

Electronic Supplementary Information for

On the reactivity of complexes $[\text{Ni}(\text{NHC})_2]$ with CS_2

Martin S. Luff^[a], Celine S. Corsei, Udo Radius^{*[a]}

[a] Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

*Corresponding author Email address: u.radius@uni-wuerzburg.de

Table of Content

1	NMR Spectra	2
2	IR Spectra.....	8
3	High Resolution Mass Spectrometry (HRMS) Data.....	11
4	Cartesian Coordinates of Geometry Optimized Complexes.....	13

1 NMR Spectra

[Ni(*l*iPr^{Me})₂(η^2 -CS₂)] (1a)

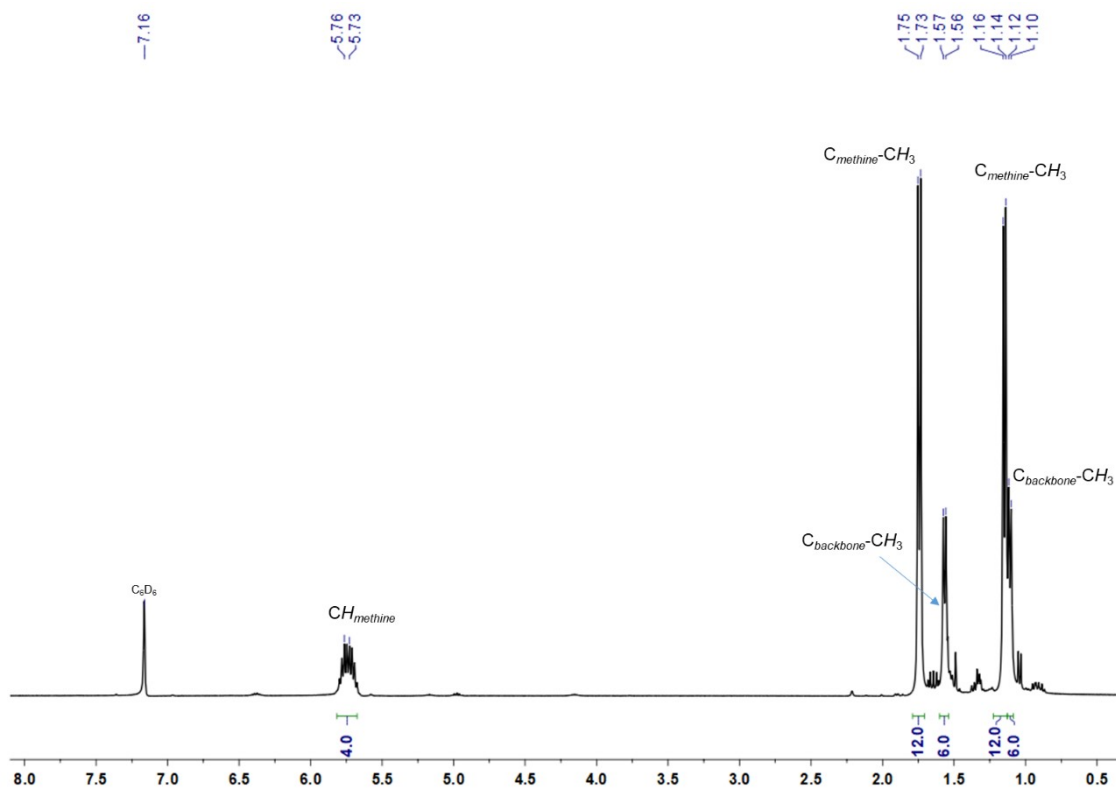


Figure S1. ¹H NMR spectrum of [Ni(*l*iPr^{Me})₂(η^2 -CS₂)] (1a) in C₆D₆.

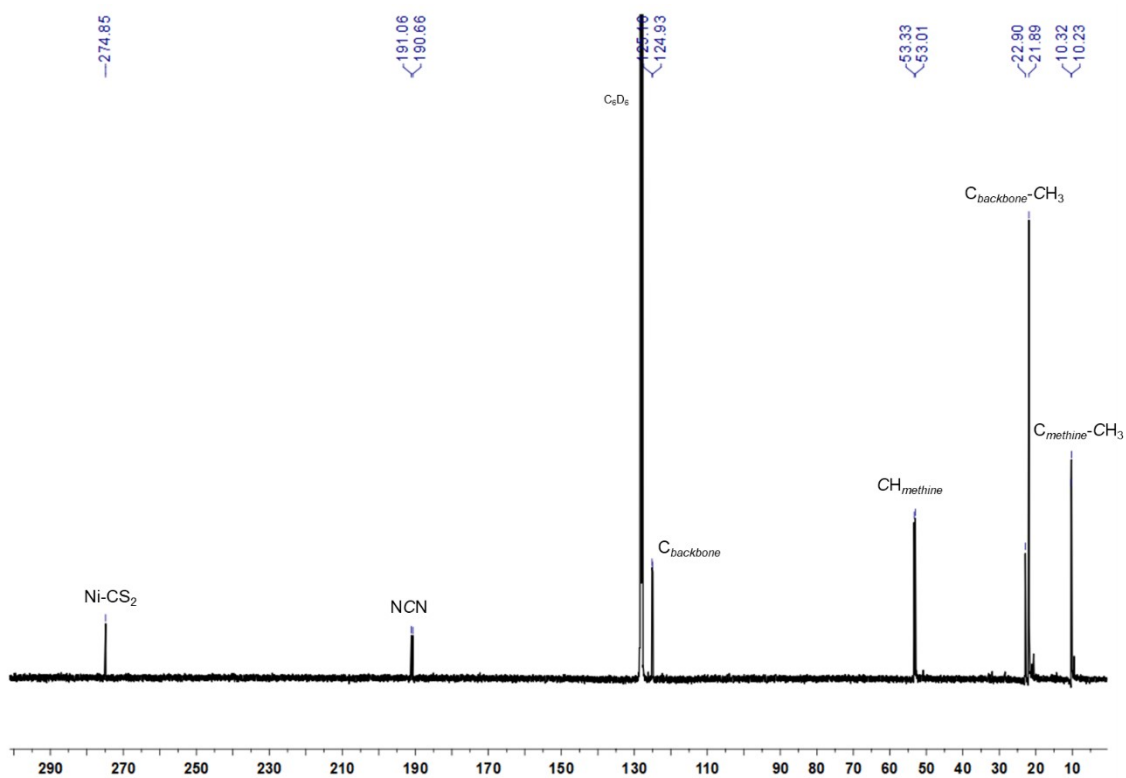


Figure S2. ¹³C{¹H} NMR spectrum of [Ni(*l*iPr^{Me})₂(η^2 -CS₂)] (1a) in C₆D₆.

[Ni(*l*iPr)₂(η^2 -CS₂)] (1b)

