Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Quantitative insights into intermolecular interactions in fluorine and trifluoromethyl substituted isomeric *N*-phenylacetamides and *N*-methylbenzamides

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Table S1: Melting Points (in °C) of the solid compounds determined from DSC data and compared with the reported values in the literature (the exact reference is provided in superscript):

Compound Code	% Yield after column chromatography	M.P. (Onset Value)
AC-0	**92**	**114.2**[a]
AC-1	**88**	**75.0**[b]
AC-2	**91**	**85.4**[c]
AC-3	**94**	**152.3**[d]
AC-4	**86**	**92.7**[e]
AC-5	**89**	**101.7**[f]
AC-6	**93**	**151.2**[g]
BZ-0	**87**	**79.7**[h]
BZ-1	**84**	**46.0**
BZ-2	**91**	**89.6**[i]
BZ-3	**91**	**128.6**[i]
BZ-4	**85**	**115.5**
BZ-5	**90**	**81.2**[i]
BZ-6	**93**	**157.0**

Figure S1: IR-Spectra of the compounds: All IR spectra were recorded with KBr pellet on Perkin Elmer instrument.

Figure S1(a): AC-0

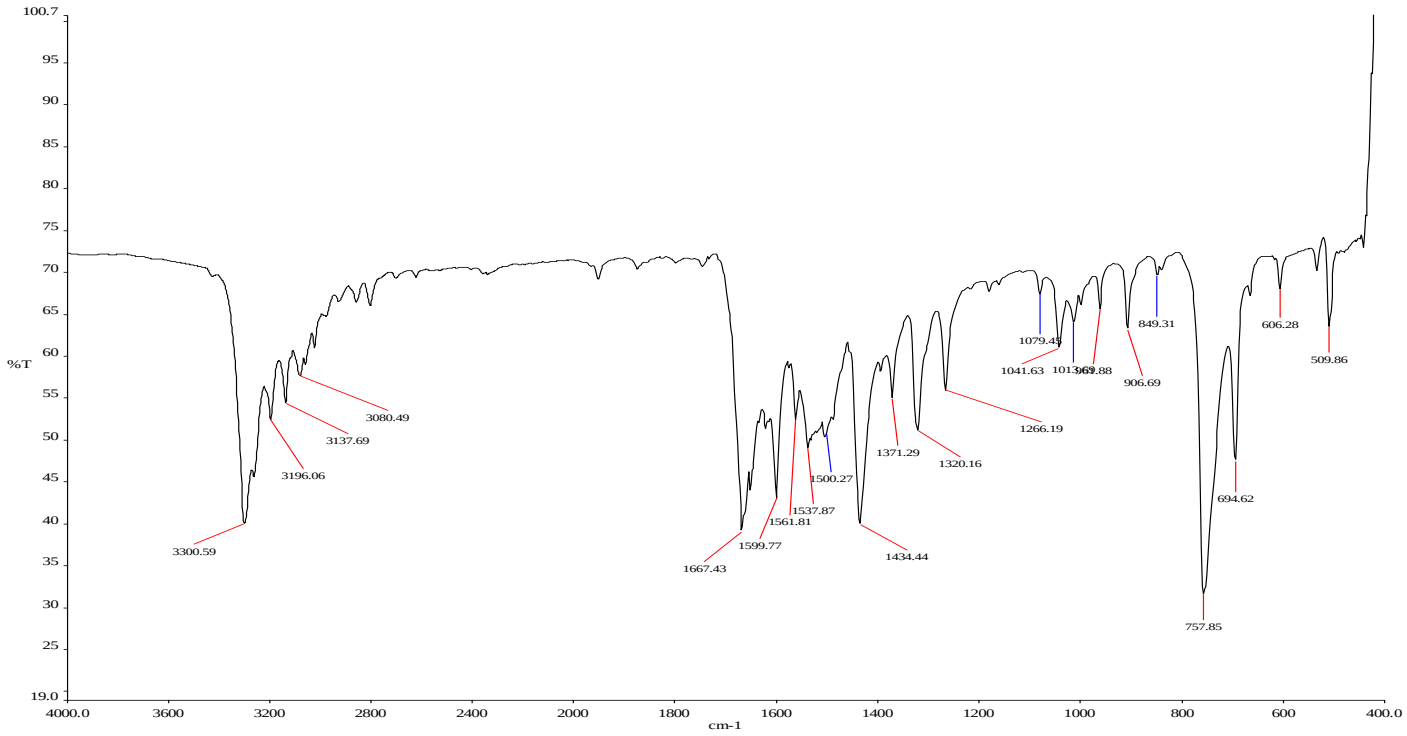


Figure S1(b): AC-1

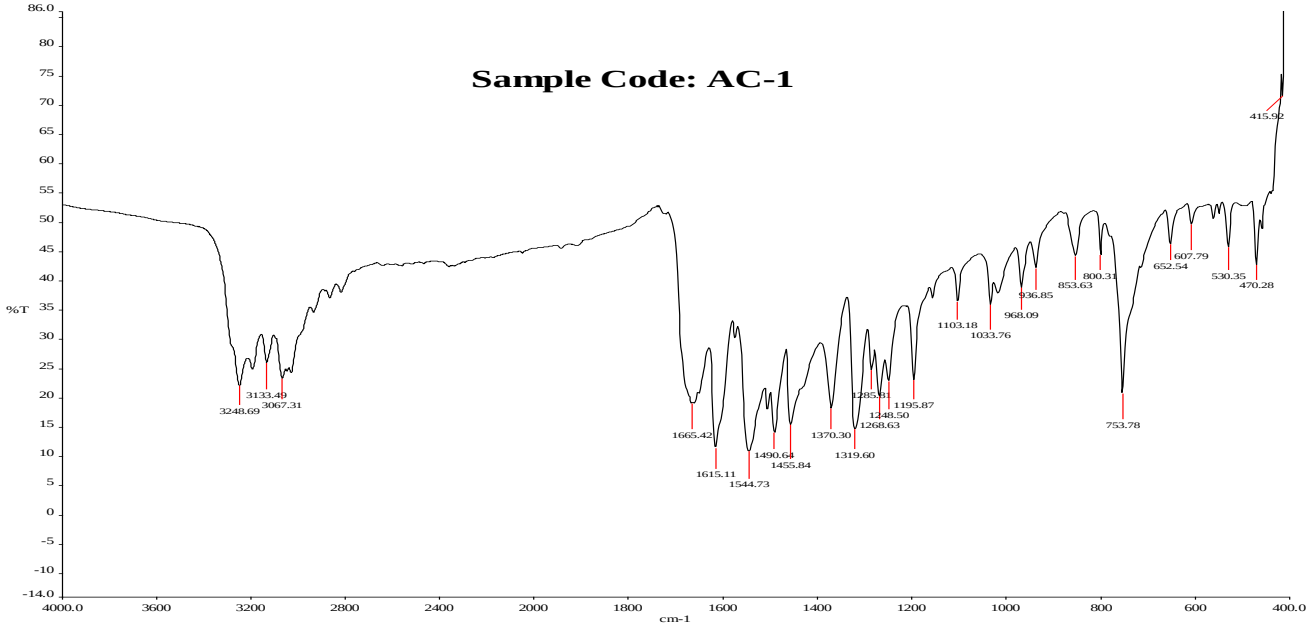


Figure S1(c): AC-2

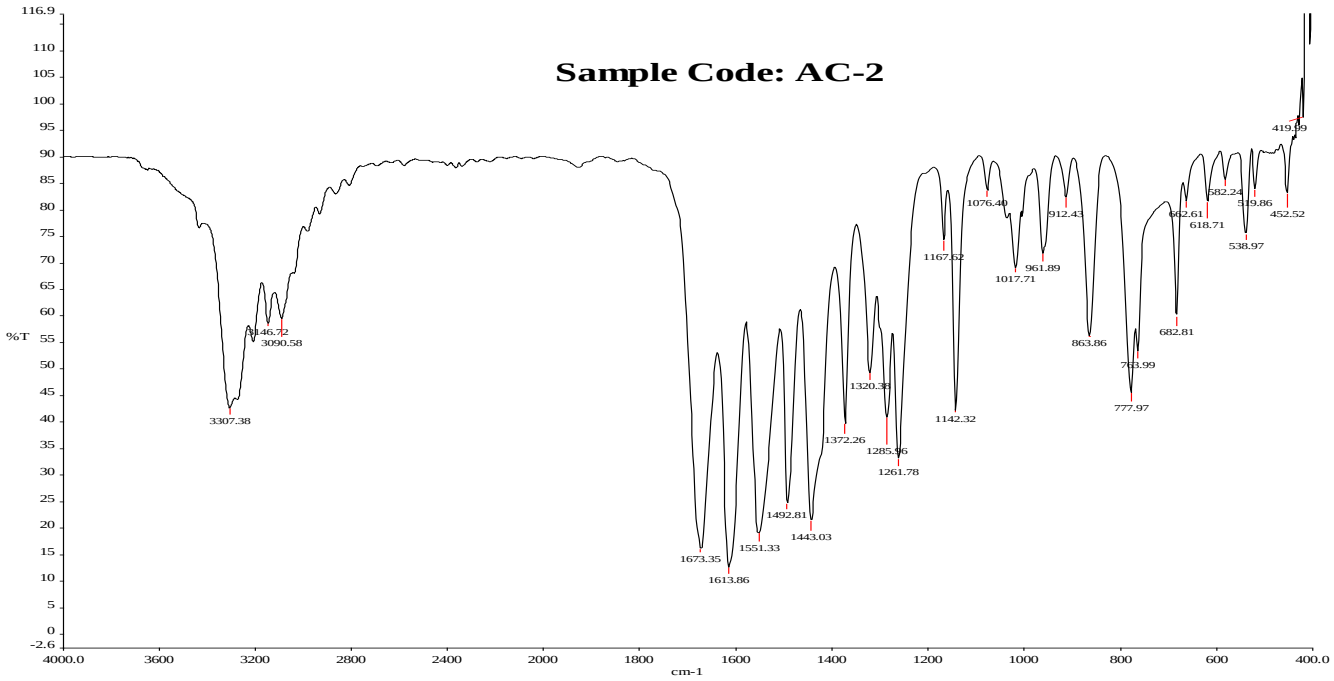


Figure S1(d): AC-3

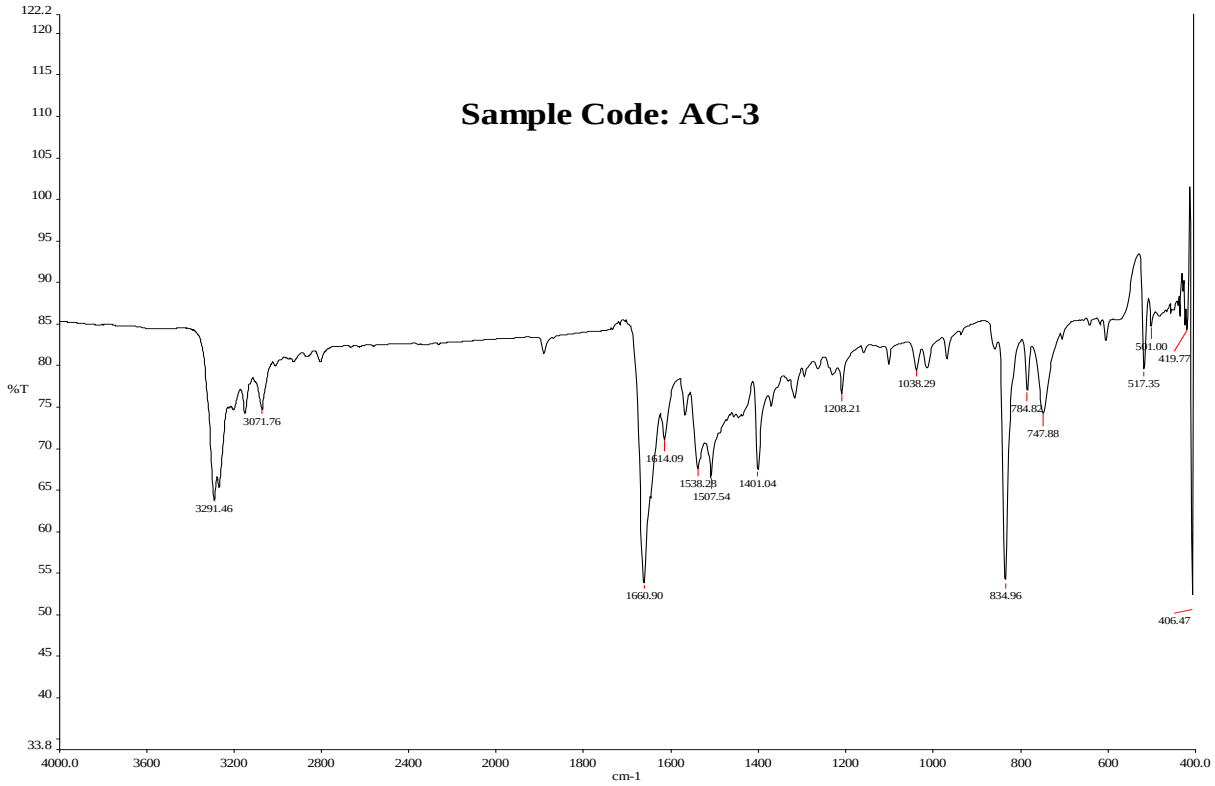


Figure S1(e): AC-4

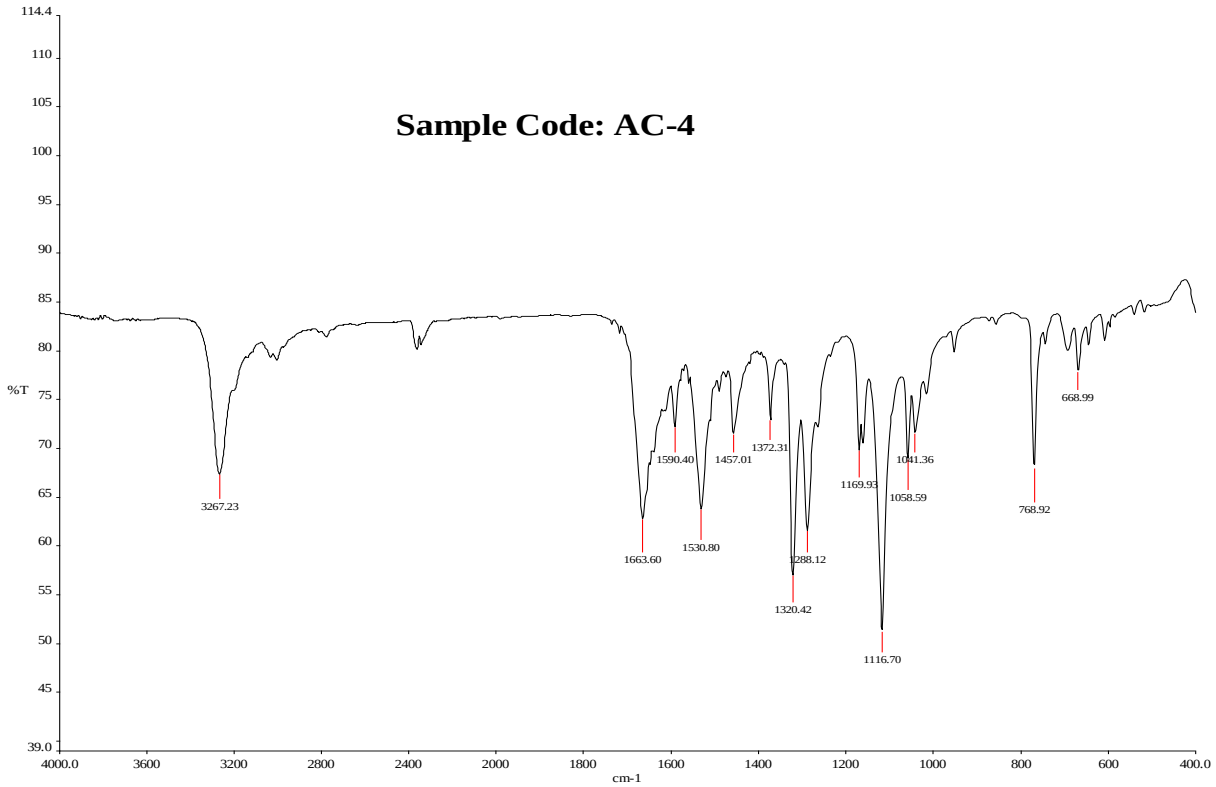


Figure S1(f): AC-5:

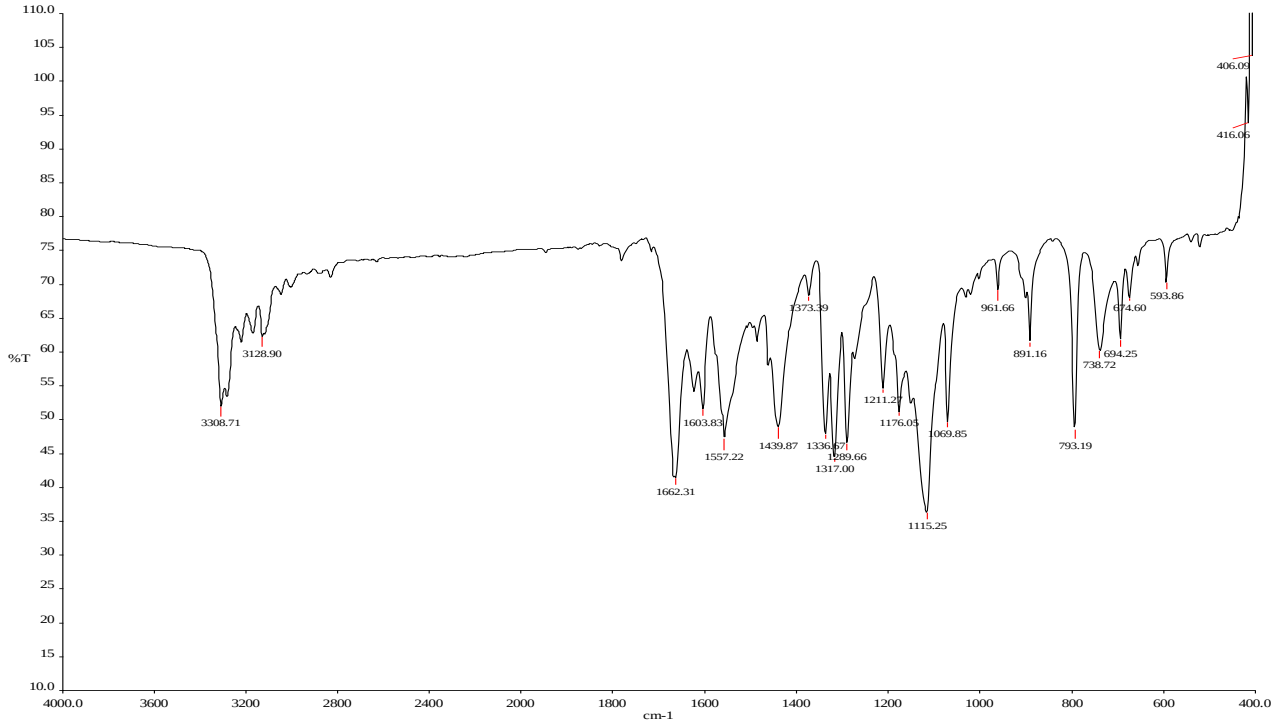


Figure S1(g): AC-6:

