Supplementary Information

Azothiophene-Based Molecular Switches: Influence of Substituent Position and Solvent Environment on Photophysical Behaviour

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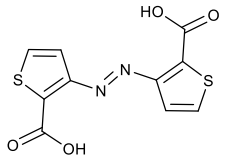
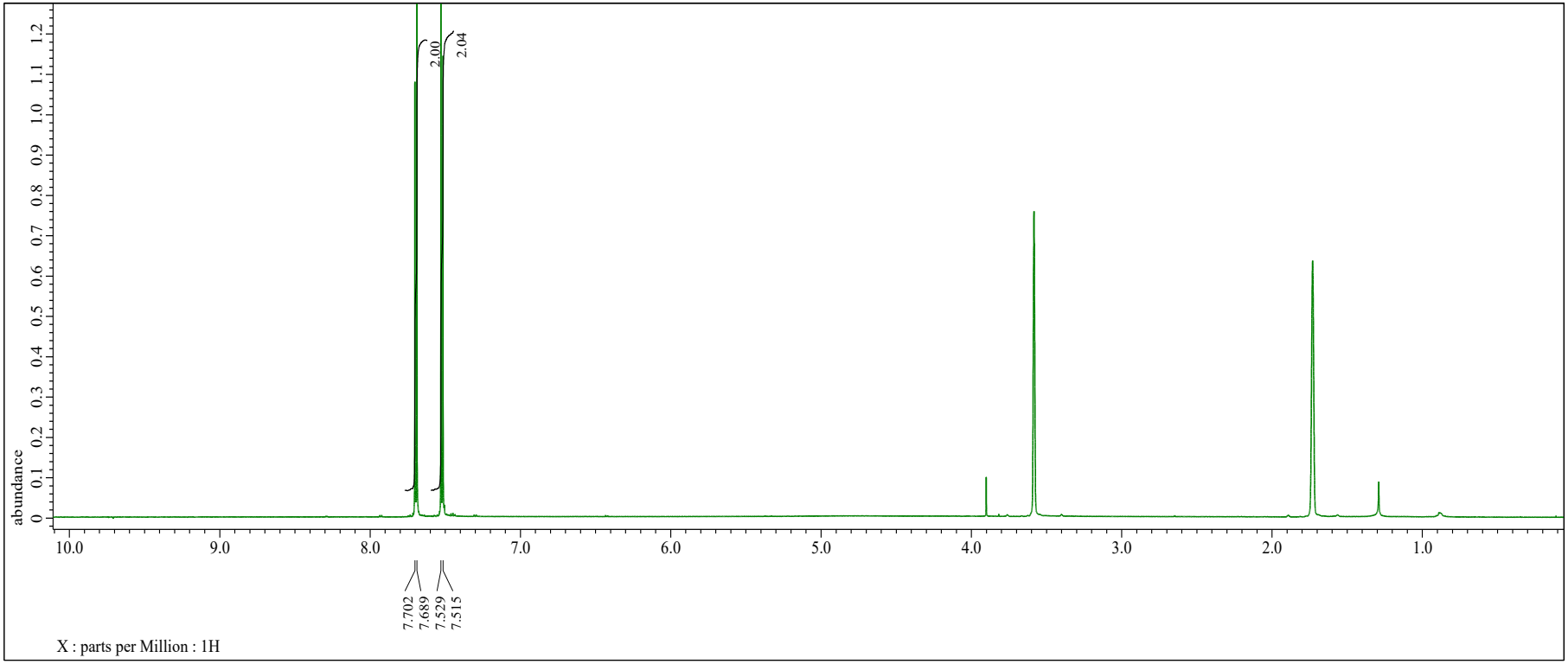
NMR and IR Spectra for compounds (1a) - (5a), and (1b).

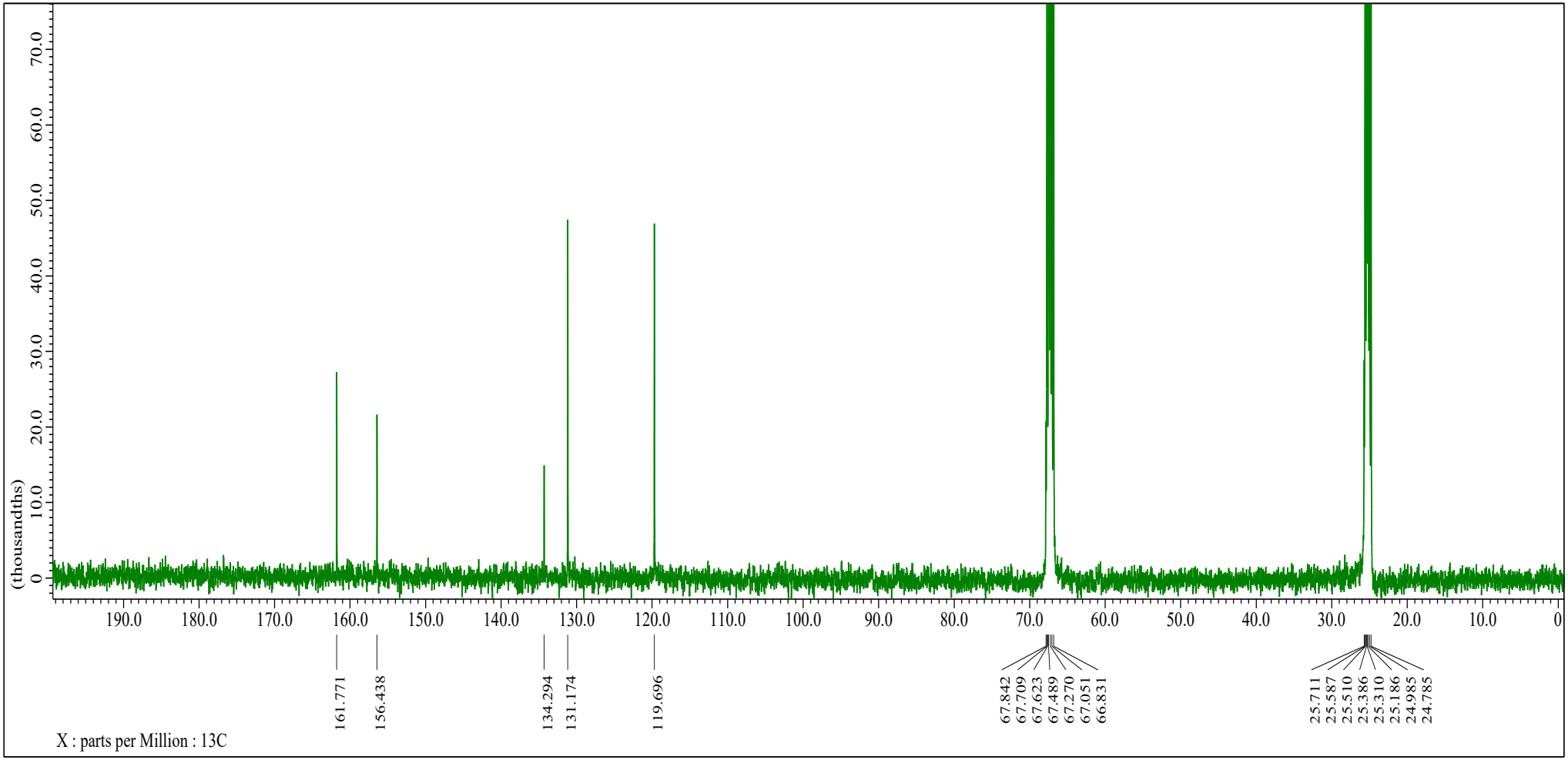
(*E*)-3,3'-Azothiophene-2,2'-dicarboxylic acid (1a).



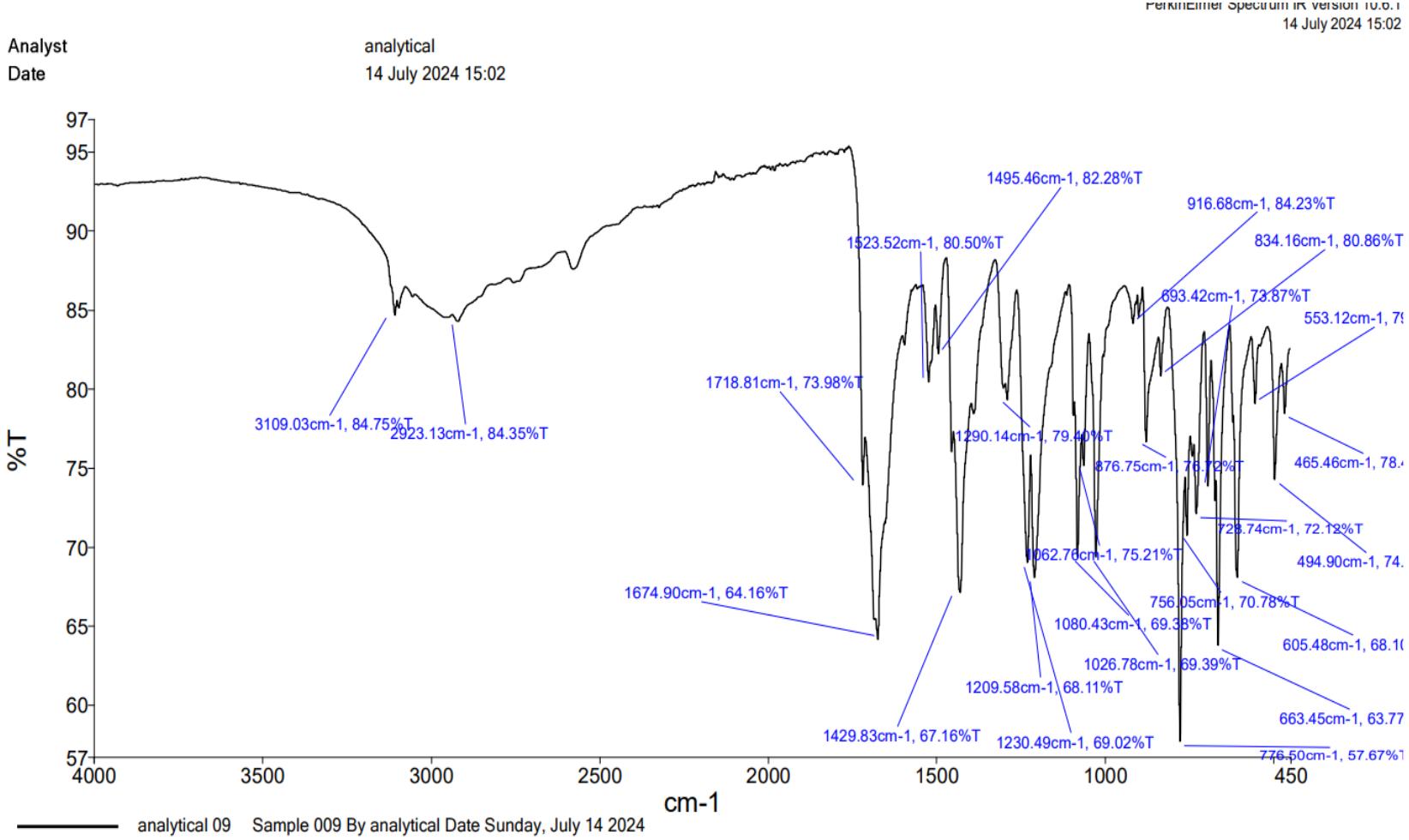
^{1}H NMR **(1a)**.



^{13}C NMR **(1a)**.


(thousandths)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.771
156.438
134.294
131.174
119.696
67.842
67.709
67.623
67.489
67.270
67.051
66.831
25.711
25.587
25.510
25.386
25.310
25.186
24.985
24.785
X : parts per Million : 13C

IR **(1a)**.


PerkinElmer Spectrum IR version 10.6.1
14 July 2024 15:02
Analyst analytical
Date 14 July 2024 15:02
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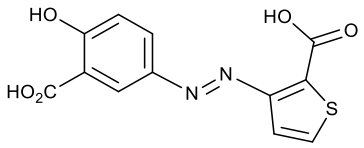
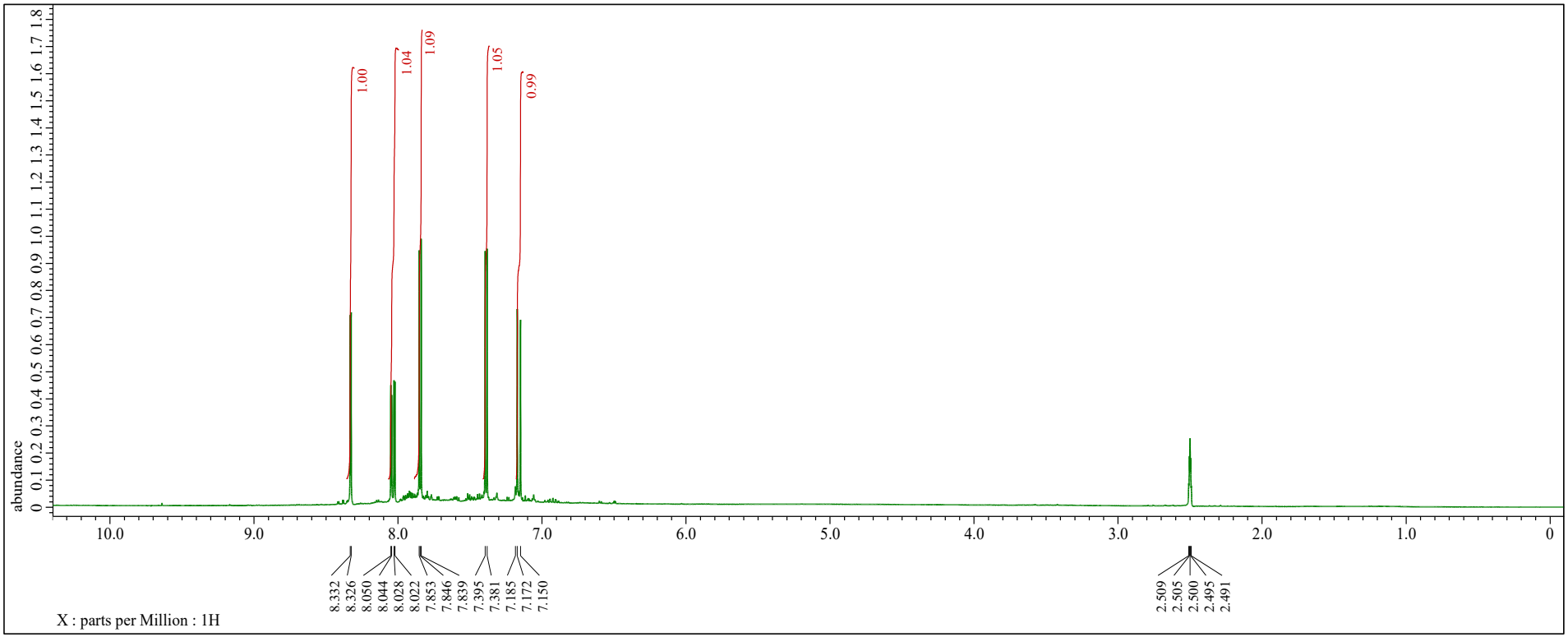
cm-1
3109.03cm-1, 84.75%T
2923.13cm-1, 84.35%T
1718.81cm-1, 73.98%T
1674.90cm-1, 64.16%T
1523.52cm-1, 80.50%T
1495.46cm-1, 82.28%T
1429.83cm-1, 67.16%T
1290.14cm-1, 79.40%T
1230.49cm-1, 69.02%T
1209.58cm-1, 68.11%T
1080.43cm-1, 69.38%T
1062.76cm-1, 75.21%T
1026.78cm-1, 69.39%T
916.68cm-1, 84.23%T
876.75cm-1, 78.72%T
834.16cm-1, 80.86%T
756.05cm-1, 70.78%T
728.74cm-1, 72.12%T
693.42cm-1, 73.87%T
663.45cm-1, 63.77
605.48cm-1, 68.1
553.12cm-1, 7
494.90cm-1, 74.
465.46cm-1, 78.
analytical 09 Sample 009 By analytical Date Sunday, July 14 2024

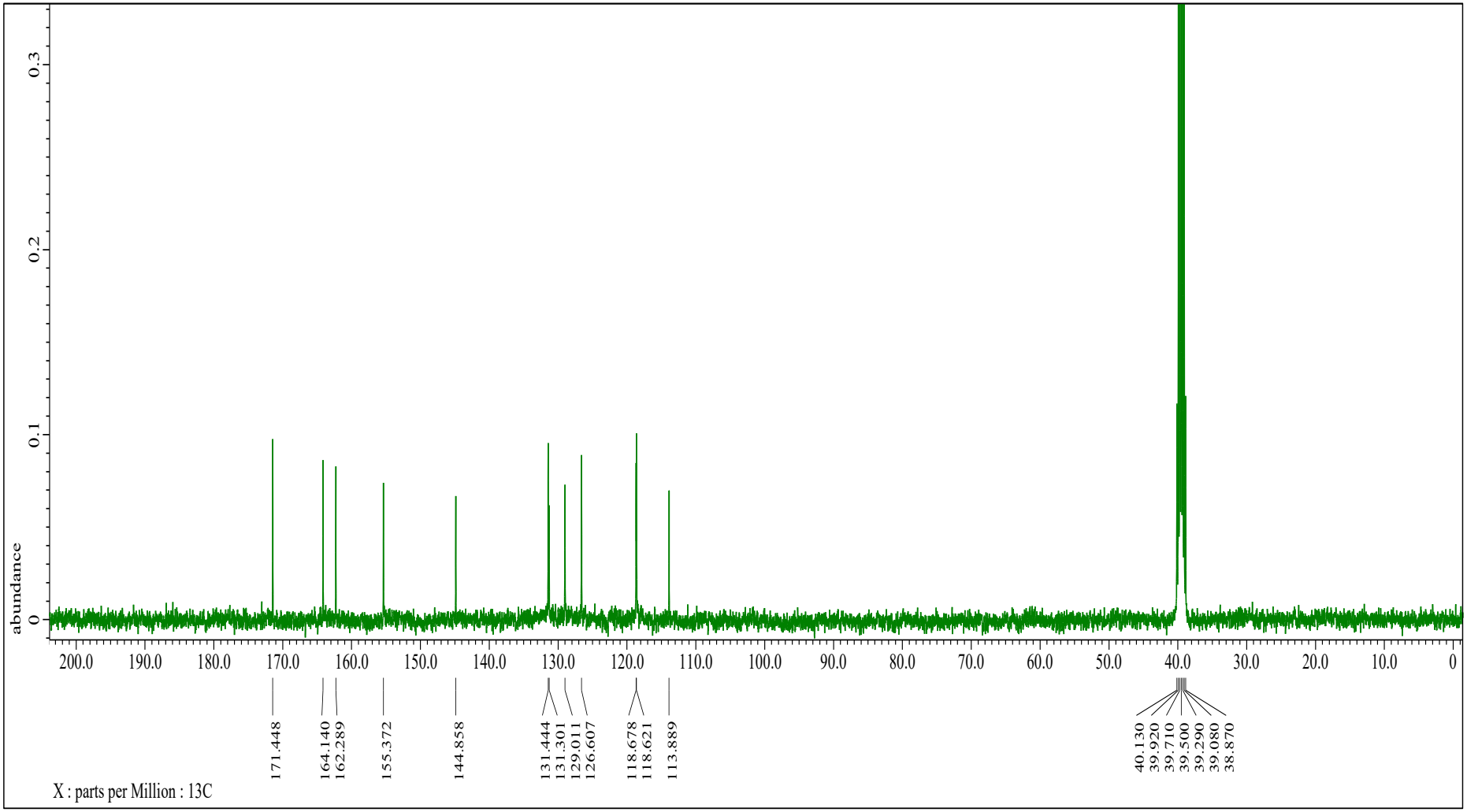
(*E*)-3-((3'-Carboxy-4'-hydroxyphenyl)diazenyl)thiophene-2-carboxylic acid (2a).



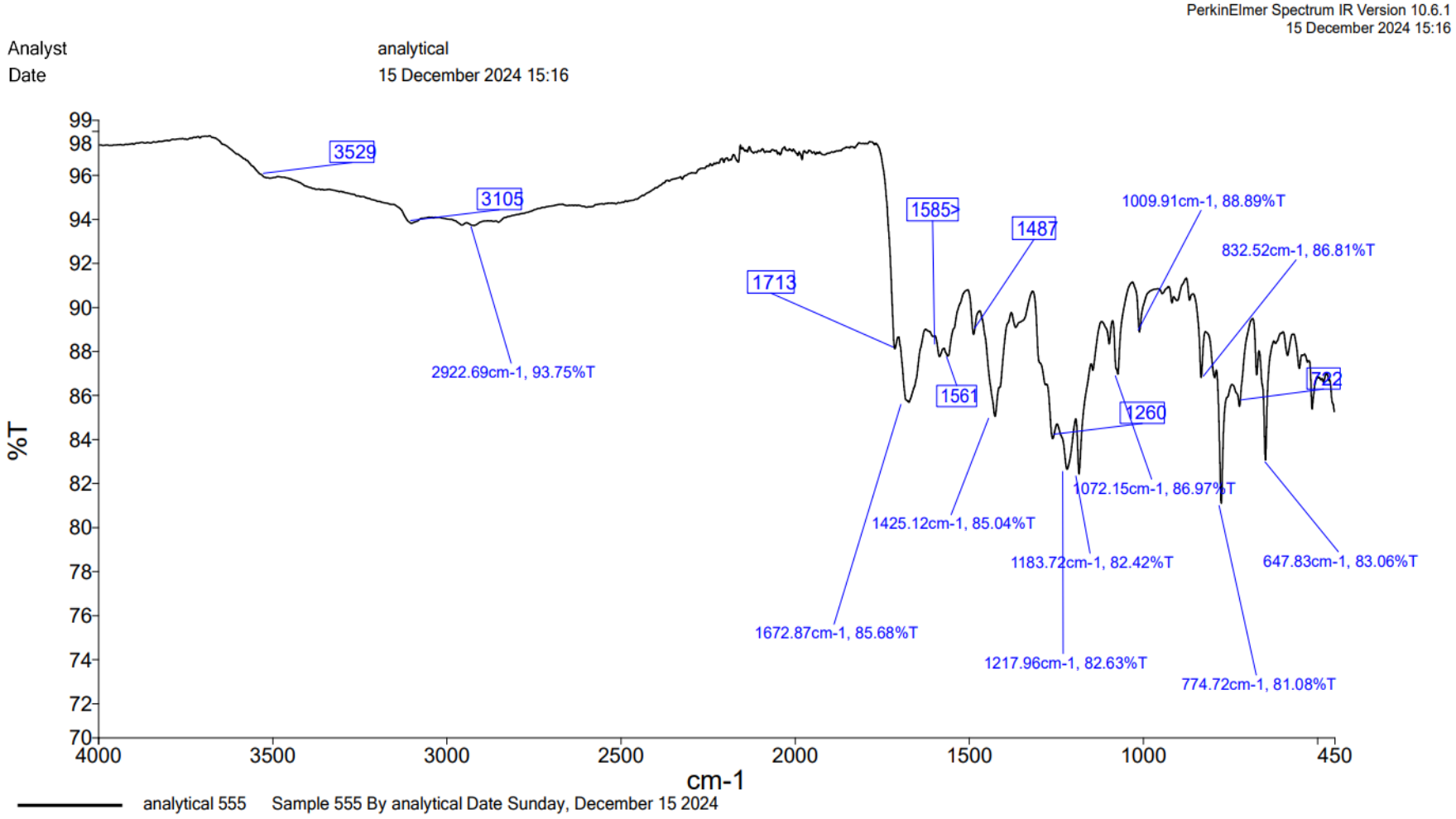
^{1}H NMR **(2a)**.



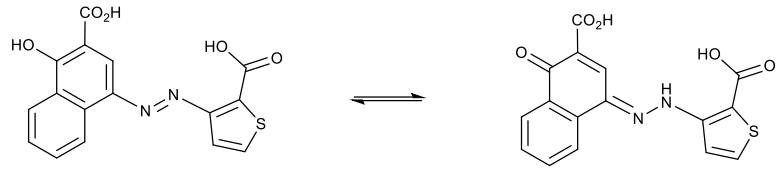
^{13}C NMR **(2a)**.


abundance
0
0.1
0.2
0.3
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.448
164.140
162.289
155.372
144.858
131.444
131.301
129.011
126.607
118.678
118.621
113.889
40.130
39.920
39.710
39.500
39.290
39.080
38.870
X : parts per Million : 13C

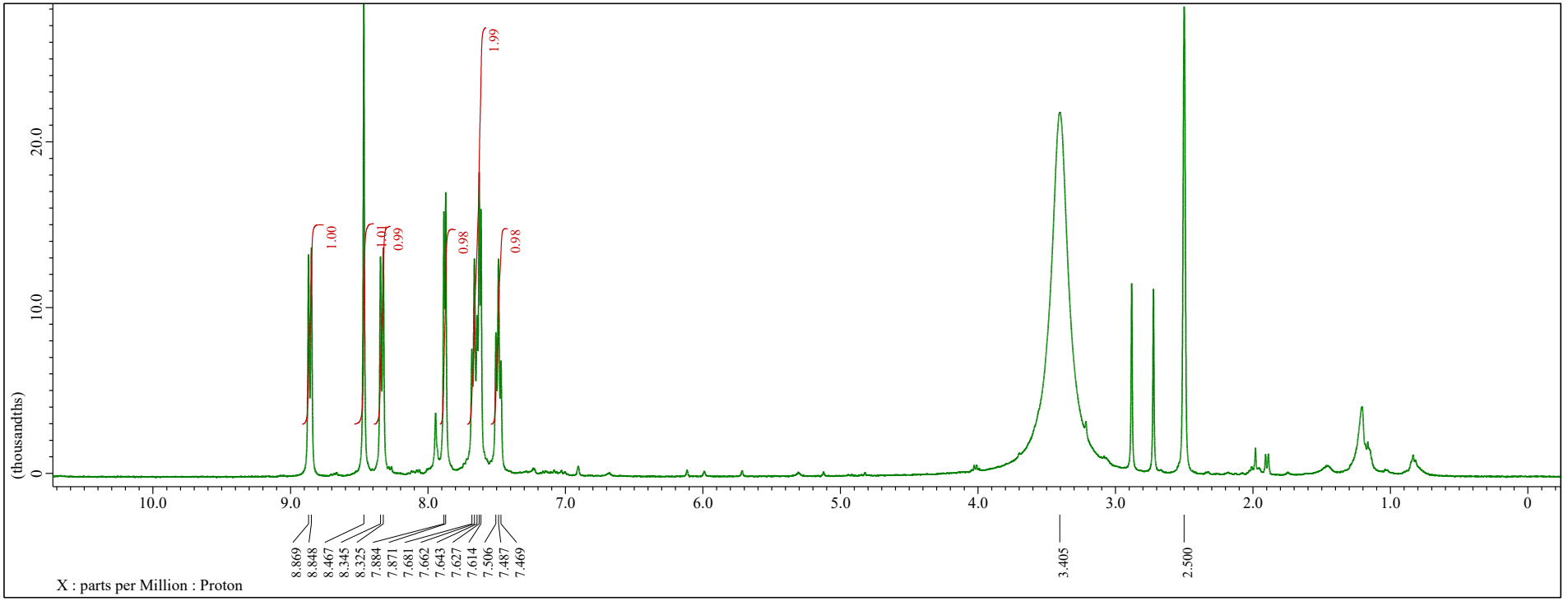
IR **(2a)**.


