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Tandem A_N-A_N reactions in the synthesis of tetrahydrothiazolo-[4,5-*e*][1,2,4]triazines

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General. Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were measured on the instrument Boetius. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal reference. For products **3a-d** mass spectra were recorded on a SHIMADZU GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. The structure of compound **3a** was determined on an Xcalibur E X-ray diffractometer.

Starting 3-aryl-1,2,4-triazines **1a-c** were synthesized as described in literature [1].

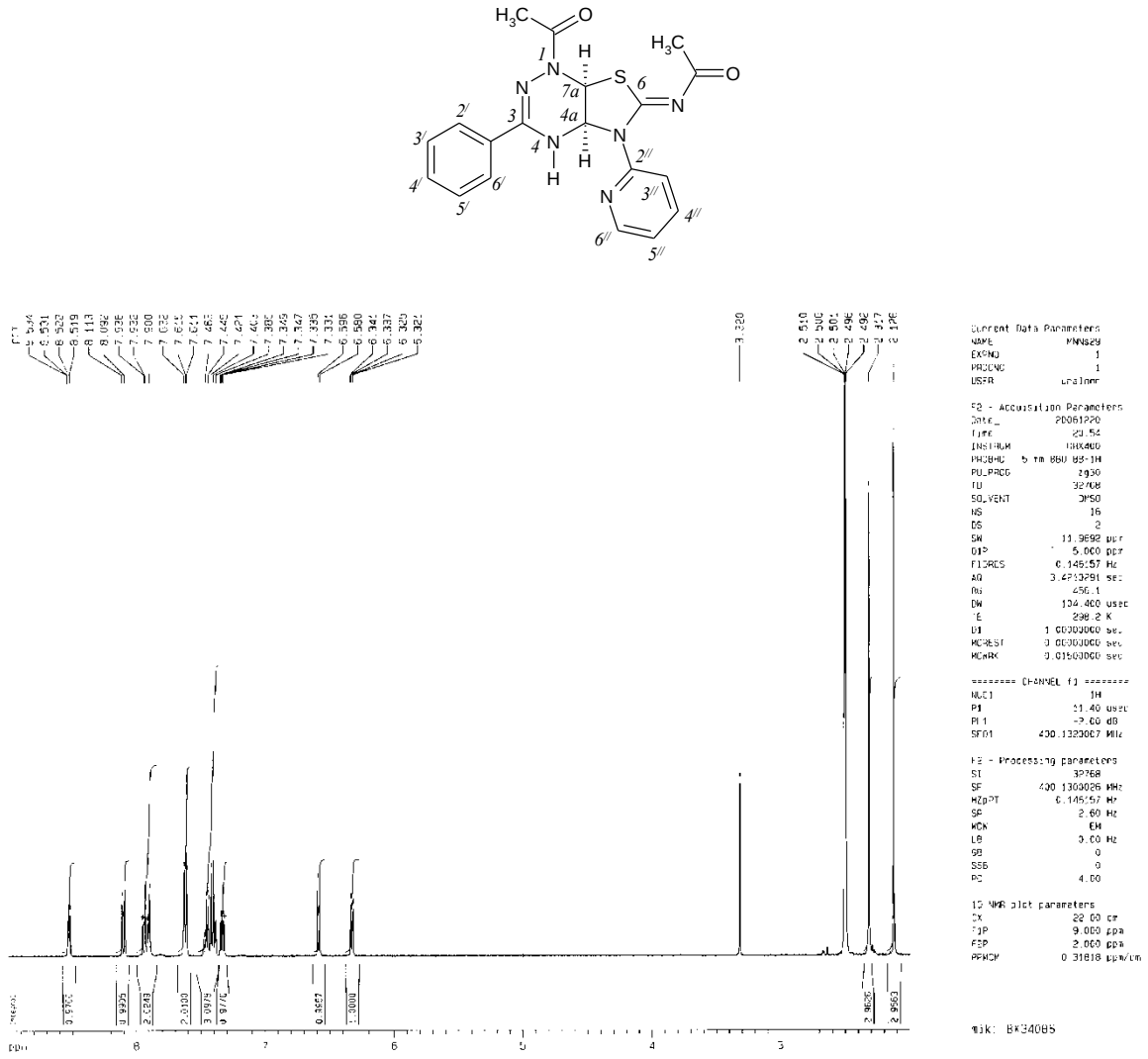


Figure S1 ^{1}H NMR (400.13 MHz) spectrum of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3a** in DMSO-d_6.

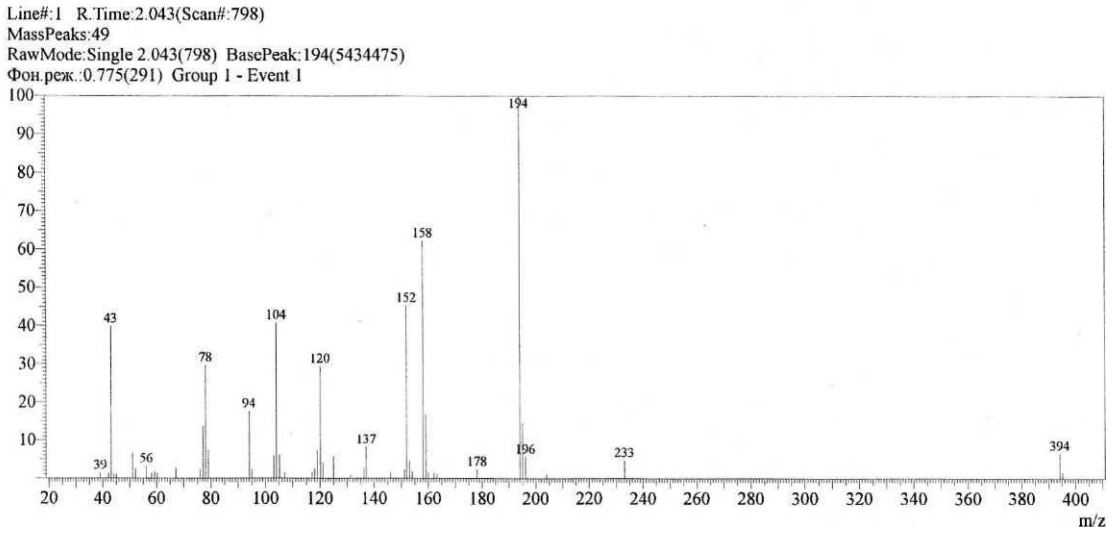
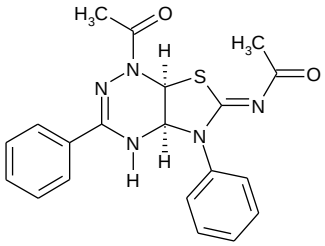