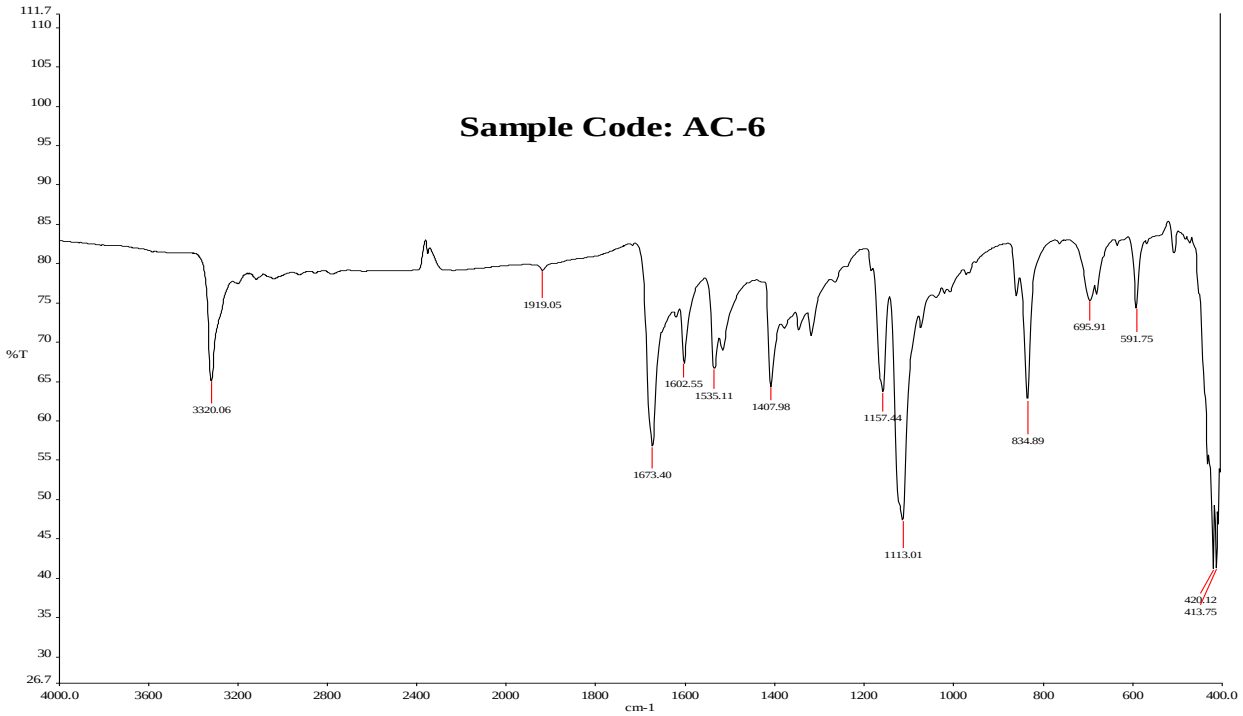


Figure S1(h): BZ-0

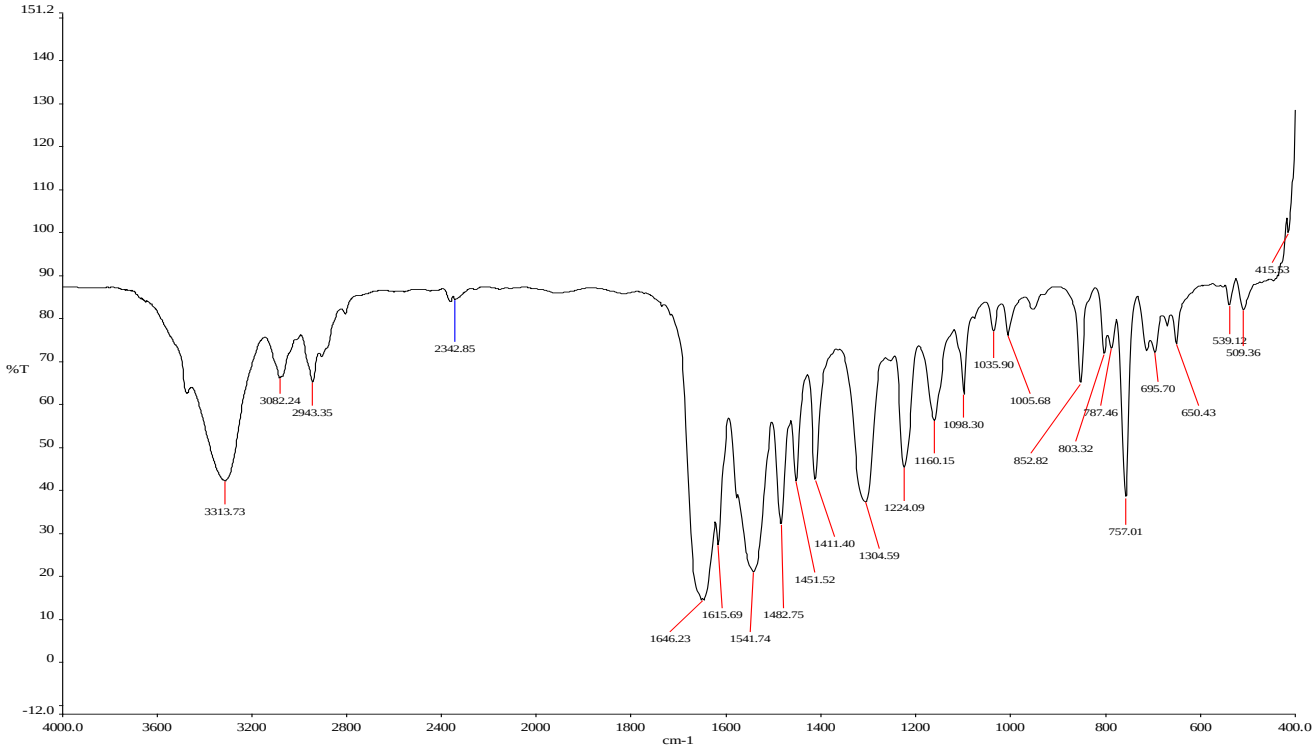


Figure S1(i): BZ-1

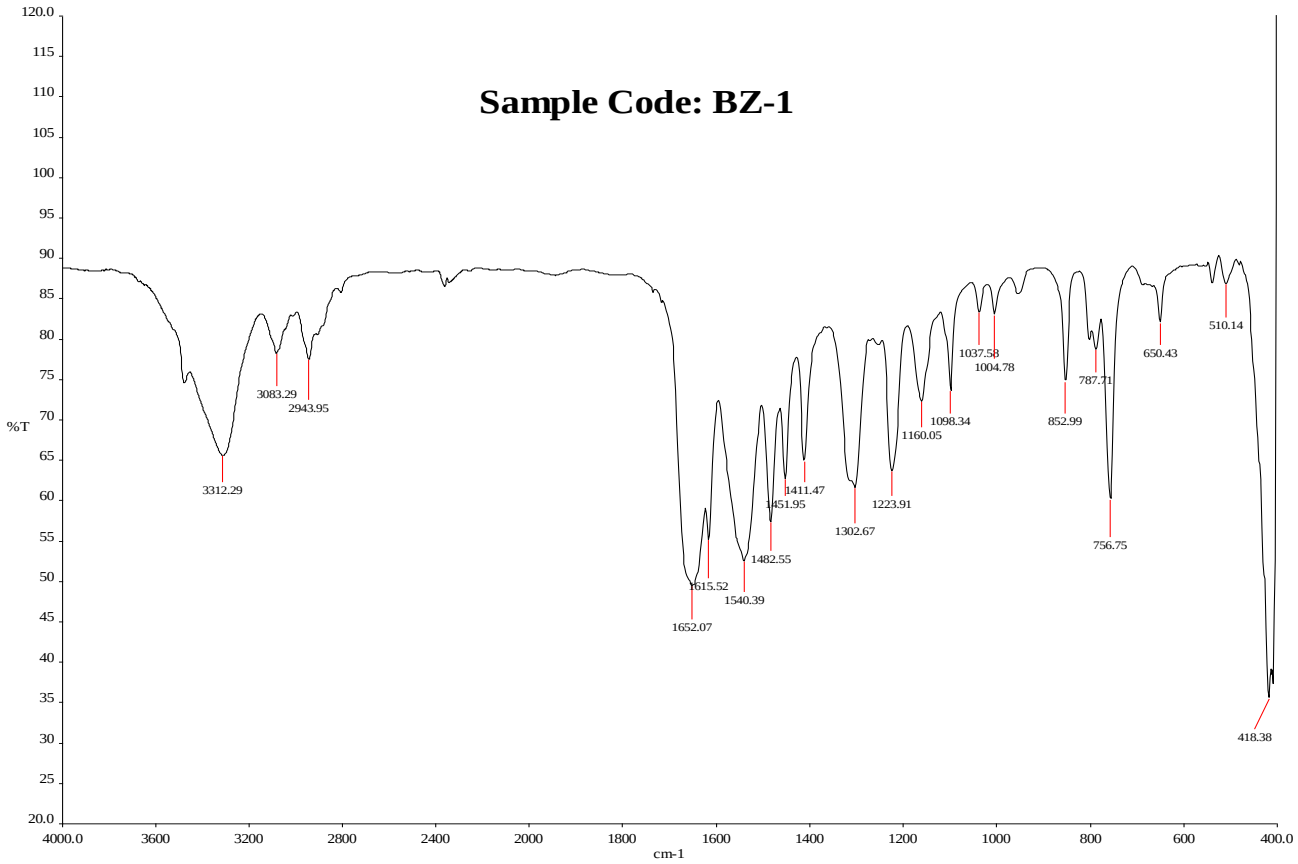


Figure S1(j): BZ-2

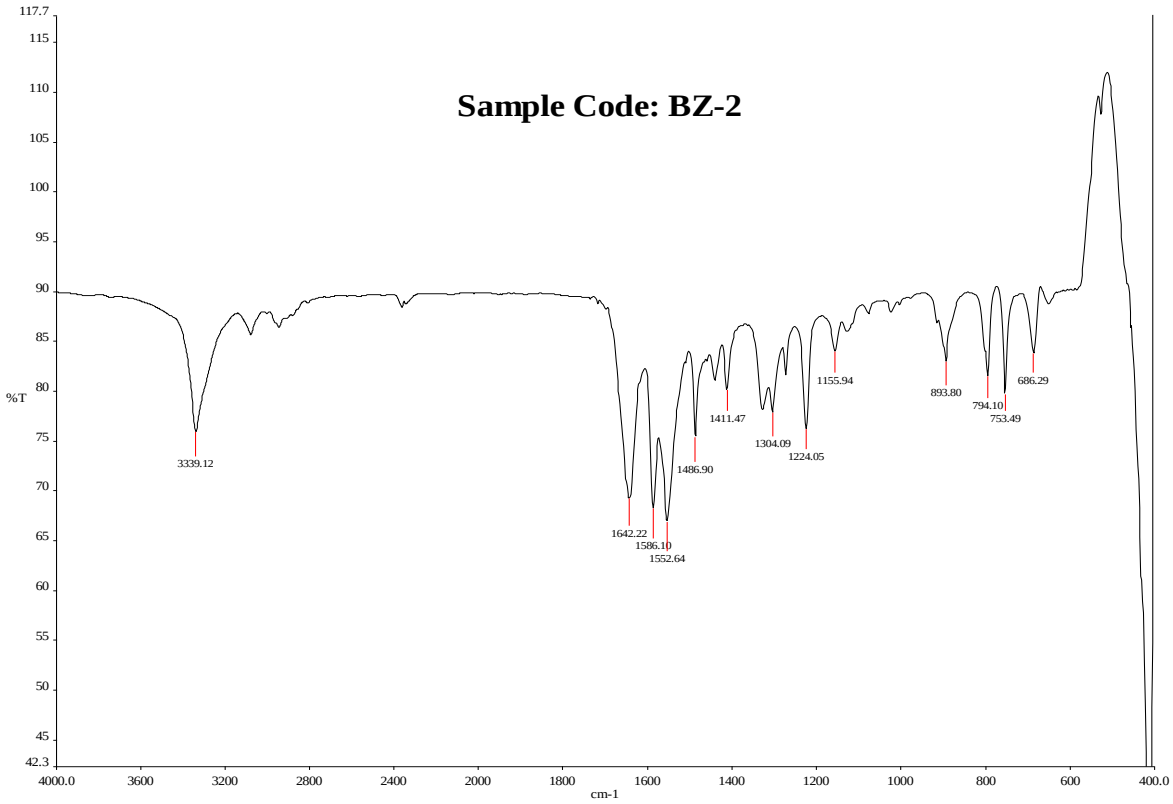


Figure S1(k): BZ-3

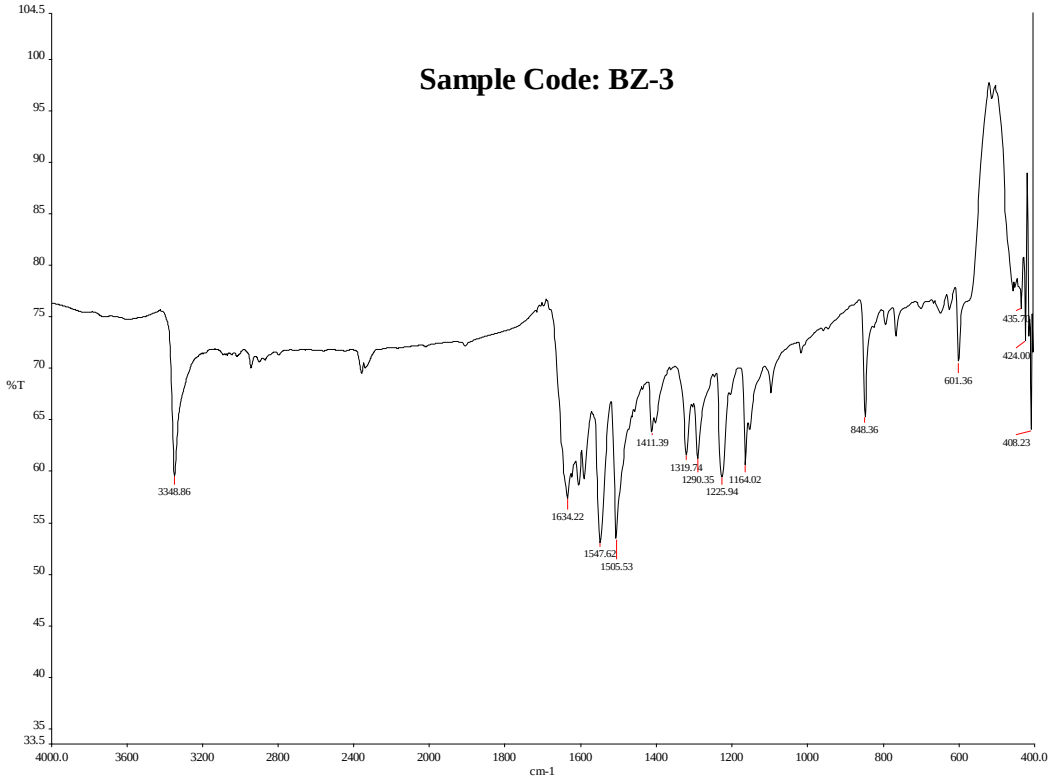


Figure S1(l): BZ-4

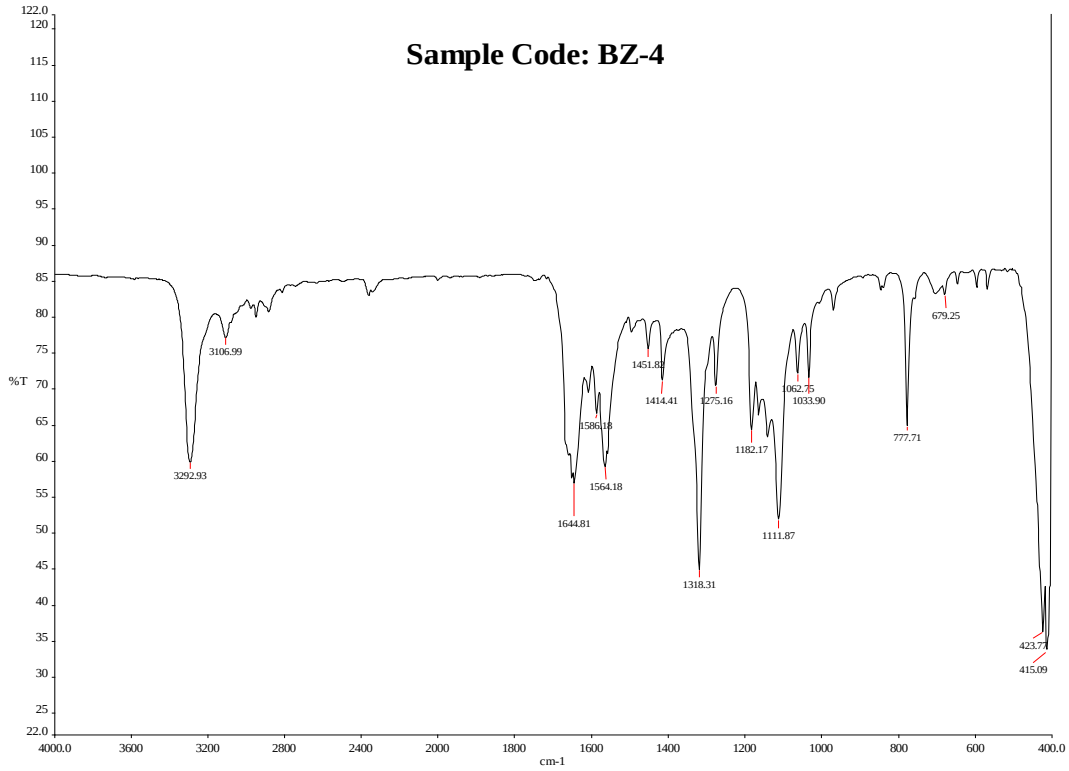


Figure S1(m): BZ-5

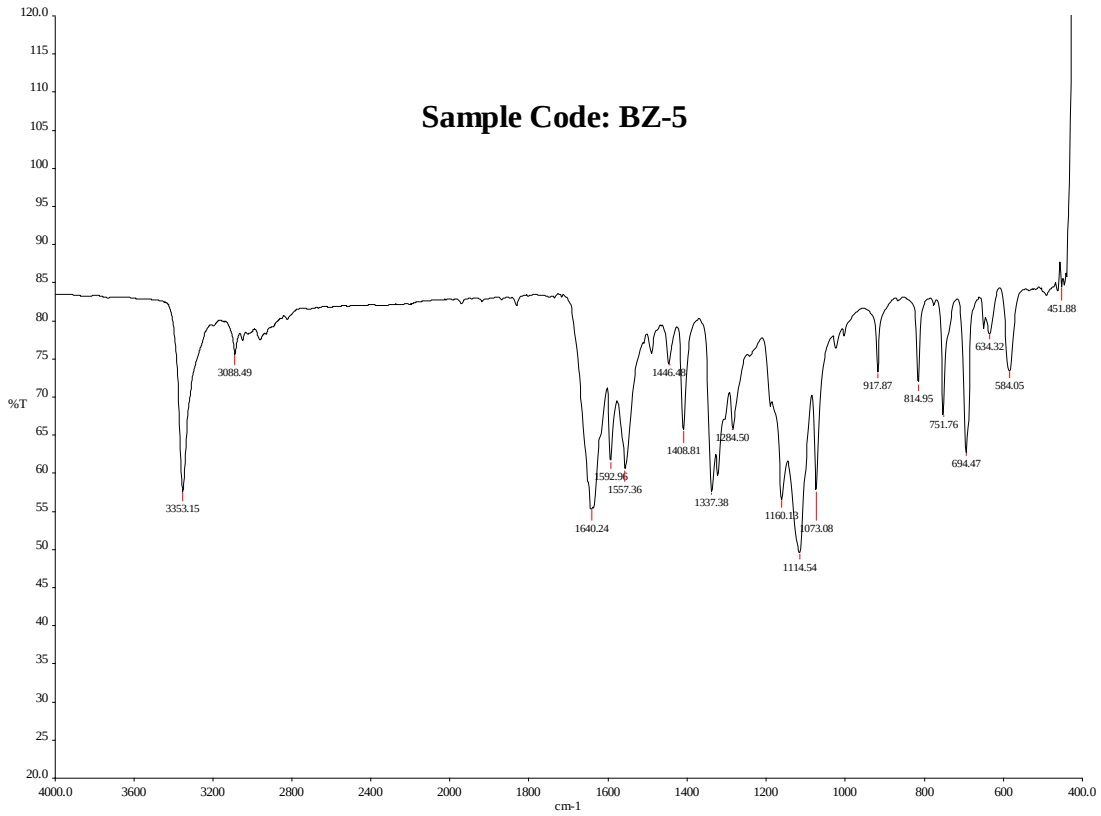


Figure S1(n): BZ-6

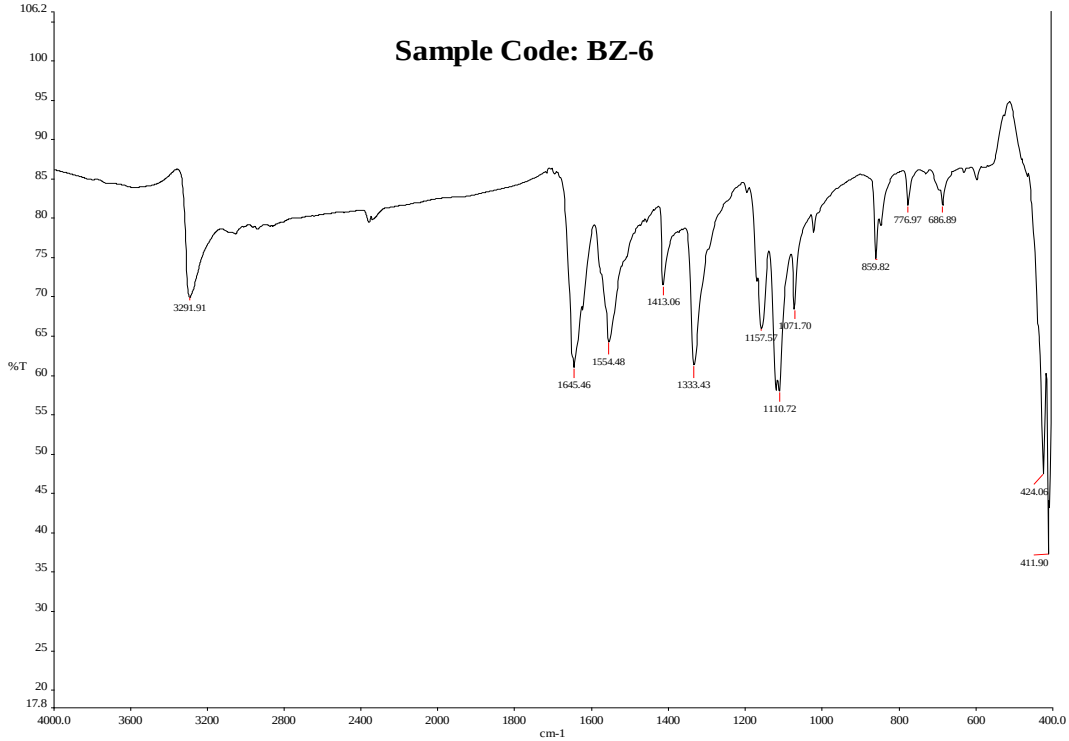
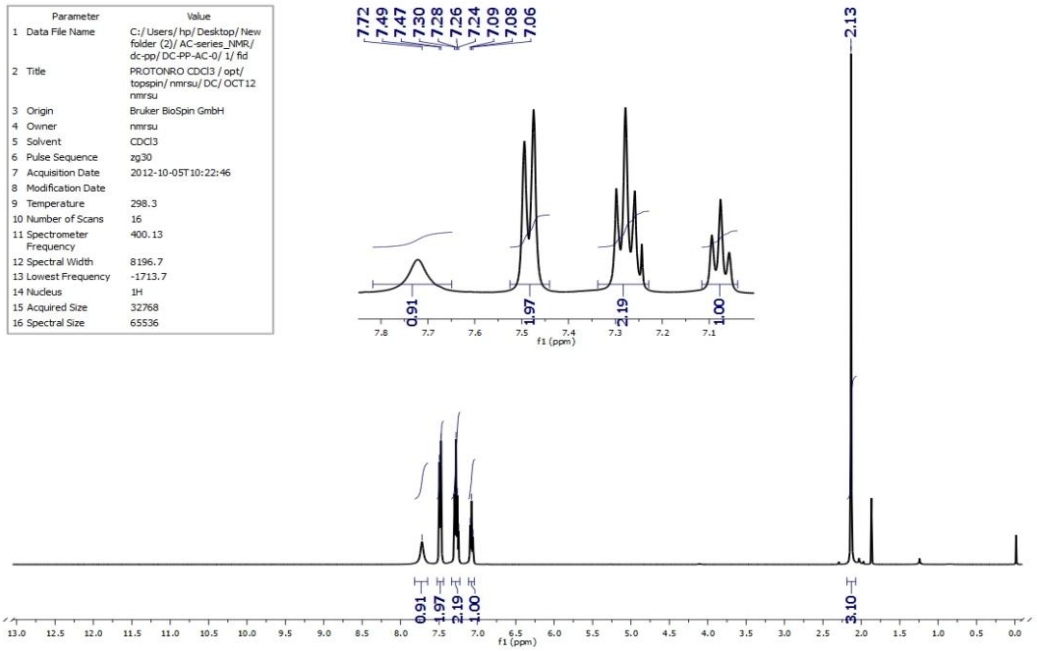
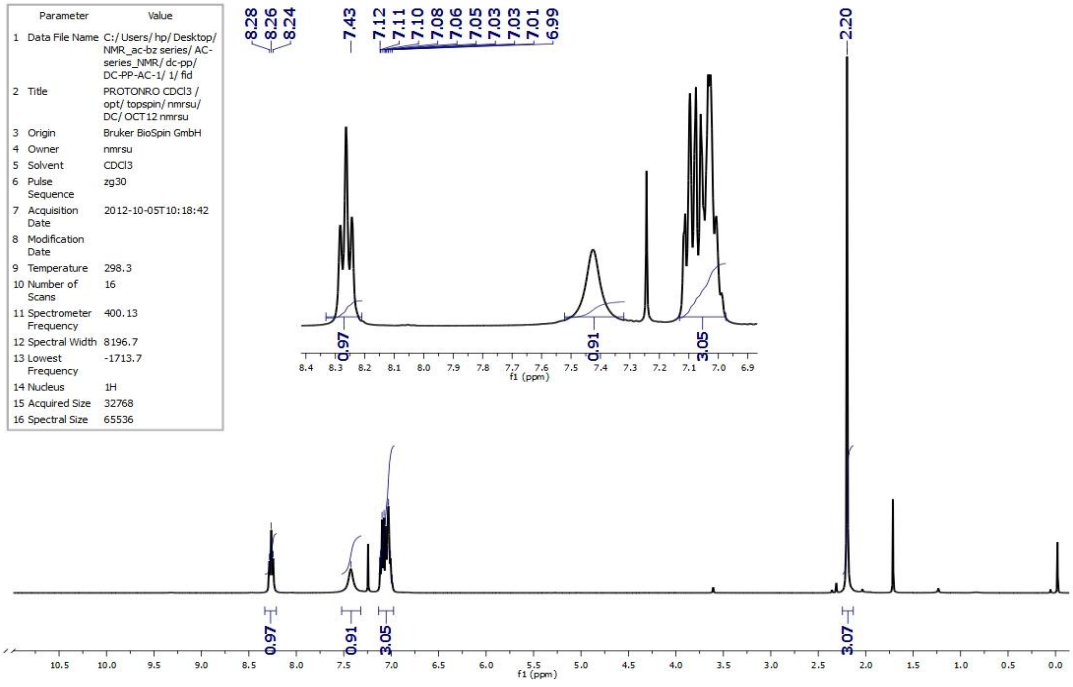


Figure S2: ^{1}H NMR of all compounds: All NMR experiments were recorded on 400MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

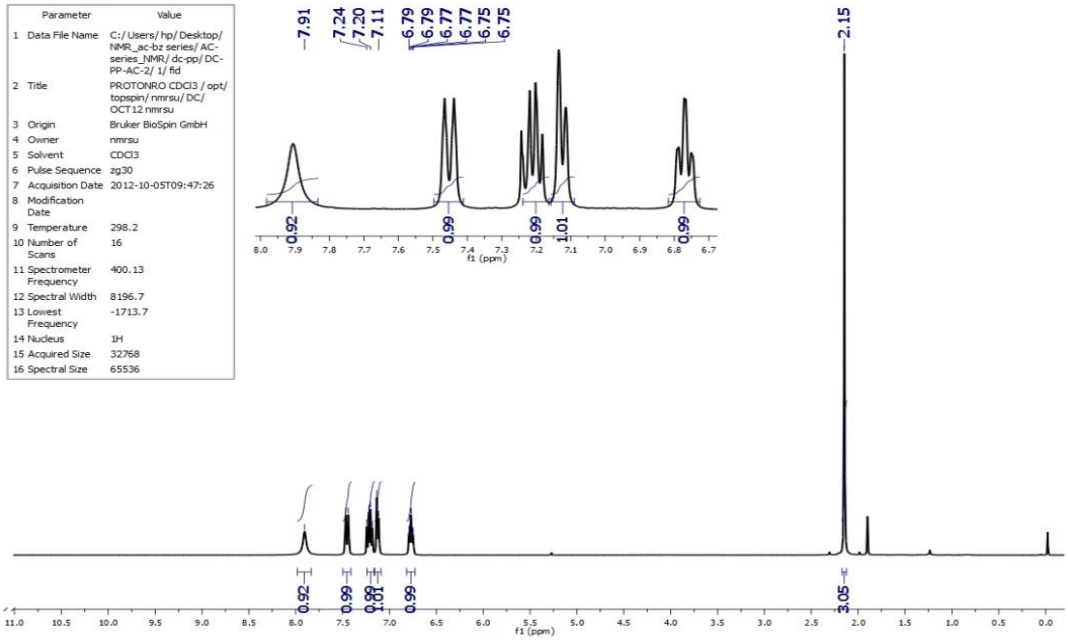
(a) AC-0: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.48 (d, *J* = 7.91 Hz, 2H), 7.27 (m, 2H), 7.08 (t, *J* =7.37 Hz, 1H), 2.13 (s, 3H).



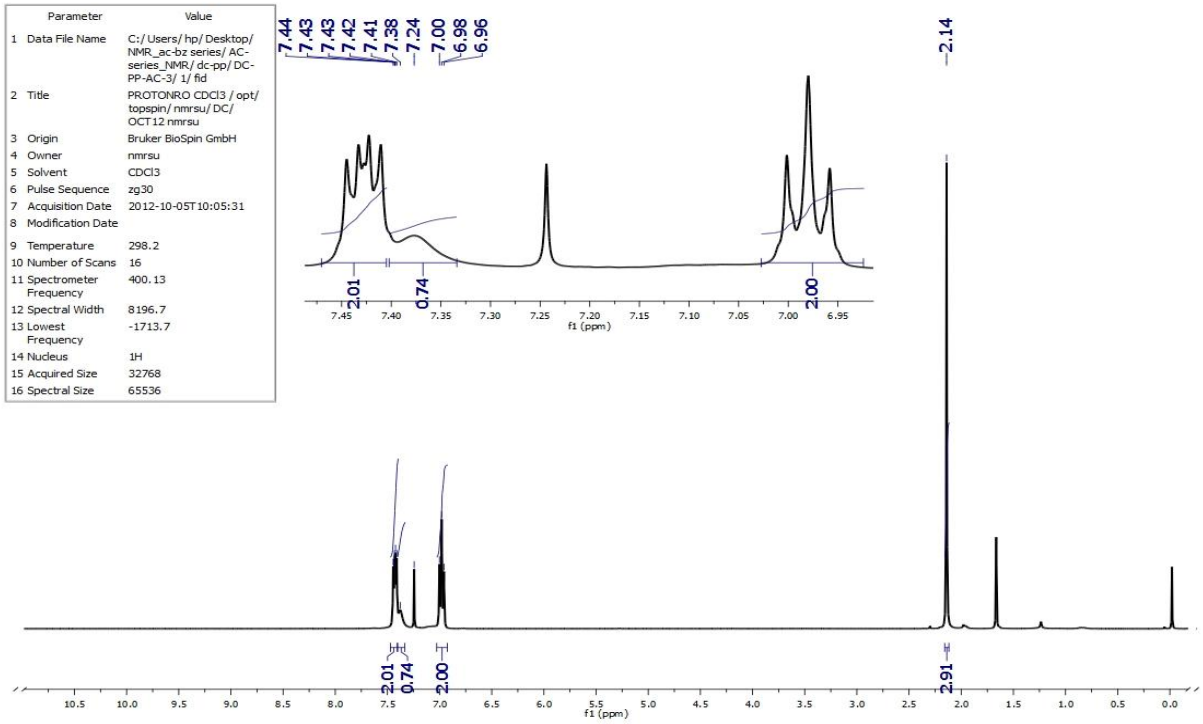
(b) AC-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (t, *J*=7.72 Hz, 1H), 7.43 (s, 1H), 7.06 (m, 3H), 2.20 (s, 3H).



