

Supporting Information

for

**Synthesis and Coordination Chemistry of Phenanthridine-
Containing Monoanionic $N^{\wedge}N^{\wedge}N$ Pincer Motifs**

By

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fulfilment of the requirements of the degree of

Doctor of Philosophy

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Chapter 2:

2.1. NMR Spectra:

PMA-01-104-B3H.1.fid

^1H NMR (300MHz, CDCl_3)

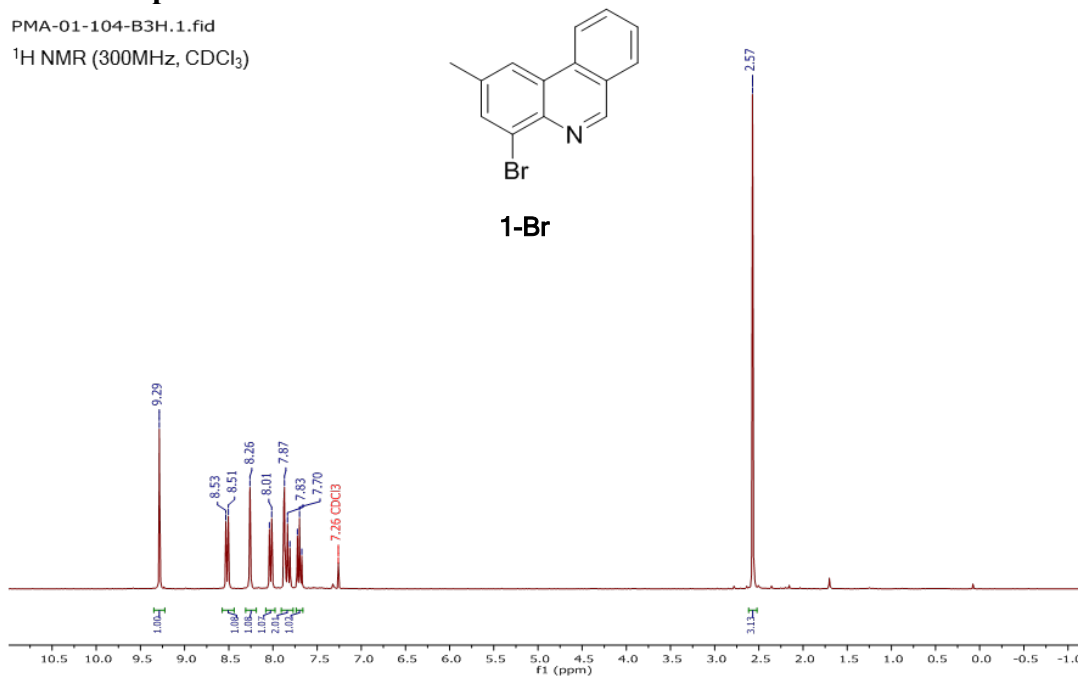


Figure S2.1. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of **1-Br**.

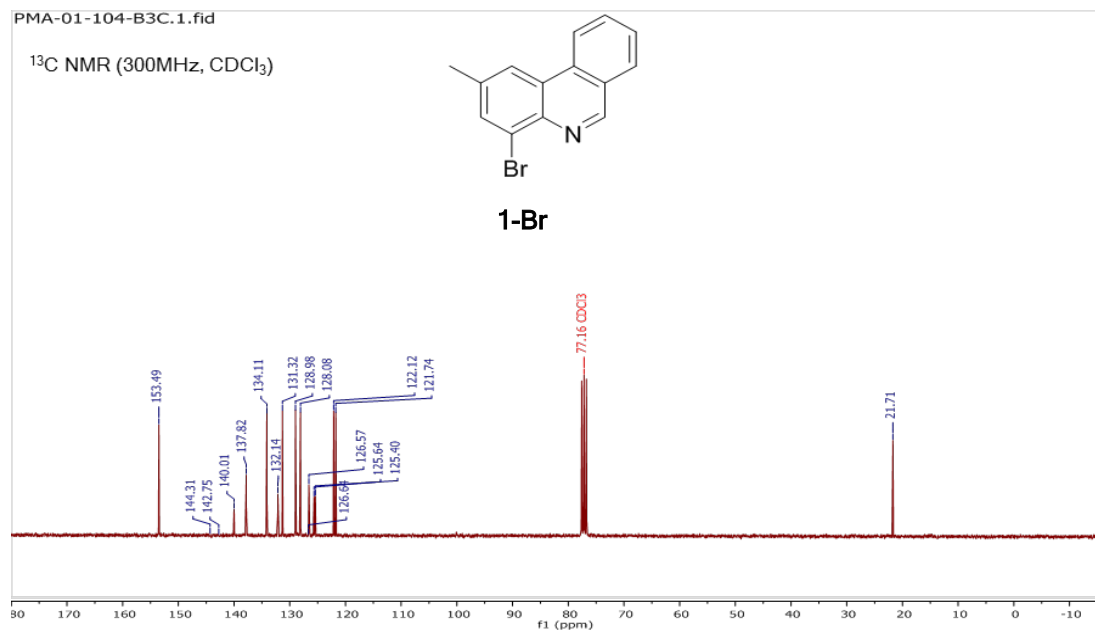


Figure S2.2. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 22 °C) spectrum of **1-Br**.

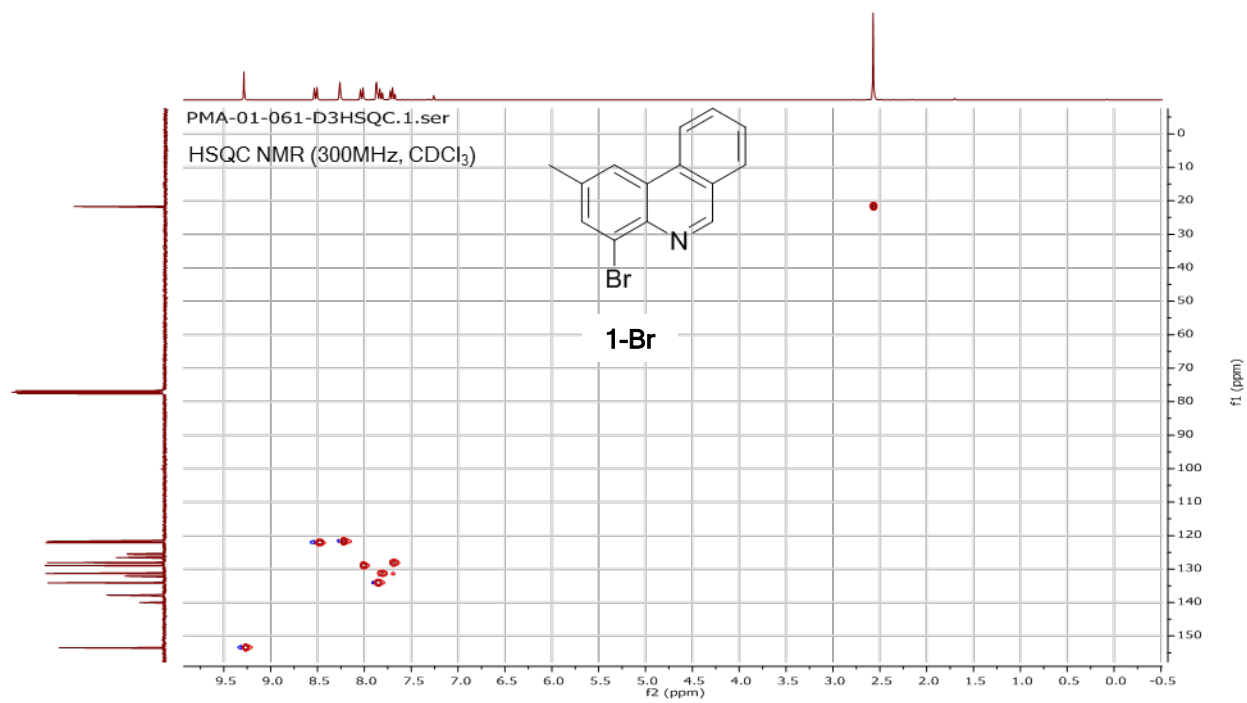


Figure S2.3. HSQC NMR spectrum of **1-Br** in CDCl₃.

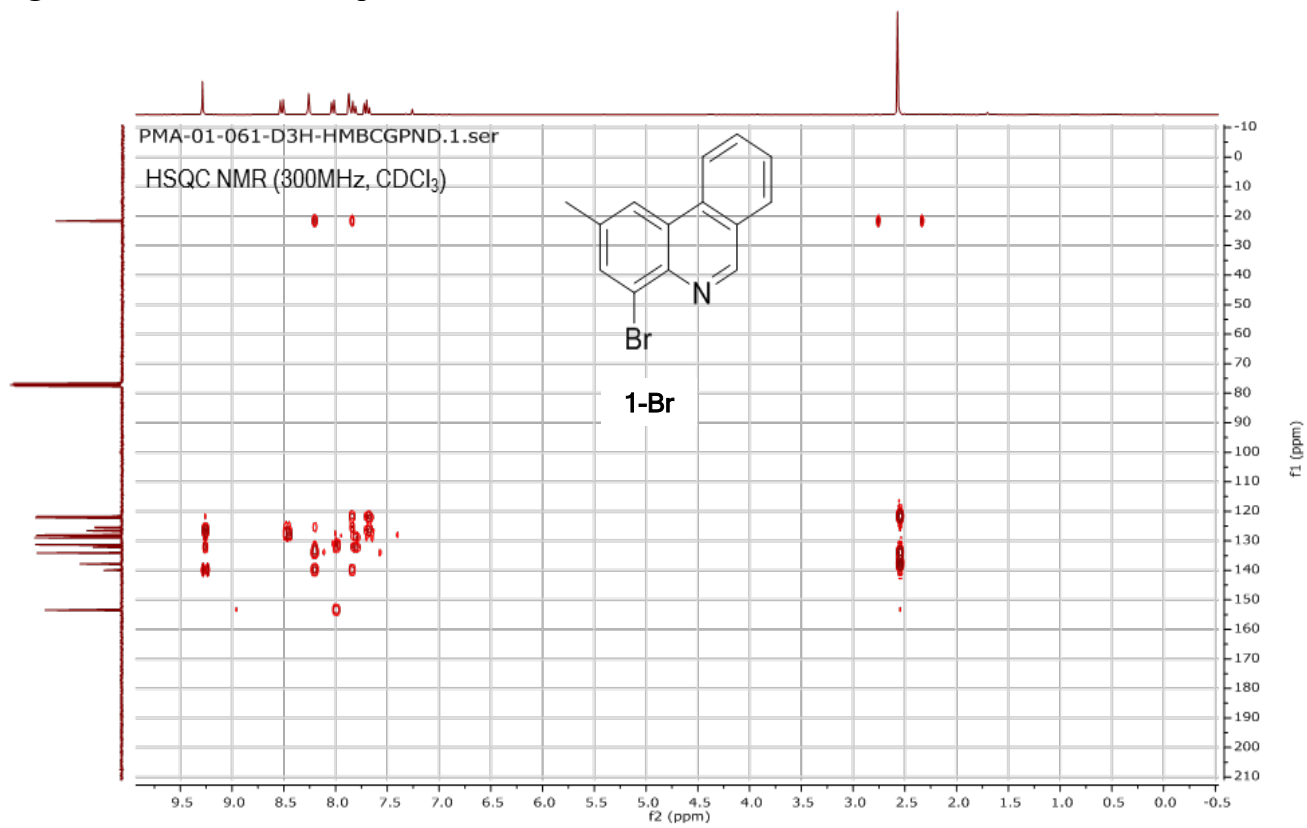


Figure S2.4. HMBC NMR spectrum of **1-Br** in CDCl₃.

PMA-03-063-D3H.1.fid
 ^1H NMR (300MHz, CDCl_3)

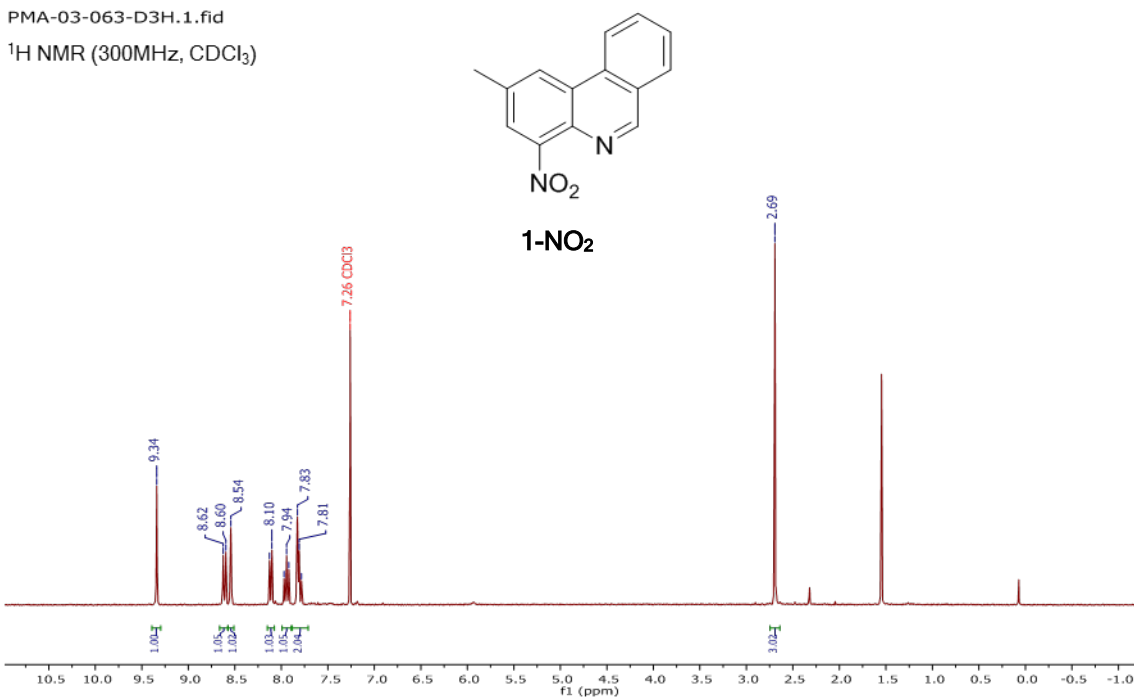


Figure S2.5. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of 1-NO₂.

PMA-03-063-D3C.1.fid
 ^{13}C NMR (300MHz, CDCl_3)

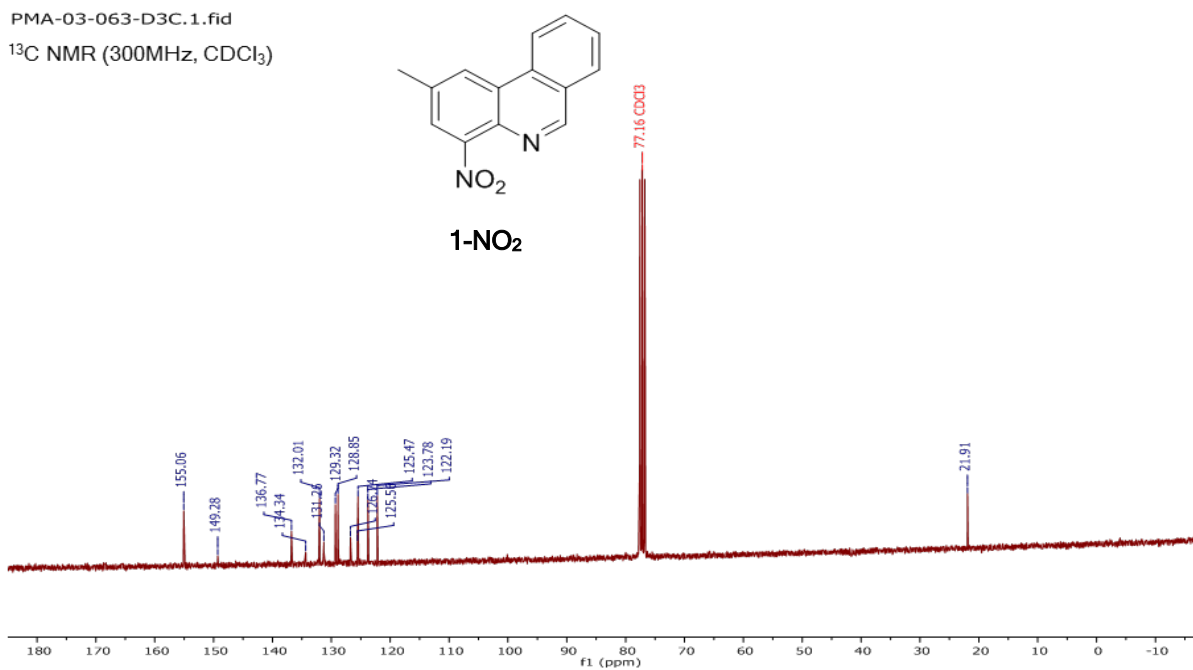


Figure S2.6. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 22 °C) spectrum of 1-NO₂.

pma-01-102-C3H.1.fid
 ^1H NMR (300MHz, CDCl_3)

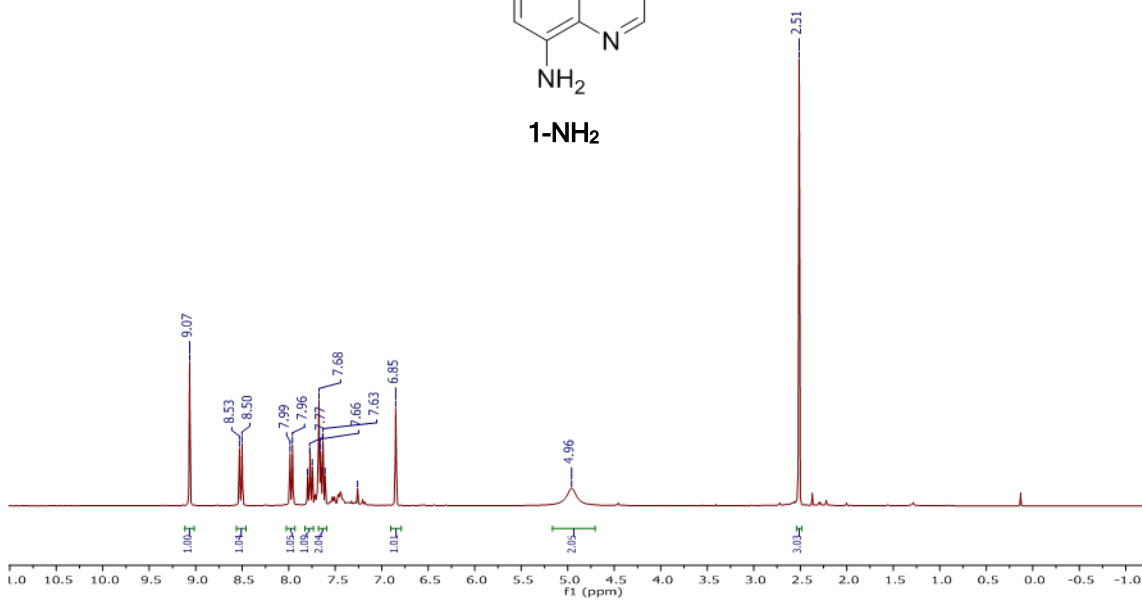
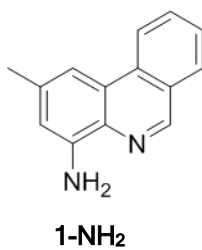


Figure S2.7. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of **1-NH₂**.

pma-01-102-A3C.1.fid
 ^{13}C NMR (300MHz, CDCl_3)

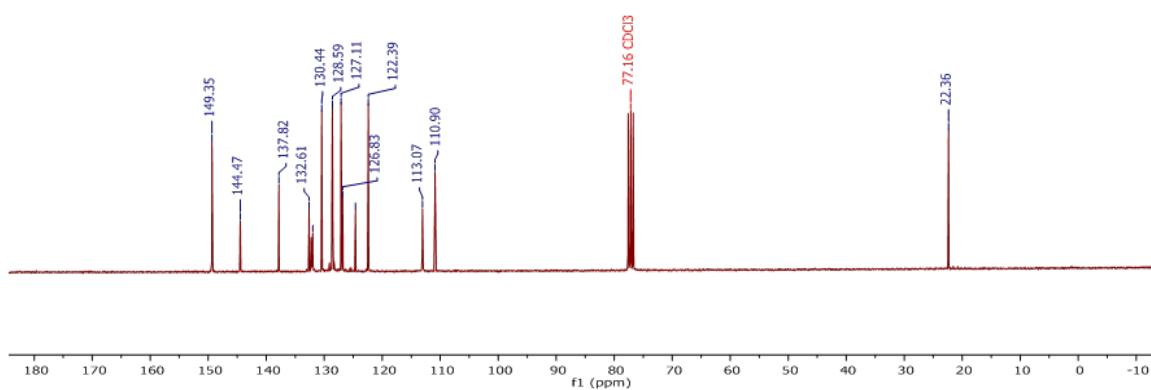
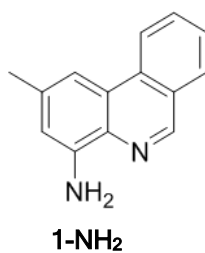


Figure S2.8. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 22 °C) spectrum of **1-NH₂**.

BBH_02_011_A3H.1.fid
lodination
PROTON CDCl3 {C:\Bruker\TOPSPIN1.3} Herbert 21

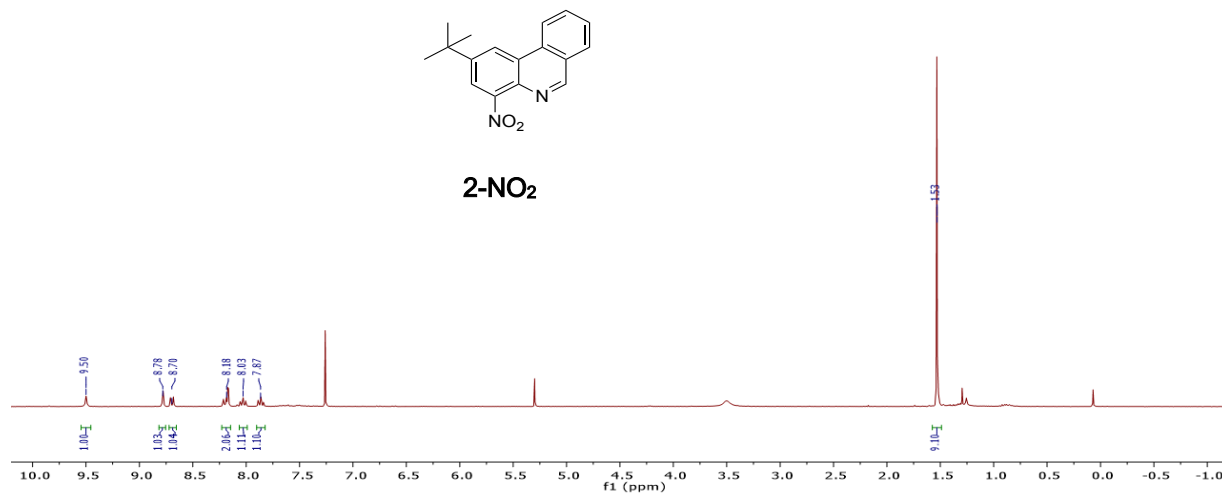


Figure S2.9. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of 2-NO₂.

JDB-03-47-E3C.1.fid
C13CPD CDCl3 {C:\Bruker\TOPSPIN1.3} Herbert 50

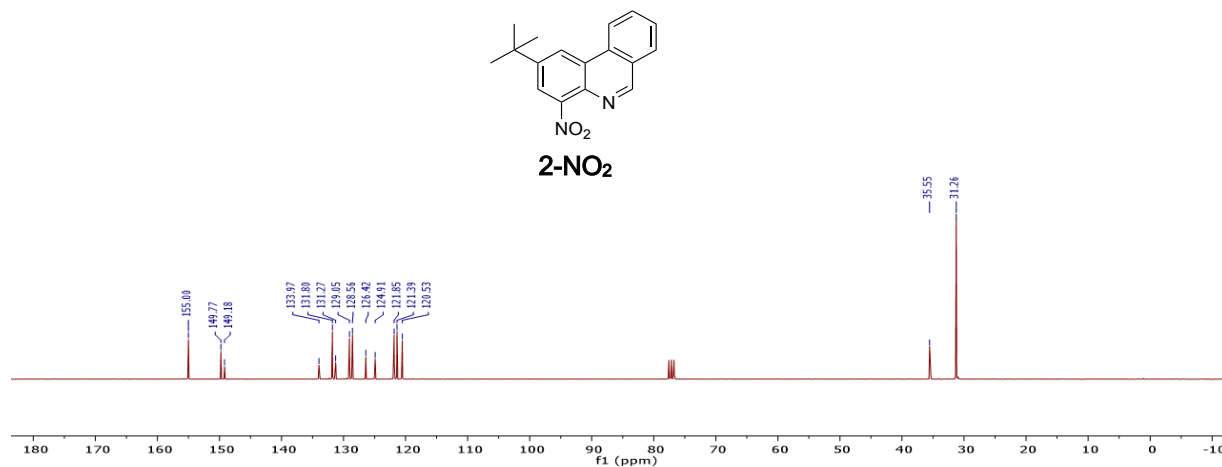


Figure S2.10. ¹³C{¹H} (75 MHz, CDCl₃, 22 °C) spectrum of 2-NO₂.

JDB-02-20-B3H.1.fid
PROTON CDCl₃ {C:\Bruker\TOPSPIN1.3} Herbert 54

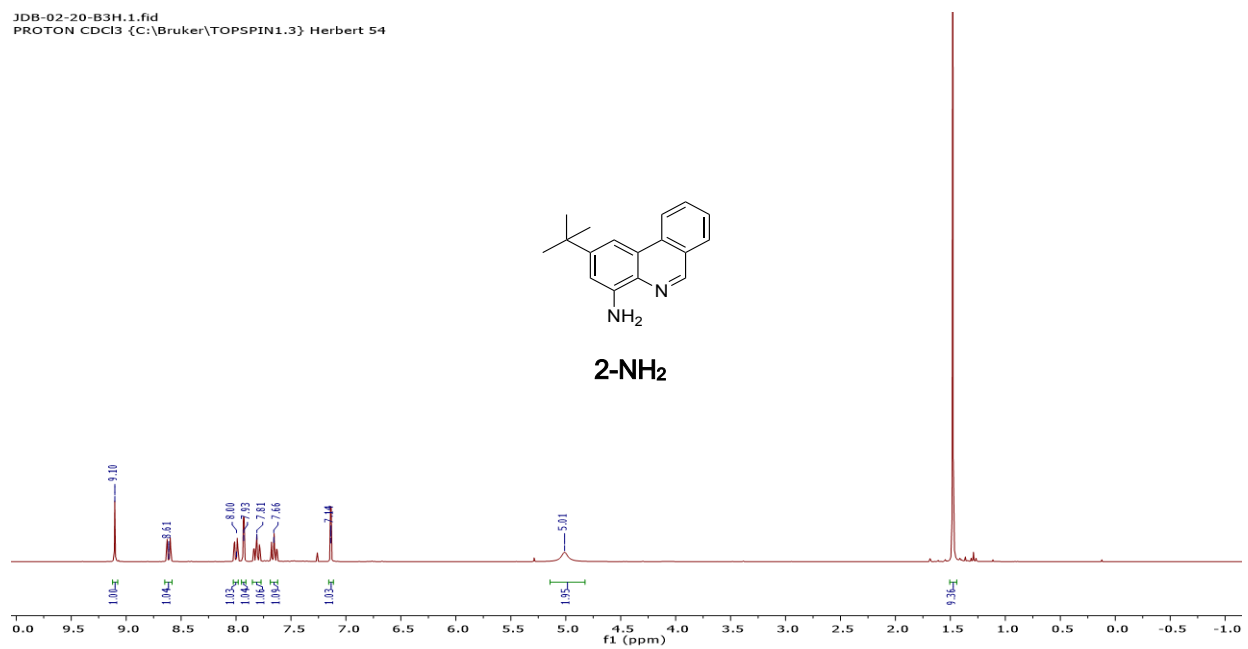


Figure S2.11. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of 2-NH₂.

JDB-02-20-B3C.1.fid
C13CPD32 CDCl₃ {C:\Bruker\TOPSPIN1.3} Herbert 54"

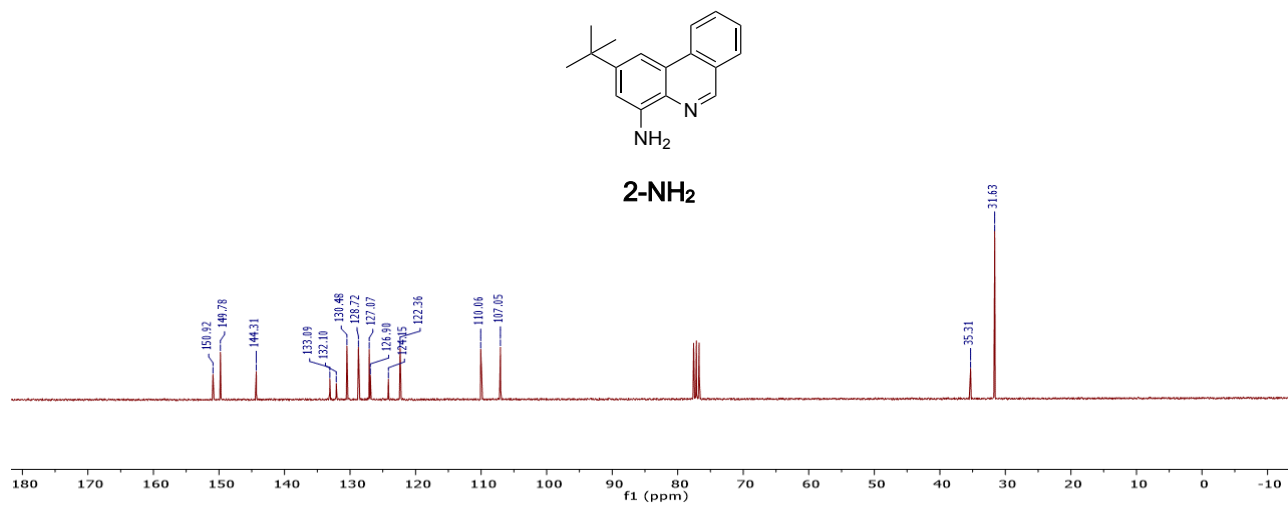


Figure S2.12. ¹³C{¹H} (75 MHz, CDCl₃, 22 °C) spectrum of 2-NH₂.

PMA-01-116-A5H.1.fid

^1H NMR (500MHz, CDCl_3)

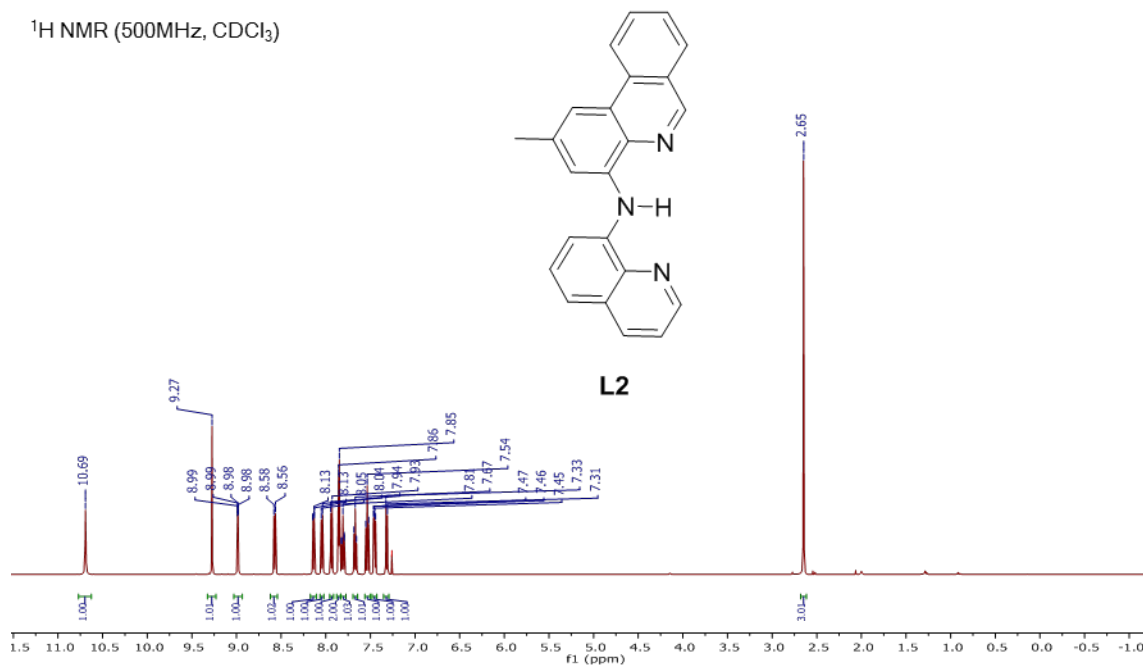


Figure S2.13. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of spectrum of **L2**.

PMA-01-116-A5C.1.fid

^{13}C NMR (500MHz, CDCl_3)

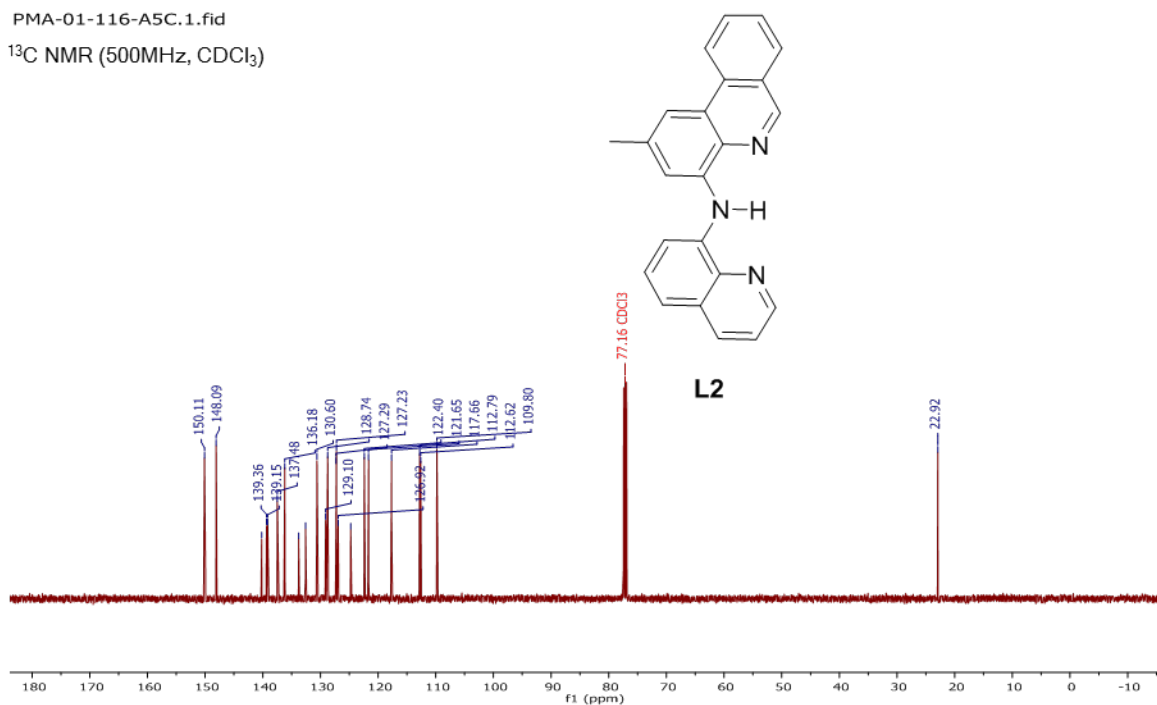


Figure S2.14. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 22 °C) spectrum of spectrum of **L2**.

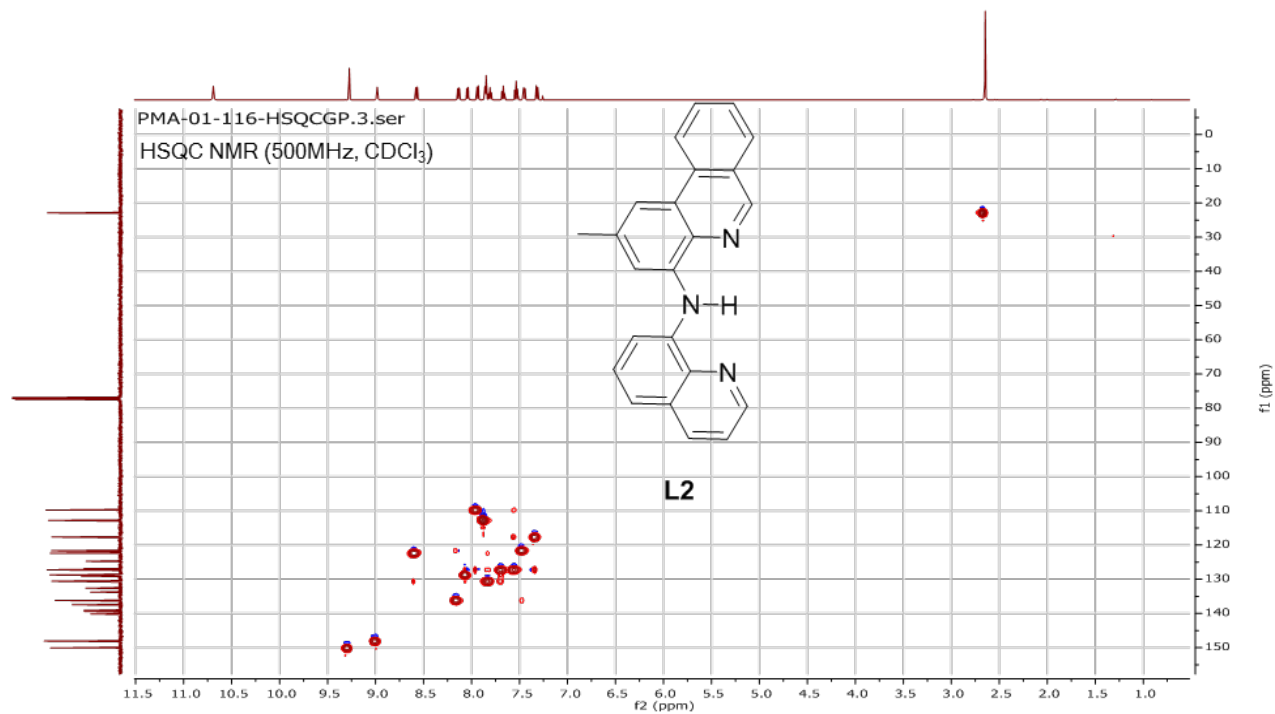


Figure S2.15. HSQC NMR spectrum of **L2** in CDCl₃.

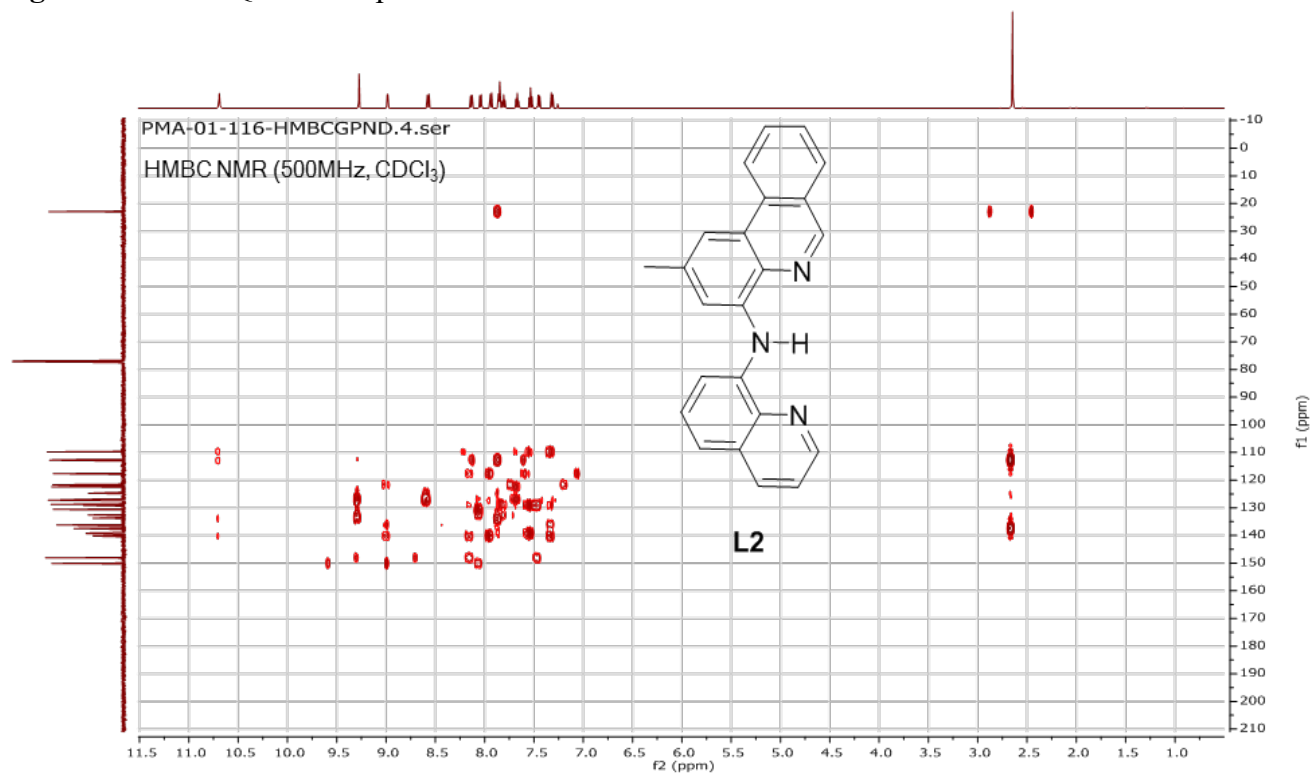


Figure S2.16. HMBC NMR spectrum of **L2** in CDCl₃.

PMA-02-025-C3H.1.fid
 ^1H NMR (300MHz, CDCl_3)

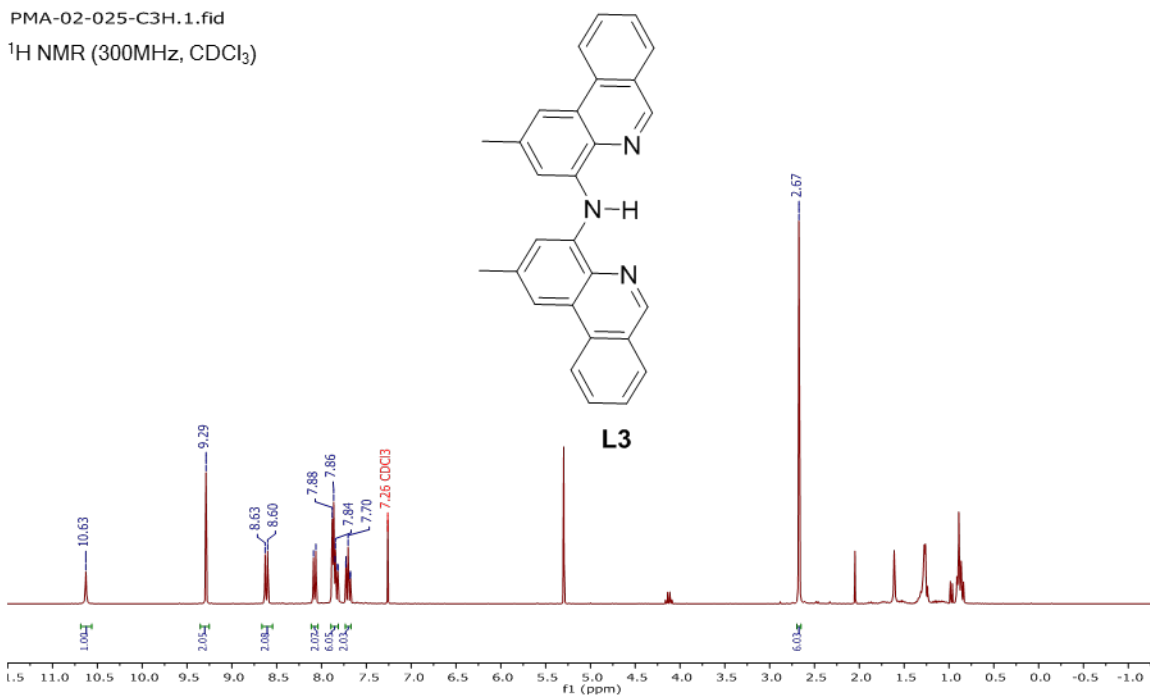


Figure S2.17. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of spectrum of **L3**.

PMA-02-125-A3C.1.fid
 ^{13}C NMR (300MHz, CDCl_3)

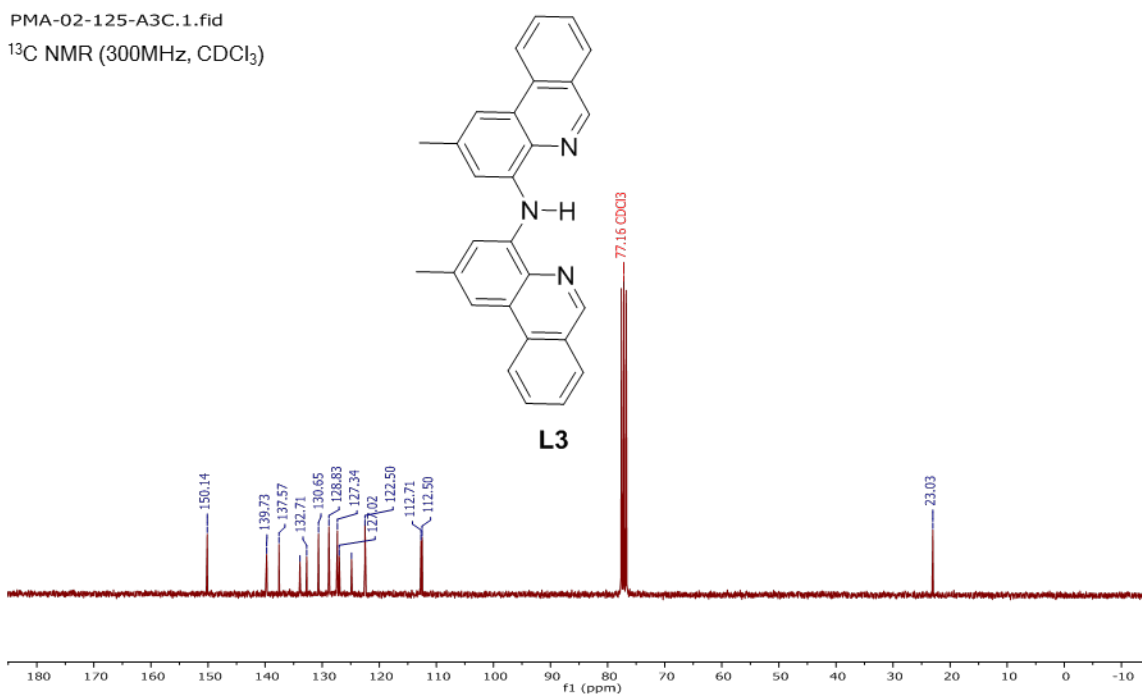


Figure S2.18. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 22 °C) spectrum of spectrum of **L3**.

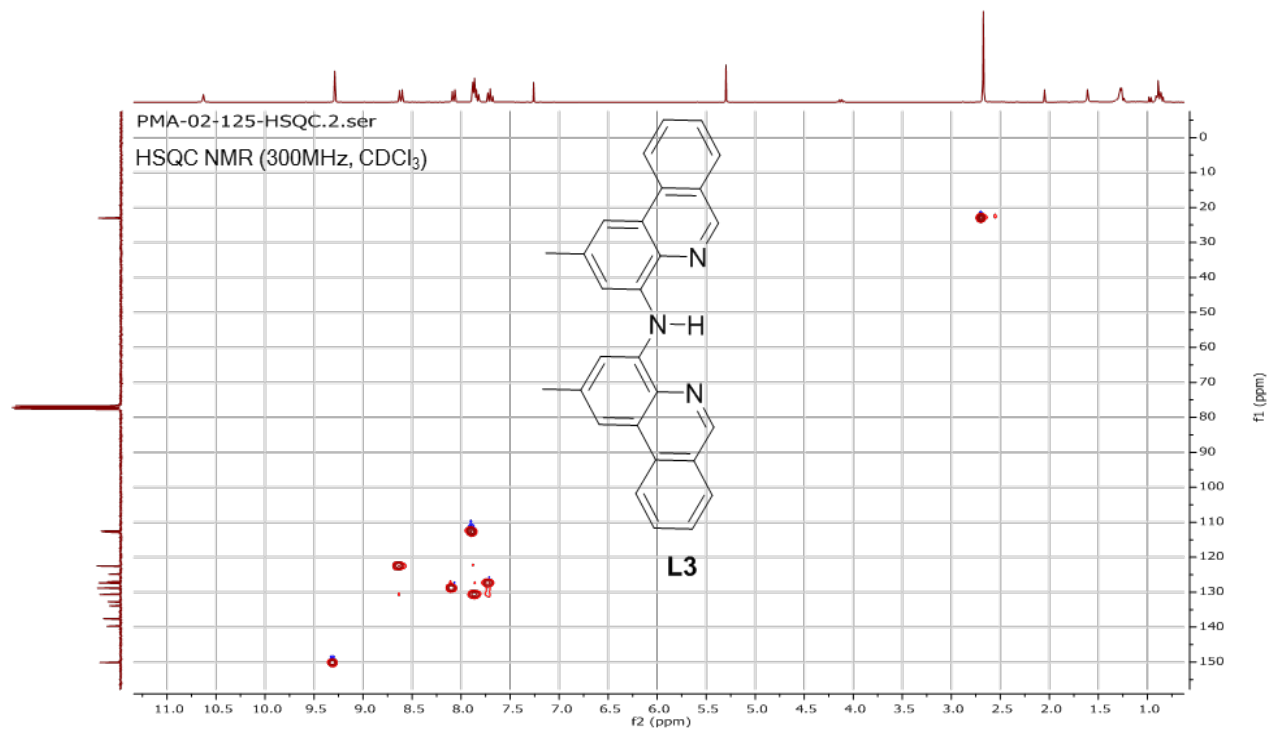


Figure S2.19. HSQC NMR spectra of **L3** in CDCl₃.