Figure S2 Mass spectrum (EI) of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3a.**



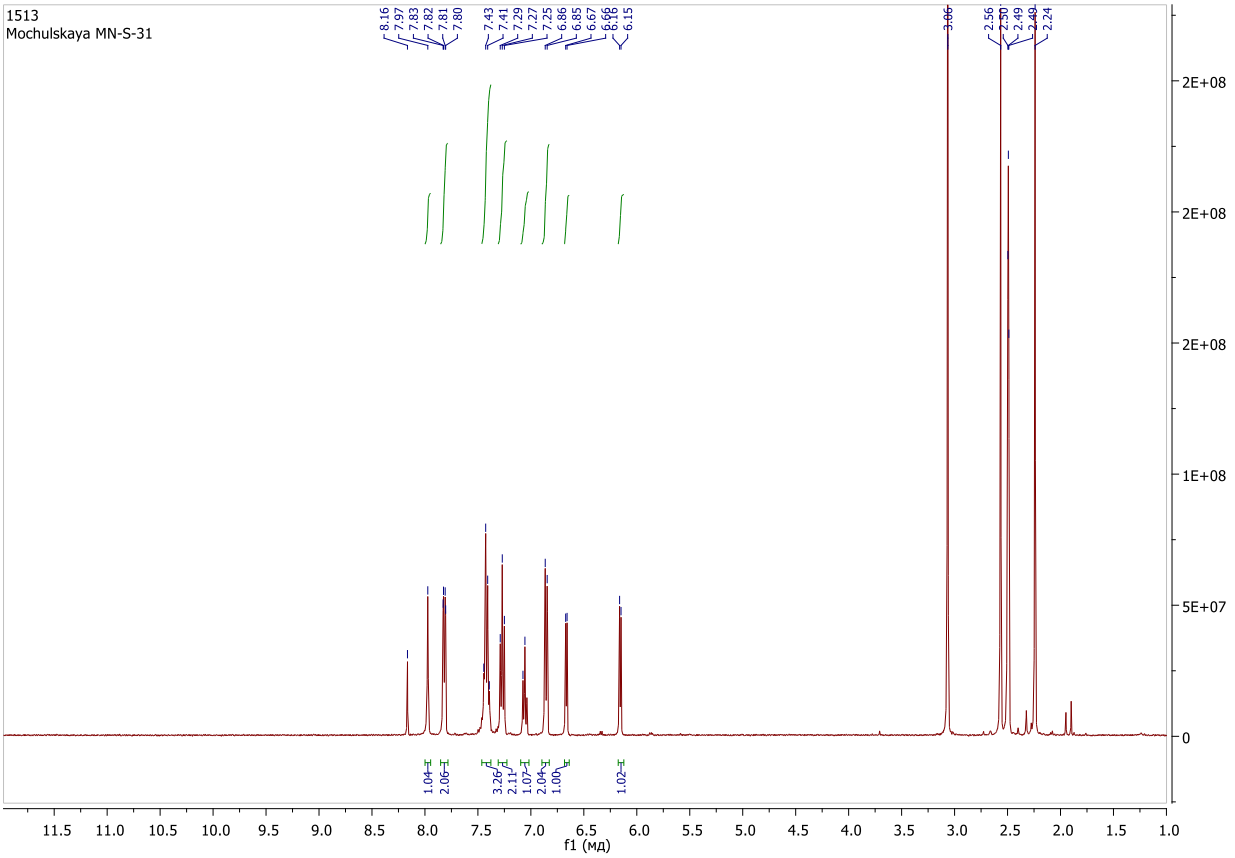


Figure S3 ^{1}H NMR (400.13 MHz) spectrum of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3b** in DMSO-d_6.

