Electronic Supplementary Information for
Highly efficient solvent free synthesis of α-aminophosphonates catalyzed by recyclable nano magnetic sulfated zirconia (Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$)

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1. Experimental
All chemicals used, such as salts of iron (III) chloride, iron (II) chloride, zirconium (IV) chloride, ammonium sulfate, aldehydes, ketones, amines, and dimethyl phosphate 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 Ka, (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 Fe₃O₄@ZrO₂/SO₄²⁻ nanoparticles were measured with a vibrating magnetometer/ Alternating Gradient Force Magnetometer (VSM/, MDKFD). In this project, the nano magnetic sulfated zirconia Fe₃O₄@ZrO₂/SO₄²⁻ 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 Fe₃O₄@ZrO₂/SO₄²⁻ 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

2.1 Preparation of the magnetic Fe₃O₄ nanoparticles (MNP)

Ferric acid and ferrous salts were employed as precursors for the synthesis of Fe₃O₄ nanoparticles. Briefly, FeCl₃·6H₂O (12.2 g, 0.04 mol) and FeCl₂·4H₂O (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 °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 °C in vacuo.

2.2 General procedure for preparation of Fe₃O₄@ZrO₂/SO₄²⁻:

Initially 30g ZrCl₄ were dissolved in 1000 ml EtOH: H₂O (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 Fe₃O₄NPs 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
confirmed by AgNO₃ test. Subsequently the obtained solid was dipped in (NH₄)₂SO₄ (3 mol.L⁻¹) aqueous solution at room temperature for 24 h. Then the solid was filtered, dried without washing overnight at 100 °C and calcined at 600 °C, for 6 h in the N₂ atmosphere.

3. Synthesis of α-aminophosphonate derivatives:

A mixture of aldehydes or ketones (2.0 mmol), amine (Table S1) (2.0 mmol), dimethylphosphite (2.4 mmol) was added with Fe₃O₄@ZrO₂/SO₄²⁻ (120.0 mg) and stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ¹H,¹³C 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 filtration) 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 of catalyst Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$

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<th>Carbonyls</th>
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4. Back titration in aqueous media catalyst Fe₃O₄@ZrO₂/SO₄²⁻

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, ¹H and ¹³C NMR, MS:

5.1.1-Dimethyl [(phenyl) (phenylamino) methyl] phosphonate

8, 41 (1a): The mixture of PhCHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν max cm⁻¹): 3305, 1600, 1500, 1240, 1027; ¹H NMR (500 MHz, CDCl₃):
5.1.2-Dimethyl [(2-chlorophenyl) (phenylamino) methyl] phosphonate (1b) \(^{42}\): The mixture of 2-(Cl)C\(_6\)H\(_4\)CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe\(_2\)O\(_4\)/ZrO\(_2\)/SO\(_4\)\(^2-\) (160 mg) as a catalyst stirred at 80\(^\circ\)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 filtration). 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[(2-chlorophenyl)(phenylamino)methyl]phosphonate (93%) afforded as colorless crystals, mp 128–129\(^\circ\)C. IR (KBr, \(\nu\)\(_{\text{max}}\) cm\(^{-1}\)) 3311 (N-H), 1602, 1519, 1232, 1033; \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) = 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): \(\delta\) = 51.04, 52.26, 54.24 (m), 114.02, 119.13, 127.87, 129.39, 129.72, 130.05, 134.18, 134.41 (d, \(J_{P,C}\) =7.12 Hz), 145.87 (d, \(J_{P,C}\) =14.7 Hz) ppm.

