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Electronic Supplementary Information

Concomitant Polymorphism in Oxime-Bridged Pyrazole–Tetrazole Energetic Materials

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1. General Experimental

All reagents (analytical grade) were purchased from AK Scientific or VWR and were used as supplied. ^{1}H, and ^{13}C spectra were recorded using a 500 MHz (Bruker Advance) NMR spectrometer operating at 500.19, and 125.78 respectively. Chemical shifts in the ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si as internal standard. The decomposition temperatures (onset) were obtained on a differential scanning calorimeter (TA Instruments Company, Q2000) at a scan rate of 5 °C min^{-1}. Infra-red spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The room temperature densities were measured at 25 °C by employing a gas pycnometer (Micromeritics AccuPyc II 1340). The impact and friction sensitivities were determined by using a standard BAM drop hammer and BAM friction tester. Elemental analyses were carried out on a Vario Micro cube Elemental Analyzer.

Suitable single crystals of **3-α** and **3-β** were obtained for SC-XRD analysis from mixed solvent systems. Yellow plate-shaped crystals of 3-α were grown from a EtOH-H_2O mixture, and crystals of **3-β** were obtained from a MeOH-H_2O system. Crystals of **3-α** (0.12 × 0.09 × 0.01 mm^3) and **3-β** (0.13 × 0.08 × 0.02 mm^3) were selected and mounted on nylon loops with Paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystals were kept at a constant **T = 100 K** during data collection. The structures were solved with the ShelXT[S1] solution program using dual methods and by using Olex2.[S2] The models were refined with ShelXL[S3] using full matrix least squares minimization on **F²**. The packing coefficient was calculated using PLATON version 90622.

Crystallographic data (including the structure factor files) for **3-α** and **3-β** in this paper were deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers **CCDC 2511981** and **CCDC 2511983**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

2. Experimental Section

Caution. All the compounds prepared are energetic materials and sensitive towards external stimuli. Mechanical actions involving scratching or scraping must be avoided. While we have not encountered any issues in the handling of these compounds, proper protective measures (face shield, eye protection, apron and leather gloves) should be taken at all times. In addition, all of the energetic compounds must be prepared only on a small scale and handled using a plastic spatula.

Synthesis of compound 1: (E)-N-hydroxy-3,4-dinitro-1*H*-pyrazole-5- carbimidoyl chloride (**1**) was prepared according to the literature procedure.[S4]

Synthesis of compound 2. In an oven-dried 100 mL round-bottom flask, sodium cyanide (0.52 g, 10.6 mmol) was dissolved in water (20 mL) and cooled to 0 °C. A solution of compound **1** (1 g, 4.2 mmol) in ethyl acetate (10 mL) was then added dropwise to the cold aqueous NaCN solution. The reaction mixture was stirred overnight, after which it was acidified to pH ≈ 3 with 20% H_2SO_4. The product was extracted with ethyl acetate (20 mL), and the combined organic layers were dried over sodium sulfate. Removal of the solvent under a gentle air stream gave compound 2 as a yellow solid.

Safety Precautions and Neutralization of Sodium Cyanide

Caution: Sodium cyanide (NaCN) is highly toxic and must be handled with extreme care. All operations involving NaCN were carried out in a well-ventilated fume hood with the sash lowered. Appropriate personal protective equipment was worn at all times, including a lab coat, safety goggles, and double nitrile gloves.

After completion of the reaction, residual cyanide in the aqueous phase was oxidatively neutralized under basic conditions prior to acidification. An aqueous sodium hypochlorite solution was added slowly with stirring to the basic reaction mixture until complete oxidation of cyanide to non-volatile cyanate was ensured. Acidification was performed only after this neutralization step to prevent the formation of hydrogen cyanide gas.

All cyanide-containing waste was collected and disposed of in accordance with institutional hazardous waste disposal protocols. In the event of spills, solid cyanide was immediately covered with an alkaline hypochlorite solution prior to cleanup.

2: Yellow solid; Yield: 77%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 14.89 (br, 1H), 13.44 (br, 1H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 147.7, 133.1, 124.5, 121.3, 107.8 ppm. FTIR (cm^{-1}) ῦ 3202, 3112, 2952, 2249, 1578, 1560, 1537, 1502, 1455, 1413, 1373, 1330, 1215, 1113, 1062, 958, 848, 815. Elemental analysis: Calcd (%) for $C_5H_2N_6O_5$ (226.01): C, 26.56; H, 0.89; N, 37.17; Found: C 27.09, H 1.01, N 37.33.

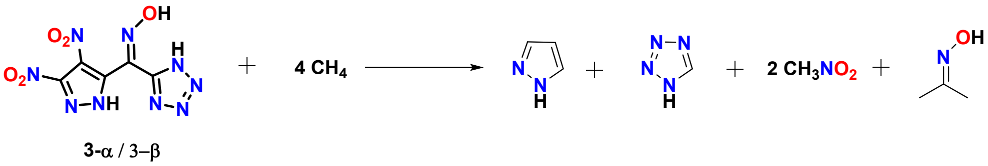
Synthesis of 3-α and 3-β. An oven-dried 100 mL round-bottomed flask was charged with compound **2** (0.45 g, 2 mmol), sodium azide (0.26 g, 4 mmol), zinc chloride (0.545 g, 4 mmol), and distilled water (10 mL). The reaction mixture was heated to reflux and stirred overnight. After completion, the mixture was cooled to room temperature, acidified with 2 N HCl, and stirred for an additional 20 minutes. The precipitated solid corresponding to **3-α** was collected by filtration and washed with cold water to give a yellow powder. The filtrate was then extracted with ethyl acetate (2 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate. Evaporation of the solvent under a gentle stream of air afforded **3-β** as a pale yellow solid, which was further dried in an oven. The combined yield of the two polymorphs was 69%, with a **3-α : 3-β** ratio of 57:43.

