

Supporting Information

New 4-(2-(4-alkoxyphenyl)-6-methoxypyridin-4-yl)benzonnitriles: Synthesis, liquid crystalline behavior and photophysical properties

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Contents

- 1. Materials and methods**
- 2. Synthetic procedures**
- 3. Single crystal X-ray crystallography studies**
- 4. DSC profile of 4a**
- 5. Powder X-ray diffraction studies**

1. Materials and methods

All the reagents were obtained from commercial sources and used without further purification. The organic solvents were commercial and all were dried by traditional methods. All the compounds were purified by recrystallization from analytical grade solvents. The purity of sample was confirmed by thin layer chromatography (Merck 60 Kieselgel F 254). Elemental analyses were carried out on a Flash EA1112 analyzer (Thermo Electron Corporation). Infrared spectra of all compounds were recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV-visible and photoluminescence spectra were taken in GBC Cintra 101 and Perkin Elmer LS55 fluorescence spectrophotometers respectively. The photoluminescence

quantum yield (Φ_f) in the solution state was calculated according to equation, *i.e.* $\Phi_f = \Phi_{f\text{ std}}(I_{\text{unk}}/A_{\text{unk}})(A_{\text{std}}/I_{\text{std}})(\eta_{\text{unk}}/\eta_{\text{std}})^2$, where $\Phi_{f\text{ std}}$ is the photoluminescence quantum yield of the standard quinine sulphate ($\Phi_{f\text{ std}}=0.546$; 1N H₂SO₄); I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively; A_{unk} and A_{std} are the absorbance of the sample and the standard, respectively, at the desired excitation wavelength $\lambda_{\text{exc}}=330$ nm; η_{unk} and η_{std} are the refractive indexes of the sample and the standard solutions. Absolute quantum yield in the solid phase was measured using a calibrated integrating sphere in Perkin Elmer LS55 fluorescence spectrophotometers. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance DPX spectrometer at 400 MHz using CDCl₃ as the solvent, with tetramethylsilane as internal standard. Mass spectra (ESI) were recorded on Waters ZQ-4000 liquid chromatography-mass spectrometer. Polarized light microscopic studies were carried out using a Leitz Ortholux II Pol-BK microscope equipped with a Mettler FP82HT hot stage. The phase transition temperatures were determined using a SHIMADZU DSC-60 differential scanning calorimeter with a heating rate of 10 °C min⁻¹ (the apparatus was calibrated with indium, 156.6 °C). The about 3 mg of sample was hermetically sealed in an aluminium pan and placed in a nitrogen atmosphere. The sequence of phases and phase transition temperatures were identified by observing the textures and their changes under the polarizing optical microscope (POM). Polarized light microscopic studies were carried out using a Leitz Ortholux II Pol-BK microscope equipped with a Mettler FP82HT hot stage was used for temperature control, which enabled temperature stabilization within ± 0.1 K. X-ray diffraction (XRD) studies were carried out on powder samples in Lindemann capillaries with CuK α radiation using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focusing optics. The electrochemical studies were carried out using AUTOLAB PGSTAT-30 electrochemical analyzer.

2. Synthetic procedures

General procedure for synthesis of 1a-f.

The 4-n-alkoxyacetophenones **1a-f** were prepared from 4-hydroxyacetophenone by reaction with the corresponding alkyl bromide following the standard procedures.^{1, 2} Further, all the obtained analytical data were in agreement with the reported data.

General procedure for synthesis of chalcone derivatives (3a-f).

The respective 4-n-alkoxyacetophenones **1a-f** (1 equivalent) and 4-cyanobenzaldehyde **2** (1 equivalent) were taken in ethanol. To this added aqueous solution of potassium hydroxide (1.2 equivalents). Reaction mixture was stirred at room temperature for 4 h. The precipitated product was filtered. The crude product was purified by recrystallization from a suitable solvent.

