Electronic Supplementary Information. Additional table T1 and figures S1, S2, S3A, S3B, S3C and S4 are presented here. X-ray crystallographic information files (CIFs) are also available for the two polymorphic forms of the compound under study. This information is available free of charge via the Internet at http://pubs.rsc.org.

Table T1. Main Crystallographic Data for Low-Temperature SCXRD of Polymorph II.

		LT-Polymorph II
Crystal data	Empirical formula	$C_{14}H_{12}N_2O_4$
	Fw	272.26
	Crystal system	Orthorhombic
	Space group	Pbca (No. 61)
	a, b, c (Å)	12.4915(15) 7.5972(14) 26.1737(18)
	α, β, γ (°)	90 90 90
	V (Å^3)	2483.9(6)
	Z	8
	ρ_{calcd} (g/cm^3)	1.456
	Mu (MoKα) (/mm)	0.109
	F(000)	1136
	Crystal size (mm)	0.40 / 0.35 / 0.20
	T (K)	105
Collection data	Radiation (Å)	Mo Kα : 0.71073
	θ min. & max. (°)	3.2 – 29.3
	Tot., Uniq., R(int)	9181, 3027, 0.026
	Obs. data	2561
Refinement	R[I > 2σ(I)]	0.0419
	wR2[all]	0.1043
	GoF	1.09
	Residual density	-0.21, 0.27

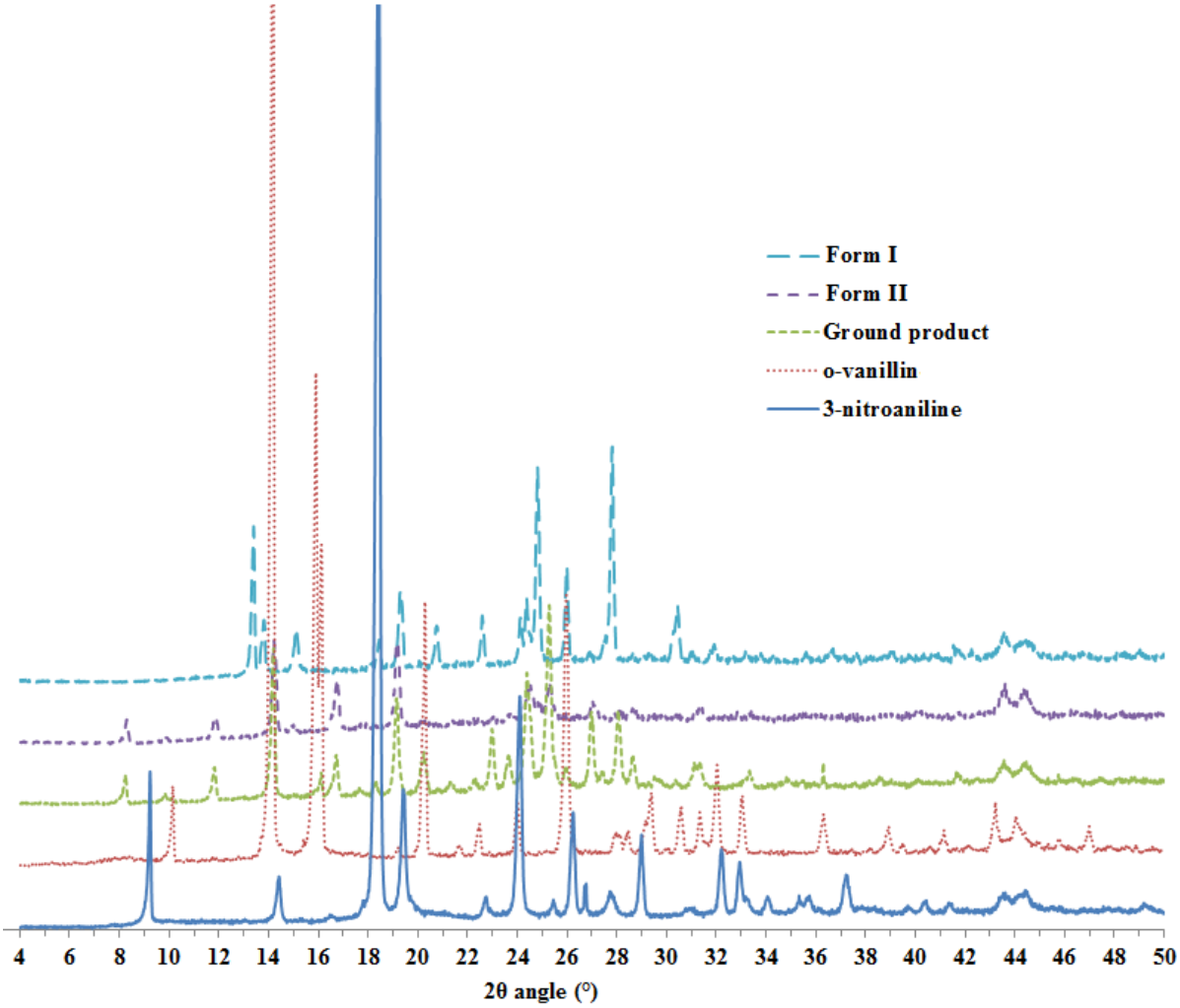

Figure S1. PXRD patterns of 3-nitroaniline (blue, on the bottom), o-vanillin (red) and dry-ground samples (green) are compared with experimental patterns for Form I and II, showing that form produced by dry-grinding is Form I.