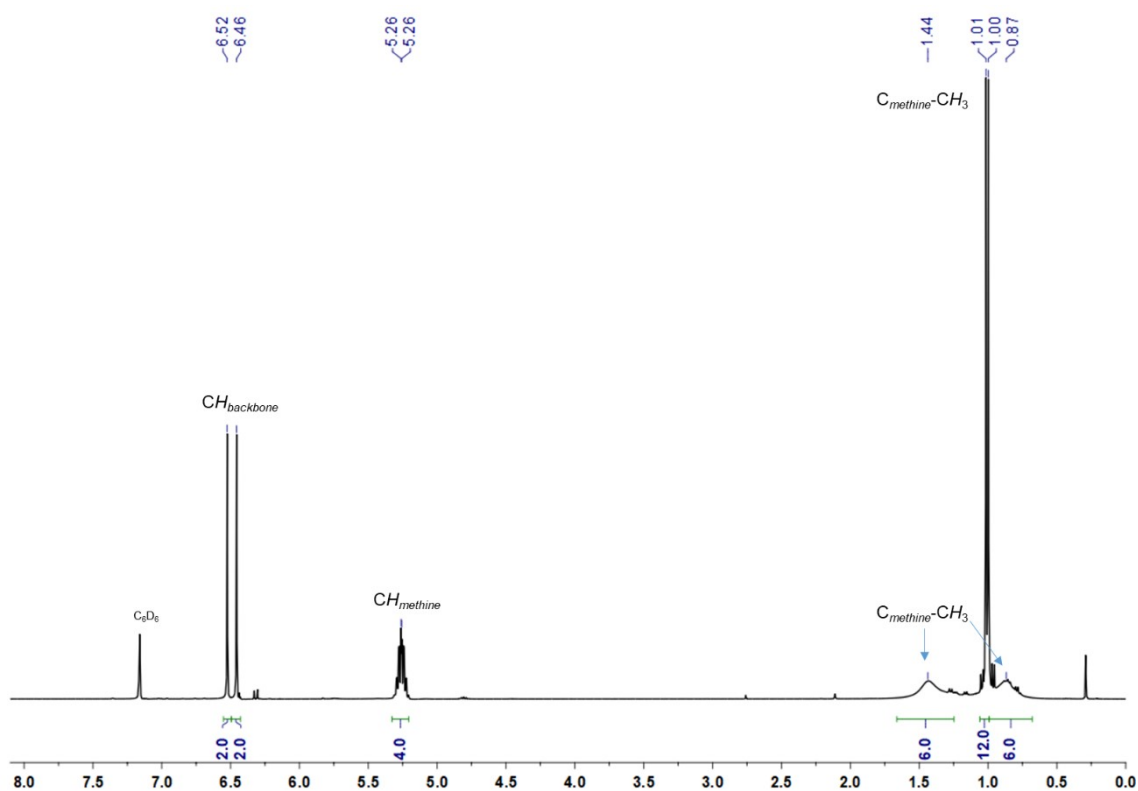


Figure S3. ¹H NMR spectrum of [Ni(*l*iPr)₂(η^2 -CS₂)] (1b) in C₆D₆.

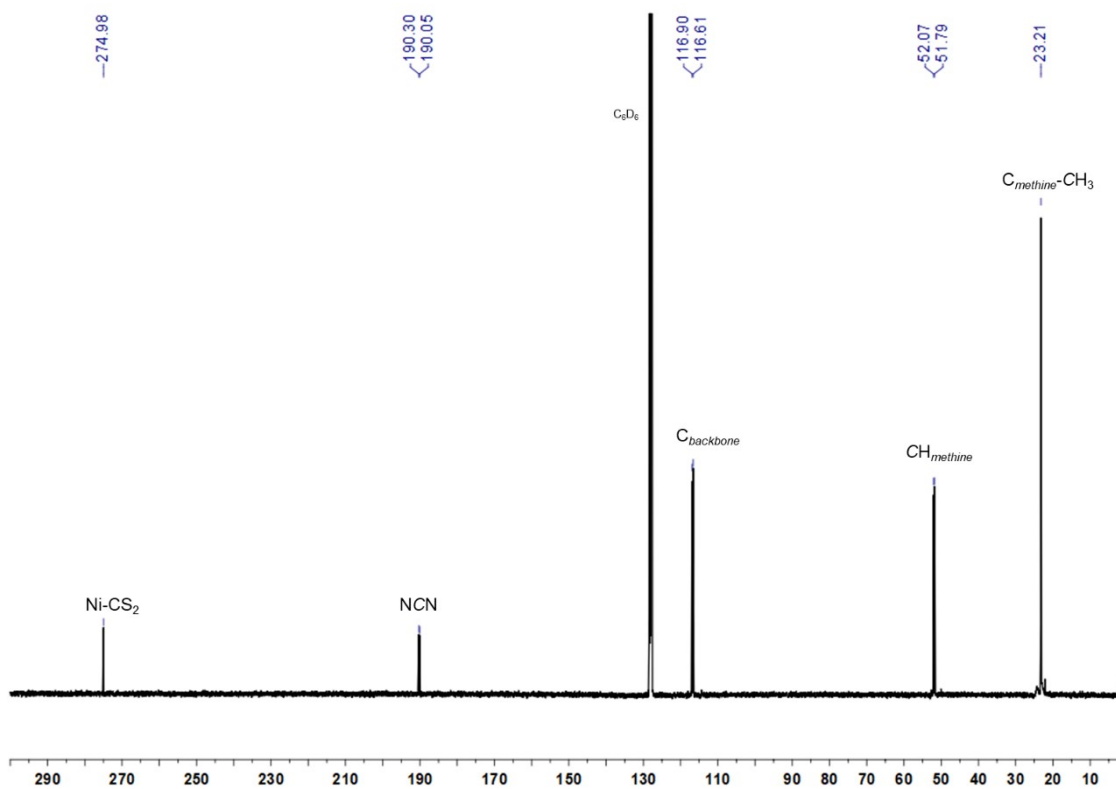


Figure S4. ¹³C{¹H} NMR spectrum of [Ni(*l*iPr)₂(η^2 -CS₂)] (1b) in C₆D₆.

[{Ni(IDipp)(μ^2 -CS₂)₂}]₂ (2c)

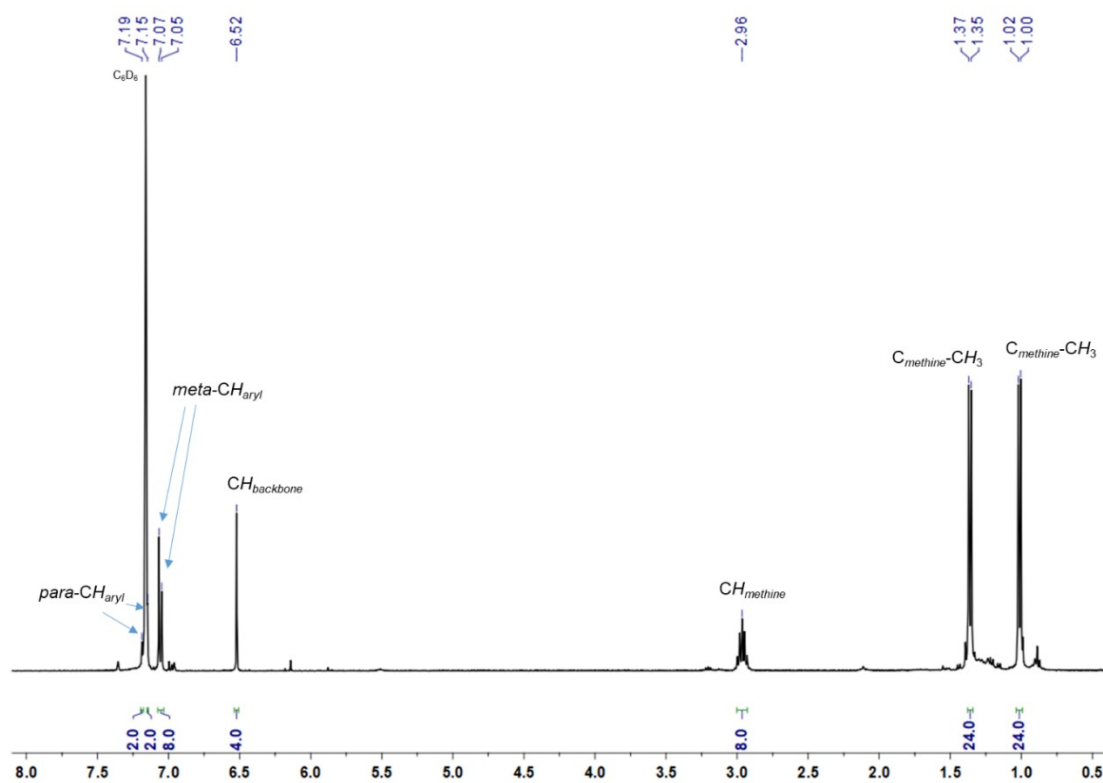


Figure S5. ¹H NMR spectrum of **[{Ni(IDipp)(μ^2 -CS₂)₂}]₂ (2c)** in C₆D₆.

