

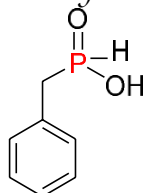
Supplementary Materials

General Information

^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a 400.13, 100.61, and 161.98 MHz instrument, respectively, equipped with an inverse gradient 5 mm probe in CDCl_3 or DMSO. The ^1H NMR chemical shifts are expressed with respect to residual protonated CDCl_3 (7.27 ppm), which served as an internal standard. The ^{13}C NMR shifts are expressed with respect to the CDCl_3 (77.0 ppm). The 85% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$ was used as external standard for ^{31}P NMR. The assignment of signals in the ^1H NMR spectrum was made using 2D COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on 2D ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments. Coupling constants (J) were measured from one-dimensional spectra, and multiplicities were abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), and m (multiplet). IR spectra were recorded on a two-beam Bruker Vertex 70 spectrometer, in a microlayer from chloroform. The C, H microanalyses were performed on a Flash EA 1112 SHNS-O/MAS analyzer. Melting points were established using a Kofler micro hot-stage apparatus (Wagner & Munz GmbH, Germany). Commercially available red phosphorus (KSAN Sia, China) was purified by consecutive washing with aq. NaOH (1-2%), H_2O , EtOH, and Et $_2\text{O}$ to remove all acidic impurities, dried in vacuum at 25-30 °C to constant weight and stored under inert atmosphere (N_2). Usual commercial toluene, KOH·0.5 H_2O (~15% water), catalysts and arylmethyl halogenides were used without further purification. The 4-Methoxybenzylchloride, 3-acylbenzylchloride, and 2-thienylmethylchloride were prepared according to the reported procedures [1-3], correspondingly. All reagents were commercially available.

Experimental Procedures, Spectral and Analytical data

Benzyl-H-phosphinic acid (2a)



A mixture of P_{red} (3.10 g, 0.1 mol), KOH·0.5 H_2O (20.00 g), H_2O (10.9 mL), Triton-X-100 (0.31 g), and (1-chloromethyl)benzene (**1a**, 2.50 g, 20 mmol) in 60 mL of toluene was stirred (700-800 rpm) at 90-95 °C for 3 h under argon atmosphere. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was thoroughly separated, washed by DCM (3×10 mL), acidified with hydrochloric acid (35%) to pH 2–3, extracted with chloroform (3×30 mL), dried with Na_2SO_4 , and the solvent was distilled off. The residue was dried in vacuum to give **2a** (2.02 g, 65%) as pale yellow oil.

IR (film): 3085, 3062, 3030, 3007, 2912, 2850, 2630, 2368, 2189, 1960, 1880, 1659, 1601, 1496, 1454, 1401, 1240, 1200, 1170, 1124, 1070, 986, 821, 779, 720, 698, 598, 481, 443 cm^{-1} .

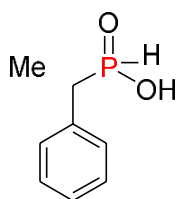
^1H NMR (400.13 MHz, CDCl_3): 3.12 (d, $^2J_{\text{PH}} = 18.7$ Hz, 2H, PCH_2), 6.94 (d, $^1J_{\text{PH}} = 560.3$ Hz, 1H, PH), 7.22-7.24 (m, 2H H_o from Ph), 7.27-7.28 (m, 1H, H_p from Ph), 7.30-7.34 (m, 2H H_m from Ph), 12.69 (brs, 1H, OH) ppm.

^{13}C NMR (100.62 MHz, CDCl_3): 36.97 (d, $^1J_{\text{PC}} = 88.7$ Hz, PCH_2), 127.01 (d, $^5J_{\text{PC}} = 3.8$ Hz, C_p from Ph), 129.68 (d, $^3J_{\text{PC}} = 6.3$ Hz, C_o from Ph), 128.65 (d, $^4J_{\text{PC}} = 3.2$ Hz, C_m from Ph), 129.90 (d, $^3J_{\text{PC}} = 6.0$ Hz, C_i from Ph) ppm.

^{31}P NMR (161.98 MHz, CDCl_3): 34.25 (d, $^1J_{\text{PH}} = 558.9$ Hz) ppm.

Elemental analysis for $\text{C}_7\text{H}_9\text{O}_2\text{P}$ (156.12): calcd. C, 53.85; H, 5.81; found: C, 53.82; H, 5.80.

1-Phenylethyl-H-phosphinic acid (**2b**).



A mixture of P_{red} (3.10 g, 0.1 mol), KOH·0.5H₂O (20.00 g), H₂O (4.5 mL), Triton- X-100 (0.63 g), and (1-chloroethyl)benzene (**1c**) (1.4 g, 10 mmol) in 40 mL of toluene was stirred (700-800 rpm) at 82-85 °C for 3 h under argon atmosphere. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was thoroughly separated, washed by DCM (3×10 mL), acidified with hydrochloric acid to pH 2–3, extracted with chloroform (3×30 mL), dried with Na₂SO₄, the solvent was distilled off, and the residue was dried in vacuum to give **2b** (0.83 g, 49%) as a pale yellow oil.

IR (film): 3061, 3030, 2974, 2932, 2878, 2852, 2365, 2164, 1959, 1716, 1704, 1651, 1602, 1562, 1543, 1494, 1455, 1378, 1340, 1317, 1227, 1194, 1168, 1064, 967, 794, 766, 699, 602, 506 cm⁻¹.

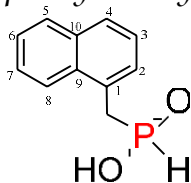
¹H NMR (400.13 MHz, CDCl₃): 1.53 (dd, ³J_{HH} = 7.4 Hz, ³J_{PH} = 18.9 Hz, 3H, CH₃CH), 3.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{PH} = 17.5 Hz, 1H, PCH), 6.80 (d, ¹J_{PH} = 552.8 Hz, 1H, PH), 7.24-7.27 (m, 3H H_{o,p} from Ph), 7.31-7.35 (m, 2H, H_m from Ph), 11.22 (brs, 1H, OH) ppm.

¹³C NMR (100.62 MHz, CDCl₃): 12.33 (d, ²J_{PC} = 2.0 Hz, CH₃), 40.50 (d, ¹J_{PC} = 89.3 Hz, PCH), 127.38 (d, ⁵J_{PC} = 3.4 Hz, C_p from Ph), 128.63 (d, ³J_{PC} = 6.3 Hz, C_o from Ph), 128.73 (d, ⁴J_{PC} = 2.8 Hz, C_m from Ph), 135.91 (d, ²J_{PC} = 5.0 Hz, C_i from Ph) ppm.

³¹P NMR (161.98 MHz, CDCl₃): 41.42 (d, ¹J_{PH} = 552.6 Hz) ppm.

Elemental analysis for C₈H₁₁O₂P (170.15): calcd. C, 56.47; H, 6.52; found: C, 56.43; H, 6.51.

1-Naphthylmethyl-H-phosphinic acid (**2c**)



A mixture of P_{red} (3.10 g, 0.1 mol), KOH·0.5H₂O (20.00 g), H₂O (10.9 mL), Triton-X-100 (0.31 g), and (1-chloromethyl)naphthalene (**1d**) (0.88 g, 5 mmol) in 40 mL of toluene was stirred (700-800 rpm) at 82-85 °C for 3 h under argon atmosphere. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was thoroughly separated, washed by DCM (3×10 mL), acidified with hydrochloric acid to pH 4–5, extracted with chloroform (3×30 mL), and dried with Na₂SO₄. The solvent was distilled off and the residue was dried in a vacuum to give **2c** (0.52 g, 50%) as light beige powder, mp 117-119 °C.

IR (KBr): 3444, 3045, 3013, 2952, 2917, 2851, 2628, 2370, 2308, 2158, 1685, 1595, 1510, 1396, 1350, 1270, 1255, 1238, 1130, 1018, 979, 960, 798, 775, 590, 445 cm⁻¹.

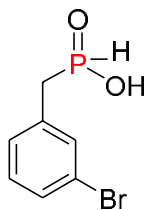
¹H NMR (400.13 MHz, DMSO-d₆): 3.60 (d, ²J_{PH} = 18.8 Hz, 2H, PCH₂), 7.02 (d, ¹J_{PH} = 532.1 Hz, 1H, PH), 7.45-7.48 (m, 2H, H-2,6 from Naph), 7.51-7.57 (m, 2H, H-3,7 from Naph), 7.83 (d, ³J_{HH} = 7.6 Hz, 1H, H-5 from Naph), 7.92 (d, ³J_{HH} = 7.6 Hz, 1H, H-4 from Naph), 8.13 (d, ³J_{HH} = 7.8 Hz, 1H, H-8 from Naph) ppm.

¹³C NMR (100.62 MHz, DMSO-d₆): 35.06 (d, ¹J_{PC} = 85.7 Hz, PCH₂), 124.69 (C-8), 125.59 (d, ⁶J_{PC} = 3.1 Hz, C-6), 125.81 (C-3), 126.06 (C-7), 127.13 (d, ⁵J_{PC} = 3.1 Hz, C-5), 128.16 (d, ³J_{PC} = 7.2 Hz, C-2), 128.41 (C-4), 128.76 (d, ³J_{PC} = 7.9 Hz, C-9), 131.91 (d, ²J_{PC} = 4.0 Hz, C-1), 133.54 (C-10) ppm.

³¹P NMR (161.98 MHz, DMSO-d₆): 28.10 (d, ¹J_{PH} = 534.0 Hz) ppm.

Elemental analysis for C₁₁H₁₁O₂P (206.18): calcd. C, 64.08; H, 5.38; found: C, 64.04; H, 5.37.

3-Bromobenzyl-*H*-phosphinic acid (**2d**)



A mixture of P_{red} (3.10 g, 0.1 mol), $KOH \cdot 0.5 H_2O$ (20.00 g), H_2O (10.9 mL), Triton-X-100 (0.63 g), and 1-bromo-3-(bromomethyl)benzene (**1e**) (2.50 g, 10 mmol) in 40 mL of toluene was stirred (700-800 rpm) at 75 °C for 3 h under argon atmosphere. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was thoroughly separated, washed by DCM (3×10 mL), acidified with hydrochloric acid to pH 4–5, extracted with chloroform (3×30 mL) and dried with Na_2SO_4 . The solvent was distilled off and the residue was dried in avacuum, obtaining **2d** (0.82 g, 35%) of light beige powder, mp 105-107 °C.

IR (KBr): 3442, 3057, 2954, 2907, 2648, 2366, 2260, 2144, 1868, 1659, 1597, 1569, 1473, 1426, 1402, 1256, 1209, 1183, 1134, 1102, 1074, 999, 983, 966, 892, 853, 816, 786, 689, 668, 518, 449 cm^{-1} .

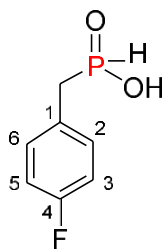
1H NMR (400.13 MHz, $CDCl_3$): 3.09 (d, $^2J_{PH} = 18.3$ Hz, 2H, PCH_2), 6.98 (d, $^1J_{PH} = 563.9$ Hz, 1H, PH), 7.16-7.20 (m, 1H, H-6 from C_6H_4), 7.21 (t, $^3J_{5,6} \sim ^3J_{5,4} = 7.6$ Hz, 1H, H-5 from C_6H_4), 7.40-7.42 (m, 2H, H-2,4 from C_6H_4), 10.99 (brs, 1H, OH) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): 37.04 (d, $^1J_{PC} = 88.2$ Hz, PCH_2), 122.81 (d, $^4J_{PC} = 4.2$ Hz, C-3), 128.54 (d, $^3J_{PC} = 6.2$ Hz, C-6), 130.36 (d, $^4J_{PC} = 3.3$ Hz, C-5), 130.48 (t, $^5J_{PC} = 3.7$ Hz, C-4), 131.91 (d, $^2J_{PC} = 7.3$ Hz, C-1), 132.75 (d, $^3J_{PC} = 6.4$ Hz, C-2) ppm.

^{31}P NMR (161.98 MHz, $CDCl_3$): 34.96 (d, $^1J_{PH} = 566.4$ Hz) ppm.

Elemental analysis for $C_7H_8BrO_2P$ (235.02): calcd. C, 35.77; H, 3.43. found: C, 35.72; H, 3.41.

(4-fluorobenzyl)phosphinic acid (**2e**)



A mixture of P_{red} (3.10 g, 0.1 mol), KOH·0.5H₂O (20.00 g), H₂O (13 mL), Triton- X-100 (0.63 g), and 1-(chloromethyl)-4-fluorobenzene (**1f**) (1.44 g, 10 mmol) in 40 mL of toluene was stirred (700-800 rpm) at 75 °C for 3 h under argon atmosphere. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was thoroughly separated, washed by DCM (3×10 mL), acidified with hydrochloric acid to pH 4–5, extracted with chloroform (3×30 mL), dried with Na₂SO₄, the solvent was distilled off, and the residue was dried in a vacuum, obtaining **2e** (0.54 g, 31%) of light beige powder, mp 75-76 °C.

IR (KBr): 3426, 3051, 2903, 2661, 2624, 2421, 2283, 2166, 2044, 1900, 1684, 1605, 1512, 1418, 1399, 1309, 1260, 1228, 1207, 1183, 1159, 1127, 1089, 983, 839, 763, 748, 696, 534, 493, 449 cm⁻¹.

¹H NMR (400.13 MHz, CDCl₃): 3.09 (d, ²J_{PH} = 18.1 Hz, 2H, PCH₂), 6.94 (d, ¹J_{PH} = 560.2 Hz, 1H, PH), 7.01 (t, ³J_{HH} ~ ³J_{HF} = 8.5 Hz, 2H, H-3,5 from C₆H₄), 7.19-7.26 (m, 2H, H-2,6 from C₆H₄), 12.53 (brs, 1H, OH) ppm.

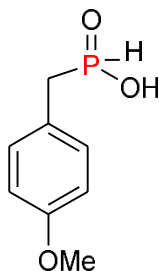
¹³C NMR (100.62 MHz, CDCl₃): 36.39 (d, ¹J_{PC} = 89.1 Hz, PCH₂), 115.72 (d, ²J_{FC} = 22.1 Hz, C-3,5), 125.38 (d, ²J_{PC} ~ ⁴J_{FC} = 4.3 Hz, C-1), 131.32 (d, ³J_{PC} ~ ³J_{FC} = 7.0 Hz, C-2,6), 162.08 (d, ¹J_{FC} = 246.4 Hz, C-4) ppm.

³¹P NMR (161.98 MHz, CDCl₃): 34.18 (dt, ¹J_{PH} = 560.4 Hz, ²J_{PH} = 18.0 Hz) ppm

¹⁹F NMR (376.5 MHz, CDCl₃): δ -114.9 ppm.

Elemental analysis for C₇H₈FO₂P (174.11): calcd. C, 48.29; H, 4.63; found: C, 48.26; H, 4.62.

4-Methoxybenzyl-H-phosphinic acid (**2f**)



To a mixture of P_{red} (1.03 g, 0.03 mol), KOH·0.5H₂O (9.16 g), H₂O (5 mL), Triton-X-100 (0.21 g), toluene (15 mL), and 1-(chloromethyl)-4-methoxybenzene (1.04 g, 6.67 mmol) in 5 mL of toluene was added dropwise (40 min) and stirred (700- 800 rpm) at 90-95 °C for 3 h. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was thoroughly separated, washed by DCM (3×5 mL), acidified with hydrochloric acid to pH 4–5, extracted with chloroform (3×20 mL), dried with Na₂SO₄, the solvent was distilled off, and the residue was dried in a vacuum, obtaining the (4-methoxybenzyl)-H-phosphinic acid (0.12 g, 10%) as white powder, mp 78-80 °C;

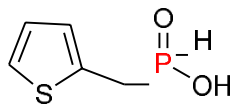
¹H NMR (400.13 MHz, CDCl₃): 2.92 (m, 2H, CH₂P), 3.68 (s, 3H, OMe), 6.76-7.09 (4H, C₆H₄), 7.27 (d, ¹J_{PH} = 564 Hz, 1H, PH).

³¹P NMR (161.98 MHz, CDCl₃): 35.1 (d, ¹J_{PH} = 564 Hz) ppm.

Elemental analysis for C₈H₁₁O₃P (186.15): calcd. C, 51.62; H, 5.96; found: C, 50.28; H, 6.10.

This is a known compound: see J.-L. Montchamp and Y. R. Dumond, J. Am. Chem. Soc., 2001, 123, 3, 510-511.

2-Thienylmethyl-*H*-phosphinic acid



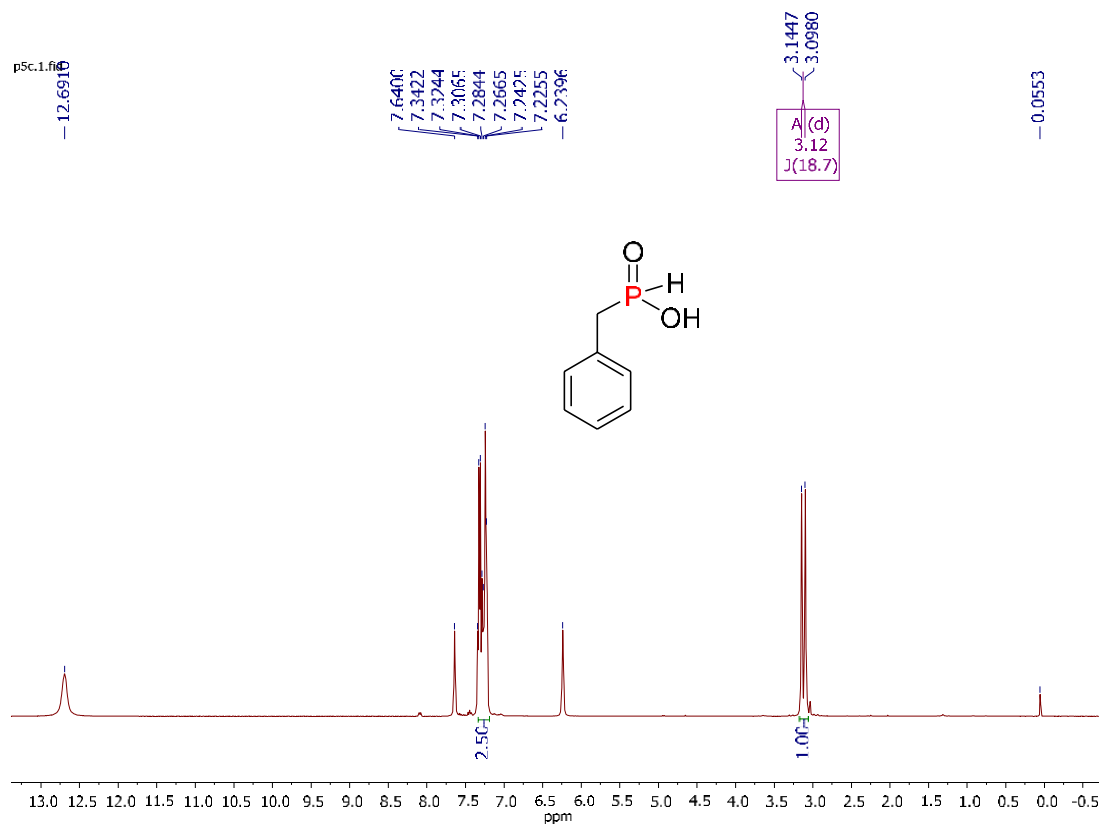
A mixture of P_{red} (3.1 g, 0.1 mol), $\text{KOH} \cdot 0.5\text{H}_2\text{O}$ (20 g), H_2O (10.9 mL), Triton-X- 100 (0.63 g), and 2-(chloromethyl)thiophene (1.3 g, 0.01 mol) in 40 mL of toluene was stirred at 82-83 °C for 3 h. The reaction mixture was cooled to r.t., diluted in two times with water, the aqueous alkaline fraction was separated, acidified with hydrochloric acid to pH 4–5, extracted with chloroform (3×30 mL), dried with Na_2SO_4 , the solvent was distilled off, and the residue was dried in a vacuum to give 2- thienylmethyl-*H*-phosphinic acid (0.10 g, 6%) as slightly yellow oil. From toluene phase, tris(2-thienylmethyl)phosphine oxide (0.45 g, 40%) was isolated as pale yellow oil.

^1H NMR (400.13 MHz, CDCl_3): 3.22 (d, $^2J_{\text{PH}} = 16.0$ Hz, 2H, PCH_2), 6.91-7.26 (m, 3H from thiophene), 6.88 (d, 1H, $^1J_{\text{PH}} = 563$ Hz, PH), 12.46 (m, 1H, OH) ppm.

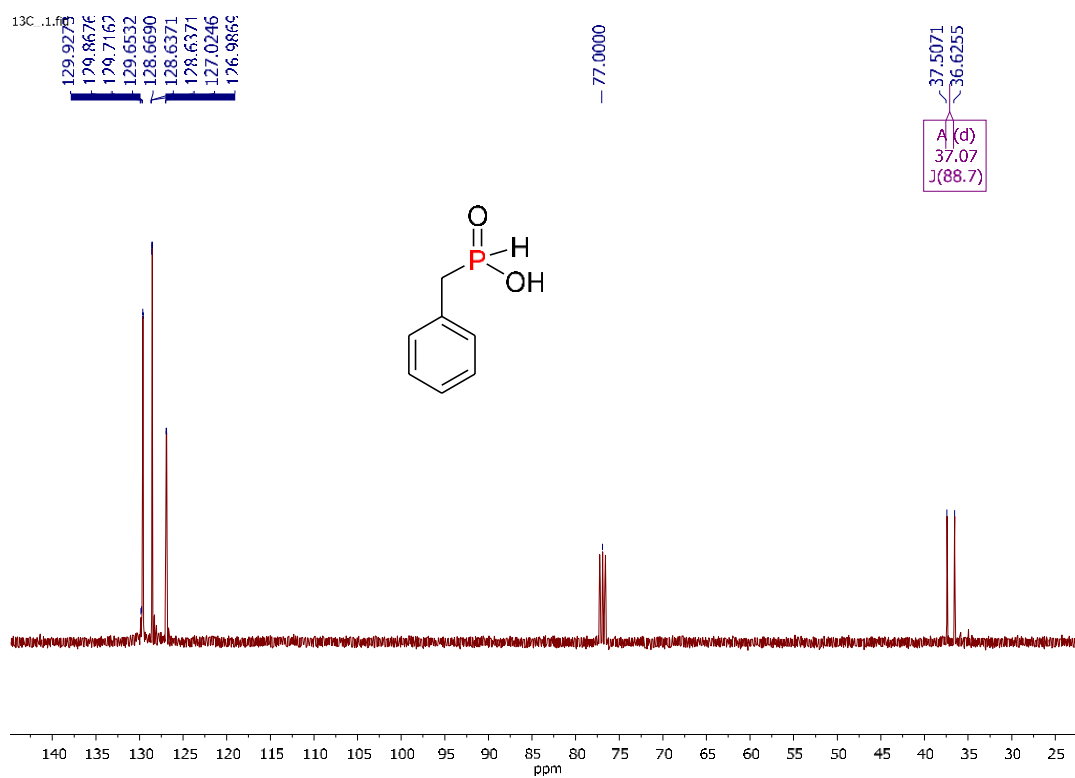
^{31}P NMR (161.98 MHz, CDCl_3): 33.3 ppm (d, 1H, $^1J_{\text{PH}} = 560$ Hz, PH).

Elemental analysis for $\text{C}_5\text{H}_7\text{O}_2\text{PS}$ (162.14): calcd. C, 37.04; H, 4.35; found: C, 37.01; H, 4.39

Copies of NMR Spectra

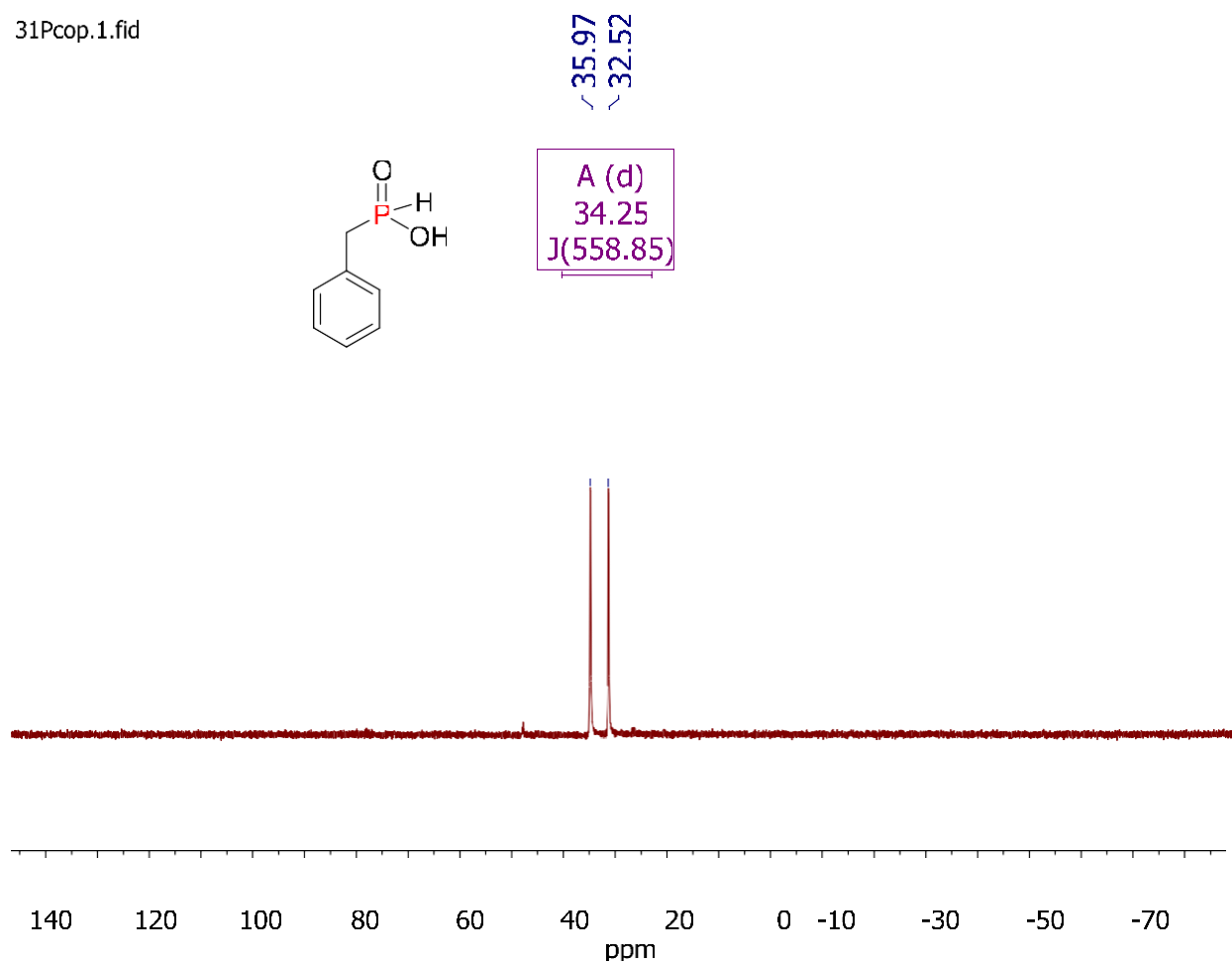


¹H NMR spectrum of compound **2a** (400.13 MHz, CDCl₃)

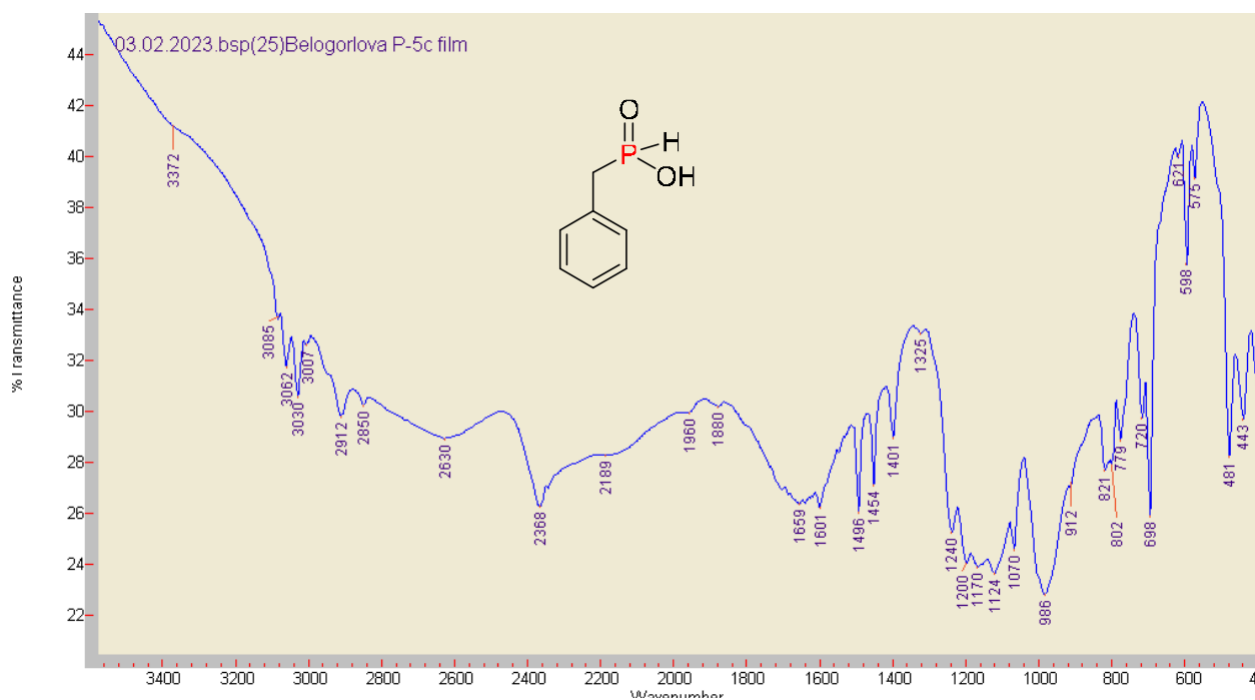


¹³C NMR spectrum of compound **2a** (100.62 MHz, CDCl₃)

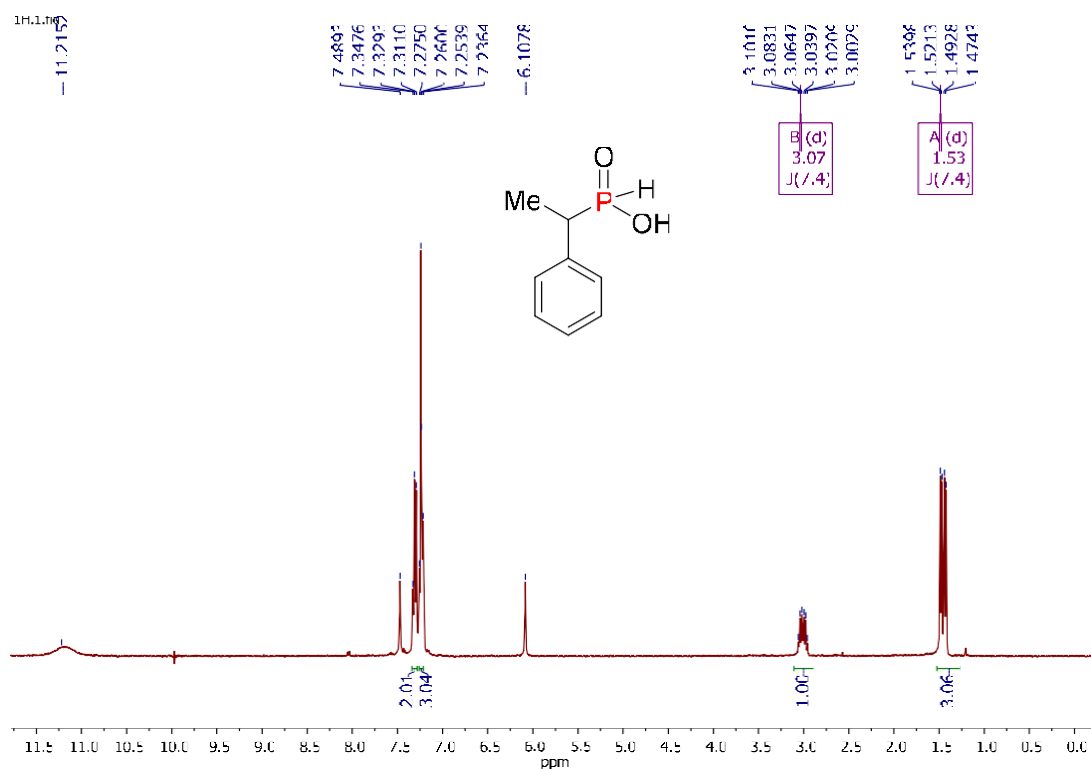
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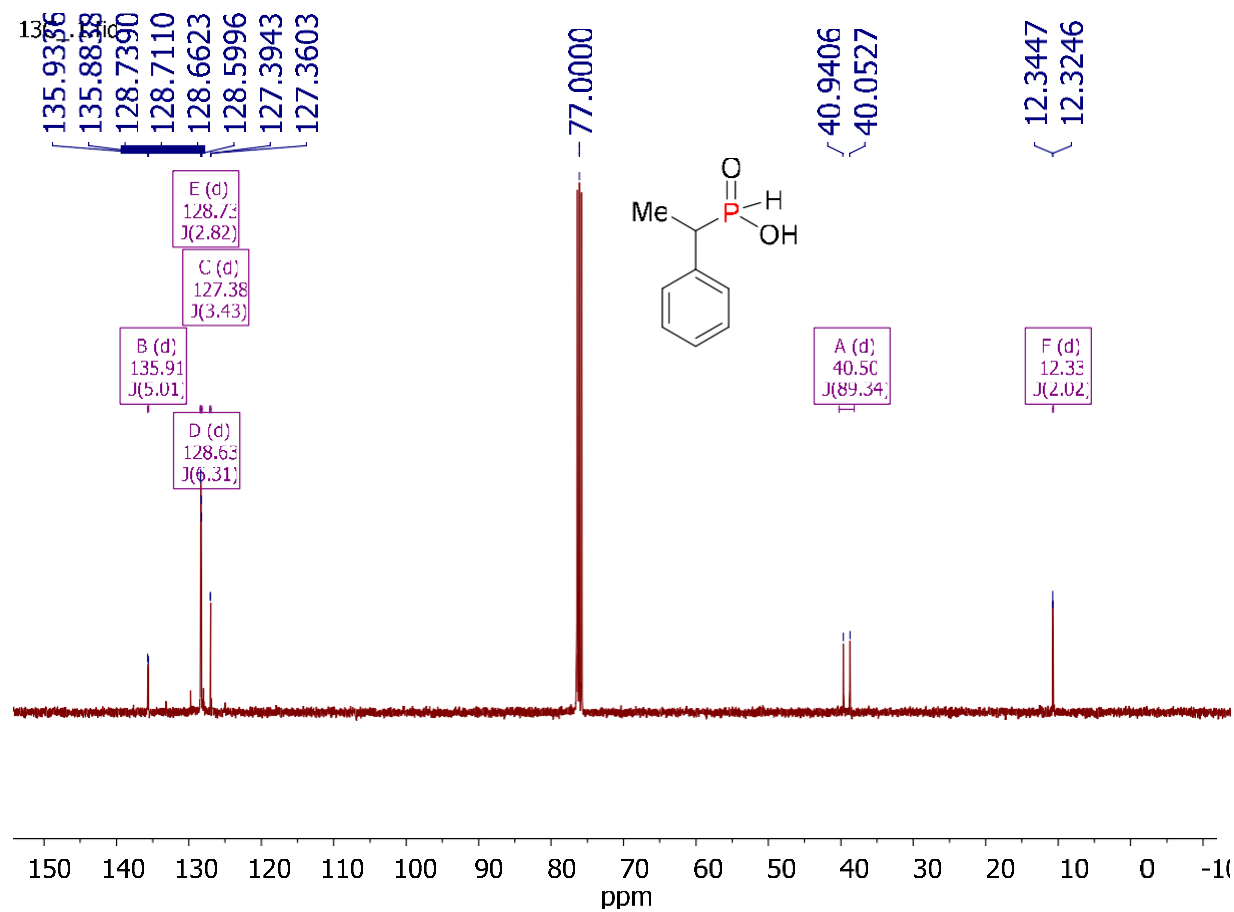
^{31}P NMR spectrum of compound 2a (161.98 MHz, CDCl_3)



IR spectrum of compound 2a (film, cm^{-1})

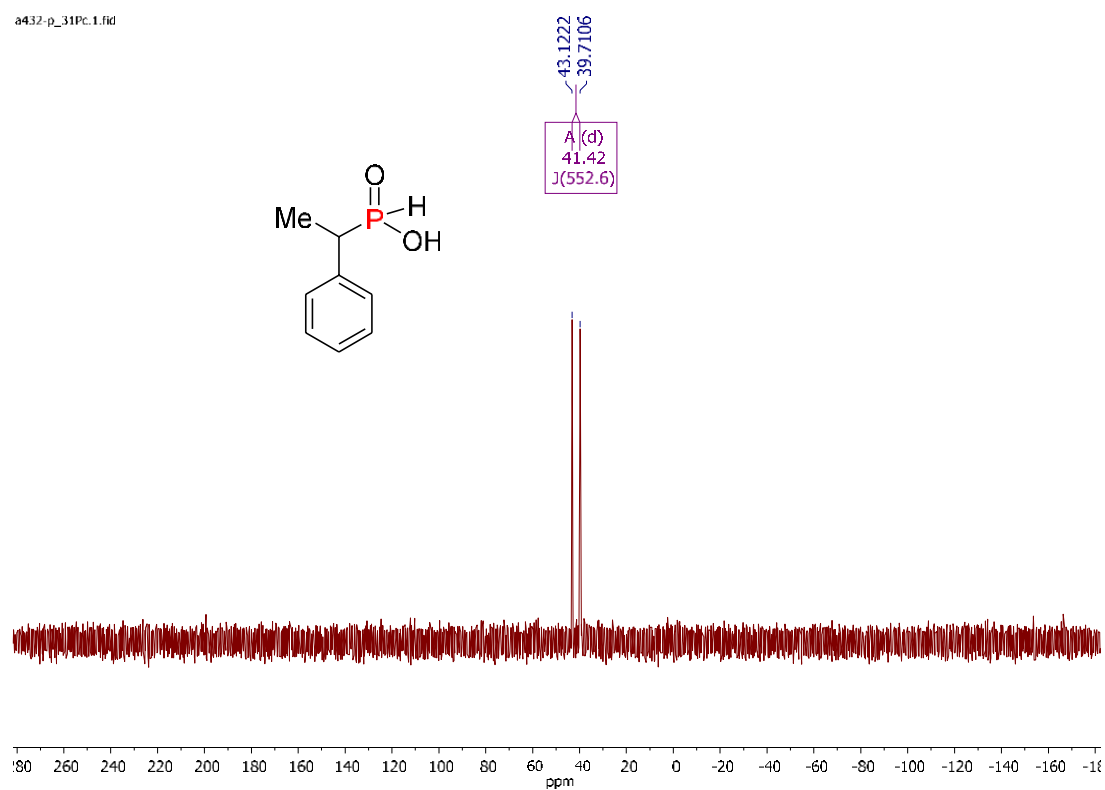


¹H NMR spectrum of compound **2b** (400.13 MHz, CDCl₃)

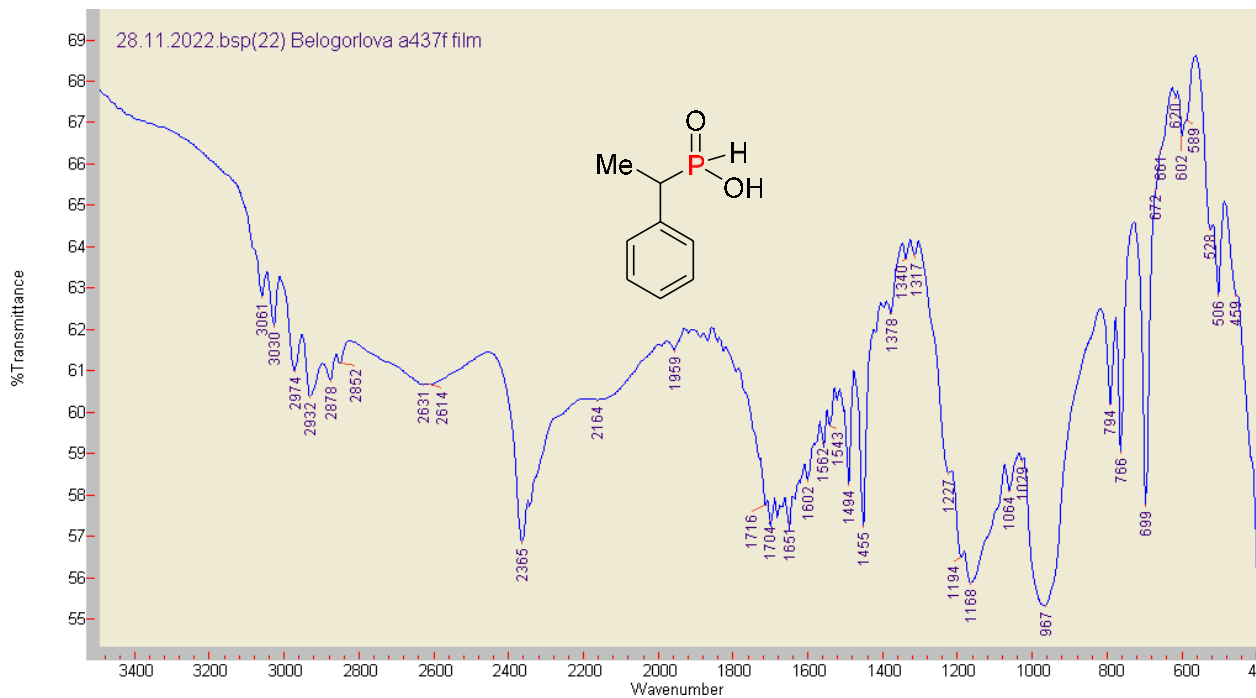


¹³C NMR spectrum of compound **2b** (100.62 MHz, CDCl₃)

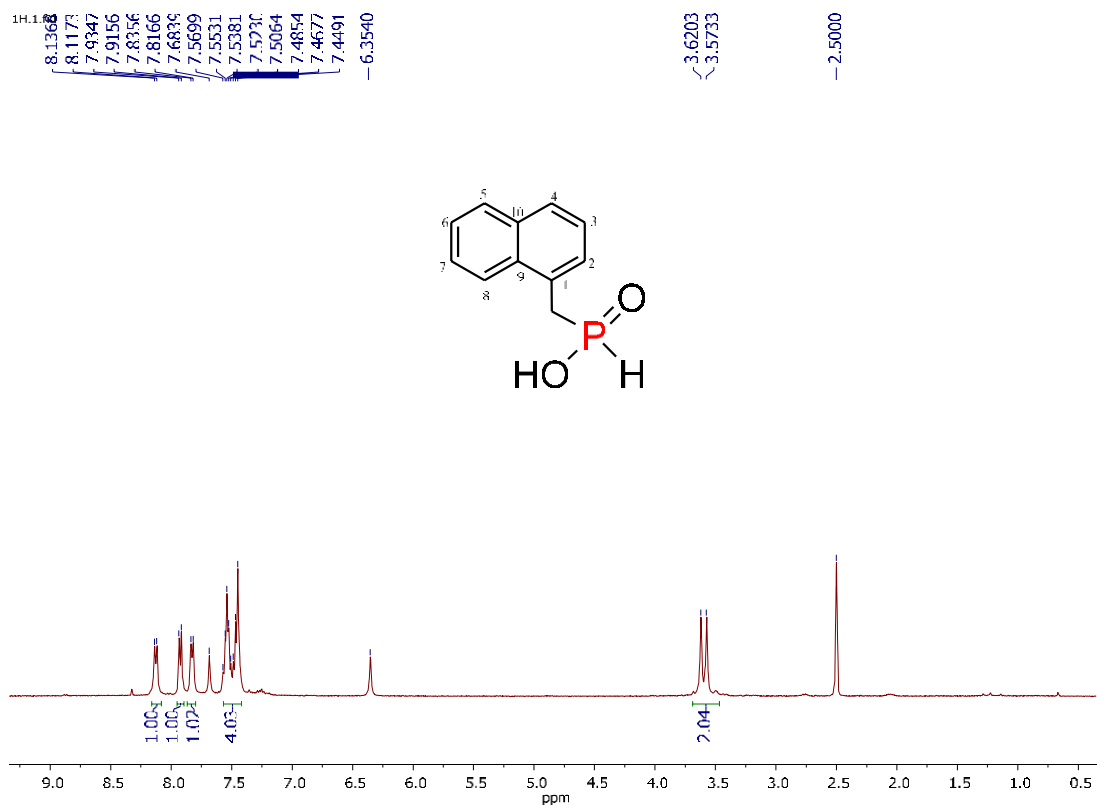
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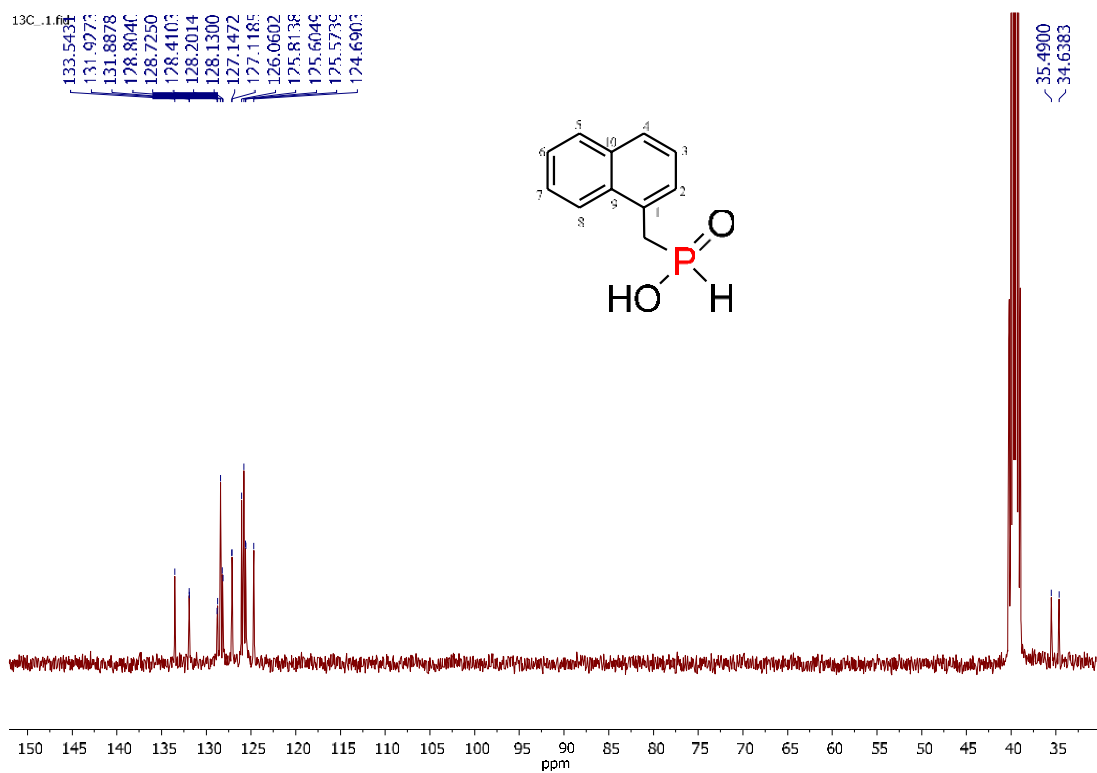
³¹P NMR spectrum of compound **2b** (161.98 MHz, CDCl₃)



IR spectrum of compound **2b** (film, cm⁻¹)

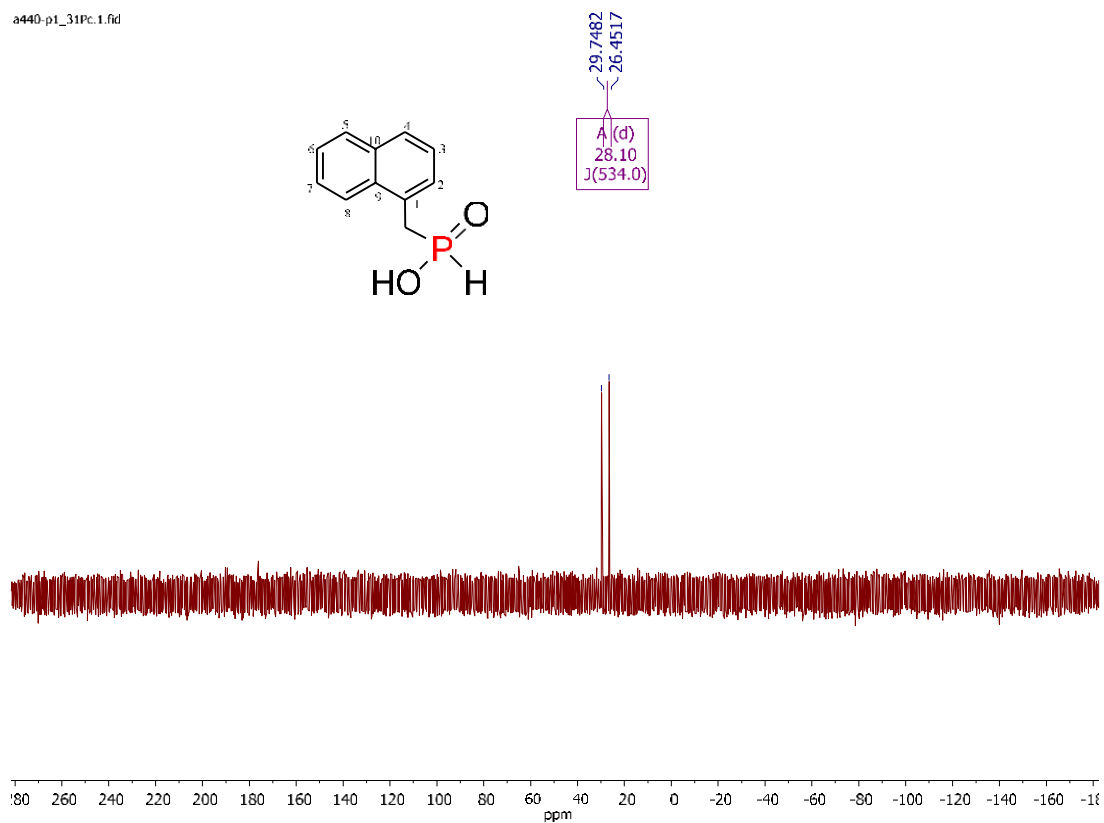


¹H NMR spectrum of compound **2c** (400.13 MHz, CDCl₃)

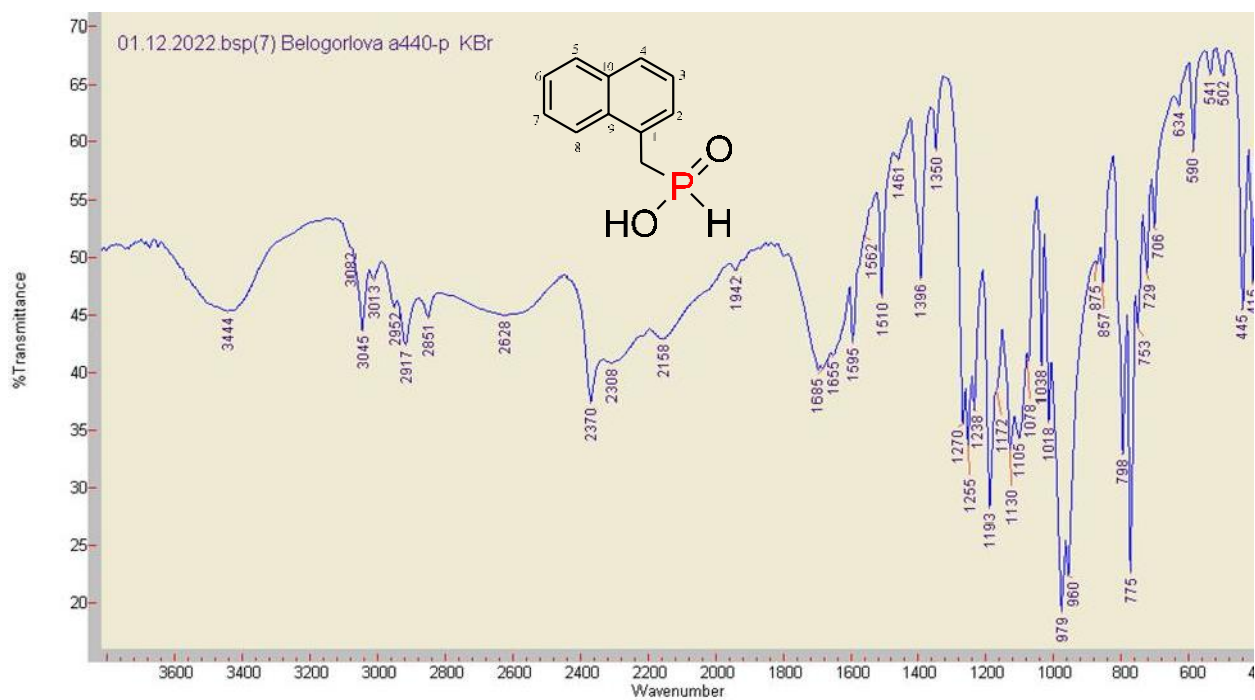


¹³C NMR spectrum of compound **2c** (100.62 MHz, CDCl₃)

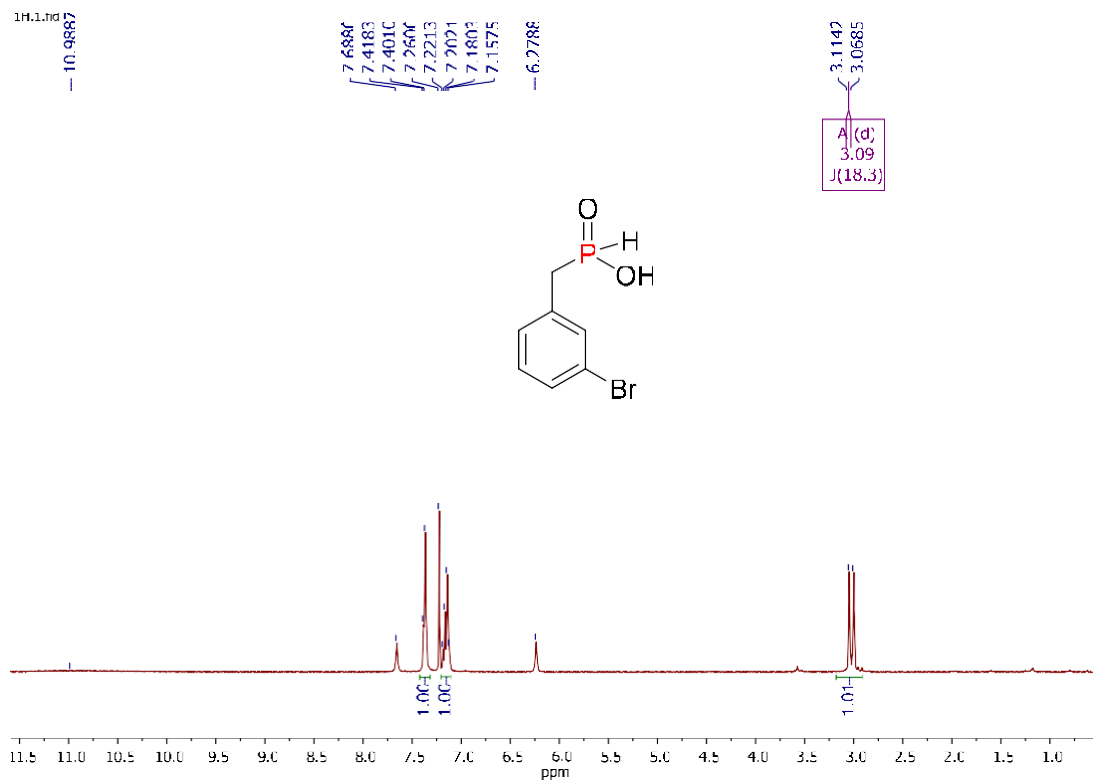
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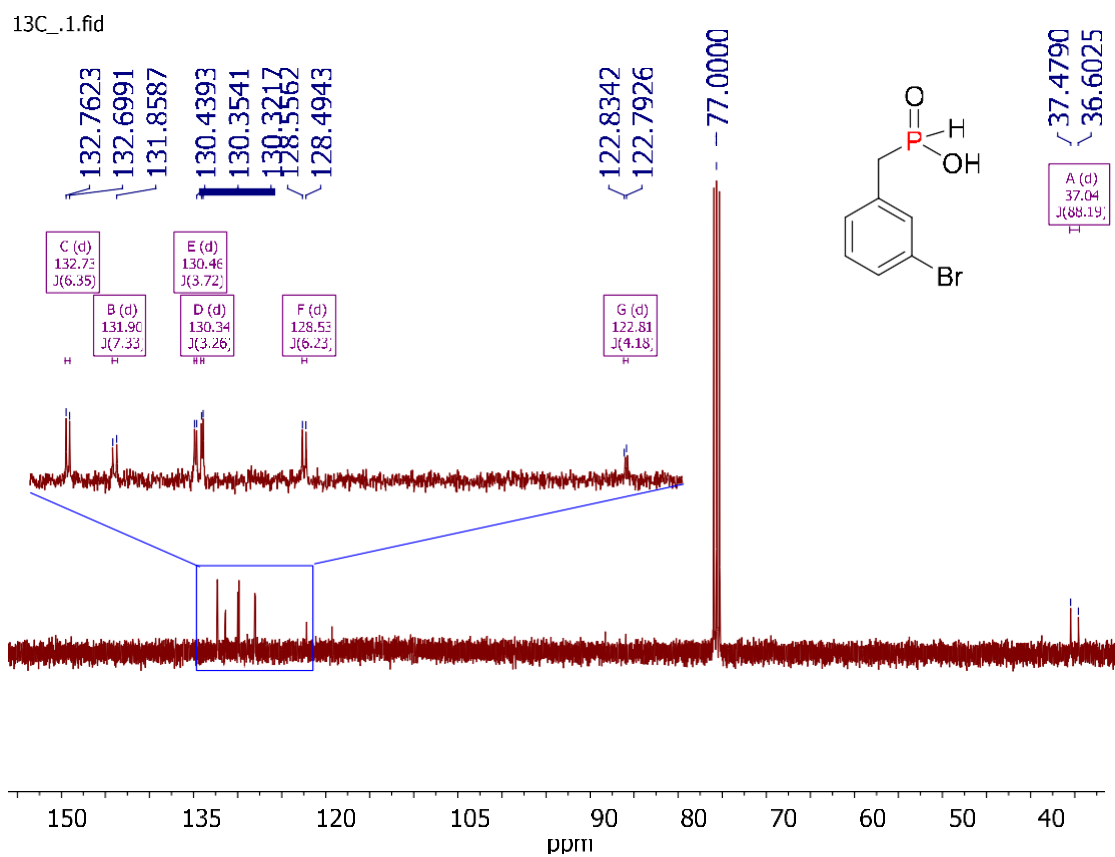
^{31}P NMR spectrum of compound **2c** (161.98 MHz, CDCl_3)



IR spectrum of compound **2c** (KBr, cm^{-1})

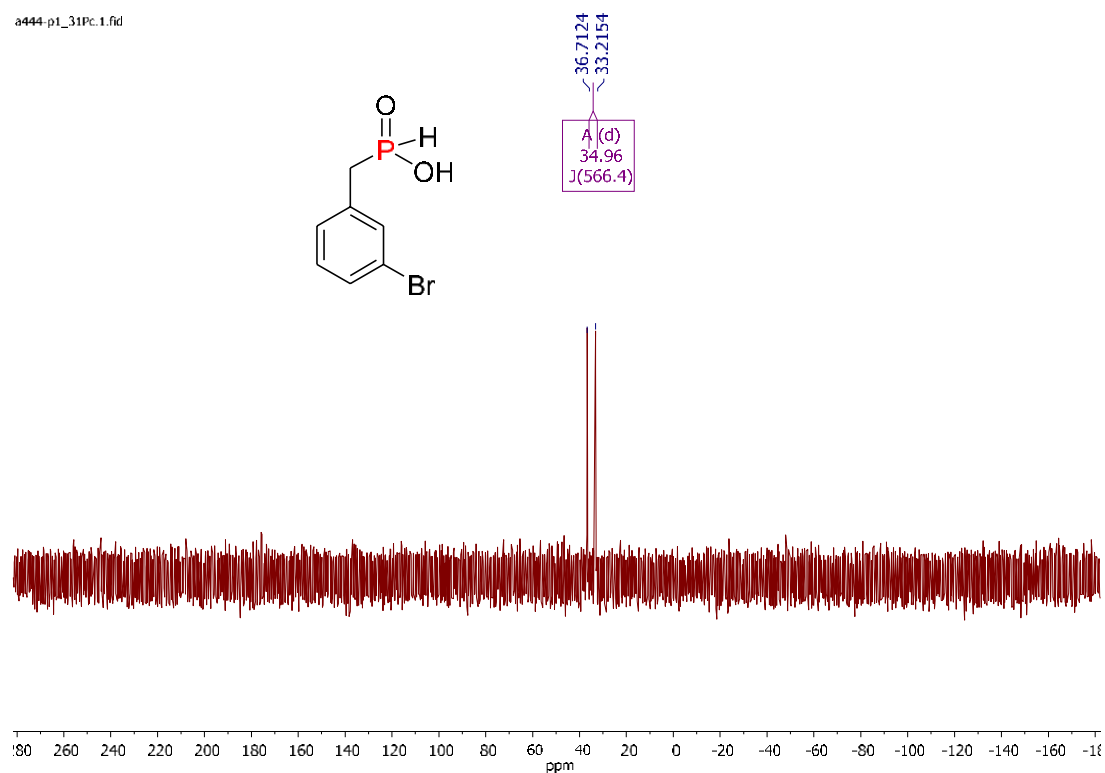


¹H NMR spectrum of compound **2d** (400.13 MHz, CDCl₃)

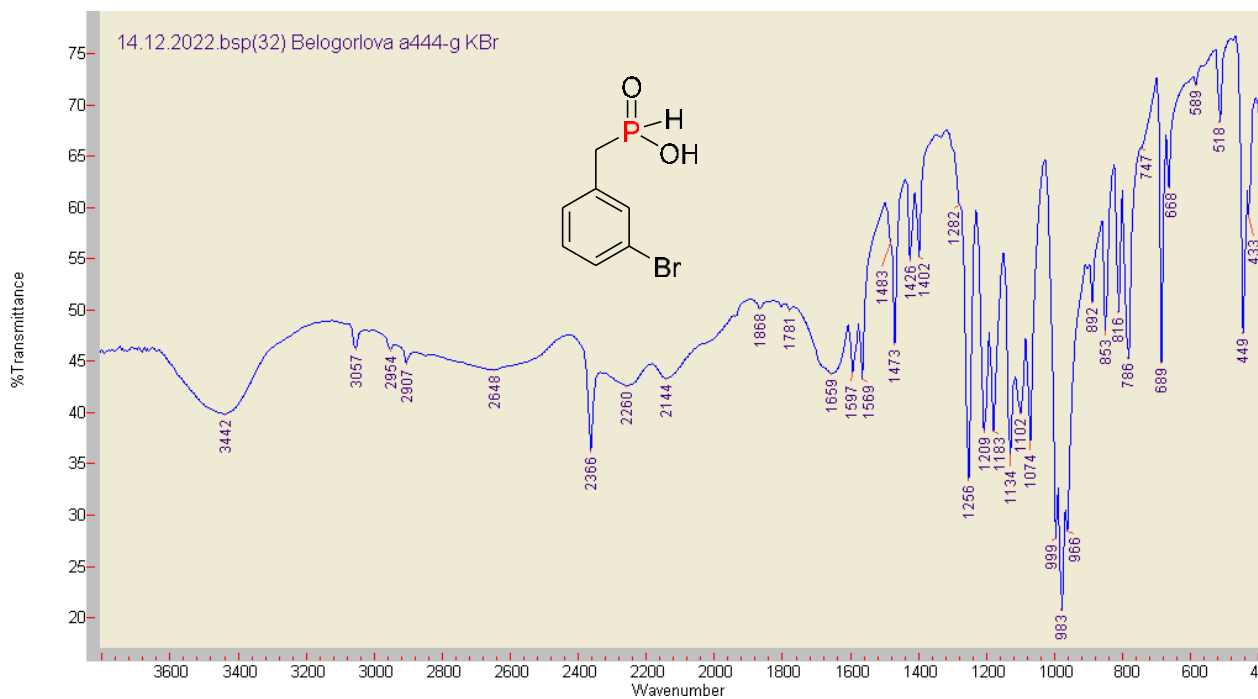


¹³C NMR spectrum of compound **2d** (100.62 MHz, CDCl₃)

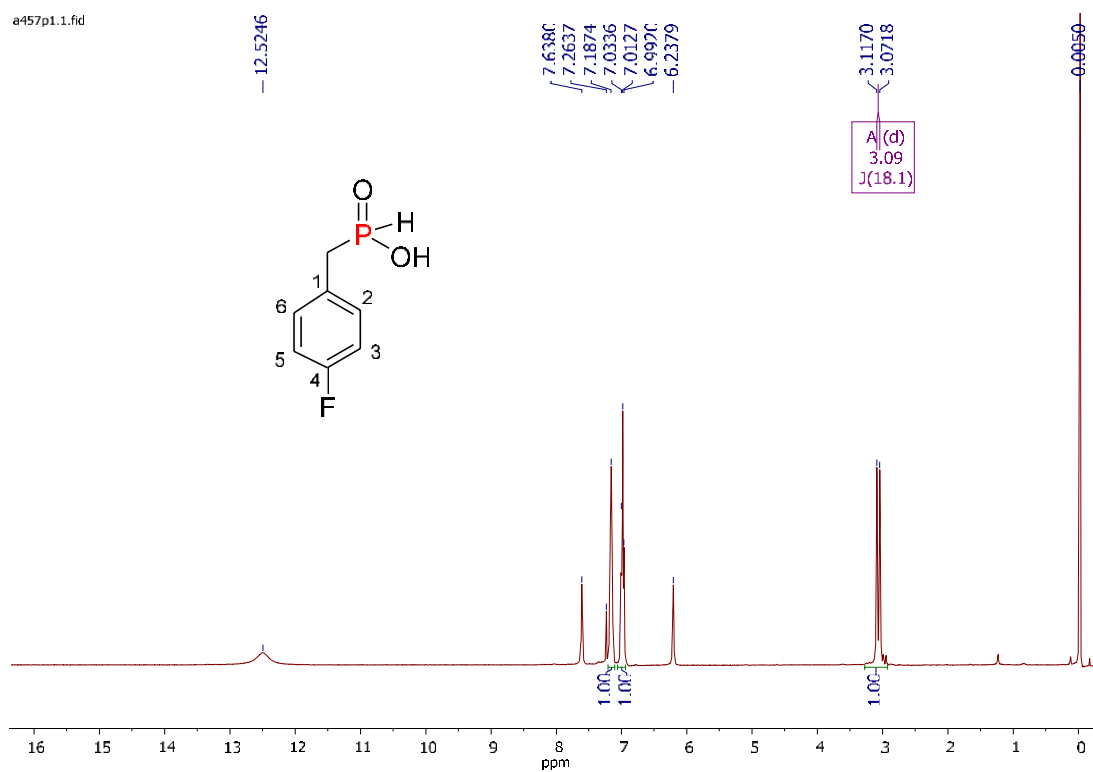
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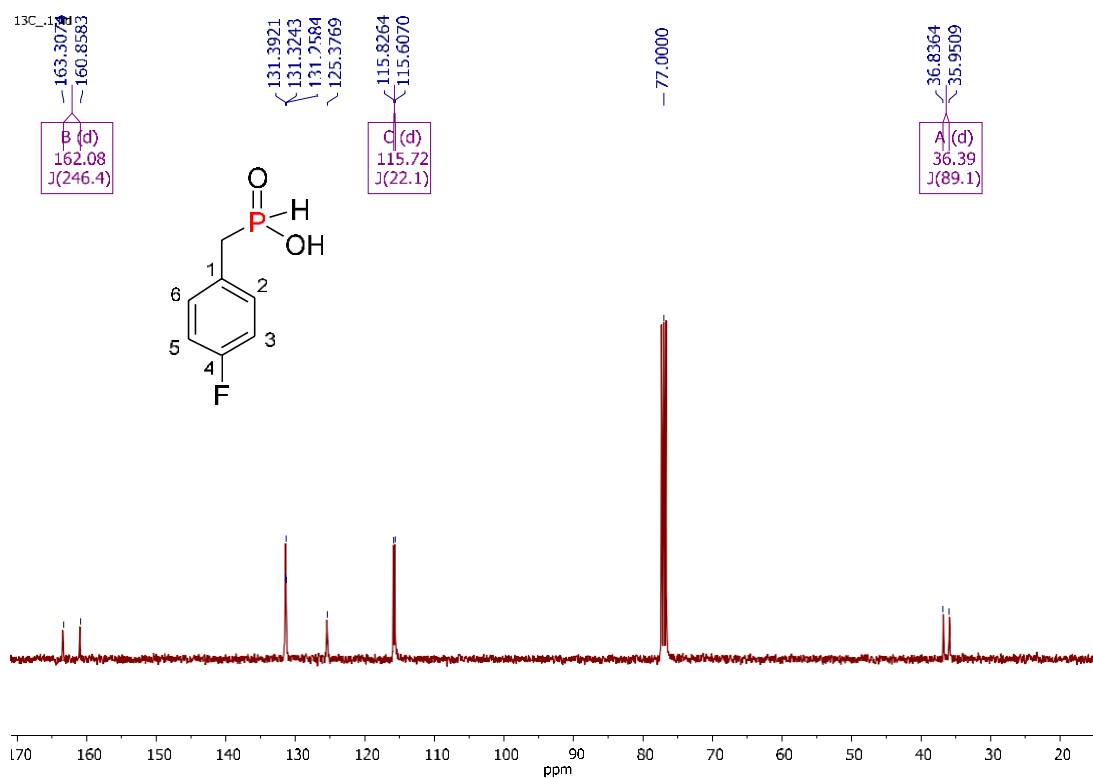
³¹P NMR spectrum of compound **2d** (161.98 MHz, CDCl₃)



IR spectrum of compound **2d** (KBr, cm⁻¹)

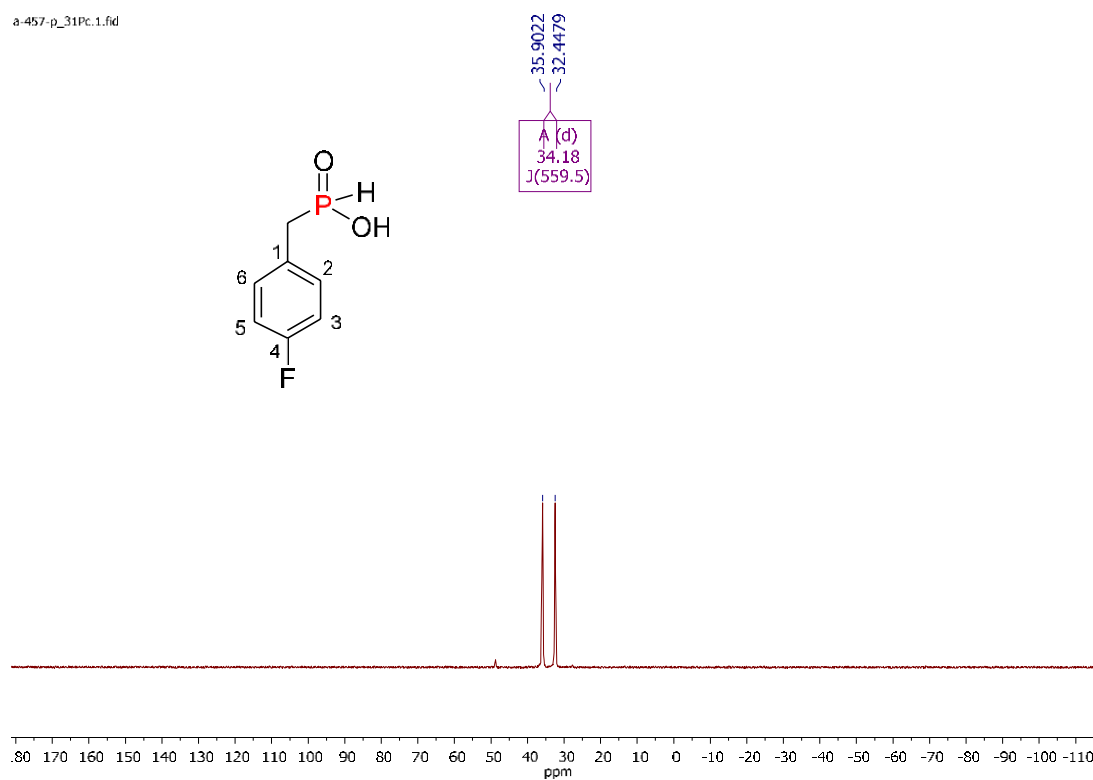


¹H NMR spectrum of compound **2e** (400.13 MHz, CDCl₃)



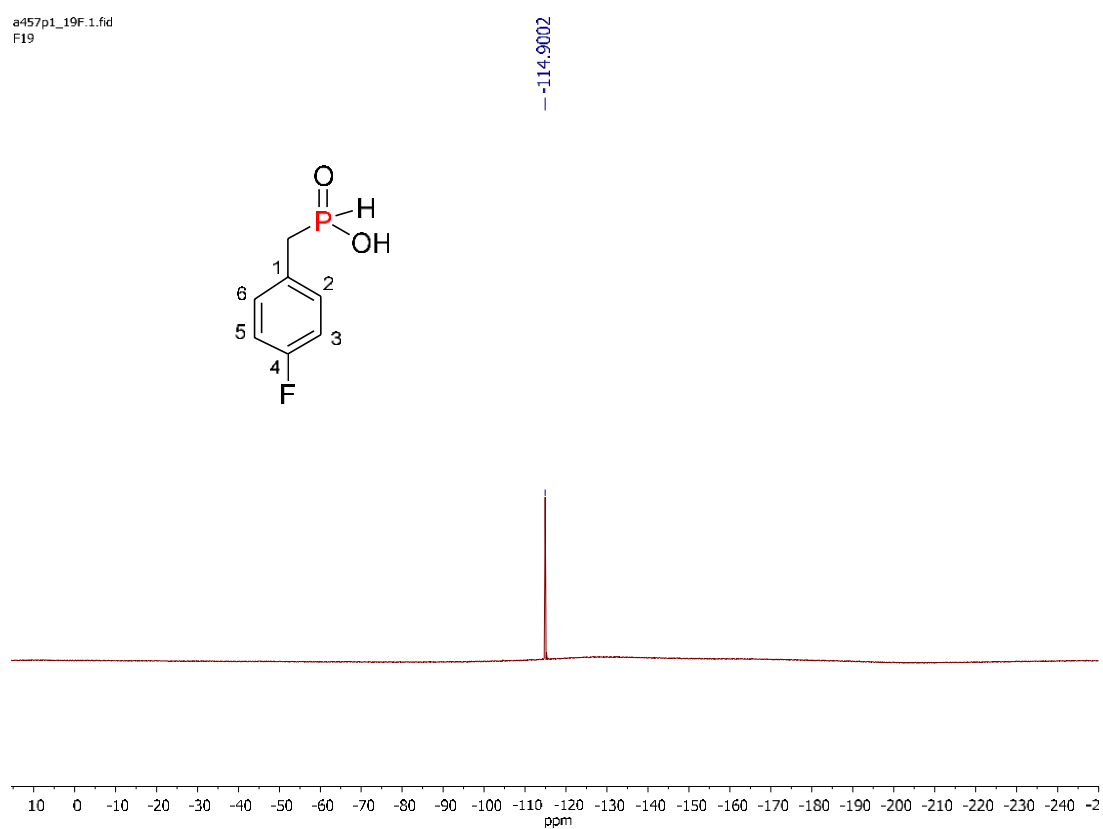
¹³C NMR spectrum of compound **2e** (100.62 MHz, CDCl₃)

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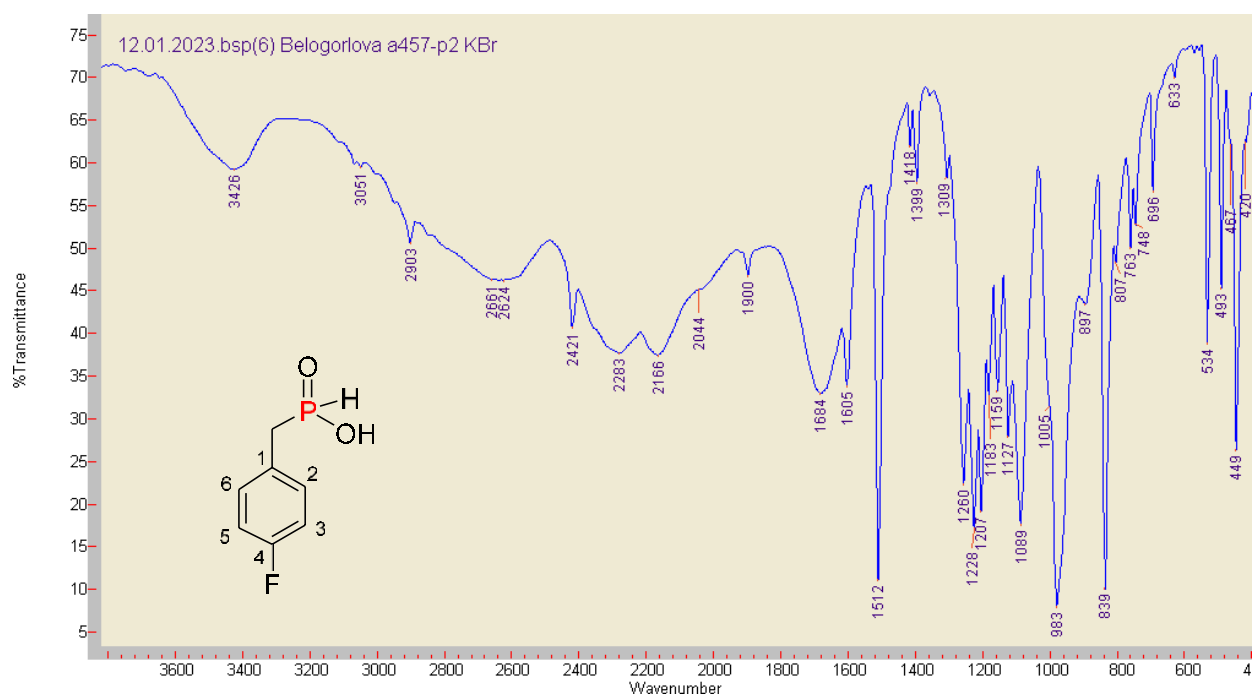


³¹P NMR spectrum of compound **2e** (161.98 MHz, CDCl₃)

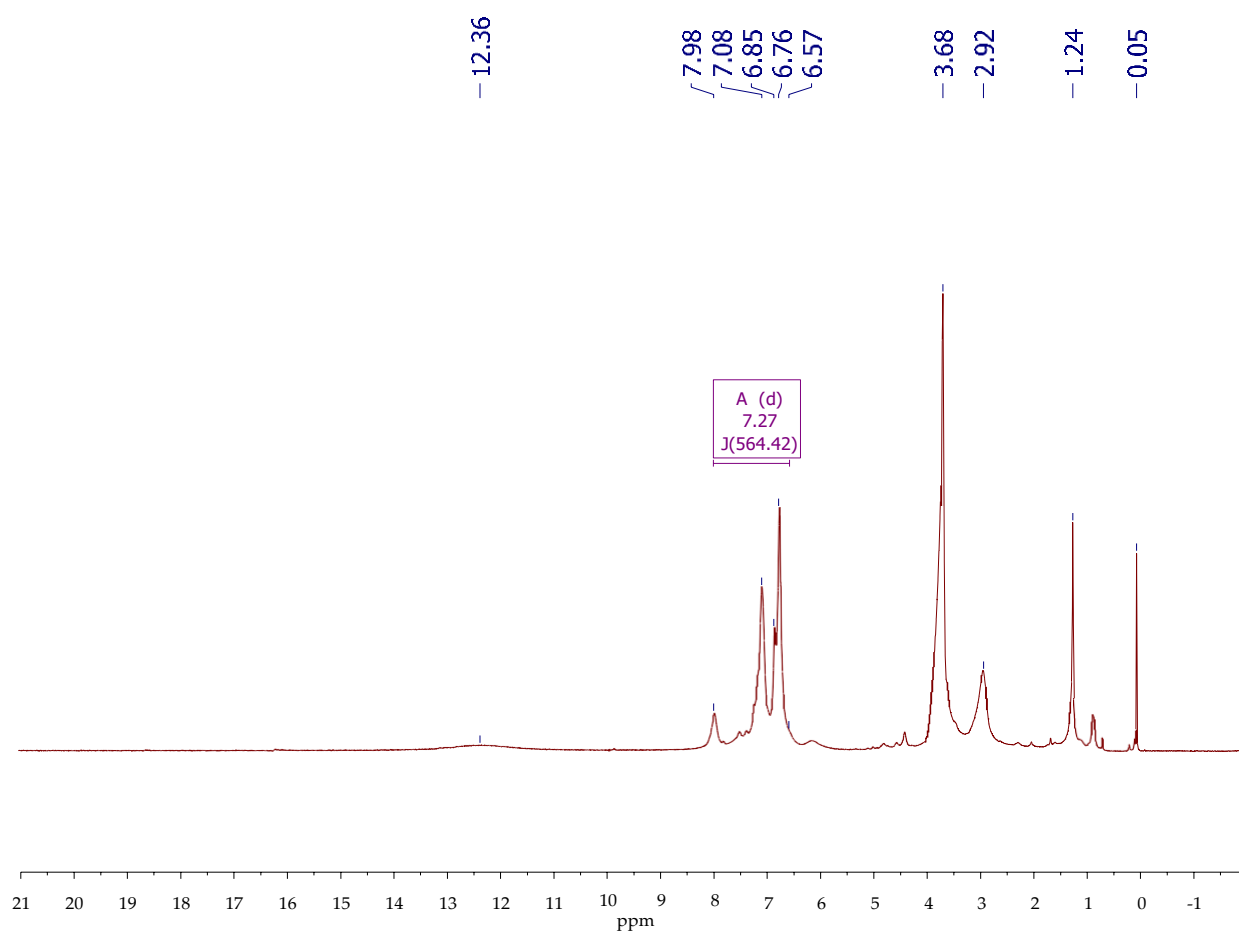
a457p1_19F.1.fid
F19



¹⁹F NMR spectrum of compound **2e** (376.5 MHz, CDCl₃)

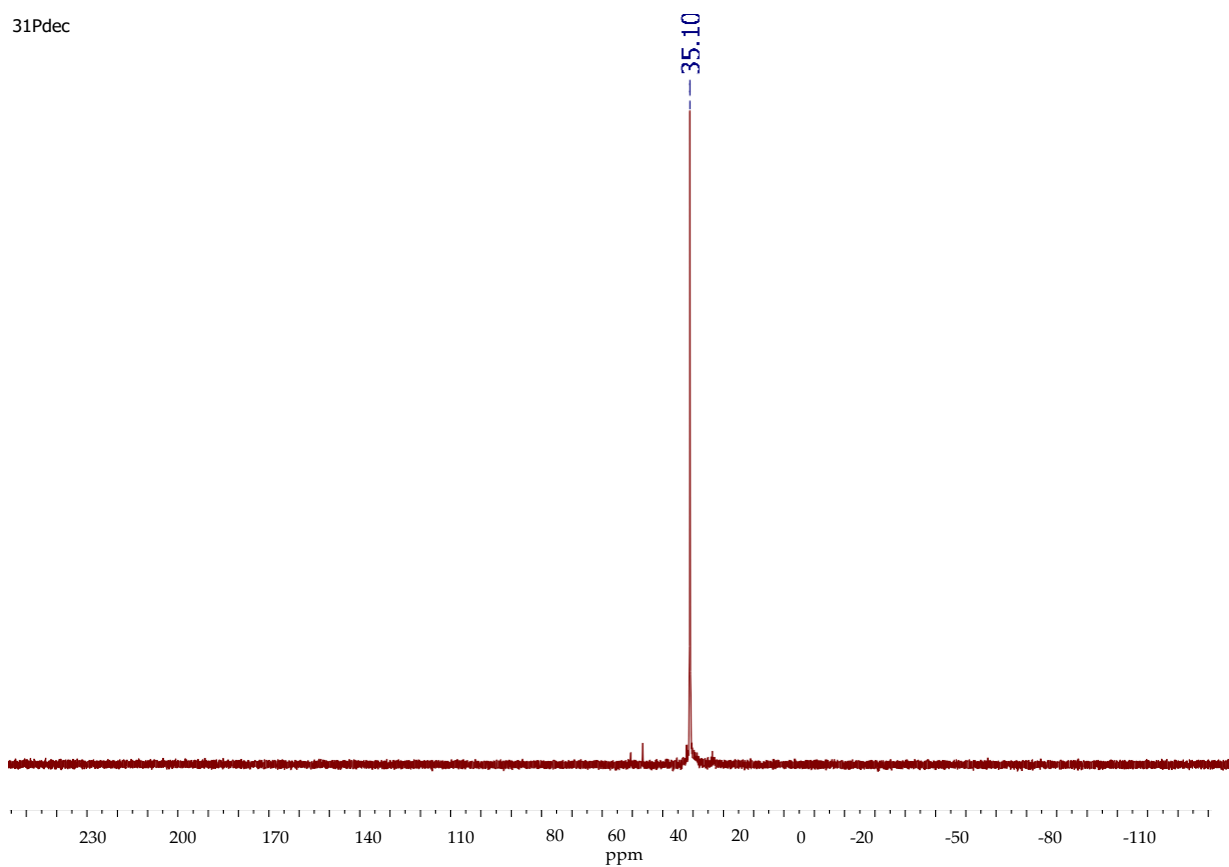


IR spectrum of compound **2e** (KBr, cm⁻¹)



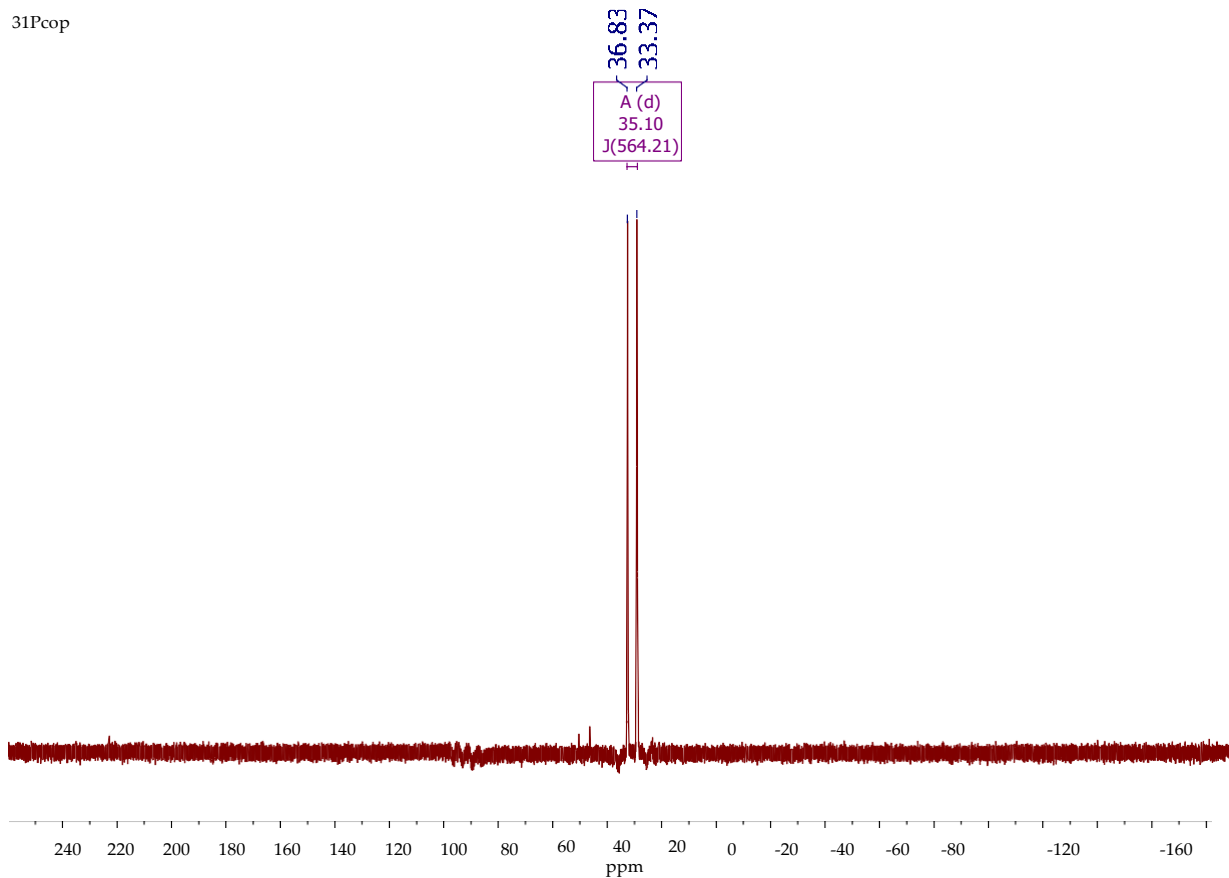
¹H NMR spectrum of 4-Methoxybenzyl-H-phosphonic acid (400.13 MHz, CDCl₃)

³¹Pdec

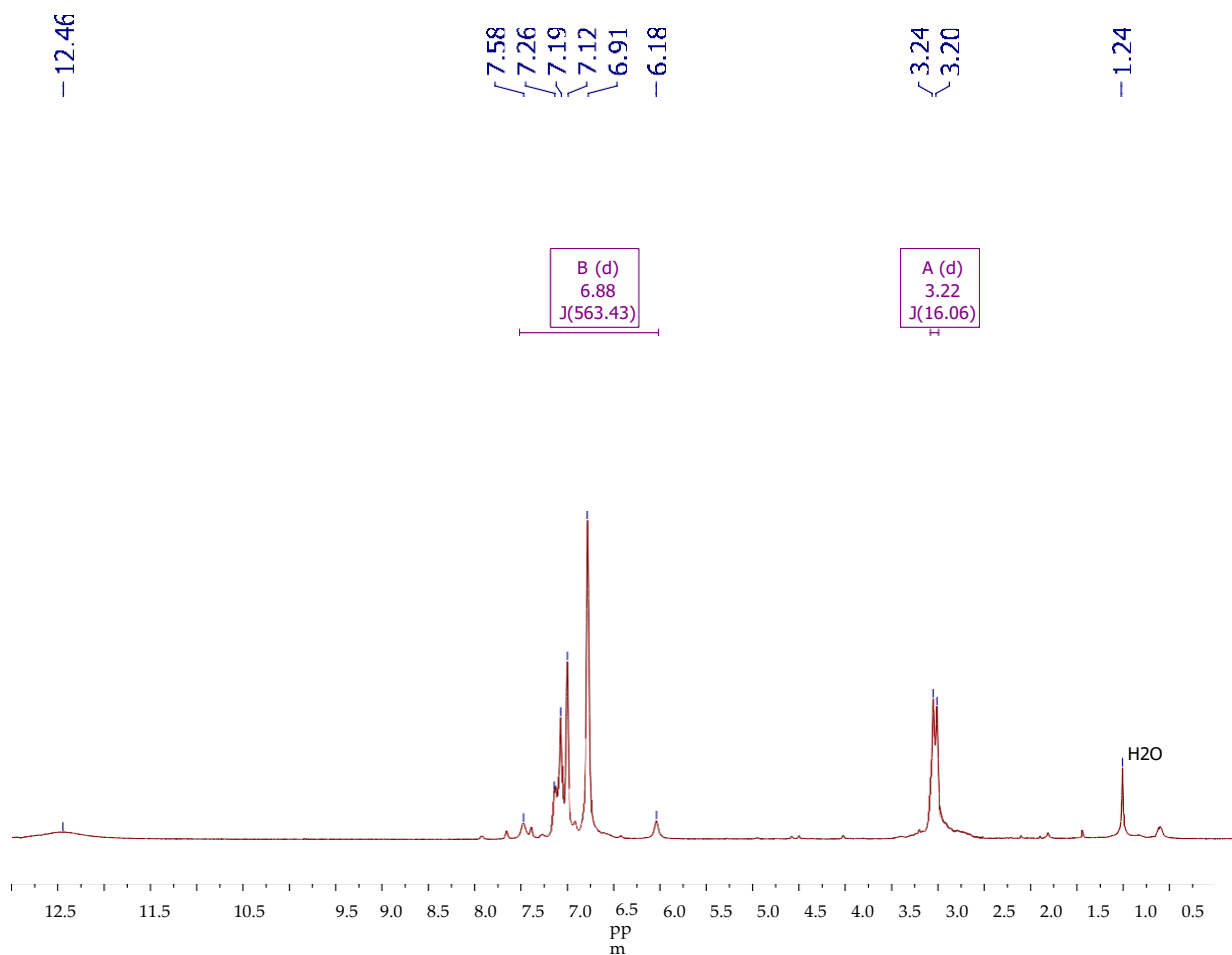


³¹P{H} NMR spectrum of 4-Methoxybenzyl-H-phosphinic acid (161.98 MHz, CDCl₃)

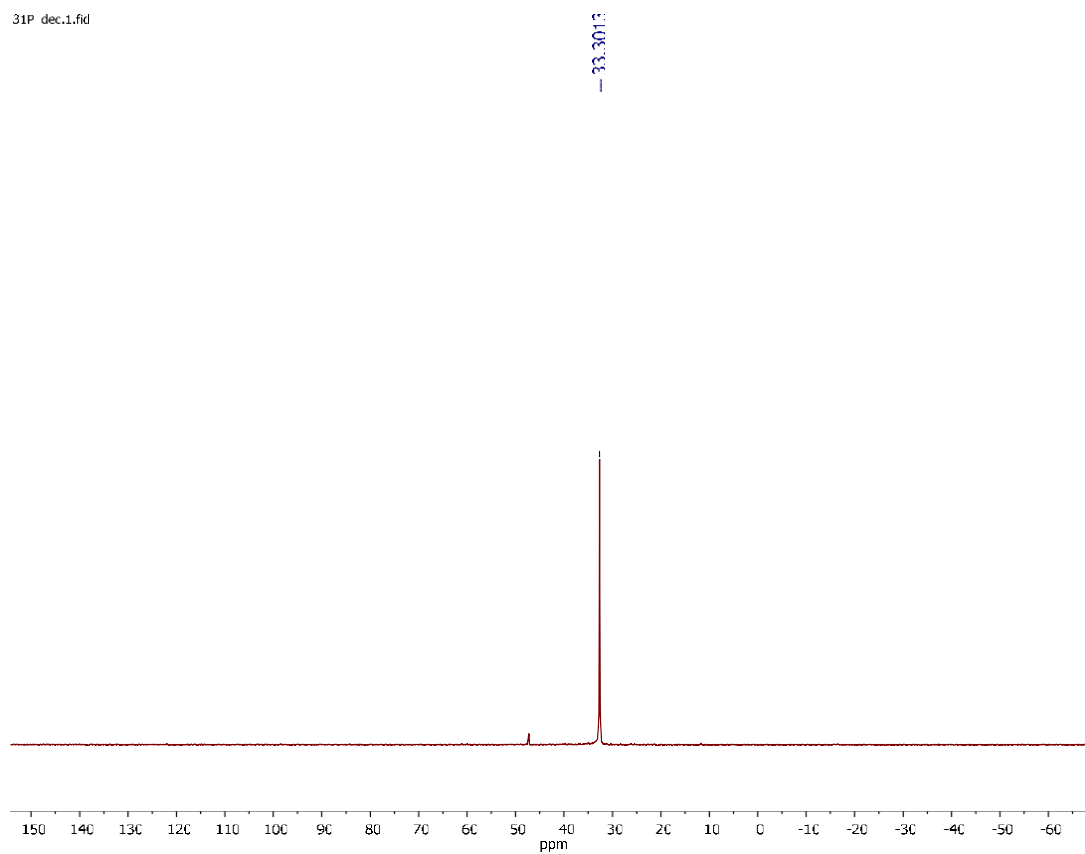
³¹Pcop

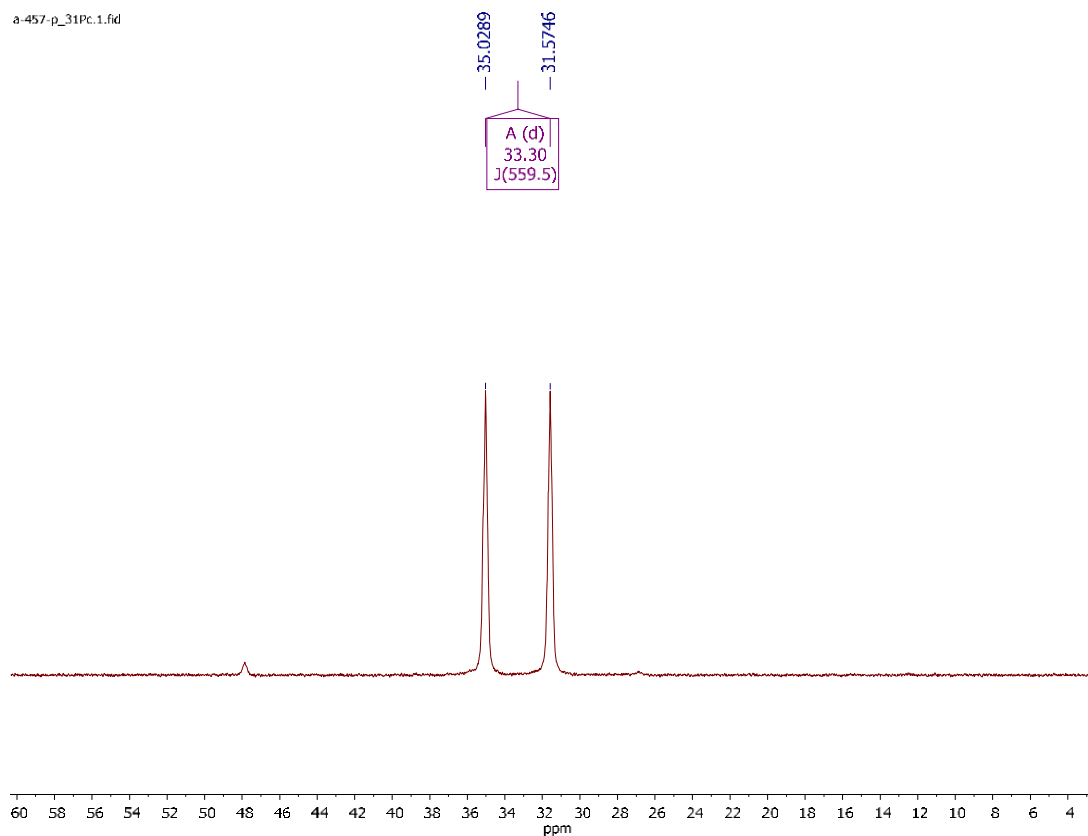


³¹P NMR spectrum of 4-Methoxybenzyl-H-phosphinic acid (161.98 MHz, CDCl₃)



31P dec.1.fid





^{31}P NMR spectrum of 2-Thienylmethyl-H-phosphinic acid (161.98 MHz, CDCl_3)

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