4-(3-(4-Butoxyphenyl)-3-oxoprop-1-enyl)benzotrile (3a). Yield 85 %, m.p. 139-140 °C. FTIR (cm⁻¹): 2927, 2862, 2219, 1656, 1596, 1266, 1166, 1018, 816. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.04 (d, *J*=9 Hz, 2H, Ar-H), 7.77 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.75-7.71 (m, 4H, Ar-H), 7.62 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.00 (d, *J*=9 Hz, 2H, Ar-H), 4.07 (t, *J*=6.5 Hz, 2H, -OCH₂-), 1.84-1.80 (m, 2H, -OCH₂CH₂-), 1.56-1.51 (m, 2H, -CH₂-), 1.02 (t, *J*=7.2 Hz, 3H, -CH₃). MS (m/z): 306.1 (M+H)⁺. Anal. Calcd. For. C₂₀H₁₉NO₂: C. 78.66; H. 6.27; N. 4.59; Found: C. 78.95; H. 6.24; N. 4.55.

4-(3-(4-(Hexyloxy)phenyl)-3-oxoprop-1-enyl)benzotrile (3b). Yield 84 %, m.p. 115-116 °C. FTIR (cm⁻¹): 2912, 2850, 2217, 1653, 1598, 1263, 1165, 1015, 816. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.04 (d, *J*=9 Hz, 2H, Ar-H), 7.77 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.75-7.71 (m, 4H, Ar-H), 7.63 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.00 (d, *J*=9 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH₂-), 1.85-1.82 (m, 2H, -OCH₂CH₂-), 1.51-1.36 (m, 6H, -CH₂-), 0.93 (t, *J*=7 Hz, 3H, -CH₃). MS (m/z): 334.2 (M+H)⁺. Anal. Calcd. For. C₂₂H₂₃NO₂: C. 79.25; H. 6.95; N. 4.20; Found: C. 79.46; H. 6.98; N. 4.24.

4-(3-(4-(Octyloxy)phenyl)-3-oxoprop-1-enyl)benzotrile (3c). Yield 81 %, m.p. 95-97 °C. FTIR (cm⁻¹): 2921, 2858, 2223, 1654, 1601, 1250, 1179, 987, 816. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.04 (d, *J*=8.5 Hz, 2H, Ar-H), 7.77 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.75-7.71 (m, 4H, Ar-H), 7.63 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.00 (d, *J*=8.5 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH₂-), 1.87-1.81 (m, 2H, -OCH₂CH₂-), 1.51-1.32 (m, 10H, -CH₂-), 0.91 (t, *J*=7 Hz, 3H, -CH₃). MS (m/z): 362.2 (M+H)⁺. Anal. Calcd. For. C₂₄H₂₇NO₂: C. 79.74; H. 7.53; N. 3.87; Found: C. 79.97; H. 7.58; N. 3.84.

4-(3-(4-(Decyloxy)phenyl)-3-oxoprop-1-enyl)benzotrile (3d). Yield 79 %, m.p. 93-94 °C. FTIR (cm⁻¹): 2920, 2855, 2223, 1654, 1600, 1246, 1178, 985, 815. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.04 (d, *J*=8.5 Hz, 2H, Ar-H), 7.77 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.75-7.71 (m, 4H, Ar-

H), 7.63 (d, $J=15.5$ Hz, 1H, Olefinic-H), 6.99 (d, $J=8.5$ Hz, 2H, Ar-H), 4.06 (t, $J=6.5$ Hz, 2H, -OCH₂-), 1.86-1.81 (m, 2H, -OCH₂CH₂-), 1.50-1.30 (m, 14H, -CH₂-), 0.90 (t, $J=7$ Hz, 3H, -CH₃). MS (m/z): 390.2 (M+H)⁺. Anal. Calcd. For. C₂₆H₃₁NO₂: C. 80.17; H. 8.02; N. 3.60; Found: C. 80.43; H. 8.05; N. 3.56.

