

Supplementary Materials: Spectroscopic, DFT and XRD Studies of Hydrogen Bonds in *N*-Unsubstituted 2-Aminobenzamides

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S1: ^1H -NMR spectra for ABB, AIB, ABBB and ABIB with peak pickings

S2: Computed GIAO NMR chemical shift of conformers (A) and (B) of ABB, AIB, ABBB and ABIB

S3: Experimental IR spectra for ABB, AIB, ABBB and ABIB

S4: Experimental Raman spectra for ABB, AIB, ABBB and ABIB

S5: Computed IR and Raman frequency values of ABB, AIB, ABBB and ABIB

1. Supplementary S1: Detailed ^1H -NMR Spectra for ABB, AIB, ABBB and ABIB

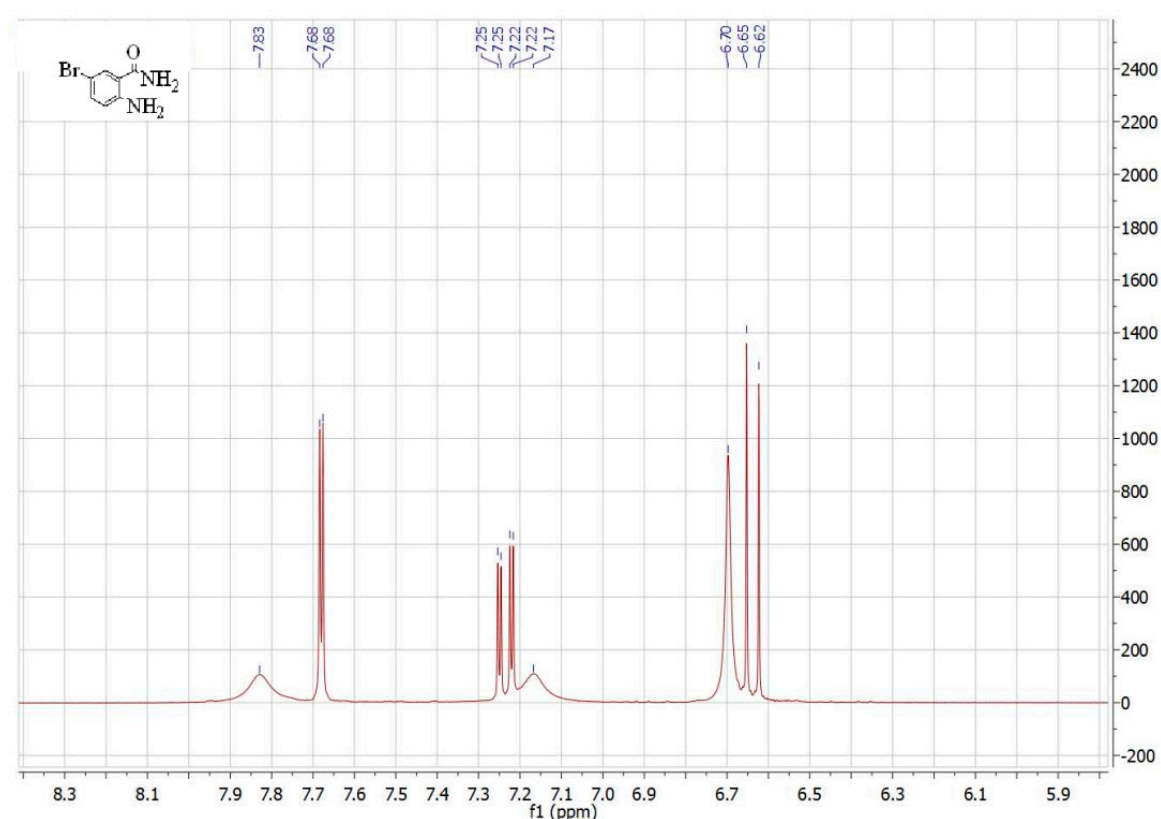


Figure S1. ^1H -NMR spectrum of ABB in $\text{DMSO}-d_6$ at 500 MHz showing peak pickings.

