Electronic Supplementary Information for

Investigation of the Titanium-Mediated Catalytic Enantioselective Oxidation of Aryl Benzyl Sulfides Contatining Heterocyclic Groups.

Maria Annunziata M. Capozzi,*[a] Angel Alvarez-Larena,[b] Joan F. Piniella Febrer,[c] and Cosimo Cardellicchio.*[d]

(a) Dipartimento di Chimica, Università di Bari, via Orabona 4, 70125 Bari, Italy. E-mail maria.capozzi@uniba.it

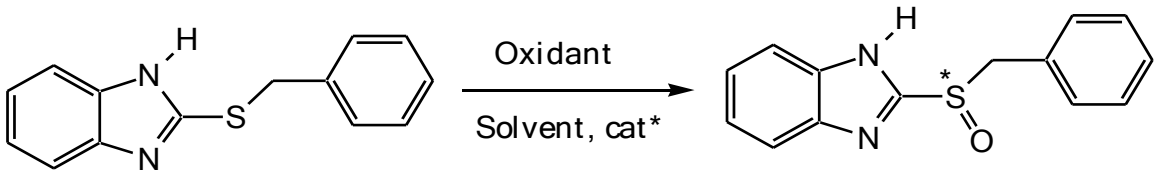
(b) Servei de Difracció de Raigs X, Universitat Autònoma de Barcelona, 08193 Bellaterra, Cerdanyola del Vallès, Barcelona, Spain.

(c) Departament de Geologia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Cerdanyola del Vallès, Barcelona, Spain.

(d) CNR ICCOM, Dipartimento di Chimica, Università di Bari, via Orabona 4, 70125 Bari, Italy.

Index of Electronic Supplementary Information

Table S1. Enantioselective oxidation of benzimidazolyl benzyl sulfide **5a** to obtain benzimidazolyl benzyl sulfoxide **5b** with hydroperoxides in the presence of a complex between titanium and (*S*,*S*)-hydrobenzoin. Other solvents.



cat* = 5% 1:2 complex Ti(O-*i*-Pr)$_4$/(*S*, *S*)-hydrobenzoin

Entry	Oxidant	Solvent	Yield	ee
1	TBHP	Propylene carbonate	21	12
2	TBHP	Methylene chloride	90	21
3	TBHP	Dimethyl carbonate	70	20
4	CHP	Dimethyl carbonate	58	7
5	TBHP	Cyclopentyl methyl ether	62	7
6	CHP	Cyclopentyl methyl ether	55	22

Table S2. Crystal data and structure refinement for (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-thiophene **2b.**

Empirical formula	$C_{11}H_5F_5OS_2$	
Formula weight	312.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2_1 2_1 2_1	
Unit cell dimensions	a = 5.4947(11) Å	α= 90°.
	b = 9.2154(18) Å	β= 90°.
	c = 23.473(5) Å	γ = 90°.
Volume	1188.6(4) $Å^3$	
Z	4	
Density (calculated)	1.745 Mg/m^3	
Absorption coefficient	0.499 mm^{-1}	
F(000)	624	
Crystal size	0.800 x 0.520 x 0.270 mm^3	
Theta range for data collection	1.735 to 28.709°.	
Index ranges	-7<=h<=7, -12<=k<=11, -31<=l<=31	
Reflections collected	9421	
Independent reflections	2891 [R(int) = 0.0126]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.84	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2891 / 0 / 172	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1218	
R indices (all data)	R1 = 0.0420, wR2 = 0.1236	
Absolute structure parameter	0.023(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.534 and -0.308 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for (*R*)-2-(benzylsulfinyl)-*1H*-benzo[d]imidazole **5b.**

Empirical formula	$C_{14}H_{12}N_2OS$	
Formula weight	256.32	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P 6_4	
Unit cell dimensions	a = 13.2625(10) Å	α= 90°.
	b = 13.2625(10) Å	β= 90°.
	c = 12.4674(10) Å	γ = 120°.
Volume	1899.1(3) $Å^3$	
Z	6	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	804	
Crystal size	0.240 x 0.080 x 0.070 mm^3	
Theta range for data collection	1.773 to 28.744°.	
Index ranges	-17<=h<=17, -17<=k<=17, -16<=l<=16	
Reflections collected	17934	
Independent reflections	3030 [R(int) = 0.0778]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.8538	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3030 / 1 / 166	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0659, wR2 = 0.0907	
R indices (all data)	R1 = 0.1141, wR2 = 0.1026	
Absolute structure parameter	0.10(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.243 and -0.199 e.$Å^{-3}$	

Table S4. Crystal data and structure refinement for (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-*1H*-benzo[d]imidazole **9b.**

Empirical formula	$C_{14}H_7F_5N_2OS$	
Formula weight	346.28	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 8.1880(4) Å	α= 90°.
	b = 7.0323(4) Å	β= 102.82(3)°.
	c = 12.3527(7) Å	γ= 90°.
Volume	693.55(10) $Å^3$	
Z	2	
Density (calculated)	1.658 Mg/m^3	
Absorption coefficient	0.296 mm^{-1}	
F(000)	348	
Crystal size	0.580 x 0.280 x 0.210 mm^3	
Theta range for data collection	1.691 to 28.509°.	
Index ranges	-10<=h<=10, -9<=k<=9, -16<=l<=16	
Reflections collected	5473	
Independent reflections	3134 [R(int) = 0.0107]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3134 / 1 / 212	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0965	
R indices (all data)	R1 = 0.0361, wR2 = 0.0976	
Absolute structure parameter	0.065(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.230 and -0.181 e.$Å^{-3}$	

Table S5. Crystal data and structure refinement for benzylsulfinyl-*1H*-methyl-benzo[d]imidazole (*R*)-**10b.**

Empirical formula	$C_{15}H_{14}N_2OS$	
Formula weight	270.34	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 4.7062(4) Å	α= 90°.
	b = 23.5001(18) Å	β= 107.6410(10)°.
	c = 6.3164(5) Å	γ = 90°.
Volume	665.72(9) $Å^3$	
Z	2	
Density (calculated)	1.349 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	284	
Crystal size	0.600 x 0.400 x 0.300 mm^3	
Theta range for data collection	1.733 to 28.697°.	
Index ranges	-6<=h<=6, -31<=k<=31, -8<=l<=8	
Reflections collected	5272	
Independent reflections	3065 [R(int) = 0.0195]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.799	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3065 / 1 / 173	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1116	
R indices (all data)	R1 = 0.0481, wR2 = 0.1142	
Absolute structure parameter	0.10(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.453 and -0.203 $e.Å^{-3}$	

ORTEP plot and packing plot of sulfoxides (2b), (5b), (9b) and (10b)

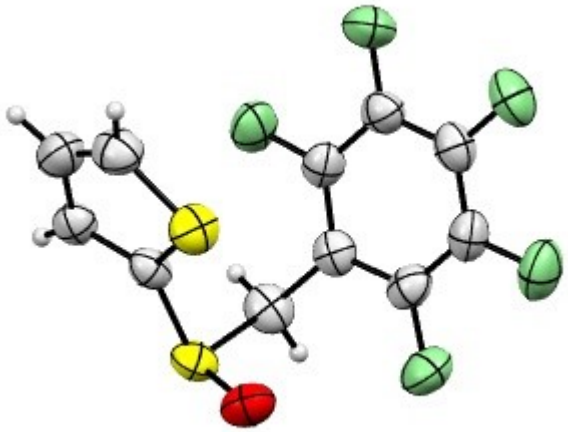


Figure S1. ORTEP plot (50% probability level) of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-thiophene **2b.**

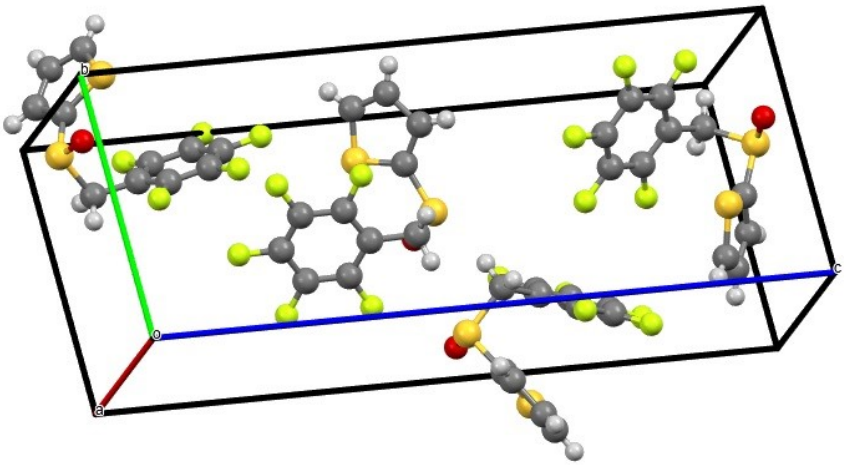


Figure S2. Packing plot of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-thiophene **2b.**

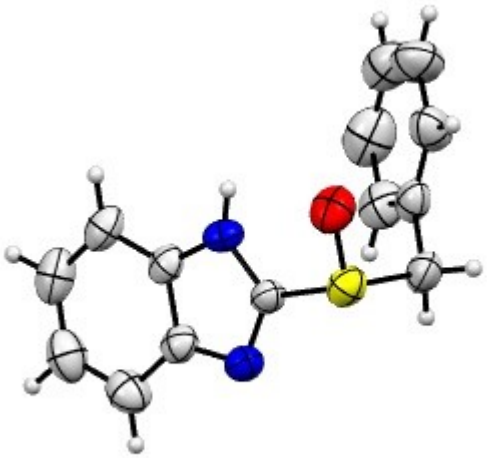


Figure S3. ORTEP plot (50% probability level) of (*R*)-2-(benzylsulfinyl)-1H-benzo[d]imidazole **5b.**

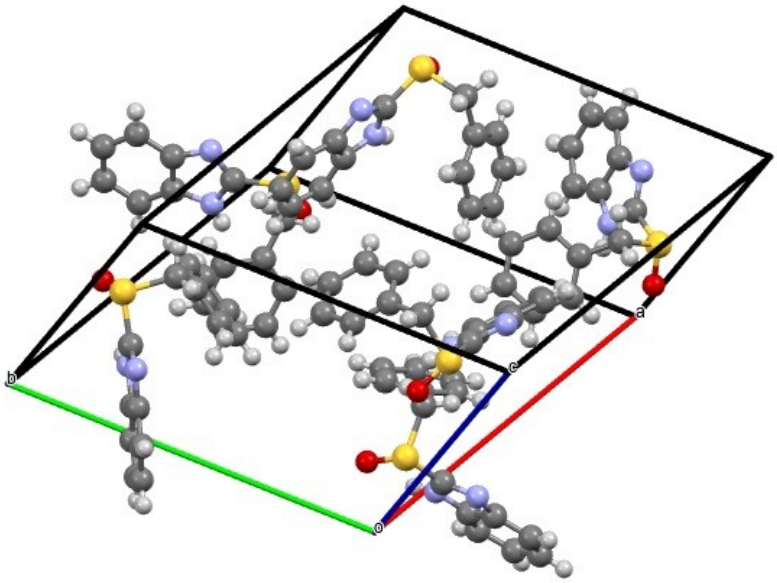


Figure S4. Packing plot of (*R*)-2-(benzylsulfinyl)-1H-benzo[d]imidazole **5b.**

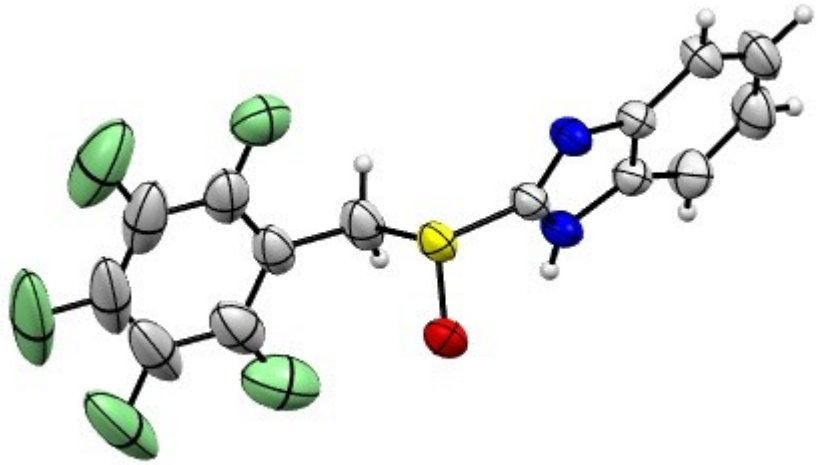


Figure S5. ORTEP plot (50% probability level) of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1H-benzo[d]imidazole **9b.**

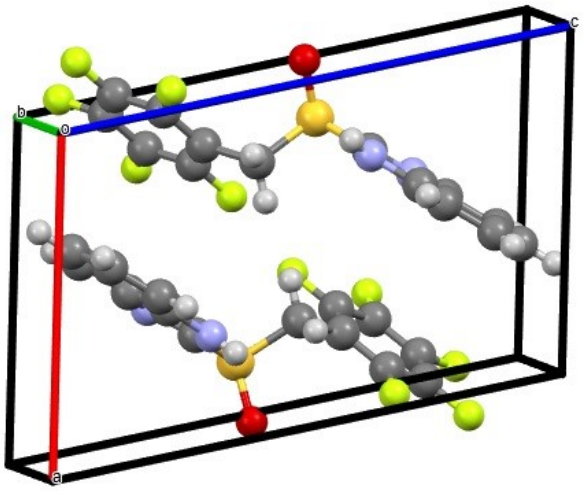


Figure S6. Packing plot of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1H-benzo[d]imidazole **9b.**

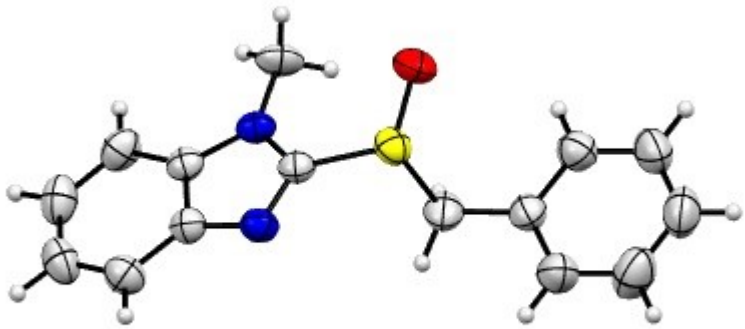


Figure S7. ORTEP plot (50% probability level) of 2-benzylsulfinyl-1-methyl-1-H-benzo[d]imidazole **10b.**

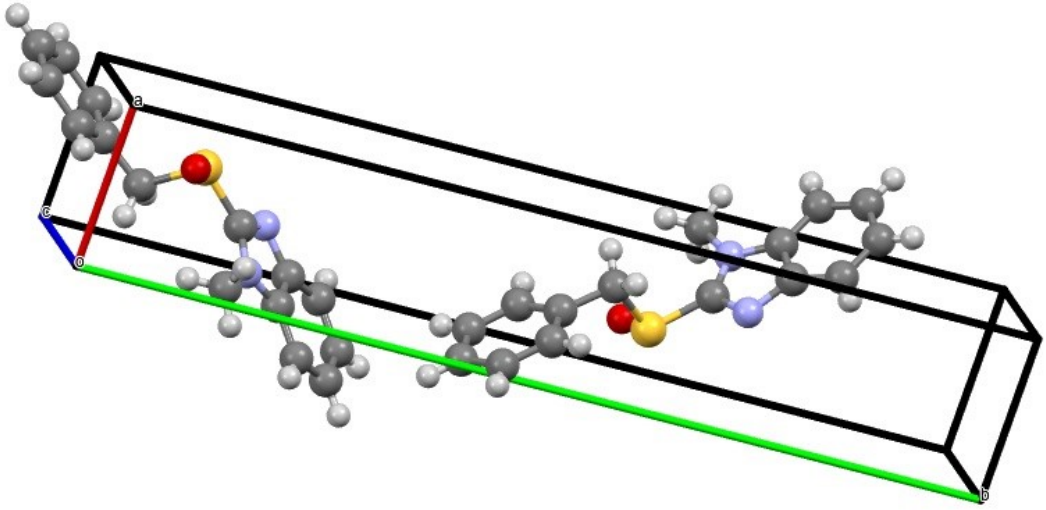


Figure S8. Packing plot of 2-benzylsulfinyl-1-methyl-1-H-benzo[d]imidazole **10b.**

Outputs of pairwise lattice energy calculations.