4-(3-(4-(Dodecyloxy)phenyl)-3-oxoprop-1-enyl)benzotrile (3e). Yield 84 %, m.p. 95-96 °C. FTIR (cm⁻¹): 2909, 2847, 2221, 1650, 1596, 1258, 1171, 988, 816. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.04 (d, $J=9$ Hz, 2H, Ar-H), 7.77 (d, $J=15.5$ Hz, 1H, Olefinic-H), 7.74-7.73 (m, 4H, Ar-H), 7.63 (d, $J=15.5$ Hz, 1H, Olefinic-H), 7.01 (d, $J=9$ Hz, 2H, Ar-H), 4.06 (t, $J=6.7$ Hz, 2H, -OCH₂-), 1.87-1.81 (m, 2H, -OCH₂CH₂-), 1.51-1.29 (m, 18H, -CH₂-), 0.90 (t, $J=7$ Hz, 3H, -CH₃). MS (m/z): 418.2 (M+H)⁺. Anal. Calcd. For. C₂₈H₃₅NO₂: C. 80.53; H. 8.45; N. 3.35; Found: C. 80.75; H. 8.48; N. 3.37.

4-(3-Oxo-3-(4-(tetradecyloxy)phenyl)prop-1-enyl)benzotrile (3f). Yield 82 %, m.p. 98-99 °C. FTIR (cm⁻¹): 2909, 2847, 2219, 1651, 1597, 1258, 1172, 977, 816. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.04 (d, $J=9$ Hz, 2H, Ar-H), 7.77 (d, $J=15.5$ Hz, 1H, Olefinic-H), 7.75-7.71 (m, 4H, Ar-H), 7.63 (d, $J=15.5$ Hz, 1H, Olefinic-H), 7.00 (d, $J=9$ Hz, 2H, Ar-H), 4.06 (t, $J=6.7$ Hz, 2H, -OCH₂-), 1.87-1.81 (m, 2H, -OCH₂CH₂-), 1.51-1.29 (m, 22H, -CH₂-), 0.90 (t, $J=6.7$ Hz, 3H, -CH₃). MS (m/z): 446.3 (M+H)⁺. Anal. Calcd. For. C₃₀H₃₉NO₂: C. 80.86; H. 8.82; N. 3.14; Found: C. 81.03; H. 8.87; N. 3.12.

General procedure for synthesis of 4-(2-(4-alkoxyphenyl)-6-methoxypyridin-4-yl)benzotriles (4a-f).

Compound **3a-f** (1 g, 1.9 mmol) was added slowly to a freshly prepared solution of sodium methoxide (20 mmol of sodium in 10 ml of methanol) while stirring. Malononitrile (0.12 g, 1.9 mmol) was then added with continuous stirring at room temperature until the precipitate separates out. The solid separated was collected by filtration, washed with methanol and recrystallized from an appropriate solvent.

4-(2-(4-Butoxyphenyl)-6-methoxypyridin-4-yl)benzotrile (4a). Yield 74 %. FTIR (cm⁻¹): 2944, 2859, 2219, 1577, 1237, 1170, 1008, 823. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.05 (d, $J=8$ Hz, 2H, Ar-H), 7.84 (d, $J=8$ Hz, 2H, Ar-H), 7.77 (d, $J=8.5$ Hz, 2H, Ar-H), 7.46 (s, 1H, Ar-

H(Pyridine)), 7.01 (d, $J=8.5$ Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H(Pyridine)), 4.22 (s, 3H, -OMe of Pyridine), 4.06 (t, $J=7$ Hz, 2H, -OCH₂-), 1.86-1.81 (m, 2H, -OCH₂CH₂-), 1.28 (t, $J=8.5$ Hz, 2H, -CH₂-), 1.01 (t, $J=7.5$ Hz, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.47, 160.31, 155.57, 149.90, 143.56, 132.70, 129.19, 128.97, 118.53, 115.19, 112.05, 110.57, 106.31, 68.25, 54.67, 31.89, 19.63, 14.08. MS (m/z): 359.1 (M+H)⁺. Anal. Calcd. For. C₂₃H₂₂N₂O₂: C. 77.07; H. 6.19; N. 7.82; Found: C. 77.31; H. 6.14; N. 7.86.