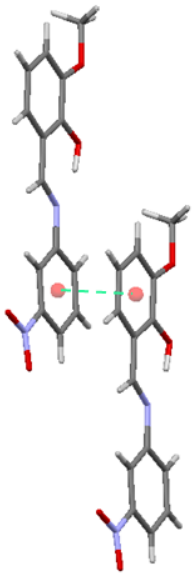

Figure S2. Highlighted π-π stacking interactions in Form I.

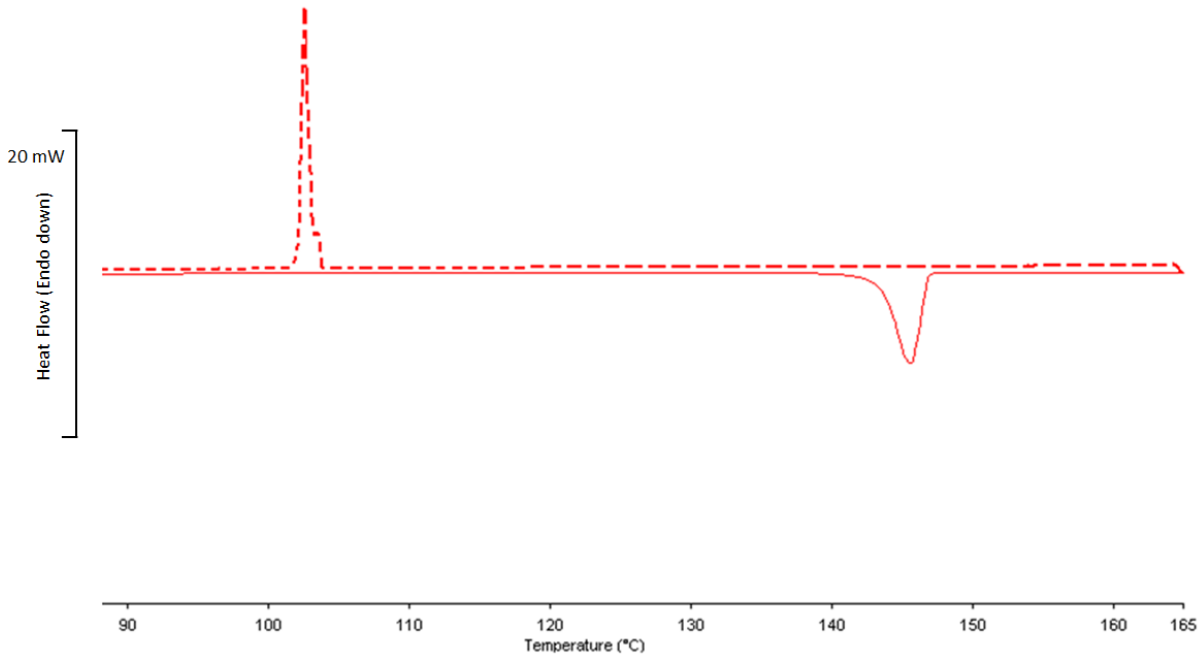

Figure S3A. DSC heating/cooling (dotted line) cycle for Form I (5°C/min, T_m: 143.5°C, T_{cryst}: 109.8 °C)

