

Supporting Information

A one-pot three-component synthesis of novel α -sulfamidophosphonates under ultrasound irradiation and catalyst-free conditions

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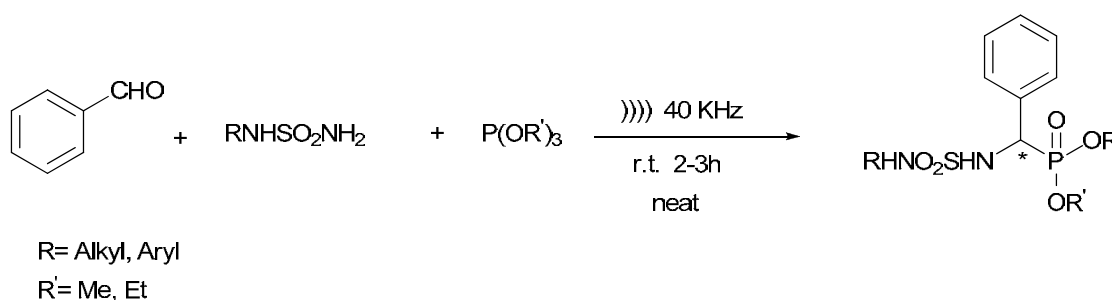
1. Apparatus

Melting points were measured in open capillary tubes on an Electro thermal apparatus and uncorrected. Mass spectra were recorded on a shimadzu QP 1100 Ex mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded as KBr pellets on a Perkin Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded in DMSO-d₆ or CDCl₃ solvents on a 250, 300 or 400MHz Bruker spectrometer with tetramethylsilane as internal reference.

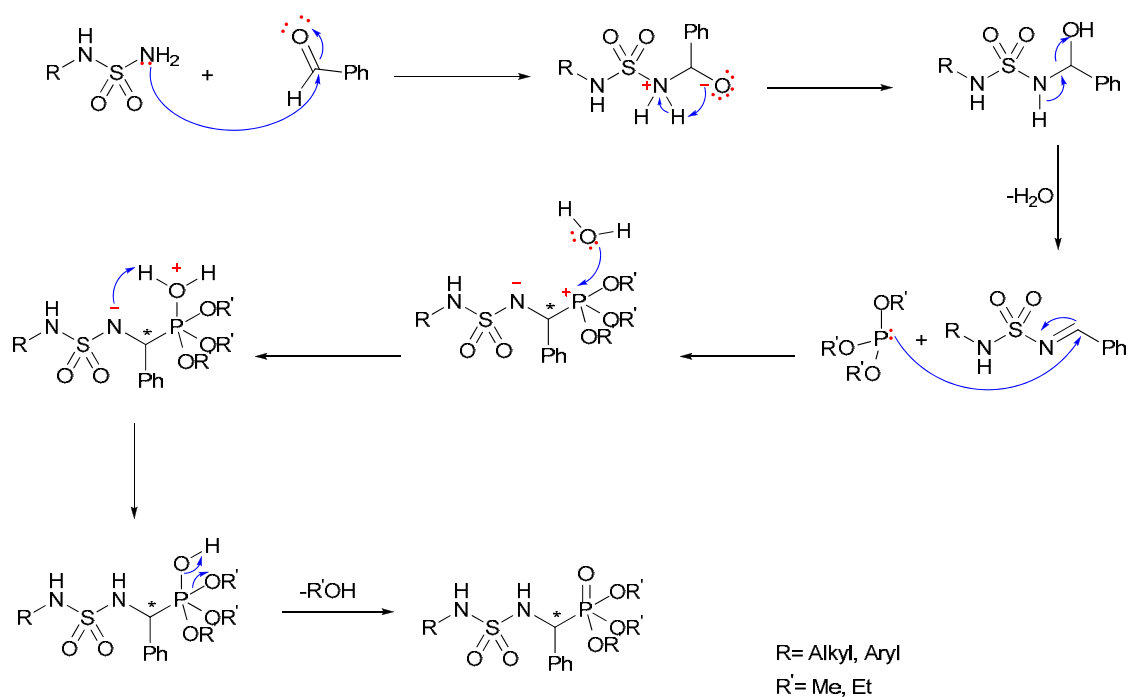
Ultrasound assisted reactions were carried out using a FUNGILAB ultrasonic bath with a frequency of 40 kHz and a nominal power of 250 W. The reactions were carried out in an open glass tube (diameter: 25 mm; thickness: 1 mm; volume: 20 mL) at room temperature. All reactions were monitored by thin layer chromatography (TLC) on silica Merck 60 F254 percolated aluminum plates.

2. General procedure

In a 10 ml round bottom flask taken a mixture of aldehyde (1 mmol) and sulfonamide (1 mmol) at room temperature and then triethylphosphite (1 mmol) was added. Then reaction mixture was subjected to the ultrasonication for appropriate time. After completion of the reaction, as indicated by TLC, silica gel; dichloromethane:methanol (9:1), a (4:1) mixture of diethyl ether and *n*-hexane was added and the mixture was cooled to 6° C overnight. The product was finally filtered and dried.

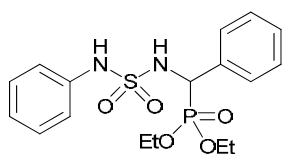


Scheme 1: One-potsynthesis of α -sulfamidophosphonate under ultrasound irradiations.



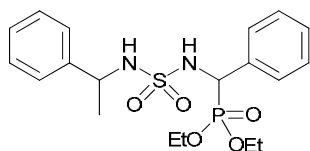
Scheme 2: Mechanistic proposal for synthesis of α -sulfamidophosphonate.

3. Selected Spectral data:



diethyl phenyl(*N*-phenylsulfamoylamino)methylphosphonate (Table 1, Entry 2a)

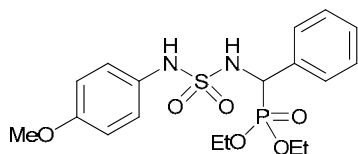
White crystal. m.p = 152-154 °C. Yield 95%. R_f (DCM-MeOH : 95/5) = 0.32. Ms (m/z): 399 [M+1]. ν_{\max} (KBr)/ cm^{-1} 3210, 1675, 1387, 1262, 1151, 1023. δ_p (160 MHz, CDCl_3) 19.61. δ_H (400 MHz, CDCl_3) 1.03 (t, J 7.2 Hz, 3H, CH_3), 1.29 (t, J 6.8 Hz, 3H, CH_3), 3.59–3.67 (m, 1H, CH_2), 3.82–3.89 (m, 1H, CH_2), 4.06–4.17 (m, 2H, CH_2), 4.81 (dd, J 8.8 Hz, 1H, CH), 5.92 (t, J 6.8 Hz, 1H, NH), 6.47 (s, 1H, NH), 6.79–6.81 (m, 2H, H-Ar), 7.01–7.25 (m, 8H, H-Ar). δ_c (100 MHz, CDCl_3) 16.3, 16.5, 54.8, 63.9, 64.1, 119.7, 124.4, 128.3, 128.4, 128.7, 128.9, 129.3, 134.2, 136.8. Anal. Calc. for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_5\text{P}$: C 51.25, H 5.82, N 7.03. Found: C 51.15, H 5.80, N 7.20%. $M = 398$.



diethyl phenyl(*N*-(1-phenylethyl)sulfamoylamino)methylphosphonate (Table 1, Entry 2c)

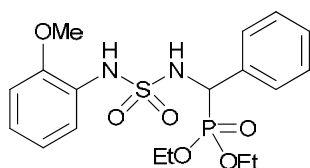
White powder. m.p = 138-140 °C. Yield 90%. R_f (DCM-MeOH : 95/5) = 0.36. Ms (m/z): 427 [M+1]. ν_{\max} (KBr)/ cm^{-1} 3330, 3040, 1622, 1355, 1230, 1155, 1103. δ_p (160 MHz, CDCl_3) 20.16. δ_H (400 MHz, CDCl_3) 1.08 (t, J 7.2 Hz, 3H, CH_3), 1.12 (d, J 6.6 Hz, 3H, CH_3), 1.32 (t, J 7 Hz, 3H, CH_3), 3.69 (m,

1H, CH), 3.92 (m, 1H, CH), 4.10–4.19 (m, 2H, CH₂), 4.27–4.39 (m, 2H, CH₂), 4.73 (dd, *J* 11.2 Hz, 1H, CH), 5.41 (t, *J* 7.7 Hz, 1H, NH), 7.15–7.27 (m, 5H, H-Ar), 7.28–7.45 (m, 5H, H-Ar). δ_c (100 MHz, CDCl₃) 17, 21.3, 48.2, 56, 62.2, 115.7, 122.8, 124, 126.3, 128.5, 129.4, 142.5, 145.1. Anal. Calc. for C₁₉H₂₇N₂O₅PS: C 53.51, H 6.38, N 6.57. Found: C 53.02, H 6.21, N 6.35%. M=426.



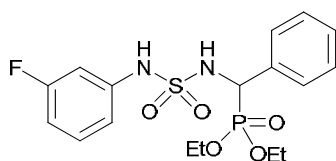
diethyl (N-(4-methoxyphenyl)sulfamoylamino)(phenyl)methylphosphonate (Table 1, Entry 2d)

Oil. Yield 87%. R_f (DCM-MeOH : 95/5) = 0.39. Ms (*m/z*): 429 [M+1]. ν_{max} (KBr)/cm⁻¹ 3323, 1610, 1315, 1236, 1167, 1050. δ_p (160 MHz, CDCl₃) 21.37. δ_H (400 MHz, CDCl₃) 1.21 (t, *J* 7 Hz, 3H, CH₃), 1.26 (t, *J* 7 Hz, 3H, CH₃), 3.75 (s, 3H, CH₃), 3.94–4.01 (m, 2H, CH₂), 4.00–4.15 (m, 2H, CH₂), 5.03 (d, *J* 10.8 Hz, 1H, CH), 6.62–6.81 (2d, *J* 8.9 Hz, 2H, H-Ar), 7.24–7.49 (m, 7H, H-Ar). δ_c (100 MHz, CDCl₃) 16.3, 16.4, 55.4, 63.1, 63.3, 70, 71.6, 114.1, 123.2, 127, 127.1, 128, 128.1, 128.2, 128.3, 128.5, 129.6, 136.5, 136.6. Anal. Calc. for C₁₈H₂₅N₂O₆PS: C 50.46, H 5.88, N 6.54. Found: C 50.99, H 6.15, N 6.80%. M=428.