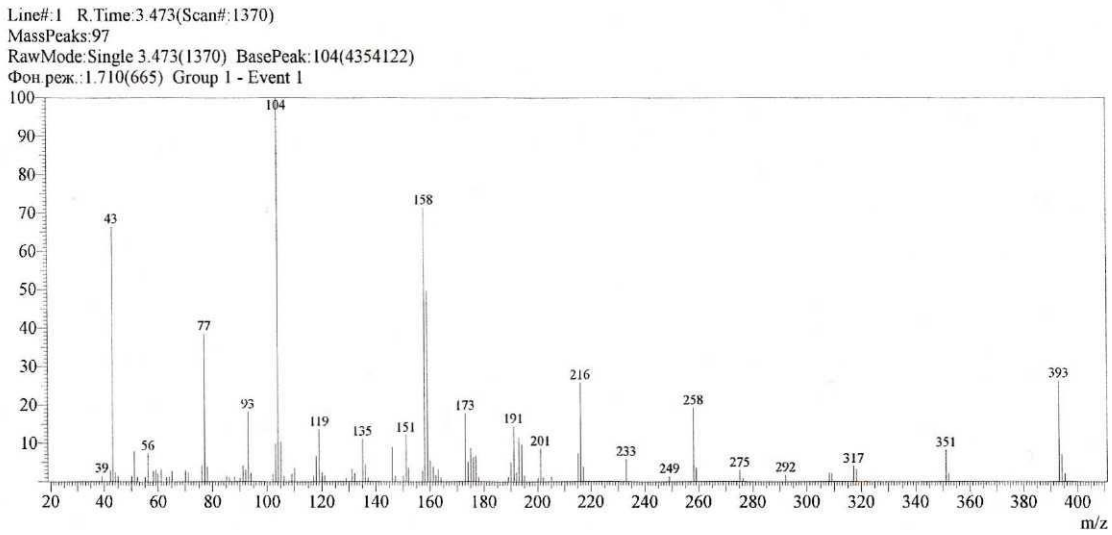
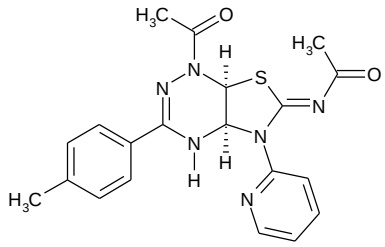


Figure S4 Mass spectrum (EI) of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3b.**



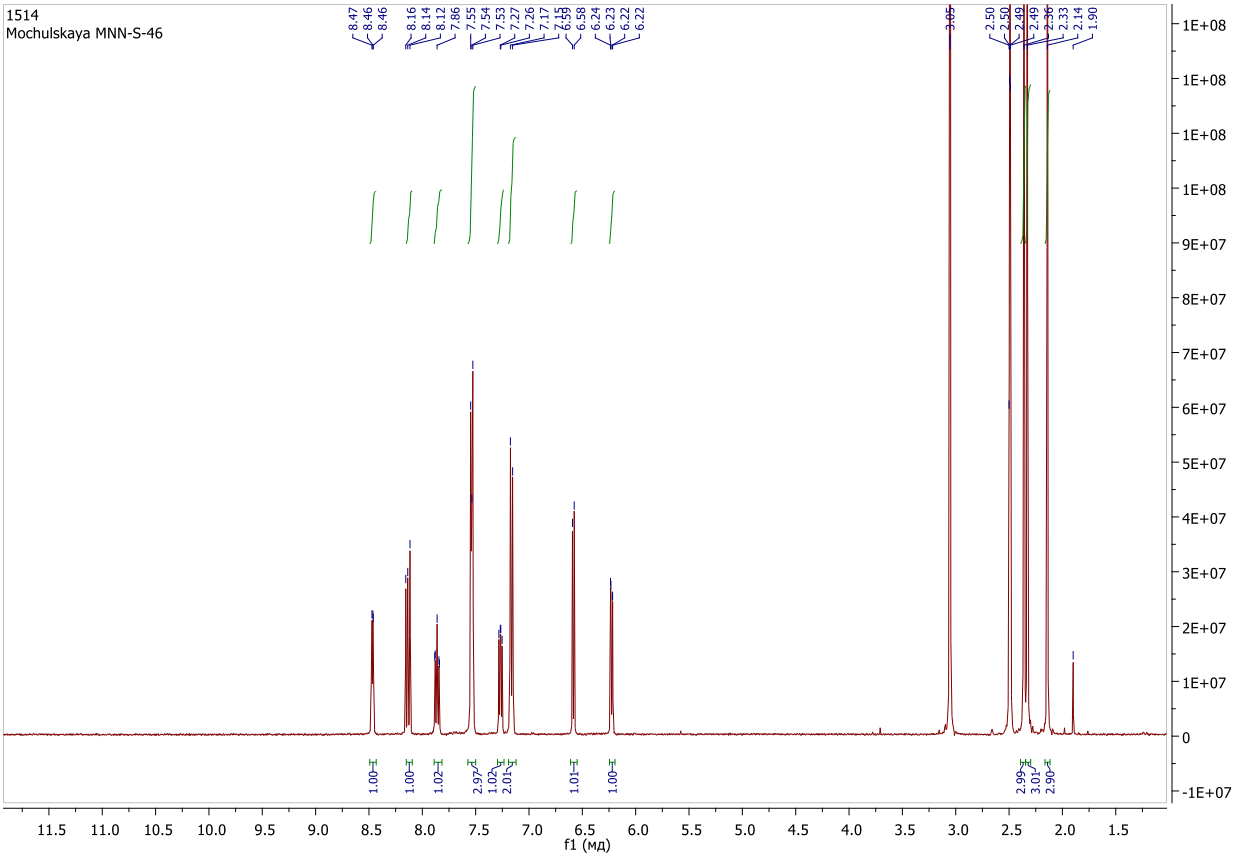


Figure S5 ^{1}H NMR (400.13 MHz) spectrum
of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3c** in DMSO-d_6.

