Supporting information

Pyridine-grafted graphene oxide: a reusable acid-base bifunctional catalyst for the one-pot synthesis of β-phosphonomalonates via cascade Knoevenogel-phospha Michael addition reaction in water

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1) General information

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded on a Bruker Advance DPX-400, 300 and 250 in $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A and Agilent Technology (HP). The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV254 plates. FT-IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). TEM analysis was performed using TEM microscope (Philips CM30). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were determined by using a SEM Phenom, model PROX. Thermo gravimetric analysis (TGA) was performed using a Shimadzu thermo gravimetric analyzer (TG-50). Elemental analysis was carried out on a Costech 4010 CHNS elemental analyzer. Power X-ray diffraction (XRD) was performed on a X'Pert Pro MPD diffractometer with Cu Kα (λ = 0.154 nm) radiation. The UV-Vis spectra were carried out by using a Shimadzu UV-160 A spectrophotometer.

2) General procedure for the synthesis of β-phosphonomalonates

A mixture of aldehyde (1 mmol), malononitrile (1 mmol), diethyl phosphite (2 mmol) and Py-GO (3 mol%) was refluxed at 100 °C for an appropriate time (Table 2). The catalyst was separated by centrifugation. The supernatant was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulting product (**1-15**) was purified by chromatography on silica (*n*-hexane/EtOAc: 1/1).

3) Spectral data of β-phosphonomalonates

[1-Phenyl-2,2-dicyanoethyl] phosphonic acid diethyl ester (1)

Yellow solid, mp 53-54 °C; R_f = 0.40 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.08-1.18 (m, 3H), 1.25-1.37 (m, 3H), 3.65 (dd, 1H, $^3J_{HH}$ = 8.0, $^2J_{HP}$ = 21.0 Hz), 4.02-4.19 (m, 4H), 4.55 (t, 1H, $^3J_{HH}$ = 8.3 Hz), 7.43 (s, 5H) ppm; ^{13}C NMR (62 MHz,$CDCl_3$): δ 16.1 (d, $^3J_{CP}$ = 5.6 Hz), 16.2 (d, $^3J_{CP}$ = 5.6 Hz), 25.5, 44.6 (d, $^1J_{CP}$ = 144.0 Hz), 63.4 (d, $^2J_{CP}$ = 7.5 Hz), 64.4 (d, $^2J_{CP}$ = 7.0 Hz), 111.1 (d, $^3J_{CP}$ = 12.5 Hz), 111.3 (d, $^3J_{CP}$ = 10.0 Hz), 129.1, 129.2, 129.3, 129.4, 129.5, 129.6 ppm; MS (70 eV): *m/z* = 292 [5%, M^+], 155 [18%, M^+ – $P(O)(OEt)_2$], 129 {100%, M^+ – [$P(O)(OEt)_2$ and CN]}.

[1-(4-Methyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (2)

Yellow solid, mp 97 °C; R_f = 0.44 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, 3H, $^3J_{HH}$ = 7.2 Hz), 1.38 (t, 3H, $^3J_{HH}$ = 7.2 Hz), 2.39 (s, 3H), 3.57 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^2J_{HP}$ = 21.2 Hz), 3.74-3.84 (m, 1H), 3.99-4.08 (m, 1H), 4.14-4.24 (m, 2H), 4.50 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HP}$ = 9.0 Hz), 7.28 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.38 (d, 2H, $^3J_{HH}$ = 8.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.1 (d, 2H, $^3J_{CP}$ = 5.2 Hz), 16.2 (d, 2H, $^3J_{CP}$ = 6.0 Hz), 21.2, 25.6, 44.2 (d, $^1J_{CP}$ = 143.2 Hz), 63.3 (d, $^2J_{CP}$ = 7.5 Hz), 64.3 (d, $^2J_{CP}$ = 7.5 Hz), 111.3 (d, $^3J_{CP}$ = 12.7 Hz), 111.5 (d, $^3J_{CP}$ = 10.5 Hz), 127.1 (d, J_{CP} = 6.0 Hz), 129.1 (d, J_{CP} = 6.0 Hz), 130.1, 139.5 ppm; MS (70 eV): *m/z* = 306 [6%, M^+], 169 [7%, M^+ – $P(O)(OEt)_2$], 143 {100%, M^+ – [$P(O)(OEt)_2$ and CN]}.

[1-(4-Methoxy)-2,2-dicyanoethyl] phosphonic acid diethyl ester (3)

Yellow solid, mp 61 °C; R_f = 0.50 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, 3H, $^3J_{HH}$ = 7.2 Hz), 1.37 (t, 3H, $^3J_{HH}$ = 7.2 Hz), 3.57 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^2J_{HP}$ = 21.2 Hz), 3.84 (s, 3H), 4.00-4.24 (m, 4H), 4.51 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HP}$ = 8.8 Hz), 6.97 (d, 2H, $^3J_{HH}$ = 8.8 Hz), 7.42 (d, 2H, $^3J_{HH}$ = 8.8 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0 (d, $^3J_{CP}$ = 6.7 Hz), 16.2 (d, $^3J_{CP}$ = 6.0 Hz), 25.5, 44.3 (d, $^1J_{CP}$ = 142.5 Hz), 55.2, 63.3 (d, $^2J_{CP}$ = 6.0 Hz), 64.2 (d, $^2J_{CP}$ = 6.7 Hz), 111.4 (d, $^3J_{CP}$ = 8.2 Hz), 114.5 (d, $^3J_{CP}$ = 6.0 Hz), 121.4 (d, J_{CP} = 8.2 Hz), 130.3, 131.8, 160.0 ppm; MS (70 eV): *m/z* = 323 [4%, M^+ + 1], 322 [23%, M^+], 185 [18%, M^+ – $P(O)(OEt)_2$] 121 {100%, M^+ – [$P(O)(OEt)_2$ and $CH(CN)_2$]}.

[1-(3-Methoxyphenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (4)

Yellow liquid; R_f = 0.50 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.10 (t, 3H, $^3J_{HH}$ = 6.7 Hz), 1.31 (t, 3H, $^3J_{HH}$ = 6.5 Hz), 3.56 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^2J_{HP}$ = 21.0 Hz), 3.78 (s, 3H), 3.94-4.15 (m,4H), 4.56 (t, 1H, $^3J_{HH}$ = 8.0 Hz), 6.91 (d, 2H, $^3J_{HH}$ = 7.5 Hz), 7.00 (s, 1H), 7.30 (t, 1H, $^3J_{HH}$ = 7.5 Hz) ppm;^{13}C NMR (62 MHz, $CDCl_3$): δ 16.1 (d, $^3J_{CP}$ = 6.3 Hz), 16.2 (d, $^3J_{CP}$ = 6.9 Hz), 25.5, 44.5 (d, $^1J_{CP}$ = 144.9 Hz), 55.3, 63.4 (d, $^2J_{CP}$ = 7.6 Hz), 64.4 (d, $^2J_{CP}$ = 6.9 Hz), 111.2 (d, $^3J_{CP}$ = 11.2 Hz) , 111.3 (d, $^3J_{CP}$ = 10.0 Hz), 114.9 (d, J_{CP} = 6.8 Hz), 121.4, 130.4, 131.6, 160.0, 160.3 ppm; MS (70 eV): *m/z* = 323 [3%, M^+ + 1], 322 [13%, M^+], 185 [8%, M^+ – $P(O)(OEt)_2$], 121 {100%, M^+ – [$P(O)(OEt)_2$ and $CH(CN)_2$}.

[1-(4-Chlorophenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (5)

Yellow solid, mp 98°C; R_f = 0.53 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.16 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 1.33 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 3.62 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^2J_{HP}$ = 21.5 Hz), 3.82-4.19 (m, 4 H), 4.55 (t, 1H, $^3J_{HH}$ = 7.7 Hz), 7.42 (s, 4H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ 16.1 (d, $^3J_{CP}$ = 5.0 Hz), 16.2 (d, $^3J_{CP}$ = 5.6 Hz), 25.5, 43.9 (d, $^1J_{CP}$ = 144.7 Hz), 63.5 (d, $^2J_{CP}$ = 7.0 Hz), 64.4 (d, $^2J_{CP}$ = 7.0 Hz), 111.0 (d, $^3J_{CP}$ = 11.9 Hz), 111.2 (d, $^3J_{CP}$ = 11.3 Hz), 128.8, 129.6, 130.7, 135.7 ppm; MS (70 eV): *m/z* = 326 [16%, M^+], 328 [5%, M^+ + 2], 189 [31%, M^+ – $P(O)(OEt)_2$], 191 [10%, (M^+ + 2) – $P(O)(OEt)_2$], 163 {100%, M^+ – [$P(O)(OEt)_2$ and CN]}, 165 [33%, (M^+ + 2) – $P(O)(OEt)_2$ and CN].

[1-(3-Chlorophenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (6)

Yellow liquid; $R_f = 0.56$ (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, 3H, $^3J_{HH}$ = 7.2 Hz), 1.38 (t, 3H, $^3J_{HH}$ = 7.2 Hz), 3.60 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^2J_{HP}$ = 21.2 Hz), 3.83-3.93 (m, 1H), 4.03-4.26 (m, 3H), 4.56 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HP}$ = 9.2 Hz), 7.41-7.44 (m, 3H), 7.49 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0 (d, $^3J_{CP}$ = 5.2 Hz), 16.2 (d, $^3J_{CP}$ = 6.0 Hz), 25.3, 43.8 (d, $^1J_{CP}$ = 142.5 Hz), 63.6 (d, $^2J_{CP}$ = 6.7 Hz), 64.4 (d, $^2J_{CP}$ = 6.7 Hz), 111.3 (d, $^3J_{CP}$ = 12.0 Hz), 111.4 (d, $^3J_{CP}$ = 12.0 Hz), 127.5 (d, J_{CP} = 6.7 Hz), 129.5 (d, J_{CP} = 6.7 Hz), 129.6, 130.6, 132.6 (d, J_{CP} = 6.0 Hz), 135.0 ppm, MS (70 eV): *m/z* = 326 [12%, M^+], 328 [4%, M^+ + 2], 163 {100%, M^+ – [P(O)$(OEt)_2$ and CN]}, 165 {33%, (M^+ + 2) – [P(O)$(OEt)_2$ and CN]}.

[1-(2-Chlorophenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (7)

Yellow solid, mp 77 °C; $R_f = 0.57$ (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.11 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 1.35 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 3.75-4.30 (m, 4H), 4.46 (dd, 1H, $^3J_{HH}$ = 8.2, $^2J_{HP}$ = 21.2 Hz), 4.61 (t, 1H, $^3J_{HH}$ = 8.5 Hz), 7.35 (d, 2H, $^3J_{HH}$ = 4 Hz), 7.47 (s, 1H), 7.75 (d, 1H, $^3J_{HH}$ = 5.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.9 (d, $^3J_{CP}$ = 6.0 Hz), 16.1 (d, $^3J_{CP}$ = 6.0 Hz), 24.8, 43.7 (d, $^1J_{CP}$ = 142.5 Hz), 63.5 (d, $^2J_{CP}$ = 7.5 Hz), 64.3 (d, $^2J_{CP}$ = 7.5 Hz), 111.2 (d, $^3J_{CP}$ = 11.2 Hz), 113.8 (d, $^3J_{CP}$ = 11.2 Hz), 127.7, 128.7, 129.6, 130.3, 130.5, 135.0 ppm, ; MS (70 eV): *m/z* = 327 [100%, M^+ + 1], 329 [26%, M^+ + 3], 291 [84%, M^+ – Cl], 189 [15%, M^+ – P(O)$(OEt)_2$], 191 [5%, (M^+ + 2) – P(O)$(OEt)_2$], 163 {6%, M^+ – [P(O)$(OEt)_2$ and CN]}, 165 {3%, (M^+ + 2) – P(O)$(OEt)_2$ and CN]}.

[1-(4-Bromophenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (8)

White solid, mp 102 °C; R_f= 0.44 (*n*-hexane/EtOAc: 1/1); ^{1}HNMR (250 MHz, $CDCl_3$): δ 1.16 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 1.33 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 3.58 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^2J_{HP}$ = 21.5 Hz), 3.79-4.18 (m, 4H), 4.56 (t, 1H, $^3J_{HH}$, $^3J_{HP}$ = 7.7 Hz), 7.36 (d, 2H, $^3J_{HH}$ = 8.2 Hz), 7.56 (d, 2H, $^3J_{HH}$ = 8.0 Hz) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ 16.1 (d, $^3J_{CP}$ = 4.4 Hz), 16.2 (d, $^3J_{CP}$ = 5.7

Hz), 25.4, 43.9 (d, ${}^{1}J_{CP}$ = 144.7 Hz), 63.6 (d, ${}^{2}J_{CP}$ = 7.5 Hz), 64.4 (d, ${}^{2}J_{CP}$ = 7.5 Hz), 111.0 (d, ${}^{3}J_{CP}$ = 11.9 Hz), 111.2 (d, ${}^{3}J_{CP}$ = 10.7 Hz), 123.9, 129.4, 131.0, 132.5 ppm; MS (70 eV): *m/z* = 370 [7%, M^+], 372 [8%, M^+ + 2], 233 [12%, M^+ – P(O)$(OEt)_2$], 235 [12%, (M^+ + 2) – P(O)$(OEt)_2$], 207 {99%, M^+ – P(O)$(OEt)_2$ and CN]}, 209 {100%, (M^+ + 2) – P(O)$(OEt)_2$ and CN]}.

[1-(3-Bromophenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (9)

White solid, mp 78-79 °C; R_f = 0.46 (*n*-hexane/EtOAc: 1/1); ^{1}HNMR (400 MHz, $CDCl_3$): δ 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), 3.85-4.17 (m, 4H), 4.70 (dd, 1H, ${}^{3}J_{HH}$= 8.0 Hz, ${}^{2}J_{HP}$ = 9.2 Hz), 7.27 (t, 1H, ${}^{3}J_{HH}$ = 8.0 Hz), 7.43 (d, 1H, ${}^{3}J_{HH}$ = 7.2 Hz), 7.51 (d, 1H, ${}^{3}J_{HH}$ = 8.0 Hz), 7.62 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, J_{CP} = 6.0 Hz), 130.8, 132.4 (d, J_{CP} = 6.0 Hz), 132.6, 132.8 (d, J_{CP} = 6.0 Hz) ppm; MS (70 eV): *m/z* = 370 [7%, M^+], 372 [7%, M^+ + 2], 234 [7%, M^+ – P(O)$(OEt)_2$], 236 [6%, (M^+ + 2) – P(O)$(OEt)_2$], 207 {56%, M^+ – P(O)$(OEt)_2$ and CN]}, 209 {57%, (M^+ + 2) – P(O)$(OEt)_2$ and CN]}, 137 [100%, P(O)$(OEt)_2$].

[1-(4-Hydroxyphenyl)-2,2-dicyanoethyl] phosphonic acid diethyl ester (10)

Yellow solid, mp 129-131 °C; R_f = 0.55 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.19 (t, 3H, ${}^{3}J_{HH}$ = 7.0 Hz), 1.38 (t, 3H, ${}^{3}J_{HH}$ = 7.0 Hz), 3.53 (dd, 1H, ${}^{3}J_{HH}$ = 7.8 Hz, ${}^{2}J_{HP}$ = 21.3 Hz), 3.79-4.23 (m, 4H), 4.43 (t, 1H, ${}^{3}J_{HH}$, ${}^{3}J_{HP}$ = 8.0 Hz), 6.76 (d, 2H, ${}^{3}J_{HH}$ = 8.4 Hz), 7.25 (d, 2H, ${}^{3}J_{HH}$ = 8.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.1 (d, ${}^{3}J_{CP}$ = 5.2 Hz), 16.2 (d, ${}^{3}J_{CP}$ = 5.2 Hz), 25.7, 43.7 (d, ${}^{1}J_{CP}$ = 145.5 Hz), 63.8 (d, ${}^{2}J_{CP}$ = 7.5 Hz), 64.7 (d, ${}^{2}J_{CP}$ = 6.8 Hz), 111.2 (d, ${}^{3}J_{CP}$ = 12.7 Hz), 111.3 (d, ${}^{3}J_{CP}$ = 9.7 Hz), 116.6, 120.4 (d, J_{CP} = 6.0 Hz), 130.6 (d, J_{CP} = 6.0 Hz), 157.8 ppm; MS (70 eV): *m/z* = 308 [36%, M^+], 243 [89%, M^+ – $CH(CN)_2$], 215 [88%, M^+ – (C_6H_4OH)], 171 [31%, (M^+ – $P(O)(OEt)_2$], 145 {45%, M^+ – $P(O)(OEt)_2$ and CN]}, 107 {100%, M^+ – $P(O)(OEt)_2$ and $CH(CN)_2$]}.

[1,1-Dicyanopentan-2-yl] phosphonic acid diethyl ester (11)

Yellow liquid, R_f = 0.50 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.00 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 1.37 (t, 6H, $^3J_{HH}$ = 7.0 Hz), 1.61 (q, 2H, $^3J_{HH}$ = 7.0 Hz), 1.72-2.09 (m, 2H), 2.29-2.34 (m, 1H), 4.16-4.24 (m, 4H), 4.28-4.48 (m, 1H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ 13.7, 16.3 (d, $^3J_{CP}$ = 5.6 Hz), 20.7 (d, $^2J_{CP}$ = 7.6 Hz), 23.7, 29.2, 37.8 (d, $^1J_{CP}$ = 144.9 Hz), 63.2 (d, $^2J_{CP}$ = 6.8 Hz), 110.7 (d, $^3J_{CP}$ = 5.0 Hz), 112.2 (d, $^3J_{CP}$ = 17.0 Hz) ppm; MS (70 eV): *m/z* = 259 [5%, M^+ + 1], 138 [100%, $HP(O)(OEt)_2$], 193 [35%, M^+ – $(CN)_2$],121 [20%, M^+ – $P(O)(OEt)_2$].