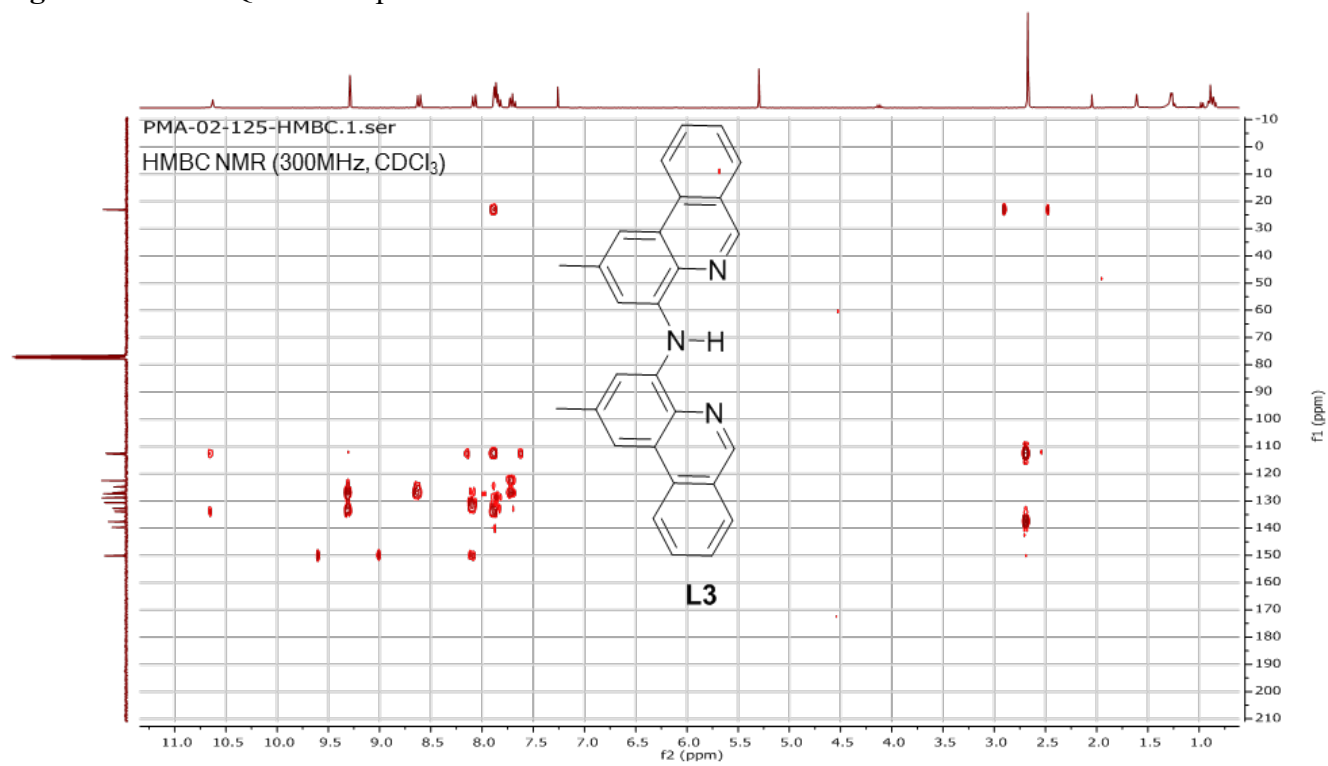


Figure S2.20. HMBC NMR spectrum of **L3** in CDCl₃.

JDB-01-24-A5H.1.fid
PROTON C6D6 C:\ Herbert 1

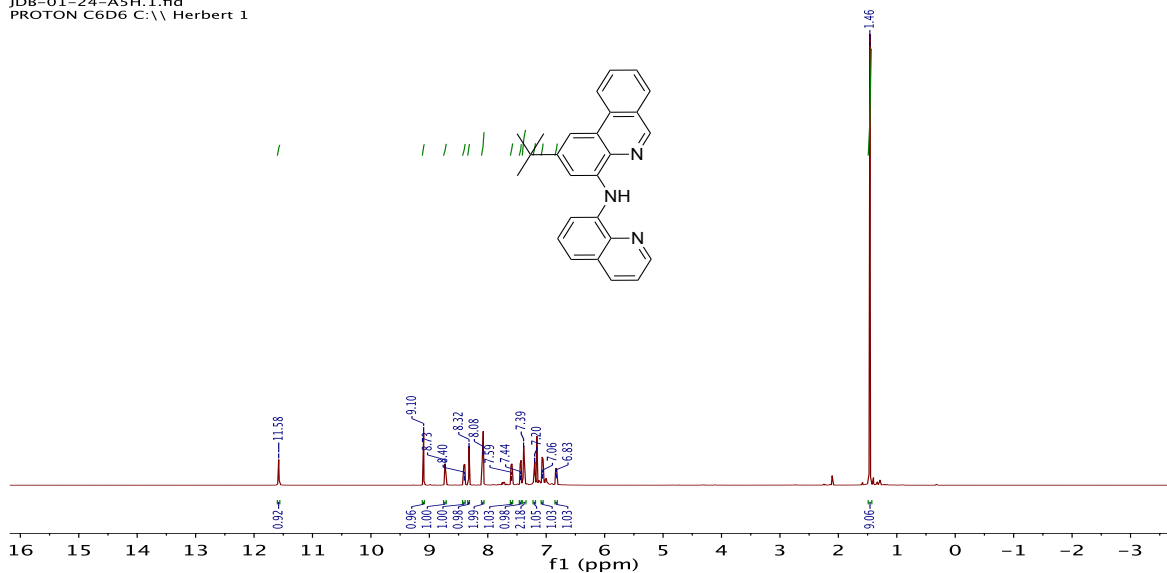


Figure S2.21. ^1H NMR (500 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of spectrum of L4.

JDB-01-24-A5C.1.fid
C13CPD32 C6D6 C:\ Herbert 1

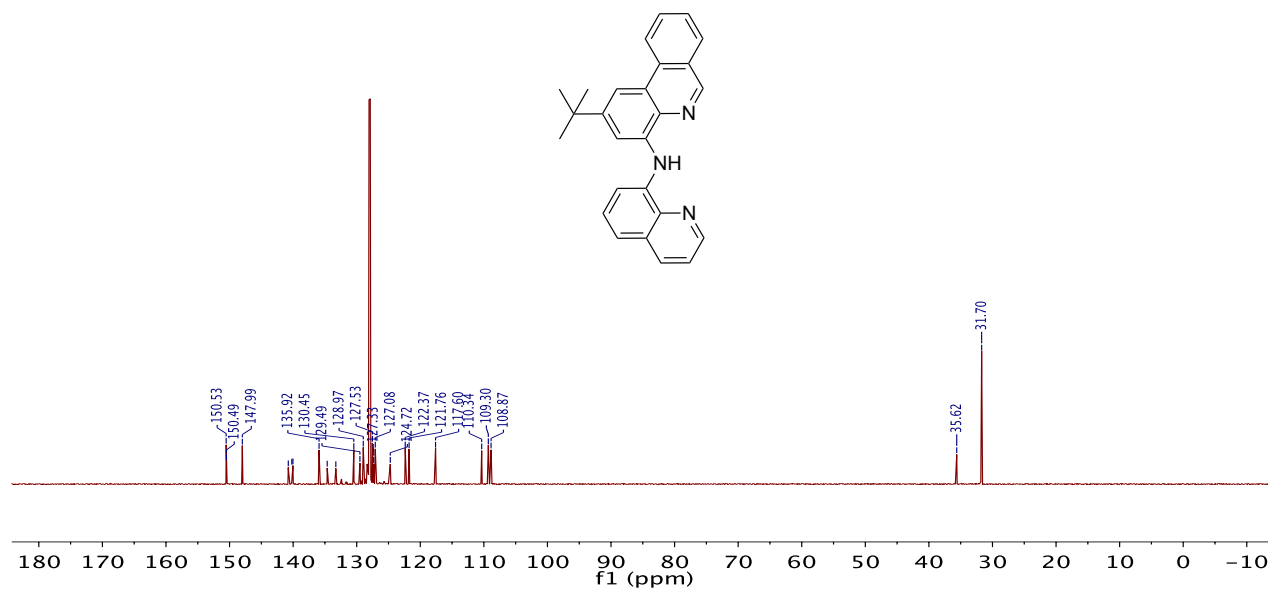


Figure S2.22. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of spectrum of L4.

PMA-01-158-A3H.1.fid
 ^1H NMR (300MHz, CDCl_3)

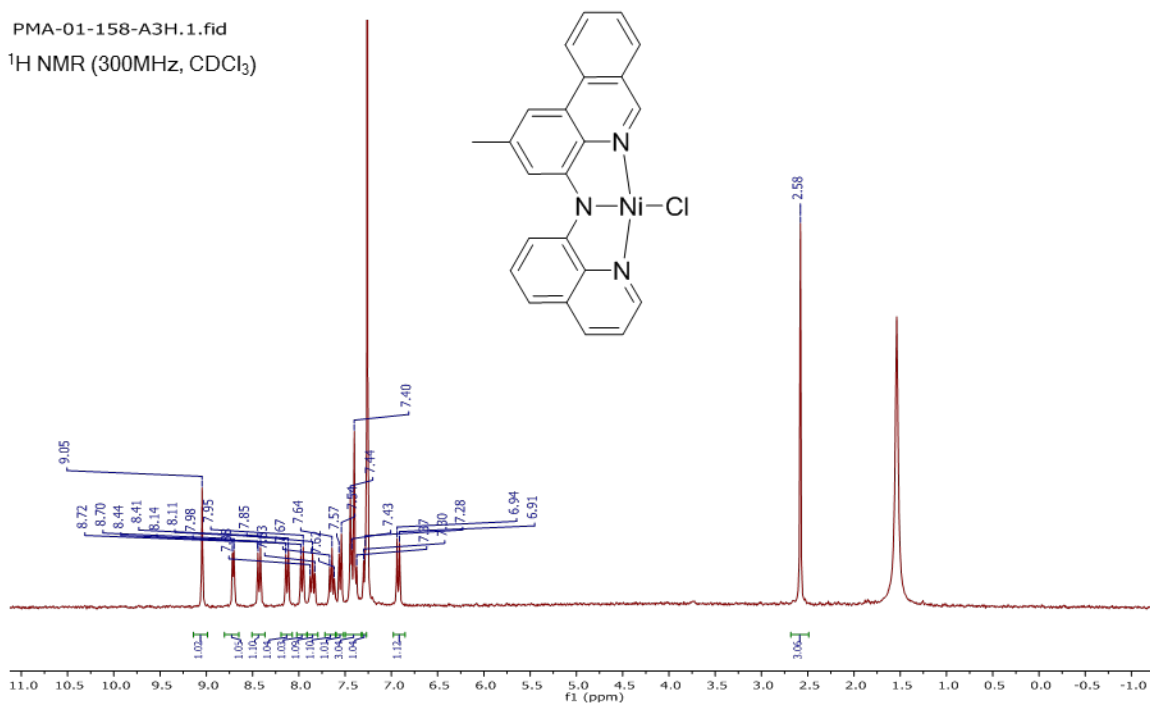


Figure S2.23. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of spectrum of L2-NiCl .

PMA-01-158-E3H.2.fid
 ^{13}C NMR (500MHz, CDCl_3)

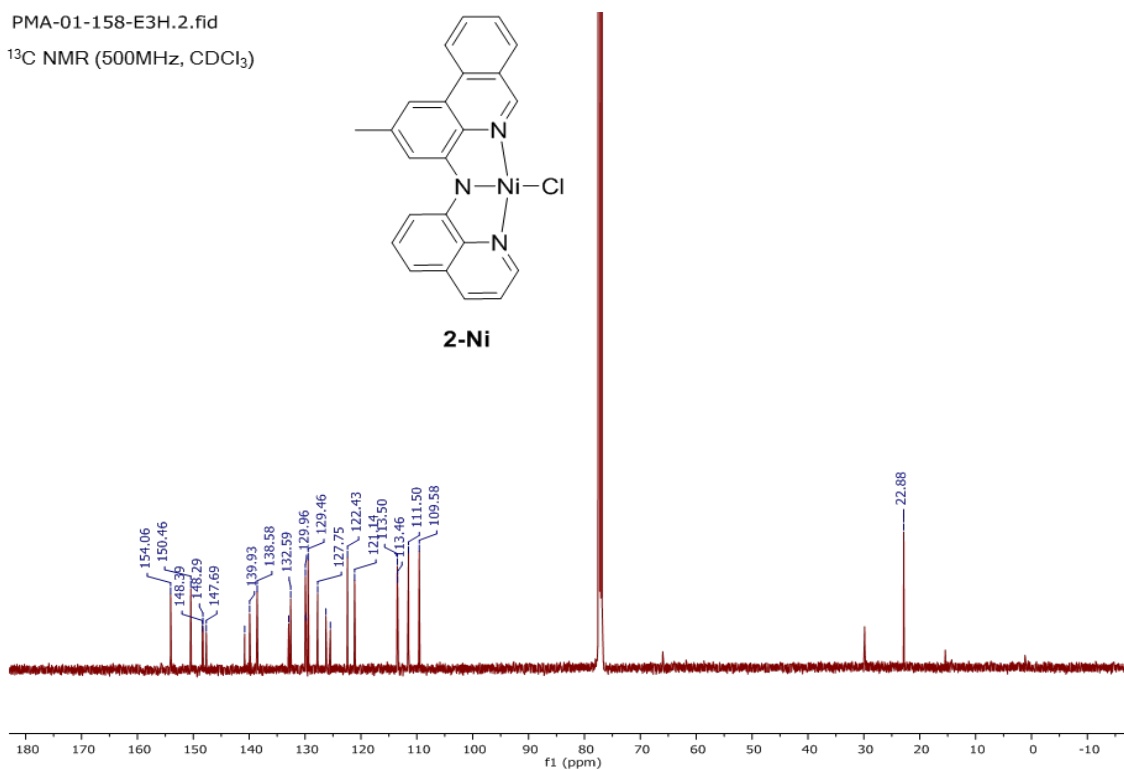


Figure S2.24. $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3 , 22 °C) spectrum of L2-NiCl .

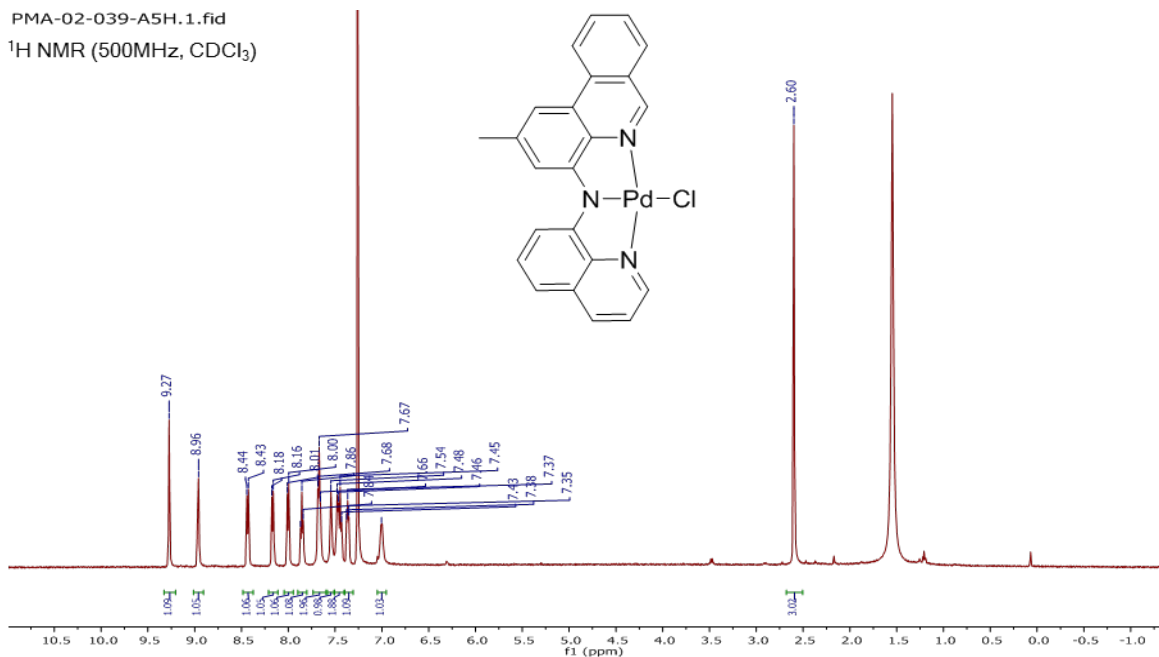


Figure S2.25. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of L2-PdCl.

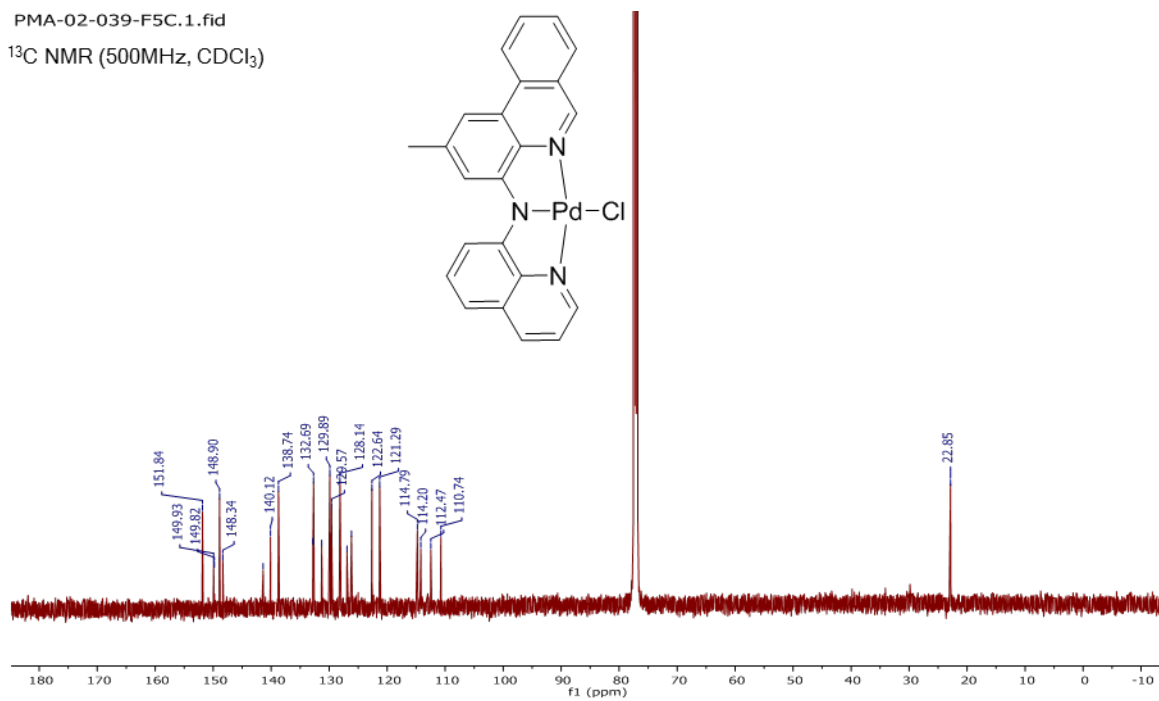


Figure S2.26. ¹³C{¹H} NMR (500 MHz, CDCl₃, 22 °C) spectrum of L2-PdCl.

PMA-02-042-B5h.1.fid
 ^1H NMR (500MHz, CDCl_3)

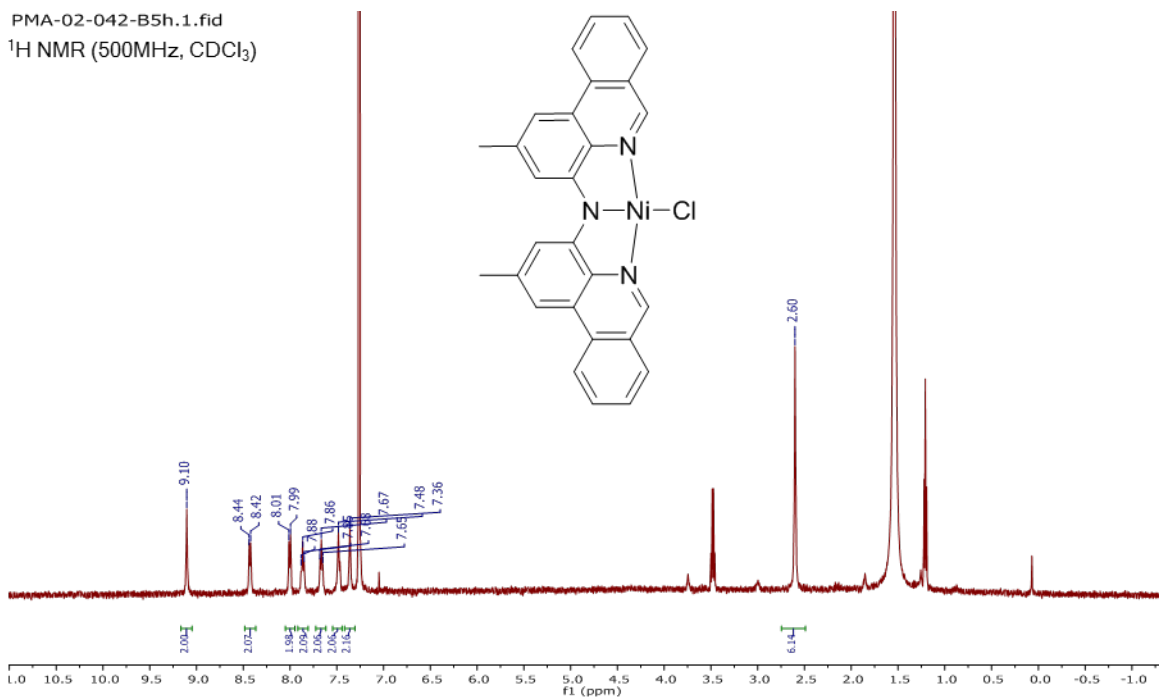


Figure S2.29. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of L3-NiCl.

PMA-03-057-A5H.1.fid
 ^{13}C NMR (500MHz, CDCl_3)

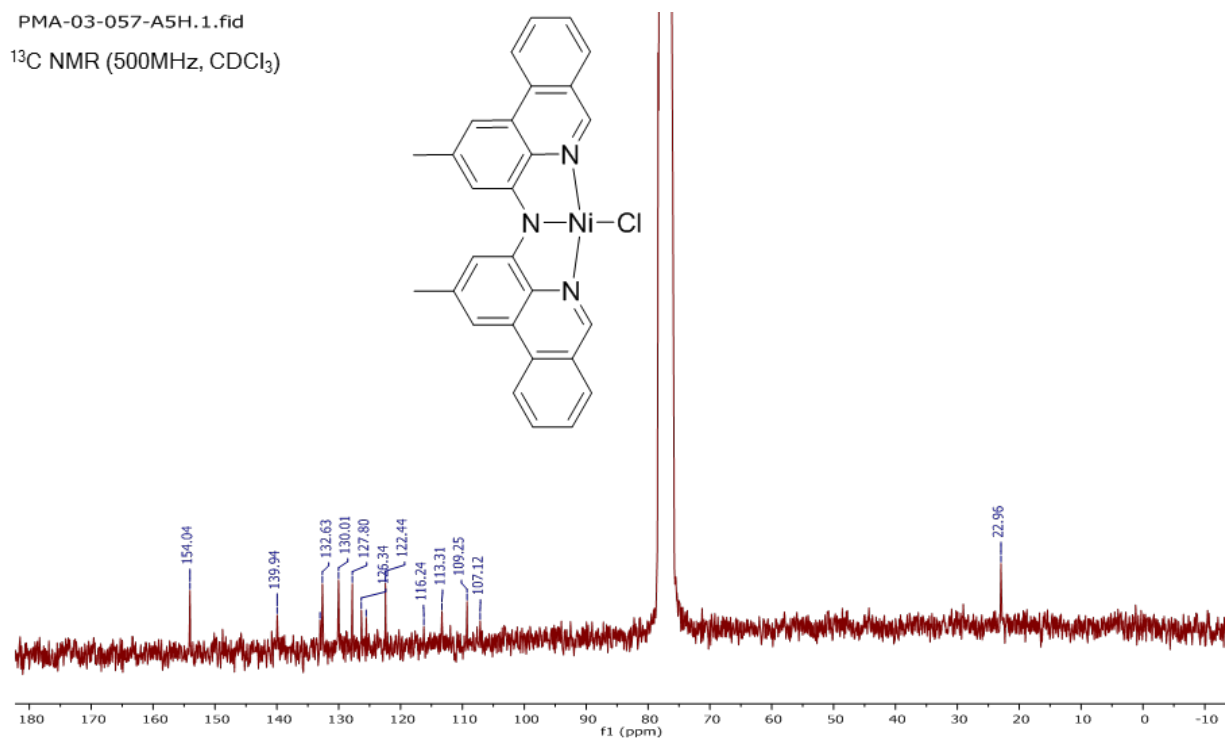


Figure S2.30. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectra of L3-NiCl in CDCl_3

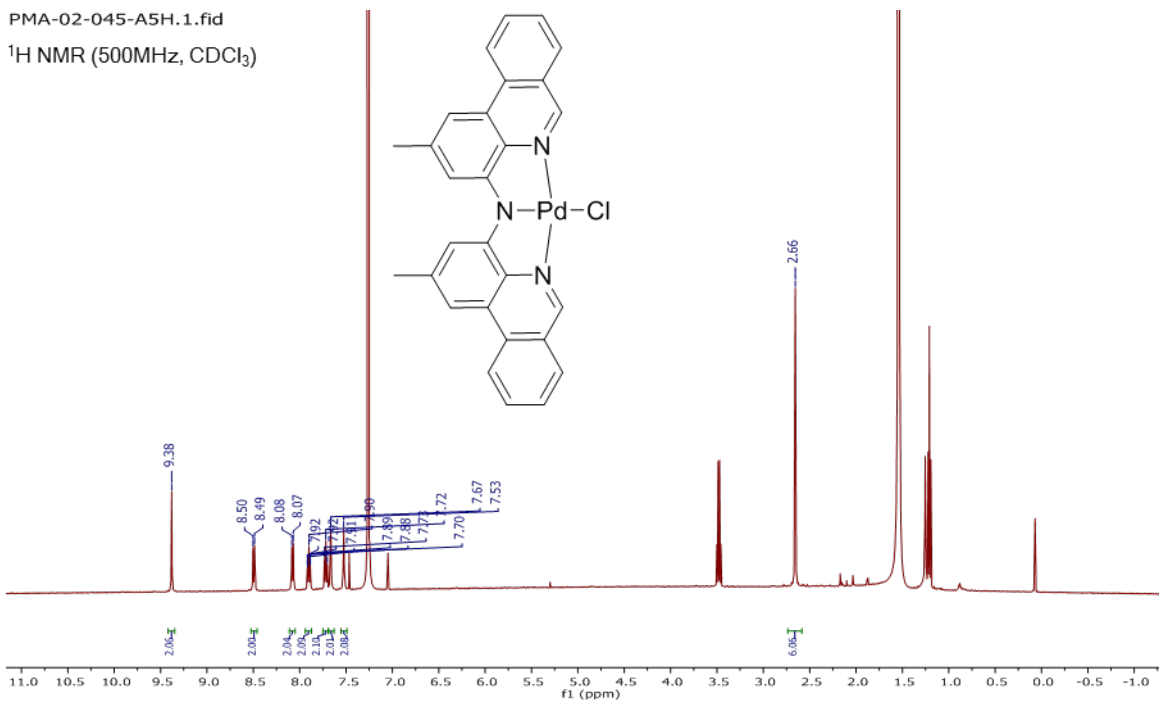


Figure S2.31. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of **L3-PdCl**.

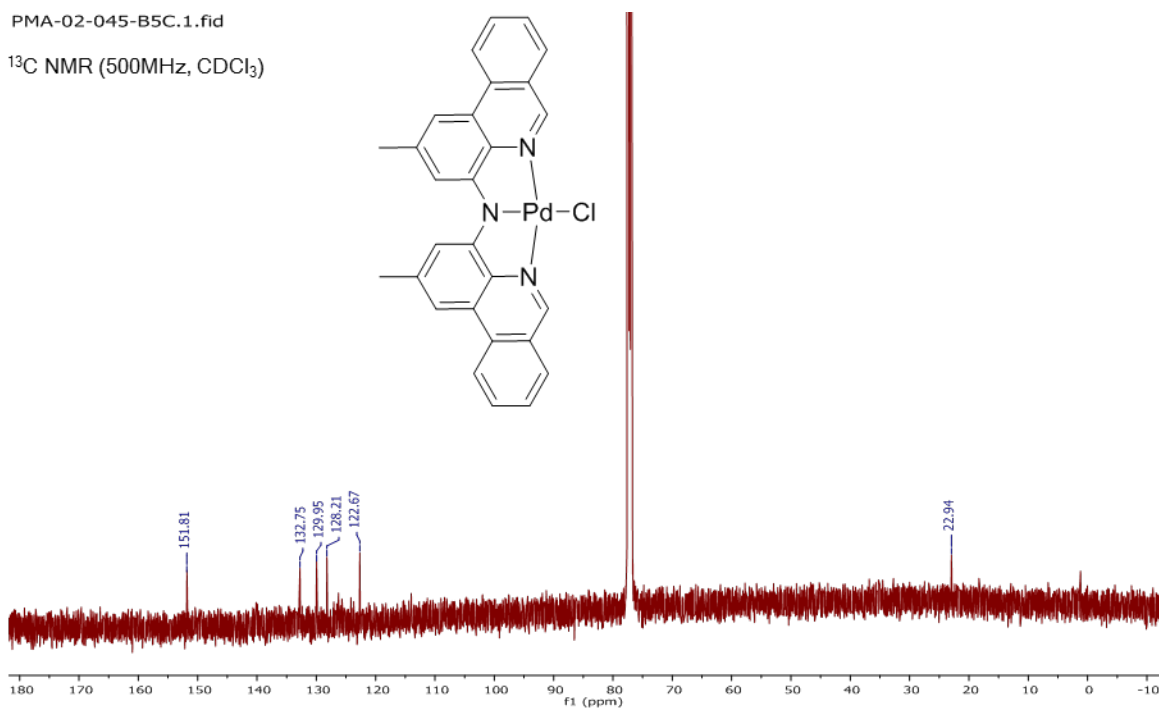


Figure S2.32. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of **L3-PdCl**.

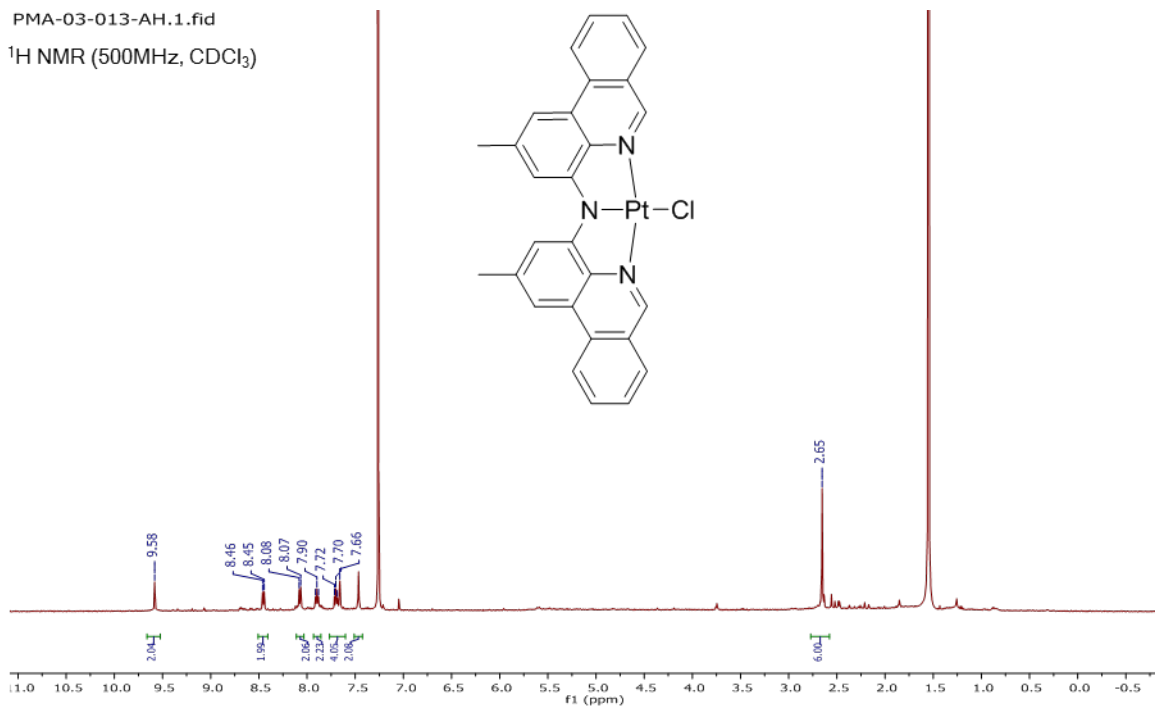


Figure S2.33. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of **L3-PtCl**.

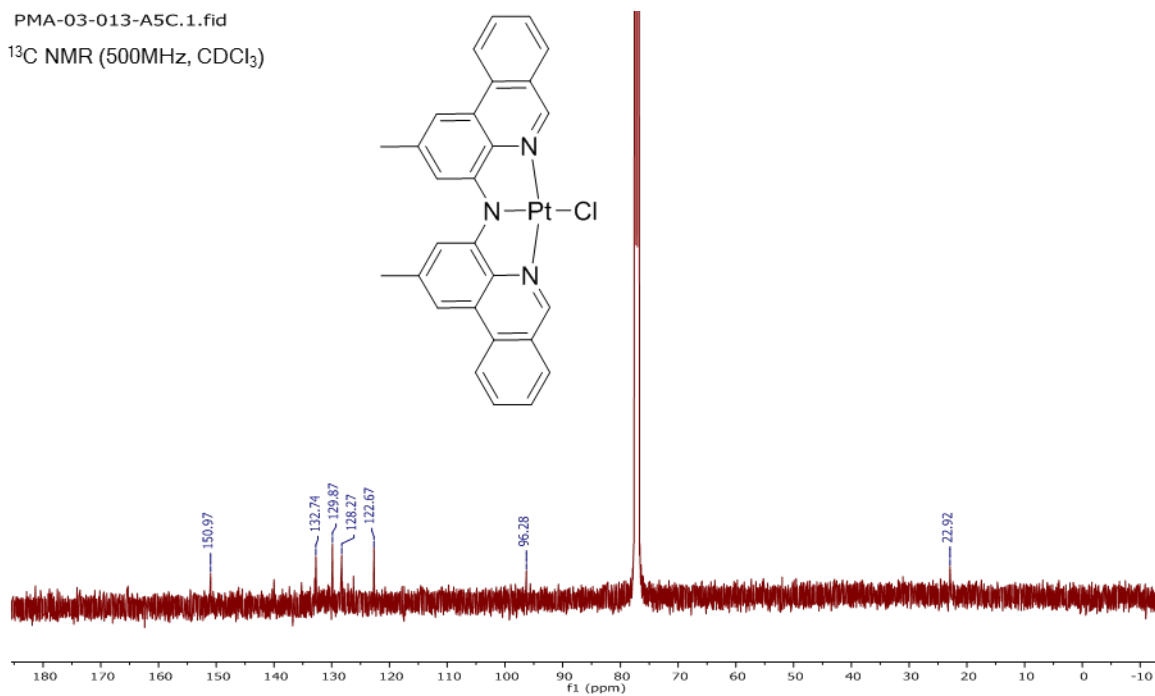


Figure S2.34. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of **L3-PtCl**.

PMA-02-093-B3H.1.fid
tAsNNN-NiCl after ether washes, filtered over celite
PROTON CDCl₃ {C:\Bruker\TOPSPIN1.3} Herbert 28

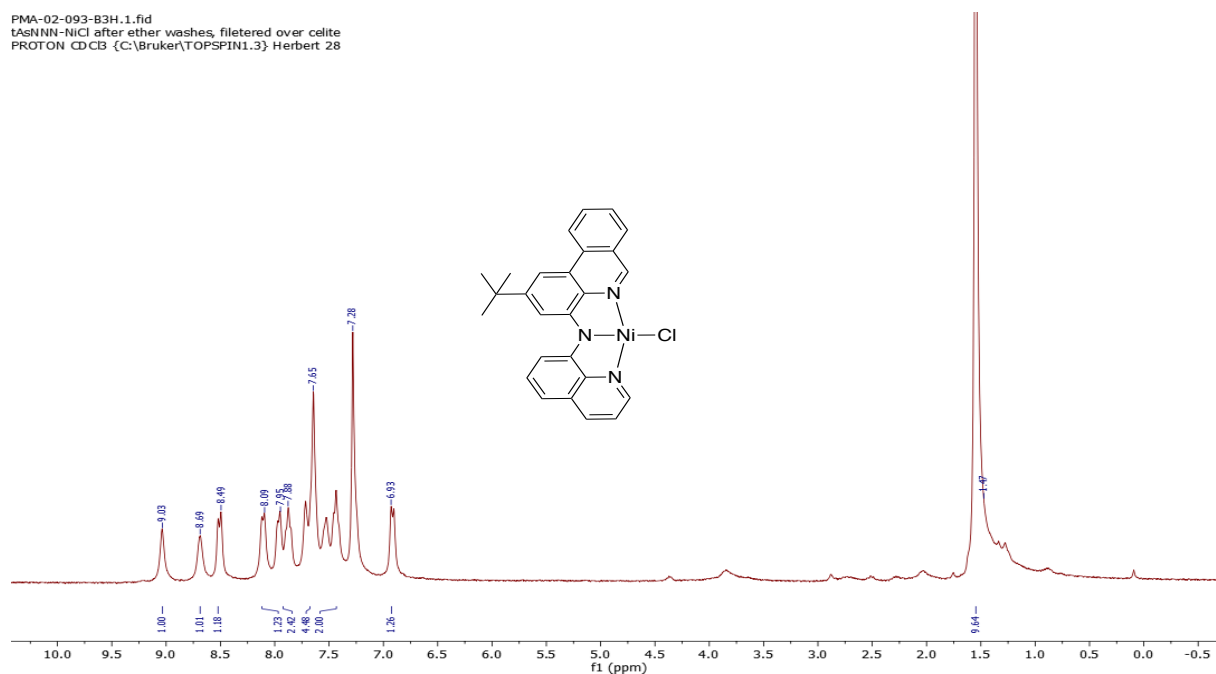


Figure S2.35. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L4-NiCl.

PMA-02-133-A3H.1.fid
tBuPhenNNNQuin-PdCl
PROTON CDCl₃ {C:\Bruker\TOPSPIN1.3} Herbert 38

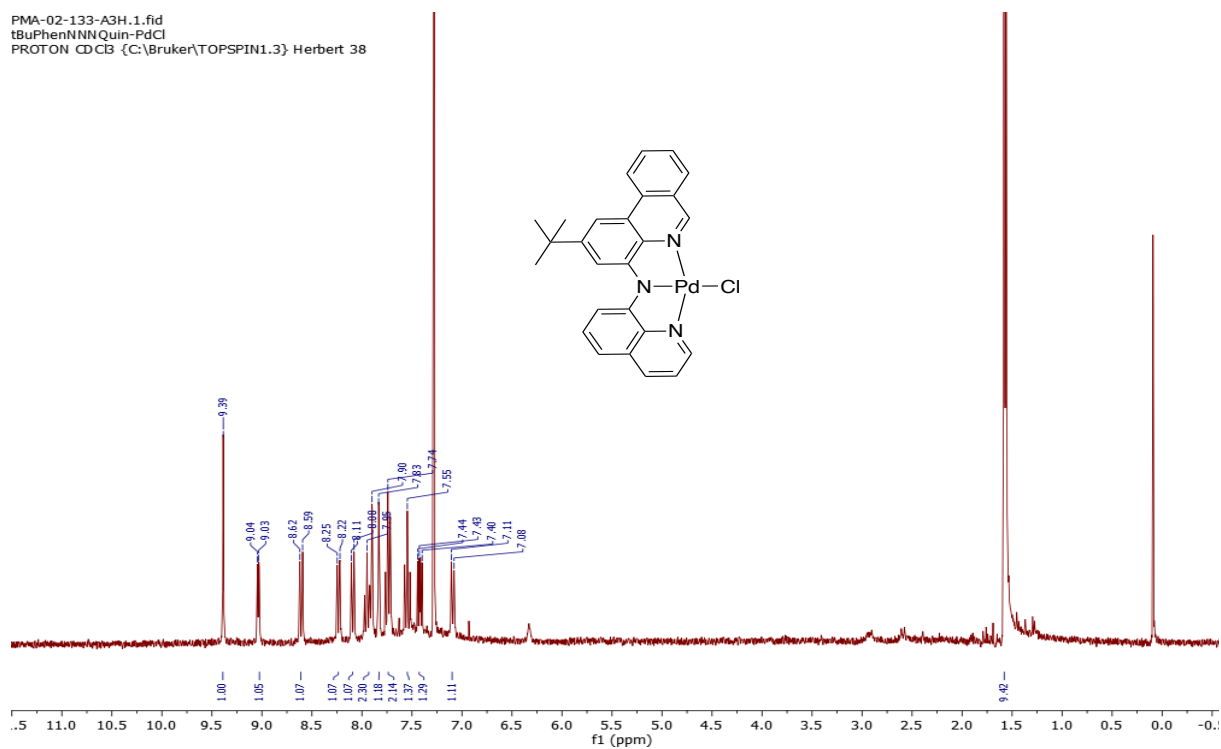


Figure S2.36. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L4-PdCl.

PMA-02-145-A3H.1.fid
tBuPhenNNNQuin-PdOAc
PROTON CDCl3 {C:\Bruker\TOPSPIN1.3} Herbert 39

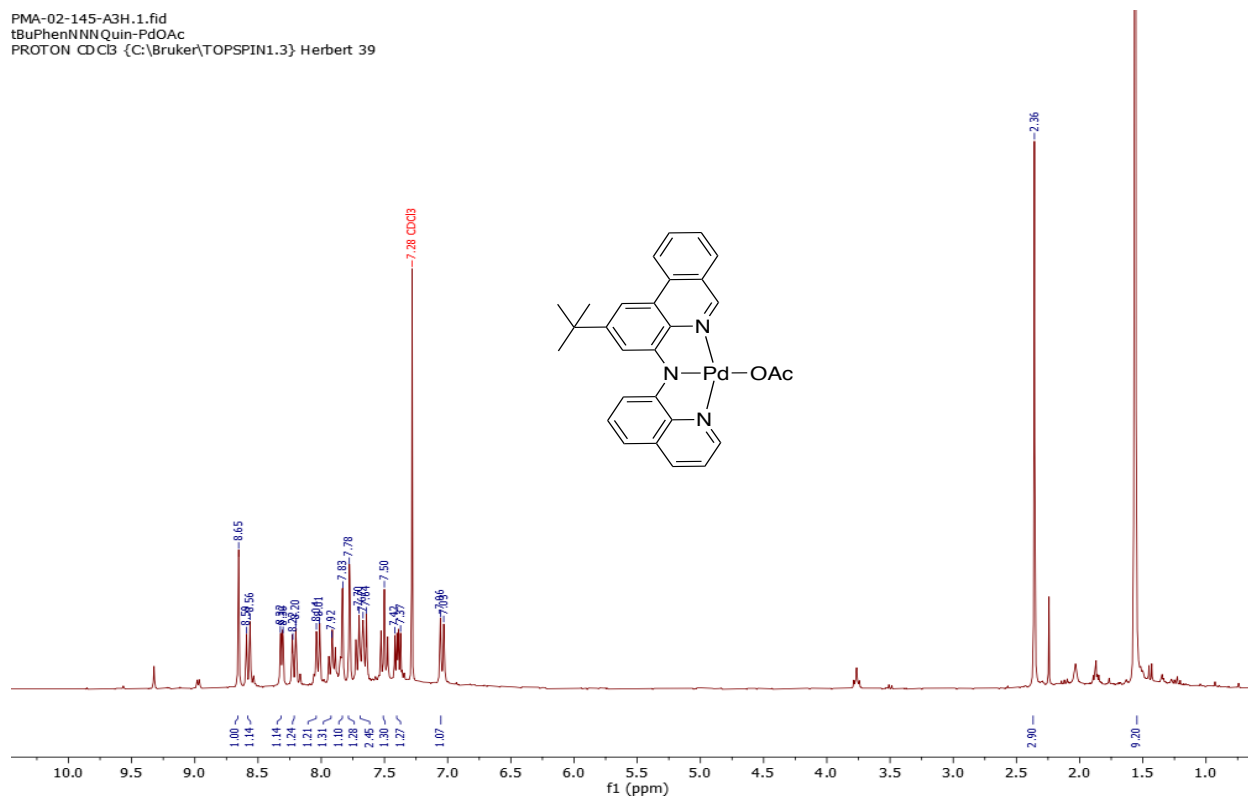


Figure S2.36. ^1H NMR (300 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of **L4-PdOAc**.

2.2. Computational Details:

Full reference for Gaussian 09 package:

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

Table S2.1. Selected Bond Distances and Angles of Optimized Structures

	1-Ni (DFT)	2-Ni (DFT)	3-Ni (DFT)
r[Ni-Cl] (Å)	2.20	2.21	2.21
r[Ni-N _{pyr}] (Å)	1.91	1.91 ^a , 1.91 ^b	1.91
r[Ni-N _{amido}] (Å)	1.87	1.87	1.86
Cl-Ni-N _{pyr} (deg)	95.5	95.4 ^a , 95.3 ^b	95.5

^a Distance and angle for the phenanthradine N, ^b Distance and angle for the quinoline N

Table S2.2. TD-DFT Summary

Compound	Transition	Assignment	λ_{calc} (nm)	Oscillator Strength	Coefficient	% Contribution
L1-NiCl	93→94	HOMO→LUMO	494.34	0.3698	0.70142	98.4
	93→95	HOMO→LUMO+1	483.13	0.0078	0.70319	98.9
L2-NiCl	110→111	HOMO→LUMO	490.66	0.2131	0.53712	57.7
	110→112	HOMO→LUMO+1			0.45206	40.9
	110→111	HOMO→LUMO	483.83	0.1722	-0.45215	40.9
	110→112	HOMO→LUMO+1			0.53581	57.4
L3-NiCl	127→128	HOMO→LUMO	496.51	0.0221	0.70183	98.5
	127→129	HOMO→LUMO+1	485.04	0.3536	0.69707	97.2

Table S2.3. TD-DFT Orbital Energies

Compound	HOMO-1 energy (eV)	HOMO energy (eV)	LUMO energy (eV)	LUMO+1 energy (eV)
L1-NiCl	-6.83	-5.35	-1.90	-1.85
L2-NiCl	-6.66	-5.32	-1.88	-1.84
L3-NiCl	-6.60	-5.28	-1.90	-1.79

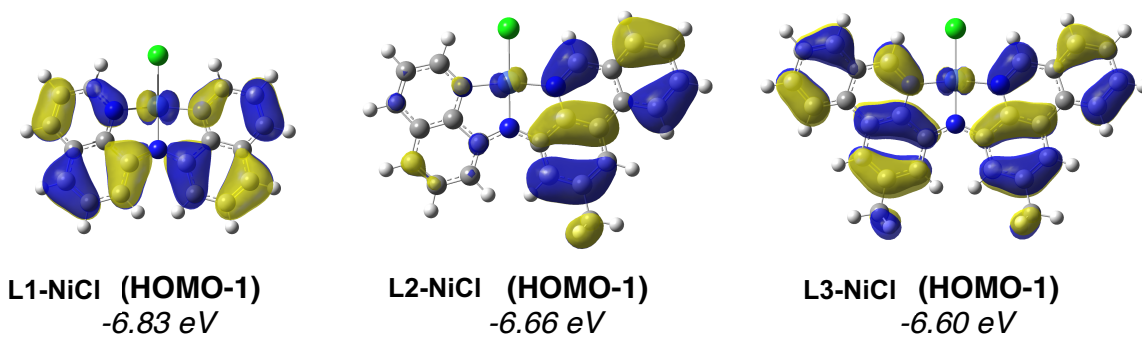


Figure S2.37. Orbital diagrams of the HOMO-1 for **L1-NiCl**, **L2-NiCl**, and **L3-NiCl**.

