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Supplementary Information

Electronic Supplementary Information for Highly efficient solvent free synthesis of α-aminophosphonates catalyzed by recyclable nano magnetic sulfated zirconia (Fe_3O_4@ZrO_2/$SO4^{2-}$)

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Table and Content

1. Experimental

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All chemicals used, such as salts of iron (III) chloride, iron (II) chloride, zirconium (IV) chloride, ammonium sulfate, aldehydes, ketones, amines, and dimethyl phosphite and solvents used were supplied by Merck and Aldrich chemical companies. FT-IR spectra were obtained over the region 400-4000 cm^{-1} with a Nicolet IR 100 FT-IR with spectroscopic grade KBr. The powder X-ray diffraction pattern was recorded using a X-PERT- PRO diffractometer with Cu Kα, (λ= 1.54 Å) irradiation, in the range of 5 to 80 (2θ) with a scan Step of 0.026. The morphology of catalyst was studied with scanning electron microscopy using SEM (KYKY, EM 3200) on gold coated samples. The magnetic properties of $Fe_3O_4@ZrO_2/SO_4^{2-}$ nanoparticles were measured with a vibrating magnetometer/ Alternating Gradient Force Magnetometer (VSM/, MDKFD).In this project, the nano magnetic sulfated zirconia $Fe_3O_4@ZrO_2/SO_4^{2-}$ was prepared and characterized by various instrumental methods. Sulfated zirconia supported on magnetic nanoparticles can act as a well-organized nano catalyst also can be easily separated by the external magnetic field from the reaction mixture. Nano $Fe_3O_4@ZrO_2/SO_4^{2-}$ is heterogeneous acidic catalyst and has special advantages such as facile synthesis procedure, high activity, easy separation and reusability. It was applied as an efficient nanocatalyst in the synthesis of α-aminophosphonate derivatives in Kabachnik-Fields reaction. These synthetic methods has several advantages including high yields, short reaction times, easy workup and environmentally benign reaction conditions.

2. General procedure

2.1Preparation of the magnetic Fe_3O_4 nanoparticles (MNPs)

Ferric acid and ferrous salts were employed as precursors for the synthesis of Fe_3O_4 nano particles. Briefly, $FeCl_3.6H_2O$ (12.2 g, 0.04 mol) and $FeCl_2.4H_2O$ (4.7 g, 0.02 mol) were dissolved in 100 ml distilled water under vigorous stirring. After 10 minutes, the solution was heated at 50 ^{0}C under nitrogen atmosphere. Consequently, the ammonium hydroxide solution (25%) was added dropwise to the reaction mixture to maintain the reaction pH about 9. Afterward, the reaction mixture was cooled at room temperature and black precipitate which was separated by external magnet from the reaction mixture, repeatedly washed with de-ionized water for several times to remove the remaining impurities. At the final step nanoparticles was dried at 60 ^{0}C in vacue.

2.2General procedure for preparation of $Fe_3O_4@ZrO_2/SO4^{2-}$:

Initially 30g $ZrCl_4$ were dissolved in 1000 ml EtOH: H_2O (1:1) to form a colorless solution and aqueous ammonia (10%) was added dropwise under vigorous stirring until the pH of the solution reached 2. Then 3g Fe_3O_4NPs was added to the mixture, after that aqueous ammonia (10%) was added dropwise again under sonication up to pH 9. The precipitate was filtered, thoroughly washed with distilled water, the absence of chloride ion was

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confirmed by $AgNO_3$ test. Subsequently the obtained solid was dipped in $(NH_4)_2SO_4$ (3 mol.L^{-1}) aqueous solution at room temperature for 24 h. Then the solid was filtered, dried without washing overnight at 100 ^{0}C and calcined at 600 ^{0}C, for 6 h in the N_2 atmosphere.

3. Synthesis of α-aminophosphonate derivatives:

A mixture of aldehydes or ketones (2.0 mmol), amine (Tabe S1) (2.0 mmol), dimethylphosphite (2.4 mmol) was added with $Fe_3O_4@ZrO_2/SO_4^{2-}$ (120.0 mg) and stirred at 80^{0C} for the appropriate reaction time (for the period of time listed in Table S1), The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane) if necessary. The products thus obtained were characterized by mp, IR, ^{1}H,^{13}C NMR and MS spectroscopy; Spectral data for selected products is presented in the below.

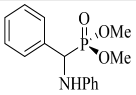
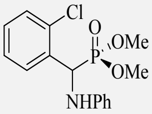
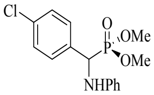
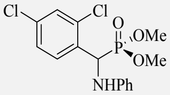
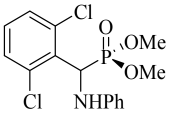
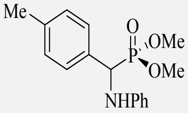
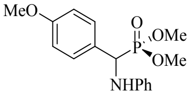
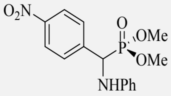
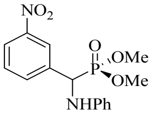
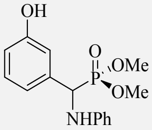
3.1 Purification process:

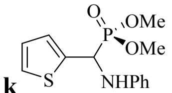
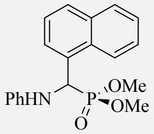
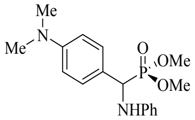
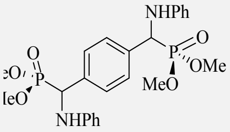
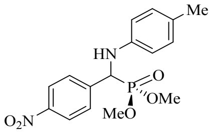
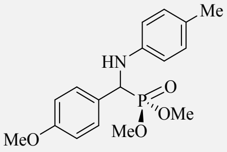
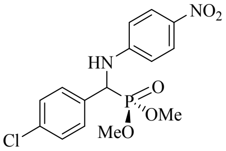
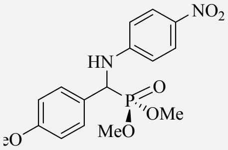
All products were provided by crystallization in the form of crystalline and no additional purification was needed.

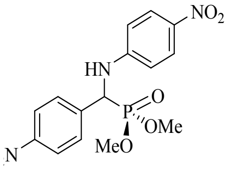
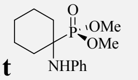
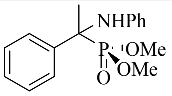
3.2 Catalyst recycling:

The catalyst was extracted by magnet (or filteration) and after that was washed with ethanol. Organic phase was removed by evaporating (by reducing the pressure) and the α-aminophosphonate product was remained in the balloon.

Table S1. synthesis derivatives of α-aminophosphonate in the presence catalyst $Fe_3O_4@ZrO_2/SO_4^{2-a}$

Entry	Carbonyls	ami	Products
1	PhCHO	Aniline	 **1a**
2	2-(Cl)C_6H_4CHO	Aniline	**1b** 
3	4-(Cl)C_6H_4CHO	Aniline	 **1c**
4	2,4-(Cl)$_2C_6H_3CHO$	Aniline	
5	2,6-(Cl)$_2C_6H_3CHO$	Aniline	
6	4-(Me)C_6H_4CHO	Aniline	**1f** 
7	4-(OMe)C_6H_4CHO	Aniline	**1g** 
8	-(NO_2)C_6H_4CHO	Aniline	
9	-(NO_2)C_6H_4CHO	Aniline	**1i** 
10	3-(OH) C_6H_4CHO	Aniline	**1j** 

11	Thiophen-2-carbaldehyde	Aniline	 **1k**
12	-naphthaldehyde	Aniline	 **1L**
13	4-(dimethyl amino) benzaldehyde	Aniline	 **1** **m**
14[c]	rephthaldehyd e	Aniline	 **1n**
15	$NO_2)C_6H_4CHO$	*p*-Toluidine	 **1o**
16	4-)Me)C_6H_4CHO	*p*-Toluidine	 **lp**
17	$(Cl)C_6H_4CHO$	4-Nitroaniline	 **q**
18	4-)Me)C_6H_4CHO	4-Nitroaniline	 **1r**

19	$(NO_2)C_6H_4CHO$	4-Nitroaniline	 **1s**
20	Cyclohexanone	Aniline	 **1t**
21	Acetophenone	Aniline	 **1u**

4. Back titration in aqueous media catalyst $Fe_3O_4@ZrO_2/SO_4^{2-}$

The amount of released [H^+] by catalyst was determined by back titration. In a container which contained 35 ml of distilled water, 0.5 g of NaCl, 0.5 g catalyst and 10 ml NaOH (0.1 M) were added and stirred for 24 h on a magnetic stirrer until neutralized [H^+] which produced from catalyst hydrolysis. Then three drops of phenolphthalein were added to the container and the solution titrated with 0.1 M solution of hydrochloric acid. The end point was reached when the colour changed from pink to colourless

5. Characterization:

5.1. FT-IR, ^{1}H and^{13}C NMR, MS:

5.1.1-Dimethyl [(phenyl) (phenylamino) methyl] phosphonate8, 41 (1a): The mixture of PhCHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0C} for 30 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl [(phenyl)(phenylamino)methyl]phosphonate* (95%) afforded as a white solid, mp 90-92 °C; IR (KBr, $\tilde{v}_{max}$ cm^{-1}): 3305, 1600, 1500, 1240, 1027; ^{1}H NMR (500 MHz, $CDCl_3$):

δ 3.51 (d, J = 10.5 Hz, 3H), 3.81 (d, J = 10.6 Hz, 3H), 4.82 (d, $^{1}J_{P\text{-}H}$ = 23.9 Hz, 1H), 4.84 (br, 1H), 6.61-6.72 (m, 3 H),7.28-7.50 (m, 7 H) , ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 53.68(d, $^{2}J_{P,C}$ = 6.6 Hz), 54.2 (d, $^{2}J_{P,C}$ = 7.8 Hz), 54.6 (d, $^{1}J_{P,C}$ =151.0 Hz), 114.2, 118.5, 122.8, 129.0, 128.9 (d, $^{2}J_{P,C}$ = 4.4 Hz),131.0, 134.8 (d, $^{2}J_{P,C}$ =2.6 Hz), 146.4 (d,$^{2}J_{P,C}$ = 14.8 Hz) ppm.

5.1.2-Dimethyl [(2-chlorophenyl) (phenylamino) methyl] phosphonate (1b) [42]**:** The mixture of 2-(Cl)C_6H_4CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0}C for 20 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl[(2-chlorophenyl)(phenylamino)methyl]phosphonate* (93%) afforded as colorless crystals, mp 128–129°C. IR (KBr, ν˜max cm−1): 3311 (N-H),1602, 1519, 1232, 1033; ^{1}H NMR ($CDCl_3$, 500 MHz): δ= 3.4 (d, J = 10.4Hz, 3H), 3.8 (d, J = 10.7 Hz, 3H), 5.0 (br, NH, 1H), 5.36 (d, J = 24.6 Hz, 1H), 6.6 (d, j=-7.6 (m, 9H) ppm.^{13}C NMR ($CDCl_3$, 125 MHz): δ= 51. 04, 52.26, 54.24 (m), 114. 02, 119.13, 127.87, 129.39, 129.72, 130.05, 134.18, 134.41 (d, $^{2}J_{P,C}$ =7.12 Hz), 145.87 (d, $^{2}J_{P,C}$ =14.7 Hz) ppm.

5.1.3-Dimethyl [(4-chlorophenyl) (phenylamino) methyl] phosphonate (1c) [51, 43]**:** The mixture of 4-(Cl) C6H4CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0}C for 15 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent:50:50EtOAC/n-hexane).*Dimethyl[(4-chlorophenyl)(phenylamino)methyl]phosphonate* (95%) afforded, mp 139-140°C, IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3319(N-H), 1602, 1494, 1232, 1033; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3. 55 (d, J = 10.8 Hz, 3H), 3.79 (d, J = 10.5 Hz,3H), 4.98(d, $^{1}J_{P\text{-}H}$ = 24 Hz, 1H), 7.3-8.2 (m, 9H) . ^{13}C NMR (125MHz,$CDCl_3$): δ = 53.8, 54.2 , 56.1, 114.3 , 126.8, 128.2(d, $^{3}J_{p\text{–}c}$ = 5.5 Hz),128.4 (d, $^{3}J_{p\text{–}c}$ = 3.0 Hz), 131.1 , 132.2, 141.0 ,146.6 (d, $^{2}J_{p\text{–}c}$ = 14.5 Hz) ppm.

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5.1.4-Dimethyl[(2,4-chlorophenyl)(phenylamino)methyl]phosphonate(1d)[42]**:** The mixture of 2,4-$(Cl)_2C_6H_3CHO$ (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (120 mg) as a catalyst stirred at 80^0C for 30 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl[(2,4-chlorophenyl)(phenylamino)methyl]phosphonate* (89%) afforded as a colorless crystals, mp 110–112°C. IR (KBr, $\tilde{v}_{max}$ cm^{-1}): 3313(N-H), 1602, 1521, 1236, 1 041; ^1H NMR (300 MHz; $CDCl_3$): δ 3.5 (d, j= 10.5 Hz, 3H), 3.9 (d, J =10.6 Hz, 3H),4.6 (br, 1H), 5.3 (d, $^1J_{P\text{-}H}$ = 24.4, 1H), 6.5- 7.5(m, 9H) ppm. ^{13}C NMR (75 MHz; $CDCl_3$) *δ*: 51.19 (d, ^1J =153.1 Hz),53.86 (d, ^{2} J =6.9 Hz), 53.96 (d, ^2Jc-p =6.9 Hz), 113.58, 118.70, 127.46 (d, ^3Jc-p =3.0 Hz),128.93 (d, ^3Jc-p =4.2 Hz), 128.25, 128.30, 128.57 (d,^3Jc-p =2.2 Hz), 132.70, 132.98 (d, ^3Jc-p =7.17 Hz), 146.47(d, ^2Jc-p =14.4 Hz) ppm.

5.1.5-Dimethyl[(2,6-chlorophenyl)(phenylamino)methyl]phosphonate(1e)[19]**:** The mixture of 2,6-$(Cl)_2C_6H_3CHO$ (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 70 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl[(2,6-chlorophenyl)(phenylamino)methyl]phosphonate* (85%) afforded, mp: 98-100°C, IR (KBr, $\tilde{v}_{max}$ cm^{-1}) 3313(N-H), 1602, 1521, 1236, 1041. ^1H NMR(500 MHz, $CDCl_3$): δ= 3.58 (d, J=10.6, 3H), 3.80 (d, J=10.6, 3H), 4.79 (d, J=24.4, 1H), 6.60 (d, J=8.0, 2H), 6.76 (m, 1H), 7.15 (t, J=7.6, 2H), 7.35 (d, J=8.2, 2H), 7.44 (m, 2H). ^{13}C NMR (125 MHz; $CDCl_3$) δ:= 54.24, 54.30, 54.38, 54.44, 54.97, 56.17, 114.31, 119.27, 129.37 (d, ^2Jc-p=27.5 Hz), 129.51 (d, ^3Jc-p= 5.5 Hz), 129.69, 134.33 (d, 4.0 Hz), 134.68 (d, 28.7 Hz), 146.16 (d, 14.6 Hz) ppm.

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5.1.6- Dimethyl (4-methylphenyl) (N-phenylamino) methylphosphonate (1f) [45]: The mixture of 4-(Me) C6H4CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 25 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl(4-methylphenyl)(N-phenylamino)methylphosphonate* (93%) afforded as a greenish-white solid, mp 128°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3313, 1602, 1498, 1232, 1031 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.52 (d, J = 10.5Hz, 3H), 3.79 (d, J = 10.6 Hz, 3H), 4.78 (d, $^1J_{P-H}$ =24.7 Hz, 1H), 6.63(d, J= 7.9, 2H), 6.75 (d, j=7.3, 1H), 7.13–7.19 (m, 3H), 7.38-7.40 (d, ^{2}Jc-p=6.4, 2H) ppm. .^{13}C NMR (125 MHz; $CDCl_3$) δ: 21.56, 54.19 (d, ^{2}Jc-p=7.0 Hz), 55.21, 56.42, 114.33, 118.93, 128.07 (d, ^{3}Jc-p= 5.6 Hz), 129.60, 129.88 (d, ^{2}Jc-p= 23.7 Hz) ppm.

5.1.7 Dimethyl (4- methoxy phenyl) (N-phenylamino) methylphosphonate (1g) [51, 41]**:** The mixture of 4-(OMe)C_6H_4CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 15 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane. *Dimethyl(4- methoxy phenyl)(N-phenylamino) methylphosphonate* (90%) afforded as a green solid, mp 123-124°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3290, 1602, 1508, 1240, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 3.47 (3H, d, J= 10.6Hz), 3.68 (s, 3H), 3.77 (d, j= 10.6 3H,),4.22 (br,s 1H), 4.70(1H, d, $^1J_{P-H}$ = 24.08 Hz). 6.58-7.39 (9H, m); ^{13}C NMR ($CDCl_3$, 75 MHz):54.01, 55.82, 57.52, 115.05, 115.74, 120.05, 128.87, 129.45, 129.73, 146.60, 146.90, 159.96 ppm.

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5.1.8-Dimethyl (4-nitrophenyl) (N-phenylamino) methylphosphonate (1h) [51, 41]**:** The mixture of 4-$(NO_2)C_6H_4CHO$ (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 20 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50EtOAC/n-hexane). *Dimethyl(4-nitrophenyl)(N-phenylamino)methylphosphonate* (96%) afforded as a yellow crystals mp 127-128°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3315, 3100, 1346, 1245,33, 1027 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.60 (d, J= 10.7 Hz, 3H), 3.78(d, J = 10.7Hz, 3H), 5.01 (H, d, $^1J_{P-H}$ = 24.04 Hz), 6.53-8.01 (9H, m) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 54.07, 55.20, 55.81, 57.30 113.84, 125.9, 119.26, 123.91, 129.0, 129.41, 143.61, 145.31, 145.41, 147.61 ppm.

5.1.9-Dimethyl (3-nitrophenyl) (N-phenylamino) methylphosphonate (1i) [45]**:** The mixture of 3-(NO_2)C6H4CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 40 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50EtOAC/n-hexane. *Dimethyl(3-nitrophenyl)(N-phenylamino)methylphosphonate* (95%) afforded, mp 122-124◦C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3301, 3106, 2940,1602, 1533, 1024 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$): δ 3.62 (d, J = 10.7 Hz, 3H), 3.81 (d,J = 10.7 Hz, 3H), 4.96 (d, $^1J_{P-H}$ = 25.0 Hz, 1H), 5.35(br s, 1H), 6.59 (d, J = 7.8 Hz, 2H), 6.71(t, J = 7.3 Hz,1H), 7.10 (t, J = 8.4 Hz, 2H), 7.49 (t, J = 7.9 Hz, 1H),7.85 (d, J = 7.4 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H),8.38 (d, J = 1.9Hz, 1H); ^{13}C NMR(75 MHz, $CDCl_3$): δ 54.17 (d, $^2J_{P-C}$ = 6.8 Hz),55.26 (d, $^2J_{P-C}$ = 6.9 Hz), 56.06 (d, $^1J_{P-C}$ =150.3 Hz), 114.81, 119.09, 122.75 (d, $^3J_{P-C}$ =5.3 Hz),123.05, 129.33, 129.66, 133.94, 138.67,145.61 (d, $^2J_{P-C}$ = 14.1 Hz), 148.51 (d, $^3J_{P-C}$ =2.8 Hz) ppm.