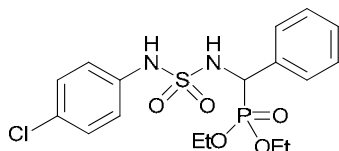
diethyl (N-(2-methoxyphenyl)sulfamoylamino)(phenyl)methylphosphonate (Table 1, Entry 2e)

White crystal. mp = 145–147 °C. Yield 85%. R_f (DCM-MeOH : 95/5) = 0.38. Ms (*m/z*): 429 [M+1]. ν_{max} (KBr)/cm⁻¹ 3300, 1655, 1311, 1228, 1151, 1080. δ_p (160 MHz, CDCl₃) 19.53. δ_H (400 MHz, CDCl₃) 1.01 (t, *J* 7.1 Hz, 3H, CH₃), 1.29 (t, *J* 7.1 Hz, 3H, CH₃), 3.81 (s, 3H, CH₃), 3.54–3.83 (m, 1H, CH₂), 3.84–3.87 (m, 1H, CH₂), 4.04–4.16 (m, 2H, CH₂), 4.74 (dd, *J* 8.8 Hz, 1H, CH), 6.00 (t, *J* 7.1 Hz, 1H, NH), 6.55–6.57 (d, *J* 8 Hz, 1H, H-Ar), 6.74 (s, 1H, NH), 6.83–6.87 (t, *J* 7.6 Hz, 1H, H-Ar), 6.91–6.95 (t, *J* 7.5 Hz, 1H, H-Ar), 7.08–7.14 (m, 5H, H-Ar), 7.39–7.43 (d, *J* 6.9 Hz, 1H, H-Ar). δ_c (100 MHz, CDCl₃) 16.3, 16.4, 55.9, 58.2, 68.2, 69, 109.9, 117.4, 120.8, 123.6, 123.9, 127.7, 127.7, 128.1, 128.3, 129.1, 138.4, 139.6. Anal. Calc. for C₁₈H₂₅N₂O₆PS: C 50.46, H 5.88, N 6.54. Found: C 50.95, H 5.71, N 6.68%. M=428.



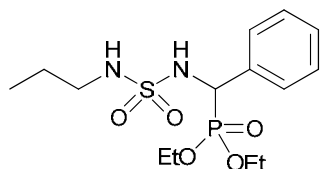
diethyl (*N*-(3-fluorophenyl)sulfamoylamino)(phenyl)methylphosphonate (Table 1, Entry 2f)

White crystal. mp = 109-111 °C. Yield 92%. R_f (DCM-MeOH : 95/5) = 0.45. Ms (m/z): 417 [M+1]. ν_{\max} (KBr)/ cm^{-1} 3315, 1688, 1319, 1225, 1140, 1032. δ_{F} (375 MHz, CDCl_3) -111.62. δ_{P} (160 MHz, CDCl_3) 22.21. δ_{H} (400 MHz, CDCl_3) 1.1 (t, J 7.1 Hz, 3H, CH_3), 1.29 (t, J 7 Hz, 3H, CH_3), 3.59–3.69 (m, 1H, CH_2), 3.87–3.96 (m, 1H, CH_2), 4.04–4.18 (m, 2H, CH_2), 4.71 (dd, J 7.7 Hz, 1H, CH), 4.97 (t, J 8.6 Hz, 1H, NH), 6.24–7.03 (m, 4H, H-Ar), 7.25–7.46 (m, 5H, H-Ar). δ_{C} (100 MHz, CDCl_3) 16.1, 16.4, 56.2, 64, 64.1, 106.5, 106.7, 110.6, 110.8, 114.7, 128.2, 128.7, 130.2, 130.3, 134, 138.5, 161.8. Anal. Calc. for $\text{C}_{17}\text{H}_{22}\text{FN}_2\text{O}_5\text{PS}$: C 49.03, H 5.33, N 6.73. Found: C 48.50, H 5.62, N 6.53%. $M=416$.



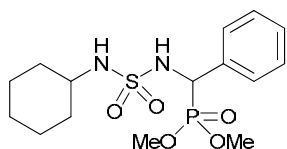
diethyl (*N*-(4-chlorophenyl)sulfamoylamino)(phenyl)methylphosphonate (Table 1, Entry 2j)

White crystal. mp = 116-118 °C. Yield 91%. R_f (DCM-MeOH : 95/5) = 0.46. Ms (m/z): 433 [M+1]. ν_{\max} (KBr)/ cm^{-1} 3210, 1675, 1387, 1262, 1151, 1023. δ_{P} (100 MHz, CDCl_3) 19.66. δ_{H} (300 MHz, CDCl_3) 1.10 (t, J 6.9 Hz, 3H, CH_3), 1.28 (t, J 7.1 Hz, 3H, CH_3), 3.61–3.69 (m, 1H, CH_2), 3.88–3.96 (m, 1H, CH_2), 4.07–4.14 (m, 2H, CH_2), 4.78 (dd, J 7.7 Hz, 1H, CH), 4.82 (t, J 8.2 Hz, 1H, NH), 6.50 (d, J 8.85 Hz, 2H, H-Ar), 7.03 (d, J 7.1 Hz, 2H, H-Ar), 7.29–7.35 (m, 5H, H-Ar). δ_{C} (75 MHz, CDCl_3) 16.3, 16.4, 55.5, 63.5, 63.7, 109.3, 111.2, 115.2, 124.1, 126.8, 128.3, 128.9, 131.4, 136.6, 148.4, 149.3, 163.2. Anal. Calc. for $\text{C}_{17}\text{H}_{22}\text{ClN}_2\text{O}_5\text{PS}$: C 47.17, H 5.12, N 6.47. Found: C 46.95, H 5.58, N 6.46%. $M=432$.



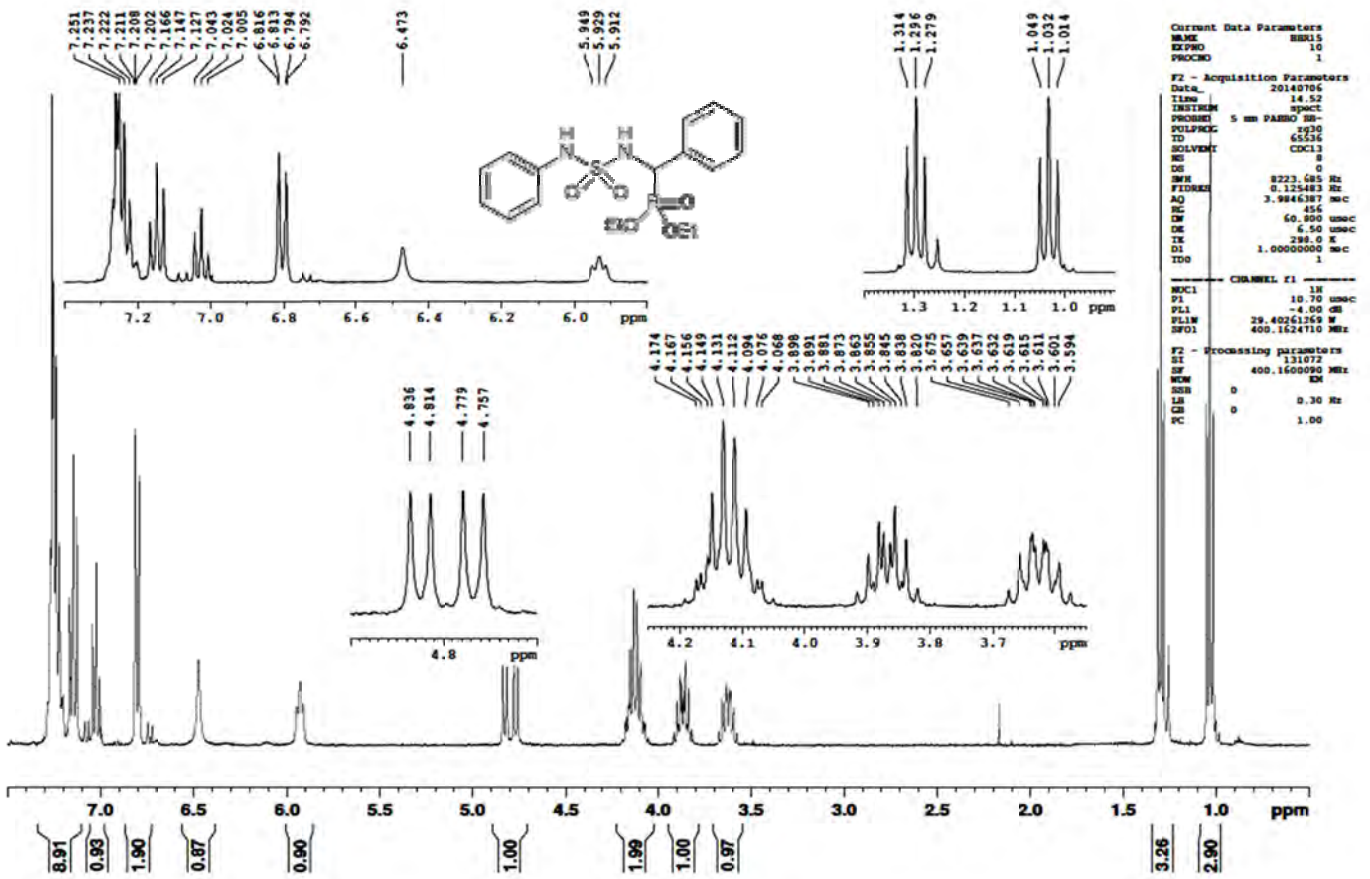
diethyl phenyl(*N*-propylsulfamoylamino)methylphosphonate (Table 1, Entry 2n)

White powder. mp = 136-138 °C. Yield 88%. R_f (DCM-MeOH : 95/5) = 0.41. Ms (m/z): 366 [M+1]. ν_{\max} (KBr)/ cm^{-1} 3265, 2978, 1593, 1372, 1264, 1154, 1077. δ_{P} (120 MHz, CDCl_3) 19.88. δ_{H} (300 MHz, CDCl_3) 0.72 (t, J 7.3 Hz, 3H, CH_3), 1.09 (t, J 7.1 Hz, 3H, CH_3), 1.14–1.29 (m, 2H, CH_2), 1.37 (t, J 7.1 Hz, 3H, CH_3), 2.54 (m, 1H, $\text{CH}_2\text{-N}$), 2.82 (m, 1H, $\text{CH}_2\text{-N}$), 3.67–3.76 (m, 1H, CH_2), 3.89–3.97 (m, 1H, CH_2), 4.07 (t, J 6 Hz, 1H, NH), 4.18–4.27 (m, 2H, CH_2), 4.75 (dd, J 8.8 Hz, 1H, CH), 6.03 (t, J 6.6 Hz, 1H, NH), 7.28–7.52 (m, 5H, H-Ar). δ_{C} (75 MHz, CDCl_3) 11.1, 16.3, 16.4, 21.7, 24.5, 55.4, 66.2, 66.3, 124.6, 127.1, 127.3, 129, 129.2, 137.1. Anal. Calc. for $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_5\text{PS}$: C 46.14, H 6.92, N 7.69. Found: C 46.10, H 7.08, N 7.55%. $M=365$.

