Understanding of the Weak Intermolecular Interactions Involving Halogens in Substituted N-benzylideneanilines: Insights from Structural and Computational Perspectives

Gurpreet Kaur, and Angshuman Roy Choudhury[*]

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, Knowledge City, S. A. S. Nagar, Manauli PO, Mohali, 140306. Punjab, India.

Keywords: Weak interactions, organic fluorine, benzylideneanilines, *in situ* crystallization, polymorphism.

Electronic Supplementary Information

Procedure for synthesis:

All the starting materials, namely *ortho*-, *meta*- and *para*- halogenated benzaldehydes and anilines were purchased from Sigma Aldrich and were used without further purification. Corresponding benzaldehyde (0.5 mmol) and aniline (0.5 mmol) were dissolved in dichloromethane (DCM) at 298 K. Anhydrous Na_2SO_4 was added to that mixture to remove the water molecules produced during the condensation reaction. The solution was stirred for ~10 minutes and then the solvent was evaporated under reduced pressure to get the condensed product. Pure crystals were obtained by recrystallization from different organic solvents like methanol, ethanol, hexane, ethyl acetate, chloroform and DCM.

Details of Powder X-ray Diffraction:

Powder X-ray Diffraction (PXRD) data were recorded on a Rigaku Ultimia IV diffractometer using parallel beam geometry, Cu – Kα radiation, 2.5° primary and secondary solar slits, 0.5° divergence slit with 10 mm height limit slit, sample rotation stage (120 rpm) attachment and DTex Ultra detector. The tube voltage and current applied were 40 kV and 40 mA respectively. The data sets were collected over 2θ ranging from 5 to 50° with a scanning speed of 5° per minute with 0.02° step for all the solid compounds.

Details of Single Crystal X-ray Diffraction Data Collection, Structure Solution and Refinement:

Single crystals of all the purified solids were grown from different organic solvents (methanol, ethanol, acetone, dichloromethane, hexane, toluene etc.) and solvent mixtures (Table 1) at low temperature (4 ^{o}C or -20 ^{o}C). All the crystallization products were checked

using optical polarizing microscope for their morphologies and those were then checked for the identification of different polymorphs, if any, by unit cell determination using single crystal X-ray diffraction (SCXRD) technique. The compounds 18, 22, 28, and 34 yielded two polymorphs each from different solvents (Table 1). Single crystal X-ray diffraction data for all the compounds were collected using Bruker AXS KAPPA APEX-II CCD diffractometer (Monochromatic Mo – K_α radiation) equipped with Oxford cryosystem 700Plus at 100.0(1) K. Data collection and unit cell refinement for the data sets were done using Bruker APEX-II[1] suit, data reduction and integration were performed by SAINT V7.685A12 (Bruker AXS, 2009) and absorption corrections and scaling was done using SADABS V2008/112 (Bruker AXS). The crystal structures were solved by using Olex2[2] or WinGx[3] packages using SHELXS97[4] and the structures were refined using SHELXL97[4]. All the hydrogen atoms have been geometrically fixed and refined using the riding model. Table 1 lists the crystal and refinement data for all the compounds. All the packing and interaction diagrams have been generated using Mercury 3.1.1. Geometric calculations have been done using PARST[5] and PLATON[6].

Crystal Growth and Data collection for Liquids:

Out of 54 synthesized compounds, compounds **20**, **23**, **27**, **29**, **30**, **38**, **44**, **45**, **47** and **48** were found to be liquids at room temperature (25 ^{o}C). Out of these, structure of compound **23** (Melting point 22 ^{o}C) could be determined when room temperature was around 20 ^{o}C. Structure of compound **44** was determined by *in situ* crystallization technique[7]. In this case, the compound was taken in 0.3 mm Lindemann quartz capillary and was sealed at both ends with glue and was mounted on Bruker AXS KAPPA APEX-II CCD diffractometer with the capillary aligned vertically. For Compound **44**, the capillary was then cooled at 200K/hr to 180K, the liquid solidified by itself at this temperature. At the same rate, then it was heated from 180 to 220K. Still images were taken from time to time to see if there is any formation of crystals. It has been seen that at 210 K, compound got converted into a polycrystalline material. After that, even by heating from 220 K to 260 K at 200 K/hr, it remained polycrystalline. Then at 260 K, a few cycles of zone melting scans using the CO_2 LASER of the OHCD[8] were repeated for 6 hours to grow single crystal in the capillary. After the formation of a single crystal, one Φ scan (scan width 0.3°, 1200 frames) data were collected keeping ω and κ fixed at 0° and the detector fixed at 30° and with a detector distance of 6.0 cm.

For rest of the liquid compounds, the single crystal structure could not be determined as all those compounds were not crystallizing even by repeated heating or cooling cycles. Rather, they were forming only glassy material. DSC's of all those compounds have not shown any features too except in compound **29**, where a sharp peak has been seen in DSC, but still could not be crystallized *in situ*.

Crystallographic modelling of disorder:

Among all the 45 compounds reported in this paper, compound number (C.N.) **33**, **51**, **52**, and **56** were found to exhibit positional disorder due to in plane flipping of the molecule around C=N bond. But C.N. **23** and **41** were found to have positional disorder due to rotation of the aniline ring around C8–N1 bond. All these positional disorders were analysed with PART command using SHELXL97 and were refined for two independent positions, namely A and B ('A' for higher occupancy). For the purpose of refinement, the position of the carbon atoms in part A and B of the phenyl rings were fixed at same position using EXYZ command in SHELXL97. Thermal parameters were also constrained to be equal for the atoms at the same position using EADP command in SHELXL97. All hydrogen atoms were then positioned geometrically and refined using a riding model with Uiso (H) = 1.2 Ueq(C,N). The occupancy ratio for the two parts in C.N. **23**, **33**, **41**, **52**, and **56** were found to be 0.617(4) : 0.383(4), 0.909(1) : 0.091(1), 0.525(2) : 0.475(2), 0.544(2) : 0.456(2), and 0.627(1) : 0.373(1) respectively. The remaining molecules didn't find to exhibit any disorder.

Crystallographic Data Tables for all the compounds reported in the manuscript

Identification code	43	25	16F1	16F2	34
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9BrFN$	$C_{13}H_9BrFN$	$C_{13}H_9ClFN$
Formula weight	233.66	278.12	278.12	278.12	233.66
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	904772	904759	904752	904753	904765
Solvent system	Acetone	Methanol	DCM+Hexane	Ethanol	Ethyl Acetate
Morphology	block	plate	rect. block	plate	block
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\ \bar{1}$	$P2_1/c$	$P2_1/c$	$Pna2_1$	$P2_1/c$
a/Å	9.240(2)	15.2489(5)	23.950(5)	11.646(4)	23.596(2)
b/Å	9.283(2)	15.6548(5)	6.3629(15)	26.988(8)	6.3391(4)
c/Å	13.168(3)	17.0477(7)	7.2093(15)	7.113(2)	7.0801(4)
α/°	81.794(5)	90.00	90.00	90.00	90.00
β/°	80.917(5)	123.158(1)	94.890(7)	90.00	95.323(4)
γ/°	77.366(5)	90.00	90.00	90.00	90.00
Volume/$Å^3$	1081.5(4)	3406.9(2)	1094.7(4)	2235.6(11)	1054.5(1)
Z	4	12	4	8	4
Z′	2	3	1	1	1
$\rho_{calc}mg/mm^3$	1.435	1.627	1.688	1.653	1.472
μ/mm^{-1}	0.334	3.602	3.737	3.659	0.343
F(000)	480	1656.0	552	1104	480
Crystal size/mm^3	0.2 × 0.2 × 0.1	0.3 × 0.1 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1
$\Theta_{min,\ max}$	1.58, 25.02°	1.93, 25.03°	2.56, 25.03°	2.31, 25.02°	2.6, 25.02°
hmin, hmax; kmin, kmax; lmin, lmax	-10, 10; -11, 10; -15, 15	-16, 18; -18, 18; 20, 14	-28, 27; -3, 7; -8, 8	-13, 13; -32, 32; -3, 8	-28, 24; -7, 7; -8, 8
No. of reflections	7091	24812	8569	12225	4831
No. of Observed Reflections	3820	6024	1945	3060	1863
No. of unique reflections	3053	5149	1681	2760	1670
R(int)	0.0206	0.0285	0.0309	0.0362	0.0197
Data/restraints/parameters	3820/0/361	6024/0/541	1945/0/145	3060/1/284	1863/0/181
Goodness-of-fit on F^2	1.042	1.040	1.031	1.038	1.126
R_obs	0.0454	0.0402	0.0262	0.0244	0.0358
wR_2(obs)	0.1064	0.1008	0.0648	0.0478	0.0824
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.057/-0.339	2.41/-1.13	0.772/-0.376	0.228/-0.248	0.273/-0.386

Identification code	44	26	35	17
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$
Formula weight	233.66	278.12	233.66	278.12
Temperature (K)	100.0K	100.0K	100.0K	100.0K
CCDC No.	904773	904760	967464	904754
Solvent system	Methanol	Ethanol	Ethyl Acetate	DCM + Hexane
Morphology	*In situ*	plate	needle	plate
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.626(2)	12.8032(8)	11.504(2)	11.664(2)
b/Å	7.004(1)	7.0146(4)	4.725(1)	4.7226(9)
c/Å	12.228(2)	12.2477(8)	24.275(4)	21.437(4)
α/°	90.00	90.00	90.00	90.00
β/°	92.568(1)	92.867(2)	127.34(1)	113.688(8)
γ/°	90.00	90.00	90.00	90.00
Volume/$Å^3$	1080.3(3)	1098.6(1)	1049.1(3)	1079.5(3)
Z	4	4	4	4
Z′	1	1	1	1
$\rho_{calc}mg/mm^3$	1.437	1.682	1.479	1.711
μ/mm^{-1}	0.335	3.723	0.345	3.789
F(000)	480	552	480	552
Crystal size/mm^3	In situ	0.3 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.1
$\Theta_{min, max}$	3.23, 25.02°	3.19, 25.02°	1.93, 25.03°	1.91, 25.03°
hmin, hmax; kmin, kmax; lmin, lmax	-15, 15; -6, 6; -14, 14	-15, 15; 0, 8; 0, 14;	-13, 13; -5, 3; -28, 27	-8, 13; -3, 5; -25, 24
No. of reflections	4852	6185	3888	5336
No. of Observed Reflections	1540	1946	1825	1882
No. of unique reflections	1475	1719	1335	1439
R(int)	0.0193	0.0283	0.0362	0.0468
Data/restraints/parameters	1540/0/181	1946/0/181	1825/0/145	1882/0/145
Goodness-of-fit on F^2	1.056	1.046	1.027	1.067
R_obs	0.0257	0.0234	0.0452	0.041
wR_2(obs)	0.0699	0.0651	0.1058	0.0726
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.038/-0.192	0.468/-0.338	0.779/-0.294	0.637/-0.656

Identification code	36F1	36F2	18F1	18F2
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9BrFN$
Formula weight	233.66	233.66	278.12	278.12
Temperature (K)	100.0K	100.0K	100.0K	100.0K
CCDC No.	904766	967465	967460	967467
Solvent system	Acetone	Methanol	Acetone + Methanol	DCM + Hexane
Morphology	plate	needle	block	plate
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$Pna2_1$	$P2_12_12_1$	$P2_1$
a/Å	6.182(2)	26.077(3)	6.1982(5)	13.424(2)
b/Å	7.123(2)	5.8390(7)	7.1066(7)	6.0702(6)
c/Å	25.074(8)	14.513(2)	25.399(2)	15.467(2)
α/°	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	115.534(6)
γ/°	90.00	90.00	90.00	90.00
Volume/$Å^3$	1104.1(6)	2209.78(4)	1118.77(2)	1137.2(2)
Z	4	8	4	4
Z′	1	2	1	1
$\rho_{calc}mg/mm^3$	1.406	1.40	1.65	1.627
μ/mm^{-1}	0.328	0.327	3.656	3.597
F(000)	480	960	552	552
Crystal size/mm^3	0.3 × 0.2 × 0.1	0.3 × 0.1 × 0.1	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.15
$\Theta_{min, max}$	2.97, 25.02°	2.10, 26.40°	1.60, 25.00°	1.46, 25.68°
hmin, hmax; kmin, kmax; lmin, lmax	-7, 7; -7, 8; -12, 29	-32, 28; -7, 7; -18, 18	-7, 7; -8, 8; -30, 29	-16, 13; -7, 6; -18, 18
No. of reflections	3797	8743	5888	7418
No. of Observed Reflections	1927	2870	1754	3850
No. of unique reflections	1776	3643	1987	3422
R(int)	0.0193	0.045	0.042	0.0368
Data/restraints/parameters	1927/0/181	3643/0/289	1927/0/145	3850/1/289
Goodness-of-fit on F^2	1.046	1.041	0.957	1.074
R_obs	0.0267	0.042	0.027	0.047
wR_2(obs)	0.0595	0.087	0.049	0.0997
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.165/-0.143	0.229/-0.300	0.461/-0.444	0.608/ -0.659

Identification code	46	28F1	28F2	37	19
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9BrFN$	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$
Formula weight	233.66	278.12	278.12	233.66	278.12
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	904774	904761	967463	904767	904755
Solvent system	Acetone	Acetone + Methanol	DCM + Hexane	Ethyl Acetate	Methanol
Morphology	block	rect. Prism	block	plate	plate
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_1/c$	$P2_1/c$
a/Å	8.371(1)	3.9096(7)	8.4843(3)	24.330(6)	24.639(3)
b/Å	5.8235(6)	10.202(2)	5.8153(2)	6.156(2)	6.1809(6)
c/Å	11.239(1)	27.608(6)	11.3383(5)	7.129(2)	7.2279(7)
α/°	90.00	90.00	90	90.00	90.00
β/°	95.359(4)	90.00	94.559(2)	96.144(3)	96.537(5)
γ/°	90.00	90.00	90	90.00	90.00
Volume/$Å^3$	545.5(1)	1101.11(3)	557.65(4)	1054.5(1)	1093.6(2)
Z	2	4	2	4	4
Z′	0.5	1	1	1	1
$\rho_{calc}mg/mm^3$	1.423	1.678	1.656	1.462	1.689
μ/mm^{-1}	0.332	3.715	3.668	0.341	3.741
F(000)	240	552	552	480	552
Crystal size/mm^3	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.1	0.4 × 0.2 × 0.2	0.5 × 0.3 × 0.2	0.2 × 0.1 × 0.1
$\Theta_{min, max}$	2.44, 25.03°	2.13, 25.02°	3.12, 32.74°	2.53, 25.02°	2.5, 24.71°
hmin, hmax; kmin, kmax; lmin, lmax	-9, 9; -6, 6; -13, 13	-4, 4; 0, 12; -15, 32	-10, 10; -7, 5; -11, 14	-21, 28; -7, 2; -8, 6	-28, 28; -7, 5; -8, 7
No. of reflections	3114	4619	2988	4982	6660
No. of Observed Reflections	1610	1913	1817	1863	1851
No. of unique reflections	1578	1769	1757	1743	1686
R(int)	0.0141	0.0196	0.0159	0.014	0.0318
Data/restraints/parameters	1610/0/181	1913/0/177	1817/1/145	1863/0/181	1851/0/145
Goodness-of-fit on F^2	1.086	1.062	1.028	1.065	1.044
R_obs	0.0212	0.0236	0.0191	0.0289	0.0259
wR_2(obs)	0.0536	0.0525	0.0463	0.0791	0.0700
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.114/ -0.177	0.41/-0.25	0.257/-0.278	0.319/-0.26	0.725/-0.368

Identification code	39	21
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$
Formula weight	233.66	278.12
Temperature (K)	100.0K	100.0K
CCDC No.	904768	967461
Solvent system	Ethanol	Acetone
Morphology	block	block
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	6.1450(1)	6.1317(4)
b/Å	12.8880(3)	13.1483(8)
c/Å	13.6233(3)	13.8815(9)
α/°	90.00	90
β/°	90.00	90
γ/°	90.00	90
Volume/$Å^3$	1078.92(4)	1119.2(2)
Z	4	4
Z′	1	1
$\rho_{calc}mg/mm^3$	1.438	1.651
μ/mm^{-1}	0.335	3.655
F(000)	480	552
Crystal size/mm^3	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.1
$\Theta_{min, max}$	2.18, 25.02°	2.13, 28.28
hmin, hmax; kmin, kmax; lmin, lmax	-7, 7; -15, 11; -16, 13	-8, 5; -16, 17; -17, 18
No. of reflections	7193	6479
No. of Observed Reflections	1897	2768
No. of unique reflections	1871	2547
R(int)	0.0161	0.0307
Data/restraints/parameters	1897/0/181	2768/0/145
Goodness-of-fit on F^2	1.046	0.992
R_obs	0.0203	0.0269
wR_2(obs)	0.0525	0.0547
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.161/ -0.14	0.41/-0.604

Identification code	49	31	40	22
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$
Formula weight	233.66	278.12	233.66	278.12
Temperature (K)	100.0K	100.0K	100.0K	100.0K
CCDC No.	904775	904762	904769	967462
Solvent system	Ethanol	Acetone	DCM + Hexane	Ethyl Acetate
Morphology	rectangular	block	irregular	needle
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	13.129(1)	13.4031(9)	3.8515(8)	3.8890(4)
b/Å	11.0236(8)	11.0048(9)	25.069(6)	24.937(3)
c/Å	7.6940(6)	7.7272(7)	10.864(2)	11.0177(10)
α/°	90.00	90.00	90.00	90.00
β/°	106.445(5)	106.161(4)	93.302(3)	93.160(5)
γ/°	90.00	90.00	90.00	90.00
Volume/$Å^3$	1068.0(1)	1094.7(2)	1047.2(4)	1066.9(2)
Z	4	4	4	4
Z′	1	1	1	1
$\rho_{calc}mg/mm^3$	1.453	1.688	1.482	1.732
μ/mm^{-1}	0.339	3.737	0.345	3.834
F(000)	480	552.0	480	552
Crystal size/mm^3	0.4 × 0.2 × 0.1	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.3 × 0.1 × 0.1
$\Theta_{min, max}$	2.46, 26.37°	2.43, 25.02	1.62, 25.12°	2.02, 25.02
hmin, hmax; kmin, kmax; lmin, lmax	-12, 16; -13, 13; -9, 7	-15, 15; -13, 10; -9, 8;	-4, 4; -29, 29; -12, 11	-4, 2; -29, 28; --13, 12
No. of reflections	9936	5574	5691	5135
No. of Observed Reflections	2186	1779	1874	1875
No. of unique reflections	1844	1925	1705	1616
R(int)	0.0439	0.0181	0.0184	0.0262
Data/restraints/parameters	2186/0/181	1925/0/181	1874/0/181	1875/1/145
Goodness-of-fit on F^2	1.077	1.038	1.12	1.036
R_obs	0.0372	0.0209	0.03	0.0254
wR_2(obs)	0.09	0.0526	0.0783	0.0602
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.283/ -0.312	0.38/-0.38	0.254/-0.304	1.025/-0.436

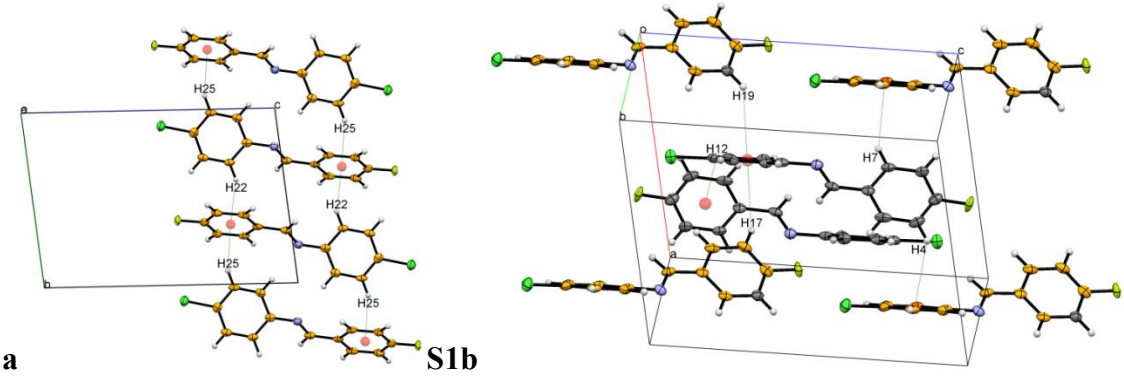
Identification code	50	32	41	23
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$
Formula weight	233.66	278.12	233.66	278.12
Temperature (K)	100.0K	100.0K	100.0K	100.0K
CCDC No.	904776	904763	904770	904757
Solvent system	Ethanol	Acetone	Hexane	Methanol
Morphology	block	plate	irregular	irregular
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a/Å	15.377(5)	15.490(1)	3.8567(2)	3.9037(9)
b/Å	3.925 (1)	3.9477(2)	12.0890(8)	12.190(3)
c/Å	22.648(8)	24.348 (2)	22.859(2)	22.760(5)
α/°	90	90.00	90.00	90
β/°	129.569(9)	133.511(3)	90.00	90
γ/°	90	90.00	90.00	90
Volume/Å^3	1053.8(6)	1079.8 (1)	1065.8(1)	1083.03(4)
Z	4	4	4	4
Z′	1	1	1	1
ρ_{calc}mg/mm^3	1.473	1.711	1.456	1.71
μ/mm^{-1}	0.343	3.788	0.339	3.777
F(000)	480	552	480	552
Crystal size/mm^3	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.05	0.5 × 0.2 × 0.1	0.4 × 0.2 × 0.1
$\Theta_{min,\ max}$	1.72, 26.37°	1.81, 25.02°	1.78, 25.02°	2.9, 25.03°
hmin, hmax; kmin, kmax; lmin, lmax	-19, 19; -4, 4; -27, 28	-17, 18; -4, 4; -28, 28;	-7, 7; -7, 8; -12, 29	-3, 4; -14, 14; -24, 27
No. of reflections	6284	7459	7013	4097
No. of Observed Reflections	2139	1798	1859	1926
No. of unique reflections	1861	1915	1748	1892
R(int)	0.0254	0.0203	0.0256	0.0130
Data/restraints/parameters	2139/0/181	1915/0/181	1859/0/175	1926/0/175
Goodness-of-fit on F^2	1.054	1.059	1.085	1.046
R_obs	0.029	0.0192	0.0273	0.0243
wR_2(obs)	0.0712	0.0483	0.0639	0.0627
$\Delta\rho_{min,max}$ / e Å^{-3}	0.281/-0.228	0.313/-0.264	0.039/ -0.238	0.21/-0.27

Identification code	51	33	42	24
Empirical formula	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$	$C_{13}H_9ClFN$	$C_{13}H_9BrFN$
Formula weight	233.66	278.12	233.66	278.12
Temperature (K)	100.0K	100.0K	100.0K	100.0K
CCDC No.	967466	904764	904771	904758
Solvent system	Methanol	Acetone	Ethanol	Methanol
Morphology	plate	block	block	plate
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pbcn$	Pbca	$P2_1/c$
a/Å	10.030(4)	12.9933(6)	12.4117(3)	12.112(2)
b/Å	3.8427(15)	11.4999(5)	9.8248(2)	3.9009(7)
c/Å	28.062(11)	14.9358(7)	17.9456(4)	23.337(5)
α/°	90	90.00	90.00	90.00
β/°	90.806(8)	90.00	90.00	104.714(4)
γ/°	90	90.00	90.00	90.00
Volume/$Å^3$	1081.4(7)	2231.7(2)	2188.33(8)	1066.5(4)
Z	4	8	8	4
Z′	1	1	2	1
$\rho_{calc}mg/mm^3$	1.435	1.656	1.418	1.732
μ/mm^{-1}	0.334	3.666	0.331	3.835
F(000)	480	1104	960	552
Crystal size/mm^3	0.4 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.2 × 0.15 × 0.1
$\Theta_{min, max}$	2.03, 25.03	2.73, 27.79°	2.27, 26.37°	2.16, 25.03
hmin, hmax; kmin, kmax; lmin, lmax	-5, 11; -4, 4; -32, 33	-7, 15; -13, 13; -17, 16;	-15, 7; -11, 12; -20, 22	-14, 12; -4, 2; -27, 25
No. of reflections	6584	12745	11432	6185
No. of Observed Reflections	1909	1712	2235	1873
No. of unique reflections	1640	1973	1979	1658
R(int)	0.0221	0.0274	0.018	0.0283
Data/restraints/parameters	1909/0/157	1973/13/157	2235/0/181	1873/0/177
Goodness-of-fit on F^2	1.043	1.058	1.039	1.051
R_obs	0.0364	0.0236	0.0279	0.0245
wR_2(obs)	0.0837	0.0513	0.0735	0.0598
$\Delta\rho_{min,max}$ / e $Å^{-3}$	0.244/-0.344	0.260/-0.316	0.261/-0.273	0.514/-0.399

Structural description of the compounds belonging to class 1a and 1c:

4-chloro-N-(4-fluorobenzylidene)aniline (43):

Compound **43** crystallizes in the centrosymmetric triclinic $P\ \bar{1}$ space group with Z = 4 and having two molecules in the asymmetric unit (Z′ = 2). The molecules have been found to form hexameric network involving two different C–H···F hydrogen bonds (one between F1 and H26 and the other between F2 and H13) and a type I C–Cl···Cl–C interactions (table 1, figure 1b). Further, a number of weak C–H···π interactions, which interconnect these molecules, have been found in the lattice (table S1a, figure S1a and S1b).

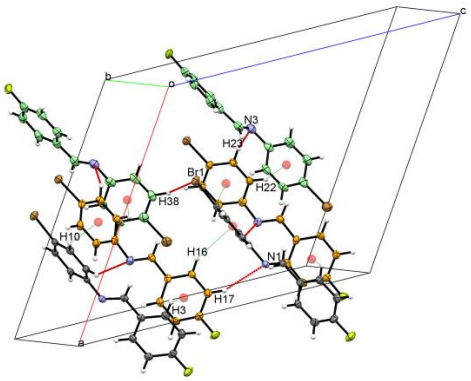


S1a **S1b**

Figure S1: (a) Chains of dimers through C–H···π interactions in **43**, **(b)** formation of network through C–H···π interactions present in **43**.

4-bromo-N-(4-fluorobenzylidene)aniline (25):

Compound **25** was found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 12 and having three molecules in the asymmetric unit. All the three molecules of the asymmetric unit pack in the lattice through type I C–F···Br interaction, which results in the formation of chains in the *bc* plane. These chains are interlinked with each other through C–H···π interactions (table 1, figure 1c). Three molecules of the asymmetric unit have also been found to interact with each other through weak C–H···N and C–H···Br hydrogen bonds (involving H9 with N1, H23 with N3, H17 with N1 and H38 with Br1) (table 1, figure S1c). These interactions (C–H···N and C–H···Br) are also further supported by C–H···π interactions (ESI, table S1, figure S1c].



S1c

Figure S1: (c) Molecules connected by C–H···N, C–H···Br hyderogen bonds and C–H···π interactions in **25.**

4-fluoro-N-(4-chlorobenzylidene)aniline (34) and **4-fluoro-N-(4-bromobenzylidene)aniline (16 Form I, 16F1):**

Compounds **34** and **16F1** (Polymorph 1 of **16**) have been found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4, while **16F2** (Polymorph 2 of **16**) was crystallized in the non-centrosymmetric orthorhombic $Pna2_1$ space group with Z = 8 and Z' = 2. Compounds **34** and **16F1** have been found to be isostructural with similar packing characteristics as described below.

Both the structures, when viewed down the *c*-axis, were found to have zigzag molecular chains through C–H···F hydrogen bonds (involving H12 with F1) in the *ab* plane by the utilization of 2_1 screws along *b*-axis. These chains have been found to run antiparallel along the *b* axis (table 1, figure 1d and 1e). A pair of antiparallel chains are found to be further interconnected by the formation of dimers by the molecules related by inversion center through C–H···Cl hydrogen bonds in case of **34** (table 1, figure 1d) and by type I C–Br···Br–C interactions in case of **16F1** (table 1, figure 1e), thus results in the formation of sheets in the *ab* plane. The homohalogen interactions found in **16F1** are in contrast to the observation made by Nayak *et al.*, in the cases of fluorinated benzenanilides, in which preference for type II geometry for homo/hetero halogen short contacts involving heavier halogens (Br and Cl) in the solid state have been revealed. The sheets thus formed have been found to interact with other sheets in the lattice through weak C–H···π interactions (involving H3 and H6 with Cg1, H13 and H10 with Cg2) (ESI, table S1, figure S1d, S1e, S1f and S1g).

The C–H···F chains found in this molecule are similar to those observed in the case of 4-fluoro-N-(4-fluorobenzylidene)aniline reported by us earlier.* In the earlier case as

fluorine was there at the para position on both the phenyl rings, both the fluorine atoms were found to be involved in the formation of chains by C–H···F hydrogen bond and no F···F contact was found.

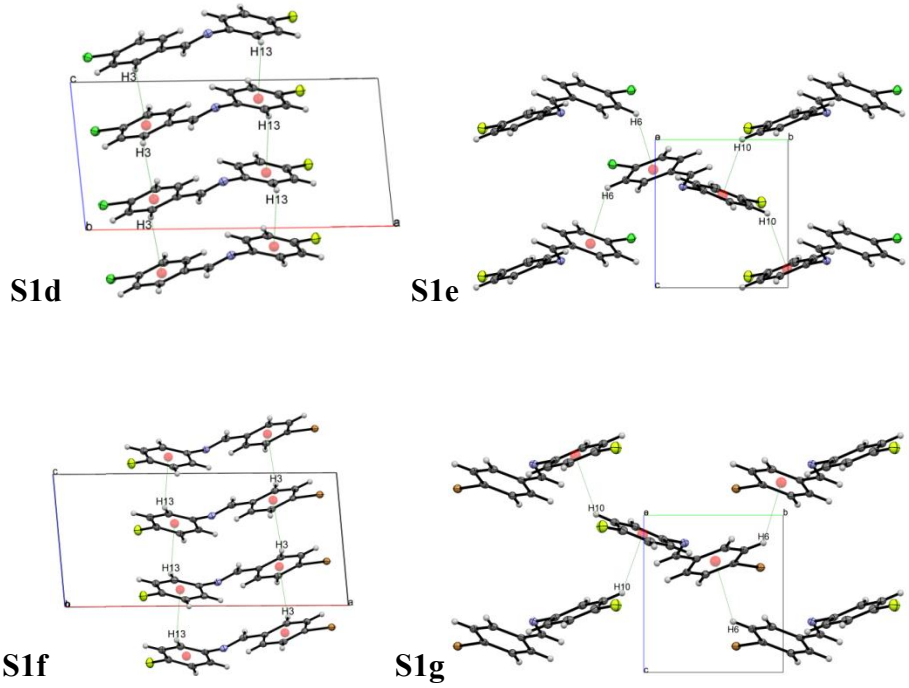
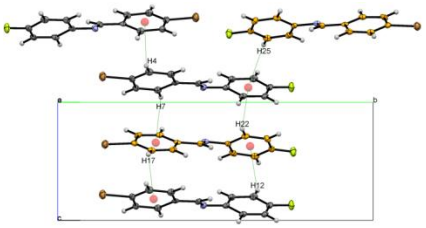


Figure S1: (d) Chains of dimers formed by C–H···π interactions along *b*-axis in **34**, **(e)** formation of molecular network *via* C–H···π interactions in **34**, **(f)** Chains of dimers formed by C–H···π interactions along *b*-axis in **16F1**, **(g)** formation of molecular network *via* C–H···π interactions in **16F1**.

4-fluoro-N-(4-bromobenzylidene)aniline (16 Form II, 16F2):

Compound **16F2** has been found to crystallize in the non-centrosymmetric orthorhombic $Pna2_1$ space group with Z = 8 and Z′ = 2. A network of chains has been found to form through weak C–H···F hydrogen bonds in both the molecules of the asymmetric unit (involving H14 with F2 and H1 with F1). Then C–H···Br (involving H23 with Br1) hydrogen bonds between the two molecules of the asymmetric unit have been found to interconnect these chains to form sheets (table 1, figure 1f). These sheets have been found to propagate along *c*-axis through weak C–H···π (ESI, table S1, figure S1h).



S1h

Figure S1: (h) Molecules interacting *via* C–H···π interactions along *c*-axis.

Table S1: Intermolecular C–H···π interactions metrics for compounds **43**, **25**, **34**, **16F1** and **16F2**

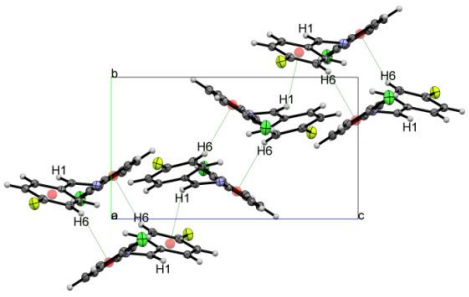
Code	C–H···π	C···π (Å)	H···π (Å)	∠C–H···π (°)	Symmetry Code
43	C4–H4···Cg4	3.46	2.78	129	x,y,1+z
	C7–H7···Cg4	3.40	2.68	133	-1+x,y,1+z
	C10–H10···Cg1	3.67	2.96	133	1-x,-y,1-z
	C12–H12···Cg1	3.59	2.88	132	1-x,1-y,1-z
	C17–H17···Cg2	3.50	2.92	121	x,y,z
	C19–H19···Cg2	3.69	2.96	135	1+x,y,z
	C22–H22···Cg3	3.42	2.74	130	2-x,1-y,-z
	C25–H25···Cg3	3.49	2.77	133	2-x,-y,-z
25	C3–H3···Cg3	3.44	2.78	127	x,1/2-y,1/2+z
	C10–H10···Cg4	3.56	2.75	143	x,1/2-y,1/2+z
	C12–H12···Cg6	3.41	2.73	129	1-x,-y,1-z
	C30–H30···Cg1	3.44	2.86	120	1-x,-y,1-z
	C16–H16··Cg2	3.55	2.68	151	x,y,z
	C22–H22···Cg6	3.59	2.89	132	x,1/2-y,-1/2+z
	C36–H36···Cg2	3.55	2.97	121	x,y,z
34	C3–H3···Cg1	3.69	2.98	133	x,1/2-y,-1/2+z
	C13–H13···Cg2	3.63	2.94	131	x,1/2-y,-1/2+z
	C6–H6···Cg1	3.50	2.85	126	x,-1/2-y,1/2+z
	C10–H10···Cg2	3.51	2.82	130	x,3/2-y,1/2+z
16F1	C6–H6···Cg1	3.55	2.90	126	x,5/2-y,1/2+z
	C10–H10···Cg2	3.54	2.84	131	x,1/2-y,1/2+z
	C13–H13···Cg2	3.68	2.98	132	x,1/2-y, 1/2+z
	C3–H3···Cg1	3.73	3.06	133	x,1/2-y, 1/2+z
16F2	C4–H4···Cg1	3.45	2.76	138	2-x,-y,-/2+z
	C7–H7···Cg3	3.59	2.93	128	x,y,z
	C12–H12···Cg4	3.50	2.84	127	x,y,-1+z
	C17–H17···Cg1	3.36	2.73	124	x,y,1+z
	C22–H22···Cg2	3.42	2.69	134	x,y,z
	C25–H25···Cg2	3.58	2.84	135	-1/2+x,1/2-y,1+z

Structural description of the compounds belonging to class 1b and 5a:

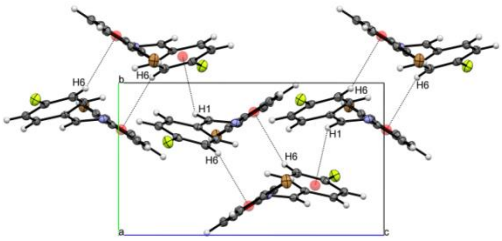
3-chloro-N-(4-fluorobenzylidene)aniline (44) and **3-bromo-N-(4-fluorobenzylidene)aniline (26)**

Both the compounds **44** and **26** were found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4 with similar unit cell dimensions. These compounds are isostructural and have similar packing features as described below.

Molecules related by *c* glide have been found to interact through weak C–H···F hydrogen bond, which resulted into the formation of chains in both. Then these chains were found to be interconnected through type II C–F···X (X = Cl or Br) hetero halogen interactions in **44** and **26** respectively and thus giving rise to a sheet like structure in the *ac* plane (table 2, figure 2b and 2c). On viewing down the *bc* plane, molecules having a center of symmetry have been found to interact by forming dimers through weak C–H···π interaction (involving H6 with Cg2). Then these dimers have been found to extend by the utilization of 2_1 screw along *b*-axis through another weak C–H···π interaction (involving H1 with Cg1) (ESI, table S2, figure S2a and S2b).



S2a



S2b

Figure S2: (a) Extension of molecular dimers, formed by C–H···π interactions, through C–H···π interaction in **44**, **(b)** Extending molecular dimers, formed by C–H···π interactions, through C–H···π interaction in **26**.

3-fluoro-N-(4-chlorobenzylidene)aniline (35) and **3-fluoro-N-(4-bromobenzylidene)aniline (17):**

The compounds **35** and **17** have been found to pack in the monoclinic centrosymmetric space group $P2_1/c$ with Z = 4. Dimers have been found to form between the two molecules related by center of inversion involving H9 and H1 with F1 in the packing of both **35** and **17** (table 2, figure 2d and 2e). The fluorine atom involved in these dimers have been found to have bifurcated C–H···F hydrogen bonds. These dimers have been found to

propagate along the *c* glide through C–H···X (X = Cl or Br) hydrogen bonds in the compounds **35** and **17** respectively (table 2, figure 2d and 2e).

Table S2: Intermolecular C–H···π interactions metrics for compounds **44** and **26**

Code	C–H···π	C···π (Å)	H···π (Å)	∠C–H···π (°)	Symmetry Code
44	C1–H1···CG1	3.50	2.84	127	-x,-1/2+y,1/2-z
	C6–H6···CG2	3.50	2.78	133	-x,1-y,1-z
26	C1–H1···Cg1	3.51	2.85	128	-x,1/2+y,1/2-z
	C6–H6··Cg2	3.53	2.81	134	-x,1-y,1-z

Structural comparison of the compounds belonging to class 1c and 6a: 2-chloro-N-(4-fluoro-benzylidene)aniline (**45**) and **2-bromo-N-(4-fluorobenzylidene)aniline** (**27**):

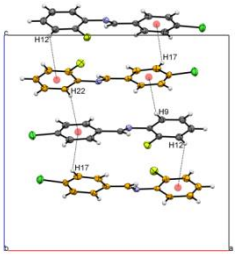
Among the compounds belonging to the group **1c** (**3**, **27**, **45**), only **3** was solid, while **27** and **45** were found to be liquids at room temperature. The DSC data on **45** and **27** didn't indicate any sharp solidification or melting feature. Several trials of crystal growth using *in situ* crystallization technique were failed to grow single crystals suitable for structural analysis.

2-fluoro-N-(4-chlorobenzylidene)aniline (36 Form I, 36F1) and **2-fluoro-N-(4-chlorobenzylidene)aniline (18 Form I, 18F1):**

Compounds **36F1** and **18F1** were found to crystallize in the orthorhombic non-centrosymmetric $P2_12_12_1$ space group with $Z = 4$. The molecules of 36F1 and 18F1 have been found to form chains through C–H···F hydrogen bonds (involving H1 with F1) along *b*-axis (table 1, figure 3c and 3d) and these chains have been found to be interconnected with each other through C–H···π interactions involving H6 with Cg1 and H9 with Cg2 by the utilization of 2_1 screw axis along *b* and *c* directions respectively (ESI, table S3), (figure 3c and 3d).

2-fluoro-N-(4-chlorobenzylidene)aniline (36 Form II, 36F2):

Compound **36F2** was found to crystallize in the orthorhombic non-centrosymmetric *Pna2₁* space group with Z = 8 and Z′ = 2. Along the *b*-axis, both the molecules of the asymmetric unit have been found to form chains through C–H···F hydrogen bonds (involving H1 with F1 and H14 with F2) (table 3, figure 3e). These chains have been found to be interlinked along the *c*-axis through C–H···π interactions (H17 and H22 with Cg1, H9 with Cg3 and H12 with Cg4) (ESI, table S3, figure S3a).

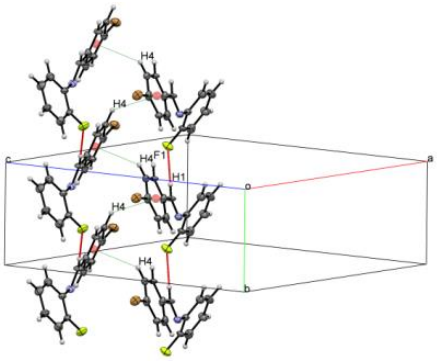


S3a

Figure S3a: C–H···π interactions, connecting the molecules belonging to different chains in **36F2**.

2-fluoro-N-(4-bromobenzylidene)aniline (18 Form II, 18F2):

Compound **18F2** has been found to crystallize in the non-centrosymmetric $P2_1$ space group with Z = 4 and Z′ = 2. The two molecules, designated as A (grey) and B (orange), present in the asymmetric unit were found to form chains of the type ···A···A···A···A··· and ···B···B···B···B··· in the lattice by C–H···F hydrogen bond along *b*-axis. But in molecule A of the asymmetric unit, the C–H···F hydrogen bond is bifurcated at the F atom. Due to this bifurcation at F1, these chains (A and B) are further interlinked forming a ladder like structure, which is has been found to extend along the *b* axis (table 3, figure 3f). The chains formed by both the molecule of asymmetric unit have been found to interact with other chains by the utilization of C–H···π interactions along the *b*-axis (ESI, table S3, figure S3b).



S3b

F**igure S3b:** C–H···π interactions present between the molecules of the two different chains, which were formed by C–H···F hydrogen bond.

Table S3: Intermolecular C–H···π interactions metrics for compounds **36F1**, **18F1**, **36F2** and **18F2**

Code	C–H···π	C···π (Å)	H···π (Å)	∠C–H···π (°)	Symmetry Code
36F1	C6–H6···Cg1	3.42	2.85	120	-x,-1/2+y,1/2-z
	C9–H9···Cg2	3.42	2.54	147	-1/2+x,1/2-y,-z
18F1	C4–H4···Cg1	3.48	2.78	132	-x,-1/2+y,1-z
	C13–H13···Cg2	3.64	2.85	141	1-x,-1/2+y,1-z
	C17–H17···Cg3	3.53	2.84	130	2-x,1/2+y,-z
	C26–H26···Cg4	3.51	2.70	144	1-x,1/2+y,-z
36F2	C6–H6···Cg4	3.58	2.94	126	-x,-y,1/2+z
	C17–H17···Cg1	3.43	2.78	127	x,y,z
	C19–H19···Cg2	3.57	2.93	126	-x,-y,-1/2+z
	C22–H22···Cg1	3.59	2.78	144	-x,1-y,-1/2+z
	C9–H9···Cg3	3.54	2.75	141	-x,1-y,1/2+z
18F2	C6–H6···Cg1	3.45	2.87	121	1-x,-1/2+y,1/2-z
	C9–H9···Cg2	3.38	2.57	143	-1/2+x,1/2-y,-z
	C12–H12···Cg2	3.50	2.71	140	x,-1/2-y,1/2+z

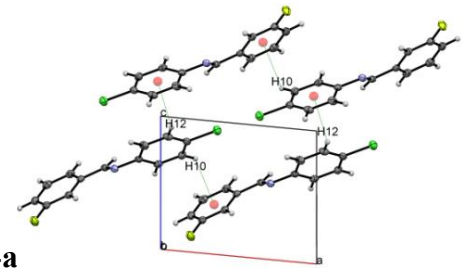
Structural description of the compounds belonging to class 2a and 4b:

4-chloro-N-(3-fluoro-benzylidene)aniline (46) and **4-bromo-N-(3-fluorobenzylidene)aniline (28 Form I, 28F1):**

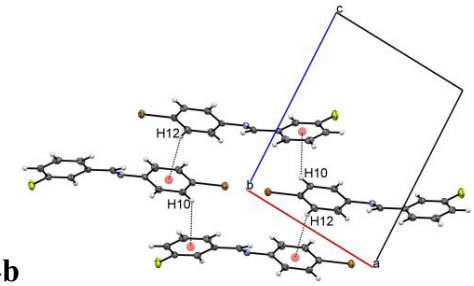
Both the compounds **46** and **28F1** were found to be crystallized in the monoclinic non-centrosymmetric $P2_1$ space group with $Z = 2$ with similar unit cell dimensions and packing features in the crystal lattice, which have been described below.

Zigzag chains were found to form by molecules through weak C–H···F hydrogen bond (involving H5 with F1), which are propagating along the 2_1 screw axis (table 4, figure 4b and 4c). A chain of hetero dimer has also been observed *via* weak C–H···F hydrogen bond

(involving H9 with F1), and C–H···π interactions (involving H7 with Cg1) (ESI, table S4, figure S4a and S4b). Further, these chains have been found to extend along the *a*-axis through C–H···π interactions (involving H10 with Cg1 and H12 with Cg2) (ESI, table S4, figure S4a and S4b). But, neither Cl nor Br was found to involve in any kind of interaction in **46** and **28F1** respectively.



S4a



S4b

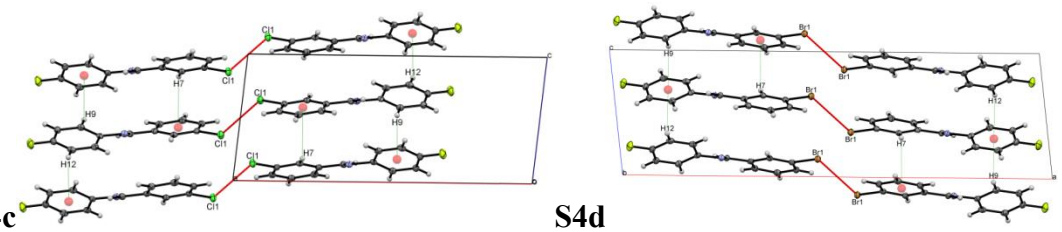
Figure S4: (a) Molecules interacting through weak C–H···π interactions in the crystal structure of **46**, **(b)** formation of molecular network *via* weak C–H···π interactions in **28F1**.

4-bromo-N-(3-fluorobenzylidene)aniline (28 Form II, 28F2):

The form II of compound **28** (referred to as **28F2**) was found to crystallize in the orthorhombic non-centrosymmetric $P2_12_12_1$ space group with Z = 4. The crystal packing of the molecules were found to involve weak C–H···N hydrogen bond (involving H4 with N1 by using 2_1 screw along *b*-axis) and type II Br1···F1 interaction (by using 2_1 screw along *c*-axis) to form of a zigzag chain in the *bc* plane (table 4, figure 4f).

4-fluoro-N-(3-chlorobenzylidene)aniline (37) and **4-fluoro-N-(3-bromobenzylidene)aniline (19):**

Both the compounds **37** and **19** were found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4. Both the molecules have been found to form ribbons in the *ab* plane by the utilization of 2_1 screw axis and involving C–H···F hydrogen bonds (involving H10 with F1) in the similar fashion as was observed in the case of compounds 34 and 16F1. Then these molecular ribbons were found to be interconnected through type I C–X···X (X = Cl or Br) interactions (table 4, figure 4g and 4h). Very weak C–H···π interactions (involving H7 with Cg1, H9 and H12 with Cg2) in the *ac* plane have also been identified in between the sheets formed by C–H···F hydrogen bonds and C–X···X interactions (table S4, figure S4c and S4d)



S4c **S4d**

Figure S4: (c) Sheets formed interact among each other by C–H···π interactions in **37**, **(b)** interactioning molecular sheets in **19** by C–H···π interactions.

Table S4: Intermolecular C–H···π interactions metrics for compounds **46** and **28F2**

Code	C–H ···π	C···π (Å)	H ···π (Å)	∠C–H ···π (°)	Symmetry Code
46	C7–H7···Cg1	3.52	2.83	130	1-x,-1/2+y,1-z
	C10–H10···Cg1	3.42	2.75	127	-1+x,y,z
	C12–H12···Cg1	3.46	2.72	135	-x,-1/2+y,-z
28F2	C7–H7···Cg1	3.54	2.86	129	-x,1/2+y,1-z
	C10–H10···Cg1	3.43	2.74	130	1+x,y,z
	C12–H12···Cg2	3.52	2.75	139	1-x,1/2+y,2-z

Structural comparison of the compounds belonging to class 2b and 5b:

All the compounds belonging to the sub-class **2b** (**5**, **47**, **29**) and **5b** (**5**, **38**, **20**) were found to be liquid at 25 °C. Among these, crystal structure of **5** could be determined using *in situ* crystallization technique, while crystals of the others could not be grown in the same way. The DSC data of compounds **20** and **47** have not shown any indication of solidification in the cooling and heating cycles (25 °C to -100 °C and heated back to 25 °C) (ESI, figure S4:5 and 32).

Structural comparison of the compounds belonging to class 2c and 6b:

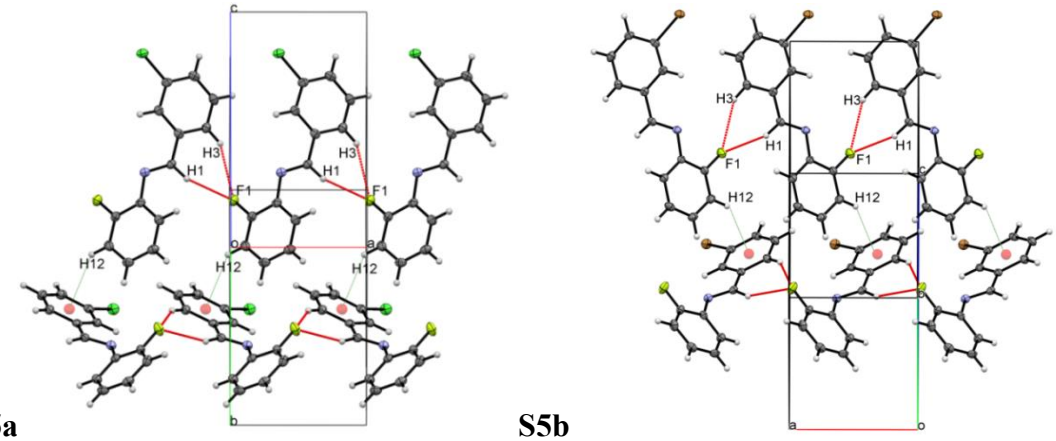
2-chloro-N-(3-fluorobenzylidene)aniline (48) and **2-bromo-N-(3-fluorobenzylidene)aniline (30)**

Among the compounds belonging to the sub-class **2c** (**6**, **30**, **48**), **6** was found to be solid at 25 °C and was found to crystallize in the monoclinic $P2_12_12_1$ space group utilizing C–H···F hydrogen bonds, and C–H···π interactions. Crystal structures of **48** and **30** could not be

determined as none of them could be crystallized when cooled from room temperature to -170 ^{o}C in a glass capillary on he diffractometer using Oxford cryosystem.

2-fluoro-N-(3-chlorobenzylidene)aniline (39) and **2-fluoro-N-(3-bromobenzylidene)aniline (21):**

Compound **39** and **21** were found to crystallize in the orthorhombic non-centrosymmetric $P2_12_12_1$ space group with Z = 4 with similar packing features. Molecules are found to extend along the *a*-axis in the form of chains through bifurcated weak C–H···F hydrogen bonds (involving H1 and H3 with F1). These chains have been found to be interlinked through type I inter-halogen C–F···X (X = Cl or Br) interactions along the *b*-axis (table 5, figure 5c and 5d). Further, weak C–H···π interactions (involving H12 with Cg1) were found to interconnect these chains by the utilization of 2_1 screw parallel to the *c*-axis (ESI, table S5, figure S5a and S5b).



S5a **S5b**

Figure S5: (a) Interconnecting molecular layers, which were found to form by weak C–H···F hydrogen bonds, through C–F···X (X = Cl or Br) interactions in **39** and **21** respectively **(b)** C–H···π interactions, which were found to interconnect these layers along *c*-axis.

Table S5: Intermolecular C–H···π interactions metrics for compounds **39** and **21**

Code	C–H ···π	C···π (Å)	H ···π (Å)	∠C–H ···π (^{o})	Symmetry Code
39	C12–H12···Cg1	3.73	2.93	143	3/2-x,-y,1/2+z
21	C12–H12···Cg1	3.75	2.94	144	1/2-x,1-,1/2+z

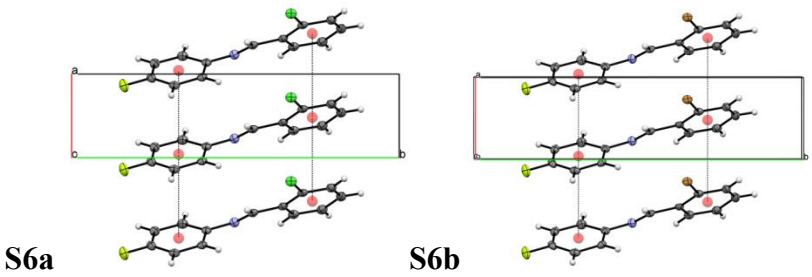
Structural comparison of the compounds belonging to class 3a and 4c:

4-chloro-N-(2-fluorobenzylidene)aniline (49) and **4-bromo-N-(2-fluorobenzylidene)aniline (31):**

Compounds **49** and **31** were found to be crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4. Chains have been found to form by the molecules *via* weak C–H···Cl and C–H···Br hydrogen bonds along *a*-axis in **49** and **31** respectively (table 6, figure 6b and 6c). Further, weak C–H···π interactions (involving H7 with Cg1) were found to hold these chains in both the compounds (ESI, table S6a), (figure 6b and 6c).

4-fluoro-N-(2-chlorobenzylidene)aniline (40) and **4-fluoro-N-(2-bromobenzylidene)aniline (22)**

Both the compounds **40** and **22** were found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4. Chains have been found to form along *c*-axis through C–H···X (X = Cl or Br) hydrogen bond in compound **40** and **22** (table 6, figure 6d and 6e). Very weak π···π interactions have been found along the *b*-axis between the two molecules of **40** or **22** in their respective crystal structures (ESI, table S6b, figure S6a and S6b).



S6a **S6b**

Figure S6: (a) weak π···π interactions between the molecules of **40** along *b*-axis. **(b)** weak π···π interactions between the molecules of **22** along *b*-axis.

Table S6a: Intermolecular C–H···π interactions metrics for compounds **49** and **31**

Code	C–H ···π	C···π (Å)	H ···π (Å)	∠C–H ···π (°)	Symmetry Code
31	C7–H7···Cg1	3.76	2.88	154	x,3/2-y,1/2+z
49	C7–H7··· Cg1	3.73	2.85	153	x,1/2-y,1/2+z

Table S6b: Intermolecular π···π interactions metrics for compounds **22**

Code	π···π	Cg1···Cg2 (Å)	(Cg1···Per)* (Å)	(Cg2···Per)**(Å)	Slippage	Symmetry Code
GK22F1	Cg1···Cg1	3.96	3.41	3.41	2.01	x,-1+y,z

Structural comparison of the compounds belonging to class 3b and 5c:

3-chloro-N-(2-fluorobenzylidene)aniline (50) and **3-bromo-N-(2-fluorobenzylidene)aniline (32):**

Compound **50** and **32** were found to be crystallized in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4. These compounds display similar structural features. Both the compounds were found to form hetero-dimers by the use of weak C–H···F hydrogen bonds, involving H9 and H1 with F1 (table 7, figure 7b and 7c) by the utilization 2_1 screw along *b*-axis. The molecular dimers have been found to be interconnected through C–H···F (again involving H9 and H1 with F1) hydrogen bonds and have been found to propagate along the crystallographic b-axis, thus generating a chain of hetero-dimers along that axis.

3-fluoro-N-(2-chlorobenzylidene)aniline (41) and **3-fluoro-N-(2-bromobenzylidene)aniline (23):**

Compounds **41** and **23** were found to crystallize in the orthorhombic non-centrosymmetric $P2_12_12_1$ space group with Z = 4. Molecules have been found to be disordered due to rotation of the aryl ring around N–C (Ar) bond. Therefore, fluorine atom is present on both the sides of the *meta* position of the ring (F1A and F1B) with 0.5 occupancy on each position. The disorder modelling has been done by partitioning the ring in two parts with 0.5 occupancies each for both **23** and **41** as described in the section under disorder refinement.

In both the compounds, linear chains have been found to form through C–H···F hydrogen bond (involving H5 with F1A) by the utilization of 2_1 screw parallel to the *c*-axis (table 7, Figure 7d and 7e). The atom F1B is found to be trifurcated and it forms hydrogen bonds with H1 and H9B, while it is also found to be involved in the type I inter-halogen C–F···X (X = Cl or Br) interactions in **41** and **23** respectively (table 7, Figure 7d and 7e).

Structural comparison of the compounds belonging to class 3c and 6c:

2-chloro-N-(2-fluorobenzylidene)aniline (51):

Compound **51** has been found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4 (Z' = 1). The molecule has been found to have a static disorder in the crystal lattice in which 55% of the molecule crystallizes in one orientation, while the remaining in other, by in plane 180^o rotation of the molecule around the C=N bond. Disorder refinement for the molecule has been explained in the disorder refinement section. Molecules have been found to form C–H···Cl hydrogen bonds (involving H6A with Cl1A). These dimers further interconnect with each other through another C–H···Cl hydrogen bond (involving H4A with Cl1A) and thus resulting into a tetrameric unit (table 8, figure 8c).

2-bromo-N-(2-fluorobenzylidene)aniline (33):

Compound **33** was found to crystallize in the monoclinic centrosymmetric *Pbcn* space group with Z = 8. The molecule is found to be disordered and displays positional disorder around C=N bond with the occupancy ratio 0.9 : 0.1. The disorder was analysed using PART command in SHELXL97 and refined for two independent positions, namely A and B ('A' for higher occupancy), which has been described. The atoms in the major conformer of the molecule are considered for intermolecular interactions analysis.