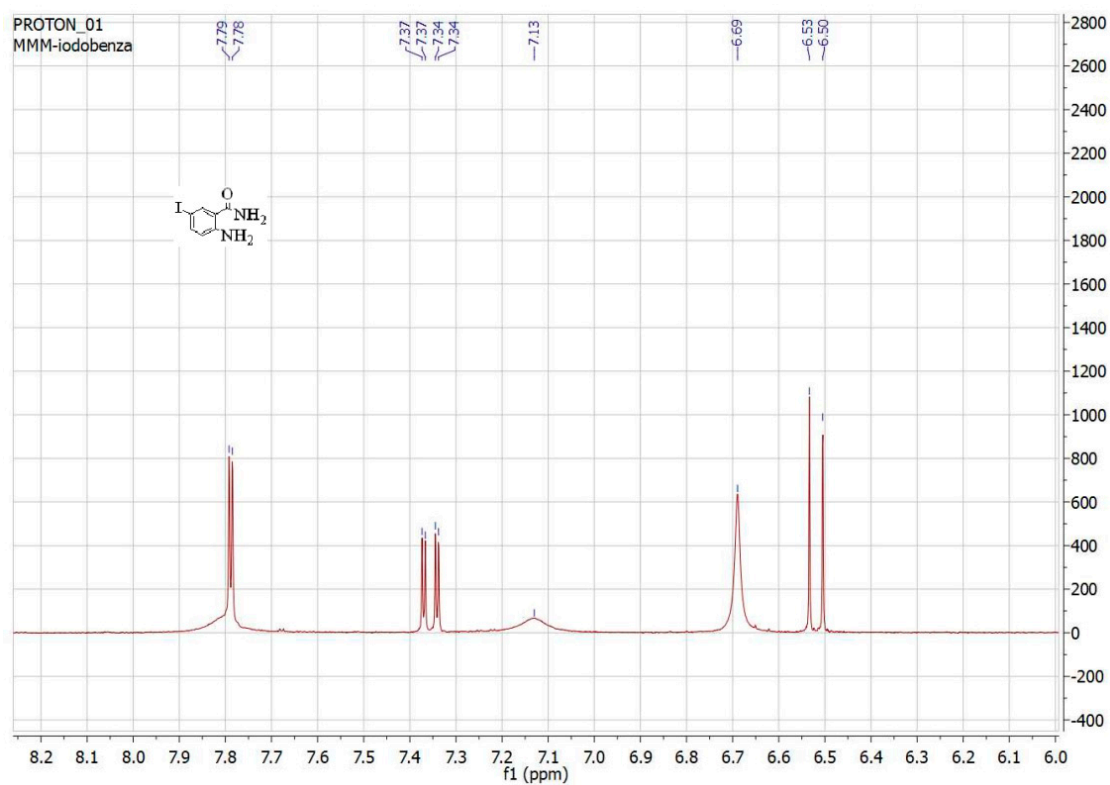


Figure S2. ^1H -NMR spectrum of AIB in $\text{DMSO}-d_6$ at 500 MHz showing peak pickings.

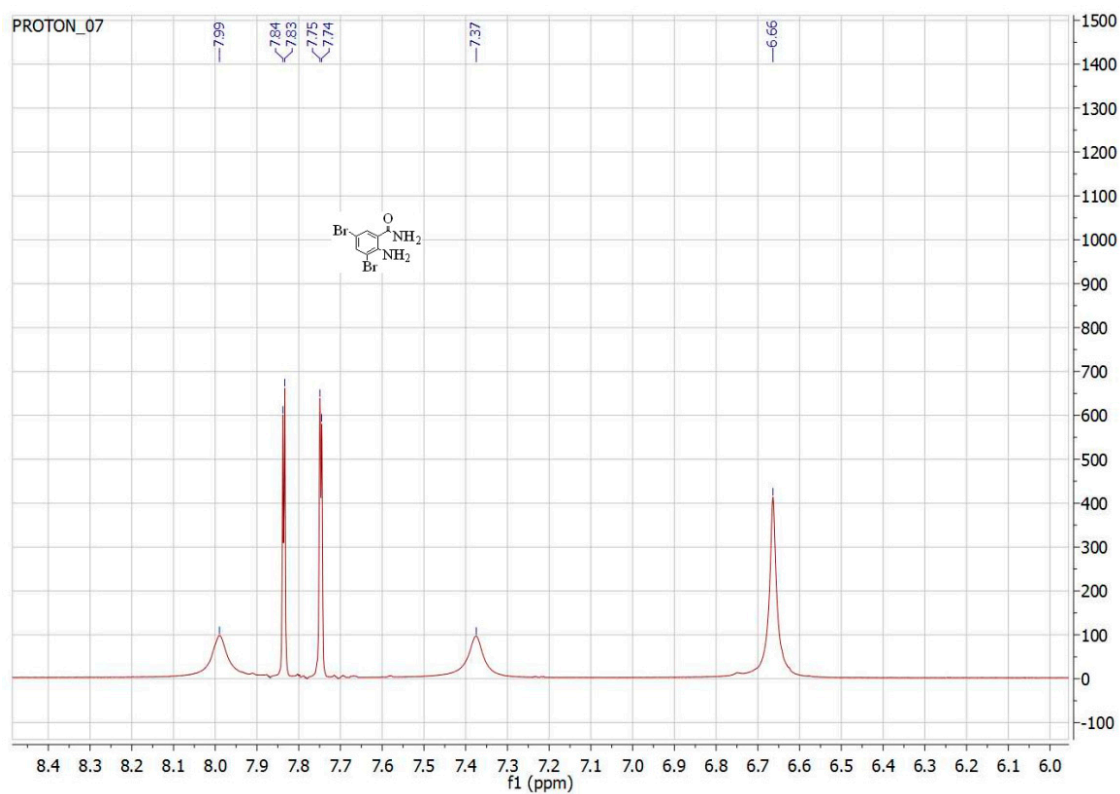


Figure S3. ^1H -NMR spectrum of ABBB in $\text{DMSO}-d_6$ at 500 MHz showing peak pickings.

