Supporting Information for:

Highly efficient one-pot multi-component synthesis of α-aminophosphonates and bis-α–aminophosphonates catalyzed by heterogeneous reusable silica supported dodecatungstophosphoric acid (DTP/SiO₂) at ambient temperature and their antitubercular evaluation against Mycobactrium Tuberculosis

Shafeek A. R. Mulla*, Mohsinkhan Y. Pathan, Santosh S. Chavan, Suwarna P. Gample, Dhiman Sarkar

aChemical Engineering & Process Development Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India.
bCombi. Chem. Bio. Resource Center, Organic Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India.

*Corresponding author Tel: +91 20 25902316
Fax: +91 20 25902676
E-mail: sa.mulla@ncl.res.in

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1. General experimental details

All chemicals and reagents required for the reactions were procured from Sigma-Aldrich with purity >98% and used without further purification. All reactions were monitored by TLC. TLC was performed on 0.25 mm E. Merck pre-coated silica gel plates (60F254). Column chromatography was performed on silica gel, Merck grade 60–120 mesh size. The products were characterized using $^1$HNMR, $^{13}$C NMR and mass spectra. NMR spectra were recorded on Bruker AC-200 spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications. Mass spectra were recorded by MALDI TOF/TOF and Electron Spray Ionization (ESI).

2. General Procedure for the preparation of DTP/SiO$_2$

DTP impregnated SiO$_2$ (20% DTP/SiO$_2$) catalyst was prepared by a incipient wetness technique\cite{1} as follows.

2 g of dry dodecatungstophosphoric acid (DTP) was weighed accurately. This was dissolved in 8 ml of methanol. The solution was added in small aliquots of 1 ml each time to the silica with constant stirring with a glass rod properly. The solution was added at time intervals of 2 min. Initially on addition of the DTP solution, silica was in a powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The performed catalyst was dried at 120 °C for removal of water and other occluded volatiles and subsequently calcined at 285 °C for 3 h.
3. General experimental procedure for 20% DTP/SiO$_2$ mediated synthesis of $\alpha$-aminophosphonates

The reaction mixture of aldehyde (10 mmol), amine (10 mmol) and Di/Tri alkyl phosphite (10 mmol) were stirred in 10 ml round bottom flask containing 5 ml acetonitrile solvent in the presence of 50 mg (0.35 mol%) 20% DTP/SiO$_2$ catalyst at room temperature for 1 h. The completion of the reaction was monitored by TLC. After completion of reaction, reaction mixture was diluted with ethyl acetate (10 ml) and catalyst was recovered by filtration. The filtrate was washed with aqueous NaHCO$_3$ and then with water followed by separation of aqueous layer and organic layer. The organic layer is dried over anhydrous Na$_2$SO$_4$ and concentrate in vacuum to gives the crude product. The crude product was purified by silica gel column chromatography using 70:30 ratio of pet ether/ethyl acetate to afford the pure $\alpha$-amino phosphonates.

4. Antitubercular testing using XTT Reduction menadione assay protocol

M. tuberculosis H37Ra (ATCC 25177) were grown to logarithmic phase (O.D.$_{595}$$\sim$1.0) in a defined medium (M. pheli medium). The stock culture was maintained at -70 °C and sub-cultured once in M. pheli medium before inoculation into experimental culture. Isoniazid, ethambutol and pyrazinamide were procured from Sigma. Drugs were solubilized in dimethyl sulfoxide (DMSO) and stored in aliquots at -20 °C. XTT sodium salt powder (Sigma) was prepared as a 1.25 mM stock solution in sterile 1x PBS and used immediately. Menadione (Sigma) was always freshly prepared as a 6 mM solution in DMSO before use. Compounds were screened for their inhibitory effect on MTB by following XTT Reduction Menadione Assay (XRMA) protocol published earlier. Briefly,
2.5 μl of these inhibitor solutions were added in a total volume of 250 μl of *M. phlei* medium consisting of 1x 10^6 bacilli. The incubation was terminated on the 8th day for MTB cultures. The XRMA was then carried out to estimate viable cells present in different wells of the assay plate. For that, in all wells of assay plate 200 μM XTT was added as a final concentration and incubated at 37 °C for 20 minutes. Then 60 μM Menadione was added as a final concentration and incubated at 37 °C for 40 minutes. The optical density was read on a micro plate reader (Spectramax plus 384 plate reader, Molecular Devices Inc) at 490 nm filter against a blank prepared from cell-free wells. Absorbance given by cells treated with the vehicle alone was taken as 100% cell growth. All experiments were performed in triplicates and the quantitative value was expressed as the average ± standard deviation and IC_{50} values were calculated from their dose response curves. For details: Sarkar D., Sing U., *J. Micro. Methods*, 211, 84, 202.