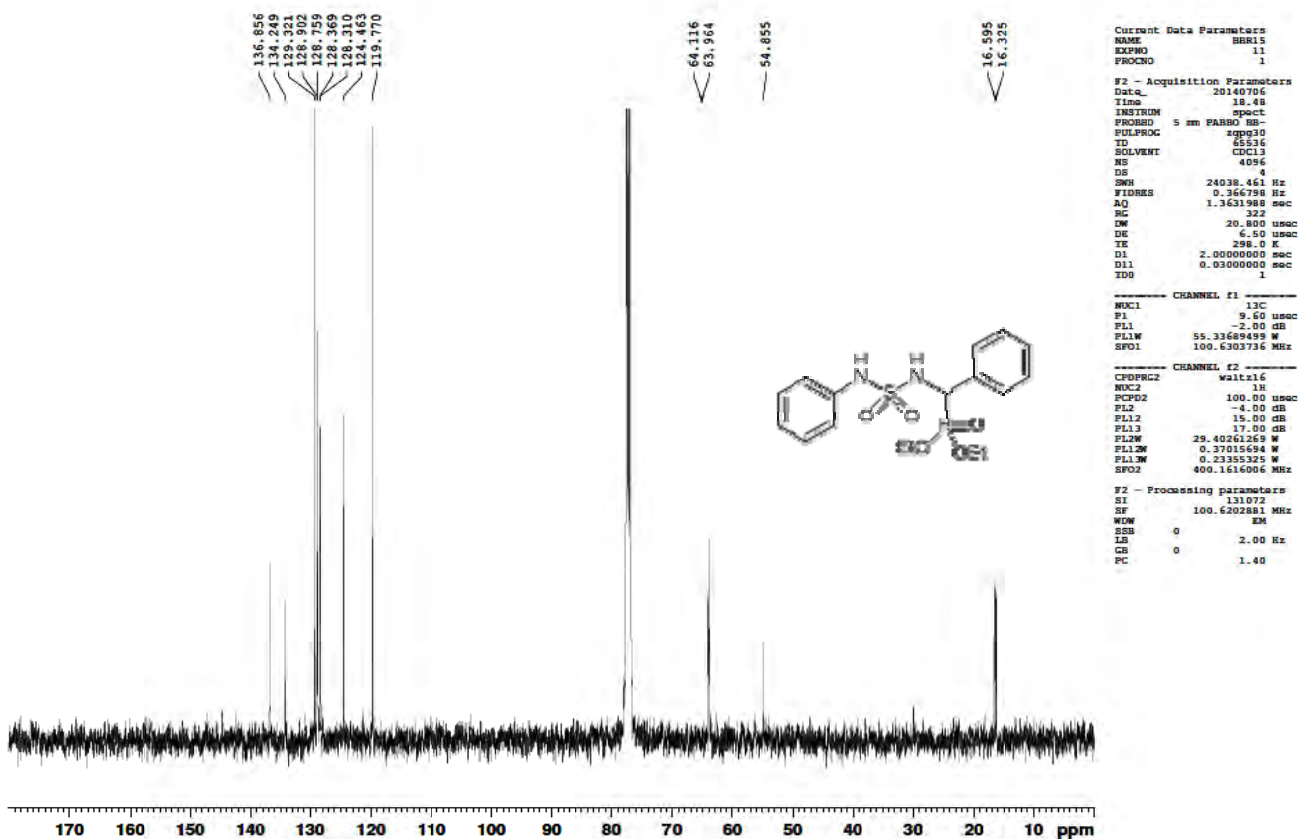


dimethyl (*N*-cyclohexylsulfamoylamino)(phenyl)methylphosphonate (Table 1, Entry 2q)

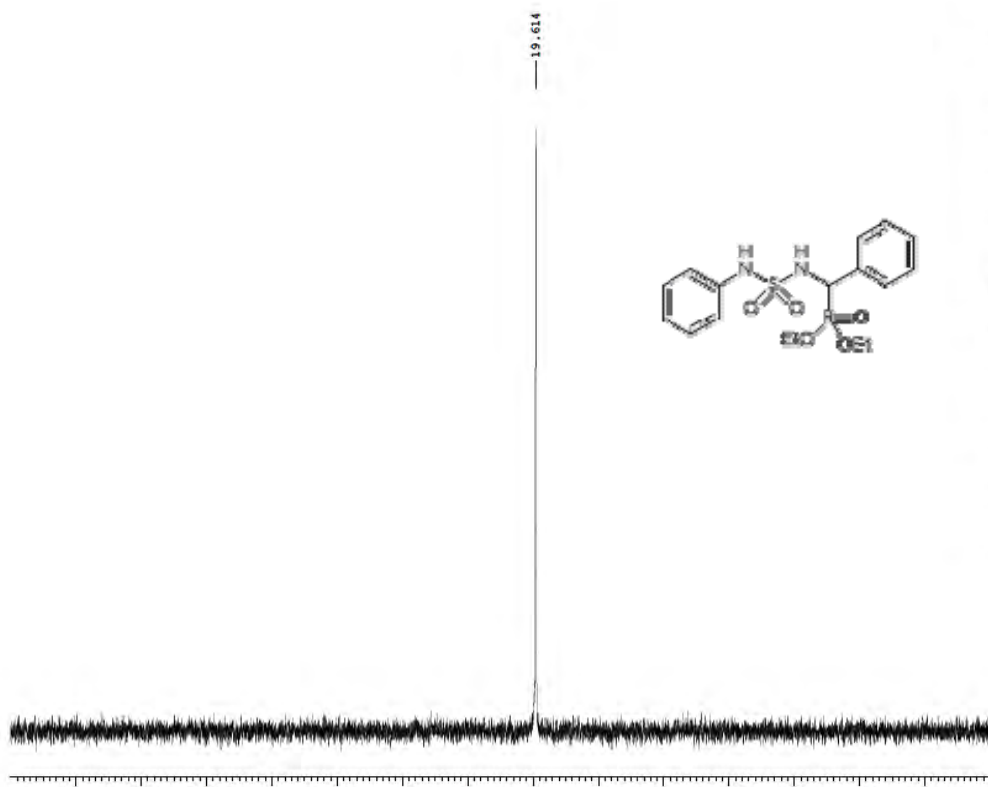
White crystal. mp = 137-139 °C. Yield 94%. R_f (DCM-MeOH : 95/5) = 0.39. Ms (m/z): 399 [M+23]. ν_{\max} (KBr)/ cm^{-1} 3468, 3065, 1631, 1368, 1259, 1152, 1100. δ_p (120 MHz, CDCl_3) 19.98. δ_H (300 MHz, CDCl_3) 0.9 (m, 4H, 2CH₂), 1.1 (m, 2H, CH₂), 1.39 (m, 2H, CH₂), 1.55 (m, 1H, CH₂), 1.84 (m, 1H, CH₂), 2.45 (m, 1H, CH), 3.47 (d, J 9 Hz, 3H, CH₃), 3.67 (d, J 7.2 Hz, 3H, CH₃), 4.61 (dd, J 6.8 Hz, 1H, CH), 6.72 (d, J 6.5 Hz, 1H, NH), 7.27-7.51 (m, 5H, H-Ar). δ_c (75 MHz, CDCl_3) 21.5, 24.6, 25.1, 33.9, 53.4, 53.5, 56.1, 126.2, 129.5, 129.8, 136.5. Anal. Calc. for C₁₅H₂₅N₂O₃PS: C 47.86, H 6.69, N 7.44. Found: C 48.03, H 6.65, N 7.40%. M=376.