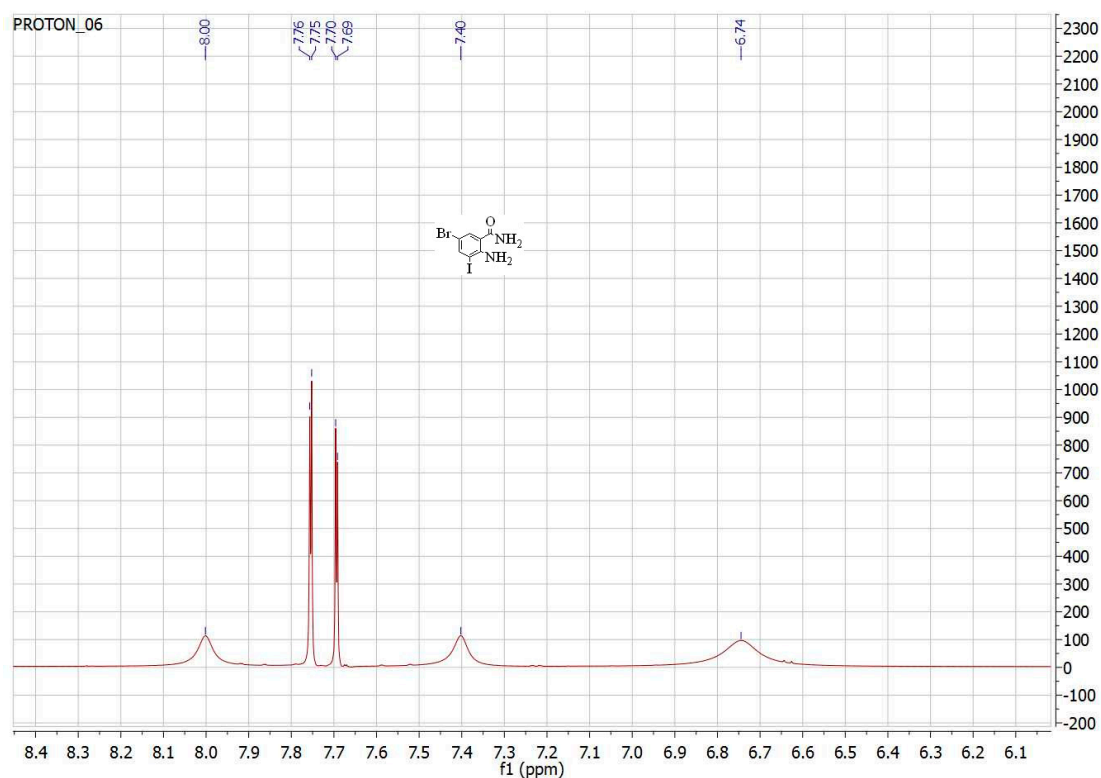
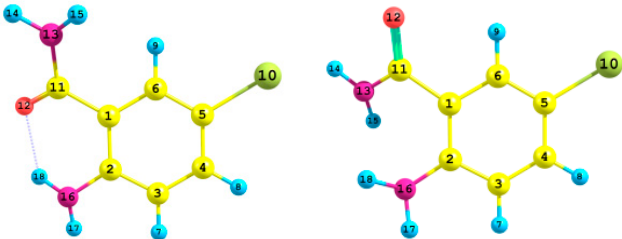
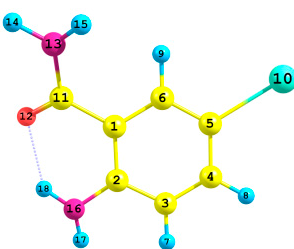


Figure S4. ^1H -NMR spectrum of AIBB in $\text{DMSO}-d_6$ at 500 MHz showing peak pickings.

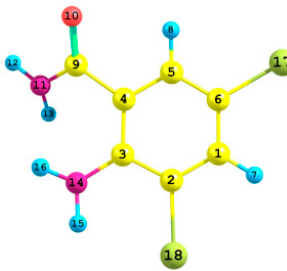
2. Supplementary S2: Computed GIAO NMR Chemical Shift of Conformers (A) and (B) of ABB, AIB, ABBB and ABIB

Table S1. Computed chemical shift (ppm) of conformers (A) and (B) of ABB, AIB, ABBB and ABIB.

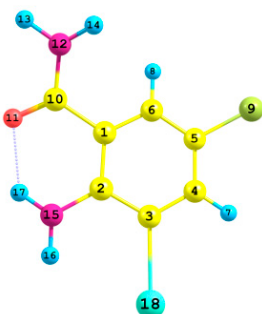
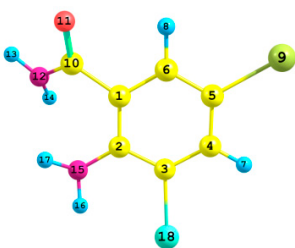
ABB				
Conformer (A)		Conformer (B)	Conformer (A)	Conformer (B)
C1	121.20	127.63		
C2	157.76	153.77		
C3	124.18	124.83		
C4	142.90	142.31		
C5	129.99	134.00		
C6	137.47	140.26		
H7	7.02	7.11		
H8	7.46	7.51		
H9	7.73	8.05		
C11	178.27	175.06		
H14	5.17	5.49		
H15	5.76	6.30		
H17	4.30	4.06		
H18	7.45	4.18		
AIB				
Conformer (A)		Conformer (B)	Conformer (A)	Conformer (B)
C1	121.71	127.87		
C2	157.89	153.95		
C3	124.35	124.87		
C4	146.94	146.45		
C5	121.64	126.00		
C6	141.70	144.67		

