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Efficient solvent free synthesis of tertiary α-aminophosphonates using $H_2Ti_3O_7$ nanotubes as a reusable solid-acid catalyst

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1. General experimental details

Photo catalyst grade titanium dioxide (TiO_2-P25 and TiO_2-LAB) was procured from Degussa Corporation, Germany and Merck, India. Sodium Hydroxide pellets (99 %) and Hydrochloric acid (35 % pure) was purchased from Merck, India. Distilled water was used for materials synthesis/solution preparation. De-ionized water used for nanotube washing process.

Solvents were purchased from Merck, India and used as received. Analytical thin layer chromatography was performed with aluminium backed plates pre-coated with silica gel 60 F254 (0.2 mm) from Merck, and visualization was achieved by inspection under 254nm UV light. Column chromatography was performed using silica gel (100 - 200 mesh) from SDFCL; eluting solvents reported as % v/v mixtures.

Powder wide-angle X-ray diffraction (WAXRD) patterns of the catalysts were recorded using a D8 ADVANCE X-ray diffractometer (Bruker) equipped with Ni-filtered Cu K_α (k = 1.5418 Å) radiation (30 kV, 50 mA). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) measurements were carried out by using a FEI Tecnai F20ST electron microscope operated at 200 keV and equipped with high angle annular dark field (HAADF) detector and energy dispersive X-ray (EDX) spectrometer. For TEM measurement, all the catalysts were sonicated in acetone or ethanol and the resulting dispersion of the powder catalysts was transferred into a holey carbon film fixed on a 3 mm copper grid (200 meshes). The specific surface area (SSA) and pore size of the catalysts were measured by N_2 adsorption-desorption isotherms at 77 K using a surface area analyzer (Micromeritics, ASAP 2020). Prior to the measurements, all the catalysts were degassed at 350 ºC under vacuum (10^{-3} mbar) for 6 h. Brunauer-Emmett-Teller method (BET) was used to calculate the SSA whereas the pore size distributions were derived from the desorption branches of the isotherms based on the Barrett-Joyner-Halenda model (BJH).

Total acidity was evaluated by temperature-programmed desorption of ammonia (TPD/NH_3) using a Micromeritics Chemisorb 2750 instrument. Before NH_3 desorption, the samples were heated to 200℃ (20° min^{-1}) in 30mL high pure Helium flow. Subsequently, the samples were cooled down to 30℃ in helium flow.NH_3 adsorption was performed under ambient conditions and saturated for about 30 min in a flow of 10% ammonia in Helium (30 ml min^{-1}). Then, the samples were purged in a Helium flow until a constant baseline level was

attained. Desorption of NH_3 was carried out with the linear heating rate (10℃ min^{-1}) in a flow of Helium from 30℃-600℃.

Infrared spectra of the title compounds were recorded on Bruker Alpha-Eco ATR-FTIR (Attenuated total reflection-Fourier transform infrared) interferometer with single reflection sampling module equipped with ZnSe crystal. NMR analysis was performed on Bruker DRX 400 (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) and Bruker DRX 500 (500 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) spectrometers. Chemical shifts are expressed as δ (ppm) values using TMS or the residual signals of the solvents as the internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating 70 eV. Melting points were recorded on Guna melting point apparatus and are uncorrected.

2. Catalyst characterization

2.1. HR-TEM image of (a) TFP, (b) TNP and (c & d) TNR

Fig. S1 Shows that the HR-TEM images of TiO_2-fine particles (TP), TiO_2-P25 nanoparticles (TNP), $H_2Ti_3O_7$ nanorods (TNR) catalysts. The **fig. S1a** represents those TiO_2 fine particles with ~150 nm and **fig. S1b** displays that TiO_2 nanoparticles with size ~ 25 nm with well dispersed manner. **Fig. S1c** depicts rod-like spherical morphology having different length > 1 μm. **Fig. S1d** confirms the clean nanorods surface with completely filled-inside, besides lattice arrangements observed.

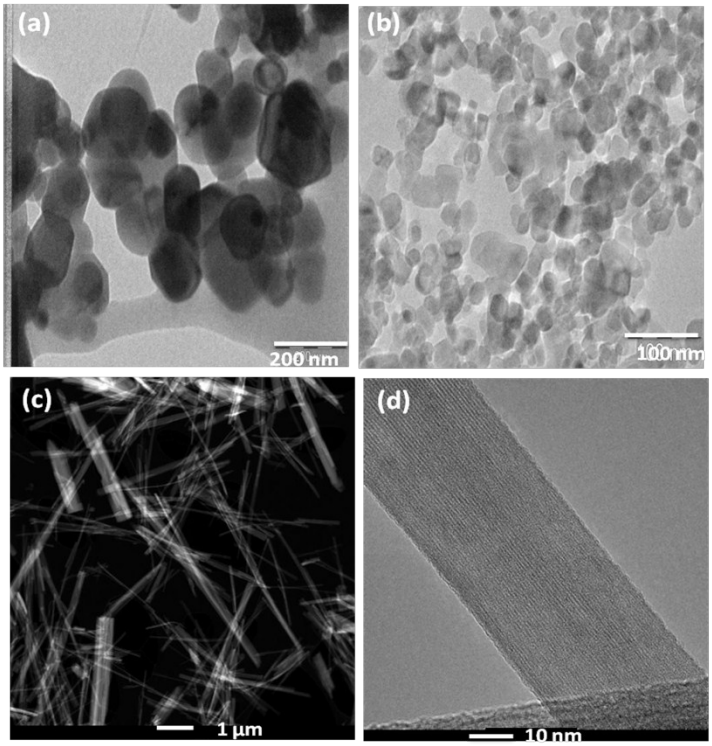


Fig. S1 HR-TEM image of (a) TP, (b) TNP and (c & d) TNR

2.2. XRD Pattern of TFP, TNP and TNR

Fig. S2 displays XRD pattern of standard TFP, TNP and TNR. TNP catalyst shows major peaks at 2θ = 25.4 and 27.5° are characteristic pattern of tetragonal structure of anatase and rutile phase respectively (JCPDS No.21-1272 & 21-1276). TFP catalyst show major peak at 2θ = 25.4 are characteristic pattern of tetragonal structure of anatase phase (JCPDS No.21-1272). The sharp peaks indicate the high crystallinity of the TiO_2 nanoparticles. The TNR catalyst shows 3 major diffraction peaks at 2θ = 10.2, 24.1, and 48.2° is matches well with hydrogen trititanate phase ($H_2Ti_3O_7$), layered type and monoclinic crystal structure (JCPDS No. 47-0561 and 31-1329). The broad diffraction pattern of TNR suggests that the poor crystallinity of the catalytic materials. These observations are matches well with our earlier reports.[1a, 1b]