[1,1-Dicyanooctan-2-yl] phosphonic acid diethyl ester (12)

Yellow liquid, R_f = 0.60 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, 3H, $^3J_{HH}$ = 6.8 Hz), 1.23-1.25 (m, 6H), 1.29 (t, 6H, $^3J_{HH}$ = 7.2 Hz), 1.44-1.50 (m, 2H), 1.66-1.78 (m, 1H), 1.85-1.98 (m, 1H), 2.24-2.34 (m, 1H), 4.07-4.16 (m, 4H),4.36 (dd, 1H, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 3.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 13.8, 16.2 (d, $^3J_{CP}$ = 5.0 Hz), 22.3, 23.7, 27.1, 27.2 (d, $^3J_{CP}$ = 6.0 Hz), 28.8, 31.2, 37.7 (d, $^1J_{CP}$ = 143.0 Hz), 63.1 (d, $^2J_{CP}$ = 7.0 Hz), 111.1 (d, $^3J_{CP}$ = 3.0 Hz), 112.3 (d, $^3J_{CP}$ = 17.0 Hz) ppm; MS (70 eV): *m/z* = 301 [1%, M^+ + 1], 163 [16%, M^+ – $P(O)(OEt)_2$], 137 [100%, $P(O)(OEt)_2$]

[1-(4-Chlorophenyl)-2,2-dicyanoethyl] phosphonic acid di*iso*-propyl ester (13)

Yellow solid, mp 111 °C; R_f = 0.62 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, 3H, $^3J_{HH}$ =6.4 Hz), 1.32 (d, 3H, $^3J_{HH}$ =6.0 Hz), 1.38 (d, 6H, $^3J_{HH}$ = 6.0 Hz), 3.51 (dd, 1H, $^3J_{HH}$ = 7.2 Hz, $^2J_{HP}$ = 21.6 Hz), 4.51-4.57 (m, 1H), 4.75-4.82 (m, 1H), 7.43-7.50 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1 (d, $^3J_{CP}$ = 6.0 Hz), 23.8 (d, $^3J_{CP}$ = 5.2 Hz), 23.9, 24.2, 25.7, 44.4

(d, $^1J_{CP}$ = 144.7 Hz), 72.9 (d, $^2J_{CP}$ = 7.5 Hz), 73.8 (d, $^2J_{CP}$ = 7.5 Hz), 111.1 (d, $^3J_{CP}$ = 11.2 Hz), 111.4 (d, $^3J_{CP}$ = 11.2 Hz), 129.1 (d, J_{CP} = 5.2 Hz), 129.6, 130.9 (d, J_{CP} = 6.7 Hz), 135.7 ppm; MS (70 eV): *m/z* = 354 [16%, M^+], 356 [5%, M^+ + 2], 189 [16%, M^+ – P(O)(O-*i*-Pr)$_2$], 191 [5%, (M^+ + 2) – P(O)(O-*i*-Pr)$_2$], 163 {100%, M^+– [P(O)(O-*i*-Pr)$_2$ and CN}, 165 {34%, (M^+ + 2) – [P(O)(O-i-Pr)$_2$ and CN]}.

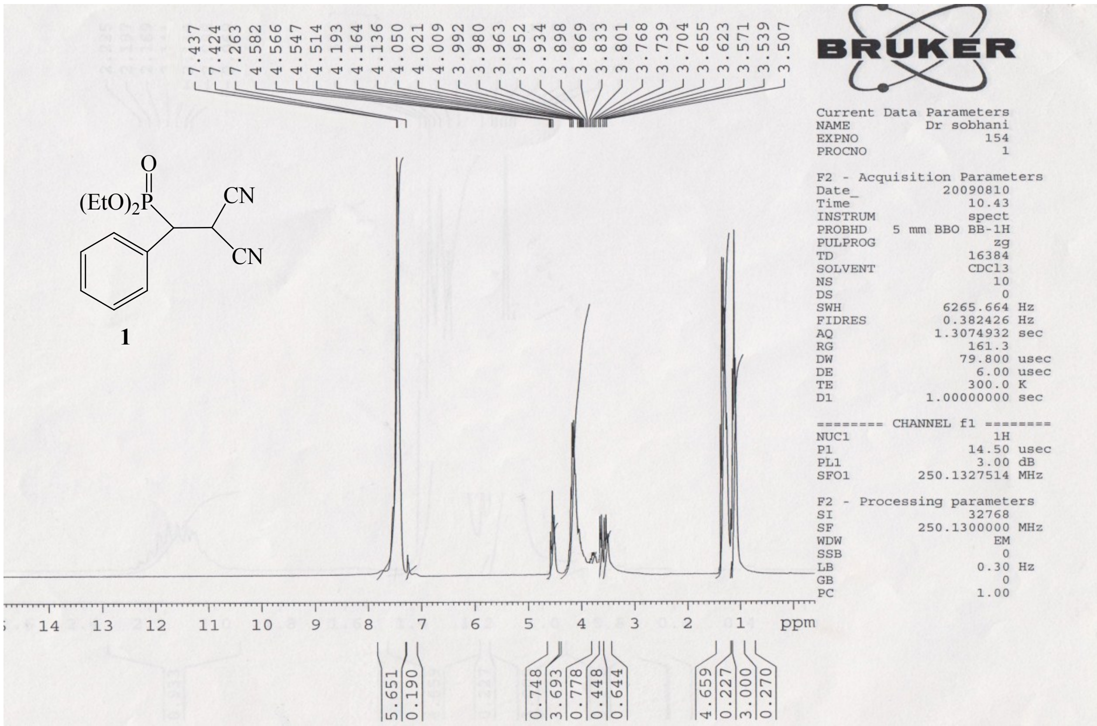
[1-(4-Chlorophenyl)-2,2-dicyanoethyl] phosphonic acid dimethyl ester (14)

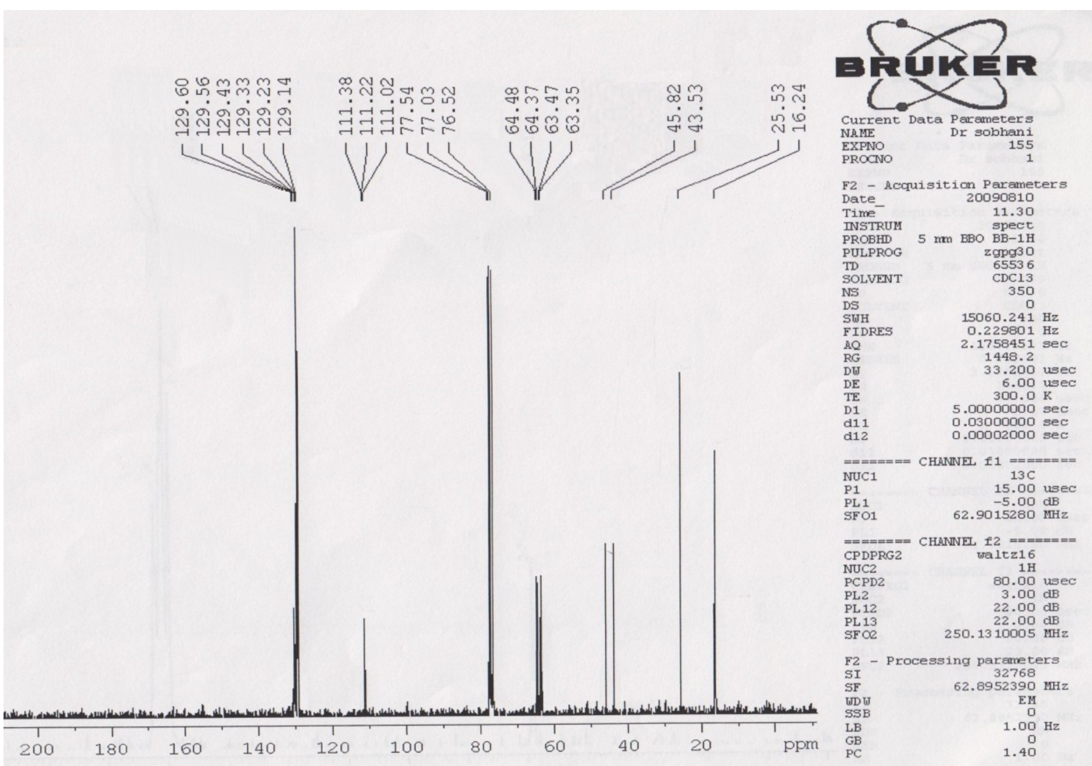
White solid, mp 118 °C; R_f = 0.31 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60-3.68 (m, 4H), 3.85 (d, 3H, $^3J_{HP}$ = 11.2 Hz), 4.51 (t, 1H, $^3J_{HH}$ = 8.0 Hz), 7.50 (s, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.4, 43.4 (d, $^1J_{CP}$ = 144.0 Hz), 53.7 (d, $^2J_{CP}$ = 7.5 Hz), 54.6 (d, $^2J_{CP}$ = 6.7 Hz), 111.2 (d, $^3J_{CP}$ = 10.5 Hz), 111.3 (d, $^3J_{CP}$ = 11.2 Hz), 129.5, 129.7, 130.7 (d, J_{CP} = 6.4 Hz), 135.8 ppm; MS (70 eV): *m/z* = 298 [6%, M^+], 300 [2%, M^+ + 2], 189 [6%, M^+ – P(O)(OMe)$_2$], 191 [2%, (M^+ + 2) – P(O)(OMe)$_2$], 109 [100%, P(O)(OMe)$_2$].

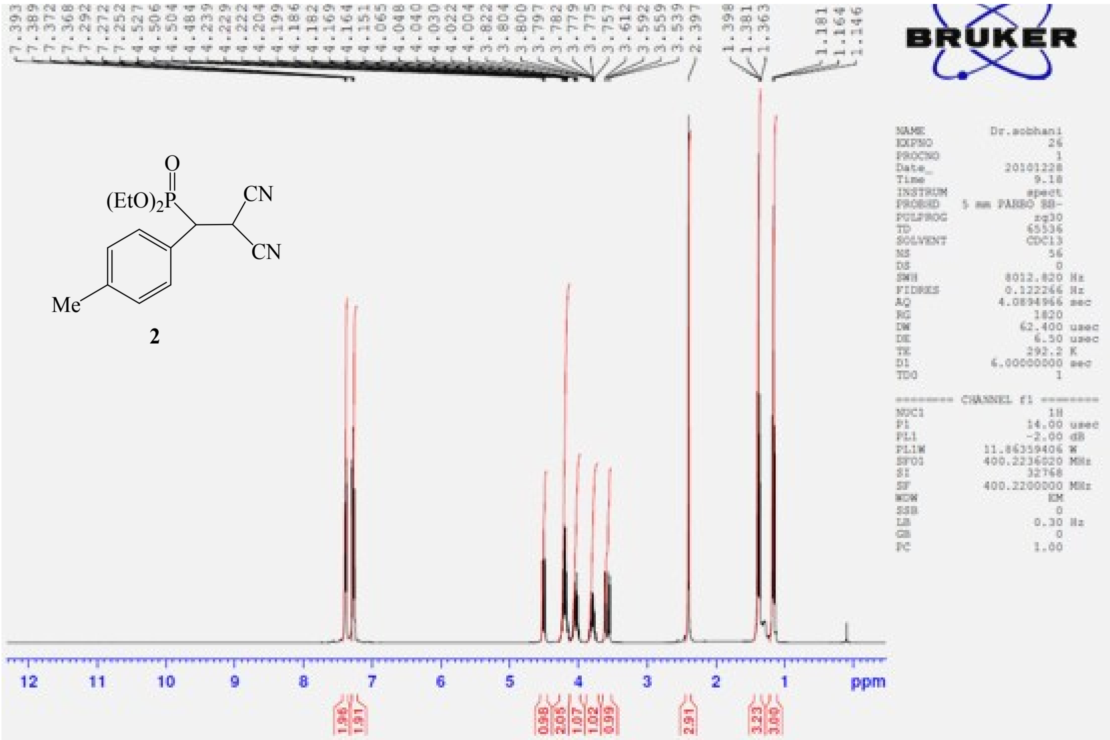
[1-(4-Chlorophenyl)-2-cyano-2-ethylcarboxylic acid ethyl ester] phosphonic acid diethyl ester (15; mixture of two diastereoisomers, ratio ~ 68:32)

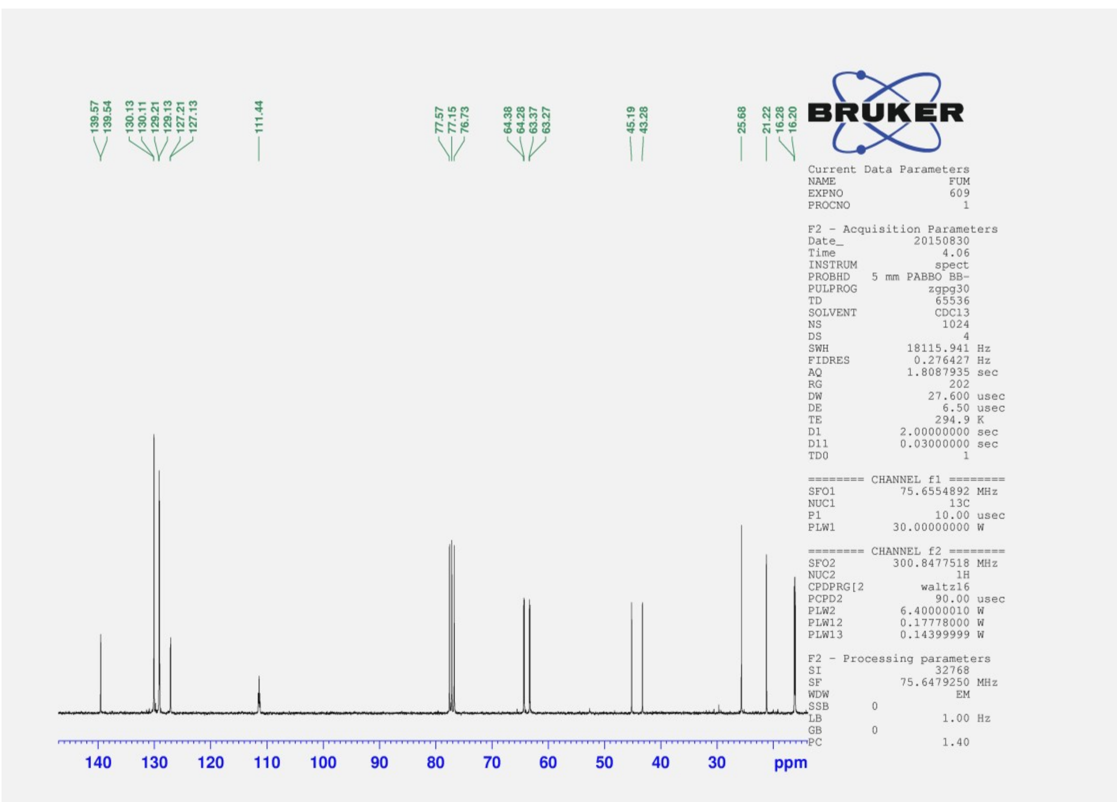
Light yellow liquid, R_f = 0.46 (*n*-hexane/EtOAc: 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10-1.15 (m, 2H), 1.19-1.30 (m, 6H), 1.34 (t, 1H, $^3J_{HH}$ = 7.2 Hz), 3.74-3.85 (m, 1H), 3.96-4.21 (m, 6H), 4.27 (dd, 1H, $^3J_{HH}$ = 6.0 Hz, $^3J_{HP}$ = 8.4 Hz), 7.33-7.35 (m, 3H), 7.44-7.47 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 13.6, 16.0-16.1, 39.0, 39.1, 42.7 (d, $^1J_{CP}$ = 142.5 Hz), 43.3 (d, $^1J_{CP}$ = 142.5 Hz), 62.9 (d, $^2J_{CP}$ = 6.7 Hz), 63.0 (d, $^2J_{CP}$ = 6.7 Hz), 63.1 (d, $^2J_{CP}$ = 5.2 Hz), 63.25, 63.6 (d, $^2J_{CP}$ = 6.7 Hz), 114.5 (d, $^3J_{CP}$ = 9.0 Hz), 114.7 (d, $^3J_{CP}$ = 4.5 Hz), 128.8, 130.1 (d, $^3J_{CP}$ = 6.0 Hz), 130.7 (d, $^3J_{CP}$ = 6.7 Hz), 130.9 (d, $^3J_{CP}$ = 6.0 Hz), 131.1 (d, $^3J_{CP}$ = 6.0 Hz), 134.3, 134.5, 163.9 (d, $^3J_{CP}$ = 12.0 Hz), 164.0 (d, $^3J_{CP}$ = 13.5 Hz) ppm; MS (70 eV): *m/z* = 373 [43%, M^+], 375 [14%, M^+ + 2], {302 [35%, (M^+ + 2) – CO_2Et]}, 300 [100%, M^+ – CO_2Et].