¹H NMR spectrum: diethyl phenyl(*N*-phenylsulfamoylamino)methylphosphonate



¹³C NMR spectrum: diethyl phenyl(*N*-phenylsulfamoylamino)methylphosphonate



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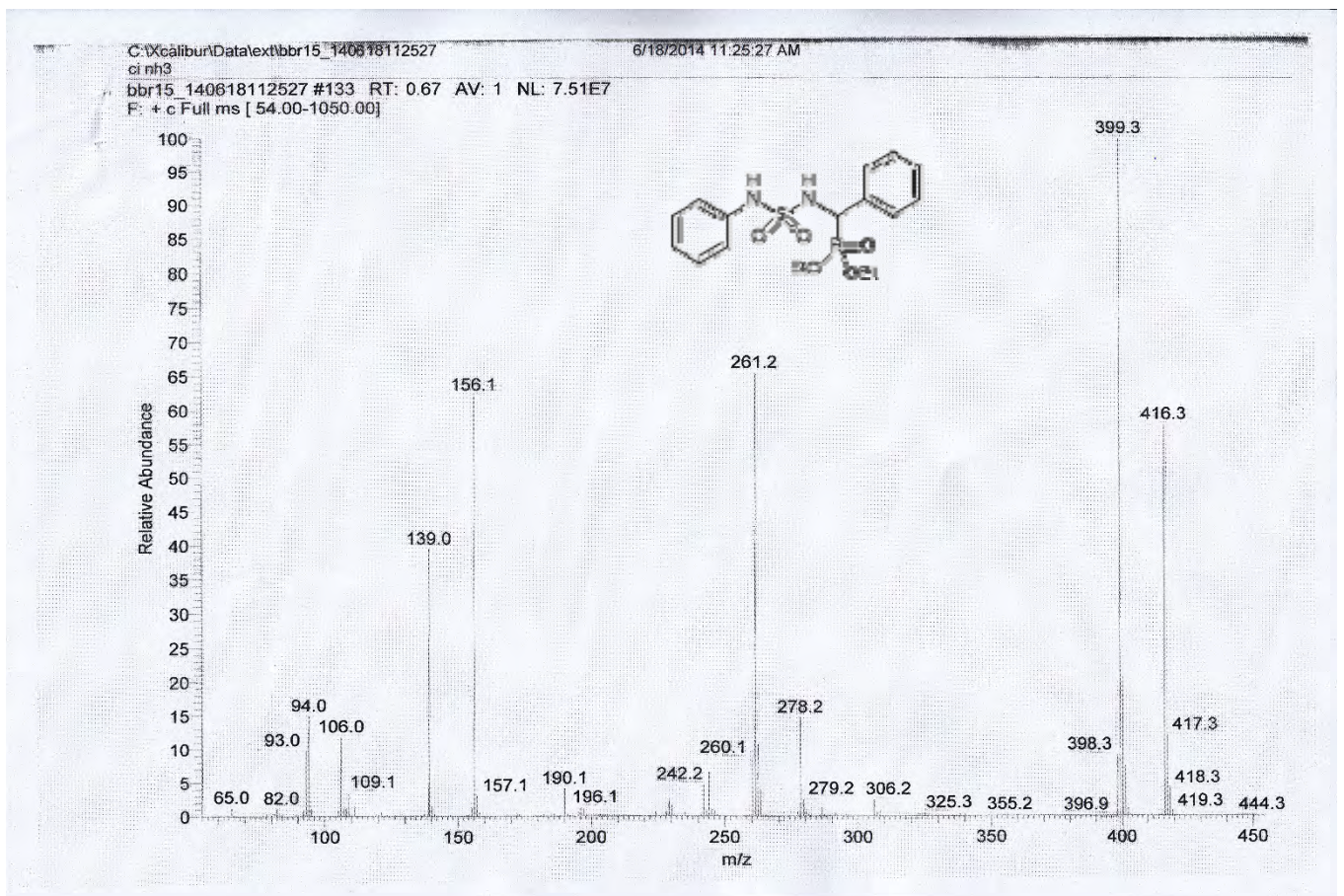
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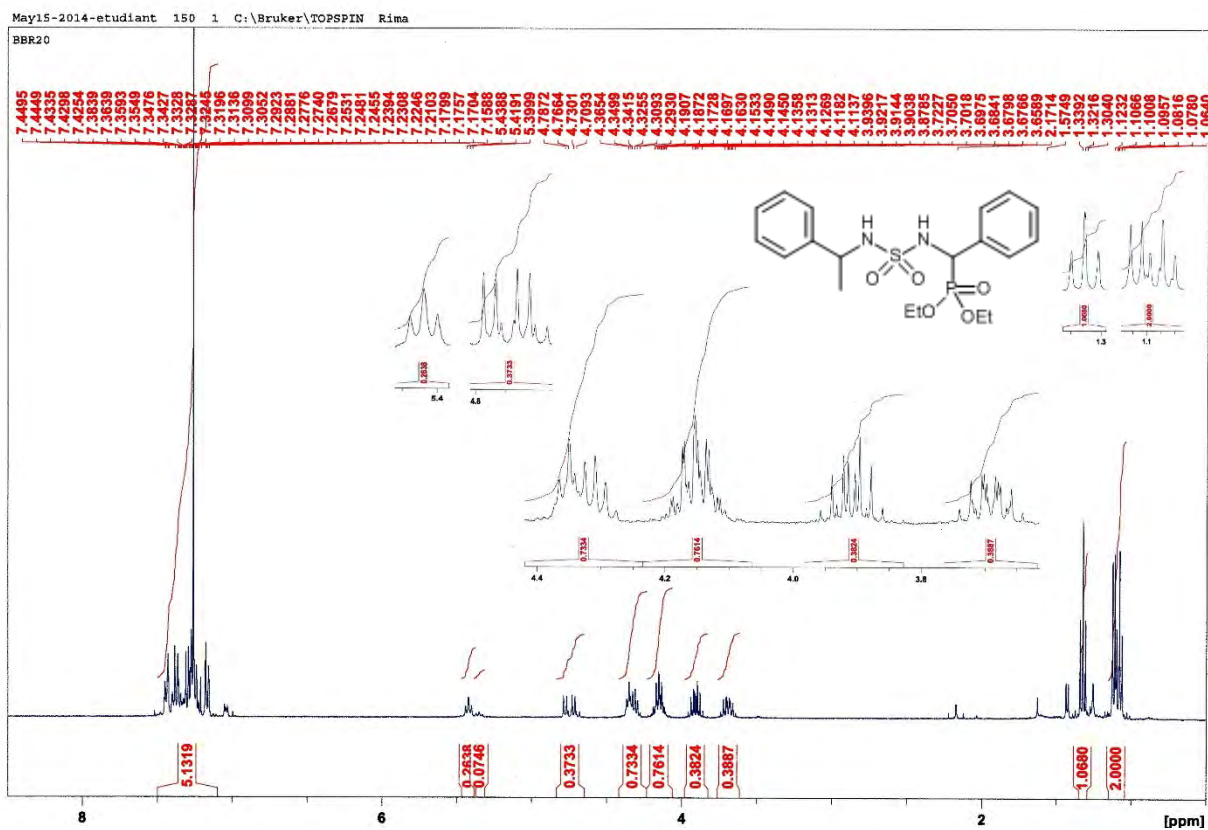
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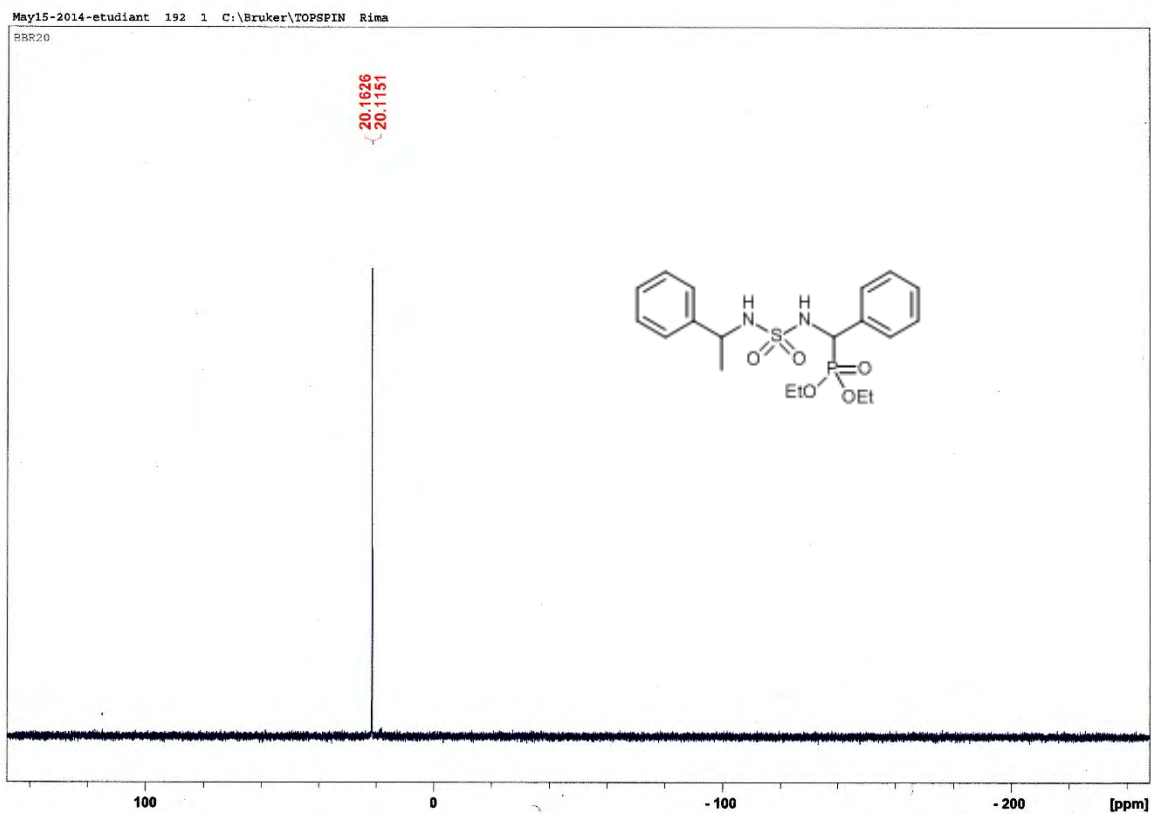
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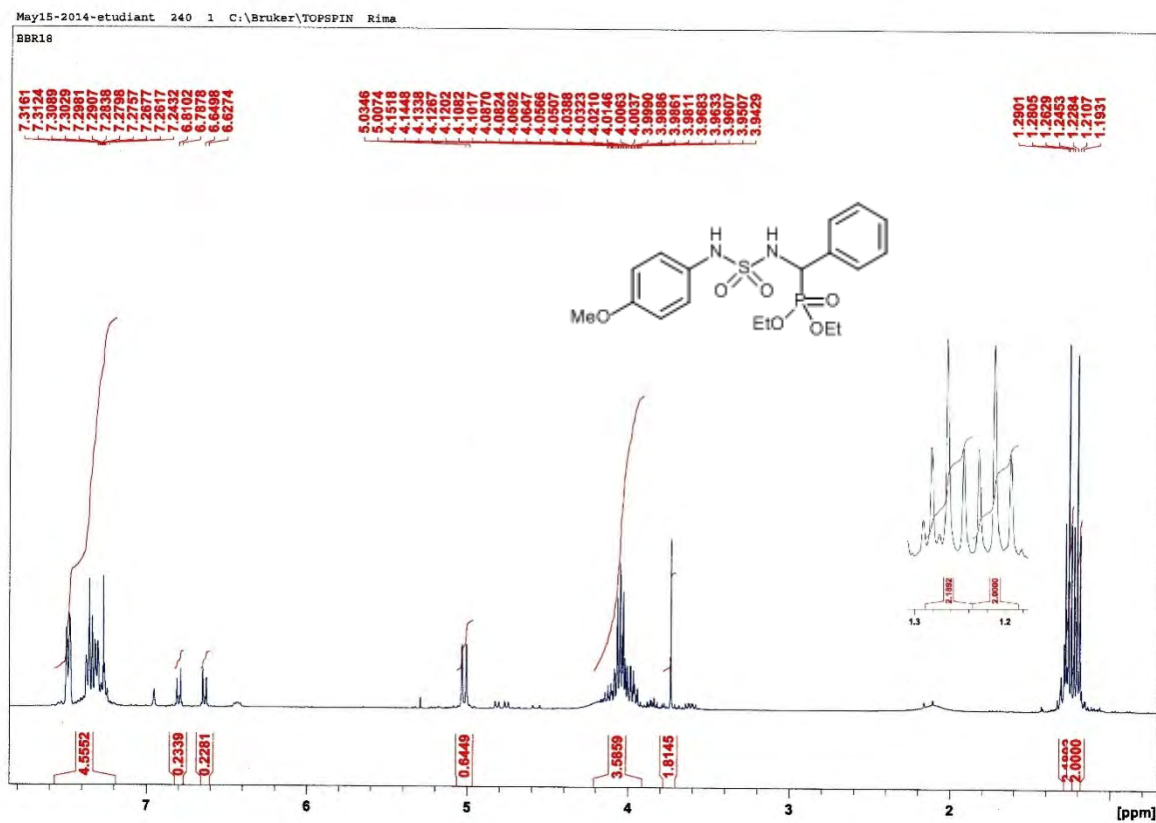