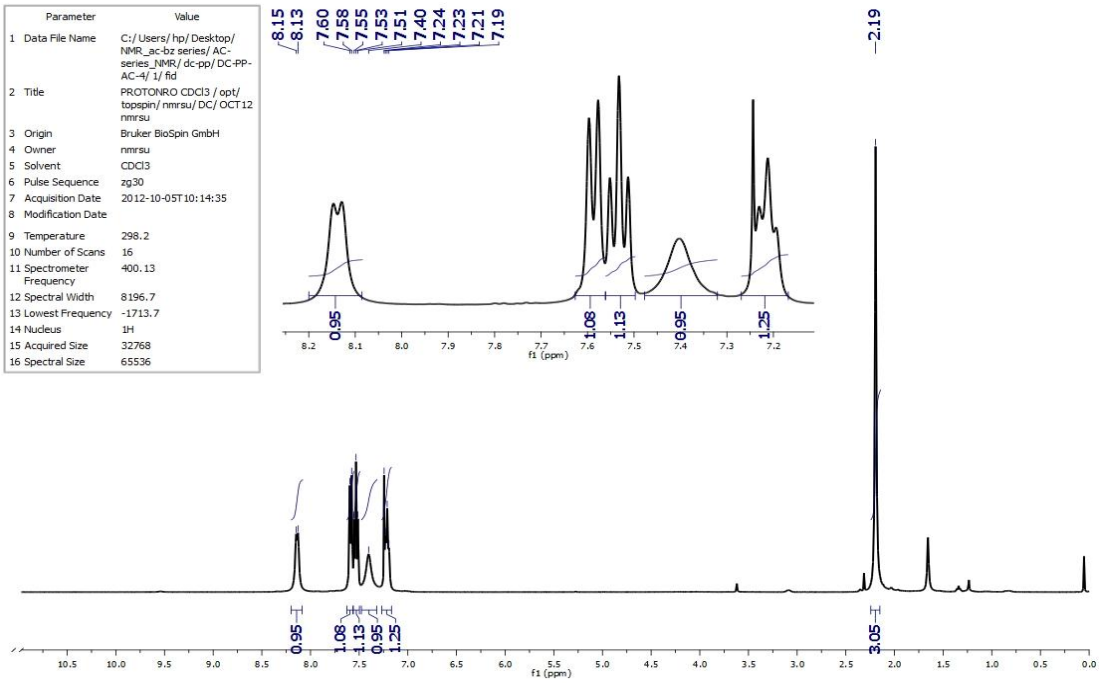
(c) AC-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.45 (d, *J* =11.59 Hz, 1H), 7.22 (m, 1H), 7.12 (d, 7.99 Hz, 1H), 6.77 (m, 1H) 2.15 (s, 3H).



(d) AC-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.38 (s, 1H), 6.98 (t, *J* = 8.53 Hz, 2H), 2.14 (s, 3H).



(e) AC-4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.98 Hz, 1H), 7.59 (d, *J*=7.88 Hz, 1H), 7.53 (t, *J*= 7.99 Hz, 1H), 7.40 (s, 1H), 7.22 (m, 1H), 2.19 (s, 3H).



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4	Owner	nmrsu
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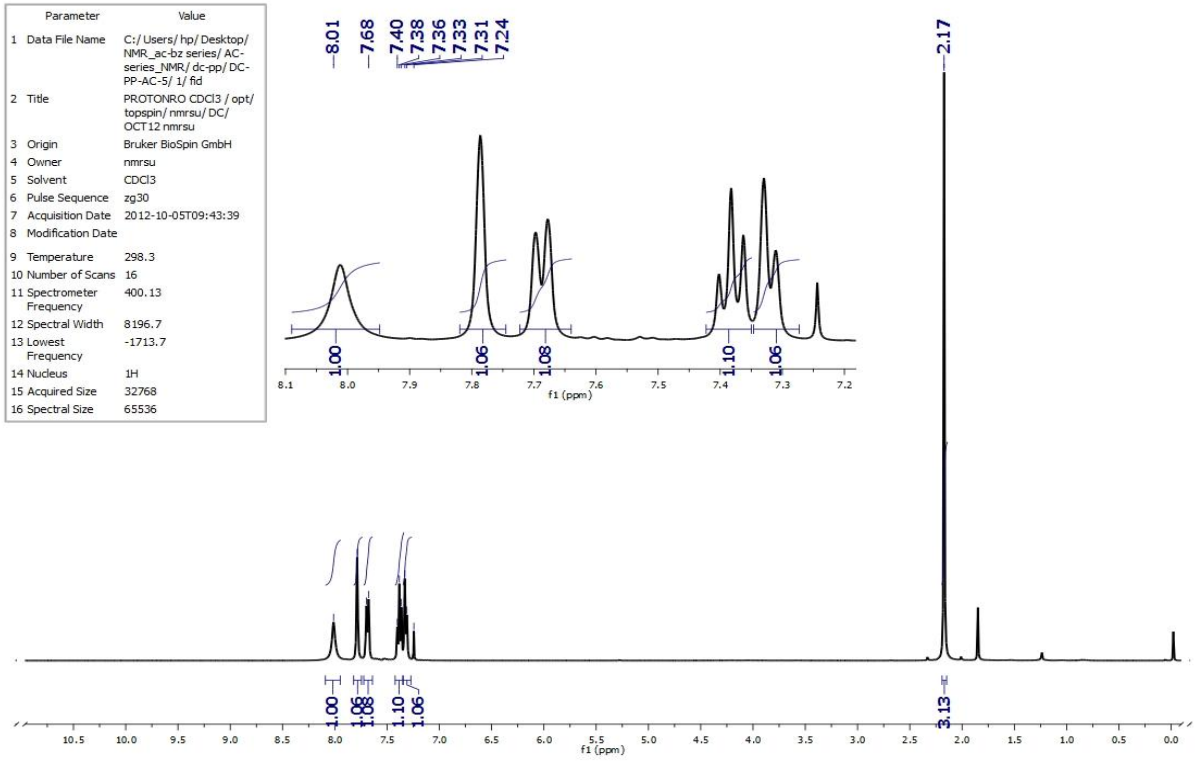
12	Spectral Width	8196.7
13	Lowest Frequency	-1713.7
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

(f) AC-5: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.79 (s, 1H), 7.69 (d, *J*=7.95 Hz, 1H), 7.38 (t, *J*=8.05 Hz, 1H), 7.32 (d, *J*=8.06 Hz, 1H), 2.17 (s, 3H).



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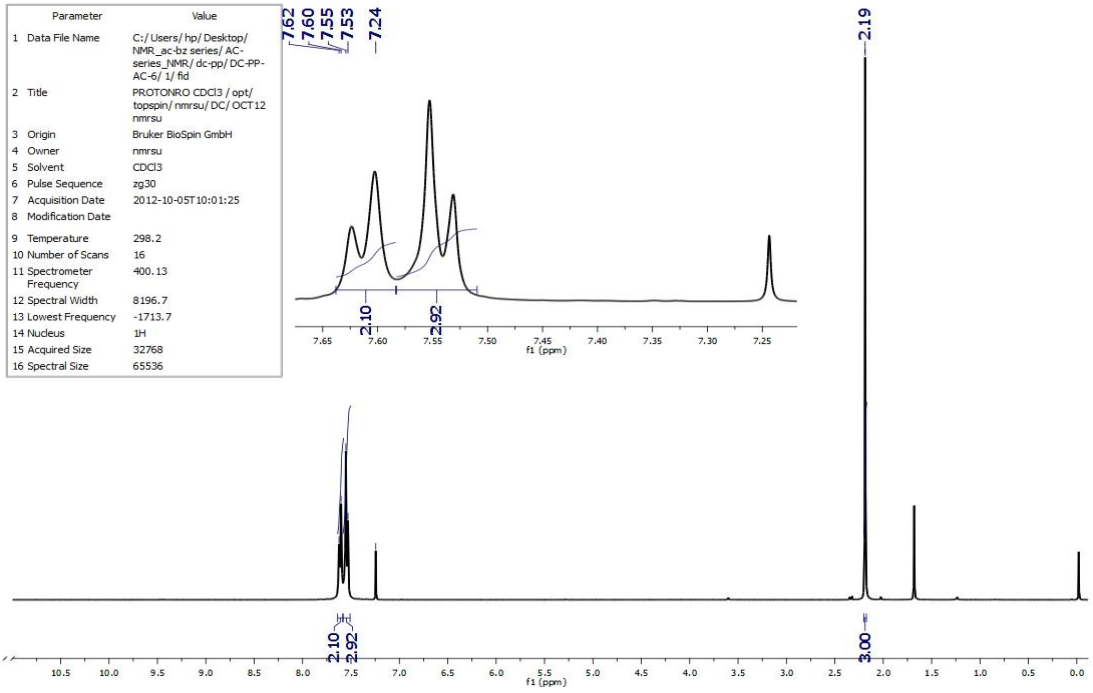
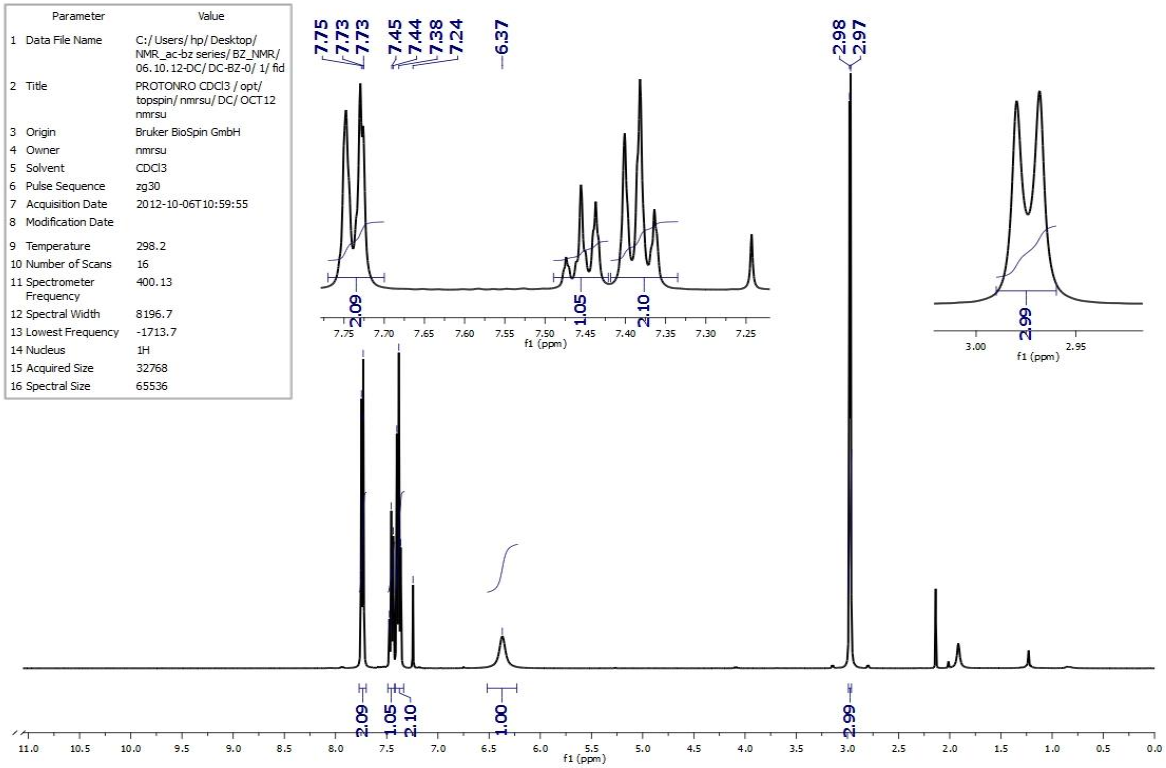
12	Spectral Width	8196.7
13	Lowest Frequency	-1713.7
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

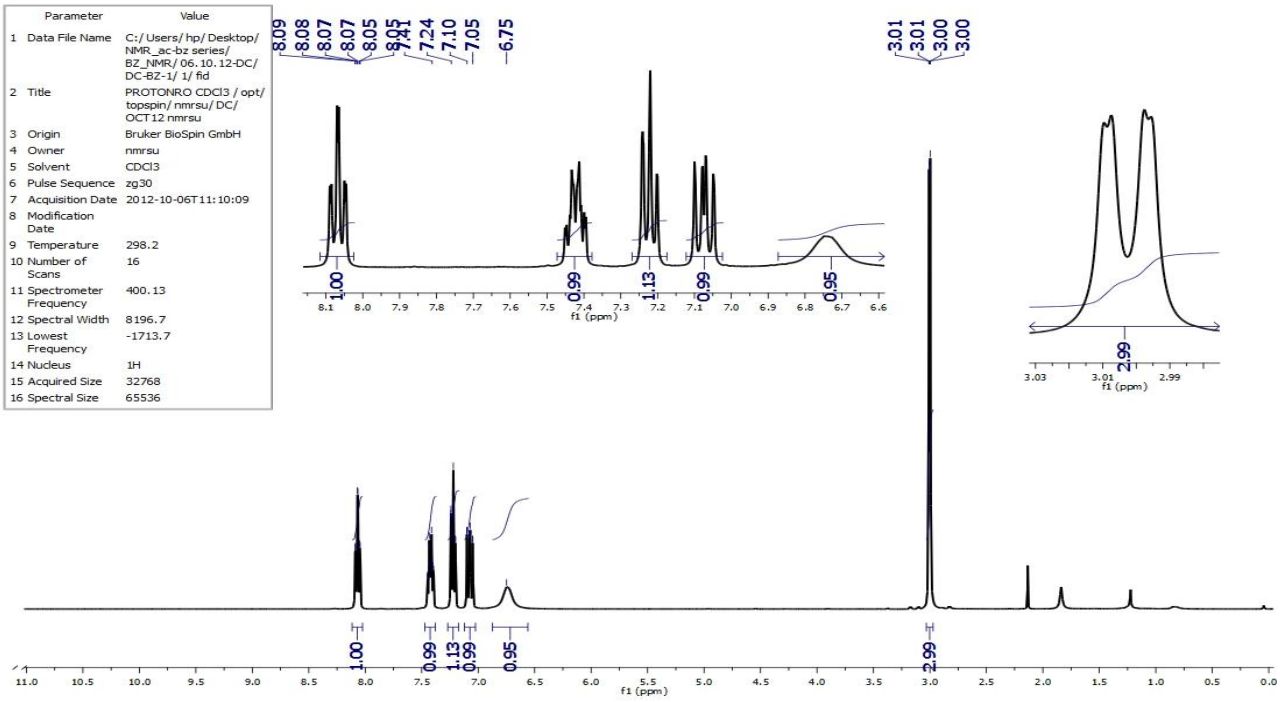
(g) AC-6: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 5H), 2.19 (s, 3H).



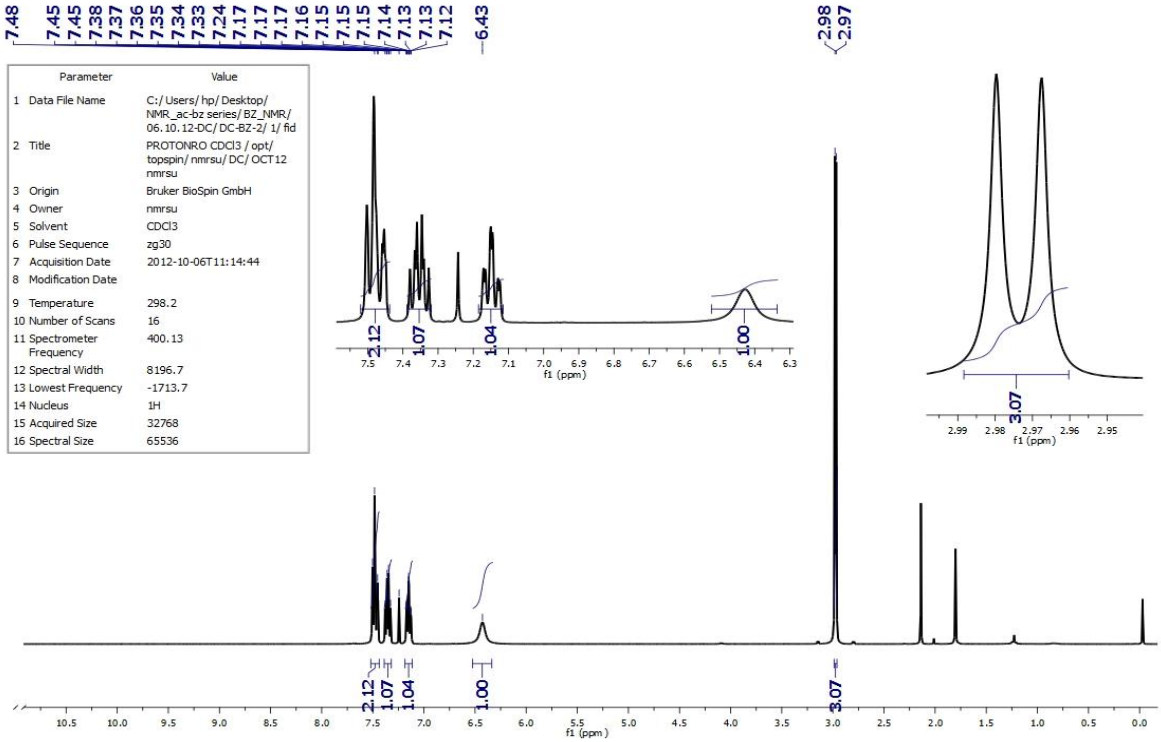
(h) BZ-0: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J*=7.93 Hz, 2H), 7.45 (t, *J*=7.50 Hz, 1H), 7.38 (t, *J*=7.54 Hz, 2H), 6.37 (s, 1H), 2.97 (d, *J*=4.61 Hz, 3H).



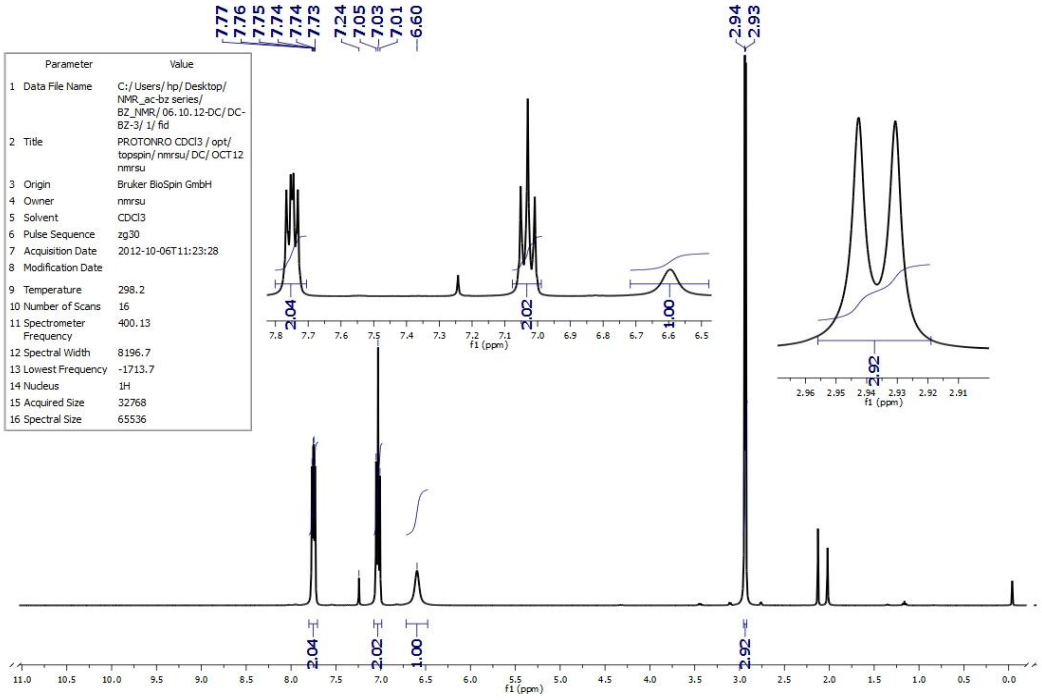
(i) BZ-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (t, *J* = 8.03 Hz, 1H), 7.41 (m, 1H), 7.10 (m, 1H), 7.07 (m, 1H), 6.75 (s, 1H), 3.00 (d, *J*=4.80 Hz, 3H).



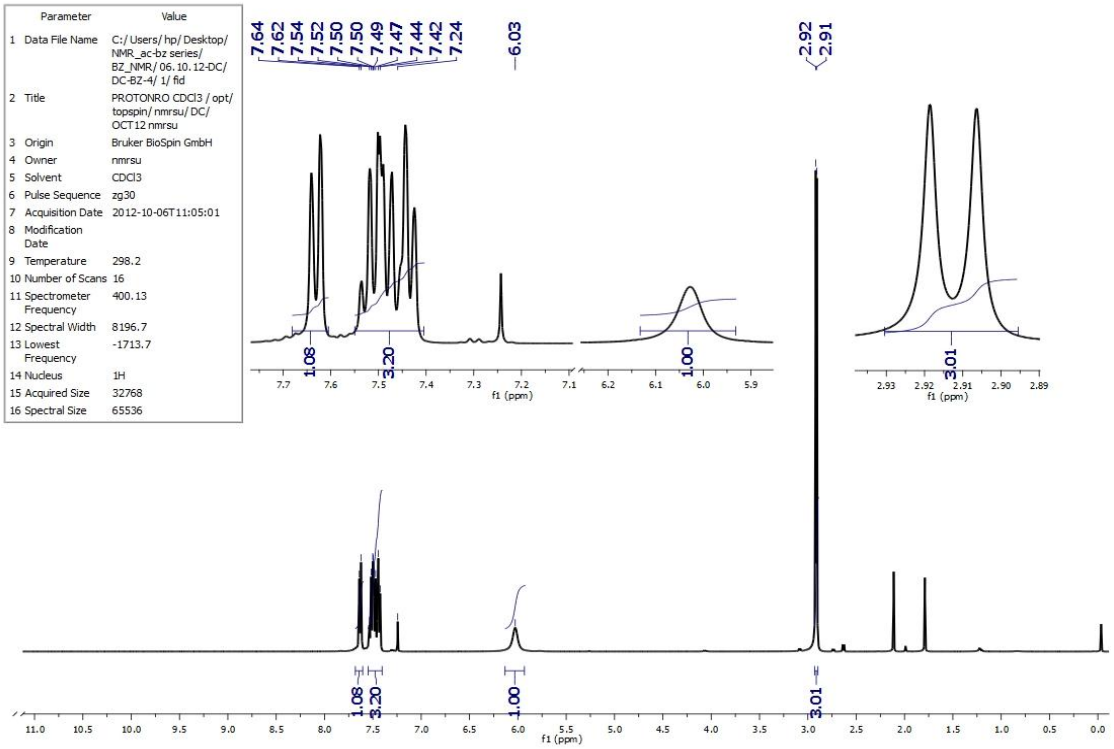
(j) BZ-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, *J* = 9.96 Hz, 2H), 7.35 (m, 1H), 7.15 (t, *J* = 8.38 Hz, 1H), 6.43 (s, 1H), 2.97 (d, *J* = 4.85 Hz, 3H).



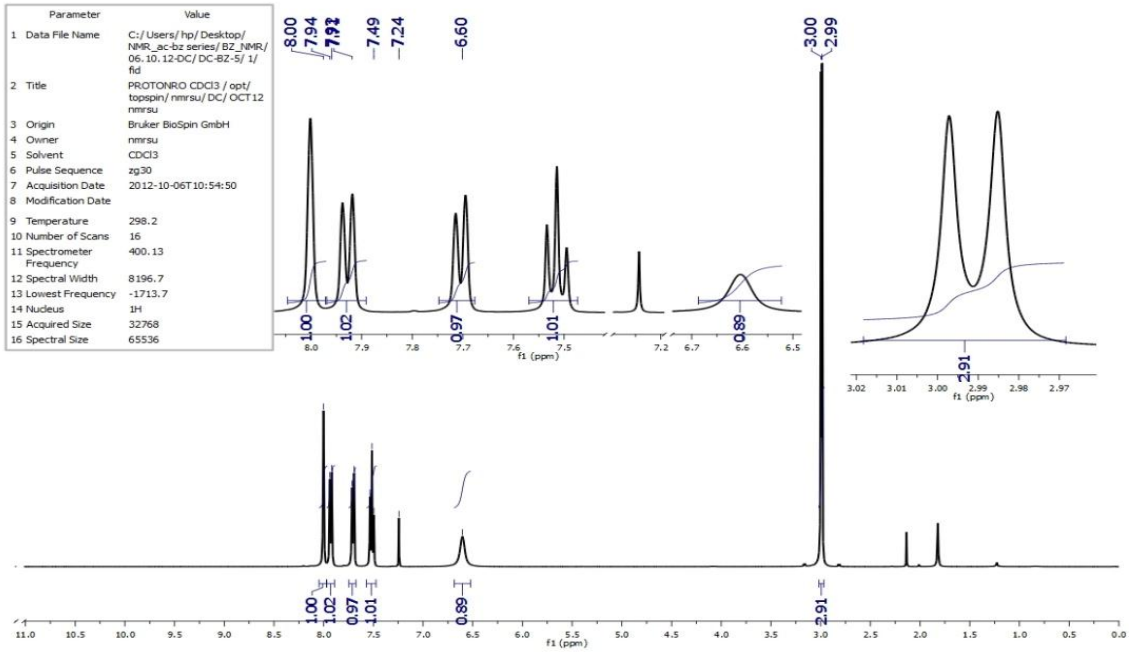
(k) BZ-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.03 (t, *J*=8.57 Hz, 2H), 6.60 (s, 1H), 2.94 (d, *J*=4.82 Hz, 3H).



(l) BZ-4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* =7.55 Hz, 1H), 7.48 (m, 3H), 6.03 (s, 1H), 2.91 (d, *J*=4.94 Hz, 3H).



(m) BZ-5: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.93 (d, *J*=7.95 Hz, 1H), 7.70 (d, *J*=7.95 Hz, 1H), 7.51 (t, *J*=7.81 Hz, 1 H), 6.60 (s, 1H), 2.99 (d, *J*=4.81 Hz, 3H).



(n) BZ-6: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.16 Hz, 2H), 7.64 (d, *J*=816 Hz, 2H), 6.46 (s, 1H), 3.00 (d, *J*=4.91, 3H).

