Supporting Information

Strong Intramolecular Calcium-π Interactions to Aryl Substituents – Requirements and Limitations

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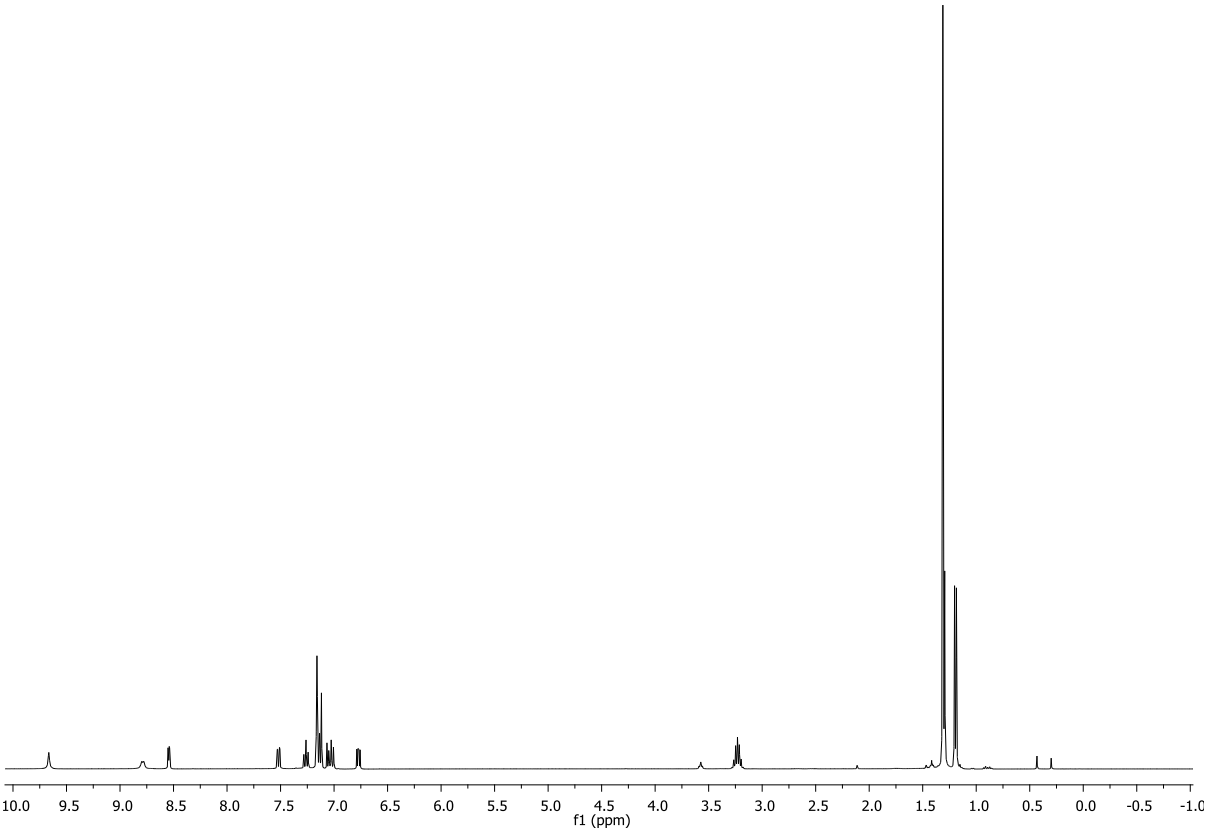
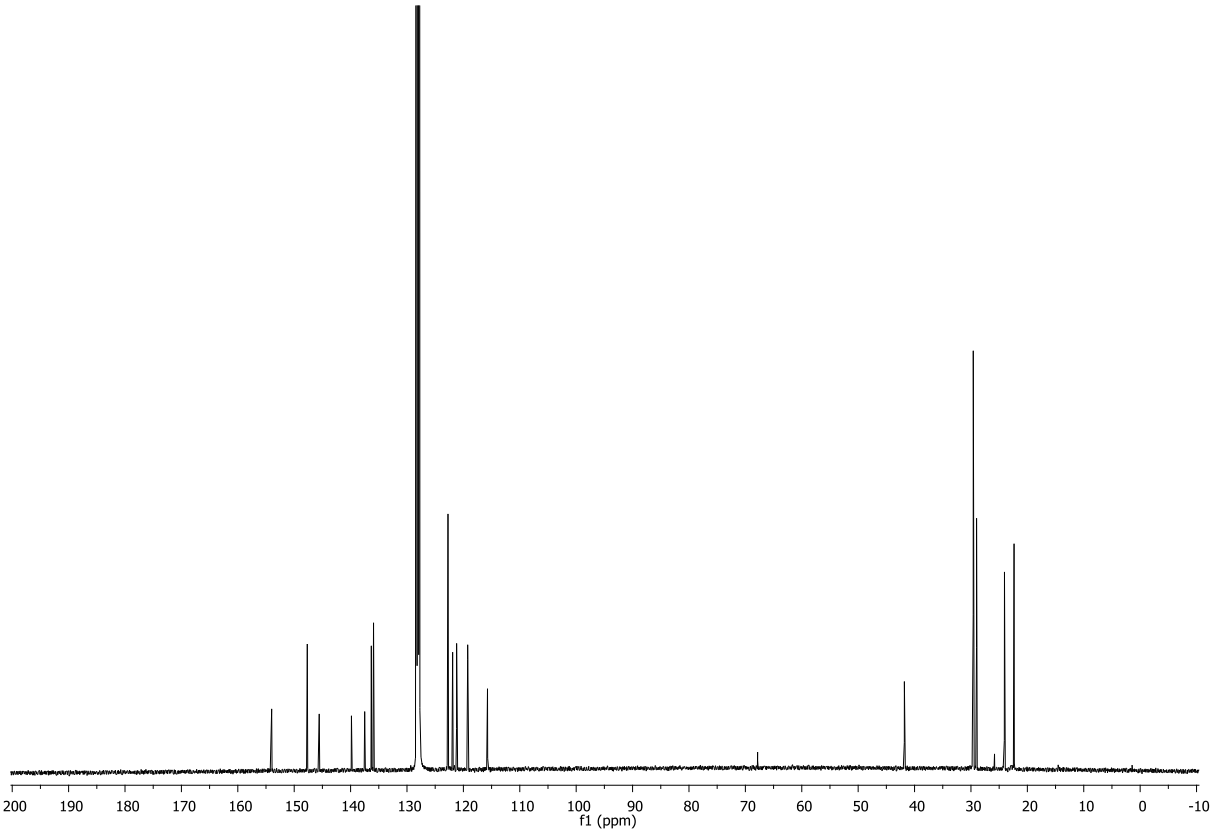
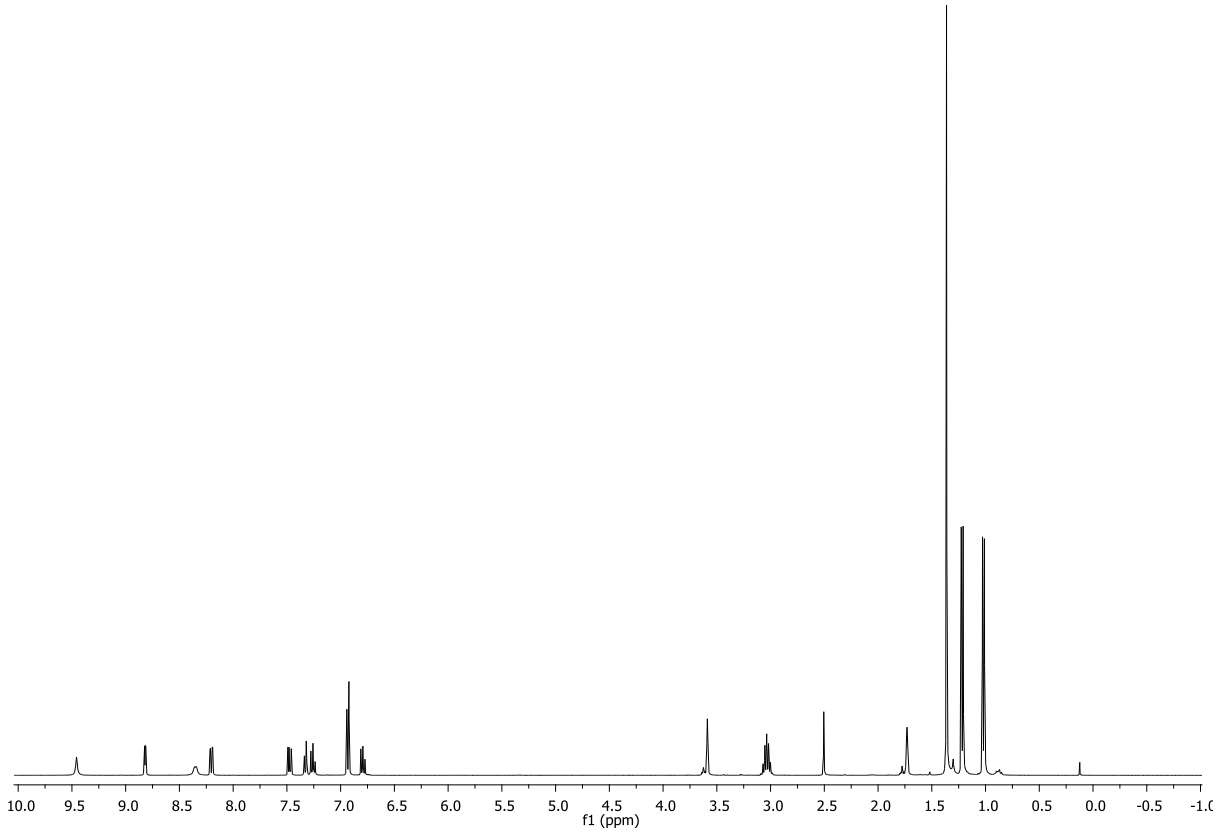
Content:



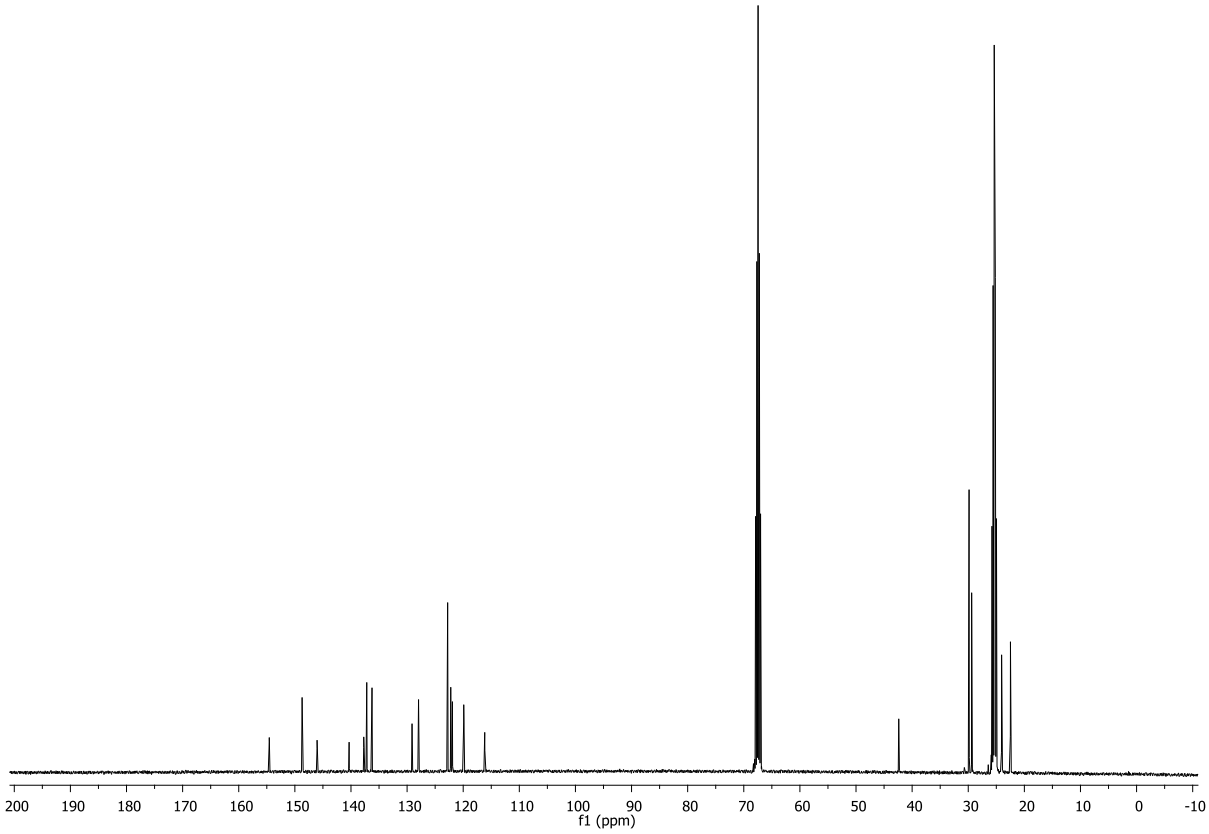
^{1}H NMR Spectrum of Compound **1a** in C_6D_6



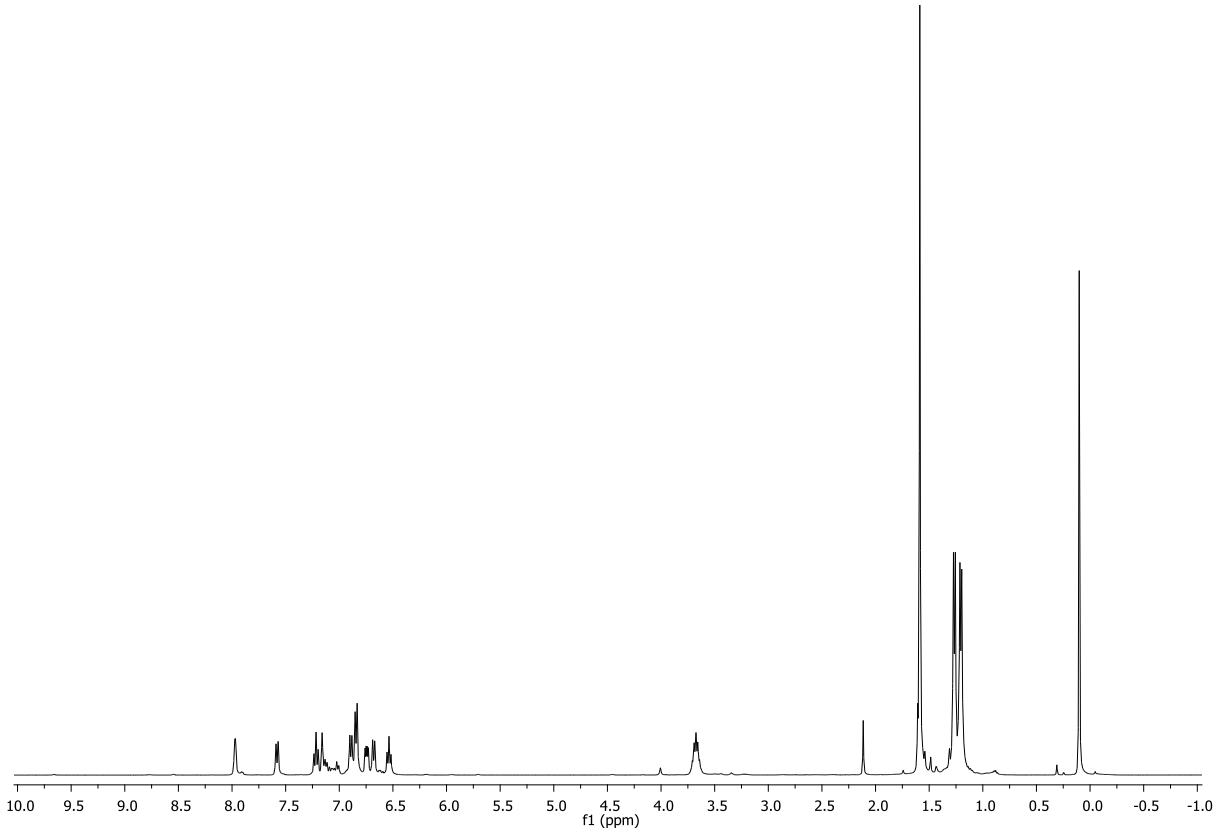
^{13}C{^{1}H} NMR Spectrum of Compound **1a** in C_6D_6