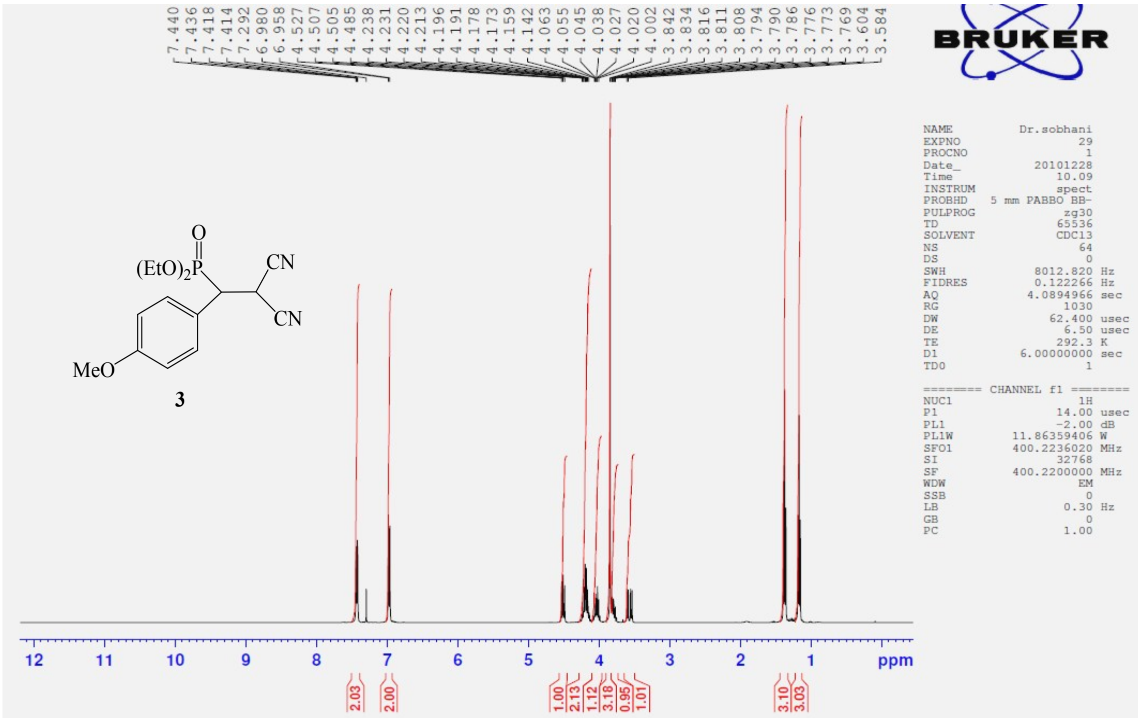
4) ^{1}H NMR and ^{13}C NMR spectra of β-phosphonomalonates



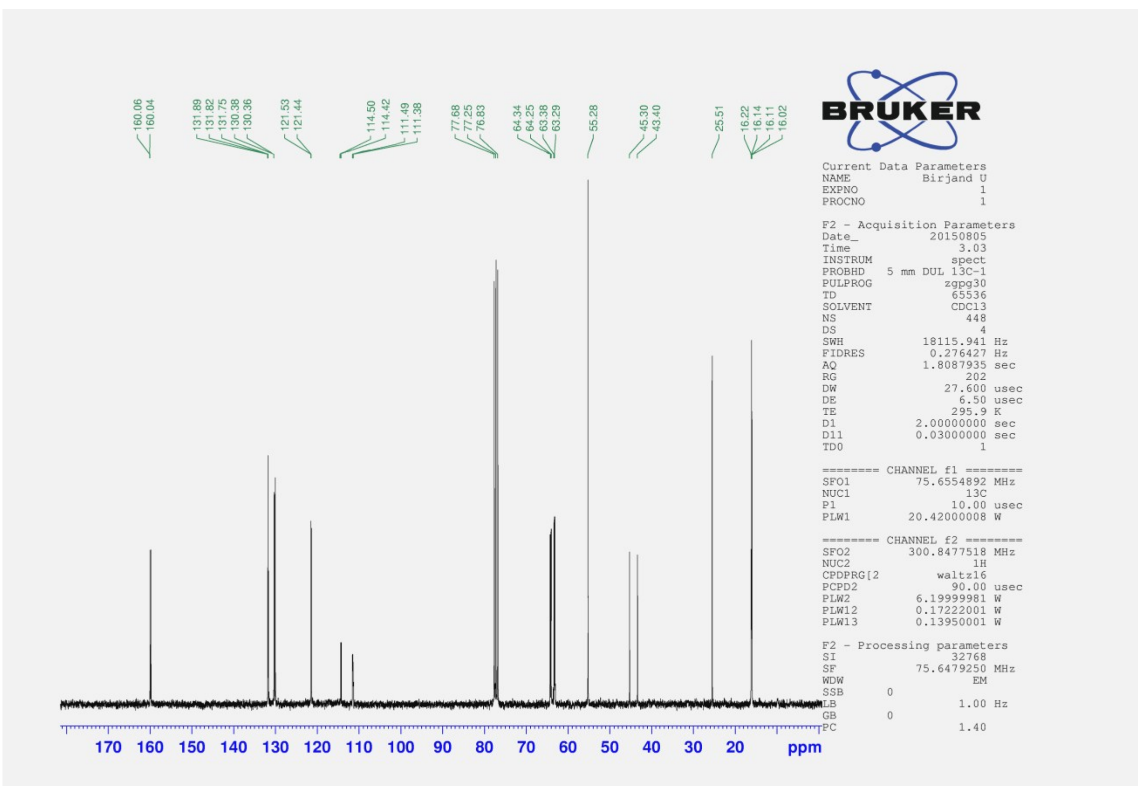








7.440 7.436 7.418 7.414 7.292 6.980 6.958 4.527 4.507 4.505 4.485 4.238 4.231 4.220 4.213 4.196 4.191 4.178 4.173 4.159 4.142 4.063 4.055 4.045 4.038 4.027 4.020 4.002 3.842 3.834 3.816 3.811 3.808 3.794 3.790 3.786 3.776 3.773 3.769 3.604 3.584
BRUKER
NAME Dr.sobhani
EXPNO 29
PROCNO 1
Date_ 20101228
Time 10.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 1030
DW 62.400 usec
DE 6.50 usec
TE 292.3 K
D1 6.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
(EtO)2P
CN
CN
MeO
3
12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.03 2.00 1.00 2.13 1.12 3.18 0.95 1.01 3.10 3.03



160.06 160.04 131.89 131.82 131.75 130.38 130.36 121.53 121.44 114.50 114.42 111.49 111.38 77.68 77.25 76.83 64.34 64.25 63.38 63.29 55.28 45.30 43.40 25.51 16.22 16.14 16.11 16.02
BRUKER
Current Data Parameters
NAME Birjand U
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150805
Time 3.03
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 448
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8087935 sec
RG 202
DW 27.600 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.6554892 MHz
NUC1 13C
P1 10.00 usec
PLW1 20.42000008 W
======== CHANNEL f2 ========
SFO2 300.8477518 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.19999981 W
PLW12 0.17222001 W
PLW13 0.13950001 W
F2 - Processing parameters
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WDW EM
SSB 0
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GB 0
PC 1.40
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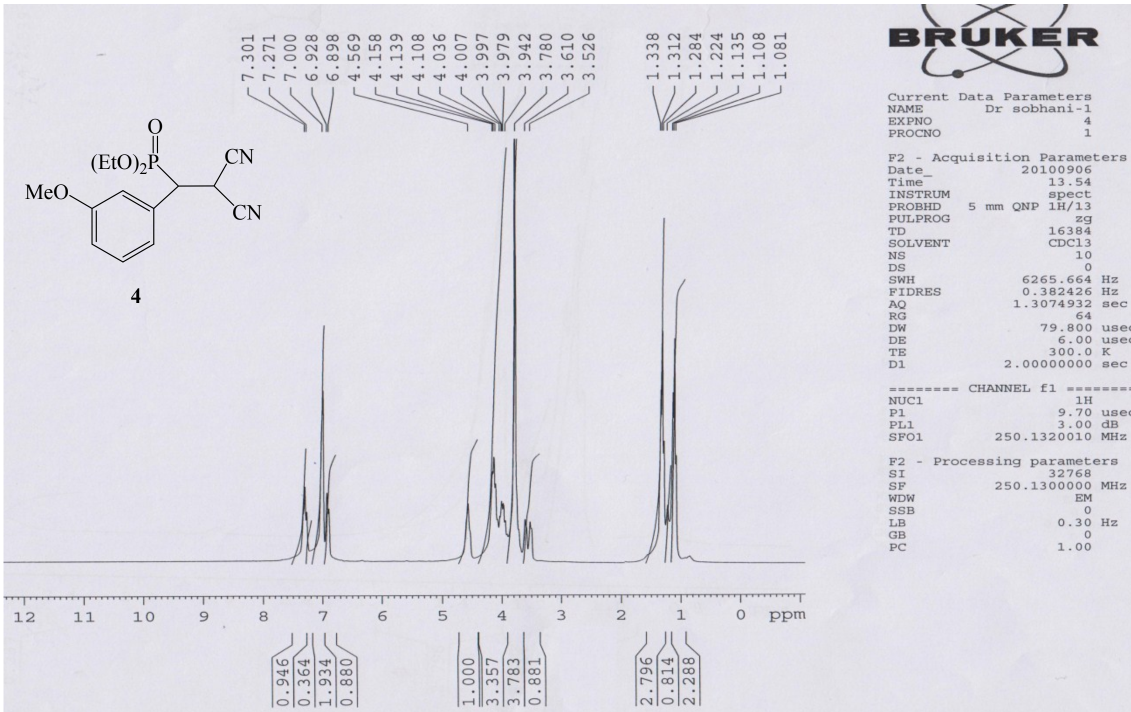

O
$(EtO)_2P$
CN
MeO
CN
4
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7.271
7.000
6.928
6.898
4.569
4.158
4.139
4.108
4.036
4.007
3.997
3.979
3.942
3.780
3.610
3.526
1.338
1.312
1.284
1.224
1.135
1.108
1.081
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.946
0.364
1.934
0.880
1.000
3.357
3.783
0.881
2.796
0.814
2.288
BRUKER
Current Data Parameters
NAME Dr sobhani-1
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100906
Time 13.54
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg
TD 16384
SOLVENT CDCl3
NS 10
DS 0
SWH 6265.664 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 64
DW 79.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.70 usec
PL1 3.00 dB
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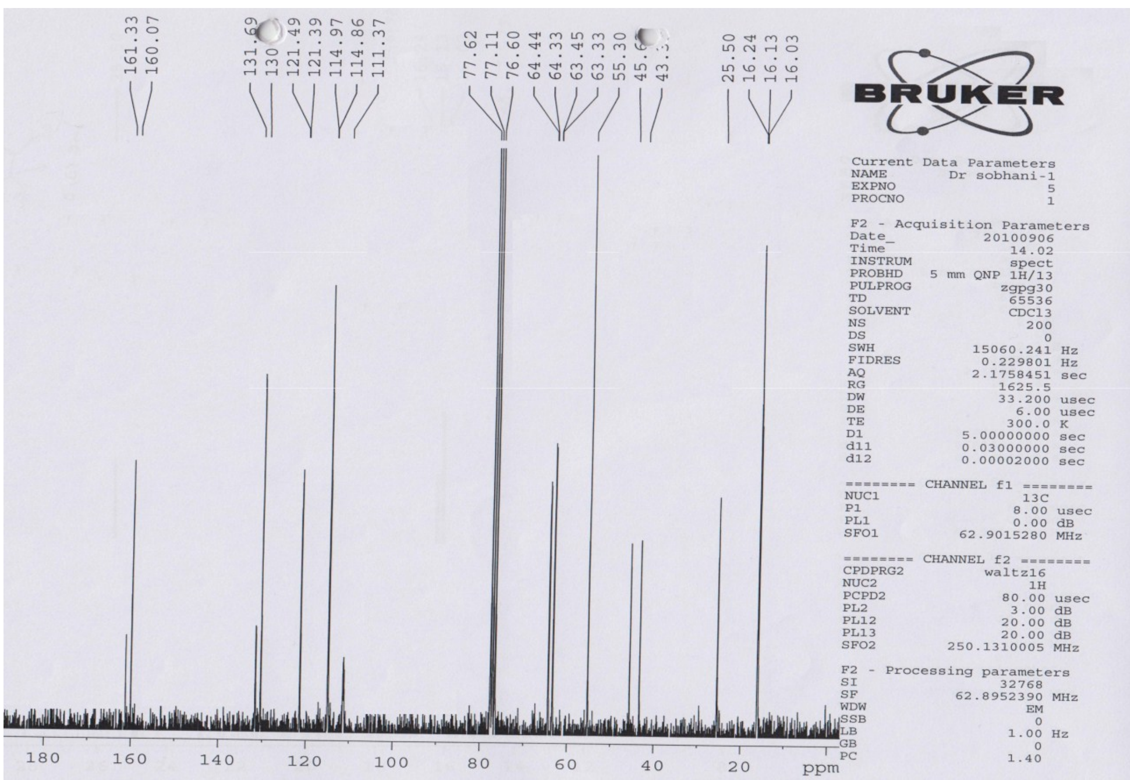
F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