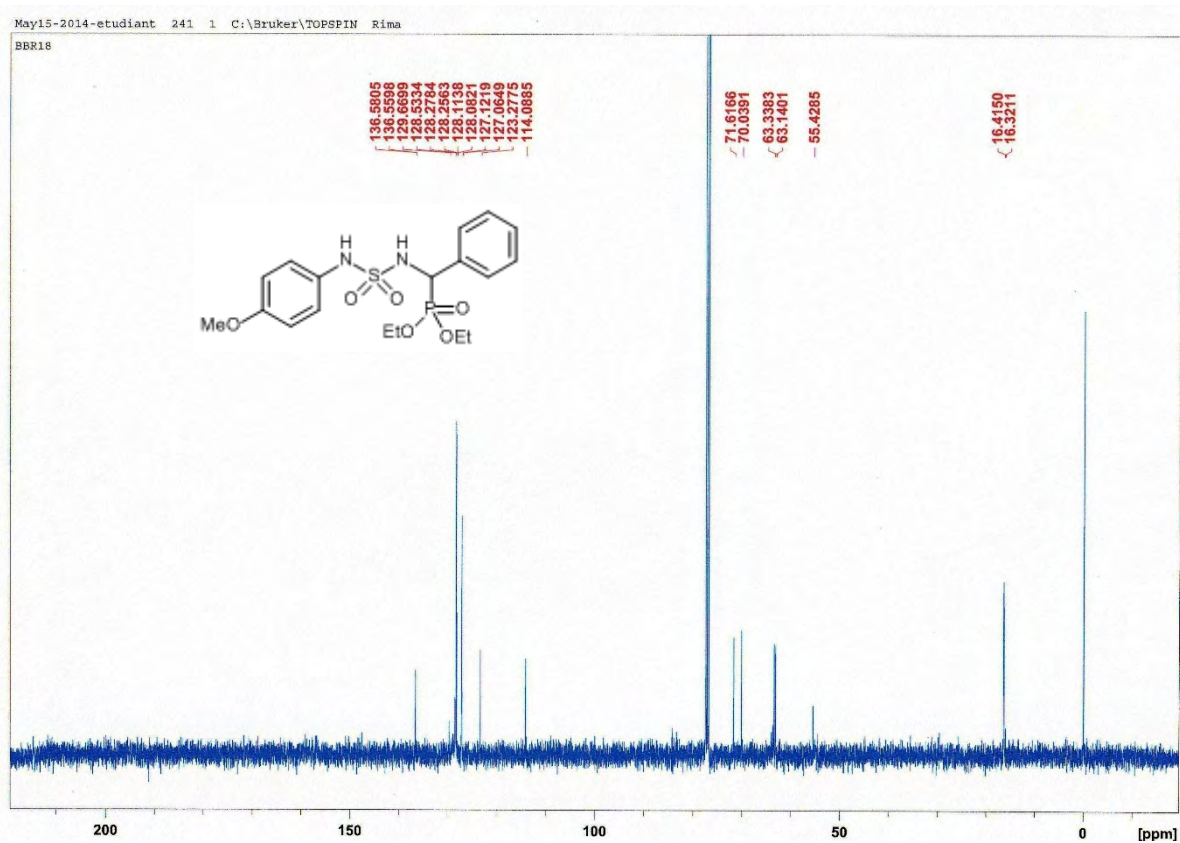
¹H NMR spectrum: diethyl phenyl(*N*-(1-phenylethyl)sulfamoylamino)methylphosphonate



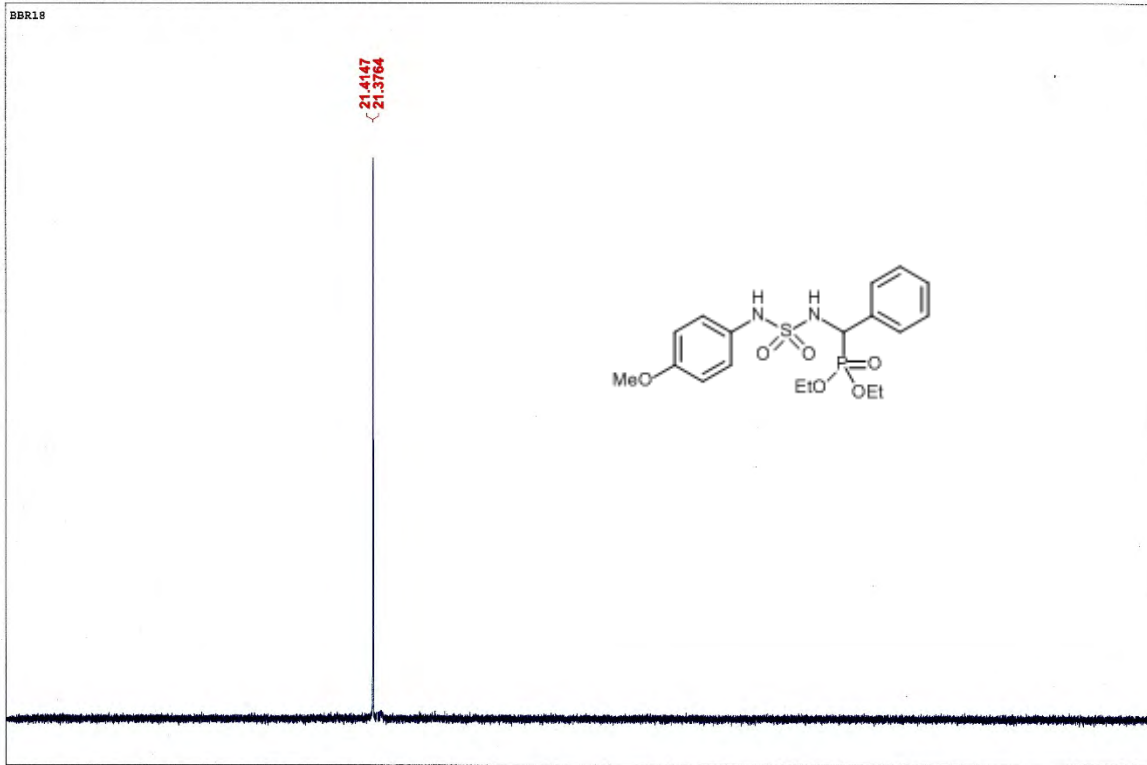
³¹P NMR spectrum: diethyl phenyl(*N*-(1-phenylethyl)sulfamoylamino)methylphosphonate



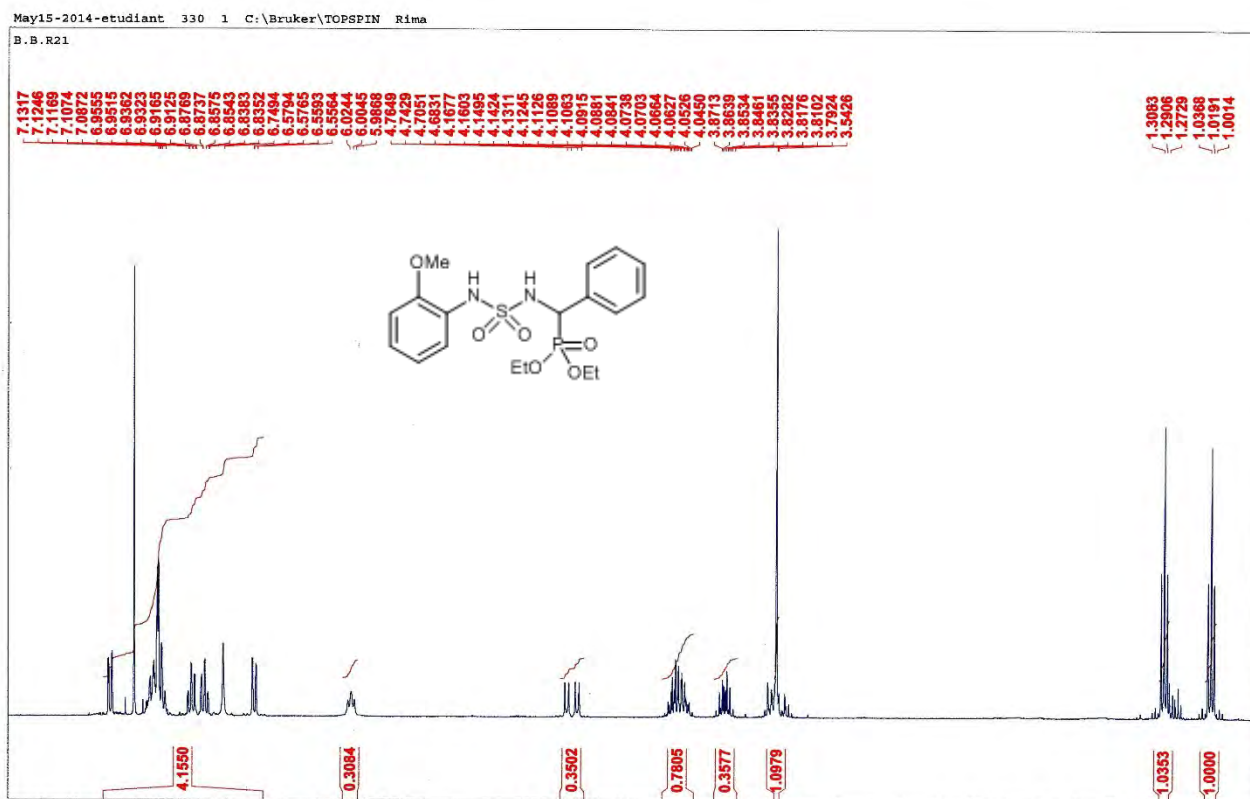
¹H NMR spectrum: diethyl (*N*-(4-methoxyphenyl)sulfamoylamino)(phenyl)methylphosphonate



