Supporting Information

Thienopentathiepine: sulfur containing fused heterocycle for conjugated systems and their electrochemical polymerization

Sashi Debnath, Anjan Bedi, and Sanjio S. Zade*

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246, India.

[*] email: sanjiozade@iiserkol.ac.in

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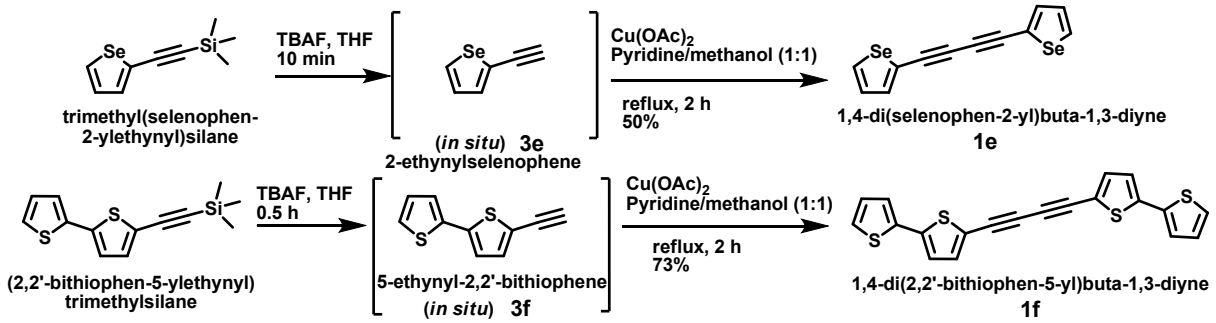


Scheme S1 Synthesis of **1e** and **1f**.

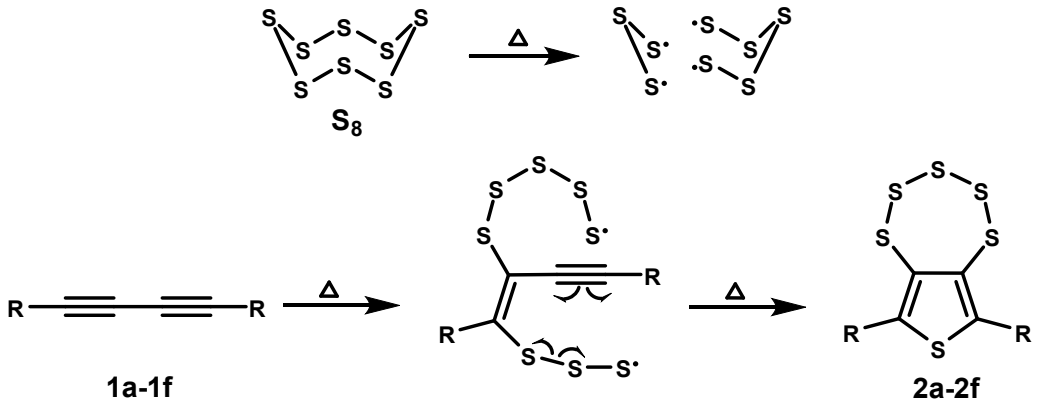
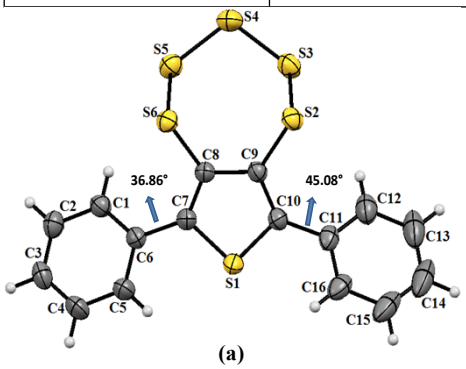


Figure S1 Proposed Mechanism.

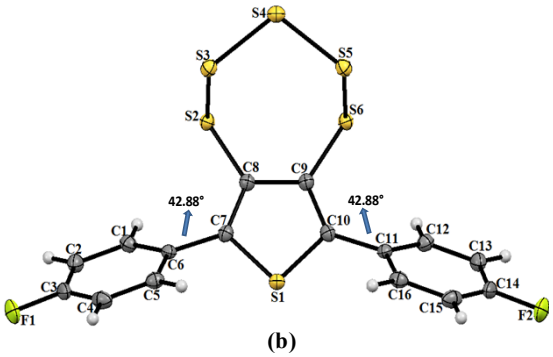
Table S1. Crystallographic data and refinement parameters for **2a**, **2c**, **2d**, and **2e**.

Parameters	**2a**	**2c**	**2d**	**2e**
Empirical formula	C16 H10 S6	C16 H8 F2 S6	C12 H6 S8	C12 H6 S6 Se2
Formula weight	394.60	430.59	406.65	500.45
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	*C2/c*	*Pnma*	$P2_1/c$	*Pbca*
T (K)	102.26(10)	293(2)	293.74(10)	295.16(10)

a (Å)	24.2039(11)	7.7840(4)	8.3161(3)	16.5074(3)
b (C)	6.2548(3)	22.5821(14)	20.2270(7)	8.21747(13)
c (Å)	22.5250(9)	9.6099(4)	9.2199(4)	23.5969(4)
α (°)	90.00	90.00	90	90.00
β (°)	103.733(4)	90.00	92.391(4)	90.00
γ (°)	90.00	90.00	90	90.00
Z	8	8	4	8
V (Å^3)	3312.6(2)	1689.21(16)	1549.53(10)	3200.90(8)
D_x (g/cm^3)	1.582	1.693	1.743	2.077
Radiation	Mo Kα (λ = 0.71073Å)	Mo Kα (λ = 0.71073Å)	Mo Kα (λ = 0.71073Å)	Cu Kα (λ = 1.54184Å)
μ(Mo Kα)/mm^{-1}	0.817	0.825	1.135	12.972
F(0 0 0)	1616.0	872	824.0	1936
Crystal size/mm	0.55× 0.35× 0.23	0.35× 0.31× 0.21	0.5225× 0.175× 0.1289	0.561× 0.315× 0.231
θ range for data collection (°)	2.82-26.37	2.29-27.52	2.4250-26.3390	3.7270-66.2240
Limiting indices	$-18 \le h \le 30$, $-3 \le k \le 7$, $-24 \le l \le 28$	$-10 \le h \le 7$, $-29 \le k \le 20$, $-12 \le l \le 9$	$-10 \le h \le 4$, $-25 \le k \le 8$, $-10 \le l \le 11$	$-19 \le h \le 19$, $-9 \le k \le 8$, $-25 \le l \le 28$
Reflections collected	5198	1654	4953	2623
Data/restraints/parameters	3341/0/199	1533/0/112	3143/0/181	2789/0/181
Unique reflections	3341	1533	3143	2789
R indices I > 2σ(I)	R_1 = 0.0362, wR_2 = 0.0986	R_1 = 0.0303, wR_2 = 0.0721	R_1 = 0.0491, wR_2 = 0.1593	R_1 = 0.0487, wR_2 = 0.1279
R indices (all data)	R_1 = 0.0402, wR_2 = 0.1014	R_1 = 0.0349, wR_2 = 0.0757	R_1 = 0.0558, wR_2 = 0.1730	R_1 = 0.0577, wR_2 = 0.1356
(Δ/σ)max	0.015	0.001	0.001	0.001
(Δ/ρ)max (e Å^{-3})	0.527	0.401	0.827	1.071
CCDC deposition number	1050201	1049965	1050203	1050202



(a)



(b)

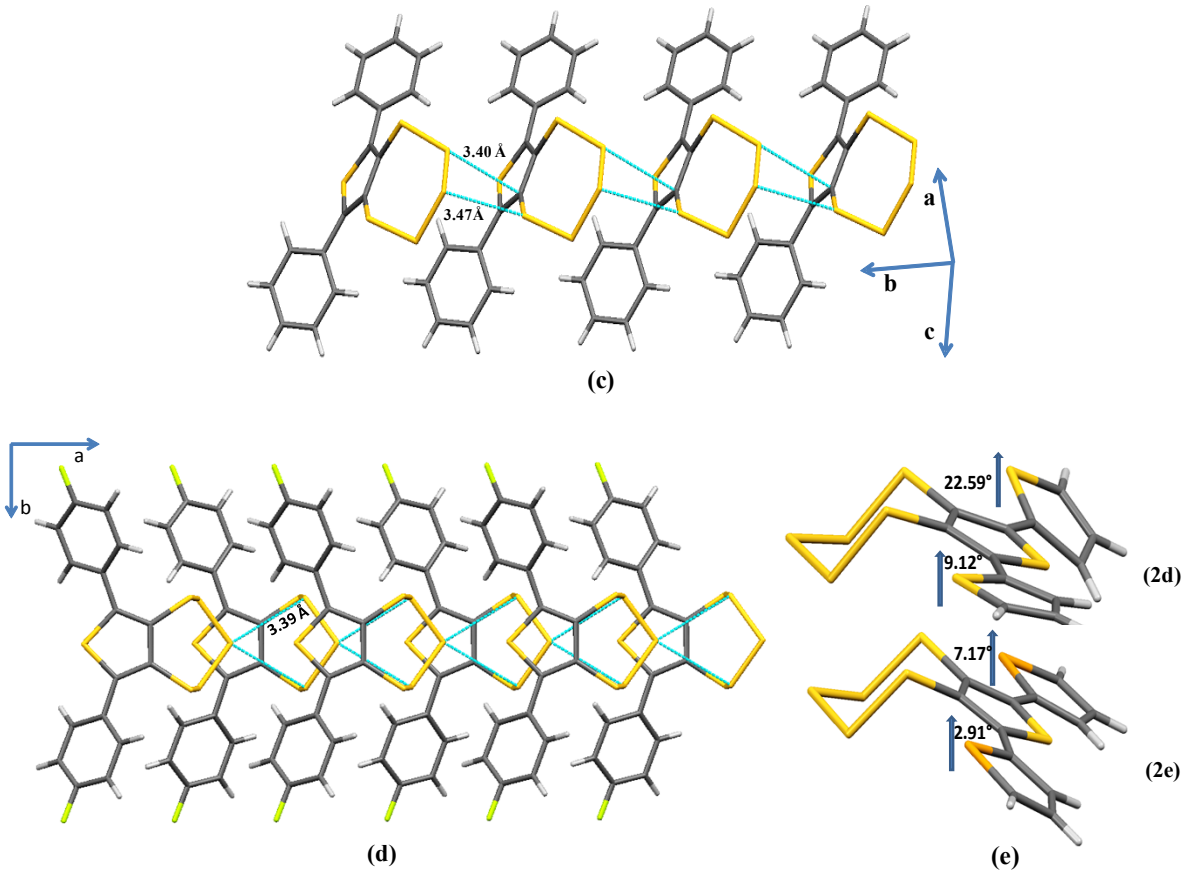


Fig. S2 (a) and (b) ORTEP diagram of **2a**,and **2c**; (c) and (d) packing of **2a** and **2c**, (e) torsional angle in **2d** and **2e**. The ellipsoids are drawn at the 50% probability level in (a).and (b).

