Supplementary Information

Electrochemically induced efficient, simple, non-catalytic synthesis of β-phosphonomalonates *via* multicomponent reaction

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Experimental Section

General Information: All chemicals were reagent grade and purchased from Aldrich, Alfa Aesar, Merck, Spectrochem and Qualigens and were used without further purification. The reactions were monitored using pre-coated Aluminium TLC plates of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F-254). NMR spectra were recorded on a Bruker Avance-II 400FT spectrometer at 300 or 500 MHz (^{1}H) and 75 or 125 MHz (^{13}C) in DMSO or $CDCl_3$ using TMS as an internal reference. Mass spectra (EIMS) were obtained on a Waters UPLC-TQD mass spectrometer. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Elemental analyses were carried out in a Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Melting points were determined by open glass capillary method and were uncorrected.

General procedure for the synthesis of β-phosphonomalonates: The mixture of benzaldehyde 1 (2.0 mmol) and malononitrile 2 (2.2 mmol) and lithium perchlorate 0.5 mmol) in ethanol (30 mL) was electrolyzed in beaker equipped with a magnetic stirrer, graphite anode and iron cathode, under constant current density of 10 mA/cm^2). After completion of the reaction (monitored by TLC). Tri ethyl phosphite (2.4 mmol) was added to the reaction mixture. The solvent was evaporated under reduced pressure and reaction mixture was added by water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate as eluent to

afford an analytically pure sample of product **4**. All the compounds are known and were characterized by comparison of their spectral data with those reported in the literature.

Diethyl 2,2-dicyano-1-phenylethylphosphonate 4a solid: mp 56-58 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) d 7.42 (br s, 5H), 4.48 (t, 1H, $^3J_{HH}$=8.4 Hz), 4.18-4.12 (m, 2H), 4.02-3.92 (m, 1H), 3.78-3.67 (m, 1H), 3.56 (dd, 1H, $^3J_{HH}$=8.1 Hz and $^2J_{HP}$=21.0 Hz), 1.33 (t, 3H, $^3J_{HH}$=7.2 Hz), 1.10 (t, 3H, $^3J_{HH}$=6.9 Hz); ^{13}C NMR (75 MHz) d 130.4, 129.5, 129.4, 129.3, 111.5 (d, $^3J_{CP}$=9.9 Hz), 111.4 (d, $^3J_{CP}$=12.6 Hz), 64.3 (d, $^2J_{CP}$=6.6 Hz), 63.3 (d, $^2J_{CP}$=7.1 Hz), 44.4 (d, $^1J_{CP}$=143.4 Hz), 25.5, 16.2 (d, $^3J_{CP}$=5.5 Hz), 16.0 (d, $^3J_{CP}$=5.5 Hz); IR (KBr) 2988, 2870, 2614, 2487, 2378, 2257, 1456, 1388, 1237, 1036 cm^{-1}; MS (m/z, EI) 292 (M+)

Diethyl 2,2-dicyano-1-m-tolylethylphosphonate (4b) ^{1}H NMR (300 MHz, $CDCl_3$) d 7.13-6.99 (m, 4H), 4.27 (t, 1H, 3JHH=8.7 Hz), 3.99-3.87 (m, 2H), 3.85-3.72 (m, 1H), 3.60-3.46 (m, 1H), 3.32 (dd, 1H, $^3J_{HH}$=8.4 Hz and $^2J_{HP}$=21.0 Hz), 2.17 (s, 3H), 1.14 (t, 3H, $^3J_{HH}$=7.2 Hz), 0.90 (t, 3H, $^3J_{HH}$=6.9 Hz); ^{13}C NMR (75 MHz) d 139.2, 130.3, 130.0, 129.9, 129.2, 126.2, 111.6 (d, $^3J_{CP}$=7.7 Hz), 111.5 (d, $^3J_{CP}$=13.1 Hz), 64.3 (d, $^2J_{CP}$=7.1 Hz), 63.4 (d, $^2J_{CP}$=7.1 Hz), 44.5 (d, $^1J_{CP}$=142.8 Hz), 25.5, 21.4, 16.2 (d, $^3J_{CP}$=5.5 Hz), 16.1 (d, $^3J_{CP}$=5.5 Hz); IR (KBr) 2979, 2906, 2609, 2480, 2257, 1605, 1466, 1387, 1241, 1026 cm^{-1}; MS (m/z, EI) 306.

Diethyl 2,2-dicyano-1-(3-methoxyphenyl) Ethylphosphonate (4c) ^{1}H NMR (300 MHz, $CDCl_3$):
d 7.24 (t, 1H, $^3J_{HH}$=7.8 Hz), 6.98 (s, 2H), 6.85 (d, 1H, $^3J_{HH}$=8.1 Hz), 4.67 (t, 1H, $^3J_{HH}$=8.7 Hz), 4.10-4.05 (m, 2H), 3.99-3.90 (m, 1H), 3.77-3.71 (m, 4H), 3.58 (dd, 1H, $^3J_{HH}$=7.8 Hz and $^2J_{HP}$=21.3 Hz),1.25 (t, 3H, $^3J_{HH}$=6.6 Hz), 1.05 (t, 3H, $^3J_{HH}$=6.9 Hz); 13C NMR (75 MHz) d 159.9, 131.7 (d, $^3J_{CP}$=6.0 Hz), 130.2, 121.4 (d, $^3J_{CP}$=6.0 Hz), 114.9, 114.8, 111.6 (d, $^3J_{CP}$=4.9 Hz), 111.5 (d, $^3J_{CP}$=7.2 Hz), 64.2 (d, $^2J_{CP}$=6.6 Hz), 63.2 (d, $^2J_{CP}$=7.1 Hz), 55.2, 44.0 (d, $^1J_{CP}$=142.8 Hz), 25.3, 16.0 (d, $^3J_{CP}$=6.0 Hz), 15.9 (d, $^3J_{CP}$=6.0 Hz); IR (neat) 2980, 2920, 2597, 2257, 1597, 1471, 1249, 1164, 1031 cm^{-1}; MS (m/z, EI) 322.