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5.1.10- Dimethyl (3-Hydroxyphenyl) (N-phenylamino) methylphosphonate (1j) [51]**:** The mixture of 3-(OH)C_6H_4CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe_3O_4@ZrO_2/SO_4^{2-} (160 mg) as a catalyst stirred at 80^0C for 20 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane. *Dimethyl(3-Hydroxyphenyl)(N-phenylamino)methylphosphonate* (96%) afforded, mp 130-132°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3413(N-H), 3176(br O-H), 1602, 1504, 1231, 1029; ^1H NMR (500 MHz, $CDCl_3$): δ 3.45 (d, J =10.5 Hz, 3H), 3.74 (d, J = 10.7 Hz, 3H), 4.73 (d, $^1J_{P-H}$ =23.8 Hz, 1H), 5.82(br 2H) 6.60 (d, J = 7.5 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.79(d, J = 8.0 Hz, 1H), 6.91 (d, J = 6.51Hz 1H), 7.07 (d,J = 7.6 Hz, 2H), 7.17(m, 2H) ppm. ^{13}C NMR($CDCl_3$, 125 MHz): 54.0, 54.1, 54.7-56.3(d, $^1Jc\text{-}p$ = 152 Hz), 113.9, 114.4, 115.8, 118.7, 119.7, 129.2,129.9, 136.7, 145.9, 146.0, 157.3 ppm.

5.1.11- Dimethyl (Thiophenyl) (N-phenylamino) methylphosphonate (1k) [19, 32]: The mixture of Thiophen-2-carbaldehyde (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe_3O_4@ZrO_2/SO_4^{2-} (160 mg) as a catalyst stirred at 80^0C for 80 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50EtOAC/n-hexane. *Dimethyl(Thiophenyl)(N-phenylamino)methylphosphonate* (80%) afforded, mp 83-86°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}) : 3303, 2952, 1602, 1498, 1315, 1240, 1180, 1051, 1029 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.30 (m, 6 H), 3.82 (m, 4 H,), 4.6 (bs, 1 H), 5.09 (dd, J = 6.9 , 23. 6 Hz, 1 H), 6.60-7.20 (m, 8 H) ppm.

5.1.12- Dimethyl (2-naphthyl) (N-phenylamino) methylphosphonate (1l) [8, 45, 51]**:** The treatment of 1-naphthaldehyde (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe_3O_4@ZrO_2/SO_4^{2-} (160 mg) as a catalyst and stirred at 80^0C for 30 min. The

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reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAc/n-hexane. *Dimethyl(2-naphthyl)(N-phenylamino)methylphosphonate* (90%) afforded as a white crystals, mp 143-145°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3310, 1602, 1498, 1237, 1027cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.18 (d, J =10.5 Hz, 3H), 3.85 (d, J = 10.6 Hz, 3H), 5.69 (d, J=24.0, 1H), 6.58 (d, J=8.0 Hz, 2H), 6.69 (t, J=7.6 Hz, 1H), 7.06 (t, J=7.7 Hz, 2H), 7.47 (t, 7.7 Hz, 1H), 7.57 (t, J=7.3 Hz, 1H), 7.65 (t, 7.8 Hz, 1H), 7.83 (d, J=7.3 Hz, 2H), 7.94 (d, J=8.1 Hz, 1H), 8.26 (d, J=8.7 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ= 50.96, 52.18, 54.13 (d, J=7.1 Hz), 114.04, 118.89, 123.03, 125.96 (m), 126.95, 129.10 (d. ^{3}Jc-p=3.6 Hz), 129.55, 129.66, 131.79 (d, ^{3}Jc-p=4.5 Hz), 134.30, 146.30 (d, ^{2}Jc-p=14.1 Hz) ppm.

5.1.13- Dimethyl (4-Dimethyl amino phenyl) (N-phenylamino) methylphosphonate (1m) [13, 32]**:** The mixture of 4-(dimethyl amino) benzaldehyde (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0}C for 20 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane. *Dimethyl(4-Dimethyl amino phenyl)(N-phenylamino)methylphosphonate* (85%) afforded as a white Solid, mp 144°C, IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}); 3446, 2926, 1350 , 1251 , 1167,1030. ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 2.9 (s, 6 H) 3.45(d, *J* = 10.4 Hz, 3 H), 3.72 (d, J = 10.6 Hz, 3 H), 4.66-4.74 (d, $^1J_{P\text{-}H}$ = 24.02 Hz, 1 H),6.59-7.32 (m, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 41.4, 54.7, 54.8, 54.9, 56.9, 56.7,113.5, 114.9, 119.2, 112.5, 128.5, 129, 146.2, 146.4, 151.2 ppm.

5.1.14-Tetramethyl((1,4-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonates) (1n)[46,53]: The mixture of Terephthaldehyde (1.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (100 mg) as a catalyst stirred at 80^{0}C for 15 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous NaHCO$_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Tetramethyl((1,4-phenylenebis(azanediyl)) bis (phenylmethylene))bis(phosphonates)* (90%) afforded, mp: 170-173 °C; IR (KBr, $\tilde{\nu}_{\max}$ cm^{-1}) 3306, 1600, 1500, 1313, 1240, 1027. ^{1}H NMR (200 MHz, CDCl$_3$+DMSO d$_6$): δ= 7.38-7.20 (m, 10H), 6.38 (s, 4H), 4.62 (d, J=24 Hz, 2H), 3.65 (d, J=10 Hz, 6H), 3.38 (d, J=10 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$+DMSO d$_6$): δ= 132.7, 128.4, 124.3, 117.7, 112.7, 53.3, 52.7, 49.2, 28.7ppm.

5.1.15-Dimethyl (4-nitrophenyl)(4-Methyphenylamino)methylphosphonate(1o)[47,52]**:** The mixture of 4-(NO$_2$)C$_6$H$_4$CHO (2.0 mmol) with *p*-Toluidine (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0}C for 10 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous NaHCO$_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50: 50 EtOAC / n-hexane. *Dimethyl(4-nitrophenyl)(4-Methyphenylamino) methylphosphonate* (92%) afforded, m.p.: 210–212°C, IR (KBr, $\tilde{\nu}_{\max}$ cm^{-1}); 3305, 31008, 1356, 1255. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 2.23 (s, 3H),3.65 (d, ^{2}J $_{\text{P-H}}$ = 10.8 Hz, 3H), 3.82 (d, ^{2}J $_{\text{P-H}}$ = 10.8 Hz, 3H), 4.89 (d,^{1}J$_{\text{P-H}}$ = 25.2 Hz, 1H), 6.49 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 7.68 (dd, , J = 8.4 Hz and 2.0 Hz, 2H), 8.23 (d, J = 8.4Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ: 20.76, 54.22 (d, J = 7.0 Hz), 54.63 (d, J =7.0 Hz), 55.66, 56.85, 114.42, 124.27 (d, J=25 Hz), 129.01 (t, 4 Hz), 130.30, 143.42 (d, 14.6 Hz), 144.24 (d, J=3 Hz), 148.07 (d, J=37.5 Hz) ppm.

5.1.16- Dimethyl (4-Methoxyphenyl) (N-4-nitrophenylamino) methylphosphonate (1p)[37, 41]**:** The mixture of 4-(OMe) C6H4CHO (2.0 mmol) with *p*-Toluidine (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0}C for 20 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl (4-Methoxyphenyl)(N-4-nitrophenylamino)methylphosphonate* (88%) afforded, mp: 96-99°C, IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}) 3301, 2950, 1612, 1514, 1458, 1337, 1238, 1178, 1058, 1027. ^{1}H NMR($CDCl_3$, 300 MHz): δ 3.46 (d, J = 11.5 Hz, 3 H), 3.76 (d, J = 10.8 Hz, 3 H), 3.78 (s,3H), 4.77-4.84 (d, $^1J_{P\text{-}H}$ = 24.67 Hz, 1 H), 6.58 (d, J = 8.2 Hz, 2 H), 6.88 (d, J = 10.1Hz, 2 H), 7.36 (m, 2 H), 8.00 (d, J = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 53.4, 53.6, 54.2, 55.3, 55.5, 112.4, 114.5, 125.9, 128.8, 132.3, 139,151.7, 151.8, 159.8 ppm.

5.1.17- Dimethyl [(4-chlorophenyl)-(4-nitrophenylamino) methyl] phosphonate (1q) [37]**:** The mixture of 4-(Cl) C6H4CHO (2.0 mmol) with 4-Nitroaniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 15 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50: 50 EtOAC / n-hexane). *Dimethyl[(4-chlorophenyl)-(4-nitrophenylamino) methyl]phosphonate* (76%) afforded, mp: 160-162°C, IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}) 3298, 3074, 2921, 2852, 2432, 1600, 1546, 1490, 1328, 1278, 1234, 1178, 1112, 1091, 1051, 1024, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.51 (d , J = 10.7 Hz, 3 H), 3.75 (d, J = 10.6Hz, 3 H), 4.65-4.82 (d, $^1J_{P\text{-}H}$ = 24.35 Hz, 1 H), 6.58 (d, J = 9.1 Hz, 2 H), 7.27-7.44 (m, 4 H),7.98 (d, J = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 53.9, 55.4, 54.7, 56.0, 112.9,126.5, 129.5, 129.7, 133.5, 135.0, 139.6, 152 ppm.

5.1.18- Dimethyl (4-Methoxyphenyl) (N-4-nitrophenylamino) methylphosphonate (1r) [13, 37]**:** The mixture of 4-(OMe) C6H4CHO (2.0 mmol) with 4-Nitroaniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 25 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane),

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Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl(4-Methoxyphenyl)(N-4-nitrophenylamino)methylphosphonate* (82%) afforded, mp: 160-162°C, IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}) 3271, 3070, 2954, 2923, 2848, 1483, 1182.^{1}H NMR(CDCl3, 300 MHz): δ 3.46 (d, J= 10.6 Hz, 3 H), 3.70 (d, J = 10.7 Hz, 3 H), 3.71 (s, 3 H), 4.77 (d, $^1J_{P\text{-}H}$ = 24.6Hz, 1H), 6.58 (d, J = 8.6 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 7.36(m, 2 H), 7.99 (d, J= 8.2 Hz, 2 H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 53.4, 53.6, 54.2, 54.9, 55.3, 112.4, 114.5, 125.9, 128.8, 132.3,139,151.7, 151.8, 159.8 ppm.

5.1.19- Dimethyl [(4-nitrophenyl)-(4-nitrophenylamino) methyl] phosphonate (1s) [13, 37]**:** The mixture of 4-(NO_2) C6H4CHO (2.0 mmol) with 4-Nitroaniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 15 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl[(4-nitrophenyl)-(4-nitrophenylamino)methyl] phosphonate* (80%) afforded, mp:170-173°C, IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}) : 3279, 2954, 1621, 1529 cm-1; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.55 (d, J = 10.7 Hz,3 H), 3.80 (d J = 10.8 Hz, 3 H), 4.77 (dd, J = 7.2 Hz, 24.6 Hz, 1 H),5.79 (bs, 1 H), 6.80 (m, 8 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 54.5, 54.7, 54.9, 56.5,108.9, 113.9, 120.0, 129.9, 130.6, 134, 135, 147.6, 147.8, 149.9 ppm.

5.1.20- Dimethyl (1-phenylaminocyclohexyl) phosphonate (1t) [8, 13, 51]: The mixture of cyclohexanone (2.0 mmol) with aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^0C for 50 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was

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extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane). *Dimethyl (1-phenylaminocyclohexyl) phosphonate* (75%) afforded as a brownish white solid, mp 99-102°C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}): 3331, 1602, 1498, 1449, 1230, 1028 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20- 1.82 (m, 10H), 3.91 (s, 1H), 3.77 (d,J = 10.2 Hz, 6H), 7.41 (m, 5H) ppm.

5.1.21- Dimethyl (1-Phenyl-1-phenylaminoethyl) phosphonate (1u) [13,37]**:** The mixture of acetophenone (2.0 mmol) with aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ (160 mg) as a catalyst stirred at 80^{0}C for 120 min. The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane. *Dimethyl(1-Phenyl-1-phenylaminoethyl)phosphonate* (70%) afforded as a brownish yellow solid, mp 125-129 °C; IR (KBr, $\tilde{\nu}_{max}$ cm^{-1}) : ^{1}H NMR($CDCl_3$, 300 MHz) δ= 1.81 (d, J= 16.5 Hz, 3 H), 3.80 (d,3 H),3.91(d,3H), 6.81-7.41 (m, 10 H)ppm.

5.2. Characterization $Fe_3O_4@ZrO_2/SO_4^{2-}$:

Figure. S1 FT-IR spectra of the Fe_3O_4, ZrO_2, $Fe_3O_4@ZrO_2$ and $Fe_3O_4@ZrO_2/SO_4^{2-}$

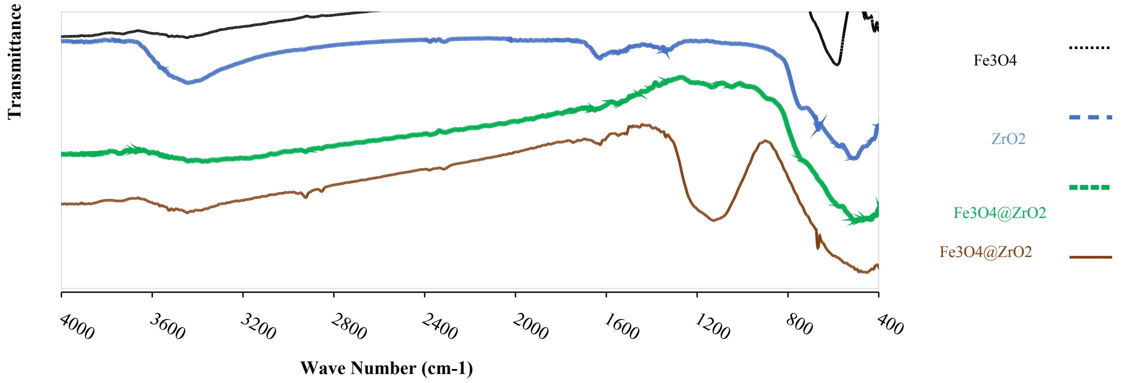

Figure. S2 SEM of $Fe_3O_4@ZrO_2/SO_4^{2-}$

Cite this: DOI: 10.1039/c0xx00000x

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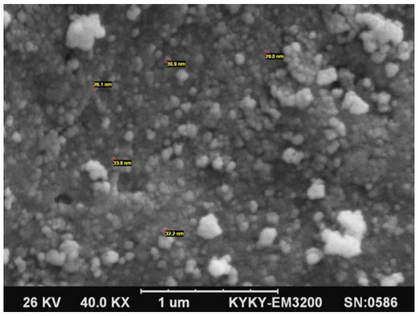

Figure. S3 TEM image of Fe_3O_4@ZrO_2/SO_4^{2-}(a,b)

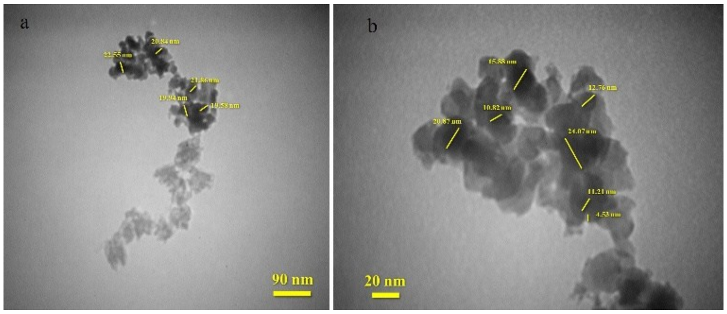

Figure S4: Nitrogen adsorption- desorption isotherm and pore- size distribution of Fe_3O_4@ZrO_2/SO_4^{2-}.

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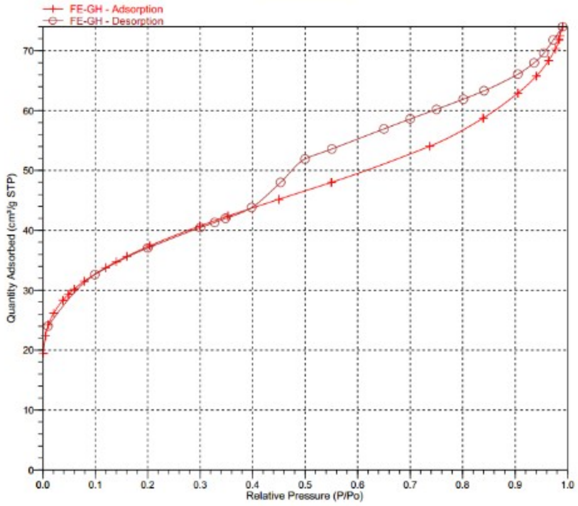

