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Synthesis, Spectroscopic Properties, and Electropolymerization of Azulene Dyads

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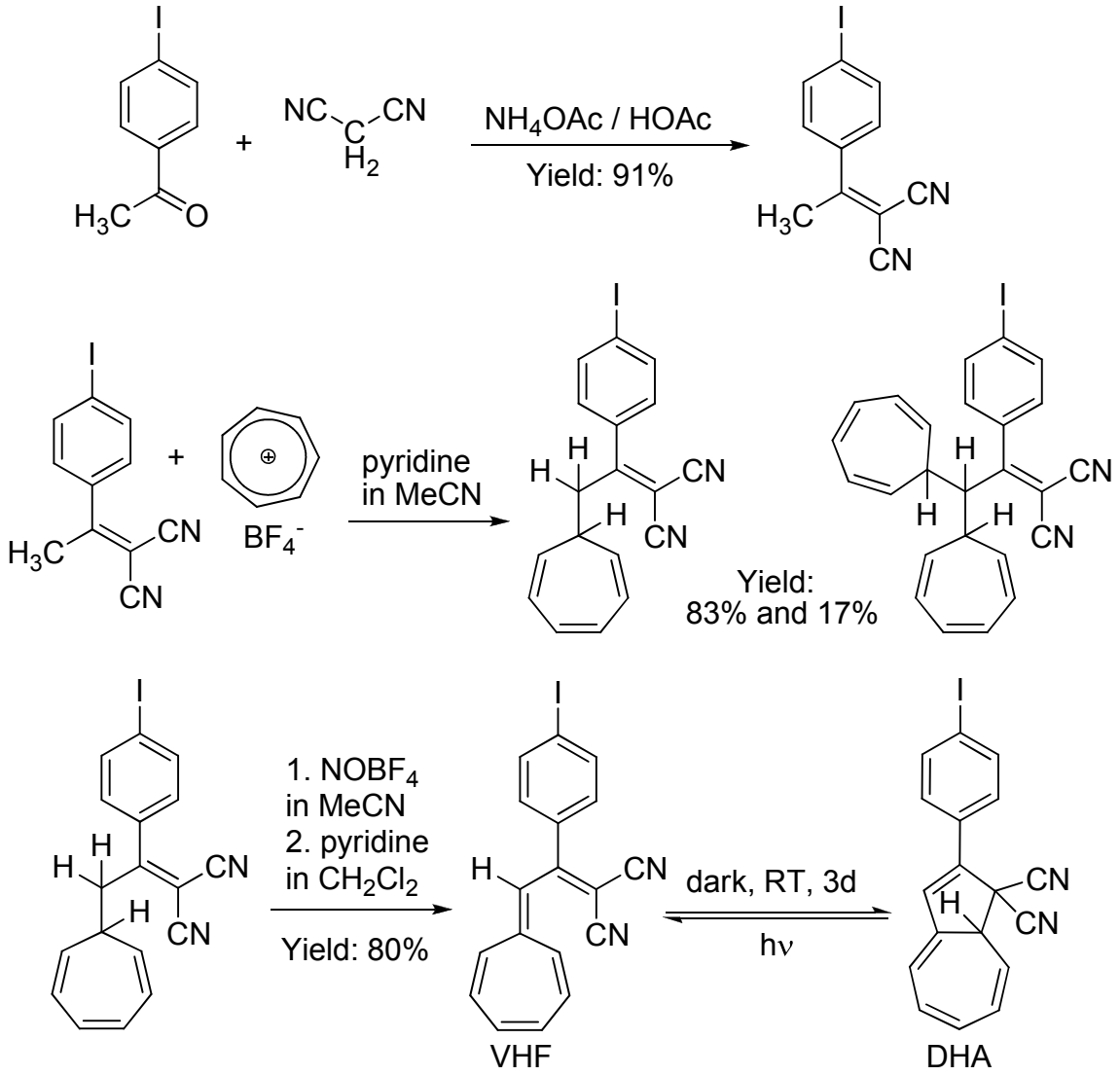
Supporting Information

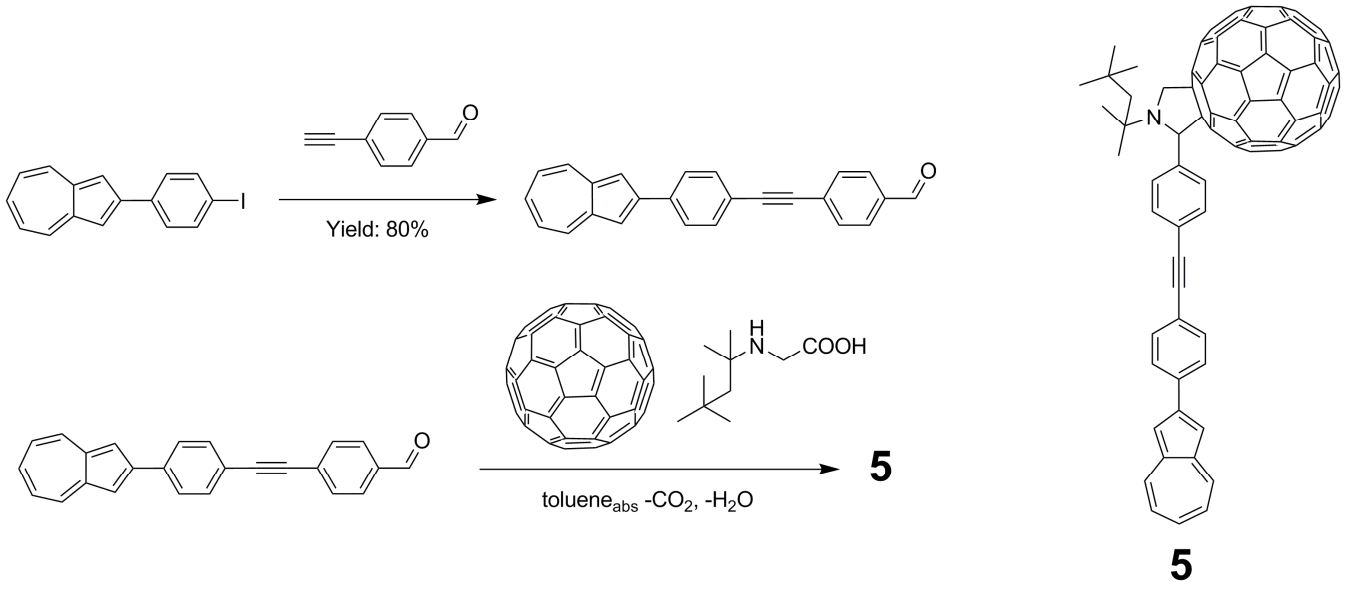
I Synthesis of DHA



Scheme S-1. Synthesis of the photochromic 2-(4-iodophenyl)-dihydroazulene (DHA) intermediate from 4-iodacetophenone.

II Synthesis of 5

We decided to synthesize the azulene-fulleropyrrolidine dyad **5** as depicted in Scheme S-2 by a 1,3-dipolar cycloaddition of an azomethine ylide[1] formed from 4-(4-azulen-2-yl-phenylethynyl)-benzaldehyde and *N*-isooctylglycine in order to introduce the fullerene subunit, which might decrease the solubility, in the last step. The precursor 4-(4-azulen-2-yl-phenylethynyl)-benzaldehyde was prepared by Pd-catalyzed cross-coupling of 2-(4-iodophenyl)-azulene and 4-ethinyl-benzaldehyde. The isooctyl group was introduced in order to increase the solubility of **5**. Although we have strong evidence from ^{1}H-NMR and mass spectroscopy that the synthesis of **5** was successful, we were not able to purify **5** due to its poor solubility. **5** was only soluble in very low concentration in toluene and CS_2.



Scheme S-2. Synthesis of the azulene-fulleropyrrolidine dyad **5**.

III Supplementary figures for electrochemical polymerization results

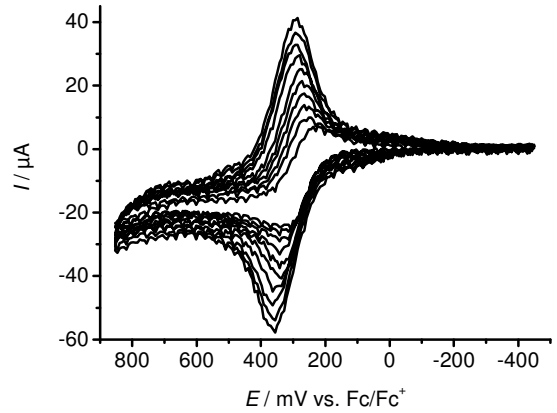


Figure S-1. Multi-cycle CV showing the potentiodynamic polymerization of **1** in CH_2Cl_2 when only the first oxidation is scanned, measured at v = 20 mV s^{-1}.

