

Electronic Supporting Information for

**Intermolecular oxidative dehydrogenative 3,3'-coupling of benzo[*b*]furans and benzo[*b*]thiophenes promoted by DDQ/H<sup>+</sup>; total synthesis of Shandougenine B**

T. Wirtanen<sup>\*a</sup>, M. Muuronen<sup>a</sup>, J. Hurmalainen<sup>b</sup>, H. M. Tuononen<sup>b</sup>, M. Nieger<sup>a</sup> and J. Helaja<sup>\*a</sup>

<sup>a</sup>*Department of Chemistry, A.I. Virtasen aukio 1, University of Helsinki, 00014, Finland.*

<sup>b</sup>*Department of Chemistry, Nanoscience Center, University of Jyväskylä, PO Box 35, FI-40014 Jyväskylä, Finland*

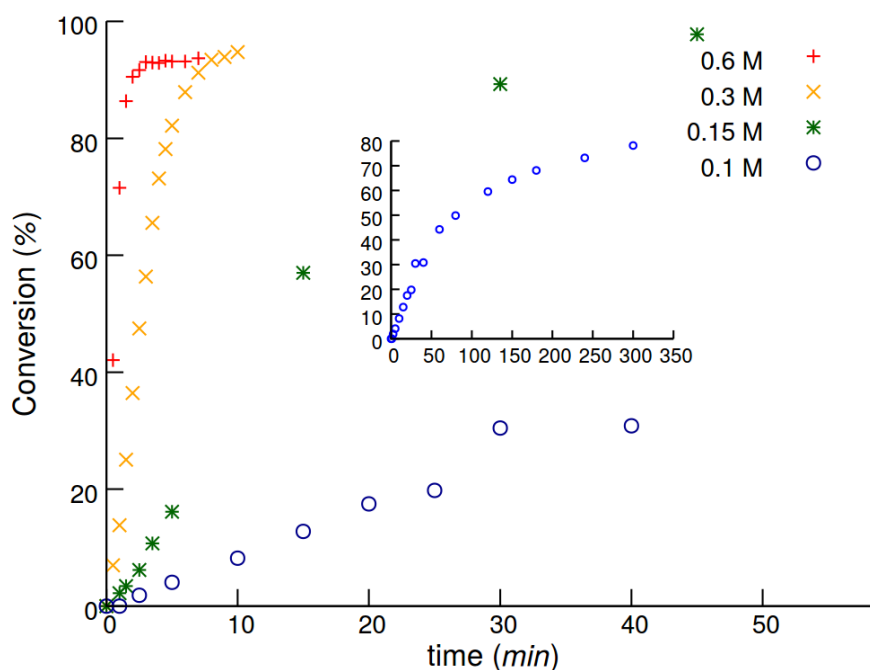
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## Kinetic, NMR and EPR studies of the reaction

### Kinetic studies with different amount of MsOH as an additive

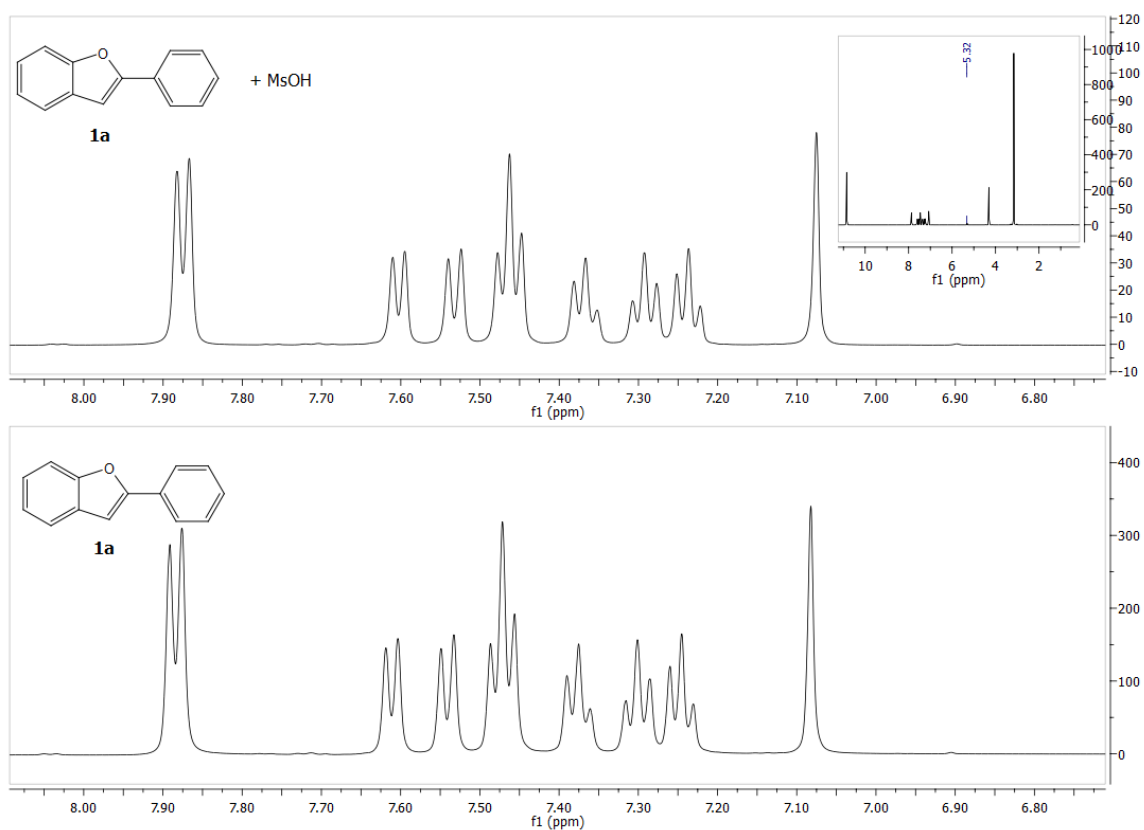
Kinetic data was obtained by quenching the reaction. Samples of the reaction mixture (25  $\mu$ l) were filtrated through  $\text{Al}_2\text{O}_3$  and washed with  $\text{CDCl}_3$ . The conversion was then determined with  $^1\text{H}$  NMR by relative integration of signals from **1a** and **2a**.



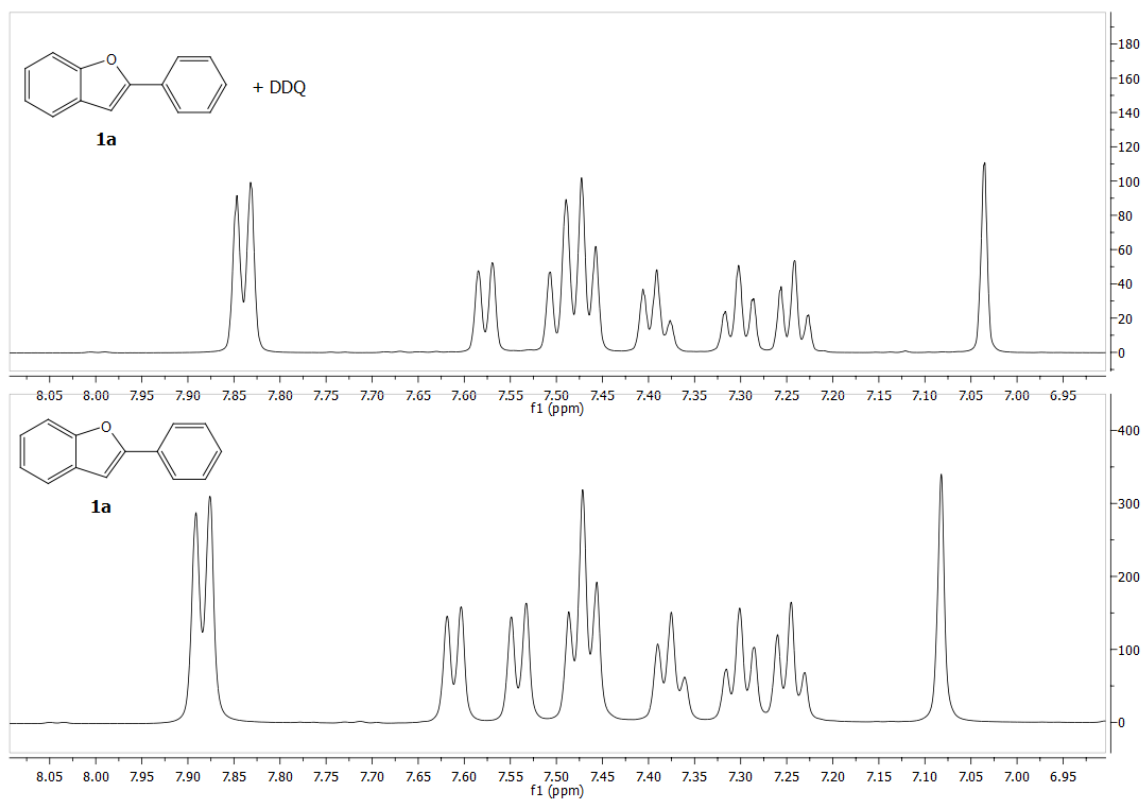
**Figure S1.** Effect of MsOH in the kinetics of oxidative dehydrogenative 3,3'-coupling of **1a** to **2a** (0.5 eq. DDQ in DCE at 0 °C). The data points were analyzed with  $^1\text{H}$  NMR after quenching the reaction.

### NMR and EPR studies of the reaction

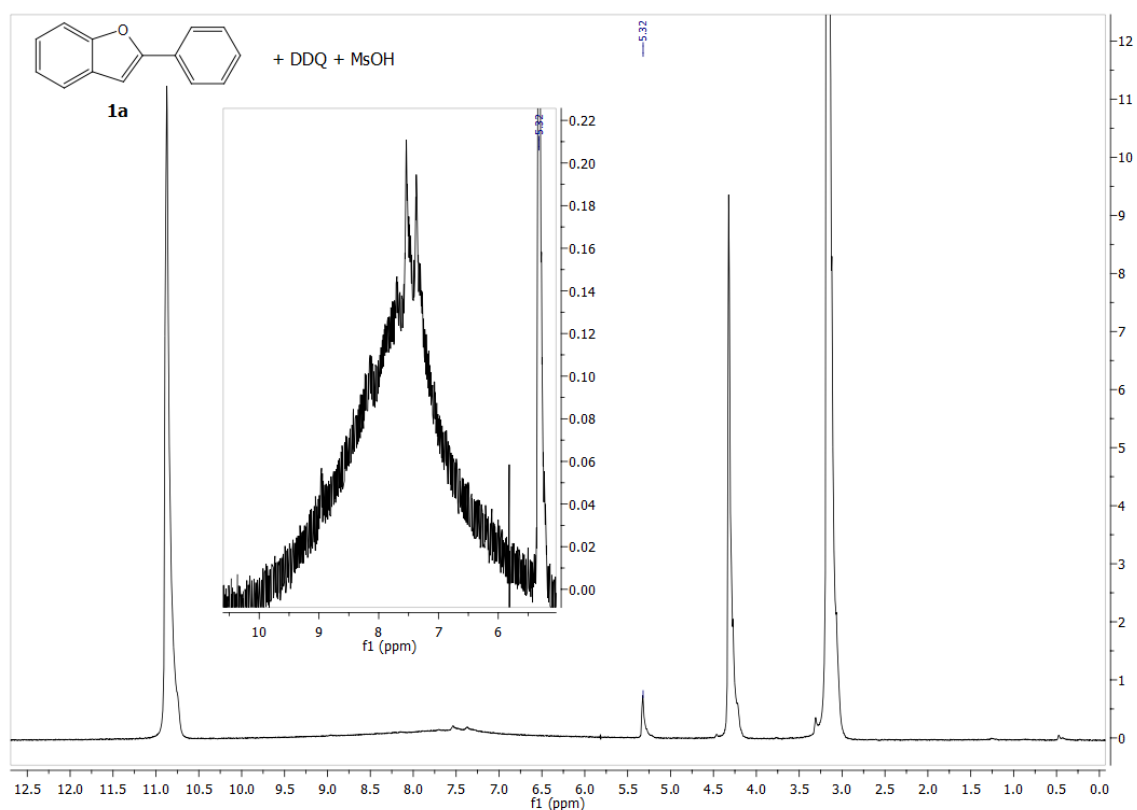
1 eq. of **1a** was measured with  $^1\text{H}$  NMR by itself (Figures S2 and S3, down), together with 3 eq. of MsOH (Figure S2), together with 0.5 eq. DDQ (Figure S3) and together with 3 eq. MsOH and 0.5 eq. of DDQ (Figure S4) in  $\text{CD}_2\text{Cl}_2$  at 0 °C. In the last case, disappearance of signals in the aromatic region was observed after adding MsOH to the green CT-complex. This event can be attributed to the increased relaxation of these nuclei caused by some paramagnetic species such as radicals.



**Figure S2.**  $^1\text{H}$  NMR of **1a** + 3 eq. MsOH (up) and pure **1a** (down) in  $d_2$ -DCM at  $0^\circ\text{C}$ .

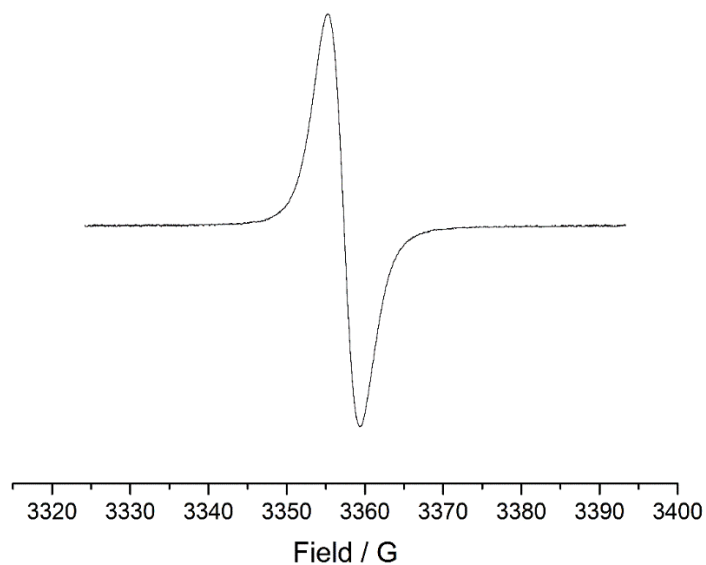


**Figure S3.**  $^1\text{H}$  NMR of **1a** + 0.5 eq. DDQ (up) and pure **1a** (down) in  $d_2$ -DCM at  $0^\circ\text{C}$ .



**Figure S4.**  $^1\text{H}$  NMR of **1a** + 0.5 eq. DDQ + 3 eq. MsOH in  $d_2$ -DCM at 0 °C.

When a sample from a mixture containing 1 eq. **1a**, 0.5 eq. DDQ and 3 eq. MsOH (0.1 M DCE at 0 °C) was measured on an X-band EPR spectrometer operating at room temperature, a featureless singlet with a  $g$ -value of 2.0023 was detected (Figure S5). This indicates the presence of radicals in the reaction mixture.



**Figure S5.** EPR-spectrum measured from a sample taken from a mixture containing 1 eq. **1a**, 0.5 eq. DDQ and 3 eq. MsOH (0.1 M DCE at 0 °C).

## Crystallographic data

### Crystal Structure Determination of 1c\_DDQ

A single crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Direct methods (SHELXS-97) [G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122] were used for structure solution and refinement was carried out using SHELXL-2014 [G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8] (full-matrix least-squares on  $F^2$ ). Hydrogen atoms were located from the difference electron density map and refined using a riding model. Semi-empirical absorption corrections were applied.

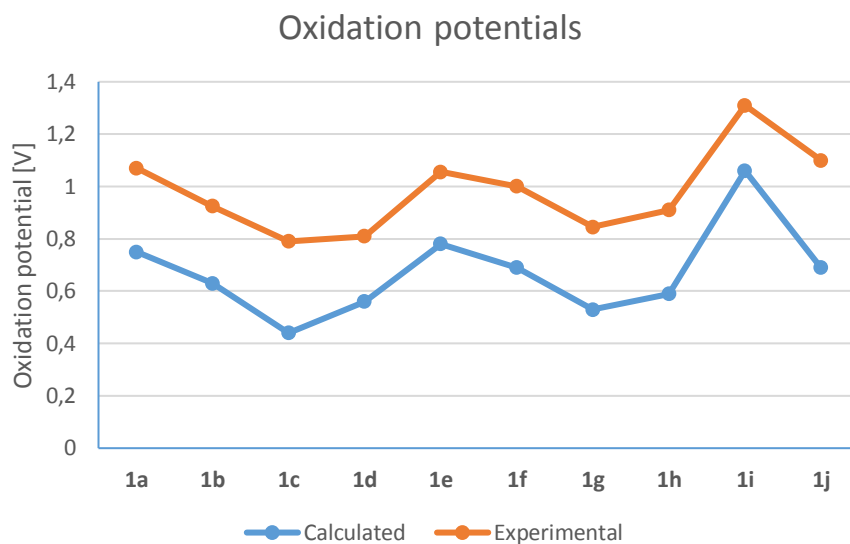
**1c\_DDQ**: green crystals,  $2(\text{C}_{15}\text{H}_{12}\text{O}_2) \cdot \text{C}_8\text{Cl}_2\text{N}_2\text{O}_2$ ,  $M_r = 675.49$ , crystal size  $0.36 \times 0.22 \times 0.06$  mm, monoclinic, space group  $P2_1/c$  (No. 14),  $a = 14.2296(4)$  Å,  $b = 6.2823(2)$  Å,  $c = 33.8457(10)$  Å,  $\beta = 90.358(1)^\circ$ ,  $V = 3025.56(16)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho = 1.483$  Mg/m<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 2.391$  mm<sup>-1</sup>,  $F(000) = 1392$ ,  $2\theta_{\text{max}} = 144.4^\circ$ , 30717 reflections, of which 5937 were independent ( $R_{\text{int}} = 0.030$ ), 435 parameters,  $R_1 = 0.055$  (for 5279  $I > 2\sigma(I)$ ),  $wR_2 = 0.157$  (all data),  $S = 1.09$ , largest diff. peak / hole = 0.831 / -0.357 e Å<sup>-3</sup>.

CCDC 1477482 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

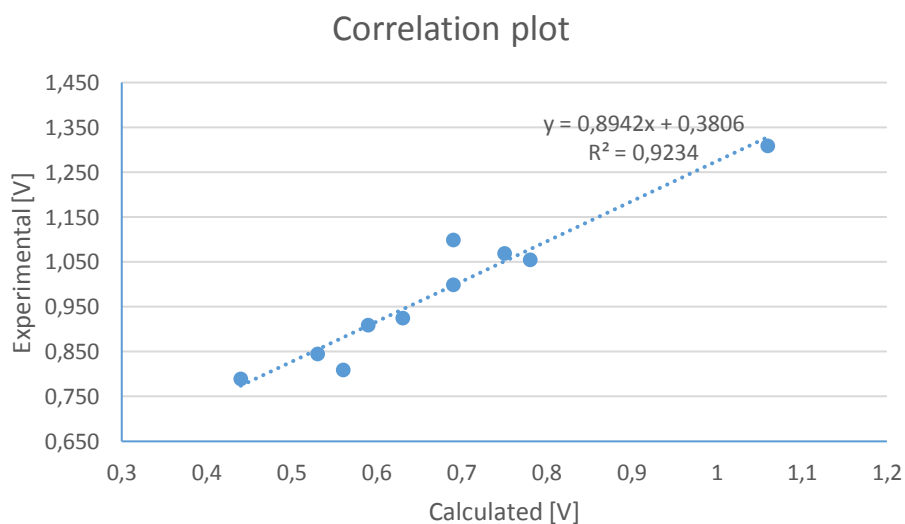


## Cyclic voltammetry

Cyclic voltammetry was performed on samples of **1a-j** to measure their oxidation potentials vs. the FcH/FcH<sup>+</sup> couple. The experimental data was compared with potentials calculated with density functional theory.



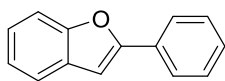
**Figure S7.** Experimental and calculated oxidation potentials of **1a-j**. Connecting lines are guides for eye.