PerkinElmer Spectrum IR Version 10.6.1
15 December 2024 15:16
Analyst
analytical
Date
15 December 2024 15:16
3529
3105
1585
1487
1713
1009.91cm-1, 88.89%T
832.52cm-1, 86.81%T
2922.69cm-1, 93.75%T
1561
1260
1072.15cm-1, 86.97%T
1425.12cm-1, 85.04%T
1183.72cm-1, 82.42%T
647.83cm-1, 83.06%T
1672.87cm-1, 85.68%T
1217.96cm-1, 82.63%T
774.72cm-1, 81.08%T
%T
cm-1
analytical 555 Sample 555 By analytical Date Sunday, December 15 2024

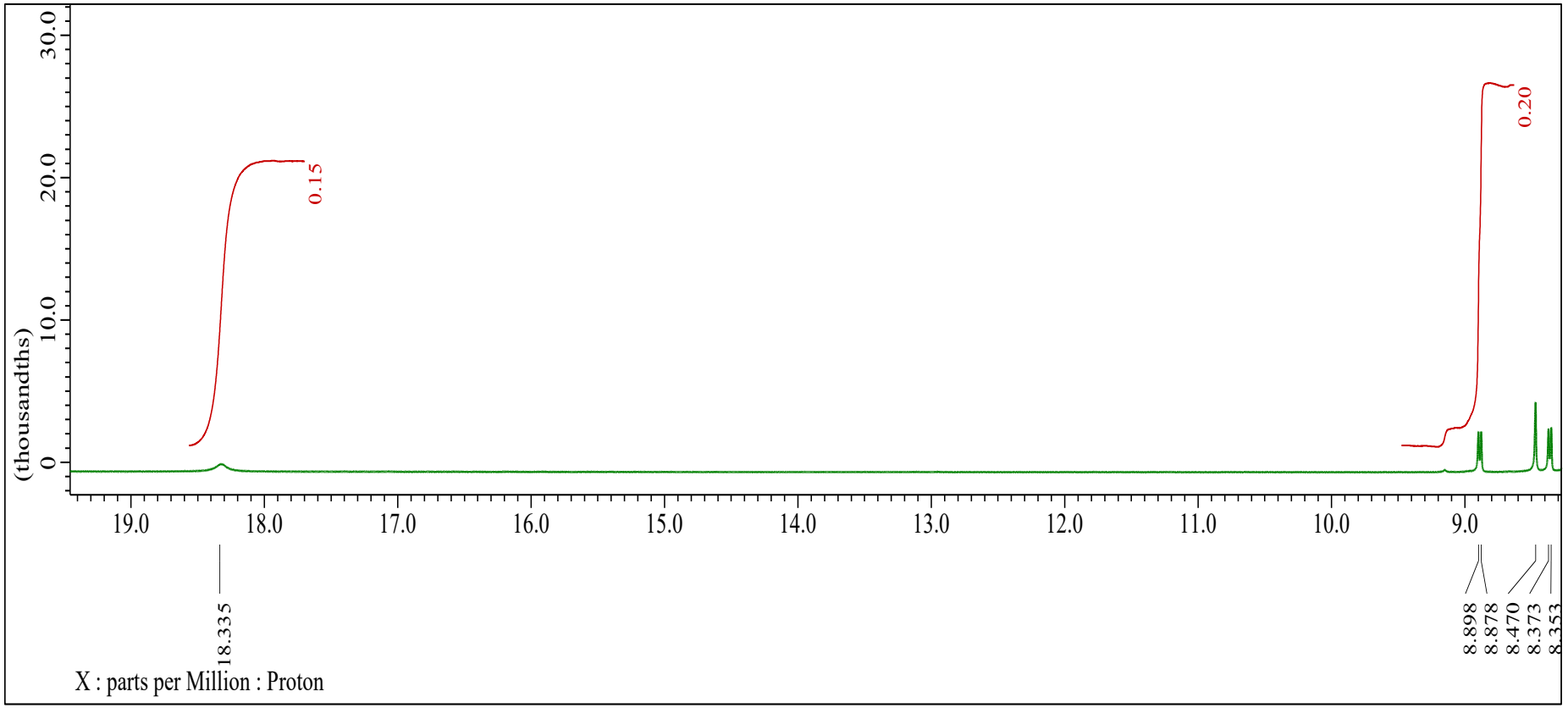
(*E*)-3-((3'-Carboxy-4'-hydroxynaphthalen-1-yl)diazenyl)thiophene-2-carboxylic acid (3a).



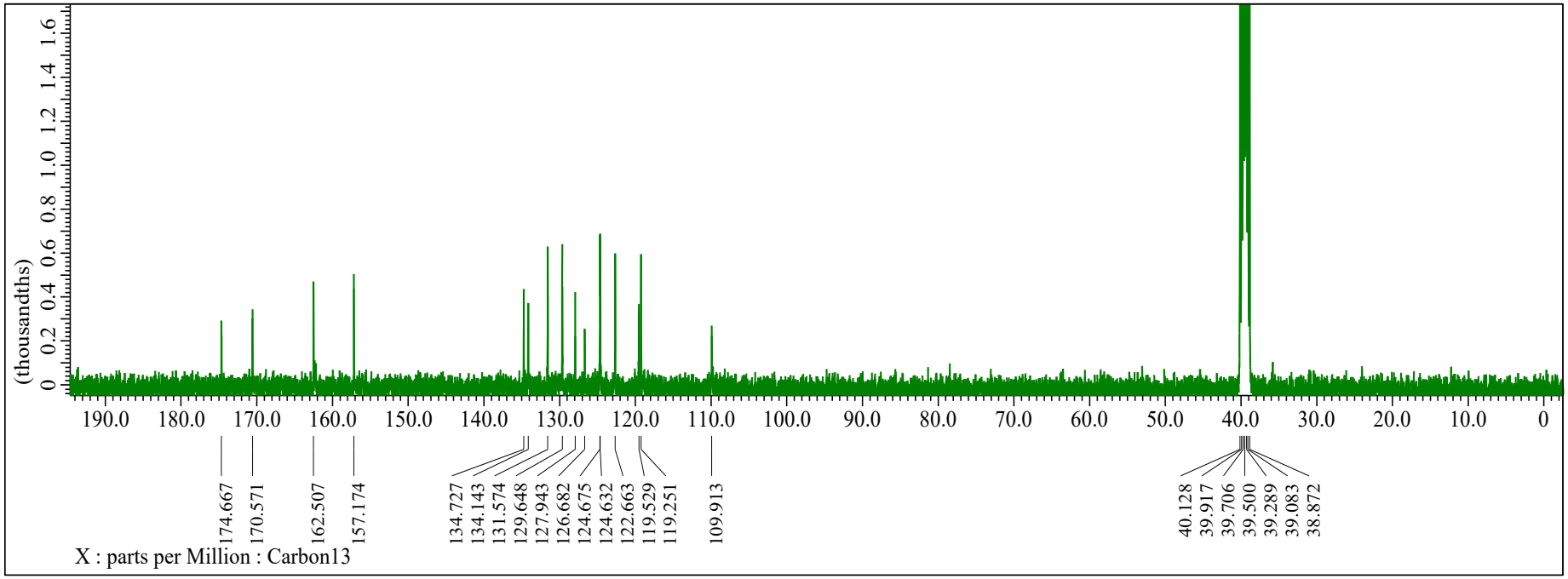
^{1}H NMR **(3a).**



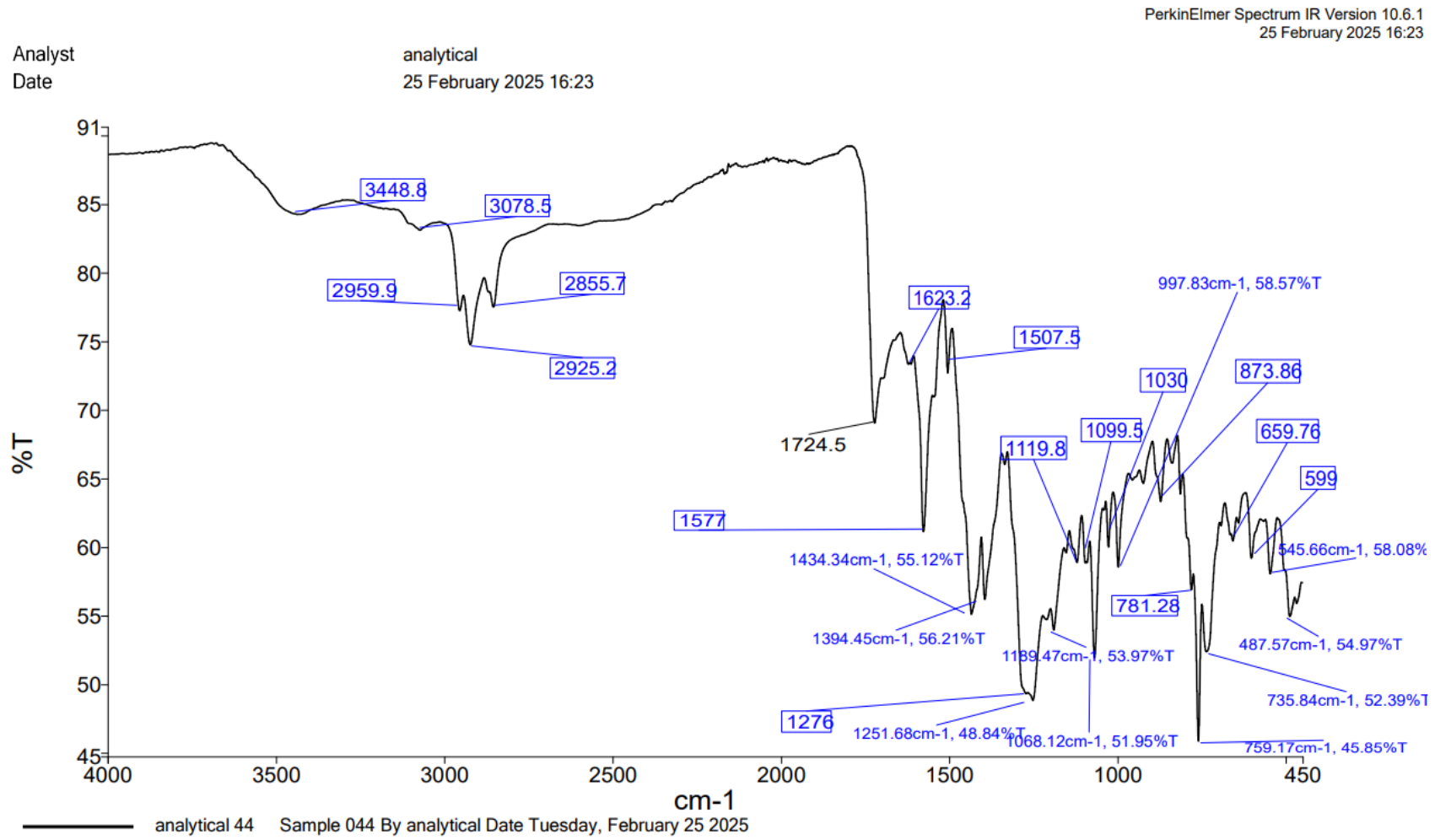
Contains small amount of DMF


30.0
20.0
10.0
0
(thousandths)
0.15
0.20
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
18.335
8.898
8.878
8.470
8.373
8.353
X : parts per Million : Proton

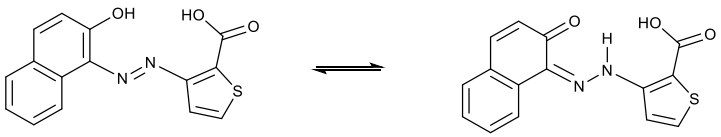
^{13}C NMR **(3a)**.


(thousandths)
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
174.667
170.571
162.507
157.174
134.727
134.143
131.574
129.648
127.943
126.682
124.675
124.632
122.663
119.529
119.251
109.913
40.128
39.917
39.706
39.500
39.289
39.083
38.872
X : parts per Million : Carbon13

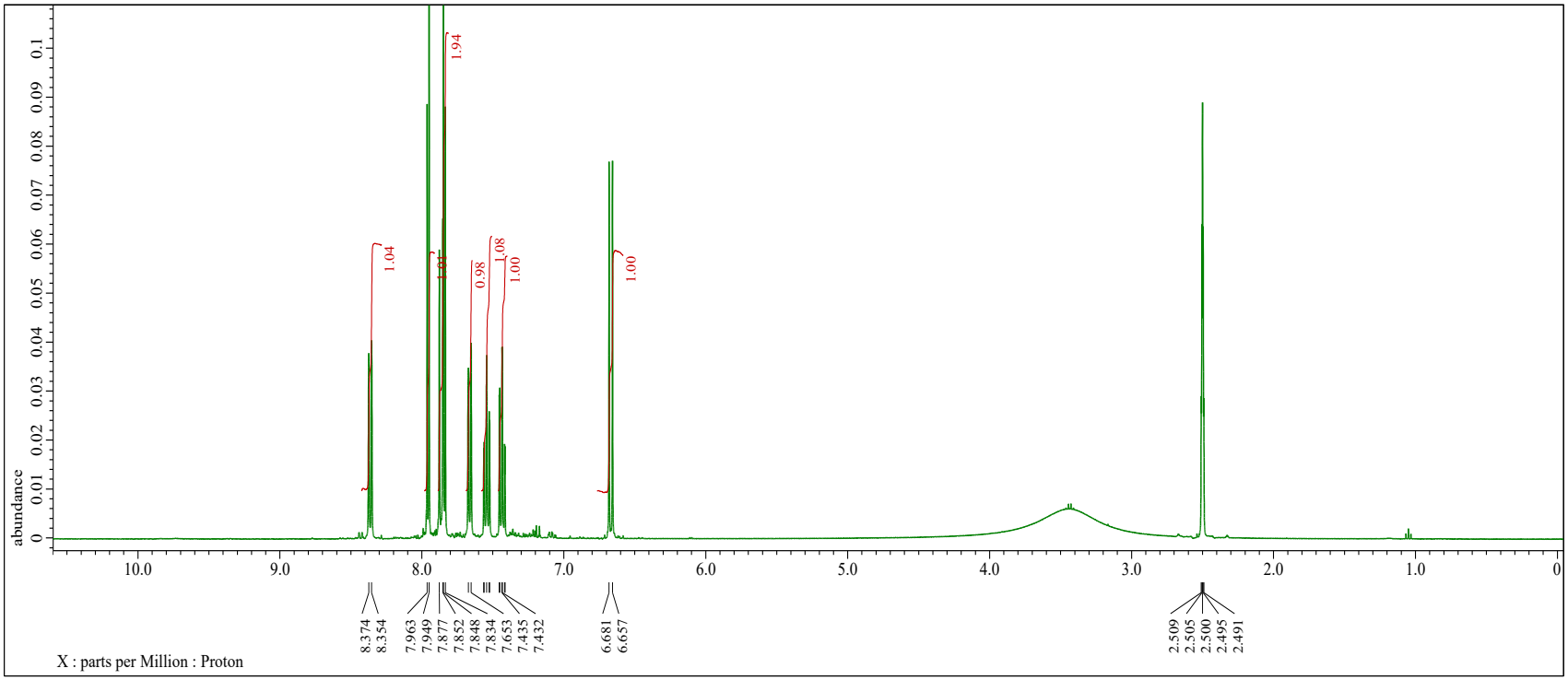
IR **(3a)**.

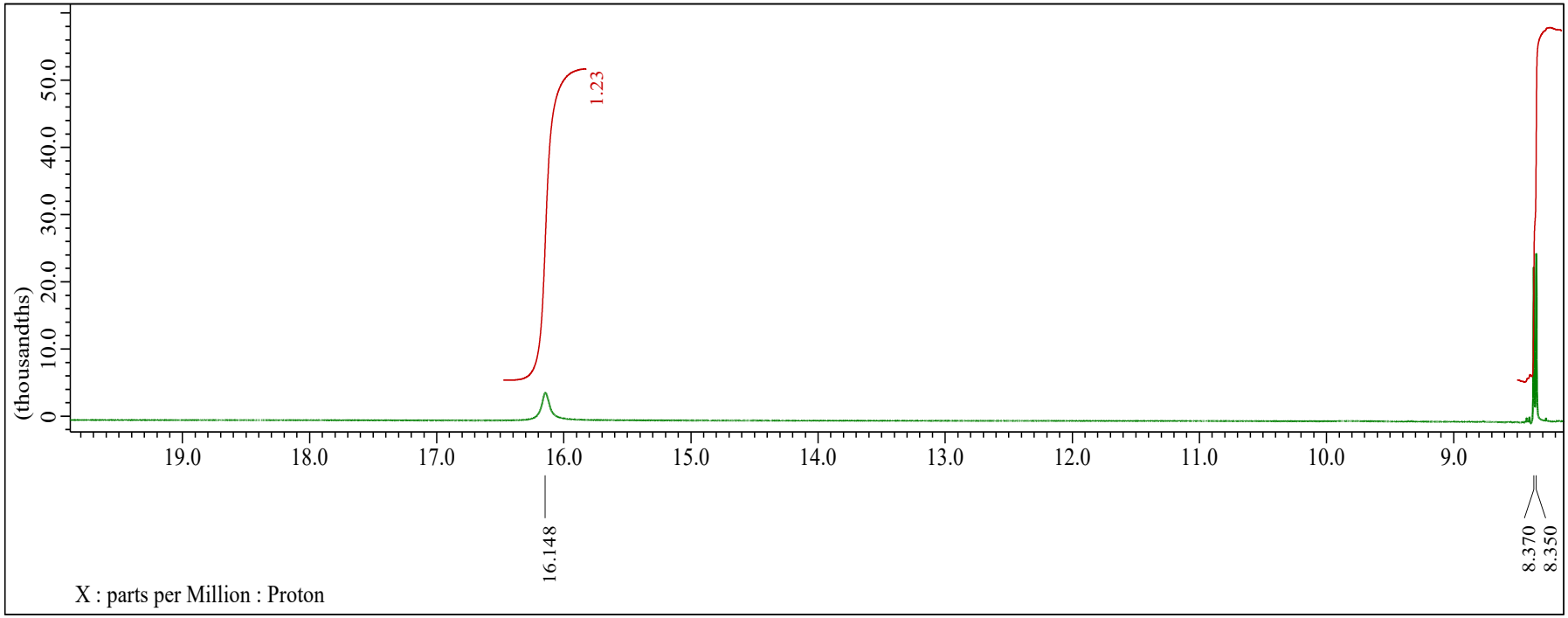

PerkinElmer Spectrum IR Version 10.6.1
25 February 2025 16:23
Analyst
analytical
Date
25 February 2025 16:23
%T
cm-1
3448.8
3078.5
2959.9
2855.7
2925.2
1724.5
1623.2
1507.5
1577
1119.8
1099.5
1030
997.83cm-1, 58.57%T
873.86
659.76
599
545.66cm-1, 58.08%
1434.34cm-1, 55.12%T
781.28
1394.45cm-1, 56.21%T
487.57cm-1, 54.97%T
1189.47cm-1, 53.97%T
735.84cm-1, 52.39%T
1276
1251.68cm-1, 48.84%T
1068.12cm-1, 51.95%T
759.17cm-1, 45.85%T
analytical 44 Sample 044 By analytical Date Tuesday, February 25 2025

(*E*)-3-(2'-Hydroxynaphth-1'-yl)diazenyl)thiophene-2-carboxylic acid (4a).

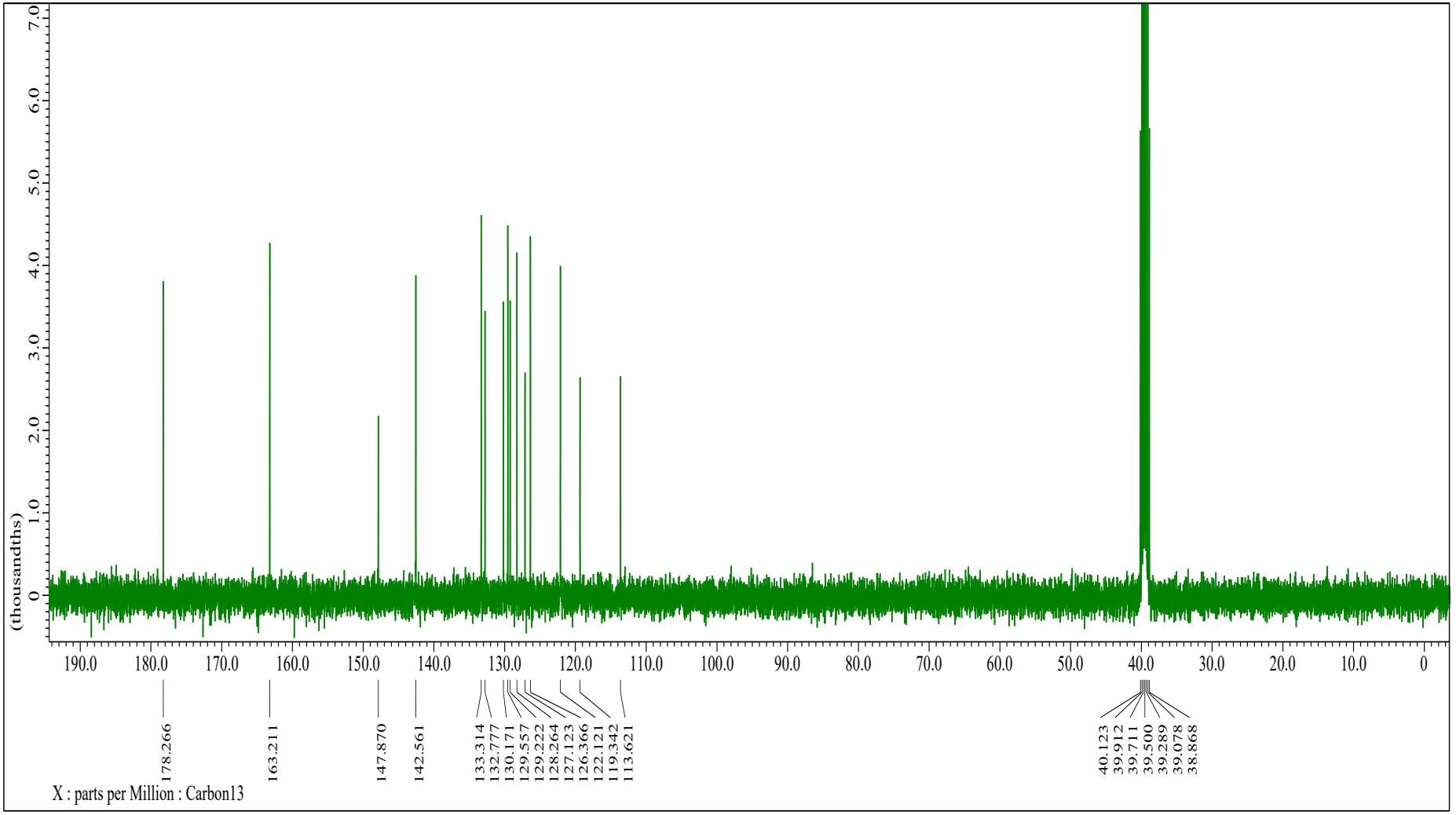


^{1}H NMR **(4a)**.

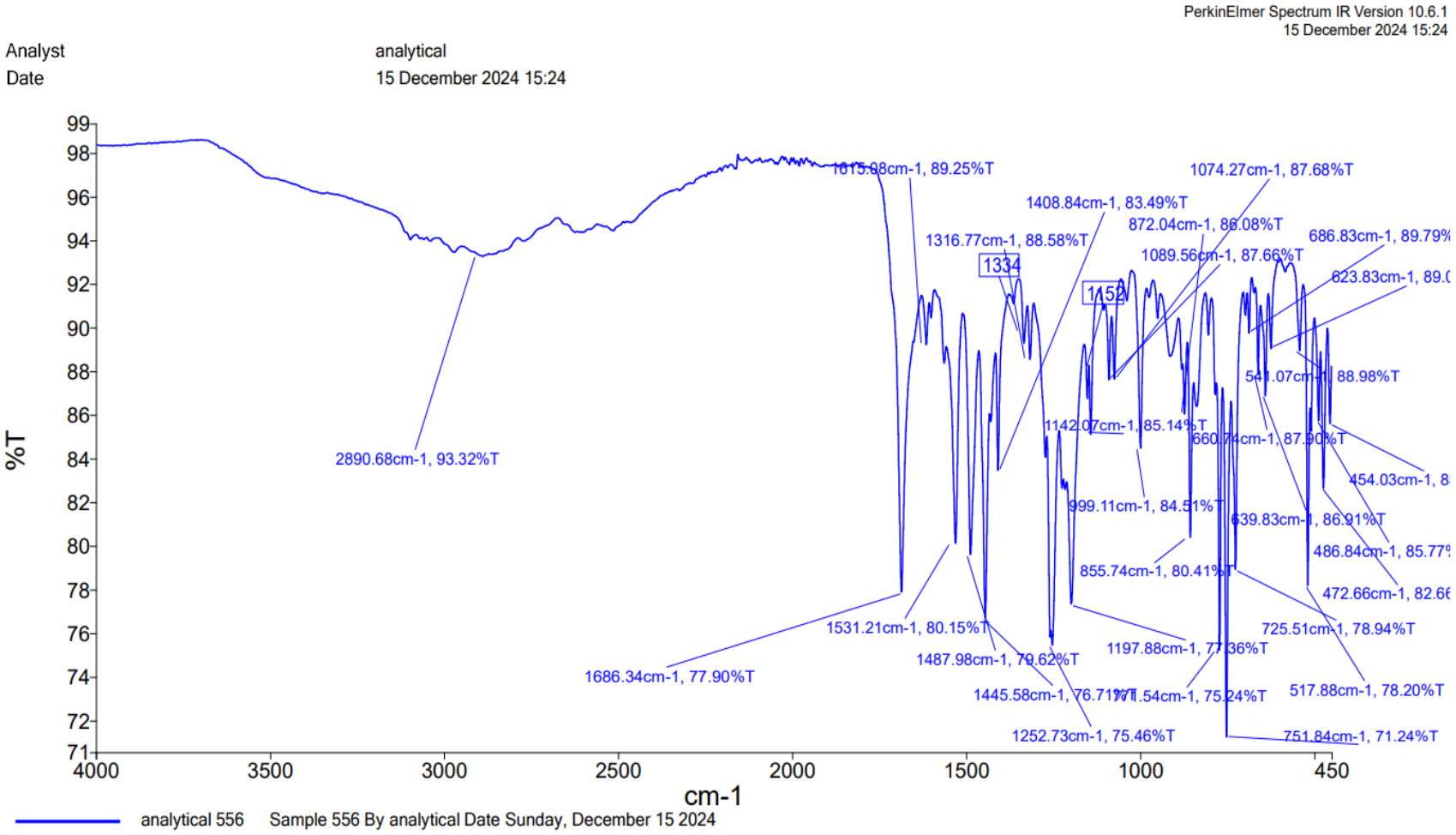



(thousandths)
0
10.0
20.0
30.0
40.0
50.0
1.23
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
16.148
8.370
8.350
X : parts per Million : Proton

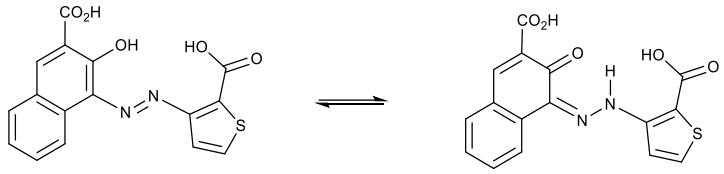
^{13}C NMR **(4a)**.


(thousandths)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
178.266
163.211
147.870
142.561
133.314
132.777
130.171
129.557
129.222
128.264
127.123
126.366
122.121
119.342
113.621
40.123
39.912
39.711
39.500
39.289
39.078
38.868
X : parts per Million : Carbon13

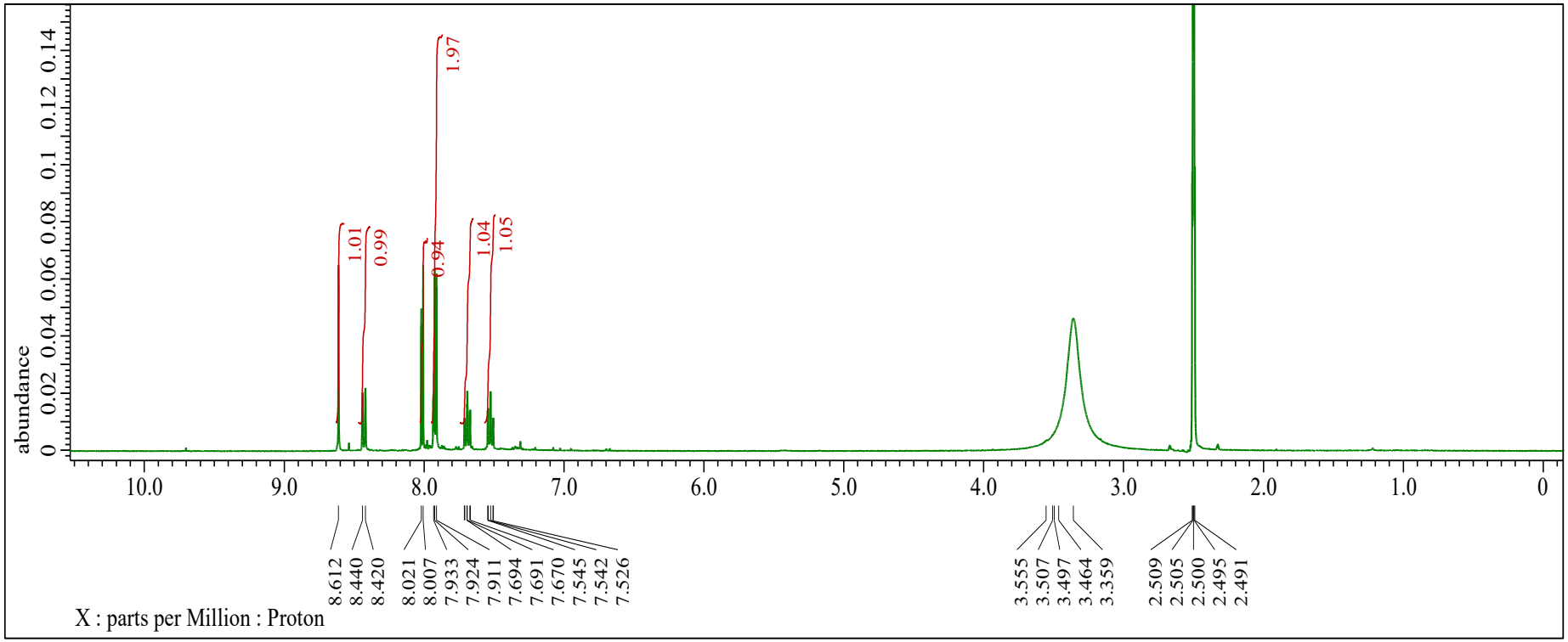
IR **(4a)**.