3-α: Pale-yellow solid; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 14.45 (br), 13.88 (br) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 148.0, 144.8, 135.4, 131.8, 125.6 ppm. FTIR (cm^{-1}) ṽ 3475, 3044, 1550, 1505, 1414, 1380, 1338, 1263, 1231, 1197, 1181, 1112, 1073, 1049, 1027, 916, 851, 814. Elemental analysis: Calcd (%) for $C_5H_3N_9O_5$ (269.03): C, 22.31; H, 1.12; N, 46.84; Found: C 22.51, H 1.41, N 47.08.

3-β: Pale-yellow solid; Yield: 75%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 13.94 (br), 13.55 (br) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 147.9, 144.7, 135.3, 131.6, 125.5 ppm. FTIR (cm^{-1}) ṽ 3554, 3062, 2145, 1557, 1522, 1490, 1410, 1258, 1336, 1206, 1182, 1116, 1059, 1005, 921, 822. Elemental analysis: Calcd (%) for $C_5H_3N_9O_5$ (269.03): C, 22.31; H, 1.12; N, 46.84; Found: C 22.57, H 1.50, N 47.11.

3. Theoretical Study and Isodesmic reactions

The heat of formation (HOF) for all compounds were calculated by using isodesmic reactions. The single crystal structures were used for the geometric optimization and frequency analyses using the B3LYP functional with the 6-31+G** basis set. The single-point energies were obtained at the MP2/6-311++G** level.[S5] The atomization energies for cations were calculated by using the G^{2}ab *initio* method.[S6] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme S1: Isodesmic Reactions.

Table S1: Calculated zero-point energy (ZPE), values of the correction (H_{Corr}), total energy (E_o) and the gas-state heat of formation.

Compound	ZPE	H_{Corr}	E_0	HOF_{gas} (kJ/mol)
3-α	0.129847	0.146182	-1058.50046	690.3
3-β	0.129567	0.146116	-1058.495705	710.3

4. X-Ray Crystallographic Data

Table S2. Crystal data and structure refinement for compounds **3-α and 3-β**.

Compound	**3-α**	**Compound**	**3-β**
CCDC	2511981	CCDC	2511983
Formula	$C_7H_{11}N_9O_7$	Formula	$C_5H_5N_9O_6$
$D_{calc.}$/ g cm^{-3}	1.656	$D_{calc.}$/ g cm^{-3}	1.687
m/mm^{-1}	1.293	*m*/mm^{-1}	1.357
Formula Weight	333.25	Formula Weight	287.18
Colour	yellow	Colour	yellow
Shape	plate-shaped	Shape	plate-shaped
Size/mm	0.12×0.09×0.01	Size/mm^3	0.13×0.08×0.02
T/K	100.00(10)	*T*/K	99.97(13)
Crystal System	triclinic	Crystal System	orthorhombic
Space Group	*P*-1	Flack Parameter	0.01(19)
a/Å	5.0699(3)	Hooft Parameter	0.07(17)
b/Å	8.4323(4)	Space Group	*Aea*2
c/Å	16.2474(6)	*a*/Å	10.1090(4)
a/°	82.100(4)	*b*/Å	22.5053(11)
b/°	84.341(4)	*c*/Å	9.9376(4)
g/°	76.871(4)	*a*/°	90
V/Å^3	668.38(6)	*b*/°	90
Z	2	*g*/°	90
Z'	1	V/Å^3	2260.87(16)
Wavelength/Å	1.54184	*Z*	8
Radiation type	Cu K_a	*Z'*	1
Q_{min}/°	2.752	Wavelength/Å	1.54184
Q_{max}/°	80.507	Radiation type	Cu K_a
Index range h	-6 ≥ h ≥ 6	Q_{min}/°	3.928
Index range k	-10 ≥ k ≥ 10	Q_{max}/°	79.865
Index range l	-19 ≥ l ≥ 20	Measured Refl's.	7766
Measured Refl's.	7636	Indep't Refl's	2223
Indep't Refl's	2784	Refl's I≥2 *s*(I)	2081
Refl's I≥2*s*(I)	2337	R_{int}	0.0453
R_{int}	0.0455	Parameters	201
Parameters	252	Restraints	1
Restraints	0	Largest Peak	0.361
Largest Peak/eÅ^3	0.508	Deepest Hole	-0.283
Deepest Hole/eÅ^3	-0.258	GooF	1.061
GooF	1.078	wR_2 (all data)	0.1097
R_1 (I≥2*s*(I) / all)	0.0609 / 0.0728	wR_2	0.1077
wR_2 (I≥2*s*(I) / all)	0.1519 / 0.1599	R_1 (all data)	0.0458
		R_1	0.0426

Table S3: Torsion Angles in ° for **3-α**.