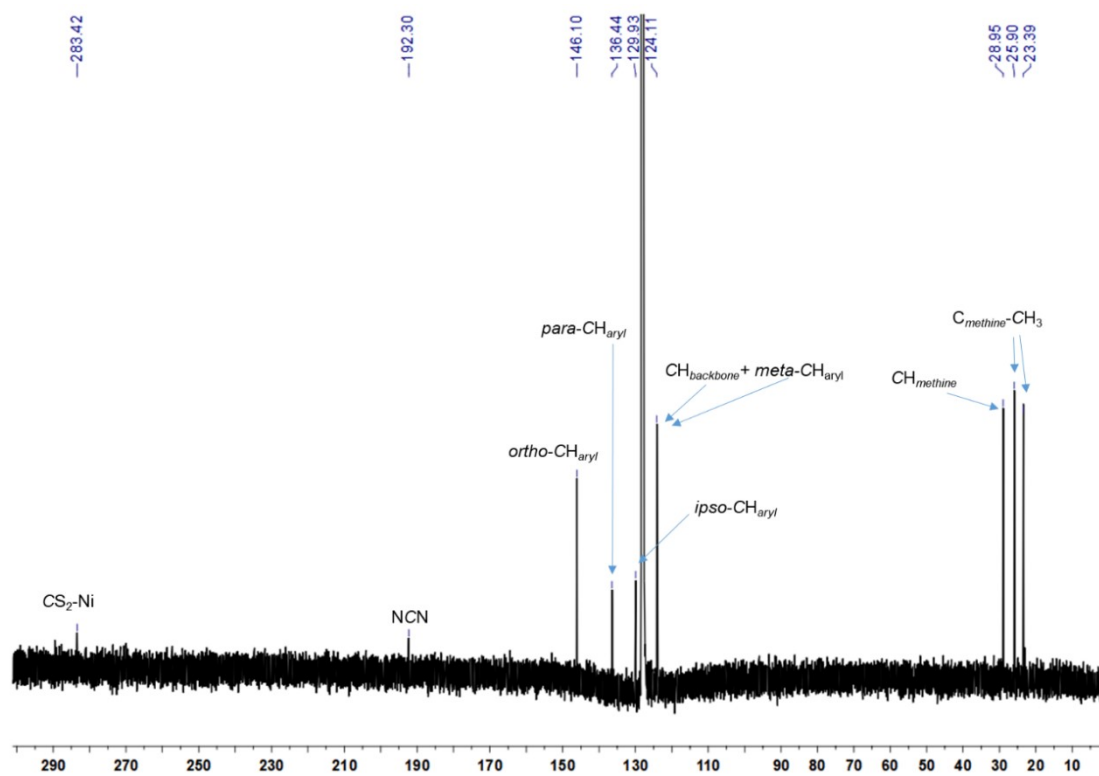


Figure S6. ¹³C{¹H} NMR spectrum of **[{Ni(IDipp)(μ^2 -CS₂)₂}]₂ (2c)** in C₆D₆.

[{Ni(IMes)(μ^2 -CS₂)₂]₂ (2d)

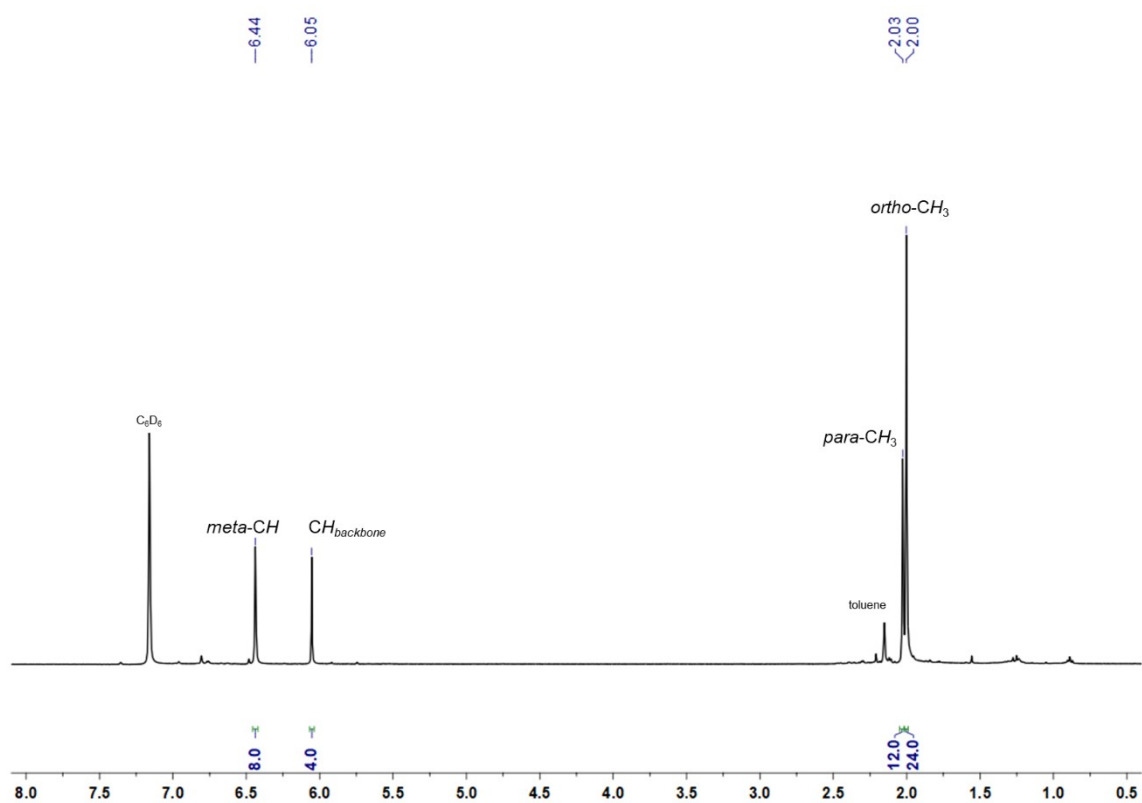


Figure S7. ¹H NMR spectrum of **[{Ni(IMes)(μ^2 -CS₂)₂]₂ (2d)** in C₆D₆.

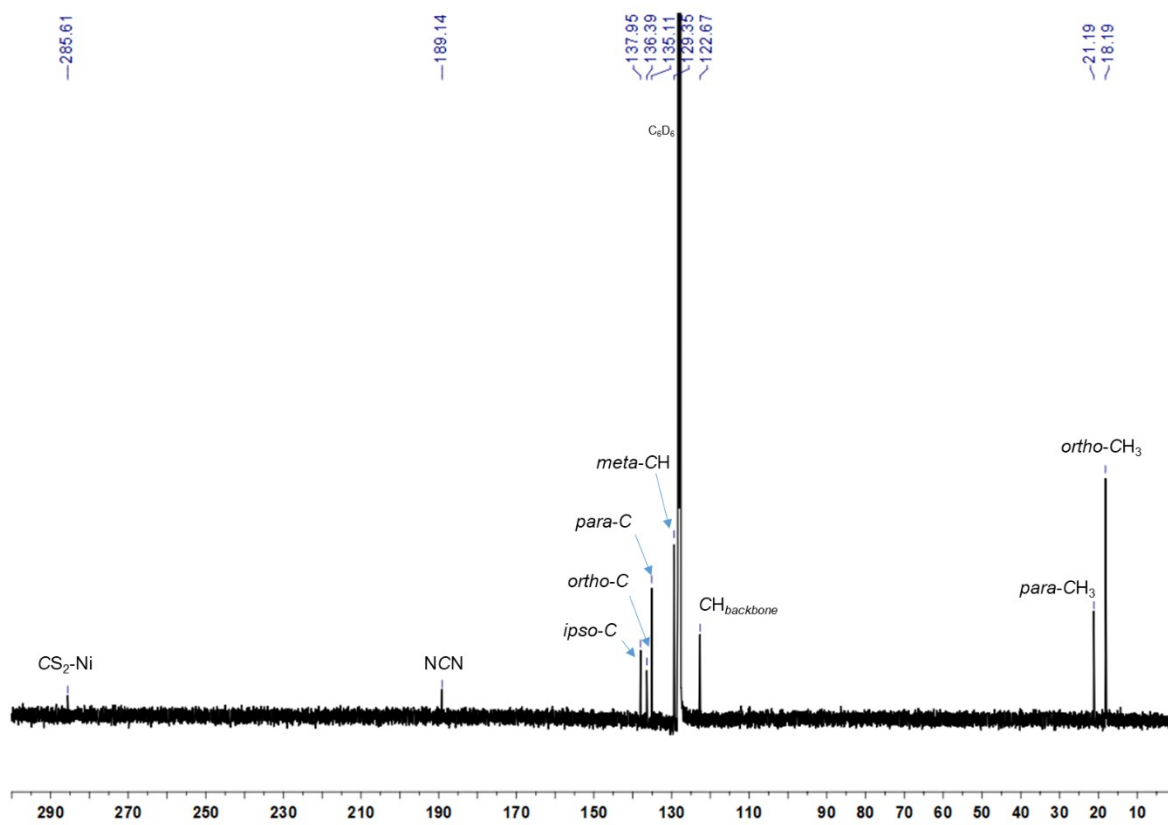


Figure S8. ¹³C{¹H} NMR spectrum of **[{Ni(IMes)(μ^2 -CS₂)₂]₂ (2d)** in C₆D₆.