B3LYP/6-31G(d,p) calculated electronic, polarisation, dispersion and repulsion energies are reported. The molecule interacting with the central molecule is identified by the distance R and the Symop. Further information on these output Tables can be obtained in the cited paper[42] and references therein.

Table S6. *Crystal Explorer 21* estimate of lattice energies (kJ/mol) for (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-thiophene **2b.**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	x, y, z	5,49	B3LYP/6-31G(d,p)	-18,1	-4,5	-36,4	25,4	-38,4	-38,4
2	-x, y+1/2, -z+1/2	7,19	B3LYP/6-31G(d,p)	-5,3	-0,7	-20,4	8,8	-18,5	-18,5
2	-x, y+1/2, -z+1/2	7,59	B3LYP/6-31G(d,p)	-2,6	-0,6	-16,9	6	-14,2	-14,2
2	x+1/2, -y+1/2, -z	9,17	B3LYP/6-31G(d,p)	-2,3	-1,3	-18,7	12,6	-12	-12
2	x+1/2, -y+1/2, -z	8,06	B3LYP/6-31G(d,p)	-3,5	-3,3	-13,3	11,2	-10,9	-10,9
2	x, y, z	10,73	B3LYP/6-31G(d,p)	-1,5	-0,2	-2	0,1	-3,5	-3,5
2	x, y, z	9,22	B3LYP/6-31G(d,p)	2,3	-0,7	-7,5	1,9	-3,4	-3,4
2	x+1/2, -y+1/2, -z	11,19	B3LYP/6-31G(d,p)	-2,2	-0,1	-0,5	0	-2,9	-2,9
2	x, y, z	10,99	B3LYP/6-31G(d,p)	-1,3	-0,1	-0,4	0	-1,7	-1,7
2	-x, y+1/2, -z+1/2	10,3	B3LYP/6-31G(d,p)	-0,6	0	-0,9	0	-1,4	-1,4
2	x+1/2, -y+1/2, -z	12,02	B3LYP/6-31G(d,p)	-0,6	-0,1	-0,6	0	-1,2	-1,2
2	x, y, z	14,34	B3LYP/6-31G(d,p)	-1	0	-0,1	0	-1,2	-1,2
2	-x+1/2, -y, z+1/2	11,79	B3LYP/6-31G(d,p)	-0,3	0	-0,8	0	-1	-1
2	-x, y+1/2, -z+1/2	15,08	B3LYP/6-31G(d,p)	-0,4	0	-0,1	0	-0,5	-0,5
2	-x+1/2, -y, z+1/2	12,78	B3LYP/6-31G(d,p)	0	0	-0,4	0	-0,4	-0,4
2	-x+1/2, -y, z+1/2	14,31	B3LYP/6-31G(d,p)	-0,2	0	-0,1	0	-0,4	-0,4
2	-x, y+1/2, -z+1/2	14,88	B3LYP/6-31G(d,p)	-0,3	0	-0,1	0	-0,4	-0,4
2	-x+1/2, -y, z+1/2	15,59	B3LYP/6-31G(d,p)	-0,3	0	-0,1	0	-0,4	-0,4
2	-x+1/2, -y, z+1/2	15,14	B3LYP/6-31G(d,p)	-0,2	0	-0,1	0	-0,3	-0,3
2	-x+1/2, -y, z+1/2	16,35	B3LYP/6-31G(d,p)	-0,1	0	-0,1	0	-0,2	-0,2
2	x, y, z	14,34	B3LYP/6-31G(d,p)	0	0	-0,1	0	-0,1	-0,1
2	-x+1/2, -y, z+1/2	15,75	B3LYP/6-31G(d,p)	0	0	-0,1	0	-0,1	-0,1
2	-x, y+1/2, -z+1/2	11,13	B3LYP/6-31G(d,p)	0,4	0	-0,5	0	0	0
2	-x+1/2, -y, z+1/2	13,24	B3LYP/6-31G(d,p)	0,2	0	-0,2	0	0	0
2	-x+1/2, -y, z+1/2	15,52	B3LYP/6-31G(d,p)	0,1	0	-0,1	0	0	0
2	x+1/2, -y+1/2, -z	17,39	B3LYP/6-31G(d,p)	0,2	0	0	0	0,2	0,2
2	x, y, z	10,73	B3LYP/6-31G(d,p)	1	-0,1	-0,7	0	0,3	0,3
2	x+1/2, -y+1/2, -z	14,68	B3LYP/6-31G(d,p)	0,4	0	-0,1	0	0,4	0,4
2	x+1/2, -y+1/2, -z	16,52	B3LYP/6-31G(d,p)	0,5	0	-0,1	0	0,5	0,5
									-111,7

Table S7. *Crystal Explorer 21* estimate of lattice energies (kJ/mol) for (*R*)-2-(benzylsulfinyl)-1H-benzo[d]imidazole **5b.**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
1	x-y, x, z+2/3	5,34	B3LYP/6-31G(d,p)	-60,7	-15,3	-42,3	78,2	-64,1	-32,05
1	y, -x+y, z+1/3	5,34	B3LYP/6-31G(d,p)	-60,7	-15,3	-42,3	78,2	-64,1	-32,05
2	-y, x-y, z+1/3	7,13	B3LYP/6-31G(d,p)	-8,8	-2,3	-27,2	18,1	-23,5	-23,5
1	-x, -y, z	6,61	B3LYP/6-31G(d,p)	-4,6	-1,3	-33,4	21,1	-21,9	-10,95
1	-x, -y, z	12	B3LYP/6-31G(d,p)	-1,8	-0,2	-6,7	0	-7,9	-3,95
2	y, -x+y, z+1/3	10,76	B3LYP/6-31G(d,p)	-1,8	-0,3	-10,9	6,2	-7,8	-7,8
2	-x+y, -x, z+2/3	9,38	B3LYP/6-31G(d,p)	-1,4	-0,3	-10,4	5	-7,7	-7,7
1	-x, -y, z	6,69	B3LYP/6-31G(d,p)	0,6	-1,6	-15,8	13,2	-6,2	-3,1
1	-x, -y, z	10,97	B3LYP/6-31G(d,p)	-0,4	-0,2	-6,4	1,9	-4,9	-2,45
2	-x+y, -x, z+2/3	10	B3LYP/6-31G(d,p)	-0,2	-0,1	-3,8	0,1	-3,4	-3,4
1	y, -x+y, z+1/3	8,96	B3LYP/6-31G(d,p)	1,9	-0,3	-5,4	1,2	-2,2	-1,1
1	x-y, x, z+2/3	8,96	B3LYP/6-31G(d,p)	1,9	-0,3	-5,4	1,2	-2,2	-1,1
1	-y, x-y, z+1/3	10,13	B3LYP/6-31G(d,p)	-0,8	-0,1	-0,7	0	-1,6	-0,8
1	-x+y, -x, z+2/3	10,13	B3LYP/6-31G(d,p)	-0,8	-0,1	-0,7	0	-1,6	-0,8
2	x, y, z	13,26	B3LYP/6-31G(d,p)	-0,6	0	-0,5	0	-1,1	-1,1
2	x-y, x, z+2/3	12,42	B3LYP/6-31G(d,p)	-0,5	0	-0,5	0	-1	-1
2	x, y, z	13,26	B3LYP/6-31G(d,p)	-0,4	0	-0,2	0	-0,6	-0,6
2	x, y, z	13,26	B3LYP/6-31G(d,p)	0	0	-0,6	0	-0,5	-0,5
2	y, -x+y, z+1/3	14,76	B3LYP/6-31G(d,p)	-0,4	0	-0,1	0	-0,5	-0,5
2	-y, x-y, z+1/3	12,32	B3LYP/6-31G(d,p)	0,1	0	-0,6	0	-0,4	-0,4
1	x-y, x, z+2/3	12,95	B3LYP/6-31G(d,p)	-0,1	0	-0,3	0	-0,4	-0,2
2	-x, -y, z	14,15	B3LYP/6-31G(d,p)	-0,3	0	-0,1	0	-0,4	-0,4
2	x-y, x, z+2/3	15,58	B3LYP/6-31G(d,p)	-0,3	0	-0,1	0	-0,4	-0,4
2	-y, x-y, z+1/3	11,83	B3LYP/6-31G(d,p)	0,2	0	-0,6	0	-0,3	-0,3
2	y, -x+y, z+1/3	12,89	B3LYP/6-31G(d,p)	0	0	-0,3	0	-0,3	-0,3
1	y, -x+y, z+1/3	12,95	B3LYP/6-31G(d,p)	0	0	-0,3	0	-0,3	-0,15
2	-y, x-y, z+1/3	14,66	B3LYP/6-31G(d,p)	-0,1	0	-0,1	0	-0,3	-0,3
2	-y, x-y, z+1/3	15,45	B3LYP/6-31G(d,p)	-0,1	0	-0,1	0	-0,3	-0,3
2	-y, x-y, z+1/3	16,33	B3LYP/6-31G(d,p)	-0,2	0	-0,1	0	-0,3	-0,3
2	y, -x+y, z+1/3	15,96	B3LYP/6-31G(d,p)	-0,1	0	-0,1	0	-0,2	-0,2
2	x-y, x, z+2/3	17,5	B3LYP/6-31G(d,p)	-0,1	0	-0,1	0	-0,2	-0,2
2	-x, -y, z	17,31	B3LYP/6-31G(d,p)	0	0	-0,1	0	-0,1	-0,1
2	-x, -y, z	14,11	B3LYP/6-31G(d,p)	0,1	0	-0,1	0	0	0
2	-x, -y, z	16,61	B3LYP/6-31G(d,p)	0	0	-0,1	0	0	0
2	x-y, x, z+2/3	17,11	B3LYP/6-31G(d,p)	0,2	0	-0,1	0	0,1	0,1
1	-x, -y, z	17,18	B3LYP/6-31G(d,p)	0,1	0	-0,1	0	0,1	0,05
2	x, y, z	18,2	B3LYP/6-31G(d,p)	0,1	0	0	0	0,1	0,1
2	x, y, z	12,47	B3LYP/6-31G(d,p)	0,4	0	-0,2	0	0,2	0,2
2	x-y, x, z+2/3	14,35	B3LYP/6-31G(d,p)	0,3	0	-0,1	0	0,2	0,2
									-137,35

Table S8. *Crystal Explorer 21* estimate of lattice energies (kJ/mol) for(*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1H-benzo[d]imidazole **9b.**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	-x, y+1/2, -z	5,13	B3LYP/6-31G(d,p)	-60,5	-16,7	-51,1	70,8	-77,1	-77,1
2	-x, y+1/2, -z	5,82	B3LYP/6-31G(d,p)	-4,4	-2	-40,7	19,1	-29,8	-29,8
2	x, y, z	7,03	B3LYP/6-31G(d,p)	-6,4	-3,1	-23,9	13,6	-21,5	-21,5
2	x, y, z	14,97	B3LYP/6-31G(d,p)	-2,3	-0,2	-6,8	0	-8,5	-8,5
2	-x, y+1/2, -z	13,5	B3LYP/6-31G(d,p)	1,8	-0,5	-10,3	0	-7,4	-7,4
2	-x, y+1/2, -z	11,76	B3LYP/6-31G(d,p)	-0,8	-0,1	-6,1	1,2	-5,5	-5,5
2	-x, y+1/2, -z	11,52	B3LYP/6-31G(d,p)	-0,8	-0,2	-4,8	1,5	-4,2	-4,2
2	x, y, z	13,22	B3LYP/6-31G(d,p)	-1,3	-0,1	-2,9	0	-4	-4
2	x, y, z	8,19	B3LYP/6-31G(d,p)	-0,7	-0,3	-2,3	0	-2,9	-2,9
2	x, y, z	10,79	B3LYP/6-31G(d,p)	-1,4	-0,1	-0,7	0	-2,2	-2,2
2	-x, y+1/2, -z	11,19	B3LYP/6-31G(d,p)	-0,6	-0,1	-1,4	0	-1,9	-1,9
2	x, y, z	14,06	B3LYP/6-31G(d,p)	-0,5	0	-0,2	0	-0,7	-0,7
2	-x, y+1/2, -z	16,76	B3LYP/6-31G(d,p)	-0,4	0	-0,2	0	-0,6	-0,6
2	-x, y+1/2, -z	18,18	B3LYP/6-31G(d,p)	-0,4	0	-0,1	0	-0,5	-0,5
2	x, y, z	19,3	B3LYP/6-31G(d,p)	-0,4	0	-0,1	0	-0,5	-0,5
2	-x, y+1/2, -z	15,4	B3LYP/6-31G(d,p)	-0,2	0	-0,1	0	-0,3	-0,3
2	x, y, z	19,5	B3LYP/6-31G(d,p)	-0,1	0	0	0	-0,2	-0,2
2	-x, y+1/2, -z	14,83	B3LYP/6-31G(d,p)	0,1	0	-0,2	0	-0,1	-0,1
2	-x, y+1/2, -z	16,7	B3LYP/6-31G(d,p)	0,2	0	-0,4	0	-0,1	-0,1
2	-x, y+1/2, -z	19,44	B3LYP/6-31G(d,p)	0	0	-0,1	0	-0,1	-0,1
2	x, y, z	18,72	B3LYP/6-31G(d,p)	0,1	0	-0,1	0	0	0
2	x, y, z	14,21	B3LYP/6-31G(d,p)	0,2	0	-0,1	0	0,1	0,1
2	-x, y+1/2, -z	14,82	B3LYP/6-31G(d,p)	0,6	0	-0,2	0	0,4	0,4
2	x, y, z	14,97	B3LYP/6-31G(d,p)	0,6	0	-0,1	0	0,5	0,5
2	-x, y+1/2, -z	13,81	B3LYP/6-31G(d,p)	0,8	0	-0,2	0	0,7	0,7
2	x, y, z	10,79	B3LYP/6-31G(d,p)	1,3	-0,1	-0,6	0	0,8	0,8
2	x, y, z	12,35	B3LYP/6-31G(d,p)	1,8	-0,1	-0,9	0	1,1	1,1
2	-x, y+1/2, -z	12,37	B3LYP/6-31G(d,p)	1,3	0	-0,2	0	1,2	1,2
2	x, y, z	14,21	B3LYP/6-31G(d,p)	2,5	0	-1,3	0	1,5	1,5
									-161,8