**Figure S8.** Correlation between the experimental and calculated oxidation potentials of **1a-j**.

## Calculated oxidation potentials and optimized xyz-coordinates

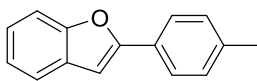
**1a**



Oxidation potential: 5.68 eV  
vs. (FcH/FcH<sup>+</sup>): 0.75 V

$\Delta E$ : 5.70 eV

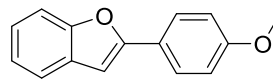
**1b**



Oxidation potential: 5.55 eV  
vs. (FcH/FcH<sup>+</sup>): 0.63 V

$\Delta E$ : 5.58 eV

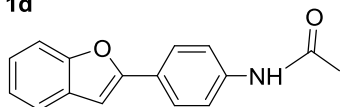
**1c**



Oxidation potential: 5.37 eV  
vs. (FcH/FcH<sup>+</sup>): 0.44 V

$\Delta E$ : 5.37 eV

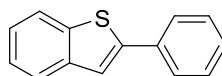
**1d**



Oxidation potential: 5.48 eV  
vs. (FcH/FcH<sup>+</sup>): 0.56 V

$\Delta E$ : 5.46 eV

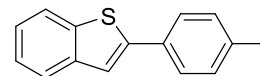
**1e**



Oxidation potential: 5.71 eV  
vs. (FcH/FcH<sup>+</sup>): 0.78 V

$\Delta E$ : 5.73 eV

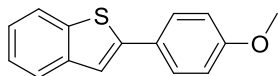
**1f**



Oxidation potential: 5.62 eV  
vs. (FcH/FcH<sup>+</sup>): 0.69 V

$\Delta E$ : 5.63 eV

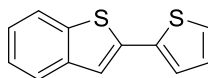
**1g**



Oxidation potential: 5.45 eV  
vs. (FcH/FcH<sup>+</sup>): 0.53 V

$\Delta E$ : 5.41 eV

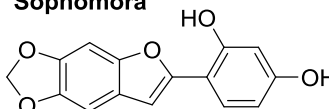
**1h**



Oxidation potential: 5.52, 5.57 eV  
vs. (FcH/FcH<sup>+</sup>): 0.59, 0.64 V

$\Delta E$ : 5.54, 5.56 eV

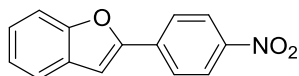
**Sophomora**



Oxidation potential: 4.97 eV  
vs. (FcH/FcH<sup>+</sup>): 0.04 V

$\Delta E$ : 4.94 eV

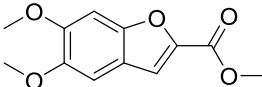
**1i**



Oxidation potential: 5.99 eV  
vs. (FcH/FcH<sup>+</sup>): 1.06 V

$\Delta E$ : 6.02 eV

**1j**

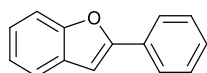


Oxidation potential: 5.61 eV  
vs. (FcH/FcH<sup>+</sup>): 0.69 V

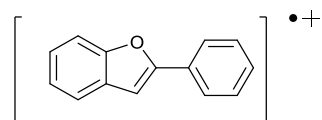
$\Delta E$ : 5.62 eV

**Figure S9.** Calculated oxidation potentials.



**1 a**

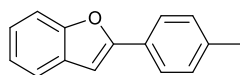
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 G(298.15): -614.9350728661



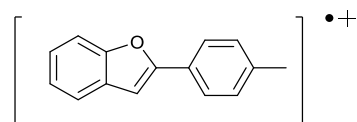
E(0): -614.8821427776  
 Chem. Pot (298.15 K): 0.158359  
 G(298.15): -614.7237837776

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| C | -3.1536137 | 1.3954855  | 0.0013640  |
| C | -2.0624513 | 0.5296499  | 0.0006429  |
| C | -0.7716067 | 1.0863221  | -0.0004636 |
| C | -0.6394707 | 2.4898242  | -0.0009690 |
| C | -1.7112809 | 3.3716010  | -0.0004360 |
| H | -1.5662813 | 4.4471354  | -0.0008455 |
| H | -3.8582840 | 3.4376749  | 0.0014288  |
| H | -4.1604366 | 0.9870546  | 0.0024470  |
| H | -2.2047955 | -0.5473050 | 0.0010466  |
| C | 0.5674722  | 0.5712148  | -0.0007581 |
| C | 1.4131369  | 1.6494293  | -0.0013297 |
| O | 0.6899726  | 2.8397056  | -0.0016224 |
| H | 0.8630344  | -0.4685094 | -0.0002975 |
| C | 2.8624004  | 1.7740793  | -0.0010862 |
| C | 3.4838946  | 3.0371393  | -0.0013613 |
| C | 3.6719774  | 0.6210672  | -0.0000739 |
| C | 5.0589665  | 0.7313226  | 0.0008409  |
| C | 5.6683266  | 1.9908138  | 0.0006346  |
| C | 4.8740958  | 3.1398155  | -0.0004268 |
| H | 2.8741460  | 3.9346531  | -0.0022474 |
| H | 3.2125370  | -0.3631614 | 0.0000451  |
| H | 5.6682062  | -0.1683381 | 0.0018071  |
| H | 6.7515035  | 2.0737881  | 0.0012570  |
| H | 5.3381457  | 4.1223344  | -0.0004204 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.9653570 | 2.7601692  | 0.0022814  |
| C | -3.1272776 | 1.3536390  | 0.0029269  |
| C | -2.0352783 | 0.5077011  | 0.0013008  |
| C | -0.7439757 | 1.0995293  | -0.0009622 |
| C | -0.6282620 | 2.5167365  | -0.0018878 |
| C | -1.7009492 | 3.3760456  | -0.0002590 |
| H | -1.5860925 | 4.4537621  | -0.0008303 |
| H | -3.8497057 | 3.3897955  | 0.0039099  |
| H | -4.1314571 | 0.9432083  | 0.0049508  |
| H | -2.1480181 | -0.5711443 | 0.0017130  |
| C | 0.5646527  | 0.6019127  | -0.0025146 |
| C | 1.4277343  | 1.7225521  | -0.0040751 |
| O | 0.7035967  | 2.8818854  | -0.0040480 |
| H | 0.8763928  | -0.4328244 | -0.0022728 |
| C | 2.8482925  | 1.8126499  | -0.0038292 |
| C | 3.4947844  | 3.0767143  | -0.0039111 |
| C | 3.6267239  | 0.6237422  | -0.0013259 |
| C | 5.0077934  | 0.7042975  | 0.0023745  |
| C | 5.6361817  | 1.9586790  | 0.0032725  |
| C | 4.8762710  | 3.1405036  | -0.0002816 |
| H | 2.9003641  | 3.9835156  | -0.0062722 |
| H | 3.1403329  | -0.3457309 | -0.0016739 |
| H | 5.6041719  | -0.2020896 | 0.0046230  |
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**1 b**

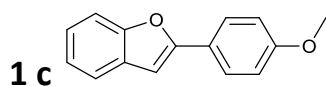
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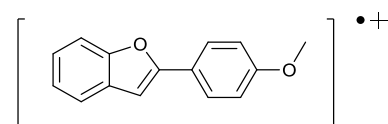
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| C | -3.0736698 | 1.4131568  | 0.0008158  |
| C | -1.9879483 | 0.5400861  | 0.0034077  |
| C | -0.6932743 | 1.0877854  | 0.0026028  |
| C | -0.5522818 | 2.4904894  | -0.0005057 |
| C | -1.6181753 | 3.3791635  | -0.0028530 |
| H | -1.4659213 | 4.4537355  | -0.0052750 |
| H | -3.7650630 | 3.4599001  | -0.0039034 |
| H | -4.0830873 | 1.0110680  | 0.0010245  |
| H | -2.1377106 | -0.5358977 | 0.0058431  |
| C | 0.6425317  | 0.5639908  | 0.0037508  |
| C | 1.4956250  | 1.6367050  | 0.0011969  |
| O | 0.7796134  | 2.8317559  | -0.0012710 |
| H | 0.9316297  | -0.4775715 | 0.0061517  |
| C | 2.9445927  | 1.7531257  | 0.0001343  |
| C | 3.5783140  | 3.0106508  | -0.0001428 |
| C | 3.7526278  | 0.6015326  | -0.0010107 |
| C | 5.1400446  | 0.7083140  | -0.0024538 |
| C | 5.7764946  | 1.9582876  | -0.0028394 |
| C | 4.9664703  | 3.1040729  | -0.0015877 |
| H | 2.9772372  | 3.9142328  | 0.0007529  |
| H | 3.2942891  | -0.3834179 | -0.0010804 |
| H | 5.7419713  | -0.1975975 | -0.0034331 |
| H | 5.4310563  | 4.0877696  | -0.0018056 |
| C | 7.2811957  | 2.0737697  | -0.0045924 |
| H | 7.7545128  | 1.0878179  | -0.0065653 |
| H | 7.6331352  | 2.6214855  | 0.8779345  |
| H | 7.6308890  | 2.6239831  | -0.8864476 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.8727675 | 2.7729427  | -0.0079855 |
| C | -3.0395989 | 1.3669165  | -0.0055243 |
| C | -1.9507534 | 0.5162218  | 0.0011129  |
| C | -0.6579526 | 1.1015530  | 0.0048255  |
| C | -0.5362816 | 2.5177659  | 0.0024941  |
| C | -1.6072324 | 3.3820397  | -0.0037644 |
| H | -1.4867212 | 4.4592120  | -0.0057378 |
| H | -3.7548747 | 3.4057469  | -0.0133776 |
| H | -4.0453048 | 0.9599265  | -0.0090851 |
| H | -2.0689990 | -0.5621023 | 0.0030839  |
| C | 0.6508167  | 0.5985988  | 0.0092778  |
| C | 1.5171152  | 1.7134829  | 0.0092709  |
| O | 0.7953018  | 2.8784124  | 0.0062317  |
| H | 0.9580064  | -0.4375061 | 0.0117762  |
| C | 2.9347603  | 1.8000100  | 0.0085694  |
| C | 3.5912888  | 3.0606521  | 0.0077379  |
| C | 3.7164172  | 0.6131483  | 0.0051886  |
| C | 5.0946279  | 0.6914709  | -0.0012093 |
| C | 5.7509362  | 1.9398917  | -0.0038518 |
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| H | 3.0028524  | 3.9714539  | 0.0113288  |
| H | 3.2320159  | -0.3574742 | 0.0064155  |
| H | 5.6846872  | -0.2200904 | -0.0049732 |
| H | 5.4644413  | 4.0854499  | 0.0005613  |
| C | 7.2453269  | 2.0305345  | -0.0129108 |
| H | 7.7125194  | 1.0438010  | -0.0195201 |
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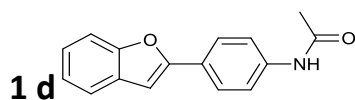
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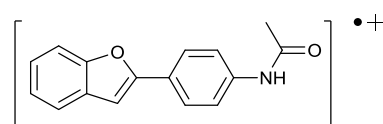
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| C | -1.4877623 | 3.3848261  | -0.0091472 |
| H | -1.3112285 | 4.4556631  | -0.0207298 |
| H | -3.6329168 | 3.5143237  | -0.0046876 |
| H | -4.0051227 | 1.0729522  | 0.0208986  |
| H | -2.0949287 | -0.5167142 | 0.0324382  |
| C | 0.7100396  | 0.5199570  | 0.0144428  |
| C | 1.5873535  | 1.5736023  | 0.0012934  |
| O | 0.8974941  | 2.7842382  | -0.0091851 |
| H | 0.9755076  | -0.5278372 | 0.0245007  |
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| C | 3.8230658  | 0.4959758  | 0.0069548  |
| C | 5.2136911  | 0.5569222  | 0.0020966  |
| C | 5.8537340  | 1.8055425  | -0.0138180 |
| C | 5.0836230  | 2.9789625  | -0.0245976 |
| H | 3.1181928  | 3.8232167  | -0.0282458 |
| H | 3.3458867  | -0.4797528 | 0.0193427  |
| H | 5.7842275  | -0.3647208 | 0.0107398  |
| H | 5.5894925  | 3.9399511  | -0.0368747 |
| O | 7.2090185  | 1.9786618  | -0.0198015 |
| C | 8.0351669  | 0.7976001  | -0.0099935 |
| H | 7.8559610  | 0.2056990  | 0.8948779  |
| H | 9.0614293  | 1.1646060  | -0.0172965 |
| H | 7.8499256  | 0.1867294  | -0.9009430 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.7773568 | 2.8451412  | -0.0002280 |
| C | -2.9870885 | 1.4528250  | 0.0144844  |
| C | -1.9207116 | 0.5555555  | 0.0209517  |
| C | -0.6138961 | 1.0734800  | 0.0122428  |
| C | -0.4423796 | 2.4727033  | -0.0025093 |
| C | -1.4877623 | 3.3848261  | -0.0091472 |
| H | -1.3112285 | 4.4556631  | -0.0207298 |
| H | -3.6329168 | 3.5143237  | -0.0046876 |
| H | -4.0051227 | 1.0729522  | 0.0208986  |
| H | -2.0949287 | -0.5167142 | 0.0324382  |
| C | 0.7100396  | 0.5199570  | 0.0144428  |
| C | 1.5873535  | 1.5736023  | 0.0012934  |
| O | 0.8974941  | 2.7842382  | -0.0091851 |
| H | 0.9755076  | -0.5278372 | 0.0245007  |
| C | 3.0369854  | 1.6610136  | -0.0037622 |
| C | 3.6986471  | 2.9065464  | -0.0196250 |
| C | 3.8230658  | 0.4959758  | 0.0069548  |
| C | 5.2136911  | 0.5569222  | 0.0020966  |
| C | 5.8537340  | 1.8055425  | -0.0138180 |
| C | 5.0836230  | 2.9789625  | -0.0245976 |
| H | 3.1181928  | 3.8232167  | -0.0282458 |
| H | 3.3458867  | -0.4797528 | 0.0193427  |
| H | 5.7842275  | -0.3647208 | 0.0107398  |
| H | 5.5894925  | 3.9399511  | -0.0368747 |
| O | 7.2090185  | 1.9786618  | -0.0198015 |
| C | 8.0351669  | 0.7976001  | -0.0099935 |
| H | 7.8559610  | 0.2056990  | 0.8948779  |
| H | 9.0614293  | 1.1646060  | -0.0172965 |
| H | 7.8499256  | 0.1867294  | -0.9009430 |



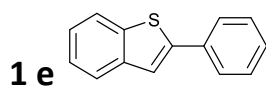
E(0): -823.2361967787  
 Chem. Pot (298.15 K): 0.205299  
 G(298.15): -823.0308977787



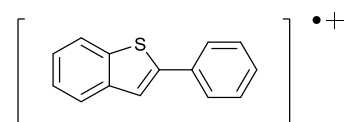
E(0): -823.0338666170  
 Chem. Pot (298.15 K): 0.207083  
 G(298.15): -822.826783617

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.9932765 | 2.9434159  | 0.0743249  |
| C | -3.2521895 | 1.5979958  | -0.2525987 |
| C | -2.2211393 | 0.6719251  | -0.3938370 |
| C | -0.9001467 | 1.1124543  | -0.2015084 |
| C | -0.6789351 | 2.4657606  | 0.1257590  |
| C | -1.6893130 | 3.4056811  | 0.2714422  |
| H | -1.4758876 | 4.4397092  | 0.5224281  |
| H | -3.8227473 | 3.6373963  | 0.1749338  |
| H | -4.2806109 | 1.2791277  | -0.3979834 |
| H | -2.4318438 | -0.3632287 | -0.6470493 |
| C | 0.3999462  | 0.5085423  | -0.2550567 |
| C | 1.3114698  | 1.4913682  | 0.0319474  |
| O | 0.6678514  | 2.7030872  | 0.2713327  |
| H | 0.6275884  | -0.5240677 | -0.4795148 |
| C | 2.7601614  | 1.5027847  | 0.1236127  |
| C | 3.4661341  | 2.6754154  | 0.4466074  |
| C | 3.5012963  | 0.3312015  | -0.1282245 |
| C | 4.8843548  | 0.3315293  | -0.0393108 |
| C | 5.5814463  | 1.5055749  | 0.2972210  |
| C | 4.8553625  | 2.6835596  | 0.5201628  |
| H | 2.9233117  | 3.5982347  | 0.6216700  |
| H | 2.9902628  | -0.5908860 | -0.3885228 |
| H | 5.4385654  | -0.5845641 | -0.2257623 |
| H | 5.3670781  | 3.6164782  | 0.7237233  |
| N | 6.9912859  | 1.4466337  | 0.3370911  |
| H | 7.4191436  | 0.7517418  | -0.2698757 |
| C | 7.9095373  | 2.0770806  | 1.1458245  |
| O | 9.1139172  | 1.8550934  | 0.9689610  |
| C | 7.4264769  | 2.9968342  | 2.2429293  |
| H | 8.1938601  | 3.0158717  | 3.0184283  |
| H | 6.4706776  | 2.6780250  | 2.6666234  |
| H | 7.3097228  | 4.0140895  | 1.8532917  |

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.0004421 | 2.9007531  | 0.0921974  |
| C | -3.2419380 | 1.5902866  | -0.3856674 |
| C | -2.2058799 | 0.6968546  | -0.5877275 |
| C | -0.8909001 | 1.1374721  | -0.2996305 |
| C | -0.6920523 | 2.4587988  | 0.1803803  |
| C | -1.7116347 | 3.3648200  | 0.3871969  |
| H | -1.5298665 | 4.3690642  | 0.7525119  |
| H | -3.8426582 | 3.5708018  | 0.2349415  |
| H | -4.2636371 | 1.2903143  | -0.5950411 |
| H | -2.3847988 | -0.3080591 | -0.9551971 |
| C | 0.3877546  | 0.5546353  | -0.3745099 |
| C | 1.3044822  | 1.5263100  | 0.0573968  |
| O | 0.6482935  | 2.6880856  | 0.3974013  |
| H | 0.6352470  | -0.4464685 | -0.6975609 |
| C | 2.7165402  | 1.4948389  | 0.1922817  |
| C | 3.4325720  | 2.6207797  | 0.6798743  |
| C | 3.4481140  | 0.3295402  | -0.1697727 |
| C | 4.8118807  | 0.2976991  | -0.0387965 |
| C | 5.5232822  | 1.4204051  | 0.4719235  |
| C | 4.8005142  | 2.5919584  | 0.8182761  |
| H | 2.8924229  | 3.5237798  | 0.9407334  |
| H | 2.9308118  | -0.5435188 | -0.5520176 |
| H | 5.3645922  | -0.5956641 | -0.3145049 |
| H | 5.3075282  | 3.4792119  | 1.1671984  |
| N | 6.8867204  | 1.2810048  | 0.5646839  |
| H | 7.2595534  | 0.4290269  | 0.1463935  |
| C | 7.9255880  | 2.0265081  | 1.1605818  |
| O | 9.0610719  | 1.5997378  | 0.9932296  |
| C | 7.6198801  | 3.2506631  | 1.9751973  |
| H | 8.5306456  | 3.5304547  | 2.5044130  |
| H | 6.8147002  | 3.0659726  | 2.6922672  |
| H | 7.3249741  | 4.0777982  | 1.3204162  |



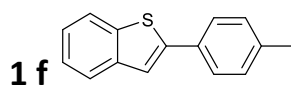
E(0): -938.0694110854  
 Chem. Pot (298.15 K): 0.153945  
 G(298.15): -937.9154660854



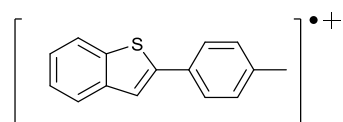
E(0): -937.86006697733  
 Chem. Pot (298.15 K): 0.154177  
 G(298.15): -937.7029698703

|   |            |            |            |
|---|------------|------------|------------|
| C | -4.4700193 | 0.7647317  | 0.0008550  |
| C | -4.3707202 | -0.6403450 | -0.0019811 |
| C | -3.1316693 | -1.2671826 | -0.0026983 |
| C | -1.9584869 | -0.4855356 | -0.0005568 |
| C | -2.0813752 | 0.9299435  | 0.0020679  |
| C | -3.3289134 | 1.5624679  | 0.0028078  |
| H | -3.4074395 | 2.6455660  | 0.0046854  |
| H | -5.4494491 | 1.2346491  | 0.0015357  |
| H | -5.2774161 | -1.2389147 | -0.0035657 |
| H | -3.0584433 | -2.3515739 | -0.0050060 |
| C | -0.5910916 | -0.9036625 | -0.0008097 |
| C | 0.3101048  | 0.1324529  | 0.0011071  |
| S | -0.5139115 | 1.6904833  | 0.0040550  |
| H | -0.2977379 | -1.9477714 | -0.0027758 |
| C | 1.7747075  | 0.0692363  | 0.0007148  |
| C | 2.5588331  | 1.2384018  | -0.0022075 |
| C | 2.4398642  | -1.1736329 | 0.0031598  |
| C | 3.8303552  | -1.2385129 | 0.0025105  |
| C | 4.5953750  | -0.0678066 | -0.0005755 |
| C | 3.9507786  | 1.1708938  | -0.0028896 |
| H | 2.0775381  | 2.2135543  | -0.0042973 |
| H | 1.8673456  | -2.0960789 | 0.0057675  |
| H | 4.3198801  | -2.2086336 | 0.0045294  |
| H | 5.6803199  | -0.1218661 | -0.0010641 |
| H | 4.5315711  | 2.0891358  | -0.0053685 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -4.4445273 | 0.7293585  | -0.0018819 |
| C | -4.3423717 | -0.6745553 | -0.0026721 |
| C | -3.1014424 | -1.2862786 | -0.0005429 |
| C | -1.9334501 | -0.4754976 | 0.0017204  |
| C | -2.0666111 | 0.9463844  | 0.0025473  |
| C | -3.3067202 | 1.5581635  | 0.0008563  |
| H | -3.4126399 | 2.6376428  | 0.0012453  |
| H | -5.4264809 | 1.1924118  | -0.0034961 |
| H | -5.2456643 | -1.2751627 | -0.0052852 |
| H | -3.0048527 | -2.3674672 | -0.0007448 |
| C | -0.5930724 | -0.8789458 | 0.0023135  |
| C | 0.3238627  | 0.2034136  | 0.0036159  |
| S | -0.5003606 | 1.7308643  | 0.0046613  |
| H | -0.2809808 | -1.9163008 | 0.0010889  |
| C | 1.7575012  | 0.1078052  | 0.0027910  |
| C | 2.5674914  | 1.2731441  | 0.0010251  |
| C | 2.3909058  | -1.1648174 | 0.0025105  |
| C | 3.7727370  | -1.2580853 | -0.0003873 |
| C | 4.5554996  | -0.0961040 | -0.0031110 |
| C | 3.9461439  | 1.1697952  | -0.0019944 |
| H | 2.1044614  | 2.2561803  | 0.0015623  |
| H | 1.7968628  | -2.0716095 | 0.0044775  |
| H | 4.2478881  | -2.2336591 | -0.0006360 |
| H | 5.6385489  | -0.1731448 | -0.0061004 |
| H | 4.5572714  | 2.0664643  | -0.0035630 |



