Supplementary Materials

Annular tautomerism of 3(5)-disubstituted-1*H*-pyrazoles with ester and amide group

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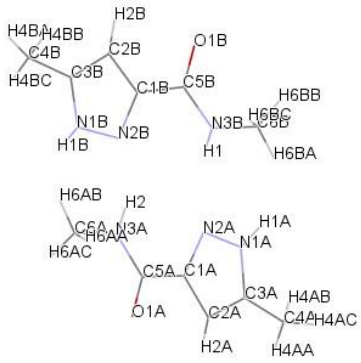
Supplementary Materials

Table 1S. Selected geometric parameters for *N*-Methyl 5-methyl-1H-pyrazole-3-carboxylamide ***(1a)*** CH_3-Pz-$CONHCH_3$ (Å, º)

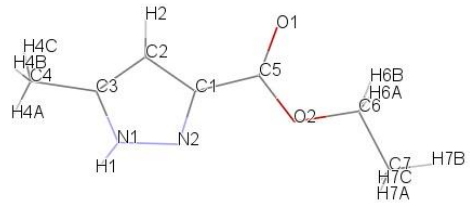


N1A—C3A	1.3512 (19)	C2B—C3B	1.375 (2)
N1A—N2A	1.3515 (17)	C2B—H2B	0.9300
N1A—H1A	0.8600	C4A—H4AA	0.9600
O1A—C5A	1.2424 (17)	C4A—H4AB	0.9600
C1A—N2A	1.3438 (18)	C4A—H4AC	0.9600
C1A—C2A	1.3952 (19)	C3B—C4B	1.490 (2)
C1A—C5A	1.477 (2)	N3B—C5B	1.3367 (19)
N1B—C3B	1.3484 (19)	N3B—C6B	1.4556 (18)
N1B—N2B	1.3505 (16)	N3B—H1	0.8600
N1B—H1B	0.8600	C4B—H4BA	0.9600
O1B—C5B	1.2395 (16)	C4B—H4BB	0.9600
C1B—N2B	1.3438 (17)	C4B—H4BC	0.9600
C1B—C2B	1.395 (2)	C6A—H6AA	0.9600
C1B—C5B	1.4817 (19)	C6A—H6AB	0.9600
C3A—C2A	1.374 (2)	C6A—H6AC	0.9600
C3A—C4A	1.494 (2)	C6B—H6BA	0.9600
N3A—C5A	1.3287 (18)	C6B—H6BB	0.9600
N3A—C6A	1.4510 (18)	C6B—H6BC	0.9600
N3A—H2	0.8600	C2A—H2A	0.9300
C3A—N1A—N2A	113.48 (12)	C2B—C3B—C4B	132.29 (14)
C3A—N1A—H1A	123.3	C5B—N3B—C6B	120.93 (12)
N2A—N1A—H1A	123.3	C5B—N3B—H1	119.5
N2A—C1A—C2A	111.91 (13)	C6B—N3B—H1	119.5
N2A—C1A—C5A	121.72 (13)	O1A—C5A—N3A	122.62 (13)
C2A—C1A—C5A	126.35 (13)	O1A—C5A—C1A	119.47 (13)
C1A—N2A—N1A	103.33 (12)	N3A—C5A—C1A	117.90 (12)
C3B—N1B—N2B	113.51 (11)	C3B—C4B—H4BA	109.5
C3B—N1B—H1B	123.2	C3B—C4B—H4BB	109.5
N2B—N1B—H1B	123.2	H4BA—C4B—H4BB	109.5
N2B—C1B—C2B	111.55 (12)	C3B—C4B—H4BC	109.5
N2B—C1B—C5B	121.71 (13)	H4BA—C4B—H4BC	109.5
C2B—C1B—C5B	126.74 (13)	H4BB—C4B—H4BC	109.5
N1A—C3A—C2A	105.99 (13)	N3A—C6A—H6AA	109.5
N1A—C3A—C4A	121.81 (14)	N3A—C6A—H6AB	109.5
C2A—C3A—C4A	132.19 (14)	H6AA—C6A—H6AB	109.5

C5A—N3A—C6A	120.94 (12)	N3A—C6A—H6AC	109.5
C5A—N3A—H2	119.5	H6AA—C6A—H6AC	109.5
C6A—N3A—H2	119.5	H6AB—C6A—H6AC	109.5
C1B—N2B—N1B	103.58 (11)	N3B—C6B—H6BA	109.5
C3B—C2B—C1B	105.48 (13)	N3B—C6B—H6BB	109.5
C3B—C2B—H2B	127.3	H6BA—C6B—H6BB	109.5
C1B—C2B—H2B	127.3	N3B—C6B—H6BC	109.5
C3A—C4A—H4AA	109.5	H6BA—C6B—H6BC	109.5
C3A—C4A—H4AB	109.5	H6BB—C6B—H6BC	109.5
H4AA—C4A—H4AB	109.5	O1B—C5B—N3B	123.08 (13)
C3A—C4A—H4AC	109.5	O1B—C5B—C1B	120.03 (13)
H4AA—C4A—H4AC	109.5	N3B—C5B—C1B	116.89 (12)
H4AB—C4A—H4AC	109.5	C3A—C2A—C1A	105.28 (13)
N1B—C3B—C2B	105.88 (12)	C3A—C2A—H2A	127.4
N1B—C3B—C4B	121.83 (13)	C1A—C2A—H2A	127.4
C2A—C1A—N2A—N1A	0.16 (15)	C6A—N3A—C5A—C1A	−178.40 (12)
C5A—C1A—N2A—N1A	−178.50 (12)	N2A—C1A—C5A—O1A	165.29 (13)
C3A—N1A—N2A—C1A	−0.35 (15)	C2A—C1A—C5A—O1A	−13.2 (2)
N2A—N1A—C3A—C2A	0.41 (16)	N2A—C1A—C5A—N3A	−15.4 (2)
N2A—N1A—C3A—C4A	179.69 (13)	C2A—C1A—C5A—N3A	166.12 (13)
C2B—C1B—N2B—N1B	−0.13 (15)	C6B—N3B—C5B—O1B	−2.0 (2)
C5B—C1B—N2B—N1B	178.95 (12)	C6B—N3B—C5B—C1B	178.53 (13)
C3B—N1B—N2B—C1B	−0.21 (15)	N2B—C1B—C5B—O1B	165.12 (13)
N2B—C1B—C2B—C3B	0.40 (16)	C2B—C1B—C5B—O1B	−16.0 (2)
C5B—C1B—C2B—C3B	−178.62 (13)	N2B—C1B—C5B—N3B	−15.4 (2)
N2B—N1B—C3B—C2B	0.46 (16)	C2B—C1B—C5B—N3B	163.51 (13)
N2B—N1B—C3B—C4B	−179.12 (12)	N1A—C3A—C2A—C1A	−0.28 (15)
C1B—C2B—C3B—N1B	−0.49 (15)	C4A—C3A—C2A—C1A	−179.45 (15)
C1B—C2B—C3B—C4B	179.02 (15)	N2A—C1A—C2A—C3A	0.08 (16)
C6A—N3A—C5A—O1A	0.9 (2)	C5A—C1A—C2A—C3A	178.66 (13)

Supplementary Materials

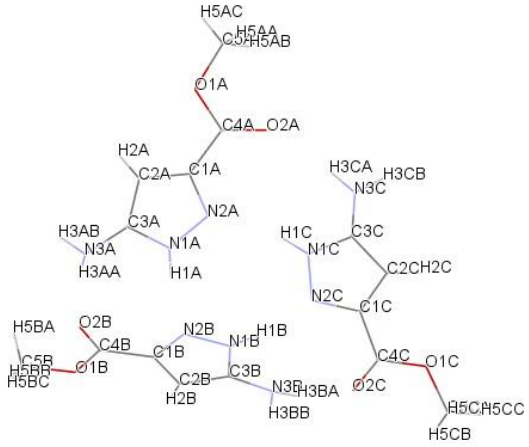
Table 2S. Selected geometric parameters for ethyl 5-methyl-1H-pyrazole-3-carboxylate (**1b**) CH_3-Pz-$COOCH_2CH_3$ (Å, º)



N1—N2	1.3458 (17)	C3—C4	1.491 (2)
N1—C3	1.3512 (19)	C4—H4A	0.9600
N1—H1	0.8600	C4—H4B	0.9600
N2—C1	1.3423 (18)	C4—H4C	0.9600
O1—C5	1.2087 (18)	C6—C7	1.501 (2)
O2—C5	1.3399 (18)	C6—H6A	0.9700
O2—C6	1.4578 (18)	C6—H6B	0.9700
C1—C2	1.400 (2)	C7—H7A	0.9600
C1—C5	1.475 (2)	C7—H7B	0.9600
C2—C3	1.377 (2)	C7—H7C	0.9600
C2—H2	0.9300		
N2—N1—C3	113.56 (12)	H4A—C4—H4C	109.5
N2—N1—H1	123.2	H4B—C4—H4C	109.5
C3—N1—H1	123.2	O1—C5—O2	124.52 (14)
C1—N2—N1	103.78 (12)	O1—C5—C1	123.77 (14)
C5—O2—C6	116.16 (11)	O2—C5—C1	111.70 (12)
N2—C1—C2	111.54 (13)	O2—C6—C7	107.29 (12)
N2—C1—C5	120.39 (13)	O2—C6—H6A	110.3
C2—C1—C5	128.06 (13)	C7—C6—H6A	110.3
C3—C2—C1	105.25 (13)	O2—C6—H6B	110.3
C3—C2—H2	127.4	C7—C6—H6B	110.3
C1—C2—H2	127.4	H6A—C6—H6B	108.5
N1—C3—C2	105.88 (13)	C6—C7—H7A	109.5
N1—C3—C4	121.39 (13)	C6—C7—H7B	109.5
C2—C3—C4	132.73 (14)	H7A—C7—H7B	109.5
C3—C4—H4A	109.5	C6—C7—H7C	109.5
C3—C4—H4B	109.5	H7A—C7—H7C	109.5
H4A—C4—H4B	109.5	H7B—C7—H7C	109.5
C3—C4—H4C	109.5		
C3—N1—N2—C1	−0.54 (16)	C1—C2—C3—C4	179.66 (16)
N1—N2—C1—C2	0.76 (16)	C6—O2—C5—O1	−0.2 (2)
N1—N2—C1—C5	−179.66 (12)	C6—O2—C5—C1	−179.37 (12)
N2—C1—C2—C3	−0.71 (17)	N2—C1—C5—O1	175.04 (15)
C5—C1—C2—C3	179.75 (15)	C2—C1—C5—O1	−5.5 (3)
N2—N1—C3—C2	0.11 (17)	N2—C1—C5—O2	−5.8 (2)
N2—N1—C3—C4	−179.30 (13)	C2—C1—C5—O2	173.72 (14)
C1—C2—C3—N1	0.35 (16)	C5—O2—C6—C7	174.94 (12)

Supplementary Materials

Table 3S. Selected geometric parameters for methyl 5-amino-1H-pyrazole-3-carboxylate (**2b**) H_2N-Pz-$COOCH_3$ (Å, º)

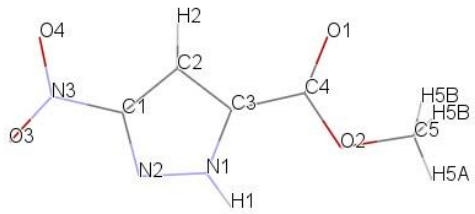


C1C—N2C	1.3351 (19)	N1B—C3B	1.3503 (19)
C1C—C2C	1.399 (2)	N1B—N2B	1.3524 (17)
C1C—C4C	1.475 (2)	N1B—H1B	0.8600
C2C—C3C	1.384 (2)	O1B—C4B	1.3386 (18)
C2C—H2C	0.9300	O1B—C5B	1.4452 (18)
C3C—N1C	1.3537 (19)	C1B—N2B	1.3411 (19)
C3C—N3C	1.370 (2)	C1B—C2B	1.402 (2)
C4C—O2C	1.2191 (18)	C1B—C4B	1.473 (2)
C4C—O1C	1.3368 (18)	N3A—C3A	1.378 (2)
C5C—O1C	1.4493 (18)	N3A—H3AB	0.895 (17)
C5C—H5CA	0.9600	N3A—H3AA	0.877 (18)
C5C—H5CB	0.9600	N3B—C3B	1.387 (2)
C5C—H5CC	0.9600	N3B—H3BA	0.892 (18)
N1A—C3A	1.3562 (19)	N3B—H3BB	0.880 (18)
N1A—N2A	1.3582 (17)	C3B—C2B	1.379 (2)
N1A—H1A	0.8600	N3C—H3CA	0.906 (18)
O1A—C4A	1.3381 (18)	N3C—H3CB	0.856 (18)
O1A—C5A	1.4459 (18)	C4B—O2B	1.2131 (18)
C1A—N2A	1.3389 (19)	C5B—H5BA	0.9600
C1A—C2A	1.400 (2)	C5B—H5BB	0.9600
C1A—C4A	1.476 (2)	C5B—H5BC	0.9600
O2A—C4A	1.2139 (18)	C5A—H5AA	0.9600
C2A—C3A	1.374 (2)	C5A—H5AB	0.9600
C2A—H2A	0.9300	C5A—H5AC	0.9600
N1C—N2C	1.3629 (17)	C2B—H2B	0.9300
N1C—H1C	0.8600		
N2C—C1C—C2C	112.41 (14)	C2B—C1B—C4B	129.00 (14)
N2C—C1C—C4C	118.92 (13)	C3A—N3A—H3AB	114.3 (11)
C2C—C1C—C4C	128.66 (14)	C3A—N3A—H3AA	115.6 (11)
C3C—C2C—C1C	104.68 (13)	H3AB—N3A—H3AA	115.7 (15)
C3C—C2C—H2C	127.7	N1A—C3A—C2A	106.98 (13)