Table S9. *Crystal Explorer 21* estimate of lattice energies (kJ/mol) for (*R*)-2-benzylsulfinyl-1-methyl-1-H-benzo[d]imidazole **10b.**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x, y, z	4.71	B3LYP/6-31G(d,p)	-12.1	-5.1	-62.6	32.8	-50.8
2	x, y, z	6.32	B3LYP/6-31G(d,p)	-13.1	-4.6	-28.5	21.5	-28.7
2	x, y, z	6.64	B3LYP/6-31G(d,p)	-12.1	-3.7	-29.7	25.4	-25.7
2	-x, y+1/2, -z	12.2	B3LYP/6-31G(d,p)	-6.7	-0.3	-9.9	0	-15.9
2	-x, y+1/2, -z	11.89	B3LYP/6-31G(d,p)	-3.2	-0.4	-11.3	7.7	-8.7
2	-x, y+1/2, -z	12.81	B3LYP/6-31G(d,p)	-0.9	-0.2	-7.6	0	-7.7
2	x, y, z	9.62	B3LYP/6-31G(d,p)	-1.6	-0.2	-1.6	0	-3.2
2	-x, y+1/2, -z	13.76	B3LYP/6-31G(d,p)	-1	0	-1	0	-2
2	x, y, z	8.95	B3LYP/6-31G(d,p)	-0.2	-0.1	-1.7	0	-1.8
2	x, y, z	9.41	B3LYP/6-31G(d,p)	-0.5	-0.1	-1.3	0	-1.8
2	-x, y+1/2, -z	13.53	B3LYP/6-31G(d,p)	-0.5	-0.1	-1.1	0	-1.6
2	-x, y+1/2, -z	14.16	B3LYP/6-31G(d,p)	-1	0	-0.5	0	-1.5
2	x, y, z	13.61	B3LYP/6-31G(d,p)	-0.7	0	-0.2	0	-0.9
2	-x, y+1/2, -z	14.88	B3LYP/6-31G(d,p)	-0.4	0	-0.3	0	-0.6
2	-x, y+1/2, -z	13.71	B3LYP/6-31G(d,p)	0	0	-0.6	0	-0.5
2	-x, y+1/2, -z	16.1	B3LYP/6-31G(d,p)	-0.3	0	-0.1	0	-0.4
2	x, y, z	13.27	B3LYP/6-31G(d,p)	0	0	-0.2	0	-0.3
2	-x, y+1/2, -z	15.69	B3LYP/6-31G(d,p)	-0.1	0	-0.2	0	-0.3
2	-x, y+1/2, -z	17.22	B3LYP/6-31G(d,p)	-0.2	0	-0.1	0	-0.3
2	-x, y+1/2, -z	13.35	B3LYP/6-31G(d,p)	0.4	0	-0.7	0	-0.2
2	-x, y+1/2, -z	16.35	B3LYP/6-31G(d,p)	-0.1	0	-0.1	0	-0.2
2	-x, y+1/2, -z	17.31	B3LYP/6-31G(d,p)	-0.1	0	-0.1	0	-0.2
2	x, y, z	12.63	B3LYP/6-31G(d,p)	0.1	0	-0.2	0	-0.1
2	-x, y+1/2, -z	16.11	B3LYP/6-31G(d,p)	0	0	-0.1	0	-0.1
2	-x, y+1/2, -z	16.32	B3LYP/6-31G(d,p)	0	0	-0.1	0	-0.1
2	-x, y+1/2, -z	17.6	B3LYP/6-31G(d,p)	-0.1	0	-0.1	0	-0.1
2	-x, y+1/2, -z	17.68	B3LYP/6-31G(d,p)	-0.1	0	-0.1	0	-0.1
2	x, y, z	12.07	B3LYP/6-31G(d,p)	0.3	0	-0.4	0	0
2	x, y, z	12.83	B3LYP/6-31G(d,p)	0.2	0	-0.2	0	0
2	-x, y+1/2, -z	15.92	B3LYP/6-31G(d,p)	0.1	0	-0.1	0	0
2	x, y, z	14.76	B3LYP/6-31G(d,p)	0.1	0	-0.1	0	0.1
2	-x, y+1/2, -z	14.09	B3LYP/6-31G(d,p)	0.5	0	-0.3	0	0.2
								-74

Table S10. Geometric characteristics of stronger hydrogen bondings

Crystal Structure		**Angle (°)**	**H···N (Å)**	**N···N (Å)**	**H-N (Å)**
5b	N122-H122-N129	162(5)	2.07	2.885	0.84
		Angle (°)	**H···O (Å)**	**N···O (Å)**	**H-N (Å)**
9b	N29-H29-O2	173(4)	2.05	2.820	0.77

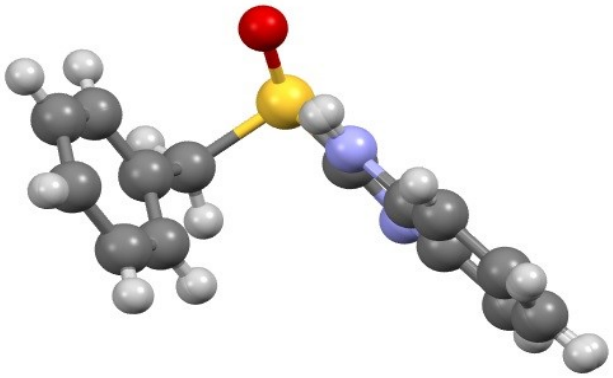


Figure S9. Overlap between the inverted reported crystal structure of "racemic" **5b** with (*R*)-**5b** synthesised in the present work.

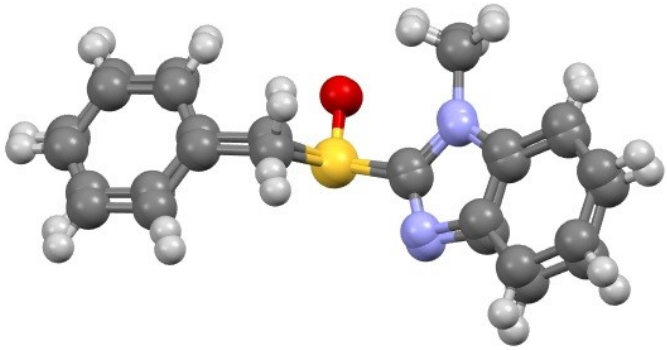


Figure S10. Overlap between the inverted reported crystal structure of (*R*)-**10b** with the "racemic" sample synthesised in the present work.

Graphical Reports of spectral data

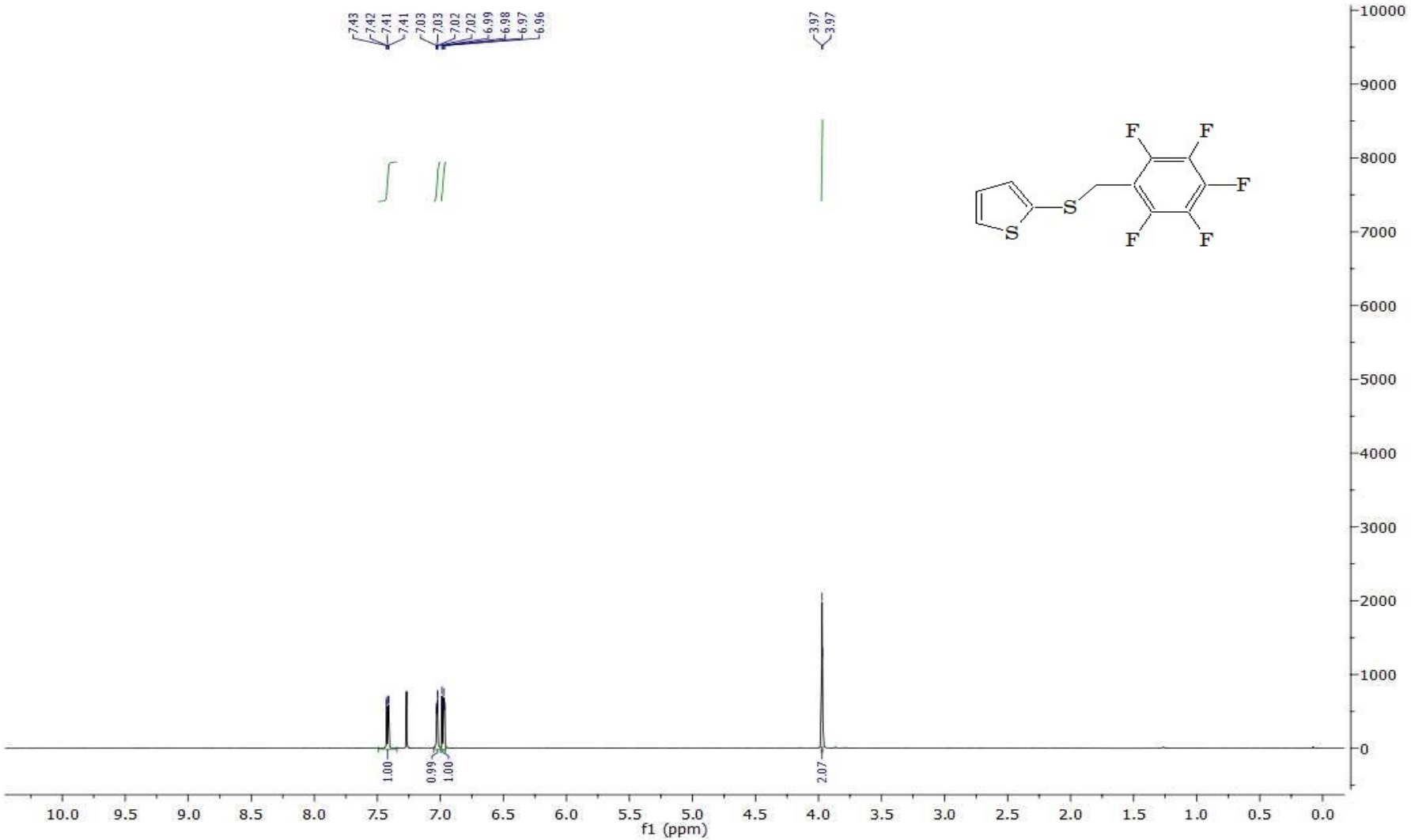


Figure S11. 400 MHz ^{1}H-NMR spectrum of (*R*)-2-(2,3,4,5,6-pentafluorobenzylthio)thiophene **2a.**

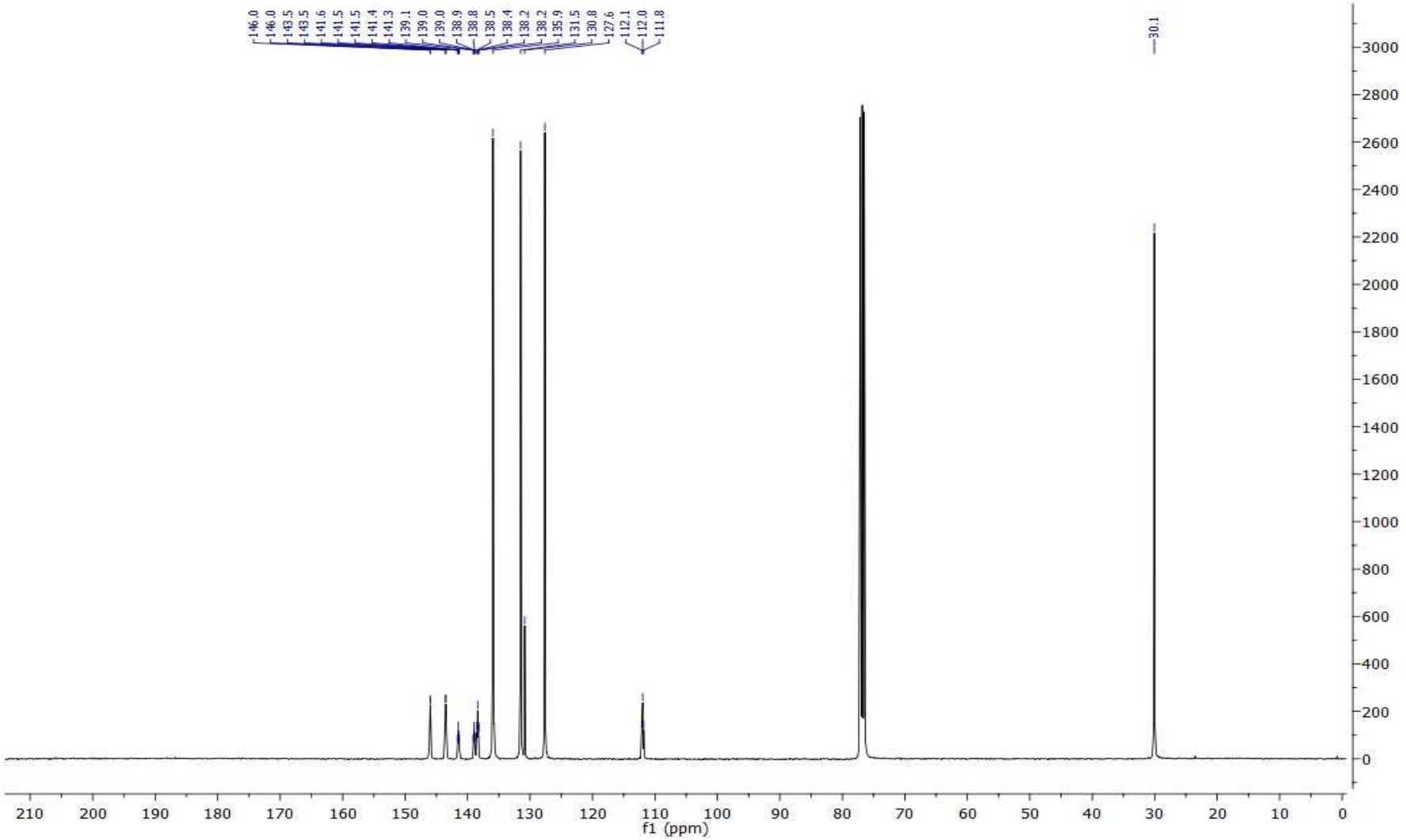


Figure S12. 100 MHz ^{13}C-NMR spectrum of (*R*)-2-(2,3,4,5,6-pentafluorobenzylthio)thiophene **2a.**