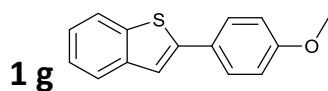
E(0): -977.4089551678  
 Chem. Pot (298.15 K): 0.178172  
 G(298.15): -977.2307831678



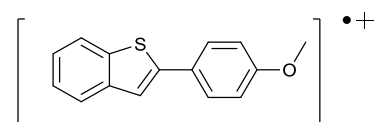
E(0): -977.2005926665  
 Chem. Pot (298.15 K): 0.178852  
 G(298.15): -977.0217406665

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.2504172 | 2.5750514  | 0.0316444  |
| C | -3.1458464 | 1.1705730  | 0.0348882  |
| C | -1.9043937 | 0.5481496  | 0.0212748  |
| C | -0.7338979 | 1.3335544  | 0.0036109  |
| C | -0.8622606 | 2.7486001  | 0.0005472  |
| C | -2.1118133 | 3.3766077  | 0.0145603  |
| H | -2.1940629 | 4.4594629  | 0.0120831  |
| H | -4.2313645 | 3.0416553  | 0.0425690  |
| H | -4.0501612 | 0.5685152  | 0.0482638  |
| H | -1.8275138 | -0.5360094 | 0.0239658  |
| C | 0.6350877  | 0.9202622  | -0.0126041 |
| C | 1.5330114  | 1.9593785  | -0.0278941 |
| S | 0.7028614  | 3.5147068  | -0.0226572 |
| H | 0.9324473  | -0.1227491 | -0.0115264 |
| C | 2.9965507  | 1.9024167  | -0.0476429 |
| C | 3.7812464  | 3.0687006  | -0.0412354 |
| C | 3.6710711  | 0.6642163  | -0.0746303 |
| C | 5.0591002  | 0.6061518  | -0.0935966 |
| C | 5.8420560  | 1.7727638  | -0.0873790 |
| C | 5.1732919  | 3.0022074  | -0.0609719 |
| H | 3.3029227  | 4.0452672  | -0.0197458 |
| H | 3.1054070  | -0.2626715 | -0.0822382 |
| H | 5.5473938  | -0.3657935 | -0.1145146 |
| H | 5.7483540  | 3.9253377  | -0.0554388 |
| C | 7.3487570  | 1.6939762  | -0.1085778 |
| H | 7.7977344  | 2.6912277  | -0.1057306 |
| H | 7.7007691  | 1.1614927  | -1.0003541 |
| H | 7.7247394  | 1.1459185  | 0.7638203  |

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.2178140 | 2.5342710  | 0.0251998  |
| C | -3.1054721 | 1.1293829  | 0.0215737  |
| C | -1.8616380 | 0.5259879  | 0.0122809  |
| C | -0.6992335 | 1.3437045  | 0.0054513  |
| C | -0.8417513 | 2.7655003  | 0.0100203  |
| C | -2.0881830 | 3.3689953  | 0.0199972  |
| H | -2.2003263 | 4.4478978  | 0.0228997  |
| H | -4.2035293 | 2.9893985  | 0.0322202  |
| H | -4.0050521 | 0.5229908  | 0.0261189  |
| H | -1.7582340 | -0.5546067 | 0.0092512  |
| C | 0.6447086  | 0.9488296  | -0.0088023 |
| C | 1.5534779  | 2.0345149  | -0.0157502 |
| S | 0.7164587  | 3.5613734  | -0.0021218 |
| H | 0.9628810  | -0.0867011 | -0.0149813 |
| C | 2.9833461  | 1.9497440  | -0.0356374 |
| C | 3.7901192  | 3.1180855  | -0.0412854 |
| C | 3.6339465  | 0.6834436  | -0.0542375 |
| C | 5.0103766  | 0.6033185  | -0.0801034 |
| C | 5.8098426  | 1.7674833  | -0.0880791 |
| C | 5.1665259  | 3.0244718  | -0.0669343 |
| H | 3.3237171  | 4.0994589  | -0.0258542 |
| H | 3.0502414  | -0.2301588 | -0.0494895 |
| H | 5.4893386  | -0.3715177 | -0.0951291 |
| H | 5.7668244  | 3.9294615  | -0.0716562 |
| C | 7.3031799  | 1.6608606  | -0.1195422 |
| H | 7.7804882  | 2.6428267  | -0.1166481 |
| H | 7.6252532  | 1.1117460  | -1.0134695 |
| H | 7.6615779  | 1.0882069  | 0.7451982  |



E(0): -1052.6621685159  
 Chem. Pot (298.15 K): 0.182196  
 G(298.15): -1052.4799725159

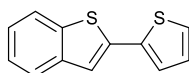


E(0): -1052.4619424721  
 Chem. Pot (298.15 K): 0.184979  
 G(298.15): -1052.2769634721

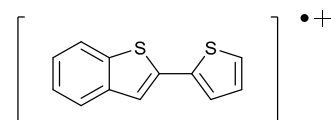
|   |            |            |            |
|---|------------|------------|------------|
| C | -3.2198711 | 2.5798982  | 0.0774254  |
| C | -3.1210565 | 1.1752715  | 0.0665184  |
| C | -1.8824428 | 0.5474972  | 0.0286841  |
| C | -0.7083507 | 1.3273156  | 0.0001194  |
| C | -0.8313528 | 2.7428698  | 0.0114881  |
| C | -2.0773498 | 3.3762227  | 0.0502655  |
| H | -2.1544180 | 4.4594728  | 0.0588435  |
| H | -4.1983669 | 3.0508030  | 0.1073442  |
| H | -4.0275738 | 0.5766547  | 0.0881600  |
| H | -1.8108859 | -0.5370548 | 0.0207751  |
| C | 0.6584342  | 0.9081779  | -0.0393094 |
| C | 1.5616386  | 1.9432690  | -0.0590449 |
| S | 0.7373622  | 3.5020917  | -0.0291939 |
| H | 0.9509910  | -0.1362367 | -0.0482728 |
| C | 3.0231831  | 1.8827826  | -0.1012664 |
| C | 3.8158533  | 3.0483672  | -0.0517457 |
| C | 3.6937557  | 0.6499989  | -0.1937848 |
| C | 5.0836345  | 0.5718599  | -0.2332210 |
| C | 5.8486833  | 1.7462973  | -0.1824008 |
| C | 5.2005998  | 2.9874458  | -0.0916707 |
| H | 3.3425127  | 4.0244628  | 0.0226003  |
| H | 3.1266503  | -0.2747502 | -0.2399943 |
| H | 5.5559419  | -0.4012483 | -0.3053392 |
| H | 5.7980746  | 3.8934809  | -0.0522843 |
| O | 7.2141499  | 1.7828552  | -0.2159968 |
| C | 7.9148692  | 0.5264973  | -0.3065333 |
| H | 8.9730224  | 0.7876173  | -0.3177228 |
| H | 7.6497854  | -0.0003850 | -1.2303012 |
| H | 7.6943262  | -0.1045442 | 0.5620382  |

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.1841059 | 2.5452566  | 0.0798154  |
| C | -3.0788552 | 1.1388981  | 0.0350417  |
| C | -1.8398612 | 0.5279668  | -0.0074145 |
| C | -0.6730048 | 1.3360091  | -0.0070841 |
| C | -0.8067449 | 2.7578289  | 0.0389853  |
| C | -2.0525375 | 3.3695111  | 0.0828074  |
| H | -2.1548823 | 4.4489592  | 0.1172921  |
| H | -4.1675856 | 3.0042239  | 0.1127620  |
| H | -3.9821860 | 0.5376656  | 0.0340807  |
| H | -1.7452288 | -0.5530361 | -0.0417671 |
| C | 0.6717956  | 0.9329343  | -0.0504323 |
| C | 1.5837080  | 2.0071782  | -0.0399650 |
| S | 0.7524917  | 3.5446539  | 0.0277483  |
| H | 0.9801655  | -0.1050109 | -0.0899036 |
| C | 3.0100600  | 1.9226417  | -0.0834482 |
| C | 3.8230664  | 3.0925038  | -0.0698914 |
| C | 3.6601514  | 0.6567050  | -0.1471374 |
| C | 5.0321690  | 0.5548243  | -0.1988677 |
| C | 5.8155434  | 1.7327435  | -0.1883055 |
| C | 5.1902517  | 3.0055385  | -0.1208343 |
| H | 3.3595699  | 4.0735943  | -0.0195240 |
| H | 3.0727689  | -0.2543531 | -0.1574372 |
| H | 5.4972944  | -0.4221301 | -0.2476907 |
| H | 5.8147239  | 3.8925853  | -0.1124950 |
| O | 7.1480322  | 1.7523361  | -0.2392199 |
| C | 7.8802484  | 0.4957823  | -0.3143257 |
| H | 8.9274782  | 0.7886241  | -0.3493934 |
| H | 7.5998011  | -0.0425613 | -1.2233945 |
| H | 7.6774725  | -0.1048831 | 0.5761786  |

1 h a



E(0): -1258.8286581062  
Chem. Pot (298.15 K): 0.121252  
G(298.15): -1258.7074061062



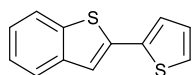
E(0): -1258.6234939383  
Chem. Pot (298.15 K): 0.121622  
G(298.15): -1258.50551762204

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.2535016 | 2.5780515  | -0.0021944 |
| C | -3.1520150 | 1.1734816  | -0.0002831 |
| C | -1.9123570 | 0.5476133  | 0.0024091  |
| C | -0.7387883 | 1.3293699  | 0.0028556  |
| C | -0.8654154 | 2.7454845  | 0.0007957  |
| C | -2.1125912 | 3.3768896  | -0.0015650 |
| H | -2.1917922 | 4.4598879  | -0.0031728 |
| H | -4.2332161 | 3.0472134  | -0.0042689 |
| H | -4.0577659 | 0.5734734  | -0.0009467 |
| H | -1.8383636 | -0.5366711 | 0.0038908  |
| C | 0.6276189  | 0.9106720  | 0.0041330  |
| C | 1.5239729  | 1.9531795  | 0.0029346  |
| S | 0.7024938  | 3.5097728  | 0.0009608  |
| H | 0.9314605  | -0.1305270 | 0.0052111  |
| S | 3.9682801  | 3.3057805  | -0.0083633 |
| C | 5.4187645  | 2.3812301  | -0.0049364 |
| C | 5.1536362  | 1.0322345  | 0.0038523  |
| C | 3.7664630  | 0.7432808  | 0.0080621  |
| C | 2.9702226  | 1.8776769  | 0.0022606  |
| H | 6.3769960  | 2.8832342  | -0.0096121 |
| H | 5.9292099  | 0.2740739  | 0.0072586  |
| H | 3.3608360  | -0.2623375 | 0.0150217  |

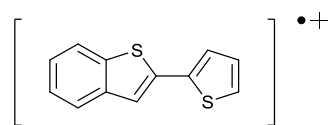
|   |            |            |            |
|---|------------|------------|------------|
| C | -3.2264204 | 2.5404979  | 0.0034835  |
| C | -3.1117494 | 1.1345314  | 0.0048450  |
| C | -1.8685530 | 0.5319747  | 0.0016818  |
| C | -0.7066442 | 1.3498397  | -0.0025916 |
| C | -0.8518500 | 2.7730083  | -0.0044576 |
| C | -2.1001770 | 3.3755785  | -0.0014522 |
| H | -2.2125503 | 4.4544053  | -0.0024036 |
| H | -4.2131427 | 2.9934723  | 0.0064059  |
| H | -4.0109011 | 0.5274330  | 0.0086252  |
| H | -1.7641747 | -0.5484764 | 0.0028455  |
| C | 0.6373222  | 0.9543026  | -0.0038973 |
| C | 1.5382031  | 2.0447989  | -0.0062848 |
| S | 0.7030227  | 3.5747437  | -0.0088399 |
| H | 0.9659914  | -0.0783249 | -0.0025033 |
| S | 3.9973452  | 3.3378797  | -0.0055935 |
| C | 5.3877622  | 2.3466404  | 0.0036438  |
| C | 5.0822316  | 0.9881910  | 0.0074937  |
| C | 3.7093154  | 0.7513438  | 0.0028570  |
| C | 2.9475649  | 1.9401171  | -0.0041525 |
| H | 6.3699507  | 2.8025266  | 0.0057575  |
| H | 5.8396677  | 0.2138128  | 0.0136526  |
| H | 3.2619337  | -0.2352318 | 0.0051881  |



1 h b



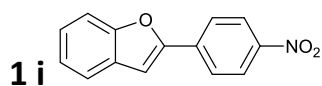
E(0): -1258.8302021305  
Chem. Pot (298.15 K): 0.12026  
G(298.15): -1258.7099421305



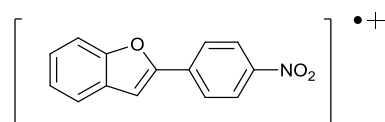
E(0): -1258.6242327095  
Chem. Pot (298.15 K): 0.121469  
G(298.15): -1258.5027637095

|   |            |            |            |
|---|------------|------------|------------|
| C | -4.0036138 | 0.6758675  | -0.0000591 |
| C | -3.9098022 | -0.7289951 | -0.0000390 |
| C | -2.6730782 | -1.3610751 | 0.0000503  |
| C | -1.4963927 | -0.5849598 | 0.0000592  |
| C | -1.6142303 | 0.8316117  | -0.0000397 |
| C | -2.8584770 | 1.4689325  | -0.0000892 |
| H | -2.9325351 | 2.5523206  | -0.0001747 |
| H | -4.9808355 | 1.1502446  | -0.0000771 |
| H | -4.8186165 | -1.3243270 | -0.0000864 |
| H | -2.6042751 | -2.4456868 | 0.0001141  |
| C | -0.1313933 | -1.0093224 | 0.0001442  |
| C | 0.7706223  | 0.0272456  | 0.0000957  |
| S | -0.0430667 | 1.5903876  | -0.0000786 |
| H | 0.1673449  | -2.0529463 | 0.0002627  |
| S | 3.0640237  | -1.5526740 | -0.0001397 |
| C | 4.6006142  | -0.7756930 | -0.0002081 |
| C | 4.4759895  | 0.5919271  | 0.0000019  |
| C | 3.1231509  | 1.0183859  | 0.0001652  |
| C | 2.2159508  | -0.0277584 | 0.0001011  |
| H | 5.5032395  | -1.3722460 | -0.0003585 |
| H | 5.3239777  | 1.2678777  | -0.0000013 |
| H | 2.8214027  | 2.0608831  | 0.0003570  |

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.9788173 | 0.6494696  | 0.0005118  |
| C | -3.8820667 | -0.7585278 | 0.0014796  |
| C | -2.6470536 | -1.3763606 | 0.0008143  |
| C | -1.4751090 | -0.5724979 | -0.0007518 |
| C | -1.6010758 | 0.8531558  | -0.0015926 |
| C | -2.8426947 | 1.4704244  | -0.0010795 |
| H | -2.9420958 | 2.5505313  | -0.0017549 |
| H | -4.9599203 | 1.1145012  | 0.0010747  |
| H | -4.7889760 | -1.3539728 | 0.0028133  |
| H | -2.5556917 | -2.4579726 | 0.0015521  |
| C | -0.1363992 | -0.9831140 | -0.0012566 |
| C | 0.7786641  | 0.0943185  | -0.0020809 |
| S | -0.0382161 | 1.6375758  | -0.0029420 |
| H | 0.1796241  | -2.0211366 | -0.0005659 |
| S | 2.9985965  | -1.5587259 | -0.0029855 |
| C | 4.5258621  | -0.8087085 | -0.0003128 |
| C | 4.4481262  | 0.5841260  | 0.0017772  |
| C | 3.1329132  | 1.0423235  | 0.0009615  |
| C | 2.1876483  | -0.0011959 | -0.0014747 |
| H | 5.4218187  | -1.4169386 | -0.0003488 |
| H | 5.3229679  | 1.2228870  | 0.0037578  |
| H | 2.8518951  | 2.0898380  | 0.0024037  |



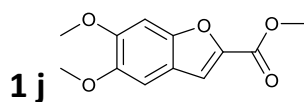
E(0): -819.7300789063  
Chem. Pot (298.15 K): 0.155886  
G(298.15): -819.5741929063



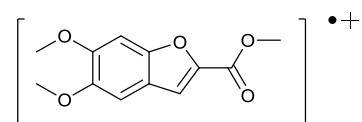
E(0): -819.5072110298  
Chem. Pot (298.15 K): 0.15586  
G(298.15): -819.3513510298

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.7679699 | 2.8345263  | 0.0090853  |
| C | -2.9679447 | 1.4383856  | 0.0172747  |
| C | -1.8967269 | 0.5513136  | 0.0158788  |
| C | -0.5949427 | 1.0846930  | 0.0060399  |
| C | -0.4327709 | 2.4860839  | -0.0022869 |
| C | -1.4871119 | 3.3892688  | -0.0010982 |
| H | -1.3221658 | 4.4616327  | -0.0073734 |
| H | -3.6304311 | 3.4946286  | 0.0107915  |
| H | -3.9832561 | 1.0523471  | 0.0248064  |
| H | -2.0585326 | -0.5225509 | 0.0229165  |
| C | 0.7292112  | 0.5417379  | 0.0035588  |
| C | 1.5980440  | 1.6046271  | -0.0056843 |
| O | 0.9020028  | 2.8092337  | -0.0100033 |
| H | 1.0028266  | -0.5039513 | 0.0081204  |
| C | 3.0425006  | 1.6917876  | -0.0098448 |
| C | 3.6936450  | 2.9435253  | -0.0293821 |
| C | 3.8234211  | 0.5154317  | 0.0072245  |
| C | 5.2061320  | 0.5830415  | 0.0064350  |
| C | 5.8214460  | 1.8387720  | -0.0125627 |
| C | 5.0784086  | 3.0207150  | -0.0311922 |
| H | 3.1073232  | 3.8552175  | -0.0428757 |
| H | 3.3422630  | -0.4568723 | 0.0223645  |
| H | 5.8096111  | -0.3164849 | 0.0209480  |
| H | 5.5839062  | 3.9787838  | -0.0462939 |
| N | 7.2815162  | 1.9152567  | -0.0117715 |
| O | 7.9255627  | 0.8546303  | 0.0106791  |
| O | 7.8126223  | 3.0361398  | -0.0330346 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.7574586 | 2.7966915  | 0.0032553  |
| C | -2.9495168 | 1.3945040  | 0.0175712  |
| C | -1.8753522 | 0.5271323  | 0.0211885  |
| C | -0.5703863 | 1.0948145  | 0.0101223  |
| C | -0.4259046 | 2.5100517  | -0.0044822 |
| C | -1.4780408 | 3.3898735  | -0.0082857 |
| H | -1.3439175 | 4.4651762  | -0.0191497 |
| H | -3.6279970 | 3.4451607  | 0.0011097  |
| H | -3.9619500 | 1.0056145  | 0.0258678  |
| H | -2.0080127 | -0.5492513 | 0.0322417  |
| C | 0.7242574  | 0.5698412  | 0.0108058  |
| C | 1.6101247  | 1.6755331  | -0.0033688 |
| O | 0.9157158  | 2.8461102  | -0.0130181 |
| H | 1.0149521  | -0.4710770 | 0.0203575  |
| C | 3.0373208  | 1.7358814  | -0.0077613 |
| C | 3.7044879  | 2.9859763  | -0.0235102 |
| C | 3.7873971  | 0.5331120  | 0.0047964  |
| C | 5.1702927  | 0.5776806  | 0.0024924  |
| C | 5.7938075  | 1.8263635  | -0.0129571 |
| C | 5.0866650  | 3.0317191  | -0.0263141 |
| H | 3.1321513  | 3.9061516  | -0.0331797 |
| H | 3.2865639  | -0.4281323 | 0.0166783  |
| H | 5.7622419  | -0.3289999 | 0.0126083  |
| H | 5.6182085  | 3.9751451  | -0.0382748 |
| N | 7.2767625  | 1.8762722  | -0.0149422 |
| O | 7.8847918  | 0.8033311  | 0.0025005  |
| O | 7.8113857  | 2.9872441  | -0.0336317 |