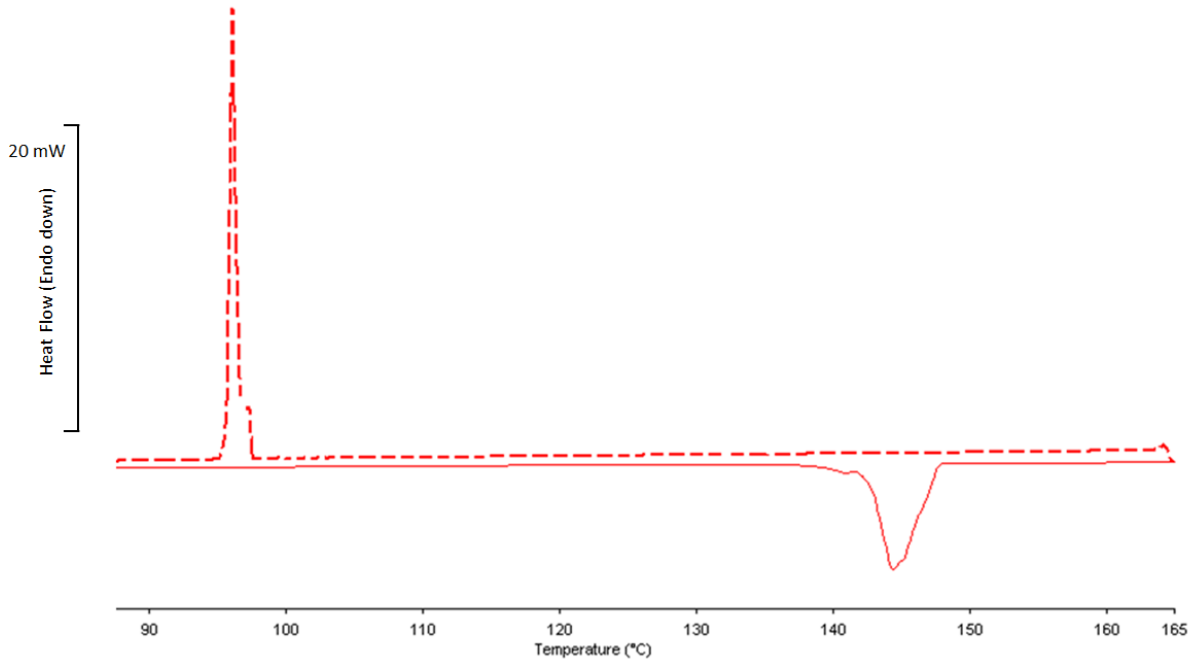

Figure S3B. DSC heating/cooling (dotted line) cycle for Form II (5°C/min, T_m: 144.5°C, T_{cryst}: 109.2°C)

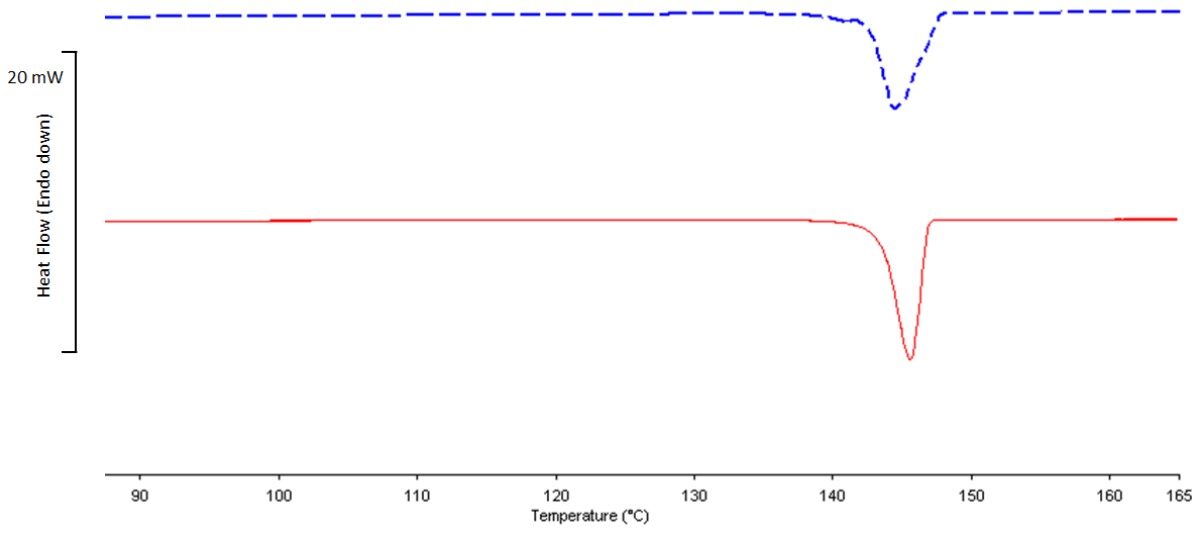

Figure S3C. Superposition of second heating step for form II (blue dotted line, (5°C/min, T_m: 144.1°C) and melting point of Form I.

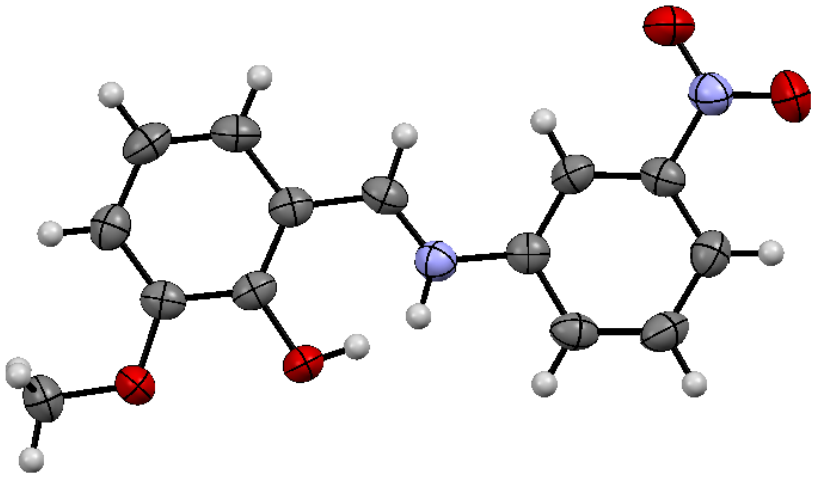

Figure S4. ORTEP diagram (50% probability ellipsoids) for compound (**1**) at low-temperature in crystals belonging to polymorph I. An average structure has been refined with highlighting of a weak residual density peak on nitrogen atom.