Supporting Information

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1-Trifluoromethyl-prop-2-yne 1-iminium salts and 1-imines: reactions with the mesoionic „Nitron“

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Contents

1. Selected ^{1}H NMR spectra

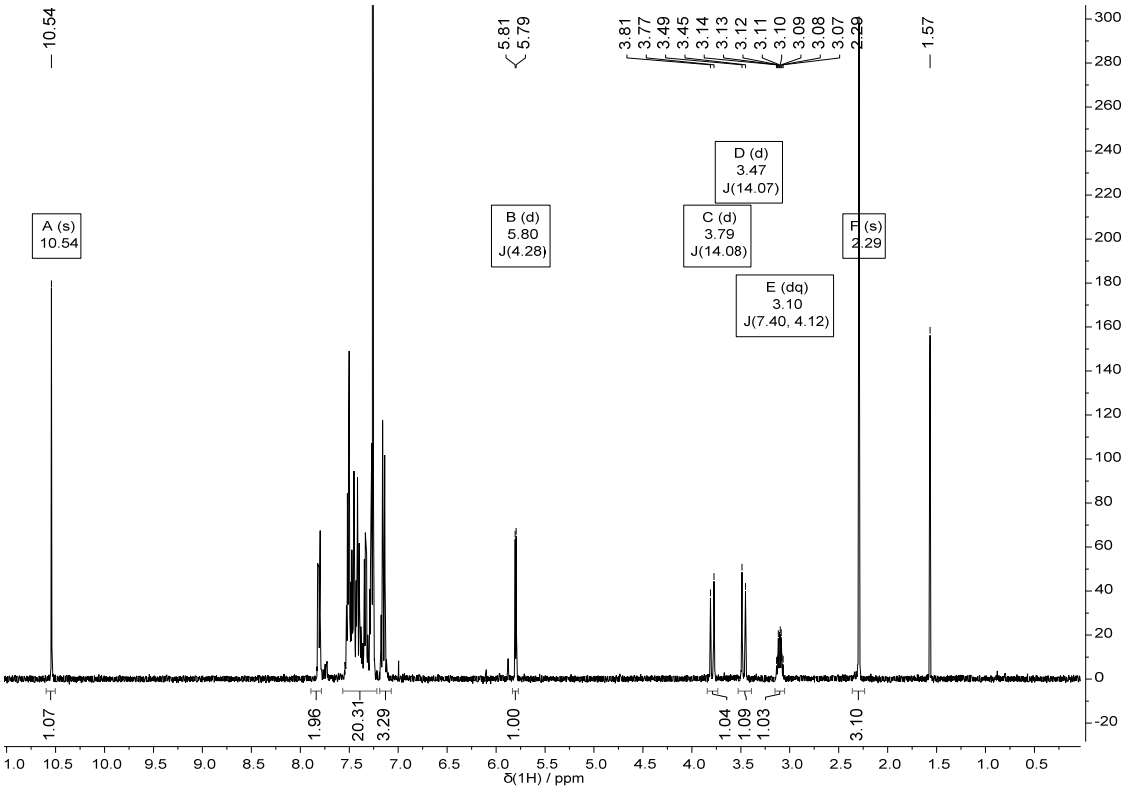

Fig. S1. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$, 298 K) of **5a**.

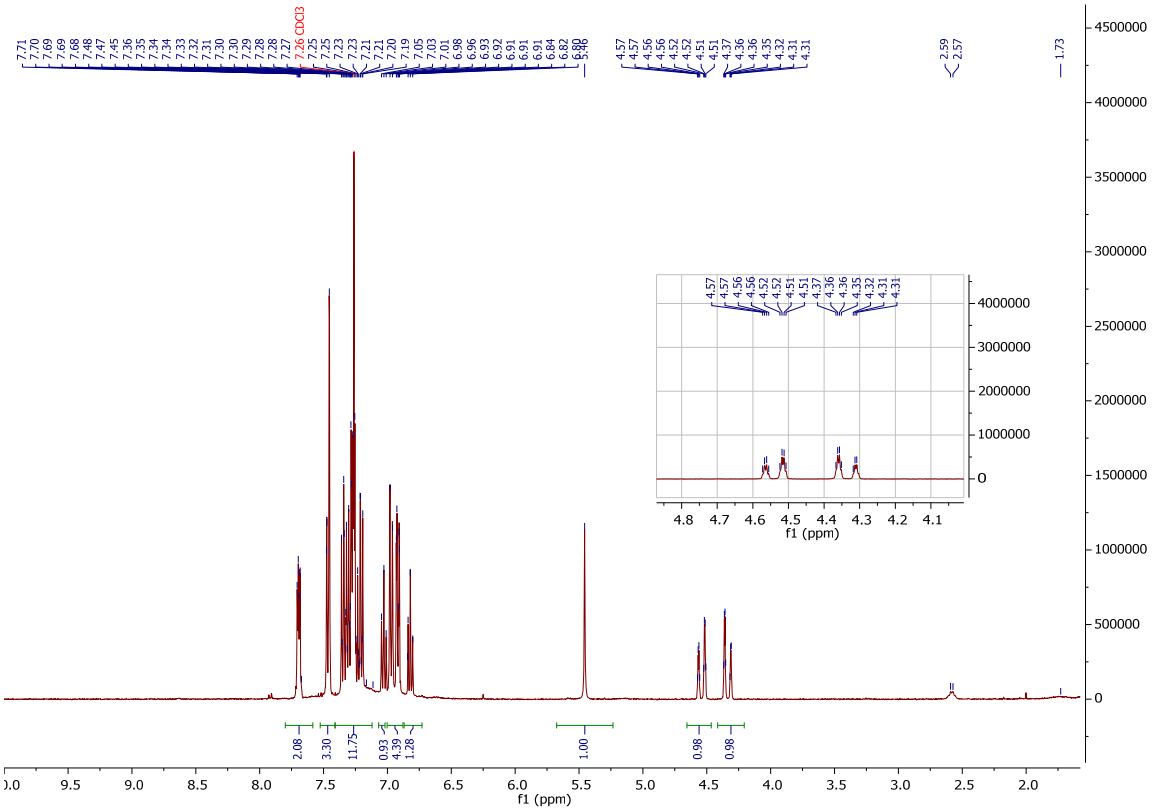

Fig. S2. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$, 298 K) of tetraazaspiro[4.4]nonadiene **6a**.

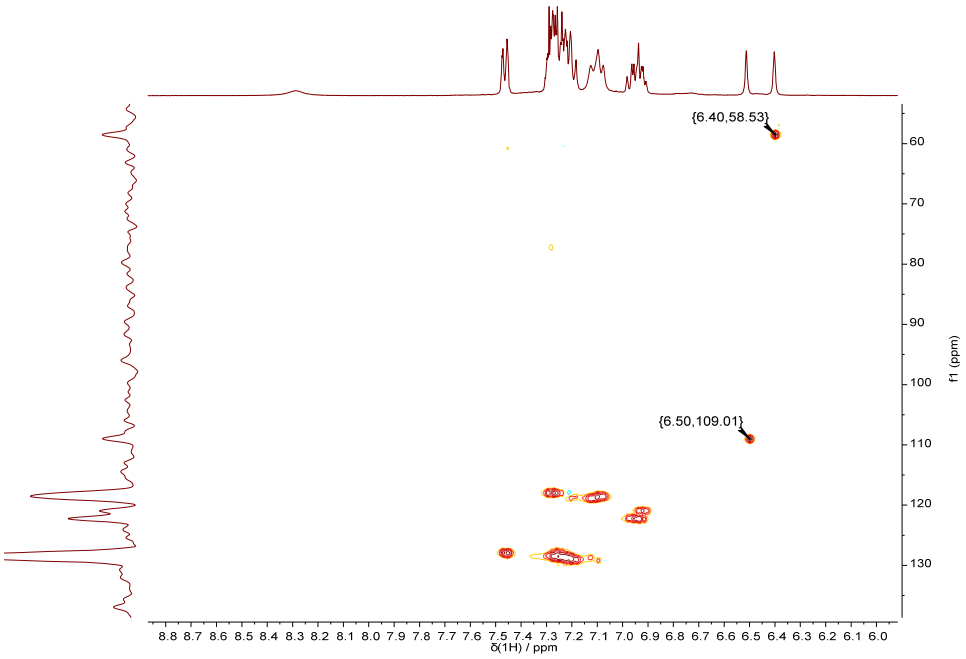

Fig. S3. HSQC $^{1}H,^{13}C$ NMR spectrum of isomerization product **7a** in $CDCl_3$; ^{13}C NMR at 125.77 MHz, ^{1}H NMR at 400.13 MHz.