Diethyl 2,2-dicyano-1-(4-fluorophenyl) Ethylphosphonate (4d) mp 80-82 ^{o}C; 1H NMR (300 MHz, $CDCl_3$) d 7.47-7.43 (m, 2H), 7.07 (t, 2H, $^3J_{HH}$=8.4 Hz), 4.57 (dd, 1H, $^3J_{HH}$=7.8 Hz and $^3J_{HP}$=8.7 Hz), 4.17-4.04 (m, 2H), 4.02-3.91 (m, 1H), 3.85-3.72 (m, 1H), 3.58 (dd, 1H, $^3J_{HH}$=7.2 Hz and $^2J_{HP}$=21.3 Hz), 1.28 (t, 3H, 3JHH=7.2 Hz), 1.10 (t, 3H, $^3J_{HH}$=6.9 Hz); 13C NMR (75 MHz, $CDCl_3$) d 131.4, 131.3, 126.4, 126.3, 116.7, 116.4, 111.5 (d, $^3J_{CP}$=10.9 Hz), 111.3 (d, $^3J_{CP}$=11.5 Hz), 64.4 (d, $^2J_{CP}$=7.1 Hz), 63.5 (d, $^2J_{CP}$=7.7 Hz), 43.7 (d, $^1J_{CP}$=144.0 Hz), 25.7, 16.3 (d, $^3J_{CP}$=6.6 Hz), 16.2 (d, $^3J_{CP}$=6.0 Hz); IR (KBr) 2993, 2922, 2261, 1606, 1512, 1387, 1244, 1029 cm^{-1}; HRMS m/z (M) calcd for $C_{14}H_{16}FN_2O_3P$: 310.0883; found: 310.0884

Diethyl 1-(4-chlorophenyl)-2,2- Dicyanoethylphosphonate (4e) solid: mp 94-96 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) d 7.41 (br s, 4H), 4.45 (t, 1H, $^3J_{HH}$=8.4 Hz), 4.19-4.11 (m, 2H), 4.07-3.97 (m, 1H), 3.90-3.77 (m, 1H), 3.53 (dd, 1H, $^3J_{HH}$=7.5 Hz and $^2J_{HP}$=21.3 Hz), 1.33 (t, 3H, $^3J_{HH}$=6.9 Hz), 1.16 (t, 3H, $^3J_{HH}$=7.2 Hz); ^{13}C NMR (75 MHz) d 135.7, 130.8, 129.6, 129.0, 111.4 (d, $^3J_{CP}$=10.9 Hz), 111.2 (d, $^3J_{CP}$=13.2 Hz), 64.4 (d, $^2J_{CP}$=7.1 Hz), 63.6 (d, $^2J_{CP}$=7.1 Hz),

43.8 (d, $^{1}J_{CP}$=143.4 Hz), 25.5, 16.3 (d, $^{3}J_{CP}$=6.6 Hz), 16.2 (d, $^{3}J_{CP}$=5.5 Hz); IR (KBr) 2993, 2854, 2612, 2257, 1931, 1587, 1493, 1239, 1021 cm^{-1}; MS (m/z, EI) 326 (M+, 16).

Diethyl 2,2-dicyano-1-(4-hydroxyphenyl) ethylphosphonate (4f)

1H NMR (250 MHz, CDCl3): 7.26 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar). 6.8 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar), 4.43 (t, 1H, $^{3}J_{HH}$, $^{3}J_{HP}$ = 8.0 Hz), 3.79-4.23 (m, 4H, CH_2), 3.53 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{HP}$ = 21.3 Hz, 1H, CH), 1.38 (t, 3*J*HH = 7.0 Hz, 3H, CH3), 1.19 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3), ^{13}C NMR (62.9 Hz, $CDCl_3$, TMS, ppm): δ = 157.6, 130.5, 120.7 116.6, 111.2 (d, $^{3}J_{CP}$ = 10.0 Hz), 111.0 (d, $^{3}J_{CP}$ = 11.2 Hz), 64.6 (d, $^{2}J_{CP}$ = 7.5 Hz), 63.8 (d, $^{2}J_{CP}$ = 7.5 Hz), 43.9 (d, $^{1}J_{CP}$ = 144.7 Hz), 25.7, 16.3 MS (*m*/*z*, EI) 308 (M+)); IR (KBr) 2993, 2854, 2612, 2257, 1931, 1587, 1493, 1239, 1021 cm^{-1};