161.33
160.07
121.49
121.39
114.97
114.86
111.37
77.62
77.11
76.60
64.44
64.33
63.45
63.33
55.30
25.50
16.24
16.13
16.03
180 160 140 120 100 80 60 40 20 ppm
BRUKER
Current Data Parameters
NAME Dr sobhani-1
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100906
Time 14.02
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 0
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 1625.5
DW 33.200 usec
DE 6.00 usec
TE 300.0 K
D1 5.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 0.00 dB
SFO1 62.9015280 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 250.1310005 MHz
F2 - Processing parameters
SI 32768
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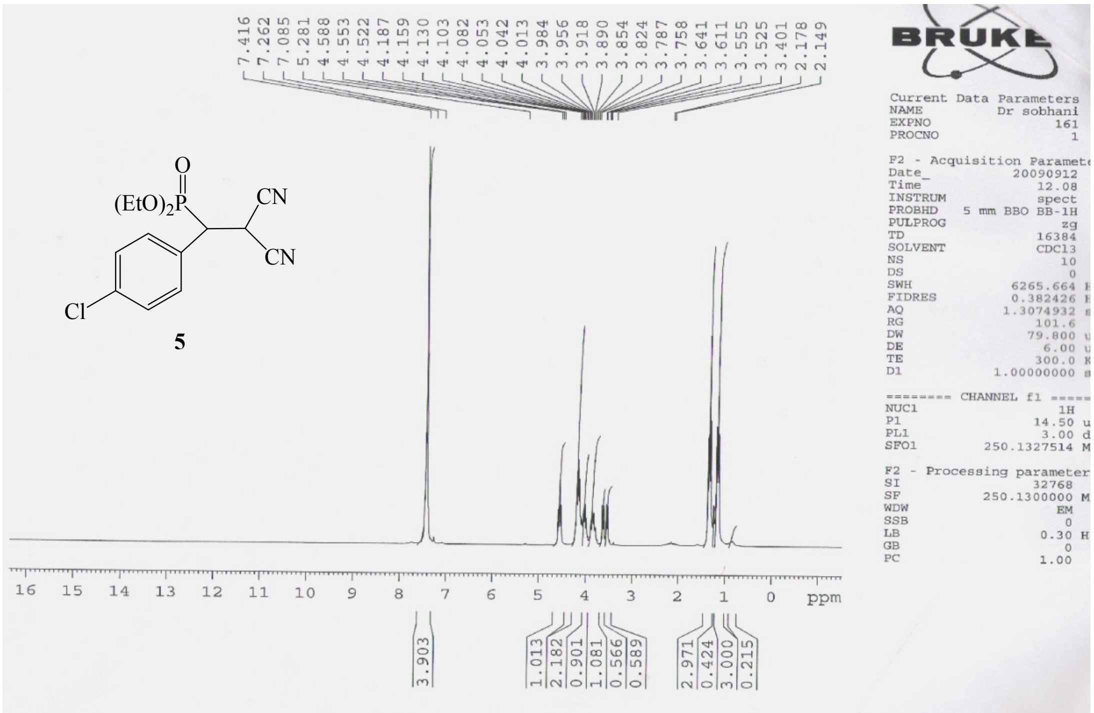
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.416 7.262 7.085 5.281 4.588 4.553 4.522 4.187 4.159 4.130 4.103 4.082 4.053 4.042 4.013 3.984 3.956 3.918 3.890 3.854 3.824 3.787 3.758 3.641 3.611 3.555 3.525 3.401 2.178 2.149
(EtO)2P
O
CN
CN
Cl
5
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.903 1.013 2.182 0.901 1.081 0.566 0.589 2.971 0.424 3.000 0.215
Current Data Parameters
NAME Dr sobhani
EXPNO 161
PROCNO 1
Date_ 20090912
SOLVENT CDCl3
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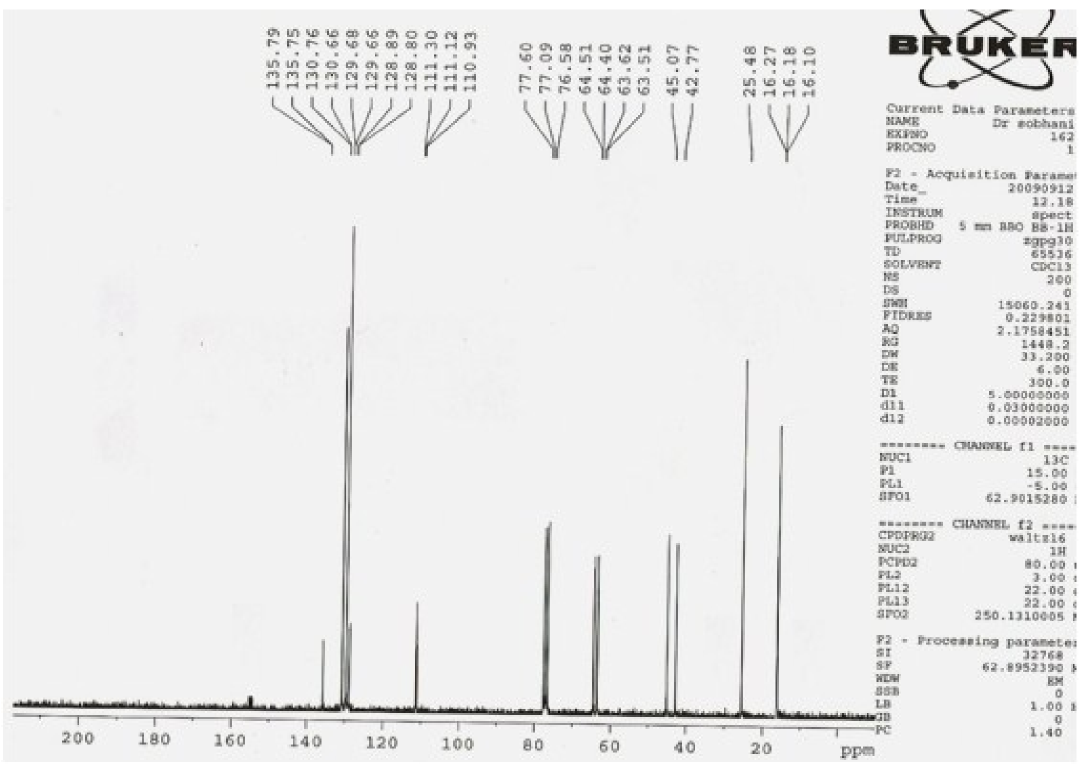
SFO1 250.1327514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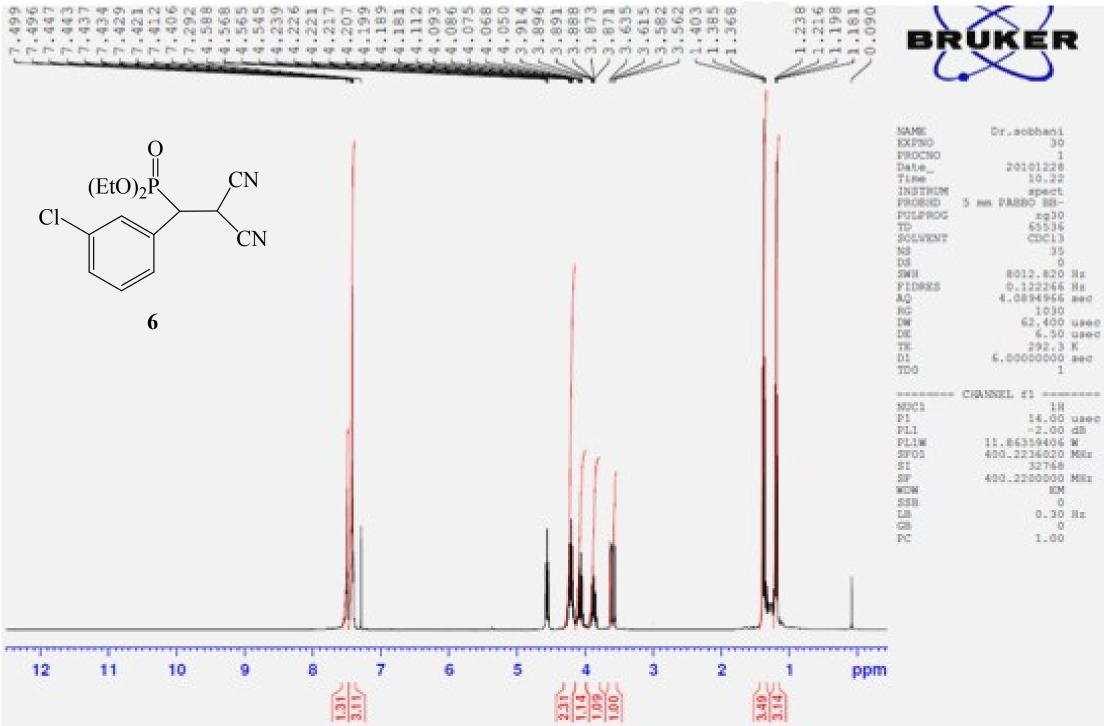
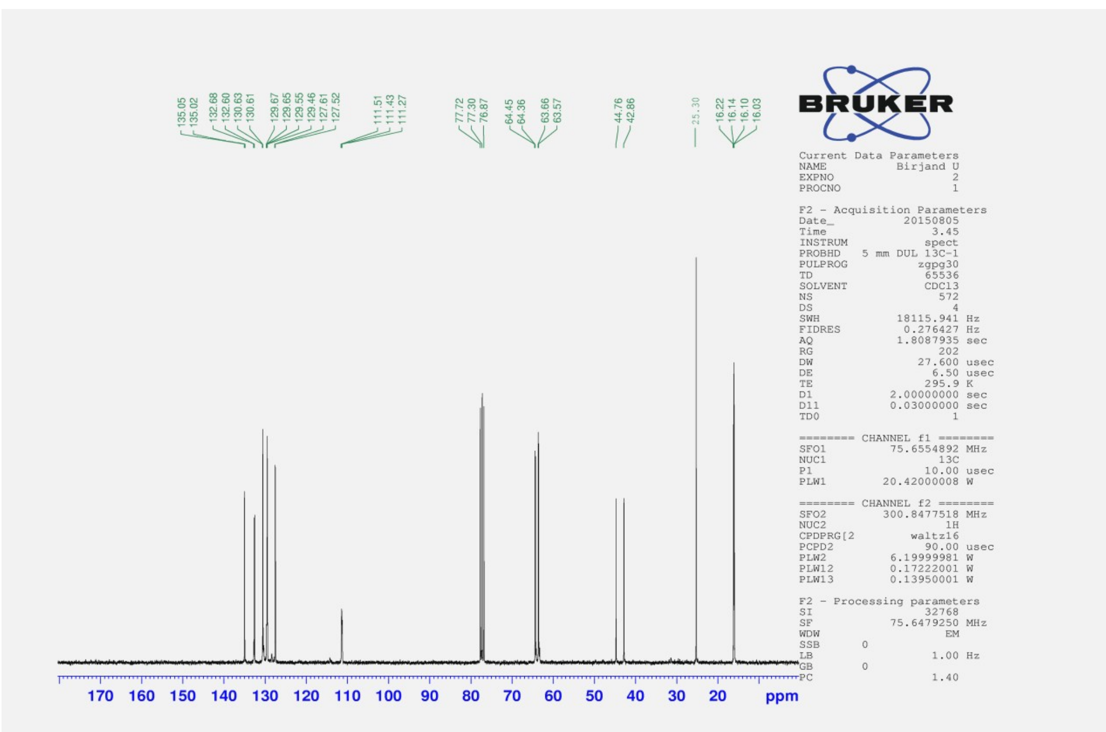
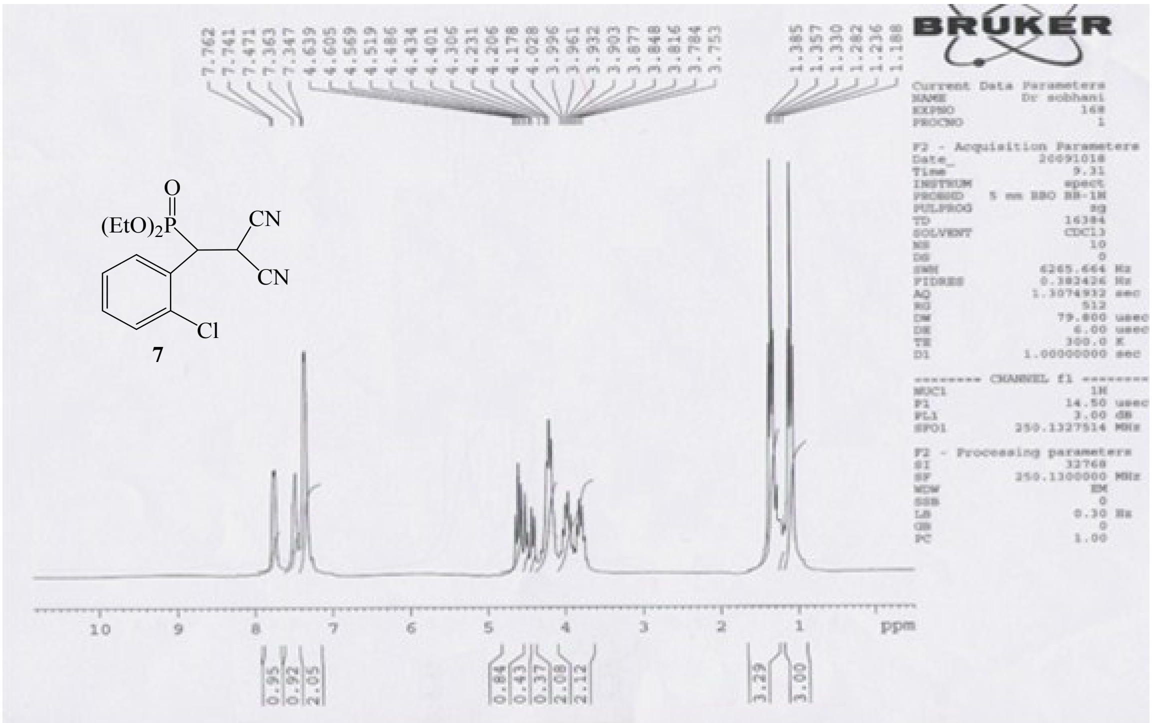
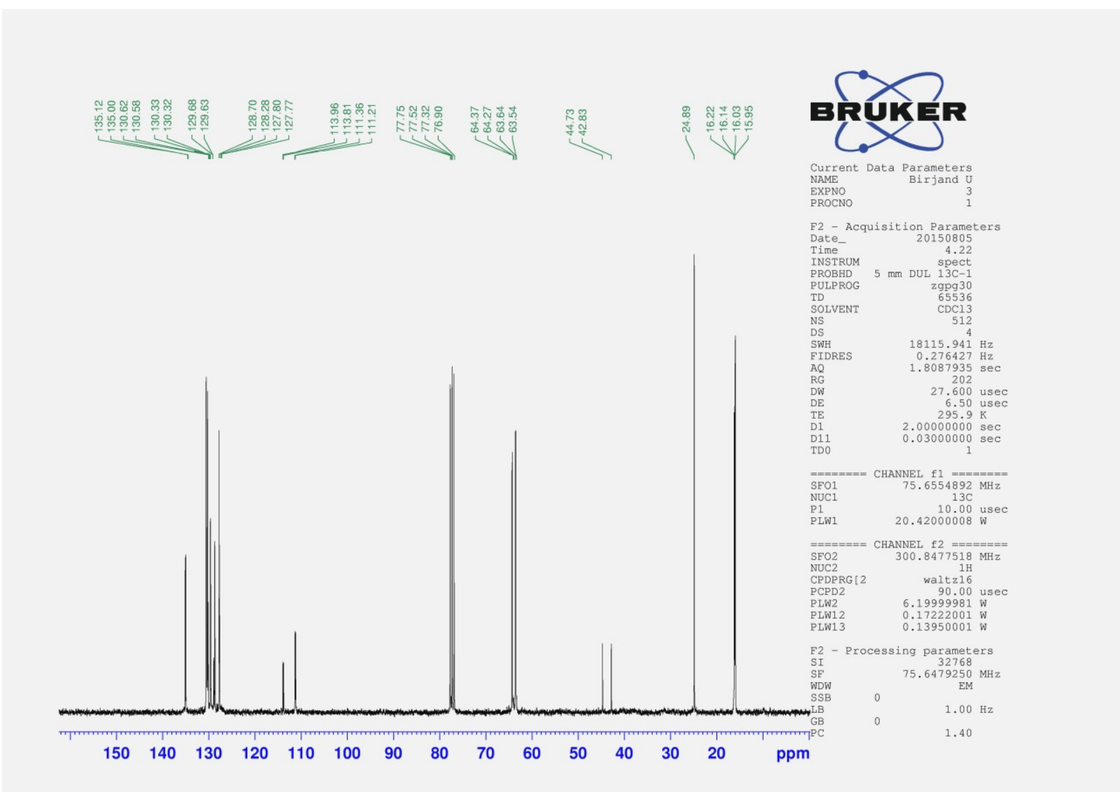
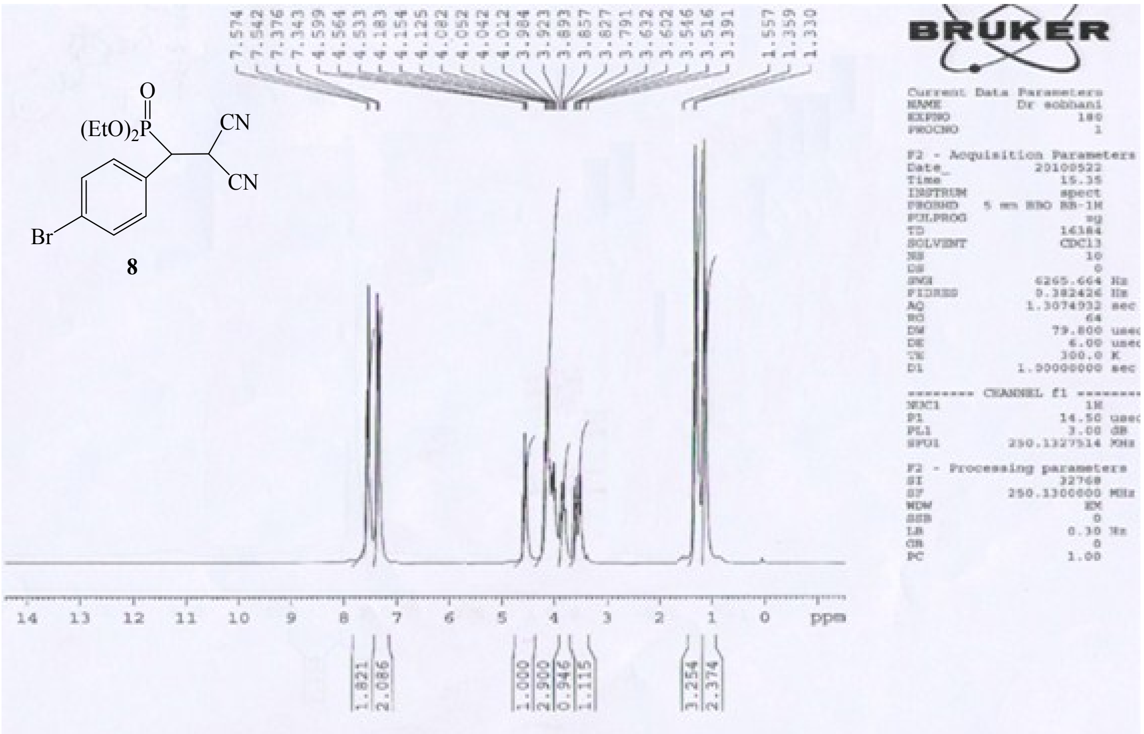
200 180 160 140 120 100 80 60 40 20 ppm
Current Data Parameters
NAME Dr sobhani
EXPNO 162
PROCNO 1
Date_ 20090912
SOLVENT CDCl3
NUC1 13C
SFO1 62.9015280

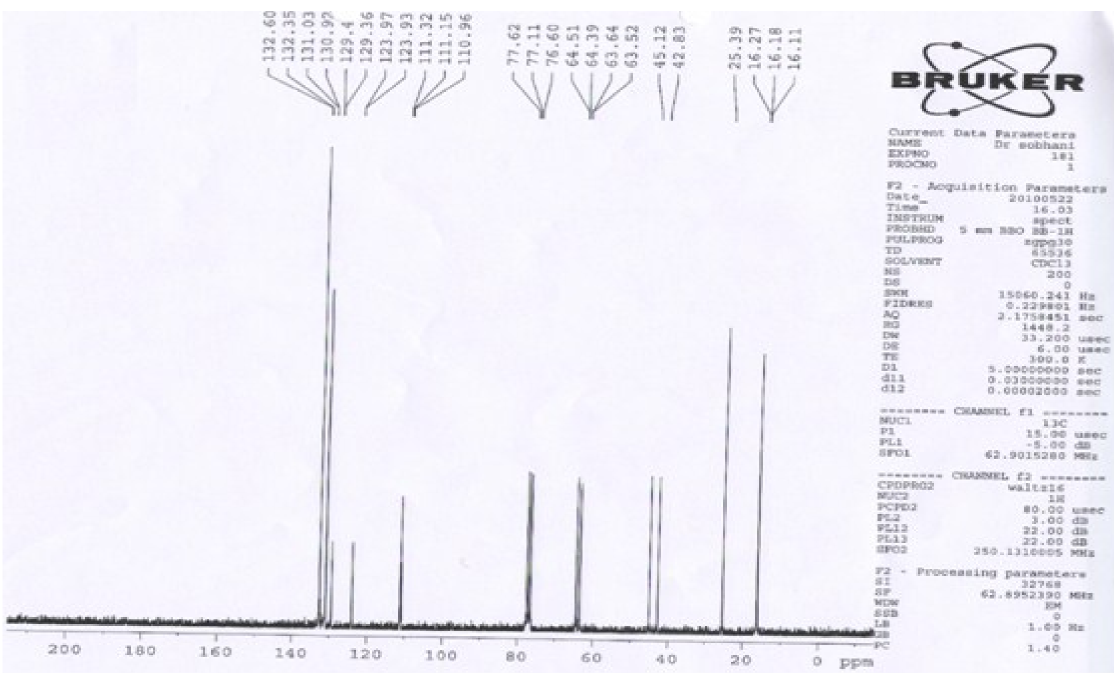

(EtO)2P
O
CN
CN
Cl
6
BRUKER
ppm

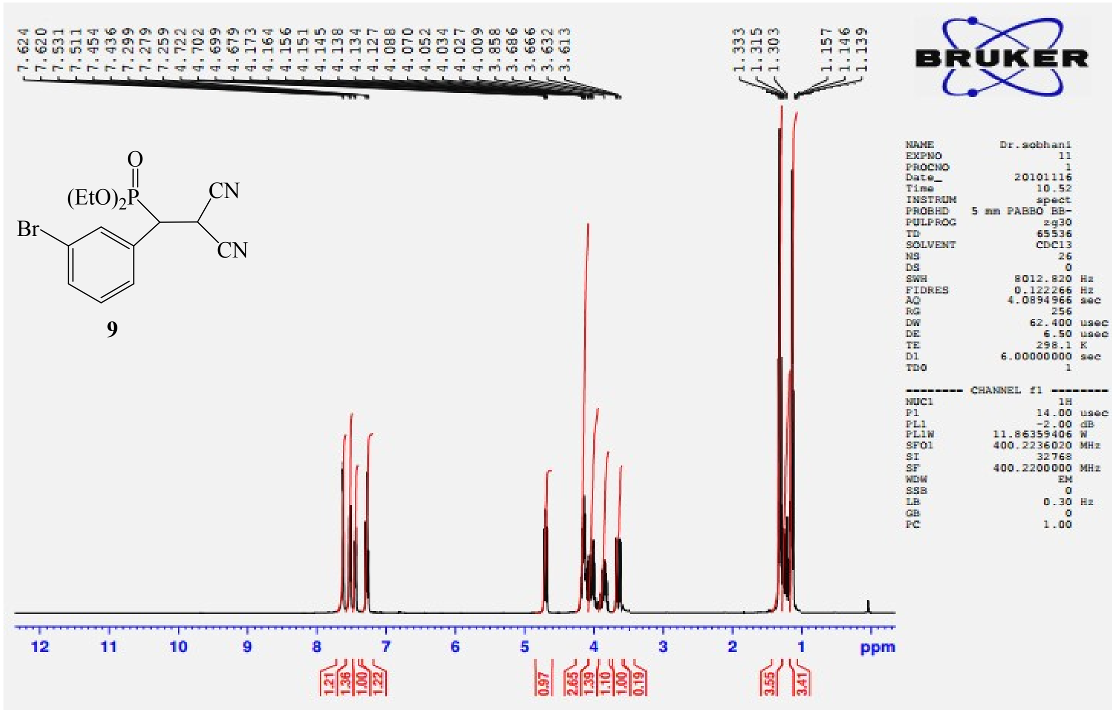

135.05
135.02
132.68
132.60
130.63
130.61
129.67
129.65
129.55
129.46
127.61
127.52
111.51
111.43
111.27
77.72
77.30
76.87
64.45
64.36
63.66
63.57
44.76
42.86
25.30
16.22
16.14
16.10
16.03
BRUKER
Current Data Parameters
ppm