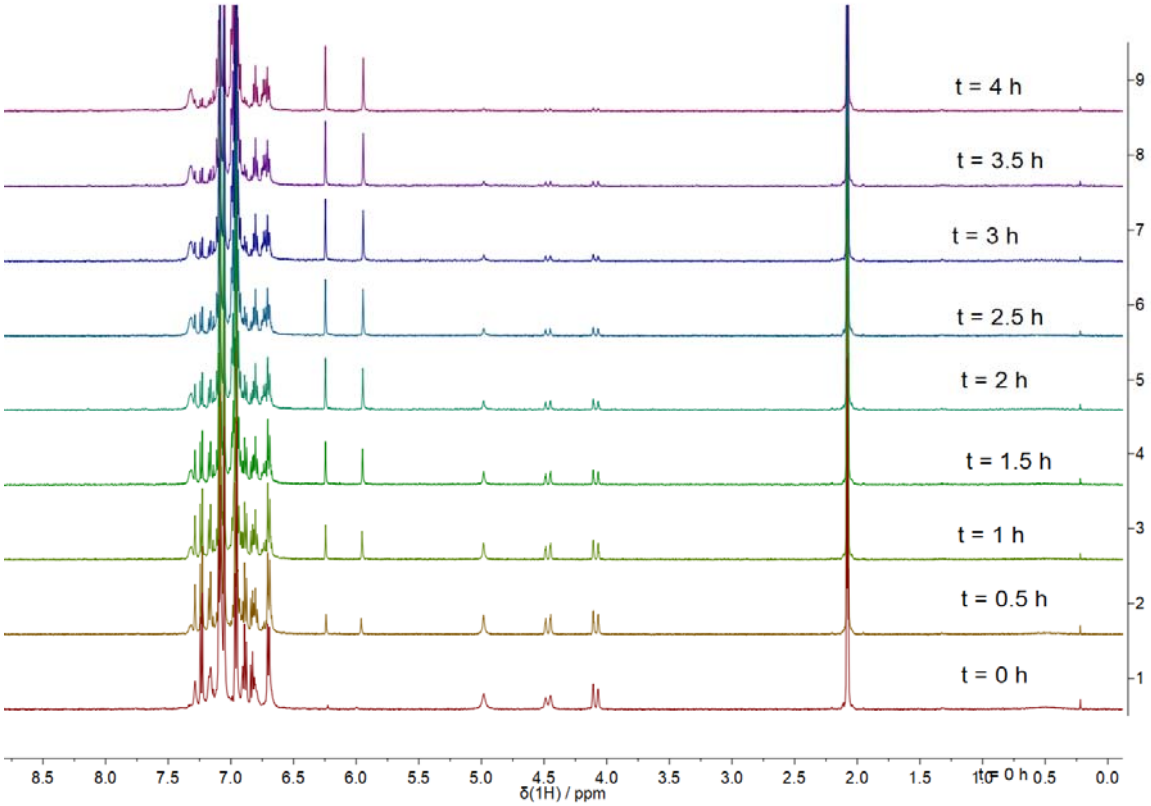

Fig. S4. ^{1}H NMR (400 MHz) monitoring of the thermal isomerization **6e** → **7e** in [D_8]toluene at 373 K). Residual proton signals of uncompletely deuterated toluene appear at 2.1 ppm and in the aromatic region.

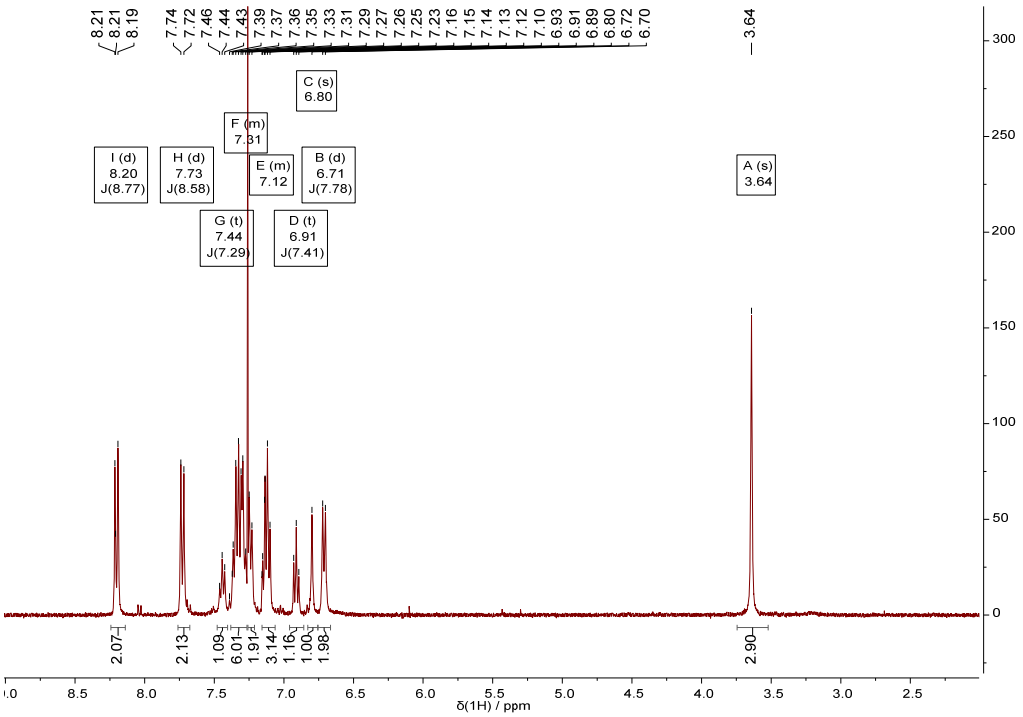

Fig. S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of *N*-methylpyrrole **8**.

2. Selected IR spectra

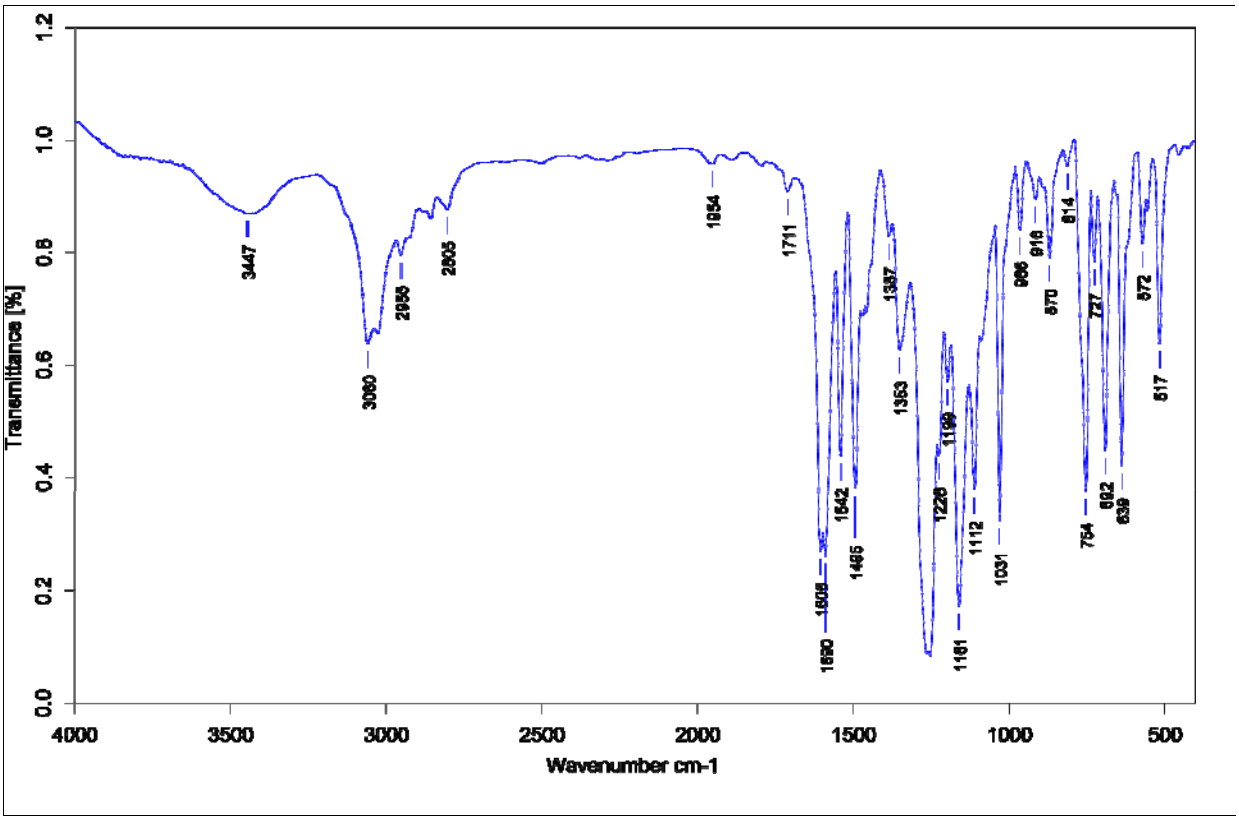

Fig. S6. IR spectrum of **5a** in KBr.

