3.08.

25p: Diethyl[(3-Bromo-5-chloro-2-hydroxy-phenyl)-(4-bromo-phenylamino)-methyl]-phosphonate
Yield 96% (Buff colour solid) Mp= 107–108°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3545 (O-H), 3329 (N-H), 1230 (P=O), 1054, 1012 (P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.22–1.26 (t, 3H, -OCH₂-CH₃), 1.29–1.33 (t, 3H, -OCH₂-CH₃), 3.96–4.04 (m, 1H, -OCH₂-CH₃), 4.09–4.23 (m, 3H, -OCH₂-CH₃), 4.72 (s, 1H, NH), 4.95 (d, 1H, CHP), 6.49–6.52 (dd, 2H, Ar), 7.24–7.28 (m, 3H, Ar), 7.47 (s, 1H, Ar), 7.97 (s, 1H, -OH). Anal. calcd. for C₁₇H₁₉Br₂ClNO₄P: C, 38.70; H, 3.63; N, 2.65; found: C, 38.62; H, 3.51; N, 2.60.

26p: Diethyl[(4-Bromo-phenylamino)-(3-hydroxy-phenyl)-methyl] phosphonate
Yield 92% (Brown oil); IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3531 (O-H), 3318 (N-H), 1226 (P=O), 1049, 1015 (P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.06–1.11 (t, 3H, -OCH₂-CH₃), 1.24–1.29 (t, 3H, -OCH₂-CH₃), 3.59–3.72 (m, 1H, -OCH₂-CH₃), 3.88–3.97 (m, 1H, -OCH₂-CH₃), 4.05–4.16 (m, 2H, -OCH₂-CH₃), 4.66–4.74 (d, 1H, CHP), 4.98 (s, 1H, NH), 6.46–6.49 (dd, 2H, Ar), 6.82–6.85 (d, 1H, Ar), 6.92–6.95 (d, 1H, Ar), 7.14–7.19 (m, 4H, Ar), 8.79 (s, 1H, -OH). Anal. calcd. for C₁₇H₂₁BrNO₄P: C, 49.29; H, 5.11; N, 3.38; found: C, 49.16; H, 5.04; N, 3.27.

27p: Diethyl[(4-Bromo-phenylamino)-(2-fluoro-phenyl)-methyl]-phosphonate
Yield 87% (White crystalline solid); Mp=101–104°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3326 (N-H), 1234 (P=O), 1054, 1021 (P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.06–1.11 (t, 3H, -OCH₂-CH₃), 1.30–1.35 (t, 3H, -OCH₂-CH₃), 3.14–3.76 (m, 1H, -OCH₂-CH₃), 3.90–3.95 (m, 1H, -OCH₂-CH₃), 4.15–4.25 (m, 2H, -OCH₂-CH₃), 5.07–5.15 (d, 1H, CHP), 6.48–6.51 (dd, 2H, Ar), 7.04–7.26 (m, 6H, Ar), 7.45–7.50 (m, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃): 16.05 (d, -OCH₂CH₃), 16.45 (d, -OCH₂CH₃), 47.23–49.33 (d, -CH), 63.41 (d, -OCH₂CH₃), 63.52 (d, -OCH₂CH₃), 114.74, 115.28, 123.49, 124.64, 128.76, 129.10, 129.69, 144.49, 159.19, 162.45. GC-MS (EI) m/z (%)

calcd. for $C_{17}H_{20}BrFNO_3P$: 416.22; found: 417[M]⁺; Anal. calcd. for $C_{17}H_{20}BrFNO_3P$: C, 49.06; H, 4.84; N, 3.37; found: C, 49.01; H, 4.79; N, 3.32.

28p: Diethyl[(4-Chloro-phenylamino)-(2-fluoro-phenyl)-methyl]-phosphonate

Yield 91% (White crystalline solid); Mp=78-80°C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3316(N-H), 1230(P=O), 1043, 1024(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.06-1.11 (t, 3H, -OCH₂-CH₃), 1.30-1.34 (t, 3H, -OCH₂-CH₃), 3.68-3.76 (m, 1H, -OCH₂-CH₃), 3.90-3.99 (m, 1H, -OCH₂-CH₃), 4.15-4.25 (m, 2H, -OCH₂-CH₃), 5.08-5.16 (d, 1H, CHP), 6.53-6.56 (dd, 2H, Ar), 7.03-7.12 (m, 4H, Ar), 7.22-7.26 (m, 1H, Ar), 7.46-7.51 (m, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃): 16.05(d, -OCH₂CH₃), 16.45(d, -OCH₂CH₃), 47.23-49.33(d, -CH), 63.41(d, -OCH₂CH₃), 63.52(d, -OCH₂CH₃), 114.74, 115.28, 123.49, 124.64, 128.76, 129.10, 129.69, 144.49, 159.19, 162.45. Anal. calcd. for $C_{17}H_{20}ClFNO_3P$: C, 54.92; H, 5.42; N, 3.77; found: C, 54.85; H, 5.33; N, 3.70.

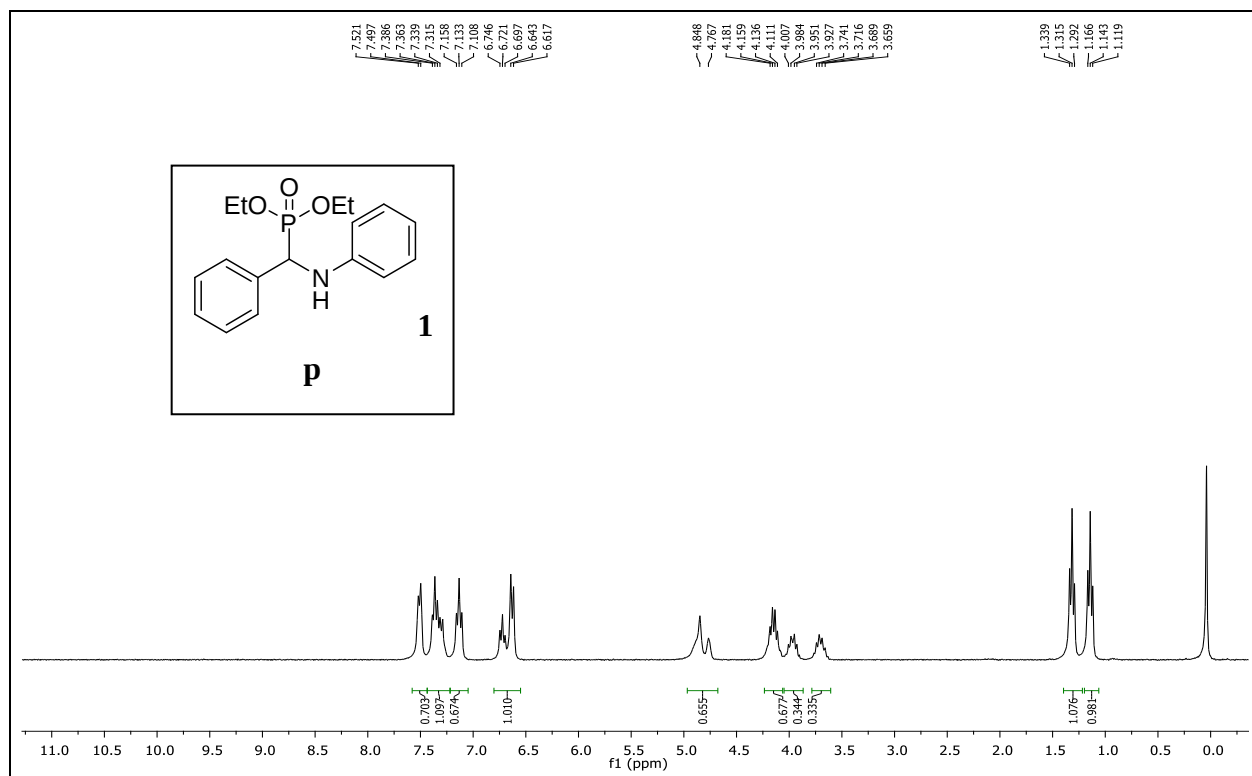
29p: Diethyl[(4-Chloro-phenylamino)-thiophen-2-yl-methyl]-phosphonate

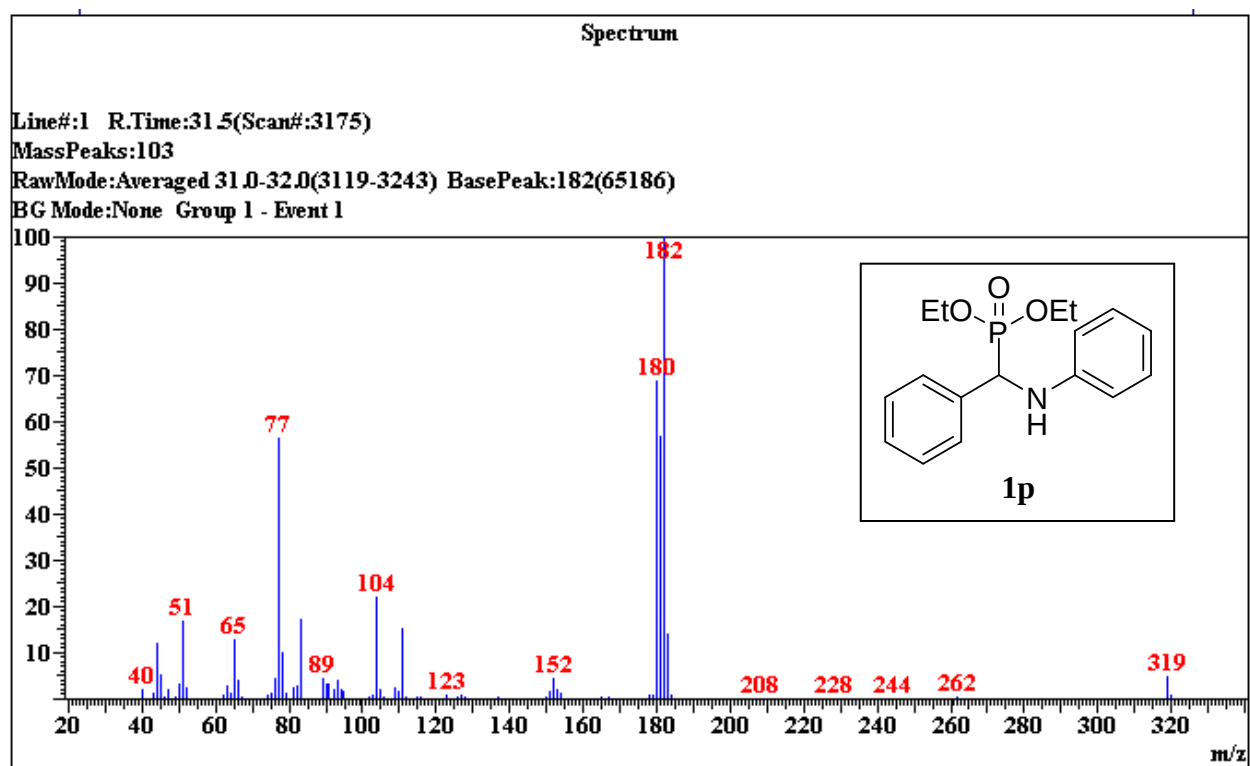
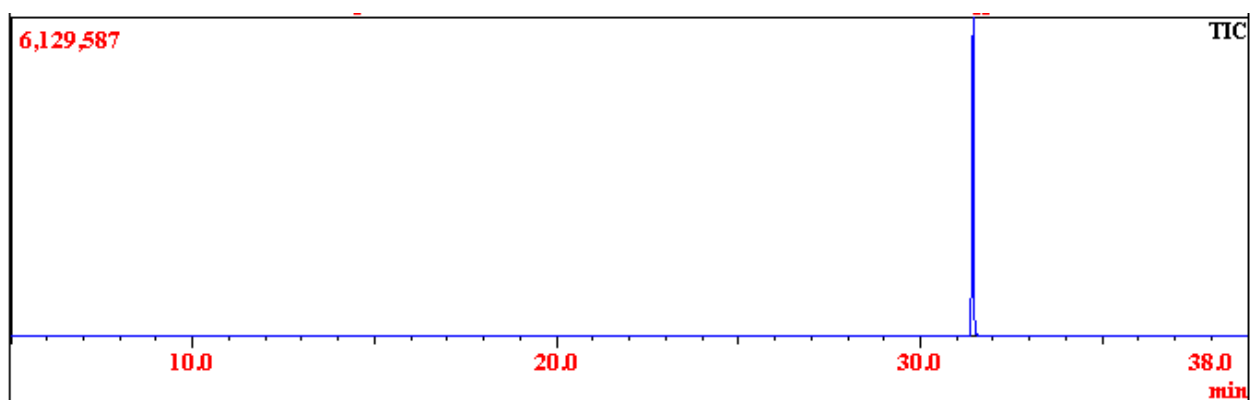
Yield 88% (White crystalline solid); Mp=96-97°C; IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3319(N-H), 1224(P=O), 1058, 1022(P-O-C); ¹H NMR (300 MHz, CDCl₃): δ = 1.19-1.24 (t, 3H, -OCH₂-CH₃), 1.29-1.33 (t, 3H, -OCH₂-CH₃), 3.84-3.94 (m, 1H, -OCH₂-CH₃), 4.03-4.22 (m, 3H, -OCH₂-CH₃), 4.95-5.03 (s, 1H, CHP), 6.60-6.63 (d, 2H, Ar), 6.98-7.01 (t, 1H, Ar), 7.09-7.17 (m, 3H, Ar); 7.24-7.26 (d, 1H, Ar); ¹³C NMR (75 MHz, CDCl₃): 16.30(d, -OCH₂CH₃), 16.47(d, -OCH₂CH₃), 51.16-53.25(d, -CH), 63.55(d, -OCH₂CH₃), 63.65 (d, -OCH₂CH₃), 115.13, 123.60, 125.44, 126.34, 127.15, 129.07, 139.39, 144.83(Ar). Anal. calcd. for $C_{15}H_{19}ClNO_3PS$: C, 50.07; H, 5.32; N, 3.89; S, 8.91; found: C, 49.94; H, 5.25; N, 3.81; S, 8.83.

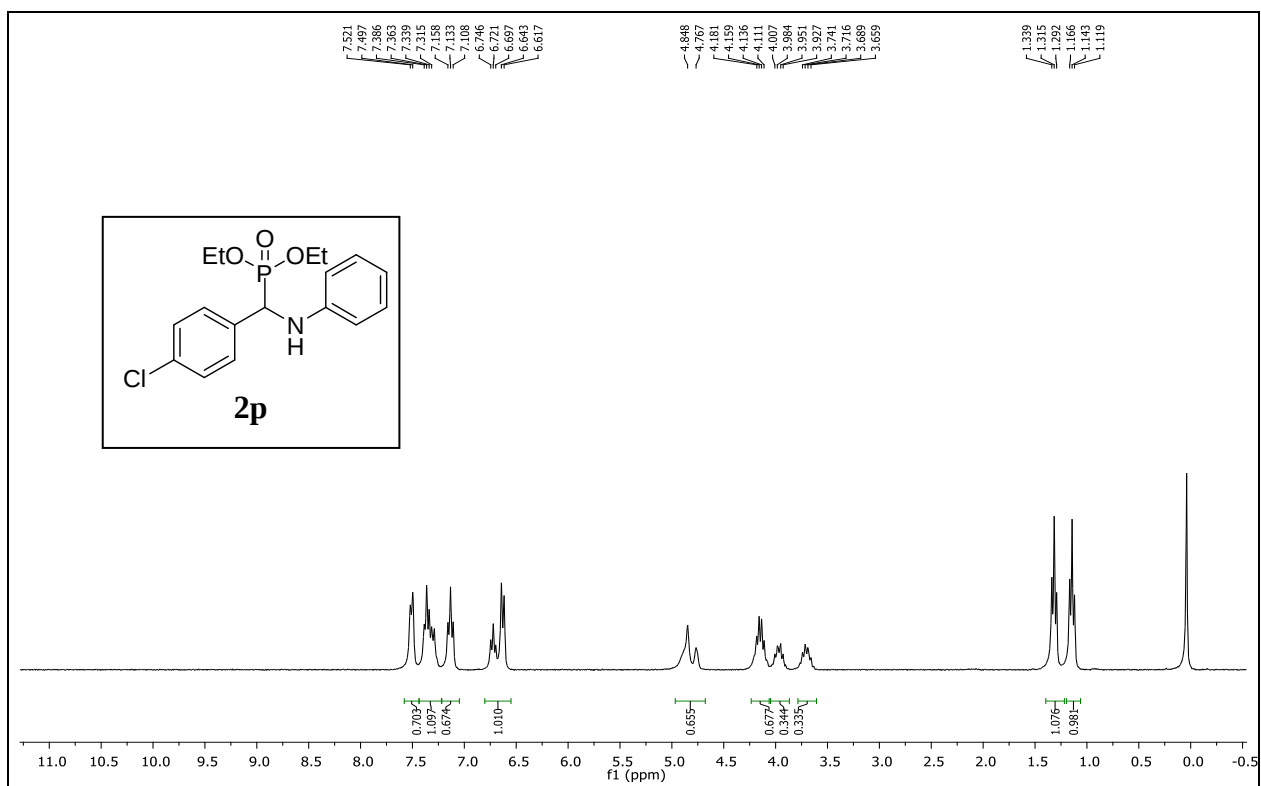
30p: Diethyl[(4-Chloro-phenylamino)-(3,5-dimethyl-phenyl)-methyl] phosphonate

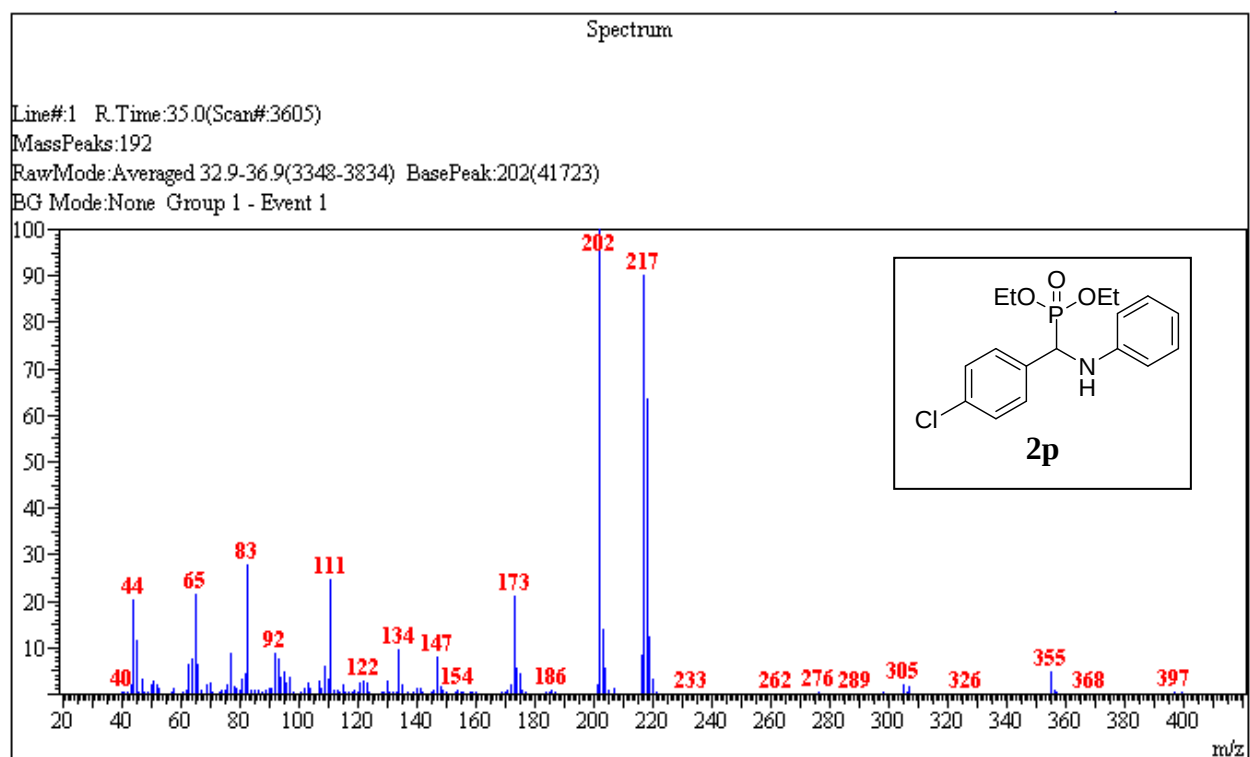
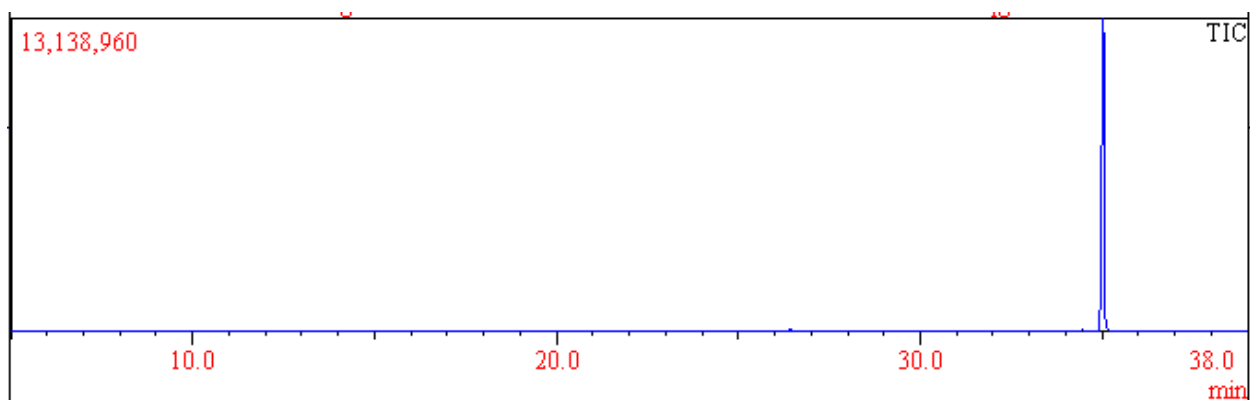
Yield 94% (Brown oil); IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3315(N-H), 1226(P=O), 1050, 1018(P-O-C), ¹H NMR (300 MHz, CDCl₃): δ = 1.10-1.15 (t, 3H, -OCH₂-CH₃), 1.28-1.33 (t, 3H, -OCH₂-CH₃), 2.29 (s, 6H, -CH₃), 3.61-3.69 (m, 1H, -OCH₂-CH₃), 3.89-3.98 (m, 1H, -OCH₂-CH₃), 4.10-4.17 (m, 2H, -OCH₂-CH₃), 4.60-4.68 (s, 1H, CHP) 4.973(s, 1H, NH), 6.54-6.56 (d, 2H, Ar), 6.91 (s, 1H, Ar), 7.04-7.06 (dd, 4H, Ar). ¹³C NMR (75 MHz, CDCl₃): 16.16(d, -OCH₂CH₃), 16.44(d, -OCH₂CH₃), 21.20(-CH₃), 55.06-57.06(d, -CH), 63.15(d, -OCH₂CH₃), 63.47(d, -OCH₂CH₃), 114.93, 122.71, 125.66, 128.93, 129.83, 135.28, 138.08, 145.32(Ar). GC-MS (EI) m/z (%) calcd. for $C_{19}H_{25}ClNO_3P$: 381.83; found: 381[M]⁺. Anal. calcd. for $C_{19}H_{25}ClNO_3P$: C, 59.77; H, 6.60; N, 3.67; found: C, 59.68; H, 6.55; N, 3.59.