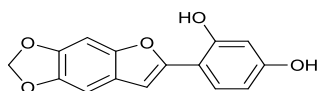
E(0): -841.0915922981  
 Chem. Pot (298.15 K): 0.178133  
 G(298.15): -840.9134592981



E(0): -840.8834583532  
 Chem. Pot (298.15 K): 0.178891  
 G(298.15): -840.7045673532

|   |            |            |            |
|---|------------|------------|------------|
| C | -3.0289971 | -1.3664961 | 0.0953906  |
| C | 0.1361232  | 0.2395418  | -0.0327769 |
| H | -0.3197621 | 2.3754360  | -0.0716379 |
| H | -2.9099146 | -2.4423298 | 0.1174517  |
| C | -3.2871754 | 1.4929480  | 0.0353805  |
| C | -4.2800250 | -0.7538138 | 0.1158213  |
| H | -3.3783867 | 2.5722129  | 0.0126536  |
| C | -4.4072287 | 0.6779974  | 0.0865758  |
| C | -2.0137750 | 0.8830201  | 0.0133691  |
| C | -1.9262868 | -0.5180840 | 0.0444606  |
| C | -0.6662712 | 1.3523242  | -0.0367956 |
| O | -0.6176856 | -0.9248171 | 0.0172128  |
| C | -5.3987242 | -2.8685424 | 0.1962890  |
| O | -5.4599241 | -1.4284560 | 0.1638161  |
| H | -6.4367926 | -3.1979672 | 0.2314919  |
| H | -4.8641639 | -3.2119383 | 1.0893012  |
| H | -4.9116352 | -3.2545840 | -0.7063948 |
| C | -5.8919143 | 2.5535936  | 0.0900064  |
| O | -5.6976529 | 1.1278698  | 0.1139036  |
| H | -6.9719239 | 2.6972708  | 0.1213815  |
| H | -5.4823575 | 2.9862515  | -0.8306011 |
| H | -5.4252523 | 3.0240239  | 0.9637227  |
| O | 2.2184681  | 1.2543284  | -0.1223248 |
| C | 1.5815276  | 0.0577801  | -0.0697052 |
| O | 2.1567696  | -1.0230466 | -0.0560990 |
| C | 3.6704016  | 1.1745655  | -0.1629557 |
| H | 4.0058210  | 2.2092602  | -0.2178589 |
| H | 4.0427657  | 0.6900775  | 0.7428790  |
| H | 3.9889633  | 0.6122914  | -1.0439191 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.9969751 | -1.3932404 | 0.0950327  |
| C | 0.1234093  | 0.2355892  | -0.0340671 |
| H | -0.3196773 | 2.3760664  | -0.0721633 |
| H | -2.8800474 | -2.4686406 | 0.1167442  |
| C | -3.2600710 | 1.5173777  | 0.0344416  |
| C | -4.2548833 | -0.7686934 | 0.1167858  |
| H | -3.3447426 | 2.5961875  | 0.0117621  |
| C | -4.3839632 | 0.7006653  | 0.0866628  |
| C | -2.0104515 | 0.8930295  | 0.0125230  |
| C | -1.9203497 | -0.5422704 | 0.0438366  |
| C | -0.6698550 | 1.3551159  | -0.0375817 |
| O | -0.6175203 | -0.9351593 | 0.0153102  |
| C | -5.4171016 | -2.8700189 | 0.1989417  |
| O | -5.4057396 | -1.4086909 | 0.1645060  |
| H | -6.4716798 | -3.1318180 | 0.2350904  |
| H | -4.8962320 | -3.2141555 | 1.0955013  |
| H | -4.9476256 | -3.2563136 | -0.7087510 |
| C | -5.9031709 | 2.5541284  | 0.0884753  |
| O | -5.6434731 | 1.1210311  | 0.1143217  |
| H | -6.9871067 | 2.6375971  | 0.1193898  |
| H | -5.5050715 | 2.9811814  | -0.8358957 |
| H | -5.4504558 | 3.0236973  | 0.9659060  |
| O | 2.2041420  | 1.2402668  | -0.1197474 |
| C | 1.5888745  | 0.0501093  | -0.0720891 |
| O | 2.1336718  | -1.0388991 | -0.0607788 |
| C | 3.6647107  | 1.1841722  | -0.1611974 |
| H | 3.9800032  | 2.2246012  | -0.2031063 |
| H | 4.0345161  | 0.6920887  | 0.7406039  |
| H | 3.9818562  | 0.6357130  | -1.0504186 |

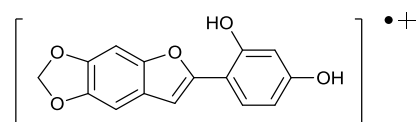


## Sophora

E(0): -954.2723874643

Chem. Pot (298.15 K): 0.175517

G(298.15): -954.0968704643



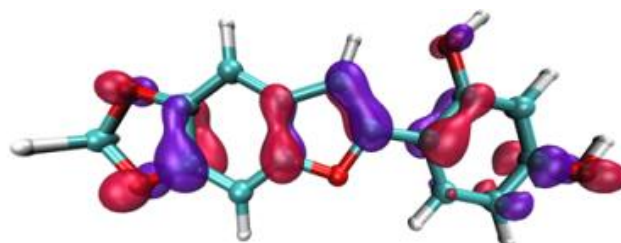
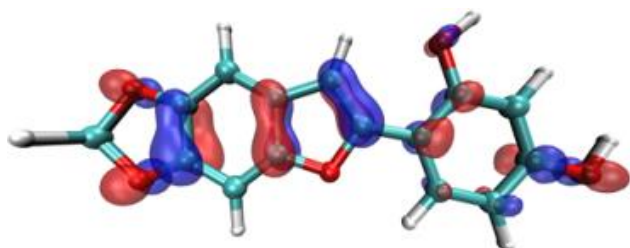
E(0): -954.0893656869

Chem. Pot (298.15 K): 0.177347

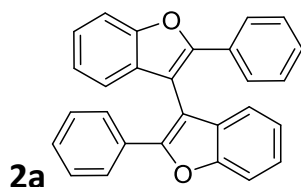
G(298.15): -953.9120186869

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.9319064 | 3.1043118  | 0.0996823  |
| C | -3.1864333 | 1.7228776  | 0.0944412  |
| C | -2.1925885 | 0.7676100  | 0.0757403  |
| C | -0.8712094 | 1.2757436  | 0.0589067  |
| C | -0.6527504 | 2.6675753  | 0.0662207  |
| C | -1.6564850 | 3.6403659  | 0.0877652  |
| H | -1.4564575 | 4.7054229  | 0.0976164  |
| H | -2.4104580 | -0.2948145 | 0.0790324  |
| C | 0.4324877  | 0.6793531  | 0.0281983  |
| C | 1.3515528  | 1.7011692  | 0.0194567  |
| O | 0.6928319  | 2.9345489  | 0.0412750  |
| H | 0.6645164  | -0.3734266 | 0.0154326  |
| C | 2.7995253  | 1.7818863  | -0.0035873 |
| C | 3.4516427  | 3.0333626  | -0.0083704 |
| C | 3.6240793  | 0.6317309  | -0.0211384 |
| C | 5.0159631  | 0.7397877  | -0.0414140 |
| C | 5.6207726  | 1.9986302  | -0.0451083 |
| C | 4.8334045  | 3.1558095  | -0.0287722 |
| H | 2.8450178  | 3.9322445  | 0.0047649  |
| H | 5.6238076  | -0.1632002 | -0.0542081 |
| H | 5.3089884  | 4.1312344  | -0.0320022 |
| C | -5.1462526 | 2.8038369  | -0.0798439 |
| O | -4.1241265 | 3.7956392  | 0.1744231  |
| H | -5.9766754 | 2.9602476  | 0.6091635  |
| H | -5.4528726 | 2.8669193  | -1.1323059 |
| O | -4.5538899 | 1.5126892  | 0.1704399  |
| H | 3.6989002  | -1.2908493 | -0.0295895 |
| O | 3.0183267  | -0.5959955 | -0.0174623 |
| O | 6.9823554  | 2.1563261  | -0.0644245 |
| H | 7.4131069  | 1.2842644  | -0.0745596 |

|   |            |            |            |
|---|------------|------------|------------|
| C | -2.9007851 | 3.0979168  | 0.0128878  |
| C | -3.1572656 | 1.6931837  | 0.0202965  |
| C | -2.1676353 | 0.7461784  | 0.0078199  |
| C | -0.8513301 | 1.2735334  | -0.0107279 |
| C | -0.6334661 | 2.6892709  | -0.0171444 |
| C | -1.6276208 | 3.6535388  | -0.0070148 |
| H | -1.4411117 | 4.7199650  | -0.0114407 |
| H | -2.3711687 | -0.3176891 | 0.0146301  |
| C | 0.4276655  | 0.6910176  | -0.0198840 |
| C | 1.3627517  | 1.7299291  | -0.0285050 |
| O | 0.7023240  | 2.9589673  | -0.0300767 |
| H | 0.6647542  | -0.3603600 | -0.0169998 |
| C | 2.7823958  | 1.7954699  | -0.0255790 |
| C | 3.4410292  | 3.0575418  | -0.0251147 |
| C | 3.6037947  | 0.6214487  | -0.0133023 |
| C | 4.9897925  | 0.7235212  | 0.0047663  |
| C | 5.5927394  | 1.9850729  | 0.0083907  |
| C | 4.8094757  | 3.1628214  | -0.0084588 |
| H | 2.8369693  | 3.9569389  | -0.0362059 |
| H | 5.5984741  | -0.1774010 | 0.0164314  |
| H | 5.3034185  | 4.1281390  | -0.0065697 |
| C | -5.1319492 | 2.7882289  | 0.0446079  |
| O | -4.0629835 | 3.7728253  | 0.0306300  |
| H | -5.7121420 | 2.9156808  | 0.9611142  |
| H | -5.7284771 | 2.9079374  | -0.8625954 |
| O | -4.5040270 | 1.4927355  | 0.0446561  |
| H | 3.6396831  | -1.2990326 | -0.0053829 |
| O | 2.9833761  | -0.5792332 | -0.0184468 |
| O | 6.9307020  | 2.1496315  | 0.0281057  |
| H | 7.3857899  | 1.2875226  | 0.0388849  |

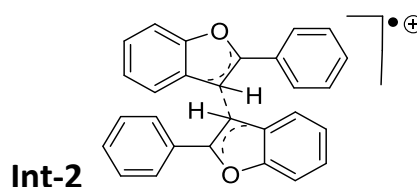


Frontier MOs of neutral and radical cation *Sophora*.



E(0): -1228.9949052129  
 Chem. Pot (298.15 K): 0.31831  
 G(298.15): -1228.6765952129

|   |            |            |            |
|---|------------|------------|------------|
| C | 1.6008603  | -2.5036249 | -2.0371161 |
| C | 0.3396350  | -4.1528445 | -0.7913584 |
| C | -1.1777991 | 0.0867075  | -1.1556590 |
| C | 0.4592356  | -3.3685375 | 0.3601608  |
| C | 3.5636285  | 1.1599002  | -1.9553267 |
| H | 2.0278088  | -2.1579955 | -2.9723497 |
| H | 0.1208681  | 2.4393804  | -1.3843276 |
| H | -0.7232688 | 1.3857042  | 0.5429761  |
| O | 3.0416218  | -0.0993668 | -2.1206479 |
| C | -1.2014212 | 0.4996547  | 0.1507627  |
| H | 0.8204524  | -4.3155565 | -2.8873604 |
| H | -3.2919027 | -1.9858708 | 3.6114442  |
| C | -3.0578577 | -2.5932957 | 0.2564941  |
| C | 0.0871037  | 0.4115794  | -4.6860372 |
| H | 4.4727481  | 1.4710678  | -3.8946137 |
| C | 3.6953043  | 2.9335770  | -0.3115373 |
| C | 0.9144926  | -3.7153248 | -1.9863235 |
| H | 3.4792636  | 3.3431794  | 0.6712680  |
| C | 2.5212044  | 0.5986532  | -0.0232057 |
| H | -3.9602036 | -3.6383398 | 1.9019982  |
| C | 4.2707782  | 1.8776696  | -2.9090174 |
| C | 4.6898332  | 3.1559199  | -2.5333236 |
| H | 1.2230182  | -1.5561719 | 1.2161816  |
| C | -0.5518620 | -0.0996631 | -3.5581259 |
| H | -0.2040390 | -5.0928292 | -0.7572162 |
| C | 1.1458557  | -2.1604942 | 0.3175647  |
| O | -1.8731458 | -1.1099900 | -1.3034633 |
| C | 4.4029694  | 3.6746009  | -1.2552396 |
| H | -1.0388663 | -1.0678910 | -3.6000870 |
| C | 1.7248141  | -1.7080979 | -0.8835970 |
| C | -3.3957363 | -2.7603149 | 1.6012802  |
| C | -2.3302322 | -1.4541335 | -0.0553556 |
| C | -0.5520814 | 0.6238838  | -2.3515757 |
| H | 0.0840909  | -0.1616974 | -5.6093169 |
| C | 3.2657537  | 1.6427675  | -0.6646799 |
| C | 0.1013034  | 1.8704107  | -2.3087061 |
| H | 0.0016541  | -3.6919839 | 1.2905240  |
| H | -3.3337623 | -3.3185745 | -0.5020277 |
| C | -1.9369018 | -0.4848802 | 0.8898083  |
| C | 2.4013643  | -0.4234161 | -0.9279909 |
| C | 0.7403527  | 2.3726458  | -3.4366786 |
| H | 5.2435530  | 3.7635203  | -3.2433739 |
| H | 1.2560165  | 3.3267400  | -3.3797498 |
| H | 4.7432848  | 4.6753922  | -1.0036083 |
| H | 2.1021547  | 0.6152574  | 0.9726047  |
| H | -1.9956902 | 0.0434750  | 2.9970334  |
| C | 0.7372327  | 1.6462781  | -4.6315813 |
| C | -3.0127152 | -1.8169351 | 2.5749915  |
| H | 1.2433746  | 2.0375604  | -5.5096412 |
| C | -2.2867476 | -0.6768574 | 2.2375627  |

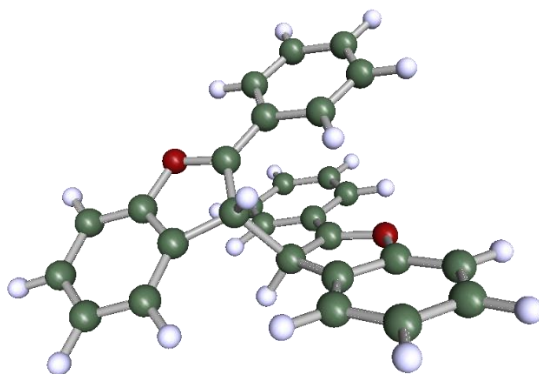


E(0): -1229.9704993022  
 Chem. Pot (298.15 K): 0.339987  
 G(298.15): -1229.6305123022

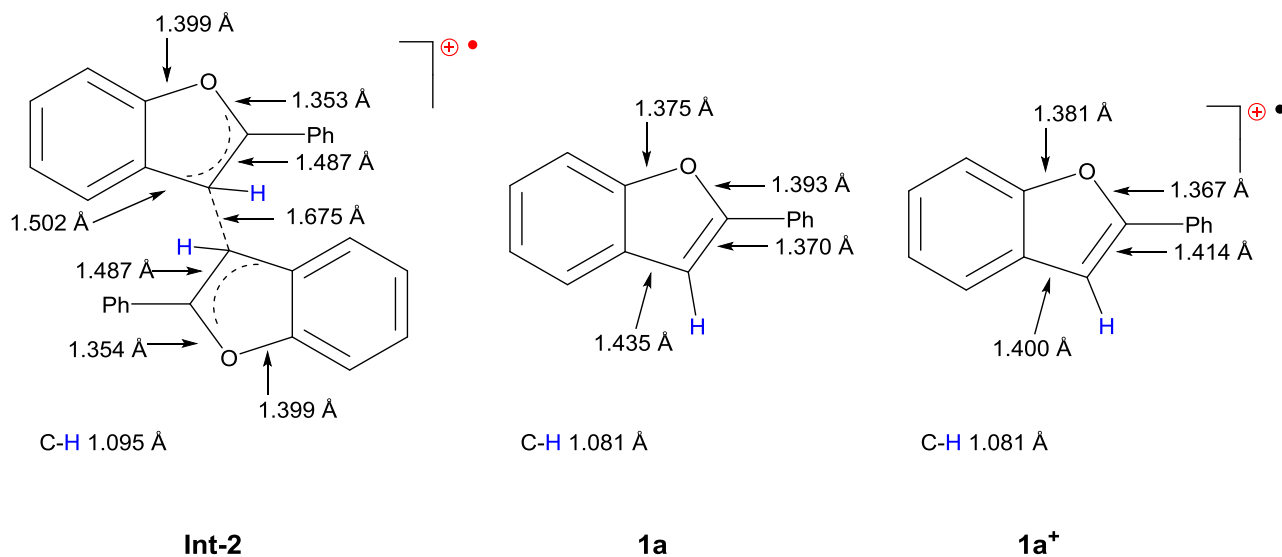
|   |            |            |            |
|---|------------|------------|------------|
| C | 2.3971477  | -2.2978891 | -2.8170060 |
| C | 0.9800071  | -4.2518628 | -2.6546097 |
| C | -0.9162209 | -0.0777720 | -1.2938247 |
| C | 0.4128315  | -3.7652833 | -1.4732076 |
| C | 3.2550882  | 1.4237872  | -1.0231238 |
| H | 3.1499132  | -1.7170605 | -3.3387182 |
| H | 0.8007893  | 1.5774465  | -2.4855894 |
| H | -0.1749927 | 1.6760378  | -0.3334833 |
| O | 3.1522511  | 0.2016932  | -1.6970419 |
| C | -0.1683125 | 0.5900825  | -0.1956533 |
| H | 2.4184851  | -3.9069008 | -4.2295559 |
| H | -1.6252714 | -0.0707981 | 4.3109997  |
| C | -2.8690275 | -1.3433340 | 1.3949272  |
| C | -0.9934178 | -0.8395899 | -4.9428112 |
| H | 4.9097924  | 2.2883998  | -2.1149463 |
| C | 2.2454048  | 2.6707113  | 0.7598008  |
| C | 1.9785680  | -3.5191056 | -3.3159163 |
| H | 1.5110489  | 2.7864189  | 1.5514685  |
| C | 1.4688932  | 0.2656076  | -0.0488078 |
| H | -3.4027466 | -1.5617862 | 3.4640763  |
| C | 4.1826602  | 2.4064061  | -1.3192227 |
| C | 4.1198358  | 3.5577129  | -0.5263965 |
| H | 0.4121877  | -2.1905995 | -0.0172967 |
| C | -1.3393341 | -0.8640857 | -3.6029990 |
| H | 0.6554536  | -5.2064506 | -3.0577187 |
| C | 0.8258177  | -2.5440918 | -0.9576135 |
| O | -1.9411451 | -0.8283705 | -0.8274296 |
| C | 3.1690076  | 3.6883470  | 0.4949644  |
| H | -2.0985326 | -1.5489220 | -3.2413369 |
| C | 1.8116301  | -1.7821295 | -1.6323767 |
| C | -2.7209833 | -1.0902051 | 2.7631769  |
| C | -1.9628640 | -0.7061855 | 0.5663469  |
| C | -0.6708611 | -0.0124667 | -2.6864946 |
| H | -1.4969217 | -1.5010423 | -5.6411264 |
| C | 2.2989910  | 1.5166033  | -0.0168597 |
| C | 0.3227616  | 0.8771518  | -3.1649047 |
| H | -0.3440419 | -4.3440255 | -0.9528453 |
| H | -3.6423000 | -1.9962118 | 1.0055713  |
| C | -0.9500492 | 0.1405591  | 1.0051955  |
| C | 2.1308653  | -0.4925648 | -1.1435396 |
| C | 0.6621631  | 0.8866549  | -4.5111499 |
| H | 4.8224749  | 4.3644818  | -0.7104904 |
| H | 1.4255493  | 1.5691417  | -4.8716674 |
| H | 3.1488502  | 4.5953663  | 1.0910253  |
| H | 1.5071385  | -0.3017207 | 0.8866091  |
| H | -0.0310092 | 1.0269270  | 2.7550866  |
| C | 0.0131170  | 0.0255376  | -5.4007125 |
| C | -1.7112658 | -0.2448331 | 3.2429623  |
| H | 0.2799163  | 0.0329892  | -6.4532573 |
| C | -0.8119448 | 0.3780624  | 2.3699586  |

## Computational analysis of the proposed intermediate Int-2

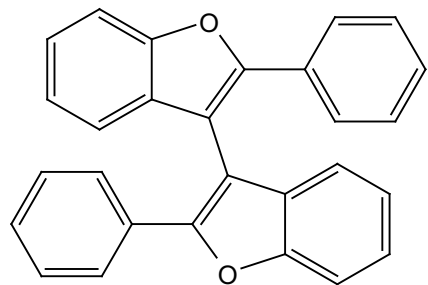
**Int-2** is a proposed intermediate structure in route from **1a** to **2a**. When the benzo[*b*]furans **1a** and **1a**<sup>+</sup> are connected together at C3-carbon, a geometry optimization yields a stable minimum with a structure that has a long C–C bond (1.675 Å). The minimum is very shallow, lying behind a very low barrier to **1a** and **1a**<sup>+</sup>. The calculated Gibbs energy change  $\Delta G = \text{Int-2} - (\mathbf{1a} + \mathbf{1a}^+)$  is endergonic by 17.8 kcal mol<sup>−1</sup> (the effects of acid and DDQ have been excluded from the calculations).