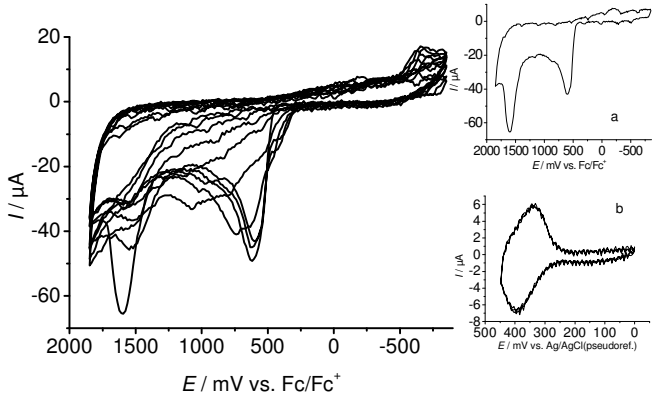


Figure S-2. Multi-cycle CVs showing the potentiodynamic polymerization of **2** in CH_2Cl_2 measured at v = 50 mV s^{-1}. Inset a: initial cycle, inset b: multi-cycle CVs of the resulting polymer film in monomer-free solution measured at v = 20 mV s^{-1}.

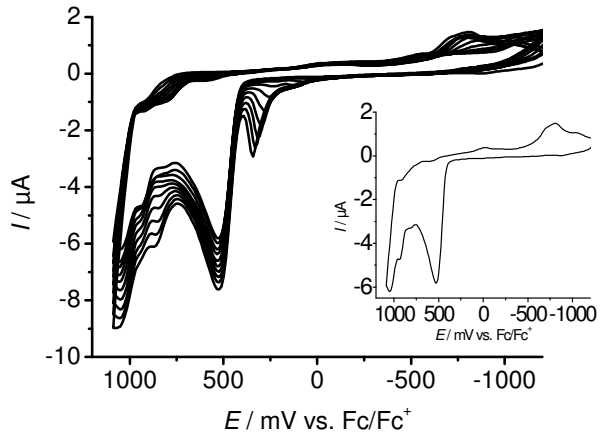


Figure S-3. Multi-cycle CVs showing the potentiodynamic polymerization of **3** in CH_2Cl_2 measured at v = 20 mV s^{-1}. Inset: initial cycle.

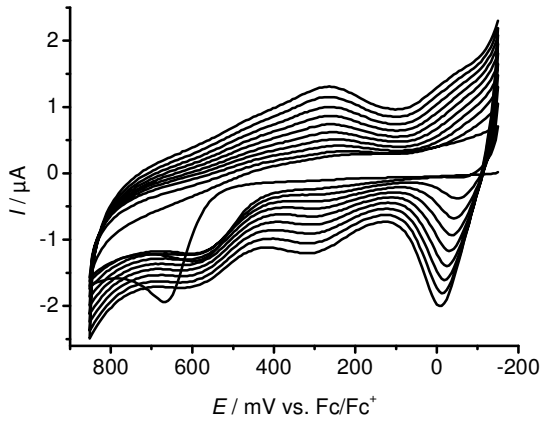


Figure S-4. Multi-cycle CVs showing the potentiodynamic polymerization of **4** in CH_2Cl_2 measured at v = 50 mV s^{-1}.

IV Atom numbering for NMR results in Experimental Section

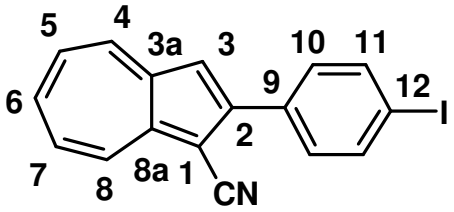


Chart S-1. 2-(4-Iodophenyl)-azulene-1-carbonitrile.

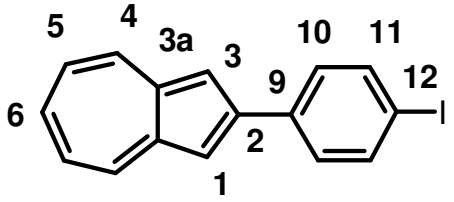


Chart S-2. 2-(4-Iodophenyl)-azulene.

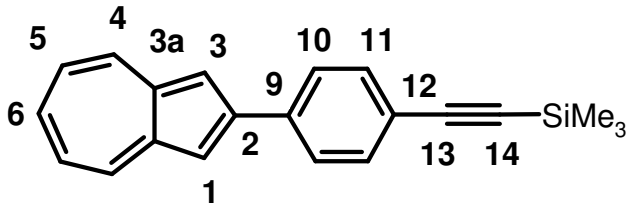


Chart S-3. (4-Azulen-2-yl-phenylethynyl)-trimethyl-silane.

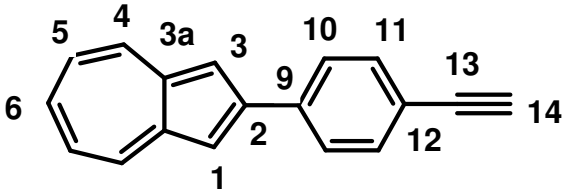
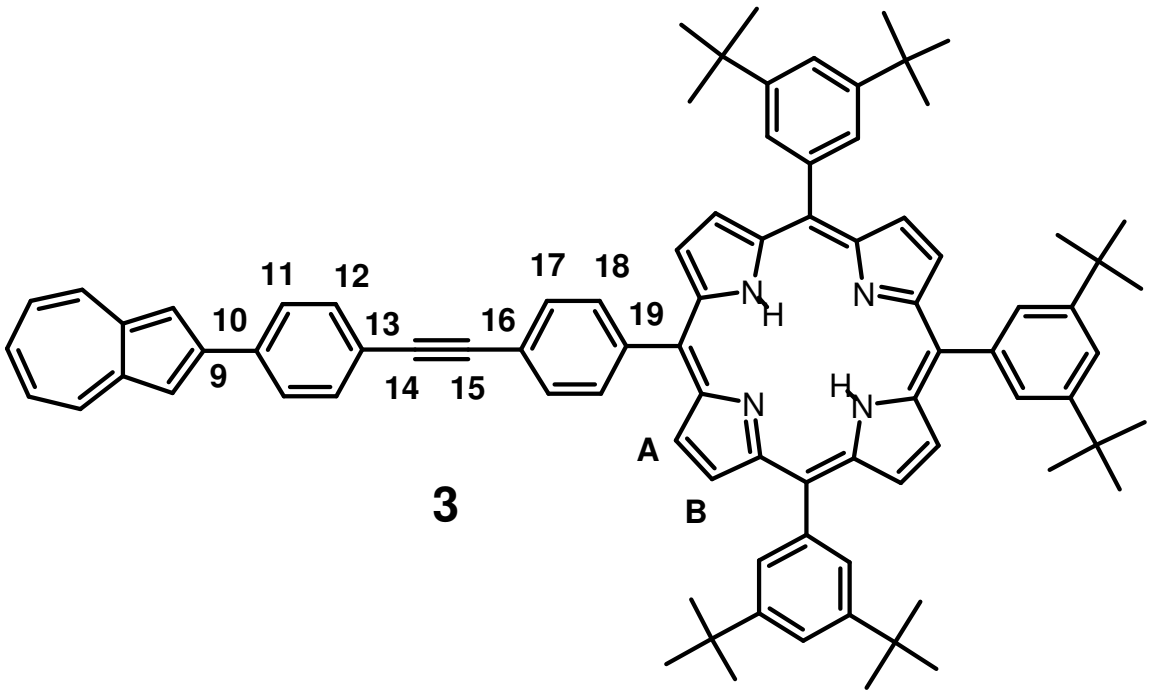


Chart S-4. 2-(4-Ethynyl-phenyl)-azulene (EPA).