4-(2-(4-(Hexyloxy)phenyl)-6-methoxypyridin-4-yl)benzotrile (4b). Yield 67 %. FTIR (cm⁻¹): 2930, 2856, 2219, 1577, 1238, 1170, 1016, 825. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.06 (d, $J=8$ Hz, 2H, Ar-H), 7.84 (d, $J=8$ Hz, 2H, Ar-H), 7.78 (d, $J=8.5$ Hz, 2H, Ar-H), 7.47 (s, 1H, Ar-H(Pyridine)), 7.01 (d, $J=8.5$ Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H(Pyridine)), 4.19 (s, 3H, -OMe of Pyridine), 4.07 (t, $J=6.7$ Hz, 2H, -OCH₂-), 1.87-1.81 (m, 2H, -OCH₂CH₂-), 1.57-1.36 (m, 6H, -CH₂-), 0.93 (t, $J=7$ Hz, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.49, 160.32, 155.58, 149.88, 143.53, 132.73, 129.19, 128.93, 127.82, 118.52, 114.88, 112.05, 110.48, 106.31, 68.29, 54.64, 31.90, 29.61, 26.03, 22.67, 14.09. MS (m/z): 387.2 (M+H)⁺. Anal. Calcd. For. C₂₅H₂₆N₂O₂: C. 77.69; H. 6.78; N. 7.25; Found: C. 77.99; H. 6.72; N. 7.22.

4-(2-Methoxy-6-(4-(octyloxy)phenyl)pyridin-4-yl)benzotrile (4c). Yield 62%. FTIR (cm⁻¹): 2916, 2852, 2220, 1578, 1237, 1171, 1013, 827. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.05 (d, $J=8$ Hz, 2H, Ar-H), 7.84 (d, $J=8$ Hz, 2H, Ar-H), 7.78 (d, $J=8$ Hz, 2H, Ar-H), 7.46 (s, 1H, Ar-H(Pyridine)), 7.01 (d, $J=8$ Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H(Pyridine)), 4.10 (s, 3H, -OMe of Pyridine), 4.06 (t, $J=7$ Hz, 2H, -OCH₂-), 1.86-1.81 (m, 2H, -OCH₂CH₂-), 1.59-1.27 (m, 10H, -CH₂-), 0.91 (t, $J=6.5$ Hz, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.50, 160.34, 155.62, 149.91, 143.55, 132.78, 129.23, 128.97, 127.82, 118.55, 114.93, 112.07, 110.50, 106.33, 68.18, 54.70, 31.94, 29.68, 29.41, 29.38, 26.07, 22.71, 14.13. MS (m/z): 415.2 (M+H)⁺. Anal. Calcd. For. C₂₇H₃₀N₂O₂: C. 78.23; H. 7.29; N. 6.76; Found: C. 78.47; H. 7.33; N. 6.79.

4-(2-(4-(Decyloxy)phenyl)-6-methoxypyridin-4-yl)benzotrile (4d). Yield 74 %. FTIR (cm⁻¹): 2915, 2852, 2221, 1580, 1240, 1171, 1020, 827. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.05 (d, $J=8$ Hz, 2H, Ar-H), 7.84 (d, $J=8$ Hz, 2H, Ar-H), 7.78 (d, $J=8$ Hz, 2H, Ar-H), 7.46 (s, 1H, Ar-H(Pyridine)), 7.01 (d, $J=8$ Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H(Pyridine)), 4.19 (s, 3H, -OMe of Pyridine), 4.06 (t, $J=6.5$ Hz, 2H, -OCH₂-), 1.86-1.81 (m, 2H, -OCH₂CH₂-), 1.63-1.30 (m, 14H, -

CH₂-), 0.91 (t, $J=6.5$ Hz, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.49, 160.31, 155.59, 149.90, 143.54, 132.70, 129.19, 128.94, 127.82, 118.53, 114.89, 112.05, 110.51, 106.31, 68.28, 54.67, 31.89, 29.56, 29.40, 29.31, 29.26, 29.17, 26.04, 22.67, 14.09. MS (m/z): 443.2 (M+H)⁺. Anal. Calcd. For. C₂₉H₃₄N₂O₂: C. 78.70; H. 7.74; N. 6.33; Found: C. 78.95; H. 7.67; N. 6.36.

