Electronic Supporting Information

for

One-pot synthesis of dimerized arenes and heteroarenes under mild condition using Co(I) as active catalyst

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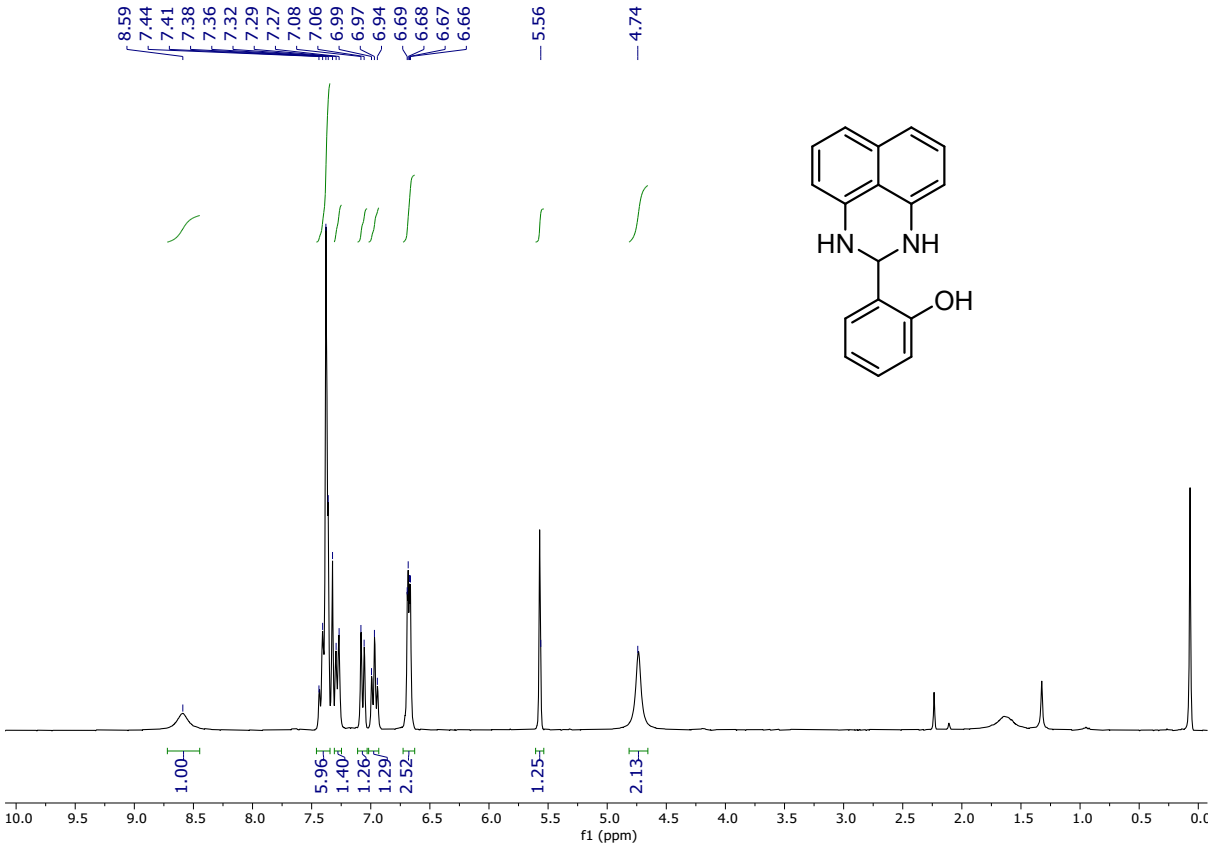


Fig S1: ^{1}H NMR spectra of ligand **L1** in $CDCl_3$.

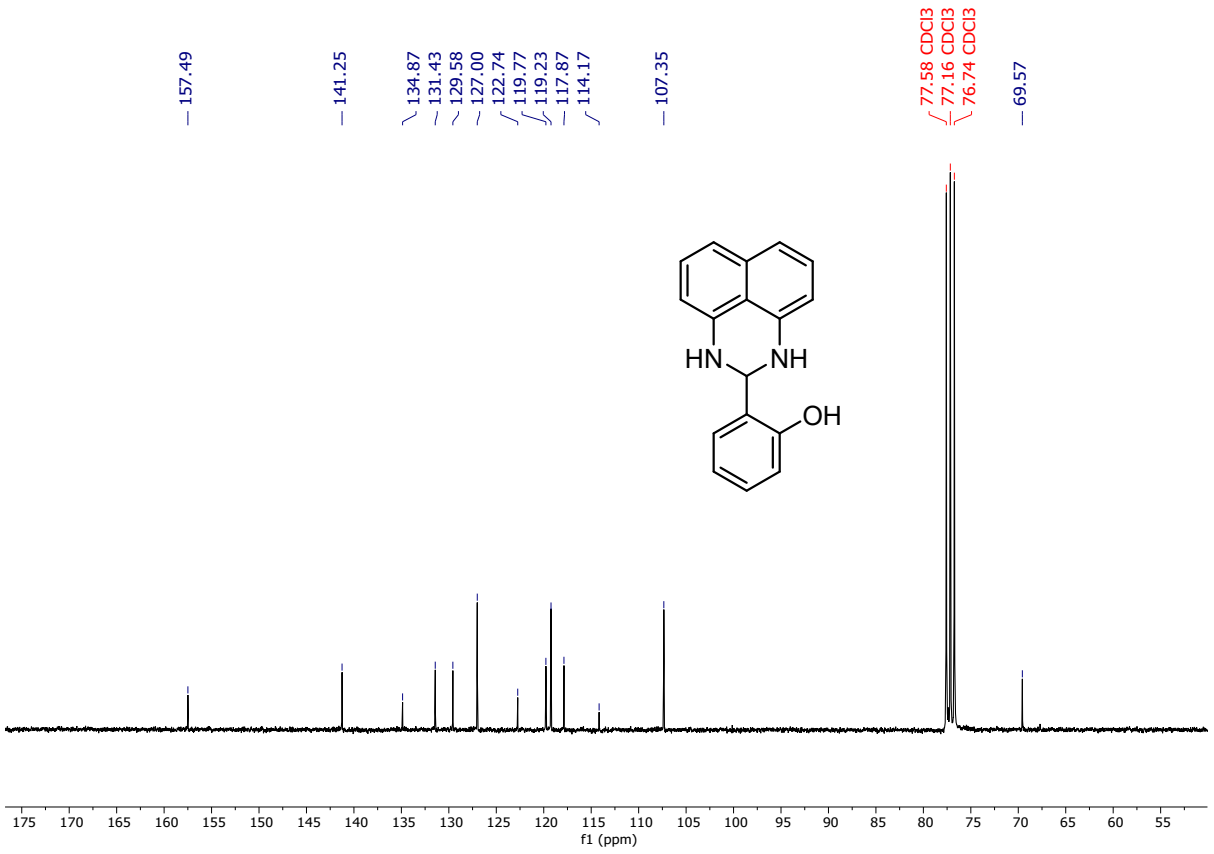


Fig S2: ^{13}C NMR spectra of ligand **L1** in $CDCl_3$.

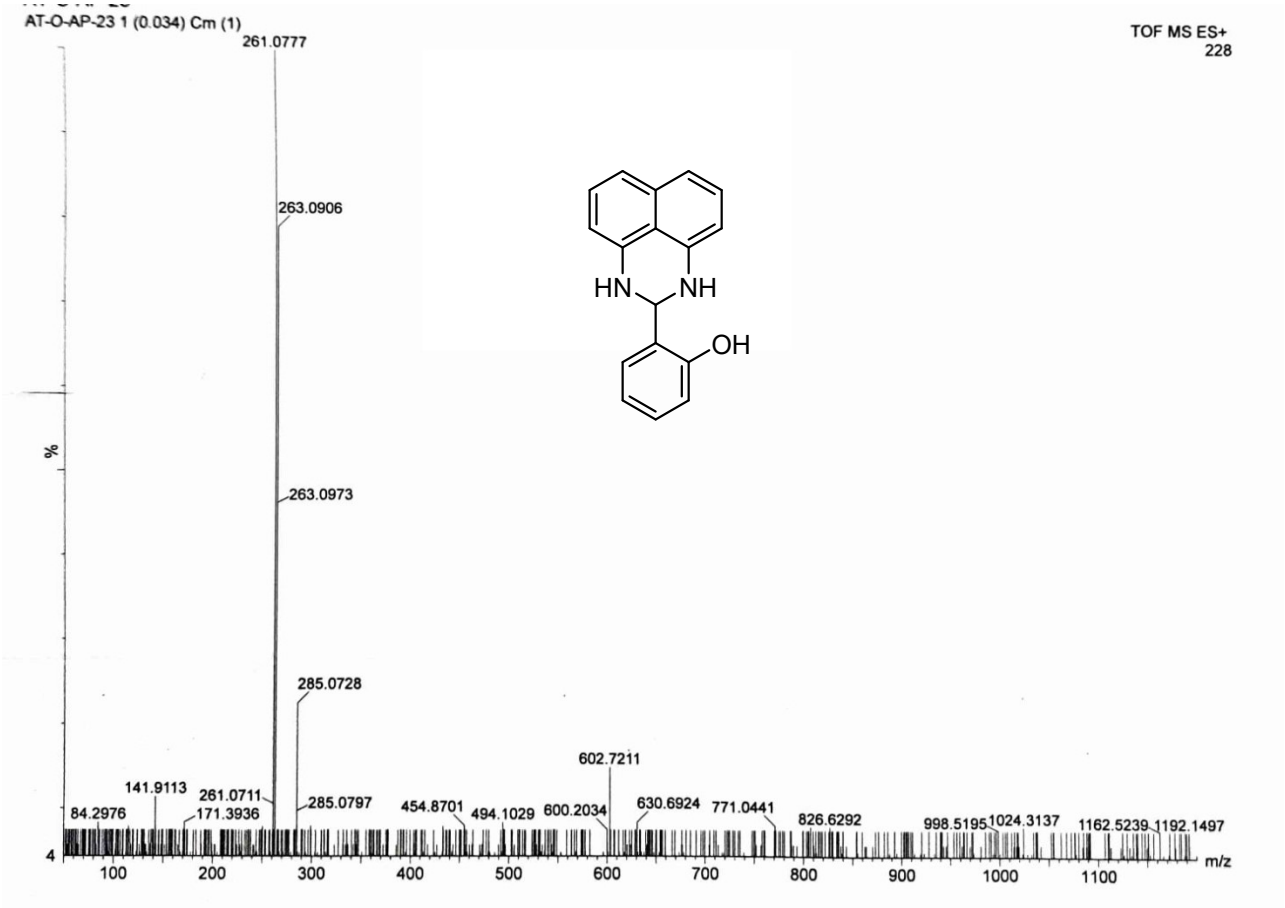


Fig S3: HRMS of ligand **L1**.

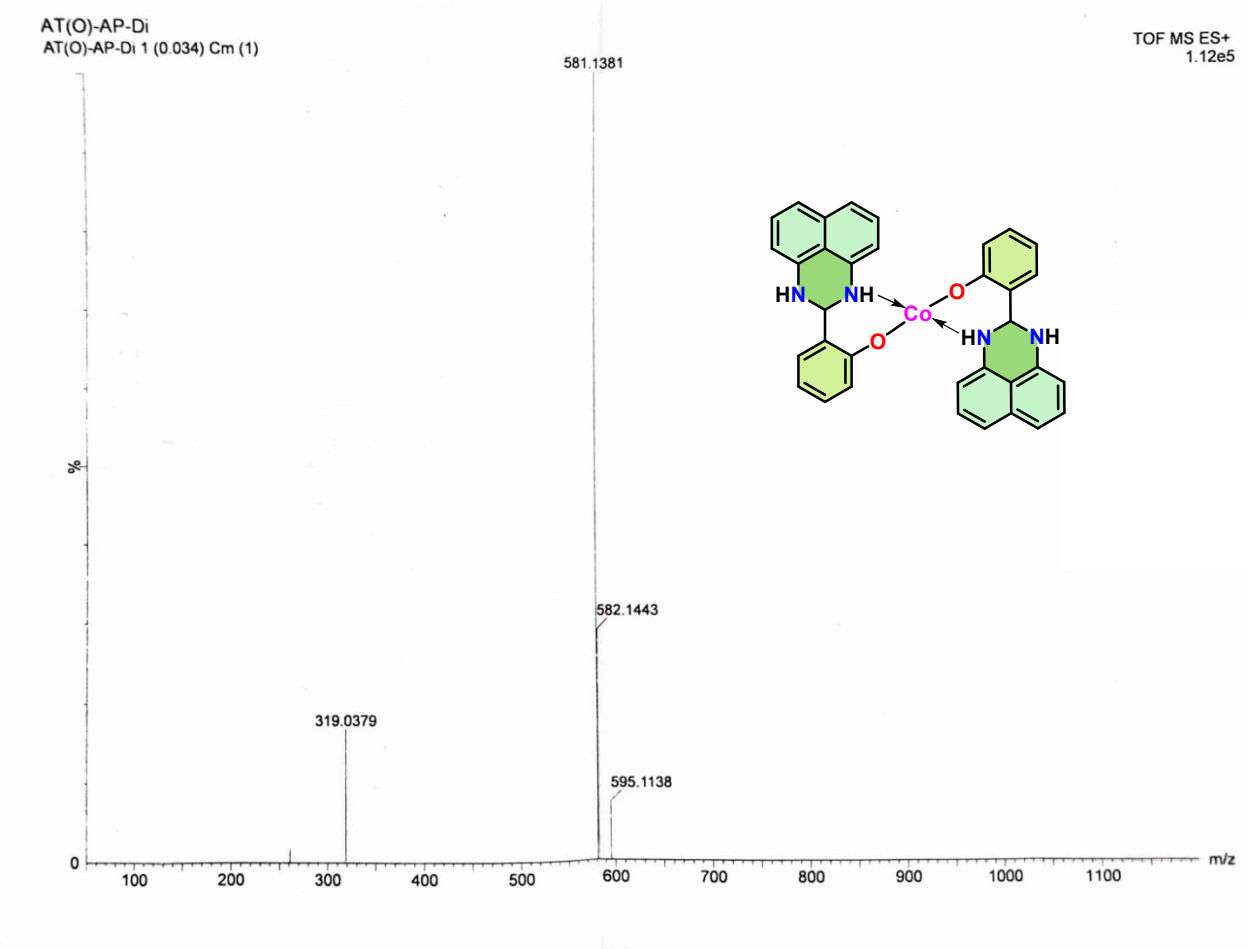


Fig S4: HRMS of complex **1**.

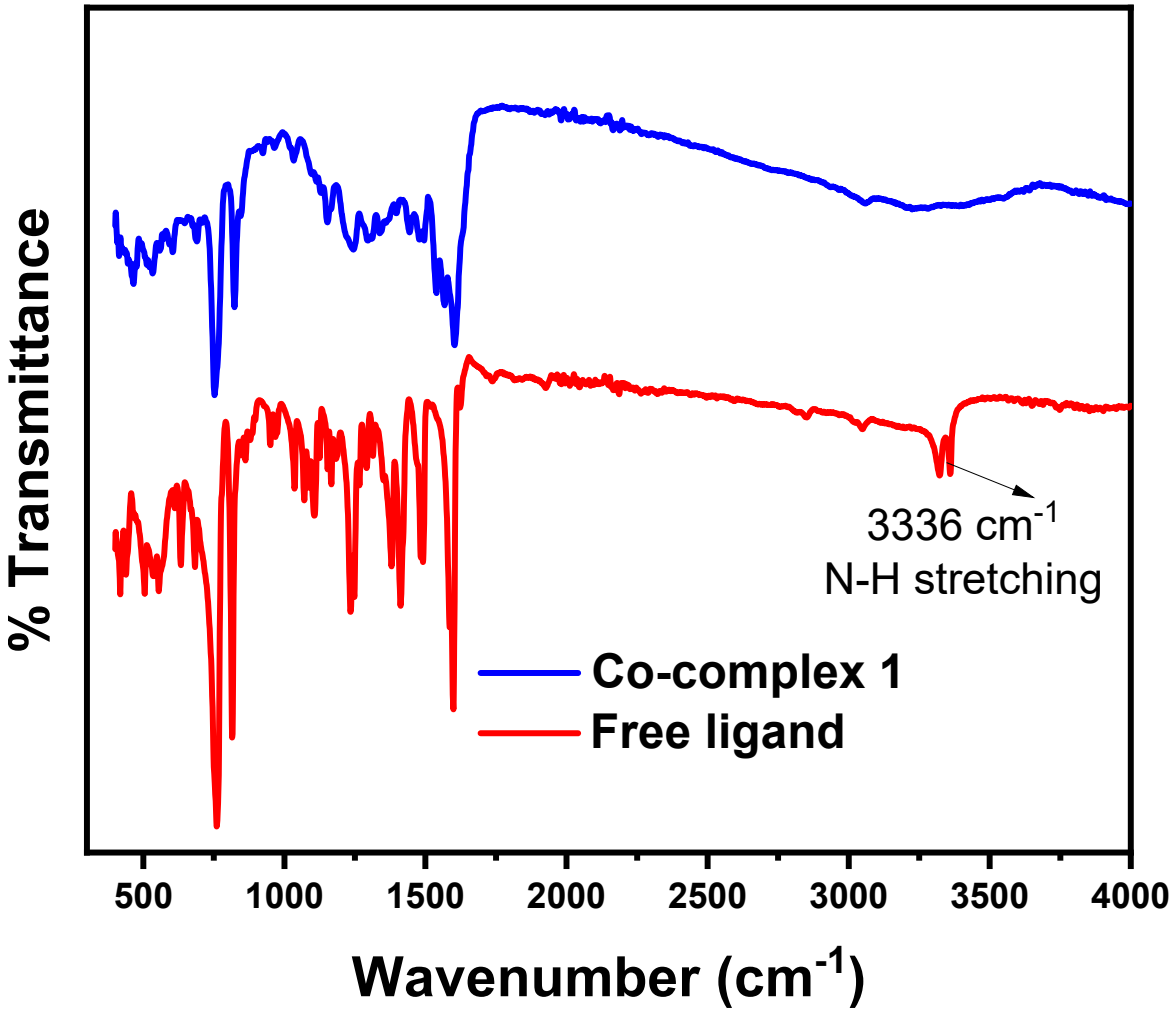


Fig S5: IR spectra of free ligand **L1** and Co-complex **1** in solid state at 22 ˚C.

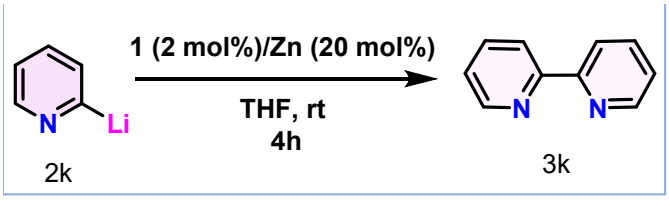
Lithiation of compounds

All reactions have been performed under N_2 atmosphere through Schlenk line using *n*-BuLi as the lithiating agent. Reactions, where -78 ˚C is required, have been done using acetone/liq N_2 mixture.

1. 1,1'-biphenyl (**3a**): Compound **3a** has been prepared from iodobenzene in THF, according to literature reported procedure.[1]
2. [1,1'-biphenyl]-2,2'-diol (**3b**): Compound **3b** has been prepared from 2-bromophenol in diethyl ether, according to literature reported procedure.[2]
3. 4,4'-dimethyl-1,1'-biphenyl (**3c**): Compound **3c** has been prepared from lithiation of 4-bromotoluene, according to literature reported procedure.[3]
4. 3,3'-dimethoxy-1,1'-biphenyl (**3d**): Compound **3d** have been prepared from 3-bromoanisole by slight modification of literature reported procedure.[4] One equivalent of *n*-BuLi (0.213 ml, 2.5 M in hexane) was added to THF solution 3-bromoanisole (100 mg, 0.534 mmol) at -78 ˚C and stirred at the same temperature for 30 min, during which time colourless precipitate could be observed.
5. 4,4'-dimethoxy-1,1'-biphenyl (**3e**): Compound **3e** have been prepared from 4-bromoanisole by slight modification of literature reported procedure.[5] One equivalent of *n*-BuLi (0.213 ml, 2.5 M in hexane) was added to THF solution 4-bromoanisole (100 mg, 0.534 mmol) at room temperature and stirred at the same temperature for 2 h, during which time colourless precipitate could be observed.
6. 6,6'-difluoro-[1,1'-biphenyl]-3,3'-diol (**3f**): The same procedure as for **3b** was followed.
7. 3,3',5,5'-tetramethoxy-1,1'-biphenyl (**3g**): Compound **3g** has been prepared from lithiation of 3,5-dimethoxy-1-bromobenzene, according to literature reported procedure.[6]
8. 1,1'-bipyrene (**3h**): Compound **3h** has been prepared from 2-bromopyrene in THF, according to literature reported procedure.[7]
9. 2,2'-dimethyl-1,1'-binaphthalene (**3i**): Compound **3i** has been prepared from lithiation of 1-bromo-2-methyl-naphthalene, according to literature reported procedure.[8]
10. 2,2',6,6'-tetramethyl-1,1'-biphenyl (**3j**): Compound **3j** has been prepared from lithiation of 1,3-dimethyl-2-bromobenzene, according to literature reported procedure.[9]
11. 2,2'-bipyridine (**3k**): Compound **3k** has been prepared from lithiation of 2-bromopyridine, according to literature reported procedure.[10]

12. 1,1'-dimethyl-1*H*,1'*H*-2,2'-bibenzo[d]imidazole (**3l**): Compound **3l** has been prepared from lithiation of 1-methylbenzimidazole, by slight modification of literature reported procedure.[11] n-BuLi (1 equivalent, 0.6 ml, 2.5 M in hexane) was added dropwise to a solution of 1-methylbenzimidazole in THF at -78 ˚C and the mixture was stirred for 2 h at -78 ˚C, after which, the temperature of the reaction mixture was allowed to rise to room temperature within another 1 h.
13. 2,2'-bibenzo[d]thiazole (**3m**): Compound **3m** has been prepared from lithiation of benzothiazole, according to literature reported procedure.[12]
14. 1,1'-dimethyl-1*H*,1'*H*-2,2'-biindole (**3n**): Compound **3n** has been prepared from lithiation of 1-methylindole, according to literature reported procedure.[13]
15. 5,5'-dimethyl-2,2'-bithiophene (**3o**): Compound **3o** has been prepared from lithiation of 2-methylthiophene, according to literature reported procedure.[14]
16. Biferrocene (**3p**): Compound **3p** has been prepared from lithiation of ferrocene, according to literature reported procedure.[15]
17. 1,1'-dimethyl-1*H*,1'*H*-2,2'-biimidazole (**3q**): Compound **3q** has been prepared from lithiation of 1-methylimidazole, according to literature reported procedure.[16]
18. 5-bromo-4,5'-bipyrimidine (**3r**): Compound **3r** has been prepared from 5-bromopyrimidine in THF, according to literature reported procedure.[17]
19. 5,5'-dibromo-2,2'-bipyridine (**3s**): Compound **3s** has been prepared from 3-bromopyridine in diethyl ether, according to procedure reported in patent.[18]
20. 3-bromo-1,1':3',1''-terphenyl (**3t**) and 3,3'''-dibromo-1,1':3',1'':3'',1'''-quaterphenyl (**3u**): Compounds **3t** and **3u** have been prepared by the lithiation of 1,3-dibromobenzene according to literature reported procedure.[19]
21. 1,1':3',1'':3'',1'''-quaterphenyl (**3v**): Compound **3v** has been prepared from lithiation of 1-iodo-3-bromobenzene, according to literature reported procedure.[20]

Table S1. Optimization of reaction conditions for the dimerization of heteroarenes.