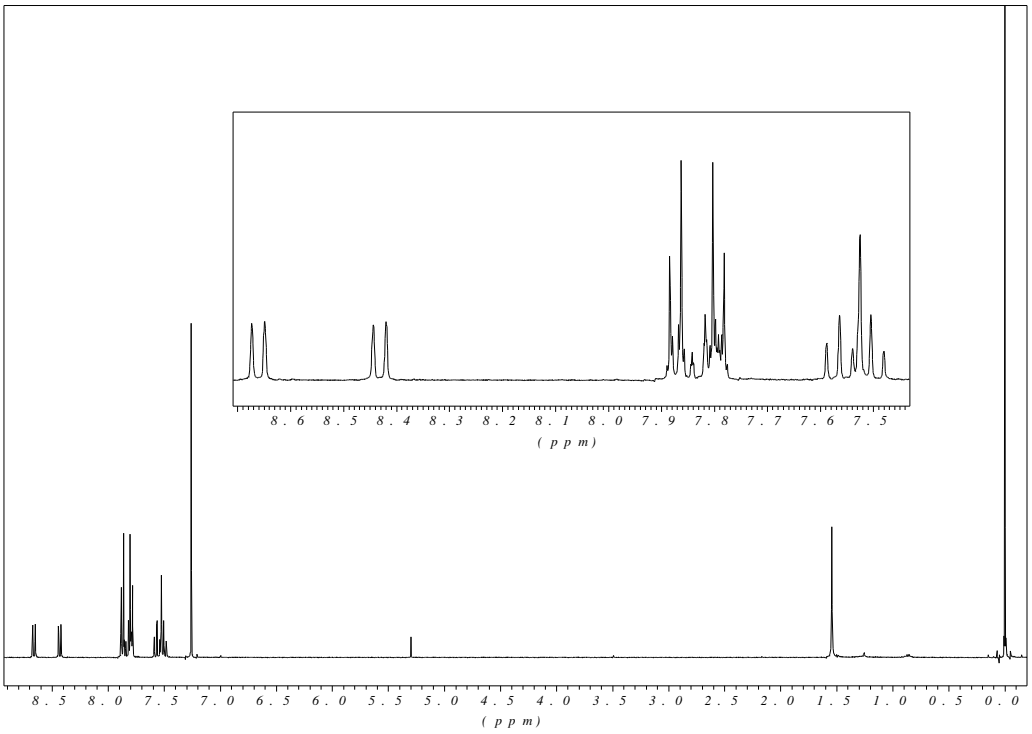
3

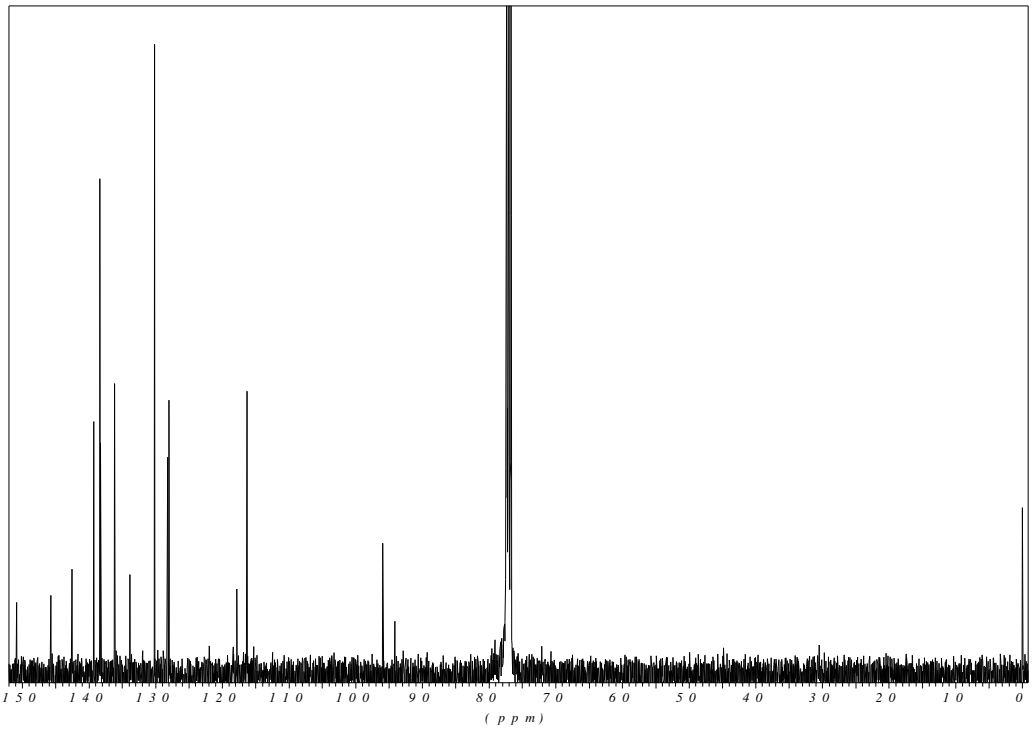
Chart S-5. 5-[4-(4-Azulen-2-yl-phenylethynyl)-phenyl]-10,15,20-tris-(3,5-di-^{t}butyl-phenyl)-porphyrin (3).

V References

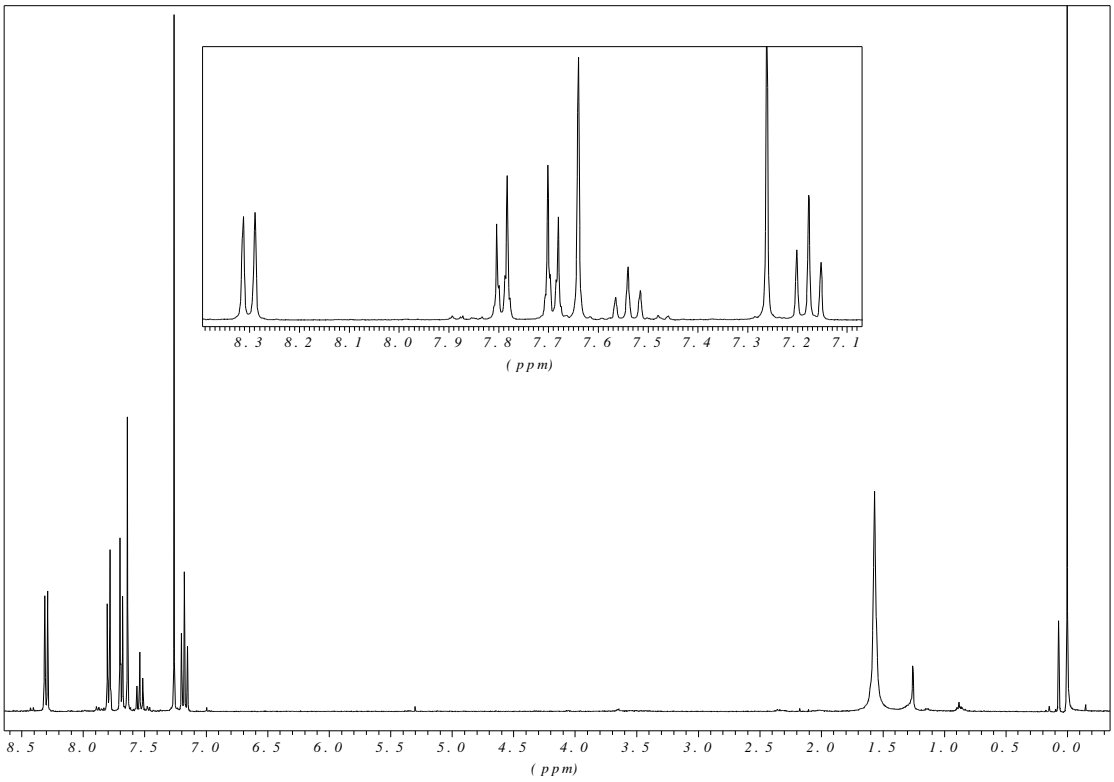
(1) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519-526.