^{1}H NMR Spectrum of Compound **1a** in [D_8]THF



^{13}C{^{1}H} NMR Spectrum of Compound **1a** in [D_8]THF



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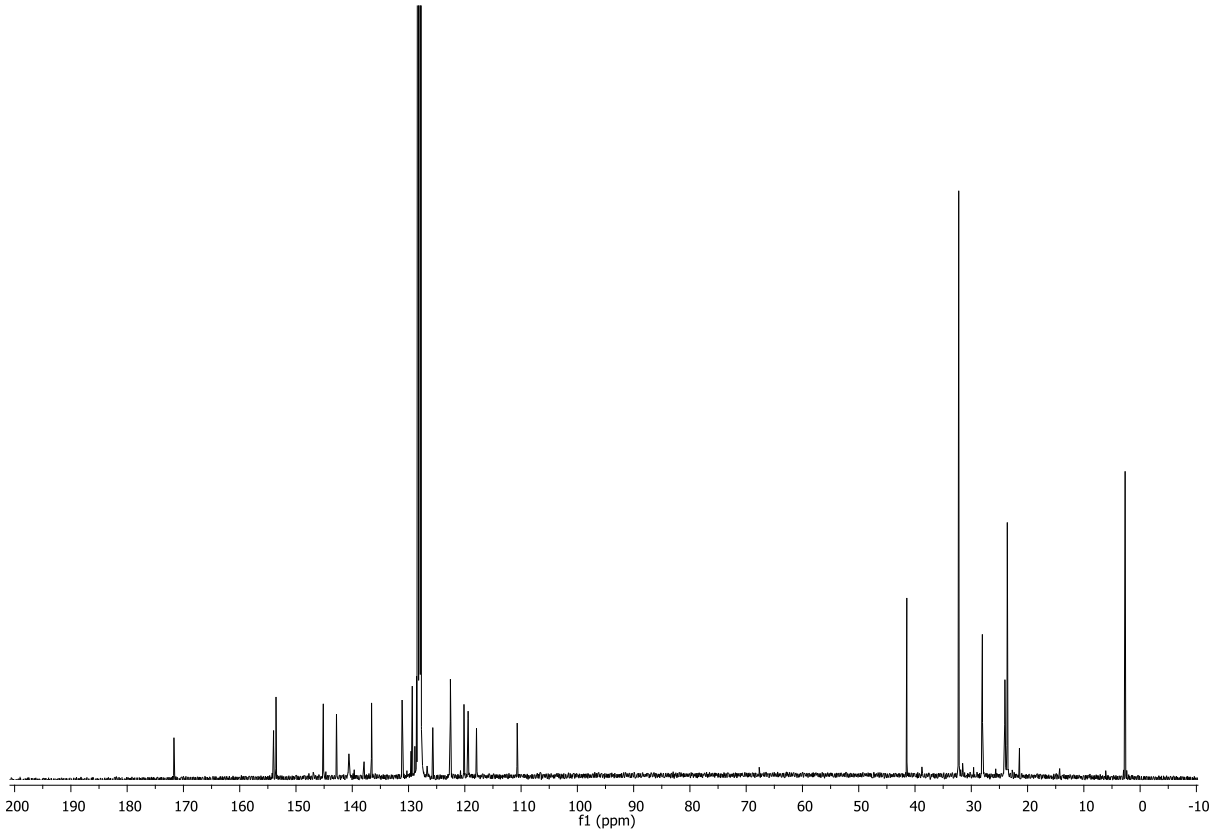
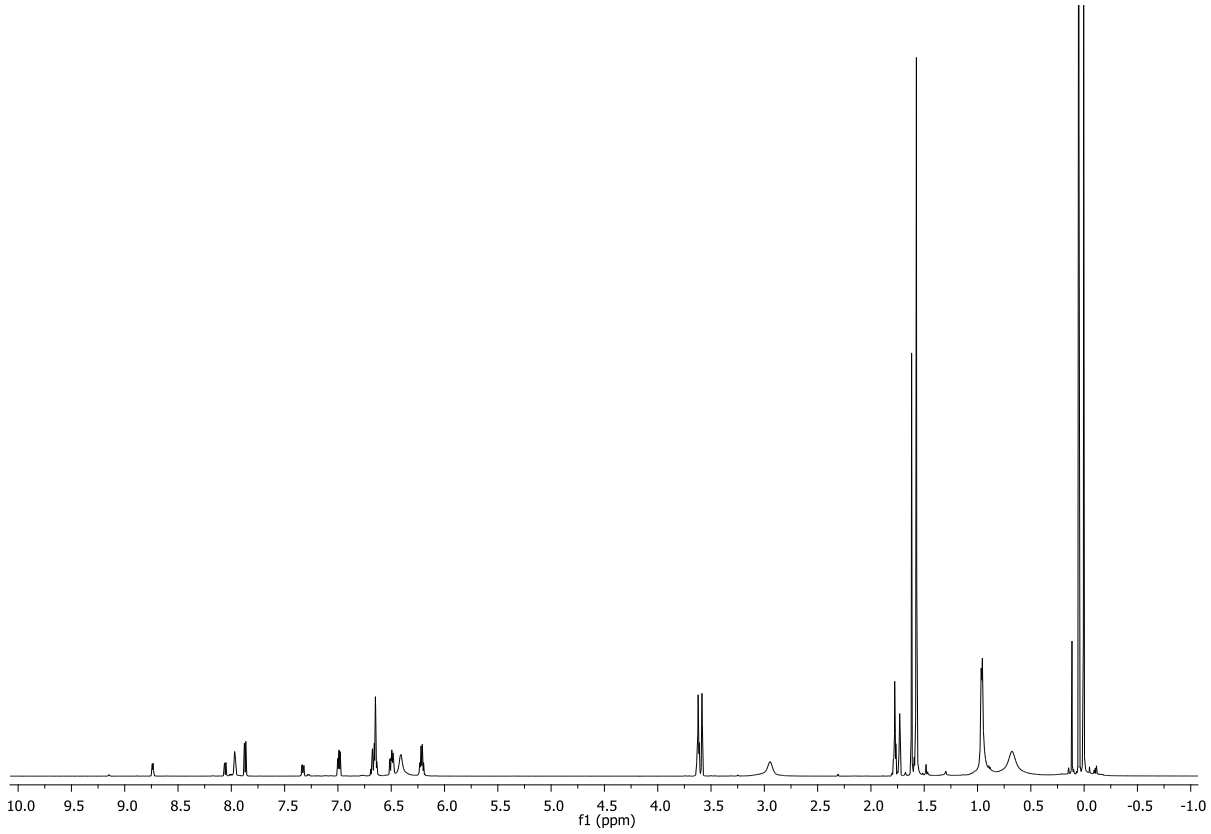
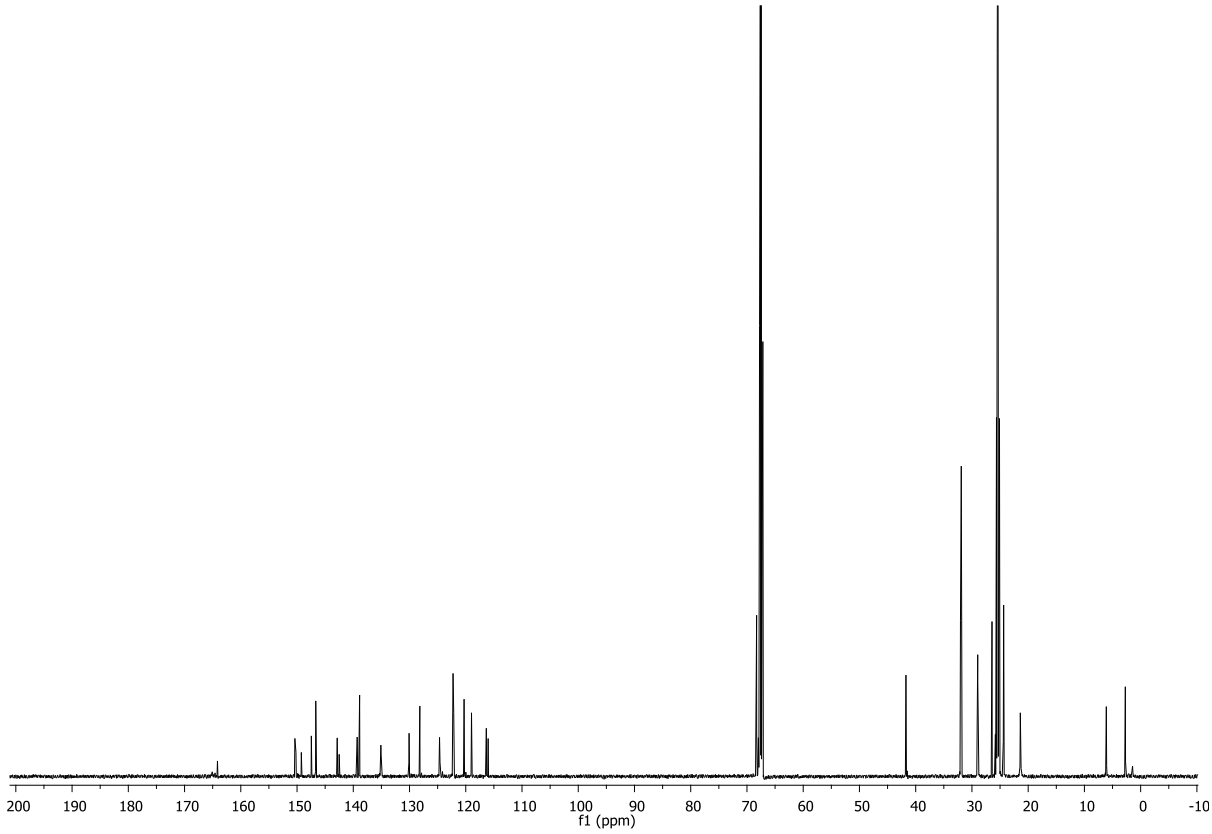