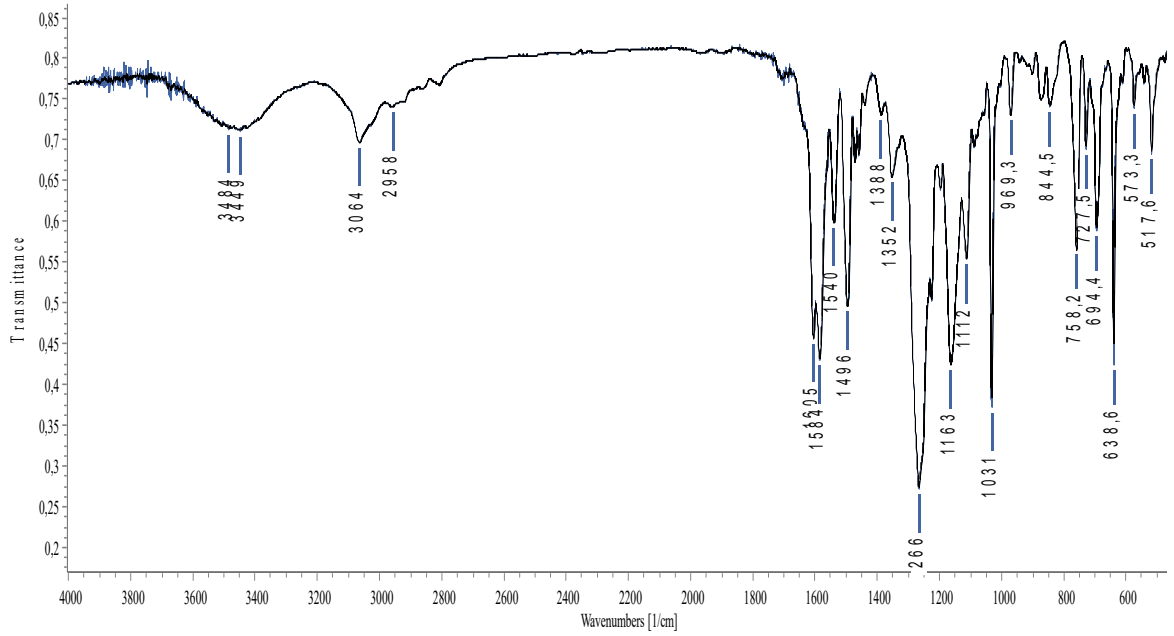

Fig. S7. IR spectrum of **5b** in KBr.

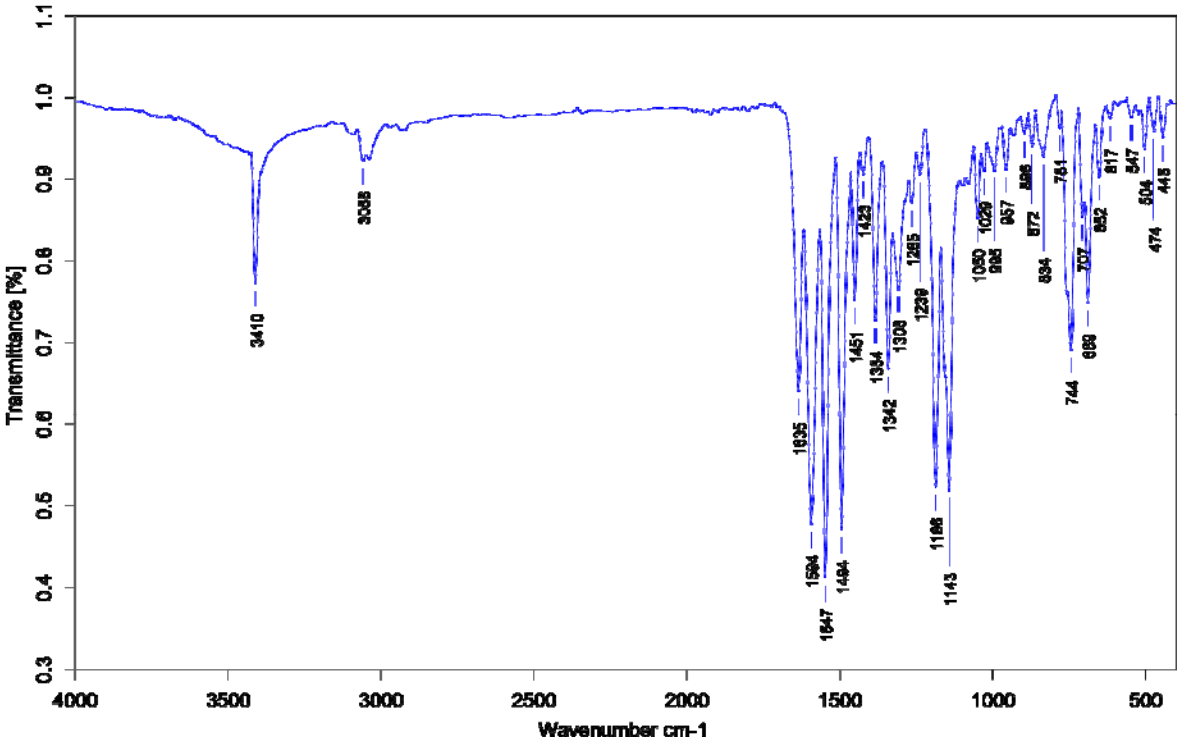

Fig. S8. IR spectrum of **6a** in KBr.

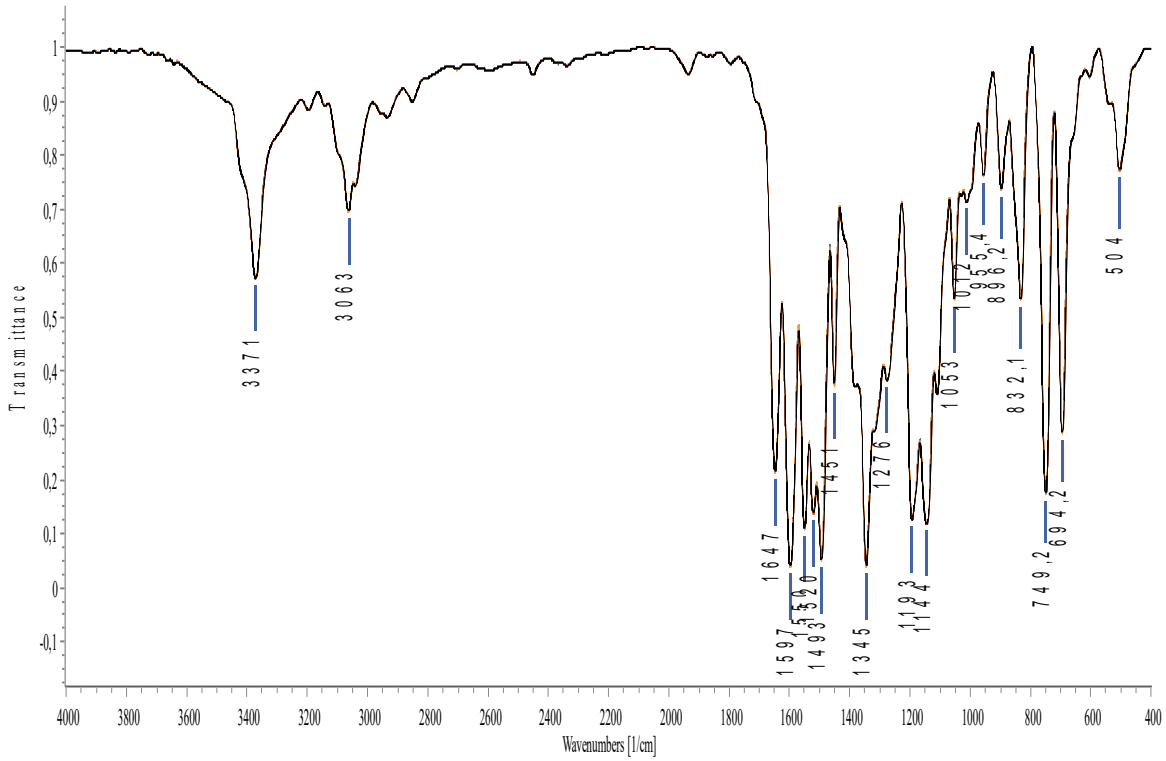

Fig. S9. IR spectrum of **6d** in KBr.