4-(2-(4-(Dodecyloxy)phenyl)-6-methoxypyridin-4-yl)benzotrile (4e). Yield 77 %. FTIR (cm⁻¹): 2915, 2849, 2221, 1581, 1240, 1171, 1020, 827. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.06 (d, $J=8$ Hz, 2H, Ar-H), 7.80-7.75 (m, 4H, Ar-H), 7.46 (s, 1H, Ar-H (Pyridine)), 7.01 (d, $J=8$ Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H (Pyridine)), 4.10 (s, 3H, -OMe of Pyridine), 4.07 (t, $J=6.7$ Hz, 2H, -OCH₂-), 1.86-1.81 (m, 2H, -OCH₂CH₂-), 1.59-1.28 (m, 18H, -CH₂-), 0.91 (t, $J=7.5$ Hz, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.48, 160.30, 155.57, 149.88, 143.52, 132.73, 129.17, 128.93, 127.80, 118.52, 114.87, 112.03, 110.48, 106.31, 68.29, 54.66, 31.91, 29.63, 29.58, 29.40, 29.34, 29.25, 26.03, 22.67, 14.09. MS (m/z): 471.3 (M+H)⁺. Anal. Calcd. For. C₃₁H₃₈N₂O₂: C. 79.11; H. 8.14; N. 5.95; Found: C. 79.33; H. 8.17; N. 5.92.

4-(2-Methoxy-6-(4-(tetradecyloxy)phenyl)pyridin-4-yl)benzotrile (4f). Yield 69 %. FTIR (cm⁻¹): 2915, 2848, 2223, 1602, 1241, 1171, 1023, 829. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.05 (d, $J=8.5$ Hz, 2H, Ar-H), 7.80-7.75 (m, 4H, Ar-H), 7.46 (s, 1H, Ar-H (Pyridine)), 7.01 (d, $J=8.5$ Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H (Pyridine)), 4.10 (s, 3H, -OMe of Pyridine), 4.06 (t, $J=7.2$ Hz, 2H, -OCH₂-), 1.85-1.82 (m, 2H, -OCH₂CH₂-), 1.51-1.28 (m, 22H, -CH₂-), 0.90 (t, $J=7.5$ Hz, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.52, 160.34, 155.61, 149.91, 143.56, 132.77, 129.21, 128.97, 127.84, 118.55, 114.91, 112.07, 110.52, 106.33, 68.19, 54.70, 31.95, 29.69, 29.62, 29.43, 29.38, 29.29, 29.20, 26.07, 22.71, 14.13. MS (m/z): 499.3 (M+H)⁺. Anal. Calcd. For. C₃₃H₄₂N₂O₂: C. 79.48; H. 8.49; N. 5.62; Found: C. 79.72; H. 8.53; N. 5.55.

3. Single crystal X-ray crystallography studies

Compounds **4a** and **4c** was recrystallized from their saturated solution in chloroform and methanol (1:1) by the slow evaporation of solvent mixture at room temperature. The single crystal X-ray data was collected using MoK α ($\lambda = 0.7107$ Å) radiation on a BRUKER APEX II diffractometer equipped with a CCD area detector. Data reduction was performed using SAINTPLUS. Scaling, absorption correction was done using SADABS, all embedded in the

Apex2 software suite.³ The crystal structure was solved by direct methods using XS and the structure refinement was done using XL in the SHELXTL package.⁴ The position and thermal parameters of all the non-hydrogen atoms were refined. The hydrogen's were fixed in geometrically calculated positions and refined isotropically. The ORTEP diagrams and packing diagrams were created using Mercury 3.0 and POV ray.⁵ Summary of the crystallographic data and structural refinement details of compounds **4a** and **4c** are given in Table 1.