Molecules related by center of inversion have been found to form dimers through weak C–H···Br hydrogen bond and these dimers were found to propagate in the lattice through C–H···π interactions by the utilization of *c* glide (table 8, figure 8d).

2-fluoro-N-(2-chlorobenzylidene)aniline (42):

Compound **42** was found to crystallize in the orthorhombic centrosymmetric *Pbca* space group with Z = 8. The molecules of **42** have been found to interact through the formation of hetero dimers using weak C–H···F and C–H···N hydrogen bonds (involving H11 with F1 and H12 with N1) by the utilization of 2_1 screw parallel to the *b*-axis in the *bc* plane (table 8, figure 8e). Heterodimers involving C–H···F and C–H···Cl hydrogen bonds (involving H5 with F1 and H6 with Cl1) have also been found to form between the molecules related by 2_1 screw along *a*-axis. Then these dimers have been found to propagate in the *ac* plane by another set of C–H···F hydrogen bonds (involving H9 with F1) and a weak C–Cl···π interactions (ESI, table S7) involving Cl1 with Cg2 through *a* glide perpendicular to *c*-axis (Table 8, figure 8f).

2-fluoro-N-(2-bromobenzylidene)aniline (24):

Compound **24** was found to crystallize in the monoclinic centrosymmetric $P2_1/c$ space group with Z = 4. The molecules related by the center of inversion have been found to form dimers through C–H···F hydrogen bonds involving H12 with F1. These dimers have been found to be interconnected by another group of C–H···F hydrogen bonds involving H6 and H5 with F1 (Table 8, figure 8g). In this case, the F atom has been found to be trifurcated and the Br atom in the A ring has not been found to get involved in any kind of intermolecular interactions.

Table S7: Intermolecular C–H···π and C–Cl···π interactions metrics for compounds **33** and **42** respectively.

Code	C–X···π (X = H, Cl)	C···π (Å)	X···π (Å)	∠C–X···π (°)	Symmetry Code
33	C4A–H4A···Cg2	3.53	2.62	160	x,-y,-1/2+z
42	C3–Cl1···Cg2	5.18	3.56	154	-1/2+x,y,1/2-z

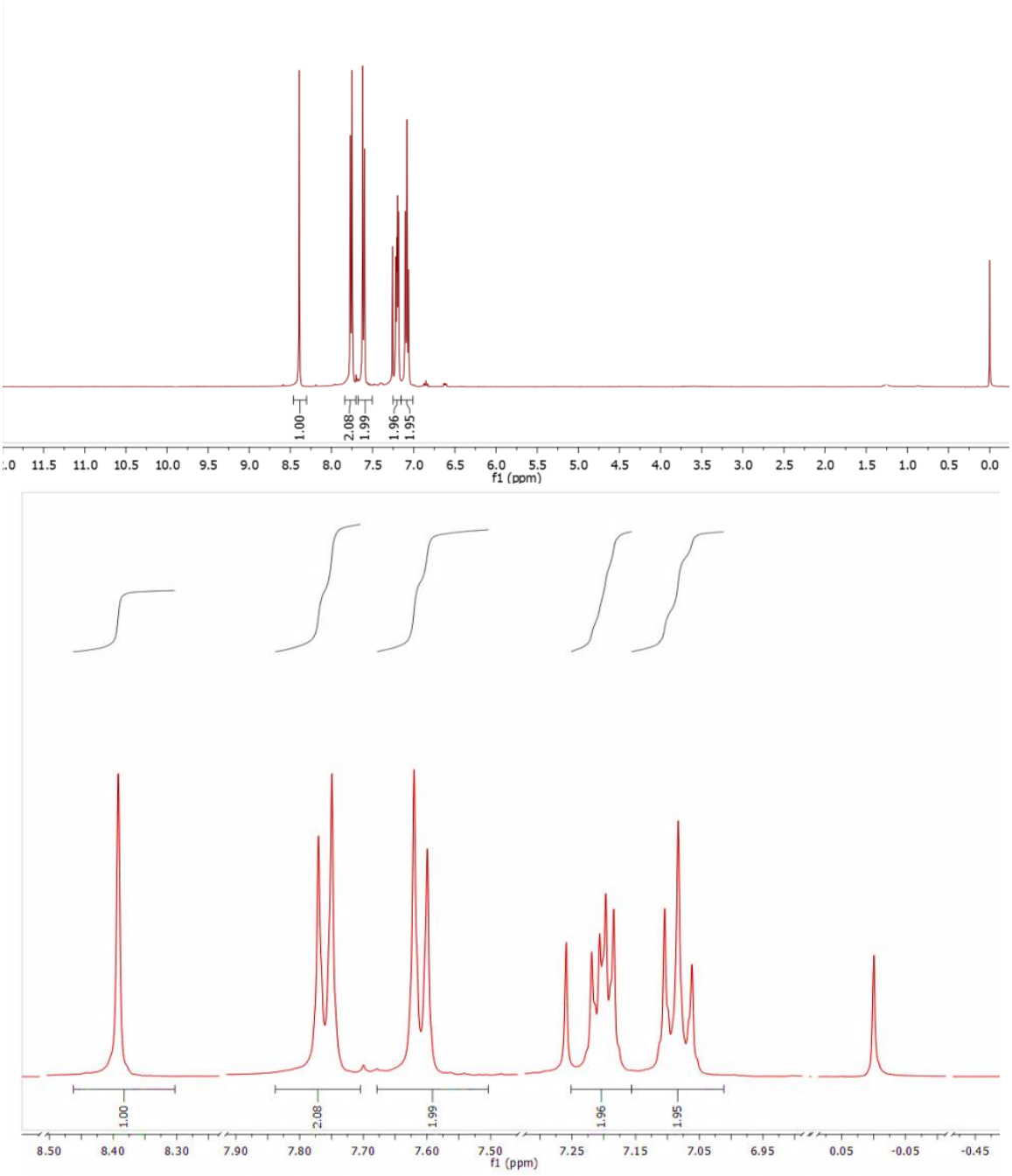
Table S8: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs and the bond paths (R_{ij}) as calculated by AIM2000, which are found in the structures reported herein

Code	C–H···F	*d* H···F /Å	θ ∠C–H···F/^{o}	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})	R_{ij}(Å)
1	C6–H6···F2	2.67	131	0.027	0.555	2.70
	C12–H12···F1	2.69	130	0.027	0.555	2.70
43	C13-H13···F2	2.44	150	0.047	0.893	2.46
	C26-H26···F1	2.51	143	0.041	0.772	2.54
34	C12–H12···F1	2.56	153	0.035	0.694	2.58
16F1	C12–H12···F1	2.57	153	0.034	0.676	2.59
16F2	C1-H1···F1	2.68	153	0.027	0.531	2.71
	C14–H14···F2	2.68	155	0.027	0.555	2.70
2	C6-H6···F1	2.52	128	0.039	0.758	2.60
	C11-H11···F2	2.55	134	0.038	0.695	2.60
	C13-H13···F2	2.55	161	0.036	0.707	2.59
44	C11-H11···F1	2.52	164	0.036	0.71	2.54
26	C11-H11···F1	2.63	166	0.027	0.548	2.65
35	C1-H1···F1	2.56	153	0.036	0.678	2.59
	C9-H9···F1	2.76	156	0.023	0.471	2.79
17	C1-H1···F1	2.58	155	0.034	0.659	2.60
	C9-H9···F1	2.66	162	0.03	0.589	2.68
3	C1-H1···F2	2.32	162	0.068	1.11	2.35
	C14-H14···F4	2.3	161	0.068	1.135	2.34
	C10-H10···F1	2.66	131	0.034	0.603	2.70
36F1	C1-H1···F1	2.4	160	0.056	0.987	2.42
18F1	C1-H1···F1	2.44	156	0.054	0.958	2.46
18F2	C1-H1···F1	2.35	168	0.06	1.045	2.38
	C14-H14···F2	2.41	159	0.054	0.958	2.43
	C23-H23···F1	2.43	142	0.049	0.927	2.46
36F2	C1-H1···F1	2.37	173	0.054	0.99	2.40
	C14-H14···F2	2.38	168	0.054	0.99	2.41
4	C13A–H13A···F3A	2.59	160	0.032	0.642	2.63
	C16A–H16A···F1A	2.62	157	0.031	0.606	2.67
	C18A–H18A···F3A	2.53	135	0.04	0.77	2.58
	C23A–H23A···F4A	2.56	140	0.035	0.69	2.61
	C5A–H5A···F1A	2.56	136	0.037	0.715	2.61
	C5A–H5A···F2A	2.7	128	0.026	0.543	2.74
46	C5-H5···F1	2.62	136	0.034	0.659	2.65
	C9-H9···F1	2.7	156	0.023	0.48	2.72
28F1	C5-H5···F1	2.65	138	0.031	0.616	2.68

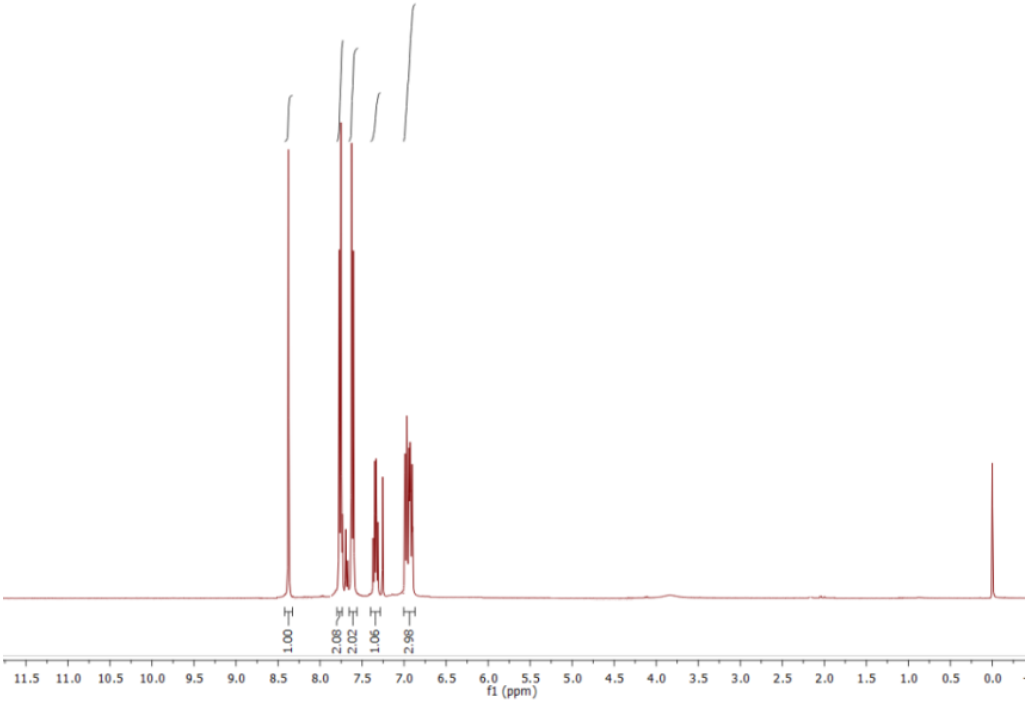
	C9-H9···F1	2.65	156	0.026	0.536	2.68
37	C10-H10···F1	2.62	126	0.031	0.623	2.67
19	C10-H10···F1	2.63	126	0.031	0.618	2.68
6	C1–H1···F1	2.47	163	0.041	0.768	2.51
39	C1-H1···F1	2.46	153	0.048	0.864	2.49
	C3-H3···F1	2.66	149	0.027	0.558	2.69
21	C1-H1···F1	2.49	152	0.045	0.823	2.52
	C3-H3···F1	2.64	150	0.029	0.594	2.66
7	C6A–H6A···F1	2.61	127	0.035	0.596	2.66
	C6A–H6A···F2	2.54	136	0.041	0.775	2.57
	C1–H1···F1	2.32	146	0.067	1.154	2.35
8	C9-H9···F1	2.55	169	0.038	0.734	2.56
	C1-H1···F1	2.67	157	0.03	0.584	2.68
50	C9-H9···F1	2.61	164	0.032	0.628	2.64
	C1-H1···F1	2.69	155	0.027	0.546	2.71
32	C9-H9···F1	2.66	163	0.029	0.57	2.68
	C1-H1···F1	2.7	154	0.026	0.531	2.72
41	C1-H1···F1B	2.61	167	0.028	0.575	2.61
	C9B-H9B···F1B	2.56	125	0.043	0.797	2.60
	C5-H5···F1A	2.57	124	0.043	0.797	2.64
23	C1-H1···F1B	2.66	163	0.025	0.521	2.68
	C9B-H9B···F1B	2.55	126	0.043	0.801	2.60
	C5-H5···F1A	2.62	124	0.029	0.716	2.67
9F1	C6–H6···F2	2.68	131	0.026	0.56	2.70
9F2	C5–H5···F2	2.62	132	0.028	0.558	2.65
	C12–H12···F2	2.64	176	0.027	0.555	2.67
42	C11-H11···F1	2.6	131	0.037	0.715	2.64
	C9-H9···F1	2.6	142	0.035	0.676	2.63
	C5-H5···F1	2.53	139	0.036	0.719	2.55
24	C5-H5···F1	2.65	124	0.029	0.608	2.70
	C6-H6···F1	2.69	122	0.029	0.601	2.74

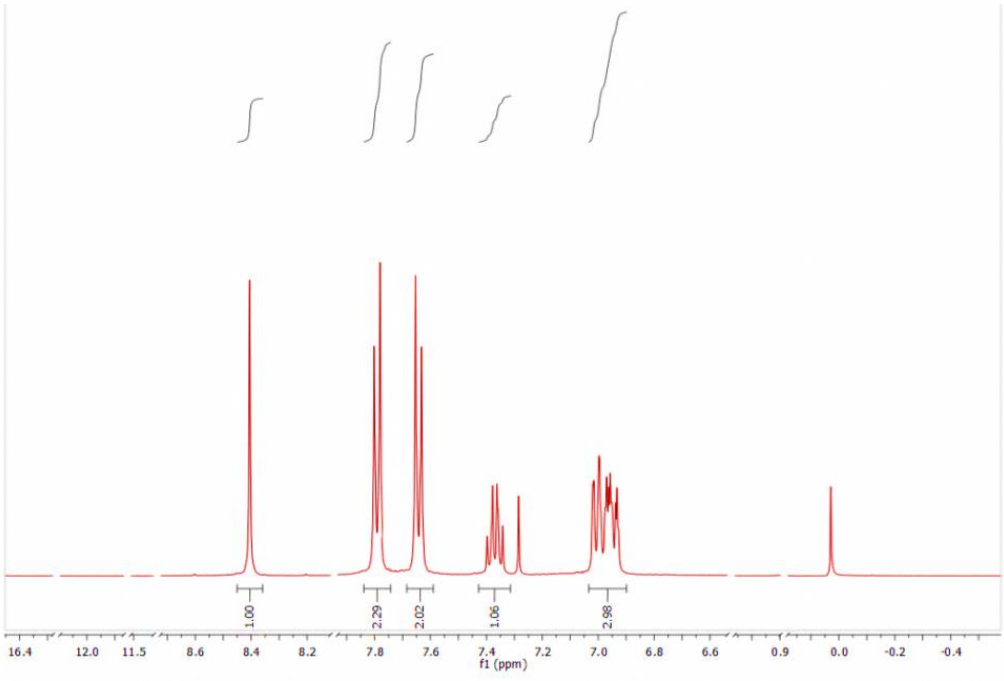
Figure S1: ^{1}H NMR of all compounds: All NMR experiments were recorded on 400 MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

FigureS1:1 **Compound 16:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 1H), 7.75-7.77 (d, 2H), 7.60-7.62 (d, 2H), 7.18-7.22 (m, 2H), 7.06-7.10 (t, 2H)

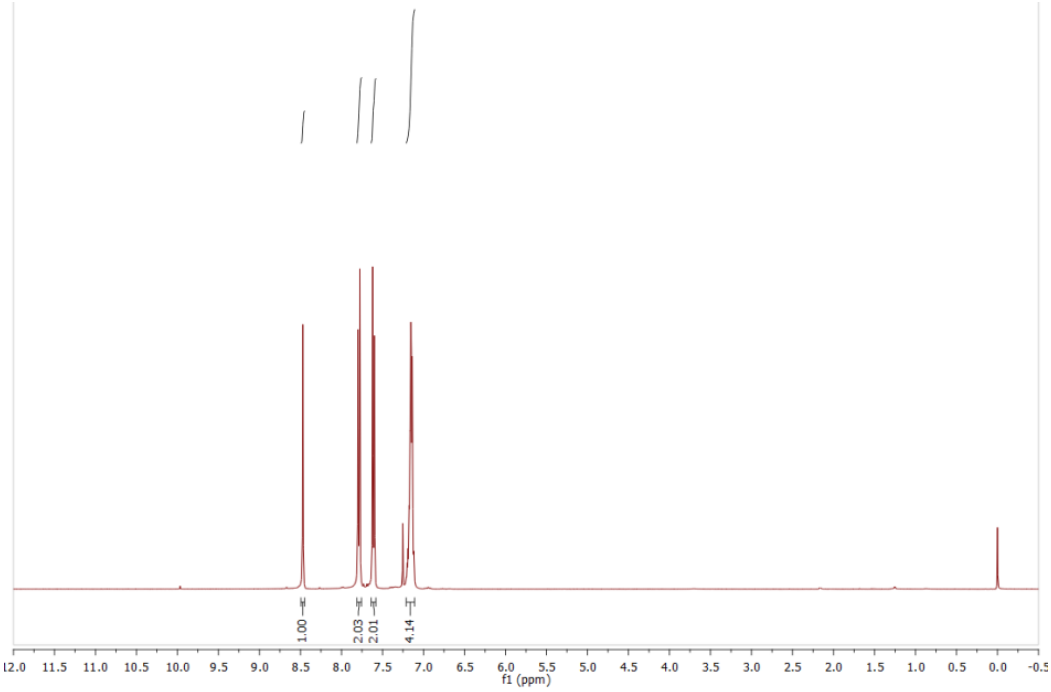


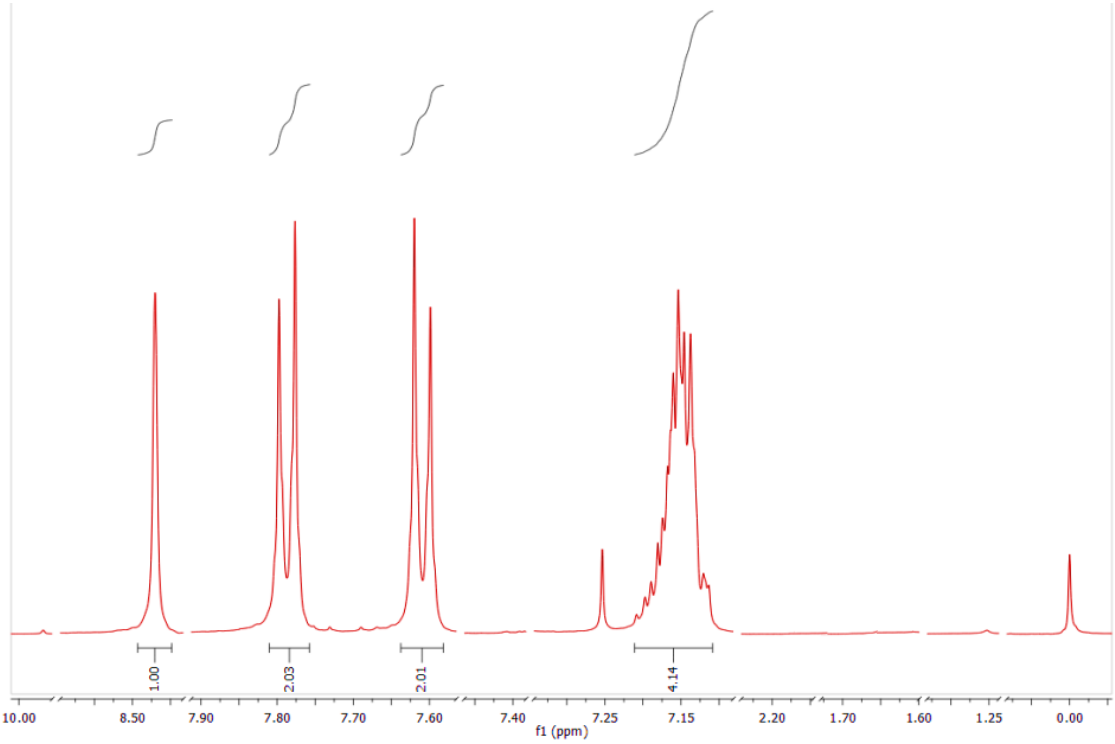
FigureS1:2 **Compound 17:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.41 (s, 1H), 7.78-7.80 (d, 2H), 7.63-7.65 (d, 2H), 7.34-7.40 (q, 1H), 6.93-7.02 (m, 3H).



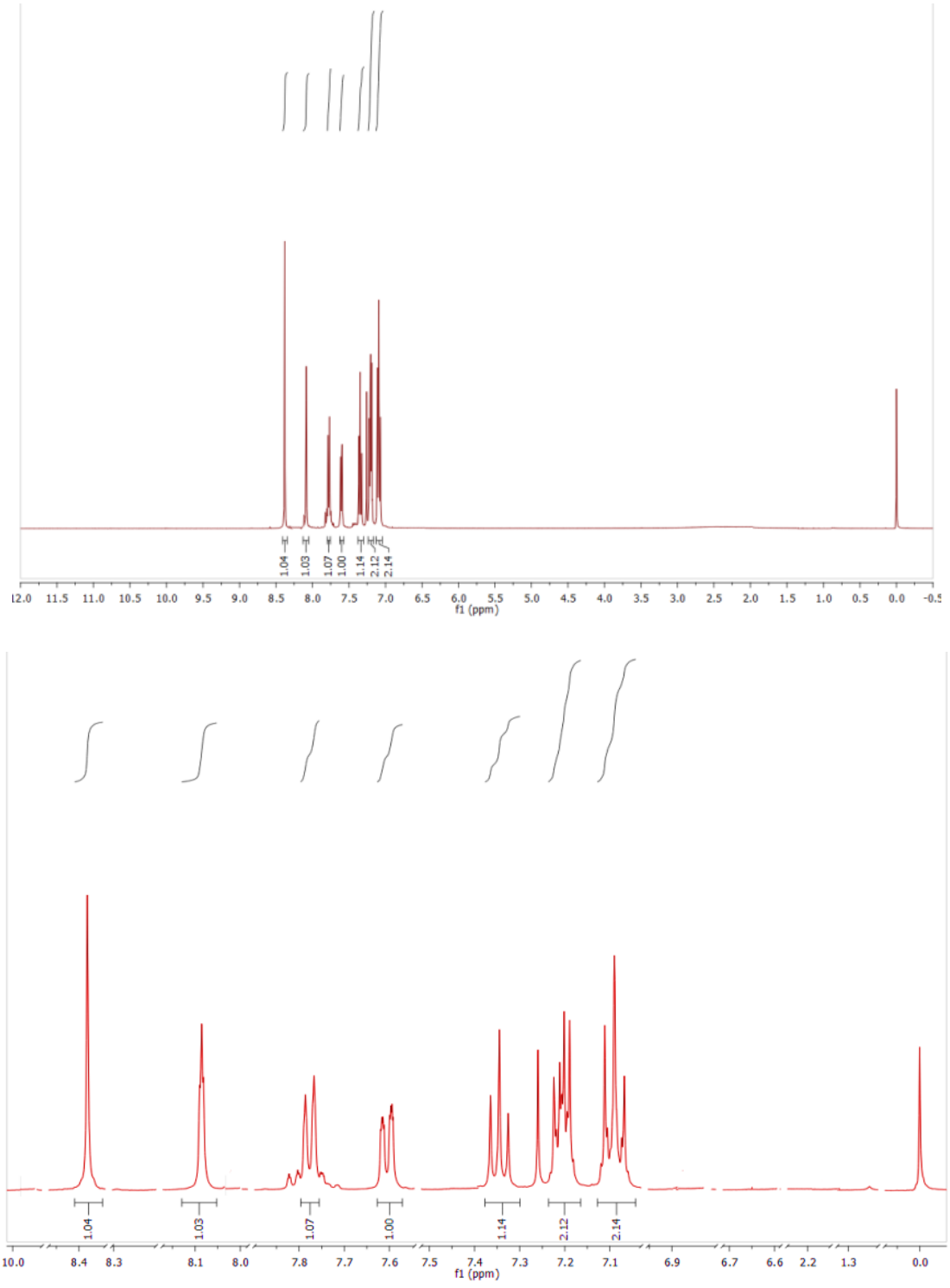


FigureS1:3 **Compound 18:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.47 (s, 1H), 7.78-7.80 (d, 2H), 7.60-7.62 (d, 2H), 7.11-7.20 (m, 4H),

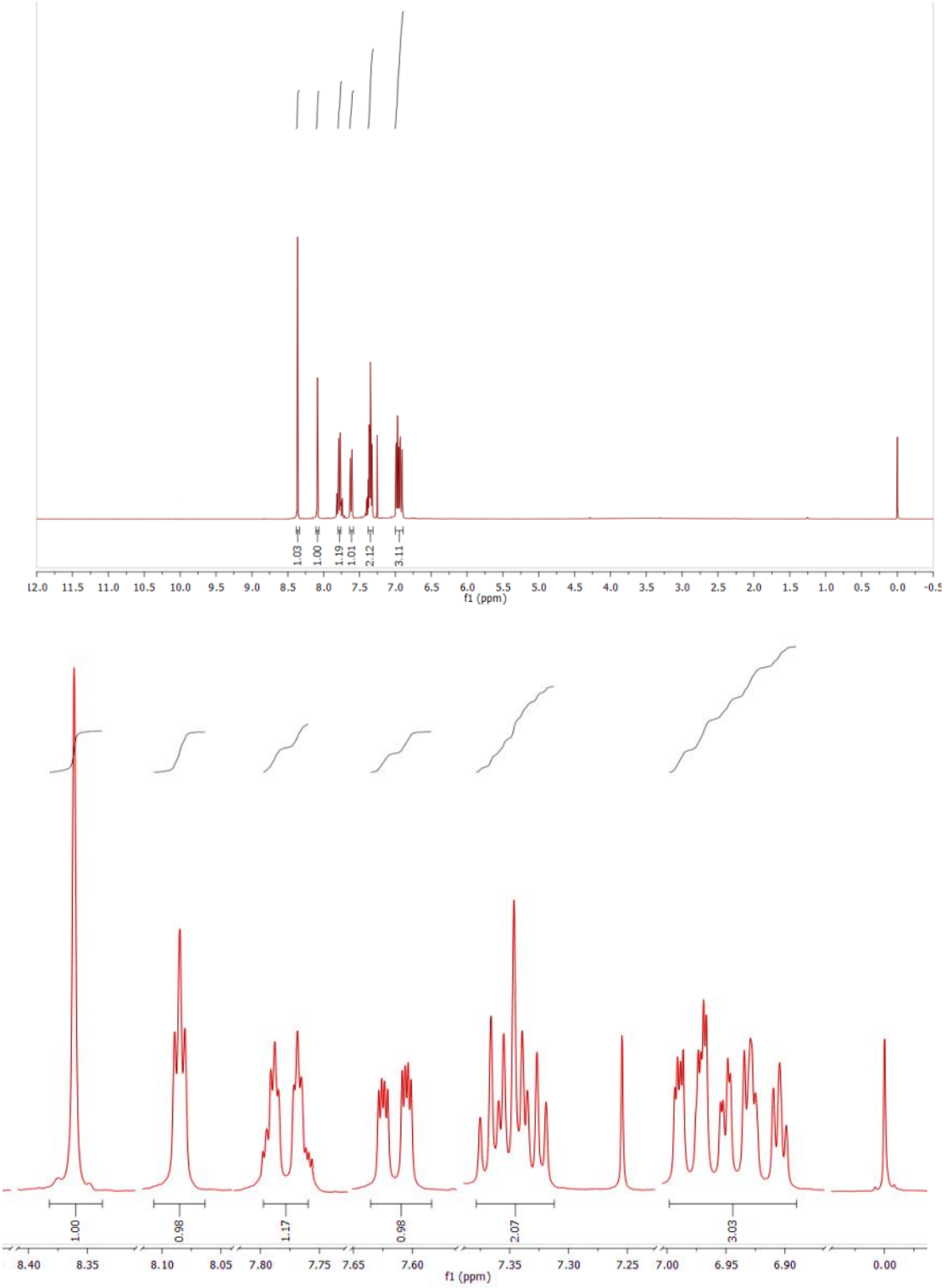




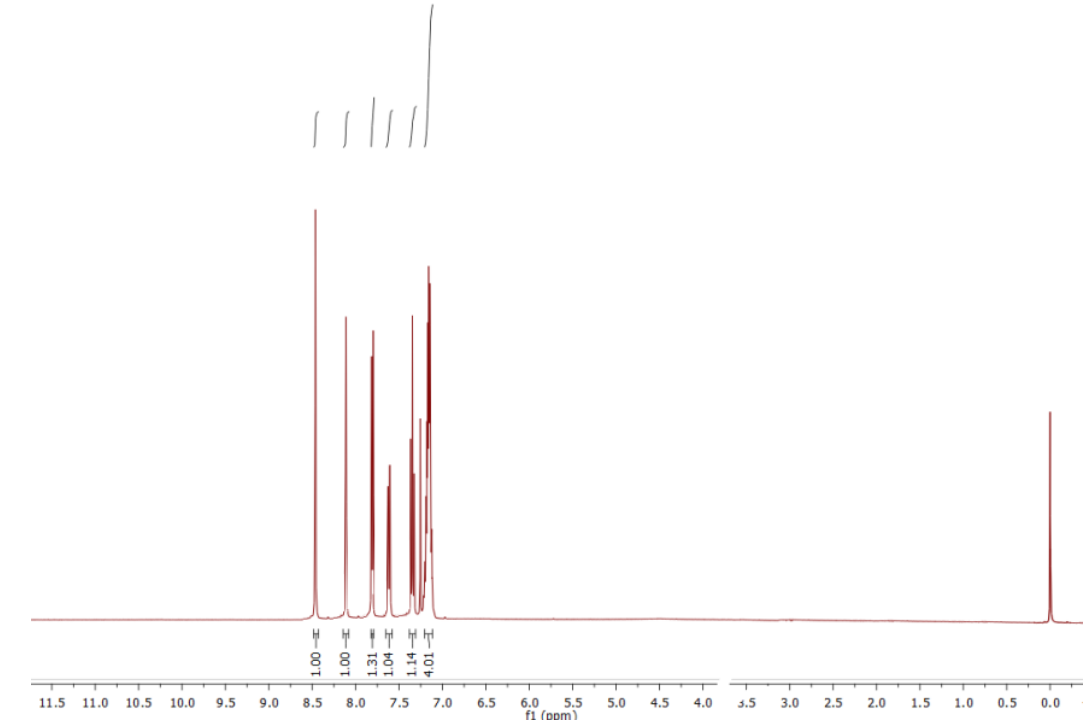
FigureS1:4 **Compound 19:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.38 (s, 1H), 8.09 (s, 1H), 7.77-7.79 (d, 1H), 7.59-7.61 (d, 1H), 7.33-7.36 (t, 1H), 7.19-7.22 (m, 2H), 7.07-7.11 (m, 2H),

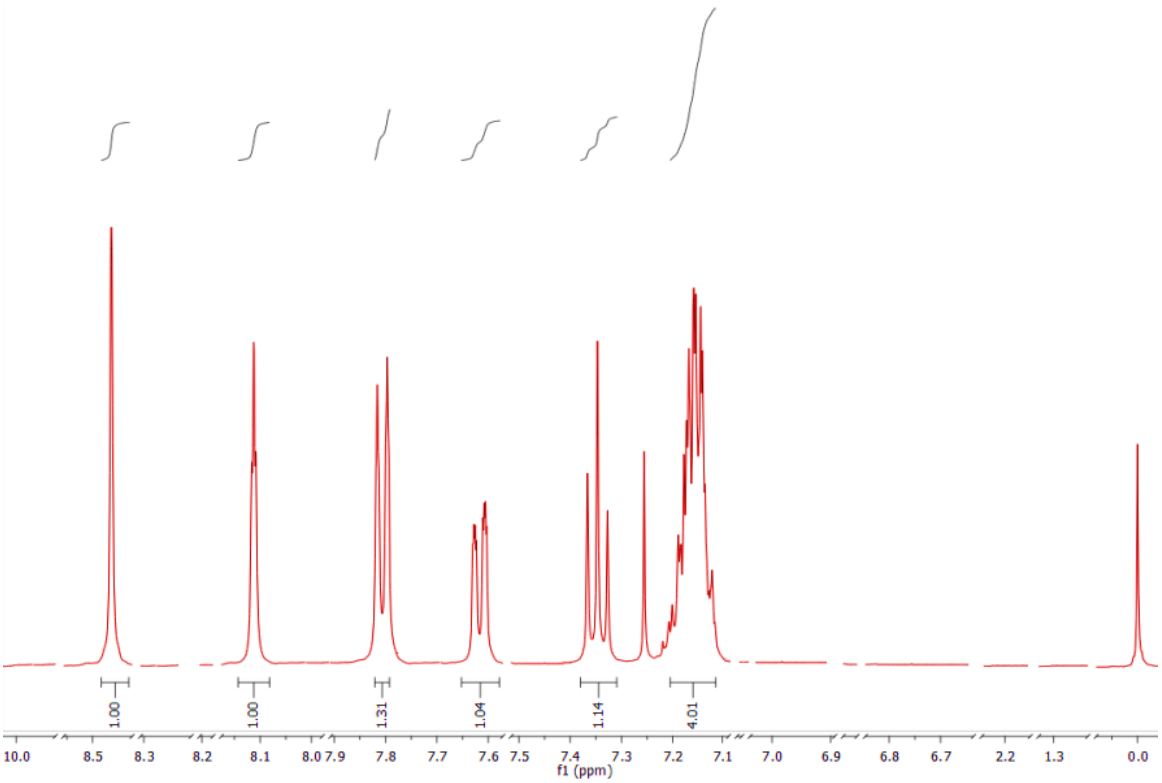


FigureS1:5 **Compound 20:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.36 (s, 1H), 8.08-8.09 (t, 1H), 7.77-7.79 (dt, 1H), 7.61-7.63 (m, 1H), 7.33-7.37 (m, 2H), 6.90-6.99 (m, 3H),

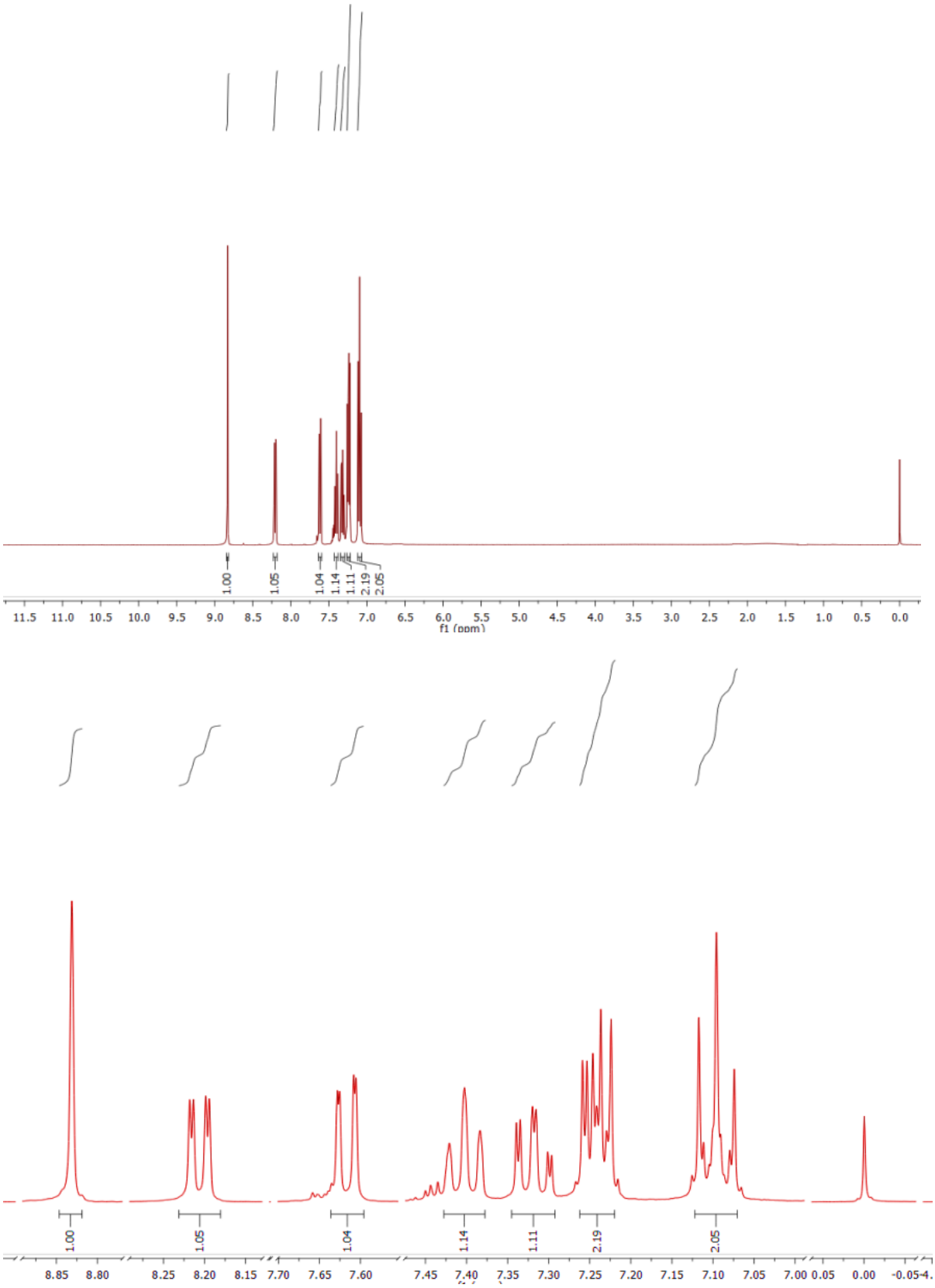


FigureS1:6 **Compound 21:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 8.14-8.15 (t, 1H), 7.83-7.85 (d, 1H), 7.63-7.66 (m, 1H), 7.36-7.40 (t, 1H), 7.15-7.24 (m, 4H)

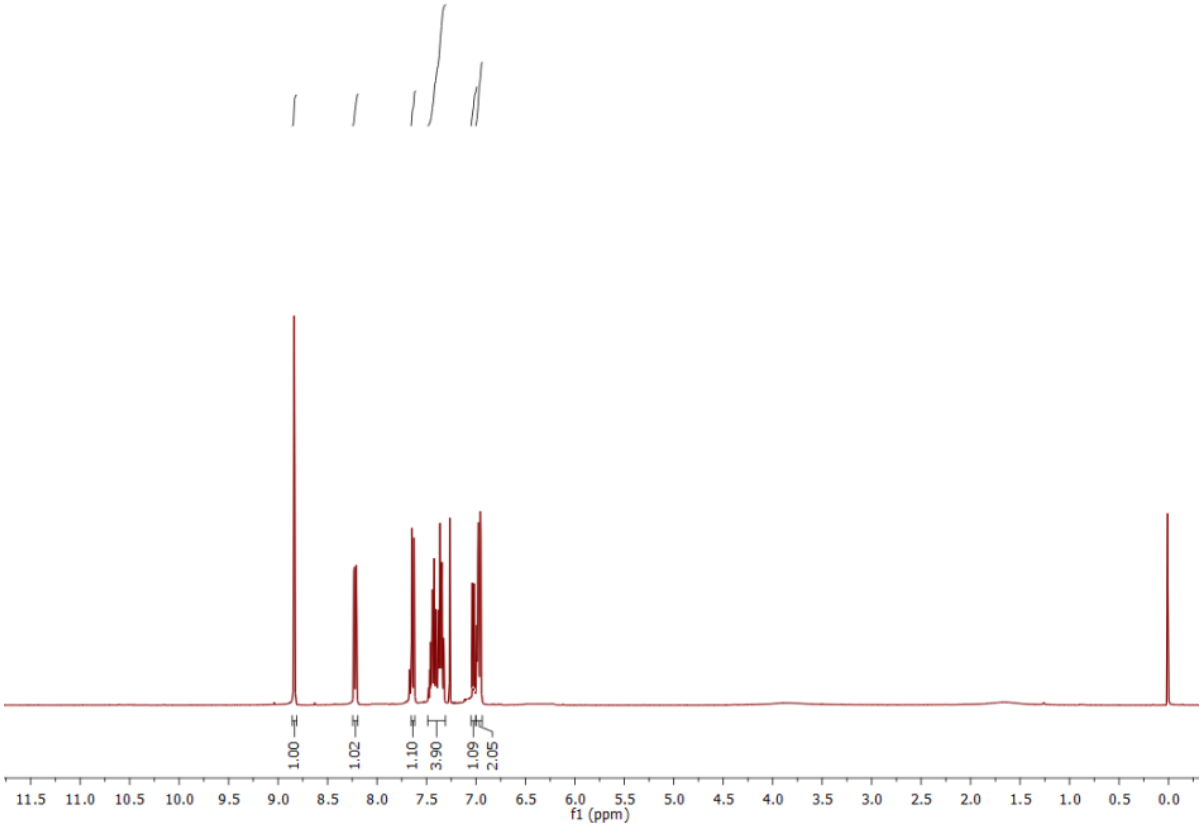


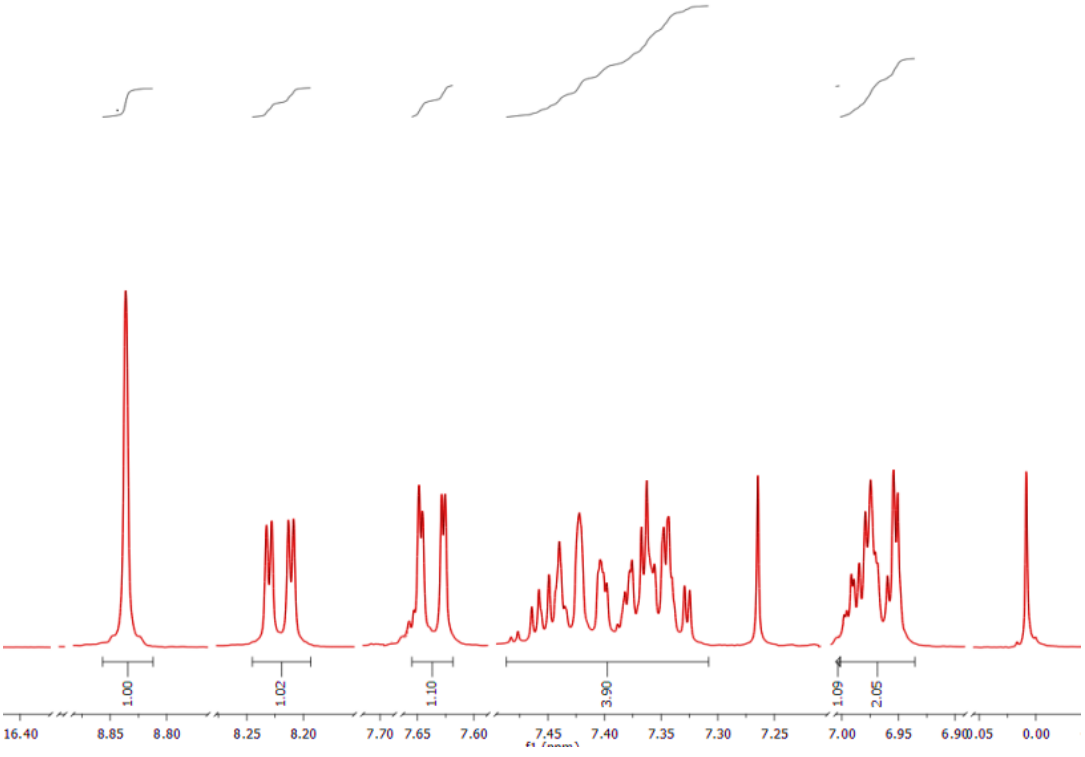


FigureS1:7 **Compound 22:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.83 (s, 1H), 8.19-8.22 (dd, 1H), 7.61-7.63 (dd, 1H), 7.38-7.42 (t, 1H), 7.30-7.34 (td, 1H), 7.22-7.25 (m, 2H), 7.07-7.13 (m, 2H)

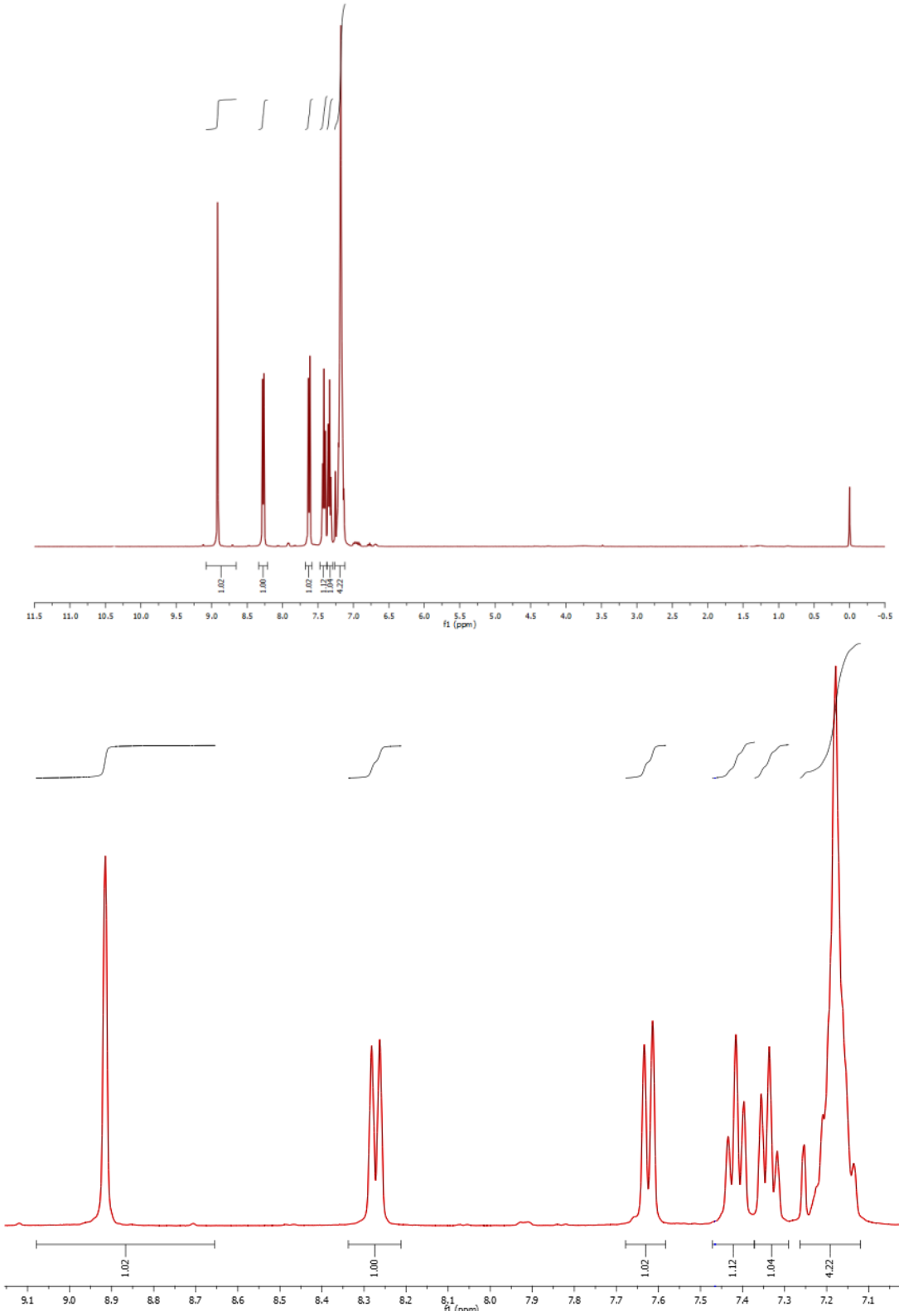


FigureS1:8 **Compound 23:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.84 (s, 1H), 8.21-8.23 (dd, 1H), 7.63-7.65 (q, 1H), 7.32-7.48 (m, 4H), 6.97-7.00 (m, 2H)

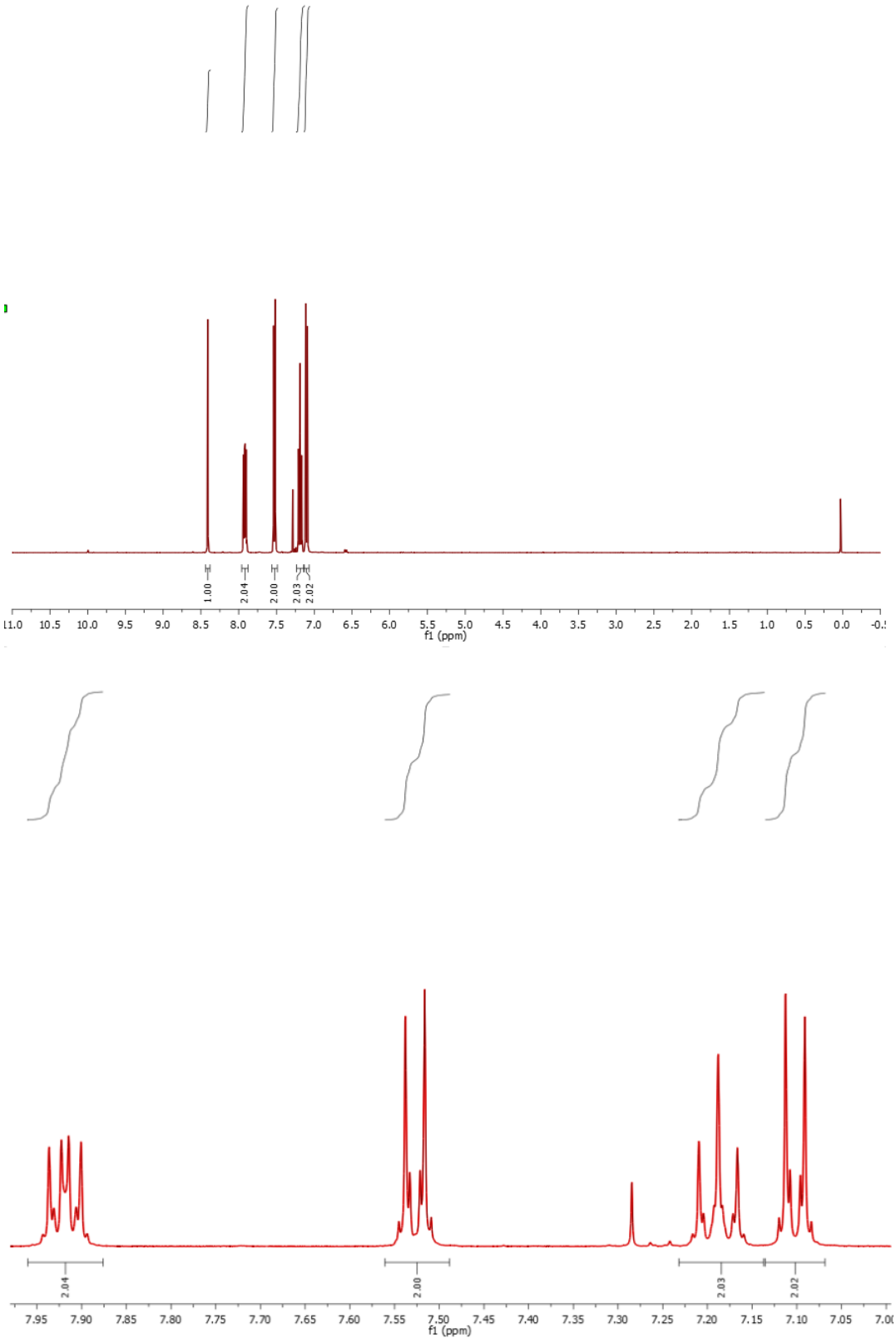




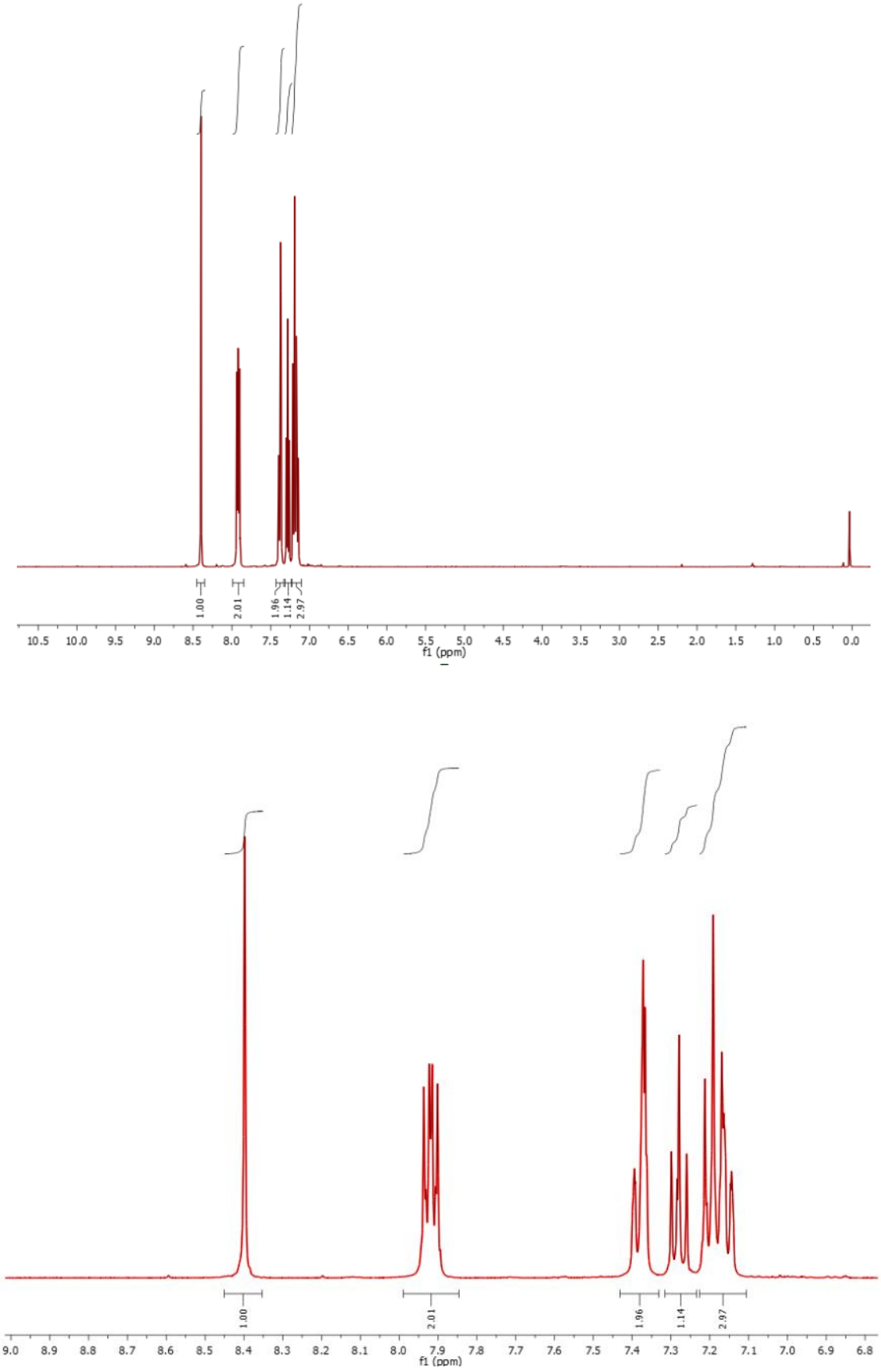
FigureS1:9 **Compound 24:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.91 (s, 1H), 8.26-8.28 (d, 1H), 7.61-7.63 (d, 1H), 7.32-7.43 (dt, 2H), 7.13-7.25 (m, 4H)



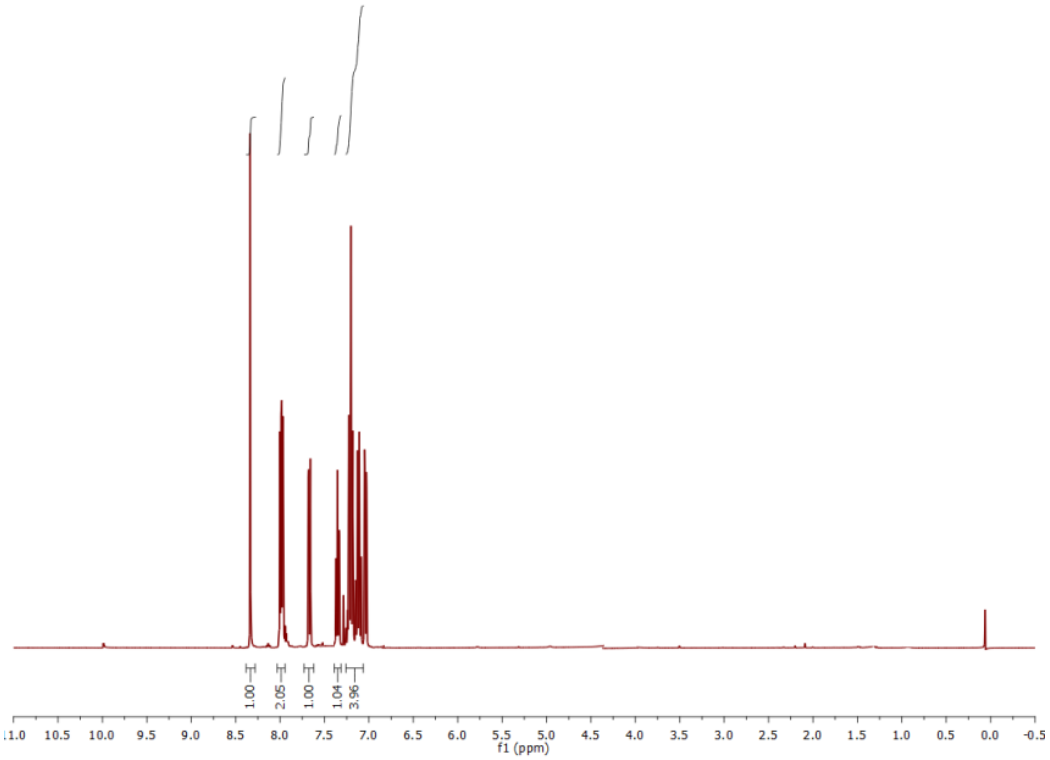
FigureS1:10 **Compound 25:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.41 (s, 1H), 8.26-8.28 (q, 2H), 7.51-7.54 (d, 2H), 7.16-7.21 (t, 2H), 7.09-7.11 (d, 2H)