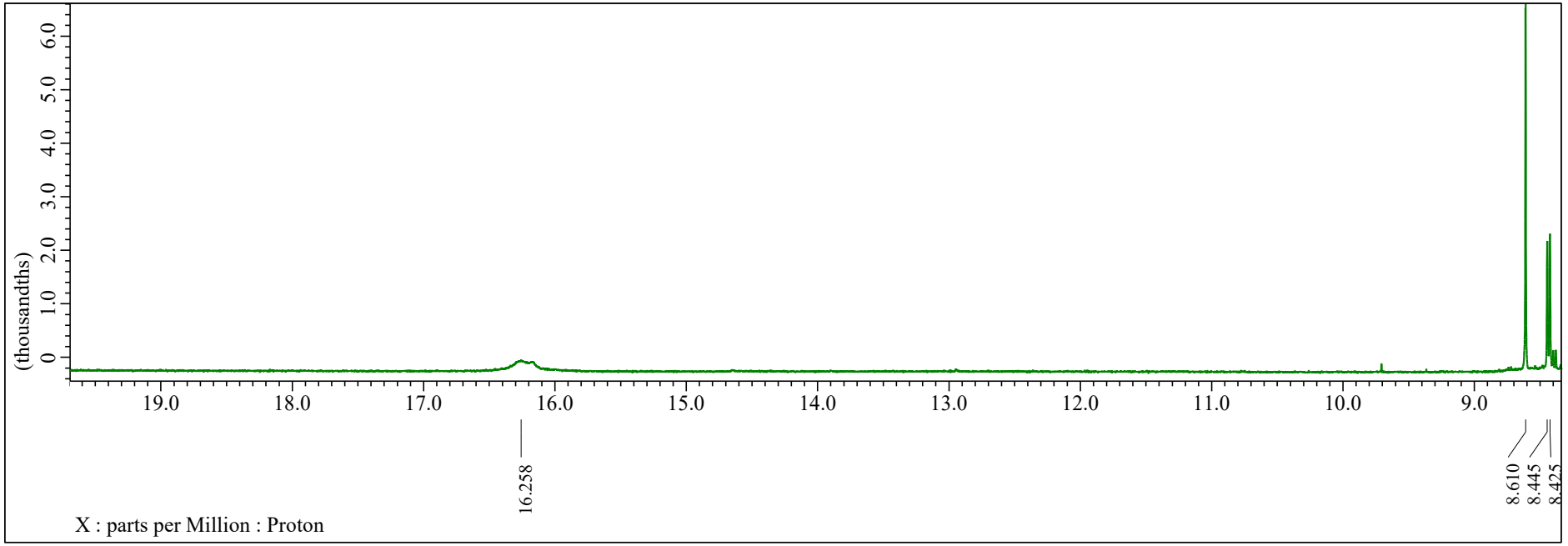

PerkinElmer Spectrum IR Version 10.6.1
15 December 2024 15:24
Analyst
analytical
Date
15 December 2024 15:24
%T
cm-1
2890.68cm-1, 93.32%T
1686.34cm-1, 77.90%T
1531.21cm-1, 80.15%T
1487.98cm-1, 79.62%T
1445.58cm-1, 76.71%T
1252.73cm-1, 75.46%T
1316.77cm-1, 88.58%T
1408.84cm-1, 83.49%T
1334
1152
1142.07cm-1, 85.14%T
999.11cm-1, 84.51%T
855.74cm-1, 80.41%T
1197.88cm-1, 77.36%T
1074.27cm-1, 87.68%T
872.04cm-1, 86.08%T
1089.56cm-1, 87.66%T
686.83cm-1, 89.79%
623.83cm-1, 89.0
88.98%T
660.74cm-1, 87.90%T
454.03cm-1, 8
639.83cm-1, 86.91%T
486.84cm-1, 85.77%
472.66cm-1, 82.66
725.51cm-1, 78.94%T
517.88cm-1, 78.20%T
771.54cm-1, 75.24%T
751.84cm-1, 71.24%T
analytical 556 Sample 556 By analytical Date Sunday, December 15 2024

(*E*)-3-(3'-Carboxy-2'-hydroxynaphth-1'-yl)diazenyl)thiophene-2-carboxylic acid (5a).

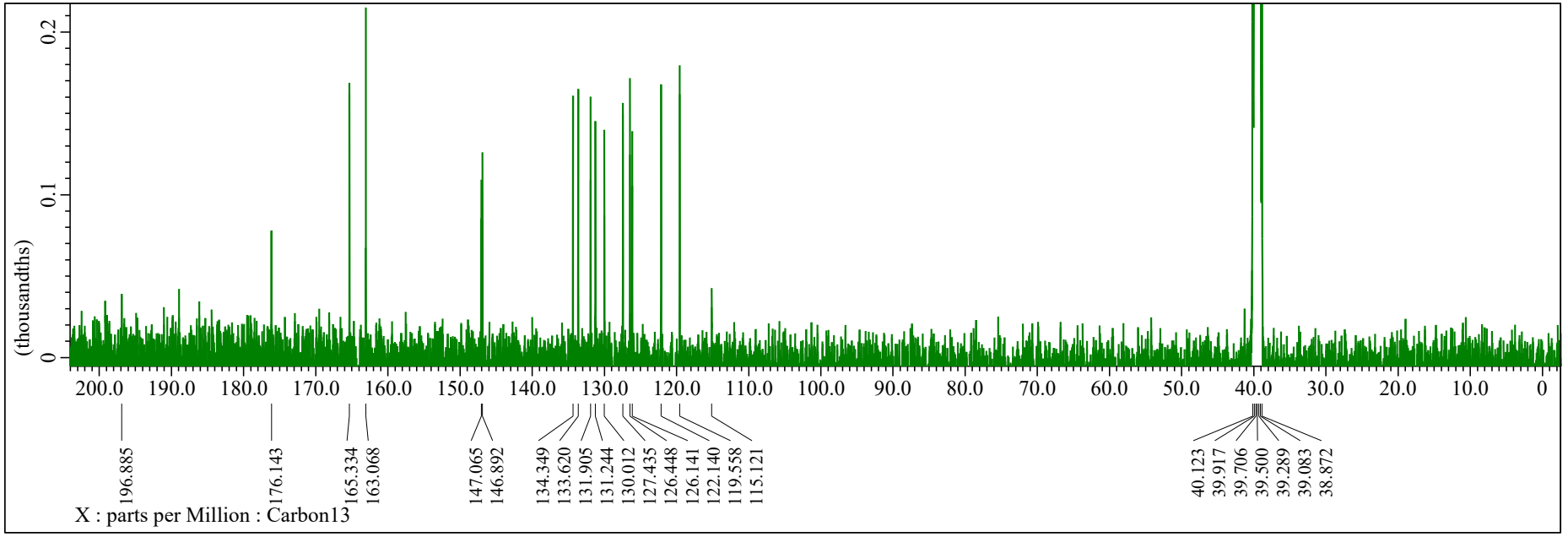


^{1}H NMR **(5a)**.

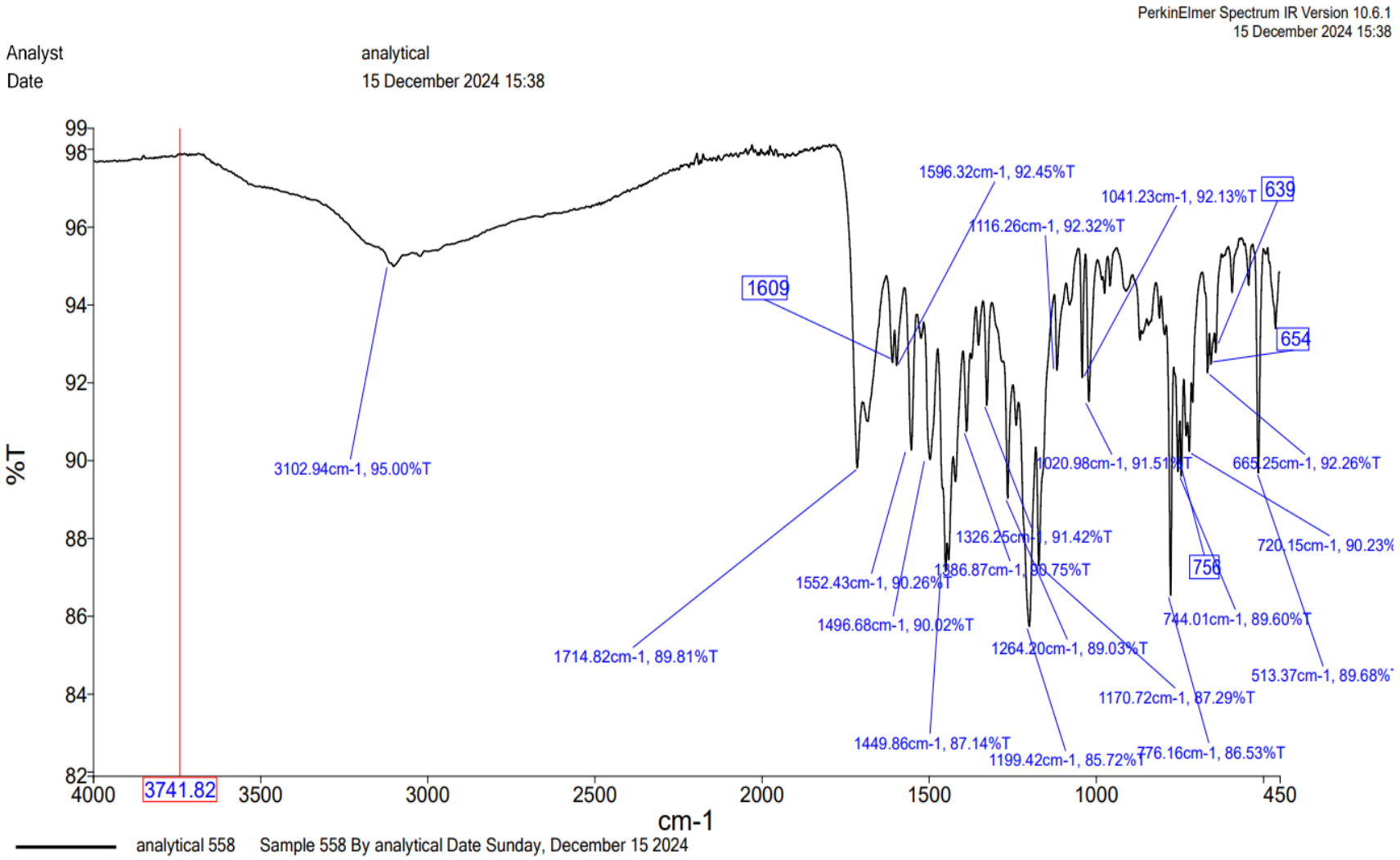



(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
16.258
8.610
8.445
8.425
X : parts per Million : Proton

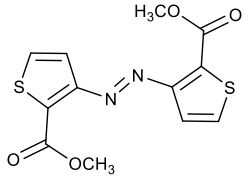
^{13}C NMR **(5a)**.


(thousandths)
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.885
176.143
165.334
163.068
147.065
146.892
134.349
133.620
131.905
131.244
130.012
127.435
126.448
126.141
122.140
119.558
115.121
40.123
39.917
39.706
39.500
39.289
39.083
38.872
X : parts per Million : Carbon13

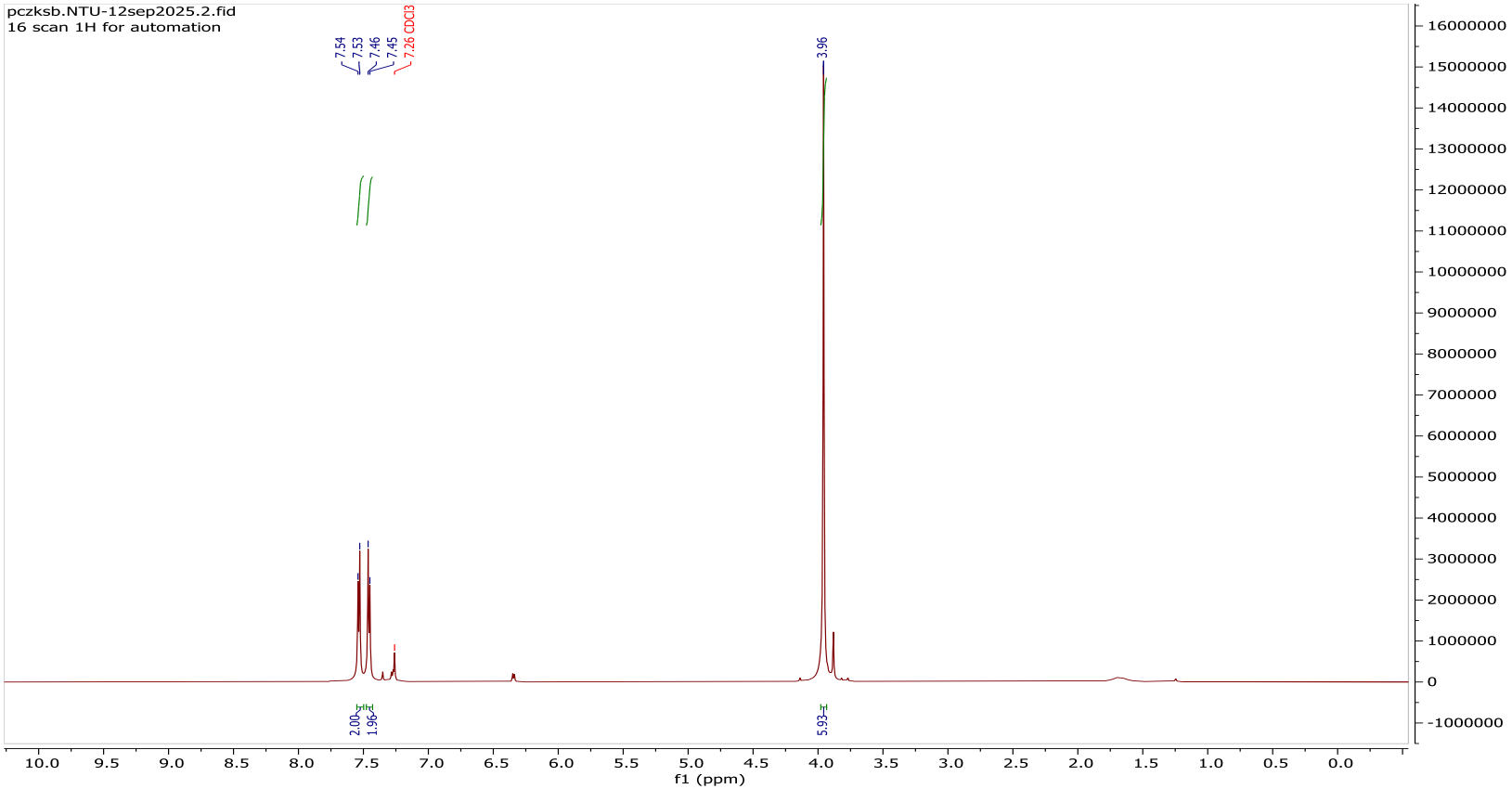
IR **(5a)**.

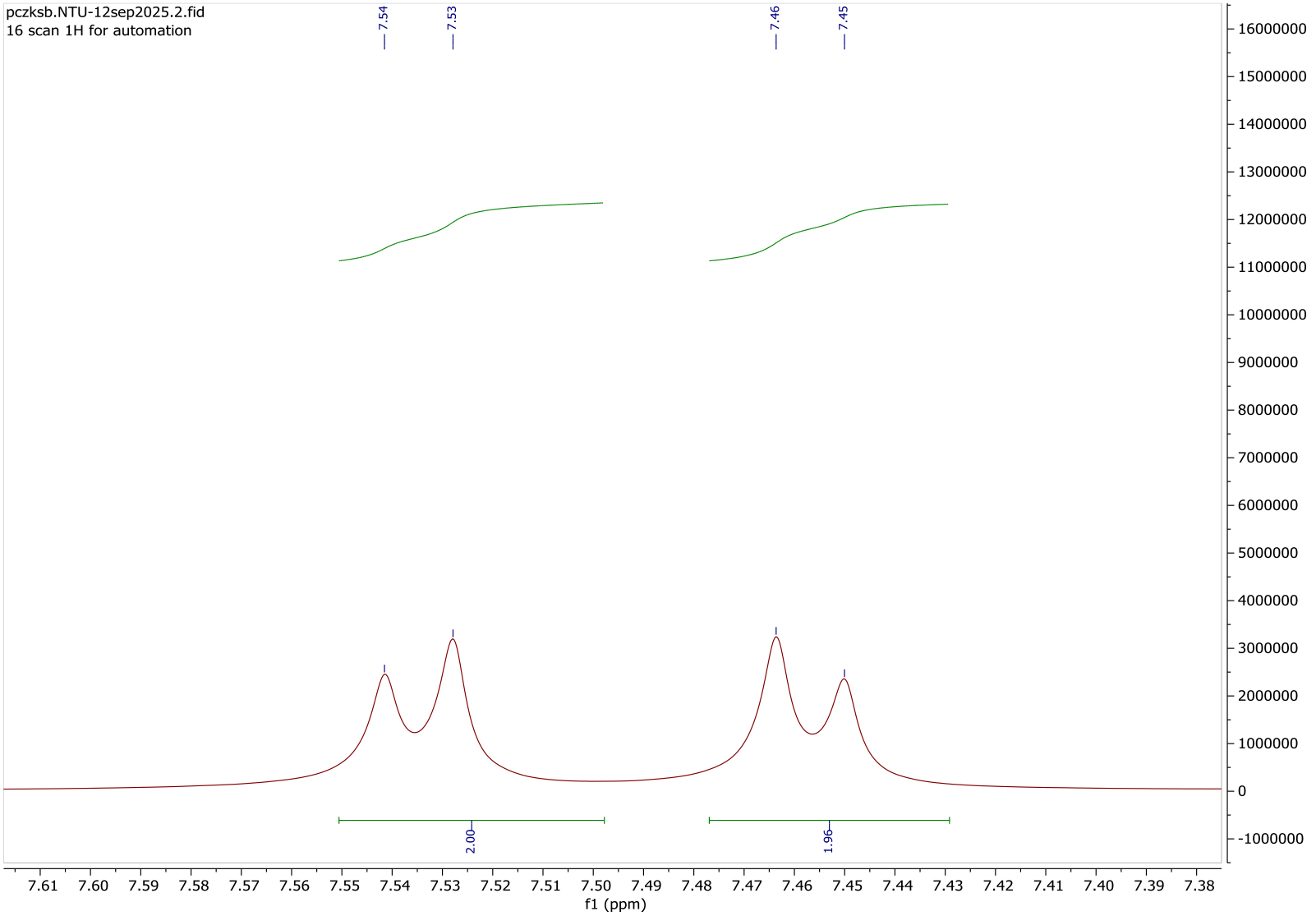

PerkinElmer Spectrum IR Version 10.6.1
15 December 2024 15:38
Analyst
Date
analytical
15 December 2024 15:38
%T
cm-1
3741.82
3102.94cm-1, 95.00%T
1596.32cm-1, 92.45%T
1041.23cm-1, 92.13%T
639
1116.26cm-1, 92.32%T
1609
654
1020.98cm-1, 91.51%T
665.25cm-1, 92.26%T
1326.25cm-1, 91.42%T
720.15cm-1, 90.23%
1552.43cm-1, 90.26%T
1386.87cm-1, 89.75%T
756
744.01cm-1, 89.60%T
1496.68cm-1, 90.02%T
1714.82cm-1, 89.81%T
1264.20cm-1, 89.03%T
513.37cm-1, 89.68%
1170.72cm-1, 87.29%T
1449.86cm-1, 87.14%T
1199.42cm-1, 85.72%T
776.16cm-1, 86.53%T
analytical 558 Sample 558 By analytical Date Sunday, December 15 2024

Dimethyl (*E*)-3,3'-azothiophene-2,2'-dicarboxylate (1b).



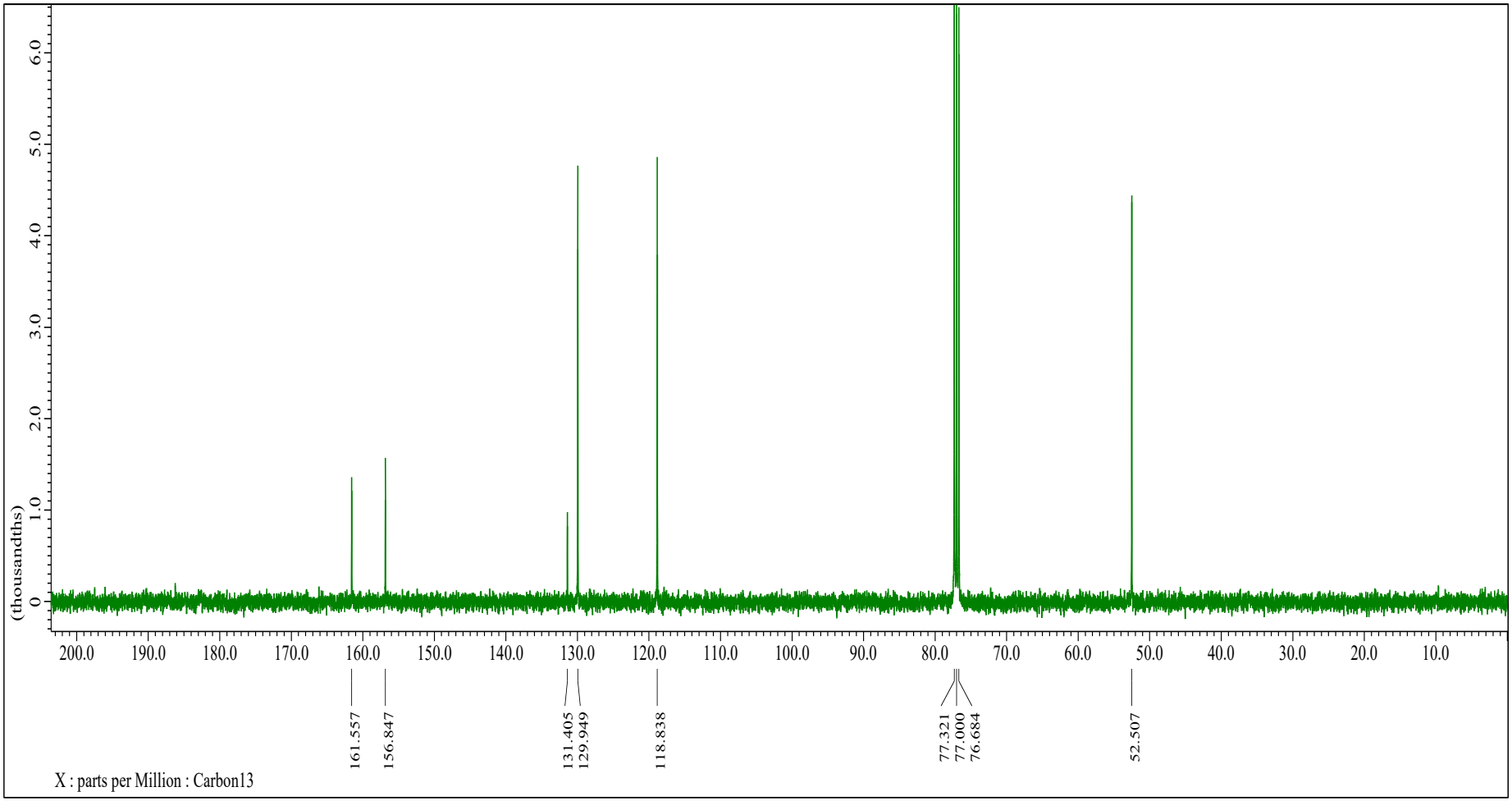
^{1}H NMR **(1b)**.



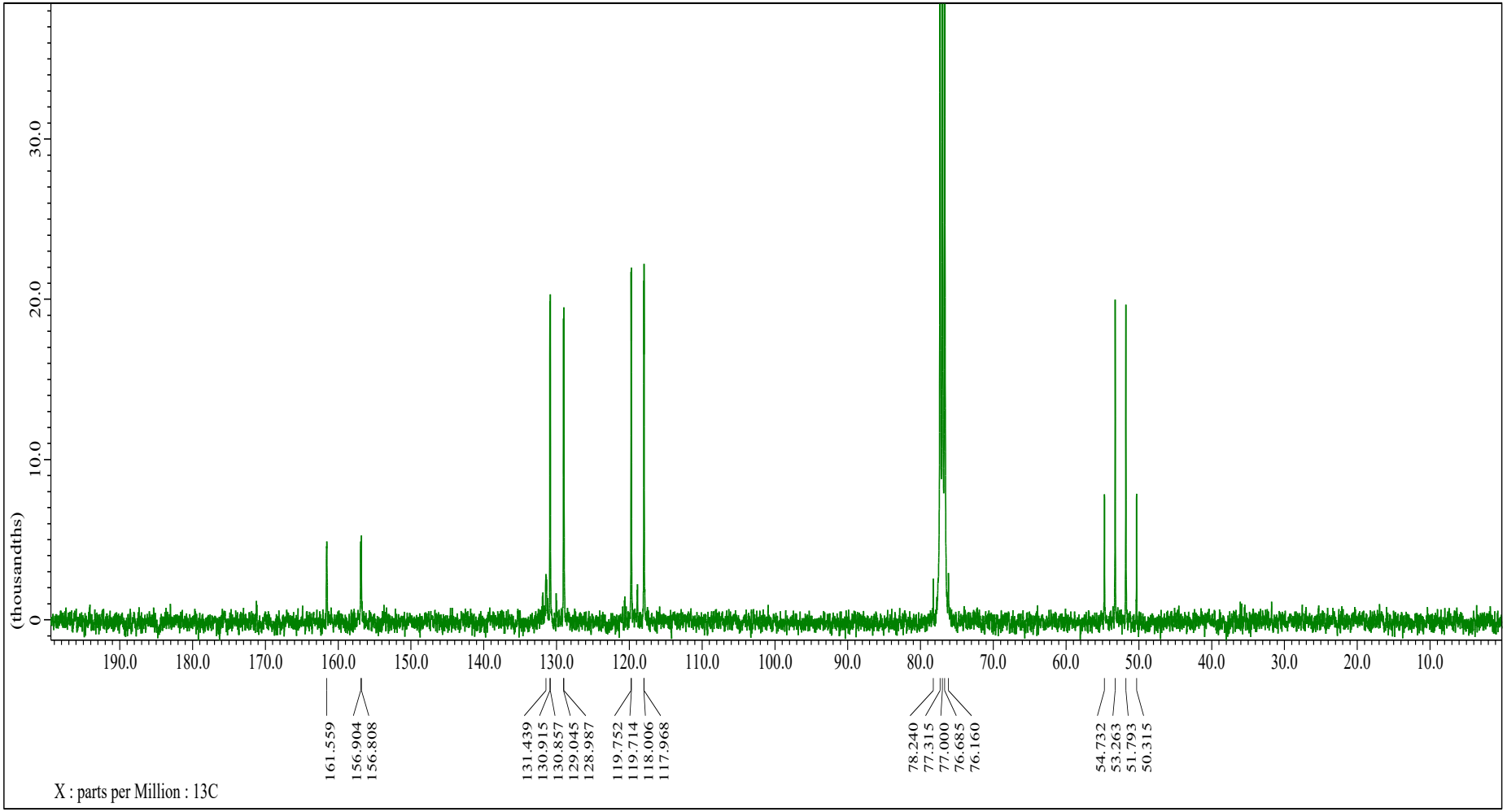

pczksb.NTU-12sep2025.2.fid
16 scan 1H for automation
7.54
7.53
7.46
7.45
2.00
1.96
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
7.61 7.60 7.59 7.58 7.57 7.56 7.55 7.54 7.53 7.52 7.51 7.50 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.39 7.38
f1 (ppm)

Expansion of aromatic region to show coupling

^{13}C NMR **(1b)**.