5. Cytotoxicity evaluation using MTT Reduction menadione assay protocol:

Cytotoxicity of compounds was tested for their inhibitory effect on THP-1 (Acquired from NCCS). In case of THP-1, cells were grown in RPMI medium. About 10,000 cells were taken per well in 96-well tissue culture plates and treated with different concentrations of test samples for 72 h. Vehicle control [dimethyl sulfoxide (DMSO), 1%] were run simultaneously. Cell viability was assessed with 10 ml from 5 mg/ml stock solution of tetrazolium salt (MTT) dissolved in cell culture medium and subsequently incubated for additional 1 h at 37 °C, 5% of CO_2 and 95% humidity in incubator. The violet colored formazan crystals formed were solubilized in 200 ml of isopropanol and incubated for another 4 h. The optical density was read on a micro plate reader at 49 nm
filter against a blank prepared from cell-free wells.

All experiments were out in triplicate, and the quantitative value was expressed as the average± standard deviation.

6. Spectral data for the products

Dimethyl phenyl(phenylamino)methylphosphonate\(^{2a}\) (4a)

\[
\text{White solid; mp: 91-93 °C; } ^1\text{H NMR (200 MHz, Acetone } d_6): \delta = 7.37-7.36 \text{ (m, 2H), 7.24-7.19 (m, 3H), 6.97-6.93 (m 2H), 6.56-6.45 (m, 3H), 4.80 (br s, 1H), 4.72 (d, } J=24 \text{ Hz, 1H), 3.68 (d, } J=10 \text{ Hz, 3H), 3.34 (d, } J=10 \text{ Hz, 3H); } ^{13}\text{C NMR (50 MHz, Acetone } d_6): \delta = 148.5, 138.1, 130.1, 129.5, 128.8, 118.7, 115.0, 57.4, 54.3.}
\]

Dimethyl (((3-chlorophenyl)amino)(4-methoxyphenyl)methylphosphonate (4b)

\[
\text{Yellow solid; mp: 92-94 °C; } ^1\text{H NMR (200 MHz, CDCl}_3): \delta = 7.45-7.27 \text{ (m, 4H), 6.66-6.49 (m, 4H), 4.70 (d, } J=24 \text{ Hz, 1H), 4.25 (br s, 1H), 3.75 (d, } J=10 \text{ Hz, 3H), 3.65 (s, 3H), 3.45 (d, } J=10 \text{ Hz, 3H); } ^{13}\text{C NMR (50 MHz, CDCl}_3): \delta = 153.4, 140.8, 140.4, 136.4, 136.3, 129.2, 128.6, 128.5, 128.4, 115.9, 115.3, 58.7, 55.9, 54.2.; MALDI TOF/TOF m/z calcd for C_{16}H_{19}ClNO_4P [M+] 355.07, observed 354.91.}
\]

Dimethyl ((4-chlorophenyl)(3-chlorophenyl)amino)methyl)phosphonates\(^{2a}\) (4c)
**Dimethyl (4-chlorophenyl) (phenylamino)methylphosphonate**

![Structure of Dimethyl (4-chlorophenyl) (phenylamino)methylphosphonate](image)

Yellow solid; mp: 134-136 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$= 7.41-7.40 (m, 1H), 7.39-7.30 (m, 2H), 7.10-7.05 (m, 2H), 6.70-6.56 (m, 1H), 6.56-6.50 (m, 2H), 4.80 (br s, 1H), 4.69 (s, 1H), 3.78 (d, $J$=10 Hz, 3H), 3.54 (d, $J$=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$= 151.9, 151.7, 137.0, 134.0, 127.6, 127.2, 127.1, 126.9, 124.7, 111.3, 54.9, 52.8, 52.6.

**Dimethyl (phenylamino)(p-tolyl)methylphosphonate**

![Structure of Dimethyl (phenylamino)(p-tolyl)methylphosphonate](image)

White solid; mp: 112-114 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$= 7.42-7.28 (m, 4H), 7.08-7.04 (m, 2H), 6.69 (t, $J$=7.02 Hz, 1H), 6.55-6.50 (m, 2H), 4.78 (br s, 1H), 4.67 (d, $J$=21 Hz, 1H), 3.79 (d, $J$=10 Hz, 3H), 3.55 (d, $J$=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$= 145.9, 134.3, 129.3, 129.2, 129.0, 118.9, 113.9, 56.8, 53.8.