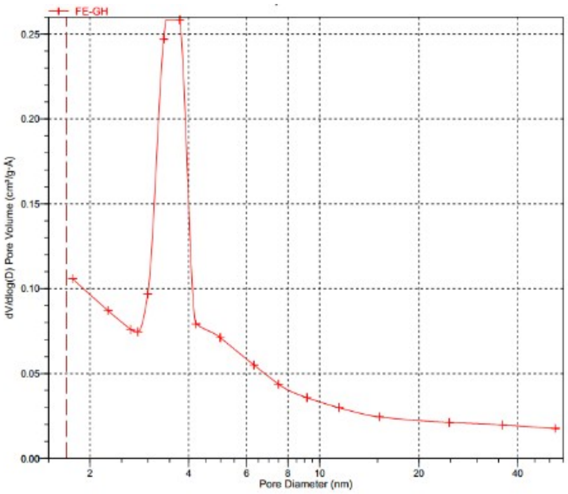

6. Scanned FT-IR, 1H NMR spectral data

6.1. IR spectra

Figure S5. IR spectra of 1b

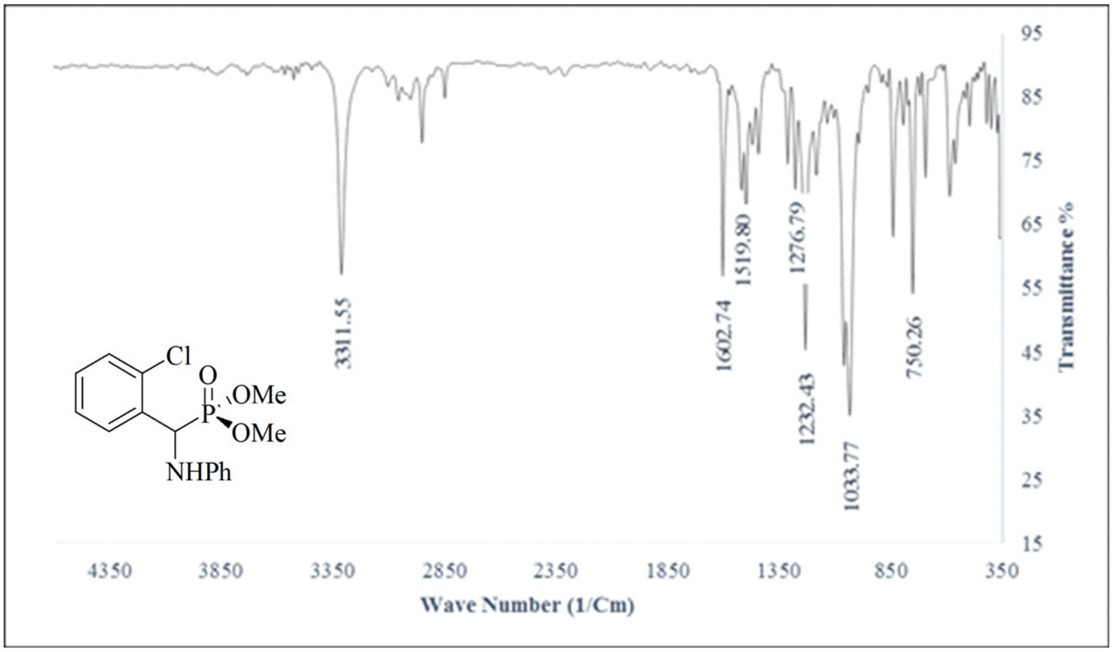

Figure S6. IR spectra of 1c

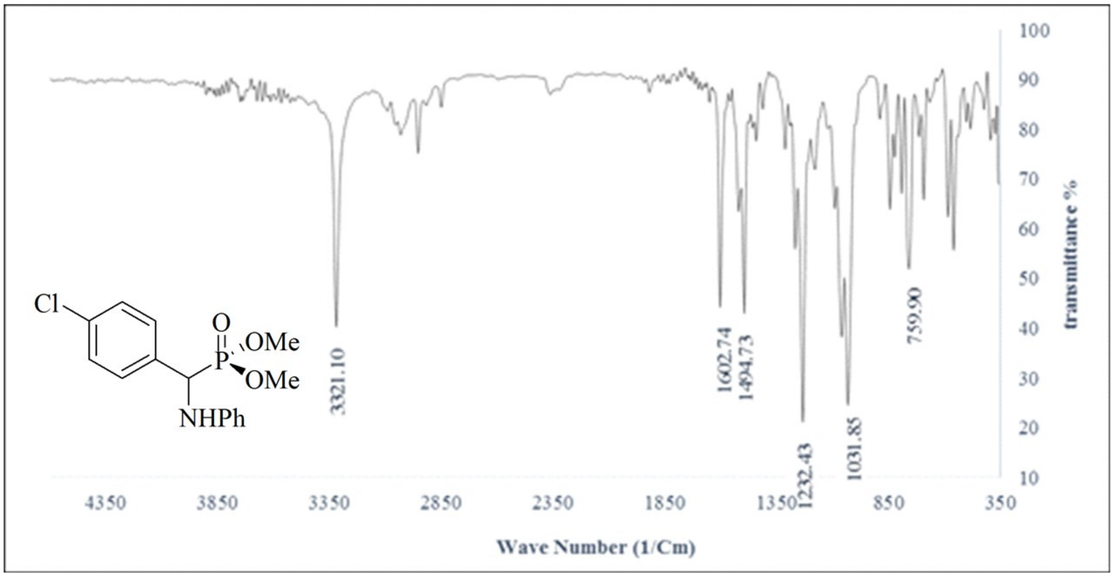

Figure S7. IR spectra of 1d

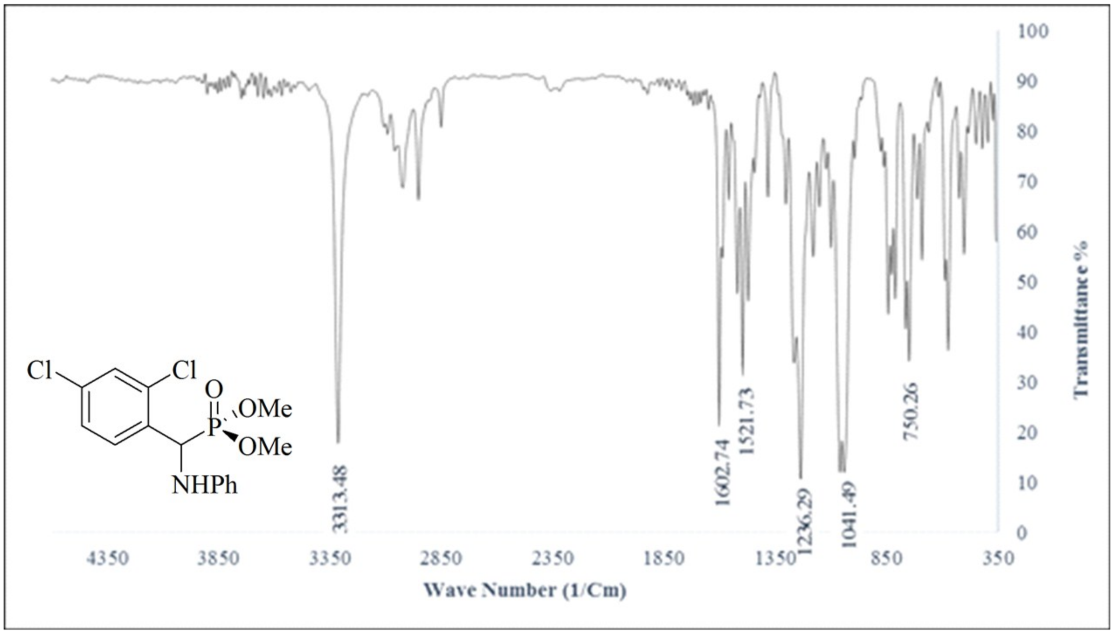

Figure S8. IR spectra of 1f

Cite this: DOI: 10.1039/c0xx00000x

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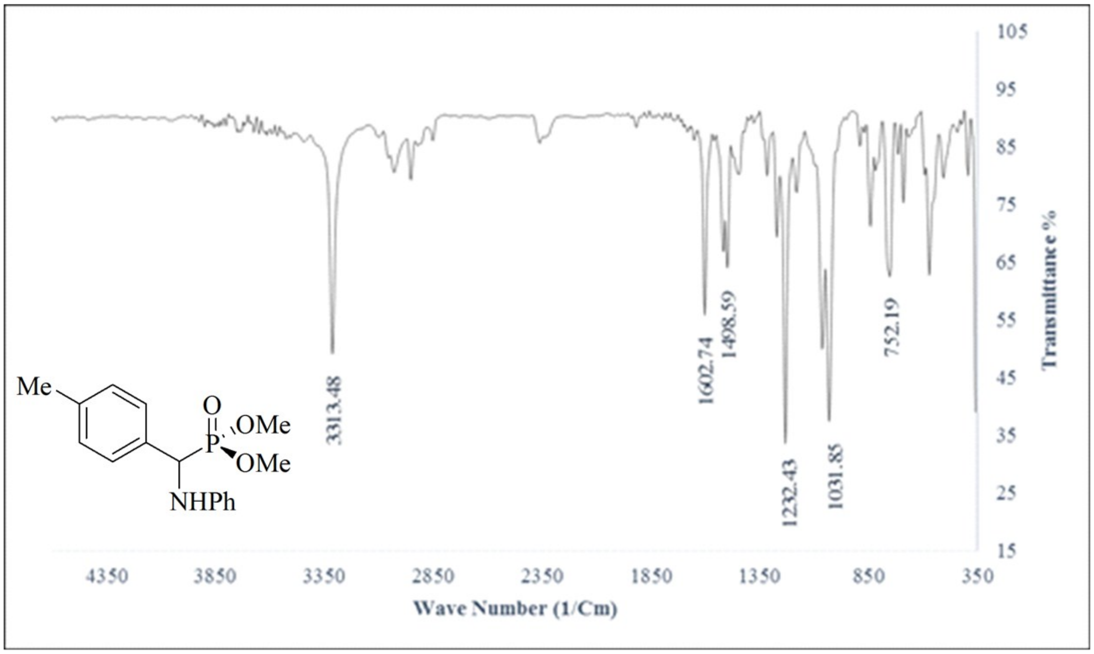