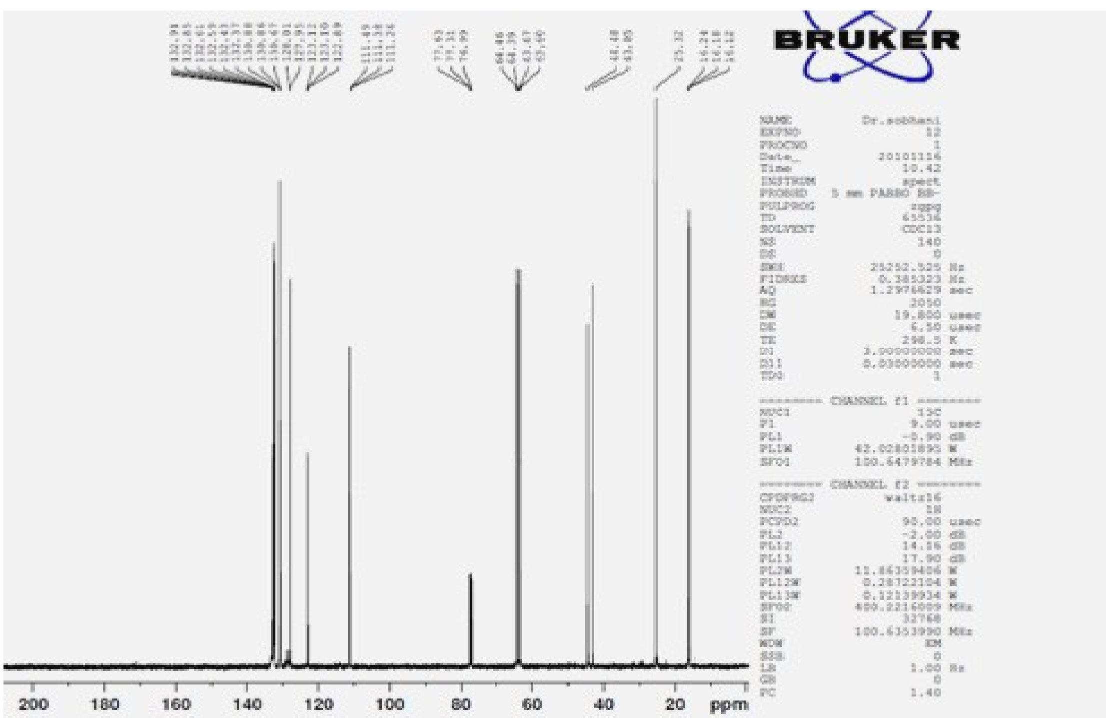

O
(EtO)2P
CN
CN
Cl
7
BRUKER
Current Data Parameters
F2 - Acquisition Parameters
CHANNEL f1
F2 - Processing parameters
ppm

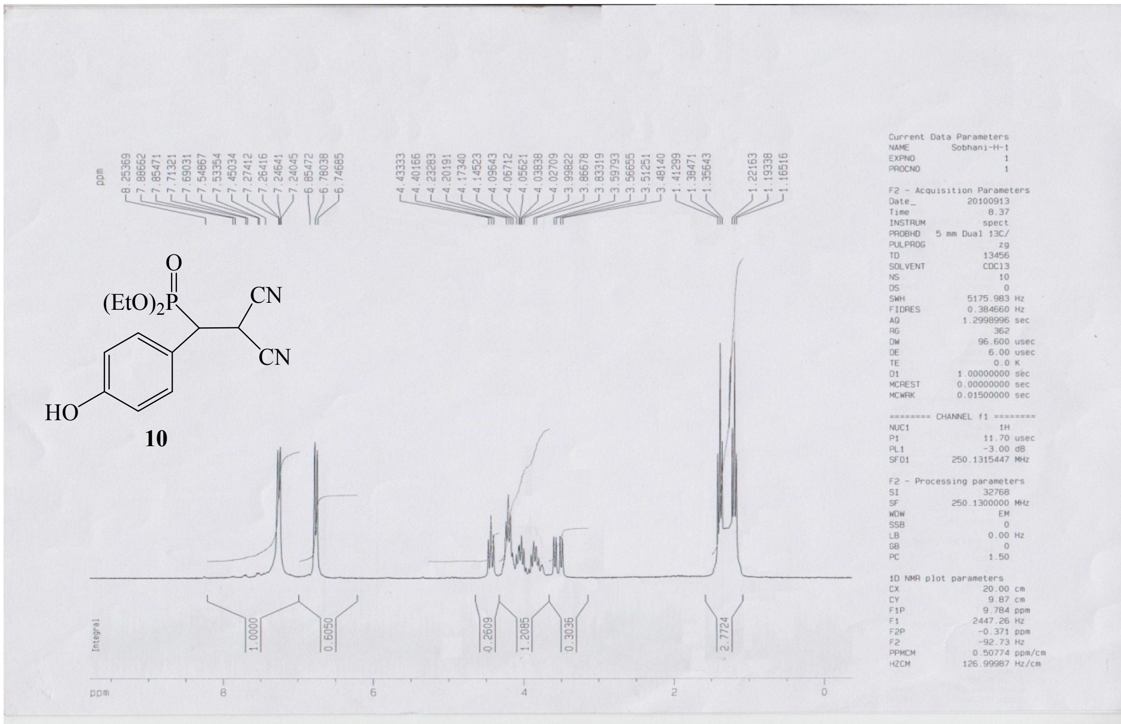

BRUKER
Current Data Parameters
NAME Birjand U
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150805
Time 4.22
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8087935 sec
RG 202
DW 27.600 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.6554892 MHz
NUC1 13C
P1 10.00 usec
PLW1 20.42000008 W
======== CHANNEL f2 ========
SFO2 300.8477518 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.19999981 W
PLW12 0.17222001 W
PLW13 0.13950001 W
F2 - Processing parameters
SI 32768
SF 75.6479250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ppm


(EtO)2P(O)
CN
CN
Br
8
BRUKER
7.574
7.542
7.376
7.343
4.599
4.564
4.533
4.183
4.154
4.125
4.082
4.052
4.042
4.012
3.984
3.923
3.893
3.857
3.827
3.791
3.632
3.602
3.546
3.516
3.391
1.557
1.359
1.330
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.821
2.086
1.000
2.900
0.946
1.115
3.254
2.374


BRUKER
132.60
132.35
131.03
130.92
129.4
129.36
123.97
123.93
111.32
111.15
110.96
77.62
77.11
76.60
64.51
64.39
63.64
63.52
45.12
42.83
25.39
16.27
16.18
16.11
200 180 160 140 120 100 80 60 40 20 0 ppm



