Electronic Supplementary Material for CrystEngComm

Co-crystallization experiments of thiocarbamides with bipyridine-type molecules†

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*** Electronic Supplementary Information ***

Table S(1). Selected bond distances (Å) for ROC(=S)N(H)R' in their pure crystalline form and in co-crystals (**1**) – (**5**).

Compound	C1=S1	C1–N1	C1–O1
MeOC(=S)N(H)Ph [1]	1.671(1)	1.329(2)	1.329(1)
MeOC(=S)N(H)Ph in (**1**)	1.6747(17)	1.336(2)	1.3345(19)
MeOC(=S)N(H)PhNO$_2$-4 [2]	1.664(2)	1.345(2)	1.322(2)
MeOC(=S)N(H)PhNO$_2$-4 in (**2**)	1.661(4)	1.363(5)	1.329(4)
EtOC(=S)N(H)Ph [3,a]	1.636(5)	1.327(7)	1.301(7)
	1.651(5)	1.324(7)	1.296(6)
	1.650(5)	1.319(7)	1.311(7)
EtOC(=S)N(H)Ph in (**3**)	1.6672(16)	1.3309(18)	1.343(2)
EtOC(=S)N(H)PhNO$_2$-4 [4]	1.672(2)	1.354(3)	1.321(3)
EtOC(=S)N(H)PhNO$_2$-4 in (**4**)	1.659(5)	1.369(6)	1.328(5)
iPrOC(=S)N(H)Ph [5]	1.6748(16)	1.334(2)	1.3216(19)
iPrOC(=S)N(H)Ph in (**5**)	1.671(3)	1.339(4)	1.330(3)

a Three independent molecules in the crystallographic asymmetric unit

References: 1. S. Y. Ho, C. S. Lai and E. R. T. Tiekink, *Acta Crystallogr. Sect. E: Struct. Reports Online*, 2003, **59**, o1155; 2. S. Y. Ho, R. P. A. Bettens, D. Dakternieks, A. Duthie and E. R.T. Tiekink, *CrystEngComm*, 2005, **7**, 682; 3. R. L. Taylor and E. R. T. Tiekink, *Z. Kristallogr*., 1994, **209**, 64; 4. R. E. Benson, G. A. Broker, L. M. Daniels, E. R. T. Tiekink, J. L. Wardell and D. J. Young, *Acta Crystallogr. Sect. E: Struct. Reports Online*, 2006, **62**, o4106; and 5. F. S. Kuan, F. Mohr, P. P. Tadbuppa and E. R.T. Tiekink, *CrystEngComm*, 2007, **9**, 574.

Table S(2). Selected bond and torsion angles (º) for ROC(=S)N(H)R' in their pure crystalline form and in co-crystals (**1**) – (**5**).

Compound	S1–C1–O1	S1–C1–N1	O1–C1–N1	S1/C1/N1/C2	C1/N1/C2/C3
MeOC(=S)N(H)Ph [1]	124.5(1)	123.0(1)	112.5(1)	178.2(1)	-60.1(2)
MeOC(=S)N(H)Ph in (**1**)	124.85(12)	121.96(12)	113.15(14)	-178.62(13)	31.3(3)
MeOC(=S)N(H)PhNO_2-4 [2]	124.5(1)	121.9(1)	113.6(2)	-175.9(1)	-176.0(2)
MeOC(=S)N(H)PhNO_2-4 in (**2**)	125.6(3)	121.5(3)	112.9(3)	173.9(3)	-21.0(6)
EtOC(=S)N(H)Ph [3,a]	125.0(4)	122.2(4)	112.8(5)	174.0(5)	37.1(9)
	124.9(4)	121.8(4)	113.3(4)	173.5(5)	158.3(6)
	124.3(4)	122.2(4)	113.6(4)	-177.0(5)	-17(1)
EtOC(=S)N(H)Ph in (**3**)	124.54(11)	122.88(11)	112.58(13)	173.39(12)	23.2(3)
EtOC(=S)N(H)PhNO_2-4 [4]	125.0(2)	121.6(2)	113.5(2)	178.9(2)	-3.8(4)
EtOC(=S)N(H)PhNO_2-4 in (**4**)	125.3(3)	122.1(3)	112.5(4)	-178.0(4)	4.0(8)
iPrOC(=S)N(H)Ph [5]	125.4(1)	121.591)	113.1(1)	178.2(1)	141.7(2)
iPrOC(=S)N(H)Ph in (**5**)	125.7(2)	122.0(2)	112.2(2)	-179.7(2)	-48.3(4)

a Three independent molecules in the crystallographic asymmetric unit

References: 1. S. Y. Ho, C. S. Lai and E. R. T. Tiekink, *Acta Crystallogr. Sect. E: Struct. Reports Online*, 2003, **59**, o1155; 2. S. Y. Ho, R. P. A. Bettens, D. Dakternieks, A. Duthie and E. R.T. Tiekink, *CrystEngComm*, 2005, **7**, 682; 3. R. L. Taylor and E. R. T. Tiekink, *Z. Kristallogr*., 1994, **209**, 64; 4. R. E. Benson, G. A. Broker, L. M. Daniels, E. R. T. Tiekink, J. L. Wardell and D. J. Young, *Acta Crystallogr. Sect. E: Struct. Reports Online*, 2006, **62**, o4106; and 5. F. S. Kuan, F. Mohr, P. P. Tadbuppa and E. R.T. Tiekink, *CrystEngComm*, 2007, **9**, 574.

Figure S(1). Unit cell contents highlighting the stacking of layers in co-crystal (**1**). The crystal structure of co-crystal (**3**) is isomorphous with co-crystal (**1**). Colour code in this and remaining diagrams: sulphur, yellow; oxygen, red; nitrogen, blue; carbon, grey; and hydrogen, green.