[Ni(cAAC^{Me}-CS₂)₂] (3e)

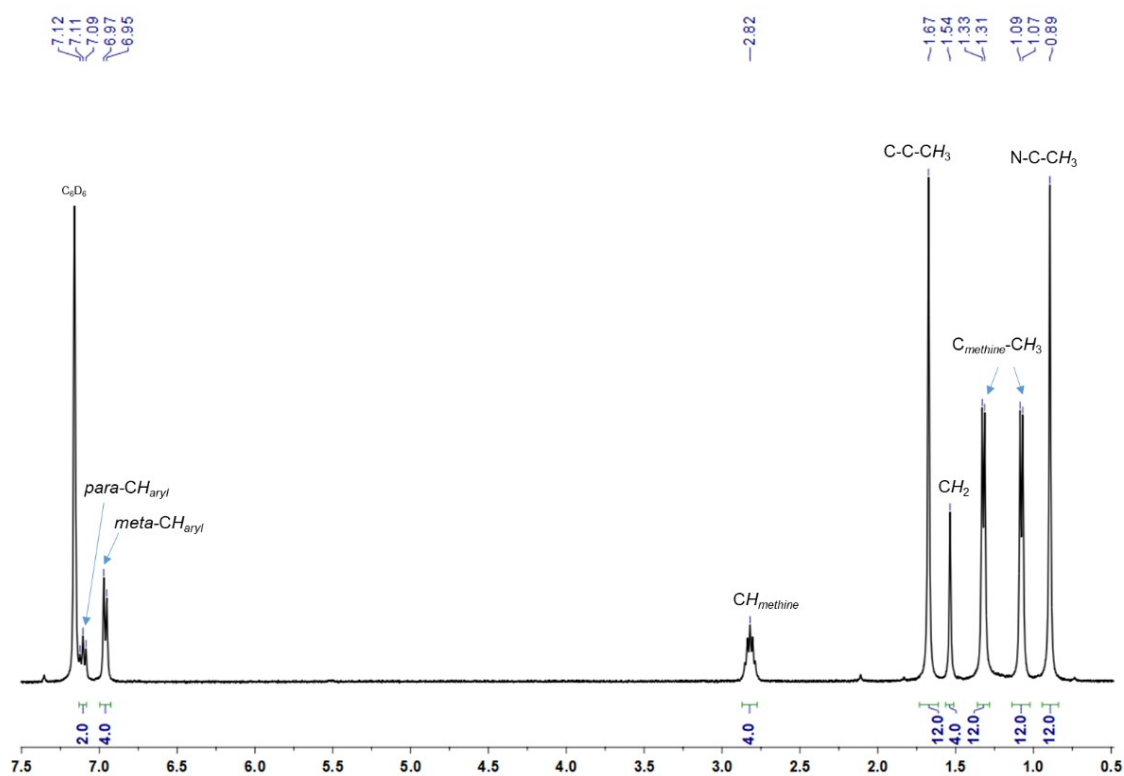


Figure S9. ¹H NMR spectrum of [Ni(cAAC^{Me}-CS₂)₂] (3e) in C₆D₆.

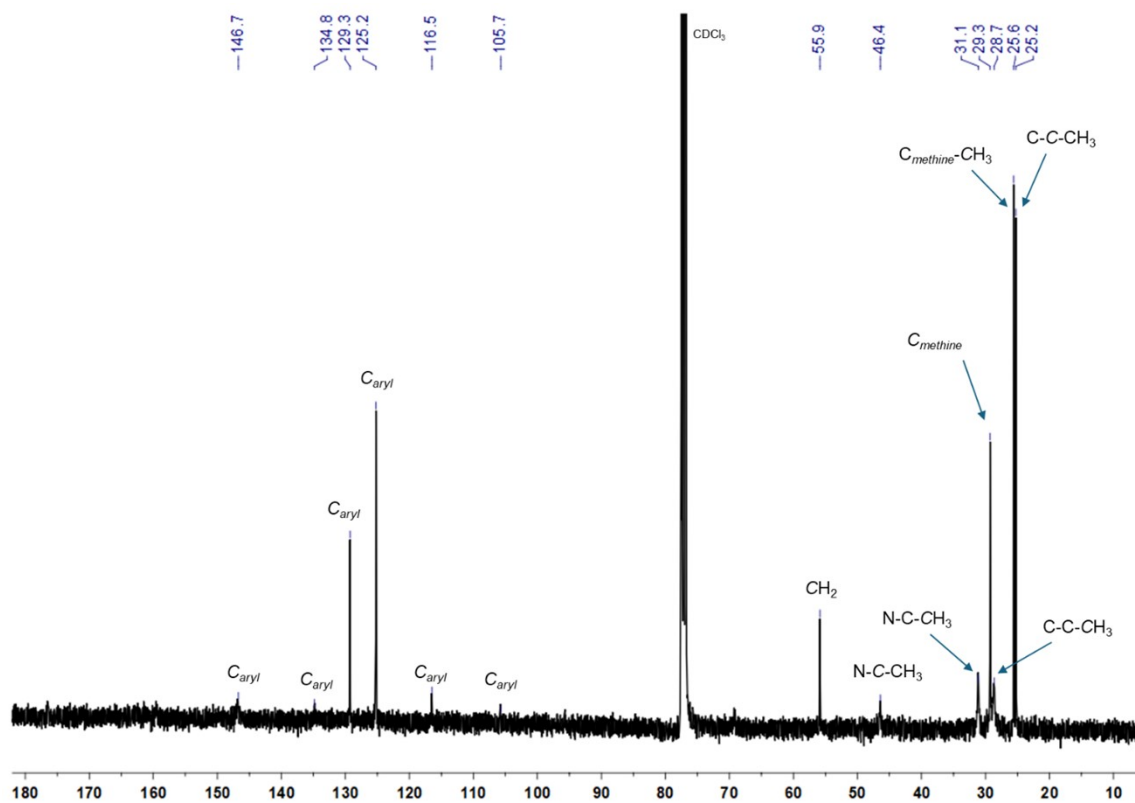


Figure S10. ¹³C{¹H} NMR spectrum of [Ni(cAAC^{Me}-CS₂)₂] (3e) in CDCl₃. Resonances of the former carbene carbon atom as well as of the CS₂ group were not detected.