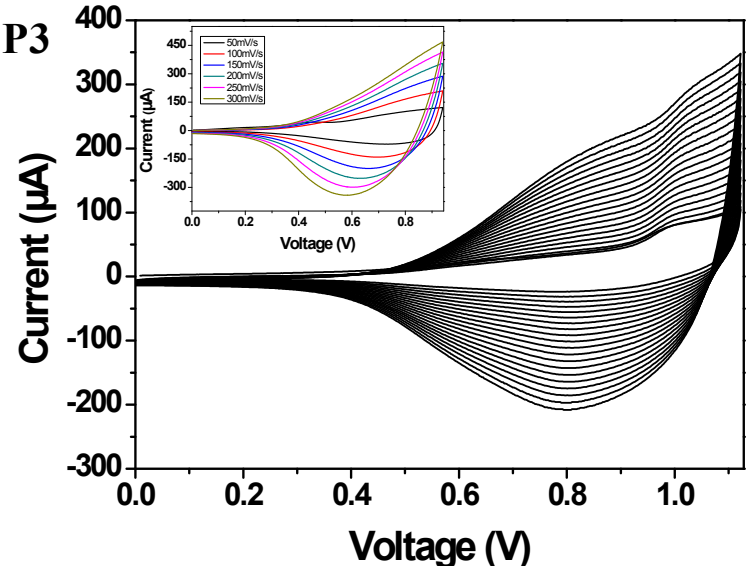


Fig. S3 Multisweep electropolymerizatio **2f** on a Pt electrode in DCM and 0.1 M $TBAPF_6$ at 50 mV s^{-1} vs Ag/AgCl wire. (Inset) CV of **P3** in monomer free DCM and 0.1 M $TBAPF_6$ as a function of scan rate.

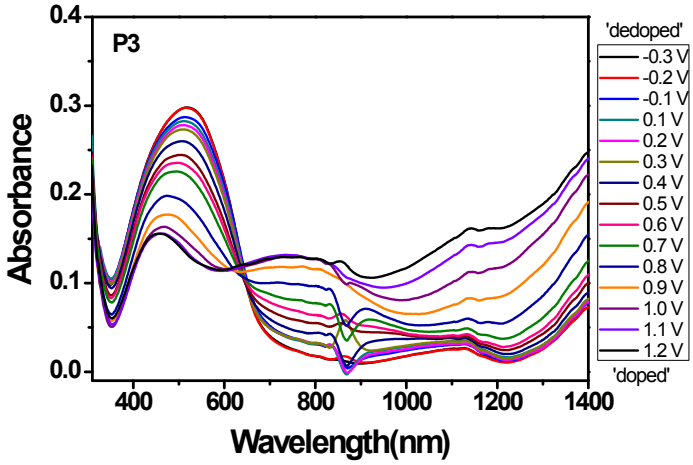


Fig. **S4** Spectroelectrochemistry of **P3** thin films prepared on ITO coated glass as a function of applied potential in DCM.

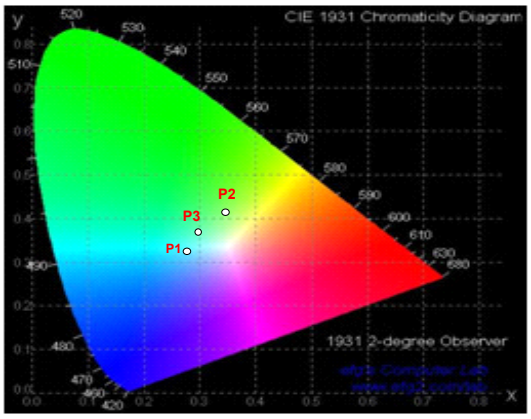


Fig. **S5** CIE color coordinates for **P1**-0.28 (x), 0.33 (y), **P2**-0.35 (x), 0.41 (y) and **P3**-0.30 (x), 0.37 (y) are obtained from absorption spectra of the polymers. The complementary colour of the coordinate points are similar to the colour of the polymers.

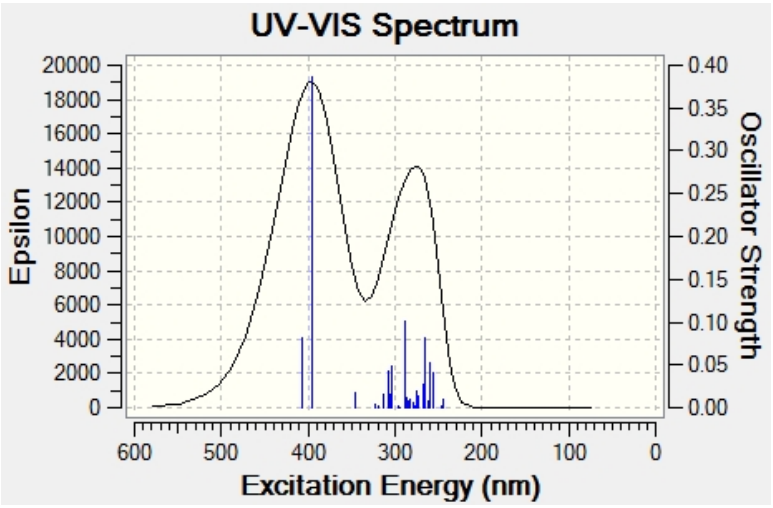


Fig. **S6** TD-DFT (at B3LYP/6-31G(d)) calculated excitation spectra of **2d**.

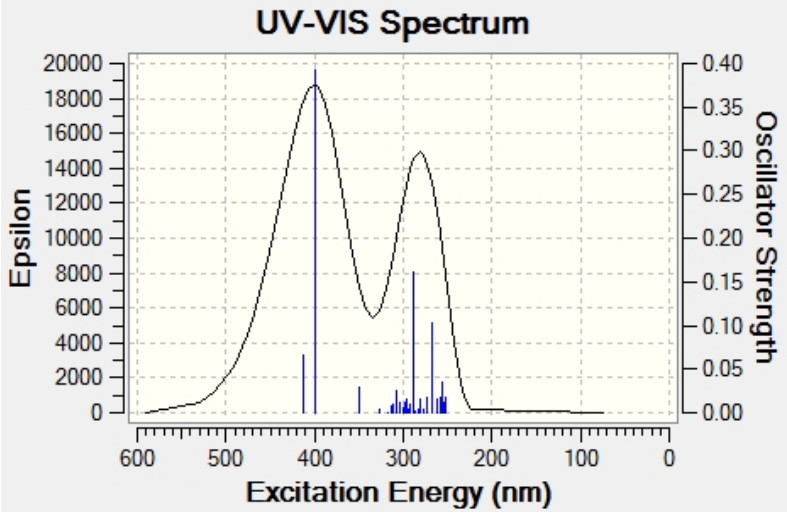


Fig. **S7** TD-DFT (at B3LYP/6-31G(d)) calculated excitation spectra of **2e**.

Table S2. TD-DFT calculated molecular orbitals and corresponding excitations of **2d**.

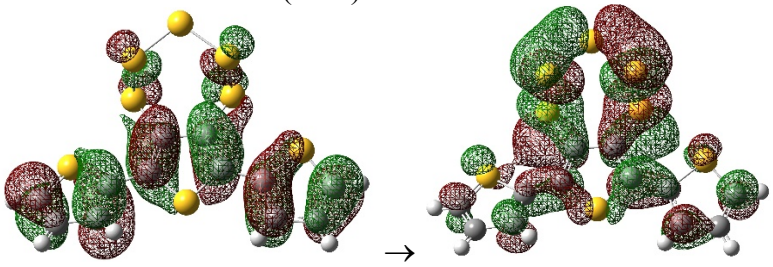
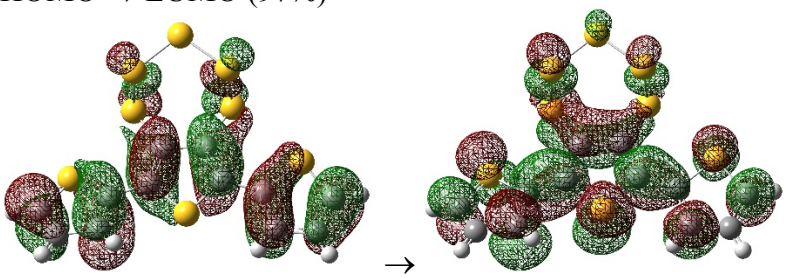
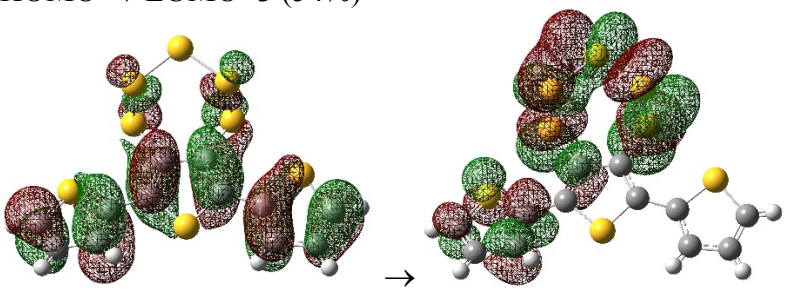
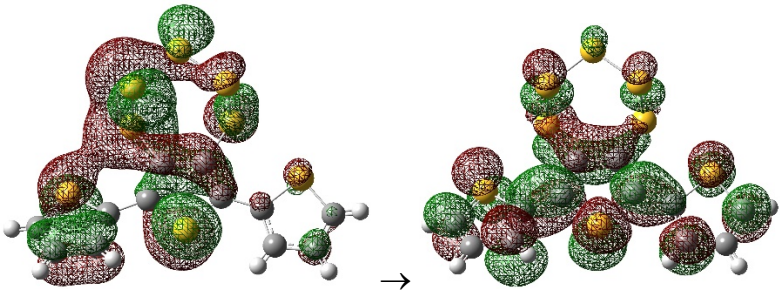
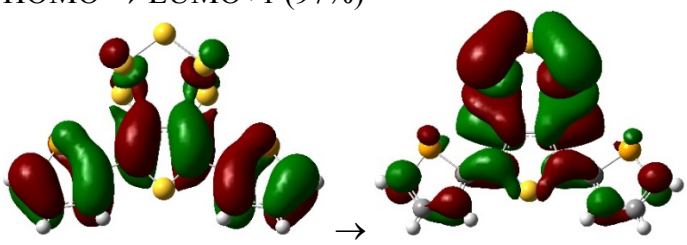
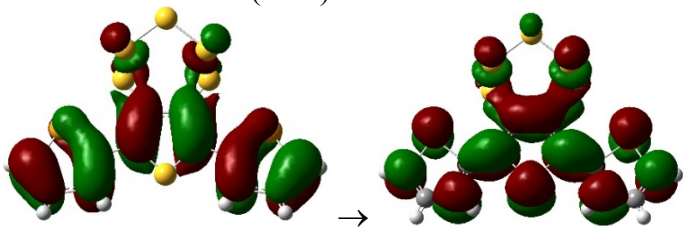
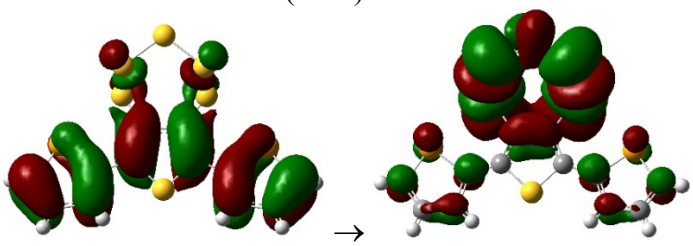
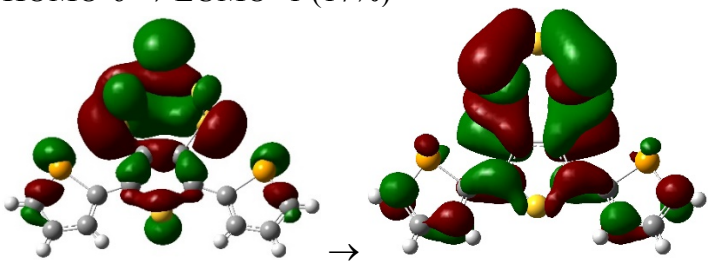
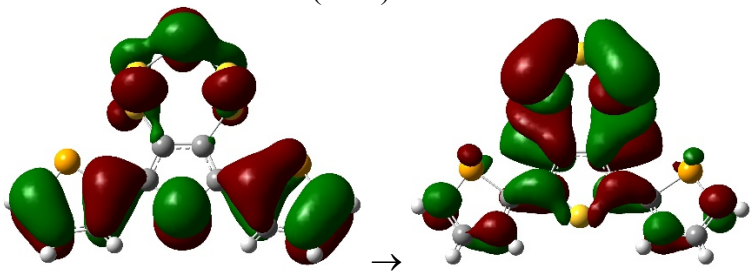
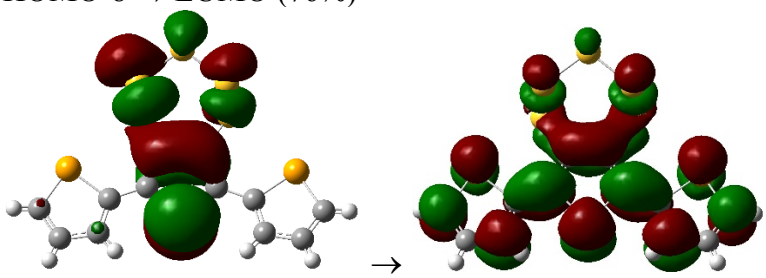
State	Excitation	*f* (oscillator strength)	λ (nm)
S1	HOMO → LUMO+1 (96%) 	0.0815	407
S2	HOMO → LUMO (97%) 	0.3865	395
S12	HOMO → LUMO+3 (54%) 	0.1013	289
S23	HOMO-8 → LUMO (58%) 	0.0808	265

