

# Photoinduced Nucleophilic Substitution of Iodocubanes with Arylthiolate and Diphenylphosphanide ions. Experimental and Computational Approaches

*Liliana B. Jimenez,\* Marcelo Puiatti, Diego Andrada,<sup>‡</sup> Federico Brigante, Karina F. Crespo Andrada, Roberto A. Rossi, Ronny Priefer,<sup>§</sup> Adriana B. Pierini<sup>#</sup>*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Argentina.

<sup>‡</sup>Krupp-Professur für Allgemeine und Anorganische Chemie, Universität des Saarlandes, 66123 Saarbrücken, Germany.

<sup>§</sup>College of Pharmacy, Western New England University, Springfield, Massachusetts 01119, United States

<sup>#</sup>Prof. Adriana B. Pierini deceased

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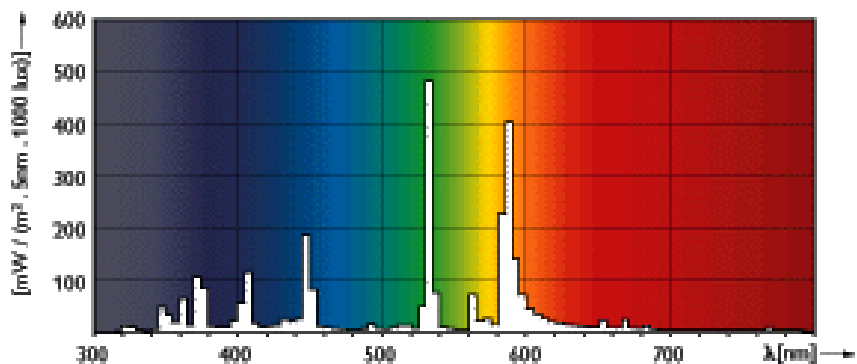
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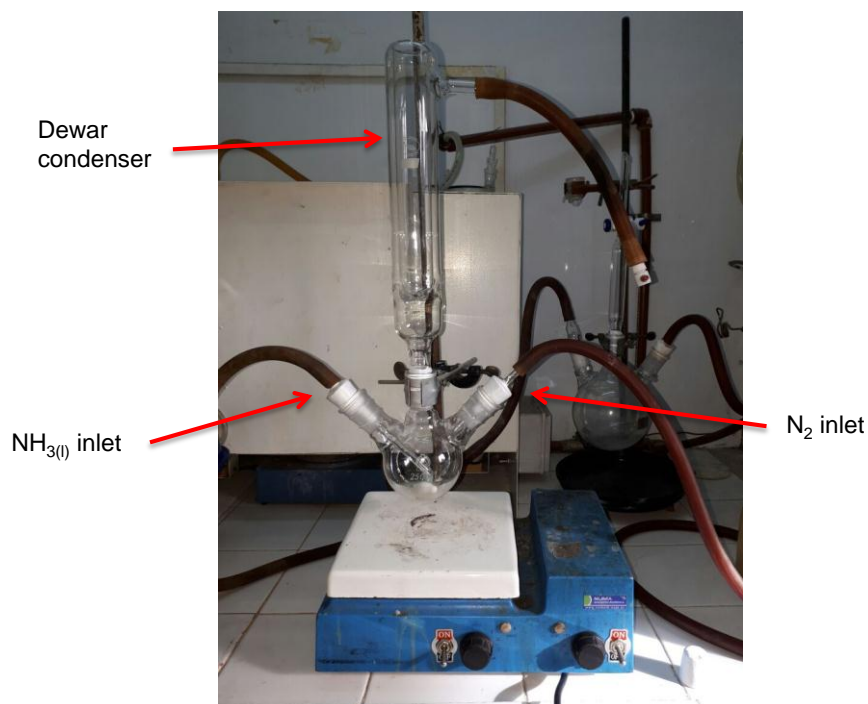
## 1. Experimental Information

### 1.1. Experimental system description for $\text{NH}_3(l)$ reaction

- Figure SI-1: Spectrum of lamps used for photoinduced  $\text{S}_{\text{RN}}1$  reactions. It was obtained from the manufacturer webpage ([http://www.lighting.philips.com.eg/prof/lamps/high-intensity-discharge-lamps/quartz-metal-halide/master-hpi-t-plus/928481600096\\_EU/product](http://www.lighting.philips.com.eg/prof/lamps/high-intensity-discharge-lamps/quartz-metal-halide/master-hpi-t-plus/928481600096_EU/product)).



- Picture SI-2: Experimental device for the  $\text{NH}_3(l)$  reactions



- Picture **SI-3**: Experimental device for the  $\text{NH}_3(l)$  reactions. Solvent drying process.



$\text{NH}_3(l)$  with Na  
before to distill it

- Picture **SI-4**: Experimental device for the  $\text{NH}_3(l)$  reactions. Distillation of  $\text{NH}_3(l)$  dry.



$\text{N}_2(l)$ - ethanol bath  
within the  
coldfinger's Dewar  
condenser

$\text{N}_2(l)$ - ethanol  
bath

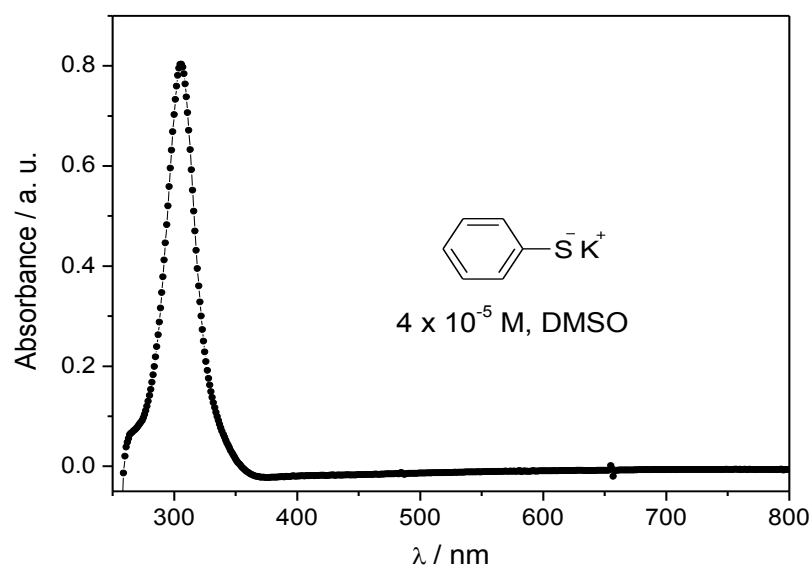
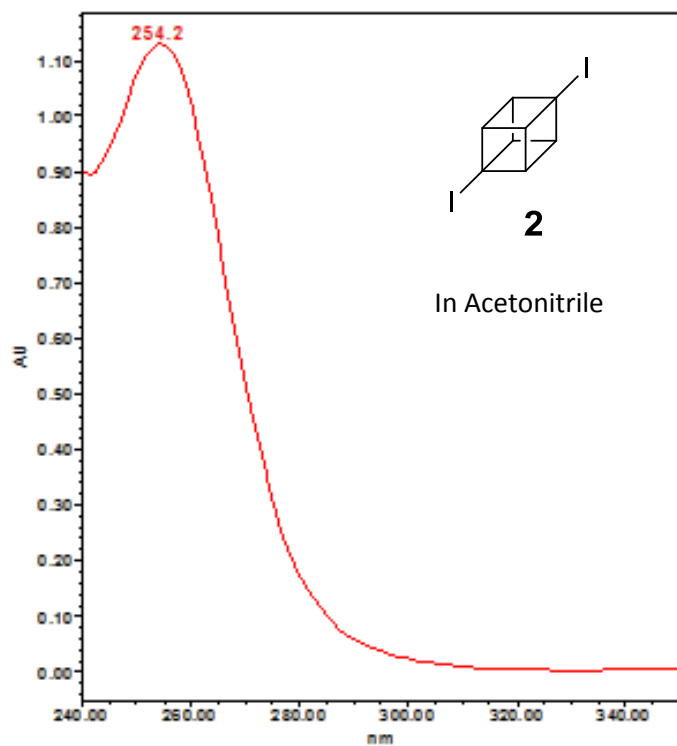
-Picture **SI-5**: Experimental device for the  $\text{NH}_3(l)$  reactions. Distilled  $\text{NH}_3(l)$  before adding the substrates.

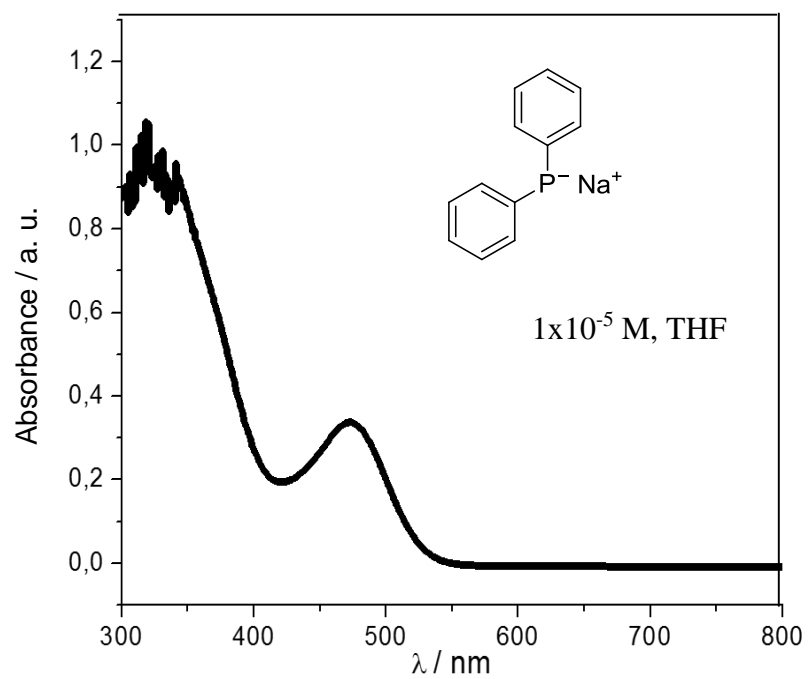


Picture **SI-6**: Experimental device for the  $\text{NH}_3(l)$  reactions. Dark reaction.



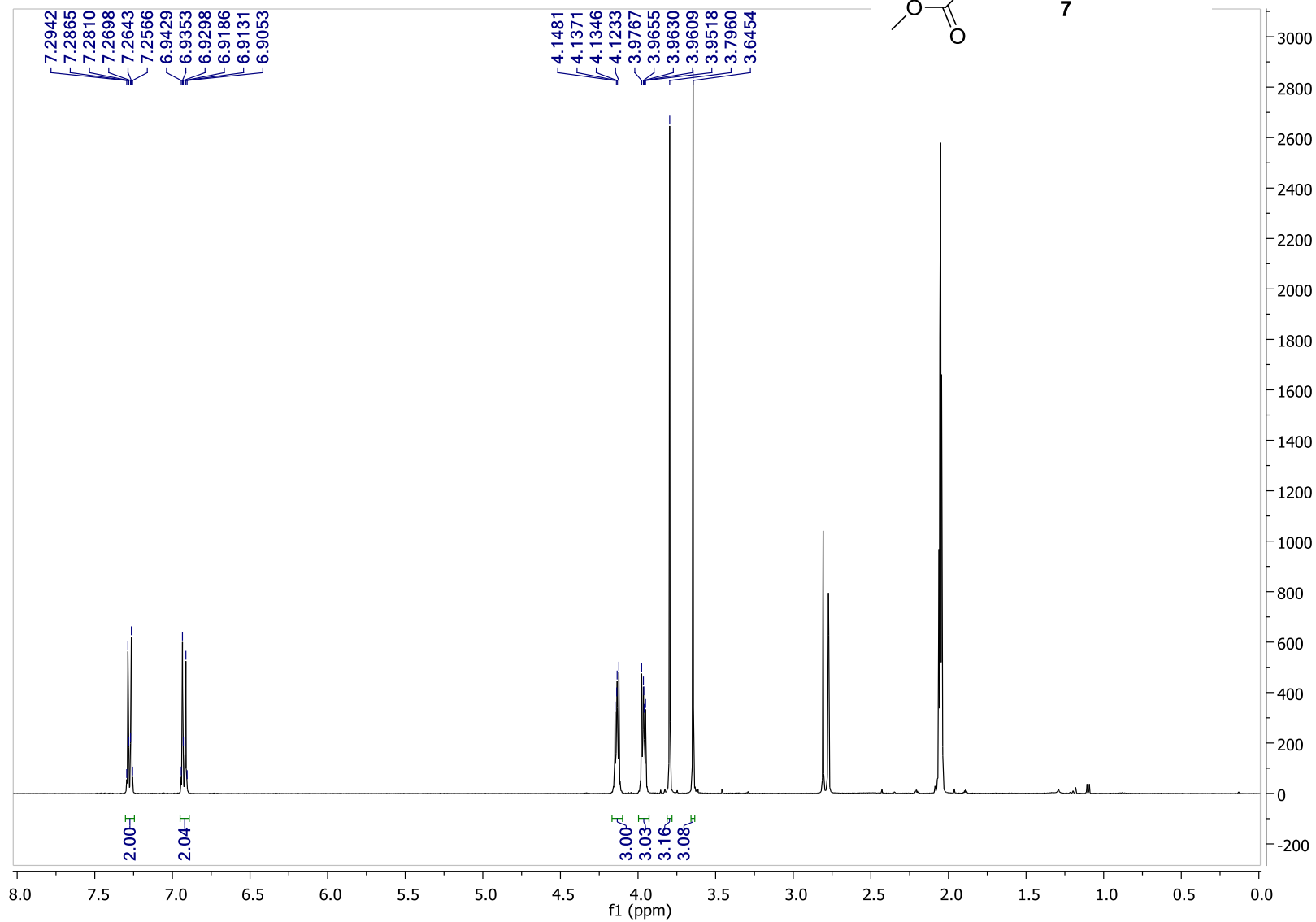
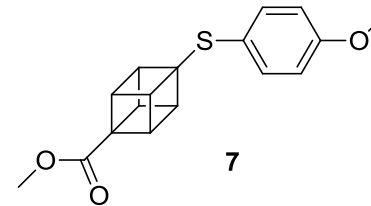
1.2 Figure SI-7: UV-visible spectra of **2**, **4**, **6**.





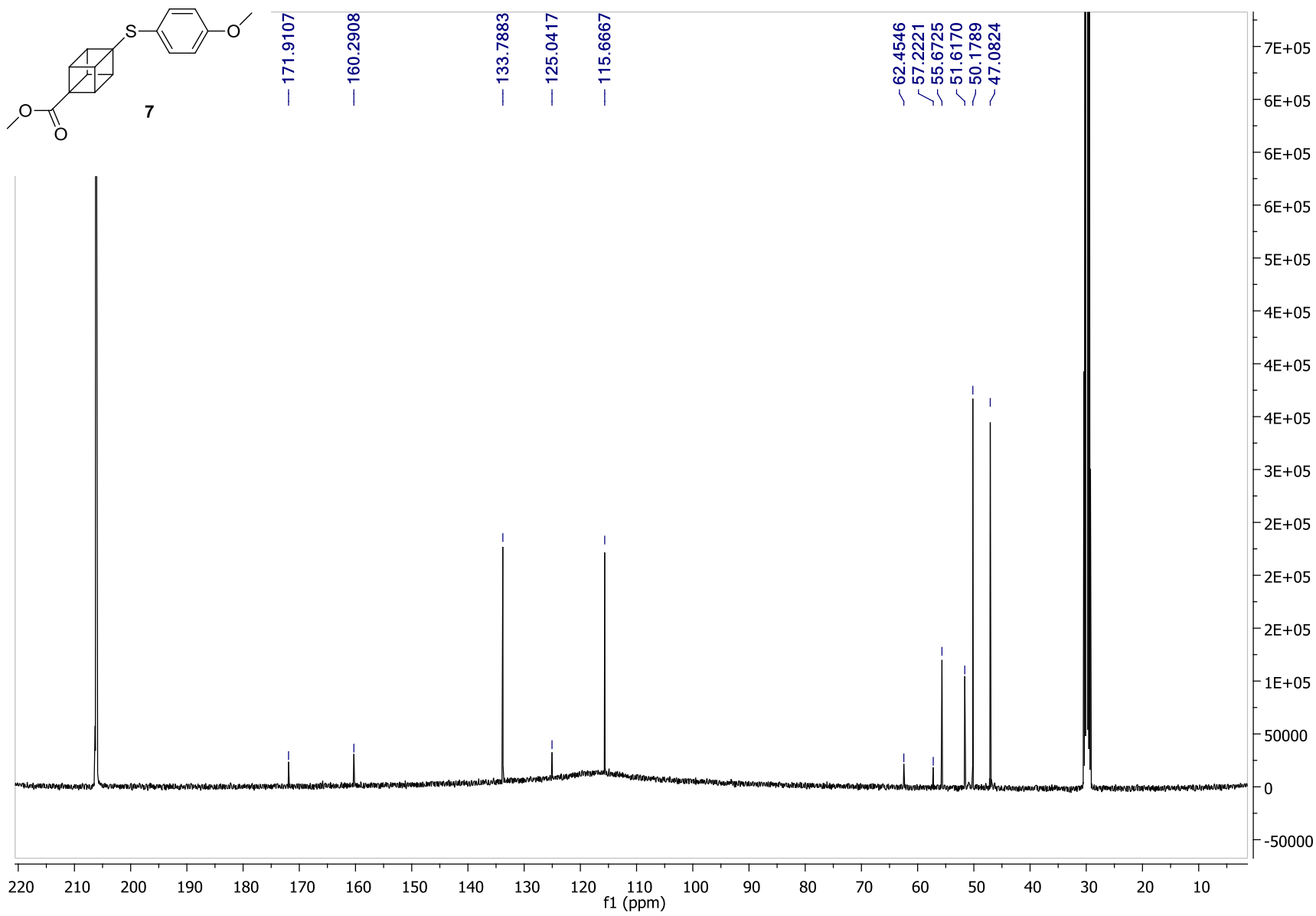
# Methyl 4-((4-methoxyphenyl)thio)cubane-1-carboxylate (7)

$^1\text{H-NMR}$  (400 MHz, acetone- $d_6$ )

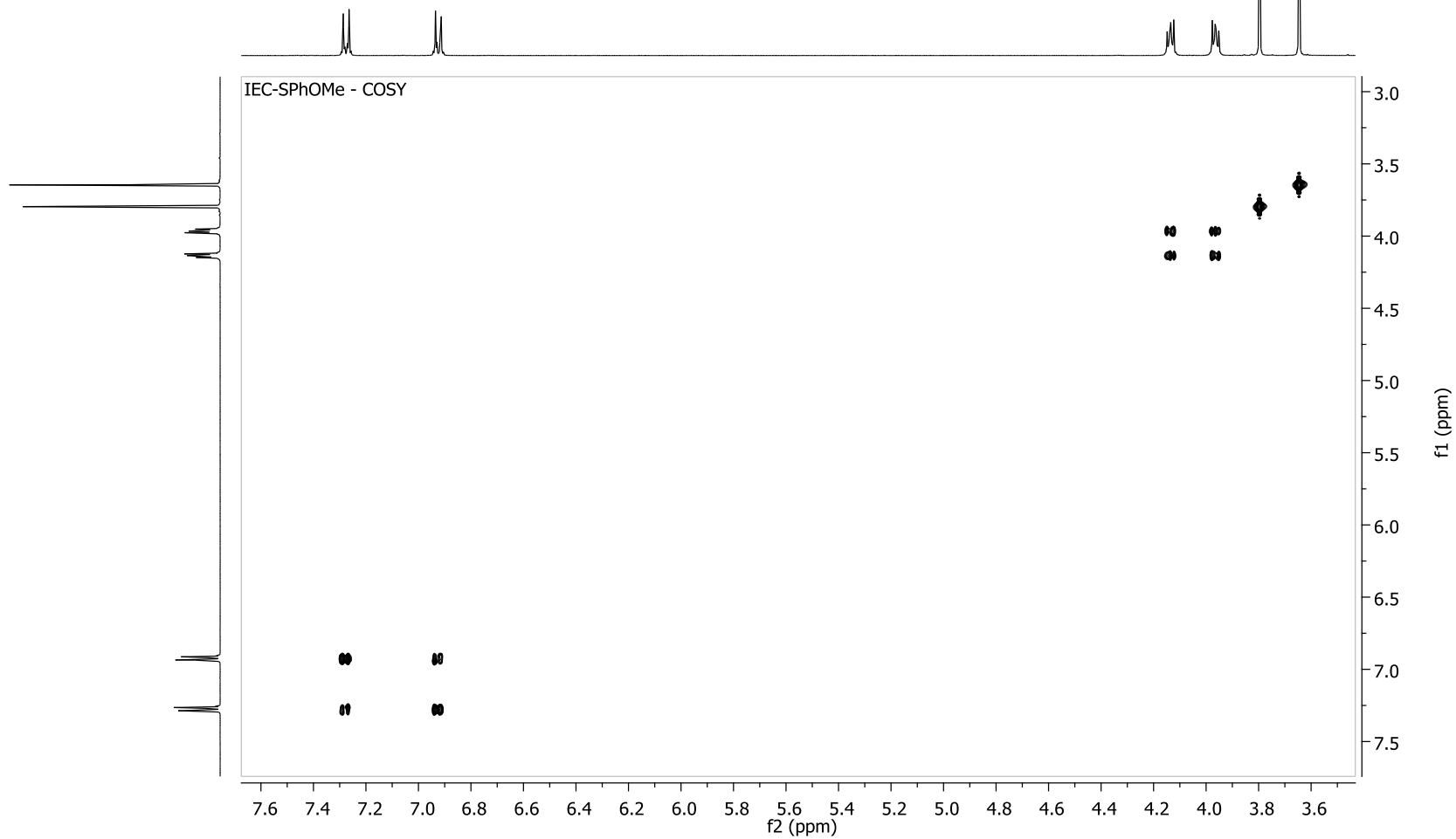
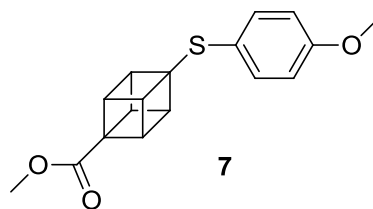


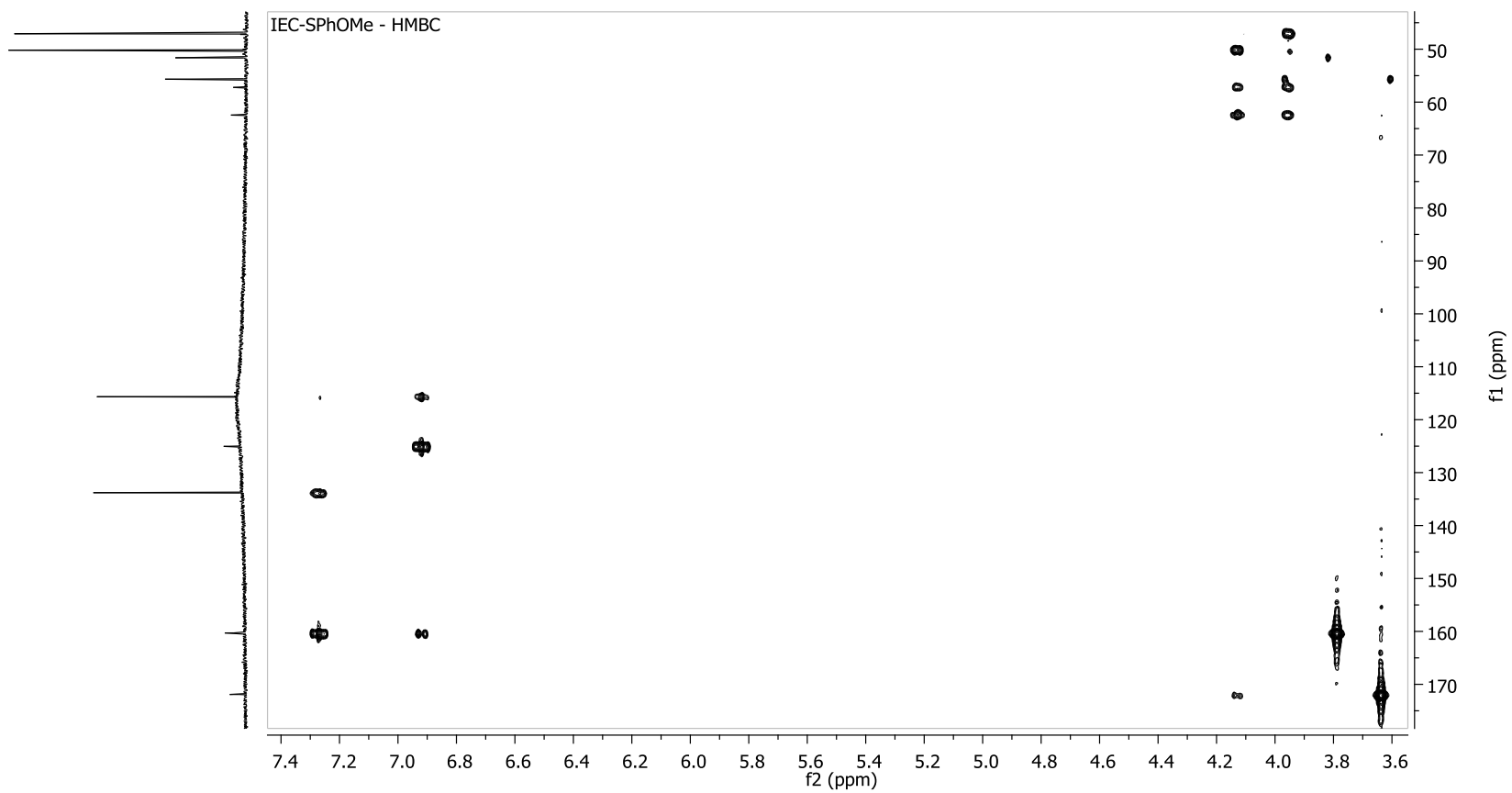
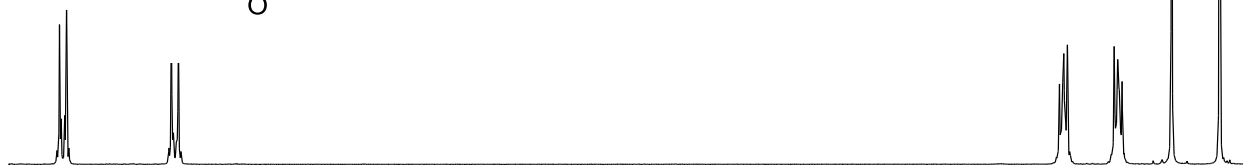
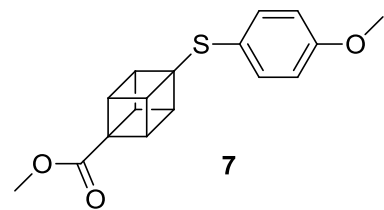


**<sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>)**

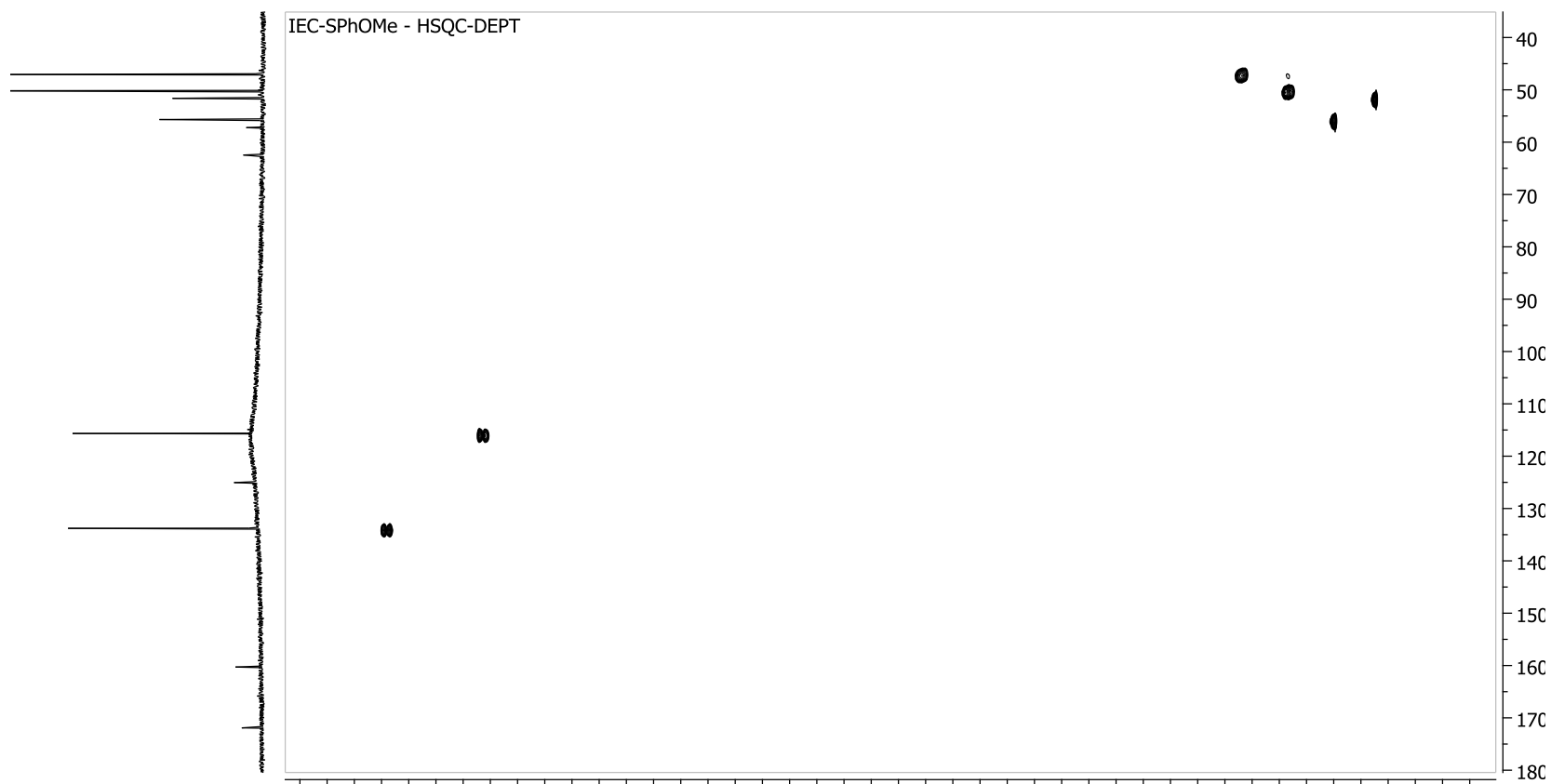
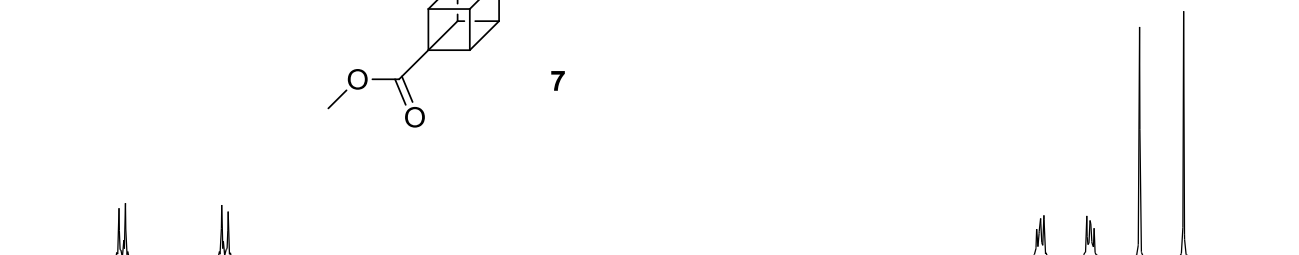
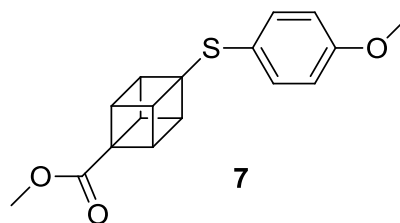


COSY (acetone-*d*<sub>6</sub>)