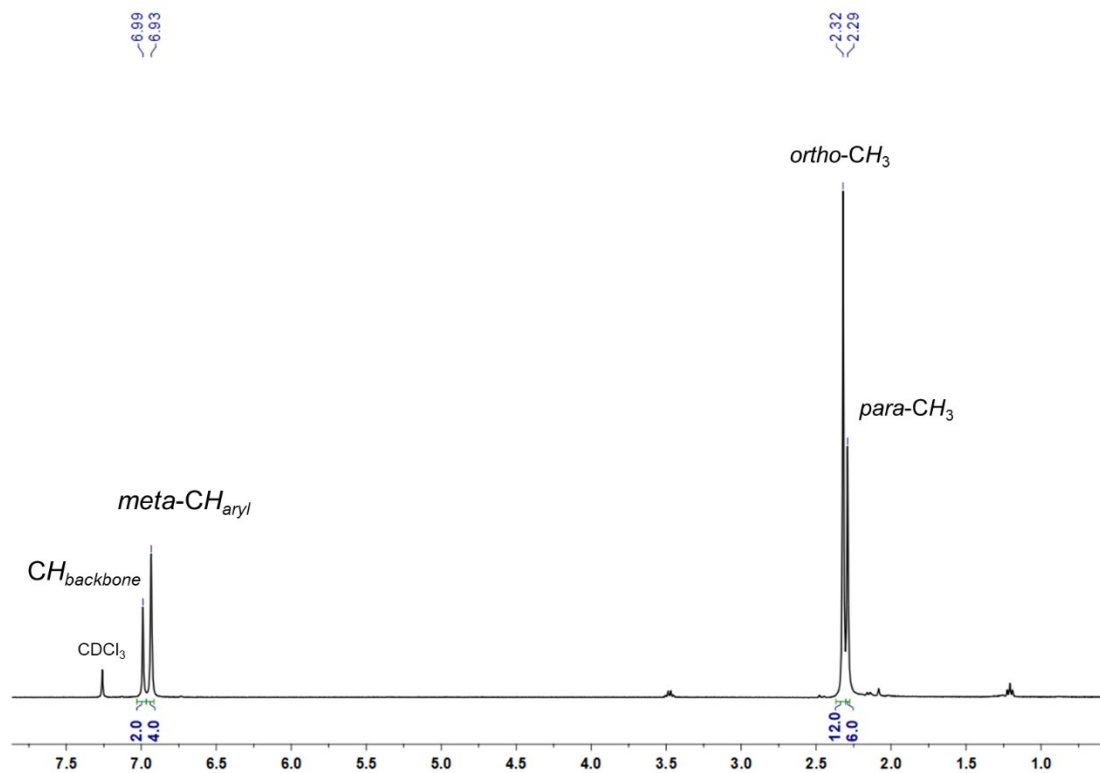


Figure S11. ^1H NMR spectrum of the isolated side-product IMes-CS₂ obtained from the reaction of [Ni(IMes)₂] with CS₂ in CDCl₃.

2 IR Spectra

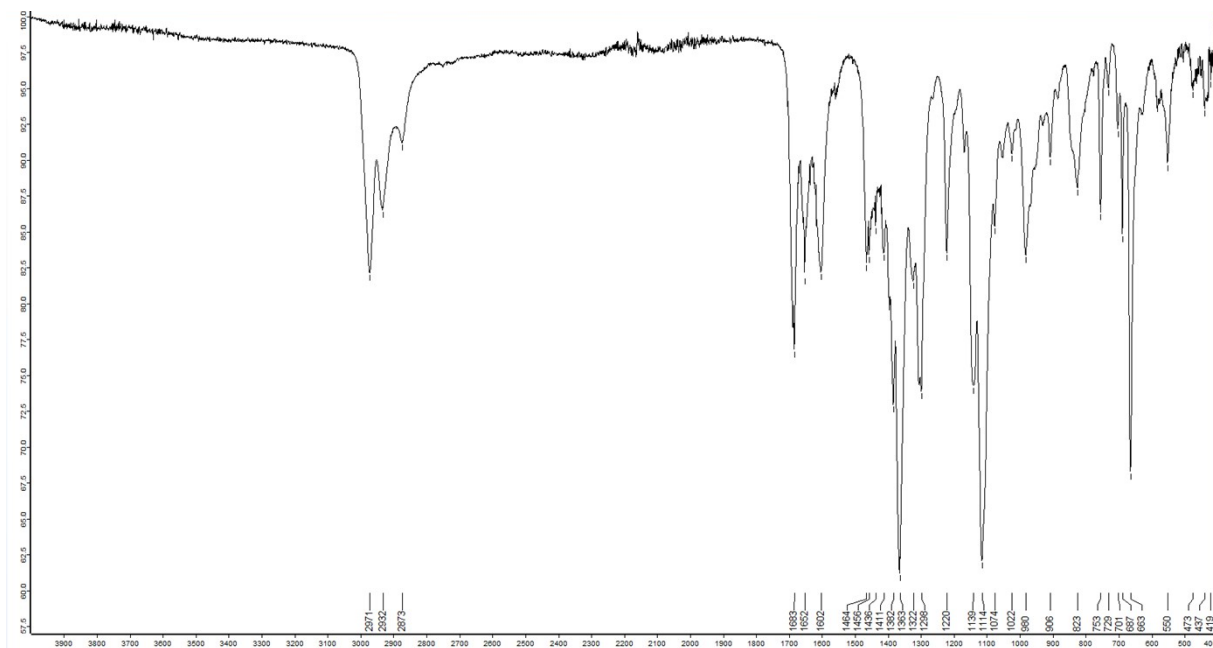


Figure S12. FT-IR spectrum (ATR) of $[\text{Ni}(\text{IIPr}^{\text{Me}})_2(\eta^2\text{-CS}_2)]$ (**1a**).

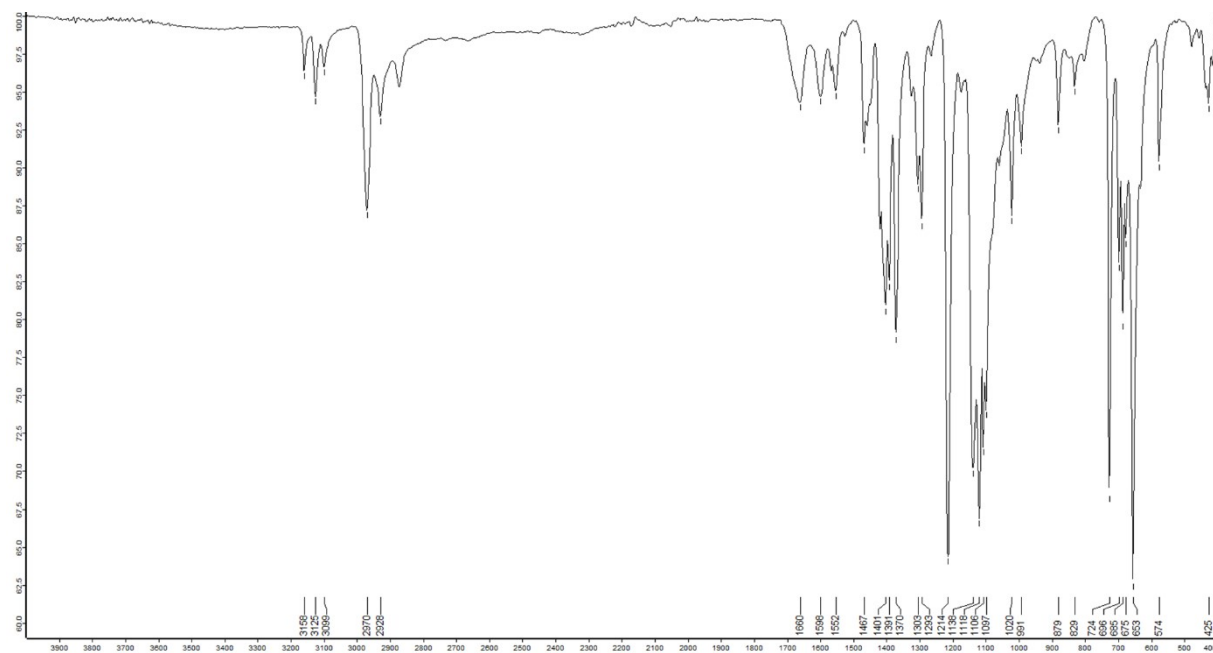


Figure S13. FT-IR spectrum (ATR) of $[\text{Ni}(\text{IIPr})_2(\eta^2\text{-CS}_2)]$ (**1b**).