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O
CN
CN
HO
10
Current Data Parameters
NAME Sobhani-H-1
ppm
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Integral
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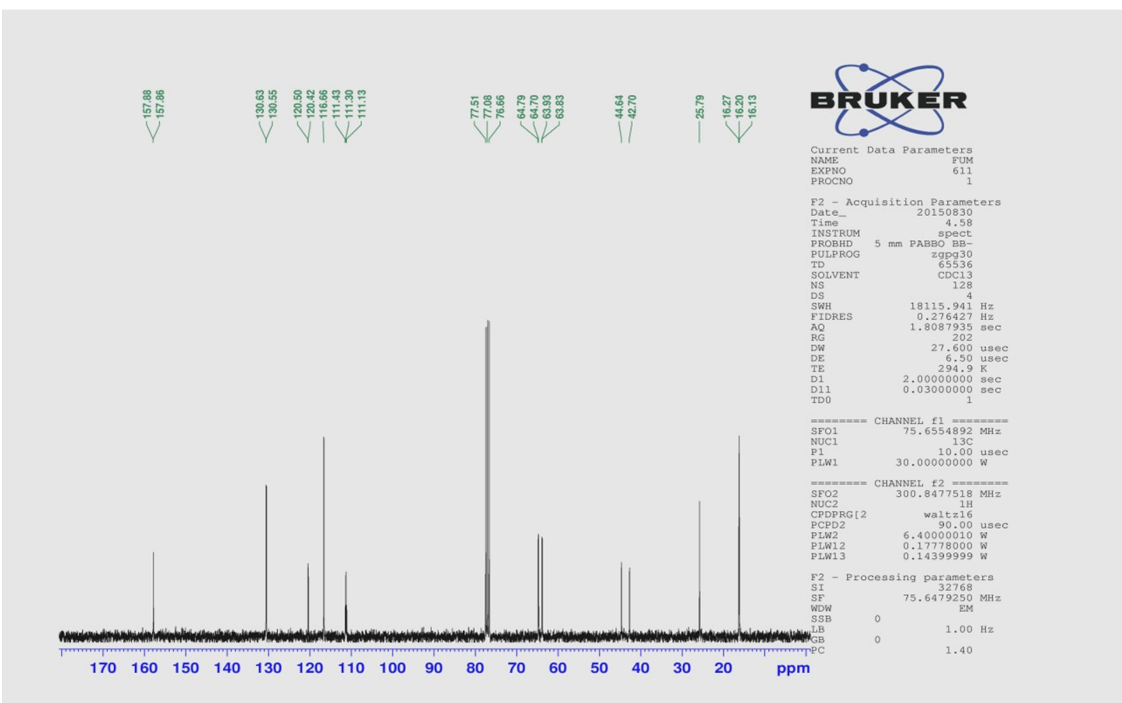
0.2609
1.2085
0.3036
2.7724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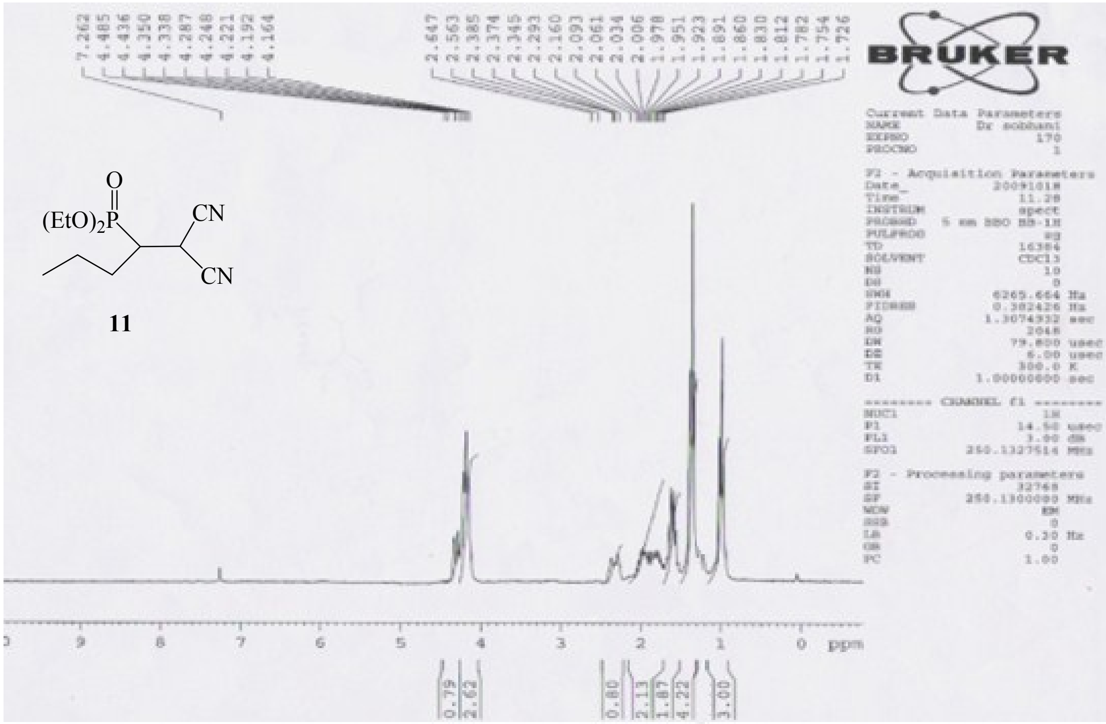
157.86
130.63
130.55
120.50
120.42
116.66
111.43
111.30
111.13
77.51
77.08
76.66
64.79
64.70
63.93
63.83
44.64
42.70
25.79
16.27
16.20
16.13
BRUKER
Current Data Parameters
NAME FUM
EXPNO 611
PROCNO 1
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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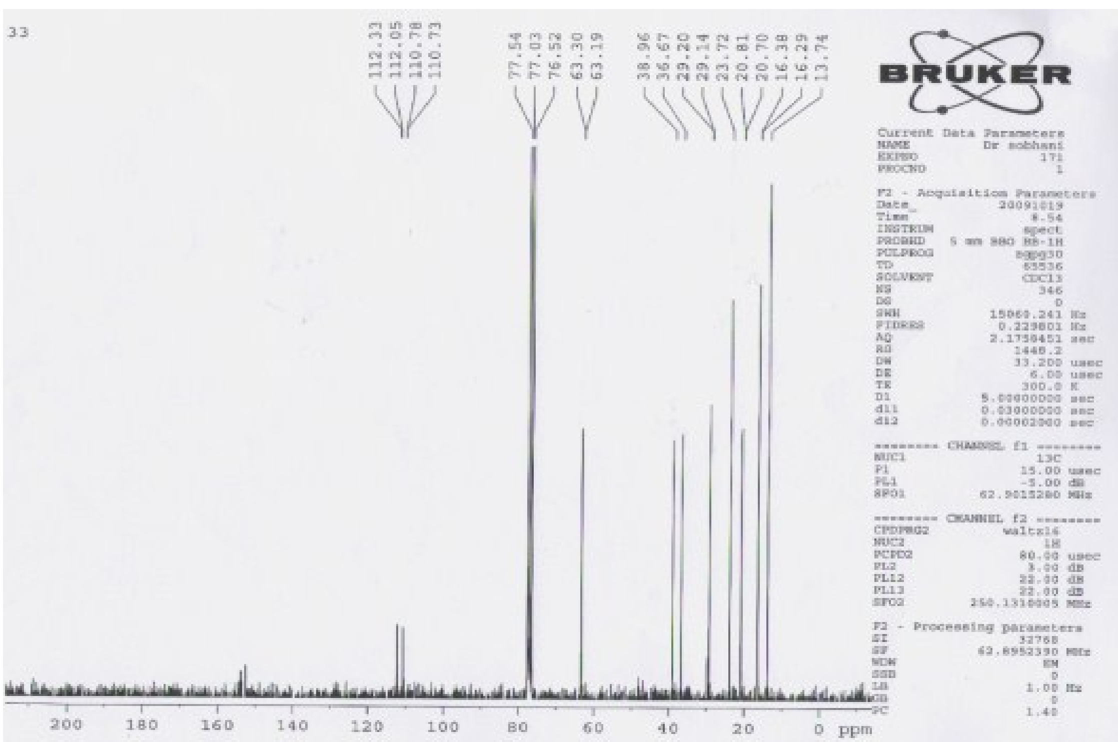
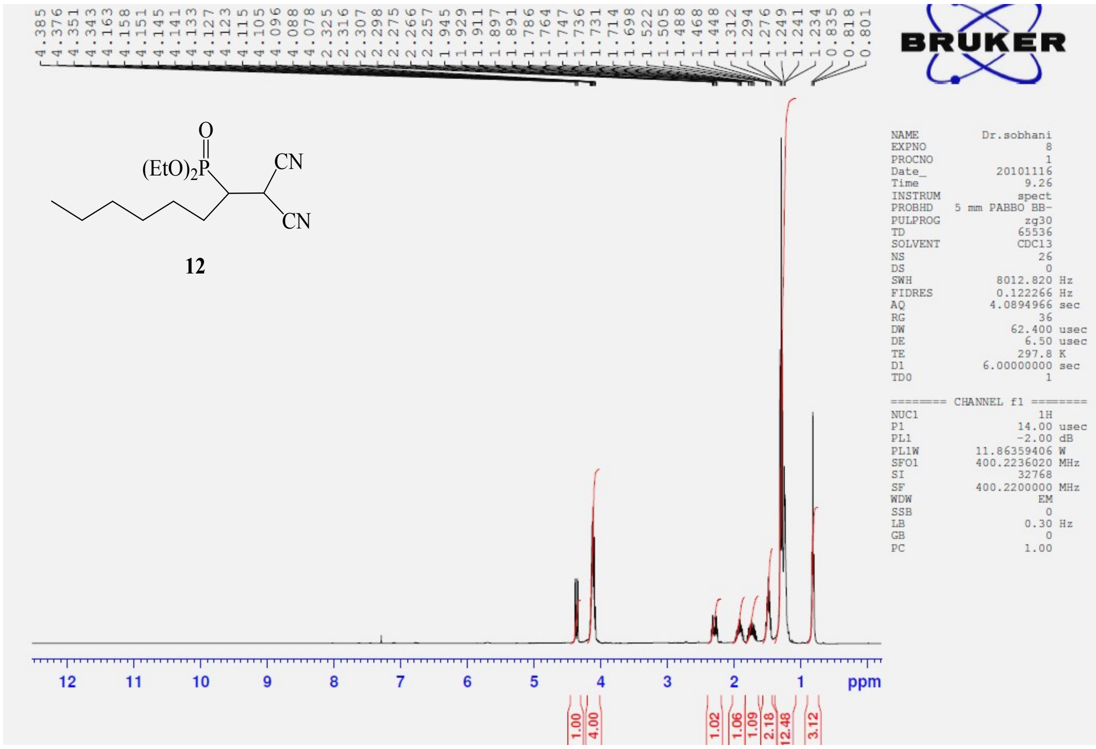
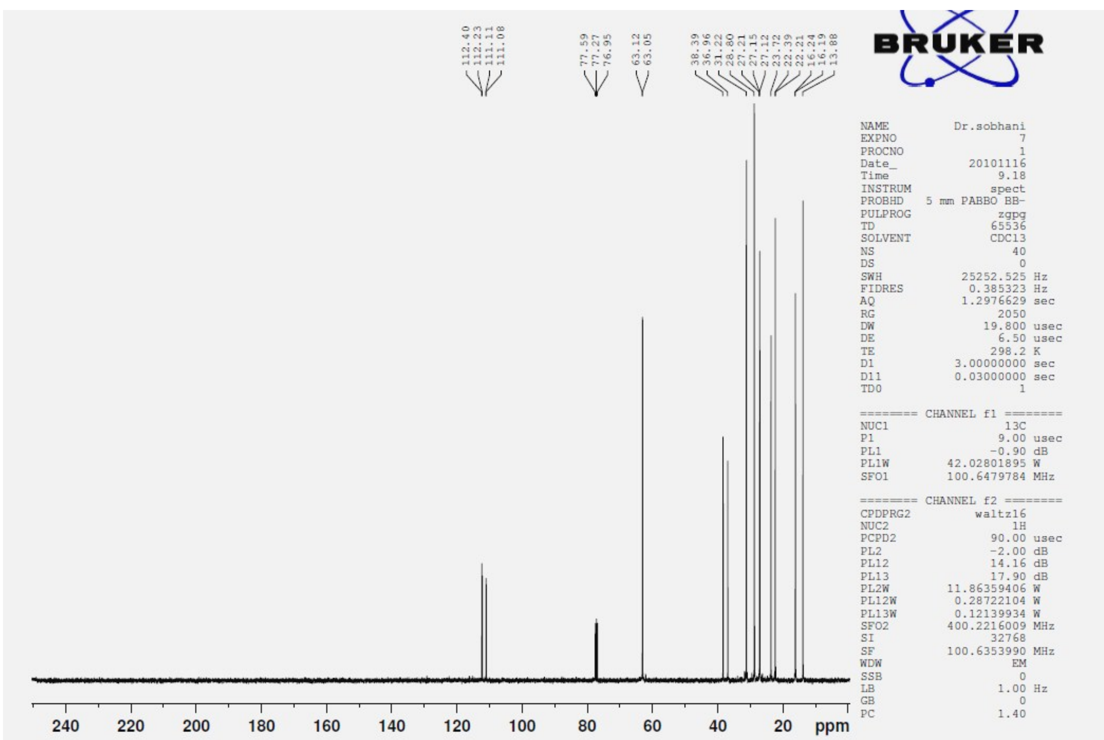
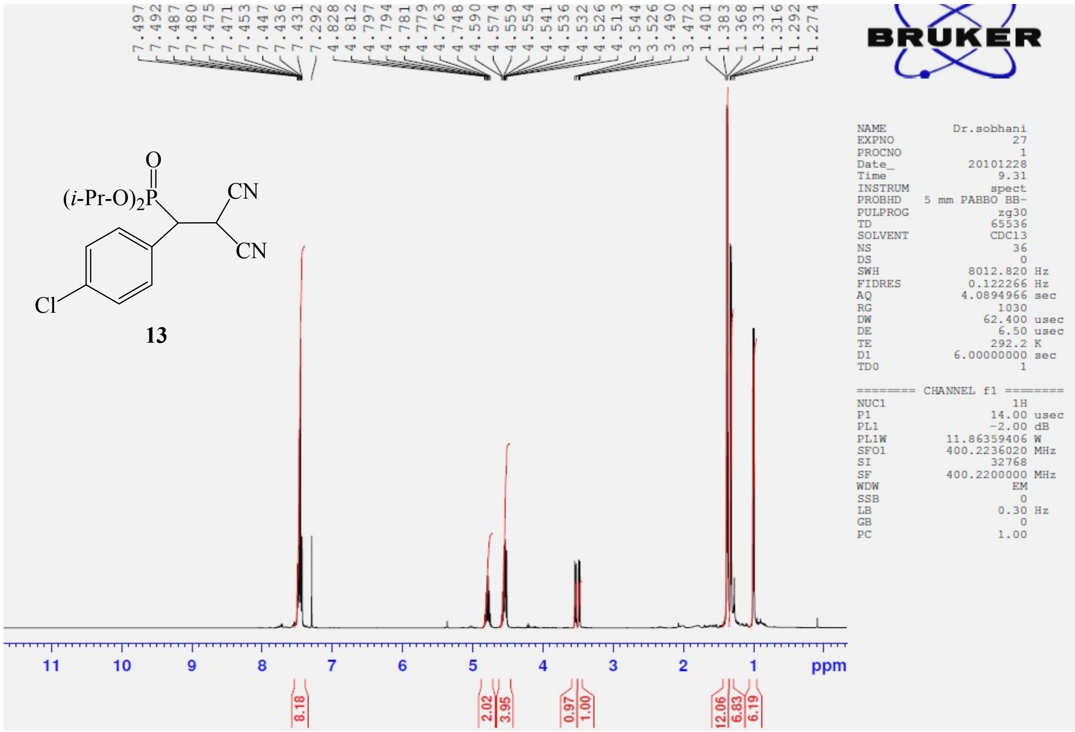
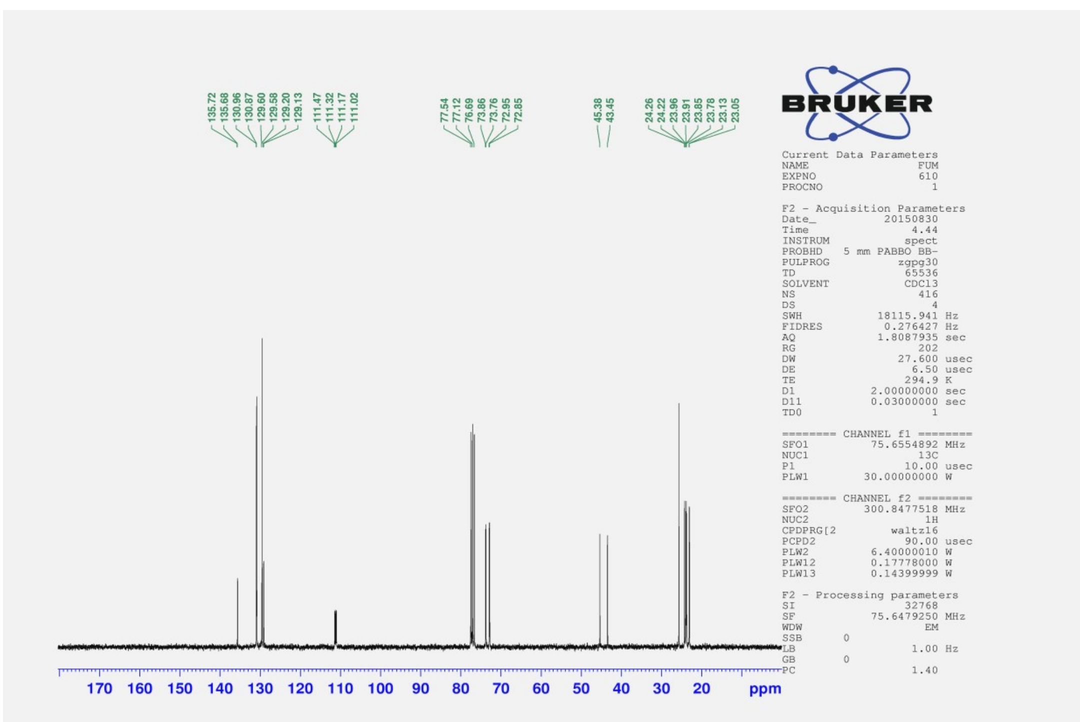
4.485
4.436
4.350
4.338
4.287
4.248
4.221
4.192
4.164
2.647
2.563
2.385
2.374
2.345
2.293
2.160
2.093
2.061
2.034
2.006
1.978
1.951
1.923
1.891
1.860
1.830
1.812
1.782
1.754
1.726
BRUKER
O
(EtO)2P
CN
CN
11
ppm
0.79
2.62
0.80
2.13
1.87
4.22
3.00

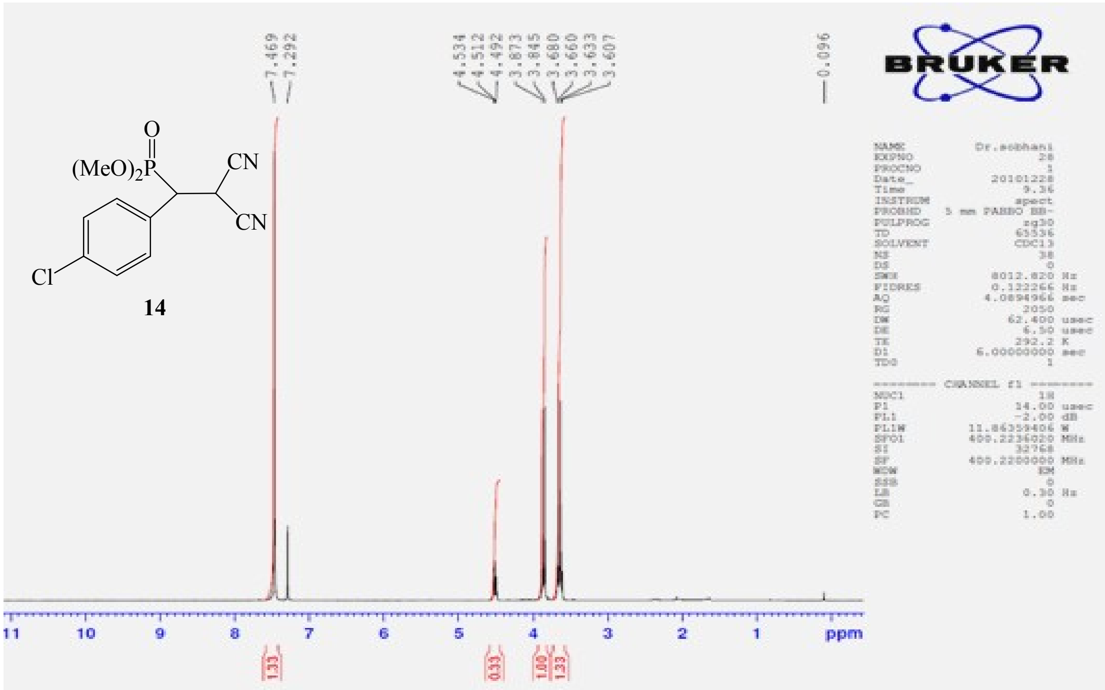

112.33
112.05
110.78
110.73
77.54
77.03
76.52
63.30
63.19
38.96
36.67
29.20
29.14
23.72
20.81
20.70
16.38
16.29
13.74
BRUKER
200
180
160
140
120
100
80
60
40
20
0
ppm

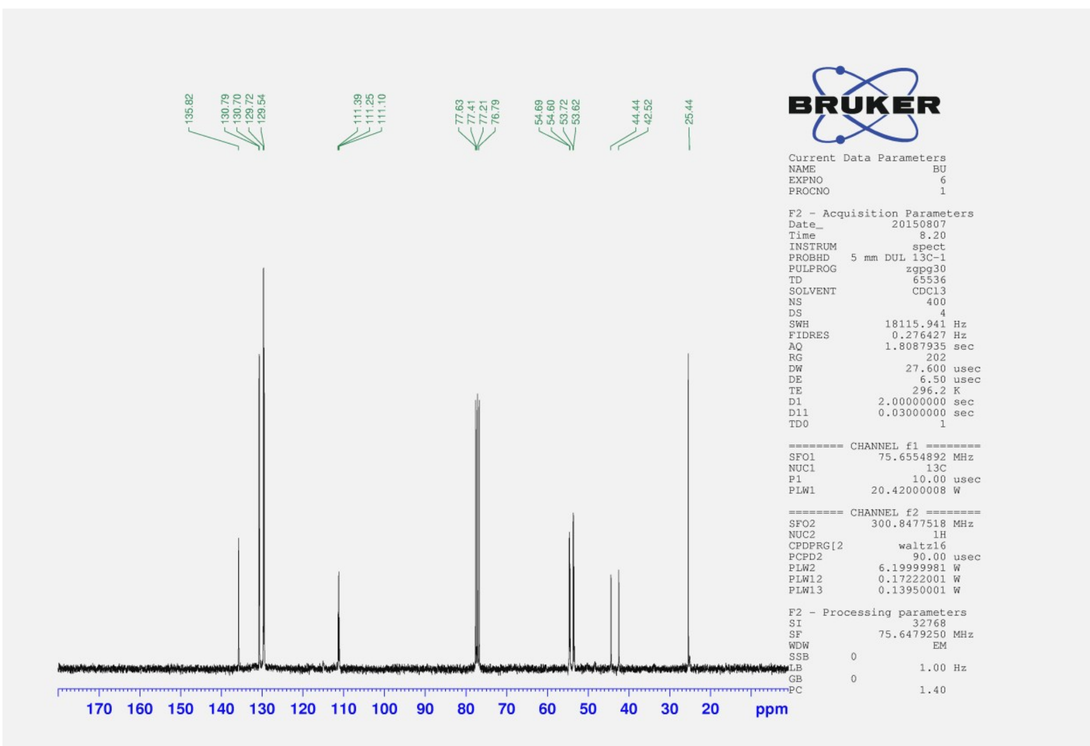

4.385 4.376 4.351 4.343 4.163 4.158 4.151 4.145 4.141 4.133 4.127 4.123 4.115 4.105 4.096 4.088 4.078 2.325 2.316 2.307 2.298 2.275 2.266 2.257 1.945 1.929 1.911 1.897 1.891 1.786 1.764 1.747 1.736 1.731 1.714 1.698 1.522 1.505 1.488 1.468 1.448 1.312 1.294 1.276 1.249 1.241 1.234 0.835 0.818 0.801
BRUKER
O
(EtO)2P
CN
CN
12
NAME Dr.sobhani
EXPNO 8
PROCNO 1
Date_ 20101116
Time 9.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 26
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 36
DW 62.400 usec
DE 6.50 usec
TE 297.8 K
D1 6.00000000 sec
TD0 1
======= CHANNEL f1 =======
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 4.00 1.02 1.06 1.09 2.18 12.48 3.12