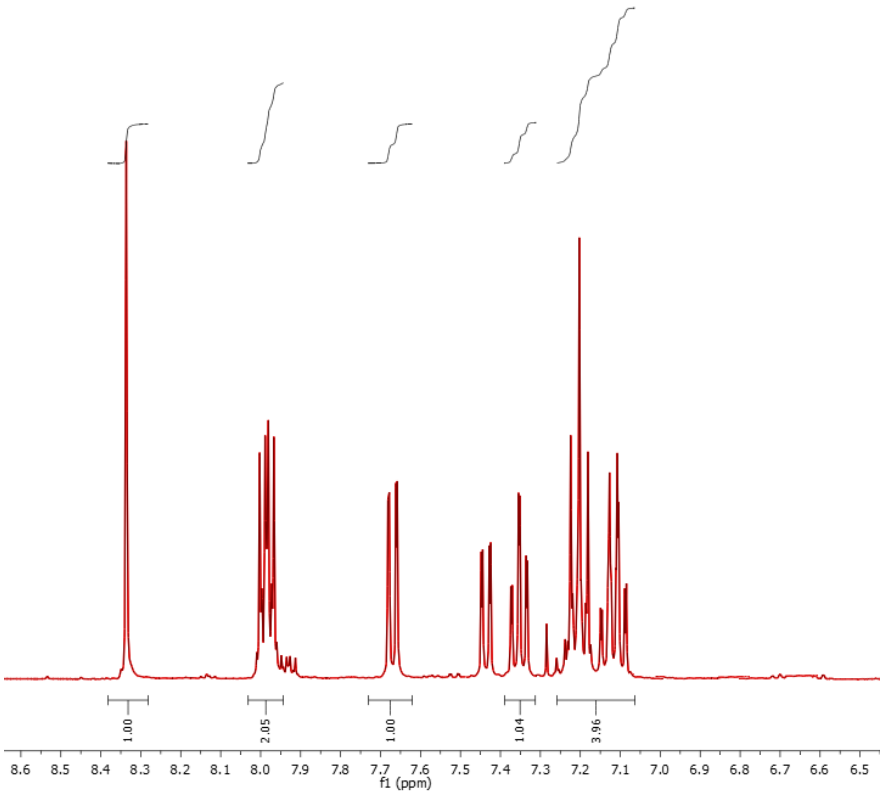


FigureS1:11 **Compound 26:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.40 (s, 1H), 7.90-7.93 (q, 2H), 7.36-7.40 (d, 2H), 7.26-7.30 (t, 1H), 7.14-7.21 (m, 3H)

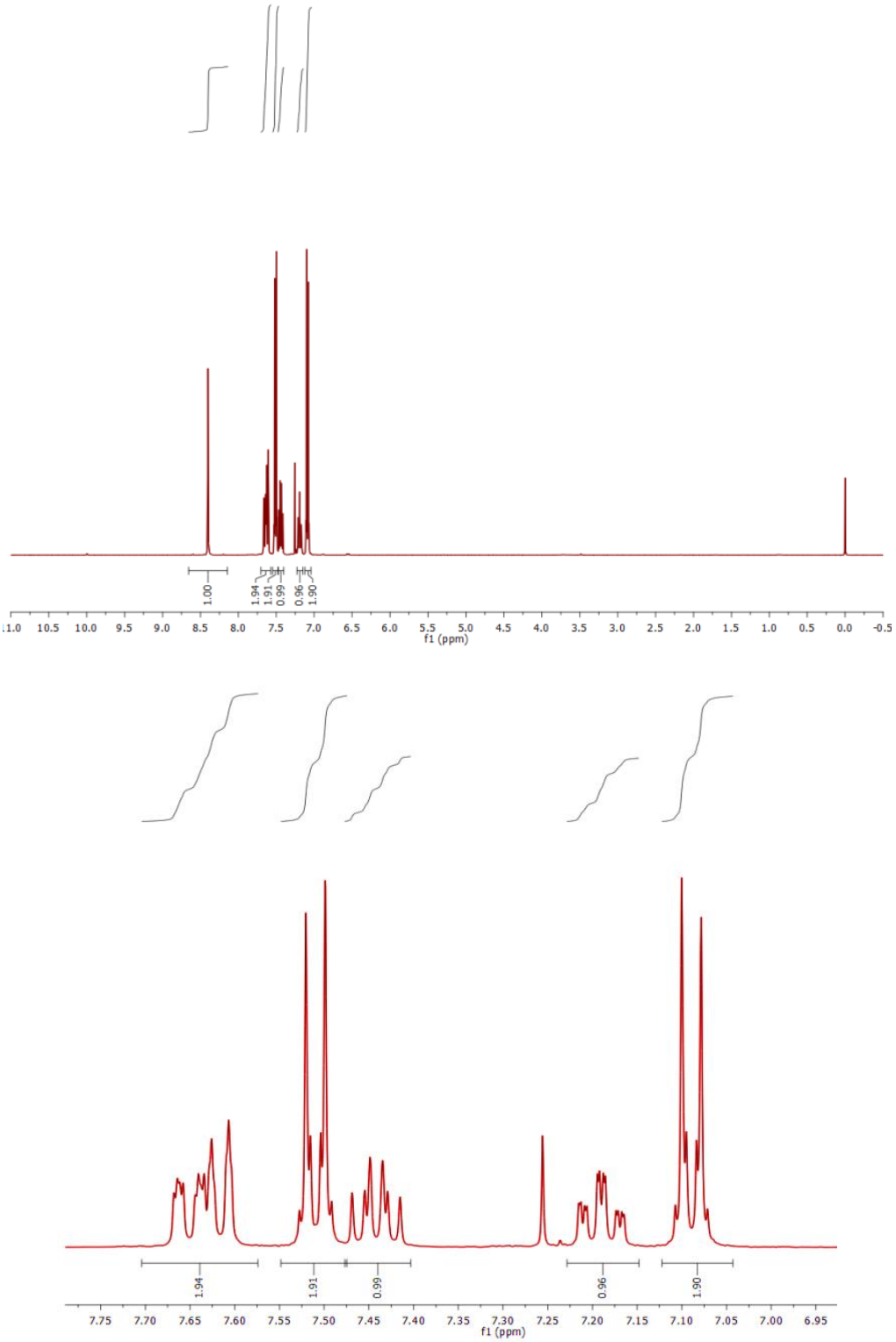


FigureS1:12 **Compound 27:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.33 (s, 1H), 7.97-8.00 (q, 2H), 7.65-7.68 (d, 1H), 7.33-7.37 (t, 1H), 7.08-7.26 (m, 4H)

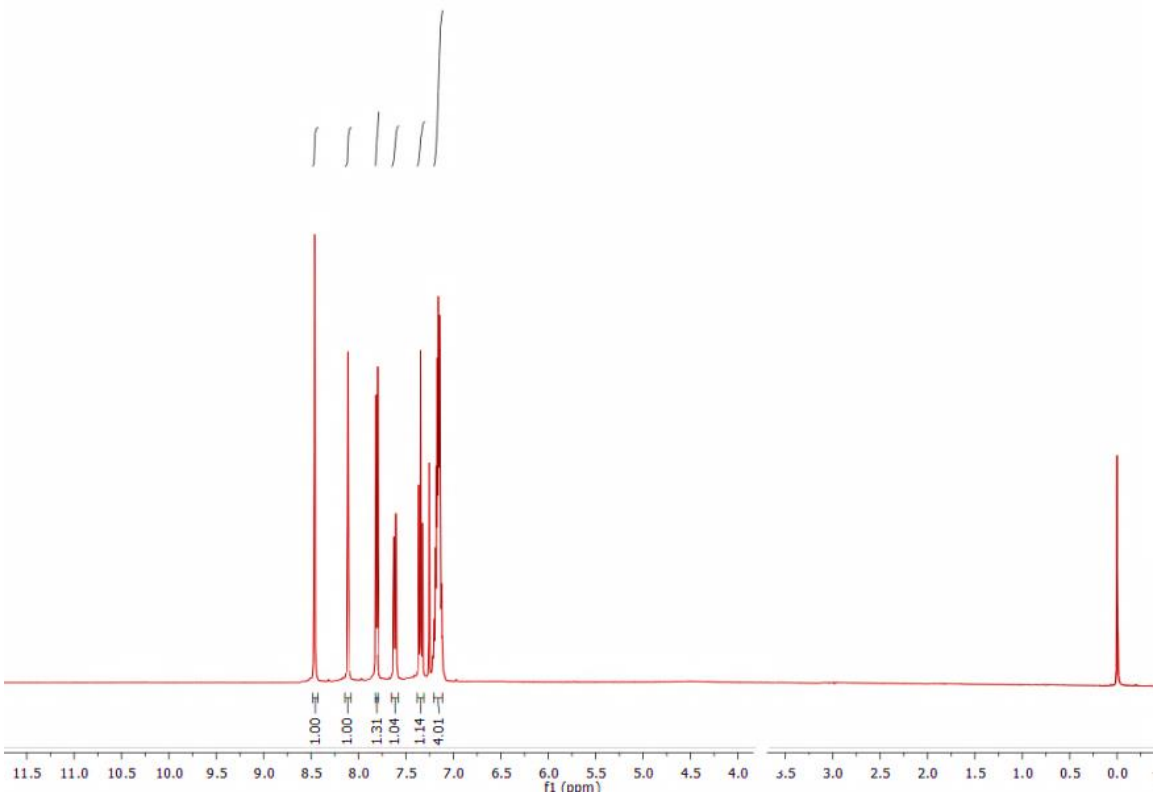


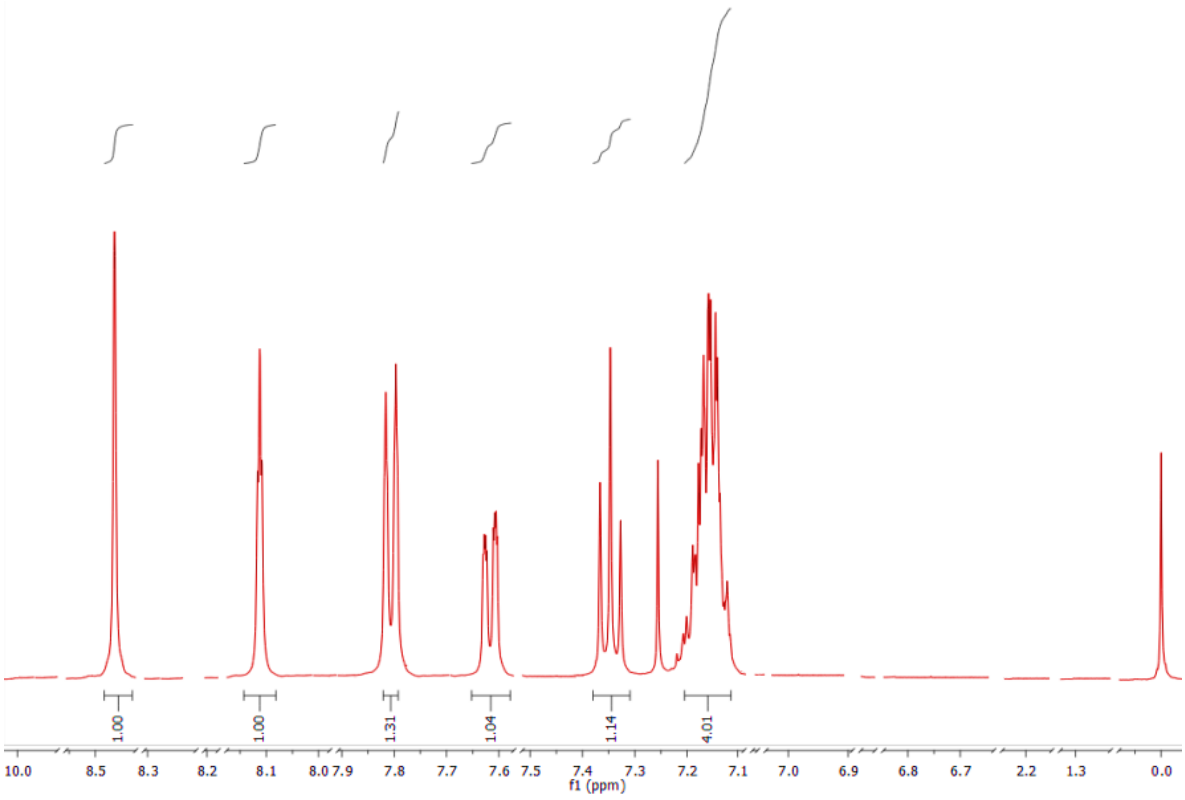


FigureS1:13 **Compound 28:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.33 (s, 1H), 7.60-7.67 (m, 2H), 7.49-7.53 (m, 2H), 7.41-7.47 (q, 1H), 7.16-7.21 (m 1H), 7.07-7.11 (m, 2H)

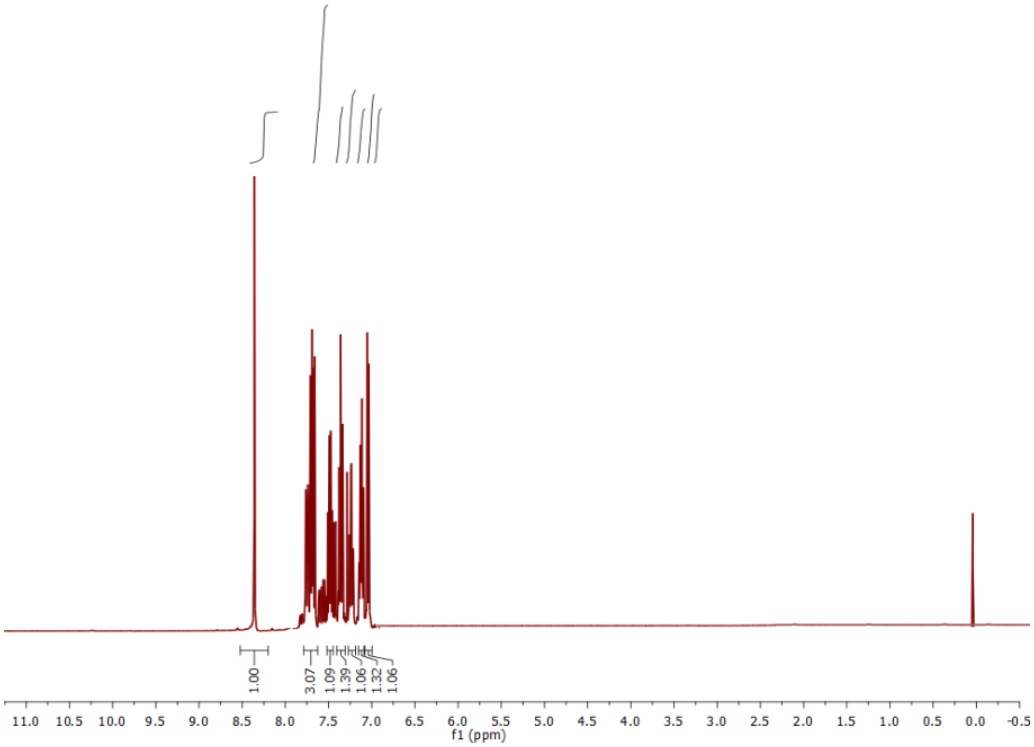


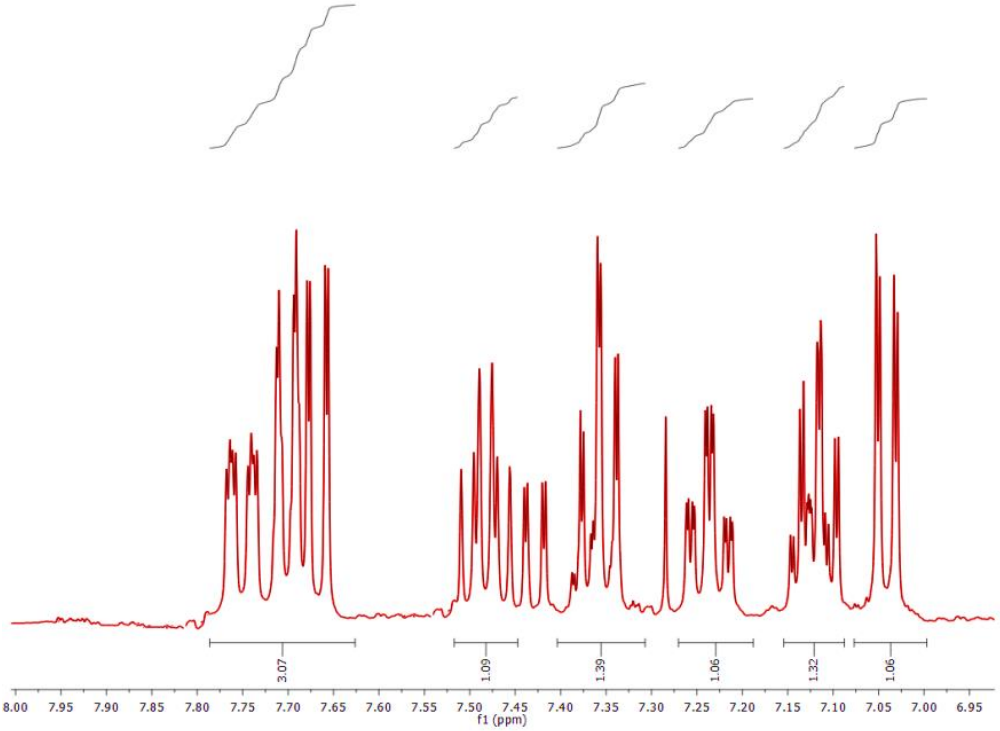
FigureS1:14 **Compound 29:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 8.14-8.15 (t, 1H), 7.83-7.85 (d, 1H), 7.63-7.66 (m, 1H), 7.36-7.40 (t, 1H), 7.15-7.24 (m, 4H)



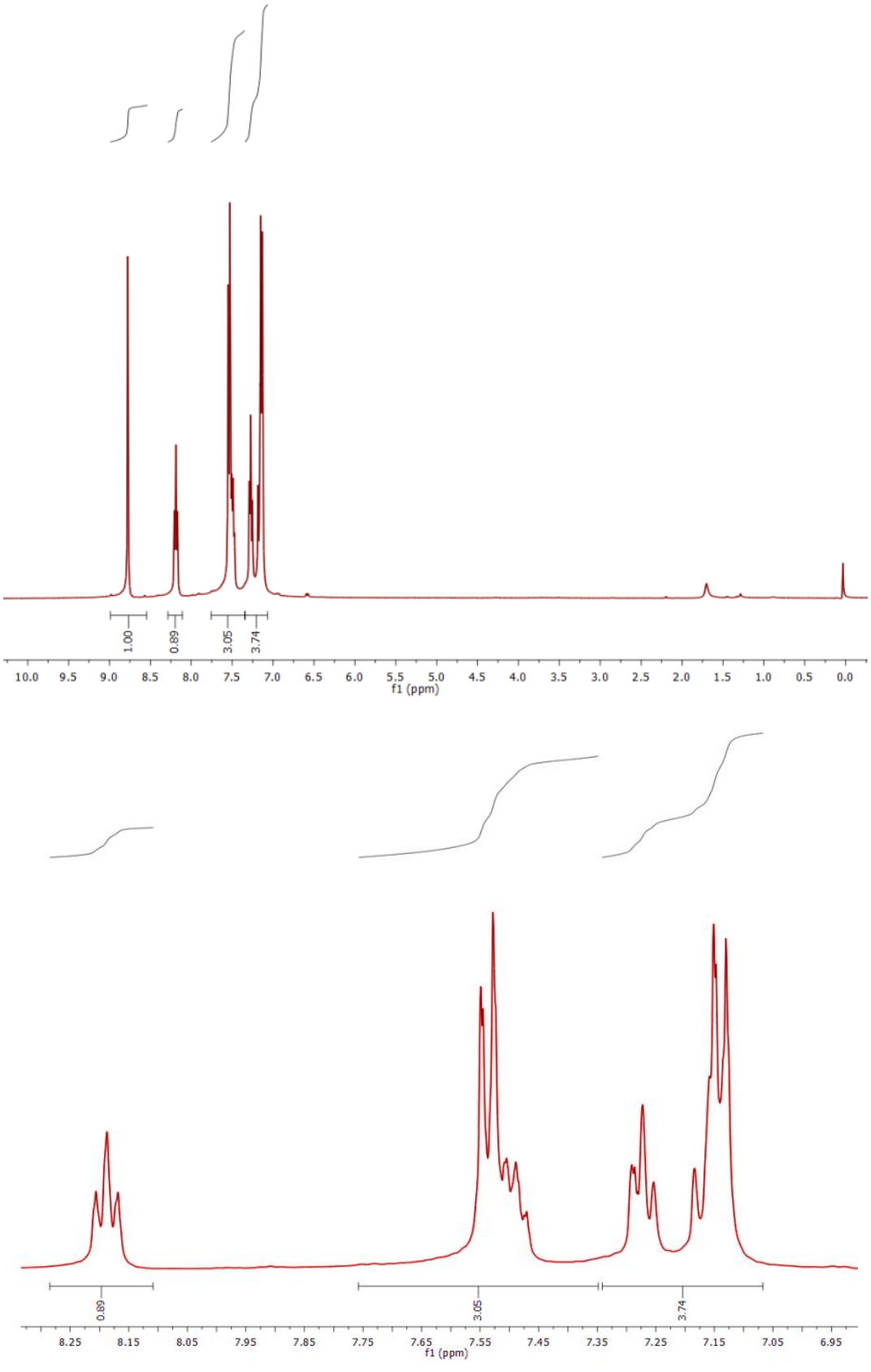


FigureS1:15 **Compound 30:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 7.66-7.77 (m, 3H), 7.45-7.51 (m, 1H), 7.33-7.38 (m, 1H), 7.21-7.26 (t, 1H), 7.02-7.05 (d, 1H)

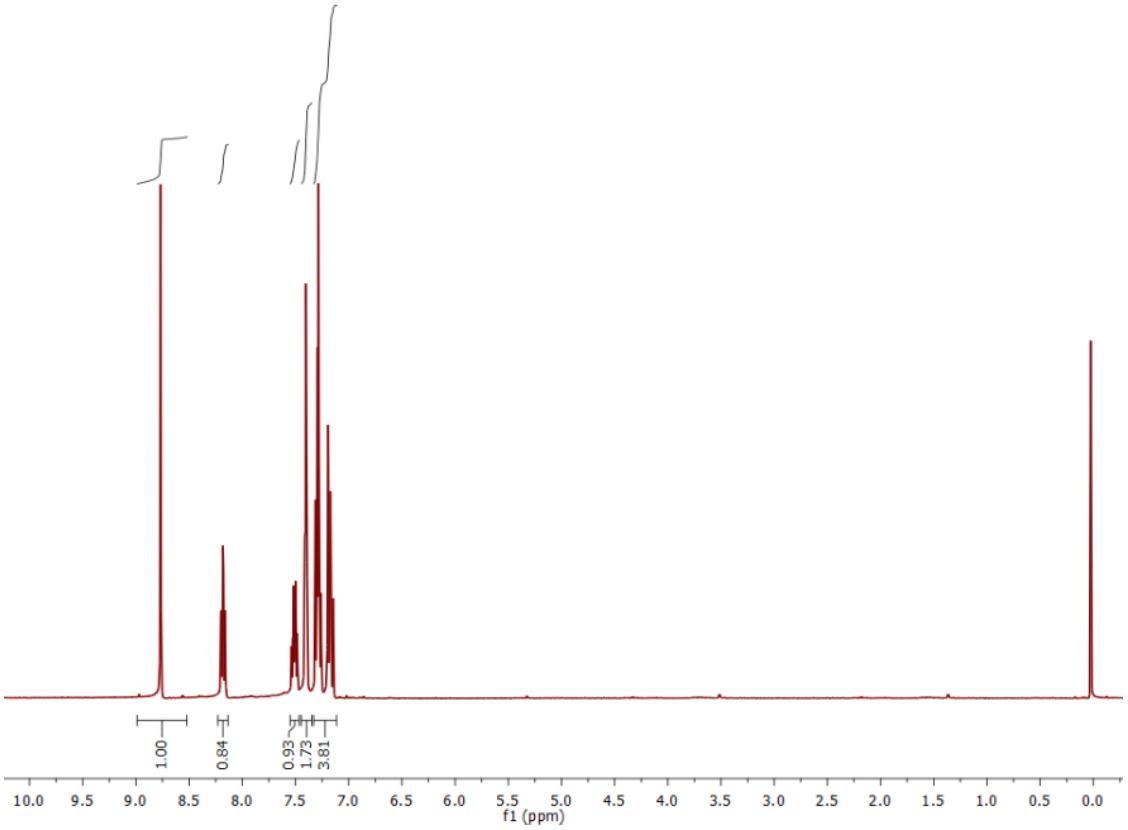


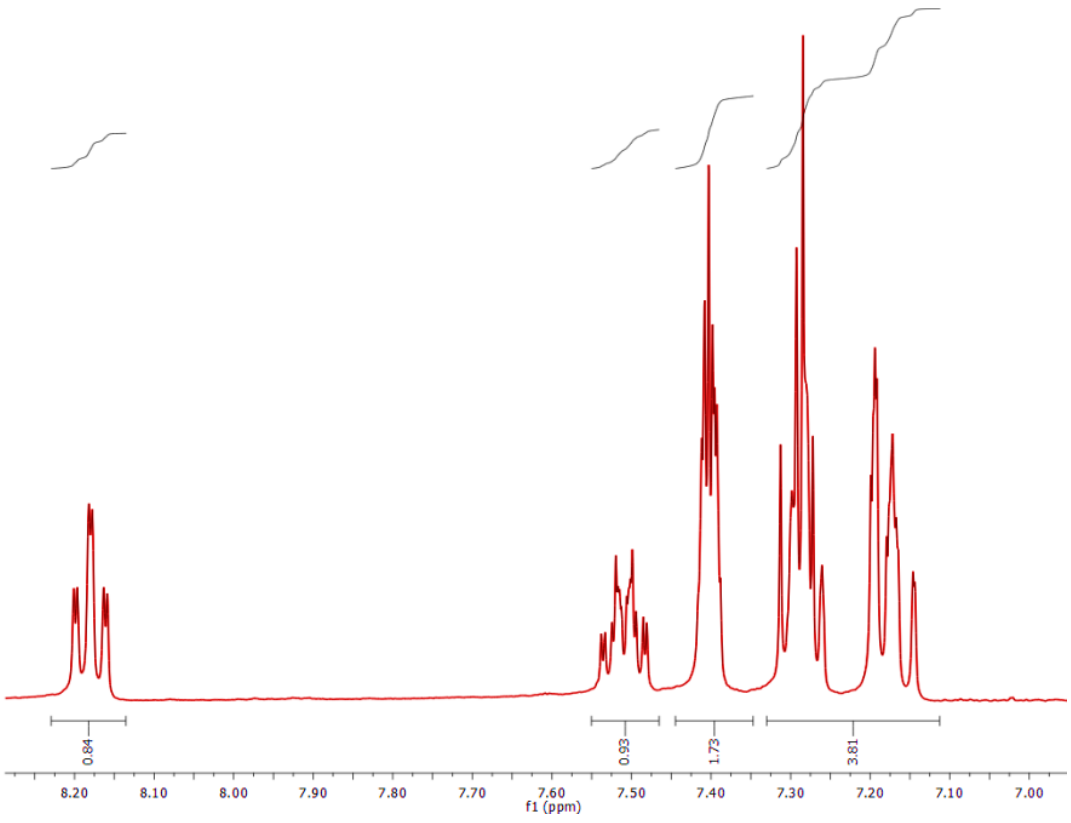


FigureS1:16 **Compound 31:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.76 (s, 1H), 8.16-8.21 (t,1H), 7.47-7.55 (m, 3H), 7.11-7.29 (m, 4H),

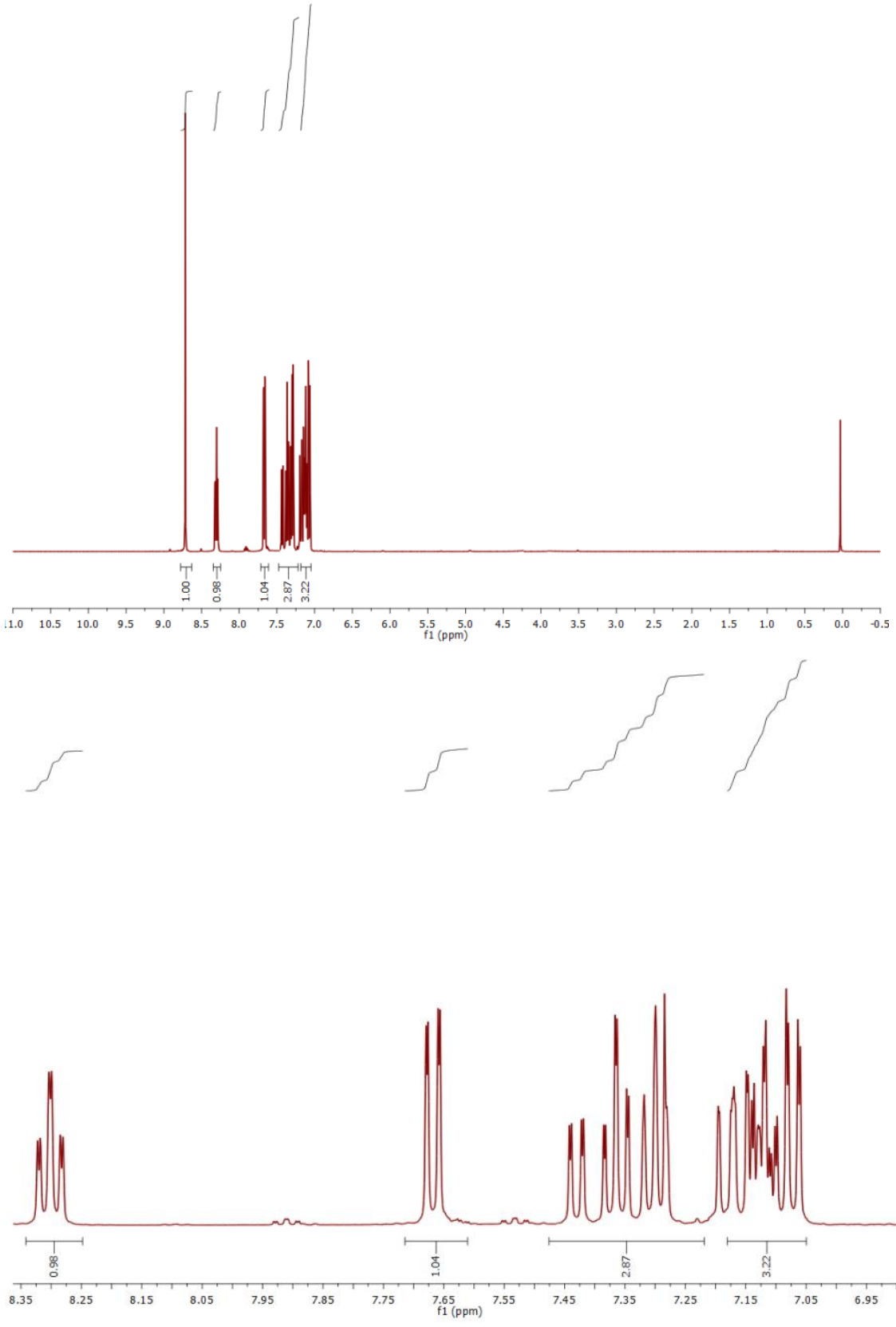


FigureS1:17 **Compound 32:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.78 (s, 1H), 8.16-8.20 (t, 1H), 7.47-7.54 (m, 1H), 7.39-7.41 (m, 2H), 7.14-7.30 (m, 4H),

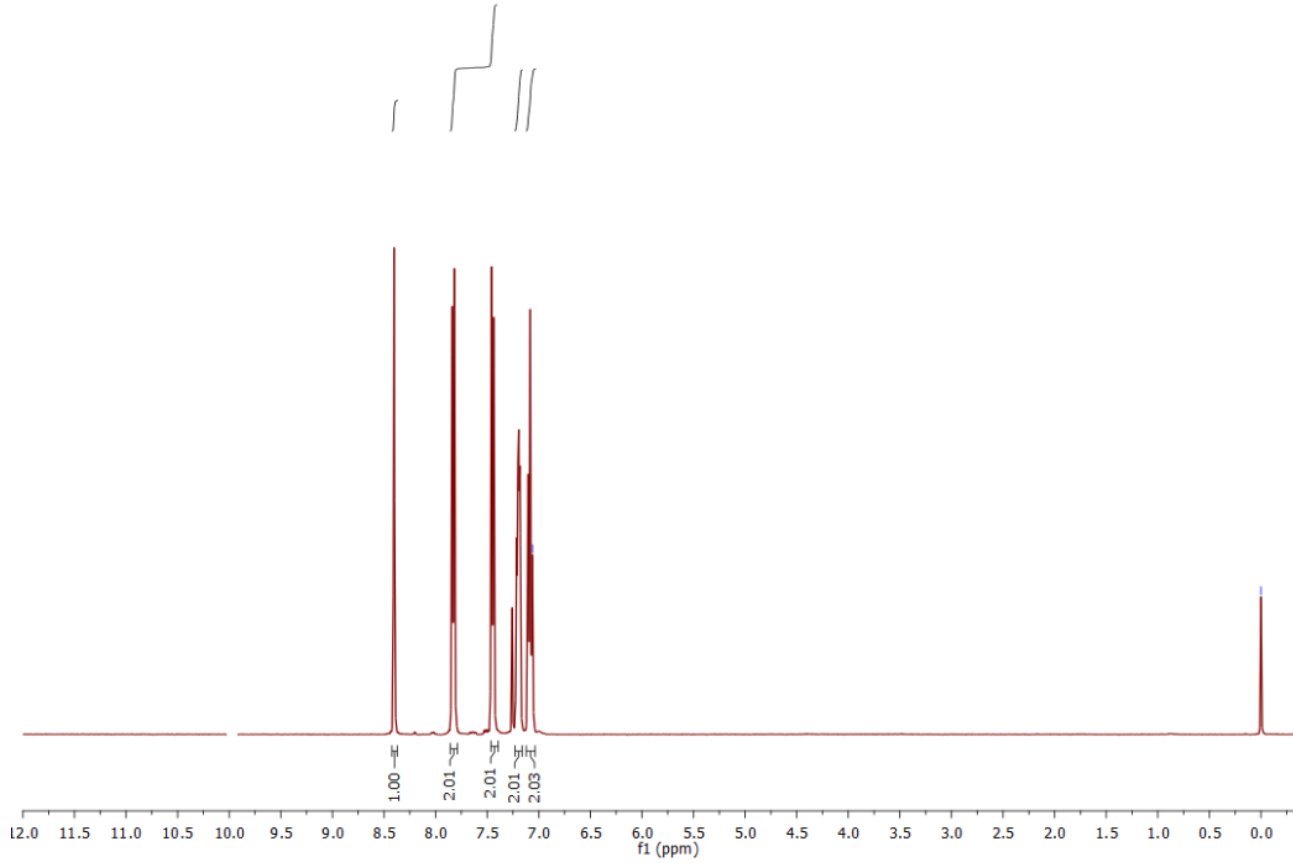


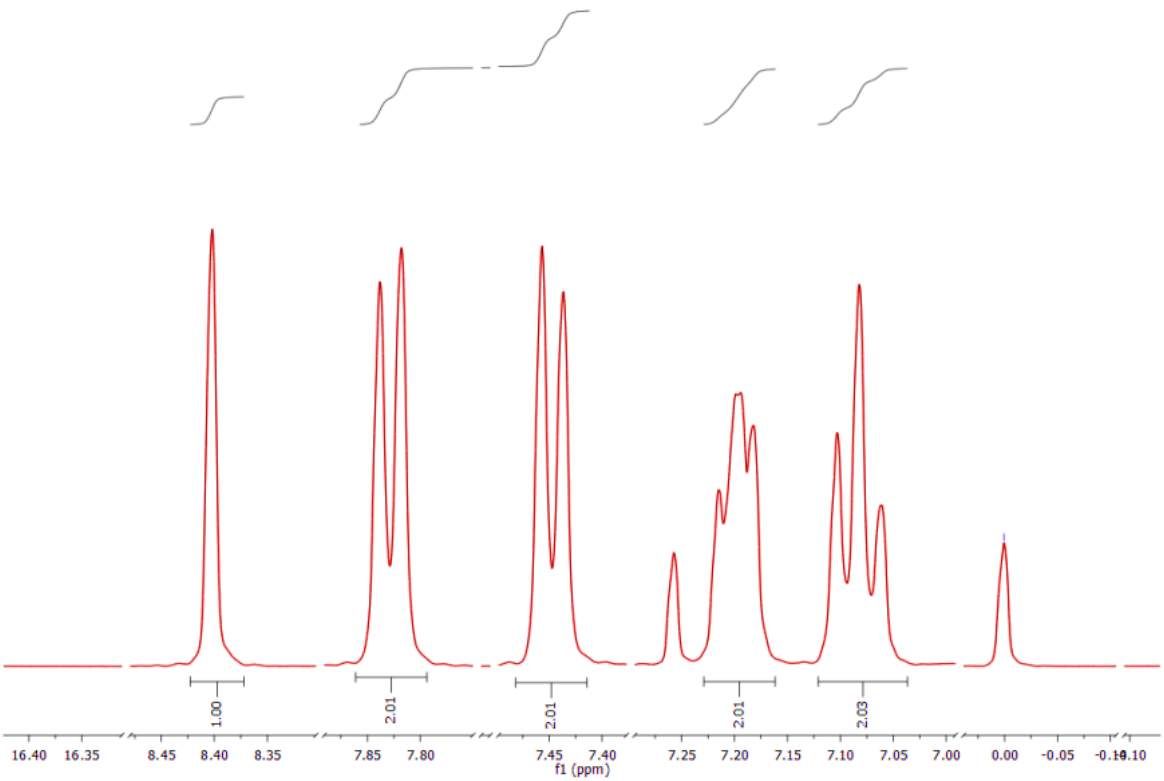


FigureS1:18 **Compound 33:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.71 (s, 1H), 8.28-8.32 (t, 1H), 7.66-7.68 (d, 1H), 7.28-7.44 (m, 3H), 7.06-7.19 (m, 3H),

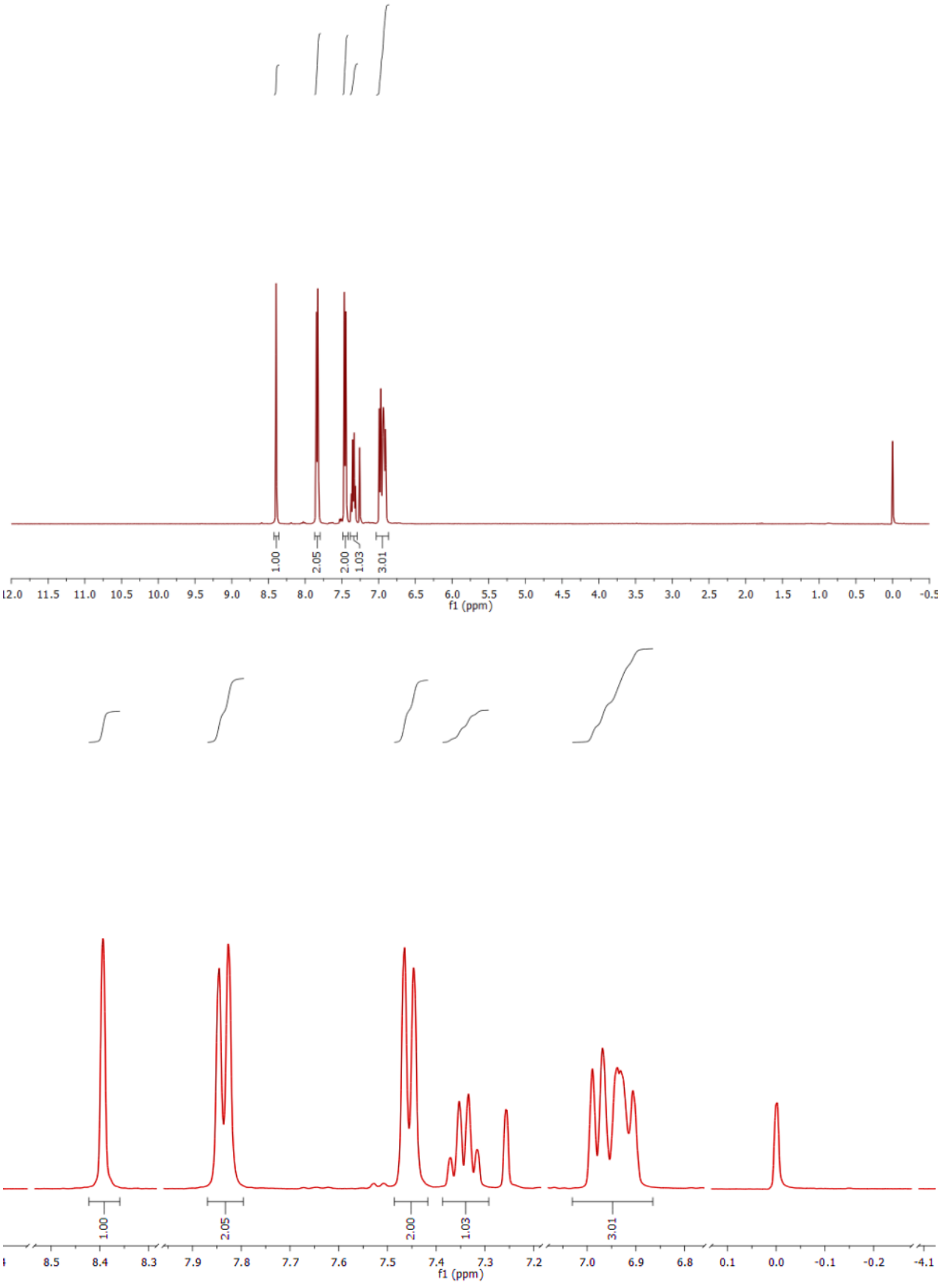


FigureS1:19 **Compound 34:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.40 (s, 1H), 7.90-7.94 (d, 2H), 7.44-7.44 (d, 2H), 7.18-7.21 (t, 2H), 7.06-7.10 (t, 2H)

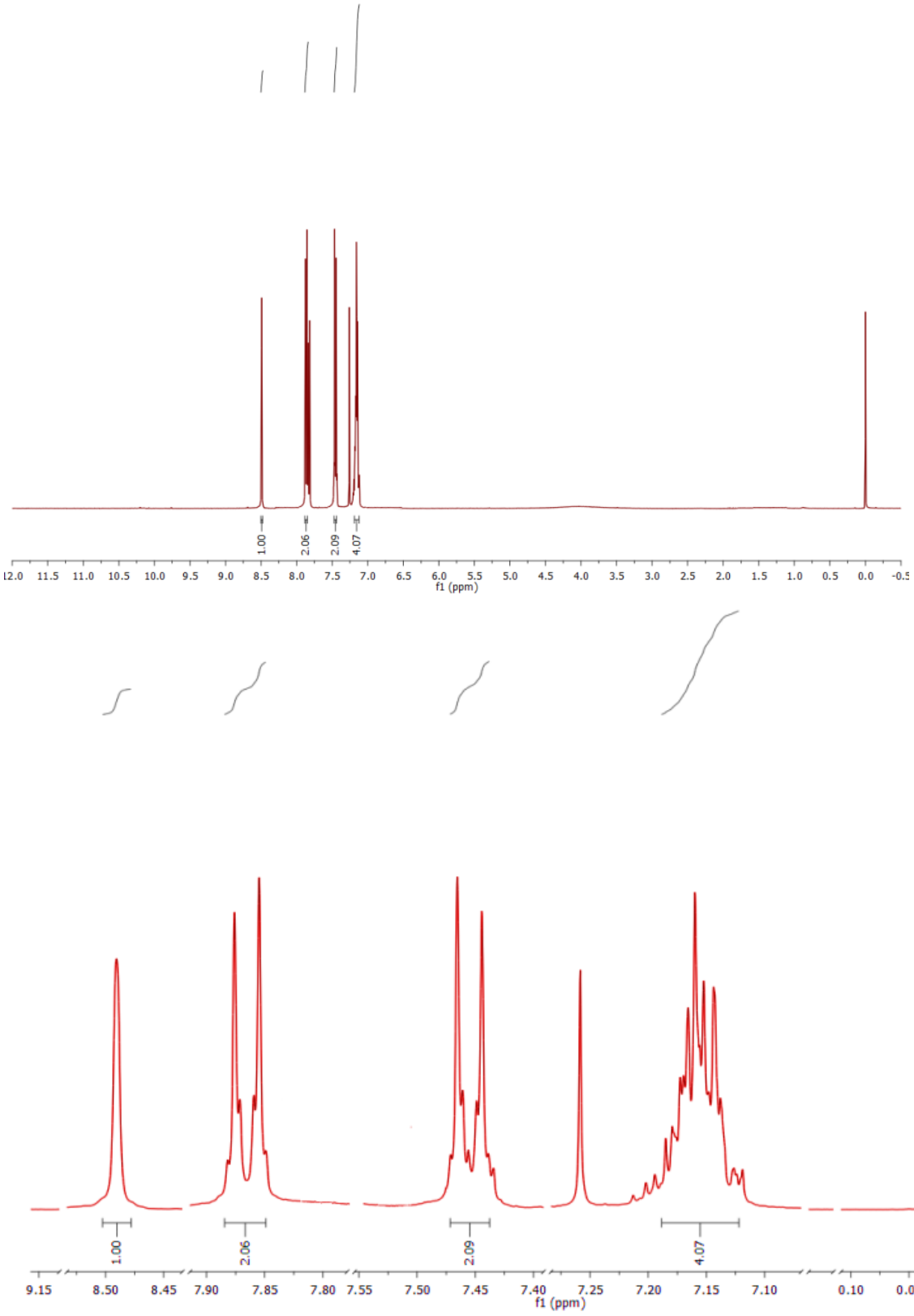




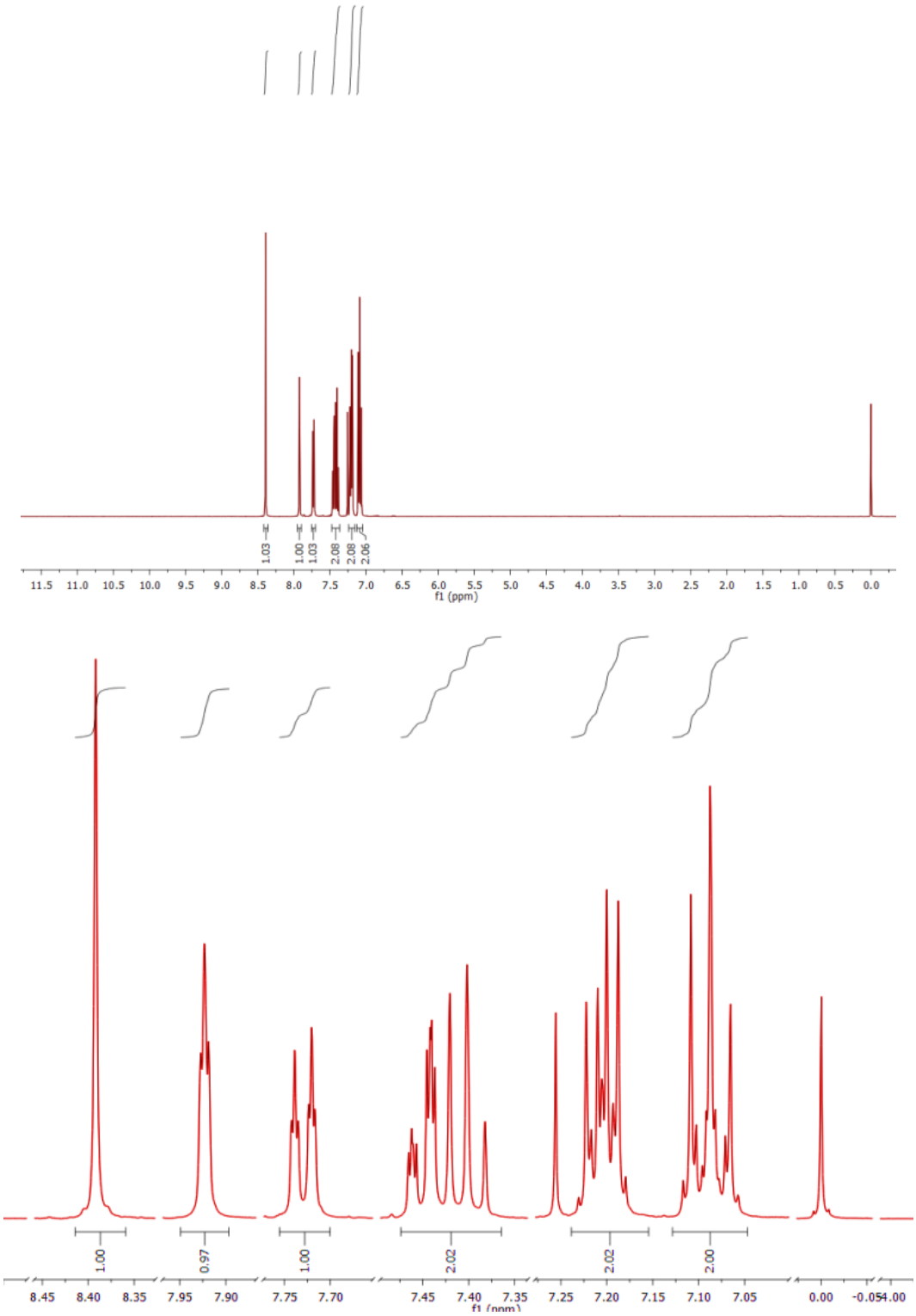
FigureS1:20 **Compound 35:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 1H), 7.83-7.85 (d, 2H), 7.45-7.46 (d, 2H), 7.32-7.37 (q, 1H), 6.91-6.99 (m, 3H)



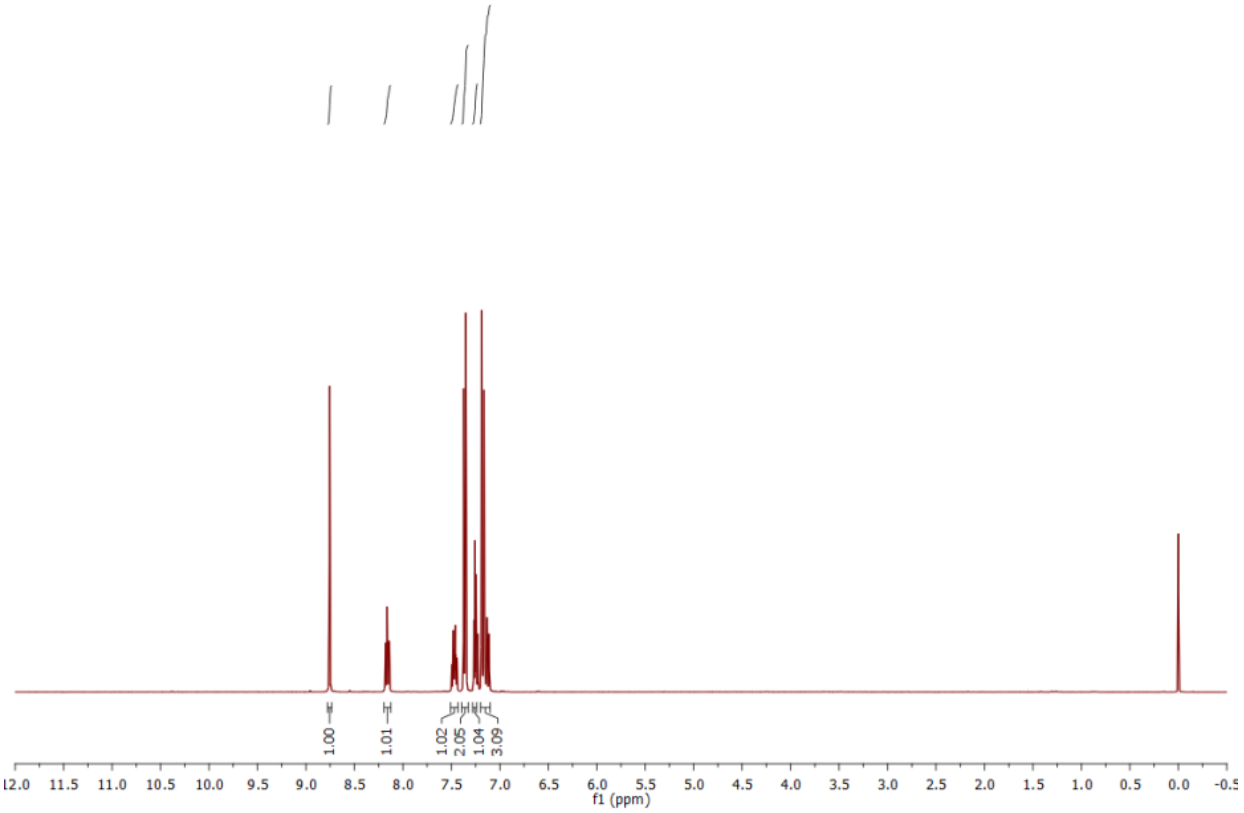
FigureS1:21 **Compound 36:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 7.85-7.88 (d, 2H), 7.44-7.47 (d, 2H), 7.12-7.21 (m, 4H)

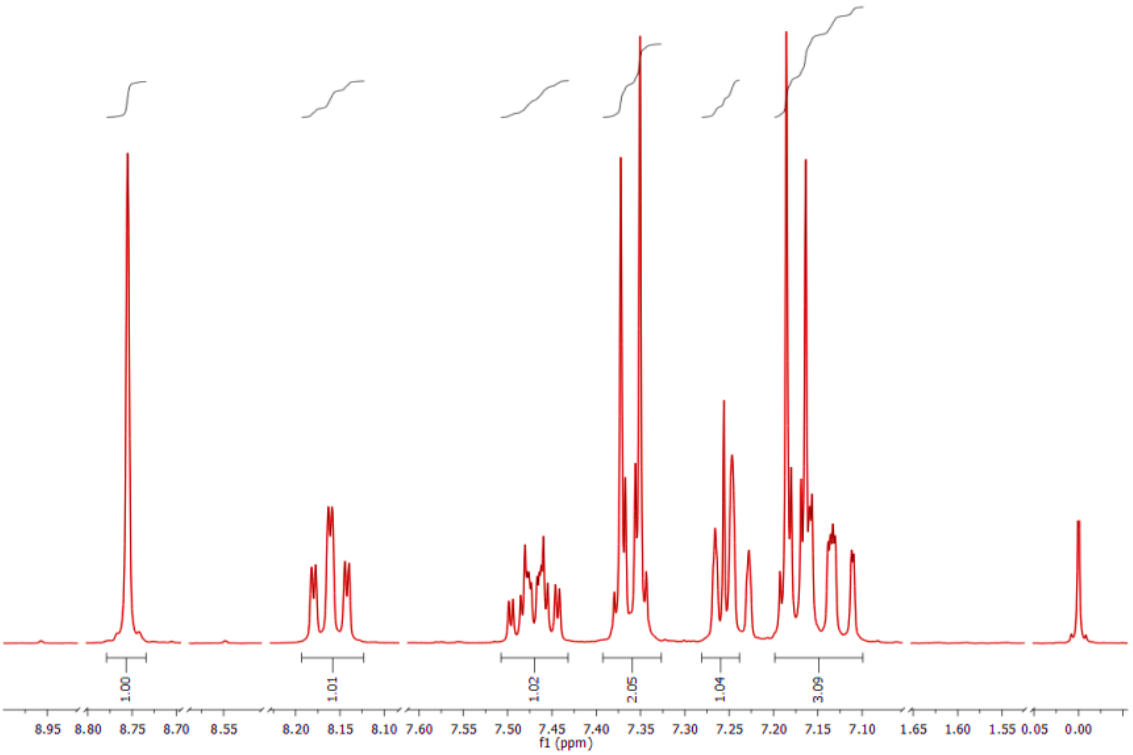


FigureS1:22 **Compound 37:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 1H), 7.92-7.93 (t, 1H), 7.72-7. 74 (dt, 1H), 7.38-7.47 (m, 2H), 7.19-7.22 (m, 2H), 7.06-7.12 (m, 2H)