^{13}C NMR with coupling to H **(1b)**.


(thousandths)
30.0
20.0
10.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
161.559
156.904
156.808
131.439
130.915
130.857
129.045
128.987
119.752
119.714
118.006
117.968
78.240
77.315
77.000
76.685
76.160
54.732
53.263
51.793
50.315
X : parts per Million : 13C

X-ray Crystallography for Diacid 1a

The crystal packing arrangement for diacid **1a** shown in Figure S1, with molecules stacked along the *a* axis with neighbours related by a centre of symmetry. The azo bond is 1.270(5) Å long and the angles at the azo nitrogens are 113.1(3)° at N1 and 114.3(3)° at N2. Other geometric features are similar to those of the diester **1b**. In the plane of each thiophene ring, the carboxylic acid group is bent away from the azo group (by 4.4 and 3.7°) and the azo group is bent towards carboxylic acid (by 4.0 and 4.4°). There is one intramolecular (1,5) contact between a carbonyl oxygen atom and an azo nitrogen atom (2.886 Å), and two (1,5) contacts between a thiophene hydrogen and an azo nitrogen (2.60 and 2.69 Å).

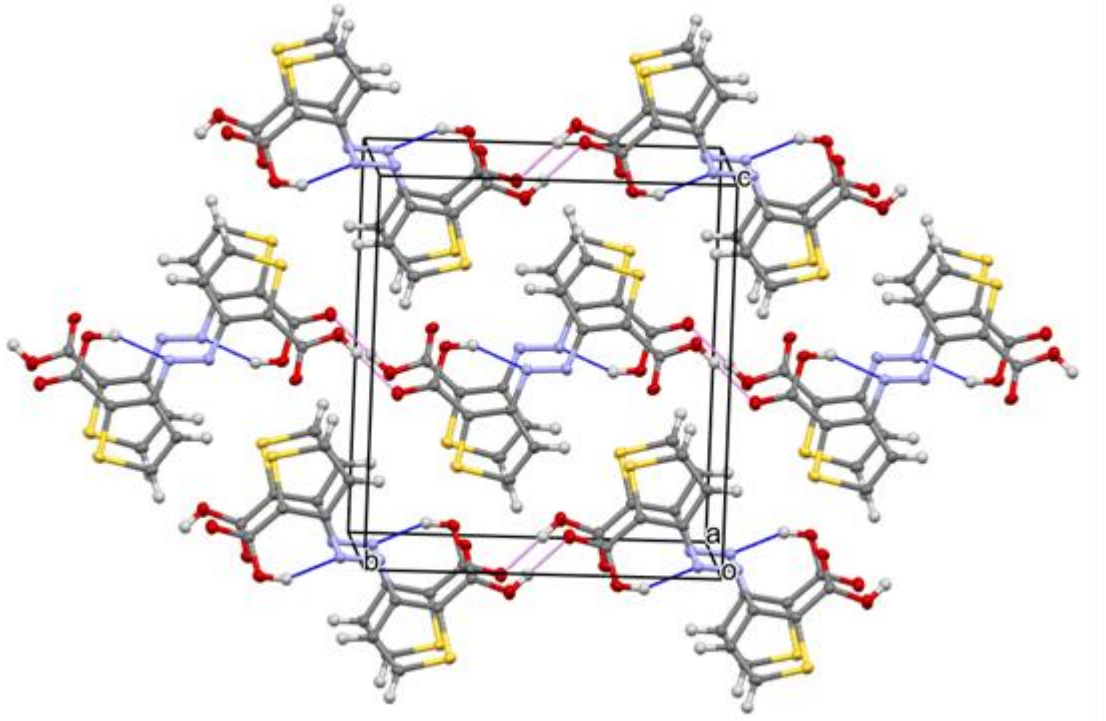


*Figure S1 View down the a axis of the crystal packing arrangement for diacid **1a**, showing how molecules lying along this axis are related by a centre of symmetry.*

Among the azobenzene series with two *ortho* CO_2H groups, one on each ring, there are two structures recorded in the Cambridge Structural Database (2023.3 release). [1] One (**A**, refcode XAJJOK)[2] shows two intramolecular hydrogen bonds from CO_2H groups to azo nitrogen atoms, the other (**B**, refcode YIRQAS)[3] shows no such intramolecular hydrogen bonds, preferring to use pairs of intermolecular hydrogen bonds to link molecules together and additional hydrogen bonds to included water molecules (Figure S2).

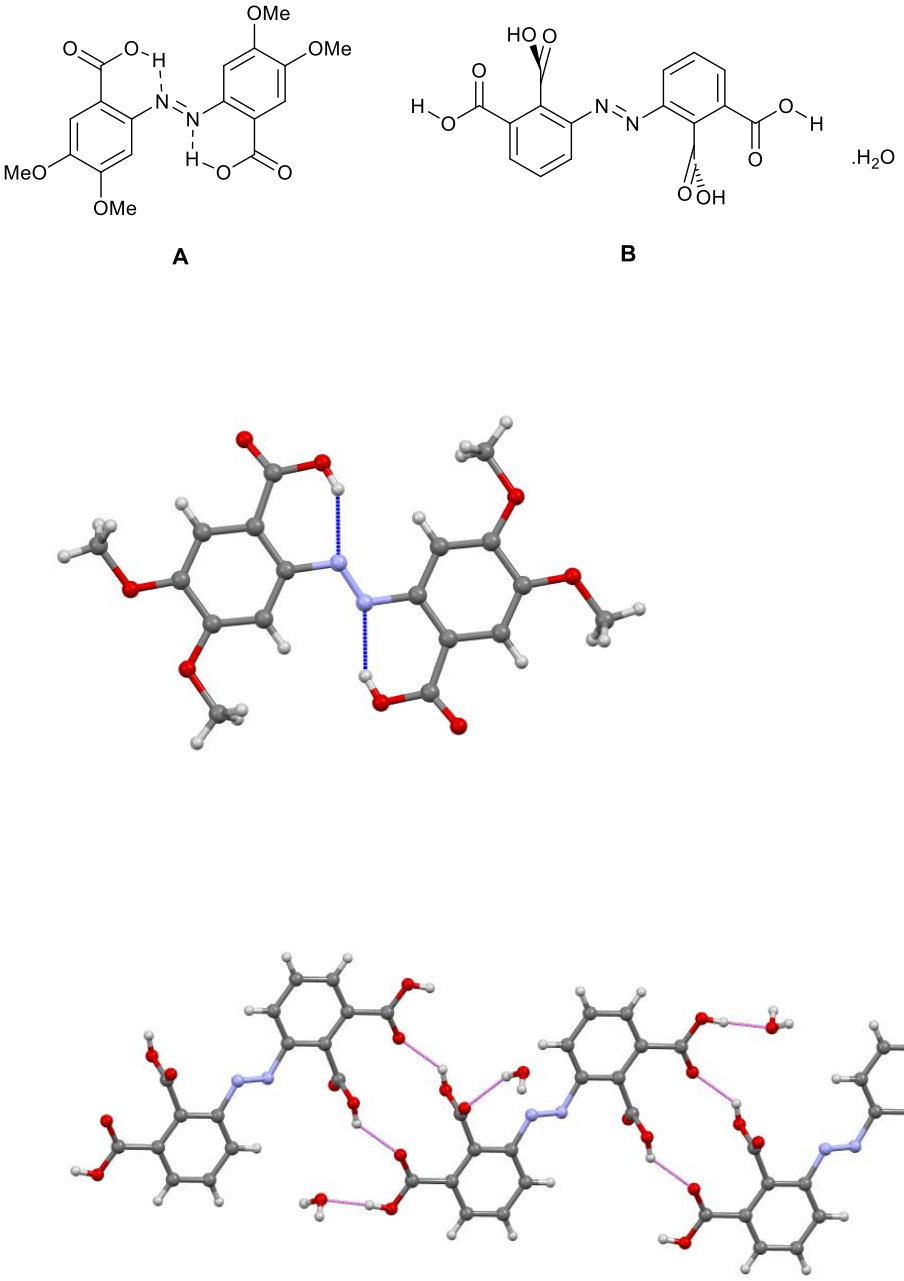


*Figure S2 Illustrations of the hydrogen bonding arrangements in **A** and **B**.*

X-ray crystallography data for 1a

Table S1 Bond Lengths for trans-3,3'-azothiophene-2,2'-dicarboxylic acid.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.713(4)	N2	C7	1.400(5)
S1	C4	1.710(4)	C1	C2	1.381(5)

S2	C6	1.712(4)	C1	C5	1.460(5)
S2	C9	1.714(4)	C2	C3	1.423(5)
O1	C5	1.218(5)	C3	C4	1.355(6)
O2	C5	1.339(5)	C6	C7	1.389(5)
O3	C10	1.208(5)	C6	C10	1.485(5)
O4	C10	1.332(5)	C7	C8	1.427(5)
N1	N2	1.270(5)	C8	C9	1.348(6)
N1	C2	1.404(5)			

Table S2 Bond Angles for trans-3,3'-azothiophene-2,2'-dicarboxylic acid.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	S1	C1	91.76(19)	O1	C5	C1	123.2(4)
C6	S2	C9	92.11(19)	O2	C5	C1	116.8(3)
N2	N1	C2	113.1(3)	C7	C6	S2	110.7(3)
N1	N2	C7	114.3(3)	C7	C6	C10	128.3(4)
C2	C1	S1	110.7(3)	C10	C6	S2	121.0(3)
C2	C1	C5	129.0(4)	N2	C7	C8	128.1(3)
C5	C1	S1	120.2(3)	C6	C7	N2	119.4(3)
N1	C2	C3	127.3(3)	C6	C7	C8	112.5(3)
C1	C2	N1	119.6(3)	C9	C8	C7	112.1(4)
C1	C2	C3	113.2(3)	C8	C9	S2	112.6(3)
C4	C3	C2	111.2(4)	O3	C10	O4	124.2(4)
C3	C4	S1	113.1(3)	O3	C10	C6	124.2(4)
O1	C5	O2	120.0(4)	O4	C10	C6	111.6(3)

Table S3 Hydrogen Bonds for trans-3,3'-azothiophene-2,2'-dicarboxylic acid.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	-H21	N1	0.87(7)	1.89(7)	2.698(4)	152(6)
O4	-H41	O1[1]	0.87(8)	1.84(8)	2.691(4)	166(6)

[1]+X,-1+Y,+Z

Table S4 Torsion Angles for trans-3,3'-azothiophene-2,2'-dicarboxylic acid.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
S1	C1	C2	N1	179.3(3)	C2	C1	C5	O1	-177.2(4)
S1	C1	C2	C3	-0.5(5)	C2	C1	C5	O2	3.3(6)
S1	C1	C5	O1	4.9(6)	C2	C3	C4	S1	0.4(5)

S1	C1	C5	O2	-174.7(3)	C4	S1	C1	C2	0.6(3)
S2	C6	C7	N2	177.7(3)	C4	S1	C1	C5	178.8(3)
S2	C6	C7	C8	-0.9(4)	C5	C1	C2	N1	1.2(6)
S2	C6	C10	O3	164.1(3)	C5	C1	C2	C3	-178.6(4)
S2	C6	C10	O4	-15.6(5)	C6	S2	C9	C8	-0.3(4)
N1	N2	C7	C6	-179.8(4)	C6	C7	C8	C9	0.7(5)
N1	N2	C7	C8	-1.5(6)	C7	C6	C10	O3	-14.2(7)
N1	C2	C3	C4	-179.7(4)	C7	C6	C10	O4	166.1(4)
N2	N1	C2	C1	179.5(4)	C7	C8	C9	S2	-0.1(5)
N2	N1	C2	C3	-0.8(6)	C9	S2	C6	C7	0.7(3)
N2	C7	C8	C9	-177.7(4)	C9	S2	C6	C10	-177.9(3)
C1	S1	C4	C3	-0.5(4)	C10	C6	C7	N2	-3.9(6)
C1	C2	C3	C4	0.1(5)	C10	C6	C7	C8	177.6(4)
C2	N1	N2	C7	179.8(3)					

X-ray Crystallography for Diester 1b

The azo-diester **1b** crystallises from THF as two polymorphs, and the crystal structures of both were investigated, with crystallographic details given in Table S5. The major polymorph is monoclinic and composed of thick orange plates and the minor one is triclinic and forms small thin colourless plates. The densities of the two forms, measured at 120 K, are very similar (1.57 g cm^{-3}). In the orange form, which is in space group $P2_1/n$, the molecule of **1b** sits on a centre of symmetry, so only half the molecule is unique, and the whole molecule is close to planar (Figure S3).

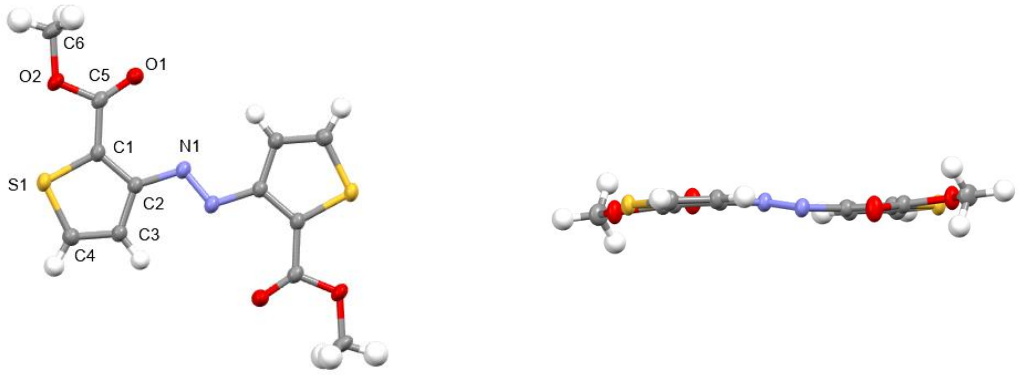


*Figure S3 Two views of the molecular conformation of **1b** in the orange polymorph, with anisotropic displacement parameters drawn at the 50% level.*

In contrast, for the colourless form, which is in space group *P*-1, the whole molecule is unique (Figure S4), and one thiophene ring is tilted at 19.6° to the best plane of the thiophene-azo skeleton.

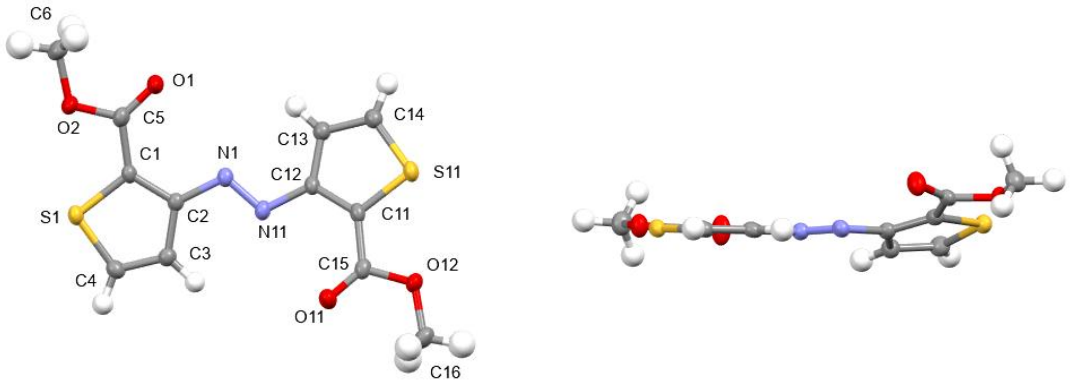


*Figure S4 Two views of the molecular conformation of **1b** in the colourless polymorph, with anisotropic displacement parameters drawn at the 50% level.*

The superposition of the two conformations is shown in Figure S5. The azo bond lengths are 1.269(3) and 1.270(3) Å, and the angles at the nitrogens are in the range 111.74(18)-112.1(2)°. In each case the ester group is bent away from the azo group by 3.5-4.3° and the azo group is bent towards the ester by 1.7-2.4° to avoid steric interactions. Both forms show long (1,5) contacts from a carbonyl oxygen atom to an azo nitrogen atom (2.951-2.965 Å) and from a thiophene hydrogen atom to an azo nitrogen atom (2.53-2.57 Å), all of the order of van der Waals contacts.

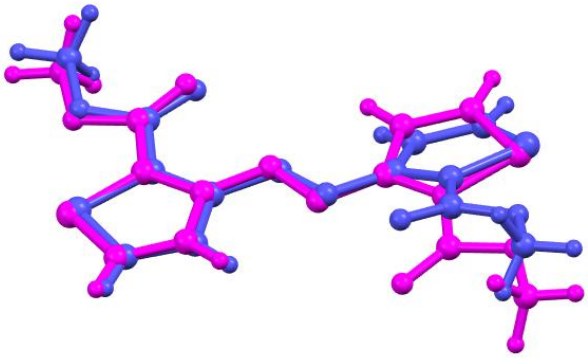


*Figure S5 Superposition of the conformers of **1b** in the two polymorphs, (orange polymorph shown in magenta, and colourless polymorph shown in blue.)*

The different packing arrangements in the two polymorphs are shown in Figure S6 and Figure S7. In the colourless form, the molecules related by a [1 0 0] translation are packed along the short *a* axis (3.873 Å) of the triclinic cell, and the view perpendicular to the molecular plane is also shown in Figure S7. In contrast, in the orange polymorph (Figure S6) there are two layers of molecules inserted between the layers related by the [0 0 1] translation along the *c* axis, though just the ester groups of these molecules lie directly between the molecules related by the cell translation. Thus, only in the colourless form are the molecules packed nearly directly on top of each other.

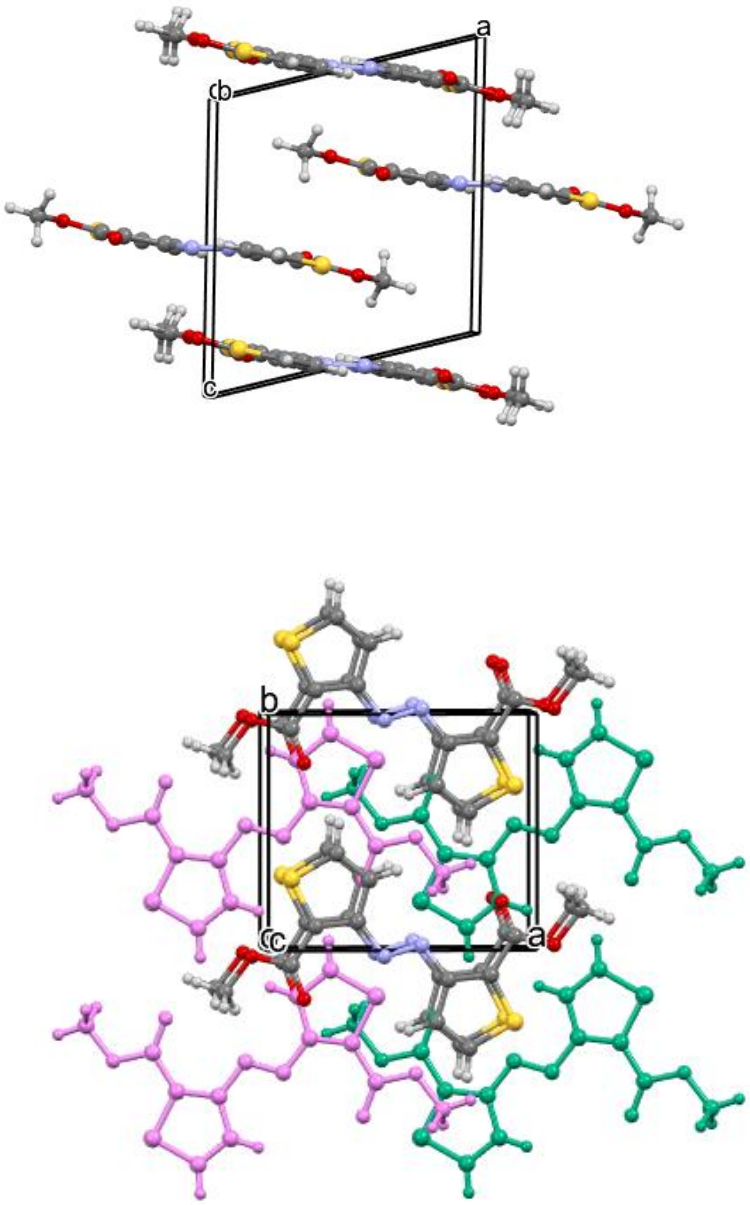


*Figure S6 Crystal packing in the orange polymorph of **1b** viewed down the b axis (upper), and down the c axis showing how two layers of molecules (in pink and green) lie in between molecules related by one cell translation along c (below).*

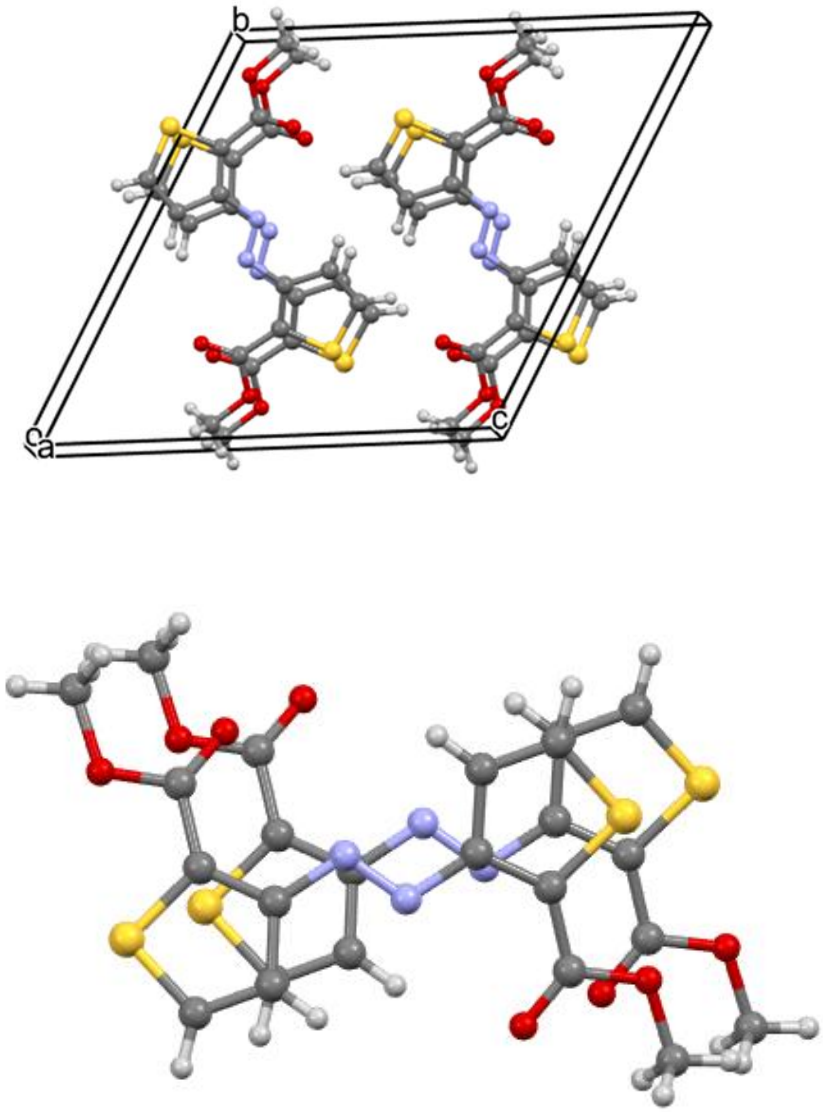


*Figure S7 Crystal packing in the colourless polymorph of **1b** viewed down the a axis (upper), and perpendicular to molecular plane (below), showing the overlap between adjacent molecules.*

Details of X-ray Crystallography

X-ray diffraction data from a single crystal of **1a** or both polymorphs of **1b** was measured on a Rigaku XtaLAB Synergy-DW VHF system equipped with a HyPix-Arc 100 detector at low temperature. (CrysAlisPro, Version 1.171.35.15 (release 03-08-2011 CrysAlis171.NET) Rigaku Corporation, Wroclaw, Poland.) Structures were solved with SHELXT, [4] and refined with SHELXL, [5] using the OLEX-2 software suite.[6] Structures were refined with non-hydrogen atoms having anisotropic displacement parameters. The positions and isotropic displacement parameters of the two carboxylate hydrogen atoms in **1a** were included in the refinement, but all other hydrogen atoms in **1a** and the polymorphs of **1b** were placed in calculated positions with displacement parameters related to the attached atom. For the orange polymorph of **1b**, a small amount (4.3%) of

a second orientation of the molecule which sits on a different centre of symmetry was included in the refinement. Illustrations were made with Mercury.[7] All crystal structures have been deposited at the Cambridge Crystallographic Data Centre, with reference number 2457289-2457291.X-ray diffraction data from a single crystal of **1a** or both polymorphs of **1b** was measured on a Rigaku XtaLAB Synergy-DW VHF system equipped with a HyPix-Arc 100 detector at low temperature. (CrysAlisPro, Version 1.171.35.15 (release 03-08-2011 CrysAlis171.NET) Rigaku Corporation, Wroclaw, Poland.) Structures were solved with SHELXT, [4] and refined with SHELXL, [5] using the OLEX-2 software suite.[6] Structures were refined with non-hydrogen atoms having anisotropic displacement parameters. The positions and isotropic displacement parameters of the two carboxylate hydrogen atoms in **1a** were included in the refinement, but all other hydrogen atoms in **1a** and the polymorphs of **1b** were placed in calculated positions with displacement parameters related to the attached atom. For the orange polymorph of **1b**, a small amount (4.3%) of a second orientation of the molecule which sits on a different centre of symmetry was included in the refinement. Illustrations were made with Mercury.[7] All crystal structures have been deposited at the Cambridge Crystallographic Data Centre, with reference number 2457289-2457291.

*Table S5 Details of the crystallographic measurements for diester **1b** and diacid **1a**.*

	Diacid 1a	Diester 1b Colourless Polymorph	Diester 1b Orange Polymorph
Formula	$C_{10}H_6N_2O_4S_2$	$C_{12}H_{10}N_2O_4S_2$	$C_{12}H_{10}N_2O_4S_2$
Formula weight	282.29	310.34	310.34
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	$P2_1/n$
a[Å]	7.4513(3)	3.87346(11)	9.0514(2)
b[Å]	11.4497(4)	13.8361(6)	7.63966(18)
c[Å]	12.7532(5)	13.9032(6)	9.7827(2)
α[°]	90	61.541(4)	90
β [°]	90.562(4)	87.776(3)	104.546(2)
γ[°]	90	87.828(3)	90
V [Å^3]	1087.99(7)	654.43(5)	654.79(3)
Z	4	2	2

ρ [g cm^{-3}]	1.723	1.575	1.574
T [K]	130	120	120
λ (Å)	1.54184	1.54184	1.54184
μ(mm^{-1})	4.560	3.846	3.844
unique refl.	2099	2469	1323
Refl, I > 2σI	1741	2056	1265
R_{int}	0.0342	0.0584	0.0273
R_1 (I > 2σI)	0.0590	0.0437	0.0339
wR_2 (all)	0.179	0.106	0.0946
$\Delta\rho$(r) [e Å^{-3}]	0.68/-0.47	0.26/ -0.37	0.36/-0.32
Crystallisation Solvent	THF/Toluene	THF	THF
CCDC number	2457289	2457291	2457290

Bidirectional photoisomerization of 1a and 1b

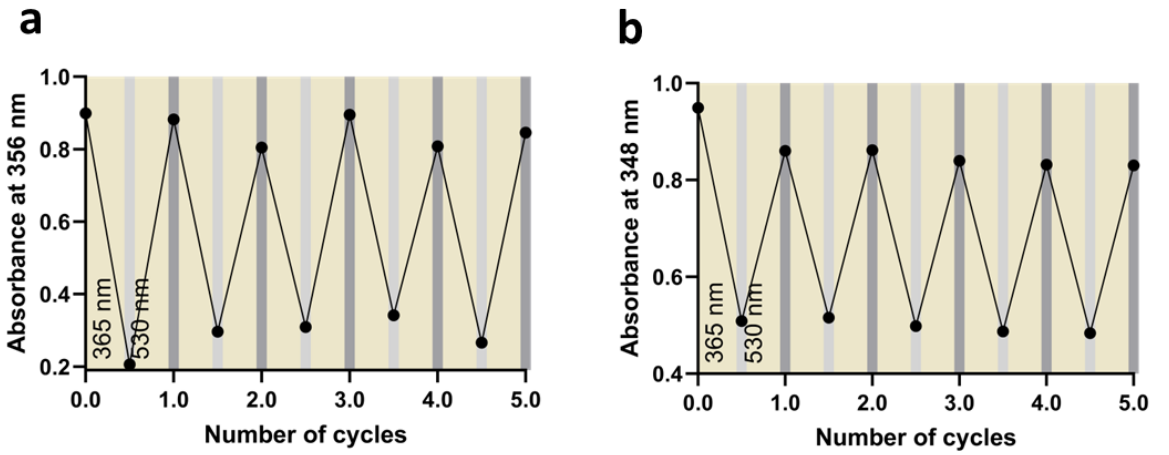


Figure S8 Multiple cycles of photoisomerization irradiation with 365 nm and 530 nm light for molecules (a) 1a in 1x10^{-4} M NaOH; (b) 1b in DCM.

