

Electronic Supplementary Information

Halogen bonded supramolecular assemblies constructed from azulene-containing molecules and perfluorinated di-/triiodobenzenes

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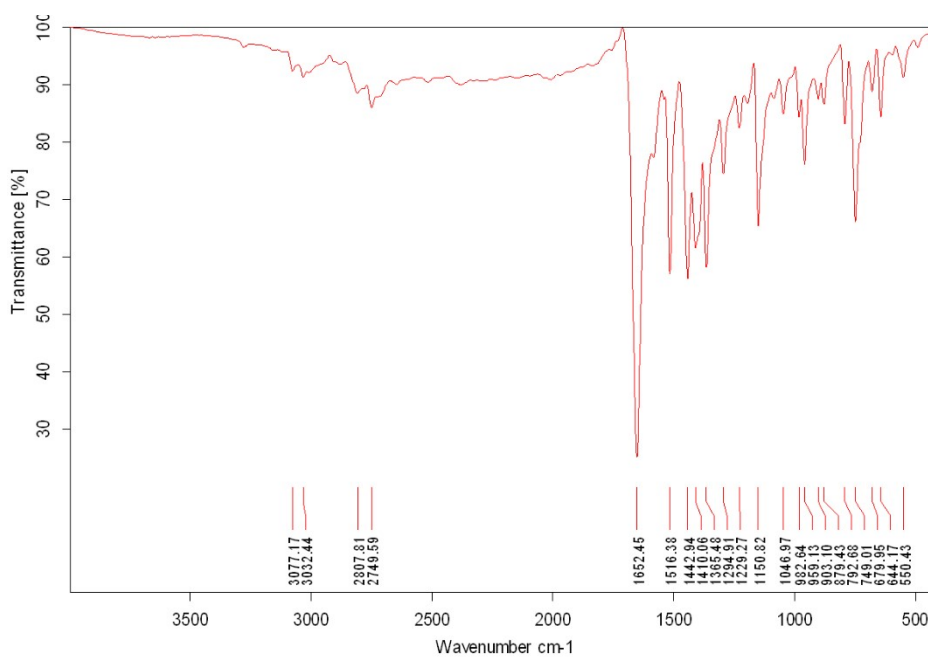


Figure S1. FT-IR spectra of compound **1**

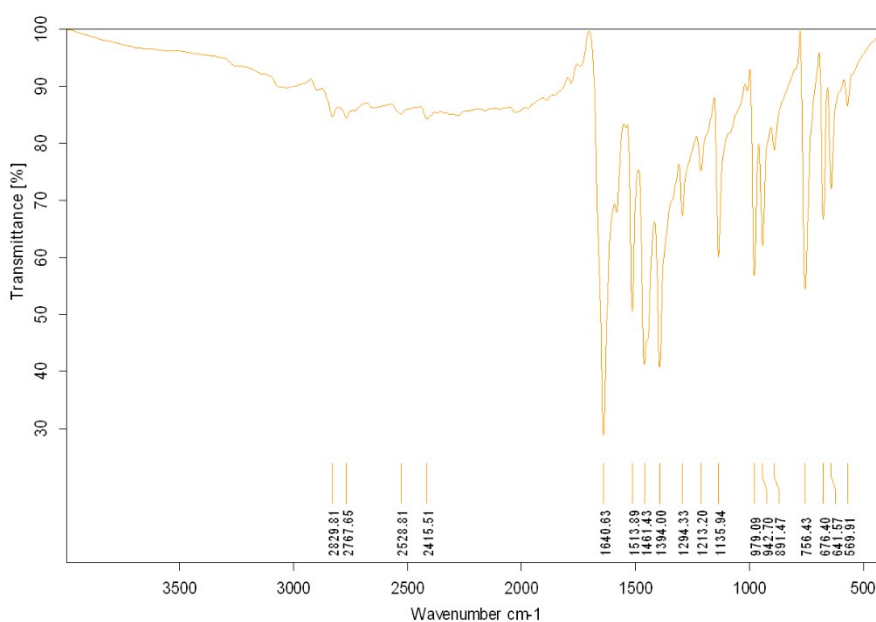


Figure S2. FT-IR spectra of co-crystal **3**

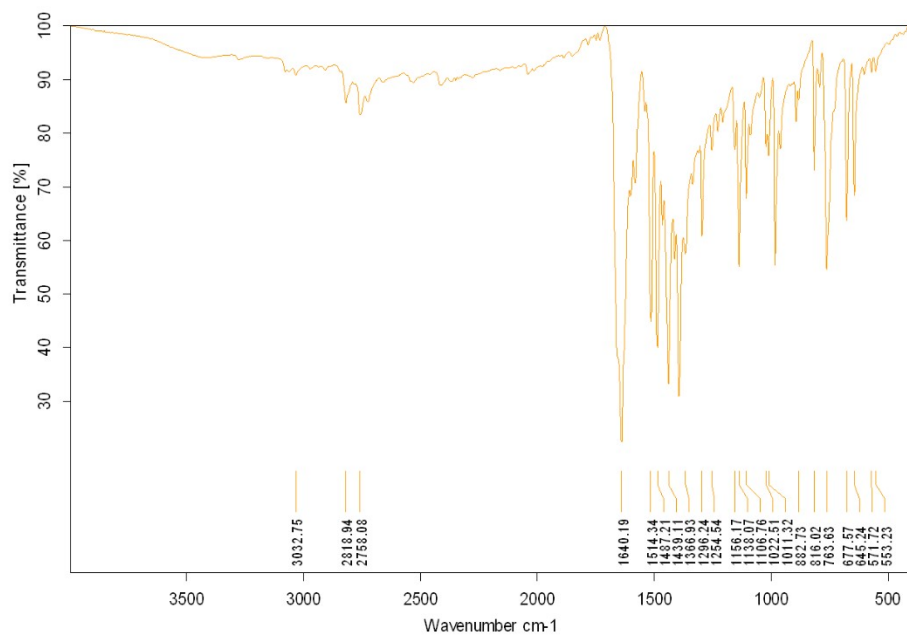


Figure S3. FT-IR spectra of co-crystal 4

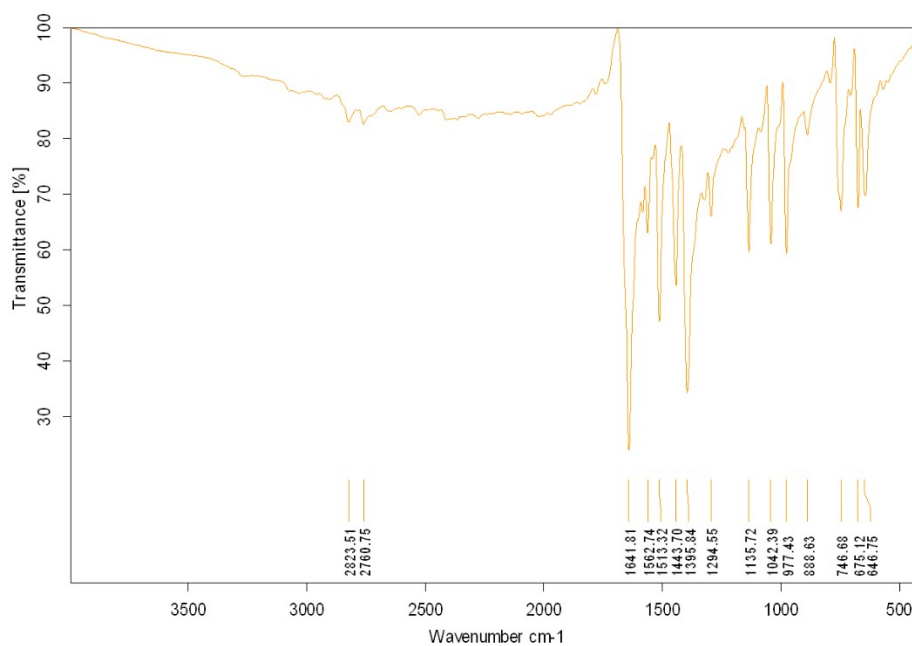


Figure S4. FT-IR spectra of co-crystal 5

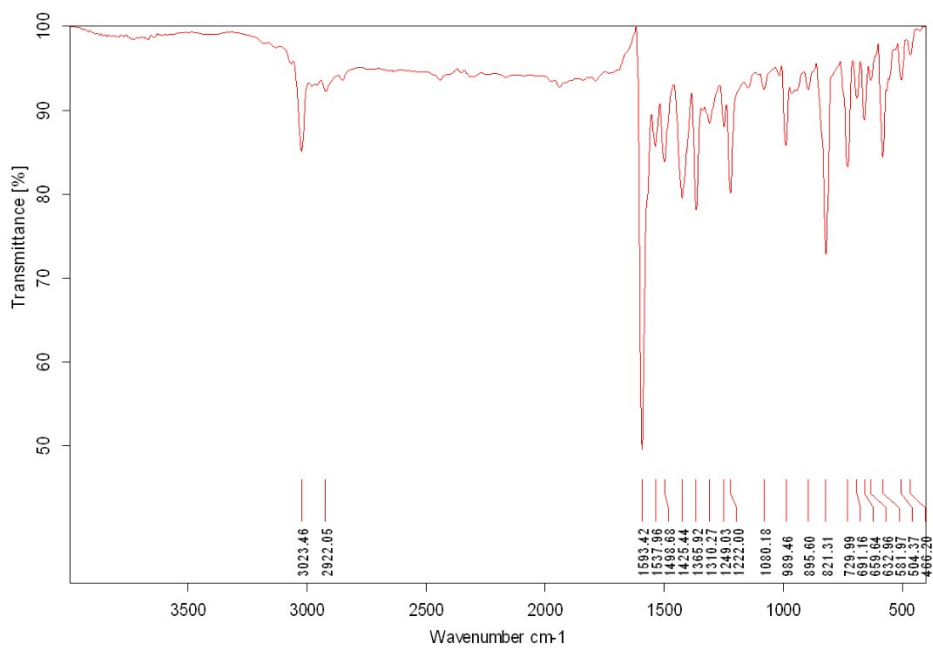


Figure S5. FT-IR spectra of compound **2**.