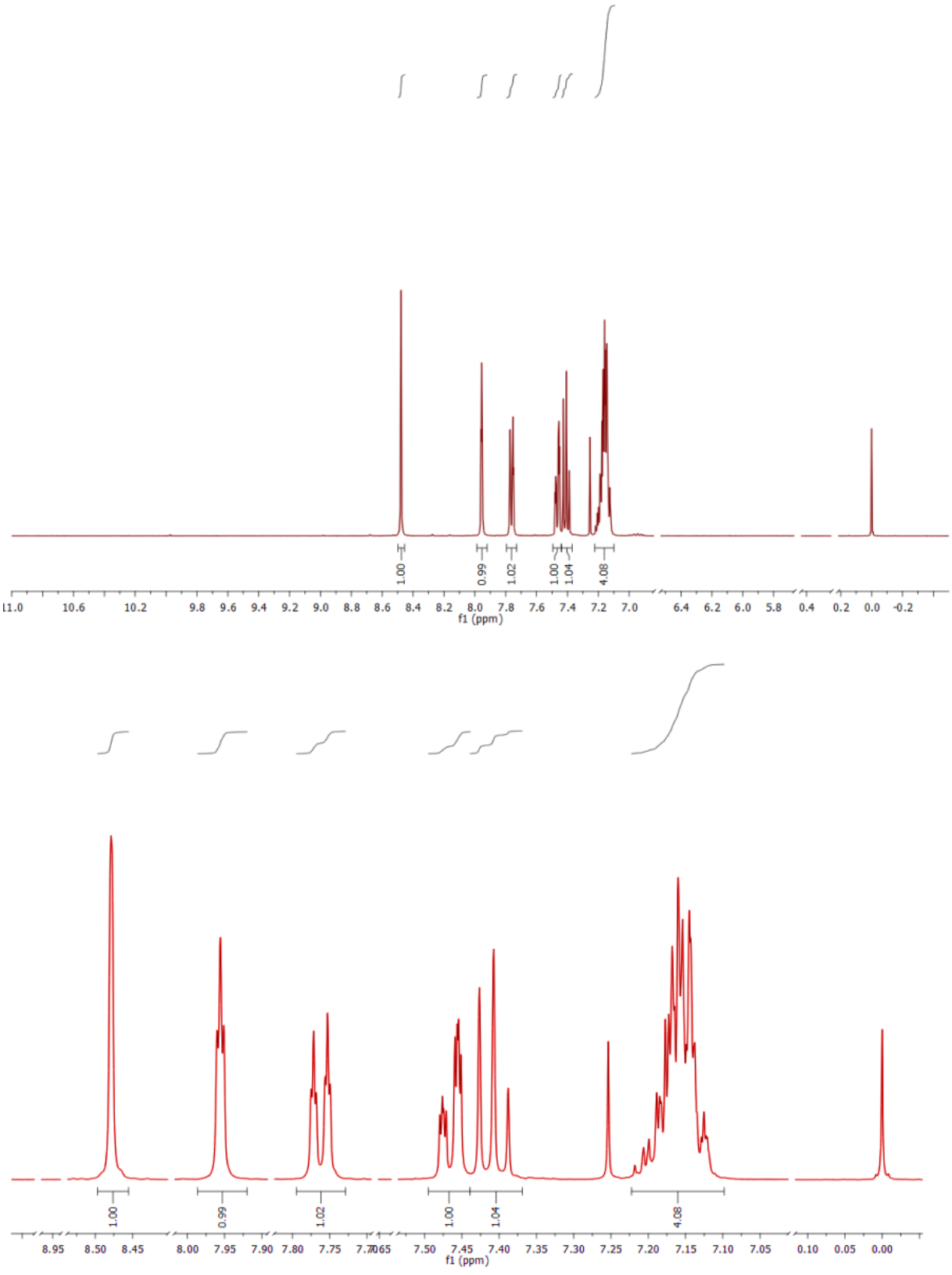


FigureS1:23 **Compound 38:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 1H), 8.14-8.18 (m, 1H), 7.44-7.50(m, 1H), 7.34-7.38 (dt, 2H), 7.23-7.27 (t, 1H), 7.11-7.19 (m,3H)

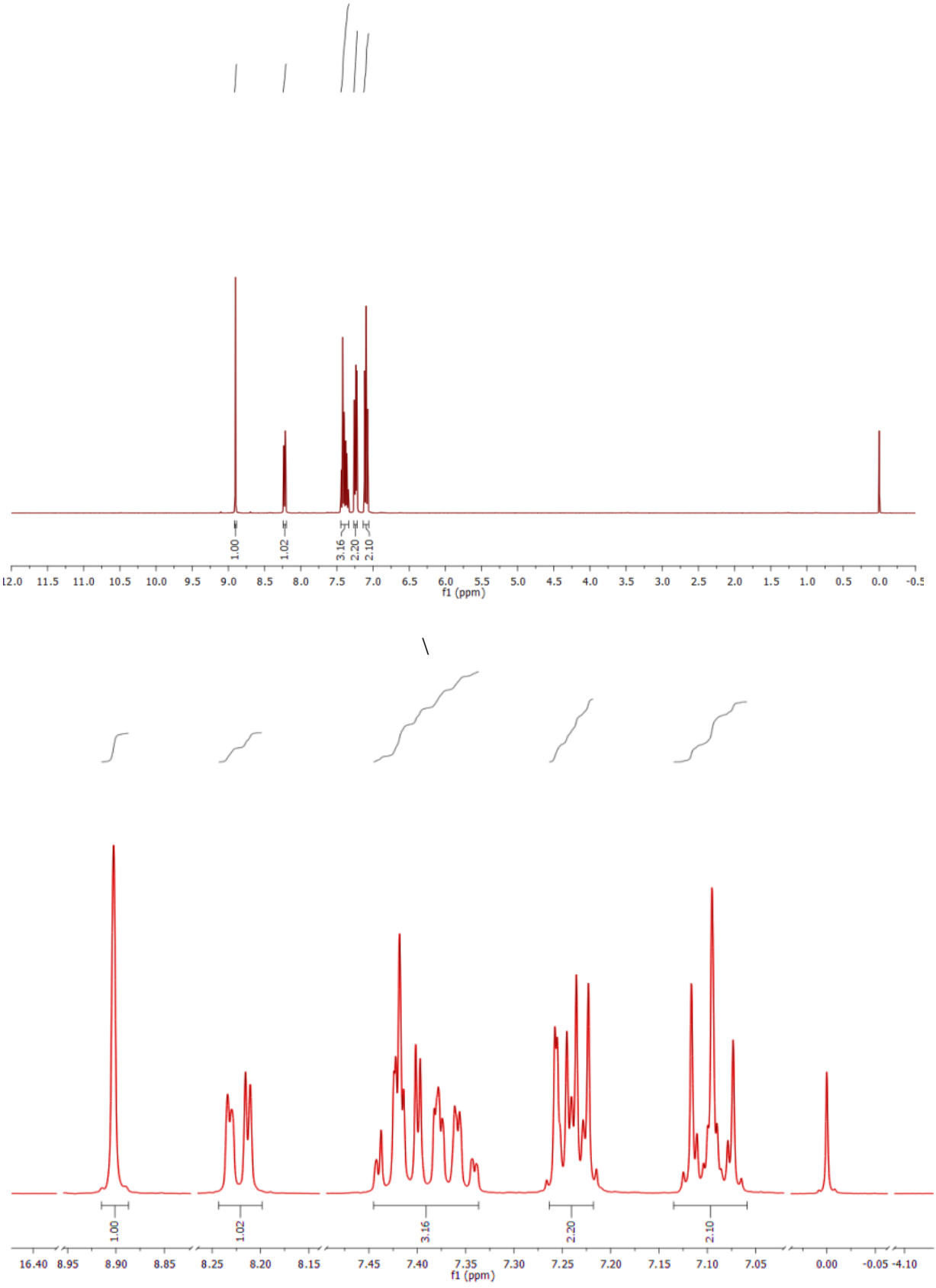




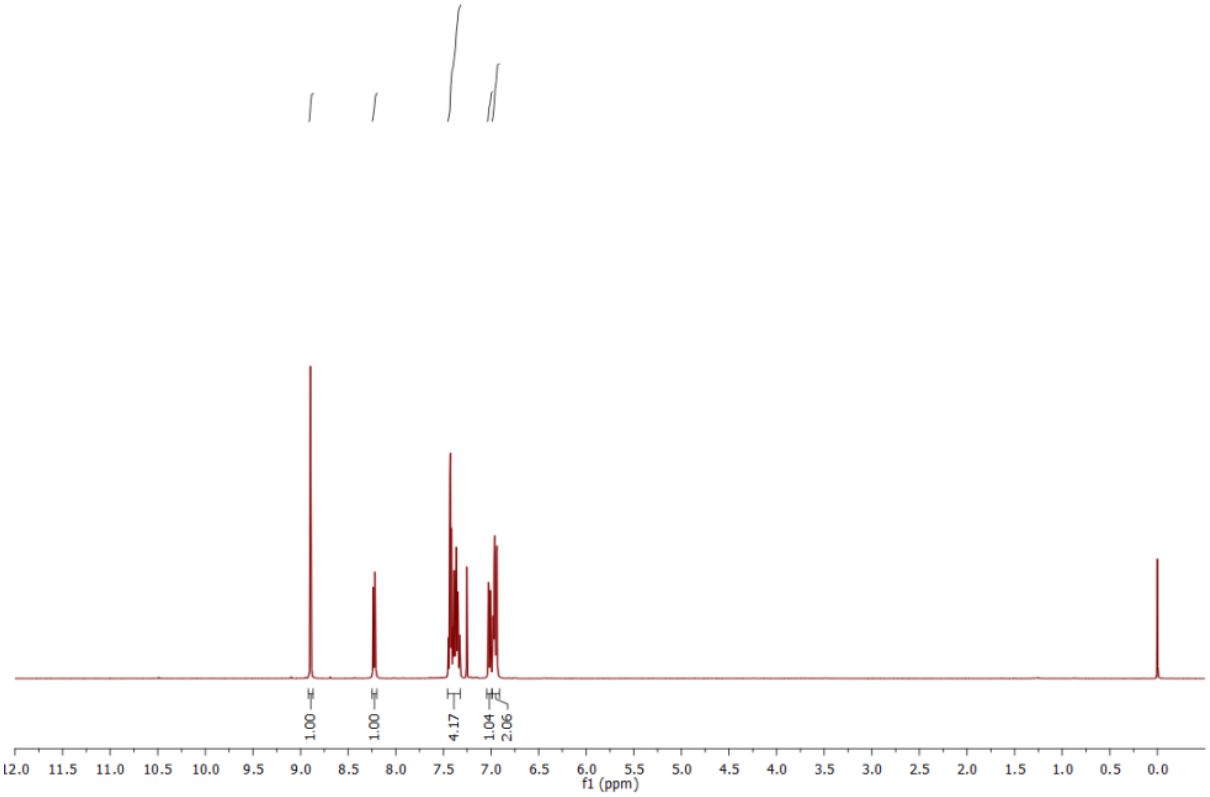
FigureS1:24 **Compound 39:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.48 (s, 1H), 7.95-7.96 (t, 1H), 7.75-7.77 (dt, 1H), 7.45-7.48 (m, 1H), 7.39-7.43 (t, 1H), 7.12-7.22 (m, 4H)

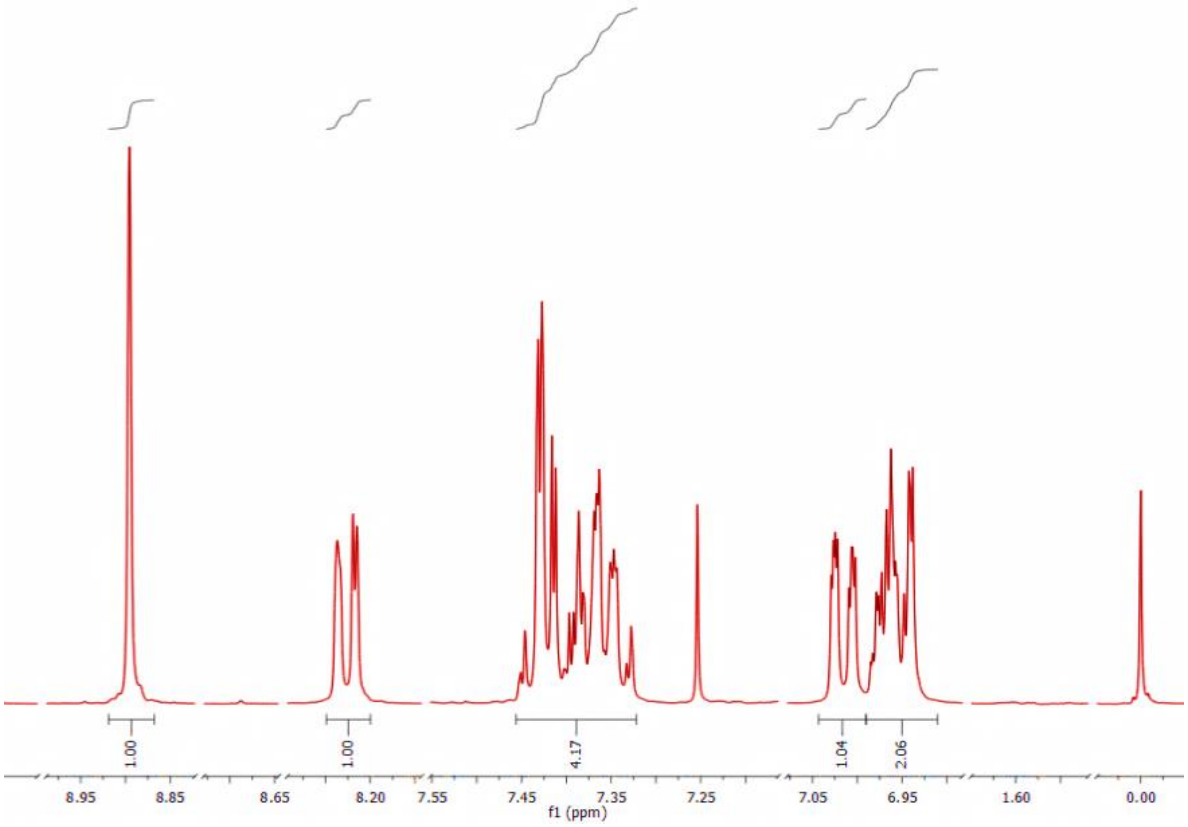


FigureS1:25 **Compound 40:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 1H), 8.21-8.23 (dd, 1H), 7.34-7.44 (m, 3H), 7.21-7.27 (m, 2H), 7.06-7.12 (m, 2H)

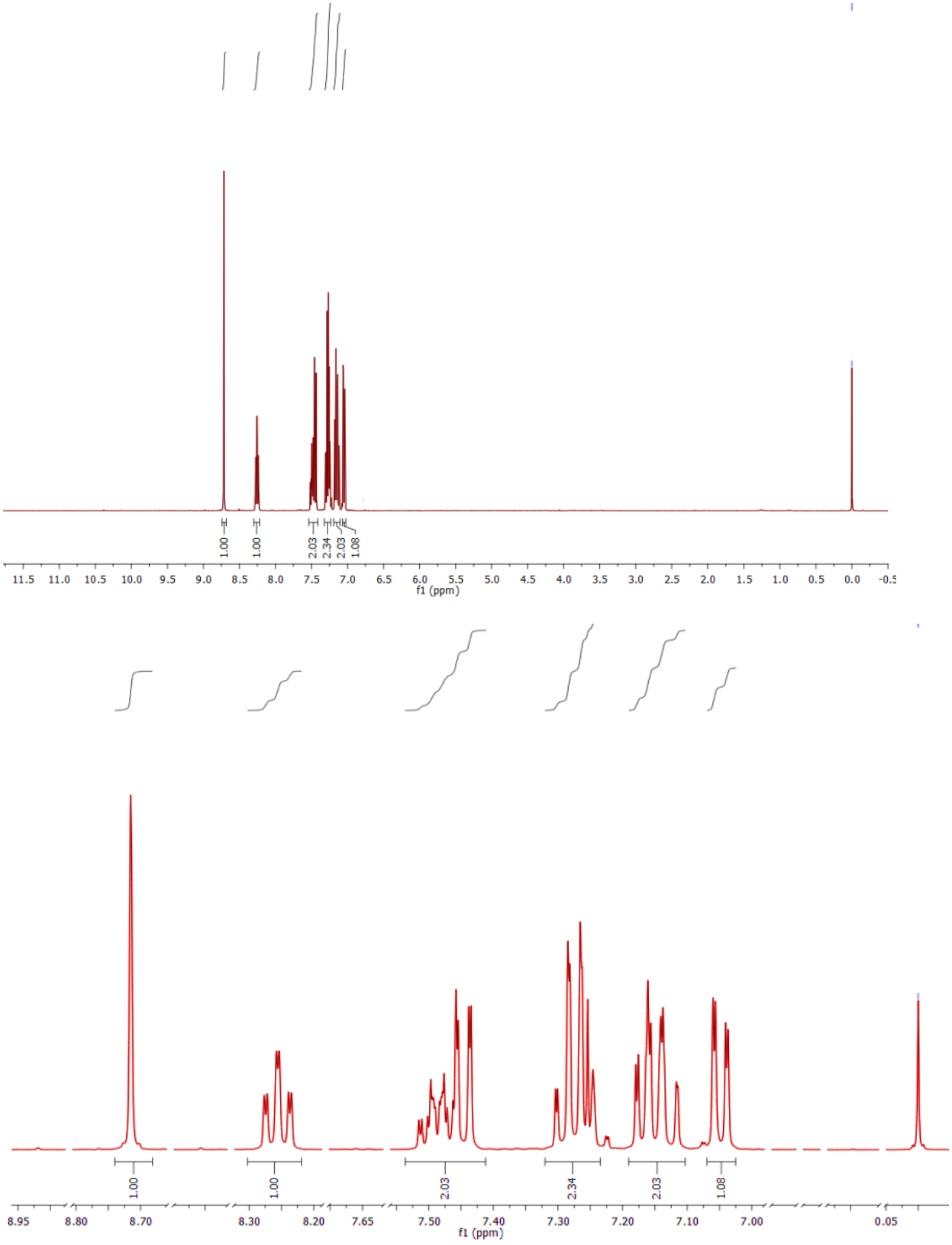


FigureS1:26 **Compound 41:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 1H), 8.21-8.24 (m, 1H), 7.33-7.45 (m, 4H), 7.00-7.03 (m, 1H), 6.94-6.18 (m, 2H)

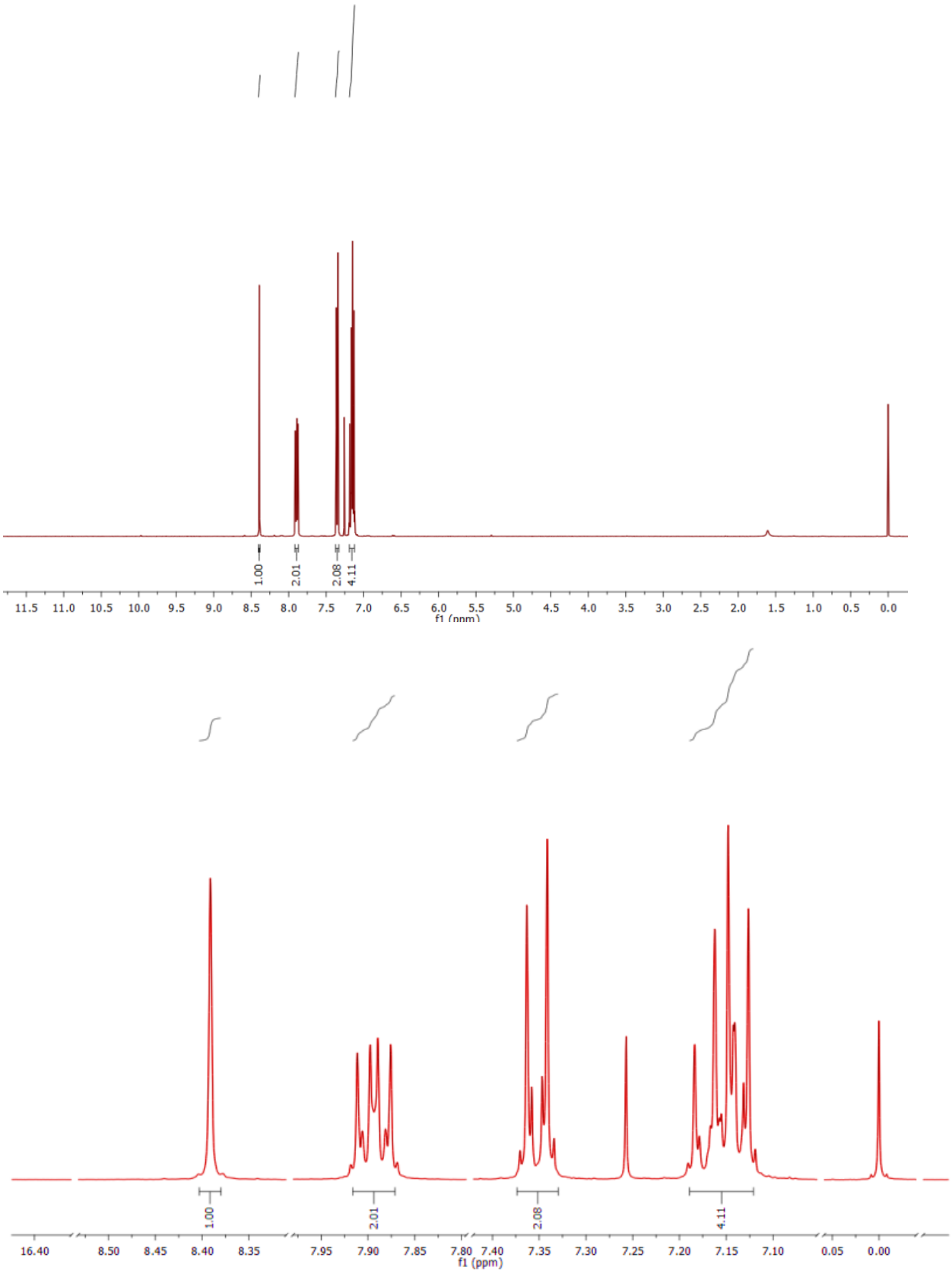




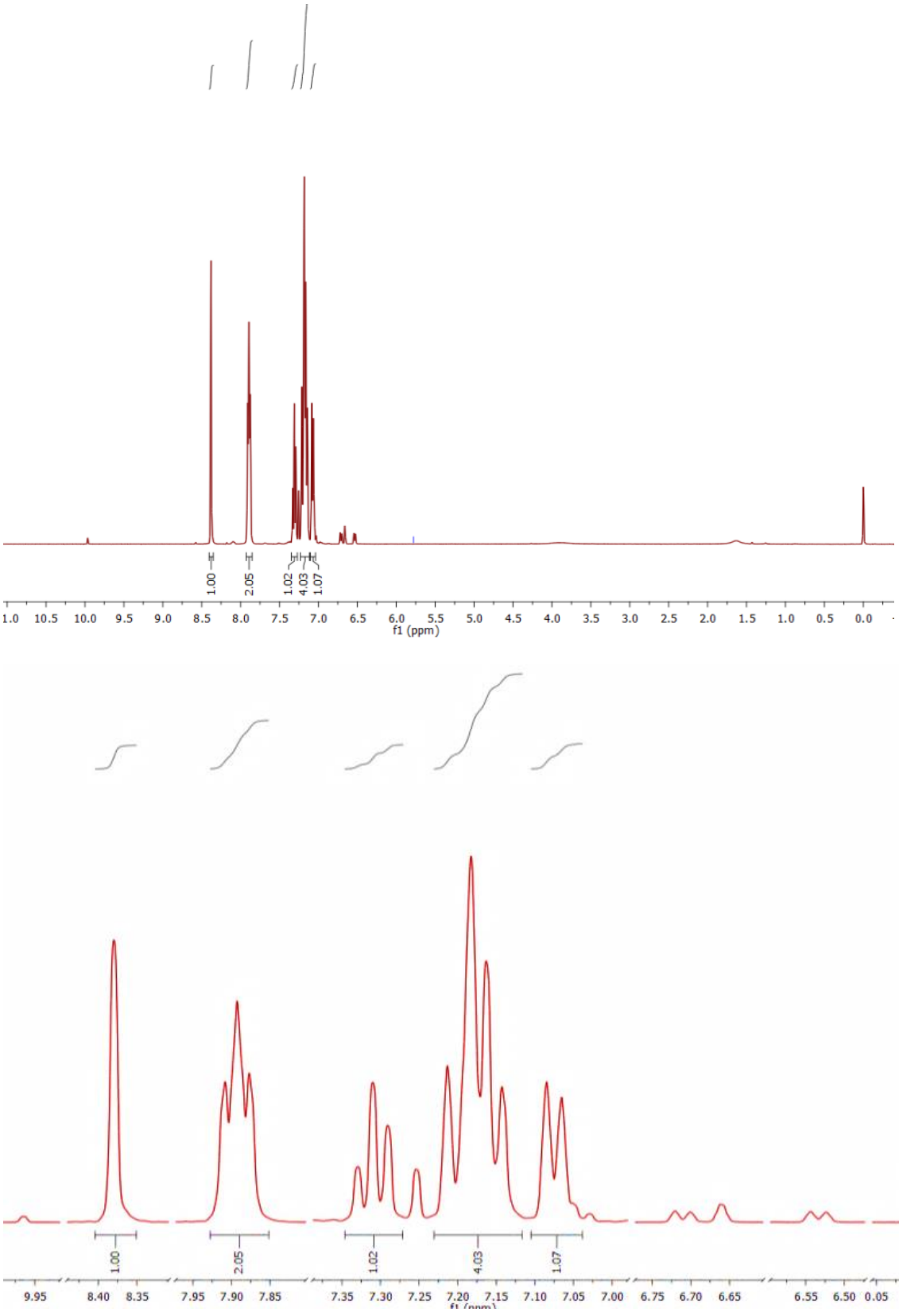
FigureS1:27 **Compound 42:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.72 (s, 1H), 8.23-8.28 (td, 1H), 7.43-7.52 (m, 2H), 7.25-7.30 (m, 2H), 7.12-7.18 (m, 2H), 7.04-7.06 (dd, 1H)



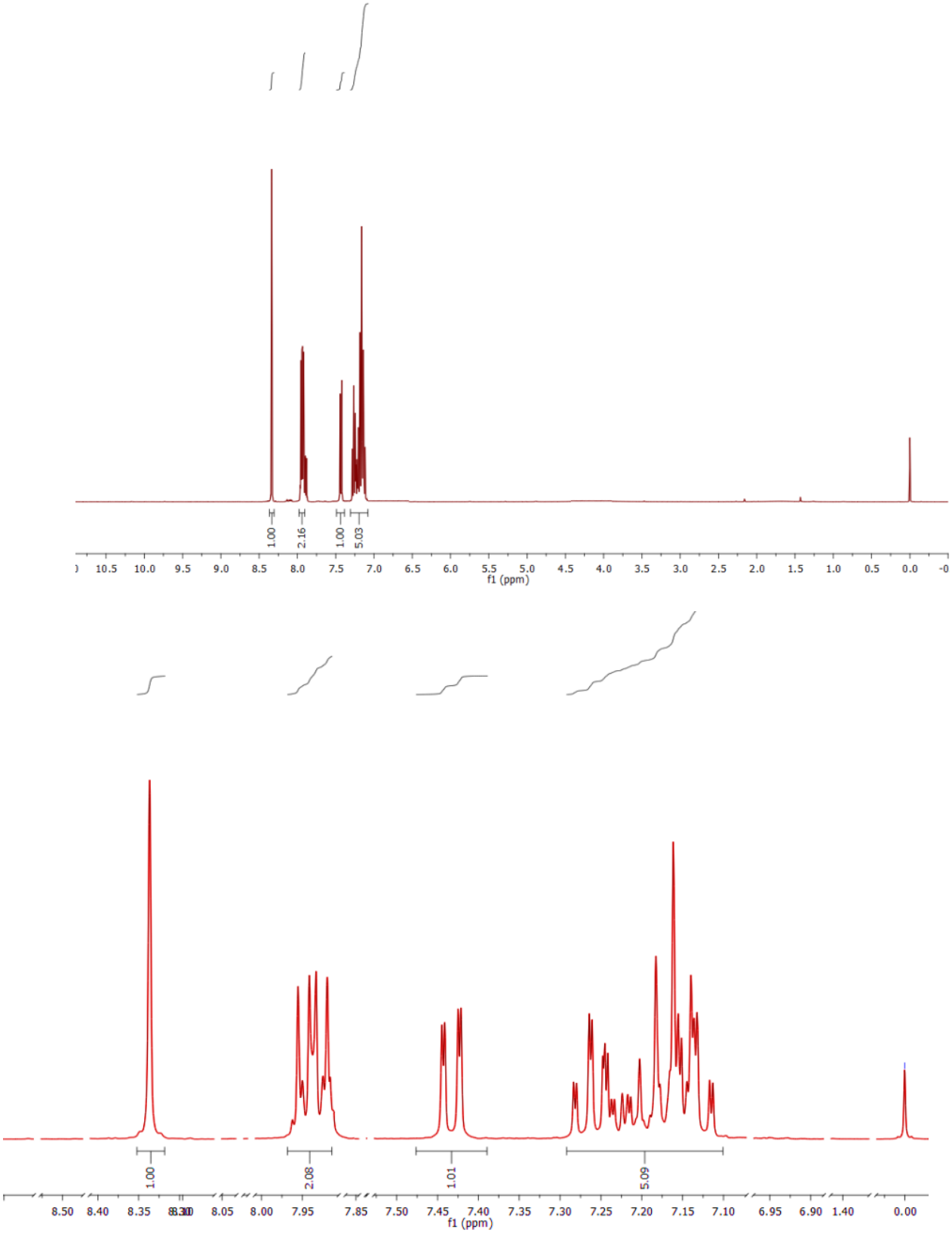
FigureS1:28 **Compound 43:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 1H), 7.87-7.92 (m, 2H), 7.33-7.37 (m, 2H), 7.12-7.19 (m, 4H)



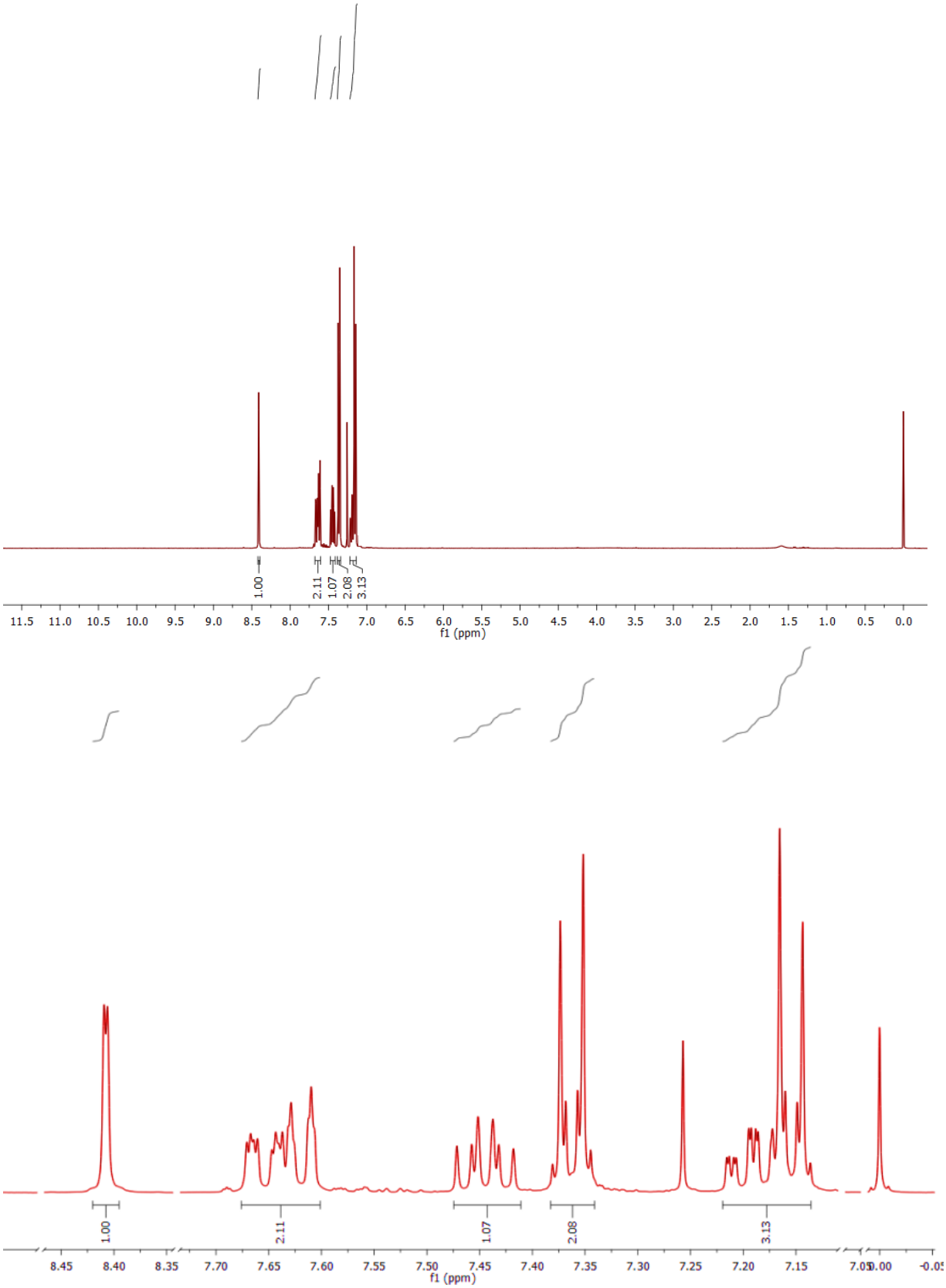
FigureS1:29 **Compound 44:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.38 (s, 1H), 7.88-7.91 (t, 2H), 7.29-7.33 (t, 1H), 7.14-7.21 (q, 4H), 7.14-7.21 (d, 1H)



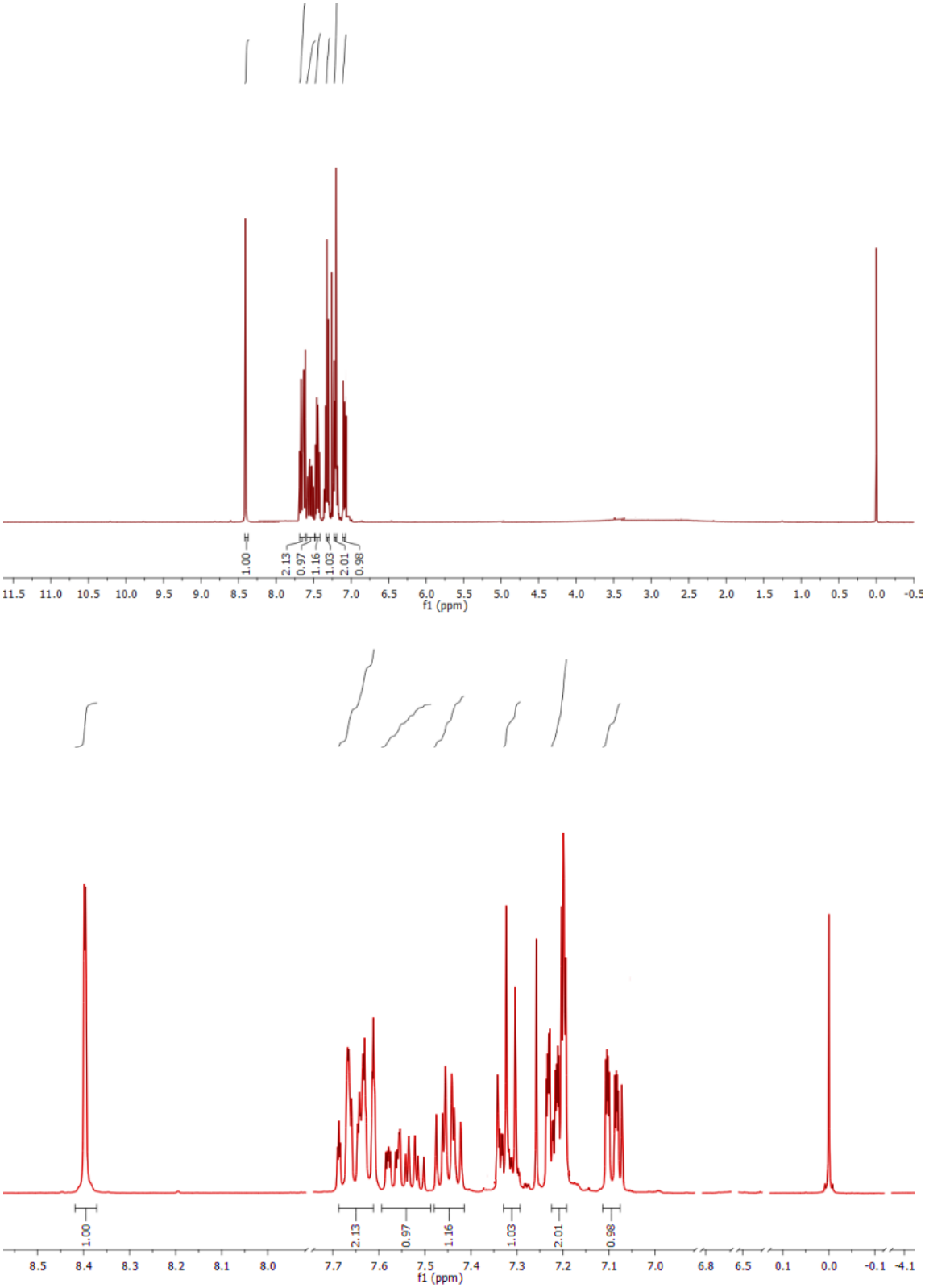
FigureS1:30 **Compound 45:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1H), 7.92-7.96 (m, 2H), 7.42-7.44 (dd, 1H), 7.11-7.28 (m, 5H)



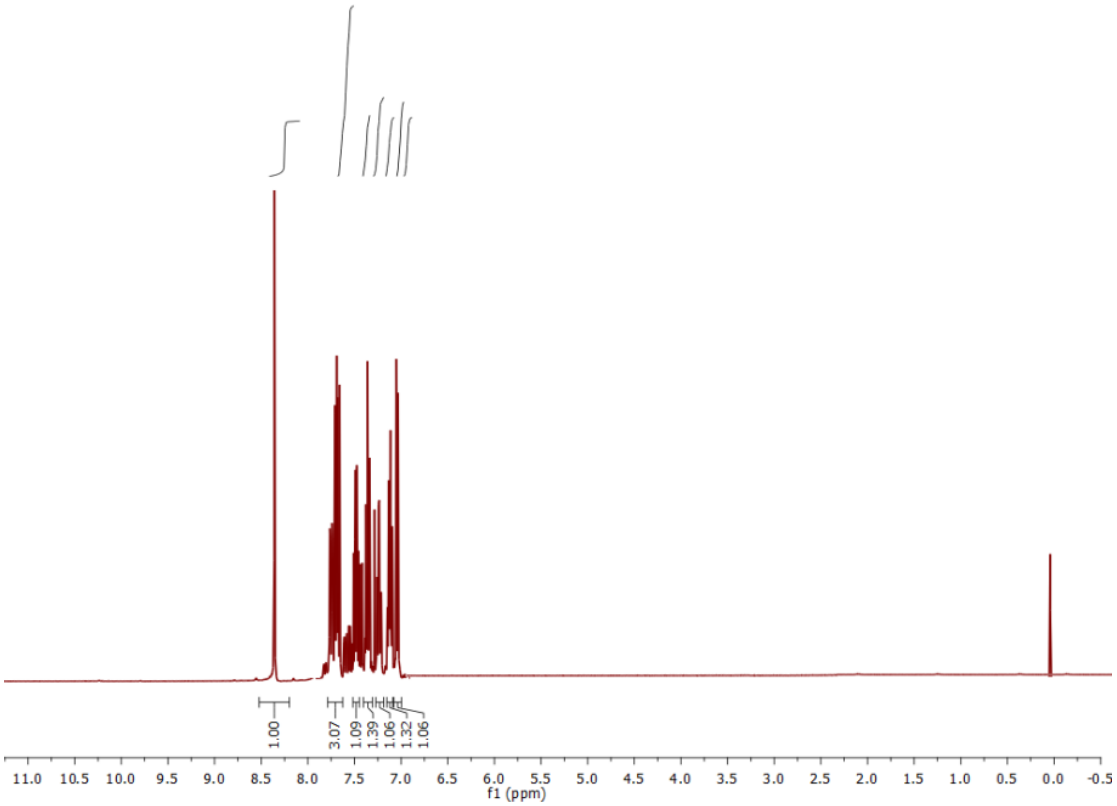
FigureS1:31 **Compound 46:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.41 (s,1H), 7.61-7.67 (m,2H), 7.42-7.47 (m, 1H), 7.34-7.38 (m, 2H), 7.14-7.22 (m, 3H)

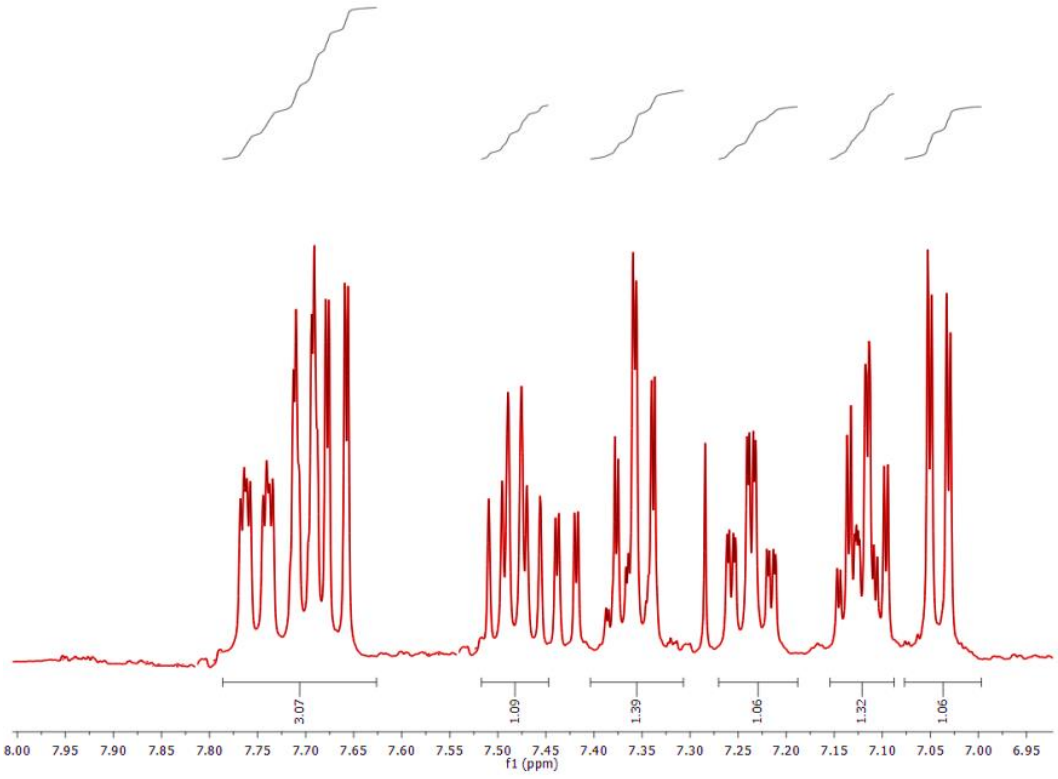


FigureS1:32 **Compound 47:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.40 (s, 1H), 7.61-7.68 (m, 2H), 7.50-7.58 (m, 1H), 7.42-7.48 (m, 1H), 7.30-7.34 (m, 1H), 7.20-7.24 (m, 2H), 7.07-7.11 (m, 1H).

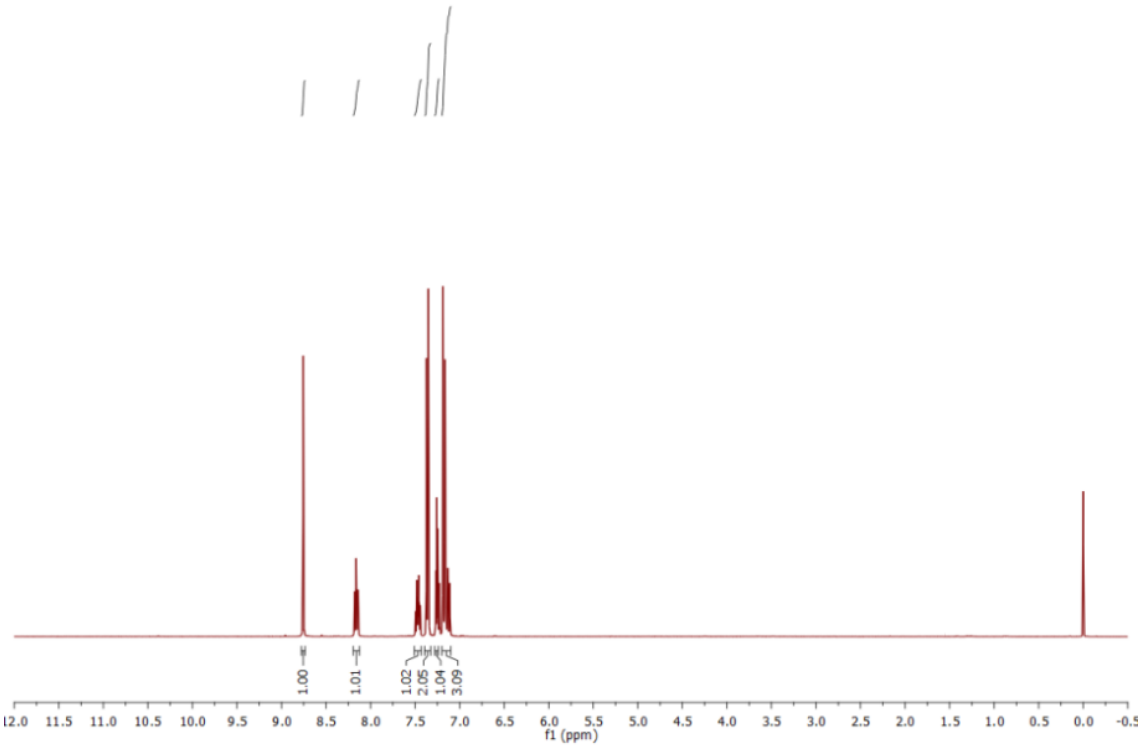


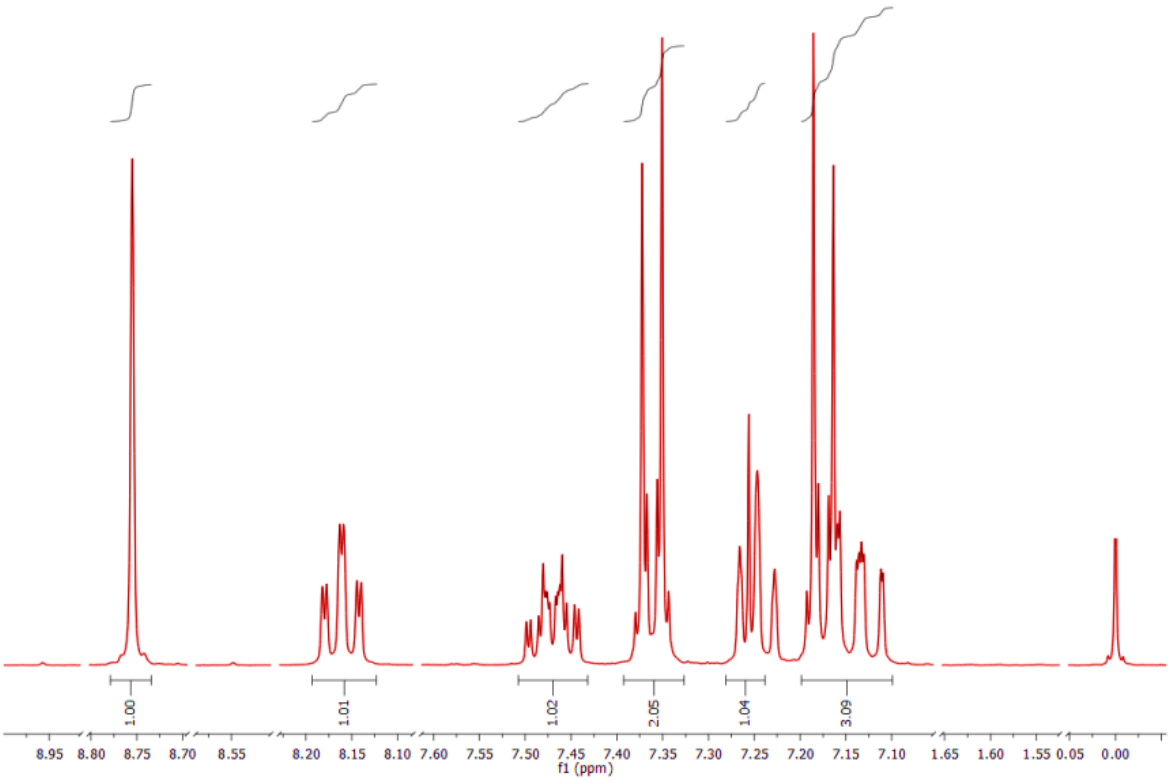
FigureS1:33 **Compound 48:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 7.66-7.77 (m, 3H), 7.45-7.51 (m, 1H), 7.33-7.38 (m, 1H), 7.21-7.26 (t, 1H), 7.02-7.05 (d, 1H).



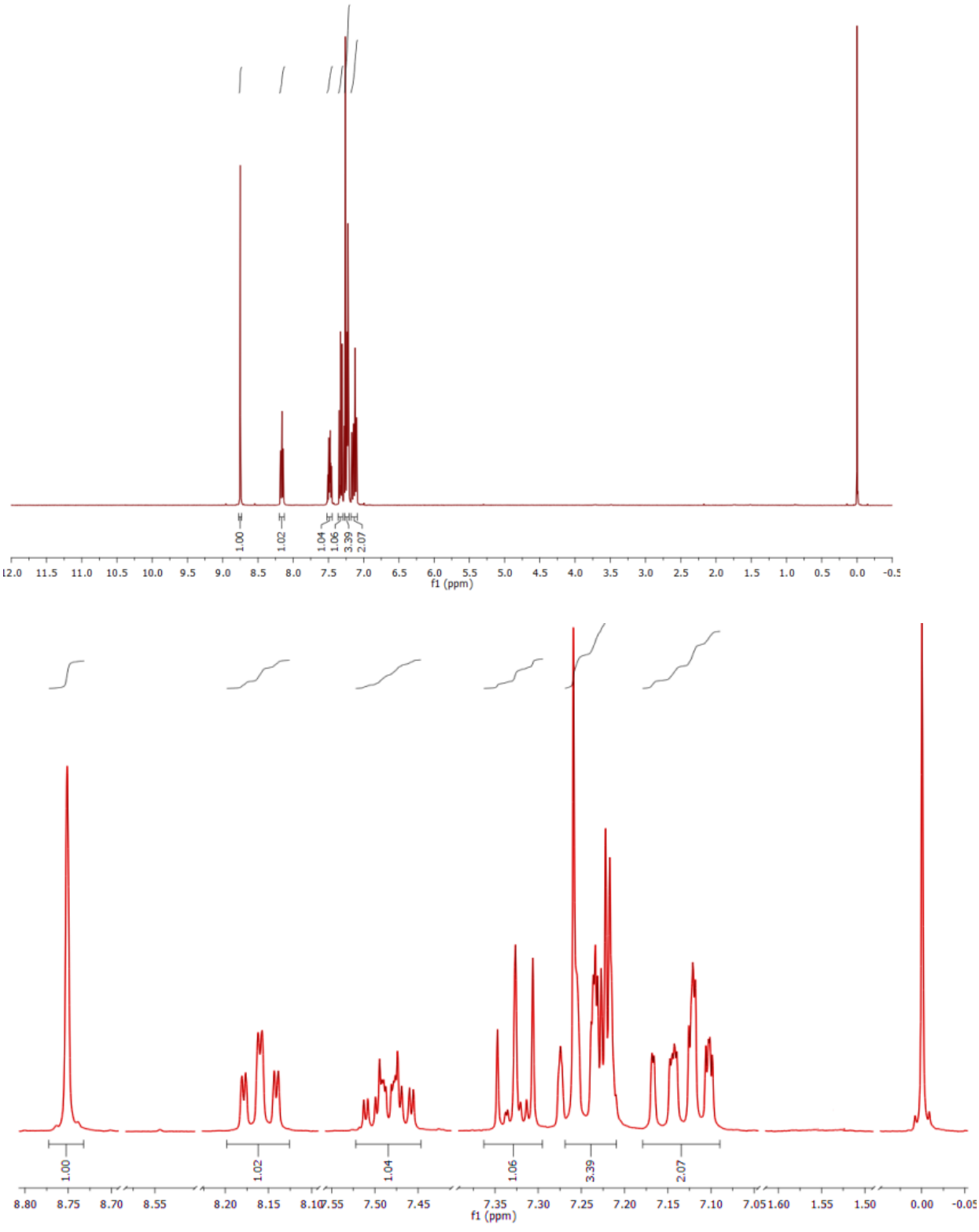


FigureS1:34 **Compound 49:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.75 (s,1H), 8.14-8.18 (m, 1H), 7.44-7.50 (m, 1H), 7.34-7.38 (dt, 2H), 7.23-7.27 (t, 1H), 7.11-7.19 (m, 3H),





FigureS1:35 **Compound 50:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 1H), 8.14-8.18 (td, 1H), 7.46-7.51 (m, 1H), 7.31-7.35 (m, 1H), 7.22-7.27 (m, 3H), 7.10-7.17 (m, 2H).



FigureS1:36 **Compound 51:** White solid. ^{1}H NMR ($CDCl_3$) δ 8.72 (s, 1H), 8.23-8.28 (td, 1H), 7.43-7.52 (m, 2H), 7.25-7.30 (m, 2H), 7.12-7.18 (m, 2H), 7.04-7.06 (dd, 1H).