Table S3. TD-DFT calculated molecular orbitals and corresponding excitations of **2e**.

State	Excitation	*f* (oscillator strength)	λ (nm)
S1	HOMO → LUMO+1 (97%) 	0.0663	412
S2	HOMO → LUMO (97%) 	0.3916	400
S16	HOMO → LUMO+3 (43%)  HOMO-6 → LUMO+1 (17%)  HOMO-4 → LUMO+1 (16%) 	0.1618	289
S23	HOMO-8 → LUMO (76%) 	0.1026	268

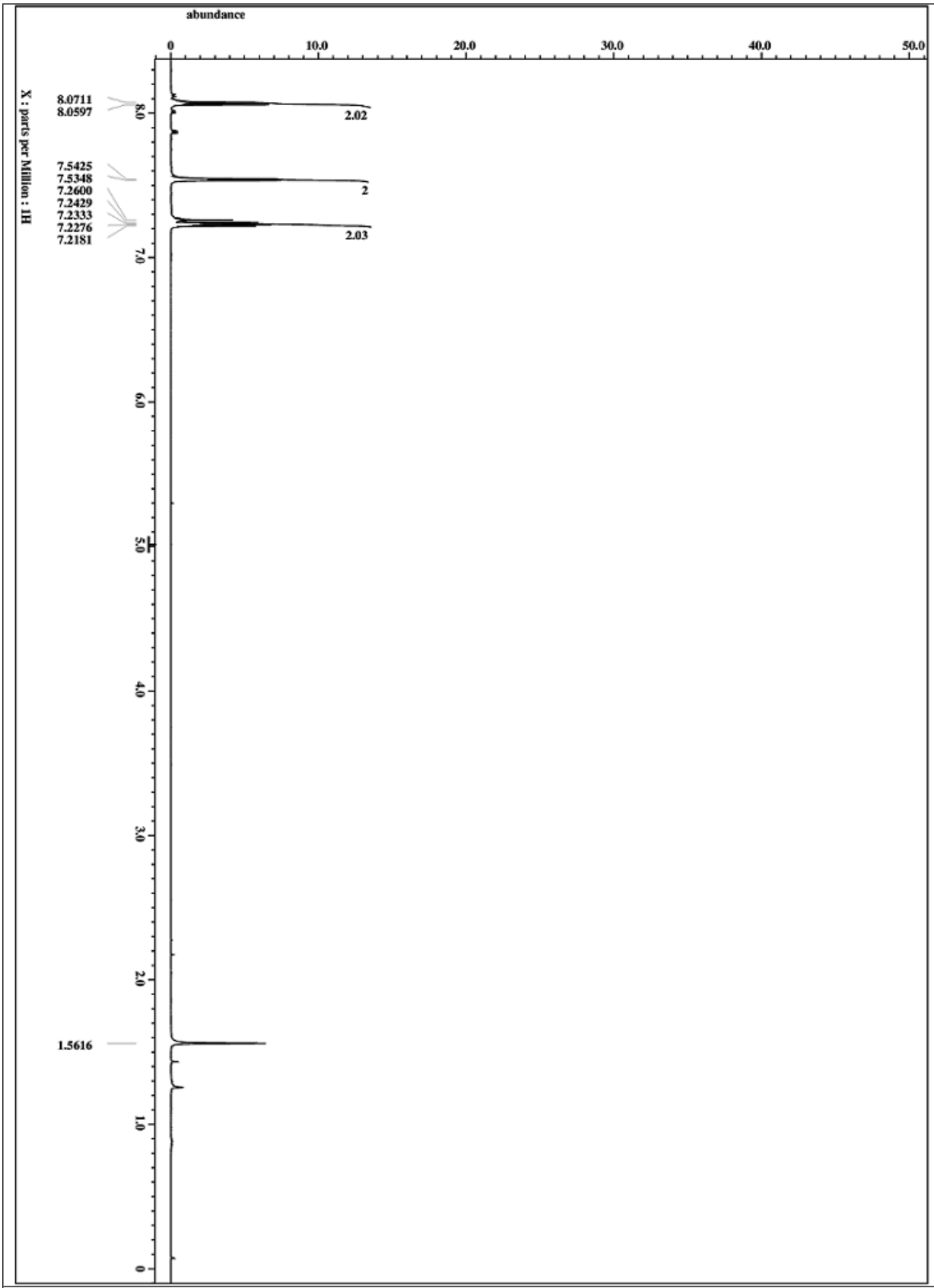


Fig. S8 ^{1}H NMR of compound **1e**.

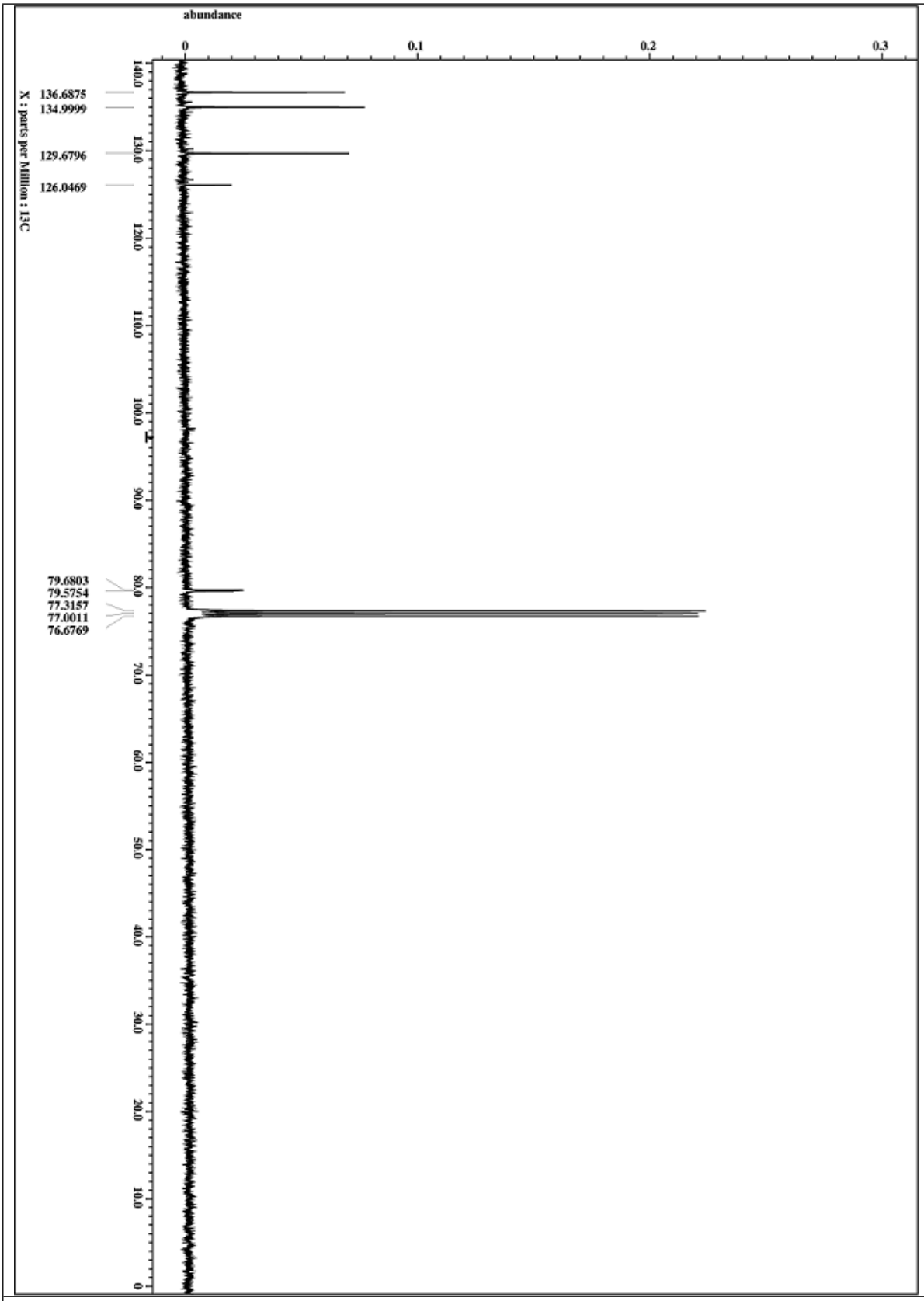


Fig. S9 ^{13}C NMR of compound **1e**.