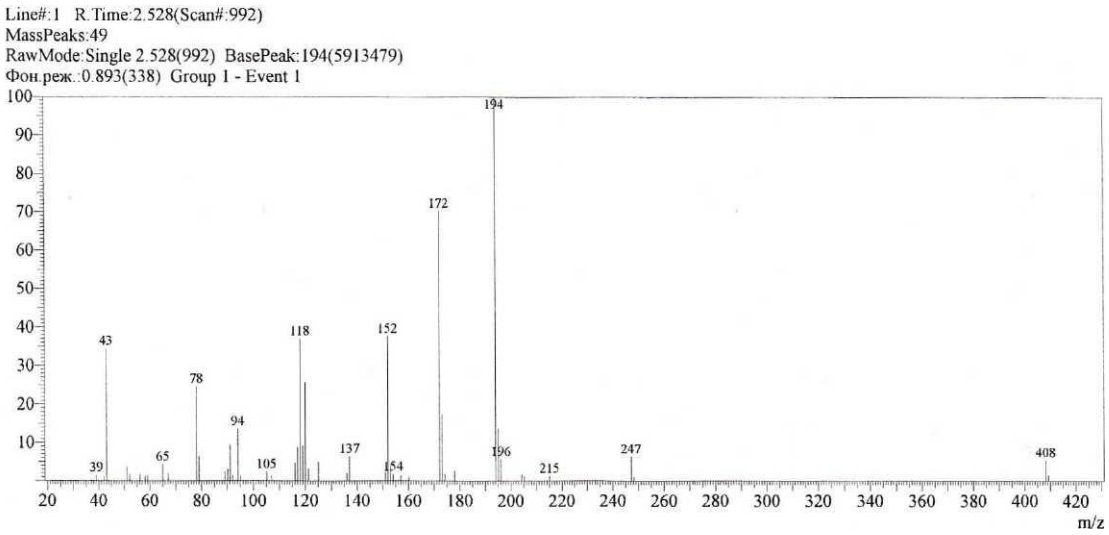


Figure S6 Mass spectrum (EI) of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3c.**

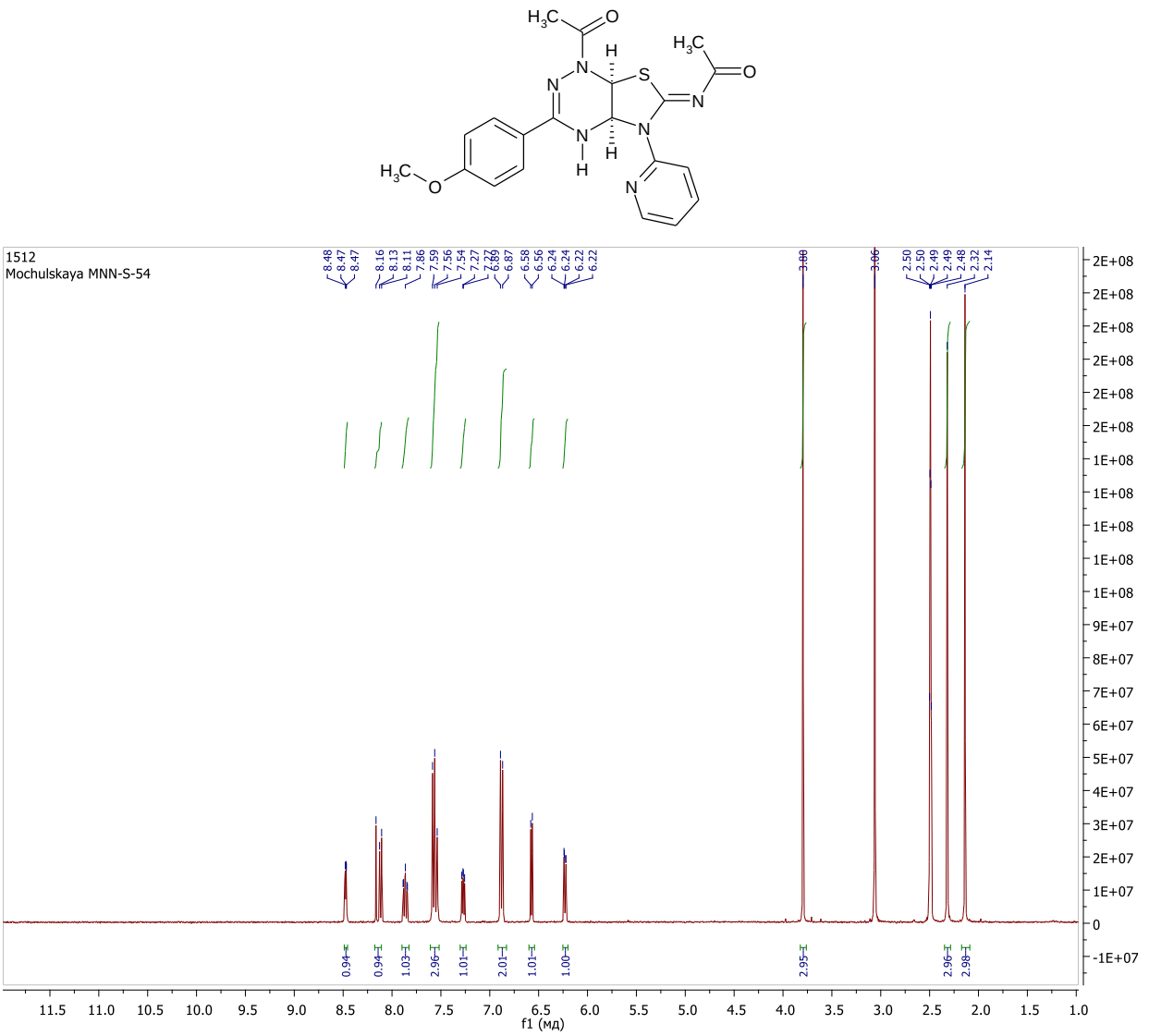


Figure S7 ^{1}H NMR (400.13 MHz) spectrum of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3d** in DMSO-d_6.