Diethyl 2,2-dicyano-1-(pyridin-3-yl)ethylphosphonate (4g). Yield 0.26 g, 89%; dark orange liquid; [Found: C, 52.71; H, 5.32; N, 14.04. $C_{13}H_{16}N_3O_3P$ requires C, 53.24; H, 5.50; N, 14.33%]; Rf (50% n-hexane/EtOAc) 0.07; ymax (KBr) 2236 (CN),1011 (P]O) cm^{-1}; dH (250MHz, CDCl3) 8.67 (s, 2H); 7.95 (d, 1H, 3JHH=6.5 Hz), 7.39 (t, 1H, 3JHH=6.5 Hz), 4.63 (t, 1H, 3JHH=8.5 Hz), 3.92-4.21 (m, 4H), 3.65 (dd, 1H, 3JHH=6.8 Hz, 2JHP=21.6 Hz), 1.33 (t, 3H, 3JHH=7.0 Hz), 1.18 (t, 3H, 3JHH=6.8 Hz), dC (62.9 MHz, CDCl3) 150.8 150.5 136.5, 126.7, 124.0, 110.8 (d, 3JCP=10.7 Hz), 111.0 (d, 3JCP=11.9 Hz), 64.5 (d, 2JCP=7.0 Hz), 63.8 (d, 2JCP=7.0 Hz), 42.1 (d, 1JCP=144.6 Hz), 25.3, 16.2 (d, 3JCP=5.0 Hz), 16.1 (d, 3JCP=5.0 Hz), MS m/z (EI) 293 .

Diethyl 2,2-dicyano-1-(naphthalen-1-yl) ethylphosphonate (4h) (172 mg, 50%) as a solid: mp 104-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) d 8.00 (d, 1H, $^{3}J_{HH}$=7.8 Hz), 7.90 (d, 2H, $^{3}J_{HH}$=7.8 Hz), 7.82-7.80 (m, 1H), 7.65-7.50 (m, 3H), 4.69-4.55 (m, 2H), 4.23-4.16 (m, 2H), 3.85-3.74 (m, 1H), 3.45-3.34 (m, 1H), 1.35 (t, 3H, $^{3}J_{HH}$=7.2 Hz), 0.81 (t, 3H, $^{3}J_{HH}$ =6.9 Hz); 13C NMR (75 MHz) d 134.2, 131.7, 130.2, 129.5, 127.6, 127.5, 126.6, 126.5, 125.3, 122.1, 111.7 (d, $^{3}J_{CP}$=7.2 Hz), 111.6 (d, $^{3}J_{CP}$=15.3 Hz), 64.5 (d, $^{2}J_{CP}$=7.1 Hz), 63.5 (d, $^{2}J_{CP}$=7.6 Hz), 38.2 (d, $^{1}J_{CP}$=142.8 Hz), 25.6, 16.3 (d, $^{3}J_{CP}$=6.6 Hz), 15.9 (d, $^{3}J_{CP}$=5.4 Hz); IR (KBr) 2985, 2857, 2612, 2366, 2260,1390,1243,1025 cm^{-1}; HRMSm/z (Mþ) calcd for $C_{18}H_{19}N_2O_3P$: 342.1133; found: 342.1134.

Diethyl 1-(2-chlorophenyl)-2,2-dicyanoethylphosphonate (4i). yellow solid, mp 77 °C; dH (400 MHz, $CDCl_3$), 7.75 (d, 1H, $^{3}J_{HH}$=5.3 Hz). 7.47 (s, 1H), 7.35 (d, 2H, $^{3}J_{HH}$=4 Hz) 4.61 (t, 1H, $^{3}J_{HH}$=8.5 Hz), 4.46 (dd, 1H, $^{3}J_{HH}$=8.2, $^{1}J_{HP}$=21.2 Hz), 3.75-4.30 (m, 4H), 1.36 (t, 3H, $^{3}J_{HH}$=7.0 Hz), 1.11 (t, 3H, $^{3}J_{HH}$=7.0 Hz), ^{13}C NMR (75 MHz) d 135.7, 130.8, 129.6, 129.0, 111.4 (d, $^{3}J_{CP}$=10.9 Hz), 111.2 (d, $^{3}J_{CP}$=13.2 Hz), 64.4 (d, $^{2}J_{CP}$=7.1 Hz), 63.6 (d, $^{2}J_{CP}$=7.1 Hz), 43.8 (d, $^{1}J_{CP}$=143.4 Hz), 25.5, 16.3 (d, $^{3}J_{CP}$=6.6 Hz), 16.2 (d, $^{3}J_{CP}$=5.5 Hz); IR (KBr) 2993, 2854, 2612, 2257, 1931, 1587, 1493, 1239, 1021 cm^{-1}; MS (m/z, EI) 326 (M+, 16).

Diethyl 2,2-dicyano-1-(4-methoxyphenyl)ethylphosphonate (4j). yellow solid, mp 61 °C; dH (400 MHz, CDCl3) 7.41-7.44 (m, 2H). 6.97 (d, 2H, $^{3}J_{HH}$=8.8 Hz), 4.51 (dd, 1H, $^{3}J_{HH}$=8.0 Hz, $^{3}J_{HP}$=8.8 Hz), 4.00-4.24 (m, 4H), 3.84 (s, 3H), 3.57 (dd, 1H, $^{3}J_{HH}$=8.0 Hz, $^{2}J_{HP}$=21.2 Hz), 1.37 (t, 3H, $^{3}J_{HH}$=7.2 Hz), 1.17 (t, 3H, $^{3}J_{HH}$=7.2 Hz), 13C NMR (75 MHz) d 159.9, 131.7 (d, $^{3}J_{CP}$=6.0 Hz), 130.2, 121.4 (d, $^{3}J_{CP}$=6.0 Hz), 114.9, 114.8, 111.6 (d, $^{3}J_{CP}$=4.9 Hz), 111.5 (d, $^{3}J_{CP}$=7.2 Hz), 64.2 (d, $^{2}J_{CP}$=6.6 Hz), 63.2 (d, $^{2}J_{CP}$=7.1 Hz), 55.2, 44.0 (d, $^{1}J_{CP}$=142.8 Hz), 25.3, 16.0 (d, $^{3}J_{CP}$=6.0 Hz), 15.9 (d, $^{3}J_{CP}$=6.0 Hz); IR (neat) 2980, 2920, 2597, 2257, 1597, 1471, 1249, 1164, 1031 cm^{-1}; MS (m/z, EI) 322.