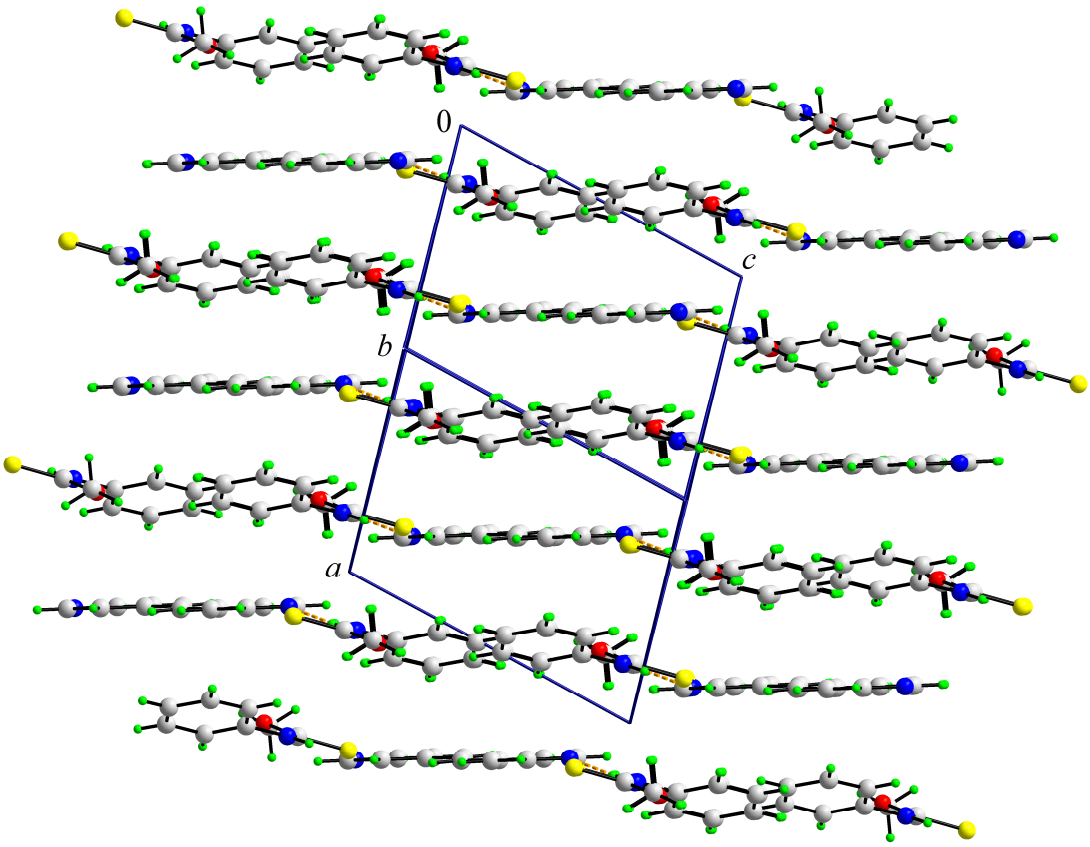

Figure S(2). Layers in the structure of co-crystal (**2**). Supramolecular chains mediated by N–H…N hydrogen bonds (orange dashed lines) and C–H…O contacts (blue dashed lines) run along the *c*-axis and are connected into layers in the *a*-direction via C-H…π and π…π interactions (not shown).