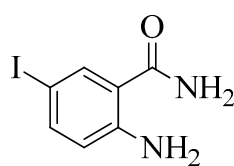
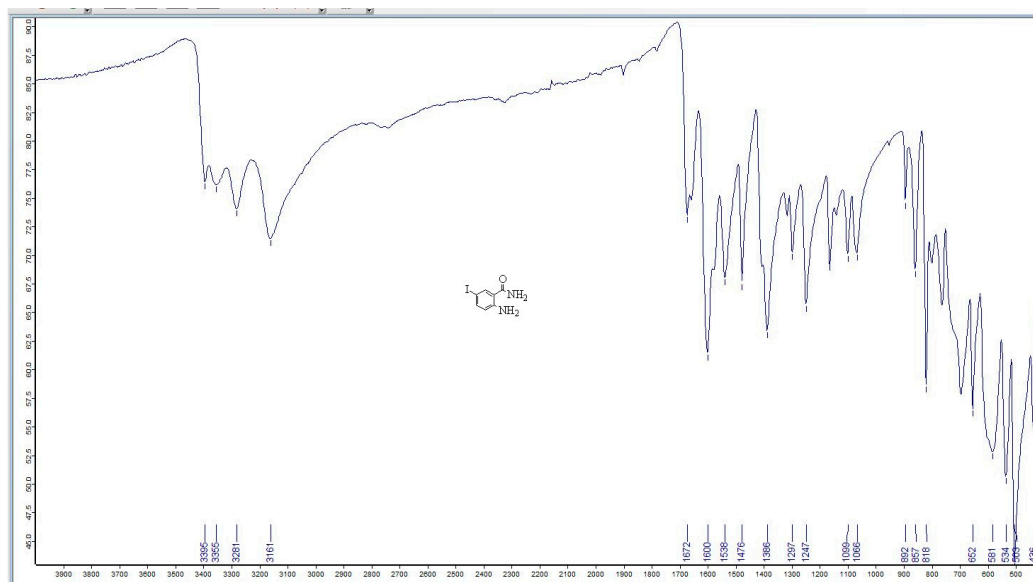
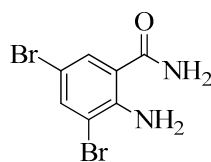
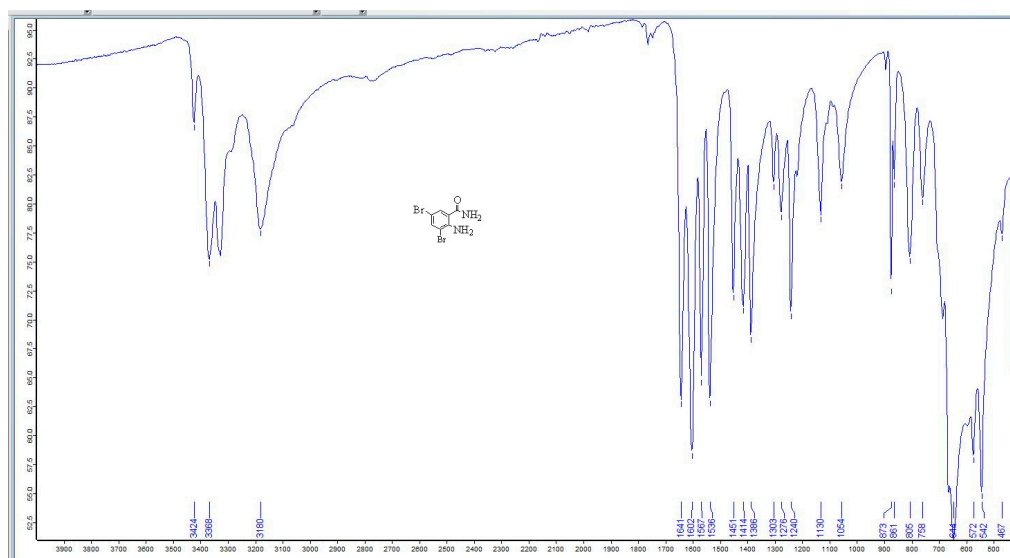
H7	6.98	7.04		
H8	7.46	7.53		
H9	7.78	8.09		
C11	178.23	175.18		
H14	5.12	5.46		
H15	5.70	6.29		
H17	4.20	3.98		
H18	7.35	4.15		

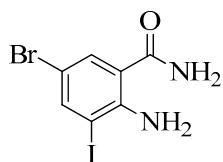
ABBB

	Conformer (A)	Conformer (B)	Conformer (A)	Conformer (B)
C1	145.08	144.58		
C2	132.99	133.38		
C3	154.55	150.52		
C4	122.75	128.84		
C5	137.32	140.51		
C6	129.53	132.73		
H7	7.73	7.75		
H8	7.63	7.90		
C9	177.31	174.11		
H12	5.26	5.56		
H13	5.75	6.00		
H15	4.87	4.80		
H16	7.97	4.70		

ABIB

	Conformer (A)	Conformer (B)	Conformer (A)	Conformer (B)
C1	122.80	129.11		
C2	156.59	152.79		
C3	127.87	128.18		
C4	149.52	148.89		
C5	129.70	132.76		
C6	138.04	140.74		
H7	7.86	7.89		
H8	7.75	7.89		
C10	177.61	174.77		
H13	5.27	5.60		
H14	5.74	6.01		
H16	4.67	4.53		
H17	7.95	4.70		

3. Supplementary S3: Experimental IR Spectra for ABB, AIB, ABBB and ABIB**AIB****Figure S5. Experimental and computed IR spectra for AIB.****ABBB****Figure S6. Experimental IR spectra for ABBB.**



ABIB

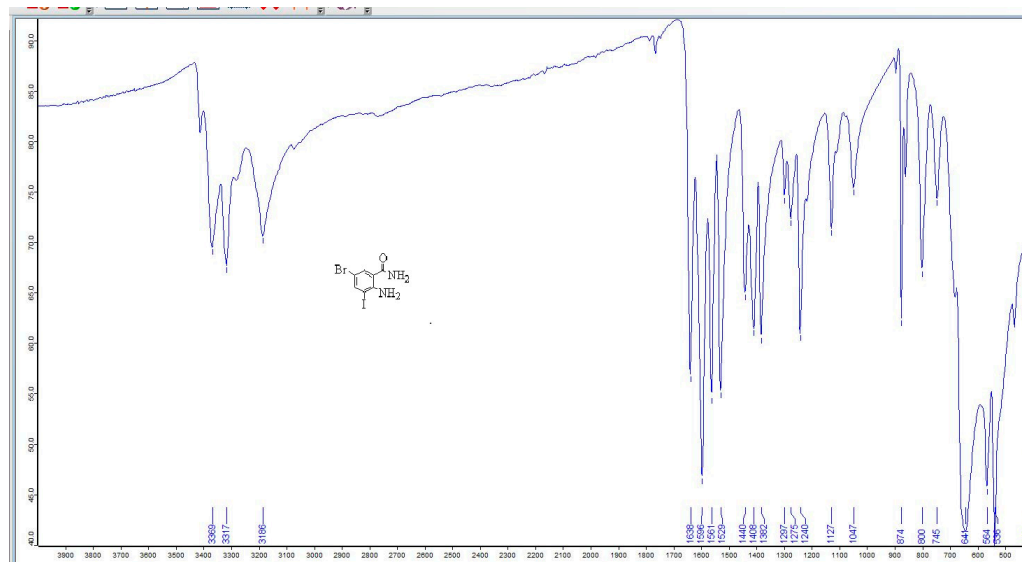
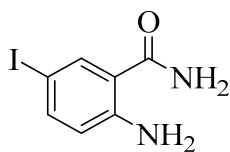


Figure S7. Experimental IR spectra for ABIB.