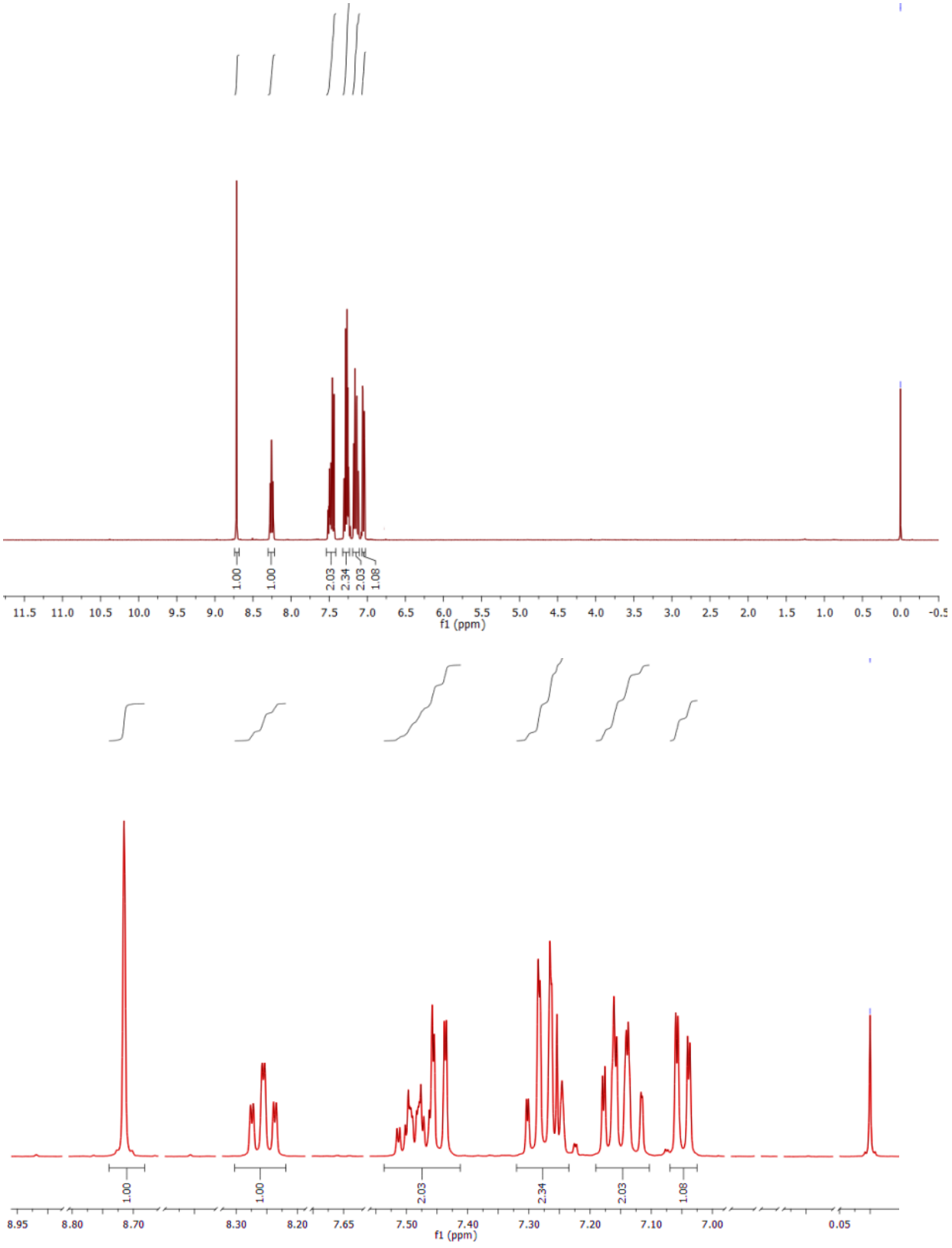


Figure S2: IR-S1pectra of the compoundS1: All IR S1pectra were recorded on

Figure S2:1 Compound 16

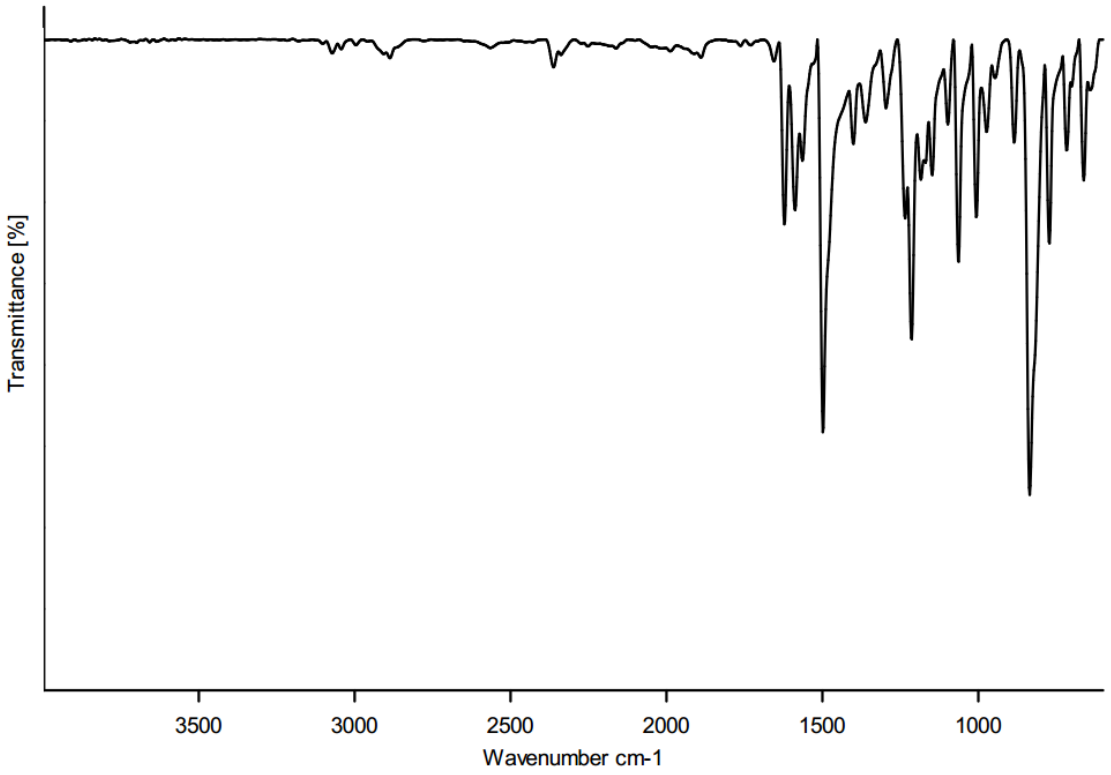


Figure S2:2 Compound 17

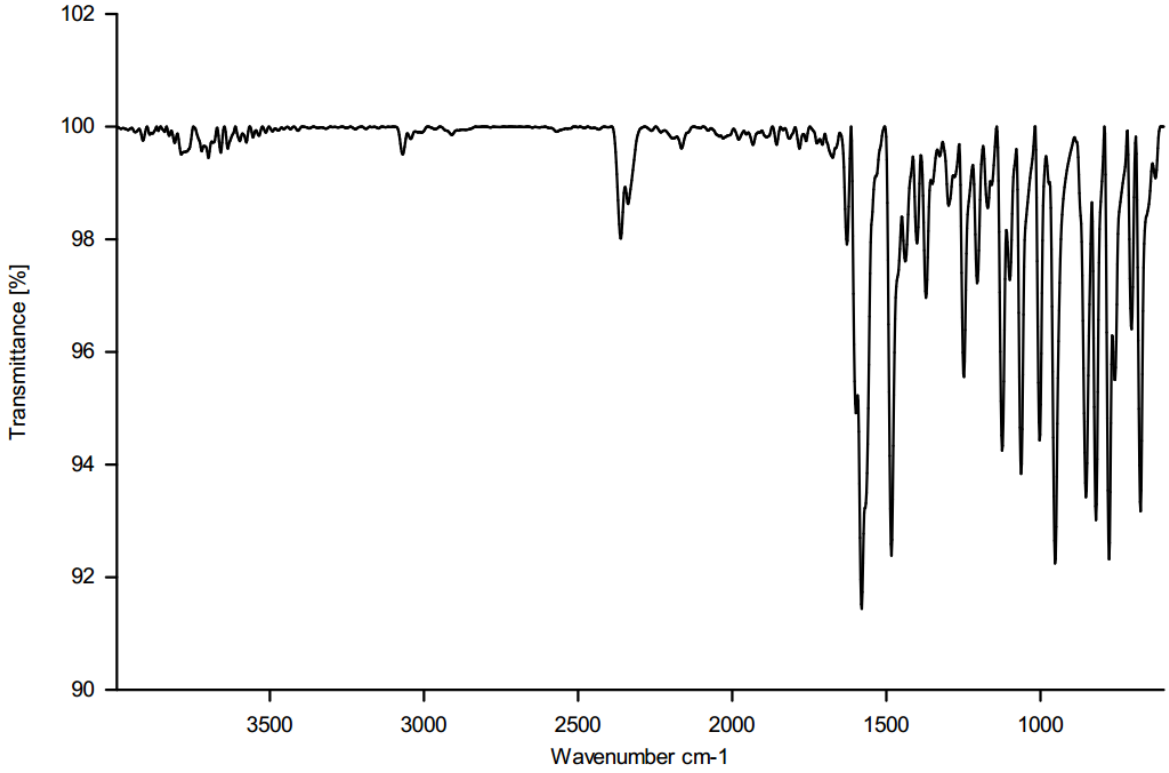


Figure S2:3 Compound 18

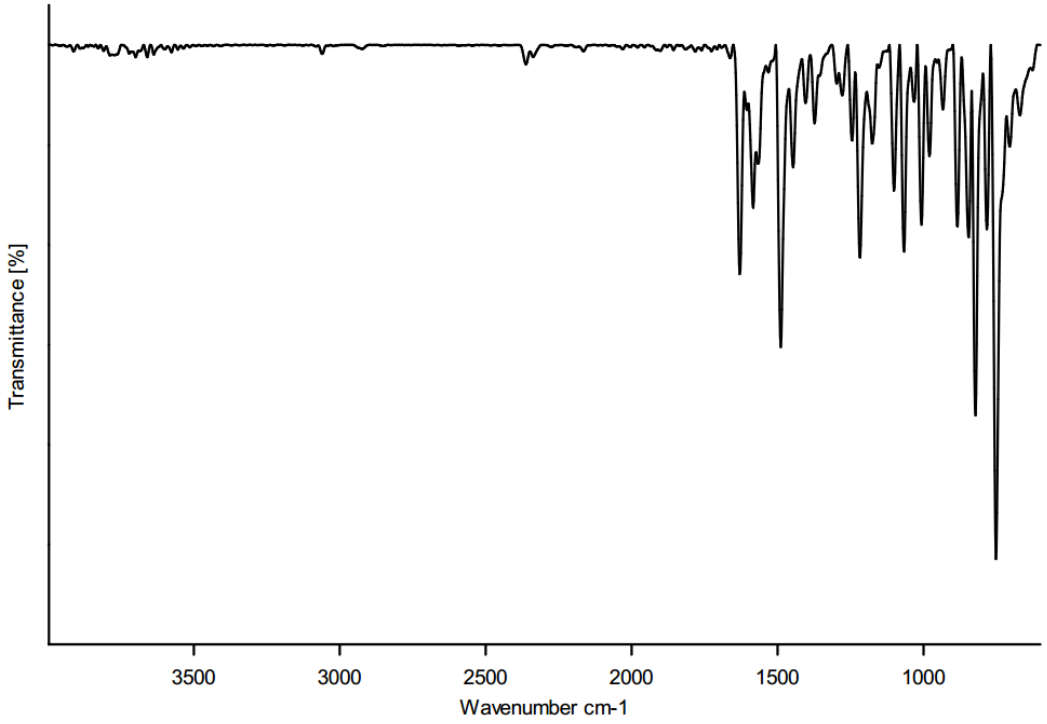


Figure S2:4 Compound 19

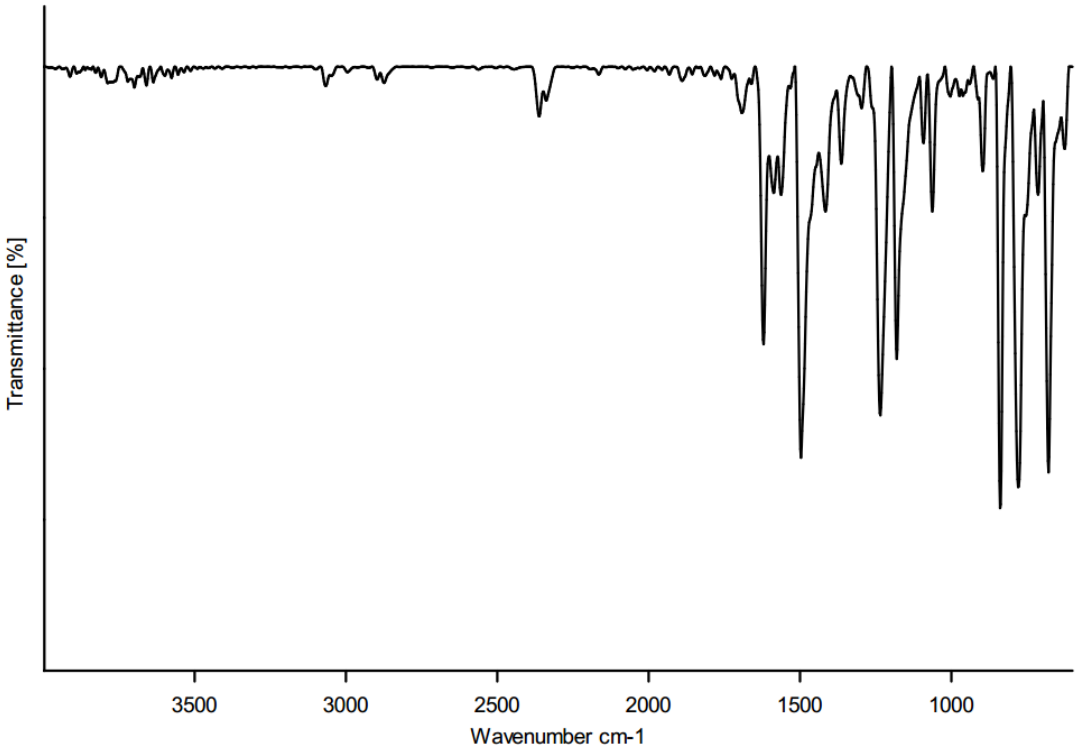


Figure S2:5 Compound 20

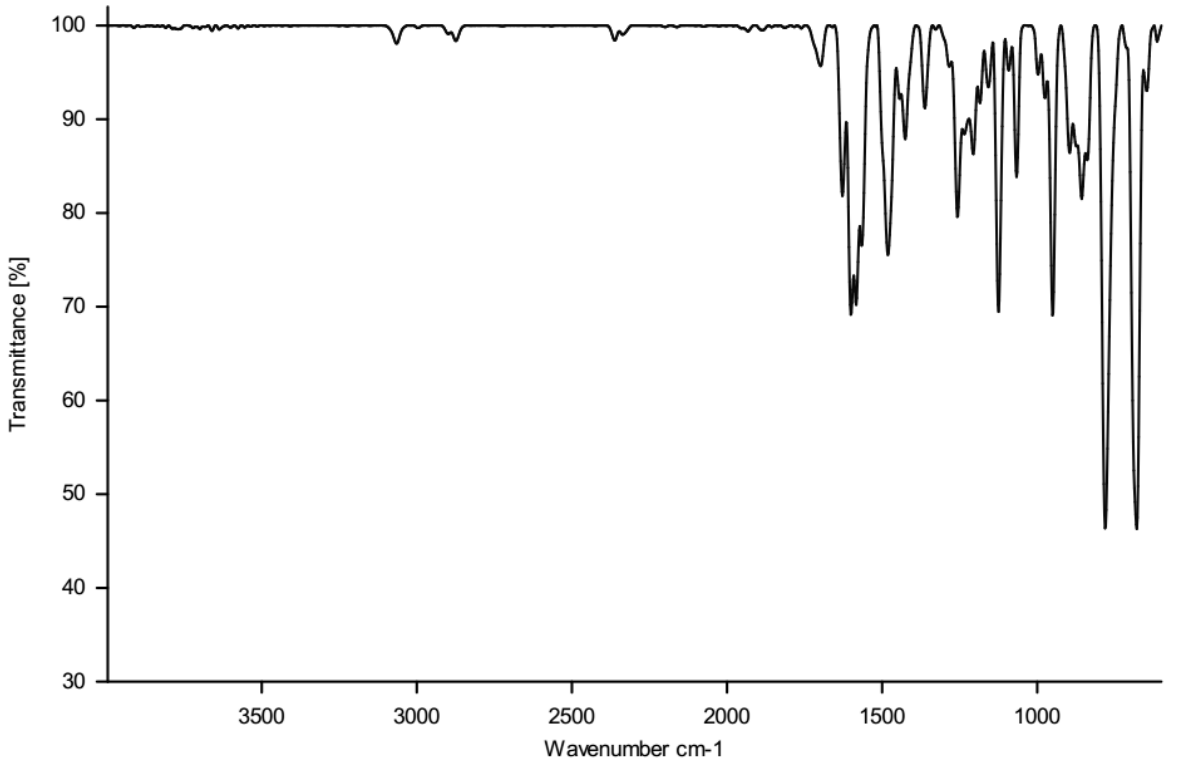


Figure S2:6 Compound 21

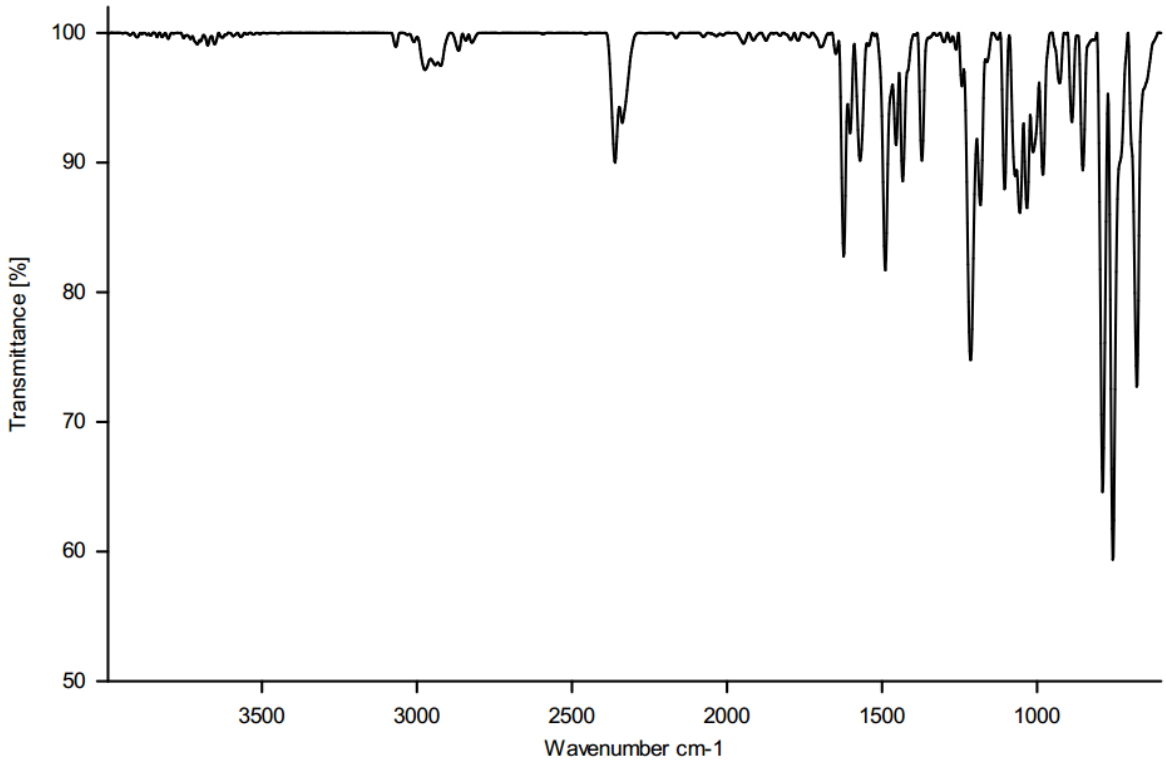


Figure S2:7 Compound 22

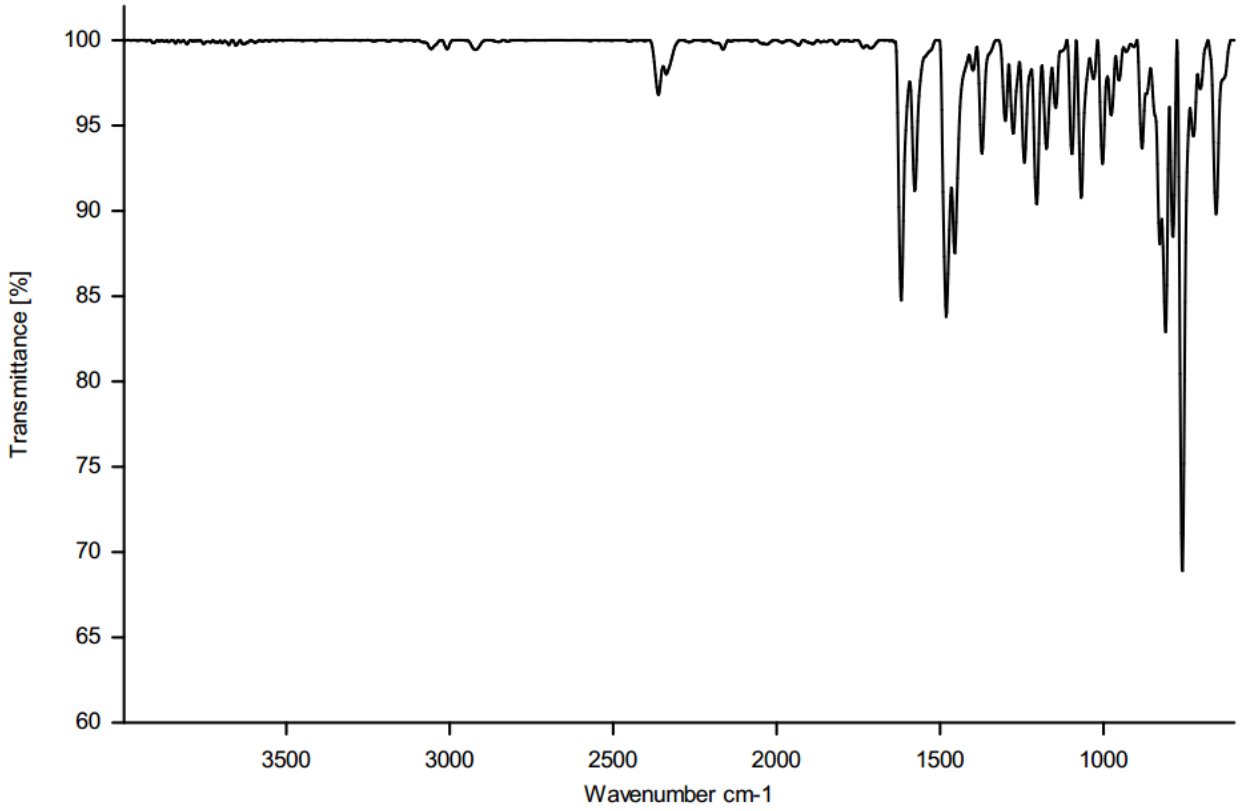


Figure S2:8 Compound 23

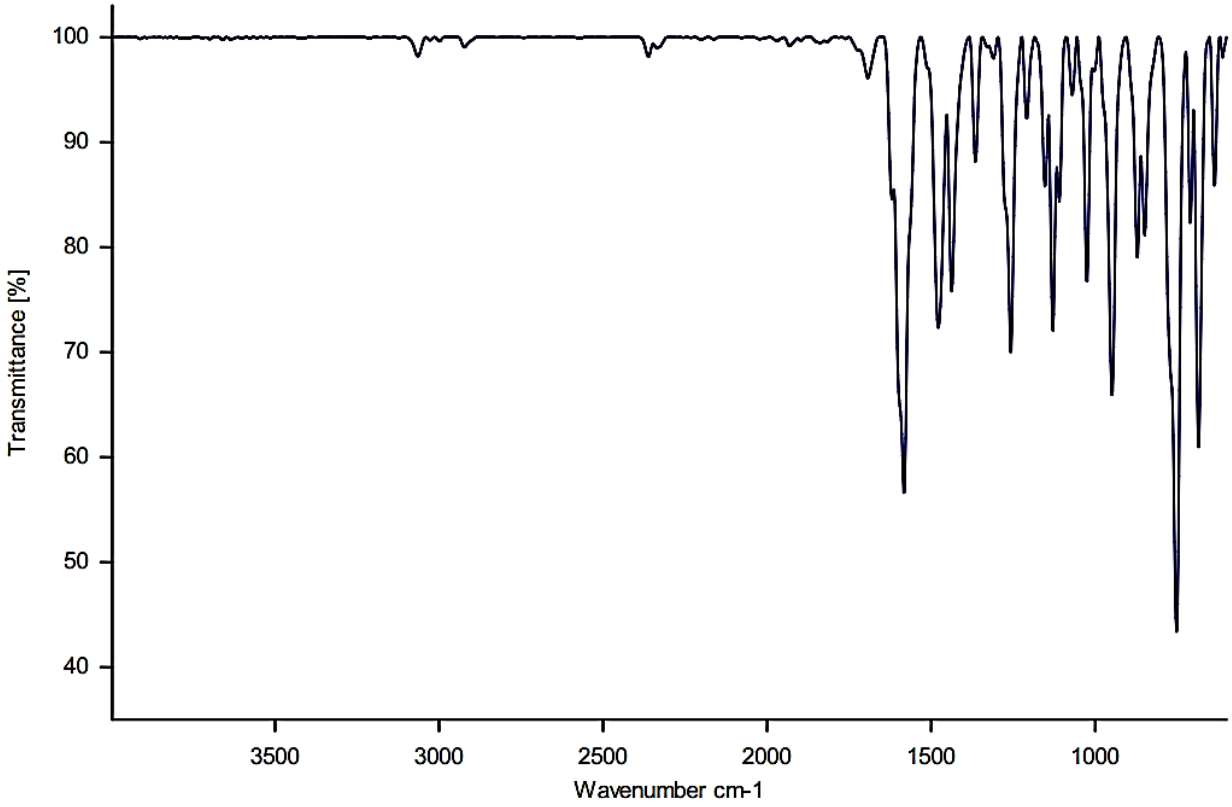


Figure S2:9 Compound 24

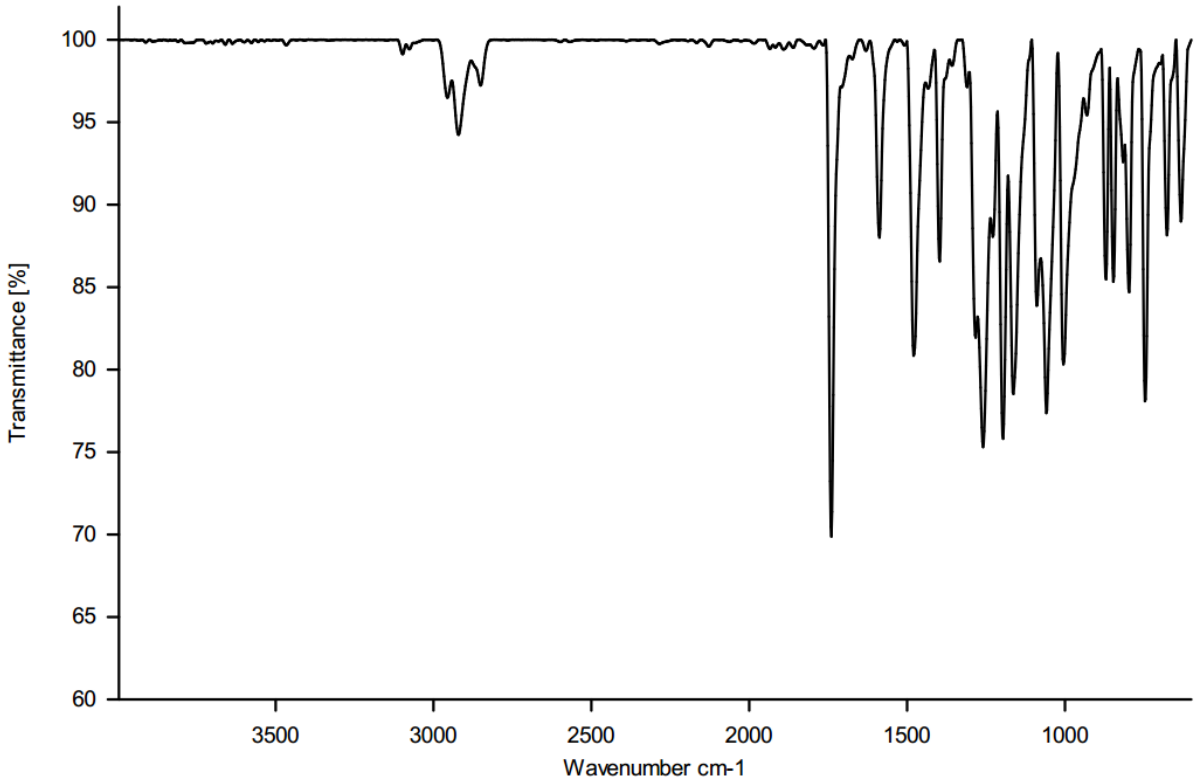


Figure S2:10 Compound 25

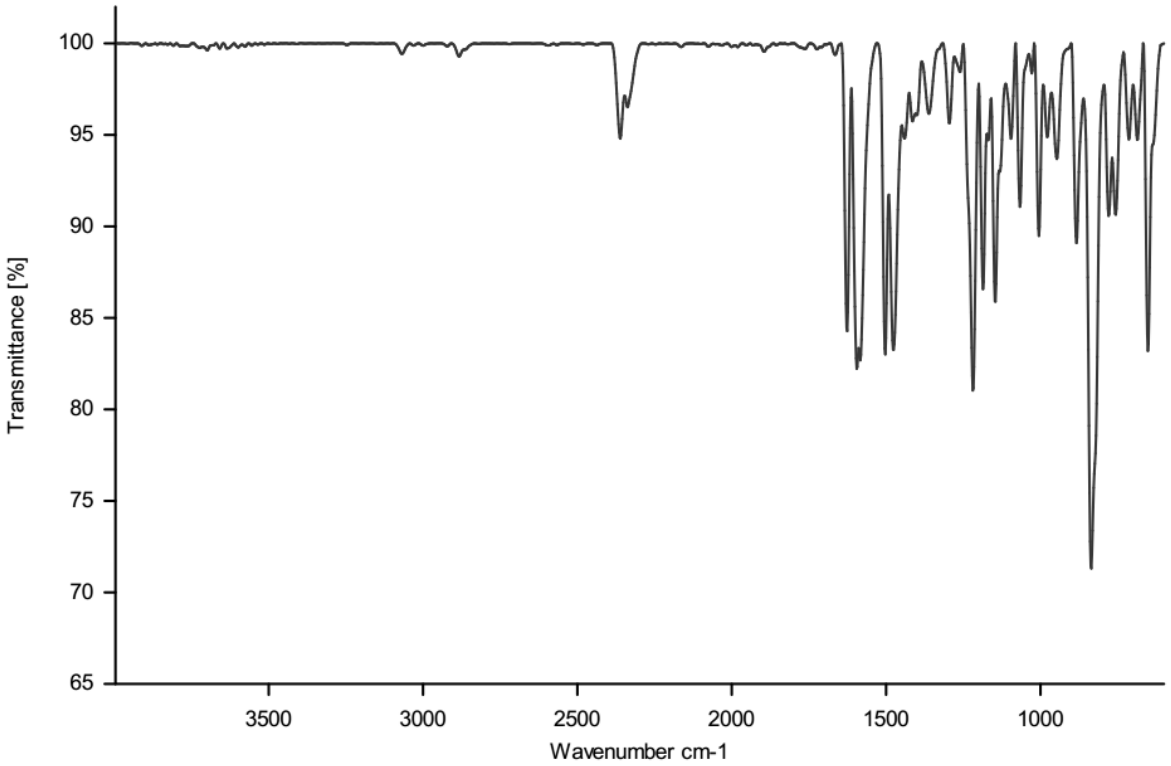


Figure S2:11 Compound 26

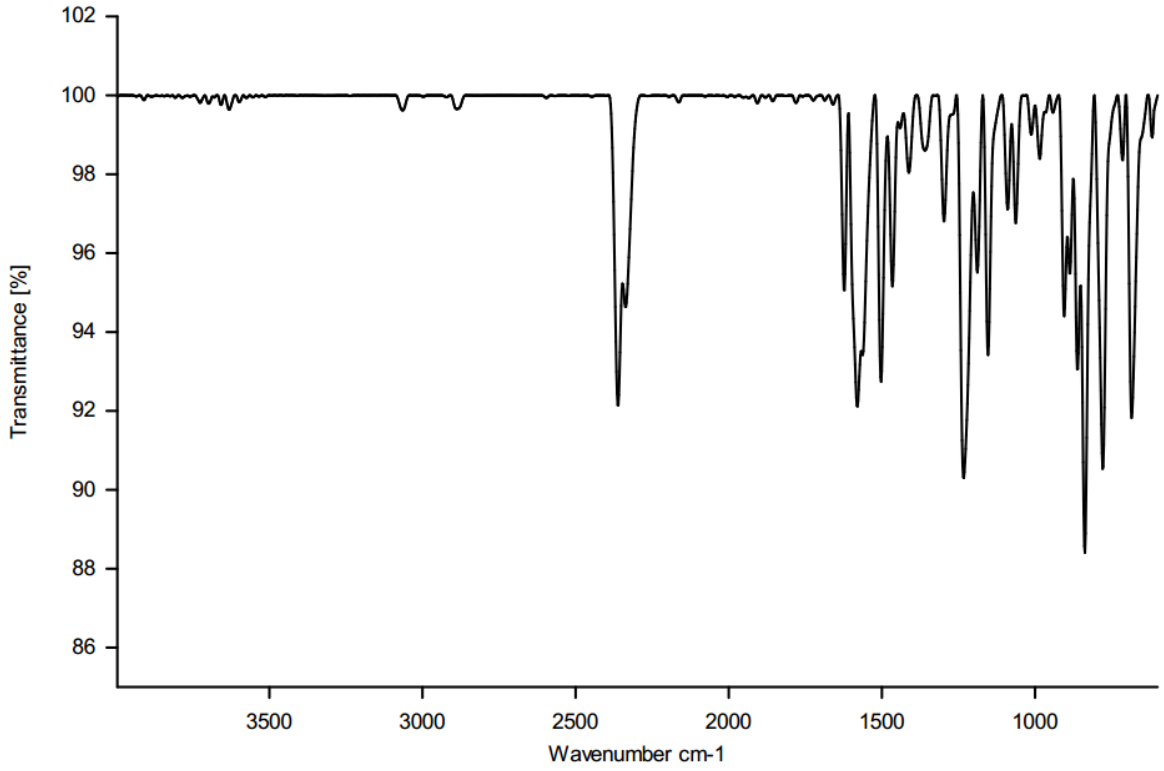


Figure S2:12 Compound 27

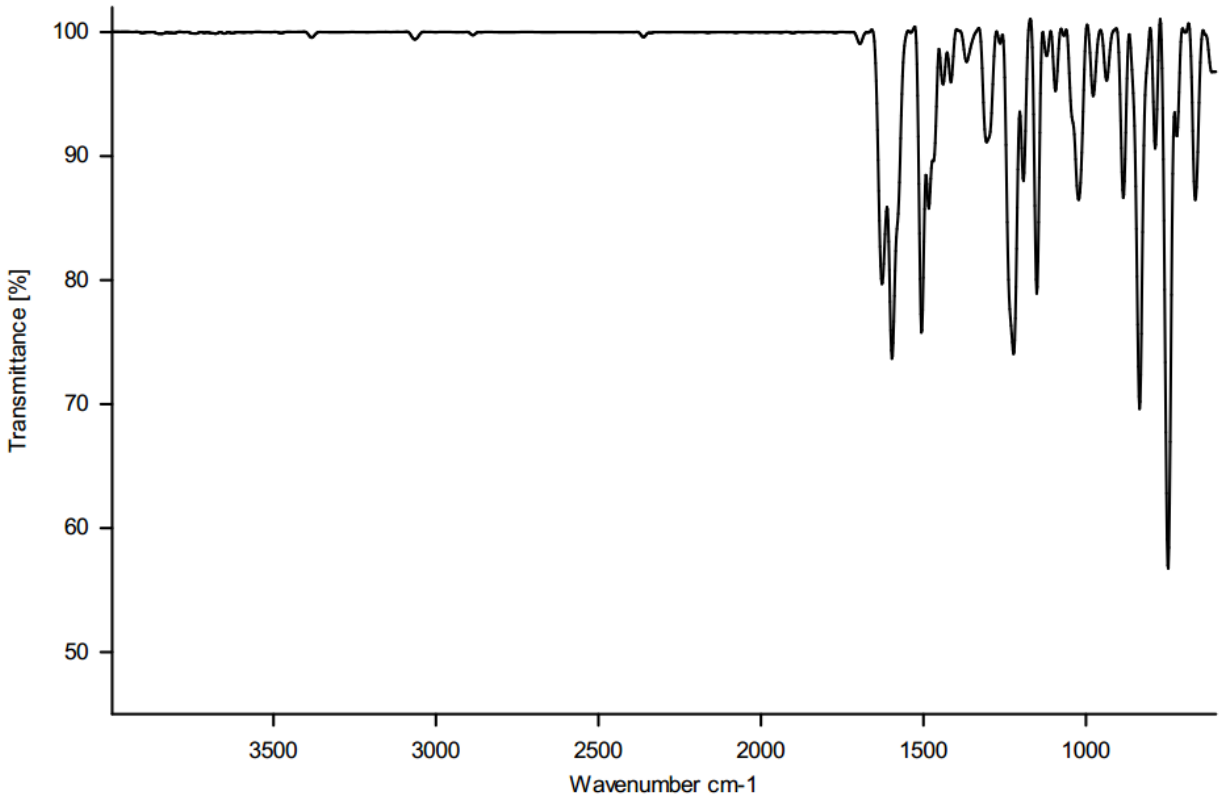


Figure S2:13 Compound 28

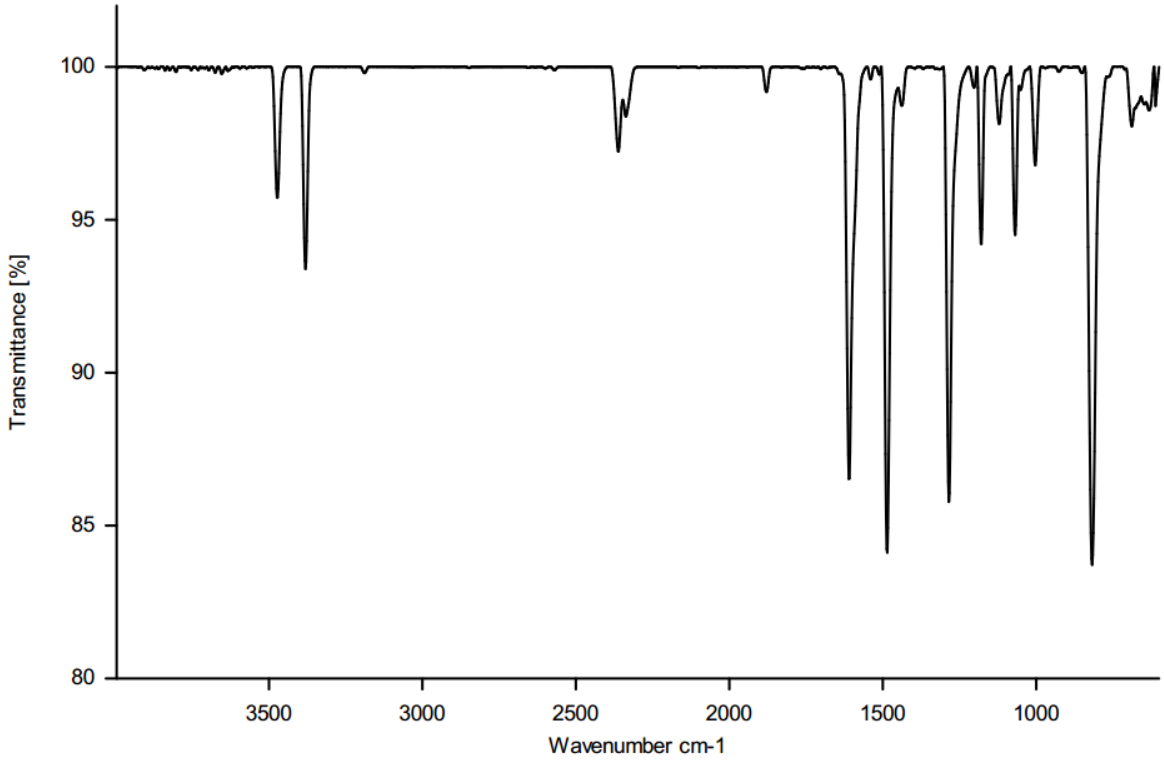


Figure S2:14 Compound 29

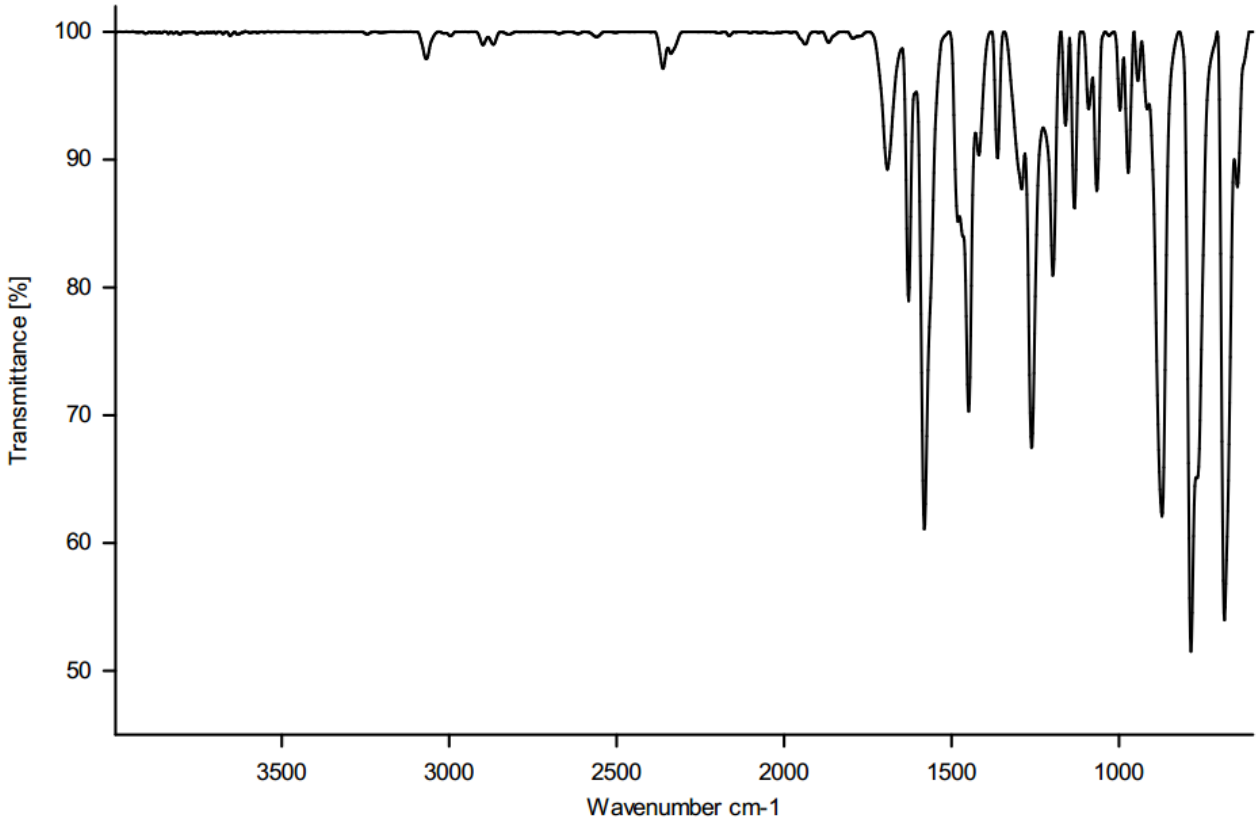


Figure S2:15 Compound 30

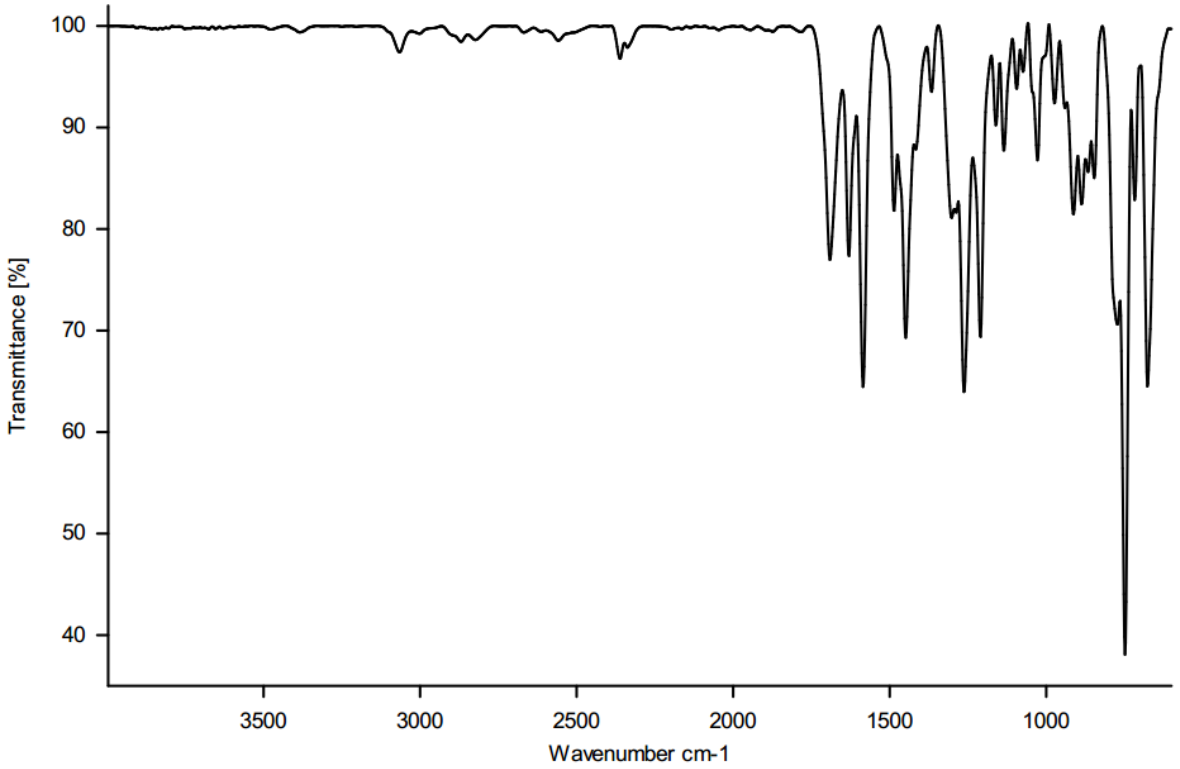


Figure S2:16 Compound 31

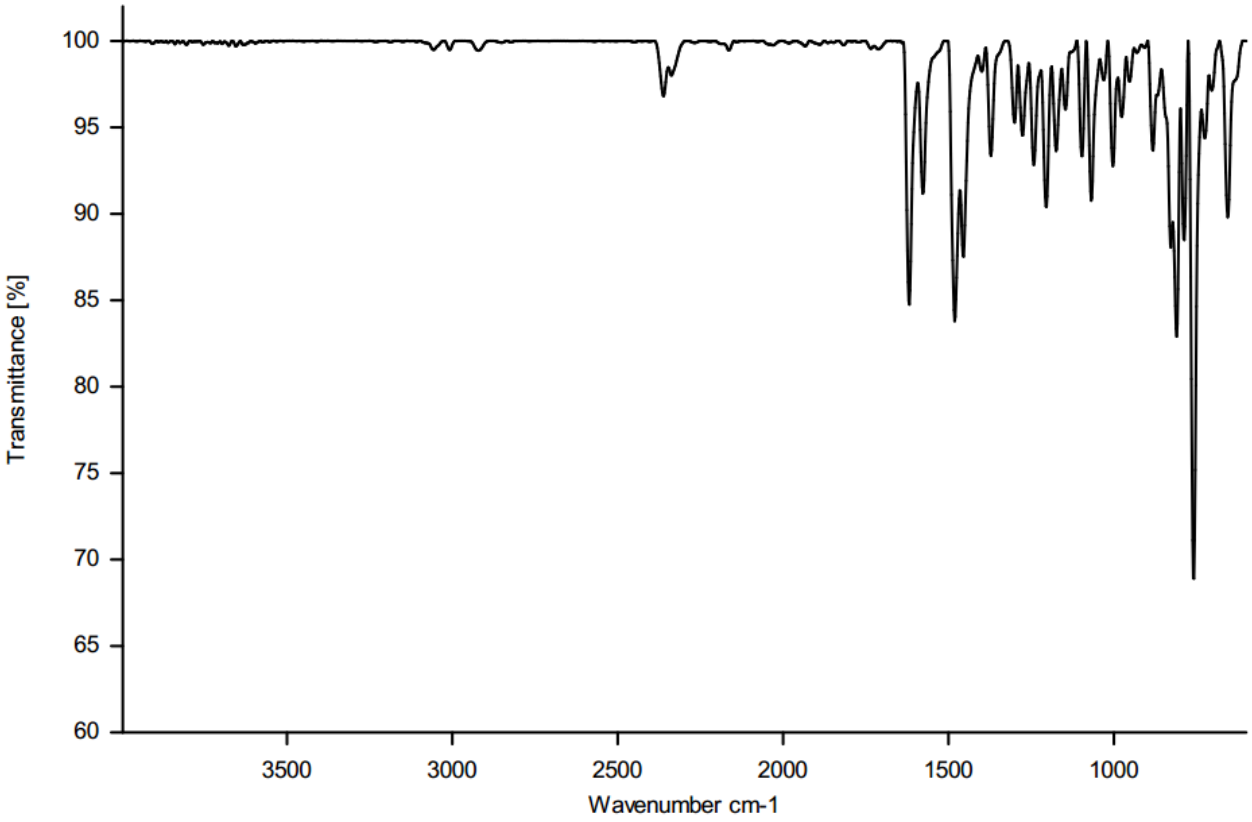


Figure S2:17 Compound 32

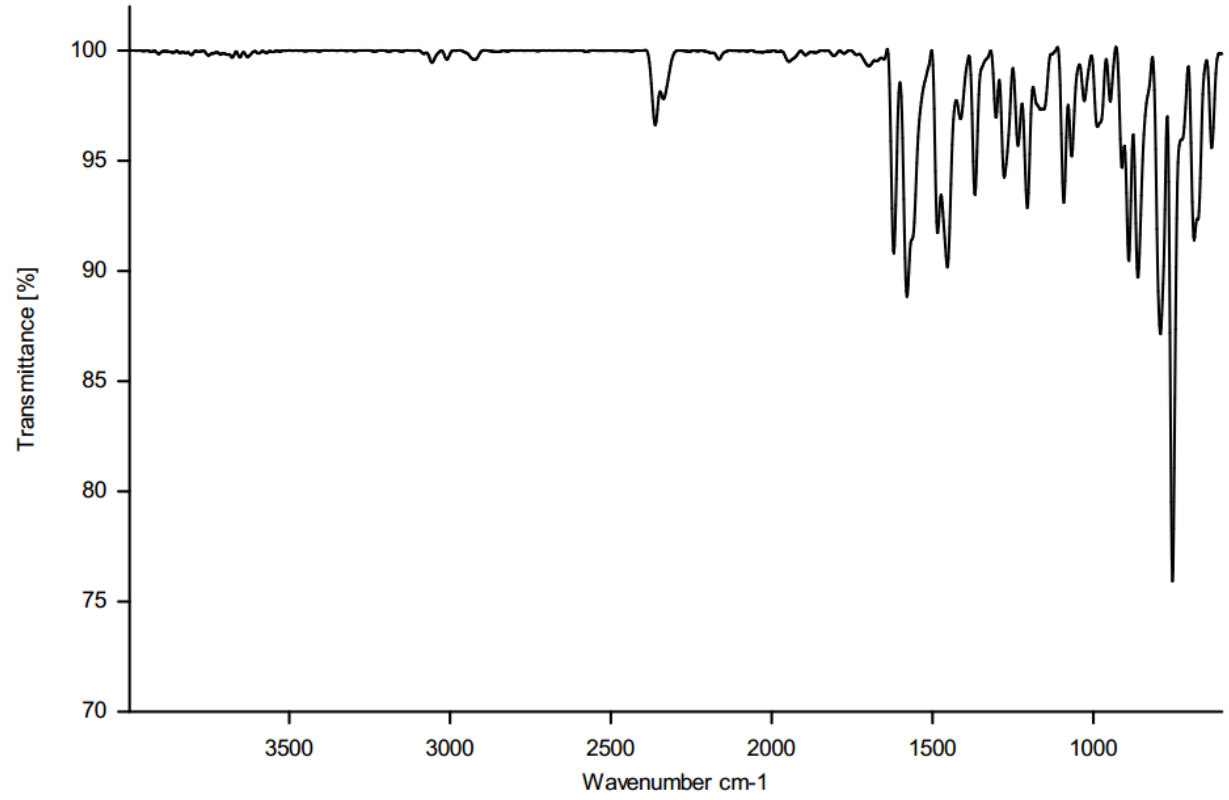


Figure S2:18 Compound 33

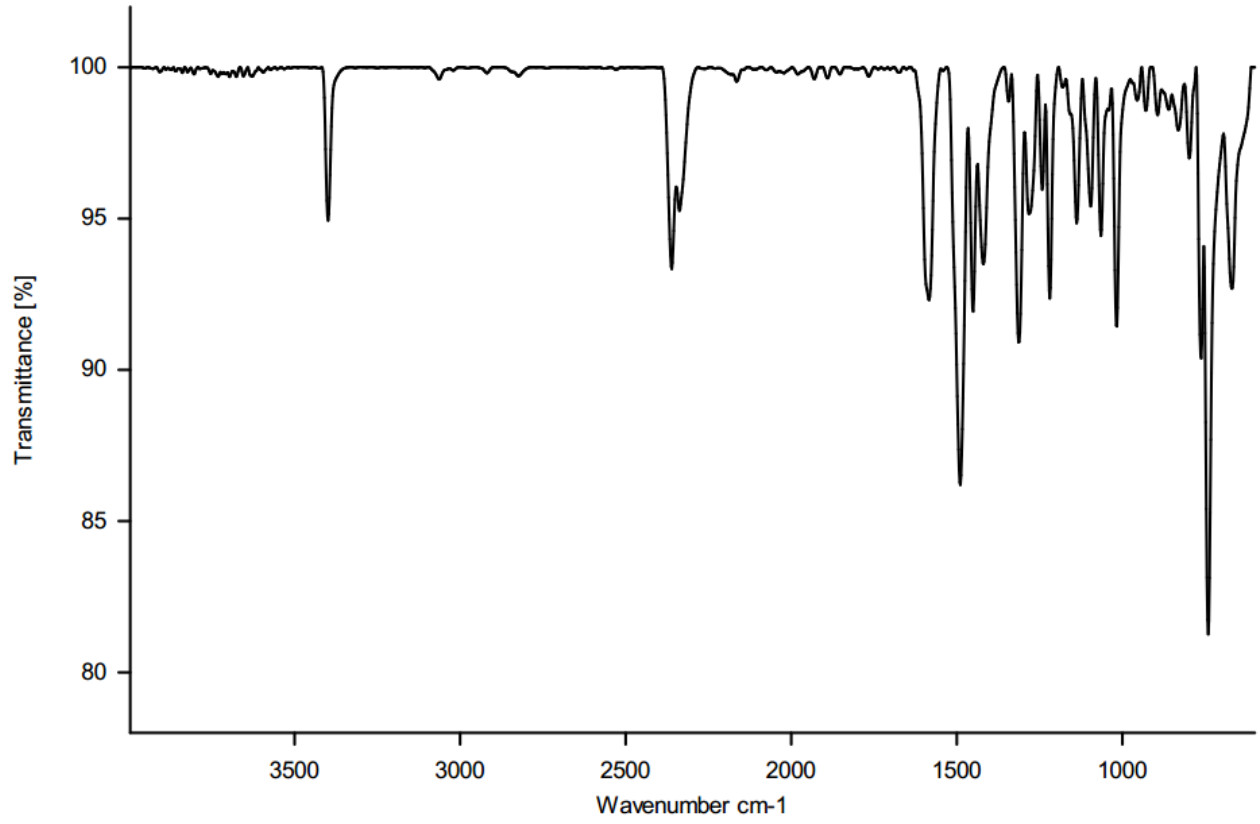


Figure S2:19 Compound 34

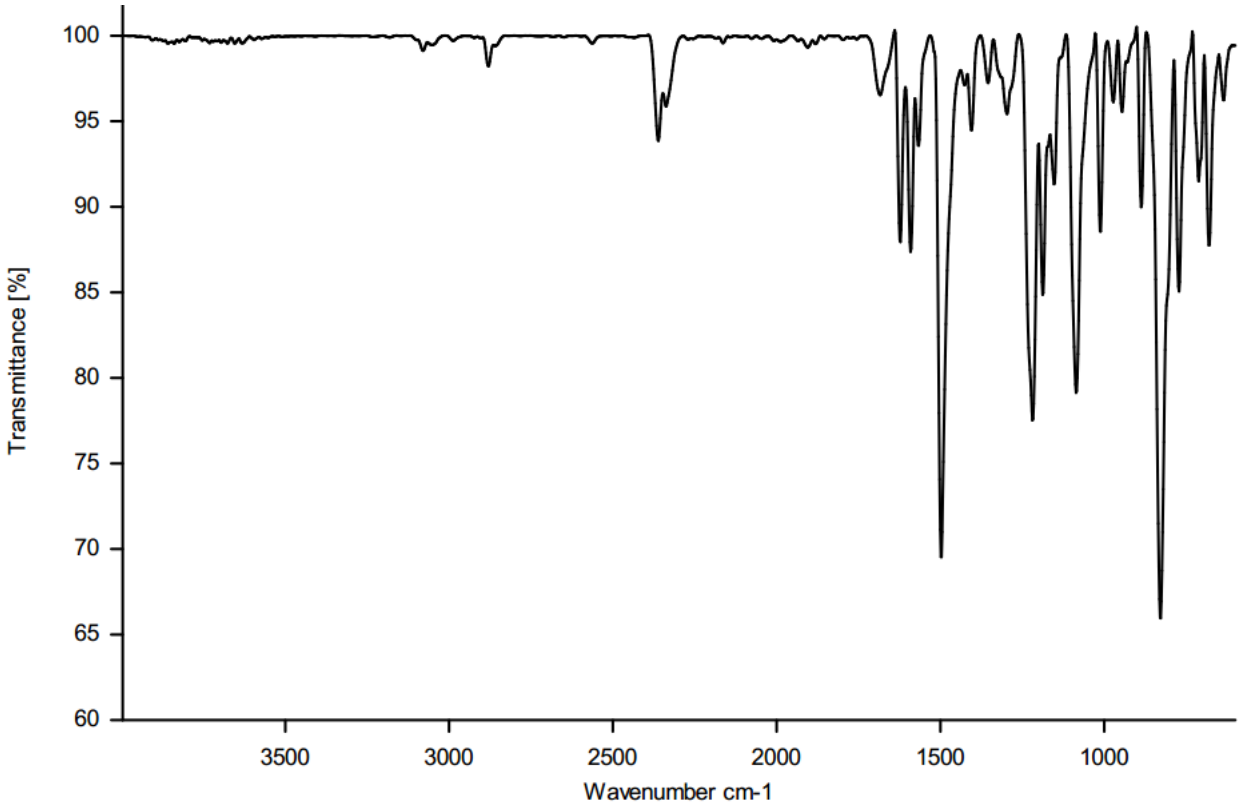


Figure S2:20 Compound 35