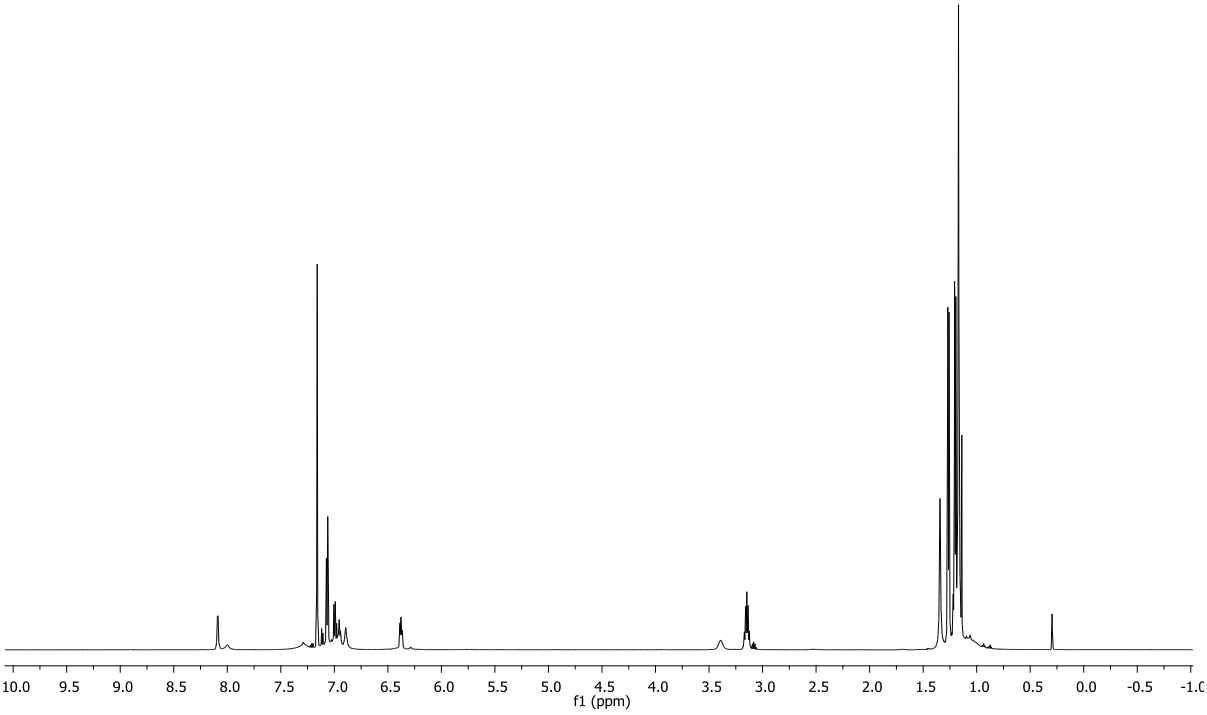
^{13}C{^{1}H} NMR Spectrum of Compound **2a** in C_6D_6



^{1}H NMR Spectrum of Compound **3a** in [D_8]THF



^{13}C{^{1}H} NMR Spectrum of Compound **3a** in [D_8]THF



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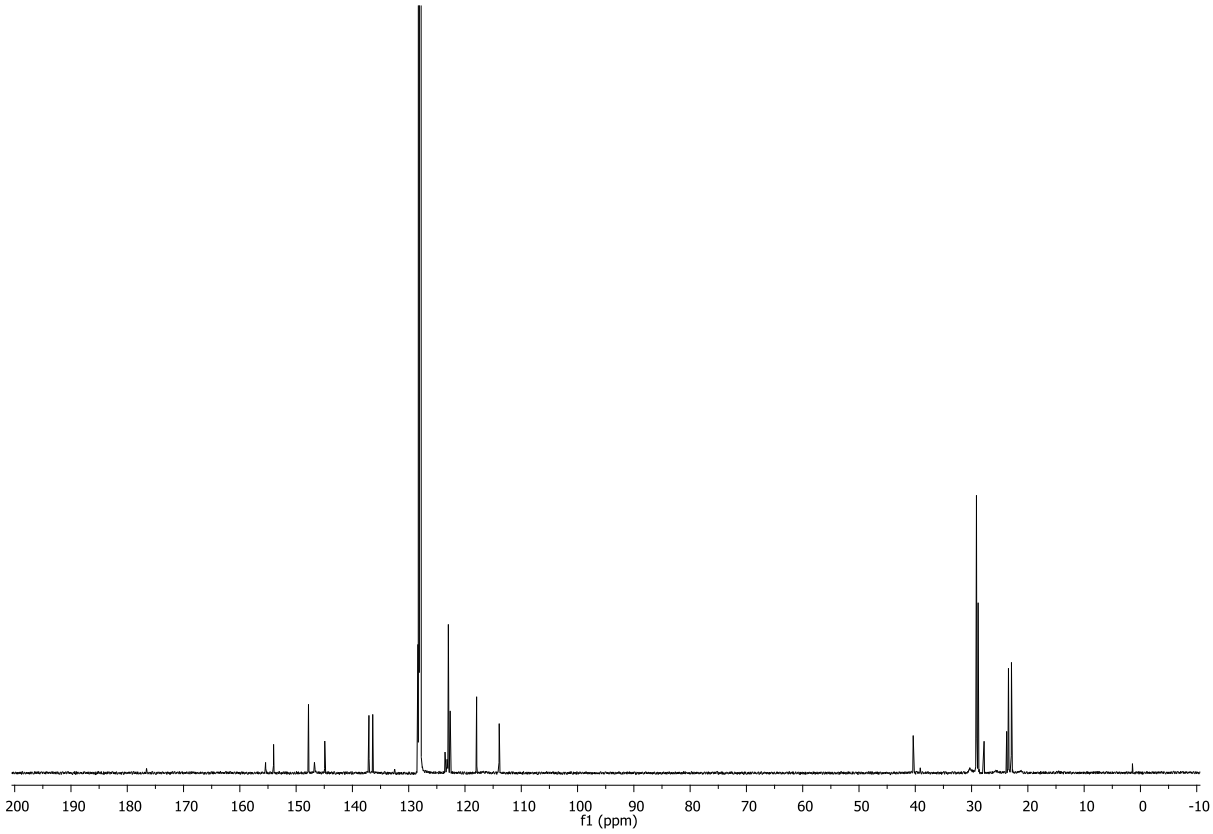
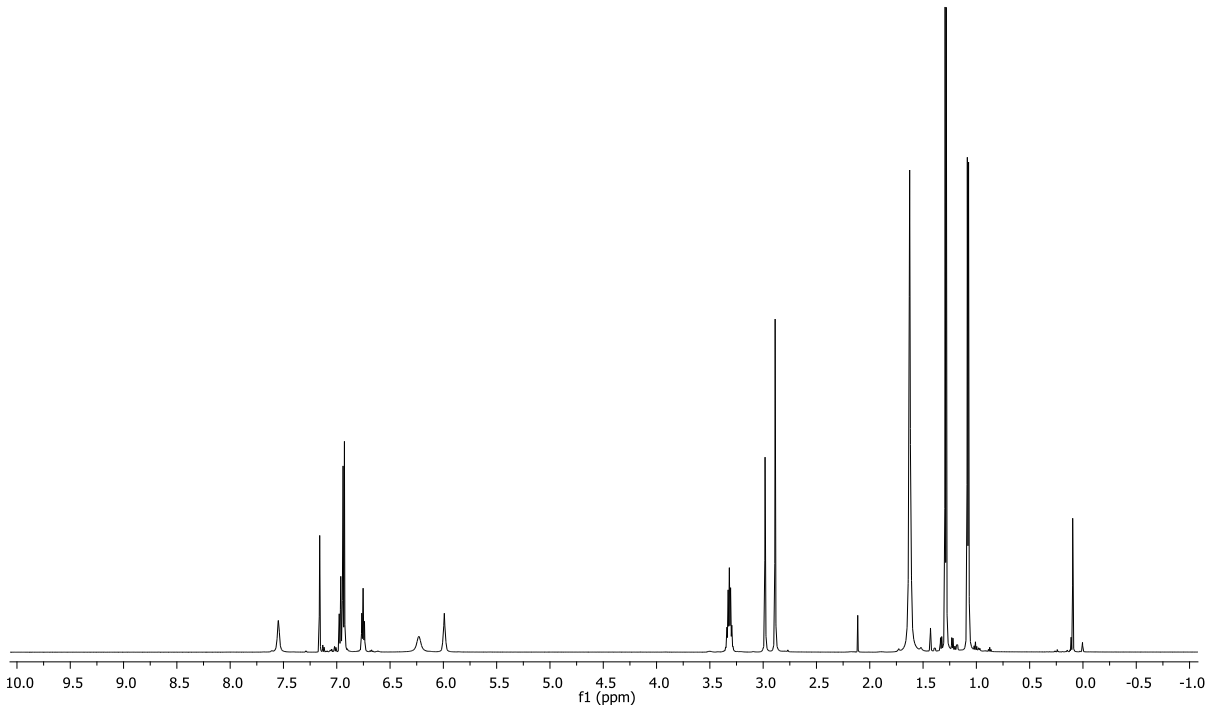
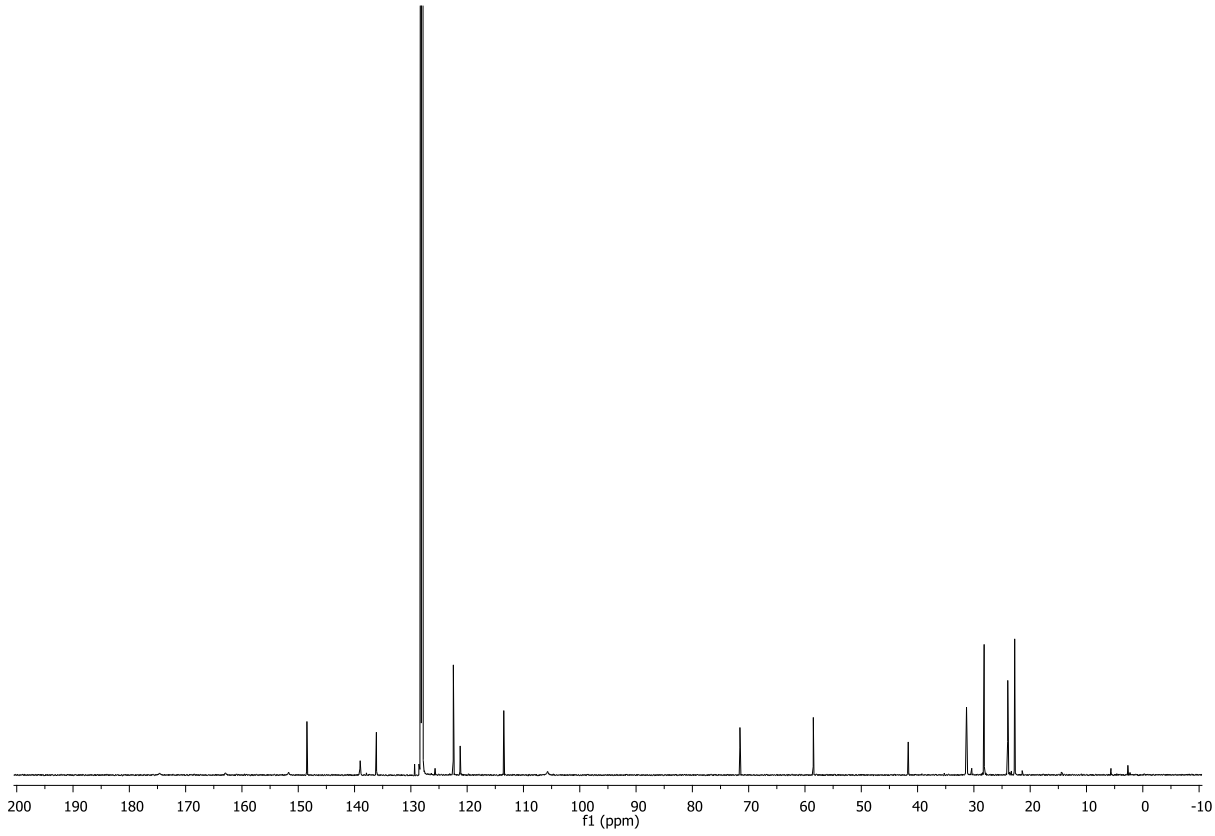