Entry	Catalyst (mol %)[a]	Zn source (equiv)	Temperature (˚C)	Time (h)	% Yield[b]
1	Catalyst **1** (2)	Zn dust (1)	rt	2	55
2	Catalyst **1** (2)	Zn dust (1)	rt	3	68
3	Catalyst **1** (2)	Zn dust (1)	rt	4	75
4	-	Zn dust (1)	rt	4	NR
5	Catalyst **1** (2)	-	rt	4	NR
6	Catalyst **1** (2)	Zn dust (1)	45	4	75
7	Catalyst **1** (2)	Zn dust (1)	60	4	75
8	Catalyst **1** (2)	Zn dust (20 mol%)	rt	2	55
9	Catalyst **1** (2)	Zn dust (20 mol%)	rt	3	68
10	Catalyst **1** (2)	Zn dust (20 mol%)	rt	4	75

[a]Reaction conditions: **2k** (1 mmol), Zn dust, cobalt catalyst, solvent THF (5 ml). [b]Isolated yield after column chromatography.

Table S2. Table for known and unknown compounds

Known Compounds	Unknown compounds
3a-3t	**3u, 3v**

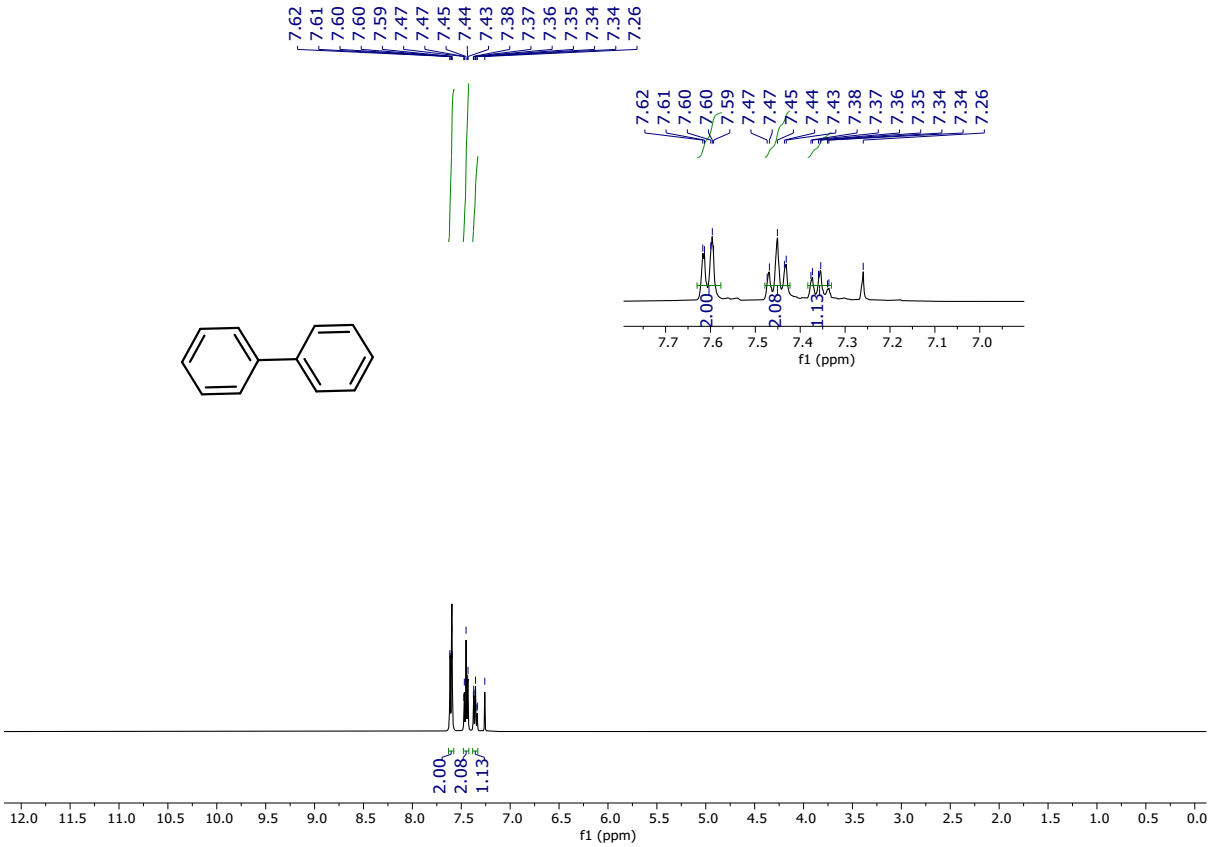


Fig S6: ^{1}H NMR spectra of compound **3a** in $CDCl_3$.

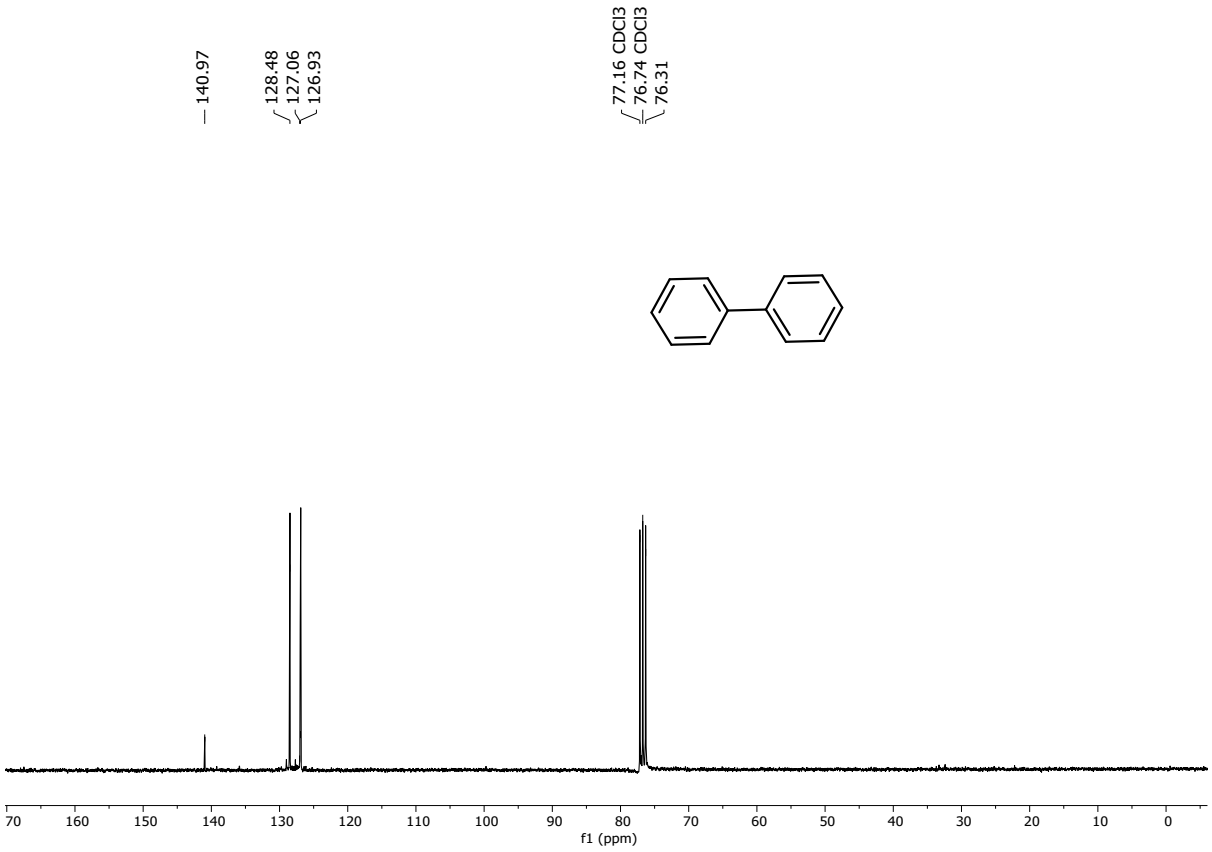


Fig S7: ^{13}C NMR spectra of compound **3a** in $CDCl_3$.

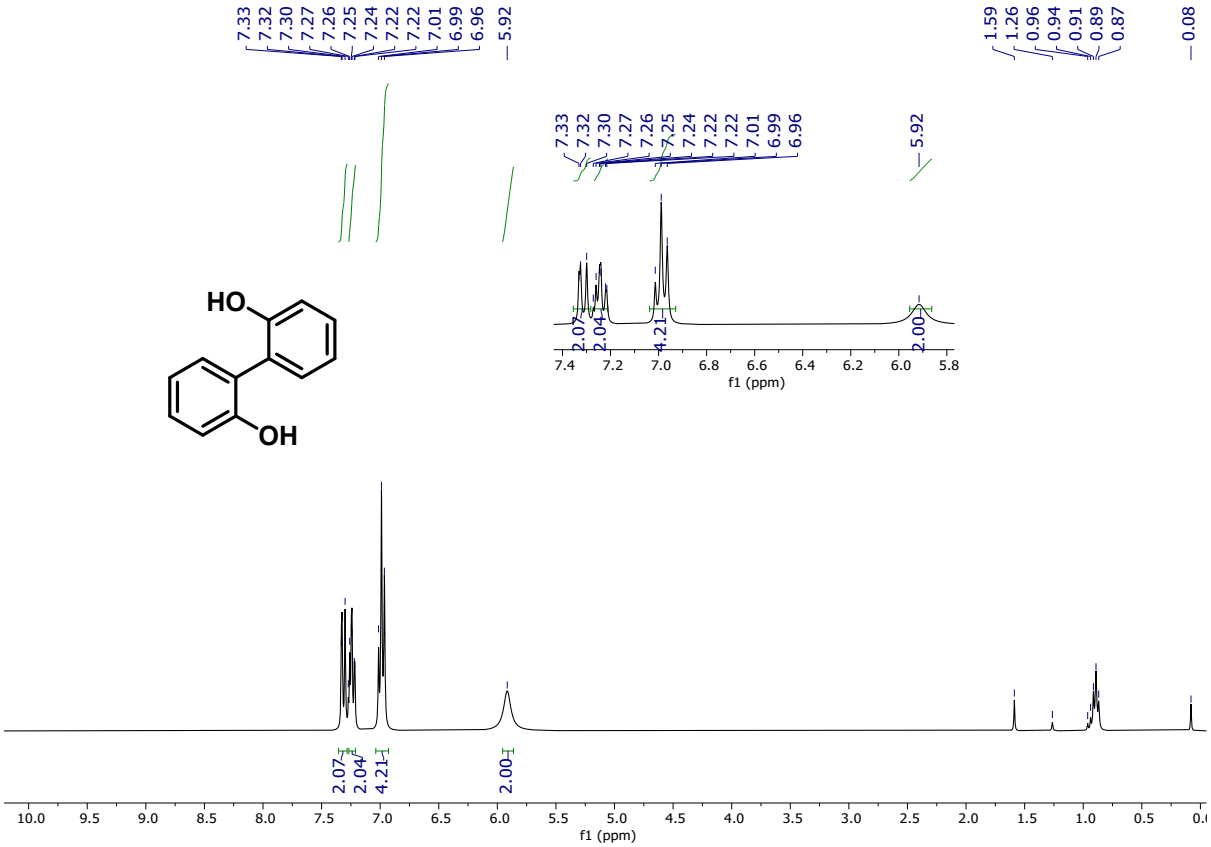


Fig S8: ^{1}H NMR spectra of compound **3b** in $CDCl_3$.

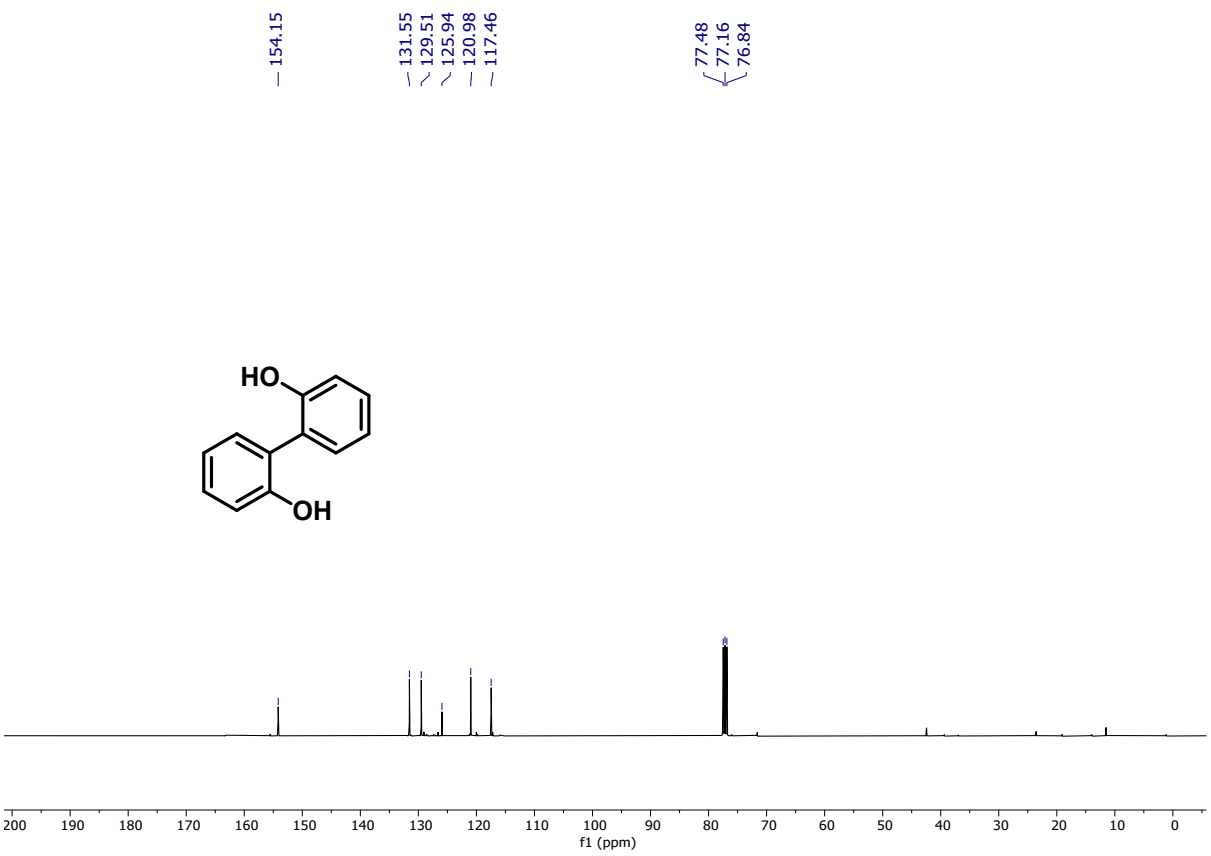


Fig S9: ^{13}C NMR spectra of compound **3b** in $CDCl_3$.

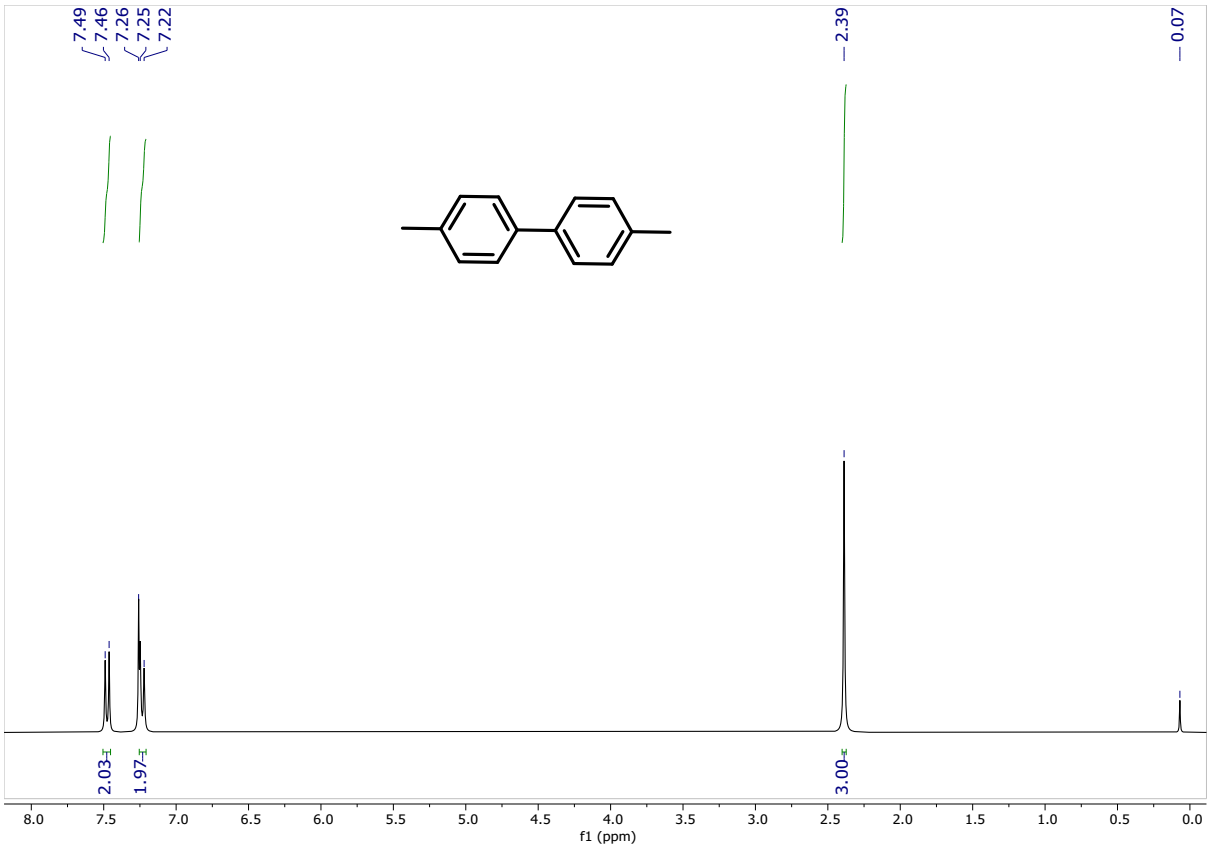


Fig S10: ^{1}H NMR spectra of compound **3c** in $CDCl_3$.

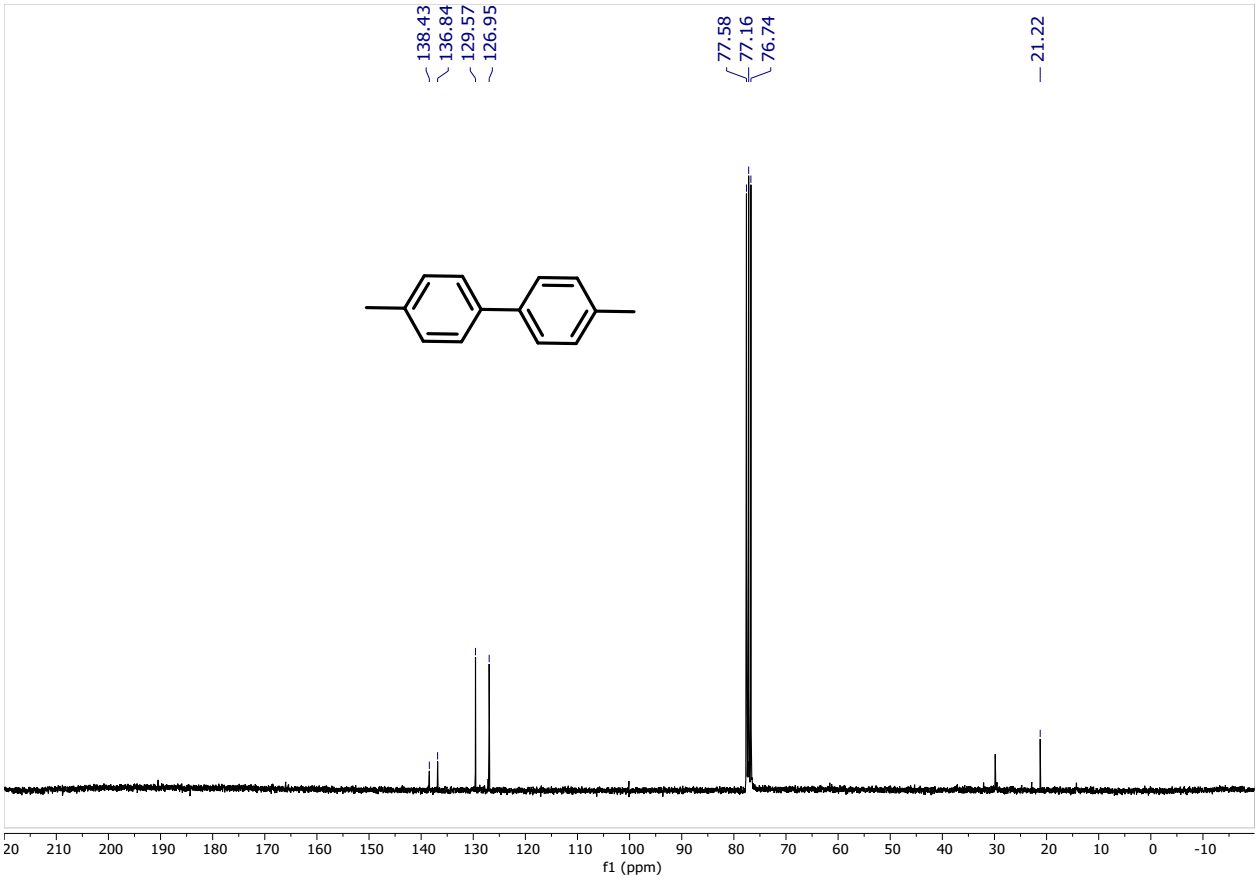


Fig S11: ^{13}C NMR spectra of compound **3c** in $CDCl_3$.