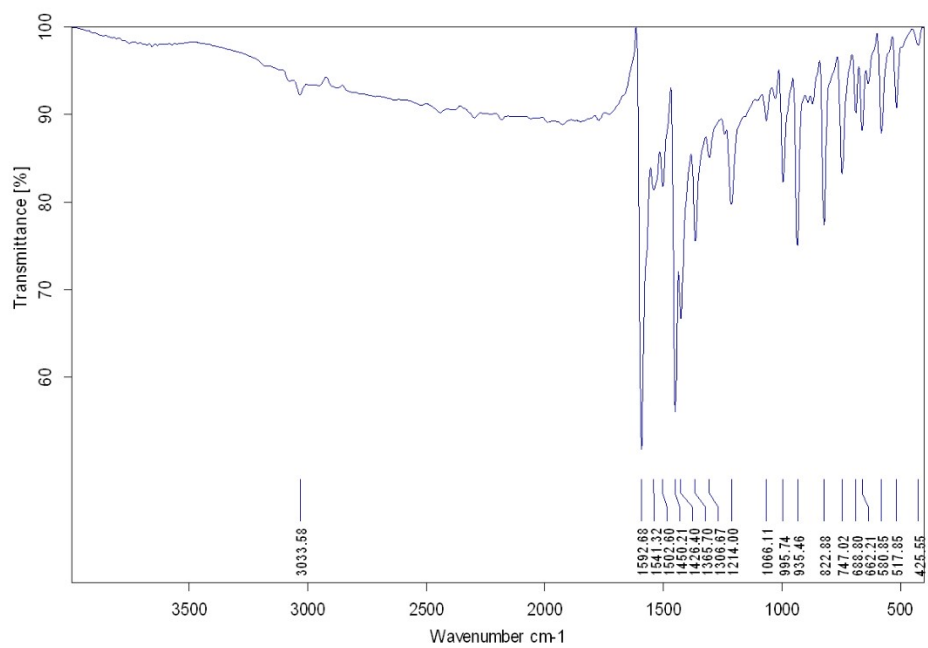


Figure S6. FT-IR spectra of co-crystal **6**

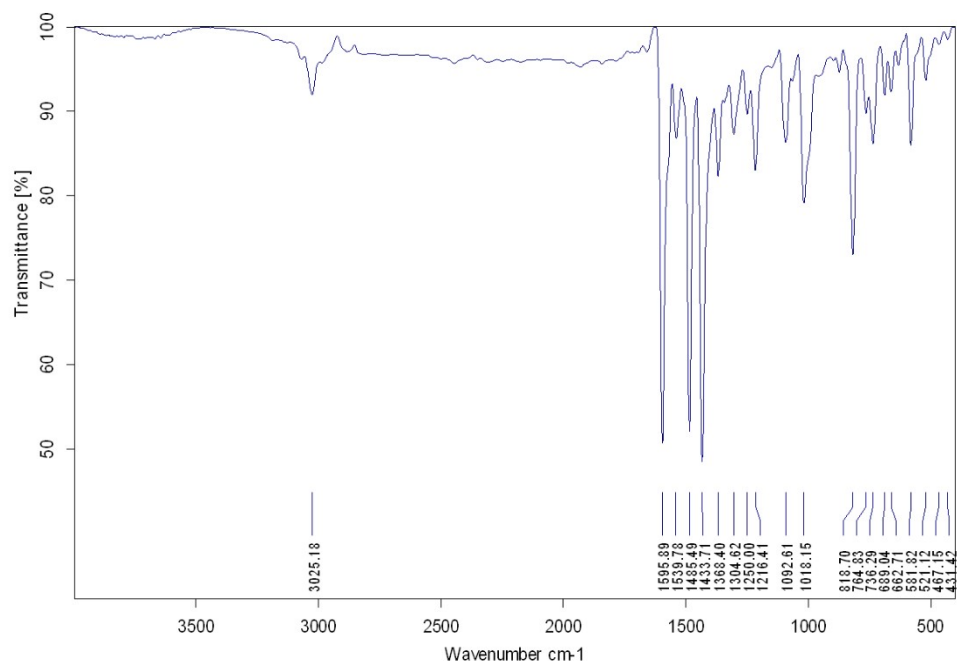


Figure S7. FT-IR spectra of co-crystal 7

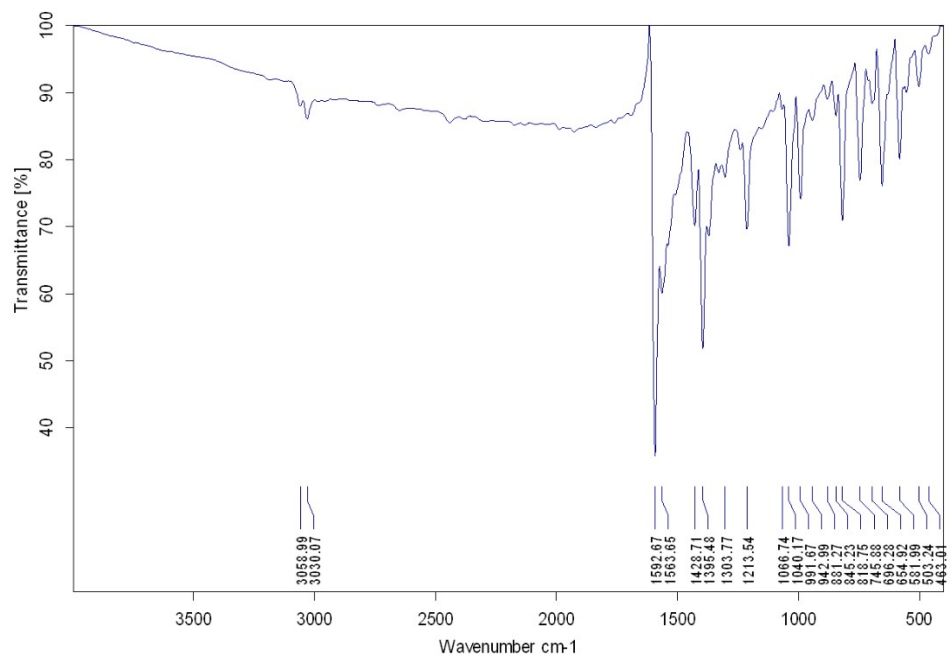


Figure S8. FT-IR spectra of co-crystal 8.

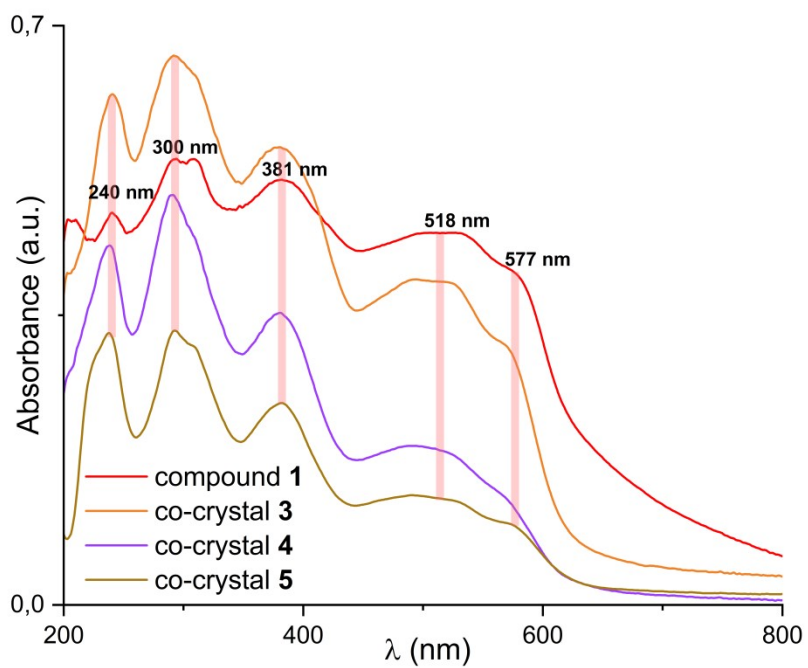


Figure S9. Electronic spectra of compounds **1**, **3**, **4** and **5**.

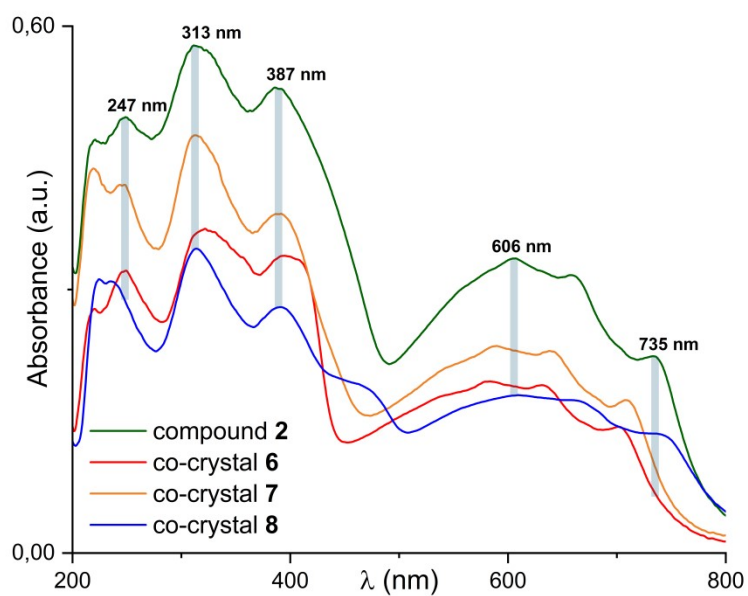


Figure S10. Electronic spectra of compounds **2**, **6**, **7** and **8**.