Atom	Atom	Atom	Atom	Angle/°
O1	N1	C1	C2	-178.73(19)
O1	N1	C1	C5	-0.4(3)
O2	N8	C3	C2	-83.6(3)
O2	N8	C3	C4	93.1(3)

Table S4: Hydrogen Bond information for **3-α**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	O6^1	0.97(4)	1.63(4)	2.596(3)	175(3)
N2	H2	N6^2	0.89(3)	2.14(3)	2.926(3)	148(3)
N2	H2	N7	0.89(3)	2.17(3)	2.691(3)	117(3)
N4	H4	O7^3	0.88(5)	1.84(5)	2.647(3)	152(4)
O6	H6	O2	0.87(5)	2.11(5)	2.895(3)	150(4)
O7	H7D	N5^4	0.81(4)	2.21(4)	3.024(3)	174(3)
O7	H7E	O5^1	0.84(5)	2.22(5)	2.941(3)	144(4)
O7	H7E	N3^1	0.84(5)	2.32(5)	3.039(3)	144(4)

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^{1}1+x,+y,+z; ^{2}-1-x,-y,1-z; ^{3}+x,1+y,+z; ^{4}-x,-y,1-z

Table S5: Torsion Angles in ° for **3-β**.

Atom	Atom	Atom	Atom	Angle/°
C1	C2	N2	N3	179.7(3)
C1	C2	C3	C4	-179.9(4)
C1	C2	C3	N5	4.6(6)
C1	C5	N6	N7	-177.2(3)
C1	C5	N9	N8	177.0(3)
N1	C1	C2	N2	-53.8(5)
N1	C1	C2	C3	125.3(4)
N1	C1	C5	N6	-15.6(5)
N1	C1	C5	N9	167.4(3)
C2	C1	N1	O1	0.1(5)
C2	C1	C5	N6	161.7(3)
C2	C1	C5	N9	-15.3(5)
C2	N2	N3	C4	0.1(4)
C2	C3	C4	N3	0.8(4)
C2	C3	C4	N4	174.4(3)
C2	C3	N5	O4	153.1(4)
C2	C3	N5	O5	-25.7(5)
N2	C2	C3	C4	-0.6(4)
N2	C2	C3	N5	-176.1(3)
N2	N3	C4	C3	-0.6(4)
N2	N3	C4	N4	-175.0(3)
C3	C2	N2	N3	0.3(4)
C3	C4	N4	O2	150.6(4)
C3	C4	N4	O3	-30.8(5)
N3	C4	N4	O2	-36.0(4)
N3	C4	N4	O3	142.5(3)
C4	C3	N5	O4	-21.2(5)
C4	C3	N5	O5	160.0(4)
C5	C1	N1	O1	177.3(3)
C5	C1	C2	N2	129.1(4)
C5	C1	C2	C3	-51.7(5)
C5	N6	N7	N8	0.0(4)

Atom	Atom	Atom	Atom	Angle/˚
N5	C3	C4	N3	176.0(3)
N5	C3	C4	N4	-10.4(6)
N6	C5	N9	N8	-0.3(4)
N6	N7	N8	N9	-0.3(4)
N7	N8	N9	C5	0.4(4)
N9	C5	N6	N7	0.2(4)

Table S6: Hydrogen Bond information for **3-β**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	O1W[1]	0.91(7)	1.78(7)	2.685(4)	172(5)
N2	H2	O1W	1.01(5)	1.72(5)	2.725(4)	172(4)
N6	H6	N9[2]	0.80(8)	2.11(8)	2.899(4)	167(6)
O1W	H1WA	N8[3]	0.88(6)	2.01(6)	2.860(4)	163(6)
O1W	H1WB	O2[4]	0.74(7)	2.20(7)	2.938(4)	175(6)

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[1] 1/2-x,+y,1/2+z; [2] 1-x,1/2-y,1/2+z; [3] -1/2+x,1/2-y,+z; [4] -1/2+x,1-y,1/2+z

5. NMR spectra (^{1}H, and ^{13}C), IR spectra, and DSC of compounds

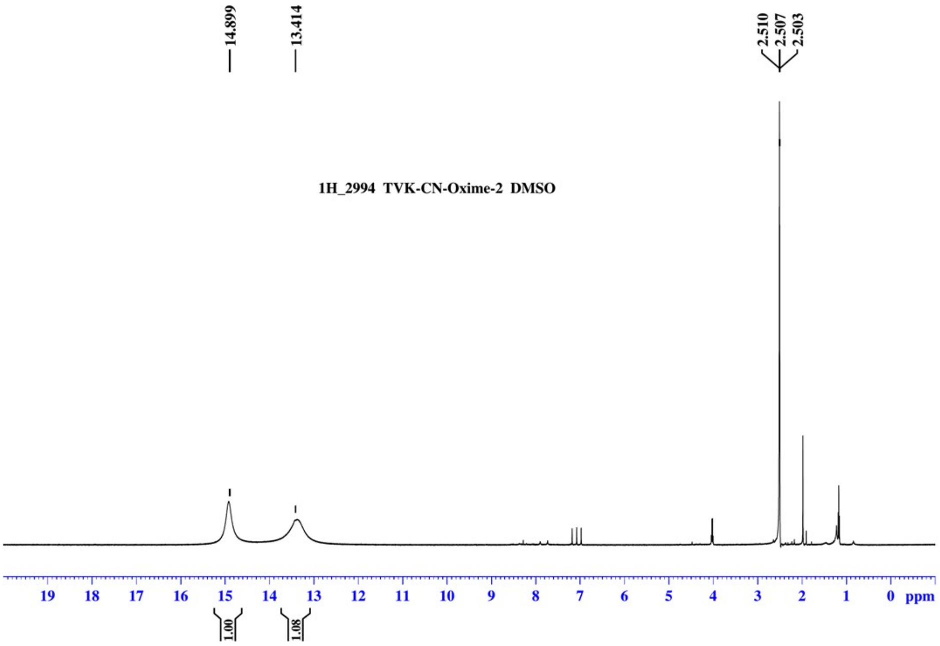

Figure S1: ^{1}H NMR spectrum of **2** in dimethyl sulfoxide-d_6.