^{13}C{^{1}H} NMR Spectrum of Compound **1b** in C_6D_6



^{1}H NMR Spectrum of Compound **2b** in C_6D_6



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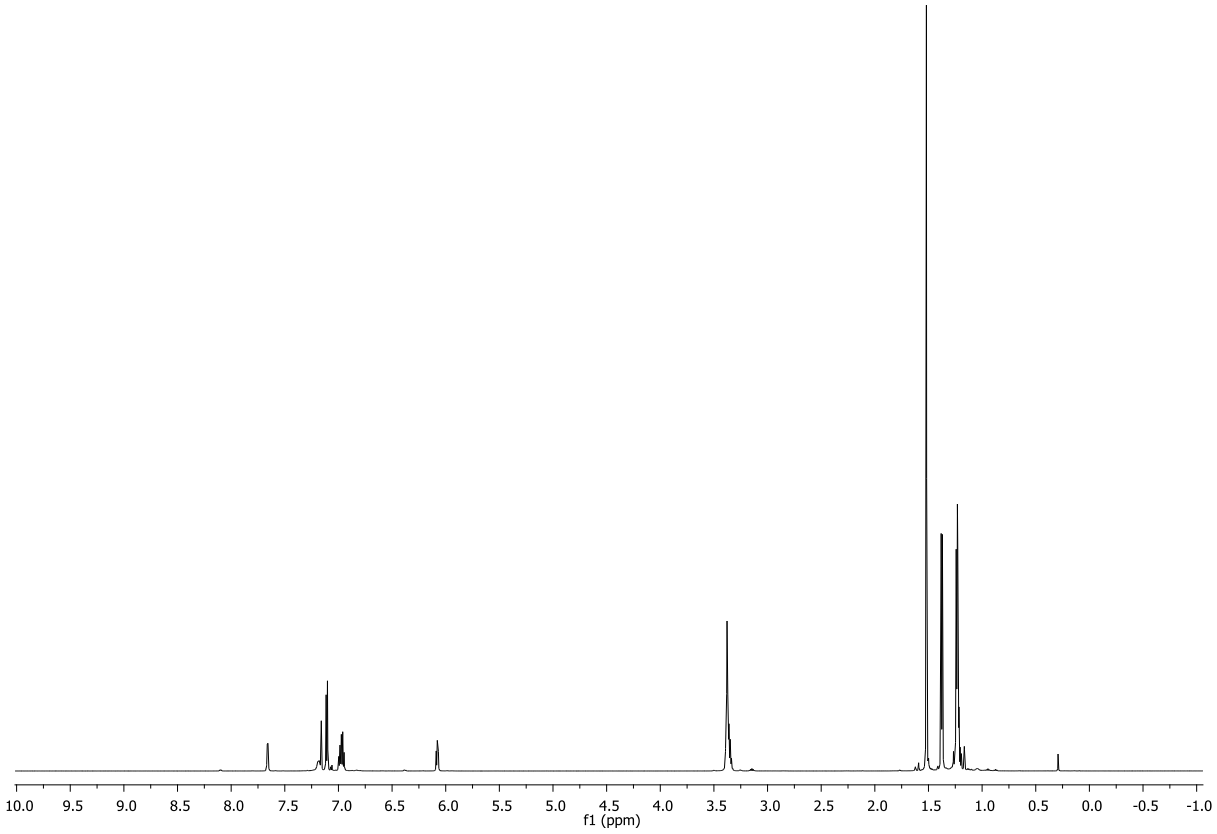
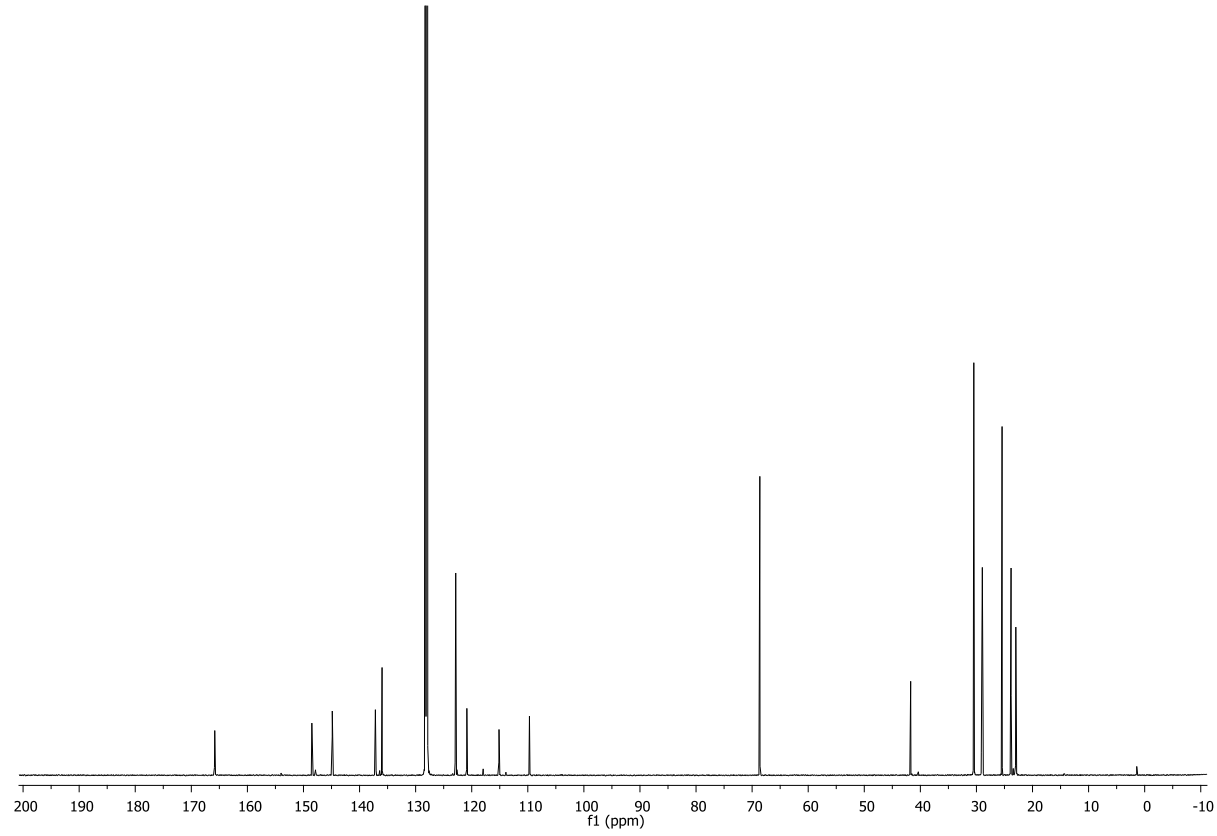
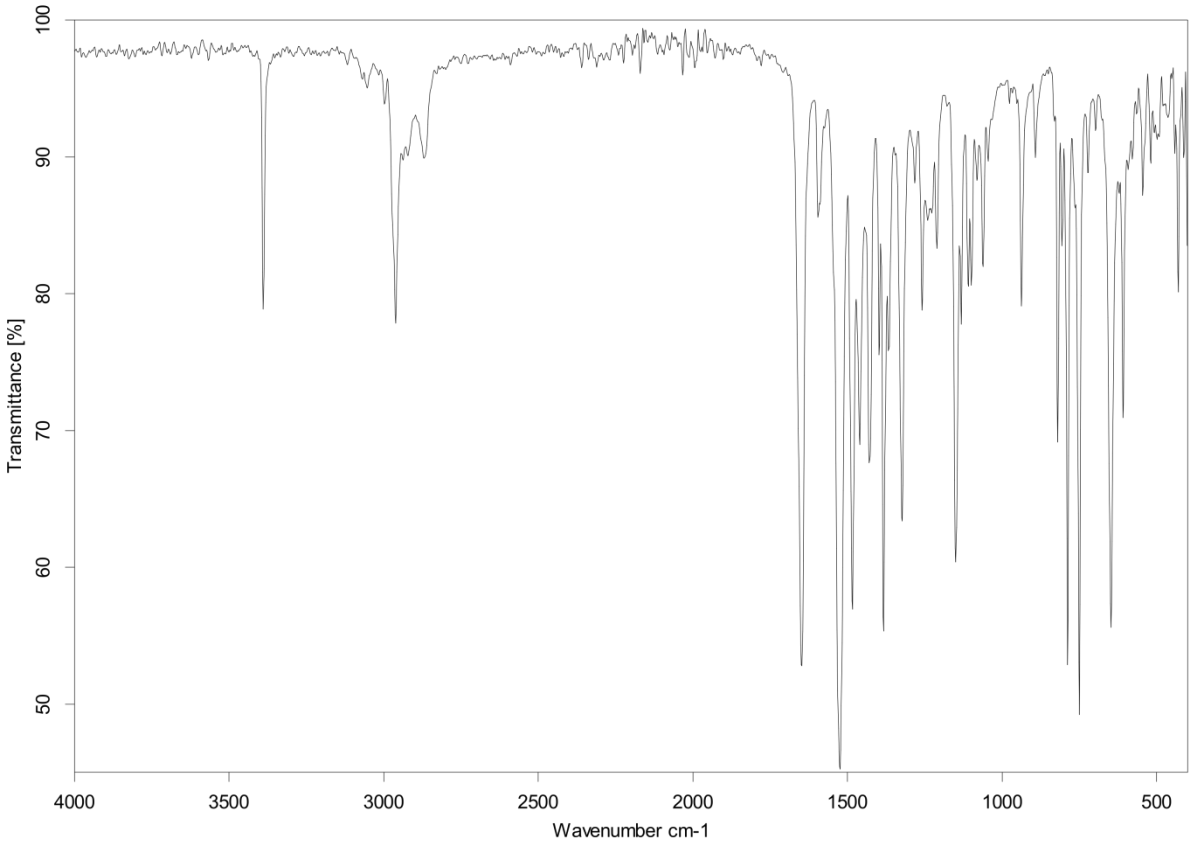