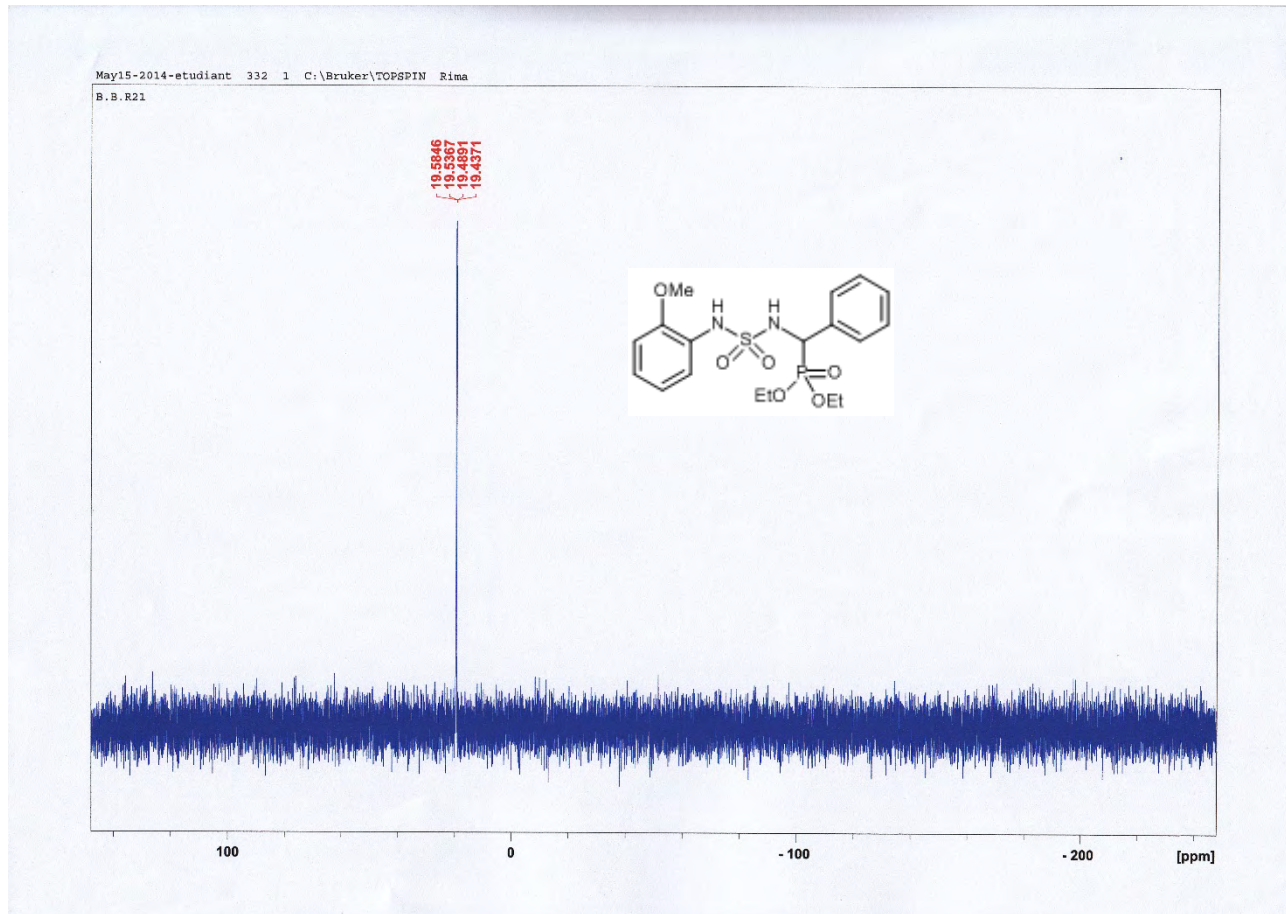
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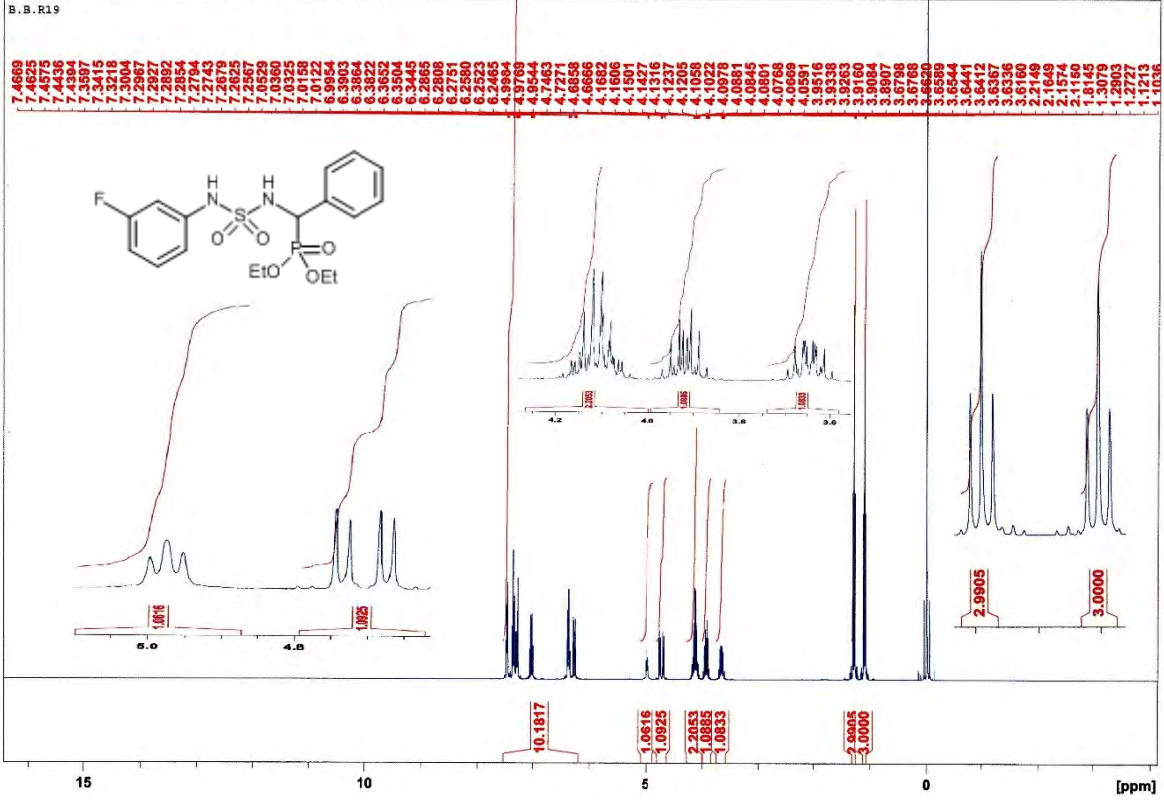
^{31}P NMR spectrum: diethyl (N-(4-methoxyphenyl)sulfamoylamino)(phenyl)methylphosphonate



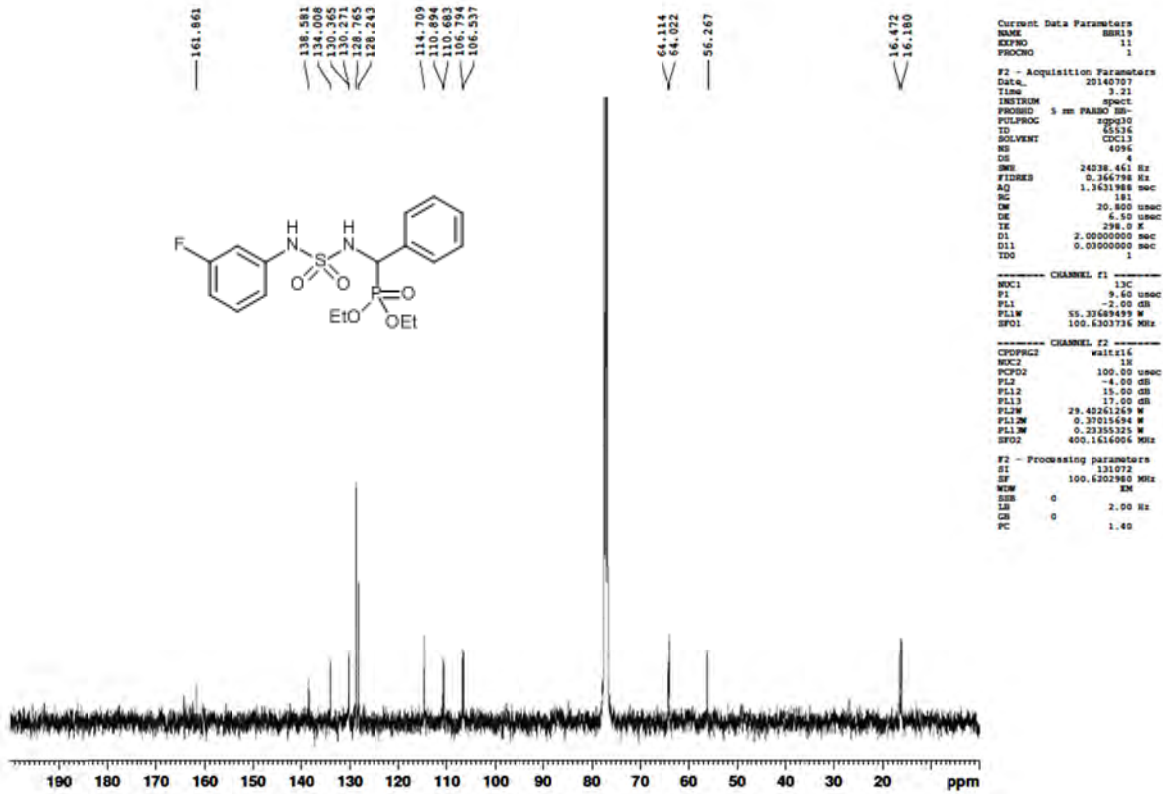
¹H NMR spectrum: diethyl (*N*-(2-methoxyphenyl)sulfamoylamino)(phenyl)methylphosphonate