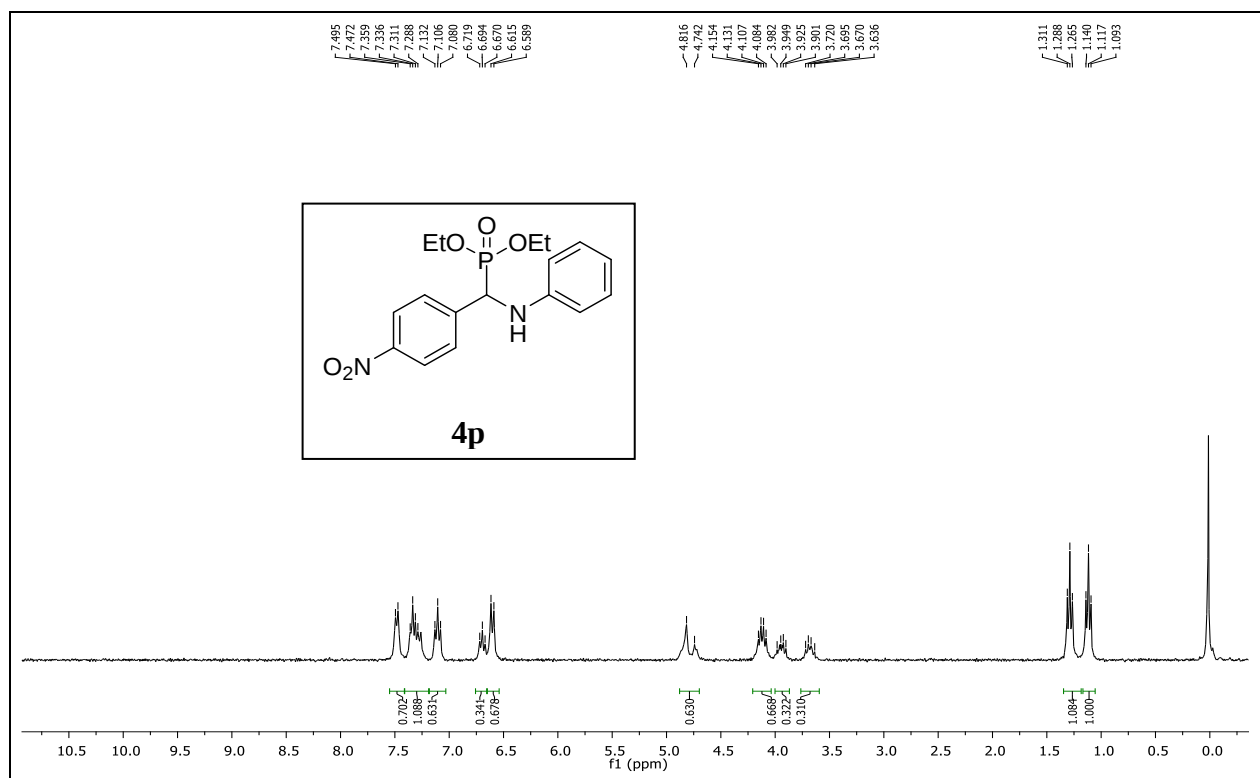
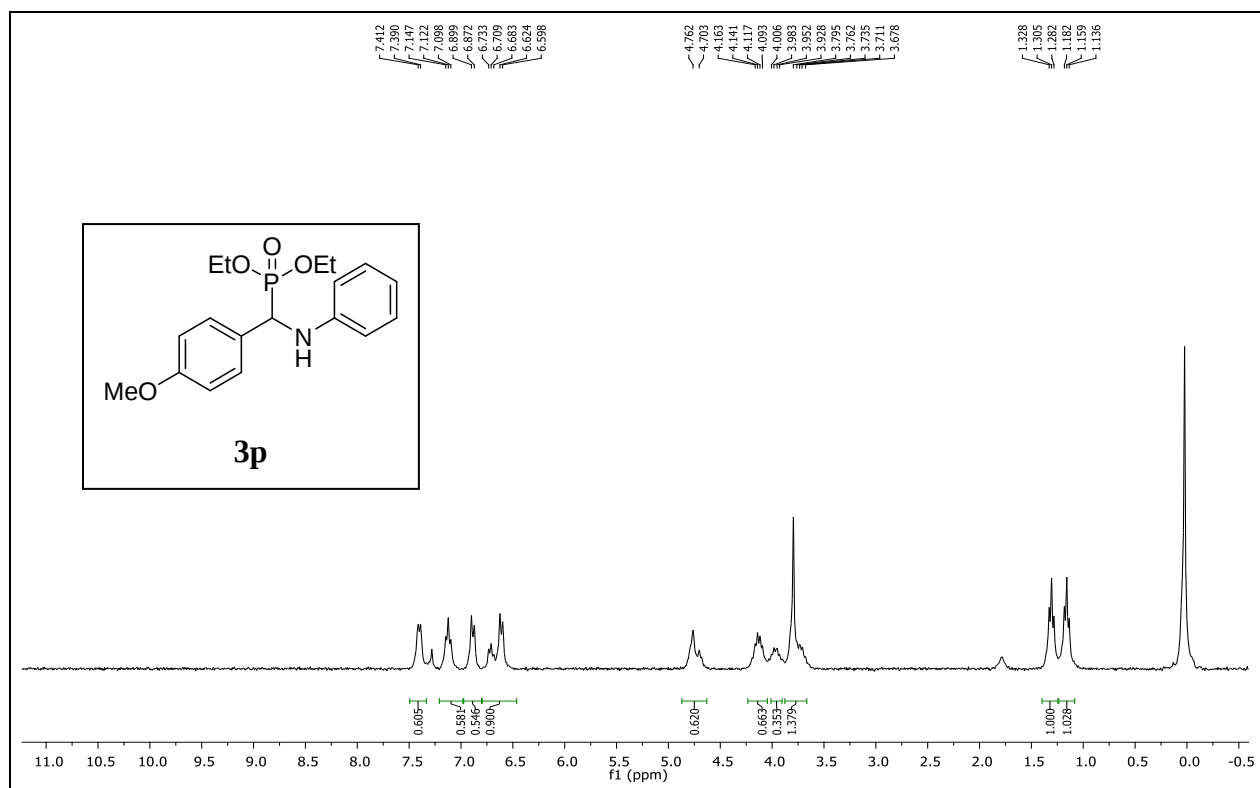
3. ^1H NMR, ^{13}C NMR and GC-MS spectra of some selected products

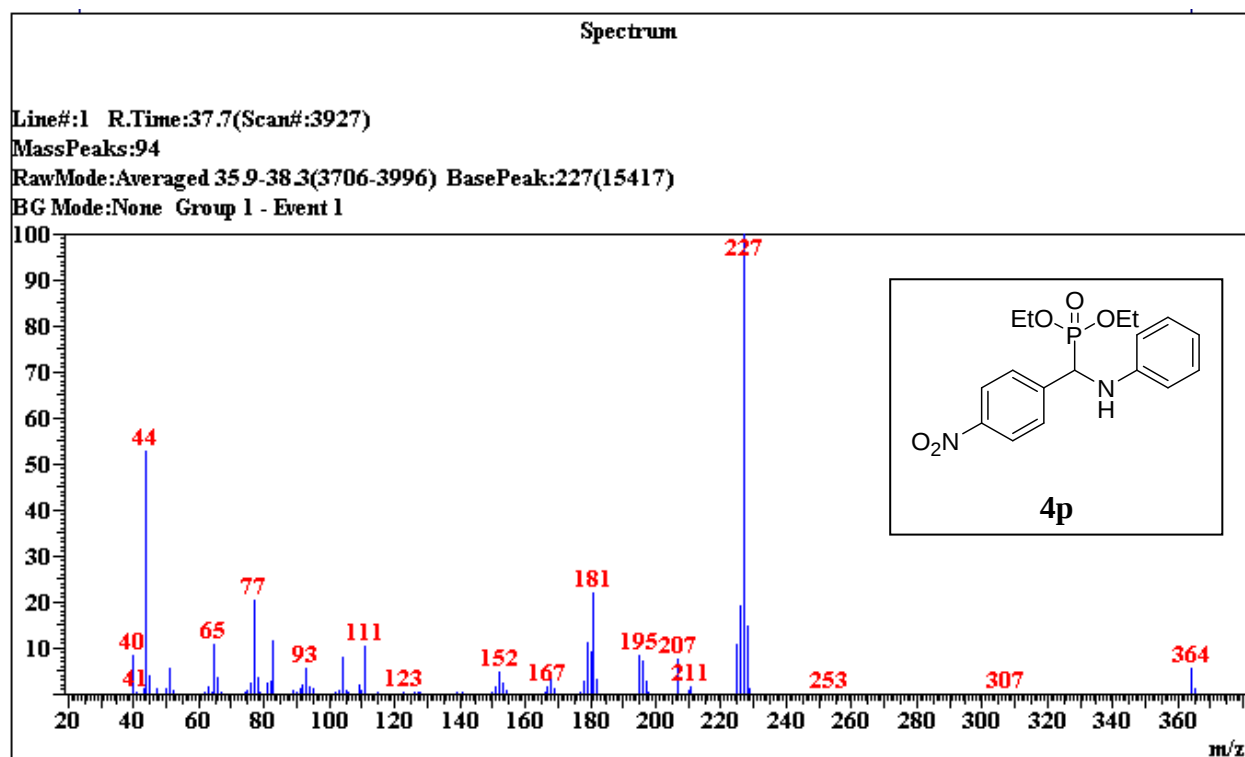
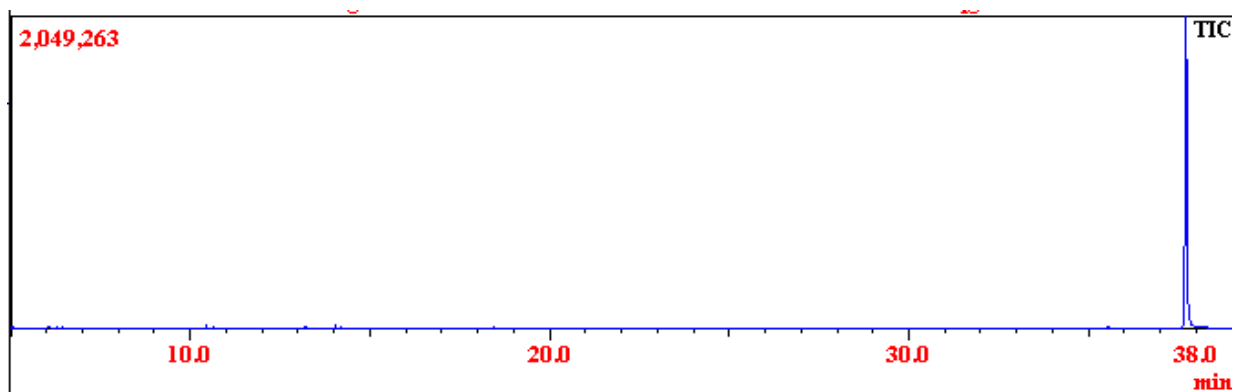


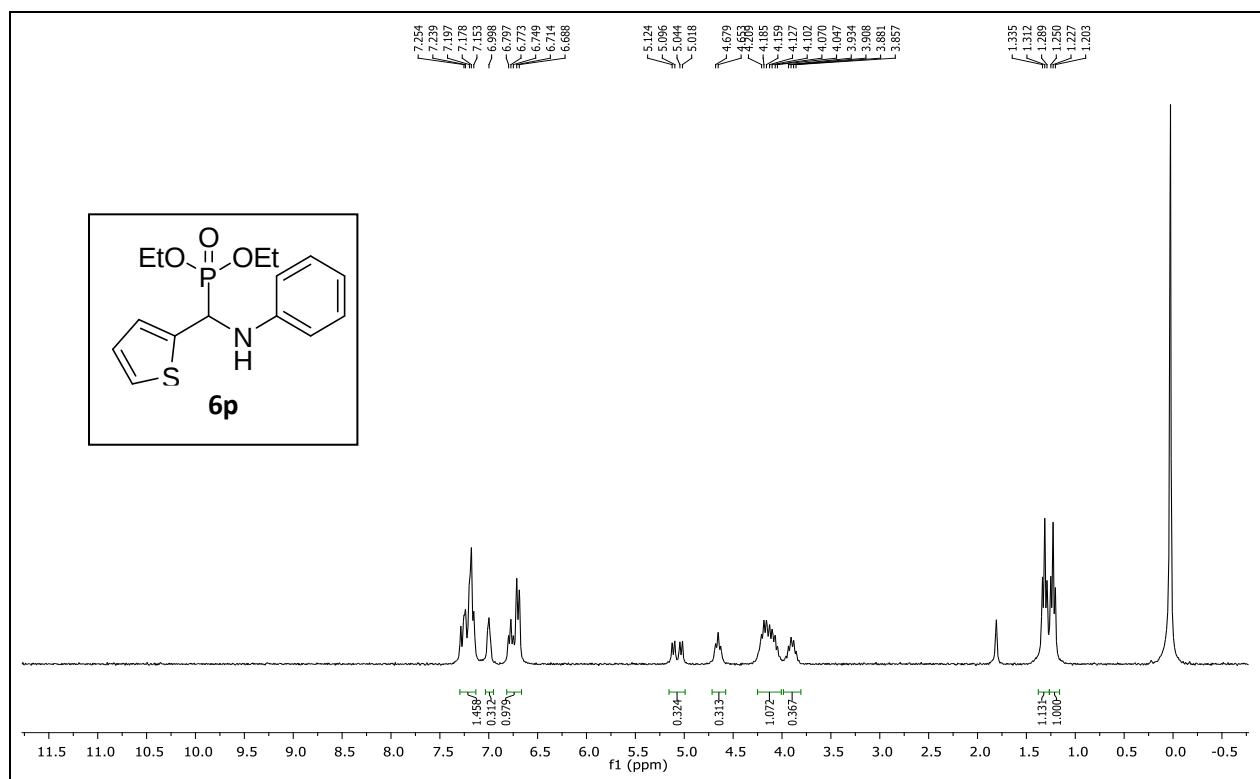
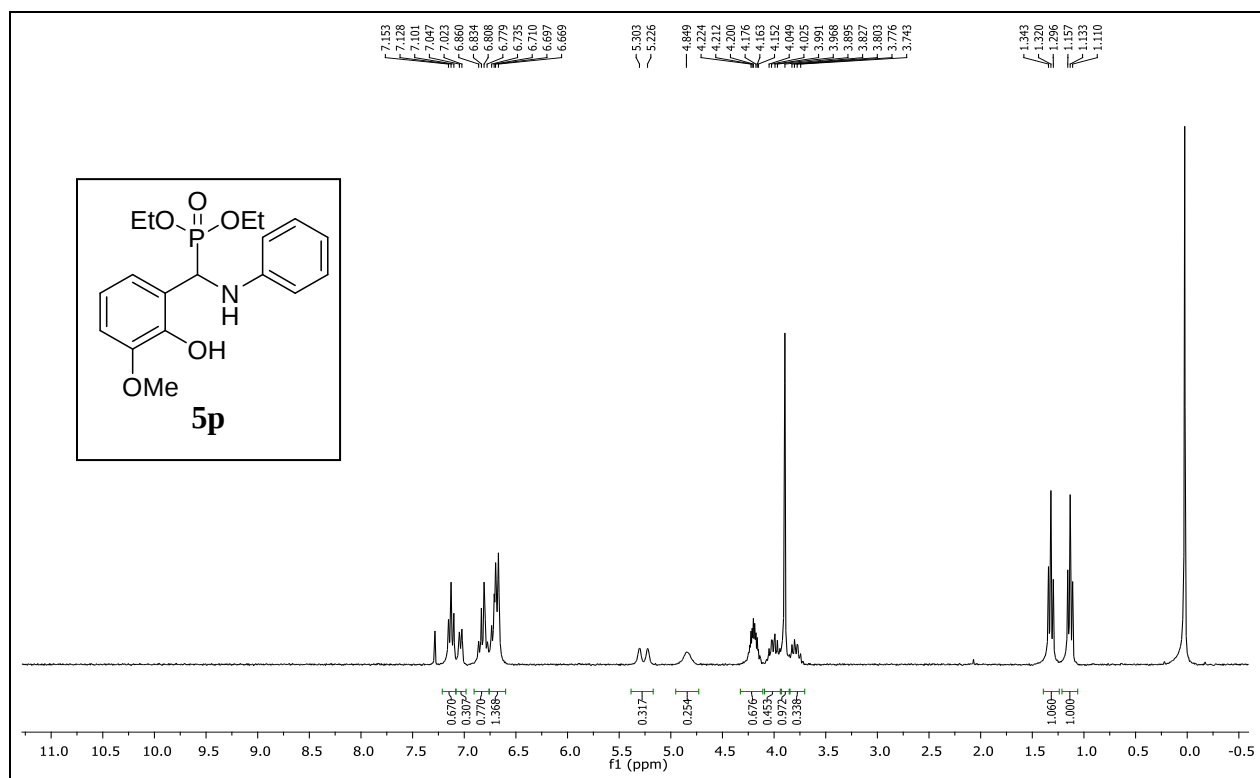


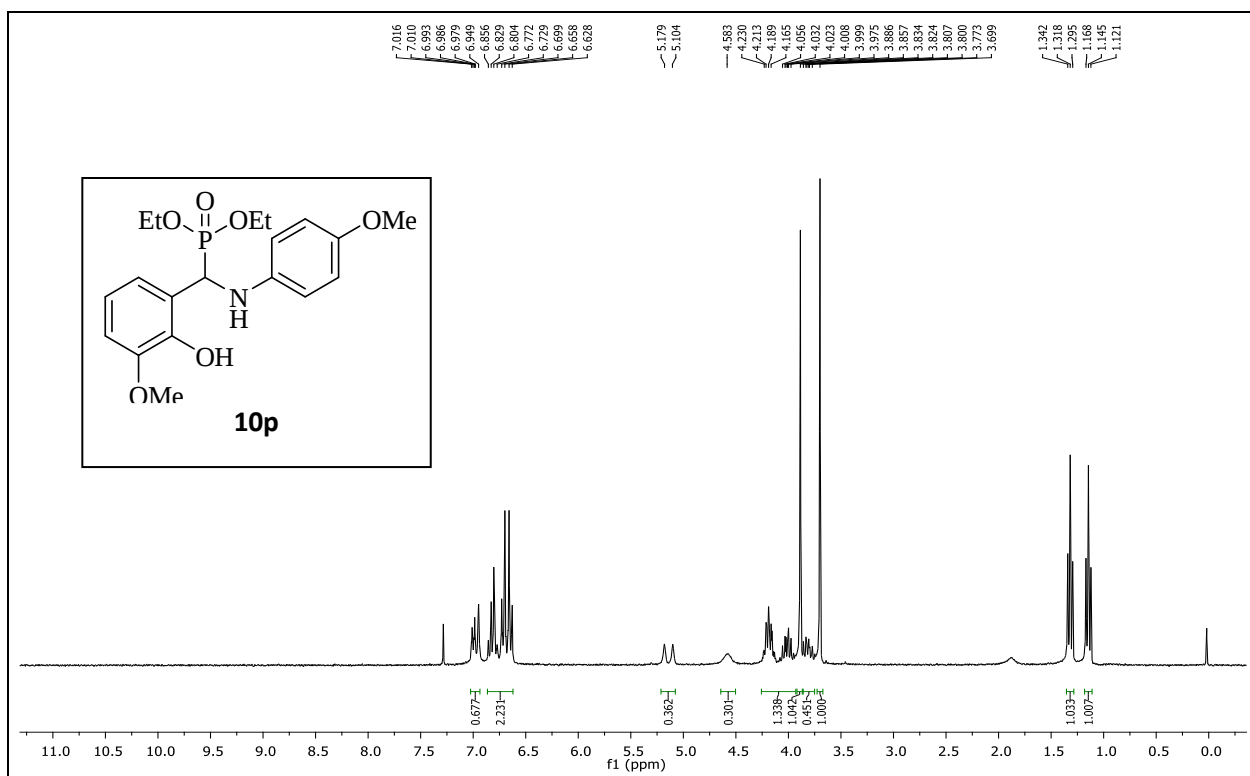
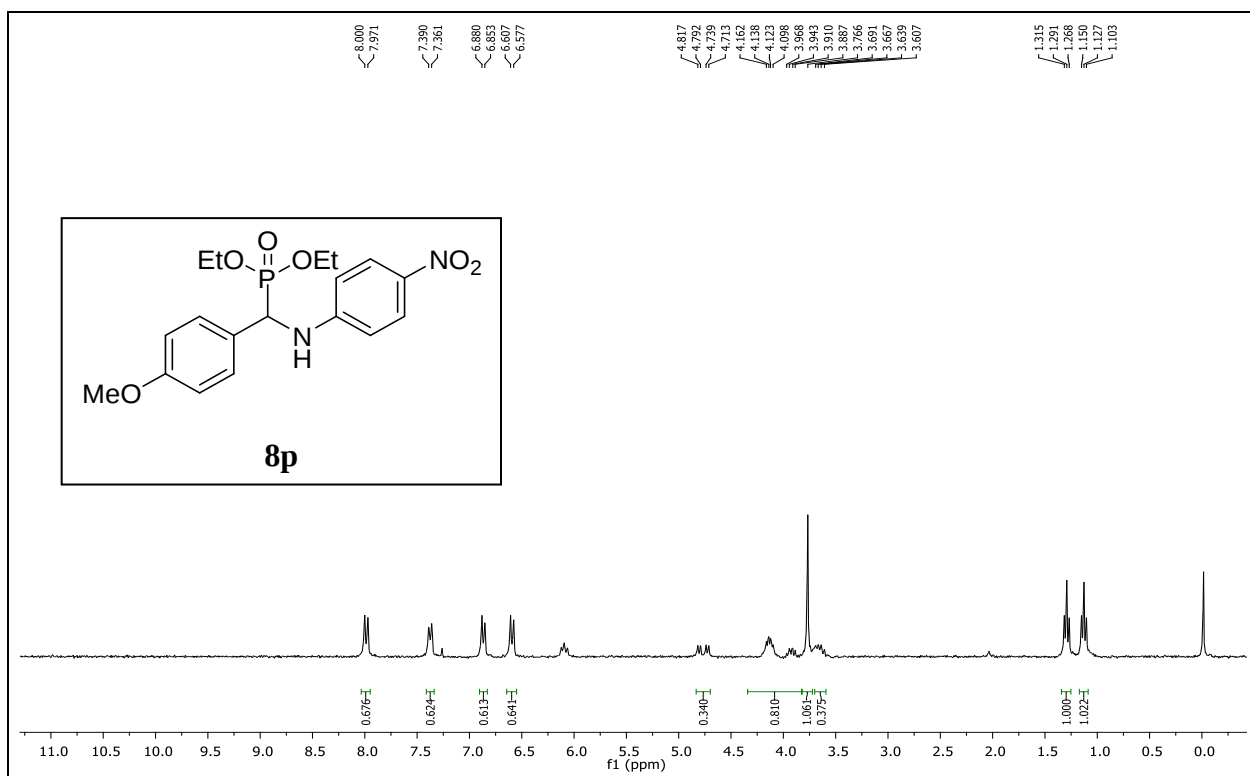