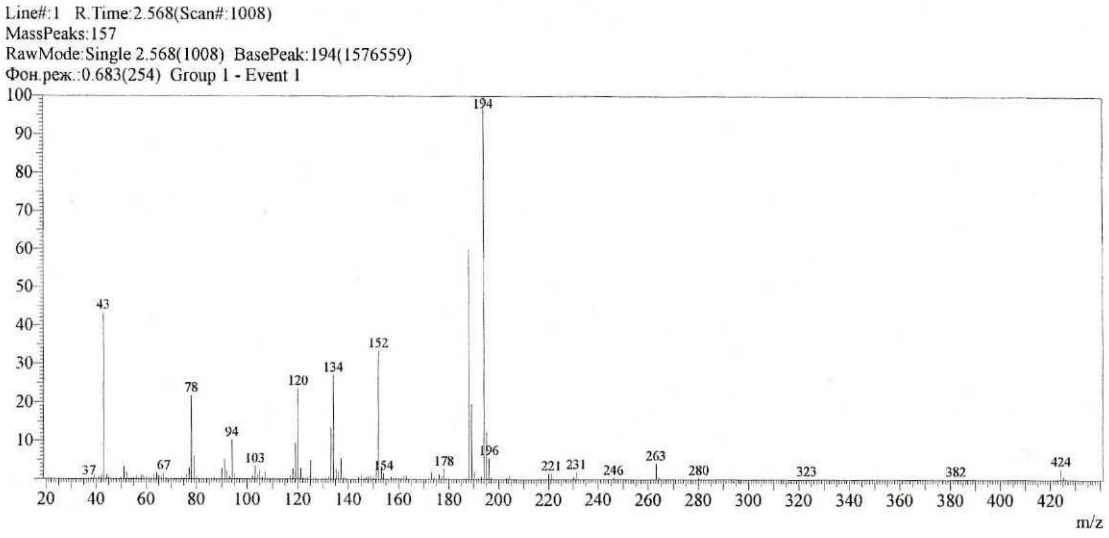


Figure S8 Mass spectrum (EI) of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3d.**

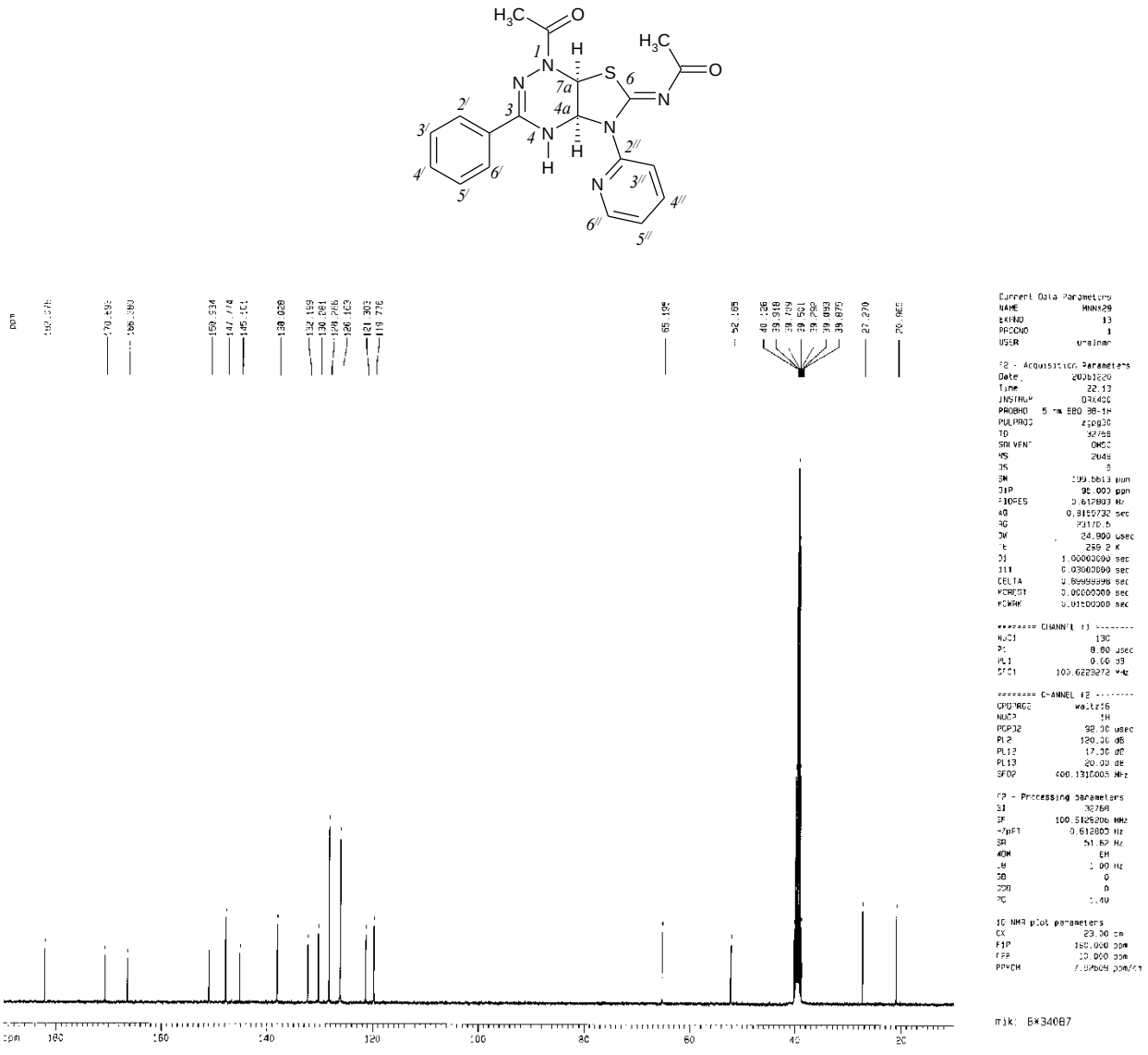


Figure S9 ^{13}C NMR (100.61 MHz) spectrum of tetrahydrothiazolo[4,5-*e*][1,2,4]triazine **3a** in DMSO-d_6.