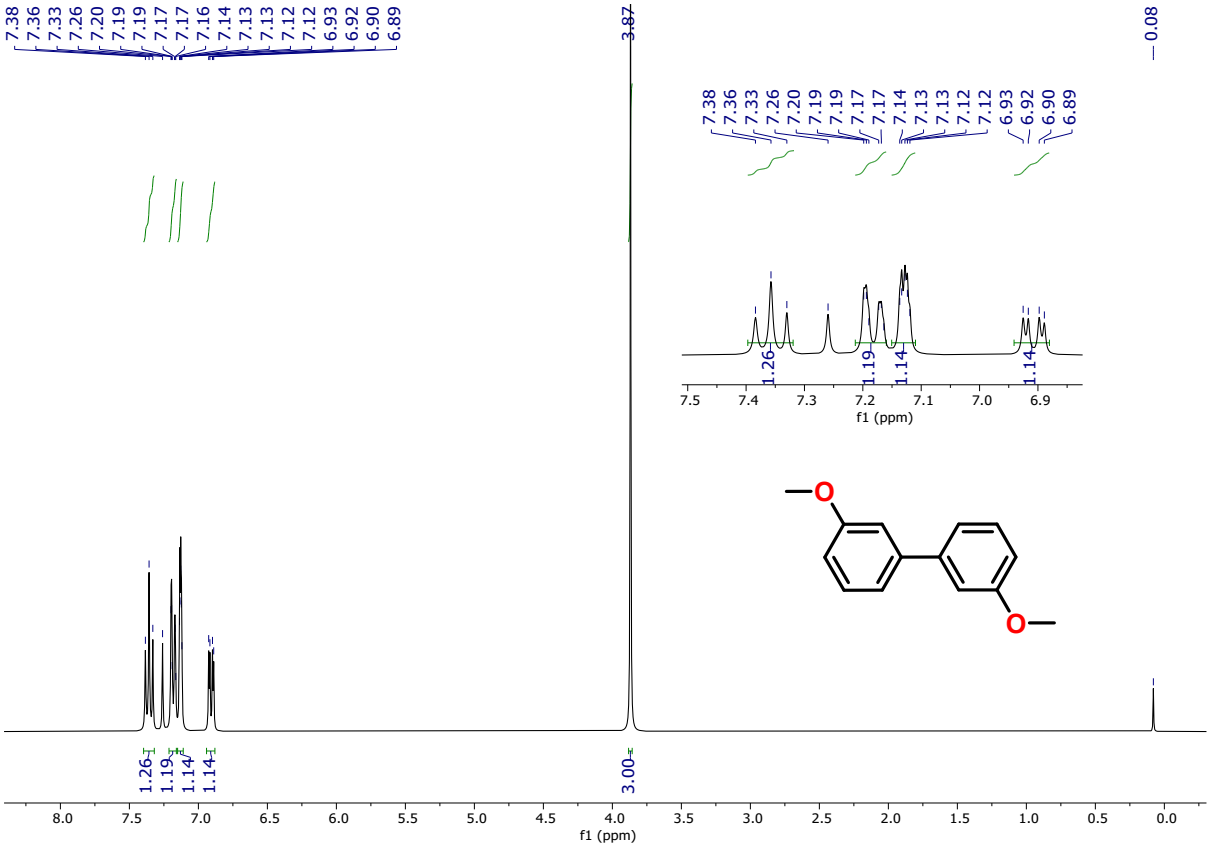


Fig S12: ^{1}H NMR spectra of compound **3d** in $CDCl_3$.

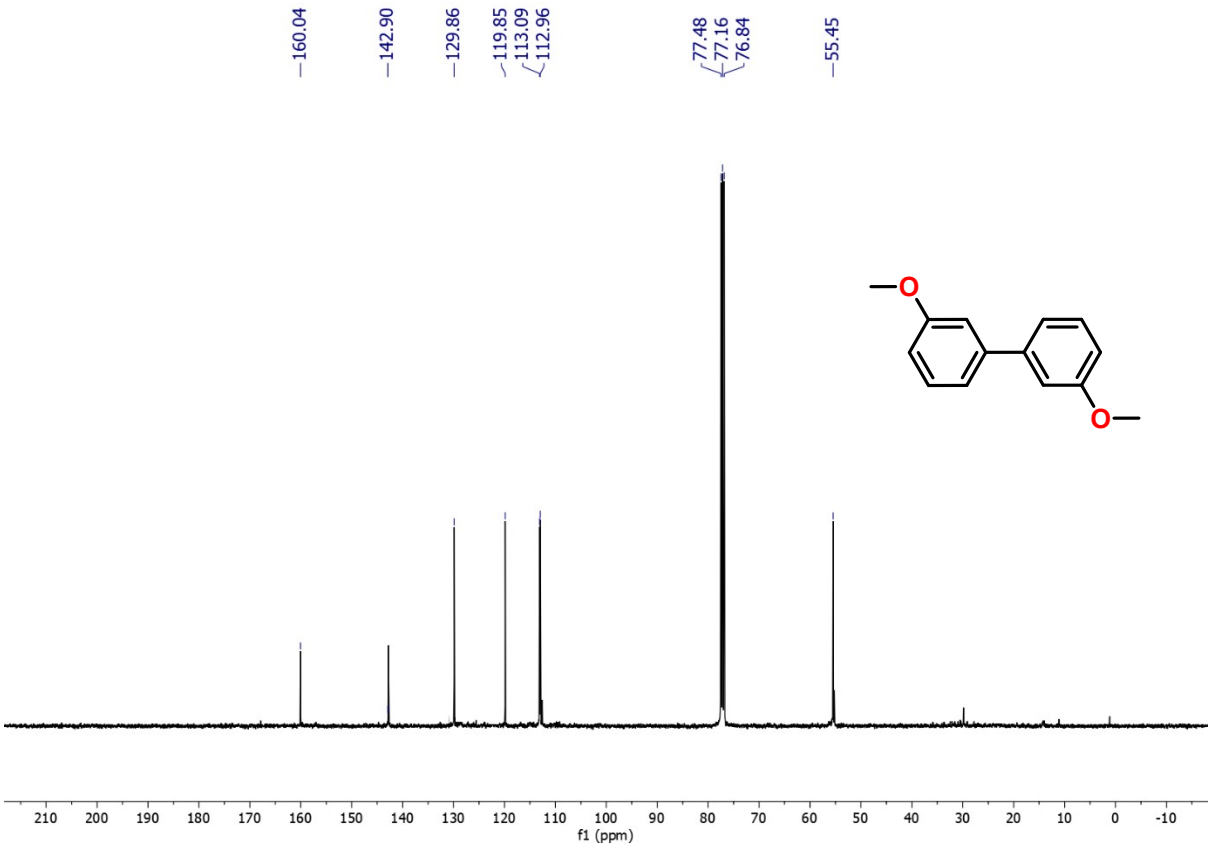


Fig S13: ^{13}C NMR spectra of compound **3d** in $CDCl_3$.

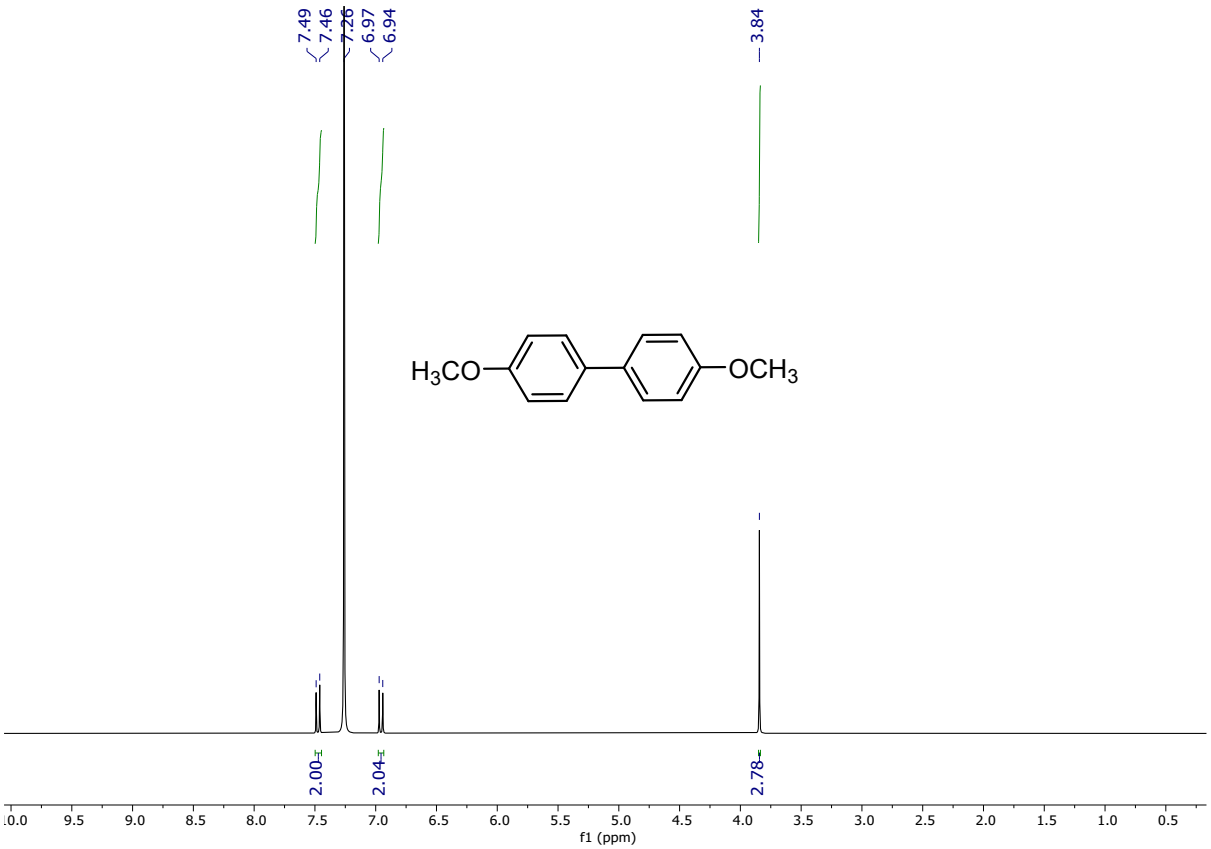


Fig S14: ^{1}H NMR spectra of compound **3e** in $CDCl_3$.

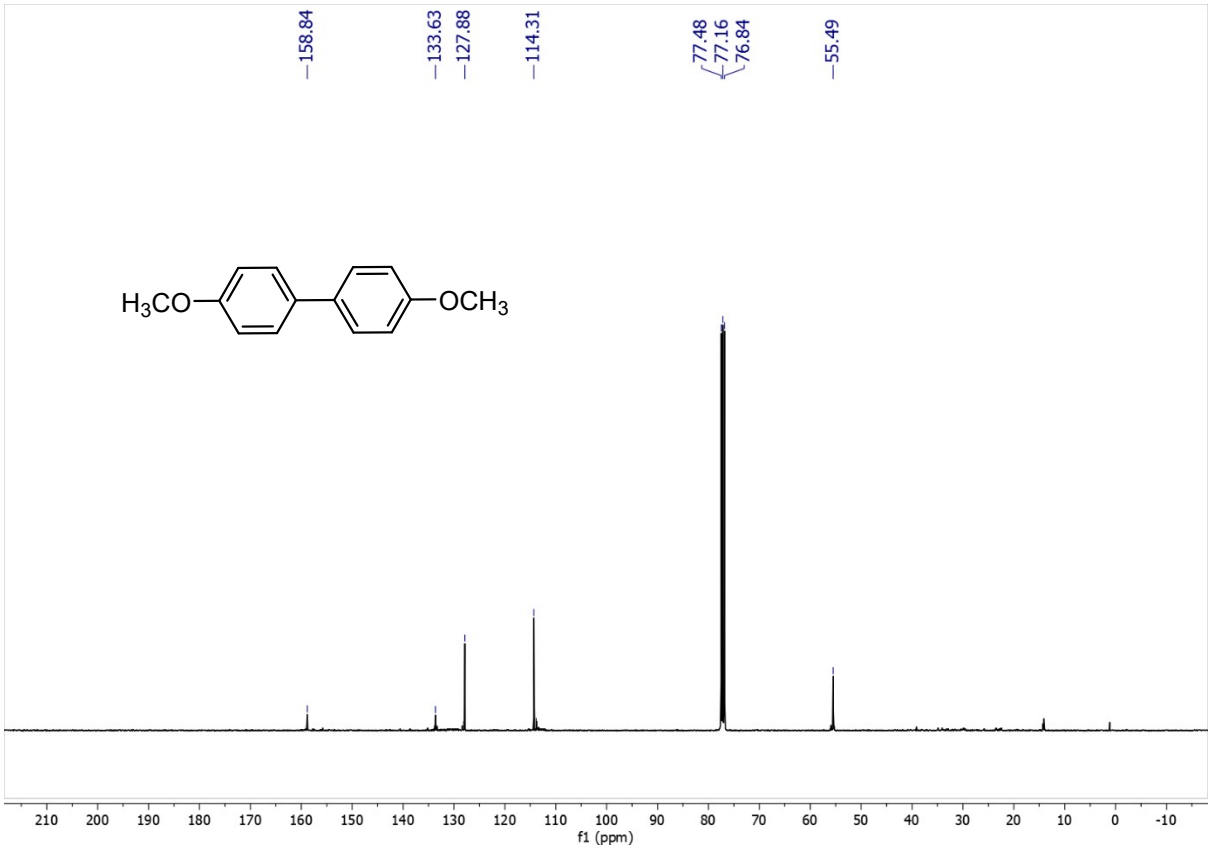


Fig S15: ^{13}C NMR spectra of compound **3e** in $CDCl_3$.

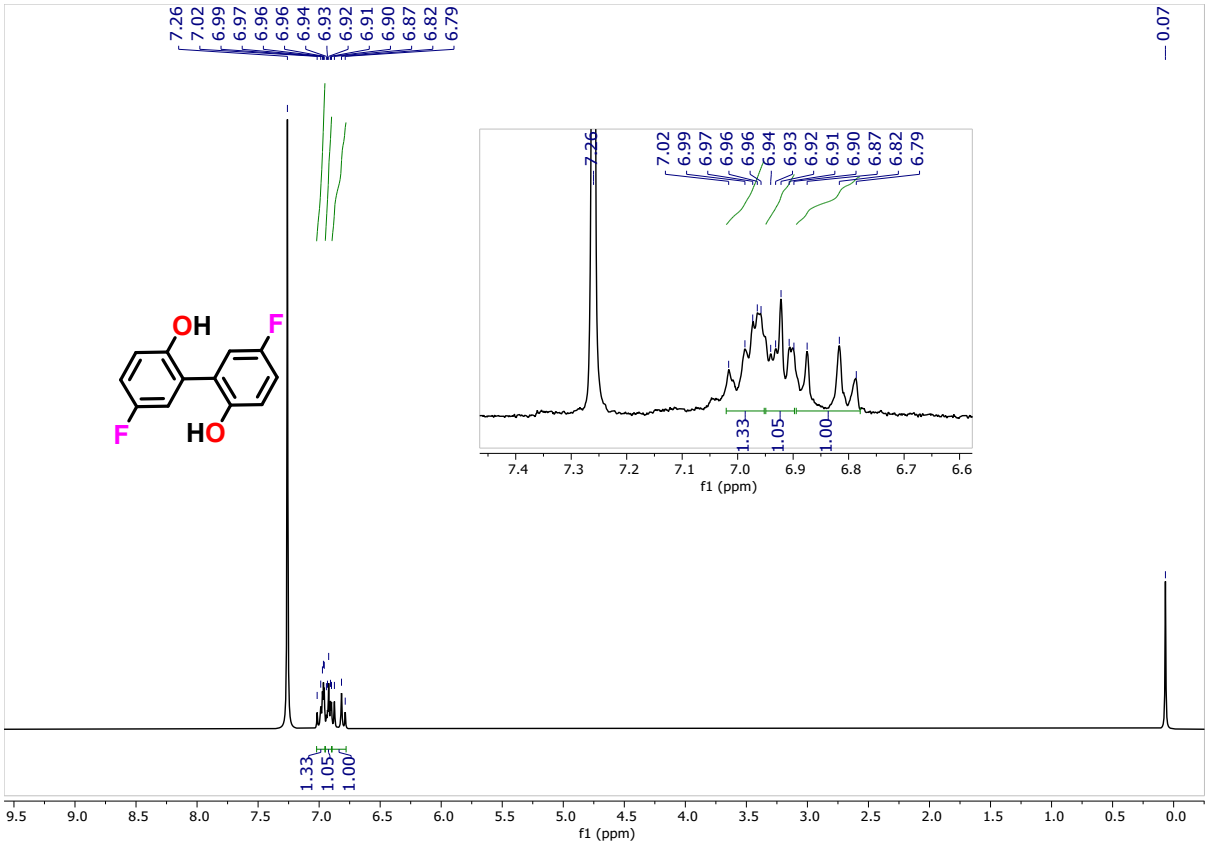


Fig S16: ^{1}H NMR spectra of compound **3f** in $CDCl_3$.

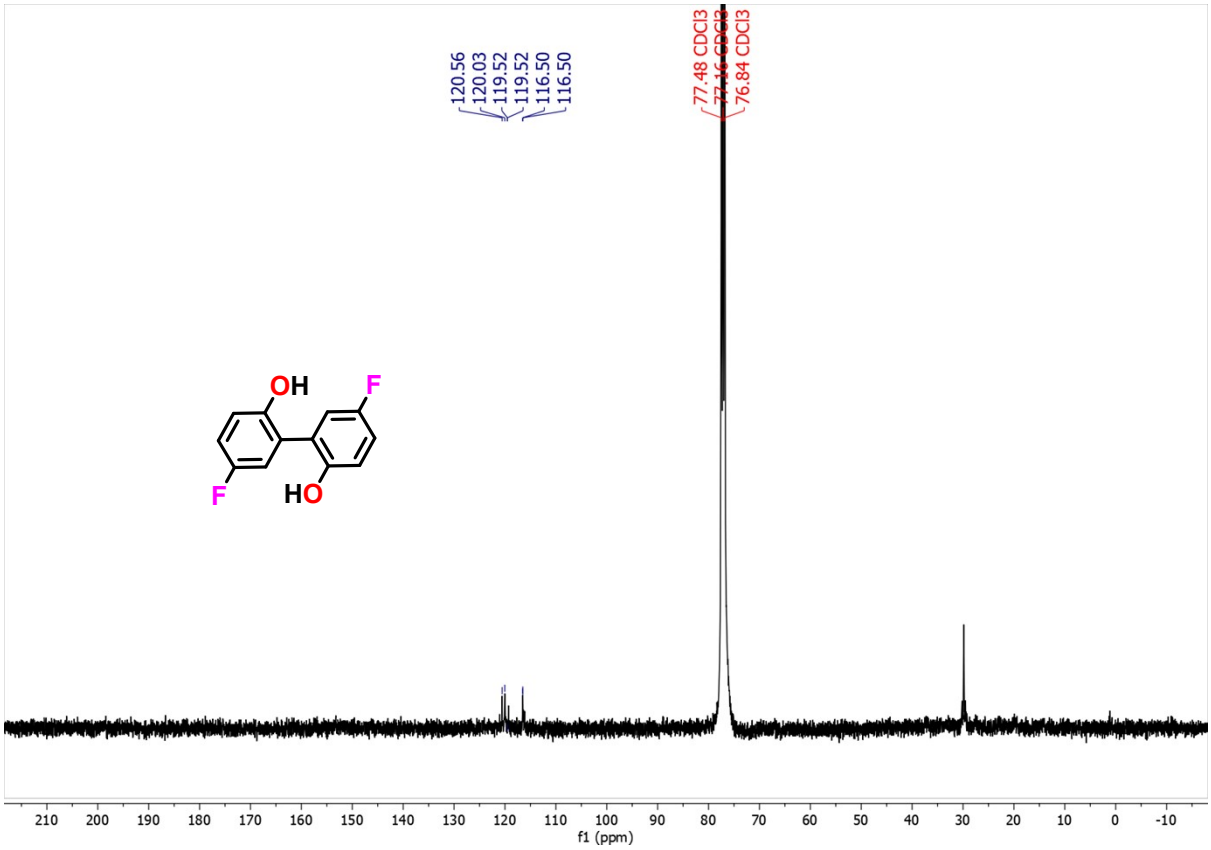


Fig S17: ^{13}C NMR spectra of compound **3f** in $CDCl_3$.

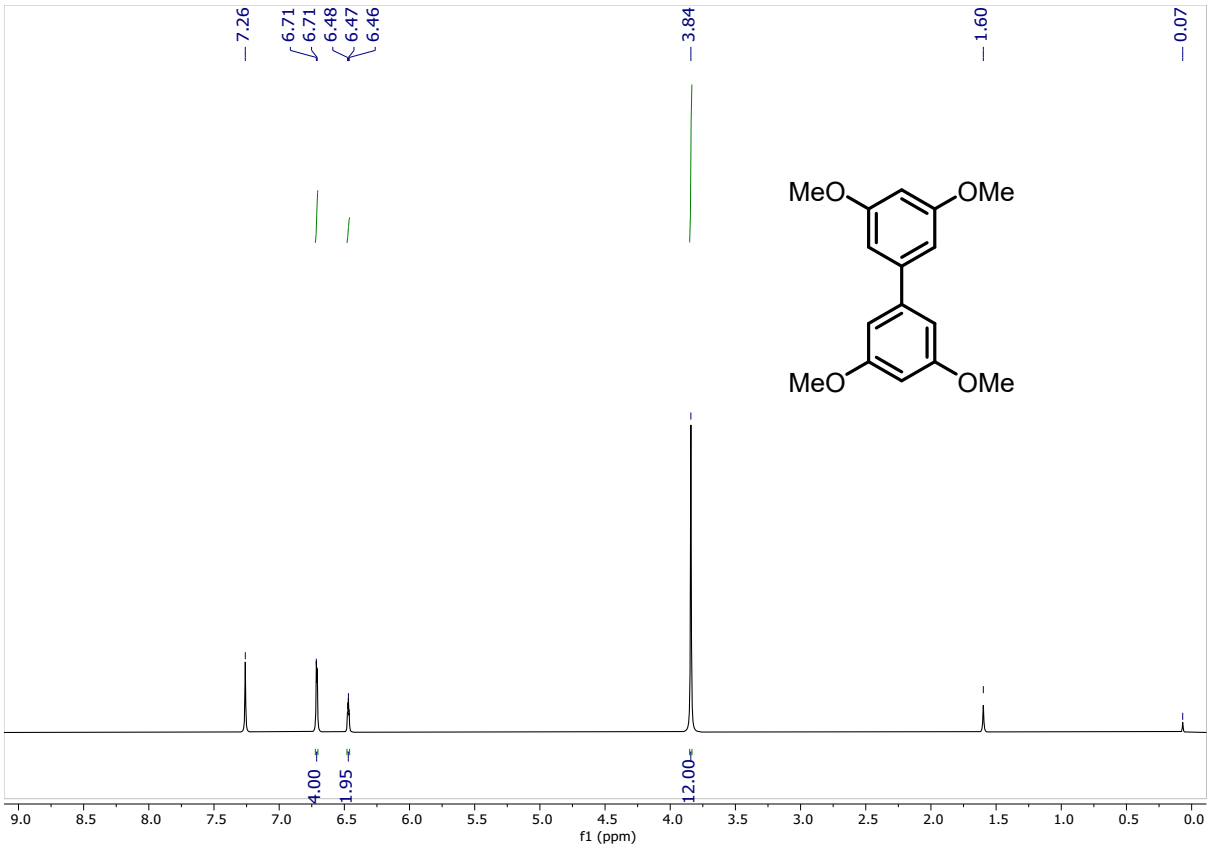


Fig S18: ^{1}H NMR spectra of compound **3g** in $CDCl_3$.