2.3. Energies and Reaction Coordinates:

2.3.1.L1-NiCl:

HF = -2825.2746691 hartrees

Zero-point correction= 0.260950 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.216236

Sum of electronic and zero-point Energies= -2825.013719

Sum of electronic and thermal Free Energies= -2825.058433

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
--------	--------	--------	-------------------------	--	--

Number	Number	Type	X	Y	Z
--------	--------	------	---	---	---

1	28	0	-0.000000	1.077475	-0.000002
2	17	0	-0.000002	3.281024	0.000001
3	7	0	0.000000	-0.792306	-0.000007

4	7	0	1.905151	0.895184	0.048416
5	6	0	1.240111	-1.379701	-0.039592
6	6	0	-1.240110	-1.379702	0.039587
7	7	0	-1.905151	0.895183	-0.048418
8	6	0	1.608196	-2.719457	-0.136014
9	1	0	0.869942	-3.506042	-0.220021
10	6	0	2.295792	-0.417337	0.004239
11	6	0	3.658176	-0.792975	-0.004696
12	6	0	4.202828	1.553017	0.101601
13	6	0	-2.295792	-0.417338	-0.004240
14	6	0	2.829113	1.843966	0.095904
15	1	0	2.468993	2.868317	0.127906
16	6	0	-2.829114	1.843965	-0.095904
17	1	0	-2.468993	2.868316	-0.127907
18	6	0	4.616026	0.244424	0.049300
19	6	0	-3.986099	-2.169118	0.076931
20	1	0	-5.031531	-2.469136	0.083486
21	6	0	-2.969622	-3.091428	0.149655
22	1	0	-3.208151	-4.150621	0.221162
23	6	0	-3.658176	-0.792977	0.004699
24	6	0	3.986100	-2.169117	-0.076925
25	1	0	5.031532	-2.469135	-0.083477
26	6	0	2.969623	-3.091427	-0.149652

27	6	0	-1.608194	-2.719458	0.136011
28	1	0	-0.869940	-3.506042	0.220016
29	6	0	-4.202829	1.553015	-0.101597
30	1	0	-4.913981	2.372342	-0.142942
31	6	0	-4.616026	0.244423	-0.049294
32	1	0	-5.674484	-0.009755	-0.045773
33	1	0	4.913980	2.372344	0.142948
34	1	0	5.674484	-0.009753	0.045782
35	1	0	3.208154	-4.150620	-0.221157

2.3.2. L2-NiCl:

HF = -3018.1050941 hartrees

Zero-point correction= 0.333731 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.283365

Sum of electronic and zero-point Energies= -3017.771363

Sum of electronic and thermal Free Energies= -3017.821729

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	28	0	-0.767469	-1.135410	0.000070
2	17	0	-0.581790	-3.333443	0.000241
3	7	0	-0.923637	0.728418	-0.000097
4	7	0	1.114079	-0.797086	-0.000056
5	6	0	0.265547	1.420153	-0.000025
6	6	0	-2.211242	1.206075	-0.000214
7	7	0	-2.680678	-1.120695	0.000179
8	6	0	0.506393	2.793025	0.000126
9	1	0	-0.299713	3.515476	0.000281
10	6	0	1.402265	0.559753	-0.000053
11	6	0	2.717557	1.054538	-0.000041
12	6	0	3.464626	-1.278907	-0.000114
13	6	0	-3.180723	0.154435	-0.000021
14	6	0	2.096001	-1.662914	-0.000081
15	1	0	1.828694	-2.717819	-0.000074
16	6	0	-3.520878	-2.146196	0.000391
17	1	0	-3.074358	-3.135799	0.000548
18	6	0	3.798897	0.097219	-0.000094
19	6	0	6.138870	-0.524633	-0.000164
20	1	0	7.186411	-0.232202	-0.000185
21	6	0	-5.021511	1.753144	-0.000318
22	1	0	-6.089617	1.958382	-0.000338

23	6	0	-4.090014	2.762889	-0.000583
24	1	0	-4.418768	3.800038	-0.000831
25	6	0	5.162434	0.451201	-0.000121
26	1	0	5.456193	1.497630	-0.000112
27	6	0	-4.571030	0.410905	-0.000047
28	6	0	2.907881	2.451318	0.000052
29	1	0	3.912109	2.868092	0.000072
30	6	0	1.820074	3.305192	0.000163
31	6	0	4.475795	-2.263718	-0.000154
32	1	0	4.186931	-3.313165	-0.000165
33	6	0	5.800976	-1.890887	-0.000179
34	1	0	6.584631	-2.644148	-0.000211
35	6	0	-2.701493	2.510660	-0.000545
36	1	0	-2.043232	3.367619	-0.000822
37	6	0	-4.914218	-1.974543	0.000406
38	1	0	-5.552539	-2.852815	0.000579
39	6	0	2.007572	4.791830	0.000365
40	1	0	1.538771	5.248497	-0.880629
41	1	0	3.067968	5.064234	0.000187
42	1	0	1.539158	5.248188	0.881727
43	6	0	-5.436861	-0.704882	0.000180
44	1	0	-6.512944	-0.540591	0.000166

2.3.3. L3-NiCl:

HF = -3210.9361927 hartrees

Zero-point correction= 0.409019 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.353212

Sum of electronic and zero-point Energies= -3210.527174

Sum of electronic and thermal Free Energies= -3210.582980

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	2.811773	1.825310	-0.130728
2	1	0	2.460941	2.853972	-0.189543
3	6	0	4.206934	1.550861	-0.126561
4	6	0	5.135316	2.610286	-0.210570
5	1	0	4.762479	3.630420	-0.282904
6	6	0	6.486343	2.345814	-0.199897
7	1	0	7.206394	3.157523	-0.265016
8	6	0	6.934557	1.015120	-0.104597
9	1	0	8.002363	0.808566	-0.096913
10	6	0	6.039801	-0.033059	-0.019895
11	1	0	6.414746	-1.050556	0.053240

12	6	0	4.652372	0.209884	-0.028879
13	6	0	3.652507	-0.829255	0.058310
14	6	0	2.302801	-0.440802	0.023021
15	6	0	1.237908	-1.385178	0.085512
16	6	0	1.579293	-2.725285	0.258039
17	1	0	0.822769	-3.490133	0.389954
18	6	0	2.928717	-3.130961	0.306148
19	6	0	3.948039	-2.201760	0.190560
20	1	0	4.981437	-2.539657	0.220434
21	6	0	3.234724	-4.586678	0.488501
22	1	0	4.313725	-4.771563	0.506123
23	1	0	2.799143	-5.186917	-0.320277
24	1	0	2.810144	-4.963433	1.427881
25	6	0	-2.811772	1.825311	0.130716
26	1	0	-2.460941	2.853973	0.189523
27	6	0	-4.206933	1.550862	0.126552
28	6	0	-5.135315	2.610288	0.210554
29	1	0	-4.762478	3.630422	0.282881
30	6	0	-6.486342	2.345815	0.199885
31	1	0	-7.206393	3.157525	0.264998
32	6	0	-6.934557	1.015121	0.104594
33	1	0	-8.002363	0.808567	0.096914
34	6	0	-6.039801	-0.033059	0.019899

35	1	0	-6.414746	-1.050556	-0.053228
36	6	0	-4.652372	0.209885	0.028879
37	6	0	-3.652507	-0.829255	-0.058304
38	6	0	-2.302801	-0.440802	-0.023019
39	6	0	-1.237908	-1.385178	-0.085508
40	6	0	-1.579294	-2.725286	-0.258027
41	1	0	-0.822770	-3.490134	-0.389942
42	6	0	-2.928718	-3.130962	-0.306130
43	6	0	-3.948039	-2.201761	-0.190545
44	1	0	-4.981437	-2.539658	-0.220418
45	6	0	-3.234725	-4.586682	-0.488464
46	1	0	-2.810068	-4.963472	-1.427795
47	1	0	-4.313727	-4.771556	-0.506171
48	1	0	-2.799221	-5.186899	0.320371
49	17	0	0.000000	3.275087	-0.000010
50	7	0	0.000000	-0.795444	-0.000001
51	7	0	1.903753	0.885467	-0.060055
52	7	0	-1.903752	0.885468	0.060047
53	28	0	0.000000	1.068110	-0.000005

Chapter 3:

3.1. NMR Spectra:

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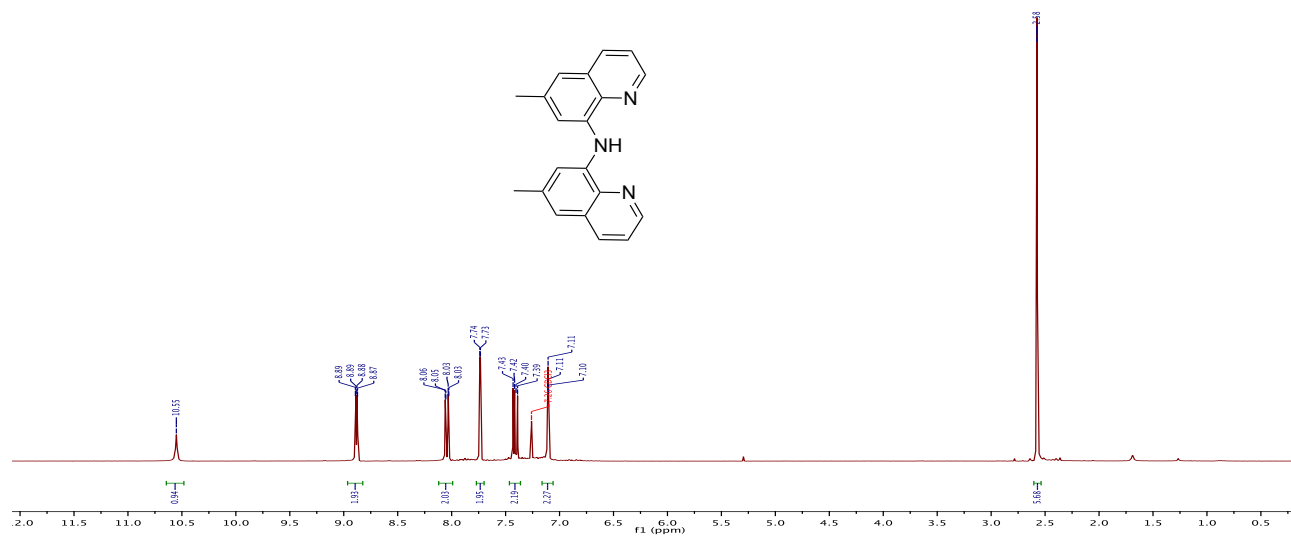


Figure S3.1. ^1H NMR (300 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L5.

PMA-04-022-C3C.1.fid

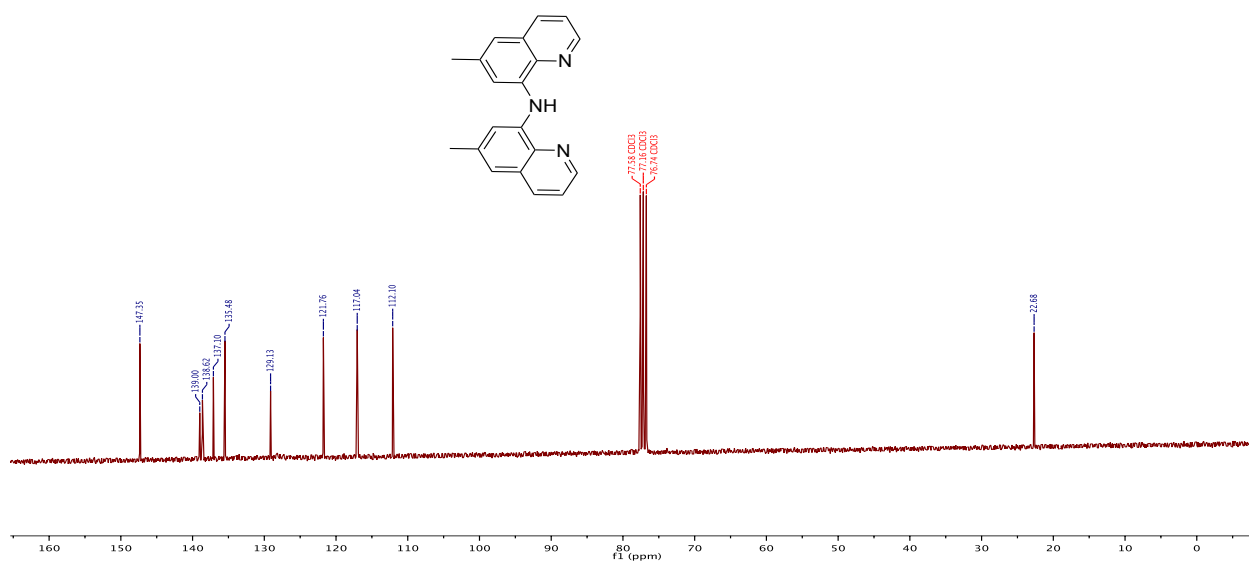


Figure S3.2. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L5.

PMA-03-091-C3H.1.fid

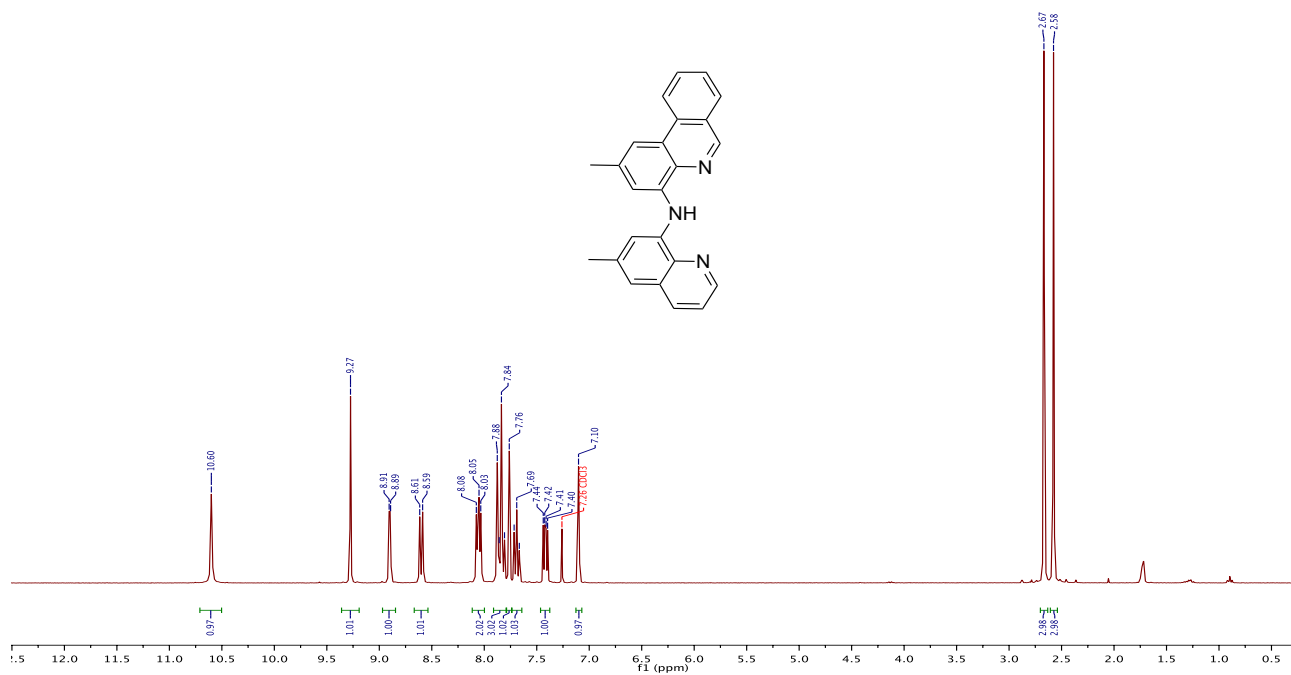


Figure S3.3. ^1H NMR (300 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L6.

PMA-03-091-C3C.1.fid

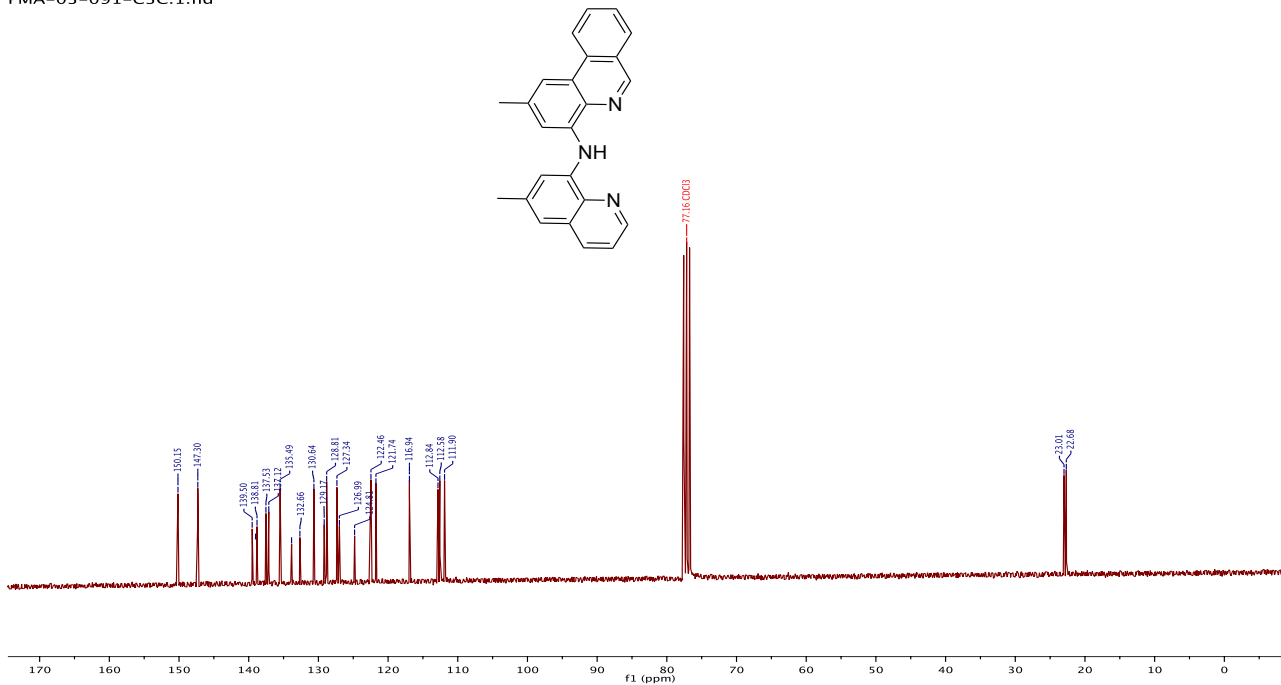


Figure S3.4. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L6.

PMA-04-076-B3H.1.fid

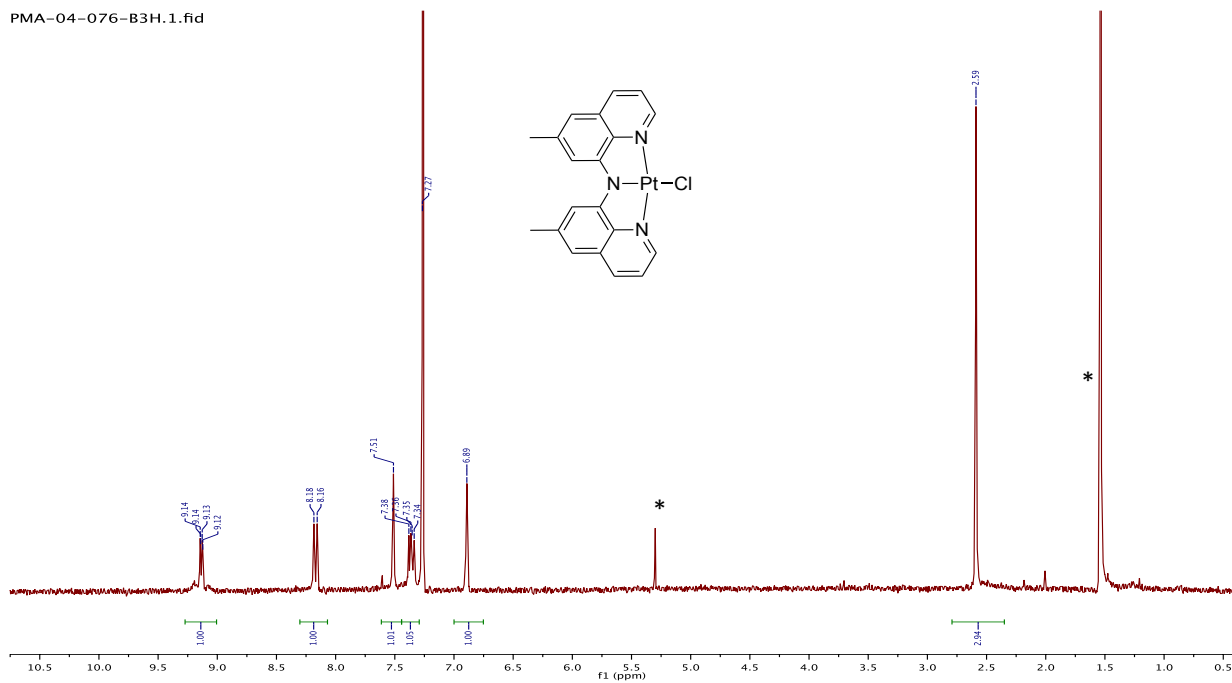


Figure S3.5. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L5-PtCl.

PMA-03-142-A3H.1.fid

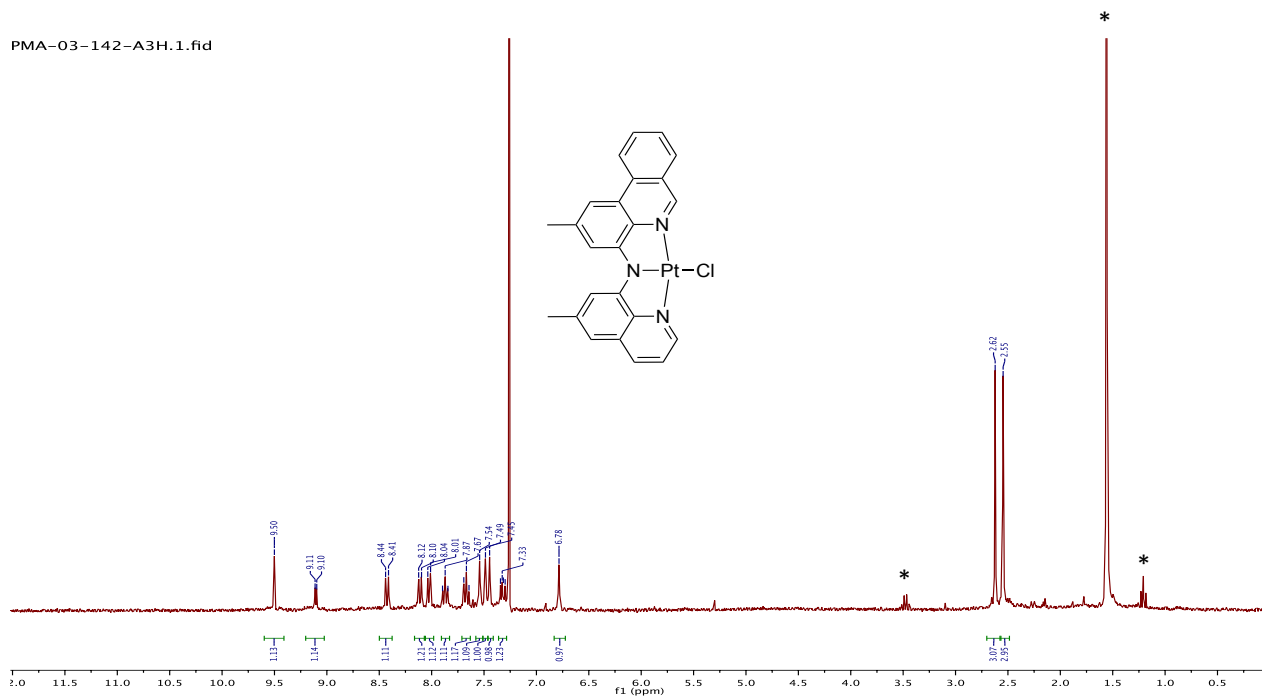


Figure S3.6. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L6-PtCl.

3.2. Energies And Reaction Coordinaties:

3.2.1. L5_S0:

HF = -935.828978 hartrees

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	7	0	-0.000000	0.302329	-0.000003	
2	7	0	2.050127	1.979386	0.317332	
3	7	0	-2.050128	1.979385	-0.317333	
4	6	0	2.361238	0.656816	0.102380	
5	6	0	-1.263129	-0.270178	0.075543	
6	6	0	2.911661	-2.067377	-0.417863	
7	6	0	1.263129	-0.270178	-0.075546	
8	6	0	3.703629	0.189399	0.035155	
9	6	0	-2.361239	0.656816	-0.102381	
10	6	0	3.962309	-1.191146	-0.217051	
11	1	0	4.990395	-1.539309	-0.261038	
12	6	0	3.040268	2.854497	0.478323	
13	1	0	2.759042	3.888885	0.643310	
14	6	0	-3.703629	0.189398	-0.035154	
15	6	0	1.561577	-1.599948	-0.350869	
16	1	0	0.776235	-2.313519	-0.563151	
17	6	0	-1.561576	-1.599949	0.350866	
18	1	0	-0.776233	-2.313520	0.563145	
19	6	0	3.151341	-3.530119	-0.718424	
20	1	0	4.219591	-3.758994	-0.752895	
21	1	0	2.710713	-3.805770	-1.683126	
22	1	0	2.688928	-4.166121	0.044623	
23	6	0	4.739431	1.153718	0.219528	
24	6	0	4.413823	2.479629	0.441083	
25	6	0	-2.911659	-2.067378	0.417862	
26	6	0	-3.962309	-1.191147	0.217052	

27	1	0	-4.990394	-1.539311	0.261040
28	6	0	-3.040269	2.854496	-0.478322
29	1	0	-2.759044	3.888884	-0.643309
30	6	0	-4.413824	2.479628	-0.441081
31	1	0	-5.177469	3.234590	-0.582778
32	6	0	-4.739432	1.153717	-0.219525
33	1	0	-5.775845	0.832022	-0.179434
34	6	0	-3.151339	-3.530119	0.718427
35	1	0	-2.688902	-4.166124	-0.044603
36	1	0	-2.710735	-3.805760	1.683143
37	1	0	-4.219589	-3.759000	0.752871
38	1	0	5.775845	0.832023	0.179438
39	1	0	5.177467	3.234591	0.582782
40	1	0	-0.000000	1.325297	-0.000003

3.2.2. L6_S0:

HF = -1089.3386594 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.902637	-0.131644	-0.051060
2	7	0	-1.408248	-1.413041	0.180255
3	7	0	2.616808	-2.148384	-0.379609
4	6	0	-1.484616	-0.032009	-0.010200
5	6	0	2.246157	0.195056	0.077131
6	6	0	-1.487990	2.744125	-0.468684
7	6	0	-0.232180	0.665987	-0.137100
8	6	0	-2.712153	0.667216	-0.095198
9	6	0	3.159458	-0.913389	-0.109093
10	6	0	-2.693706	2.069270	-0.315615
11	1	0	-3.621061	2.627787	-0.378799

12	6	0	-2.517732	-2.102314	0.303718
13	1	0	-2.429551	-3.175898	0.449709
14	6	0	4.562219	-0.705749	0.007699
15	6	0	-0.258647	2.039259	-0.384450
16	1	0	0.655549	2.590590	-0.561201
17	6	0	2.776617	1.436150	0.411344
18	1	0	2.129534	2.275002	0.633268
19	6	0	-5.238021	0.468141	-0.013732
20	1	0	-5.356237	1.533694	-0.172892
21	6	0	-1.456114	4.233606	-0.731819
22	1	0	-2.465089	4.642723	-0.827898
23	1	0	-0.908278	4.454615	-1.654422
24	1	0	-0.949150	4.762543	0.082909
25	6	0	-3.941275	-0.106543	0.045817
26	6	0	-3.833294	-1.508656	0.252301
27	6	0	4.187203	1.642409	0.527810
28	6	0	5.063576	0.593373	0.318891
29	1	0	6.136524	0.742742	0.400739
30	6	0	3.433448	-3.185476	-0.551904
31	1	0	2.971325	-4.144358	-0.759850
32	6	0	4.850897	-3.072253	-0.471209
33	1	0	5.466392	-3.950005	-0.625944
34	6	0	5.407940	-1.837851	-0.190404
35	1	0	6.484182	-1.714489	-0.114525
36	6	0	-4.996676	-2.306857	0.398708
37	1	0	-4.886943	-3.376140	0.555902
38	6	0	-6.254374	-1.723641	0.340482
39	1	0	-7.147539	-2.328458	0.451426
40	6	0	-6.370110	-0.324874	0.131149
41	1	0	-7.354422	0.128567	0.082844
42	6	0	4.683616	3.025120	0.886940
43	1	0	4.384491	3.755811	0.127029
44	1	0	4.258764	3.355414	1.841479
45	1	0	5.773120	3.046865	0.972107
46	1	0	0.714551	-1.136127	-0.084468

3.2.3. L3_S0:

HF = -1242.8479739 hartrees

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	7	0	2.078522	-1.413465	-0.280775	
2	7	0	-2.078521	-1.413465	0.280773	
3	6	0	-3.904922	1.768523	-0.473060	
4	1	0	-4.909414	2.159586	-0.590538	
5	6	0	3.063919	-2.266390	-0.432911	
6	1	0	2.806170	-3.299993	-0.649803	
7	6	0	4.457295	-1.901325	-0.326428	
8	6	0	4.788041	-0.551883	-0.026756	
9	6	0	3.698533	0.401811	0.152852	
10	6	0	3.904922	1.768524	0.473059	
11	1	0	4.909413	2.159588	0.590536	
12	6	0	2.823000	2.621697	0.659584	
13	6	0	1.498337	2.137077	0.506413	
14	1	0	0.680320	2.816552	0.710113	
15	6	0	1.253165	0.807978	0.157702	
16	7	0	-0.000000	0.226624	-0.000003	
17	6	0	-1.253165	0.807977	-0.157706	
18	6	0	-2.374935	-0.078798	-0.002331	
19	6	0	-3.063918	-2.266391	0.432910	
20	1	0	-2.806169	-3.299993	0.649802	
21	6	0	-4.457294	-1.901325	0.326428	
22	6	0	-4.788041	-0.551883	0.026756	
23	6	0	-3.698533	0.401811	-0.152853	
24	6	0	-2.823001	2.621696	-0.659586	
25	6	0	-1.498338	2.137077	-0.506417	
26	1	0	-0.680321	2.816551	-0.710119	
27	6	0	-3.030233	4.072544	-1.035013	

28	1	0	-4.090230	4.299754	-1.174678
29	1	0	-2.503748	4.312989	-1.965160
30	1	0	-2.637983	4.737369	-0.257466
31	6	0	-6.159450	-0.201767	-0.082564
32	1	0	-6.445275	0.818644	-0.310344
33	6	0	-7.150344	-1.159028	0.101633
34	1	0	-8.194179	-0.876359	0.016316
35	6	0	-6.812442	-2.504464	0.401561
36	1	0	-7.596745	-3.239807	0.542753
37	6	0	-5.478065	-2.868772	0.511949
38	1	0	-5.199675	-3.893563	0.740864
39	6	0	2.374935	-0.078798	0.002329
40	6	0	3.030232	4.072542	1.035019
41	1	0	2.503808	4.312961	1.965208
42	1	0	2.637913	4.737373	0.257511
43	1	0	4.090234	4.299770	1.174613
44	6	0	6.159450	-0.201766	0.082566
45	1	0	6.445275	0.818644	0.310346
46	6	0	7.150345	-1.159027	-0.101630
47	1	0	8.194179	-0.876358	-0.016312
48	6	0	6.812443	-2.504463	-0.401558
49	1	0	7.596746	-3.239806	-0.542749
50	6	0	5.478066	-2.868772	-0.511947
51	1	0	5.199676	-3.893562	-0.740862
52	1	0	-0.000000	-0.794635	-0.000004

3.2.4. L5-PtCl_S0:

HF = -1069.416144 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	17	0	0.000005	3.702867	0.000009

2	7	0	-0.000001	-0.762063	-0.000008
3	7	0	2.013750	0.971088	0.059521
4	7	0	-2.013749	0.971090	-0.059537
5	6	0	2.348158	-0.375305	0.022226
6	6	0	-1.266485	-1.336838	0.026200
7	6	0	2.991247	-3.102306	-0.115524
8	6	0	1.266483	-1.336839	-0.026213
9	6	0	3.705290	-0.781626	0.022813
10	6	0	-2.348159	-0.375302	-0.022234
11	6	0	4.013385	-2.171000	-0.041390
12	1	0	5.052624	-2.485603	-0.040497
13	6	0	2.957920	1.911989	0.113417
14	1	0	2.615358	2.939566	0.141133
15	6	0	-3.705291	-0.781623	-0.022824
16	6	0	1.625156	-2.683749	-0.109362
17	1	0	0.879055	-3.459657	-0.190253
18	6	0	-1.625159	-2.683748	0.109354
19	1	0	-0.879058	-3.459656	0.190249
20	6	0	3.285424	-4.582974	-0.207948
21	1	0	4.360533	-4.776665	-0.183868
22	1	0	2.883212	-5.000417	-1.137681
23	1	0	2.819587	-5.124970	0.622239
24	6	0	4.701927	0.238268	0.081984
25	6	0	4.333645	1.570089	0.130308
26	6	0	-2.991249	-3.102303	0.115528
27	6	0	-4.013388	-2.170997	0.041385
28	1	0	-5.052628	-2.485598	0.040495
29	6	0	-2.957917	1.911991	-0.113437
30	1	0	-2.615355	2.939568	-0.141145
31	6	0	-4.333643	1.570092	-0.130329
32	1	0	-5.070899	2.360885	-0.176476
33	6	0	-4.701926	0.238272	-0.081999
34	1	0	-5.749123	-0.047600	-0.086293
35	78	0	-0.000000	1.227444	0.000006
36	6	0	-3.285428	-4.582969	0.207966
37	1	0	-2.819588	-5.124975	-0.622212

38	1	0	-2.883223	-5.000403	1.137707
39	1	0	-4.360537	-4.776660	0.183883
40	1	0	5.749122	-0.047604	0.086274
41	1	0	5.070902	2.360881	0.176454

3.2.5. L5-PtCl_T1:

HF = -1069.5377801 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	17	0	0.027676	-3.693471	-0.006297
2	7	0	-0.014656	0.744339	-0.003876
3	7	0	-1.997811	-0.983827	0.119453
4	7	0	2.023207	-0.972379	-0.136281
5	6	0	-2.333091	0.360697	0.037582
6	6	0	1.260120	1.323301	0.063078
7	6	0	-2.905841	3.128636	-0.278537
8	6	0	-1.271560	1.310031	-0.068157
9	6	0	-3.697896	0.785587	0.059649
10	6	0	2.342434	0.373708	-0.054030
11	6	0	-3.950549	2.179523	-0.079481
12	1	0	-4.982037	2.524707	-0.068585
13	6	0	-3.003015	-1.934080	0.271273
14	1	0	-2.666766	-2.961012	0.340988
15	6	0	3.689428	0.802564	-0.055389
16	6	0	-1.586364	2.704608	-0.280144
17	1	0	-0.806187	3.419263	-0.501820
18	6	0	1.588478	2.661245	0.274790
19	1	0	0.820845	3.397373	0.471833
20	6	0	-3.263790	4.580495	-0.503265
21	1	0	-3.917317	4.691527	-1.375429

22	1	0	-2.371259	5.190485	-0.665528
23	1	0	-3.800770	4.985981	0.361513
24	6	0	-4.710484	-0.196519	0.208866
25	6	0	-4.331496	-1.569822	0.320956
26	6	0	2.944810	3.104724	0.284568
27	6	0	3.971869	2.191998	0.100990
28	1	0	5.006440	2.521990	0.100097
29	6	0	2.981933	-1.891403	-0.253475
30	1	0	2.656637	-2.923842	-0.307235
31	6	0	4.352330	-1.526167	-0.295425
32	1	0	5.099497	-2.301973	-0.397713
33	6	0	4.703219	-0.192959	-0.191220
34	1	0	5.745180	0.110261	-0.203947
35	78	0	-0.005036	-1.238837	-0.003161
36	6	0	3.224472	4.573973	0.502293
37	1	0	2.758338	5.179235	-0.282364
38	1	0	2.815187	4.908702	1.461487
39	1	0	4.297603	4.778032	0.499201
40	1	0	-5.753530	0.099165	0.235776
41	1	0	-5.084772	-2.339395	0.440727

3.2.6. L6-PtCl_S0:

HF = -1222.9255833 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	17	0	0.013783	-3.613783	-0.004955
2	7	0	0.736059	0.794167	-0.006437
3	7	0	-1.529729	-0.594136	0.021886
4	7	0	2.442055	-1.243578	-0.049631
5	6	0	-1.649241	0.808048	-0.004552

6	6	0	2.079579	1.155460	0.027198
7	6	0	-1.805987	3.595938	-0.116324
8	6	0	-0.422302	1.565533	-0.034211
9	6	0	-2.915556	1.428500	-0.012389
10	6	0	2.991053	0.030402	-0.012494
11	6	0	-2.974919	2.843199	-0.063600
12	1	0	-3.931328	3.352514	-0.072746
13	6	0	-2.593541	-1.369668	0.049161
14	1	0	-2.421238	-2.441448	0.065121
15	6	0	4.396480	0.208926	-0.003264
16	6	0	-0.538837	2.959939	-0.102977
17	1	0	0.329922	3.596150	-0.165149
18	6	0	2.656365	2.424900	0.110199
19	1	0	2.051046	3.315101	0.181300
20	6	0	-5.422706	1.090270	0.031788
21	1	0	-5.594698	2.159619	0.012317
22	6	0	-1.859638	5.106117	-0.192003
23	1	0	-2.890777	5.467806	-0.182909
24	1	0	-1.379316	5.466277	-1.108350
25	1	0	-1.330882	5.558361	0.653975
26	6	0	-4.100572	0.578403	0.025179
27	6	0	-3.923947	-0.831710	0.055201
28	6	0	4.072181	2.614200	0.125489
29	6	0	4.928813	1.528342	0.061311
30	1	0	6.005541	1.666924	0.068307
31	6	0	3.219987	-2.326788	-0.090982
32	1	0	2.713323	-3.284129	-0.116924
33	6	0	4.632720	-2.214664	-0.096231
34	1	0	5.231553	-3.115329	-0.130828
35	6	0	5.213266	-0.960510	-0.050351
36	1	0	6.292854	-0.848694	-0.046421
37	6	0	-5.044851	-1.701702	0.087681
38	1	0	-4.881341	-2.774753	0.108088
39	6	0	-6.329048	-1.177855	0.092267
40	1	0	-7.190868	-1.834887	0.116460
41	6	0	-6.513148	0.228522	0.065088

42	1	0	-7.518681	0.634927	0.070328
43	78	0	0.414689	-1.167147	-0.010579
44	6	0	4.603025	4.027807	0.213348
45	1	0	4.264800	4.624149	-0.641171
46	1	0	4.240756	4.522350	1.121256
47	1	0	5.695549	4.042016	0.228830

3.2.7. L6-PtCl_T1:

HF = -1223.1086669 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	17	0	0.023668	-3.611263	-0.018191
2	7	0	0.739539	0.765972	-0.015615
3	7	0	-1.534659	-0.615654	0.076496
4	7	0	2.438451	-1.238736	-0.136485
5	6	0	-1.648788	0.783678	-0.015376
6	6	0	2.064987	1.133855	0.089033
7	6	0	-1.773125	3.564754	-0.376566
8	6	0	-0.427809	1.536838	-0.109724
9	6	0	-2.904979	1.416989	-0.047579
10	6	0	2.972856	0.037467	-0.017437
11	6	0	-2.942557	2.826056	-0.213965
12	1	0	-3.894534	3.343646	-0.245335
13	6	0	-2.607474	-1.372193	0.169890
14	1	0	-2.448703	-2.444950	0.228653
15	6	0	4.386098	0.251750	-0.002333
16	6	0	-0.515660	2.913383	-0.335760
17	1	0	0.370939	3.503477	-0.525053

18	6	0	2.579901	2.458311	0.352095
19	1	0	1.909332	3.274588	0.583056
20	6	0	-5.414875	1.113521	0.069133
21	1	0	-5.580049	2.180816	-0.014912
22	6	0	-1.818284	5.058729	-0.603508
23	1	0	-2.847277	5.422243	-0.653052
24	1	0	-1.315785	5.324870	-1.539290
25	1	0	-1.307054	5.590355	0.206038
26	6	0	-4.099475	0.588030	0.068292
27	6	0	-3.933066	-0.819704	0.182234
28	6	0	3.948095	2.676784	0.394503
29	6	0	4.842339	1.587147	0.185547
30	1	0	5.913965	1.772022	0.207866
31	6	0	3.291890	-2.325417	-0.301191
32	1	0	2.807043	-3.288015	-0.404341
33	6	0	4.660916	-2.164651	-0.321539
34	1	0	5.291476	-3.035985	-0.452644
35	6	0	5.241550	-0.868115	-0.162352
36	1	0	6.317492	-0.733611	-0.163871
37	6	0	-5.059654	-1.674490	0.292475
38	1	0	-4.905818	-2.745939	0.374723
39	6	0	-6.338857	-1.137441	0.292479
40	1	0	-7.205424	-1.783152	0.375615
41	6	0	-6.511545	0.265609	0.180536
42	1	0	-7.513146	0.681315	0.181268
43	78	0	0.428991	-1.188039	-0.029122
44	6	0	4.514092	4.049795	0.680039
45	1	0	5.137840	4.393216	-0.152740
46	1	0	3.719178	4.784021	0.834432
47	1	0	5.144124	4.034447	1.576046

3.2.8. L3-PtCl_S0:

HF = -1376.4359676 hartrees

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	17	0	0.000004	3.450959	-0.000152	
2	7	0	2.012594	0.719472	0.043043	
3	7	0	-2.012596	0.719470	-0.043063	
4	6	0	-3.987612	-2.439388	0.152088	
5	1	0	-5.012613	-2.790339	0.176623	
6	6	0	2.939149	1.653584	0.096552	
7	1	0	2.598857	2.683677	0.139291	
8	6	0	4.338610	1.334556	0.095745	
9	6	0	4.738036	-0.027770	0.023746	
10	6	0	3.704371	-1.054960	-0.046513	
11	6	0	3.987616	-2.439386	-0.152035	
12	1	0	5.012618	-2.790334	-0.176566	
13	6	0	2.952563	-3.364832	-0.246930	
14	6	0	1.600504	-2.939687	-0.208893	
15	1	0	0.840773	-3.698070	-0.321924	
16	6	0	1.265160	-1.586540	-0.069167	
17	7	0	0.000001	-1.011188	0.000012	
18	6	0	-1.265158	-1.586540	0.069191	
19	6	0	-2.355323	-0.644667	0.018560	
20	6	0	-2.939153	1.653582	-0.096555	
21	1	0	-2.598864	2.683673	-0.139326	
22	6	0	-4.338615	1.334554	-0.095705	
23	6	0	-4.738039	-0.027771	-0.023676	
24	6	0	-3.704370	-1.054961	0.046573	
25	6	0	-2.952558	-3.364832	0.246981	
26	6	0	-1.600500	-2.939687	0.208927	
27	1	0	-0.840768	-3.698067	0.321962	

28	6	0	-3.244601	-4.841791	0.397260
29	1	0	-4.319771	-5.036935	0.394348
30	1	0	-2.830713	-5.225738	1.336197
31	1	0	-2.790140	-5.414054	-0.418707
32	6	0	-6.125045	-0.321736	-0.021963
33	1	0	-6.466445	-1.348615	0.028429
34	6	0	-7.064061	0.701291	-0.087205
35	1	0	-8.121543	0.459918	-0.085615
36	6	0	-6.657971	2.058796	-0.156093
37	1	0	-7.403407	2.844242	-0.206070
38	6	0	-5.306442	2.370682	-0.160331
39	1	0	-4.973538	3.402899	-0.212030
40	6	0	2.355323	-0.644667	-0.018527
41	6	0	3.244609	-4.841789	-0.397228
42	1	0	2.830704	-5.225730	-1.336161
43	1	0	2.790166	-5.414060	0.418743
44	1	0	4.319780	-5.036929	-0.394340
45	6	0	6.125042	-0.321734	0.022062
46	1	0	6.466443	-1.348614	-0.028324
47	6	0	7.064057	0.701293	0.087317
48	1	0	8.121539	0.459921	0.085744
49	6	0	6.657965	2.058799	0.156185
50	1	0	7.403400	2.844245	0.206169
51	6	0	5.306436	2.370685	0.160385
52	1	0	4.973531	3.402902	0.212061
53	78	0	-0.000000	0.971986	-0.000030

3.2.9. L3-PtCl_T1:

HF = -1376.6747587 hartrees

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	17	0	0.031343	-3.445668	-0.010853
2	7	0	2.028660	-0.737201	-0.074414
3	7	0	-1.994366	-0.729745	0.047219
4	6	0	-3.920000	2.420393	-0.263164
5	1	0	-4.940941	2.788461	-0.306701
6	6	0	2.973521	-1.649394	-0.162118
7	1	0	2.651741	-2.684242	-0.233855
8	6	0	4.368017	-1.307315	-0.156715
9	6	0	4.747594	0.057108	-0.028877
10	6	0	3.693669	1.058225	0.087556
11	6	0	3.945193	2.442755	0.274686
12	1	0	4.965264	2.806112	0.323674
13	6	0	2.901933	3.351391	0.434663
14	6	0	1.559941	2.903014	0.362483
15	1	0	0.774830	3.623898	0.543459
16	6	0	1.264088	1.558554	0.118492
17	7	0	-0.006899	0.978647	-0.005547
18	6	0	-1.258136	1.558098	-0.128607
19	6	0	-2.335798	0.605239	-0.050595
20	6	0	-3.000681	-1.690800	0.157405
21	1	0	-2.669947	-2.719280	0.232834
22	6	0	-4.358973	-1.336239	0.164607
23	6	0	-4.755176	0.047257	0.047354
24	6	0	-3.685918	1.049623	-0.084683
25	6	0	-2.870481	3.366255	-0.434643
26	6	0	-1.553190	2.931930	-0.369711
27	1	0	-0.761872	3.643896	-0.559016
28	6	0	-3.210758	4.815131	-0.700466
29	1	0	-3.822872	4.915246	-1.603540
30	1	0	-2.308070	5.417166	-0.833976
31	1	0	-3.782598	5.241627	0.131244
32	6	0	-6.122662	0.374591	0.064181
33	1	0	-6.435107	1.411011	-0.016199
34	6	0	-7.108124	-0.613569	0.184860
35	1	0	-8.157247	-0.339221	0.194887
36	6	0	-6.724875	-1.977090	0.293770

37	1	0	-7.488258	-2.743478	0.386450
38	6	0	-5.386056	-2.333812	0.285242
39	1	0	-5.090585	-3.375824	0.370109
40	6	0	2.355762	0.626574	0.033272
41	6	0	3.173369	4.815743	0.693920
42	1	0	2.741438	5.126045	1.651335
43	1	0	2.724729	5.439695	-0.086039
44	1	0	4.245678	5.022225	0.721271
45	6	0	6.128030	0.374462	-0.018940
46	1	0	6.455388	1.402952	0.074118
47	6	0	7.082090	-0.631234	-0.132156
48	1	0	8.135593	-0.373645	-0.125043
49	6	0	6.697124	-1.990181	-0.257065
50	1	0	7.454727	-2.760378	-0.343964
51	6	0	5.350706	-2.324267	-0.268414
52	1	0	5.034242	-3.358393	-0.362077
53	78	0	-0.001948	-0.993642	-0.007991

Chapter 4:

4.1. NMR Spectra:

PMA-05-078-ASH.1.fid
tBuPhen-Br
PROTON CDCl3 C:\Herbert 1

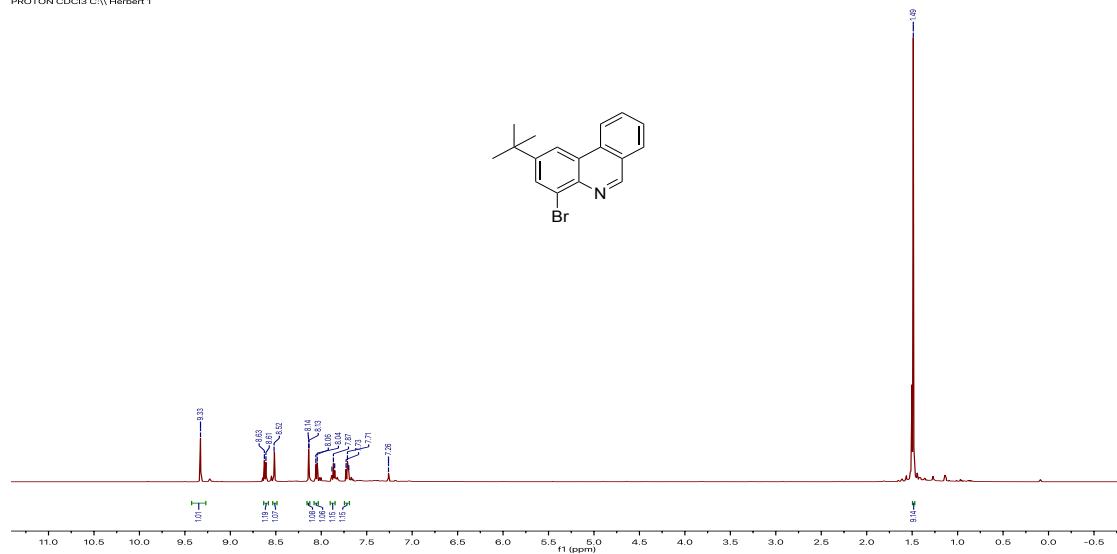


Figure S4.1. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of 2-Br.