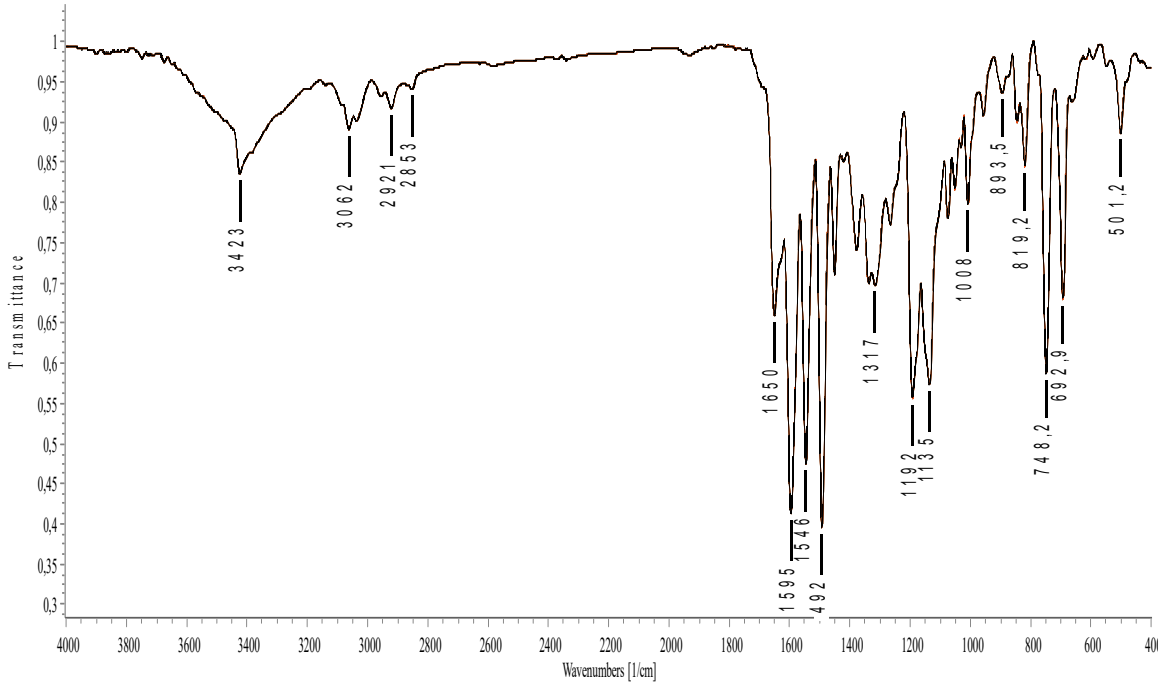

Fig. S10. IR spectrum of **6e** in KBr.

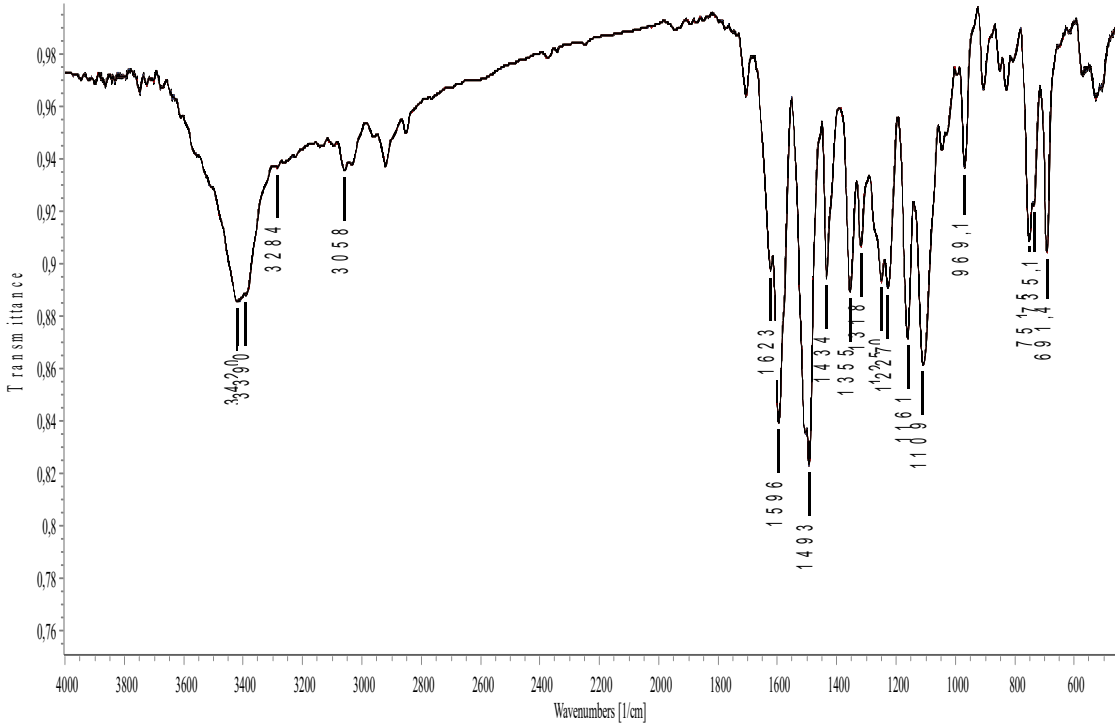

Fig. S11. IR spectrum of **7b** in KBr.

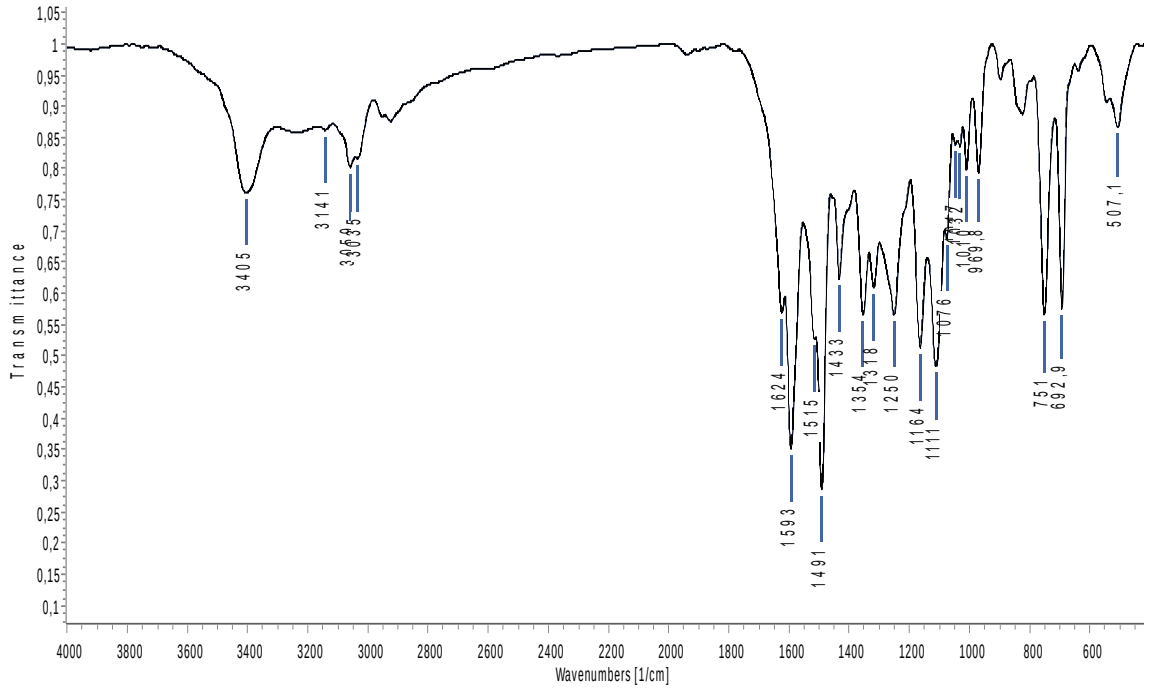

Fig. S12. IR spectrum of **7e** in KBr.

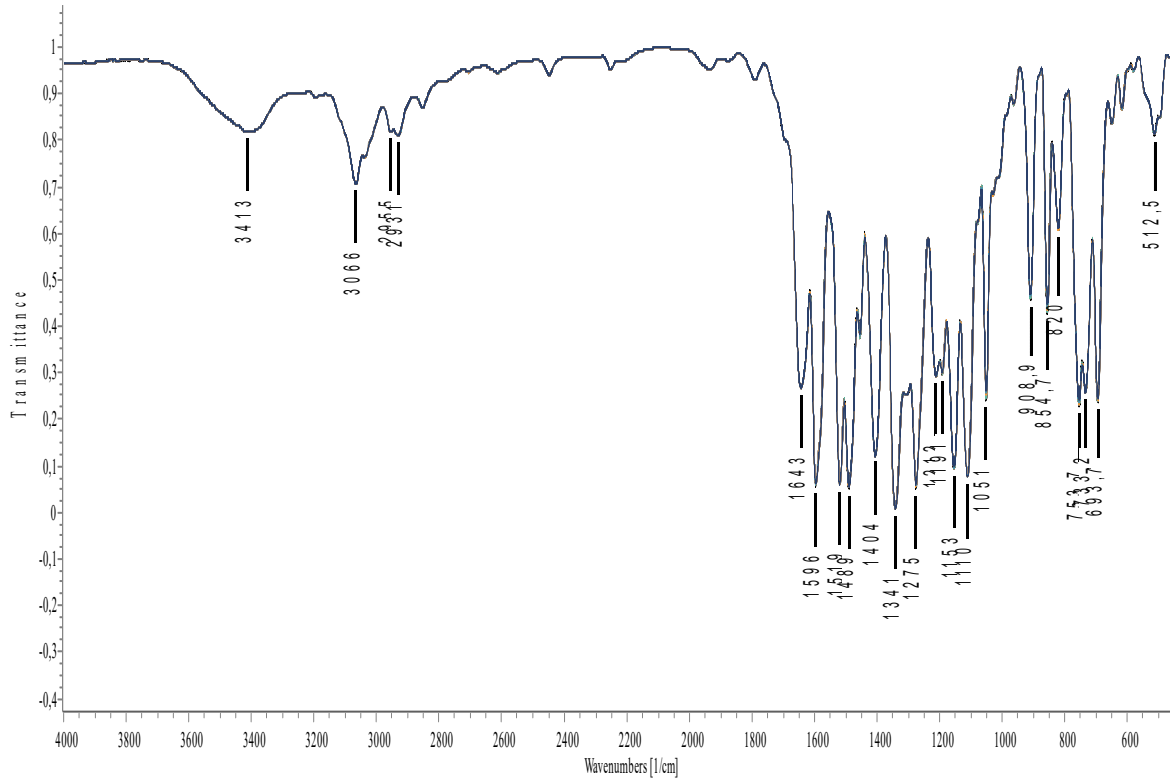

Fig. S13. IR spectrum of **8** in KBr.