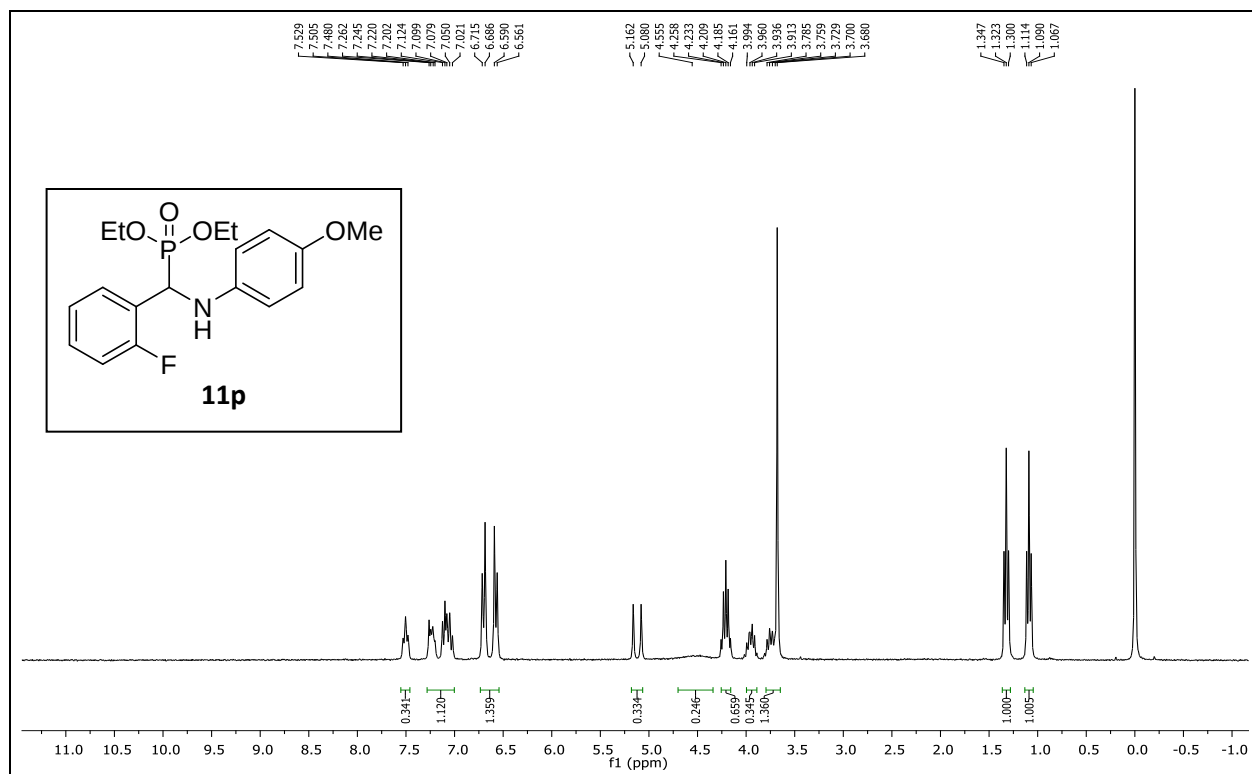
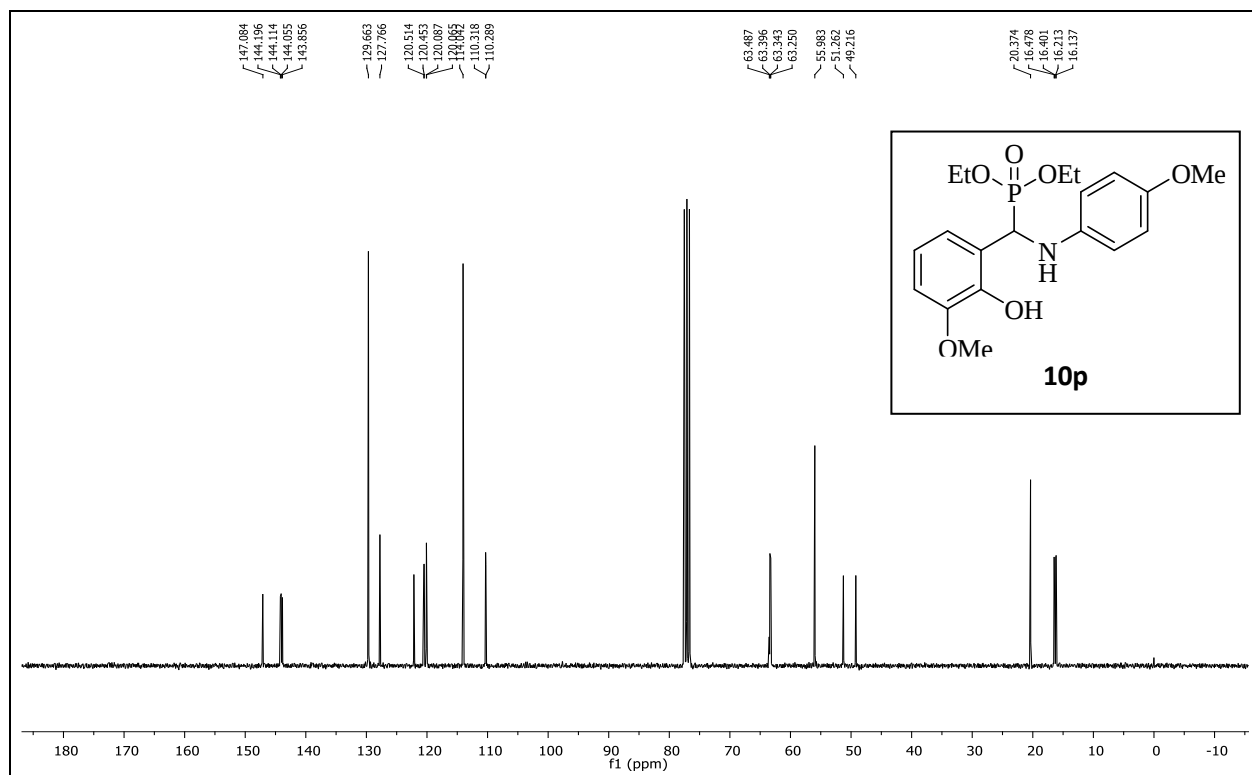


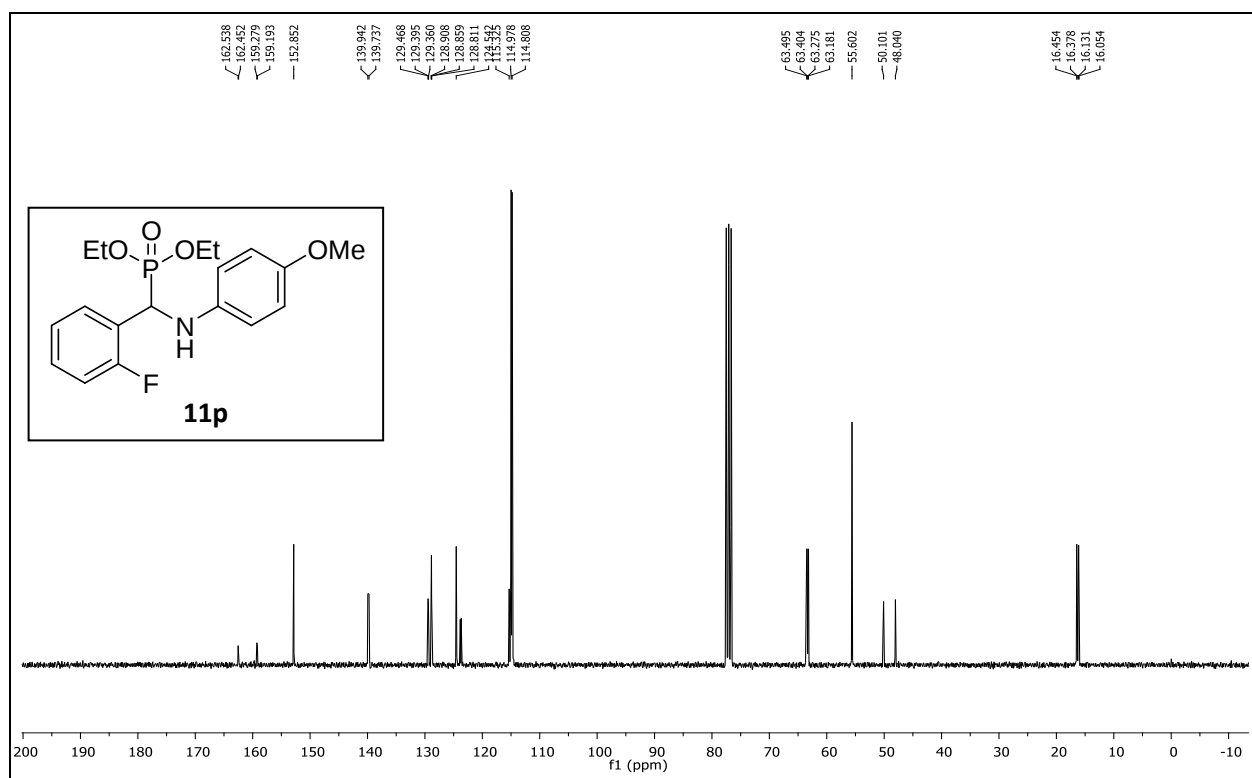


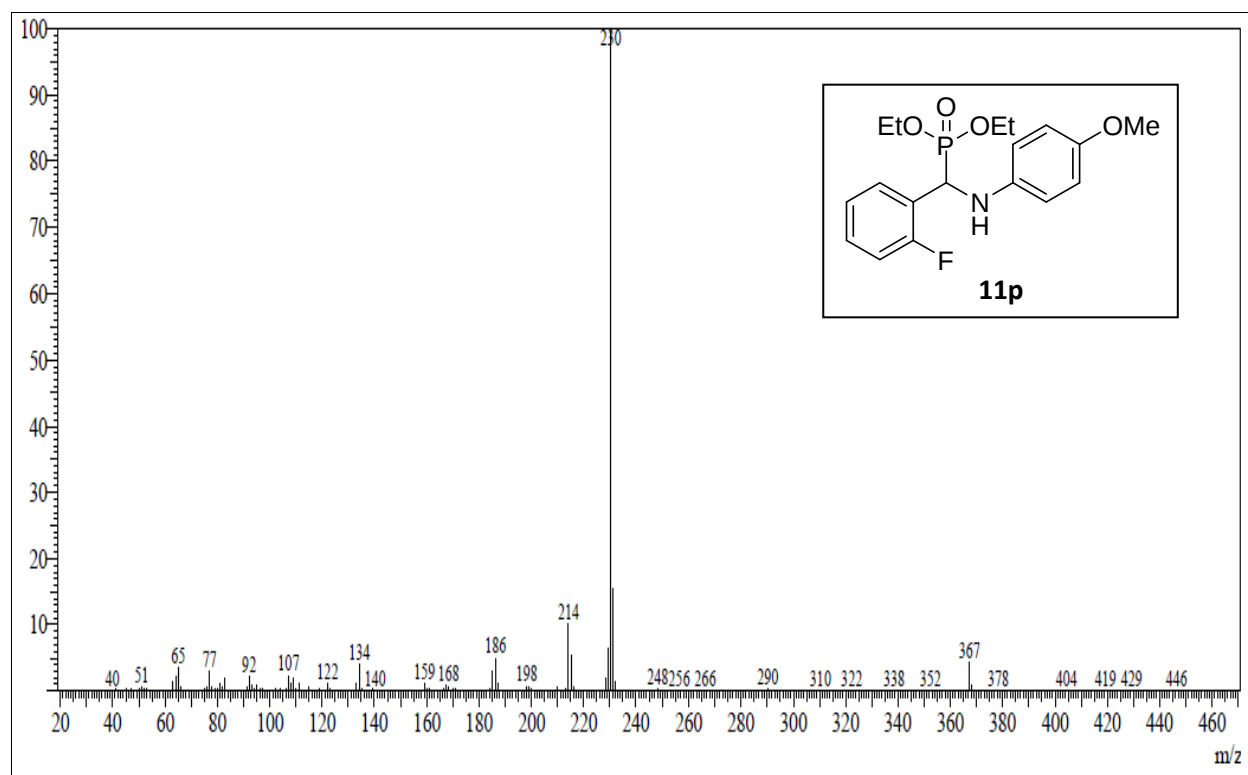
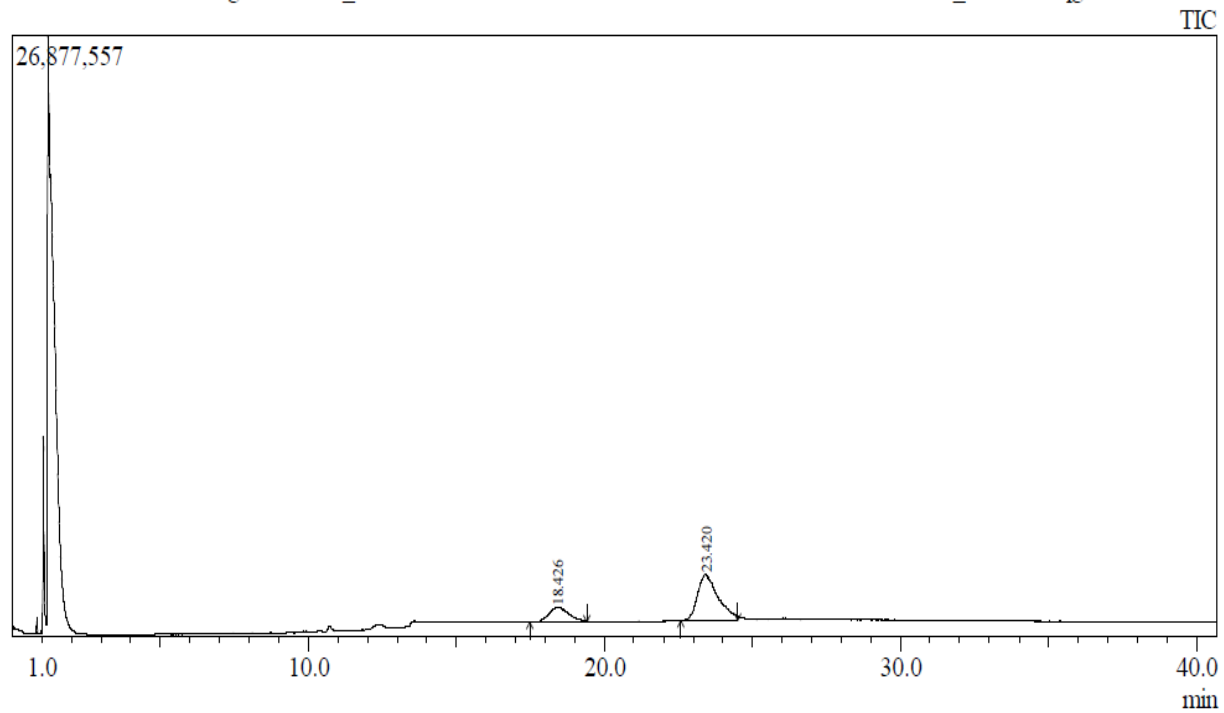


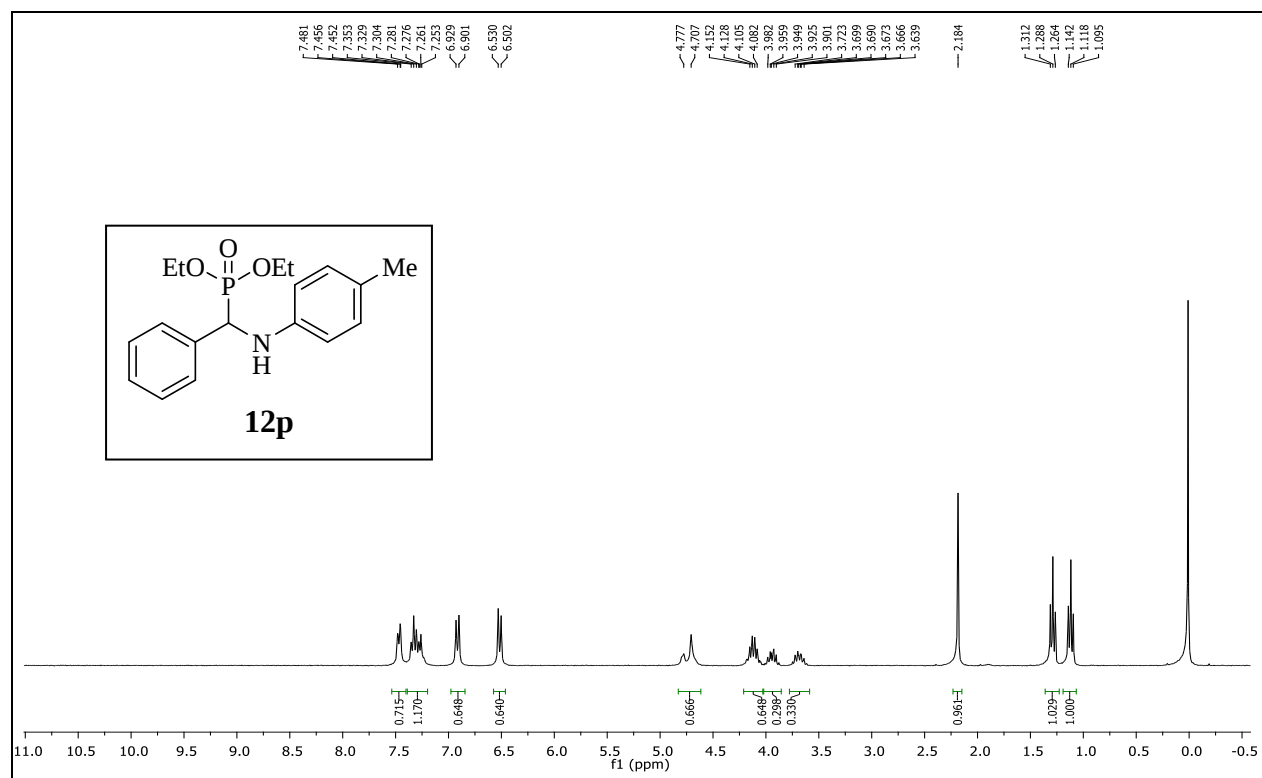


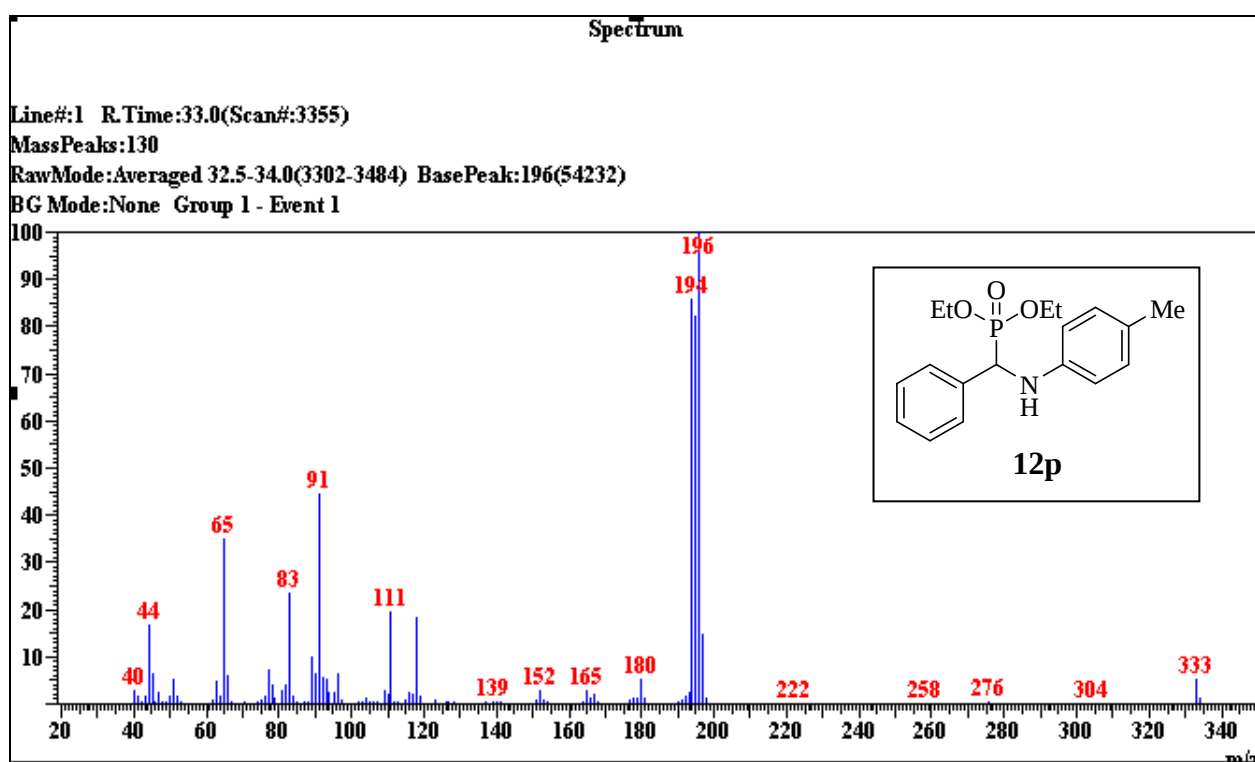


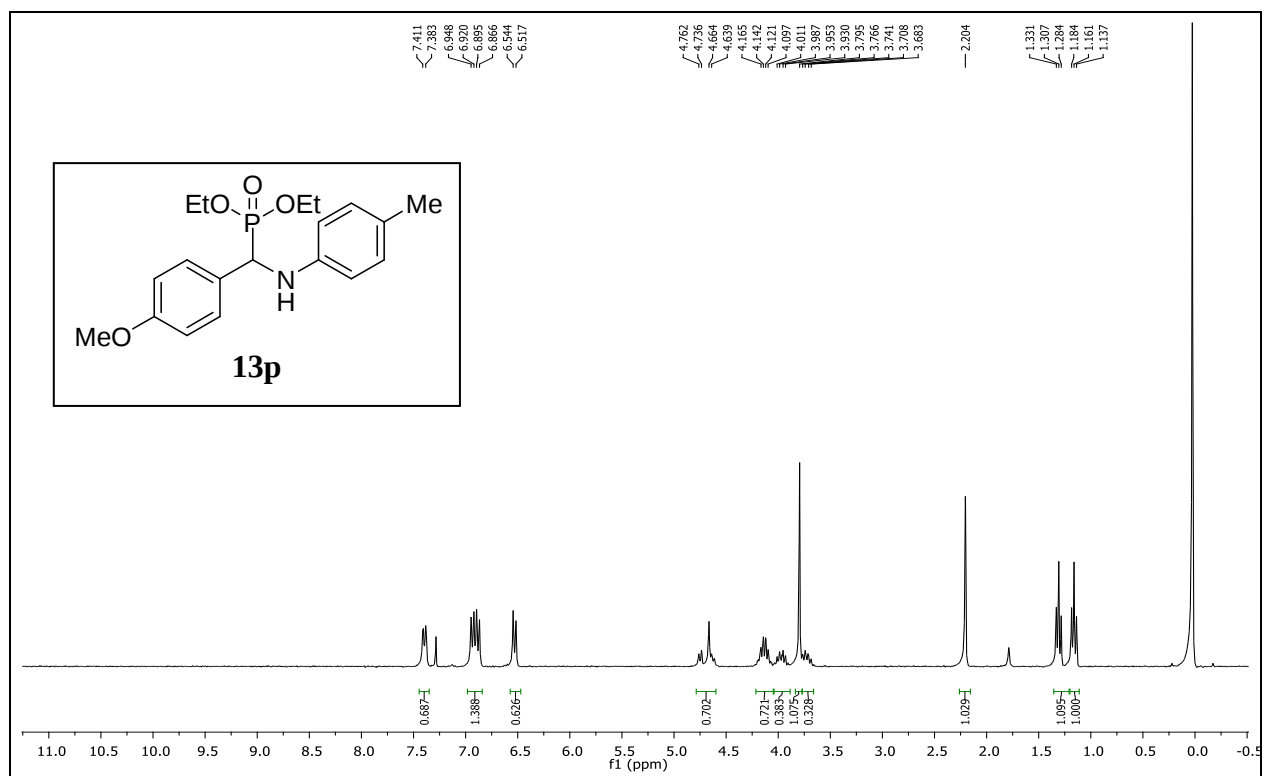


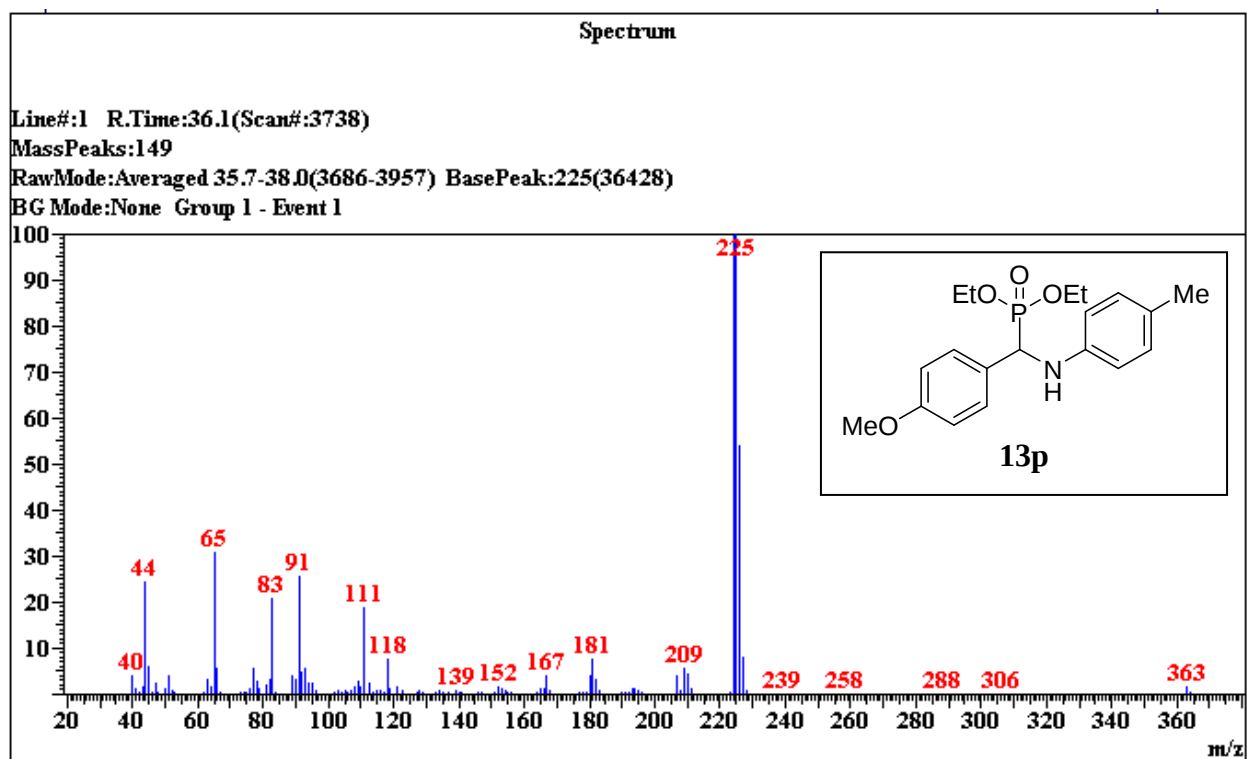
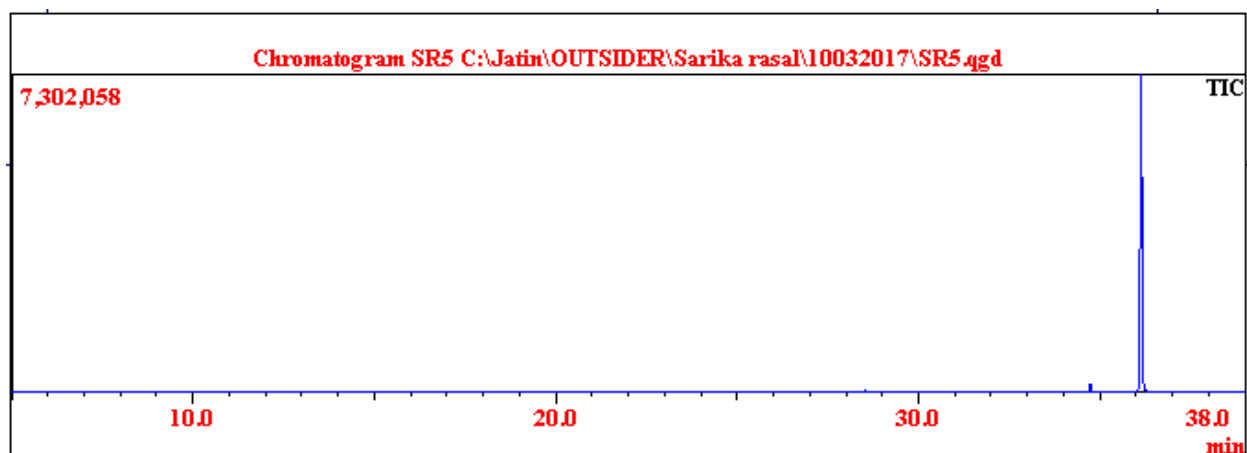