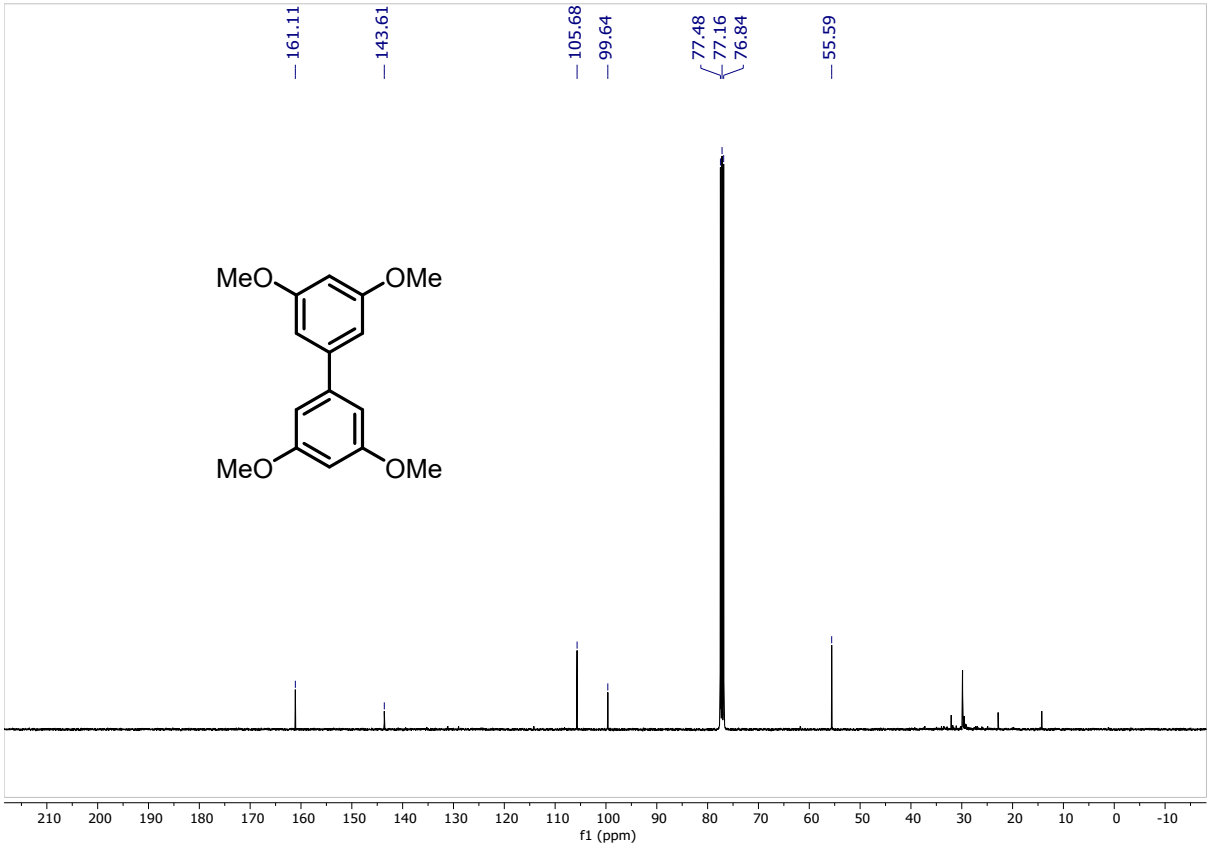


Fig S19: ^{13}C NMR spectra of compound **3g** in $CDCl_3$.

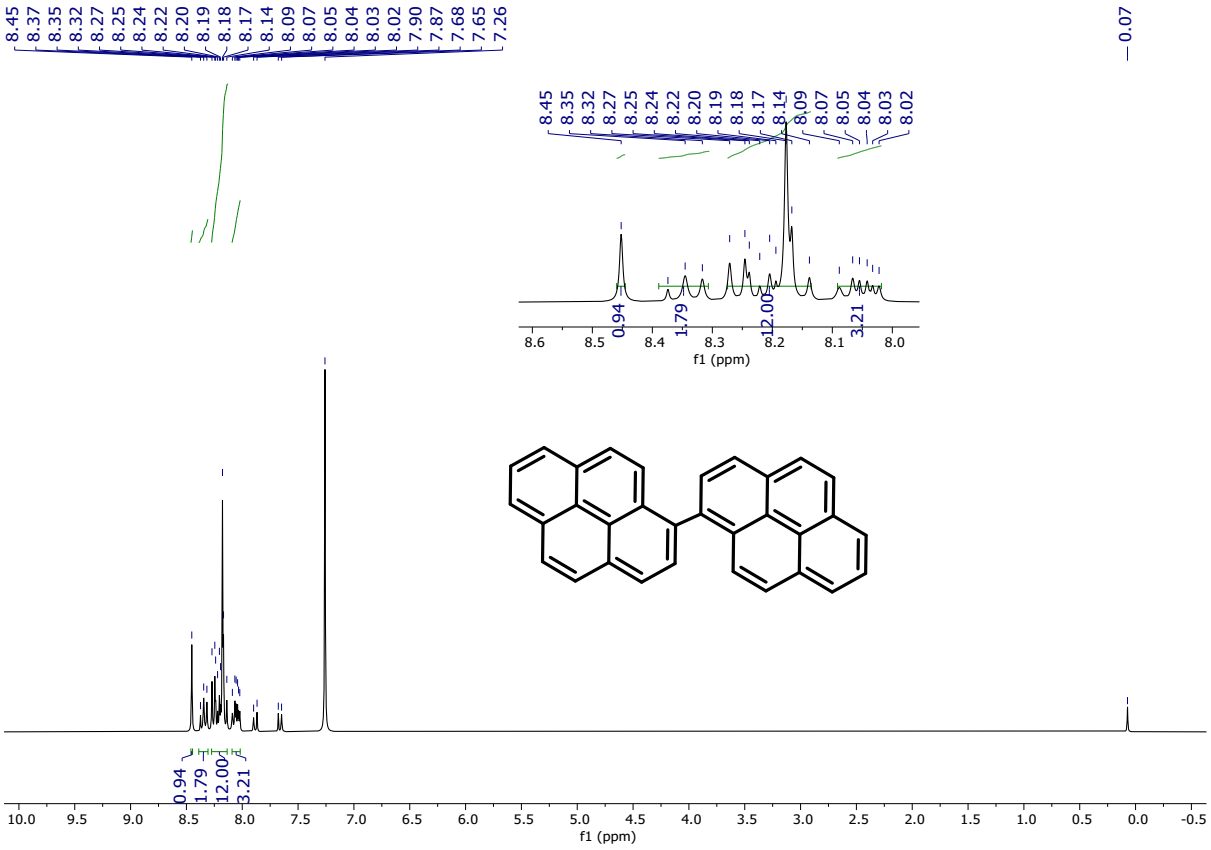


Fig S20: ^{1}H NMR spectra of compound **3h** in $CDCl_3$.

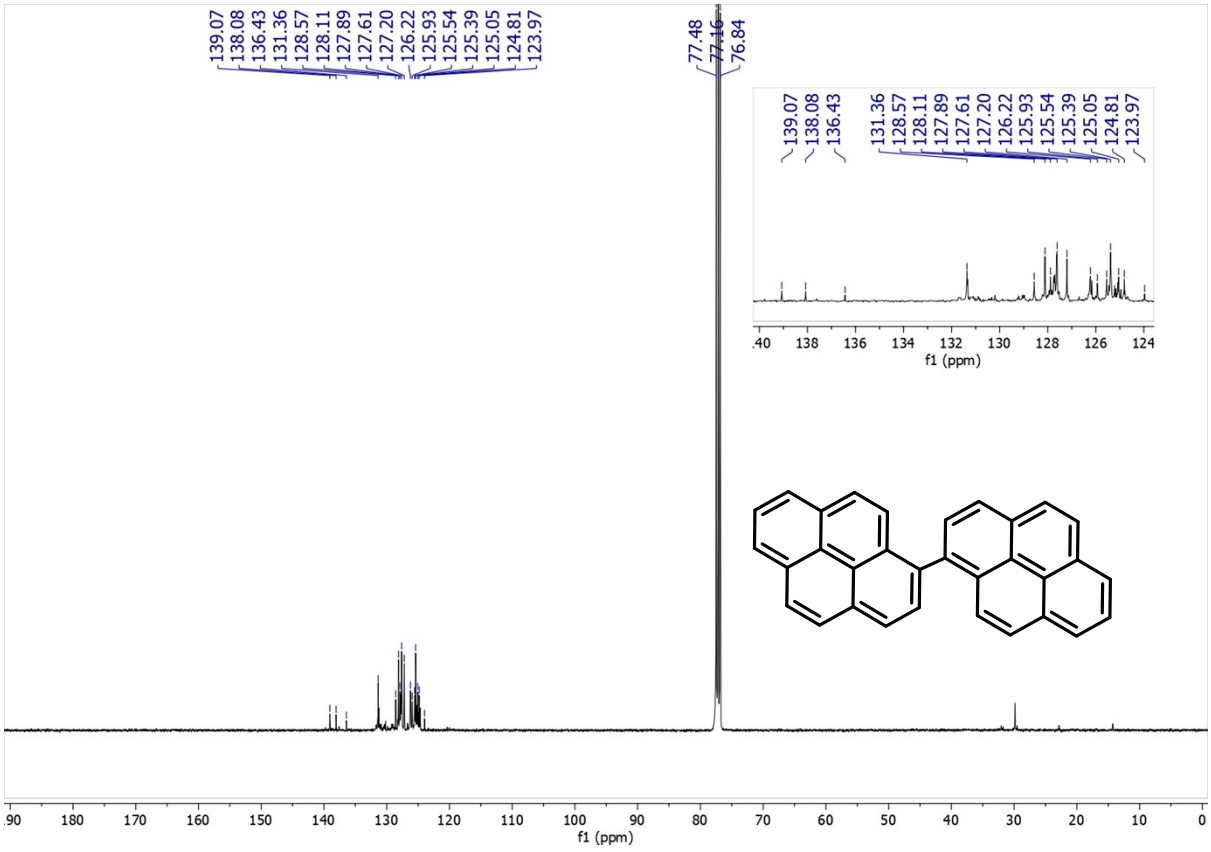


Fig S21: ^{13}C NMR spectra of compound **3h** in $CDCl_3$.

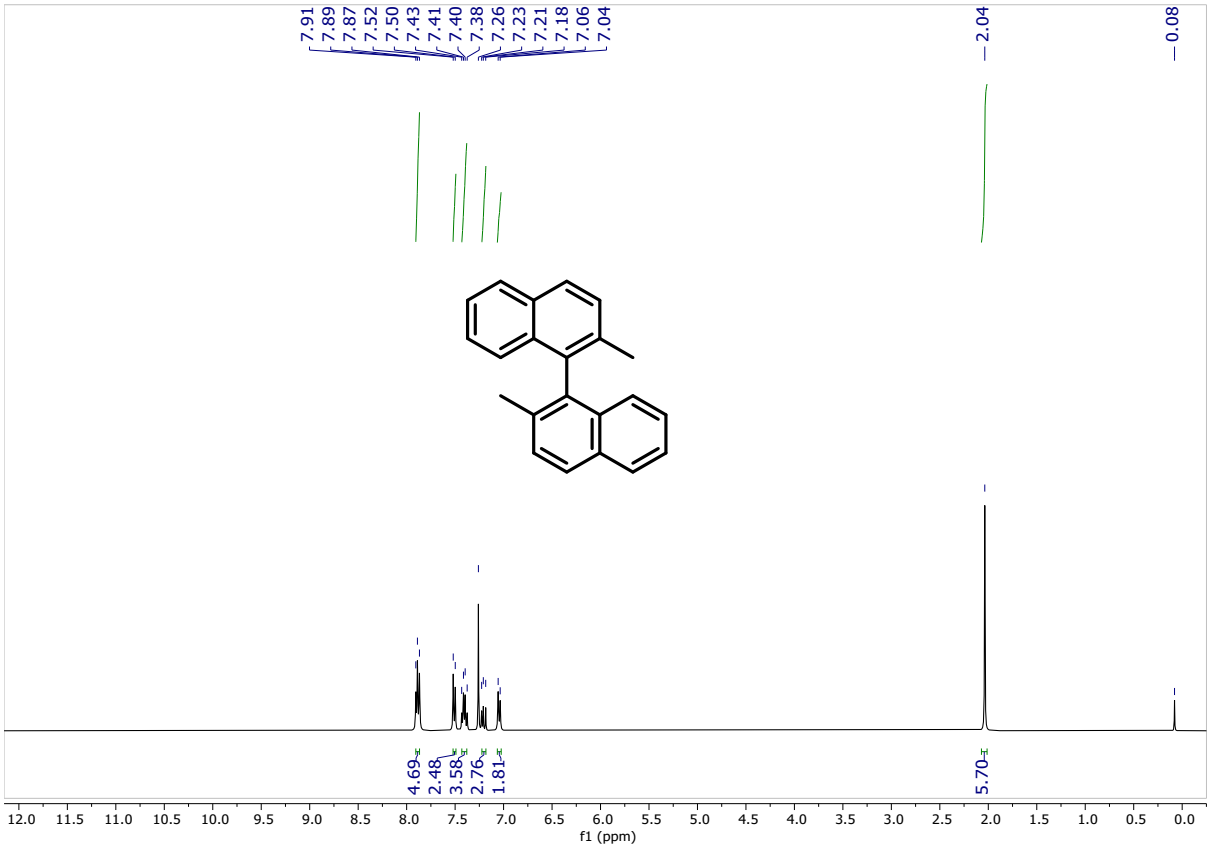


Fig S22: ^{1}H NMR spectra of compound **3i** in $CDCl_3$.

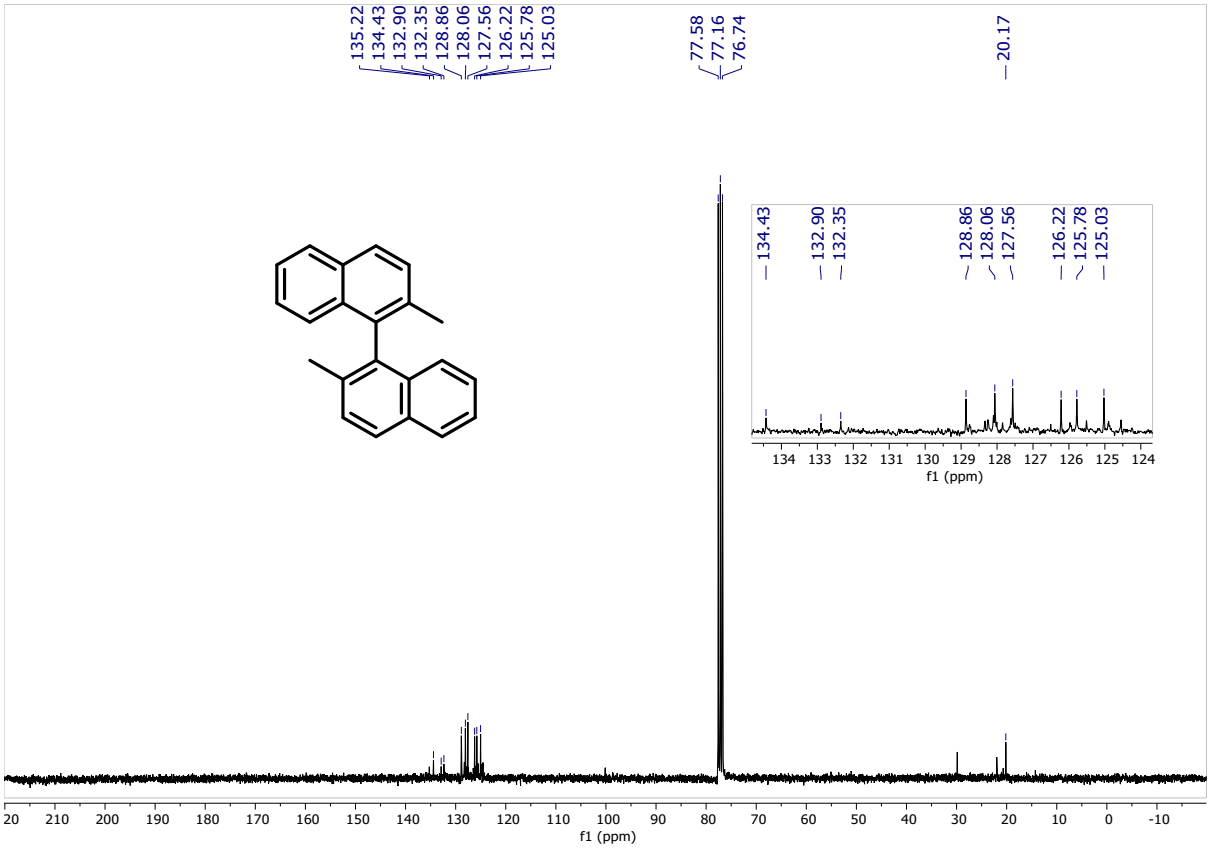


Fig S23: ^{13}C NMR spectra of compound **3i** in $CDCl_3$.

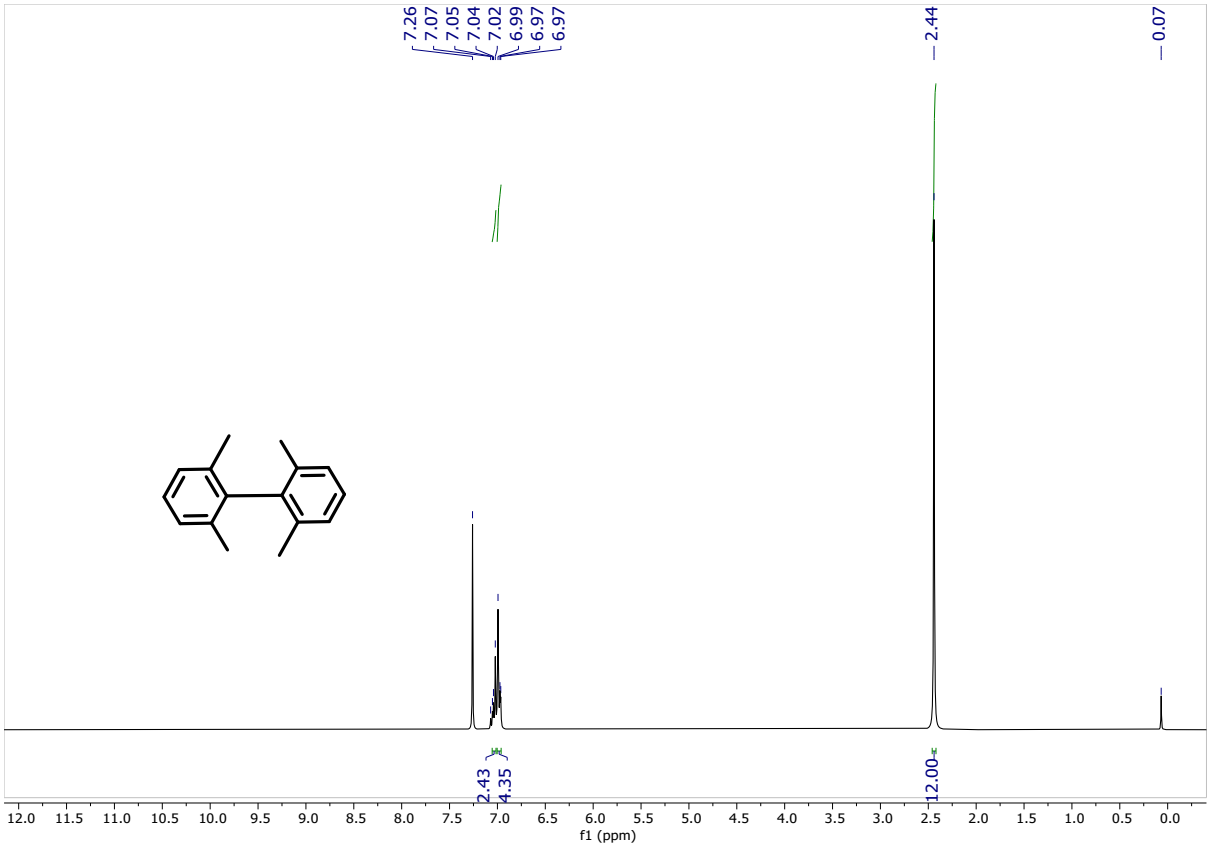


Fig S24: ^{1}H NMR spectra of compound **3j** in $CDCl_3$.