Computational analysis of 1a and 1b

Table S6 Comparison of calculated and experimental maximum absorbance values in DCM solvent.

Molecule	Calculated λ_{max} (Calc.)	Experimental λ_{max} (Exp.)	Difference between Calc. and Exp.
1a	373.6 nm	377 nm	3.4 nm
1b	346.1 nm	345 nm	1.1 nm

*Table S7 Comparison of theoretically calculated UV–Vis absorption maxima (λ_{max}) with their corresponding excited states and oscillator strengths, alongside experimental absorption maxima recorded in DCM solvent for compounds **1a** and **1b**.*

	1a		**1b**	
	Computational max absorbance and the corresponding excited states (λ_{max})	Oscillator strength	Computational max absorbance the corresponding excited states (λ_{max})	Oscillator strength
***E* isomer**	516.9 nm (N=1) 371.4 nm (N=2) 345.14 nm (N=3)	0.0459 0.3132 0.2990	504.45 nm (N=1) 379.5 nm (N=2) 346.1 nm (N=3)	0.0188 0.2327 0.4116
***Z* isomer**	479.7 nm (N=1) 330.6 nm (N=3) 299.6 nm (N=6) 253.3 nm (N = 12) 243.8 nm (N = 13)	0.0519 0.0506 0.1590 0.1562 0.1405	486.4 nm (N = 1) 315.7 nm (N = 4) 290.97 nm (N=6) 253.0 nm (N = 11) 224.5 nm (N = 20)	0.0849 0.3541 0.0582 0.0901 0.0603

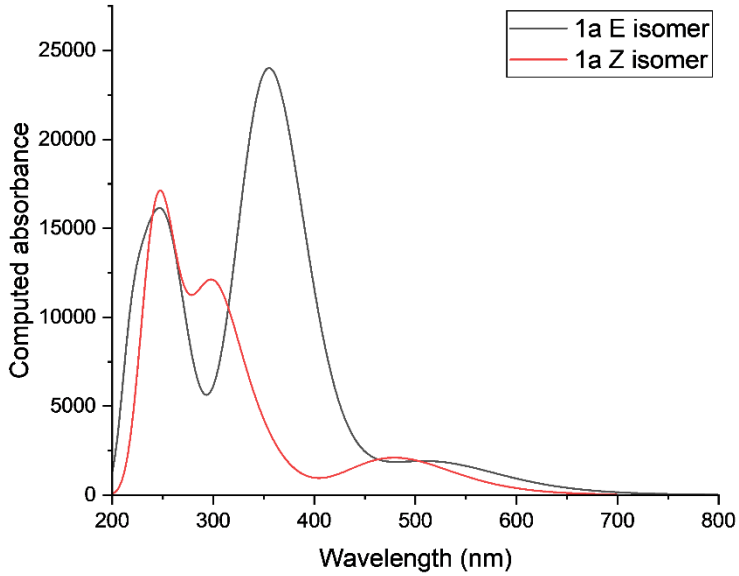


*Figure S9 TD-DFT calculated UV–Vis absorption spectra of the E and Z isomers of compound **1a** in DCM solvent.*

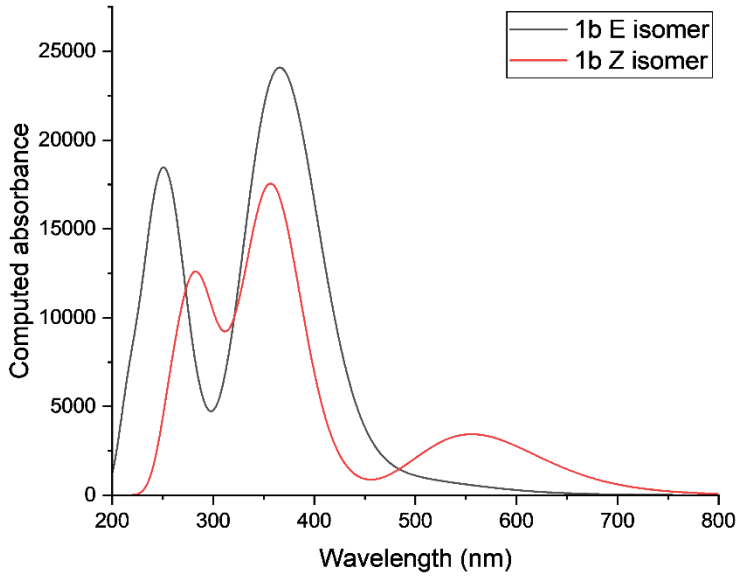
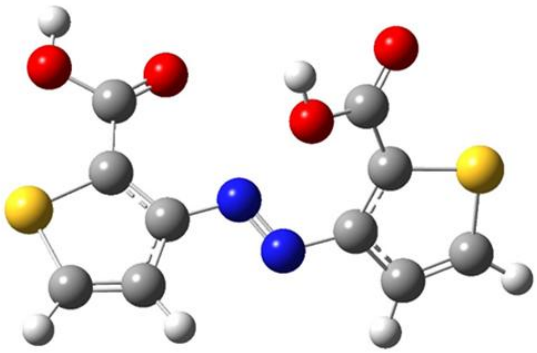


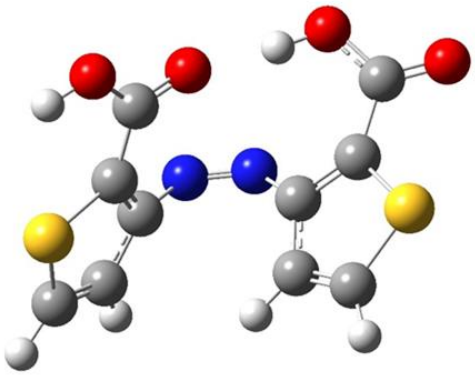
*Figure S10 TD-DFT calculated UV–Vis absorption spectra of the E and Z isomers of compound **1b** in DCM solvent.*

Thermal isomerisation in gas phase and DCM solvent phase

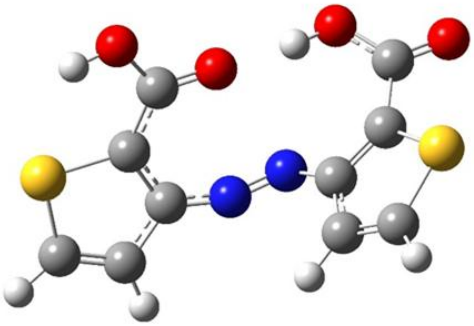
1a molecule



E isomer:
Dihedral angle: 176.43°
Optimised energy: -4.1790x10^{6} kJ mol^{-1}



Z isomer:
Dihedral angle: 0.00°
Optimised energy: -4.1789x10^{6} kJ mol^{-1}



Transition state:
Dihedral angle: 93.46°
Optimised energy: -4.1788x10^{6} kJ mol^{-1}

*Figure S10 Calculations of the energy difference based on the total electronic energies obtained from geometry optimizations of the E and Z isomers for **1a** molecule.*

- The energy difference between **1a** molecule *Z* isomer and *E* isomer = 51.64 kJ mol-1
- The energy difference between **1a** molecule *Z* isomer and transition state = 84.41 kJ mol-1

*Table S8 Calculated thermochemistry values from Gaussian output files for the isomerization of **1a** molecule in the gas phase from Z isomer to E isomer. Where E_o is the total electronic energy of the molecule, ZPE is zero-point correction, E_{tot} is Thermal correction to Energy, H_{corr} is thermal correction to Enthalpy, and G_{corr} is Thermal correction to Gibbs Free Energy.*

	E_0 (Hartrees)	ZPE (Hartrees)	E_{tot} (Hartrees)	H_{corr} (Hartrees)	G_{corr} (Hartrees)
Z isomer	-1591.66	0.1518	0.1678	0.1687	0.1068
E isomer	-1591.69	0.1520	0.1683	0.1692	0.1047
Transition state	-1591.63	0.1501	0.6609	0.1670	0.1047
	E_0+ZPE (Hartrees)	E_0+E_{tot} (Hartrees)	E_0+H_{corr} (Hartrees)	E_0+G_{corr} (Hartrees)	E_0+G_{corr} (kJ mol^{-1})

Z isomer	-1591.51	-1591.49	-1591.49	-1591.55	-4.1786E+06
E isomer	-1591.53	-1591.52	-1591.52	-1591.58	-4.1787E+06
Transition state	-1591.48	-1590.96	-1591.46	-1591.52	-4.1785E+06
Delta *Z*-*E*	-0.02672	-0.02647	-0.02647	-0.02904	**-76.25**
Delta TS-*Z*	0.03102	0.52591	0.03109	0.03067	**80.53**

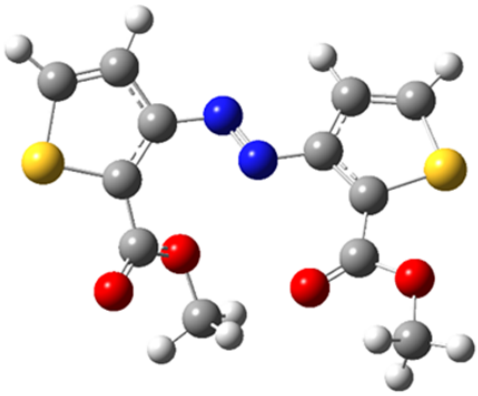
- Thermal isomerisation energy difference between **1a** molecule *Z* isomer and *E* isomer at 298 K (ΔG) = -76.25 kJ mol-1.
- Thermal activation energy difference between **1a** molecule transition state and *Z* isomer at 298 K (ΔG) = 80.53 kJ mol-1.

*Table S9 Calculated thermochemistry values from Gaussian output files for the isomerization of **1a** molecule in the DCM solvent phase from Z isomer to E isomer. Where E_o is the total electronic energy of the molecule, ZPE is zero-point correction, E_{tot} is Thermal correction to Energy, H_{corr} is thermal correction to Enthalpy, and G_{corr} is Thermal correction to Gibbs Free Energy.*

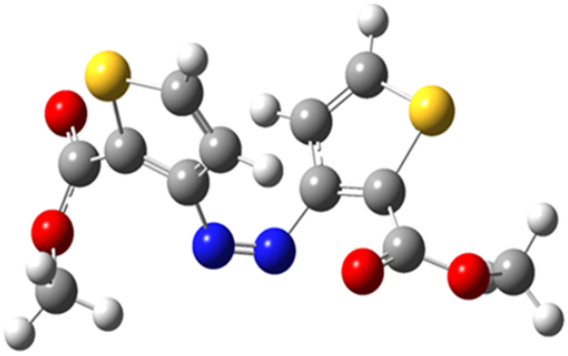
	E_0 (Hartrees)	ZPE (Hartrees)	E_{tot} (Hartrees)	H_{corr} (Hartrees)	G_{corr} (Hartrees)
Z isomer	-1591.679	0.1519	0.1677	0.1687	0.1076
E isomer	-1591.701	0.1516	0.1679	0.1688	0.1045
	E_0+ZPE (Hartrees)	E_0+E_{tot} (Hartrees)	E_0+H_{corr} (Hartrees)	E_0+G_{corr} (Hartrees)	E_0+G_{corr} (kJ mol^{-1})
Z isomer	-1591.53	-1591.51	-1591.51	-1591.57	-4.17867E+06
E isomer	-1591.55	-1591.53	-1591.53	-1591.60	-4.17874E+06
delta	-0.02187	-0.02143	-0.02142	-0.02463	**-64.67**

- Thermal isomerisation energy difference between **1a** molecule *Z* isomer and *E* isomer at 298 K (ΔG) = -64.67 kJ mol-1.

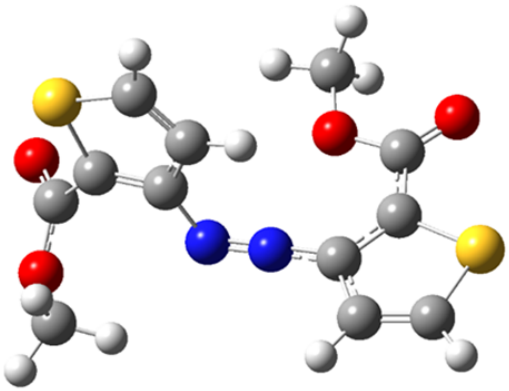
1b molecule



E isomer:
Dihedral angle: 179.50°
Optimised energy: -4.3853x10^{6} kJ mol^{-1}



Z isomer:
Dihedral angle: 0.00°
Optimised energy: -4.3854x10^{6} kJ mol^{-1}



Transition state:
Dihedral angle: 80.00°
Optimised energy: -4.3852x10^{6} kJ mol^{-1}

*Figure S11 Calculations of the energy difference based on the total electronic energies obtained from geometry optimizations of the E and Z isomers for **1b** molecule.*

- The energy difference between **1b** molecule *Z* isomer and *E* isomer = 122.78 kJ mol-1
- The energy difference between **1b** molecule *Z* isomer and transition state = 116.54 kJ mol-1

*Table S10 Calculated thermochemistry values from Gaussian output files for the isomerization of **1b** molecule in the gas phase from Z isomer to E isomer. Where E_o is the total electronic energy of the molecule, ZPE is zero-point correction, E_{tot} is Thermal correction to Energy, H_{corr} is thermal correction to Enthalpy, and G_{corr} is Thermal correction to Gibbs Free Energy.*

	E_0 (Hartrees)	ZPE (Hartrees)	E_{tot} (Hartrees)	H_{corr} (Hartrees)	G_{corr} (Hartrees)
Z isomer	-1670.2609	0.2069	0.2266	0.2275	0.1554

E isomer	-1670.3076	0.2077	0.2272	0.2281	0.1573
Transition state	-1670.2165	0.2051	0.2241	0.2250	0.1557
	E_0+ZPE (Hartrees)	E_0+E_{tot} (Hartrees)	E_0+H_{corr} (Hartrees)	E_0+G_{corr} (Hartrees)	E_0+G_{corr} (kJ mol^{-1})
Z isomer	-1670.054	-1670.034	-1670.033	-1670.105	-4.3849E+06
E isomer	-1670.053	-1670.034	-1670.033	-1670.150	-4.3850E+06
Transition state	-1670.011	-1669.992	-1669.991	-1670.061	-4.3847E+06
Delta *Z*-*E*	0.00083	0.00065	0.00064	-0.04494	**-118.00**
Delta TS-*Z*	0.04261	0.04190	0.04190	0.04466	**117.27**

- Thermal isomerisation energy difference between **1b** molecule *Z* isomer and *E* isomer at 298 K (ΔG) = -118.0 kJ mol-1.
- Thermal activation energy difference between **1b** molecule transition state and *Z* isomer at 298 K (ΔG) = 117.27 kJ mol-1.

*Table S11 Calculated thermochemistry values from Gaussian output files for the isomerization of **1b** molecule in the DCM solvent phase from Z isomer to E isomer. Where E_o is the total electronic energy of the molecule, ZPE is zero-point correction, E_{tot} is Thermal correction to Energy, H_{corr} is thermal correction to Enthalpy, and G_{corr} is Thermal correction to Gibbs Free Energy.*

	E_0 (Hartrees)	ZPE (Hartrees)	E_{tot} (Hartrees)	H_{corr} (Hartrees)	G_{corr} (Hartrees)
Z isomer	-1670.279	0.2068	0.2264	0.2273	0.1554
E isomer	-1670.308	0.2077	0.2272	0.2281	0.1573
	E_0+ZPE (Hartrees)	E_0+E_{tot} (Hartrees)	E_0+H_{corr} (Hartrees)	E_0+G_{corr} (Hartrees)	E_0+G_{corr} (kJ mol^{-1})
Z isomer	-1670.072	-1670.053	-1670.052	-1670.124	-4.3849E+06
E isomer	-1670.100	-1670.080	-1670.079	-1670.150	-4.3850E+06
delta	-0.0277	-0.0278	-0.0278	-0.0267	**-70.11**

- Thermal isomerisation energy difference between **1b** molecule *Z* isomer and *E* isomer at 298 K (ΔG) = -70.11 kJ mol-1.

*Table S12 Summarized values of the activation free energy differences for **1a** and **1b** molecules obtained using total electronic energy and thermochemistry data from Gaussian output files.*

Activation free energy difference for the isomerisation reaction		
Molecule system and the calculation method	1a molecule	1b molecule
***Z*-TS isomer (HF)**	84.41 kJ mol^{-1}	116.54 kJ mol^{-1}
***Z*-TS isomer (Thermochemistry)**	80.53 kJ mol^{-1}	117.27 kJmol^{-1}

Thermal-induced half-life studies of 1a and 1b

Thermal-induced half-life measurements of 1a

*Table S13 Parameters obtained from NMR spectroscopy, data highlighted in bold text were used for calculating thermal half-life of **1a** molecule, determined in the dark at 20˚C.*

Name of NMR data	Time for *Z-E* conversion (days)	Amount of *Z* (%)	Ln *Z* amount	Half-life (days)
XZ_diacid_sample	0	29.1	3.37073817	34.8241206
XZ_diacid_after_uv	0	65.0	4.17438727	
XZ_diacid_even_longer_uv_conc	0.099	59.7	4.08933202	
E_AND_Z_DIACID_8_DEC_1600	2.06	60.6	4.104294893	
JW_E_AND_Z_MIX_TUES_1645	4.096	56.5	4.034240638	
JW_E_and_Z_acid_WED_18_DEC	11.96	48.2	3.875359021	
JW_E_TO_Z_PAT_ACID_21_DEC	14.98	45.4	3.815512105	

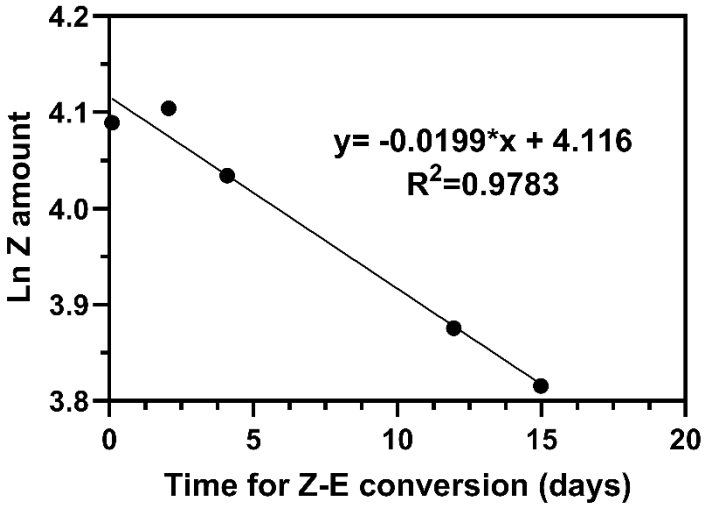
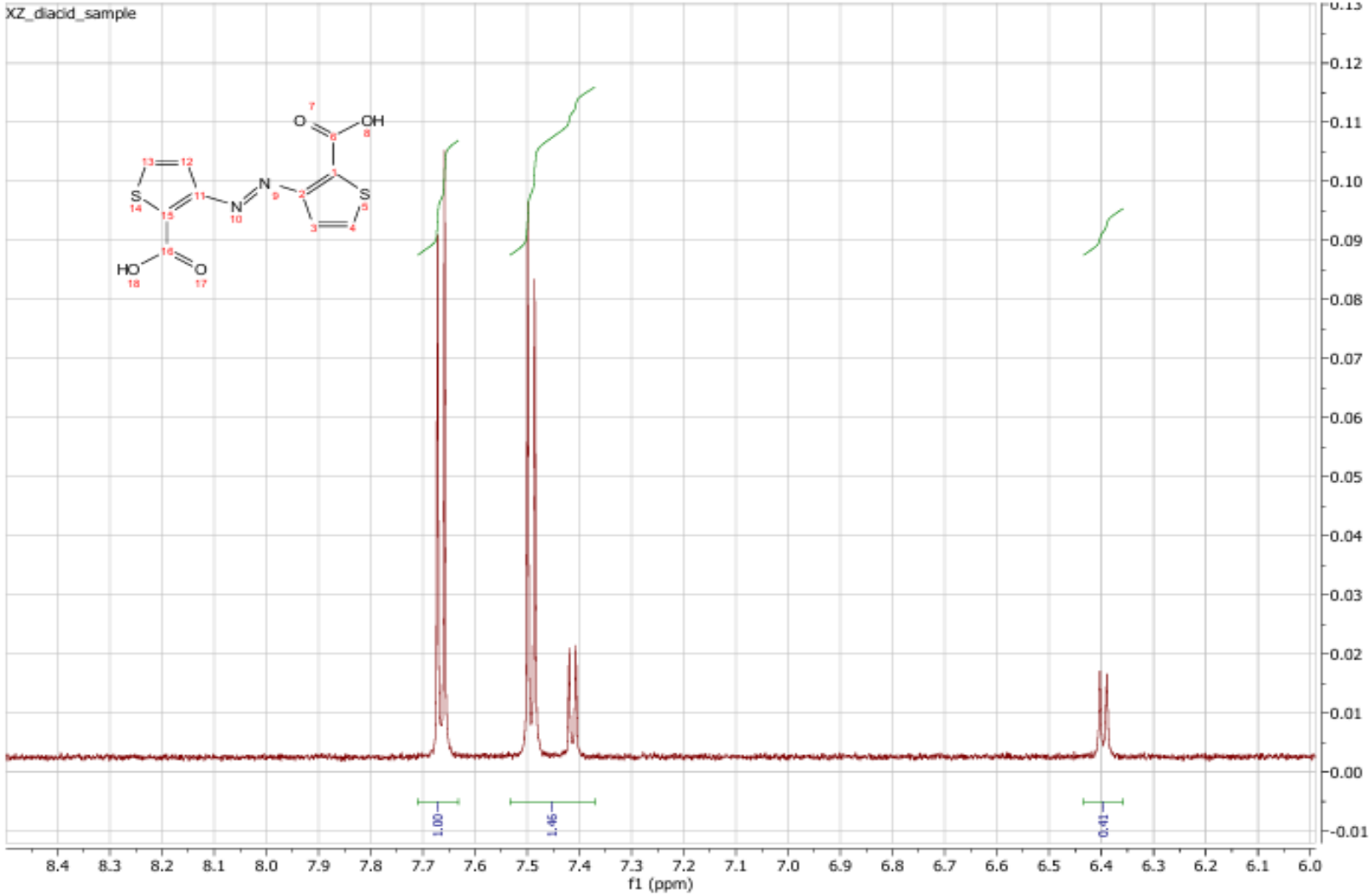
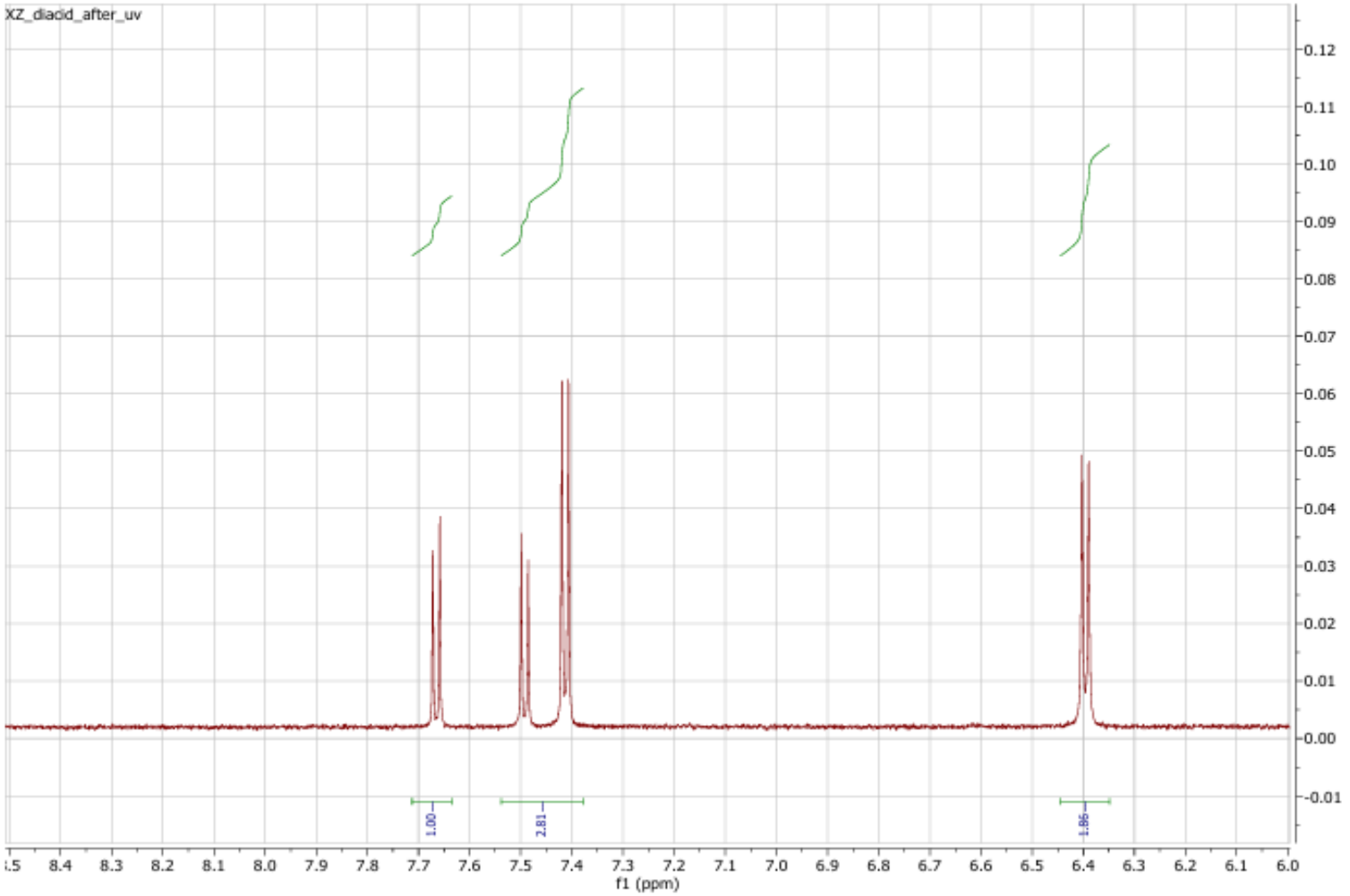
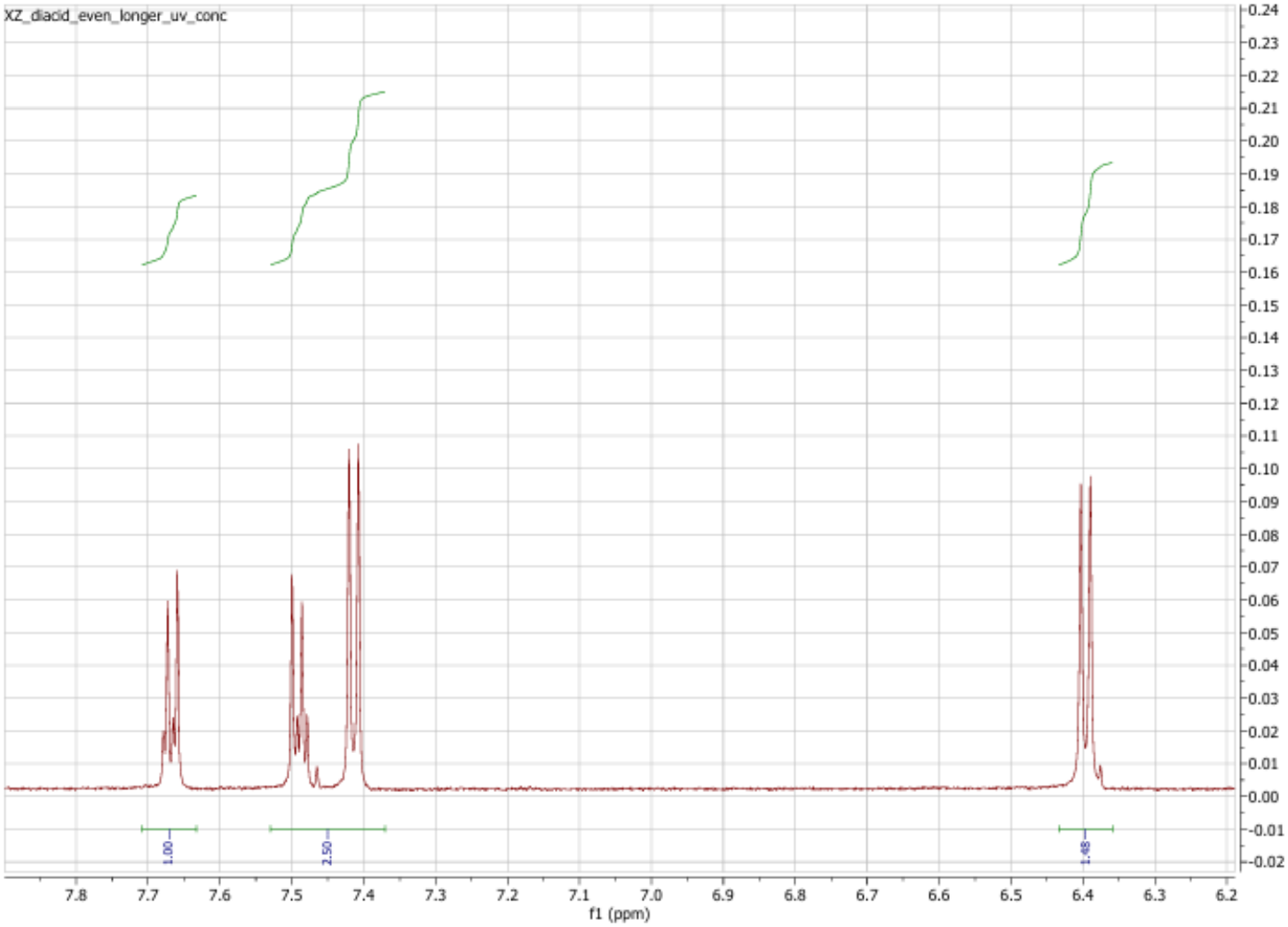