PMA-05-078-ABC-2.2.fid
C13CPD32 CDCl3 C:\Herbert 1

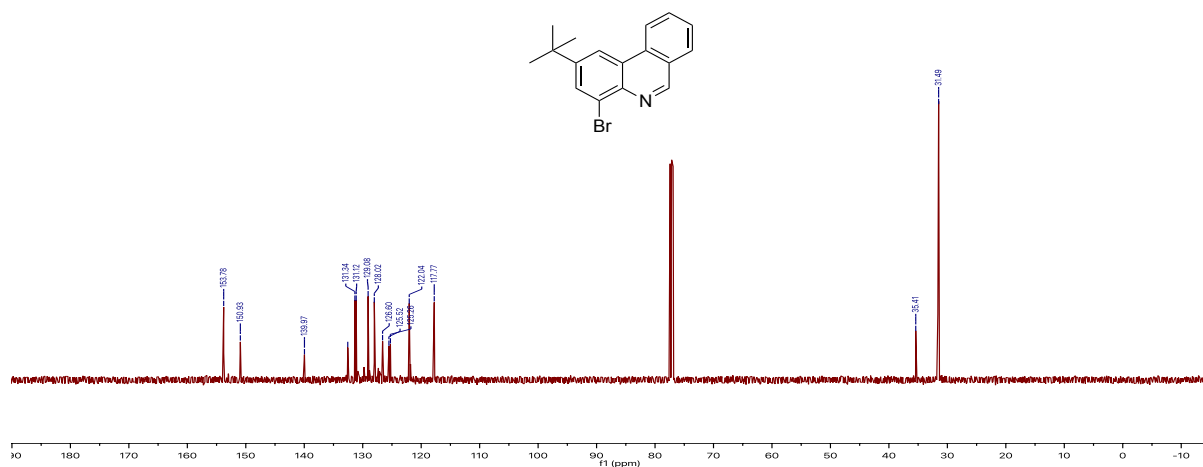
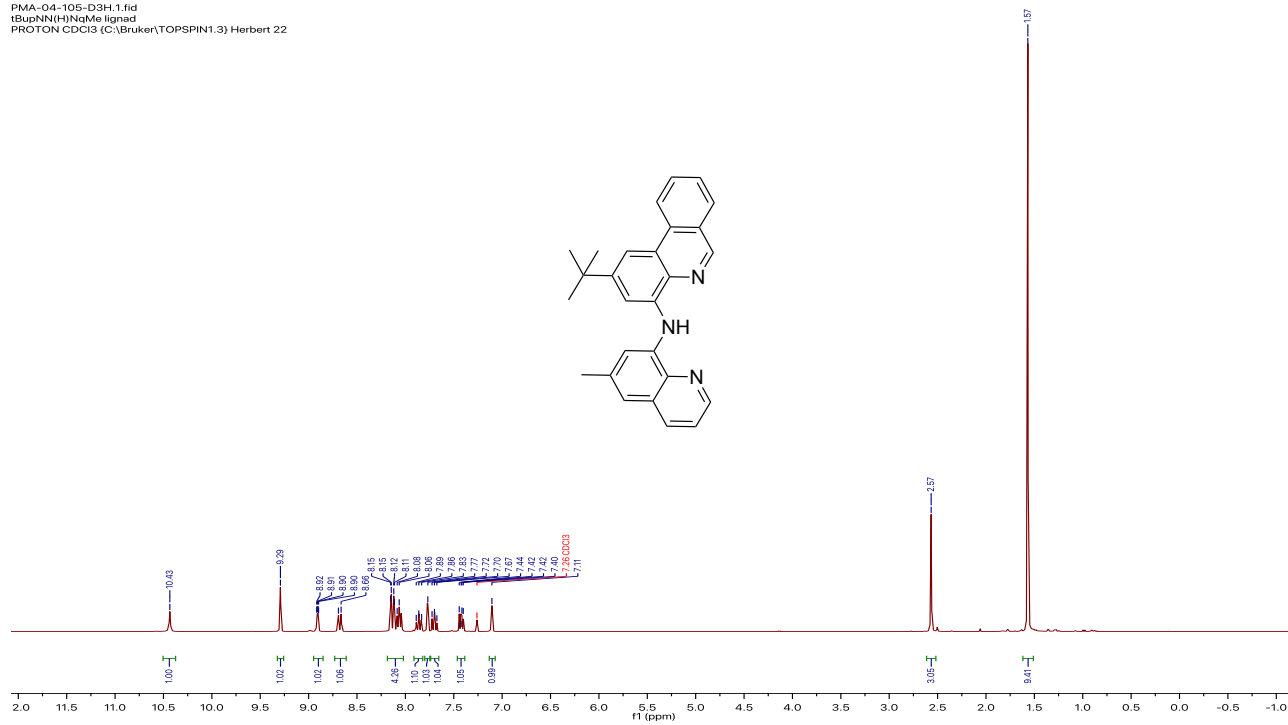


Figure S4.2. ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C) spectrum of 2-Br.

PMA-04-105-D3H.1.fid
tBupNN(H)NaMe lignad
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 22



PMA-04-020-C3H.1.fid

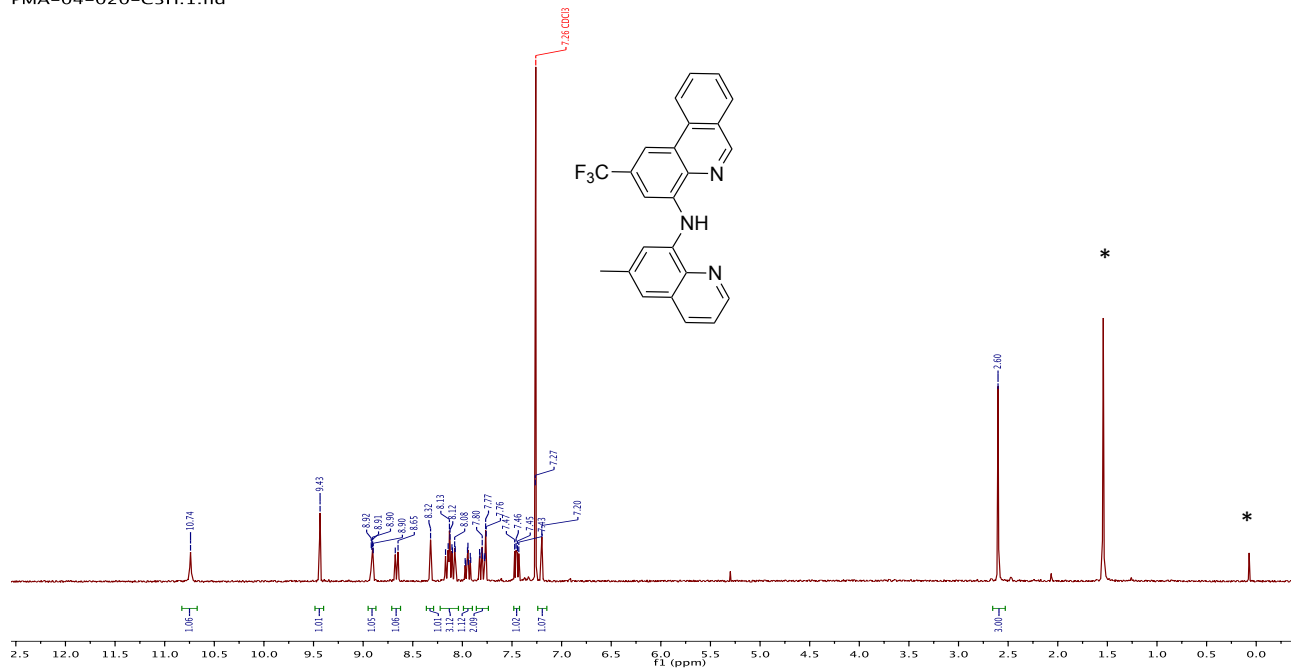


Figure S4.5. ^1H NMR (300 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L9, $^*\text{H}_2\text{O}$ and silicone grease.

PMA-04-020-D3C.2.fid

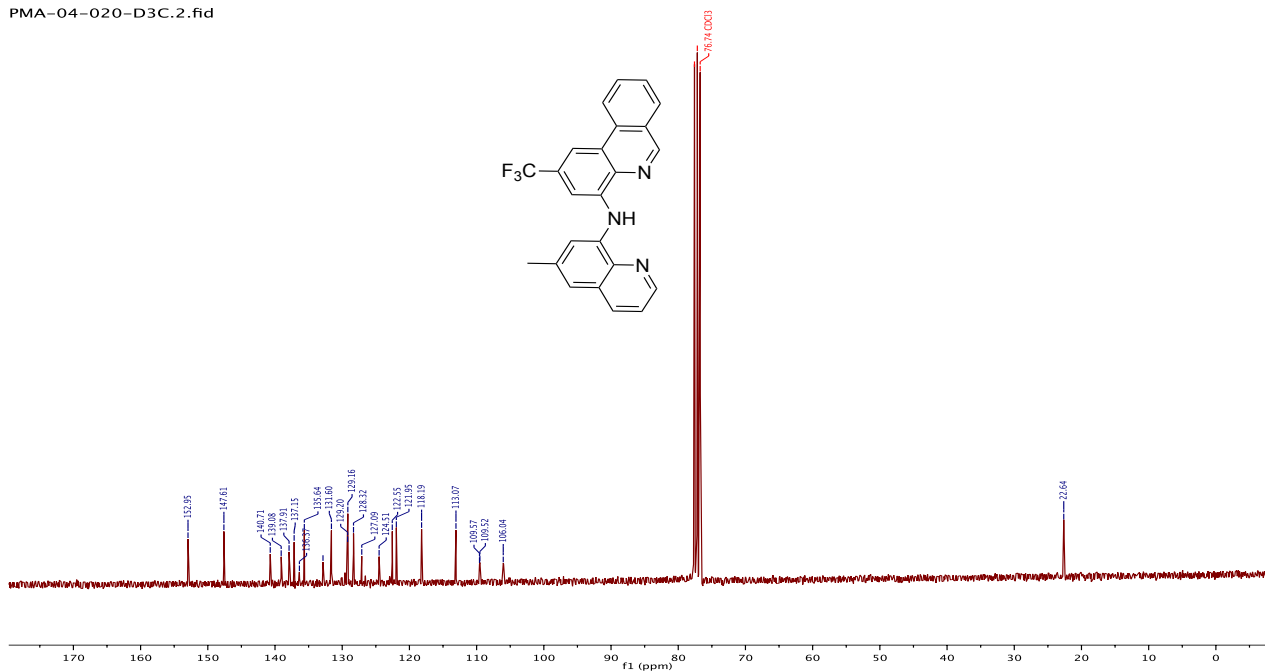


Figure S4.6. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L9.

PMA-04-020-D3F.1.fid
CF3[NNH]NaMe ligand
F19CPD CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 39

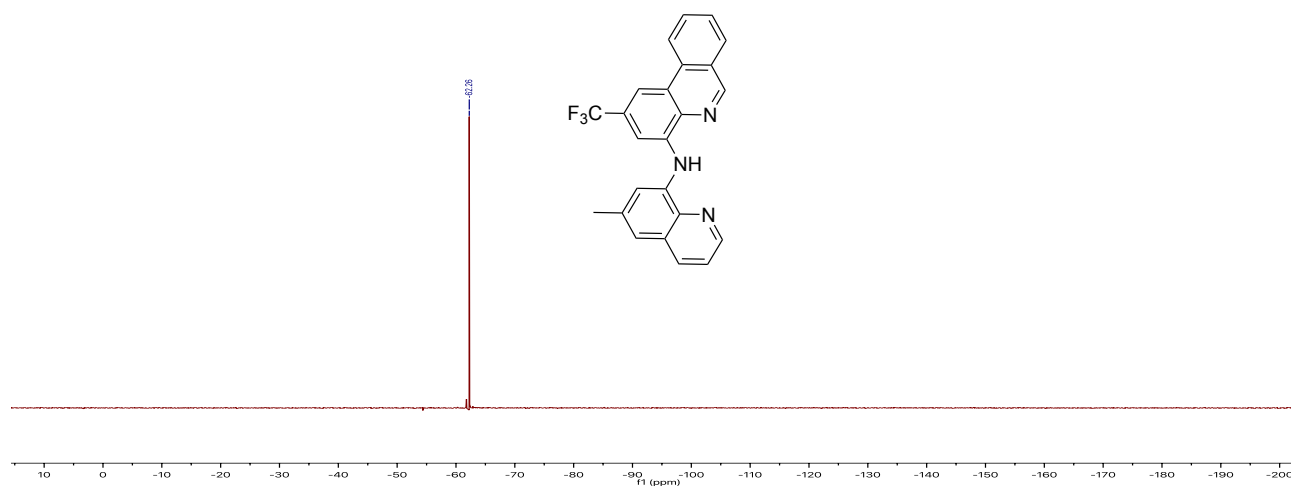


Figure S4.7. $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3 , 22 °C) spectrum of L9.

PMA-03-093-B3H.1.fid

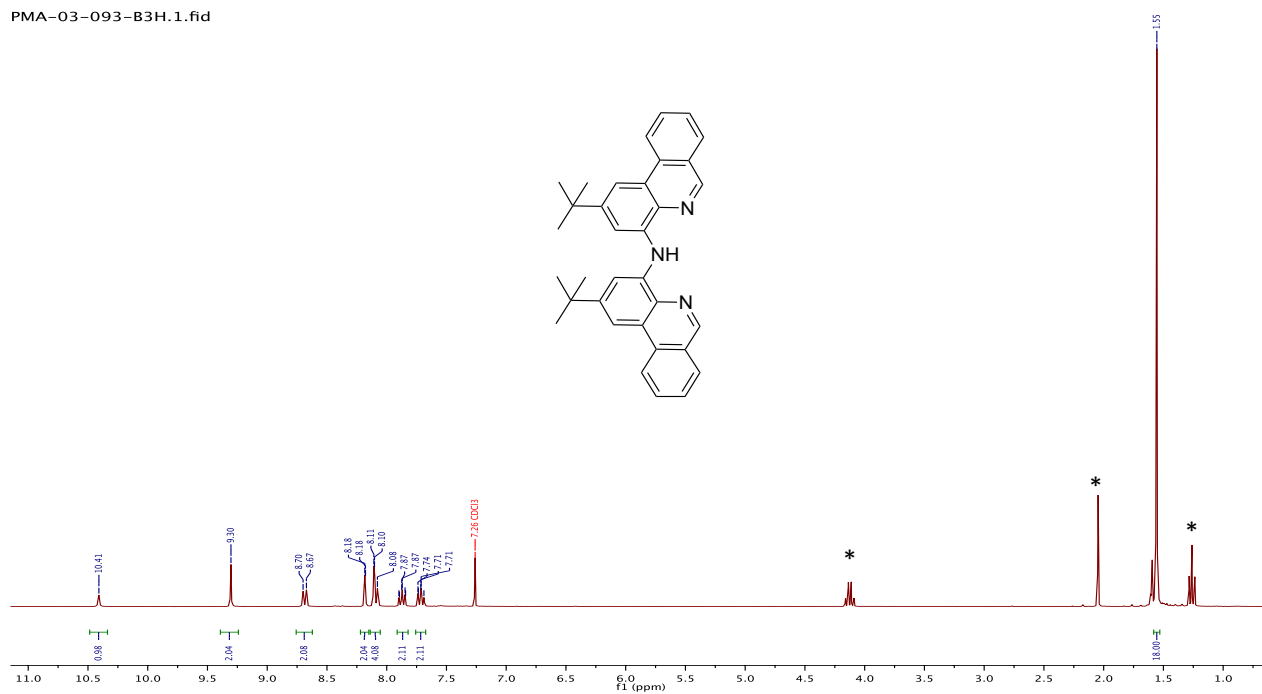


Figure S4.8. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of L10, *EtOAc and H_2O .

PMA-03-093-C3C.1.fid
tBupNNNptBu ligand
C13CPD CDCl3 {C:\Bruker\TOPSPIN1.3} Herbert 39

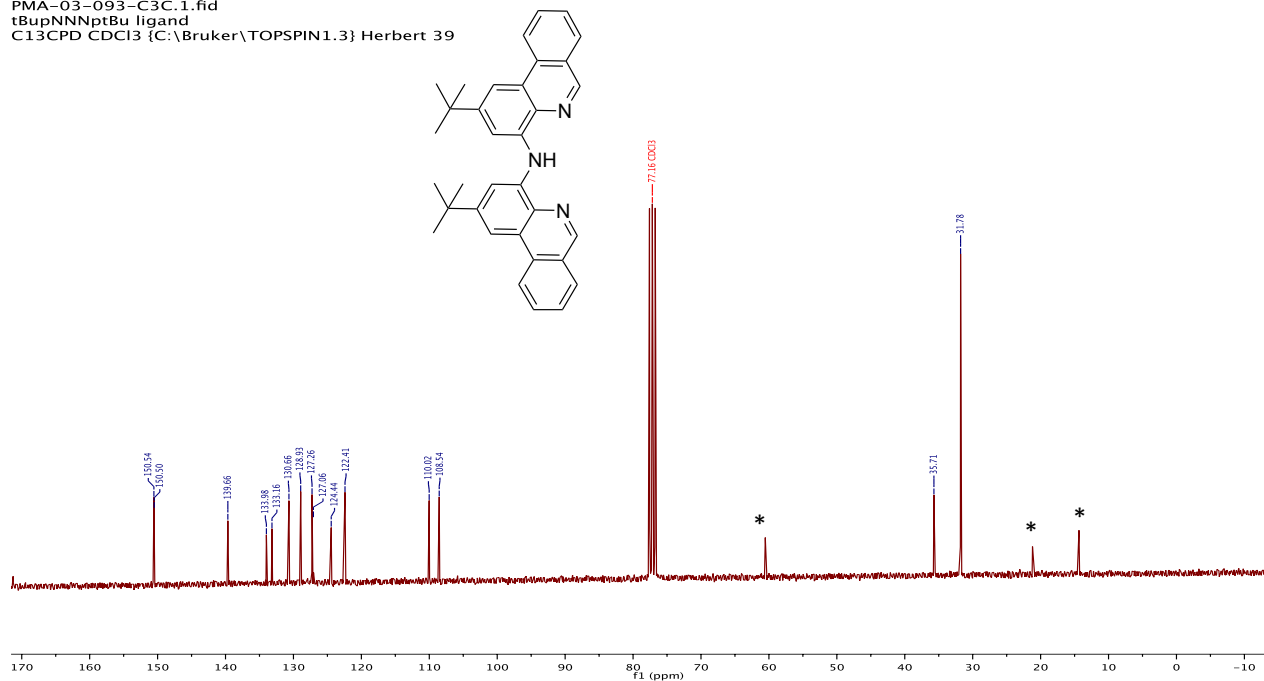


Figure S4.9. ¹³C{¹H} NMR (75 MHz, CDCl₃, 22 °C) spectrum of **L10**, *EtOAc.

PMA-05-076-E5H.1.fid
CF3,CF3bis phen ligand
PROTON CDCl3 C:\Herbert 1

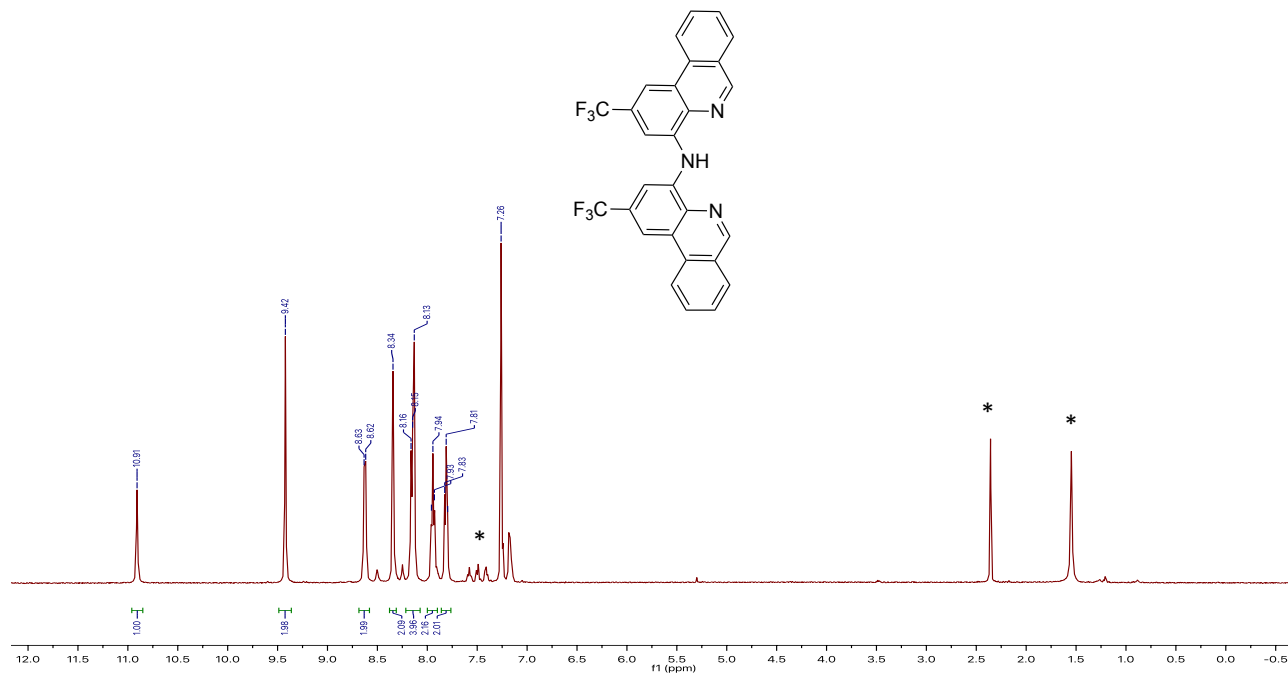


Figure S4.10. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of **L11**, *H₂O, toluene and 4-bromo-trifluoromethylphenanthridine

PMA-05-076-E5C.2.fid
CF3,CF3bis phen ligand
C13CPD.CDCl3 C:\Herbert 1

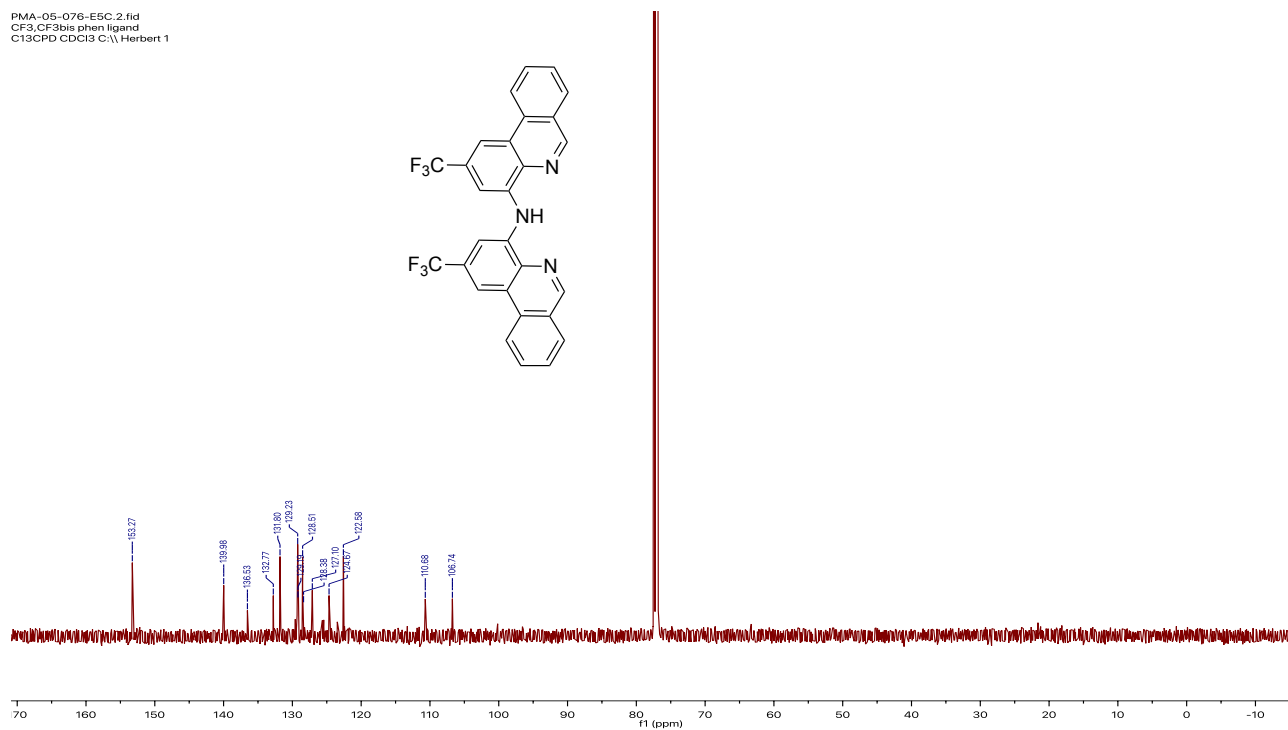


Figure S4.11. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L11.

PMA-05-076-E5F.1.fid
CF3,CF3bis phen ligand
F19CPD.CDCl3 C:\Herbert 1

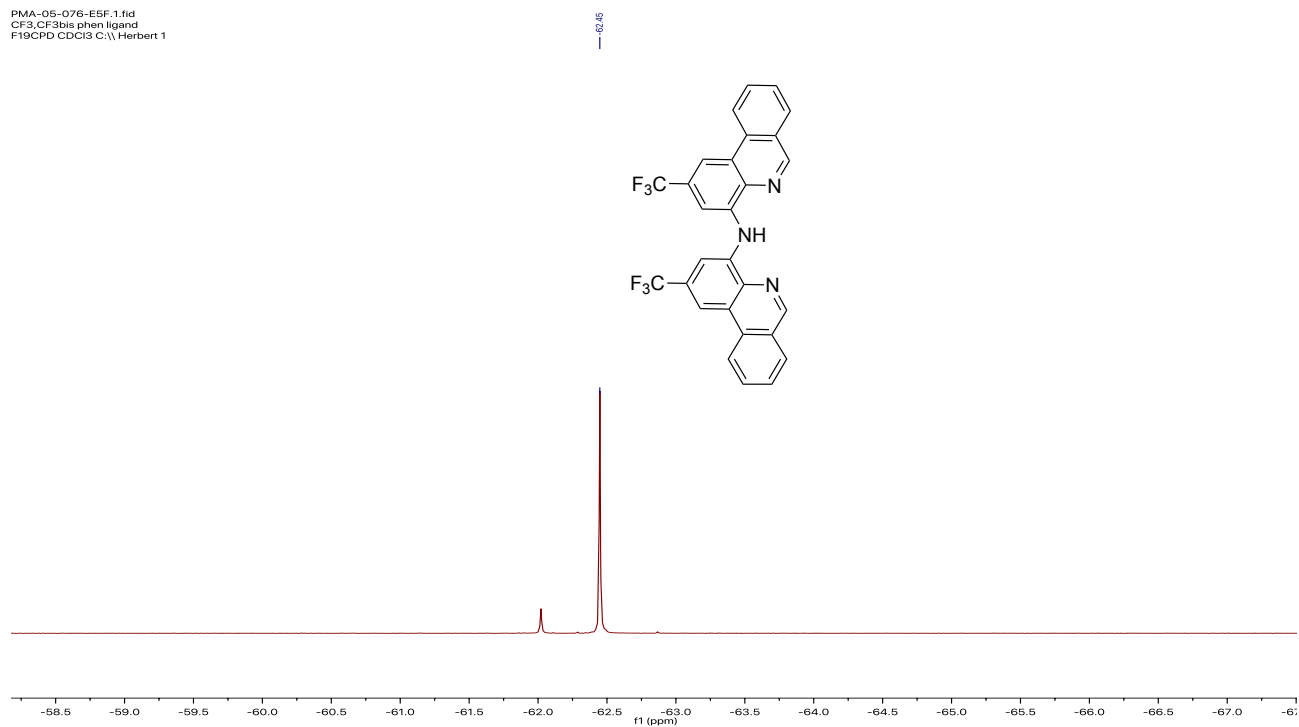


Figure S4.12. $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3 , 22 °C) spectrum of L11.

PMA-04-026-C3H.1.fid

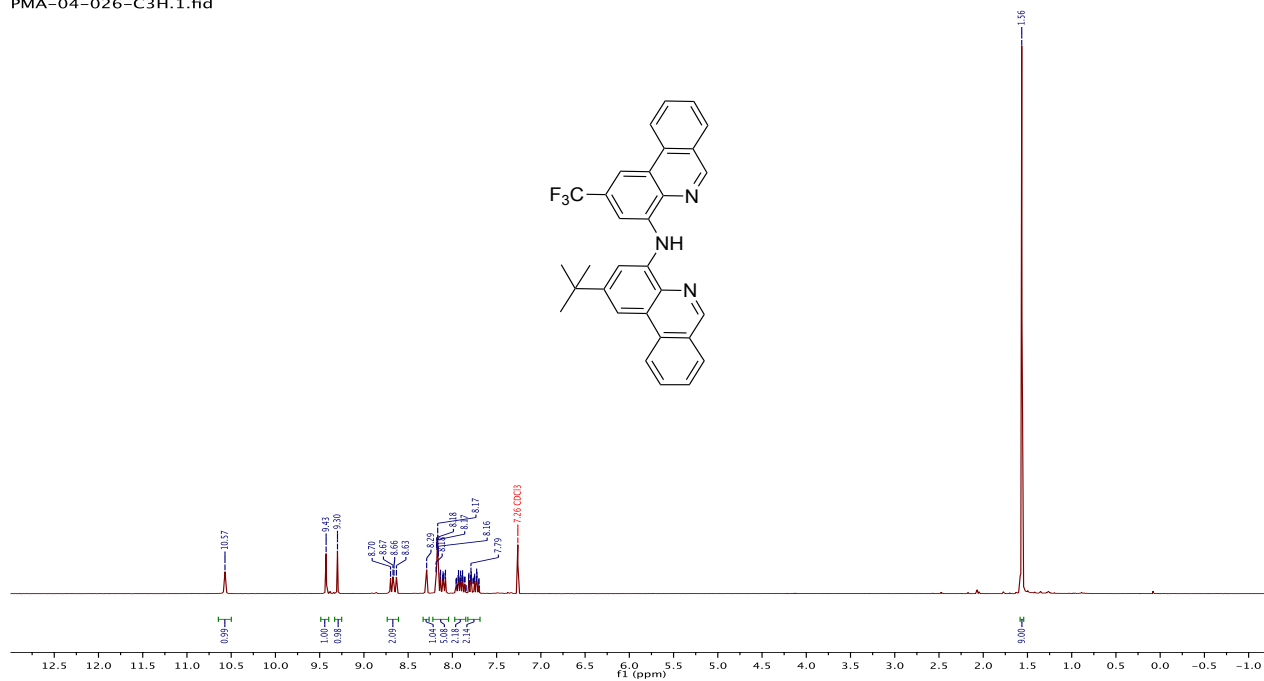


Figure S4.13. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L12.

PMA-04-026-C3C.2.fid

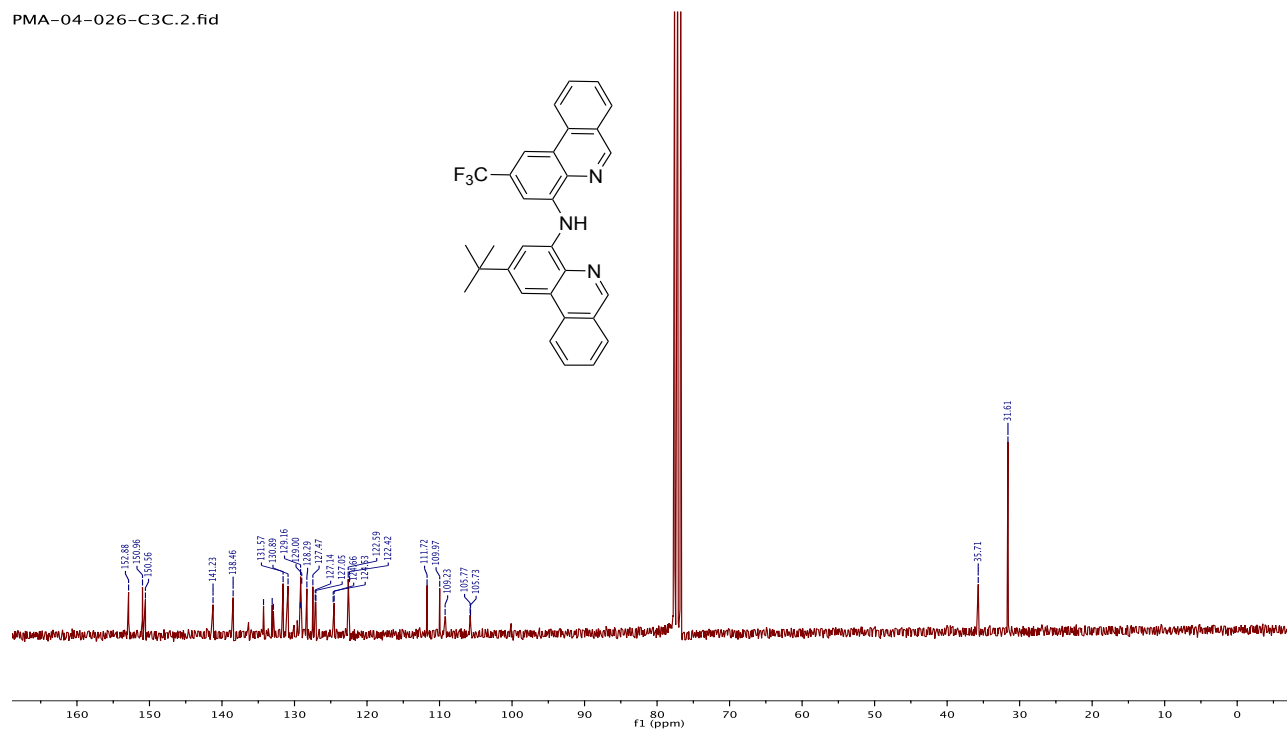


Figure S4.14. ¹³C {¹H} NMR (75 MHz, CDCl₃, 22 °C) spectrum of L12.

PMA-04-026-C3F.1.fid

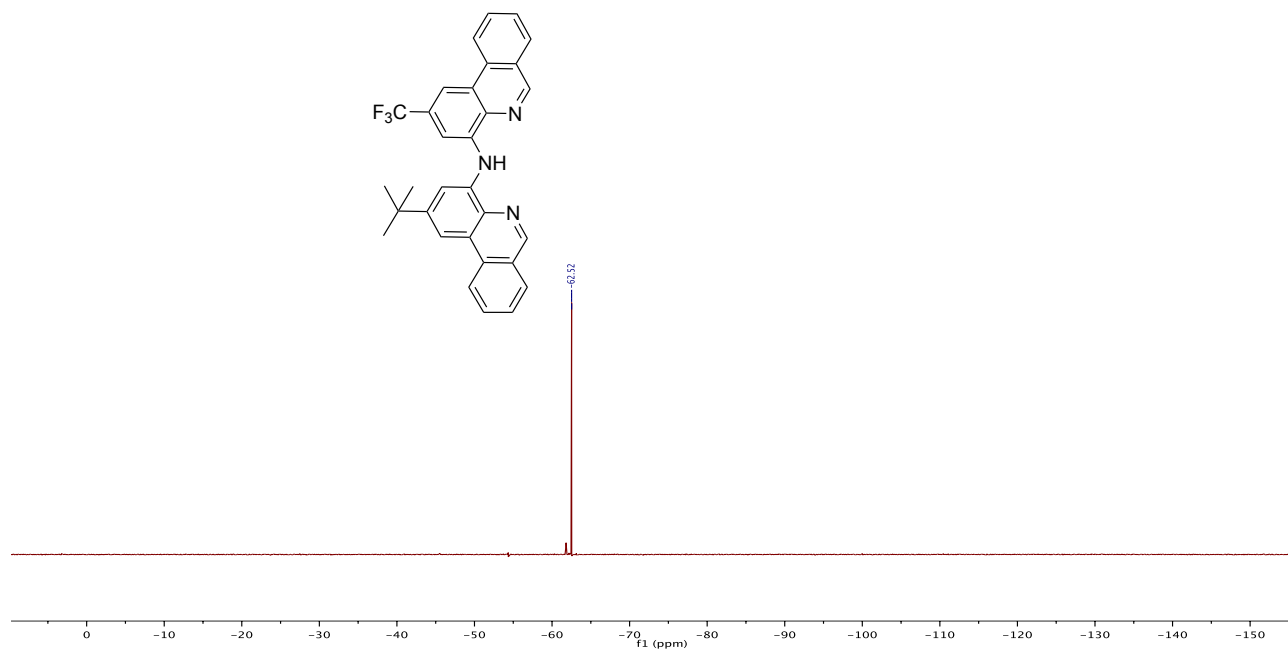


Figure S4.15. $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3 , 22 °C) spectrum of L12.

PMA-03-148-A3H.1.fid

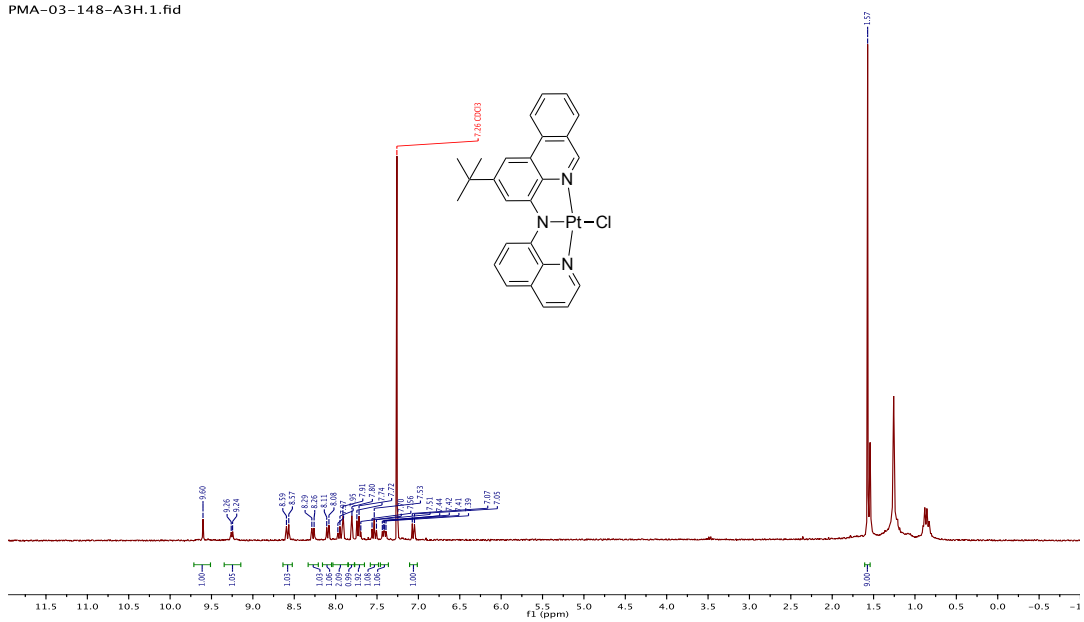


Figure S4.16. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of L4-PtCl.

PMA-04-118-C5H.1.fid
PROTON CDCl3 C:\Herbert 1

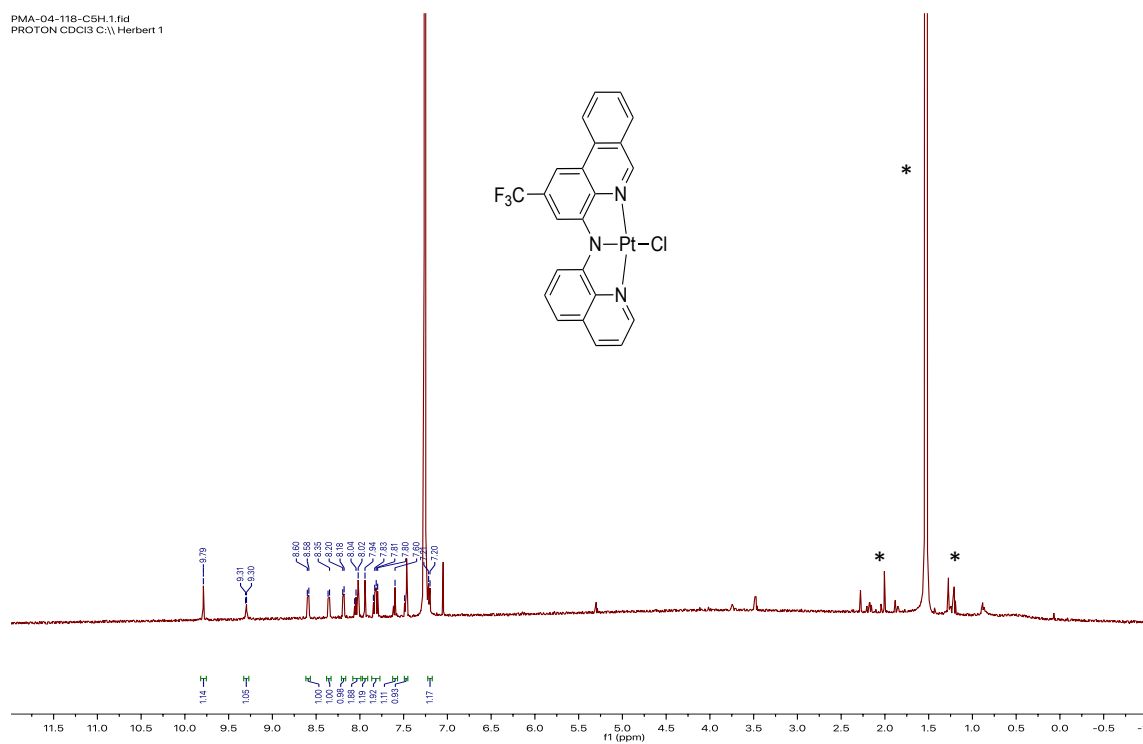


Figure S4.17. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of **L7-PtCl**, $^*\text{H}_2\text{O}$ and *n*-hexanes.

PMA-04-118-A5F.2.fid
F19CPD CDCl3 C:\Herbert 3

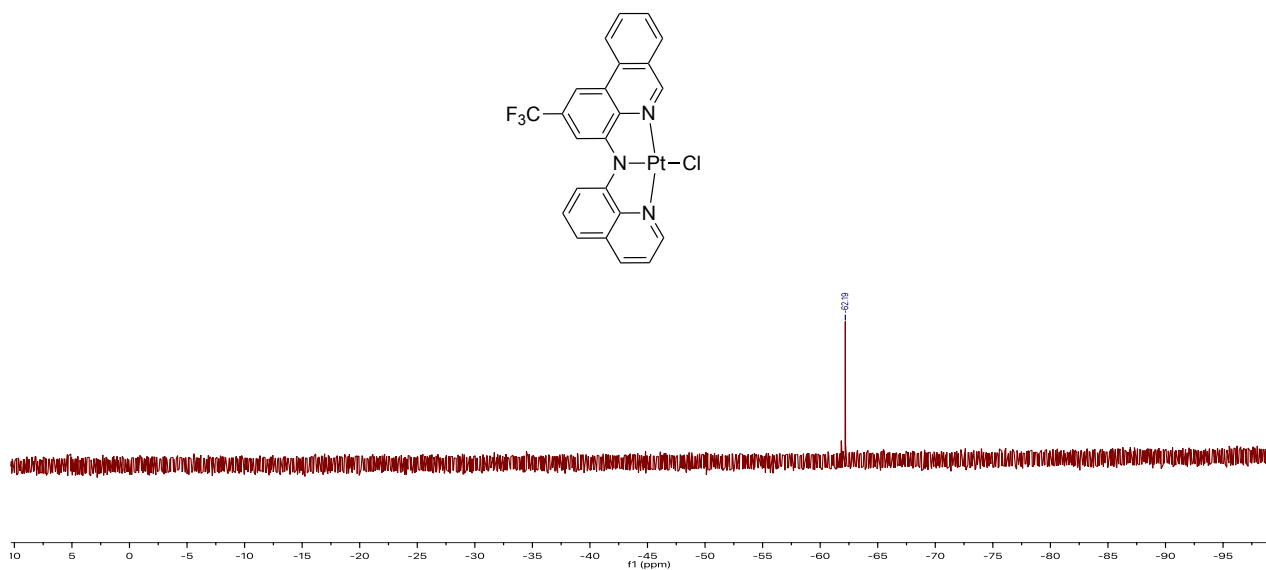


Figure S4.18. $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3 , 22 °C) spectrum of **L7-PtCl**.

PMA-04-117-C3H.1.fid
tBuPNNaMe-PtCl after ether washings
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 62

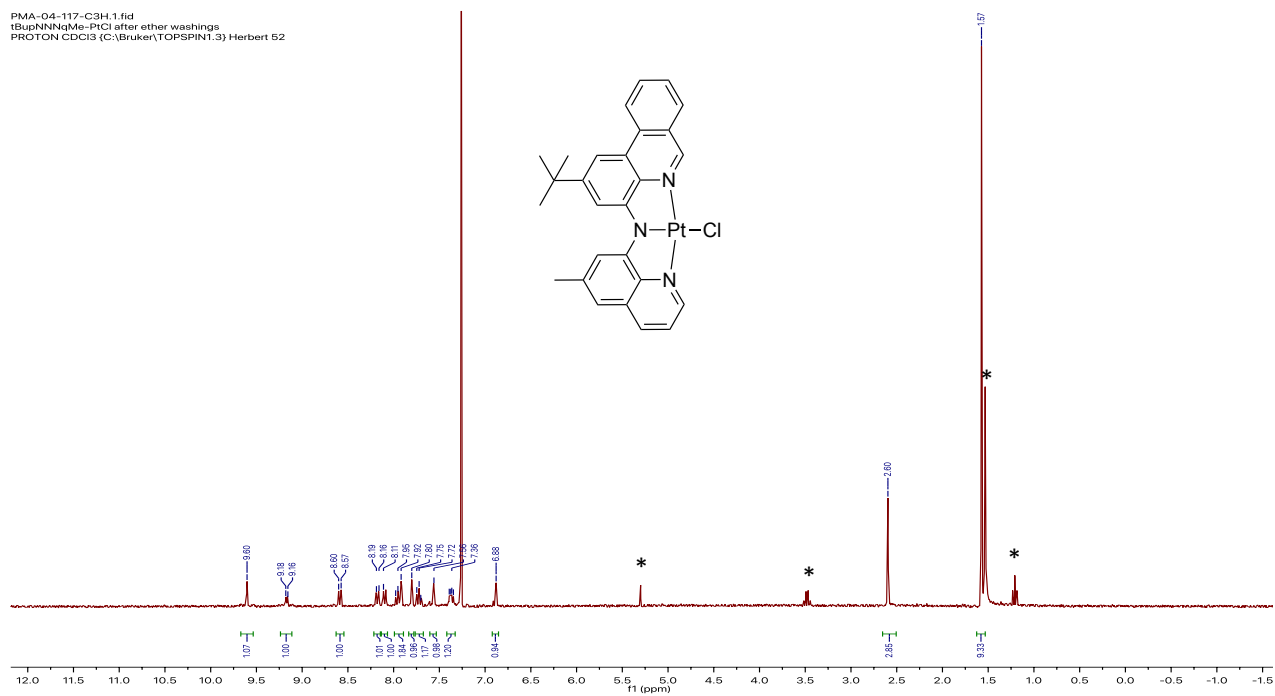


Figure S4.19. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L8-PtCl, *H₂O, CH₂Cl₂ and Et₂O.