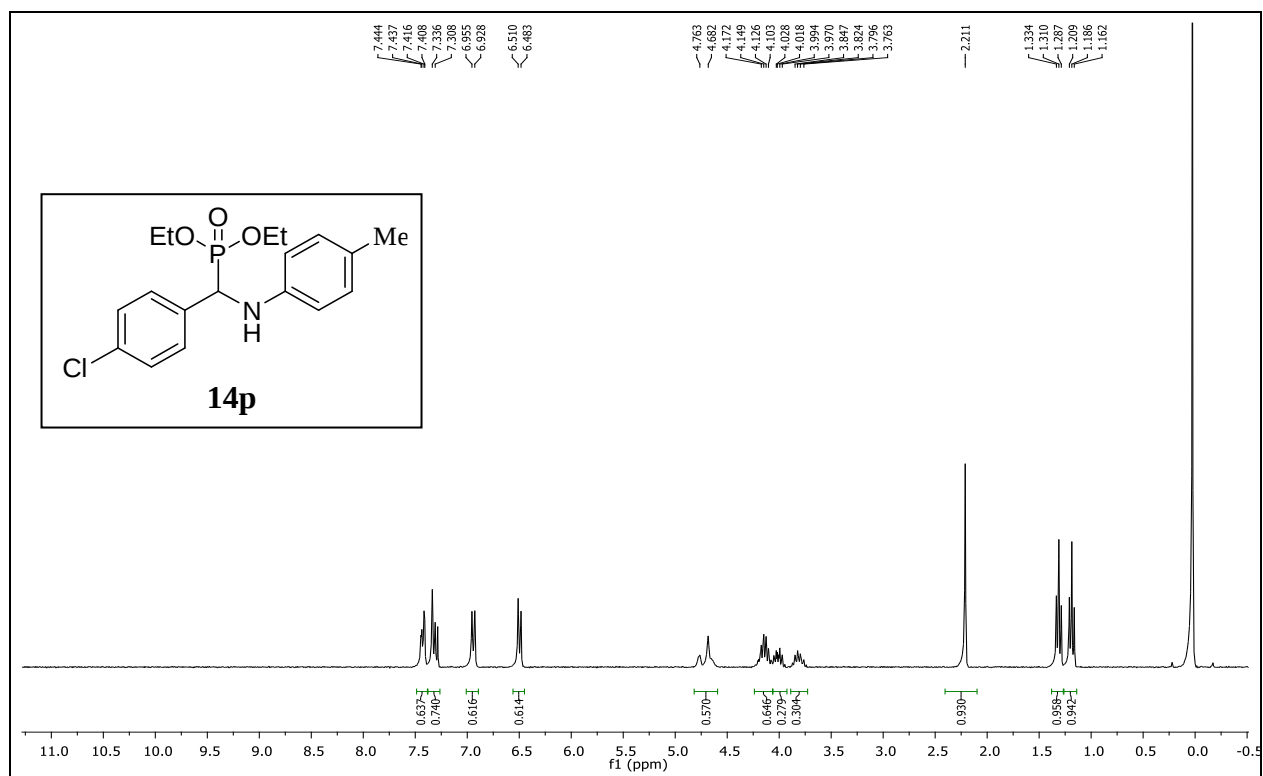


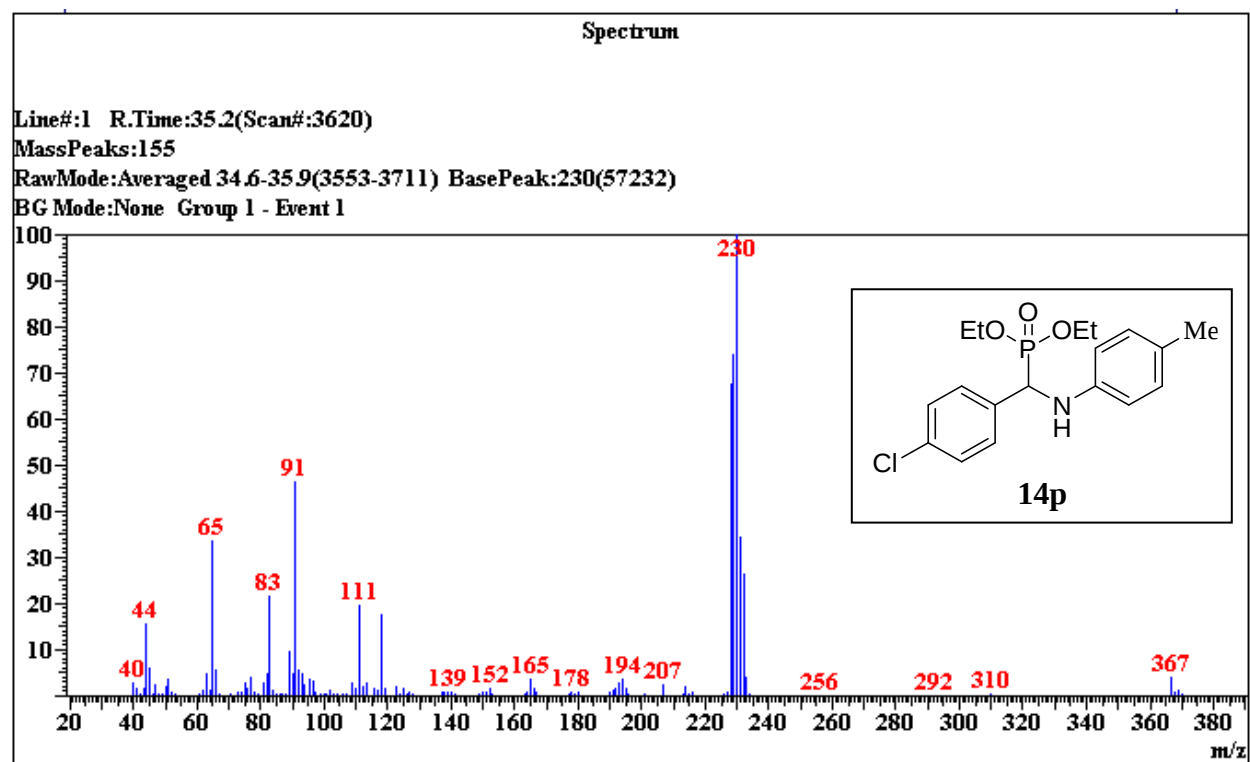
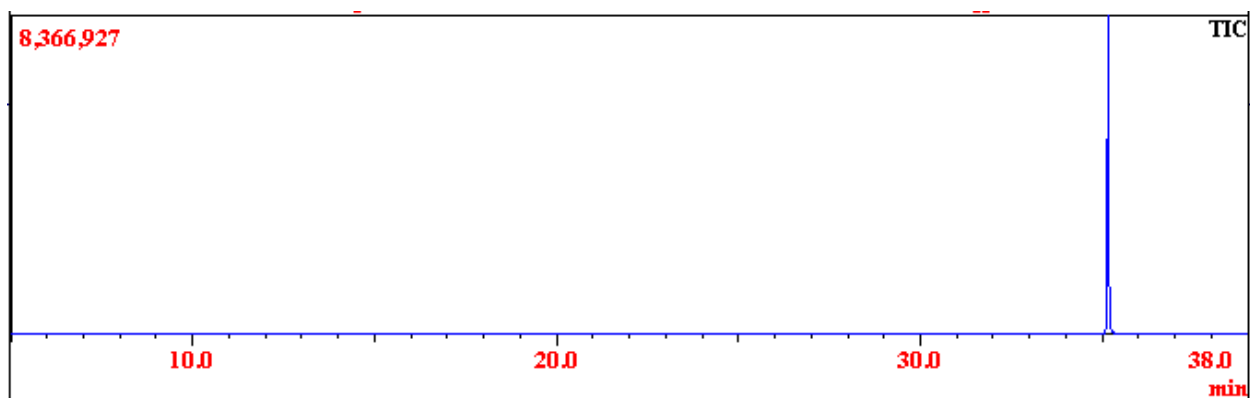


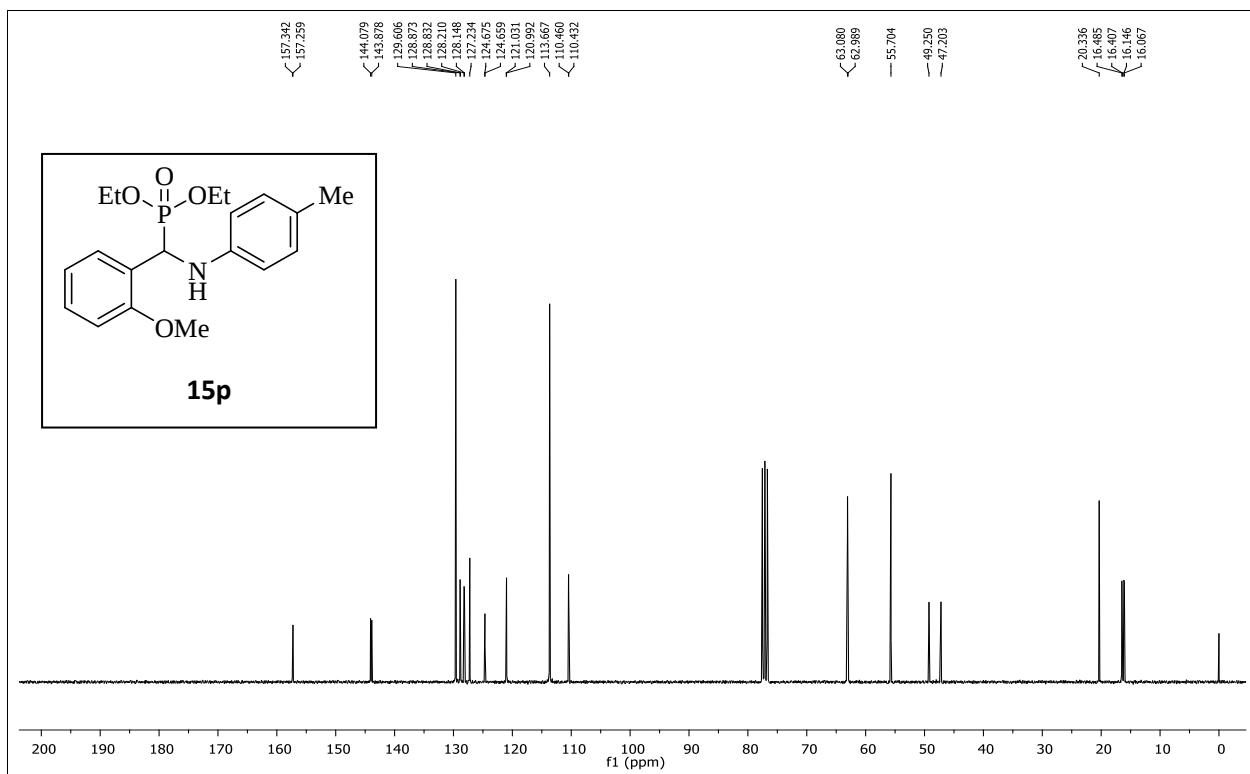
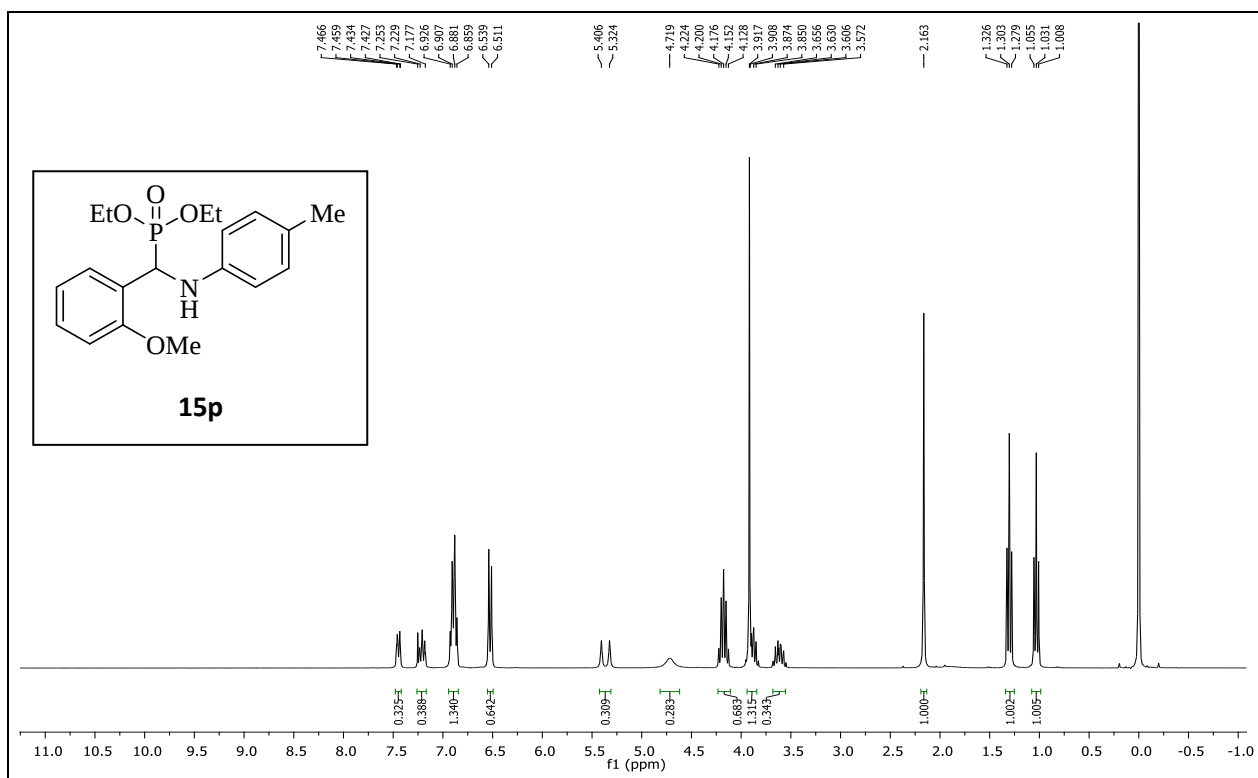


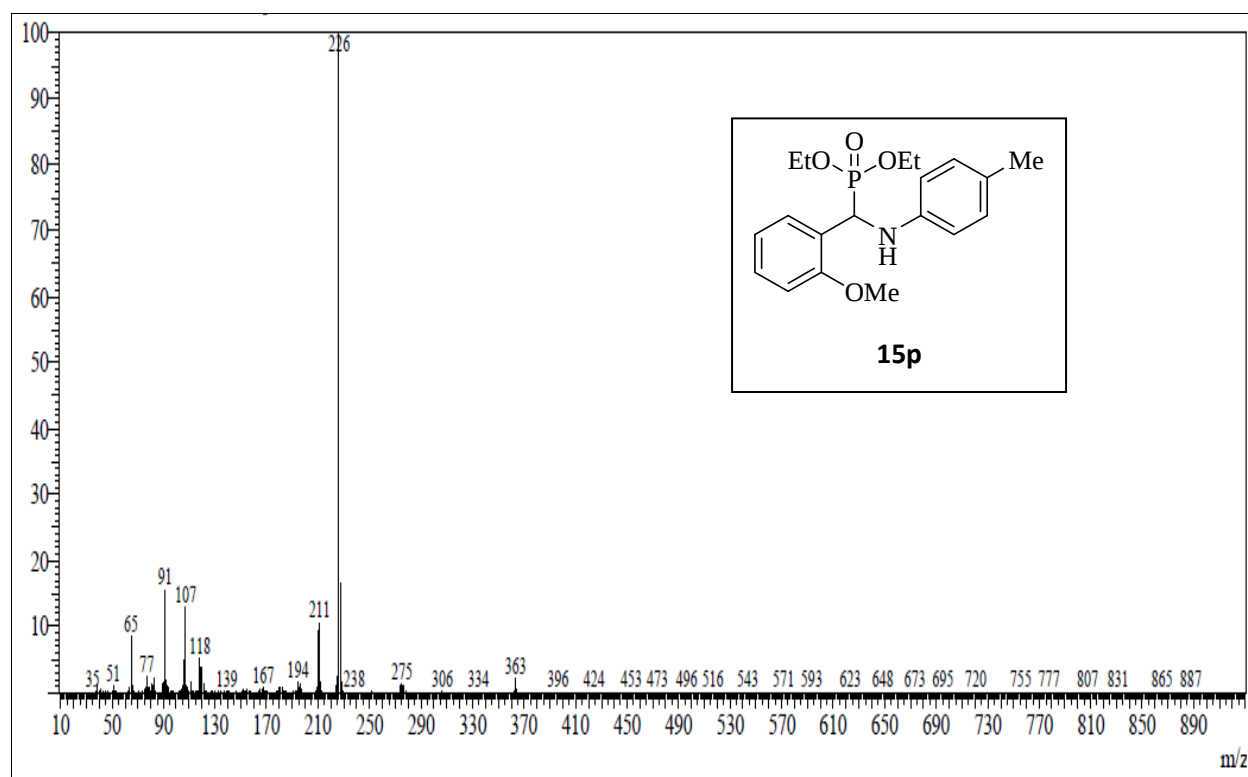
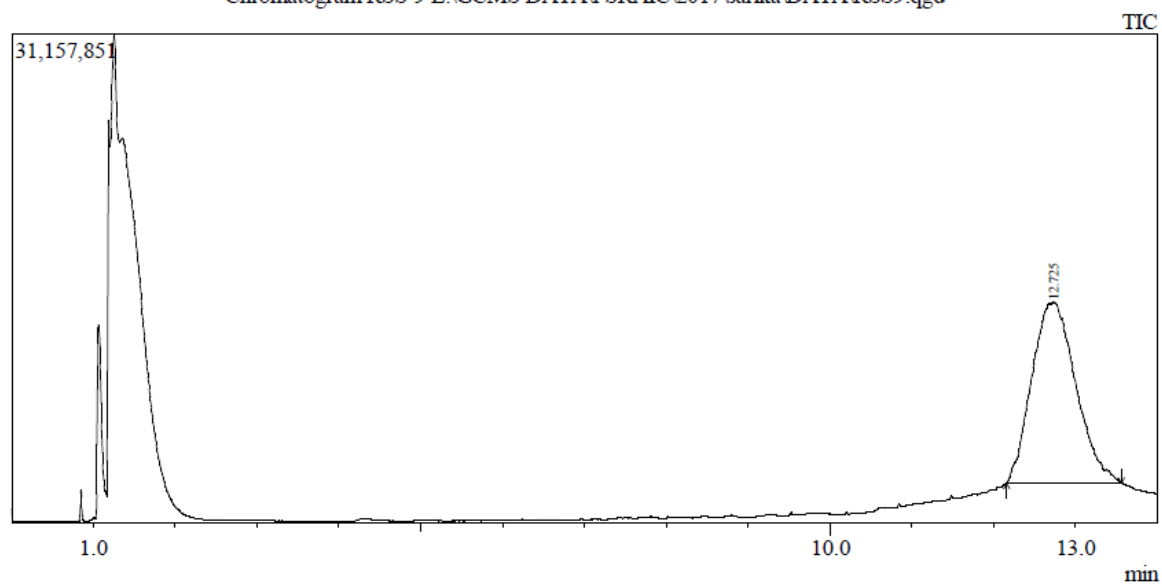


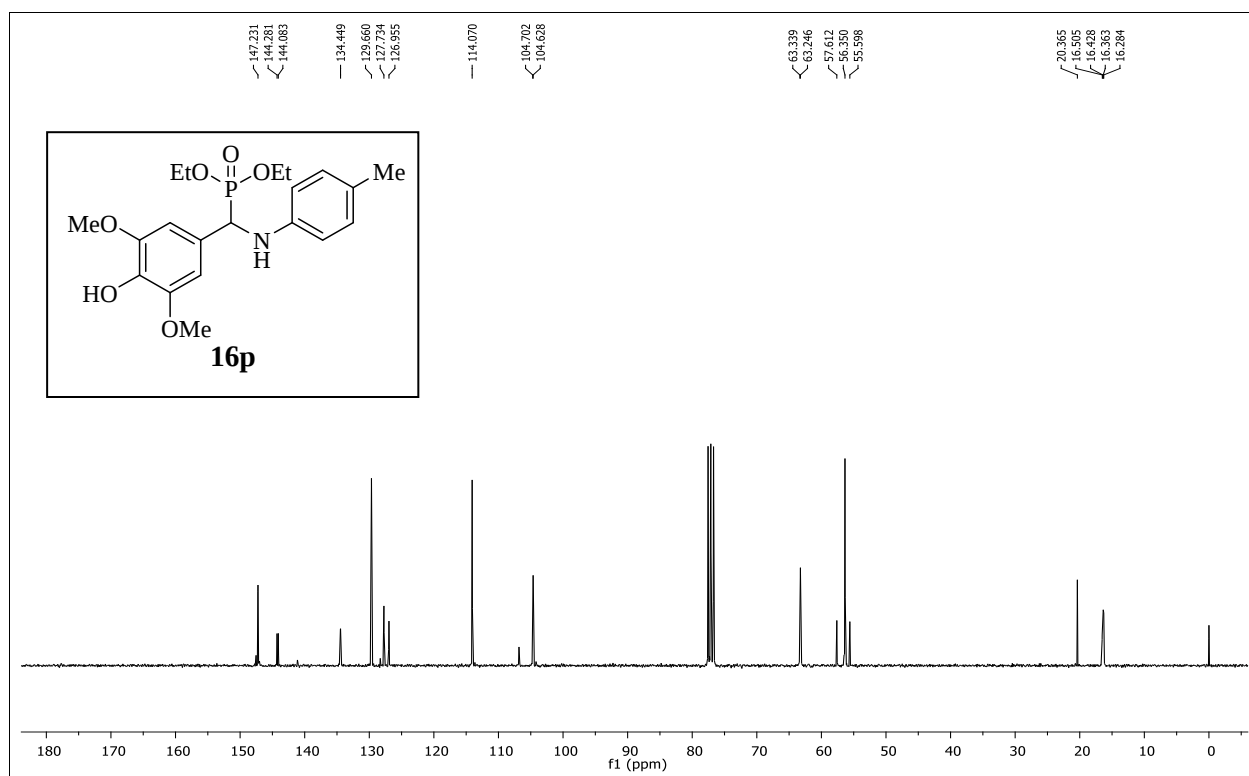
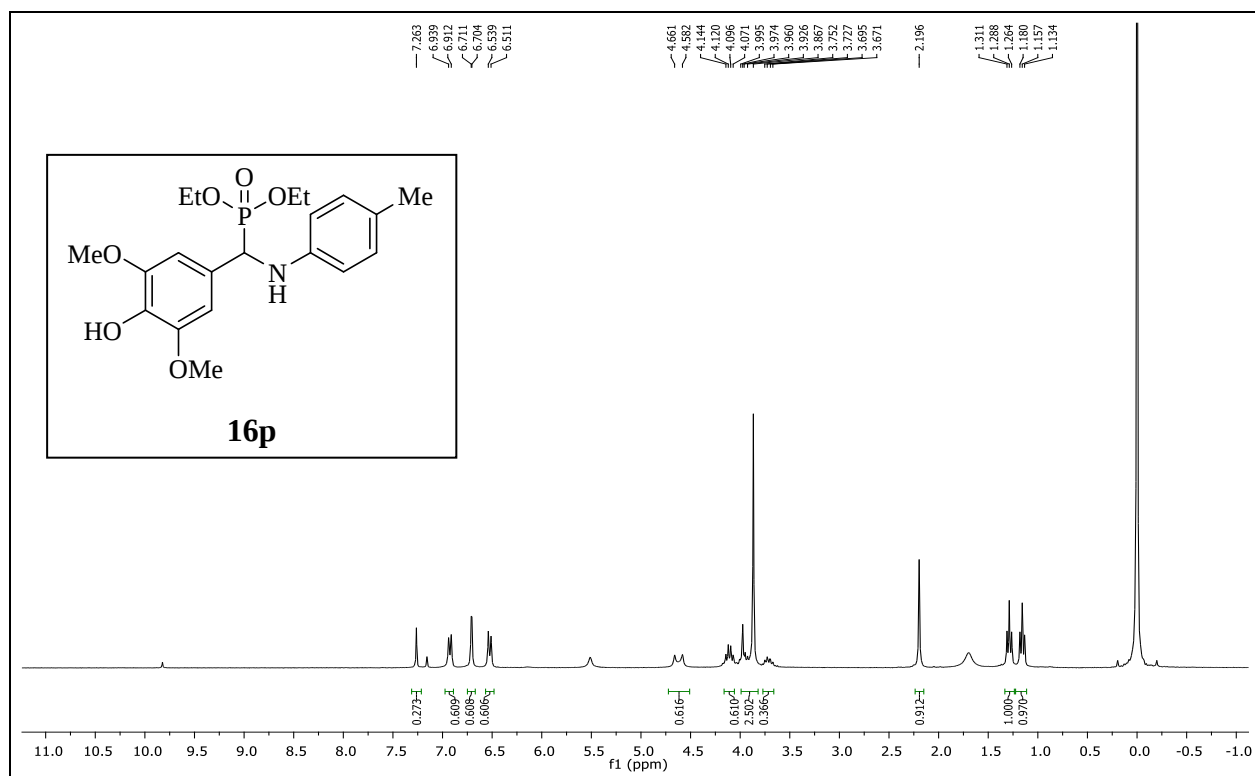