**Dimethyl (phenylamino)(p-tolyl)methylphosphonate**

![Structure of Dimethyl (phenylamino)(p-tolyl)methylphosphonate](image)

White solid; mp: 122-124 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$= 7.34-7.30 (m, 2H), 7.14-7.03 (m, 4H), 6.69-6.52 (m, 3H), 4.79 (s, 1H), 4.77 (d, $J$=21 Hz, 1H), 3.75 (d, $J$=10 Hz,
3H), 3.45 (d, J=10 Hz, 3H), 2.32 (s, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): δ= 146.0, 137.6, 132.6, 129.5, 129.2, 127.8, 118.6, 113.9, 57.0, 53.8, 21.3; MALDI TOF/TOF m/z calcd for C$_{16}$H$_{20}$NO$_3$P [M + K$^+$] 344.12, observed 344.02.

**Dimethyl (2,5-dimethoxy phenyl)(phenylamino)methylphosphonate$^{2c}$ (4f)**

![Chemical structure of dimethyl (2,5-dimethoxy phenyl)(phenylamino)methylphosphonate](image)

White solid; mp: 134-136 °C; $^1$H NMR (200 MHz, CDCl$_3$): δ= 7.11-7.01 (m, 3H) 6.79-6.55 (m, 5H) 5.40 (d, J=24 Hz, 1H), 4.78 (br s, 1H), 3.90 (s, 3H), 3.84 (d, J=10 Hz, 3H), 3.71 (s, 3H), 3.46 (d, J=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): δ= 146.2, 145.90, 135.7, 129.0, 128.6, 127.8, 118.4, 113.7, 57.1, 54.1, 53.5; MALDI TOF/TOF m/z calcd for C$_{17}$H$_{22}$NO$_5$P [M + K$^+$] 390.12, observed 390.02.

**Dimethyl (furan-2-yl)(phenylamino)methylphosphonate$^{2a}$ (4g)**

![Chemical structure of dimethyl (furan-2-yl)(phenylamino)methylphosphonate](image)

Black solid; mp: 102-105 °C; $^1$H NMR (200 MHz, CDCl$_3$): δ= 7.30 (s, 1H), 7.04-6.67 (m, 2H), 6.64-6.54 (m, 3H), 6.31-6.22 (m, 2H), 4.88 (d, J=24 Hz, 1H), 4.54 (br s, 1H), 3.75 (d, J=10 Hz, 3H), 3.55 (d, J=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): δ= 149.1, 145.7, 142.4, 129.1, 118.9, 133.8, 110.7, 108.9, 53.7, 53.4, 51.3, 48.1.

**Dimethyl (mesitylamino)(2,5-dimethoxyphenyl)methylphosphonate$^{2d}$ (4h)**

![Chemical structure of dimethyl (mesitylamino)(2,5-dimethoxyphenyl)methylphosphonate](image)
White solid; mp: 109-111 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$= 6.82-6.72 (m, 5H), 5.01 (d, $J$=23 Hz, 1H), 4.29 (br s, 1H), 3.86-3.67 (m, 9H), 3.46 (d, $J$=10 Hz, 3H), 2.24-2.14 (m, 9H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$= 153.8, 141.9, 130.5, 129.5, 128.9, 128.3, 114.4, 112.2, 56.4, 55.5, 29.8, 20.6, 18.6.

**Dimethyl (napthalen-1-ylamino)(phenyl)methylphosphonate**$^{2d}$ (4i)

White solid; mp: 128-130 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$= 8.00-7.52 (m, 1H), 7.56-7.49 (m,1H), 7.48-7.47 (m, 4H), 7.33-7.29 (m, 3H), 7.18-7.13 (m, 2H), 6.36 (d, $J$=8 Hz, 1H), 5.00 (d, $J$=24 Hz, 1H), 3.82 (d, $J$=10 Hz, 3H), 3.52 (d, $J$=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$= 159.5, 141.3, 134.3, 128.7, 126.9, 126.2, 125.8, 125.1, 124.1, 120.1, 118.8, 114.2, 106.6, 56.8, 55.00.