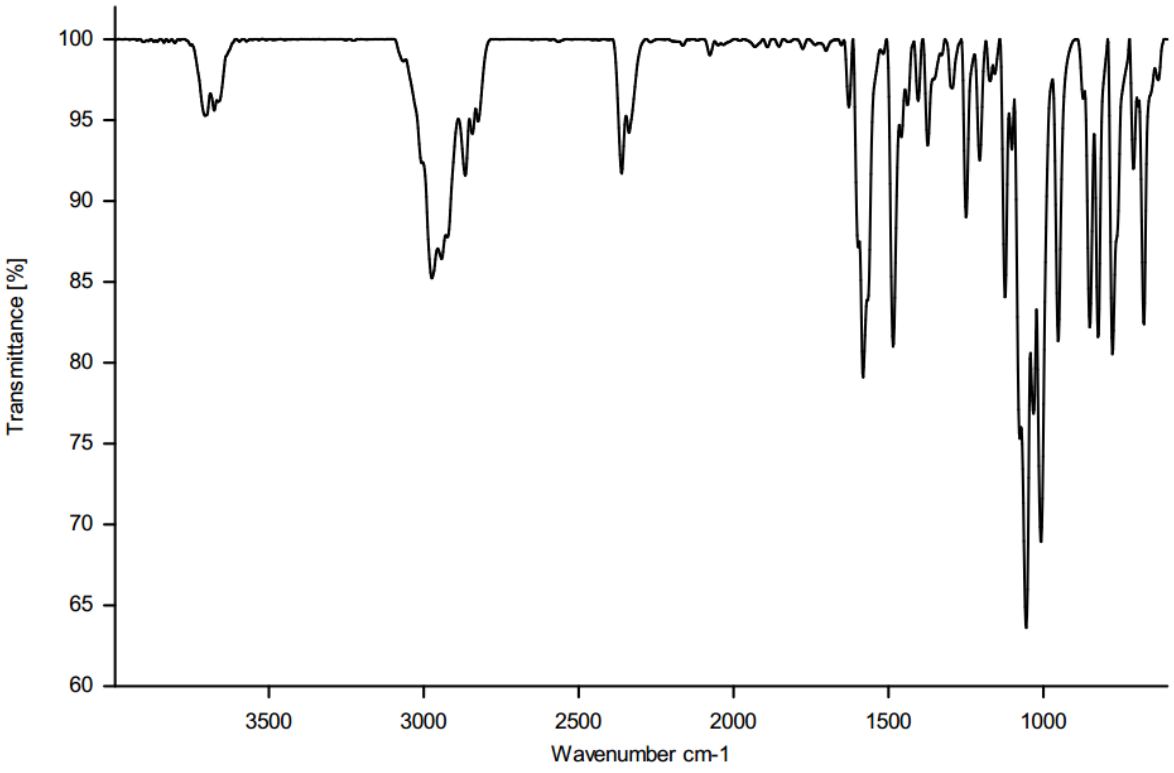


Figure S2:21 Compound 36

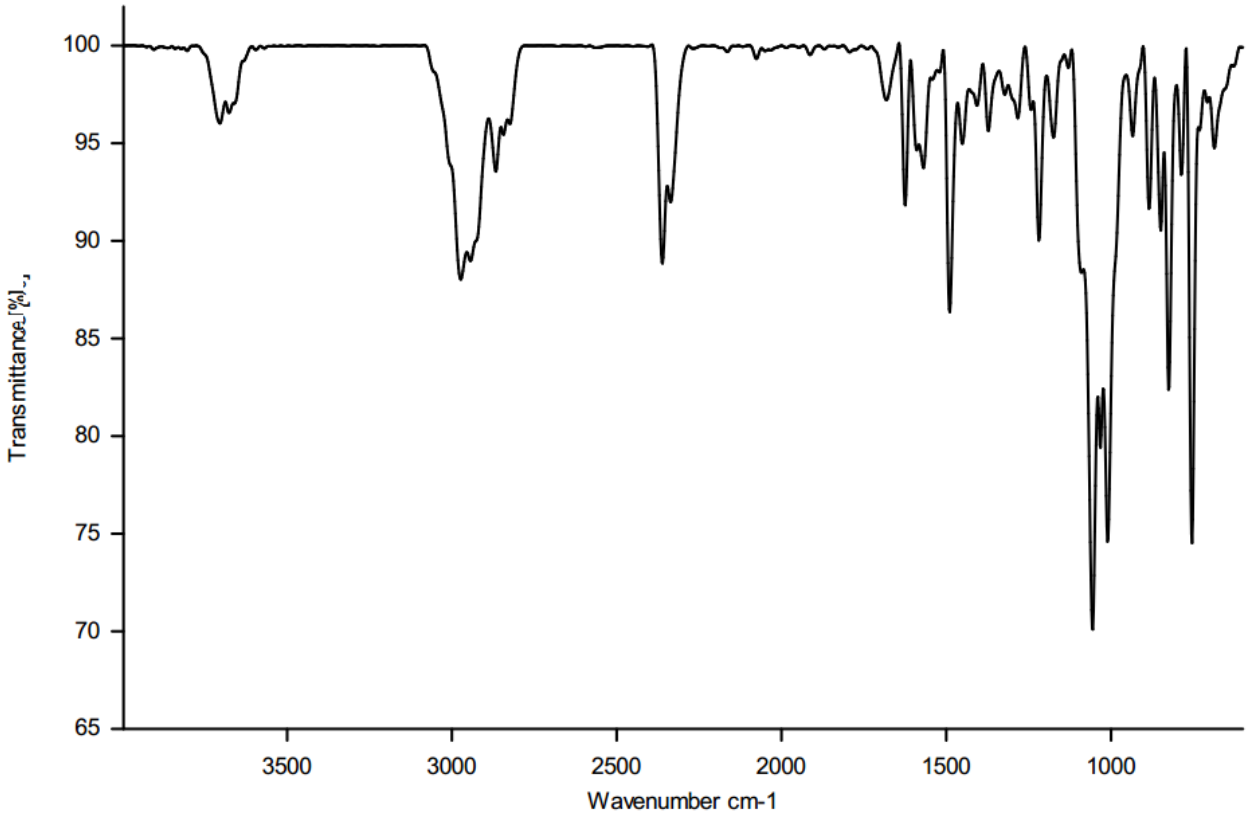


Figure S2:22 Compound 37

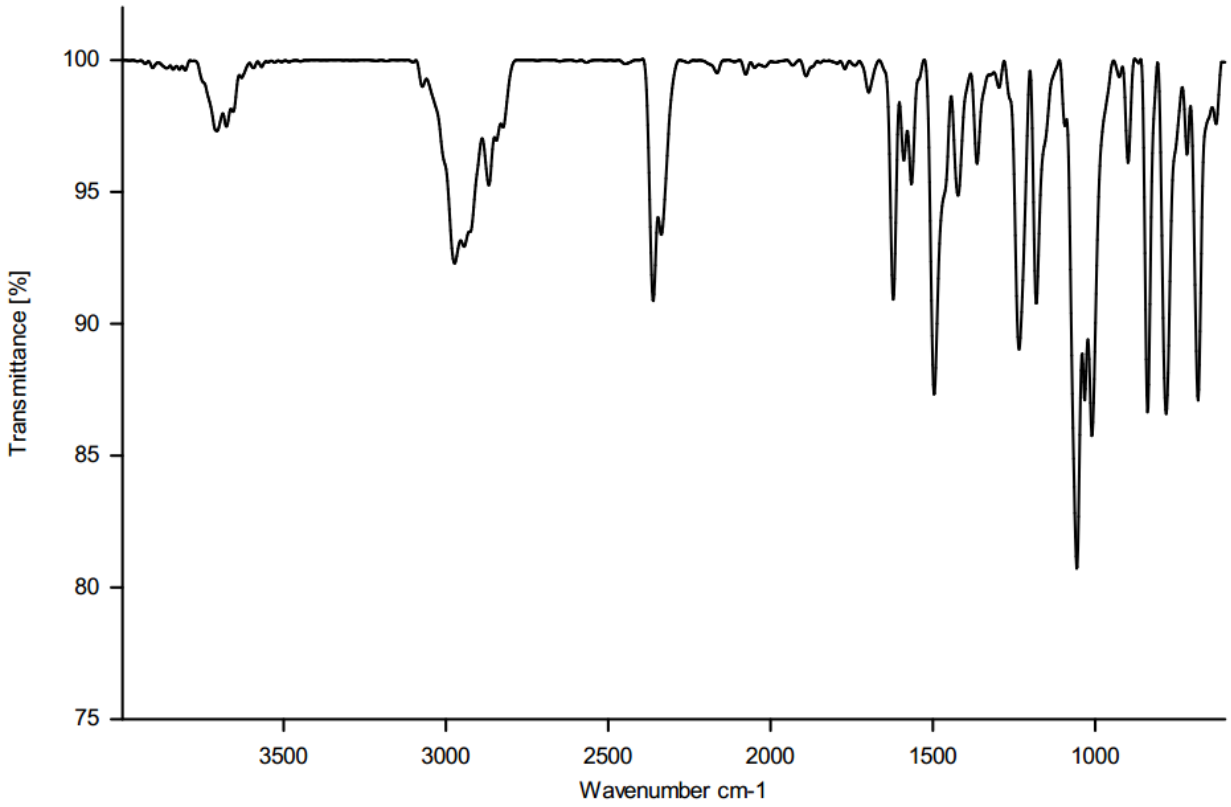


Figure S2:23 Compound 38

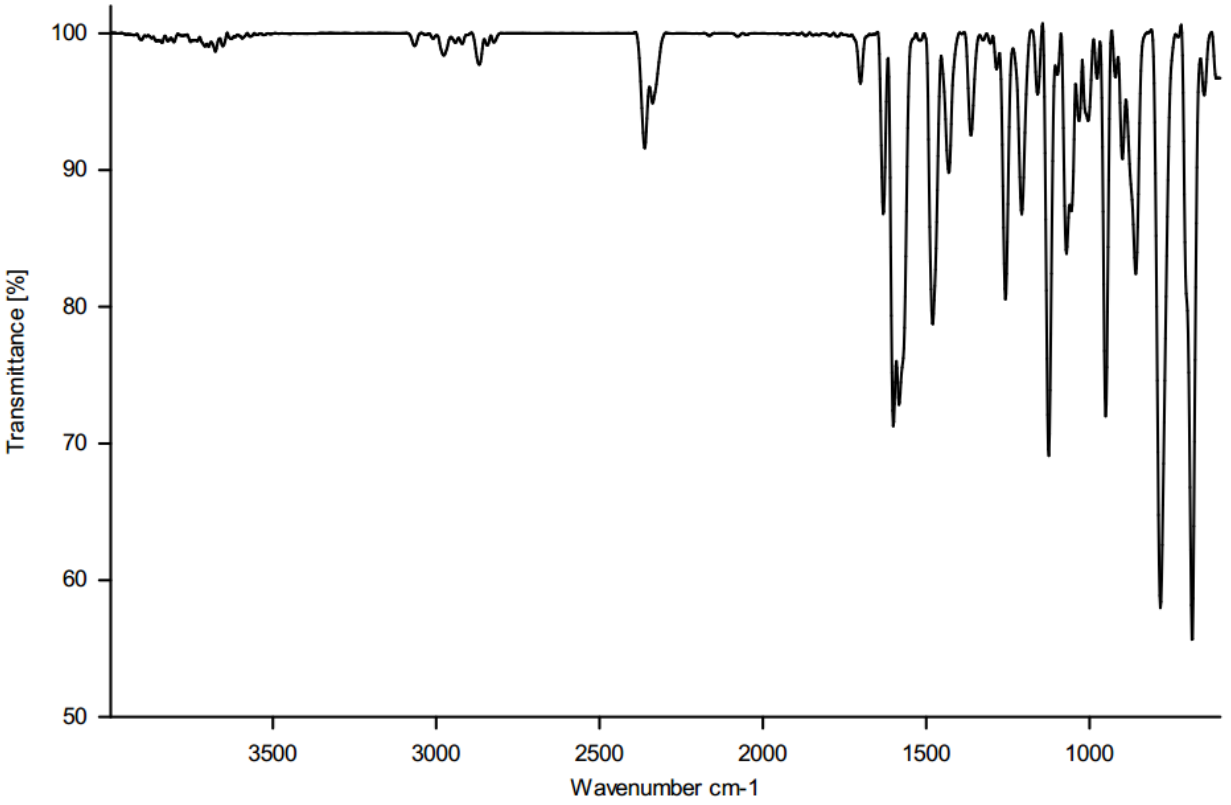


Figure S2:24 Compound 39

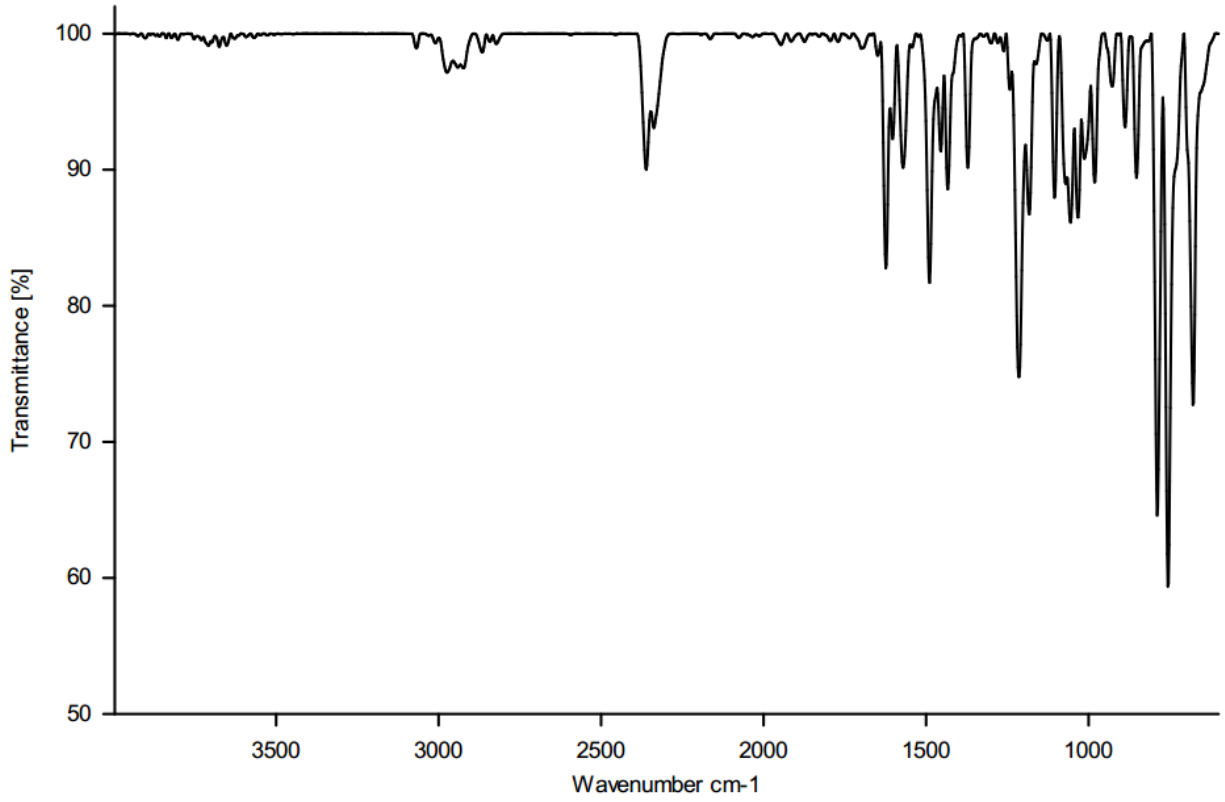


Figure S2:25 Compound 40

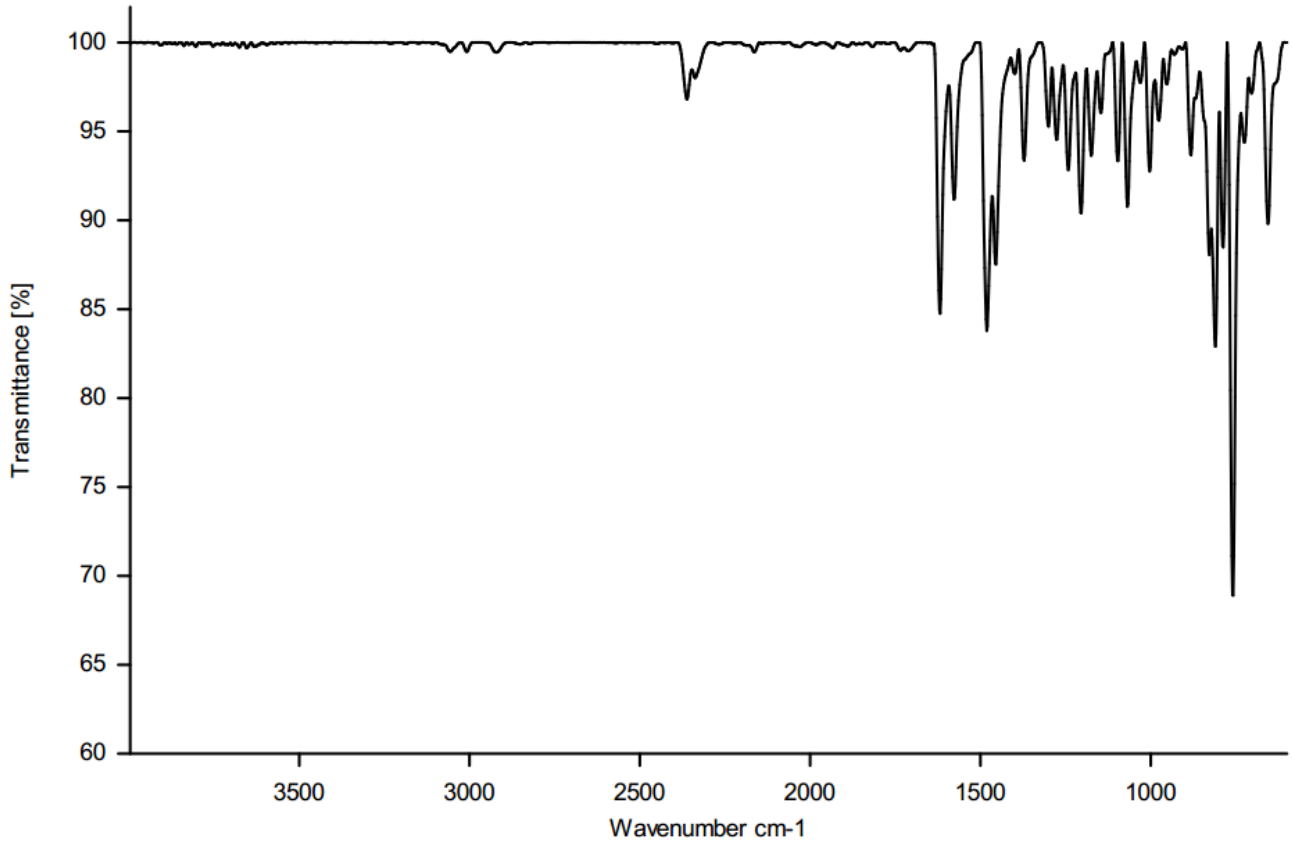


Figure S2:26 Compound 41

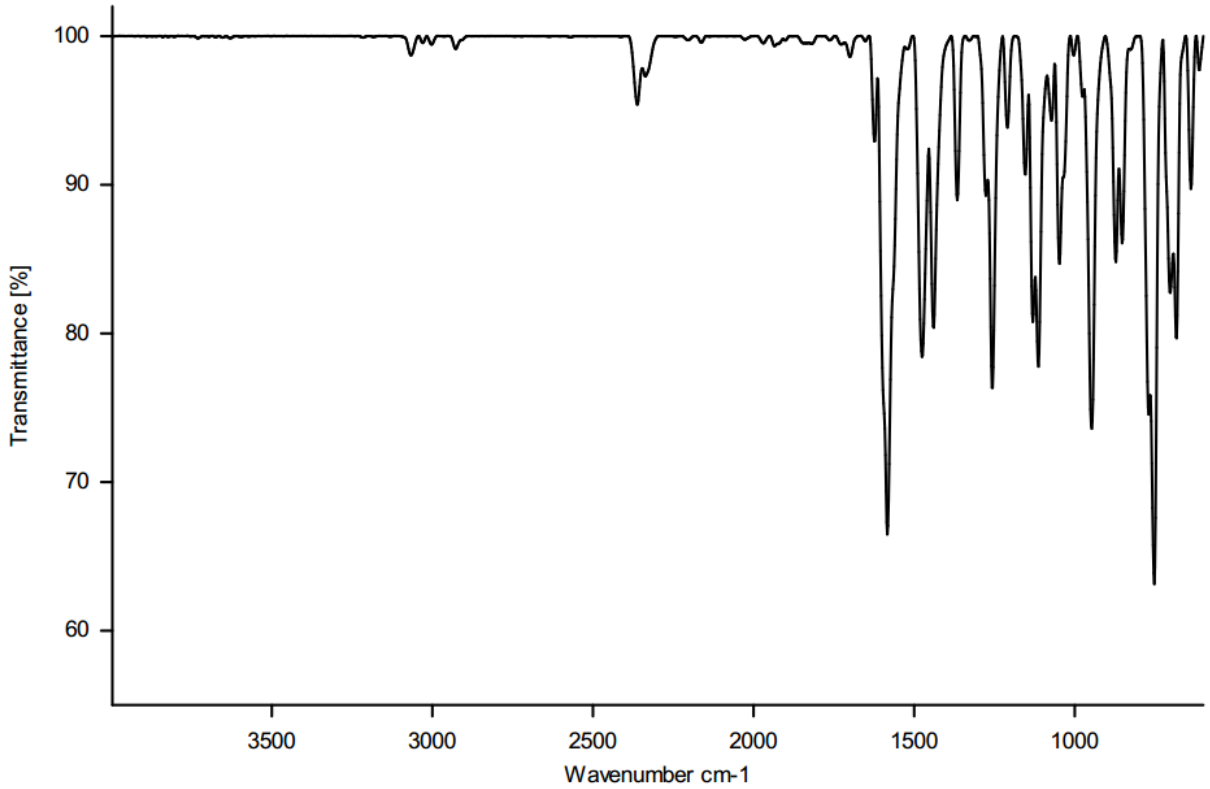


Figure S2:27 Compound 42

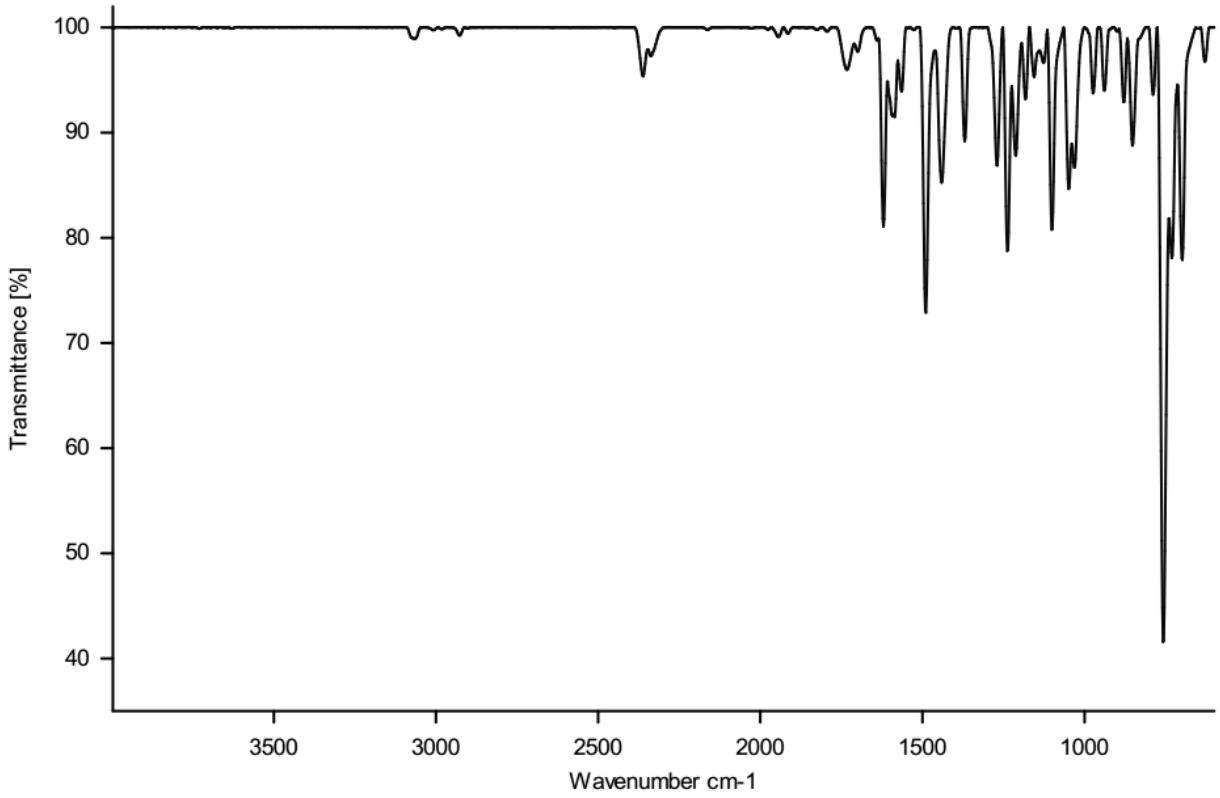


Figure S2:28 Compound 43

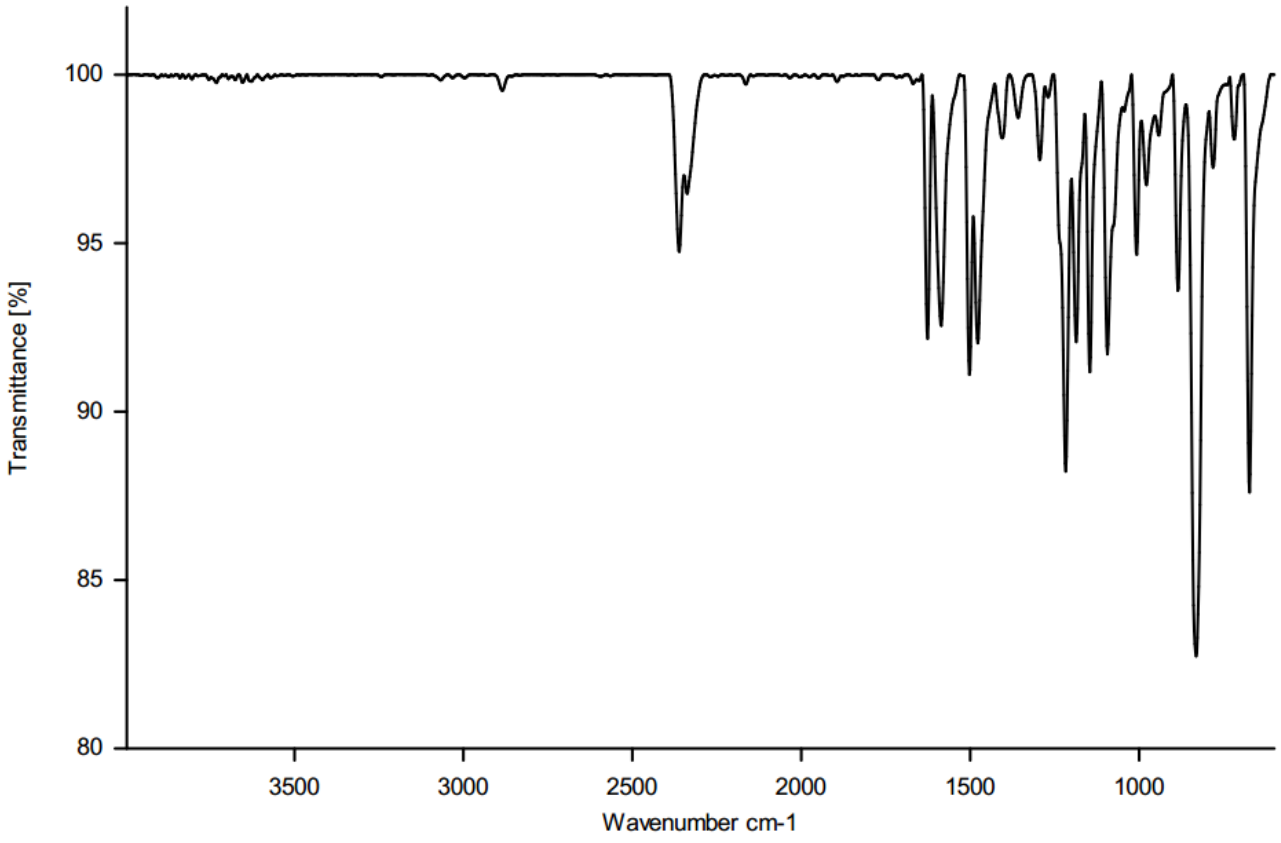


Figure S2:29 Compound 44

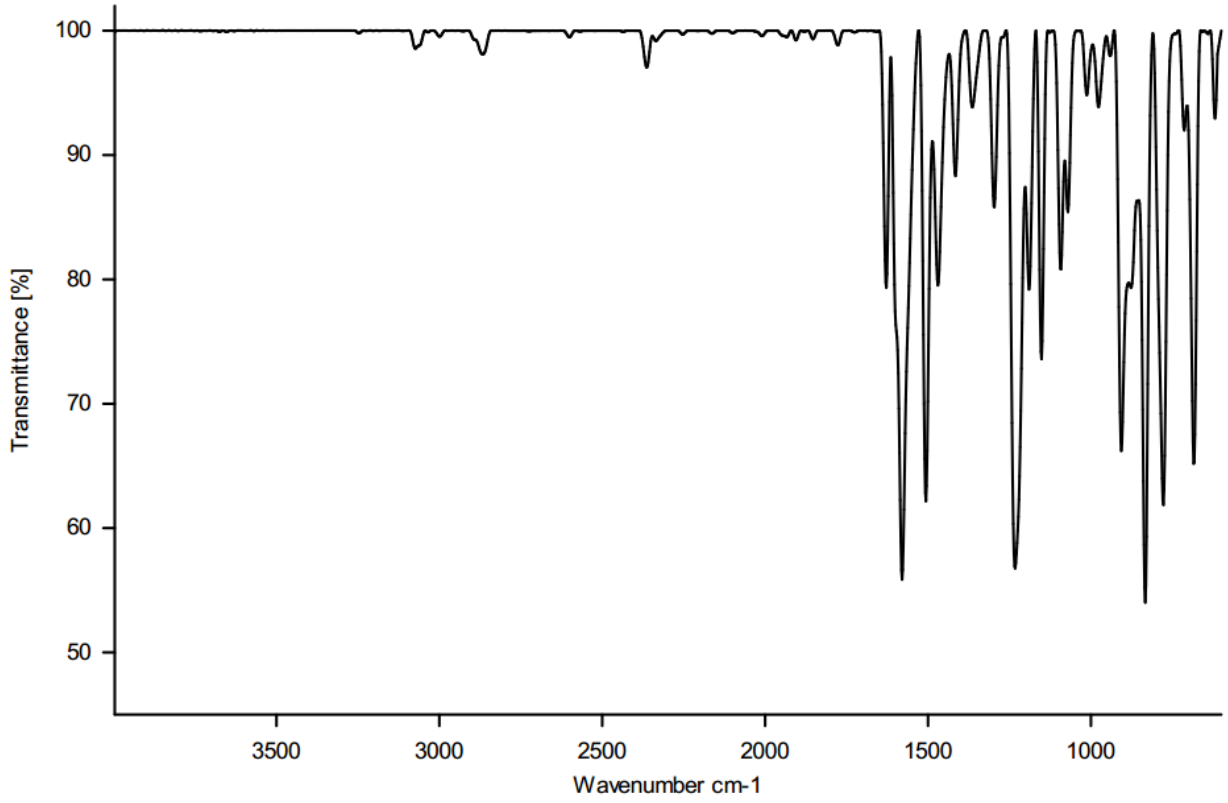


Figure S2:30 Compound 45

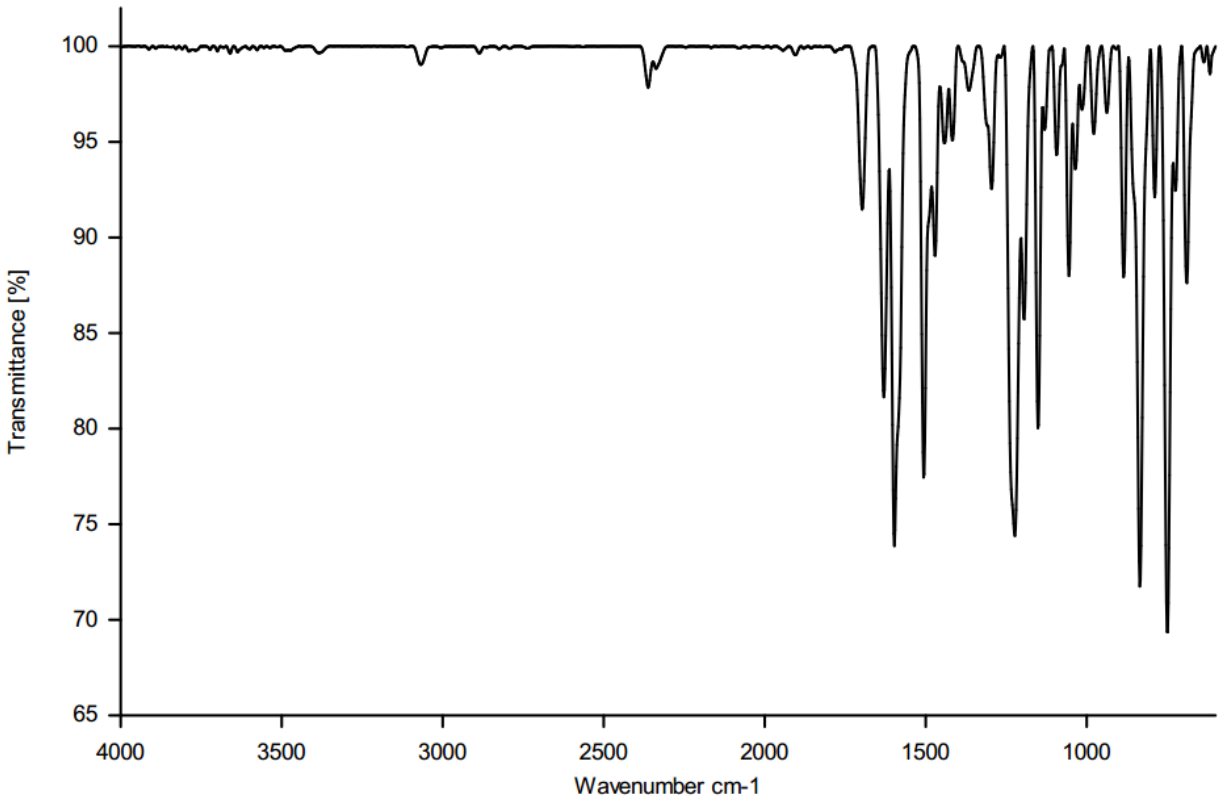


Figure S2:31 Compound 46

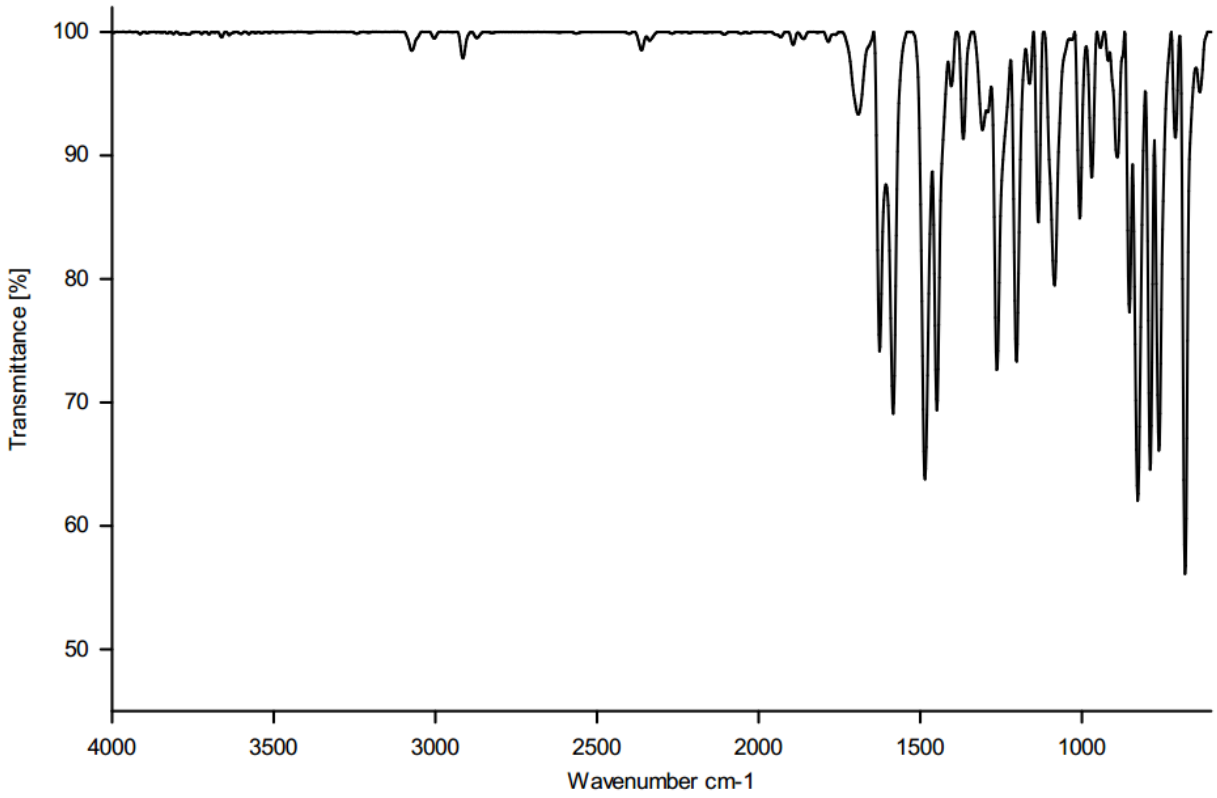


Figure S2:32 Compound 47

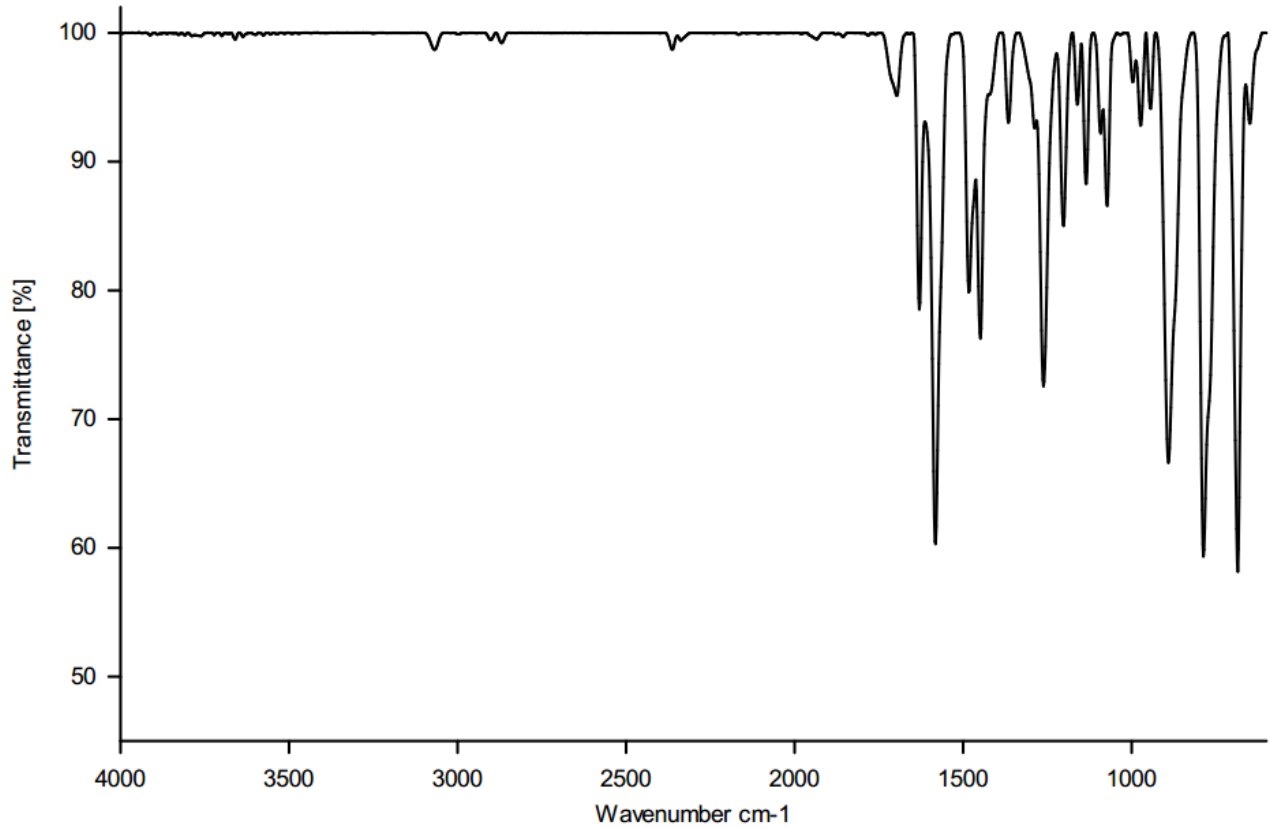


Figure S2:33 Compound 48

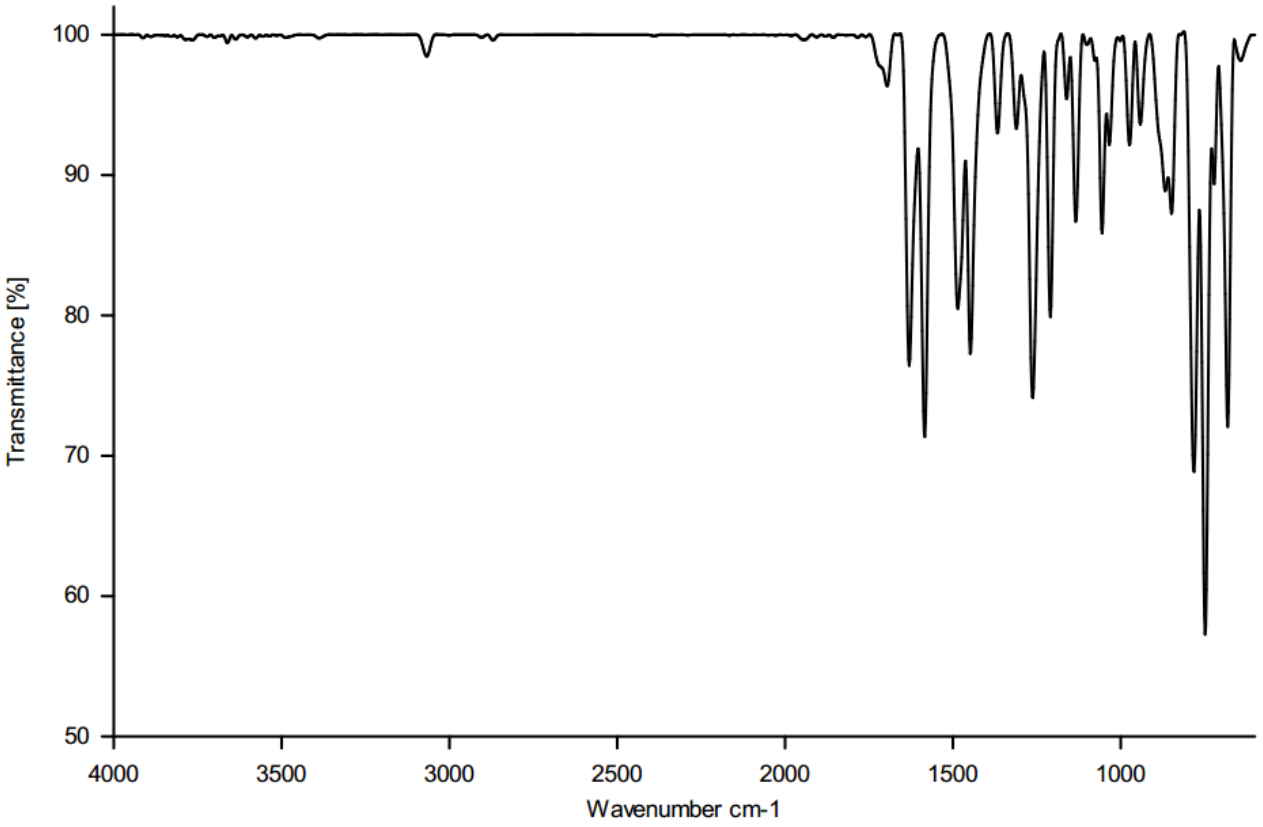


Figure S2:34 Compound 49

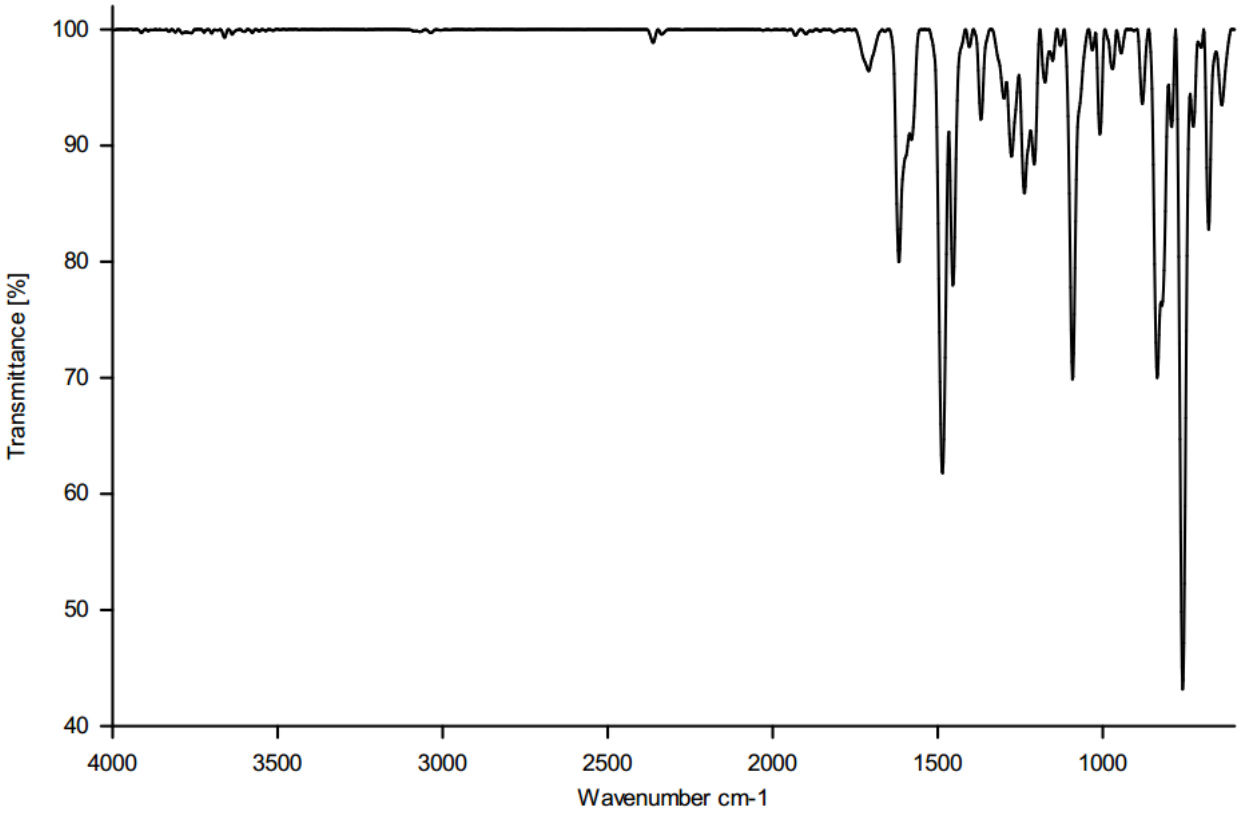


Figure S2:35 Compound 50

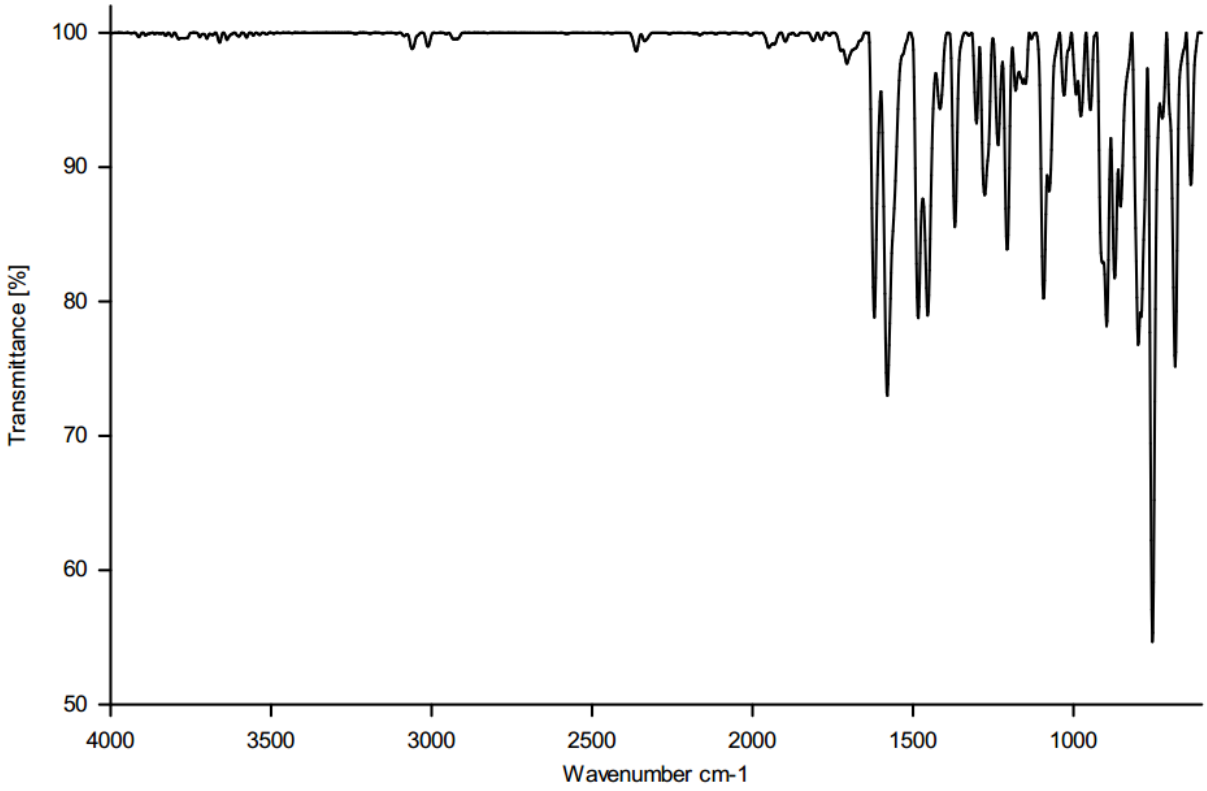


Figure S2:36 Compound 51

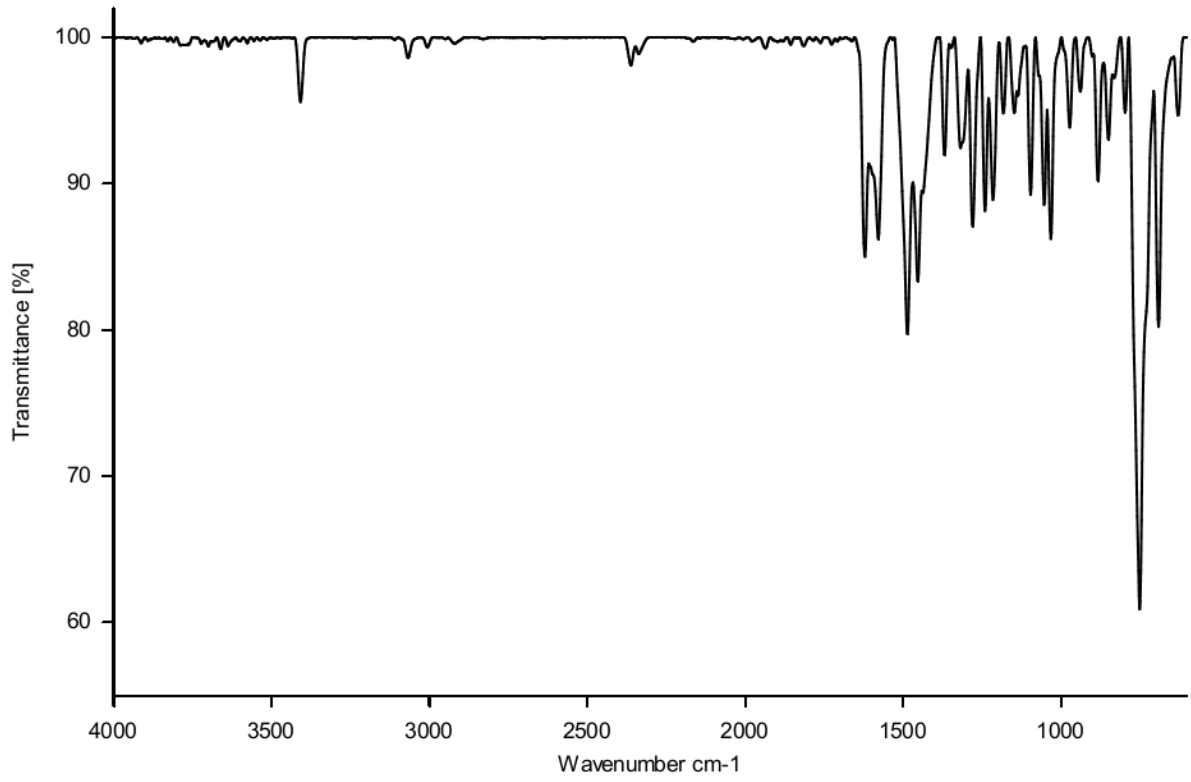


Figure S3: Powder X-ray Data for all solid compounds recorded on and their comparison with stimulated PXRD pattern. Patterns displayed in blue colour were recorded on the purified product, while the patterns simulated from the single crystal data are shown in red colour and green colour (2nd polymorph).