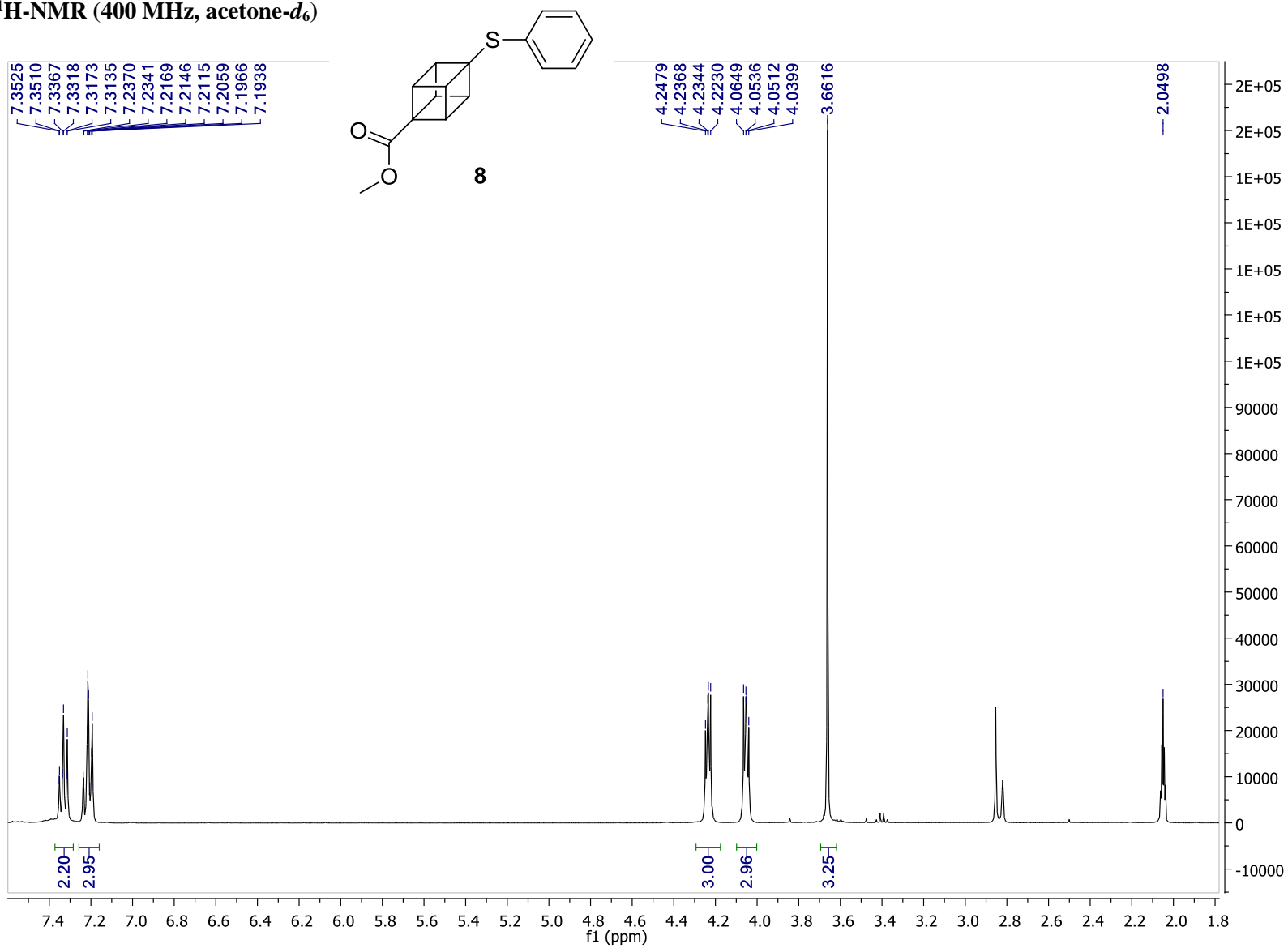


HSQC-DEPT (acetone-*d*<sub>6</sub>)

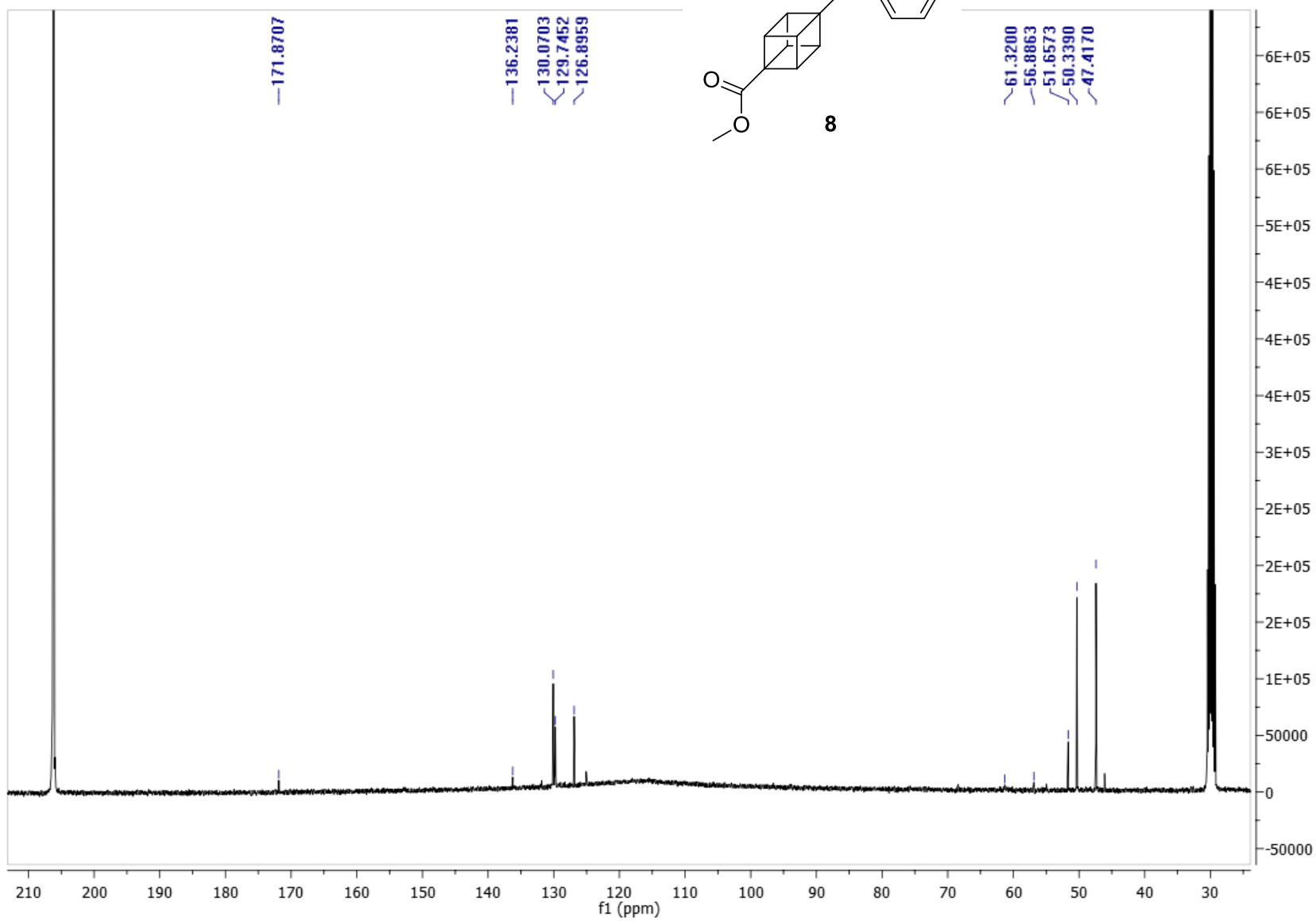


# Methyl 4-(phenylthio)cubane-1-carboxylate (8)

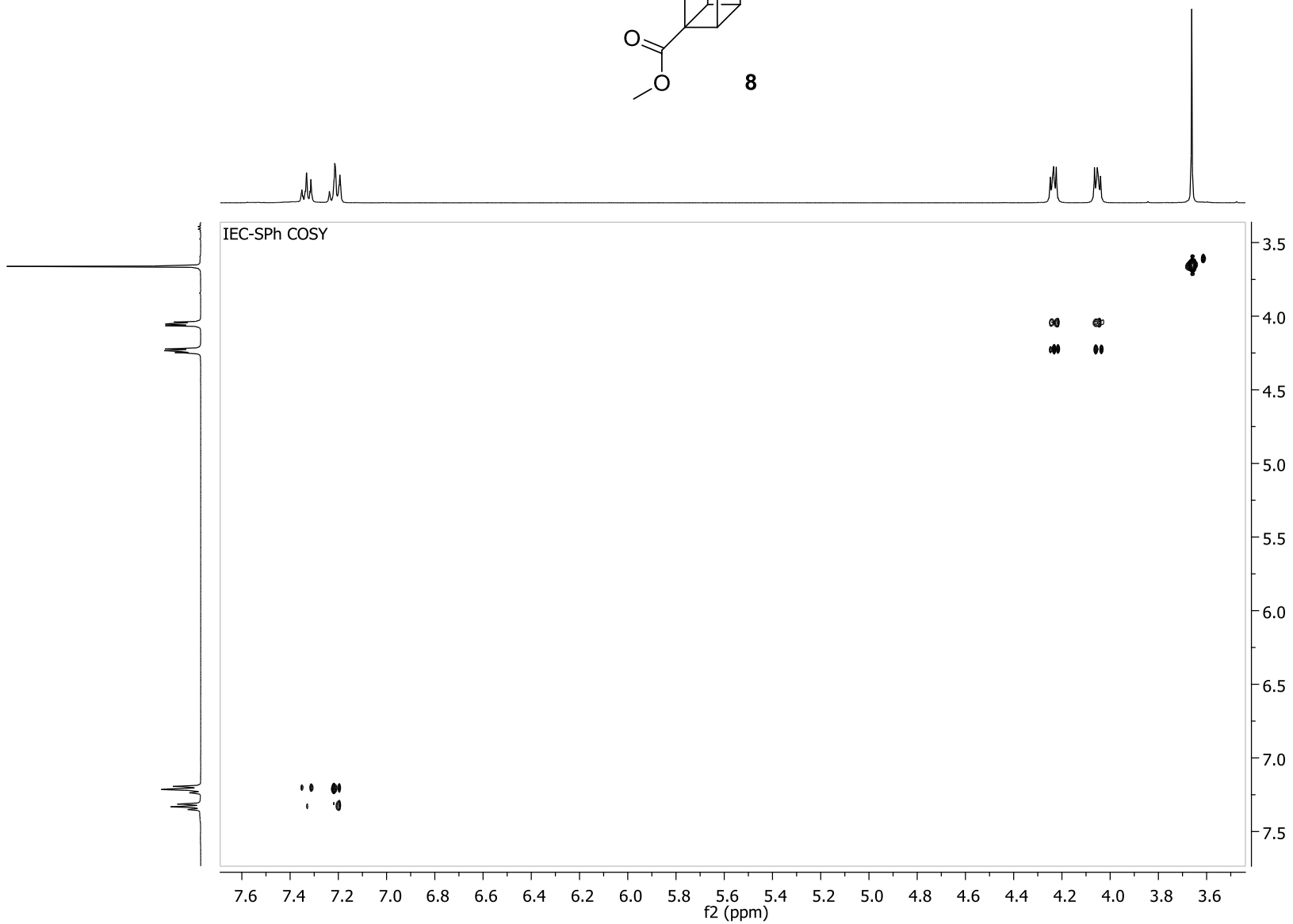
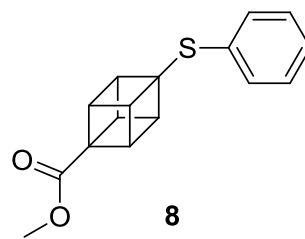
$^1\text{H-NMR}$  (400 MHz, acetone- $d_6$ )



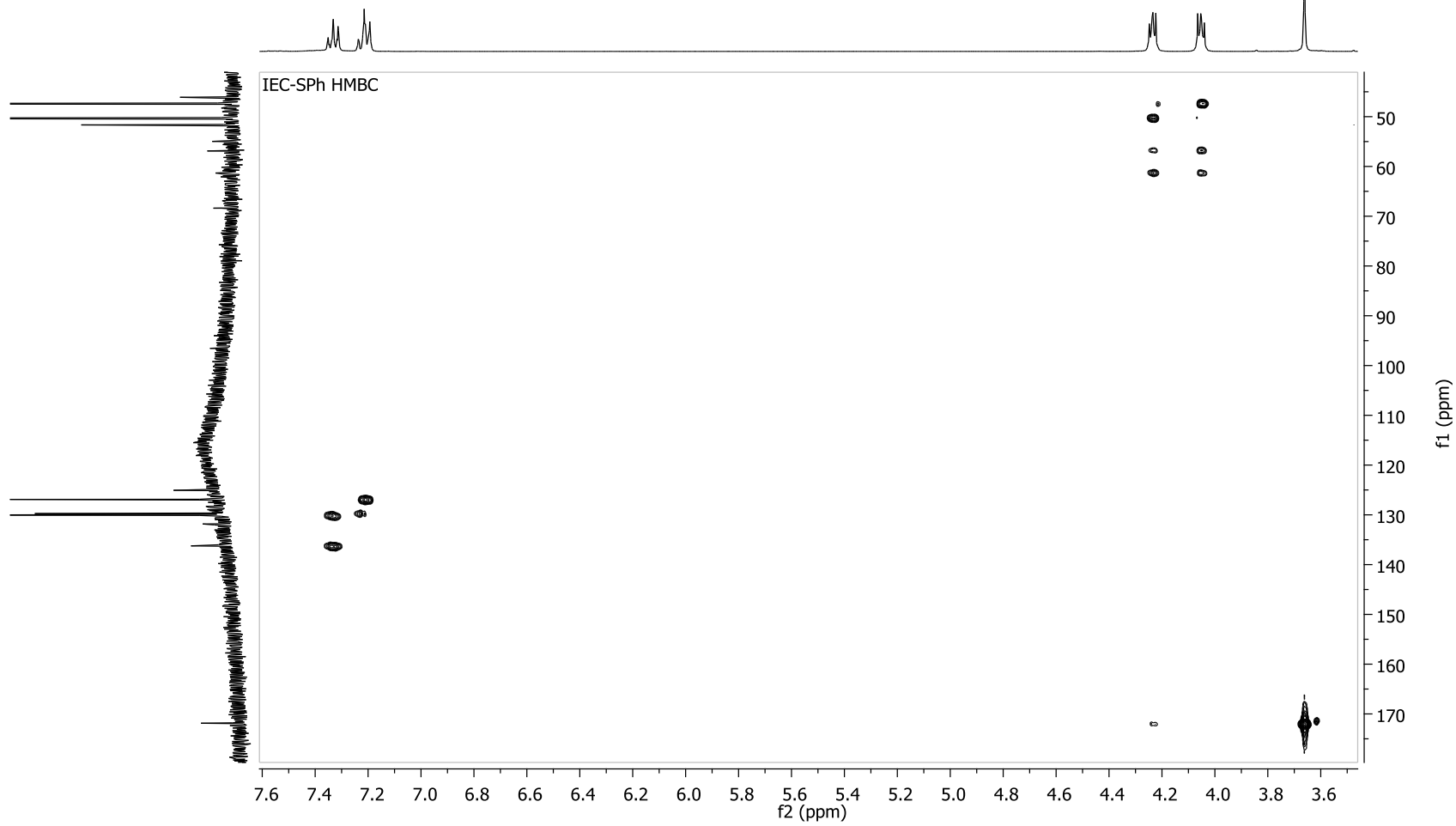
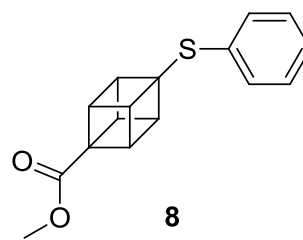
<sup>13</sup>C-NMR (100 MHz, acetone-d<sub>6</sub>)



COSY (acetone- $d_6$ )

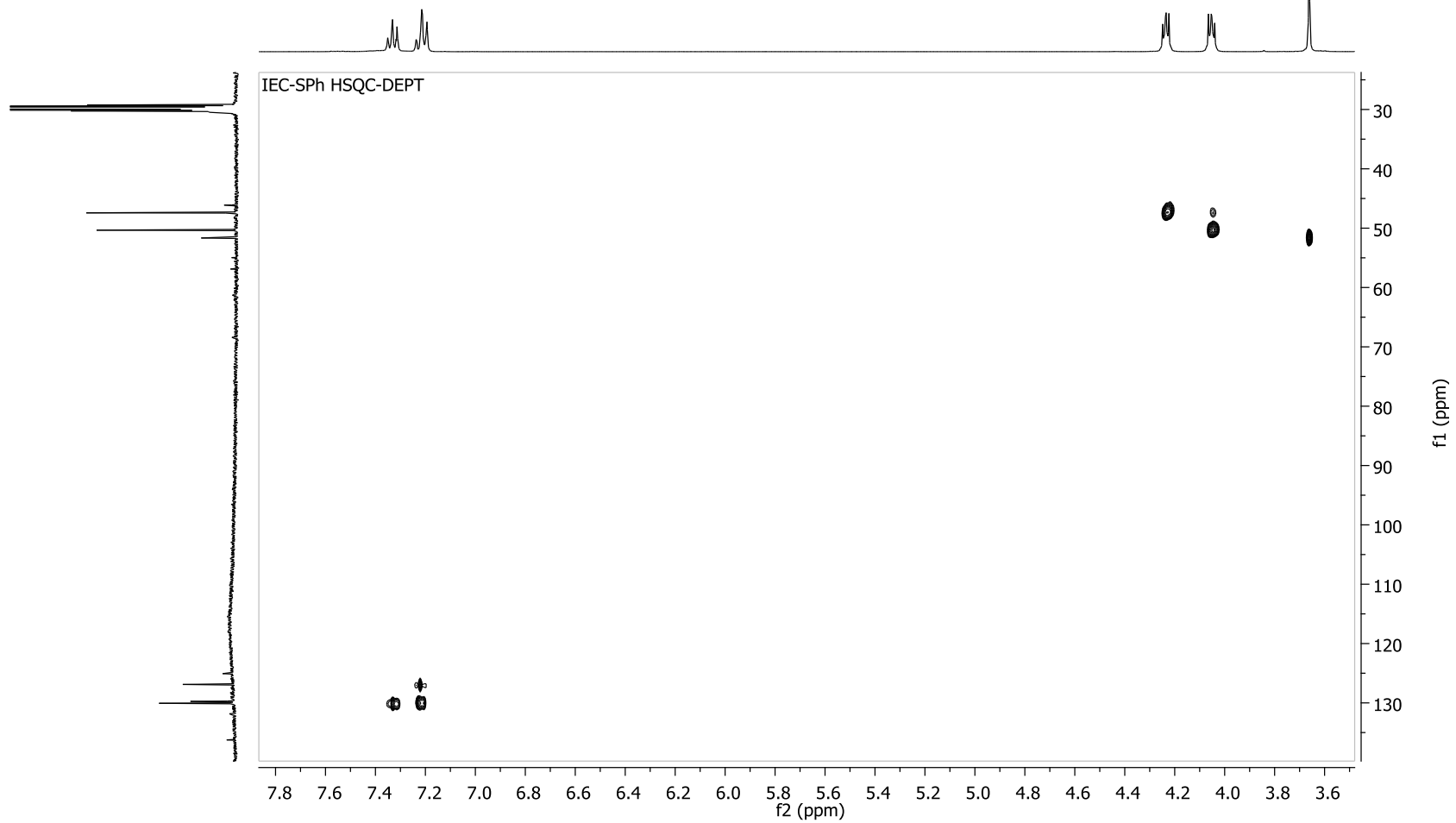
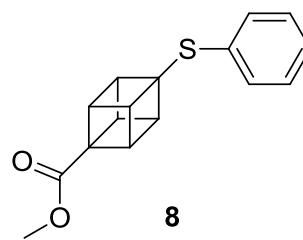


HMBC (acetone-*d*<sub>6</sub>)

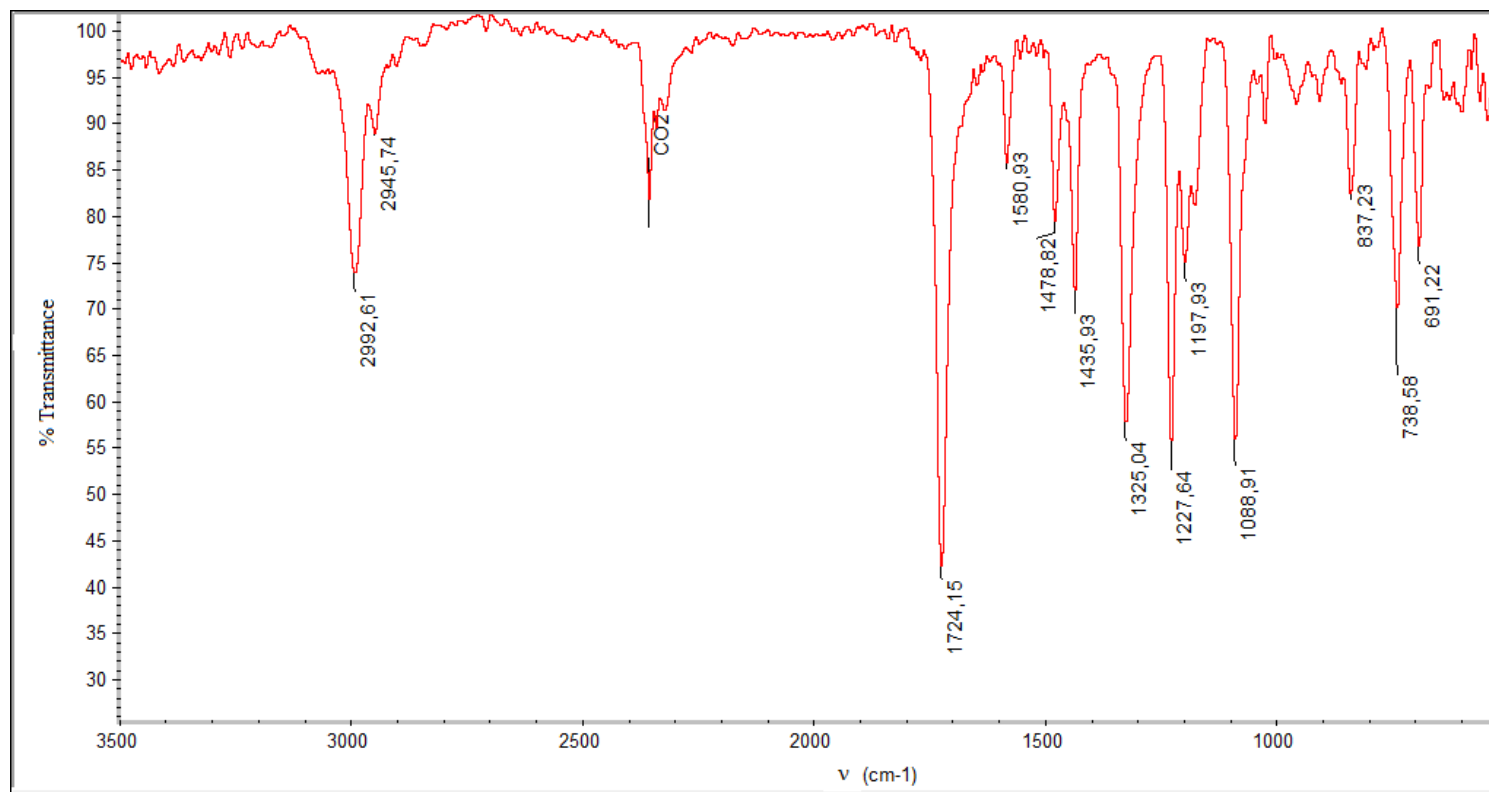
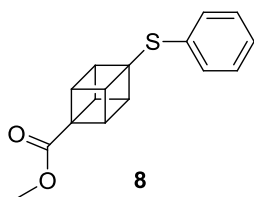




HSQC-DEPT (acetone-*d*<sub>6</sub>)

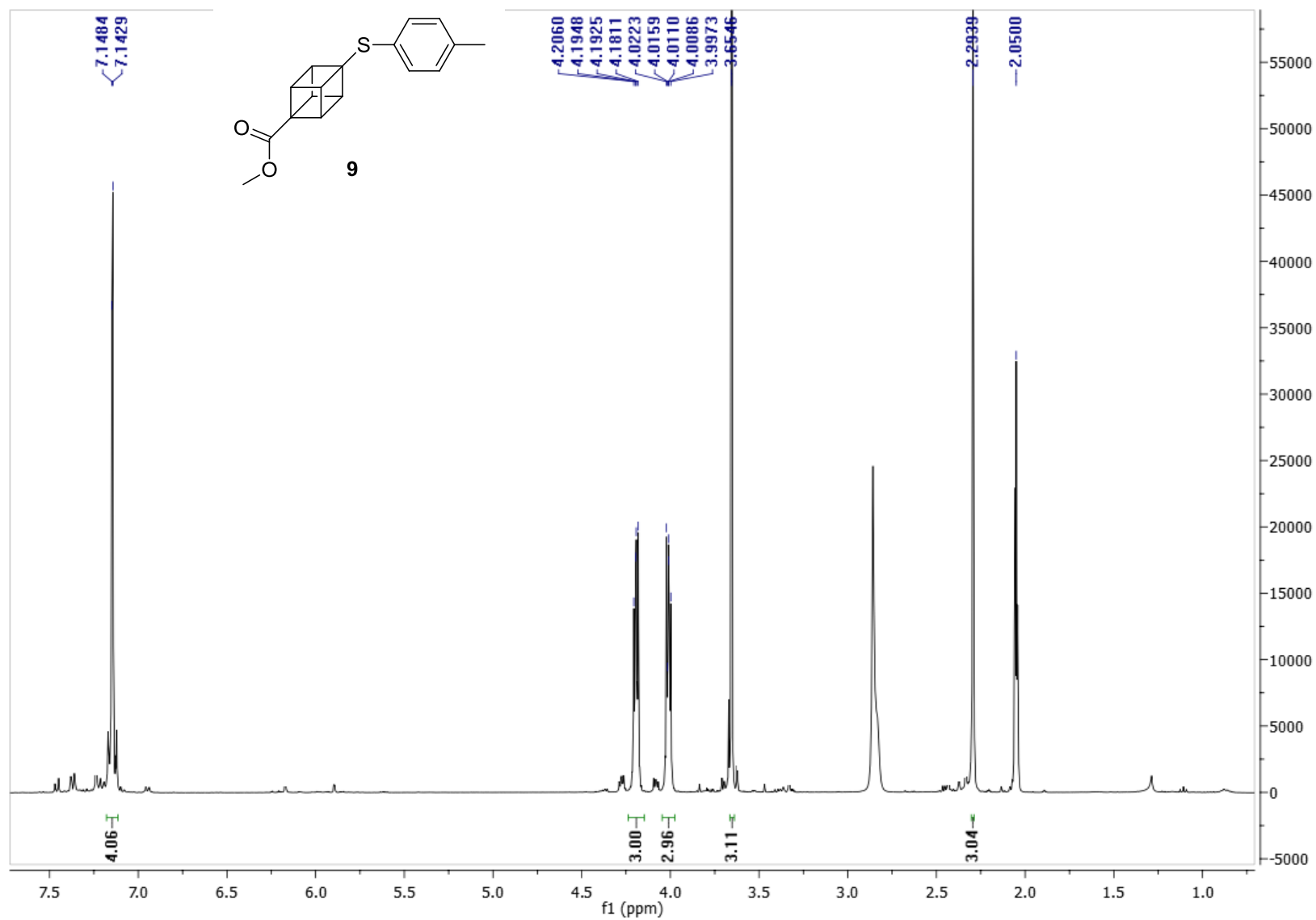


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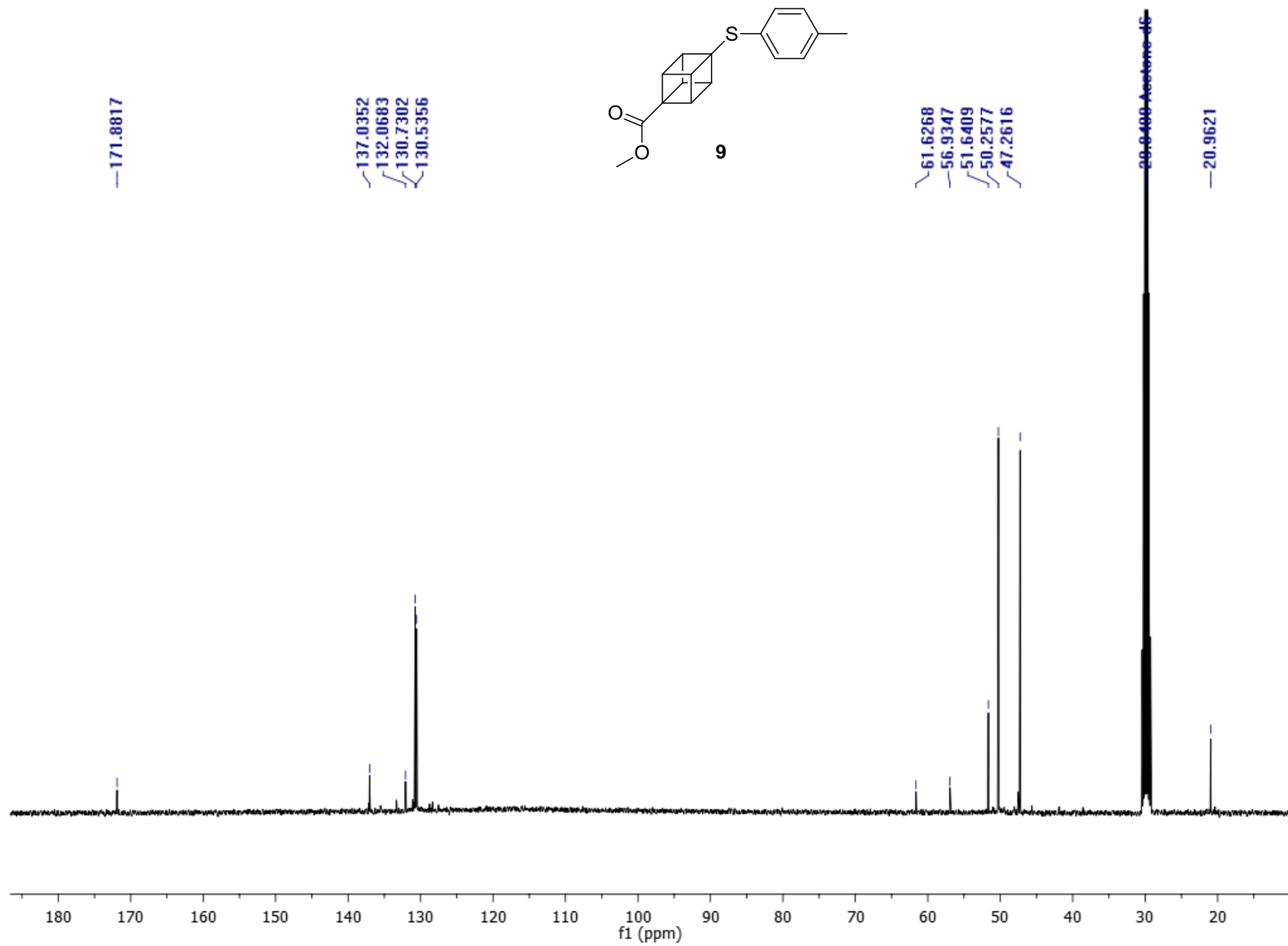


# Methyl 4-(4-methylphenylthio)cubane-1-carboxylate (9)

<sup>1</sup>H-NMR (400 MHz, acetone-d<sub>6</sub>)