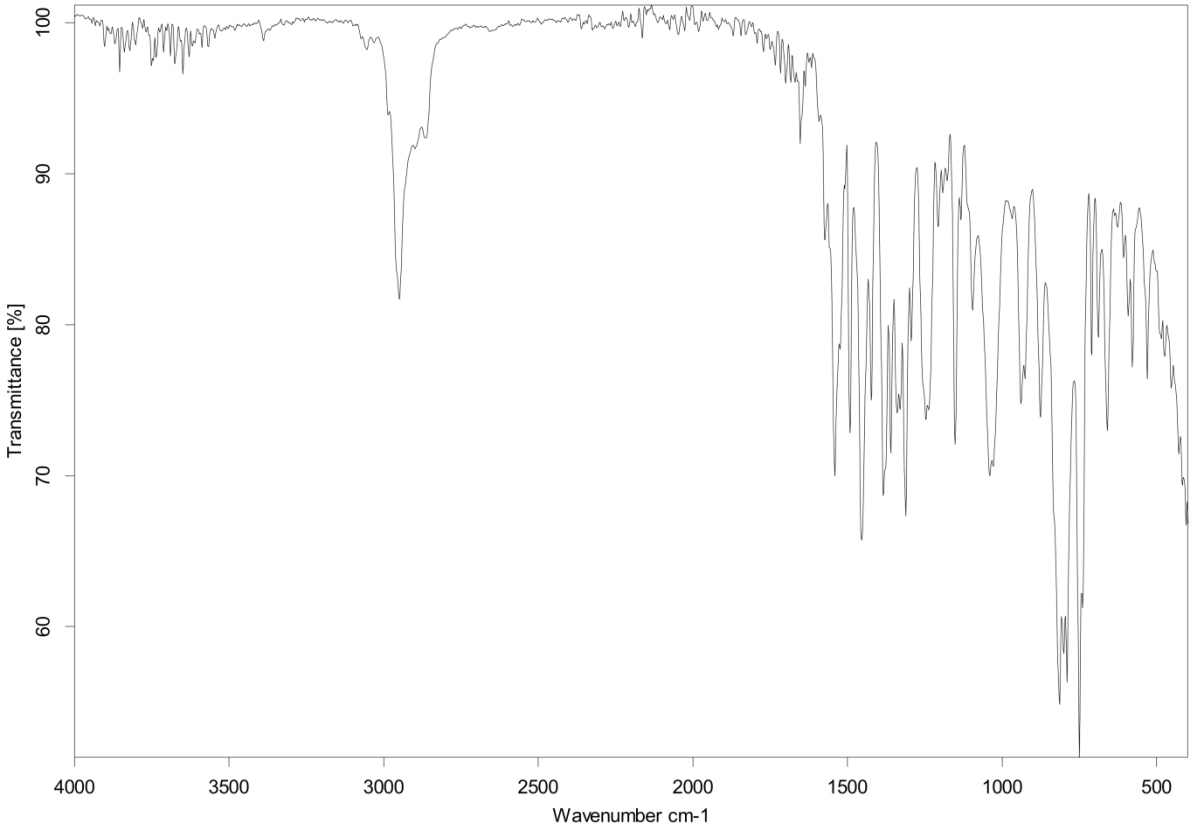
^{1}H NMR Spectrum of Compound **3b** in C_6D_6



^{13}C{^{1}H} NMR Spectrum of Compound **3b** in C_6D_6



IR-spectrum of **1a**



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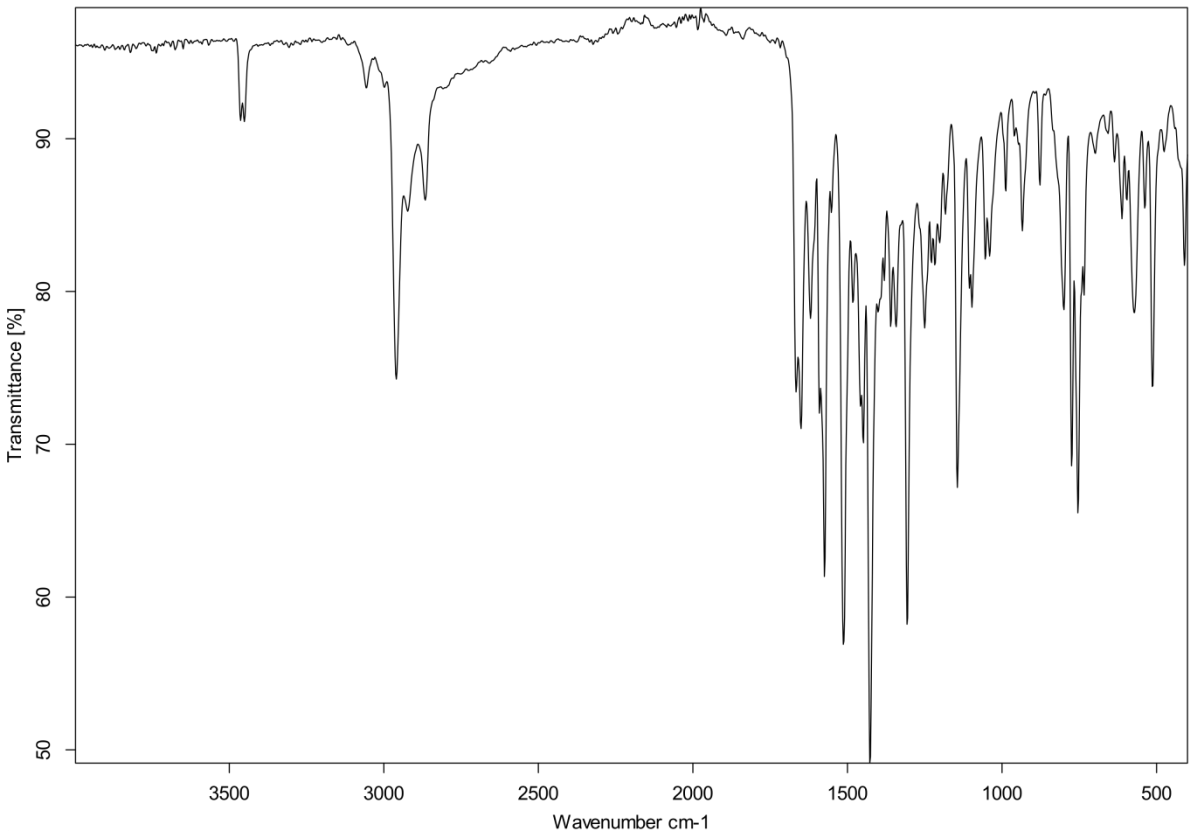