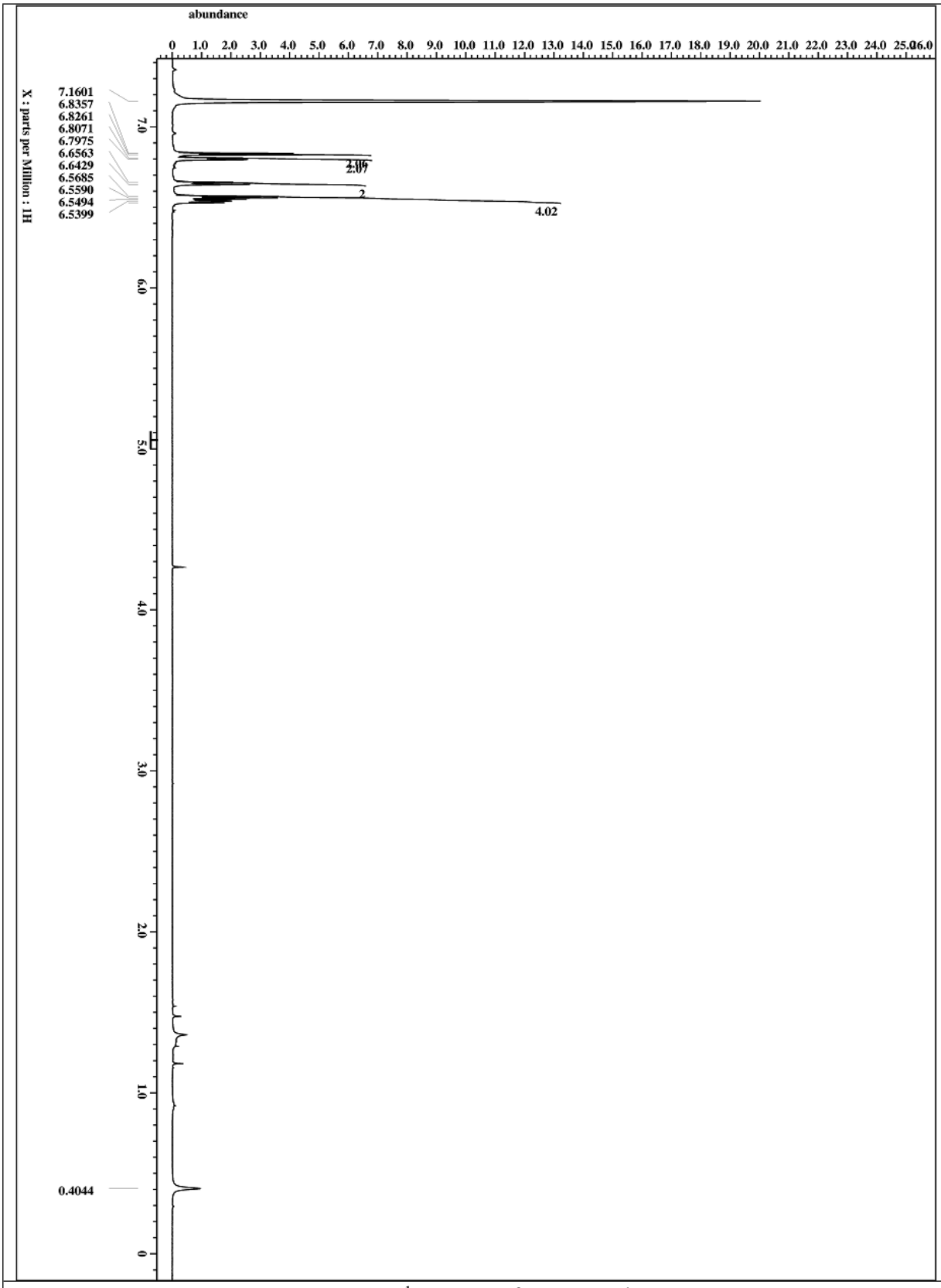


Fig. S10 ^{1}H NMR of compound **1f**.

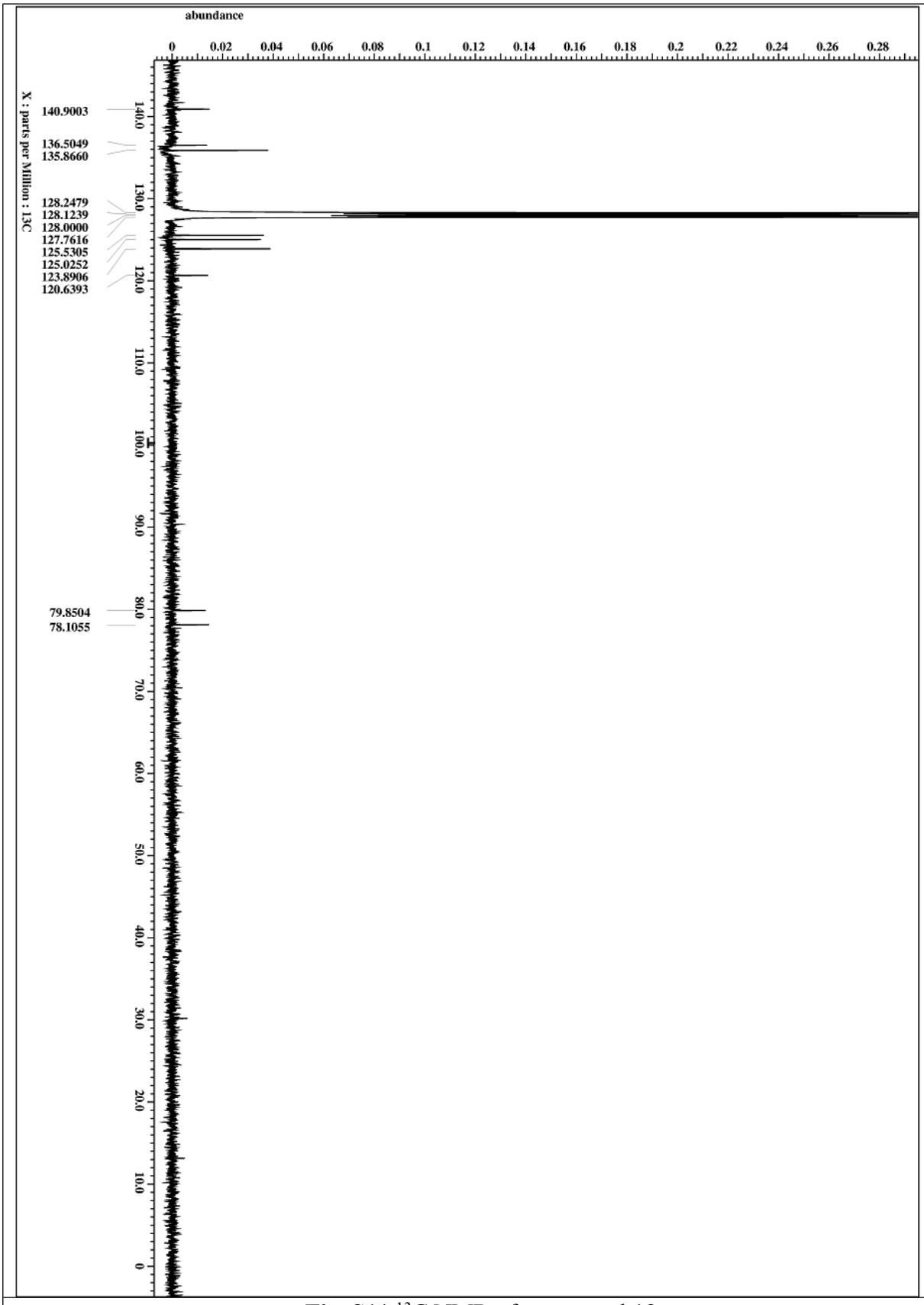


Fig. S11 ^{13}C NMR of compound **1f**.

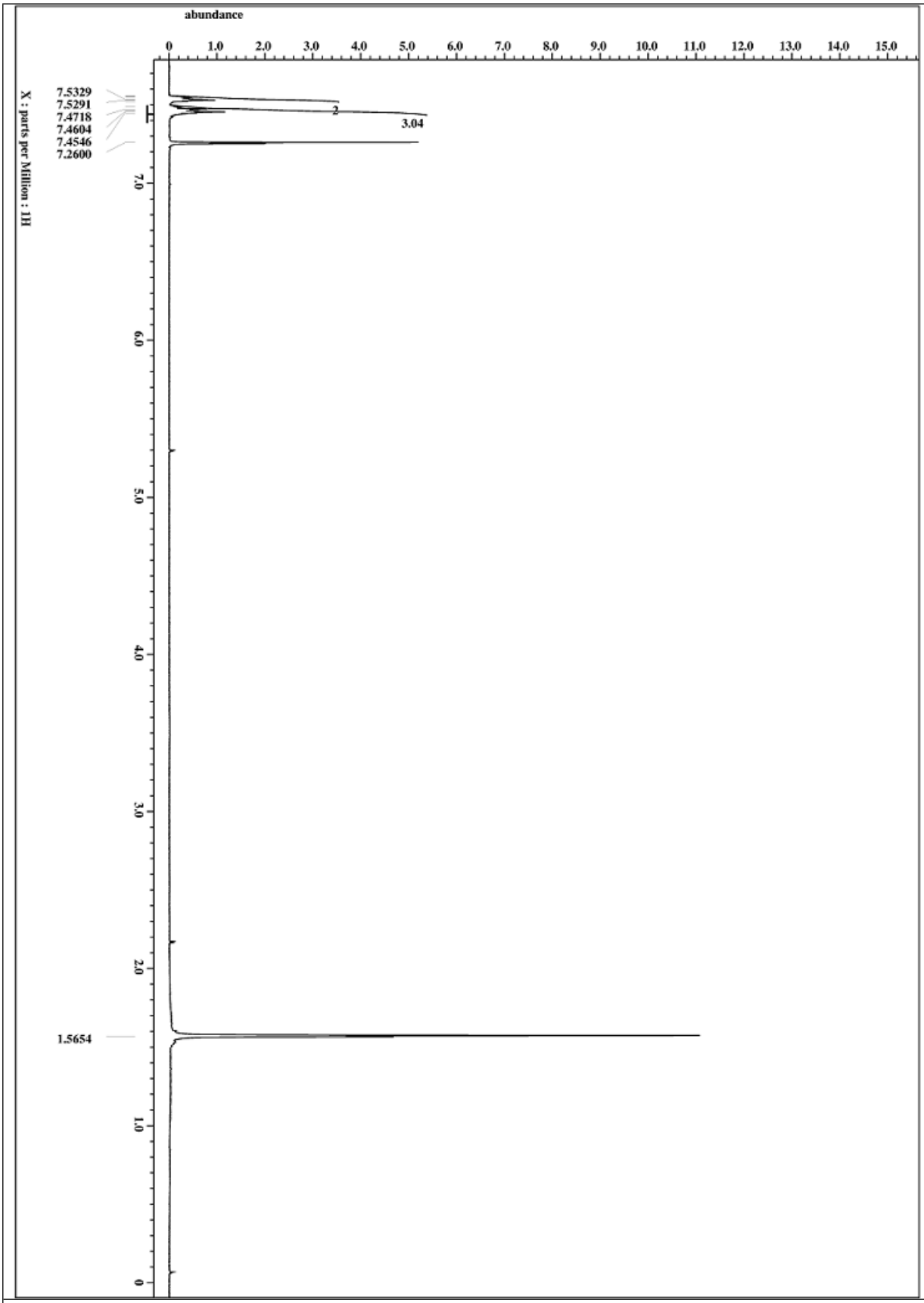


Fig. S12 ^{1}H NMR of compound **2a**.