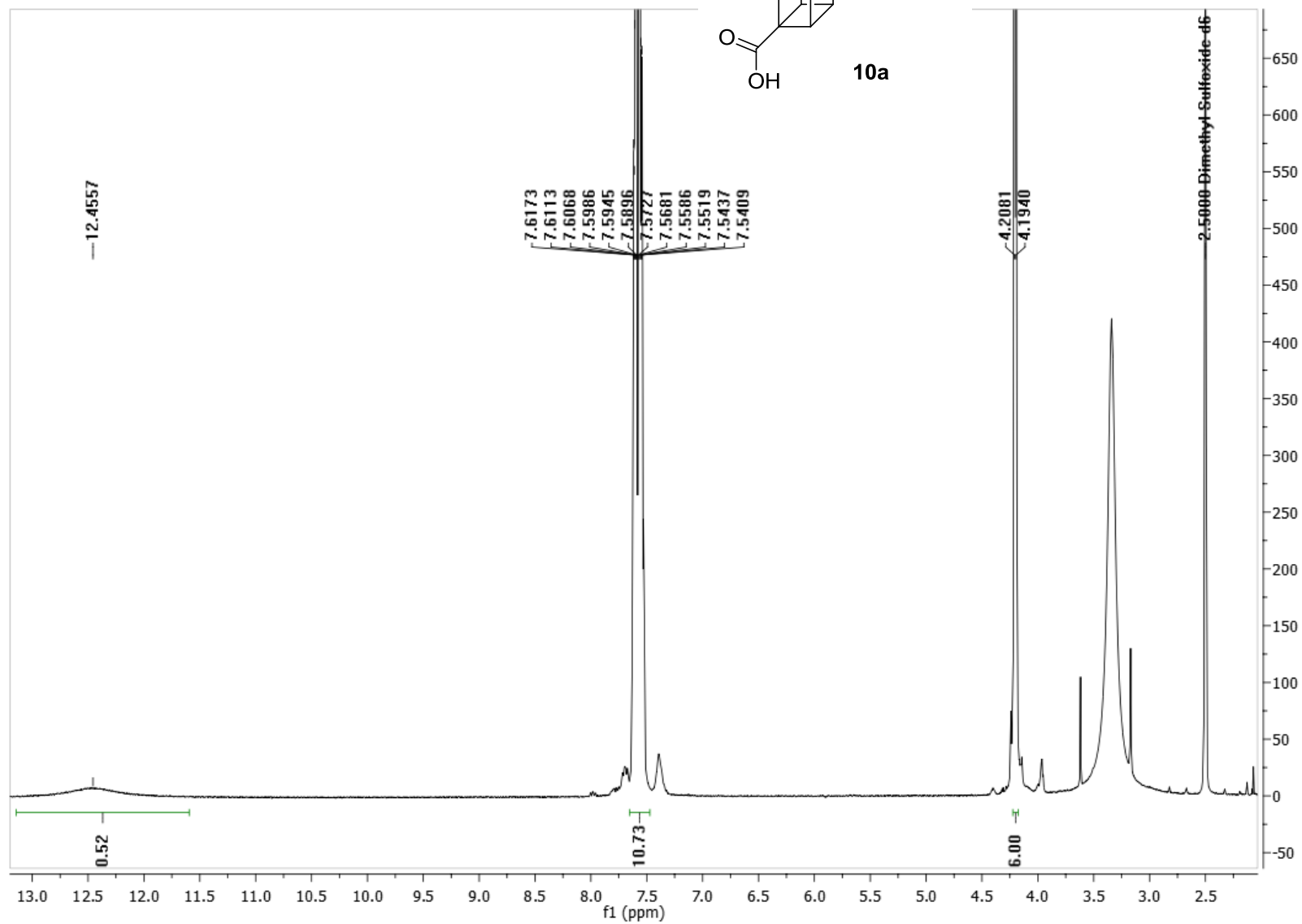
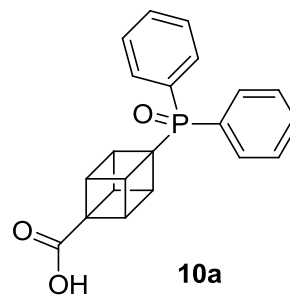


<sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>)

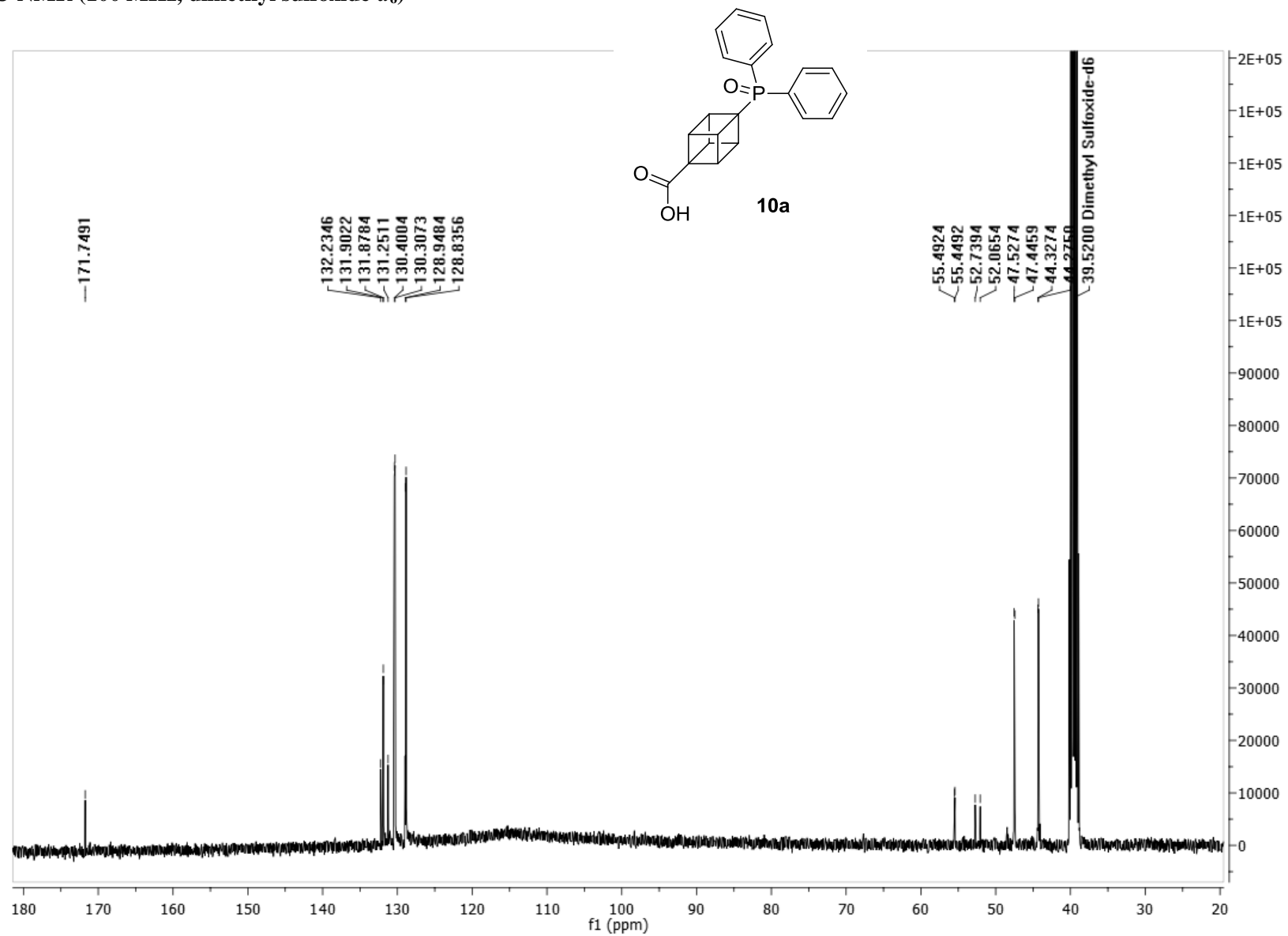


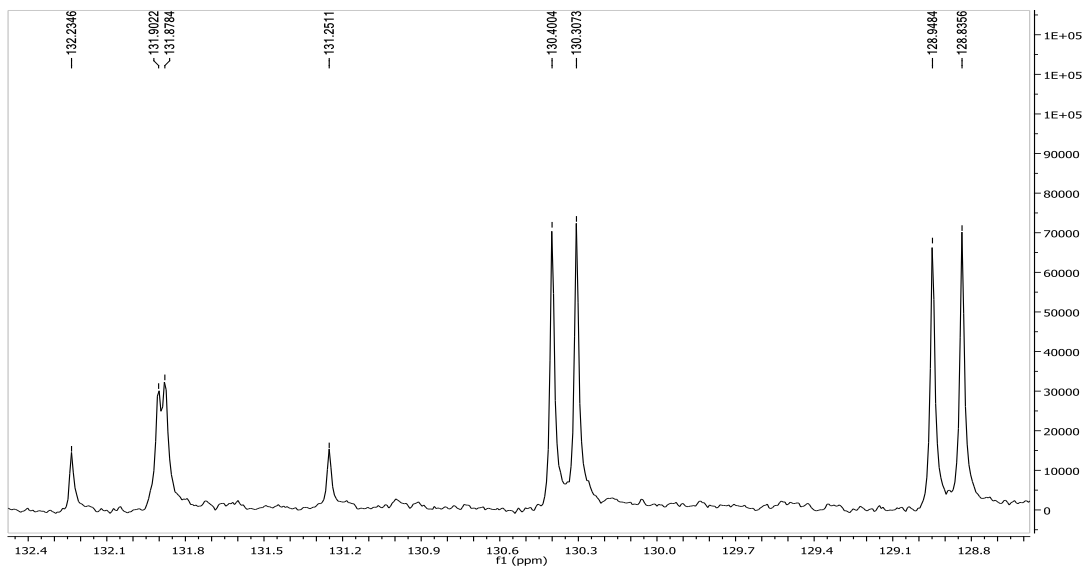
**4-(diphenylphosphoryl)cubane-1-carboxylic acid (9a)**

**<sup>1</sup>H-NMR (400 MHz, dimethyl sulfoxide-*d*<sub>6</sub>)**

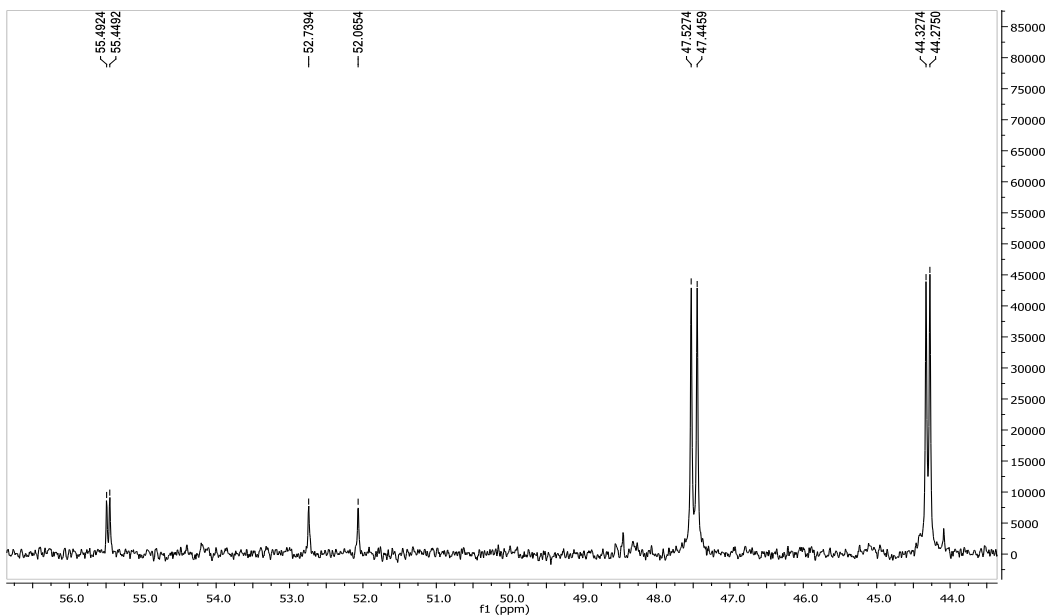
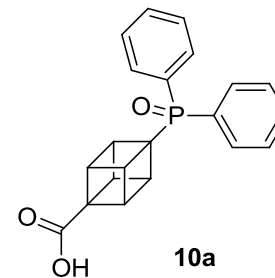


<sup>13</sup>C-NMR (100 MHz, dimethyl sulfoxide-d<sub>6</sub>)



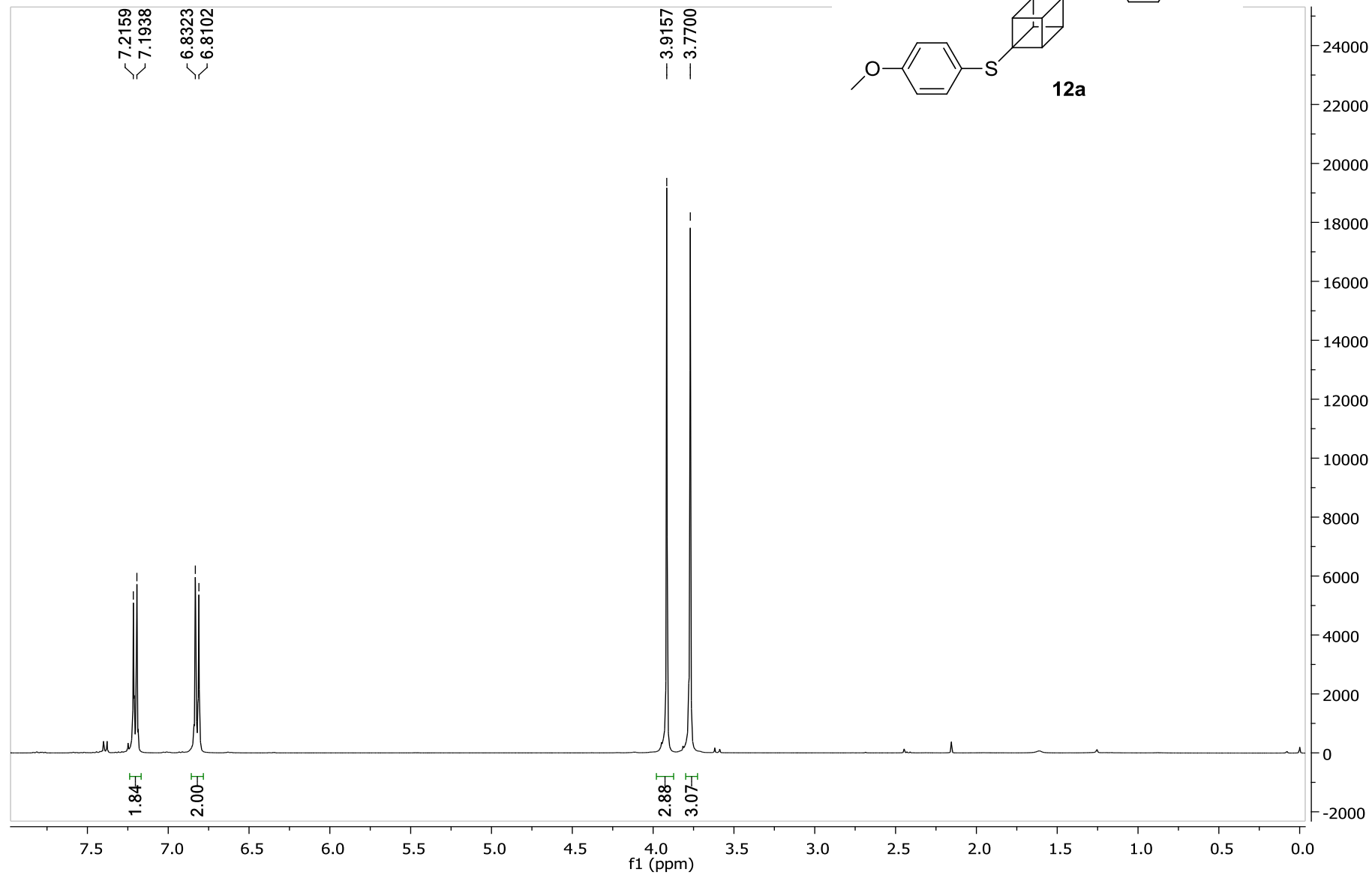


**<sup>13</sup>C-NMR (100 MHz, dimethyl sulfoxide-*d*<sub>6</sub>)**



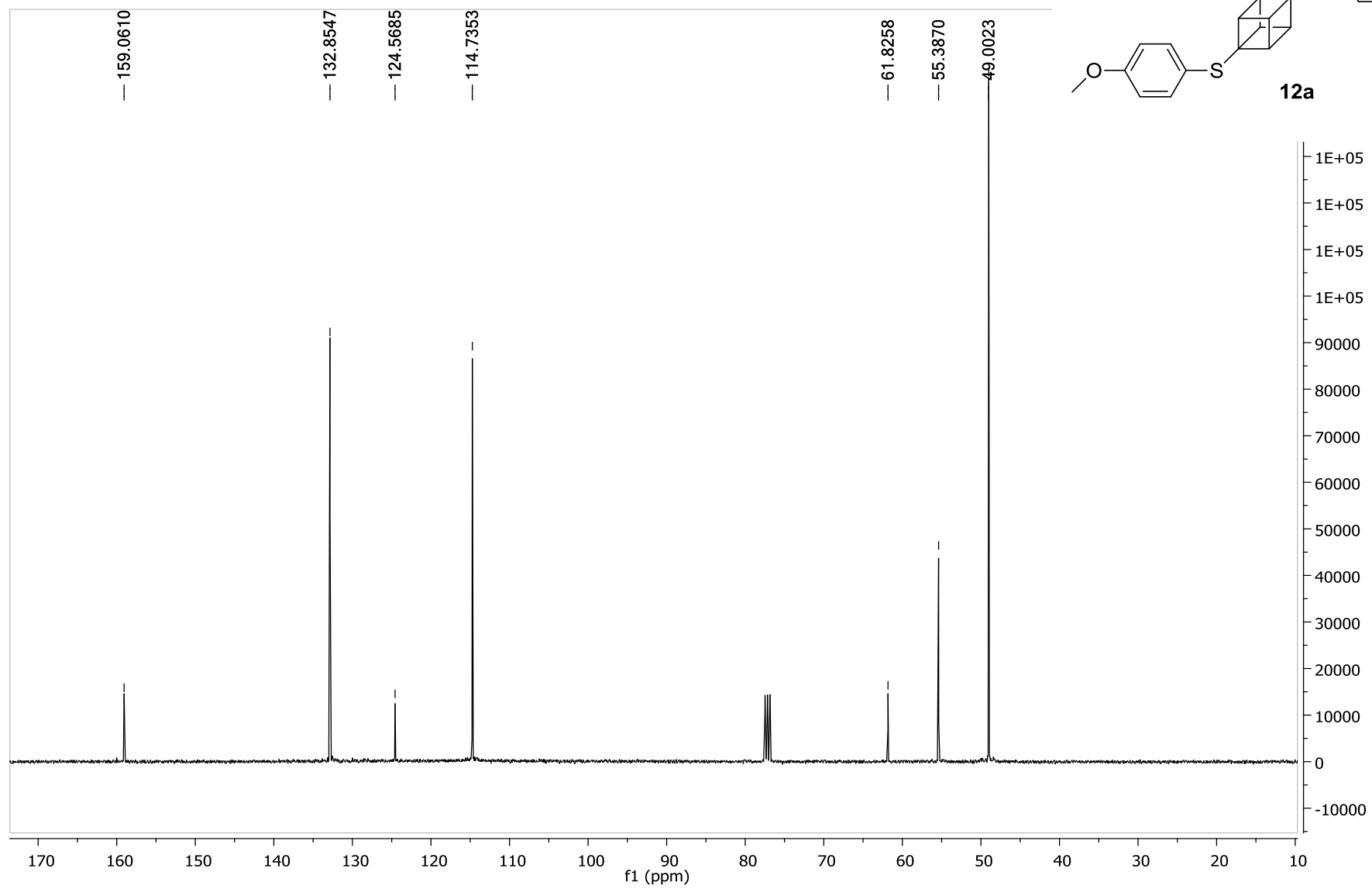
**1,4-bis((4-methoxyphenyl)thio)cubane(12a)**

**<sup>1</sup>H-NMR (400 MHz, chloroform-*d*)**



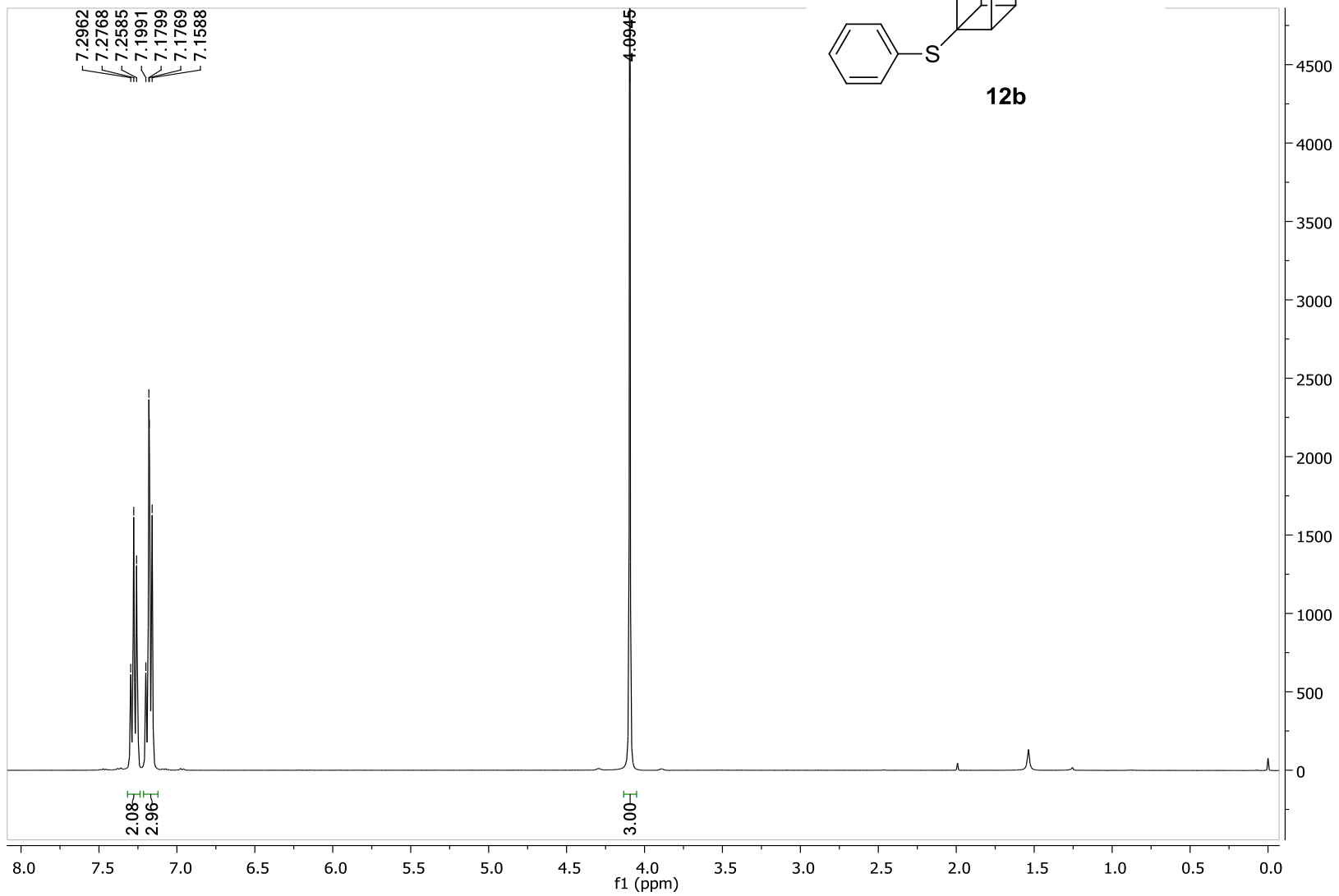


<sup>13</sup>C-NMR (100 Hz, chloroform-*d*)

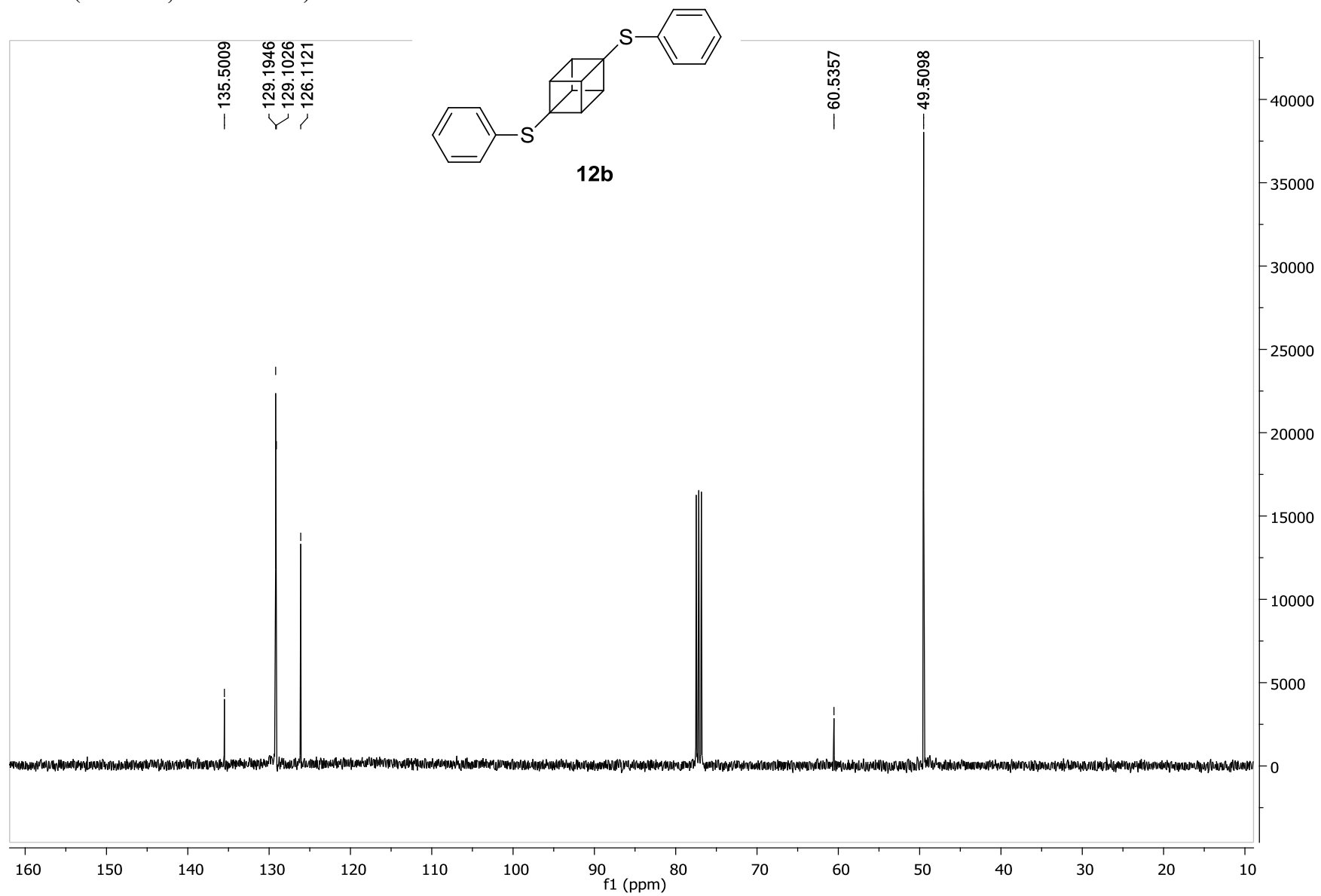


**1,4-bis(phenylthio)cubane (12b)**

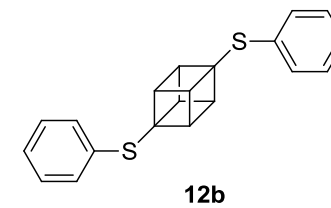
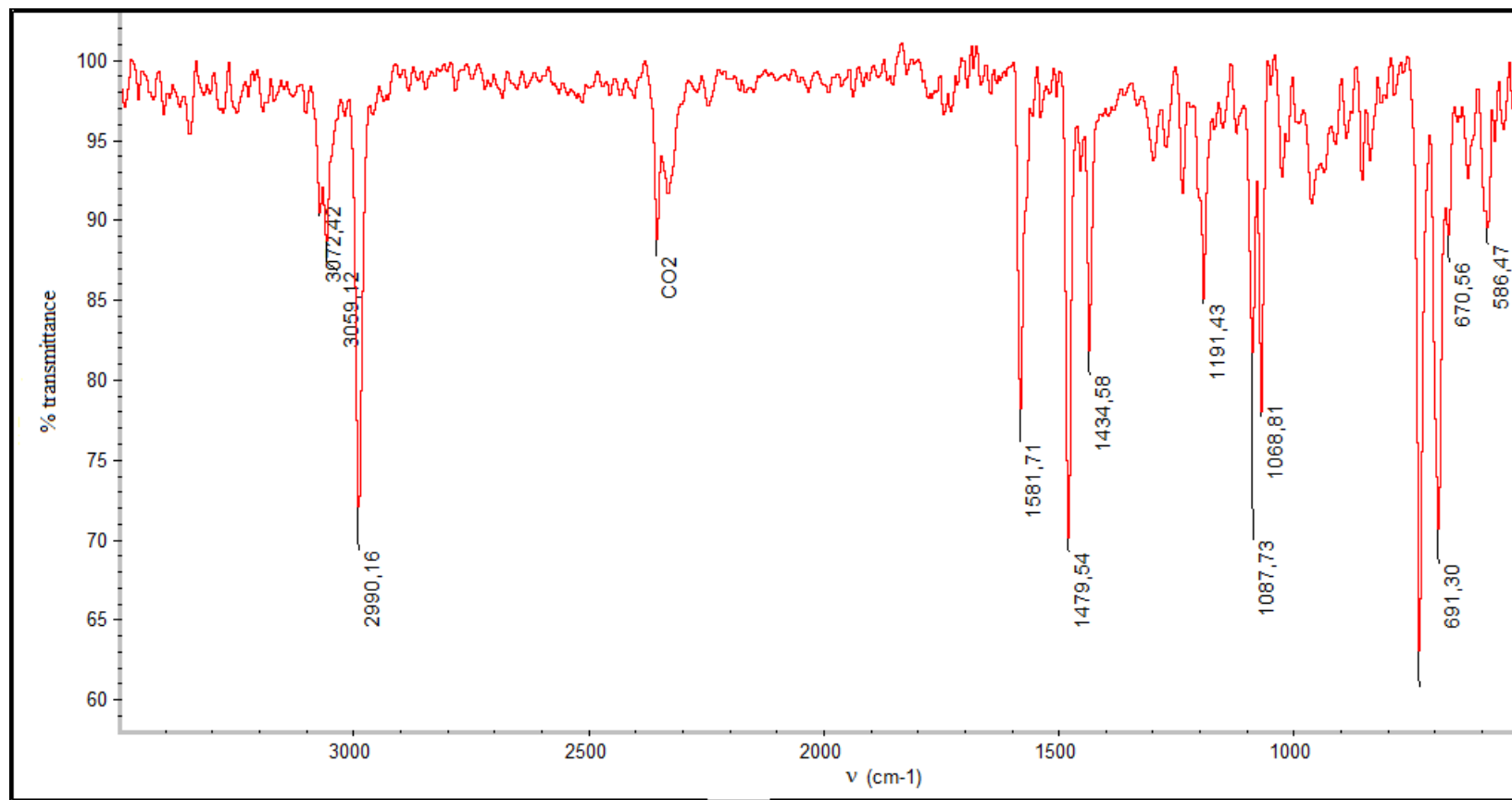
**<sup>1</sup>H-NMR (400 MHzchloroform-*d*)**



<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)