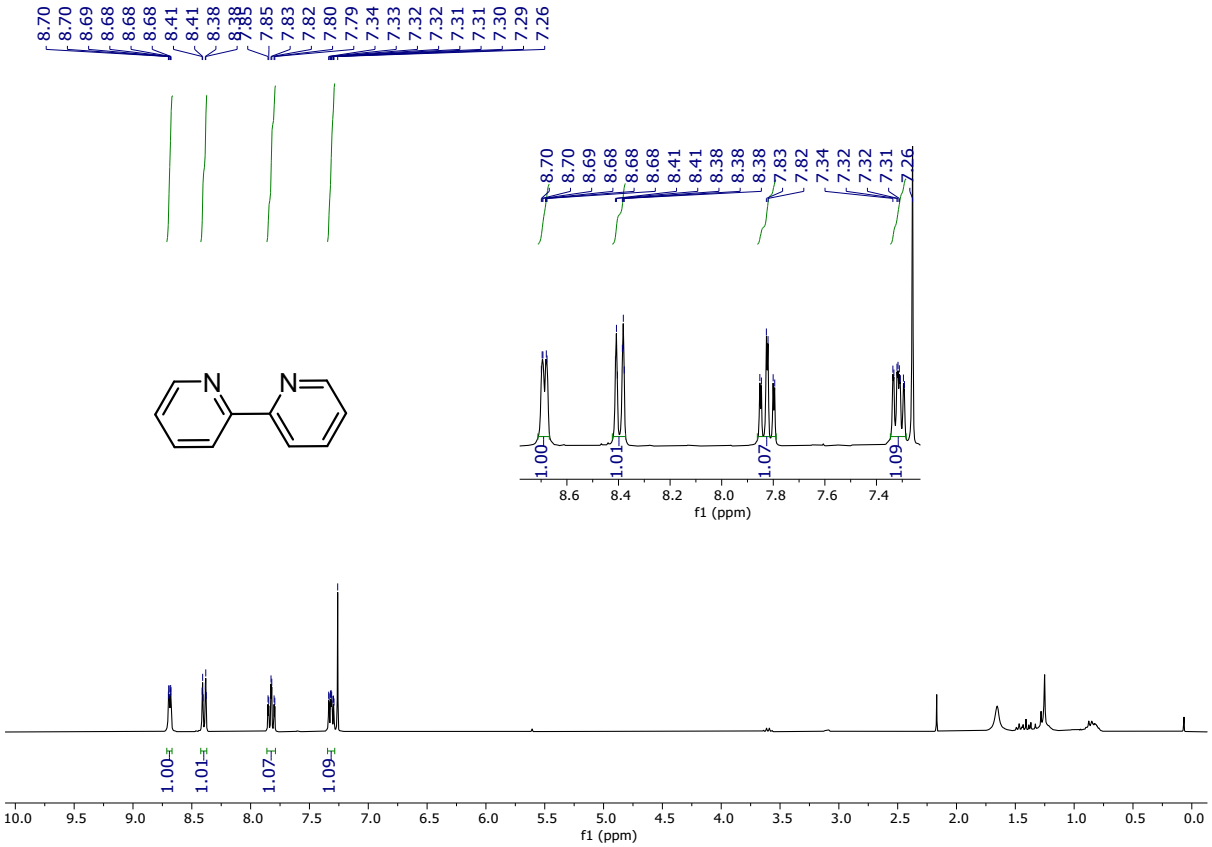


Fig S25: ^{1}H NMR spectra of compound **3k** in $CDCl_3$.

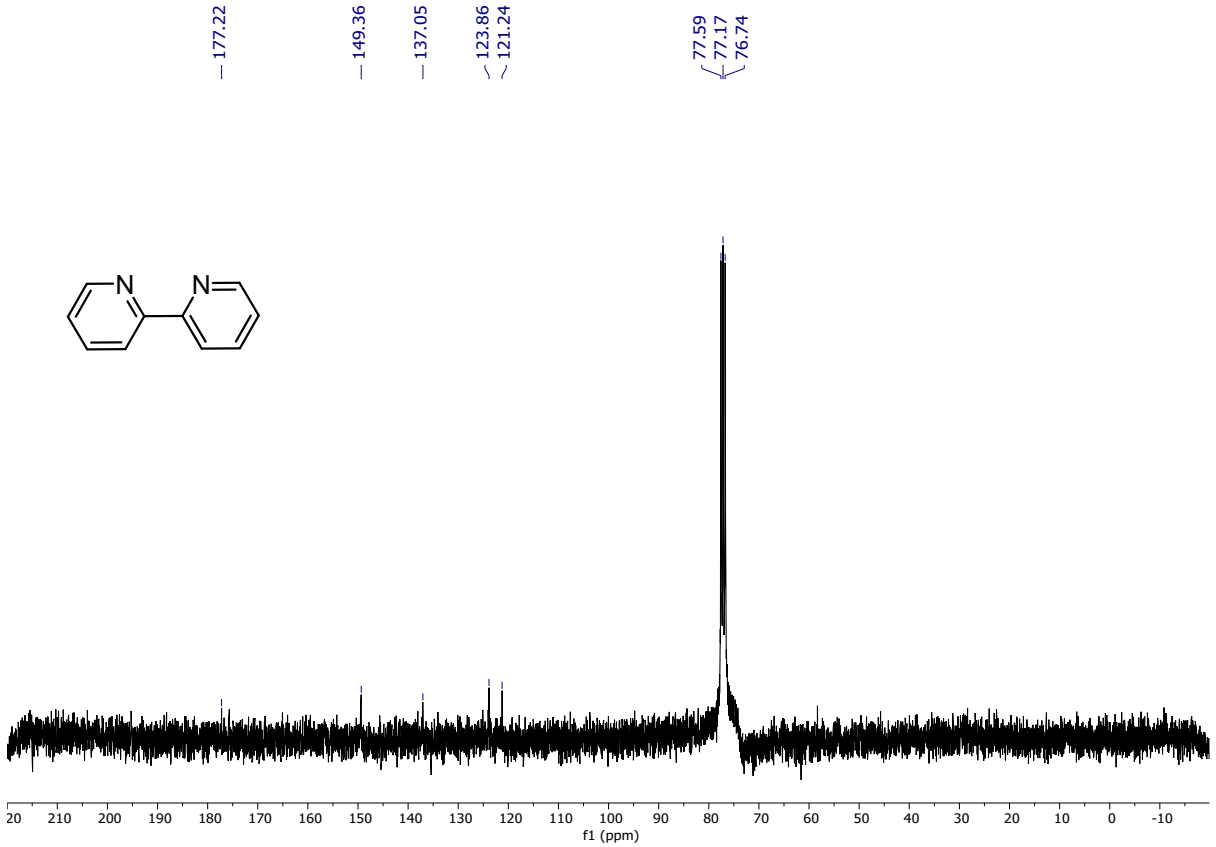


Fig S26: ^{13}C NMR spectra of compound **3k** in $CDCl_3$.

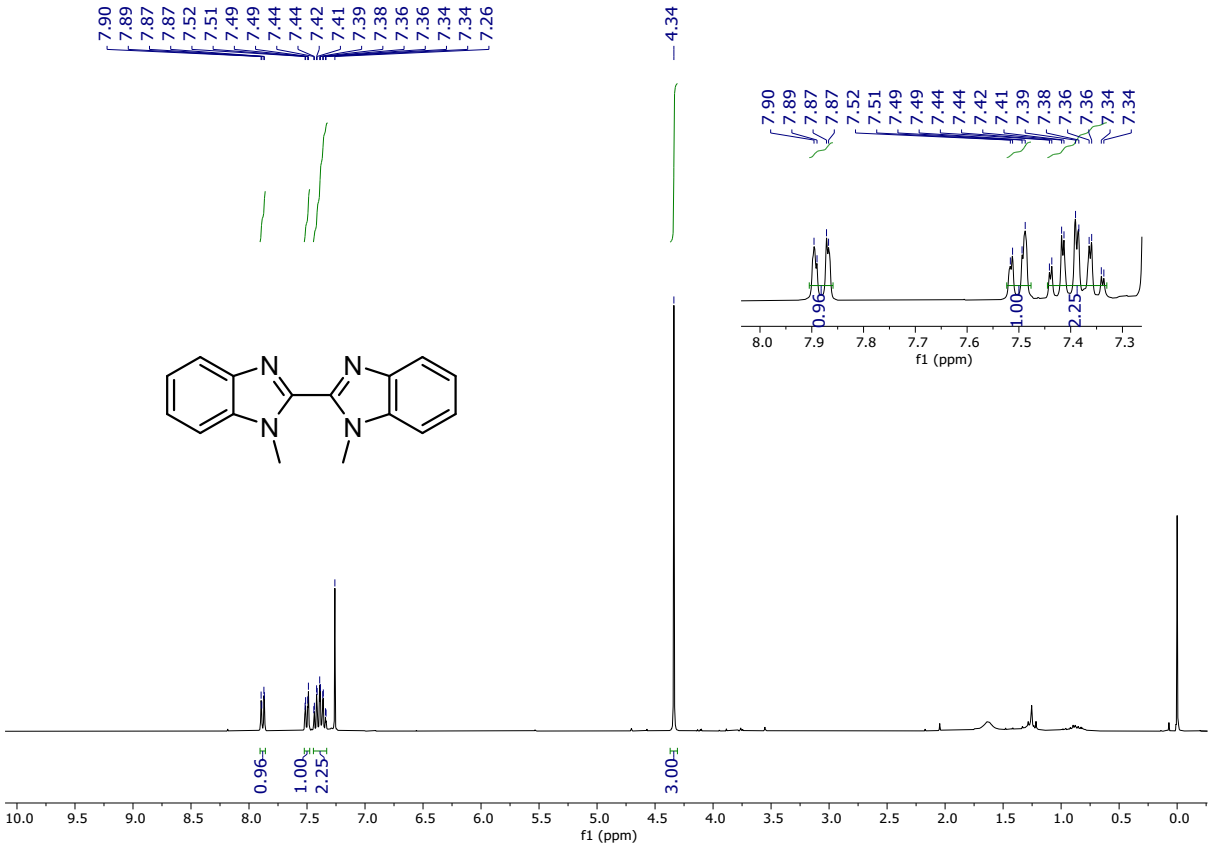


Fig S27: ^{1}H NMR spectra of compound **3l** in $CDCl_3$.

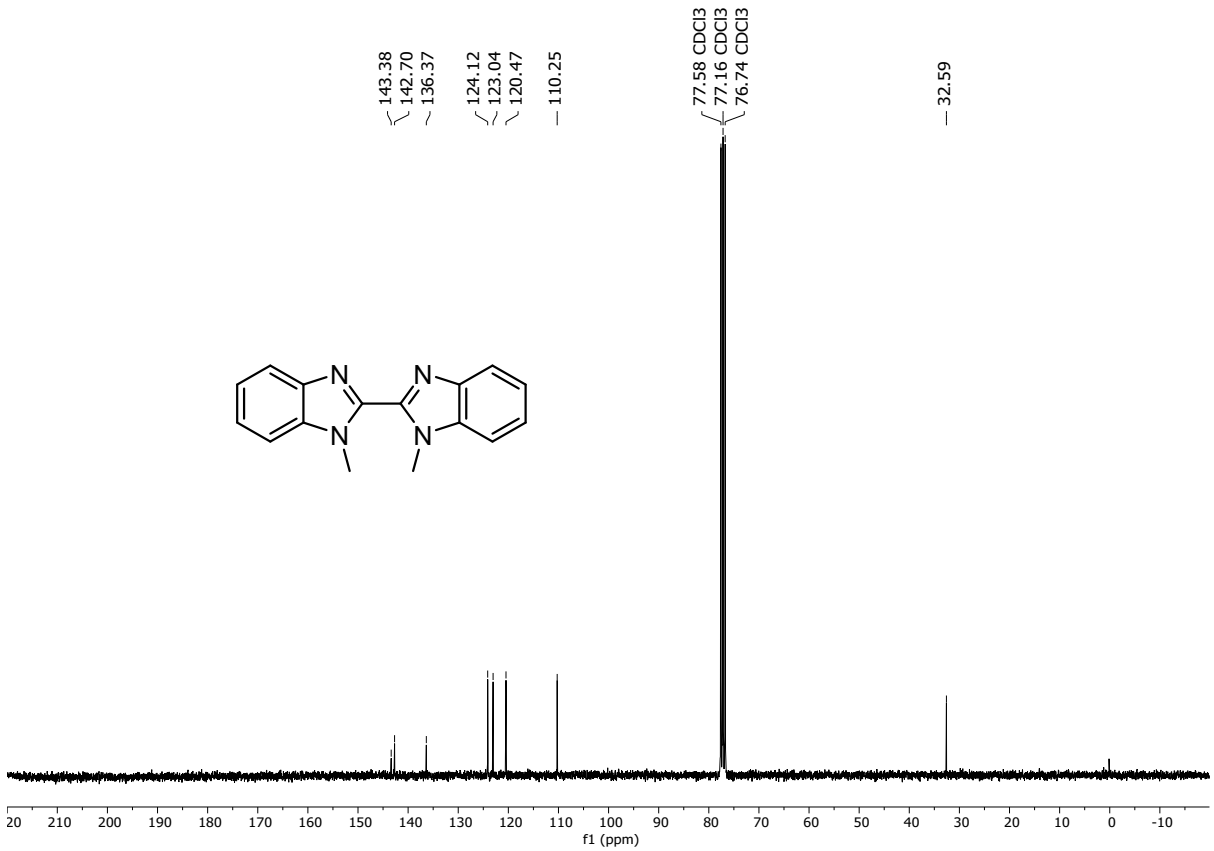


Fig S28: ^{13}C NMR spectra of compound **3l** in $CDCl_3$.

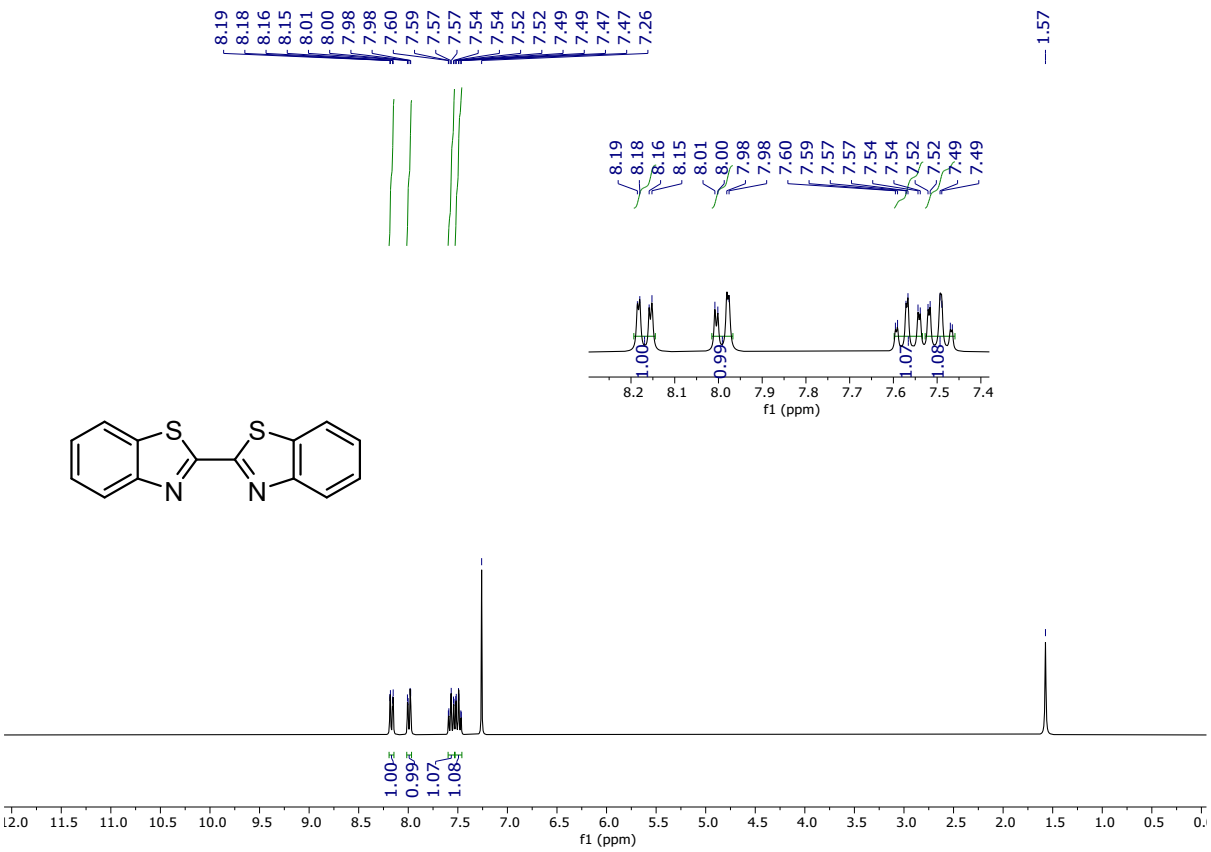


Fig S29: ^{1}H NMR spectra of compound **3m** in $CDCl_3$.

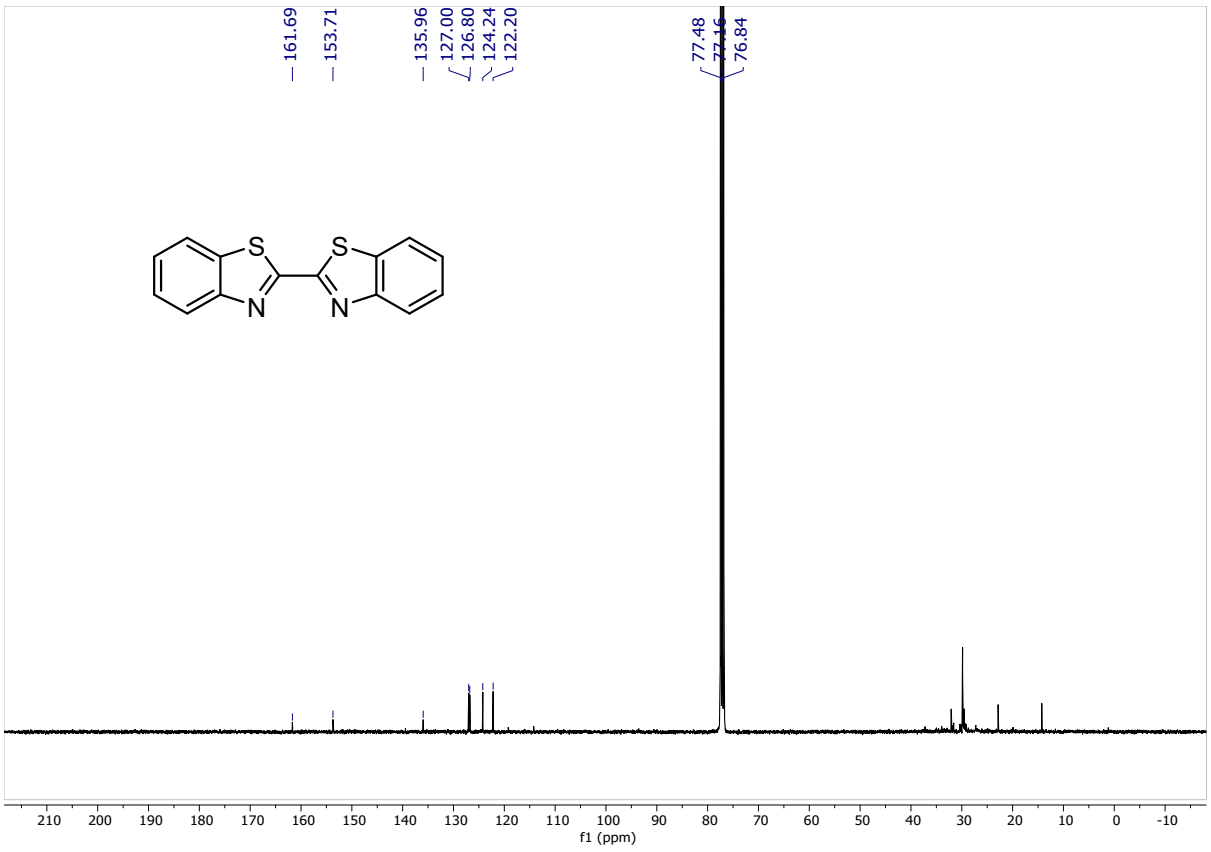


Fig S30: ^{13}C NMR spectra of compound **3m** in $CDCl_3$.

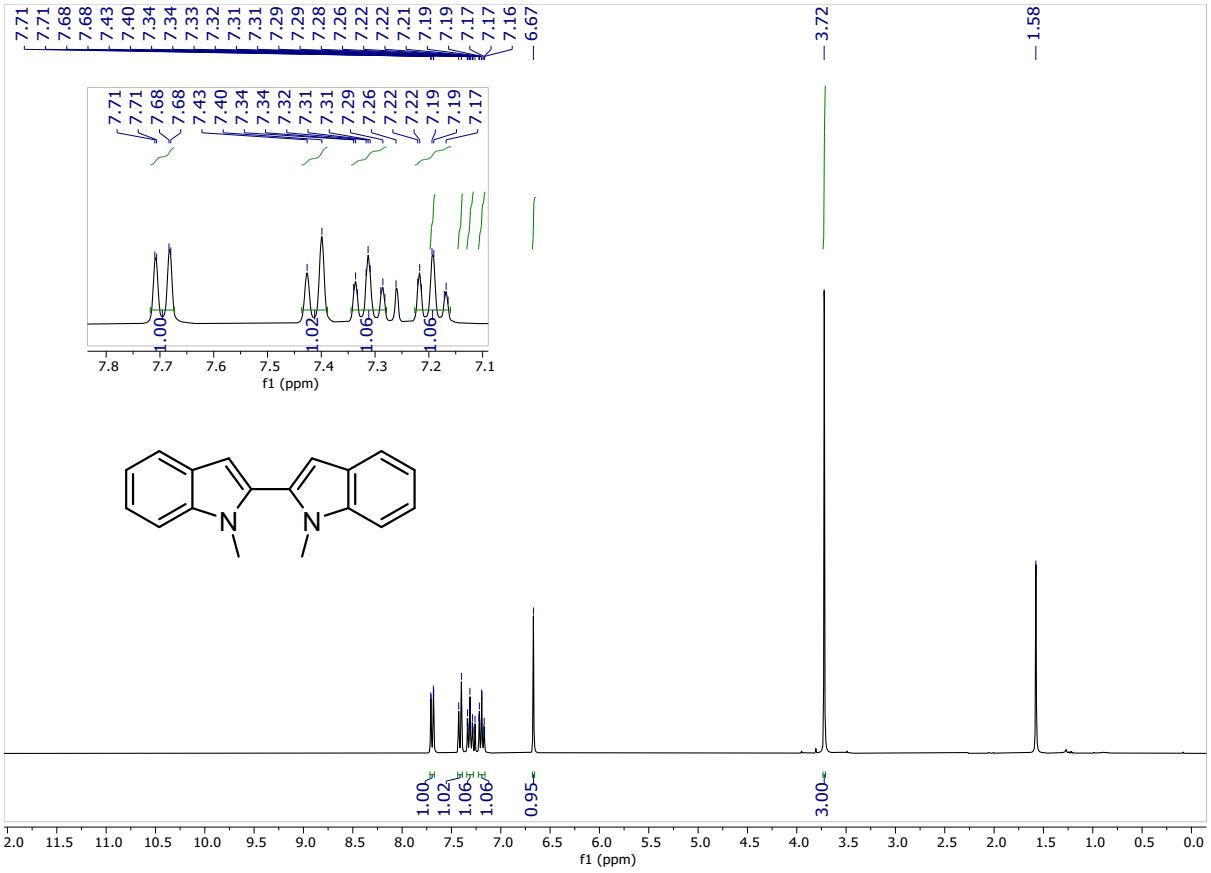


Fig S31: ^{1}H NMR spectra of compound **3n** in $CDCl_3$.