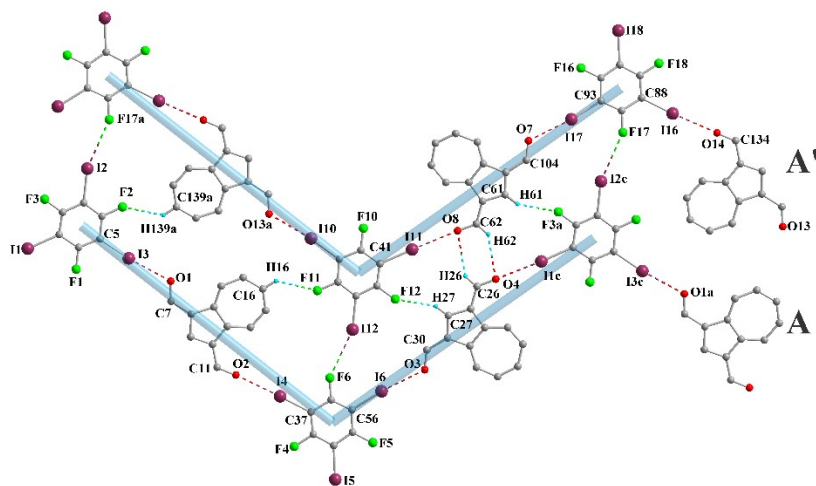


Figure S11. Assembly of supramolecular chains, **A** and **A'** in crystal structure **5**

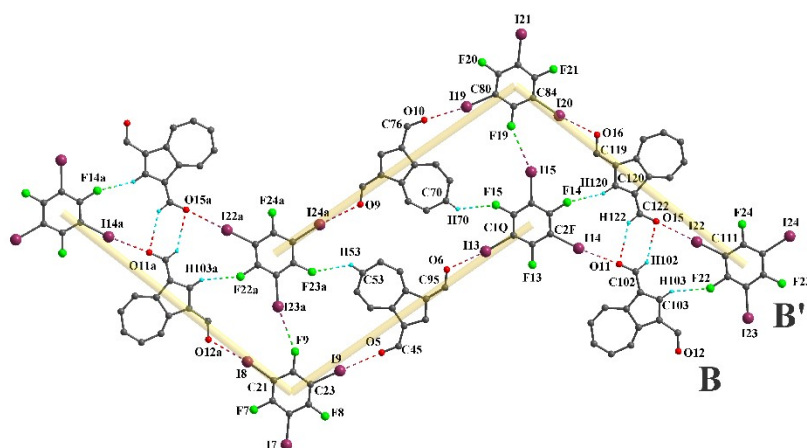


Figure S12. Assembly of supramolecular chains, **B** and **B'** in crystal structure **5**

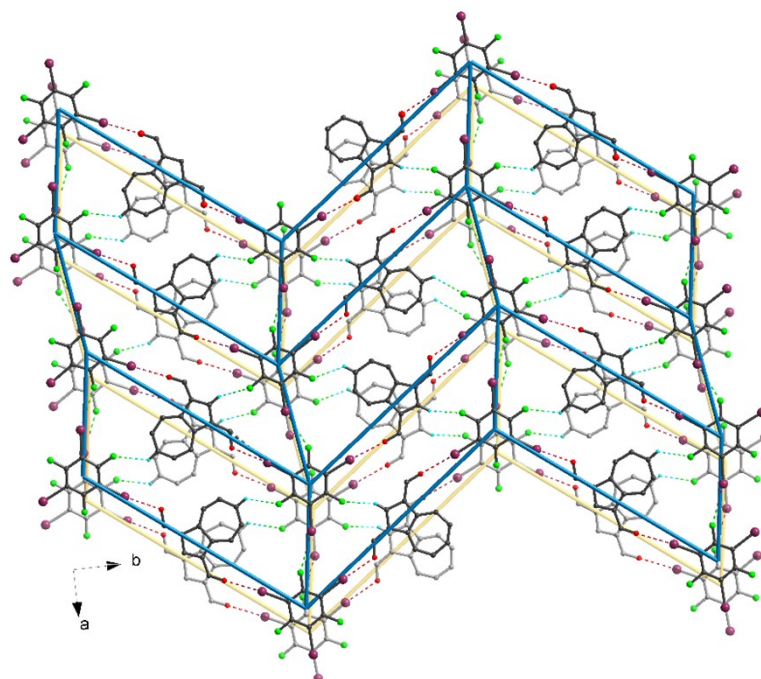


Figure S13. Crystal packing diagram in crystal structure **5**. View alongside crystallographic *c* axis.