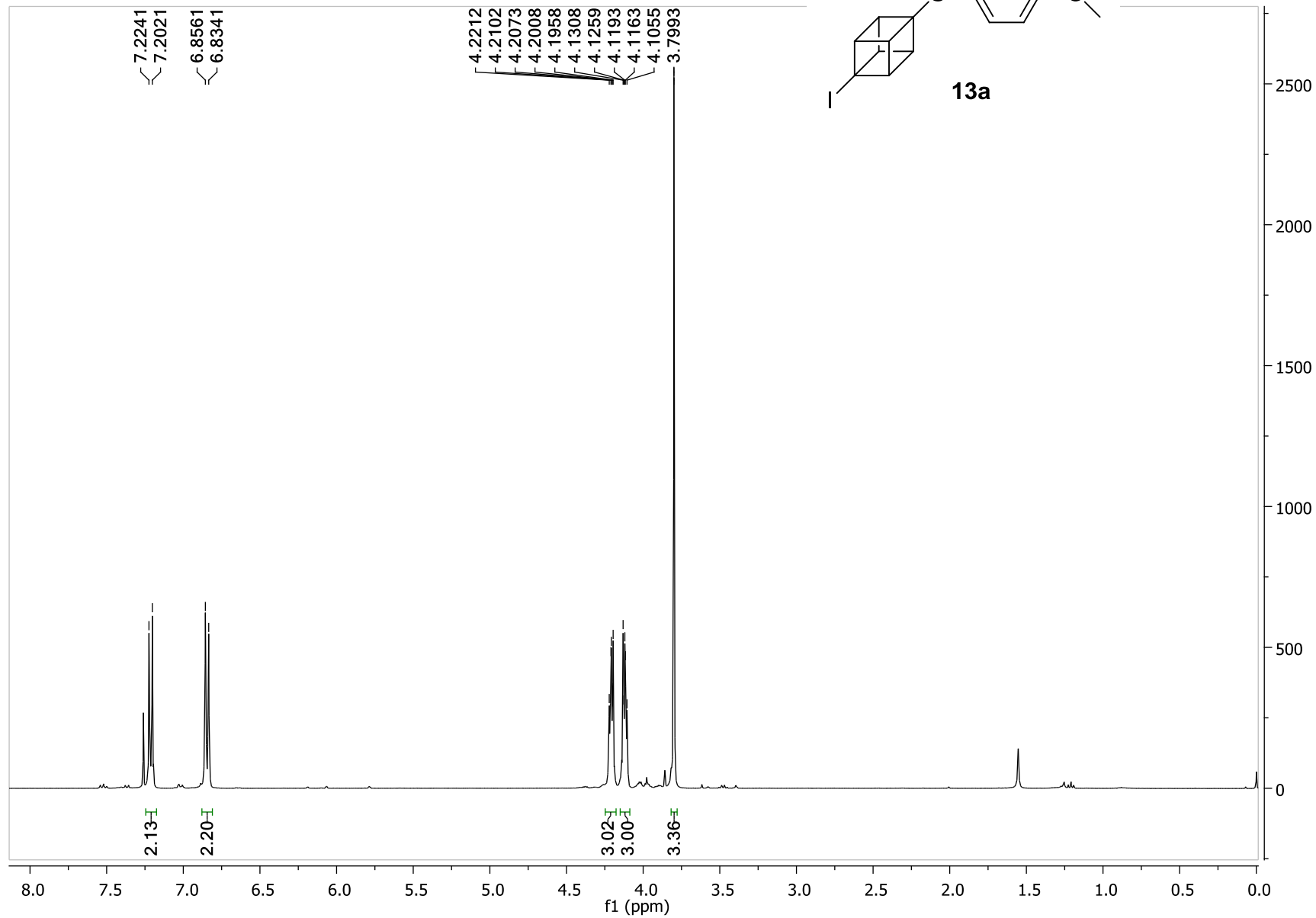


# IR

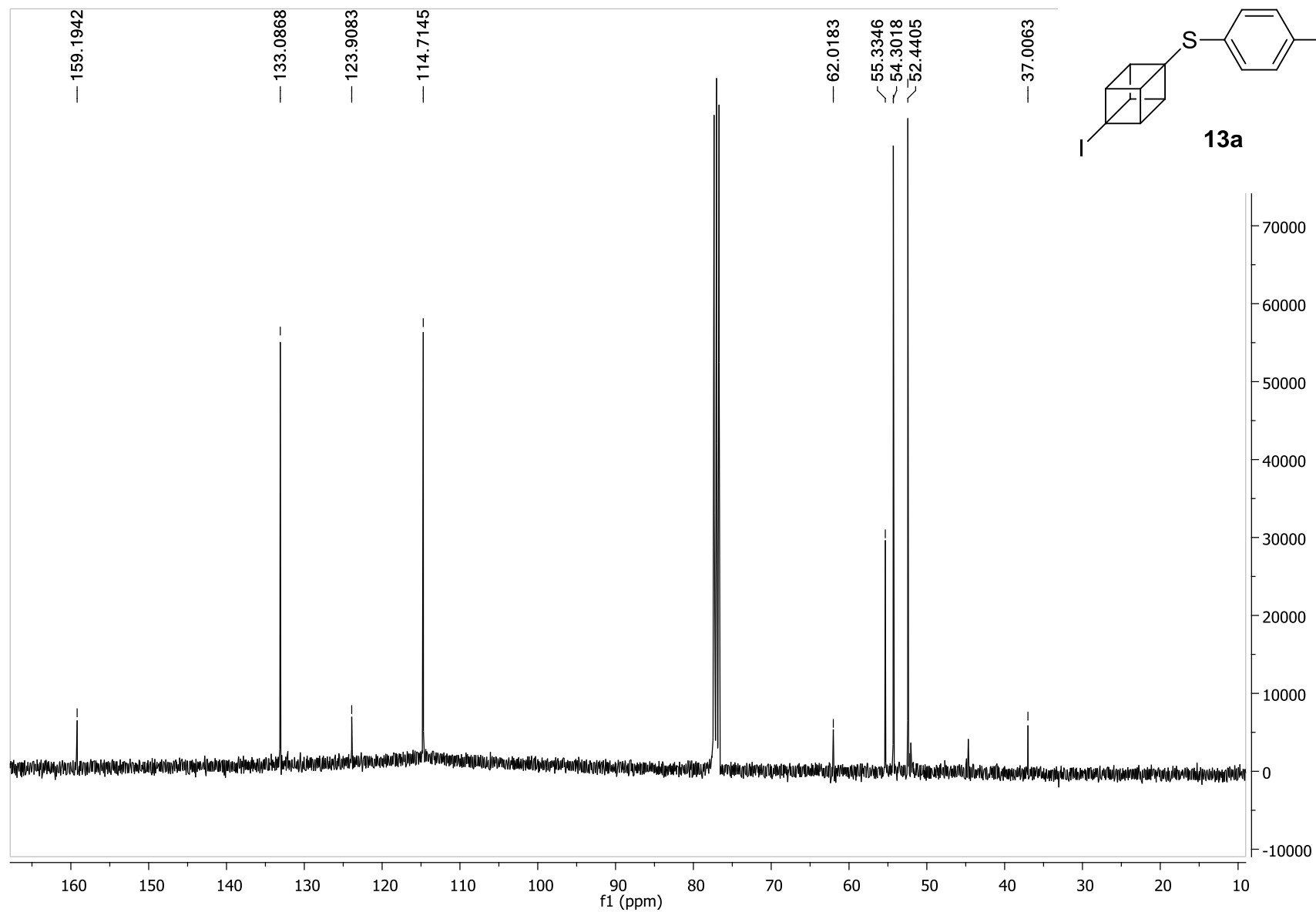


**(4-iodocuban-1-yl)(4-methoxyphenyl)sulfane (13a)**

**<sup>1</sup>H-NMR (400 MHz, chloroform-*d*)**

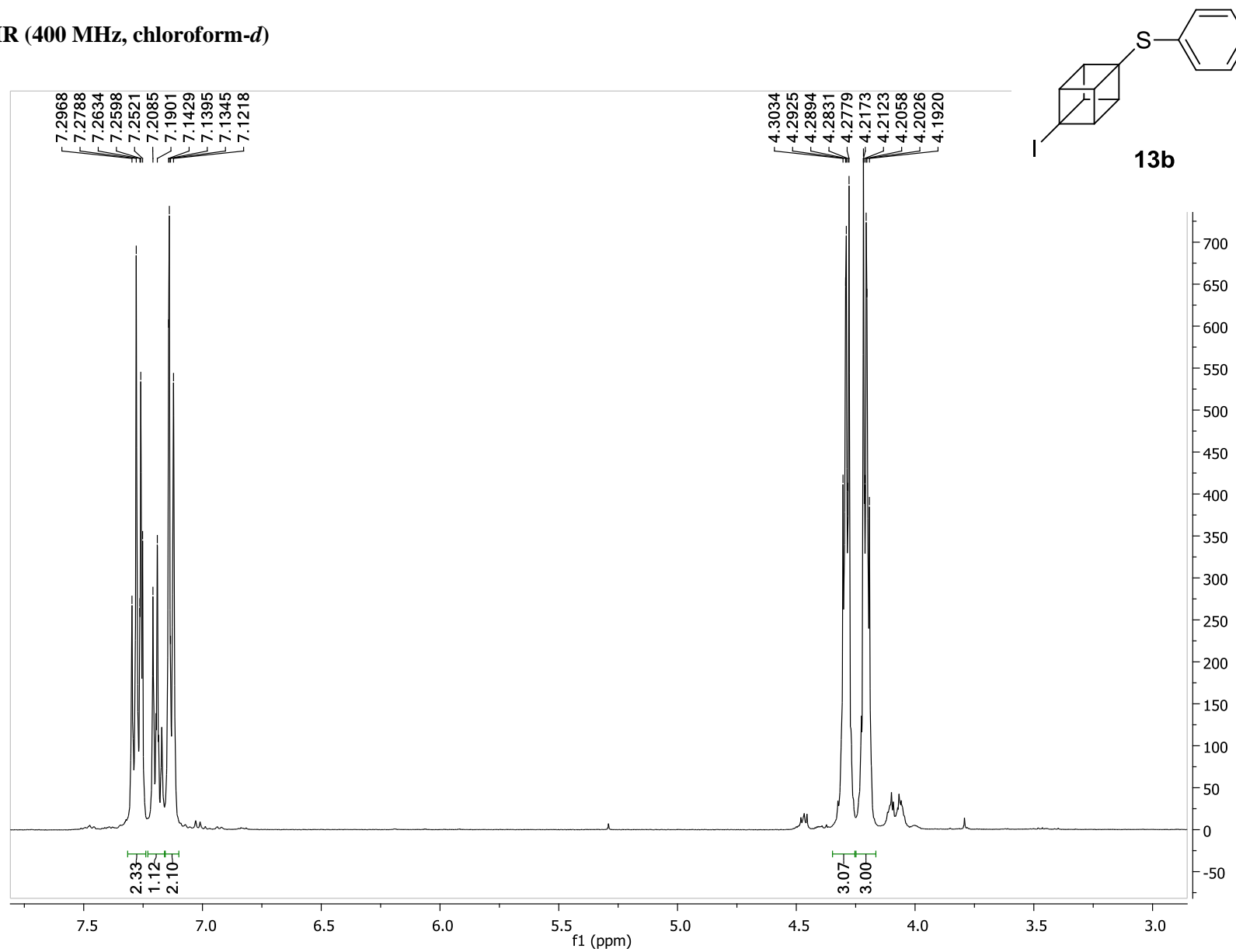


<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)

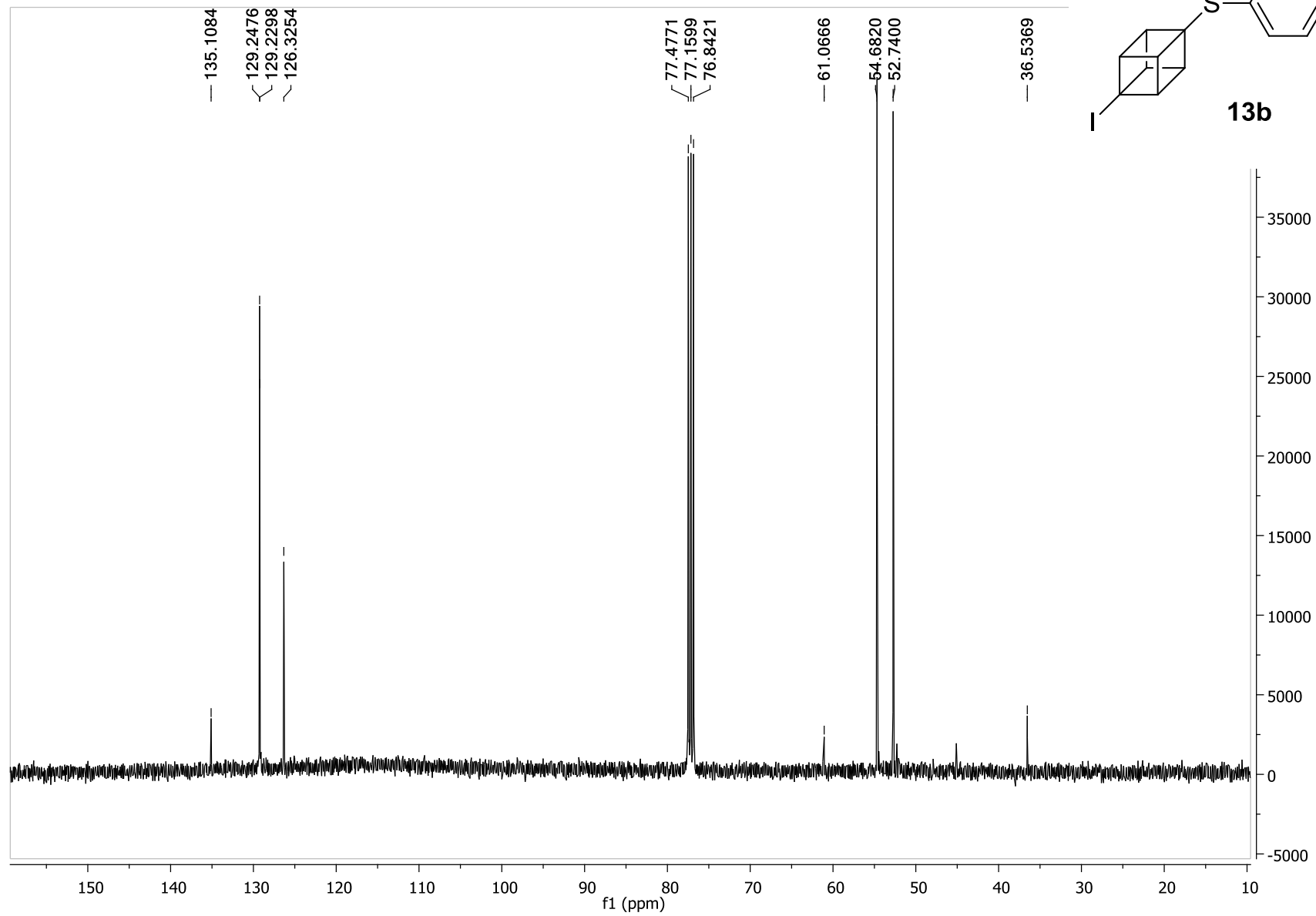


**(4-iodocuban-1-yl)(phenyl)sulfane (13b)**

**<sup>1</sup>H-NMR (400 MHz, chloroform-*d*)**



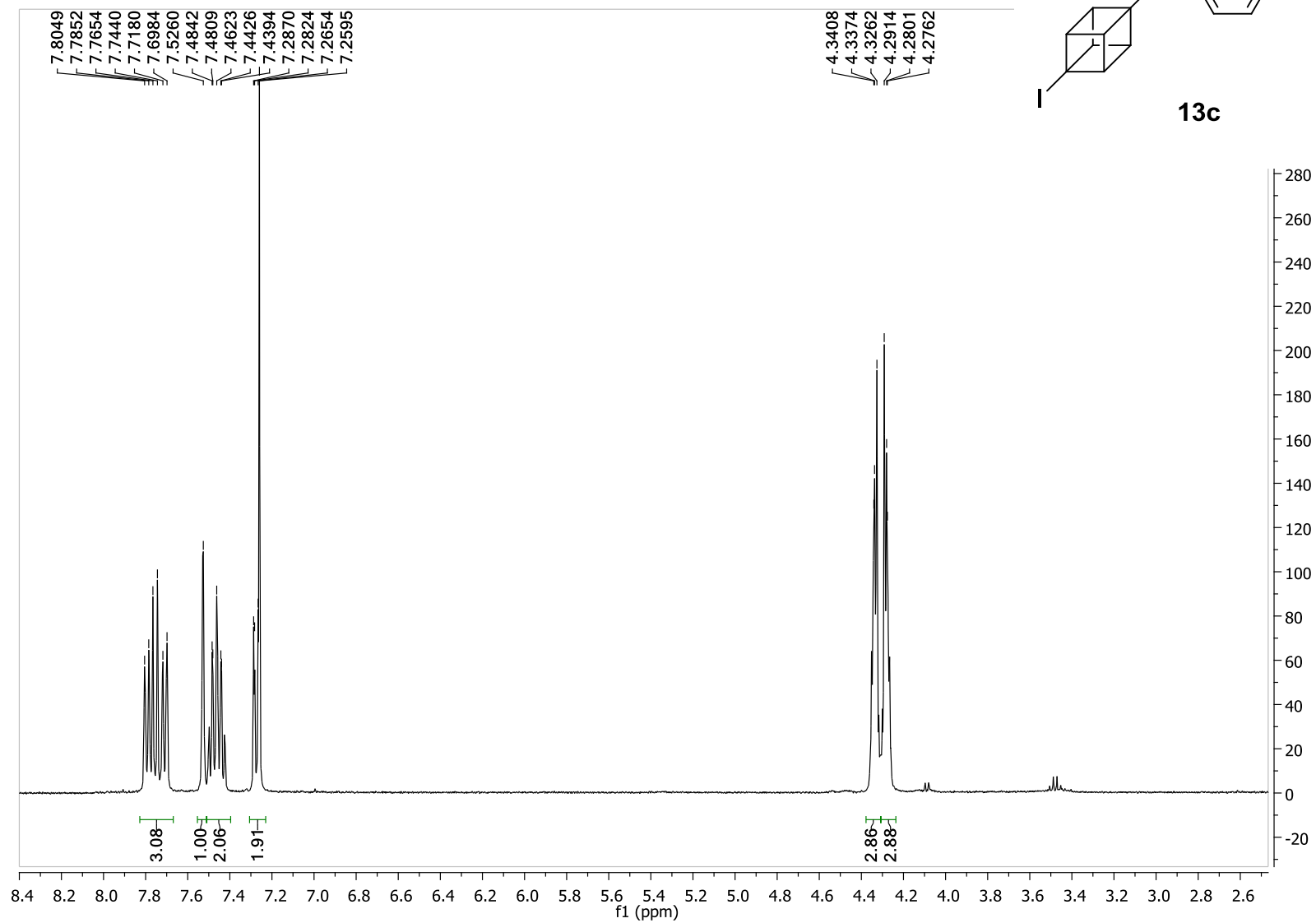
<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)



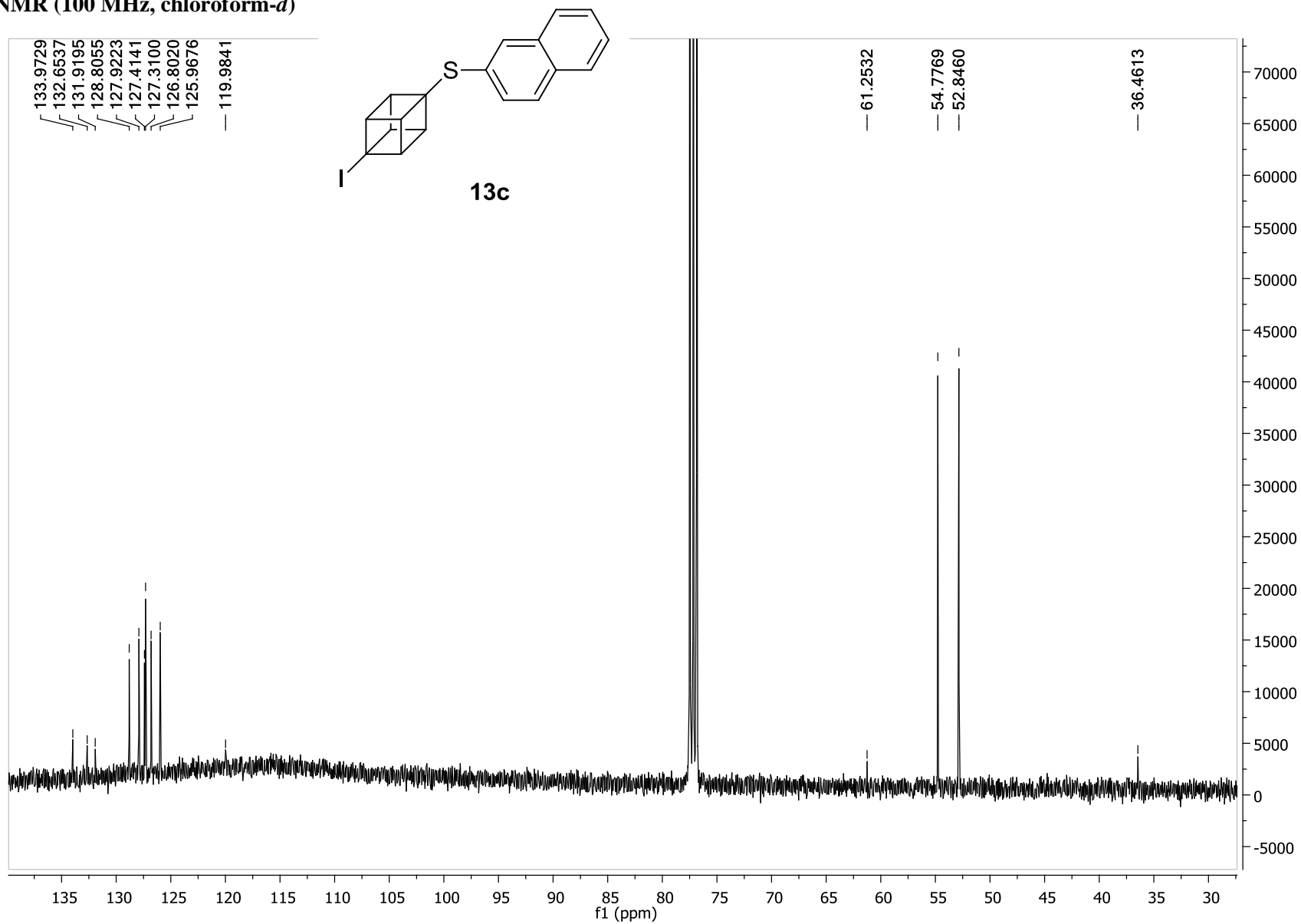


**(4-iodocuban-1-yl)(naphthalen-2-yl)sulfane (13c)**

**<sup>1</sup>H- NMR (400 MHz, chloroform-*d*)**

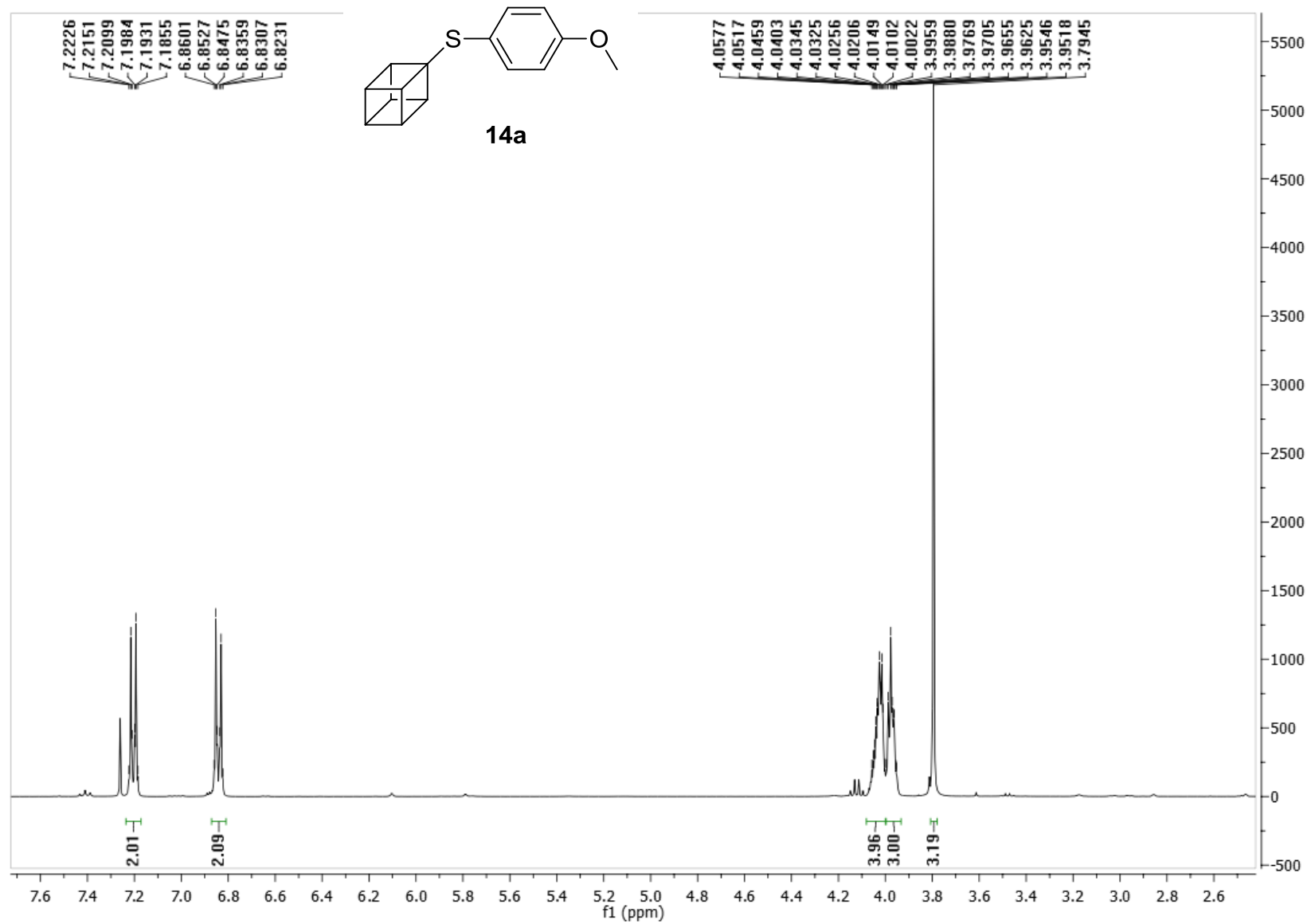


<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)

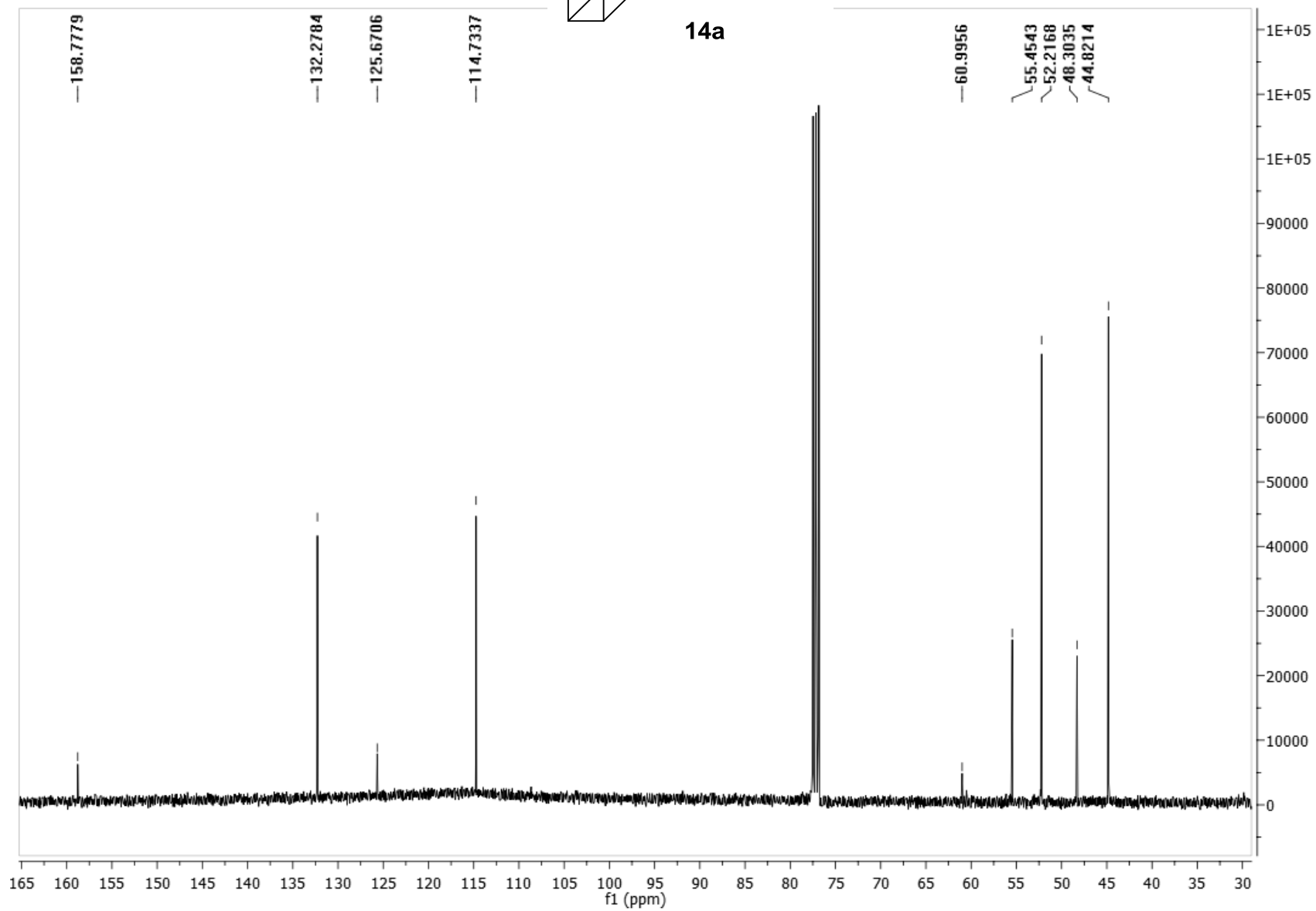
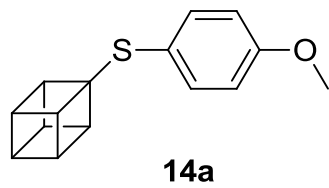