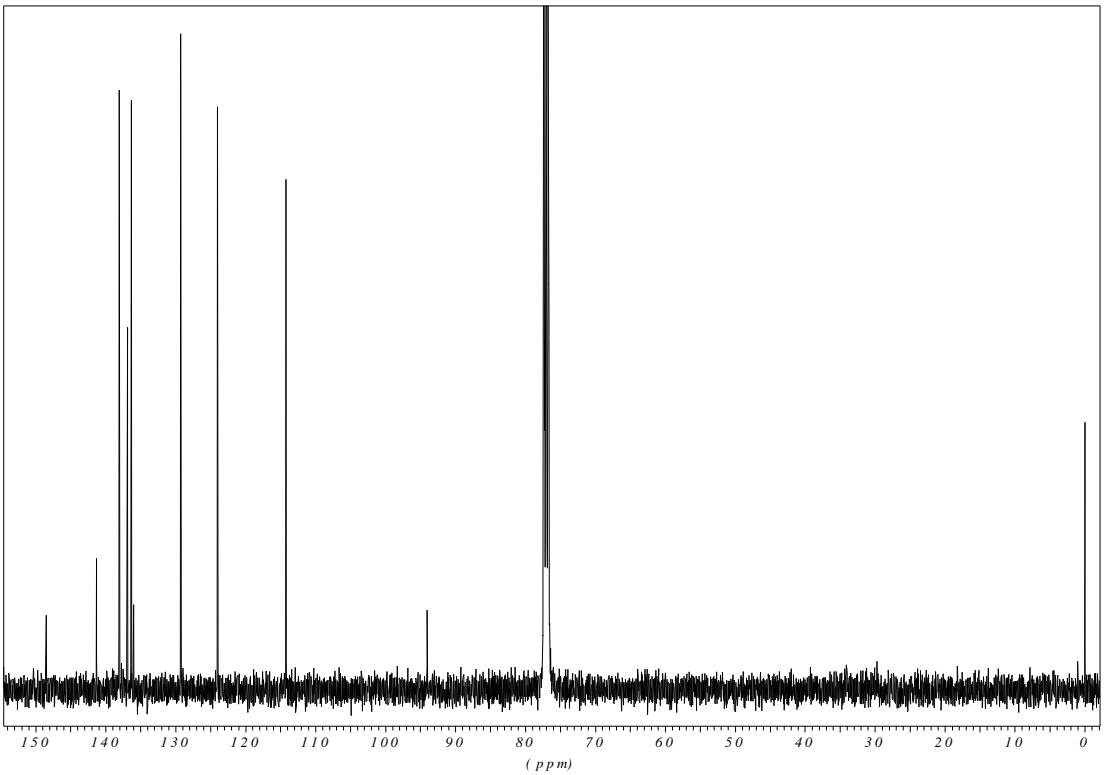
VI Copies of NMR-Spectra



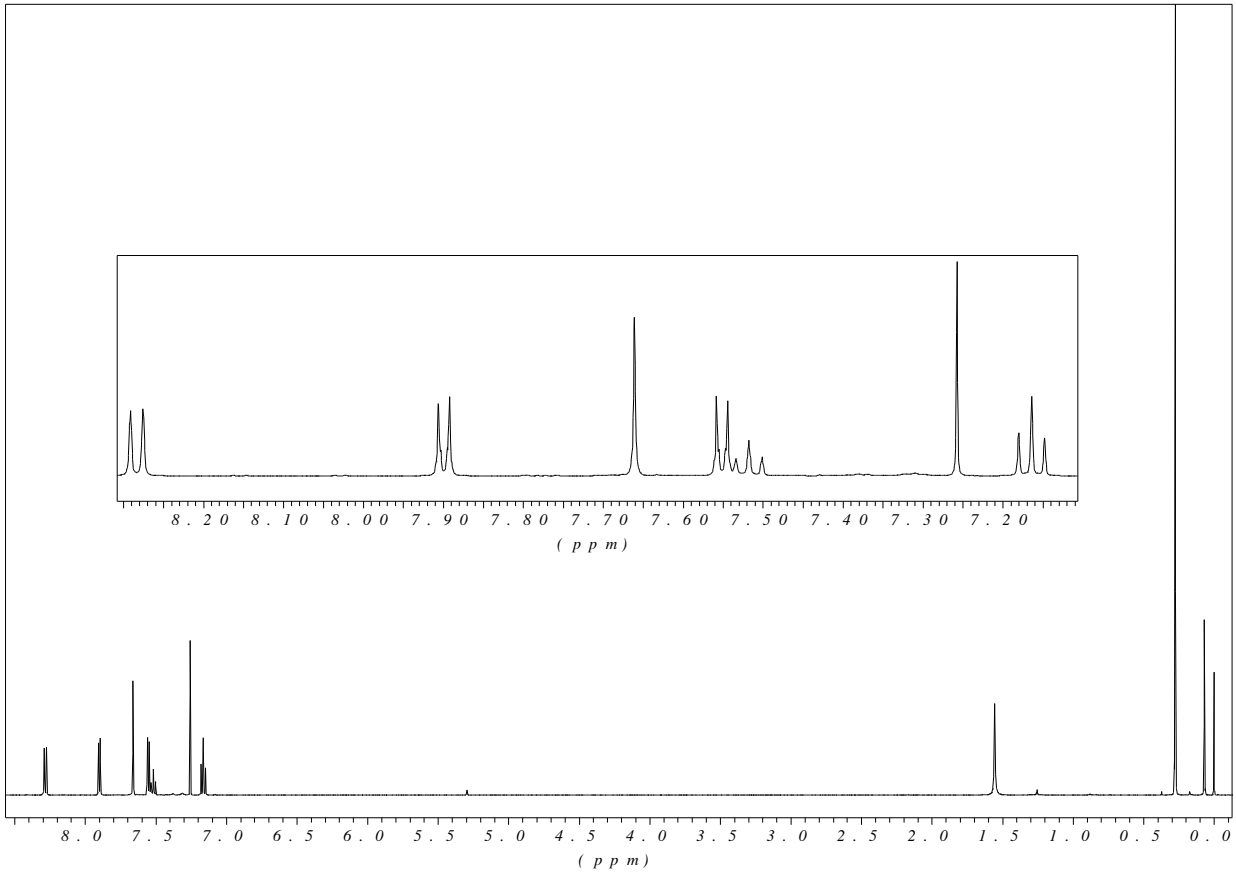


2-(4-Iodophenyl)-azulene-1-carbonitrile



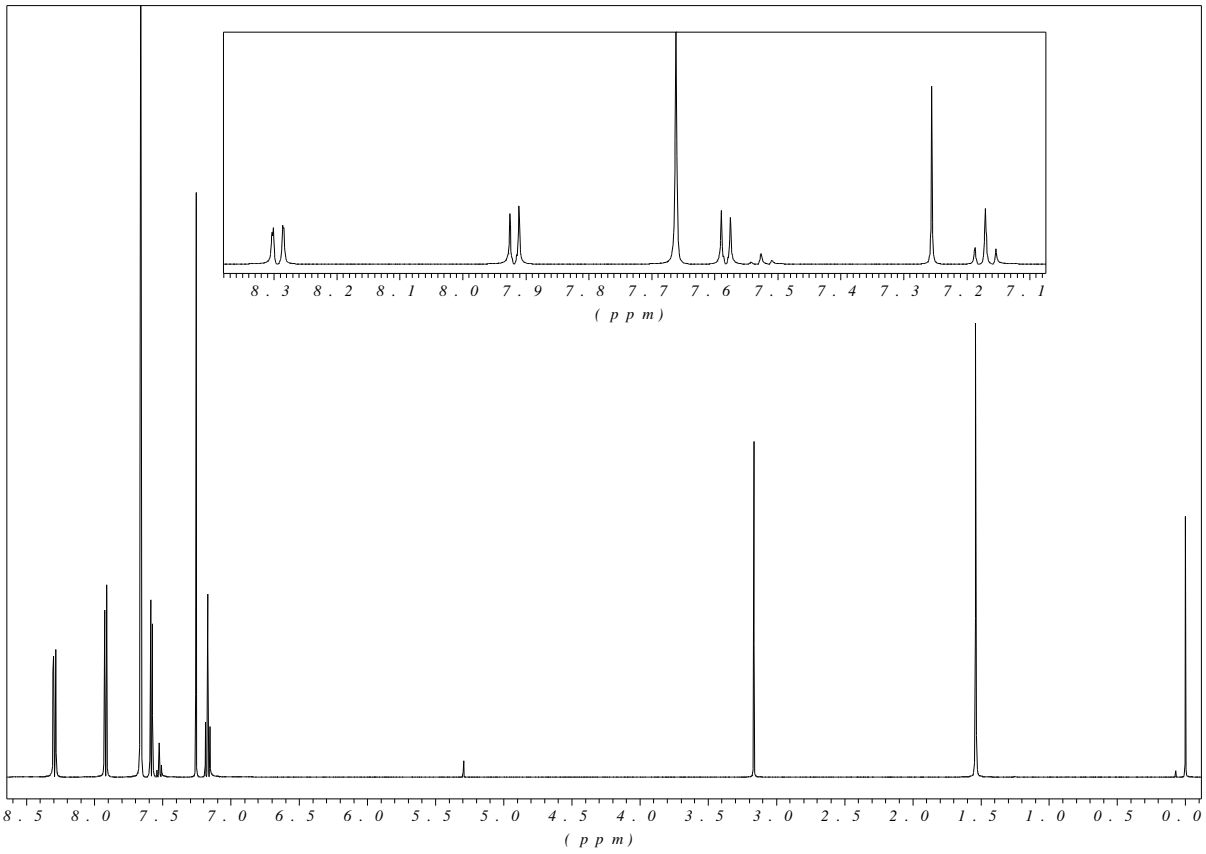


2-(4-Iodophenyl)-azulene



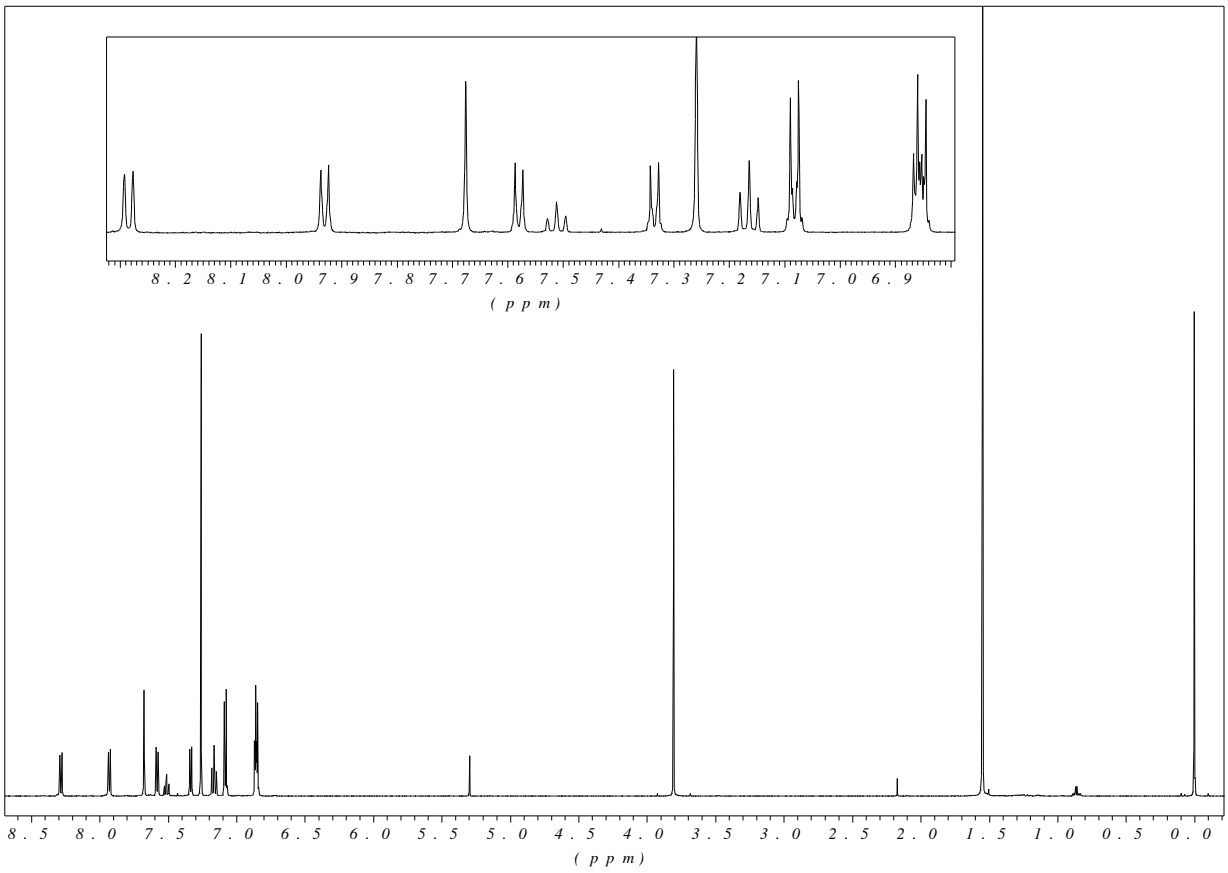
(4-Azulen-2-yl-phenylethynyl)-trimethyl-silane