PMA-04-078-E3H.1.fid

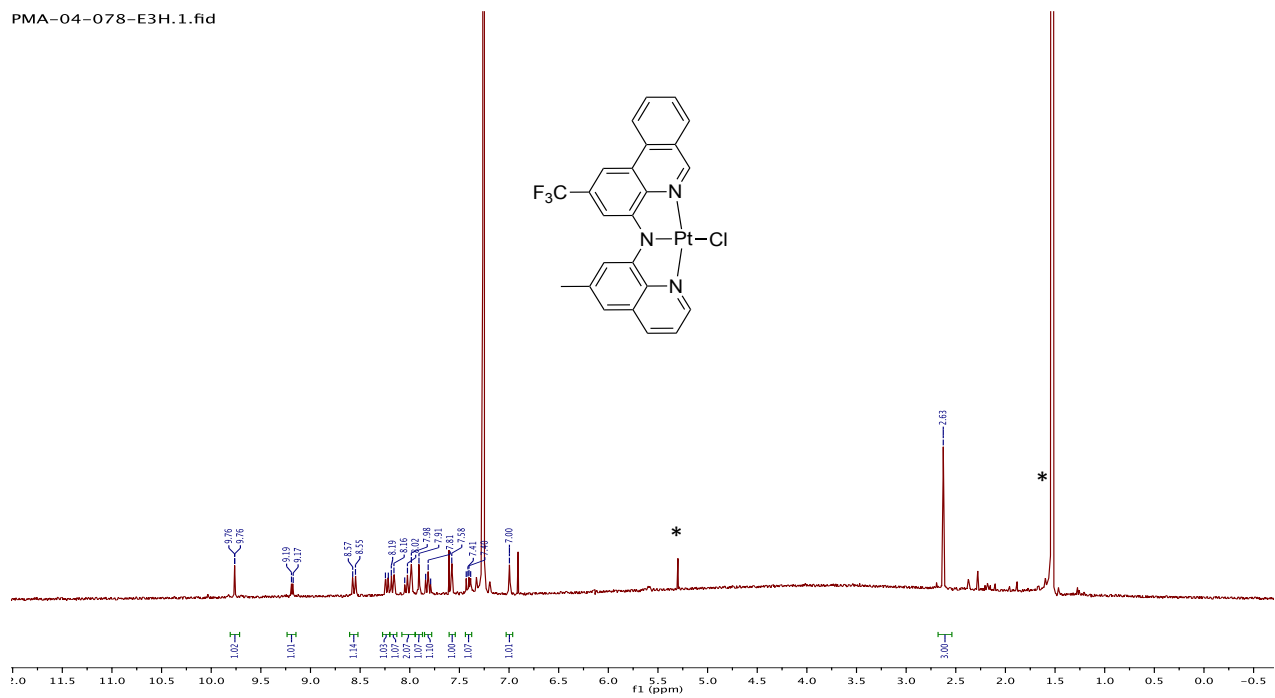


Figure S4.20. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L9-PtCl, *H₂O and CH₂Cl₂.

PMA-04-078-B5F.2.fid
F19CPD CDCl3 C:\Herbert 1

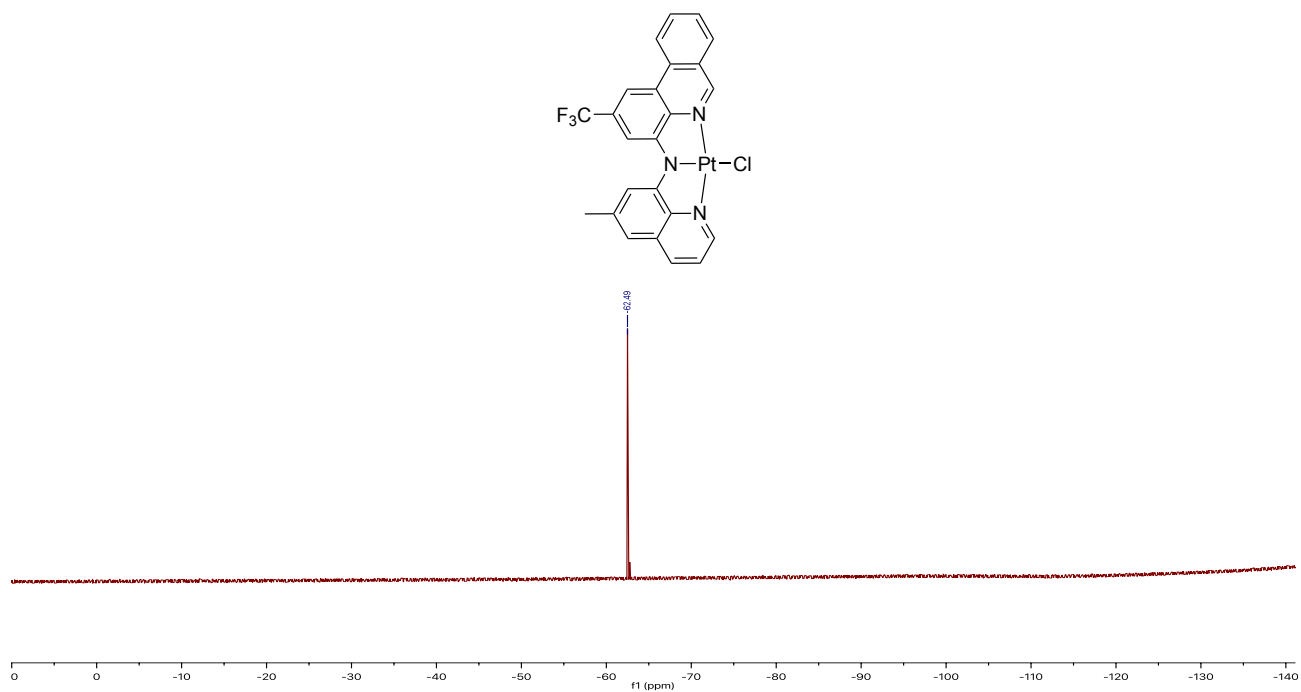


Figure S4.21. ¹⁹F{¹H} NMR (470 MHz, CDCl₃, 22 °C) spectrum of L9-PtCl.

PMA-03-144-C3H.1.fid

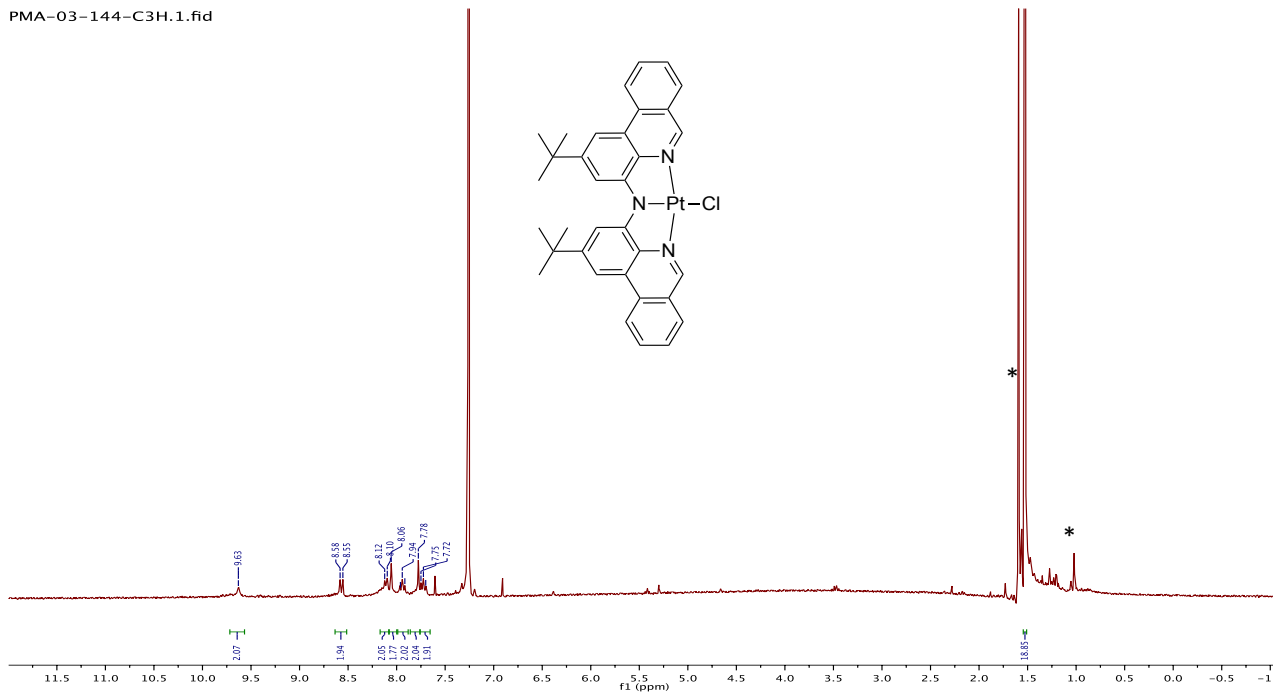


Figure S4.22. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L10-PtCl, *H₂O and *n*-hexanes.

PMA-04-072-D3H.1.fid
PROTON CDCl3 {C:\Bruker\TOPSPIN1.3} Herbert 42

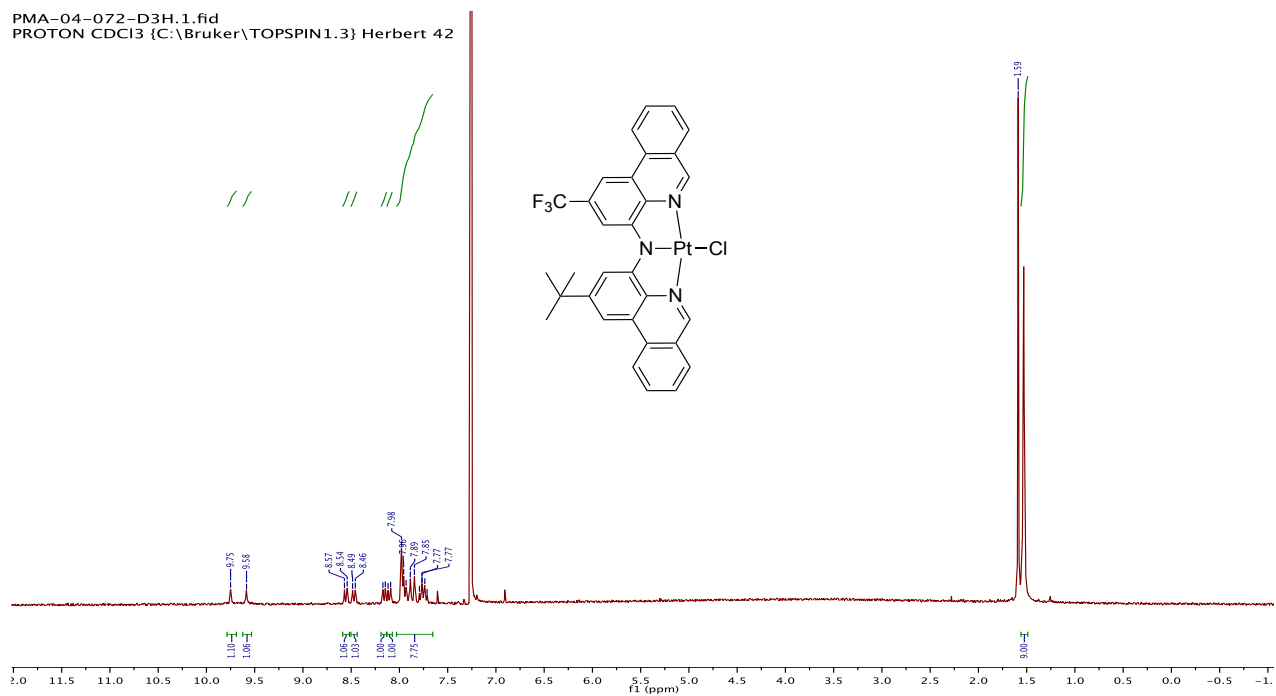


Figure S4.23. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of L12-PtCl.

PMA-05-076-GSF.1.fid
F19CPD DMSO C:\ Herbert 4

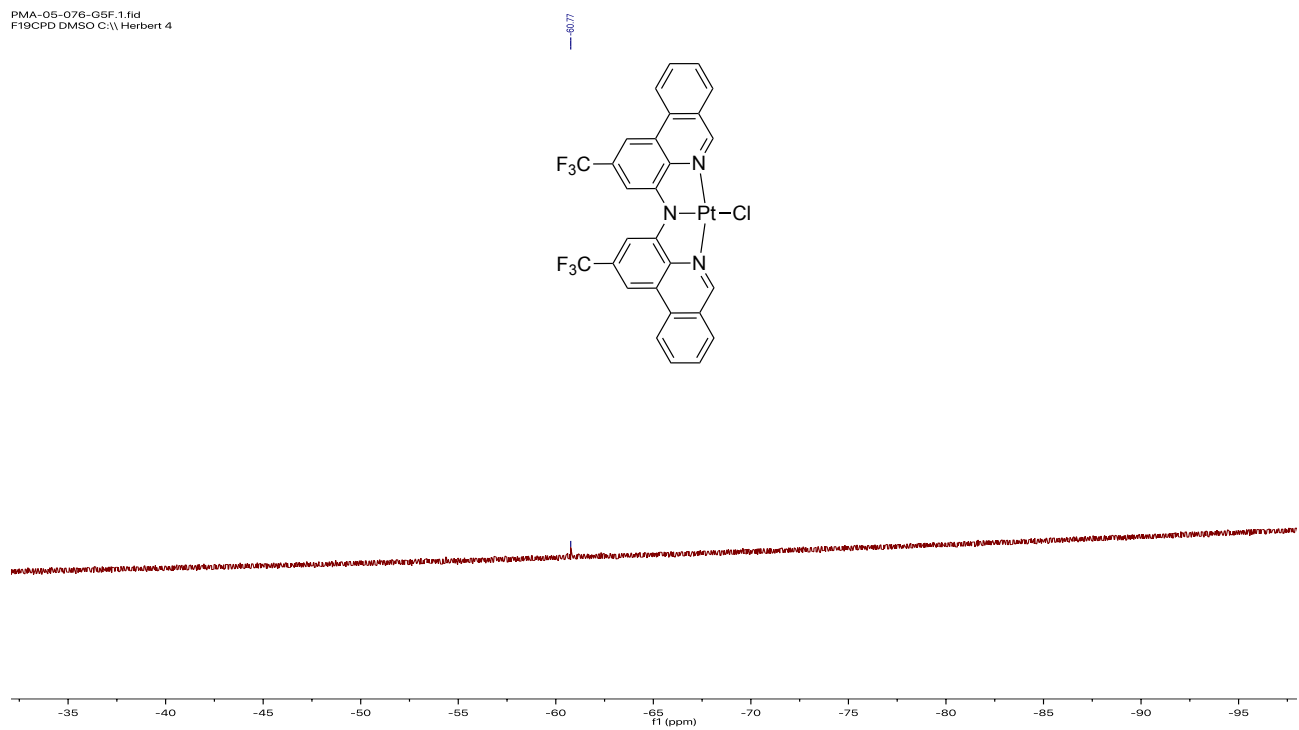


Figure S4.25. ¹⁹F{¹H} NMR (470 MHz, CDCl₃, 22 °C) spectrum of L11-PtCl.

PMA-05-076-B5F.1.fid
tBu, CF3-sPtCl
F19CPD CDCl3 C:\Herbert 2

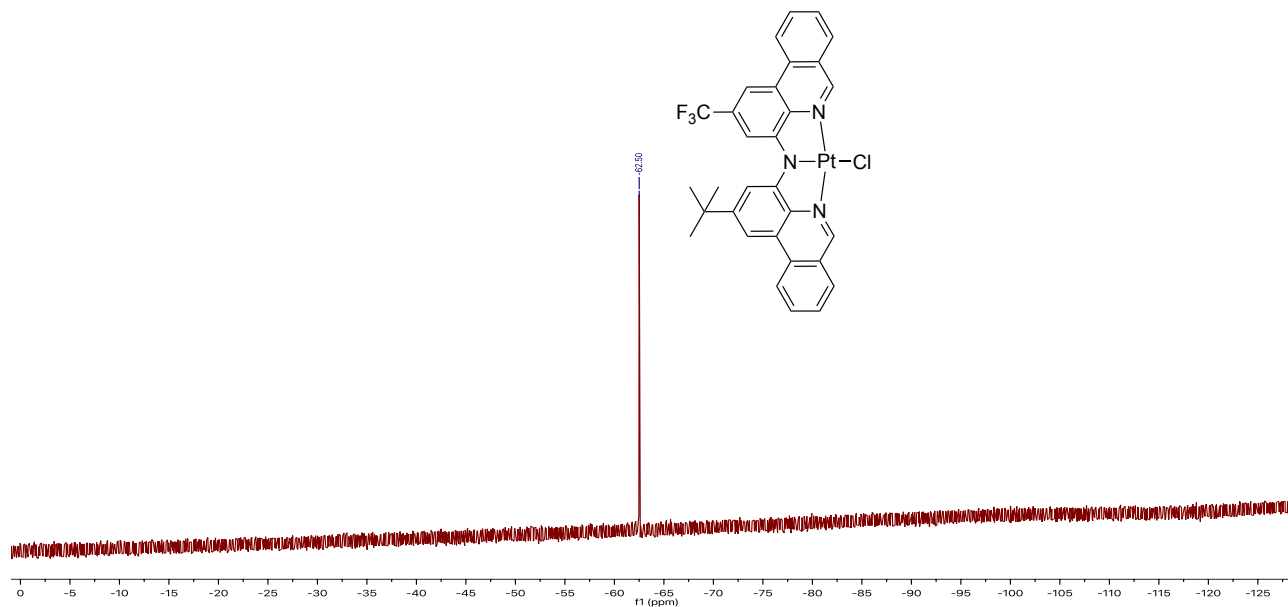


Figure S4.24. $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3 , 22 °C) spectrum of L12-PtCl.

4.2. Energies And Reaction Coordinates:

4.2.1. L9-PtCl S_0 :

HF = -1520.5737835 hartrees

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	17	0	-1.175187	-3.869005	0.055885	
2	7	0	-0.760299	0.566943	-0.011014	

3	7	0	1.071570	-1.352832	-0.028952
4	7	0	-2.927605	-0.971203	0.065465
5	6	0	1.545045	-0.029812	-0.017528
6	6	0	-1.972161	1.254932	-0.056031
7	6	0	2.395036	2.591085	0.067224
8	6	0	0.546854	1.010528	0.008253
9	6	0	2.930265	0.242391	-0.023318
10	6	0	-3.131517	0.401117	0.004023
11	6	0	3.352579	1.590292	0.013716
12	1	0	4.405546	1.845472	0.010060
13	6	0	1.912142	-2.373233	-0.060028
14	1	0	1.475550	-3.369375	-0.065768
15	6	0	-4.446170	0.934292	-0.011284
16	6	0	1.010317	2.333384	0.066772
17	1	0	0.332449	3.172489	0.136508
18	6	0	-2.201289	2.627819	-0.169970
19	1	0	-1.386228	3.333104	-0.265589
20	6	0	5.265275	-0.718034	-0.079122
21	1	0	5.709831	0.271334	-0.064977
22	6	0	2.808032	4.022161	0.126205
23	9	0	4.177288	4.211202	0.133277
24	9	0	2.320260	4.674560	1.261639
25	9	0	2.320031	4.766583	-0.951483
26	6	0	3.860229	-0.873392	-0.061664
27	6	0	3.327265	-2.193363	-0.081886
28	6	0	-3.516913	3.173078	-0.192549
29	6	0	-4.621720	2.340472	-0.104061
30	1	0	-5.628942	2.750053	-0.115297
31	6	0	-3.964227	-1.814534	0.128165
32	1	0	-3.725672	-2.871829	0.172729
33	6	0	-5.295430	-1.341769	0.131663
34	1	0	-6.106597	-2.056790	0.185680
35	6	0	-5.534014	0.018929	0.059553
36	1	0	-6.548609	0.406386	0.052783
37	6	0	4.186459	-3.319359	-0.118339
38	1	0	3.751871	-4.314936	-0.131940

39	6	0	5.561239	-3.141170	-0.135598
40	1	0	6.226308	-3.997202	-0.163785
41	6	0	6.097797	-1.831293	-0.115911
42	1	0	7.174154	-1.695159	-0.129714
43	78	0	-0.952753	-1.421429	0.024630
44	6	0	-3.669634	4.666323	-0.314776
45	1	0	-3.170187	5.180132	0.515012
46	1	0	-3.210987	5.031105	-1.241516
47	1	0	-4.722235	4.963256	-0.315784

4.2.2. L9-PtCl T₁:

HF = -1520.5081026 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	17	0	-1.182879	-3.877092	0.060560
2	7	0	-0.761720	0.561169	-0.010420
3	7	0	1.071871	-1.355961	-0.038860
4	7	0	-2.934389	-0.966592	0.083710
5	6	0	1.547391	-0.031411	-0.021170
6	6	0	-1.970970	1.256368	-0.067290
7	6	0	2.395110	2.586219	0.097800
8	6	0	0.545060	1.009259	0.015630
9	6	0	2.930100	0.240209	-0.025150
10	6	0	-3.137160	0.404658	0.008690
11	6	0	3.354420	1.590539	0.026120
12	1	0	4.405320	1.847250	0.024740
13	6	0	1.904201	-2.376081	-0.076700
14	1	0	1.464051	-3.368591	-0.085170
15	6	0	-4.448400	0.940128	-0.009330
16	6	0	1.007470	2.330369	0.096920

17	1	0	0.331320	3.164649	0.194510
18	6	0	-2.196430	2.624698	-0.212070
19	1	0	-1.381880	3.322578	-0.334070
20	6	0	5.268531	-0.723940	-0.093970
21	1	0	5.712600	0.263890	-0.075410
22	6	0	2.817290	4.019559	0.156140
23	9	0	4.183300	4.187990	0.324400
24	9	0	2.204379	4.719659	1.197210
25	9	0	2.482579	4.728299	-1.003710
26	6	0	3.860751	-0.881090	-0.074080
27	6	0	3.327071	-2.198291	-0.101330
28	6	0	-3.515790	3.174618	-0.239100
29	6	0	-4.621140	2.349378	-0.126260
30	1	0	-5.625790	2.760587	-0.138990
31	6	0	-3.965769	-1.809032	0.160880
32	1	0	-3.725469	-2.863992	0.213790
33	6	0	-5.301809	-1.334742	0.167290
34	1	0	-6.112059	-2.048703	0.234330
35	6	0	-5.539490	0.024437	0.079460
36	1	0	-6.553370	0.411347	0.072830
37	6	0	4.185161	-3.327200	-0.145860
38	1	0	3.751491	-4.322031	-0.163760
39	6	0	5.560501	-3.149650	-0.165100
40	1	0	6.224291	-4.005630	-0.199190
41	6	0	6.099701	-1.837900	-0.139430
42	1	0	7.175551	-1.703210	-0.155190
43	78	0	-0.956239	-1.415822	0.029260
44	6	0	-3.663871	4.671368	-0.394610
45	1	0	-3.161591	5.199158	0.423220
46	1	0	-3.207741	5.010498	-1.331090
47	1	0	-4.715371	4.968178	-0.399230

4.2.3. L11-PtCl S₀:

HF=-1971.7301703 hartrees

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	17	0	0.000000	0.000000	4.155543	
2	7	0	-0.115100	-2.004707	1.438842	
3	7	0	0.115100	2.004707	1.438842	
4	6	0	-0.000000	3.998436	-1.703576	
5	1	0	0.015079	5.022487	-2.057264	
6	6	0	-0.208886	-2.936319	2.372276	
7	1	0	-0.237271	-2.596332	3.404869	
8	6	0	-0.266381	-4.326377	2.057852	
9	6	0	-0.205980	-4.733791	0.694923	
10	6	0	-0.093632	-3.704652	-0.324615	
11	6	0	-0.000000	-3.998436	-1.703576	
12	1	0	-0.015079	-5.022487	-2.057264	
13	6	0	0.132360	-2.954772	-2.604895	
14	6	0	0.146518	-1.600452	-2.215925	
15	1	0	0.292578	-0.850867	-2.981224	
16	6	0	0.021084	-1.264079	-0.862289	
17	7	0	-0.000000	-0.000000	-0.295139	
18	6	0	-0.021084	1.264079	-0.862289	
19	6	0	0.068269	2.351759	0.077528	
20	6	0	0.208886	2.936319	2.372276	
21	1	0	0.237271	2.596332	3.404869	
22	6	0	0.266381	4.326377	2.057852	
23	6	0	0.205980	4.733791	0.694923	
24	6	0	0.093632	3.704652	-0.324615	
25	6	0	-0.132360	2.954772	-2.604895	
26	6	0	-0.146518	1.600452	-2.215925	
27	1	0	-0.292578	0.850867	-2.981224	

28	6	0	-0.261435	3.233222	-4.063990
29	9	0	-0.270972	4.579077	-4.377922
30	9	0	-1.430107	2.697365	-4.609140
31	9	0	0.776030	2.667957	-4.810067
32	6	0	0.257713	6.116411	0.405930
33	1	0	0.215744	6.466817	-0.619767
34	6	0	0.366334	7.047609	1.433170
35	1	0	0.406201	8.105429	1.195219
36	6	0	0.425890	6.635774	2.786274
37	1	0	0.510124	7.376984	3.573241
38	6	0	0.375705	5.285095	3.095063
39	1	0	0.418930	4.945307	4.126068
40	6	0	-0.068269	-2.351759	0.077528
41	6	0	0.261435	-3.233222	-4.063990
42	9	0	1.430107	-2.697365	-4.609140
43	9	0	-0.776030	-2.667957	-4.810067
44	9	0	0.270972	-4.579077	-4.377922
45	6	0	-0.257713	-6.116411	0.405930
46	1	0	-0.215744	-6.466817	-0.619767
47	6	0	-0.366334	-7.047609	1.433170
48	1	0	-0.406201	-8.105429	1.195219
49	6	0	-0.425890	-6.635774	2.786274
50	1	0	-0.510124	-7.376984	3.573241
51	6	0	-0.375705	-5.285095	3.095063
52	1	0	-0.418930	-4.945307	4.126068
53	78	0	0.000000	0.000000	1.699632

4.2.4. L11-PtCl T₁:

HF=-1971.6555627 hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	17	0	0.000000	-0.000000	4.142066
2	7	0	-0.194888	-2.016260	1.445985
3	7	0	0.194888	2.016260	1.445985
4	6	0	0.000000	3.957671	-1.701964
5	1	0	0.027384	4.975499	-2.074880
6	6	0	-0.386734	-2.964224	2.385230
7	1	0	-0.433226	-2.630419	3.417553
8	6	0	-0.508793	-4.331603	2.040469
9	6	0	-0.399779	-4.728989	0.668444
10	6	0	-0.175644	-3.694636	-0.328446
11	6	0	-0.000000	-3.957671	-1.701964
12	1	0	-0.027384	-4.975499	-2.074880
13	6	0	0.255524	-2.902558	-2.599401
14	6	0	0.282068	-1.569819	-2.187031
15	1	0	0.537826	-0.798925	-2.904993
16	6	0	0.047302	-1.261554	-0.831534
17	7	0	-0.000000	0.000000	-0.260749
18	6	0	-0.047302	1.261554	-0.831534
19	6	0	0.115160	2.348468	0.108948
20	6	0	0.386734	2.964224	2.385230
21	1	0	0.433226	2.630419	3.417553
22	6	0	0.508793	4.331603	2.040469
23	6	0	0.399779	4.728989	0.668444
24	6	0	0.175644	3.694636	-0.328446
25	6	0	-0.255524	2.902558	-2.599401
26	6	0	-0.282068	1.569819	-2.187031
27	1	0	-0.537826	0.798925	-2.904993
28	6	0	-0.503410	3.177660	-4.038124
29	9	0	-0.530512	4.524114	-4.349550
30	9	0	-1.714918	2.645880	-4.492292
31	9	0	0.464254	2.606664	-4.875880
32	6	0	0.515232	6.100645	0.351584
33	1	0	0.442898	6.433809	-0.678955
34	6	0	0.727885	7.045534	1.350517
35	1	0	0.815153	8.095078	1.089846

36	6	0	0.832282	6.649787	2.708568
37	1	0	0.997189	7.398406	3.476108
38	6	0	0.724465	5.312147	3.048631
39	1	0	0.802003	4.991417	4.083890
40	6	0	-0.115160	-2.348468	0.108948
41	6	0	0.503410	-3.177660	-4.038124
42	9	0	1.714918	-2.645880	-4.492292
43	9	0	-0.464254	-2.606664	-4.875880
44	9	0	0.530512	-4.524114	-4.349550
45	6	0	-0.515232	-6.100645	0.351584
46	1	0	-0.442898	-6.433809	-0.678955
47	6	0	-0.727885	-7.045534	1.350517
48	1	0	-0.815153	-8.095078	1.089846
49	6	0	-0.832282	-6.649787	2.708568
50	1	0	-0.997189	-7.398406	3.476108
51	6	0	-0.724465	-5.312147	3.048631
52	1	0	-0.802003	-4.991417	4.083890
53	78	0	0.000000	-0.000000	1.712276

Chapter 5:

5.1. NMR Spectra:

PMA-05-078-D3H.1.fid
PROTON CDCl3 C:\Herbert 1

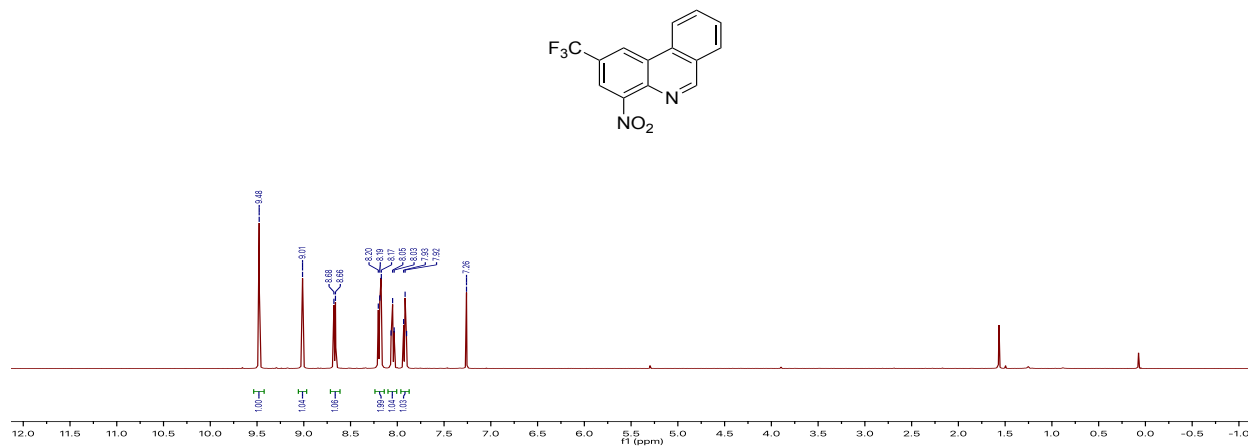


Figure S5.1. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of **3-NO₂**.

PMA-05-078-D3c.1.fid
C13CPD CDCl3 C:\Herbert 1

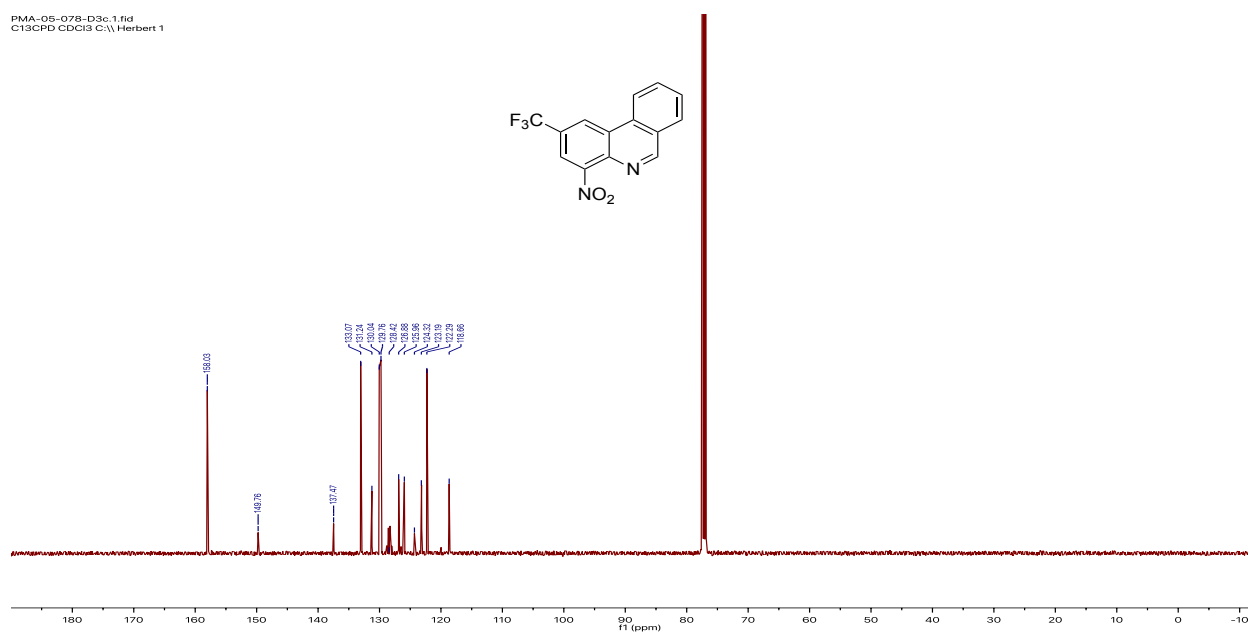


Figure S5.2. ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C) spectrum of **3-NO₂**.

PMA-05-078-D5F.1.fid
CF3phen-NO2
F19CPD.CDCI3 C:\Herbert 1

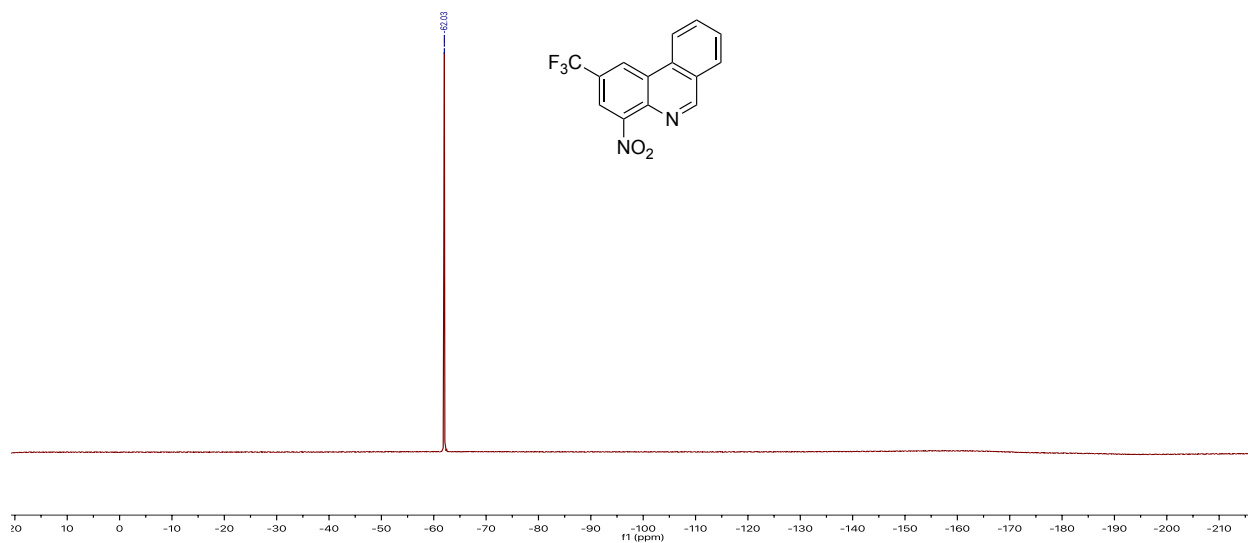


Figure S5.3. ^{19}F NMR (282 MHz, CDCl_3 , 22 °C) spectrum of **3-NO₂**.

BBH_02_047_D3H.1.fid

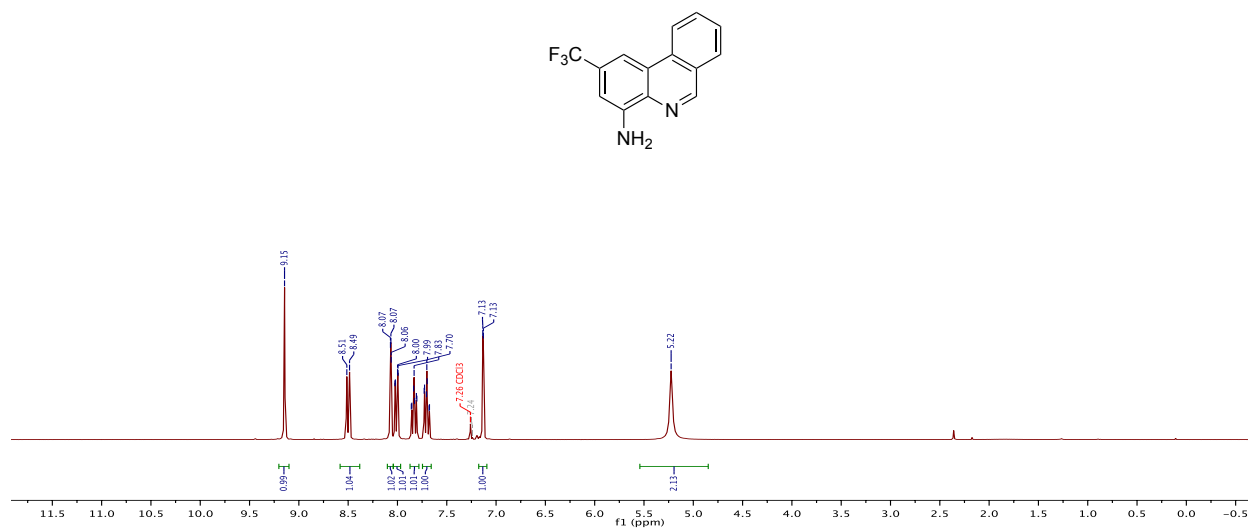


Figure S5.4. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of **3-NH₂**.

BBH_02_047_D3C.1.fid

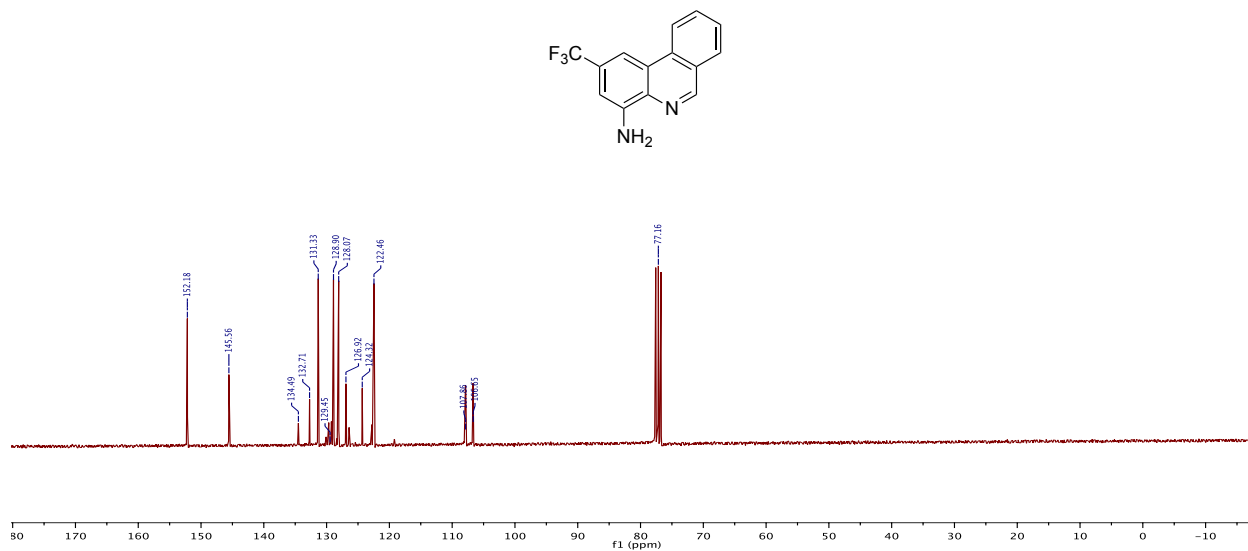


Figure S5.5. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 22 °C) spectrum of **3-NH₂**.

BBH_02_047_D3F.1.fid

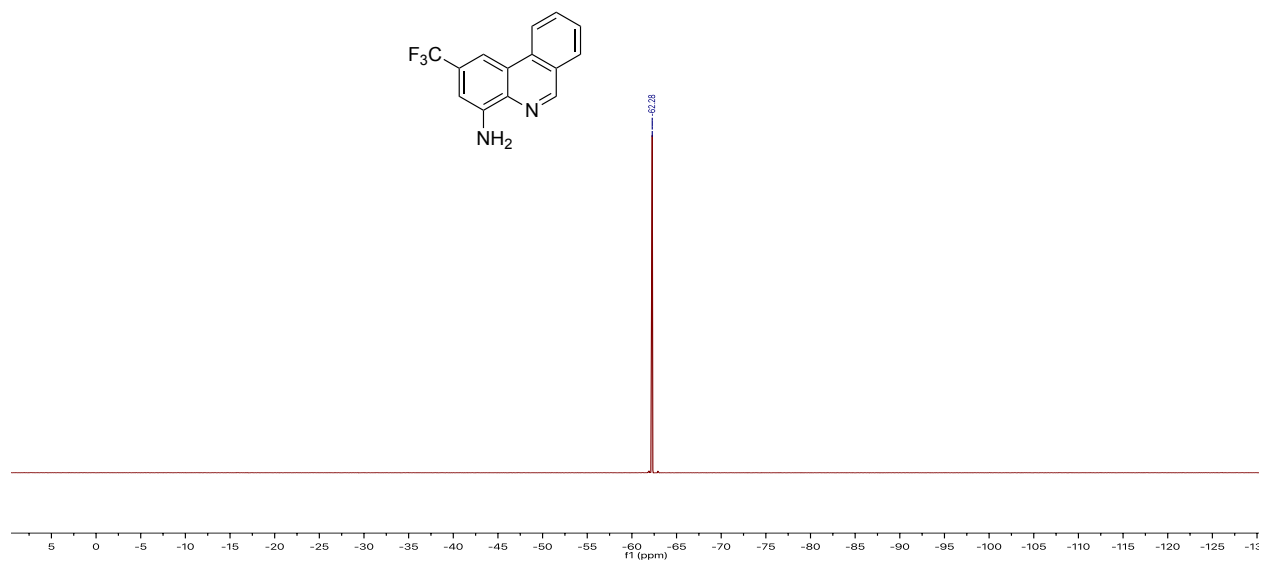


Figure S5.6. ^{19}F NMR (282 MHz, CDCl_3 , 22 °C) spectrum of **3-NH₂**.

PMA-05-135-D3H.1.fid
DCA-NME2 ligand
PROTON CDCl3 C:\Herbert 1

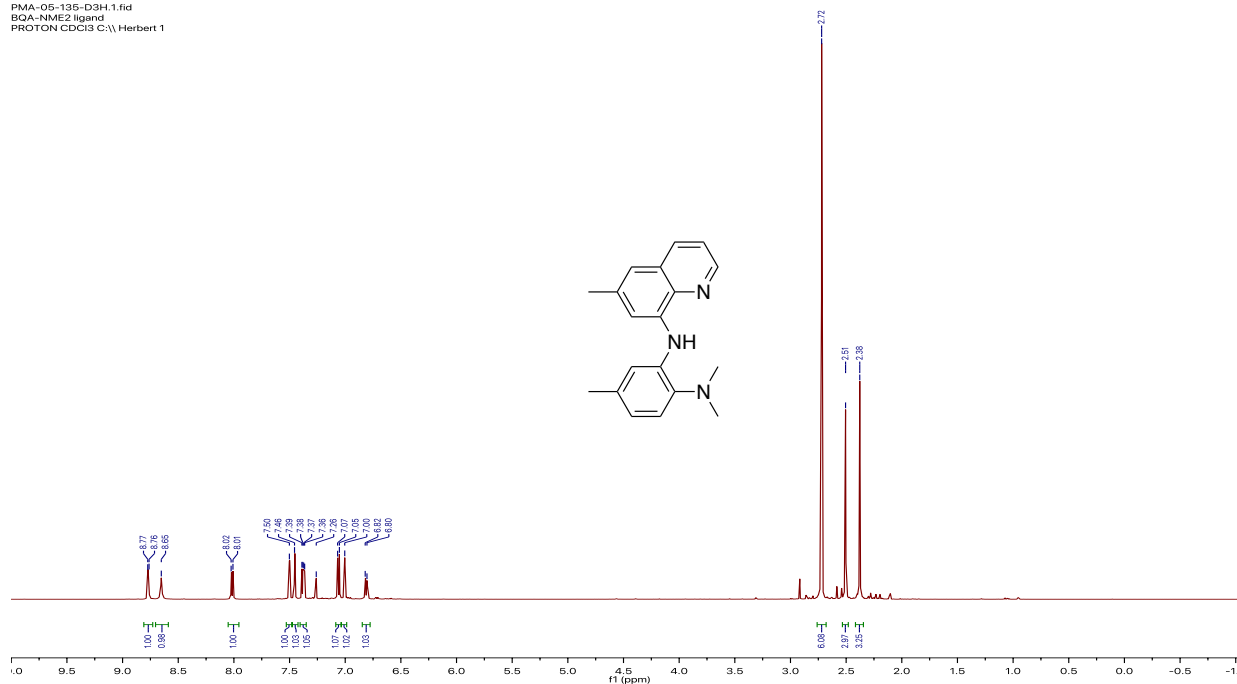


Figure S5.7. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of L13.

PMA-05-035-D5C.1.fid
DCA ligand
C13CPD CDCl3 C:\Herbert 1

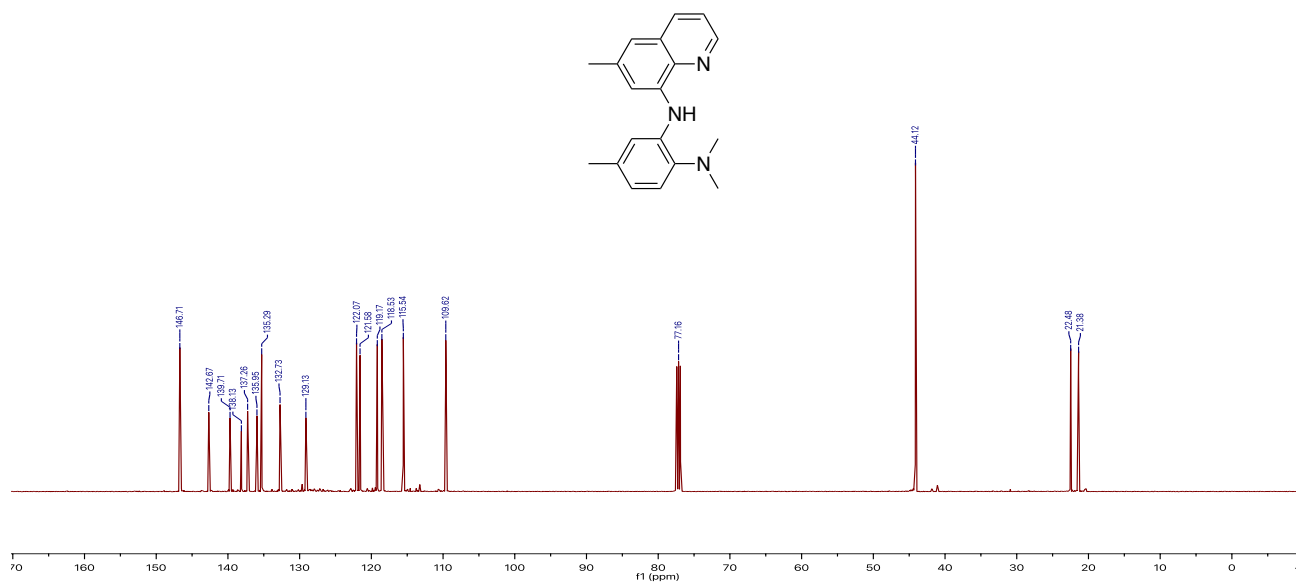


Figure S5.8. ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C) spectrum of L13.

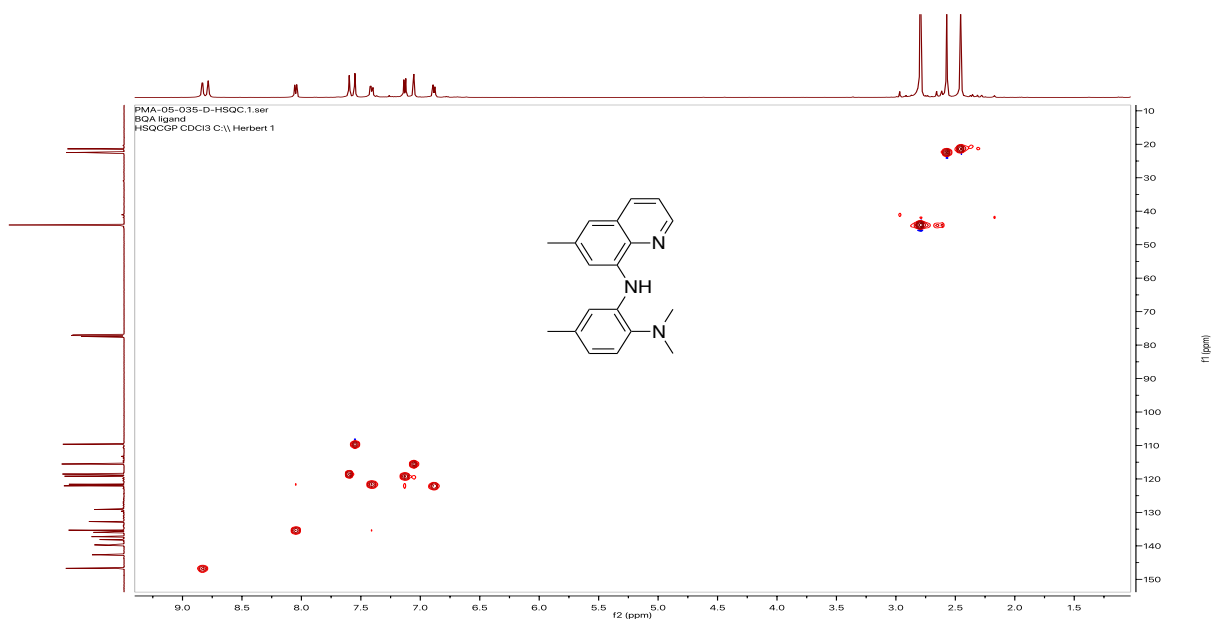


Figure S5.9. HSQC NMR (500/125 MHz, CDCl₃, 22 °C) spectrum of **L13**.