# Cuban-1-yl(4-methoxyphenyl)sulfane (14a)

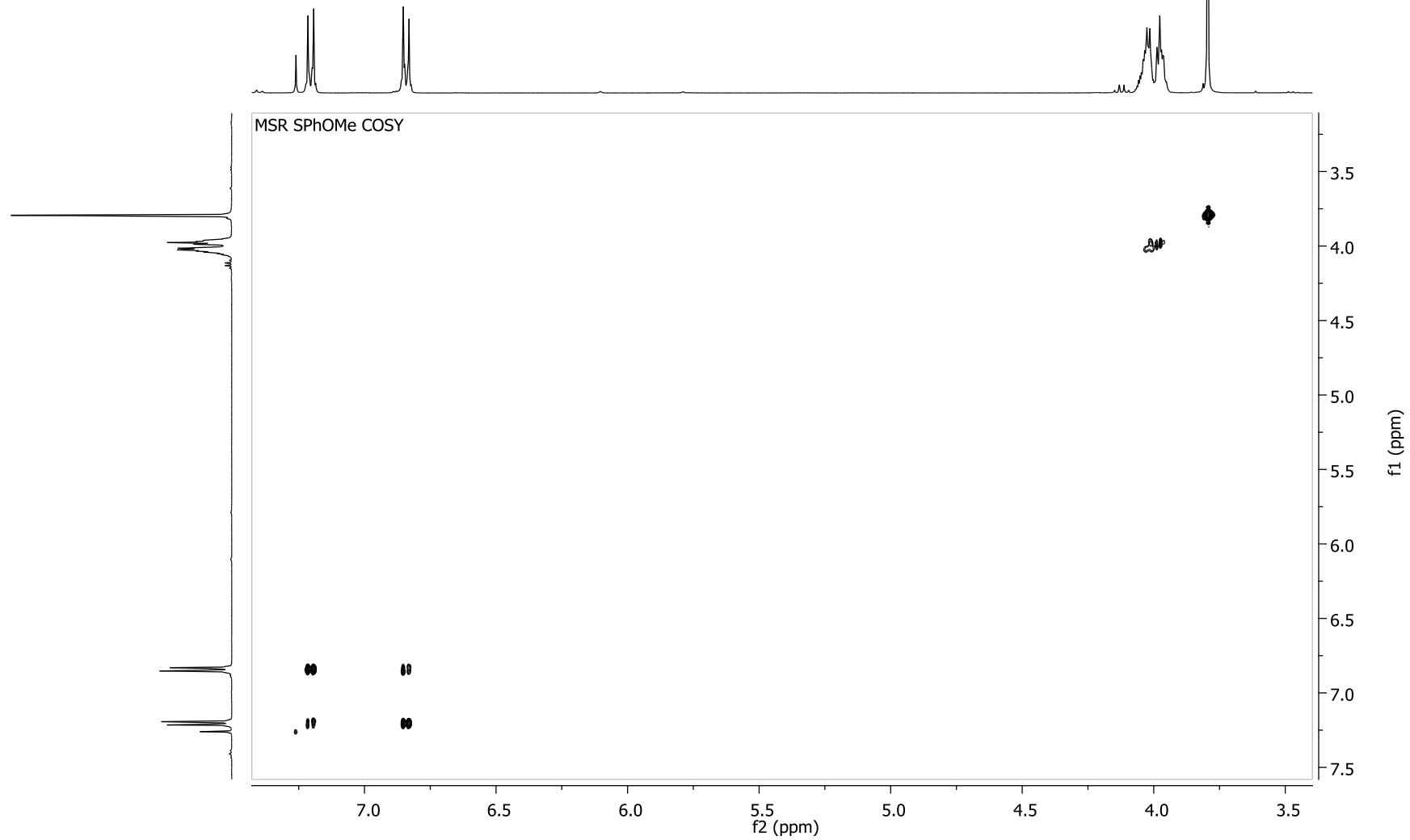
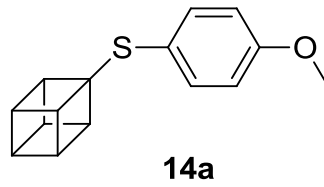
<sup>1</sup>H- NMR (400 MHz, chloroform-*d*)



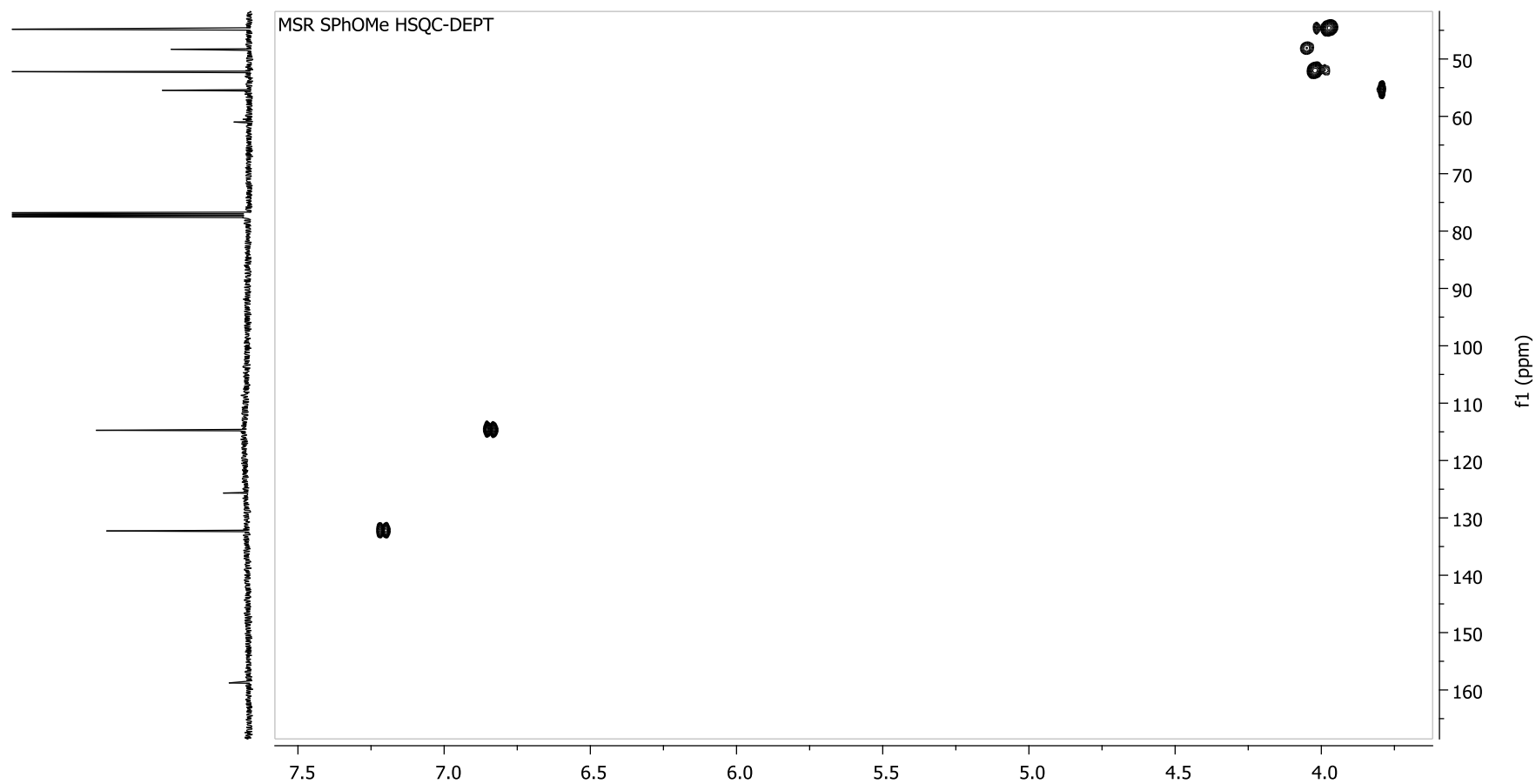
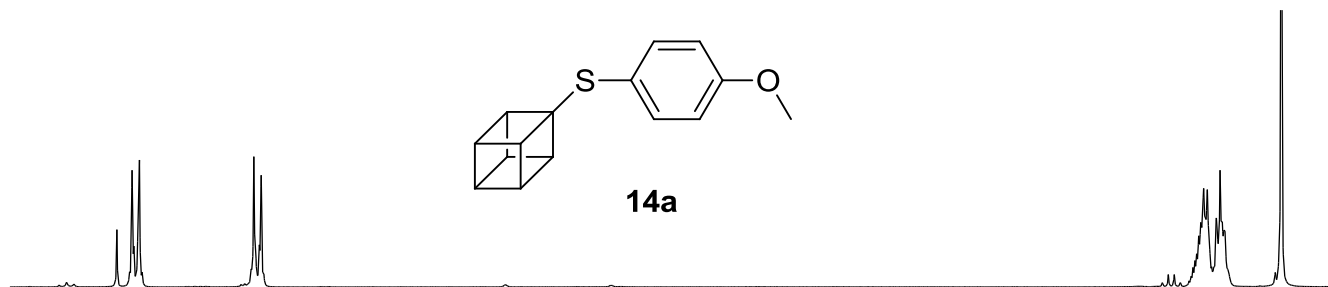
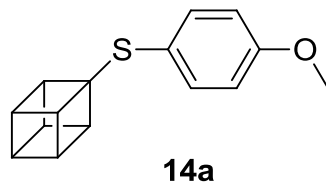
<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)



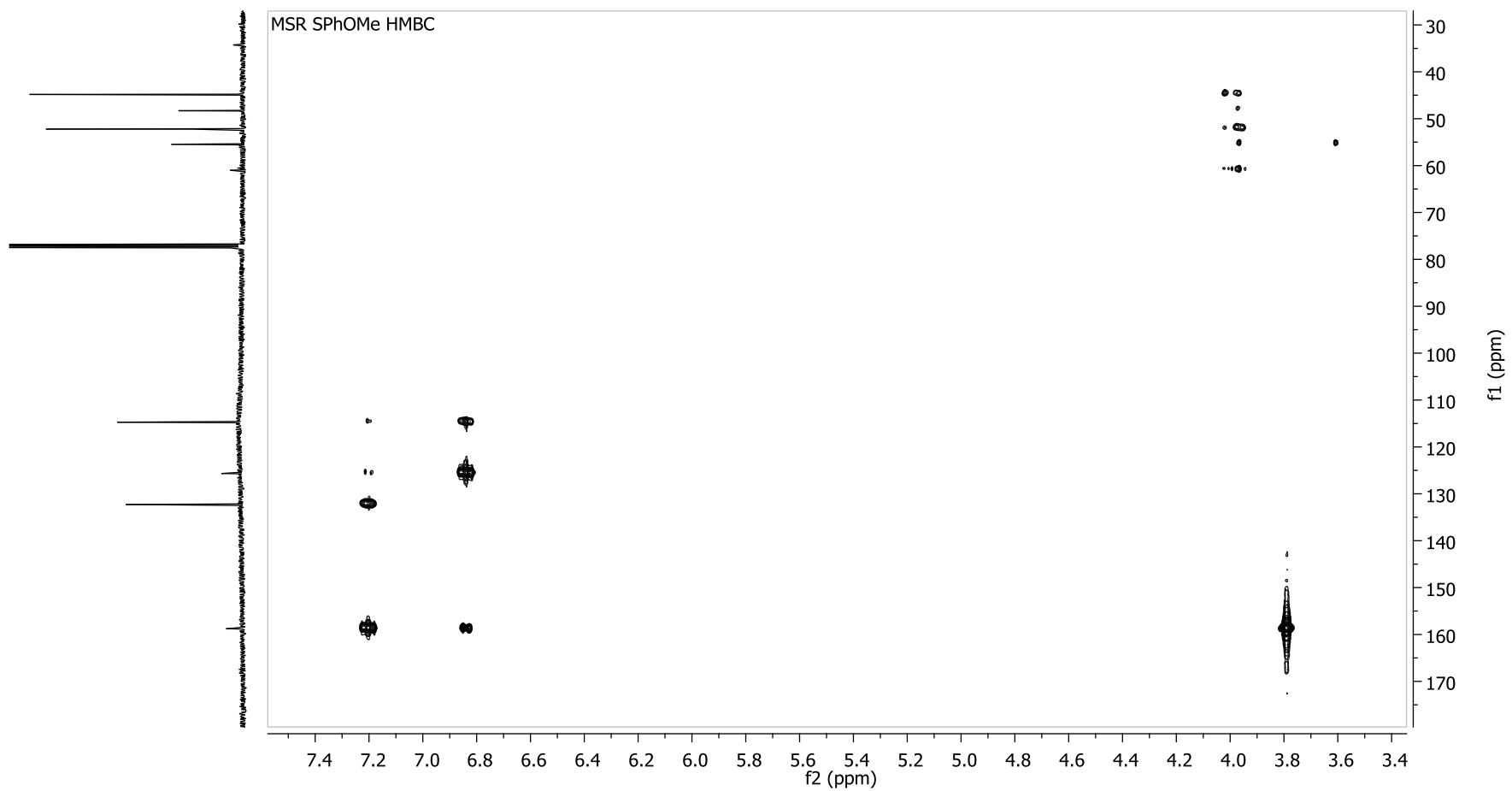
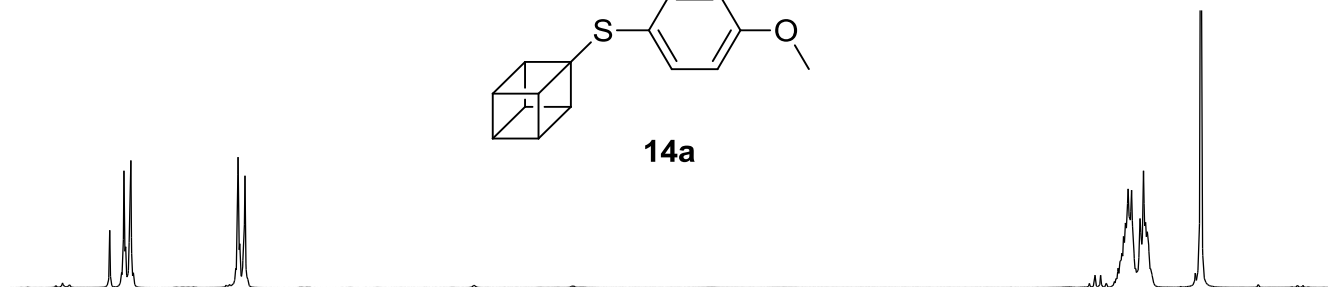
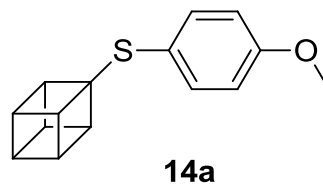
COSY (chloroform-*d*)



HSQC-DEPT (chloroform-*d*)

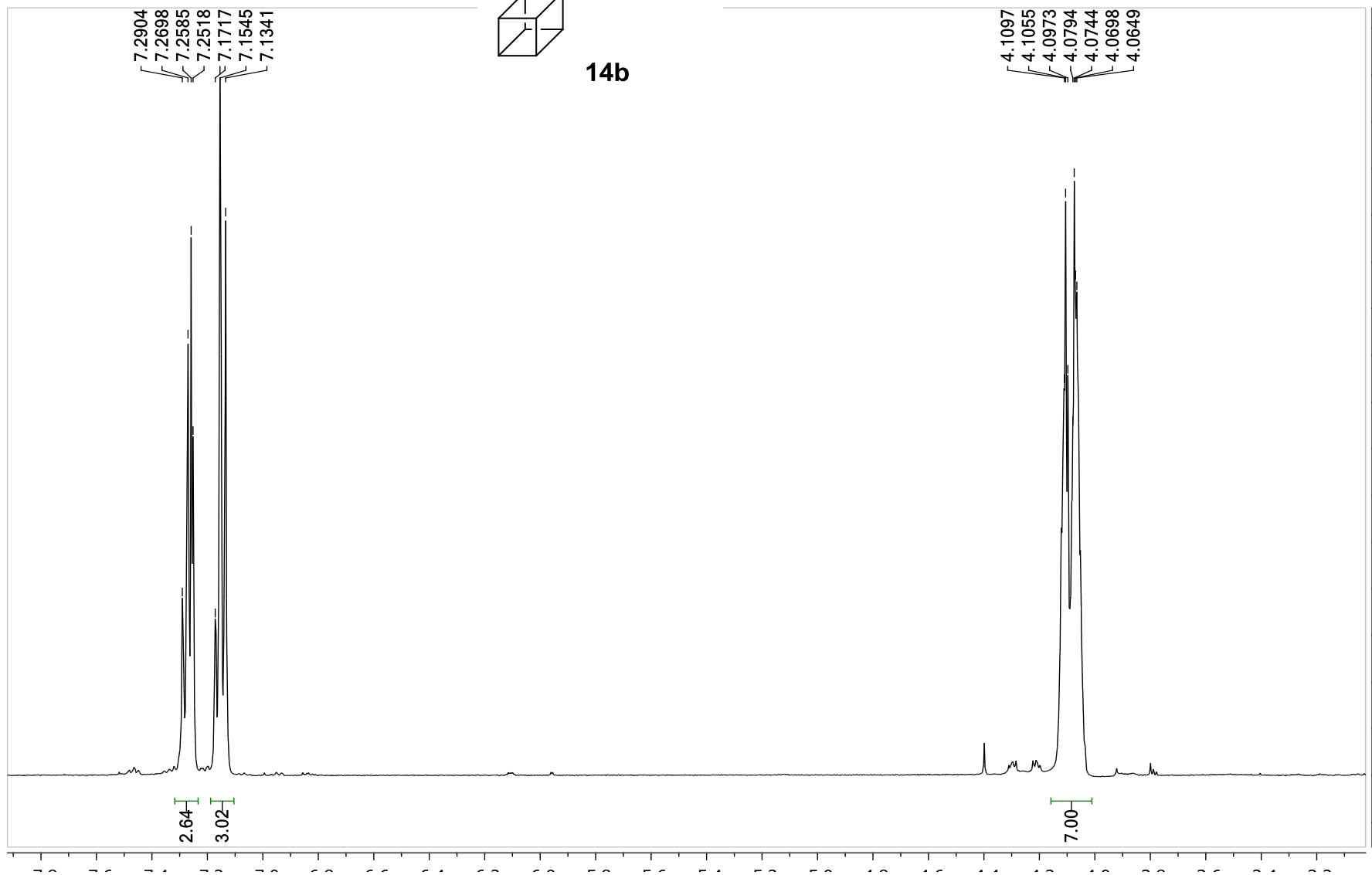
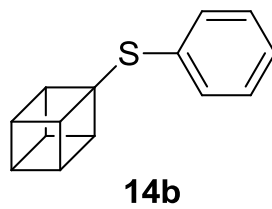


HMBC (chloroform-*d*)



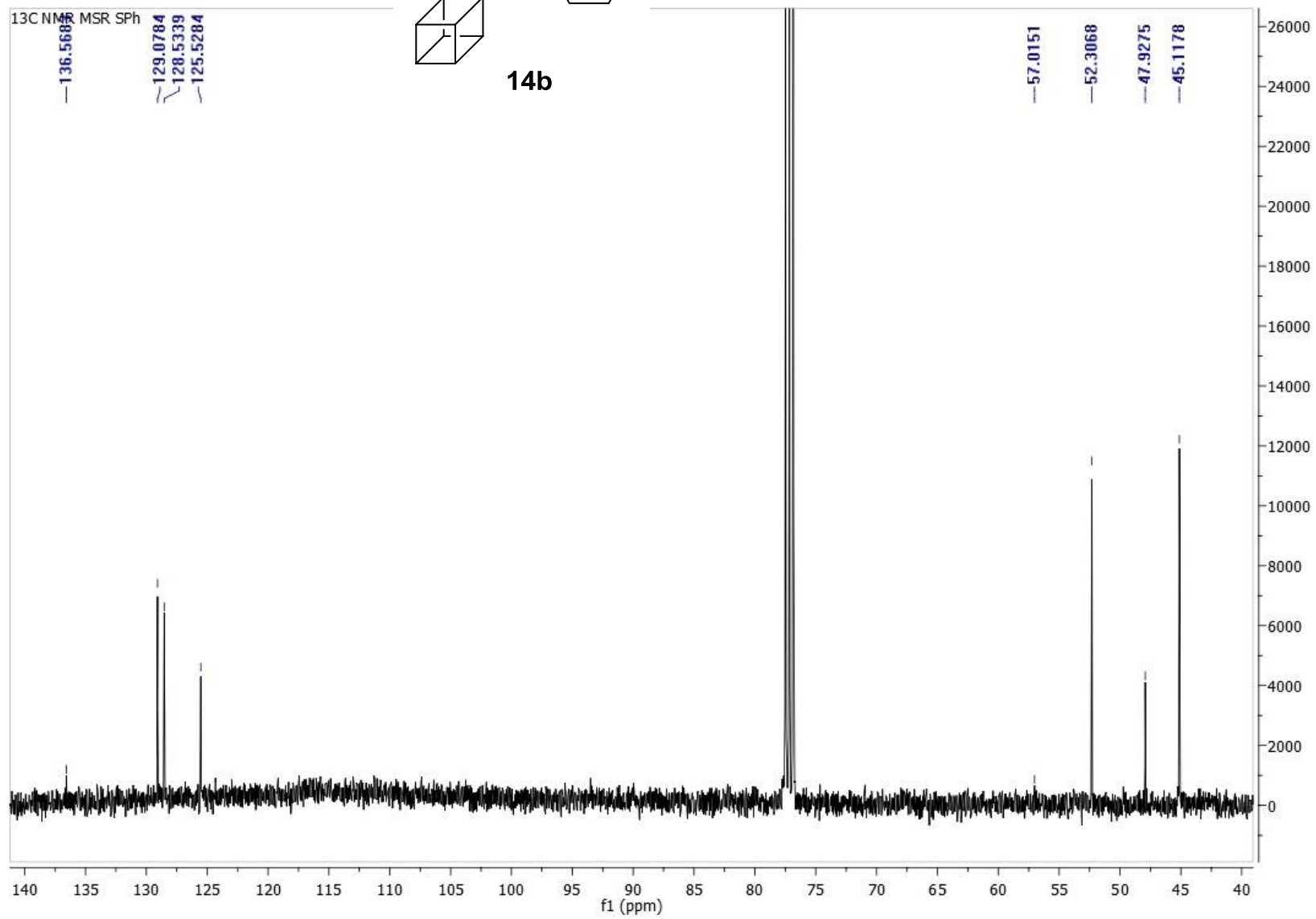
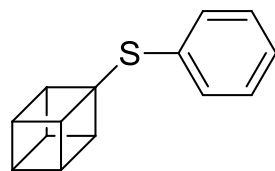
**Cuban-1-yl(phenyl)sulfane (14b)**

**<sup>1</sup>H- NMR (400 MHz, chloroform-*d*)**



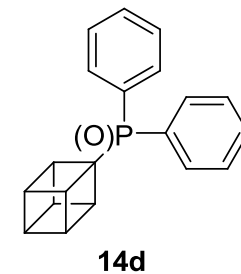
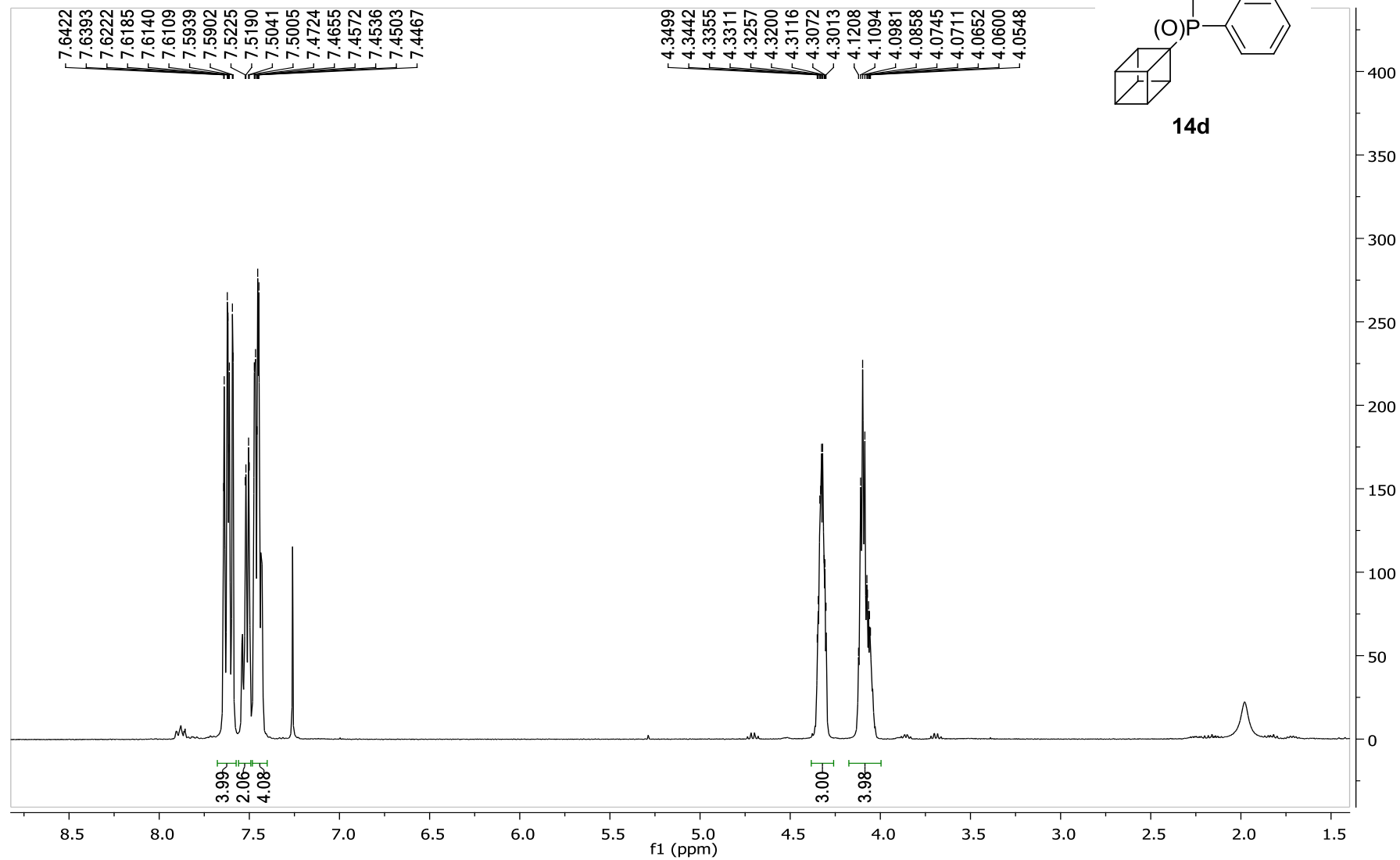


<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)

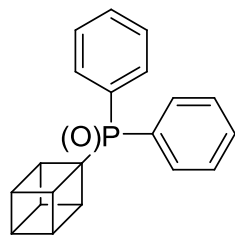


# Cuban-1-yl diphenylphosphine oxide (14d)

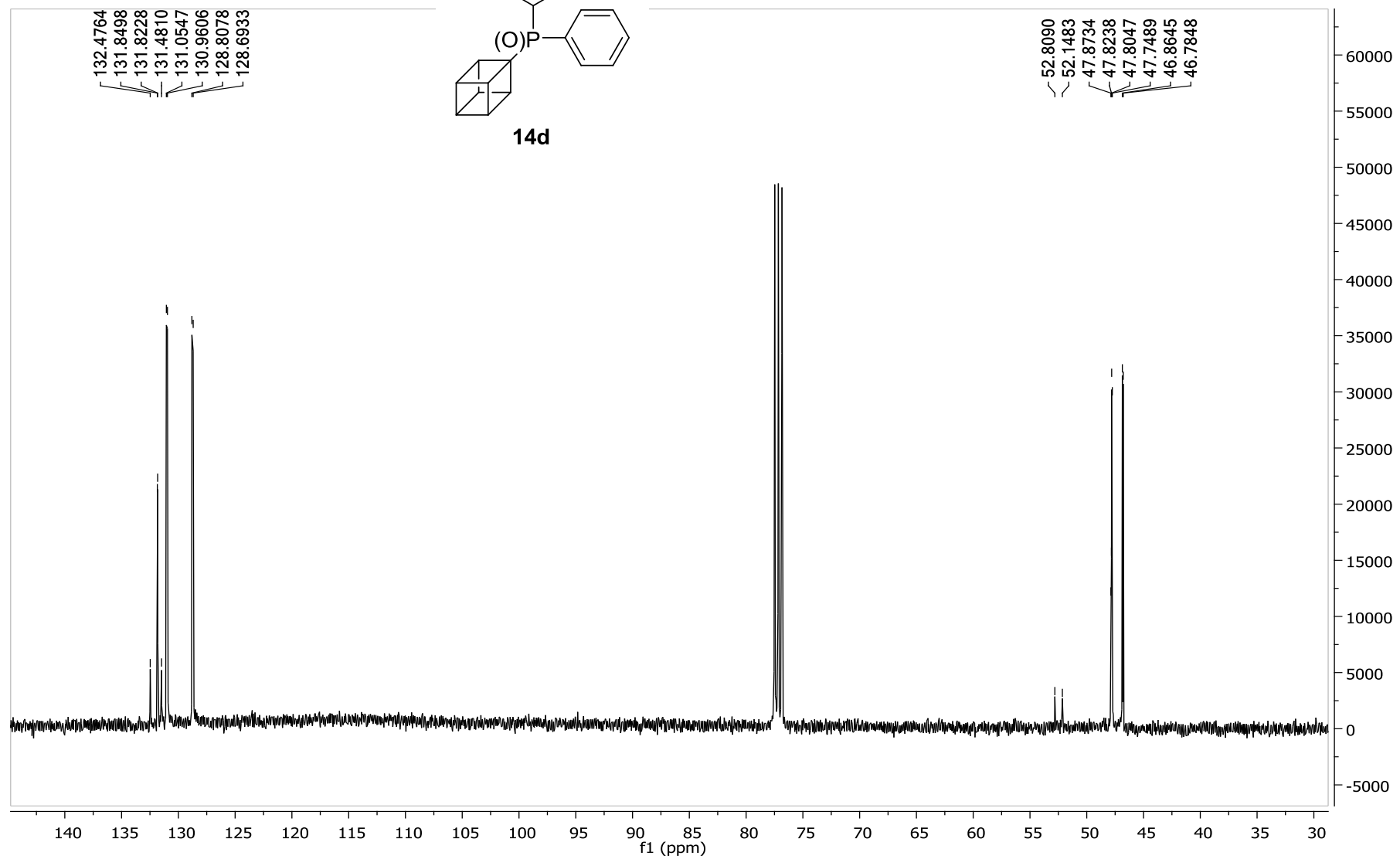
$^1\text{H}$ -NMR (400 MHz, chloroform-*d*)



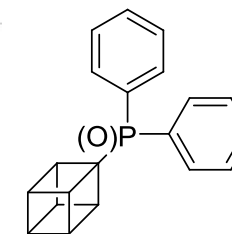
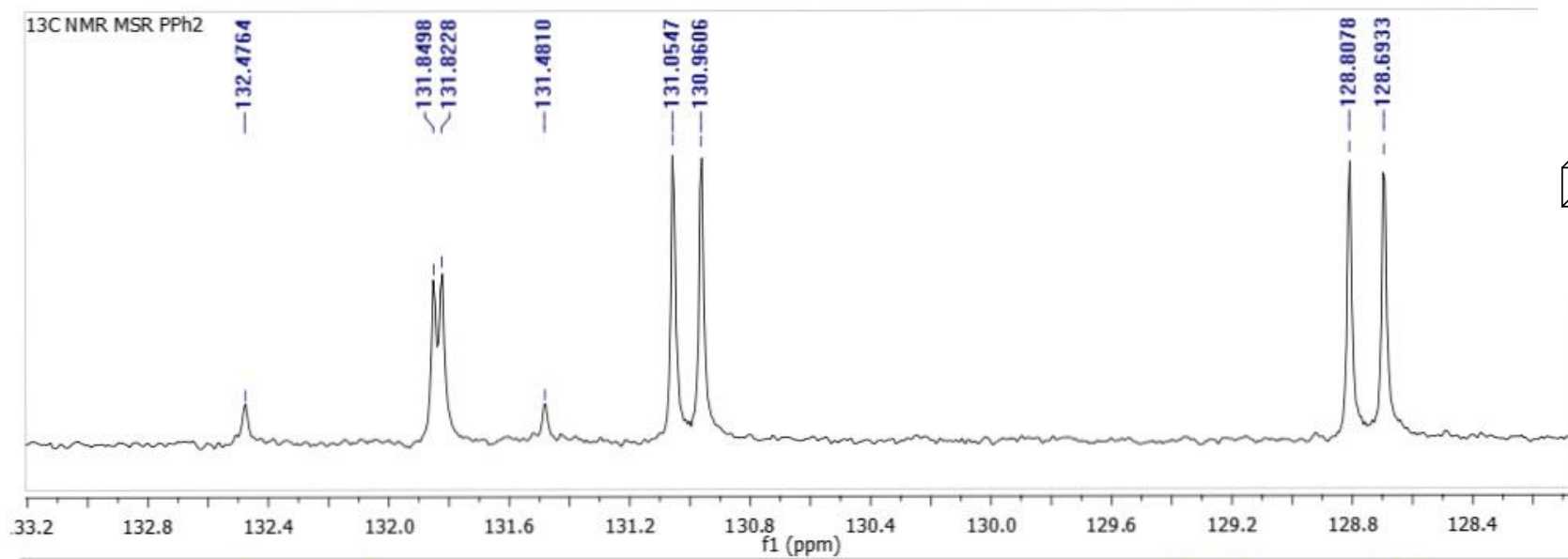
<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)



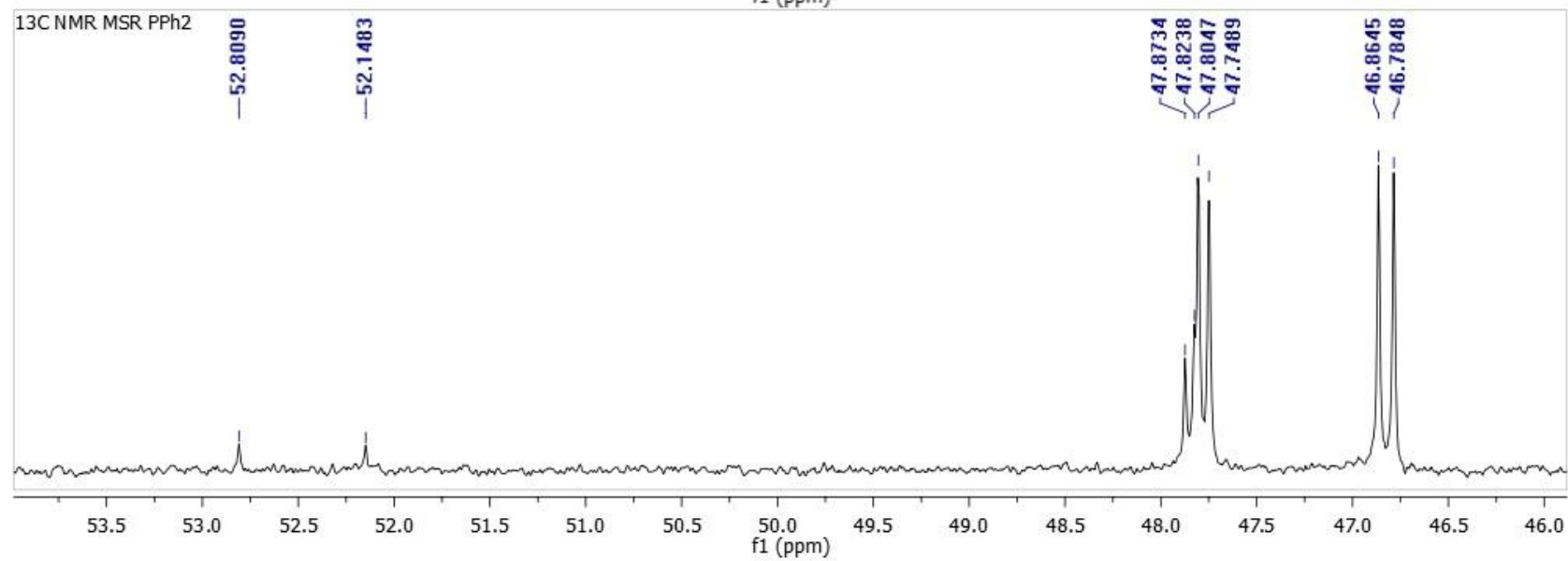
14d



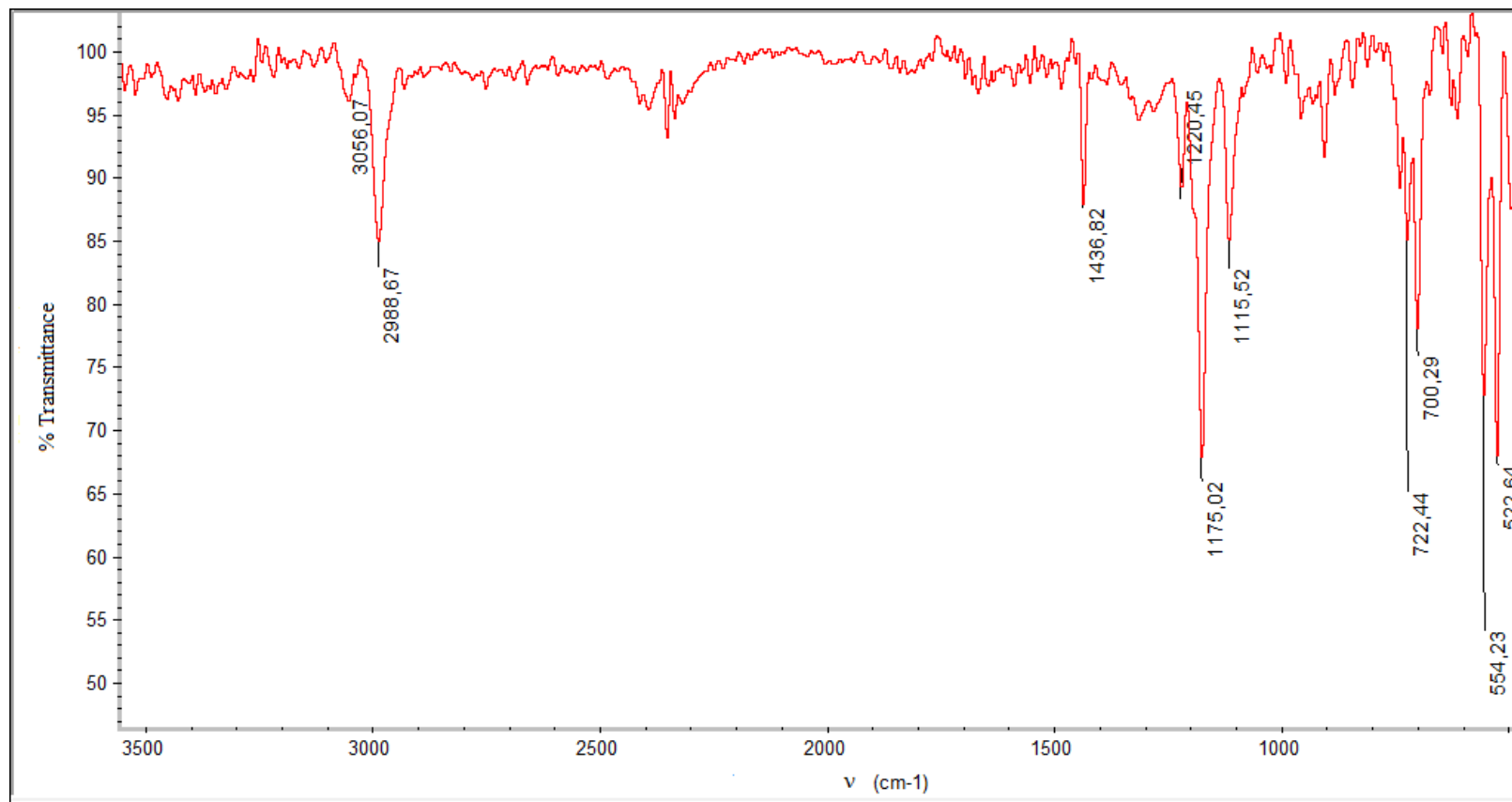
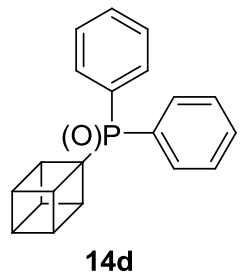
<sup>13</sup>C-NMR (100 MHz, chloroform-*d*)



**14d**



# IR



### 3. Computational Information

#### 3.1 Test of different solvent's models

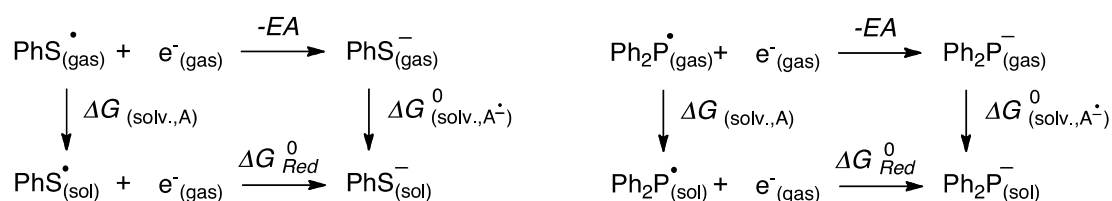
Since the reactions were carried out in liquid ammonia but this solvent was not available in g09, the solvent employed was methanol (as in previous works from the group). To check the differences arisen from different solvent approximations the energies of 3 molecules were computed with methanol, DMSO and liquid ammonia build using parameters available in literature. (Sieffert, N.; Thakkar, A.; Bühl, M. *Chem. Commun.*, 2018, **54**, 10431-10434; Budén, M. E; Dorn, V.B.; Gamba, M.; Pierini, A.B.; Rossi; R. A. *J. Org. Chem.*, 2010, **75**, 2206-2218).

Almost no differences were observed until the 4<sup>th</sup> decimal of the energy (~0.1 to 0.3 kcal/mol). With this small energy we considered that the results obtained in the study of the mechanism would not significantly change in either (DMSO, NH3, or methanol used instead of NH3)

Molecule	Solvent	SCF Energy	ZPE Corr.	Sum of ee and thermal □G
iodocubanoradical	Methanol	-605.7025463	0.111679	-605.623883
	DMSO	-605.7025935	0.111675	-605.623934
	NH3	-605.7024765	0.111684	-605.623808
15-rad	Methanol	-536.6591589	0.164962	-536.530933
	DMSO	-536.6592657	0.164956	-536.531041
	NH3	-536.6590012	0.164971	-536.530772

#### 3.2 Calculation of the redox potentials of phenylsulphide and diphenylphosphide anions

The overall calculated reaction is presented in the thermodynamic cycle shown in scheme 1 and eq. 1.



scheme 1

In previous works, this equation has been employed for the calculation of reduction.<sup>1-4</sup> In some cases the  $\Delta\Delta G_{(\text{Solv})}^0$  was calculated over the gas phase geometries, in other cases different solvent models were employed to improve its quality and hence the  $\Delta G_{\text{Red}}^0$ . In the present work the  $\Delta G_{\text{Red}}^0$  was directly calculated from the optimized geometries in solvent by employing the IEF-PCM continuum solvation model,<sup>5</sup> including the thermal corrections and the changes in enthalpy and entropy.

$$\Delta E = \Delta G_{(\text{Red})}^0 = -EA + \Delta\Delta G_{(\text{Solv})}^0 \quad (1)$$

Finally, the  $\Delta G_{red}^0$  is related to the redox potential,  $E_{Red}^0$ , by the Faraday's equation (2)

$$E_{Red}^0 = \frac{-\Delta G_{Red}^0}{n F} \quad (2)$$

where  $n$  is the number of electrons transferred (in this case is equal to 1) and  $F$  is the Faraday constant (96485 C mol<sup>-1</sup> or 23.061 kcal mol<sup>-1</sup> V<sup>-1</sup>).

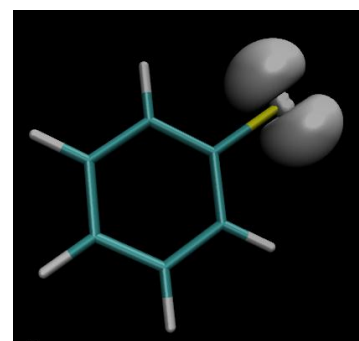
According to these equations, the Redox potential of both molecules was calculated:

Molecule	Electronic Energy (hartree)	ZPE Correction (hartree)	$\Delta G^0 + ZPE$ (hartree)	$\Delta G^0_{(red)}$ (kcal/mol)	$E^0_{red}$ (V)
PhS <sup>•</sup>	-629.6816788	0.090641	-629.621524		
PhS <sup>-</sup>	-629.8680842	0.09096	-629.806921	-116.338	~5.05
Ph <sub>2</sub> P <sup>•</sup>	-804.4192103	0.182964	-804.275287		
Ph <sub>2</sub> P <sup>-</sup>	-804.5510342	0.182091	-804.406905	-82.591	~3.58
Method: M062X/def2TZVP – PCM: methanol					

### Geometries. Spin densities of radicalary species:

#### PhS<sup>•</sup> (radical)

C	-1.444035094526	1.318789519713	-0.036036930195
C	-0.051375692512	1.311955486295	-0.035550753254
C	0.639497963100	2.522649003509	-0.036083494537
C	-0.051264232651	3.733405937645	-0.037099153054
C	-1.443924330165	3.726699608243	-0.037571706583
C	-2.144688423749	2.522776659088	-0.037044008851
H	-1.977359938134	0.379207521172	-0.035623674105
H	0.485666821540	0.373744783189	-0.034758893870
H	0.485866044717	4.671566783848	-0.037527003522
H	-1.977162370089	4.666330631850	-0.038356357947
H	-3.224486895331	2.522825927394	-0.037412261598
S	2.456870727801	2.522566748055	-0.035441172485



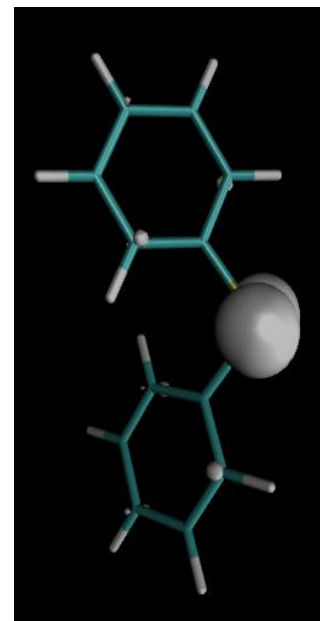
#### PhS<sup>-</sup> (anion)

C	-1.449389385640	1.321980547058	-0.036041429827
C	-0.056597265234	1.322902023100	-0.035552946870
C	0.674975060683	2.522647438050	-0.036065525356
C	-0.056486706288	3.722459947957	-0.037097438311
C	-1.449278846116	3.723509139815	-0.037570306870
C	-2.159120419136	2.522777322472	-0.037048694248
H	-1.980858736711	0.379533935875	-0.035635673038
H	0.481350075112	0.384651121853	-0.034766240143
H	0.481549806580	4.660660052191	-0.037534460315
H	-1.980661706514	4.666004276583	-0.038349085301
H	-3.239657209479	2.522826479787	-0.037415637952
S	2.487779912742	2.522566325258	-0.035427971771

#### Ph<sub>2</sub>P<sup>•</sup>

P	1.034921427728	1.059632864399	0.032440693934
C	-0.113715728954	2.478109958523	-0.260713690547

C	-1.373642491491	2.609285251139	0.341271136960
C	0.367838812084	3.527712809825	-1.056882562387
C	-2.136962271874	3.753864857544	0.133306701629
H	-1.753772331784	1.822500150571	0.978100265882
C	-0.399549919750	4.668221971335	-1.268493161214
H	1.344585930266	3.445238372685	-1.516194287456
C	-1.655016023824	4.783730176873	-0.673982947843
H	-3.105126296187	3.845141999647	0.604984156811
H	-0.018663560925	5.464583077609	-1.891618910159
H	-2.250954926517	5.670714063951	-0.834271123066
C	-0.101820057556	-0.375002609689	0.291222450011
C	0.376333661449	-1.423375412061	1.091231843267
C	-1.346794312377	-0.518893876636	-0.338348900187
C	-0.380378636545	-2.574952465485	1.279667576236
H	1.341974002627	-1.331259450436	1.571751202693
C	-2.099422786895	-1.674438150323	-0.153303581231
H	-1.723565870578	0.266565026007	-0.978740290306
C	-1.621315868876	-2.703093425210	0.657785612210
H	-0.002313051279	-3.370252037855	1.905865217513
H	-3.056093860932	-1.775098058917	-0.646021756976
H	-2.208704387809	-3.598872493497	0.799604864225



### Ph<sub>2</sub>P<sup>-</sup>

P	1.041592252280	1.055809789045	0.014801407785
C	-0.112927529885	2.485423452075	-0.288706804885
C	-1.400113143847	2.628046810623	0.265100810109
C	0.377131989662	3.570167234260	-1.043223042657
C	-2.155251299128	3.780632050307	0.063055406863
H	-1.808806222626	1.831299475695	0.872393117918
C	-0.368896286858	4.729271320389	-1.232507531536
H	1.360023791707	3.490867872363	-1.492370882703
C	-1.647881185096	4.843336799967	-0.685720822413
H	-3.141550353665	3.854867206214	0.502891262538
H	0.044282891924	5.541532152351	-1.816224998021
H	-2.233779312506	5.738678178083	-0.838281092836
C	-0.101674566898	-0.386030235897	0.304347429572
C	0.384185028471	-1.459425920934	1.077218019553
C	-1.374180480116	-0.547897865158	-0.277590029356
C	-0.352062788073	-2.626311145731	1.257739006855
H	1.355564888817	-1.365178801219	1.547983127234
C	-2.120007526720	-1.707957948536	-0.084392519722
H	-1.777890322602	0.239821702942	-0.899872640881
C	-1.616822604164	-2.759395842440	0.683045114321
H	0.057312265691	-3.429547479823	1.856367469048
H	-3.095164365464	-1.797180322813	-0.545825311718
H	-2.195243670906	-3.660765881762	0.828434014934

### 3.3 Hypothetical mechanism involving formation of 1,4-dehydrocubane A

We propose that 1,4-diiodocubane **2** receives an electron from the nucleophile (ArS<sup>-</sup>/Ph<sub>2</sub>P<sup>-</sup>) in a photoinduced process through a dissociative-ET pathway leading directly to 4-iodocubyl radical **17**. This intermediate can afford 1,4-dehydrocubane **A** by homolytic dissociation (with formation of iodine radicals) or by ET (with formation of iodide ions). Another possibility is its reaction with the anion, which is in excess, to afford the radical anion of the mono-iodosubstituted cubane **13** (Scheme 1-SI). Calculations indicated that the preferred reaction is the coupling with the



nucleophile to allow a typical  $S_{RN}1$  pathway. Relevant energetic factors ( $\Delta G^\circ$ ) of the three mechanistic possibilities are presented in the next Table 1-SI.<sup>6,7</sup>

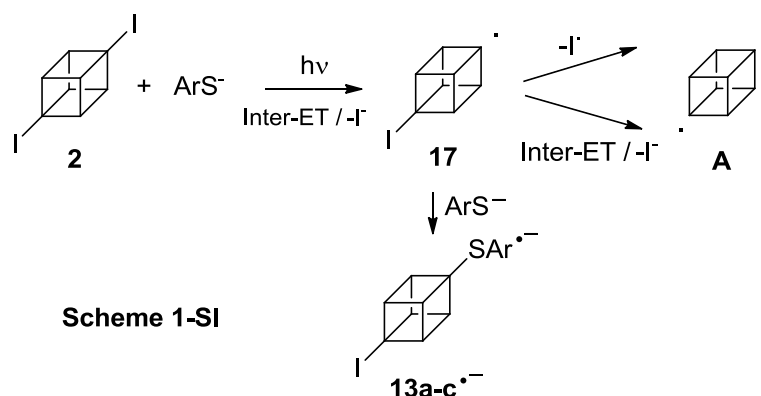


Table 1-SI. Energetic values involved in reactions shown at Scheme 1-SI

Reaction				$\Delta G^\circ$ (kcal/mol) (298 K)
				<b>53.656</b>
Compounds	Electronic Energy (hartrees)	ZPE (hartrees)	$\Delta G+ZPE$ (hartrees)	
4-Iodocubyl radical, <b>17</b>	-605.7025463	0.111679	-605.623883	
1-4 dehydrocubane diradical, <b>A</b>	-307.9851116	0.077481	-307.907631	
Iodide radical	-297.6132423	0.000000	-297.630745	
Reaction				$\Delta G^\circ$ (kcal/mol) (298 K)
				<b>41.822</b>
Compounds	Electronic Energy (hartrees)	ZPE (hartrees)	$\Delta G+ZPE$ (hartrees)	
4-Iodocubyl radical, <b>17</b>	-605.7025463	0.111679	-605.623883	
Thiophenoxide anion, <b>4<sup>-</sup></b>	-629.8680842	0.09096	-629.806921	
1-4 dehydrocubane diradical, <b>A</b>	-307.9851116	0.077481	-307.907631	
Iodide anion	-297.8181529	0.000000	-297.835001	
Thiophenyl radical, <b>4<sup>·</sup></b>	-629.6816788	0.090641	-629.621524	
Reaction				$\Delta G^\circ$ (kcal/mol) (298 K)
				<b>11.0</b>
Compounds	Electronic Energy (hartrees)	ZPE (hartrees)	$\Delta G+ZPE$ (hartrees)	

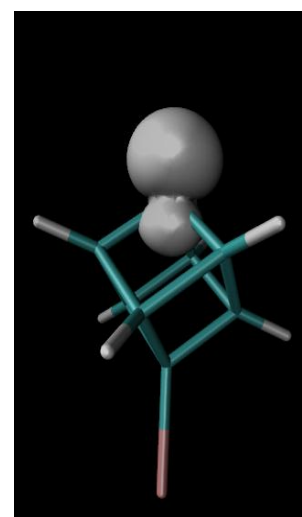
4-Iodocubyl radical, <b>17</b>	-605.7025463	0.111679	-605.623883	
Thiophenoxide anion, <b>4<sup>-</sup></b>	-629.8680842	0.09096	-629.806921	
4-iodocubyl-phenylsulfide radical anion, <b>13b<sup>-</sup></b>	-1235.5546359	0.202085	-1235.397200	
TS for the coupling	-1235.5476664	0.201420	-1235.391243	24.825 (Activation Energy)

All the calculations were performed with the Gaussian09 program,<sup>8</sup> the M06-2X DFT functional and the def2TZV basis set for C, H, O, S and P were employed. The def2TZVP<sup>9</sup> basis set and pseudo-potential was used for I. Calculations were performed with full geometry optimization including in all cases the effect of the solvent (methanol as polar solvent) through the Tomasi's polarized continuum model (IEFPCM)<sup>5,10</sup> as implemented in the Gaussian package. After refinement the characterization of stationary points was done by Hessian matrix calculations, with all positive eigenvalues for a minimum and only one negative eigenvalue for the TSs. The energy informed for TSs and radicals includes zero-point corrections.

Geometries:

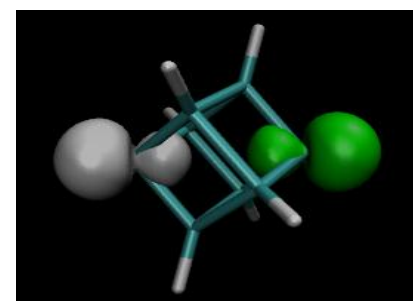
4-Iodocubyl radical, **17**

C	-0.014345381477	-0.014648103207	-0.014015286728
C	-0.005284423796	-0.005322099047	1.556420974340
C	1.570938211811	-0.007604415900	1.522880294516
C	1.555668188226	-0.011751256001	-0.053607207463
C	1.527210130492	1.563919039645	-0.098699814437
C	-0.048706777697	1.555034262158	-0.053658063307
C	-0.044915416095	1.570394609689	1.522842072205
C	1.518914870821	1.555417645645	1.466205843640
I	-1.232703670740	-1.263086986913	-1.190015814411
H	-0.620080820437	-0.634870728982	2.186070440799
H	2.129164186334	2.180378297153	-0.752199292284
H	2.207435560399	-0.624505889030	2.142328411990
H	-0.676809870119	2.192035548328	2.142267295812
H	-0.697620557750	2.147489526206	-0.685087489113
H	2.163401385395	-0.646371878440	-0.685028744015



1,4-dehydrocubane diradical, **A**

C	-0.014345381477	-0.014648103207	-0.014015286728
C	-0.005284423796	-0.005322099047	1.556420974340
C	1.570938211811	-0.007604415900	1.522880294516
C	1.555668188226	-0.011751256001	-0.053607207463
C	1.527210130492	1.563919039645	-0.098699814437
C	-0.048706777697	1.555034262158	-0.053658063307
C	-0.044915416095	1.570394609689	1.522842072205
C	1.518914870821	1.555417645645	1.466205843640
I	-1.232703670740	-1.263086986913	-1.190015814411
H	-0.620080820437	-0.634870728982	2.186070440799
H	2.129164186334	2.180378297153	-0.752199292284
H	2.207435560399	-0.624505889030	2.142328411990
H	-0.676809870119	2.192035548328	2.142267295812
H	-0.697620557750	2.147489526206	-0.685087489113
H	2.163401385395	-0.646371878440	-0.685028744015



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### 3.4 Calculations involved in Schemes 4 and 5

#### 3.4.1 Cartesian coordinates and energies (au) at PCM(methanol)-[M06-2X/def2-TZVP]. Spin densities of radicalary species. Imaginary frequencies of Transition States.

I<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -297.818216336

1

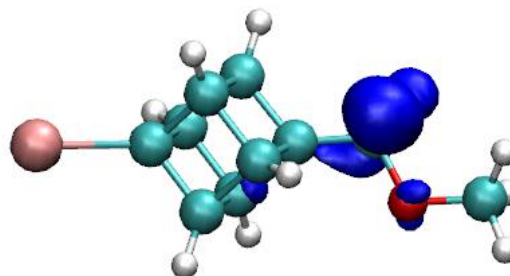
E (PCM(methanol)-[M06-2X/def2-TZVP])= -834.375006343

C	-0.842921	0.039270	0.000572
C	-0.016382	0.777171	-1.087925
C	0.829035	1.449674	0.039020
C	1.816091	0.255589	0.001191
C	0.973797	-0.499235	1.083013
C	-0.009943	0.709386	1.127832
C	0.129349	-1.172471	-0.039534
C	0.967885	-0.431247	-1.122906
H	1.395088	-1.004410	1.945455
H	-0.427500	1.278961	-1.956812
H	-0.415349	1.157082	2.028385
H	1.121419	2.493741	0.069660
H	1.384742	-0.881797	-2.017163
H	-0.166913	-2.215062	-0.071068
C	3.293718	0.350749	0.000055
O	3.927038	1.377435	-0.000804
O	3.855037	-0.860501	-0.000463
C	5.285004	-0.891206	0.000228
H	5.672579	-0.396937	-0.889046
H	5.671153	-0.394878	0.889020
H	5.559512	-1.941097	0.001771
I	-2.954814	-0.108626	0.000012

I<sup>•</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -834.419503826

C	-0.833862	0.045533	0.014886
C	-0.031674	1.213529	-0.615357
C	0.842727	1.269391	0.677178
C	1.835989	0.233211	0.076504
C	0.997722	-0.931553	0.677676
C	0.016943	0.105182	1.311215
C	0.125695	-0.995673	-0.616210
C	0.934812	0.172257	-1.251113
H	1.422821	-1.790192	1.189332
H	-0.468753	2.070291	-1.118559
H	-0.383704	0.078437	2.319416
H	1.143869	2.179517	1.188120

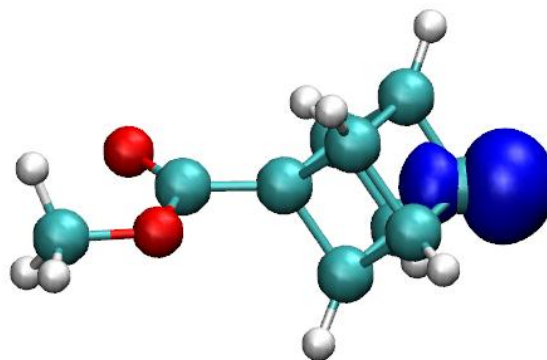


H	1.300582	0.198863	-2.273334
H	-0.186852	-1.903409	-1.122446
C	3.297738	0.368931	0.188075
O	3.897896	1.451065	-0.136092
O	3.892960	-0.870190	-0.206650
C	5.271480	-0.932650	0.050290
H	5.821130	-0.163694	-0.496717
H	5.472226	-0.799903	1.122116
H	5.622436	-1.917319	-0.259254
I	-2.958793	-0.111104	-0.016709

### 15•

E (PCM(methanol)-[M06-2X/def2-TZVP])= -536.659167544

C	2.626399	-0.320808	0.000431
C	1.915106	0.466606	1.118990
C	1.164723	1.266981	0.005177
C	0.057926	0.183732	-0.000136
C	0.807720	-0.624150	-1.111108
C	1.917484	0.475490	-1.113309
C	1.555446	-1.431185	-0.005150
C	0.805388	-0.632995	1.105611
H	0.329827	-1.046074	-1.989877
H	2.353444	0.897826	2.012967
H	2.357804	0.913811	-2.002850
H	0.981653	2.336837	0.009150
H	0.325641	-1.062027	1.979912
H	1.712240	-2.504659	-0.009289
C	-1.399667	0.440217	-0.000270
O	-1.917271	1.529824	-0.000127
O	-2.091646	-0.702208	-0.000420
C	-3.516120	-0.573266	0.000261
H	-3.844230	-0.036985	0.889123
H	-3.845246	-0.037545	-0.888560
H	-3.906223	-1.585850	0.000818



### PhS<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -629.954663140

C	-0.580831	0.000001	0.000024
C	0.160880	-1.194996	0.000003
C	0.160880	1.194996	0.000003
C	1.548483	-1.195343	0.000002
H	-0.374823	-2.137034	-0.000005
C	1.548485	1.195342	0.000002
H	-0.374820	2.137036	-0.000005
C	2.259241	0.000000	0.000006
H	2.079707	-2.140269	-0.000004

H	2.079709	2.140268	-0.000004
H	3.341416	-0.000002	0.000004
S	-2.333375	0.000000	-0.000014

**Ph<sub>2</sub>P<sup>-</sup>**

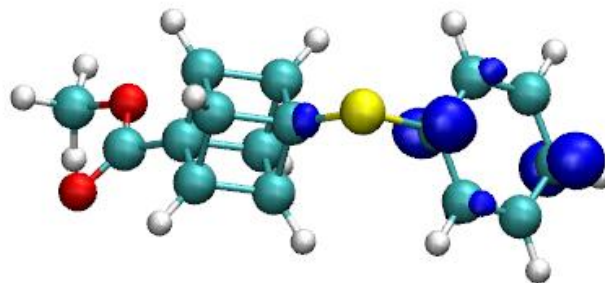
E (PCM(methanol)-[M06-2X/def2-TZVP])= -804.712954471

P	-0.000070	-1.618637	0.000344
C	-1.439373	-0.501883	-0.016730
C	-2.661345	-0.988224	0.486791
C	-1.476465	0.779453	-0.596968
C	-3.835036	-0.252444	0.414152
H	-2.681974	-1.969664	0.950110
C	-2.644829	1.524702	-0.654964
H	-0.571775	1.192961	-1.026284
C	-3.839219	1.018367	-0.150953
H	-4.751961	-0.669598	0.814639
H	-2.624990	2.508660	-1.109908
H	-4.750492	1.600553	-0.196816
C	1.439422	-0.502055	0.017076
C	1.476762	0.779116	0.597691
C	2.661057	-0.988157	-0.487392
C	2.645130	1.524360	0.655327
H	0.572272	1.192450	1.027597
C	3.834793	-0.252369	-0.415126
H	2.681435	-1.969397	-0.951144
C	3.839262	1.018197	0.150478
H	2.625545	2.508165	1.110609
H	4.751498	-0.669347	-0.816298
H	4.750546	1.600392	0.196044

**8<sup>-</sup>**

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1166.61393893

C	-4.573523	1.928233	0.387639
C	-4.096895	1.653551	-0.925148
C	-3.337870	0.545083	-1.197936
C	-2.999992	-0.403081	-0.167073
C	-3.445310	-0.090344	1.167162
C	-4.203075	1.023162	1.421944
S	-1.943806	-1.743388	-0.478954
C	-0.293669	-1.082898	-0.223641
C	0.249220	-0.463727	1.103665
C	1.538779	-1.334856	0.974273
C	2.216019	-0.199134	0.166608
C	1.669391	-0.800588	-1.171616
C	1.000523	-1.947661	-0.356168
C	0.381986	0.066605	-1.040454

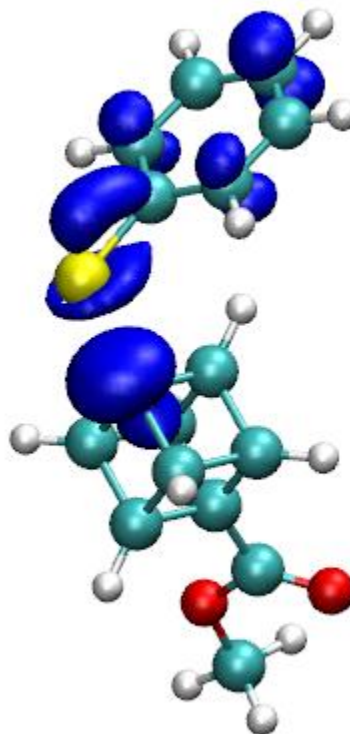


C	0.922087	0.677947	0.284996
H	2.268431	-0.921375	-2.069289
H	-0.338493	-0.326512	2.006522
H	1.018473	-3.001103	-0.620797
H	2.021260	-1.883400	1.777476
H	0.924515	1.732229	0.544712
H	-0.098997	0.619033	-1.842103
H	-2.989104	0.363770	-2.209585
H	-3.179543	-0.761315	1.977779
H	-4.339245	2.334245	-1.735733
H	-4.529214	1.212289	2.440349
H	-5.158298	2.812701	0.599567
C	3.591596	0.304960	0.366722
O	4.366878	-0.085535	1.206167
O	3.889347	1.271455	-0.508215
C	5.197646	1.836065	-0.398739
H	5.330610	2.292255	0.580977
H	5.954146	1.066712	-0.544510
H	5.265073	2.587421	-1.179122