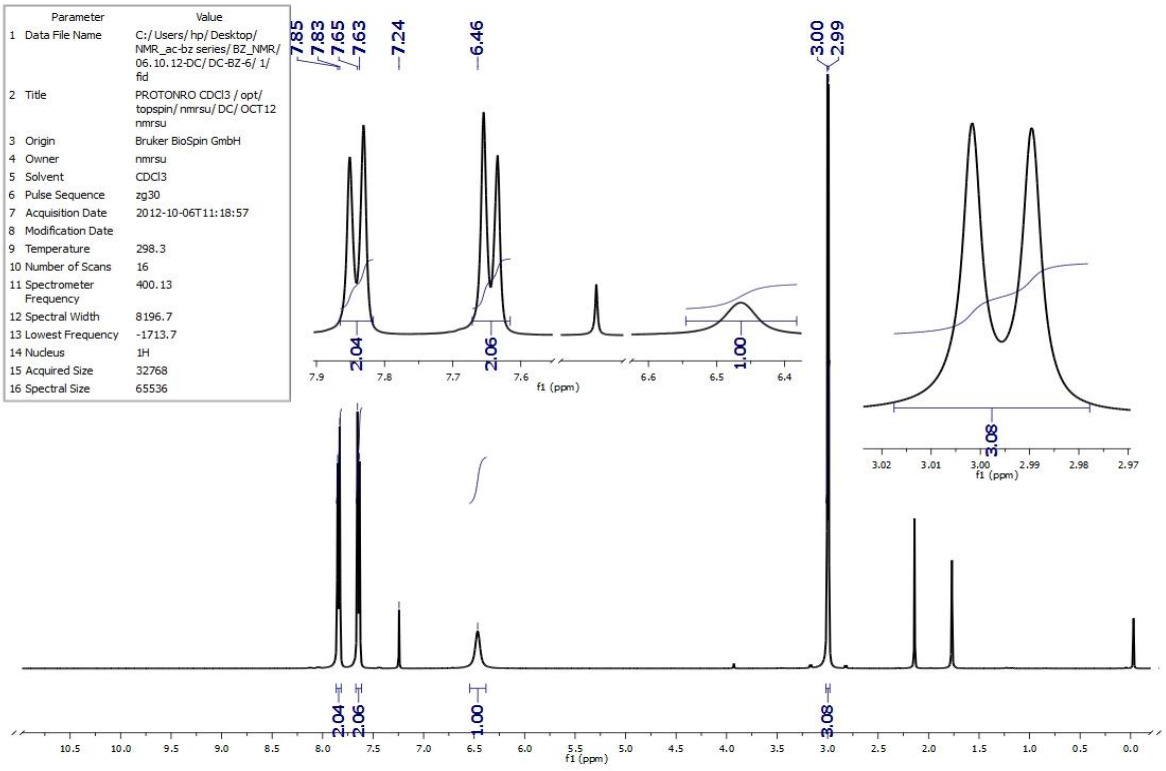
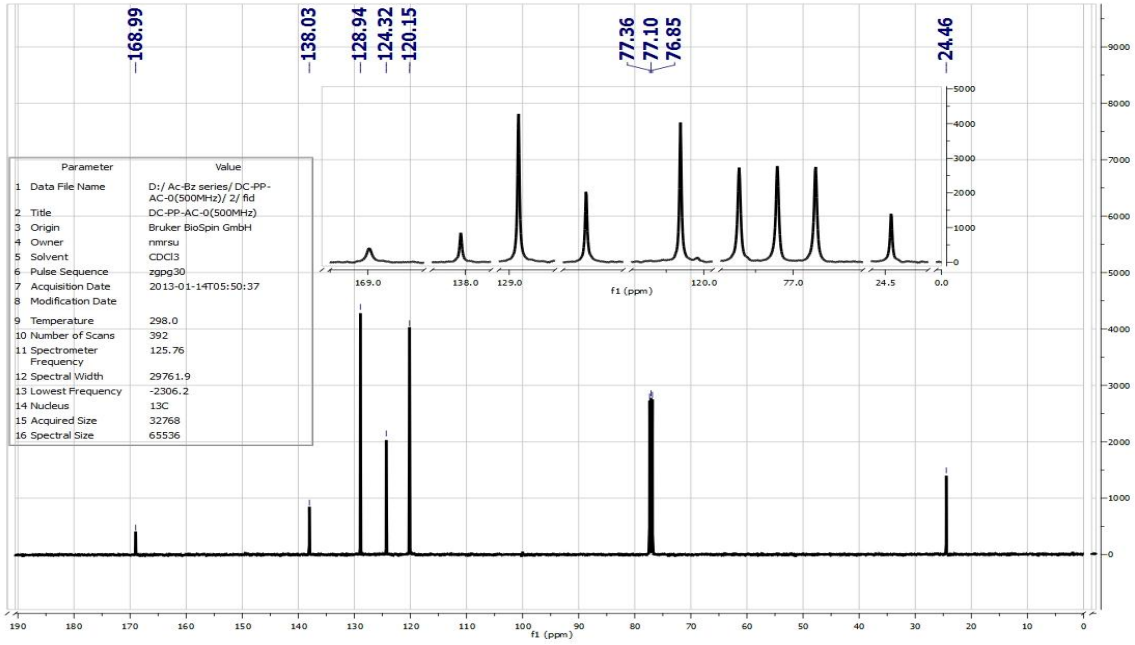
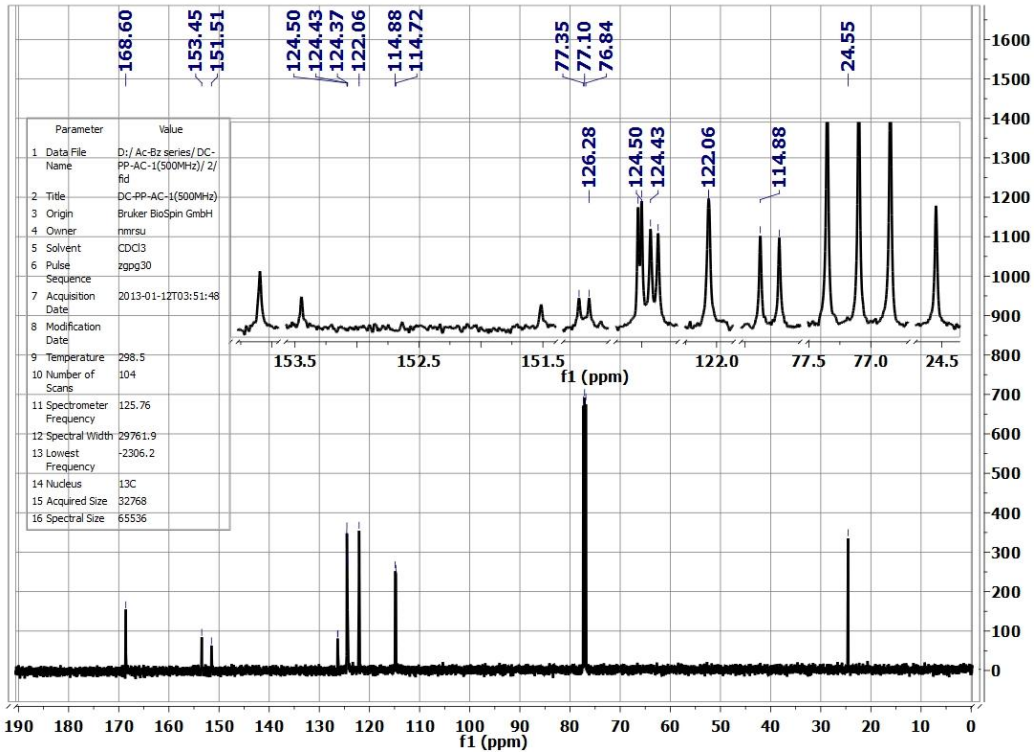


Figure S3: ^{13}C NMR of all compounds: All NMR experiments were recorded on 125MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

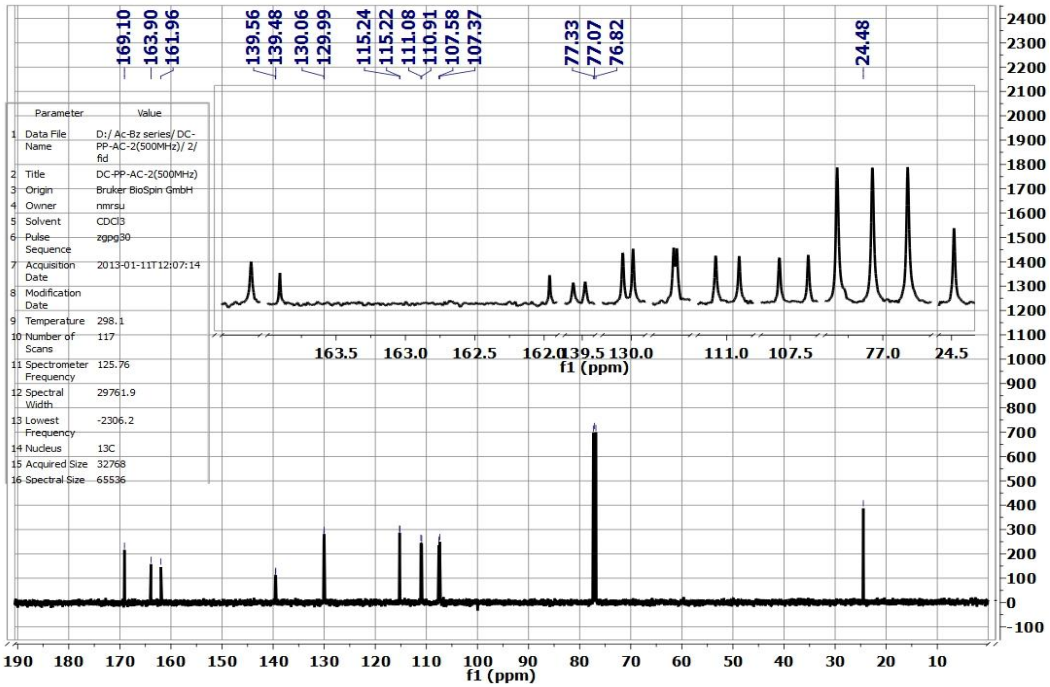
(a) AC-0^{j}: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.99, 138.03, 128.94, 124.32, 120.15, 24.46.



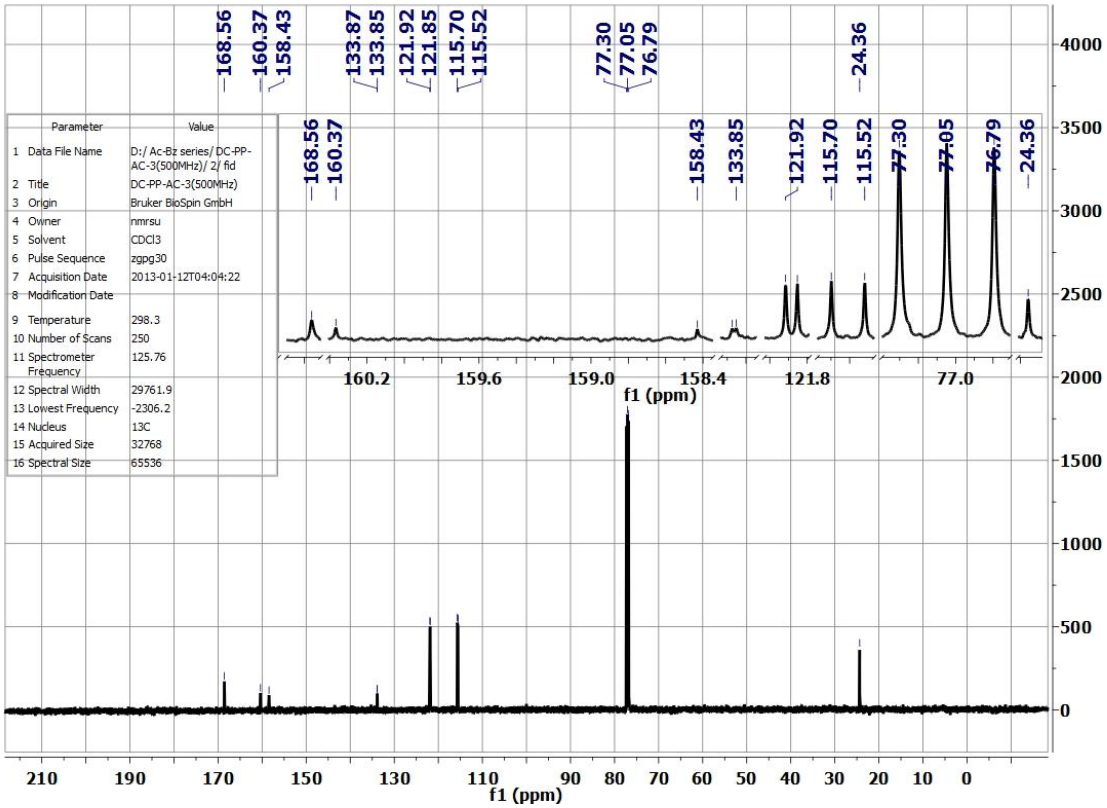
(b) AC-1^{k}: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.60, 152.48 (d, J = 243.18Hz), 126.31(d, J = 10.07 Hz), 124.52 (d, J = 3.57 Hz), 124.40 (d, J = 7.72 Hz), 122.06, 114.80 (d, J = 19.39 Hz), 24.55.



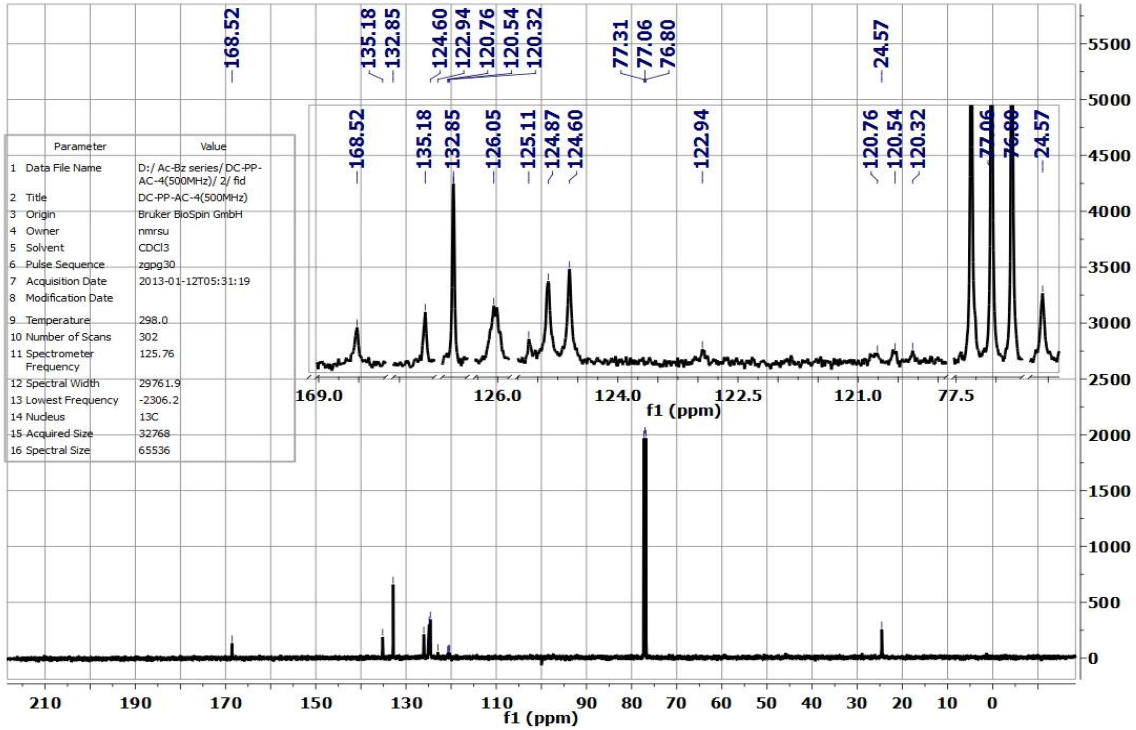
(c) AC-2: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 169.10, 162.93(d, *J* = 245.22 Hz), 139.52 (d, *J* = 10.77Hz), 130.02 (d, *J* = 9.45 Hz), 115.23 (d, *J* = 2.81 Hz), 111.00 (d, *J* = 21.40Hz), 107.47 (d, *J* = 26.14 Hz), 24.48.



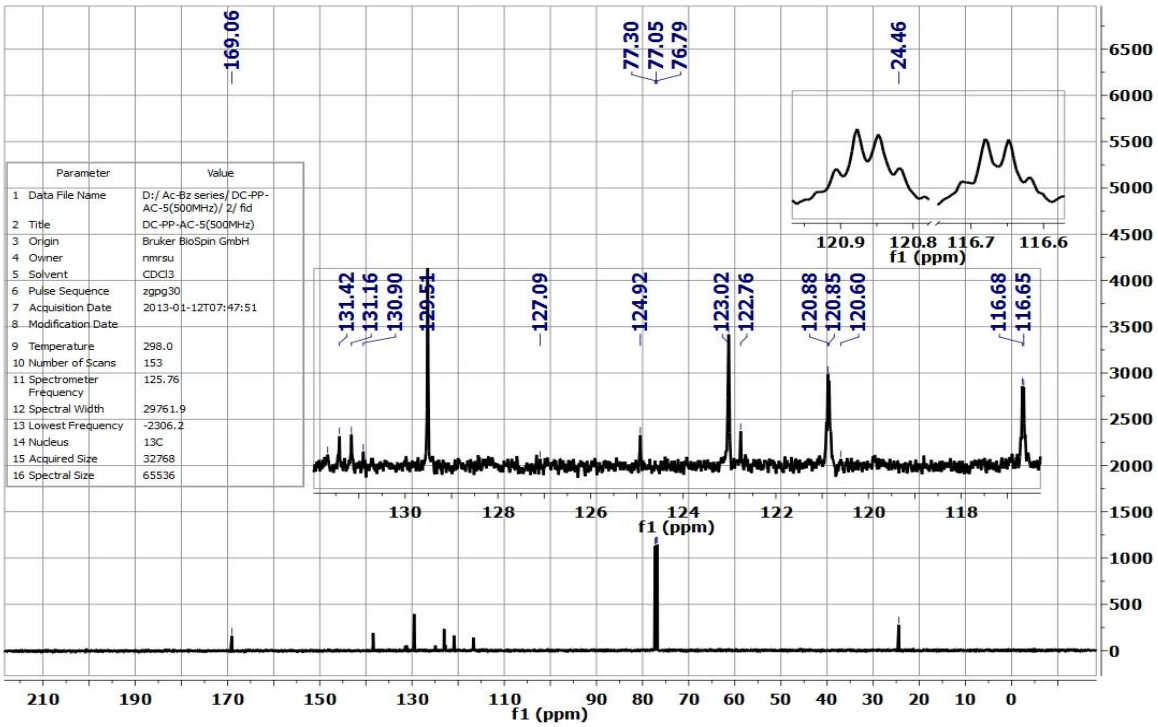
(d) AC-3: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.56, 159.40 (d, *J* = 244.32 Hz), 133.86 (d, *J* = 2.52Hz), 121.88 (d, *J* = 7.69 Hz), 115.61 (d, *J* = 22.51 Hz), 24.36.



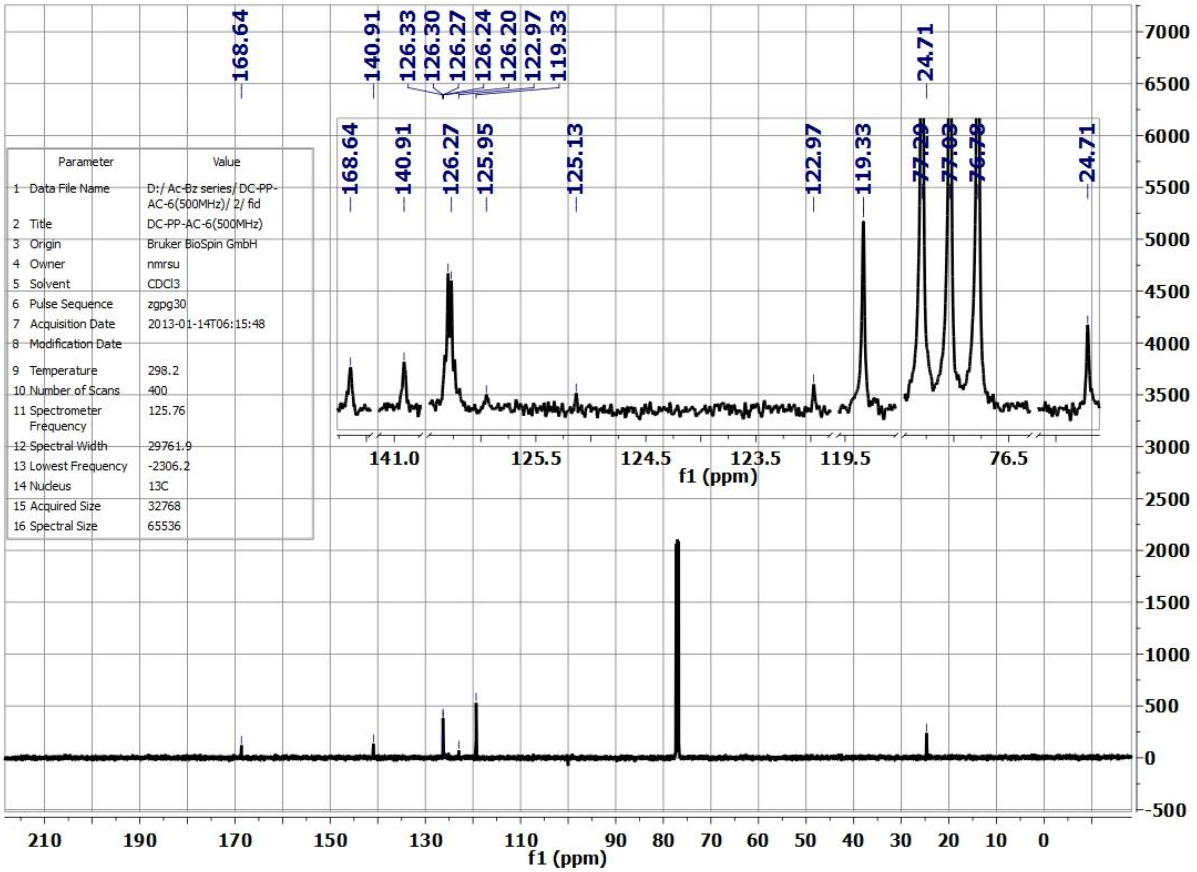
(e) AC-4: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.52, 135.18, 132.85, 126.03 (q, *J* = 4.87 Hz), 125.11, 124.74 (q, *J* = 33.21), 123.53 (q, *J* = 272.95 Hz), 120.54, 120.32, 24.57.



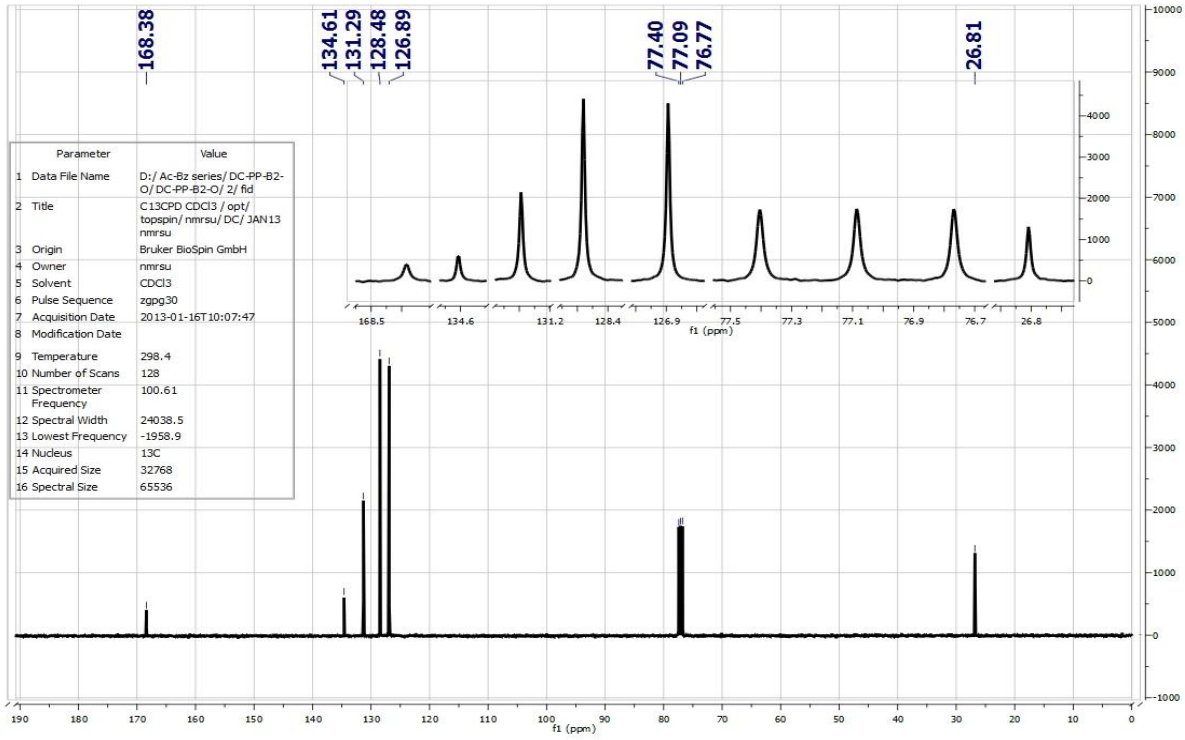
(f) AC-5^{f}: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 169.06, 138.44, 131.29 (q, *J* = 32.69 Hz), 129.51, 123.84 (q, *J* = 272.62 Hz), 123.02, 120.86 (q, *J* =3.69 Hz), 116.66 (q, *J* =3.90 Hz), 24.46.



(g) AC-6[l]: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.64, 140.91, 126.29 (q, *J* = 3.76), 125.95, 124.05 (q, *J* = 271.37 Hz), 119.33, 24.71.



(h) BZ-0[m]: ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 168.38, 134.61, 131.29, 128.48, 126.89, 26.81.