3. Crystallographic and structural data

3.1. 3-((2-Methyl-3-(trifluoromethyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-5-yl)(phenyl)amino)-1,4-diphenyl-1*H*-1,2,4-triazol-4-ium triflate (5a)

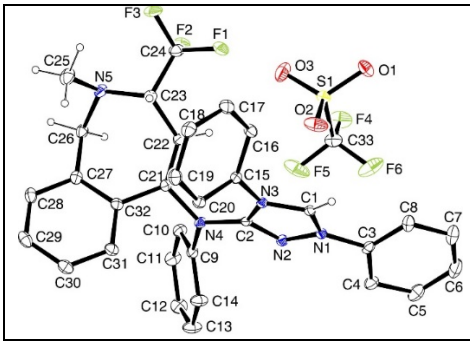	Colorless needle-shaped crystals were obtained from acetone solution.

Table S1. Crystal data and structure refinement for **5a**.

Identification code	RK337
Empirical formula	C33 H27 F6 N5 O3 S
Formula weight	687.65
Temperature	150.00(10) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\,\bar{1}$
Unit cell dimensions	a = 13.7635(6) Å α = 75.030(4)° b = 16.0887(7) Å β = 77.557(4)° c = 16.1849(8) Å γ = 66.605(4)°
Volume	3151.8(3) Å^3
Z	4
Density (calculated)	1.449 Mg/m^3
Absorption coefficient	0.182 mm^{-1}
F(000)	1416
Crystal size	0.22 x 0.12 x 0.06 mm^3
Theta range for data collection	2.798 to 25.681°.
Index ranges	–16<=h<=16, –19<=k<=19, –19<=l<=19
Reflections collected	30836
Independent reflections	11942 [R(int) = 0.0476]
Completeness to theta = 25.242°	99.9 %
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.91887
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	11942 / 0 / 867
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0636, wR2 = 0.1564
R indices (all data)	R1 = 0.1015, wR2 = 0.1824
Extinction coefficient	n/a
Largest diff. peak and hole	0.742 and –0.515 e.Å^{-3}

Table S2. Bond lengths [Å] and angles [deg] for **5a**.

S(1)–O(2)	1.422(3)	C(23)–C(24)	1.511(5)
S(1)–O(3)	1.427(3)	C(26)–C(27)	1.499(5)
S(1)–O(1)	1.428(3)	C(27)–C(28)	1.389(5)
S(1)–C(33)	1.813(4)	C(27)–C(32)	1.396(5)
N(1)–C(1)	1.311(4)	C(28)–C(29)	1.377(5)
N(1)–N(2)	1.369(3)	C(29)–C(30)	1.384(5)
N(1)–C(3)	1.442(4)	C(30)–C(31)	1.384(5)
N(2)–C(2)	1.313(4)	C(31)–C(32)	1.393(5)
N(3)–C(1)	1.345(4)	S(2)–O(5)	1.435(3)
N(3)–C(2)	1.384(4)	S(2)–O(6)	1.436(2)
N(3)–C(15)	1.448(4)	S(2)–O(4)	1.437(2)
N(4)–C(2)	1.359(4)	S(2)–C(66)	1.822(4)
N(4)–C(21)	1.444(4)	N(6)–C(34)	1.311(4)
N(4)–C(9)	1.460(4)	N(6)–N(7)	1.378(3)
N(5)–C(26)	1.463(4)	N(6)–C(36)	1.433(4)
N(5)–C(23)	1.463(4)	N(7)–C(35)	1.311(4)
N(5)–C(25)	1.464(4)	N(8)–C(34)	1.337(4)
F(1)–C(24)	1.341(4)	N(8)–C(35)	1.386(4)
F(2)–C(24)	1.334(4)	N(8)–C(42)	1.441(4)
F(3)–C(24)	1.344(4)	N(9)–C(35)	1.365(4)
F(4)–C(33)	1.323(4)	N(9)–C(48)	1.431(4)
F(5)–C(33)	1.316(5)	N(9)–C(54)	1.463(4)
F(6)–C(33)	1.320(5)	N(10)–C(58)	1.452(6)
C(3)–C(4)	1.366(5)	N(10)–C(59)	1.472(6)
C(3)–C(8)	1.374(5)	N(10)–C(56)	1.474(5)
C(4)–C(5)	1.393(5)	F(7)–C(66)	1.332(4)
C(5)–C(6)	1.354(6)	F(8)–C(66)	1.322(4)
C(6)–C(7)	1.353(6)	F(9)–C(66)	1.316(4)
C(7)–C(8)	1.381(5)	F(10)–C(57)	1.341(5)
C(9)–C(10)	1.369(5)	F(11)–C(57)	1.321(5)
C(9)–C(14)	1.369(5)	F(12)–C(57)	1.355(6)
C(10)–C(11)	1.386(5)	C(36)–C(41)	1.379(5)
C(11)–C(12)	1.366(6)	C(36)–C(37)	1.379(5)
C(12)–C(13)	1.363(6)	C(37)–C(38)	1.378(5)
C(13)–C(14)	1.389(5)	C(38)–C(39)	1.372(6)
C(15)–C(16)	1.376(4)	C(39)–C(40)	1.378(6)
C(15)–C(20)	1.379(4)	C(40)–C(41)	1.389(5)
C(16)–C(17)	1.380(5)	C(42)–C(43)	1.372(5)
C(17)–C(18)	1.374(5)	C(42)–C(47)	1.375(4)
C(18)–C(19)	1.378(5)	C(43)–C(44)	1.380(5)
C(19)–C(20)	1.387(4)	C(44)–C(45)	1.369(5)
C(21)–C(22)	1.328(4)	C(45)–C(46)	1.376(5)
C(21)–C(32)	1.483(4)	C(46)–C(47)	1.377(5)
C(22)–C(23)	1.513(4)	C(48)–C(49)	1.385(5)
		C(48)–C(53)	1.391(5)

C(49)–C(50)	1.379(5)
C(50)–C(51)	1.379(5)
C(51)–C(52)	1.371(5)
C(52)–C(53)	1.371(5)
C(54)–C(55)	1.324(5)
C(54)–C(65)	1.515(5)
C(55)–C(56)	1.509(5)
C(56)–C(57)	1.508(6)
C(59)–C(60)	1.494(6)
C(60)–C(65)	1.387(5)
C(60)–C(61)	1.401(6)
C(61)–C(62)	1.379(6)
C(62)–C(63)	1.363(6)
C(63)–C(64)	1.383(5)
C(64)–C(65)	1.392(5)