### 8-TS<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1166.60040615 Neg-Freq= -270.3

C	-4.608566	1.474490	1.157768
C	-4.241819	1.812749	-0.151198
C	-3.551465	0.926829	-0.952914
C	-3.185859	-0.371195	-0.492539
C	-3.572130	-0.692790	0.840934
C	-4.261991	0.203788	1.632061
S	-2.203483	-1.420149	-1.426290
C	-0.123410	-0.892731	-0.844382
C	0.018940	0.296988	0.140509
C	1.047774	-0.527088	0.979489
C	2.192334	0.044751	0.106624
C	2.050278	-1.146483	-0.900269
C	0.904288	-1.723199	-0.014552
C	1.025876	-0.319901	-1.731904
C	1.169426	0.873889	-0.741611
H	2.898900	-1.700734	-1.295182
H	-0.812147	0.870892	0.547146
H	0.804720	-2.768348	0.272026
H	1.087323	-0.591905	2.064262
H	1.320145	1.918239	-1.005321
H	1.018898	-0.239637	-2.816891
H	-3.271118	1.216609	-1.959276
H	-3.308999	-1.667785	1.235171
H	-4.500084	2.789629	-0.545968



H	-4.535849	-0.085732	2.641036
H	-5.148785	2.173163	1.782273
C	3.483840	0.567661	0.595156
O	3.838264	0.610614	1.749278
O	4.246243	1.004372	-0.415316
C	5.521514	1.538128	-0.055723
H	5.399556	2.394649	0.605575
H	6.122388	0.779493	0.443433
H	5.990649	1.841774	-0.986281

## 8

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1166.56808560

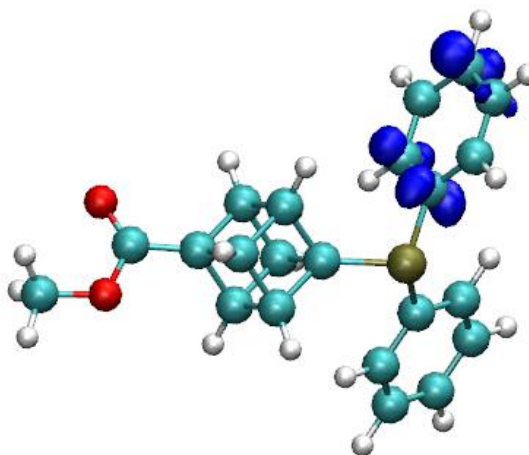
C	-4.428077	1.950033	0.367756
C	-3.996377	1.678151	-0.924109
C	-3.246435	0.538363	-1.182306
C	-2.923657	-0.333067	-0.145067
C	-3.360882	-0.060848	1.148755
C	-4.110448	1.079868	1.402919
S	-1.949251	-1.787245	-0.470114
C	-0.335650	-1.090930	-0.212103
C	0.204652	-0.462791	1.110811
C	1.494587	-1.332951	0.985372
C	2.169637	-0.203168	0.166977
C	1.622671	-0.817423	-1.164859
C	0.955379	-1.957134	-0.338724
C	0.334909	0.050166	-1.041550
C	0.874018	0.671813	0.279506
H	2.215449	-0.949509	-2.064001
H	-0.378053	-0.318646	2.015334
H	0.970078	-3.011860	-0.593855
H	1.974173	-1.877085	1.792157
H	0.868955	1.727681	0.529726
H	-0.144197	0.595427	-1.848587
H	-2.911615	0.318057	-2.188013
H	-3.115952	-0.745577	1.950782
H	-4.244831	2.351663	-1.734118
H	-4.448730	1.286480	2.410127
H	-5.014120	2.837708	0.568098
C	3.545687	0.304829	0.364654
O	4.314131	-0.073272	1.214846
O	3.845285	1.255394	-0.524777
C	5.154067	1.821950	-0.421429
H	5.286083	2.289063	0.553112
H	5.909947	1.050505	-0.558459
H	5.221008	2.563870	-1.210643



10<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1341.41737877

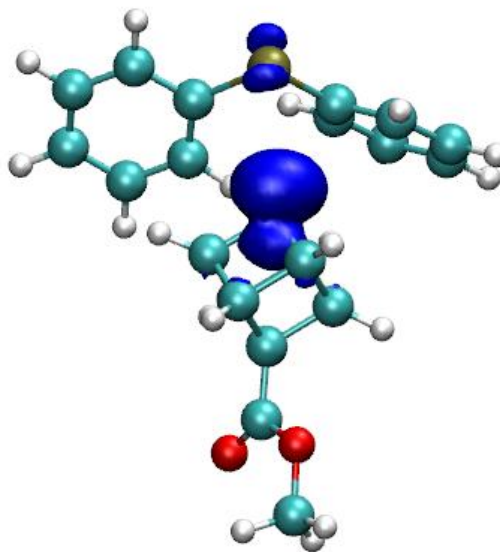
C	-1.557154	0.992353	-0.798798
C	-1.479392	-0.615304	1.379781
C	-2.790167	0.338356	-0.122856
C	-1.006475	1.392934	0.602951
C	-2.240212	0.737585	1.291674
C	-0.228295	0.039899	0.691497
C	-2.031967	-1.025529	-0.016977
C	-0.801626	-0.369219	-0.710496
H	-1.605526	1.639854	-1.669320
H	-1.442303	-1.255328	2.257614
H	-0.578018	2.358023	0.860313
H	-2.851109	1.180726	2.072664
H	-2.473896	-1.985009	-0.270391
H	-0.223221	-0.825537	-1.509290
P	1.513304	-0.043802	1.307739
C	1.960955	-1.597519	0.393627
C	3.186179	-1.713719	-0.261898
C	1.112350	-2.707540	0.404711
C	3.554721	-2.899297	-0.887166
H	3.848593	-0.855072	-0.285198
C	1.478690	-3.897199	-0.212172
H	0.148263	-2.644688	0.900494
C	2.703405	-3.997328	-0.862482
H	4.507363	-2.965408	-1.399077
H	0.807352	-4.747159	-0.187894
H	2.990141	-4.922123	-1.346972
C	2.332416	1.260622	0.448001
C	2.154050	1.497496	-0.971669
C	3.190176	2.163894	1.137484
C	2.802667	2.548435	-1.594421
H	1.513894	0.841012	-1.550726
C	3.827166	3.202331	0.506648
H	3.342266	2.018818	2.204308
C	3.646714	3.420048	-0.899048
H	2.648452	2.699729	-2.659578
H	4.470569	3.860792	1.079690
H	4.144572	4.236431	-1.405241
C	-4.201534	0.507875	-0.528076
O	-4.603456	1.268269	-1.375782
O	-5.011563	-0.284801	0.182994
C	-6.407460	-0.175190	-0.102509
H	-6.753429	0.839102	0.090760
H	-6.601820	-0.431005	-1.142899
H	-6.902782	-0.877788	0.560117



**10-TS\***

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1341.37921878. Neg-Freq= -135.27

C	1.329391	-0.654727	-0.623631
C	1.595702	0.511120	1.825587
C	2.661243	-0.217475	0.038342
C	0.883578	-1.295650	0.728783
C	2.220780	-0.852091	1.402432
C	0.275198	0.067936	1.136999
C	2.036968	1.147987	0.473292
C	0.697356	0.713303	-0.202061
H	1.251402	-1.119387	-1.603436
H	1.708687	0.973193	2.802411
H	0.423047	-2.274888	0.831428
H	2.868616	-1.475307	2.013661
H	2.532394	2.107603	0.349980
H	0.085132	1.351198	-0.836285
P	-2.853239	0.184953	1.381910
C	-2.462687	1.590894	0.294642
C	-2.791569	1.679592	-1.067452
C	-1.840268	2.716011	0.861919
C	-2.482168	2.802617	-1.822969
H	-3.301290	0.850954	-1.545172
C	-1.548568	3.848646	0.116600
H	-1.558381	2.685349	1.909484
C	-1.853990	3.898392	-1.240042
H	-2.742412	2.825402	-2.875180
H	-1.062131	4.692026	0.593158
H	-1.610972	4.773629	-1.828892
C	-2.699659	-1.277770	0.321958
C	-1.933016	-1.373788	-0.853764
C	-3.294353	-2.472781	0.774529
C	-1.782573	-2.574440	-1.532533
H	-1.430407	-0.493029	-1.233584
C	-3.133329	-3.675598	0.105498
H	-3.896288	-2.448211	1.677759
C	-2.378393	-3.740287	-1.063011
H	-1.178753	-2.601069	-2.433091
H	-3.607324	-4.569803	0.493802
H	-2.257928	-4.676672	-1.592214
C	4.014925	-0.391697	-0.526720
O	4.283559	-0.988126	-1.541798
O	4.942268	0.186169	0.245726
C	6.296832	0.046974	-0.187224
H	6.574609	-1.005284	-0.225645
H	6.426210	0.491109	-1.172836



H 6.899352 0.571537 0.547521

**10**

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1341.36694700

C	-1.704124	1.154179	-0.411943
C	-1.347063	-1.063010	1.108655
C	-2.809806	0.132311	-0.040442
C	-1.204301	1.139601	1.062857
C	-2.308369	0.111577	1.445574
C	-0.225164	-0.035560	0.723384
C	-1.846278	-1.054852	-0.366643
C	-0.743020	-0.023848	-0.756658
H	-1.864219	2.041346	-1.016430
H	-1.196024	-1.948487	1.718813
H	-0.933770	2.016089	1.644489
H	-2.963748	0.170098	2.308502
H	-2.131543	-1.929405	-0.943383
H	-0.115427	-0.083162	-1.641048
P	1.485362	-0.015542	1.340293
C	2.244140	-1.419296	0.443453
C	3.633199	-1.561940	0.500937
C	1.501859	-2.383676	-0.235758
C	4.264224	-2.629047	-0.119069
H	4.226012	-0.825764	1.033557
C	2.132968	-3.462342	-0.846979
H	0.423365	-2.307501	-0.296857
C	3.513356	-3.585448	-0.794403
H	5.342026	-2.719373	-0.070787
H	1.541216	-4.203200	-1.369508
H	4.003909	-4.422352	-1.274466
C	2.077403	1.421356	0.356900
C	2.456947	1.330150	-0.983177
C	2.082350	2.672511	0.973468
C	2.827020	2.466265	-1.689383
H	2.470599	0.365249	-1.476385
C	2.443179	3.811997	0.264611
H	1.804886	2.755843	2.018511
C	2.817284	3.709508	-1.068302
H	3.122470	2.381576	-2.727586
H	2.439702	4.776291	0.756605
H	3.105706	4.594267	-1.621360
C	-4.235134	0.212258	-0.431061
O	-4.752328	1.142221	-1.000528
O	-4.903675	-0.882893	-0.058483
C	-6.300305	-0.901440	-0.364574
H	-6.806147	-0.076349	0.134145

H	-6.450790	-0.821713	-1.439900
H	-6.672810	-1.852462	0.002110

### 16-reduction

E (PCM(methanol)-[M06-2X/def2-TZVP])= -537.333453462

C	2.650969	-0.296539	0.000799
C	1.873122	0.482026	1.107059
C	1.102641	1.278086	0.007267
C	-0.002119	0.191251	-0.000406
C	0.771000	-0.605314	-1.106095
C	1.876642	0.494566	-1.098908
C	1.541754	-1.394893	-0.007235
C	0.767542	-0.617897	1.098057
H	0.300448	-1.032759	-1.986057
H	2.309868	0.915533	2.000995
H	2.316338	0.938166	-1.986425
H	0.910334	2.346404	0.012853
H	0.294162	-1.055459	1.971503
H	1.715788	-2.465951	-0.013055
C	-1.461302	0.432916	-0.000550
O	-1.993592	1.516565	-0.000107
O	-2.145123	-0.716471	-0.000753
C	-3.569748	-0.599698	0.000523
H	-3.903066	-0.066191	0.889275
H	-3.904873	-0.066771	-0.887886
H	-3.952087	-1.615371	0.001272
H	3.719796	-0.485381	0.001334

### 16-reduction-TS

E (PCM(methanol)-[M06-2X/def2-TZVP])= -593.192486780, Neg.Freq=-1693.1

C	1.295859	0.599476	-1.215033
C	0.353078	-0.441733	1.103901
C	2.137167	-0.063992	-0.089051
C	0.277960	-0.577493	-1.101397
C	1.133515	-1.243346	0.018649
C	-0.503076	0.237236	-0.020664
C	1.373874	0.733442	1.000079
C	0.516061	1.399535	-0.122736
H	1.673524	1.010744	-2.145216
H	-0.059159	-0.848250	2.022031
H	-0.191056	-1.094171	-1.932753
H	1.384401	-2.297427	0.074125
H	1.815627	1.253160	1.844009
H	0.249161	2.450222	-0.175871
H	3.389337	-0.194380	-0.142174
N	4.698599	-0.385662	0.028820

H	4.829624	0.241887	0.826907
H	4.649754	-1.314656	0.456055
C	-1.975884	0.373674	0.031124
O	-2.581090	1.415273	0.099466
O	-2.572039	-0.821415	0.001044
C	-4.000853	-0.814166	0.055584
H	-4.340810	-0.350463	0.980213
H	-4.406871	-0.268370	-0.794605
H	-4.304909	-1.855322	0.018725

### NH<sub>3</sub>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -56.5551042794

N	0.00000	0.00000	0.115302
H	0.00000	0.938000	-0.269038
H	-0.812332	-0.469000	-0.269038
H	0.812332	-0.469000	-0.269038

### NH<sub>2</sub><sup>•</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -55.8743600454

N	0.00000	0.00000	0.141016
H	0.00000	0.804431	-0.493556
H	0.00000	-0.804431	-0.493556

### 2

E (PCM(methanol)-[M06-2X/def2-TZVP])= -903.519254608

C	-0.445663	-0.209862	1.263676
C	0.445679	0.209956	-1.263662
C	-1.325956	0.000423	0.000065
C	0.444880	-1.199292	0.449767
C	-0.445666	-0.988949	-0.813539
C	1.325962	-0.000386	-0.000066
C	-0.444909	1.199366	-0.449781
C	0.445685	0.989018	0.813489
H	-0.821170	-0.376448	2.267170
H	0.821238	0.376565	-2.267137
H	0.819883	-2.152323	0.806327
H	-0.821604	-1.774916	-1.459173
H	-0.819906	2.152397	-0.806337
H	0.821670	1.774992	1.459096
I	3.435168	-0.000040	0.000033
I	-3.435171	0.000004	-0.000026

### 17

E (PCM(methanol)-[M06-2X/def2-TZVP])= -605.806842164

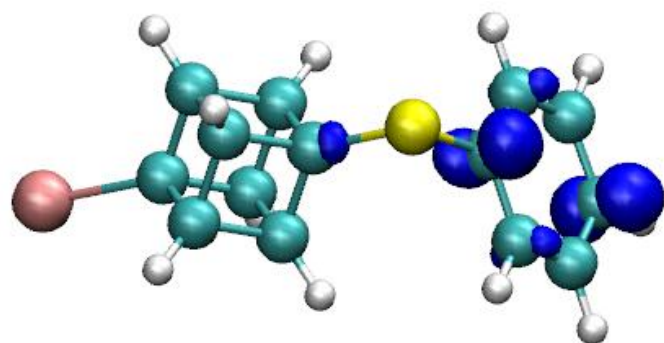
C	-2.142416	-0.866181	0.955982
C	-1.257694	0.863326	-0.952827

C	-2.988006	-0.000773	-0.000479
C	-1.256712	-1.257180	-0.270899
C	-2.142111	-0.395187	-1.228185
C	-0.387569	0.000219	0.000350
C	-2.143578	1.260937	0.271667
C	-1.258022	0.393923	1.224108
H	-2.492275	-1.555197	1.717194
H	-0.878889	1.545969	-1.706240
H	-0.877414	-2.250794	-0.485088
H	-2.491137	-0.709386	-2.205949
H	-2.494371	2.264333	0.488027
H	-0.880198	0.705375	2.192305
I	1.727753	0.000098	0.000027

### 13b<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1235.76278131

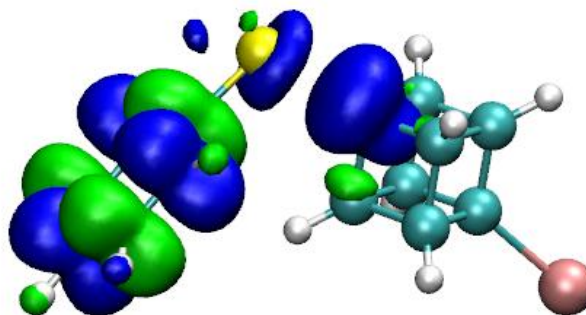
C	-4.927640	-2.031408	0.000188
C	-4.550439	-1.396082	1.216166
C	-3.872330	-0.204677	1.225884
C	-3.528479	0.471384	0.000081
C	-3.871794	-0.205085	-1.225650
C	-4.549889	-1.396497	-1.215833
S	-2.491245	1.863589	0.000075
C	-0.836234	1.165881	0.000030
C	-0.238415	0.238881	-1.106933
C	1.061298	1.102068	-1.109788
C	1.639296	0.183736	-0.000051
C	1.061275	1.101837	1.109866
C	0.469813	2.024561	0.000129
C	-0.238438	0.238650	1.106809
C	0.353281	-0.686337	-0.000154
I	3.618784	-0.590014	-0.000121
H	1.603022	1.433877	1.989493
H	-0.775372	-0.099694	-1.987612
H	0.504364	3.109747	0.000243
H	1.603063	1.434291	-1.989334
H	0.327882	-1.770981	-0.000269
H	-0.775414	-0.100110	1.987405
H	-3.595689	0.252850	2.170427
H	-3.594739	0.252131	-2.170224
H	-4.804536	-1.861474	2.163789
H	-4.803559	-1.862209	-2.163414
H	-5.452495	-2.976601	0.000231



### 13b<sup>-</sup>-TS

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1235.74940822. Neg-Freq= -246.9

C	0.604475	-0.119185	1.028537
C	0.431485	1.676301	-1.002728
C	1.714371	0.232261	0.002780
C	0.324270	1.406579	1.199850
C	1.449771	1.750217	0.176305
C	-0.698212	1.334567	0.020790
C	0.711377	0.151323	-1.178926
C	-0.415346	-0.182456	-0.151091
H	0.704702	-0.848639	1.827215
H	0.370243	2.395796	-1.816076
H	0.177016	1.909214	2.153028
H	2.221149	2.504140	0.306076
H	0.895656	-0.363361	-2.117730
H	-1.177067	-0.948796	-0.279136
C	-3.682780	0.422658	-0.008310
C	-3.981424	-0.262871	1.204762
C	-4.003869	-0.268592	-1.212386
C	-4.551686	-1.520075	1.205149
H	-3.747743	0.223961	2.144731
C	-4.574996	-1.524259	-1.197043
H	-3.786011	0.212833	-2.159014
C	-4.857900	-2.179338	0.008942
H	-4.761791	-2.002826	2.153663
H	-4.803851	-2.011181	-2.138965
H	-5.302170	-3.165512	0.015552
S	-2.838992	1.913609	-0.016955
I	3.656915	-0.642003	-0.007506



### 13b

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1235.71640352

C	-4.885132	-1.989128	0.000061
C	-4.524495	-1.395369	1.202779
C	-3.800559	-0.210429	1.204923
C	-3.432469	0.382738	0.000038
C	-3.800323	-0.210599	-1.204837
C	-4.524251	-1.395543	-1.202670
S	-2.474991	1.883565	0.000024
C	-0.856914	1.150647	-0.000007
C	-0.258373	0.228939	-1.108883
C	1.036751	1.098200	-1.109505
C	1.620943	0.181762	-0.000020
C	1.036749	1.098169	1.109492
C	0.440568	2.017084	0.000006
C	-0.258375	0.228909	1.108841
C	0.336075	-0.691834	-0.000033

I	3.595972	-0.584418	-0.000031
H	1.572867	1.436205	1.989441
H	-0.789831	-0.111785	-1.991757
H	0.463418	3.101697	0.000020
H	1.572870	1.436261	-1.989444
H	0.310635	-1.775974	-0.000049
H	-0.789843	-0.111838	1.991701
H	-3.520066	0.259445	2.139070
H	-3.519655	0.259150	-2.138995
H	-4.808487	-1.852868	2.141744
H	-4.808048	-1.853180	-2.141625
H	-5.451678	-2.911274	0.000070

### 13d

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1410.51551002

C	3.047426	-3.804228	-1.136560
C	3.073719	-2.559377	-1.754270
C	2.786077	-1.413226	-1.026488
C	2.473632	-1.496071	0.331397
C	2.458943	-2.749327	0.943154
C	2.737799	-3.898604	0.213235
C	0.273901	0.092463	0.794659
C	-0.758540	-1.029421	1.156941
C	-1.780929	0.054862	1.609984
C	-2.324603	0.107007	0.156510
C	-1.319982	1.232910	-0.211371
C	-0.764883	1.177787	1.245673
C	-0.301200	0.141714	-0.663485
C	-1.314512	-0.983314	-0.296678
I	-4.382224	0.127402	-0.350154
H	-1.565065	2.135862	-0.761095
H	-0.517732	-1.934680	1.706338
H	-0.537315	2.041729	1.862549
H	-2.390966	0.017853	2.505949
H	-1.553834	-1.845987	-0.909120
H	0.291036	0.177163	-1.572796
H	2.814048	-0.446852	-1.516407
H	2.232464	-2.826735	2.000826
H	3.318656	-2.481362	-2.806029
H	2.721628	-4.864414	0.701972
H	3.274553	-4.696849	-1.705282
P	2.000669	-0.038334	1.347357
C	2.811083	1.325747	0.434477
C	2.107015	2.352324	-0.192442
C	4.207819	1.368956	0.424483
C	2.782936	3.393840	-0.820096

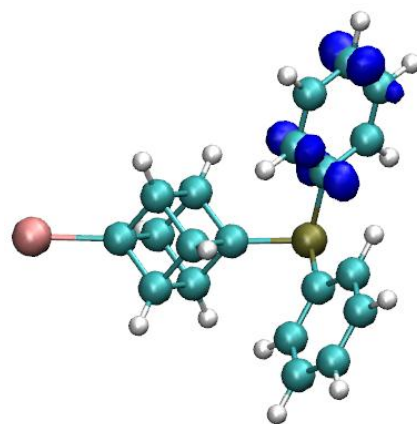


H	1.024299	2.355089	-0.199128
C	4.882296	2.399269	-0.211640
H	4.771962	0.583466	0.916271
C	4.169417	3.417825	-0.835572
H	2.220938	4.183566	-1.302483
H	5.964708	2.412093	-0.216373
H	4.693972	4.225960	-1.328881

### 13d<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= E=-1123.9904298

C	0.591041780680	0.280063216859	-0.346703968358
C	0.832990251243	0.005053769053	1.007311216925
C	2.115780280099	-0.001147507851	1.542414963775
C	3.258218410717	0.286669619490	0.693379427027
C	2.997709641957	0.557914564658	-0.678979797414
C	1.720731077962	0.560416634217	-1.197159554054
C	4.957651308741	-1.277180526702	2.429189473696
C	4.338494722321	-2.651859855339	1.979303190317
C	5.626629777202	-3.403372414789	2.481724019273
C	4.958005794252	-3.547141936209	3.893553039542
C	5.586128693785	-2.187897116969	4.363121079646
C	6.246723296041	-2.034212207483	2.944285648228
C	4.297856478943	-1.446472997927	3.852746795046
C	3.666517926907	-2.810628401083	3.390621970776
I	4.950294641849	-5.341074182291	5.054726084197
H	6.078626056533	-2.022701406232	5.313458913116
H	3.844178838925	-2.813340668208	1.028570390362
H	7.268173376641	-1.721598478955	2.759221202070
H	6.149476320066	-4.193607578824	1.957632276658
H	2.650536558209	-3.136295796762	3.574126758423
H	3.780103751159	-0.662077946453	4.392066327184
H	2.265815412872	-0.208617360458	2.594959058358
H	3.838888016332	0.768592323460	-1.333045251812
H	-0.006946993445	-0.212180964196	1.659763222808
H	1.565139088489	0.771657132220	-2.247894392796
H	-0.414163510151	0.277476430138	-0.744550639963
P	4.958227774208	0.245101118986	1.316746214086
C	4.997327747262	1.485158859739	2.750736315937
C	5.983627417392	1.363078511424	3.735419697697
C	4.097110564500	2.548247851449	2.825720897558
C	6.074149937720	2.290655931248	4.771679879452
H	6.686713969258	0.538933942009	3.694713217754
C	4.180072956042	3.475283547884	3.866147868456
H	3.328315497563	2.638912908759	2.068167729613
C	5.170010119397	3.350347320843	4.840208745248
H	6.845299603958	2.186822778353	5.523003910991

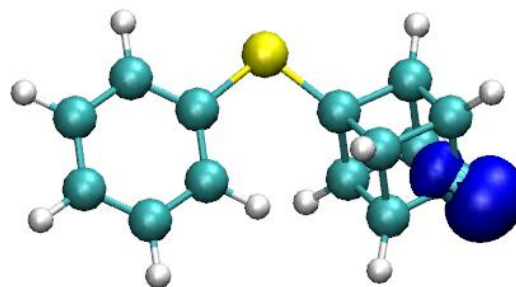


H	3.471267317632	4.290579174178	3.918960556834
H	5.236946786741	4.070846371765	5.643261213344

**14b\***

E (PCM(methanol)-[M06-2X/def2-TZVP])= -938.002171856

C	2.970692	-0.047820	-1.118146
C	1.531427	0.559140	1.116788
C	3.334317	0.949579	0.000059
C	2.567875	-1.058770	0.000139
C	2.970577	-0.047687	1.118345
C	1.128200	-0.458023	0.000029
C	1.927823	1.579595	-0.000049
C	1.531542	0.559009	-1.116808
H	3.548139	-0.293621	-2.003003
H	0.940128	0.786439	1.998864
H	2.788174	-2.122256	0.000212
H	3.547935	-0.293383	2.003289
H	1.673791	2.635120	-0.000124
H	0.940336	0.786205	-1.998973
C	-1.646076	-0.517844	-0.000021
C	-2.897525	-1.137163	0.000012
C	-1.571126	0.872852	-0.000106
C	-4.053771	-0.374400	-0.000039
H	-2.961596	-2.218763	0.000078
C	-2.737771	1.629187	-0.000151
H	-0.616560	1.380179	-0.000143
C	-3.980553	1.014297	-0.000119
H	-5.016888	-0.868723	-0.000012
H	-2.665924	2.709412	-0.000216
H	-4.884352	1.608971	-0.000157
S	-0.234186	-1.577581	0.000037

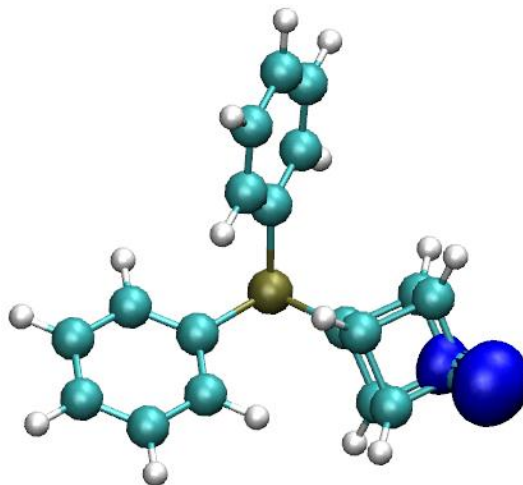


**14d\***

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1112.79997302

C	2.805981	-0.726842	0.936382
C	1.325576	-2.436001	-0.582312
C	3.028084	-2.239082	0.724551
C	2.583411	-0.609366	-0.602270
C	2.840475	-2.134435	-0.802776
C	1.060578	-0.903878	-0.390618
C	1.539883	-2.565361	0.959959
C	1.292225	-1.035063	1.153509
H	3.399265	-0.043439	1.535726
H	0.720534	-3.102754	-1.190809
H	2.976068	0.183892	-1.233311
H	3.461380	-2.569022	-1.579593

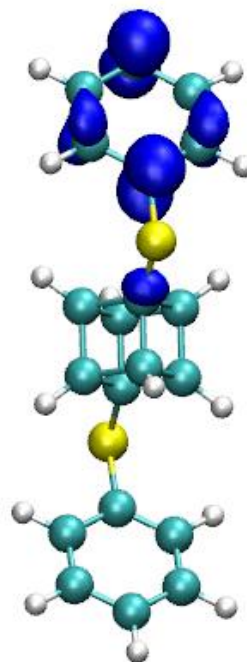
H	1.123666	-3.349935	1.585111
H	0.665618	-0.592634	1.923436
P	-0.175863	0.077618	-1.289097
C	-1.749965	-0.477880	-0.536899
C	-2.913751	0.215247	-0.880544
C	-1.853211	-1.574230	0.317096
C	-4.144336	-0.163590	-0.367760
H	-2.853333	1.065402	-1.551910
C	-3.089603	-1.963251	0.822259
H	-0.972828	-2.137476	0.599801
C	-4.235558	-1.257526	0.486423
H	-5.034093	0.390799	-0.637950
H	-3.151854	-2.817484	1.484521
H	-5.196066	-1.558809	0.884170
C	0.098768	1.676417	-0.421504
C	-0.452472	1.970843	0.825934
C	0.943569	2.610433	-1.021487
C	-0.164588	3.172205	1.458471
H	-1.116344	1.259588	1.303289
C	1.240981	3.809170	-0.384181
H	1.368416	2.401237	-1.997174
C	0.684542	4.092684	0.855474
H	-0.602787	3.389467	2.424462
H	1.899565	4.524061	-0.860819
H	0.907215	5.029870	1.349275



### 12b<sup>-</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1567.95513041

C	0.337040	1.329061	-0.000306
C	-0.423071	-1.269607	0.000199
C	0.692781	0.292711	1.107123
C	0.692747	0.292296	-1.107355
C	-0.776633	-0.234105	-1.109244
C	-0.776603	-0.233682	1.109255
H	0.616465	2.378582	-0.000507
H	-0.712307	-2.316911	0.000402
H	1.300457	0.493530	1.984552
H	1.300396	0.492789	-1.984877
H	-1.384356	-0.431008	-1.988000
H	-1.384297	-0.430253	1.988104
C	1.050284	-0.750650	0.000073
C	-1.131446	0.804619	-0.000190
S	2.470901	-1.847362	0.000245
C	3.842569	-0.785868	0.000157
C	4.398041	-0.271121	1.226219
C	4.398044	-0.271336	-1.225994

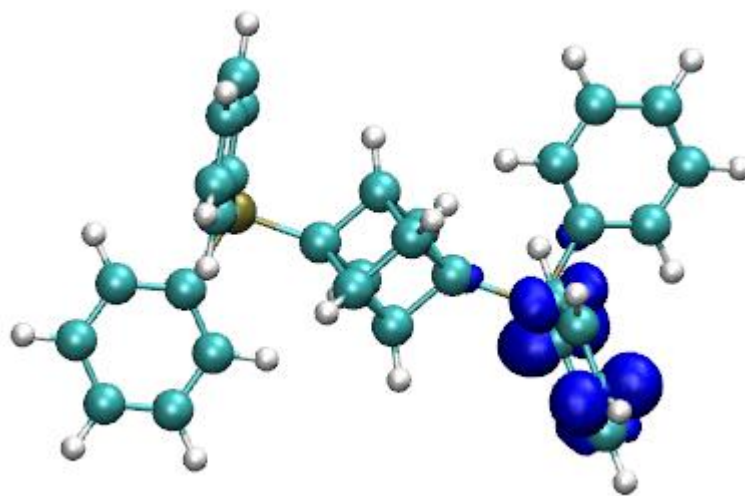


C	5.440396	0.619176	1.216756
H	3.985681	-0.612098	2.170532
C	5.440395	0.618966	-1.216684
H	3.985681	-0.612472	-2.170247
C	6.009827	1.090600	-0.000005
H	5.837366	0.970938	2.164376
H	5.837362	0.970569	-2.164365
H	6.826610	1.798939	-0.000066
S	-2.517484	1.918951	-0.000407
C	-3.830352	0.716449	-0.000151
C	-4.343436	0.241261	1.204608
C	-4.342752	0.240007	-1.204703
C	-5.357593	-0.707046	1.202872
H	-3.948104	0.619647	2.138833
C	-5.356914	-0.708293	-1.202551
H	-3.946850	0.617378	-2.139097
C	-5.864564	-1.183045	0.000264
H	-5.752647	-1.072498	2.142113
H	-5.751417	-1.074745	-2.141635
H	-6.657256	-1.920163	0.000421