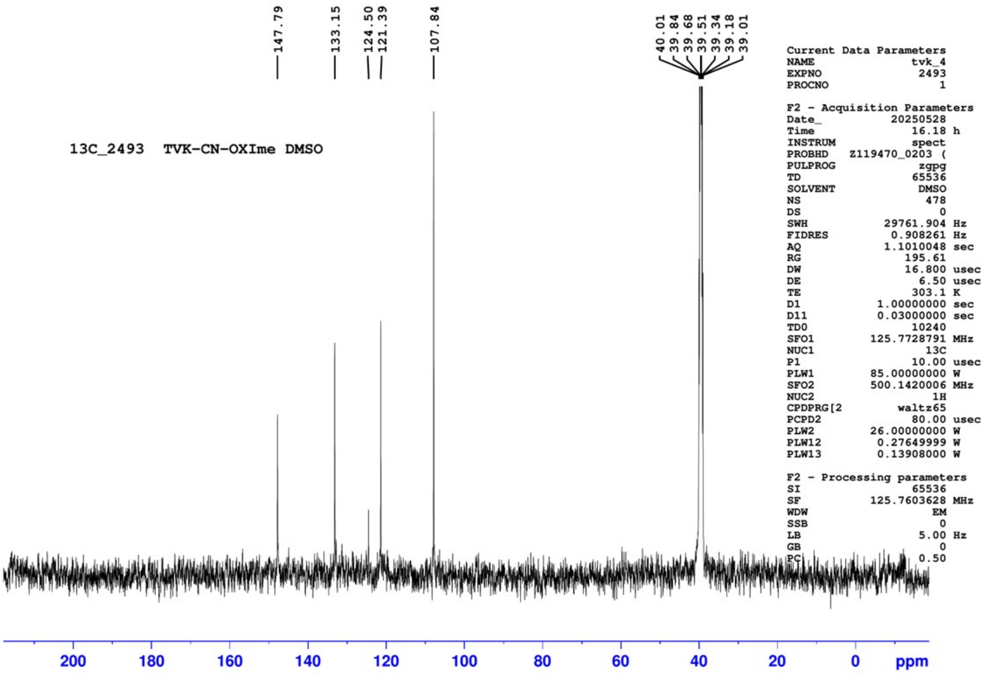

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Figure S2: ^{13}C NMR spectrum of **2** in dimethyl sulfoxide-d_6.

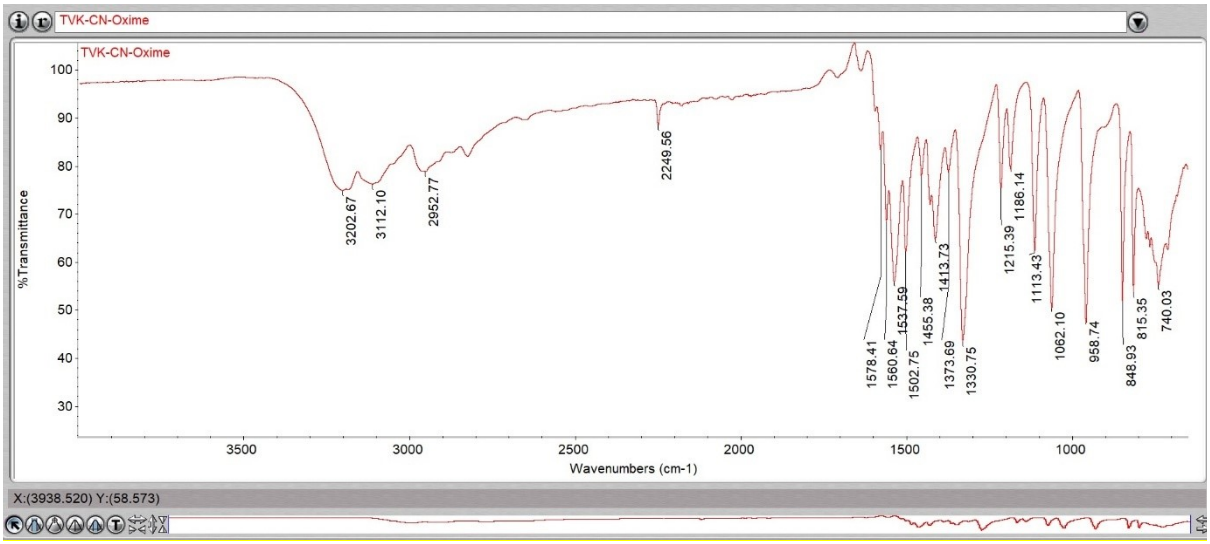
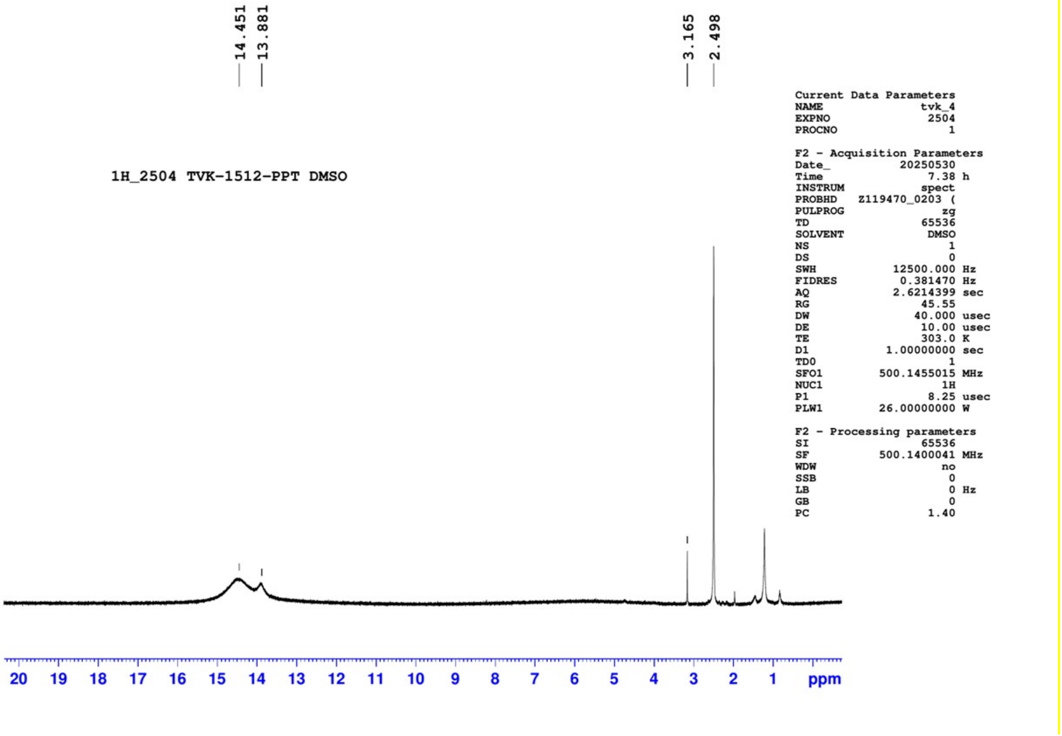