O(2)–S(1)–O(3)	115.5(2)
O(2)–S(1)–O(1)	114.88(18)
O(3)–S(1)–O(1)	113.92(19)
O(2)–S(1)–C(33)	104.51(18)
O(3)–S(1)–C(33)	101.72(18)
O(1)–S(1)–C(33)	104.16(18)
C(1)–N(1)–N(2)	112.6(2)
C(1)–N(1)–C(3)	127.8(3)
N(2)–N(1)–C(3)	119.4(2)
C(2)–N(2)–N(1)	103.7(2)
C(1)–N(3)–C(2)	106.4(2)
C(1)–N(3)–C(15)	121.9(2)
C(2)–N(3)–C(15)	131.7(2)
C(2)–N(4)–C(21)	123.0(2)
C(2)–N(4)–C(9)	115.9(2)
C(21)–N(4)–C(9)	117.4(2)
C(26)–N(5)–C(23)	115.0(2)
C(26)–N(5)–C(25)	112.2(3)
C(23)–N(5)–C(25)	112.3(3)
N(1)–C(1)–N(3)	106.5(3)
N(2)–C(2)–N(4)	122.7(3)
N(2)–C(2)–N(3)	110.8(3)
N(4)–C(2)–N(3)	126.4(3)
C(4)–C(3)–C(8)	121.9(3)
C(4)–C(3)–N(1)	118.5(3)
C(8)–C(3)–N(1)	119.5(3)
C(3)–C(4)–C(5)	118.0(4)
C(6)–C(5)–C(4)	120.4(4)
C(7)–C(6)–C(5)	120.7(4)
C(6)–C(7)–C(8)	120.6(4)
C(3)–C(8)–C(7)	118.2(4)
C(10)–C(9)–C(14)	120.7(3)
C(10)–C(9)–N(4)	119.5(3)
C(14)–C(9)–N(4)	119.7(3)
C(9)–C(10)–C(11)	119.3(3)
C(12)–C(11)–C(10)	120.7(4)
C(13)–C(12)–C(11)	119.4(3)
C(12)–C(13)–C(14)	121.0(4)
C(9)–C(14)–C(13)	118.9(4)
C(16)–C(15)–C(20)	122.7(3)
C(16)–C(15)–N(3)	118.0(3)
C(20)–C(15)–N(3)	119.2(3)
C(15)–C(16)–C(17)	118.3(3)
C(18)–C(17)–C(16)	120.5(3)
C(17)–C(18)–C(19)	120.2(3)
C(18)–C(19)–C(20)	120.7(3)
C(15)–C(20)–C(19)	117.7(3)
C(22)–C(21)–N(4)	119.6(3)
C(22)–C(21)–C(32)	126.8(3)
N(4)–C(21)–C(32)	113.5(3)
C(21)–C(22)–C(23)	126.3(3)
N(5)–C(23)–C(24)	106.9(3)
N(5)–C(23)–C(22)	118.3(3)
C(24)–C(23)–C(22)	109.4(3)
F(2)–C(24)–F(1)	107.3(3)
F(2)–C(24)–F(3)	106.6(3)
F(1)–C(24)–F(3)	106.0(3)
F(2)–C(24)–C(23)	113.1(3)
F(1)–C(24)–C(23)	111.8(3)
F(3)–C(24)–C(23)	111.6(3)
N(5)–C(26)–C(27)	114.9(3)
C(28)–C(27)–C(32)	118.9(3)
C(28)–C(27)–C(26)	121.1(3)
C(32)–C(27)–C(26)	120.0(3)
C(29)–C(28)–C(27)	120.9(3)
C(28)–C(29)–C(30)	120.2(3)
C(29)–C(30)–C(31)	119.7(4)
C(30)–C(31)–C(32)	120.2(3)
C(31)–C(32)–C(27)	120.0(3)
C(31)–C(32)–C(21)	120.3(3)
C(27)–C(32)–C(21)	119.8(3)
F(5)–C(33)–F(6)	107.4(4)
F(5)–C(33)–F(4)	106.8(3)
F(6)–C(33)–F(4)	108.0(3)
F(5)–C(33)–S(1)	111.2(3)
F(6)–C(33)–S(1)	111.8(3)
F(4)–C(33)–S(1)	111.4(3)
O(5)–S(2)–O(6)	115.11(16)
O(5)–S(2)–O(4)	114.60(15)
O(6)–S(2)–O(4)	114.57(16)
O(5)–S(2)–C(66)	103.86(16)
O(6)–S(2)–C(66)	103.44(16)

O(4)–S(2)–C(66)	103.05(16)	C(50)–C(49)–C(48)	119.0(3)
C(34)–N(6)–N(7)	111.9(2)	C(51)–C(50)–C(49)	121.0(3)
C(34)–N(6)–C(36)	127.9(3)	C(52)–C(51)–C(50)	119.6(3)
N(7)–N(6)–C(36)	120.2(2)	C(53)–C(52)–C(51)	120.4(3)
C(35)–N(7)–N(6)	103.6(2)	C(52)–C(53)–C(48)	120.0(3)
C(34)–N(8)–C(35)	106.0(2)	C(55)–C(54)–N(9)	114.9(3)
C(34)–N(8)–C(42)	123.7(3)	C(55)–C(54)–C(65)	131.9(3)
C(35)–N(8)–C(42)	130.1(3)	N(9)–C(54)–C(65)	113.2(3)
C(35)–N(9)–C(48)	121.9(3)	C(54)–C(55)–C(56)	129.1(3)
C(35)–N(9)–C(54)	118.1(2)	N(10)–C(56)–C(57)	107.4(3)
C(48)–N(9)–C(54)	116.3(3)	N(10)–C(56)–C(55)	119.0(3)
C(58)–N(10)–C(59)	114.9(4)	C(57)–C(56)–C(55)	110.0(3)
C(58)–N(10)–C(56)	111.4(4)	F(11)–C(57)–F(10)	106.7(4)
C(59)–N(10)–C(56)	114.9(3)	F(11)–C(57)–F(12)	106.6(4)
N(6)–C(34)–N(8)	107.4(3)	F(10)–C(57)–F(12)	105.1(4)
N(7)–C(35)–N(9)	124.5(3)	F(11)–C(57)–C(56)	112.7(4)
N(7)–C(35)–N(8)	111.1(3)	F(10)–C(57)–C(56)	111.3(4)
N(9)–C(35)–N(8)	124.5(3)	F(12)–C(57)–C(56)	113.9(4)
C(41)–C(36)–C(37)	122.3(3)	N(10)–C(59)–C(60)	114.1(4)
C(41)–C(36)–N(6)	118.3(3)	C(65)–C(60)–C(61)	118.9(4)
C(37)–C(36)–N(6)	119.4(3)	C(65)–C(60)–C(59)	120.4(4)
C(38)–C(37)–C(36)	118.2(4)	C(61)–C(60)–C(59)	120.7(4)
C(39)–C(38)–C(37)	120.7(4)	C(62)–C(61)–C(60)	120.3(4)
C(38)–C(39)–C(40)	120.5(3)	C(63)–C(62)–C(61)	120.5(4)
C(39)–C(40)–C(41)	120.0(4)	C(62)–C(63)–C(64)	120.0(4)
C(36)–C(41)–C(40)	118.3(3)	C(63)–C(64)–C(65)	120.4(4)
C(43)–C(42)–C(47)	122.1(3)	C(60)–C(65)–C(64)	119.7(4)
C(43)–C(42)–N(8)	118.5(3)	C(60)–C(65)–C(54)	120.7(3)
C(47)–C(42)–N(8)	119.4(3)	C(64)–C(65)–C(54)	119.6(3)
C(42)–C(43)–C(44)	118.8(3)	F(9)–C(66)–F(8)	107.8(3)
C(45)–C(44)–C(43)	120.2(3)	F(9)–C(66)–F(7)	107.2(3)
C(44)–C(45)–C(46)	120.1(3)	F(8)–C(66)–F(7)	107.5(3)
C(45)–C(46)–C(47)	120.8(3)	F(9)–C(66)–S(2)	111.5(2)
C(42)–C(47)–C(46)	118.0(3)	F(8)–C(66)–S(2)	111.4(3)
C(49)–C(48)–C(53)	119.9(3)	F(7)–C(66)–S(2)	111.3(3)
C(49)–C(48)–N(9)	121.7(3)		
C(53)–C(48)–N(9)	118.3(3)		

Table S3. Hydrogen bonds for **5a** [Å and deg].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
C(1)–H(1)...O(4)#1	0.95	2.11	3.052(4)	172.8
C(10)–H(10)...F(10)#2	0.95	2.45	3.372(5)	163.8
C(14)–H(14)...O(6)	0.95	2.59	3.458(5)	151.8
C(20)–H(20)...O(6)	0.95	2.57	3.444(4)	152.3
C(25)–H(25B)...F(3)	0.98	2.46	3.030(5)	116.6
C(34)–H(34)...O(1)#1	0.95	2.14	3.079(4)	169.9
C(41)–H(41)...F(4)#3	0.95	2.62	3.214(4)	120.8
C(47)–H(47)...O(3)#3	0.95	2.44	3.189(5)	135.2
C(49)–H(49)...O(5)	0.95	2.63	3.575(4)	173.8
C(55)–H(55)...O(3)#3	0.95	2.44	3.296(5)	150.3
C(59)–H(59A)...F(12)	0.99	2.49	3.108(5)	119.8

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1,-y,-z$ #2 $x,y-1,z$ #3 $x,y+1,z$

3.2. (*Z*)-9-Benzylidene-*N*,1,4-triphenyl-8-(trifluoromethyl)-1,2,4,7-tetraazaspiro[4.4]nona-2,7-dien-3-amine (6a)

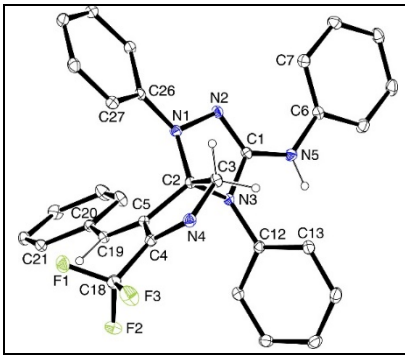	Dark red prisms were obtained from CH_2Cl_2/*n*-pentane by a vapor diffusion method.

Table S4. Crystal data and structure refinement for **6a**.

Identification code	RK340	
Empirical formula	C31 H24 F3 N5	
Formula weight	523.55	
Temperature	150.00(10) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.07997(17) Å	α = 90°
	b = 14.1001(2) Å	β = 92.545(1)°
	c = 16.1470(2) Å	γ = 90°
Volume	2520.14(6) Å^3	
Z	4	
Density (calculated)	1.380 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	1088	
Crystal size	0.23 x 0.13 x 0.10 mm^3	
Theta range for data collection	2.889 to 25.680°	
Index ranges	–13<=h<=13, –17<=k<=16, –19<=l<=19	
Reflections collected	24622	
Independent reflections	4769 [R(int) = 0.0268]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.93578	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	4769 / 0 / 356	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0841	
R indices (all data)	R1 = 0.0432, wR2 = 0.0892	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.215 and –0.233 e·Å^{-3}	

Table S5. Bond lengths [Å] and angles [deg] for **6a**.