**Dimethyl (4-chlorophenyl)(napththalene-1-ylamino)methylphosphonate** (4j)
White solid; mp: 127-129 °C; \(^1\)H NMR (200 MHz, CDCl\(_3\)): δ= 7.96 (d, \(J=7\) Hz, 1H), 7.78-7.74 (m, 1H), 7.44-7.42 (m, 4H), 7.32-7.13 (m, 4H), 6.32 (d, \(J=7\) Hz, 1H), 5.40 (s, 1H), 4.94 (d, \(J=24\) Hz, 1H), 3.80 (d, \(J=10\) Hz, 3H), 3.58 (d, \(J=10\) Hz, 3H); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): δ= 140.7, 134.1, 129.0, 128.9, 128.8, 125.9, 125.3, 124.1, 119.9, 119.2, 106.7, 57.1, 54.1; MALDI TOF/TOF m/z calcd for C\(_{19}\)H\(_{19}\)ClNO\(_3\)P [M +] 375.07, observed 375.02.

**Dimethyl (4-methoxyphenyl)(naphthalene-1-ylamino)methylphosphonate\(^2\) (4k)**

![Chemical Structure]

White solid; mp: 113-115 °C; \(^1\)H NMR (200 MHz, CDCl\(_3\)): δ= 7.98-7.91 (m, 1H), 7.76-7.12 (m, 1H), 7.53-7.38 (m, 4H), 7.25-7.09 (m, 2H), 6.83 (d, \(J=8\) Hz, 2H), 6.38 (d, \(J=8\) Hz, 1H), 4.90 (d, \(J=23\) Hz, 1H), 3.78 (d, \(J=10\) Hz, 3H), 3.75 (s, 3H), 3.51 (d, \(J=10\) Hz, 3H); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): δ= 159.5, 141.3, 134.3, 128.7, 126.9, 126.2, 125.8, 125.1, 124.1, 120.1, 118.8, 114.2, 106.6, 56.8, 55.0, 53.7.

**Dimethyl (2,5-dimethoxyphenyl)(naphthalene-1-ylamino)methylphosphonate\(^2\) (4l)**

![Chemical Structure]

White solid; mp: 130-132 °C; \(^1\)H NMR (200 MHz, CDCl\(_3\)): δ= 8.03-7.91 (m, 1H), 7.77-
7.72 (m, 1H), 7.55-7.40 (m, 2H), 7.20-7.05 (m, 3H), 6.88-6.70 (m, 2H), 6.48-6.43 (m, 1H), 5.55 (d, J=24 Hz, 1H), 3.94 (s, 3H), 3.87 (d, J=10 Hz, 3H), 3.65 (s, 3H), 3.49 (d, J=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$= 154.1, 151.5, 141.0, 134.3, 128.6, 126.4, 125.7, 125.0, 123.9, 120.2, 118.6, 114.1, 113.5, 111.8, 105.9, 56.4, 55.4, 53.7, 49.9, 46.8.

**Dimethyl (4-nitrophénylamino)(phenyl)methylphosphonate**$^{2f}$ (4m)

Yellow solid; mp: 124-126 °C; $^1$H NMR (200 MHz, CDCl$_3$+DMSO d$_6$): $\delta$= 7.90 (d, J=9 Hz, 2H), 7.45-7.20 (m, 5H), 6.70 (d, J=9 Hz, 2H), 4.90 (dd, 1H), 4.40 (br s, 1H), 3.69 (d, J=10 Hz, 3H), 3.46 (d, J=10 Hz, 3H); $^{13}$C NMR (50MHz, CDCl$_3$+DMSO d$_6$): $\delta$= 151.9, 137.1, 133.9, 127.6, 127.1, 124.7, 111.3, 54.9, 52.7, 51.9.

**Dimethyl (mesitylamino)(phenyl)methylphosphonate** (4n)

Yellow solid; mp: 93-95 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$= 7.44-7.30 (m, 2H), 7.25-7.17-7.19 (m, 3H), 6.61 (s, 2H), 4.73 (s, 1H), 4.37 (d, J=22 Hz, 1H), 3.74 (d, J=10 Hz, 3H), 3.34 (d, J=10 Hz, 3H), 2.09 (s, 3H), 2.06 (s, 6H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$= 141.4, 136.9, 131.1, 130.1, 129.6, 129.1, 128.4, 60.8, 57.8, 53.8, 29.7, 20.6, 18.7; MALDI TOF/TOF m/z calcd for C$_{18}$H$_{24}$NO$_3$P [M + K$^+$] 372.14, observed 372.03.
Dimethyl (4-methoxyphenylamino)(phenyl)methylphosphonate^{2g} (4o)

![Image of dimethyl (4-methoxyphenylamino)(phenyl)methylphosphonate]