Figure S9. IR spectra of 1g

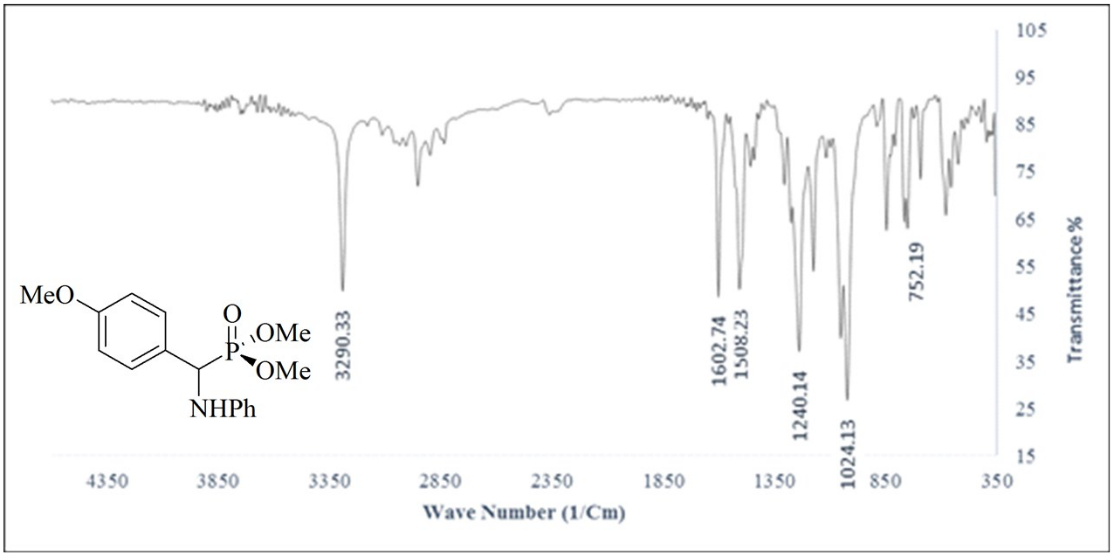

Figure S10. IR spectra of 1h

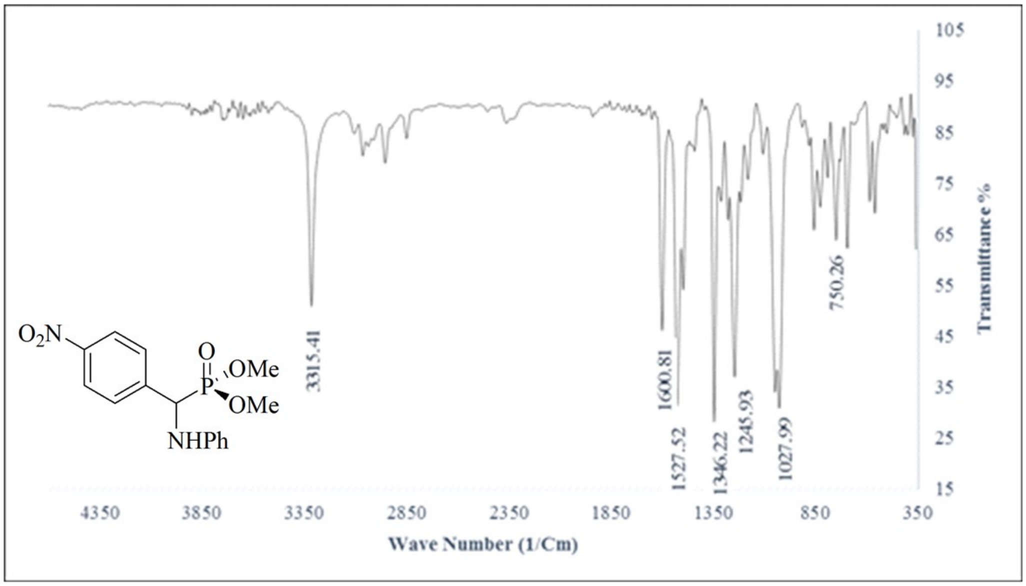

Figure S11. IR spectra of 1j

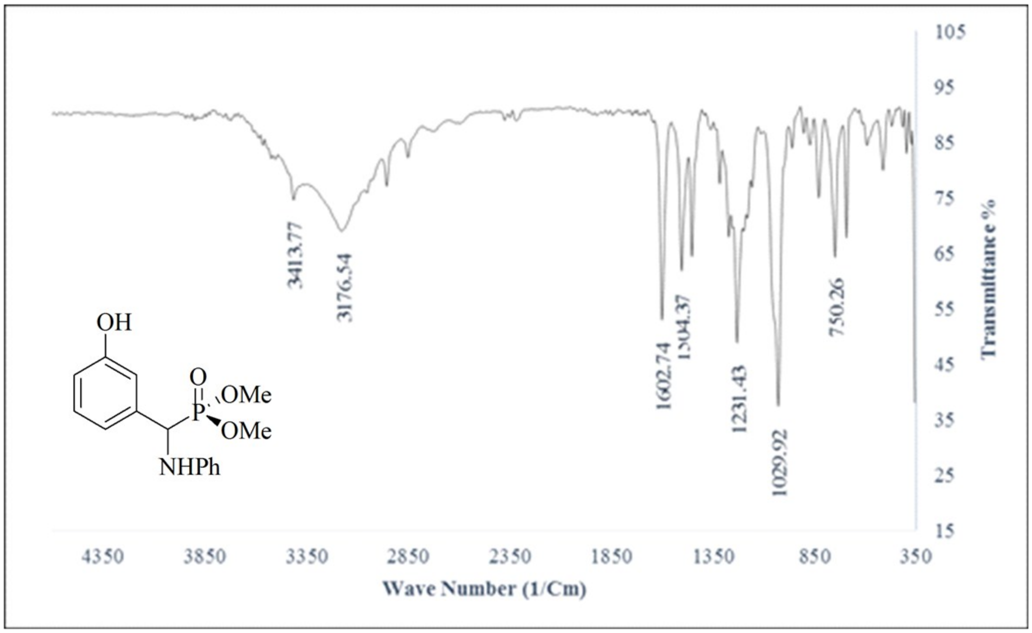

Figure S12. IR spectra of 1k

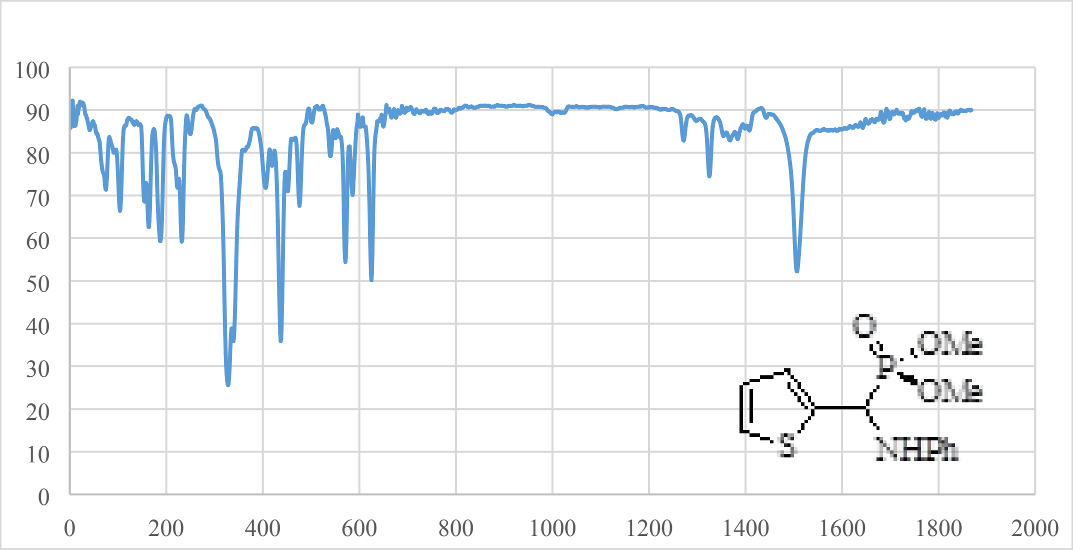

Figure S13. IR spectra of 1n

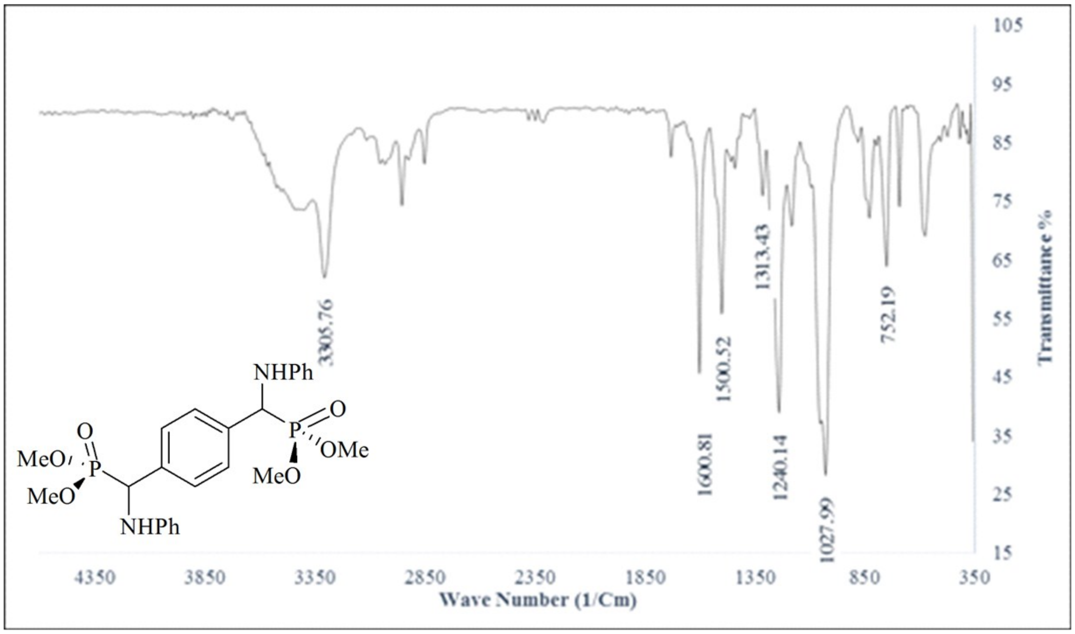

Figure S14. IR spectra of 1p

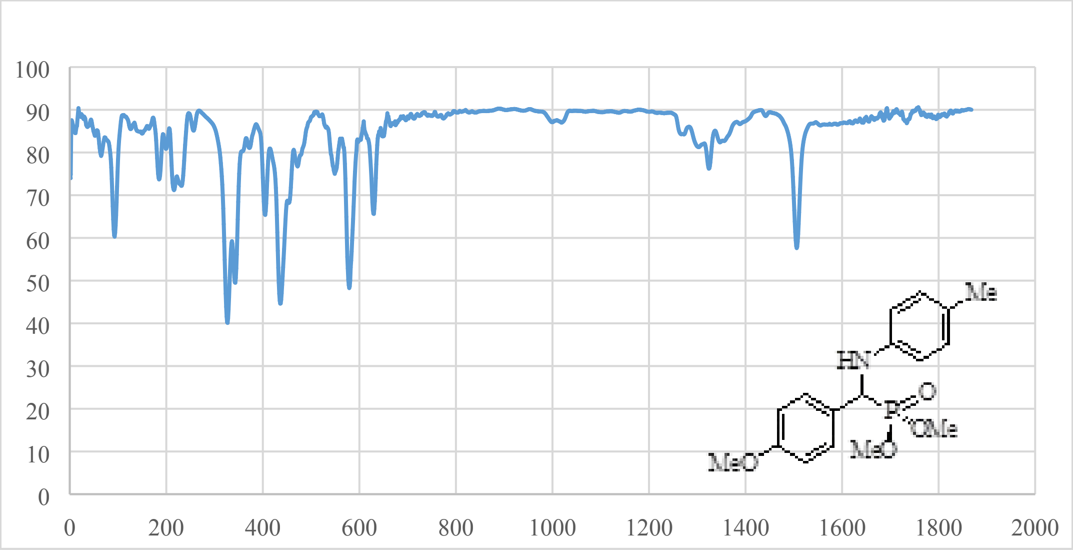

Figure S15. IR spectra of 1q

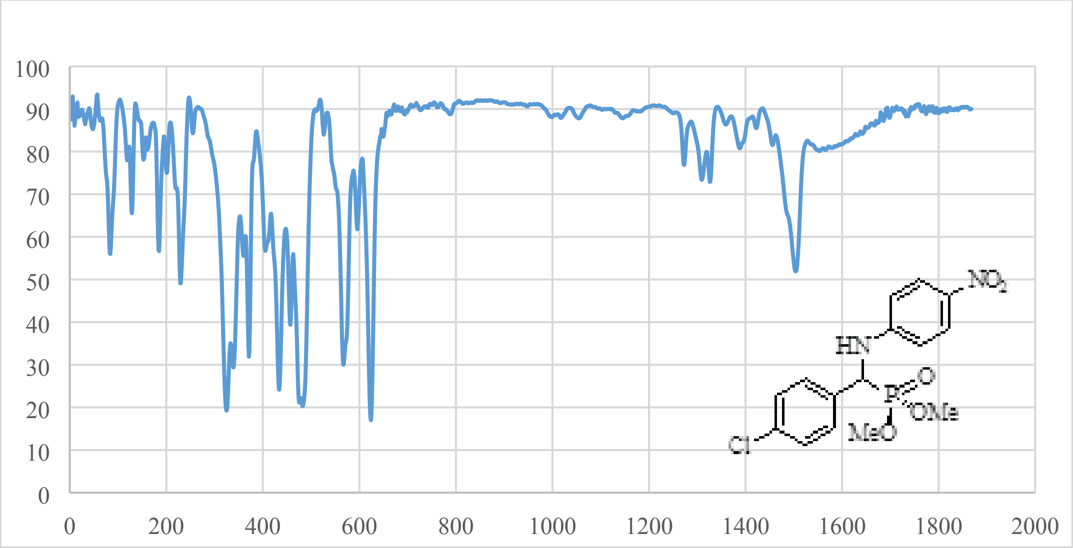

Figure S16. IR spectra of 1s

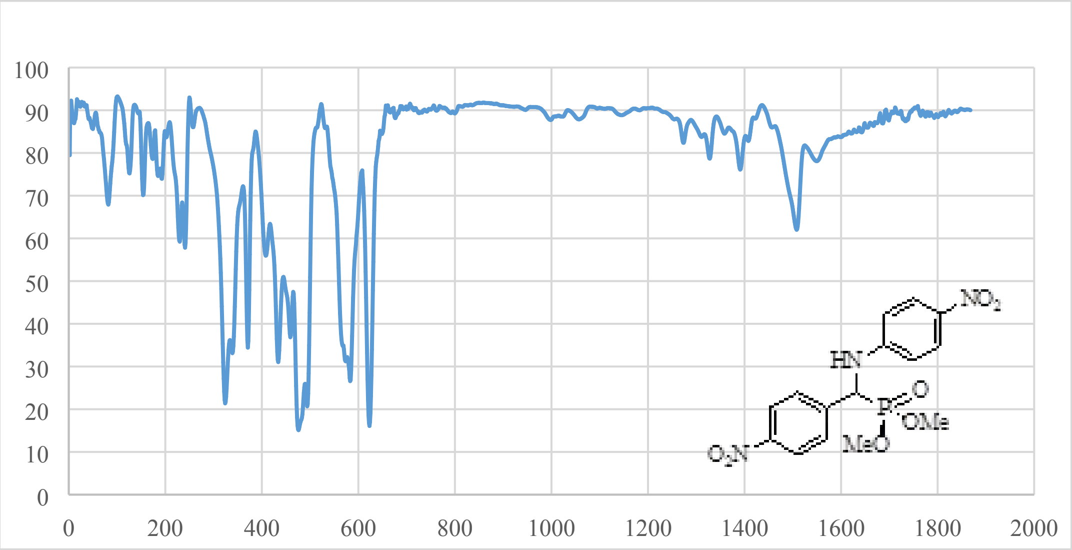

Figure S17. IR spectra of 1t

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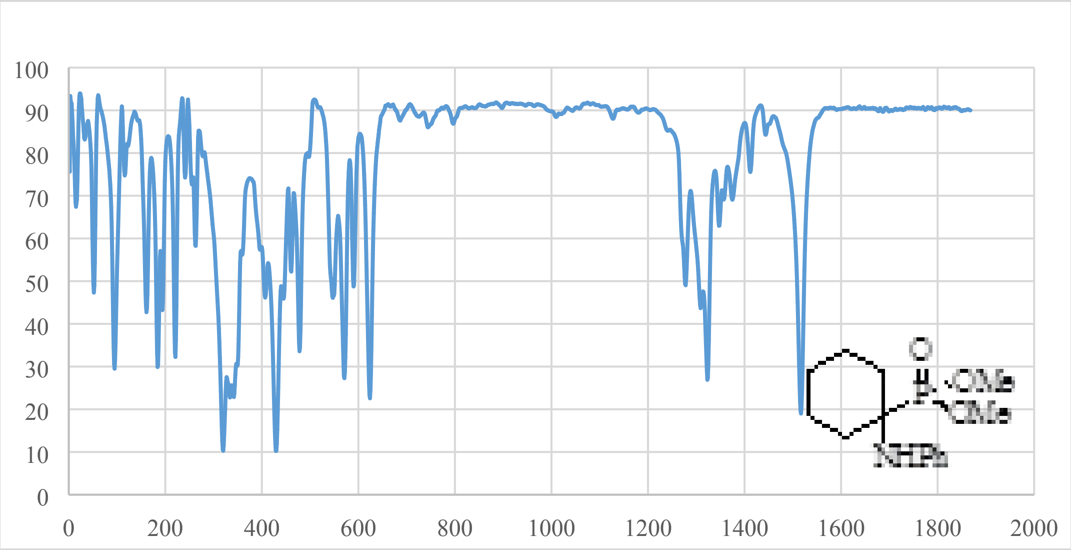
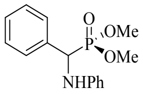
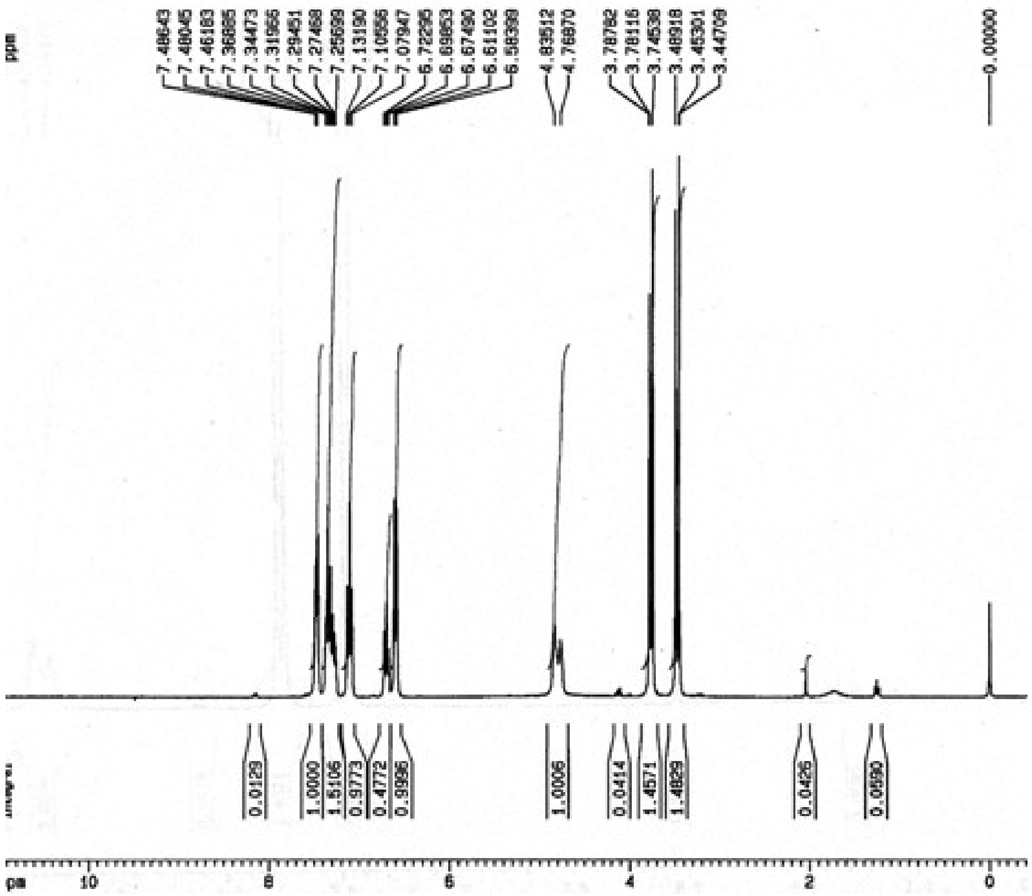


6.2. NMR spectra

Figure S18. NMR spectra of 1a

Figure S18. NMR spectra of 1a

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7.10556
7.07947
6.72295
6.69863
6.67490
6.61102
6.58399
4.83512
4.76870
3.78762
3.78115
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3.48918
3.45301
3.44709
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1.0000
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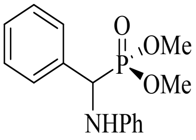
2
0


O
P
OMe
OMe
NHPh

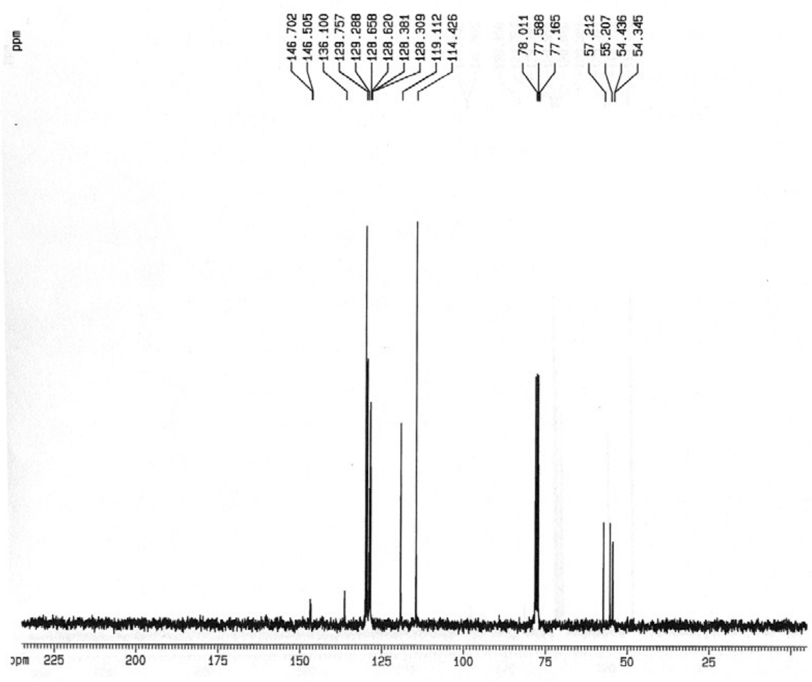
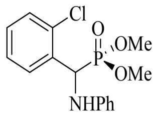
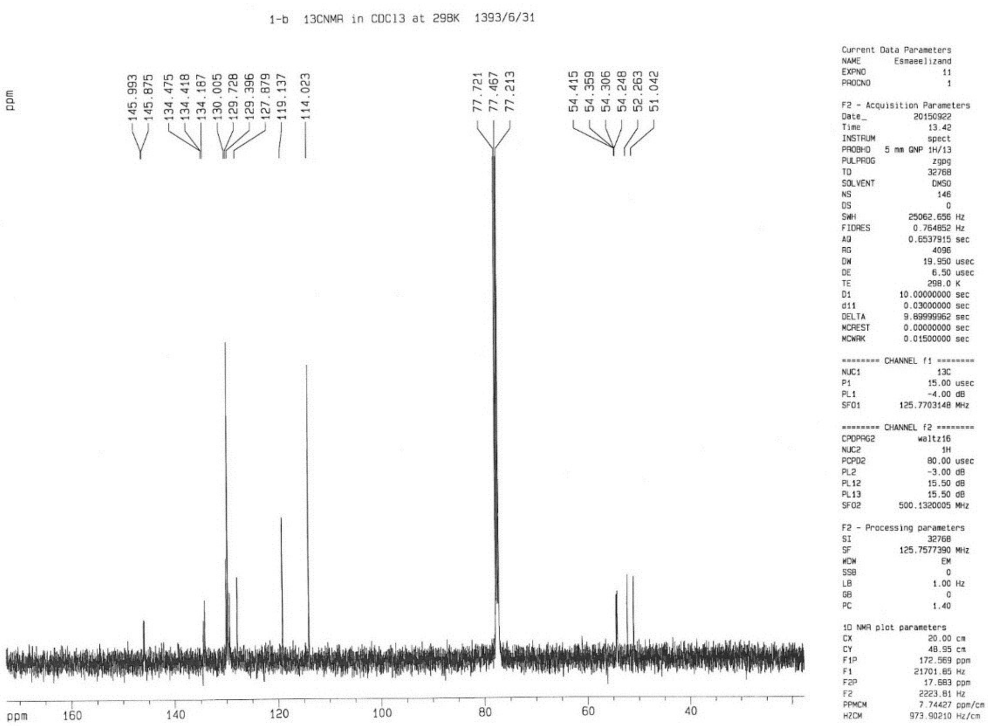


Figure S19. NMR spectra of 1b

Figure S19. NMR spectra of 1b




1-b 13CNMR in CDCl3 at 298K 1393/6/31

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PROCNO                  1

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PULPROG              zgpg
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FIDRES           0.764852 Hz
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DE                   6.50 usec
TE                  298.0 K
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d11            0.03000000 sec
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MCWRK          0.01500000 sec

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PL1                 -4.00 dB
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PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                15.50 dB
PL13                15.50 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
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SF            125.7577390 MHz
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SSB                     0
LB                   1.00 Hz
GB                      0
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1D NMR plot parameters
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F1                21701.85 Hz
F2P                17.683 ppm
F2                2223.81 Hz
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Cite this: DOI: 10.1039/c0xx00000x

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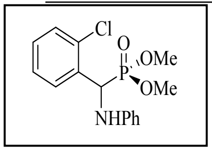
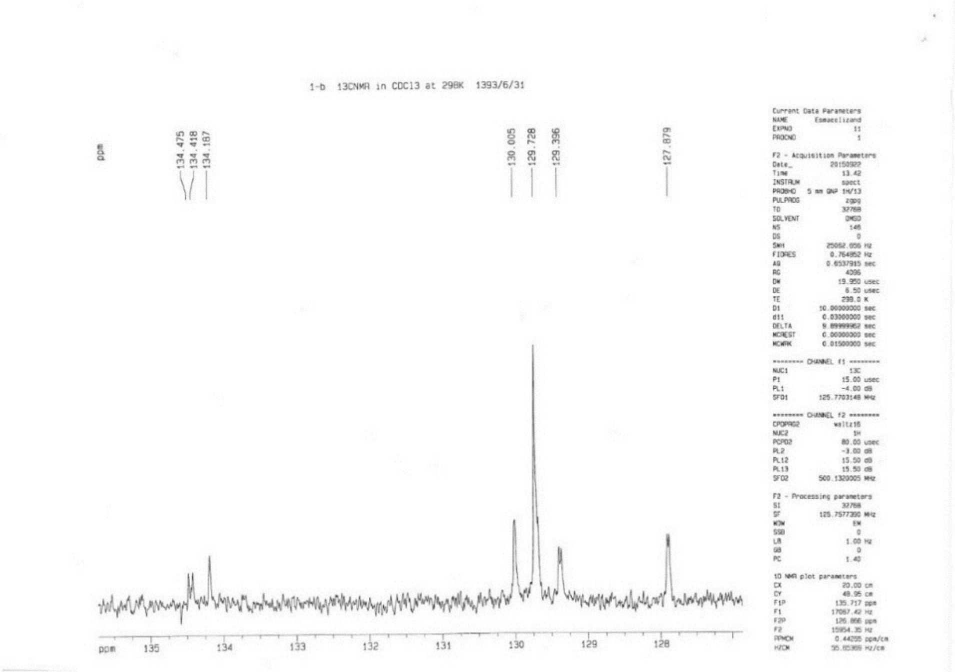
Supplementary Information





1-b 13CNMR in CDCl3 at 298K 1393/6/31

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PL1                -4.00 dB
SFO1         125.7703148 MHz

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NUC2                  1H
PCPD2              80.00 usec
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PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
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CY                 48.95 cm
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F1              17067.42 Hz
F2P              126.866 ppm
F2              15954.35 Hz
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HZCM            55.65369 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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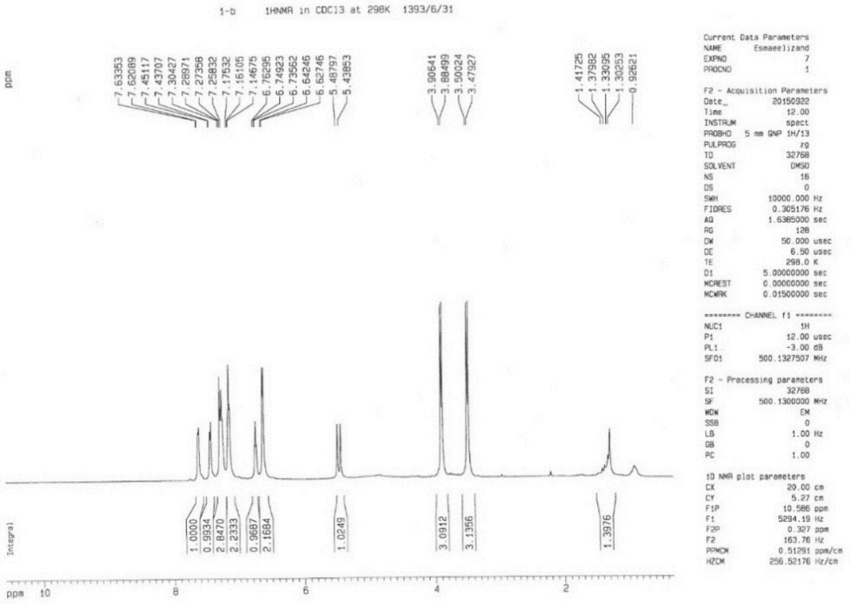
Supplementary Information