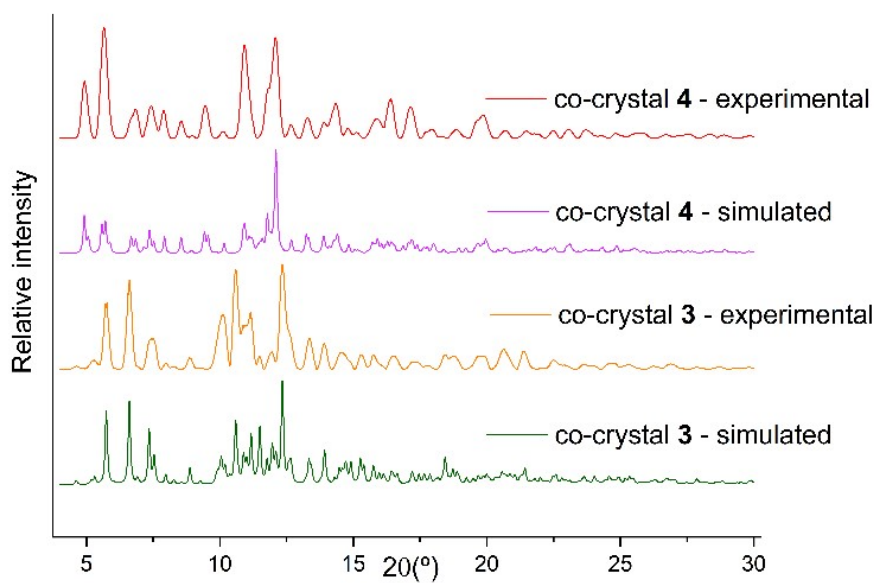


Figure S14 Powder X-ray diffractograms for compounds **3** and **4**

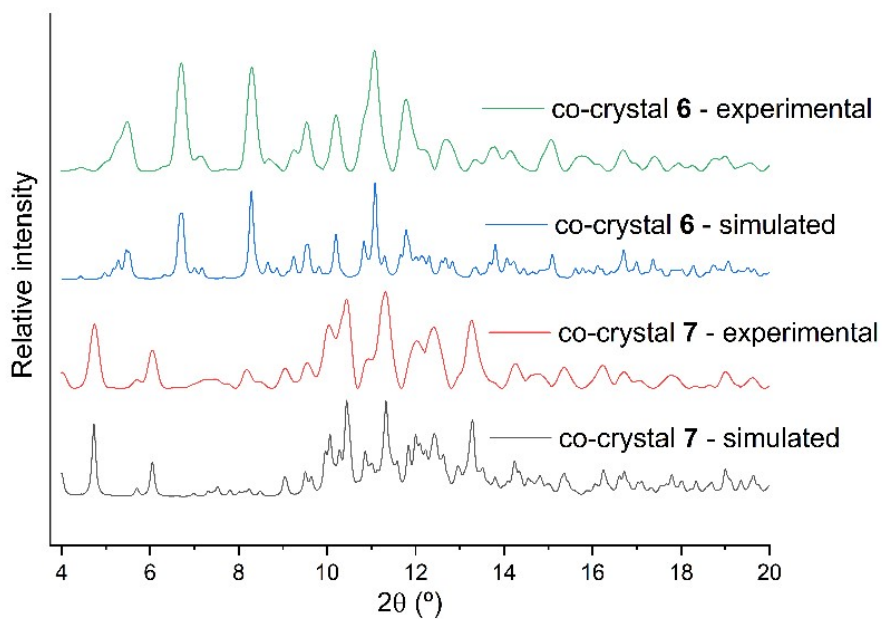


Figure S15 Powder X-ray diffractograms for compounds **6** and **7**

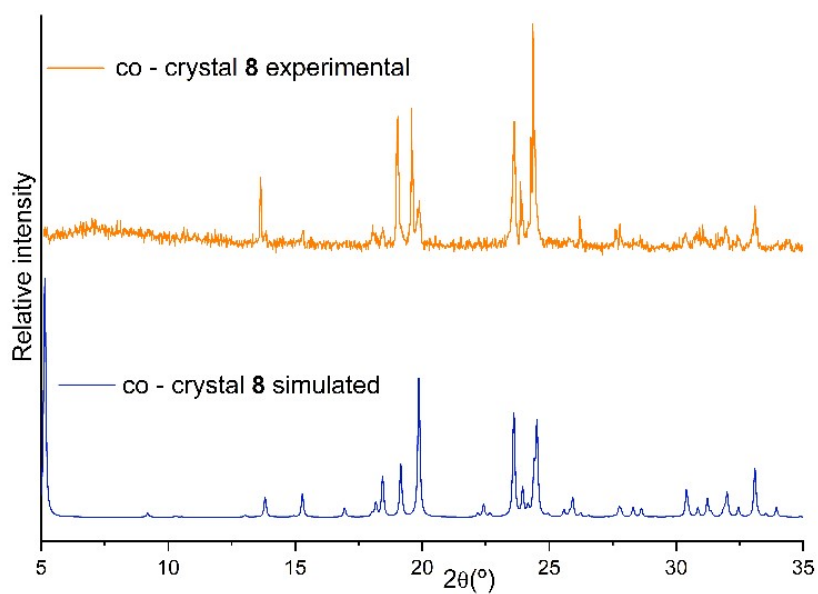


Figure S16 Powder X-ray diffractograms for compounds **8**

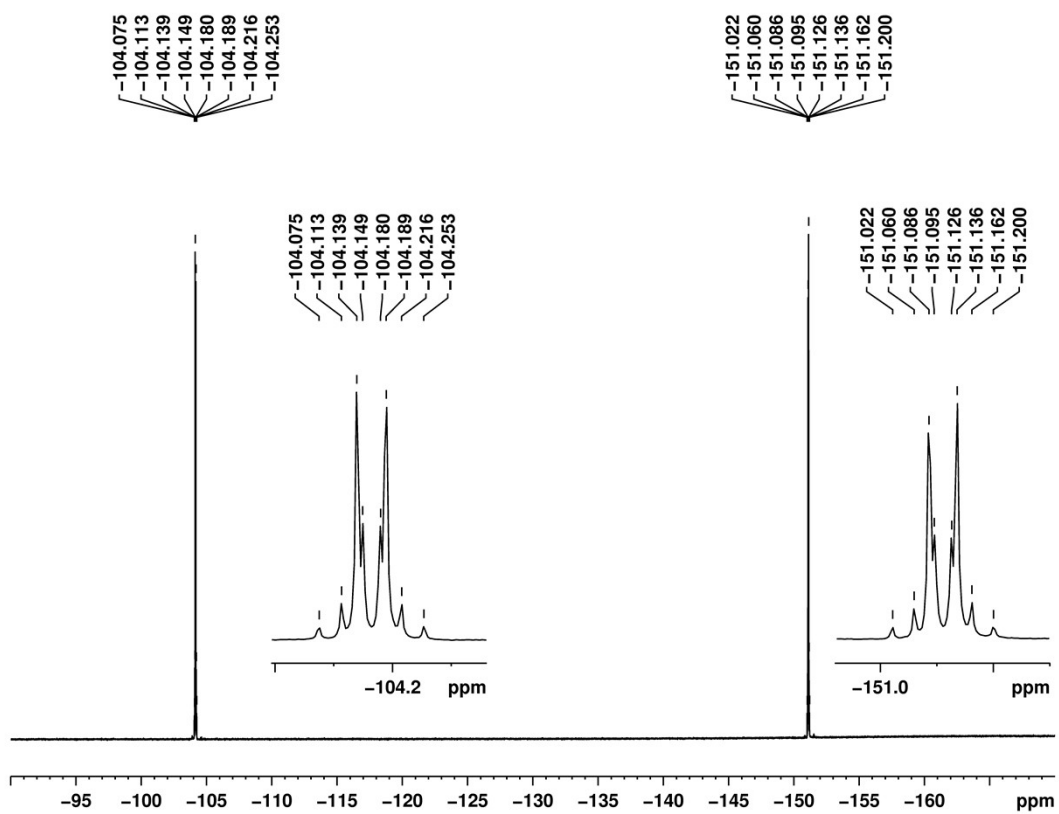


Figure S18. ^{19}F -NMR spectrum of co-crystal 4

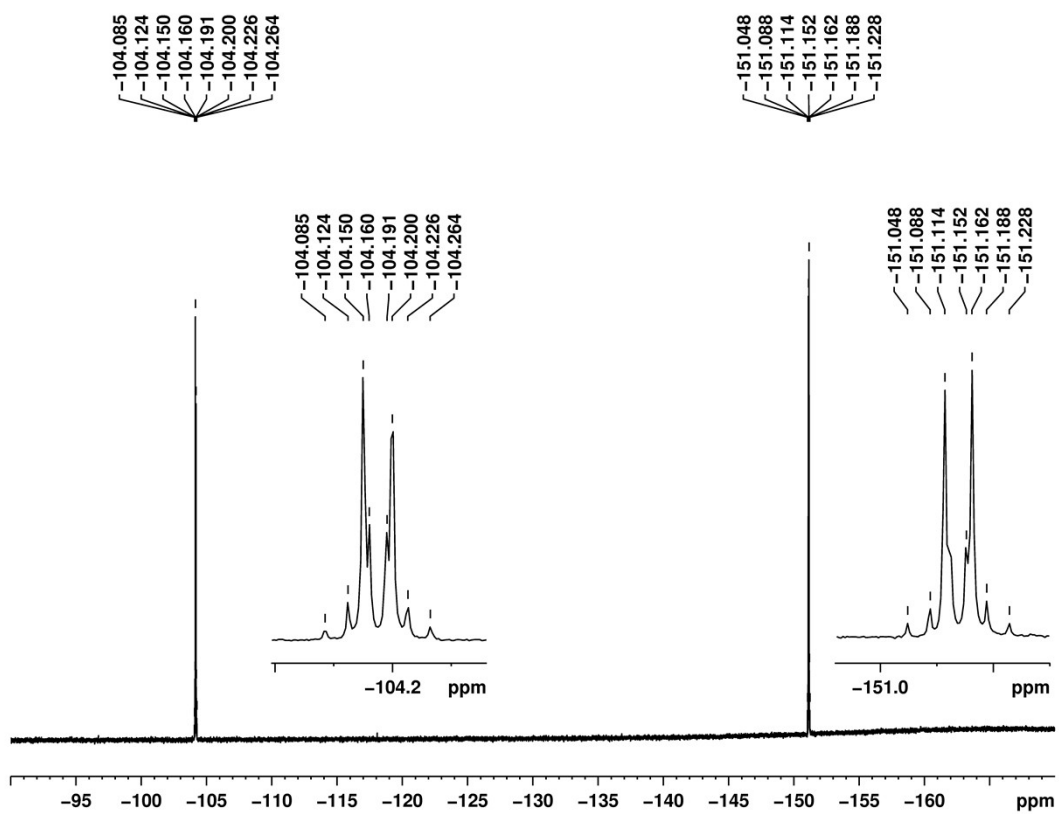


Figure S19. ^{19}F -NMR spectrum of co-crystal 7

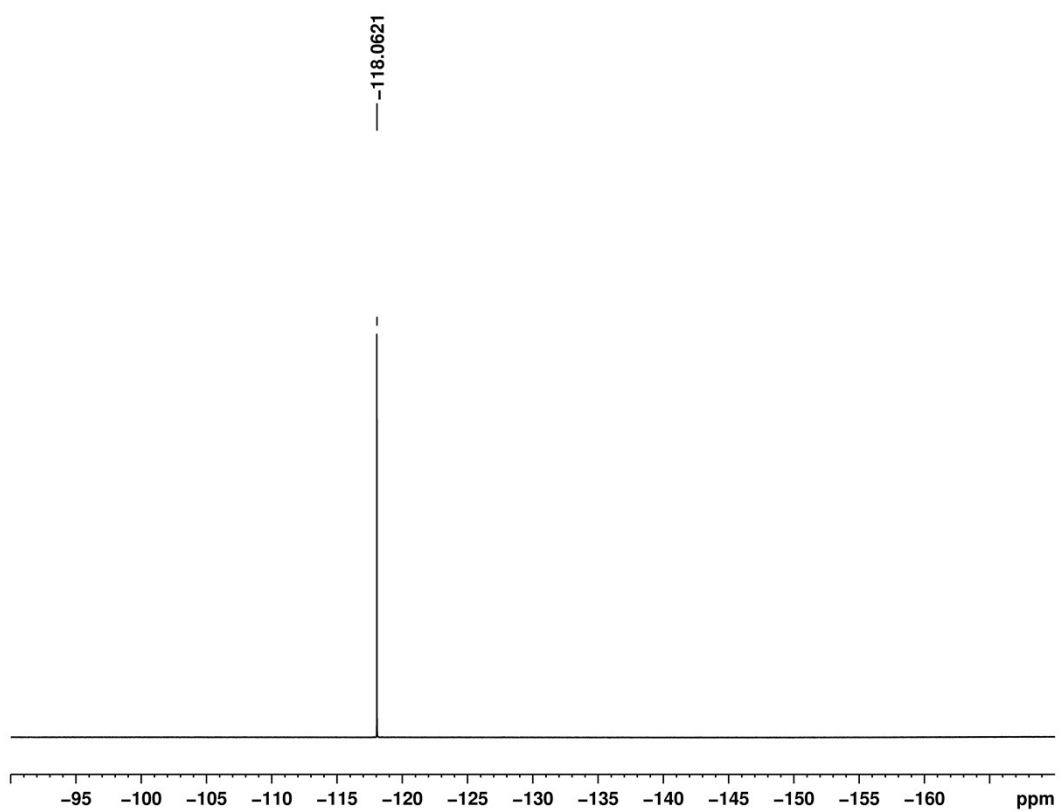


Figure S20. ^{19}F -NMR spectrum of 1,4-diiodopertetrafluorobenzene (1,4-ditfb)