C1C—C2C—H2C	127.7	N1A—C3A—N3A	121.33 (14)
N1C—C3C—N3C	121.78 (14)	C2A—C3A—N3A	131.52 (15)
N1C—C3C—C2C	106.44 (13)	C1C—N2C—N1C	103.77 (12)
N3C—C3C—C2C	131.54 (15)	C3B—N3B—H3BA	113.5 (11)
O2C—C4C—O1C	123.72 (15)	C3B—N3B—H3BB	113.8 (11)
O2C—C4C—C1C	125.03 (14)	H3BA—N3B—H3BB	110.2 (16)
O1C—C4C—C1C	111.25 (13)	N1B—C3B—C2B	106.73 (14)
O1C—C5C—H5CA	109.5	N1B—C3B—N3B	120.63 (14)
O1C—C5C—H5CB	109.5	C2B—C3B—N3B	132.55 (15)
H5CA—C5C—H5CB	109.5	C3C—N3C—H3CA	115.4 (11)
O1C—C5C—H5CC	109.5	C3C—N3C—H3CB	116.5 (12)
H5CA—C5C—H5CC	109.5	H3CA—N3C—H3CB	112.8 (16)
H5CB—C5C—H5CC	109.5	O2B—C4B—O1B	123.40 (14)
C3A—N1A—N2A	112.41 (12)	O2B—C4B—C1B	125.50 (14)
C3A—N1A—H1A	123.8	O1B—C4B—C1B	111.09 (13)
N2A—N1A—H1A	123.8	O2A—C4A—O1A	123.97 (14)
C4A—O1A—C5A	115.06 (12)	O2A—C4A—C1A	125.53 (14)
N2A—C1A—C2A	112.38 (14)	O1A—C4A—C1A	110.47 (13)
N2A—C1A—C4A	118.68 (14)	O1B—C5B—H5BA	109.5
C2A—C1A—C4A	128.93 (14)	O1B—C5B—H5BB	109.5
C1A—N2A—N1A	103.74 (12)	H5BA—C5B—H5BB	109.5
C3A—C2A—C1A	104.49 (13)	O1B—C5B—H5BC	109.5
C3A—C2A—H2A	127.8	H5BA—C5B—H5BC	109.5
C1A—C2A—H2A	127.8	H5BB—C5B—H5BC	109.5
C3C—N1C—N2C	112.68 (13)	O1A—C5A—H5AA	109.5
C3C—N1C—H1C	123.7	O1A—C5A—H5AB	109.5
N2C—N1C—H1C	123.7	H5AA—C5A—H5AB	109.5
C4C—O1C—C5C	115.80 (12)	O1A—C5A—H5AC	109.5
C3B—N1B—N2B	112.86 (13)	H5AA—C5A—H5AC	109.5
C3B—N1B—H1B	123.6	H5AB—C5A—H5AC	109.5
N2B—N1B—H1B	123.6	C1B—N2B—N1B	103.87 (12)
C4B—O1B—C5B	115.12 (12)	C3B—C2B—C1B	104.54 (14)
N2B—C1B—C2B	111.97 (14)	C3B—C2B—H2B	127.7
N2B—C1B—C4B	118.99 (13)	C1B—C2B—H2B	127.7
N2C—C1C—C2C—C3C	0.21 (17)	C3C—N1C—N2C—C1C	−1.09 (16)
C4C—C1C—C2C—C3C	−178.98 (15)	N2B—N1B—C3B—C2B	1.16 (17)
C1C—C2C—C3C—N1C	−0.85 (16)	N2B—N1B—C3B—N3B	178.19 (13)
C1C—C2C—C3C—N3C	173.41 (16)	C5B—O1B—C4B—O2B	0.6 (2)
N2C—C1C—C4C—O2C	3.8 (2)	C5B—O1B—C4B—C1B	−178.37 (12)
C2C—C1C—C4C—O2C	−177.06 (15)	N2B—C1B—C4B—O2B	−3.9 (2)
N2C—C1C—C4C—O1C	−175.76 (13)	C2B—C1B—C4B—O2B	178.40 (15)
C2C—C1C—C4C—O1C	3.4 (2)	N2B—C1B—C4B—O1B	175.00 (13)
C2A—C1A—N2A—N1A	−0.87 (16)	C2B—C1B—C4B—O1B	−2.7 (2)
C4A—C1A—N2A—N1A	−179.72 (12)	C5A—O1A—C4A—O2A	1.0 (2)
C3A—N1A—N2A—C1A	0.51 (15)	C5A—O1A—C4A—C1A	−177.21 (12)
N2A—C1A—C2A—C3A	0.90 (17)	N2A—C1A—C4A—O2A	−13.4 (2)
C4A—C1A—C2A—C3A	179.60 (14)	C2A—C1A—C4A—O2A	167.97 (15)

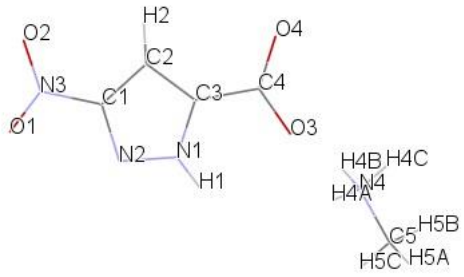
N3C—C3C—N1C—N2C	−173.69 (13)	N2A—C1A—C4A—O1A	164.82 (12)
C2C—C3C—N1C—N2C	1.25 (16)	C2A—C1A—C4A—O1A	−13.8 (2)
O2C—C4C—O1C—C5C	2.4 (2)	C2B—C1B—N2B—N1B	0.84 (16)
C1C—C4C—O1C—C5C	−177.99 (12)	C4B—C1B—N2B—N1B	−177.20 (12)
N2A—N1A—C3A—C2A	0.03 (16)	C3B—N1B—N2B—C1B	−1.24 (16)
N2A—N1A—C3A—N3A	−175.67 (13)	N1B—C3B—C2B—C1B	−0.57 (16)
C1A—C2A—C3A—N1A	−0.53 (16)	N3B—C3B—C2B—C1B	−177.10 (16)
C1A—C2A—C3A—N3A	174.56 (16)	N2B—C1B—C2B—C3B	−0.18 (17)
C2C—C1C—N2C—N1C	0.51 (16)	C4B—C1B—C2B—C3B	177.61 (14)
C4C—C1C—N2C—N1C	179.78 (13)		

Table 4S. Selected geometric parameters for methyl 3-nitro-1H-pyrazole-5-carboxylate (**3b**) N_2O-Pz-$COOCH_3$ (Å, º)



O1—C4	1.2135 (19)	O2—C5	1.464 (2)
N1—N2	1.3363 (19)	C2—C3	1.376 (2)
N1—C3	1.360 (2)	C2—H2	0.9300
N1—H1	0.8600	O4—N3	1.2279 (18)
C1—N2	1.328 (2)	C4—C3	1.479 (2)
C1—C2	1.393 (2)	O3—N3	1.2233 (18)
C1—N3	1.453 (2)	C5—H5B	0.997 (15)
O2—C4	1.3226 (19)	C5—H5A	0.98 (2)
N2—N1—C3	112.57 (12)	O1—C4—C3	123.30 (14)
N2—N1—H1	123.7	O2—C4—C3	111.55 (13)
C3—N1—H1	123.7	N1—C3—C2	107.37 (14)
N2—C1—C2	114.17 (14)	N1—C3—C4	122.70 (14)
N2—C1—N3	119.22 (14)	C2—C3—C4	129.93 (14)
C2—C1—N3	126.61 (15)	O3—N3—O4	125.44 (14)
C1—N2—N1	103.21 (12)	O3—N3—C1	118.22 (14)
C4—O2—C5	115.28 (12)	O4—N3—C1	116.34 (14)
C3—C2—C1	102.68 (13)	O2—C5—H5B	109.0 (8)
C3—C2—H2	128.7	O2—C5—H5A	104.4 (12)
C1—C2—H2	128.7	H5B—C5—H5A	112.3 (10)
O1—C4—O2	125.15 (15)		
C2—C1—N2—N1	0.000 (1)	C1—C2—C3—C4	180.000 (1)
N3—C1—N2—N1	180.000 (1)	O1—C4—C3—N1	180.000 (1)
C3—N1—N2—C1	0.000 (1)	O2—C4—C3—N1	0.000 (1)
N2—C1—C2—C3	0.000 (1)	O1—C4—C3—C2	0.000 (1)
N3—C1—C2—C3	180.000 (1)	O2—C4—C3—C2	180.000 (1)
C5—O2—C4—O1	0.000 (1)	N2—C1—N3—O3	0.000 (1)
C5—O2—C4—C3	180.000 (1)	C2—C1—N3—O3	180.000 (1)
N2—N1—C3—C2	0.000 (1)	N2—C1—N3—O4	180.000 (1)
N2—N1—C3—C4	180.000 (1)	C2—C1—N3—O4	0.000 (1)
C1—C2—C3—N1	0.000 (1)		

Table 5S. Selected geometric parameters for Methylammonium 3-nitro-1H-pyrazole-5-carboxylate (**4**) $N_2OPzCOO^-MeNH_3^+$ (Å, º)



O1—N3	1.2314 (13)	C3—C4	1.4981 (18)
C1—N2	1.3309 (16)	O3—C4	1.2502 (16)
C1—C2	1.3902 (18)	C4—O4	1.2537 (15)
C1—N3	1.4441 (16)	N4—C5	1.4811 (16)
N1—N2	1.3379 (15)	N4—H4A	0.8900
N1—C3	1.3568 (16)	N4—H4B	0.8900
N1—H1	0.8600	N4—H4C	0.8900
O2—N3	1.2247 (14)	C5—H5A	0.9600
C2—C3	1.3766 (18)	C5—H5B	0.9600
C2—H2	0.9300	C5—H5C	0.9600
N2—C1—C2	114.22 (11)	O3—C4—O4	126.23 (12)
N2—C1—N3	118.07 (11)	O3—C4—C3	114.88 (11)
C2—C1—N3	127.70 (12)	O4—C4—C3	118.88 (12)
N2—N1—C3	113.31 (11)	C5—N4—H4A	109.5
N2—N1—H1	123.3	C5—N4—H4B	109.5
C3—N1—H1	123.3	H4A—N4—H4B	109.5
C3—C2—C1	103.08 (12)	C5—N4—H4C	109.5
C3—C2—H2	128.5	H4A—N4—H4C	109.5
C1—C2—H2	128.5	H4B—N4—H4C	109.5
C1—N2—N1	102.63 (10)	N4—C5—H5A	109.5
N1—C3—C2	106.76 (11)	N4—C5—H5B	109.5
N1—C3—C4	119.15 (11)	H5A—C5—H5B	109.5
C2—C3—C4	134.08 (12)	N4—C5—H5C	109.5
O2—N3—O1	124.14 (11)	H5A—C5—H5C	109.5
O2—N3—C1	117.43 (11)	H5B—C5—H5C	109.5
O1—N3—C1	118.43 (11)		
N2—C1—C2—C3	0.23 (15)	N2—C1—N3—O2	172.97 (11)
N3—C1—C2—C3	−178.55 (13)	C2—C1—N3—O2	−8.3 (2)
C2—C1—N2—N1	0.17 (14)	N2—C1—N3—O1	−7.09 (18)
N3—C1—N2—N1	179.07 (11)	C2—C1—N3—O1	171.64 (13)
C3—N1—N2—C1	−0.53 (14)	N1—C3—C4—O3	−0.02 (18)
N2—N1—C3—C2	0.70 (15)	C2—C3—C4—O3	−178.86 (14)
N2—N1—C3—C4	−178.43 (11)	N1—C3—C4—O4	179.45 (12)
C1—C2—C3—N1	−0.53 (14)	C2—C3—C4—O4	0.6 (2)
C1—C2—C3—C4	178.42 (14)		

Table 6S. Selected hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
1a				
N1A—H1A···O1A^{i}	0.86	1.90	2.7454 (15)	166.9
N1B—H1B···O1B^{ii}	0.86	1.95	2.7815 (15)	163.1
N3A—H2···N2B	0.86	2.20	3.0254 (17)	159.6
C4A—H4AC···O1A^{iii}	0.96	2.51	3.2622 (19)	135.1
N3B—H1···N2A	0.86	2.22	3.0532 (17)	164.1
C2A—H2A···N2A^{iv}	0.93	2.65	3.5627 (19)	166.0
1b				
C4—H4C···O1^{v}	0.96	2.66	3.5453 (19)	153.9
N1—H1···N2^{vi}	0.86	2.17	2.9852 (18)	157.2
N1—H1···O2^{vi}	0.86	2.48	3.0998 (16)	129.3
2b				
C5C—H5CA···O2A^{vii}	0.96	2.60	3.255 (2)	125.4
N1A—H1A···N2B	0.86	2.05	2.8559 (18)	155.2
N1C—H1C···N2A	0.86	2.06	2.8957 (18)	165.1
N1B—H1B···N2C	0.86	2.00	2.8519 (18)	169.5
N3A—H3AB···O2C^{viii}	0.895 (17)	2.361 (18)	3.1325 (18)	144.4 (14)
N3A—H3AA···O2B	0.877 (18)	2.057 (19)	2.9198 (19)	167.5 (16)
N3B—H3BA···O2C	0.892 (18)	2.126 (19)	3.0023 (19)	166.8 (16)
N3C—H3CA···O2A	0.906 (18)	2.059 (19)	2.9602 (19)	173.0 (16)
N3C—H3CB···N3B^{ix}	0.856 (18)	2.495 (18)	3.203 (2)	140.6 (15)
C5A—H5AB···N3A^{viii}	0.96	2.65	3.511 (2)	150.1
3b				
N1—H1···O1^{x}	0.86	2.01	2.8274 (17)	159.0
C2—H2···N2^{xi}	0.93	2.35	3.250 (2)	163.6
C5—H5A···O4^{xii}	0.98 (2)	2.63 (2)	3.563 (2)	158.9 (16)
4				
N1—H1···O3^{xiii}	0.86	2.54	3.0467 (14)	118.5
N1—H1···O4^{xiii}	0.86	2.08	2.9340 (15)	175.1
C2—H2···O2^{xiv}	0.93	2.53	3.3703 (16)	151.2
N4—H4A···O4^{xv}	0.89	1.96	2.8146 (15)	160.6
N4—H4B···O3	0.89	1.85	2.7299 (14)	167.8
N4—H4C···N2^{xvi}	0.89	2.22	3.0874 (16)	166.3

Symmetry code(s): (i) *x*, −*y*+1/2, *z*+1/2; (ii) *x*, *y*−1, *z*; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) −*x*+1, *y*−1/2, −*z*+1/2; (v) −*x*+1/2, *y*+1/2, −*z*+1/2; (vi) −*x*+3/2, *y*+1/2, −*z*+1/2; (vii) −*x*+1/2, *y*+1/2, −*z*+3/2; (viii) −*x*+3/2, *y*−1/2, −*z*+3/2; (ix) −*x*+1/2, *y*−1/2, −*z*+3/2; (x) *x*−1, *y*, *z*; (xi) *x*+1, *y*, *z*; (xii) *x*, *y*, *z*+1; (xiii) *x*−1/2, −*y*+3/2, *z*−1/2; (xiv) −*x*+1, −*y*+1, −*z*+1; (xv) *x*+1/2, −*y*+3/2, *z*−1/2; (xvi) *x*+3/2, −*y*+3/2, *z*+1/2.

Supplementary Materials

Table 7S. Selected parameter of the 3(5) substituted pyrazole structures with carbonyl (amide/ester) as substituent