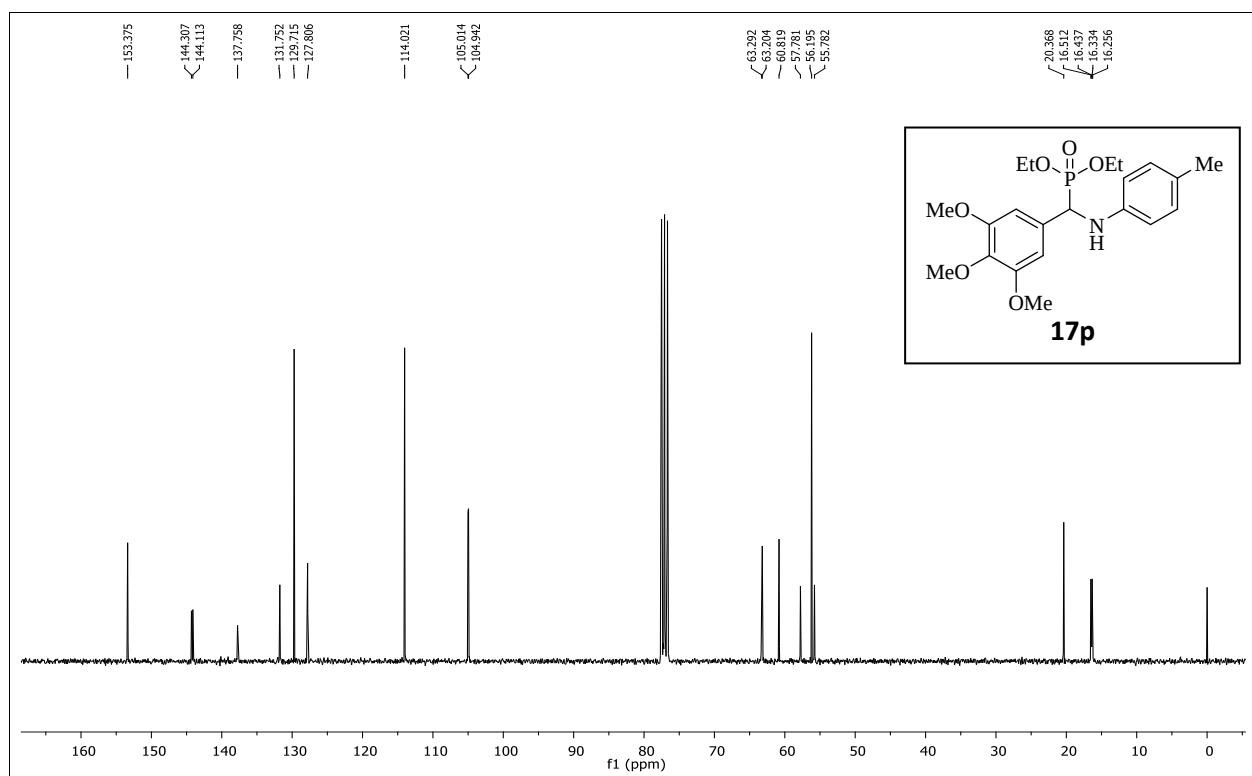
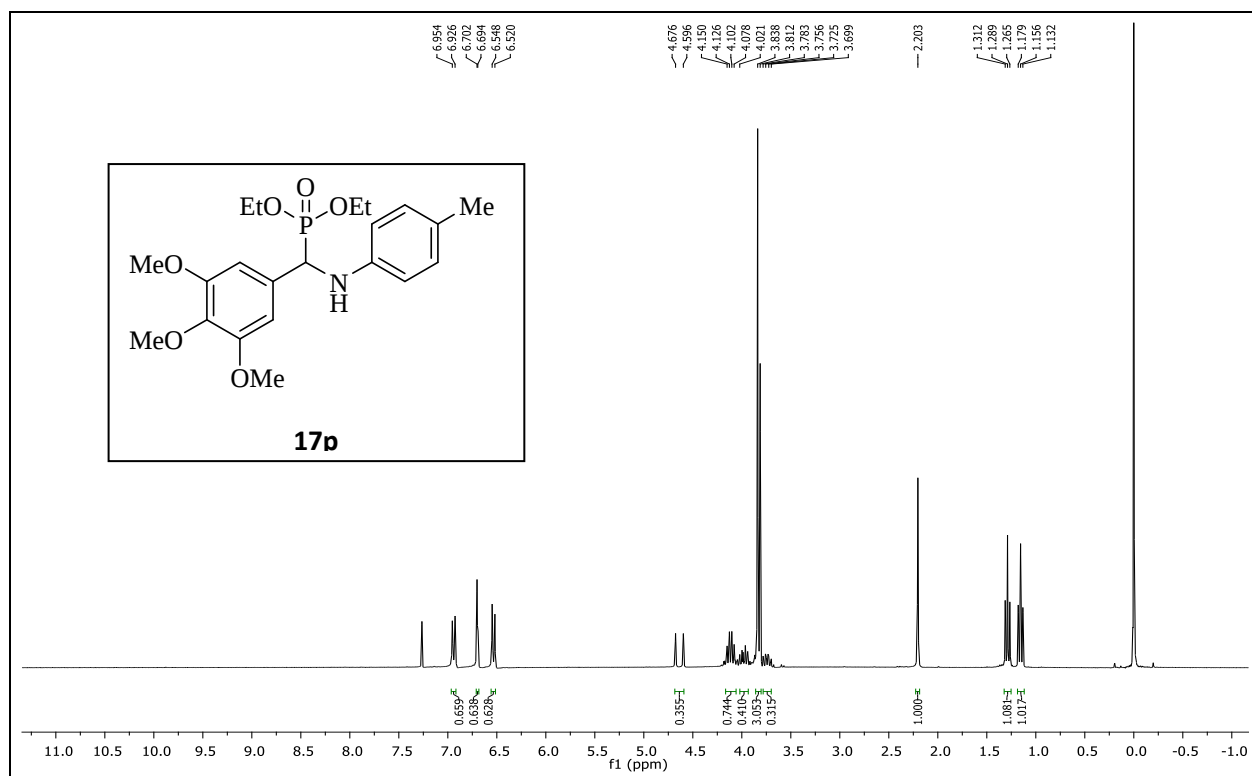


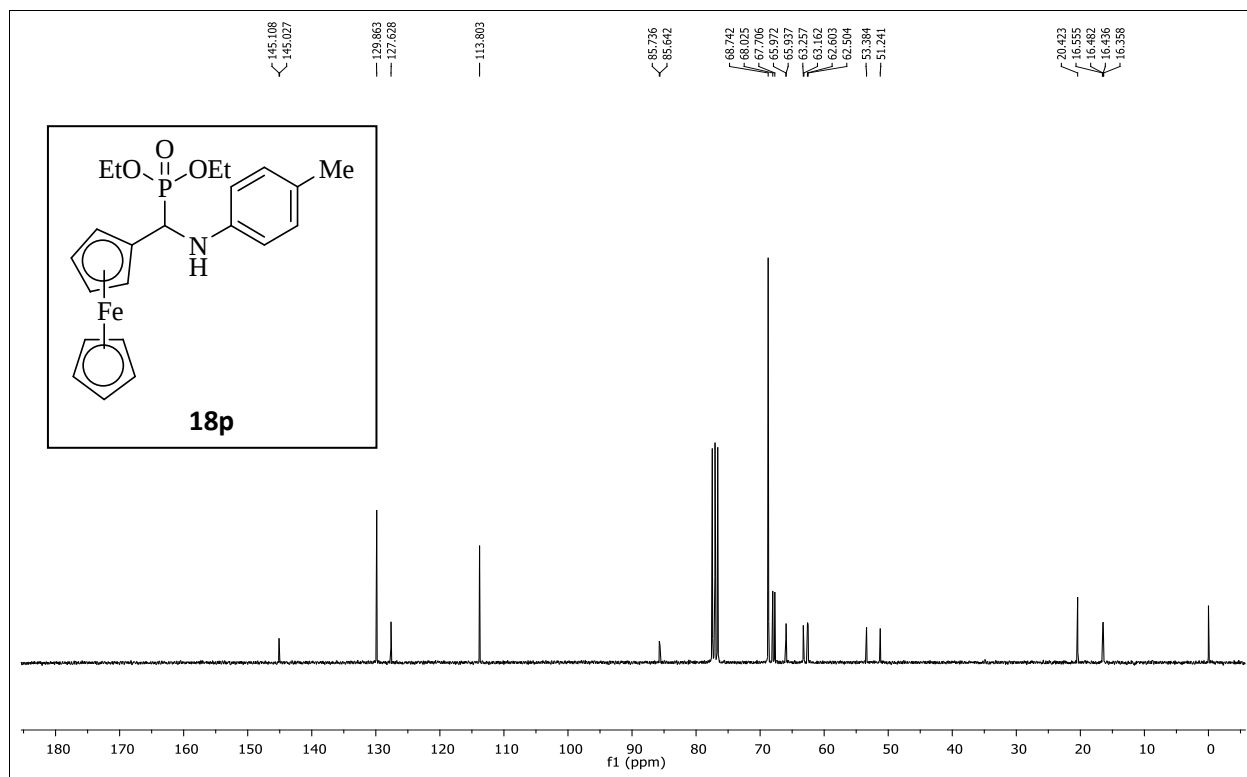
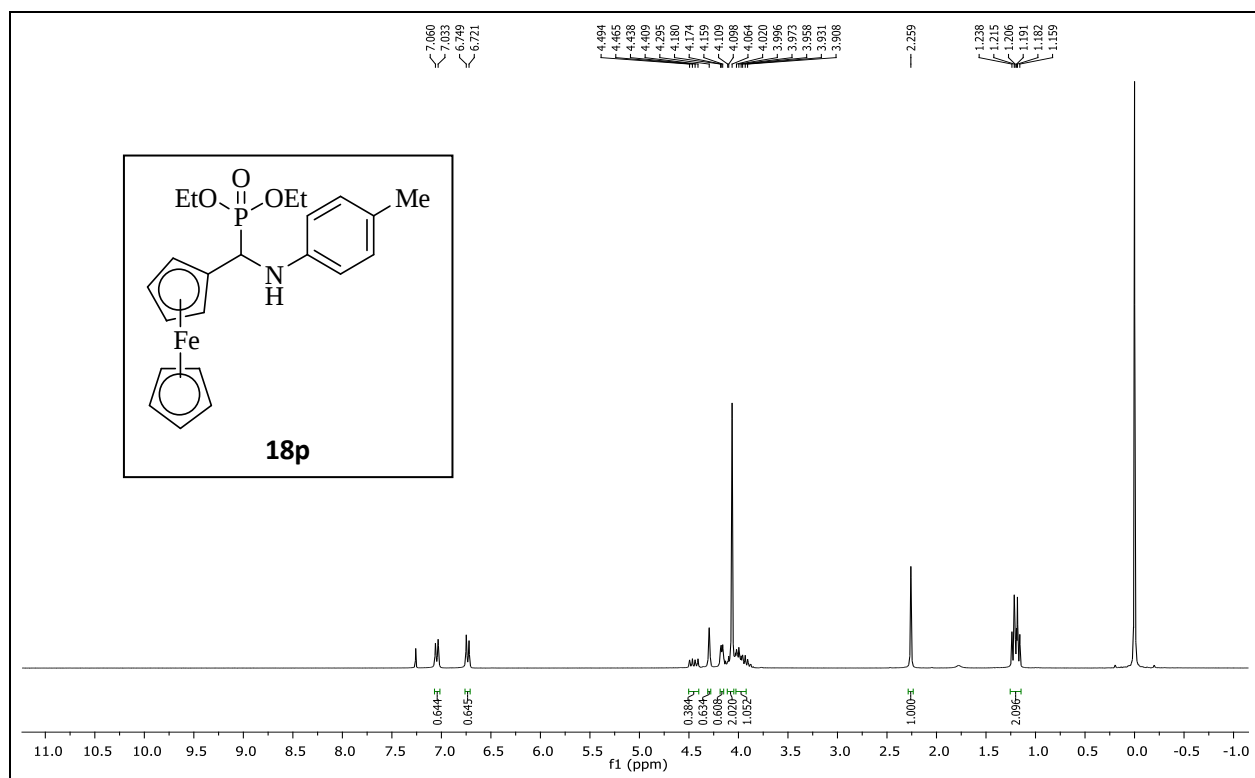


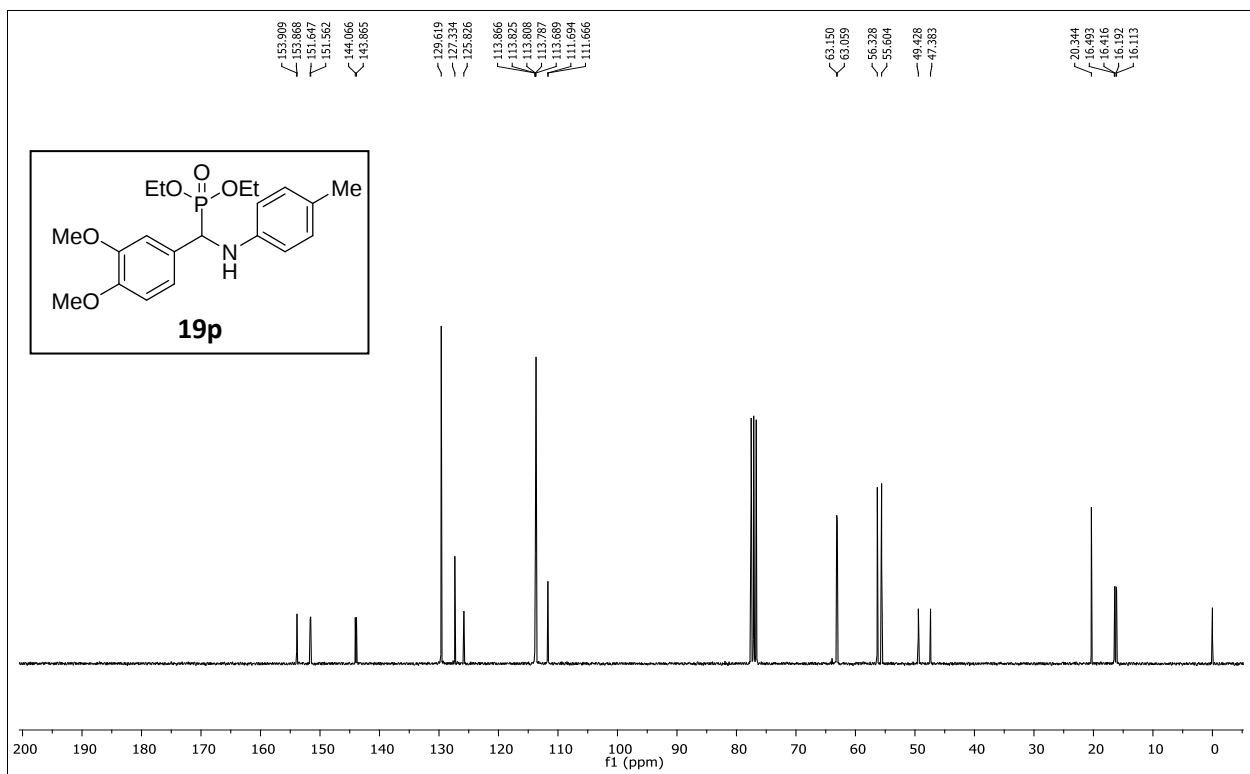
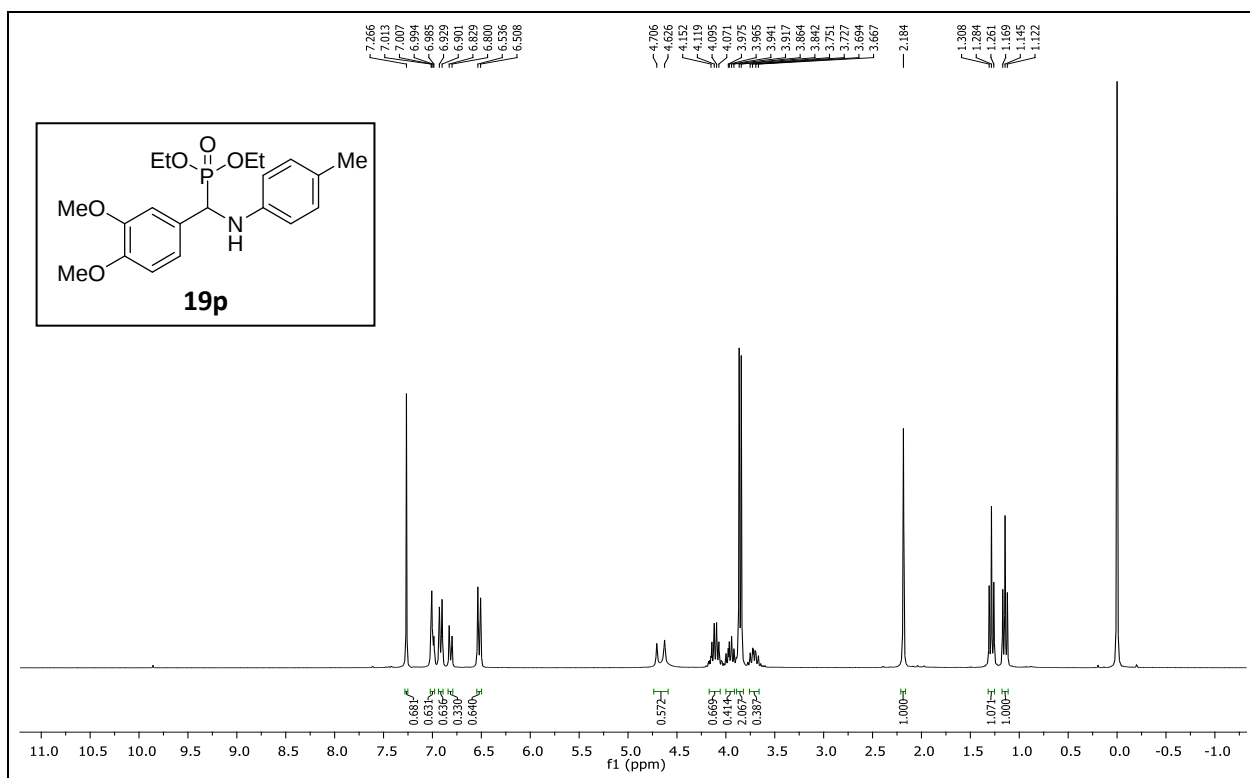


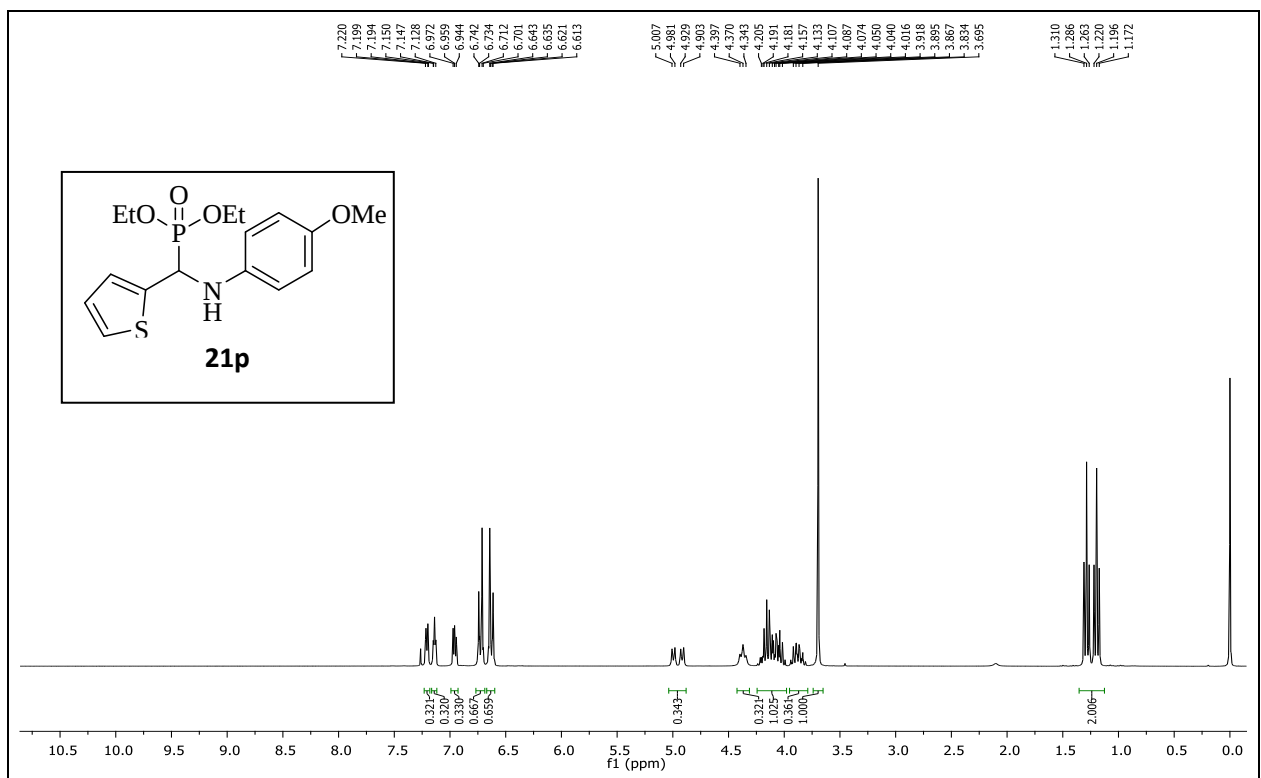
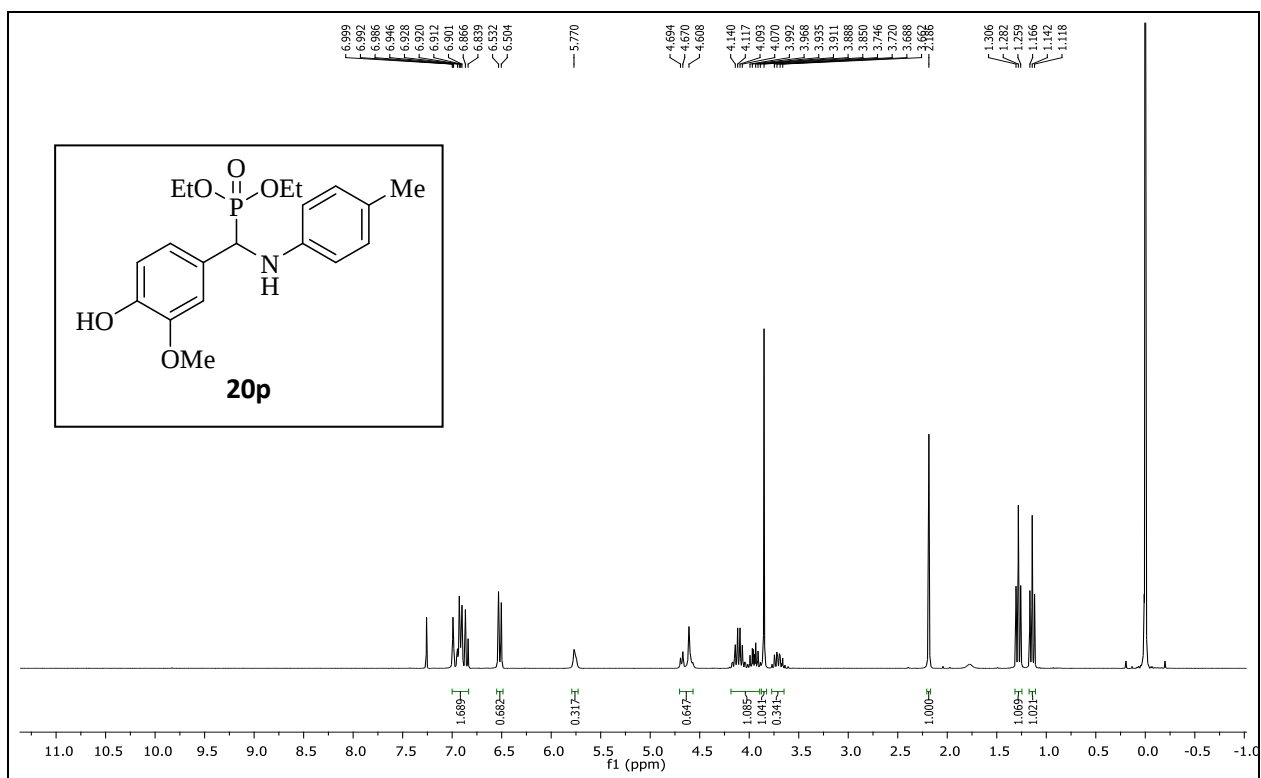