For this compound, no one-dimensional ^{13}C-NMR spectrum was measured. The ^{13}C shifts were determined from the HMBC-spectrum.



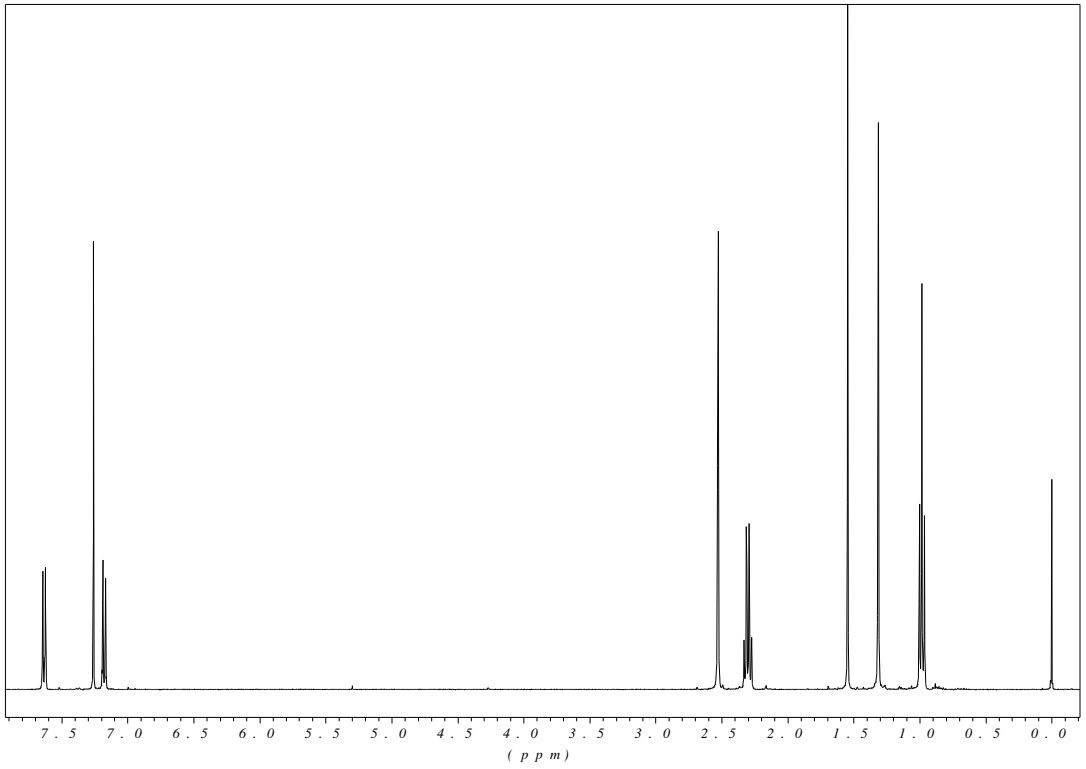
EPA

For this compound, no one-dimensional ^{13}C-NMR spectrum was measured. The ^{13}C shifts were determined from the HMBC-spectrum.