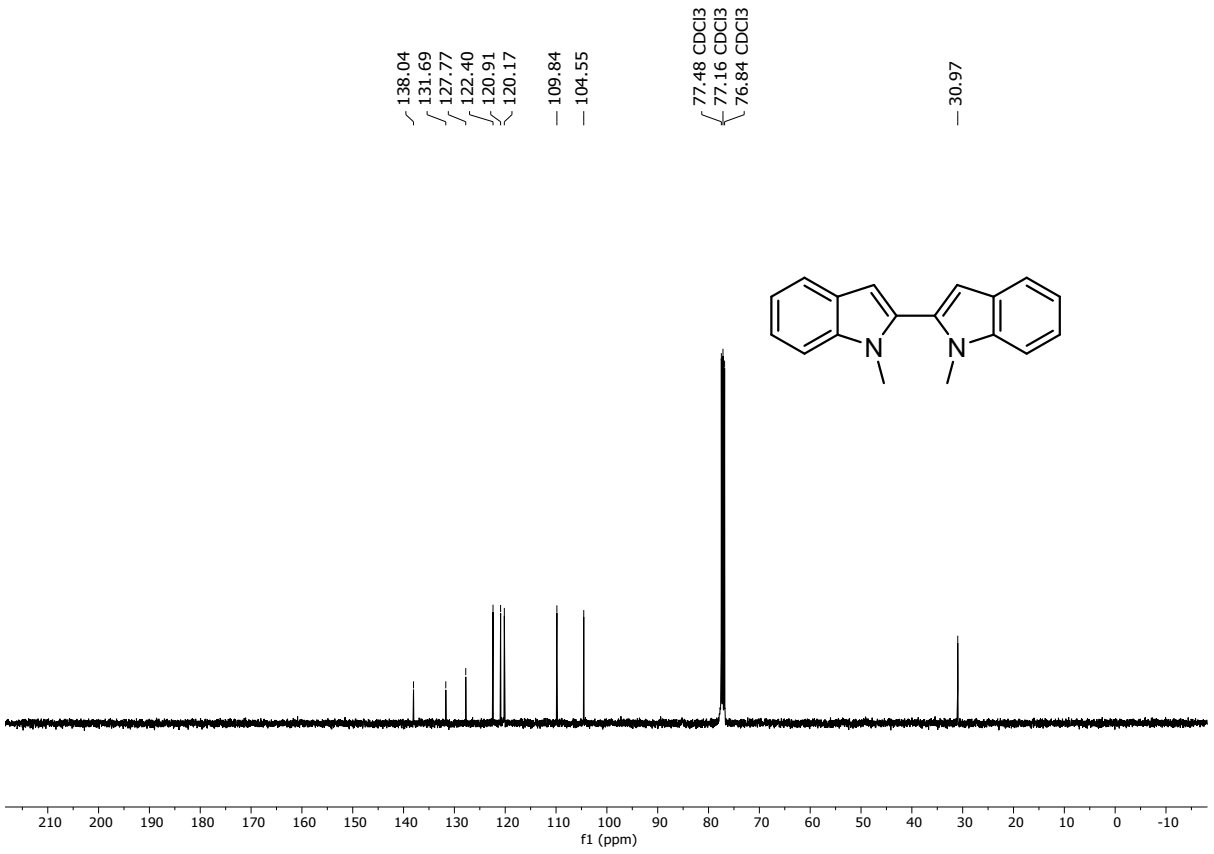


Fig S32: ^{13}C NMR spectra of compound **3n** in $CDCl_3$.

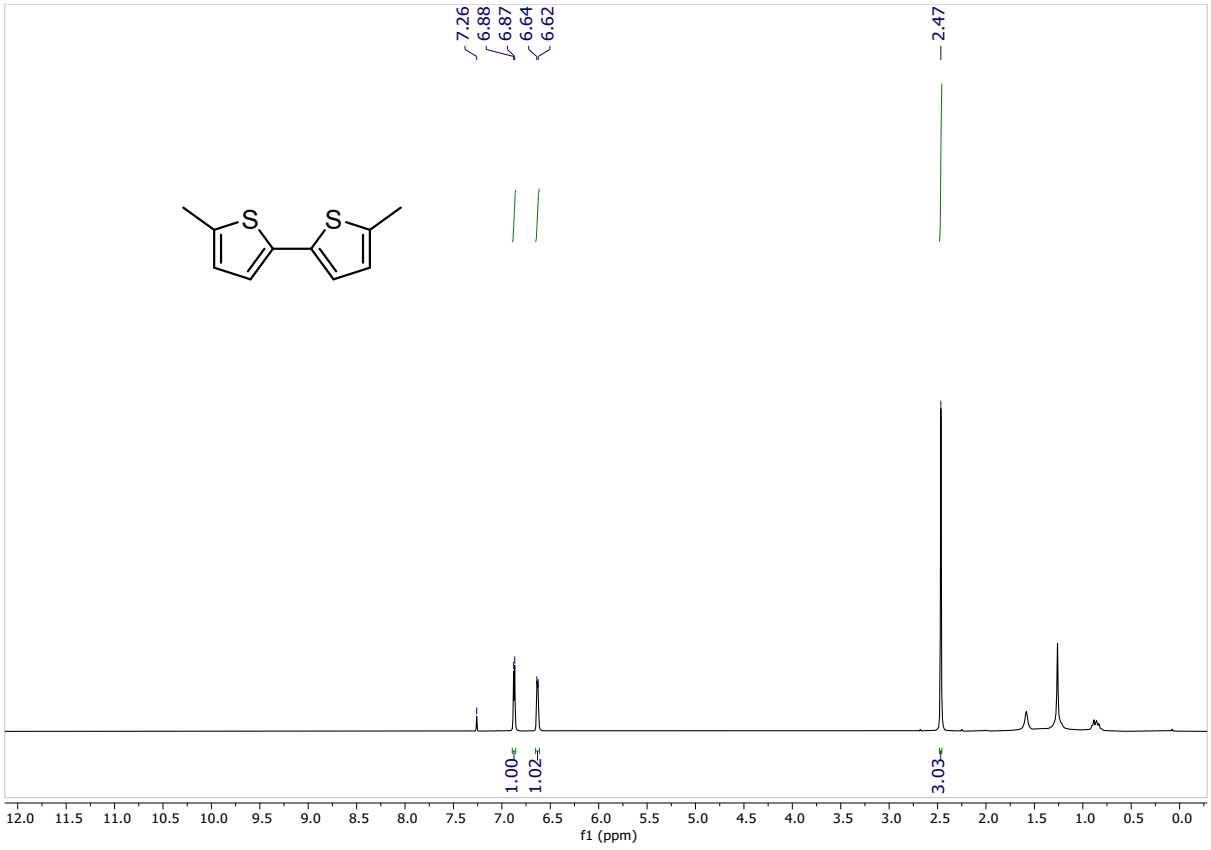


Fig S33: ^{1}H NMR spectra of compound **3o** in $CDCl_3$.

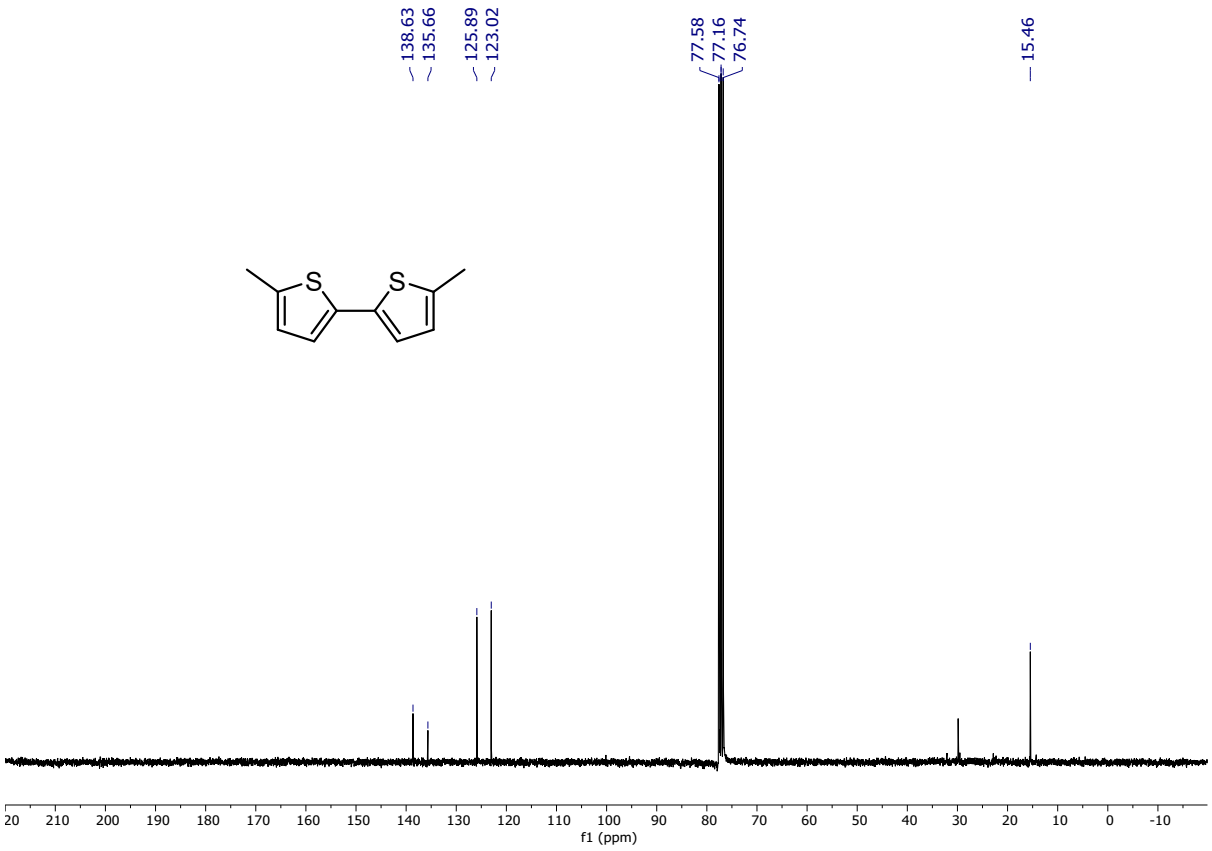


Fig S34: ^{13}C NMR spectra of compound **3o** in $CDCl_3$.

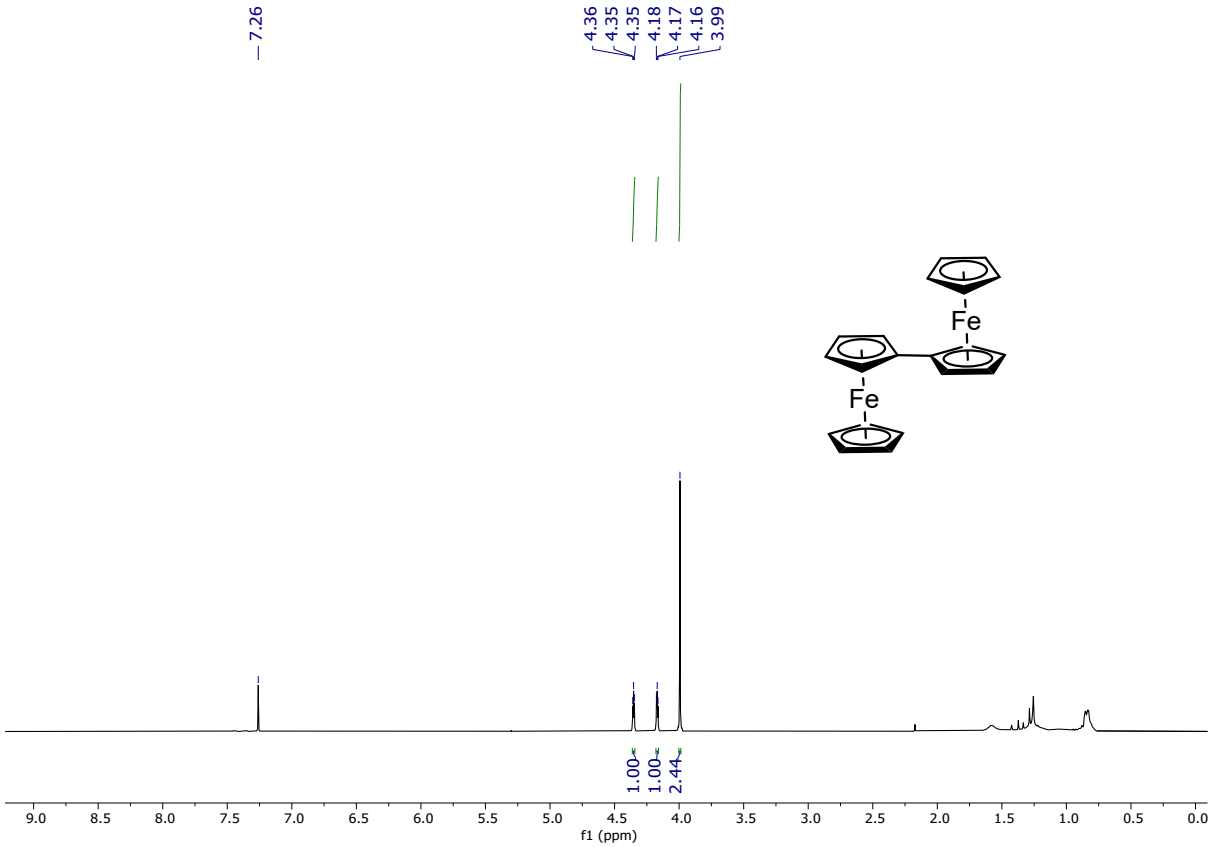


Fig S35: ^{1}H NMR spectra of compound **3p** in $CDCl_3$.

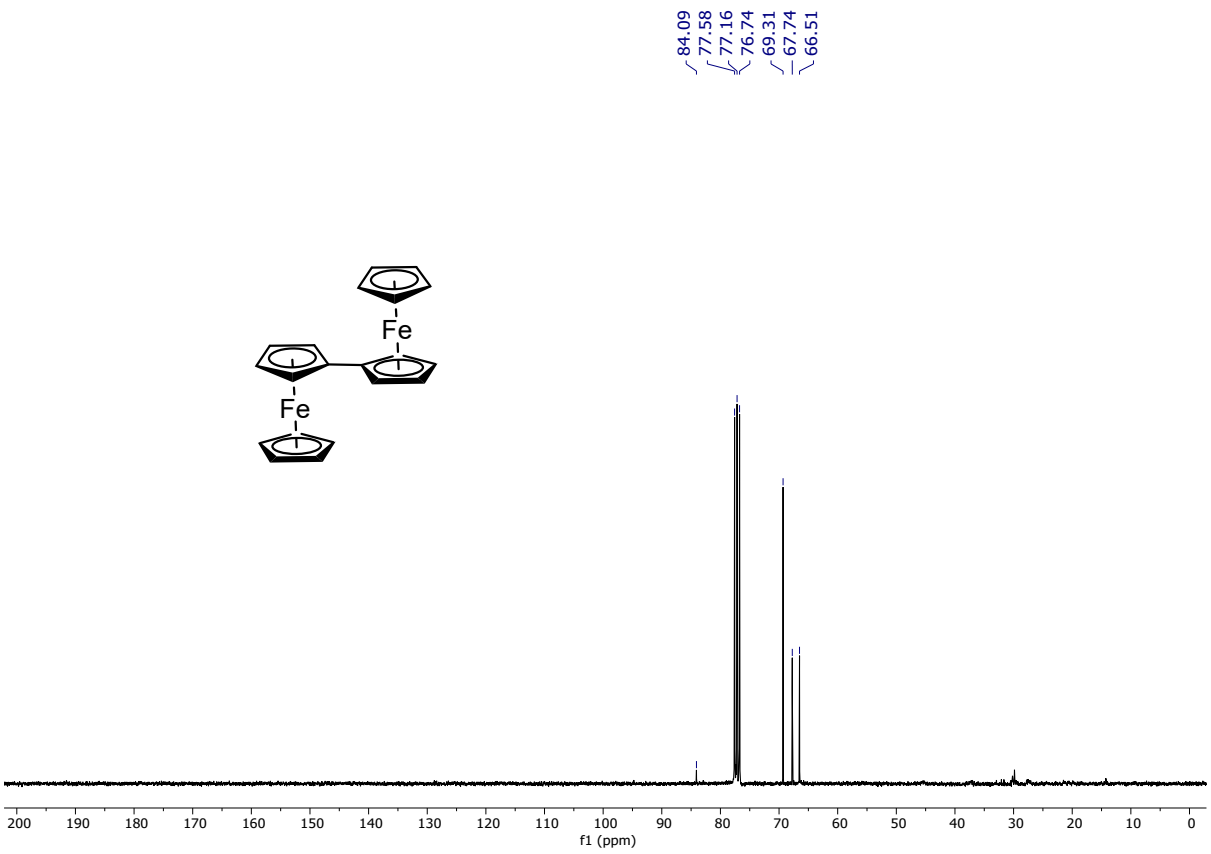


Fig S36: ^{13}C NMR spectra of compound **3p** in $CDCl_3$.

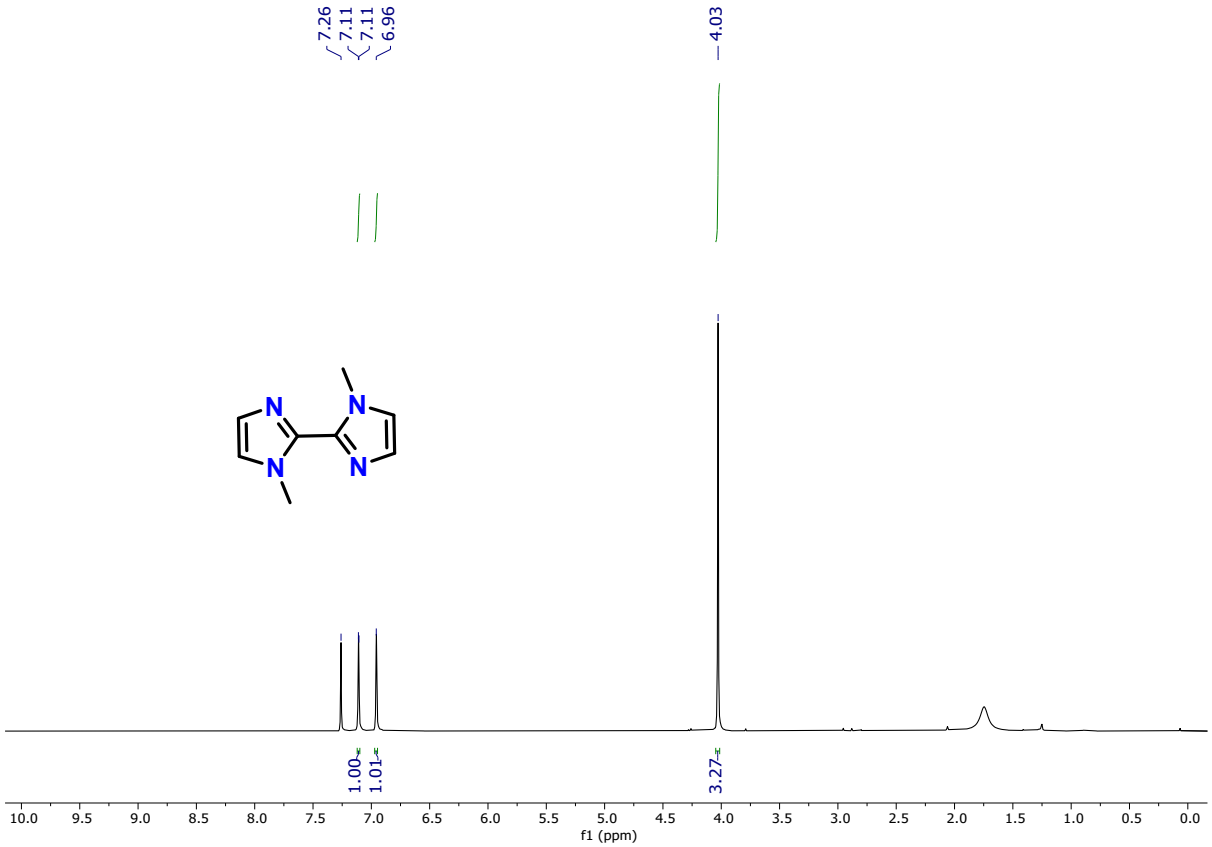


Fig S37: ^{1}H NMR spectra of compound **3q** in $CDCl_3$.