4. Supplementary S4: Experimental Raman Spectra for AIB, ABBB and ABIB



AIB

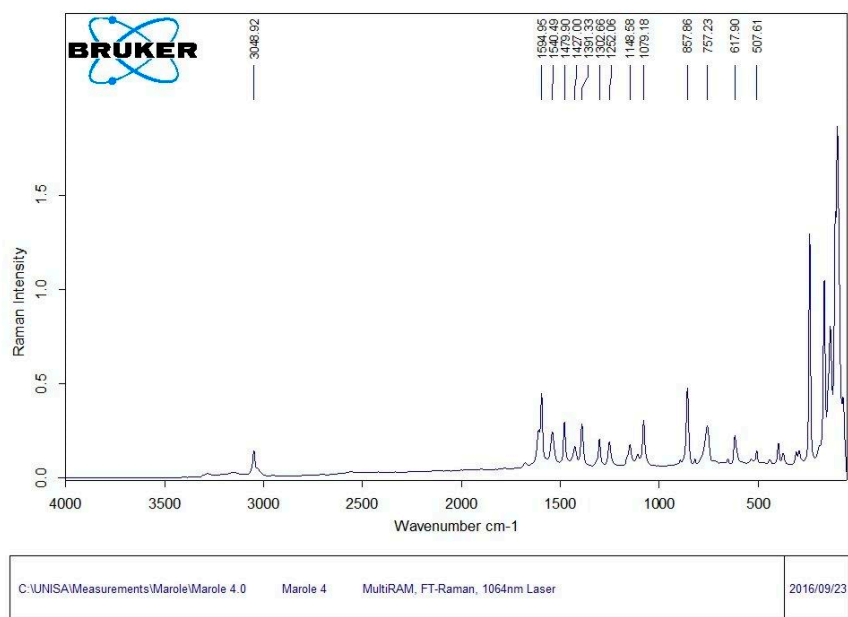


Figure S8. Experimental Raman spectrum of AIB.

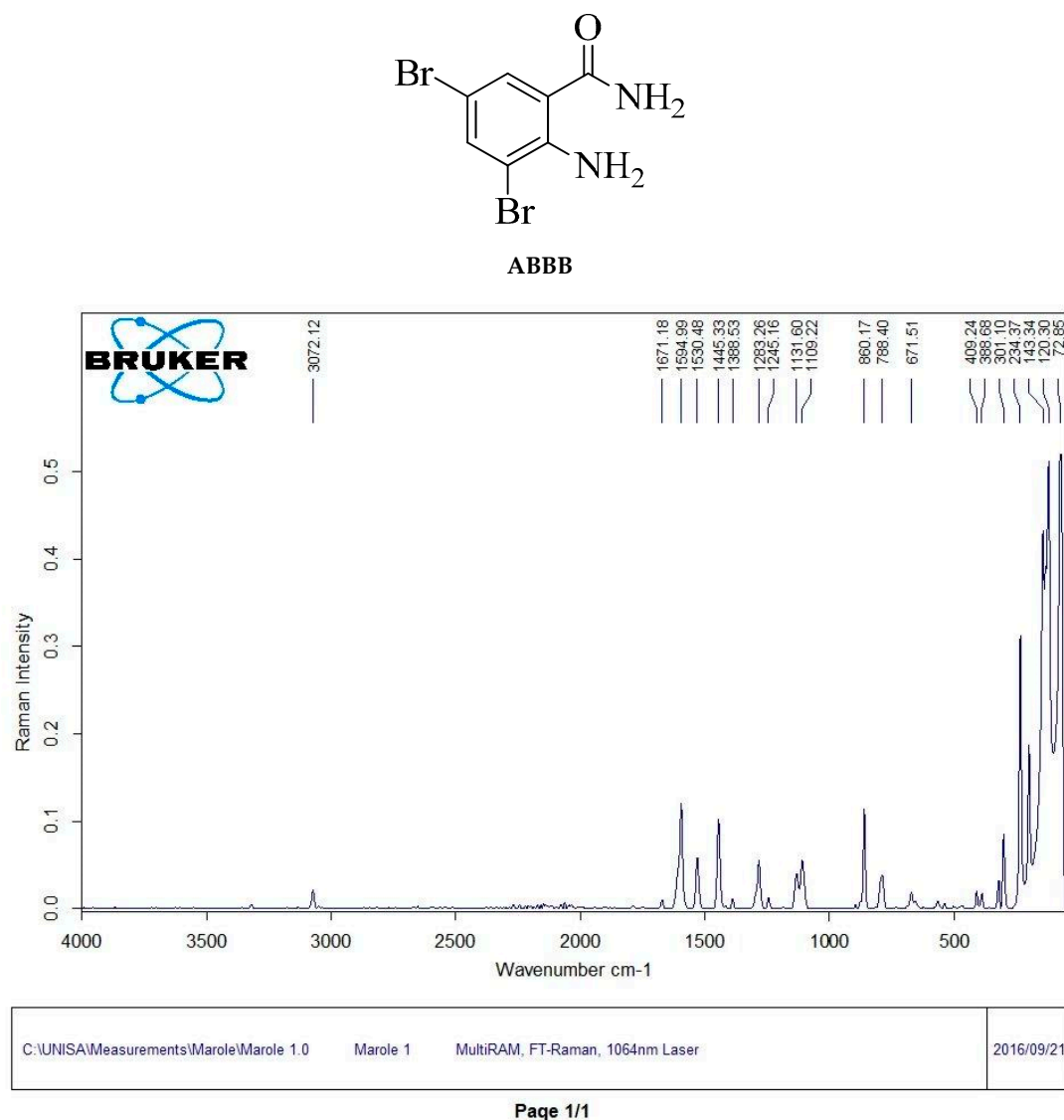
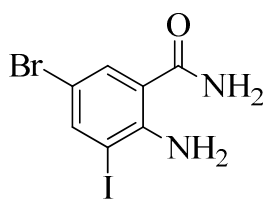


Figure S9. Experimental Raman spectrum of **ABBB**.