Figure S3: IR spectrum of **2**.



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NUC1                   1H
P1                   8.25 usec
PLW1          26.00000000 W

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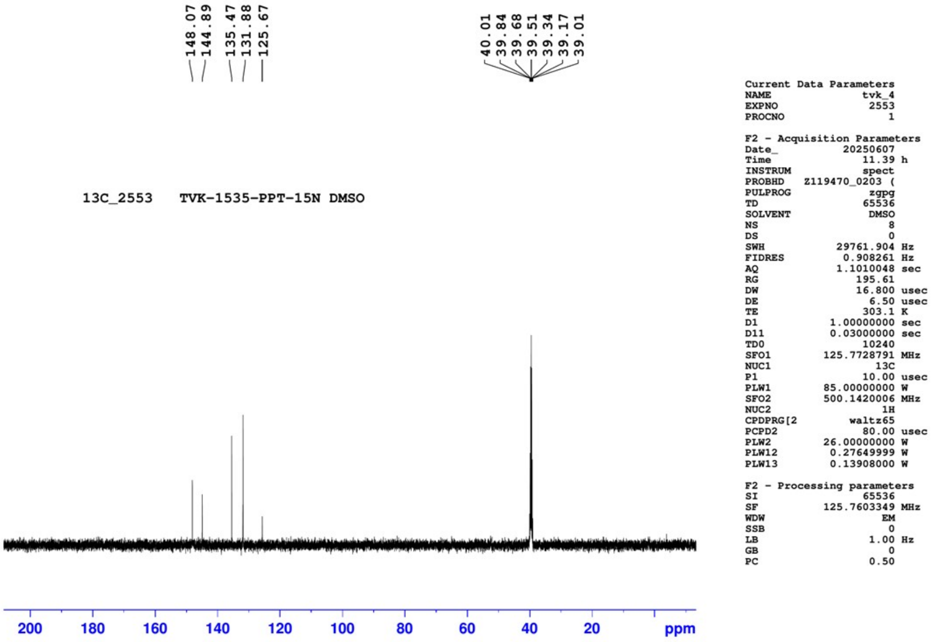
Figure S4: ^{1}H NMR spectrum of **3-α** in dimethyl sulfoxide-*d*$_6$.



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RG                  195.61
DW                  16.800 usec
DE                    6.50 usec
TE                   303.1 K
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P1                   10.00 usec
PLW1           85.00000000 W
SFO2           500.1420006 MHz
NUC2                    1H
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PLW12           0.27649999 W
PLW13           0.13908000 W

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Figure S5: ^{13}C NMR spectrum of **3-α** in dimethyl sulfoxide-d_6.