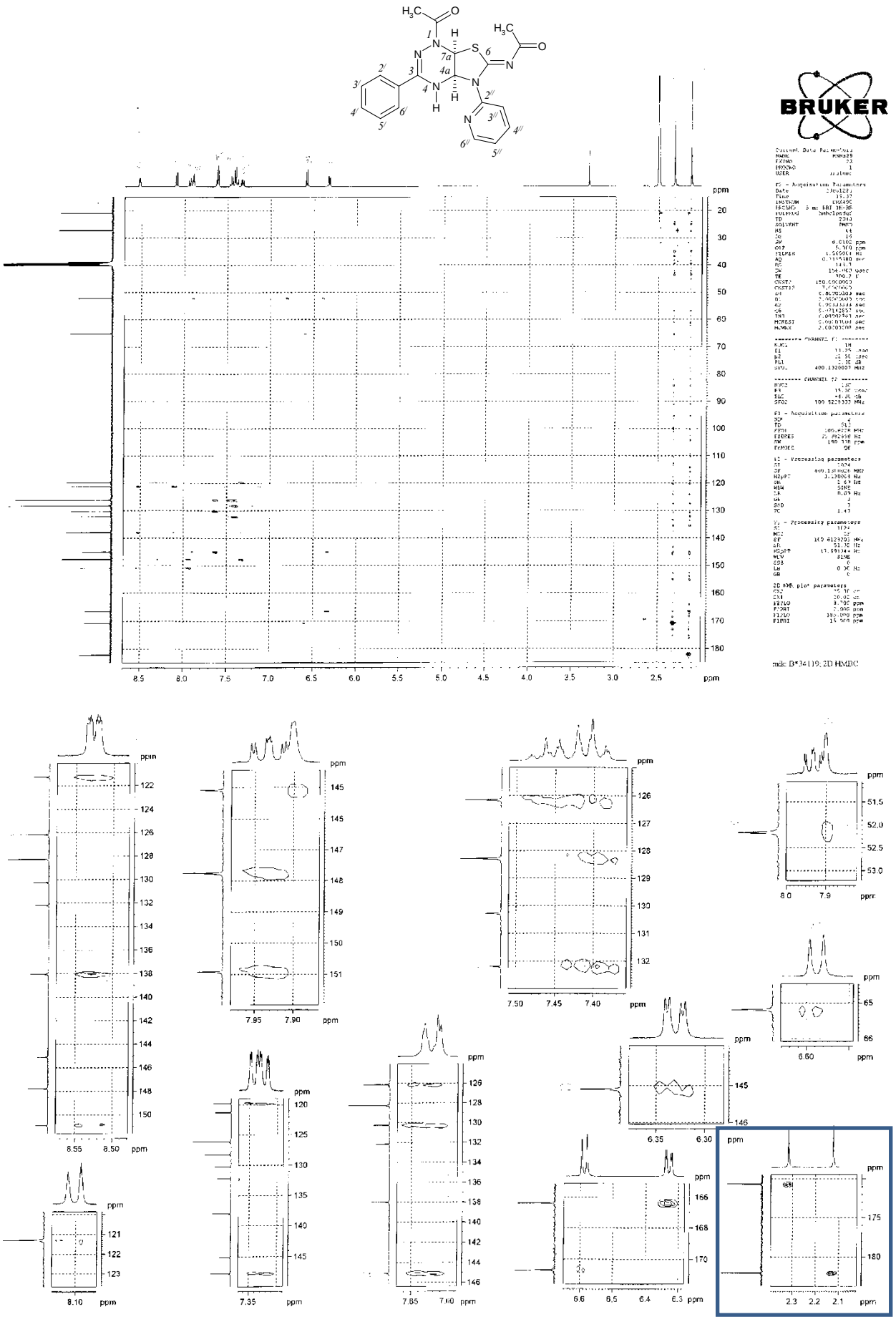


Figure S10 2D HMBS spectra of tetrahydrotniazolo[4,5-*e*][1,2,4]triazine **3a** in DMSO-d_6.