5.1.3-Dimethyl [(4-chlorophenyl) (phenylamino) methyl] phosphonate (1c) \(^{51, 43}\): The mixture of 4-(Cl) C\(_6\)H\(_4\)CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe\(_2\)O\(_4\)/ZrO\(_2\)/SO\(_4\)\(^2-\) (160 mg) as a catalyst stirred at 80\(^\circ\)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 filtration). 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:50:50EtOAC/n-hexane). Dimethyl[(4-chlorophenyl)(phenylamino)methyl]phosphonate (95%) afforded, mp 139–140\(^\circ\)C, IR (KBr, \(\nu\)\(_{\text{max}}\) cm\(^{-1}\)): 3319(N-H), 1602, 1494, 1232, 1033; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.55 (d, J = 10.8 Hz, 3H), 3.79 (d, J = 10.5 Hz,3H), 4.98(d, \(J_{P,H}\) = 24 Hz, 1H), 7.3-8.2 (m, 9H). \(^{13}\)C NMR (125MHz,CDCl\(_3\)): \(\delta\) = 53.8, 54.2 , 56.1, 114.3 , 126.8, 128.2(d, \(J_{P.C}\) = 5.5 Hz),128.4 (d, \(J_{P.C}\) = 3.0 Hz), 131.1 , 132.2, 141.0 ,146.6 (d, \(J_{P.C}\) = 14.5 Hz) ppm.
5.1.4-Dimethyl[(2,4-chlorophenyl)(phenylamino)methyl]phosphonate (1d)^12: The mixture of 2,4-(Cl)₂C₆H₃CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₂O₄@ZrO₂/SO₄²⁻ (120 mg) as a catalyst stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν̃ max cm⁻¹): 3313(N-H), 1602, 1521, 1236, 1041; ¹H NMR (300 MHz; CDCl₃): 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-H = 24.4, 1H), 6.5- 7.5(m, 9H) ppm. ¹³C NMR (75 MHz; CDCl₃) δ: 51.19 (d, ¹J =153.1 Hz), 53.86 (d, ²J =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)^13: The mixture of 2,6-(Cl)₂C₆H₃CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₂O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν̃ max cm⁻¹) 3313(N-H), 1602, 1521, 1236, 1041. ¹H NMR(500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz; CDCl₃) 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.
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 Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν max cm⁻¹): 3313, 1602, 1498, 1232, 1031 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 2.35 (s, 3H), 3.52 (d, J = 10.5Hz, 3H), 3.79 (d, J = 10.6 Hz, 3H), 4.78 (d, Jp-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, 2Jc-p = 6.4, 2H) ppm. ¹³C NMR (125 MHz; CDCl₃) δ: 21.56, 54.19 (d, 2Jc-p = 7.0 Hz), 55.21, 56.42, 114.33, 118.93, 128.07 (d, 3Jc-p = 5.6 Hz), 129.60, 129.88 (d, 3Jc-p = 23.7 Hz) ppm.