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RG                     128
DW                  50.000 usec
DE                    6.50 usec
TE                   298.0 K
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MCREST          0.00000000 sec
MCWRK           0.01500000 sec

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PL1                  -3.00 dB
SFO1           500.1327507 MHz

F2 - Processing parameters
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SF             500.1300000 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                    5.27 cm
F1P                 10.586 ppm
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F2                  163.76 Hz
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Cite this: DOI: 10.1039/c0xx00000x

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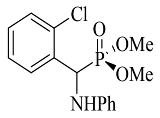
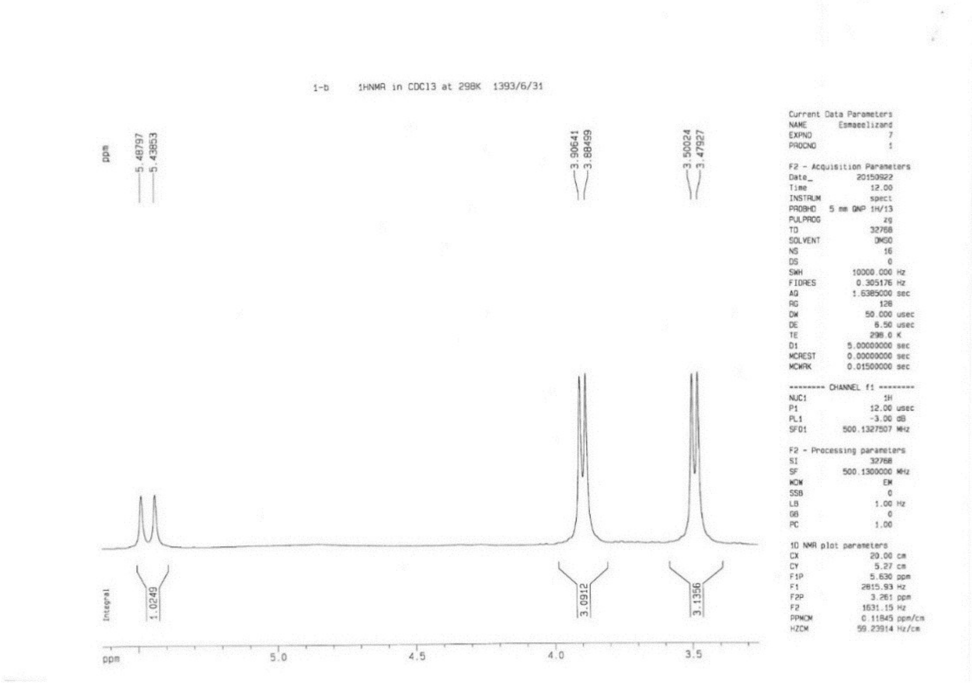
Supplementary Information





1-b 1HNMR in CDCl3 at 298K 1393/6/31

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PROCNO                  1

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RG                    128
DW                 50.000 usec
DE                   6.50 usec
TE                  298.0 K
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MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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PL1                 -3.00 dB
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F2 - Processing parameters
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SF            500.1300000 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                   5.27 cm
F1P                 5.630 ppm
F1                2815.93 Hz
F2P                 3.261 ppm
F2                1631.15 Hz
PPMCM             0.11845 ppm/cm
HZCM             59.23914 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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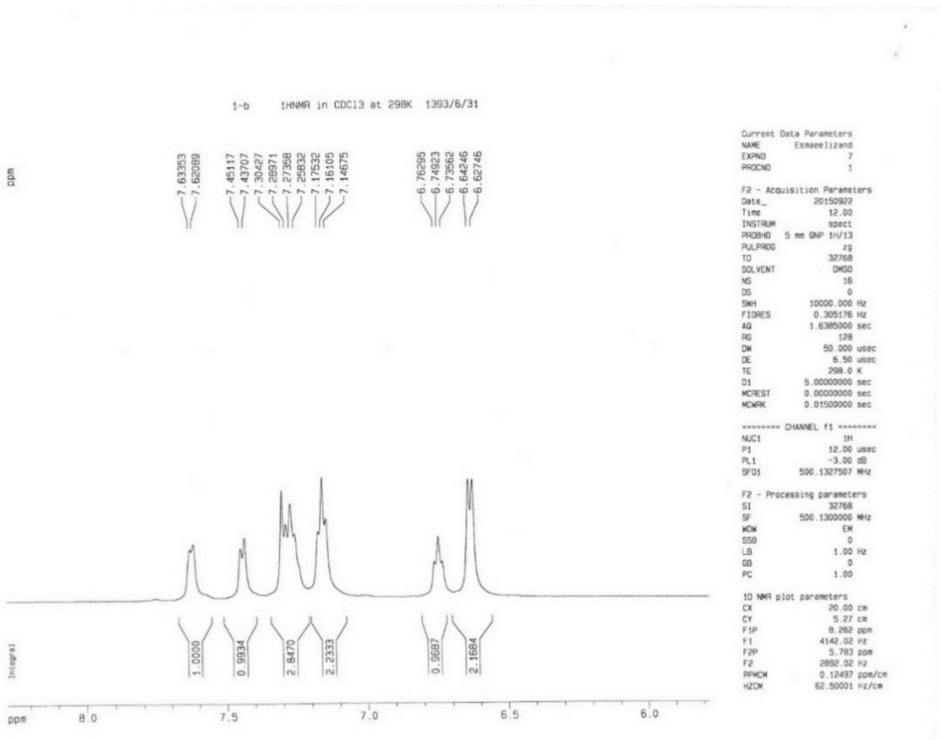
Supplementary Information



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RG                    128
DW                 50.000 usec
DE                   6.50 usec
TE                  298.0 K
D1             5.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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PL1                 -3.00 dB
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1D NMR plot parameters
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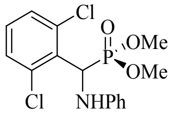
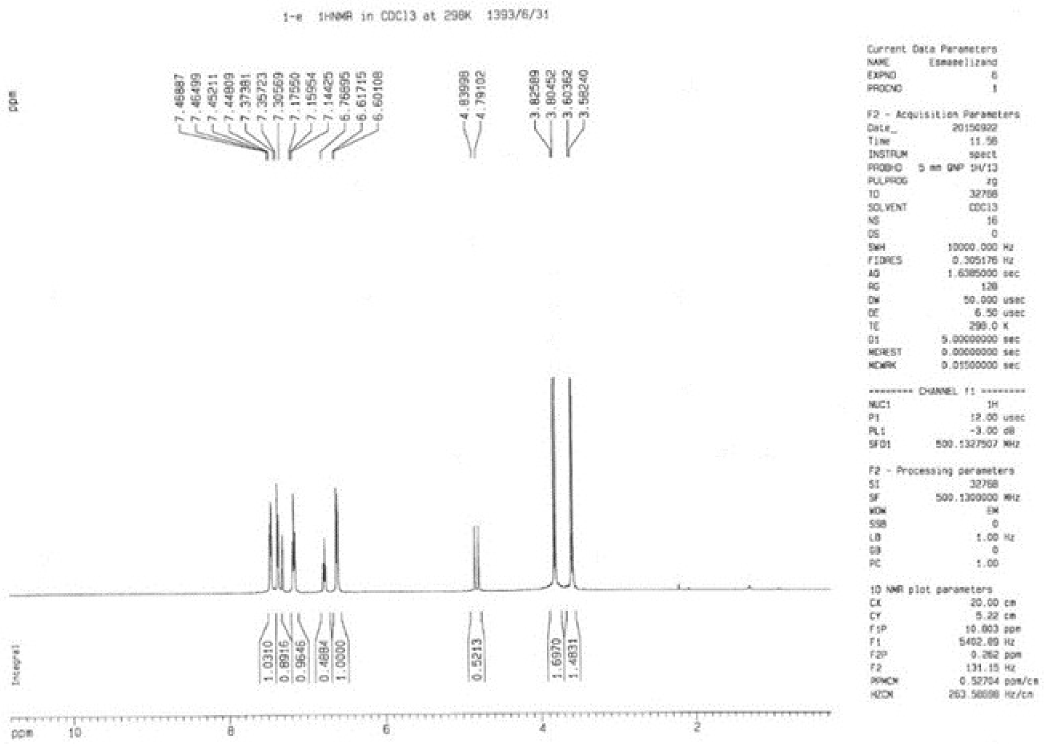
Figure S20. NMR spectra of 1e





1-e 1HNMR in CDCl3 at 298K 1393/6/31

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PROCNO                   1

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AQ            1.6385000 sec
RG                     128
DW               50.000 usec
DE                 6.50 usec
TE                298.0 K
D1           5.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
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PL1               -3.00 dB
SFO1        500.1327507 MHz

F2 - Processing parameters
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SF          500.1300000 MHz
WDW                     EM
SSB                      0
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GB                       0
PC                    1.00

1D NMR plot parameters
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CY                  5.22 cm
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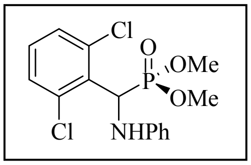

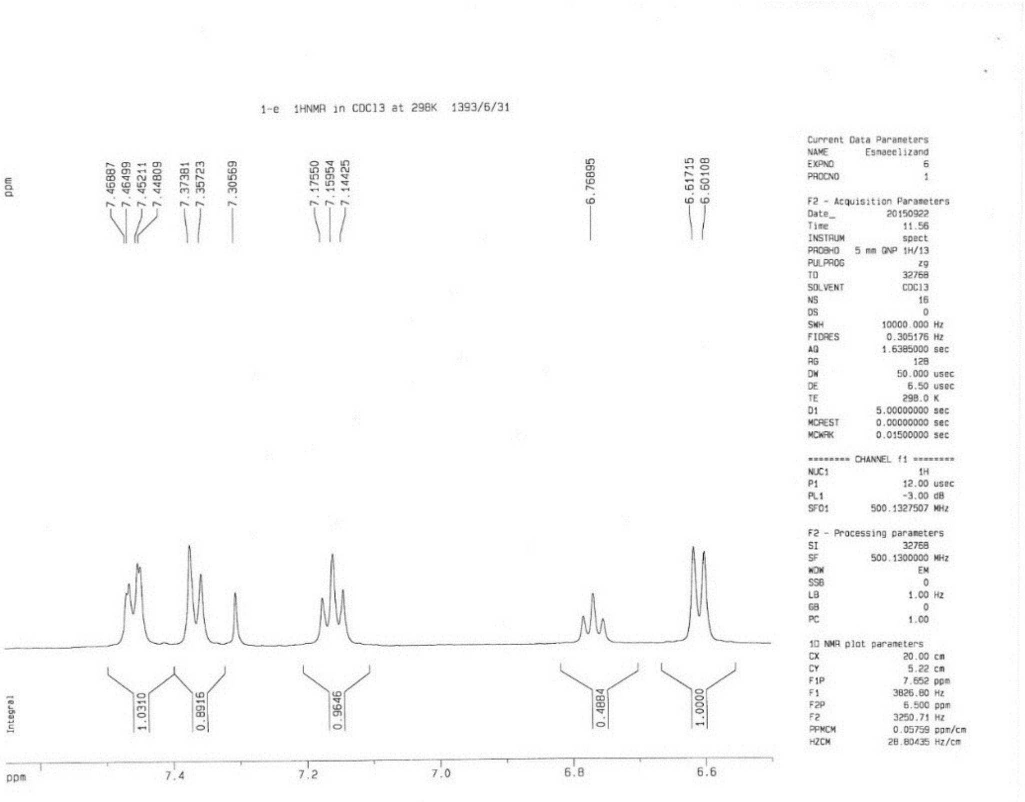

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SOLVENT           CDC13
NS                   16
DS                    0
SWH          10000.000 Hz
FIDRES        0.305176 Hz
AQ           1.6385000 sec
RG                  128
DW              50.000 usec
DE                6.50 usec
TE               298.0 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
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P1               12.00 usec
PL1              -3.00 dB
SFO1       500.1327507 MHz

F2 - Processing parameters
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WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
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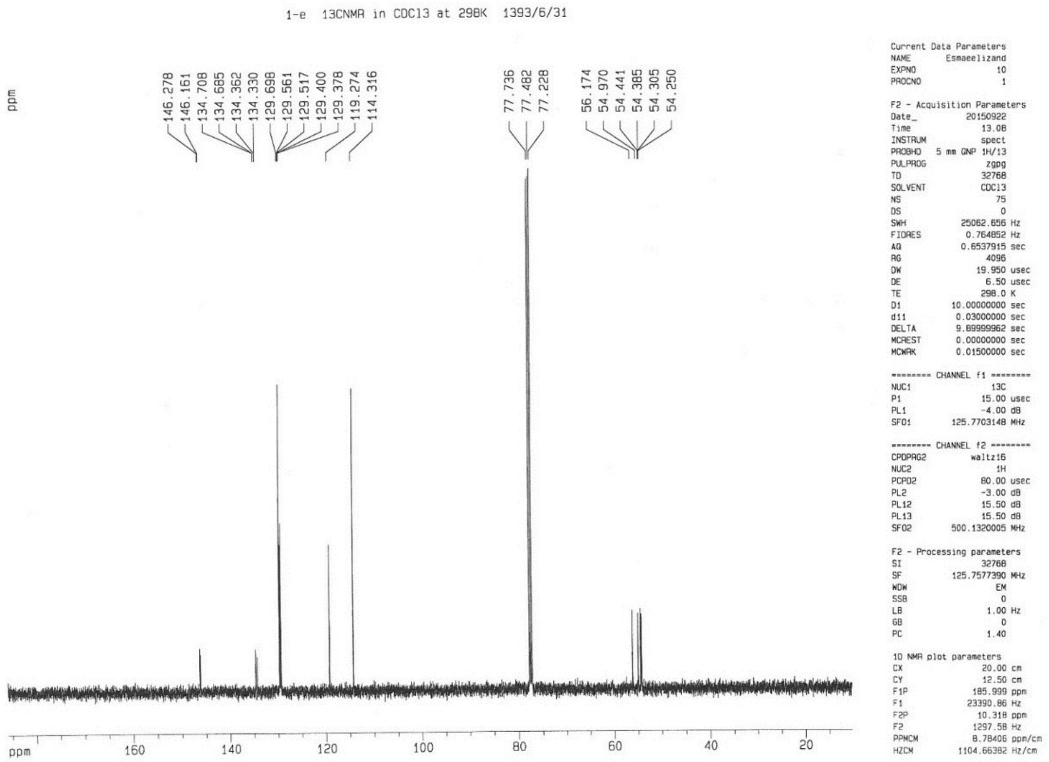
F2P               6.500 ppm
F2              3250.71 Hz
PPMCM           0.05759 ppm/cm
HZCM           28.80435 Hz/cm
```



1-e 13CNMR in CDCl3 at 298K 1393/6/31

```
Current Data Parameters
NAME          Esmaeelizand
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150922
Time                 13.08
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG               zgpg
TD                   32768
SOLVENT              CDCl3
NS                      75
DS                       0
SWH              25062.656 Hz
FIDRES            0.764852 Hz
AQ               0.6537915 sec
RG                    4096
DW                  19.950 usec
DE                    6.50 usec
TE                   298.0 K
D1             10.00000000 sec
d11             0.03000000 sec
DELTA           9.89999962 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   15.00 usec
PL1                  -4.00 dB
SFO1           125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 15.50 dB
PL13                 15.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF             125.7577390 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
CY                   12.50 cm
F1P                185.999 ppm
F1                23390.86 Hz
F2P                 10.318 ppm
F2                 1297.58 Hz
PPMCM              8.78406 ppm/cm
HZCM            1104.66382 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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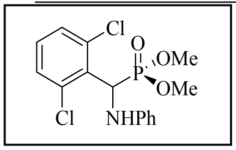
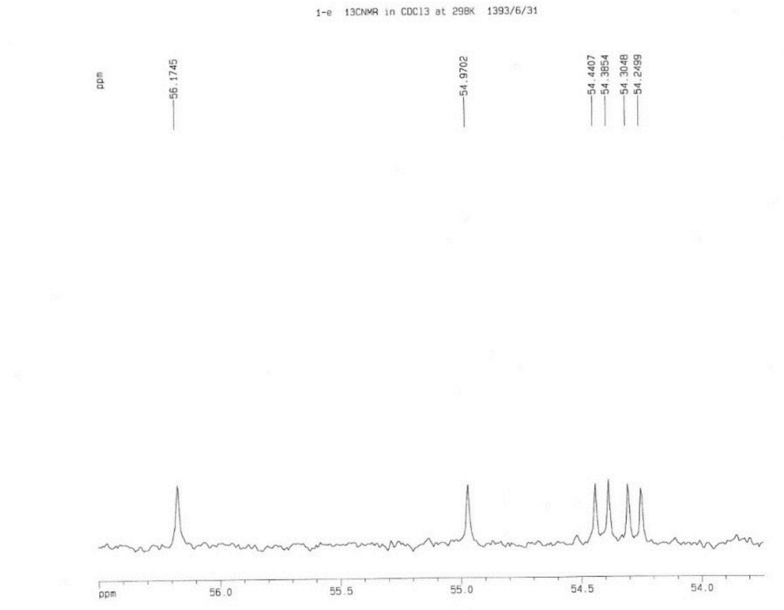
Supplementary Information





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Current Data Parameters
NAME          Esmaeelizand
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150922
Time                 13.08
INSTRUM              spect
PROBHD    5 mm GNP 1H/13
PULPROG               zgpg
TD                   32768
SOLVENT              CDCl3
NS                      75
DS                       0
SWH             25062.656 Hz
FIDRES           0.764852 Hz
AQ              0.6537915 sec
RG                    4096
DW                  19.950 usec
DE                    6.50 usec
TE                   298.0 K
D1             10.00000000 sec
d11             0.03000000 sec
DELTA           9.89999962 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   15.00 usec
PL1                  -4.00 dB
SFO1           125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 15.50 dB
PL13                 15.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF             125.7577390 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
CY                   12.50 cm
F1P                 56.503 ppm
F1                 7105.63 Hz
F2P                 53.739 ppm
F2                 6758.10 Hz
PPMCM              0.13817 ppm/cm
HZCM              17.37653 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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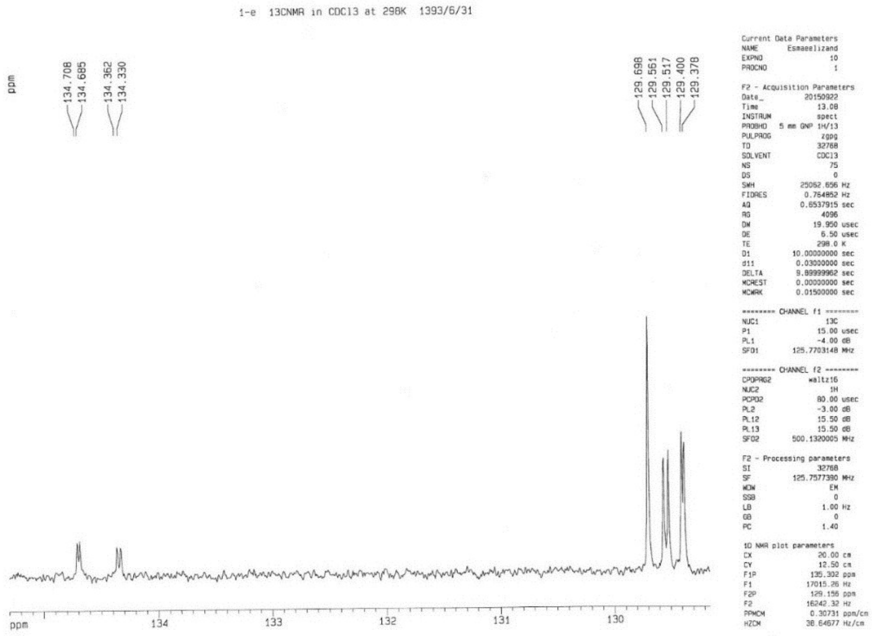
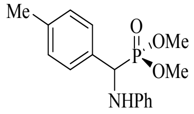
Supplementary Information



```
Current Data Parameters
NAME        Esmaeelizand
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               13.08
INSTRUM            spect
PROBHD   5 mm GNP 1H/13
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                    75
DS                     0
SWH            25062.656 Hz
FIDRES          0.764852 Hz
AQ             0.6537915 sec
RG                  4096
DW                19.950 usec
DE                  6.50 usec
TE                 298.0 K
D1           10.00000000 sec
d11           0.03000000 sec
DELTA         9.89999962 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PL1                -4.00 dB
SFO1         125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577390 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              135.302 ppm
F1              17015.26 Hz
F2P              129.156 ppm
F2              16242.32 Hz
PPMCM            0.30731 ppm/cm
HZCM            38.64677 Hz/cm
```