### 12d<sup>+</sup>

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1917.55528892

C	-0.760397	-0.635645	0.111865
C	0.546892	0.554422	-1.941231
C	-1.419616	0.285432	-0.971630
C	0.020916	-1.374357	-1.012884
C	-0.622743	-0.459524	-2.098579
C	1.212547	-0.368216	-0.862312
C	-0.232769	1.296413	-0.817759
C	0.405331	0.380458	0.267748
H	-1.292430	-1.116146	0.928897
H	1.085977	1.034353	-2.754058
H	0.144660	-2.453001	-1.085725
H	-1.052683	-0.795702	-3.038702
H	-0.359642	2.373956	-0.739828
H	0.807342	0.720436	1.217399
P	2.937813	-0.975735	-0.981361
C	3.830890	0.646420	-1.041959
C	5.150809	0.638157	-1.503521
C	3.302330	1.865148	-0.607460
C	5.916681	1.794232	-1.530809
H	5.581813	-0.297089	-1.847981
C	4.065707	3.029095	-0.632088
H	2.282662	1.917608	-0.244689
C	5.374268	2.999468	-1.092808



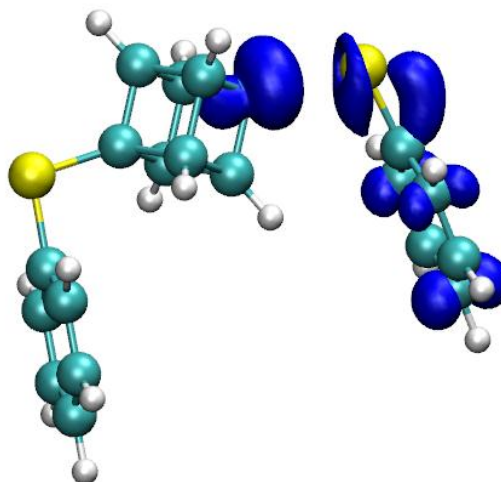
H	6.934693	1.759517	-1.899332
H	3.634806	3.961322	-0.286464
H	5.967765	3.904754	-1.111319
C	3.326370	-1.636265	0.616376
C	3.290284	-0.851963	1.832941
C	3.855918	-2.960532	0.741992
C	3.718346	-1.377873	3.031481
H	2.937898	0.172724	1.794319
C	4.269730	-3.473595	1.944104
H	3.924182	-3.577272	-0.150371
C	4.205960	-2.692959	3.137825
H	3.677140	-0.754429	3.920395
H	4.650560	-4.488774	1.983861
H	4.534865	-3.093562	4.087084
P	-3.127594	0.891868	-1.088003
C	-4.106516	-0.645762	-0.917042
C	-3.554528	-1.917801	-1.060101
C	-5.481994	-0.534090	-0.697385
C	-4.358127	-3.050742	-0.980566
C	-6.281242	-1.662599	-0.604496
C	-5.720034	-2.927316	-0.748755
H	-2.492378	-2.039839	-1.234142
H	-5.929880	0.448336	-0.590264
H	-3.913374	-4.031270	-1.095461
H	-7.343741	-1.556766	-0.425328
H	-6.343286	-3.809913	-0.683880
C	-3.260790	1.606732	0.601357
C	-3.045516	2.977562	0.743921
C	-3.495112	0.840992	1.744491
C	-3.050920	3.570619	2.000536
C	-3.511342	1.433709	2.999419
C	-3.285759	2.799135	3.130261
H	-2.874470	3.586712	-0.136851
H	-3.671980	-0.224243	1.652373
H	-2.879917	4.635442	2.095209
H	-3.698727	0.828785	3.877743
H	-3.298608	3.259522	4.109960

### 12b<sup>-</sup>-TS

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1567.94122128 Neg-Freq=-265.7

C	-0.700762	-2.853041	0.144067
C	0.379469	-0.387849	-0.127337
C	0.156068	-2.379857	-1.069639
C	0.305721	-2.201127	1.140325
C	-0.482270	-0.854656	1.086754
C	-0.631280	-1.033596	-1.125618

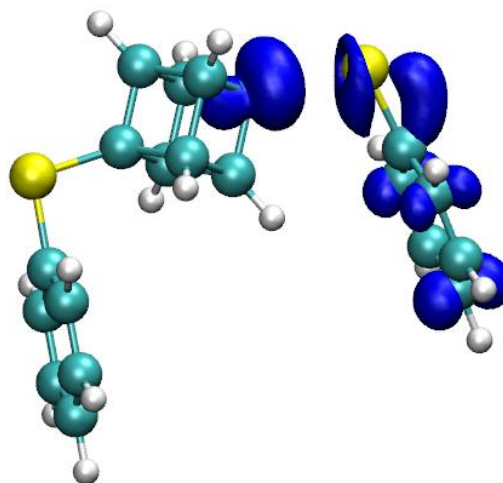
H	-1.170578	-3.828207	0.255066
H	0.832149	0.596242	-0.236426
H	0.413595	-2.993564	-1.930440
H	0.683086	-2.672950	2.045438
H	-0.776036	-0.243285	1.937541
H	-1.041994	-0.562290	-2.016158
C	1.163520	-1.725770	-0.072689
C	-1.486219	-1.508291	0.088638
S	3.381209	-1.563935	-0.228103
C	3.705122	0.112759	-0.083272
C	3.823989	0.746228	1.187579
C	3.746234	0.975119	-1.216940
C	3.978000	2.113385	1.304731
H	3.791485	0.129470	2.078523
C	3.901970	2.339523	-1.085273
H	3.648654	0.536366	-2.203660
C	4.018596	2.939612	0.175787
H	4.067753	2.550657	2.293565
H	3.930154	2.955339	-1.977897
H	4.137642	4.010320	0.273975
S	-3.261739	-1.474490	0.204581
C	-3.510654	0.281751	0.062987
C	-3.672194	0.866387	-1.191067
C	-3.533616	1.080344	1.204310
C	-3.850447	2.238976	-1.301543
H	-3.661119	0.242206	-2.075535
C	-3.713261	2.452611	1.090294
H	-3.412723	0.622258	2.177918
C	-3.870624	3.033247	-0.161836
H	-3.975917	2.687388	-2.278824
H	-3.730203	3.067441	1.981036
H	-4.011649	4.102885	-0.249307



### 12d<sup>-</sup>-TS

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1917.51809151 Neg-Freq= -135.1

C	0.647462	-0.866950	0.542411
C	-0.369953	0.807329	2.416364
C	1.440024	-0.066899	1.602084
C	-0.361703	-1.272724	1.661828
C	0.452159	-0.478846	2.727774
C	-1.199788	0.012555	1.349860
C	0.639042	1.223104	1.299686
C	-0.175125	0.426929	0.235870
H	1.063041	-1.546180	-0.200267
H	-0.805339	1.475077	3.157373
H	-0.791575	-2.263469	1.794737



H	0.699159	-0.839120	3.722888
H	1.042360	2.222643	1.155042
H	-0.444715	0.793920	-0.752809
P	-3.015095	-0.004242	1.344578
C	-3.373848	1.461157	0.296293
C	-4.493429	1.492951	-0.535542
C	-2.571825	2.600880	0.382475
C	-4.799662	2.631260	-1.269071
H	-5.128682	0.618432	-0.618353
C	-2.878238	3.739476	-0.351926
H	-1.695254	2.605096	1.021145
C	-3.993059	3.758493	-1.180446
H	-5.670133	2.635584	-1.913069
H	-2.240481	4.611626	-0.279534
H	-4.231143	4.645122	-1.753790
C	-3.401642	-1.372787	0.186298
C	-2.523141	-1.814838	-0.805244
C	-4.634094	-2.010552	0.322909
C	-2.874884	-2.866807	-1.639649
H	-1.557881	-1.338959	-0.930509
C	-4.995426	-3.051950	-0.523207
H	-5.317404	-1.689764	1.101411
C	-4.113653	-3.483722	-1.503921
H	-2.181674	-3.205279	-2.399509
H	-5.959433	-3.530896	-0.407747
H	-4.386493	-4.302232	-2.157627
P	4.474548	-0.005980	0.784112
C	3.861259	-1.491345	-0.067174
C	3.568152	-2.626125	0.708749
C	3.714568	-1.629812	-1.456715
C	3.140083	-3.815498	0.138477
C	3.266264	-2.811476	-2.030633
C	2.970448	-3.916678	-1.238911
H	3.657038	-2.557890	1.788257
H	3.959737	-0.793554	-2.100983
H	2.918120	-4.664935	0.774312
H	3.156131	-2.872882	-3.107418
H	2.619764	-4.838148	-1.685829
C	3.864094	1.383007	-0.207143
C	4.483292	2.635677	-0.021493
C	2.741156	1.366195	-1.054585
C	4.014133	3.787379	-0.632606
C	2.279248	2.515538	-1.679001
C	2.907660	3.740130	-1.477244
H	5.353462	2.697602	0.625057
H	2.203207	0.438013	-1.205370

H	4.520245	4.729632	-0.456186
H	1.404938	2.457087	-2.318356
H	2.543760	4.636506	-1.962617

### 14b

E (PCM(methanol)-[M06-2X/def2-TZVP])= -938.676890058

C	2.936836	-0.091751	-1.104579
C	1.499903	0.514140	1.111328
C	3.360094	0.925133	0.000002
C	2.514370	-1.106057	0.000046
C	2.936807	-0.091691	1.104628
C	1.075661	-0.501508	0.000011
C	1.920546	1.526763	-0.000033
C	1.499932	0.514080	-1.111350
H	3.515180	-0.339769	-1.988582
H	0.912992	0.747980	1.994583
H	2.725962	-2.171183	0.000078
H	3.515128	-0.339661	1.988660
H	1.680210	2.585679	-0.000065
H	0.913044	0.747871	-1.994633
C	-1.700977	-0.514301	0.000001
C	-2.965613	-1.106936	0.000007
C	-1.598059	0.875081	-0.000025
C	-4.106025	-0.320662	-0.000012
H	-3.052119	-2.186998	0.000027
C	-2.748992	1.655230	-0.000043
H	-0.632475	1.361413	-0.000031
C	-4.004457	1.066230	-0.000037
H	-5.079263	-0.794883	-0.000007
H	-2.654910	2.733818	-0.000062
H	-4.895966	1.679260	-0.000052
S	-0.309078	-1.599439	0.000026
H	4.277308	1.505000	-0.000002

### 14b-TS

E (PCM(methanol)-[M06-2X/def2-TZVP])= -994.535682288. Neg-Freq: -1689.01

C	2.500108	-0.578280	-1.053701
C	1.083875	0.167710	1.140966
C	2.990681	0.338615	0.096354
C	1.915057	-1.550929	0.015159
C	2.422784	-0.632676	1.167943
C	0.572345	-0.755949	-0.012011
C	1.664362	1.143816	0.068530
C	1.159570	0.219249	-1.085200
H	3.073909	-0.878073	-1.924321



H	0.502125	0.457413	2.010857
H	1.985135	-2.634204	-0.008656
H	2.933392	-0.973297	2.062368
H	1.568658	2.224881	0.091805
H	0.638789	0.547225	-1.979845
C	-2.177789	-0.402256	-0.033622
C	-3.509956	-0.820586	-0.011443
C	-1.888924	0.960593	-0.029391
C	-4.533535	0.112278	0.012806
H	-3.740791	-1.879317	-0.012193
C	-2.923482	1.888455	-0.003766
H	-0.867222	1.313361	-0.047848
C	-4.246338	1.473197	0.016829
H	-5.561501	-0.226828	0.029891
H	-2.685428	2.944660	-0.001182
H	-5.047443	2.200079	0.036597
S	-0.941481	-1.662897	-0.072609
H	4.132482	0.869603	0.171572
N	5.318710	1.456368	0.027473
H	5.713626	0.810814	-0.661770
H	5.014446	2.256046	-0.534554

#### 14d

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1113.47198784

C	-2.126877	-1.735122	1.181255
C	-2.714336	-0.211473	-0.969377
C	-3.564736	-1.442153	0.646773
C	-1.646662	-2.011252	-0.275390
C	-3.079913	-1.716281	-0.809946
C	-1.266687	-0.498722	-0.432990
C	-3.196817	0.066283	0.486692
C	-1.766250	-0.224895	1.027840
H	-1.887808	-2.350681	2.043664
H	-2.937793	0.401733	-1.838712
H	-1.010917	-2.836702	-0.584082
H	-3.608120	-2.313624	-1.546491
H	-3.818759	0.903823	0.788465
H	-1.237416	0.381159	1.759018
C	0.462175	1.697885	-0.454084
C	1.699839	2.154478	-0.004076
C	-0.647124	2.538531	-0.332507
C	1.824885	3.419865	0.557489
H	2.572348	1.516231	-0.081491
C	-0.522751	3.800098	0.231740
H	-1.621128	2.204860	-0.675219

C	0.715862	4.245798	0.678057
H	2.792684	3.757660	0.906395
H	-1.394815	4.435281	0.323917
H	0.814811	5.229552	1.118595
P	0.249230	0.066357	-1.271541
H	-4.483610	-1.820889	1.083428
C	1.545095	-0.929691	-0.441771
C	1.409762	-1.434929	0.853225
C	2.712985	-1.207150	-1.150523
C	2.418730	-2.199098	1.421458
C	3.732153	-1.958865	-0.577224
C	3.583952	-2.458925	0.708641
H	0.513323	-1.230998	1.426600
H	2.824760	-0.833477	-2.162121
H	2.297947	-2.590971	2.423450
H	4.635129	-2.161578	-1.138830
H	4.371214	-3.053023	1.154848

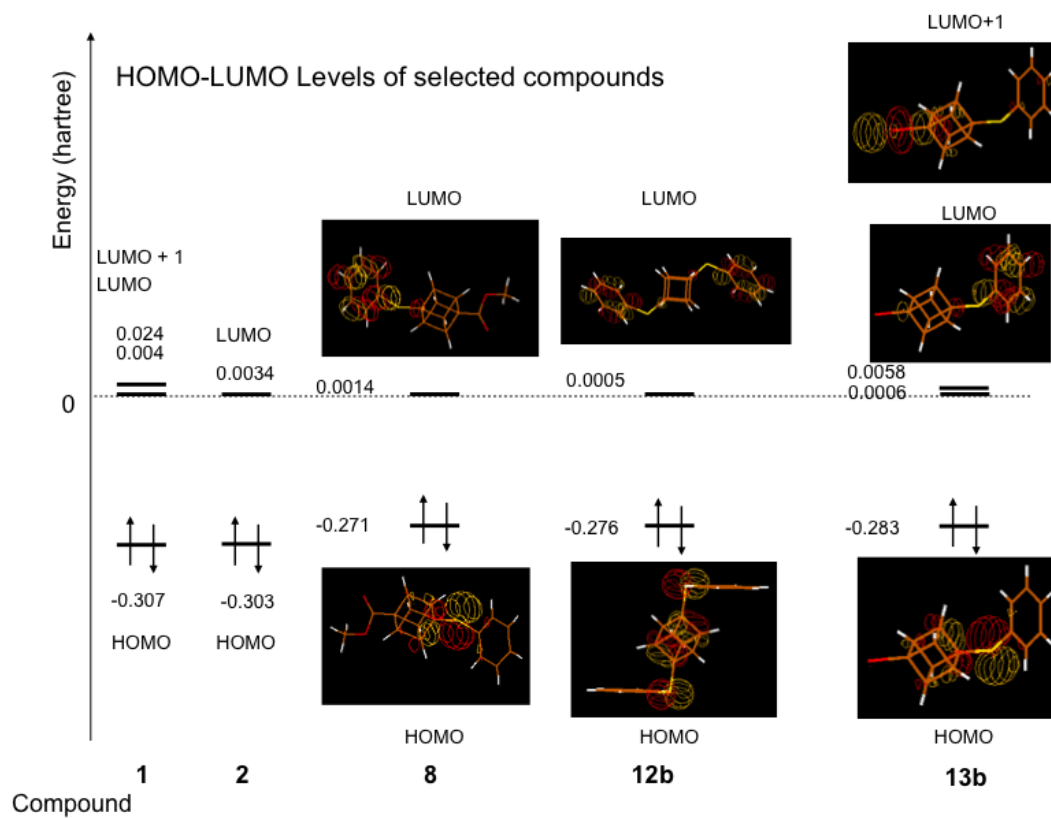
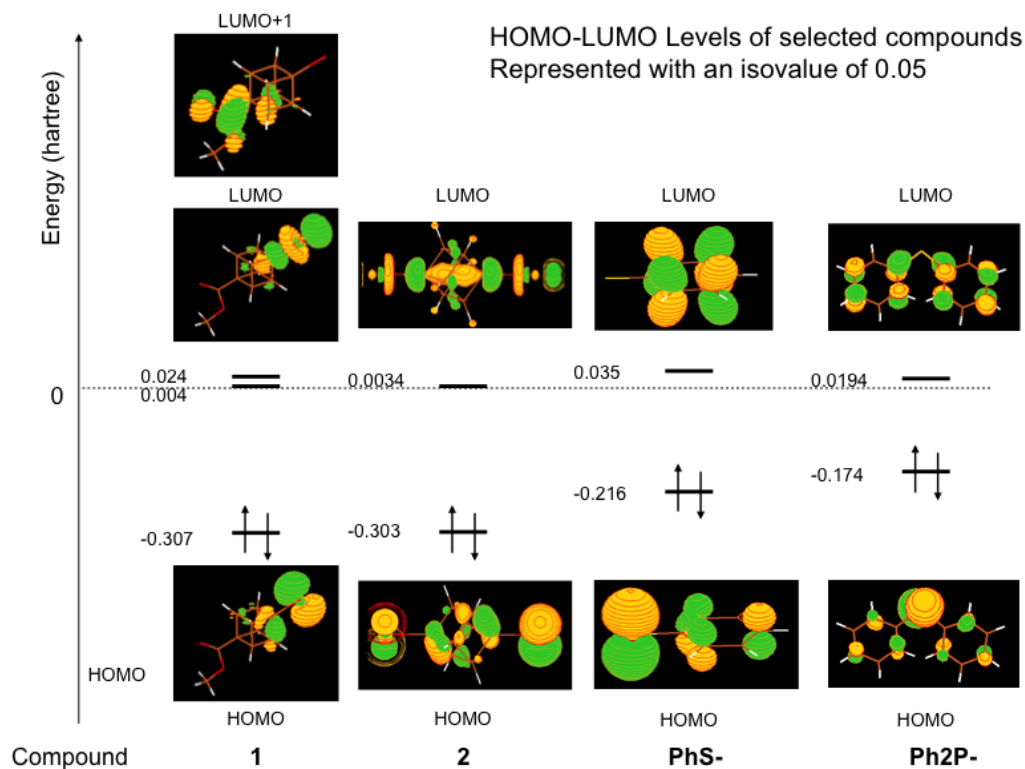
#### 14d-TS

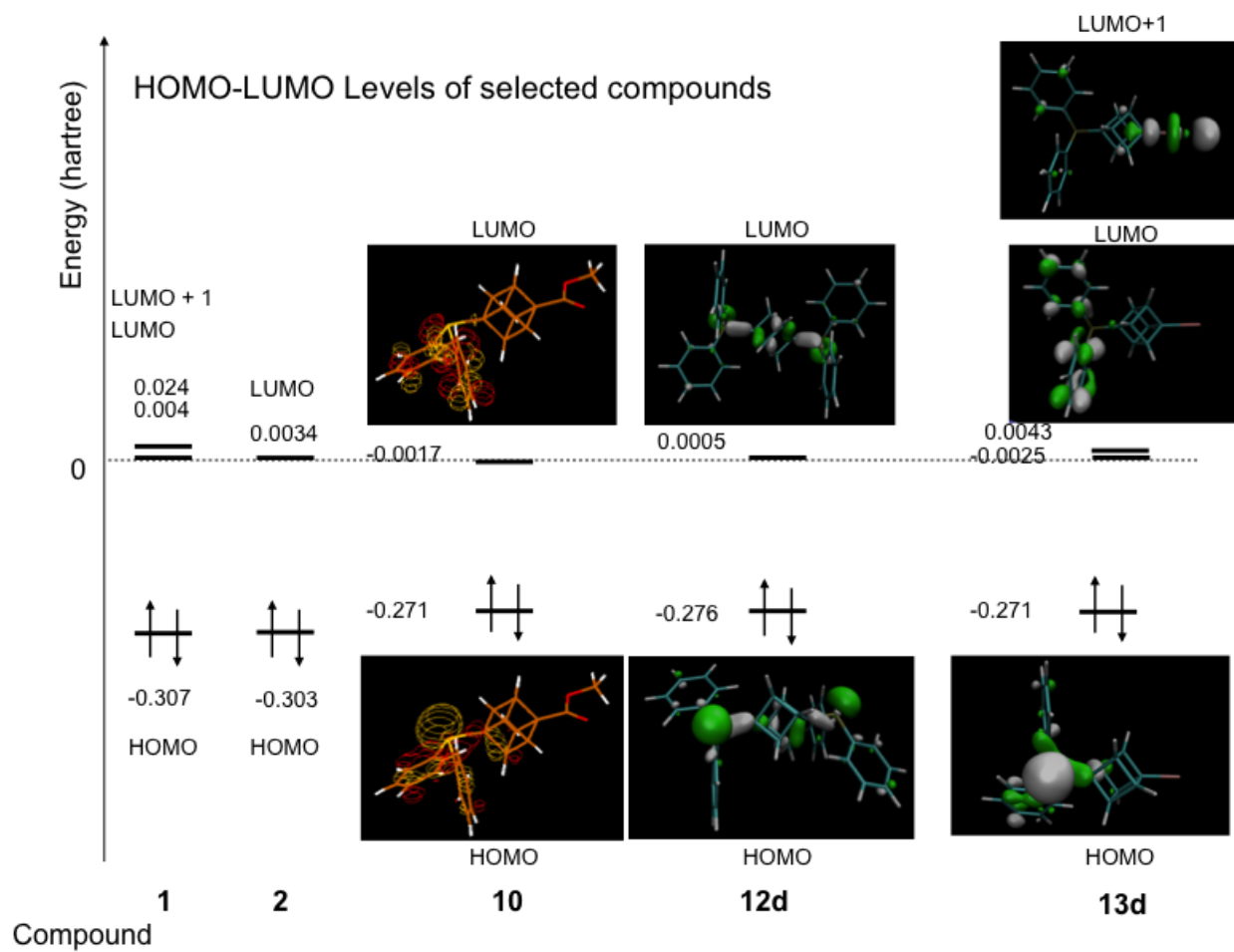
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1169.33306707. Neg-Freq=-1660.3

C	2.489093	0.715949	0.584473
C	1.902451	-1.364623	-1.054723
C	3.444829	-0.434691	0.171909
C	2.047772	0.837021	-0.904804
C	3.019057	-0.309680	-1.317155
C	0.917361	-0.215722	-0.646963
C	2.341078	-1.493275	0.437683
C	1.372599	-0.339804	0.847498
H	2.730533	1.551127	1.234432
H	1.654535	-2.194804	-1.710261
H	1.906887	1.770645	-1.442866
H	3.681666	-0.295084	-2.176267
H	2.466077	-2.429156	0.974031
H	0.708094	-0.352926	1.706765
C	-1.732500	-1.226421	-0.467113
C	-3.125931	-1.131535	-0.513629
C	-1.159301	-2.324932	0.171051
C	-3.923993	-2.097467	0.078555
H	-3.590472	-0.287701	-1.012663
C	-1.959594	-3.301290	0.755249
H	-0.082728	-2.432931	0.220028
C	-3.341322	-3.188656	0.714896
H	-5.001800	-2.002613	0.040293
H	-1.497351	-4.147853	1.247001
H	-3.963271	-3.946198	1.174074
P	-0.746797	0.053595	-1.327504

H	4.636549	-0.566450	0.540326
N	5.850427	-0.635463	1.115025
H	5.949962	0.356480	1.347791
H	5.559173	-1.063152	1.998449
C	-1.172852	1.561047	-0.365392
C	-1.581009	1.529759	0.968991
C	-1.017434	2.796810	-0.993492
C	-1.827756	2.709220	1.657682
C	-1.254448	3.978720	-0.302017
C	-1.662904	3.935564	1.023788
H	-1.713367	0.577636	1.469417
H	-0.712153	2.833722	-2.033440
H	-2.147992	2.672196	2.691328
H	-1.128956	4.930830	-0.801681
H	-1.857596	4.854588	1.561689

### 3.4.2 HOMO-LUMO Levels of selected compounds





### 3.4.3 Estimation of the Activation barrier by Marcus and Savéant's models

There can be different scenarios for dissociative electron transfer (DET) from the nucleophiles to the cubane derivatives. If ET and cleavage of the C-I bond in the iodocubane occur in different steps and involve the formation of the cubane-halide radical anion, the outer-sphere ET model is applicable and the activation barrier may be estimated from the outer-sphere Marcus-Hush model. Otherwise, when the ET and aryl halide bond cleavage are concerted (concerted dissociative ET), Savéant's model is used.

The reorganization energy  $\lambda_0$  according to Marcus equation can be calculated with:

$$\lambda_0 = (332 \text{ kcal/mol}) \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right) \quad (1)$$

where  $a_1$  and  $a_2$  are the radii of the reactant molecules and  $R = a_1 + a_2$ .  $\epsilon_{op}$  is the optical dielectric constant and  $\epsilon$  is the static dielectric constant. The inner reorganization energy was estimated to be  $\lambda_i \approx 0$ .

The Marcus equation is:

$$\Delta G_{ET}^\ddagger = \Delta G_0^\ddagger \left( 1 + \frac{\Delta G_r}{4\Delta G_0^\ddagger} \right)^2 \quad (2)$$

where  $\Delta G_r$  is the reaction energy and  $\Delta G_0^\ddagger$  is the intrinsic barrier. Within the Marcus Model the equation 3 was used, while in the Savéant Model equation 4 was used:

$$\Delta G_0^\ddagger = \frac{\lambda}{4} = \frac{\lambda_i + \lambda_0}{4} \quad (3)$$

$$\Delta G_0^\ddagger = \frac{\lambda}{4} = \frac{\lambda_i + \lambda_0 + BDFE}{4} \quad (4)$$

where BDFE stand for bond dissociation free energy of diiodocubane (60.0 kcal/mol).

#### Single Electron Transfer from 8<sup>-</sup> to 1 by Marcus-Hush Model

Solvent	$\Delta G$ (kcal/mol)	$\epsilon_{op}$	$\epsilon$	$\lambda_0$ (kcal/mol)	$\lambda_i$ (kcal/mol)	$\lambda$ (kcal/mol)	$\Delta G_{ET}^\ddagger$
Methanol	+3.1	32.6	1.76	17.6	0.0	17.6	+6.1
$a_0(7^-)$	5.38 Å						
$a_0(1a)$	4.79 Å						

#### Single Electron Transfer from 10<sup>-</sup> to 1 by Marcus-Hush Model

Solvent	$\Delta G$ (kcal/mol)	$\epsilon_{op}$	$\epsilon$	$\lambda_0$ (kcal/mol)	$\lambda_i$ (kcal/mol)	$\lambda$ (kcal/mol)	$\Delta G$ S75
Methanol	+6.1	32.6	1.76	17.6	0.0	17.6	+8.0
$a_0(9^-)$	5.51 Å						
$a_0(1a)$	4.79 Å						

### Single Electron Transfer from 13b<sup>-</sup> to 2 by Savéant Model

Solvent	$\Delta G$ (kcal/mol)	$\epsilon_{op}$	$\epsilon$	$\lambda_0$ (kcal/mol)	$\lambda_i$ (kcal/mol)	$\lambda$ (kcal/mol)	$\Delta G_{ET}^\ddagger$
Methanol	-44.5	32.6	1.76	18.6	0.0	79.0	+3.8
$a_0(12b^{\cdot-})$	5.05 Å						
$a_0(1b)$	4.55 Å						

### Single Electron Transfer from 13d<sup>-</sup> to 2 by Savéant Model

Solvent	$\Delta G$ (kcal/mol)	$\epsilon_{op}$	$\epsilon$	$\lambda_0$ (kcal/mol)	$\lambda_i$ (kcal/mol)	$\lambda$ (kcal/mol)	$\Delta G_{ET}^\ddagger$
Methanol	-40.2	32.6	1.76	18.2	0.0	78.6	+4.7
$a_0(12d^{\cdot-})$	5.36 Å						
$a_0(1b)$	4.55 Å						

### **3.3.3 DFT functional and post-HF methods for Activation Gibb Energies ( $\Delta G^\ddagger$ , in kcal/mol), Activation Enthalpy ( $\Delta H^\ddagger$ , in kcal/mol)**

Table 1. Computed Activation Gibb Energies ( $\Delta G^\ddagger$ , in kcal/mol), Activation Enthalpy ( $\Delta H^\ddagger$ , in kcal/mol) in the solvent and Kinetic parameters computed (log k) for the reaction between radical **15** and <sup>-</sup>SPh. The numbers in parenthesis are in the gas phase.

Functional	$\Delta H^\ddagger$	$\Delta G^\ddagger$	Log k
M06-2X/def2-TZVP (results presented in the manuscript)	8.7 (-5.2)	17.6 (4.2)	1.6
M06-HF/def2-TZVP	6.3(-8.3)	15.9 (1.6)	3.8
M06-L/def2-TZVP	9.2 (-4.7)	17.9 (5.0)	1.2
M06/def2-TZVP	7.2 (-5.8)	18.4 (5.5)	3.0
B3LYP/def2-TZVP	10.9 (-2.9)	19.2 (6.5)	-0.3
B3LYP+D3(BJ)/def2-TZVP	5.8 (-8.2)	14.3 (2.2)	4.3
B3PW91+D3(BJ)/def2-TZVP	4.1 (-9.0)	12.9 (1.4)	5.9
BH&HLYP/def2-TZVP	15.6 (2.0)	27.1 (12.4)	-4.6
PBE0/def2-TZVP	8.2 (-4.7)	16.3 (5.1)	2.1
PBE0+D3(BJ)/def2-TZVP	4.9 (-8.0)	14.0 (1.8)	5.1
TSPPH+D3(BJ)/def2-TZVP	3.4 (-9.5)	12.0 (1.4)	6.4
wB97/def2-TZVP	12.0 (-1.8)	22.6 (8.7)	-1.4
wB97X/def2-TZVP	11.6(-2.1)	22.8 (7.8)	-1.0

wB97XD/def2-TZVP	9.5 (-4.4)	21.3 (4.4)	1.0
DPLNO-CCSD(T)/cc-pVTZ//M06-2X/def2-TZVP	7.2 (-5.8)	16.0 (3.0)	3.0

Kinetic parameters computed ( $\log k$ ) were calculated from the Eyring-Polanyi equation (see below). This equation comes actually from the extension of Arrhenius equation but employing the Transition State Theory. The logarithmic expression is

$$\log k = \log \kappa \frac{k_B T}{h} - \frac{\Delta G^\ddagger}{2.303RT}$$

$$\log k = \log \kappa \frac{k_B T}{h} + \frac{\Delta S^\ddagger}{2.303R} - \frac{\Delta H^\ddagger}{2.303RT}$$

where  $\kappa$  is the transmission coefficient (normally taken as the unit),  $k_B$  is the Boltzmann's constant,  $h$  is Planck's constant,  $\Delta S^\ddagger$  activation entropy and  $\Delta H^\ddagger$  activation enthalpy.