Compound **1**

For this compound, no one-dimensional ^{13}C-NMR spectrum was measured. The ^{13}C shifts were determined from the HMBC-spectrum.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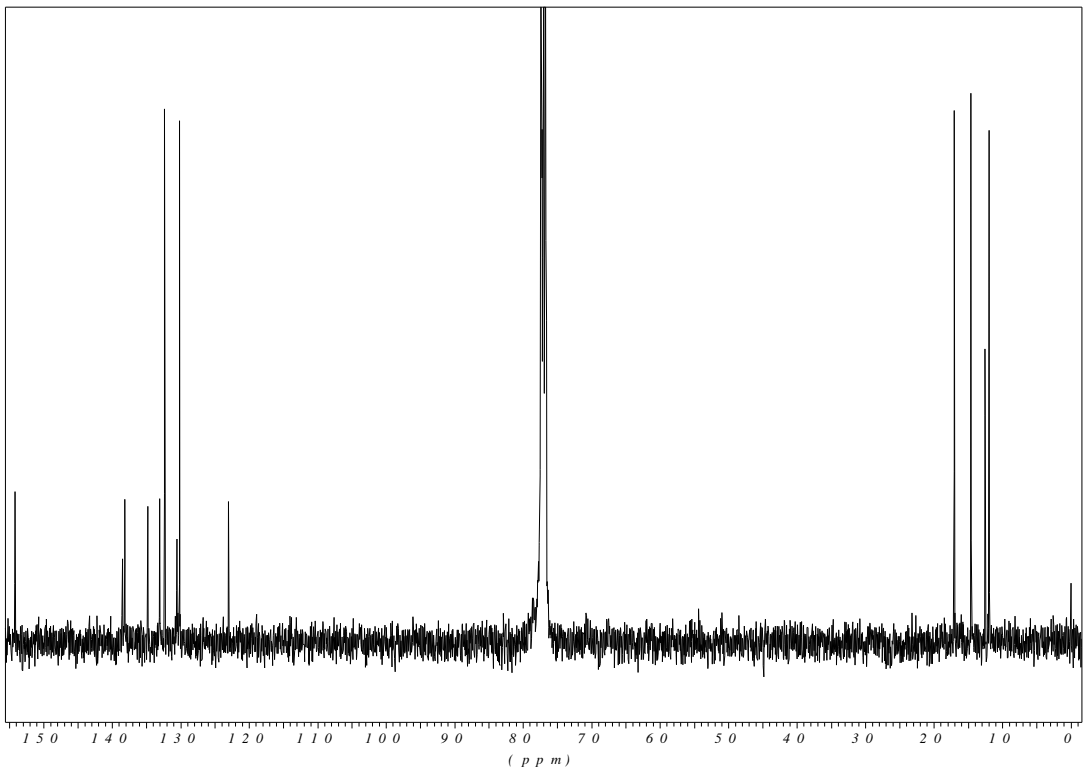
(ppm)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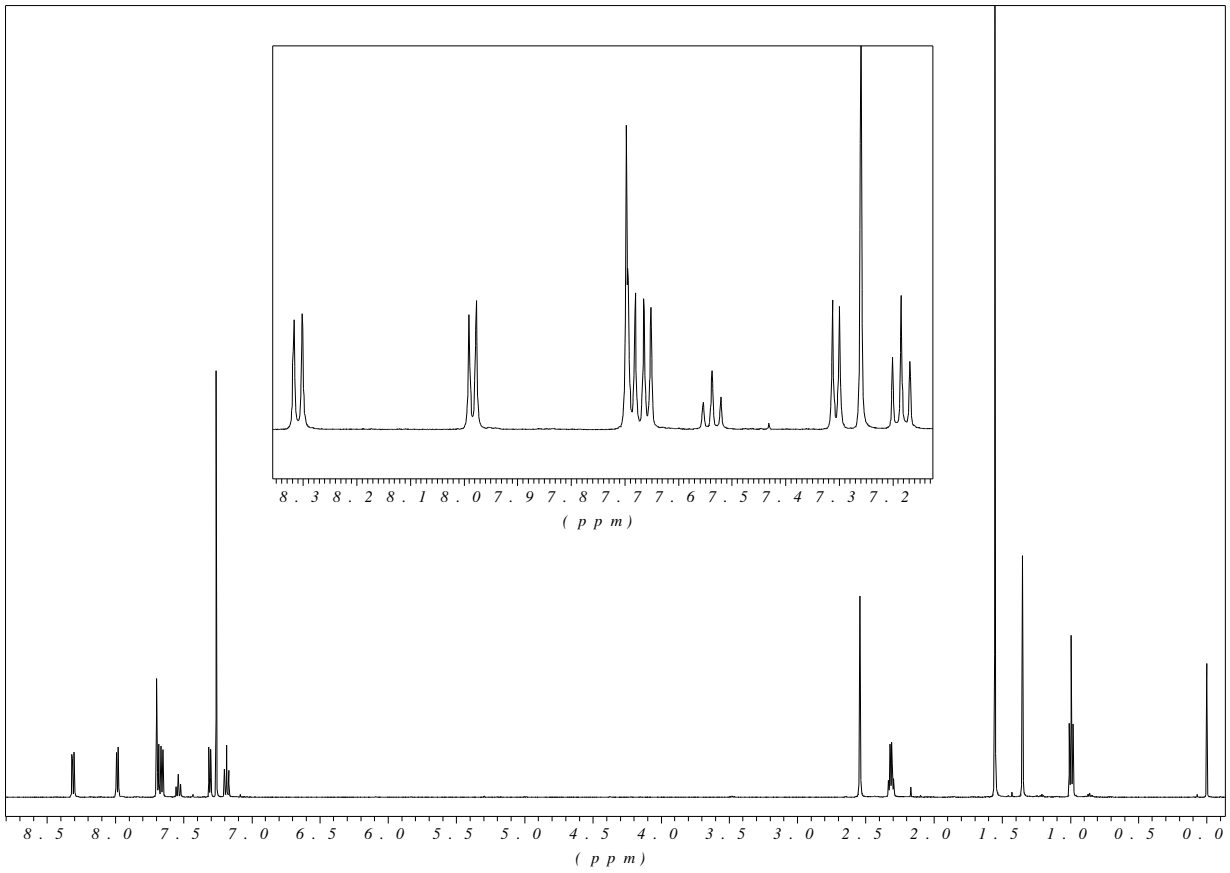
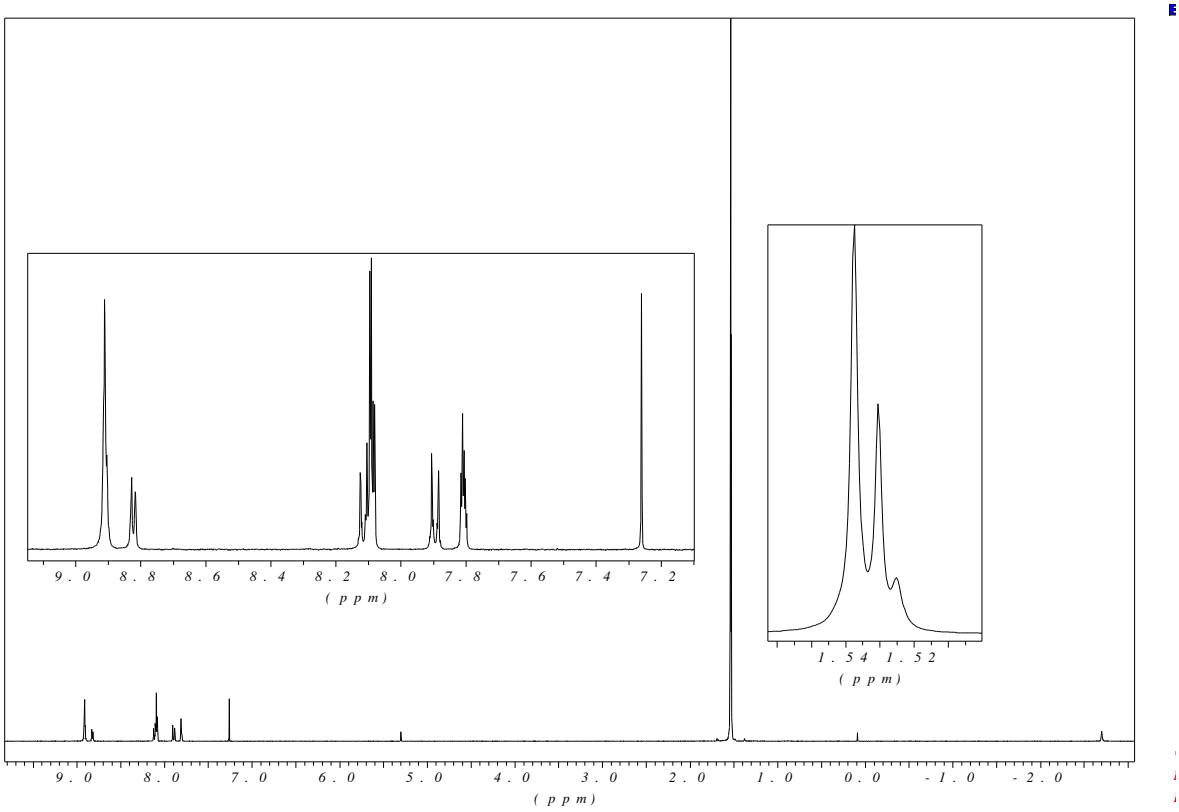
(ppm)

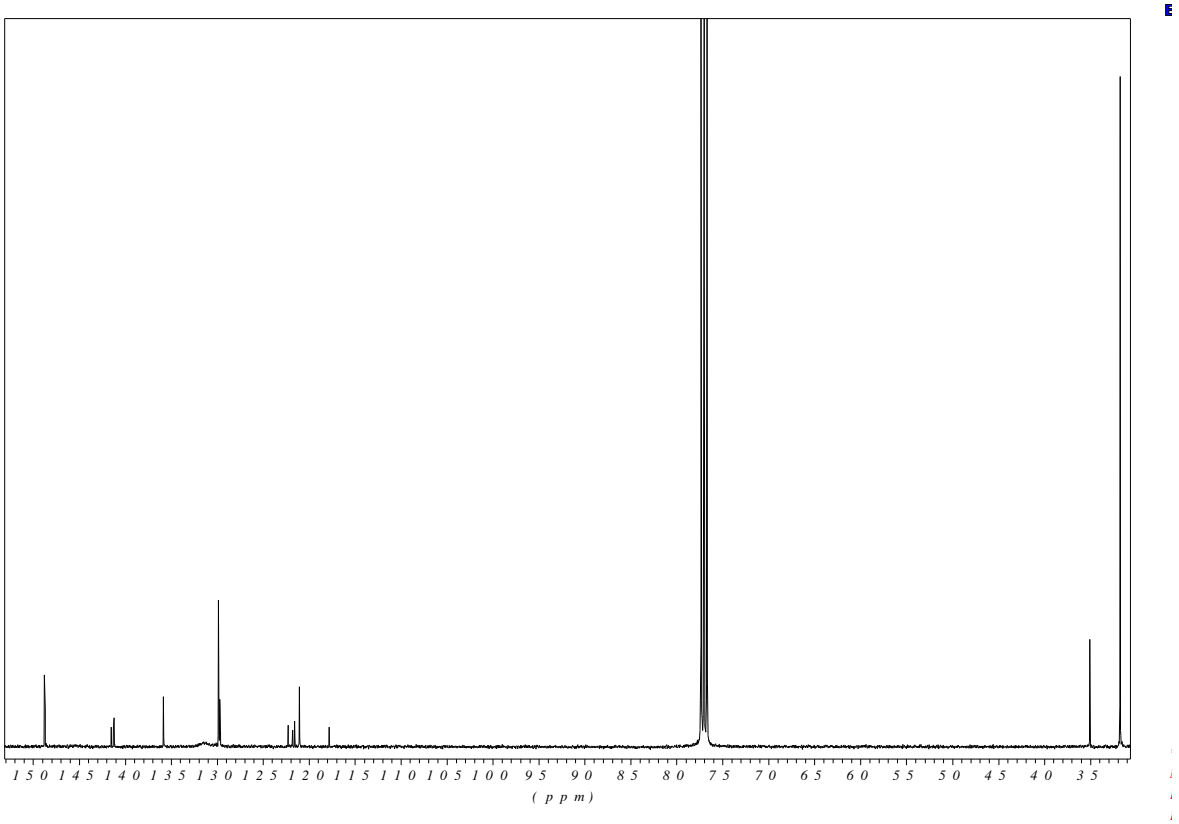
Compound **2a**



Compound **2**

For this compound, no one-dimensional ^{13}C-NMR spectrum was measured. The ^{13}C shifts were determined from the HMBC-spectrum.