Figure S21. NMR spectra of 1f

Figure S21. NMR spectra of 1f



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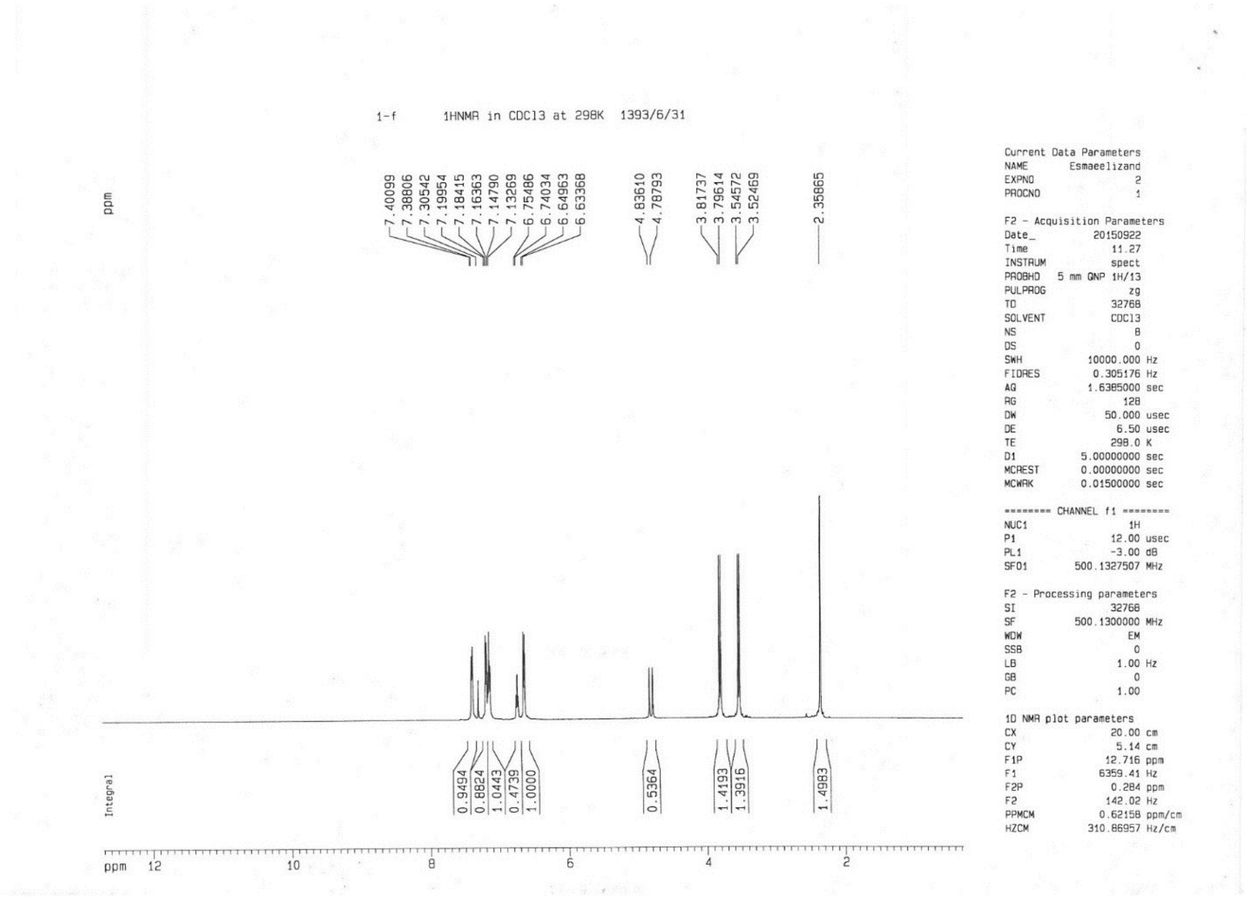

1-f 1HNMR in CDCl3 at 298K 1393/6/31

```
Current Data Parameters
NAME         Esmaeelizand
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150922
Time                11.27
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.305176 Hz
AQ              1.6385000 sec
RG                    128
DW                 50.000 usec
DE                   6.50 usec
TE                  298.0 K
D1             5.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -3.00 dB
SFO1          500.1327507 MHz

F2 - Processing parameters
SI                  32768
SF            500.1300000 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                   5.14 cm
F1P                12.716 ppm
F1                6359.41 Hz
F2P                 0.284 ppm
F2                 142.02 Hz
PPMCM             0.62158 ppm/cm
HZCM            310.86957 Hz/cm
```

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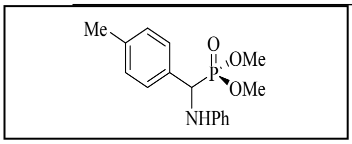

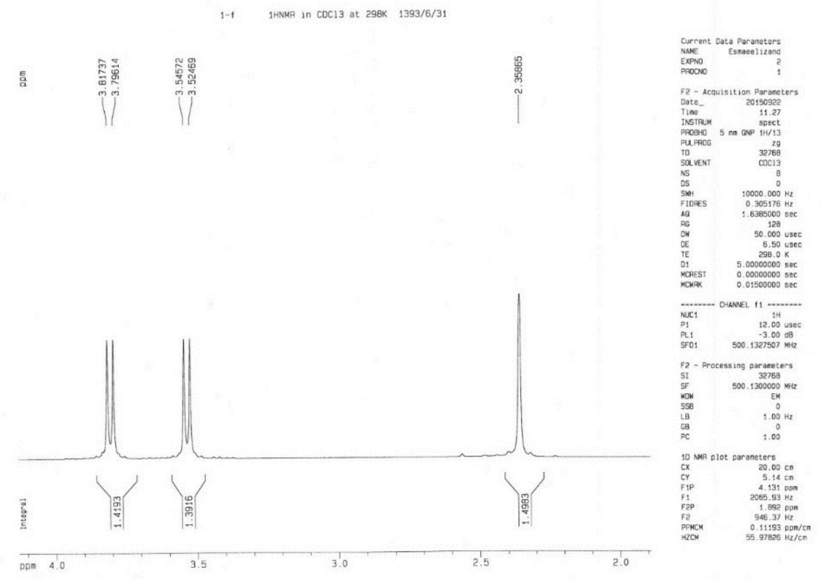

```
Current Data Parameters
NAME        Esmaeelizand
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               11.27
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ             1.6385000 sec
RG                   128
DW                50.000 usec
DE                  6.50 usec
TE                 298.0 K
D1            5.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -3.00 dB
SFO1         500.1327507 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  5.14 cm
F1P                4.131 ppm
F1               2065.93 Hz
F2P                1.892 ppm
F2                946.37 Hz
PPMCM            0.11193 ppm/cm
HZCM            55.97826 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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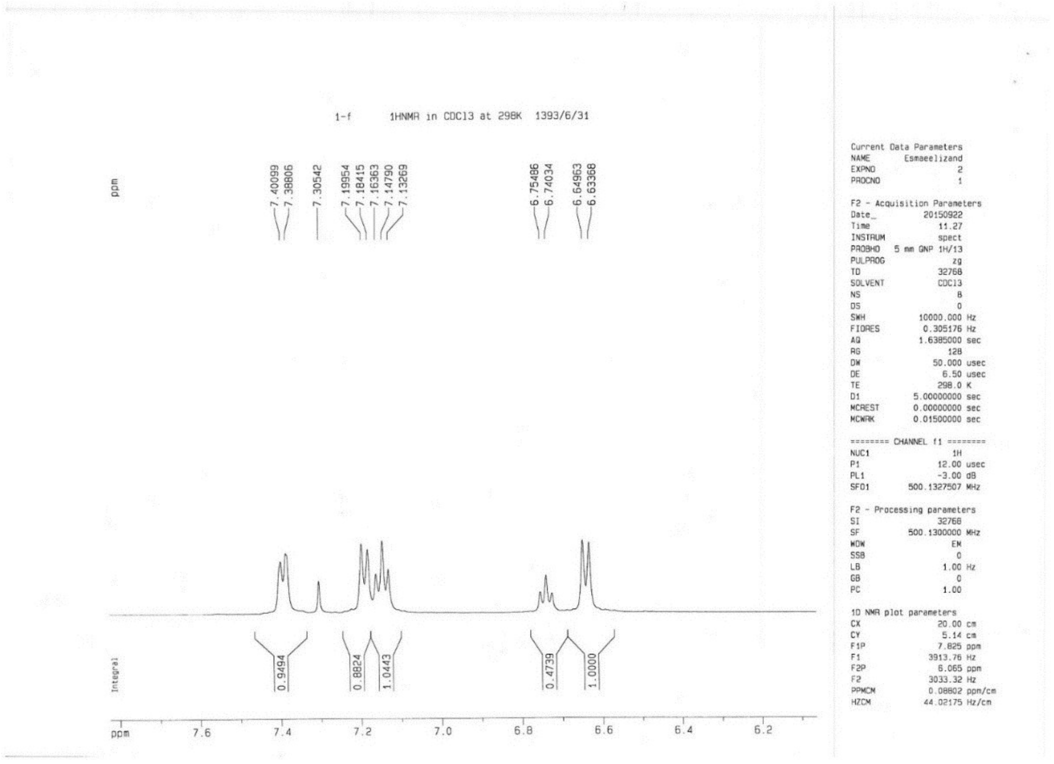
Supplementary Information



```
Current Data Parameters
NAME       Esmaeelizand
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150922
Time              11.27
INSTRUM           spect
PROBHD   5 mm GNP 1H/13
PULPROG              zg
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            1.6385000 sec
RG                  128
DW               50.000 usec
DE                 6.50 usec
TE                298.0 K
D1           5.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -3.00 dB
SFO1        500.1327507 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                 5.14 cm
F1P               7.825 ppm
F1              3913.76 Hz
F2P               6.065 ppm
F2              3033.32 Hz
PPMCM           0.08802 ppm/cm
HZCM           44.02175 Hz/cm
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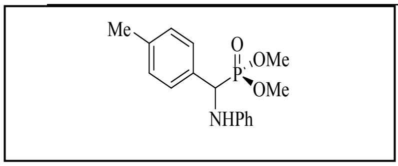
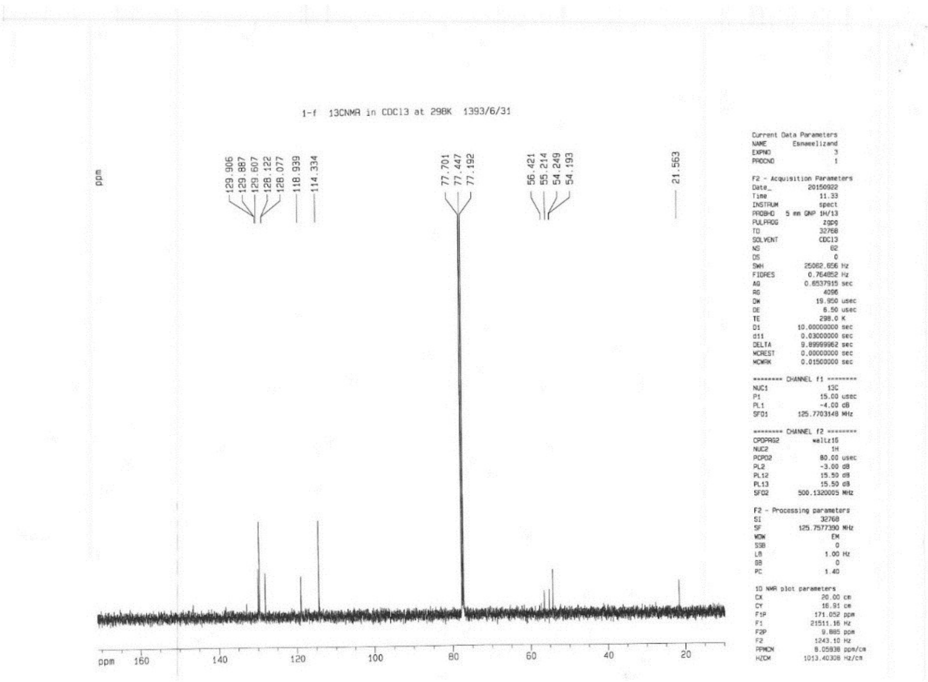
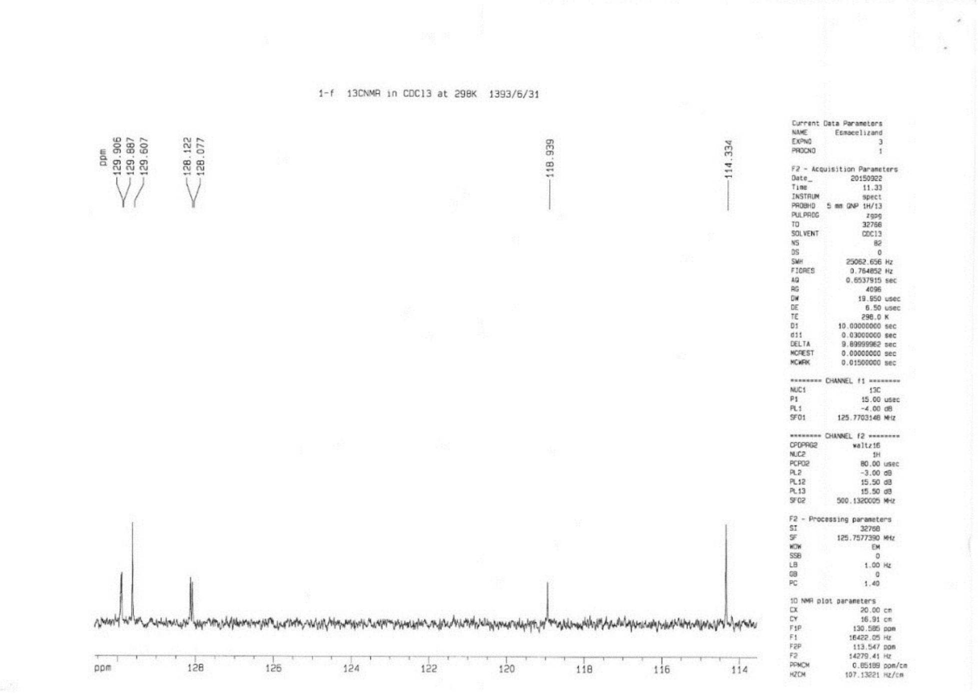
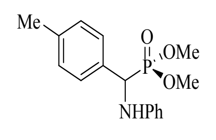
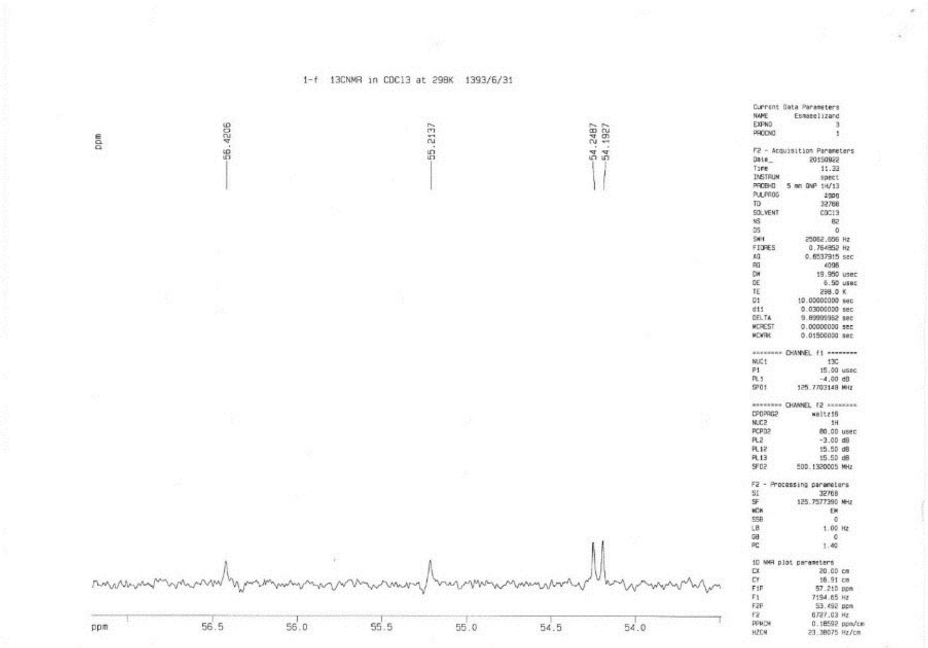






```
Current Data Parameters
NAME        Esmaeelizand
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               11.33
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                    82
DS                     0
SWH            25062.656 Hz
FIDRES          0.764852 Hz
AQ             0.6537915 sec
RG                  4096
DW                19.950 usec
DE                  6.50 usec
TE                 298.0 K
D1           10.00000000 sec
d11           0.03000000 sec
DELTA         9.89999962 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PL1                -4.00 dB
SFO1         125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577390 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 16.91 cm
F1P              130.585 ppm
F1              16422.05 Hz
F2P              113.547 ppm
F2              14279.41 Hz
PPMCM            0.85189 ppm/cm
HZCM           107.13221 Hz/cm
```