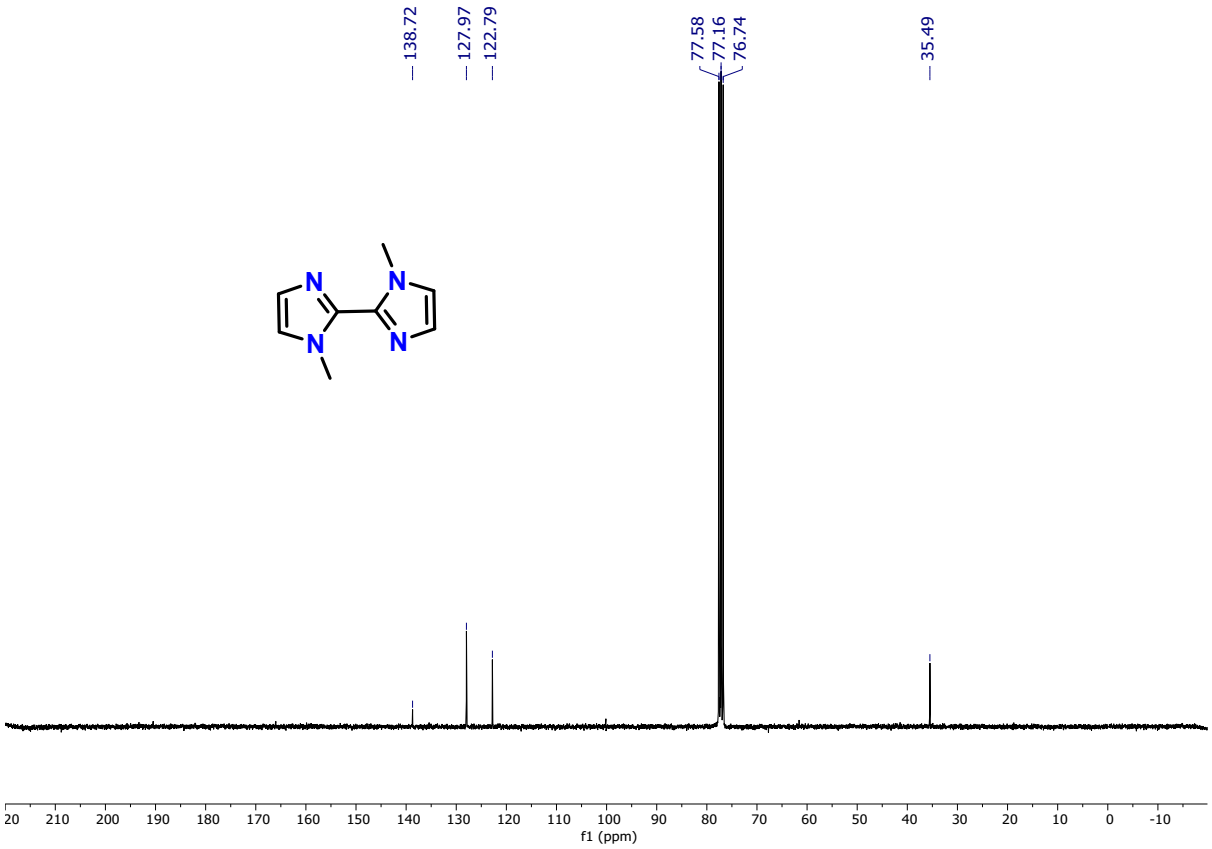


Fig S38: ^{13}C NMR spectra of compound **3q** in $CDCl_3$.

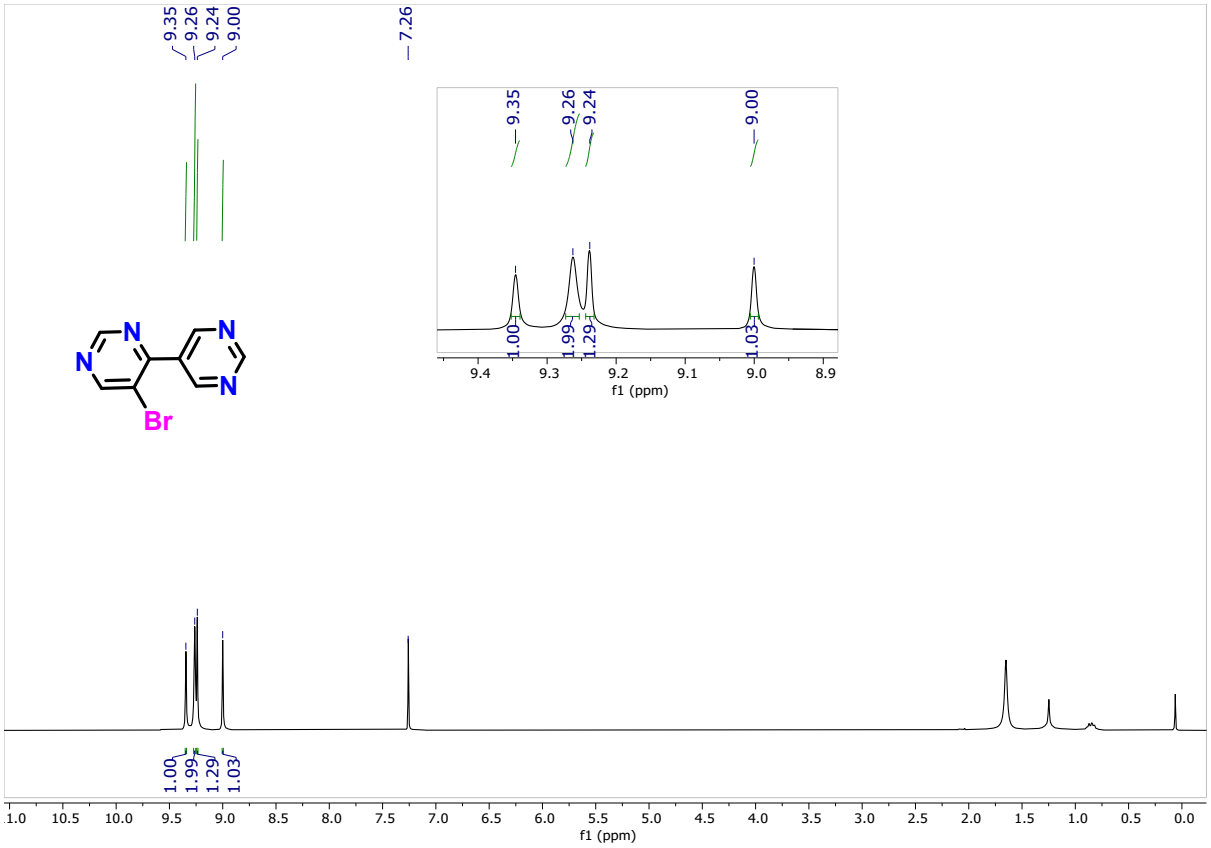


Fig S39: ^{1}H NMR spectra of compound **3r** in $CDCl_3$.

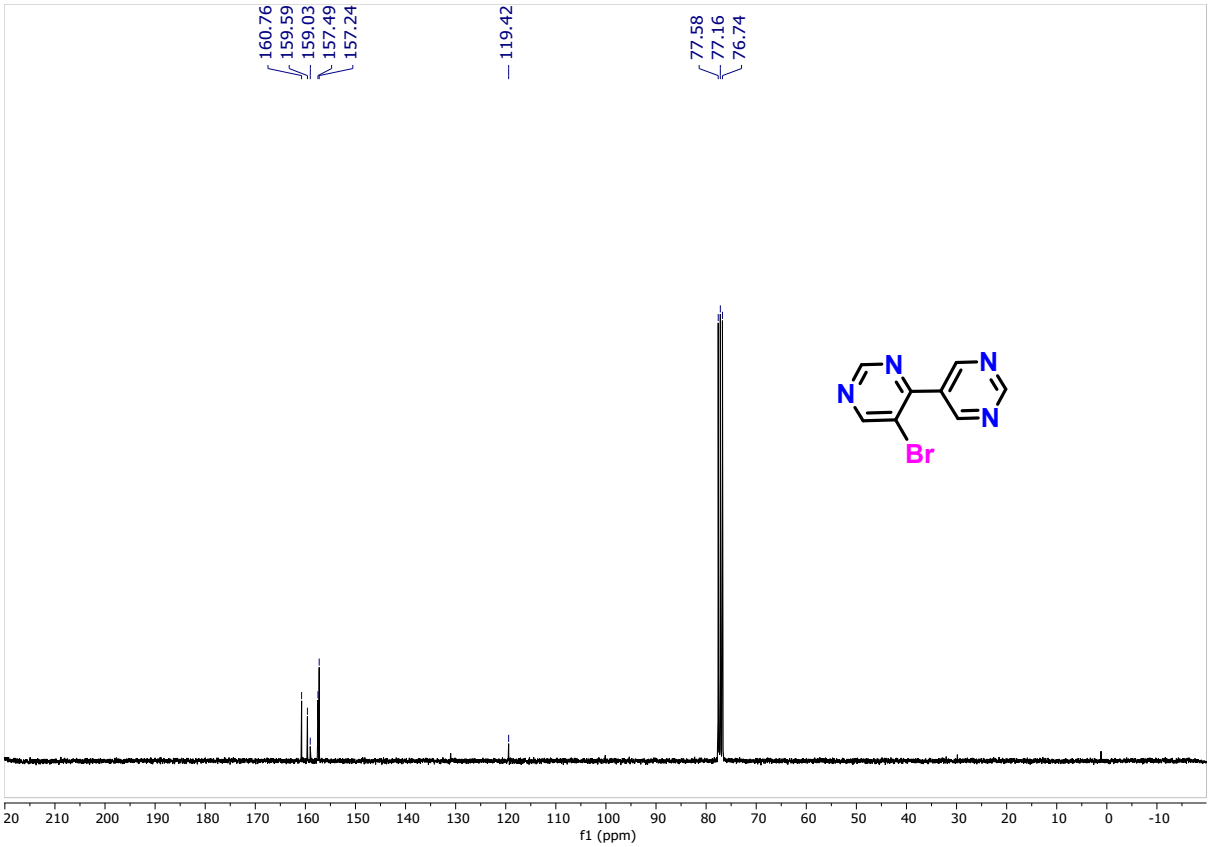
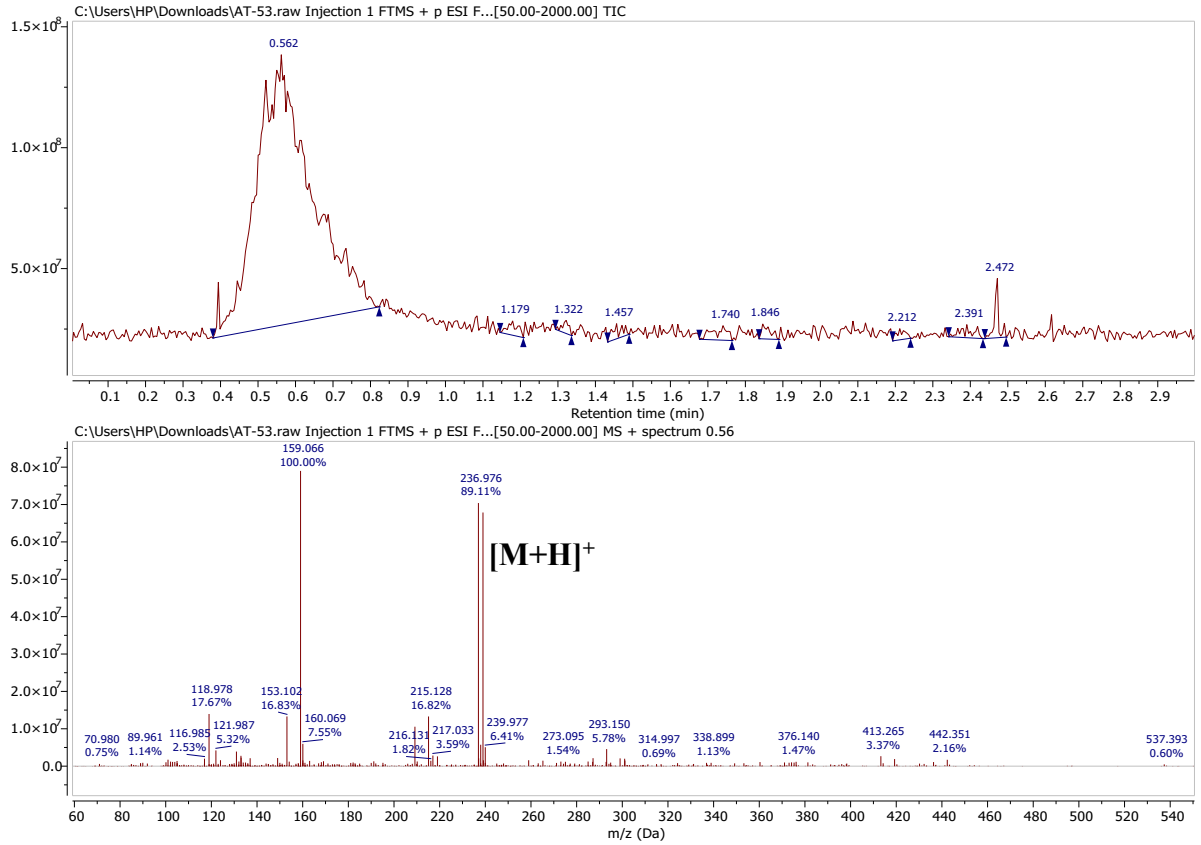


Fig S40: ^{13}C NMR spectra of compound **3r** in $CDCl_3$.



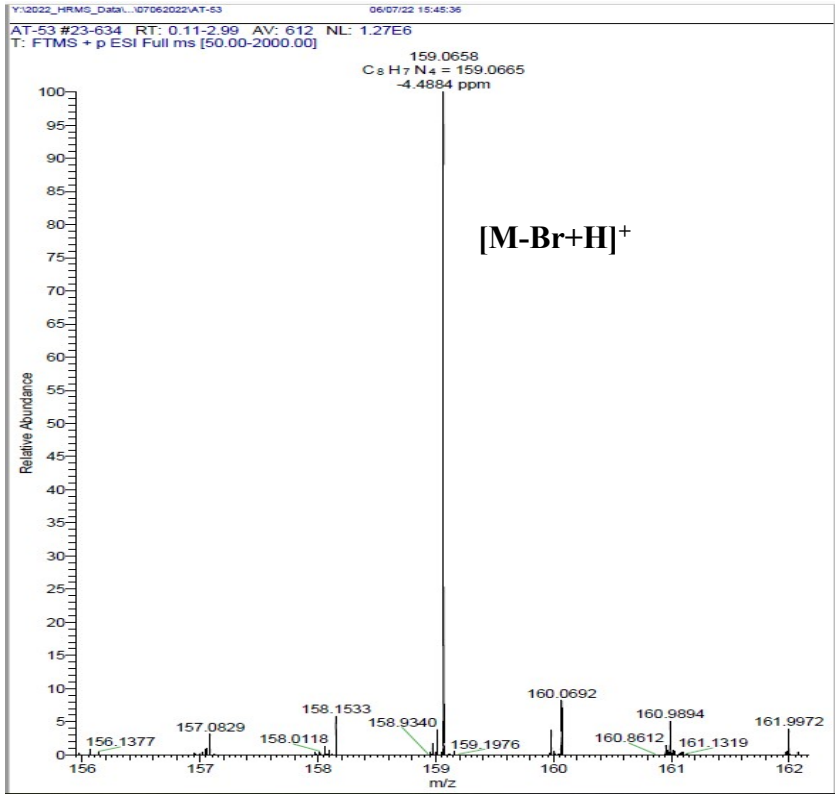


Fig S41: HRMS of compound **3r**.

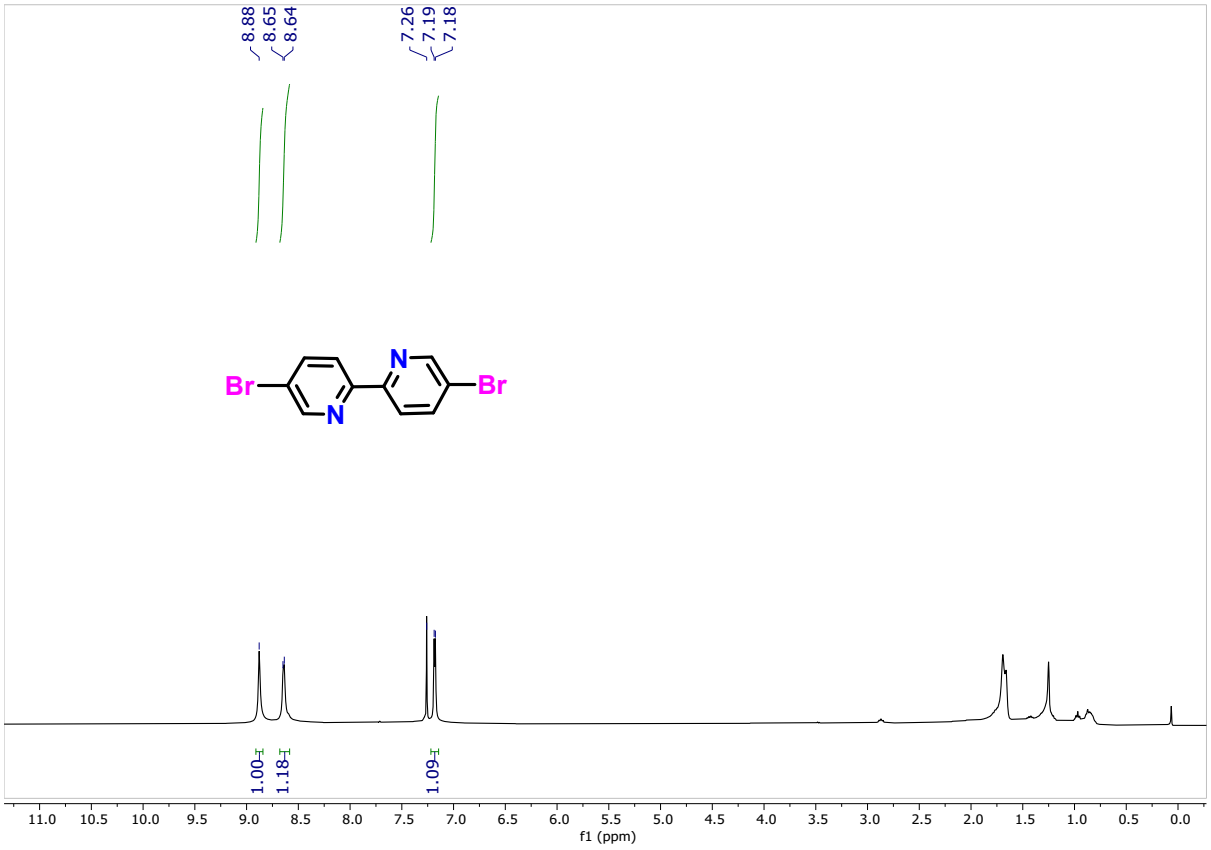


Fig S42: ^{1}H NMR spectra of compound **3s** in $CDCl_3$.

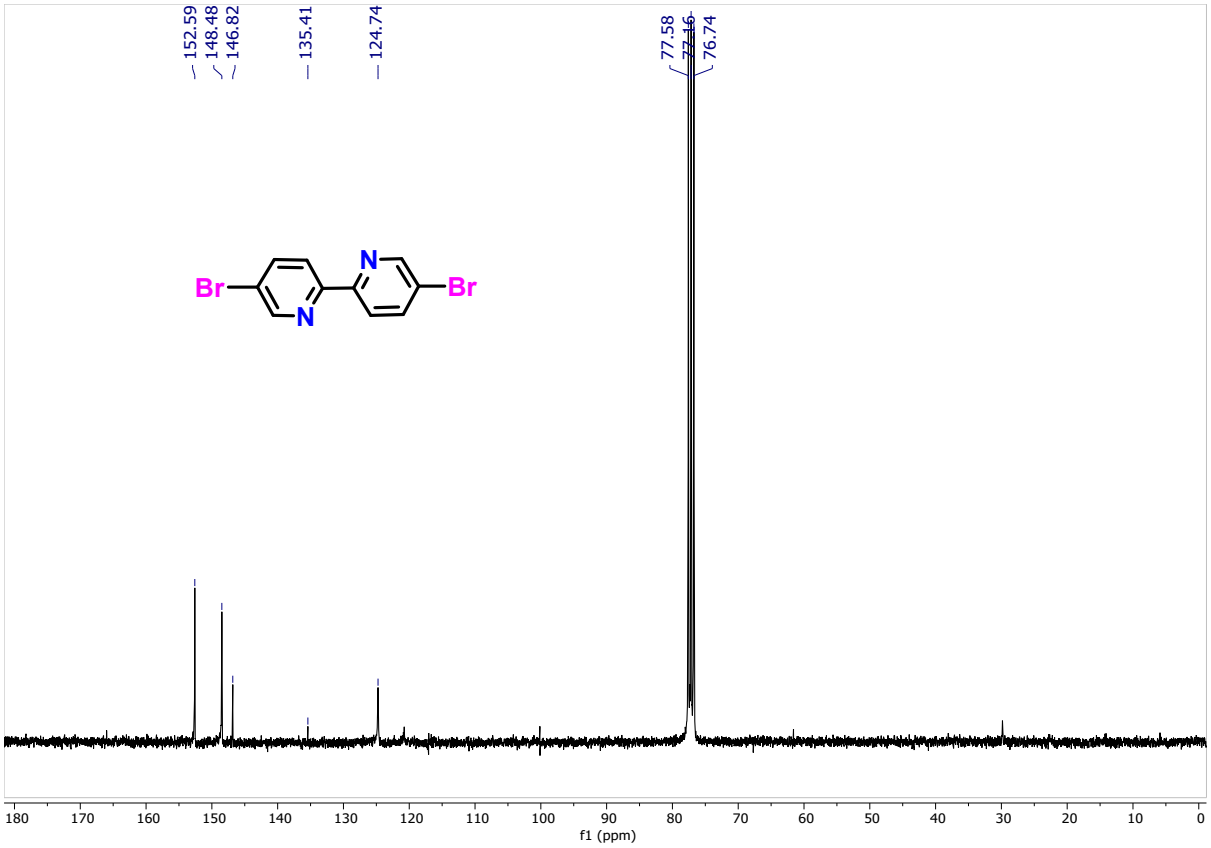


Fig S43: ^{13}C NMR spectra of compound **3s** in $CDCl_3$.