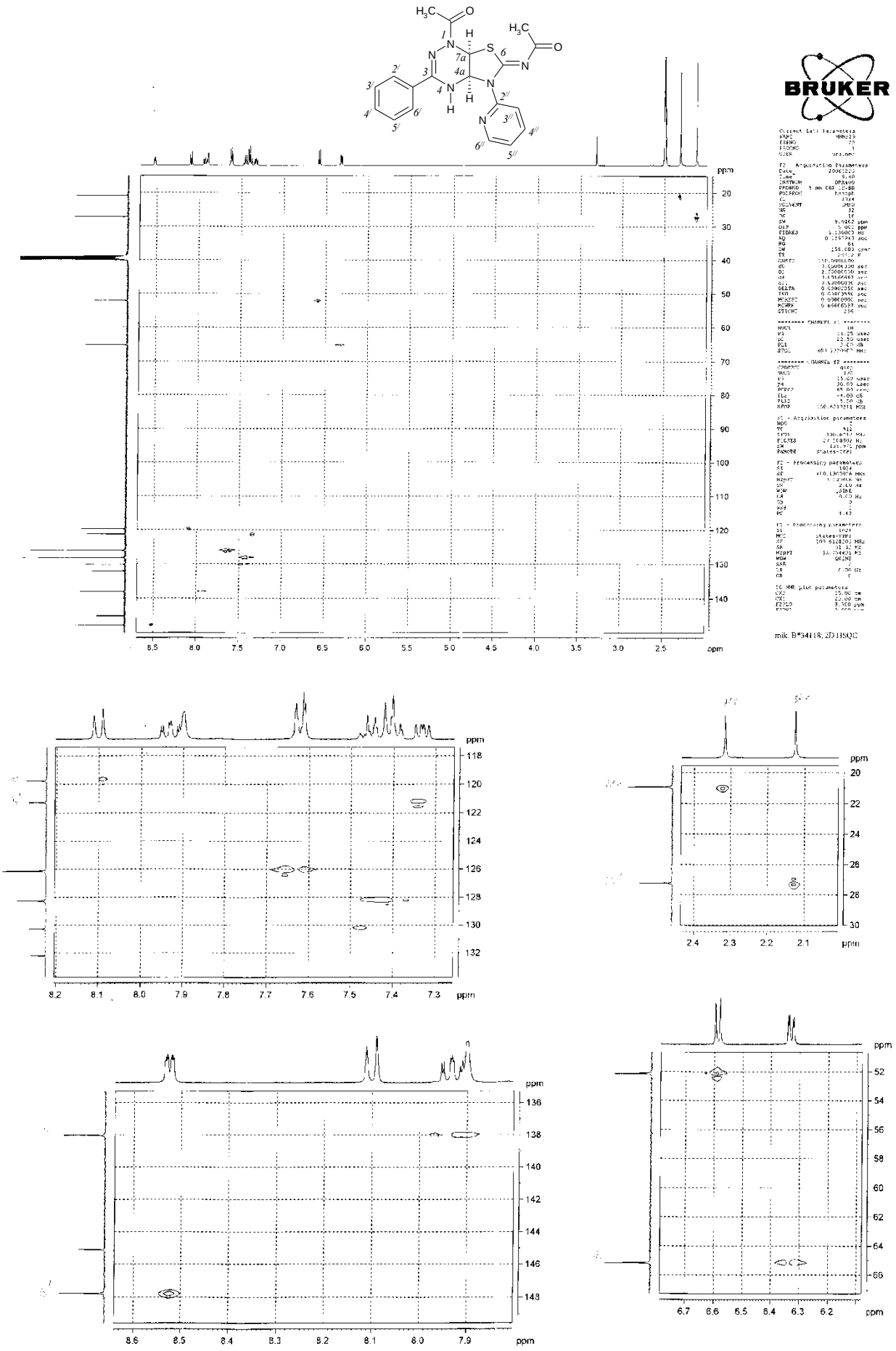


Figure S11 2D HSQC spectra of tetrahydrotniazolo[4,5-*e*][1,2,4]triazine **3a** in DMSO-d_6.