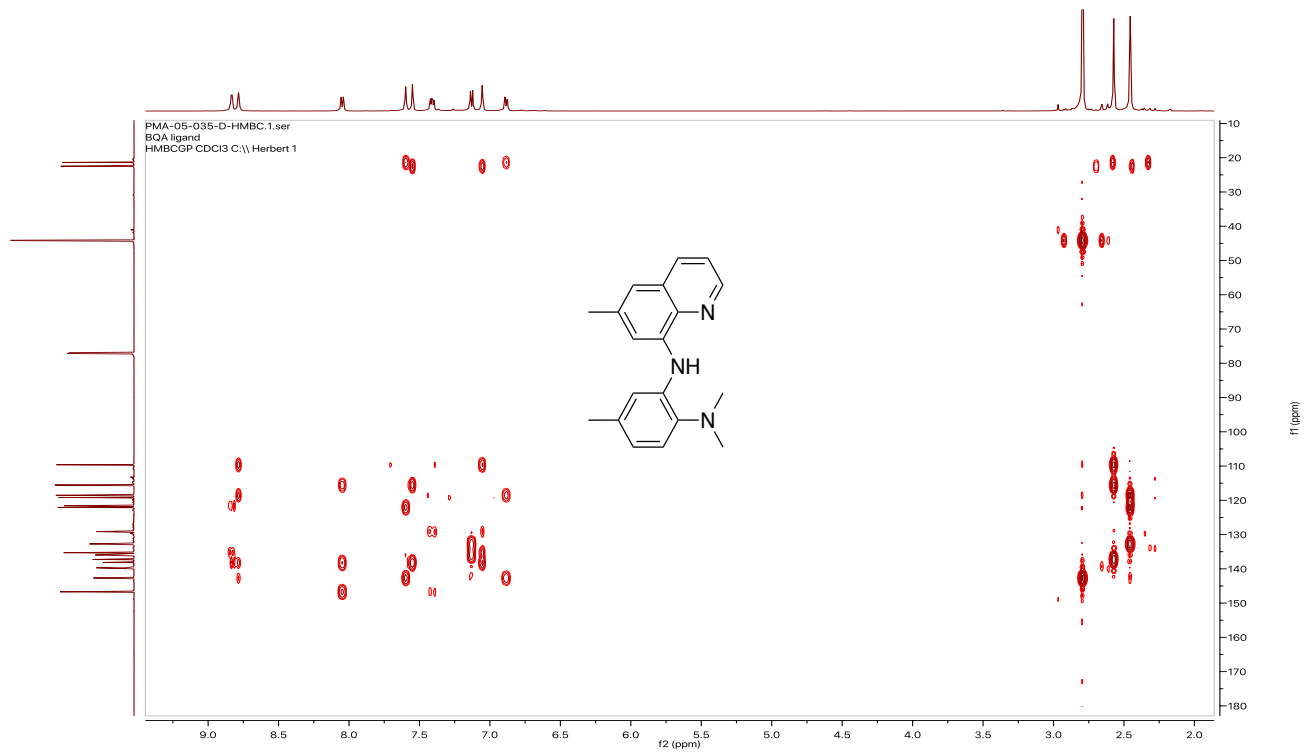


Figure S5.10. HMBC NMR (500/125 MHz, CDCl₃, 22 °C) of **L13**.

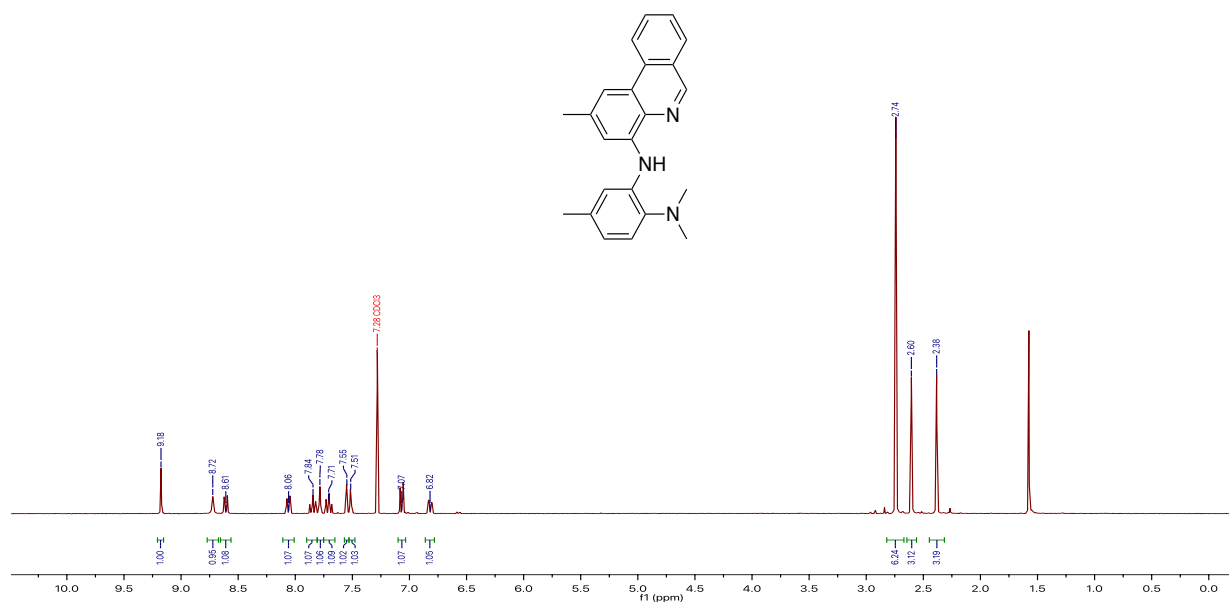


Figure S5.11. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of L14.

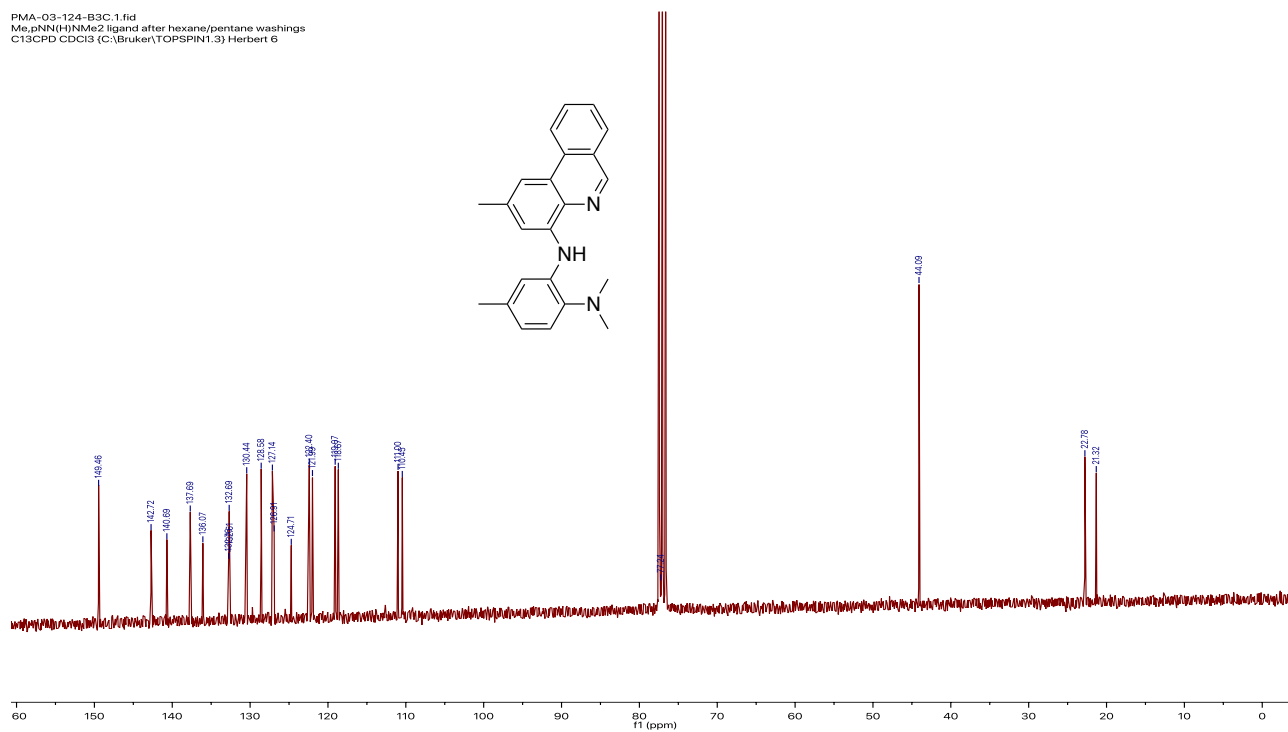


Figure S5.12. ¹³C {¹H} NMR (75 MHz, CDCl₃, 22 °C) spectrum of L14.

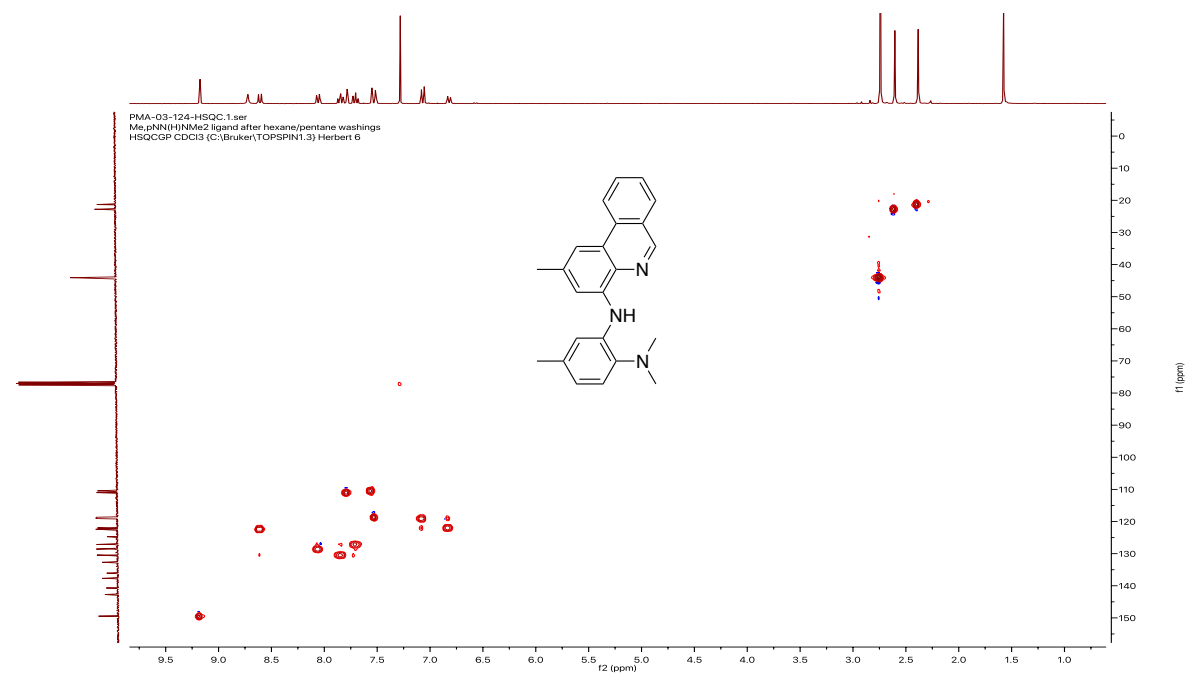


Figure S5.13. HSQC NMR (500/125 MHz, CDCl₃, 22 °C) spectrum of L14.

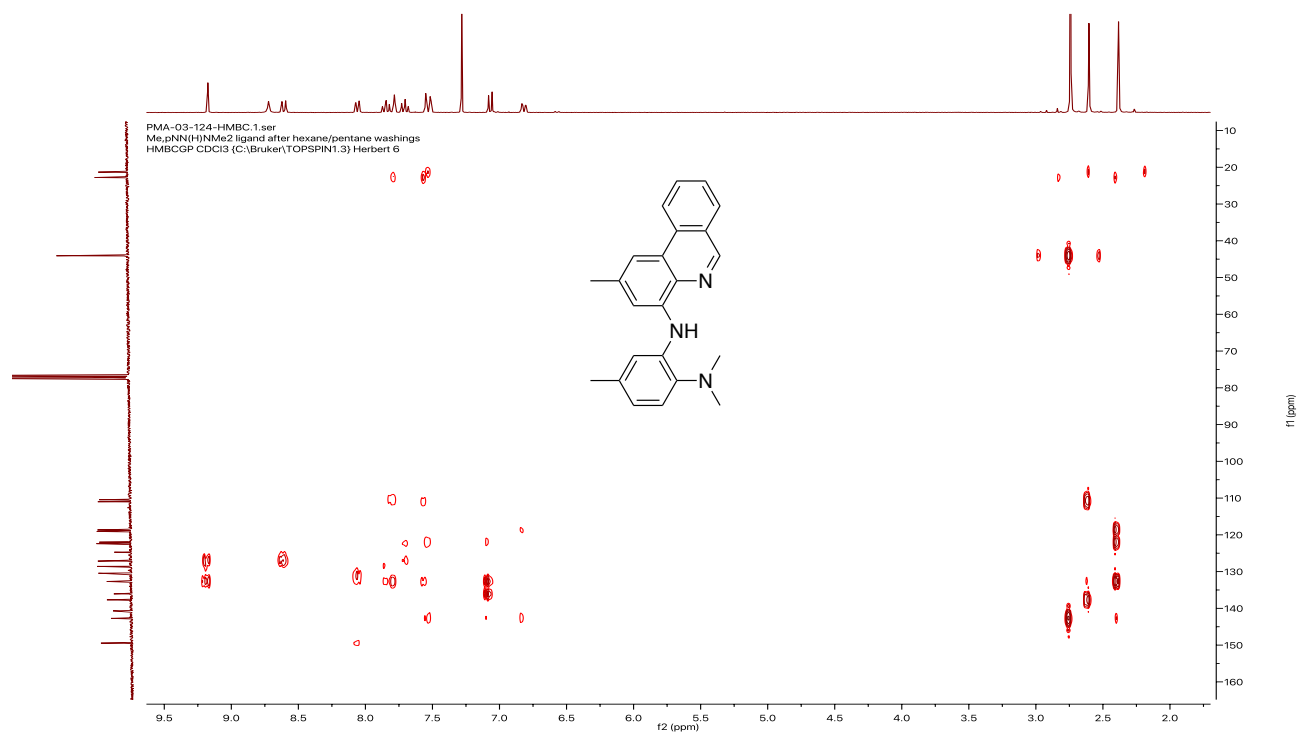


Figure S5.14. HMBC NMR (500/125 MHz, CDCl₃, 22 °C) spectrum of L14.

PMA-04-113-D3H.1.fid
(Bup)NN(H)NME2 crystals
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 38

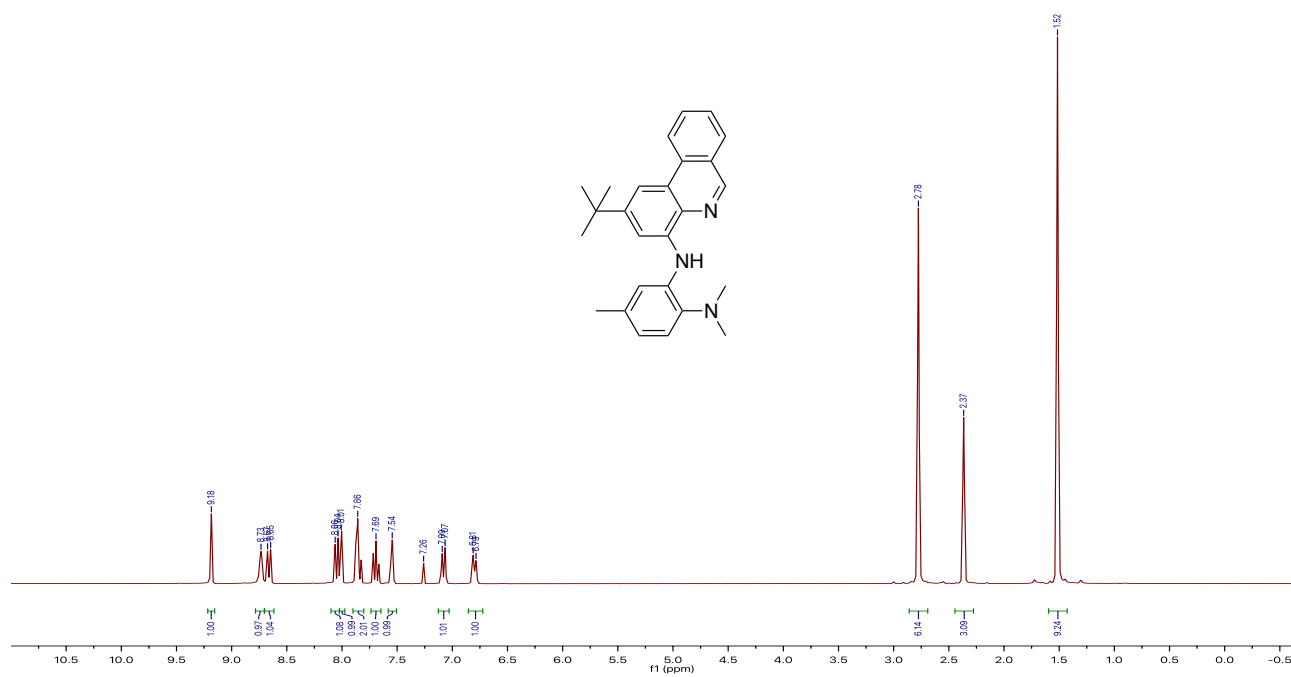


Figure S5.15. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of L15.

PMA-04-113-D3C.1.fid
(Bup)NN(H)NME2 crystals
C13CPD CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 38

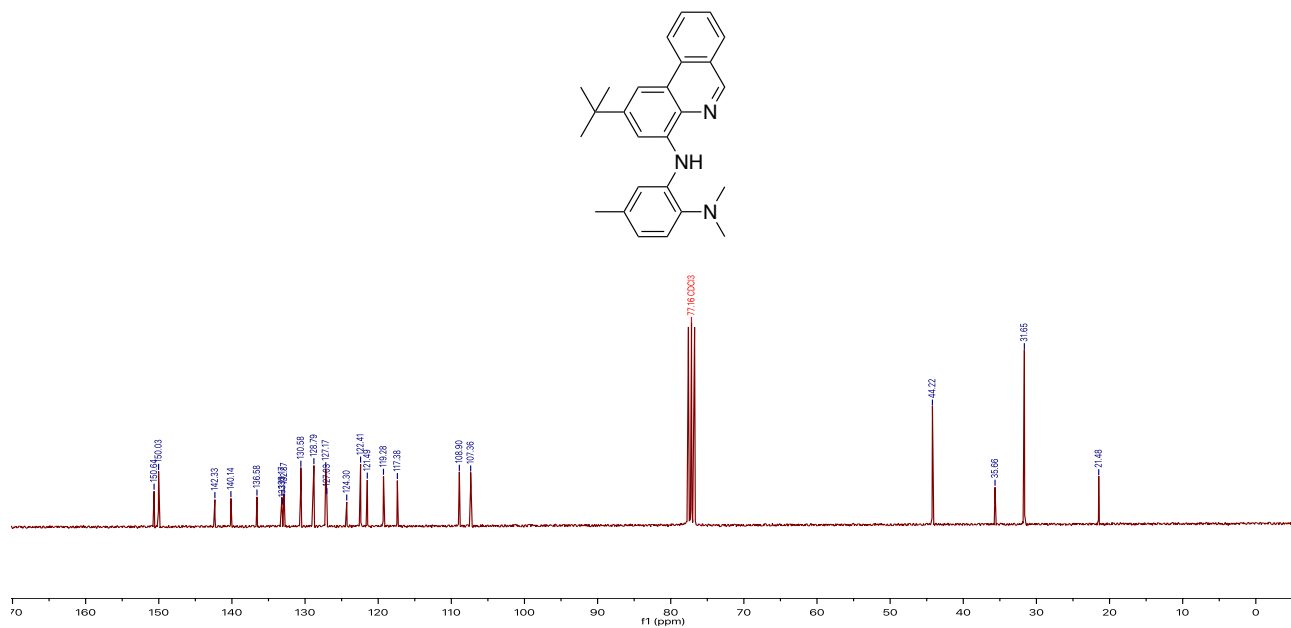


Figure S5.16. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 22 °C) spectrum of L15.

PMA-04-092-B3H.1.fid
CF3pNN(H)NMe2 after column
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 32

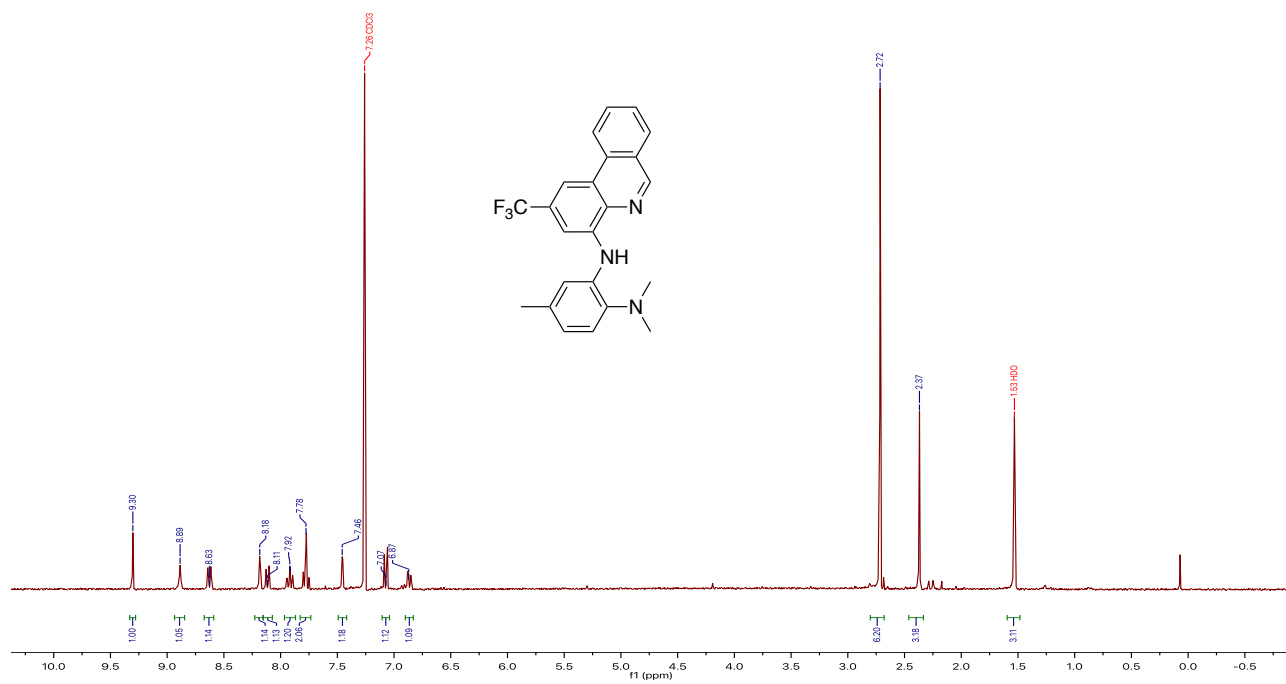


Figure S5.17. ^1H NMR (300 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L16.

PMA-04-092-A5C.1.fid
CF3NN(H)NMe2 ligand
C13CPD CDCl3 C:\Herbert 1

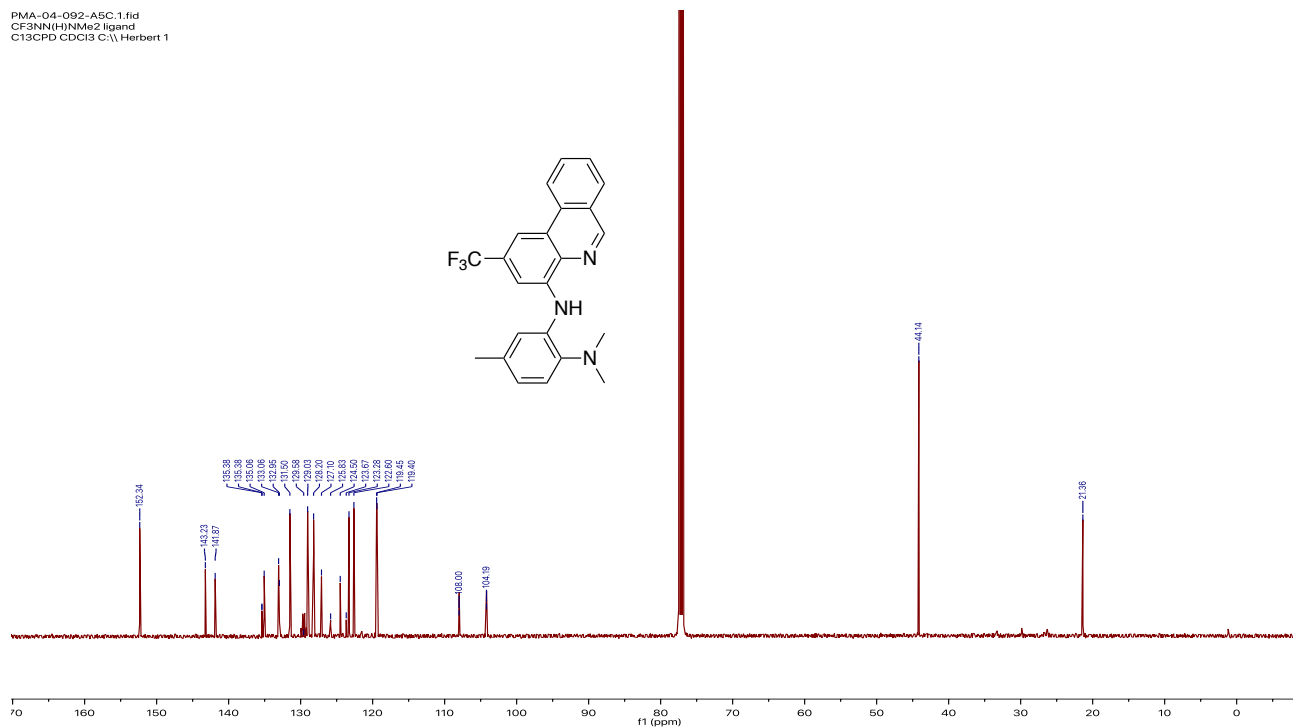


Figure S5.18. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 $^\circ\text{C}$) spectrum of L16.

PMA-05-035-H5F.1.fid
CFENMe2-ligand
F19CPD CDCl3 C:\Herbert 3

-62.37

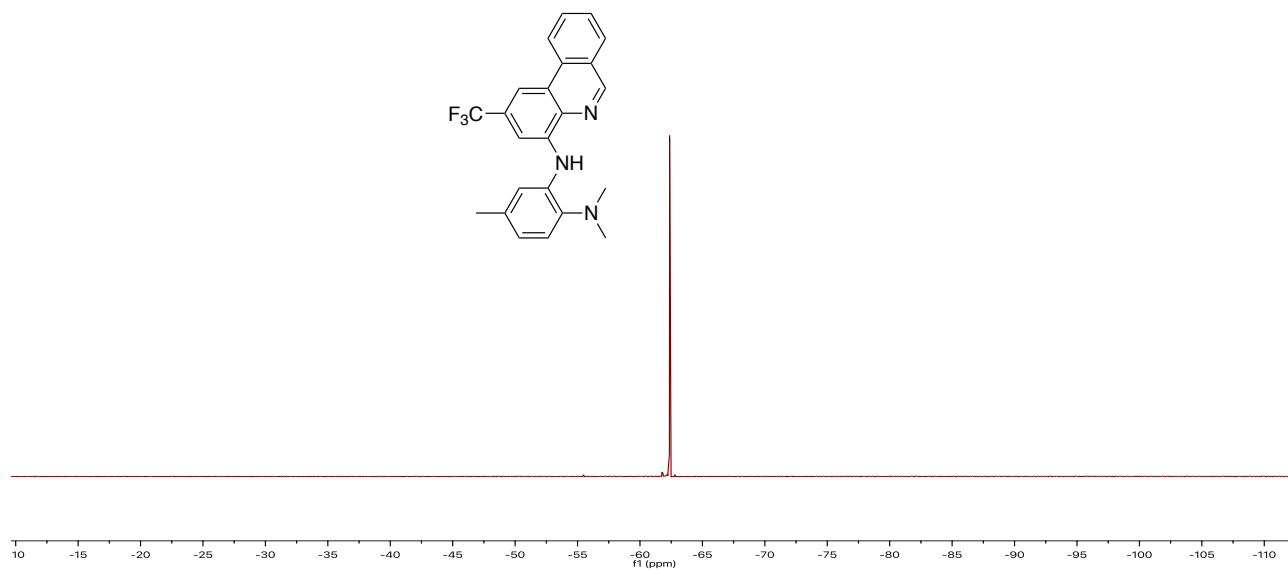


Figure S5.19. $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3 , 22 °C) spectrum of L16.

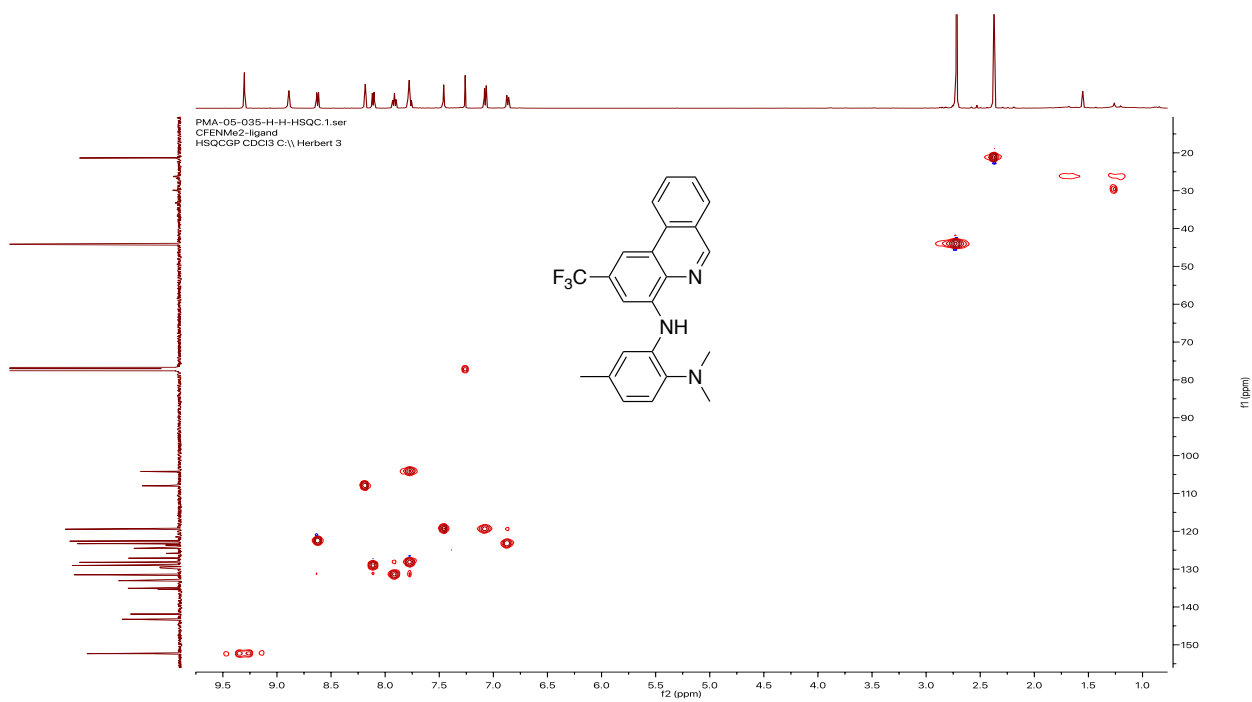


Figure S5.20. HSQC NMR (500/125 MHz, CDCl_3 , 22 °C) spectrum of L16.

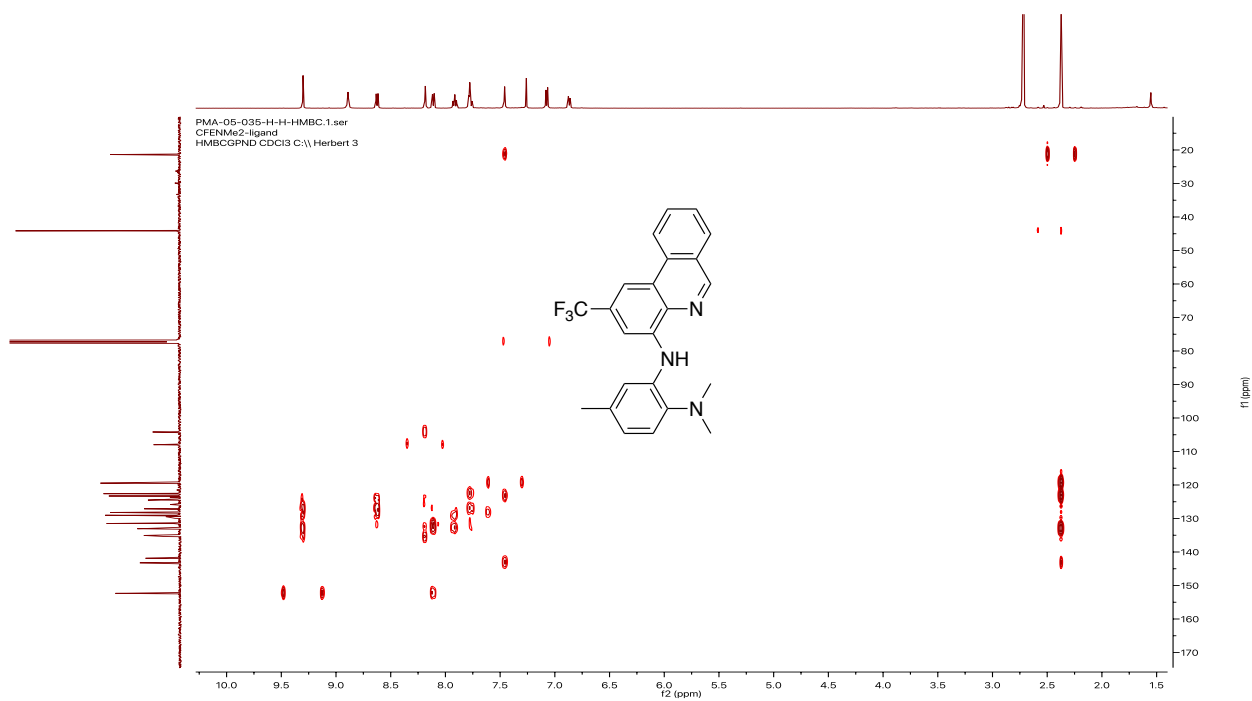


Figure S5.21. HMBC (500/125 MHz, CDCl₃, 22 °C) spectrum of **L16**.

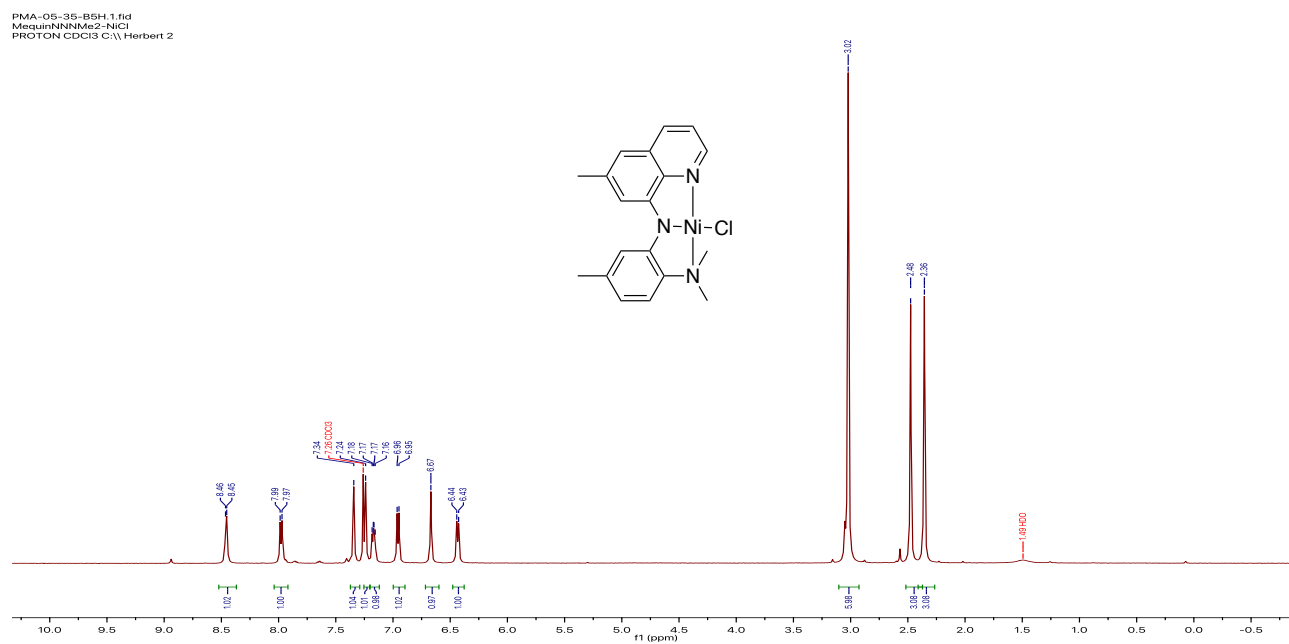


Figure S5.22. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of **L13-NiCl**.

PMA-04-152-A5C.1.fid
MeQuinNNiMe2-NiCl
C13CPD CDCl3 C:\Herbert 4

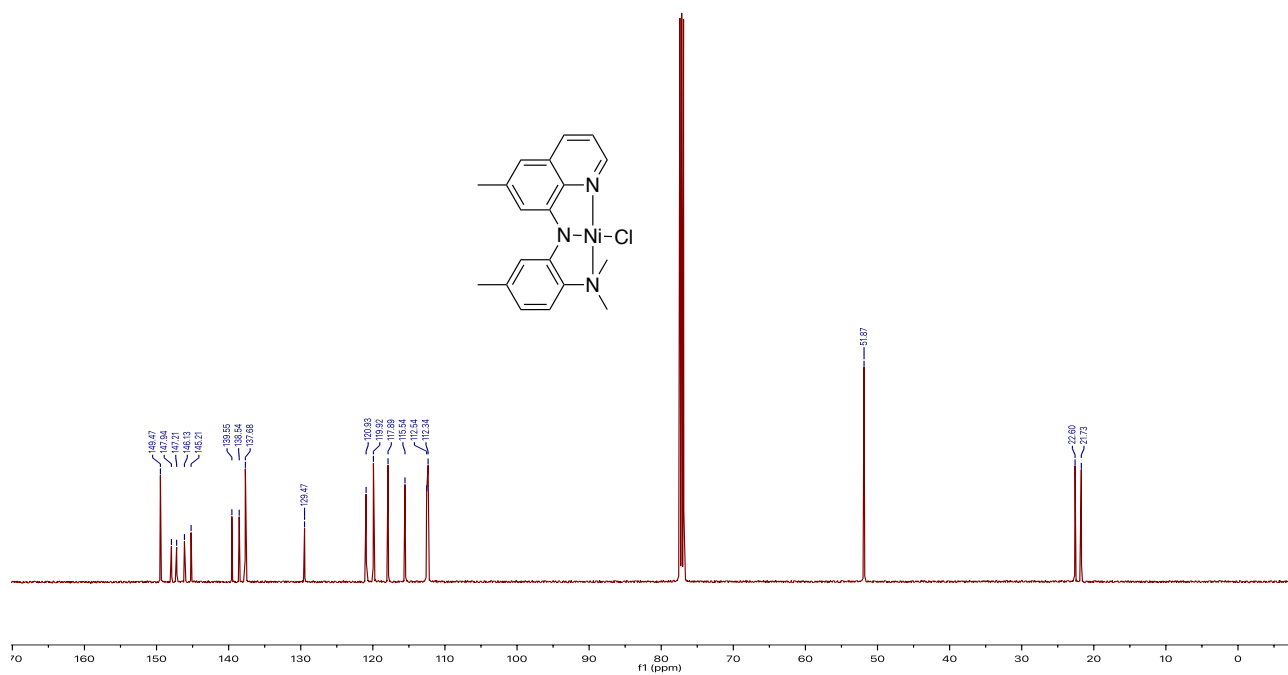


Figure S5.23. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L13-NiCl.

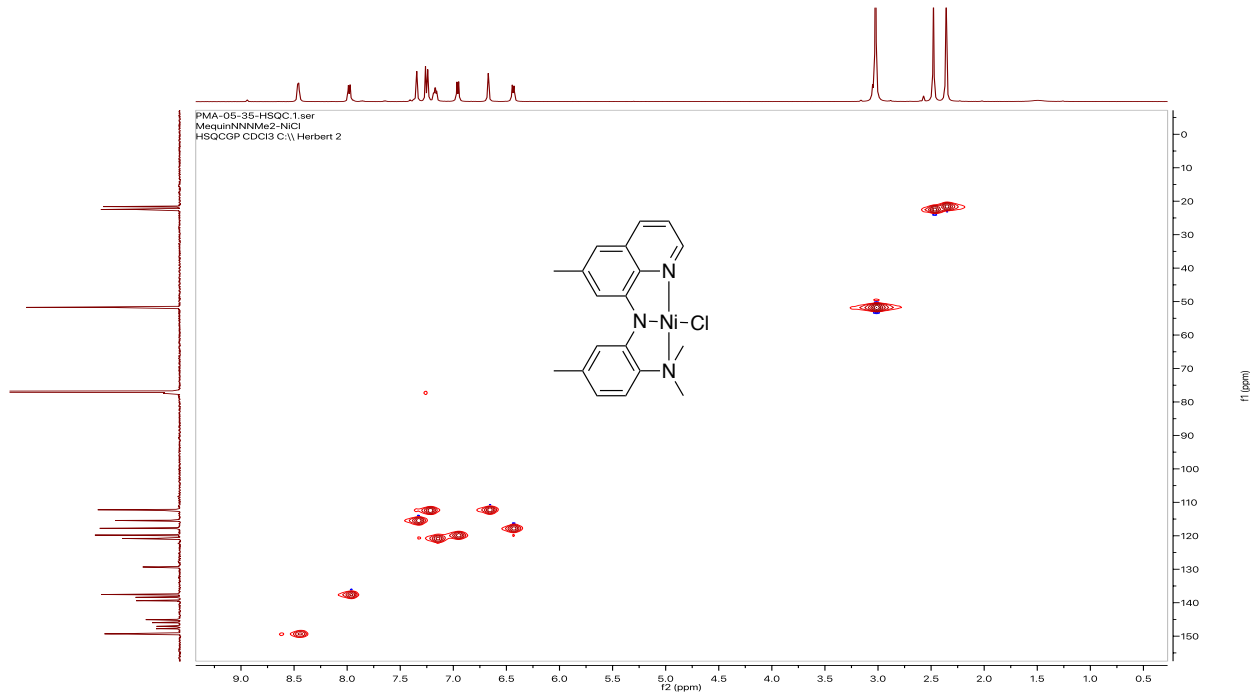


Figure S5.24. HSQC (500/125 MHz, CDCl_3 , 22 °C) spectrum of L13-NiCl.

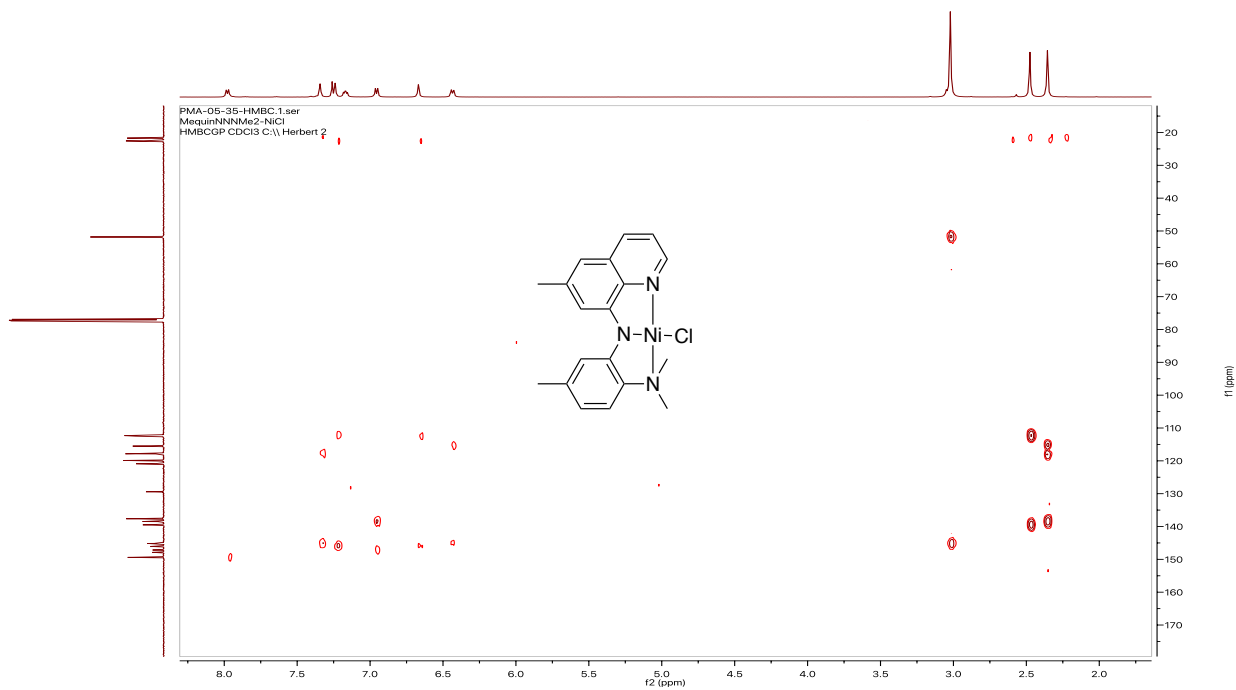


Figure S5.25. HMBC (500/125 MHz, CDCl_3 , 22 °C) spectrum of **L13-NiCl**.

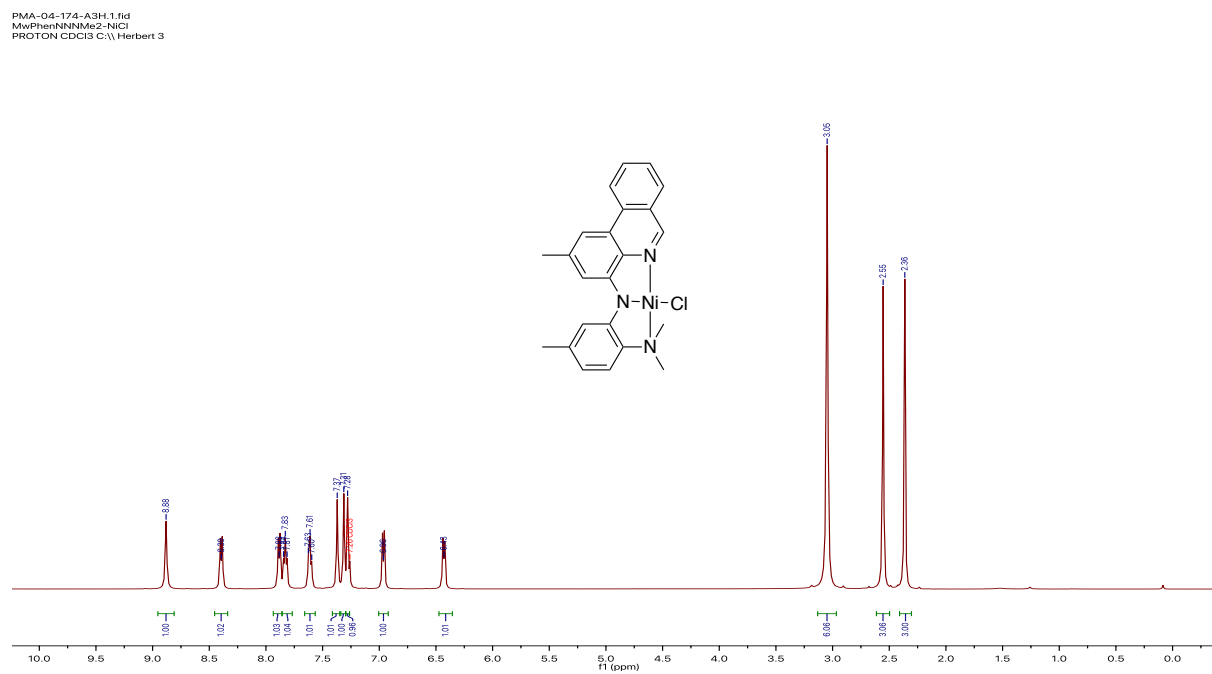


Figure S5.26. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of **L14-NiCl**.