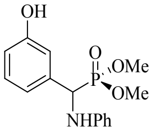


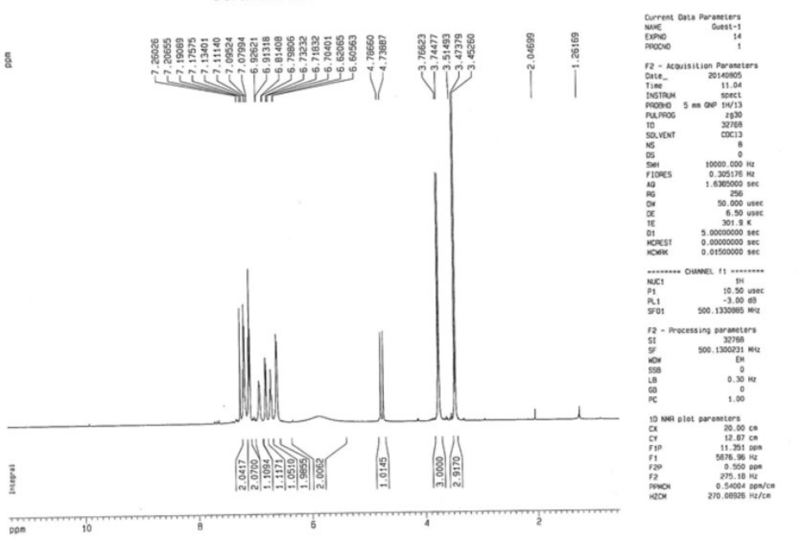


```
Current Data Parameters
NAME          Esmaeelizand
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150822
Time                 11.33
INSTRUM              spect
PROBHD   5 mm DNP 1H/13
PULPROG               zgpg
TD                   32768
SOLVENT              CDCl3
NS                      82
DS                       0
SWH           25062.656 Hz
FIDRES         0.764852 Hz
AQ            0.6537915 sec
RG                    4096
DW              19.950 usec
DE               6.50 usec
TE               298.0 K
D1         10.00000000 sec
d11         0.03000000 sec
DELTA       9.89999952 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1               15.00 usec
PL1               -4.00 dB
SFO1        125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            80.00 usec
PL2               -3.00 dB
PL12              15.50 dB
PL13              15.50 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF          125.7577390 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                20.00 cm
CY                16.91 cm
F1P             57.210 ppm
F1              7194.65 Hz
F2P             53.492 ppm
F2              6727.03 Hz
PPMCM        0.18592 ppm/cm
HZCM        23.38075 Hz/cm
```

Figure S22. NMR spectra of 1j

Figure S22. NMR spectra of 1j





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Current Data Parameters
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EXPNO                14
PROCNO                1

F2 - Acquisition Parameters
Date_          20140805
Time              11.04
INSTRUM           spect
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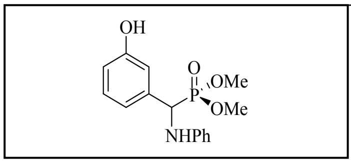
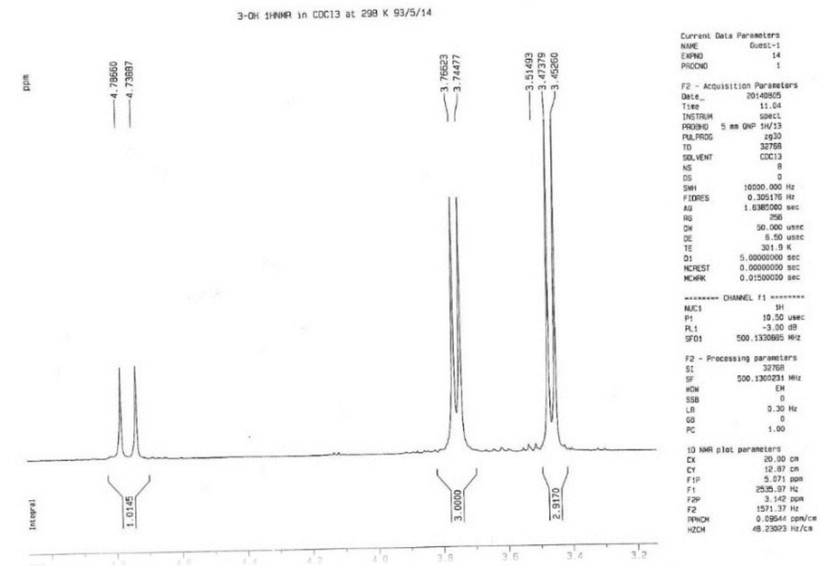
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            1.6385000 sec
RG                  256
DW               50.000 usec
DE                 6.50 usec
TE                301.9 K
D1           5.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                10.50 usec
PL1               -3.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300231 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                12.87 cm
F1P              11.351 ppm
F1              5676.96 Hz
F2P               0.550 ppm
F2               275.18 Hz
PPMCM           0.54004 ppm/cm
HZCM          270.08926 Hz/cm
```


OH
O
P
OMe
OMe
NHPh


3-OH 1HNMR in CDCl3 at 298 K 93/5/14
ppm
4.78660
4.73887
3.76623
3.74477
3.51493
3.47379
3.45260
Integral
1.0145
3.0000
2.9170
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
Current Data Parameters
NAME Guest-1
EXPNO 14
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140805
Time 11.04
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 256
DW 50.000 usec
DE 6.50 usec
TE 301.9 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300231 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.87 cm
F1P 5.071 ppm
F1 2535.97 Hz
F2P 3.142 ppm
F2 1571.37 Hz
PPMCM 0.09644 ppm/cm
HZCM 48.23023 Hz/cm

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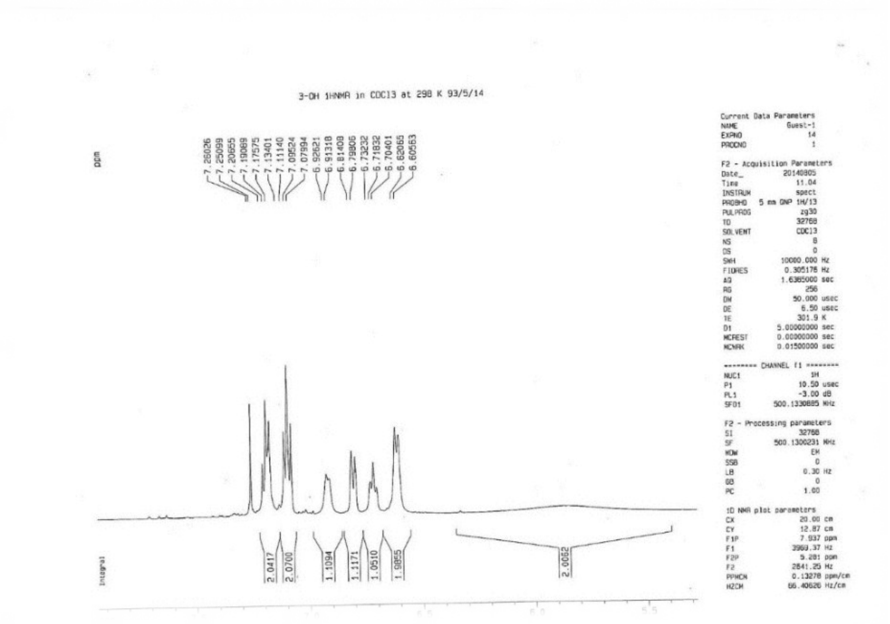
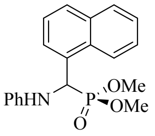


Current Data Parameters	
NAME	Guest-1
EXPNO	14
PROCNO	1
F2 - Acquisition Parameters	
Date_	20140805
Time	11.04
INSTRUM	spect
PROBHD	5 mm DNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	1.6385000 sec
RG	256
DW	50.000 usec
DE	6.50 usec
TE	301.9 K
D1	5.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	10.50 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz
F2 - Processing parameters	
SI	32768
SF	500.1300231 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00
1D NMR plot parameters	
CX	20.00 cm
CY	12.87 cm
F1P	7.937 ppm
F1	3969.37 Hz
F2P	5.281 ppm
F2	2841.25 Hz
PPMCM	0.13278 ppm/cm
HZCM	66.40626 Hz/cm

Figure S23. NMR spectra of 1l

Figure S23. NMR spectra of 1l



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Cite this: DOI: 10.1039/c0xx00000x

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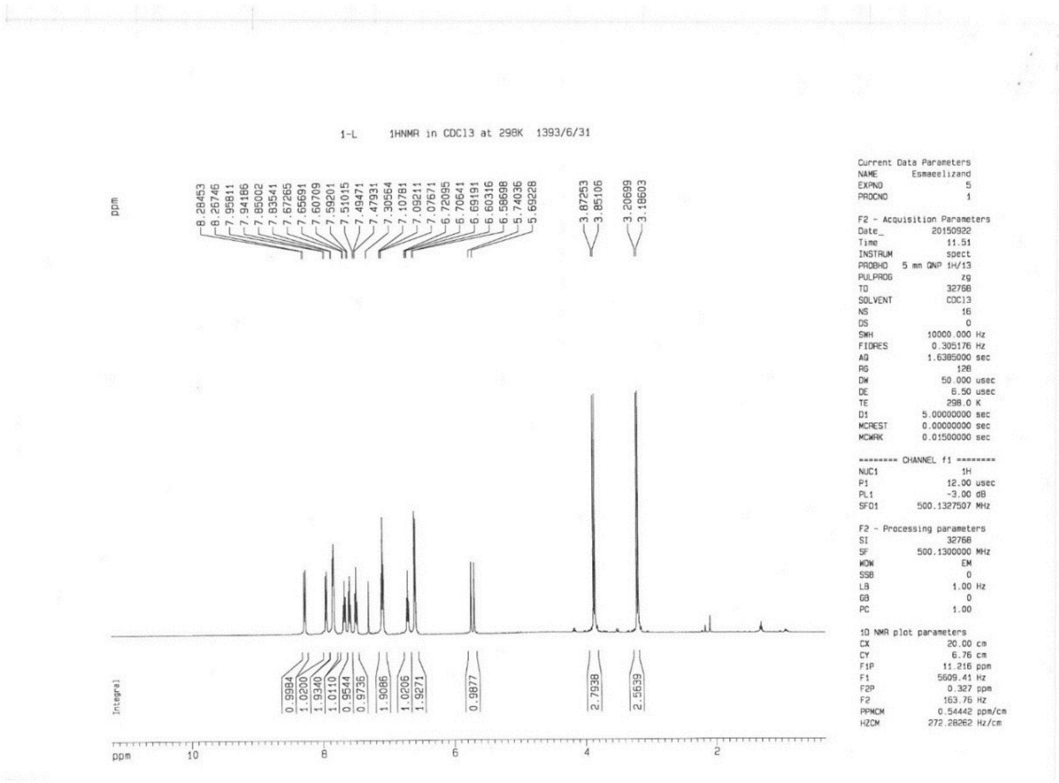
Supplementary Information



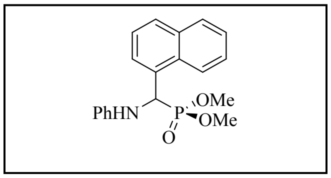
```
Current Data Parameters
NAME         Esmaeelizand
EXPNO                   5
PROCNO                  1

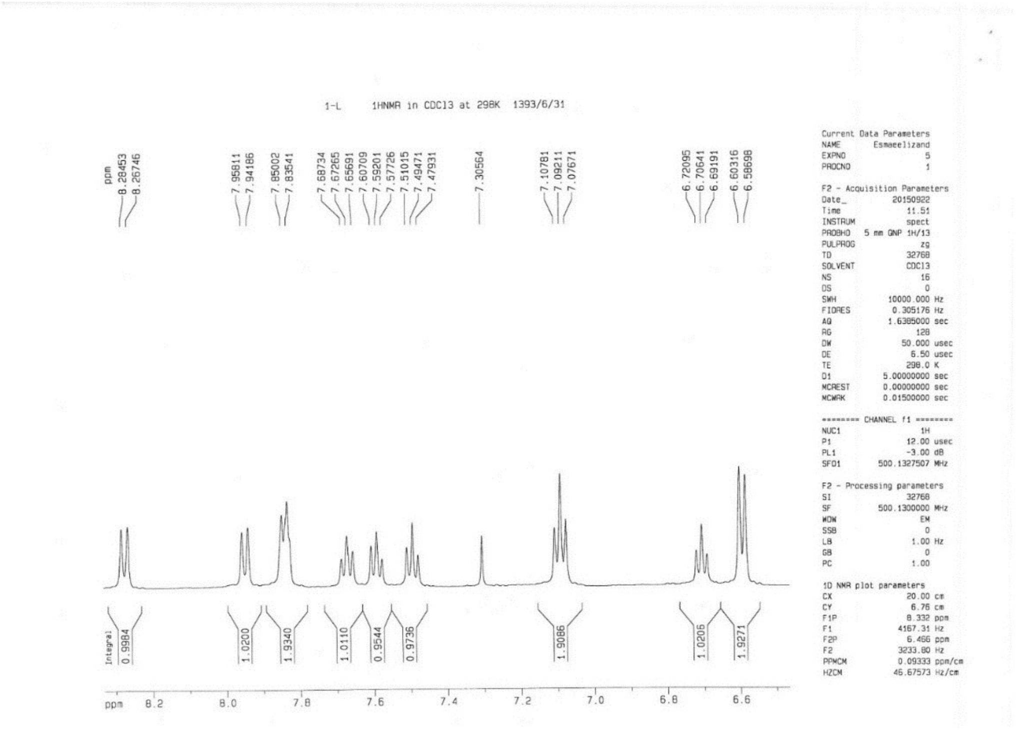
F2 - Acquisition Parameters
Date_            20150922
Time                11.51
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg
TD                  32768
SOLVENT             CDC13
NS                     16
DS                      0
SWH             10000.000 Hz
FIDRES           0.305176 Hz
AQ              1.6385000 sec
RG                    128
DW                 50.000 usec
DE                   6.50 usec
TE                  298.0 K
D1             5.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -3.00 dB
SFO1          500.1327507 MHz

F2 - Processing parameters
SI                  32768
SF            500.1300000 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                   6.76 cm
F1P                11.216 ppm
F1                5609.41 Hz
F2P                 0.327 ppm
F2                 163.76 Hz
PPMCM             0.54442 ppm/cm
HZCM            272.28262 Hz/cm
```




1-L 1HNMR in CDCl3 at 298K 1393/6/31

```
Current Data Parameters
NAME          Esmaeelizand
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150922
Time                 11.51
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG                 zg
TD                   32768
SOLVENT              CDC13
NS                      16
DS                       0
SWH          10000.000 Hz
FIDRES        0.305176 Hz
AQ           1.6385000 sec
RG                     128
DW              50.000 usec
DE                6.50 usec
TE               298.0 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1               12.00 usec
PL1              -3.00 dB
SFO1       500.1327507 MHz

F2 - Processing parameters
SI                   32768
SF         500.1300000 MHz
WDW                     EM
SSB                      0
LB                1.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX               20.00 cm
CY                6.76 cm
F1P              8.332 ppm
F1             4167.31 Hz
F2P              6.466 ppm
F2             3233.80 Hz
PPMCM          0.09333 ppm/cm
HZCM          46.67573 Hz/cm
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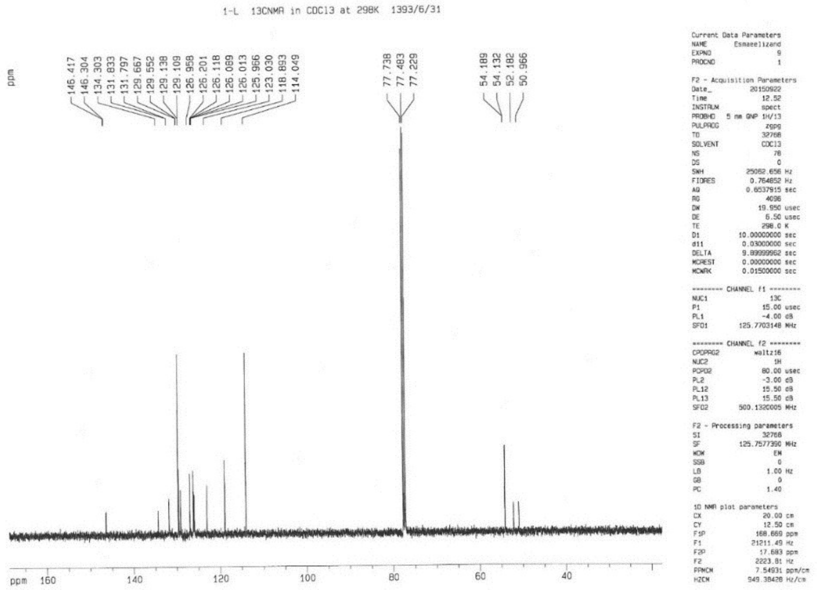

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Current Data Parameters
NAME        Esmaeelizand
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               12.52
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                    78
DS                     0
SWH            25062.656 Hz
FIDRES          0.764852 Hz
AQ             0.6537915 sec
RG                  4096
DW                19.950 usec
DE                  6.50 usec
TE                 298.0 K
D1           10.00000000 sec
d11           0.03000000 sec
DELTA         9.89999962 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PL1                -4.00 dB
SFO1         125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577390 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              168.669 ppm
F1              21211.49 Hz
F2P               17.683 ppm
F2               2223.81 Hz
PPMCM            7.54931 ppm/cm
HZCM           949.38428 Hz/cm
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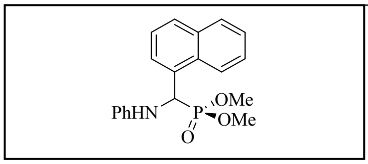

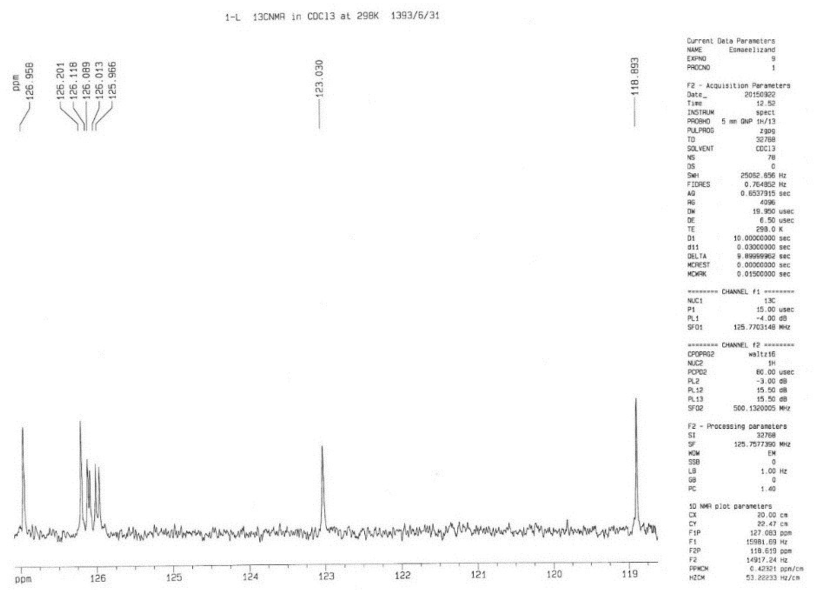
1-L 13CNMR in CDCl3 at 298K 1393/6/31

```
Current Data Parameters
NAME        Esmaeelizand
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               12.52
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                    78
DS                     0
SWH            25062.656 Hz
FIDRES          0.764852 Hz
AQ             0.6537915 sec
RG                  4096
DW                19.950 usec
DE                  6.50 usec
TE                 298.0 K
D1           10.00000000 sec
d11           0.03000000 sec
DELTA         9.89999962 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PL1                -4.00 dB
SFO1         125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577390 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 22.47 cm
F1P              127.083 ppm
F1              15981.69 Hz
F2P              118.619 ppm
F2              14917.24 Hz
PPMCM            0.42321 ppm/cm
HZCM            53.22233 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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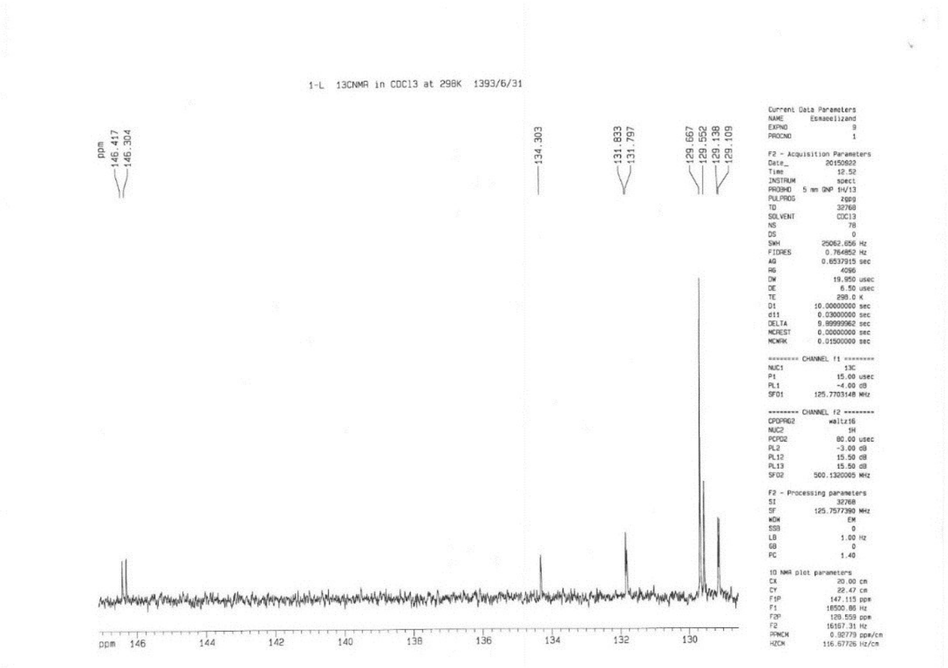
Supplementary Information



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Current Data Parameters
NAME         Esmaeelizand
EXPNO                   9
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150922
Time                12.52
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg
TD                  32768
SOLVENT             CDCl3
NS                     78
DS                      0
SWH             25062.656 Hz
FIDRES           0.764852 Hz
AQ              0.6537915 sec
RG                   4096
DW                 19.950 usec
DE                   6.50 usec
TE                  298.0 K
D1            10.00000000 sec
d11            0.03000000 sec
DELTA          9.89999962 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.00 usec
PL1                 -4.00 dB
SFO1          125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                15.50 dB
PL13                15.50 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                  32768
SF            125.7577390 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
CY                  22.47 cm
F1P               147.115 ppm
F1               18500.86 Hz
F2P               128.559 ppm
F2               16167.31 Hz
PPMCM             0.92779 ppm/cm
HZCM            116.67726 Hz/cm
```
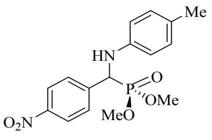

Figure S24. NMR spectra of 1o

Figure S24. NMR spectra of 1o



Cite this: DOI: 10.1039/c0xx00000x

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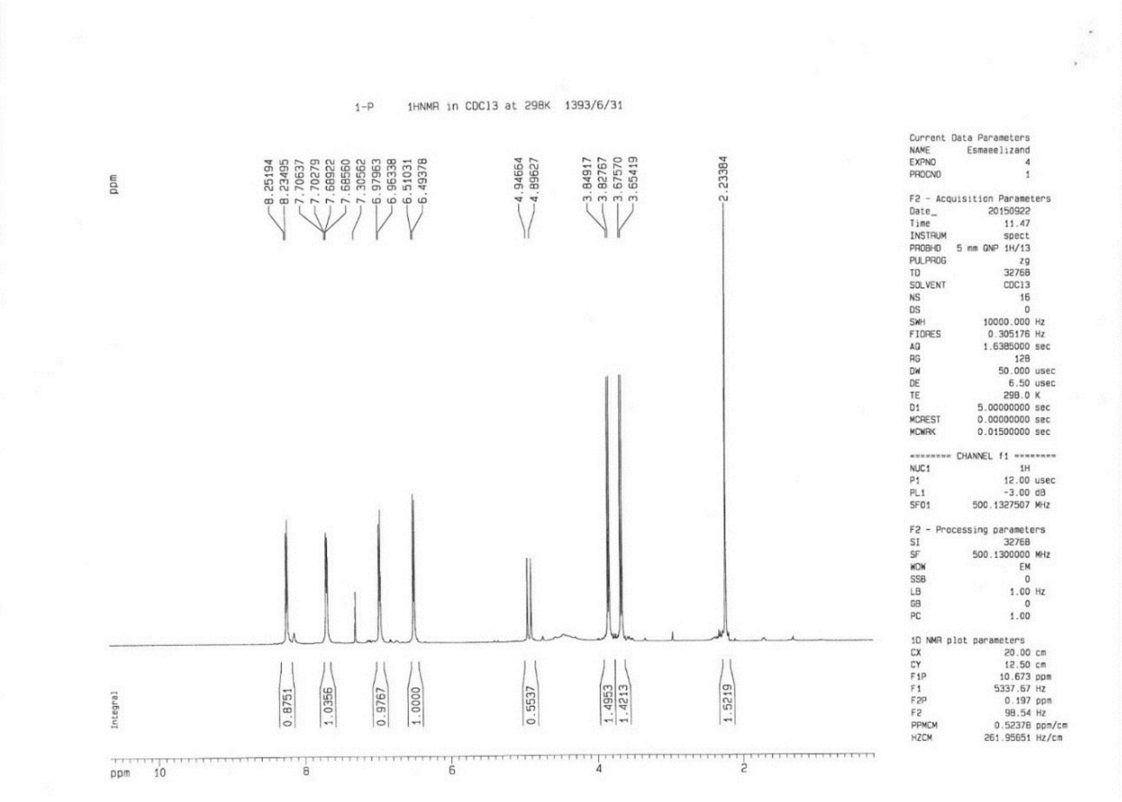

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Current Data Parameters
NAME       Esmaeelizand
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20150922
Time              11.47
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG              zg
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH          10000.000 Hz
FIDRES        0.305176 Hz
AQ           1.6385000 sec
RG                  128
DW              50.000 usec
DE                6.50 usec
TE               298.0 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -3.00 dB
SFO1        500.1327507 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P              10.673 ppm
F1              5337.67 Hz
F2P               0.197 ppm
F2                98.54 Hz
PPMCM           0.52378 ppm/cm
HZCM          261.95651 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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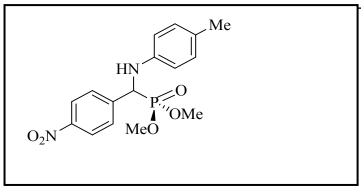

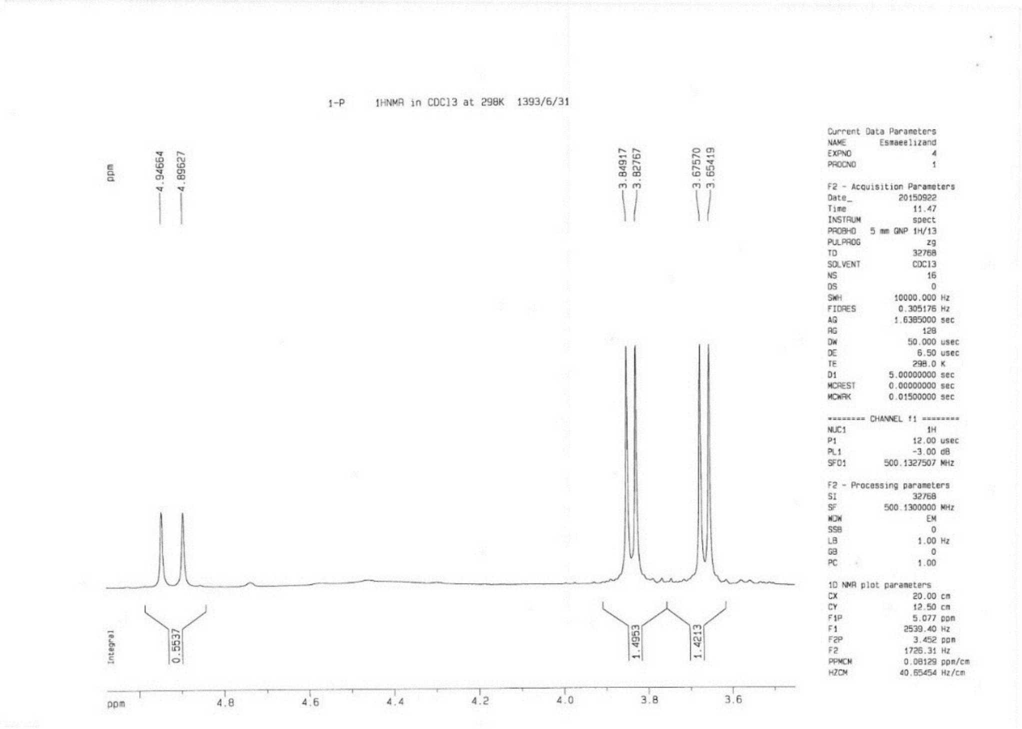

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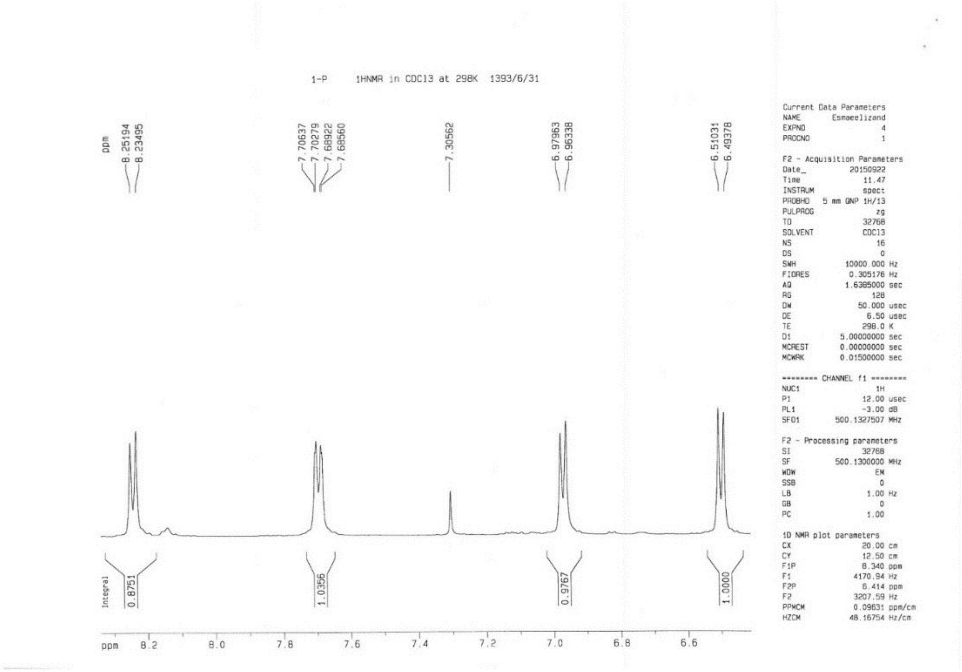
Current Data Parameters
NAME        Esmaeelizand
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               11.47
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AG             1.6385000 sec
RG                   128
DW                50.000 usec
DE                  6.50 usec
TE                 298.0 K
D1            5.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -3.00 dB
SFO1         500.1327507 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                5.077 ppm
F1               2539.40 Hz
F2P                3.452 ppm
F2               1726.31 Hz
PPMCM            0.08129 ppm/cm
HZCM            40.65454 Hz/cm
```


1-P   1HNMR in CDC13 at 298K 1393/6/31

```
Current Data Parameters
NAME          Esmaeelizand
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150922
Time                 11.47
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG                 zg
TD                   32768
SOLVENT              CDC13
NS                      16
DS                       0
SWH          10000.000 Hz
FIDRES        0.305176 Hz
AQ          1.6385000 sec
RG                     128
DW            50.000 usec
DE              6.50 usec
TE               298.0 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1             12.00 usec
PL1              -3.00 dB
SFO1       500.1327507 MHz

F2 - Processing parameters
SI                   32768
SF         500.1300000 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P              8.340 ppm
F1              4170.94 Hz
F2P              6.414 ppm
F2              3207.59 Hz
PPMCM        0.09631 ppm/cm
HZCM        48.16754 Hz/cm
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Cite this: DOI: 10.1039/c0xx00000x

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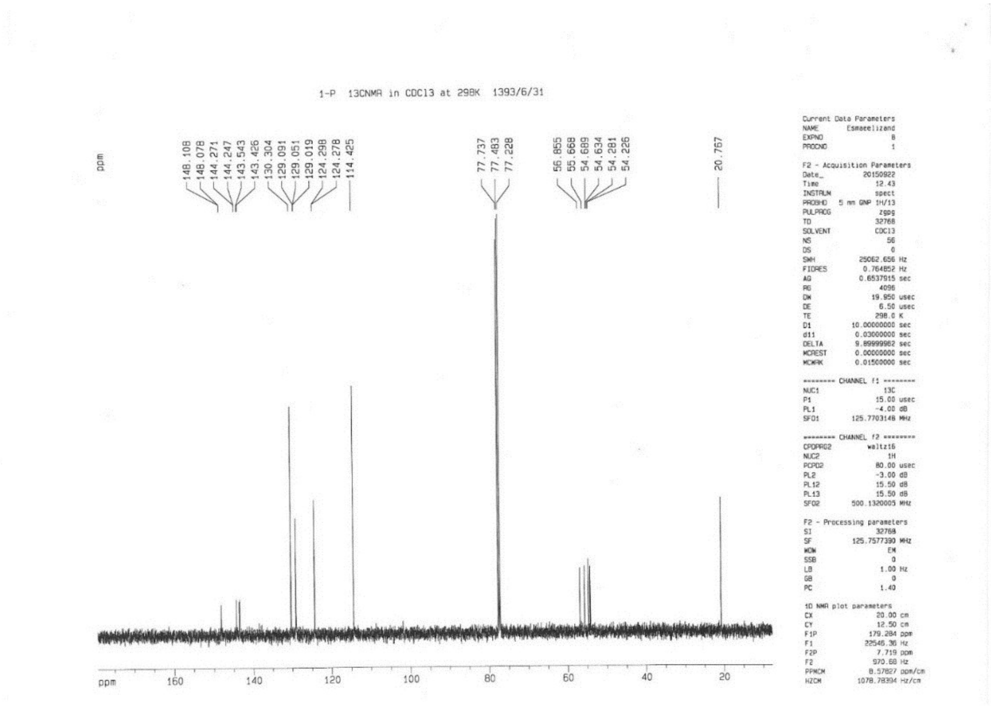

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Current Data Parameters
NAME        Esmaeelizand
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150922
Time               12.43
INSTRUM            spect
PROBHD   5 mm GNP 1H/13
PULPROG             zgpg
TD                 32768
SOLVENT            CDC13
NS                    56
DS                     0
SWH            25062.656 Hz
FIDRES          0.764852 Hz
AQ             0.6537915 sec
RG                  4096
DW                19.950 usec
DE                  6.50 usec
TE                 298.0 K
D1           10.00000000 sec
d11           0.03000000 sec
DELTA         9.89999962 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PL1                -4.00 dB
SFO1         125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577390 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              179.284 ppm
F1              22546.36 Hz
F2P                7.719 ppm
F2                970.68 Hz
PPMCM            8.57827 ppm/cm
HZCM          1078.78394 Hz/cm
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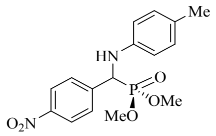

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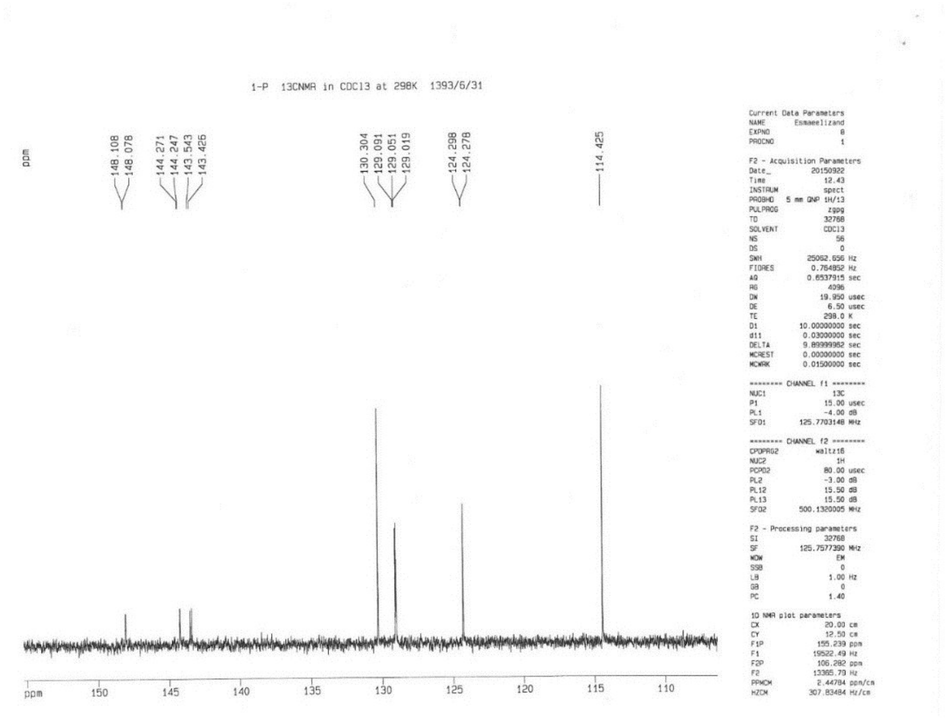

1-P 13CNMR in CDCl3 at 298K 1393/6/31

```
Current Data Parameters
NAME       Esmaeelizand
EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20150922
Time              12.43
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg
TD                32768
SOLVENT           CDCl3
NS                   56
DS                    0
SWH          25062.656 Hz
FIDRES        0.764852 Hz
AQ           0.6537915 sec
RG                 4096
DW              19.950 usec
DE                6.50 usec
TE               298.0 K
D1         10.00000000 sec
d11         0.03000000 sec
DELTA       9.89999962 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                15.00 usec
PL1               -4.00 dB
SFO1        125.7703148 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              15.50 dB
PL13              15.50 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577390 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P             155.239 ppm
F1             19522.49 Hz
F2P             106.282 ppm
F2             13365.79 Hz
PPMCM           2.44784 ppm/cm
HZCM          307.83484 Hz/cm
```