White solid; mp: 85-87 °C; $^1$HNMR (200 MHz, CDCl$_3$): δ= 7.45-7.23 (m, 5H), 6.64 (d, J=9 Hz, 2H), 6.51 (d, J=9 Hz, 2H), 4.75 (d, J=24 Hz, 1H), 4.22 (br s, 1H), 3.79 (d, J=10 Hz, 3H), 3.65 (s, 3H), 3.47 (d, J=10 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): δ= 152.7, 139.8, 135.8, 128.6, 128.0, 127.9, 127.8, 115.2, 114.7, 58.1, 55.3, 53.6; MALDI TOF/TOF m/z calcd for C$_{16}$H$_{20}$NO$_4$P [M +]$^+$ 321.11, observed 321.04.

Dibenzyl (phenylamino)(3,4,5-trimethoxyphenyl)methylphosphonate (4p)

![Image of dibenzyl (phenylamino)(3,4,5-trimethoxyphenyl)methylphosphonate]

White solid; mp: 103-105 °C; $^1$HNMR (200 MHz, CDCl$_3$): δ= 7.34-7.29 (m, 8H), 7.17-7.10 (m, 4H), 6.74 (t, J=7 Hz, 1H), 6.64 (d, J=2 Hz, 2H), 6.60 (d, J=7 Hz, 2H), 5.09-5.04 (m, 2H), 4.93 (dd, J=7 Hz, 1H), 4.77-4.65 (m, 2H), 3.85 (s, 3H), 3.76 (s, 6H); $^{13}$CNMR (50 MHz, CDCl$_3$): δ= 153.4, 146.2, 131.1, 129.2, 128.6, 128.5, 128.2, 127.9, 118.8, 113.9, 104.8, 104.6, 68.6, 60.7, 58.2, 55.9; MALDI TOF/TOF m/z calcd for C$_{30}$H$_{32}$NO$_6$P [M + $K^+$] 572.19, observed 572.06.

Dibenzyl (4-chlorophenyl)(phenylamino)methylphosphonate (4q)
Yellow solid; mp: 131-133 °C; $^1$HNMR (200 MHz, CDCl$_3$): $\delta$ = 7.37-7.26 (m, 12H), 7.11-7.07 (m, 4H), 6.73 (t, $J$=7 Hz, 1H), 6.50 (d, $J$=7 Hz, 2H), 5.07-4.68 (m, 5H); $^{13}$CNMR (50 MHz, CDCl$_3$):$\delta$ = 145.9, 134.3, 129.2, 128.8, 128.6, 128.2, 128.1, 118.8, 113.9, 68.9, 57.3, 54.3; MALDI TOF/TOF m/z calcd for C$_{27}$H$_{25}$ClNO$_3$P [M + K$^+$] 516.12, observed 515.98.

**Dibenzyl (phenylamino)(p-tolyl)methylphosphonate (4r)**

Greenish solid; mp: 137-139 °C; $^1$HNMR (200 MHz, CDCl$_3$): $\delta$ = 7.38-7.30 (m, 10H), 7.18-7.07 (m, 6H), 6.73 (t, $J$=7 Hz, 1H), 6.58 (d, $J$=7 Hz, 2H), 5.07-4.58 (m, 5H), 2.37(s, 3H); $^{13}$CNMR (50 MHz, CDCl$_3$):$\delta$ = 146.1, 137.5, 136.1, 132.6, 129.4, 129.1, 128.5, 127.9, 127.8, 118.5, 113.9, 68.5, 57.5, 54.5, 21.3; MALDI TOF/TOF m/z calcd for C$_{28}$H$_{28}$NO$_3$P [M + K$^+$] 496.18, observed 496.05.

**Dibenzyl ((4-chlorophenyl)((3-chlorophenyl)amino)methyl)phosphonates (4s)**
Yellow solid; mp: 99-101 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta =$ 7.30-7.32 (m, 11H), 7.21-7.18 (m, 3H), 7.17-6.90 (m, 1H), 6.52-6.39 (m, 3H), 4.99 (br, s 1H), 4.95-4.55 (m, 5H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 147.0, 135.4, 134.8, 133.6, 130.1, 129.1, 128.9, 128.6, 128.1, 128.0, 127.8, 118.7, 113.7, 111.9, 68.8, 56.3, 54.8; MALDI TOF/TOF m/z calcd for C$_{27}$H$_{24}$Cl$_2$NO$_3$P $[M + K^+]$ 550.08, observed 549.98.