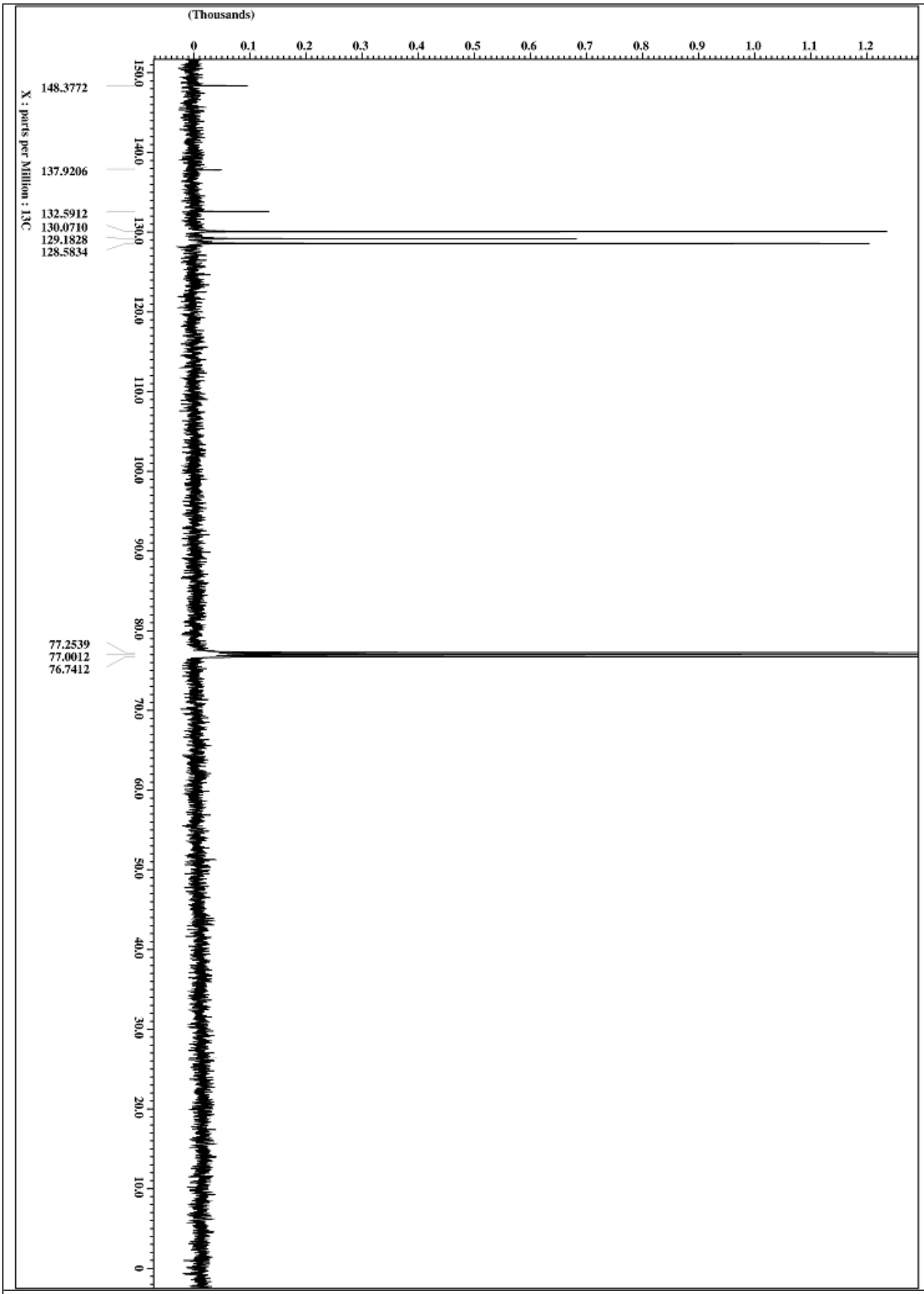


Fig. S13 ^{13}C NMR of compound **2a**.

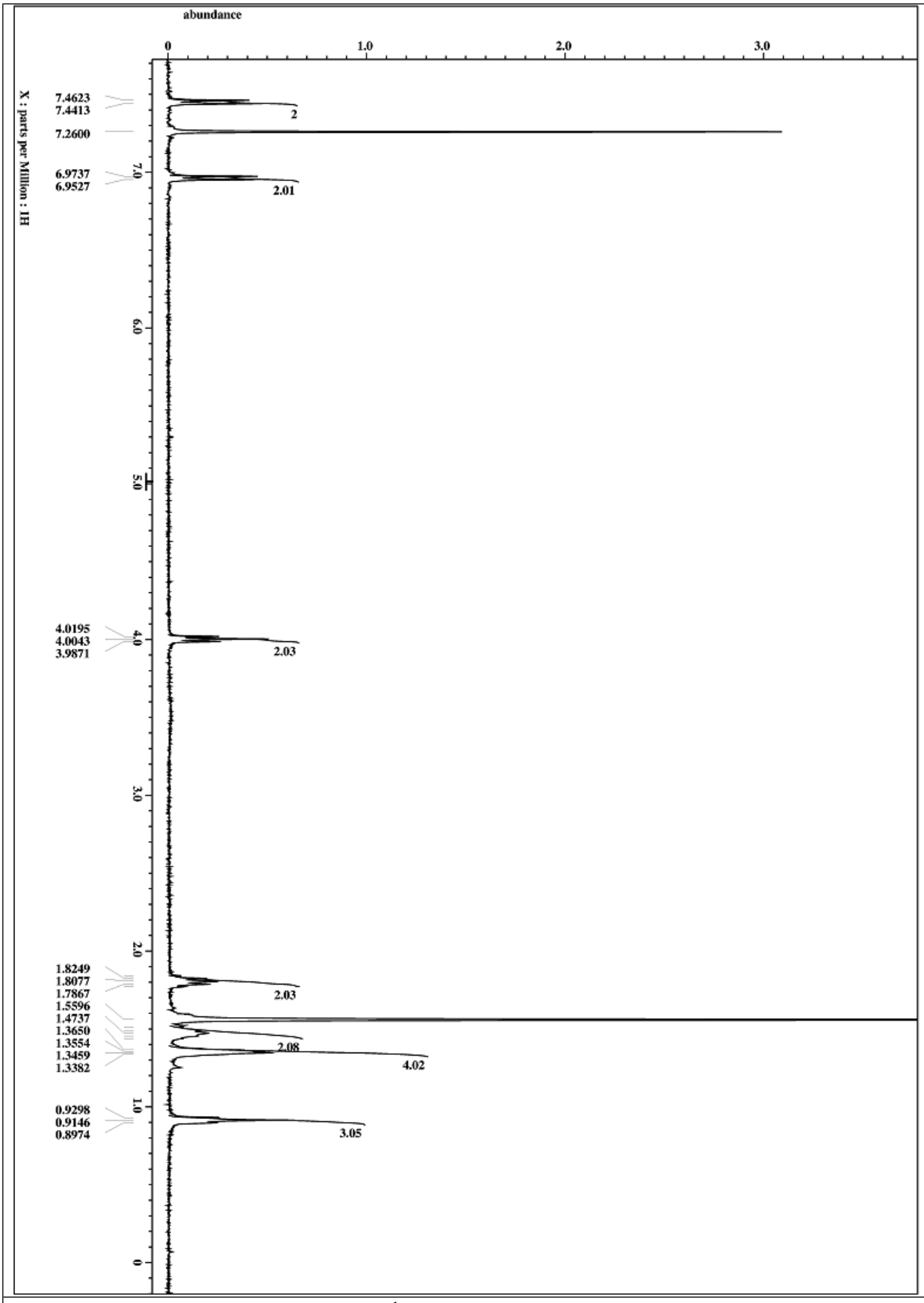


Fig. S14 ^{1}H NMR of compound **2b**.