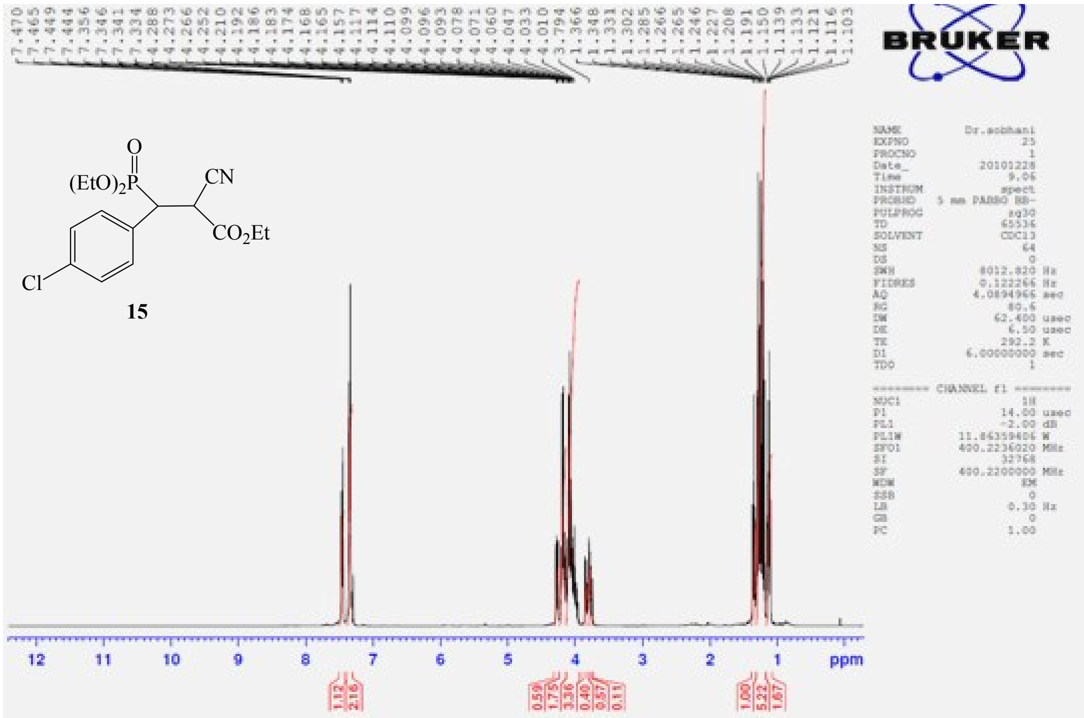

112.40 112.23 111.11 111.08 77.59 77.27 76.95 63.12 63.05 38.39 36.96 31.22 28.80 27.21 27.15 27.12 23.72 22.39 22.21 16.24 16.19 13.88
BRUKER
NAME Dr.sobhani
EXPNO 7
PROCNO 1
Date_ 20101116
Time 9.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 40
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 298.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======= CHANNEL f1 =======
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6479784 MHz
======= CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.16 dB
PL13 17.90 dB
PL2W 11.86359406 W
PL12W 0.28722104 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
SI 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
240 220 200 180 160 140 120 100 80 60 40 20 ppm


7.497
7.492
7.487
7.480
7.475
7.471
7.453
7.447
7.436
7.431
7.292
4.828
4.812
4.797
4.794
4.781
4.779
4.763
4.748
4.590
4.574
4.559
4.554
4.541
4.536
4.532
4.526
4.513
3.544
3.526
3.490
3.472
1.401
1.383
1.368
1.331
1.316
1.292
1.274
BRUKER
O
(i-Pr-O)2P
CN
CN
Cl
13
NAME Dr.sobhani
EXPNO 27
PROCNO 1
Date_ 20101228
Time 9.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 36
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 1030
DW 62.400 usec
DE 6.50 usec
TE 292.2 K
D1 6.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11
10
9
8
7
6
5
4
3
2
1
ppm
8.18
2.02
3.95
0.97
1.00
12.06
6.83
6.19

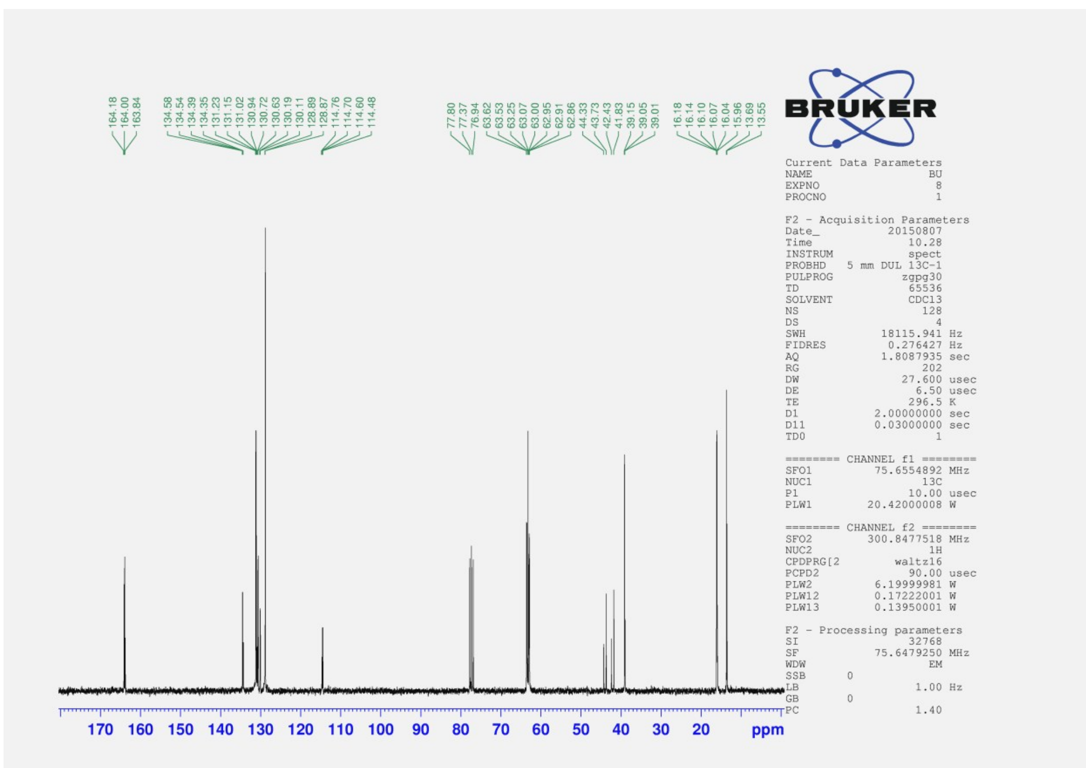

135.72
135.68
130.96
130.87
129.60
129.58
129.20
129.13
111.47
111.32
111.17
111.02
77.54
77.12
76.69
73.86
73.76
72.95
72.85
45.38
43.45
24.26
24.22
23.96
23.91
23.85
23.78
23.13
23.05
BRUKER
Current Data Parameters
NAME FUM
EXPNO 610
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150830
Time 4.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 416
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8087935 sec
RG 202
DW 27.600 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.6554892 MHz
NUC1 13C
P1 10.00 usec
PLW1 30.00000000 W
======== CHANNEL f2 ========
SFO2 300.8477518 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.40000010 W
PLW12 0.17778000 W
PLW13 0.14399999 W
F2 - Processing parameters
SI 32768
SF 75.6479250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.469
7.292
4.534
4.512
4.492
3.873
3.845
3.680
3.660
3.633
3.607
0.096
BRUKER
(MeO)2P
O
CN
CN
Cl
14
11 10 9 8 7 6 5 4 3 2 1 ppm
1.33
0.33
1.00
1.33


135.82
130.79
130.70
129.72
129.54
111.39
111.25
111.10
77.63
77.41
77.21
76.79
54.69
54.60
53.72
53.62
44.44
42.52
25.44
BRUKER
Current Data Parameters
NAME BU
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150807
Time 8.20
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8087935 sec
RG 202
DW 27.600 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.6554892 MHz
NUC1 13C
P1 10.00 usec
PLW1 20.42000008 W
======== CHANNEL f2 ========
SFO2 300.8477518 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.19999981 W
PLW12 0.17222001 W
PLW13 0.13950001 W
F2 - Processing parameters
SI 32768
SF 75.6479250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

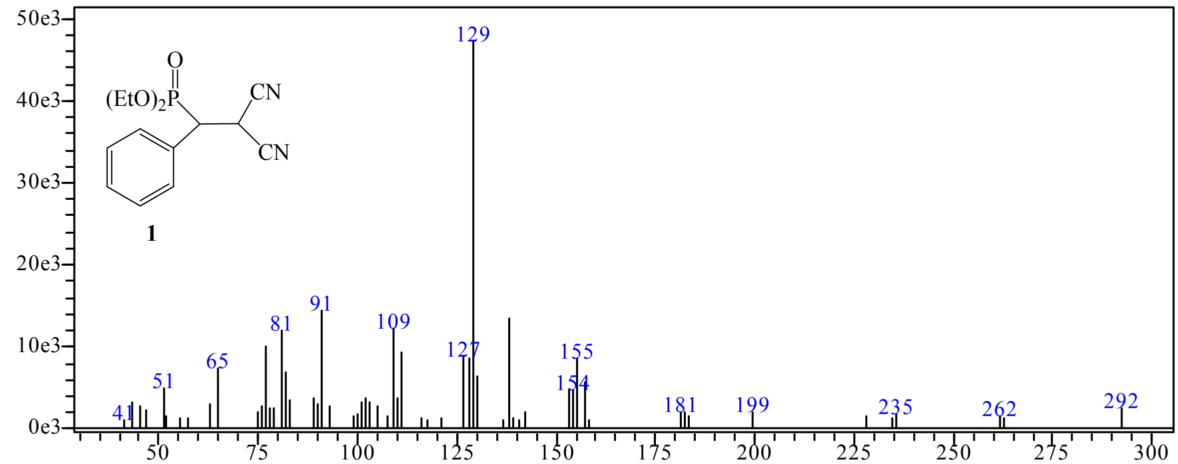


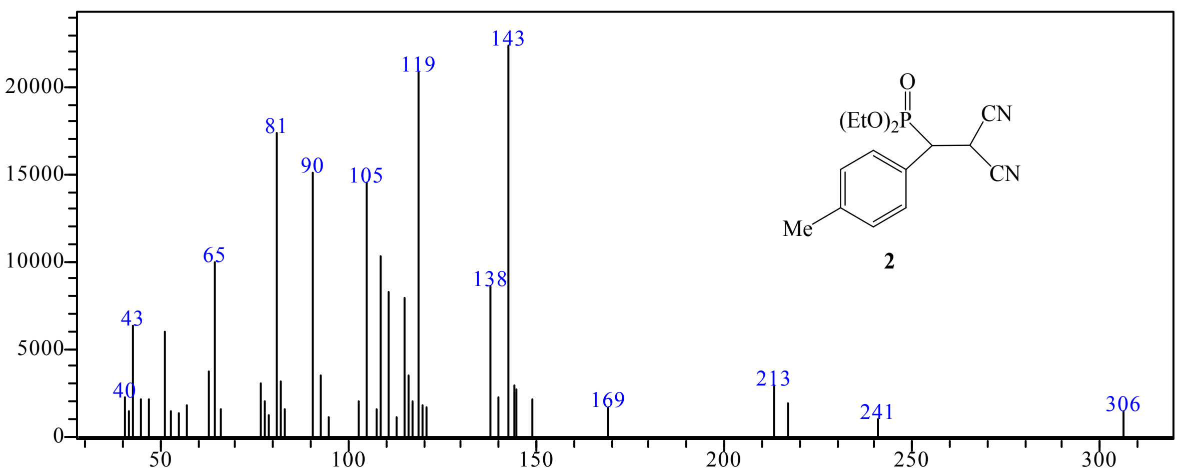
BRUKER
(EtO)2P
O
CN
CO2Et
Cl
15
ppm

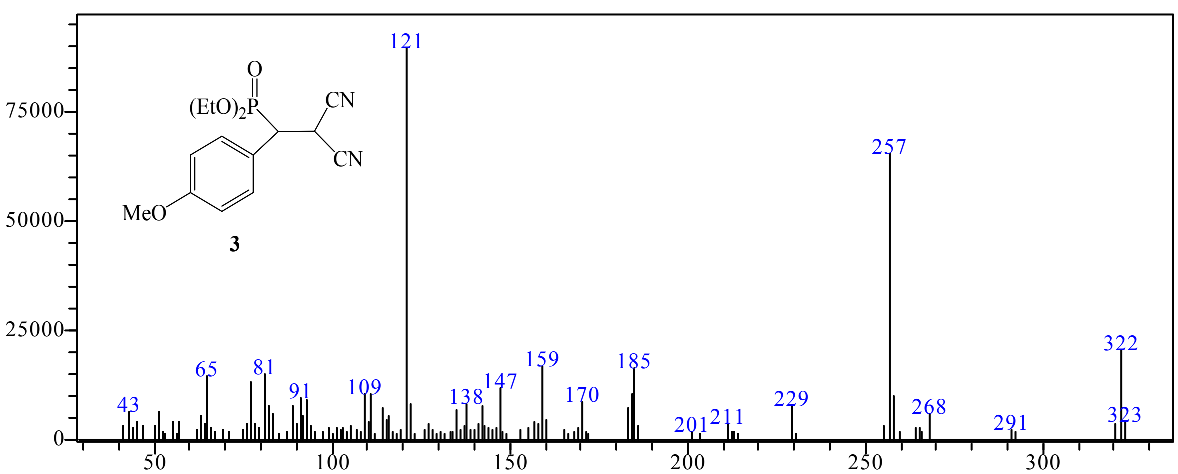


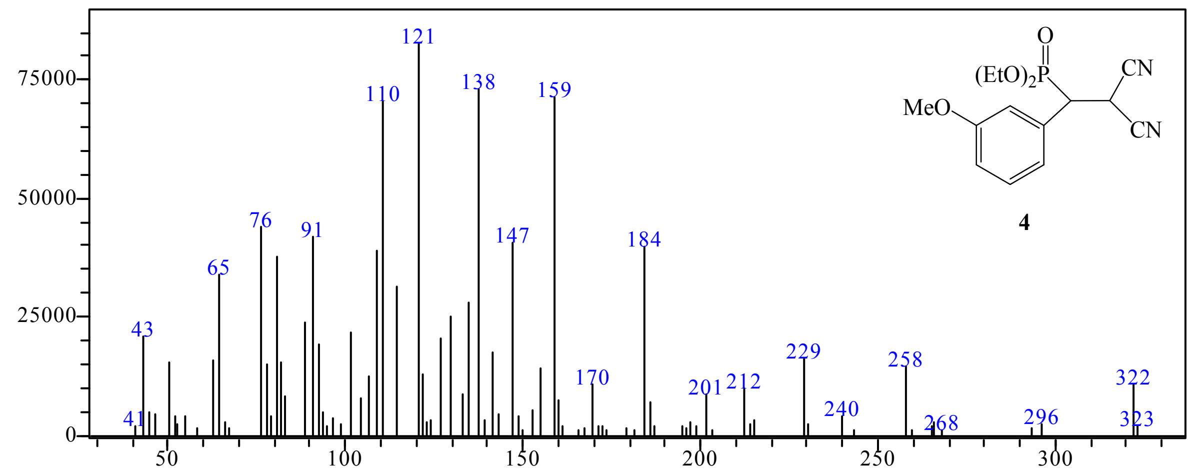
BRUKER
ppm

5) Mass spectra of β-phosphonomalonates

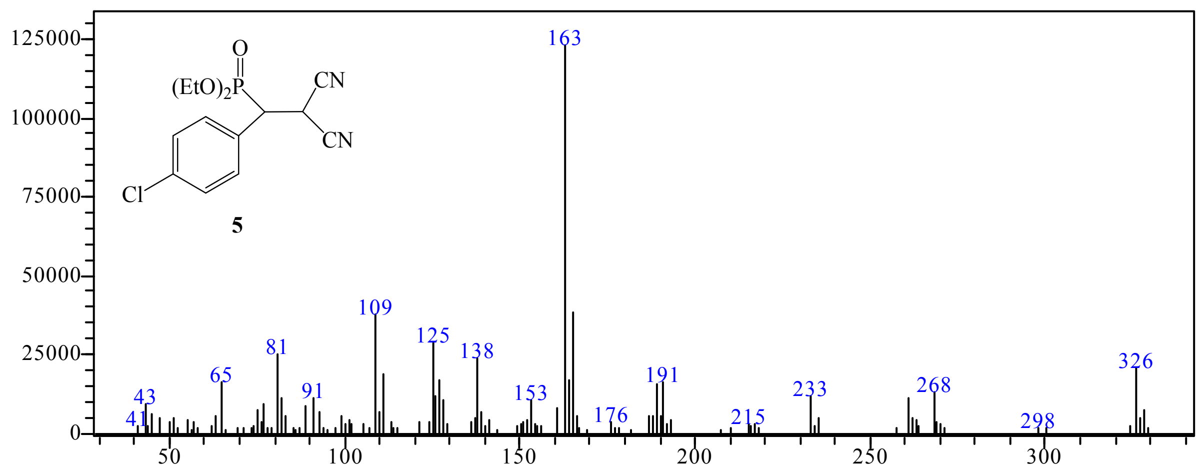




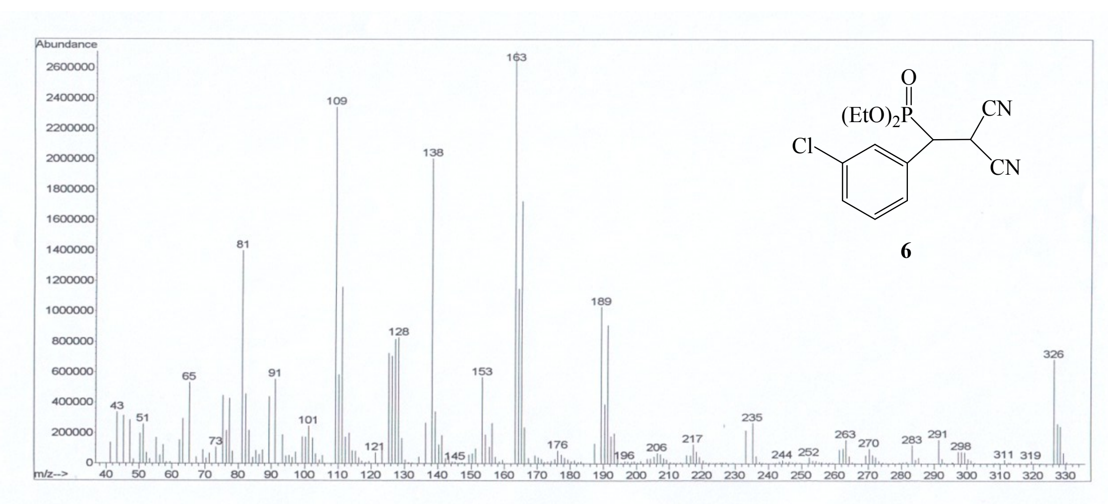




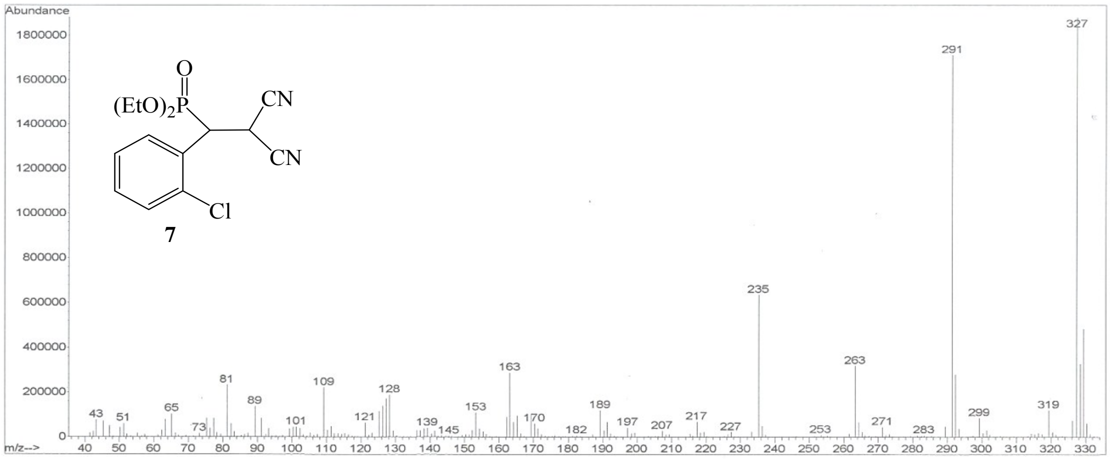
0
25000
50000
75000
50
100
150
200
250
300
41
43
65
76
91
110
121
138
147
159
170
184
201
212
229
240
258
268
296
322
323
(EtO)2P
O
CN
CN
MeO
4