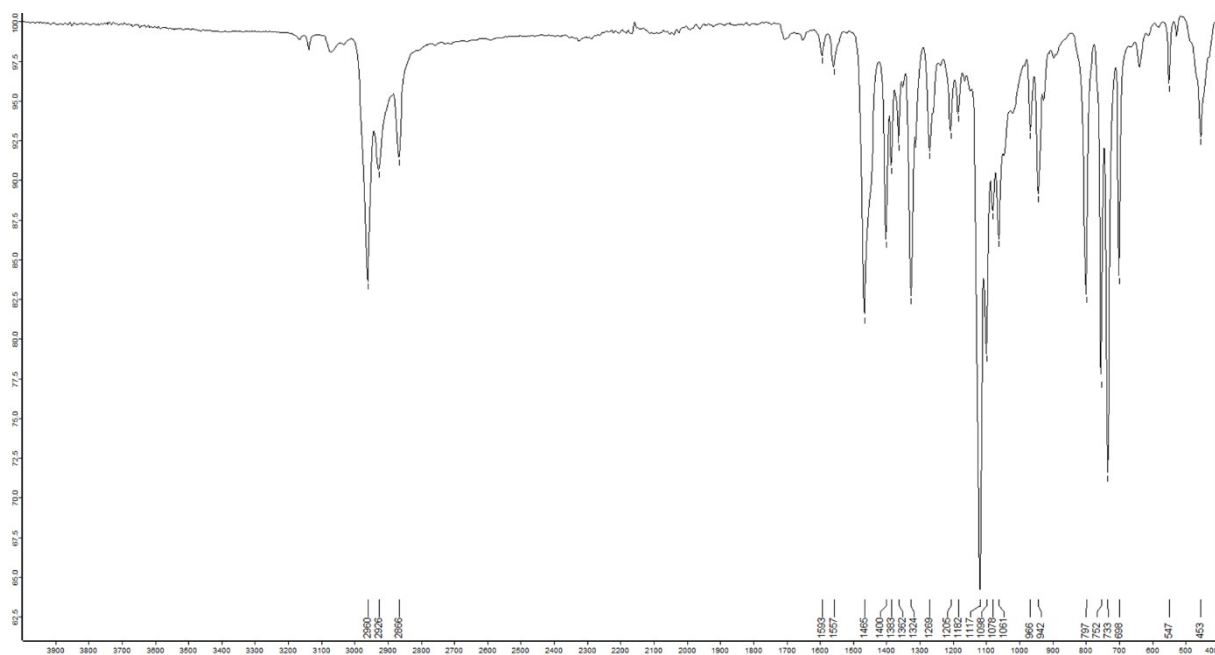


Figure S14. FT-IR spectrum (ATR) of $[\{\text{Ni}(\text{IDipp})(\mu^2\text{-CS}_2)\}_2]$ (**2c**).

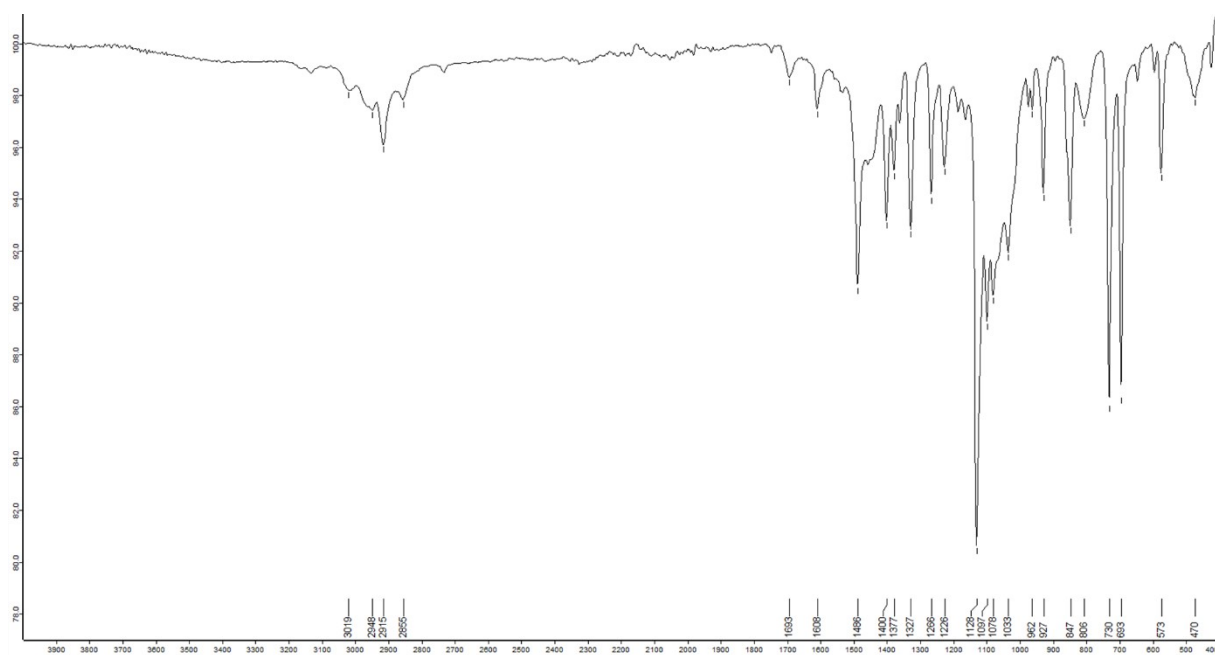


Figure S15. FT-IR spectrum (ATR) of $[\{\text{Ni}(\text{IMes})(\mu^2\text{-CS}_2)\}_2]$ (**2d**).

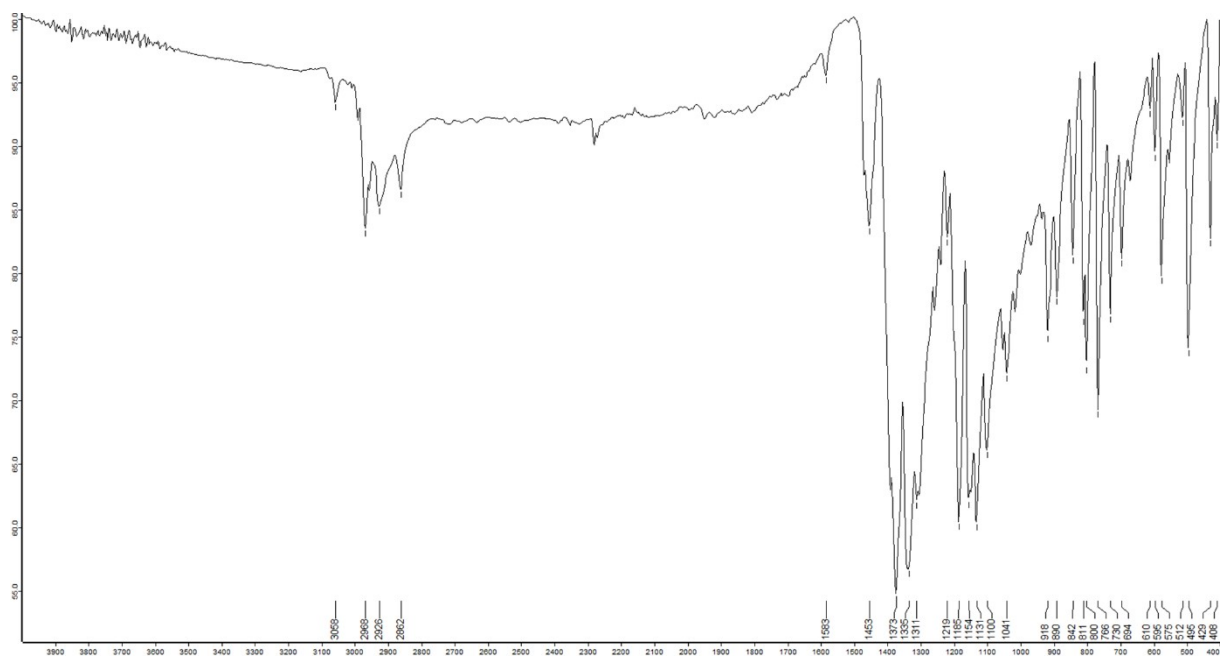


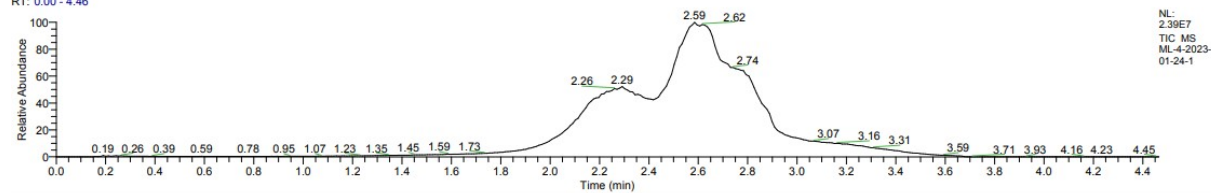
Figure S16. FT-IR spectrum (ATR) of [Ni(cAAC^{Me}-CS₂)₂] (**3e**).