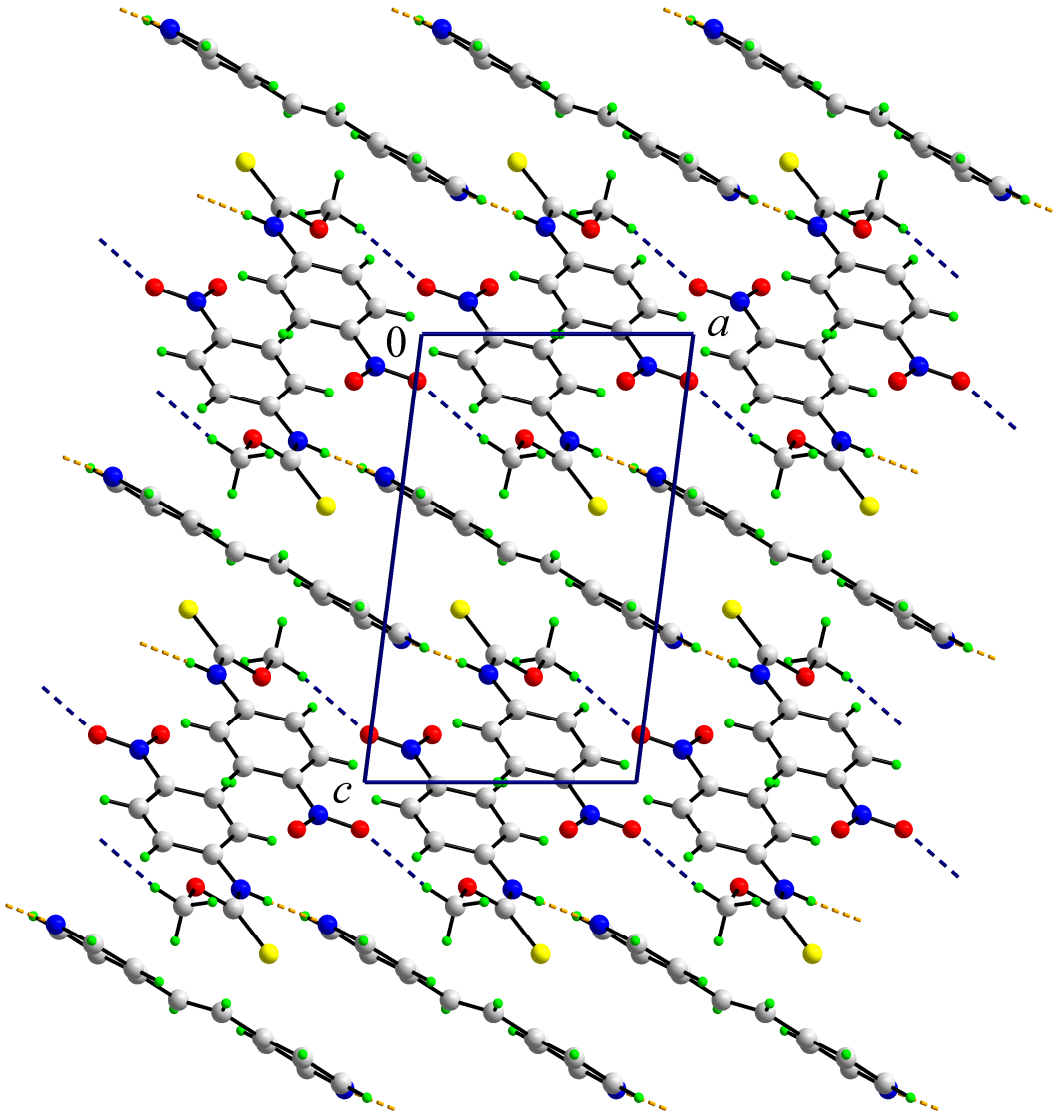

Figure S(3). Unit cell contents for co-crystal (**4**) viewed down the *b*-axis highlighting the stacking of layers along the *c*-direction.

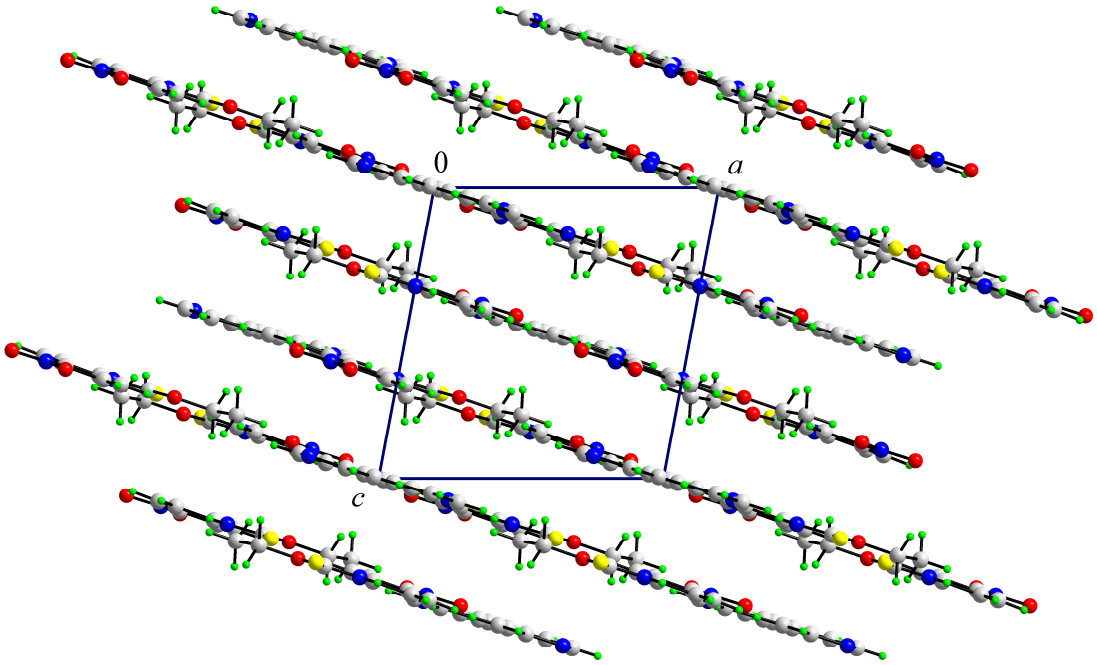

Figure S(4). PXRD patterns for co-crystal (**1**): MeOC(=S)N(H)Ph (black trace); *trans*-1,2-bis(4-pyridyl)ethene (red trace); 2:1 mixture (grinding) of MeOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene (green trace); and 2:1 mixture (solvent drop grinding) of MeOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene (blue trace).

Summary: Evidence for co-crystal formation.