Diethyl 1-(3-bromophenyl)-2,2-dicyanoethylphosphonate (4k). Yield 0.31 g, 84%; white solid, mp 78-79 °C; MS (m/z, EI) 372 (M+). Found: C, 44.33; H, 4.12; N, 7.39. $C_{14}H_{16}BrN_2O_3P$ requires C, 45.30; H, 4.34; N, 7.55%]; Rf (50% n-hexane/EtOAc) 0.46; ymax (KBr) 2242 (CN), 1003 (P]O) cm^{-1}; dH (400 MHz, $CDCl_3$) 1.14 (t, 3H, $^{3}J_{HH}$=7.2 Hz), 1.31 (t, 3H, $^{3}J_{HH}$=7.2 Hz), 3.65 (dd, 1H, $^{3}J_{HH}$=7.6 Hz, $^{2}J_{HP}$=21.6 Hz), 3.81-4.19 (m, 4H), 4.7 (dd, 1H, $^{3}J_{HH}$=8.0 Hz, $^{2}J_{HP}$=9.2 Hz), 7.28 (t, 1H, $^{3}J_{HH}$=8.0 Hz), 7.44 (d, 1H, $^{3}J_{HH}$=7.2 Hz), 7.52 (d, 1H, $^{3}J_{HH}$=8.0 Hz), 7.62 (s, 1H); dC (100 MHz, CDCl3) 16.1 (d, $^{3}J_{CP}$=5.0 Hz), 16.2 (d, $^{3}J_{CP}$=6.0 Hz), 25.3, 43.8 (d, $^{1}J_{CP}$=143.0 Hz), 63.6 (d, $^{2}J_{CP}$=7.0 Hz), 64.4 (d, $^{2}J_{CP}$=7.0 Hz), 111.3 (d, $^{3}J_{CP}$=12.1 Hz), 111.4 (d, $^{3}J_{CP}$=11.1 Hz), 123.1, 127.9 (d, $^{3}J_{CP}$=6.0 Hz), 130.8, 132.4 (d, $^{2}J_{CP}$=6.0 Hz), 132.6, 132.8 (d, $^{3}J_{CP}$=6.0 Hz); IR (neat) 2980, 2920, 2597, 2257, 1597, 1471, 1249, 1164, 1031 cm^{-1}; MS (m/z, EI) 370 .

Diethyl 1-(4-bromophenyl)-2,2- Dicyanoethylphosphonate (4l) solid: mp 96-98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) d 7.56 (d, 2H, $^{3}J_{HH}$=8.4 Hz), 7.35 (d, 2H, $^{3}J_{HH}$=8.4 Hz), 4.45 (dd, 1H, $^{3}J_{HH}$=7.8 Hz and $^{3}J_{HP}$=8.7 Hz), 4.19-4.11 (m, 2H), 4.07-3.97 (m, 1H), 3.88-3.77 (m, 1H), 3.52 (dd, 1H, $^{3}J_{HH}$=7.5 Hz and $^{2}J_{HP}$=21.3 Hz), 1.33 (t, 3H, $^{3}J_{HH}$=6.9 Hz), 1.16 (t, 3H, $^{3}J_{HH}$=7.2 Hz); ^{13}C NMR (75 MHz) d 132.6, 131.0 (d, $^{3}J_{CP}$=6.0 Hz), 129.5 (d, $^{3}J_{CP}$=6.0 Hz), 124.0, 111.4 (d, $^{3}J_{CP}$=10.5 Hz), 111.2 (d, $^{3}J_{CP}$ =11.5 Hz), 64.5 (d, $^{2}J_{CP}$=7.1 Hz), 63.6 (d, $^{2}J_{CP}$ =6.6 Hz), 44.0 (d, $^{1}J_{CP}$=143.4 Hz), 25.4, 16.3 (d, $^{3}J_{CP}$=6.1 Hz), 16.2 (d, $^{3}J_{CP}$=5.5 Hz); IR (KBr) 2991, 2853, 2613, 2377, 2256,1492,1238,1020 cm^{-1};MS (m/z, EI) 371 .