F(1)–C(18)	1.3379(17)	C(26)–N(1)–C(2)	126.22(11)
F(2)–C(18)	1.3384(18)	N(2)–N(1)–C(2)	110.74(10)
F(3)–C(18)	1.3302(17)	C(1)–N(2)–N(1)	103.98(11)
N(1)–C(26)	1.3919(18)	C(1)–N(3)–C(12)	125.45(11)
N(1)–N(2)	1.4280(15)	C(1)–N(3)–C(2)	105.65(10)
N(1)–C(2)	1.4589(18)	C(12)–N(3)–C(2)	120.51(11)
N(2)–C(1)	1.2916(18)	C(4)–N(4)–C(3)	107.72(12)
N(3)–C(1)	1.3885(18)	C(1)–N(5)–C(6)	128.22(12)
N(3)–C(12)	1.4329(17)	N(2)–C(1)–N(5)	126.28(13)
N(3)–C(2)	1.4818(17)	N(2)–C(1)–N(3)	114.67(12)
N(4)–C(4)	1.2800(19)	N(5)–C(1)–N(3)	118.97(12)
N(4)–C(3)	1.4598(19)	N(1)–C(2)–N(3)	98.03(10)
N(5)–C(1)	1.3659(18)	N(1)–C(2)–C(5)	115.32(11)
N(5)–C(6)	1.4116(18)	N(3)–C(2)–C(5)	113.91(11)
C(2)–C(5)	1.5274(18)	N(1)–C(2)–C(3)	115.40(11)
C(2)–C(3)	1.5603(19)	N(3)–C(2)–C(3)	112.37(11)
C(4)–C(5)	1.4665(19)	C(5)–C(2)–C(3)	102.39(11)
C(4)–C(18)	1.505(2)	N(4)–C(3)–C(2)	108.17(11)
C(5)–C(19)	1.346(2)	N(4)–C(4)–C(5)	117.62(13)
C(6)–C(7)	1.383(2)	N(4)–C(4)–C(18)	118.97(13)
C(6)–C(11)	1.391(2)	C(5)–C(4)–C(18)	123.40(13)
C(7)–C(8)	1.391(2)	C(19)–C(5)–C(4)	123.43(13)
C(8)–C(9)	1.380(2)	C(19)–C(5)–C(2)	132.89(13)
C(9)–C(10)	1.381(2)	C(4)–C(5)–C(2)	103.67(11)
C(10)–C(11)	1.378(2)	C(7)–C(6)–C(11)	119.60(14)
C(12)–C(17)	1.389(2)	C(7)–C(6)–N(5)	123.86(13)
C(12)–C(13)	1.392(2)	C(11)–C(6)–N(5)	116.54(13)
C(13)–C(14)	1.387(2)	C(6)–C(7)–C(8)	119.23(13)
C(14)–C(15)	1.379(2)	C(9)–C(8)–C(7)	121.29(15)
C(15)–C(16)	1.384(2)	C(8)–C(9)–C(10)	118.95(15)
C(16)–C(17)	1.390(2)	C(11)–C(10)–C(9)	120.49(14)
C(19)–C(20)	1.4611(19)	C(10)–C(11)–C(6)	120.43(15)
C(20)–C(25)	1.397(2)	C(17)–C(12)–C(13)	120.09(13)
C(20)–C(21)	1.399(2)	C(17)–C(12)–N(3)	118.16(12)
C(21)–C(22)	1.386(2)	C(13)–C(12)–N(3)	121.73(13)
C(22)–C(23)	1.379(2)	C(14)–C(13)–C(12)	119.51(14)
C(23)–C(24)	1.385(2)	C(15)–C(14)–C(13)	120.63(15)
C(24)–C(25)	1.386(2)	C(14)–C(15)–C(16)	119.79(14)
C(26)–C(27)	1.399(2)	C(15)–C(16)–C(17)	120.36(14)
C(26)–C(31)	1.400(2)	C(12)–C(17)–C(16)	119.60(14)
C(27)–C(28)	1.389(2)	F(3)–C(18)–F(1)	107.10(12)
C(28)–C(29)	1.379(2)	F(3)–C(18)–F(2)	106.93(12)
C(29)–C(30)	1.388(2)	F(1)–C(18)–F(2)	107.22(12)
C(30)–C(31)	1.384(2)	F(3)–C(18)–C(4)	112.80(13)
		F(1)–C(18)–C(4)	111.06(12)
C(26)–N(1)–N(2)	117.98(11)	F(2)–C(18)–C(4)	111.43(12)

C(5)–C(19)–C(20)	134.18(13)
C(25)–C(20)–C(21)	118.05(13)
C(25)–C(20)–C(19)	126.11(13)
C(21)–C(20)–C(19)	115.83(13)
C(22)–C(21)–C(20)	121.47(14)
C(23)–C(22)–C(21)	119.74(14)
C(22)–C(23)–C(24)	119.60(14)
C(23)–C(24)–C(25)	120.99(15)
C(24)–C(25)–C(20)	120.16(14)
N(1)–C(26)–C(27)	122.47(13)
N(1)–C(26)–C(31)	118.93(13)
C(27)–C(26)–C(31)	118.51(13)
C(28)–C(27)–C(26)	120.07(14)
C(29)–C(28)–C(27)	121.28(14)
C(28)–C(29)–C(30)	118.77(14)
C(31)–C(30)–C(29)	120.94(14)
C(30)–C(31)–C(26)	120.41(14)

3.3. (1*Z*,1*E*)-*N*-(1-methyl-3-(4-nitrophenyl)-5-(trifluoromethyl)-1*H*-pyrrol-2-yl)-*N*,*N*‘,2-triphenyldiazene-1-carboximidamide (8)

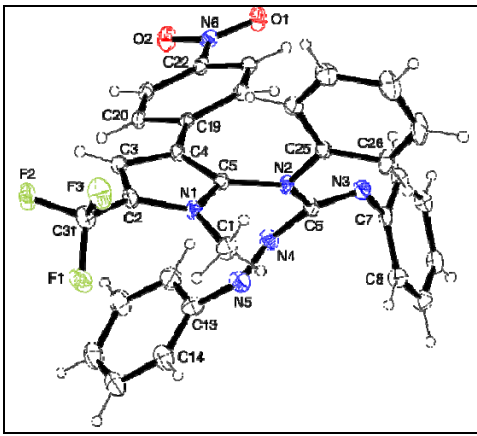	Yellow-brown crystals were obtained by slow evaporation of a pentane solution of **8**.

Table S6. Crystal data and structure refinement for **8**.

Identification code	RK362	
Empirical formula	C31 H23 F3 N6 O2	
Formula weight	568.55	
Temperature	150.00(10) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 14.5130(12) Å	α = 65.941(6)°
	b = 14.5721(10) Å	β = 72.349(6)°
	c = 15.0086(9) Å	γ = 85.745(6)°
Volume	2757.4(4) Å^3	
Z	4	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	1176	
Crystal size	0.22 x 0.20 x 0.17 mm^3	
Theta range for data collection	2.821 to 25.681°	
Index ranges	–17<=h<=17, –17<=k<=17, –18<=l<=18	
Reflections collected	31467	
Independent reflections	10470 [R(int) = 0.0356]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.91120	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	10470 / 0 / 759	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1637	
R indices (all data)	R1 = 0.0822, wR2 = 0.1783	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.095 and –0.389 e.Å^{-3}	

Table S7. Bond lengths [Å] and angles [deg] for **8**.