Refcode	Tautomer		Substituent position		Conformer			References	Compound name
	T3	T5	C-3	C-5	cis	trans			
ANIKIT	3		Me-	CONHN-	-9.22		T3c	K.Karrouchi, Y.Ramli, J.Taoufik, S.Radi, M.Ansar, J.T.Mague Unknown (2016), 1, x160793	(Z)-5-Methyl-N'-(4-methylbenzylidene)-1H-pyrazole-3-carbohydrazide
EZIYES	3		Me-	CONHN-	-9.30		T3c	S.K.Seth, N.C.Saha, S.Ghosh, T.Kar Chem.Phys.Lett. (2011), 506, 309	5-Methyl-1H-pyrazole-3-carbohydrazide monohydrate
RISHEH	3		Me-	CONHCH2	-11.78		T3c	Jing Hu, Guofeng Chen, Guochun Ma, Hongguang Song Acta Crystallogr.,Sect.E:Struct.Rep.Online (2007), 63, o4806	5,5'-Dimethyl-N,N'-(iminodiethylene)di-1H-pyrazole-3-carboxamide
VEYQIB	3		Me-	CONHN-	3.24		T3c	S.Konar, A.Jana, K.Das, S.Ray, S.Chatterjee, S.K.Kar S.Konar, A.Jana, K.Das, S.Ray, S.Chatterjee, S.K.Kar	Methyl (((5-methyl-1H-pyrazol-3-yl)carbonyl)hydrazono)(phenyl)acetate
VUXQEM	3		Me-	CONHN-	-5.50		T3c	K.Karrouchi, M.Ansar, S.Radi, M.Saadi, L.El Ammari Acta Cryst. E (2015), 71, o890	N'-(Diphenylmethylene)-5-methyl-1H-pyrazole-3-carbohydrazide
FAQSAR	3		Me-	COOEt	5.45		T3c	L.Infantes, C.Foces-Foces, R.M.Claramunt, C.Lopez, N.Jagerovic, J.Elguero Heterocycles (1999), 50, 227	3-Ethoxycarbonyl-5-methylpyrazole
MUXMIC	3		H-	CONHPh	9.40		T3c	M.Kissane, S.E.Lawrence, A.R.Maguire M.Kissane, S.E.Lawrence, A.R.Maguire	N-(4-Methylphenyl)-1H-pyrazole-3-carboxamide
NIJCOZ	3		H-	CONHtBu	1.88		T3c	R.M.Claramunt, M.A.Garcia, C.Lopez, S.Trofimenko, G.P.A.Yap, I.Alkorta, J.Elguero Magn.Reson.Chem. (2005), 43, 89	1H-Pyrazole-3-(N-t-butyl)carboxamide
FAQROE	3		H-	COOEt		179.40	T3t	L.Infantes, C.Foces-Foces, R.M.Claramunt, C.Lopez, N.Jagerovic, J.Elguero Heterocycles (1999), 50, 227	3-Ethoxycarbonylpyrazole
RUNJIV	3		H-	CONH2		-167.29	T3t	T.T.Talele, F.R.Fronczek Private Communication (2015), ,	1H-pyrazole-3-carboxamide
RUNJER	3		H-	COOMe		-178.99	T3t	T.T.Talele, F.R.Fronczek Private Communication (2015), ,	methyl 1H-pyrazole-3-carboxylate
AFEQOS	3		Ph-	COOH	-8.95		T3c	Xiao-Yuan Zhang, Wei Liu, Wei Tang, Yue-Bo Lai Acta Crystallogr.,Sect.E:Struct.Rep.Online (2007), 63, o3764	5-Phenyl-1H-pyrazole-3-carboxylic acid
EMUNEH	3		Ph-	CONHN-	-7.27		T3c	K.Karrouchi, Y.Ramli, J.Taoufik, S.Radi, M.Ansar, J.T.Mague Unknown (2016), 1, x160830	N'-[(1E)-(4-bromophenyl)methylidene]-5-phenyl-1H-pyrazole-3-carbohydrazide
FAQSIZ	3		Ph-	COOEt	0.96		T3c	L.Infantes, C.Foces-Foces, R.M.Claramunt, C.Lopez, N.Jagerovic, J.Elguero Heterocycles (1999), 50, 227	3-Ethoxycarbonyl-5-phenylpyrazole
LEPRII	3		Ph-	CONHN-	-29.63		T3c	Fang-Fang Jian, Tong-Ling liang, Ying-Qi Qin, Huan-Qing Yu, Hai-Lian Xiao Acta Crystallogr.,Sect.E:Struct.Rep.Online (2006), 62, o4364	2'-(4-Methylbenzylidene)-5-phenyl-1H-pyrazole-3-carbohydrazide
MIRYUI	3		Ph-	CONHN-	0.19		T3c	Yongqi Qin, Fangfang Jian, Hailian Xiao, Jing Zhang Acta Crystallogr.,Sect.E:Struct.Rep.Online (2008), 64, o320	(E)-5-Phenyl-N'-(1-phenylethylidene)-1H-pyrazole-3-carbohydrazide
QAJKUK	3		Ph-	CONHN-	-12.14		T3c	K.Karrouchi, S.Radi, M.Ansar, J.Taoufik, H.A.Ghabbour, Y.N.Mabkhot Z.Kristallogr.-New Cryst.Struct. (2016), 231,	N'-(4-Nitrobenzylidene)-5-phenyl-1H-pyrazole-3-carbohydrazide
SEZDUX	3		Ph-	CONHBz	-7.88		T3c	Yan-Qing Ge, Yong Xia, Fang Wei, Wen-Liang Dong, Bao-Xiang Zhao Acta Crystallogr.,Sect.E:Struct.Rep.Online (2007), 63, o1186	N-Benzyl-5-phenyl-1H-pyrazole-3-carboxamide
UJODII	3		Ph-	CONHN-	21.58		T3c	K.Karrouchi, S.Radi, M.Ansar, J.Taoufik, H.A.Ghabbour, Y.N.Mabkhot Z.Kristallogr.-New Cryst.Struct. (2016), 231,	N'-(4-(Dimethylamino)benzylidene)-5-phenyl-1H-pyrazole-3-carbohydrazide
HUPDAY	3		4-Me-OPh-	CONHN-	12.43		T3c	Yue An, Pingping Mu, Zhiping Guo, Yongheng Xing, Guanghua Zhou, Jun Ning, Jianzhou Lu, Jiehan Hu Youji Huaxue(Chin.)(Chin.J.Org.Chem.) (2009), 29, 730	N'-(4-Methoxybenzylidene)-5-(4-methoxyphenyl)-1H-pyrazole-3-carbohydrazide
LAQNOI	3		4-Me-OPh-	CONH-	-2.50		T3c	Guangqian Han, Jiaguo Lv, Ju Zhu, Youjun Zhou, Defeng Wu Acta Crystallogr.,Sect.E:Struct.Rep.Online (2012), 68, o901	N-(2-Hydroxyethyl)-5-(4-methoxyphenyl)-1H-pyrazole-3-carboxamide

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VACYUW	3		4-Me-OPh-	CONHN-	28.07		T3c	K.Karrouchi, S.Radi, M.Ansar, J.Taoufik, H.A.Ghabbour, Y.N.Mabkhot Z.Kristallogr.-New Cryst.Struct. (2016), 231,	N'-(4-Methoxybenzylidene)-5-phenyl-1H-pyrazole-3-carbohydrazide
GINPOJ	3		Ph-	COOMe	3.94		T3c	Guanghua Zhou, Yue An, Jing Han, Maofa Ge, Yongheng Xing Acta Crystallogr.,Sect.E:Struct.Rep.Online (2007), 63, o4474	Methyl 5-phenyl-1H-pyrazole-3-carboxylate
RIXVOK	3		4-Me-Ph-	COOEt	-11.37		T3c	T.T.Dang, T.T.Dang, C.Fischer, H.Gorls, P.Langer Tetrahedron (2008), 64, 2207	Ethyl 5-(4-tolyl)-1H-pyrazole-3-carboxylate
TORTOL	3		4-F-Ph-	COOEt	7.28		T3c	V.Markovic, M.D.Joksovic Green Chemistry (2015), 17, 842	Ethyl 5-(4-fluorophenyl)-1H-pyrazole-3-carboxylate
FAQSIZ	3		Ph-	COOEt		-156.83	T3t	L.Infantes, C.Foces-Foces, R.M.Claramunt, C.Lopez, N.Jagerovic, J.Elguero Heterocycles (1999), 50, 227	3-Ethoxycarbonyl-5-phenylpyrazole
LOBKEU		5	4-Me-OPh-	COOEt	11.57		T5c	Nana Shao, Tong Chen, Taotao Zhang, Huajian Zhu, Qunxiong Zheng, Hongbin Zou Tetrahedron (2014), 70, 795	Ethyl 3-(4-methoxyphenyl)-1H-pyrazole-5-carboxylate
SEZNAN		5	2-OH-5-Me-Ph-	COOEt	0.78		T5c	Yan-Qing Ge, Wen-Liang Dong, Yong Xia, Fang Wei, Bao-Xiang Zhao Acta Crystallogr.,Sect.E:Struct.Rep.Online (2007), 63, o1313	Ethyl 3-(2-hydroxy-5-methylphenyl)-1H-pyrazole-5-carboxylate
VOJZEB		5	4-Br-Ph-	CONHN-	-4.16		T5c	Juan Sun, Peng-Cheng Lv, Yong Yin, Rong-Ju Yuan, Jian Ma, Hai-Liang Zhu Unknown (2013), 8, e69751	3-(4-bromophenyl)-N'-(2-chlorobenzoyl)-1H-pyrazole-5-carbohydrazide
HUPDEC		5	4-MeO-Ph-	CONHN-		-155.04	T5t	Yue An, Pingping Mu, Zhiping Guo, Yongheng Xing, Guanghua Zhou, Jun Ning, Jianzhou Lu, Jiehan Hu Youji Huaxue(Chin.)(Chin.J.Org.Chem.) (2009), 29, 730	N'-(4-Hydroxy-3-methoxybenzylidene)-3-(4-methoxyphenyl)-1H-pyrazole-5-carbohydrazide
UKUVUS		5	Ph-	COC=C		162.16	T5t	V.V.Khlturina, Yu.V.Shklyaev, Z.A.Aliev, A.N.Maslivets Zh.Org.Khim.(Russ.)(Russ.J.Org.Chem.) (2009), 45, 1535	2-(8,8-Dimethyl-2,3,8,9-tetrahydro[1,4]dioxino[2,3-g]isoquinolin-6(7H)-ylidene)-1-(3-phenyl-1H-pyrazol-5-yl)ethanone
EWAHUH	3		COO-	COOH	-7.40		T3c	S.Packiaraj, A.Pushpaveni, S.Govindarajan, J.M.Rawson CrystEngComm (2016), 18, 7978	guanidinium 3-carboxy-1H-pyrazole-5-carboxylate monohydrate
LIGKIX	3		COO-	COOH	3.99		T3c	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	N,N,N',N'-Tetramethylethane-1,2-diaminium bis(3-carboxy-1H-pyrazole-5-carboxylate)
LIGKOD	3		COO-	COOH	-5.58		T3c	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	1,4-bis(2-Hydroxyethyl)piperazinediium bis(3-carboxy-1H-pyrazole-5-carboxylate)
LIGKUJ	3		COO-	COOH	-4.45		T3c	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	2-Isopropylanilinium 3-carboxy-1H-pyrazole-5-carboxylate
LIGLIY	3		COO-	COOH	0.61		T3c	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	2-Ethoxyanilinium 3-carboxy-1H-pyrazole-5-carboxylate
MUPDOR	3		COO-	COOH	-6.57		T3c	O.Ugono, N.P.Rath, A.M.Beatty Cryst.Growth Des. (2009), 9, 4595	2-Phenoxyanilinium 3-carboxy-1H-pyrazole-5-carboxylate
QUCRUC	3		COO-	COOH	13.84		T3c	O.Ugono, N.P.Rath, A.M.Beatty Cryst.Growth Des. (2009), 9, 4595	2-(4-Methoxyphenyl)ethanaminium 3-carboxy-1H-pyrazole-5-carboxylate
QUCSAJ	3		COO-	COOH	-16.02		T3c	O.Ugono, N.P.Rath, A.M.Beatty Cryst.Growth Des. (2009), 9, 4595	2-(4-Methylphenyl)ethanaminium 3-carboxy-1H-pyrazole-5-carboxylate
QUCSEN	3		COO-	COOH	18.77		T3c	O.Ugono, N.P.Rath, A.M.Beatty Cryst.Growth Des. (2009), 9, 4595	2-(4-Fluorophenyl)ethanaminium 3-carboxy-1H-pyrazole-5-carboxylate
QUCSIR	3		COO-	COOH	10.23		T3c	O.Ugono, N.P.Rath, A.M.Beatty Cryst.Growth Des. (2009), 9, 4595	1-(1-Naphthyl)ethanaminium 3-carboxy-1H-pyrazole-5-carboxylate
MZCPYZ10	3		COO-	COOMe	-6.34		T3c	R.L.Harlow, S.H.Simonsen Acta Crystallogr.,Sect.B:Struct.Crystallogr.Cryst.Chem. (1974), 30, 2505	1,1,1-Trimethylhydrazinium 3-carbomethoxy-5-pyrazolecarboxylate
LIGKET	3		COO-	COOH		178.42	T3t	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	Hexane-1,6-diaminium bis(3-carboxy-1H-pyrazole-5-carboxylate)
LIGLAQ	3		COO-	COOH		-175.29	T3t	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	2,6-Diethylanilinium 3-carboxy-1H-pyrazole-5-carboxylate monohydrate
LIGLEU	3		COO-	COOH		-162.73	T3t	O.Ugono, N.P.Rath, A.M.Beatty CrystEngComm (2011), 13, 753	2-Ethylanilinium 3-carboxy-1H-pyrazole-5-carboxylate monohydrate
MARVIM	3		COO-	COOH		176.84	T3t	Xiu-Ying Li, Ling Liu, Shan-Shan Wang, Miao-Miao Wang, Guang-Bo Che Z.Kristallogr.-New Cryst.Struct. (2012), 227, 73	4,4'-bipyridinium bis(3-carboxy-1H-pyrazole-5-carboxylate) tetrahydrate
PEVQUD	3		COO-	COOH		179.14	T3t	V.S.S.Kumar, T.Premkumar, N.P.Rath, S.Govindarajan Indian J.Chem.,Sect.B:Org.Chem.Incl.Med.Chem. (2007), 46, 141	Hydrazonium bis(3-carboxypyrazol-5-carboxylate)
KUZQOM		5	COO-	COOH	-3.18		T5c	Xin-Hui Zhou Acta Crystallogr.,Sect.E:Struct.Rep.Online (2010), 66, o2578	Piperazine-1,4-diium bis(2-carboxy-1H-pyrazole-4-carboxylate) tetrahydrate

Supplementary Materials

OFUZIY		5	COO-	COOH		-179.15	T5t	A.M.Beatty, C.M.Schneider, A.E.Simpson, J.L.Zaher CrystEngComm (2002), 4, 282	Propane-1,3-diammonium bis(5-carboxypyrazole-3-carboxylate) trihydrate
OFUZOE		5	COO-	COOH		179.14	T5t	A.M.Beatty, C.M.Schneider, A.E.Simpson, J.L.Zaher CrystEngComm (2002), 4, 282	Butane-1,4-diammonium bis(5-carboxypyrazole-3-carboxylate) tetrahydrate
MUNZIG		5	CN	COOiPro	0.74		T5c	P.K.Mykhailiuk Eur.J.Org.Chem. (2015), , 7235	Isopropyl 3-cyano-1H-pyrazole-5-carboxylate
MUNZOM		5	CN	COCH2Ph		179.36	T5t	P.K.Mykhailiuk Eur.J.Org.Chem. (2015), , 7235	5-(Phenylacetyl)-1H-pyrazole-3-carbonitrile
MUNZUS		5	CN	COcBu		177.74	T5t	P.K.Mykhailiuk Eur.J.Org.Chem. (2015), , 7235	5-(Cyclobutylcarbonyl)-1H-pyrazole-3-carbonitrile
MUPBAC		5	CN	COCH2Bzl		-174.71	T5t	P.K.Mykhailiuk Eur.J.Org.Chem. (2015), , 7235	5-(3-Phenylpropanoyl)-1H-pyrazole-3-carbonitrile
APUROU		5	CF3CHF	COOMe	-1.03		T5c	P.Mykhailiuk Private Communication (2016), ,	methyl 3-(1,2,2,2-tetrafluoroethyl)-1H-pyrazole-5-carboxylate
APURUA		5	CF3CHF	COOtBu	-4.94		T5c	P.Mykhailiuk Private Communication (2016), ,	t-butyl 3-(1,2,2,2-tetrafluoroethyl)-1H-pyrazole-5-carboxylate
GOWLEL		5	CHF2	COOMe	0.00		T5c	P.Mykhailiuk Angew.Chem.,Int.Ed. (2015), 54, 6558	methyl 3-(difluoromethyl)-1H-pyrazole-5-carboxylate
GOWLOV		5	CHF2	COOEt	1.30		T5c	P.Mykhailiuk Angew.Chem.,Int.Ed. (2015), 54, 6558	ethyl 3-(difluoromethyl)-1H-pyrazole-5-carboxylate
KORWIZ		5	CHF2CF2	COOiPro	-10.46		T5c	P.K.Mykhailiuk Org.Biomol.Chem. (2015), 13, 3438	isopropyl 3-(1,1,2,2-tetrafluoroethyl)-1H-pyrazole-5-carboxylate
WIXLUM		5	CF3	COOMe	0.00		T5c	Evgeniy Y.Slobodyanyuk, O.S.Artamonov, O.V.Shishkin, P.K.Mykhailiuk Eur.J.Org.Chem. (2014), , 2487	methyl 3-(trifluoromethyl)-1H-pyrazole-5-carboxylate
VOVXIP		5	CHF2	COMe		176.94	T5t	P.Mykhailiuk Angew.Chem.,Int.Ed. (2015), 54, 6558	1-(3-(Difluoromethyl)-1H-pyrazol-5-yl)ethanone
APUSAH		5	CF3CHF	CONMe2		153.61	T5t	P.Mykhailiuk Private Communication (2016), ,	N,N-dimethyl-3-(1,2,2,2-tetrafluoroethyl)-1H-pyrazole-5-carboxamide
VOVXIP		5	CHF2	COMe		176.94	T5t	Angew.Chem.,Int.Ed. (2015), 54, 6558 Angew.Chem.,Int.Ed. (2015), 54, 6558	1-(3-(Difluoromethyl)-1H-pyrazol-5-yl)ethanone
QARVOU		5	HO-	COOEt		174.26	T5t	L.Infantes, C.Foces-Foces, R.M.Claramunt, C.Lopez, J.Elguero J.Mol.Struct. (1998), 447, 71	5-Ethoxycarbonyl-3-hydroxypyrazole
APUSEL	3		difluorovinyl	COOMe	0.00		T3c	P.Mykhailiuk Private Communication (2016)	methyl 5-(1,2-difluorovinyl)-1H-pyrazole-3-carboxylate dihydrate
BIYJIE	3		pherrocenyl	COOMe	-16.33		T3c	C.Obuah, A.Munyaneza, I.A.Guzei, J.Darkwa Dalton Trans. (2014), 43, 8940	3-(Ethoxycarbonyl)-5-ferrocenylpyrazole
VIXPAV	3		Py	CONHN-	12.22		T3c	S.Bala, A.Goswami, Satirtha Sengupta, Sumi Ganguly, S.Bhattacharya, S.Khanra, R.Mondal S.Bala, A.Goswami, Satirtha Sengupta, Sumi Ganguly, S.Bhattacharya, S.Khanra, R.Mondal	5-(Pyridin-2-yl)-N'-(pyridin-2-ylmethylene)-1H-pyrazole-3-carbohydrazide acetonitrile solvate
ICEQAK	3		CONHPh	COOEt		175.88	T3t	Jing-Jing Qi, You-Jun Zhou, Xue-Fei Liu, Li-Li Ding, Can-Hui Zheng, Chun-Quan Sheng, Jia-Guo Lv, Ju Zhu Jiegou Huaxue(Chin.)(Chinese J.Struct.Chem.) (2011), 30, 1604	Ethyl 5-(4-((phenylacetyl)amino)phenyl)-1H-pyrazole-3-carboxylate
PUJLIR		5	4-NO2PhCO-	COOEt		-178.37	T5t	Wen-Ming Shu, Jun-Rui Ma, Kai-Lu Zheng, Hui-Ying Sun, Mei Wang, Yan Yang, An-Xin Wu Tetrahedron (2014), 70, 9321	ethyl 3-(4-nitrobenzoyl)-1H-pyrazole-5-carboxylate
PUJLIR		5	4-NO2PhCO-	COOEt		-178.37	T5t	Wen-Ming Shu, Jun-Rui Ma, Kai-Lu Zheng, Hui-Ying Sun, Mei Wang, Yan Yang, An-Xin Wu Tetrahedron (2014), 70, 9321	ethyl 3-(4-nitrobenzoyl)-1H-pyrazole-5-carboxylate
YOTHIZ		5	NHCSNH	COOMe		-171.40	T5t	B.Huang, P.-P.Kung, A.L.Rheingold, A.DiPasquale, A.Yanovsky Acta Crystallogr.,Sect.E:Struct.Rep.Online (2009), 65, o1249	Methyl 3-(3-(ethoxycarbonyl)thioureido)-1H-pyrazole-5-carboxylate