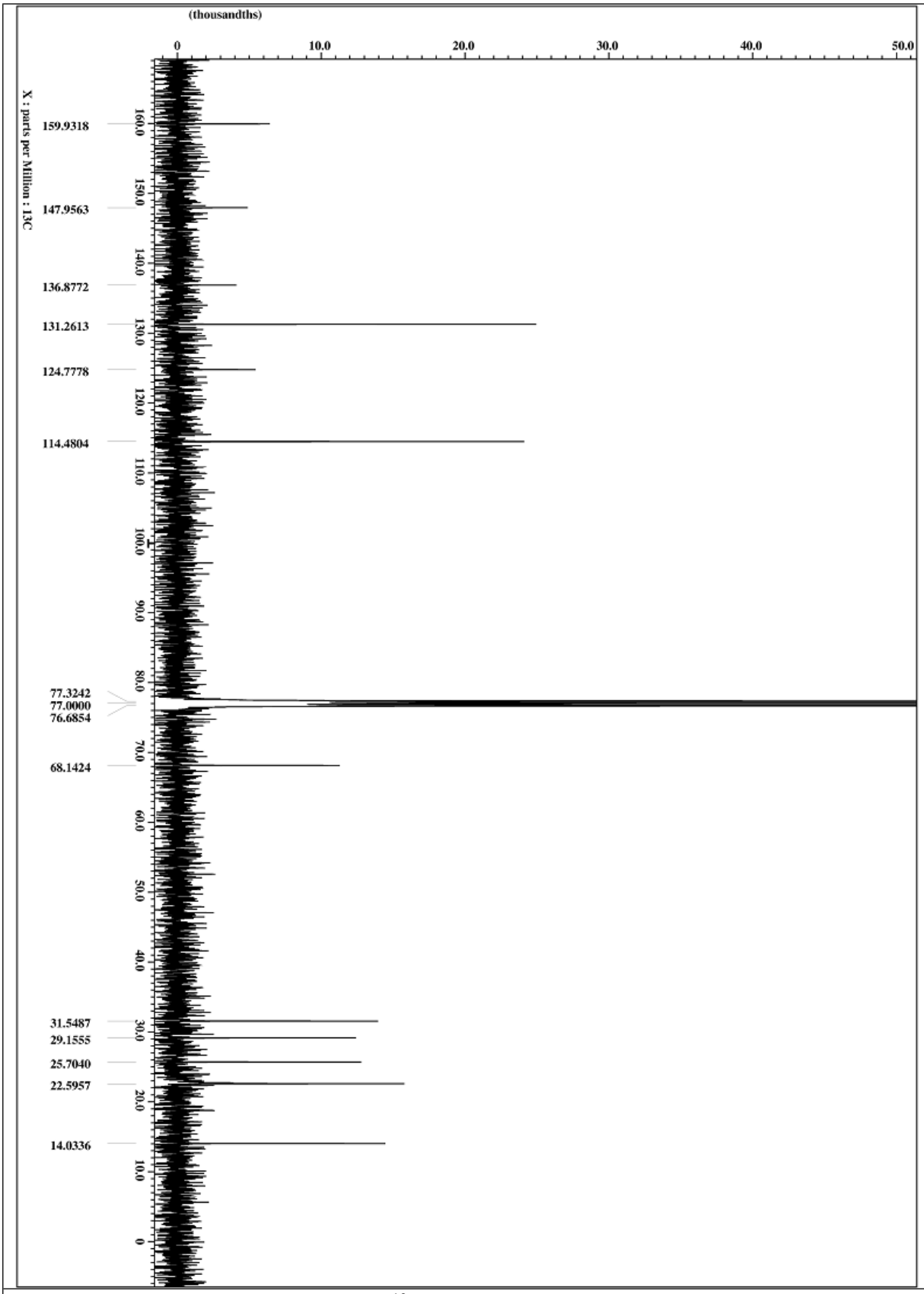


Fig. S15 ^{13}C NMR of compound **2b**.

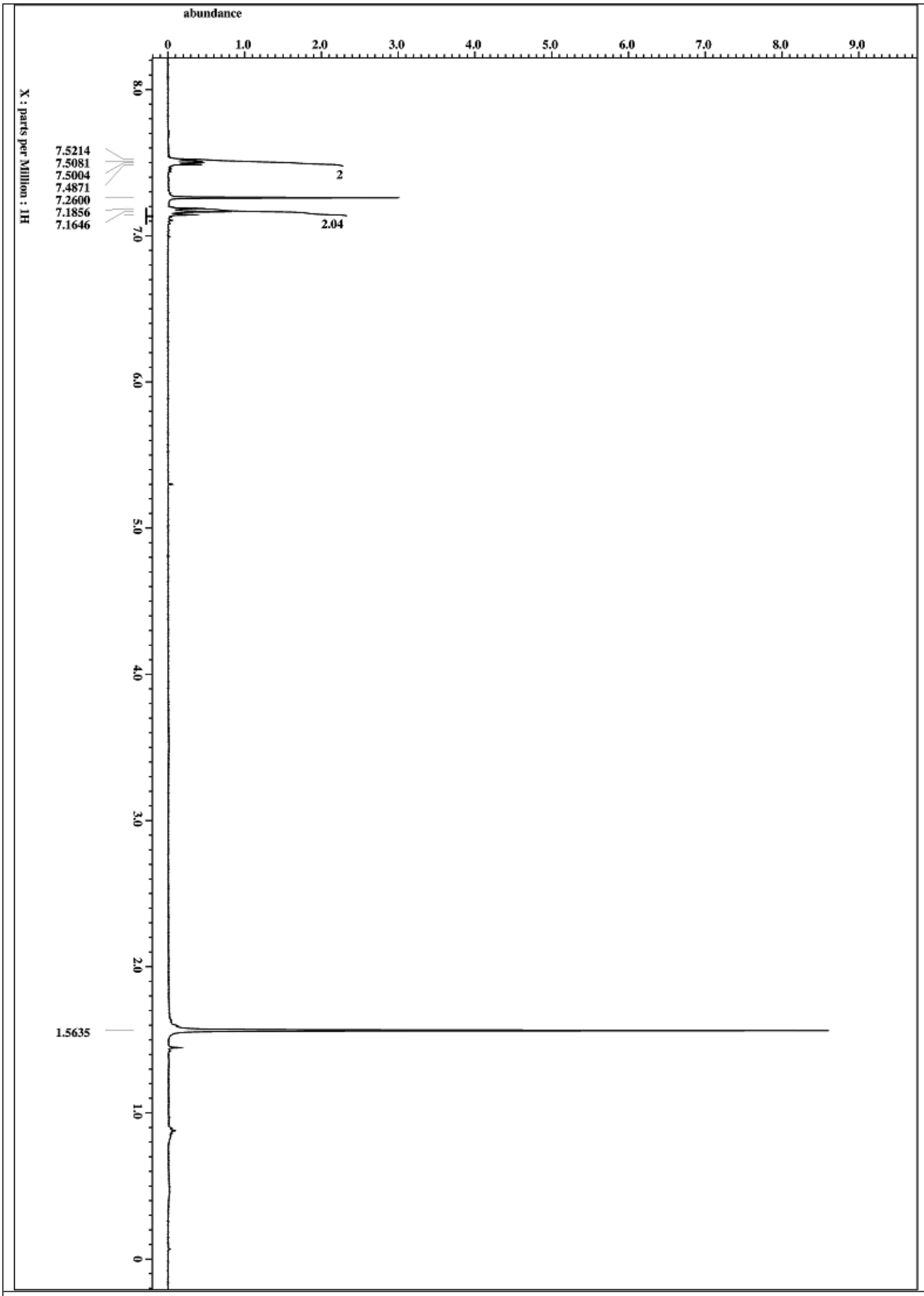


Fig. S16 ^{1}H NMR of compound **2c**.

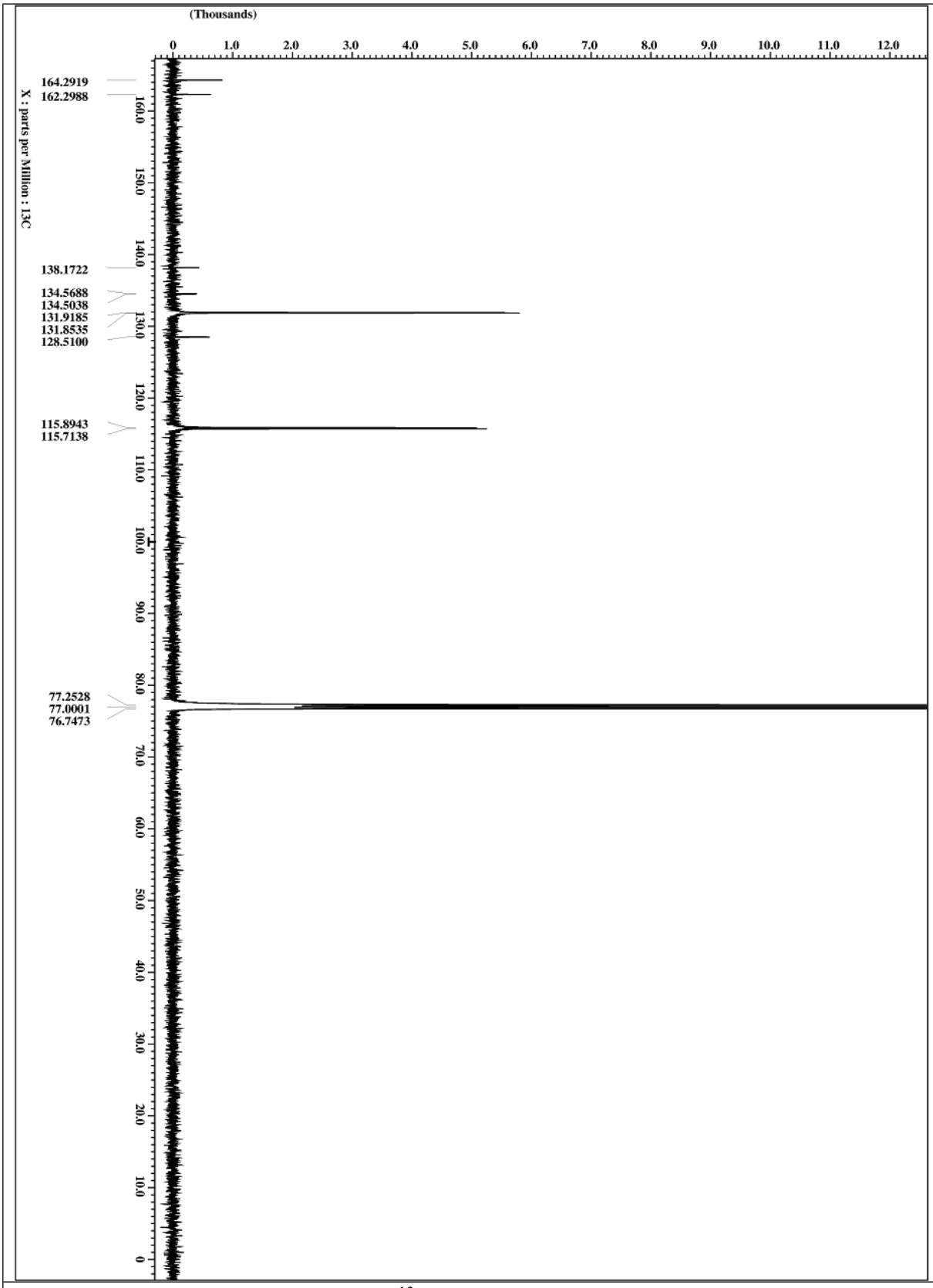


Fig. S17 ^{13}C NMR of compound **2c**.