3 High Resolution Mass Spectrometry (HRMS) Data

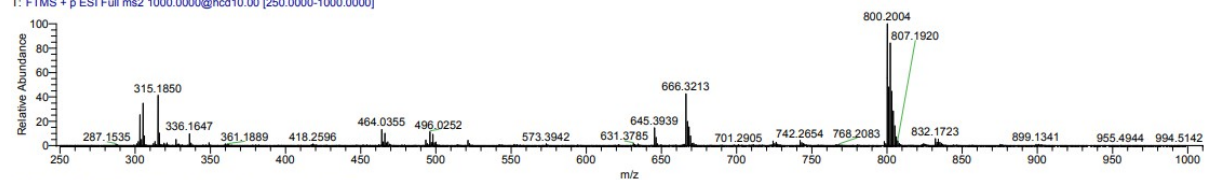
$[\{\text{Ni}(\text{IMes})(\mu^2\text{-CS}_2)\}_2] (\mathbf{2d})$

LIFDI

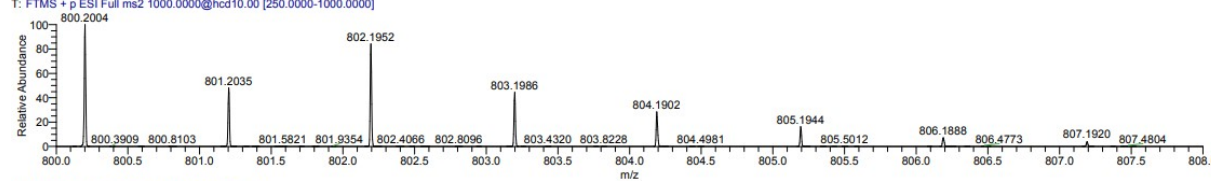
RT: 0.00 - 4.46



ML-4-2023-01-24-1 #180-248 RT: 1.88-2.60 AV: 69 NL: 1.04E6
T: FTMS + p ESI Full ms2 1000.0000@hcd10.00 [250.0000-1000.0000]



ML-4-2023-01-24-1 #180-248 RT: 1.88-2.60 AV: 69 NL: 1.04E6
T: FTMS + p ESI Full ms2 1000.0000@hcd10.00 [250.0000-1000.0000]



C43H48N4Ni2S2: C43 H48 N4 Ni2 S2 pa Chrg 1

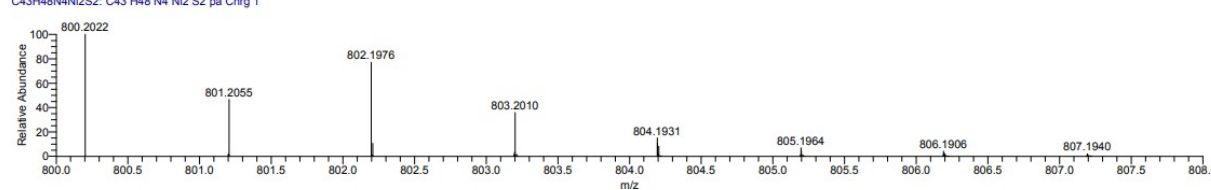


Figure S17. Results of the mass spectrometric investigations of $[\{\text{Ni}(\text{IMes})(\mu^2\text{-CS}_2)\}_2] (\mathbf{2d})$.

[Ni(cAAC^{Me}-CS₂)₂] (3e)

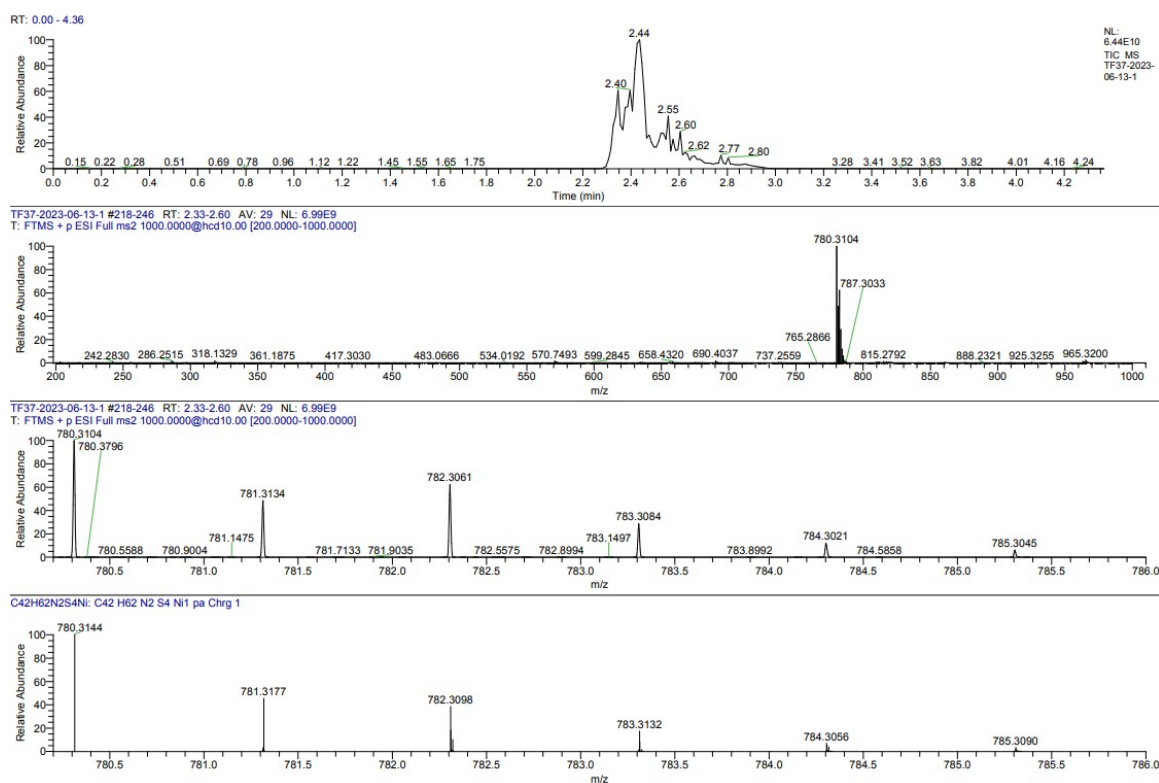


Figure S18. Results of the LIFDI mass spectrometric investigations of [Ni(cAAC^{Me}-CS₂)₂] (**3e**) dissolved in THF.