Figure S3:1 Compound 16, 16F1, 16F2

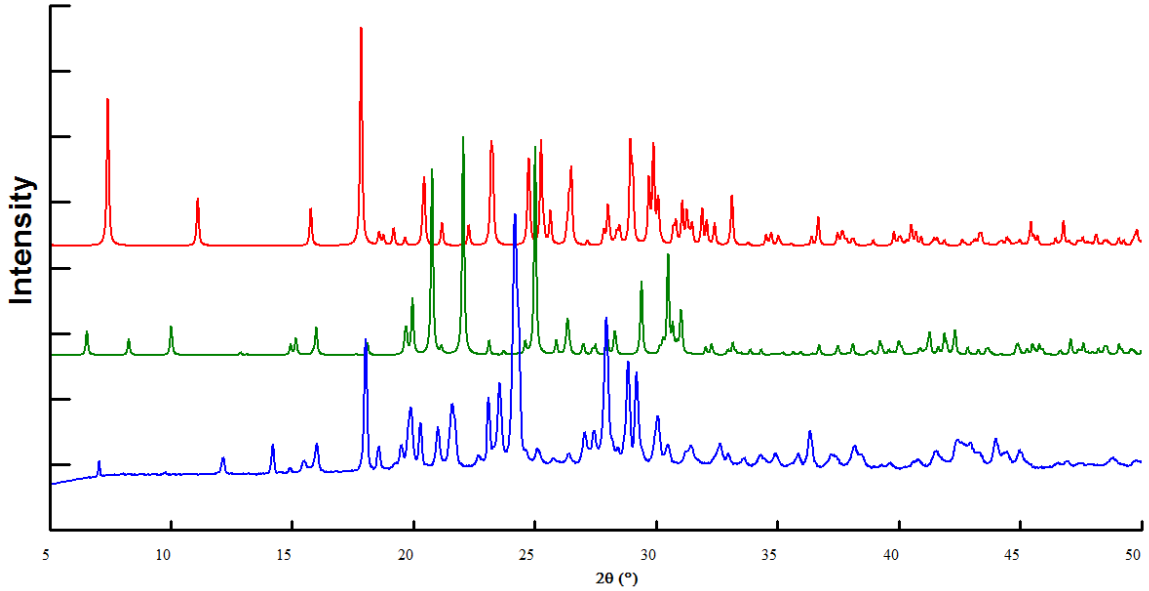


Figure S3:2 Compound 17

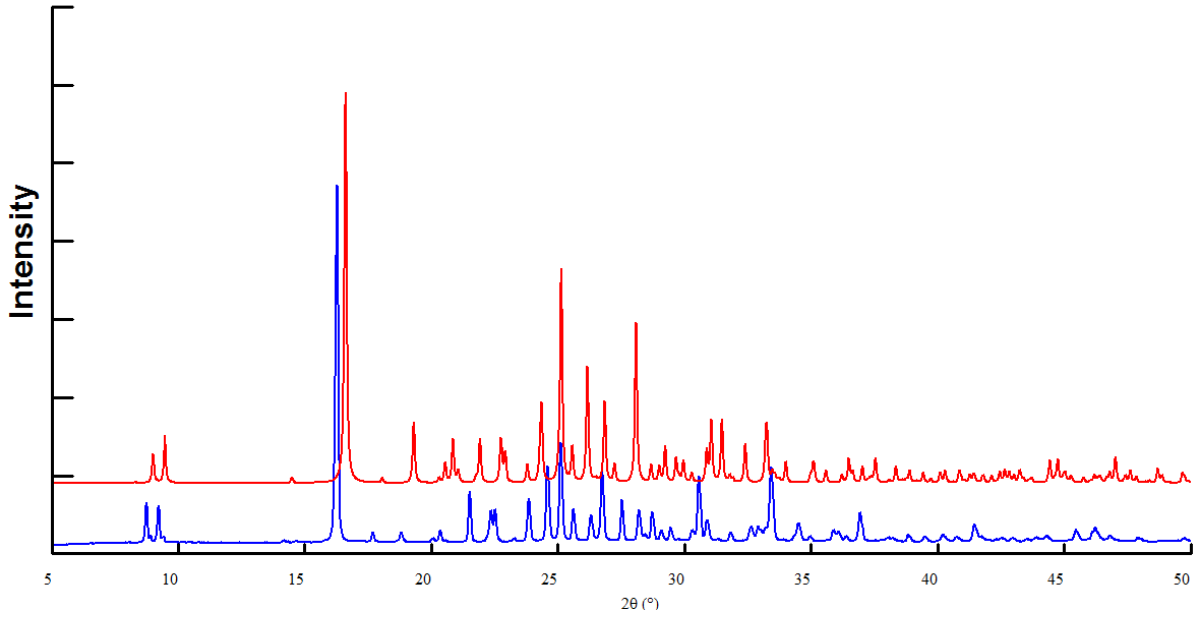


Figure S3:3 Compound 18

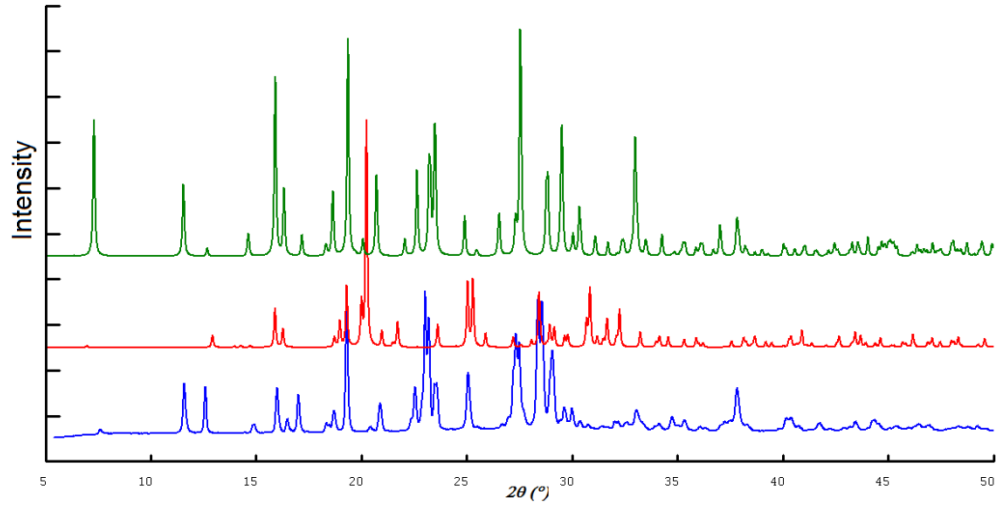


Figure S3:4 Compound 19

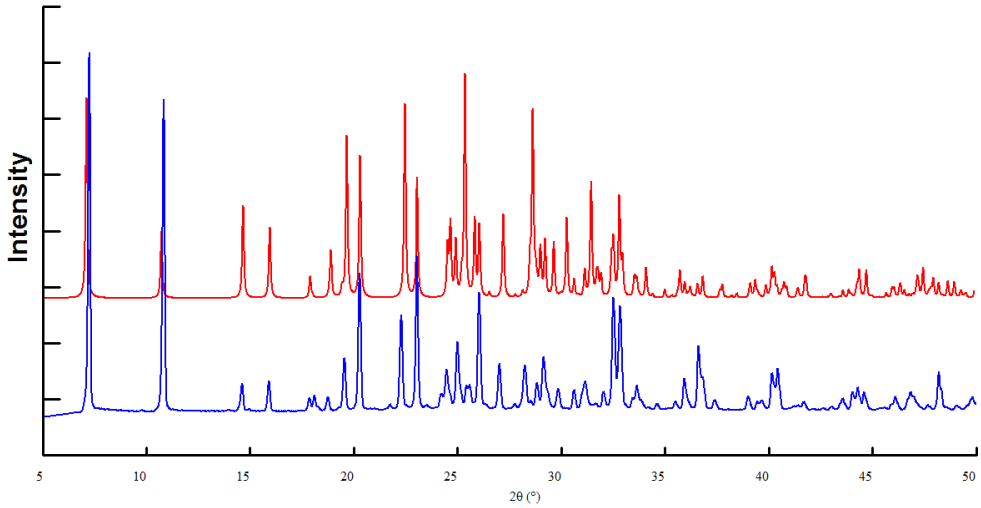


Figure S3:5 Compound 21

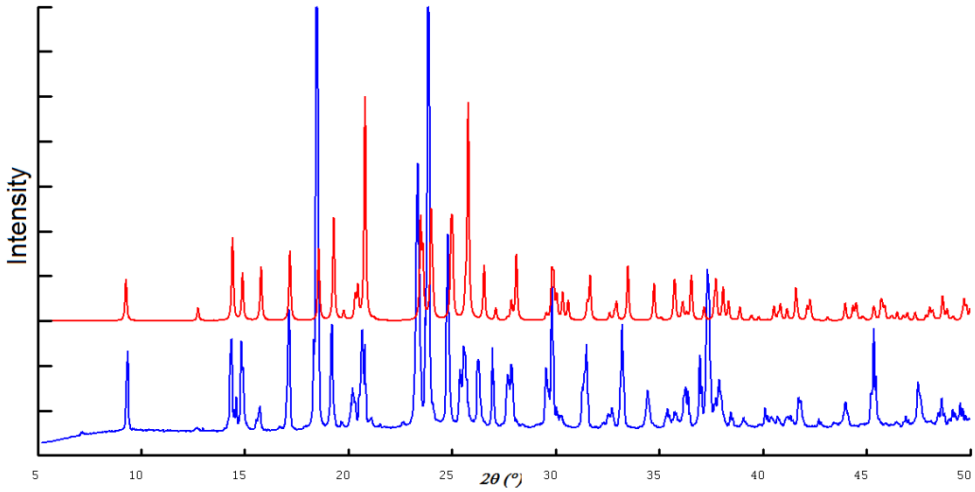


Figure S3:6 Compound 22

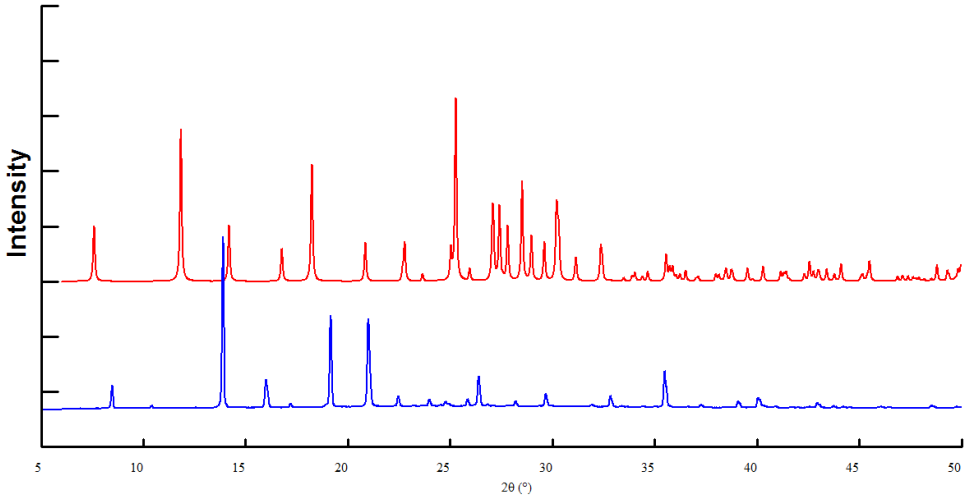


Figure S3:7 Compound 23

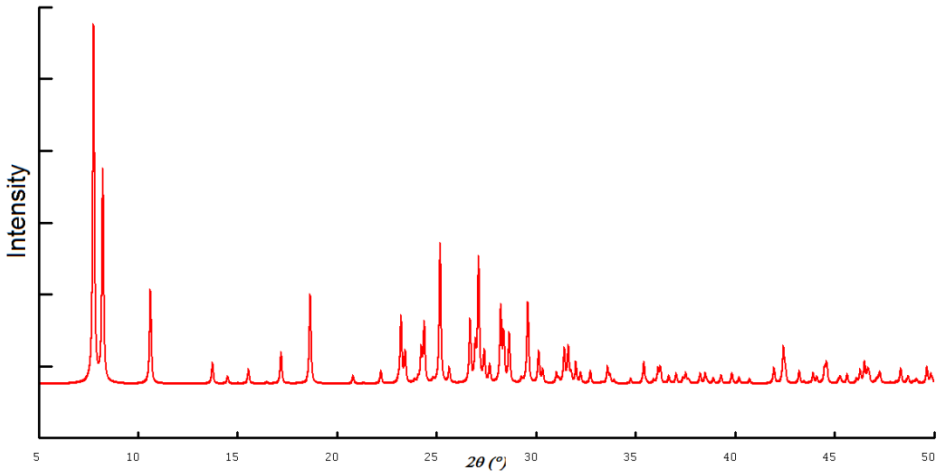


Figure S3:8 Compound 24

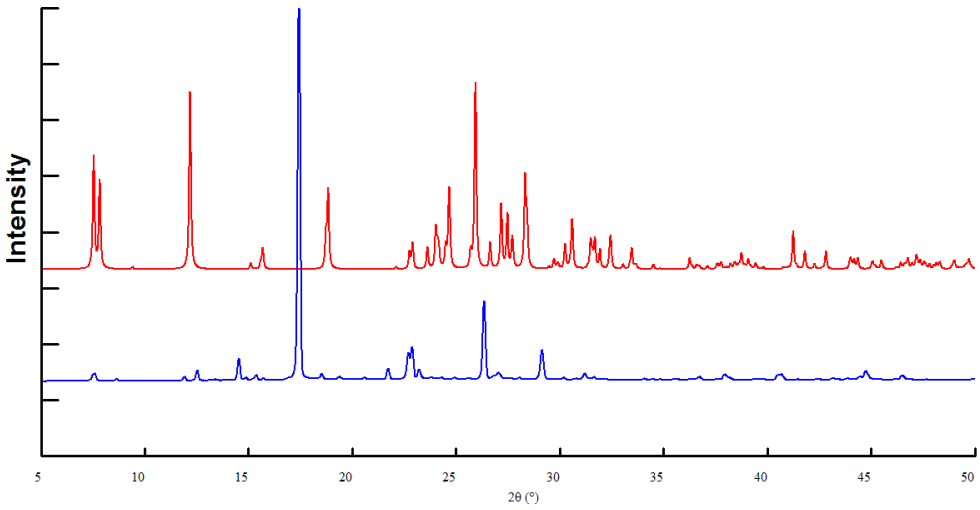


Figure S3:9 Compound 25

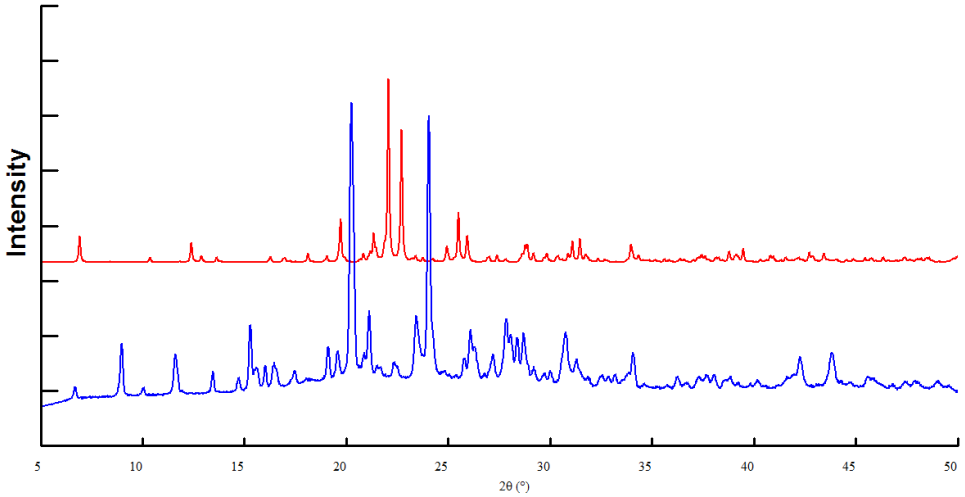


Figure S3:10 Compound 26

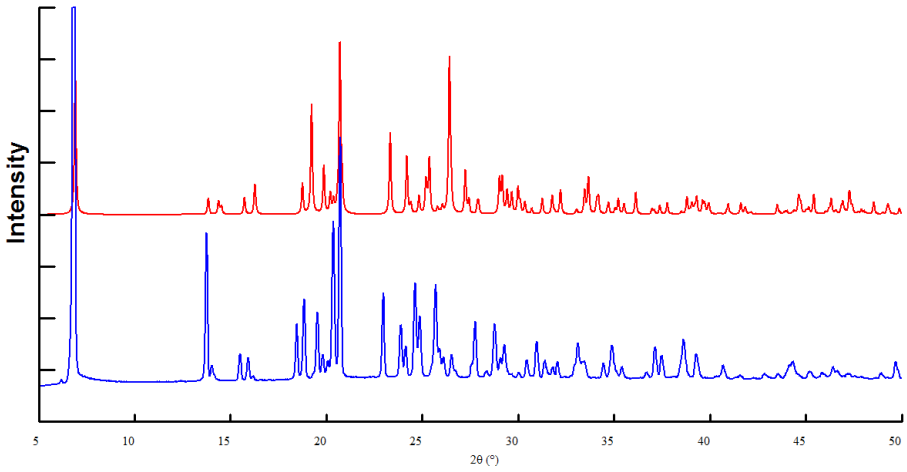


Figure S3:11 Compound 28, 28F1, 28F2

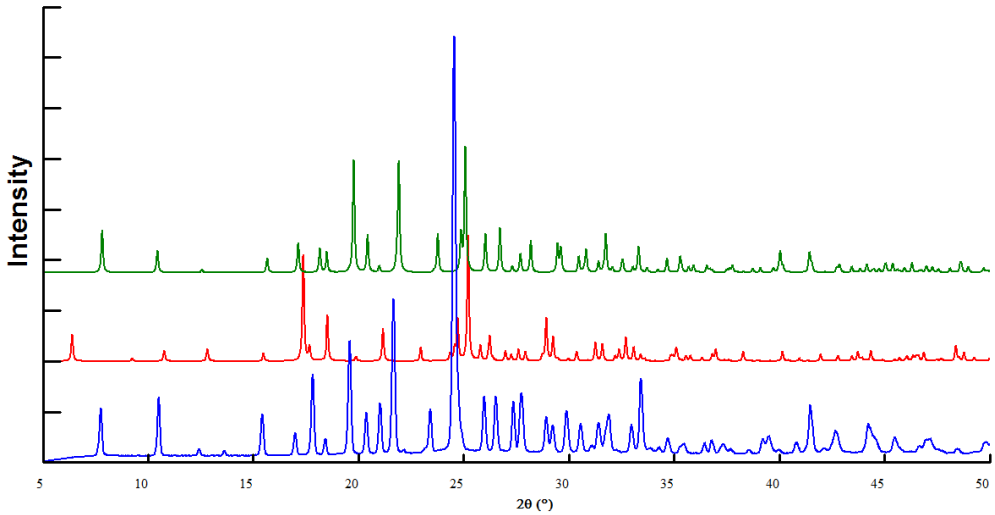


Figure S3:12 Compound 31

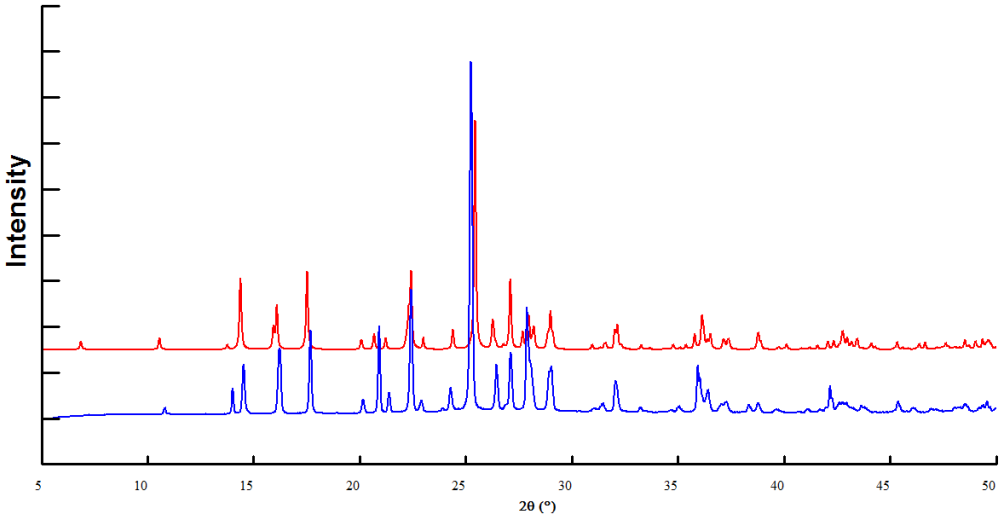


Figure S3:13 Compound 32

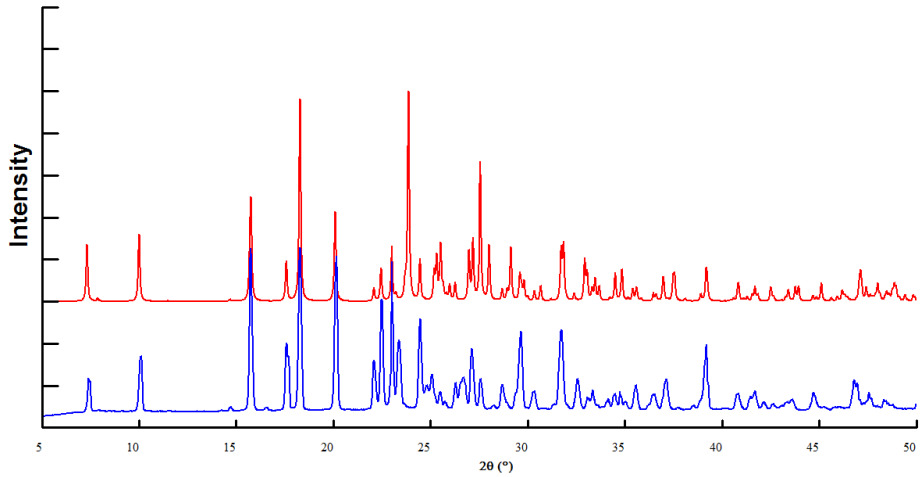


Figure S3:14 Compound 33

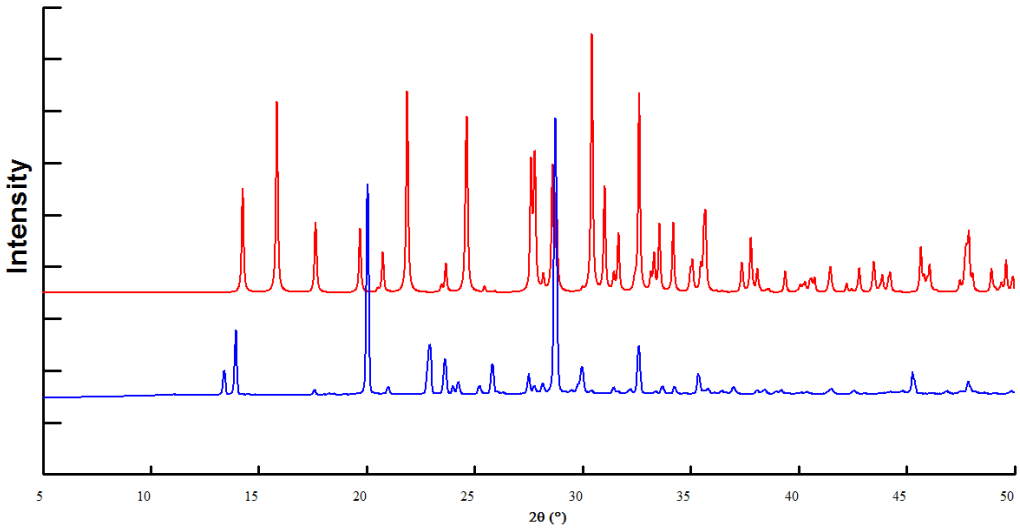


Figure S3:15 Compound 34

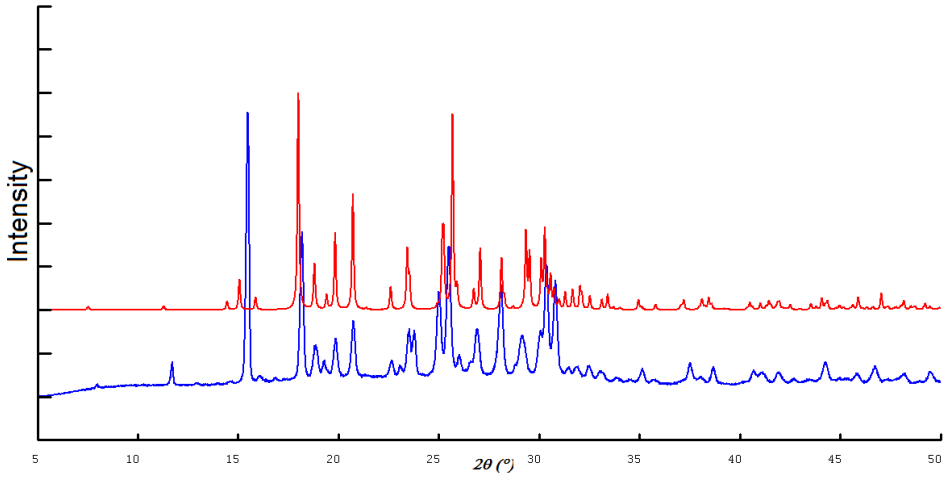


Figure S3:16 Compound 35

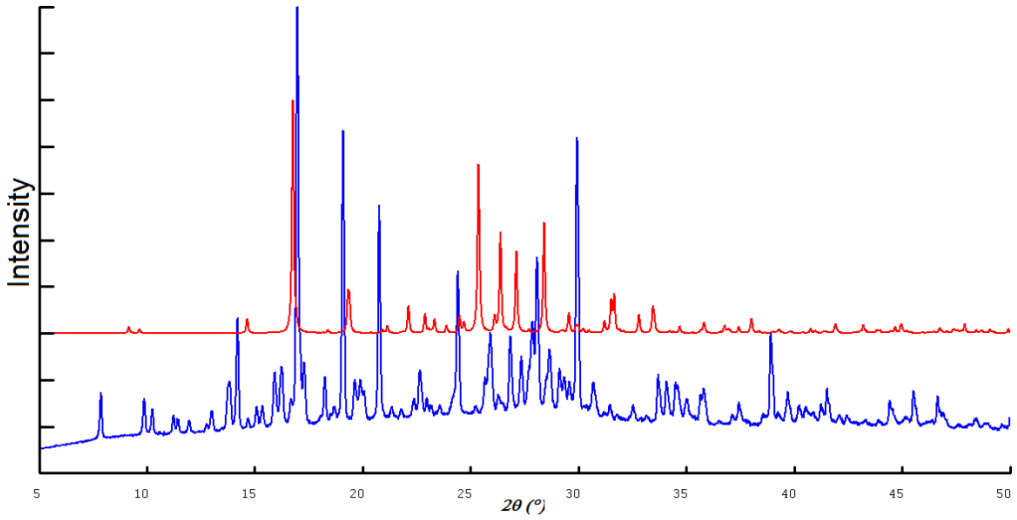


Figure S3:17 Compound 36

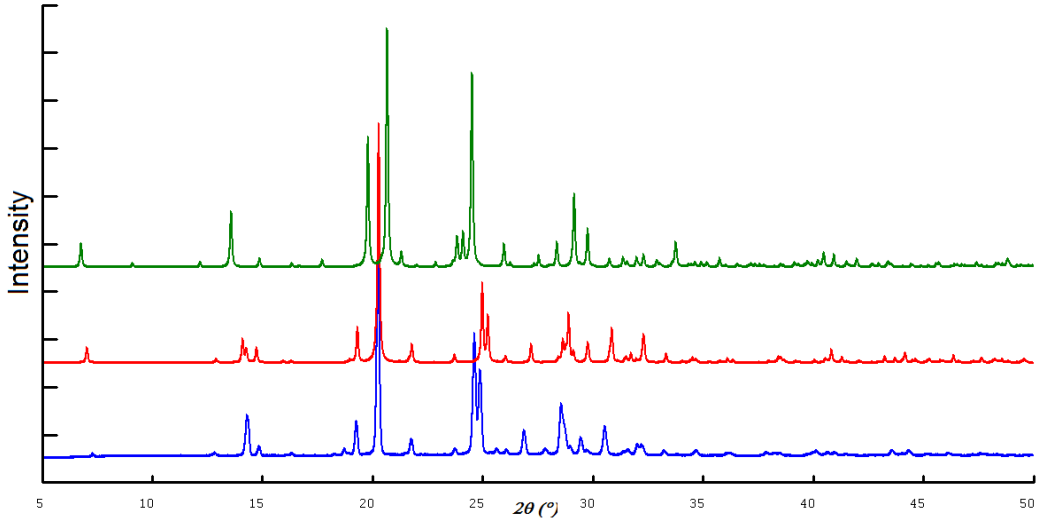


Figure S3:18 Compound 37

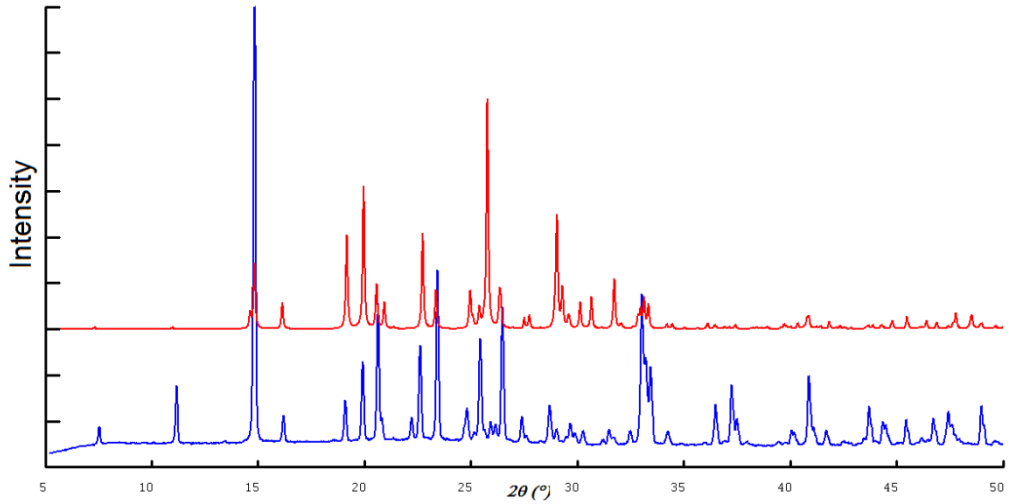


Figure S3:19 Compound 39

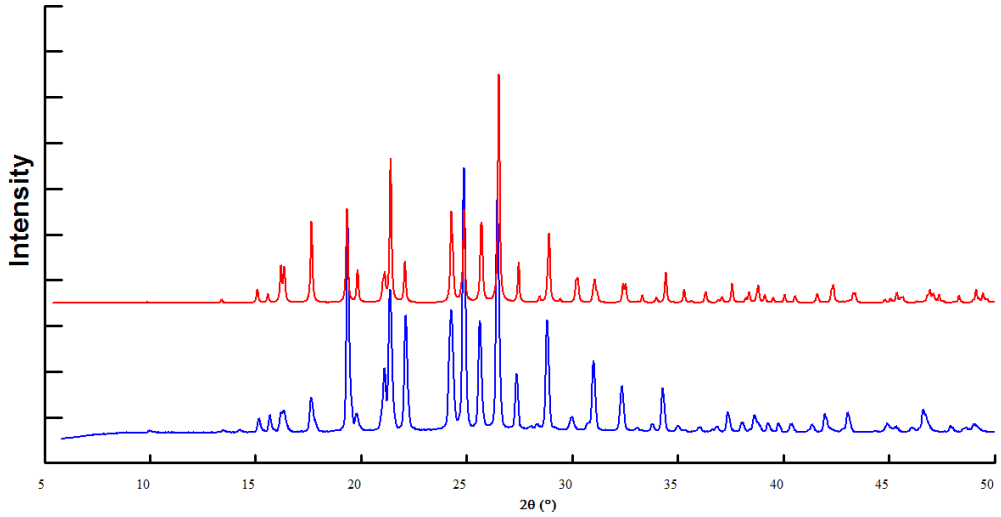


Figure S3:20 Compound 40

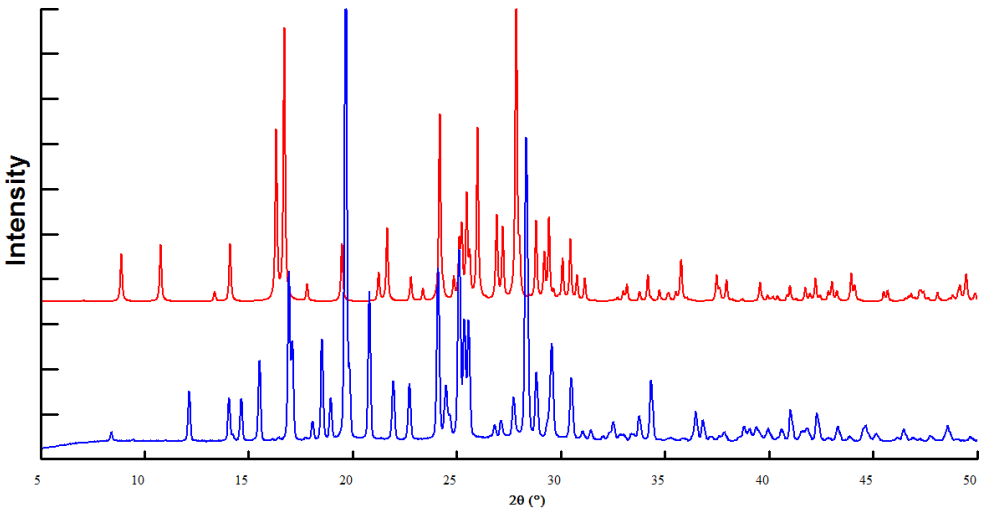


Figure S3:21 Compound 41

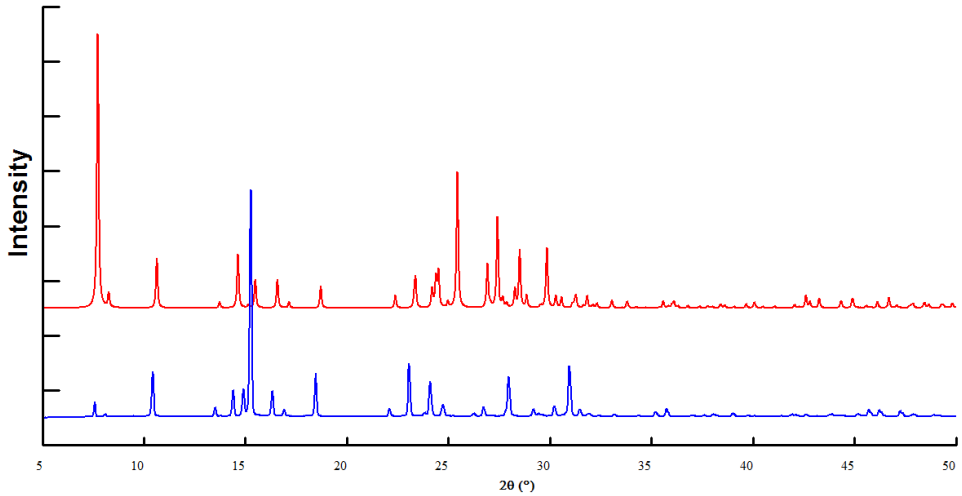


Figure S3:22 Compound 42

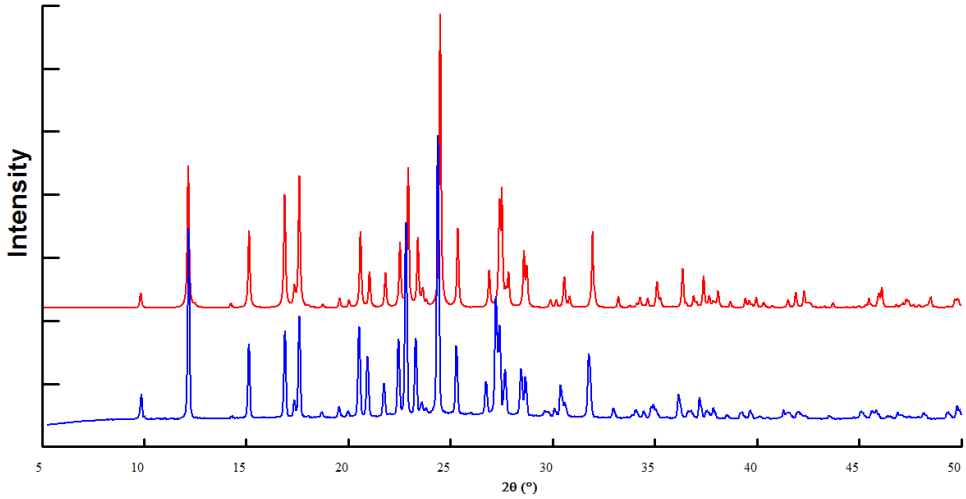


Figure S3:23 Compound 43

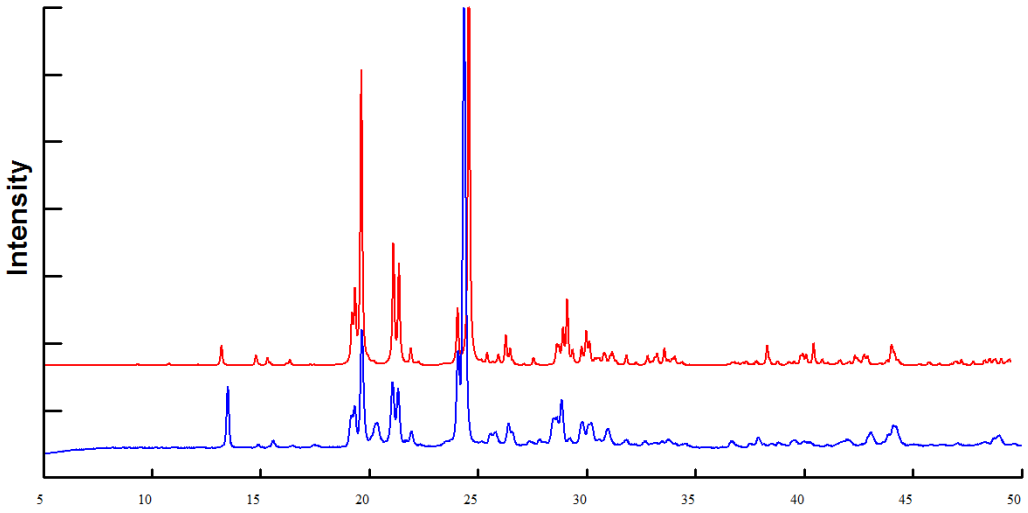


Figure S3:24 Compound 44

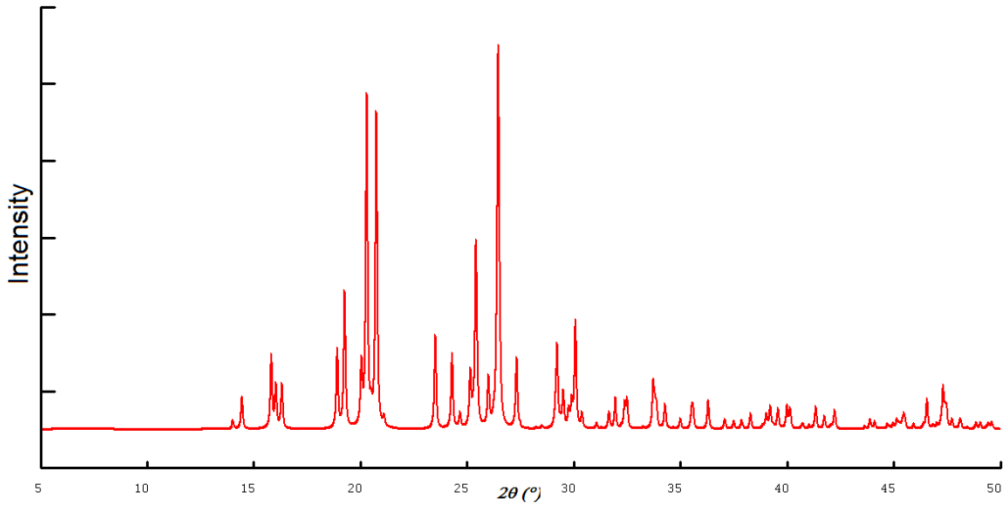


Figure S3:25 Compound 46

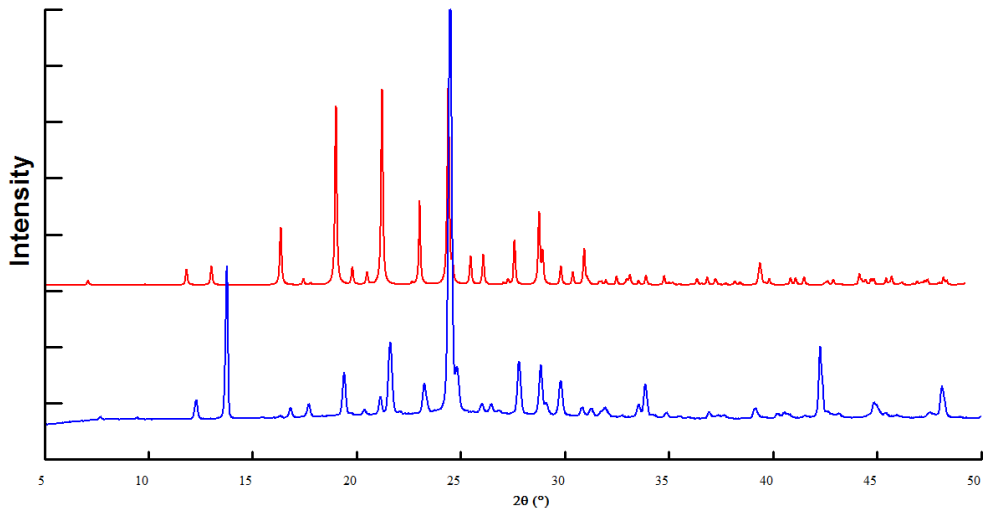


Figure S3:26 Compound 49

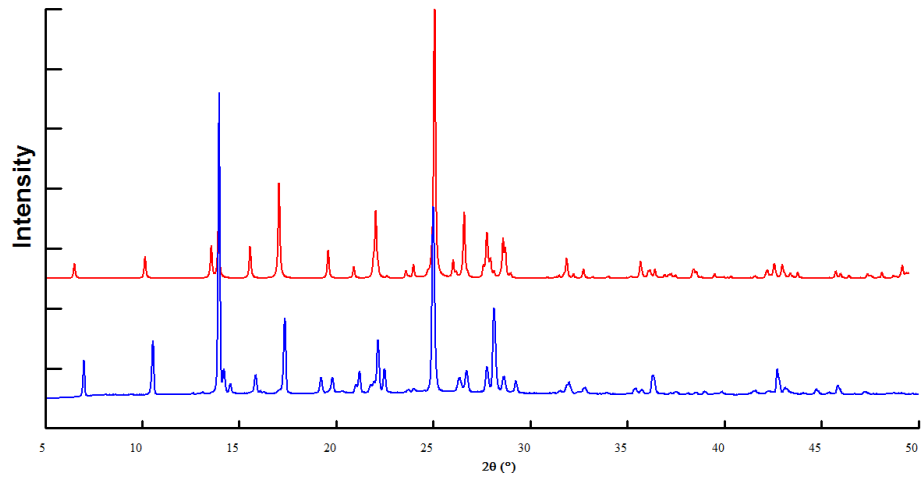


Figure S3:27 Compound 50

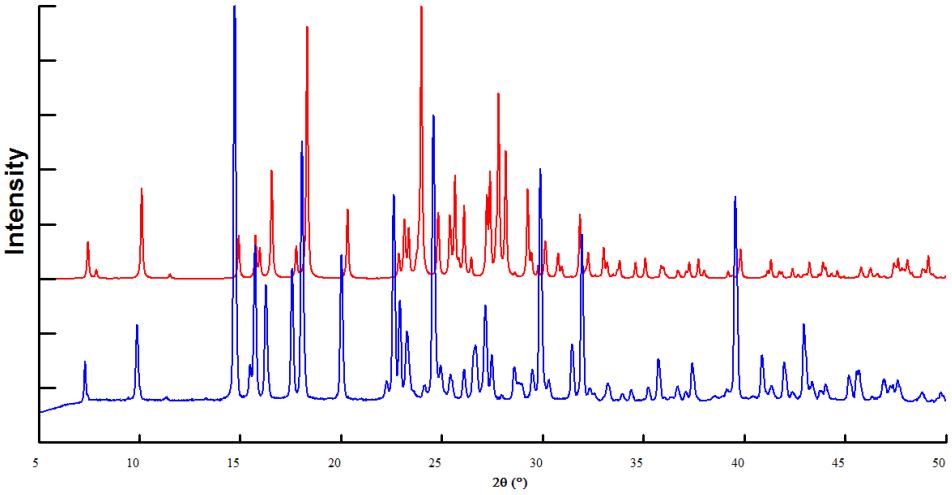


Figure S3:28 Compound 51

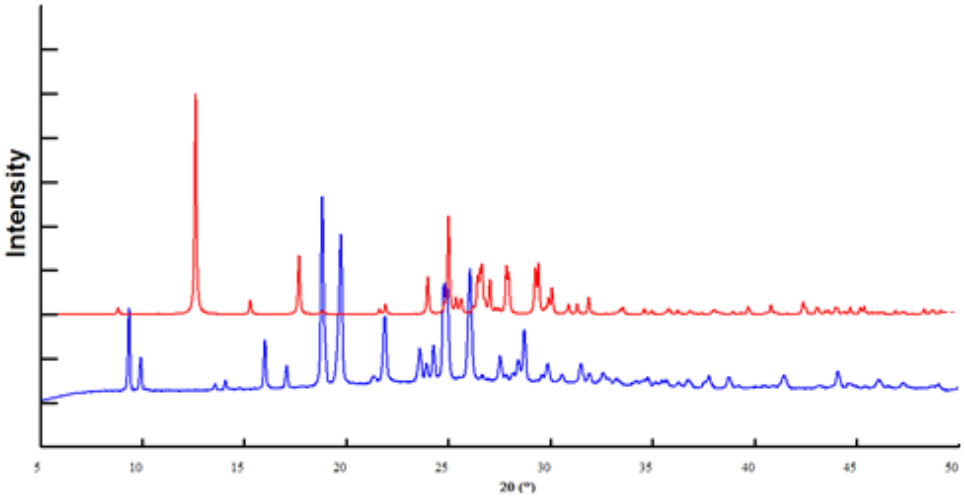


Table S1: Melting Point (in ^{0}C) of solid compounds determined from DSC data:

Compound Code	Melting point (M.P.) /^{0}C (Onset value from DSC)	ΔH (J/g)
16	62.46	63.70
17	51.41	81.05
18	68.39	73.85
19	34.44, 33.05	66.14, 16.42
20	--	--
21	40.29	65.07
22	49.07	72.33
23	29.07	59.47
24	47.72	61.89
25	57.22	64.05
26	35.38	65.62
27	--	--
28	69.84	80.02
29	-7.42	45.12
30	--	--
31	65.63	60.36
32	65.34	93.39
33	45.45	93.27
34	46.51	66.35
35	43.25	46.62
36	47.34	74.16
37	36.70	96.92
38	14.36	54.11
39	54.15	91.70
40	55.98	98.05
41	26.33	77.25
42	48.38	90.72
43	72.68	95.40
44	20.02	25.83
45	-8.50	251.02
46	43.72, 49.45	46.31, 28.90
47	--	--
48	--	--
49	52.03	94.98
50	60.75	101.92
51	48.65, 35.46	96.66, 81.74

The symbol "--" signifies that the compound has not shown any characteristic in its DSC traces.