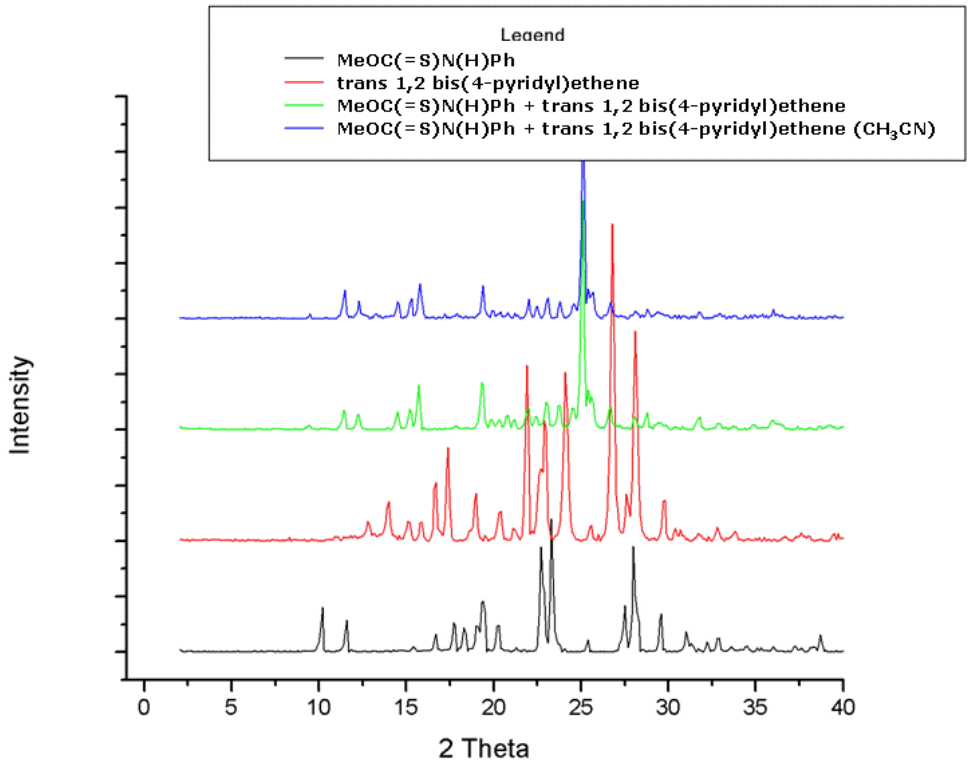

Figure S(5). PXRD patterns for co-crystal (**1**): 2:1 mixture (grinding) MeOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene (black trace); 2:1 mixture (solvent drop grinding) MeOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene (red trace) isolated single crystals of 2:1 MeOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (green trace); and calculated pattern from single crystal data for 2:1 MeOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (blue trace).

Summary: Bulk material corresponds to structure determined by single crystal X-ray crystallography.

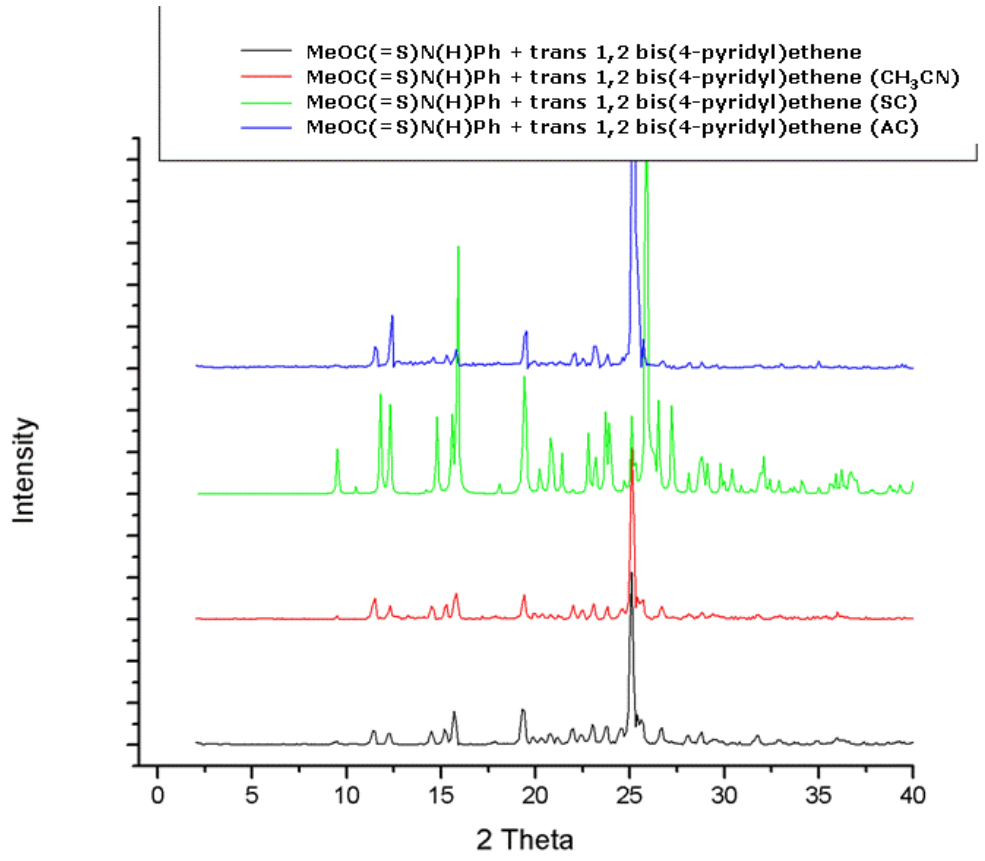

Figure S(6). PXRD patterns for co-crystal (**2**): MeOC(=S)N(H)PhNO$_2$-4 (black trace); *trans*-1,2-bis(4-pyridyl)ethene (red trace); 2:1 mixture (grinding) of MeOC(=S)N(H)PhNO$_2$-4 and *trans*-1,2-bis(4-pyridyl)ethene (green trace); and 2:1 mixture (solvent drop grinding) of MeOC(=S)N(H)PhNO$_2$-4 and *trans*-1,2-bis(4-pyridyl)ethene (blue trace).

Summary: Evidence for co-crystal formation by solvent drop grinding.