ABIB

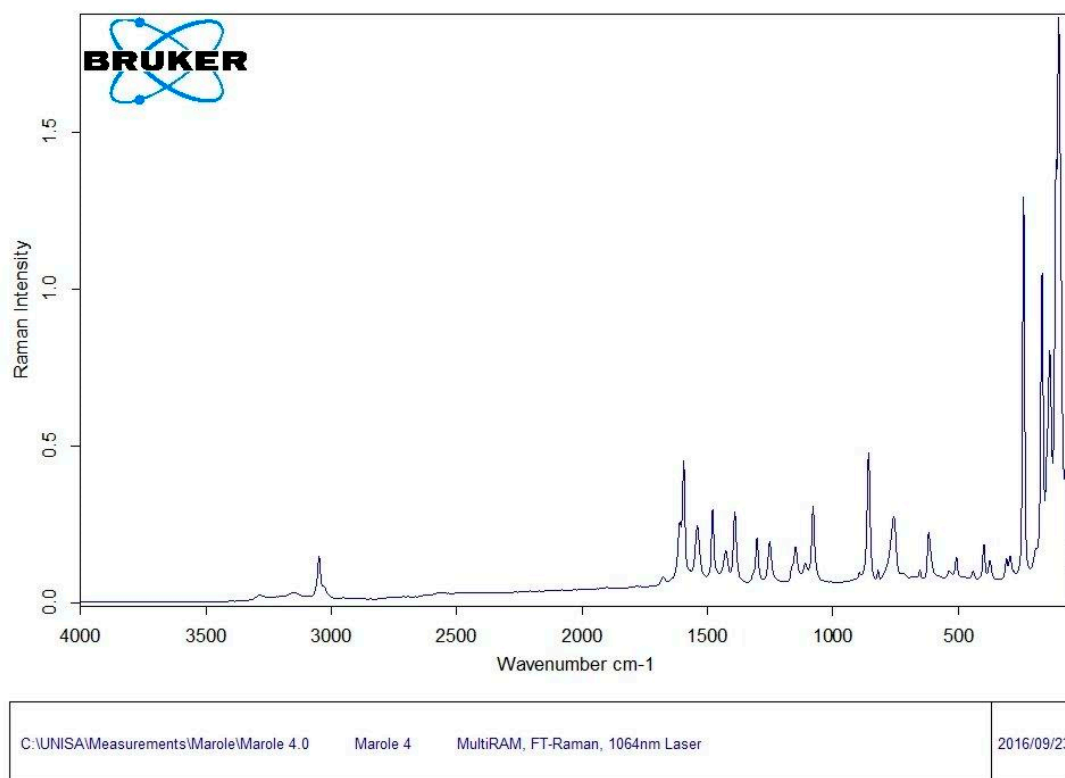


Figure S10. Experimental Raman spectrum of ABIB.

5. Supplementary S5: Computed IR and Raman Frequency Values and Intensities of ABB, AIB, ABIB and ABIB

Table S2. Computed IR frequency, IR intensity and Raman activity of conformer (A) for ABB.

Frequency (cm ⁻¹)	IR Intensity (Km ⁻¹ mol ⁻¹)	Raman Activity (Å ⁴ amu ⁻¹)	Selected Assignment
59.6	4.2	1.2	
110.3	0.6	1.5	
137.1	4.6	1.5	
144.6	1.0	1.7	
278.1	2.1	6.7	
293.0	11.7	1.9	
301.6	3.8	0.6	
360.6	201.5	1.4	
378.2	92.0	1.1	
385.0	69.4	2.5	
409.9	7.5	3.0	
431.6	5.9	1.9	
504.1	2.1	0.5	
530.2	4.4	0.3	

554.2	50.7	0.5	
617.7	81.8	1.2	
641.3	11.1	2.1	
651.7	39.4	4.7	
708.9	7.8	0.5	
755.9	6.1	18.3	
795.2	4.3	0.2	
827.5	38.8	0.7	
870.8	11.1	19.6	
900.9	6.7	0.3	
961.5	0.1	0.1	
1066.1	4.4	0.8	
1079.4	17.6	21.0	
1113.5	6.4	7.5	
1132.7	19.2	21.6	
1186.2	29.4	3.9	
1287.4	98.1	14.1	
1333.4	44.3	16.4	
1341.5	84.9	4.8	
1380.4	154.6	33.1	
1435.1	23.2	9.0	
1506.2	64.6	22.0	
1578.9	110.1	29.6	
1609.5	62.0	1.8	
1624.6	233.5	17.4	
1647.8	156.1	31.6	
1715.3	319.1	48.7	C=O str
3164.4	11.6	104.7	
3198.6	2.7	82.2	
3200.2	0.1	67.6	N-H antisym str
3524.7	129.7	166.6	N-H antisym str
3589.5	51.4	153.9	N-H sym str
3687.9	63.8	82.8	N-H sym str
3713.5	40.5	44.8	C=O str

Table S3. Computed IR frequency, IR intensity and Raman activity of conformer (B) for ABB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
61.4	9.2	1.2	
113.5	0.4	1.0	
131.7	6.7	1.7	
143.0	3.6	1.3	
268.3	38.7	4.1	
274.9	2.6	1.1	
284.5	6.6	5.5	
312.6	7.8	2.5	
367.6	3.6	2.3	
375.6	2.3	2.3	
437.9	9.2	0.4	
514.2	36.3	0.7	
542.0	59.0	0.4	
562.7	39.2	5.0	
585.9	28.1	1.4	