4. DSC profile of **4a**

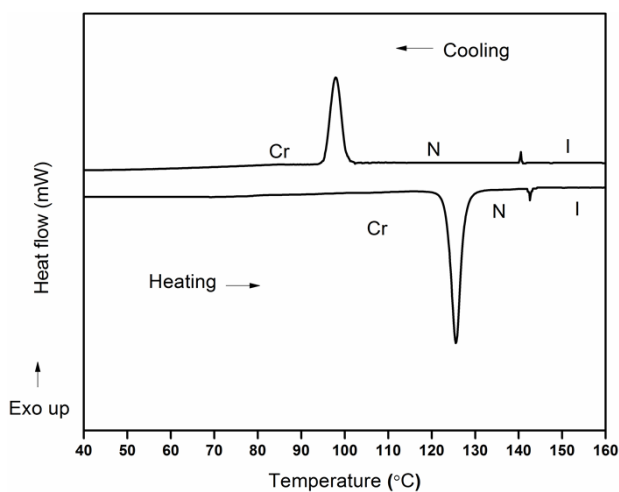


Figure S1. DSC trace of **4a**

5. Powder X-ray diffraction studies

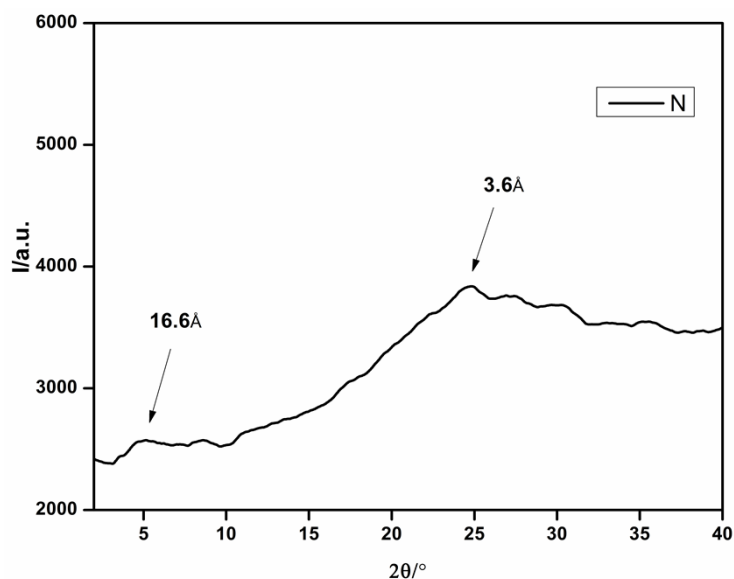


Figure S2 Powder X-ray diffraction pattern of **4a** at 132 °C.

Table S1. Space group, unit cell dimensions, measured and calculated spacings, and Miller indices data for Compound **4e**

Space group: P222

a: 43.43 Å, b: 14.47 Å, c: 4.49 Å and cell Volume: 2824 Å³

No.	d _{meas} [Å]	d _{calc} [Å]	(hkl)
1	21.96	21.58	2 0 0
2	12.11	12.10	2 1 1
3	10.28	10.25	3 1 0
4	7.48	7.43	5 1 0
5	7.26	7.30	0 2 0
6	6.49	6.51	3 2 0
7	6.04	6.05	4 2 0
8	5.13	5.13	6 2 0
9	4.72	4.71	7 2 0
10	4.50	4.48	0 0 1
11	4.35	4.34	8 2 0
12	4.23	4.24	5 3 0
13	4.09	4.10	3 1 1
14	3.93	3.93	11 0 0
15	3.78	3.79	11 1 0
16	3.68	3.68	6 1 1
17	3.42	3.42	9 3 0
18	3.22	3.21	3 3 1

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