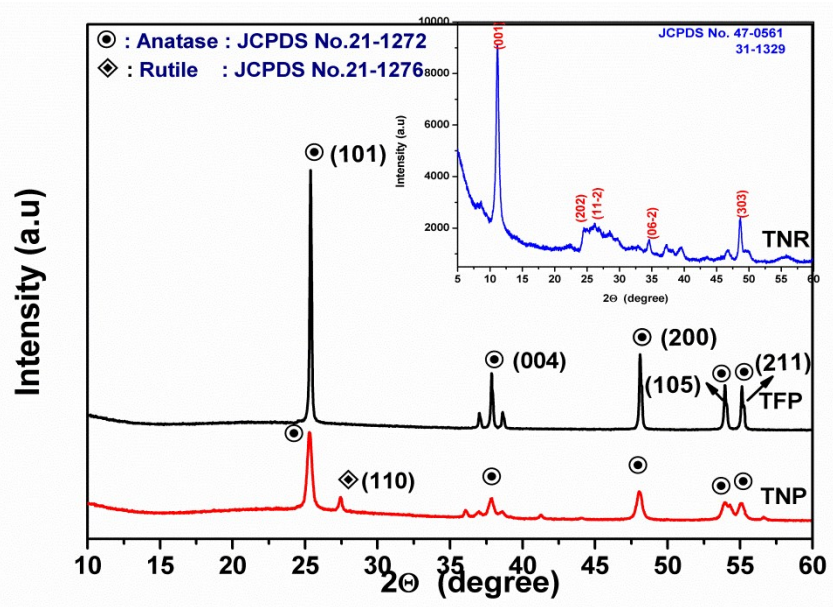


Fig. S2 XRD Pattern of TFP, TNP and TNR

2.3. N_2 Adsorption-desorption Isotherm of TNP, TNR and TN

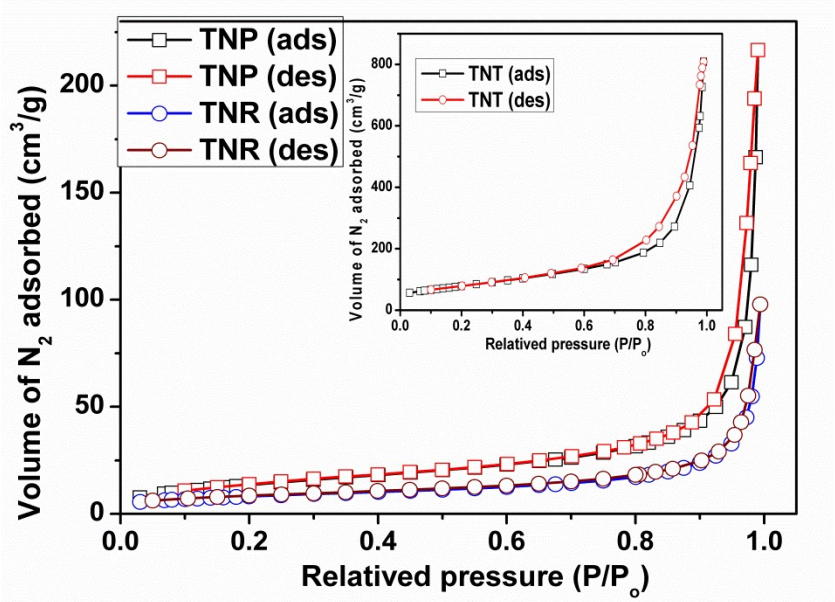


Fig. S3 N_2 Adsorption-desorption Isotherm of TNP, TNR and TNT

2.4. BJH pore size distributions for TNP, TNR and TNT

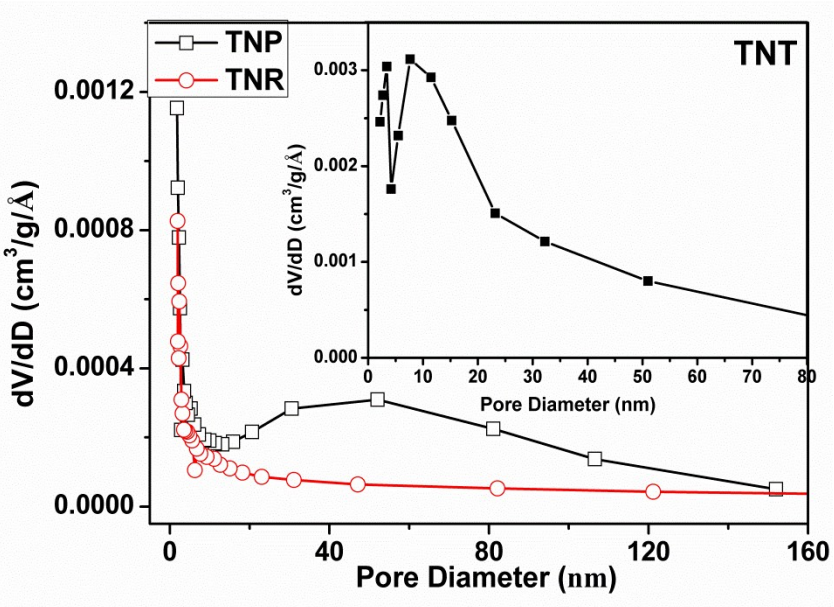


Fig. S4 BJH pore size distributions for TNP, TNR and TNT

2.5. NH_3-TPD of TFP, TNP, TNR and TNT

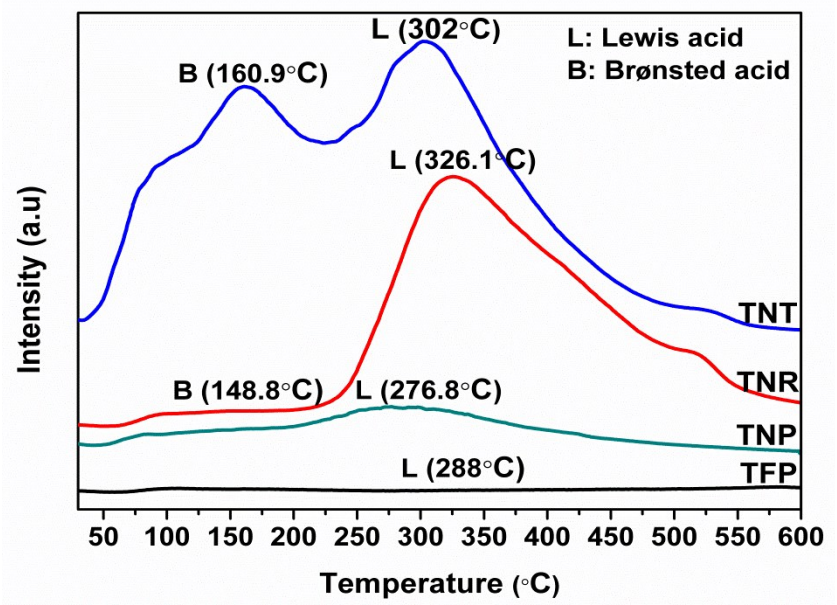


Fig. S5 NH_3-TPD of TFP, TNP, TNR and TNT

3. Characterization data of novel α-aminophosphonates

Diethyl [5,8-dioxa-10-azadispiro[2.0.4.3]undec-10-yl(2-thienyl)methyl]phosphonate (17)

Brown colour oil; IR, *v*max (ZnSe)/cm^{-1}: 3081 (Ar-C-H), 2980 (ali-C-H), 1225 (P=O), 1222 (C-N), 960 (P-O), 795 (P-C); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.29 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 7.02 (t, *J* = 12.4 Hz, Ar-H), 4.29-4.15 (m, 3H, -P(O)CH- & -P(O)OC$\underline{H_2}$$CH_3$), 4.07-3.89 (m, 2H, -P(O)OC$\underline{H_2}$$CH_3$), 3.87-3.72 (m, 4H, -OCH_2CH_2O-), 3.11 (d, *J* = 10 Hz, 1H, -N-CH_2), 2.93 (d, *J* = 7.6 Hz, -N-CH_2), 2.03 (d, *J* = 9.6 Hz, -N-CH_2), 1.39-1.25 (m, 3H, -P(O)$OCH_2C\underline{H_3}$), 1.17-1.14 (m, 3H, -P(O)$OCH_2C\underline{H_3}$), 0.83-0.81 (m, 2H, cyclopropyl-CH_2), 0.53-0.46 (m, 2H, cyclopropyl-CH_2); ^{13}NMR (100 MHz, $CDCl_3$, δ ppm): 133.85 (Ar-C), 128.80 (Ar-C), 126.70 (Ar-C), 125.88 (Ar-C), 113.42 (CH_2O-$\underline{C}$-OCH_2), 64.50 (-P(O)OC$\underline{H_2}$$CH_3$), 63.39 (-$OCH_2CH_2O$-), 62.82 (-N-$CH_2$), 61.12 (-N-$CH_2$), 60.51 (qr, *J* = 144.5, -P(O)-CH-N-), 16.50 (-P(O)$OCH_2C\underline{H_3}$), 9.31 (cyclopropyl-CH_2); ^{31}P NMR (161 MHz, $CDCl_3$, δ ppm): 19.89 (s); MS (ESI): 388.1348 ($[M+H]^+$). Anal.Calcd for $C_{17}H_{27}NO_5PS$: C, 52.70; H, 6.76; N, 3.62%; Found: C, 52.75; H, 5.70; N, 3.68%.

Dibutyl [5,8-dioxa-10-azadispiro[2.0.4.3]undec-10-yl(2-thienyl)methyl]phosphonate (18)

Brown colour oil; IR, *v*max (ZnSe)/cm^{-1}: 3082 (Ar-C-H), 2959 (ali-C-H), 1230 (P=O), 1218 (C-N), 981 (P-O), 781 (P-C); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.28 (m, 1H, Ar-H), 7.15 (s, 1H, Ar-H), 7.00-6.98 (qr, *J* = 4.0 Hz, 1H, Ar-H), 4.27 (d, 1H, *J* = 21.0 Hz, -P(O)CH-), 4.18-3.73 (m, 8H, -P(O)OC$\underline{H_2}$$CH_2CH_2CH_3$ & -OCH_2CH_2O-), 3.09 (d, 1H, -N-CH_2), 2.91-2.88 (qr, *J* = 6.5 Hz, 2H, -N-CH_2), 2.80 (d, *J* = 9.0 Hz, 1H, -N-CH_2), 1.65-1.62 (m, 2H, -P(O)$OCH_2C\underline{H_2}CH_2CH_3$), 1.48-1.45 (m, 2H, -P(O)$OCH_2C\underline{H_2}CH_2CH_3$), 1.39-1.35 (m, 2H, -P(O)$OCH_2CH_2C\underline{H_2}CH_3$), 1.26-1.21 (m, 2H, -P(O)$OCH_2CH_2C\underline{H_2}CH_3$), 0.92 (t, *J* = 9 Hz, 3H, -P(O)$OCH_2CH_2CH_2C\underline{H_3}$), 0.83-0.79 (m, 5H, -P(O)$OCH_2CH_2CH_2C\underline{H_3}$ & cyclopropyl-CH_2), 0.48-0.47 (m, 2H, cyclopropyl-CH_2); ^{13}NMR (100 MHz, $CDCl_3$, δ ppm): 134.00 (Ar-C), 128.76 (Ar-C), 126.69 (Ar-C), 125.82 (Ar-C), 113.45 (CH_2O-$\underline{C}$-OCH_2), 67.05 (-P(O)OC$\underline{H_2}$$CH_2$-$CH_2CH_3$), 66.40 (-$OCH_2CH_2O$-), 64.52 (-N-$CH_2$), 61.11 (-N-$CH_2$), 60.31 (qr, *J* = 153.75, -P(O)-CH-N-), 32.62 (-P(O)$OCH_2C\underline{H_2}CH_2CH_3$), 18.70 (-P(O)$OCH_2CH_2C\underline{H_2}CH_3$), 13.59 (-P(O)$OCH_2CH_2$-$CH_2C\underline{H_3}$), 9.32 (cyclopropyl-$CH_2$); ^{31}P NMR (202 MHz, $CDCl_3$, δ ppm): 19.90-19.80 (qr); HRMS: Anal. Calcd for $C_{24}H_{19}N_2O_4PS$ (M+H): 444.19681; found: 444.19620.