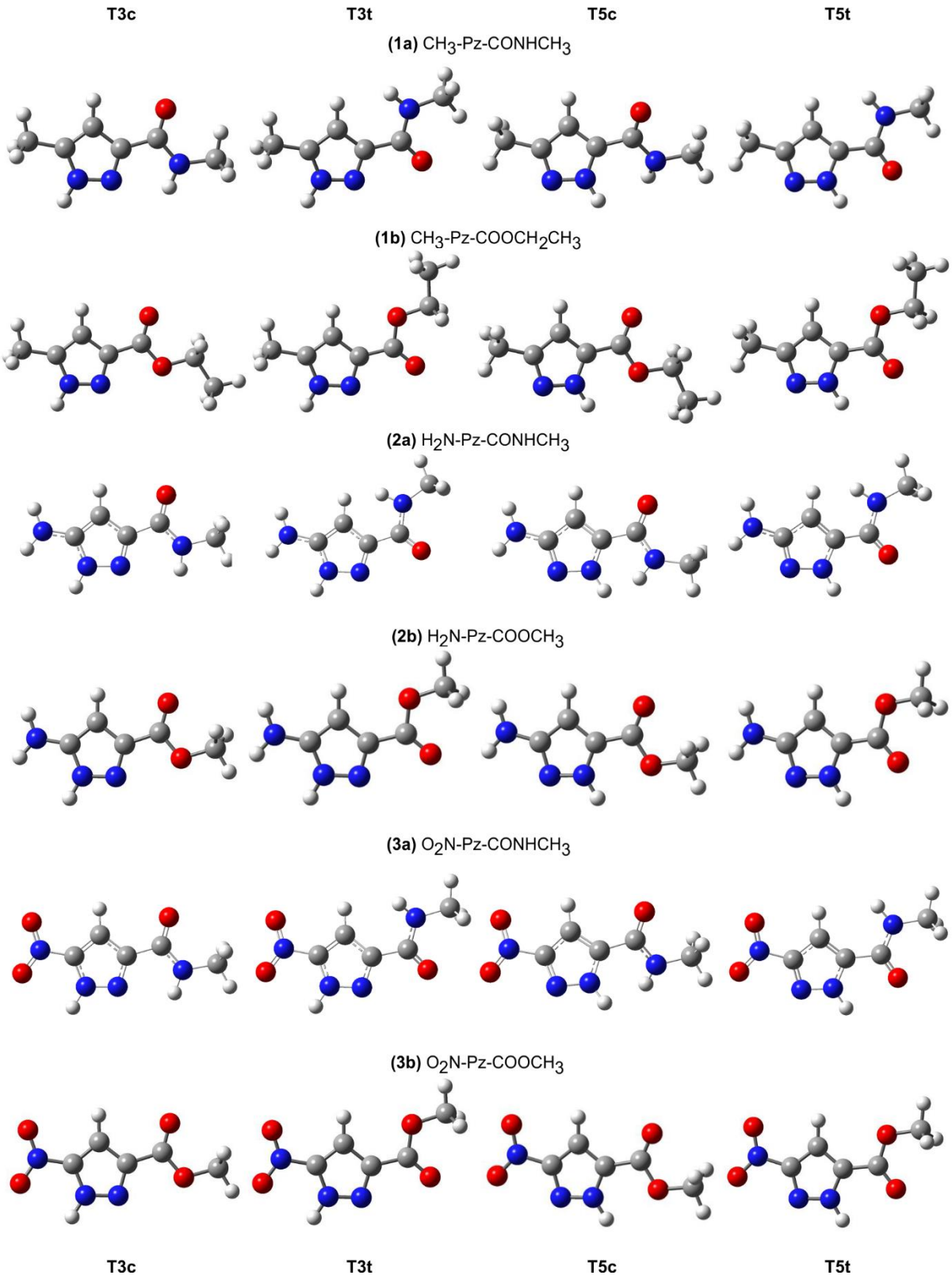

Figure 1S. Tautomers and conformers of the studied molecules calculated *in vacuo*.

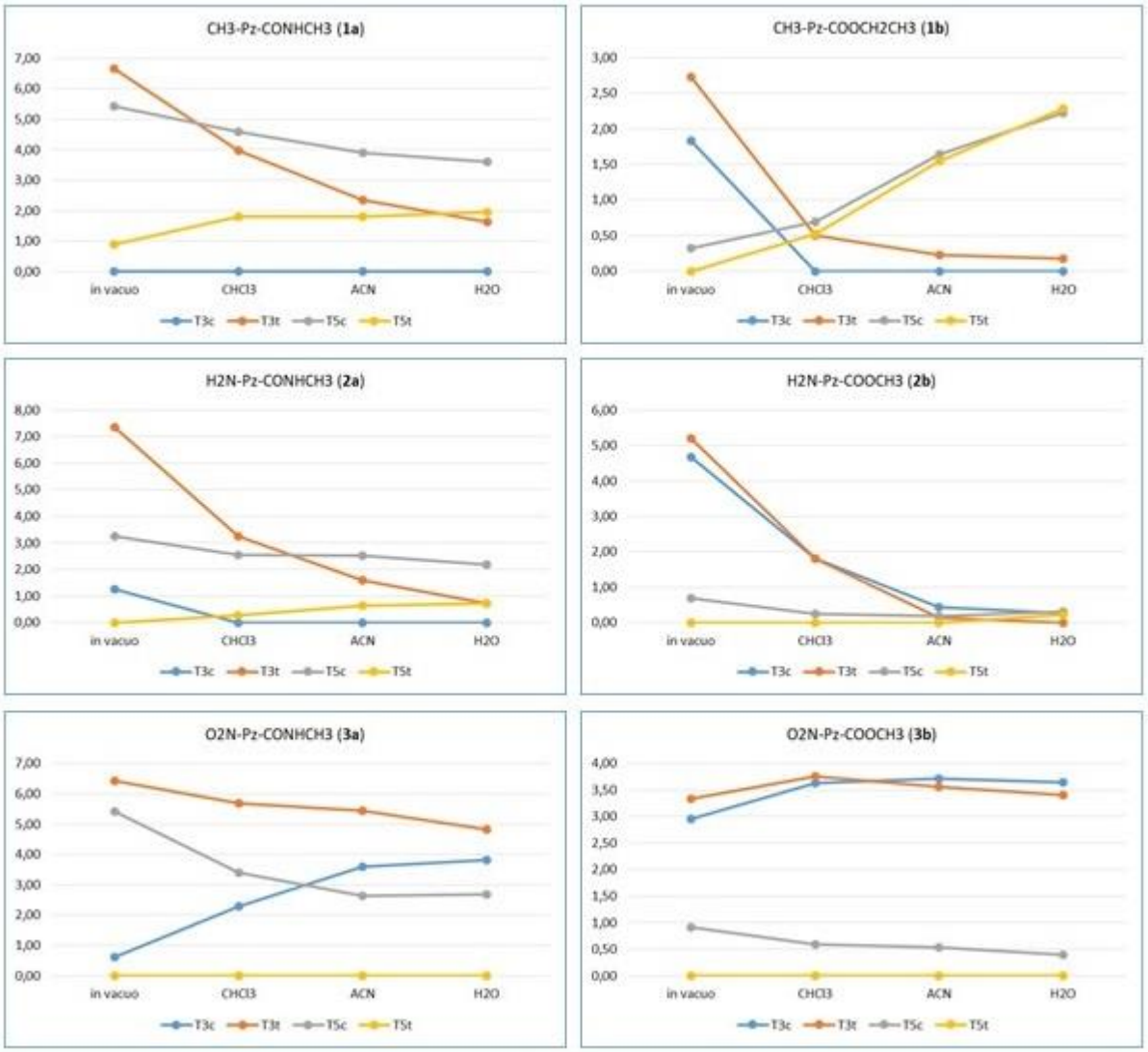

Figure 2S. The change of relative energy (kcal/mol) for the structures (see Table 3) od the studied compounds **1-3**.

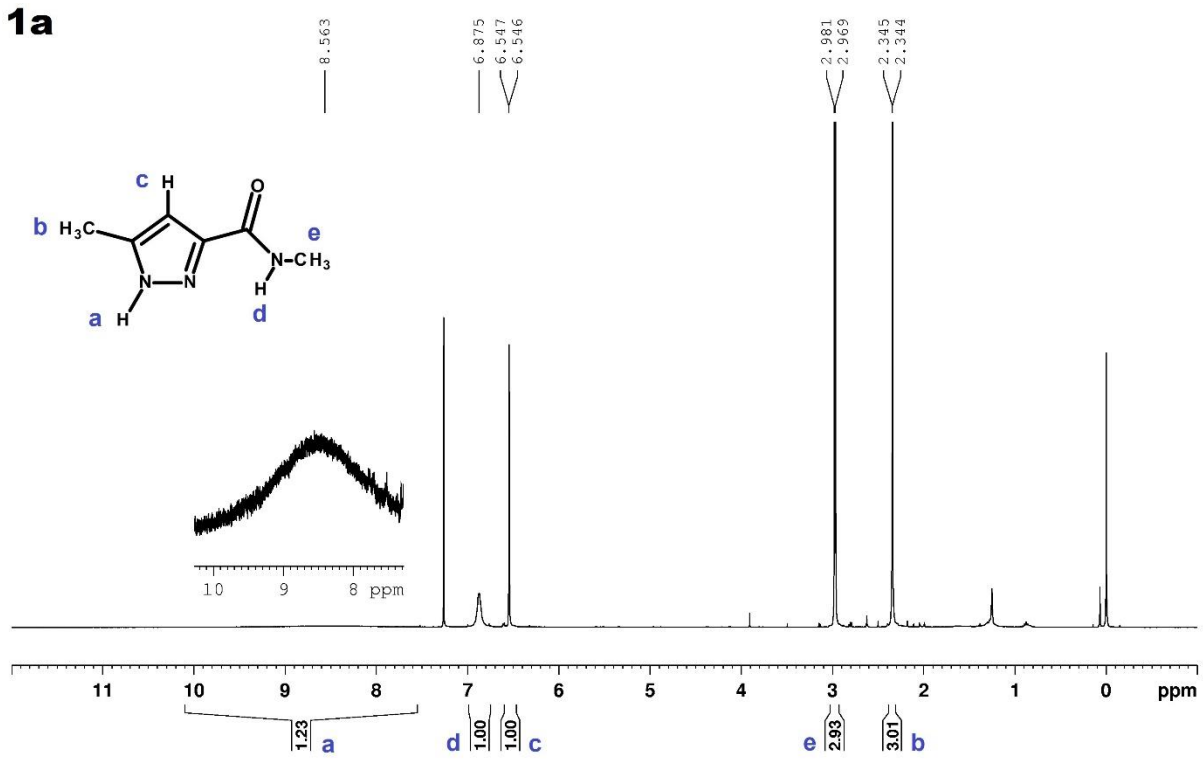

Figure 3S. ^{1}H NMR spectrum of *N*-methyl 5-methyl-1*H*-pyrazole-3-carboxylamide (**1a**) in $CDCl_3$.

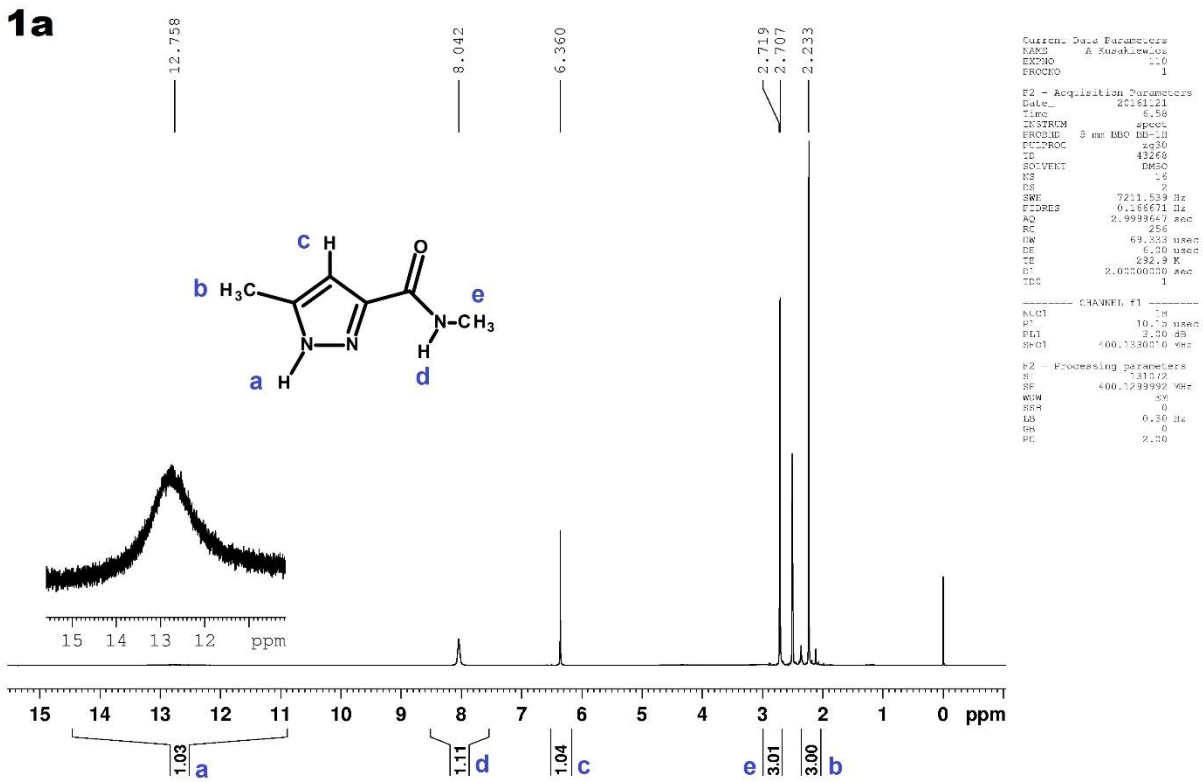

Figure 4S. ^{1}H NMR spectrum of *N*-methyl 5-methyl-1*H*-pyrazole-3-carboxylamide (**1a**) in DMSO-d_6.