**Diethyl (naphthalene-1-ylamino)(phenyl)methylphosphonate$^{2h}$ (4t)**

White solid; mp: 114-116 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta =$ 7.96-6.99 (m, 11H), 6.25 (dd, $J=$7 Hz, 1H), 5.39 (br s, 1H), 4.87 (d, $J=$24 Hz, 1H), 3.53-4.12 (m, 4H), 1.20 (t, $J=$7 Hz, 3H), 1.05 (t, $J=$7 Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta =$ 159.4, 141.5, 134.4, 128.7, 127.4, 126.2, 125.7, 125.0, 124.1, 120.1, 118.6, 114.0, 106.6, 63.2, 57.2, 54.9, 54.2, 16.5.

**Diethyl (4-methoxyphenyl)(phenylamino)methylphosphonate$^{2e}$ (4u)**

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White solid; mp: 96-98 °C; \( ^1H \) NMR (200 MHz, CDCl\(_3\)): \( \delta = 7.92 \) (d, \( J=7 \) Hz, 1H), 7.67-7.62 (m, 1H), 7.40-7.29 (m, 4H), 7.08-7.04 (m, 2H), 6.75 (d, \( J=8 \) Hz, 2H), 6.31 (dd, \( J=7 \) Hz, 1H), 4.78 (d, \( J=23 \) Hz, 1H), 4.10-3.83 (m, 4H), 3.67 (s, 3H), 1.22 (t, \( J=7 \) Hz, 3H), 1.09 (t, \( J=7 \) Hz, 3H); \( ^{13}C \) NMR (50 MHz, CDCl\(_3\)): \( \delta = 141.4, 135.7, 134.4, 128.6, 127.9, 127.7, 126.1, 125.7, 125.0, 124.1, 120.1, 118.7, 106.5, 63.2, 57.8, 54.8, 16.5.

**Tetramethyl((1,4-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonates)**

(4v)

Brown solid; mp: 178-180 °C; \( ^1H \) NMR (200 MHz, CDCl\(_3\)+DMSO d\(_6\)): \( \delta = 7.38-7.20 \) (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\(_6\)): \( \delta = 132.7, 128.4, 124.3, 117.7, 112.7, 53.3, 52.7, 49.2, 28.7\); MALDI TOF/TOF m/z calcd for C\(_{24}H_{30}N_{2}O_{6}P_{2}\) [M + K\(^{+}\)] 543.15, observed 543.07.

**Tetraethyl ((1,4-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonates)**

(4w)
White solid; mp: 152-154 °C; $^1$H NMR (200 MHz, CDCl$_3$+DMSO d$_6$): $\delta$= 7.34-7.17 (m, 10H), 6.28 (s, 4H), 4.44 (d, $J$=24 Hz, 2H), 4.03 (s, 2H), 4.01-3.56 (m, 8H), 1.19 (t, $J$=7 Hz, 6H), 1.01 (t, $J$=7 Hz, 6H); $^{13}$C NMR (50 MHz, CDCl$_3$+DMSO d$_6$): $\delta$= 158.7, 128.7, 127.5, 114.9, 113.4, 54.5, 52.7, 29.1.

**Tetramethyl ((1,4-phenylenebis(azanediyl))bis((4-methoxyphenyl)methylene)) bis(phosphonate)$^{2e}$ (4x)**

White solid; mp: 161-163 °C; $^1$H NMR (200 MHz, CDCl$_3$+DMSO d$_6$): $\delta$= 7.32-7.26 (m, 4H), 6.80-6.76 (m, 4H), 6.40 (s, 4H), 4.62 (d, $J$=24 Hz, 2H), 4.23 (br s, 2H), 3.73 (s, 6H), 3.67 (d, $J$=10 Hz, 6H), 3.46 (d, $J$=10 Hz, 6H); $^{13}$C NMR (50 MHz, CDCl$_3$+DMSO d$_6$): $\delta$= 136.4, 128.5, 128.0, 127.9, 115.5, 62.9, 16.5, 16.4, 16.3.

**Reference**


Electronic Supplementary Material (ESI) for RSC Advances
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The image represents a chart from a chemical analysis, showing the normalized intensity on the y-axis and chemical shift (ppm) on the x-axis. The peaks at various ppm values correspond to different chemical compounds or functional groups. The diagram includes a molecular structure labeled with chemical elements and shifts. The TMS reference point is marked at 0.00 ppm, and the Y35 peak is indicated at 3.23 ppm. The ESI (Electronic Supplementary Material) for RSC Advances is noted on the journal page.