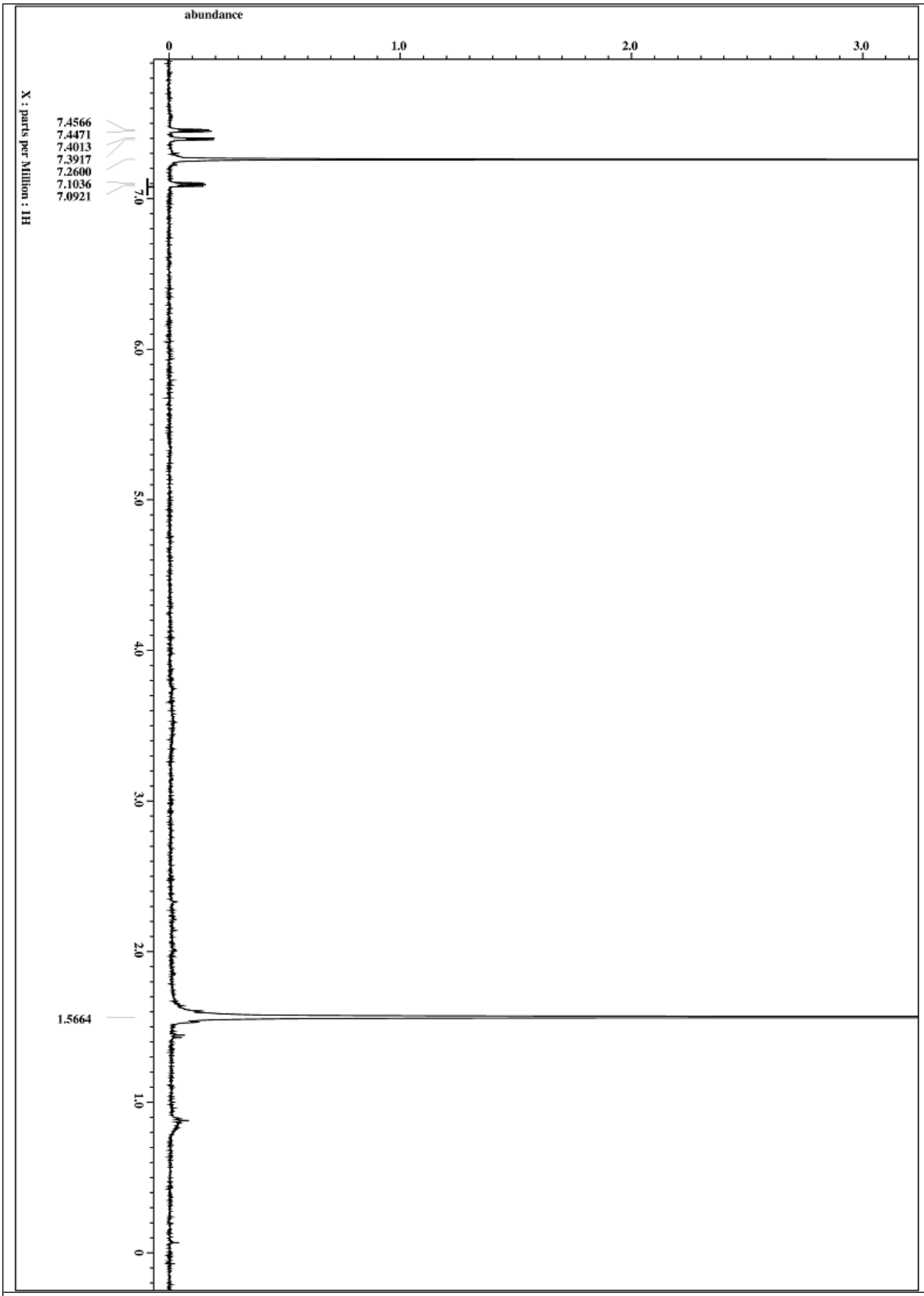


Fig. S18 ^{1}H NMR of compound **2d**.

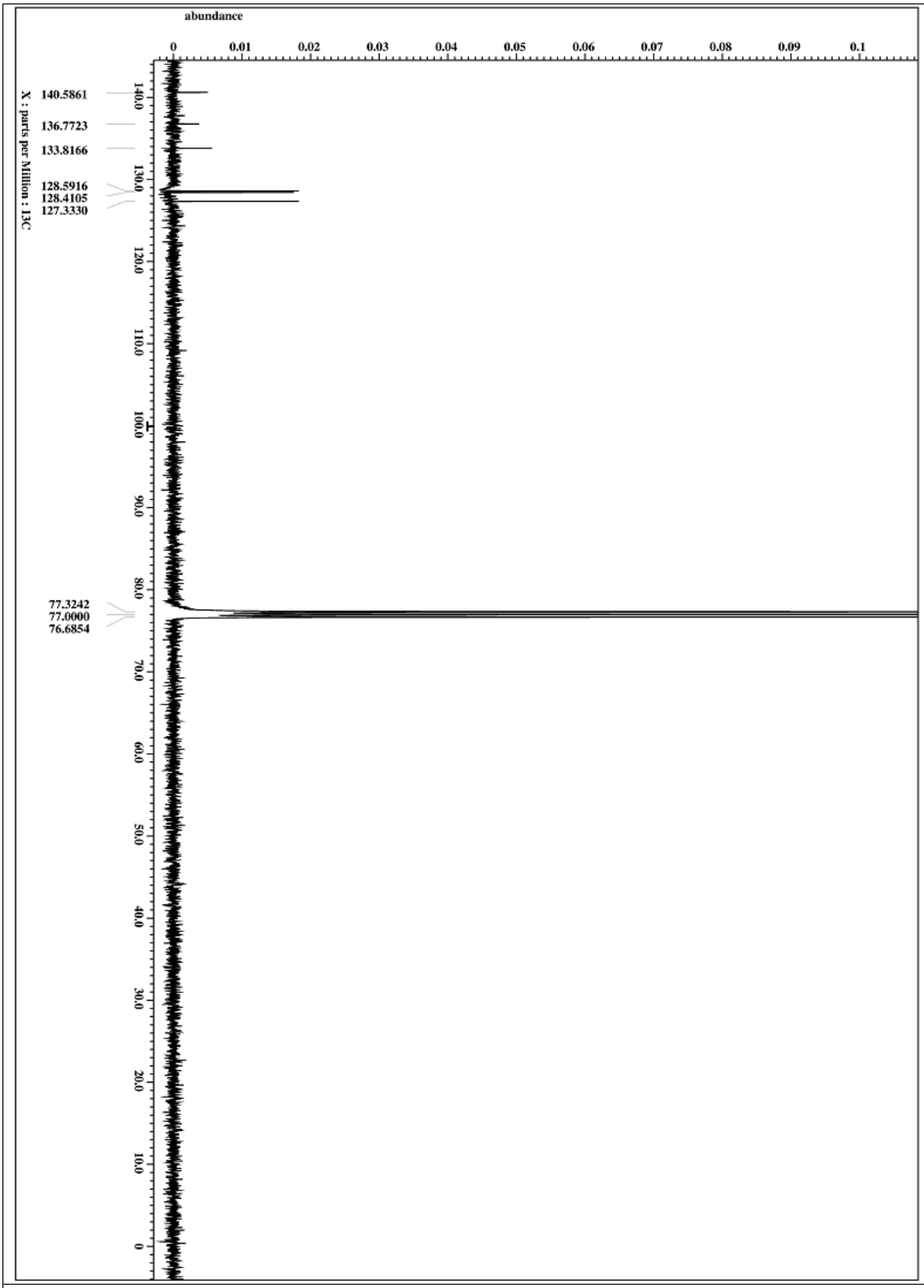


Fig. S19 ^{13}C NMR of compound **2d**.

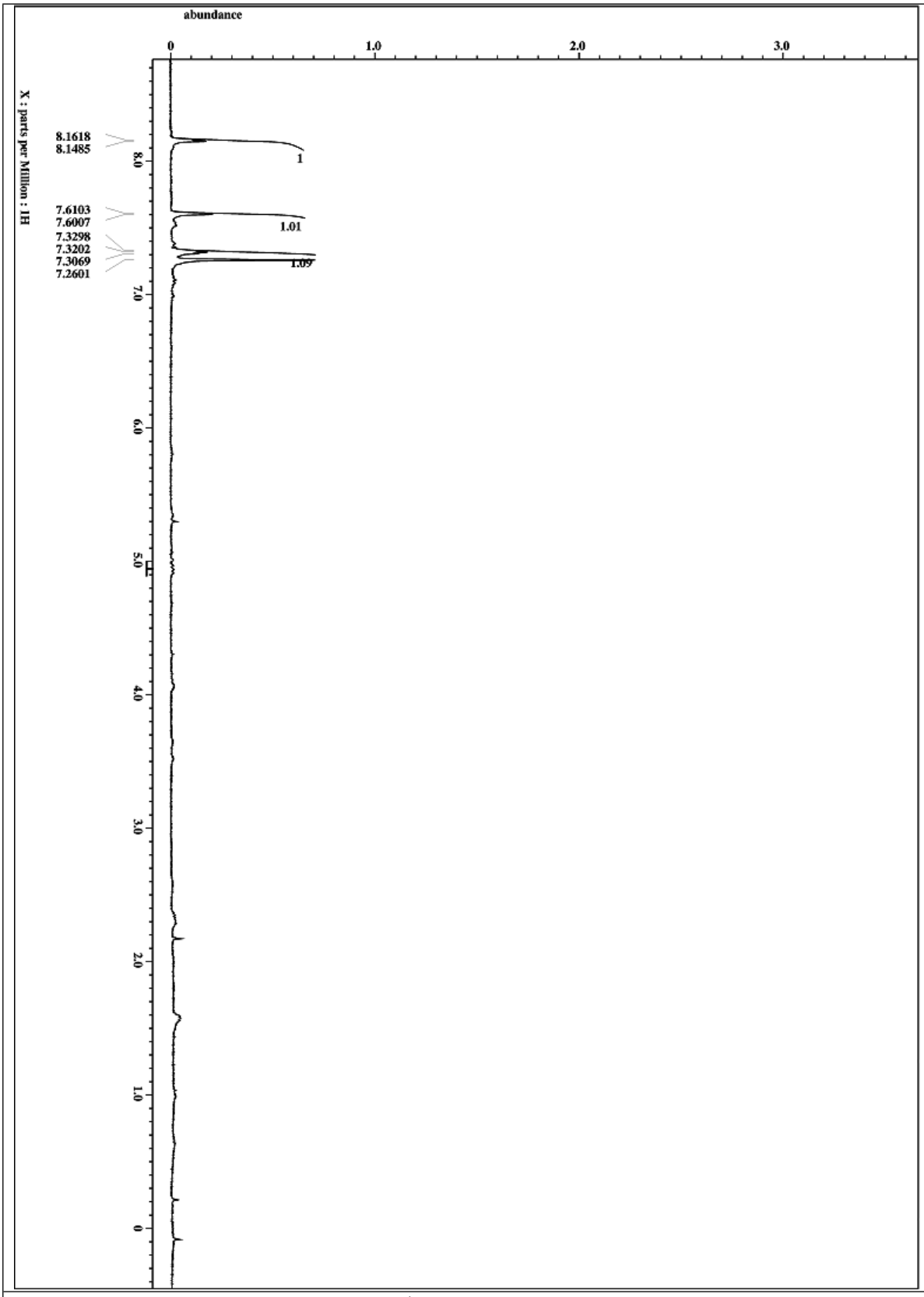


Fig. S20 ^{1}H NMR of compound **2e**.