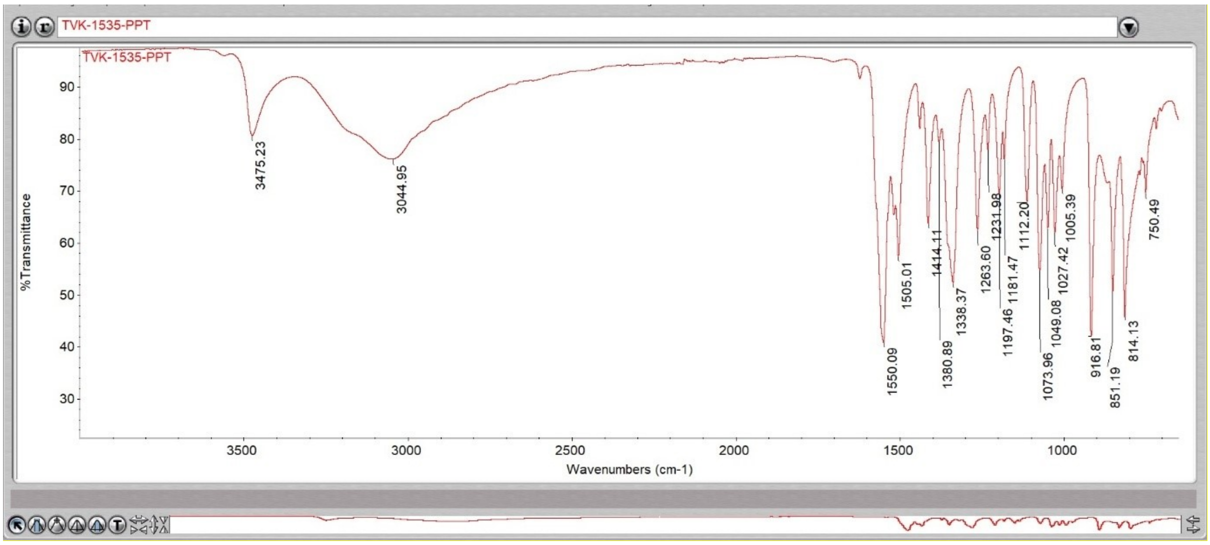

Figure S6: IR spectrum of **3-α**.

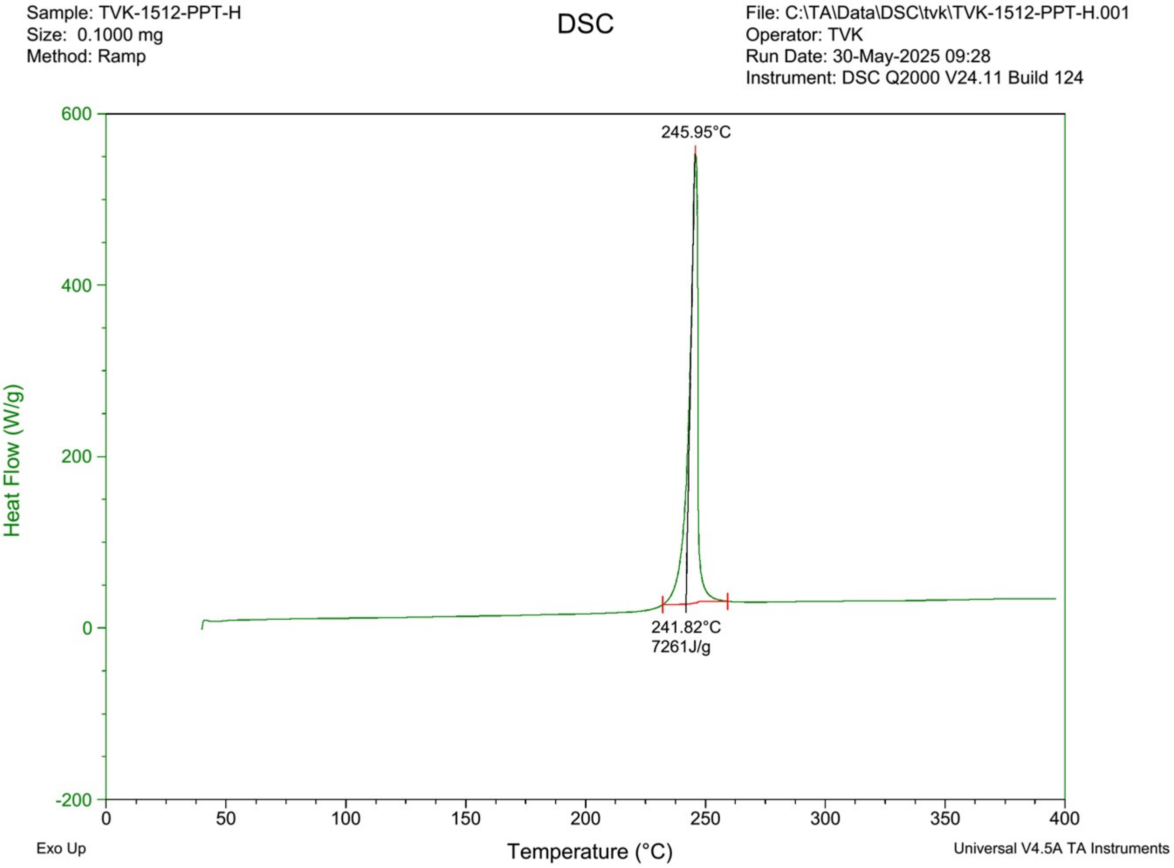

Figure S7: Thermal behavior of **3-α** at 5 °C/min.