F(1)–C(31)	1.339(4)	C(28)–C(29)	1.369(5)
F(2)–C(31)	1.337(3)	C(29)–C(30)	1.380(4)
F(3)–C(31)	1.350(3)	O(3)–N(12)	1.226(3)
F(4)–C(62)	1.331(3)	O(4)–N(12)	1.229(3)
F(5)–C(62)	1.341(4)	N(7)–C(36)	1.360(3)
F(6)–C(62)	1.350(3)	N(7)–C(33)	1.379(3)
O(1)–N(6)	1.225(3)	N(7)–C(32)	1.456(3)
O(2)–N(6)	1.228(3)	N(8)–C(37)	1.392(3)
N(1)–C(5)	1.365(3)	N(8)–C(36)	1.415(3)
N(1)–C(2)	1.378(3)	N(8)–C(56)	1.439(3)
N(1)–C(1)	1.457(3)	N(9)–C(37)	1.269(3)
N(2)–C(6)	1.396(3)	N(9)–C(38)	1.415(3)
N(2)–C(5)	1.412(3)	N(10)–N(11)	1.243(3)
N(2)–C(25)	1.438(3)	N(10)–C(37)	1.442(3)
N(3)–C(6)	1.248(3)	N(11)–C(50)	1.424(3)
N(3)–C(7)	1.416(3)	N(12)–C(47)	1.462(3)
N(4)–N(5)	1.262(3)	C(33)–C(34)	1.362(4)
N(4)–C(6)	1.442(3)	C(33)–C(62)	1.475(4)
N(5)–C(13)	1.402(4)	C(34)–C(35)	1.418(3)
N(6)–C(22)	1.461(3)	C(35)–C(36)	1.387(3)
C(2)–C(3)	1.362(4)	C(35)–C(44)	1.460(4)
C(2)–C(31)	1.473(4)	C(38)–C(39)	1.389(4)
C(3)–C(4)	1.420(3)	C(38)–C(43)	1.390(4)
C(4)–C(5)	1.387(3)	C(39)–C(40)	1.384(4)
C(4)–C(19)	1.463(3)	C(40)–C(41)	1.385(4)
C(7)–C(8)	1.382(4)	C(41)–C(42)	1.377(5)
C(7)–C(12)	1.392(4)	C(42)–C(43)	1.387(4)
C(8)–C(9)	1.386(4)	C(44)–C(49)	1.399(3)
C(9)–C(10)	1.385(4)	C(44)–C(45)	1.401(3)
C(10)–C(11)	1.383(4)	C(45)–C(46)	1.377(4)
C(11)–C(12)	1.379(4)	C(46)–C(47)	1.386(4)
C(13)–C(14)	1.373(4)	C(47)–C(48)	1.383(4)
C(13)–C(18)	1.427(4)	C(48)–C(49)	1.379(4)
C(14)–C(15)	1.399(4)	C(50)–C(55)	1.386(4)
C(15)–C(16)	1.388(5)	C(50)–C(51)	1.395(4)
C(16)–C(17)	1.405(5)	C(51)–C(52)	1.382(4)
C(17)–C(18)	1.363(4)	C(52)–C(53)	1.385(4)
C(19)–C(24)	1.399(3)	C(53)–C(54)	1.383(4)
C(19)–C(20)	1.402(3)	C(54)–C(55)	1.379(4)
C(20)–C(21)	1.377(4)	C(56)–C(61)	1.386(4)
C(21)–C(22)	1.385(4)	C(56)–C(57)	1.389(4)
C(22)–C(23)	1.387(3)	C(57)–C(58)	1.386(4)
C(23)–C(24)	1.381(4)	C(58)–C(59)	1.380(4)
C(25)–C(26)	1.380(4)	C(59)–C(60)	1.383(4)
C(25)–C(30)	1.389(4)	C(60)–C(61)	1.377(4)
C(26)–C(27)	1.387(4)	C(5)–N(1)–C(2)	107.6(2)
C(27)–C(28)	1.365(5)	C(5)–N(1)–C(1)	125.1(2)

C(2)–N(1)–C(1)	127.4(2)	C(26)–C(25)–C(30)	119.4(2)
C(6)–N(2)–C(5)	119.68(19)	C(26)–C(25)–N(2)	122.1(2)
C(6)–N(2)–C(25)	122.3(2)	C(30)–C(25)–N(2)	118.3(2)
C(5)–N(2)–C(25)	116.4(2)	C(25)–C(26)–C(27)	119.1(3)
C(6)–N(3)–C(7)	120.5(2)	C(28)–C(27)–C(26)	121.7(3)
N(5)–N(4)–C(6)	113.3(2)	C(27)–C(28)–C(29)	119.0(3)
N(4)–N(5)–C(13)	113.3(2)	C(28)–C(29)–C(30)	120.7(3)
O(1)–N(6)–O(2)	123.5(2)	C(29)–C(30)–C(25)	120.1(3)
O(1)–N(6)–C(22)	118.5(2)	F(2)–C(31)–F(1)	106.8(2)
O(2)–N(6)–C(22)	118.0(2)	F(2)–C(31)–F(3)	107.0(3)
C(3)–C(2)–N(1)	109.2(2)	F(1)–C(31)–F(3)	105.4(2)
C(3)–C(2)–C(31)	128.2(2)	F(2)–C(31)–C(2)	110.7(2)
N(1)–C(2)–C(31)	122.5(2)	F(1)–C(31)–C(2)	114.1(3)
C(2)–C(3)–C(4)	107.8(2)	F(3)–C(31)–C(2)	112.4(2)
C(5)–C(4)–C(3)	105.8(2)	C(36)–N(7)–C(33)	107.4(2)
C(5)–C(4)–C(19)	127.5(2)	C(36)–N(7)–C(32)	124.6(2)
C(3)–C(4)–C(19)	126.7(2)	C(33)–N(7)–C(32)	127.5(2)
N(1)–C(5)–C(4)	109.7(2)	C(37)–N(8)–C(36)	119.24(19)
N(1)–C(5)–N(2)	119.7(2)	C(37)–N(8)–C(56)	122.78(19)
C(4)–C(5)–N(2)	130.7(2)	C(36)–N(8)–C(56)	116.54(19)
N(3)–C(6)–N(2)	122.9(2)	C(37)–N(9)–C(38)	118.4(2)
N(3)–C(6)–N(4)	120.6(2)	N(11)–N(10)–C(37)	114.3(2)
N(2)–C(6)–N(4)	115.0(2)	N(10)–N(11)–C(50)	113.9(2)
C(8)–C(7)–C(12)	119.3(2)	O(3)–N(12)–O(4)	123.3(2)
C(8)–C(7)–N(3)	122.5(2)	O(3)–N(12)–C(47)	118.8(2)
C(12)–C(7)–N(3)	118.1(2)	O(4)–N(12)–C(47)	117.9(2)
C(7)–C(8)–C(9)	120.3(3)	C(34)–C(33)–N(7)	109.3(2)
C(10)–C(9)–C(8)	120.4(3)	C(34)–C(33)–C(62)	128.8(2)
C(11)–C(10)–C(9)	118.9(3)	N(7)–C(33)–C(62)	121.9(2)
C(12)–C(11)–C(10)	121.1(3)	C(33)–C(34)–C(35)	107.7(2)
C(11)–C(12)–C(7)	119.9(3)	C(36)–C(35)–C(34)	105.7(2)
C(14)–C(13)–N(5)	116.5(3)	C(36)–C(35)–C(44)	127.3(2)
C(14)–C(13)–C(18)	119.9(3)	C(34)–C(35)–C(44)	127.0(2)
N(5)–C(13)–C(18)	123.3(3)	N(7)–C(36)–C(35)	109.9(2)
C(13)–C(14)–C(15)	121.2(3)	N(7)–C(36)–N(8)	119.5(2)
C(16)–C(15)–C(14)	118.9(3)	C(35)–C(36)–N(8)	130.5(2)
C(15)–C(16)–C(17)	119.7(3)	N(9)–C(37)–N(8)	122.2(2)
C(18)–C(17)–C(16)	121.7(3)	N(9)–C(37)–N(10)	119.3(2)
C(17)–C(18)–C(13)	118.4(3)	N(8)–C(37)–N(10)	118.2(2)
C(24)–C(19)–C(20)	118.3(2)	C(39)–C(38)–C(43)	119.7(2)
C(24)–C(19)–C(4)	122.7(2)	C(39)–C(38)–N(9)	121.7(2)
C(20)–C(19)–C(4)	118.9(2)	C(43)–C(38)–N(9)	118.5(2)
C(21)–C(20)–C(19)	121.3(2)	C(40)–C(39)–C(38)	120.3(3)
C(20)–C(21)–C(22)	118.7(2)	C(39)–C(40)–C(41)	120.0(3)
C(21)–C(22)–C(23)	121.8(2)	C(42)–C(41)–C(40)	119.6(3)
C(21)–C(22)–N(6)	119.1(2)	C(41)–C(42)–C(43)	121.0(3)
C(23)–C(22)–N(6)	119.1(2)	C(42)–C(43)–C(38)	119.3(3)
C(24)–C(23)–C(22)	118.8(2)	C(49)–C(44)–C(45)	118.0(2)
C(23)–C(24)–C(19)	121.0(2)	C(49)–C(44)–C(35)	119.3(2)

C(45)–C(44)–C(35)	122.7(2)	C(55)–C(50)–C(51)	120.5(2)
C(46)–C(45)–C(44)	121.3(2)	C(55)–C(50)–N(11)	116.5(2)
C(45)–C(46)–C(47)	118.6(2)	C(51)–C(50)–N(11)	122.9(2)
C(48)–C(47)–C(46)	122.1(2)	C(52)–C(51)–C(50)	119.0(3)
C(48)–C(47)–N(12)	119.1(2)	C(51)–C(52)–C(53)	120.4(3)
C(46)–C(47)–N(12)	118.8(2)	C(54)–C(53)–C(52)	120.3(3)
C(49)–C(48)–C(47)	118.4(2)	C(55)–C(54)–C(53)	119.7(3)
C(48)–C(49)–C(44)	121.5(2)		
C(54)–C(55)–C(50)	120.0(3)		
C(61)–C(56)–C(57)	119.6(2)		
C(61)–C(56)–N(8)	118.2(2)		
C(57)–C(56)–N(8)	122.1(2)		
C(58)–C(57)–C(56)	119.4(3)		
C(59)–C(58)–C(57)	121.3(3)		
C(58)–C(59)–C(60)	118.6(3)		
C(61)–C(60)–C(59)	121.0(3)		
C(60)–C(61)–C(56)	120.1(3)		
F(4)–C(62)–F(5)	107.0(2)		
F(4)–C(62)–F(6)	107.3(2)		
F(5)–C(62)–F(6)	105.1(2)		
F(4)–C(62)–C(33)	110.9(2)		
F(5)–C(62)–C(33)	113.9(2)		
F(6)–C(62)–C(33)	112.2(2)		