Diethyl 2,2-dicyano-1-(naphthalen-2-yl) ethylphosphonate (4m) solid: mp 88-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) d 7.88 (s, 1H), 7.80-7.74 (m, 3H), 7.49-7.40 (m, 3H), 4.68 (t, 1H, $^{3}J_{HH}$=8.4 Hz), 4.07-4.05 (m, 2H), 3.95-3.82 (m, 1H), 3.79-3.76 (m, 1H), 3.67 (dd, 1H, $^{3}J_{HH}$=8.1 Hz and $^{2}J_{HP}$=19.2 Hz),1.23 (t, 3H, $^{3}J_{HH}$=6.6 Hz), 0.96 (t, 3H, $^{3}J_{HH}$=6.9 Hz); 13C NMR (75 MHz) d 133.3, 133.2, 129.3, 129.1, 128.1, 127.8, 127.7, 127.1, 126.8, 126.0 (d, $^{3}J_{CP}$=4.9 Hz), 111.6 (d, $^{3}J_{CP}$=7.6 Hz), 111.5 (d, $^{3}J_{CP}$=12.0 Hz), 64.3 (d, $^{2}J_{CP}$=6.6 Hz), 63.4 (d, $^{2}J_{CP}$=7.2 Hz),

44.5 (d, $^{1}J_{CP}$=142.8 Hz), 25.6, 16.2 (d, $^{3}J_{CP}$=5.4 Hz), 16.0 (d, $^{3}J_{CP}$=5.4 Hz); IR (KBr) 3056, 2984, 2864, 2612, 2494, 2255, 1711, 1605, 1386, 1237, 1015 cm^{-1}; MS (m/z, EI) 342 (M+) .

Diethyl 1,1-dicyanopentan-2-ylphosphonate (4n) dH (250 MHz, $CDCl_3$) 4.29-4.35 (m,1H); 4.25 - 4.16 (m, 4H) 2.34- 2.29, (m, 1H), 2.10- 1.73 (m, 2H), 1.61 (q, 2H, $^{3}J_{HH}$=7.0 Hz), 1.37 (t, 6H, $^{3}J_{HH}$=7.0 Hz),1.00 (t, 3H, $^{3}J_{HH}$=7.0 Hz); dC (75 MHz,$CDCl_3$) 112.2 (d, $^{3}J_{CP}$=17.0 Hz); 110.7 (d, $^{3}J_{CP}$=5.0 Hz), 37.8 (d, $^{1}J_{CP}$=144.9 Hz), 29.2, 20.7 (d, $^{2}J_{CP}$=7.6 Hz), 16.3 (d, $^{3}J_{CP}$=5.6 Hz), 13.73 MS(m/z (EI,) 259(M+) . IR (KBr) 2240, 1011 cm^{-1}

Structural data of compounds 6

General procedure for the synthesis of 2 amino-3-cyno 4 H -chromen -4-yl phosphonate. : The mixture of salicylaldehyde **5**(2.0 mmol) and malononitrile 2 (2.2 mmol) and lithium perchlorate 0.5 mmol) in ethanol (30 mL) was electrolyzed in beaker equipped with a magnetic stirrer, graphite anode and iron cathode, under constant current density of 10 mA/cm^2). After completion of the reaction (monitored by TLC). Tri ethyl phosphite (2.4 mmol) was added to the reaction mixture. The solvent was evaporated under reduced pressure and reaction mixture was added by water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate as eluent to afford an analytically pure sample of product **6**. All the compounds are known and were characterized by comparison of their spectral data with those reported in the literature.

Diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate(6a): (mg, 90%) as a solid: mp 143-145 ^{o}C; ^{1}H NMR (300 MHz, acetone-d6) d 7.39-7.35 (1H, m), 7.33-7.27 (1H, m), 7.19-7.13 (1H, m), 7.00 (1H, d, J=8.1 Hz), 6.36 (2H, br s), 4.09-3.90 (5H, m), 1.27 (3H, t, J=6.9 Hz), 1.17 (3H, t, J=6.9 Hz); 13C NMR (75 MHz, DMSO-d6) d 162.6, 149.9, 129.5, 128.7, 124.2, 120.1, 117.7, 115.9, 62.3 (d, $^{2}J_{CP}$=7.2 Hz), 62.1 (d, $^{2}J_{CP}$ =7.1 Hz), 47.4 (d, $^{2}J_{CP}$ =7.6 Hz), 34.5 (d, $^{1}J_{CP}$ =144.9), 16.2, 16.1; IR (KBr) 3343, 3167, 2985, 2190, 1656, 1418, 1236, 1034, 967, 766 cm^{-1}; MS (m/z, EI) 308.

Diethyl 2-amino-3-cyano-6-methoxy-4H-chromen-4- ylphosphonate (6b):: solid: mp 180-182 ^{o}C; ^{1}H NMR (300 MHz, acetone-d6) d 6.96 (1H, s), 6.93-6.91 (1H, m), 6.87-6.84 (1H, m), 6.30 (2H, br s), 4.08-3.89 (4H, m), 3.92 (1H, d, $^{2}J_{PH}$=18.0 Hz), 3.78 (3H, s), 1.28 (3H, t, J=6.9 Hz), 1.19 (3H, t, J=6.9 Hz); ^{13}C NMR (75 MHz, DMSO-d6) d

163.0, 155.5, 144.0, 120.4, 118.7, 118.6, 116.8, 114.2, 62.5 (d, $^{2}J_{CP}$=7.1 Hz), 62.3 (d, $^{2}J_{CP}$ =7.1 Hz), 55.5, 47.0 (d, 2JCP=7.6 Hz), 34.9 (d, $^{1}J_{CP}$ =144.5 Hz), 16.3, 16.2; IR (KBr) 3420, 3151, 2983, 2187, 1647, 1509, 1408, 1221, 1036, 963 cm^{-1}; HRMSm/z (Mþ) calcd for $C_{15}H_{19}N_2O_5P$: 338.1032; found: 338.1035.