617.5	132.8	1.9	
641.0	10.8	2.7	
705.4	19.9	2.2	
715.4	164.9	1.7	
763.2	3.5	15.7	
797.3	7.4	0.8	
826.4	47.5	0.5	
865.8	22.4	19.0	
930.7	6.9	0.2	
963.8	1.3	0.1	
1073.9	9.1	1.2	
1095.9	7.0	1.6	
1110.2	8.9	29.8	
1138.9	10.5	12.0	
1183.1	21.1	7.0	
1267.1	32.8	12.8	
1313.1	42.7	11.9	
1326.3	135.8	8.7	
1347.3	72.3	18.3	
1439.0	110.2	2.6	
1506.4	129.3	3.9	
1601.5	7.4	15.6	
1619.6	153.3	24.3	
1633.3	8.2	27.4	
1663.4	105.9	24.0	
1741.7	345.8	40.0	C=O str
3160.6	12.5	107.1	
3200.1	1.7	107.3	
3212.1	4.5	42.1	N-H antisym str
3545.1	43.9	290.8	N-H antisym str
3548.7	13.2	62.0	N-H sym str
3644.5	28.3	53.8	N-H sym str
3671.2	51.1	62.7	C=O str

Table S4. Computed IR frequency, IR intensity and Raman activity of conformer (A) for AIB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
58.5	3.5	1.4	
102.9	1.2	1.9	
124.8	1.0	1.9	
135.1	4.2	1.5	
228.0	0.3	9.5	
284.3	14.9	1.1	
289.8	1.2	1.4	
361.3	185.2	1.5	
377.1	110.6	1.3	
385.5	64.2	2.2	
408.6	10.4	3.0	
429.7	6.3	1.7	
502.6	2.3	0.8	
528.6	5.9	0.8	
552.4	55.1	2.2	
611.8	66.8	2.5	

626.2	22.9	1.1	
649.9	38.4	3.5	
709.4	7.1	3.1	
751.0	4.5	17.9	
795.3	3.7	0.1	
825.4	36.4	1.4	
862.7	13.4	25.2	
899.1	3.8	0.8	
959.5	0.2	0.8	
1061.1	7.3	1.5	
1079.7	16.0	20.8	
1108.2	8.4	6.0	
1129.8	15.5	13.1	
1189.7	30.3	4.2	
1289.7	104.0	15.4	
1333.9	39.6	12.9	
1340.5	82.9	5.3	
1378.4	165.9	27.8	
1430.7	22.0	9.7	
1504.5	59.9	23.1	
1576.2	107.6	26.6	
1607.2	66.4	1.9	
1623.8	220.0	22.3	
1645.2	173.7	23.6	
1714.8	320.5	52.1	C=O str
3162.0	11.8	112.3	
3195.9	3.7	37.6	
3197.1	0.4	98.6	N-H antisym str
3525.3	130.7	167.4	N-H antisym str
3589.0	51.1	156.0	N-H sym str
3687.9	63.4	84.9	N-H sym str
3712.7	40.2	45.3	C=O str

Table S5. Computed IR frequency, IR intensity and Raman activity of conformer (B) for AIB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
60.0	9.3	1.5	
106.6	0.8	1.1	
124.1	0.8	1.6	
131.3	8.9	1.7	
228.5	1.1	8.4	
268.1	40.0	2.6	
272.5	3.6	1.1	
303.5	10.1	3.4	
365.1	3.1	2.2	
374.6	2.1	2.1	
436.1	8.7	0.5	
512.5	40.0	1.1	
540.9	54.3	0.6	
562.2	47.8	5.1	
583.8	19.3	2.7	
604.1	126.2	1.8	
636.0	11.0	2.5	

707.2	44.8	3.1	
712.5	149.1	2.4	
758.8	3.9	14.3	
796.5	6.8	0.5	
823.1	44.5	0.7	
857.5	25.3	23.9	
930.6	4.4	1.3	
962.4	1.6	0.5	
1069.1	11.2	2.3	
1093.5	7.1	0.8	
1110.7	8.5	27.7	
1135.7	9.1	7.4	
1186.3	23.0	7.6	
1269.2	36.8	12.5	
1315.2	53.8	10.0	
1325.3	119.0	9.7	
1345.4	90.7	16.1	
1435.1	112.2	1.9	
1504.9	121.9	5.2	
1598.7	7.5	15.3	
1619.2	155.7	29.8	
1630.1	8.6	21.7	
1663.4	108.0	21.4	
1741.2	340.1	38.3	C=O str
3158.1	13.0	114.7	
3197.7	2.6	96.9	
3208.8	3.8	38.7	N-H antisym str
3545.3	44.4	299.4	N-H antisym str
3549.0	13.4	65.1	N-H sym str
3644.5	28.1	54.8	N-H sym str
3671.5	50.5	64.5	C=O str

Table S6. Computed IR frequency, IR intensity and Raman activity of conformer (A) for ABBB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
55.5	3.3	1.8	
84.1	1.1	0.5	
113.9	0.4	1.3	
123.4	0.2	2.3	
151.9	1.3	1.0	
183.1	1.6	1.5	
252.0	2.7	9.2	
295.3	6.5	4.4	
319.9	2.2	0.3	
342.2	22.2	0.7	
371.5	189.8	0.6	
383.6	62.8	0.4	
400.6	61.4	0.7	
418.5	19.2	2.3	
461.8	9.4	0.7	
551.7	1.4	0.5	
555.9	30.8	0.6	
558.2	15.0	0.4	

636.7	38.1	0.3	
656.0	54.7	4.4	
688.5	60.1	4.0	
724.4	2.6	5.5	
795.8	9.0	9.8	
801.1	16.4	0.7	
869.1	11.8	32.5	
889.4	17.8	0.3	
911.9	0.6	0.4	
1077.9	75.9	1.9	
1083.0	4.5	23.4	
1127.2	8.2	3.4	
1137.7	5.7	18.1	
1271.5	77.7	1.6	
1308.2	104.7	27.4	
1334.3	45.4	5.8	
1374.2	189.3	23.0	
1430.6	6.5	0.9	
1467.2	92.6	50.9	
1558.1	107.8	22.6	
1597.2	95.9	3.0	
1620.7	193.2	18.3	
1639.9	176.5	27.5	
1715.6	288.9	44.1	C=O str
3205.8	0.1	37.6	
3213.7	1.1	50.7	
3518.3	145.6	144.7	N-H antisym str
3589.1	58.5	168.9	N-H antisym str
3679.1	106.5	30.3	N-H sym str
3713.2	42.4	48.1	N-H sym str