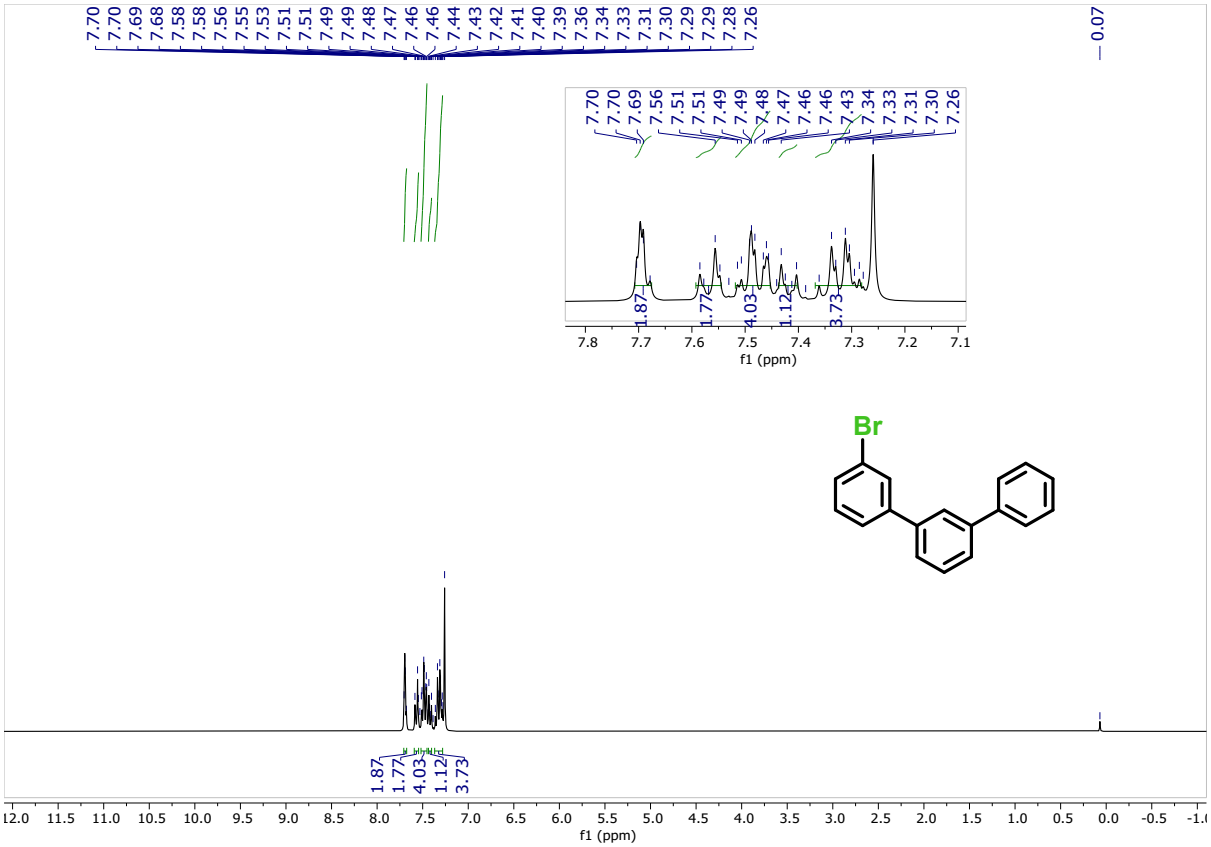


Fig S44: ^{1}H NMR spectra of compound **3t** in $CDCl_3$.

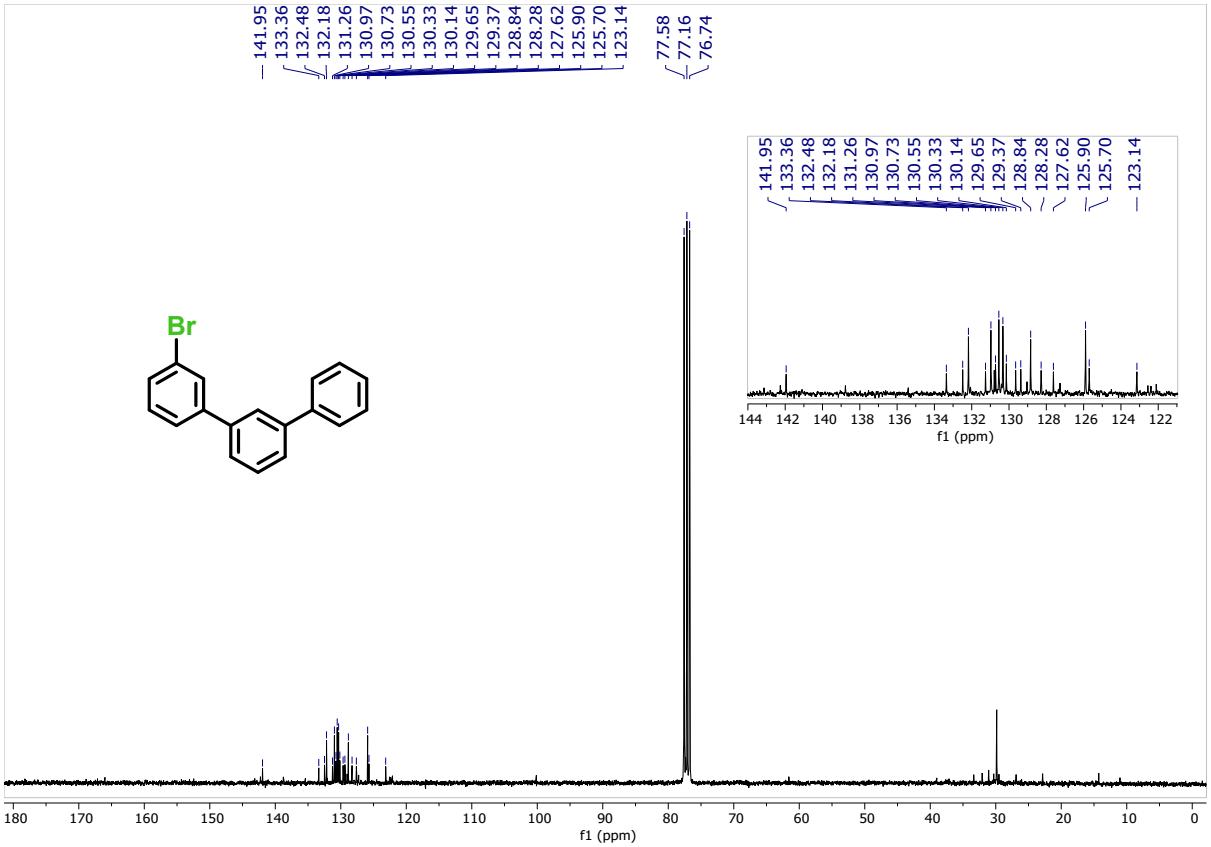


Fig S45: ^{13}C NMR spectra of compound **3t** in $CDCl_3$.

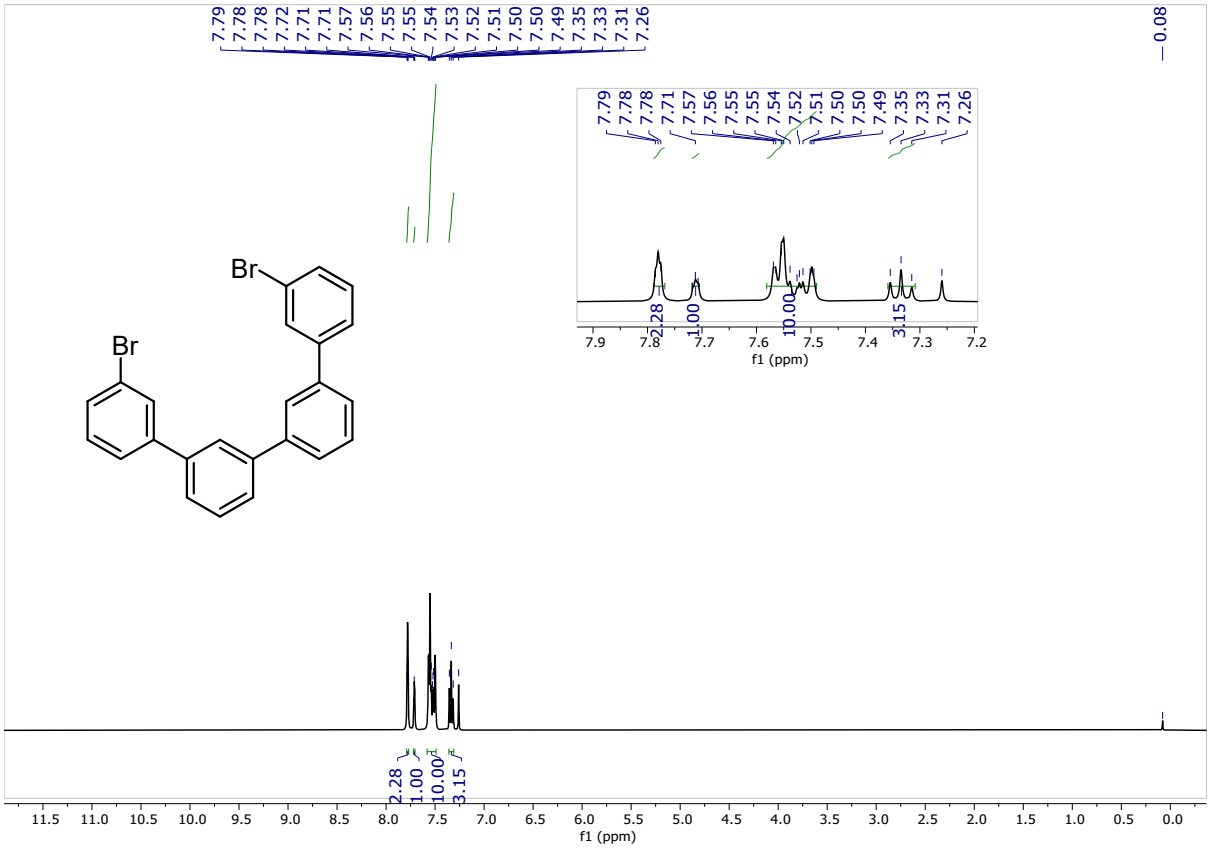


Fig S46: ^{1}H NMR spectra of compound **3u** in $CDCl_3$.

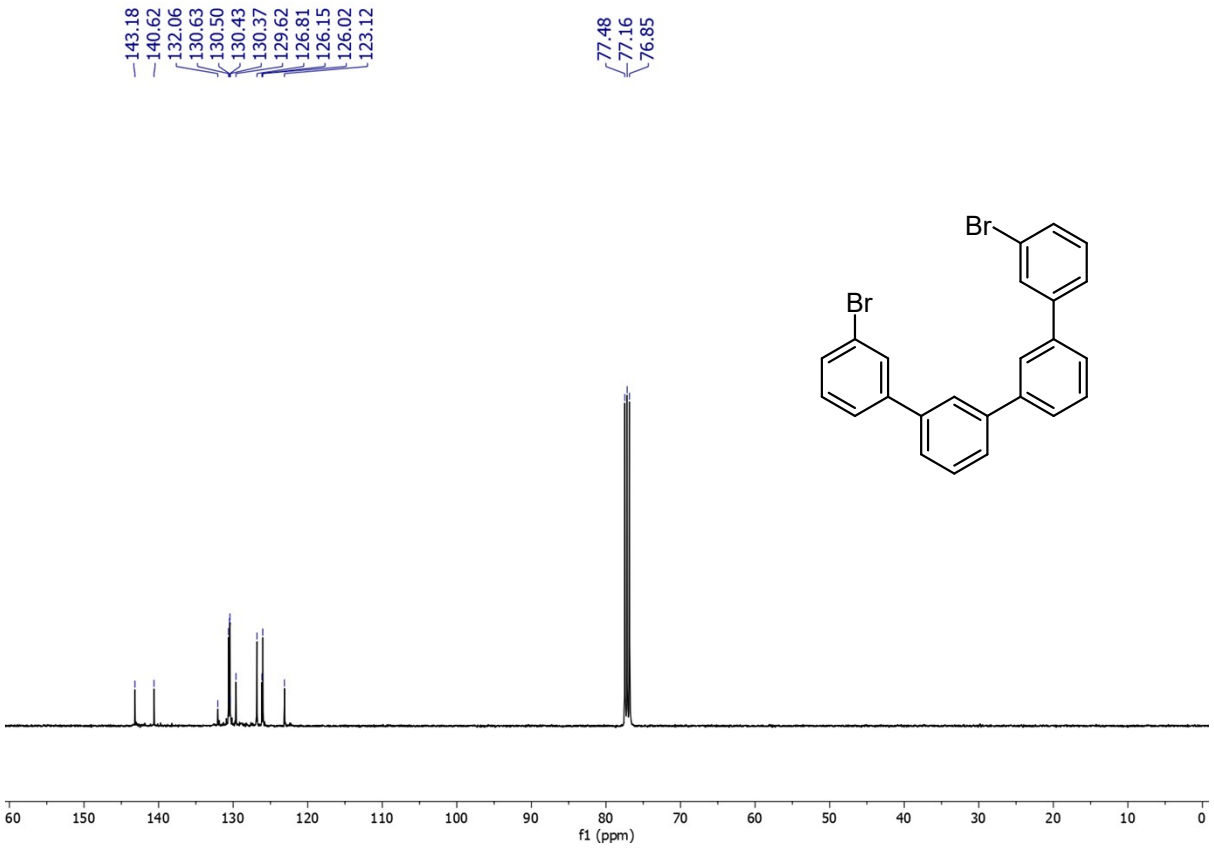


Fig S47: ^{13}C NMR spectra of compound **3u** in $CDCl_3$.

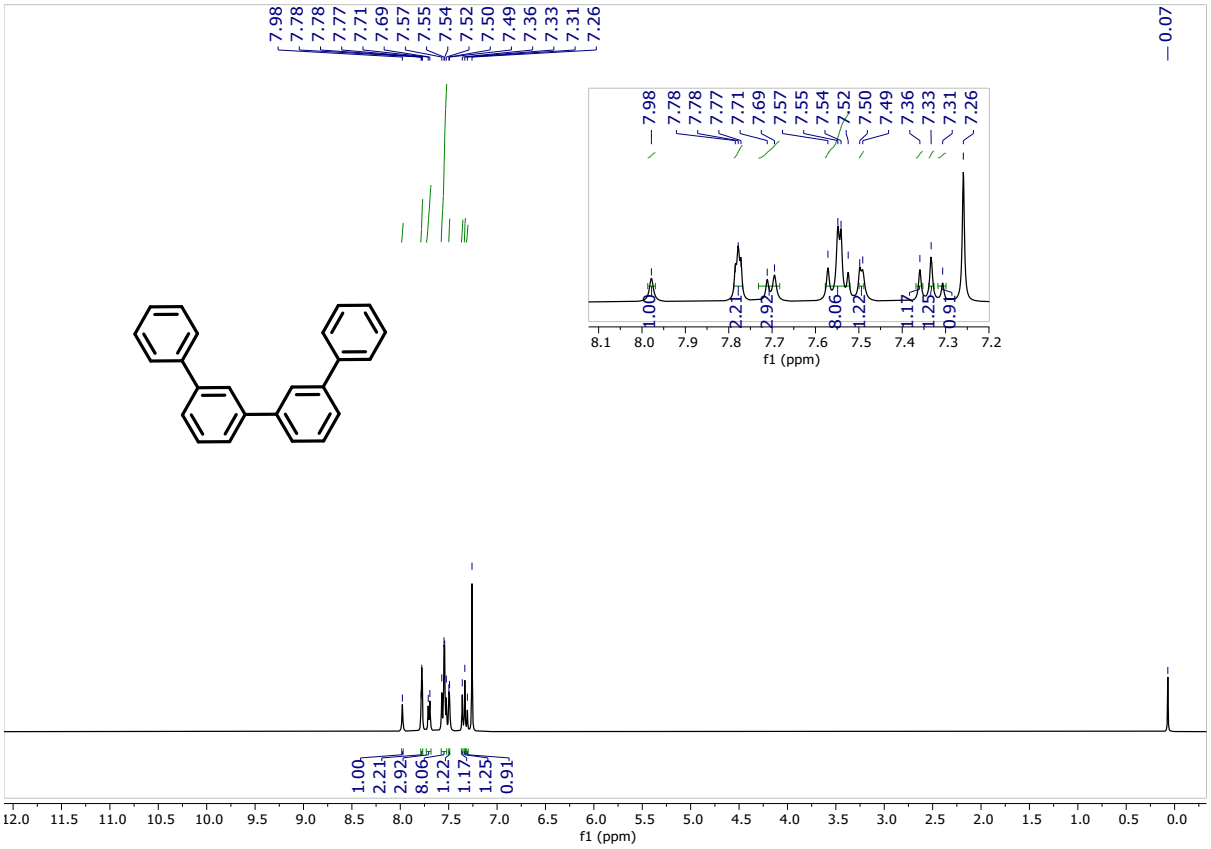


Fig S48: ^{1}H NMR spectra of compound **3v** in $CDCl_3$.

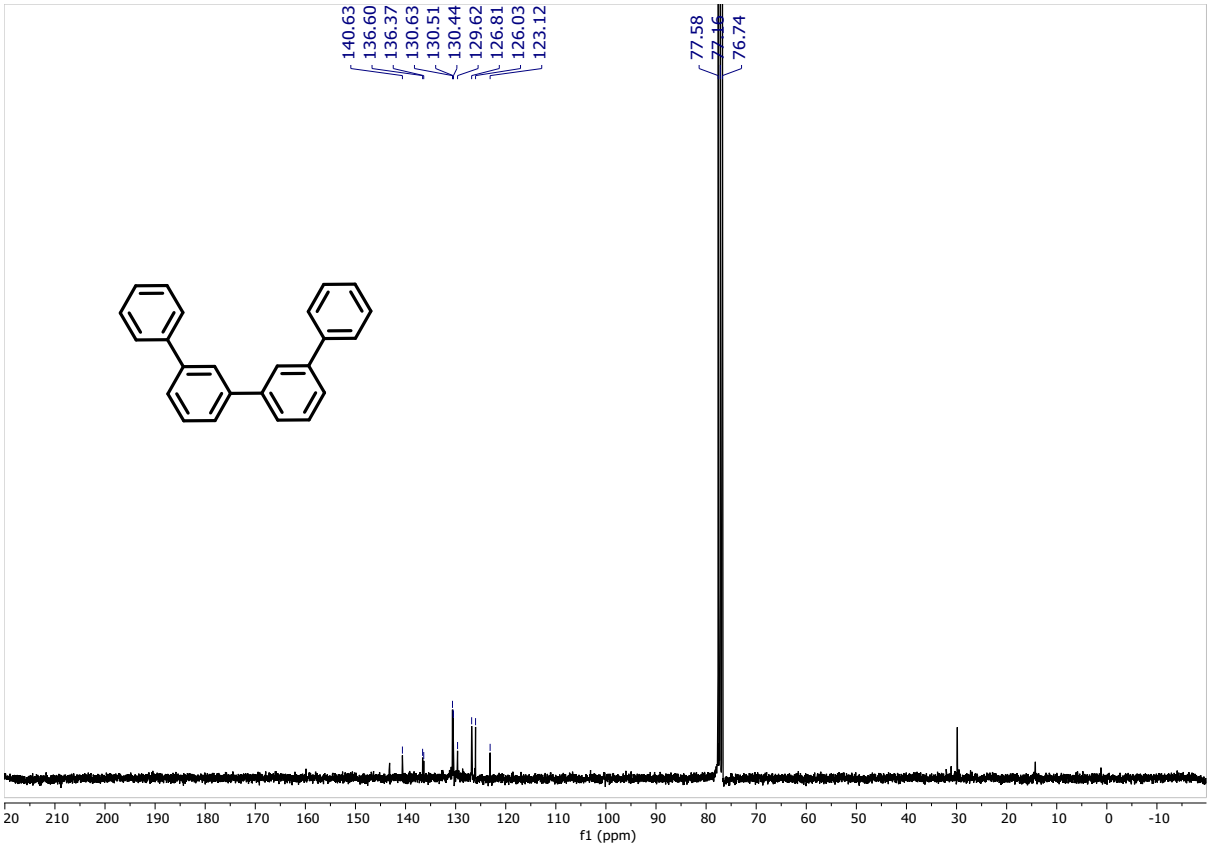


Fig S49: ^{13}C NMR spectra of compound **3v** in $CDCl_3$.

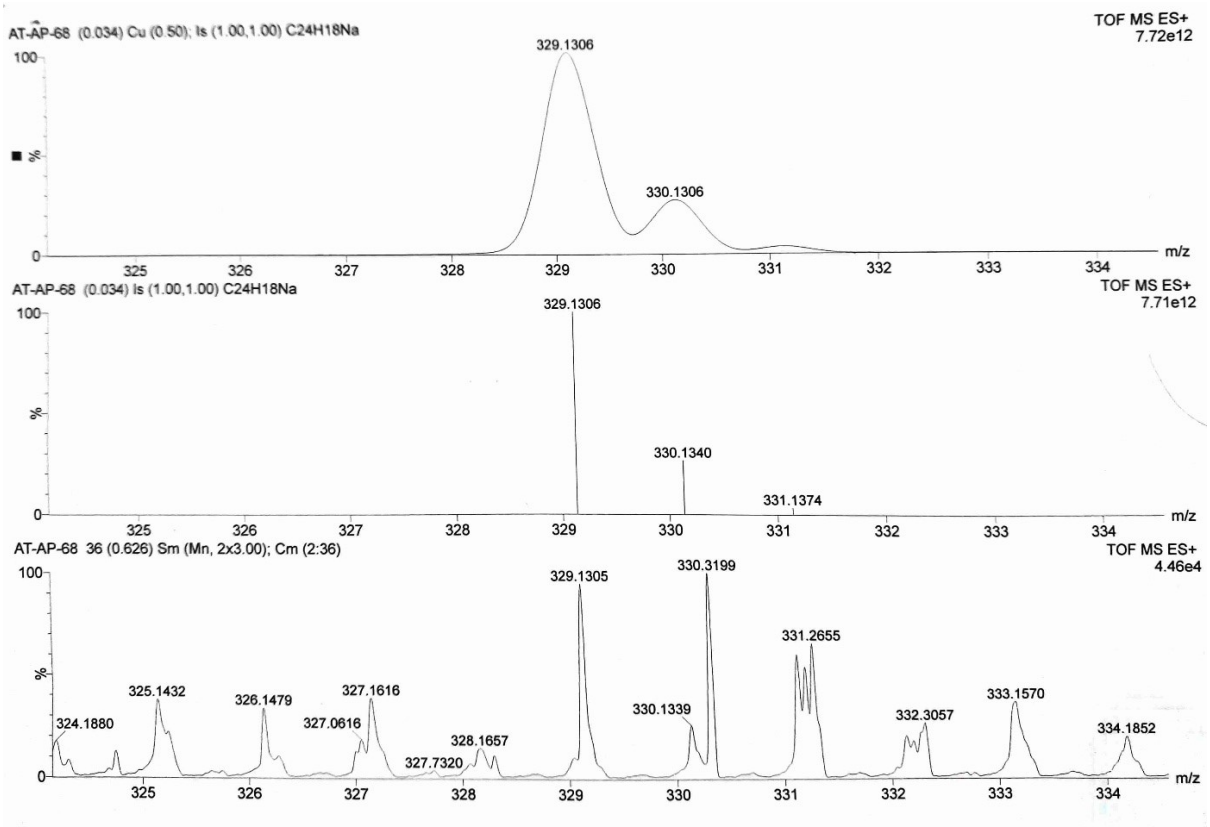


Fig S50: HRMS of compound **3v** $[M+Na]^+$.

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