5.1.7 Dimethyl (4-methoxy phenyl) (N-phenylamino) methylphosphonate (1g) ⁵¹, ⁴¹: The mixture of 4-(OMe)C₆H₄CHO (2.0 mmol) with Aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν max cm⁻¹): 3290, 1602, 1508, 1240, 1024 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): 3.47 (3H, d, J = 10.6Hz), 3.68 (s, 3H), 3.77 (d, J = 10.6 Hz), 4.22 (br, s 1H), 4.70(1H, d, ¹Jp-h = 24.08 Hz). 6.58-7.39 (9H, m); ¹³C NMR (CDCl₃, 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.
5.1.8-Dimethyl (4-nitrophenyl) (N-phenylamino) methylphosphonate (1h) \(^{51, 41}\): The mixture of 4-(NO\(_2\))C\(_6\)H\(_4\)CHO (2.0 mmol) with Aniline (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\(^{\circ}\)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 filtration). 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) (elucent: 50:50EtOAC/n-hexane). Dimethyl(4-nitrophenyl)(N-phenylamino)methylphosphonate (96%) afforded as a yellow crystals mp 127-128\(^{\circ}\)C; IR (KBr, \(\nu^{\text{max}}\) cm\(^{-1}\)): 3315, 3100, 1346, 1245,33, 1027 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\): 3.60 (d, J= 10.7 Hz, 3H), 3.78(d, J = 10.7Hz, 3H), 5.01 (H, d, \(^{1}\)J\(_{P-H}\) = 24.04 Hz), 6.53-8.01 (9H, m) ppm. \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\): 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\(_2\))C\(_6\)H\(_4\)CHO (2.0 mmol) with Aniline (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\(^{\circ}\)C 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 filtration). 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) (elucent: 50:50EtOAC/n-hexane). Dimethyl(3-nitrophenyl)(N-phenylamino)methylphosphonate (95%) afforded, mp 122-124\(^{\circ}\)C; IR (KBr, \(\nu^{\text{max}}\) cm\(^{-1}\)): 3301, 3106, 2940,1602, 1533, 1024 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz,CDCl\(_3\)): \(\delta\) 3.62 (d, J = 10.7 Hz, 3H), 3.78(d, J = 10.7Hz, 3H), 4.96 (d, \(^{1}\)J\(_{P-H}\) = 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\(_3\)): \(\delta\) 54.17 (d, \(^{2}\)J\(_{P-C}\) = 6.8 Hz),55.26 (d, \(^{2}\)J\(_{P-C}\) = 6.9 Hz), 56.06 (d, \(^{1}\)J\(_{P-C}\) =150.3 Hz), 114.81, 119.09, 122.75 (d, \(^{3}\)J\(_{P-C}\) =5.3 Hz),123.05, 129.33, 129.66, 133.94, 138.67,145.61 (d, \(^{2}\)J\(_{P-C}\) = 14.1 Hz), 148.51 (d, \(^{3}\)J\(_{P-C}\) =2.8 Hz) ppm.
5.1.10- Dimethyl (3-Hydroxyphenyl) (N-phenylamino) methylphosphonate (1j) \(^{51}\): The mixture of 3-(OH)C\(_6\)H\(_4\)CHO (2.0 mmol) with Aniline (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\(^\circ\)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 filtration). 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(3-Hydroxyphenyl)(N-phenylamino)methylphosphonate (96%) afforded, mp 130-132\(^\circ\)C; IR (KBr, \(\nu^\text{max}\) cm\(^{-1}\)) : 3413(N-H), 3176(br O-H), 1602, 1504, 1231, 1029; \(^1\)H NMR (500 MHz, CDCl\(_3\)) : \(\delta\) 3.45 (d, \(J = 10.5\) Hz, 3H), 3.74 (d, \(J = 10.7\) Hz, 3H), 4.73 (d, \(J_{P-H} = 23.8\) 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, \(J = 6.51\)Hz 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, \(J_{c-p} = 152\) 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\(_3\)O\(_4@\)ZrO\(_2/\)SO\(_4^2-\) (160 mg) as a catalyst stirred at 80\(^\circ\)C 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 filtration). 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: 50:50EtOAC/n-hexane. Dimethyl(Thiophenyl)(N-phenylamino)methylphosphonate (80%) afforded, mp 83-86\(^\circ\)C; IR (KBr, \(\nu^\text{max}\) cm\(^{-1}\)) : 3303, 2952, 1602, 1498, 1315, 1240, 1180, 1051, 1029 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 1.30 (m, 6 H), 3.82 (m, 4 H,), 4.6 (bs, 1 H), 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, \(J = 6.51\)Hz 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, \(J_{c-p} = 152\) Hz), 113.9, 114.4, 115.8, 118.7, 119.7, 129.2,129.9, 136.7, 145.9, 146.0, 157.3 ppm.

5.1.12- 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\(_3\)O\(_4@\)ZrO\(_2/\)SO\(_4^2-\) (160 mg) as a catalyst and stirred at 80\(^\circ\)C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν˜ max cm⁻¹): 3310, 1602, 1498, 1237, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 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. ¹³C NMR (CDCl₃, 125 MHz): δ= 50.96, 52.18, 54.13 (d, Jc-p=7.1 Hz), 114.04, 118.89, 123.03, 125.96 (m), 126.95, 129.10 (d, Jc-p=3.6 Hz), 129.55, 129.66, 131.79 (d, Jc-p=4.5 Hz), 134.30, 146.30 (d, 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 Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν˜ max cm⁻¹); 3446, 2926, 1350, 1251, 1167,1030. ¹H NMR (CDCl₃, 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, 1Jp,h = 24.02 Hz, 1 H)6.59-7.32 (m, 9 H); ¹³C NMR (CDCl₃, 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 Fe₃O₄@ZrO₂/SO₄²⁻ (100 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν˜ max cm⁻¹) 3306, 1600, 1500, 1313, 1240, 1027. ¹H NMR (200 MHz, CDCl₃+DMSO d₆): 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); ¹³C NMR (125 MHz, CDCl₃+DMSO d₆): δ= 132.7, 128.4, 124.3, 117.7, 112.7, 53.3, 52.7, 49.2, 28.7 ppm.