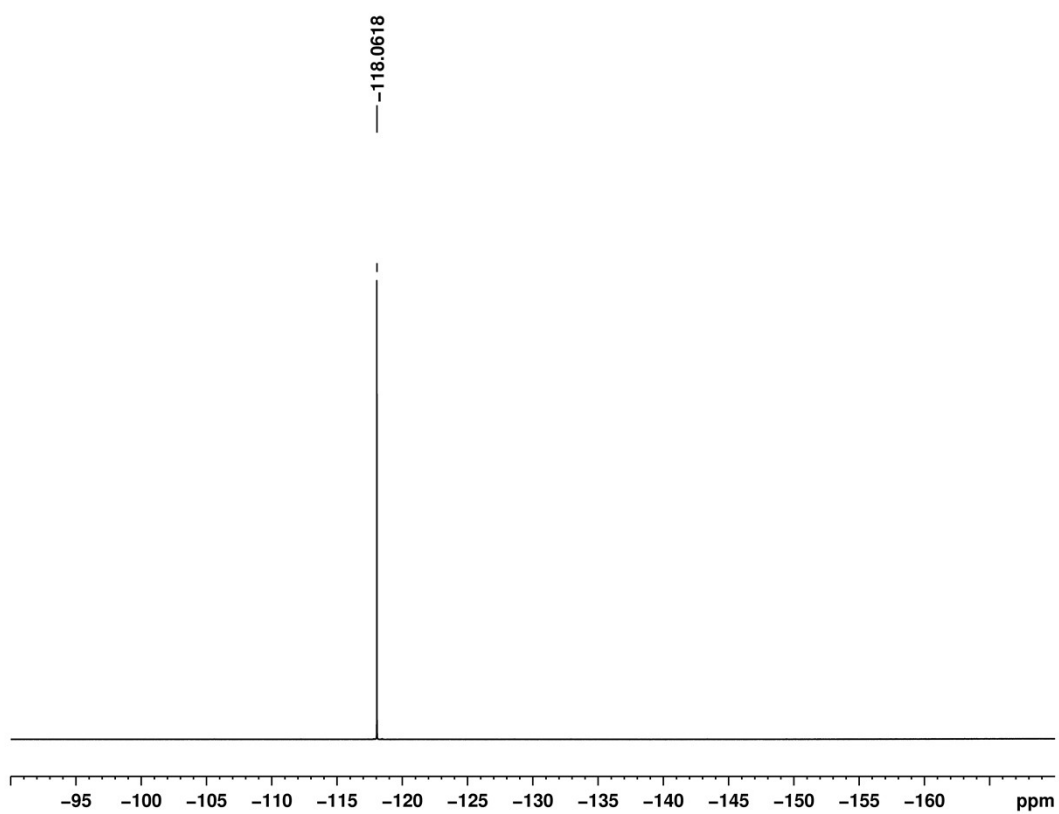


Figure S21. ^{19}F -NMR spectrum of co-crystal **3**

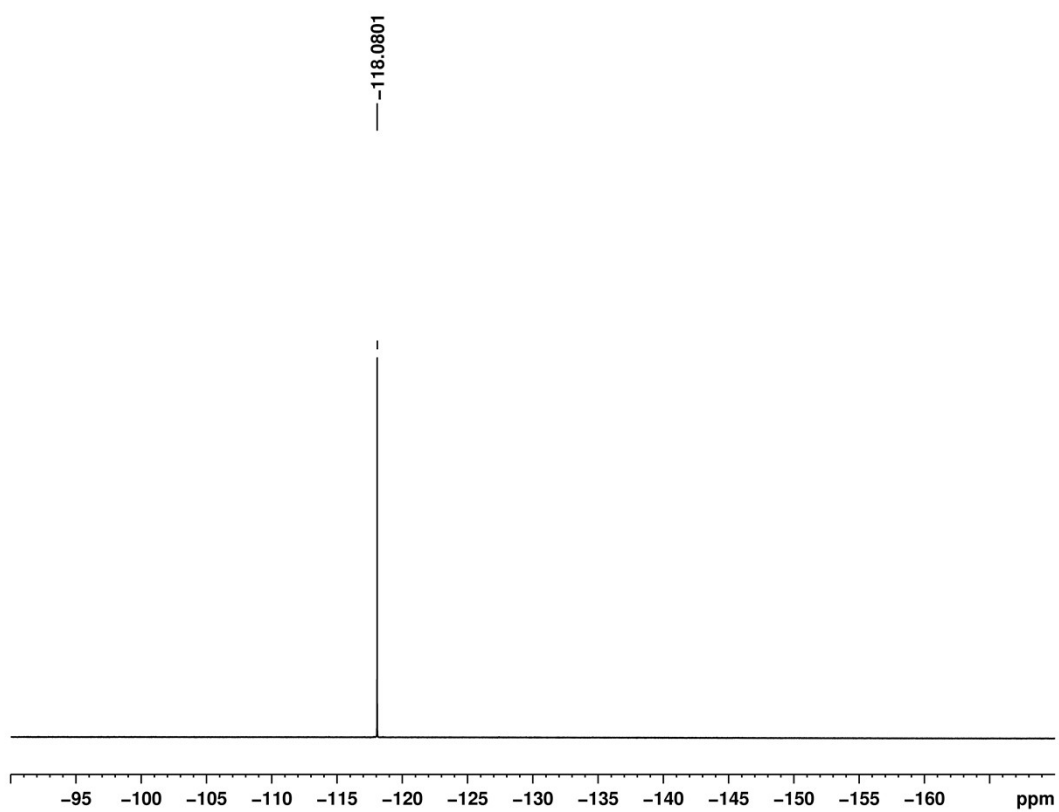


Figure S22. ^{19}F -NMR spectrum of co-crystal **6**

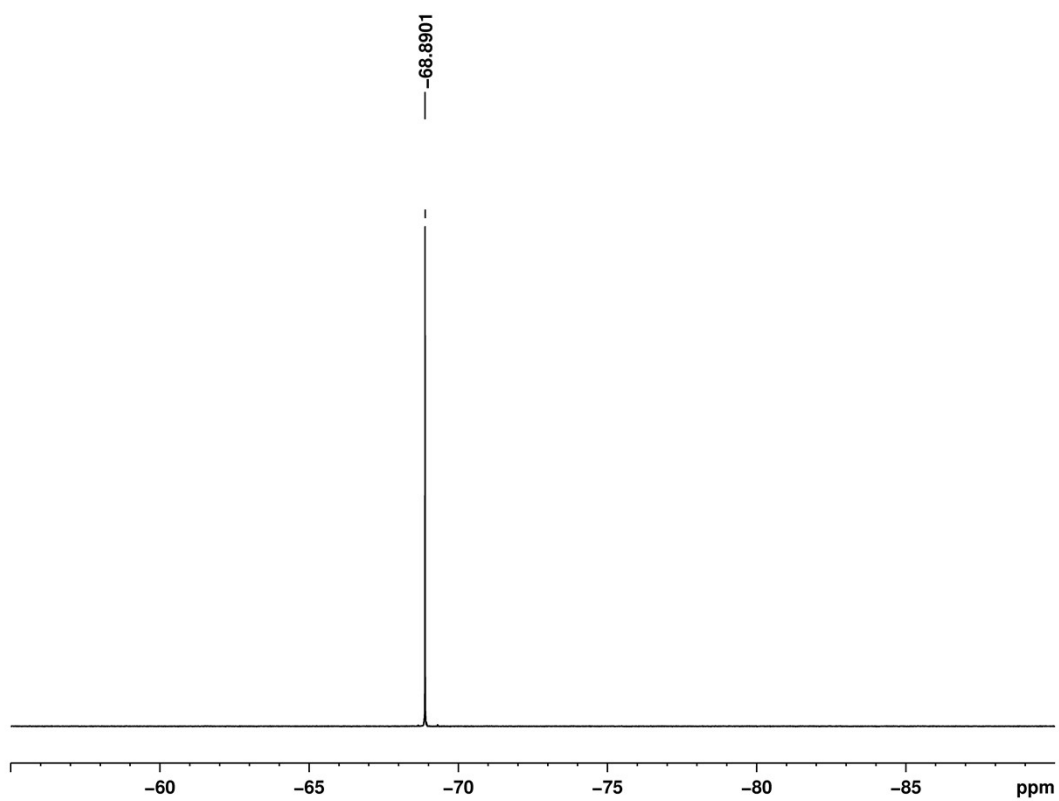


Figure S23. ^{19}F -NMR spectrum of triiodopertrifluorobenzene (1,3,5-titfb)