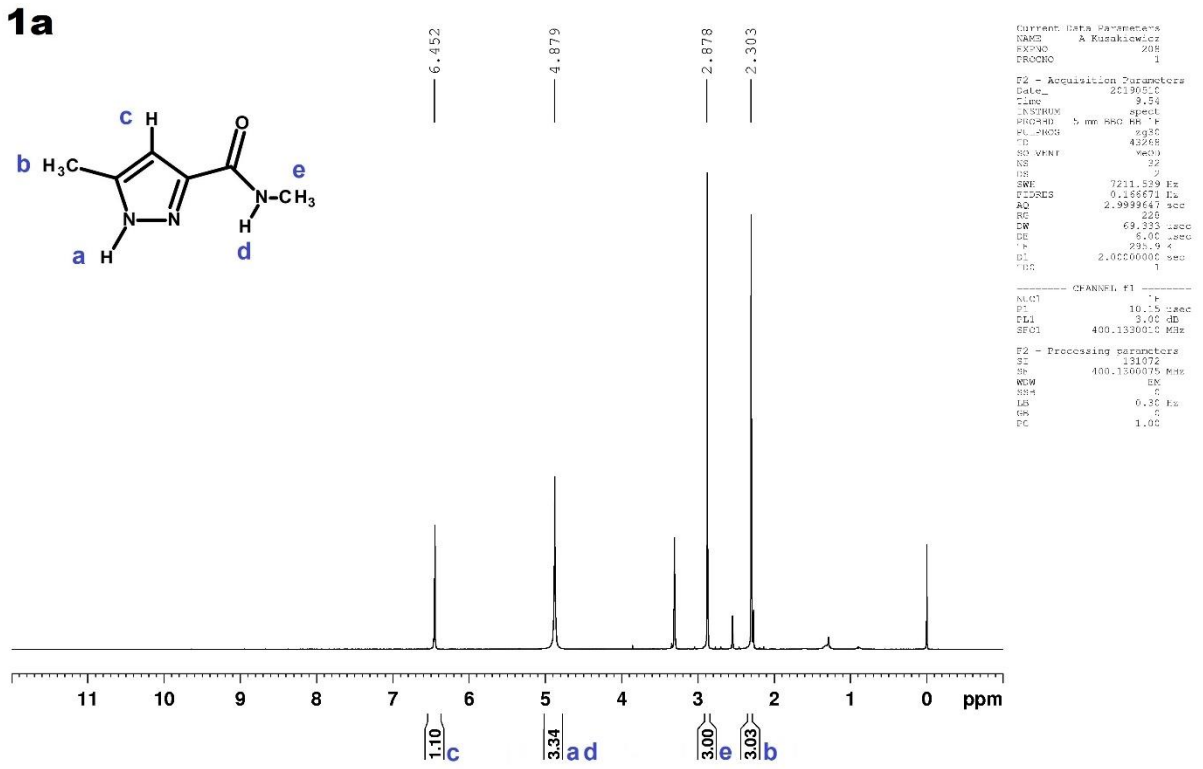

Figure 5S. ^{1}H NMR spectrum of *N*-methyl 5-methyl-1*H*-pyrazole-3-carboxylamide (**1a**) in CD_3OD.

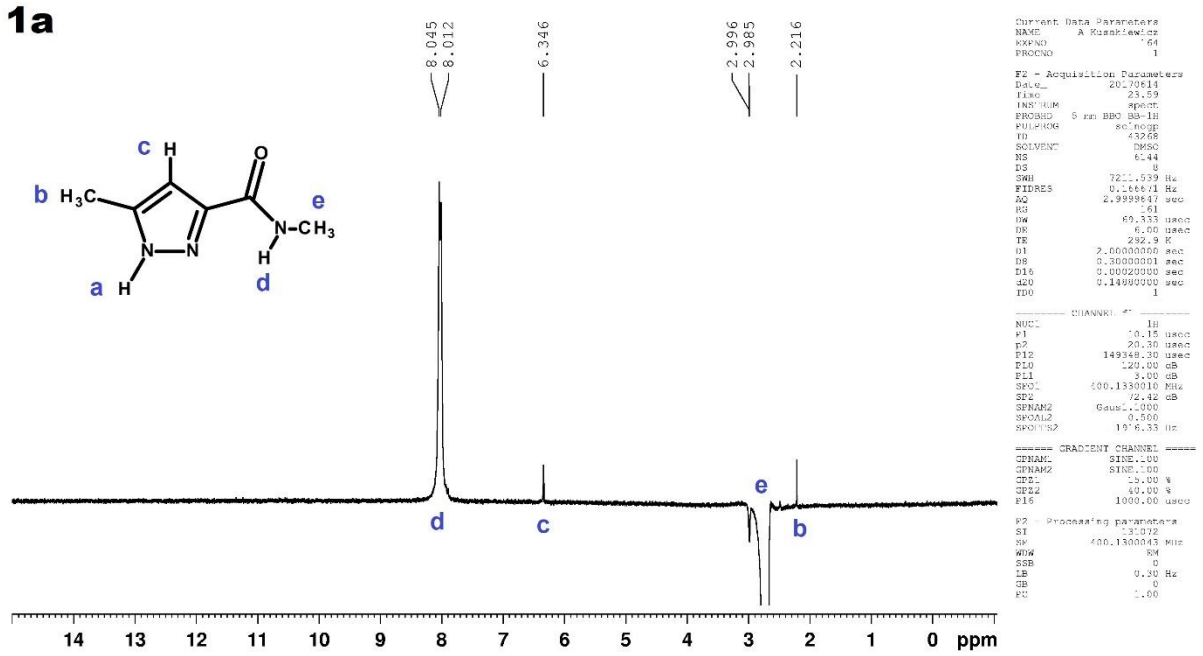

Figure 6S. NOE spectrum of *N*-methyl 5-methyl-1*H*-pyrazole-3-carboxylamide (**1a**) in DMSO-d_6.

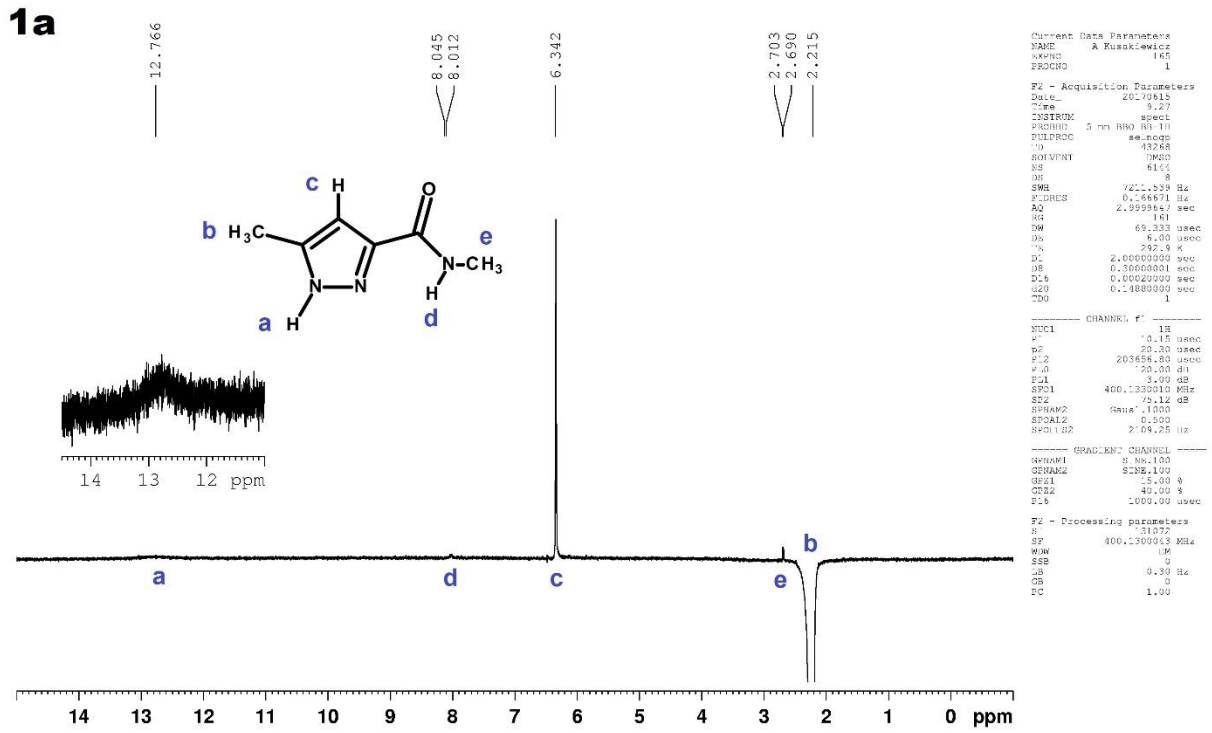

Figure 7S. NOE spectrum of *N*-methyl 5-methyl-*1H*-pyrazole-3-carboxylamide (**1a**) in DMSO-d_6.

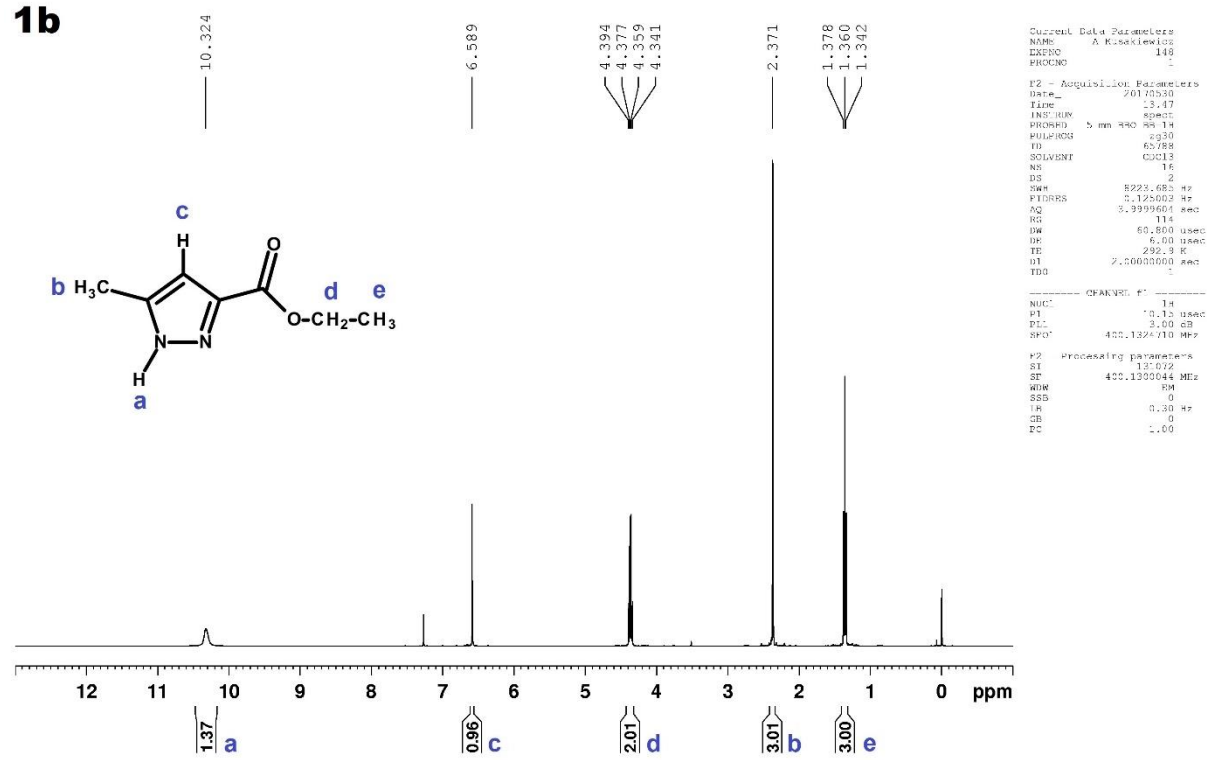

Figure 8S. ^{1}H NMR spectrum of ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (**1b**) in $CDCl_3$.

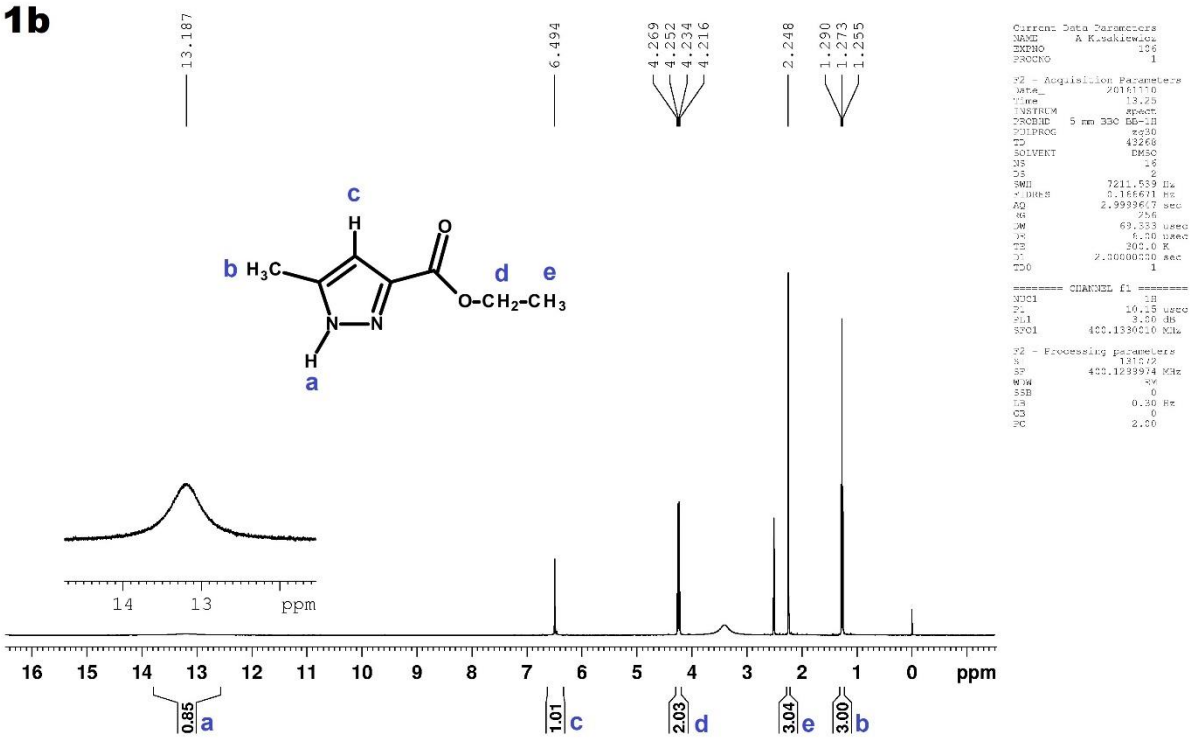

Figure 9S. ^{1}H NMR spectrum of ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (**1b**) in DMSO-d_6.