PMA-04-174-A5C.1.fid
MwPhenNNMe2-NiCl
C13CPD CDCl3 C:\ Herbert 3

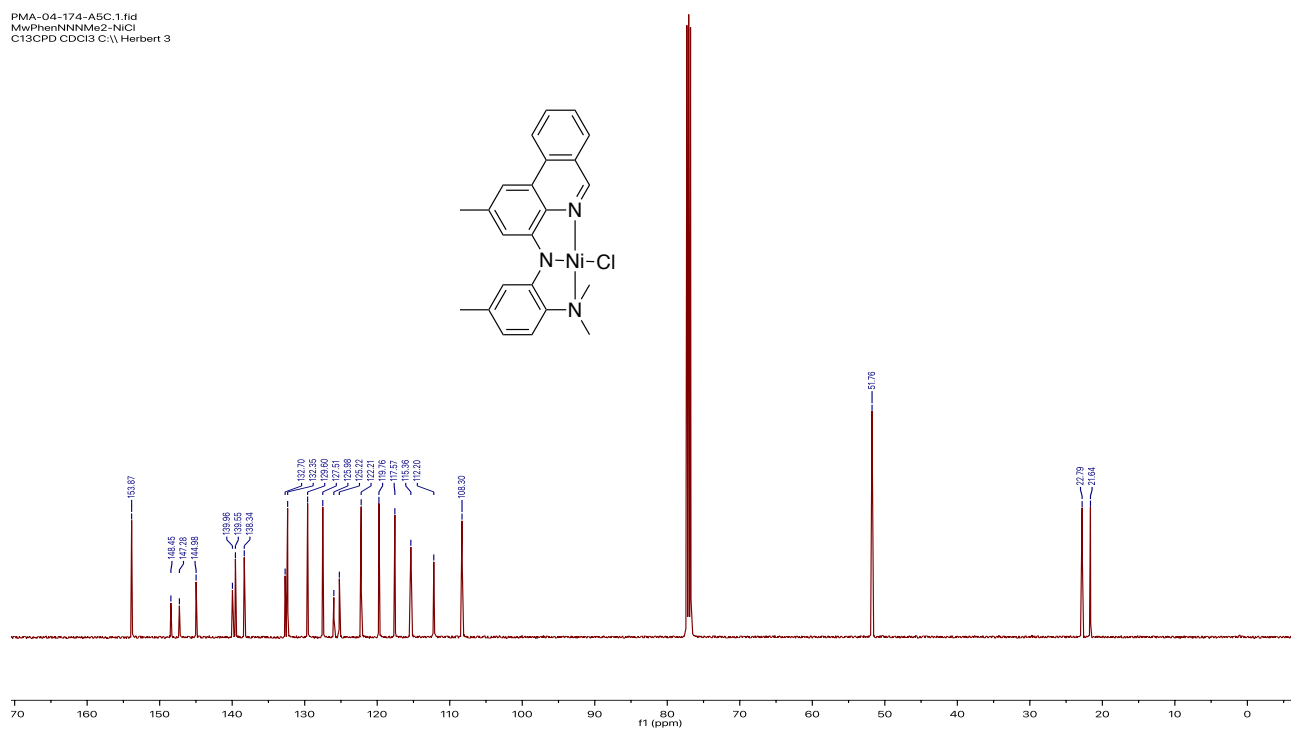


Figure S5.27. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L14-NiCl.

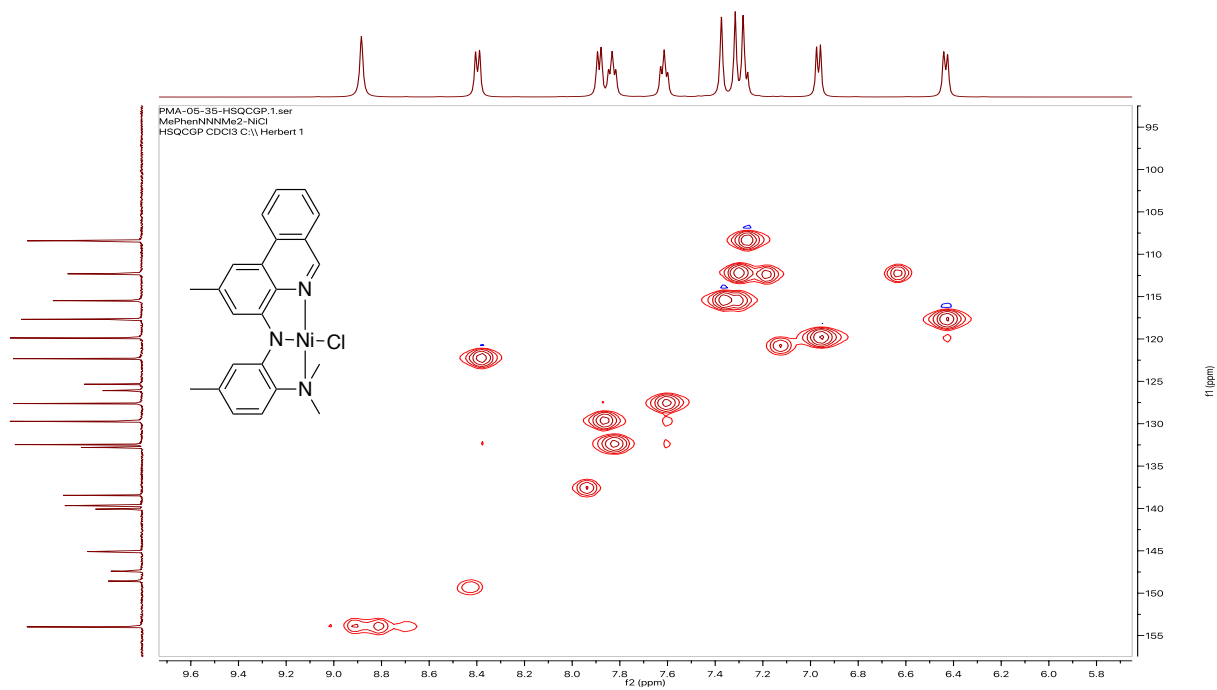


Figure S5.28. HSQC (500/125 MHz, CDCl_3 , 22 °C) spectrum of L14-NiCl.

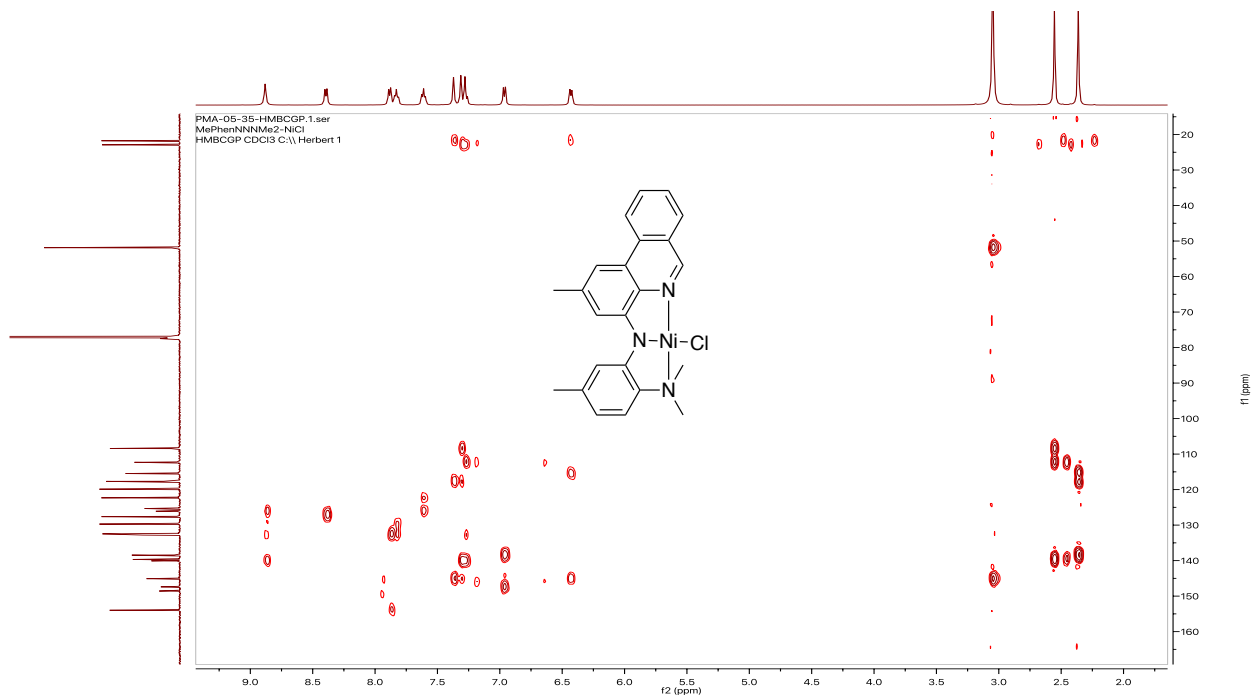


Figure S5.29. HMBC (500/125 MHz, CDCl₃, 22 °C) spectrum of **L14-NiCl**.

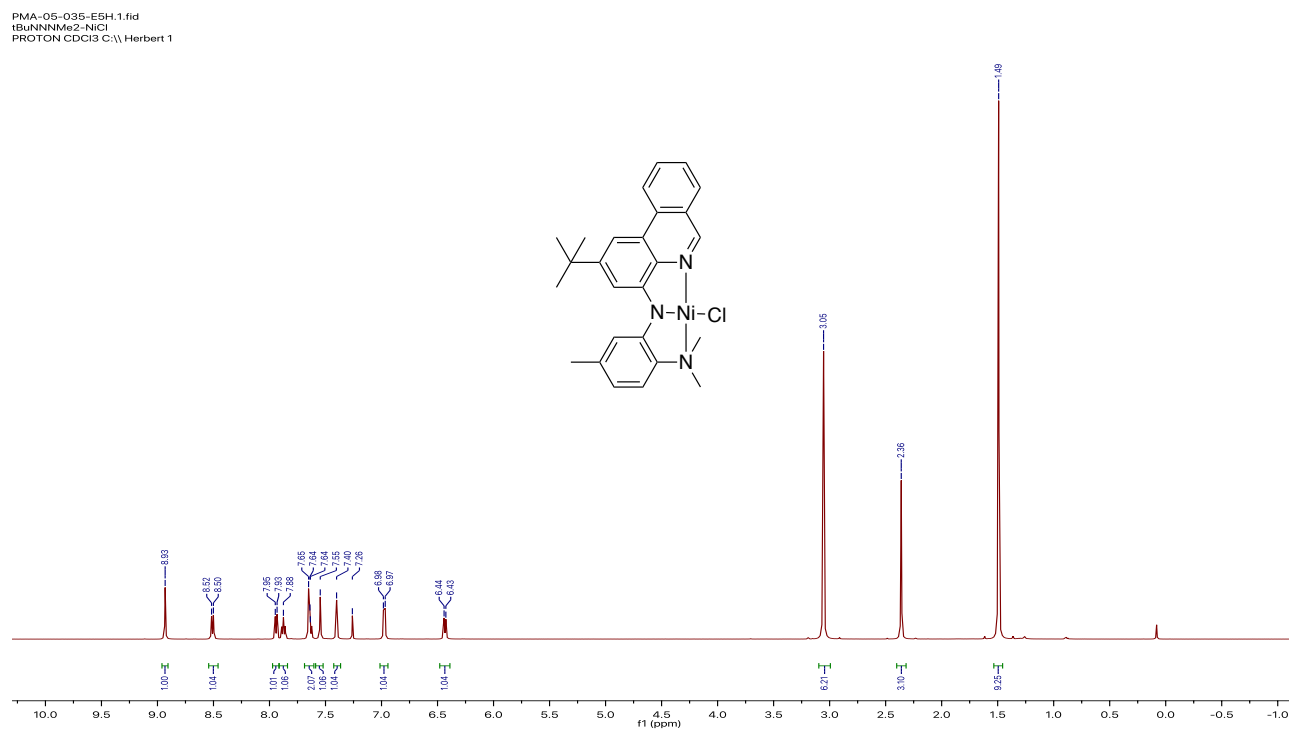


Figure S5.30. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of **L15-NiCl**.

PMA-04-tBuNiCl2.fid
tBuNNMe2-NiCl complex
C13CPD CDCl3 C:\ Herbert 1

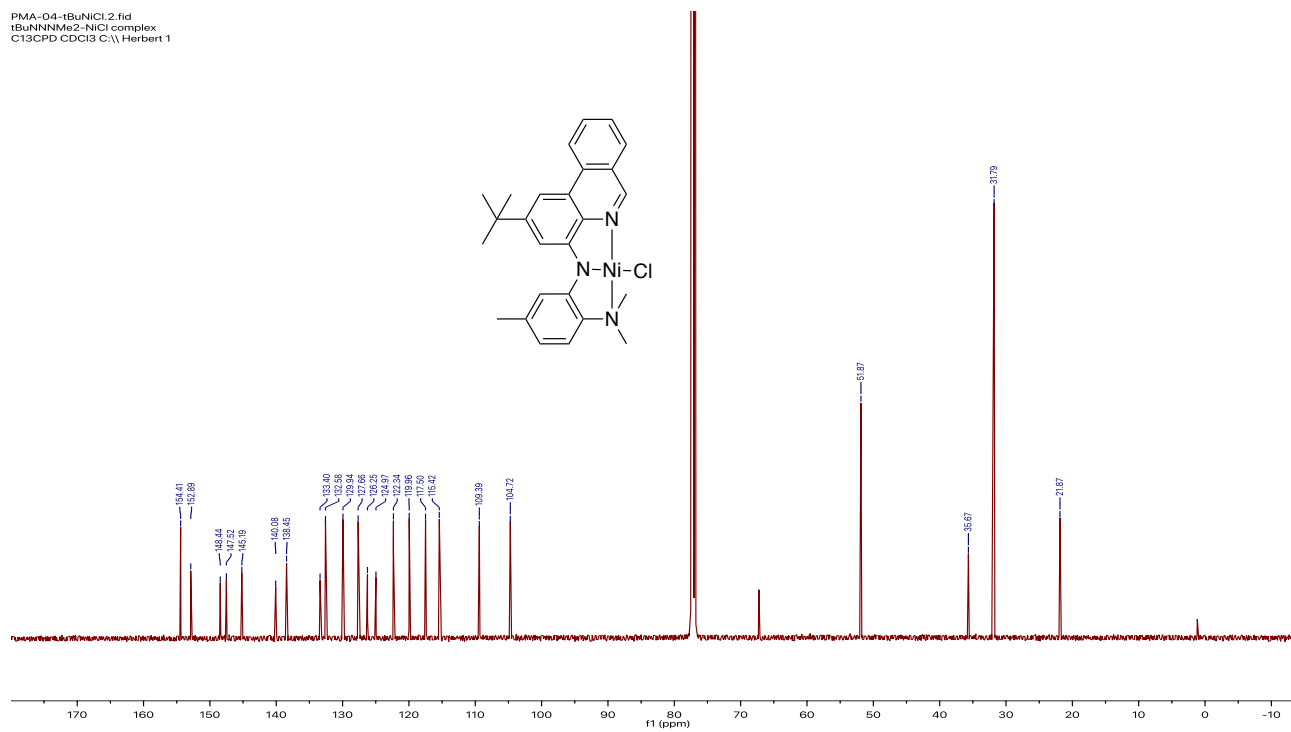


Figure S5.31. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L15-NiCl.

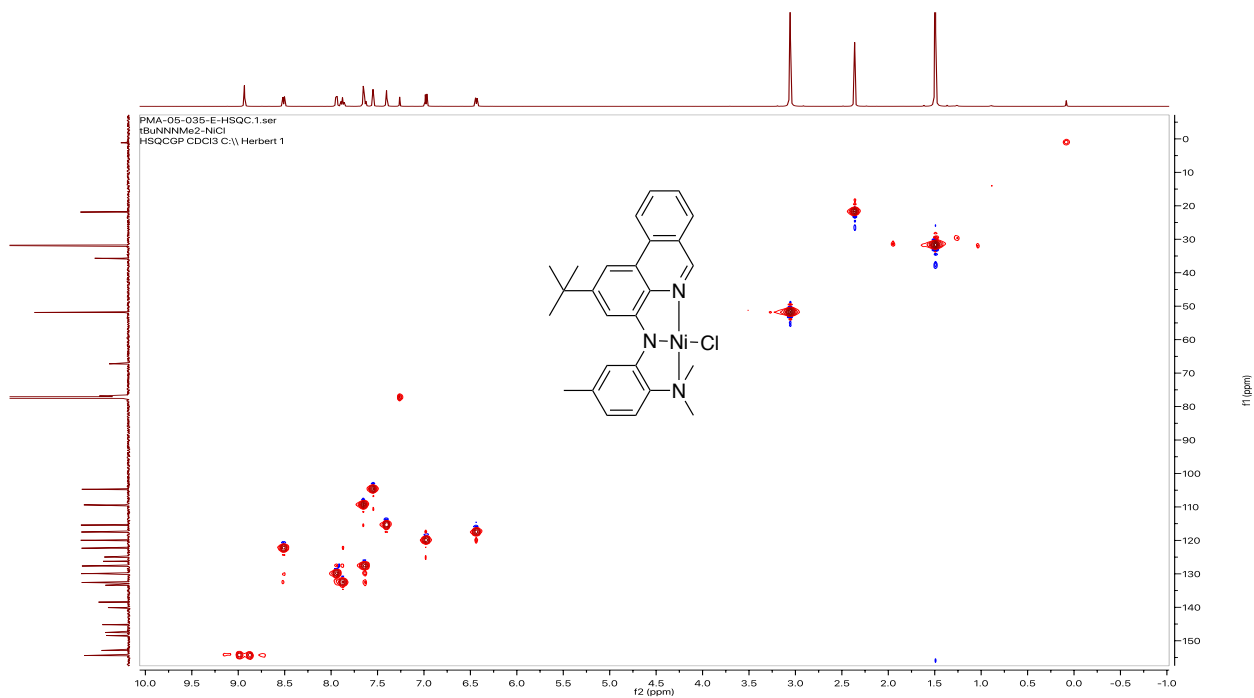


Figure S5.32. HSQC (500/125 MHz, CDCl_3 , 22 °C) spectrum of L15-NiCl.

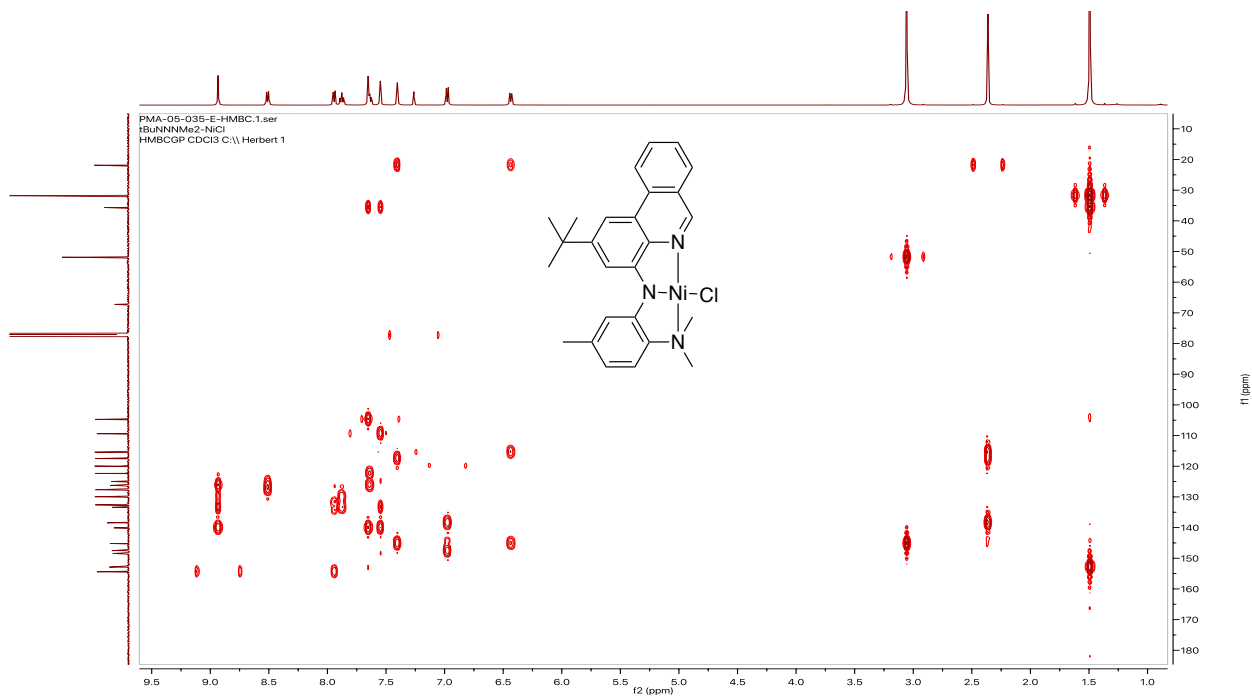


Figure S5.33. HMBC (500/125 MHz, CDCl₃, 22 °C) spectrum of **L15-NiCl**.

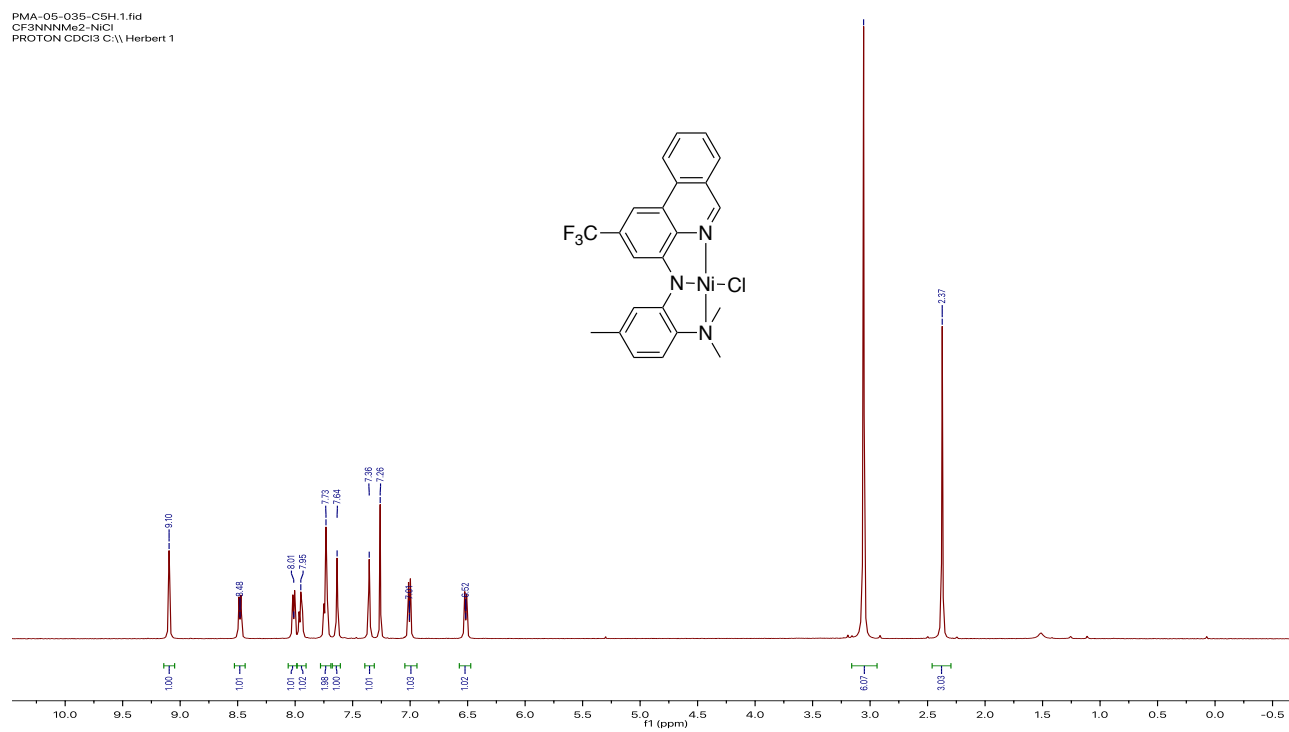


Figure S5.34. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of **L16-NiCl**.

PMA-05-035-C5C.1.fid
CF3NHNiMe2-NiCl
C13CPD CDCl3 C:\Herbert 1

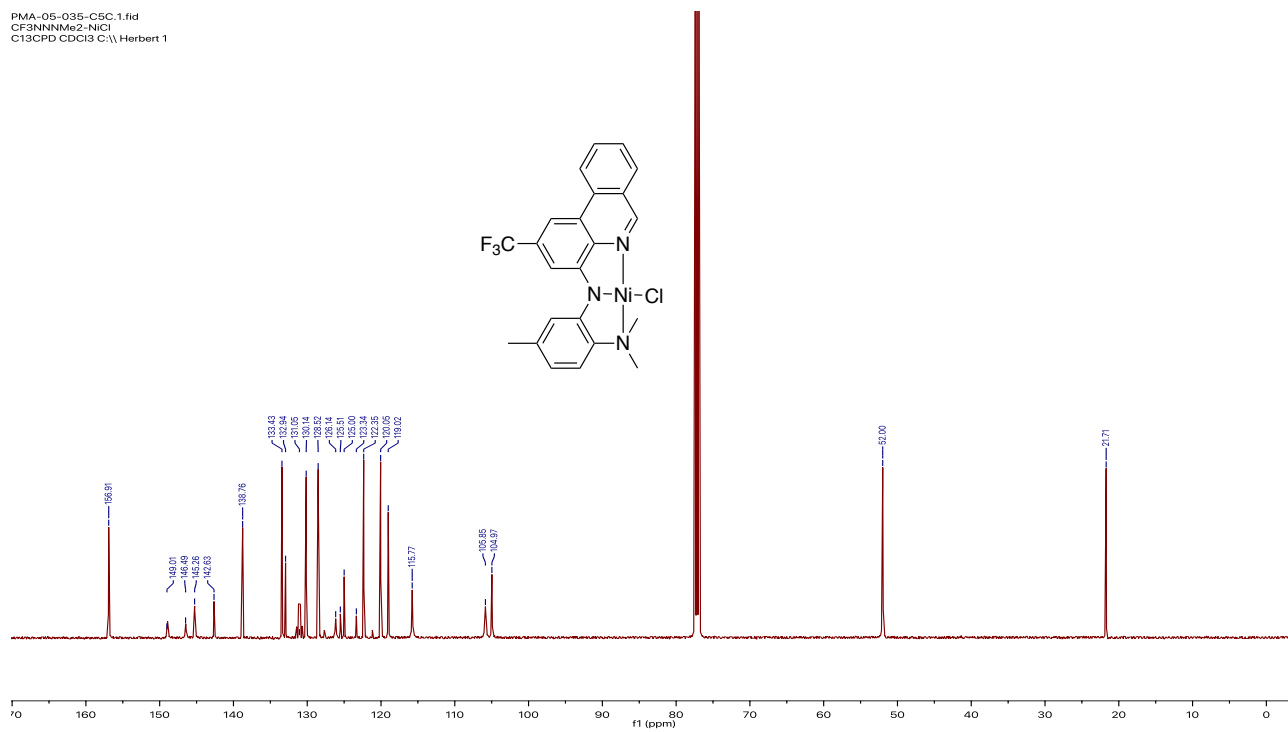


Figure S5.35. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃, 22 °C) spectrum of L16-NiCl.

PMA-04-169-A5F.1.fid
CF3phenNNiMe2-NiCl
F19CPD CDCl3 C:\Herbert 2

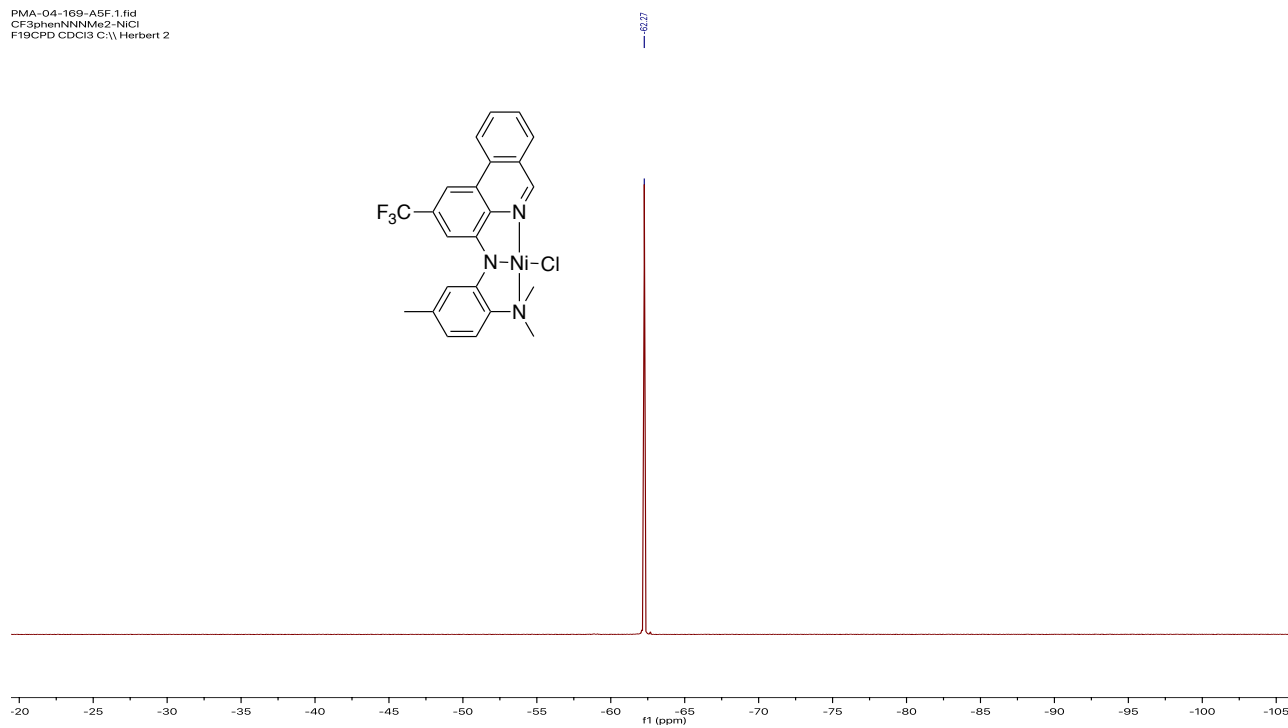


Figure S5.36. $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl₃, 22 °C) spectrum of L16-NiCl.

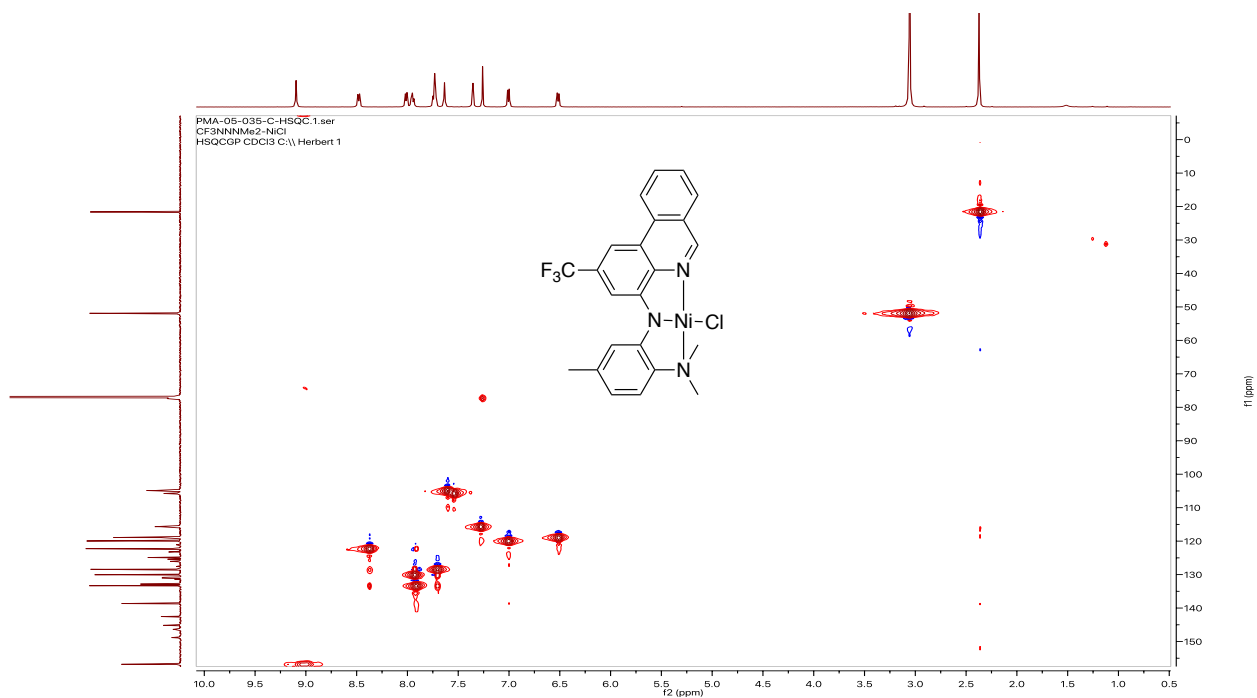


Figure S5.37. HSQC (500/125 MHz, CDCl₃, 22 °C) spectrum of **L16-NiCl**.

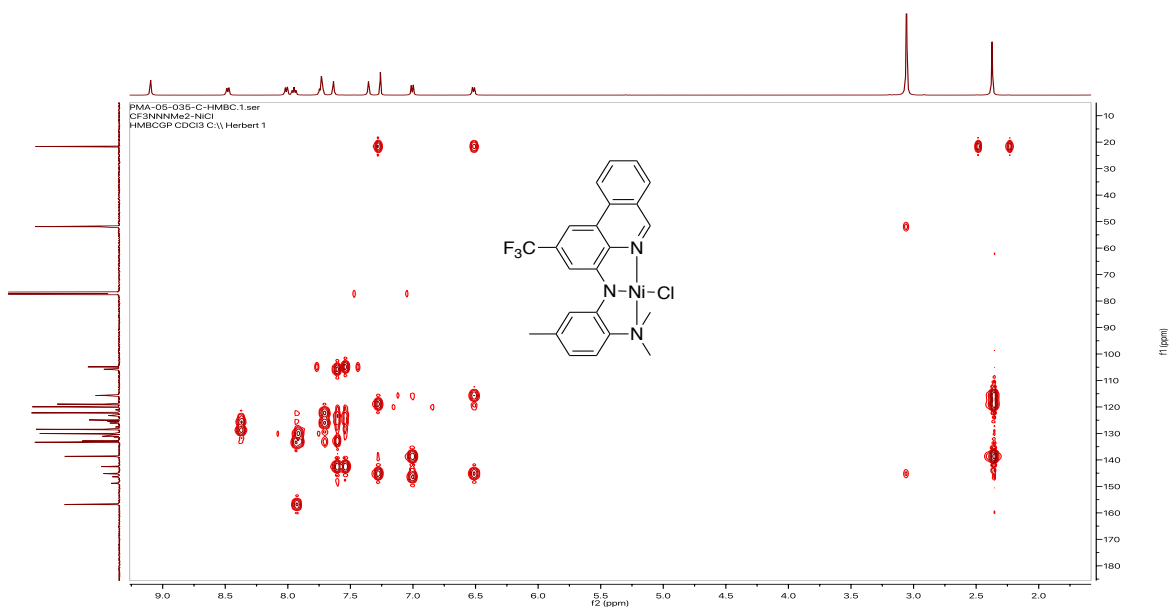


Figure S5.38. HMBC (500/125 MHz, CDCl₃, 22 °C) spectrum of **L16-NiCl**.

PMA-04048-D3H.1.fid
Column fraction
PROTON CDCl3 {C:\Bruker\TOPSPIN1.3} Herbert 22

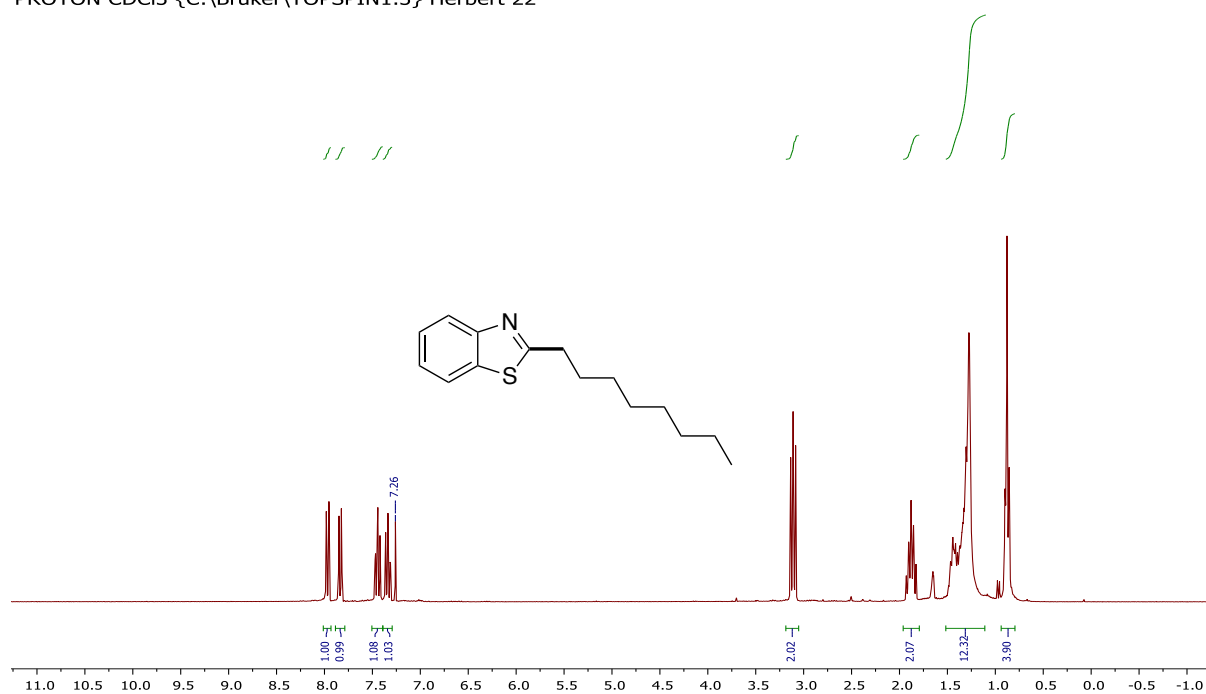


Figure S5.39. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of 2-octylbenzo[d]thiazole (P1).

PMA-04-064-ASH.1.fid
column fractions 4-8
PROTON CDCl3 C:\ Herbert 5

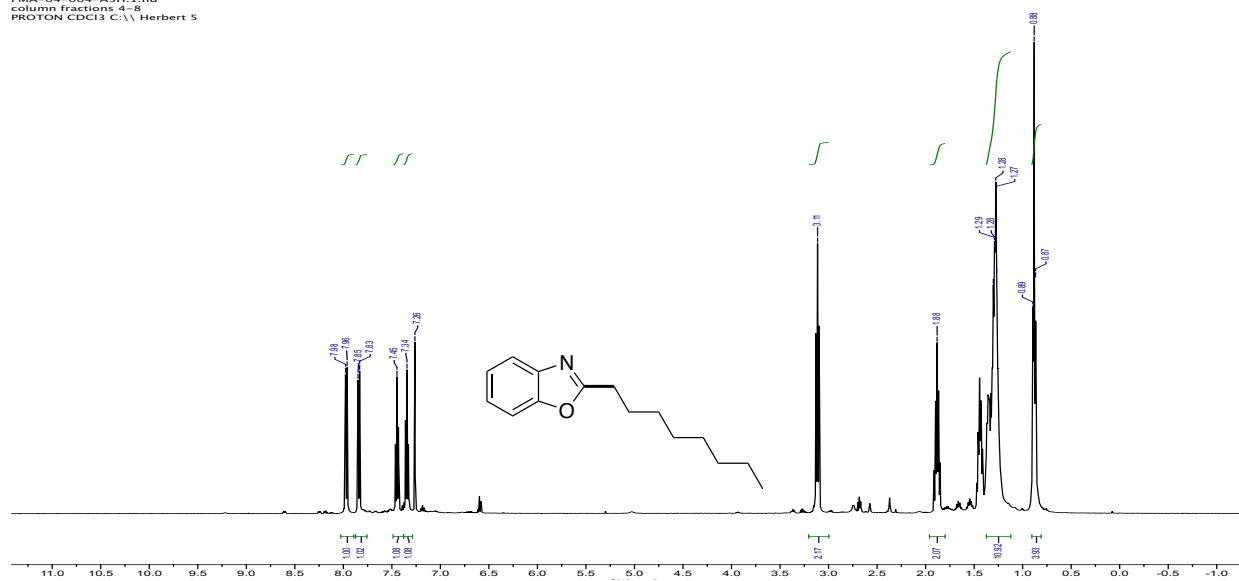


Figure S5.40. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of 2-octylbenzo[d]oxazole (P2).

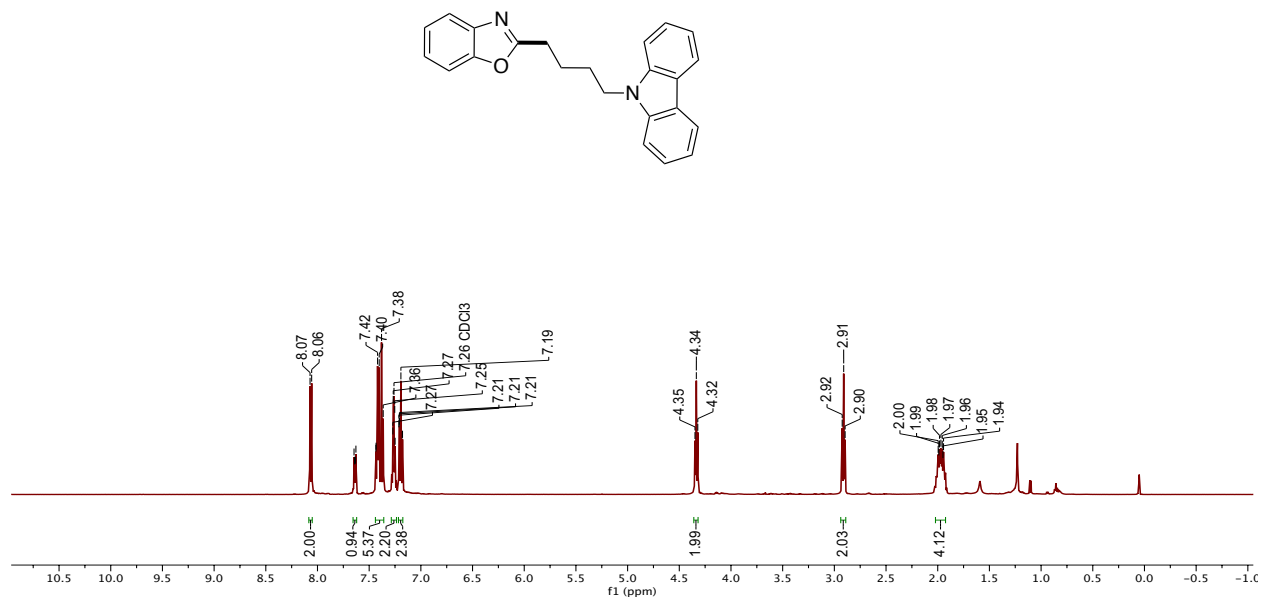


Figure S5.41. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of P3.

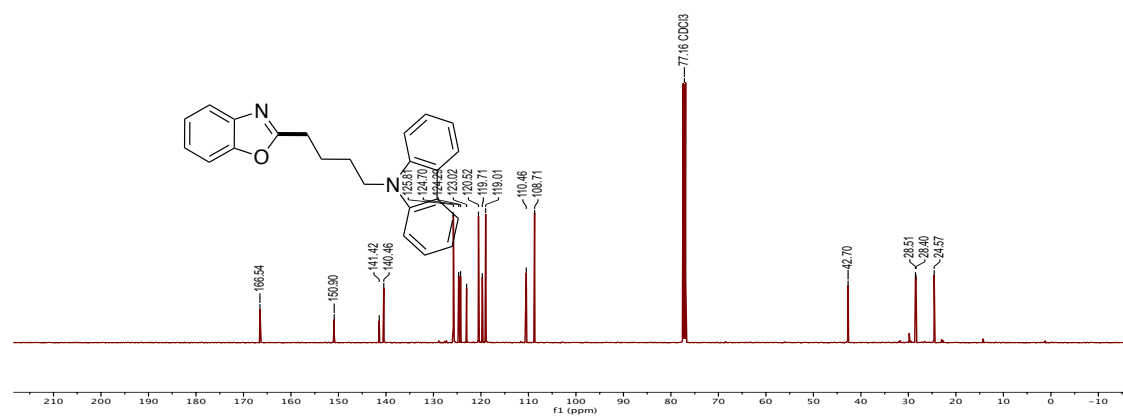


Figure S5.42. ¹³C {¹H} NMR (500 MHz, CDCl₃, 22 °C) spectrum of P3.

Generic Display Report (all)

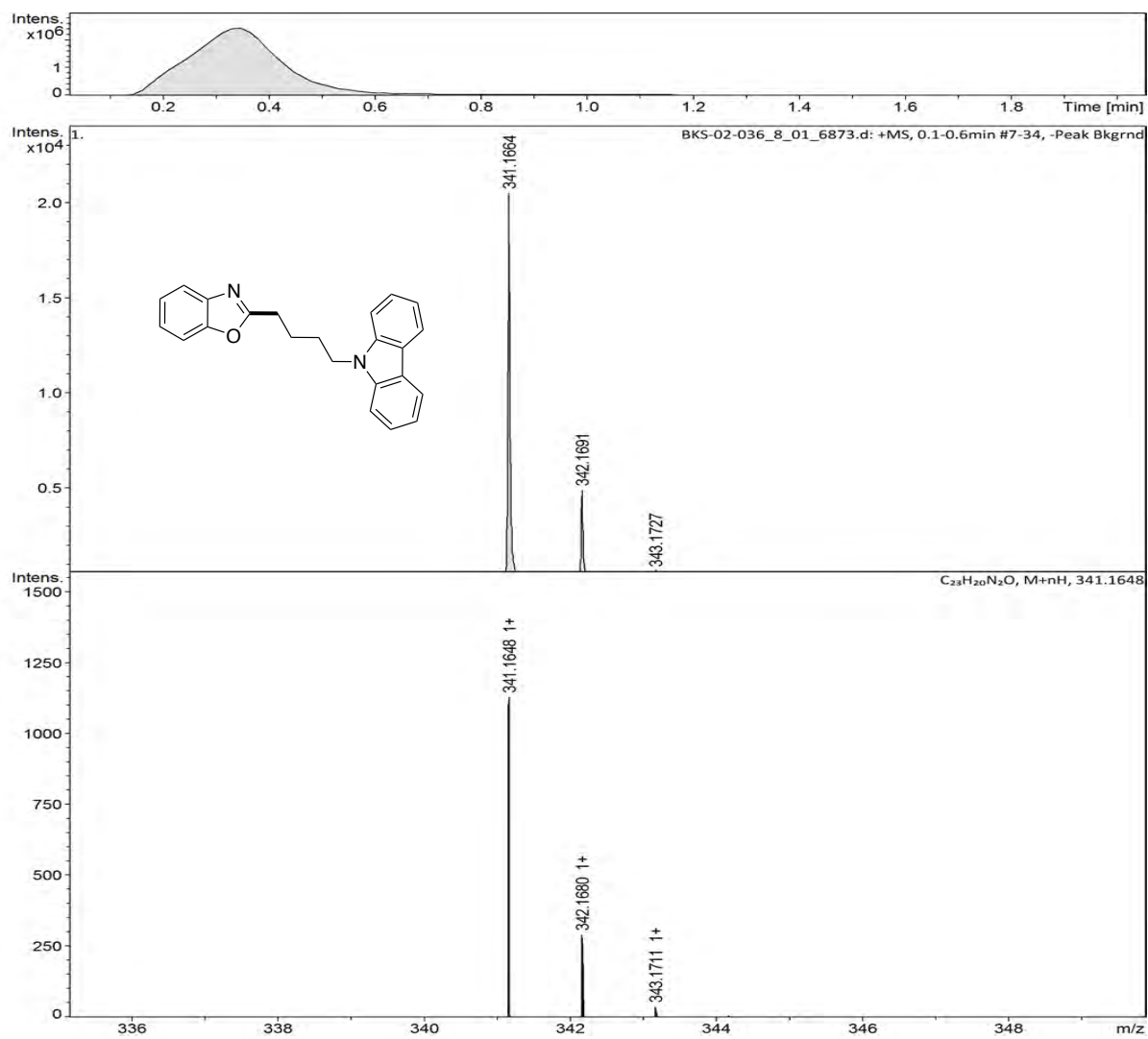


Figure S5.43. HR-MS spectrum of P3.