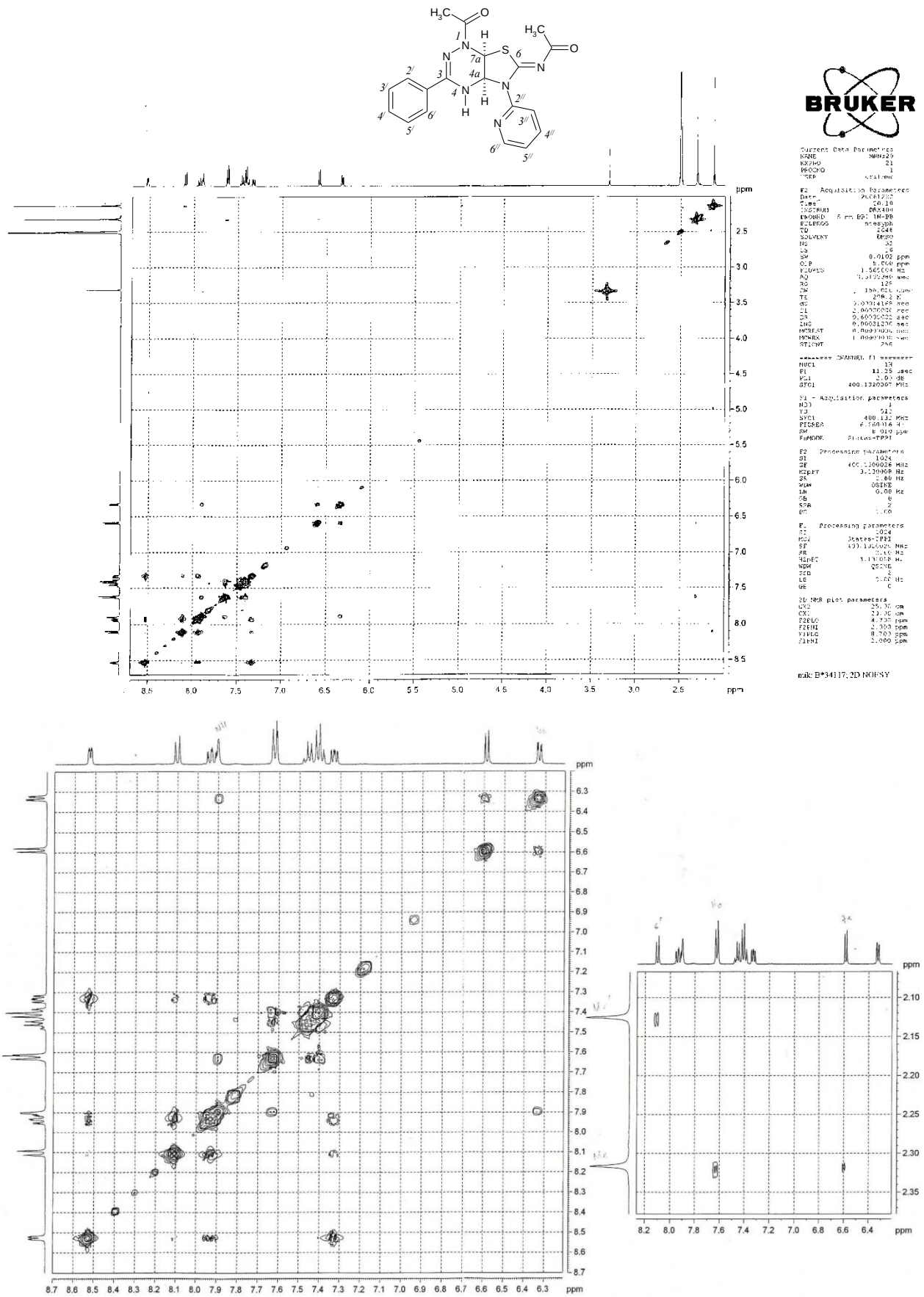


Figure S12 2D NOESY spectra of tetrahydrotniazolo[4,5-*e*][1,2,4]triazine **3a** in DMSO-d_6.

Table S1 Selected bond lengths (d) in the structure of **3a.**

Bond	d(Å)	Bond	d(Å)
S(1)-C(13)	1.753(2)	C(6)-C(7)	1.378(3)
S(1)-C(15)	1.837(2)	C(6)-C(11)	1.380(3)
N(5)-C(13)	1.293(3)	O(2)-C(18)	1.215(3)
N(5)-C(16)	1.385(3)	C(7)-C(8)	1.390(4)
N(1)-C(18)	1.367(3)	C(1)-N(6)	1.318(3)
N(1)-N(2)	1.397(3)	C(1)-C(2)	1.365(3)
N(1)-C(15)	1.441(3)	C(11)-C(10)	1.380(3)
O(1)-C(16)	1.219(3)	C(15)-C(14)	1.504(3)
N(2)-C(12)	1.284(3)	C(16)-C(17)	1.498(3)
C(13)-N(4)	1.375(3)	C(18)-C(19)	1.498(3)
N(3)-C(12)	1.354(3)	N(6)-C(5)	1.339(4)
N(3)-C(14)	1.450(3)	C(3)-C(4)	1.372(4)
N(3)-H(3)	0.81(3)	C(3)-C(2)	1.363(4)
C(12)-C(6)	1.488(3)	C(9)-C(8)	1.367(4)
N(4)-C(1)	1.426(3)	C(4)-C(5)	1.354(4)
N(4)-C(14)	1.459(3)	C(17)-H(17C)	1.372(4)

Table S2 Selected bond angles (ω) in the structure of **3a.**

Angle	ω (deg)	Angle	ω (deg)
C(13)-S(1)-C(15)	91.49(11)	C(2)-C(1)-N(4)	123.9(2)
C(13)-N(5)-C(16)	117.5(2)	C(6)-C(11)-C(10)	120.8(3)
C(18)-N(1)-N(2)	117.98(19)	N(1)-C(15)-C(14)	111.67(19)
C(18)-N(1)-C(15	119.66(19)	N(1)-C(15)-S(1)	112.62(16)
N(2)-N(1)-C(15)	121.80(18)	C(14)-C(15)-S(1)	105.70(15)
C(12)-N(2)-N(1)	114.93(19)	O(1)-C(16)-N(5)	124.3(2)
N(5)-C(13)-N(4)	121.3(2)	O(1)-C(16)-C(17)	121.7(2)
N(5)-C(13)-S(1	127.17(17)	N(5)-C(16)-C(17)	114.0(2)
N(4)-C(13)-S(1)	111.49(17)	O(2)-C(18)-N(1)	120.6(2)
C(12)-N(3)-C(14)	123.4(2)	O(2)-C(18)-C(19)	122.7(2)
N(2)-C(12)-N(3)	125.2(2)	N(1)-C(18)-C(19)	116.7(2)
N(2)-C(12)-C(6)	117.5(2)	C(1)-N(6)-C(5)	116.8(2)
N(3)-C(12)-C(6)	117.2(2)	N(3)-C(14)-N(4)	109.59(19)
C(13)-N(4)-C(1)	125.57(19)	N(3)-C(14)-C(15)	110.0(2)
C(13)-N(4)-C(14)	115.22(19)	N(4)-C(14)-C(15)	106.86(18)
C(1)-N(4)-C(14)	117.70(18)	C(4)-C(3)-C(2)	120.2(3)
C(7)-C(6)-C(11	118.5(2)	C(8)-C(9)-C(10)	119.4(3)
C(7)-C(6)-C(12)	122.1(2)	C(1)-C(2)-C(3)	118.1(2)
C(11)-C(6)-C(12)	119.4(2)	C(9)-C(10)-C(11)	120.4(3)
C(6)-C(7)-C(8)	120.5(2)	C(9)-C(8)-C(7)	120.4(3)
N(6)-C(1)-C(2)	123.3(2)	C(5)-C(4)-C(3)	117.2(3)
N(6)-C(1)-N(4)	112.7(2)	N(6)-C(5)-C(4)	124.5(3)

References

1 M.O′Rourke, S.A. Lang, Jr. and E.Cohen, *J. Med. Chem.*, 1977, **20**, 723.