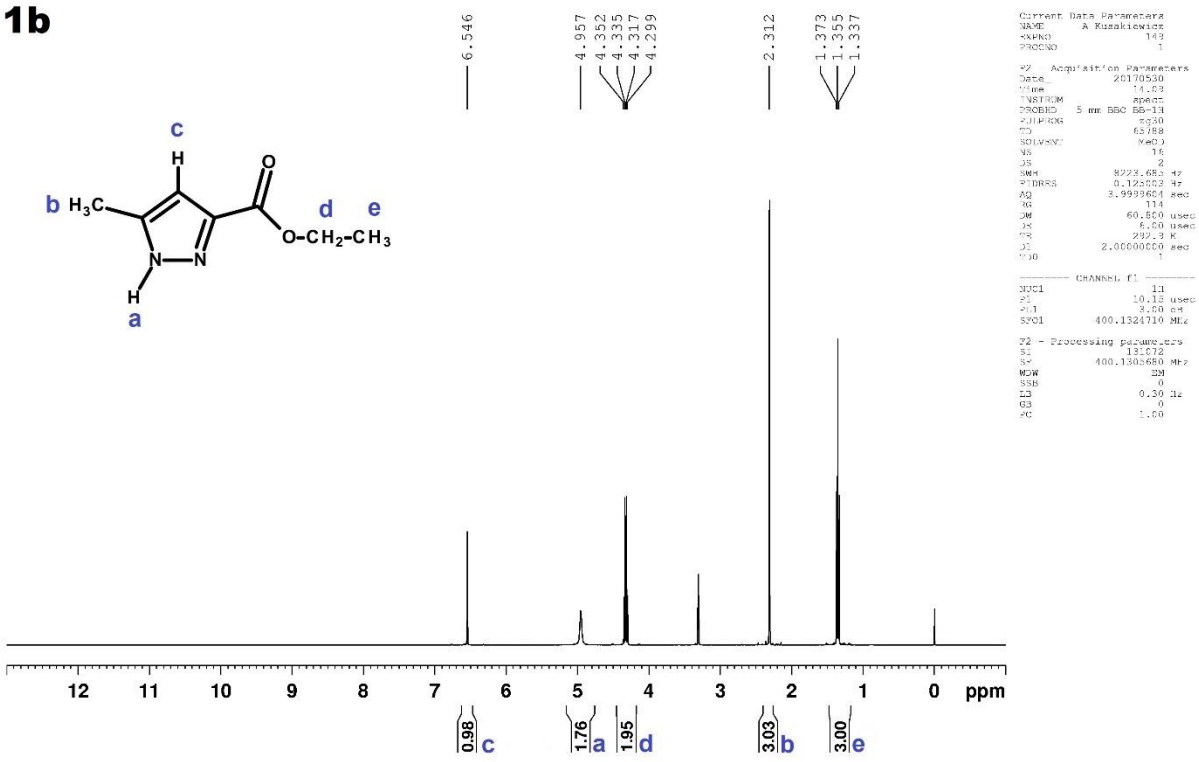

Figure 10S. ^{1}H NMR spectrum of ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (**1b**) in CD_3OD.

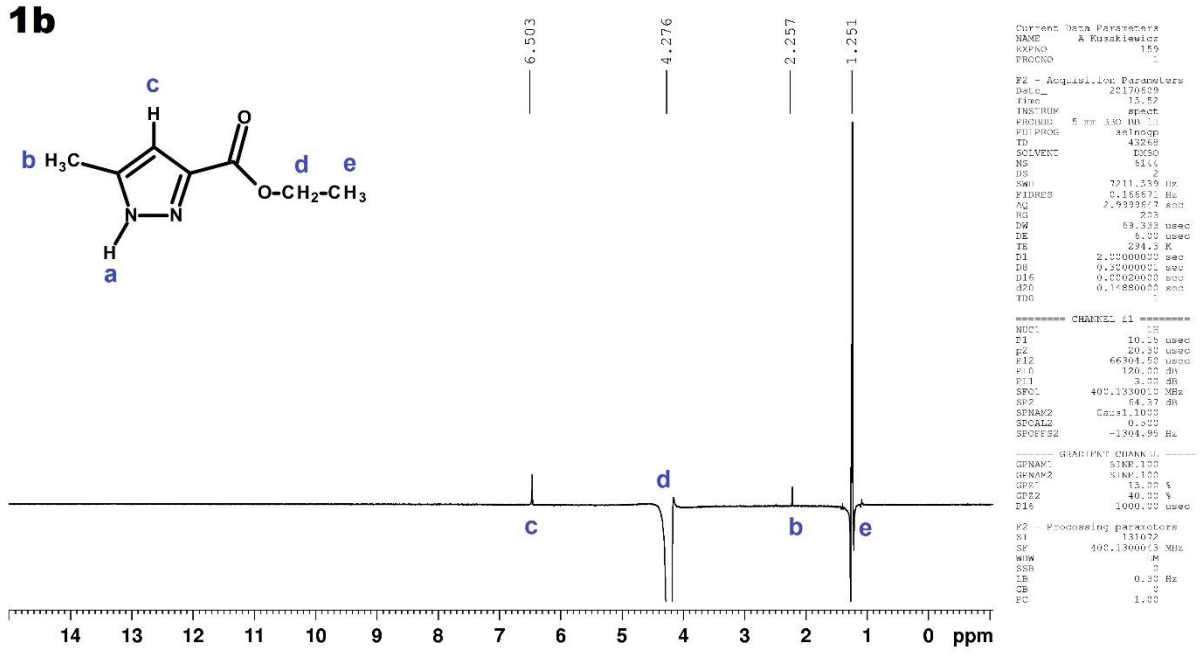

Figure 11S. NOE spectrum of ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (**1b**) in DMSO-d_6.

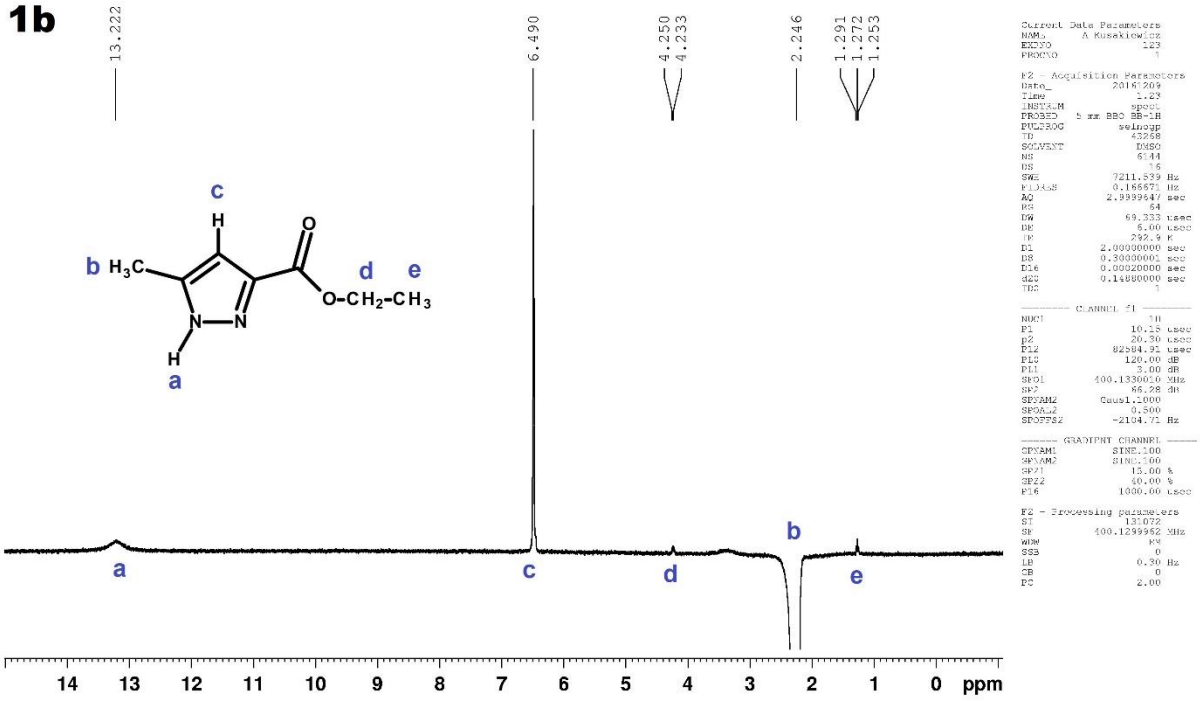

Figure 12S. NOE spectrum of ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (**1b**) in DMSO-d_6.

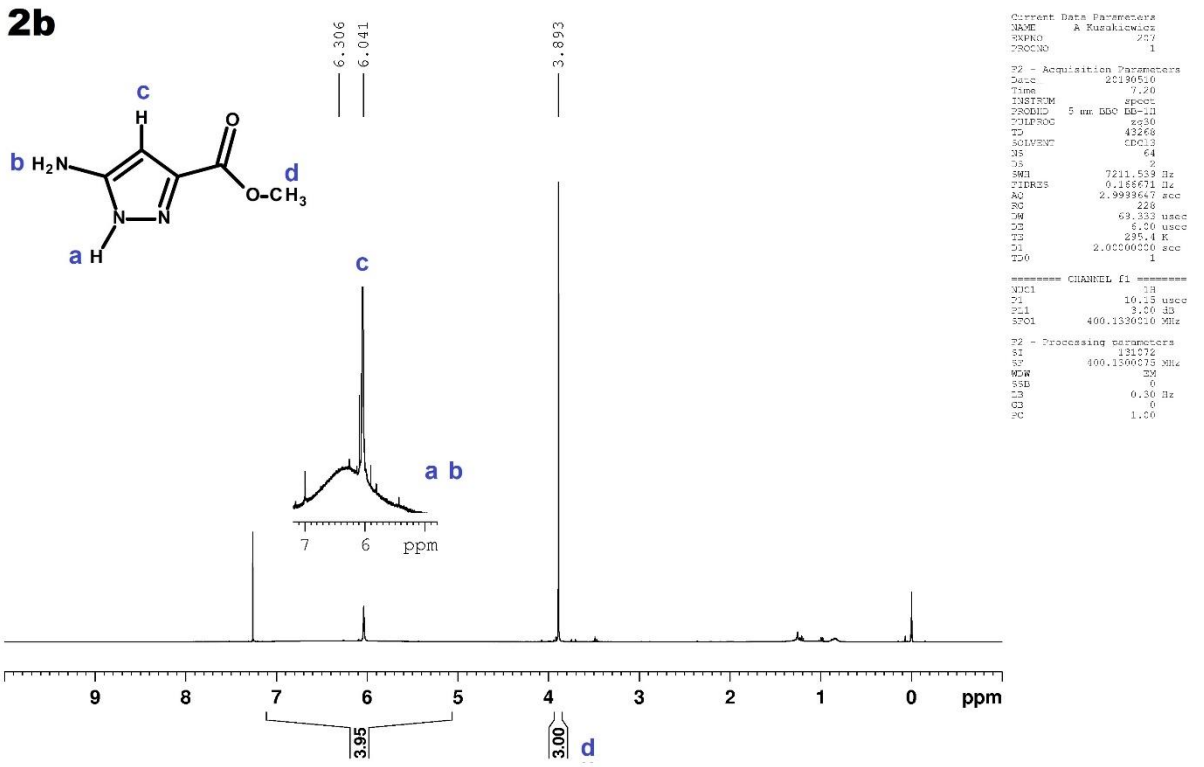

Figure 13S. ^{1}H NMR spectrum of methyl 5(3)-amino-1*H*-pyrazole-3(5)-carboxylate (**2b**) in $CDCl_3$.

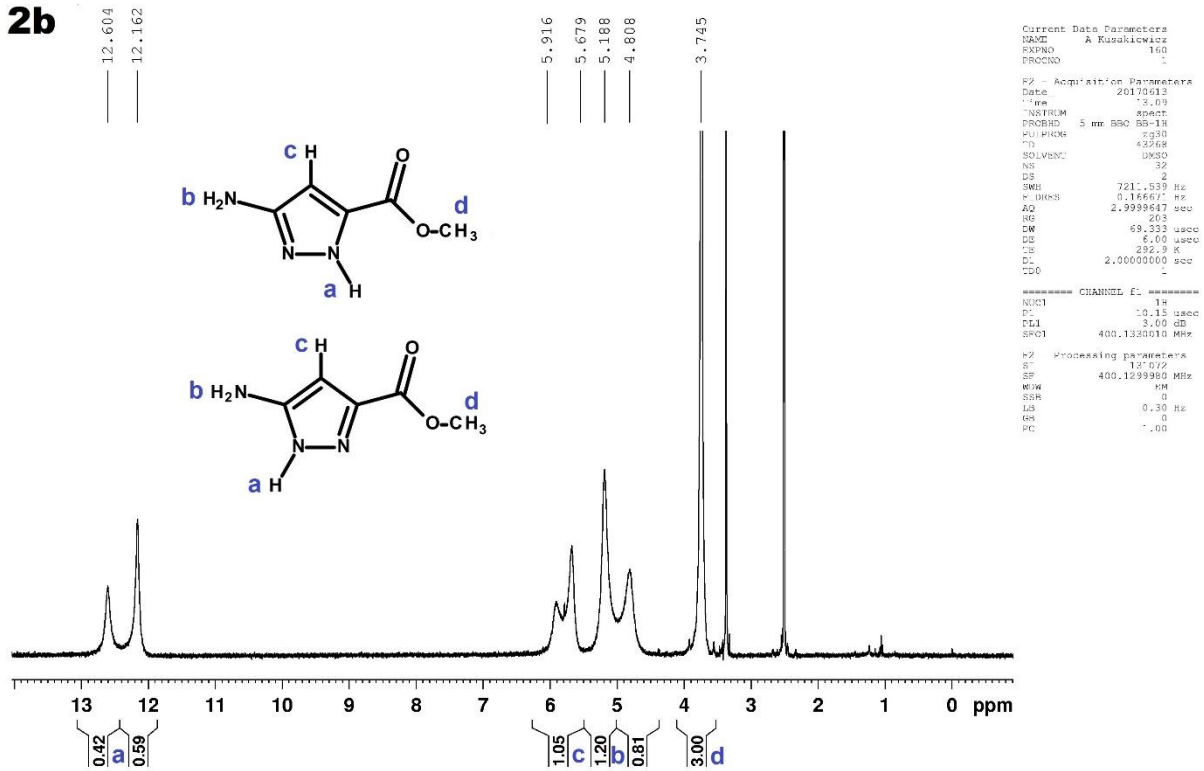

Figure 14S. ^{1}H NMR spectrum of methyl 5(3)-amino-1*H*-pyrazole-3(5)-carboxylate (**2b**) in DMSO-d_6.