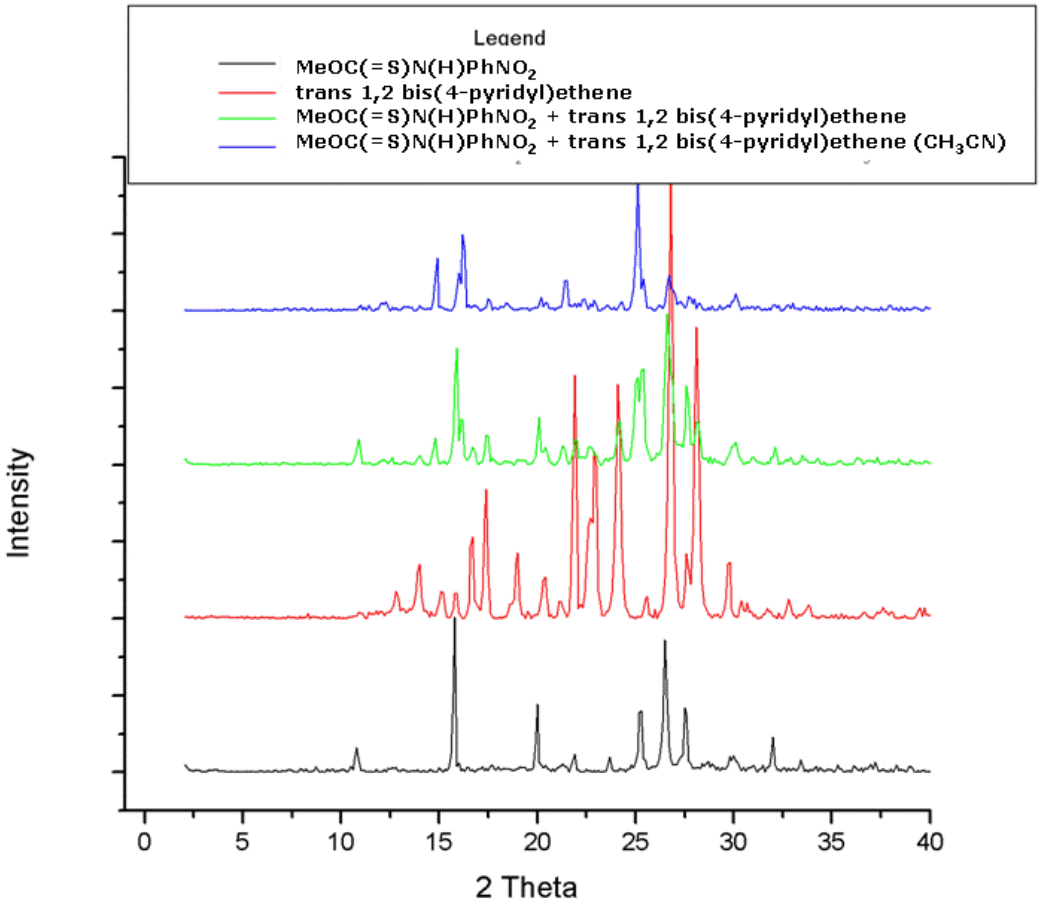

Figure S(7). PXRD patterns for co-crystal (**2**): 2:1 mixture (grinding) MeOC(=S)N(H)PhNO$_2$-4 and *trans*-1,2-bis(4-pyridyl)ethene (black trace); 2:1 mixture (solvent drop grinding) MeOC(=S)N(H)PhNO$_2$-4 and *trans*-1,2-bis(4-pyridyl)ethene (red trace); isolated single crystals of 2:1 MeOC(=S)N(H)PhNO$_2$-4 and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (green trace); and calculated pattern from single crystal data for 2:1 MeOC(=S)N(H)PhNO$_2$-4 and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (blue trace).

Summary: The solvent drop grinded bulk material corresponds to structure determined by single crystal X-ray crystallography.

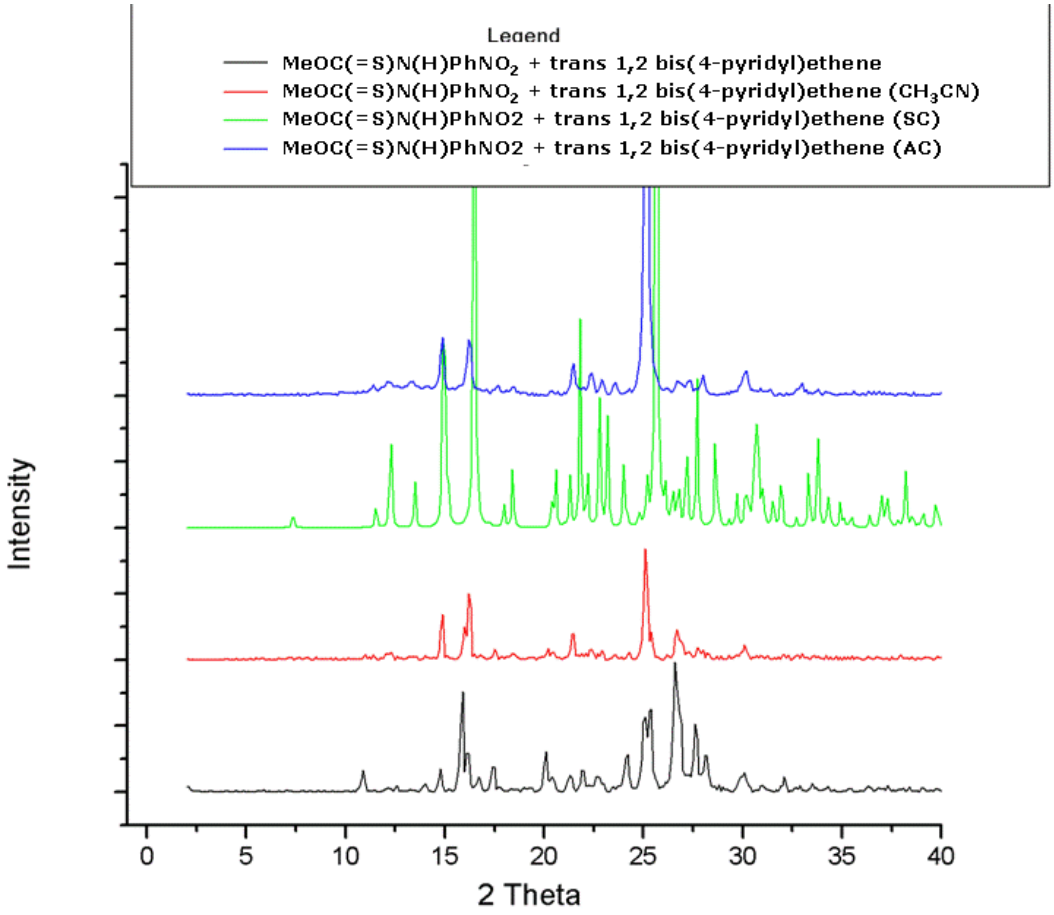

Figure S(8). PXRD patterns for co-crystal (**3**): isolated single crystals of 2:1 EtOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (black trace); and 2:1 mixture (grinding) of EtOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene (red trace).