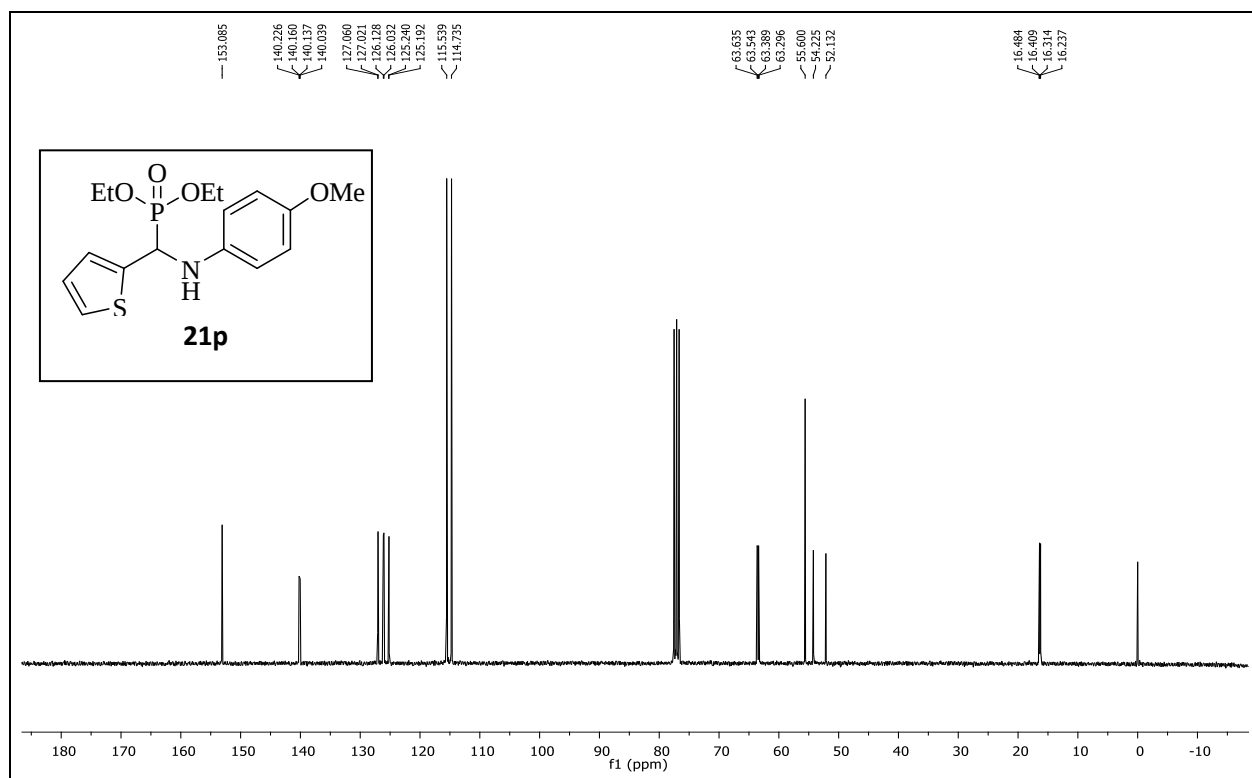


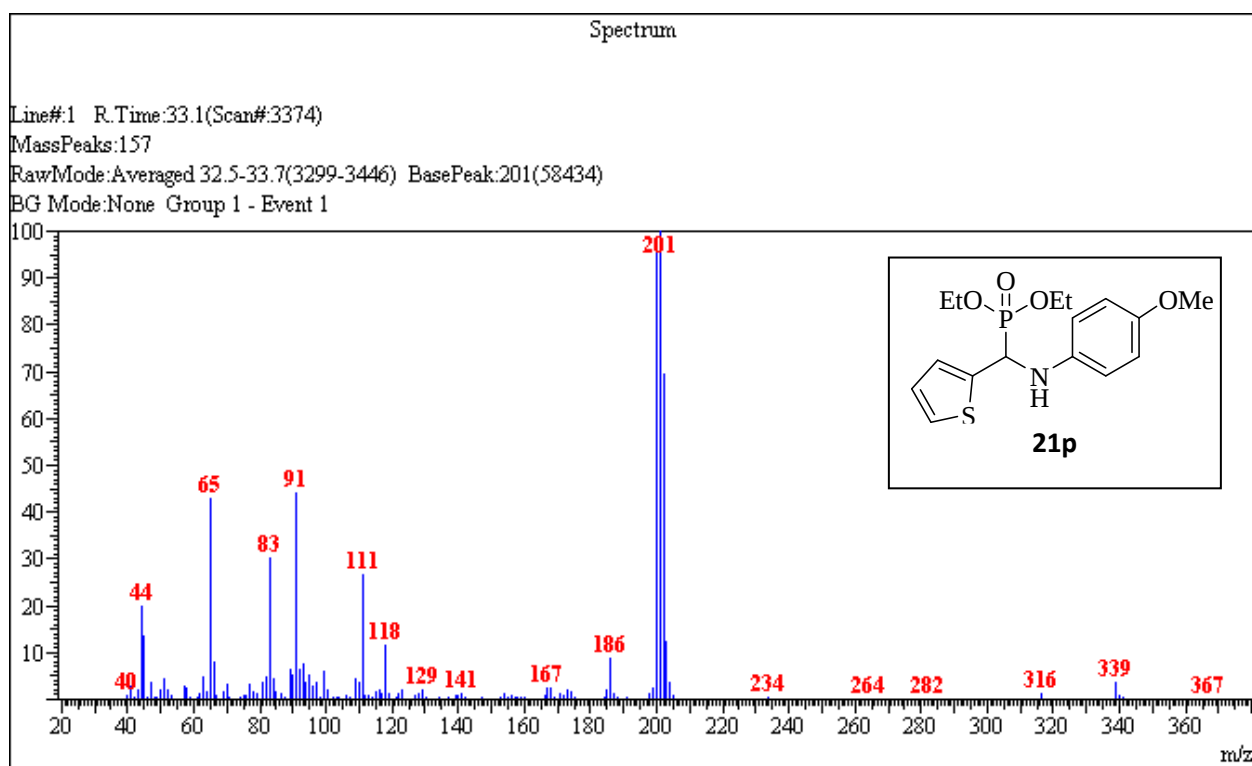
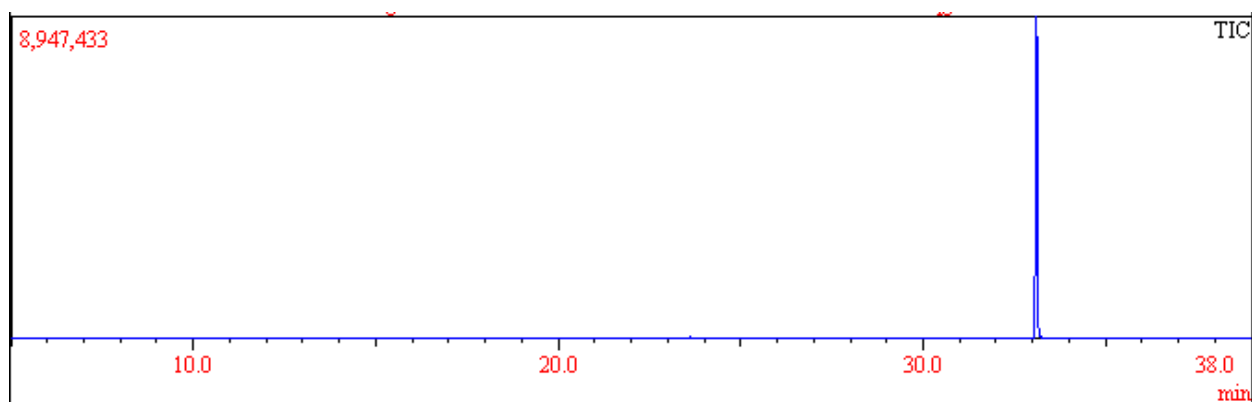


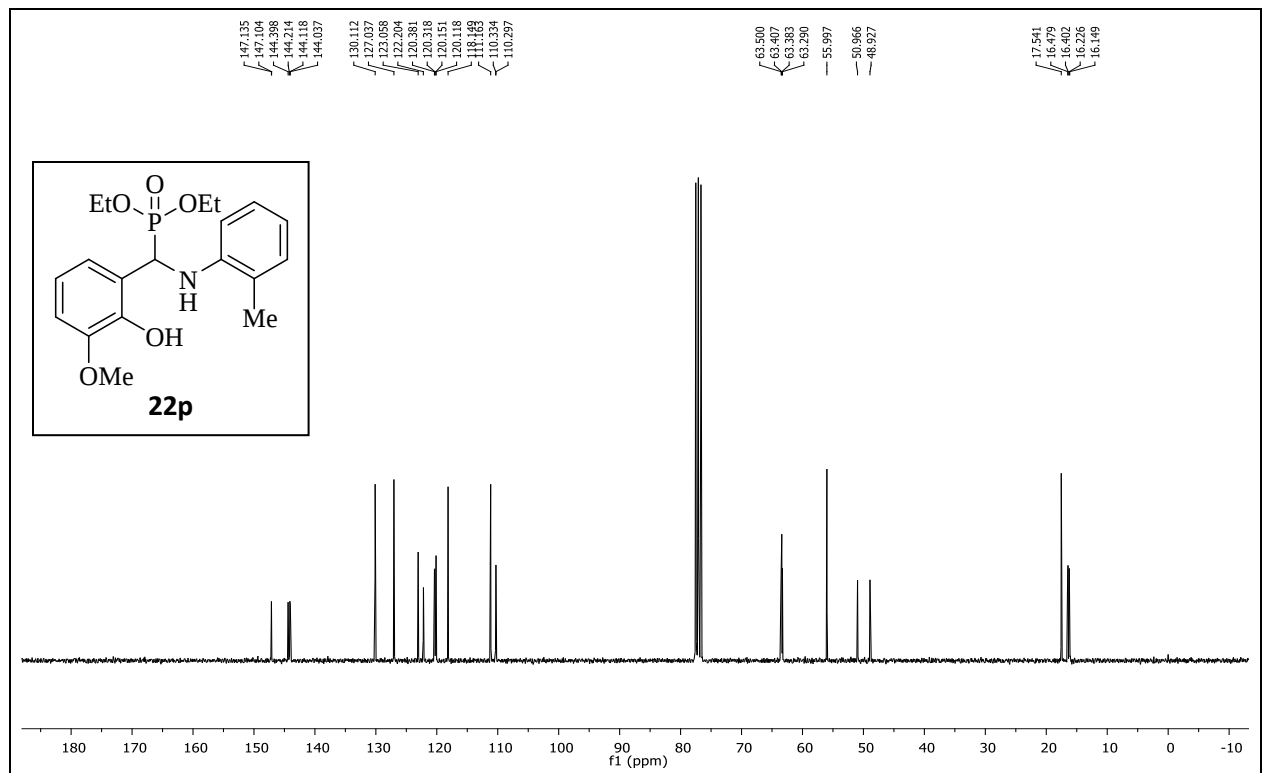
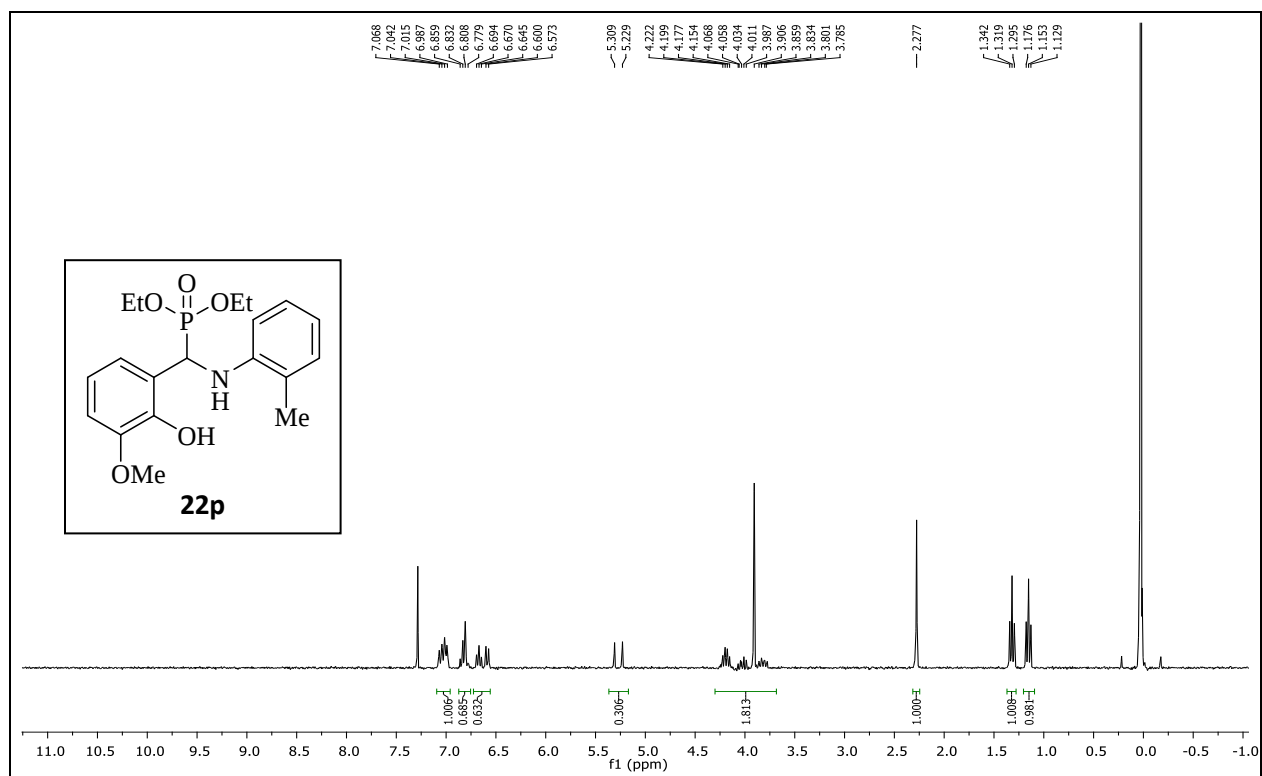


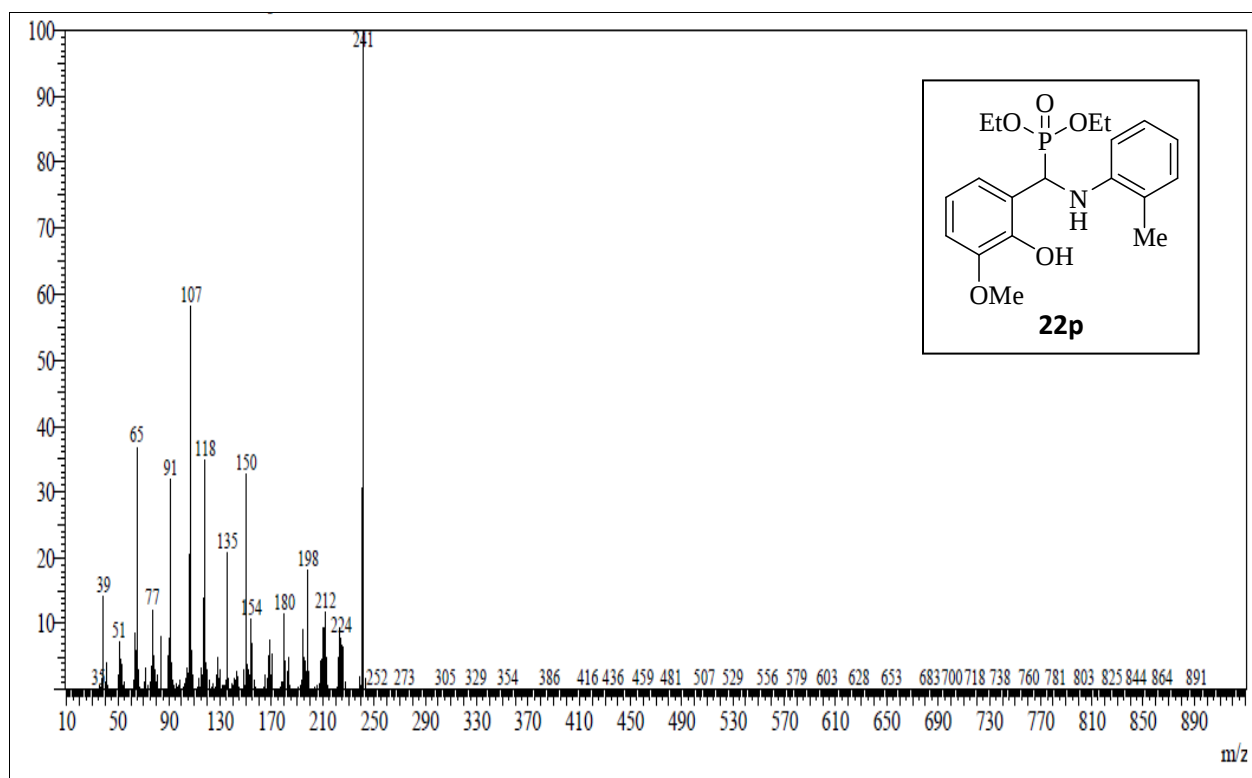
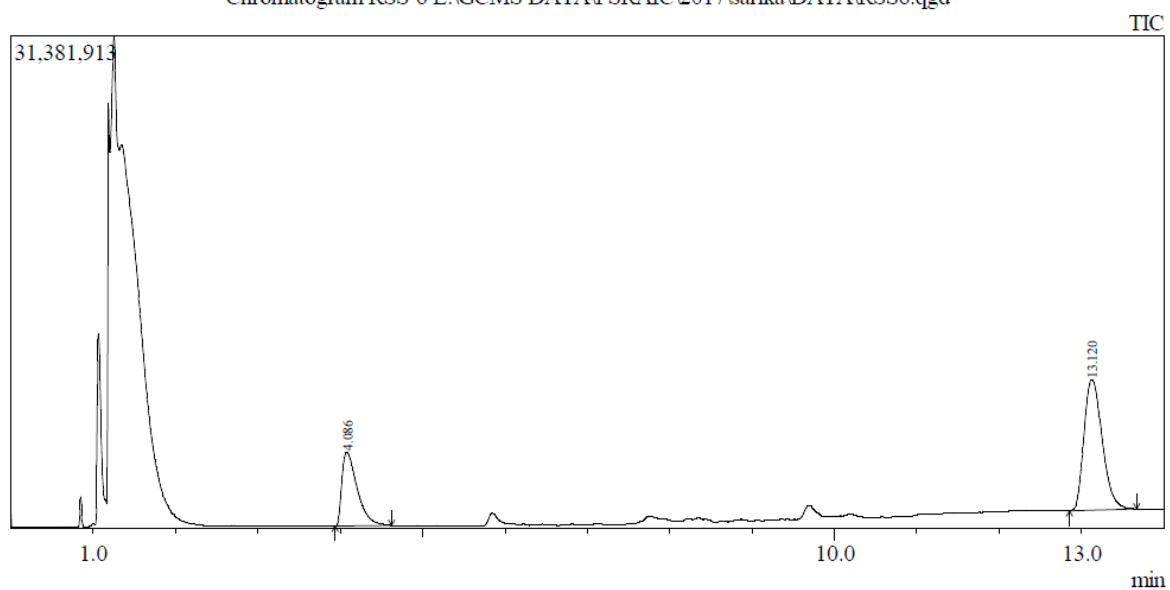