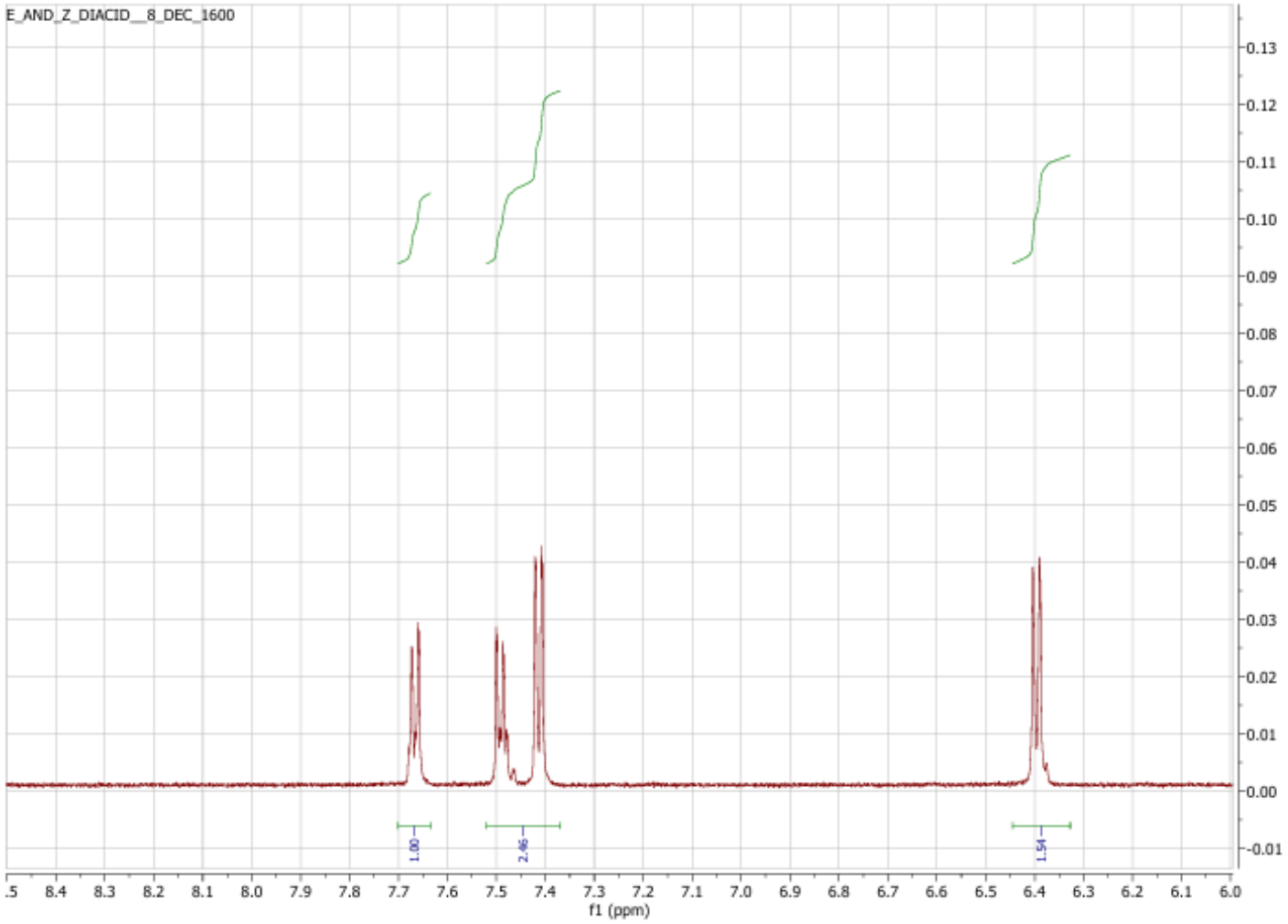
*Figure S12 Plot of Ln amount of Z versus time recorded for Z-E isomer conversion, with the gradient used for determining the thermal half-life time of azothiophene **1a**.*

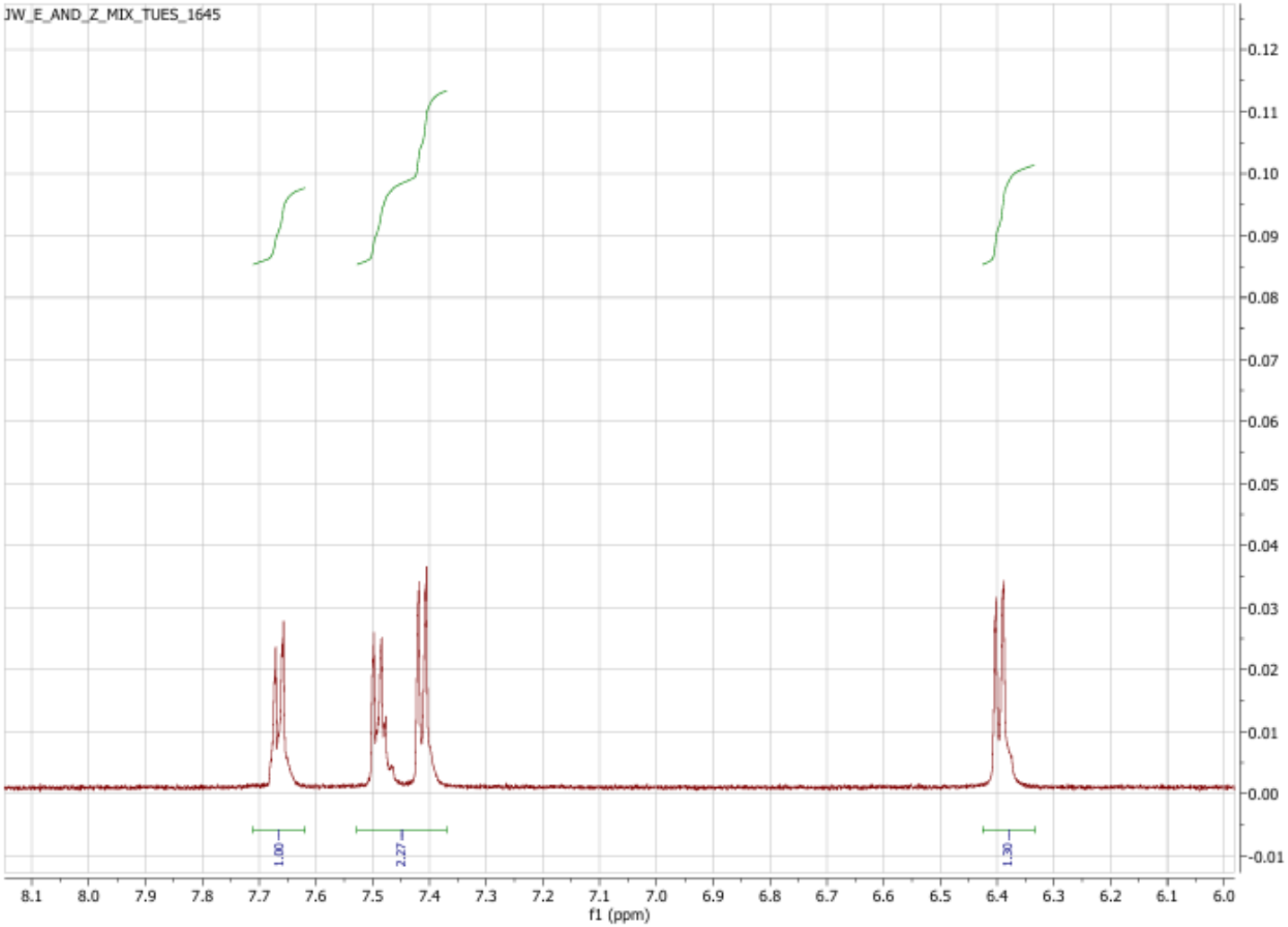
^{1}H NMR

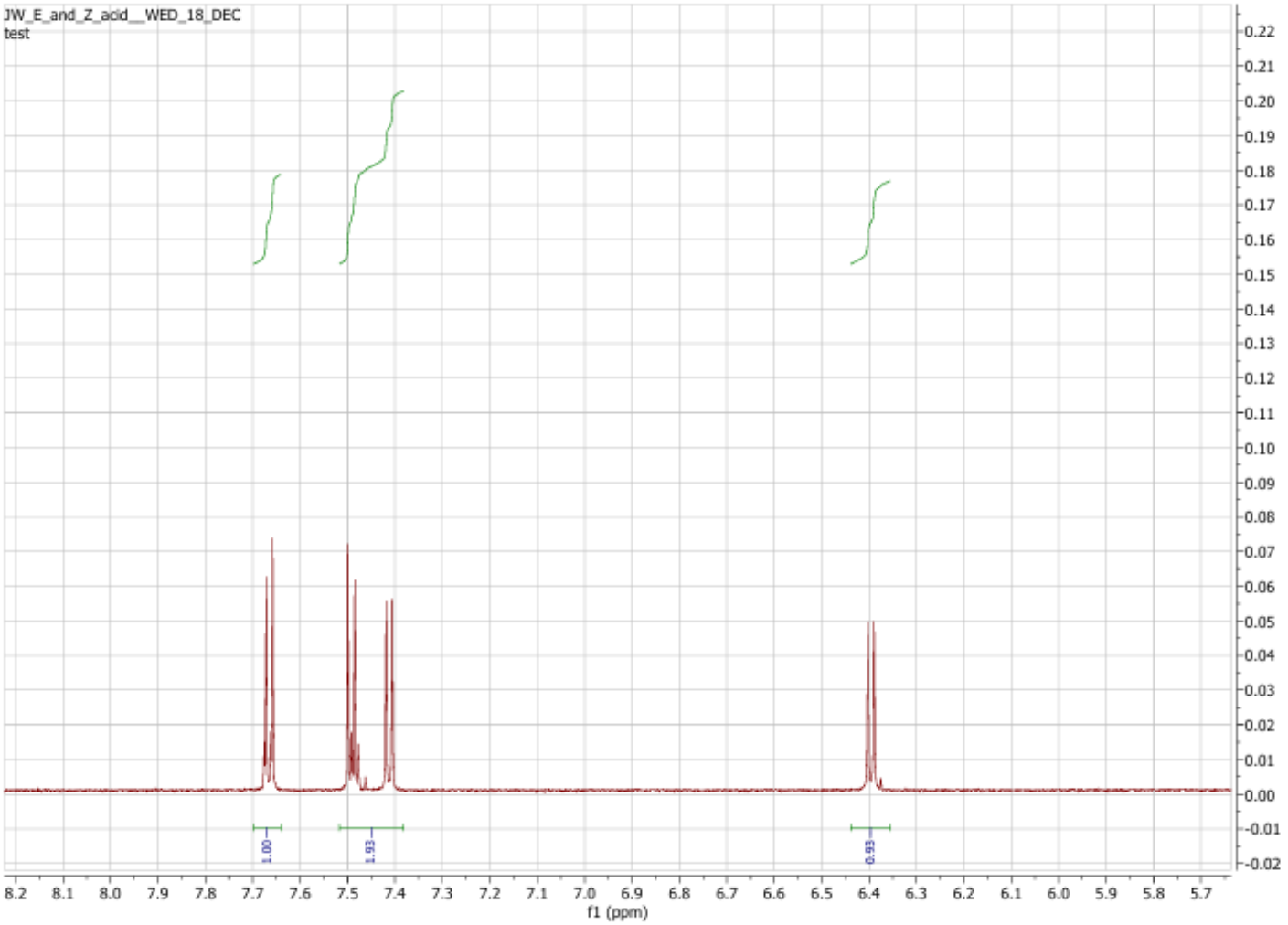


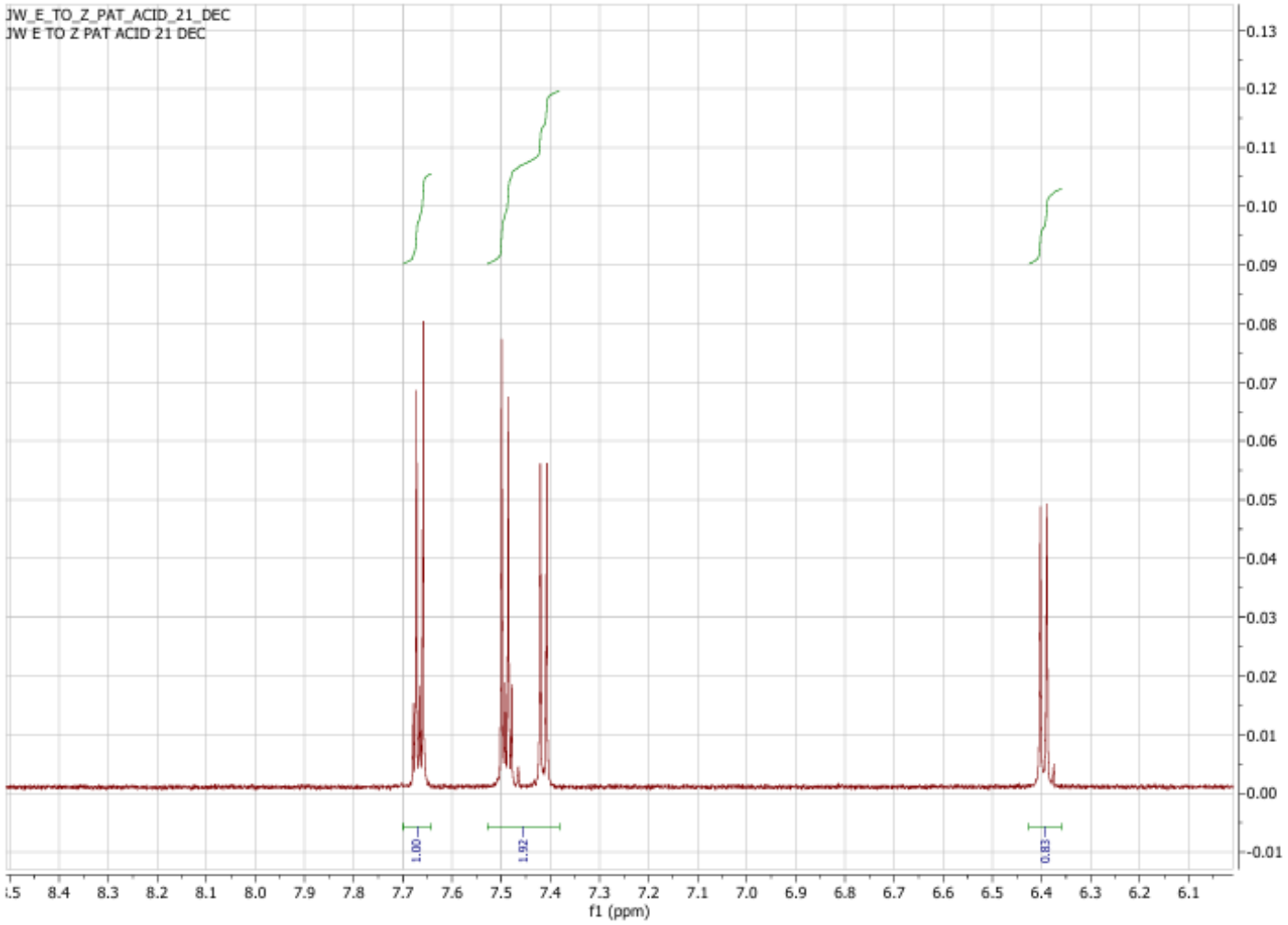

XZ_diacid_after_uv
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
1.00
2.81
1.86
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0
f1 (ppm)


XZ_diacid_even_longer_uv_conc
1.00
2.50
1.48
f1 (ppm)


E_AND_Z_DIACID__8_DEC_1600
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
1.00
2.46
1.54
.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0
f1 (ppm)


JW_E_AND_Z_MIX_TUES_1645
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
1.00
2.27
1.30
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)


JW_E_and_Z_acid__WED_18_DEC
test
1.00
1.93
0.93
f1 (ppm)


JW_E_TO_Z_PAT_ACID_21_DEC
JW E TO Z PAT ACID 21 DEC
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
1.00
1.92
0.83
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1
f1 (ppm)

Thermal-induced half-life measurements of 1b

*Table S14 Parameters obtained from NMR spectroscopy, data highlighted in bold text were used for calculating thermal half-life of **1b** molecule, determined in the dark at 20˚C.*

Name of NMR data	Time for *Z*-*E* conversion (days)	Amount of *Z* (%)	Ln *Z* amount	Half-life (days)
XZ_diester_initial	0	0.99009	-0.00995	**26.65384615**
XZ_diester_UV4	0	37.10692	3.61380	
XZ_diesterdark6	**3.02**	**34.21053**	**3.53253**	
XZ_diesterdark7	**3.04**	**33.77483**	**3.51972**	
XZ_diesterdark8	**3.86**	**32.43243**	**3.47916**	
XZ_diesterdark9	**3.95**	**32.88591**	**3.49304**	
XZ_diesterdark11	**5.81**	**31.97279**	**3.46489**	
XZ_diesterdark13	**6.07**	**31.03448**	**3.43510**	
XZ_diesterdark14	**6.94**	**30.06993**	**3.40353**	
XZ_diesterdark15	**7.05**	**29.57747**	**3.38701**	
XZ_diesterdark16	**9.71**	**28.57143**	**3.35241**	
XZ_diesterdark20	**13.03**	**25.92593**	**3.25524**	
XZ_diesterdark22	**14.06**	**25.37313**	**3.23369**	

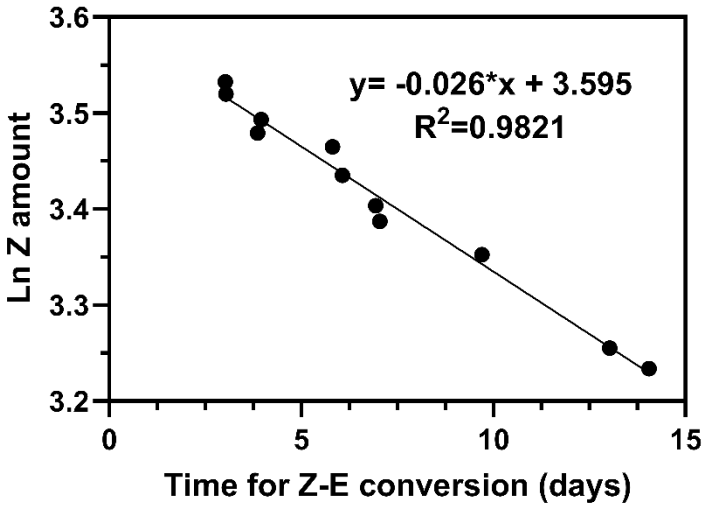
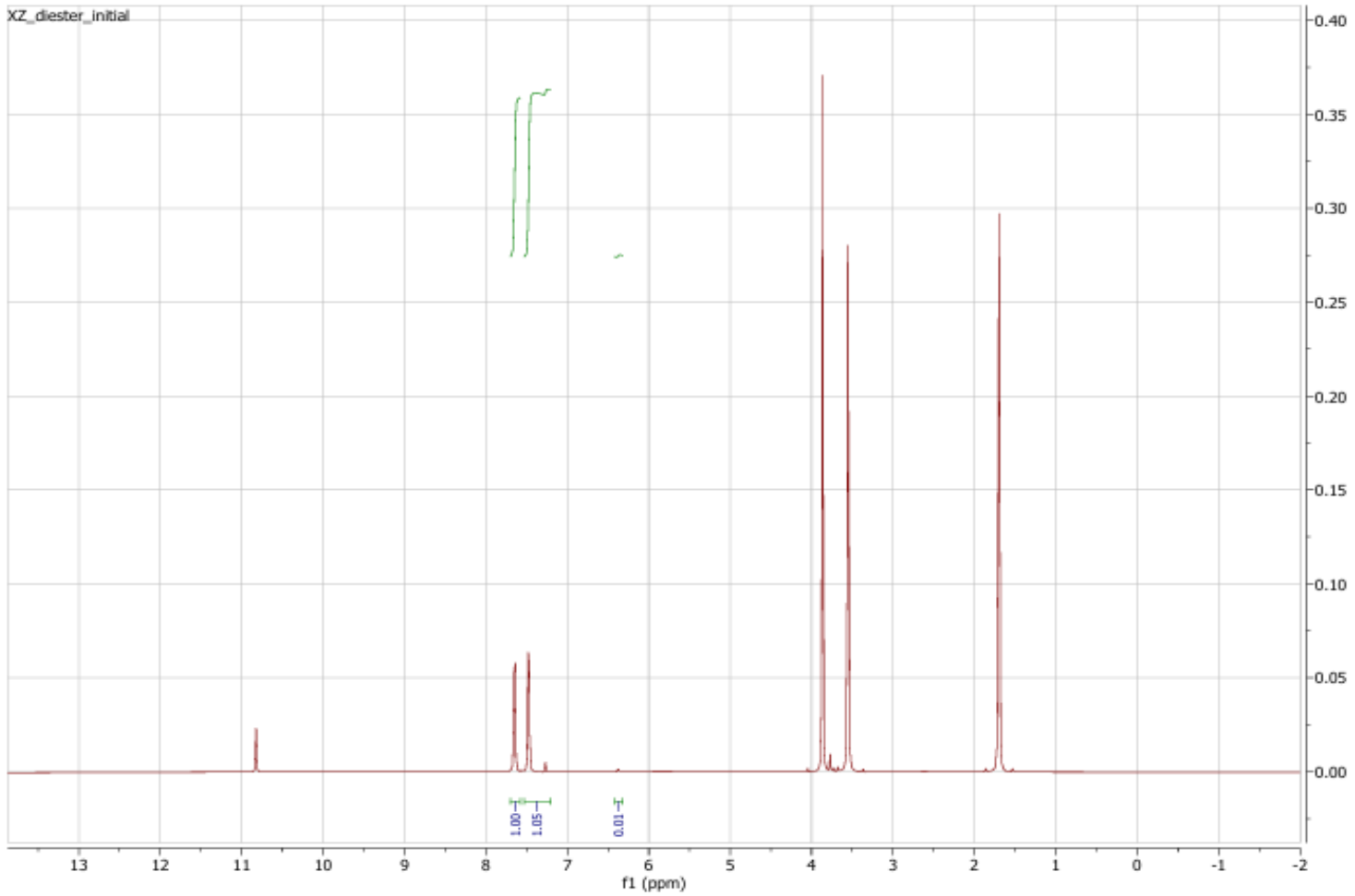
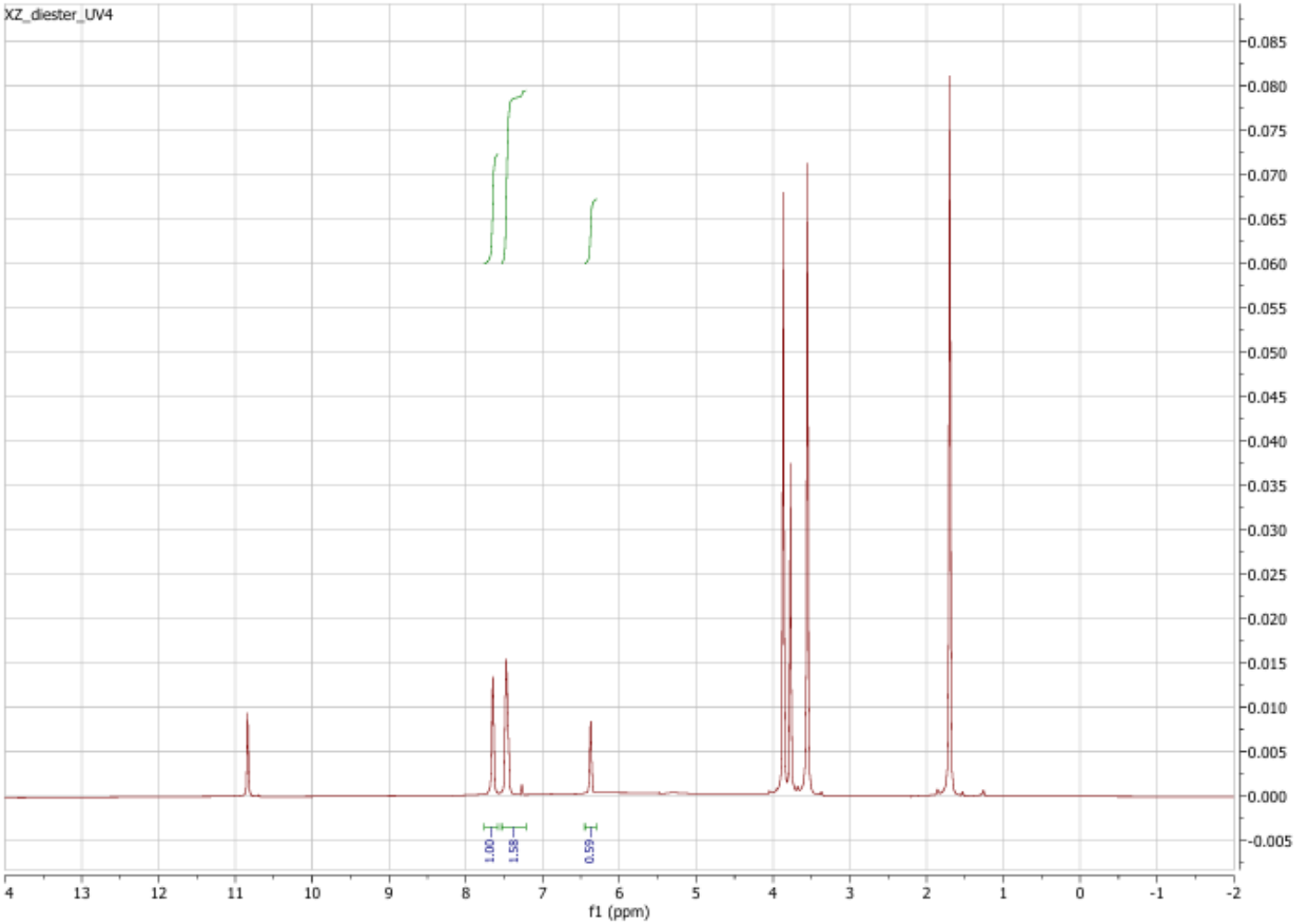
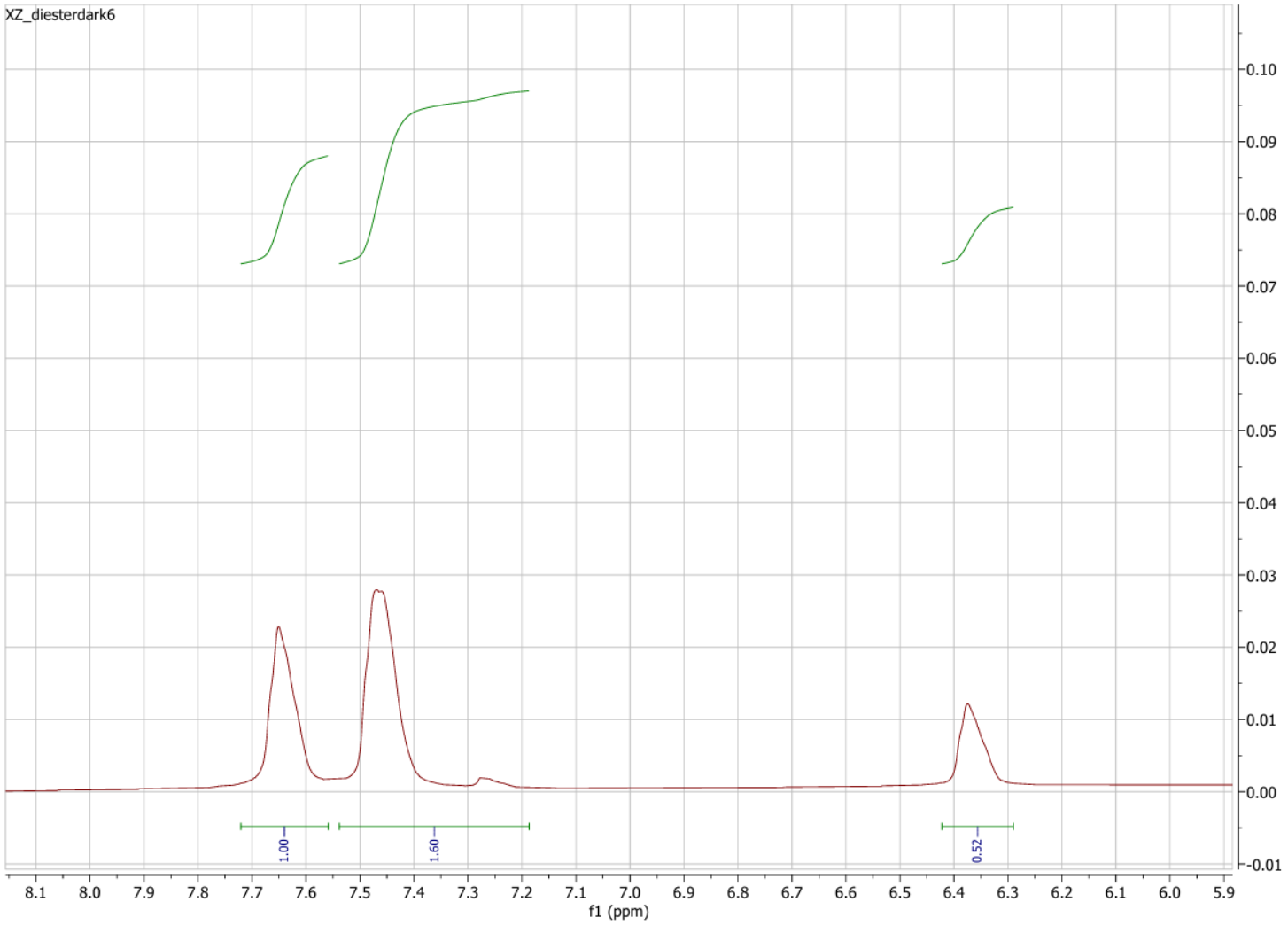