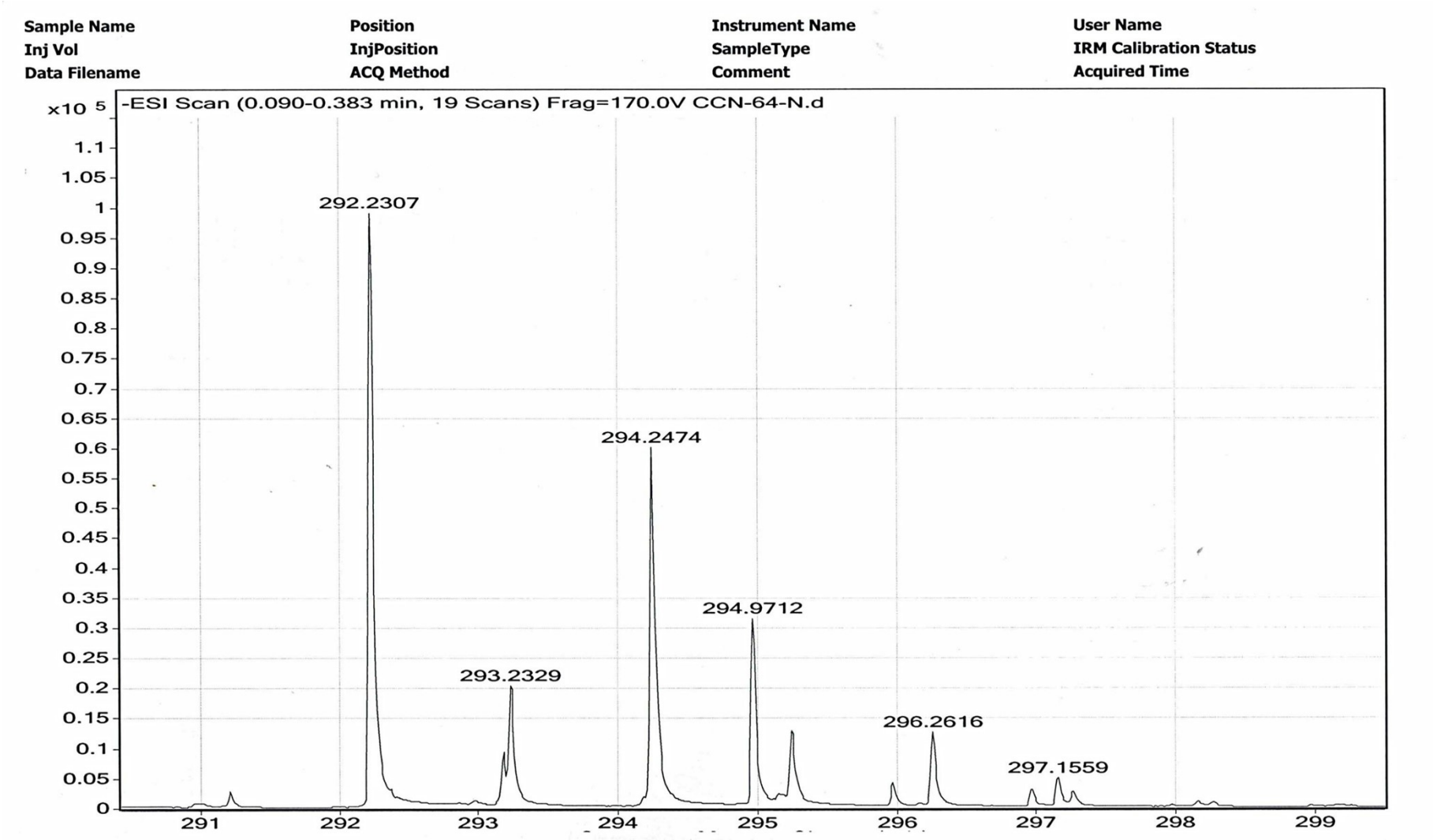


Figure S13. QTOF MS spectrum of (*R*)-2-(2,3,4,5,6-pentafluorobenzylthio)thiophene **2a.**

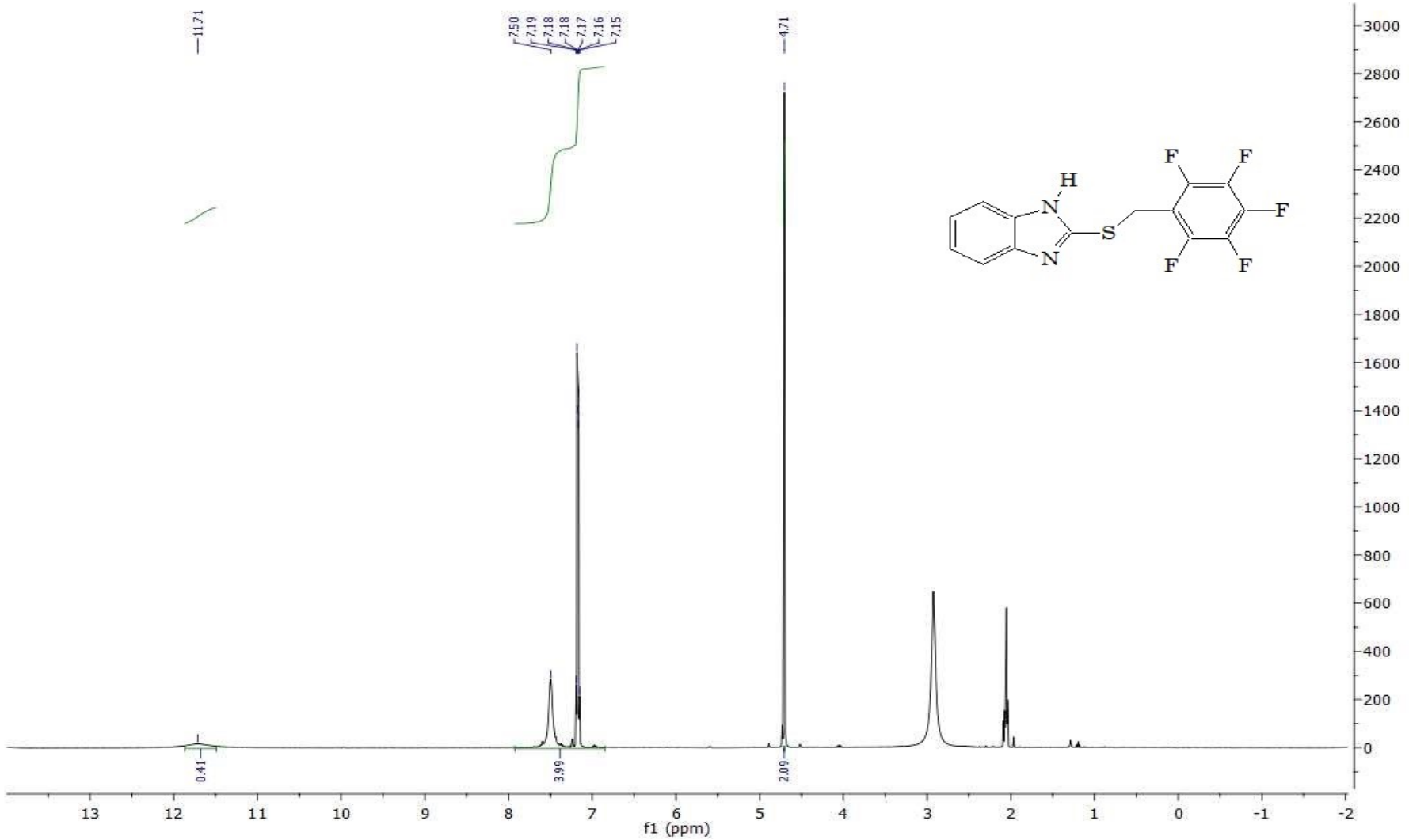


Figure S14. 400 MHz ^{1}H-NMR spectrum of 2-(2,3,4,5,6-pentafluorobenzylthio)-1H-benzo[d]imidazole **9a.**

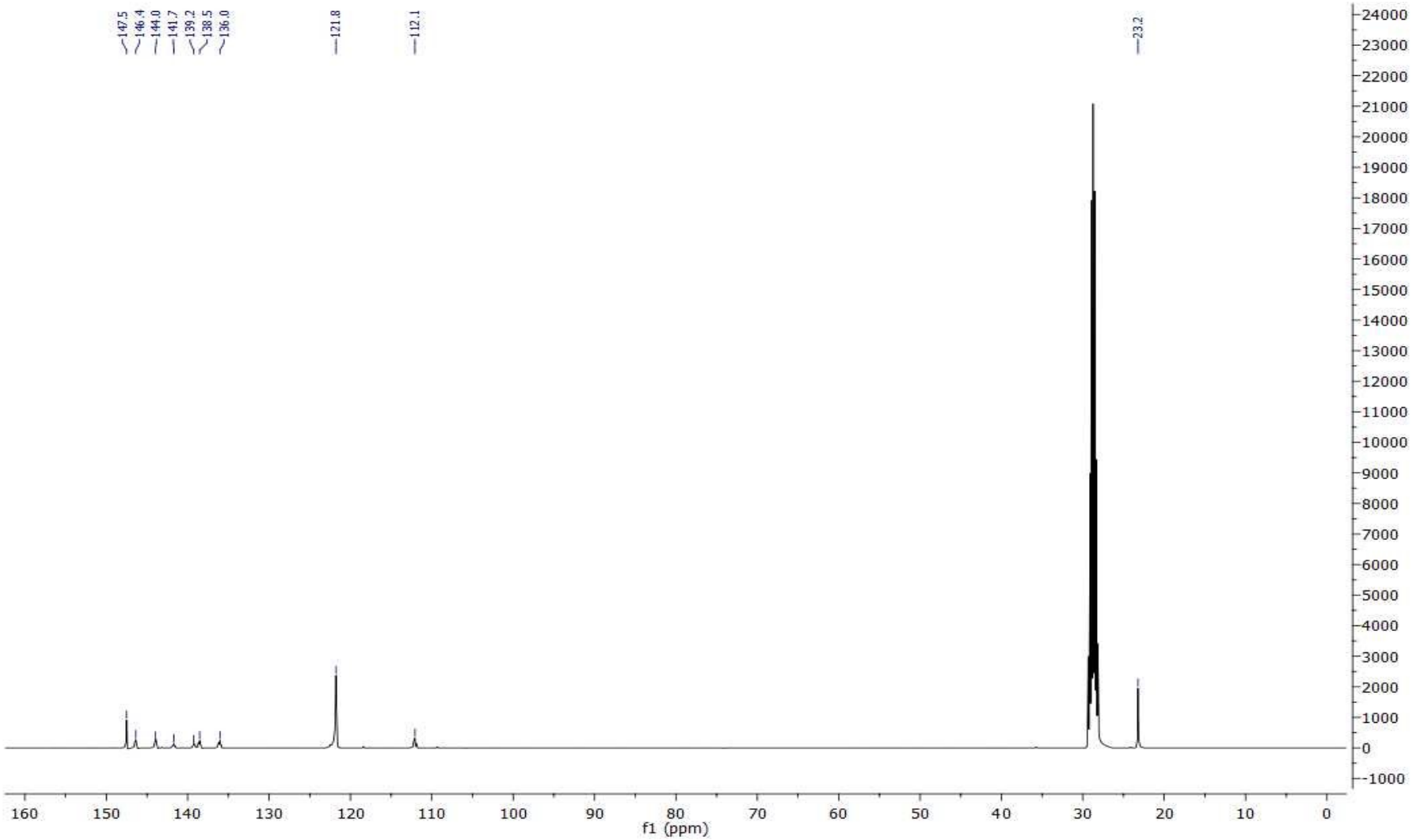


Figure S15. 100 MHz ^{13}C-NMR spectrum of 2-(2,3,4,5,6-pentafluorobenzylthio)-1H-benzo[d]imidazole **9a.**

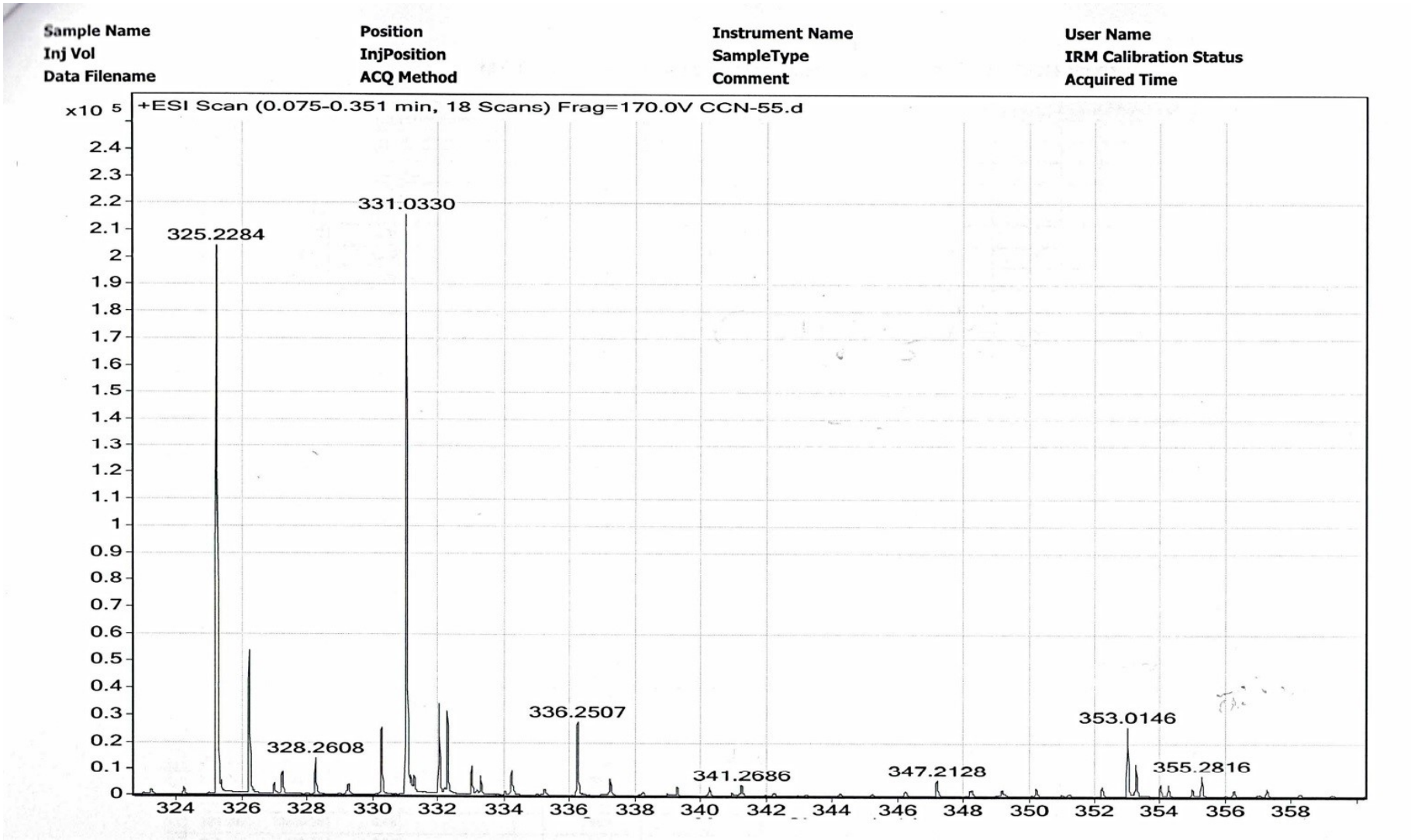


Figure S16. QTOF MS spectrum of 2-(2,3,4,5,6-pentafluorobenzylthio)-1H-benzo[d]imidazole **9a.**