Table S7. Computed IR frequency, IR intensity and Raman activity of conformer (B) for ABBB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
56.4	11.0	1.4	
88.7	0.6	0.5	
116.7	0.8	1.1	
123.1	0.6	2.1	
149.7	1.5	0.9	
178.5	9.6	1.6	
251.8	1.2	10.2	
292.9	10.6	2.7	
303.3	44.7	4.6	
320.8	9.4	1.7	
331.8	3.5	0.4	
387.8	0.9	0.8	
388.7	6.6	1.3	
468.4	9.7	0.4	
537.3	68.9	1.3	
559.2	30.9	0.5	
580.5	40.5	0.9	
597.8	23.8	1.0	
620.8	105.2	1.1	

677.9	146.8	4.7	
702.9	56.0	4.5	
726.7	4.9	0.6	
790.8	14.8	2.2	
800.1	11.9	4.1	
864.4	16.8	29.5	
890.5	17.0	0.1	
936.0	3.7	0.1	
1085.6	56.3	2.4	
1102.8	8.1	5.7	
1123.5	0.5	17.9	
1138.8	9.2	12.4	
1260.0	29.3	2.3	
1289.8	17.7	25.5	
1319.2	119.9	1.5	
1342.2	111.5	12.7	
1429.1	23.0	8.7	
1470.6	249.7	4.2	
1577.2	10.5	15.3	
1612.1	75.5	36.3	
1624.0	88.2	3.3	
1657.5	122.4	28.5	
1745.1	345.9	39.2	C=O str
3215.1	1.5	48.8	
3215.8	5.4	43.2	
3545.7	45.4	240.7	N-H antisym str
3550.6	21.8	84.2	N-H antisym str
3646.2	61.4	24.9	N-H sym str
3672.9	50.6	63.9	N-H sym str

Table S8. Computed IR frequency, IR intensity and Raman activity of conformer (A) for ABIB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
50.6	3.2	2.1	
77.6	1.0	0.6	
108.2	0.0	2.5	
113.1	0.4	1.3	
139.3	1.4	1.1	
174.4	2.1	1.9	
215.1	1.9	8.8	
290.9	2.9	5.5	
317.0	3.7	0.7	
332.1	13.6	0.7	
350.4	223.8	0.8	
374.8	25.5	0.4	
398.1	70.2	1.1	
417.3	10.3	2.5	
458.2	9.0	1.2	
547.7	0.2	0.8	
555.0	2.4	0.3	
556.0	49.6	1.4	
635.4	43.0	0.2	
656.4	54.1	3.7	

670.7	65.3	5.2	
729.7	0.9	9.4	
782.9	1.8	7.7	
803.0	24.4	2.8	
868.2	10.7	36.0	
890.9	14.3	0.9	
912.5	1.1	0.6	
1067.3	71.2	6.9	
1083.7	12.4	24.9	
1125.1	9.5	3.8	
1137.3	3.1	15.1	
1274.1	84.1	2.5	
1308.5	103.9	23.6	
1331.1	29.6	12.6	
1372.3	206.7	19.9	
1428.2	8.8	2.1	
1462.6	91.8	51.6	
1553.1	94.8	25.5	
1597.7	85.6	4.3	
1620.9	198.7	18.6	
1639.0	203.7	28.5	
1715.3	269.1	41.6	C=O str
3206.0	0.2	38.6	
3211.2	1.2	43.6	
3512.2	146.0	149.5	N-H antisym str
3588.4	59.2	174.4	N-H antisym str
3673.9	109.0	29.8	N-H sym str
3712.3	42.1	50.1	N-H sym str

Table S9. Computed IR frequency, IR intensity and Raman activity of conformer (B) for ABIB.

Frequency (cm ⁻¹)	IR Intensity (Km·mol ⁻¹)	Raman Activity (Å ⁴ ·amu ⁻¹)	Selected Assignment
54.3	10.5	1.4	
83.3	1.0	0.7	
108.7	0.0	2.5	
115.3	1.0	1.2	
139.3	1.5	0.9	
169.0	11.7	2.1	
214.7	0.0	9.9	
287.4	22.3	4.1	
294.7	33.5	4.7	
319.8	9.8	1.7	
325.7	2.4	0.3	
382.4	1.0	0.8	
389.3	8.1	2.0	
466.6	7.6	0.2	
527.4	69.2	1.4	
556.1	24.3	0.7	
580.7	54.7	1.6	
591.5	19.4	1.3	
621.0	113.5	1.2	
665.5	114.0	7.4	
698.4	80.4	3.5	

732.1	0.8	2.3	
784.6	3.9	3.3	
801.5	22.2	1.7	
863.5	15.5	31.7	
891.3	12.0	0.4	
938.7	4.5	0.2	
1074.7	59.0	6.7	
1103.3	12.2	5.1	
1122.4	0.3	18.3	
1137.1	7.0	11.4	
1262.2	27.9	4.5	
1289.4	13.3	25.7	
1316.2	102.9	2.0	
1340.1	133.6	11.0	
1426.4	18.9	11.0	
1466.1	249.5	3.2	
1571.8	14.5	17.9	
1610.0	77.1	40.6	
1623.4	93.5	3.9	
1660.4	119.3	28.7	
1744.4	346.6	40.6	C=O str
3213.4	1.5	42.1	
3216.4	5.3	43.6	
3543.0	36.3	226.6	N-H antisym str
3550.7	26.2	112.5	N-H antisym str
3642.3	64.2	22.0	N-H sym str
3673.5	51.6	66.7	N-H sym str