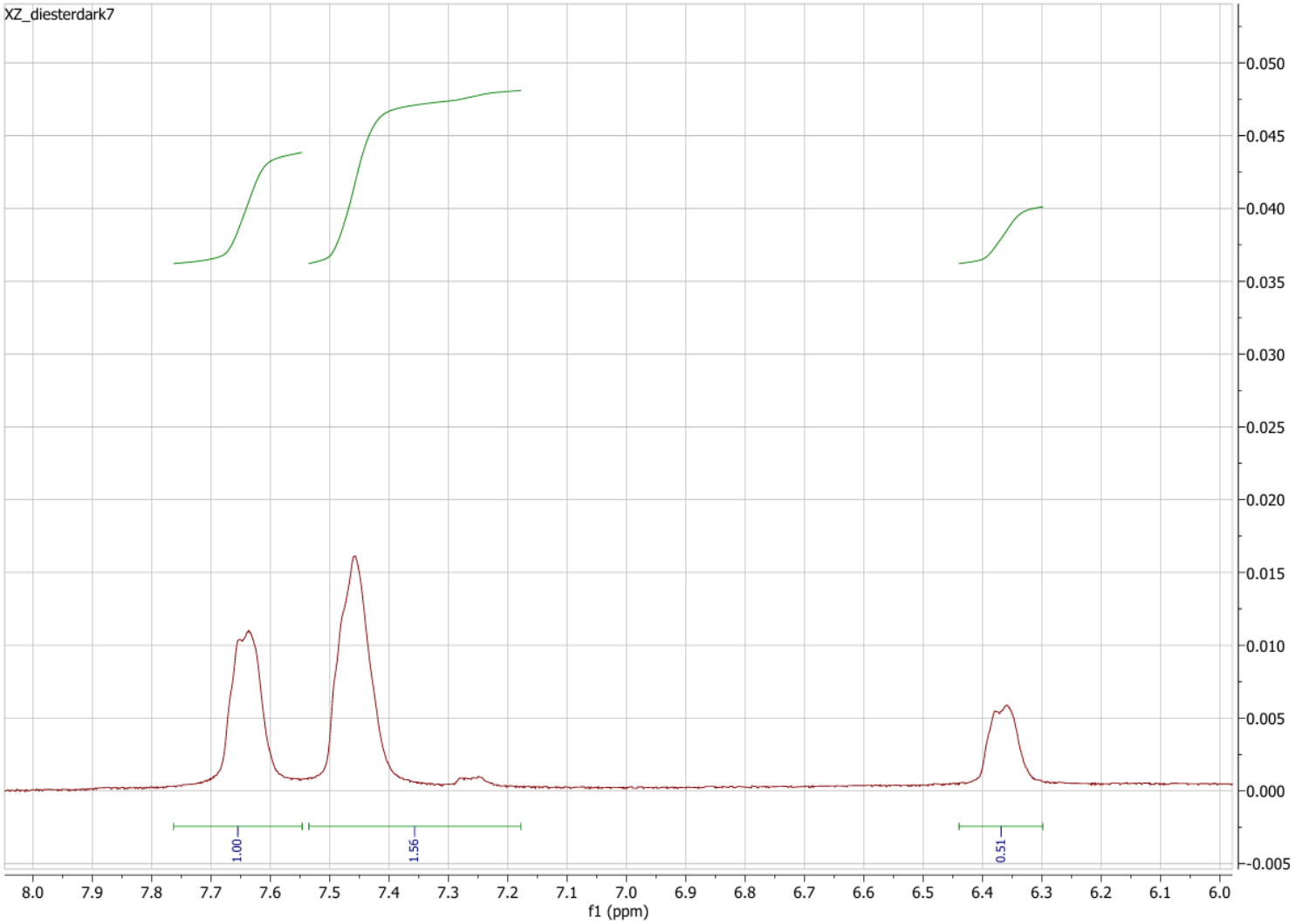
Figure S13 Plot of Ln amount of Z versus time recorded for Z-E isomer conversion, with the gradient used for determining the thermal half-life time of azothiophene ***1b****.*

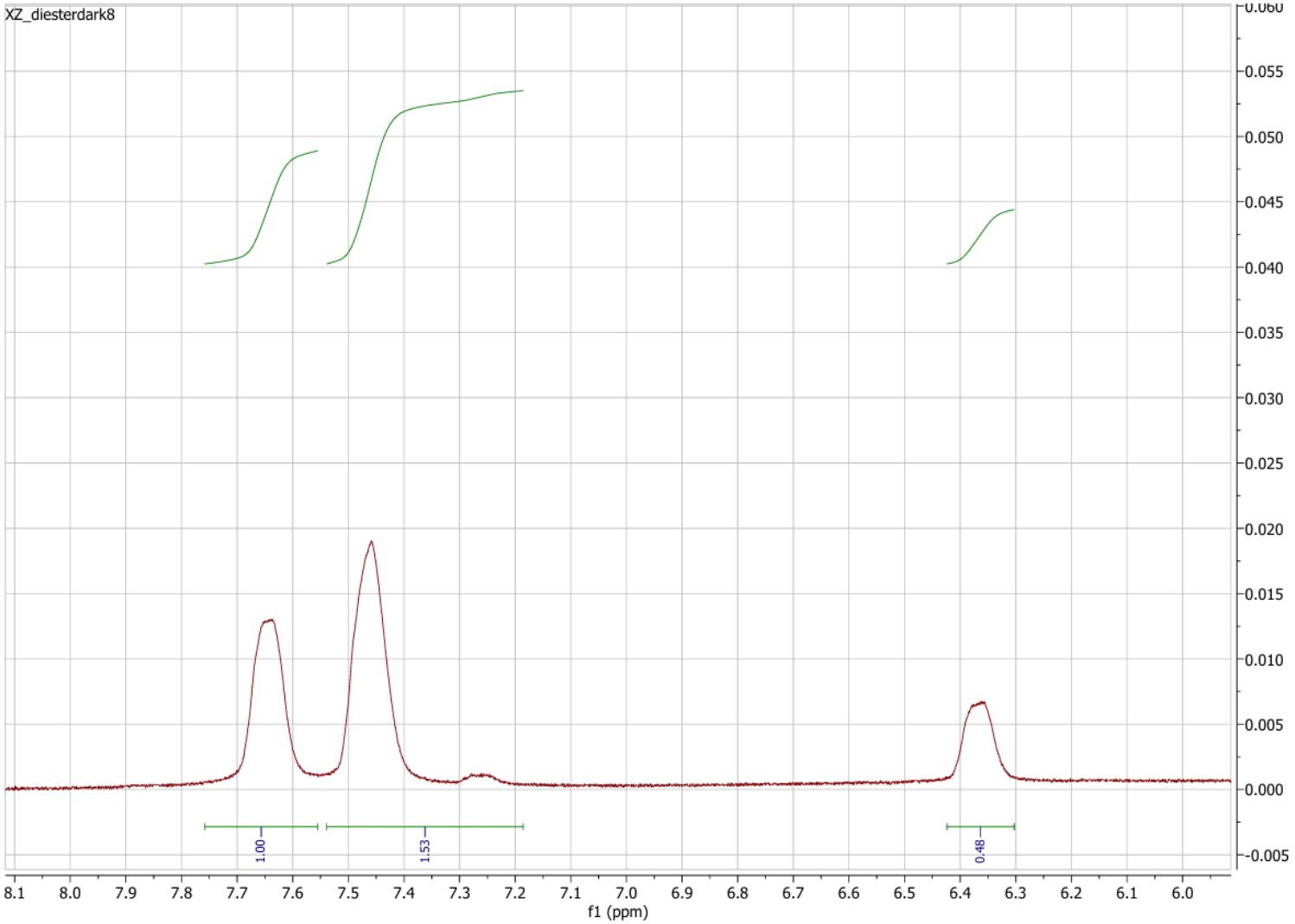
^{1}H NMR

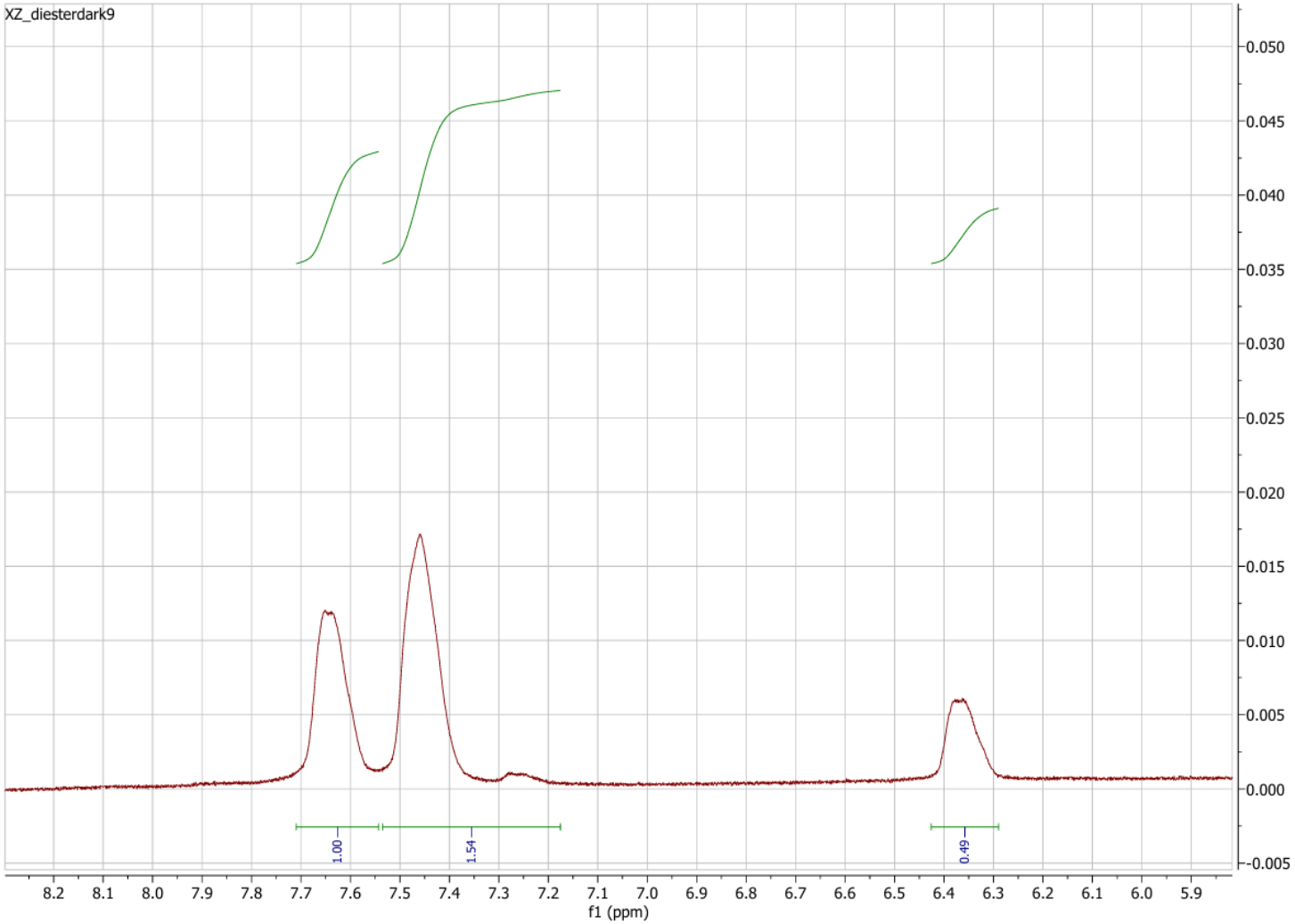

XZ_diester_initial
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
1.00
1.05
0.01
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

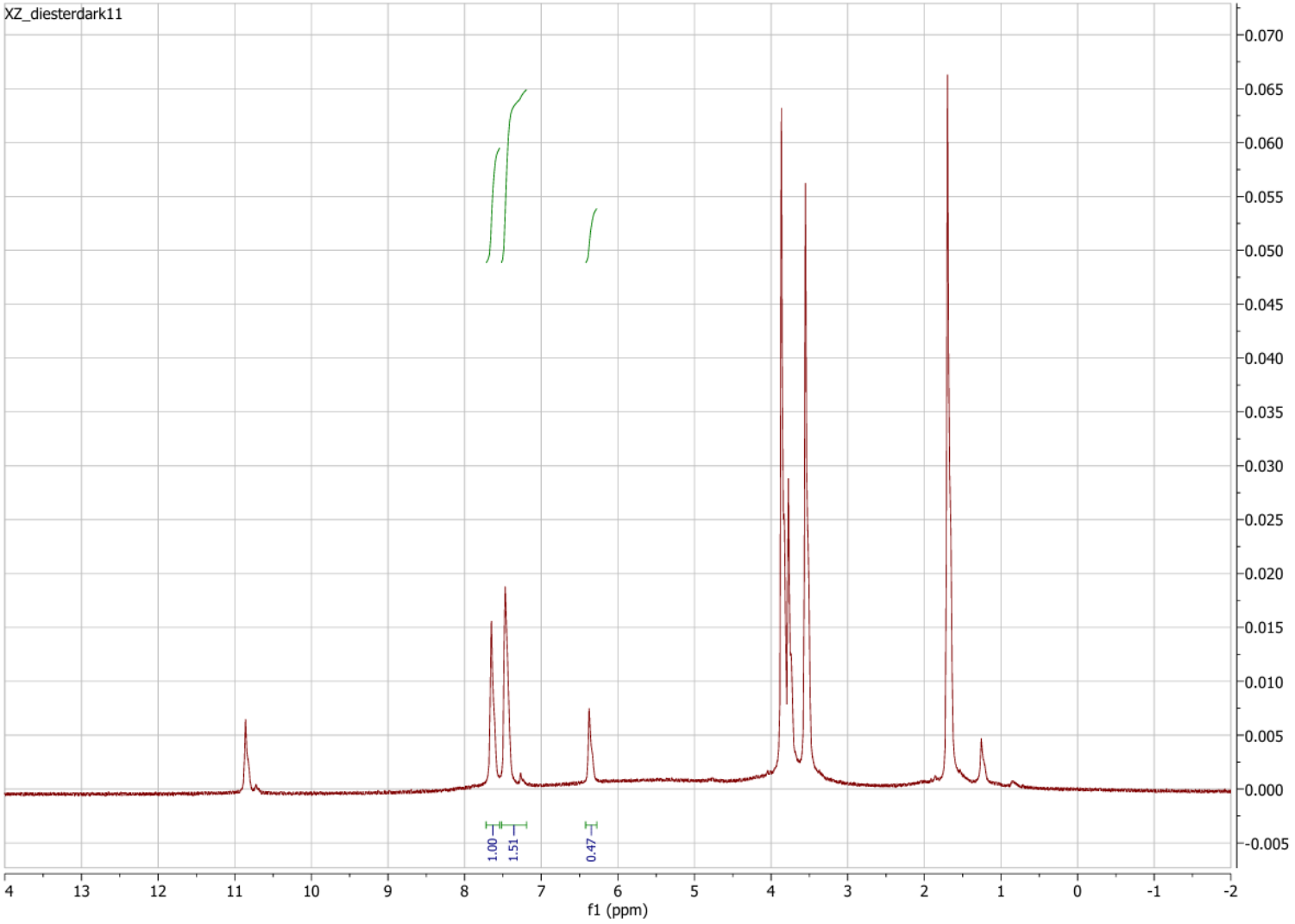

XZ_diester_UV4
0.085
0.080
0.075
0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.58
0.59
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

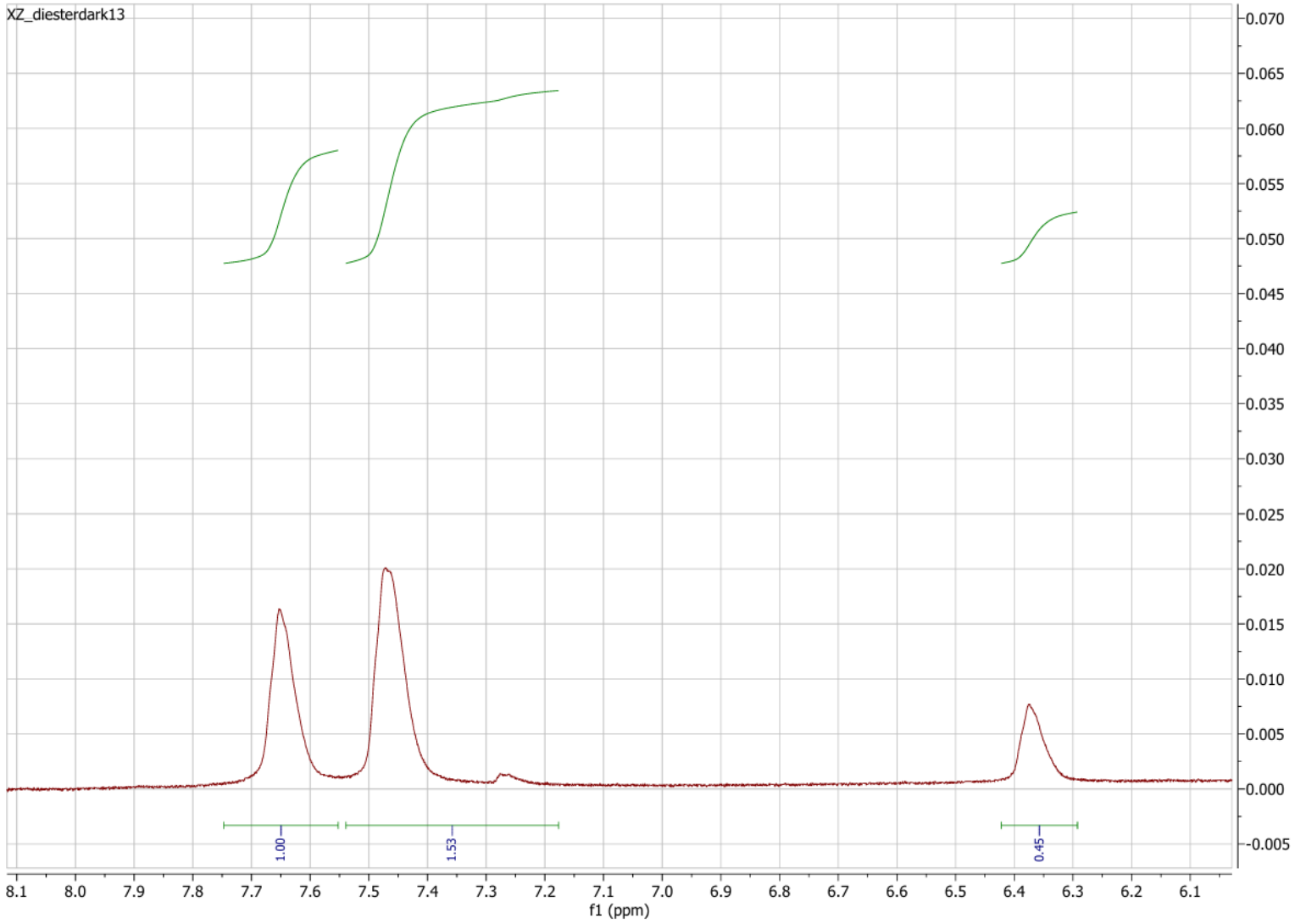

XZ_diesterdark6
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
1.00
1.60
0.52
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
f1 (ppm)

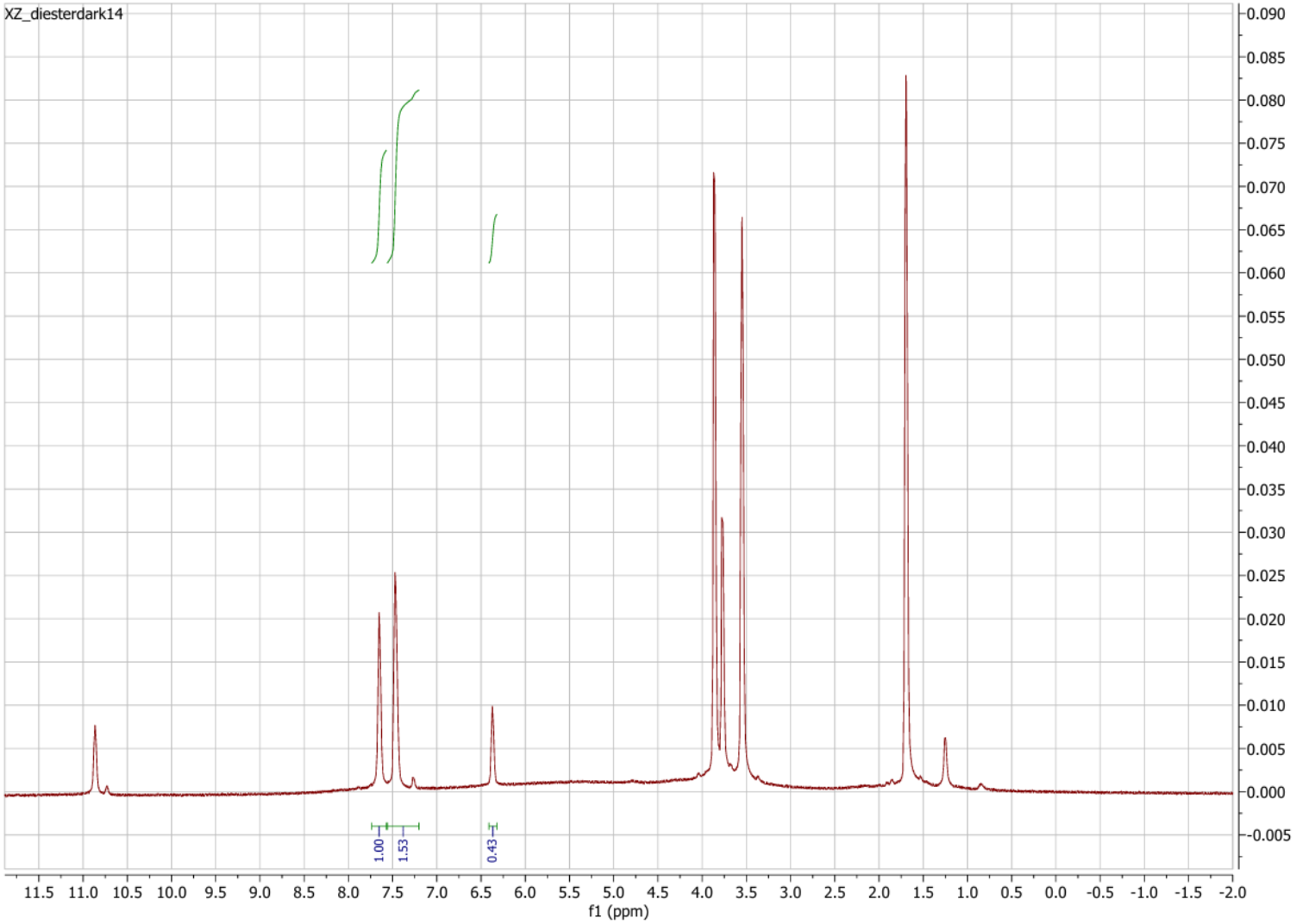

XZ_diesterdark7
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.56
0.51
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)