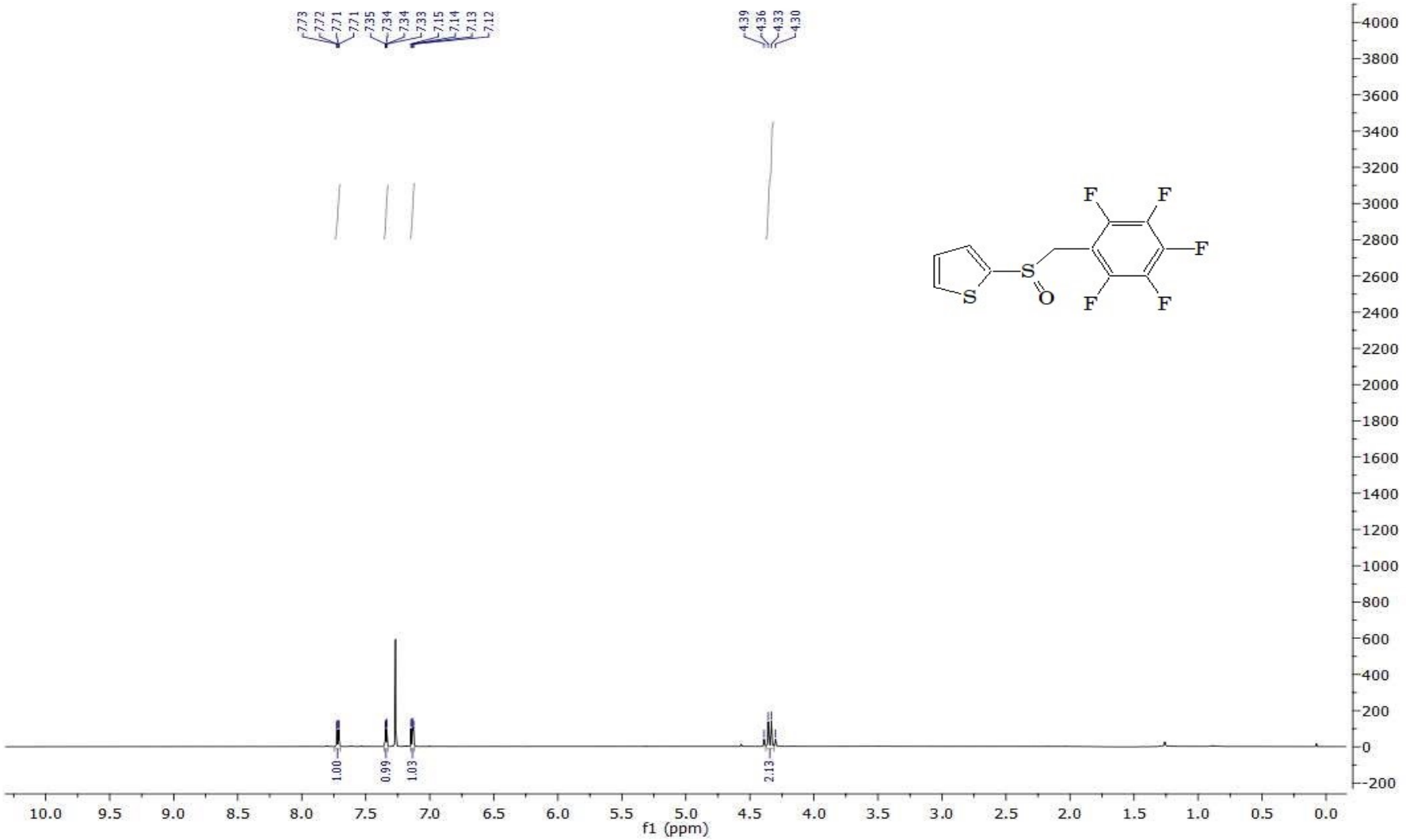


Figure S17. 400 MHz ^{1}H-NMR spectrum of of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)thiophene **2b**

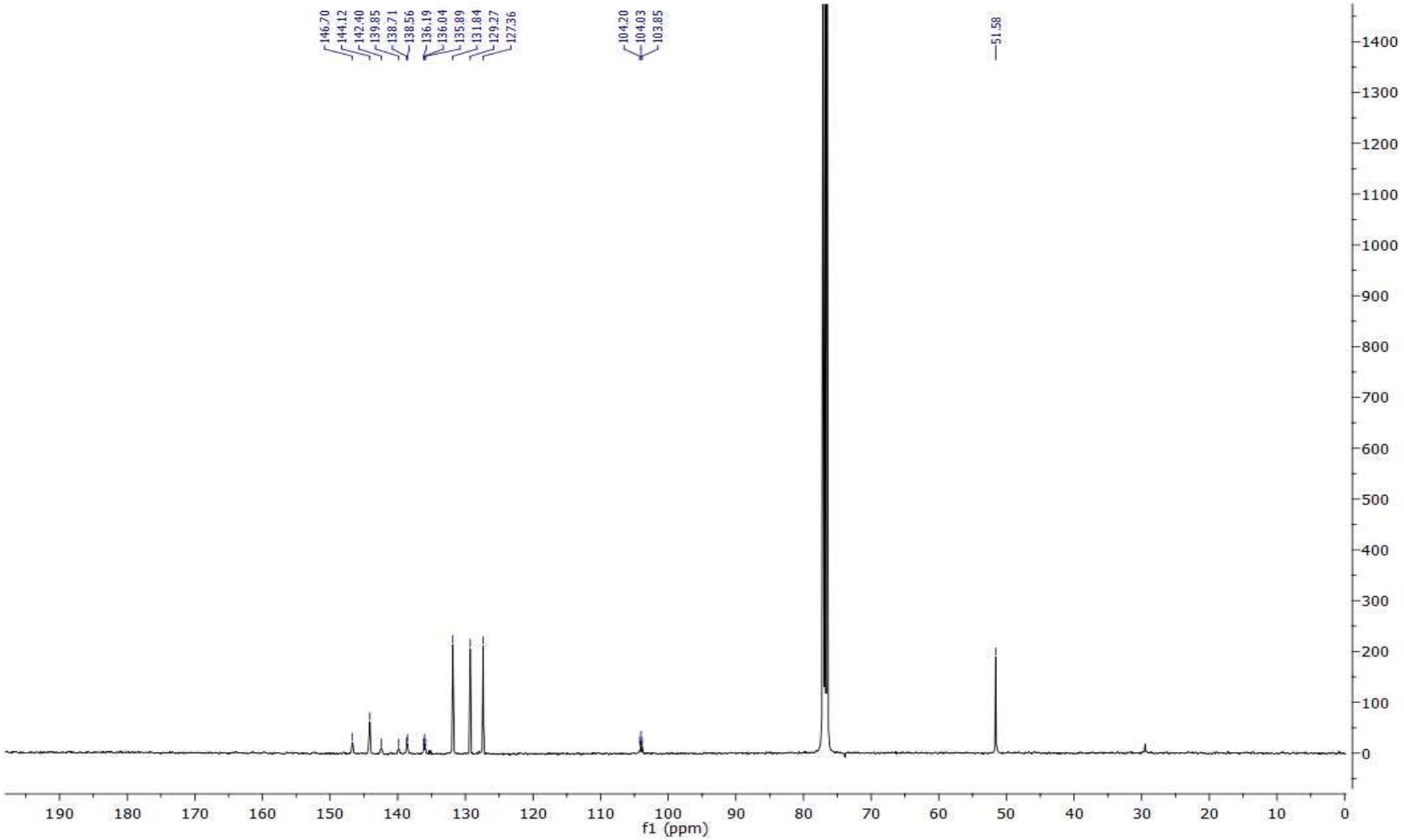


Figure S18. 100 MHz ^{13}C-NMR spectrum of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)thiophene **2b**

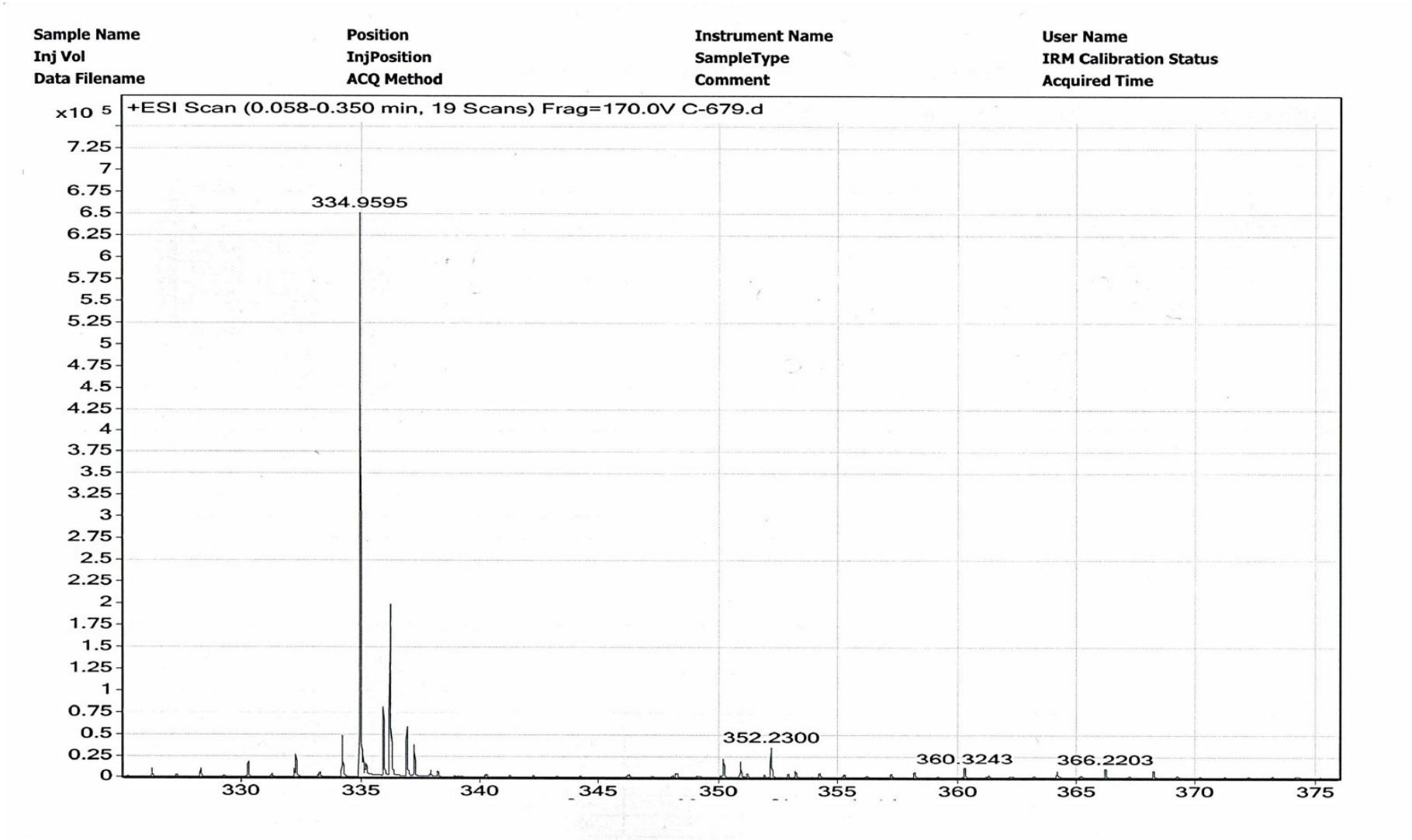


Figure S19 QTOF MS spectrum of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)thiophene **2b**

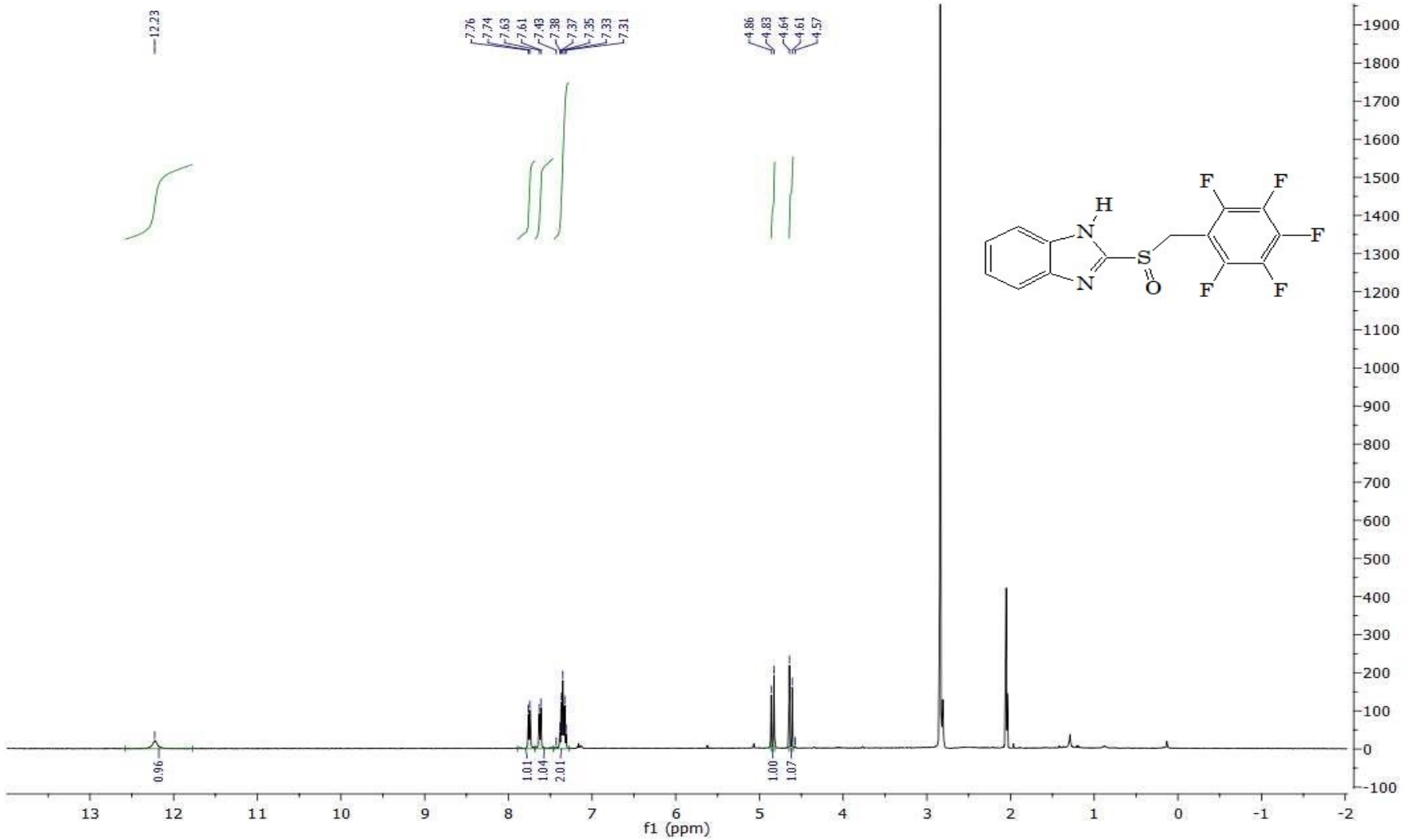


Figure S20. 400 MHz ^{1}H-NMR spectrum of 2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1H-benzo[d]imidazole **9b.**