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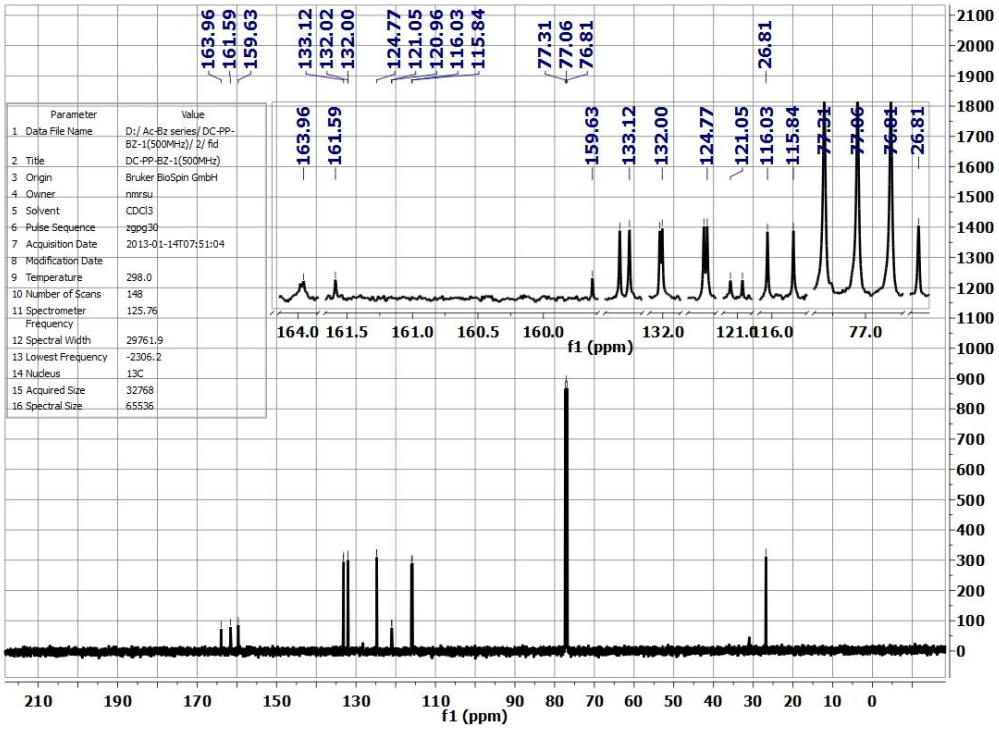
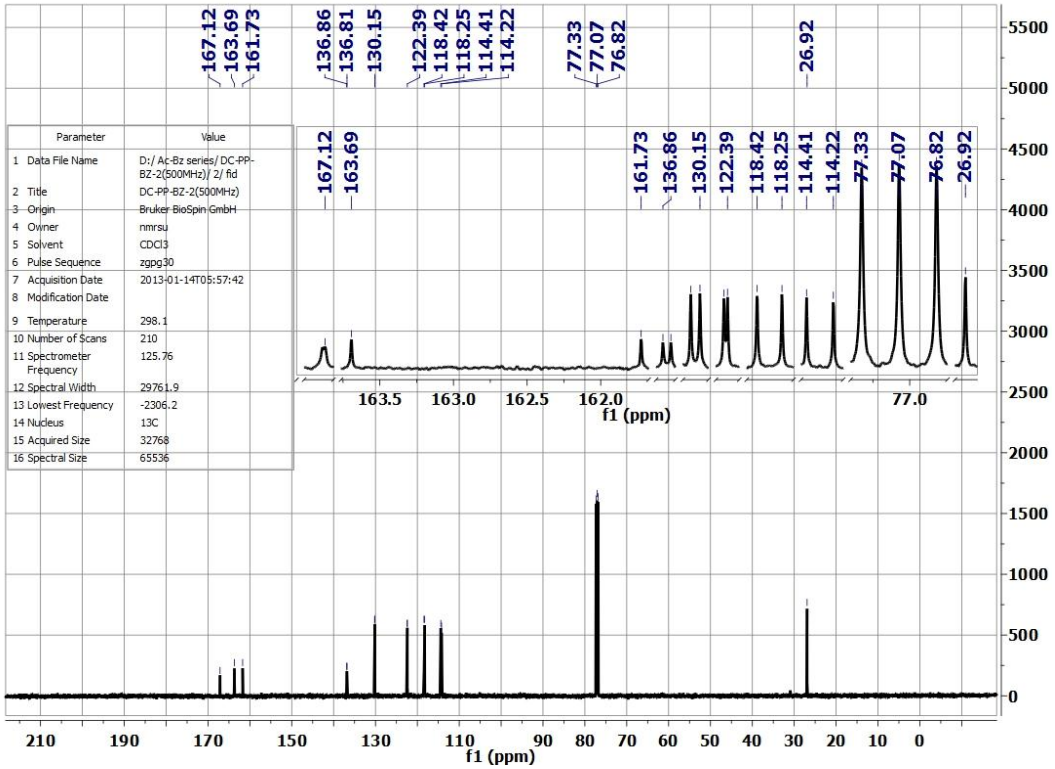
13 Lowest Frequency	-1958.9
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

(i) BZ-1^{n}: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 163.96, 161.61 (d, 246.47 Hz), 133.16 (d, 9.37 Hz), 132.01 (d, 2.37 Hz), 124.78 (d, 3.21 Hz), 115.94 (d, 24.91 Hz), 26.81.

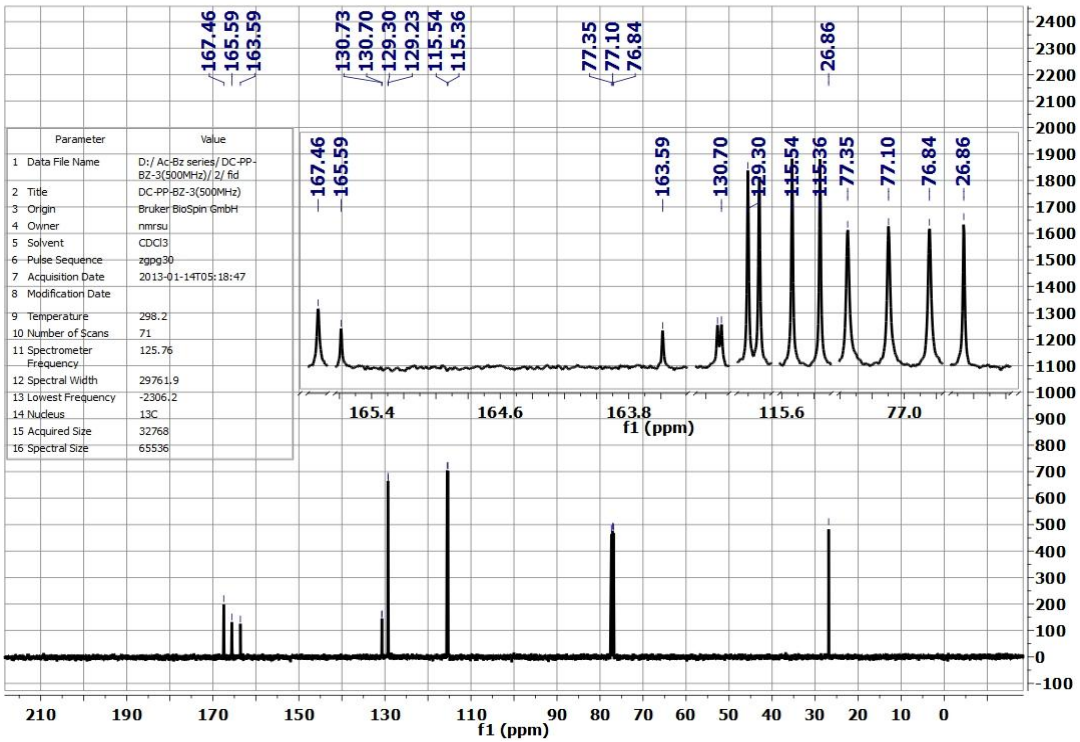


Parameter	Value
1 Data File Name	D:/ Ac-Bz series/ DC-PP-BZ-1(500MHz)/ 2/ fid
2 Title	DC-PP-BZ-1(500MHz)
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Solvent	CDCl3
6 Pulse Sequence	zgpg30
7 Acquisition Date	2013-01-14T07:51:04
8 Modification Date	
9 Temperature	298.0
10 Number of Scans	148
11 Spectrometer Frequency	125.76
12 Spectral Width	29761.9
13 Lowest Frequency	-2306.2
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

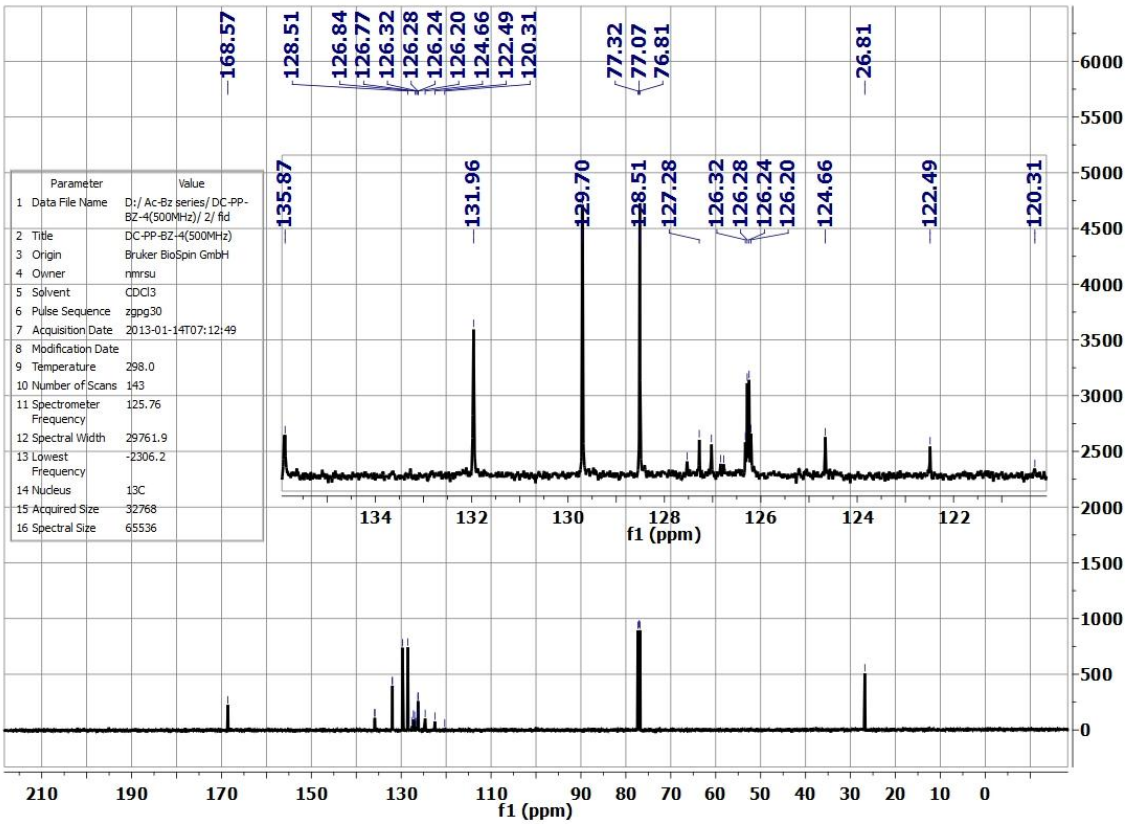
(j) BZ-2^{i}: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.12, 161.71 (d, 247.17 Hz), 136.83 (d, 6.83 Hz), 130.19 (d, 7.90 Hz), 122.41 (d, 3.06 Hz), 118.33 (d, 21.31 Hz), 114.32 (d, 22.79 Hz), 26.92.



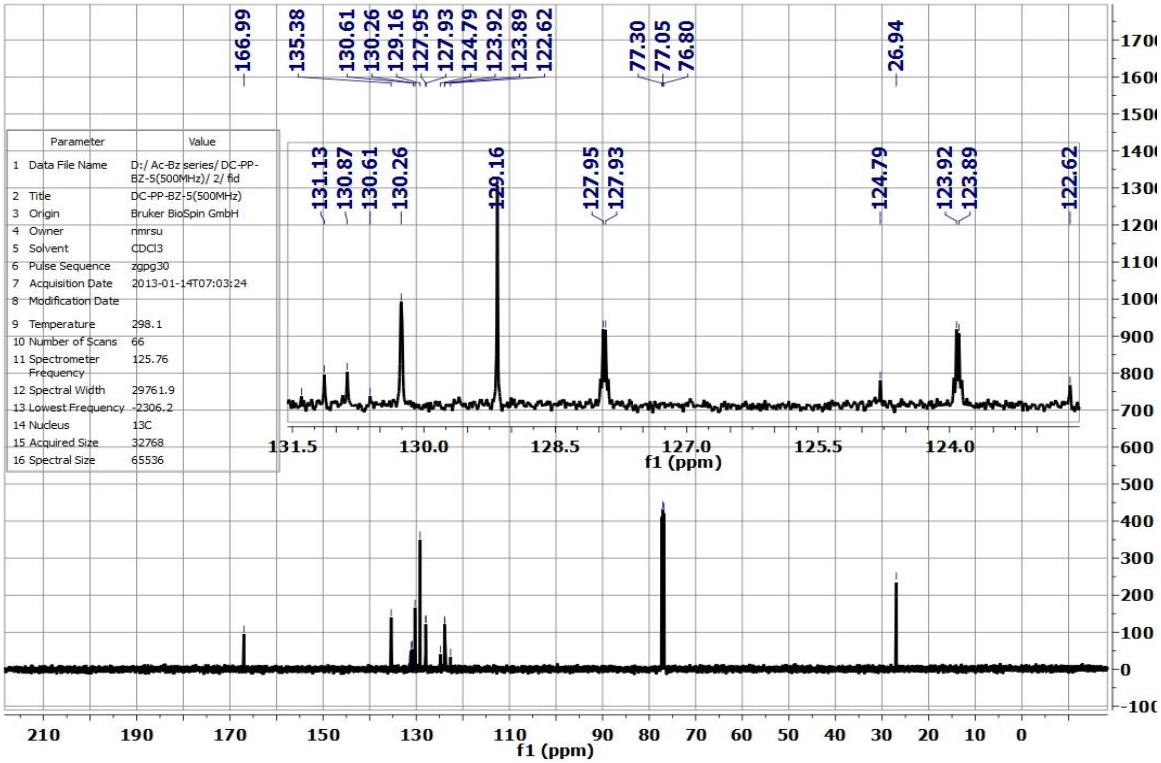
(k) BZ-3[i]: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.46, 165.59, 163.59, 130.73, 130.70, 129.30, 129.23, 115.54, 115.36, 26.86.



(l) BZ-4: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.57, 135.87, 137.96, 129.10 (d, 149.47 Hz), 127.15 (q, 32.02 Hz), 126.26 (q, 4.93 Hz), 124.66, 122.49, 26.81.



(m) BZ-5[i]: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.99, 135.38, 131.00 (d, *J* = 33.16 Hz), 130.26, 129.16, 127.94 (q, *J* = 3.65 Hz), 123.91 (q, *J* = 3.75 Hz), 123.71 (q, *J* = 272.75 Hz), 26.94.



(n) BZ-6: ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.04, 137.86, 133.12 (d, *J* = 32.38 Hz), 127.35, 125.61 (q, *J* = 3.75 Hz), 123.66 (q, *J* = 273.94Hz), 26.98.

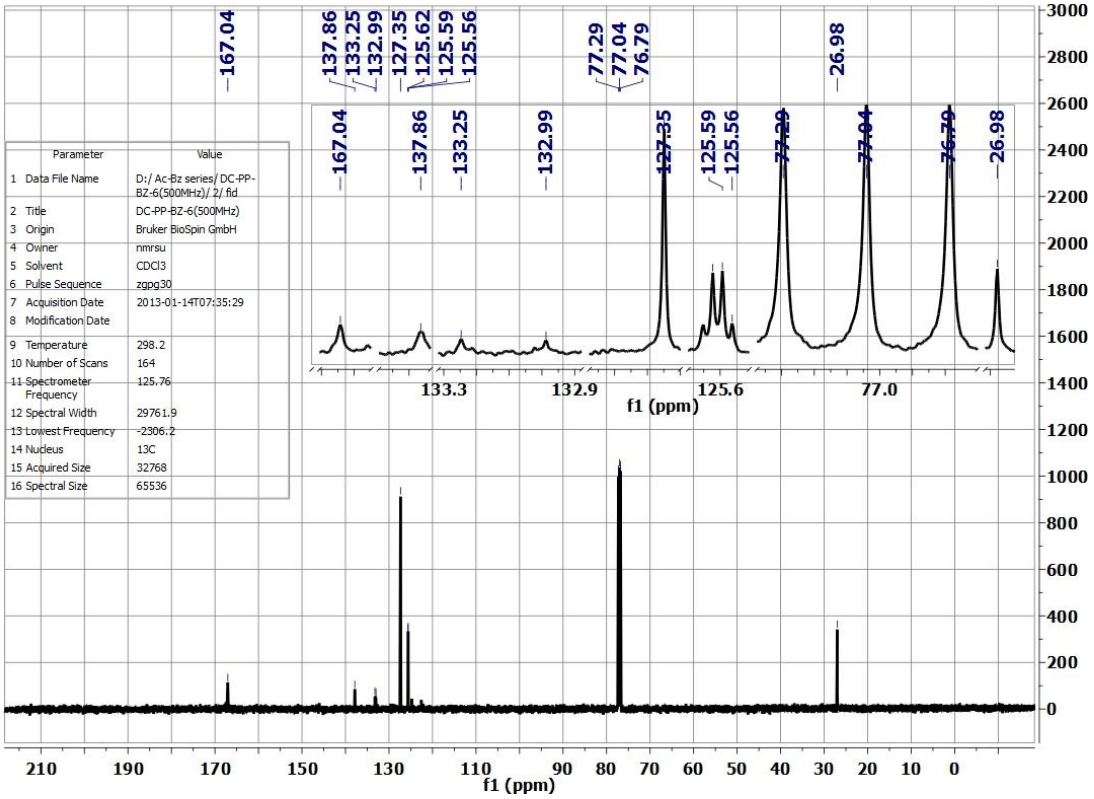
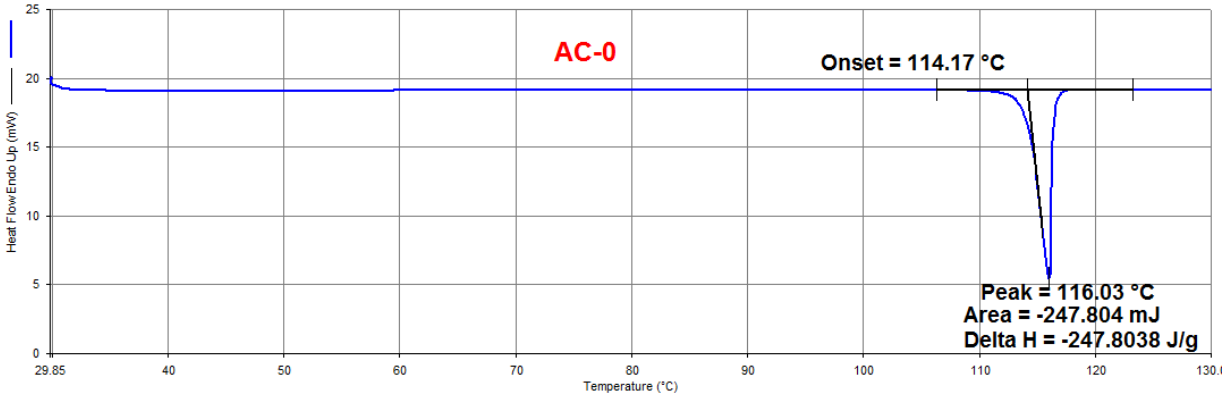
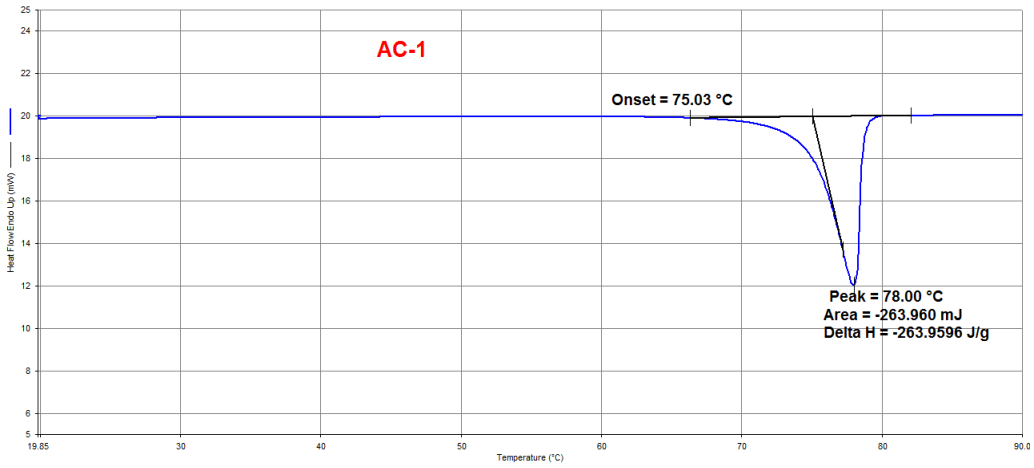


Figure S4: DSC curves of solids (@ 5°C/min) recorded on Perkin Elmer DSC 6000.

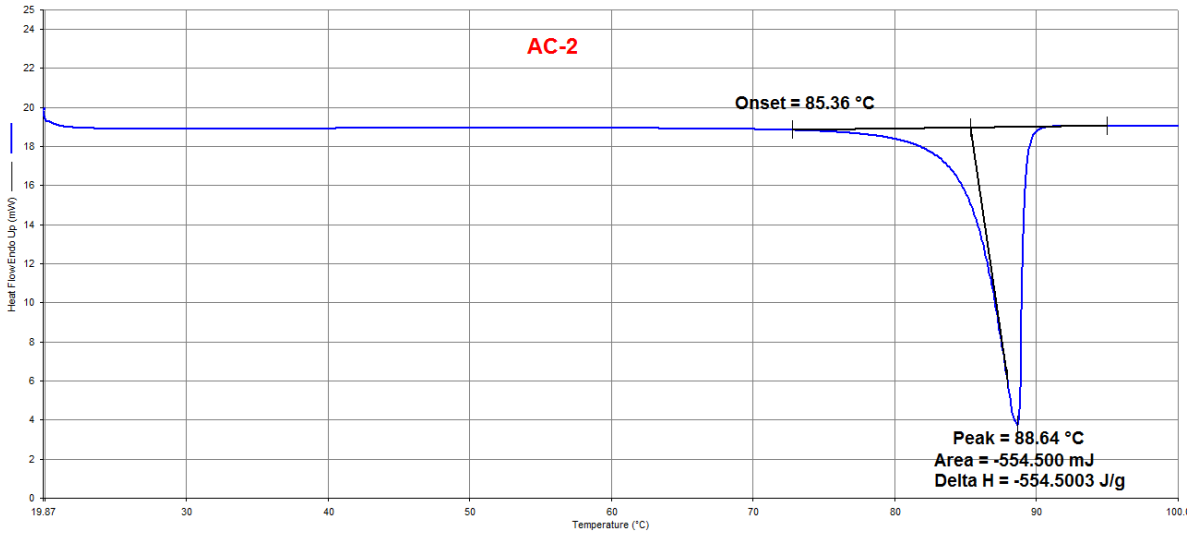
(a) AC-0:



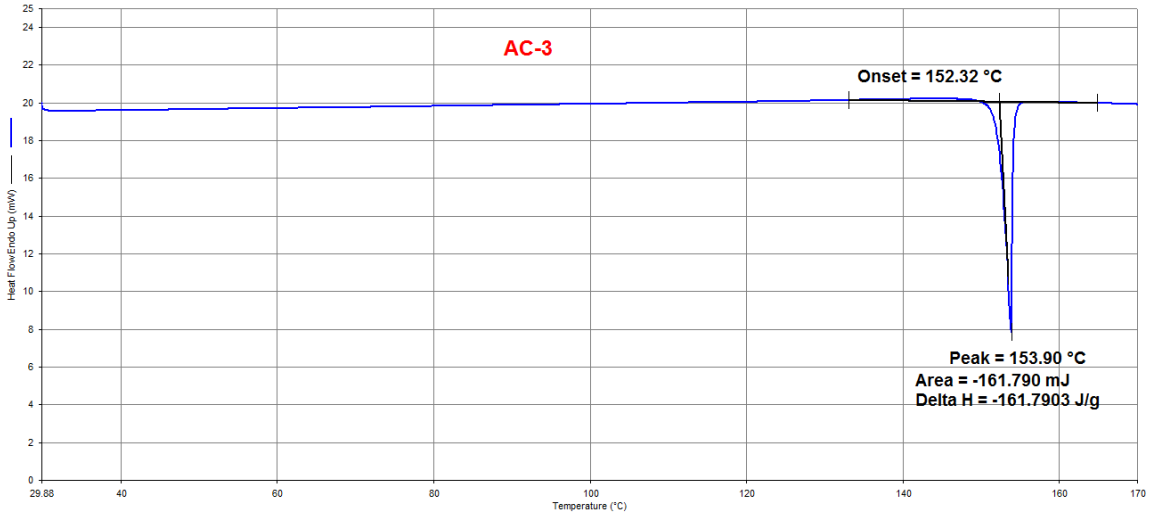
(b)AC-1:

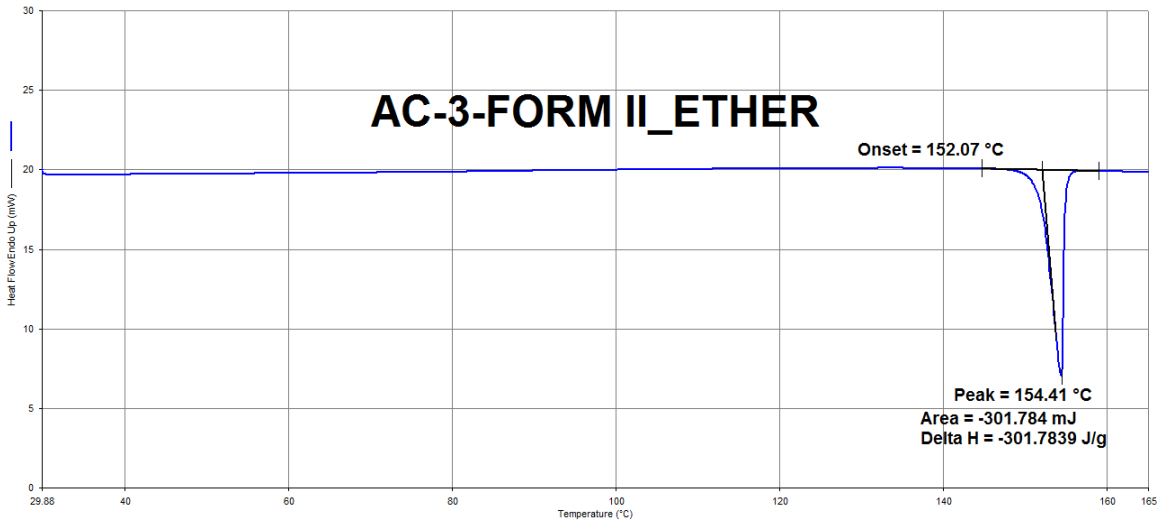


(c) AC-2:

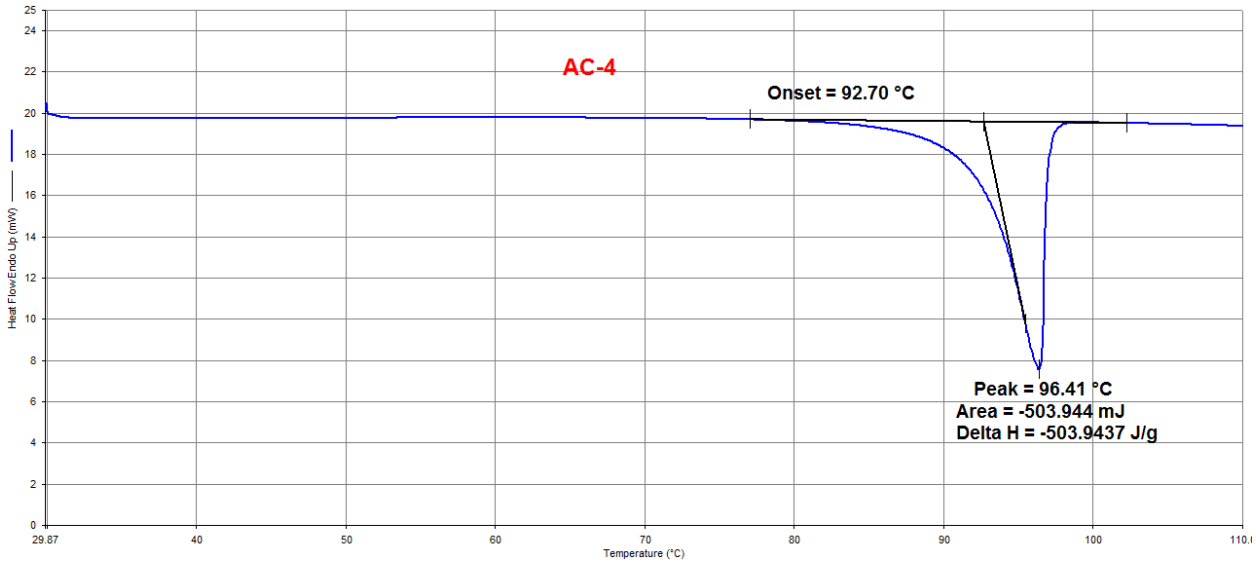


(d) AC-3_Bulk powder:

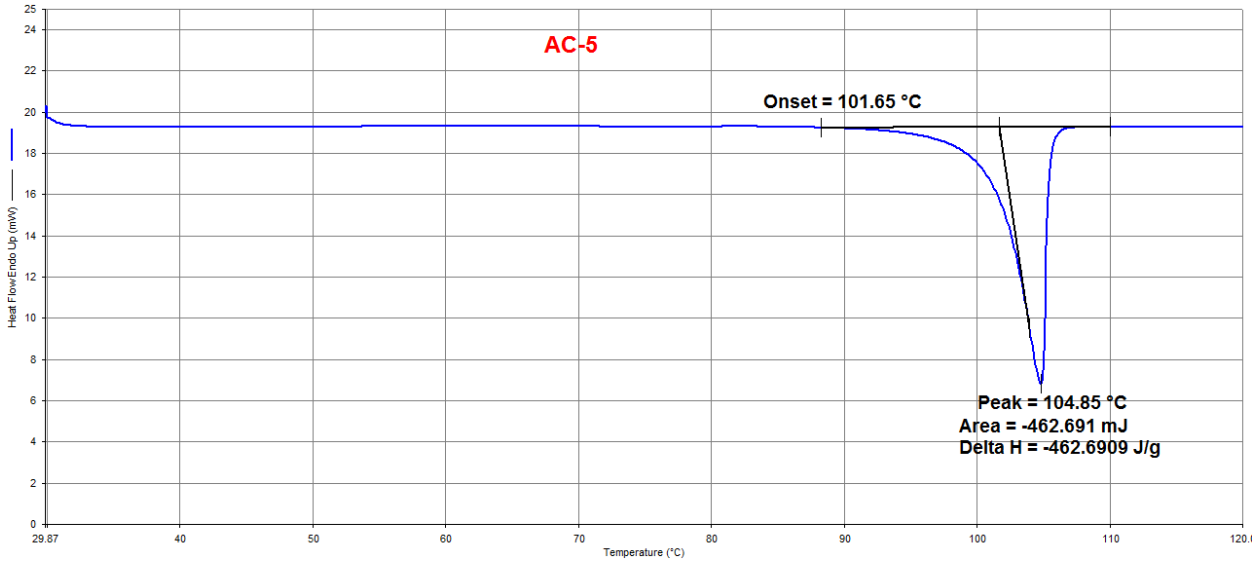




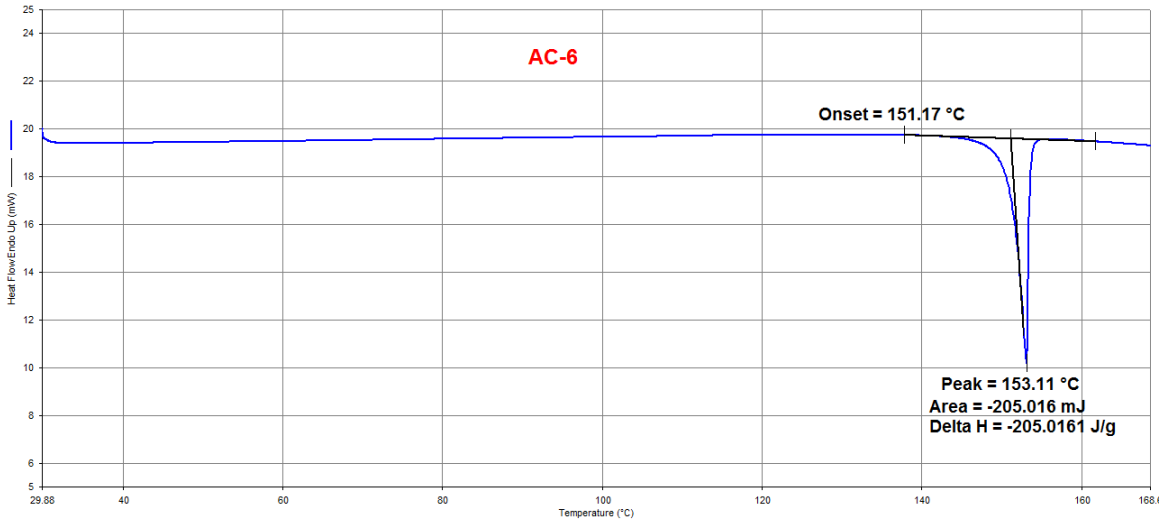
(e) AC-4:



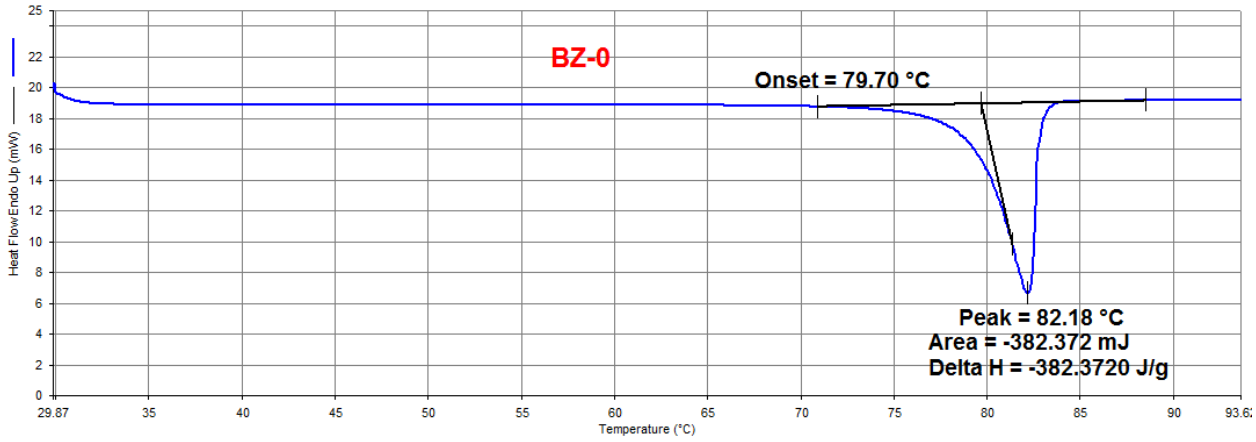
(f) AC-5:



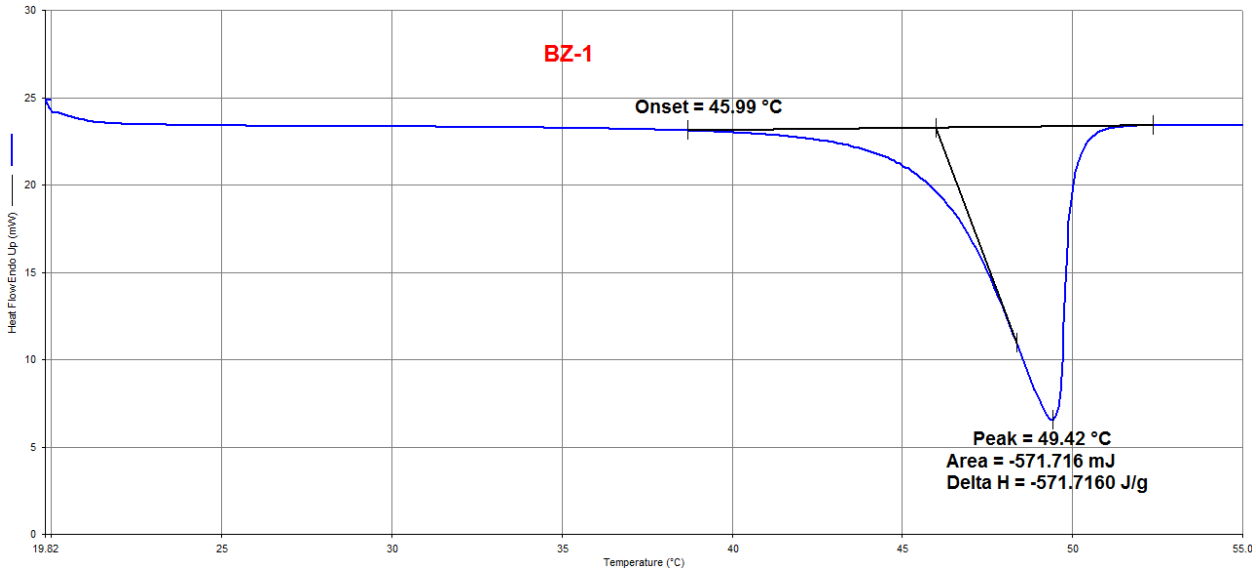
(g) AC-6:



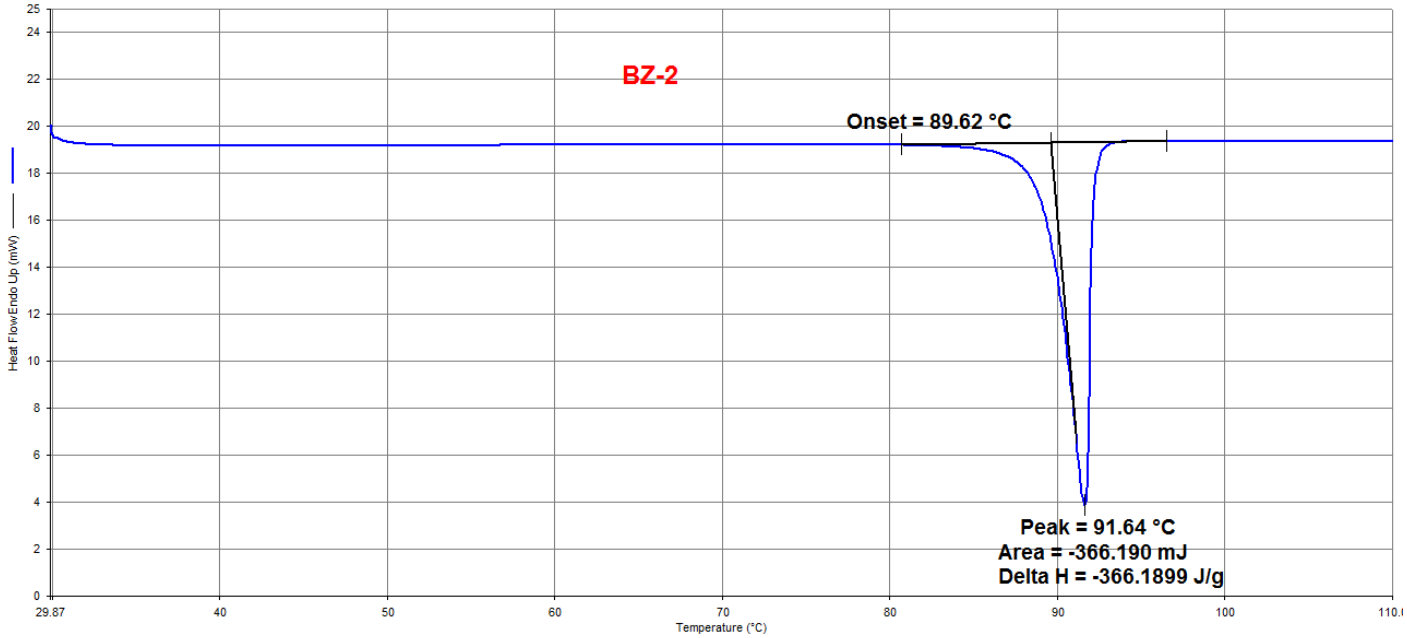
(h) BZ-0:



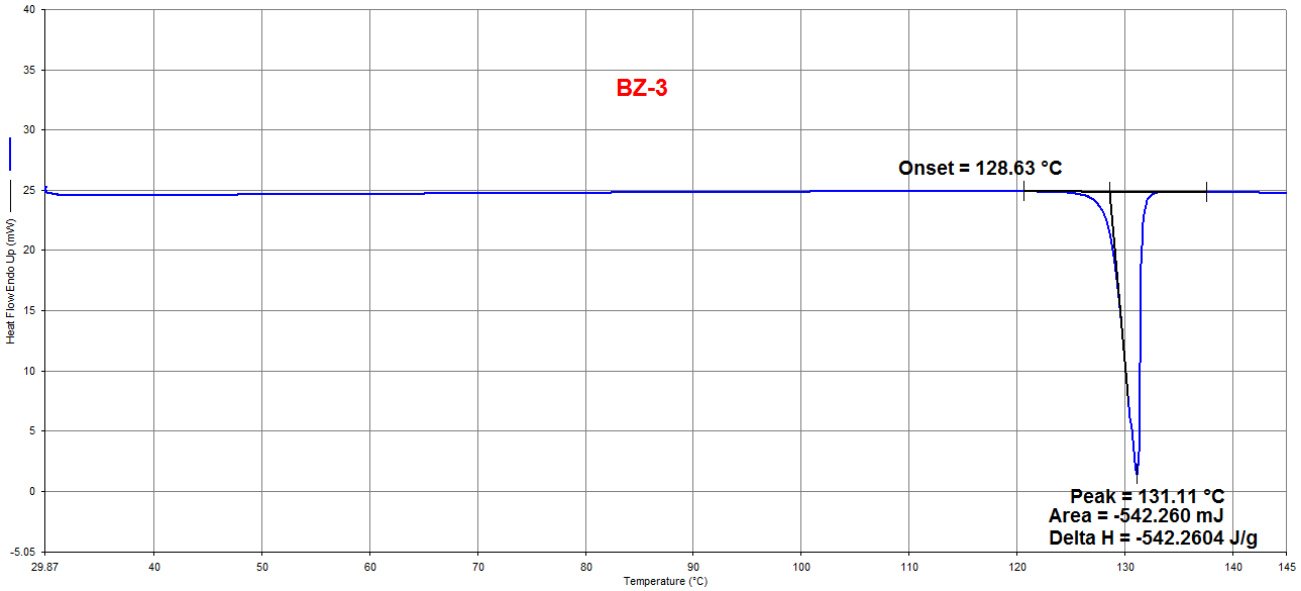
(i) BZ-1:



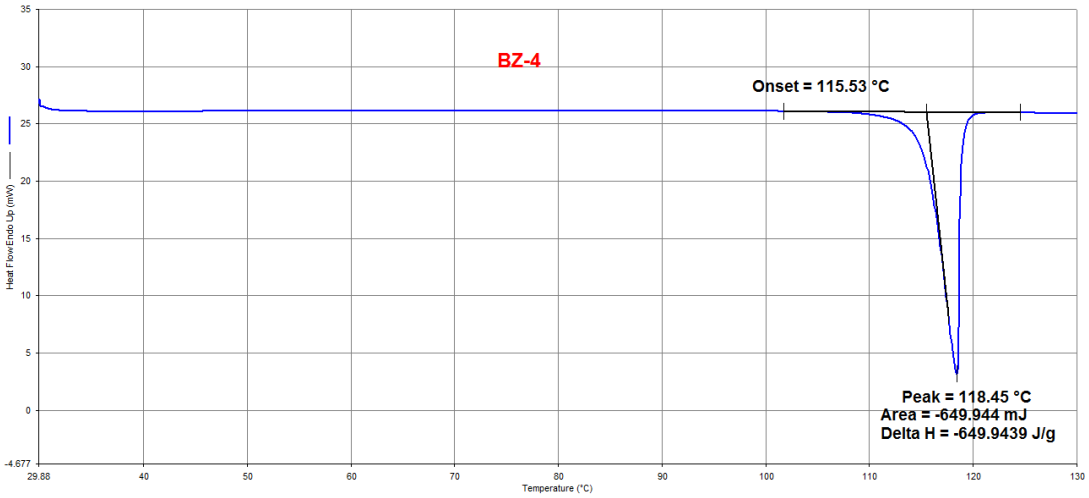
(j) BZ-2:



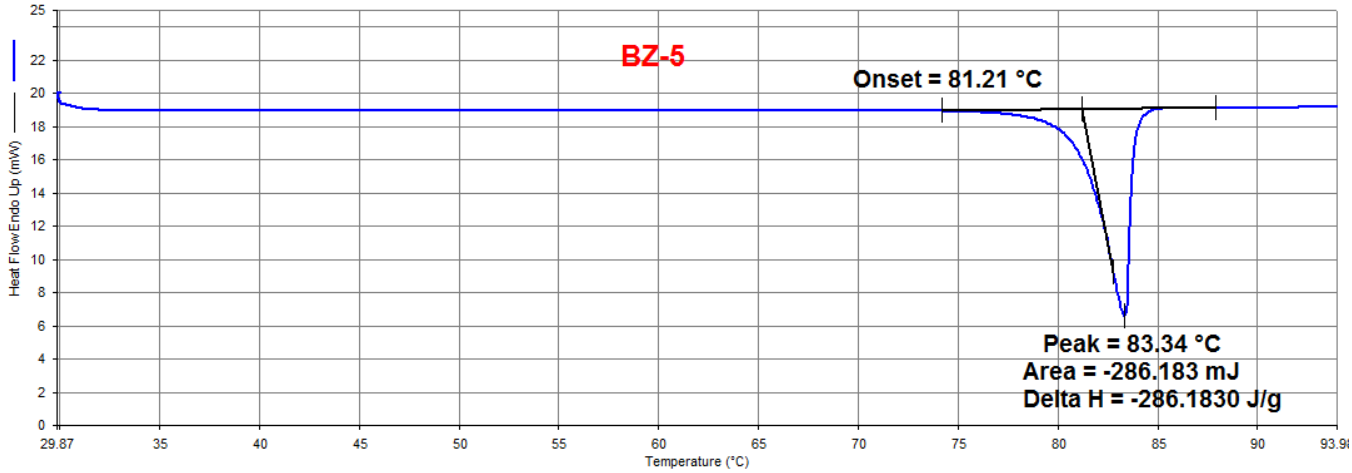
(k) BZ-3:



(l) BZ-4:



(m) BZ-5:



(n) BZ-6:

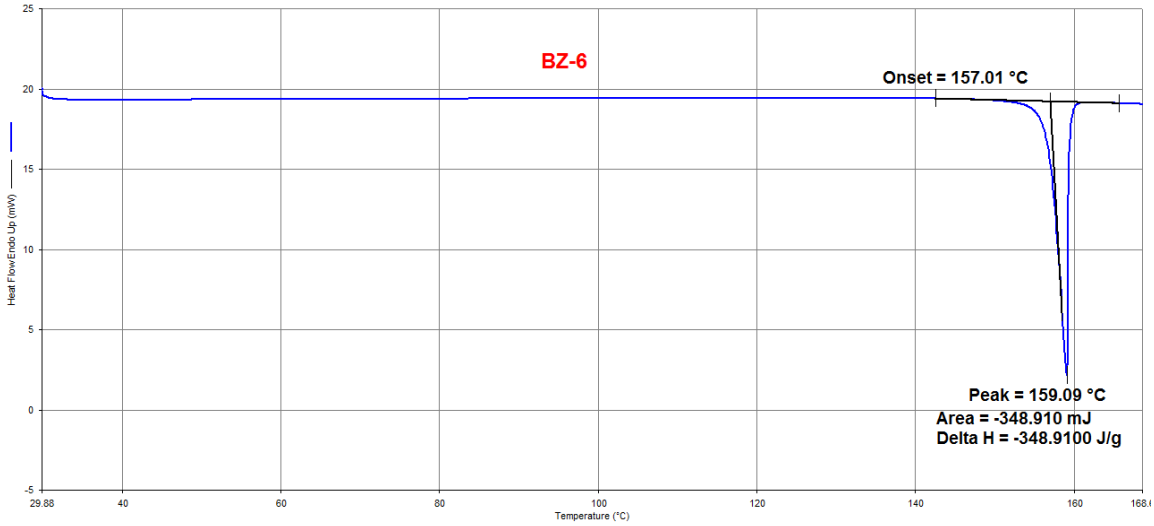
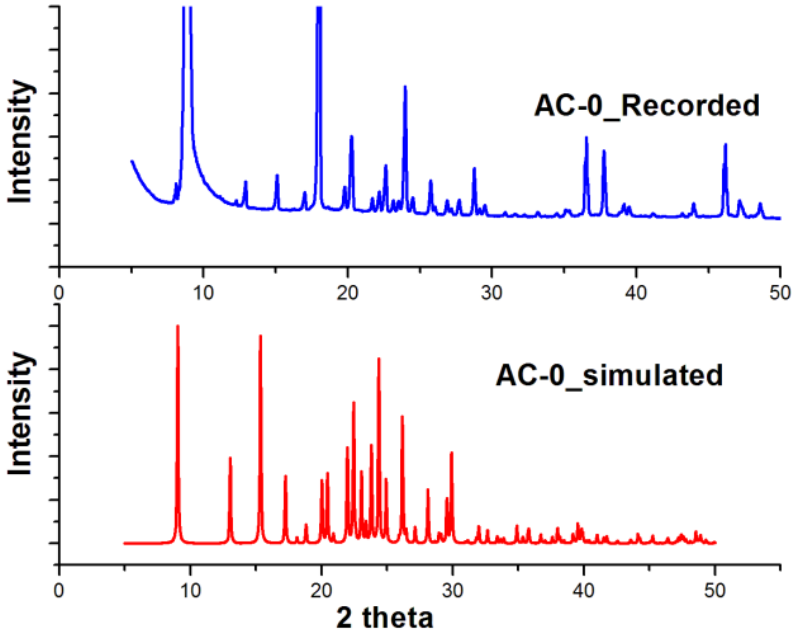
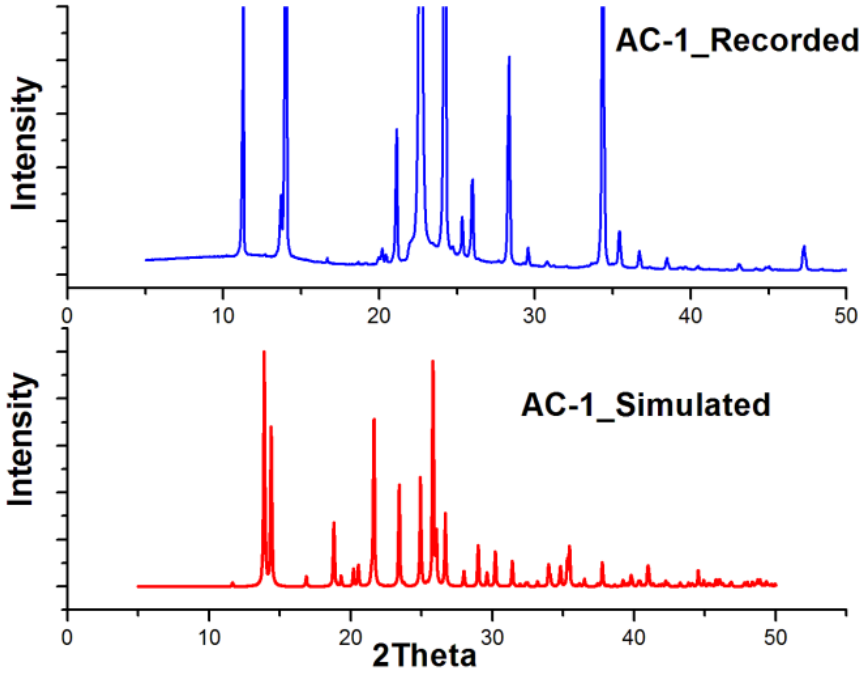


Figure S5: Powder X-ray Data for all solid compounds (recorded on Empyrean, Pan Analytical):