Figure S4: DSC traces for all solid compounds

Figure S4:1

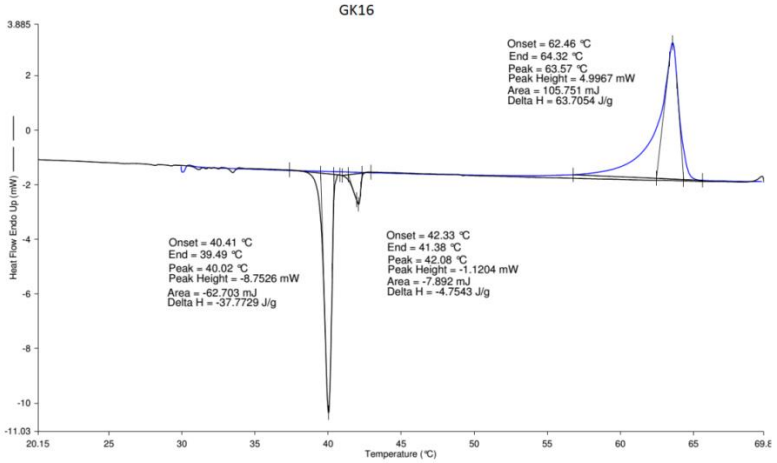


Figure S4:2

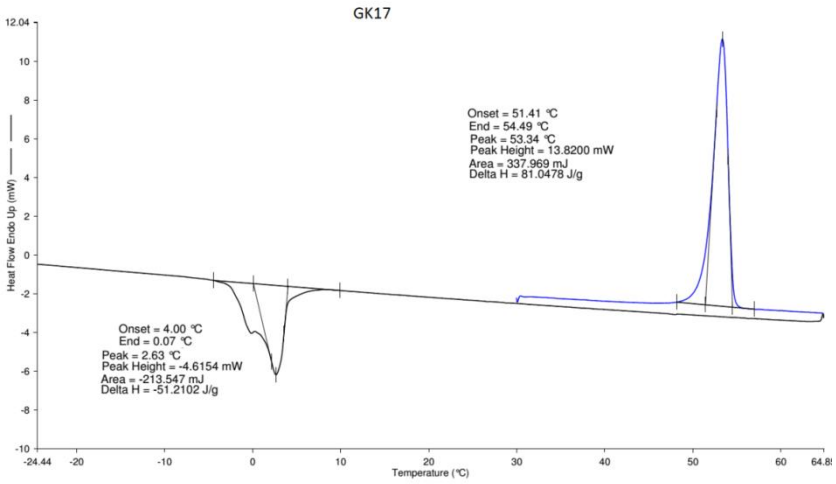


Figure S4:3

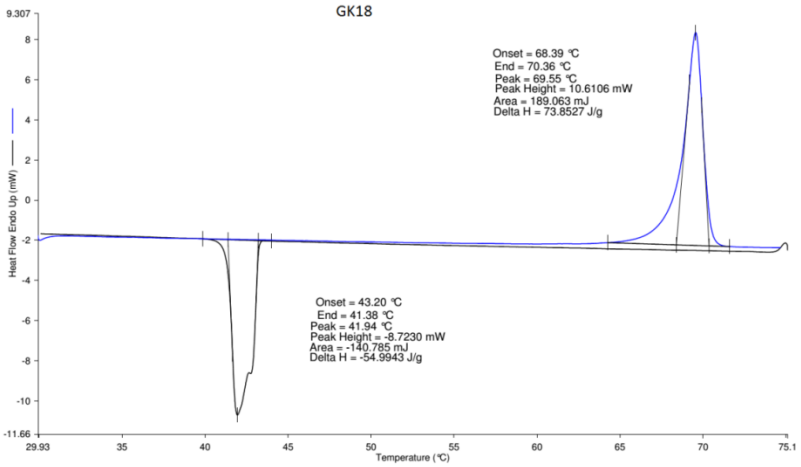


Figure S4:4

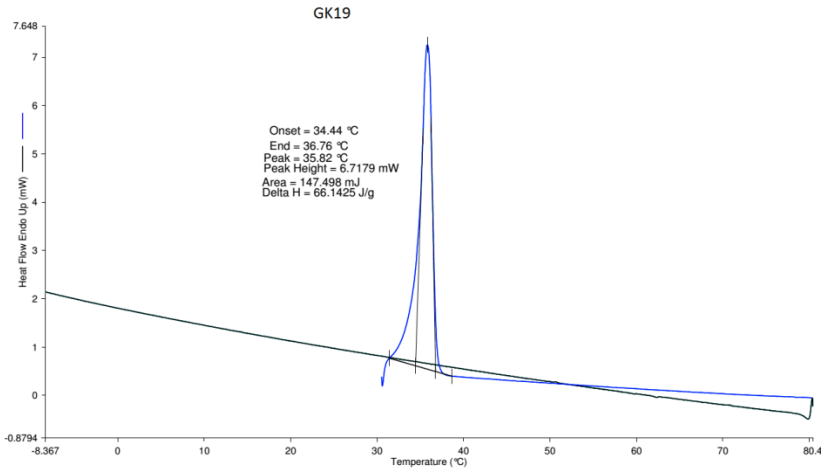


Figure S4:5

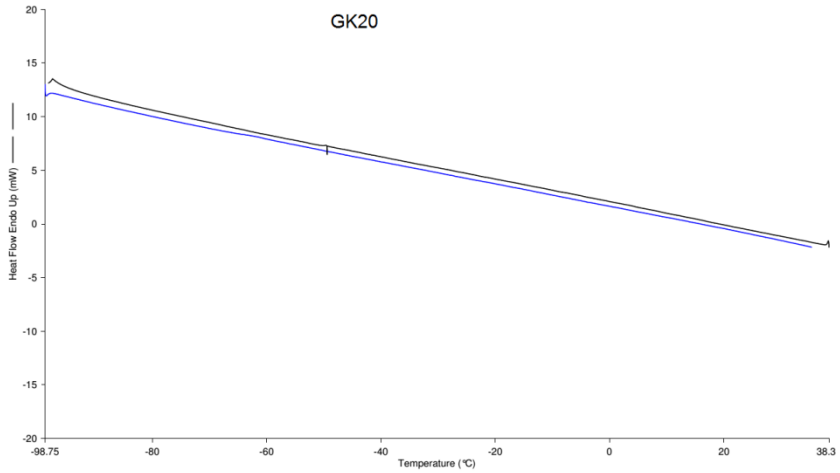


Figure S4:6

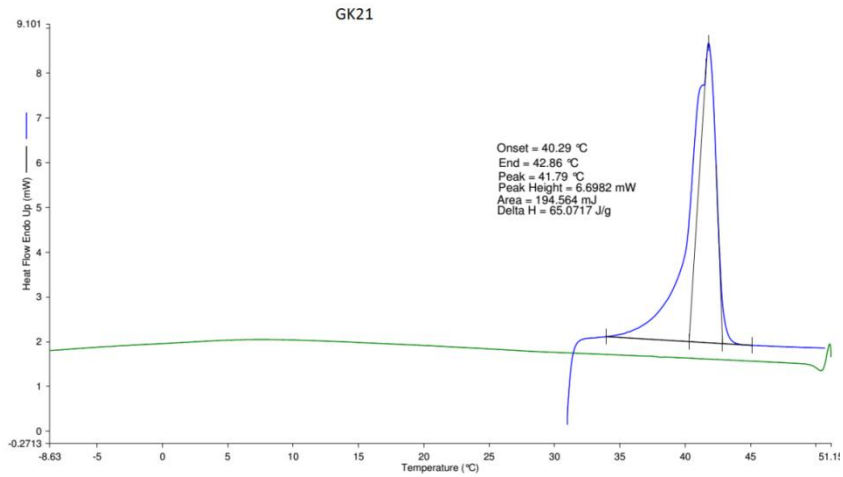


Figure S4:7

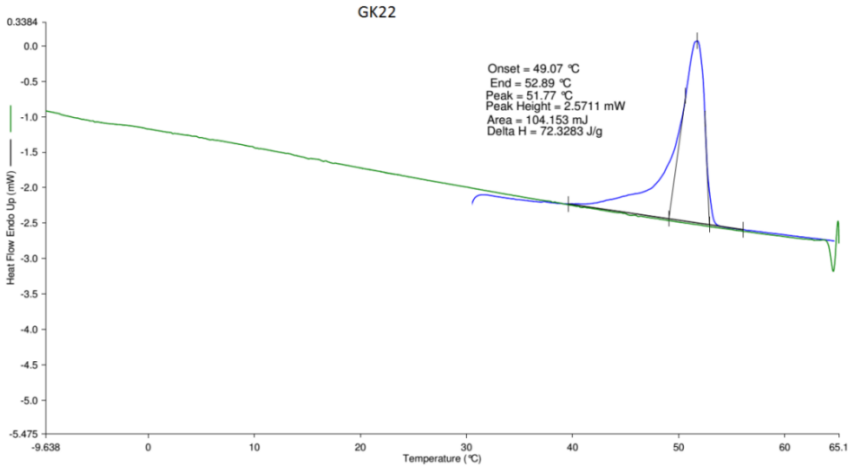


Figure S4:8

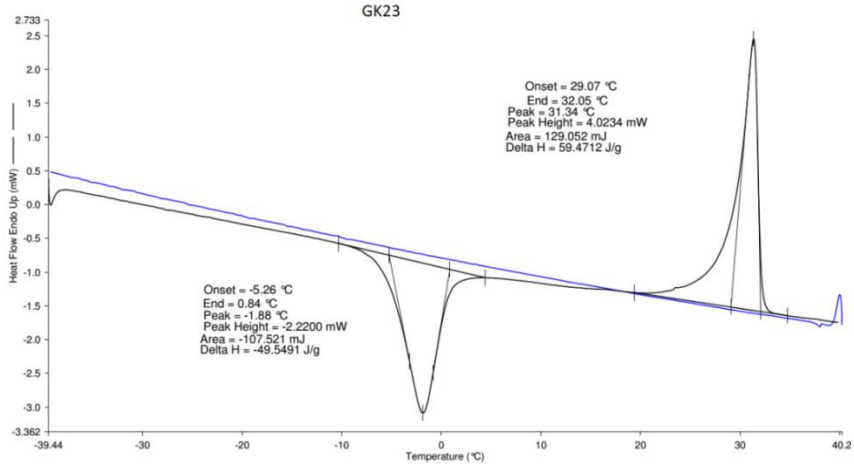


Figure S4:9

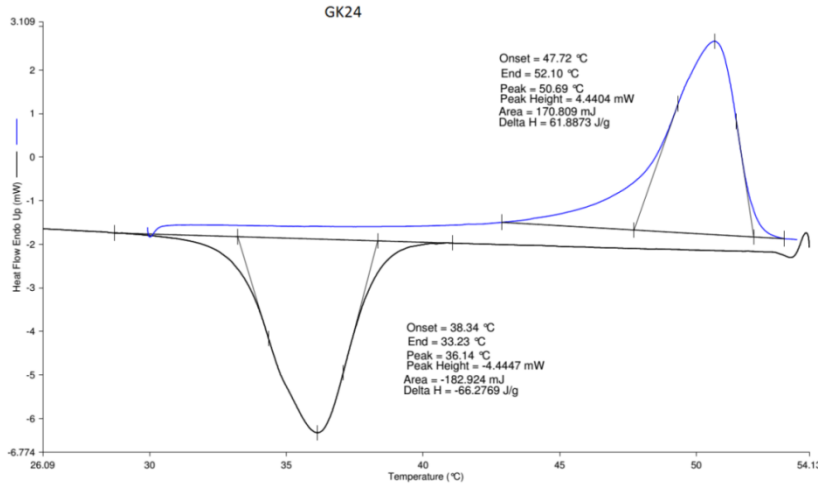


Figure S4:10

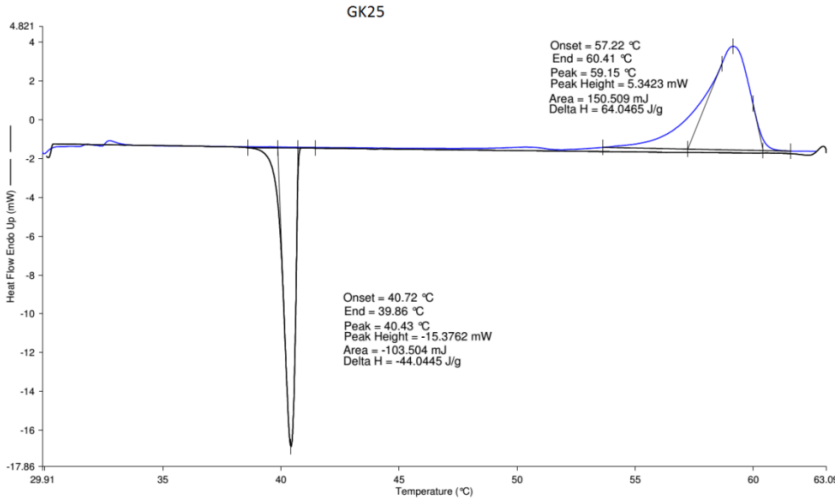


Figure S4:11

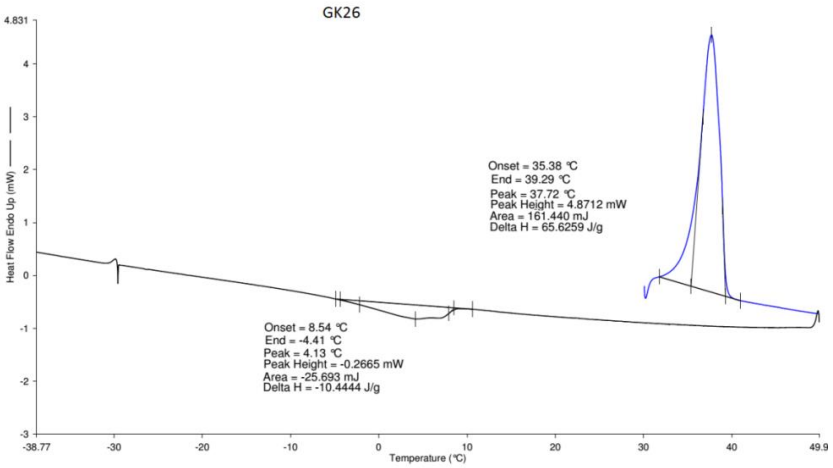


Figure S4:12

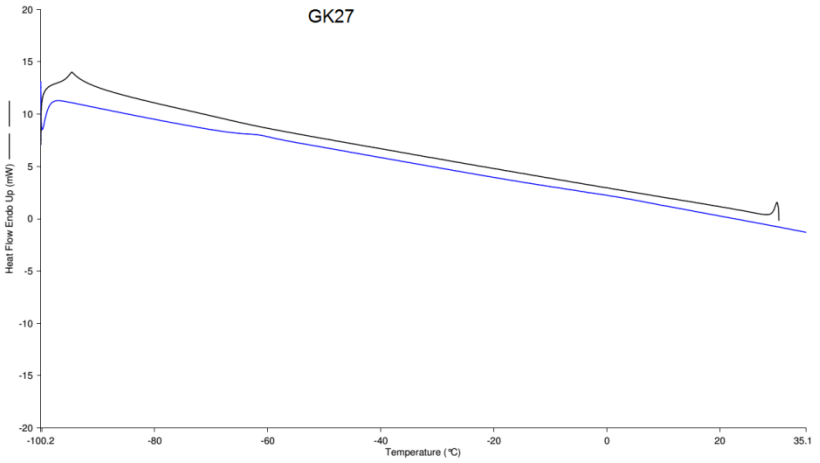


Figure S4:13

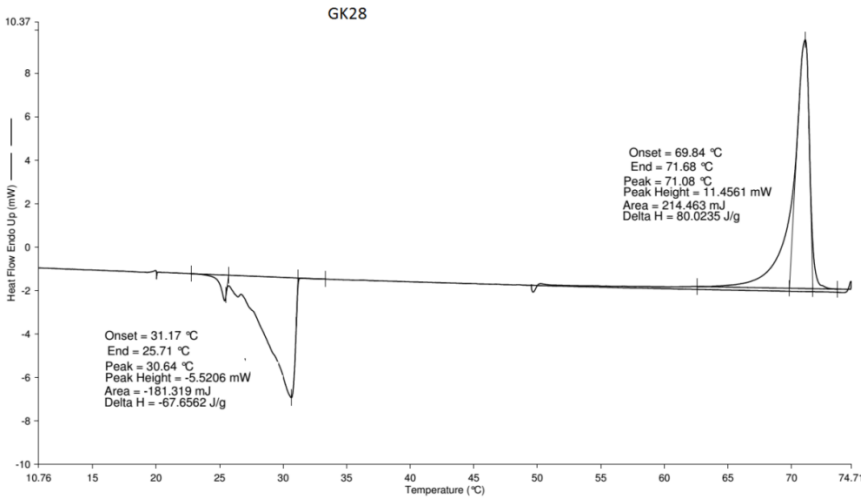


Figure S4:14

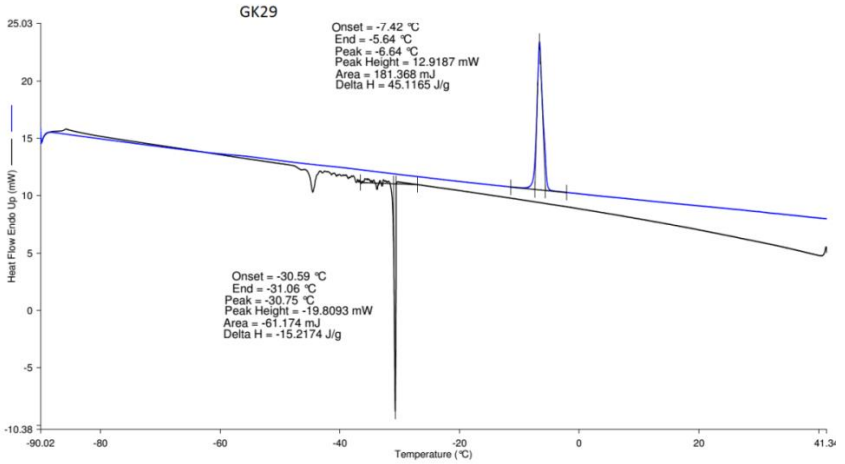


Figure S4:15

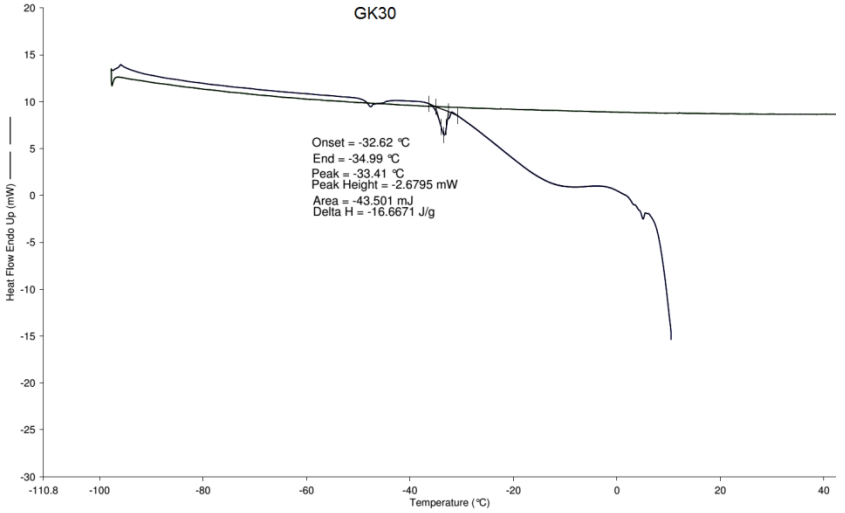


Figure S4:16

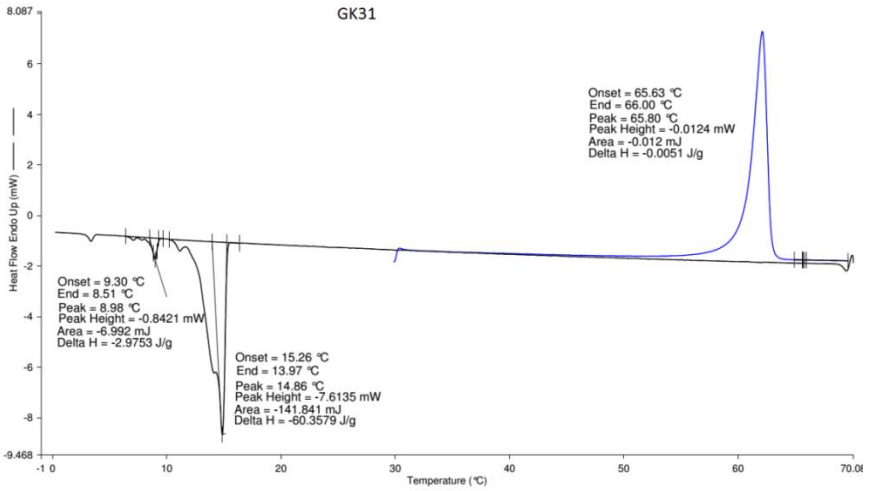


Figure S4:17

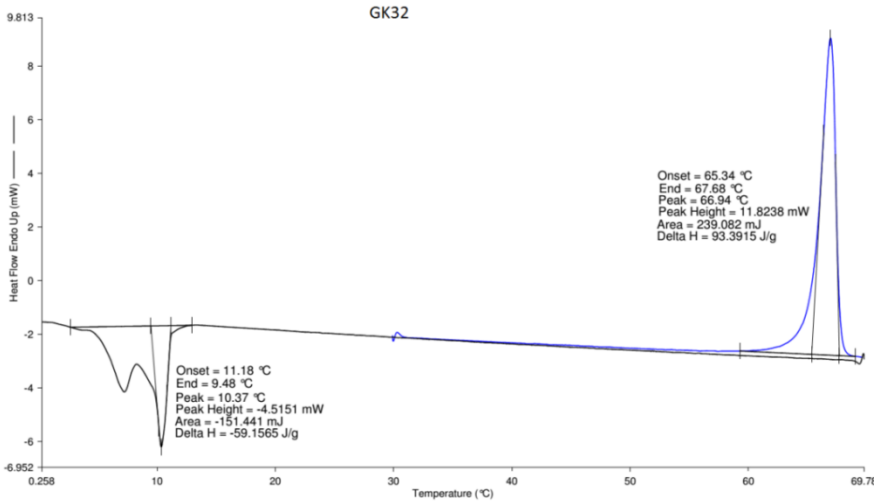
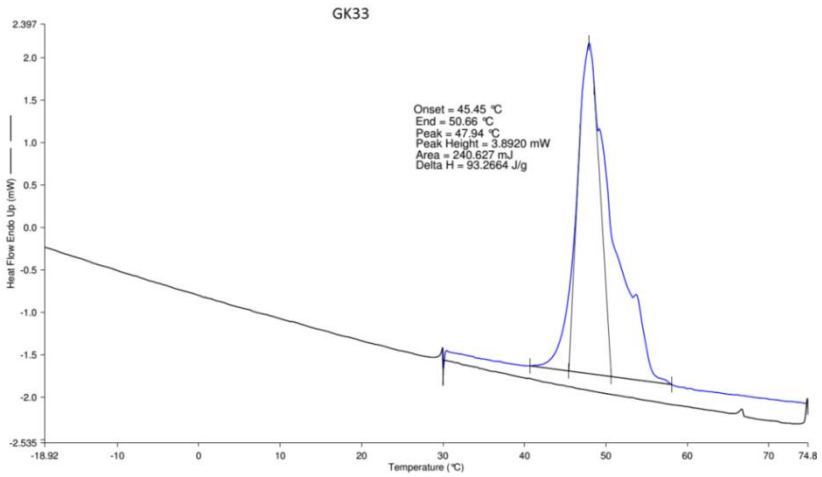


Figure S4:18



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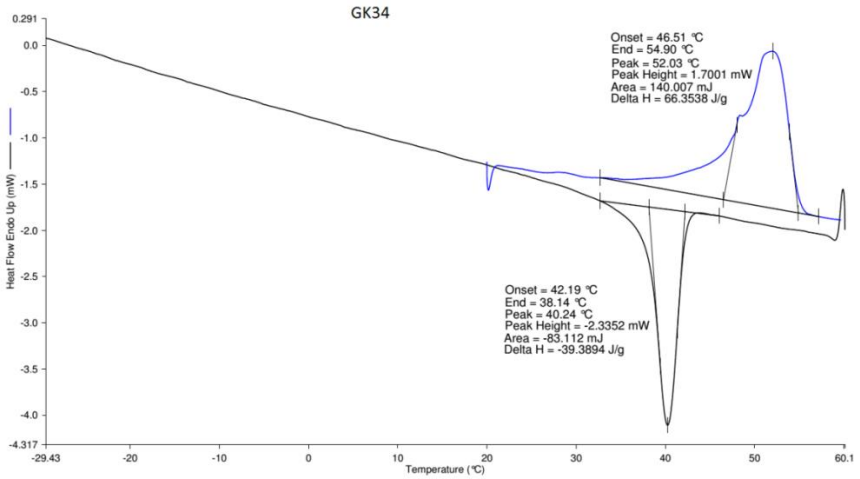
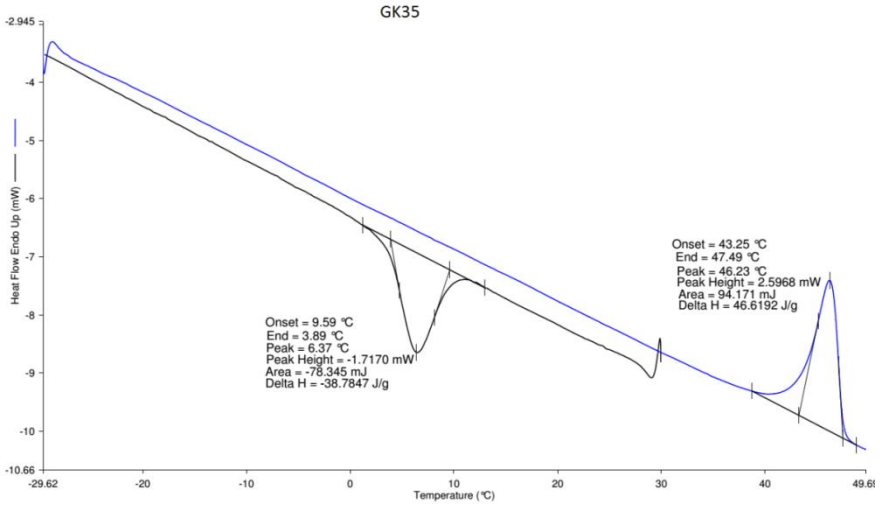


Figure S4:20



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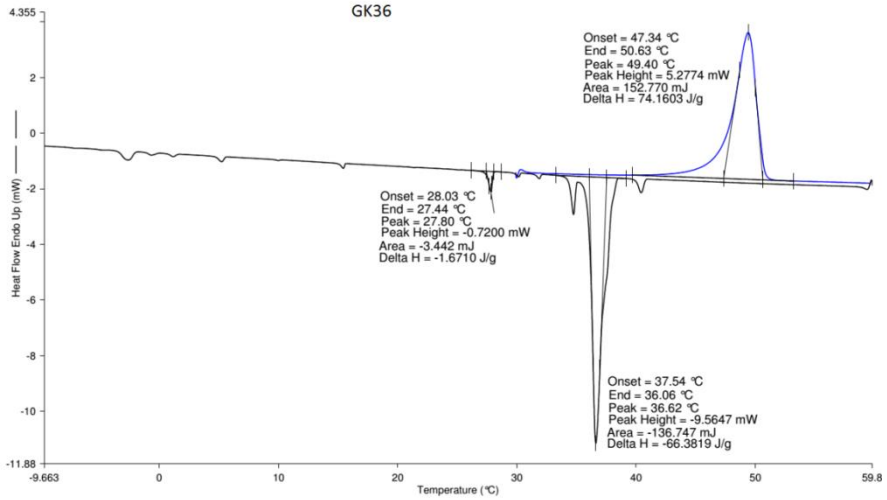

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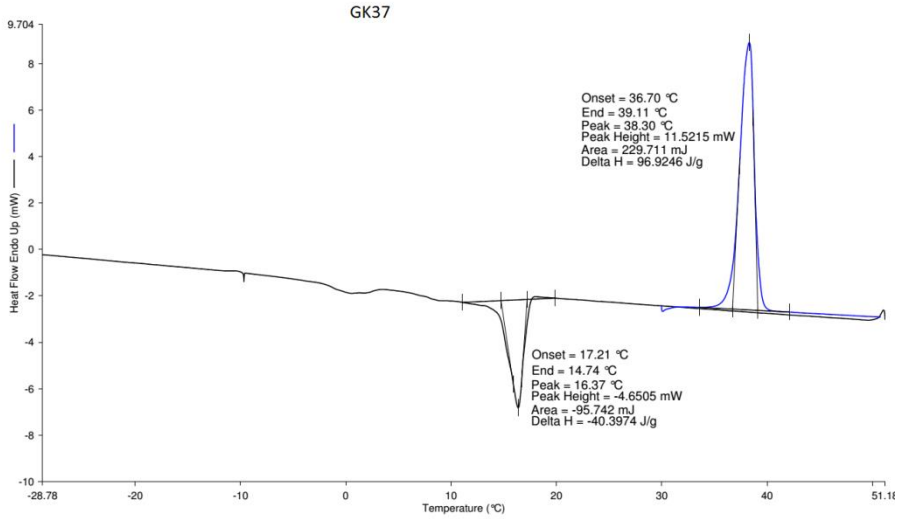

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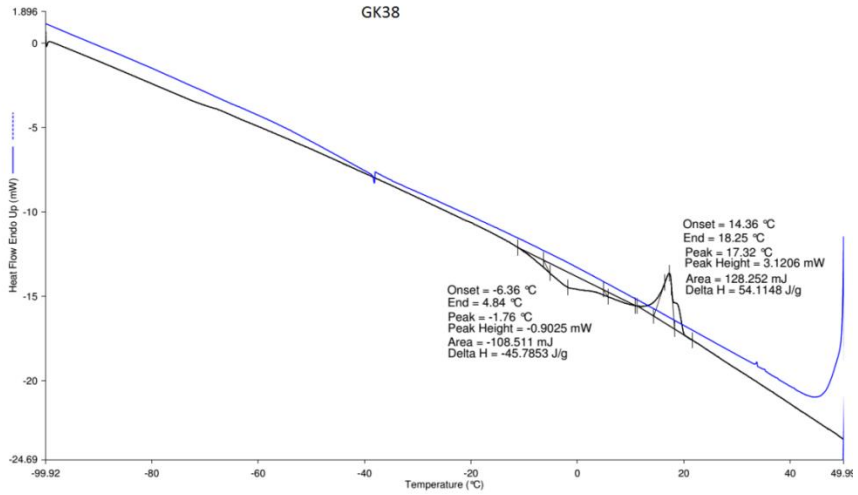

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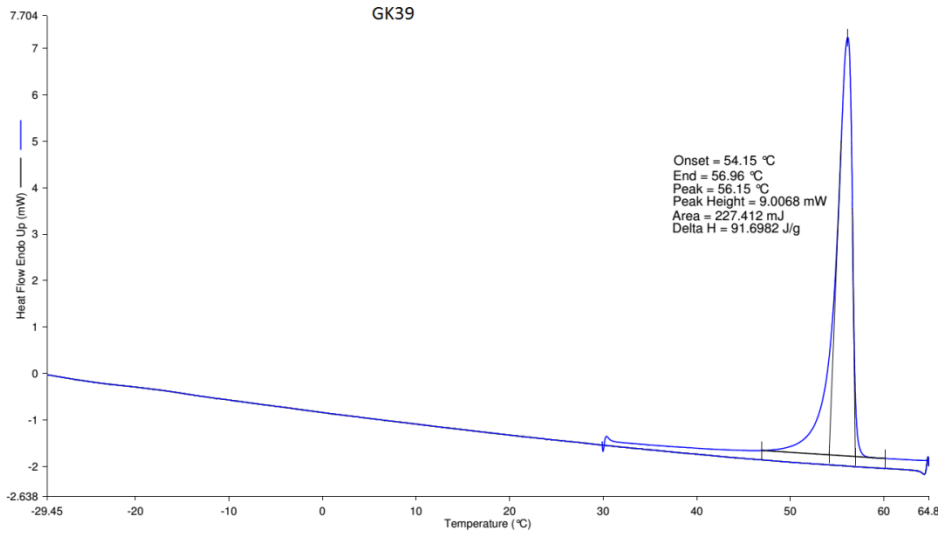


Figure S4:25

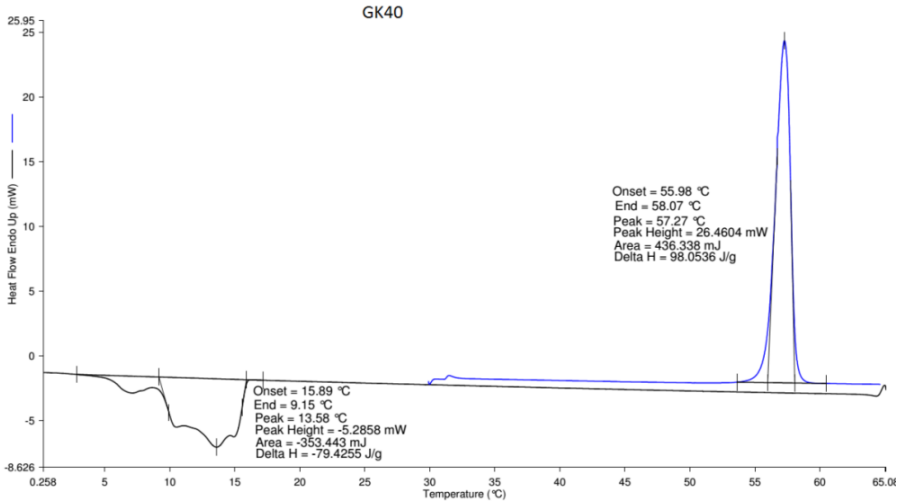
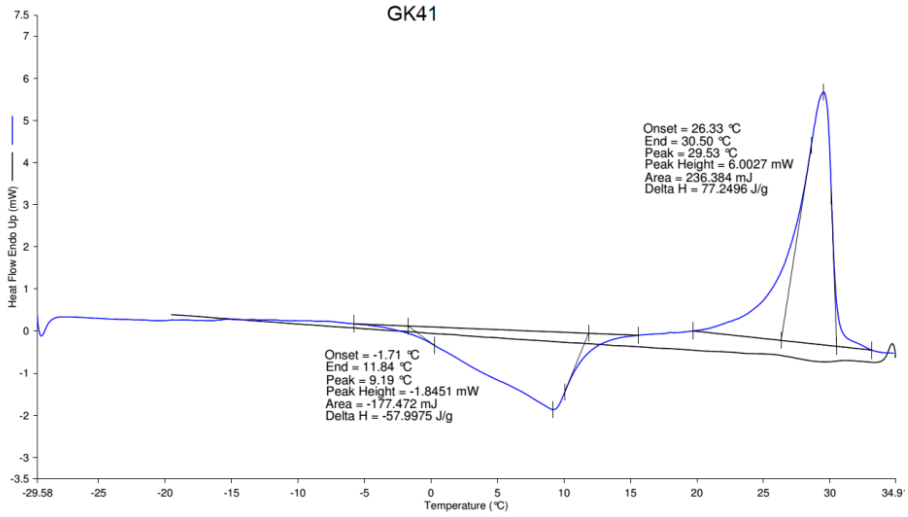


Figure S4:26



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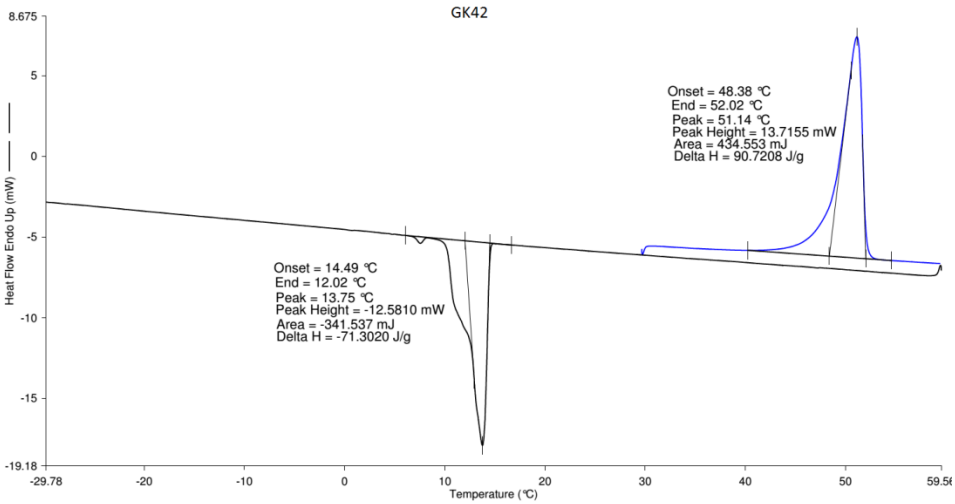


Figure S4:28

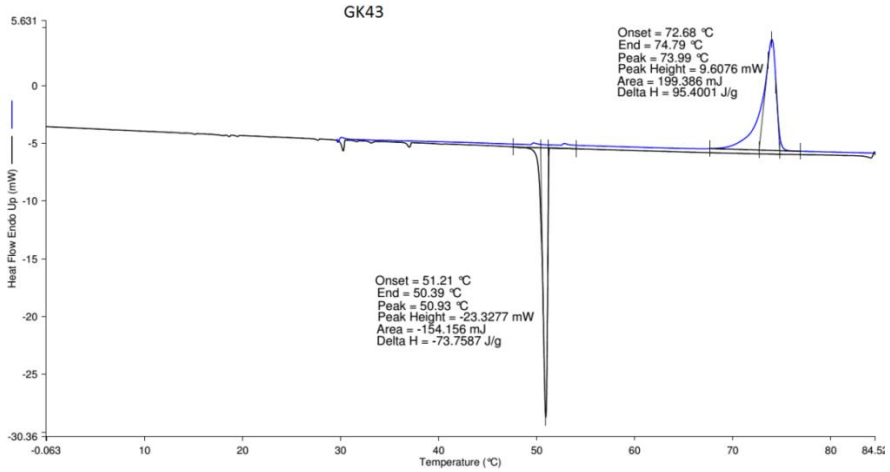


Figure S4:29

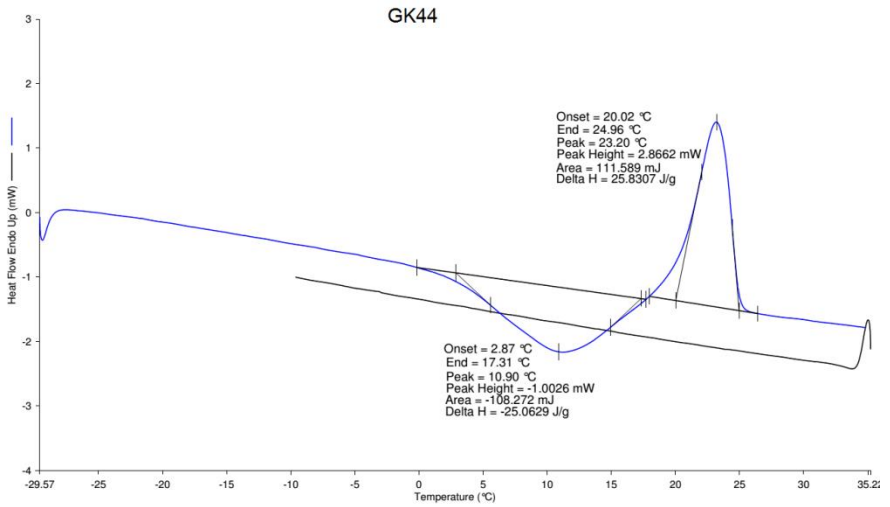


Figure S4:30

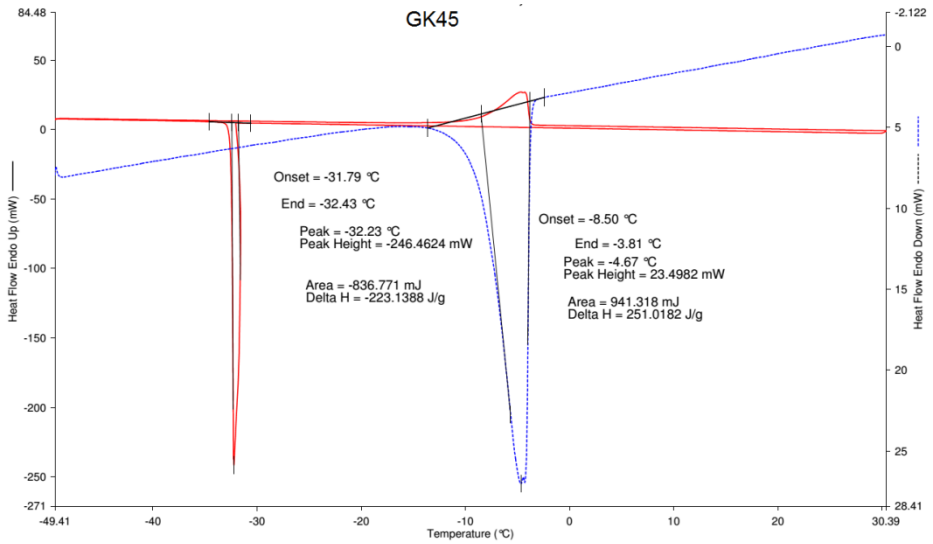


Figure S4:31

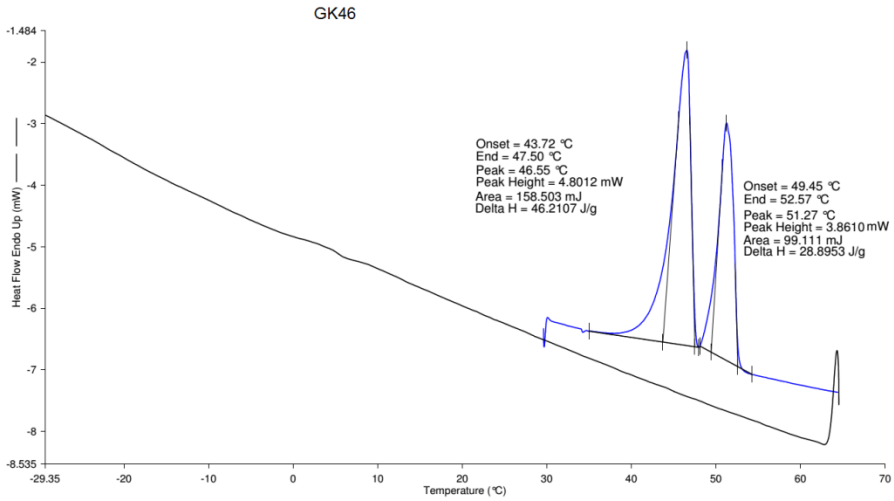


Figure S4:32

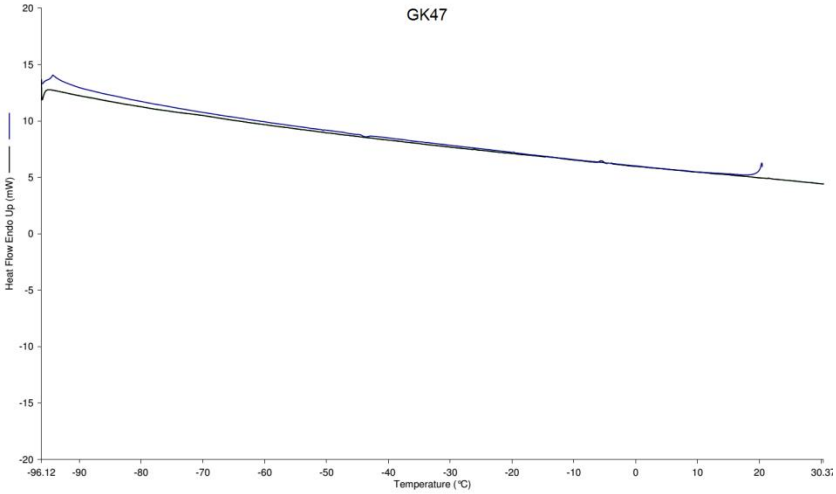


Figure S4:33

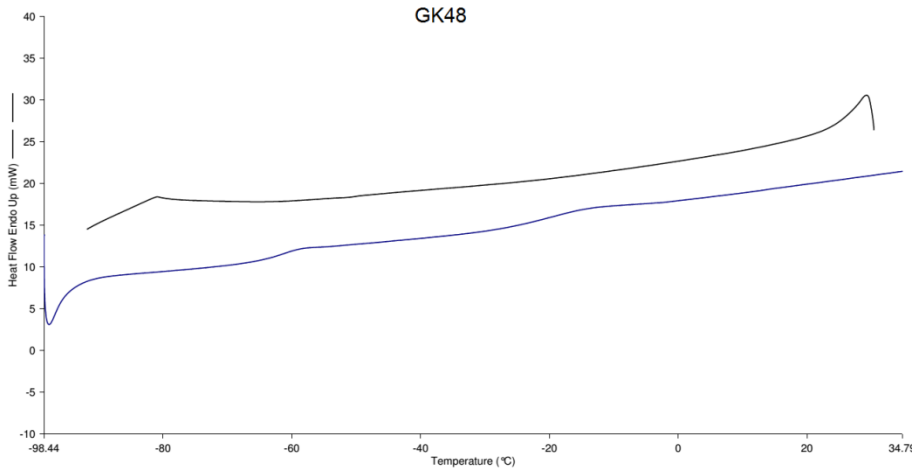


Figure S4:34

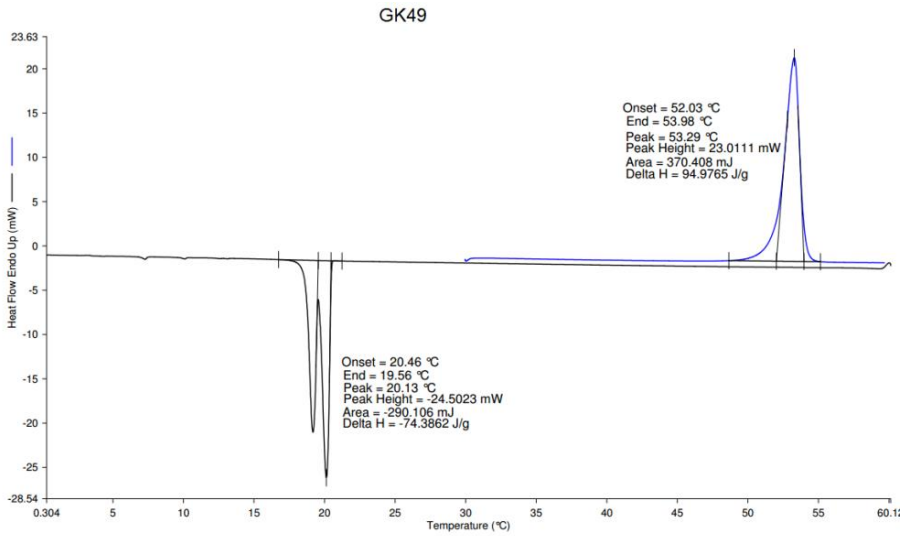


Figure S4:35

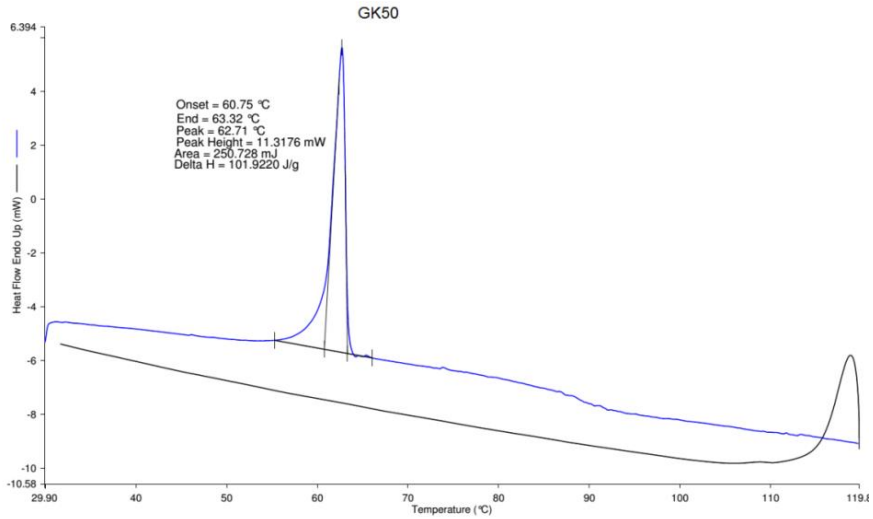


Figure S4:36

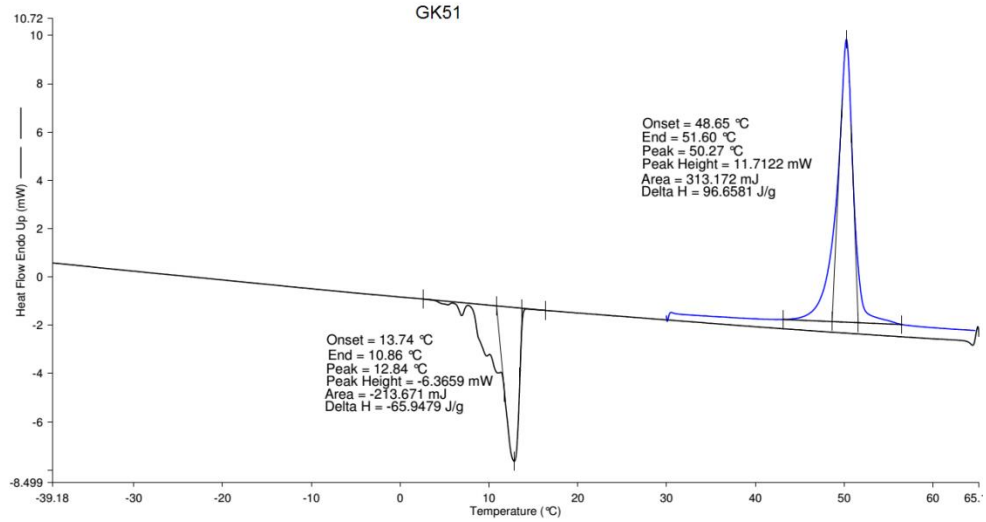


Figure S4: *ORTEP* of all compounds drawn with 50% ellipsoidal probability with atom-numbering scheme.

Figure S5:1 Compound 16F1

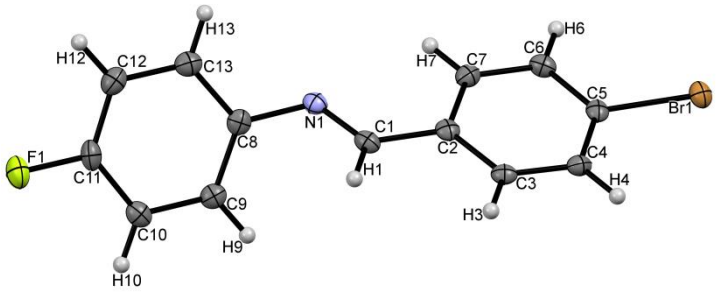


Figure S5:2 Compound 16F2

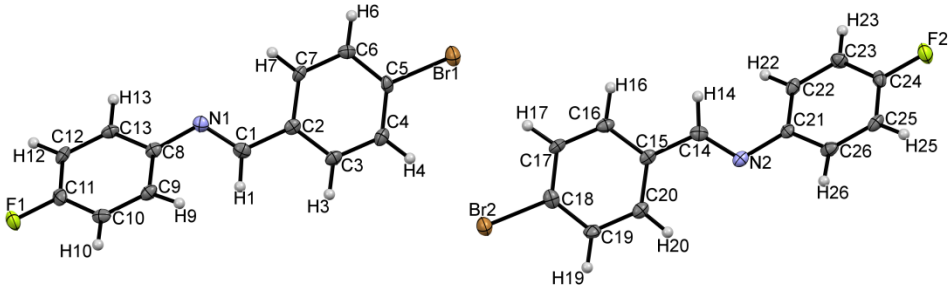


Figure S5:3 Compound 17

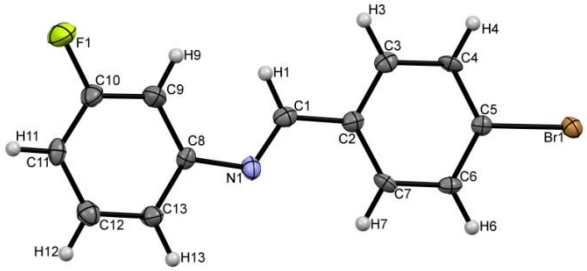


Figure S5:4 Compound 18F1

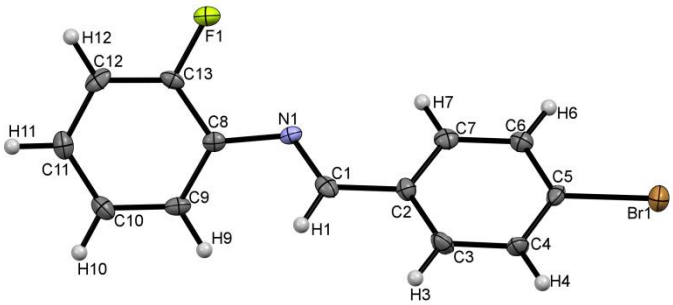


Figure S5:5 Compound 18F2

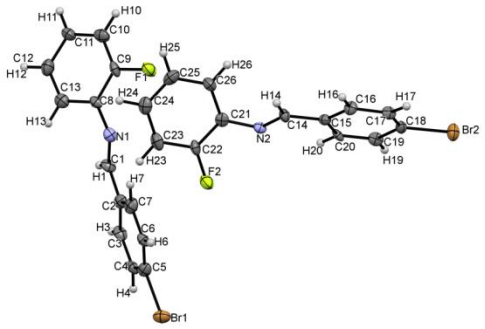


Figure S5:6 Compound 19

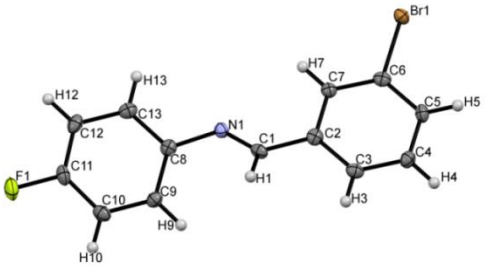


Figure S5:7 Compound 21

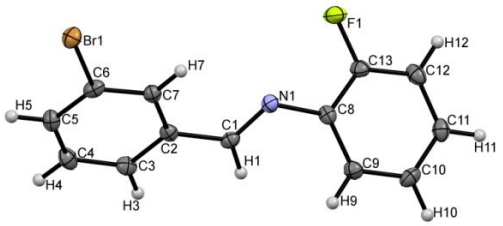


Figure S5:8 Compound 22

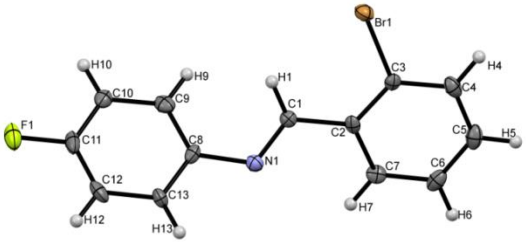


Figure S5:9 Compound 23

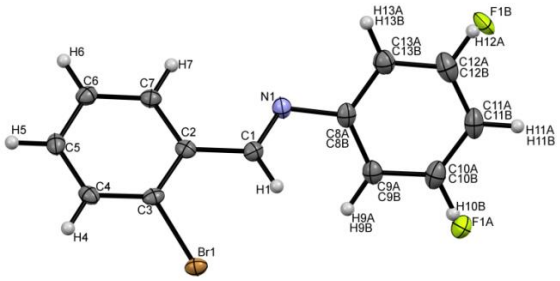


Figure S5:10 Compound 24

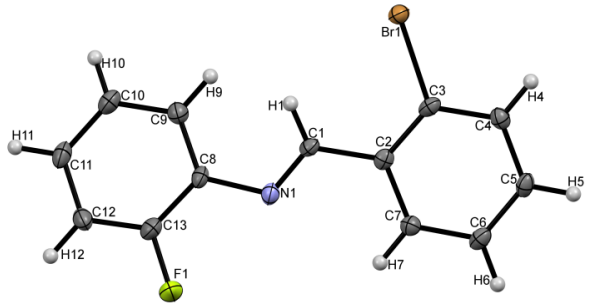


Figure S5:11 Compound 25

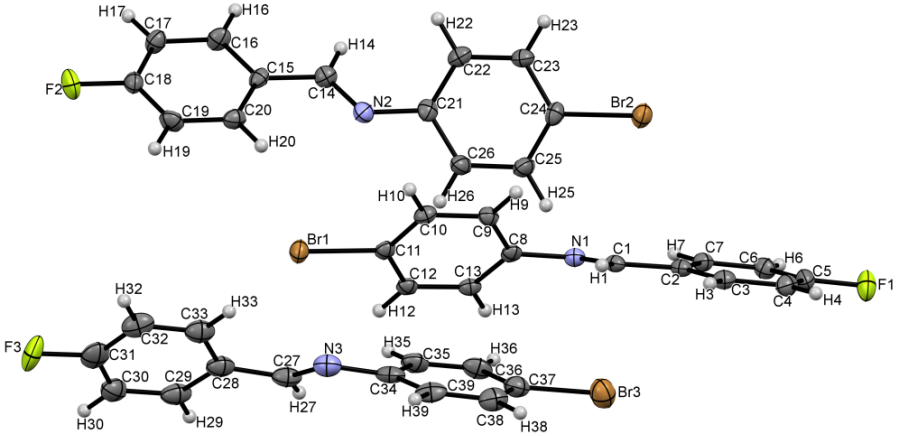


Figure S5:12 Compound 26

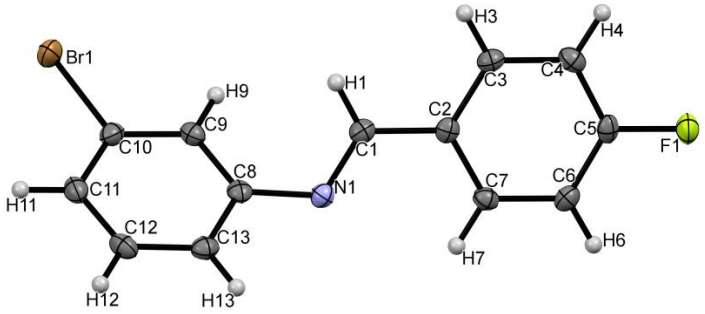


Figure S5:13 Compound 28F1

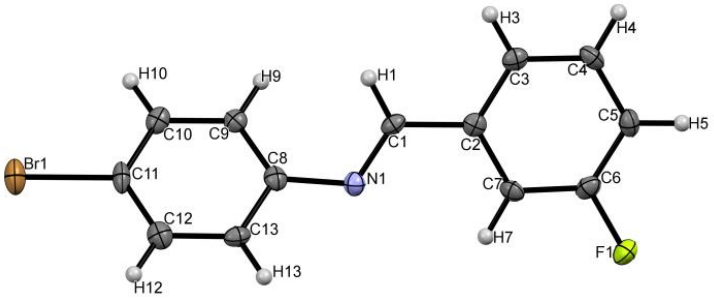


Figure S5:14 Compound 28F2

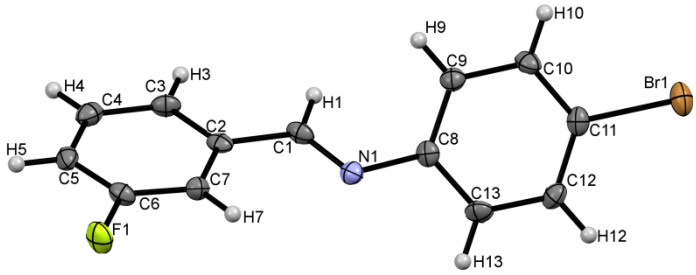


Figure S5:15 Compound 31

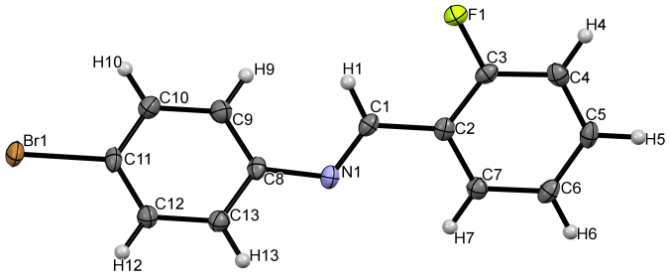


Figure S5:16 Compound 32

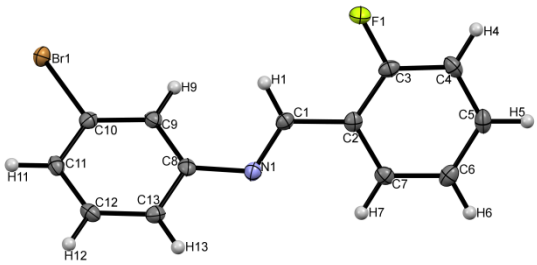


Figure S5:17 Compound 33

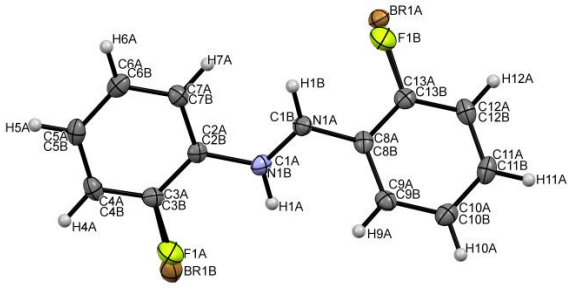


Figure S5:18 Compound 34

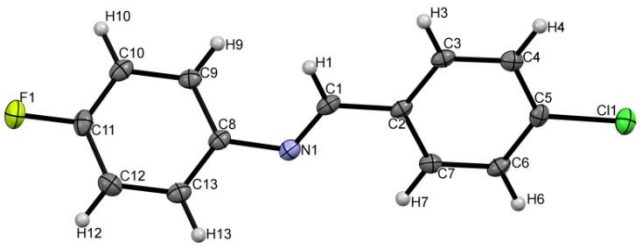


Figure S5:19 Compound 35

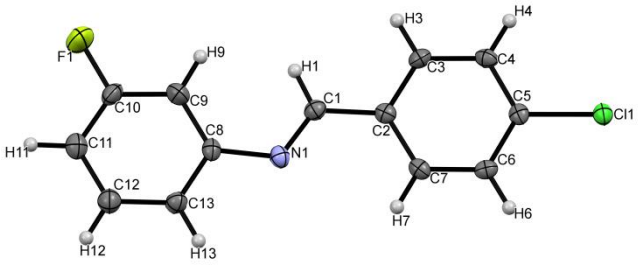


Figure S5:20 Compound 36F1

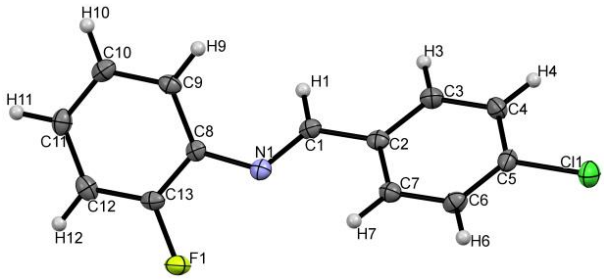


Figure S5:21 Compound 36F2

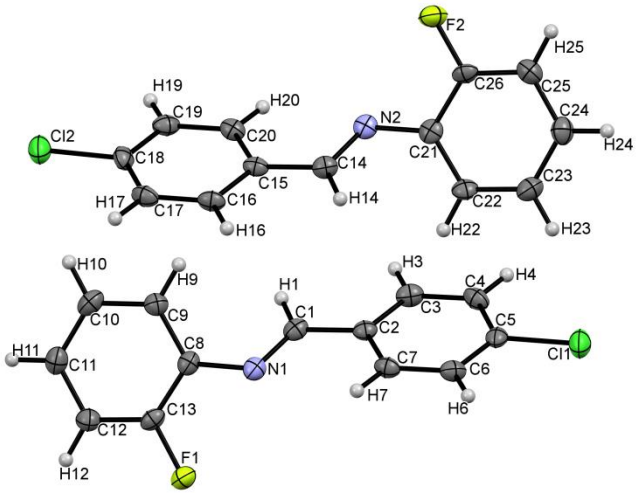


Figure S5:22 Compound 37

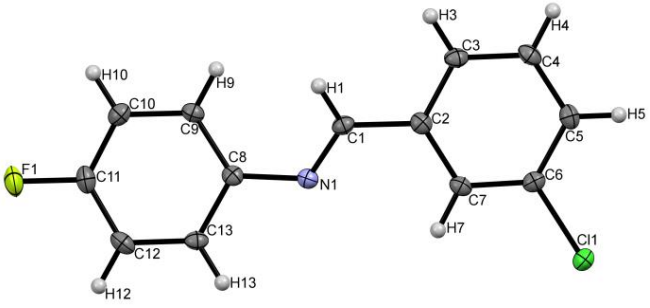


Figure S5:23 Compound 39

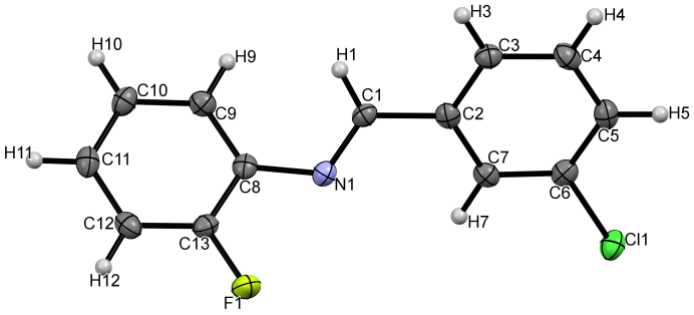


Figure S5:24 Compound 40

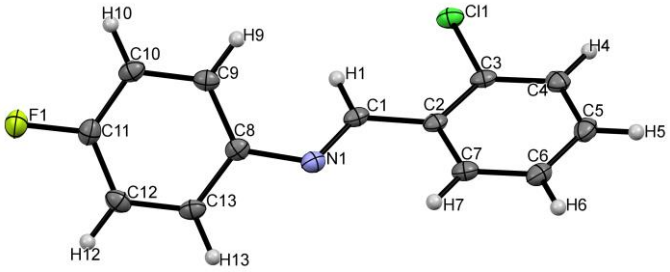


Figure S5:25 Compound 41

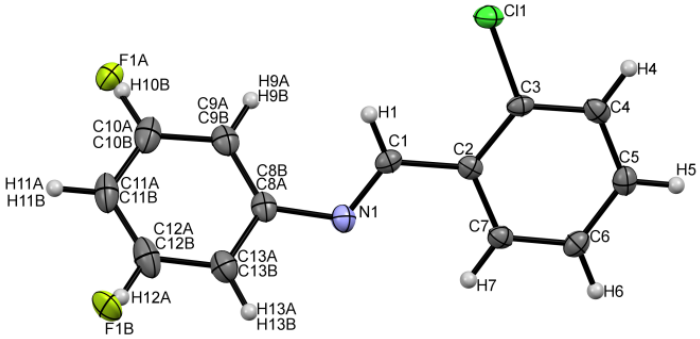


Figure S5:26 Compound 42

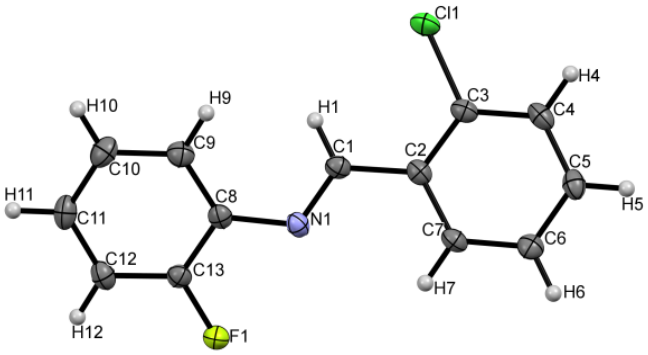


Figure S5:27 Compound 43

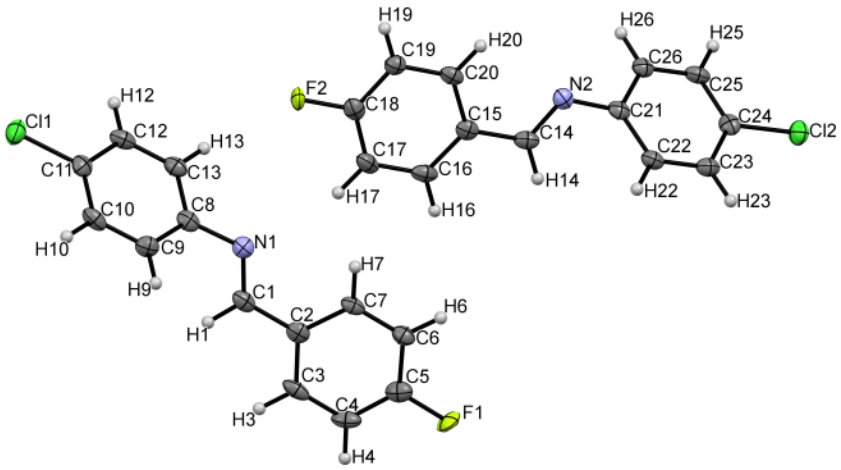


Figure S5:28 Compound 44

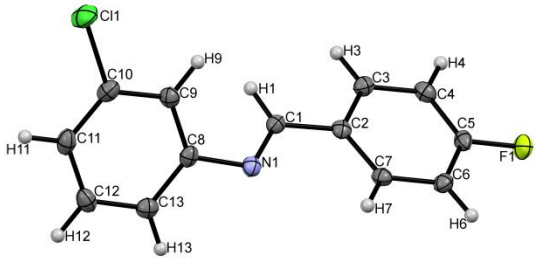


Figure S5:29 Compound 46

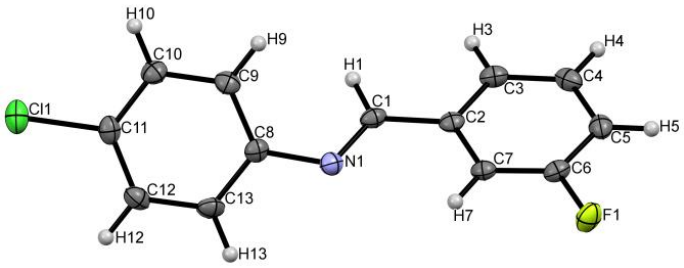


Figure S5:30 Compound 49

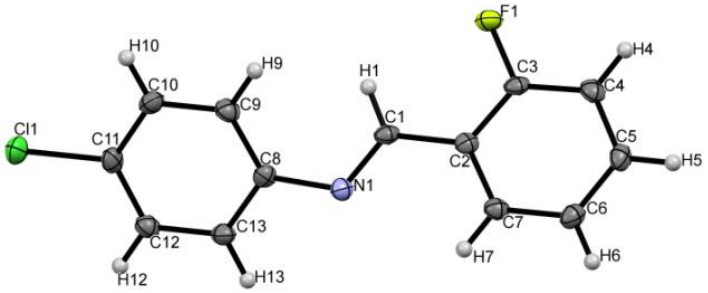


Figure S5:31 Compound 50

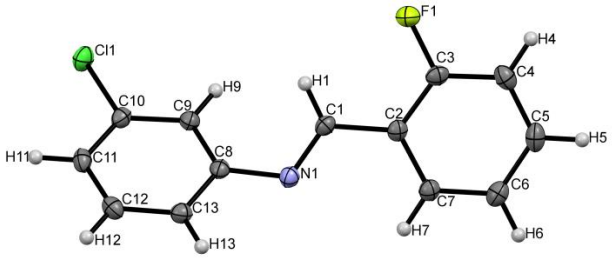
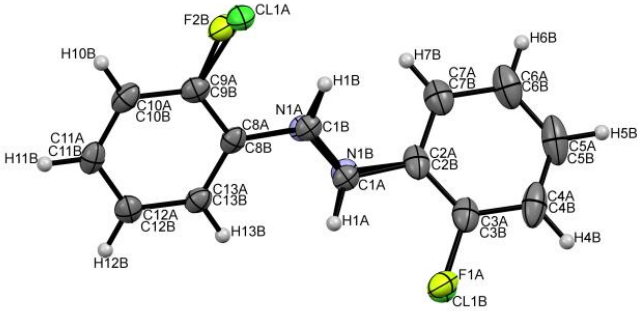


Figure S5:32 Compound 51



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