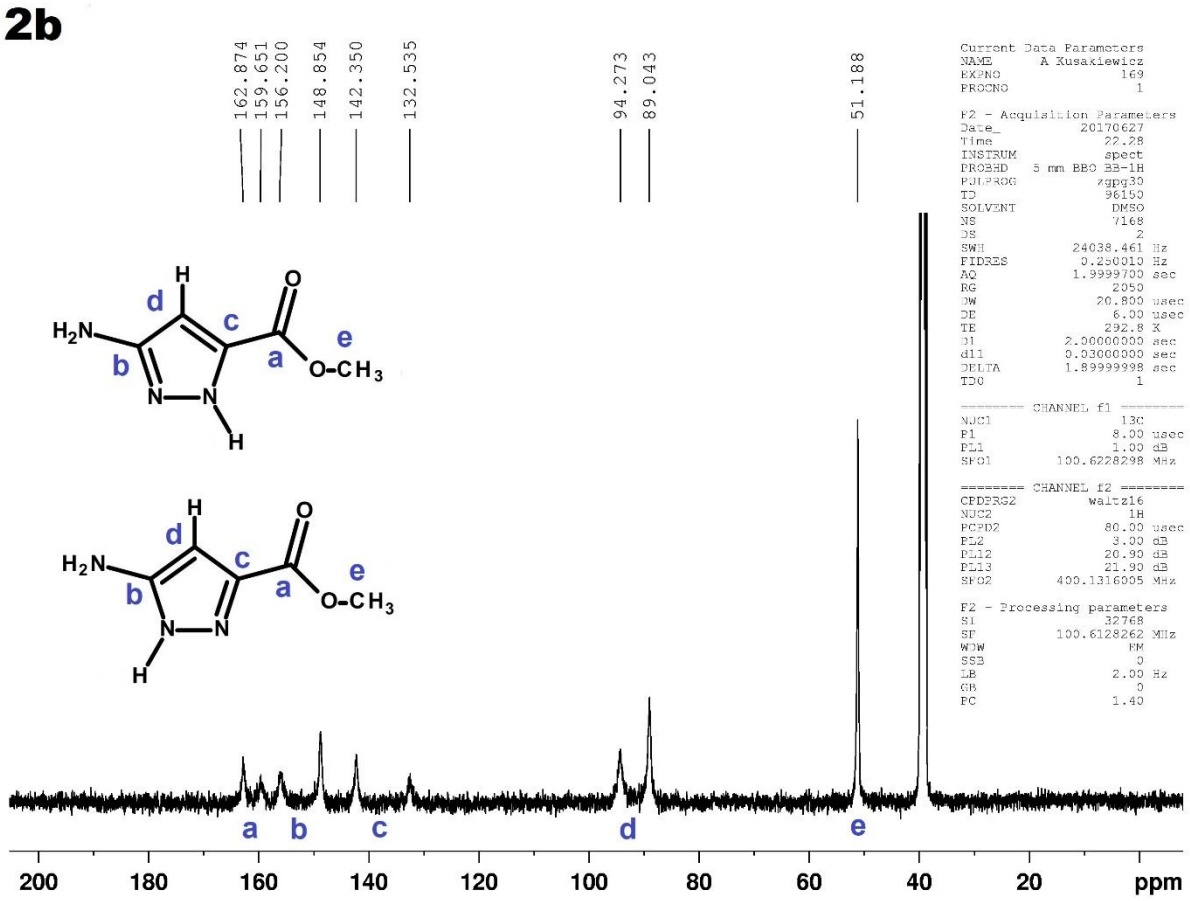

Figure 15S. ^{13}C NMR spectrum of methyl 5(3)-amino-1*H*-pyrazole-3(5)-carboxylate (**2b**) in DMSO-d_6.

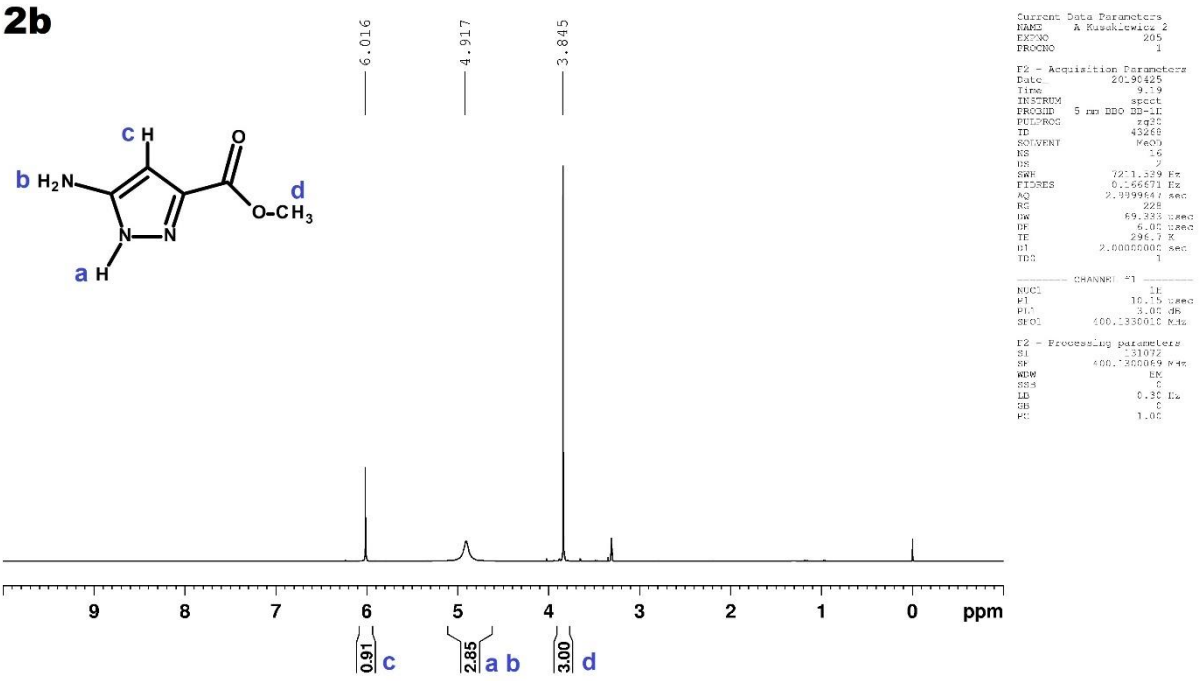

Figure 16S. ^{1}H NMR spectrum of methyl 5(3)-amino-1*H*-pyrazole-3(5)-carboxylate (**2b**) in CD_3OD.

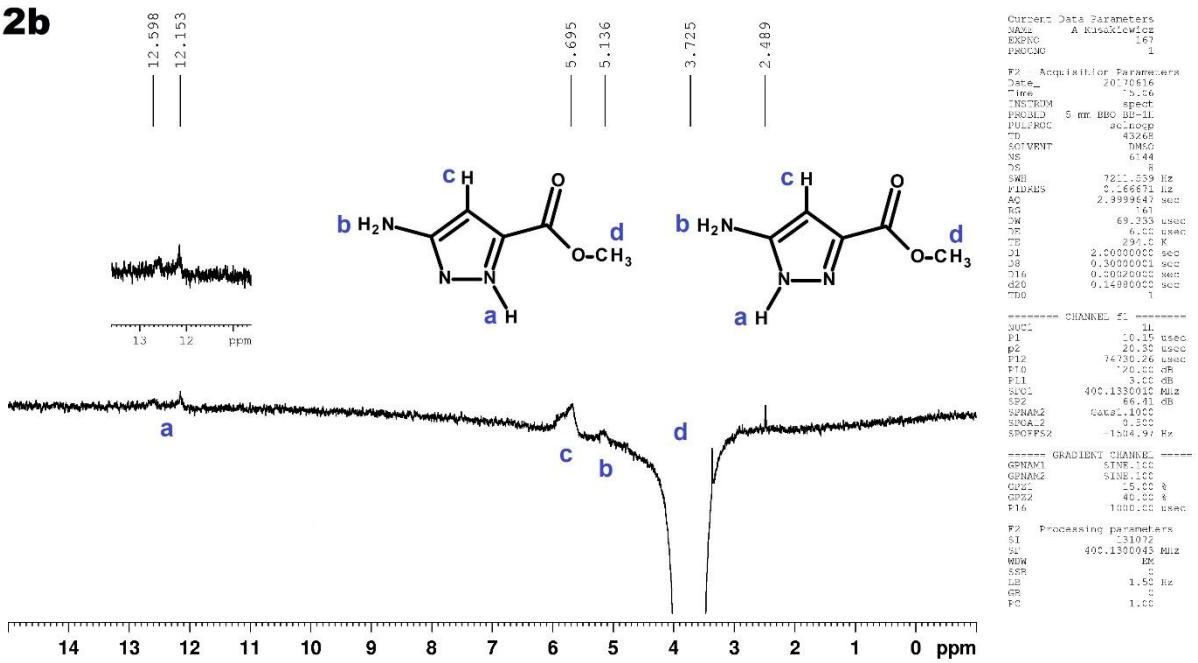

Figure 17S. NOE spectrum of methyl 5(3)-amino-1*H*-pyrazole-3(5)-carboxylate (**2b**) in DMSO-d_6.

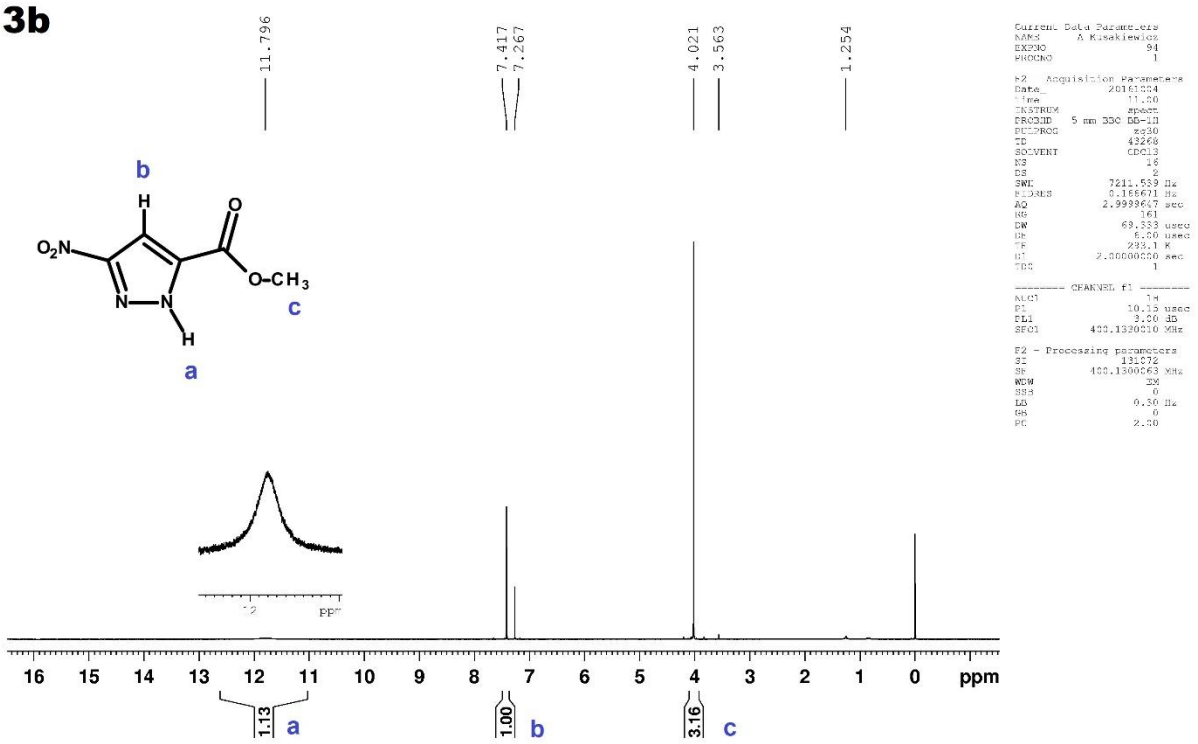

Figure 18S. ^{1}H NMR spectrum of methyl 3-nitro-1*H*-pyrazole-5-carboxylate (**3b**) in $CDCl_3$.

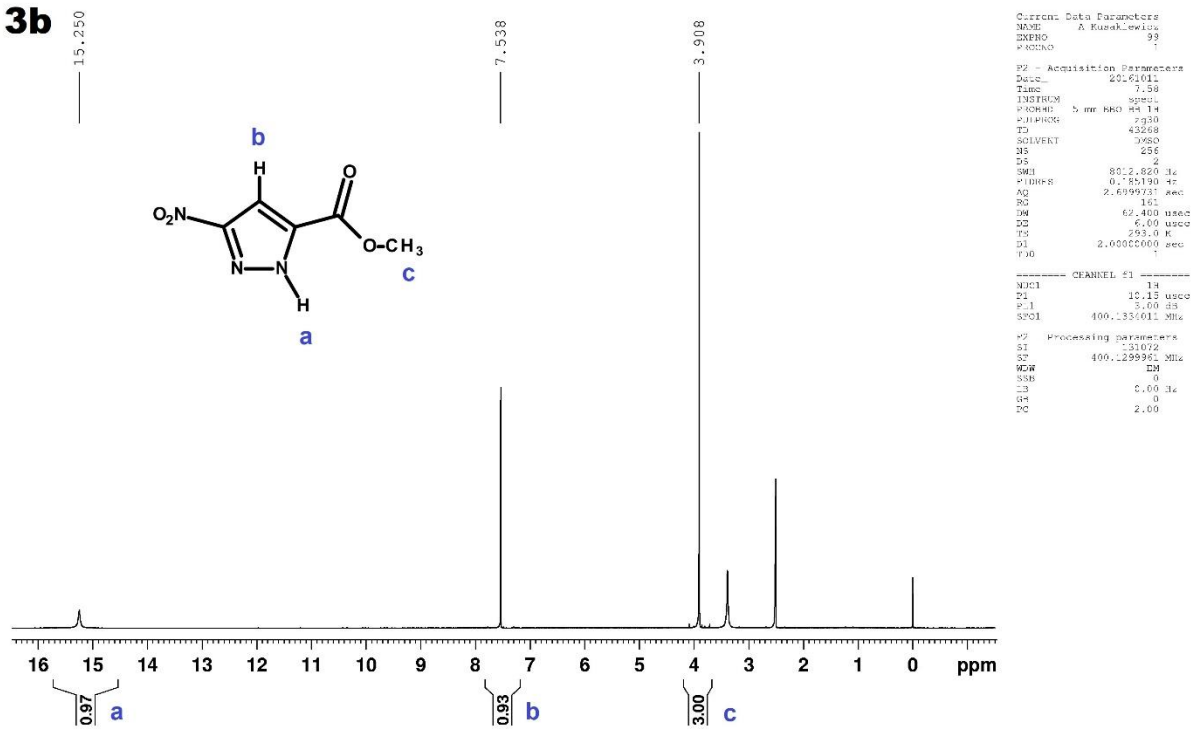

Figure 19S. ^{1}H NMR spectrum of methyl 3-nitro-1*H*-pyrazole-5-carboxylate (**3b**) in DMSO-d_6.

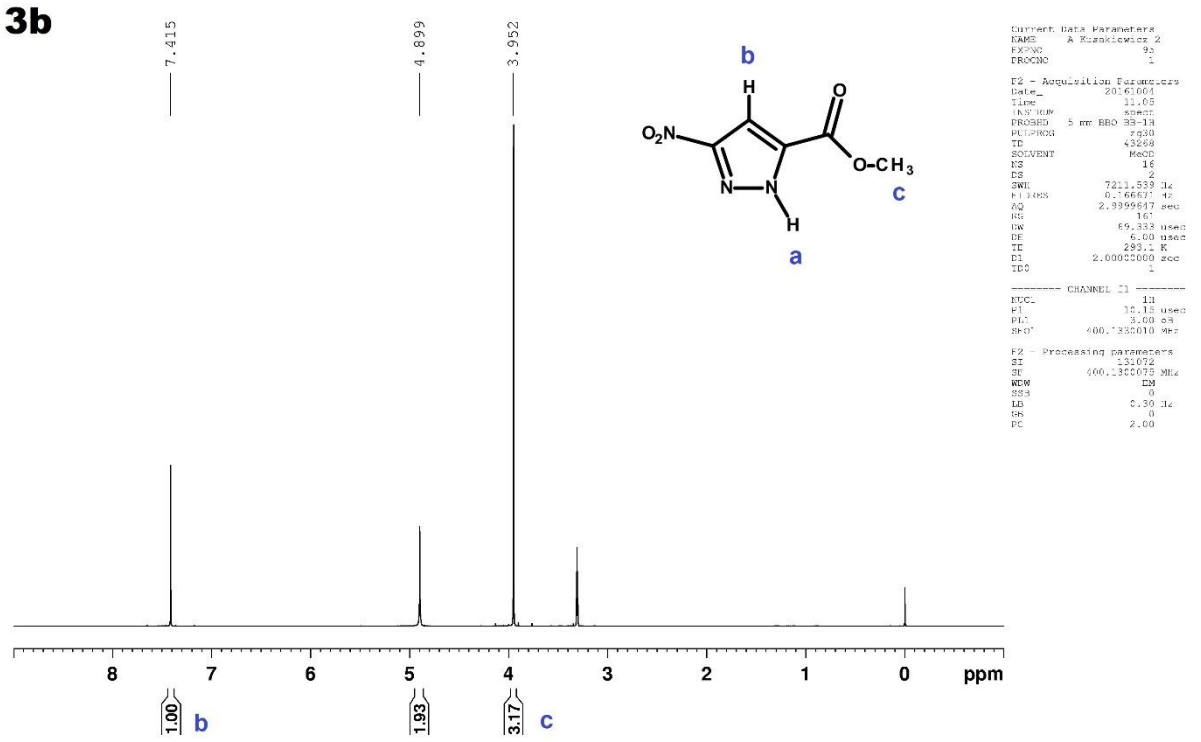

Figure 20S. ^{1}H NMR spectrum of methyl 3-nitro-1*H*-pyrazole-5-carboxylate (**3b**) in CD_3OD.