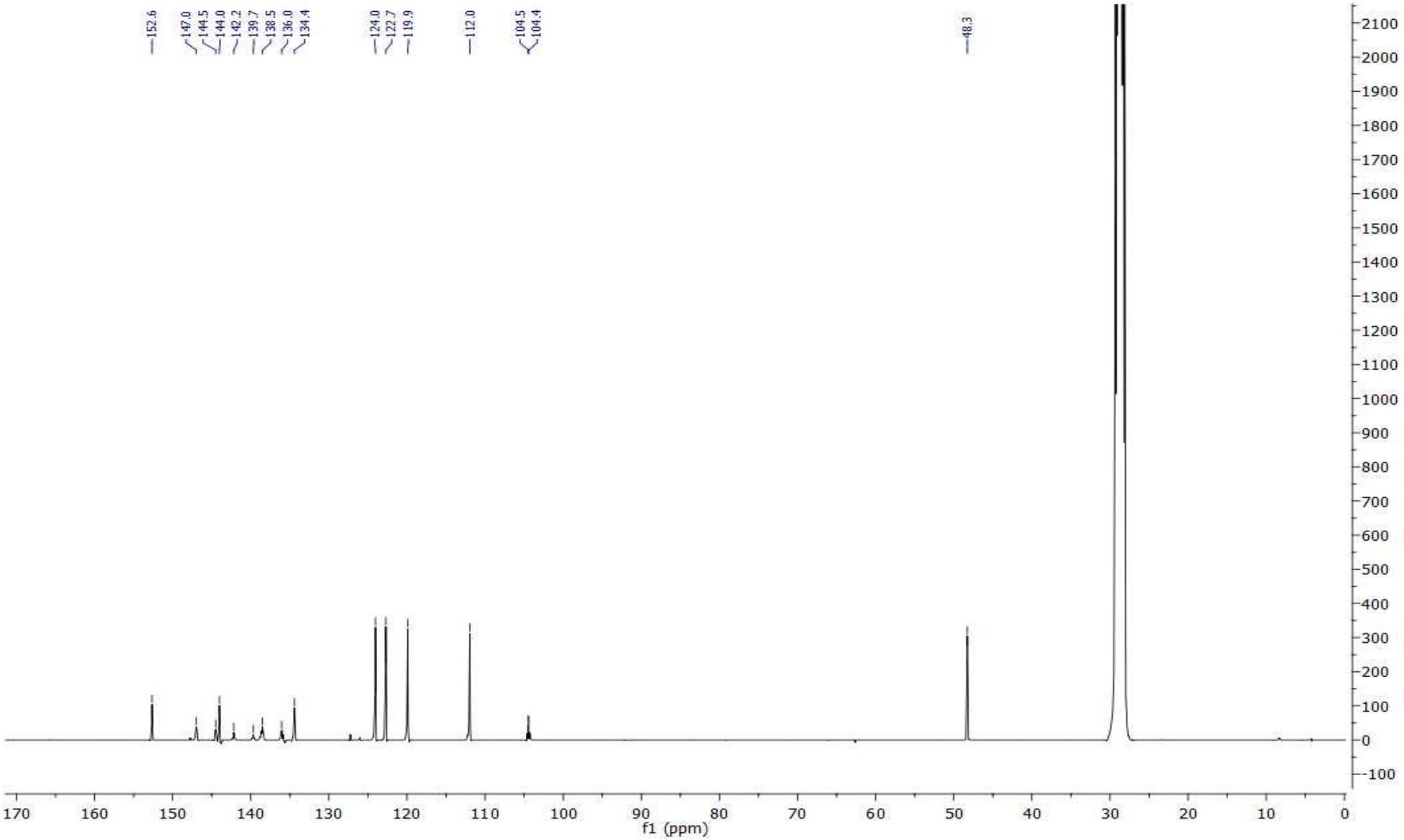


Figure S21. 100 MHz ^{13}C-NMR spectrum of 2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1H-benzo[d]imidazole **9b.**

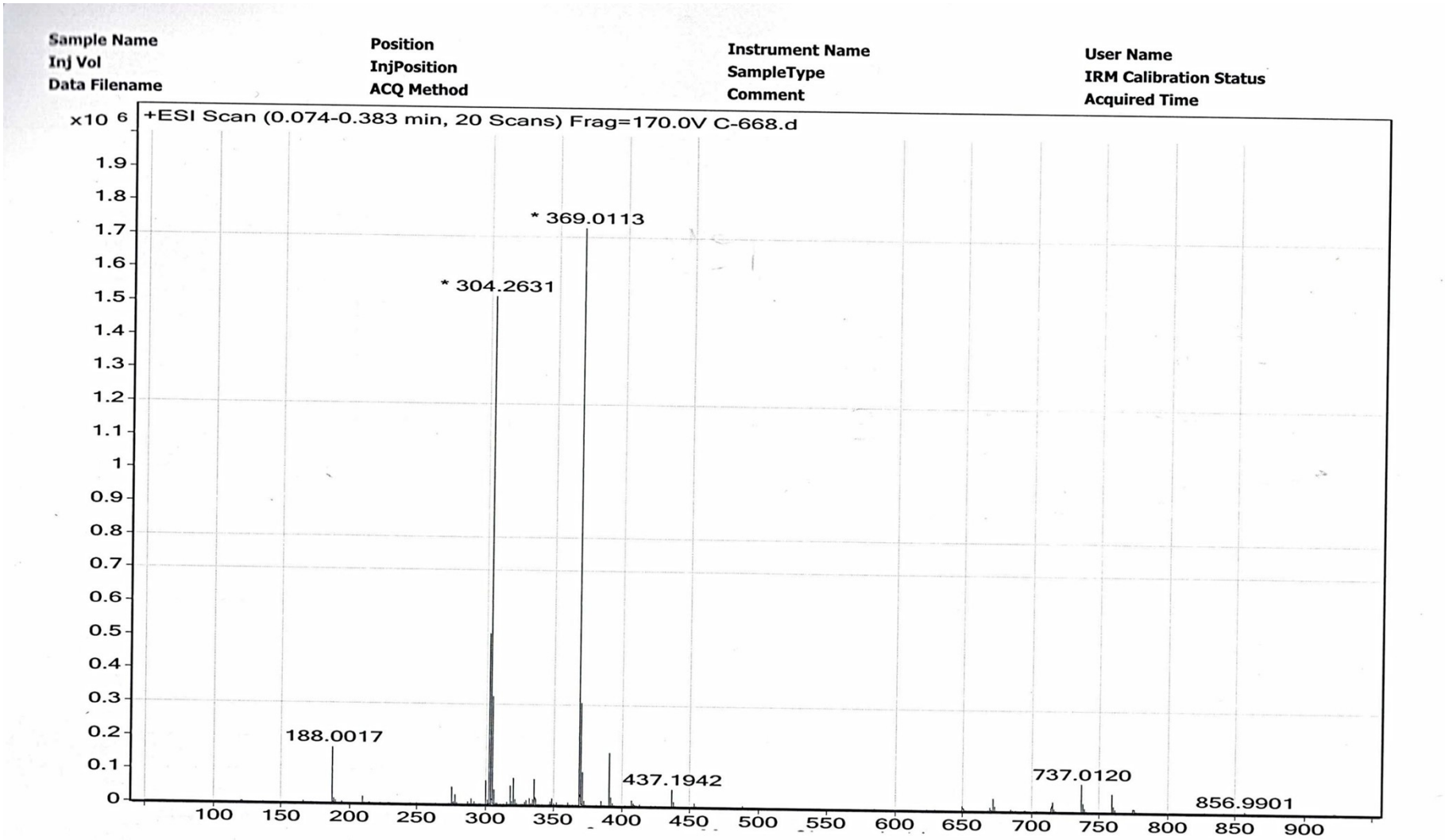
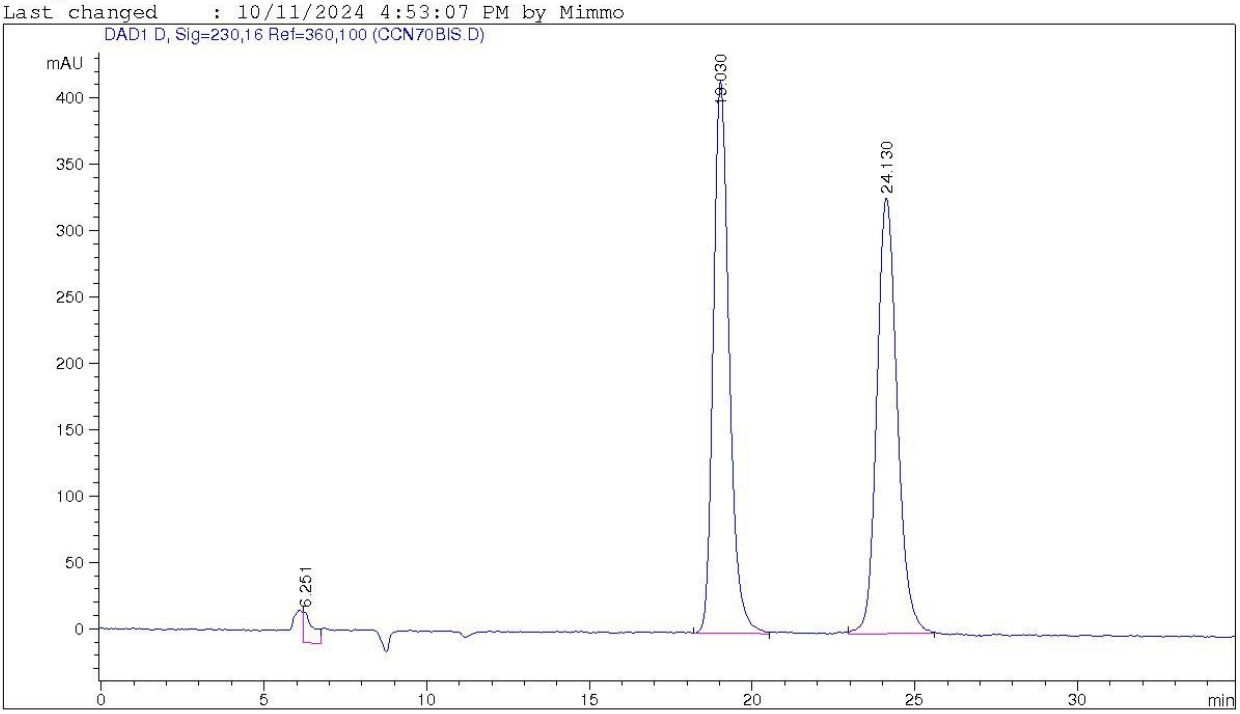


Figure S22. QTOF MS spectrum of 2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1H-benzo[d]imidazole **9b.**

Data File C:\HPCHEM\1\DATA\CCN70BIS.D Sample Name: ThSOCH2Ph_rac

ccn70bis ThSOCH2Ph racemico
Chiralcel OD-H esano:IPA 80:20 0.5 ml/min

```
==================================================================
Injection Date  : 9/29/2022 10:47:14 AM
Sample Name     : ThSOCH2Ph_rac                  Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 9/29/2022 8:34:43 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.251 VB    0.2851  485.30112   22.72493   1.6788
   2  19.030 VB    0.5201 1.41173e4   415.81421  48.8349
   3  24.130 VB    0.6686 1.43056e4   328.18442  49.4863

Totals :                  2.89081e4   766.72356

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```

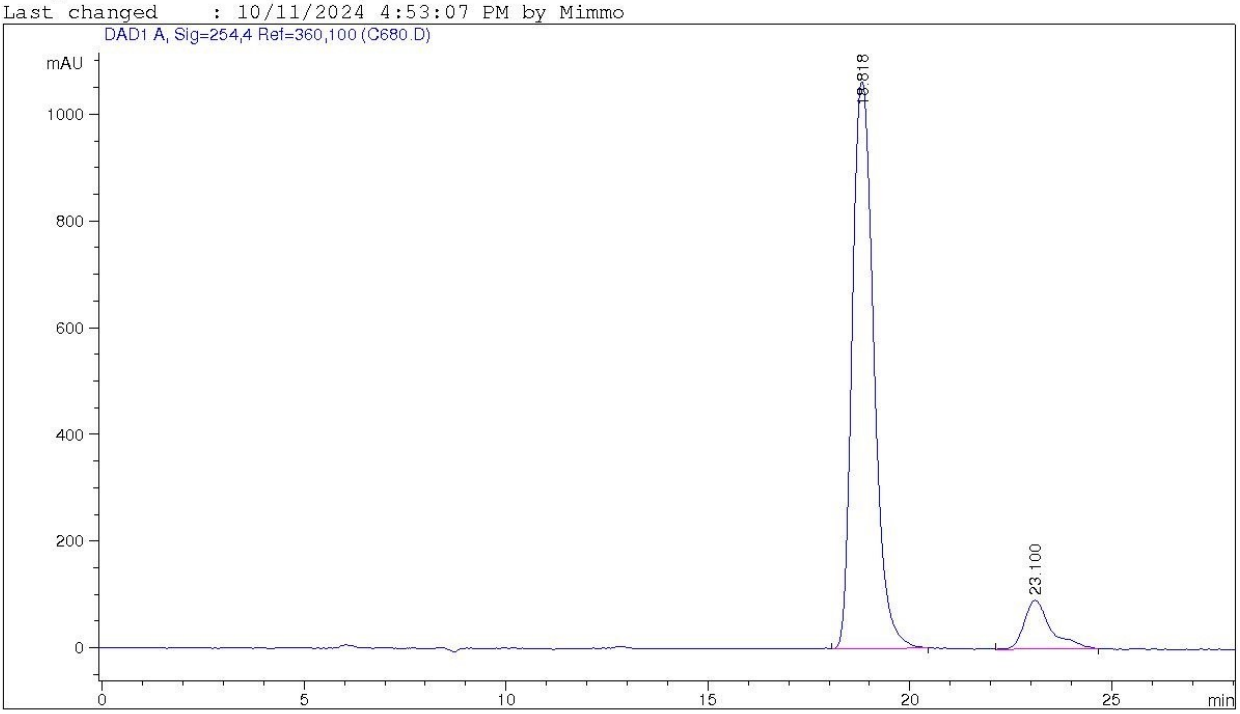
Page 1 of 1

Figure S23. HPLC of racemic 2-(Benzylsulfinyl)thiophene **1b.**

Data File C:\HPCHEM\1\DATA\C680.D Sample Name: ThSOCH2Ph_ch

c608 ThSOCH2Ph chirale
Chiralcel OD-H esano:IPA 80:20 0.5 ml/min

```
==================================================================
Injection Date  : 9/29/2022 11:24:03 AM
Sample Name     : ThSOCH2Ph_ch                    Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 9/29/2022 8:34:43 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```



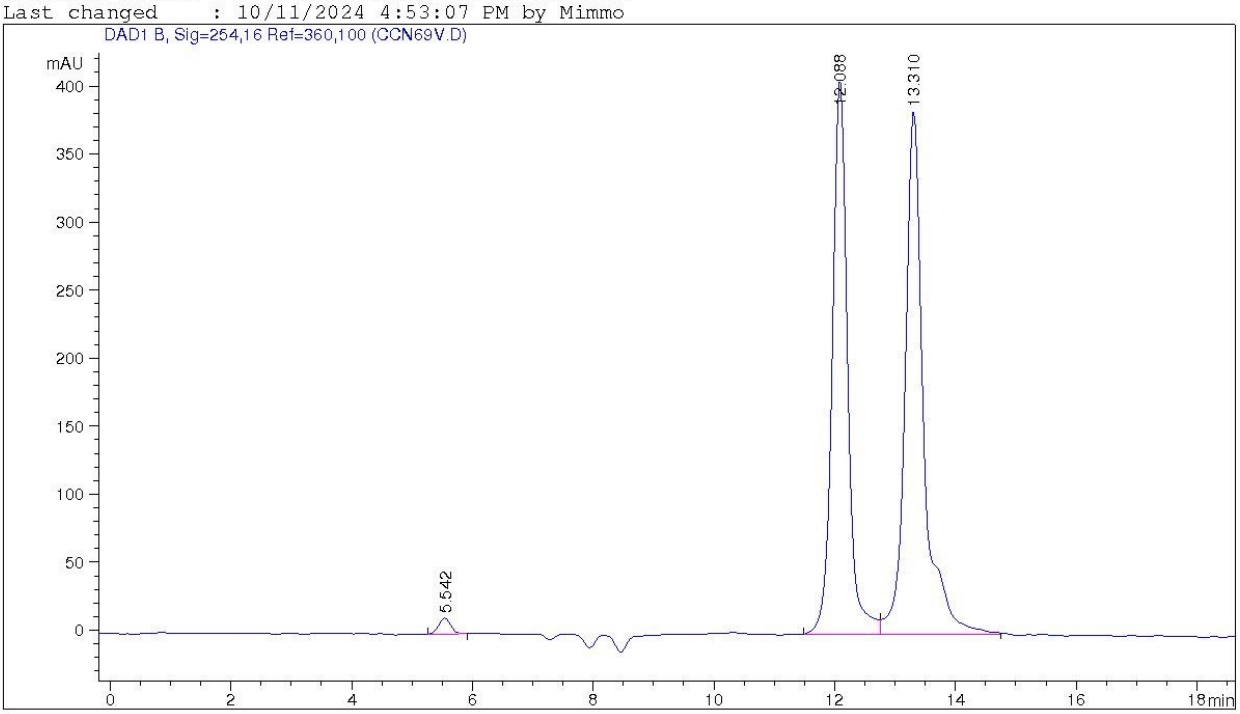

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.818 VB    0.5847 3.94050e4  1062.47437  90.4178
   2  23.100 VB    0.6446 4176.01660   91.47438   9.5822

Totals :                  4.35810e4  1153.94875

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```


Figure S24. HPLC of (*R*)-2-(Benzylsulfinyl)thiophene **1b**.