4 Cartesian Coordinates of Geometry Optimized Complexes (PBE0-D3(BJ)//def2-TZVP(Ni)/def2-SVP(C,H,N,S))

[Ni(IIPr^{Me})₂(η²-CS₂)] (1a)

Energy = -3421.559356860

Ni	-0.0676394	-0.1156625	1.3457645
C	1.3207145	-0.5464111	0.1354872
N	2.5573944	0.0019701	0.0353959
C	3.3030239	-0.6278628	-0.9582029
C	2.5004646	-1.6004722	-1.4871389
N	1.2902829	-1.5213630	-0.8038557
C	3.0154290	1.0088654	0.9986024
H	2.1003989	1.2184881	1.5774659
C	4.0405829	0.4369234	1.9670338
H	3.6611774	-0.5000256	2.4011672
H	4.2109744	1.1523520	2.7851535
H	5.0110604	0.2488006	1.4831561
C	3.4771384	2.3013517	0.3396345
H	4.4427317	2.1883933	-0.1734819
H	3.6069423	3.0741274	1.1113901
H	2.7421272	2.6711000	-0.3887977
C	0.1467854	-2.4310037	-0.8738754
H	-0.5888055	-1.9285896	-0.2252679
C	0.4736251	-3.7715497	-0.2324229
H	1.2004932	-4.3504026	-0.8227993
H	-0.4408481	-4.3770789	-0.1427123
H	0.8867654	-3.6094029	0.7750693
C	-0.4546060	-2.5258110	-2.2672103
H	-0.6601352	-1.5235459	-2.6728305
H	-1.4085145	-3.0715678	-2.2156729
H	0.1887001	-3.0662595	-2.9757379
C	-1.4395696	0.6589987	0.1668253
N	-1.3456058	1.6534175	-0.7513331
C	-2.5385339	1.8225818	-1.4473772
C	-3.4093156	0.8974171	-0.9405266
N	-2.7116407	0.1981921	0.0383674
C	-0.0792329	2.3499227	-0.9656594
H	0.5405077	1.9652896	-0.1431782
C	0.5767538	1.9254862	-2.2726025
H	0.6913035	0.8323215	-2.3038666
H	1.5780089	2.3733240	-2.3561569
H	-0.0012002	2.2434877	-3.1531382
C	-0.1901795	3.8575378	-0.7947028
H	-0.7023954	4.3463105	-1.6353717
H	0.8183196	4.2925689	-0.7299392
H	-0.7246977	4.1036173	0.1342773
C	-3.2243557	-0.8589624	0.9150983
H	-2.3220255	-1.1979098	1.4479738
C	-4.1651362	-0.3038571	1.9726194
H	-3.6705982	0.5073079	2.5253222
H	-4.4174460	-1.0952960	2.6935033
H	-5.1055680	0.0775262	1.5460841
C	-3.7918089	-2.0454185	0.1499662
H	-4.7779044	-1.8422390	-0.2911477
H	-3.9107300	-2.8939458	0.8394377
H	-3.1097658	-2.3573877	-0.6546823
C	0.6003822	-0.9943712	2.8165588
C	-2.7847621	2.8451297	-2.4991039
H	-2.0165690	2.8321382	-3.2860078
H	-3.7501523	2.6539699	-2.9849146
H	-2.8193892	3.8661083	-2.0876464
C	-4.8206505	0.6441514	-1.3361171
H	-4.9369045	-0.3042968	-1.8833877

H	-5.4953425	0.6099920	-0.4687153
H	-5.1743820	1.4491795	-1.9930063
C	4.6802430	-0.2445586	-1.3661156
H	4.7049321	0.7266180	-1.8859303
H	5.3661732	-0.1804020	-0.5097656
H	5.0863205	-0.9951020	-2.0566035
C	2.7954130	-2.5499096	-2.5924026
H	2.5438208	-3.5864384	-2.3250518
H	2.2475041	-2.3022068	-3.5157255
H	3.8668069	-2.5243622	-2.8299822
S	-0.7606097	-0.2009960	3.4318888
S	1.7230187	-2.0769979	3.3084220

[[Ni(IMes)(μ²-CS₂)]₂] (2d)

Energy = -6529.247110910

Ni	8.0267690	3.8083571	6.3404149
S	8.1841686	6.9266518	7.5045918
S	6.6394931	5.2673016	5.4327349
N	8.6060972	1.2365196	4.9096418
N	6.6636277	1.2541317	5.8025393
C	5.5110687	1.7041409	6.5166061
C	7.7758376	2.0154274	5.6478515
C	9.9166039	1.6402236	4.5078734
C	10.0489560	2.5716793	3.4710099
C	11.0248800	1.1098721	5.1861809
C	4.4523445	2.2641231	5.7921680
C	5.4981129	1.6095467	7.9148673
C	8.0225609	0.0187455	4.6026484
H	8.5329507	-0.7327990	4.0073476
C	12.2916503	1.5397493	4.7941004
H	13.1651217	1.1471141	5.3224203
C	3.3474628	2.7282282	6.5081065
H	2.5143604	3.1757587	5.9590047
C	11.3413501	2.9713979	3.1194361
H	11.4630010	3.7034793	2.3161225
C	12.4713583	2.4703527	3.7660676
C	6.7903616	0.0288631	5.1721479
H	5.9992973	-0.7152649	5.1884475
C	4.5317805	2.3968170	4.3012819
H	5.4197770	2.9832353	4.0161885
H	3.6427908	2.9037600	3.9036626
H	4.6185751	1.4175737	3.8046076
C	3.2882707	2.6500061	7.9010917
C	4.3704101	2.0876164	8.5838474
H	4.3422707	2.0233864	9.6754907
C	7.7610038	5.5821565	6.6253698
C	10.8513895	0.1572094	6.3312174
H	10.3193438	0.6533680	7.1591572
H	11.8264222	-0.1761239	6.7103528
H	10.2700808	-0.7340920	6.0504248
C	8.8501727	3.1500983	2.7815802
H	9.1352239	3.6208004	1.8309921
H	8.3707513	3.9158911	3.4147575
H	8.0876719	2.3835747	2.5768668
C	6.6705096	1.0526851	8.6637675
H	7.5076276	1.7716996	8.6614592
H	7.0457690	0.1251058	8.2056817
H	6.4053373	0.8421275	9.7084987
C	2.1057312	3.1827907	8.6566413
H	2.3598674	4.1289253	9.1614112

H	1.7757739	2.4788125	9.4356574	H	11.9055611	7.1172664	11.7966434
H	1.2543605	3.3795103	7.9901676	H	13.6306665	7.2953530	12.2082250
C	13.8511517	2.9066704	3.3674634	H	12.5335841	8.6939699	12.3036148
H	13.8218893	3.7871428	2.7105553	C	14.5855199	8.0376706	8.3735957
H	14.3800662	2.1038807	2.8277486	C	13.5772405	8.5941714	7.5815529
H	14.4588619	3.1586290	4.2498033	H	13.7687491	8.7804116	6.5208368
Ni	9.7012984	6.3970011	8.9880891	C	10.0392581	4.6480066	8.6353415
S	9.6518141	3.3155041	7.7194373	C	6.7283279	9.9333735	8.9054910
S	11.1071651	4.9469318	9.8803182	H	7.4914635	9.6305940	8.1708105
N	8.7547551	8.7495386	10.5473599	H	5.8289864	10.2316540	8.3508516
N	10.8162270	8.9499675	10.0161863	H	7.1112720	10.8177964	9.4371768
C	12.1005532	8.6632809	9.4617792	C	8.2731030	6.5207705	12.3022743
C	9.7532461	8.1202596	9.8756315	H	7.8508532	5.9091322	13.1111285
C	7.4272019	8.2276372	10.6362873	H	8.9171987	5.8734966	11.6830219
C	7.1843421	7.1312664	11.4723219	H	8.9258694	7.2865018	12.7470285
C	6.4255454	8.7956979	9.8340797	C	11.2317198	9.4564179	7.2271664
C	13.0778738	8.1004916	10.2906656	H	10.4767818	8.6784822	7.0212827
C	12.3213441	8.9117425	8.1005678	H	10.7033300	10.2945445	7.7061500
C	9.1869917	9.9423764	11.1006467	H	11.6344204	9.8025093	6.2658699
H	8.5306248	10.5807511	11.6849151	C	15.9114670	7.6724240	7.7722463
C	5.1545882	8.2262261	9.8822984	H	15.8239449	6.7577721	7.1630157
H	4.3689049	8.6428480	9.2458148	H	16.2862278	8.4679267	7.1106033
C	14.3174820	7.8001432	9.7234208	H	16.6689530	7.4843218	8.5459409
H	15.0905361	7.3524379	10.3541543	C	3.4927631	6.5269841	10.7090623
C	5.8936523	6.5951450	11.4792135	H	3.4929227	5.5247893	11.1604930
H	5.6896681	5.7295428	12.1157746	H	2.7955155	7.1541836	11.2889378
C	4.8705613	7.1217469	10.6908736	H	3.0850235	6.4444948	9.6902176
C	10.4951404	10.0714292	10.7609194				
H	11.2204847	10.8507621	10.9760936				
C	12.7765661	7.7883989	11.7257028				