5.1.15-Dimethyl (4-nitrophenyl)(4-Methyphenylamino)methylphosphonate (1o)⁴⁷,⁵²: The mixture of 4-(NO₂)C₆H₄CHO (2.0 mmol) with p-Toluidine (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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.: 170–173 °C; IR (KBr, ν˜ max cm⁻¹) 3306, 1600, 1500, 1313, 1240, 1027. ¹H NMR (200 MHz, CDCl₃+DMSO d₆): 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); ¹³C NMR (125 MHz, CDCl₃+DMSO d₆): δ= 132.7, 128.4, 124.3, 117.7, 112.7, 53.3, 52.7, 49.2, 28.7 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 Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν̲max cm⁻¹) 3301, 2950, 1612, 1514, 1458, 1337, 1238, 1178, 1058, 1027. ¹H NMR (CDCl₃, 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, ¹JP-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); ¹³C NMR (CDCl₃, 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]phophonate (1q): 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 Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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]phophonate (76%) afforded, mp: 160-162°C, IR (KBr, ν̲max cm⁻¹) 3298, 3074, 2921, 2852, 2432, 1600, 1546, 1490, 1328, 1278, 1234, 1178, 1112, 1091, 1051, 1024, ¹H NMR (CDCl₃, 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, ¹JP-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); ¹³C NMR (CDCl₃, 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): 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 Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν max cm⁻¹) 3271, 3070, 2954, 2923, 2848, 1483, 1182.¹H 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, 1 J_P-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).¹³C NMR (CDCl₃, 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-(NO₂) C₆H₄CHO (2.0 mmol) with 4-Nitroaniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν max cm⁻¹) : 3279, 2954, 1621, 1529 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°C 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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν_max cm⁻¹): 3331, 1602, 1498, 1449, 1230, 1028 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.20- 1.82 (m, 10H), 3.91 (s, 1H), 3.77 (d, J = 10.2 Hz, 6H), 7.41 (d, m, 5H) ppm.

5.1.21- **Dimethyl (1-Phenyl-1-phenylaminoethyl) phosphonate (1u)**: The mixture of acetophenone (2.0 mmol) with aniline (2.0 mmol) and dimethyl phosphite (2.4 eq) in the presence of Fe₃O₄@ZrO₂/SO₄²⁻ (160 mg) as a catalyst stirred at 80°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 filtration). A saturated aqueous NaHCO₃ 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 Na₂SO₄. 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, ν_max cm⁻¹) : ¹H NMR(CDCl₃, 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$_3$O$_4$/ZrO$_2$/SO$_4^{2-}$:

Figure. S1 FT-IR spectra of the Fe$_3$O$_4$, ZrO$_2$, Fe$_3$O$_4$/ZrO$_2$ and Fe$_3$O$_4$/ZrO$_2$/SO$_4^{2-}$

Figure. S2 SEM of Fe$_3$O$_4$/ZrO$_2$/SO$_4^{2-}$
Figure. S3 TEM image of Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$(a,b)

Figure S4: Nitrogen adsorption-desorption isotherm and pore-size distribution of Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$. 


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
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
6.2. NMR spectra

Figure S18. NMR spectra of 1a
Figure S19. NMR spectra of 1b
Supplementary Information
Figure S20. NMR spectra of 1e
Supplementary Information
Supplementary Information
Figure S21. NMR spectra of 1f
Figure S22. NMR spectra of 1j
Supplementary Information
Figure S23. NMR spectra of 1l
Figure S24. NMR spectra of 1o