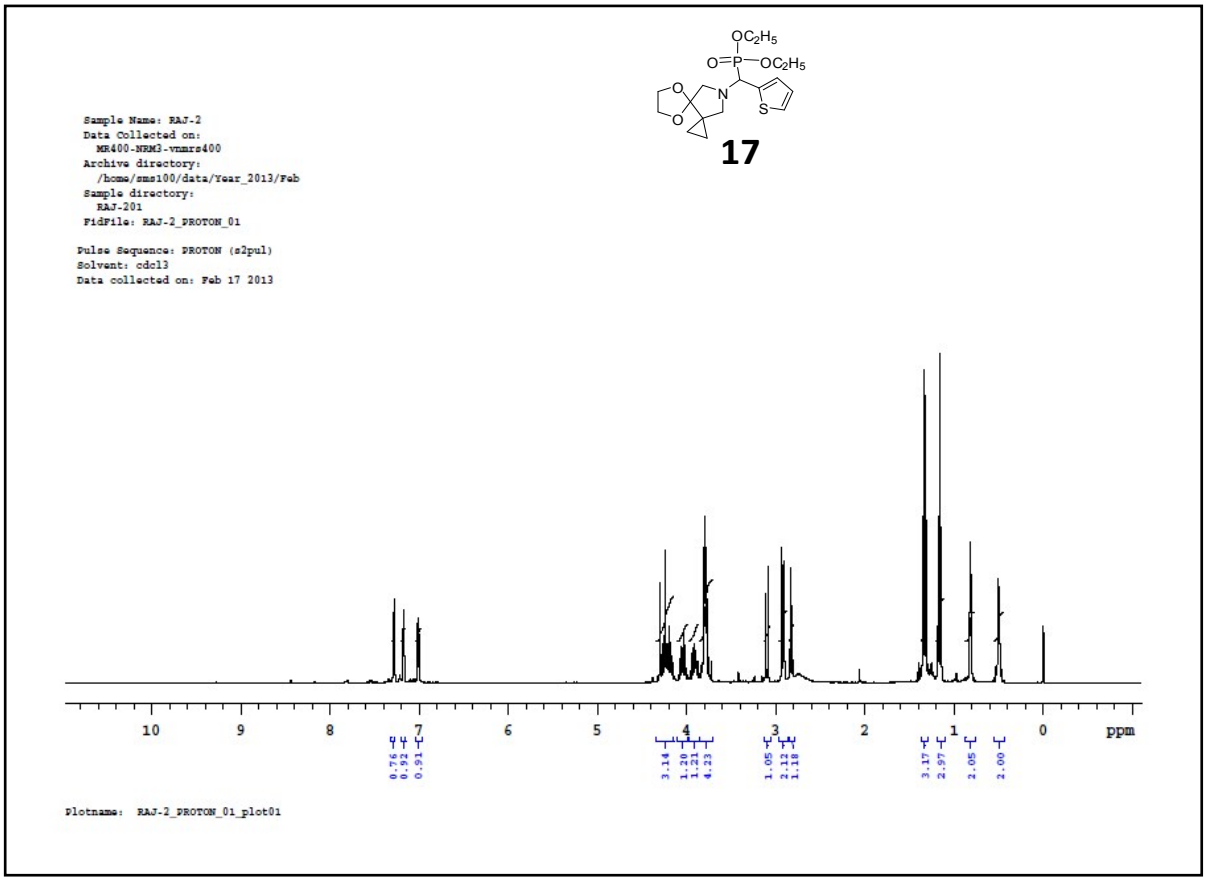
Dibutyl[(2,6-dimethoxy-3-pyridyl)(5,8-dioxa-10-azadispiro[2.0.4.3]undec-10-yl)methyl] phosphonate (19)

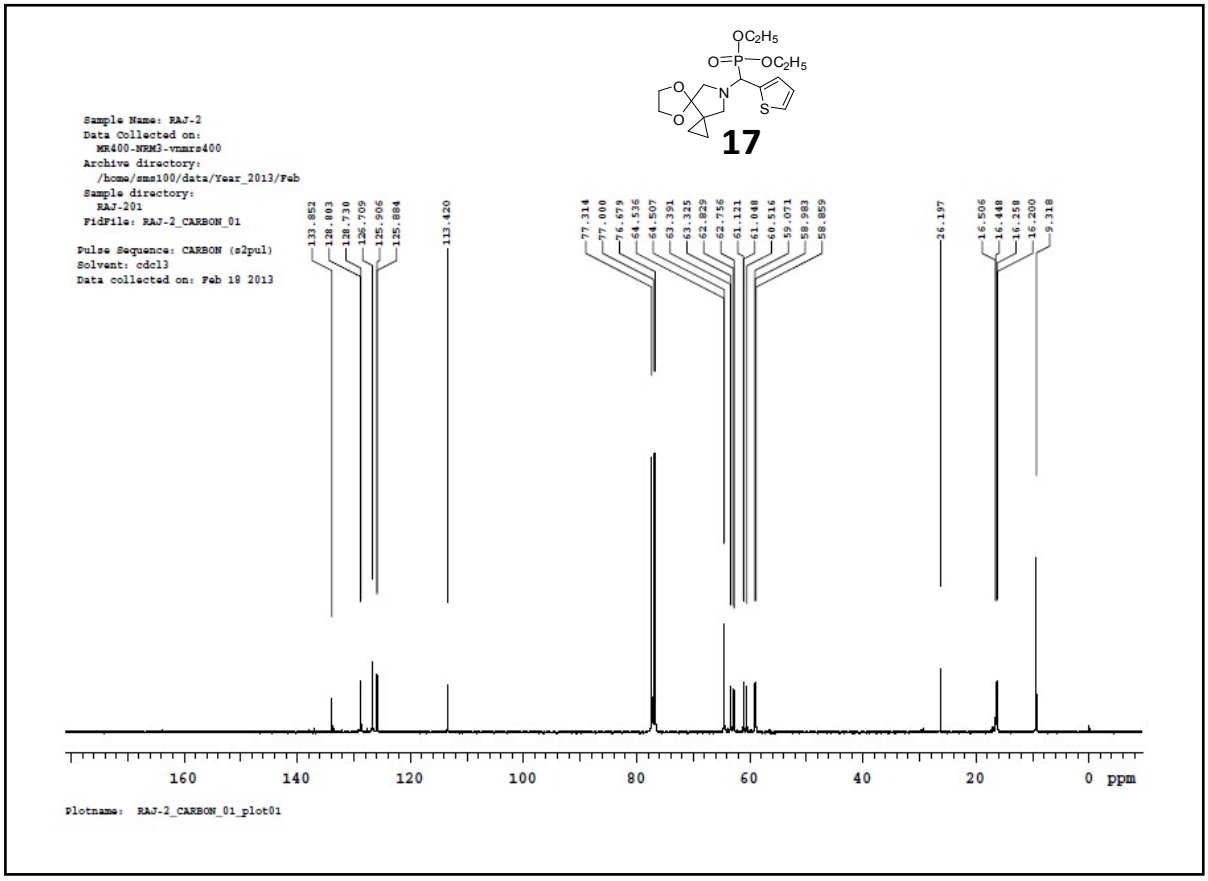
Brown colour oil; IR, *v*max (ZnSe)/cm^{-1}: 3026 (Ar-C-H),2892 (ali-C-H), 1548 (C=N), 1265 (P=O), 1175 (C-O), 1087 (C-N), 967 (P-O), 788 (P-C); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.96 (d, *J* = 10.0 Hz, 1H, Ar-H), 6.36 (d, *J* = 7.6 Hz, 1H, Ar-H), 4.57 (d, *J* = 18.8 Hz, 1H, -P(O)CH-), 4.15-3.75 (m, 14H, -P(O)OC$\underline{H_2}$$CH_2CH_2CH_3$ & -OCH_2CH_2O- & Ar-OCH_3), 3.33 (s, 2H, -N-CH_2), 3.15 (d, *J* = 9.2 Hz, 1H, -N-CH_2), 3.08 (d, *J* = 9.2 Hz, -N-CH_2), 1.67-1.60 (m, 2H, -P(O)$OCH_2C\underline{H_2}CH_2CH_3$), 1.45-1.34 (m, 6H, -P(O)$OCH_2C\underline{H_2}CH_2CH_3$ & -P(O)$OCH_2CH_2C\underline{H_2}CH_3$), 1.25-1.20 (m, 6H, -P(O)$OCH_2CH_2CH_2C\underline{H_3}$), 0.85-0.83 (t, *J* = 16.0 Hz, 4H, cyclopropyl-CH_2); ^{13}NMR (100 MHz, $CDCl_3$, δ ppm): 162.76 (Ar-C), 160.88 (Ar-C), 142.52 (Ar-C), 105.88 (CH_2O-$\underline{C}$-OCH_2), 101.03 (Ar-C), 66.48 (-P(O)OC$\underline{H_2}$$CH_2CH_2CH_3$), 60.73 (Ar-$OCH_3$), 57.04 (-$OCH_2CH_2$O-), 55.37 (-P(O)-CH-N-), 53.52 (-N-CH_2), 32.56 (-P(O)$OCH_2C\underline{H_2}CH_2CH_3$), 18.69 (-P(O)$OCH_2CH_2C\underline{H_2}CH_3$), 16.57 (-P(O)$OCH_2CH_2CH_2C\underline{H_3}$), 13.57 (cyclopropyl -$CH_2$); ^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 22.05 (s); MS (ESI): 499.1573 ($[M+H]^+$). Anal.Calcd for $C_{24}H_{40}N_2O_7P$: C, 57.70; H, 8.07; N, 5.61%; Found: C, 57.75; H, 8.09; N, 5.75%.