Diethyl 2-amino-3-cyano-8-methyl-4H-chromen-4- ylphosphonate (6c): solid: mp 160-162 °C; ^{1}H NMR (300 MHz, acetone-d6) d 7.18-7.13 (2H, m), 7.06-7.01 (1H, m), 6.40 (2H, br s), 4.05-3.94 (4H, m), 3.90 (1H, d, $^{2}J_{PH}$=15.3 Hz), 2.25 (3H, s), 1.26 (3H, t, J=6.9 Hz), 1.17 (3H, t, J=6.9 Hz); 13C NMR (75 MHz, DMSO-d6) d 162.8, 148.3, 129.9, 126.9, 124.9, 123.6, 120.1, 117.5, 62.3 (d, $^{2}J_{CP}$=7.1 Hz), 62.1 (d, $^{2}J_{CP}$=7.1 Hz), 47.5 (d, $^{2}J_{CP}$ =7.1 Hz), 34.8 (d, $^{1}J_{CP}$ =144.5 Hz), 16.2, 16.1, 15.0; IR (KBr) 3348, 3183, 2985, 2189, 1651, 1597, 1412, 1223, 1038, 968 cm-^{1}; HRMS m/z (M) calcd for $C_{15}H_{19}N_2O_4P$: 322.1082; found: 322.1085.

Diethyl 2-amino-3-cyano-7-methoxy-4H-chromen-4- ylphosphonate (6d): solid: mp 218-220 °C; ^{1}H NMR (300 MHz, DMSO-d6) d 7.22 (1H, dd, J=8.4 and 1.8 Hz), 7.01 (2H, br s), 6.75 (1H, dd, J=8.4 and 2.1 Hz), 6.57 (1H, d, J=2.1 Hz), 4.05-3.90 (5H, m), 3.78 (3H, s), 1.23 (3H, t, J=7.2 Hz), 1.16 (3H, t, J=7.2 Hz); ^{13}C NMR (75 MHz, DMSO-d6) d 162.6, 159.6, 150.7, 130.2, 120.2, 110.6, 109.3, 101.3, 62.3 (d, $^{2}J_{CP}$=7.2 Hz), 62.2 (d, $^{2}J_{CP}$=6.5 Hz), 55.5, 47.7 (d, 2JCP=7.1 Hz), 33.8 (d, $^{1}J_{CP}$=145.5 Hz),16.4,16.3; IR (KBr) 3420, 3151, 2983, 2187, 1647, 1509, 1408, 1221, 1158, 1036 cm_1; HRMS m/z (M) calcd for $C_{15}H_{19}N_2O_5P$: 338.1032; found: 338.1029

Diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4- ylphosphonate (6e): ^{1}H NMR (300 MHz, acetone-d6) d 7.53 (1H, s), 7.46 (1H, d, J=8.7 Hz), 6.99 (1H, d, J=8.7 Hz), 6.46 (2H, br s), 4.12-3.98 (5H, m), 1.28 (3H, t, J=6.9 Hz), 1.20 (3H, t, J=6.9 Hz); 13C NMR (75 MHz, acetone-d6) d 163.2, 150.6, 133.2, 132.5, 121.5, 119.7, 119.1, 117.0, 63.5 (d, $^{2}J_{CP}$=7.1 Hz), 63.3 (d, $^{2}J_{CP}$ =7.2 Hz), 50.6 (d, $^{2}J_{CP}$ =8.2 Hz), 36.1 (d, $^{1}J_{CP}$ =146.1 Hz), 16.8, 16.7; IR (KBr) 3342, 3158, 2981, 2919, 2188, 1653, 1420, 1242, 1036, 963 cm-^{1}; MS (m/z, EI) 386 (M.)

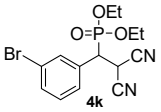
Diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4- ylphosphonate (6f) 165-175 °C; ^{1}H NMR (300 MHz, acetone-d6) d 7.15-7.12 (2H, m), 7.03-7.01 (1H, m), 6.43 (2H, br s), 4.05-3.94 (4H, m), 3.90 (1H, d, $^{2}J_{PH}$=15.3 Hz), 2.27 (3H, s), 1.28 (3H, t, J=6.9 Hz), 1.18 (3H, t, J=6.9 Hz); ^{13}C NMR (75 MHz, DMSO-d6) d 162.8, 148.3, 129.9, 126.9, 124.9, 123.6, 120.1, 117.5, 62.3 (d, $^{2}J_{CP}$=7.1 Hz), 62.1 (d, $^{2}J_{CP}$=7.1 Hz), 47.5 (d, $^{2}J_{CP}$ =7.1 Hz), 34.8 (d, $^{1}J_{CP}$ =144.5 Hz), 16.2, 16.1, 15.0; IR (KBr) 3348, 3183, 2985, 2189, 1651, 1597, 1412, 1223, 1038, 968 cm-^{1}; HRMS m/z (M) calcd for $C_{15}H_{19}N_2O_4P$: 322.1082; found: 322.1085.

Diethyl 2-amino-6,8-dibromo-3-cyano-4H-chromen-4- ylphosphonate (6g):
solid: mp 198-200 °C; ^{1}H NMR (300 MHz, acetone-d6) d 7.76 (1H, t, J=2.1 Hz), 7.54-7.53 (1H, m), 6.73 (2H, br s), 4.12-3.98 (5H, m),1.28 (3H, t, J=7.2 Hz),1.20 (3H, t, J=6.9 Hz); 13C NMR (75 MHz, DMSO-d6) d162.1,146.5,134.1,131.5,122.1, 119.4, 116.0, 110.6, 62.7 (d, $^{2}J_{CP}$=7.1 Hz), 62.6 (d, $^{2}J_{CP}$=7.1 Hz), 47.5 (d, $^{2}J_{CP}$ =7.7

Hz), 34.6 (d, $^{1}J_{CP}$ =144.5 Hz), 16.3, 16.2; IR (KBr) 3341, 3159, 2984, 2198, 1662, 1412, 1235, 1165, 1040, 861 cm-^{1}; MS (m/z, EI) 466 .

Diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4- ylphosphonate (6h): solid: mp 180-182 ^{o}C; ^{1}H NMR (300 MHz, acetone-d6) d 7.16 (1H, s), 7.10 (1H, d, J=8.4 Hz), 6.90 (1H, d, J=8.4 Hz), 6.48 (2H, br s), 4.08-3.92 (4H, m), 3.88 (1H, d, $^{2}J_{PH}$=17.7 Hz), 2.30 (3H, s), 1.26 (3H, t, J=7.2 Hz), 1.18 (3H, t, J=7.2 Hz); ^{13}C NMR (75 MHz, DMSO-d6) d 162.8, 148.0, 133.3, 129.7, 129.2, 120.2, 117.4, 115.7, 62.3 (d, $^{2}J_{CP}$=7.2 Hz), 62.2 (d, $^{2}J_{CP}$=7.1 Hz), 47.3 (d, $^{2}J_{CP}$=7.6 Hz), 34.5 (d, $^{1}J_{CP}$ =144.4 Hz), 20.3, 16.3, 16.2; IR (KBr) 3355, 3166, 2985, 2188, 1646, 1496, 1420, 1231, 1030, 811 cm_1; MS (m/z, EI) 322 .