Summary: Evidence for co-crystal formation with solvent drop grinding.

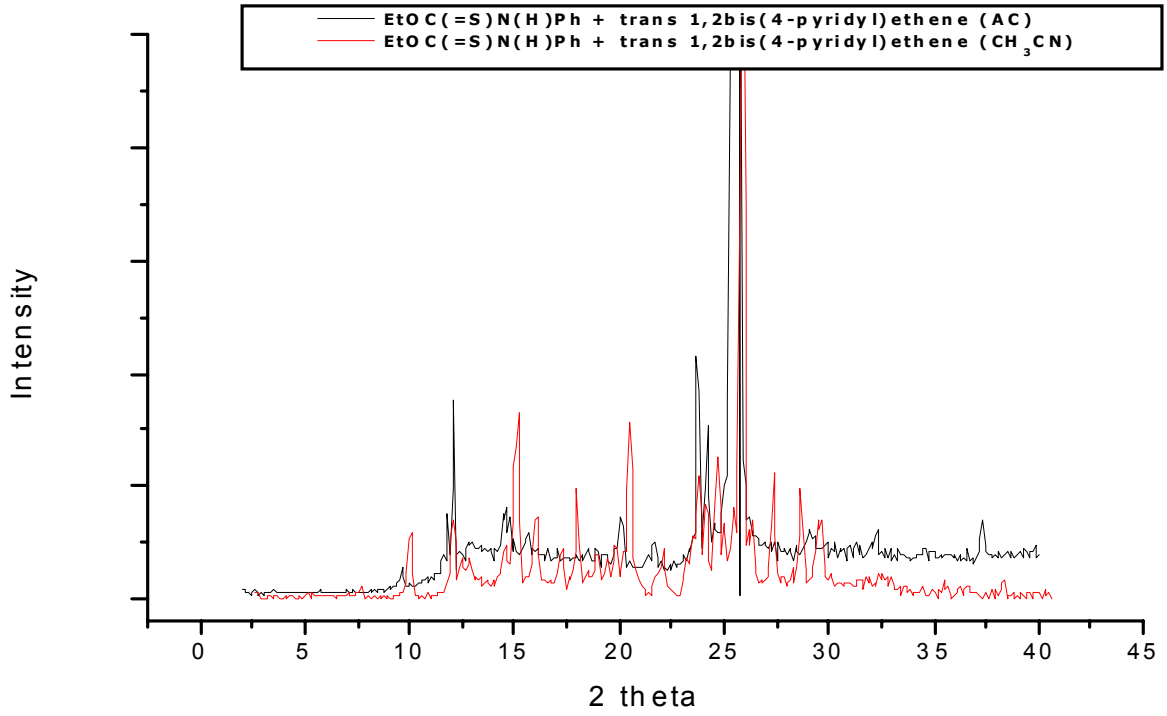

Figure S(9). PXRD patterns for co-crystal (**3**): isolated single crystals of 2:1 EtOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (black trace); and calculated pattern from single crystal data for 2:1 EtOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (red).

Summary: Bulk material corresponds to structure determined by single crystal X-ray crystallography.