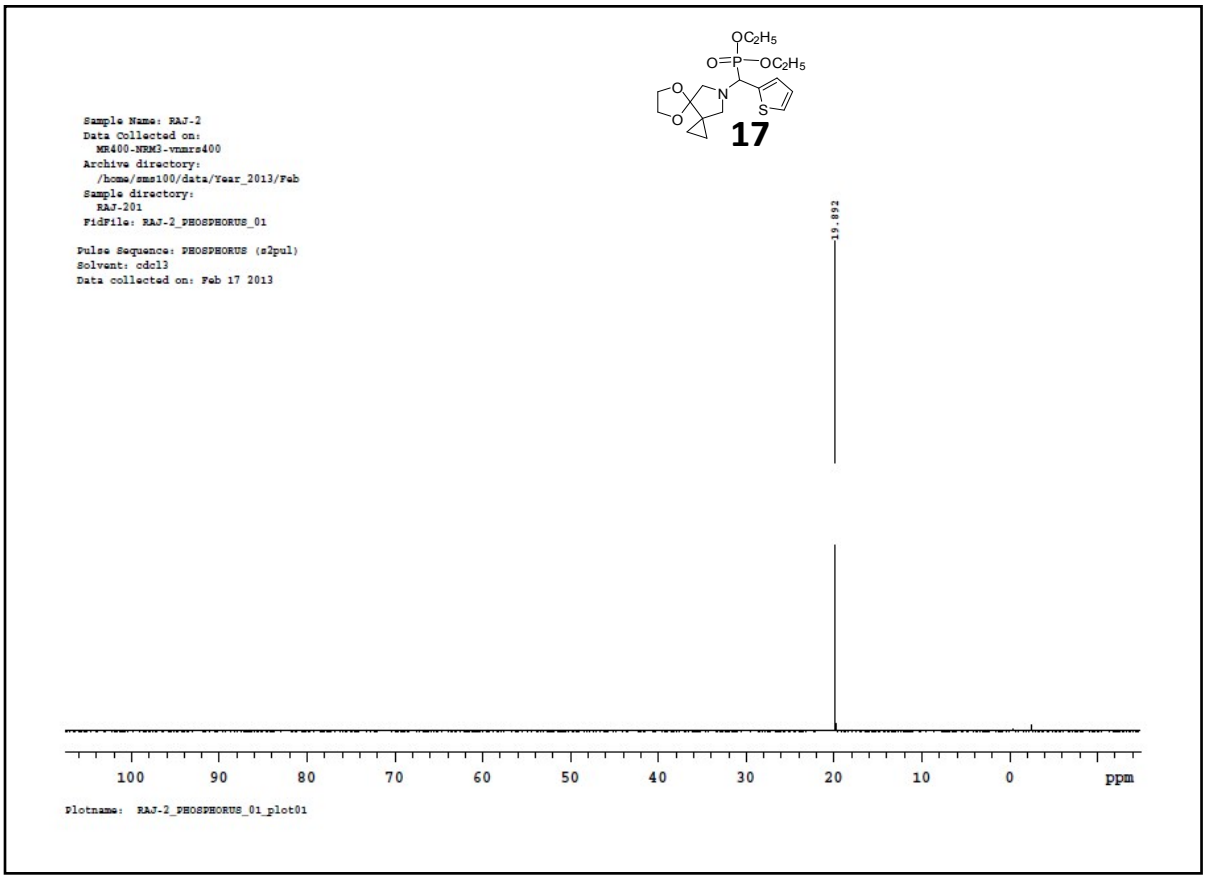
Diethyl[5,8-dioxa-10-azadispiro[2.0.4.3]undec-10-yl[3-(5-pyrimidinyl)phenyl]methyl] phosphonate (20)

Brown colour oil; IR, *v*max (ZnSe)/cm^{-1}: 3087 (Ar-C-H), 2935 (ali-C-H),1620 (C=N), 1236(P=O), 1175 (C-O), 1027 (C-N), 965 (P-O), 788 (P-C); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.22 (s, 1H, Ar-H), 8.96 (s, 2H, Ar-H), 7.73-7.69 (m, 1H, Ar-H), 7.58-7.55 (m, 1H, Ar-H), 7.53-7.26 (m, 2H, Ar-H), 4.29-4.15 (m, 3H, -(P)CH- & -P(O)OC$\underline{H_2}$$CH_3$), 4.07-3.89 (m, 2H, -P(O)OC$\underline{H_2}$$CH_3$), 3.87-3.72 (m, 4H, -OCH_2CH_2O-), 3.11 (d, *J* = 10.0 Hz, 1H, -N-CH_2), 2.93 (d, *J* = 7.6 Hz, -N-CH_2), 2.03 (d, *J* = 9.6 Hz, -N-CH_2), 1.39-1.25 (m, 3H, -P(O)$OCH_2C\underline{H_3}$), 1.17-1.14 (m, 3H, -P(O)$OCH_2C\underline{H_3}$), 0.83-0.81 (m, 2H, cyclopropyl-CH_2), 0.53-0.46 (m, 2H, cyclopropyl-CH_2); ^{13}NMR (100 MHz, $CDCl_3$, δ ppm): 157.53 (Ar-C), 154.94 (Ar-C), 136.13 (Ar-C), 134.21 (Ar-C), 130.70 (Ar-C), 129.31 (Ar-C), 128.43 (Ar-C), 126.57 (Ar-C), 113.40 (CH_2O-$\underline{C}$-OCH_2), 66.49 (-P(O)OC$\underline{H_2}$$CH_3$), 64.60 (-$OCH_2CH_2$O-), 63.04 (-N-$CH_2$), 60.85 (-P(O)-CH-N-), 32.53 (-P(O)$CH_2C\underline{H_3}$), 9.58 (cyclopropyl-CH_2); ^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 20.83 (t, *J* = 13.4 Hz); MS (ESI): 460.2001 ($[M+H]^+$). Anal.Calcd for $C_{23}H_{31}N_3O_5P$: C, 59.99; H, 6.79; N, 9.13%; Found: C, 60.05; H, 6.84; N, 9.18%.

4. ^{1}H, ^{13}C and Mass spectra of novel α-aminophosphonates



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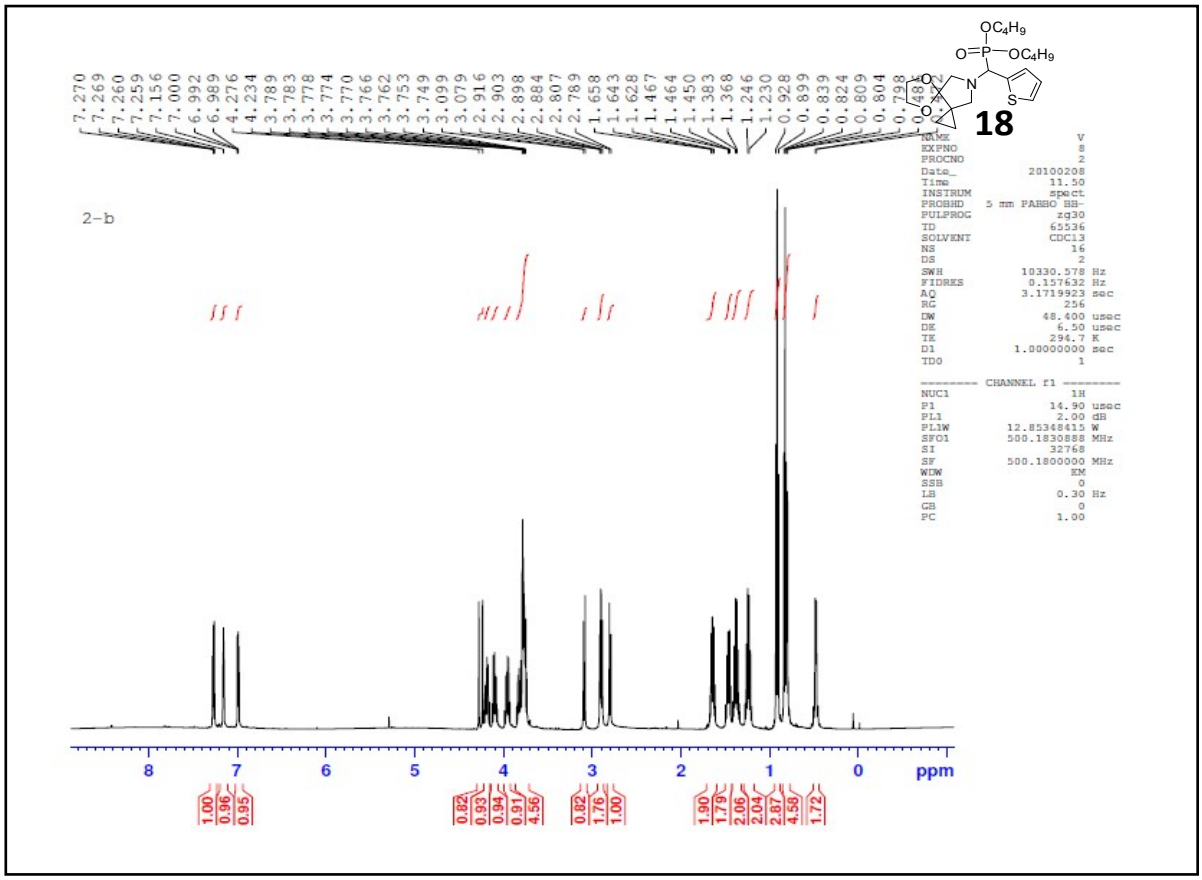
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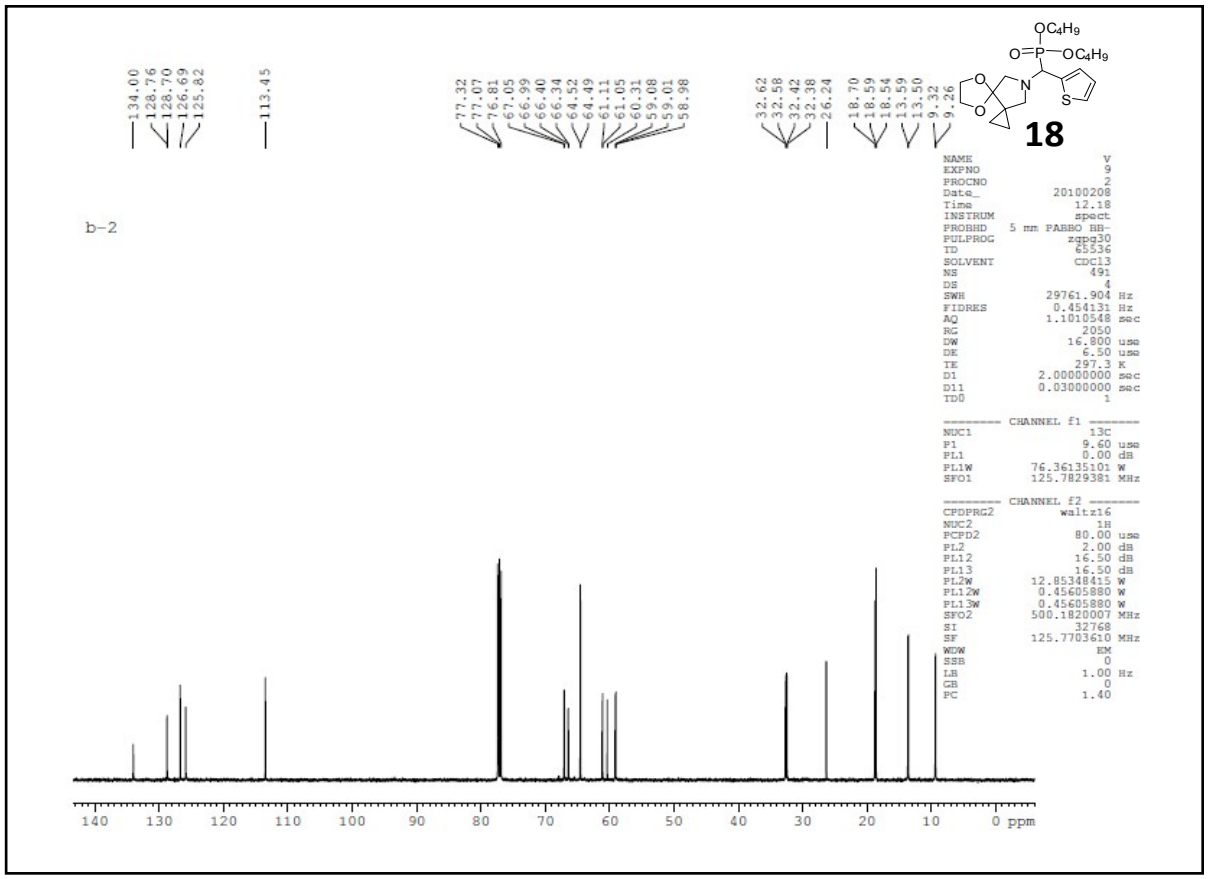
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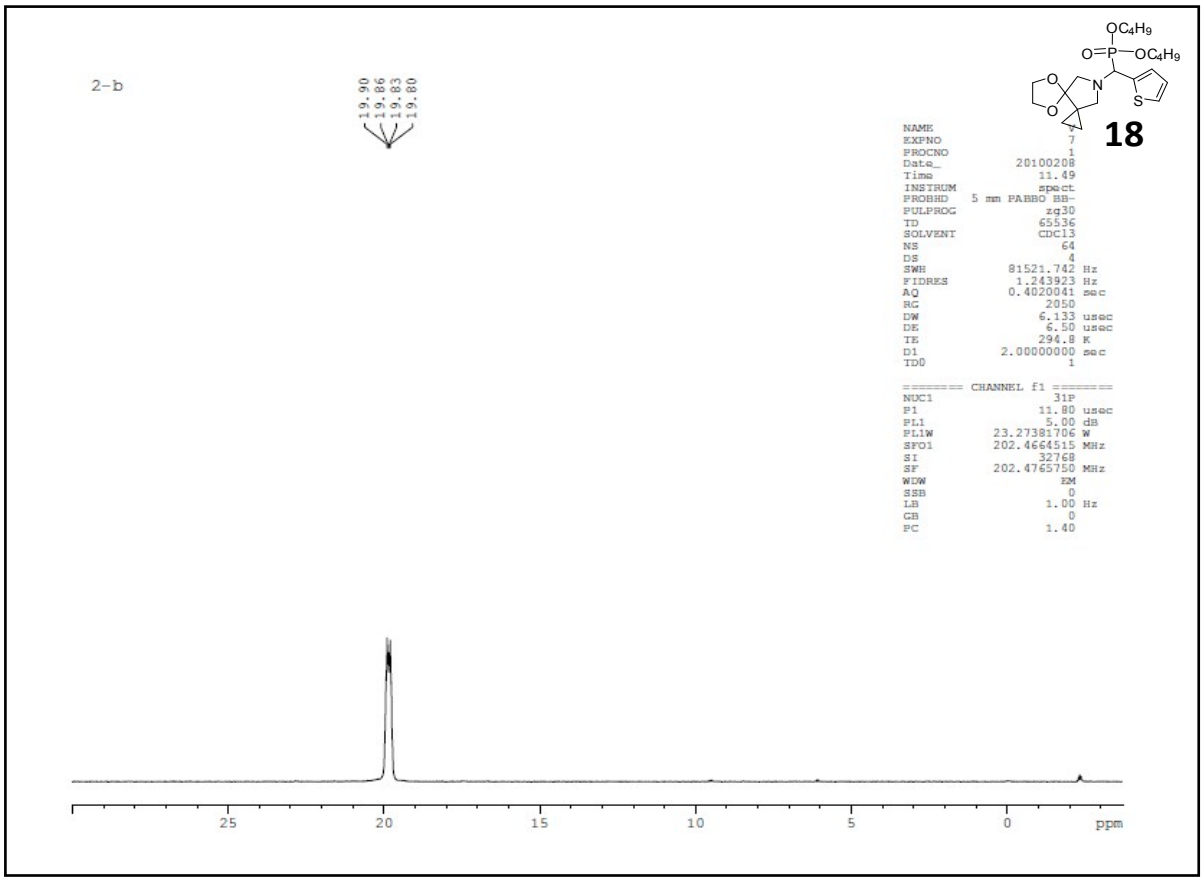
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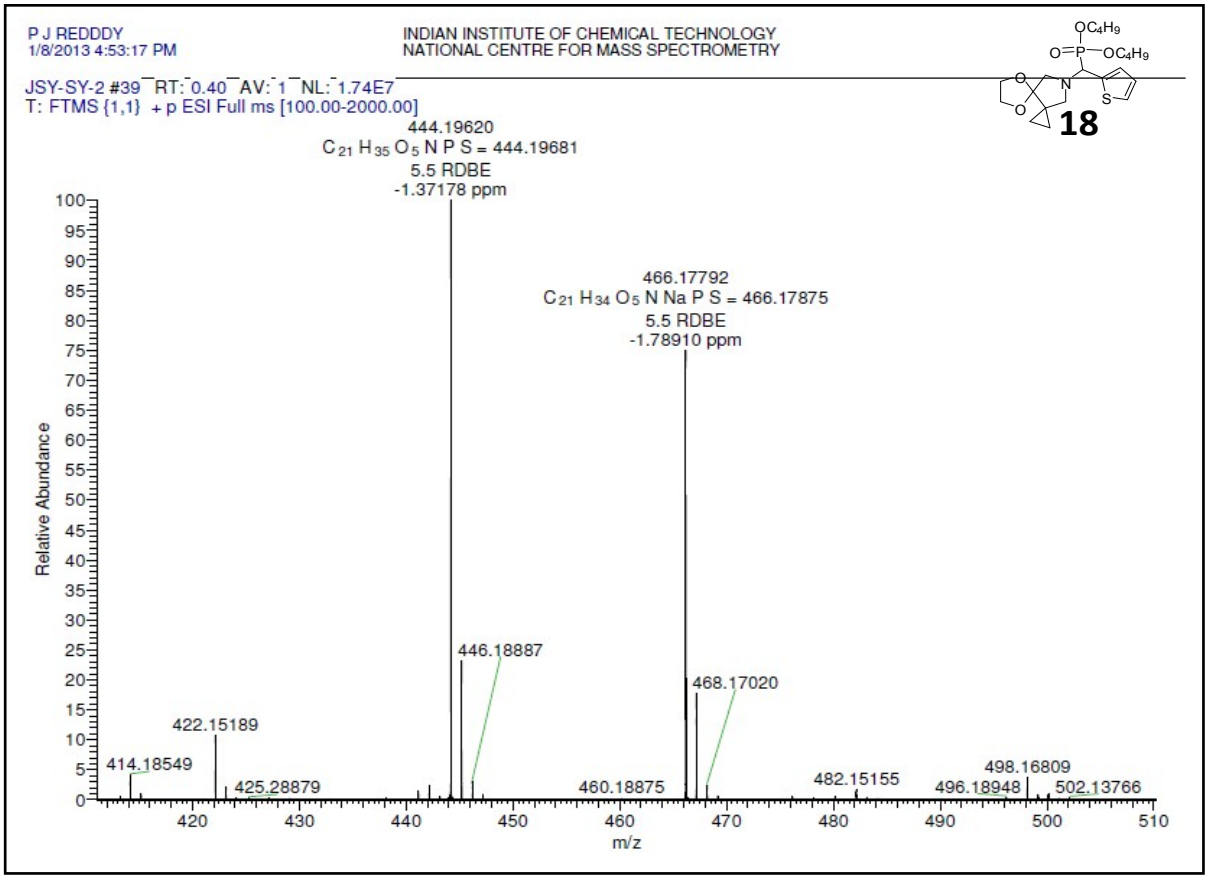
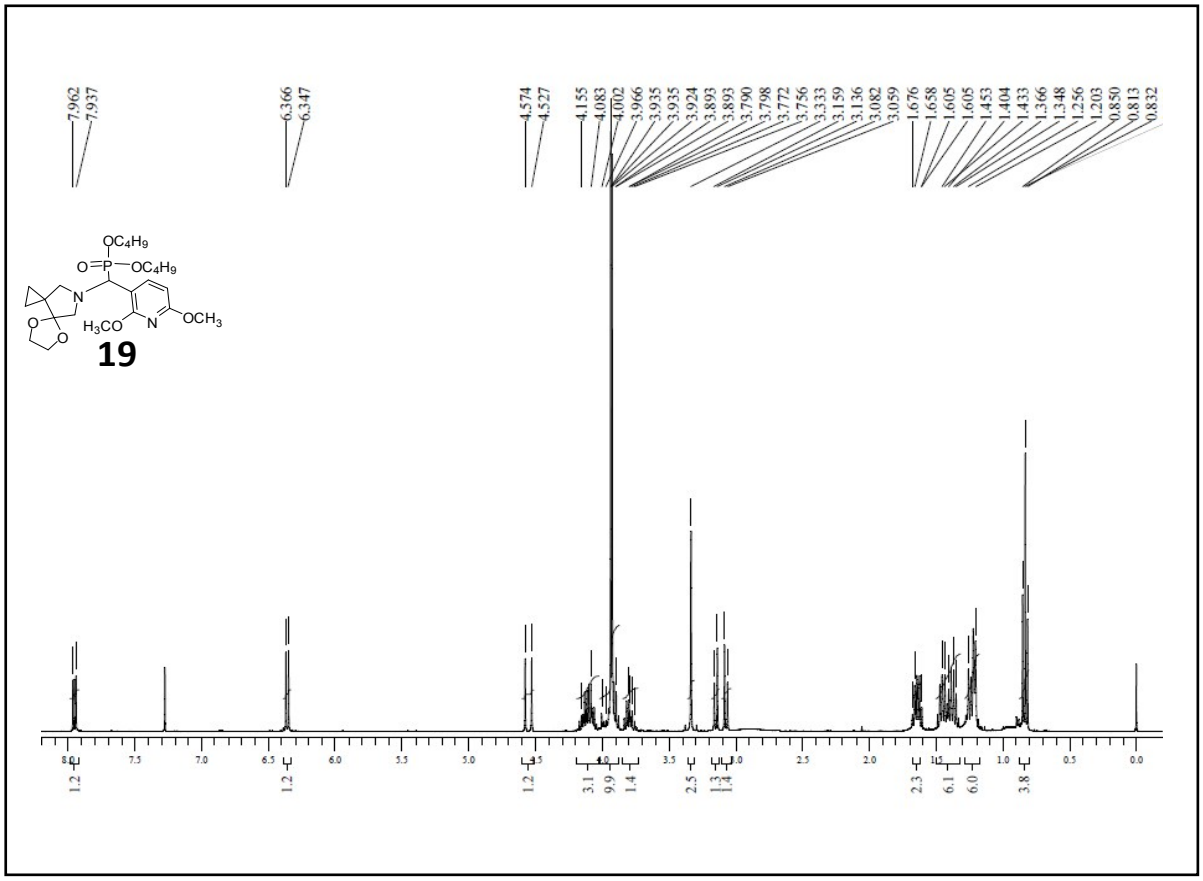
PC 1.40
25 20 15 10 5 0 ppm


P J REDDDY
1/8/2013 4:53:17 PM
INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
NATIONAL CENTRE FOR MASS SPECTROMETRY
JSY-SY-2 #39 RT: 0.40 AV: 1 NL: 1.74E7
T: FTMS {1,1} + p ESI Full ms [100.00-2000.00]
444.19620
C21 H35 O5 N P S = 444.19681
5.5 RDBE
-1.37178 ppm
466.17792
C21 H34 O5 N Na P S = 466.17875
5.5 RDBE
-1.78910 ppm
446.18887
468.17020
422.15189
414.18549
425.28879
460.18875
482.15155
498.16809
496.18948
502.13766
Relative Abundance
m/z
18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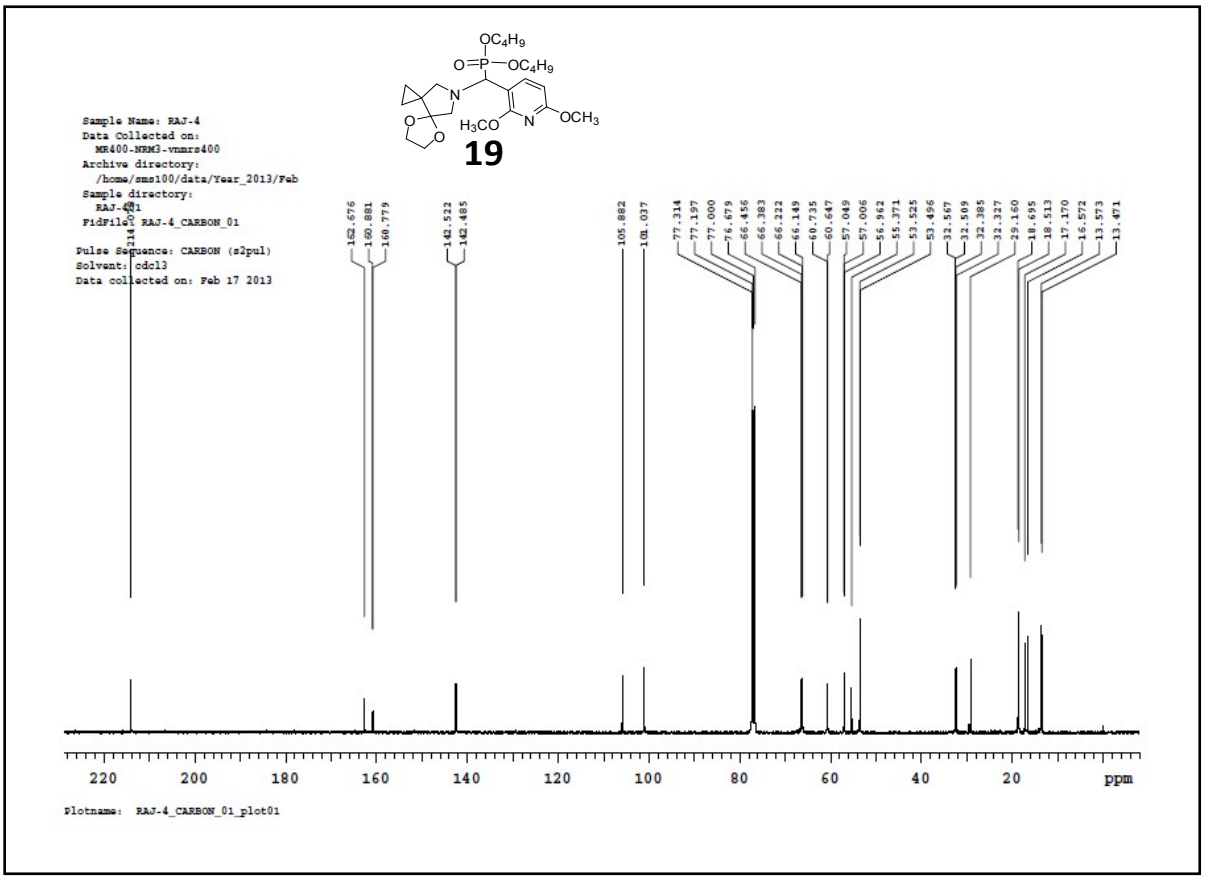
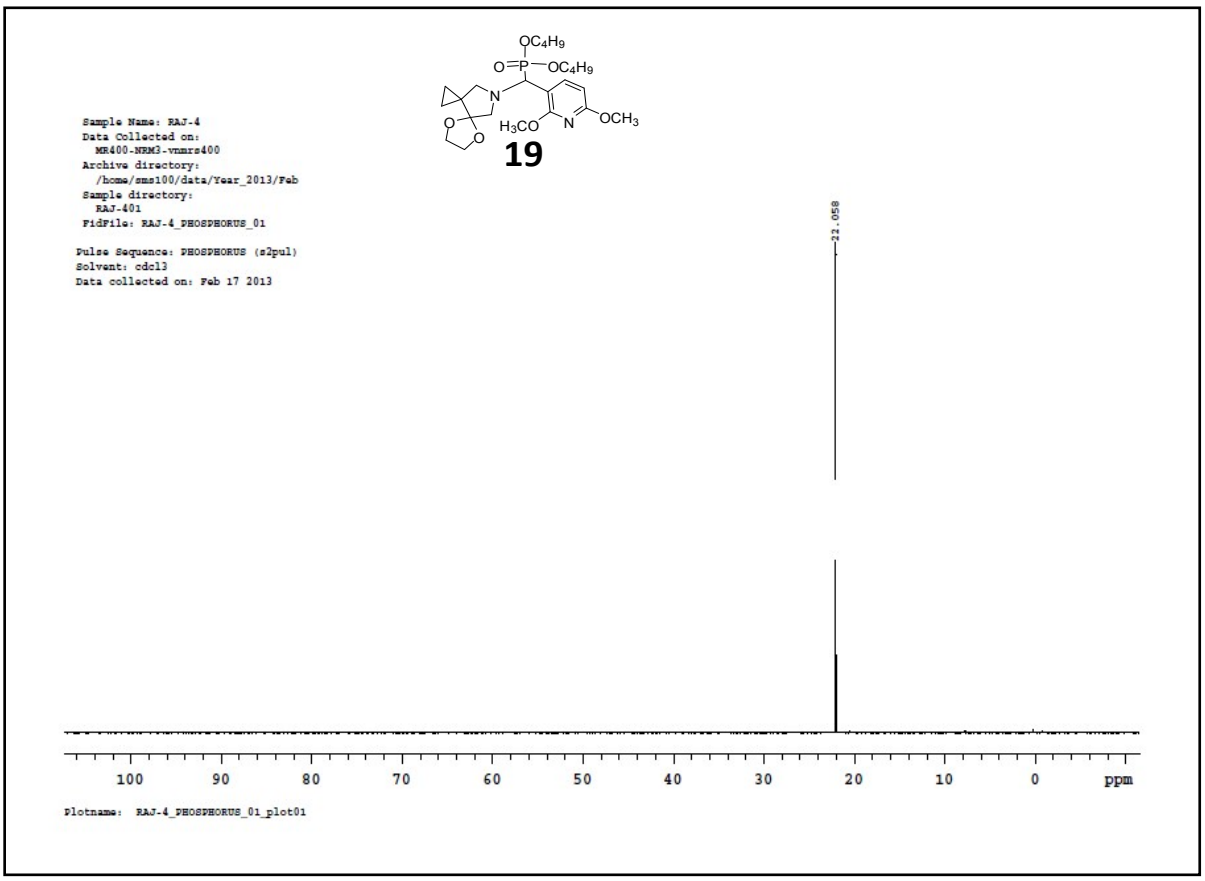
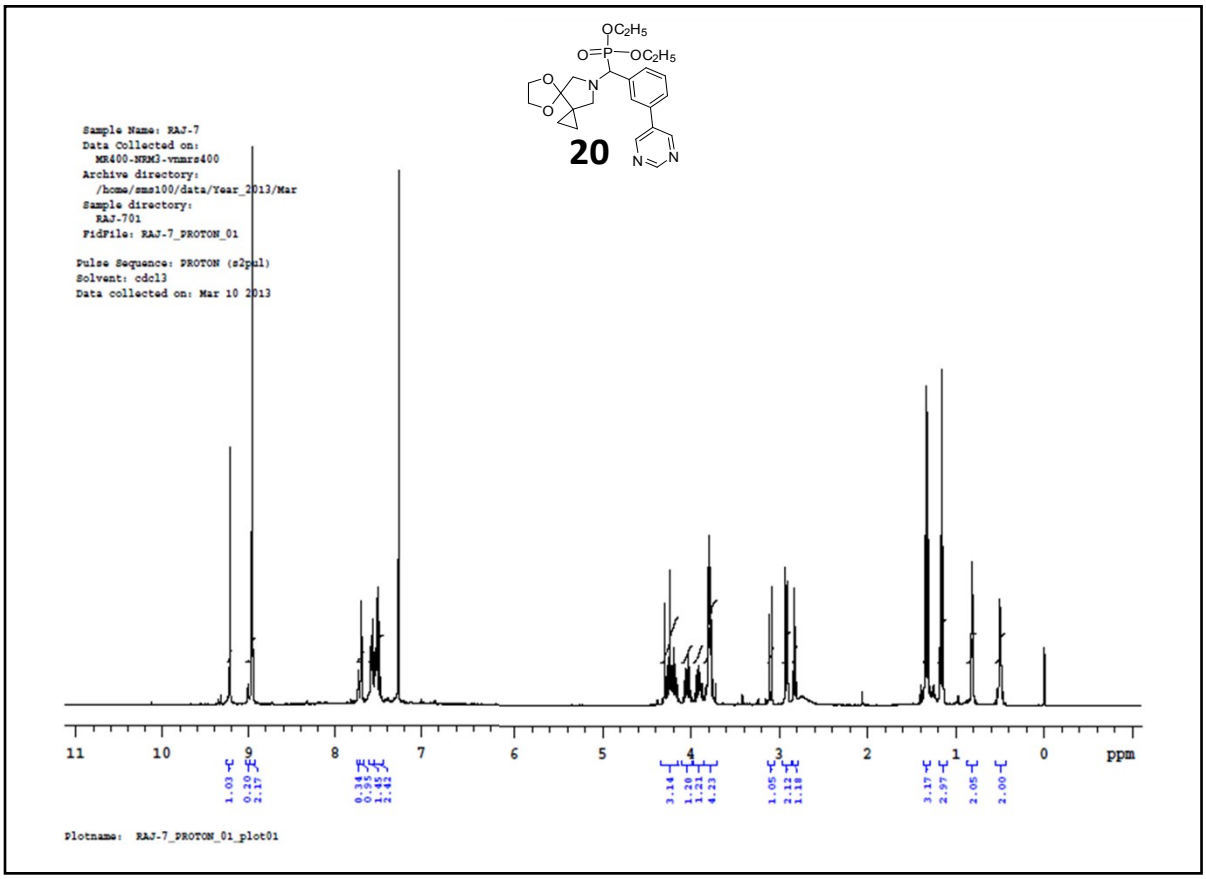
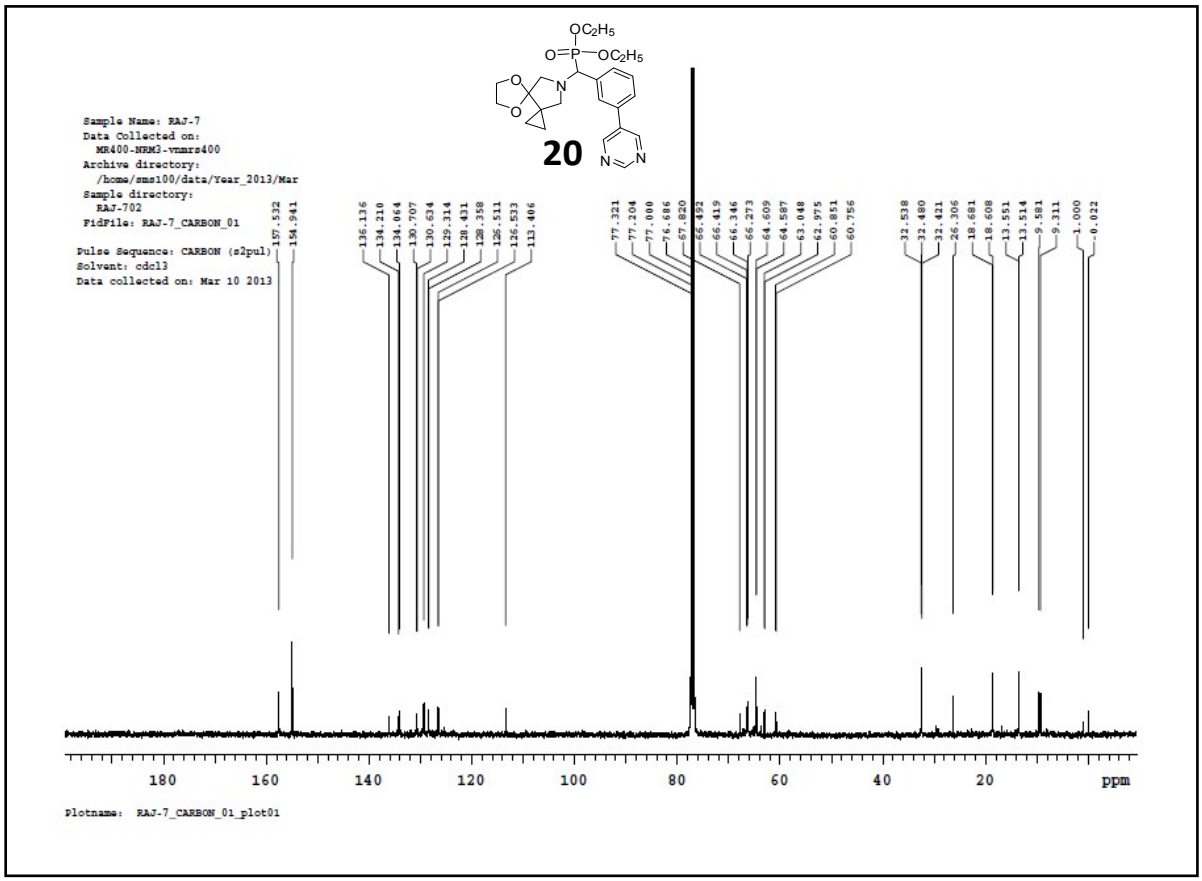
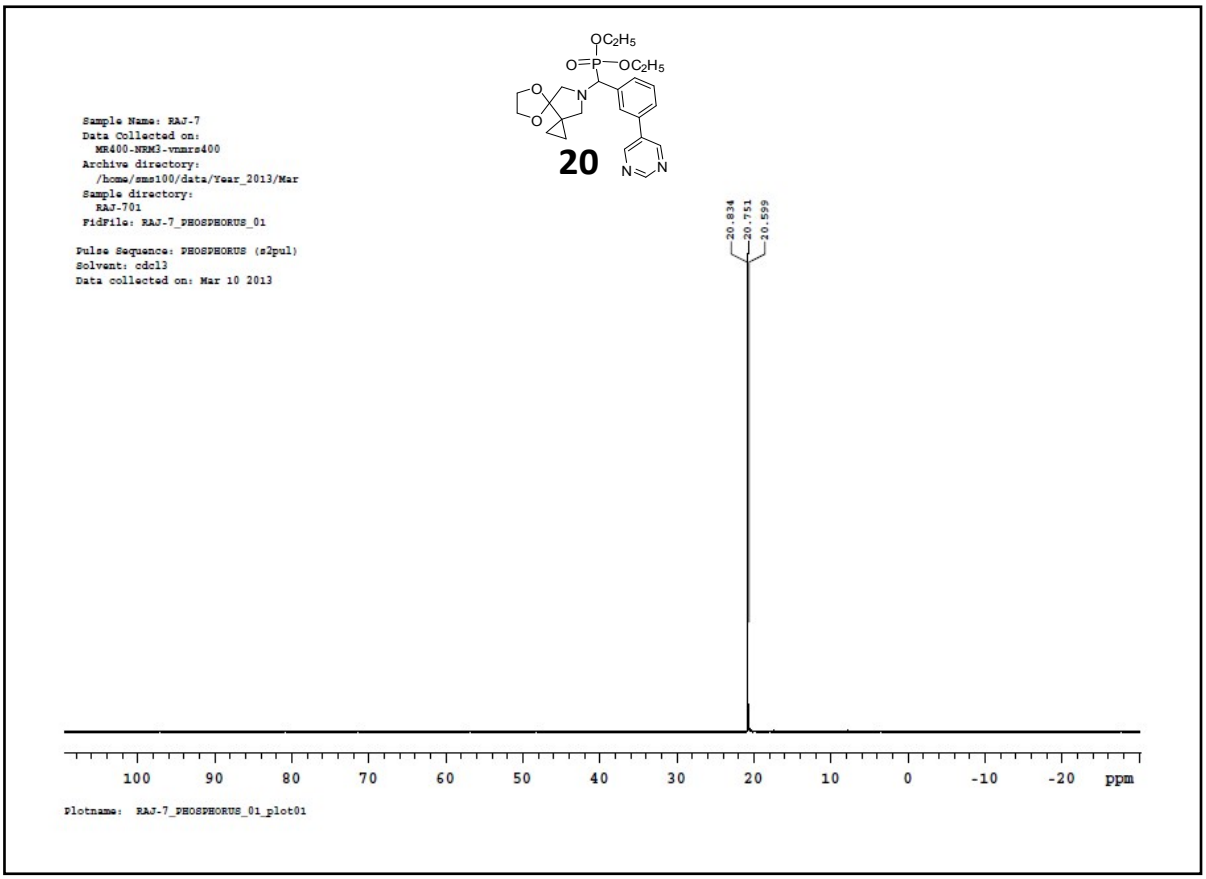

19
Sample Name: RAJ-4
Data Collected on:
MR400-NRM3-vnmrs400
Archive directory:
/home/sms100/data/Year_2013/Feb
Sample directory:
RAJ-401
FidFile: RAJ-4_CARBON_01
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 17 2013
162.676
160.881
160.779
142.522
142.485
105.882
101.037
77.314
77.197
77.000
76.679
66.456
66.383
66.222
66.149
60.735
60.647
57.049
57.006
56.962
55.371
53.525
53.496
32.567
32.509
32.385
32.327
29.160
18.695
18.513
17.170
16.572
13.573
13.471
220
200
180
160
140
120
100
80
60
40
20
ppm
Plotname: RAJ-4_CARBON_01_plot01


19
Sample Name: RAJ-4
Data Collected on:
MR400-NRM3-vnmrs400
Archive directory:
/home/sms100/data/Year_2013/Feb
Sample directory:
RAJ-401
FidFile: RAJ-4_PHOSPHORUS_01
Pulse Sequence: PHOSPHORUS (s2pul)
Solvent: cdcl3
Data collected on: Feb 17 2013
22.058
100
90
80
70
60
50
40
30
20
10
0
ppm
Plotname: RAJ-4_PHOSPHORUS_01_plot01


20
Sample Name: RAJ-7
Data Collected on:
MR400-NRM3-vnmrs400
Archive directory:
/home/sms100/data/Year_2013/Mar
Sample directory:
RAJ-701
FidFile: RAJ-7_PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 10 2013
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.03 0.20 2.17 0.34 0.65 1.42 3.14 1.20 1.21 4.23 1.05 2.12 1.18 3.17 2.97 2.05 2.00
Plotname: RAJ-7_PROTON_01_plot01


20
Sample Name: RAJ-7
Data Collected on:
MR400-NRM3-vnmrs400
Archive directory:
/home/sms100/data/Year_2013/Mar
Sample directory:
RAJ-702
FidFile: RAJ-7_CARBON_01
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 10 2013
157.532 154.941 136.136 134.210 134.064 130.707 130.634 129.314 128.431 128.358 126.511 126.533 113.406
77.321 77.204 77.000 76.686 67.820 66.492 66.419 66.346 66.273 64.609 64.587 63.048 62.975 60.851 60.756
32.538 32.480 32.421 26.306 18.681 18.608 13.551 13.514 9.581 9.311 1.000 -0.022
180 160 140 120 100 80 60 40 20 ppm
Plotname: RAJ-7_CARBON_01_plot01



5. References

1 (a) Shankar, M. V.; Anandan, S.; Venkatachalam, N.; Arabindoo, B.; Murugesan, V.; *Chemosphere*, **2006**, *63*, 1014-1021; (b) Praveen Kumar, D.; Lakshmana Reddy, N.; Mamatha Kumari, M.; Srinivas, B.; Durga kumari, V.; Sreedhar, B.; Roddatis, V.; Bondarchuk, O.; Karthik, M.; Neppolian, B.; Shankar, M. V. *Sol. Energy Mater. Sol. Cells*, **2015**, *136*, 154-166.