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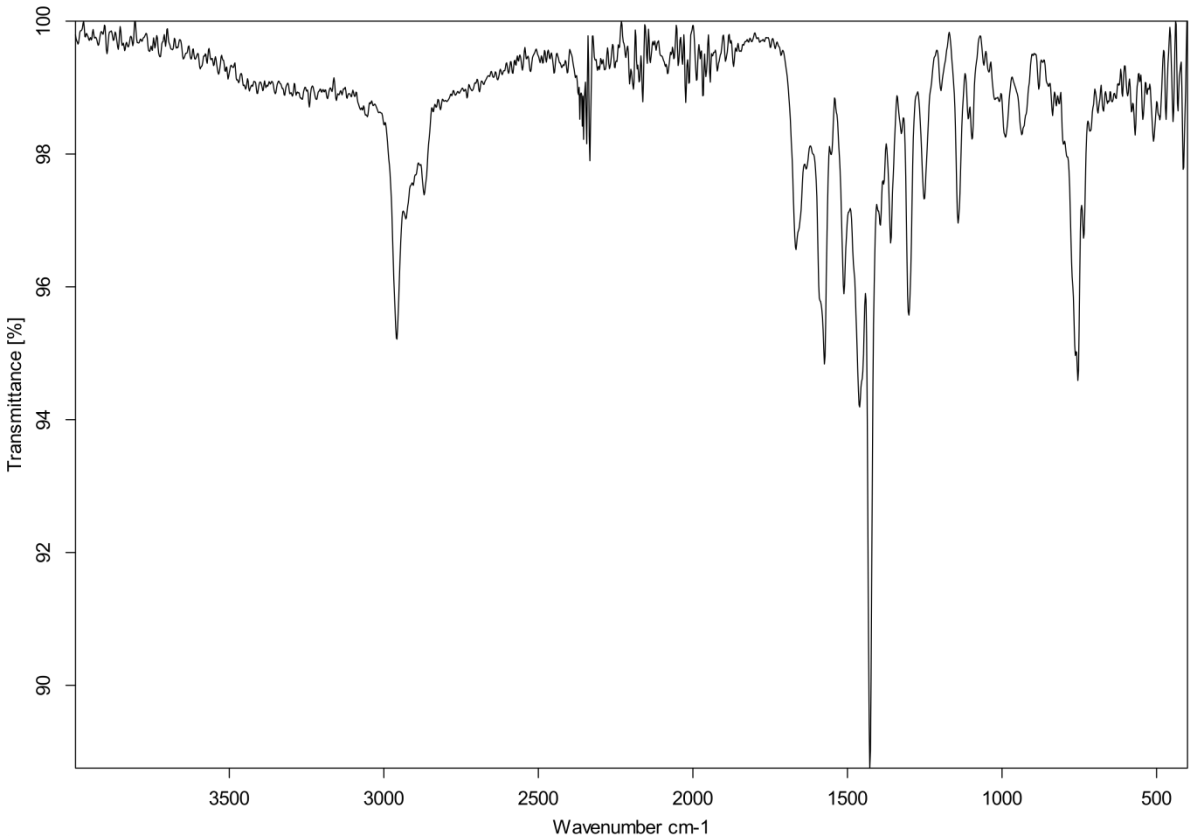
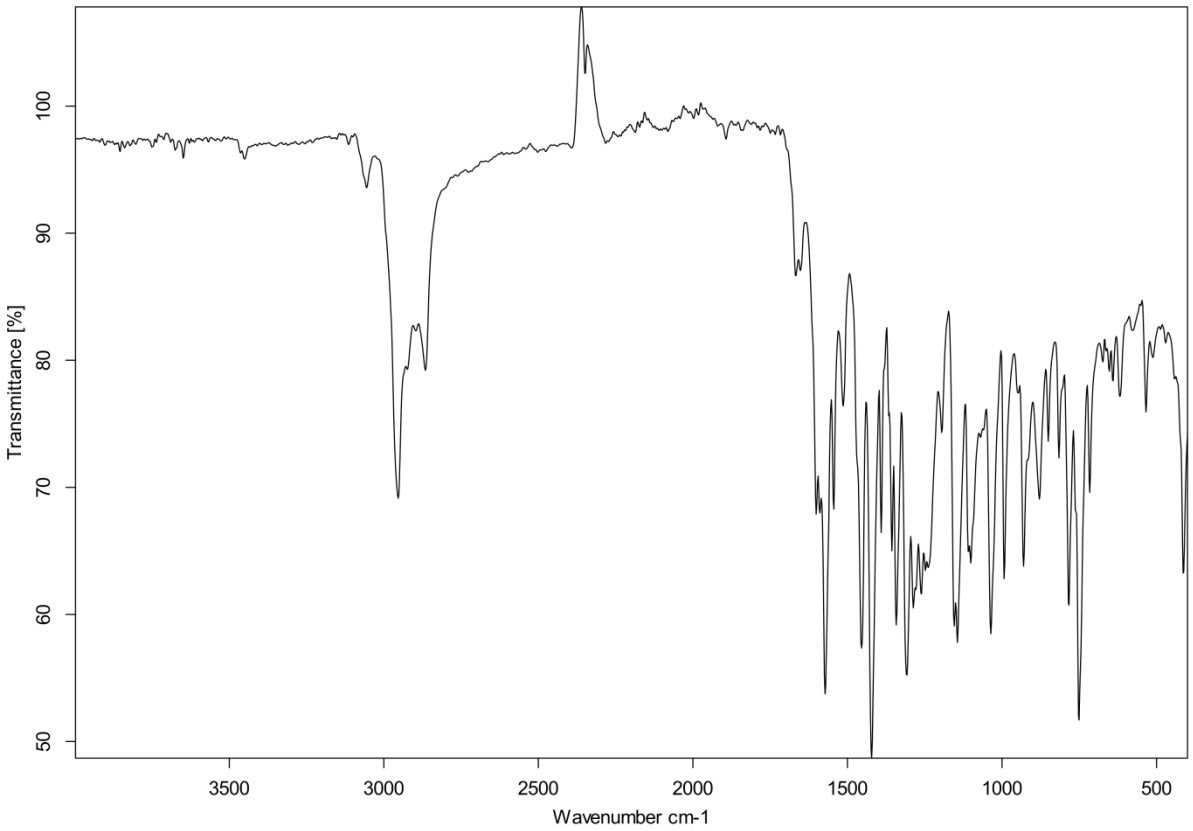
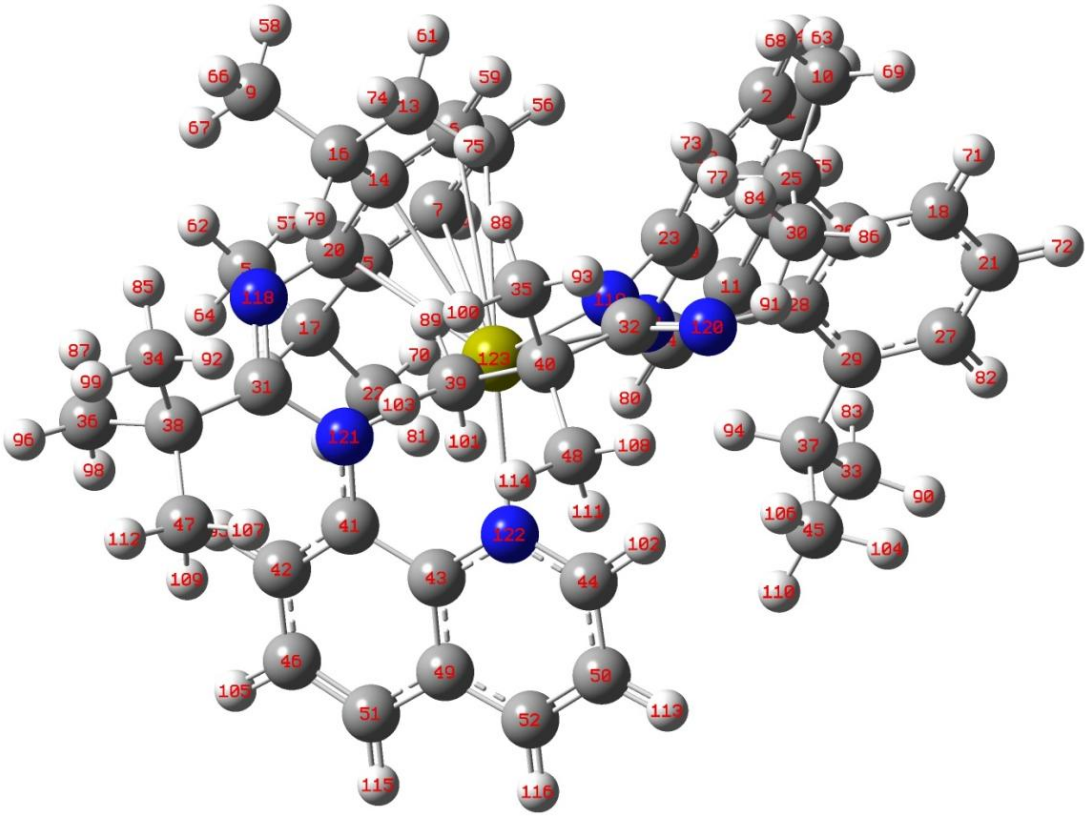