9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2
(ppm)
1.54 1.52
(ppm)
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
(ppm)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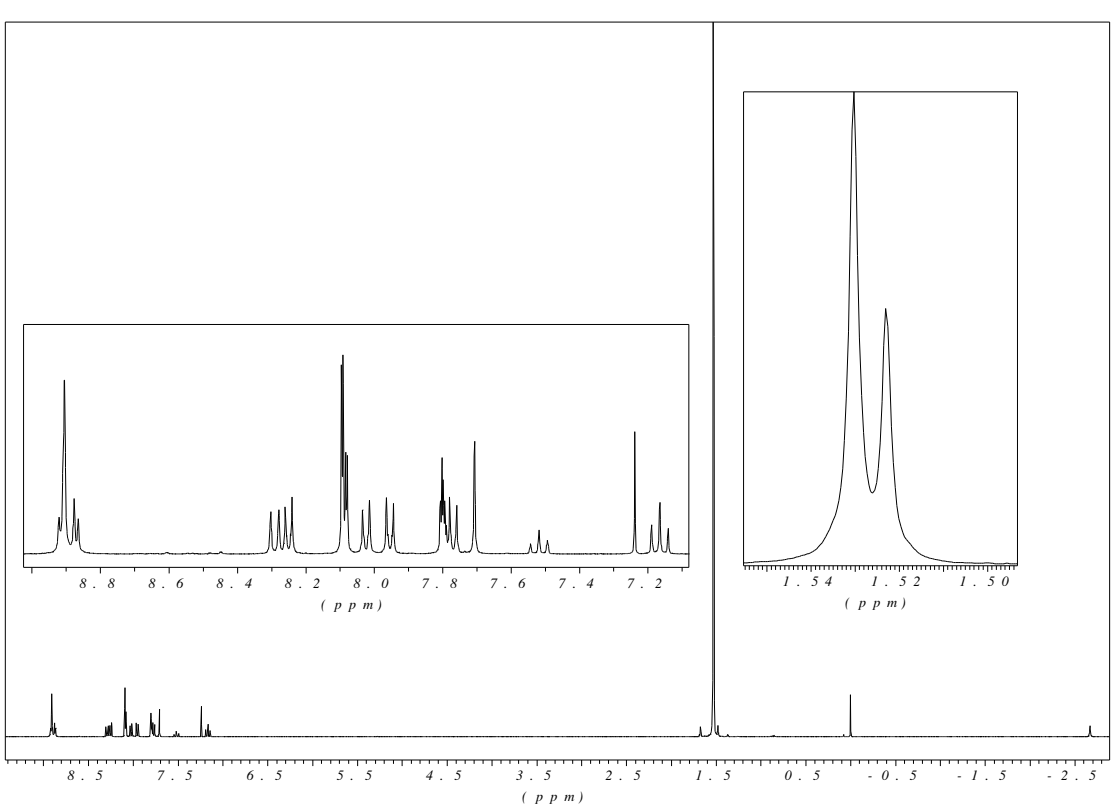
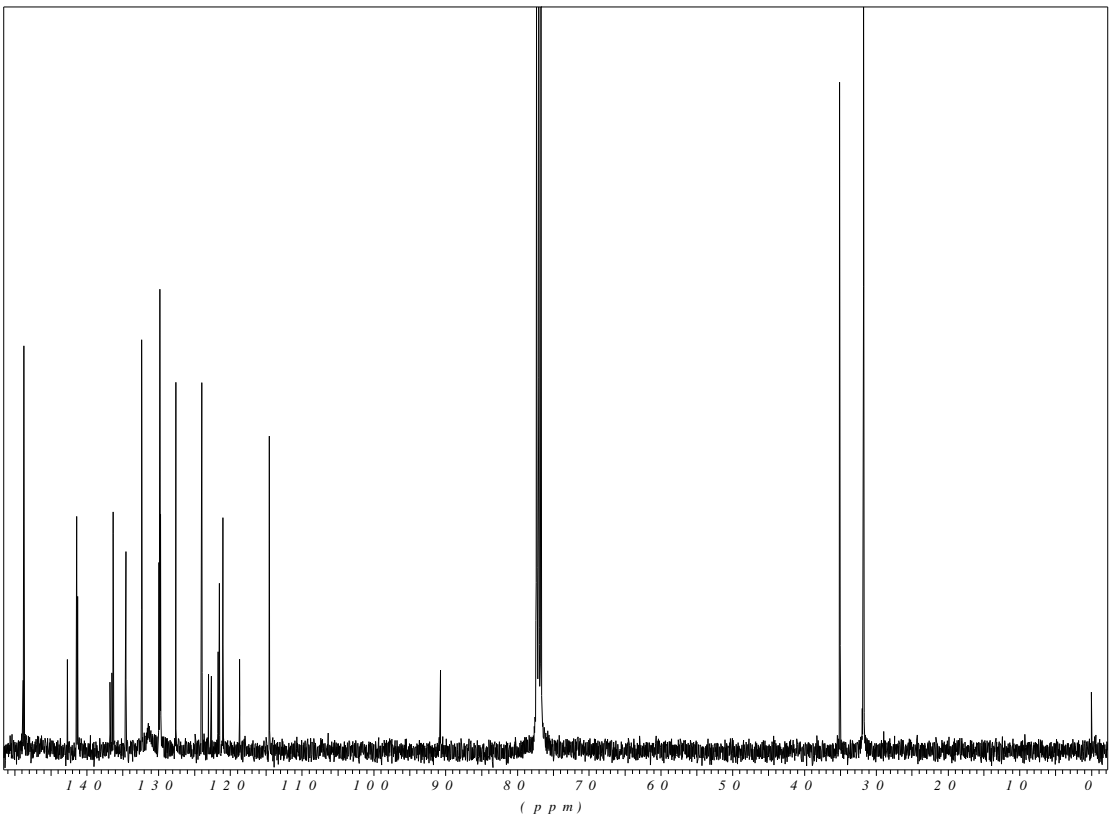
Compound **3a**


8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2
(ppm)
1.54 1.52 1.50
(ppm)
8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5 -2.5
(ppm)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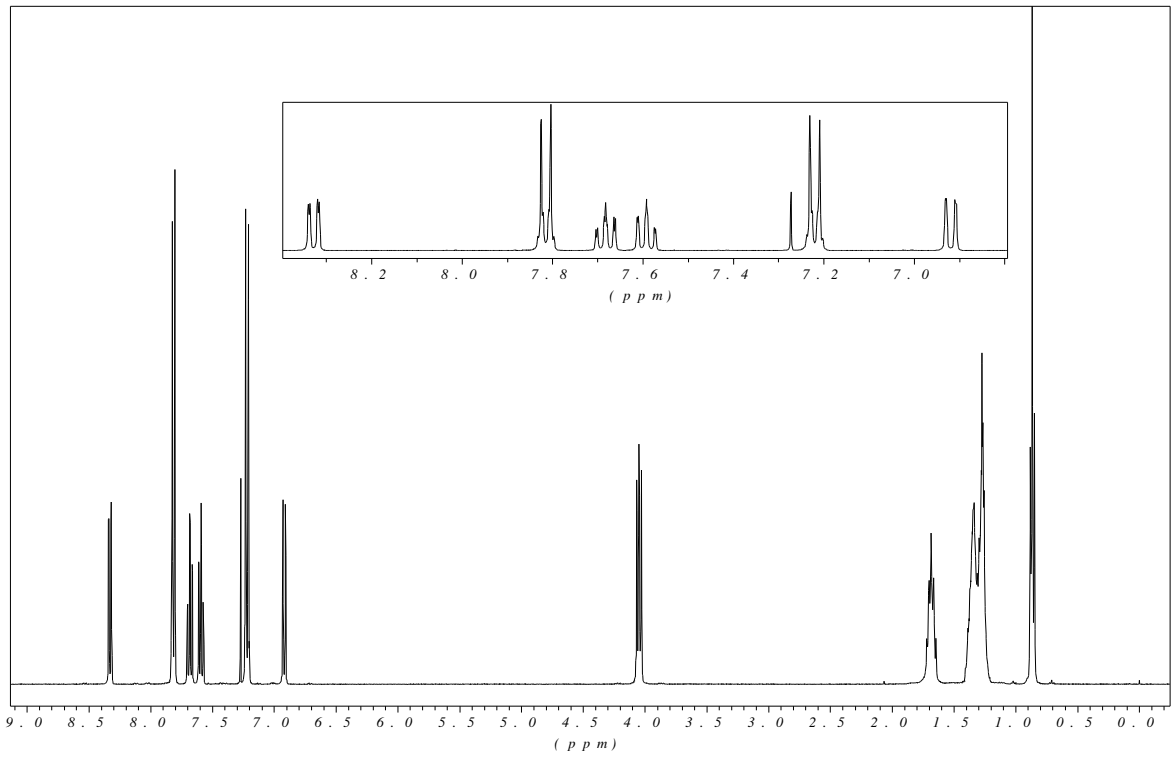
(ppm)