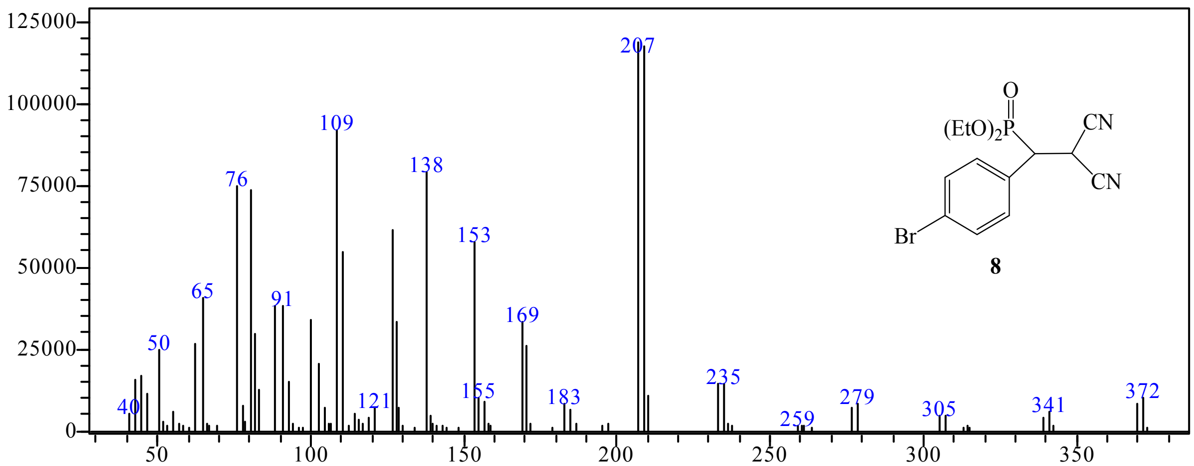


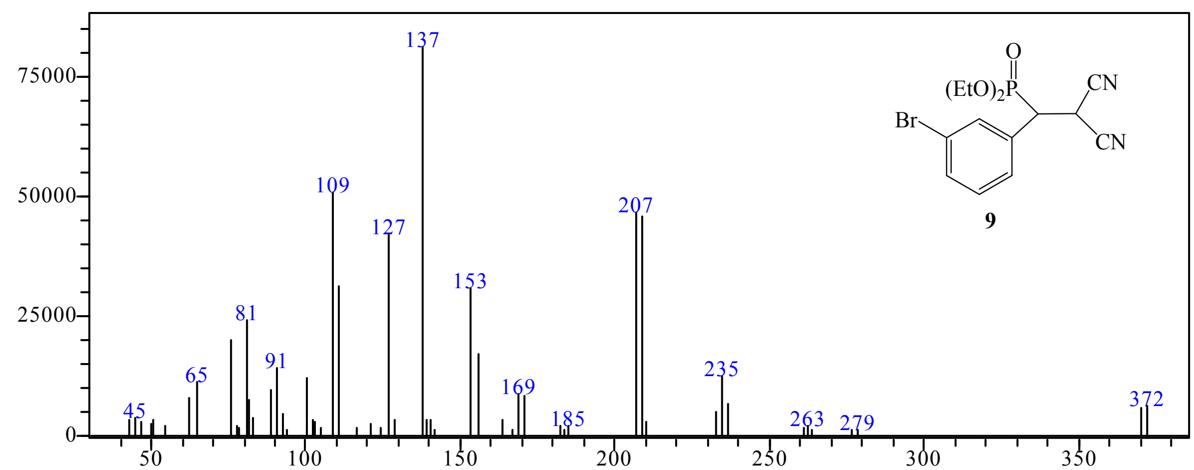
0
25000
50000
75000
100000
125000
50
100
150
200
250
300
41
43
65
81
91
109
125
138
153
163
176
191
215
233
268
298
326
(EtO)2P
O
CN
CN
Cl
5

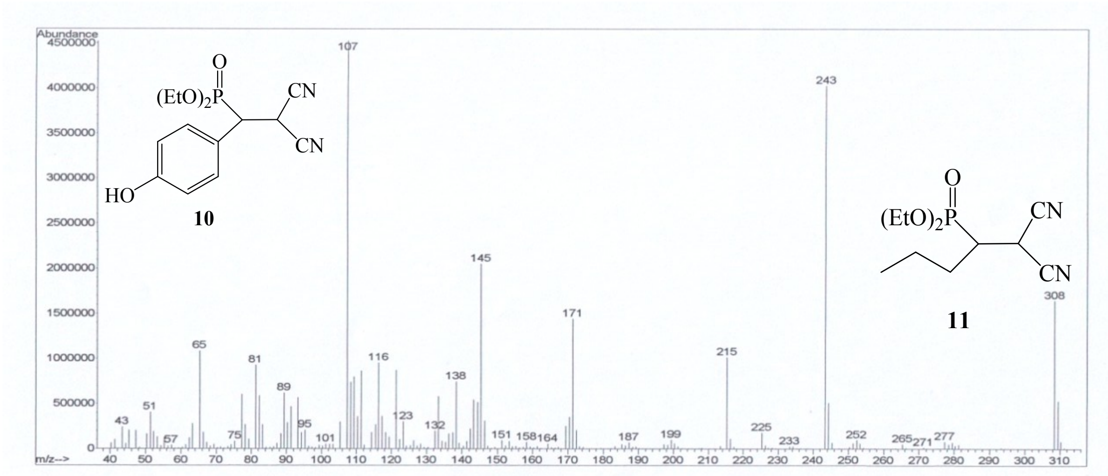


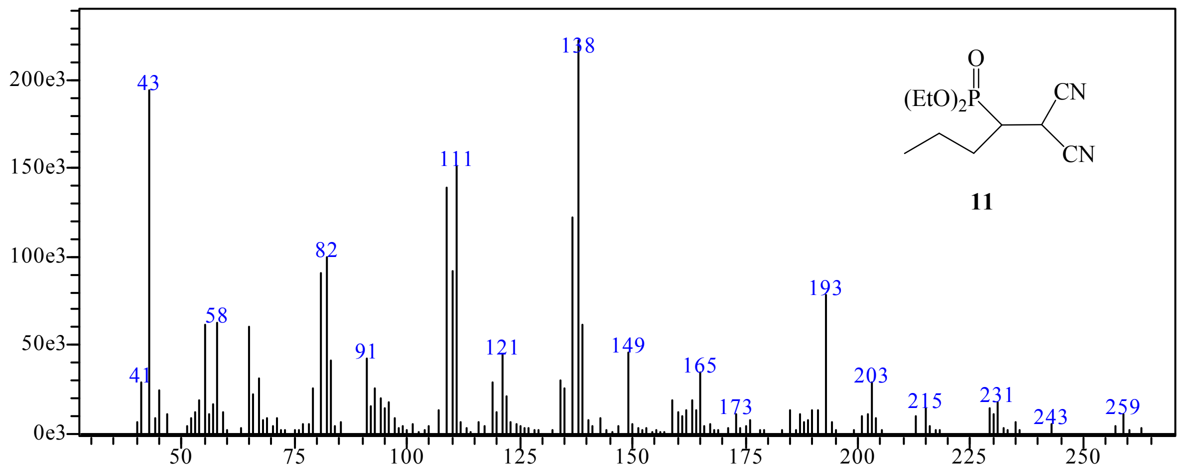
Abundance
m/z-->
43
51
65
73
81
91
101
109
121
128
138
145
153
163
176
189
196
206
217
235
244
252
263
270
283
291
298
311
319
326
(EtO)2P
O
CN
CN
Cl
6

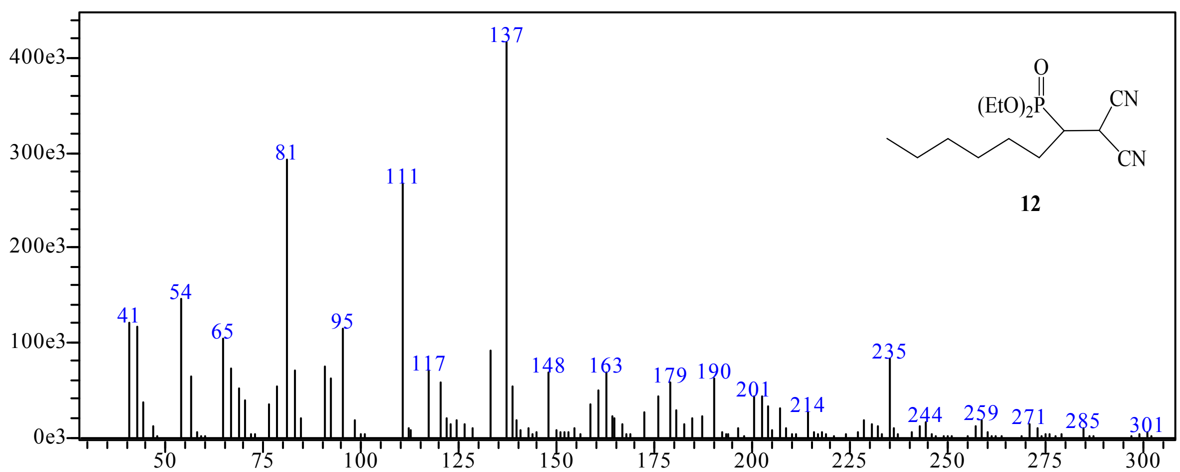

Abundance
(EtO)2P
O
CN
CN
Cl
7
m/z-->

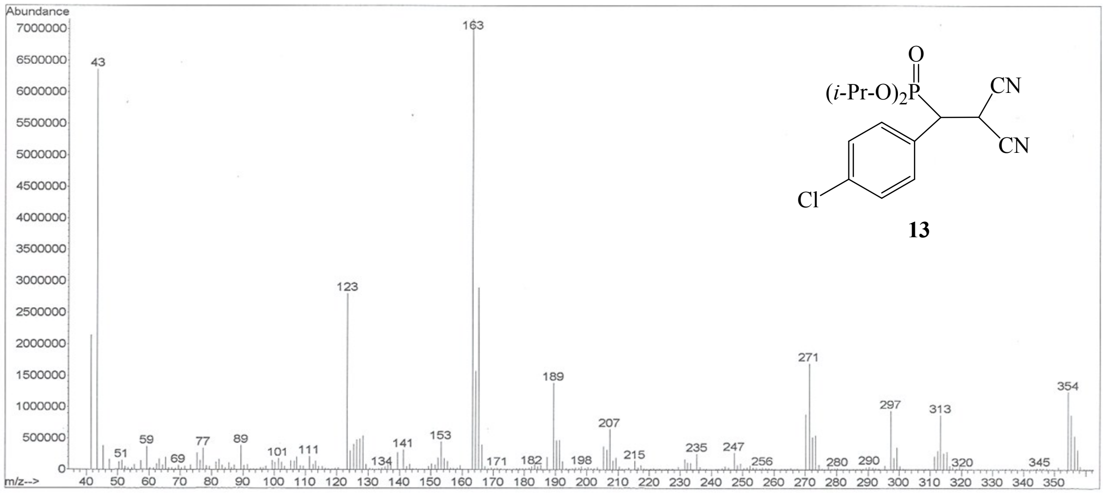

(EtO)2P
O
CN
CN
Br
8

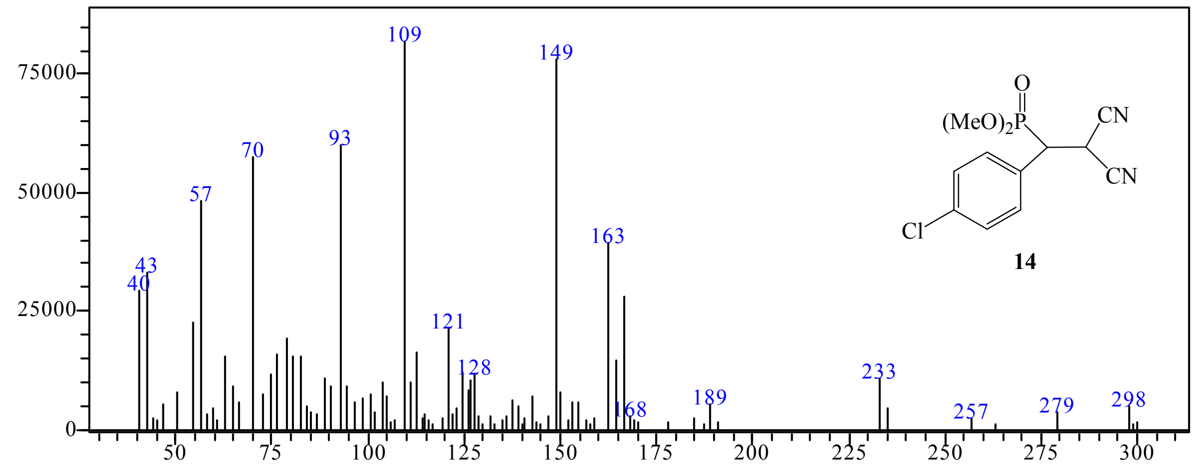

(EtO)2P
O
CN
CN
Br
9

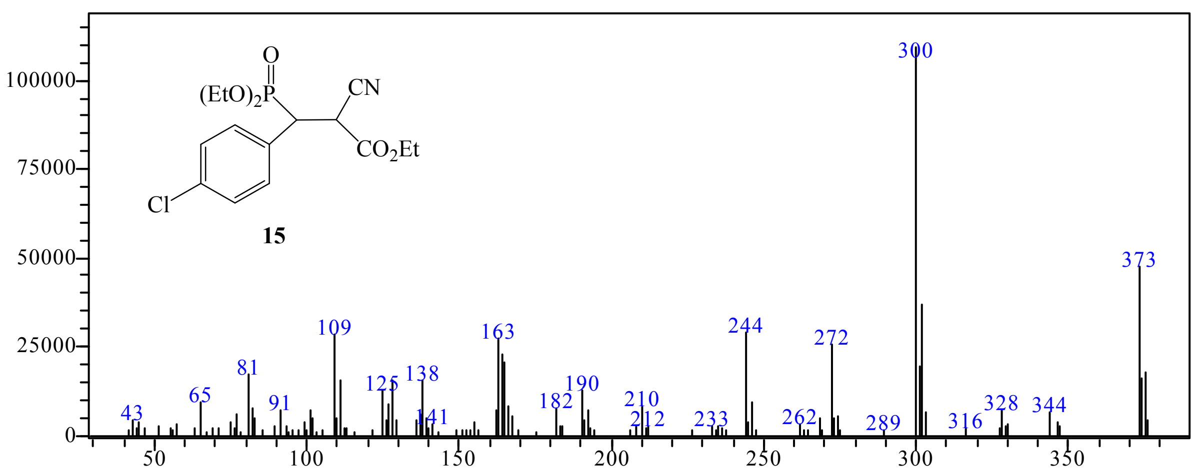

Abundance
m/z-->
(EtO)2P
O
CN
CN
HO
10
(EtO)2P
O
CN
CN
11
43 51 57 65 75 81 89 95 101 107 116 123 132 138 145 151 158 164 171 187 199 215 225 233 243 252 265 271 277 308


(EtO)2P
O
CN
CN
11
41 43 58 82 91 111 121 138 149 165 173 193 203 215 231 243 259


(EtO)2P
O
CN
CN
12
41 54 65 81 95 111 117 137 148 163 179 190 201 214 235 244 259 271 285 301


Abundance
m/z-->
43
123
163
189
207
271
297
313
354
(i-Pr-O)2P(O)
CN
CN
Cl
13


40
43
57
70
93
109
121
128
149
163
168
189
233
257
279
298
(MeO)2P(O)
CN
CN
Cl
14


43
65
81
91
109
125
138
141
163
182
190
210
212
233
244
262
272
289
300
316
328
344
373
(EtO)2P(O)
CN
CO2Et
Cl
15