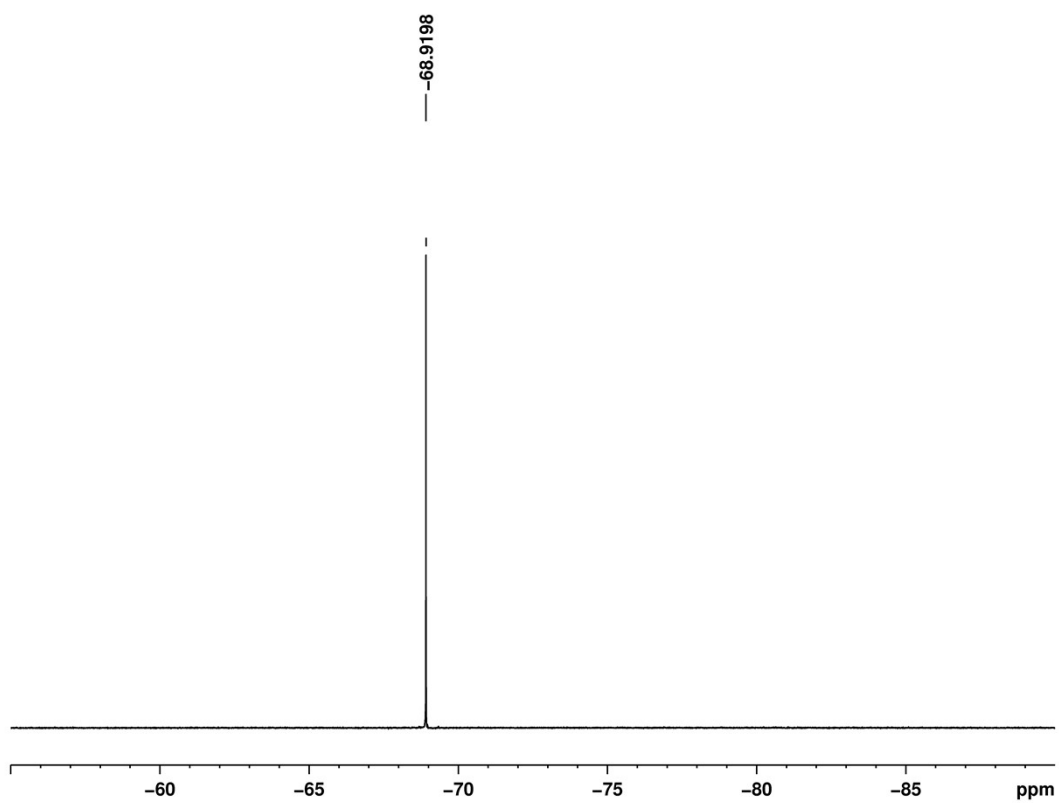


Figure S24. ^{19}F -NMR spectrum of co-crystal **8**

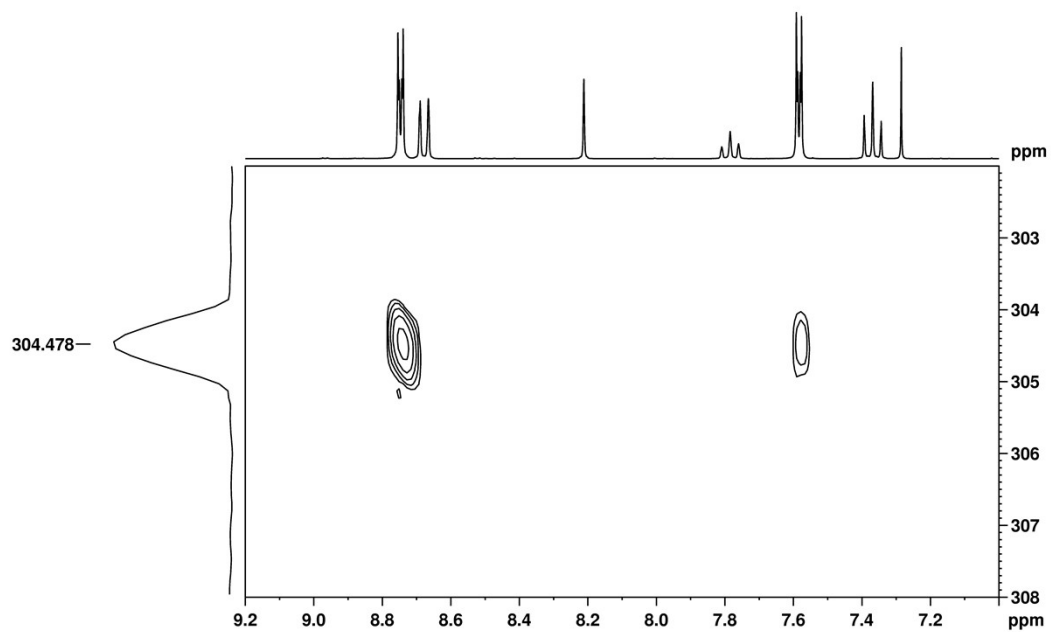


Figure S25. ^1H - ^{15}N HMBC NMR spectrum of azbipy, **2**

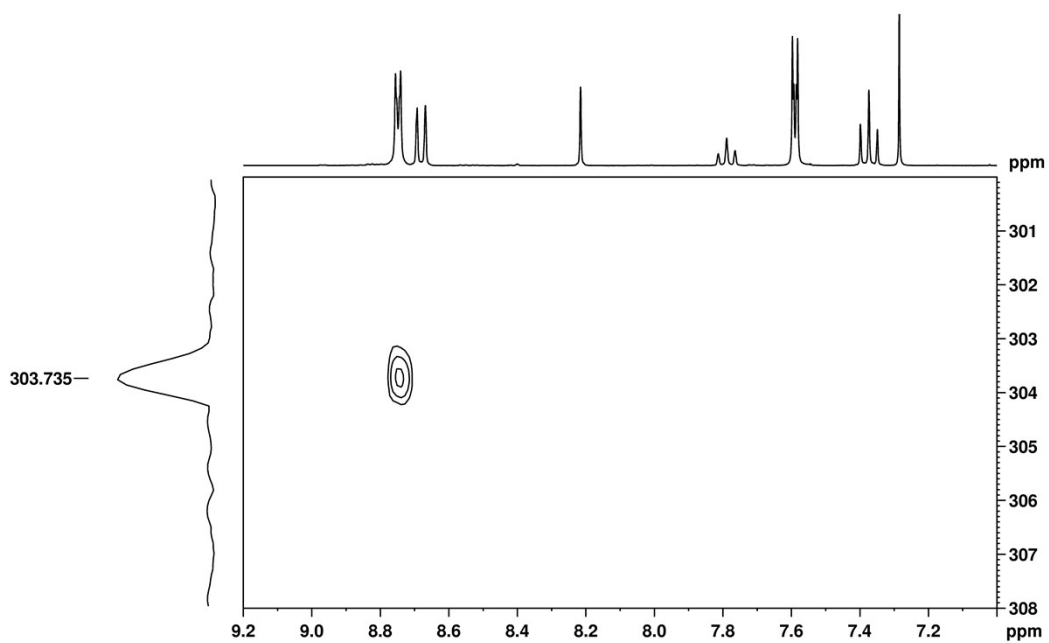


Figure S26. ^1H - ^{15}N HMBC NMR spectrum of co-crystal **6**

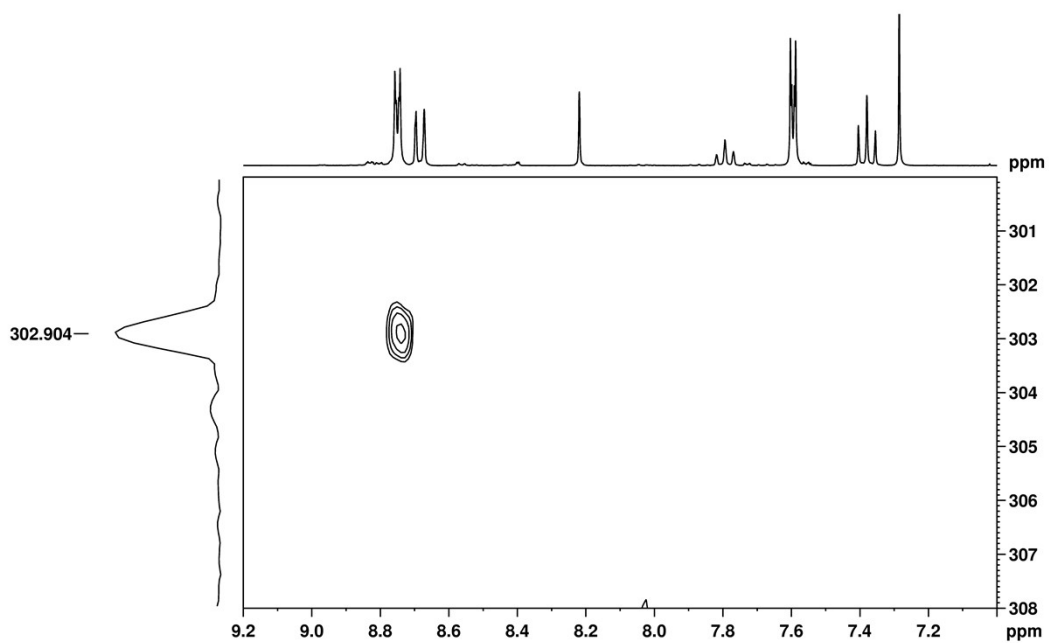


Figure S27. ^1H - ^{15}N HMBC NMR spectrum of co-crystal **7**

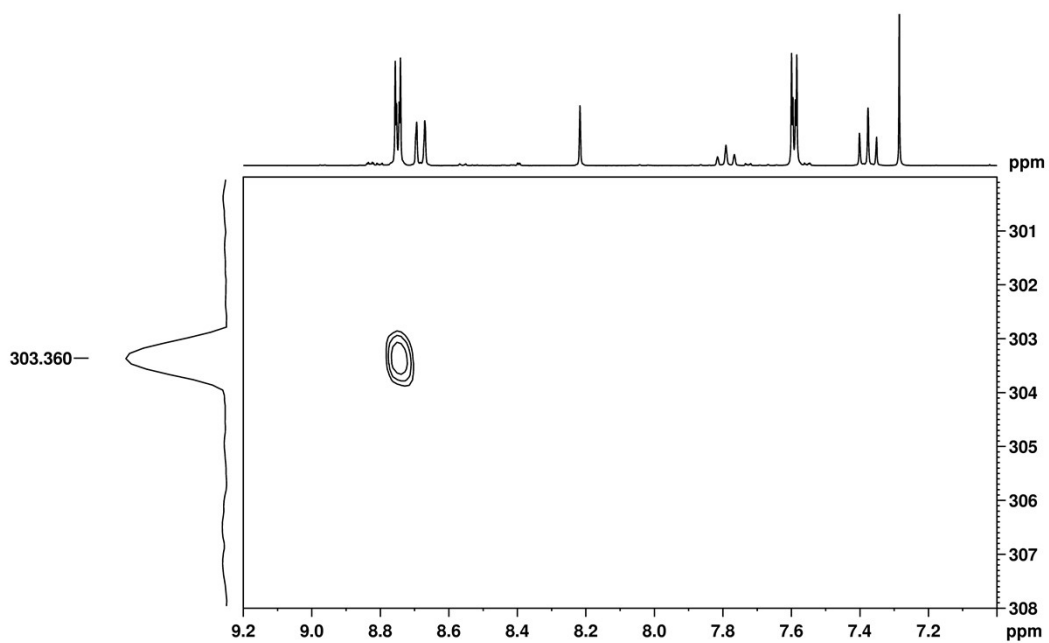


Figure S28. ^1H - ^{15}N HMBC NMR spectrum of co-crystal **8**

Table S1. Cartesian atomic coordinates for model supramolecular associates.