PMA-05-019A-A5H.1.fid
pure after vacuum
PROTON CDCl3 C:\Herbert 3

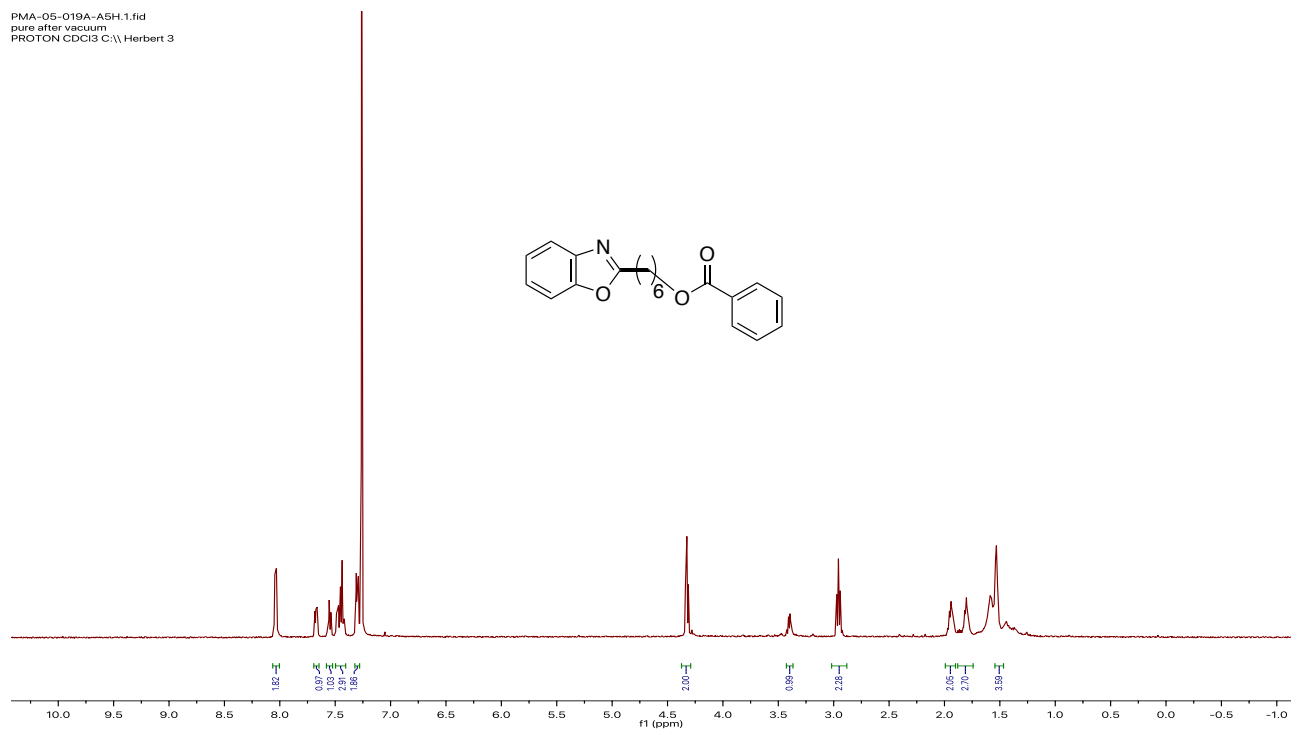


Figure S5.44. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of **P4**.

PMA-05-015A-13H.1.fid
after vacuum pure
PROTON CDCl3 C:\Bruker\TOPSPIN1.3\ Herbert 51

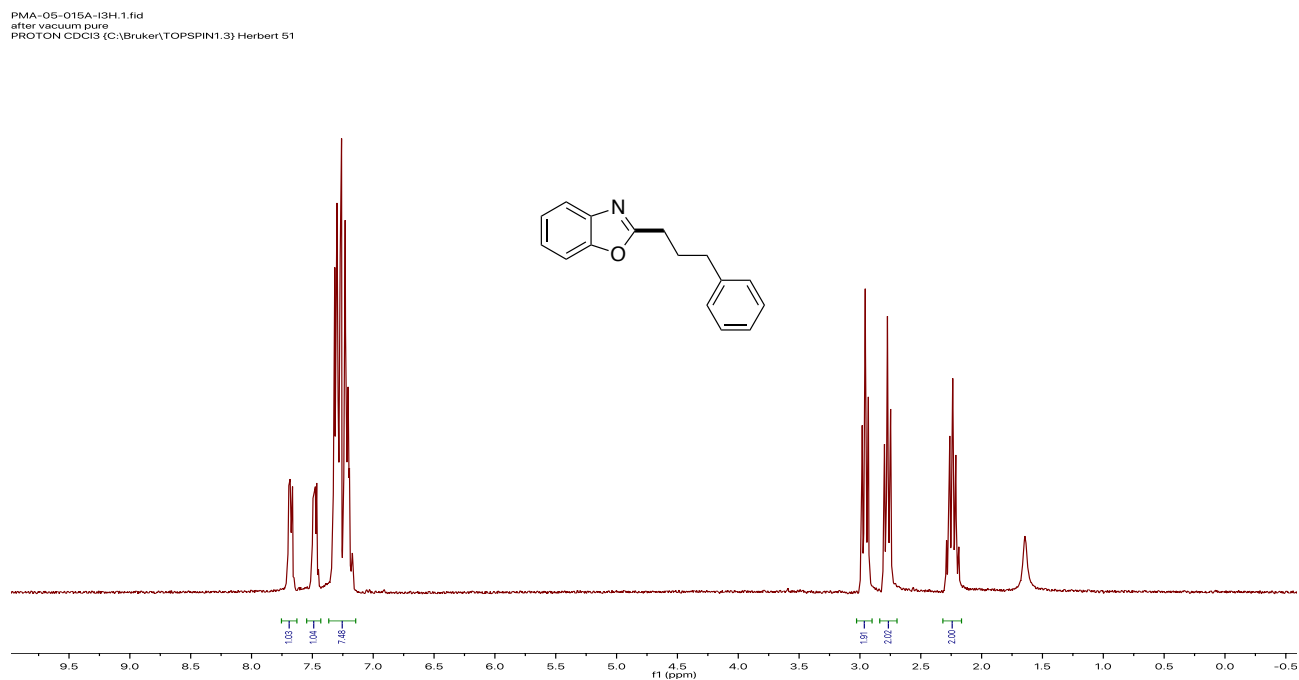


Figure S5.45. ^1H NMR (300 MHz, CDCl_3 , 22 °C) spectrum of **P5**.

PMA-05-018A-A5H.1.fid
pure after vacuum
PROTON CDCl3 C:\Herbert 1

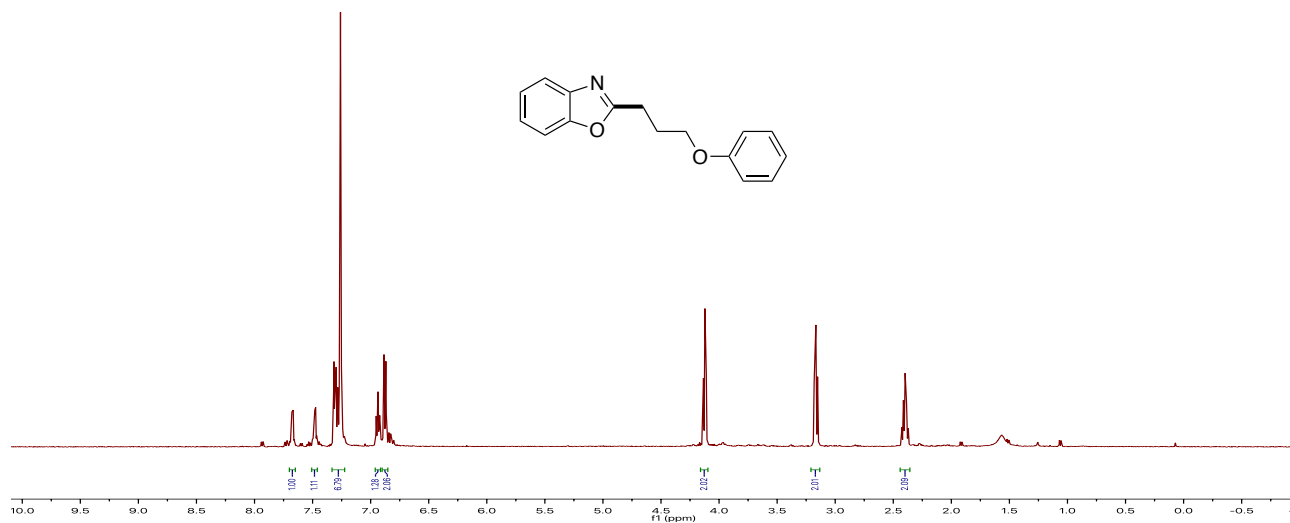


Figure S5.46. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of **P6**.

PMA-05-018B-A5H.1.fid
pure after vacuum
PROTON CDCl3 C:\Herbert 2

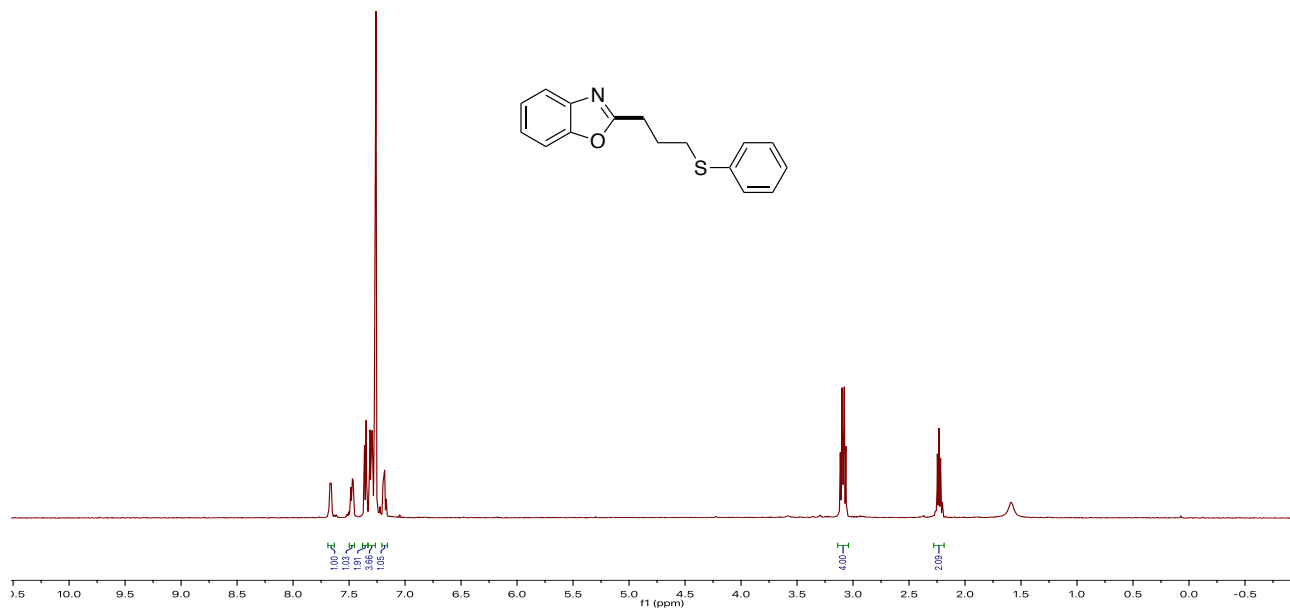


Figure S5.47. ¹H NMR (500 MHz, CDCl₃, 22 °C) spectrum of **P7**.

PMA-05-017A-G3H.1.fid
after vacuum pure
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 52

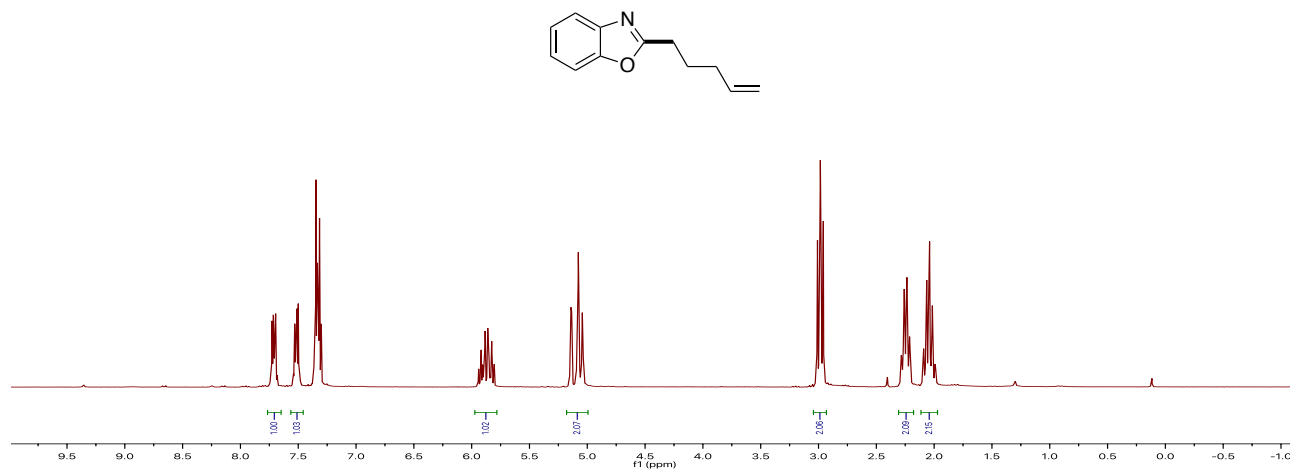


Figure S5.48. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of **P8**.

PMA-05-016A-F3H.1.fid
pure after vacuum
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 34

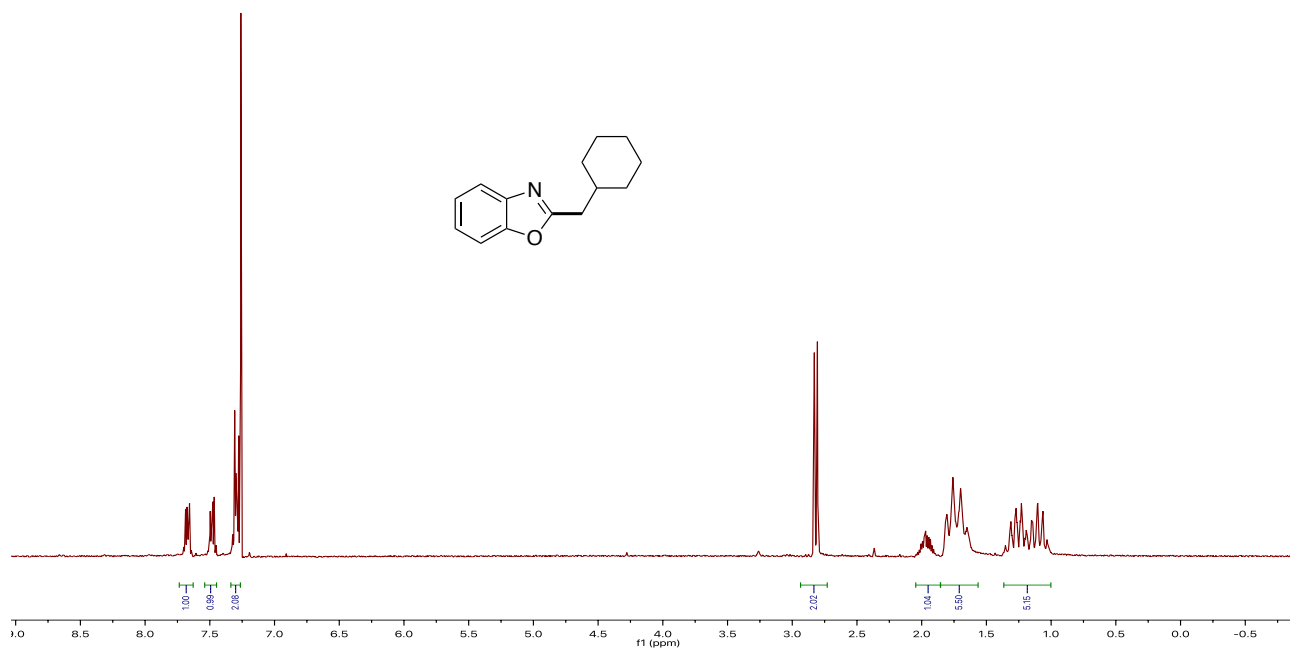


Figure S5.49. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of **P9**.

PMA-05-016B-E3H.1.fid
pure after vacuum
PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 35

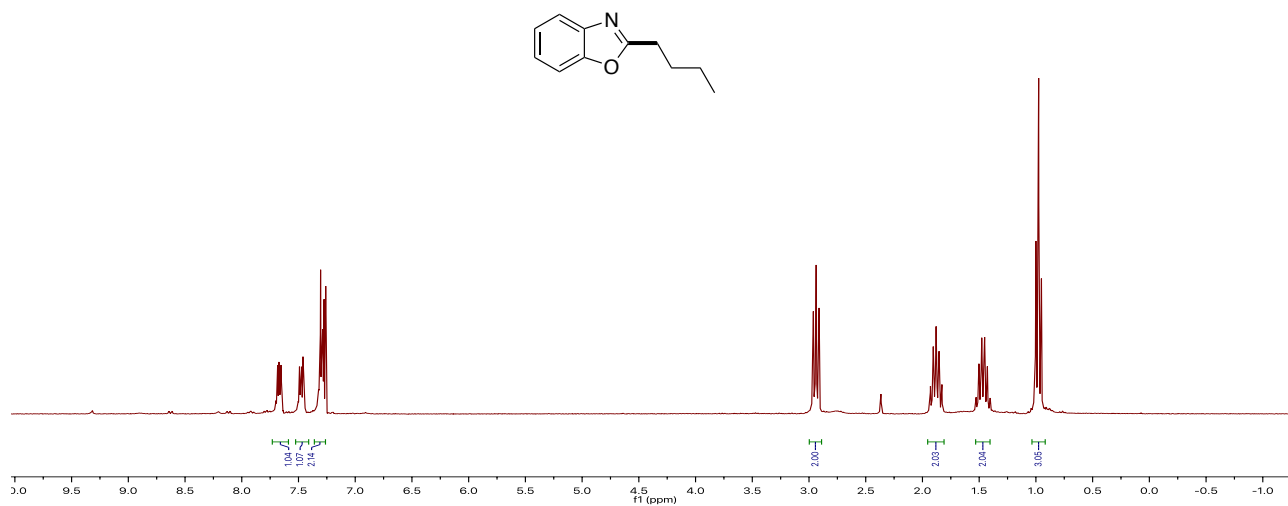


Figure S5.50. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of **P10**.

PMa05-042-B5H.1.fid
MeQuinNMe2-PdCl
PROTON CDCl3 C:\\ Herbert 2

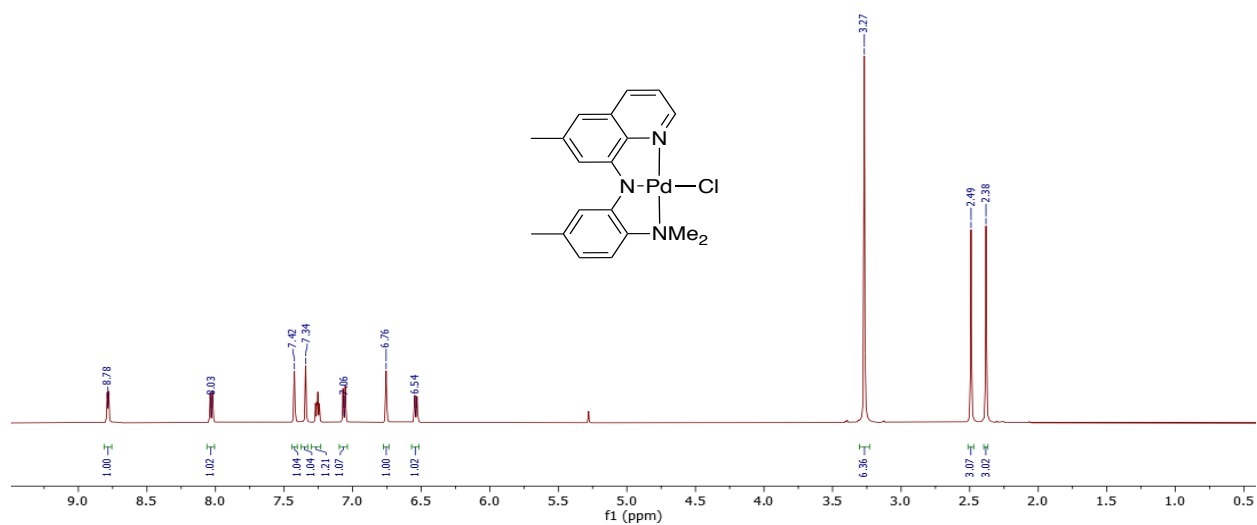


Figure S5.51. ¹H NMR (300 MHz, CDCl₃, 22 °C) spectrum of **L13-PdCl**.

PMa05-042-B5C.1.fid
MeQuinNMe2-PdCl
Cl3CPD CDCl3 C:\ Herbert 2

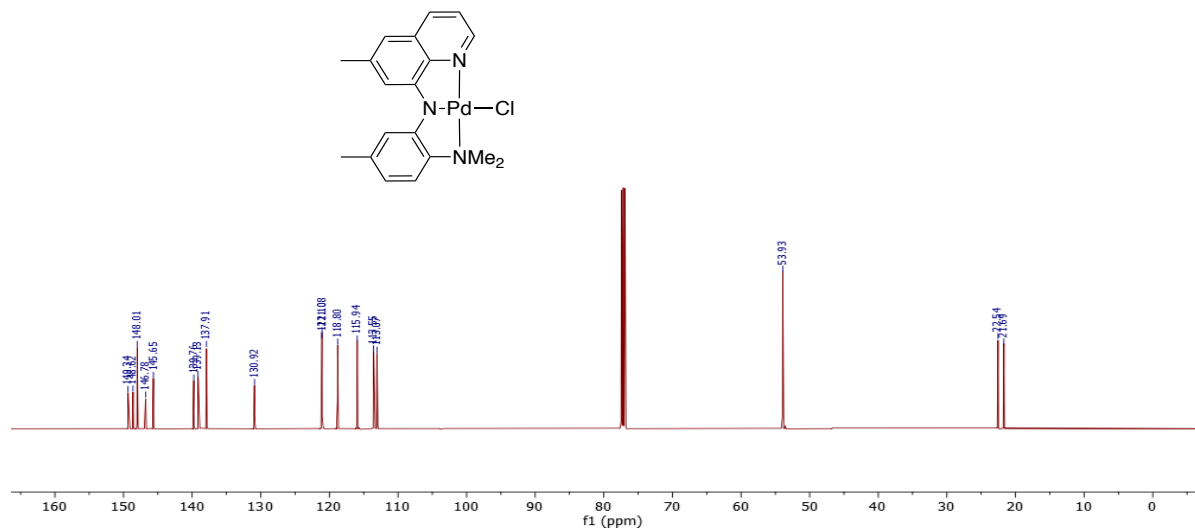


Figure S5.52. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L13-PdCl.

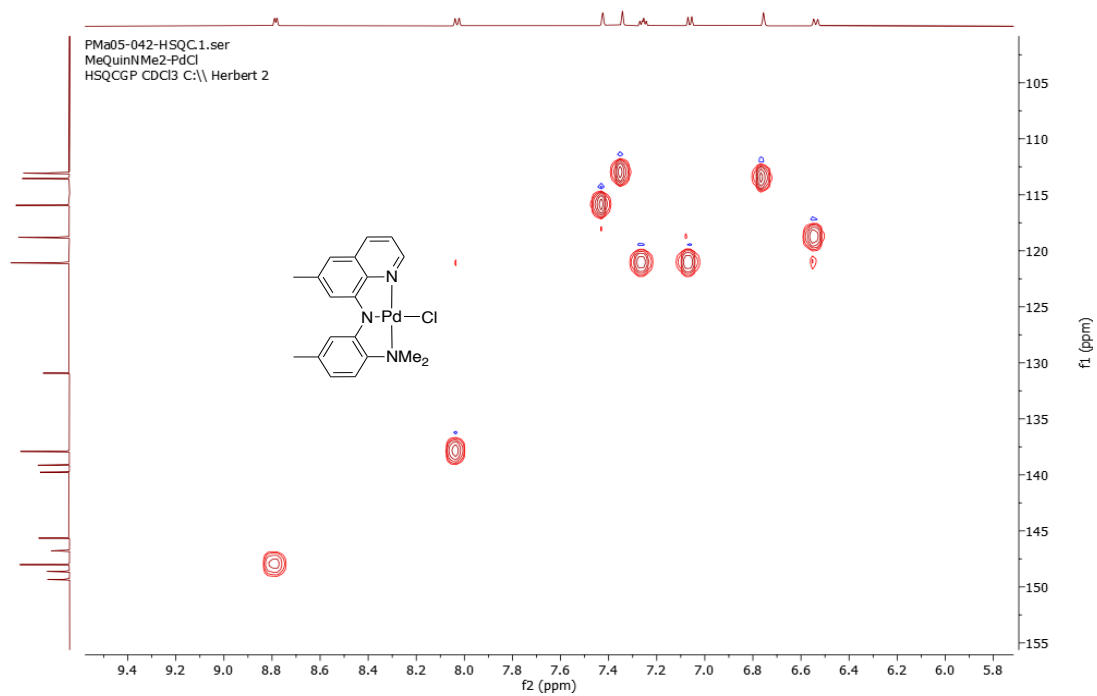
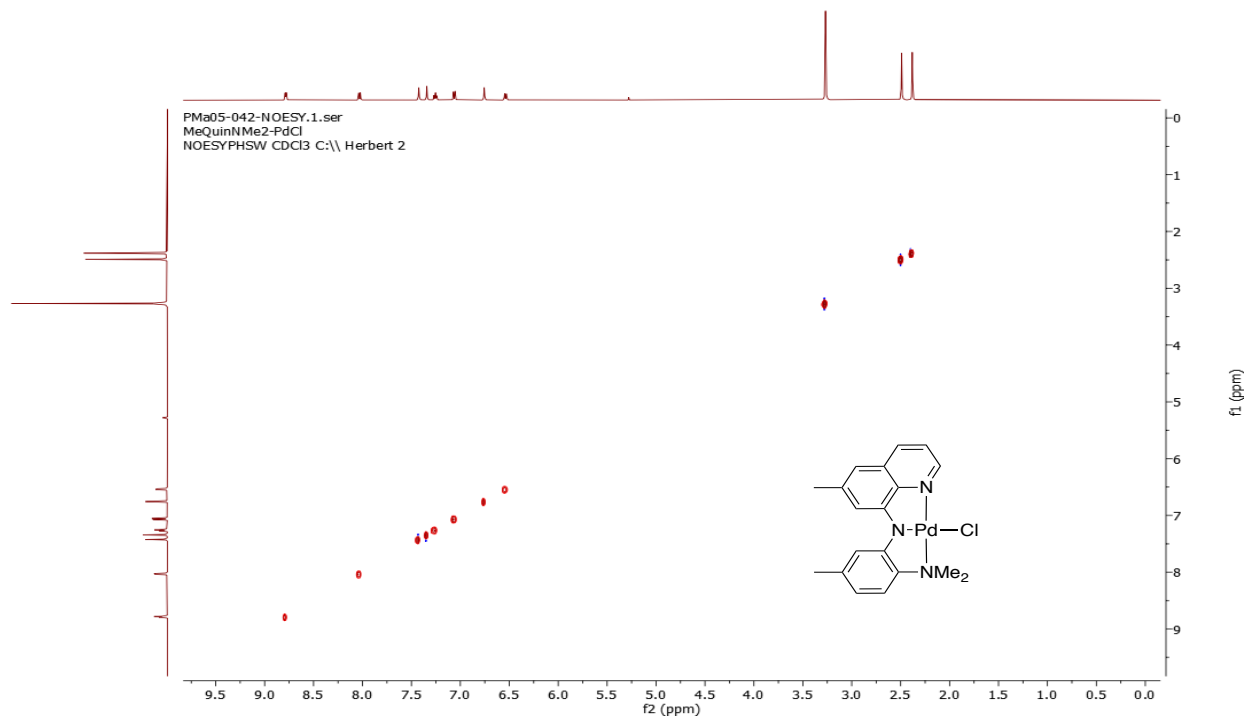
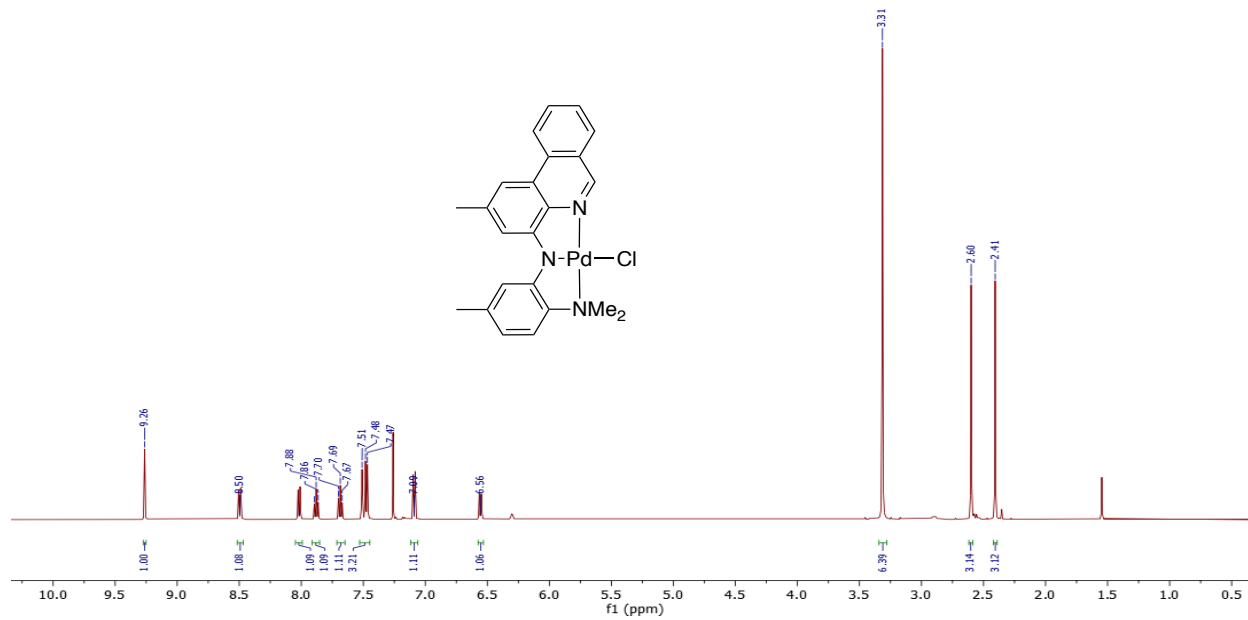


Figure S5.53. HSQC NMR (500/125 MHz, CDCl_3 , 22 °C) spectrum of L13-PdCl.



PMA-05-043-D5H.1.fid
MePhenNMe2-PdCl after cleaning
PROTON CDCl3 C:\ Herbert 1



PMA-05-043-D5C.1.fid
MePhenNMe2-PdCl after cleaning
Cl3CPD CDCl3 C:\ Herbert 1

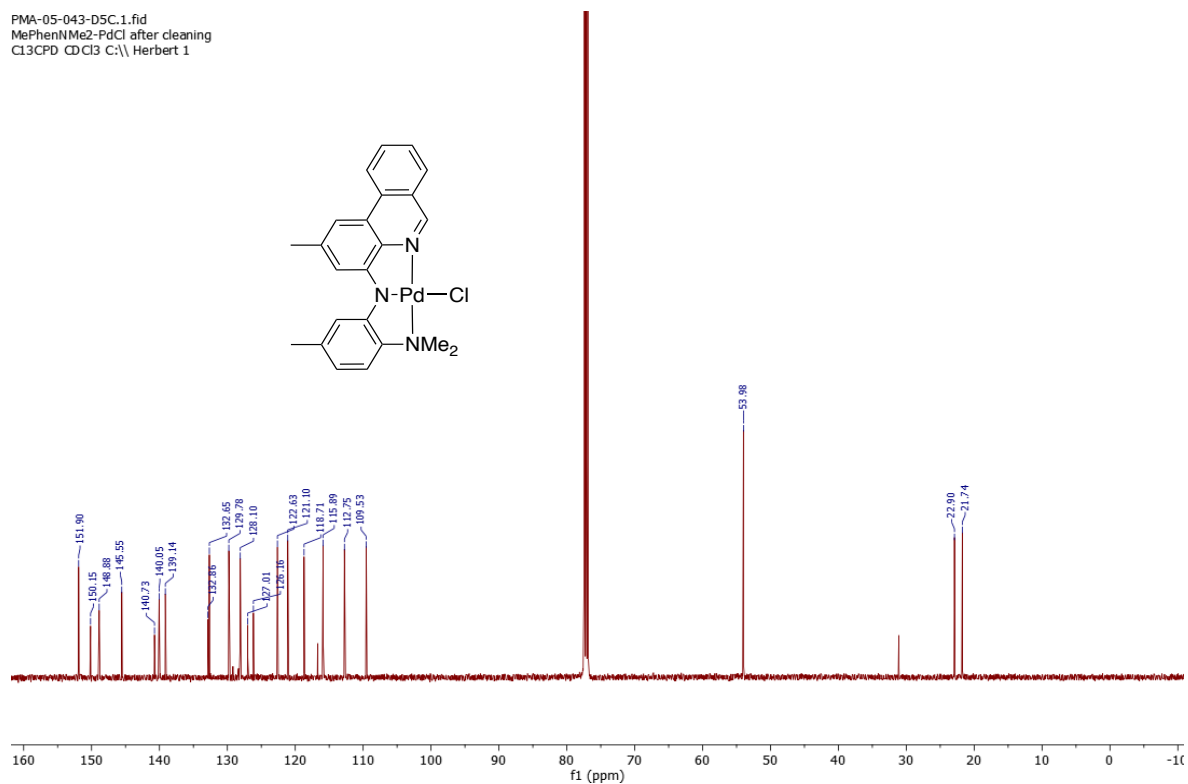


Figure S5.56. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L13-PdCl.

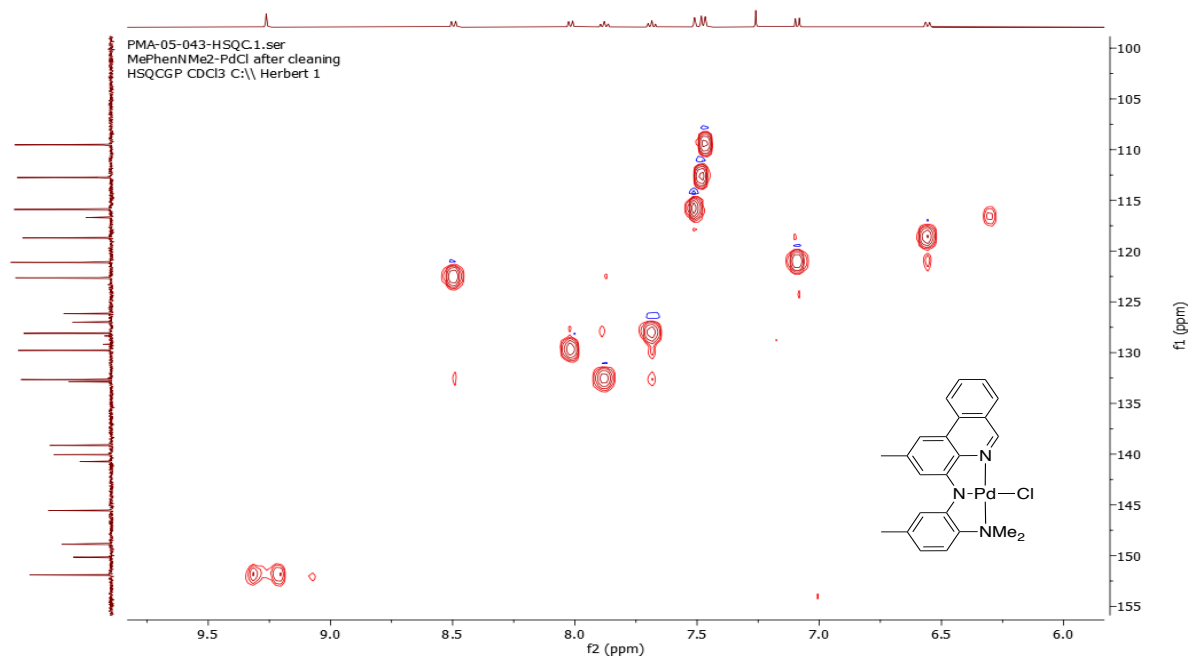


Figure S5.57. HSQC NMR (500/125 MHz, CDCl_3 , 22 °C) spectrum of L14-PdCl.

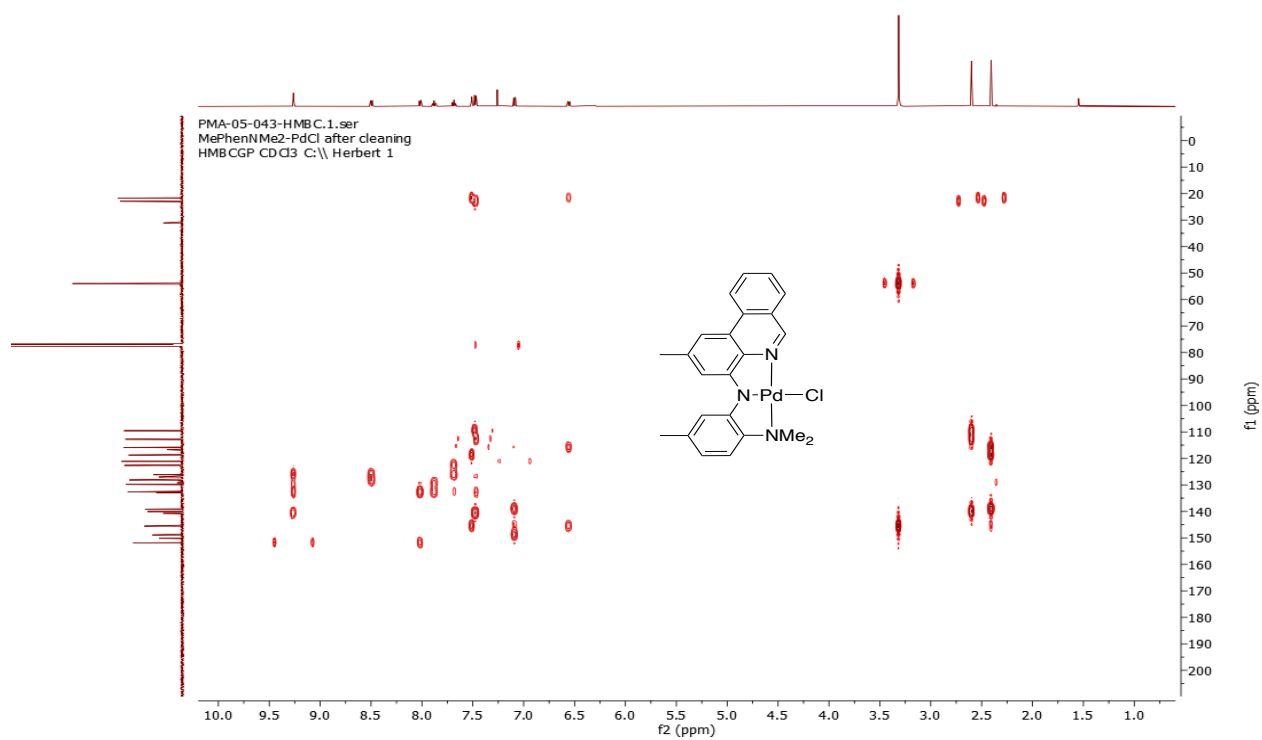


Figure S5.58. HMBC NMR (500/125 MHz, CDCl₃, 22 °C) spectrum of **L14-PdCl**.

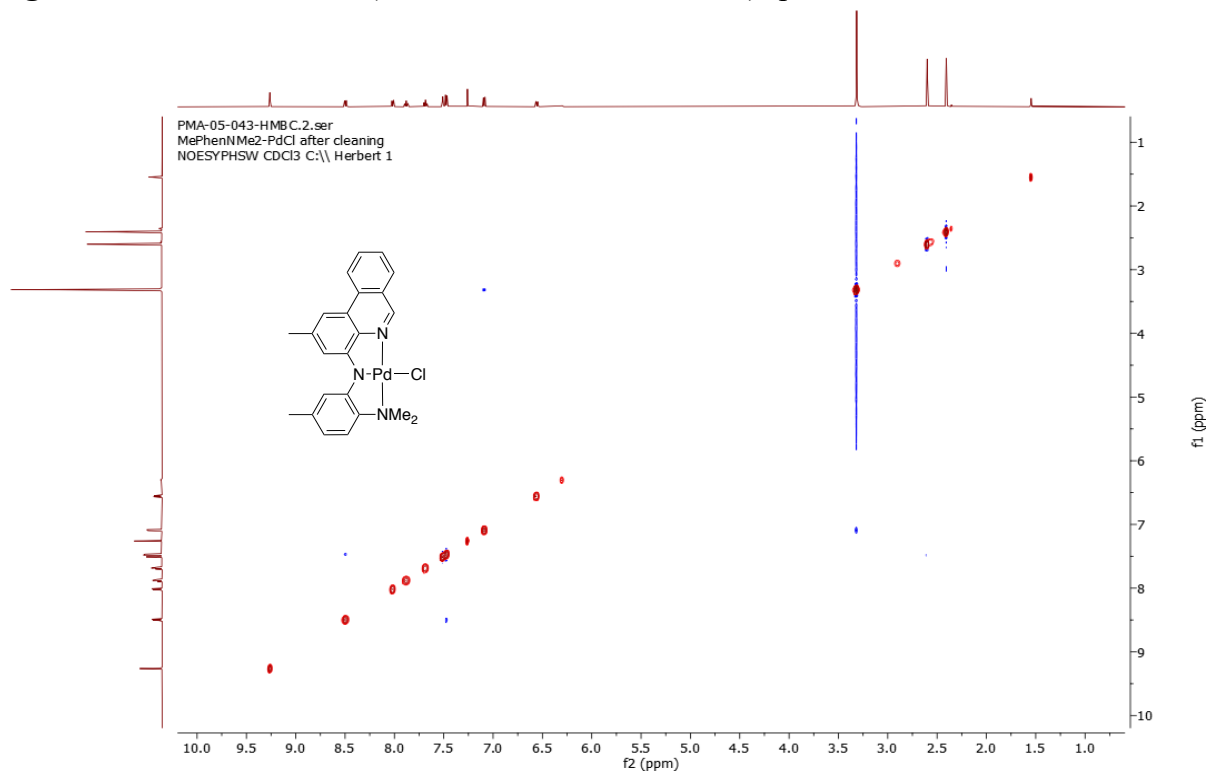


Figure S5.59. NOESY NMR (500 MHz, CDCl₃, 22 °C) spectrum of **L14-PdCl**.

PMA-05-047-B5H.1.fid
CF3,MeNMe2-PdCl
PROTON CDCl3 C:\ Herbert 1

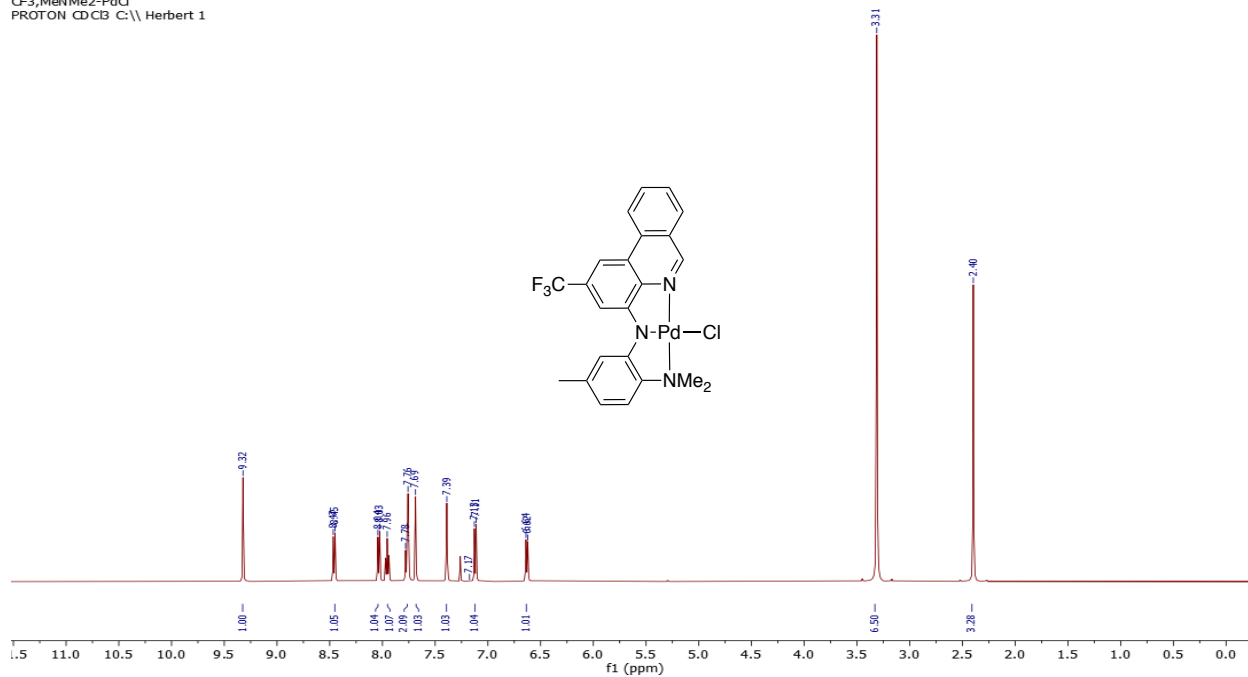


Figure S5.60. ^1H NMR (500 MHz, CDCl_3 , 22 °C) spectrum of L16-PdCl.

PMA-05-047-B5C.1.fid
CF3,MeNMe2-PdCl
Cl3CPD32 CDCl3 C:\ Herbert 1

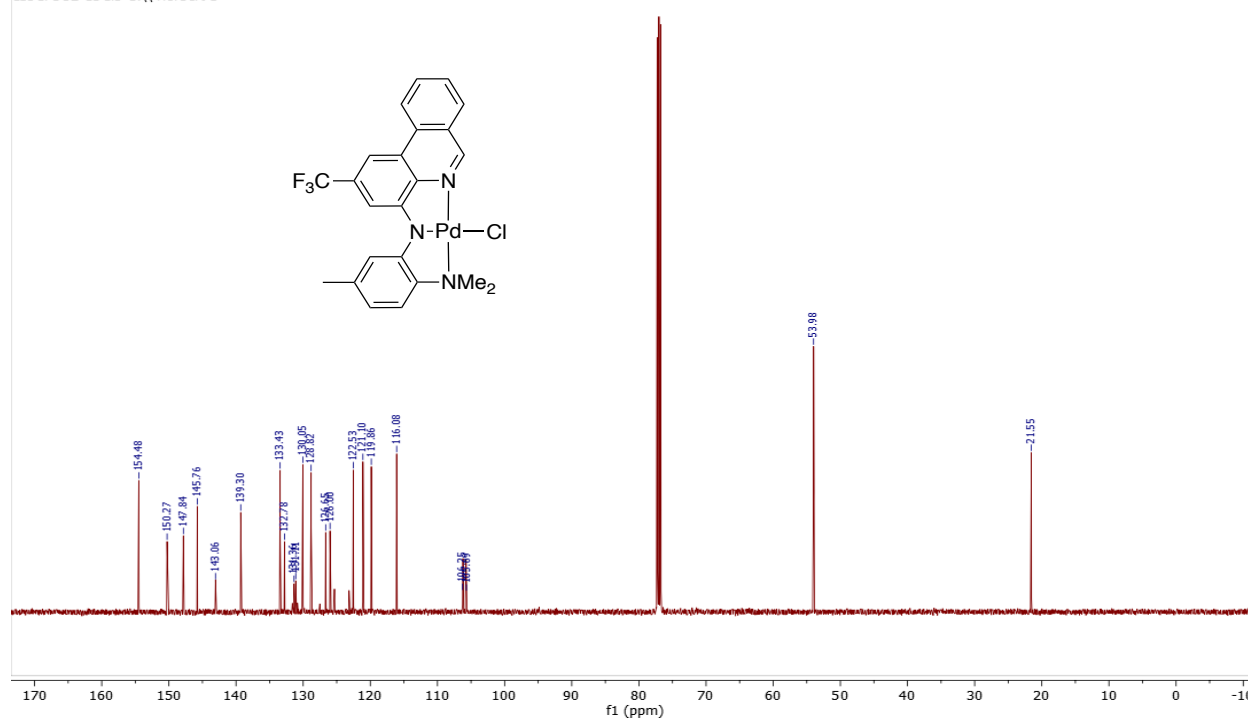


Figure S5.61. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 22 °C) spectrum of L13-PdCl.