Data File C:\HPCHEM\1\DATA\CCN69V.D Sample Name: ThSOCH2C6F5

CCN69 2-ThiophSOCH2C6F5 verifica
Chiralpak IA n-Esano/i-Propanolo 70:30

```
==================================================================
Injection Date  : 10/11/2024 12:12:20 PM
Sample Name     : ThSOCH2C6F5                    Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 11:41:05 AM by Mimmo
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```



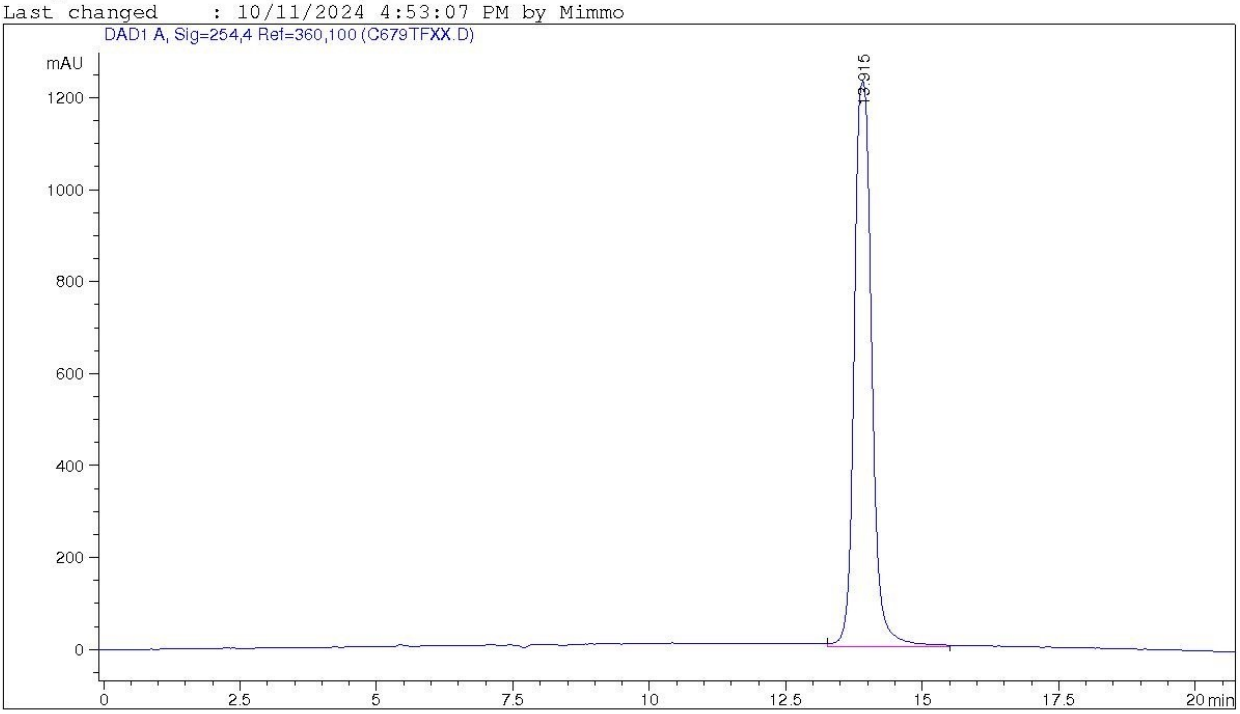

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.542 BB    0.2206  166.62471   11.80993   1.0688
   2  12.088 BV    0.2702 7224.01465  408.64069  46.3375
   3  13.310 VB R  0.3109 8199.34180  384.63553  52.5937

Totals :                  1.55900e4   805.08614

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```


Figure S25. HPLC of racemic 2-(2,3,4,5,6-pentafluorobenzylsulfinyl)thiophene **2b.**

Data File C:\HPCHEM\1\DATA\C679TFXX.D Sample Name: C679ThienFluorXX

C679 THienylSOCH2C6F5 cristallizzato
Chiralpak IA 70:30

```
==================================================================
Injection Date  : 1/13/2023 10:34:26 AM
Sample Name     : C679ThienFluorXX              Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 1/13/2023 9:17:48 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.915 VV    0.3490 2.74959e4  1229.25037 100.0000

Totals :                  2.74959e4  1229.25037

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```

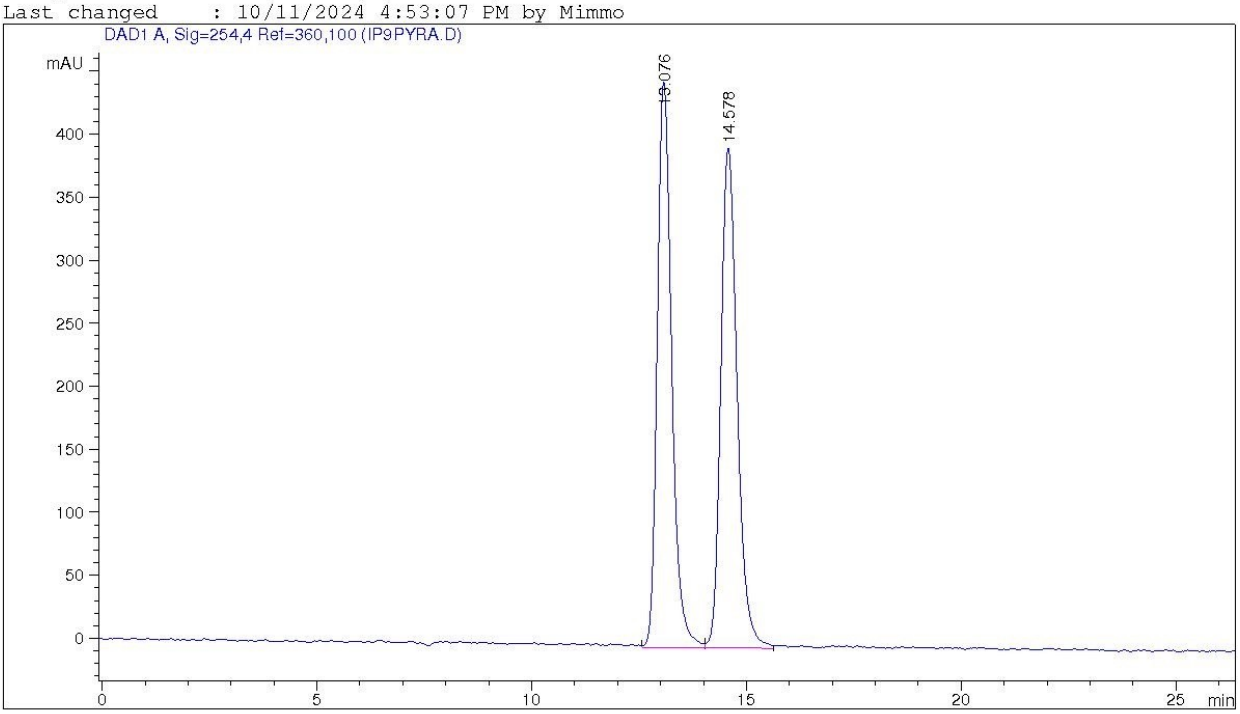
Page 1 of 1

Figure S26. HPLC of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)thiophene **2b**

Data File C:\HPCHEM\1\DATA\IP9PYRA.D Sample Name: IP9BrPhSOCH2Pyra

IP9 p-Bromofenil SOCH2 2Py racemico
Chiralcel OD-H esano:IPA 70:30 0.5 ml/min

```
==========================================================================
Injection Date  : 6/18/2019 10:47:04 AM
Sample Name     : IP9BrPhSOCH2Pyra                Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 6/18/2019 8:52:36 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```



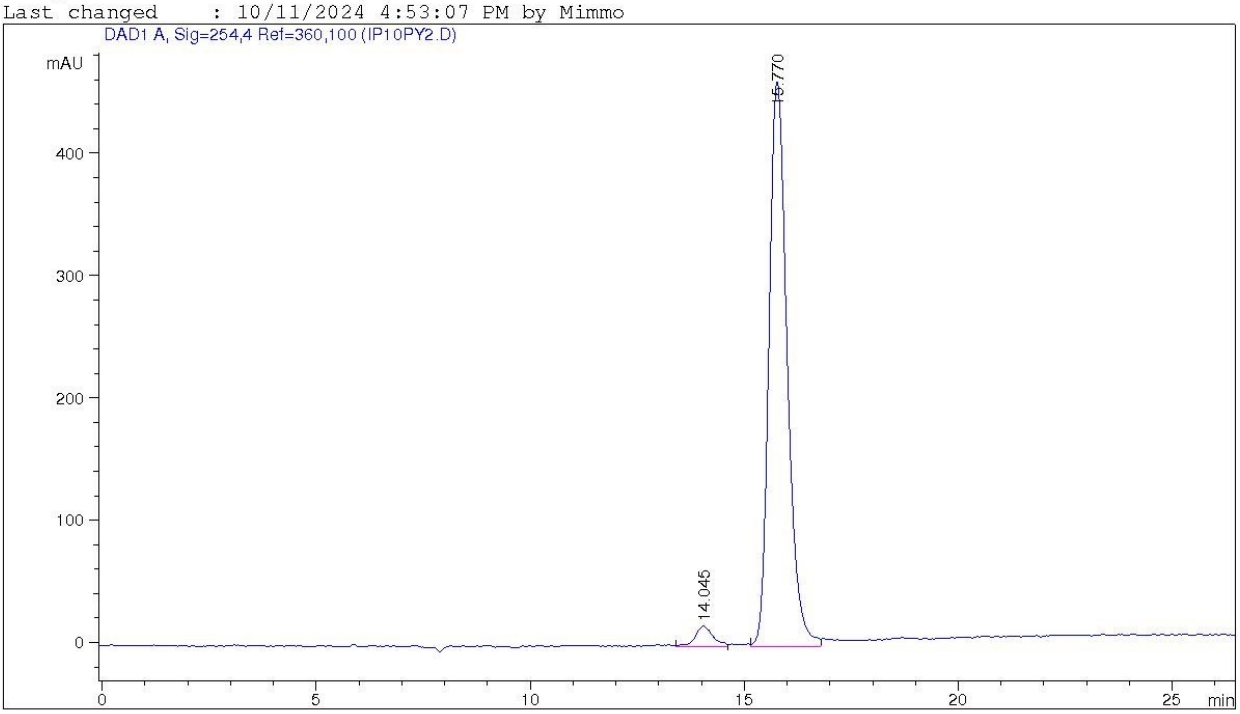

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.076 VV    0.3639 1.04661e4   449.01904  49.9125
   2  14.578 VV    0.4046 1.05028e4   397.03339  50.0875

Totals :                  2.09689e4   846.05243

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```


Figure S27.HPLC of racemic 2-(4-bromophenylmethylsulfinyl)pyridine **4b.**

Data File C:\HPCHEM\1\DATA\IP10PY2.D Sample Name: IP10-2PycristBis

ip10 pBrPhSOCH2-2Py cristallizzato Bis
Chiralcel OD-H 70:30

```
==================================================================
Injection Date  : 1/24/2023 10:28:37 AM
Sample Name     : IP10-2PycristBis              Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 1/24/2023 8:59:11 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```



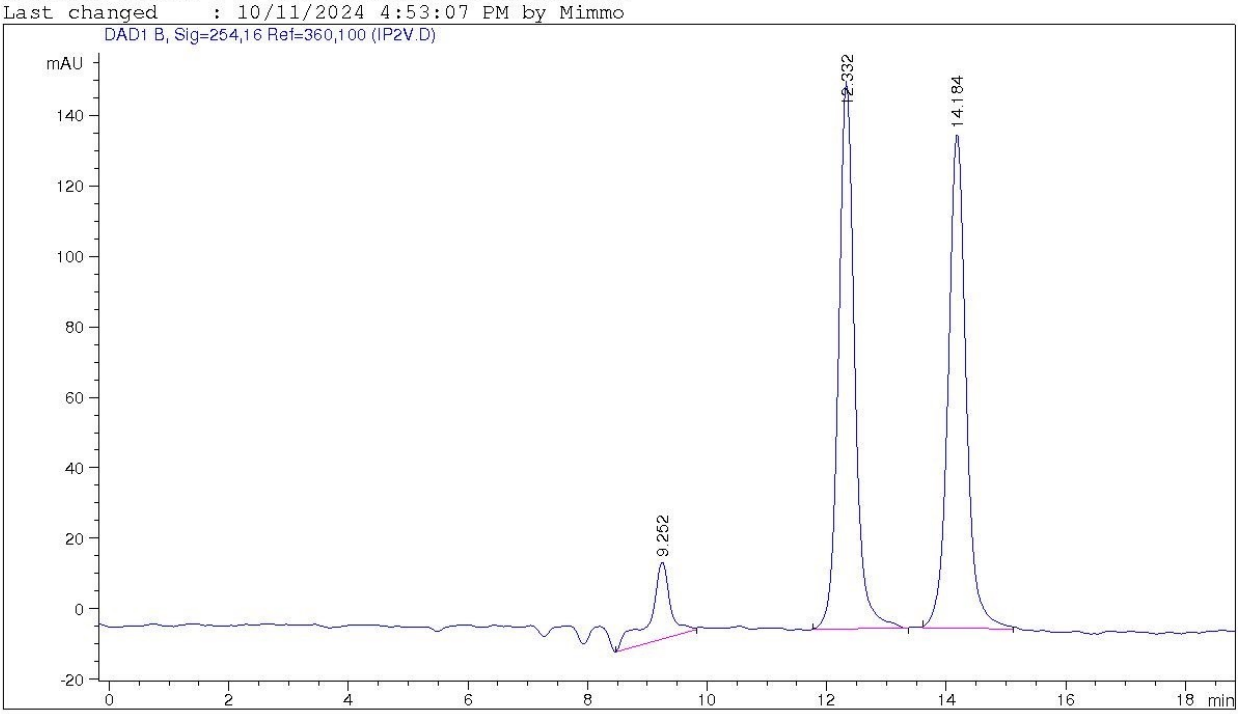

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.045 BV    0.3889  480.18973   16.62938   3.3990
   2  15.770 VV    0.4529 1.36474e4   461.65616  96.6010