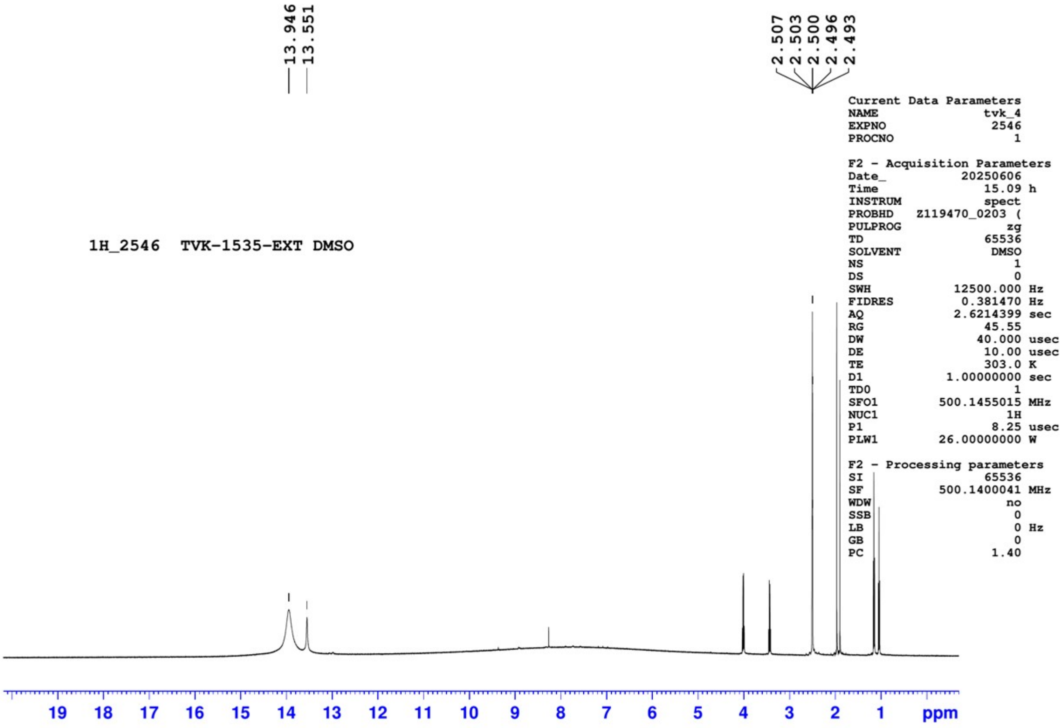

Figure S8: ^{1}H NMR spectrum of **3-β** in dimethyl sulfoxide-d_6.

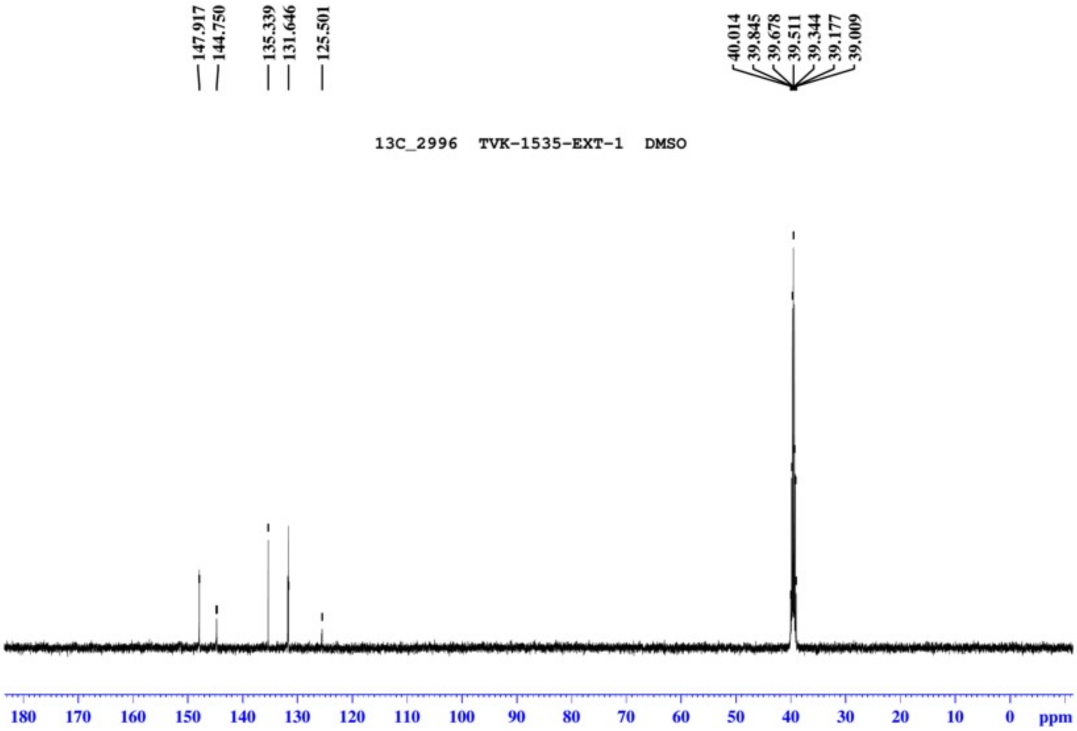

Figure S9: ^{13}C NMR spectrum of **3-β** in dimethyl sulfoxide-d_6.