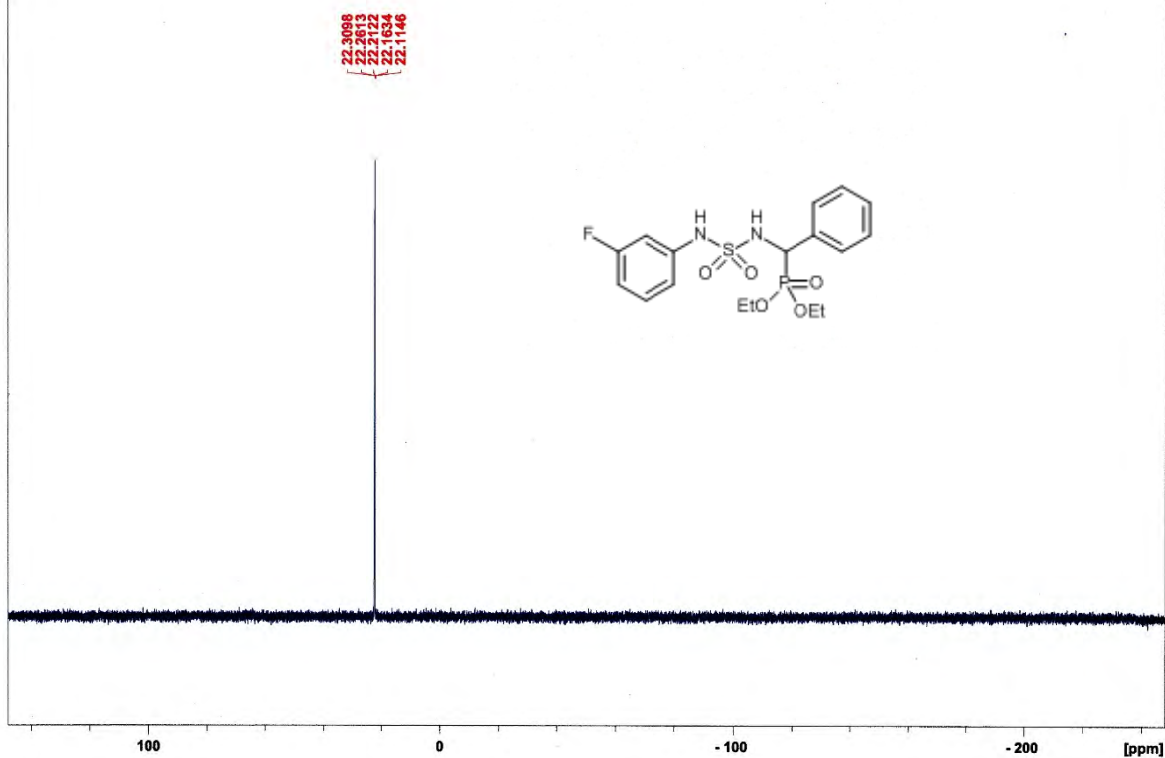
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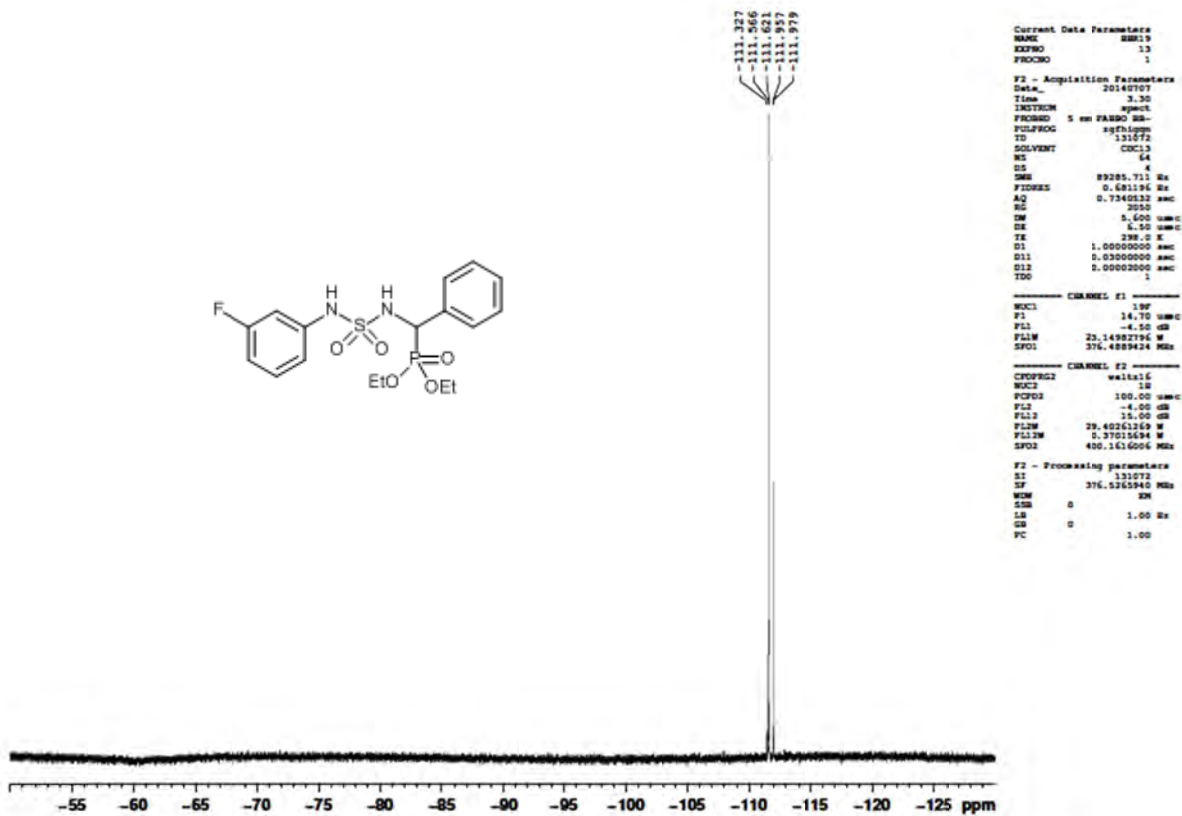
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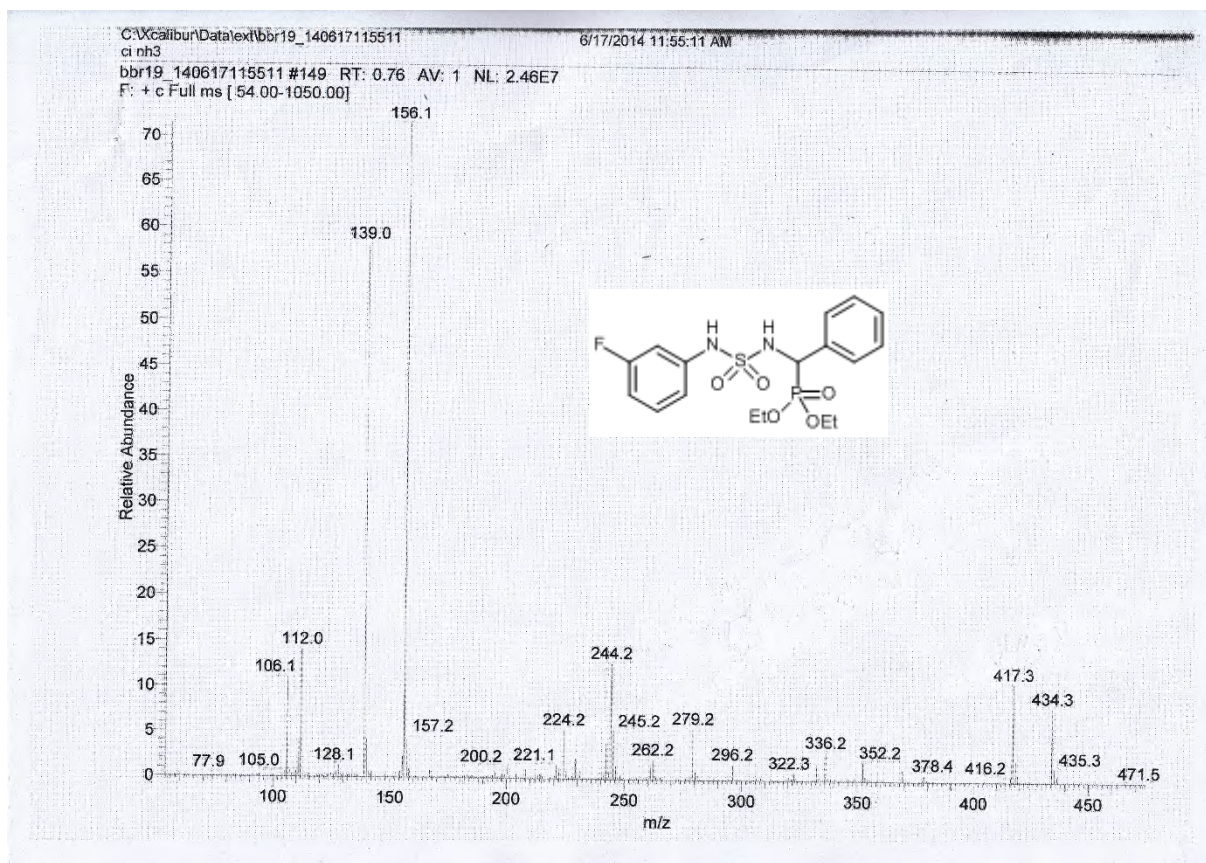
¹³C NMR spectrum: diethyl (N-(3-fluorophenyl)sulfamoylamino)(phenyl)methylphosphonate



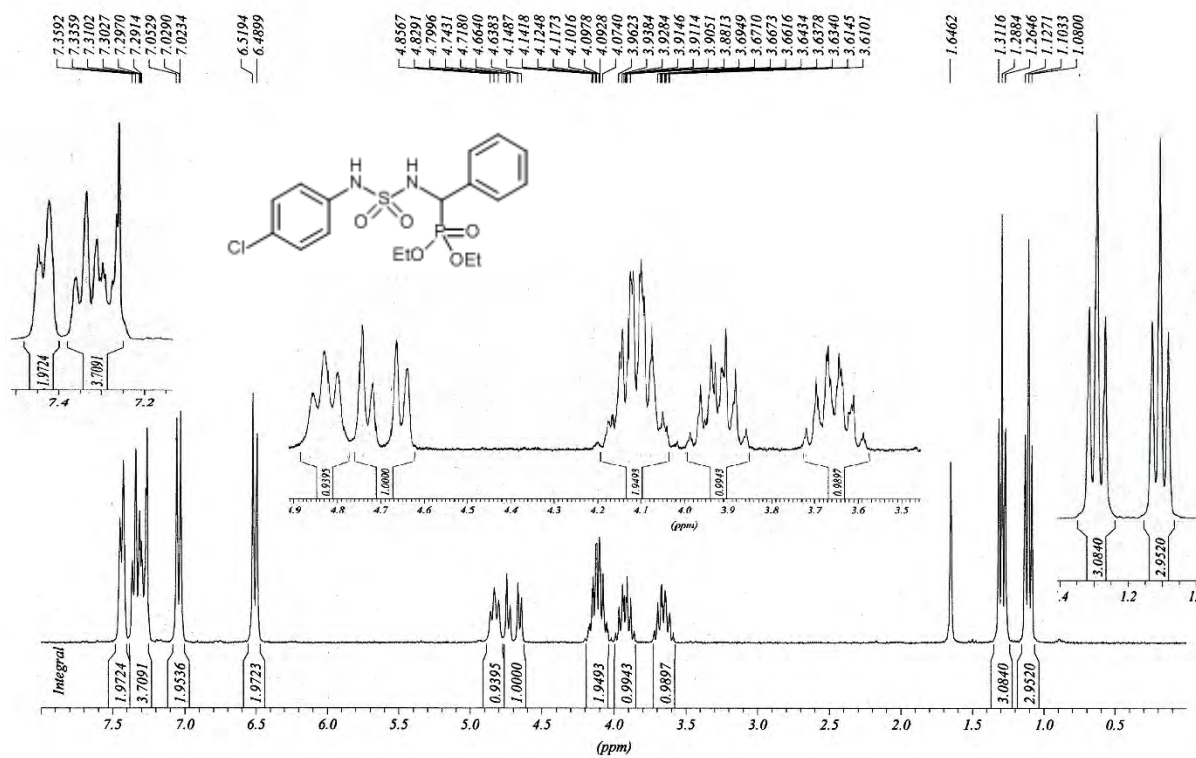
³¹P NMR spectrum: diethyl (*N*-(3-fluorophenyl)sulfamoylamino)(phenyl)methylphosphonate