Totals :                  1.41276e4   478.28554

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```


Figure S28. HPLC of (*R*)- 2-(4-bromophenylmethylsulfinyl)pyridine **4b.**

Data File C:\HPCHEM\1\DATA\IP2V.D Sample Name: BzImSOCH2Ph

IP2 BzImSOCH2Ph verifica
Chiralpak IA n-Esano/i-Propanolo 70:30

```
==================================================================
Injection Date  : 10/11/2024 12:33:55 PM
Sample Name     : BzImSOCH2Ph                    Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 11:41:05 AM by Mimmo
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```



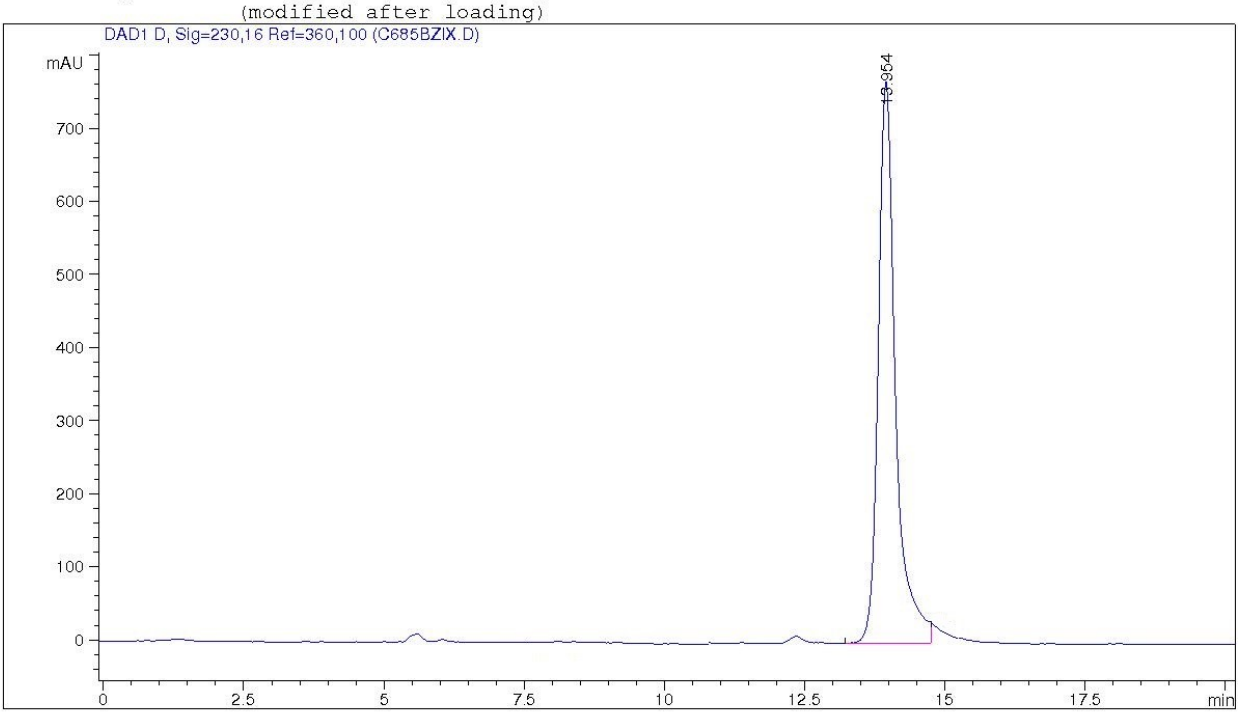

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.252 VB    0.3304  515.55560   21.92036   8.0977
   2  12.332 BP    0.2918 2925.08203  155.23112  45.9438
   3  14.184 BB    0.3228 2926.01514  140.57578  45.9585

Totals :                  6366.65277  317.72726

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```


Figure S29.HPLC of racemic 2-Benzylsulfinyl-1*H*-benzo[d]imidazole **5b.**

Data File C:\HPCHEM\1\DATA\C685BZIX.D Sample Name: C685BzIm_xx

C685 BzImSOCH2-Ph Toluene CHP cristallizzato
Chiralpak IA 70:30

```
==================================================================
Injection Date  : 1/24/2023 12:16:00 PM
Sample Name     : C685BzIm_xx                    Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 1/24/2023 11:10:20 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/25/2024 6:00:30 PM by Mimmo
                  (modified after loading)
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.954 PV    0.3225 1.65057e4   768.86505 100.0000

Totals :                  1.65057e4   768.86505

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

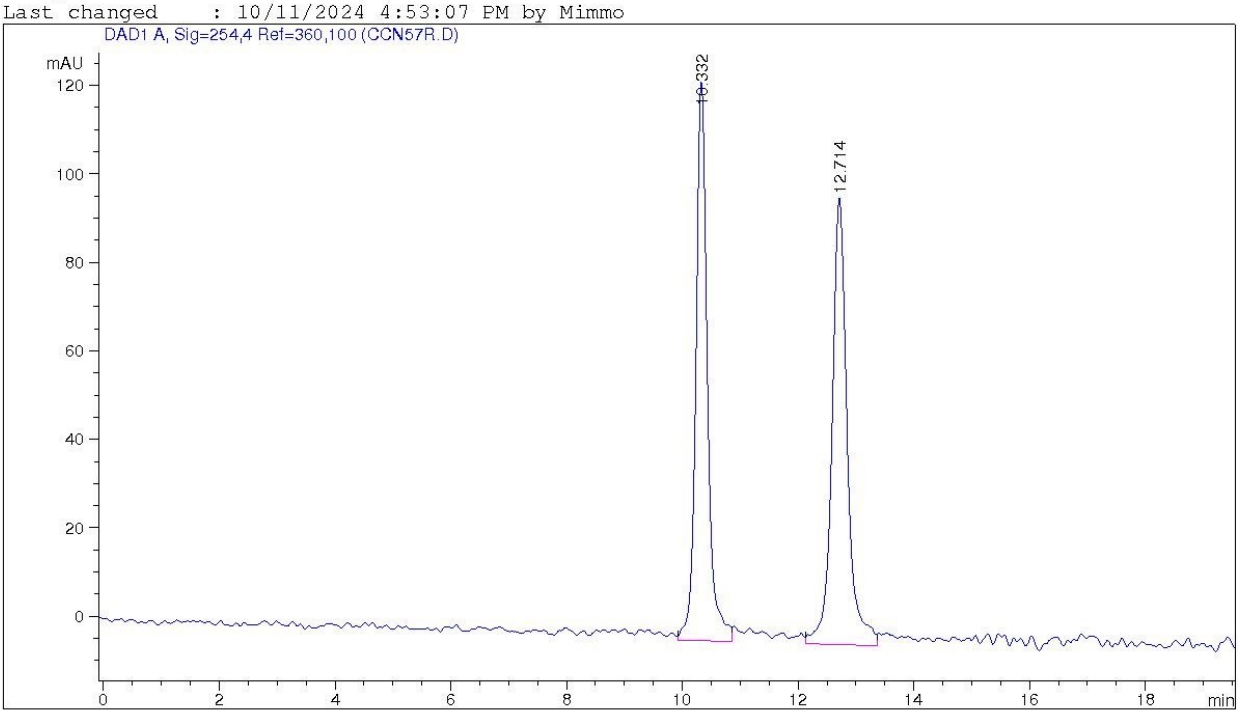
Page 1 of 1

Figure S30. HPLC of (*R*)-2-Benzylsulfinyl-1*H*-benzo[d]imidazole **5b**

Data File C:\HPCHEM\1\DATA\CCN57R.D Sample Name: BzImSOCH2C6F5rac

ccn57 BzImSOpentafluorobenzil racemico
Chiralpak IA esano:IPA 70:30 0.5 ml/min

```
======================================================================
Injection Date  : 2/4/2022 11:17:47 AM
Sample Name     : BzImSOCH2C6F5rac              Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 2/4/2022 8:32:45 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.332 VV    0.2107 1763.33301  126.46920  48.8257
   2  12.714 VV    0.2696 1848.15369  100.94040  51.1743

Totals :                  3611.48669  227.40960

 Results obtained with enhanced integrator!
======================================================================
                          *** End of Report ***
```

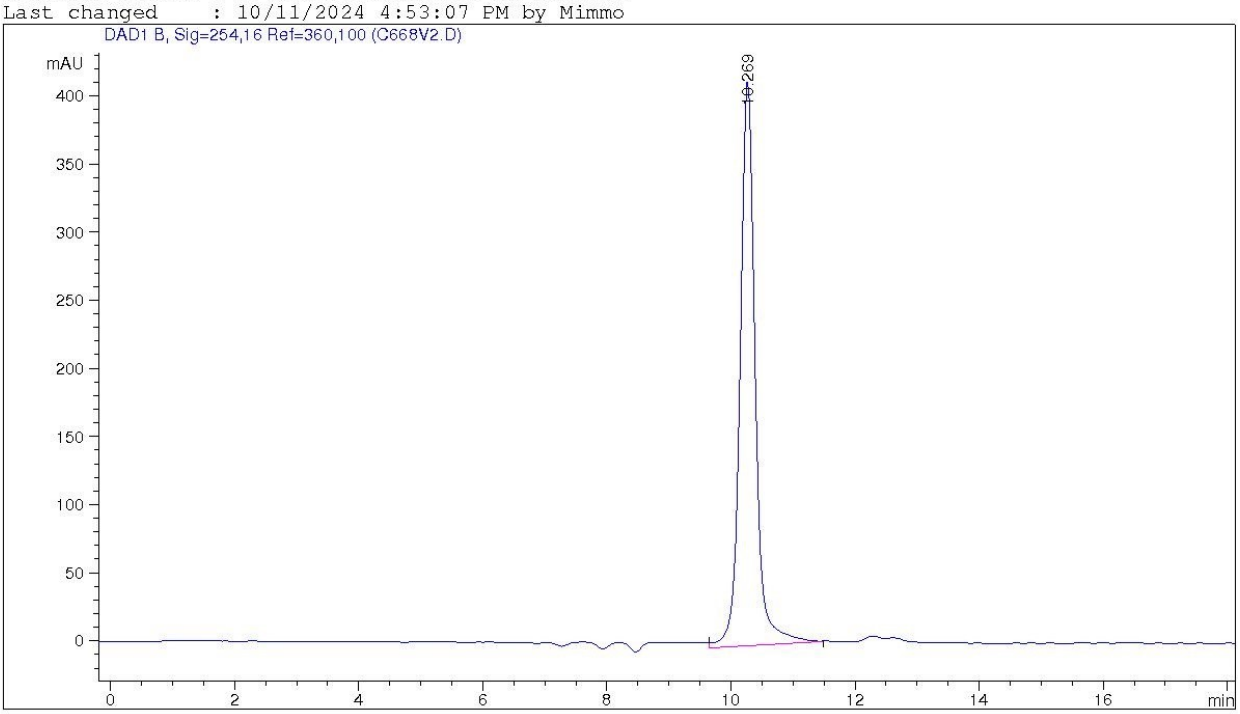
Page 1 of 1

Figure S31. HPLC of racemic 2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1*H*-benzo[d]imidazole **9b**

Data File C:\HPCHEM\1\DATA\C668V2.D Sample Name: ThSOCH2C6F5

C668 2-THiophSOCH2C6F5 verifica
Chiralpak IA n-Esano/i-Propanolo 70:30

```
==================================================================
Injection Date  : 10/11/2024 11:43:25 AM
Sample Name     : ThSOCH2C6F5                    Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 11:41:05 AM by Mimmo
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```



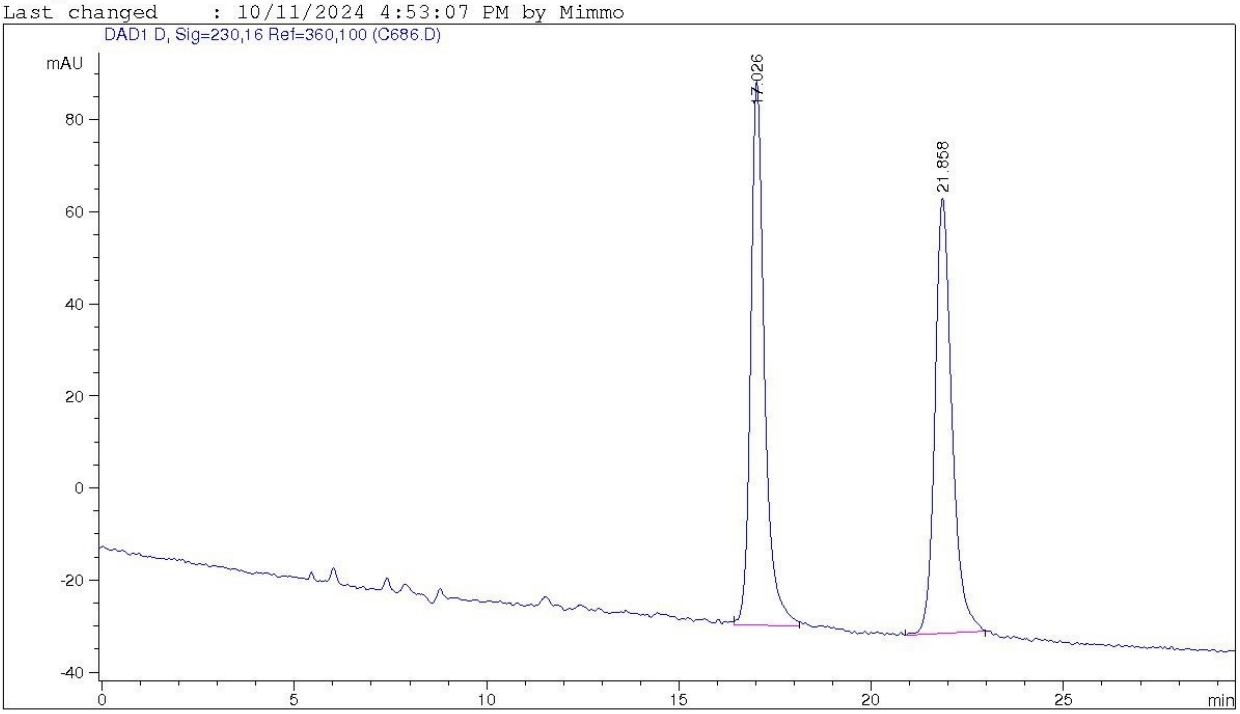

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.269 VB    0.2538 7034.26318  414.81137 100.0000

Totals :                  7034.26318  414.81137

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```


Figure S32. HPLC of (*R*)-2-(2,3,4,5,6-pentafluorobenzylsulfinyl)-1*H*-benzo[d]imidazole **9b**

Data File C:\HPCHEM\1\DATA\C686.D Sample Name: c686Nmetracem

C686 BzIm_N-Met-SOBz racemo
Chiralpak IA esano: i-propanolo 70:30

```
==================================================================
Injection Date  : 2/24/2023 9:33:22 AM
Sample Name     : c686Nmetracem                  Location : Vial 1
Acq. Operator   : Mimmo
Acq. Method     : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 2/24/2023 8:51:04 AM by Mimmo
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ESANOIPA.M
Last changed    : 10/11/2024 4:53:07 PM by Mimmo
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.026 BB    0.3713 2948.19946  118.07216  50.3596
   2  21.858 VB    0.4583 2906.09326   94.62715  49.6404

Totals :                  5854.29272  212.69931

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```


Figure S33. HPLC of racemic 2-Benzylsulfinyl-1-methyl-1*H*-benzo[d]imidazole **10b**