Compound **3**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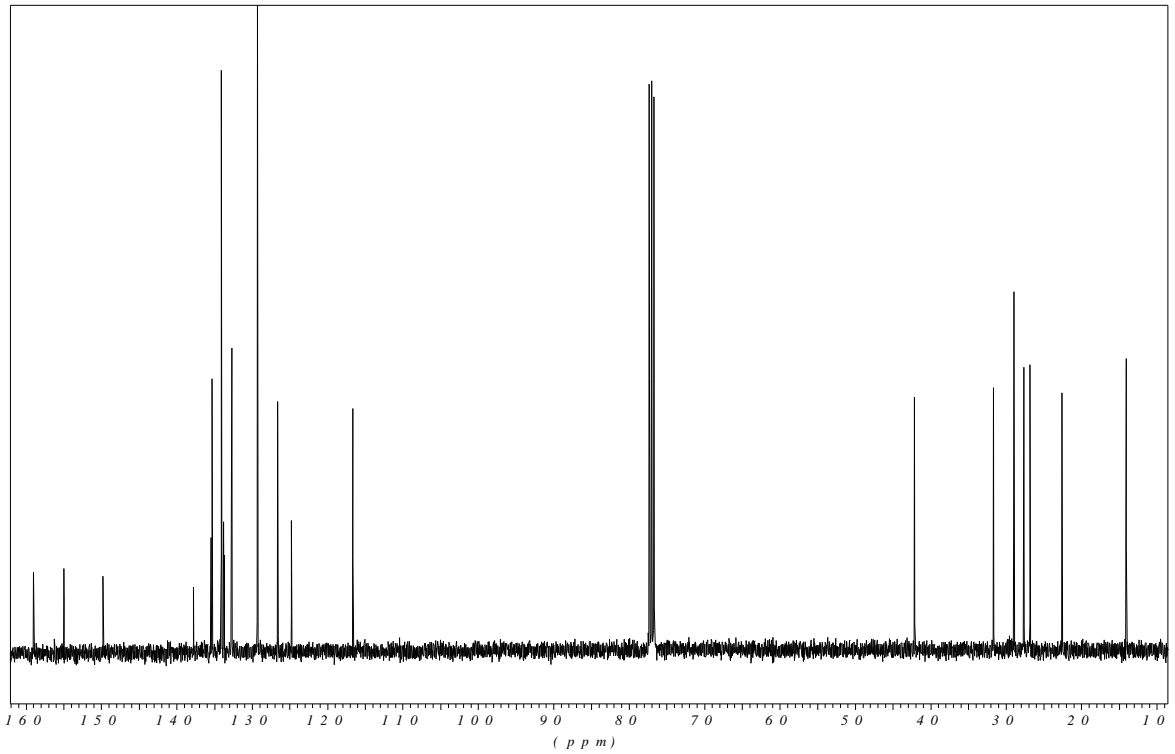
(ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)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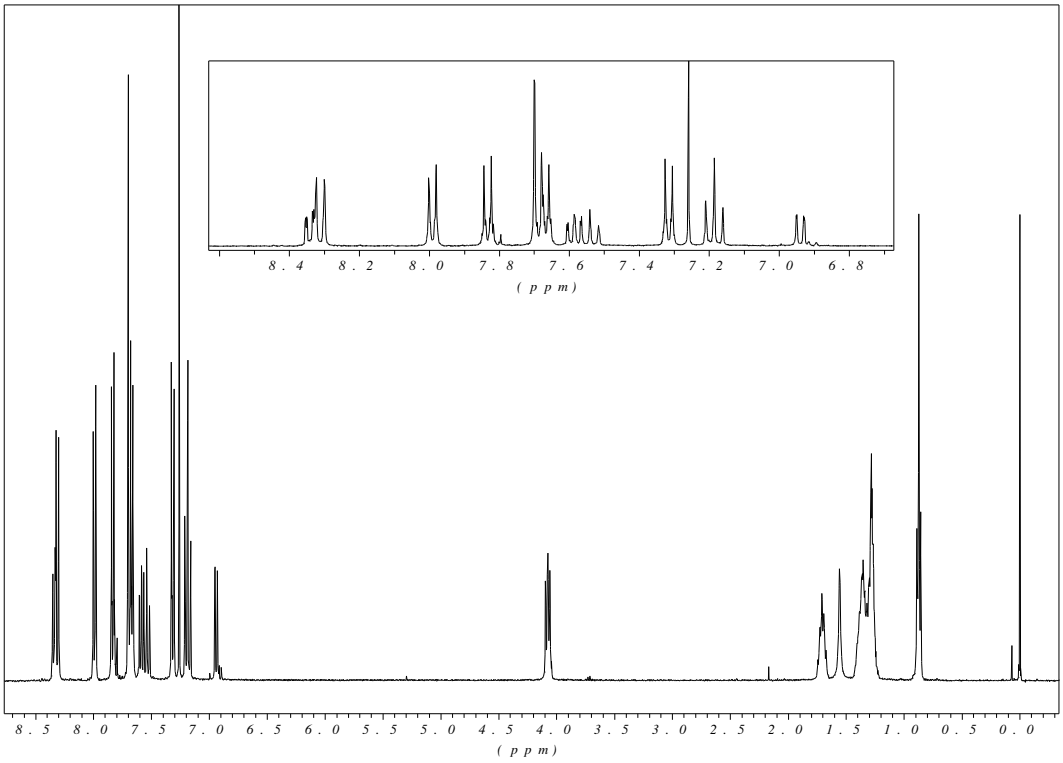
Compound 4a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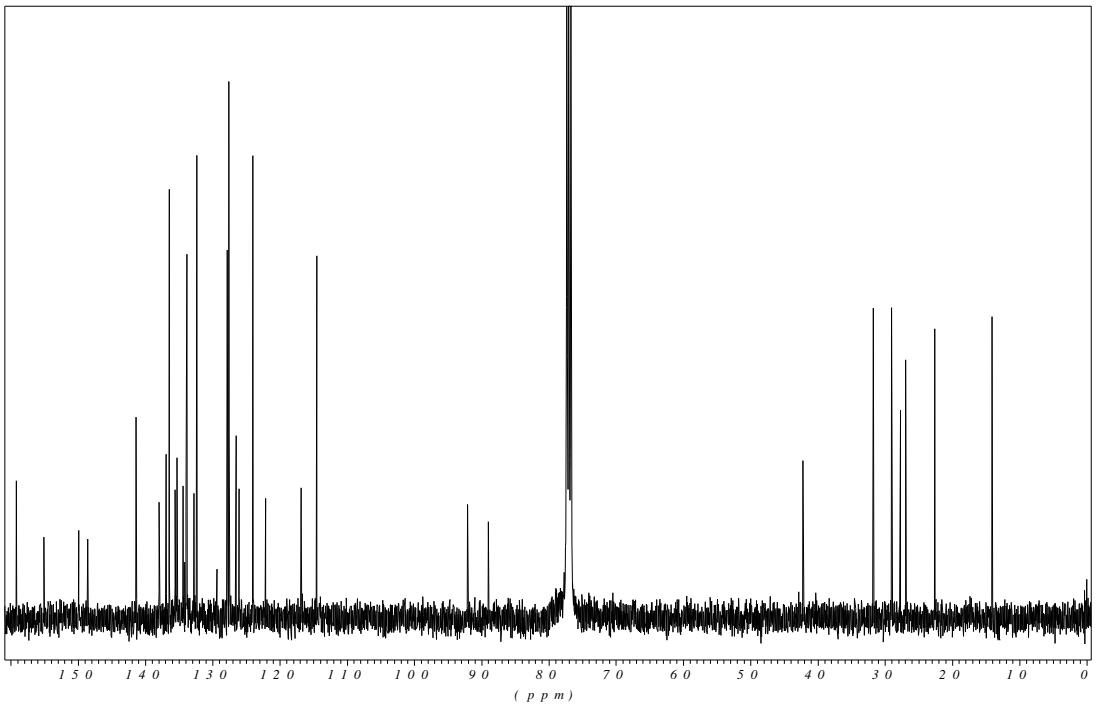
(ppm)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(ppm)

Compound **4**