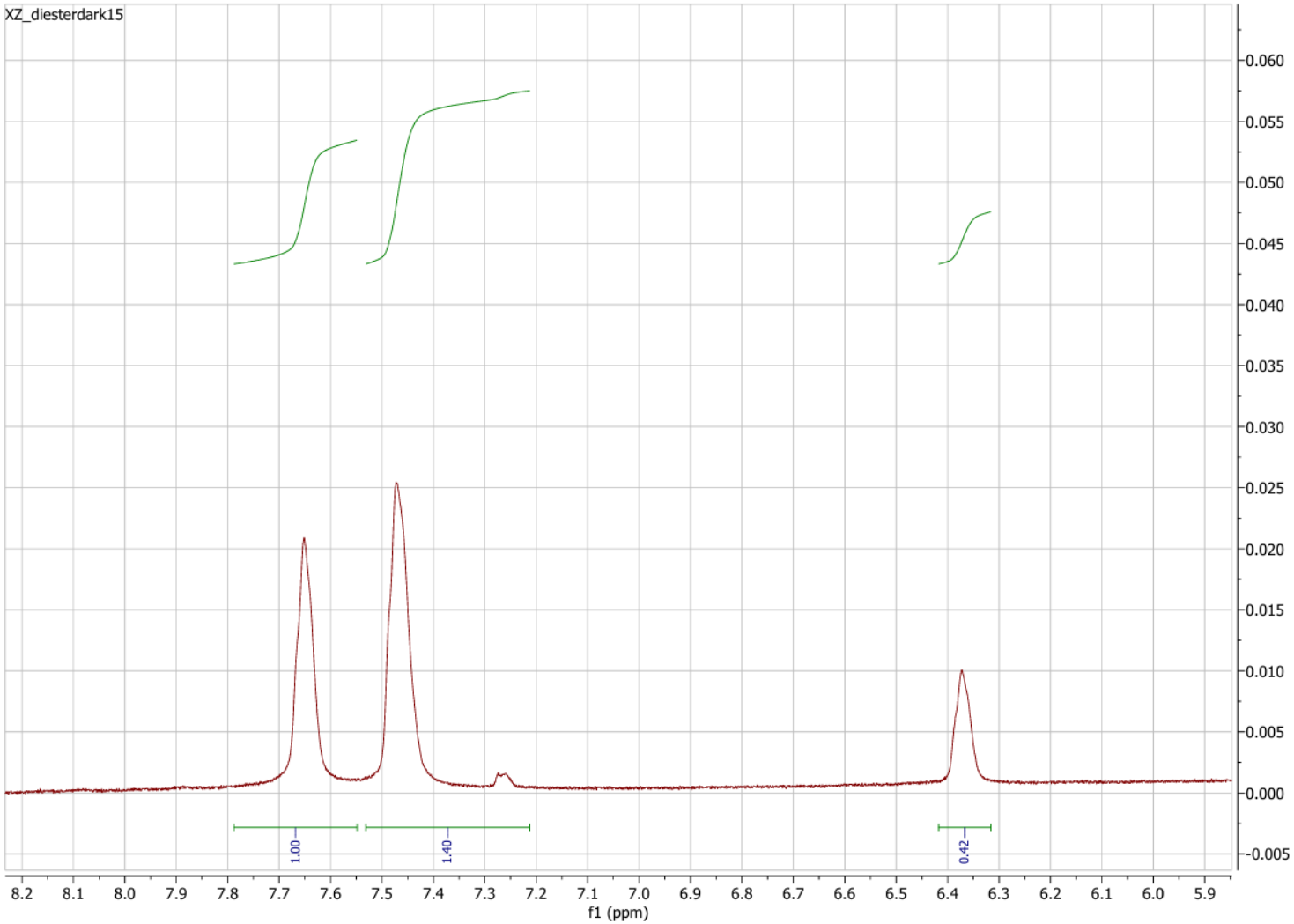

XZ_diesterdark8
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.53
0.48
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)

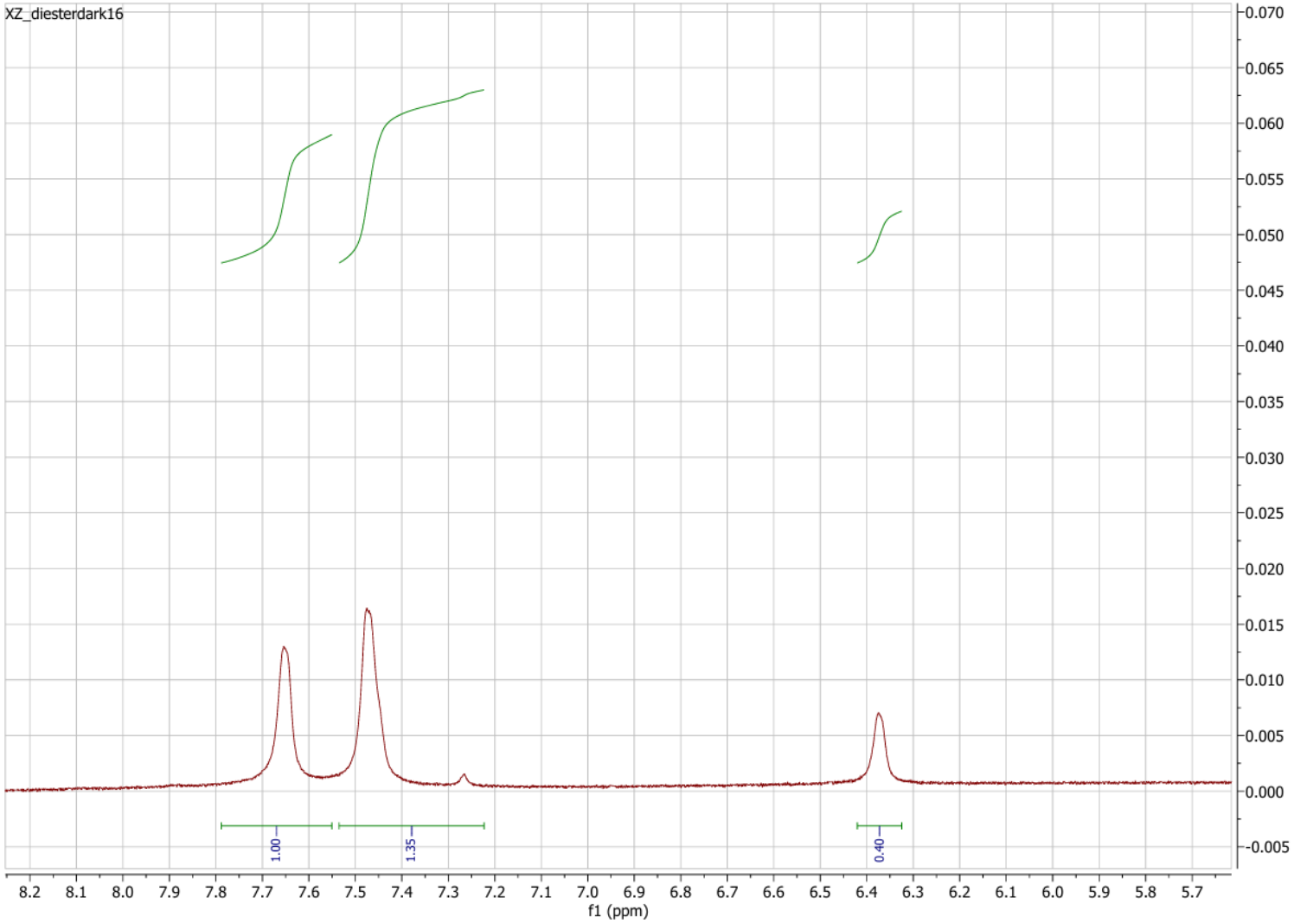

XZ_diesterdark9
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.54
0.49
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9
f1 (ppm)


XZ_diesterdark11
0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.51
0.47
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


XZ_diesterdark13
0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.53
0.45
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
f1 (ppm)


XZ_diesterdark14
1.00
1.53
0.43
f1 (ppm)


XZ_diesterdark15
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.40
0.42
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
f1 (ppm)


XZ_diesterdark16
0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
1.00
1.35
0.40
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7
f1 (ppm)

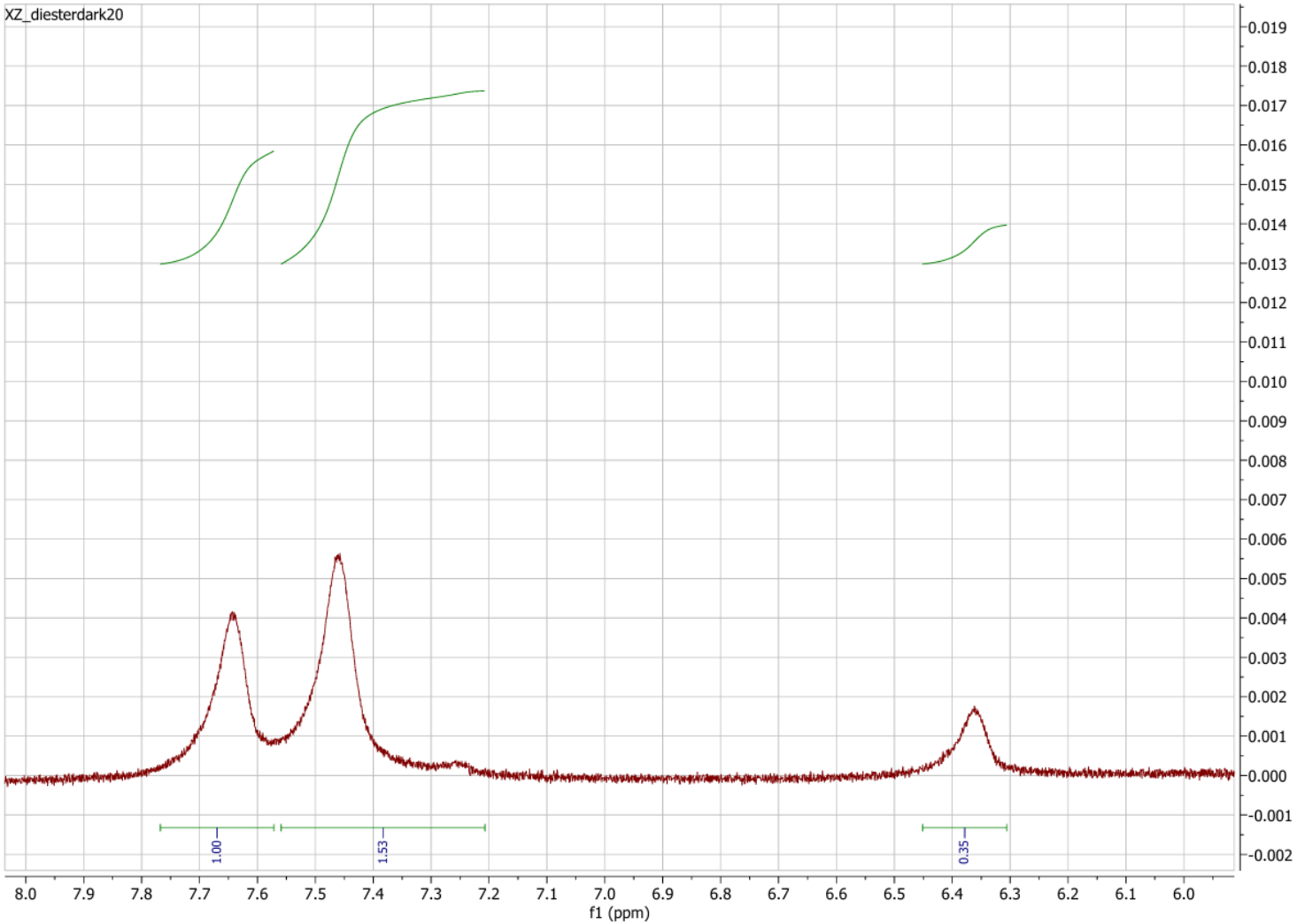

XZ_diesterdark20
0.019
0.018
0.017
0.016
0.015
0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
-0.002
1.00
1.53
0.35
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)

Photo-induced half-life studies of 1a

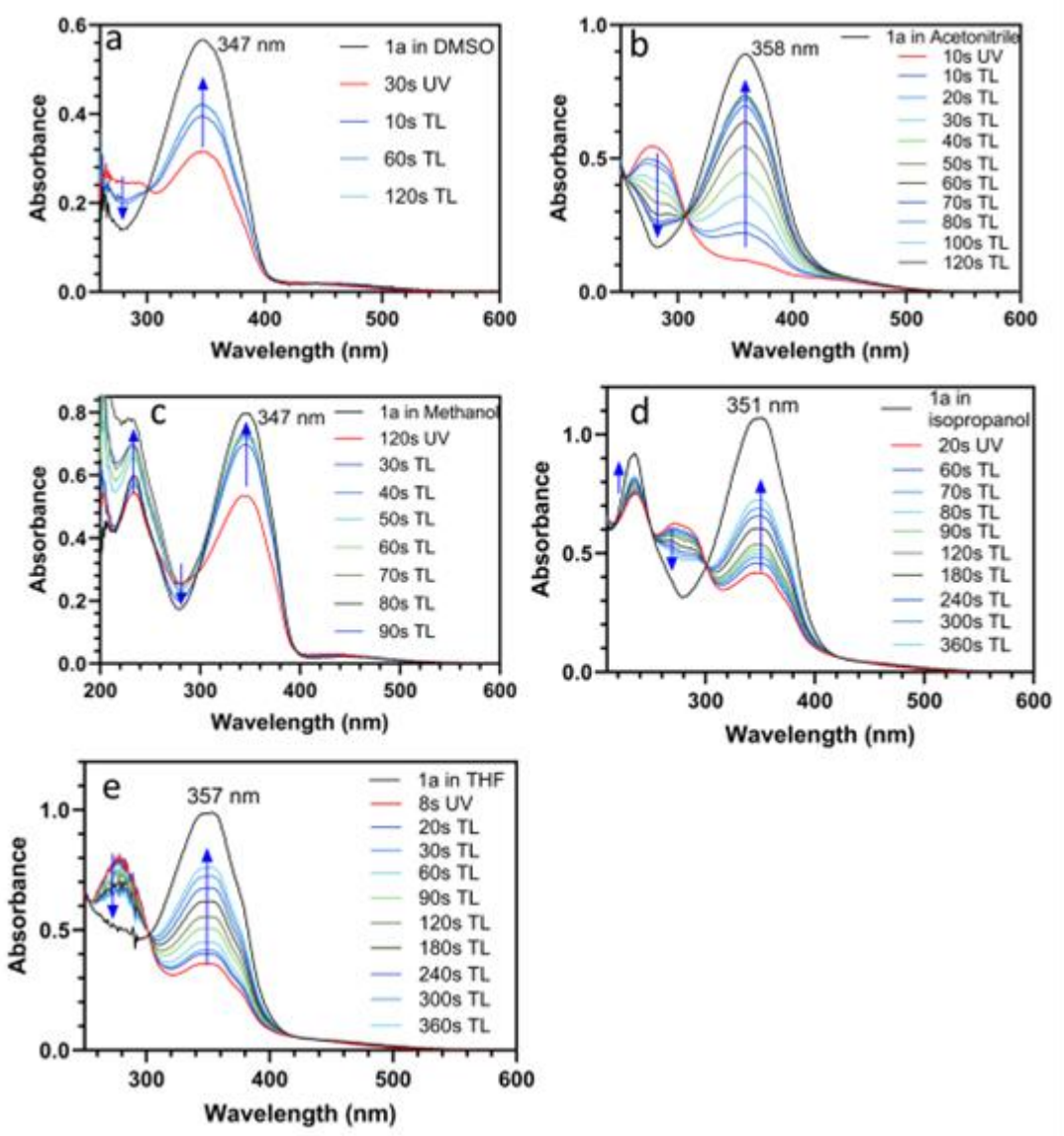


*Figure S14 Time-resolved UV-vis spectroscopy showing photoisomerization of **1a** in various solvents, upon illumination with tungsten lamp for different range of time. The concentrations were adjusted to achieve comparable absorbance values and were recorded as: a) 2.6 x 10^{-5} M DMSO, b) 4 x 10^{-5} M acetonitrile, c) 3.6 x 10^{-5} M methanol, d) 4.9 x 10^{-5} M isopropanol, e) 4.4 x 10^{-5} M THF.*

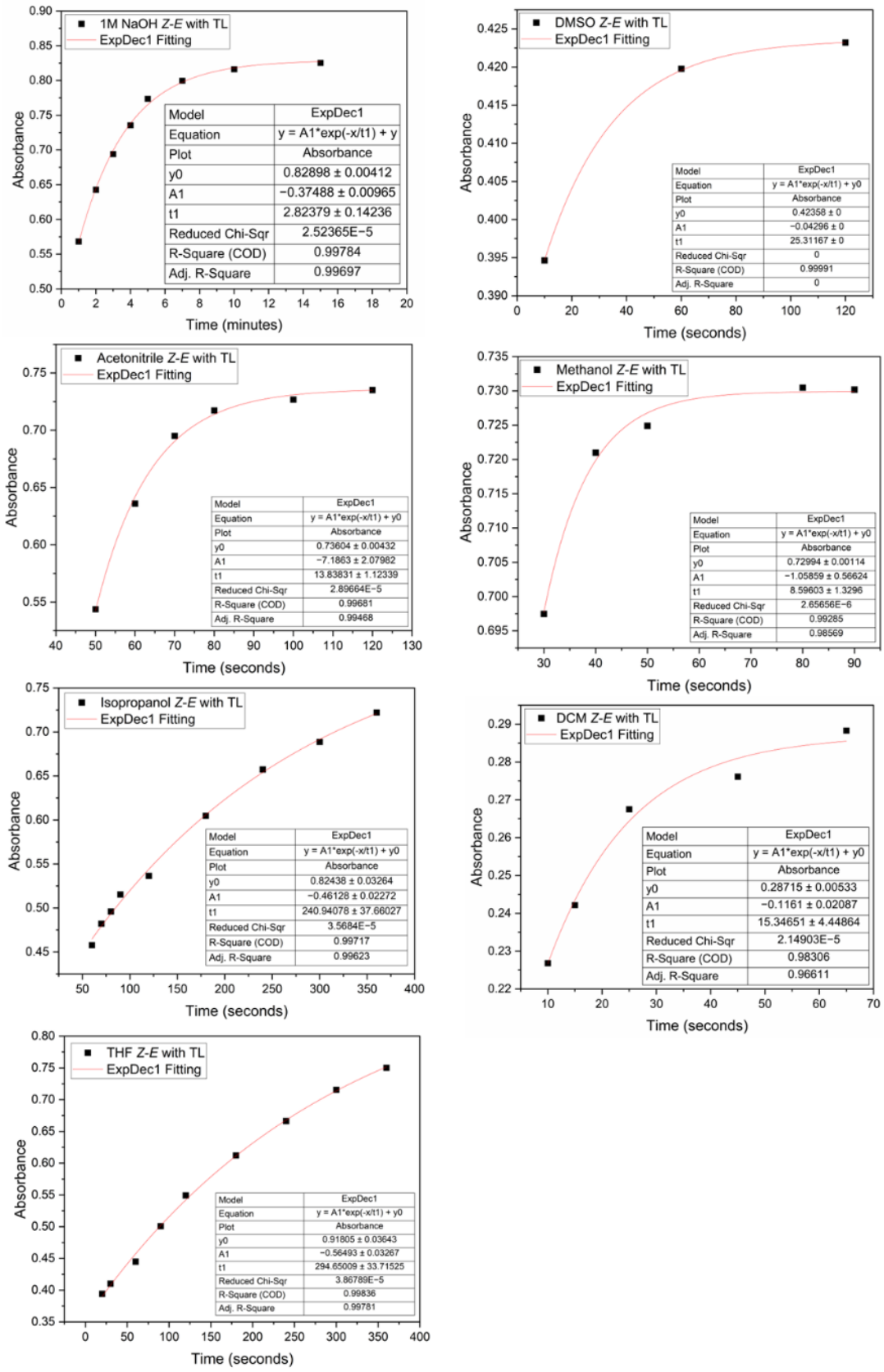


*Figure S15 ExpDec1 function individually fitted to the absorption versus time elapsed upon Z-E irradiation for **1a** in seven different solvents, to determine their exponential time t_1 values.*

Solvatochromic behaviours of molecules 1a-5a

Table S15 Concentrations of solutions used for Solvatochromic studies corresponding to Figure 7.

	DMSO	**Methanol**	**Acetone**	**Isopropanol**	**DCM**	**THF**
1a	2.5 x 10^{-5} M	3.8 x 10^{-5} M	3.7 x 10^{-5} M	6.6 x 10^{-5} M	2.8 x 10^{-5} M	5.6 x 10^{-5} M
2a	4.9 x 10^{-5} M	8.1 x 10^{-5} M	1.6 x 10^{-5} M	4.9 x 10^{-5} M	4.9 x 10^{-5} M	4.8 x 10^{-5} M
3a	3.1 x 10^{-5} M	3.9 x 10^{-5} M	3.5 x 10^{-5} M	3.1 x 10^{-5} M	2.5 x 10^{-5} M	3.8 x 10^{-5} M
4a	5.0 x 10^{-5} M	5.6 x 10^{-5} M	5.5 x 10^{-5} M	3.7 x 10^{-5} M	4.0 x 10^{-5} M	3.9 x 10^{-5} M
5a	9.1 x 10^{-5} M	4.2 x 10^{-5} M	7.2 x 10^{-5} M	2.5 x 10^{-5} M	1.2 x 10^{-5} M	3.3 x 10^{-5} M

Table S16 Solvatochromic parameters taken from literature. [8,9]

Solvent	**π**	**α**	**β**	**Ɛ**
DMSO	1	0	0.76	46.45
Methanol	0.6	0.93	0.62	32.66
Acetone	0.71	0.08	0.48	20.56
isopropanol	0.48	0.76	0.95	18.3
DCM	0.73	0.13	0.1	8.93
THF	0.58	0	0.55	7.4

Table S17 Regression fitting to solvatochromic characteristics by employing KAT equation.

Molecule	V_0 (10^3 cm^{-1})	s (10^3 cm^{-1})	a (10^3 cm^{-1})	b (10^3 cm^{-1})	R^2	F statistic
1a	26.588 (±1.438)	0.139 (±1.800)	0.010 (±0.850)	2.399 (±1.000)	0.78	2.36
2a	30.502 (±0.774)	-2.526 (±0.969)	-0.023 (±0.457)	-1.916 (±0.538)	0.92	7.35
3a	27.899 (±5.690)	-9.072 (±7.123)	-3.751 (±3.362)	-0.620 (±3.959)	0.48	0.62
4a	21.128 (±0.788)	-0.817 (±0.986)	-0.393 (±0.465)	0.037 (±0.548)	0.32	0.31
5a	17.072 (±1.446)	2.557 (±1.811)	0.345 (±0.855)	0.387 (±1.006)	0.55	0.80

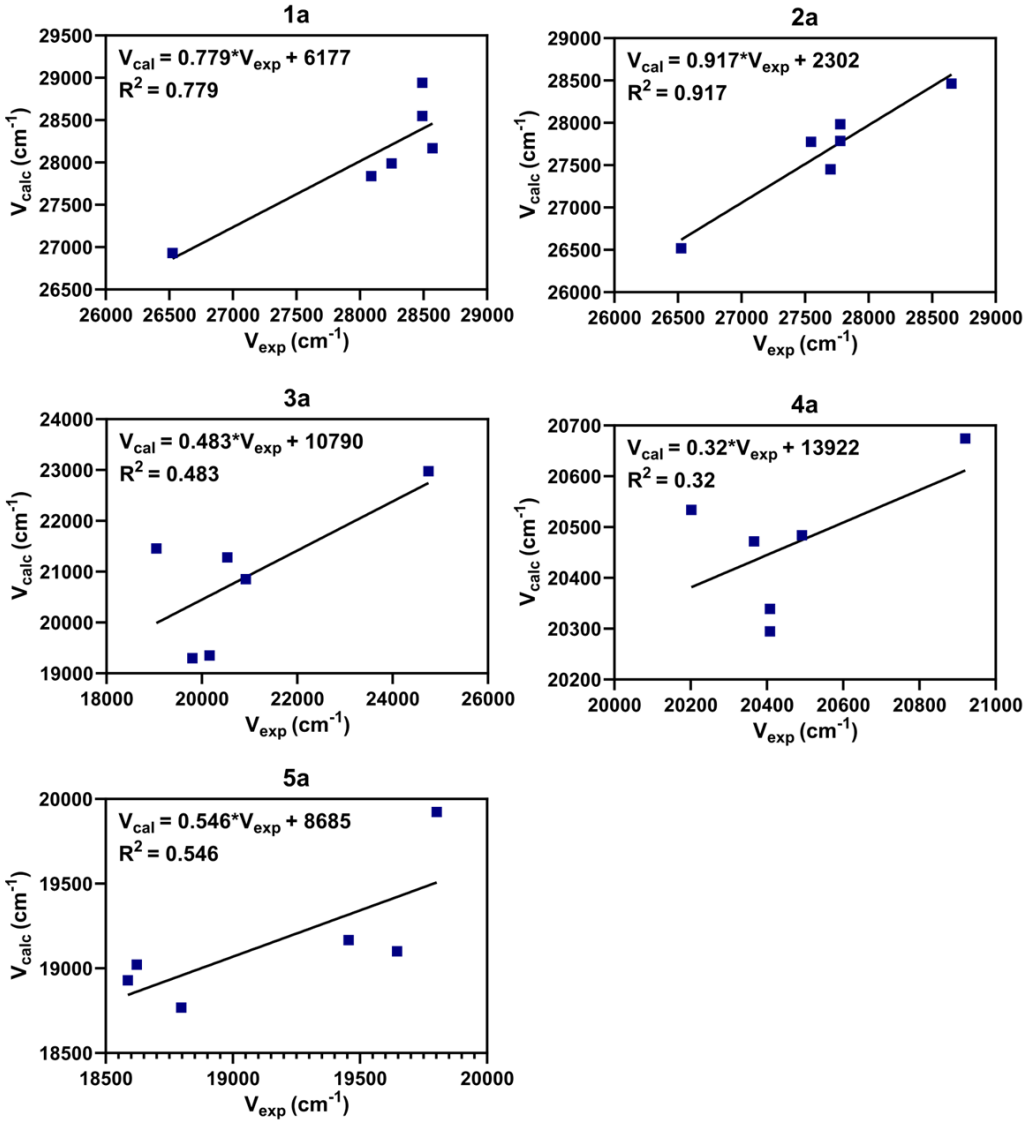


Figure S16 V_{calc} determined using KAT equation, plotted against observed values V_{exp}, for all 5 molecules.

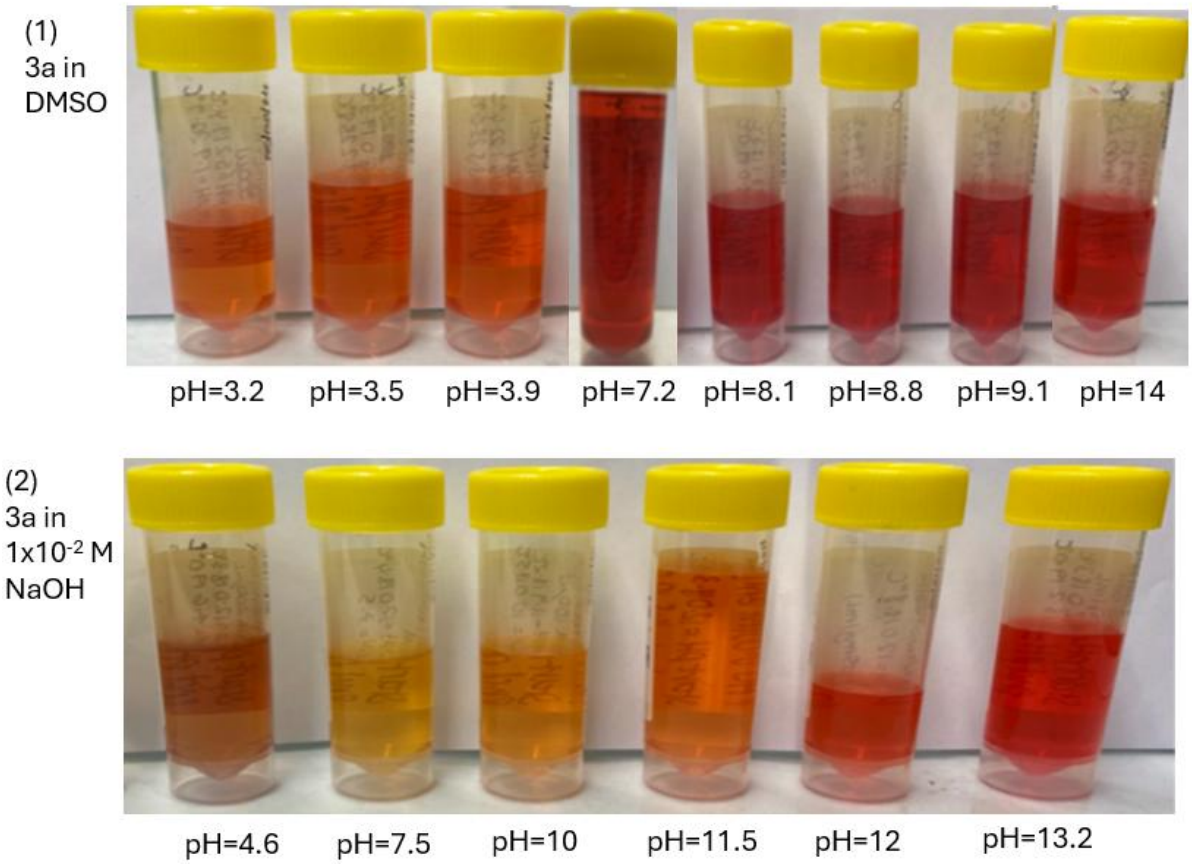


*Figure S17 Photos showing azo-hydrazone tautomerism accompanied by solution colour change, for azothiophene **3a** in the DMSO, and NaOH aq. solution.*

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