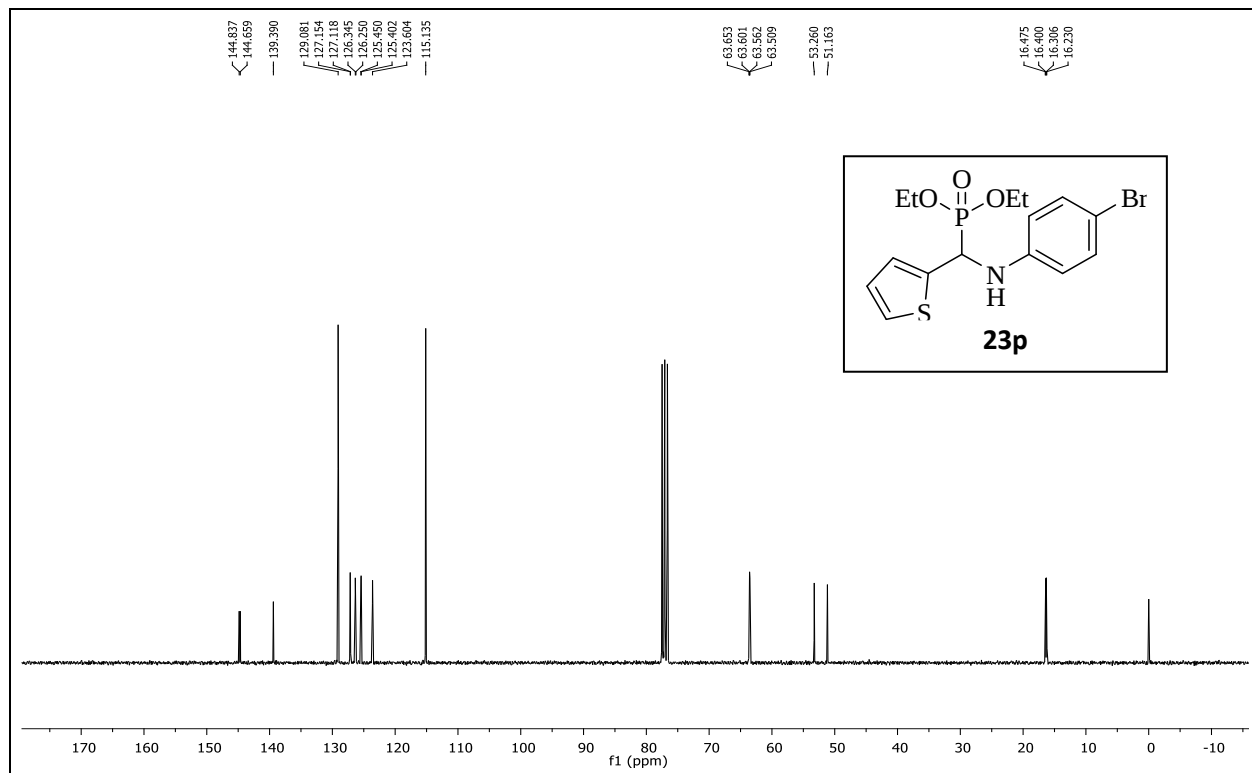
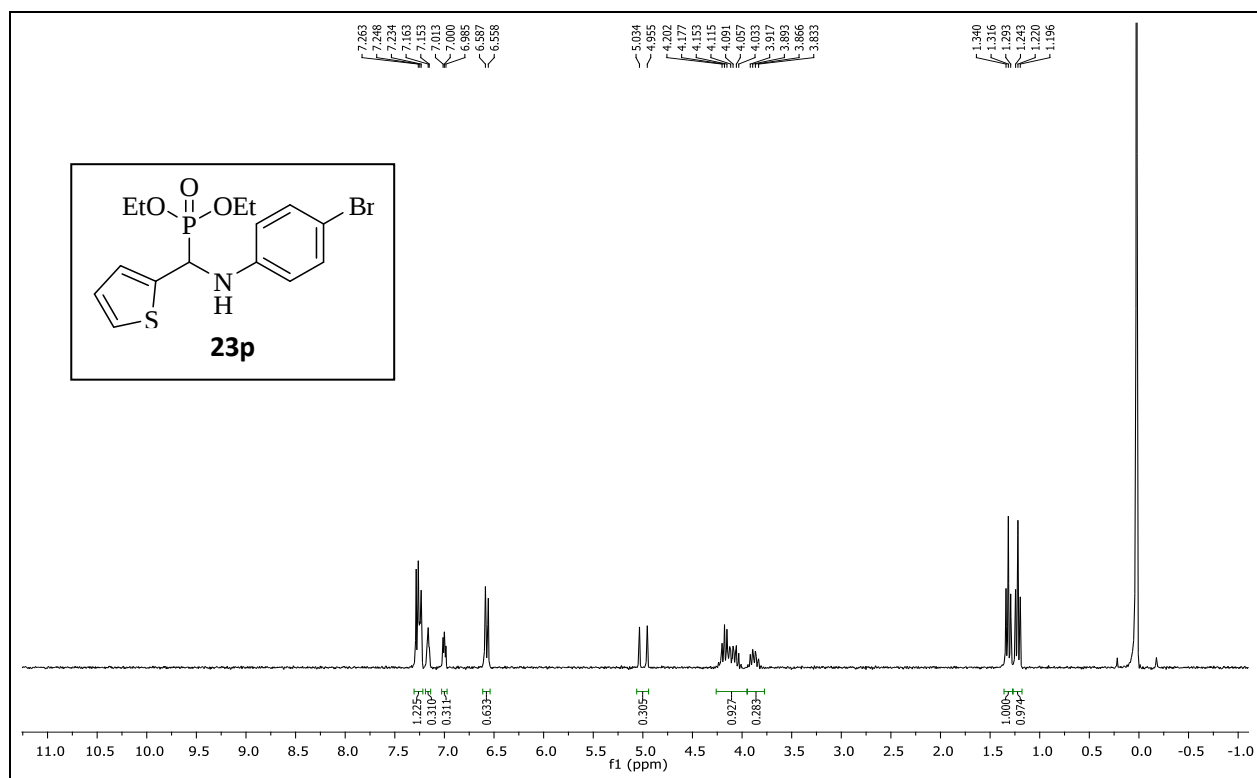


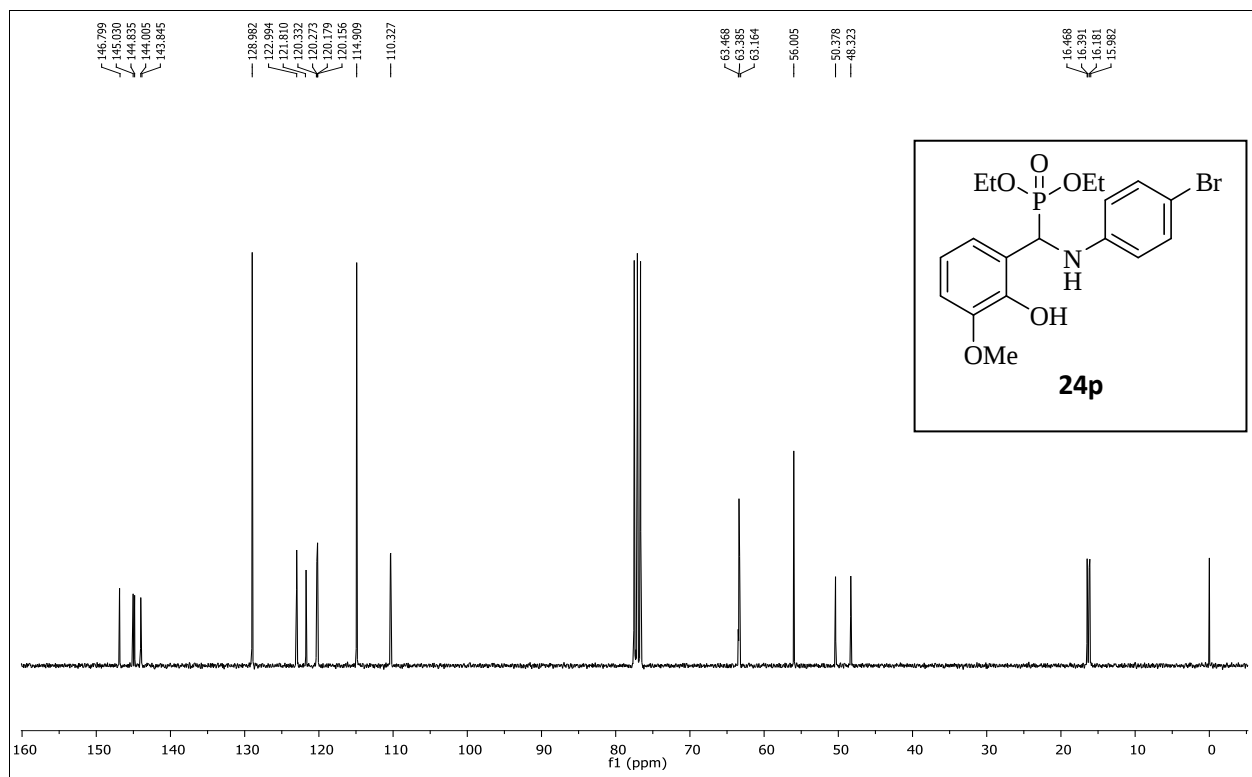
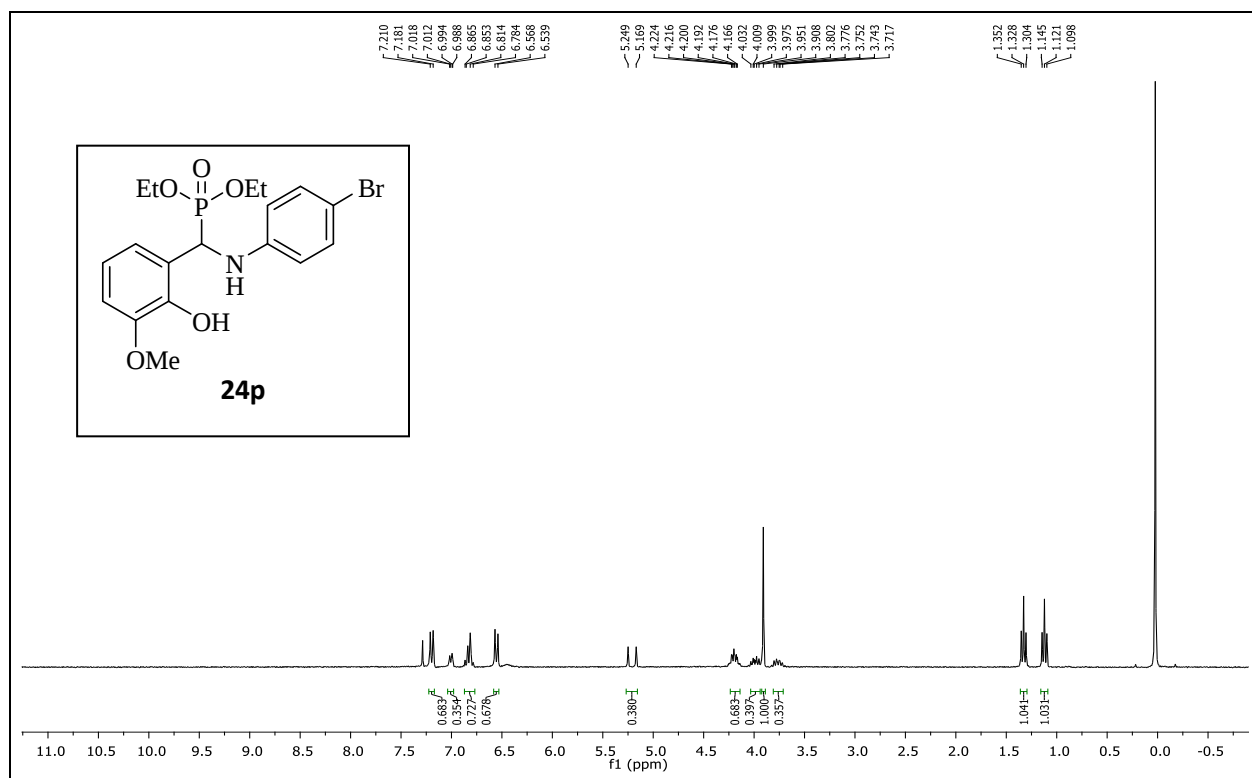


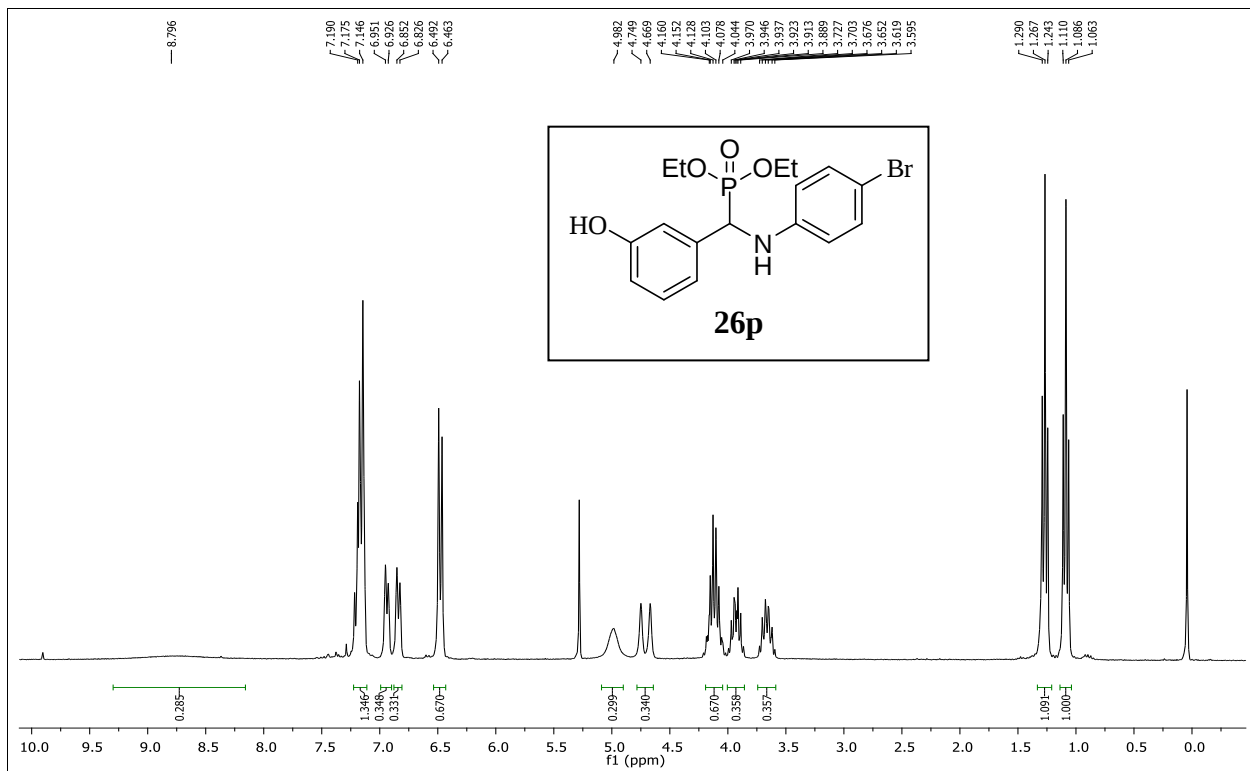
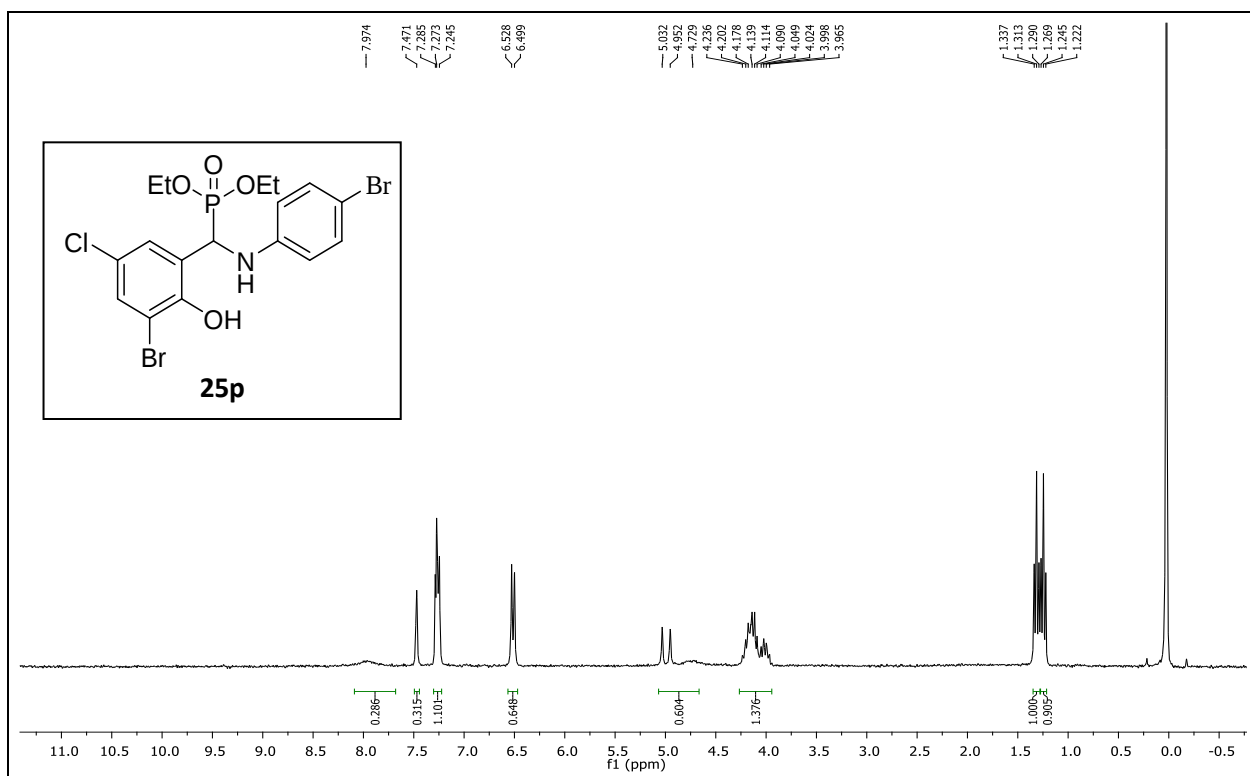


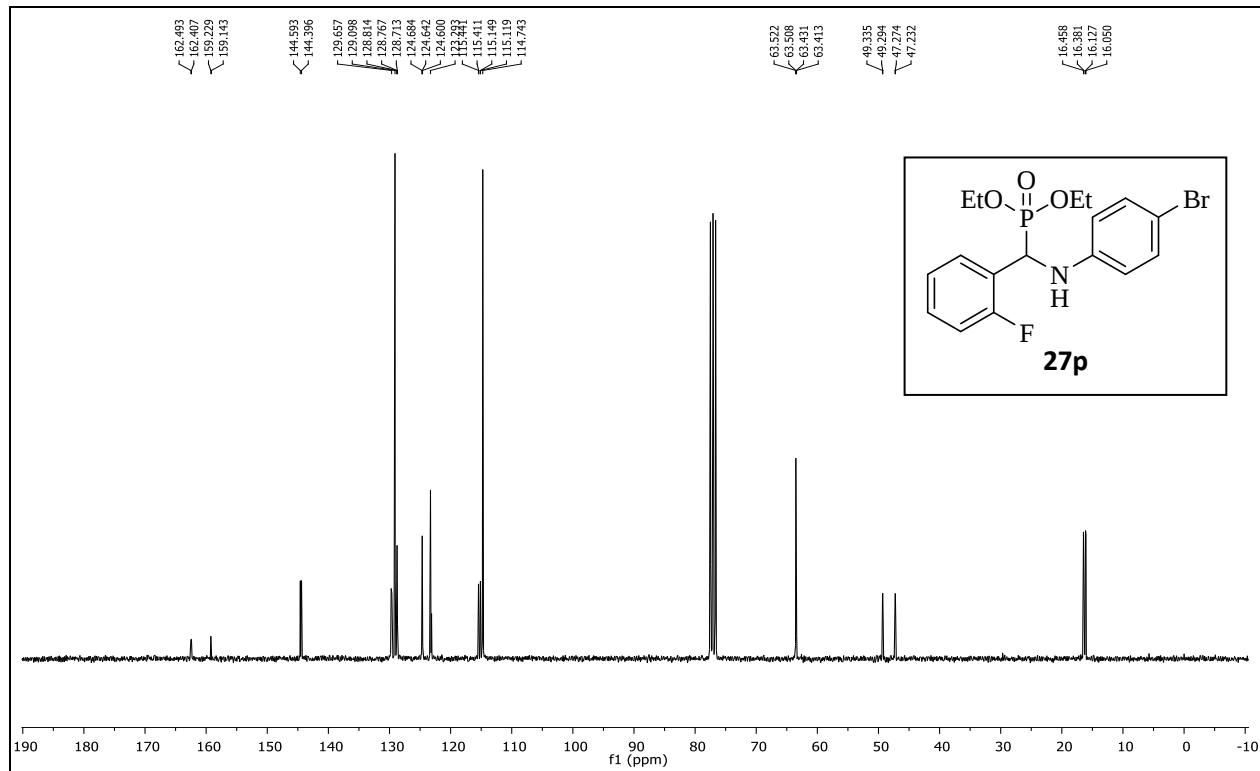
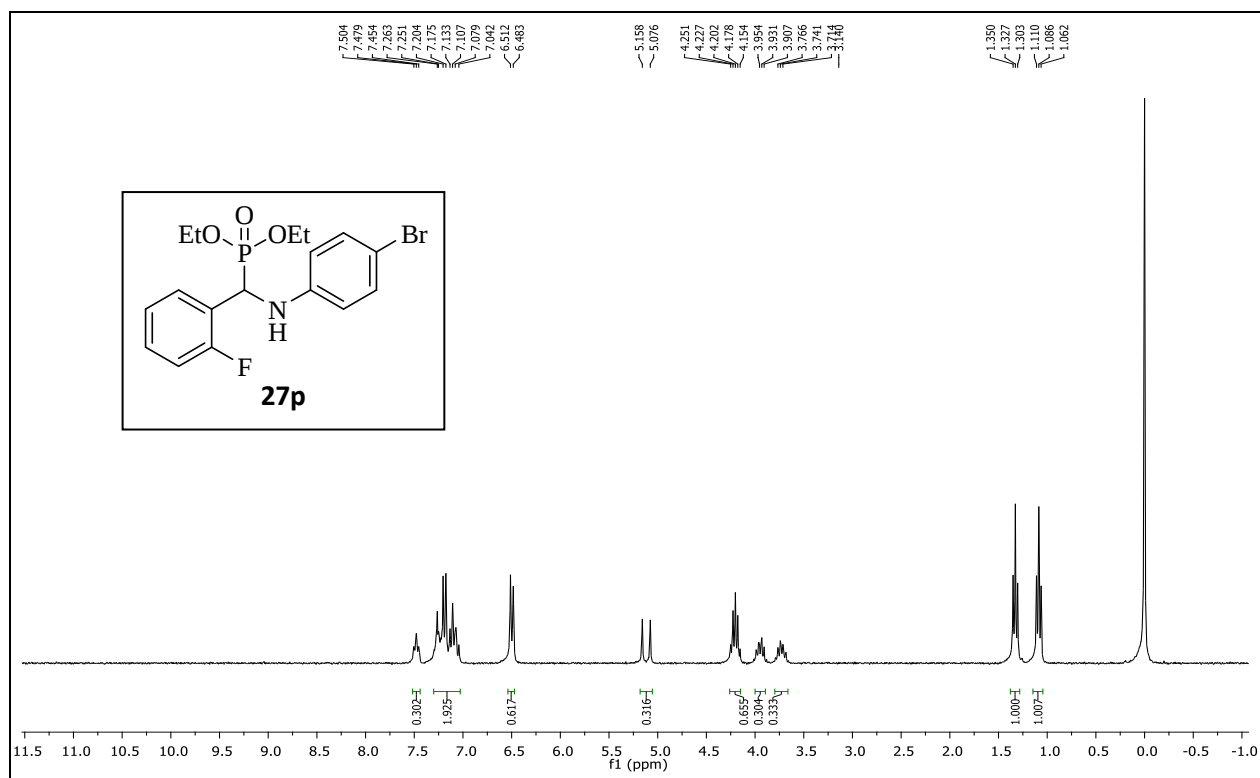