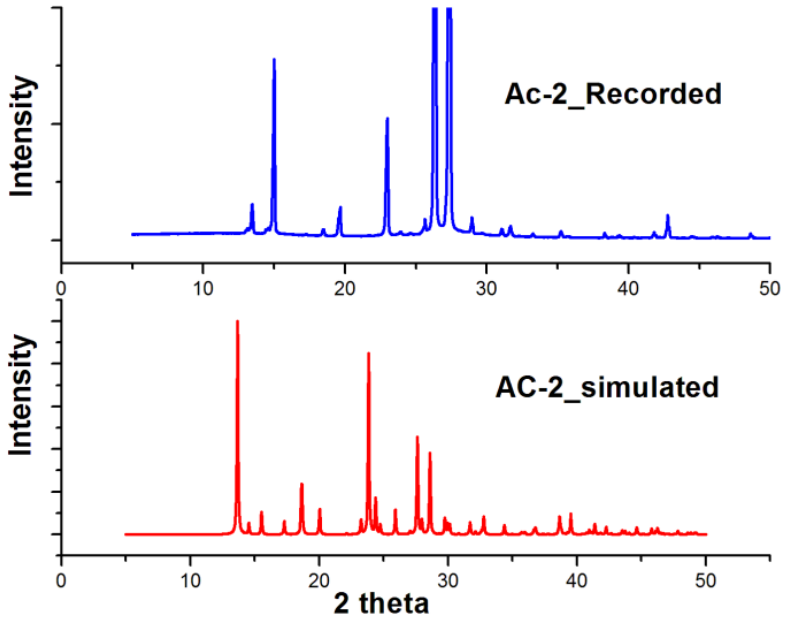
(a) AC-0:



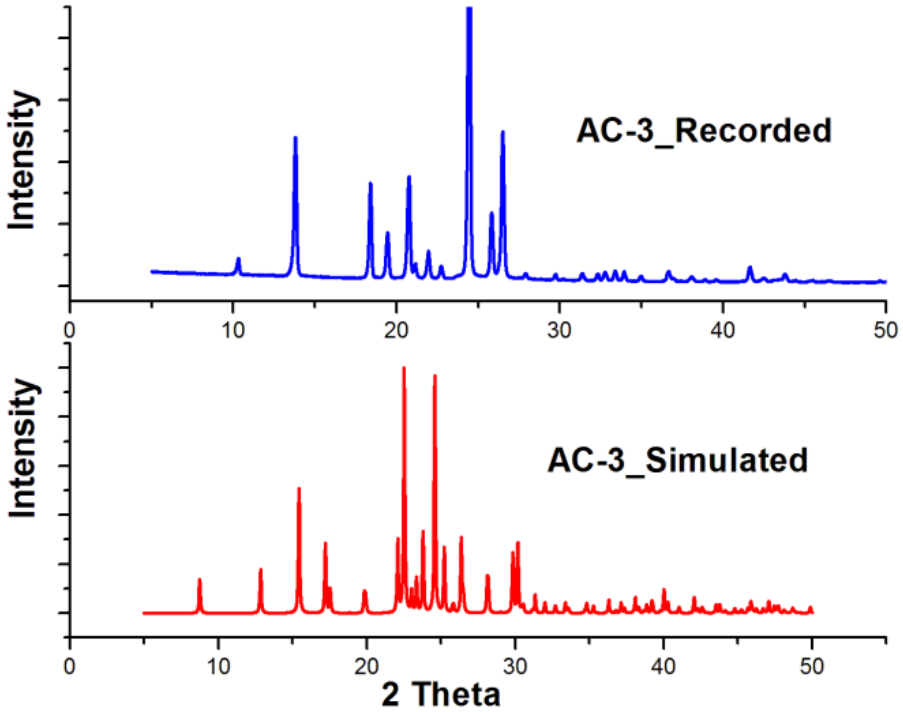
(b) AC-1:



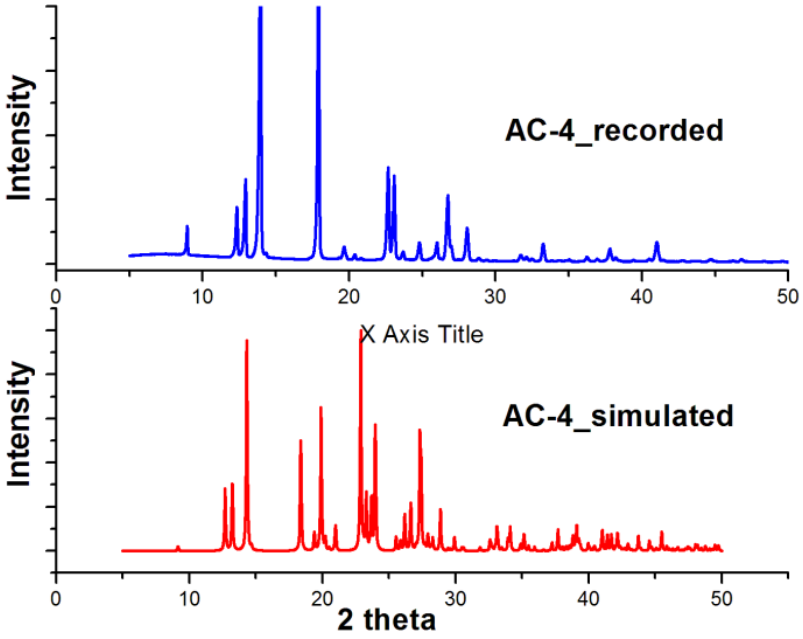
(c) AC-2:



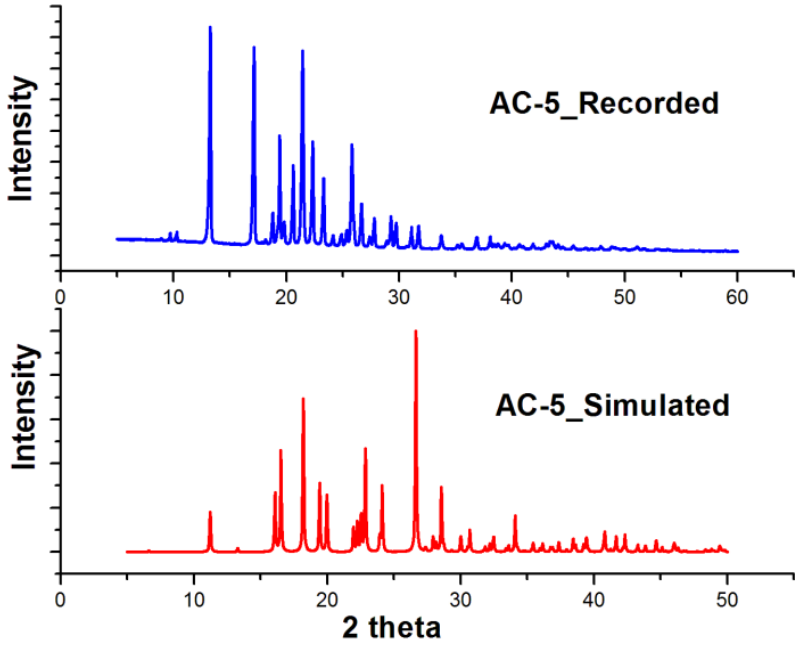
(d) AC-3:



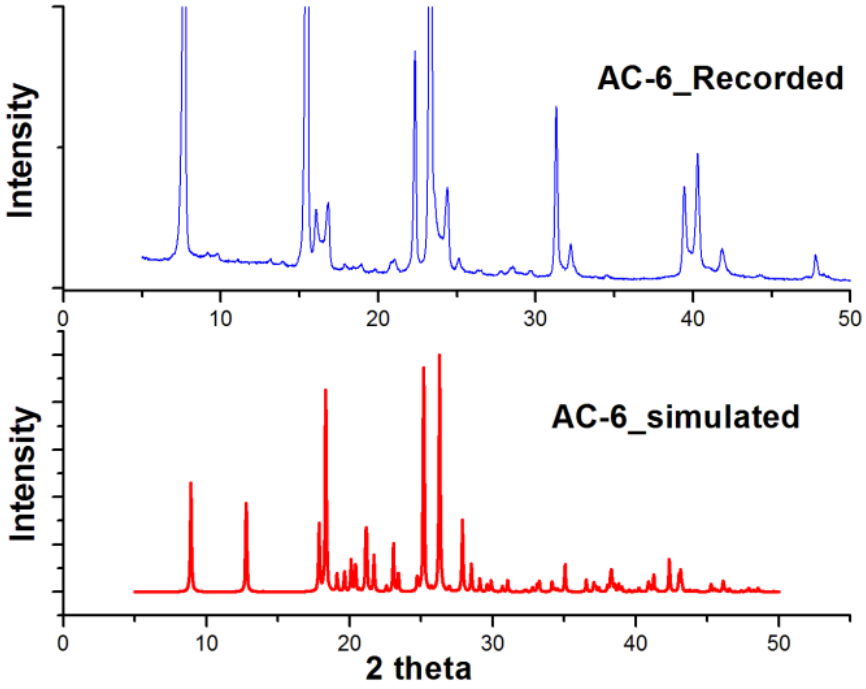
(e) AC-4:



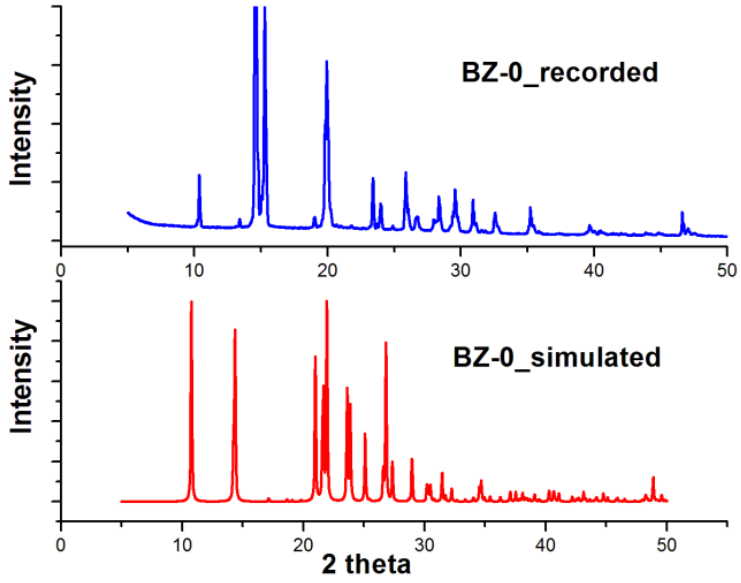
(f) AC-5:



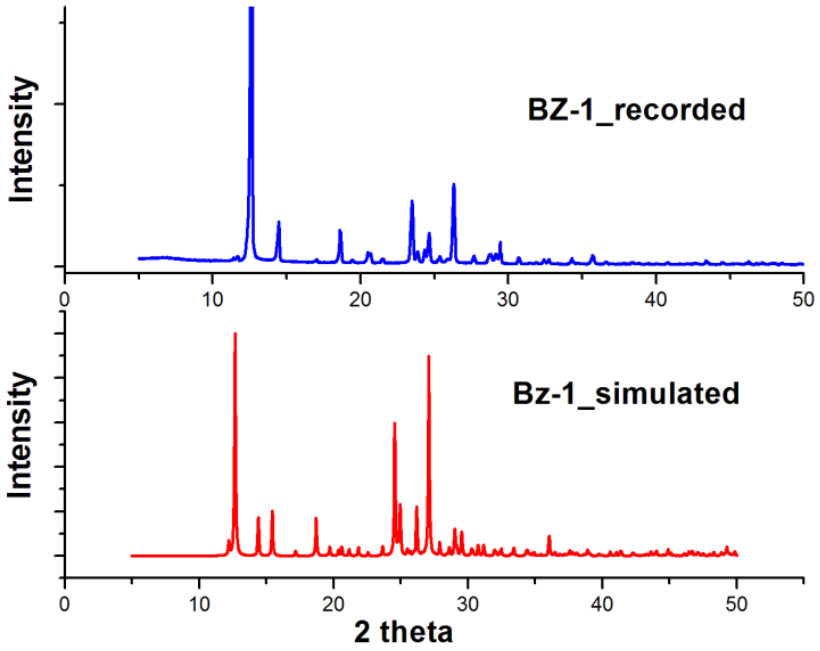
(g) AC-6:



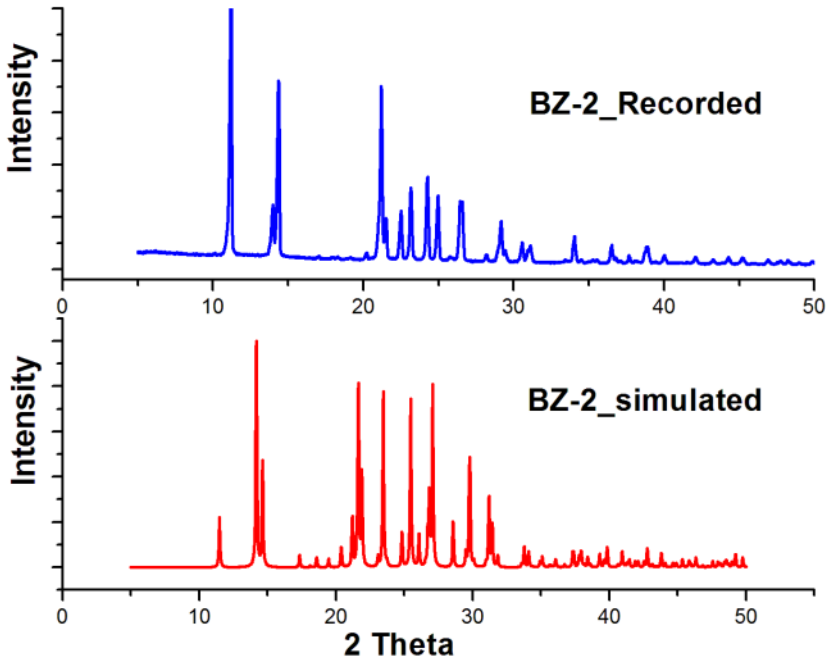
(h) BZ-0:



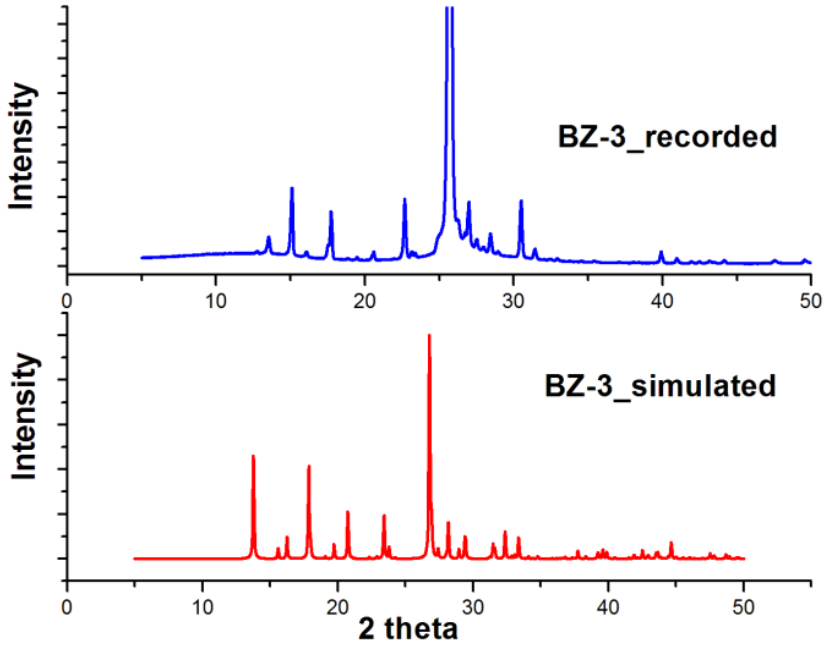
(i) BZ-1:



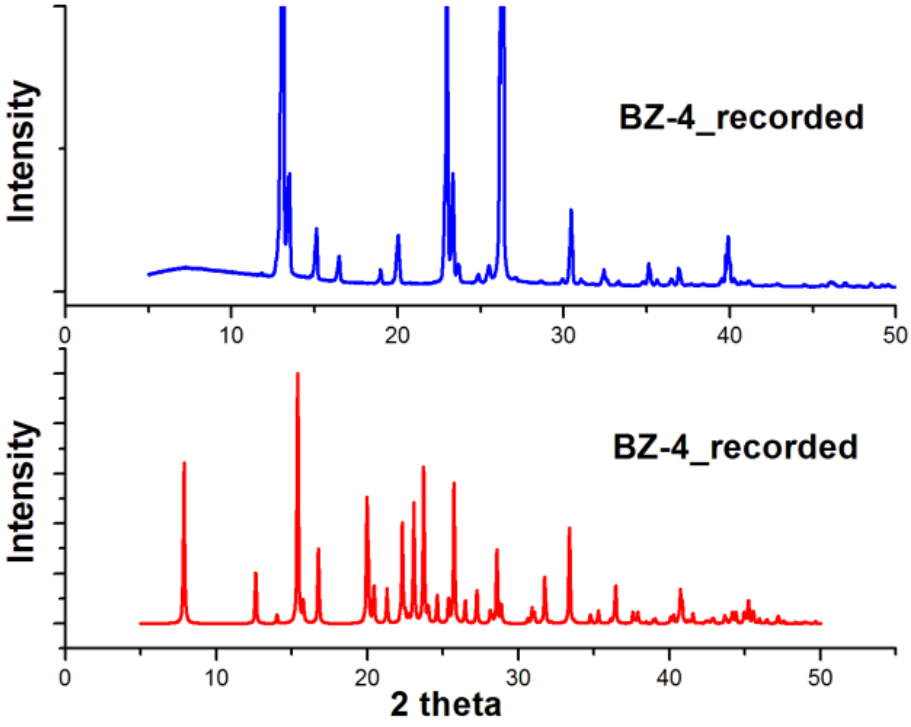
(j) BZ-2:



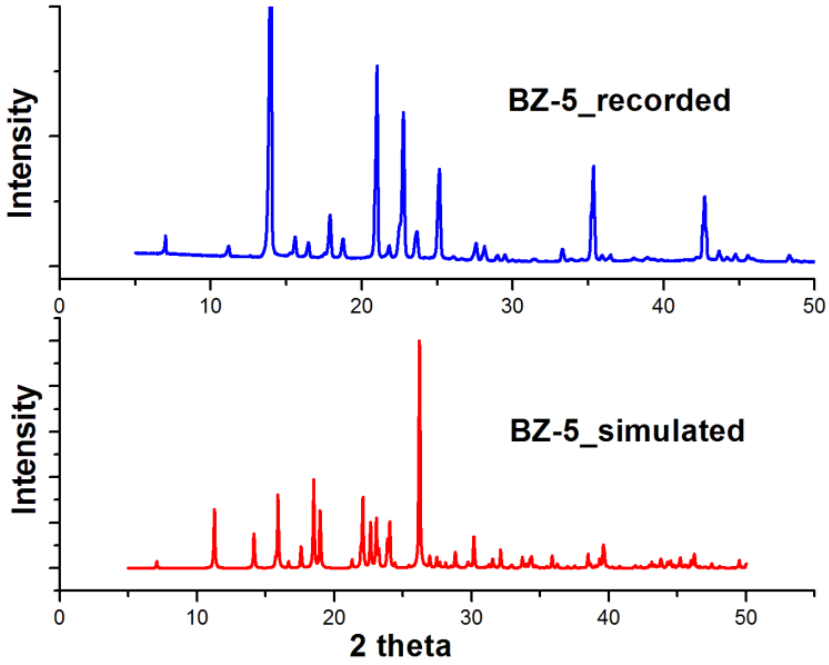
(k) BZ-3:



(l) BZ-4:



(m) BZ-5:



(n) BZ-6:

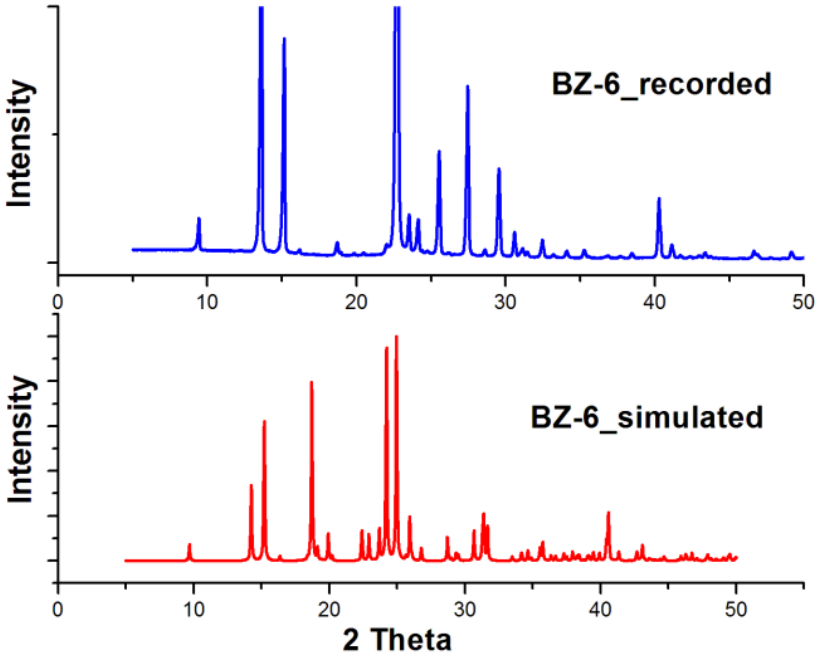
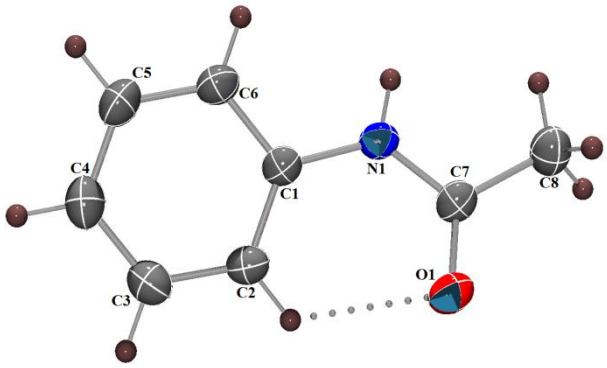
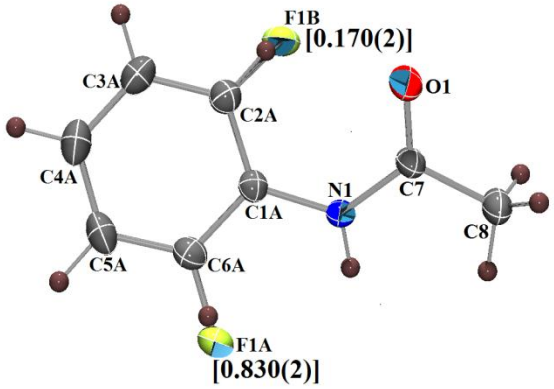


Figure S6: *ORTEP* of all compounds drawn with 50% ellipsoidal probability with atom-numbering scheme.