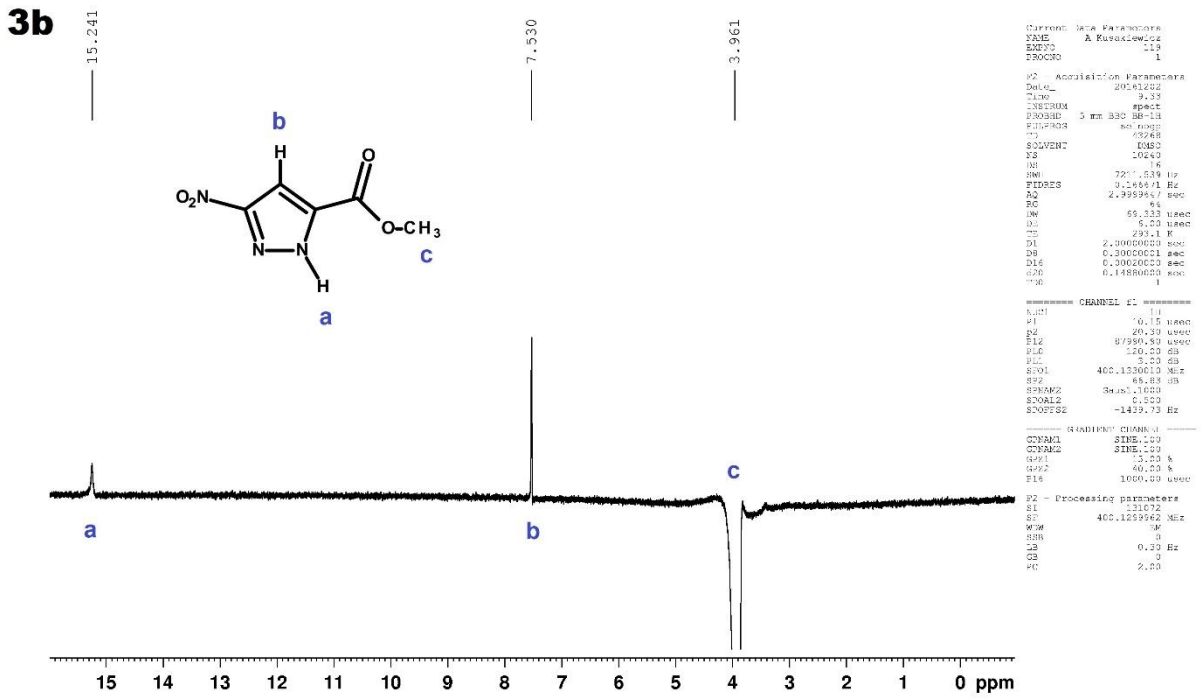

Figure 21S. NOE spectrum of methyl 3-nitro-1*H*-pyrazole-5-carboxylate (**3b**) in DMSO-d_6.

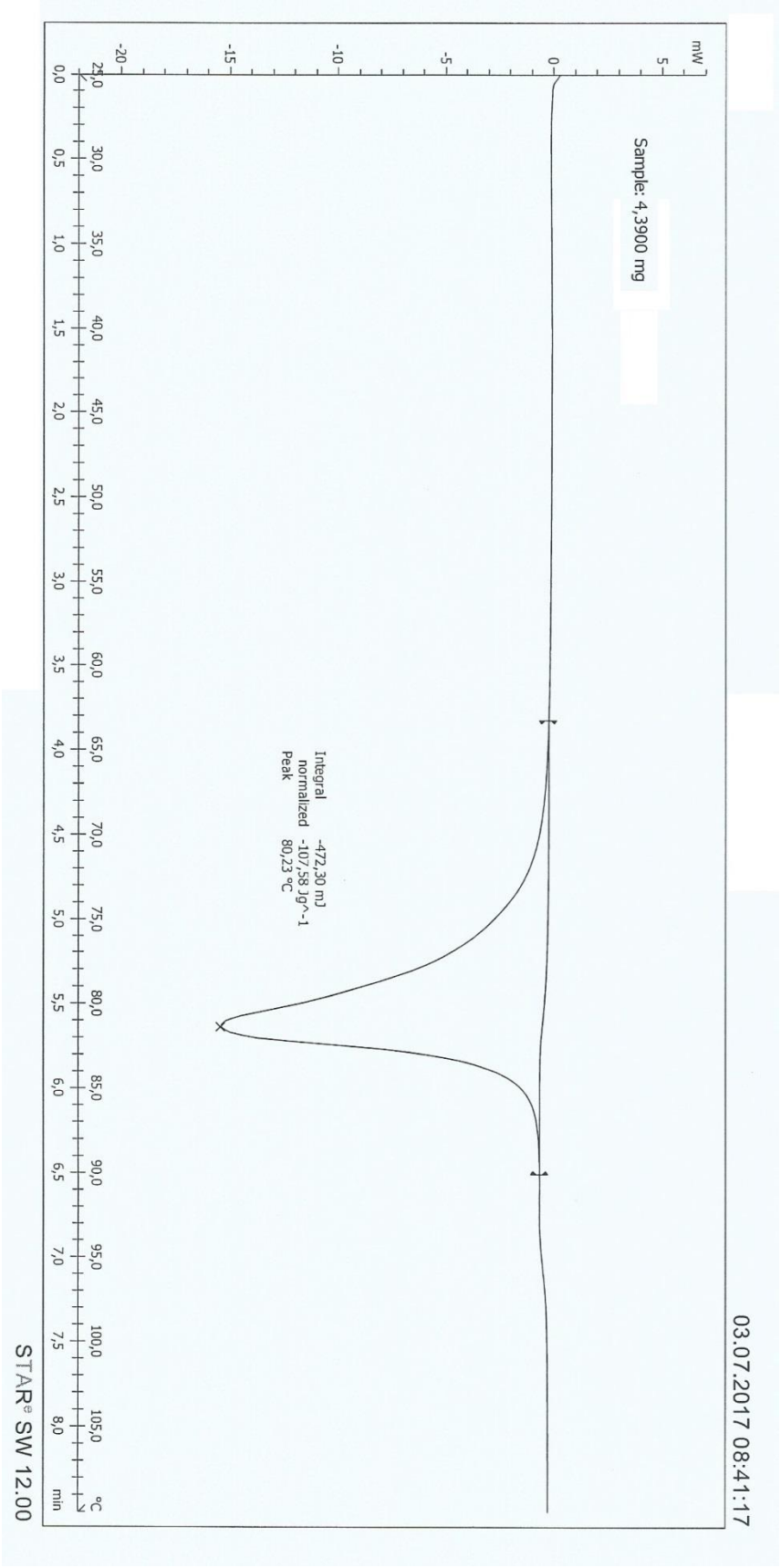

Figure 22S. DSC of ethyl 5-methyl-1H-pyrazole-3-carboxylate (**1b**)

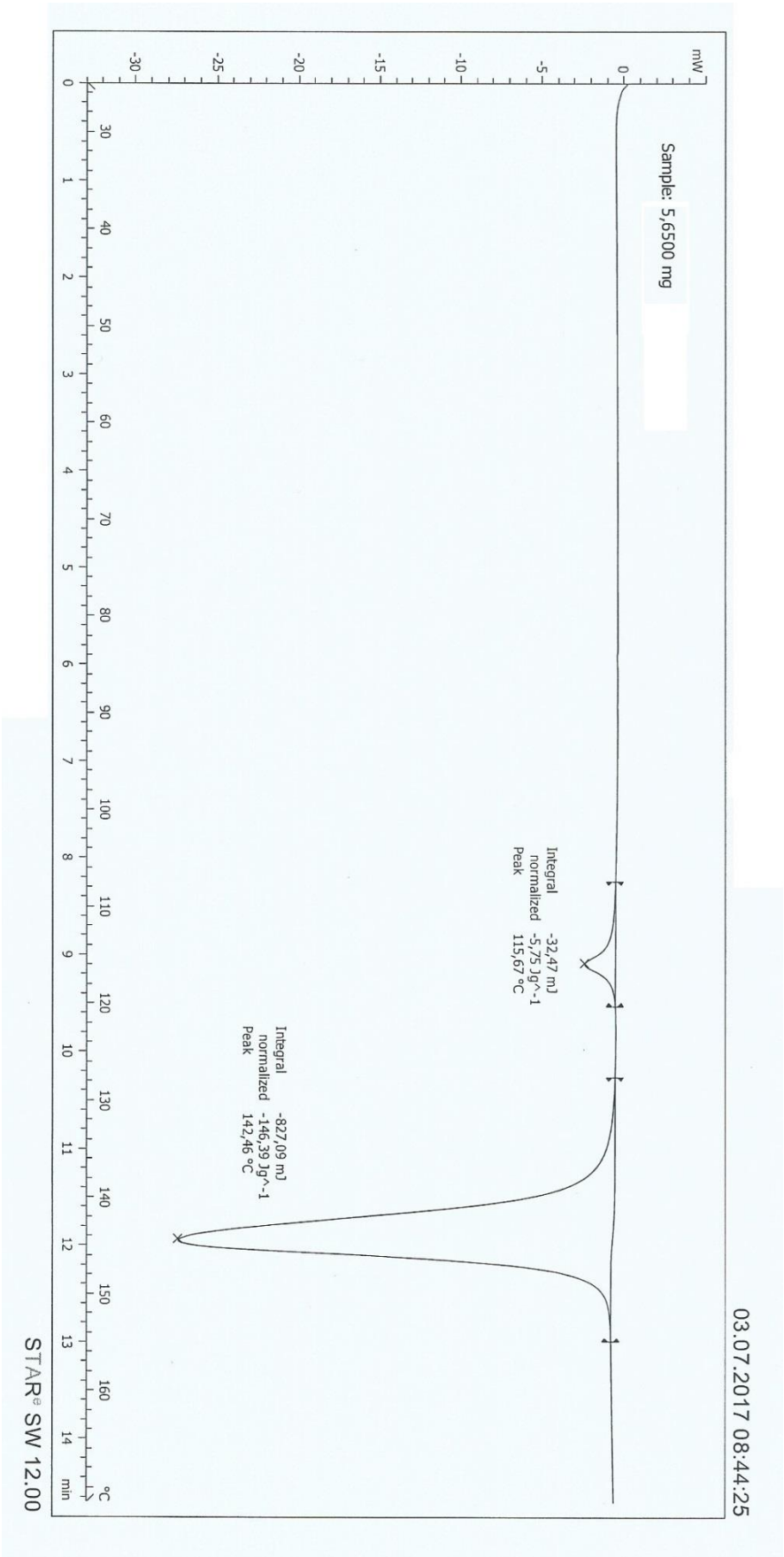

Figure 23S. DSC of methyl 5(3)-amino-1H-pyrazole-3(5)-carboxylate (**2b**)

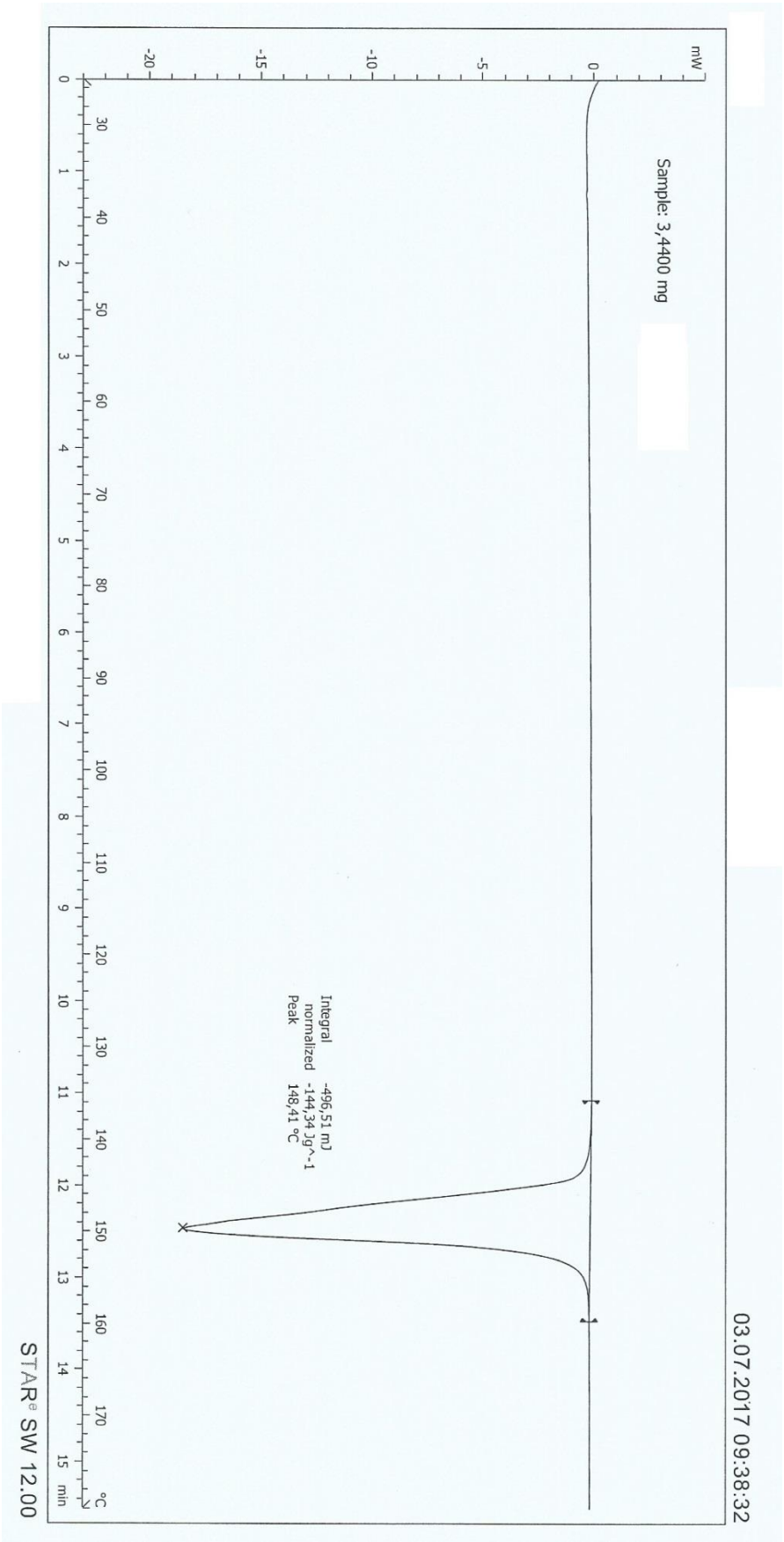

Figure 24S. DSC of methyl 3-nitro-1*H*-pyrazole-5-carboxylate (**3b**).