| 3 | | | |
|----------|-----------|-----------|-----------|
| I | 12.985538 | 6.000650 | 1.721057 |
| F | 14.240994 | 6.174341 | -1.253918 |
| F | 15.518262 | 8.103018 | -2.551791 |
| C | 14.461139 | 7.332195 | -0.612982 |
| C | 15.135435 | 8.340916 | -1.275620 |
| C | 14.027384 | 7.507847 | 0.687282 |
| I | 16.458462 | 11.052950 | -1.721057 |
| F | 15.203006 | 10.879259 | 1.253918 |
| F | 13.925738 | 8.950582 | 2.551791 |
| C | 14.982861 | 9.721405 | 0.612982 |
| C | 14.308565 | 8.712684 | 1.275620 |
| C | 15.416616 | 9.545753 | -0.687282 |
| I | 7.601467 | 1.402232 | 15.021084 |
| F | 5.215702 | 0.545033 | 19.770266 |
| F | 5.634912 | 0.075889 | 17.201003 |
| C | 7.164720 | 1.863958 | 17.021504 |
| C | 6.057645 | 1.353203 | 19.103030 |
| C | 6.285393 | 1.104221 | 17.774076 |
| I | 6.236360 | 2.861168 | 21.761491 |
| F | 8.622125 | 3.718367 | 17.012309 |
| F | 8.202915 | 4.187511 | 19.581571 |
| C | 6.673107 | 2.399442 | 19.761070 |
| C | 7.780182 | 2.910197 | 17.679545 |
| C | 7.552434 | 3.159179 | 19.008499 |
| C | 10.380414 | 0.423782 | 8.638388 |
| C | 12.262060 | -0.862912 | 5.752611 |
| H | 12.423516 | -0.409389 | 4.957040 |
| C | 10.418892 | 1.513507 | 7.760388 |
| H | 10.009113 | 2.332694 | 7.919895 |
| C | 11.596179 | -0.138134 | 6.726613 |
| C | 9.692901 | 0.471532 | 9.936629 |
| C | 11.106470 | -0.633541 | 8.039567 |
| C | 12.611159 | -3.108019 | 6.810478 |
| H | 13.033891 | -3.921902 | 6.655972 |
| C | 12.611426 | 2.208441 | 4.815023 |
| H | 13.311102 | 1.641418 | 5.047857 |
| C | 11.157358 | 1.205690 | 6.608541 |
| C | 11.956345 | -2.997170 | 8.022280 |
| H | 11.971886 | -3.759398 | 8.555333 |
| C | 12.723859 | -2.176039 | 5.796750 |
| H | 13.172154 | -2.467468 | 5.035663 |
| N | 11.828201 | 3.960699 | 3.382526 |
| C | 11.277752 | -1.908298 | 8.557466 |
| H | 10.880006 | -2.057014 | 9.384945 |

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| N | 8.352487 | 0.768265 | 12.403820 |
| C | 11.399637 | 2.149606 | 5.508007 |
| C | 12.763733 | 3.112282 | 3.782720 |
| H | 13.579858 | 3.125968 | 3.337007 |
| C | 10.098828 | -0.208054 | 11.080199 |
| H | 10.833086 | -0.777857 | 11.050239 |
| C | 8.577167 | 1.290105 | 10.087805 |
| H | 8.242020 | 1.751976 | 9.353514 |
| C | 7.964100 | 1.422270 | 11.314504 |
| H | 7.239230 | 2.000549 | 11.383821 |
| C | 9.401376 | -0.029844 | 12.265150 |
| H | 9.688765 | -0.502246 | 13.012921 |
| C | 10.428165 | 3.063679 | 5.108548 |
| H | 9.607765 | 3.089226 | 5.545893 |
| C | 10.678447 | 3.931707 | 4.067049 |
| H | 10.009703 | 4.531866 | 3.826215 |
| 4 | | | |
| I | 1.172716 | 29.113266 | 13.981182 |
| I | 1.601243 | 32.178963 | 16.012720 |
| F | 0.238165 | 34.487450 | 14.443254 |
| F | -0.467606 | 30.039968 | 11.459734 |
| F | -1.180854 | 34.588044 | 12.173885 |
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| C | -0.638802 | 33.431905 | 12.566689 |
| C | 0.086826 | 33.355771 | 13.732829 |
| C | -0.804431 | 32.312628 | 11.819220 |
| I | 5.146257 | 13.950143 | 12.332146 |
| I | 3.764840 | 11.893139 | 15.065122 |
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| F | 6.962819 | 9.258066 | 10.481448 |
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| F | 5.730643 | 7.761218 | 12.370068 |
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| C | 6.038193 | 11.199662 | 11.420935 |
| C | 4.745018 | 11.087356 | 13.400742 |
| C | 4.863231 | 9.726929 | 13.353615 |
| C | 6.199302 | 9.861284 | 11.415894 |
| C | 5.594387 | 9.101319 | 12.378178 |
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| N | 2.070792 | 26.601179 | 14.642287 |
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| H | 3.496204 | 23.575582 | 17.859736 |
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| H | 5.144139 | 18.999533 | 16.873756 |

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| C | 3.435147 | 21.594920 | 14.455090 |
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| C | 4.762153 | 19.187905 | 13.000704 |
| H | 5.013987 | 19.994894 | 12.613488 |
| C | 4.201534 | 19.169302 | 14.254523 |
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| H | 3.427102 | 17.866063 | 15.598192 |
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| H | 5.681985 | 19.307068 | 18.967854 |
| C | 1.659771 | 25.958000 | 15.725350 |
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| C | 4.063981 | 16.811207 | 14.009020 |
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| C | 2.846199 | 25.916660 | 13.807357 |
| H | 3.143900 | 26.339670 | 13.035206 |
| C | 4.967682 | 21.090573 | 19.396936 |
| H | 5.255897 | 21.004345 | 20.277459 |
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| I | 17.169700 | 1.579127 | 6.919269 |
| I | 20.153794 | 2.239373 | 12.167554 |
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| F | 19.507870 | 1.816530 | 9.035733 |
| C | 17.169700 | 1.812076 | 8.992281 |
| C | 18.344451 | 1.895220 | 9.703665 |
| C | 17.169700 | 2.124606 | 11.728226 |
| C | 18.381537 | 2.056310 | 11.066831 |
| I | 14.185606 | 2.239373 | 12.167554 |
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| C | 15.994949 | 1.895220 | 9.703665 |
| C | 15.957863 | 2.056310 | 11.066831 |
| C | 26.355146 | 3.090403 | 17.780952 |
| H | 26.165936 | 2.726429 | 16.946402 |
| C | 25.252851 | 3.486818 | 18.518677 |
| N | 22.218965 | 2.658355 | 14.252679 |
| C | 23.104922 | 3.711750 | 19.226600 |
| C | 23.900222 | 3.391797 | 18.118379 |

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| C | 23.378950 | 3.287868 | 14.399570 |
| H | 23.810665 | 3.591593 | 13.634063 |
| C | 23.980920 | 3.517254 | 15.615075 |
| H | 24.798507 | 3.959049 | 15.652240 |
| C | 22.152690 | 2.423773 | 16.633893 |
| H | 21.698449 | 2.102944 | 17.379327 |
| C | 23.369335 | 3.091145 | 16.785783 |
| C | 28.285707 | 3.711750 | 19.226600 |
| H | 29.215755 | 3.711735 | 19.226638 |
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| H | 20.813694 | 1.806516 | 15.301759 |
| H | 22.172951 | 3.711750 | 19.226600 |
| C | 26.355146 | 4.333097 | 20.672248 |
| H | 26.165936 | 4.697071 | 21.506798 |
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| H | 21.698449 | 5.320556 | 21.073873 |
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| C | 21.630731 | 5.178634 | 23.077688 |
| H | 20.813694 | 5.616984 | 23.151441 |
| 6 | | | |
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| I | 6.789264 | 5.390588 | 11.454634 |
| F | 4.251498 | 8.901284 | 8.324928 |
| F | 5.337693 | 8.092110 | 10.600521 |
| F | 5.621412 | 4.904133 | 6.253280 |
| F | 6.638629 | 4.063478 | 8.553407 |
| C | 6.019759 | 6.050038 | 9.645201 |
| C | 4.921020 | 6.938700 | 7.211666 |
| C | 5.416005 | 7.277441 | 9.531728 |
| C | 4.864054 | 7.718008 | 8.355596 |
| C | 6.056529 | 5.261264 | 8.502804 |
| C | 5.534305 | 5.714518 | 7.322072 |
| O | 0.554388 | 13.416775 | -1.298805 |
| O | 3.552679 | 8.486079 | 2.698816 |
| C | 2.454381 | 10.161889 | 1.415345 |
| C | 2.182268 | 10.893327 | -0.759042 |
| C | 2.796889 | 9.848153 | 0.061337 |