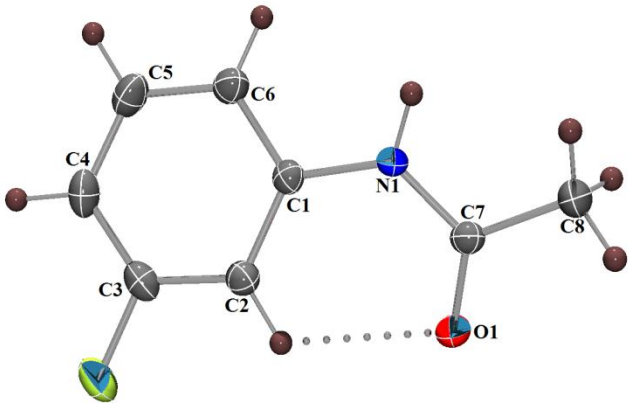
(a) AC-0:



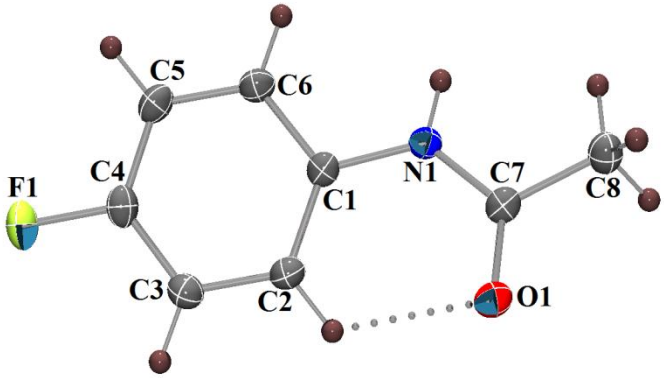
(b) AC-1:



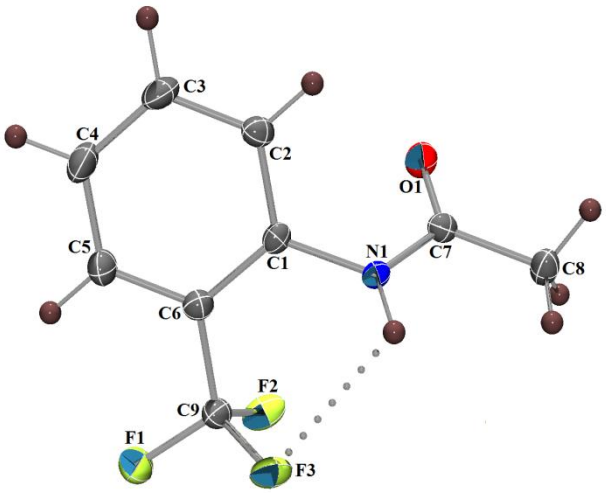
(c) AC-2:



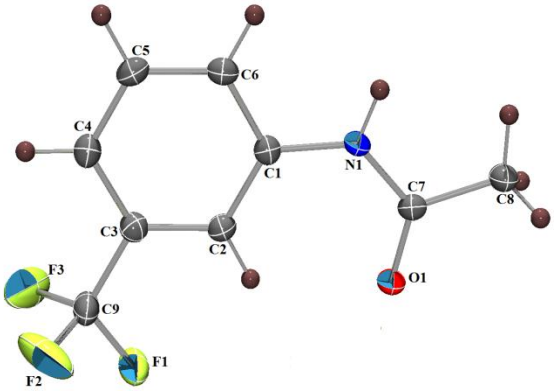
(d) AC-3:



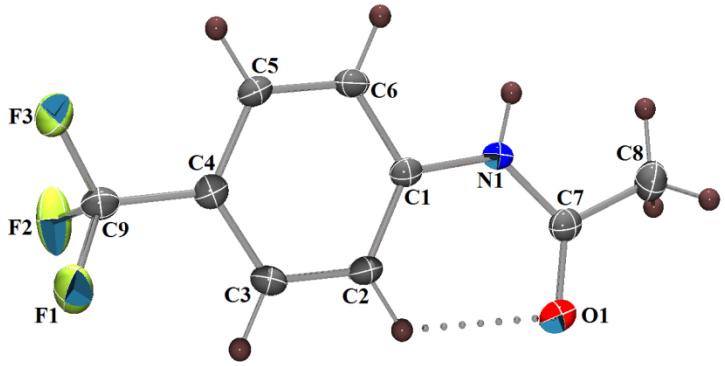
(e) AC-4:



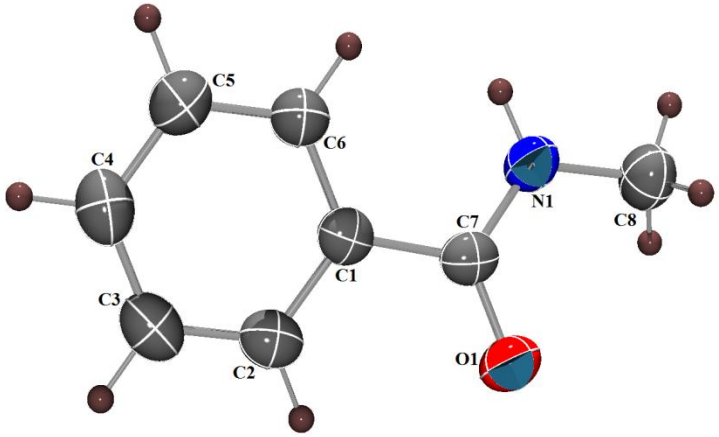
(f) AC-5:



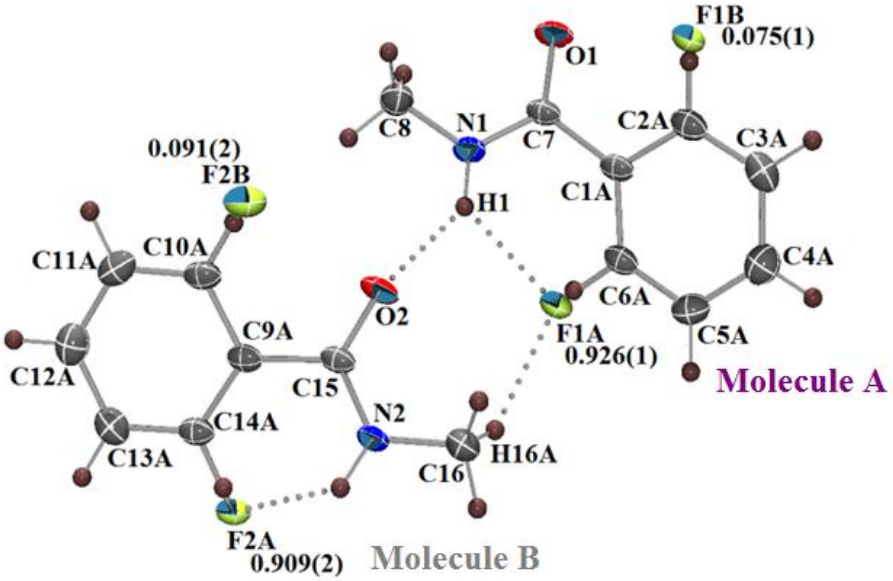
(g) AC-6:



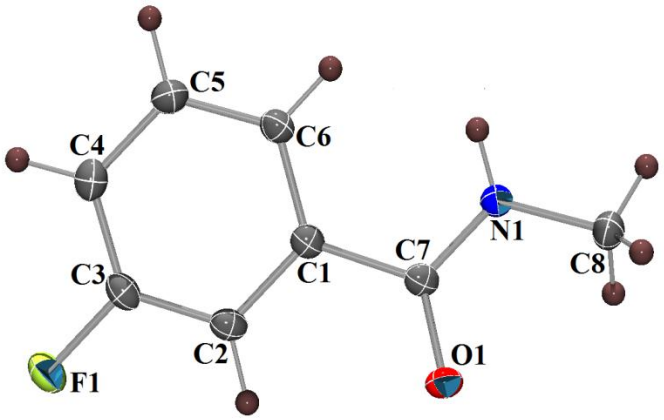
(h) BZ-0:



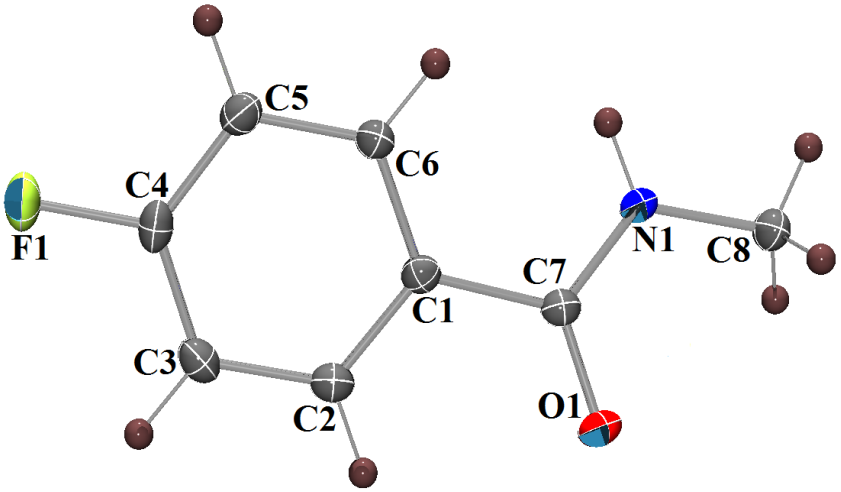
(i) BZ-1:



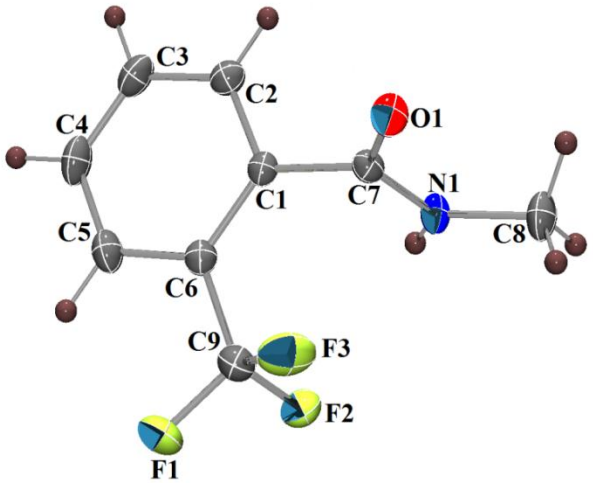
(j) BZ-2:



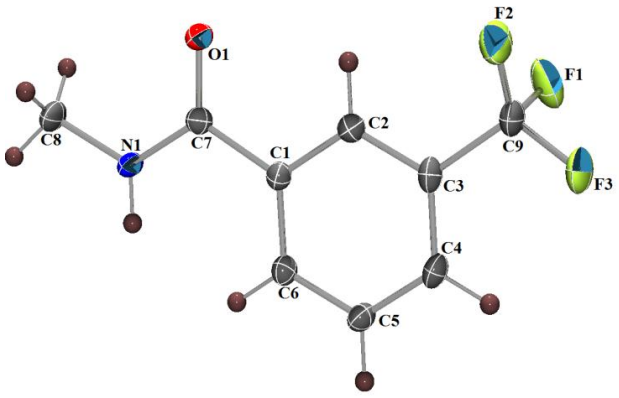
(k) BZ-3:



(l) BZ-4:



(m) BZ-5:



(n) BZ-6:

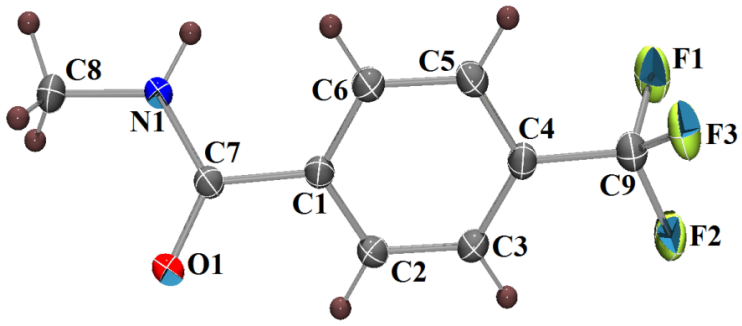


Table S2: **Intra- and intermolecular Interactions:** Cg1 refers to the center of gravity of the ring formed by C1-C6.

	D-H···A	D-H(Å)	D···A (Å)	H···A (Å)	∠D-H···A(°)	SYMMETRY CODE
AC-0(*Pbca*)	C2-H2···O1	1.08	2.865(1)	2.25	114	x, y, z
	N1-H1···O1	1.03	2.925(1)	1.91	167	x-1/2, -y+1/2, -z+1
	C6-H6···O1	1.08	3.407(1)	2.55	135	x-1/2, -y+1/2, -z+1
	C8-H8B···O1	1.08	3.733(1)	2.83	141	x-1/2, -y+1/2, -z+1
	C8-H8A···O1	1.08	3.448(2)	2.54	141	-x+3/2, y+1/2, z
	C3-H3···Cg1	1.08	3.623(1)	2.82	143	-x+3/2, y+1/2, z
	C8-H8C··· Cg1	1.08	3.615(1)	3.00	122	-x+1, -y, -z+1
AC-1(*Pbca*)	N1-H1···O1	1.03	2.850(1)	1.83	170	-x+3/2, y+1/2, z
	C8-H8B···O1	1.08	3.282(2)	2.33	146	-x+3/2, y+1/2, z
	C5A-H5A···O1	1.08	3.534(2)	2.56	150	-x+2, y+1/2, -z+3/2
	C3A-H3A···O1	1.08	3.706(2)	2.90	132	x+1/2, -y+3/2, -z+1
	C5A-H5A···F1A	1.08	3.505(2)	2.78	125	x+1/2, y, -z+3/2
	C4A-H4A···F1A	1.08	3.541(2)	2.85	122	x+1/2, y, -z+3/2
	C8-H8C···F1A	1.08	3.373(2)	2.46	142	-x+3/2, y-1/2, z
AC-2(*Pbca*)	C2-H2···O1	1.08	2.850(2)	2.21	115	x, y, z
	N1-H1···O1	1.03	2.828(1)	1.81	168	-x+3/2, y-1/2, z
	C8-H8B···O1	1.08	3.339(2)	2.61	124	-x+3/2, y-1/2, z

	C5-H5···O1	1.08	3.634(2)	2.81	133	-x+1, y-1/2, -z+3/2
	C6-H6···F1	1.08	3.402(2)	2.84	113	-x+1, y-1/2, -z+3/2
	C5-H5···F1	1.08	3.268(2)	2.64	116	-x+1/2, y-1/2, z
	C8-H8A···F1	1.08	3.709(2)	2.77	145	x+1/2, -y+1/2, -z+1
AC-3Form II(*Pbca*)	**C2-H2···O1**	1.08	2.850(1)	2.23	114	x, y, z
	N1-H1···O1	1.03	2.896(1)	1.89	166	x+1/2, -y+3/2, -z
	C6-H6···O1	1.08	3.413(1)	2.57	135	x+1/2, -y+3/2, -z
	C8-H8A···O1	1.08	3.442(1)	2.55	140	-x+1/2, y-1/2, z
	C6-H6···F1	1.08	3.126(1)	2.56	112	-x+1, y-1/2, -z+1/2
	C5-H5···F1	1.08	3.193(1)	2.72	106	-x+1, y-1/2, -z+1/2
	C8-H8A···F1	1.08	3.344(1)	2.73	116	x, -y+3/2, z-1/2
	C3-H3···Cg1	1.08	3.509(1)	2.76	137	-x+1/2, y+1/2, z
AC-4($P2_1/n$)	**N1-H1···F3**	1.03	2.879(1)	2.38	109	x, y, z
	N1-H1···O1	1.03	2.892(1)	1.92	156	x-1, y, z
	C8-H8B···O1	1.08	3.248(2)	2.27	150	x-1, y, z
	C3-H3···O1	1.08	3.461(2)	2.52	145	-x+1,-y+2,-z
	C3-H3···F2	1.08	3.413(2)	2.74	120	x+1/2, -y+3/2, z-1/2
	C4-H4···F2	1.08	3.385(2)	2.67	123	x+1/2, -y+3/2, z-1/2
	C8-H8A···F1	1.08	3.875(2)	2.86	157	x+1/2, -y+3/2, z+1/2
	C8-H8C···F3	1.08	3.408(2)	2.52	131	-x+1/2, y+1/2, -z+1/2
	C8-H8C···F2	1.08	3.630(2)	2.83	131	-x-1/2, y+1/2, -z+1/2
	C9-F3···Cg1	1.339(2)	4.072(2)	3.220(1)	121(1)	x+1, y, z
AC-5($P2_1/c$)	**C2-H2···O1**	1.08	2.881(2)	2.21	118	x, y, z
	N1-H1···O1	1.03	2.938(2)	1.91	176	-x, y-1/2, -z+1/2
	C8-H8B···O1	1.08	3.403(2)	2.43	150	-x, y-1/2, -z+1/2
	C8-H8A···O1	1.08	3.472(2)	2.68	130	-x, -y+2, -z+1
	C4-H4···F3	1.08	3.612(3)	2.76	136	-x+1,-y+2,-z
	C4-H4···F2	1.08	3.543(3)	2.83	124	-x+1, y-1/2, -z+1/2
	Cg1···Cg1	-	-	3.742(1)	-	x, -y+3/2, z-1/2
AC-6(*Pbca*)	**C2-H2···O1**	1.08	2.869(2)	2.20	118	x, y, z
	N1-H1···O1	1.03	2.853(2)	1.86	161	x-1/2, y, -z+1/2
	C8-H8C···O1	1.08	3.501(2)	2.58	143	x-1/2, y, -z+1/2
	C6-H6···O1	1.08	3.461(2)	2.63	133	x-1/2, y, -z+1/2
	C3-H3···F1	1.08	3.482(2)	2.52	149	-x+2, -y+2, -z+1
	C5-H5···F3	1.08	3.464(2)	2.44	158	-x+1, -y+2, -z+1
	C8-H8B···F1	1.08	3.716(2)	2.66	165	x, -y+3/2, z-1/2
BZ-0(*Pbca*)	**N1-H1···O1**	1.03	2.916(2)	1.93	159	x+1/2, -y+1/2, -z+1
	C6-H6···O1	1.08	3.313(3)	2.27	163	x+1/2, -y+1/2, -z+1
	C8-H8A···O1	1.08	3.447(3)	2.44	154	-x+1/2, y+1/2, z
BZ-1(*P*-1)	**N1-H1···F1A**	1.03	2.762(1)	2.06	124	x, y, z
	N2-H2···F2A	1.03	2.760(1)	2.09	121	x, y, z
	N1-H1···O2	1.03	2.833(1)	2.03	132	x, y, z

	C16-H16A···F1A	1.08	3.432(2)	2.50	144	x, y, z
	N2-H2···O1	1.03	2.844(1)	2.01	136	x, y+1, z
	C3A-H3A···O2	1.08	3.356(1)	2.52	134	-x+1, -y+1, -z+1
	C11A-H11A···O1	1.08	3.422(1)	2.43	152	-x+1, -y+1, -z
	C8-H8C···F2A	1.08	3.440(2)	2.44	154	x, y+1, z
	C4A-H4A···F2A	1.08	3.451(1)	2.75	122	-x+2, -y, -z+1
	C13-H13···F1A	1.08	3.422(1)	2.79	117	-x+2,-y,-z
	C8-H8B···F2A	1.08	3.673(1)	2.77	141	-x+2,-y,-z
BZ-2(*Pbca*)	**N1-H1···O1**	1.03	2.901(2)	1.91	161	x+1/2, -y+3/2, -z+1
	C6-H6···O1	1.08	3.326(2)	2.30	159	x+1/2, -y+3/2, -z+1
	C8-H8A···O1	1.08	3.516(2)	2.48	162	-x+1/2, y-1/2, z
	C4-H4···F1	1.08	3.288(2)	2.63	119	x+1/2, y, -z+3/2
	C5-H5···F1	1.08	3.348(2)	2.74	116	x+1/2, y, -z+3/2
	C5-H5···F1	1.08	3.485(2)	2.85	118	-x+1, y-1/2, -z+3/2
BZ-3(*Pbca*)	**N1-H1···O1**	1.03	2.859(1)	1.88	157	-x+1/2, y+1/2, z
	C6-H6···O1	1.08	3.463(1)	2.52	145	-x+1/2, y+1/2, z
	C5-H5···O1	1.08	3.557(2)	2.87	122	-x+1, y+1/2, -z+1/2
	C3-H3···O1	1.08	3.672(1)	2.91	128	x+1/2, -y+3/2, -z+1
	C8-H8B···F1	1.08	3.473(1)	2.64	133	x-1, y, z
	C3-H3···F1	1.08	3.330(1)	2.71	117	-x+3/2, y-1/2, z
	C6-H6···F1	1.08	3.315(1)	2.80	109	x-1/2, y, -z+1/2
	C8-H8C···F1	1.08	3.535(1)	2.88	119	-x+1, -y+2, -z+1
	C8-H8A···Cg1	1.08	3.442(1)	2.73	130	x+1/2, y, -z+1/2
BZ-4($P2_1/c$)	**N1-H1···O1**	1.03	2.827(1)	1.92	146	x, -y+3/2, z-1/2
	C8-H8B···O1	1.08	3.362(1)	2.85	109	x, -y+3/2, z-1/2
	C2-H2···O1	1.08	3.365(1)	2.37	153	-x+1, -y+2, -z+2
	C5-H5···F3	1.08	3.293(1)	2.44	135	-x, y+1/2, -z+3/2
	C5-H5···F2	1.08	3.536(1)	2.59	147	-x, -y+2, -z+1
	C8-H8C···Cg1	1.08	3.528(1)	2.86	126	x, -y+3/2, z+1/2
BZ-5($P2_1/c$)	**N1-H1···O1**	1.03	2.909(2)	1.91	163	-x, y-1/2, -z+1/2
	C6-H6···O1	1.08	3.300(3)	2.24	166	-x, y-1/2, -z+1/2
	C8-H8A···O1	1.08	3.559(3)	2.60	148	-x, -y+2, -z+1
	C5-H5···F3	1.08	3.360(3)	2.59	128	-x+1, y-1/2, -z+1/2
	C4-H4···F2	1.08	3.674(3)	2.63	162	-x+1, y-1/2, -z+1/2
BZ-6($P2_1/n$)	**N1-H1···O1**	1.03	2.869(2)	1.92	152	x+1, y, z
	C6-H6···O1	1.08	3.434(2)	2.83	116	-x, -y+1, -z+2
	C3-H3···O1	1.08	3.492(2)	2.53	148	-x-1/2, y-1/2, -z+3/2
	C2-H2···F2	1.08	3.549(2)	2.51	161	-x-1/2, y+1/2, -z+3/2
	C3-H3···F1	1.08	3.454(2)	2.66	130	x-1, y, z
	C5-H5···F3	1.08	3.445(2)	2.40	162	-x+1, -y, -z+2
	C8-H8A···F2	1.08	3.226(2)	2.76	106	x, y+1, z

Table S3: List of intermolecular contacts involving non-hydrogen atoms in the crystal.

	C-X···Y-C	X…Y(Å)	∠C-X…Y(°)	∠C-Y…X(°)	Symmetry Code
AC-4	**C9-F2···F3-C9**	3.108(1)	103(1)	143(1)	x-1, y, z
	C9-F3···O1-C7	3.172(1)	135(1)	109(1)	x+1, y, z
AC-5	**C9-F2···F2-C9**	3.096(2)	122(1)	122(1)	-x+1, -y+2, -z+1
	C9-F3···F3-C9	2.988(2)	134(1)	134(1)	-x+1, -y+2, -z
	C9-F2···F3-C9	3.113(2)	118(1)	113(1)	x, -y+5/2, z+1/2
AC-6	**C9-F1···F1-C9**	2.881(2)	134(1)	134(1)	-x+2, -y+2, -z+1
	C9-F3···F3-C9	2.895(2)	140(1)	140(1)	-x+1, -y+2,-z+1
BZ-4	**C9-F1···F2-C9**	3.130(1)	116(1)	119(1)	-x, y-1/2, -z+3/2
	C9-F2···F3-C9	3.109(1)	162(1)	160(1)	x, -y+3/2, z-1/2
BZ-5	**C9-F1···F2-C9**	3.019(2)	138(1)	168(1)	x, -y+5/2, z-1/2
	C9-F1···F3-C9	3.018(2)	132(1)	112(1)	-x+1, -y+2, -z
	C9-F2···F3-C9	3.072(2)	90(1)	127(1)	-x+1, -y+2, -z+1
	C9-F3···F3-C9	3.007(2)	93(1)	93(1)	-x+1, -y+2, -z+1
BZ-6	**C9-F1···F2-C9**	2.987(2)	154(1)	128(1)	x+1, y, z
	C9-F3···F3-C9	2.814(1)	104(1)	104(1)	-x, -y, -z+2
	C9-F3···F3-C9	3.061(1)	110(1)	110(1)	-x+1, -y, -z+2

Table S4: Comparison of interaction energies calculated by PIXEL and DFT-D3/B-97 methods in different molecular pairs of AC-1 and BZ-5 with those obtained with counterpoise corrected DFT-D2 and MP2/cc-pVTZ calculation.

Motif	**Total PIXEL Energy**	**DFT-D3/B-97D**	DFT-D2/ B-97D	**DFT-D2^{cp}**	MP2/ cc-pVTZ	**MP2^{cp}**
AC-1						
1	**-8.6**	**-8.50**	-8.37	**-8.02**	-10.46	**-8.21**
2	**-3.9**	**-5.76**	-6.20	**-5.78**	-7.85	**-5.58**
3	**-3.2**	**-3.45**	-3.82	**-3.49**	-4.93	**-3.21**
4	**-2.2**	**-2.56**	-2.95	**-2.76**	-3.65	**-2.46**
5	**-2.1**	**-2.33**	-2.30	**-2.19**	-2.53	**-1.84**
BZ-5						
1	**-8.7**	**-8.24**	-8.07	**-7.66**	-9.72	**-7.79**
2	**-5.6**	**-7.72**	-8.50	**-8.03**	-11.35	**-8.60**
3	**-5.6**	**-6.50**	-7.18	**-6.74**	-8.41	**-5.93**
4	**-4.6**	**-5.87**	-6.00	**-5.74**	-6.54	**-5.14**
5	**-2.0**	**-1.80**	-3.11	**-2.73**	-3.45	**-1.89**
6	**-1.6**	**-1.45**	-2.11	**-1.87**	-2.37	**-1.23**
7	**-1.1**	**-0.93**	-1.77	**-1.56**	-2.00	**-0.92**

Table S5: Analysis of weak C(sp^3/sp^2)-H···F-C(sp^3/sp^2) intermolecular interactions.

Compound Code	C-H···F interactions	Geometry (Å, º)	Total PIXEL energy(kcal/mol)	DFT-D3/B97-D (kcal/mol)
Compounds with F-atom connected with sp^2 C-atom [**C-H···F-C(sp^2)**]				
AC-1	C4A(sp^2)-H4A···F1 C5A(sp^2)-H5A···F1	2.85, 122 2.78, 125	-3.2	-3.45
AC-2	C5(sp^2)-H5···F1	2.64, 116	-1.1	-0.93
	C8(sp^3)-H8A···F1	2.77, 145	-0.9	-1.00
AC-3 Form I	C6(sp^2)-H6···F1	--	-2.3	-2.44
	C8(sp^3)-H8A···F1	--	-0.9	-1.27
	C8(sp^3)-H8C···F1	--	-0.7	-0.72
AC-3 Form II	C5(sp^2)-H5···F1 C6(sp^2)-H6···F1	2.72, 106 2.56, 112	-2.2	-2.02
	C8(sp^3)-H8A···F1	2.73, 116	-0.8	-0.73
BZ-1	C4A(sp^2)-H4A···F2A C16(sp^3)-H16B···F1A	2.75, 122 2.50Å, 144	-2.7	-2.42
	C8(sp^3)-H8B···F2A C11A(sp^2)-H11A···F1A	2.77Å, 141 2.79Å, 117	-2.6	-2.33
BZ-2	C4(sp^2)-H4···F1 C5(sp^2)-H5···F1	2.63Å, 119 2.85Å, 118	-2.0	-1.99
	C8(sp^3)-H8C···F1	2.86Å, 167	-1.2	-1.45
BZ-3	C2(sp^2)-H2···F1 C3(sp^2)-H3···F1	 2.71Å, 117	-1.6	-1.43
	C8(sp^3)-H8B···F1	2.88Å, 119	-1.0	-1.1
Compounds with F-atom connected with sp^3 C-atom **C-H···F-C(sp^3)**				
AC-4	C3(sp^2)-H3···F2 C4(sp^2)-H4···F2	2.74, 120 2.67, 123	-2.7	-2.50
	C8(sp^3)-H8C···F3	2.52, 131	-1.4	-1.22
	C8(sp^3)-H8C···F2	2.83, 131	-0.9	-0.90
AC-5	C4(sp^2)-H4···F2	2.83, 124	-1.5	-1.36

	C4(sp^2)-H4···F3 dimer with F…F	2.76, 136	-1.5	-1.55
AC-6	C5(sp^2)-H5···F3 dimer with F…F	2.44, 158	-1.8	-1.91
	C3(sp^2)-H3···F1 dimer with F…F	2.52, 149	-1.0	-1.07
	C8(sp^3)-H8B···F1	2.66, 165	-1.4	-1.63
BZ-4	C5(sp^2)-H5···F2 dimer	2.59, 147	-2.7	-2.56
	C5(sp^2)-H5···F3 with F…F	2.44, 135	-2.6	-2.49
BZ-5	C4(sp^2)-H4···F2 C5(sp^2)-H5···F3	2.63, 162 2.59, 128	-1.6	-1.45
BZ-6	C5(sp^2)-H5···F3 dimer with F···F	2.40, 162	-2.3	-2.11
	CH_3···CF_3		-1.4	-1.15

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