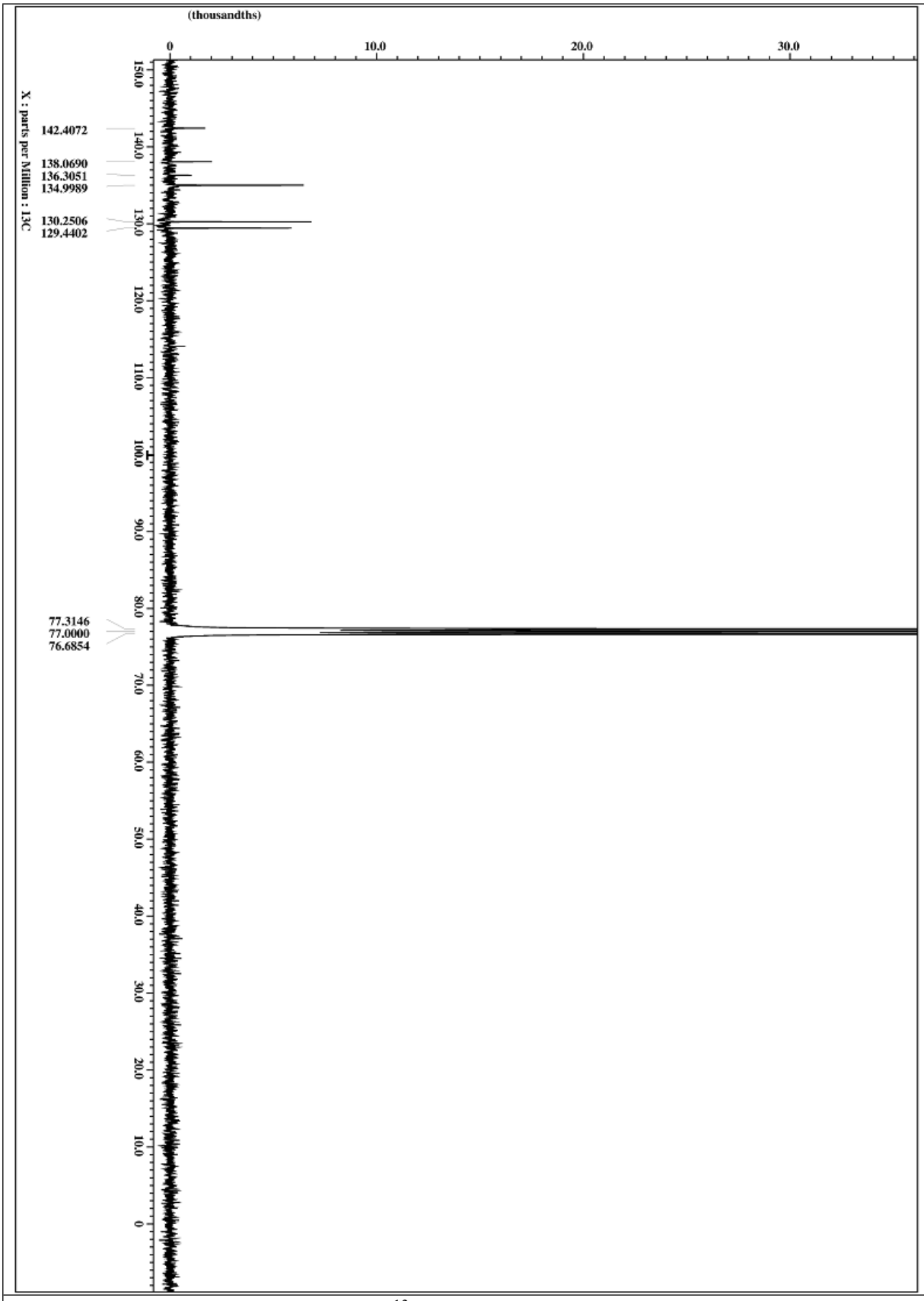


Fig. S21 ^{13}C NMR of compound **2e**.

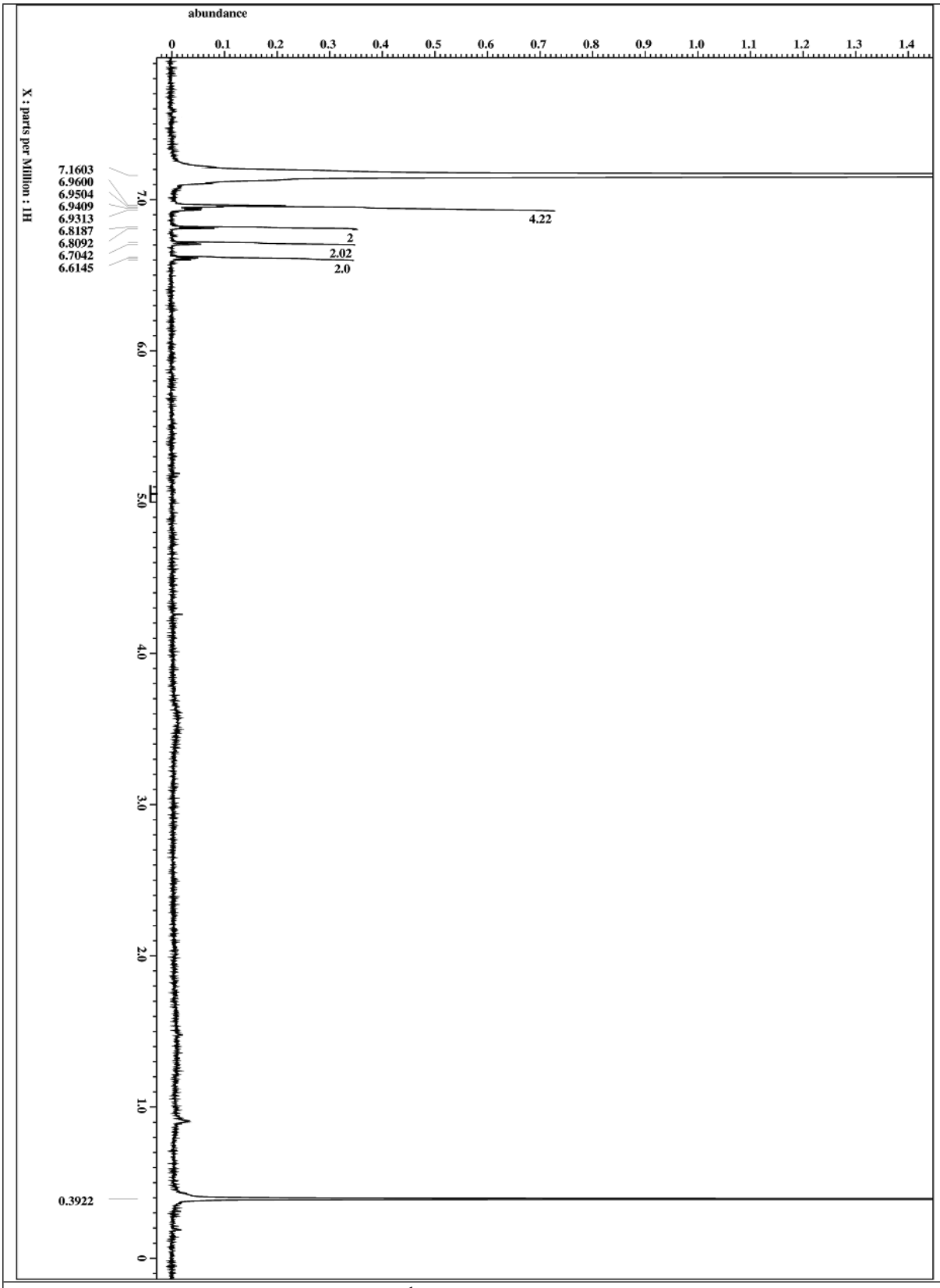


Fig. S22 ^{1}H NMR of compound **2f**.

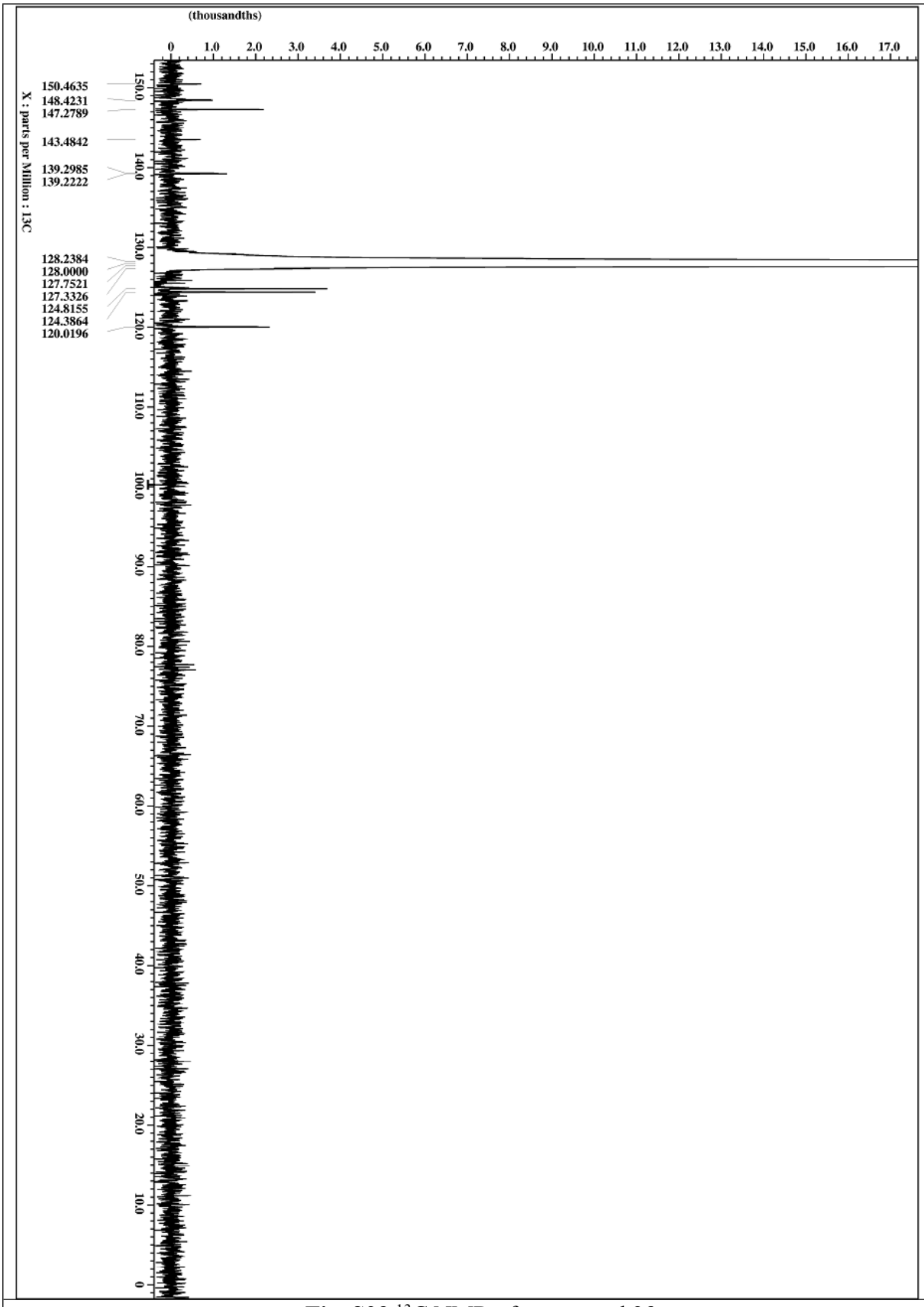


Fig. S23 ^{13}C NMR of compound **2f**.