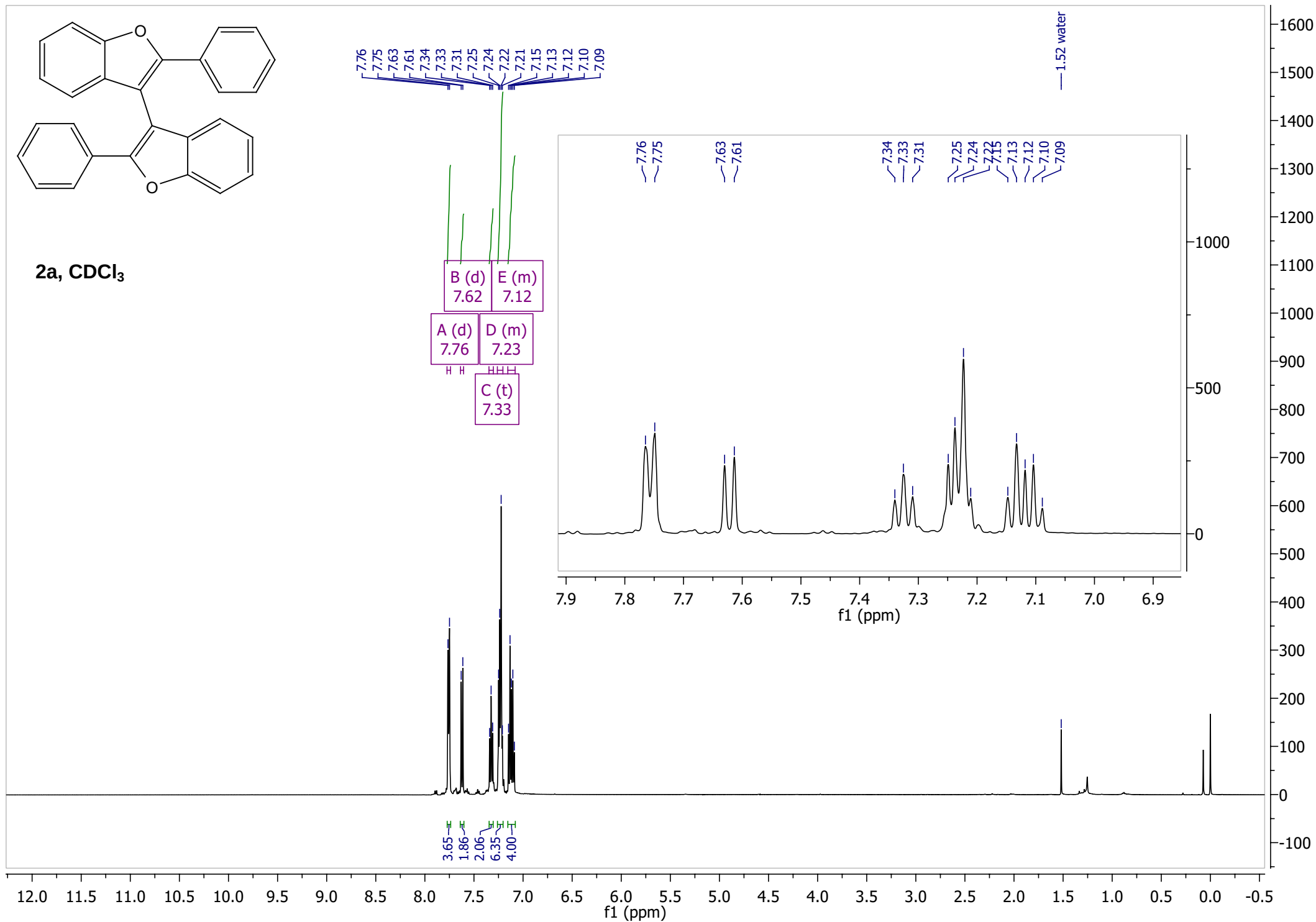
**Figure S10.** Optimized structure of **Int-2**.

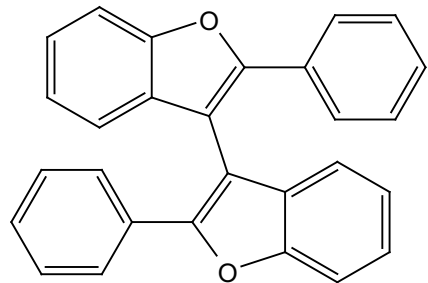


**Figure S11.** Optimized bond lengths of **Int-2**, **1a** and **1a**<sup>+</sup>.

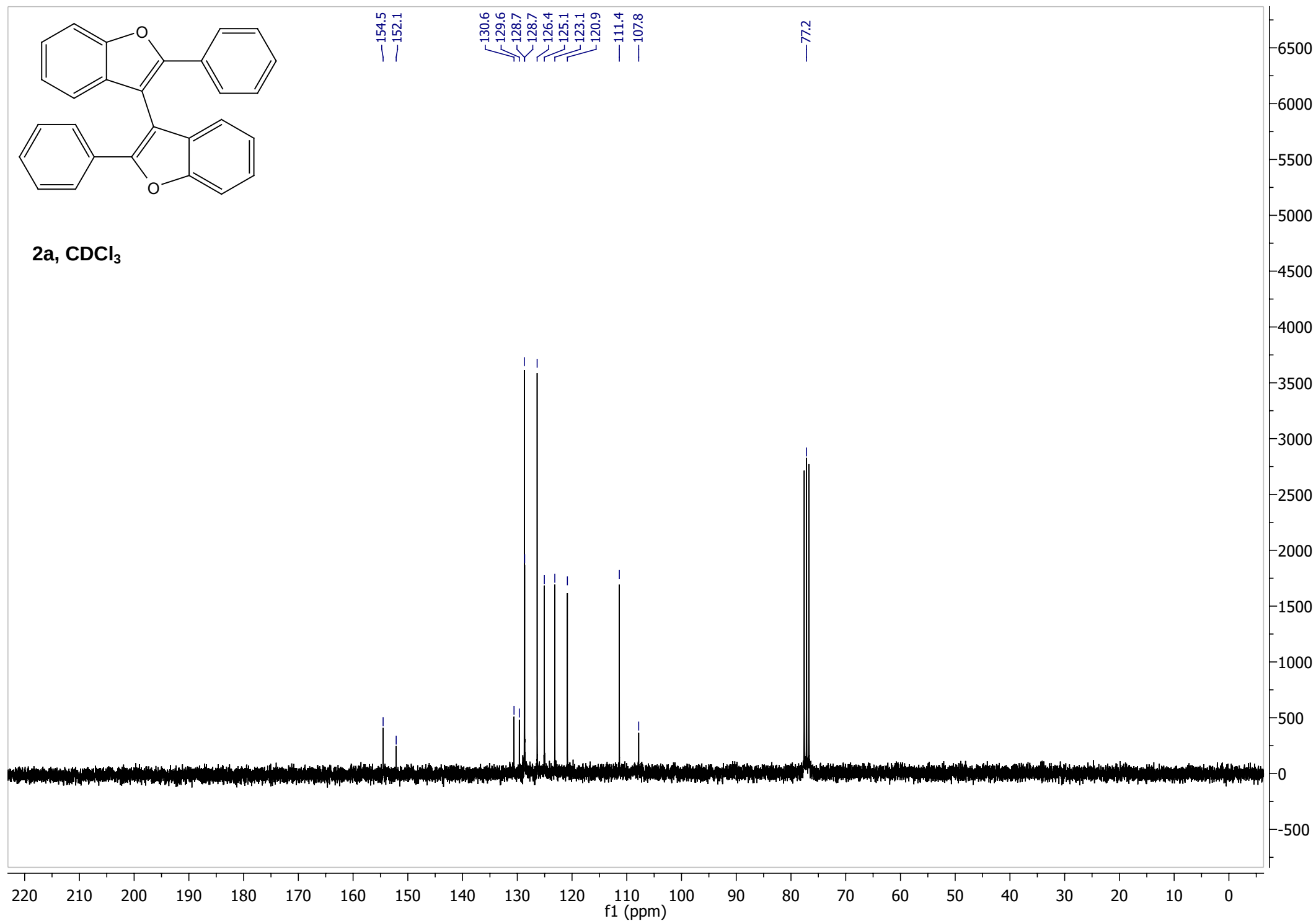


2a, CDCl<sub>3</sub>

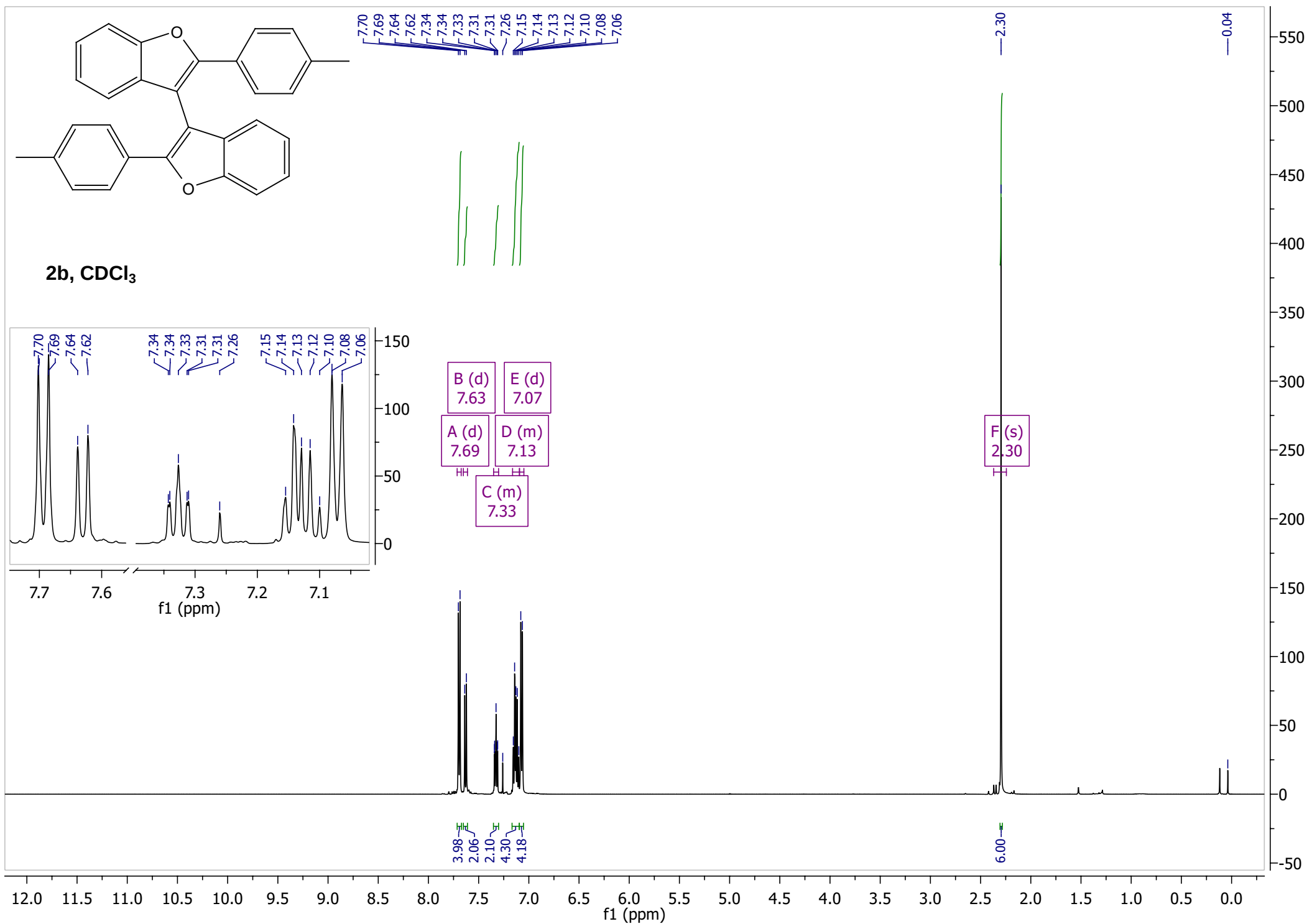


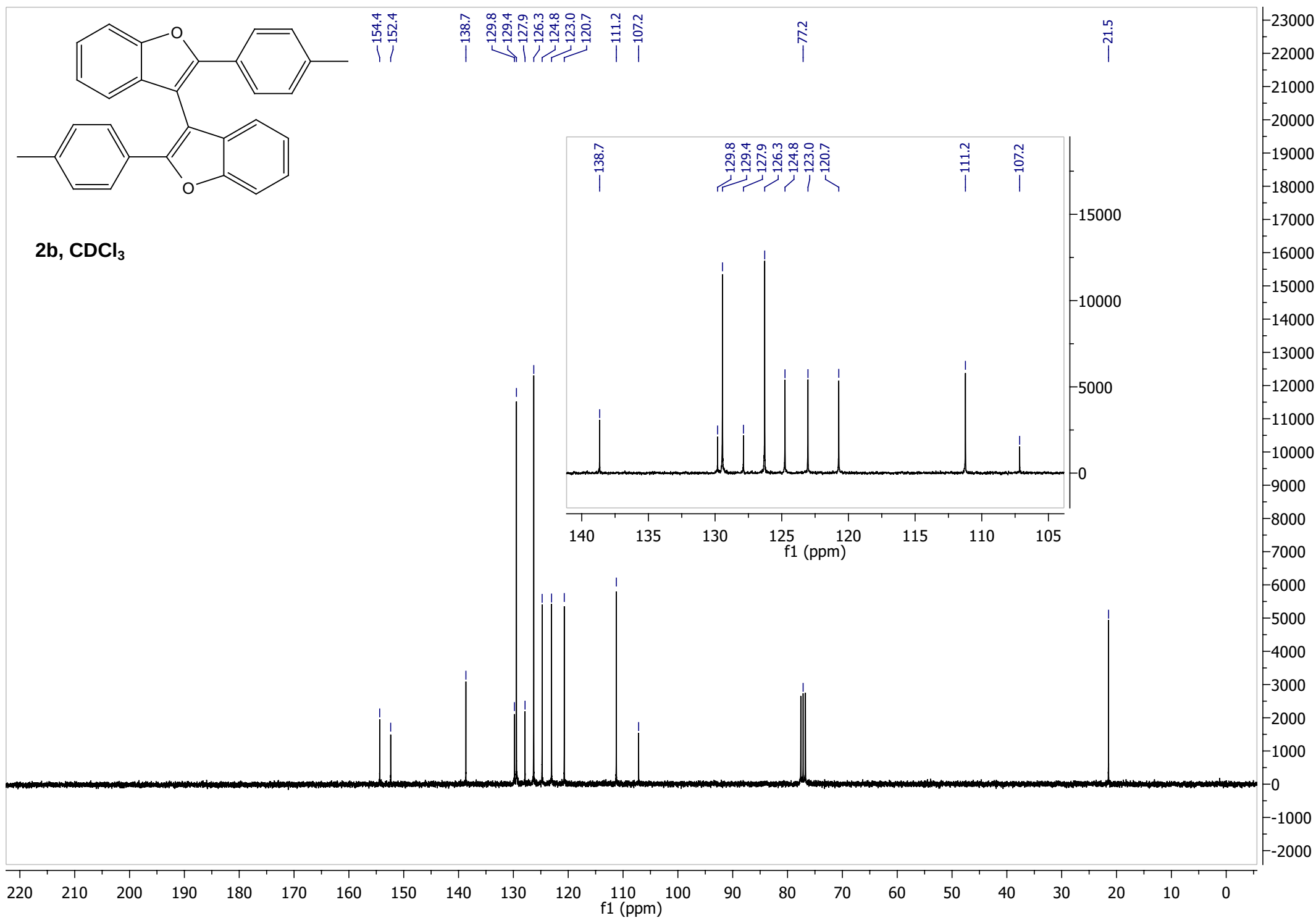


2a, CDCl<sub>3</sub>

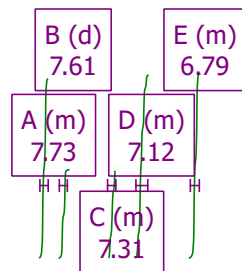
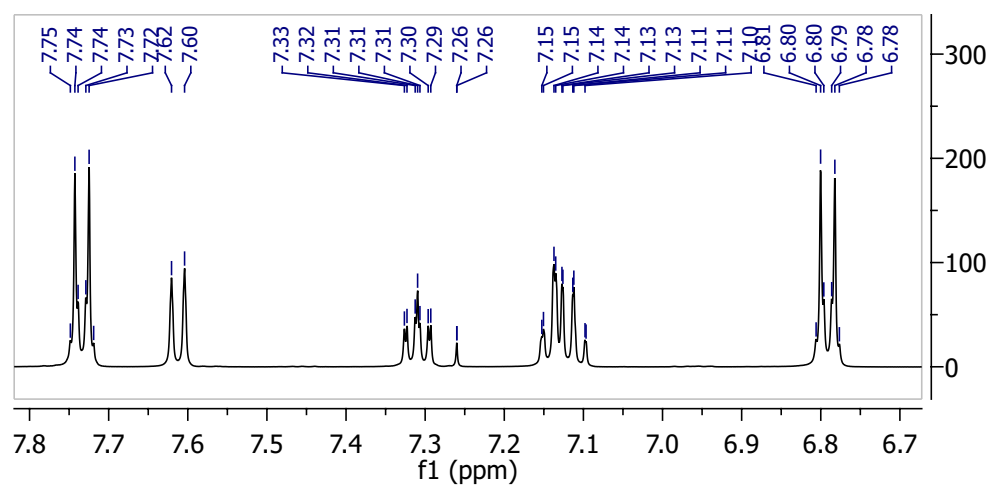
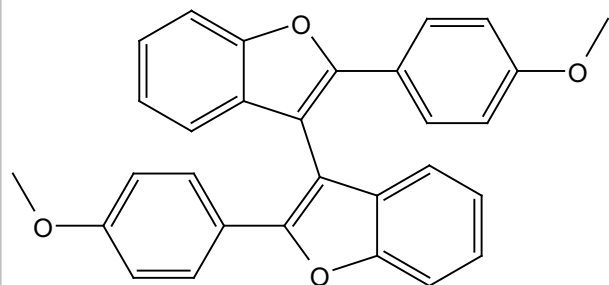






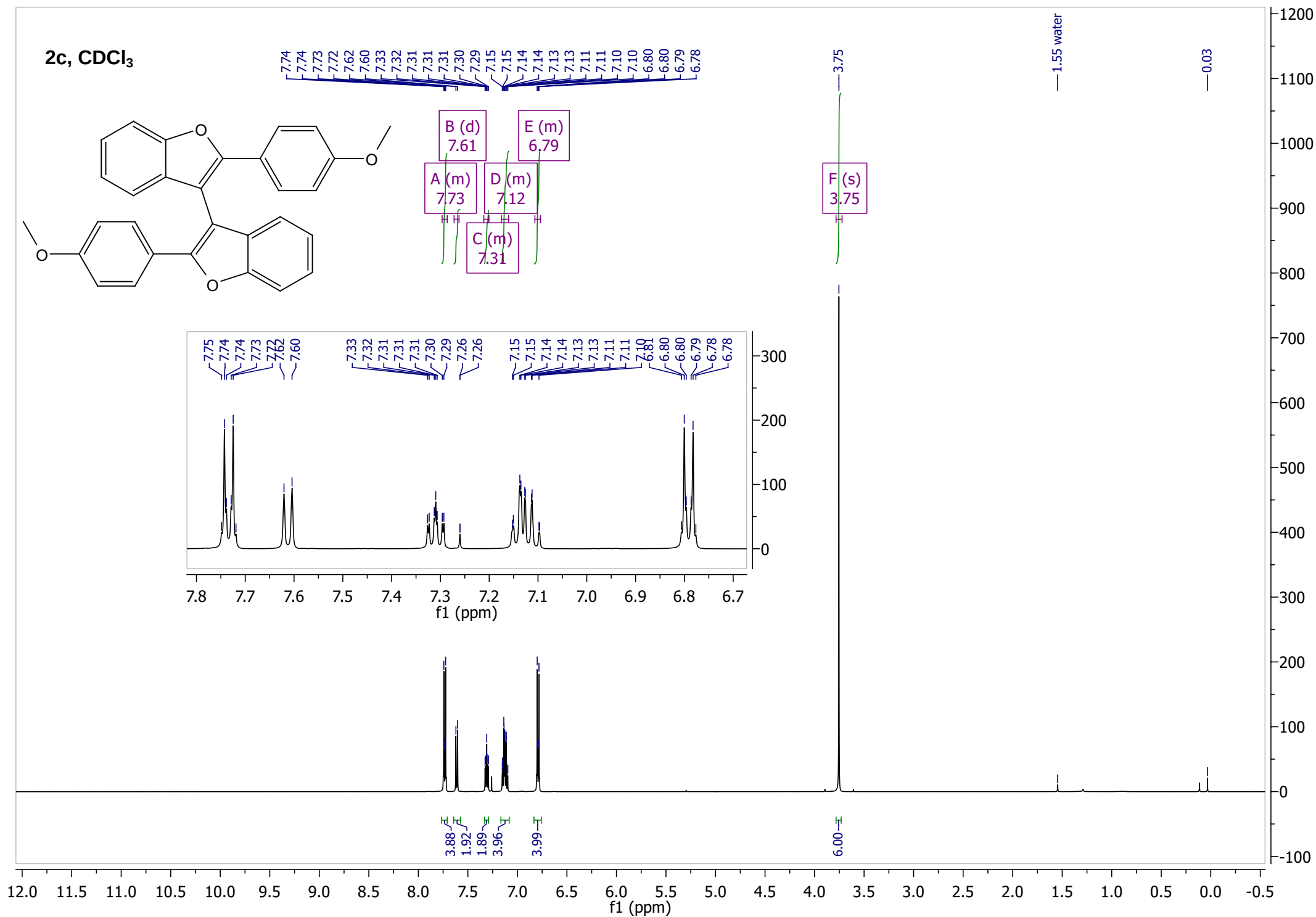


2c, CDCl<sub>3</sub>

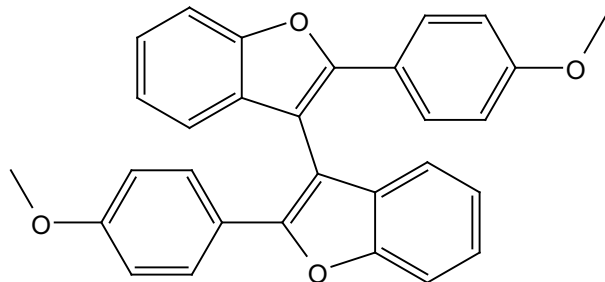


— 1.55 water

— 0.03



2c, CDCl<sub>3</sub>

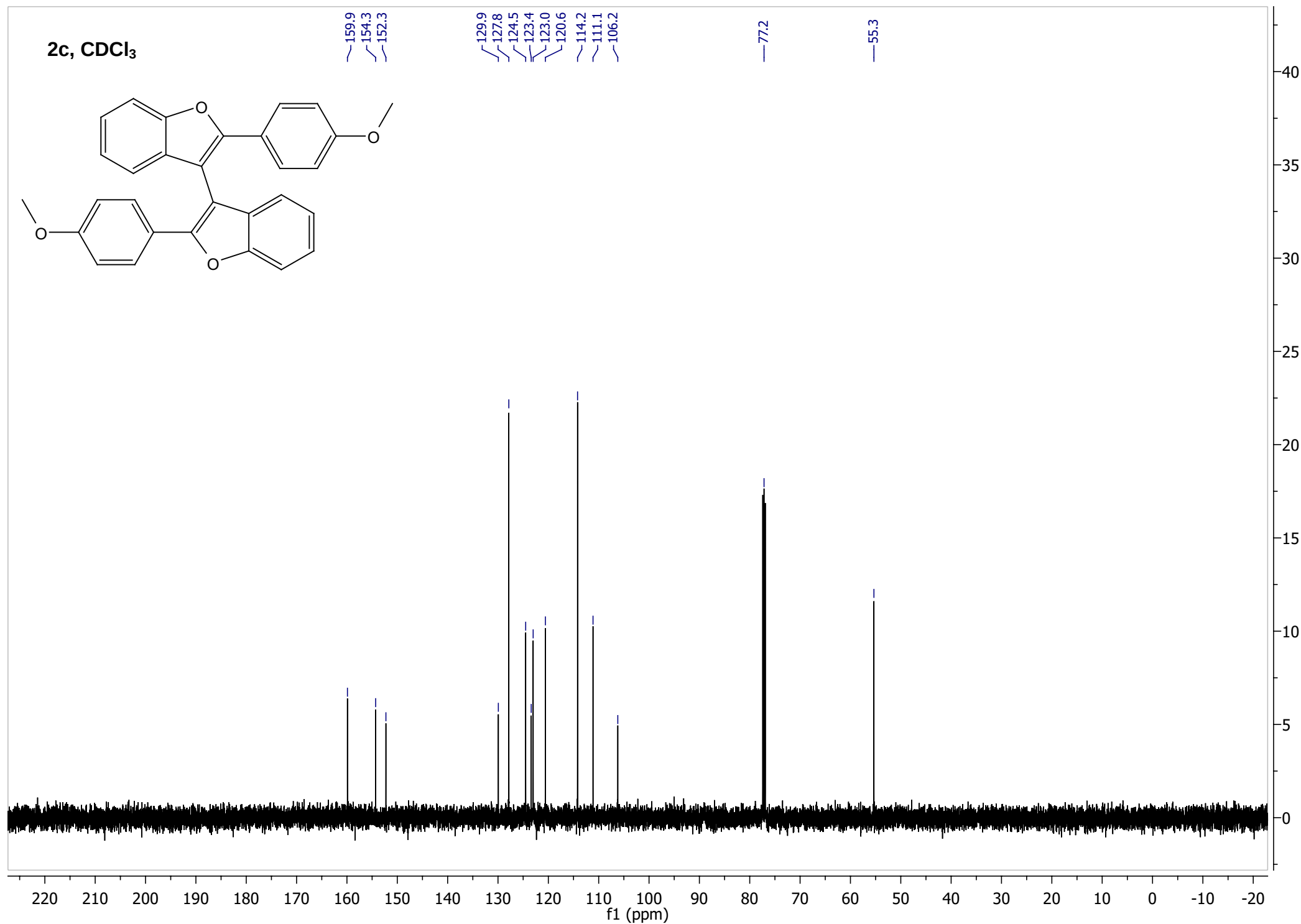


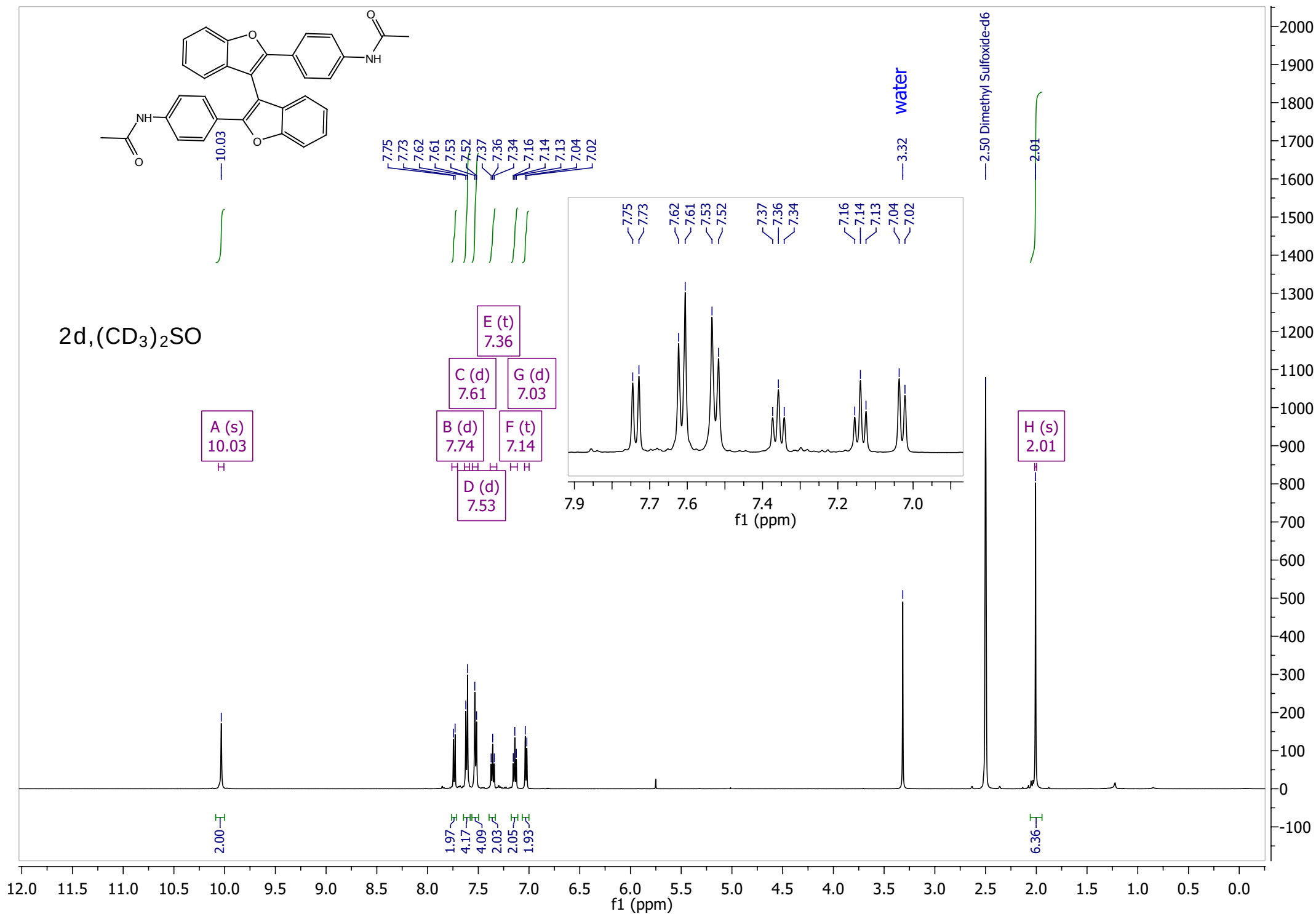
159.9  
154.3  
152.3

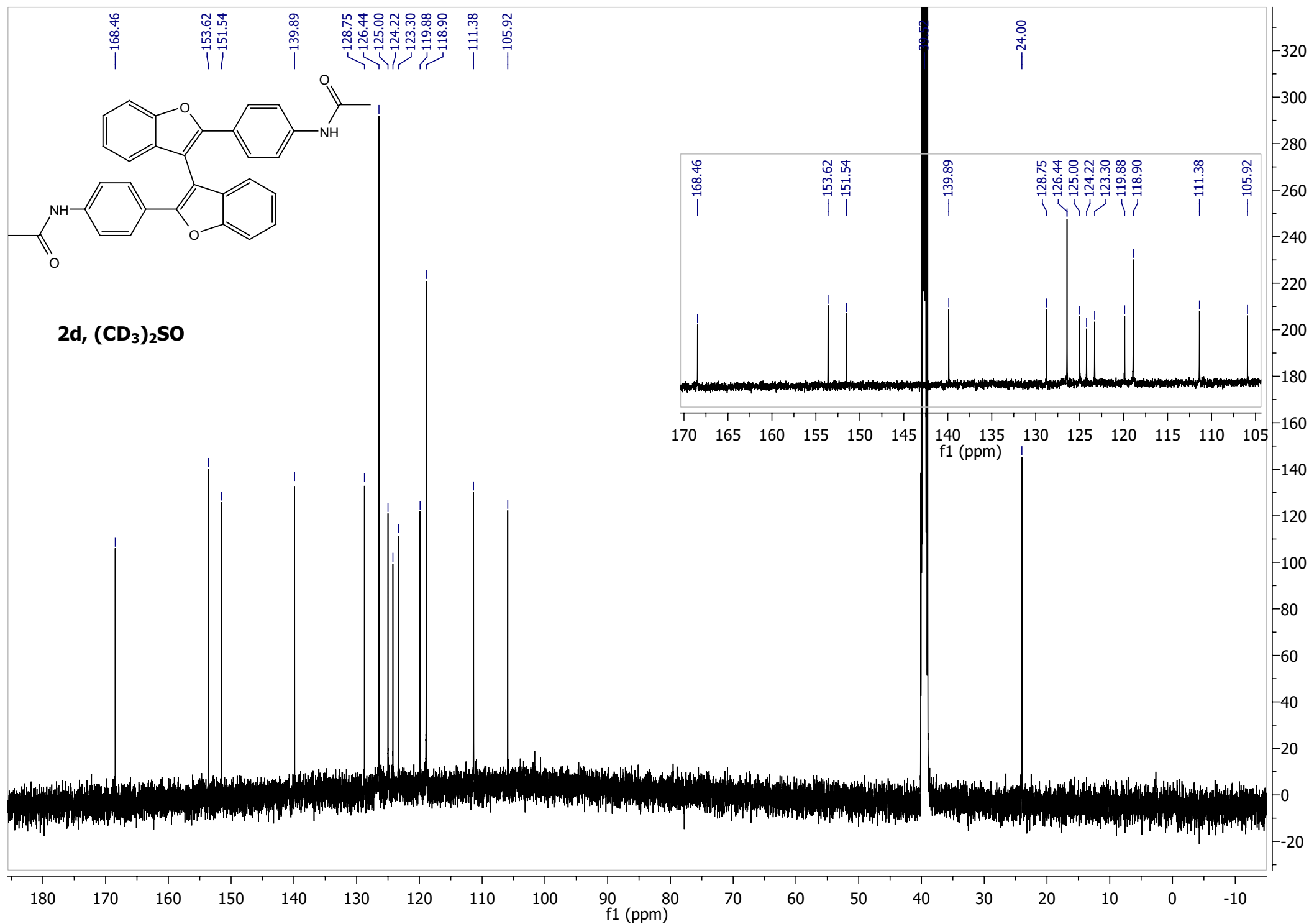
129.9  
127.8  
124.5  
123.4  
123.0  
120.6  
114.2  
111.1  
106.2

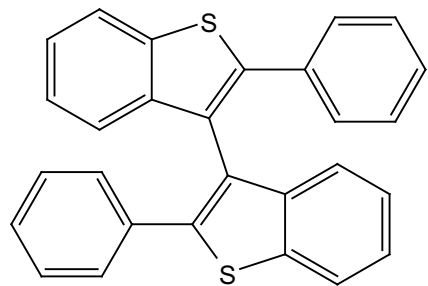
77.2

55.3

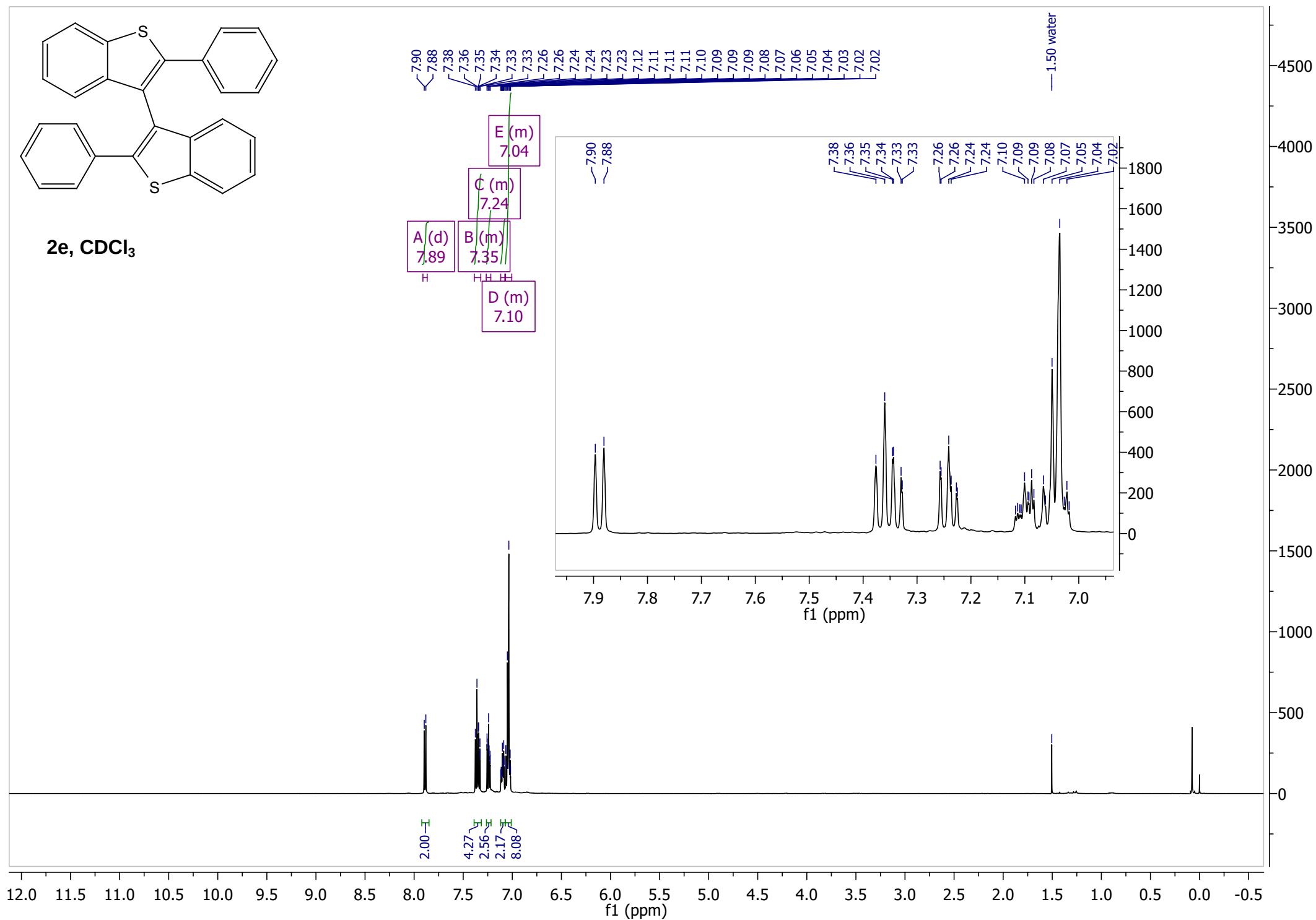


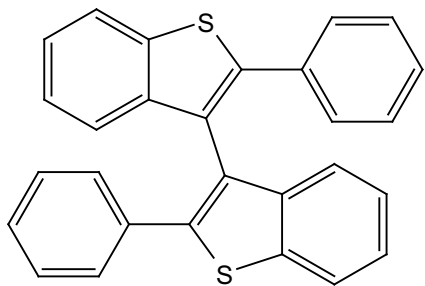




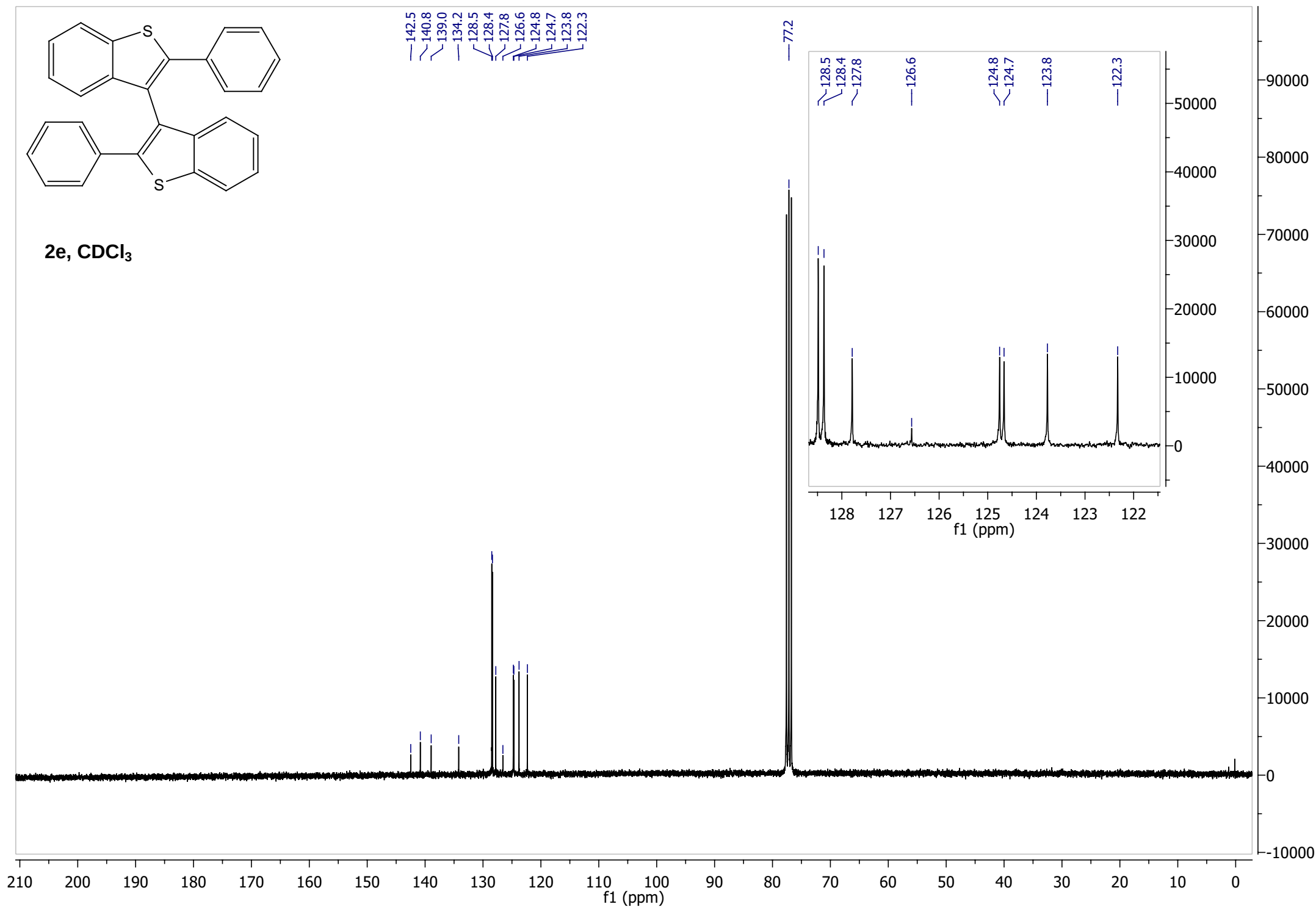


2e, CDCl<sub>3</sub>

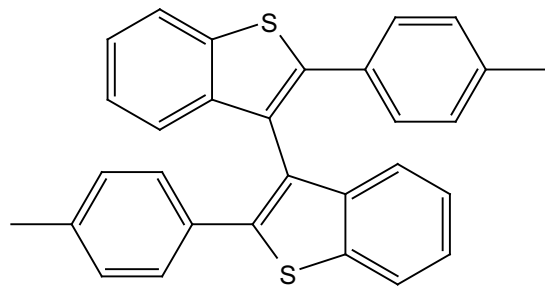




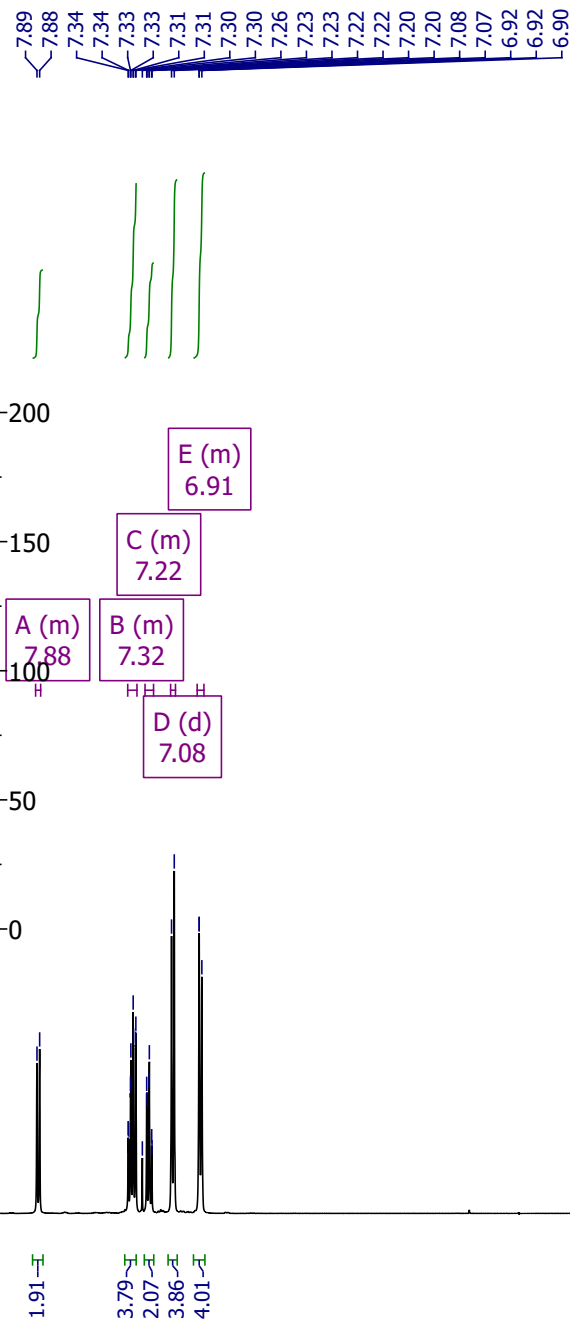
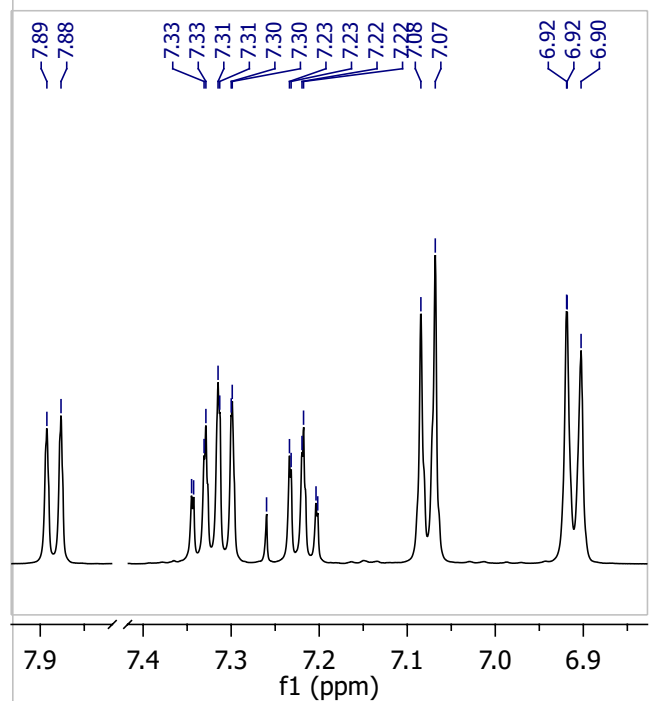
2e, CDCl<sub>3</sub>







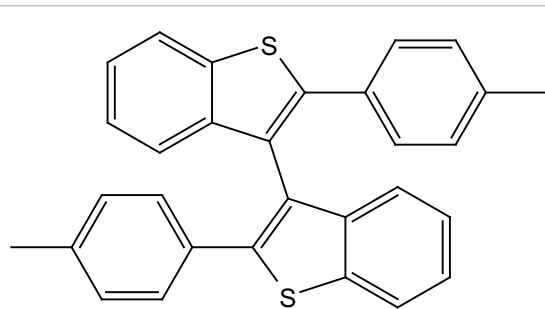
2f, CDCl<sub>3</sub>



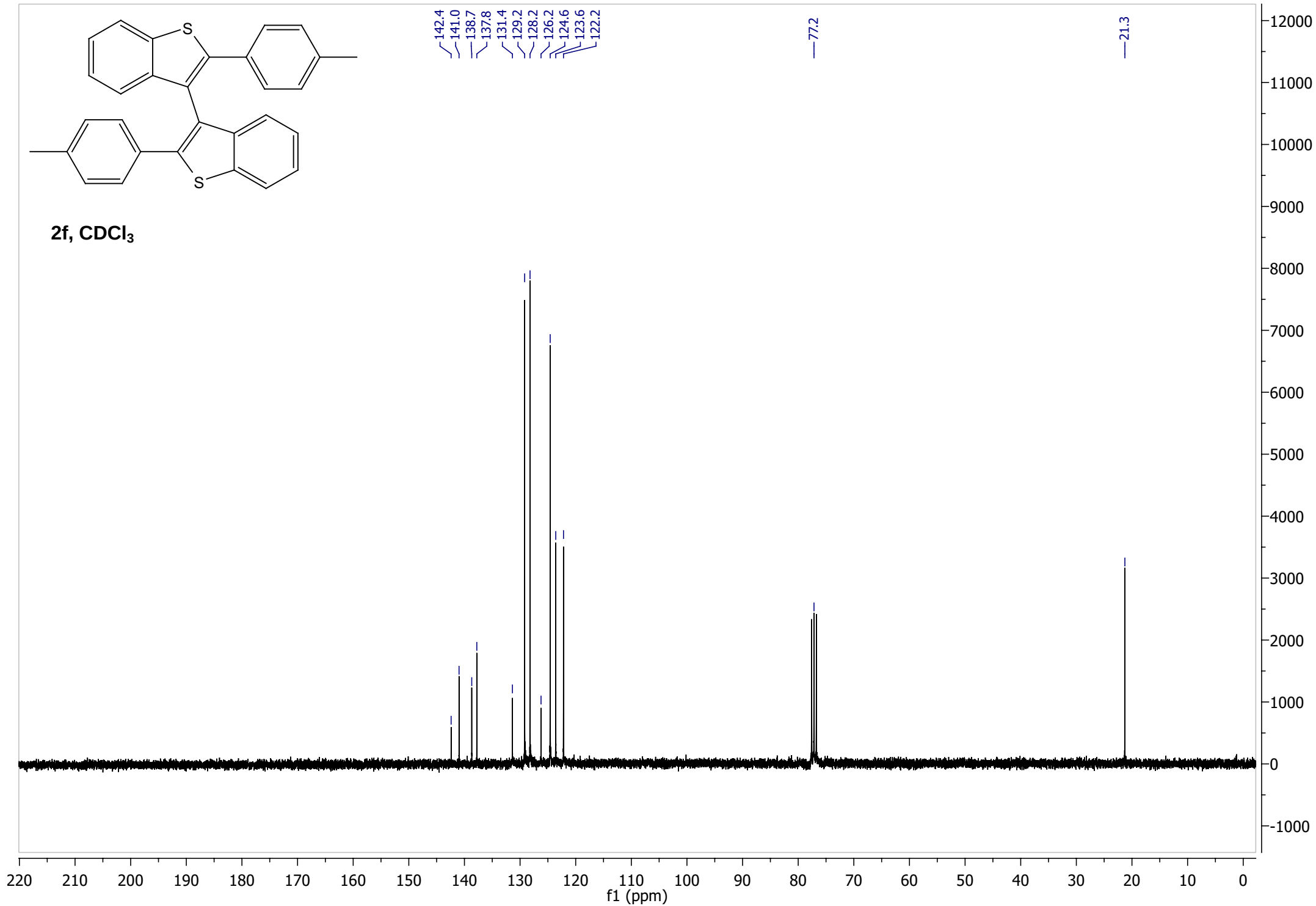
F(s)  
2.24

1.52 water

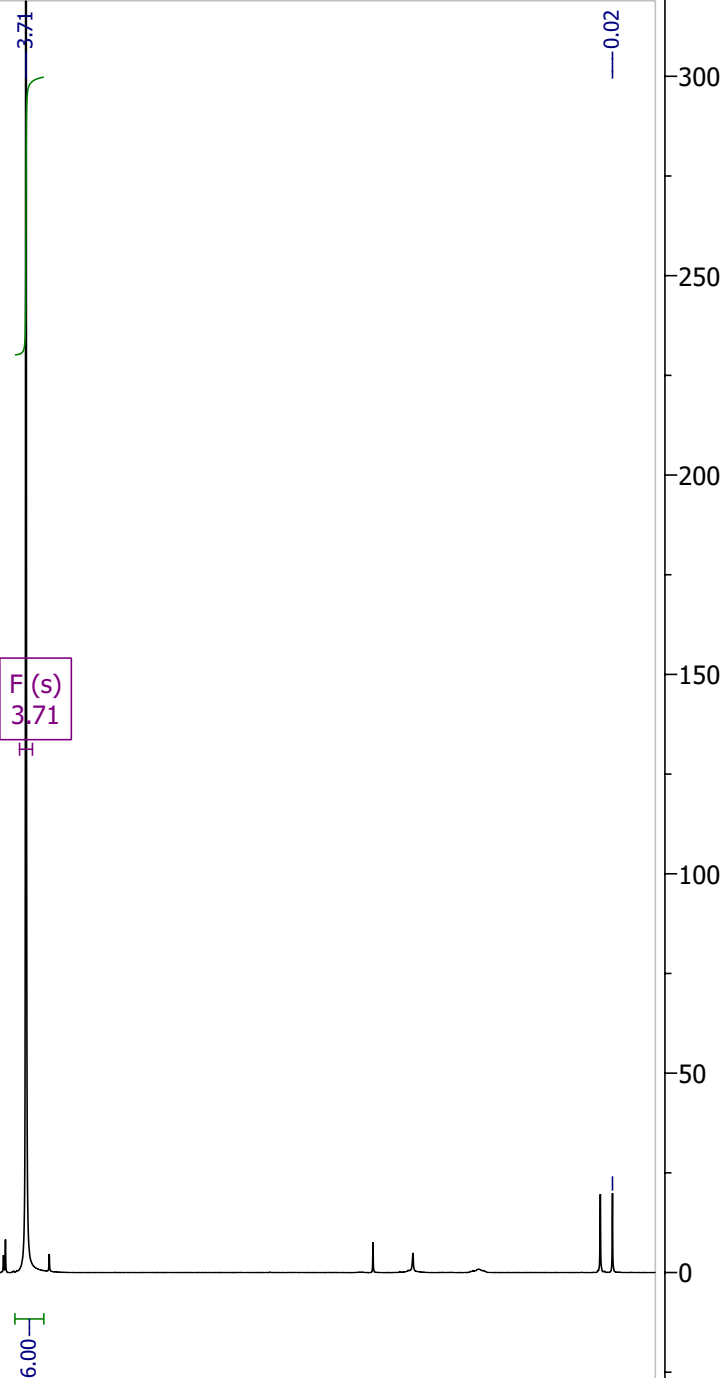
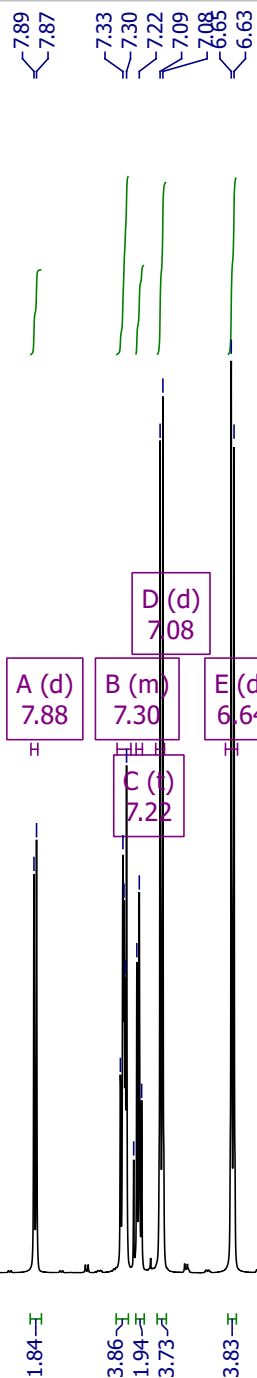
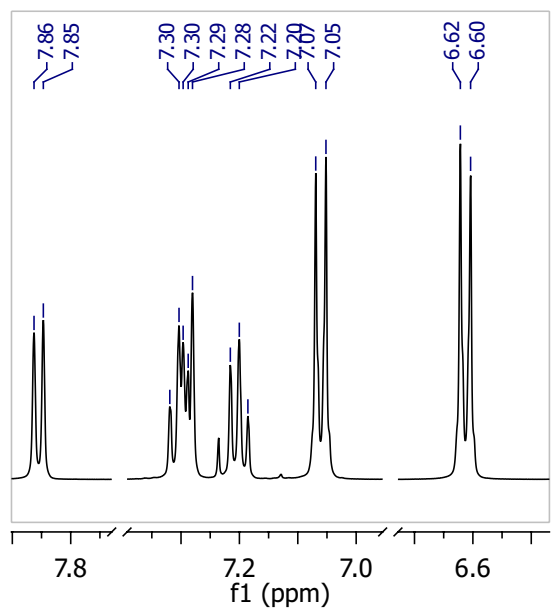
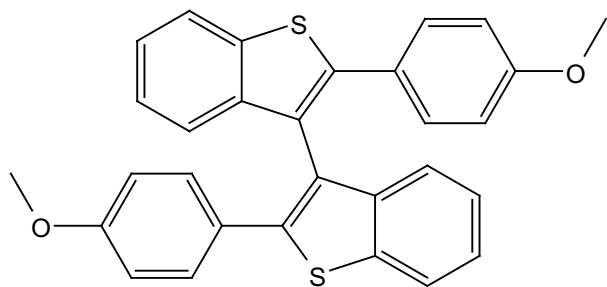
0.03



2f, CDCl<sub>3</sub>

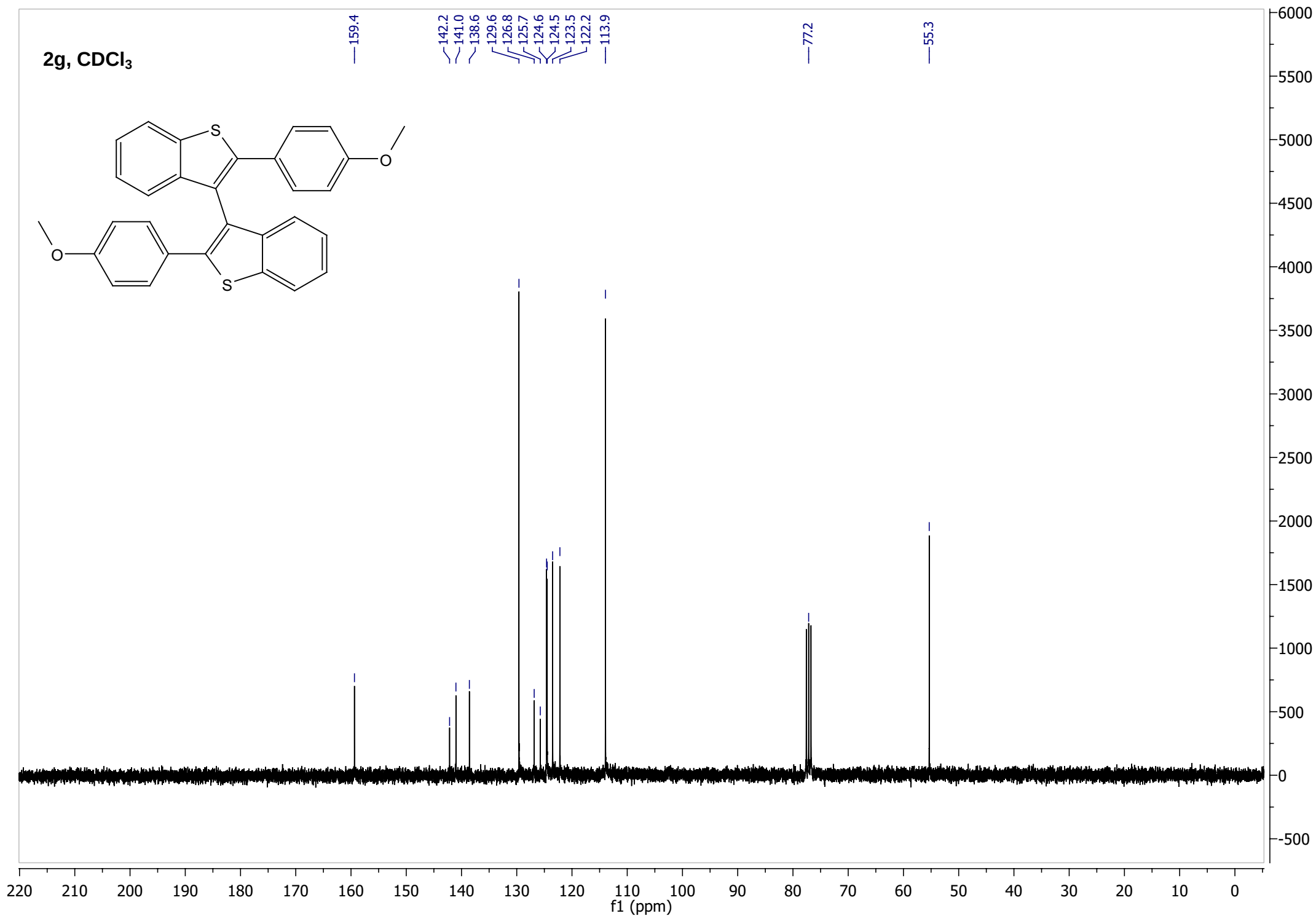
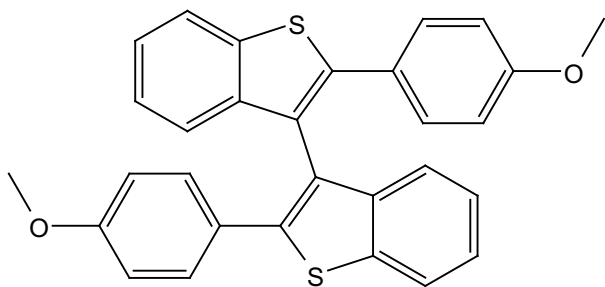