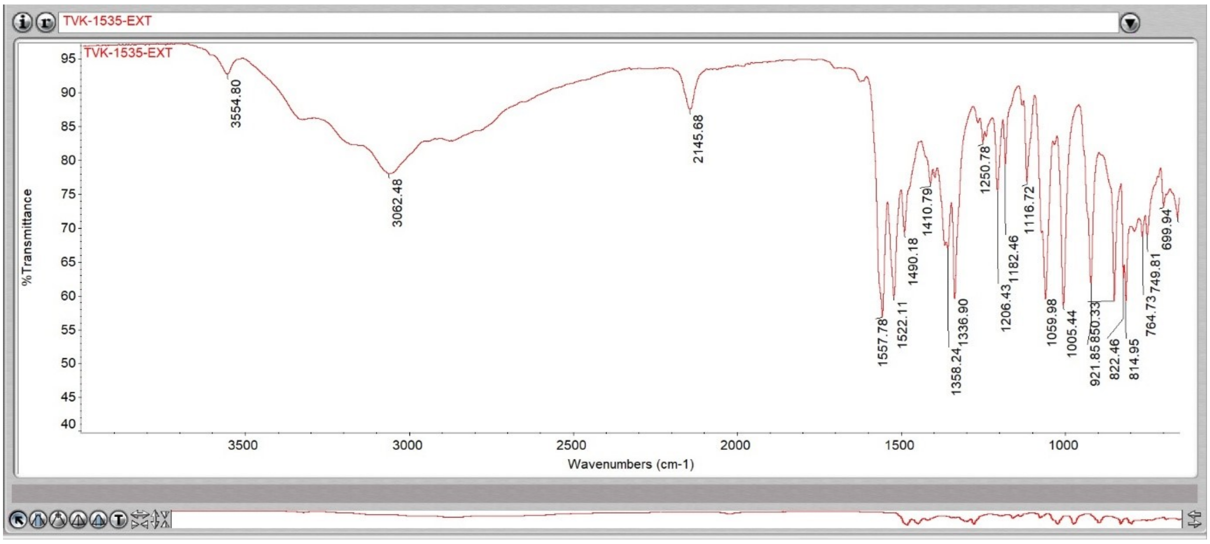

Figure S10: IR spectrum of **3-β**.

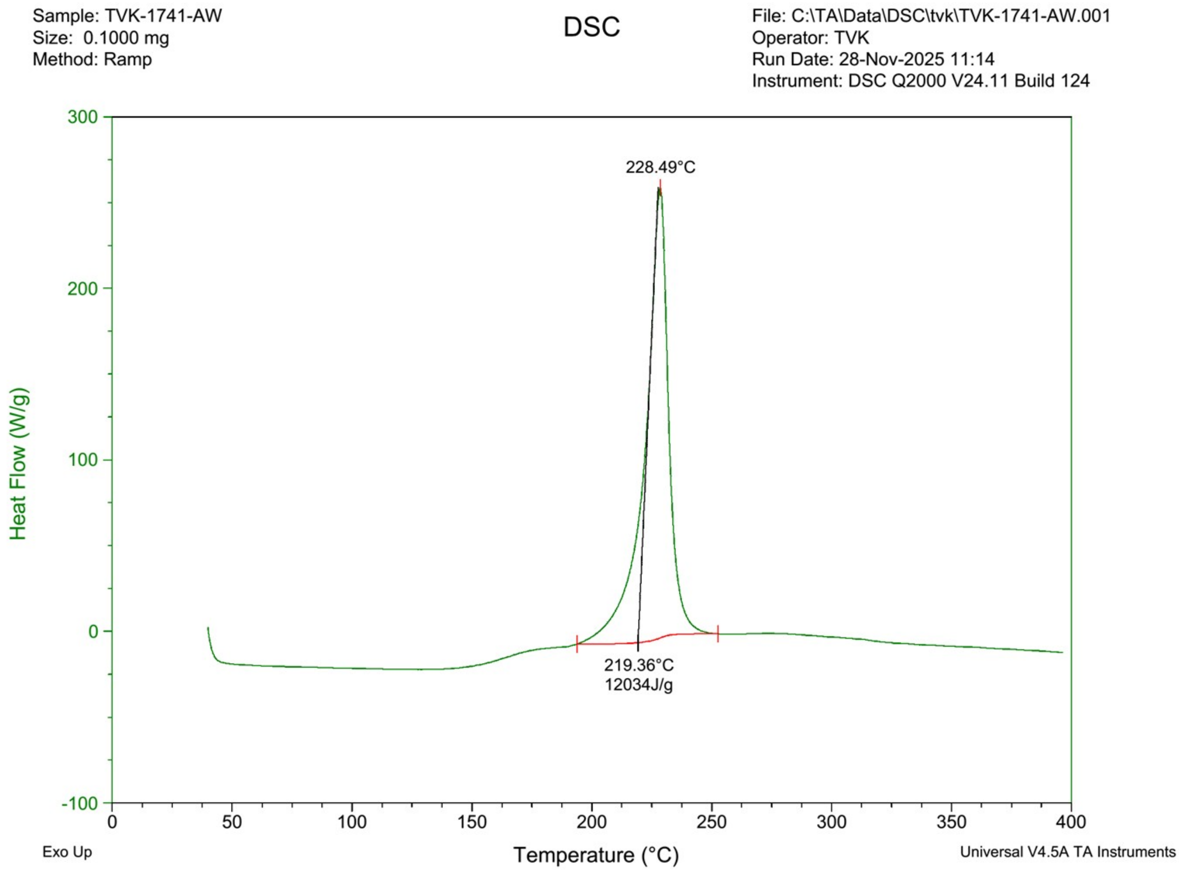

Figure S11: Thermal behavior of **3-β** at 5 ^{o}C/min.

6. References

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S2. G. M. Sheldrick, Acta Crystallogr., Sect. A Found. Adv., 2015, 71, 3.
S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
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