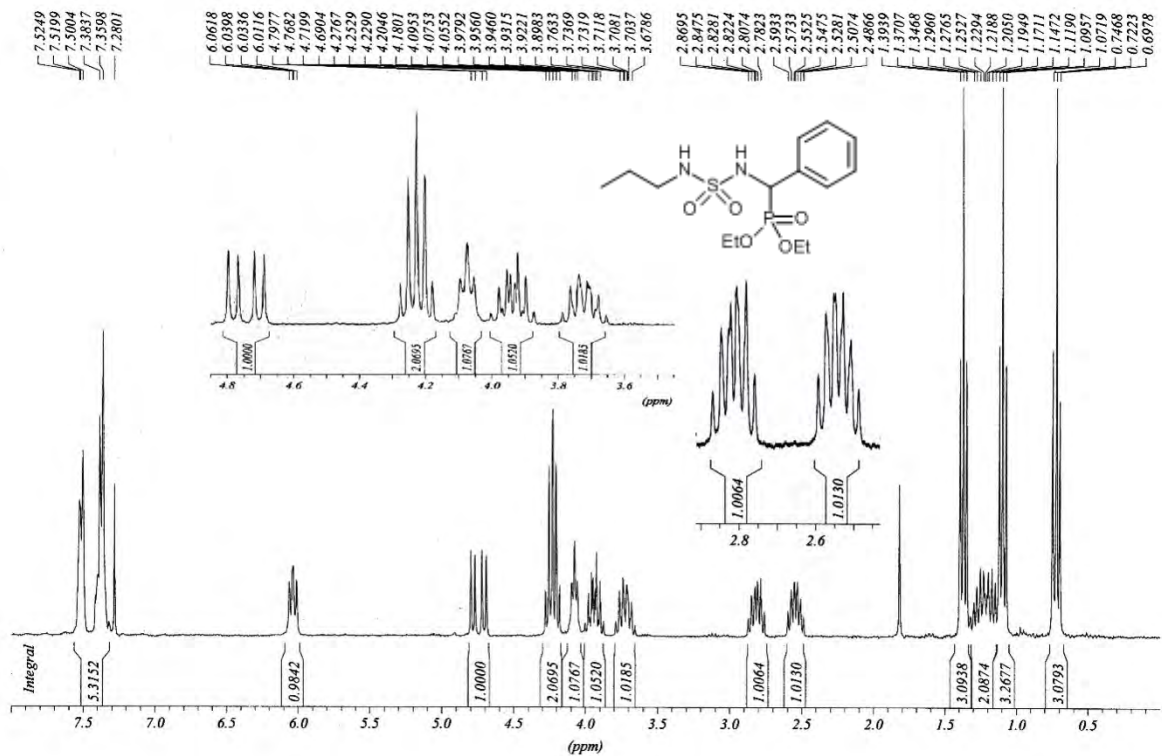
¹⁹F NMR spectrum: diethyl (*N*-(3-fluorophenyl)sulfamoylamino)(phenyl)methylphosphonate



Mass spectrum: diethyl (N-(3-fluorophenyl)sulfamoylamino)(phenyl)methylphosphonate

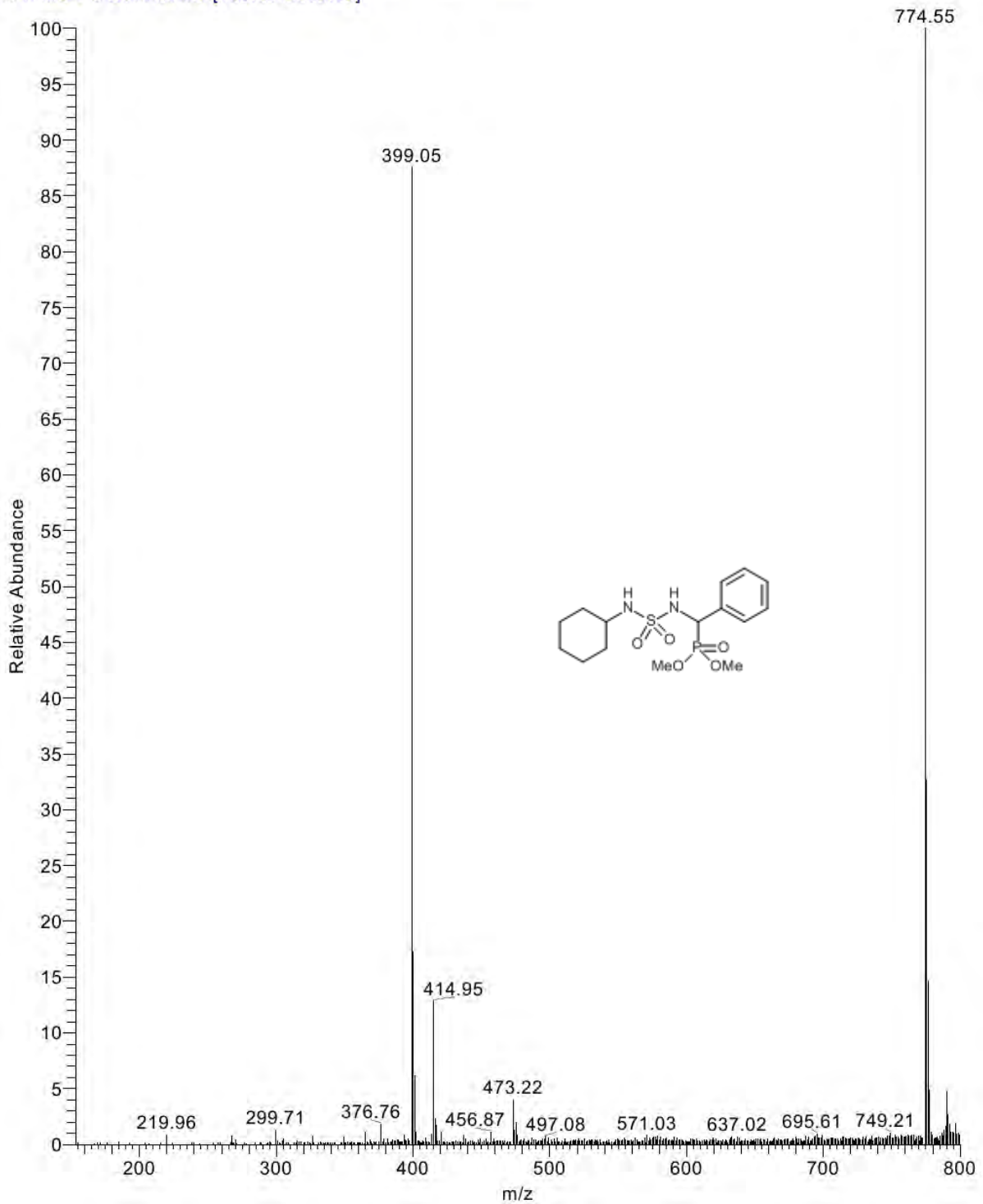


¹H NMR spectrum: diethyl (N-(4-chlorophenyl)sulfamoylamino)(phenyl)methylphosphonate

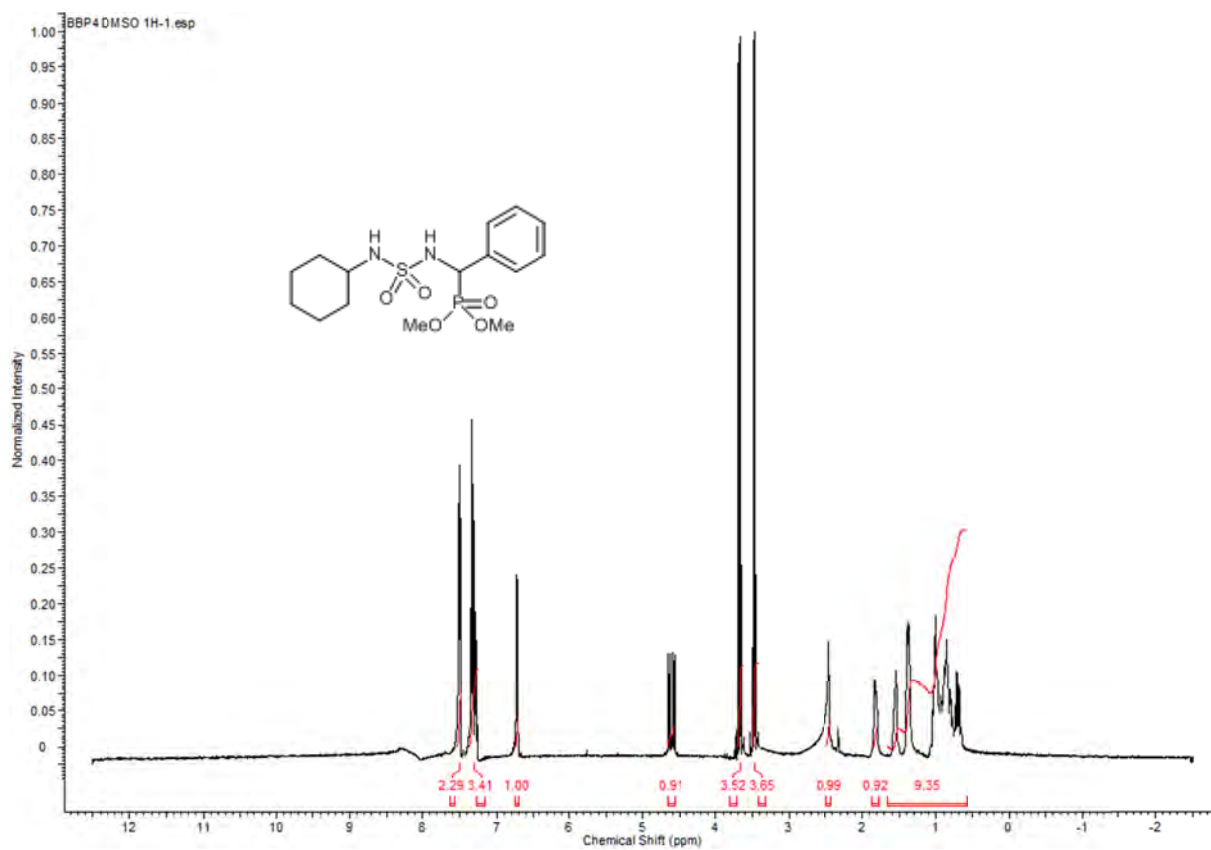


¹H NMR spectrum: diethyl phenyl(N-propylsulfamoylamino)methylphosphonate

BPP4 ESI+ 140328162401 #1 RT: 0.00 AV: 1 NL: 1.32E5
T: ITMS + c ESI Full ms [150.00-2000.00]



Mass spectrum: dimethyl (N-cyclohexylsulfamoylamino)(phenyl)methylphosphonate



¹H NMR spectrum: dimethyl (N-cyclohexylsulfamoylamino)(phenyl)methylphosphonate