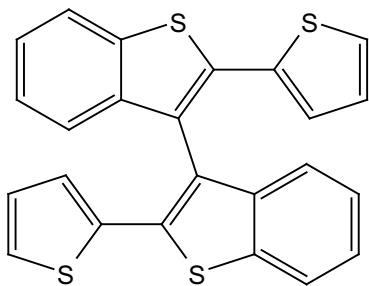
2g, CDCl<sub>3</sub>



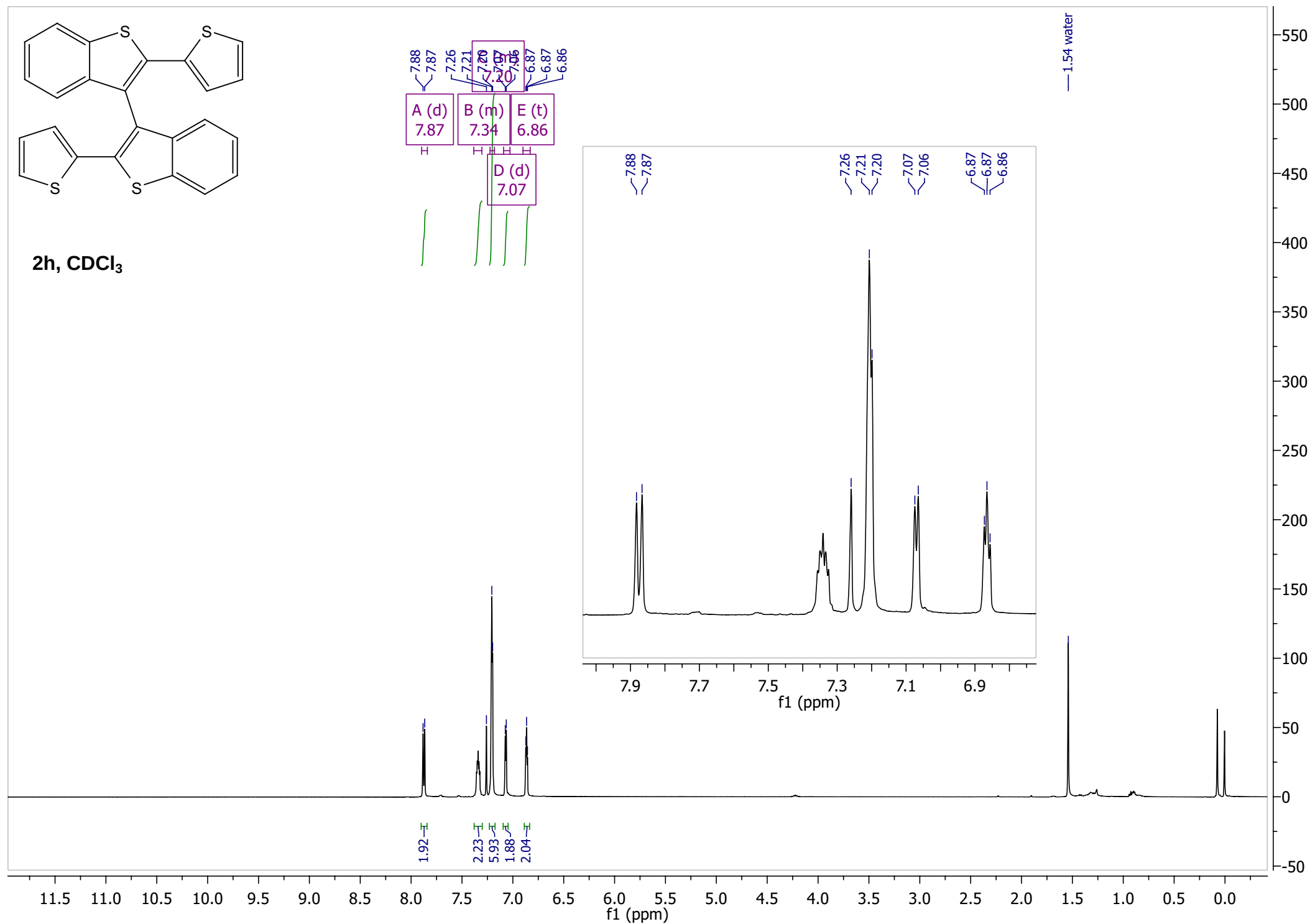
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

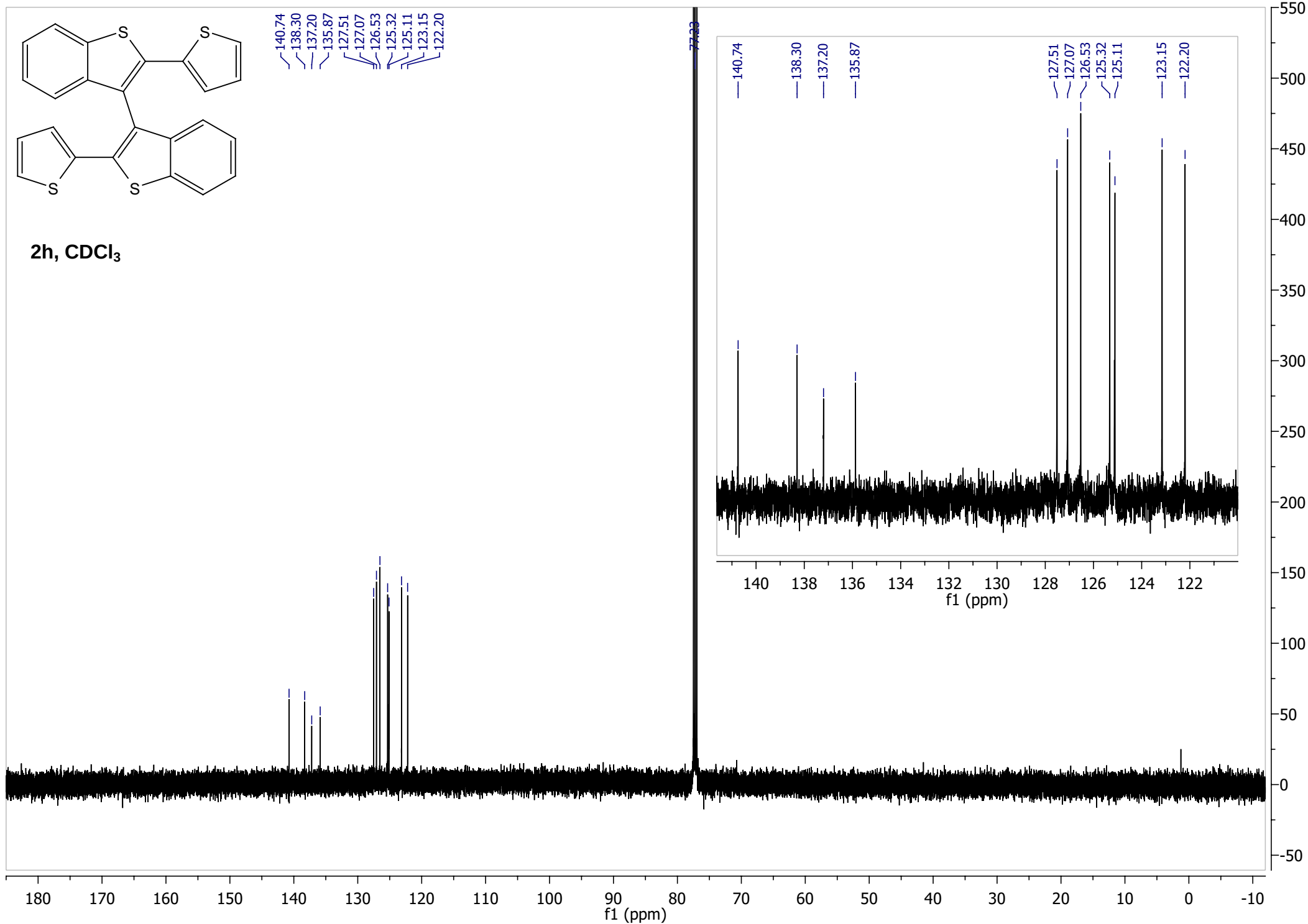
2g, CDCl<sub>3</sub>

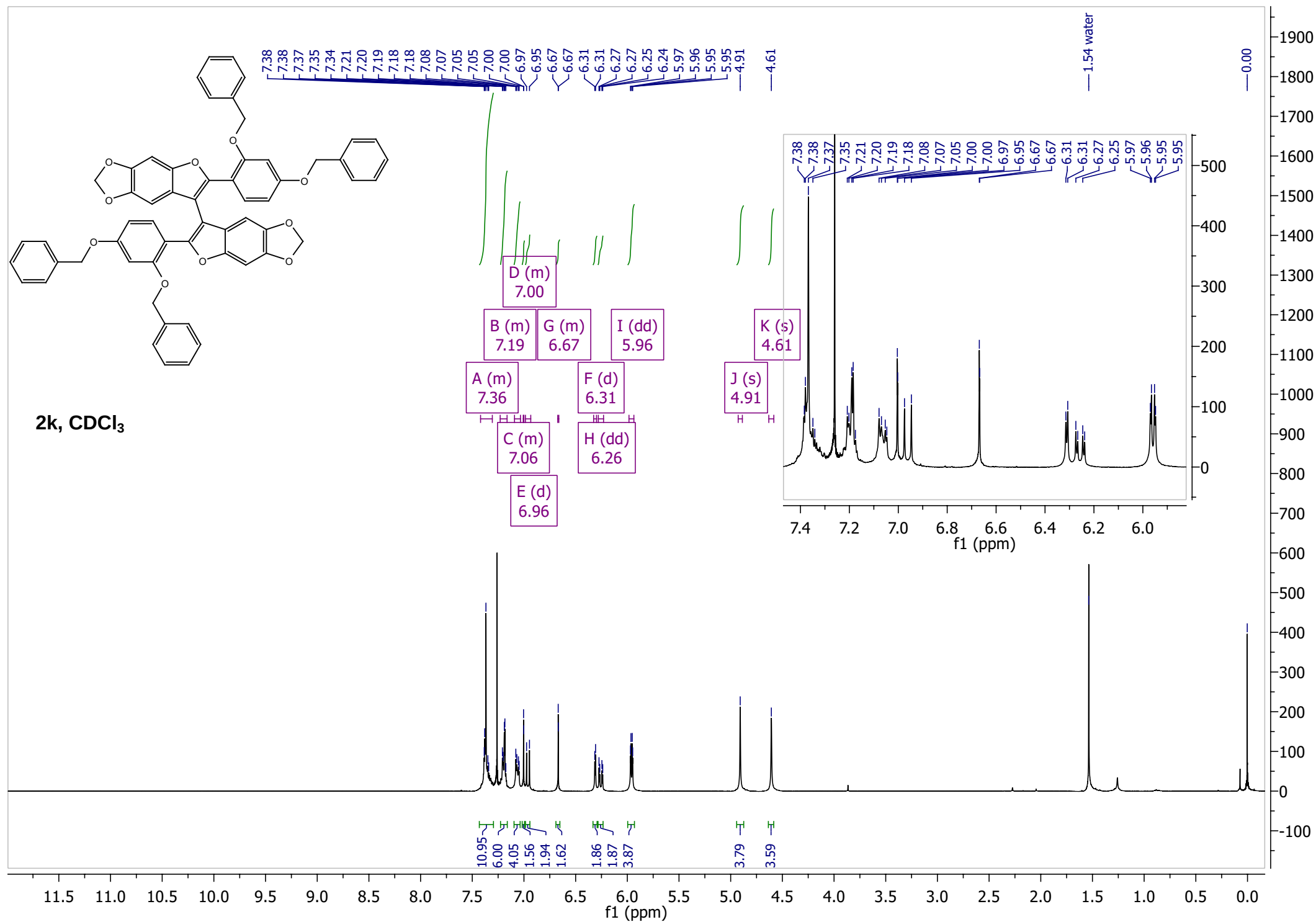
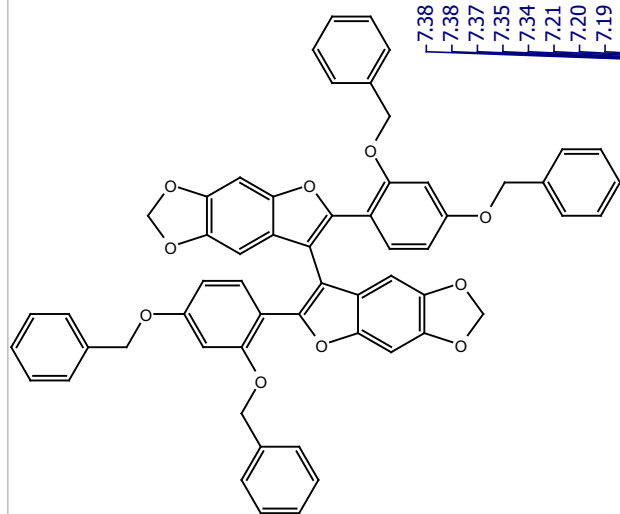




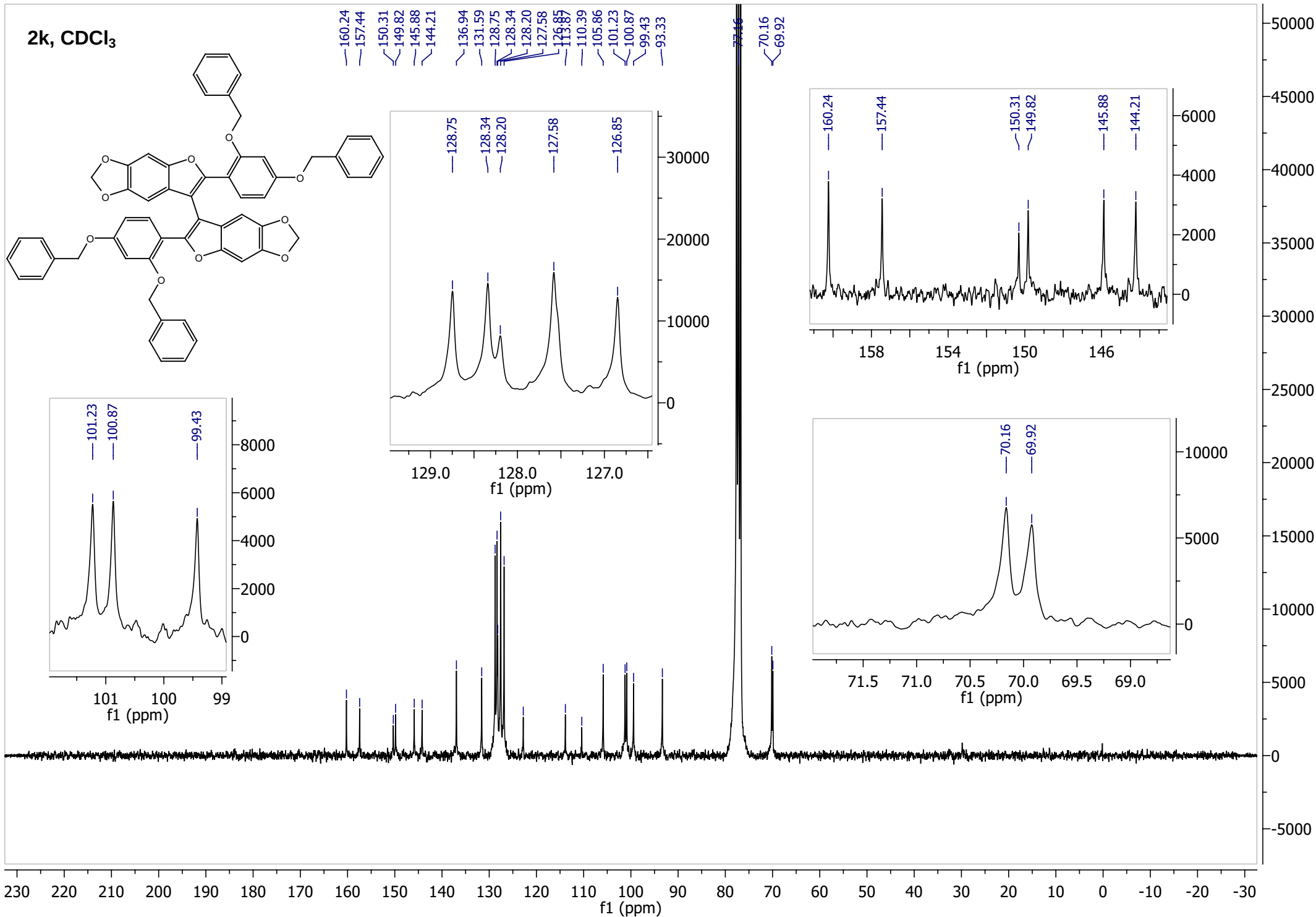
2h, CDCl<sub>3</sub>





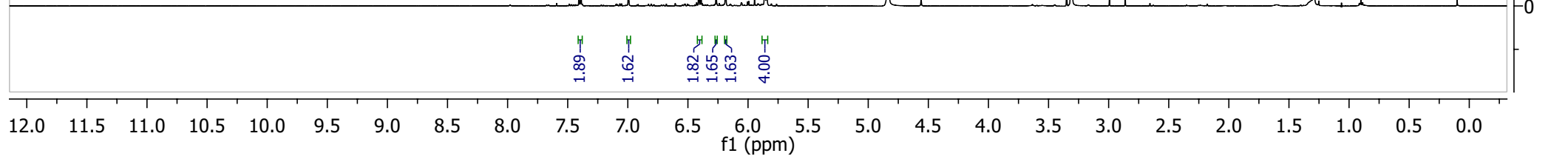
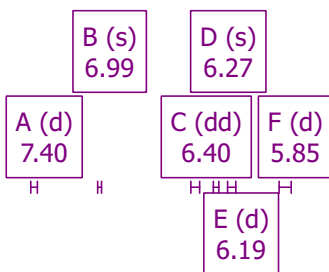
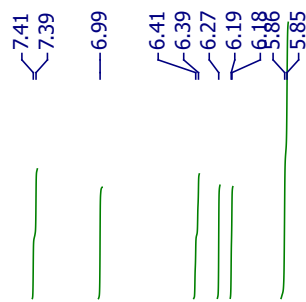
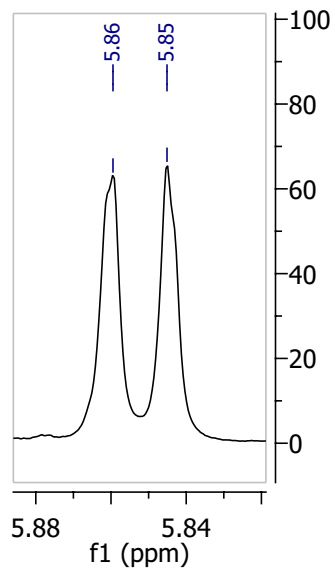
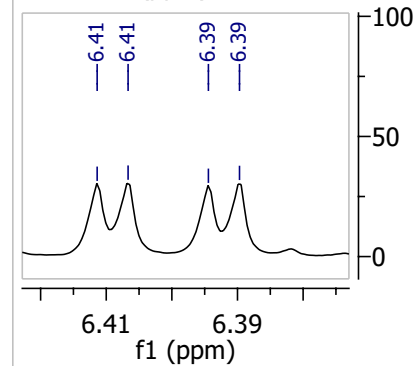
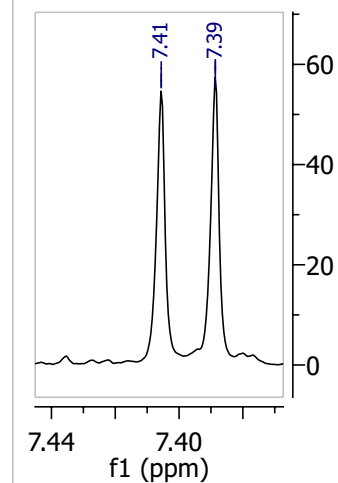
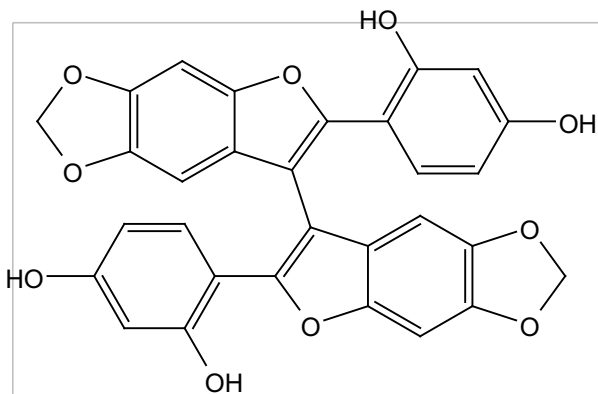


2k, CDCl<sub>3</sub>





# Shandougenine B, CD<sub>3</sub>OD



# Shandougine B, CD<sub>3</sub>OD