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|---|-----------|-----------|-----------|
| C | 1.497980 | 11.772933 | 0.118073 |
| C | 1.672990 | 11.313683 | 1.409211 |
| H | 1.318709 | 11.719104 | 2.166720 |
| C | 0.715463 | 12.946605 | -0.203945 |
| H | 0.296778 | 13.379818 | 0.506028 |
| C | 2.259666 | 11.028813 | -2.143719 |
| H | 1.826961 | 11.769859 | -2.502539 |
| C | 2.839257 | 9.464562 | 2.612945 |
| H | 2.503898 | 9.802934 | 3.411856 |
| C | 3.556524 | 8.768870 | -0.361887 |
| H | 3.869585 | 8.208207 | 0.311284 |
| C | 3.910365 | 8.415155 | -1.649958 |
| H | 4.425329 | 7.644525 | -1.726629 |
| C | 2.898720 | 10.200881 | -3.053036 |
| H | 2.839489 | 10.465230 | -3.942418 |
| C | 3.608707 | 9.042274 | -2.827623 |
| H | 3.932361 | 8.622770 | -3.592799 |
| I | -3.021440 | 16.585546 | -9.950351 |
| I | -0.430793 | 14.355800 | -3.879548 |
| F | -2.968560 | 17.866497 | -7.009255 |
| F | -1.882365 | 17.057323 | -4.733662 |
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| F | -0.581429 | 13.028690 | -6.780776 |
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| C | -2.299038 | 15.903913 | -8.122517 |
| C | -1.804052 | 16.242654 | -5.802455 |
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| C | -1.163529 | 14.226477 | -6.831378 |
| C | -1.685753 | 14.679730 | -8.012110 |
| | 7 | | |
| I | 4.011190 | 9.659645 | 1.781327 |
| I | 4.540432 | 8.499962 | 5.274706 |
| F | 1.996619 | 6.931862 | 6.053213 |
| F | 1.237842 | 8.571128 | 0.954604 |
| F | -0.209285 | 6.210211 | 4.723141 |
| F | -0.614669 | 7.039938 | 2.200161 |
| C | 2.814208 | 8.123619 | 4.173101 |
| C | 2.625417 | 8.533584 | 2.872124 |
| C | 1.821252 | 7.364023 | 4.775790 |
| C | 1.457923 | 8.163470 | 2.220943 |
| C | 0.697181 | 7.012890 | 4.128765 |
| C | 0.517071 | 7.420898 | 2.840258 |
| O | 6.916959 | 8.592640 | 7.074321 |
| O | 8.313740 | 6.470859 | 13.638781 |
| C | 10.672329 | 9.629818 | 8.968288 |
| H | 11.050315 | 10.105079 | 8.263946 |
| C | 7.777558 | 7.140475 | 11.423379 |
| C | 7.337116 | 7.800303 | 9.293879 |

| | | | |
|----------|-----------|------------|-----------|
| C | 8.913855 | 7.882656 | 10.984178 |
| C | 8.626681 | 8.307731 | 9.601458 |
| C | 6.847189 | 7.099236 | 10.382875 |
| H | 6.024706 | 6.666895 | 10.416002 |
| C | 9.432116 | 9.057471 | 8.771548 |
| H | 9.074427 | 9.206076 | 7.926675 |
| C | 10.018090 | 8.165956 | 11.717104 |
| H | 10.007286 | 7.811004 | 12.576482 |
| C | 7.537022 | 6.501685 | 12.717429 |
| H | 6.714708 | 6.084764 | 12.840488 |
| C | 6.590152 | 7.938465 | 8.038623 |
| H | 5.785708 | 7.476290 | 7.978437 |
| C | 11.142090 | 8.878269 | 11.419223 |
| H | 11.792033 | 8.942547 | 12.081820 |
| C | 11.406404 | 9.535038 | 10.179208 |
| H | 12.217746 | 9.989909 | 10.162305 |
| I | 6.916211 | 4.639121 | 15.636244 |
| I | 7.445453 | 3.479438 | 19.129623 |
| F | 4.901640 | 1.911338 | 19.908131 |
| F | 4.142863 | 3.550605 | 14.809521 |
| F | 2.695736 | 1.189687 | 18.578059 |
| F | 2.290352 | 2.019415 | 16.055078 |
| C | 5.719229 | 3.103095 | 18.028018 |
| C | 5.530438 | 3.513061 | 16.727042 |
| C | 4.726273 | 2.343500 | 18.630707 |
| C | 4.362944 | 3.142947 | 16.075861 |
| C | 3.602202 | 1.992367 | 17.983683 |
| C | 3.422092 | 2.400375 | 16.695175 |
| 8 | | | |
| I | 8.601607 | 6.222983 | 12.808023 |
| I | 8.882937 | 0.176382 | 12.425585 |
| I | 13.939718 | 3.408830 | 12.821143 |
| F | 11.715836 | 5.655865 | 12.947040 |
| F | 7.767246 | 3.157118 | 12.670680 |
| F | 11.943892 | 1.001336 | 12.609267 |
| C | 11.852414 | 3.325538 | 12.773966 |
| C | 9.701592 | 4.437113 | 12.787924 |
| C | 11.184384 | 2.128222 | 12.651139 |
| C | 11.090485 | 4.470797 | 12.832588 |
| C | 9.824751 | 2.033294 | 12.606475 |
| C | 9.126022 | 3.196926 | 12.670680 |
| I | 9.952740 | -13.558459 | 12.012162 |
| I | 9.405215 | -7.520432 | 11.898268 |
| I | 4.502928 | -10.987444 | 12.239112 |
| F | 6.839772 | -13.136795 | 12.179374 |
| F | 6.392644 | -8.482266 | 12.084462 |
| F | 10.649063 | -10.439006 | 11.939304 |
| C | 6.573579 | -10.809531 | 12.173791 |

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| C | 8.768620 | -11.820053 | 12.081671 |
| C | 8.544010 | -9.403985 | 12.003508 |
| C | 7.391632 | -11.902733 | 12.157042 |
| C | 7.185713 | -9.587717 | 12.076088 |
| C | 9.322069 | -10.570680 | 12.023049 |
| O | 16.333070 | -0.829853 | 11.925346 |
| O | 10.610990 | -4.841322 | 11.456372 |
| C | 12.961853 | -2.122098 | 11.741106 |
| H | 12.434297 | -1.356305 | 11.753193 |
| C | 14.329230 | -2.091476 | 11.808102 |
| C | 14.787205 | -3.444964 | 11.777396 |
| C | 15.086631 | -0.842102 | 11.894639 |
| H | 14.625817 | -0.033745 | 11.923224 |
| C | 13.550945 | -5.652803 | 11.562449 |
| H | 12.705258 | -6.026941 | 11.460056 |
| C | 12.443000 | -3.392907 | 11.648986 |
| C | 16.109342 | -3.852235 | 11.916971 |
| H | 16.744142 | -3.180176 | 12.015903 |
| C | 11.098754 | -3.769556 | 11.548492 |
| H | 10.493536 | -3.061761 | 11.553963 |
| C | 13.597572 | -4.290128 | 11.657361 |
| C | 15.981392 | -6.292800 | 11.777396 |
| H | 16.532584 | -7.041383 | 11.790544 |
| C | 14.616954 | -6.553087 | 11.601530 |
| H | 14.388516 | -7.448532 | 11.498356 |
| C | 16.580357 | -5.156728 | 11.922554 |
| H | 17.497927 | -5.227679 | 12.053197 |
| O | 7.287604 | 8.714993 | 12.572977 |
| O | 1.567795 | 12.799954 | 11.936512 |
| C | 4.574947 | 12.196703 | 12.184957 |
| C | 5.276160 | 10.016423 | 12.369197 |
| C | 3.889259 | 9.998050 | 12.285451 |
| H | 3.350617 | 9.241873 | 12.328050 |
| C | 5.570101 | 14.520905 | 12.081671 |
| H | 5.360568 | 15.419474 | 11.974365 |
| C | 4.532735 | 13.608372 | 12.034215 |
| H | 3.690097 | 13.971242 | 11.883920 |
| C | 6.080515 | 8.794610 | 12.472483 |
| H | 5.613637 | 7.990356 | 12.459279 |
| C | 3.413414 | 11.385222 | 12.123543 |
| C | 5.757858 | 11.354601 | 12.288243 |
| C | 2.049101 | 11.709815 | 12.073296 |
| H | 1.453171 | 11.000183 | 12.151263 |
| C | 7.635866 | 13.041867 | 12.352448 |
| H | 8.562753 | 13.114502 | 12.388039 |
| C | 7.050899 | 11.764934 | 12.388737 |
| H | 7.660102 | 11.073032 | 12.499644 |
| C | 6.872172 | 14.193251 | 12.271494 |

| | | | |
|---|----------|-----------|-----------|
| H | 7.398465 | 14.955001 | 12.372491 |
|---|----------|-----------|-----------|