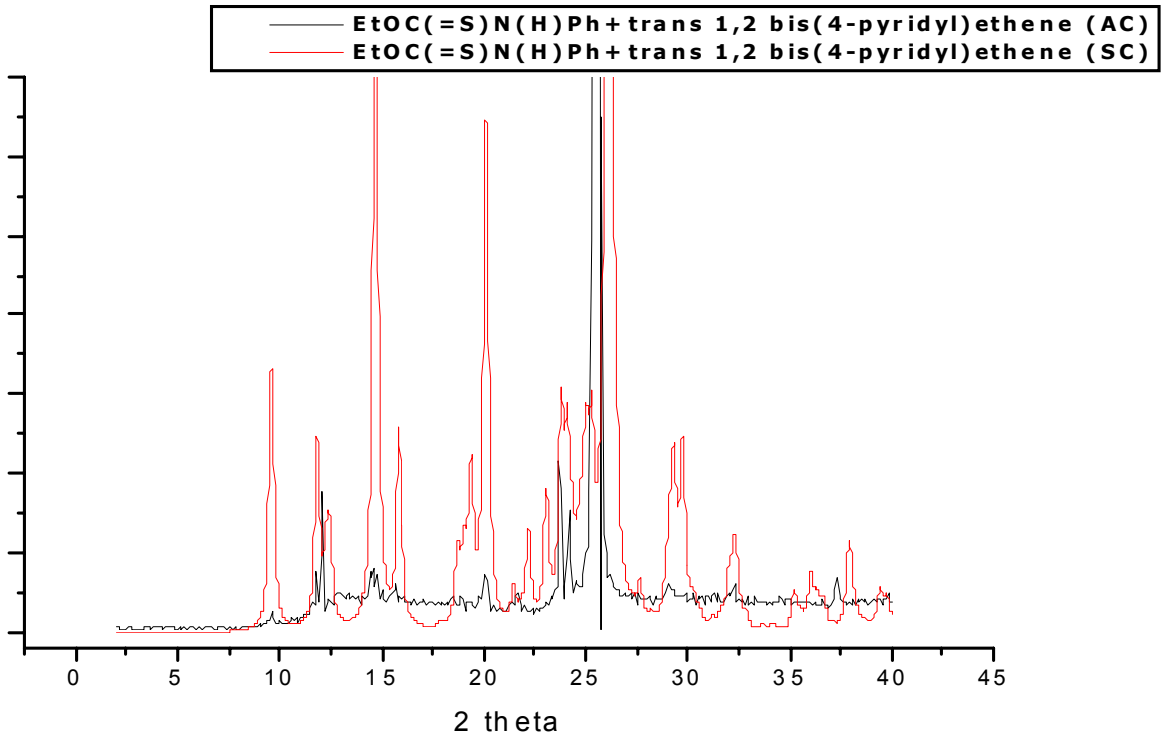

Figure S(10). PXRD patterns for co-crystal (**4**): EtOC(=S)N(H)PhNO$_2$-4 (black trace); 4,4'-bipyridine (red trace); 2:1 mixture (grinding) of EtOC(=S)N(H)PhNO$_2$-4 and 4,4'-bipyridine (green trace); and 2:1 mixture (solvent drop grinding) of EtOC(=S)N(H)PhNO$_2$-4 and 4,4'-bipyridine (blue trace).

Summary: Evidence for co-crystal formation with solvent drop grinding.

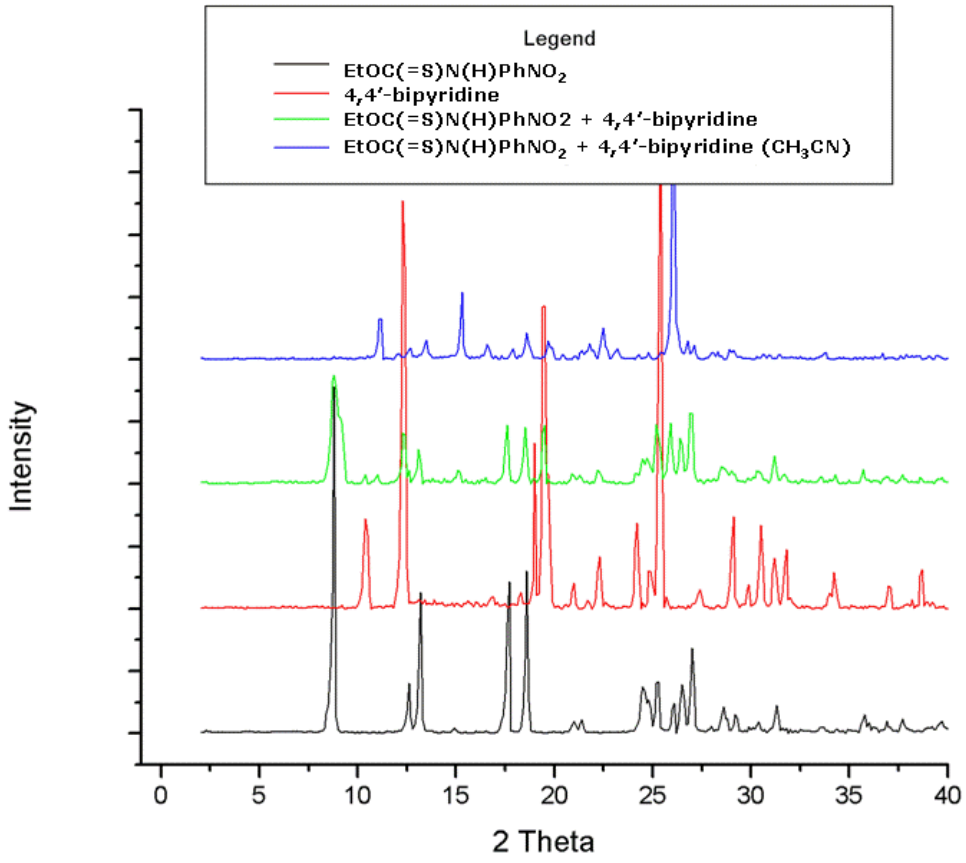

Figure S(11). PXRD patterns for co-crystal (**4**): 2:1 mixture (grinding) of EtOC(=S)N(H)PhNO$_2$-4 and 4,4'-bipyridine EtOC(=S)N(H)PhNO$_2$-4 (black trace); 2:1 mixture (solvent drop grinding) of EtOC(=S)N(H)PhNO$_2$ and 4,4'-bipyridine EtOC(=S)N(H)PhNO$_2$-4 (red trace); isolated single crystals of 2:1 EtOC(=S)N(H)PhNO$_2$-4 and 4,4'-bipyridine co-crystal (green trace); and calculated pattern from single crystal data for 2:1 EtOC(=S)N(H)PhNO$_2$-4 and 4,4'-bipyridine co-crystal (blue trace).

Summary: The bulk material obtained by solvent drop grinding corresponds to structure determined by single crystal X-ray crystallography.