Diethyl 3-amino-2-cyano-1H-benzo[f]chromen-1- ylphosphonate (6i) solid: mp 220-222 ^{o}C; ^{1}H NMR (300 MHz, acetone-d6) d 8.23 (1H, d, J=8.7 Hz), 7.92 (2H, d, J=8.4 Hz), 7.63-7.58 (1H, m), 7.52-7.47 (1H, m), 7.26 (1H, d, J=8.7 Hz), 6.81 (2H, br s), 4.65 (1H, d, $^{2}J_{PH}$=16.5 Hz), 4.00-3.83 (4H, m), 1.16-1.09 (6H, m); 13C NMR (75 MHz, DMSO-d6) d 163.3, 148.5, 130.7, 130.3, 129.6, 128.0, 126.6, 125.2, 124.9, 120.3, 116.7, 112.0, 62.4 (d, $^{2}J_{CP}$=7.1 Hz), 62.1 (d, $^{2}J_{CP}$=6.6 Hz), 48.2 (d, $^{2}J_{CP}$=7.1 Hz), 31.9 (d, $^{1}J_{CP}$=145.5 Hz), 16.3 (d, $^{3}J_{CP}$=5.5 Hz), 16.2 (d, $^{3}J_{CP}$=5.5 Hz); IR (KBr) 3361, 3169, 2981, 2191, 1660, 1418, 1237, 1035, 812 cm_1; HRMS m/z (M+) calcd for $C_{18}H_{19}N_2O_4P$: 358.1082; found: 358.1080.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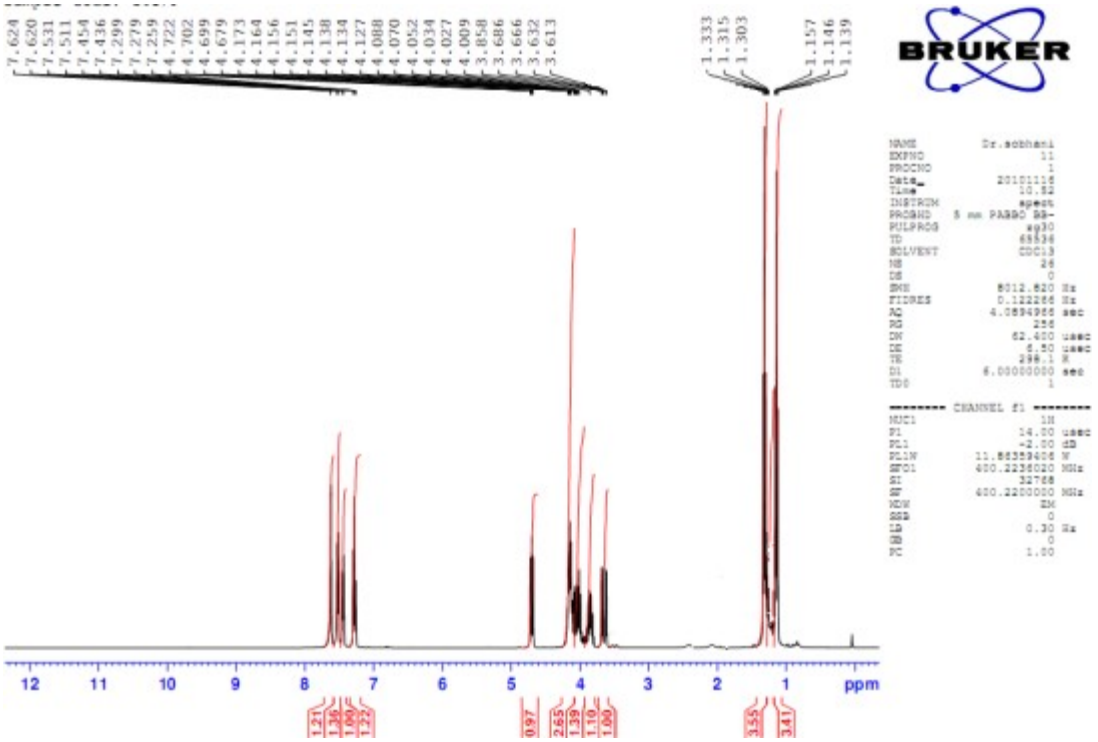
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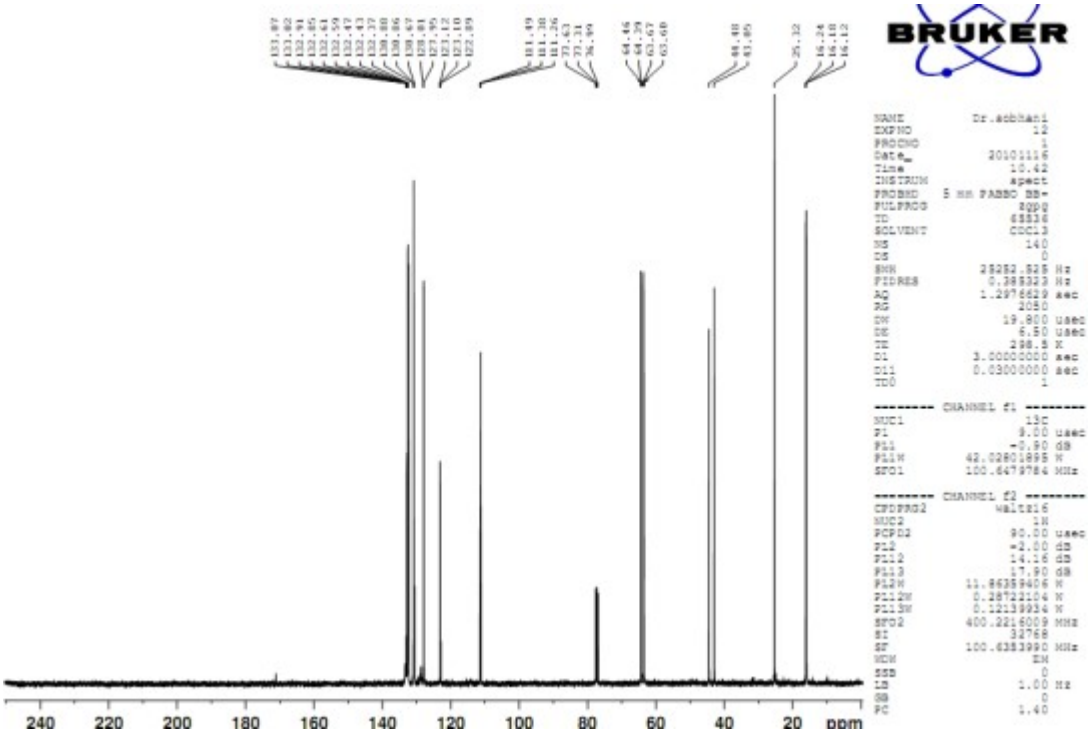
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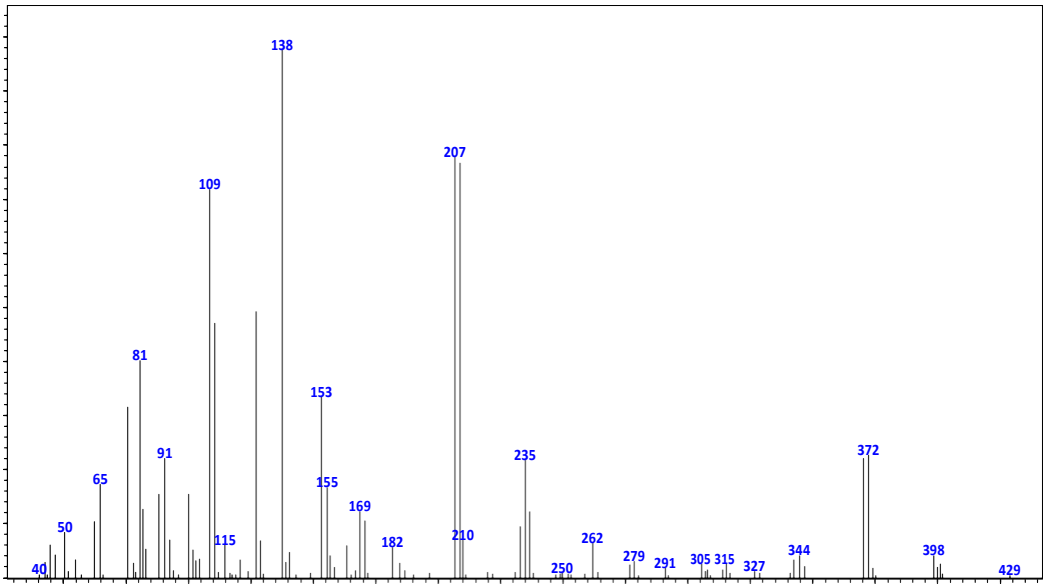
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