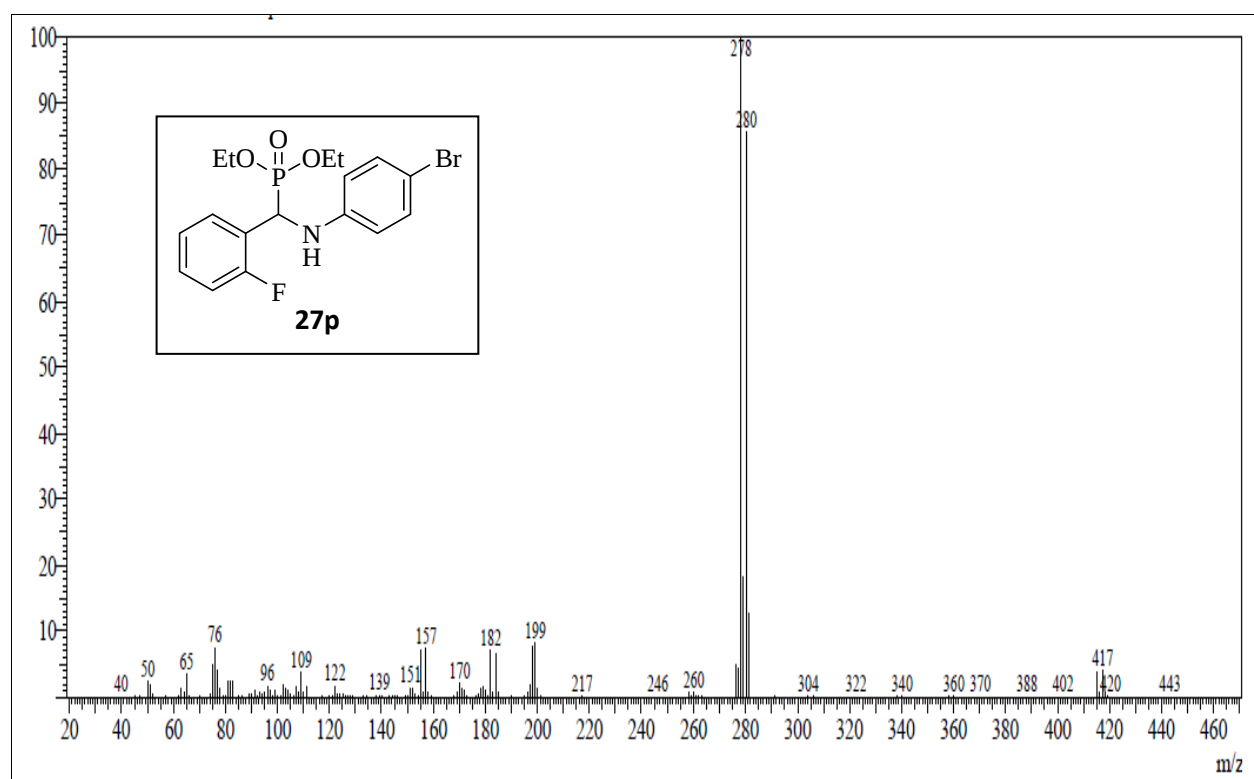
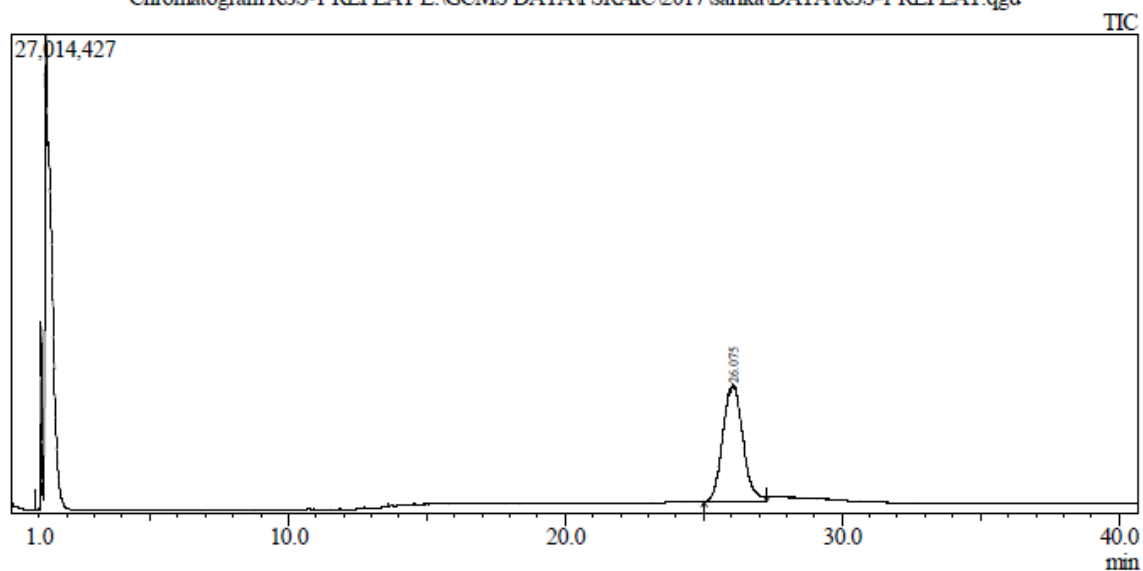


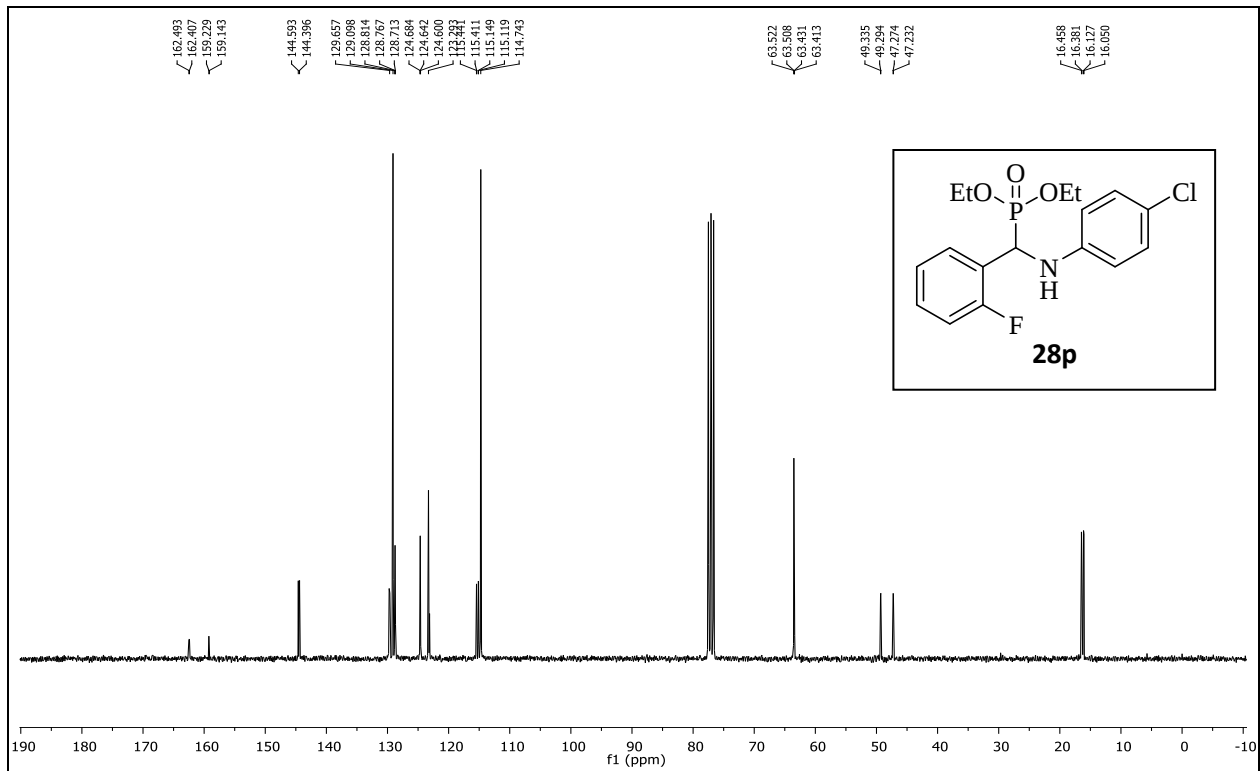
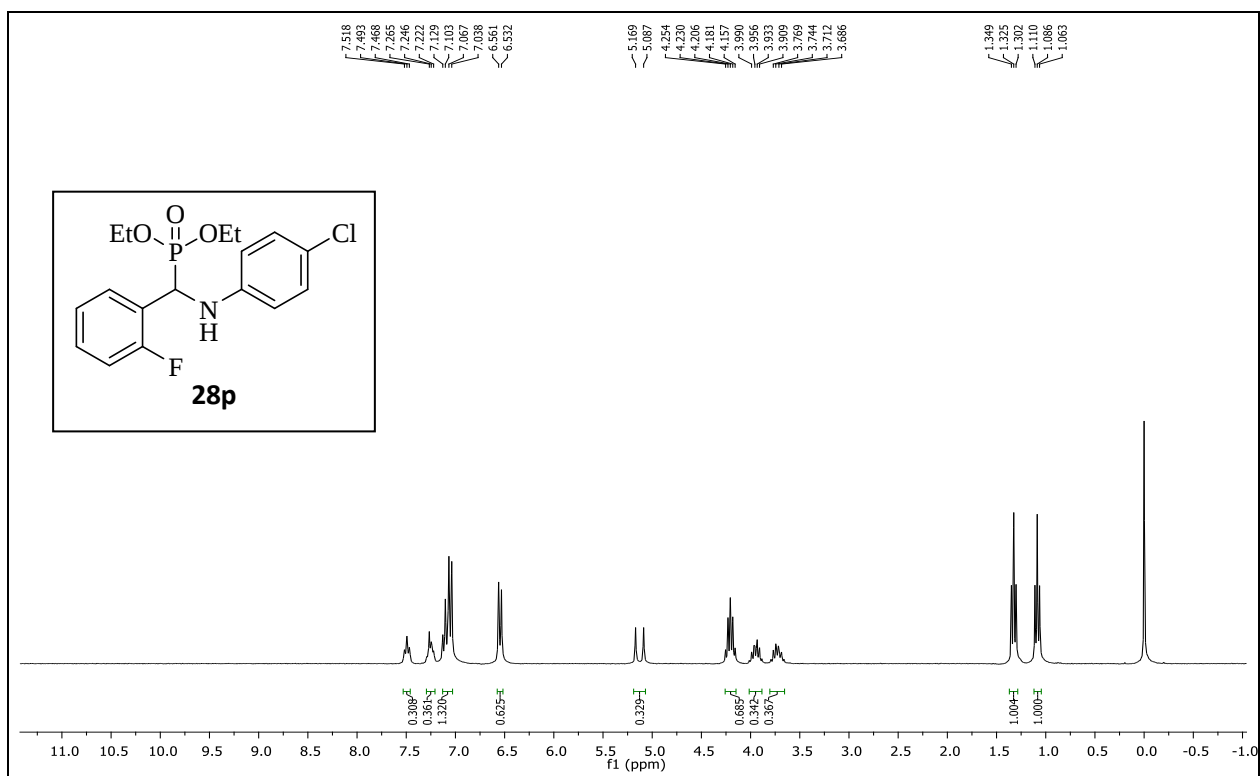


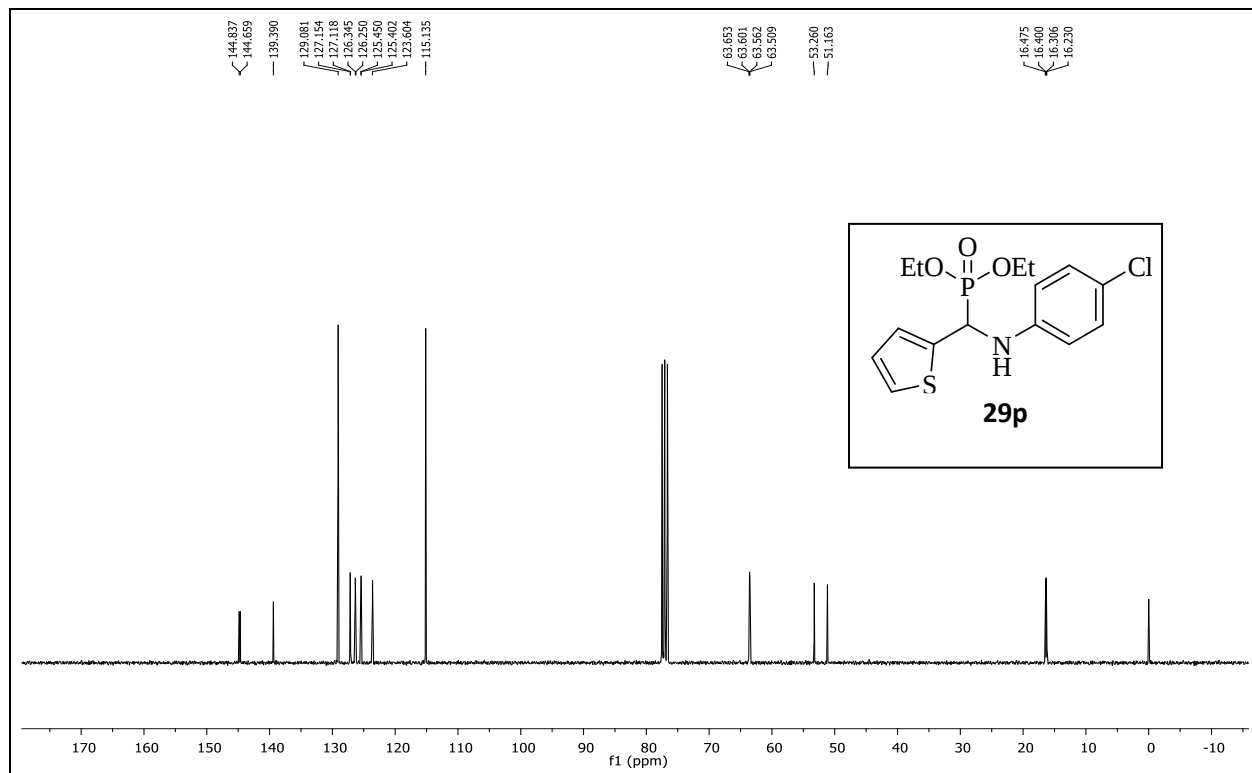
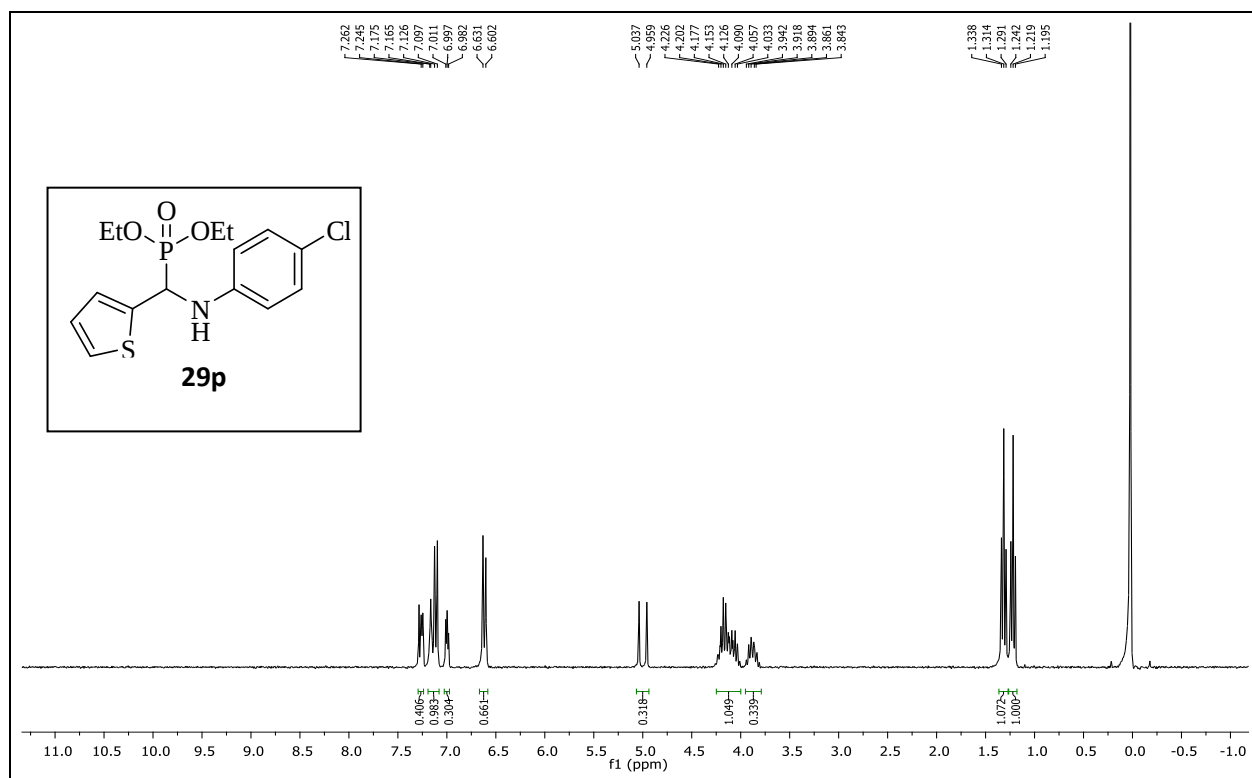


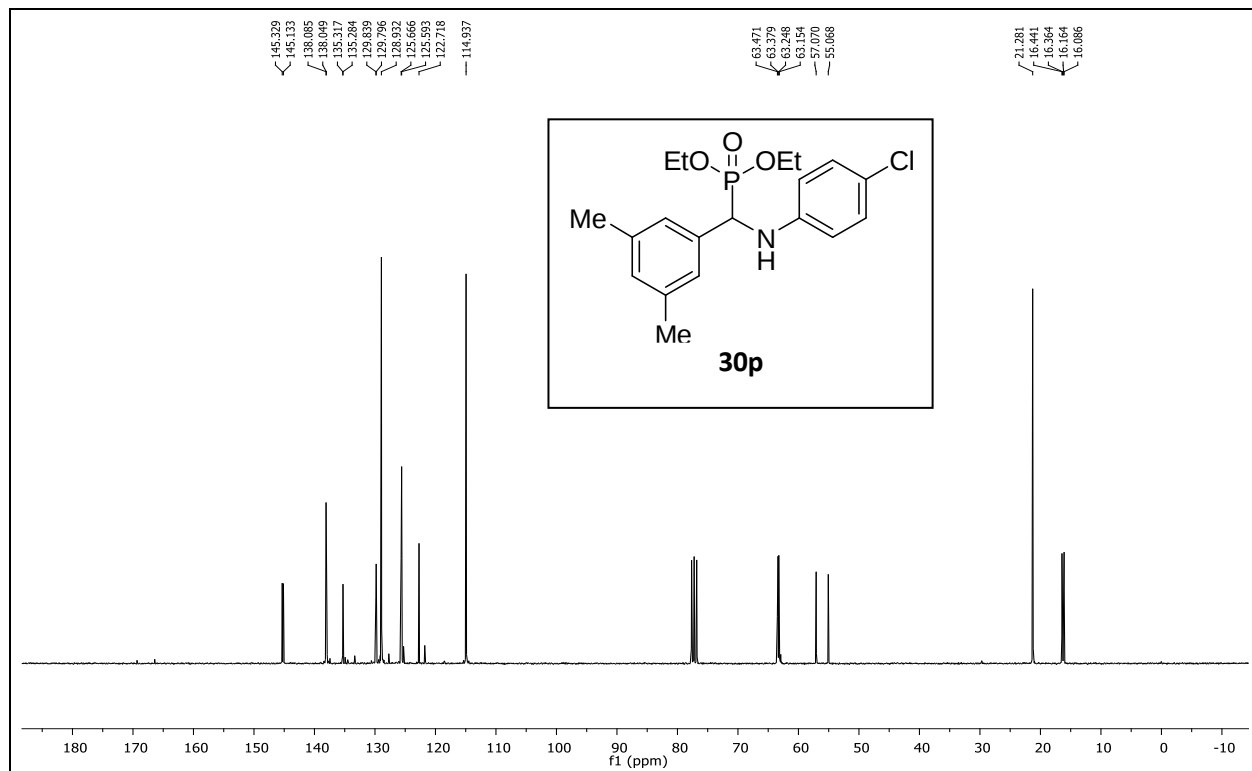
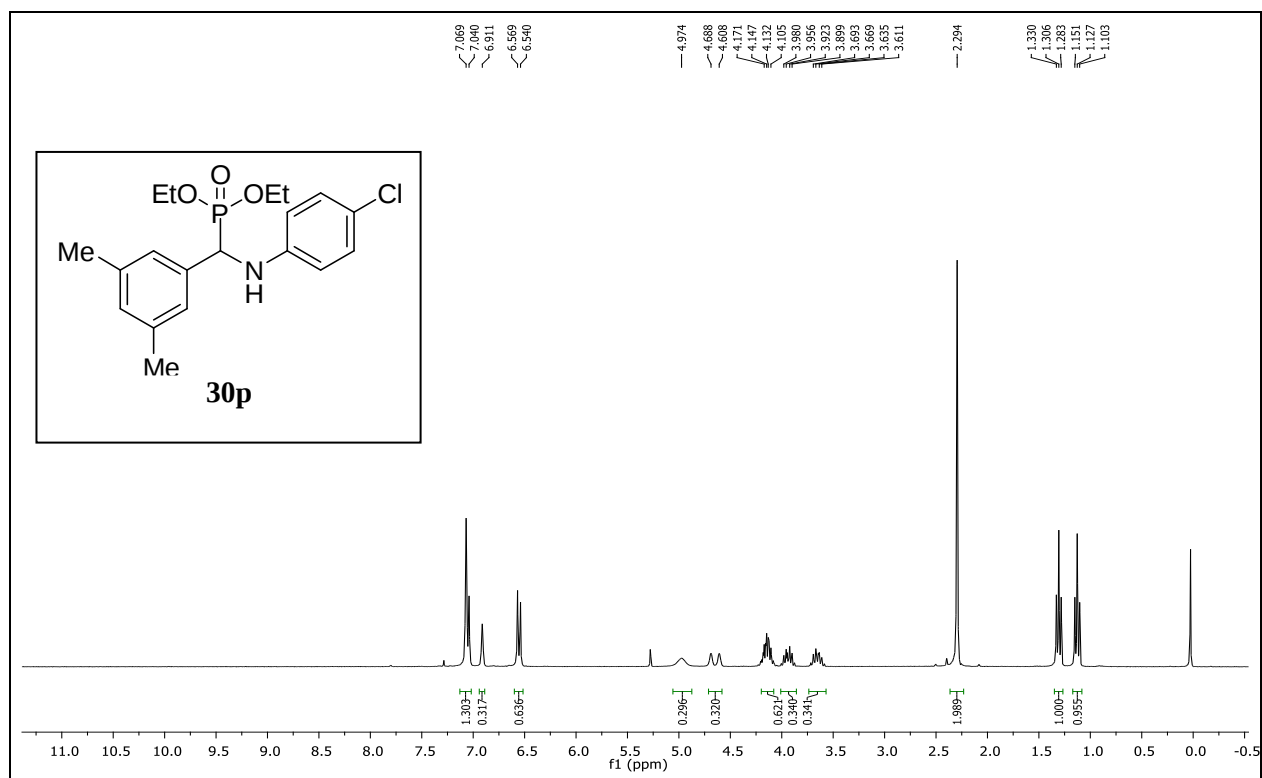


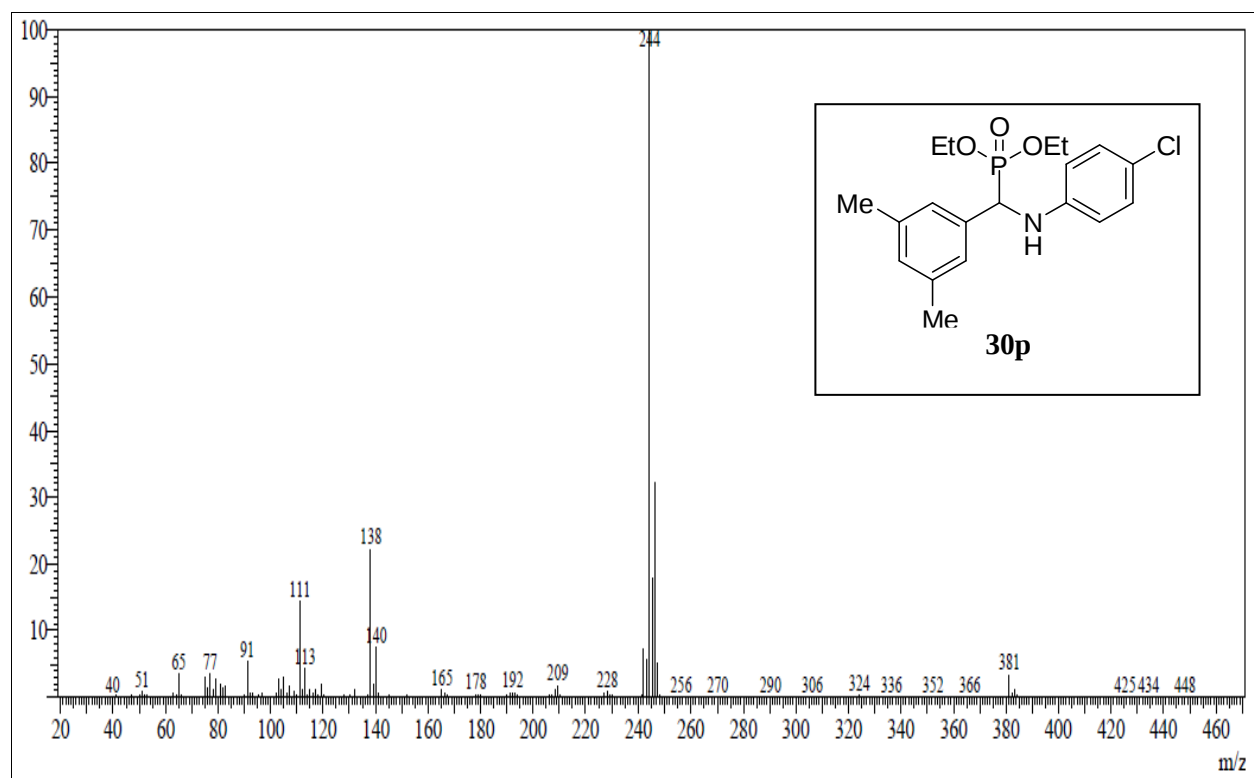












4. References

- [1] Mohammad, Z. K.; Farnaz, M.; Hassan, M.; *Synlett*, **2009**, 8, 1326-1330.
- [2] Shaterian, H. R.; Javad, F.; Majid, M.; *Phosphorus, Sulfur, and Silicon*, **2013**, 188,850-854.
- [3] Anguo, Y.; Shuo, L.; Jianguo, Y.; Huanan, H.; *Ind. Eng. Chem. Res.*, **2014**, 16143-16147, 53.