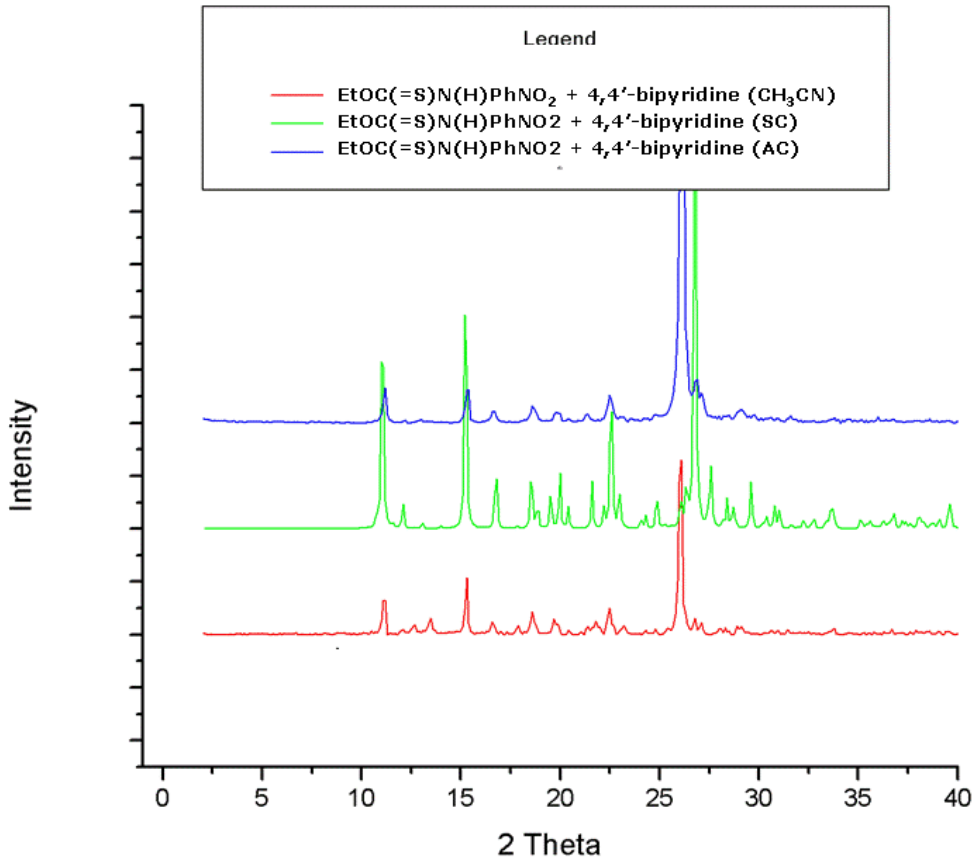

Figure S(12). PXRD patterns for co-crystal (**5**): isolated single crystals of 2:1 MeOC(=S)N(H)PhNO$_2$ and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (black trace); and calculated pattern from single crystal data for 2:1 MeOC(=S)N(H)PhNO$_2$ and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (red trace).

Summary: Bulk material corresponds to structure determined by single crystal X-ray crystallography.

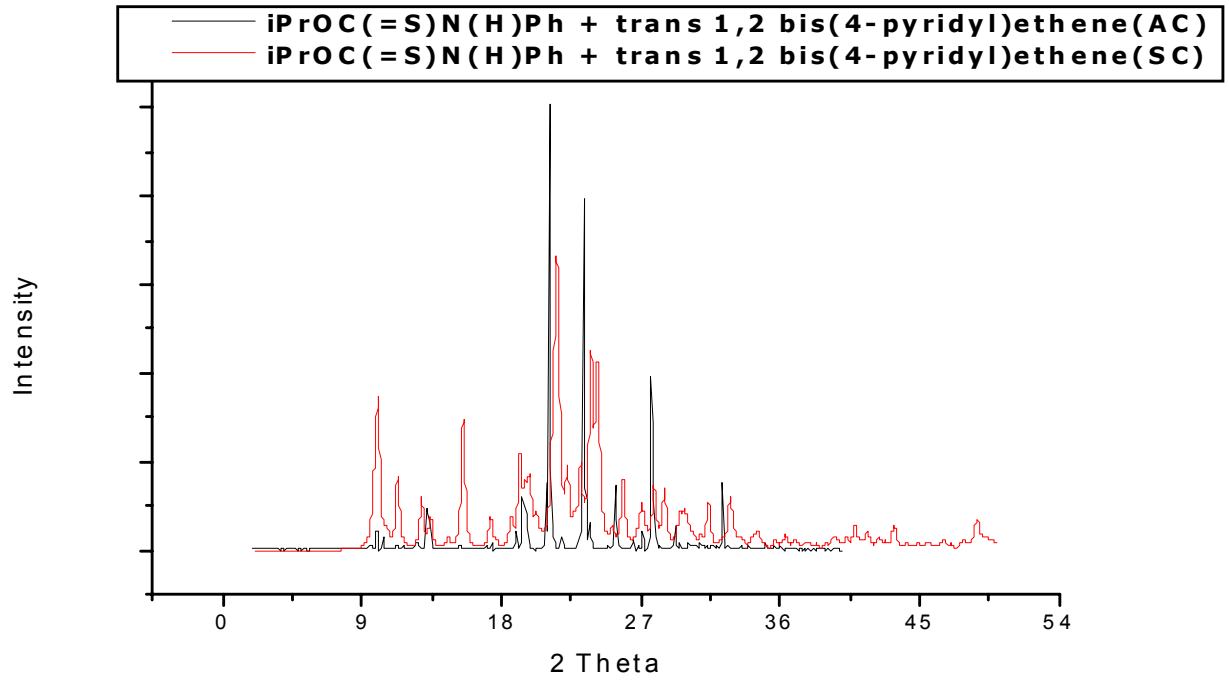

Figure S(13). PXRD patterns for co-crystal (**5**): isolated single crystals of 2:1 MeOC(=S)N(H)PhNO$_2$ and *trans*-1,2-bis(4-pyridyl)ethene co-crystal (black trace) and 2:1 mixture (grinding) of iPrOC(=S)N(H)Ph and *trans*-1,2-bis(4-pyridyl)ethene (red trace).

Summary: The phases are distinct indicating that the new phase formed by grinding is not the same as that deposited as crystals from solution.