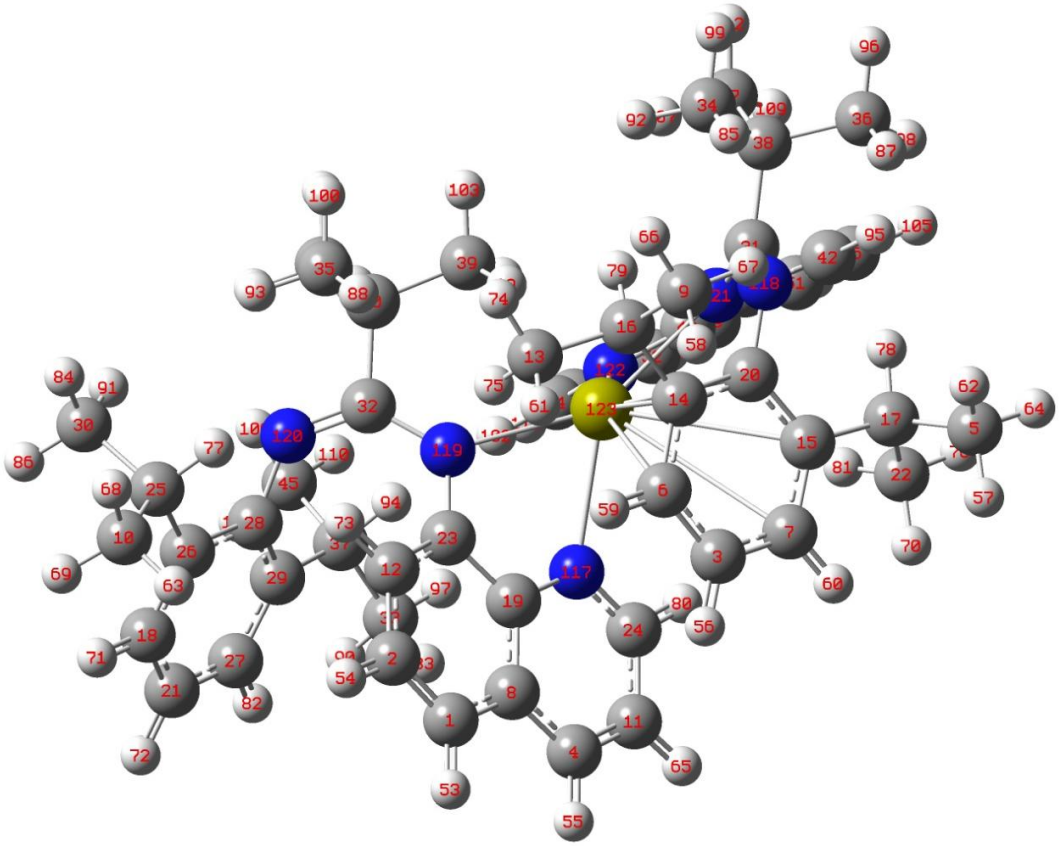
IR-spectrum of **2b**

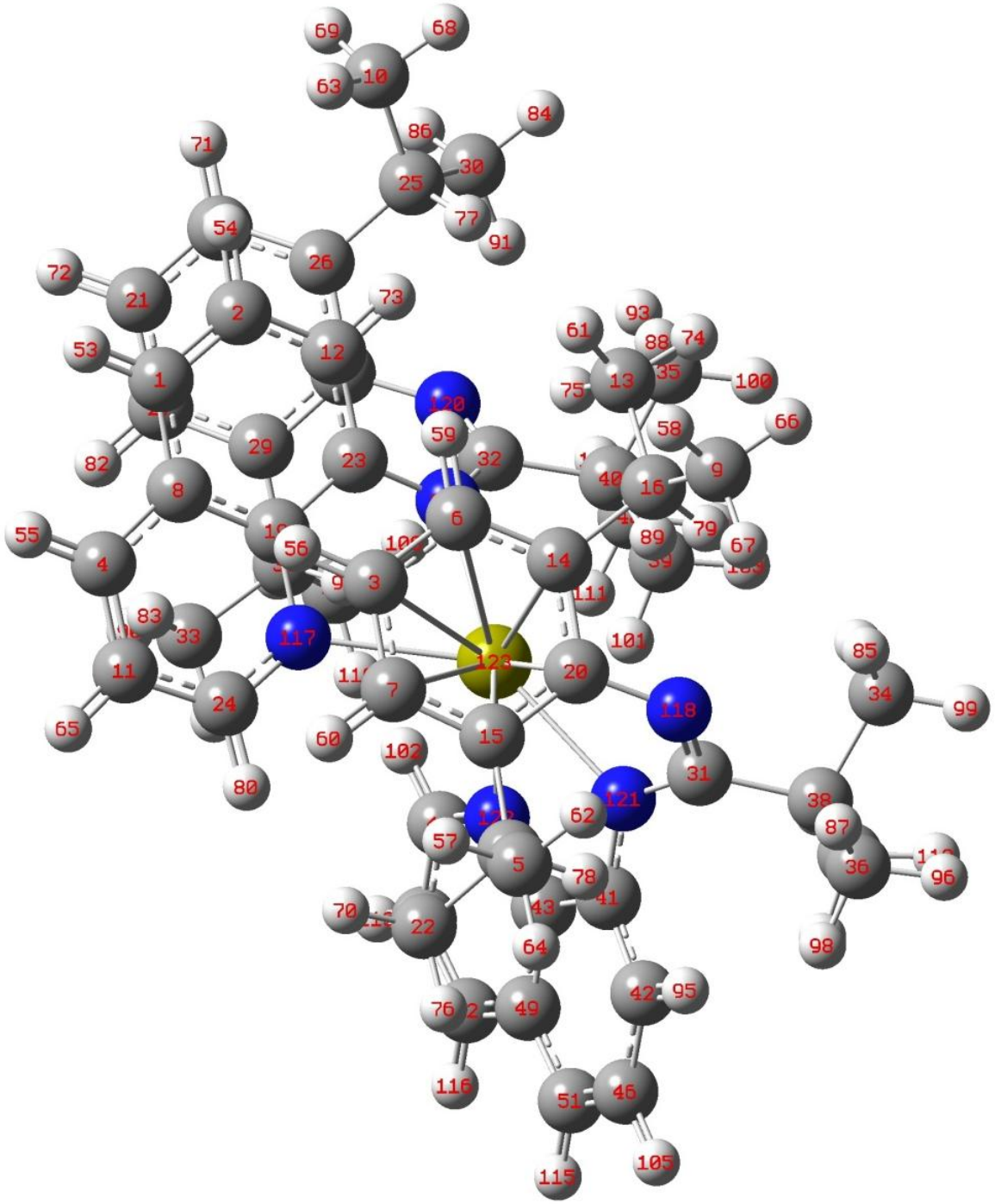


IR-spectrum of **3b**

Quantum Chemical Calculations: Gaussian09, DFT/B3LYP, 6-31G(d,p) charge analyze: NBO (color code: grey carbon, white hydrogen, blue nitrogen, yellow calcium)



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XYZ-Data (coordinates of optimized structure):

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N	-3.09932781	-0.37337967	1.12047755
N	-0.87000014	-1.57871246	2.20255343
Ca	-0.86621805	-0.19115103	0.09348013

Charge distribution:

Number	Atom	Charge
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7	C	-0,23538
8	C	-0,07969
9	C	-0,67446
10	C	-0,68144
11	C	-0,29171
12	C	-0,25288
13	C	-0,68857
14	C	-0,10615
15	C	-0,05384
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17	C	-0,2605
18	C	-0,23807
19	C	0,1701
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55	H	0,24671
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57	H	0,22701
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59	H	0,25187
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64	H	0,23321
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Literature

Gaussian09

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009

B3LYP:

D. Becke, “Density-functional thermochemistry. III. The role of exact exchange,” *J. Chem. Phys.*, **98** (1993) 5648-52.

NBO:

NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold