Supporting Information

Biaryl Formation via Base-Promoted Direct Coupling Reactions of Arenes with Aryl Halides

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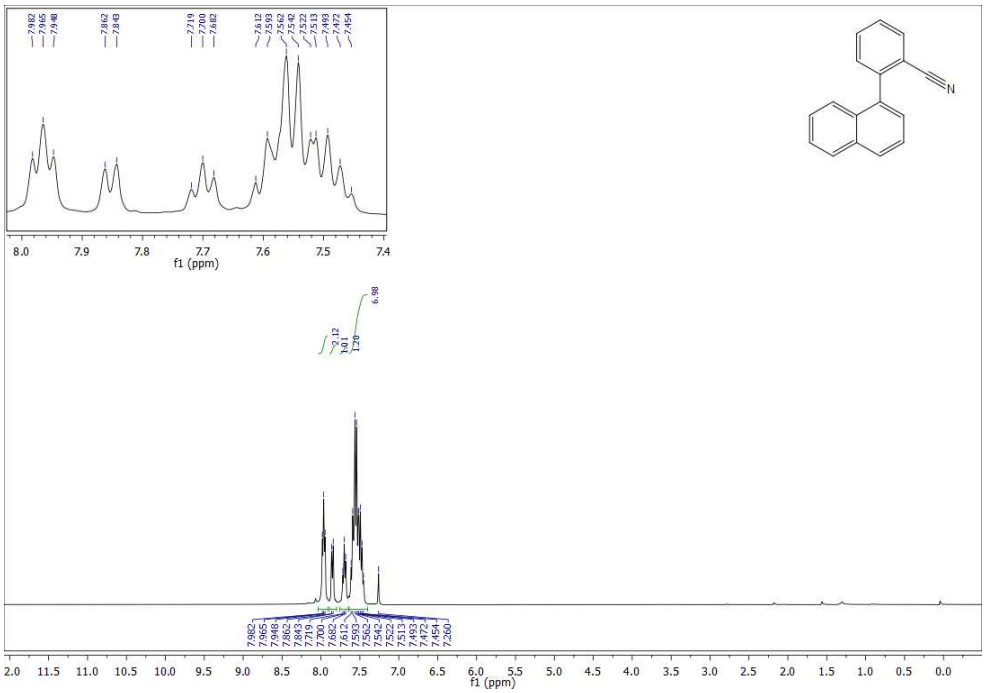


Figure S2: ^{13}C-NMR spectrum of **3aa** (100 MHz, $CDCl_3$)

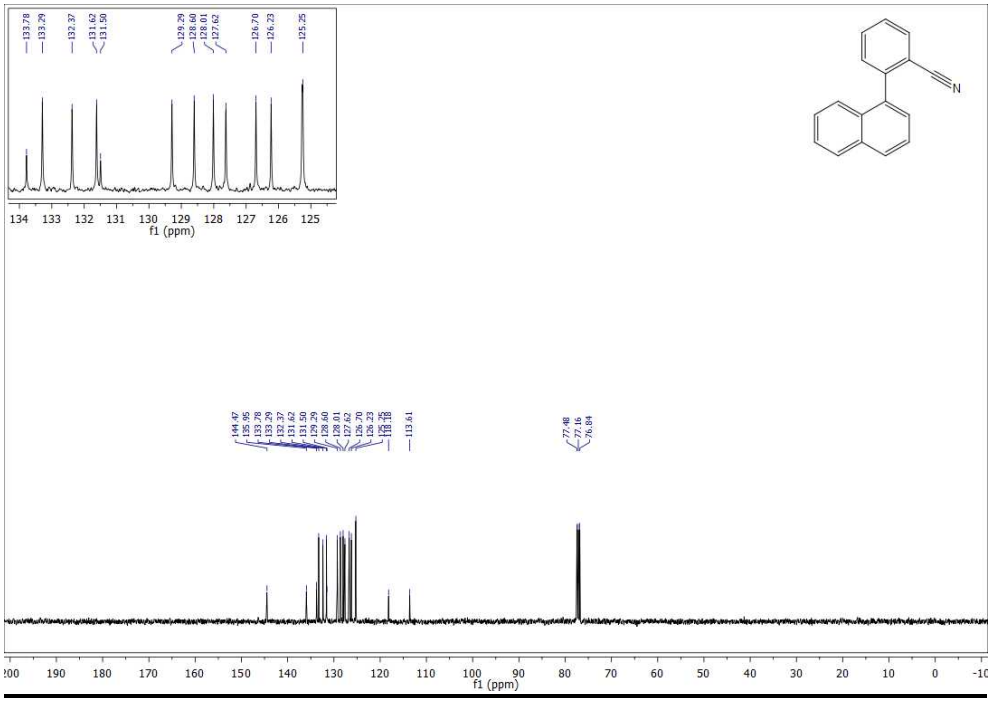


Figure S3: ^{1}H-NMR spectrum of **3ab** (400 MHz, $CDCl_3$)

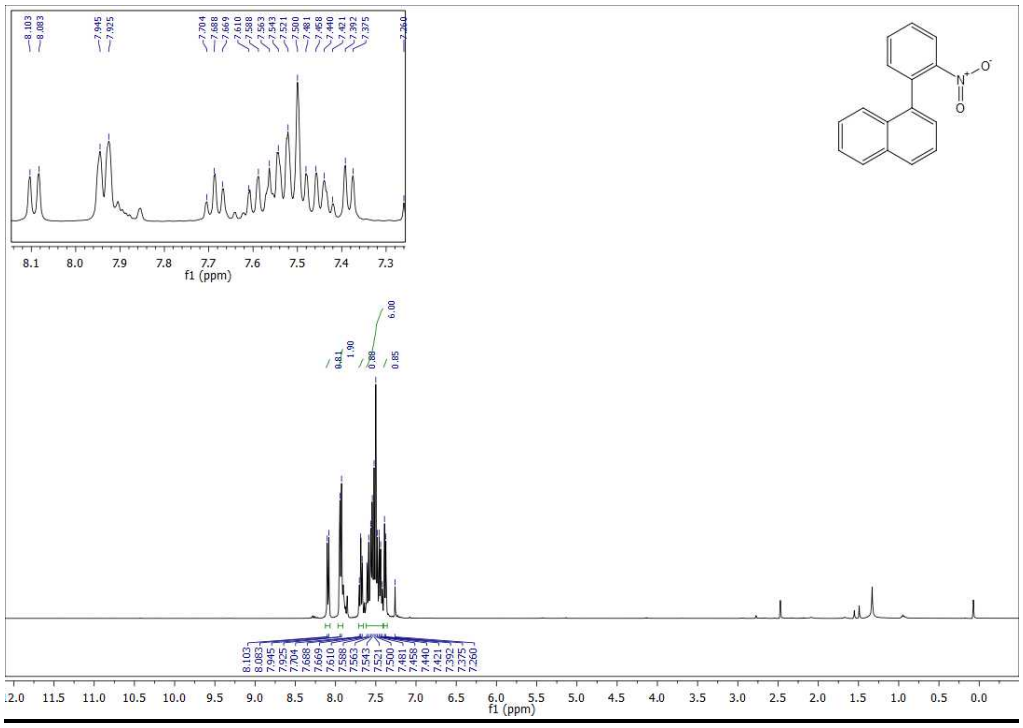
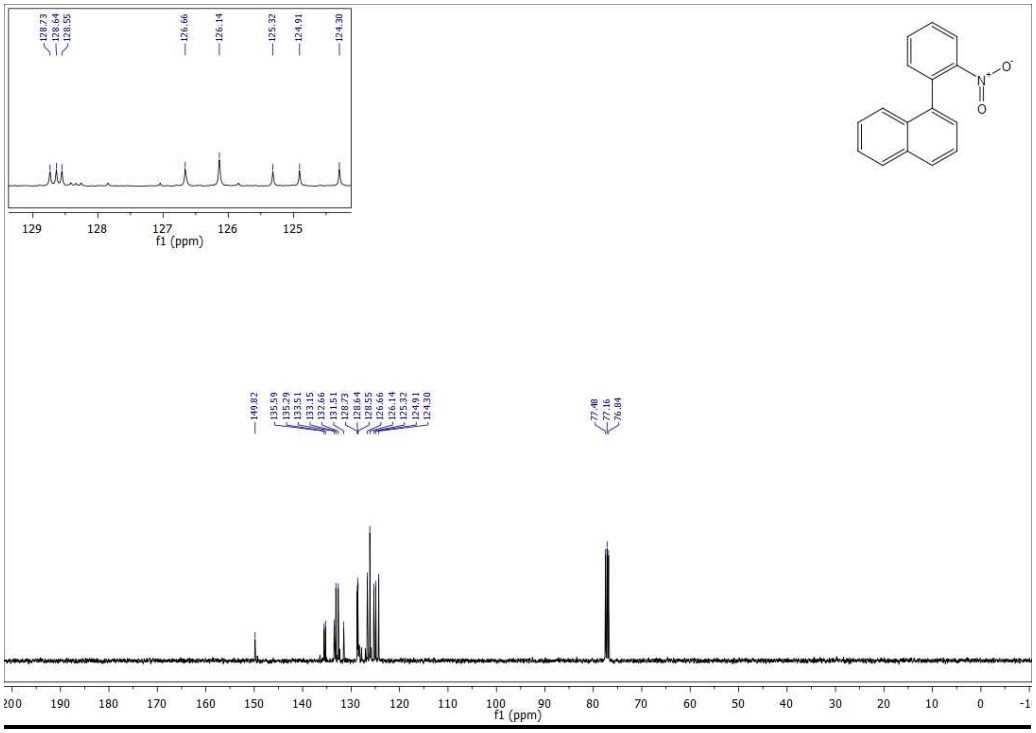


Figure S4: ^{13}C-NMR spectrum of **3ab** (100 MHz, $CDCl_3$)



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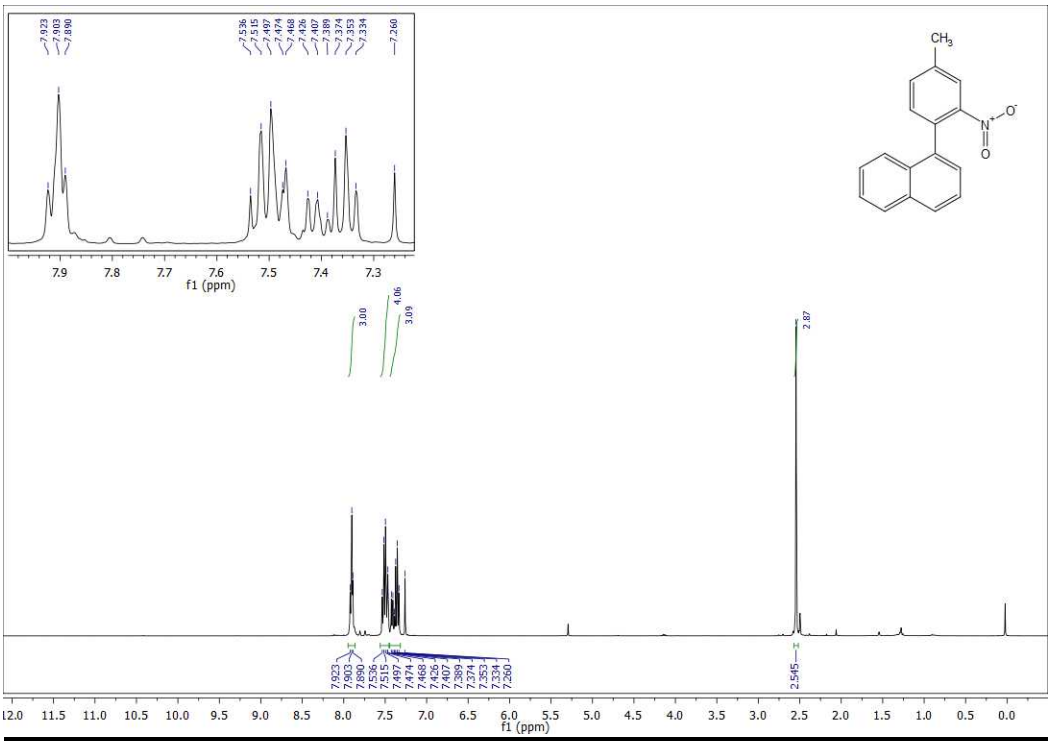

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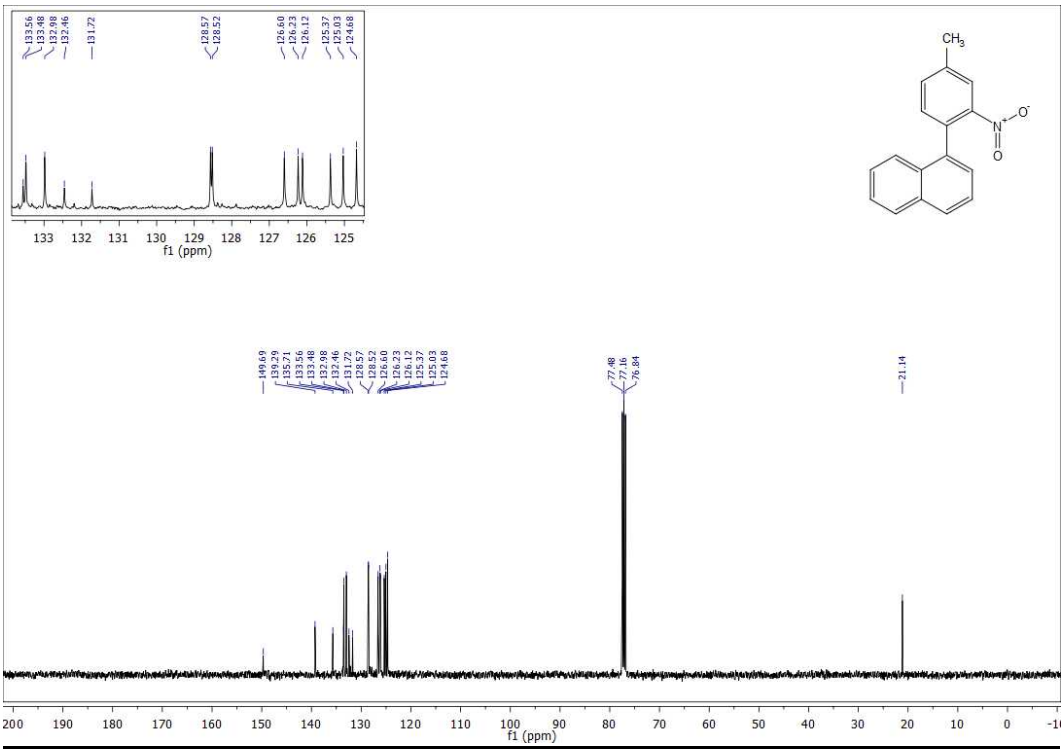

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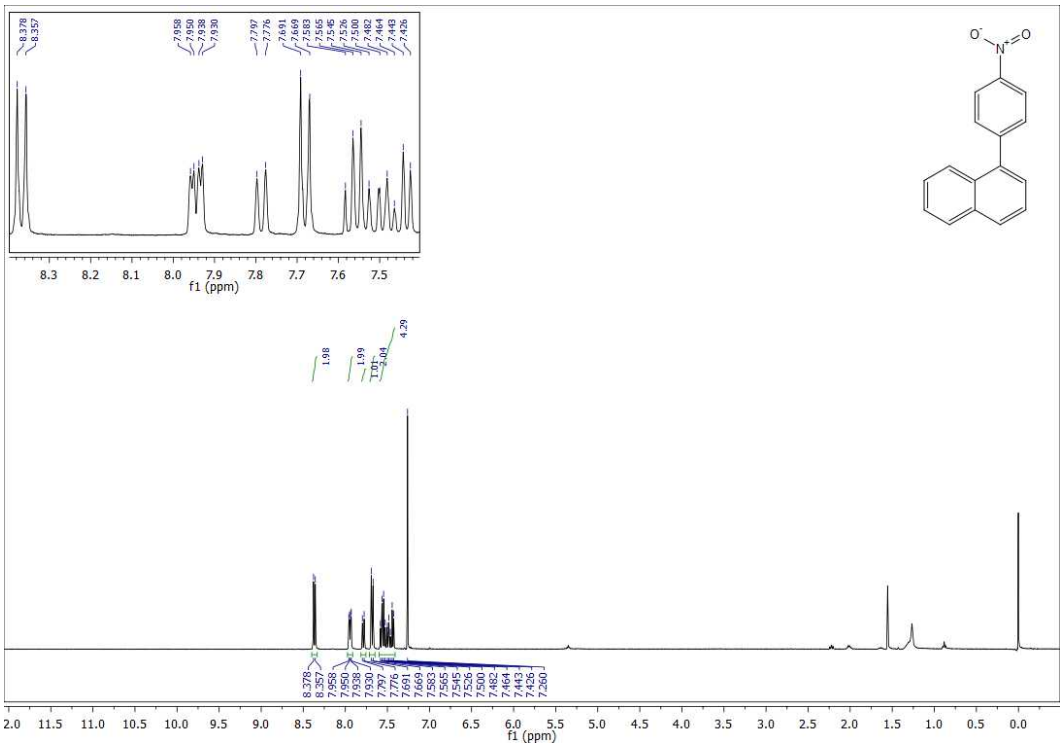

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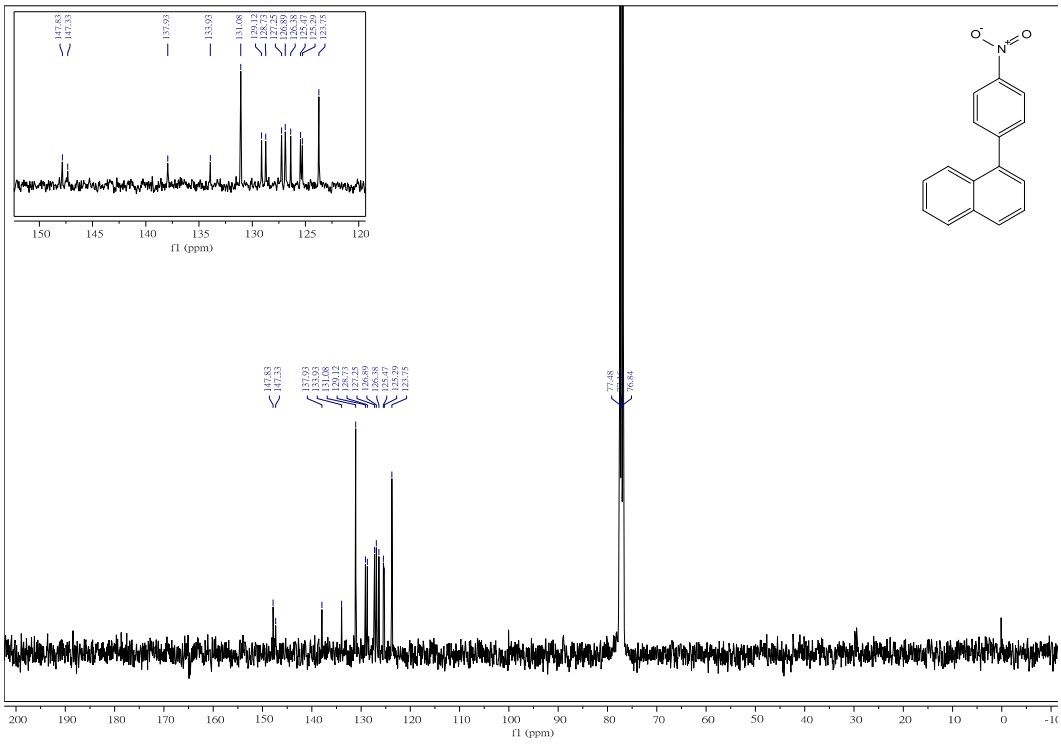

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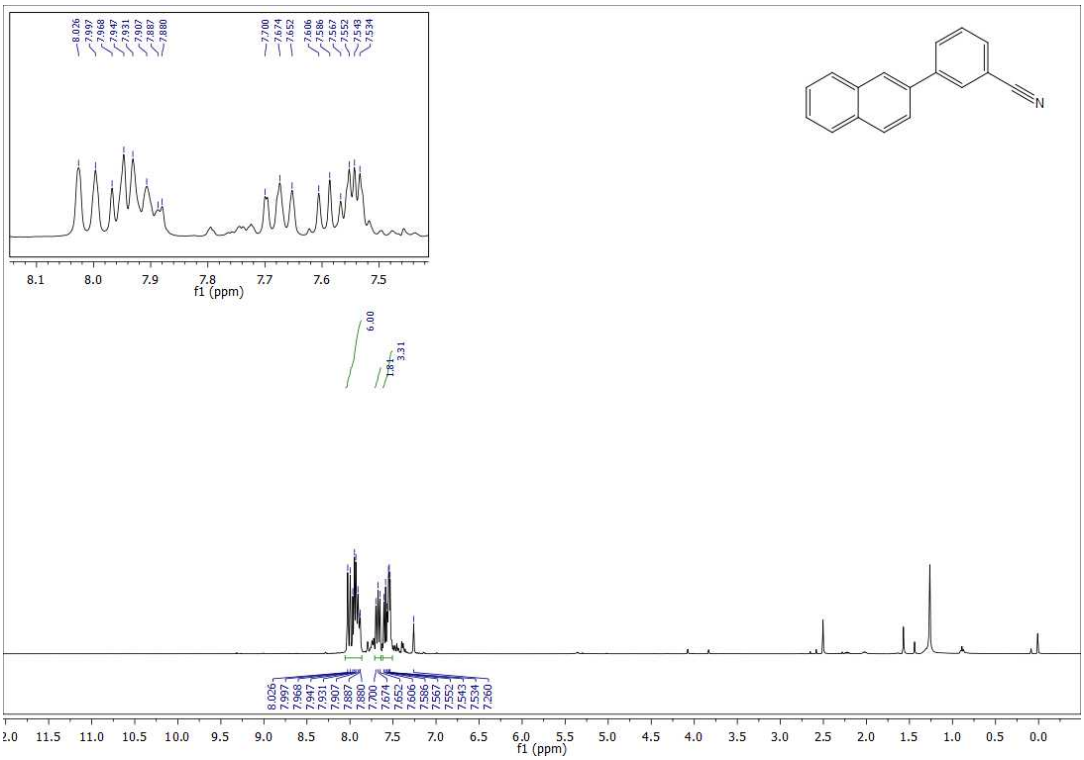

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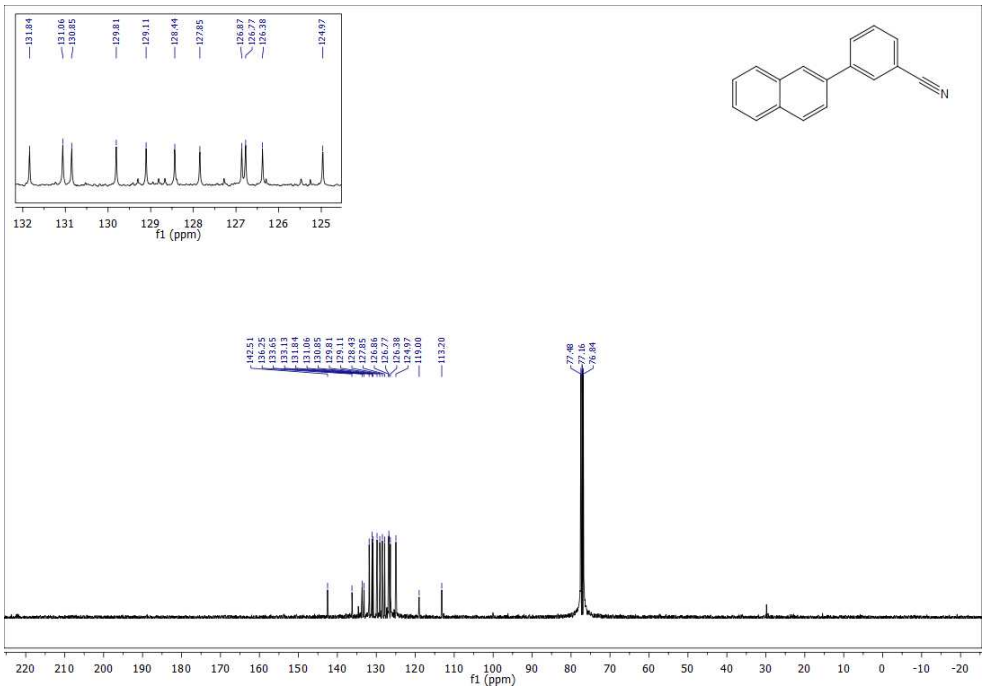


Figure S11: ^{1}H-NMR spectrum of **3af** (400 MHz, $CDCl_3$)

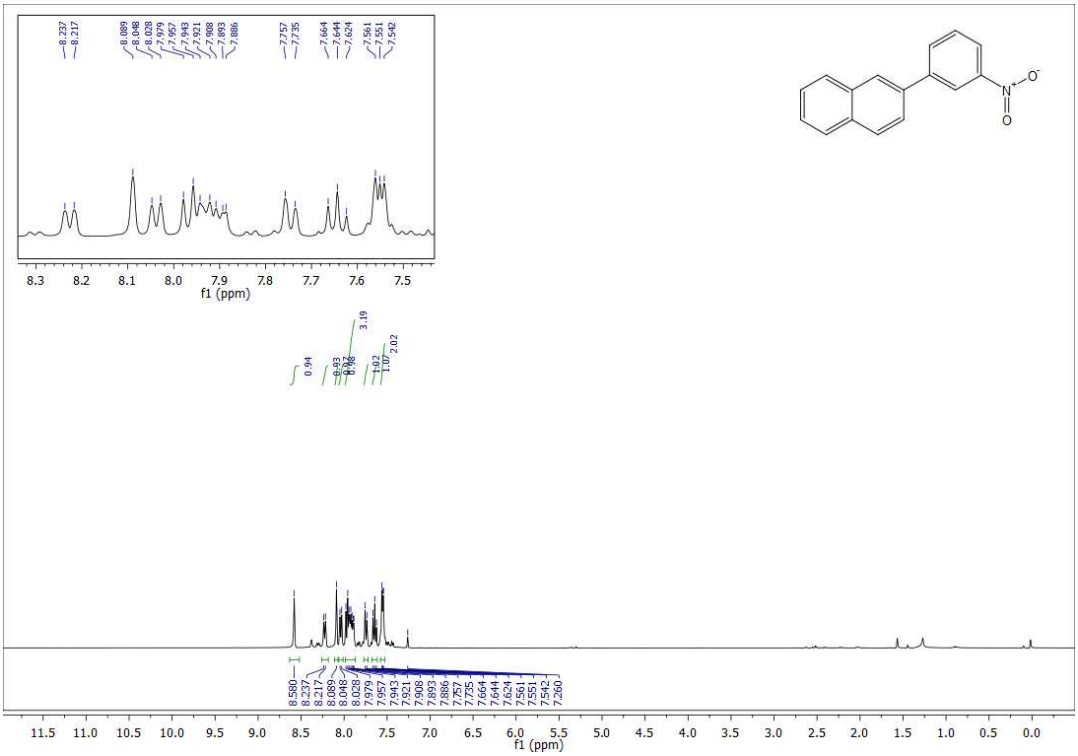
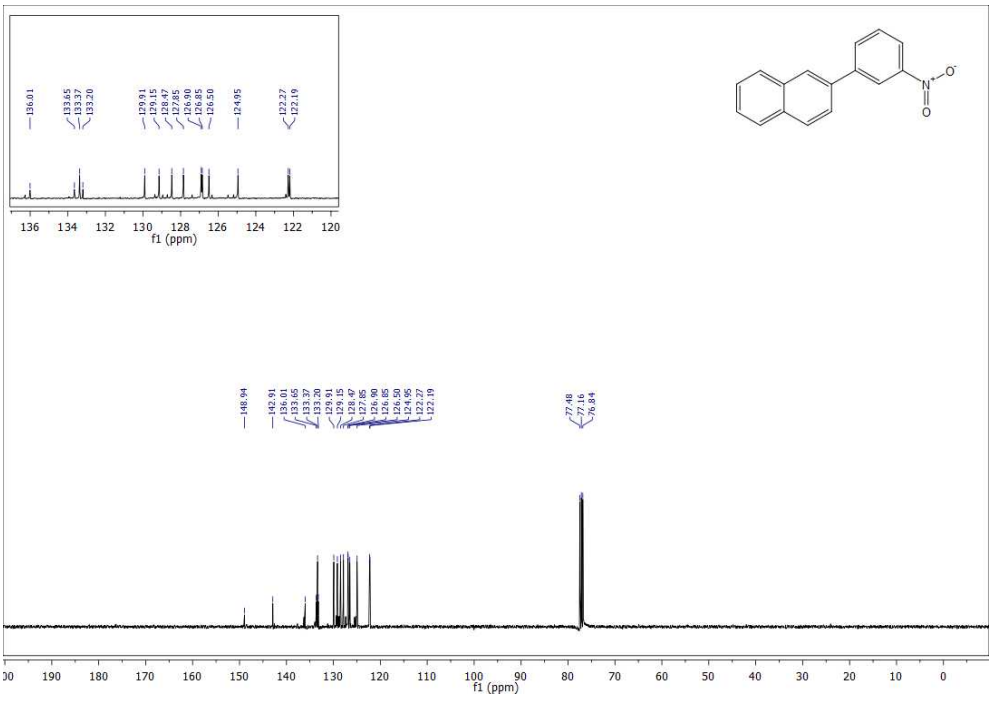


Figure S12: ^{13}C-NMR spectrum of **3af** (100 MHz, $CDCl_3$)



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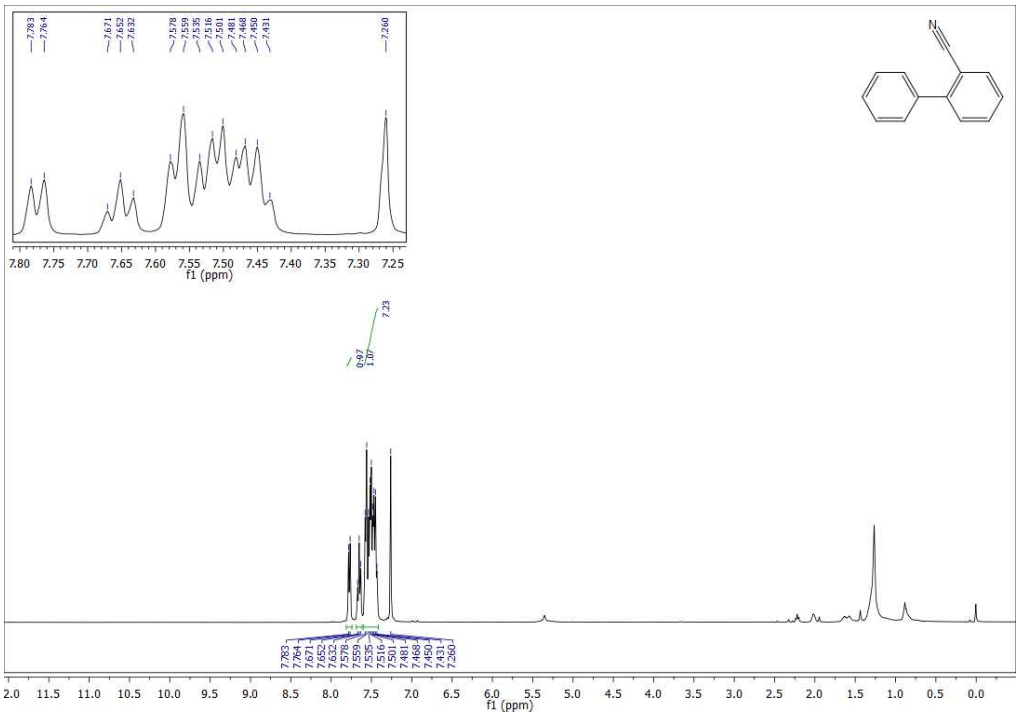

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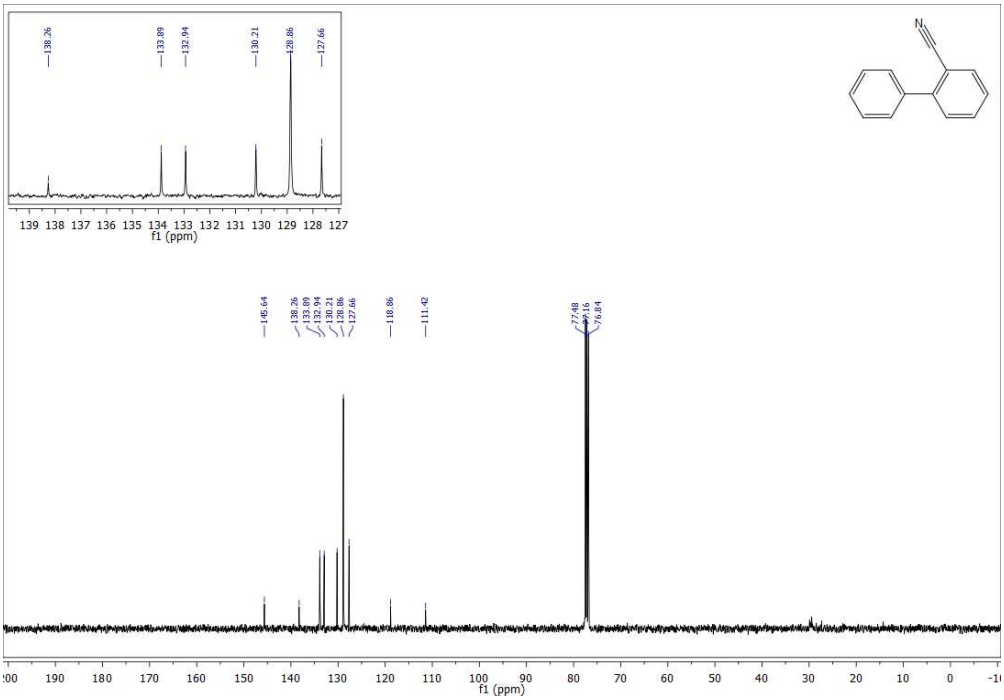
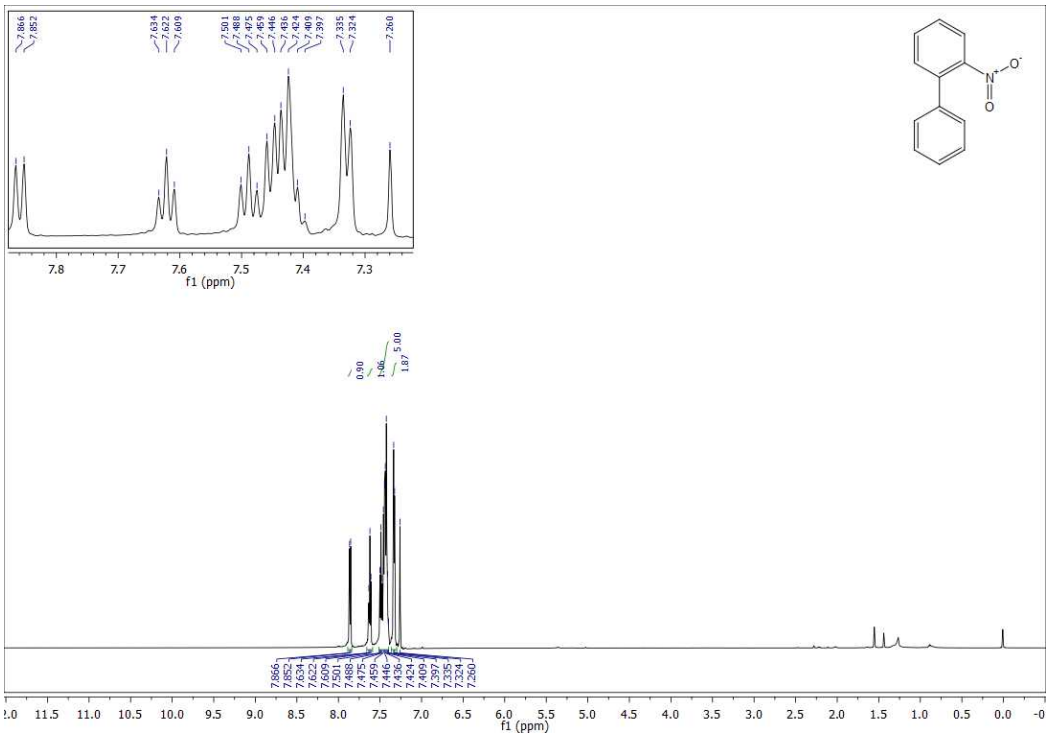


Figure S15: ^{1}H-NMR spectrum of **3bb** (600 MHz, $CDCl_3$)



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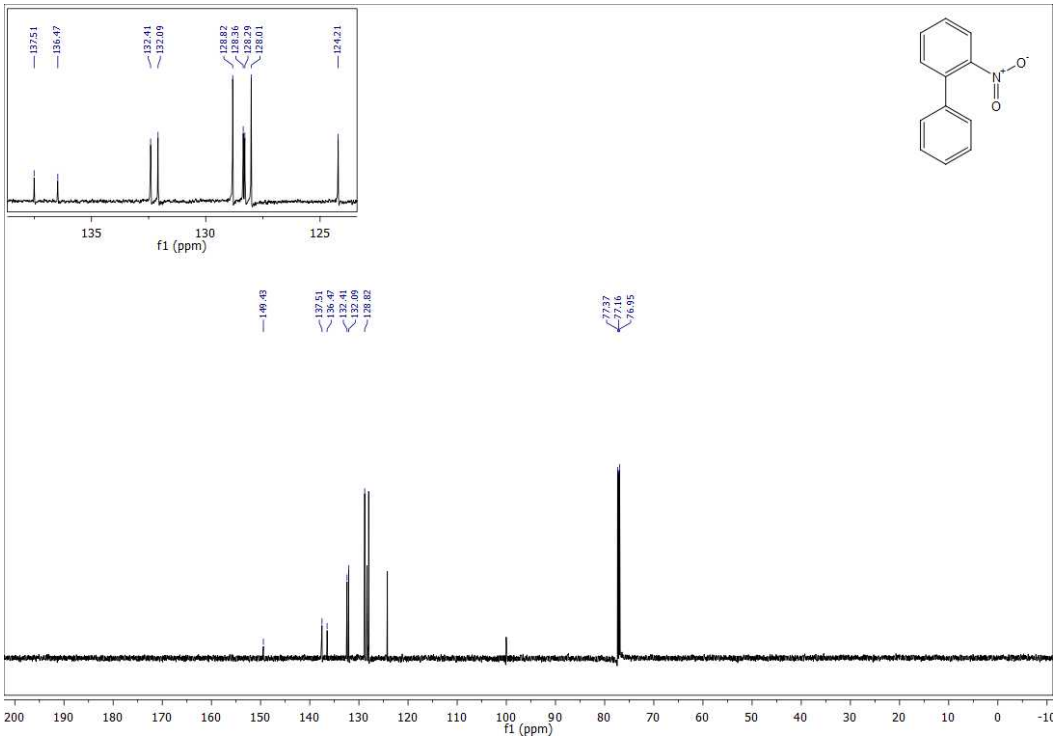

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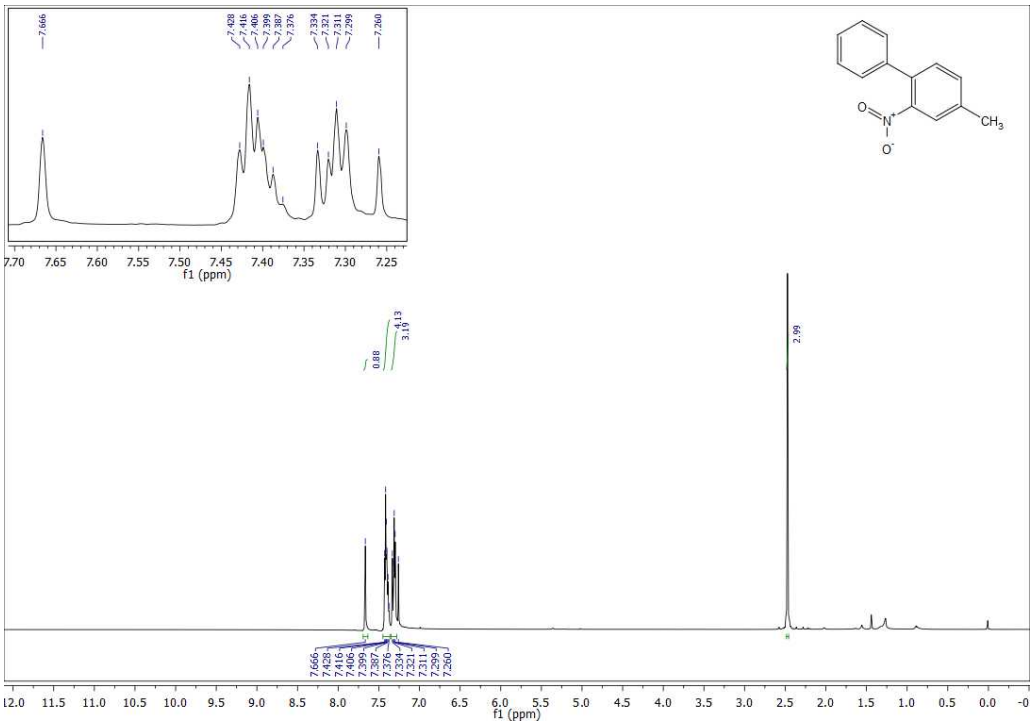

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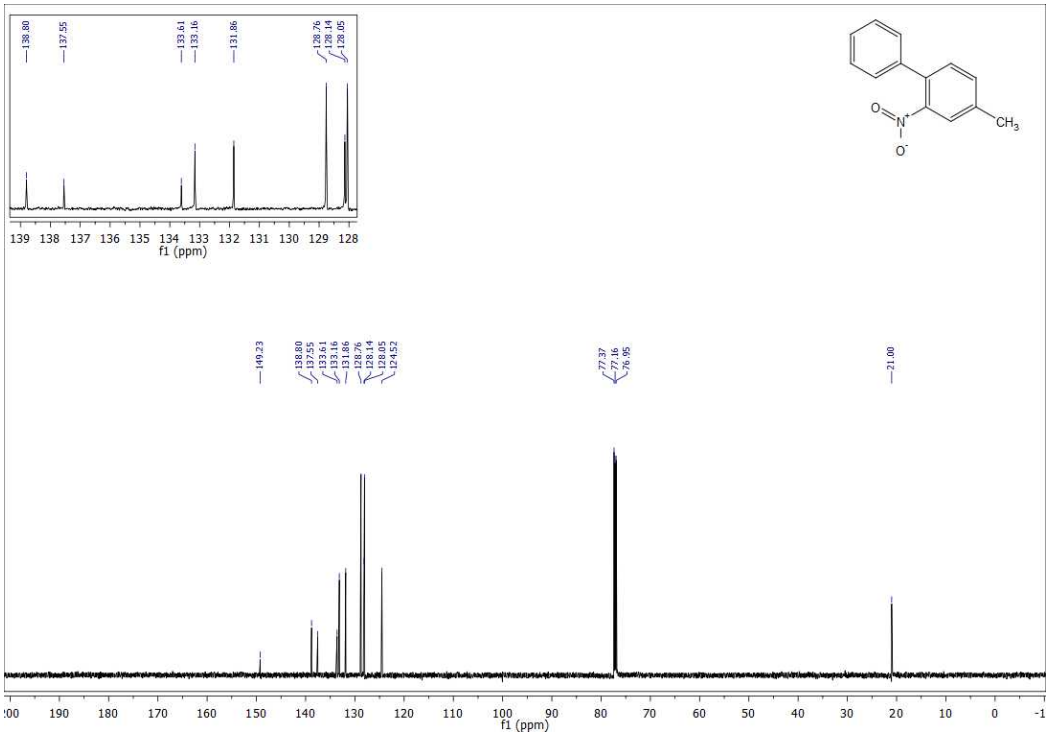

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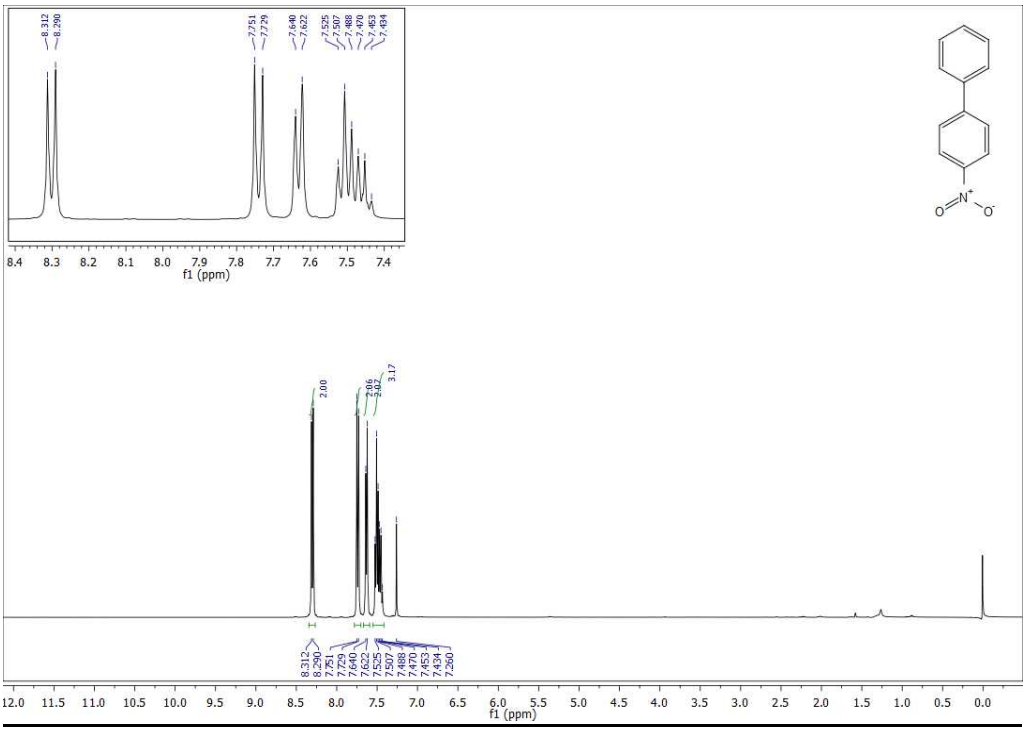

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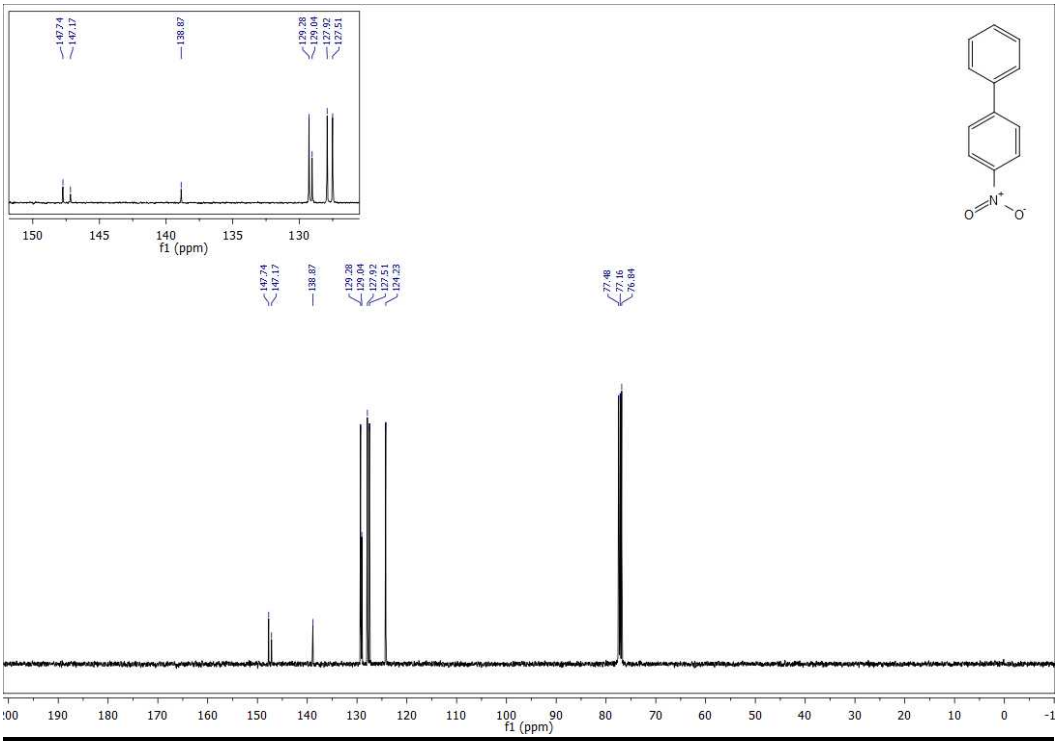

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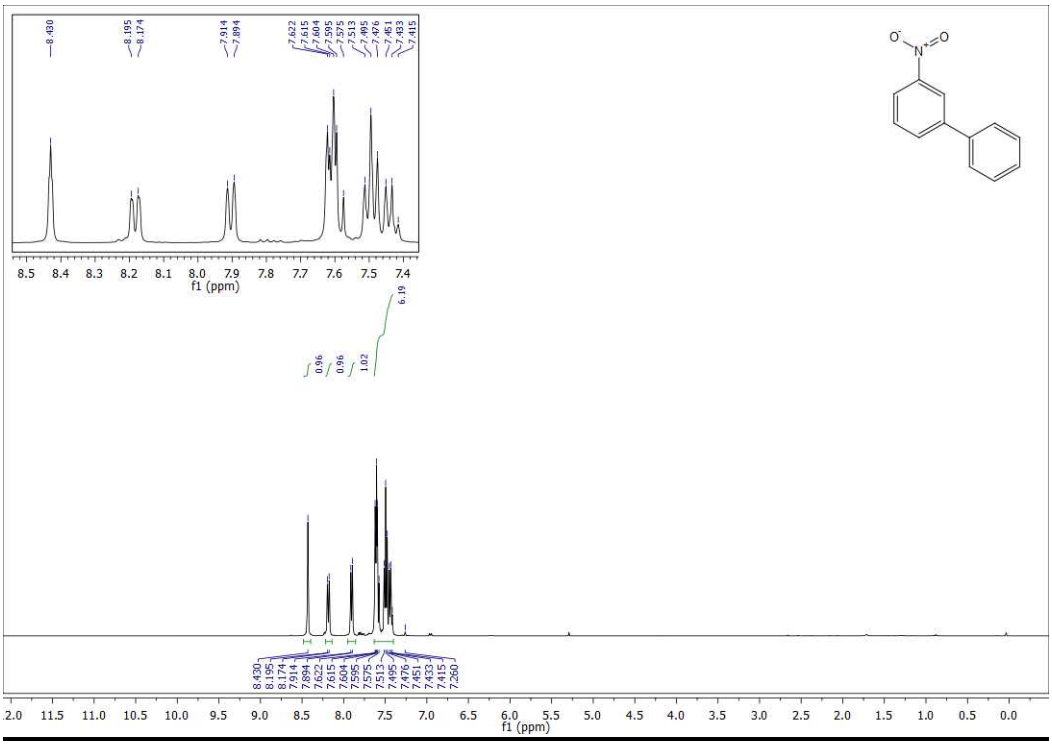

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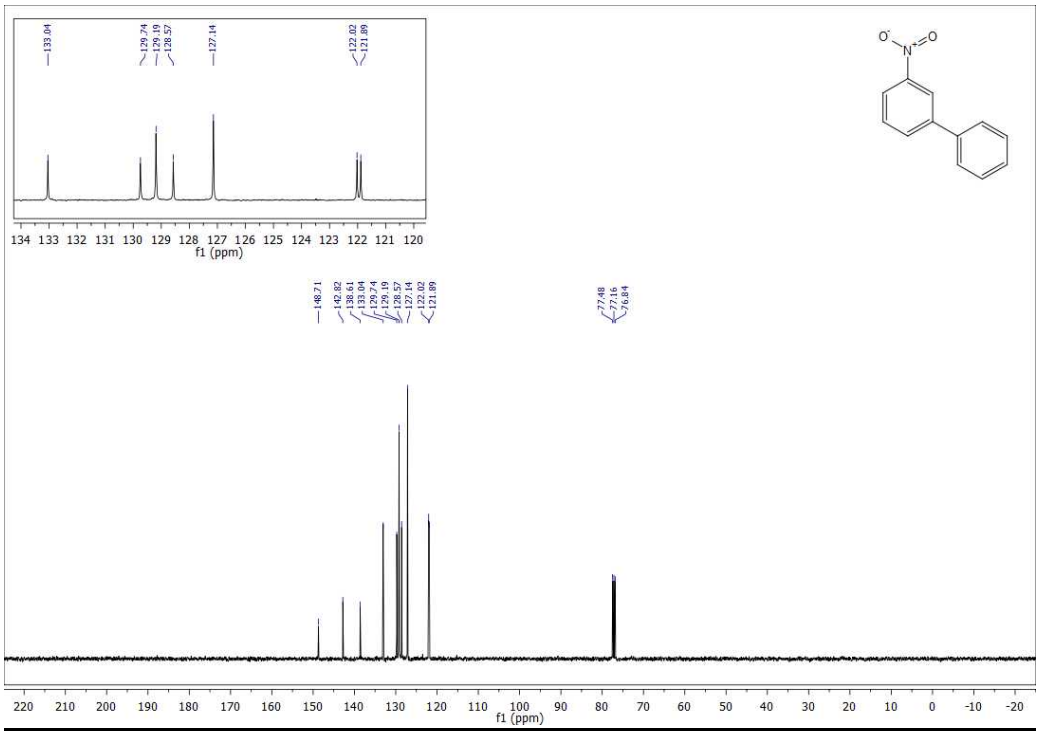

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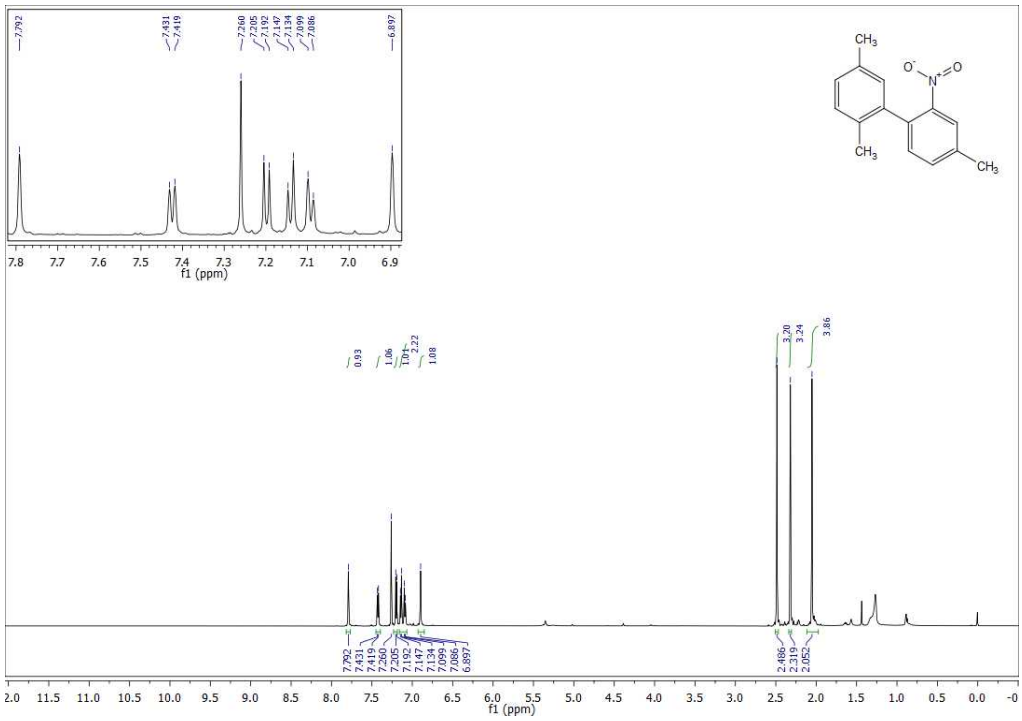

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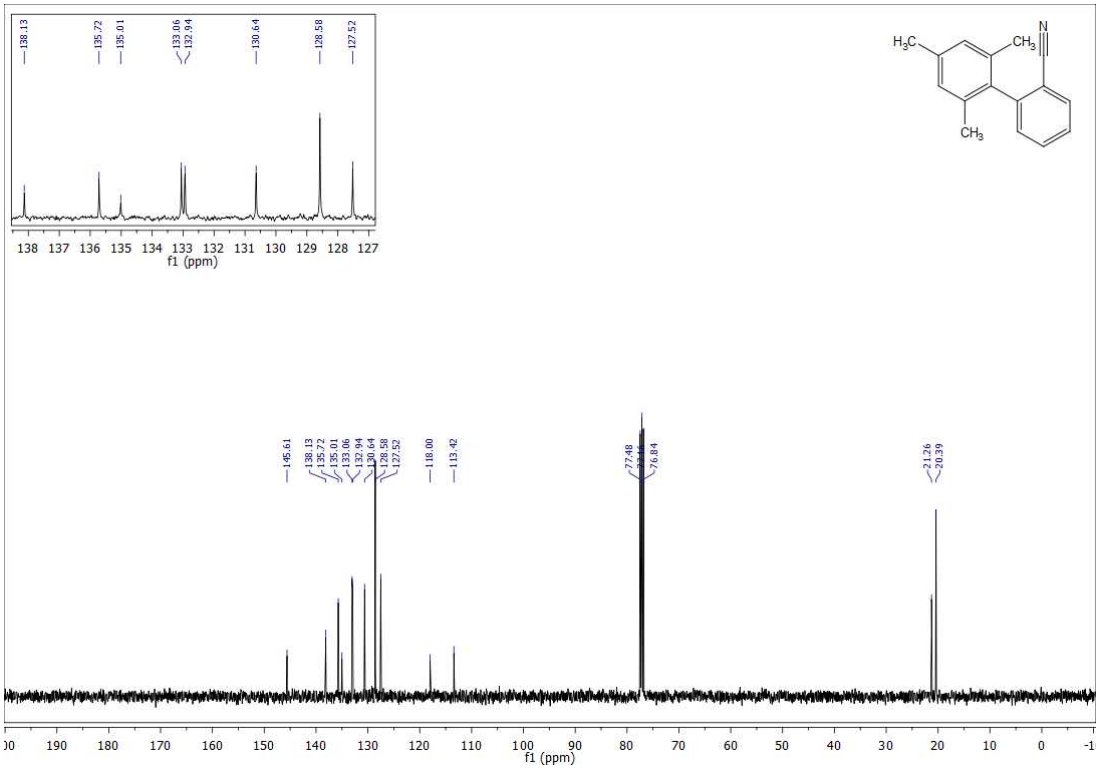

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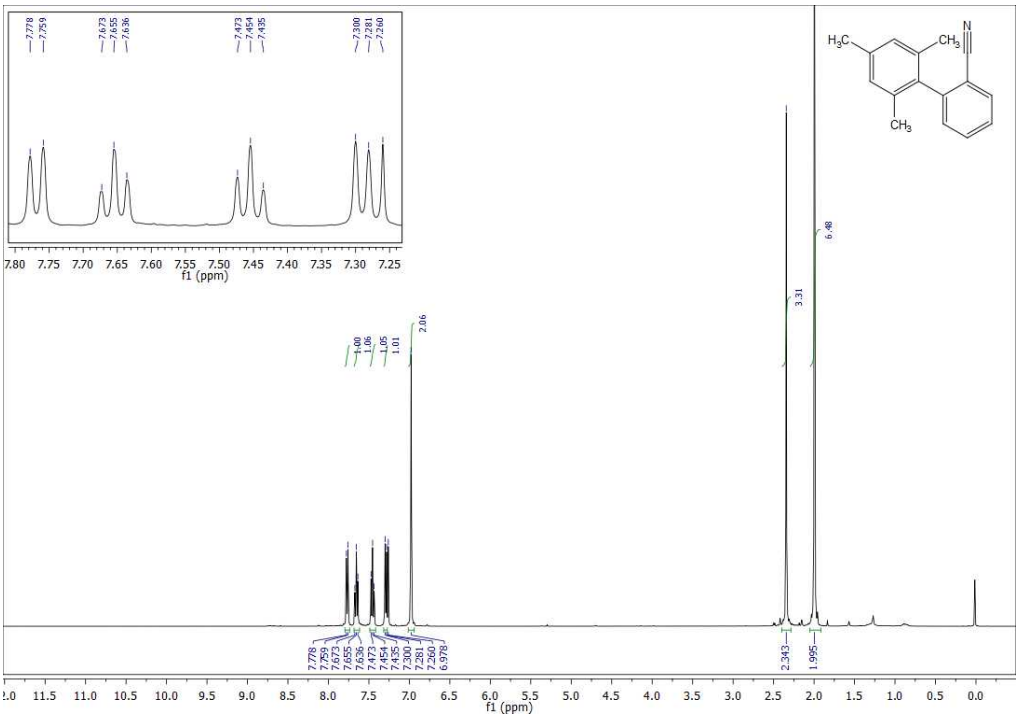

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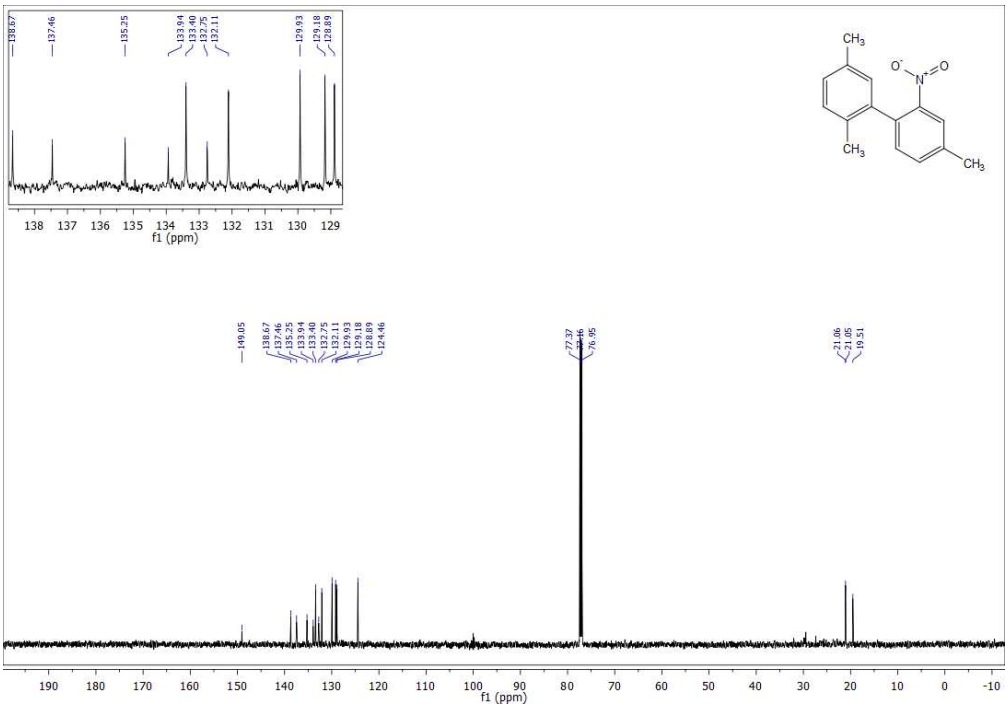

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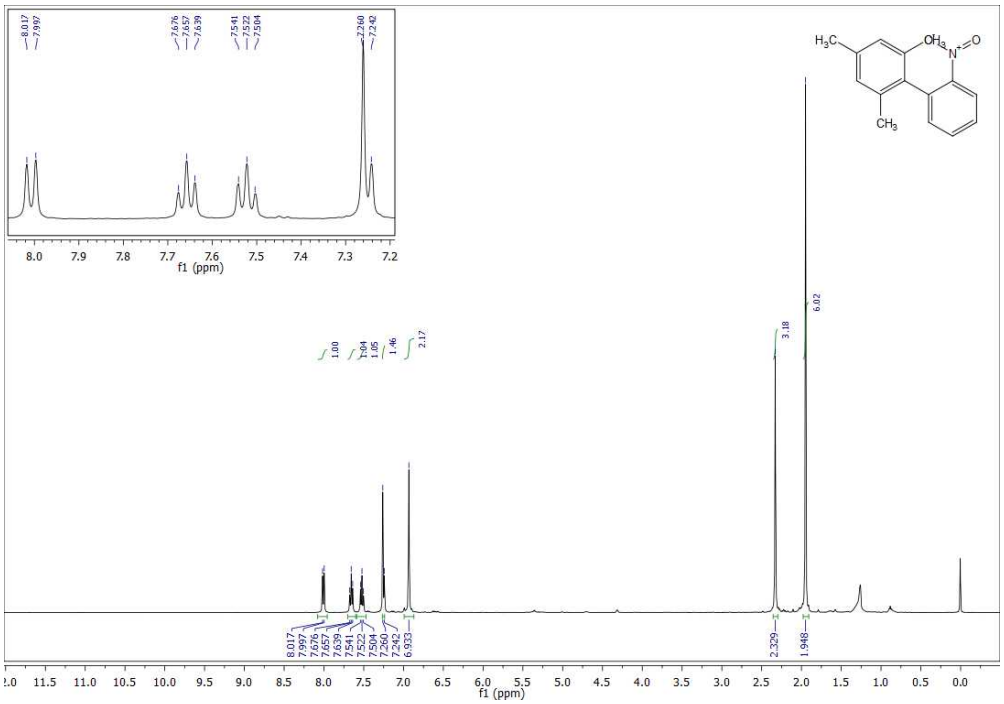

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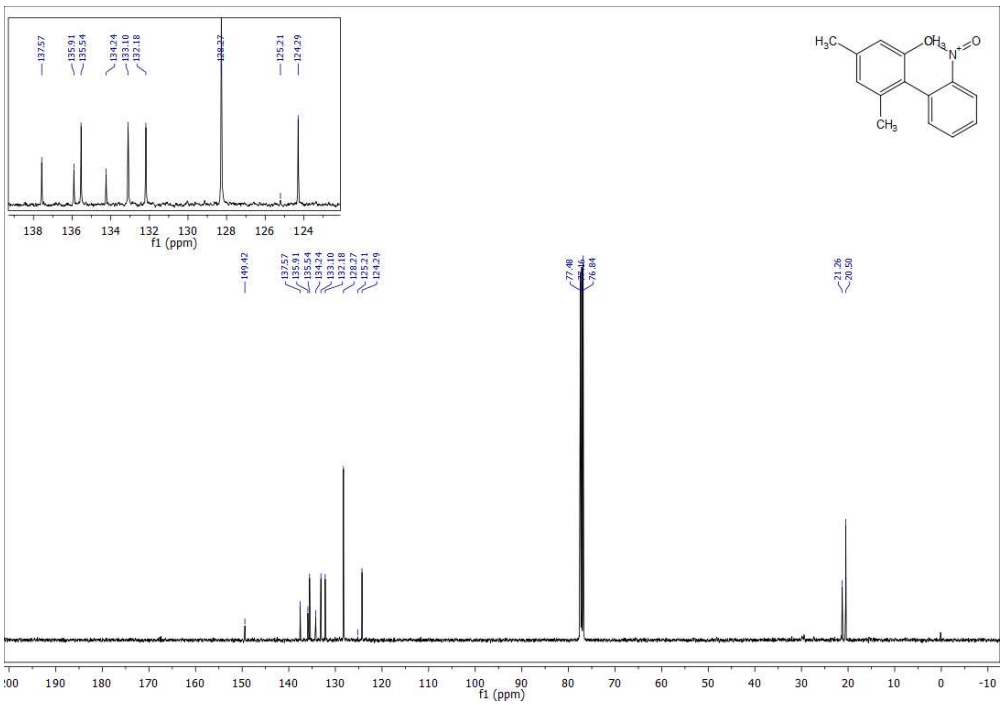

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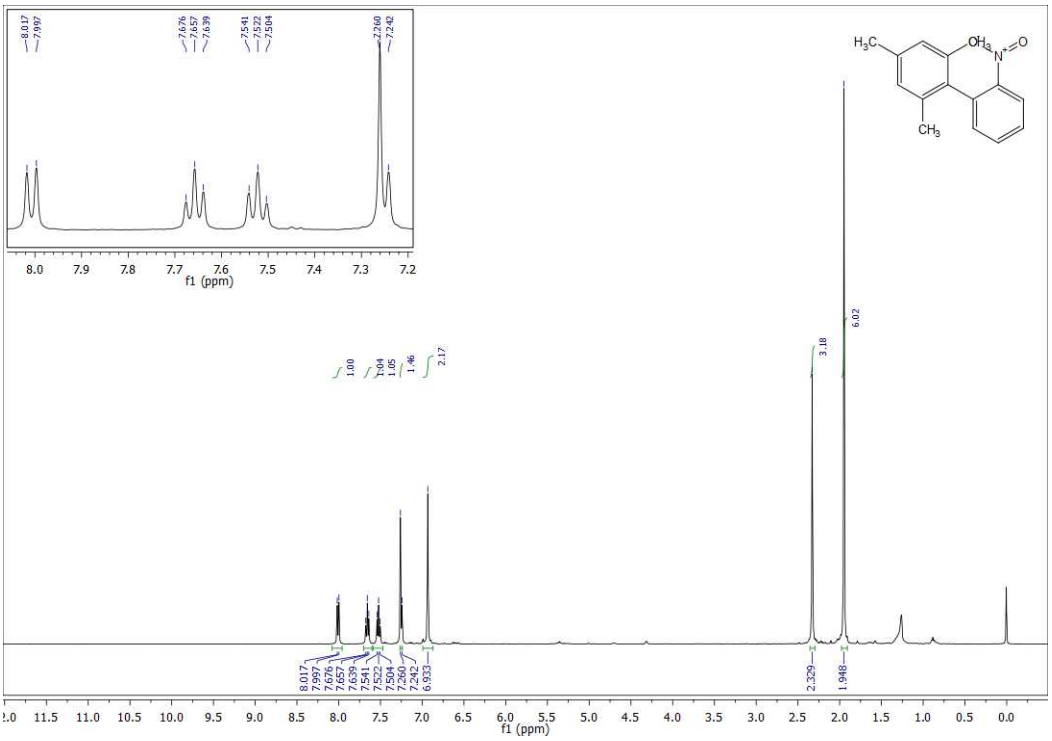

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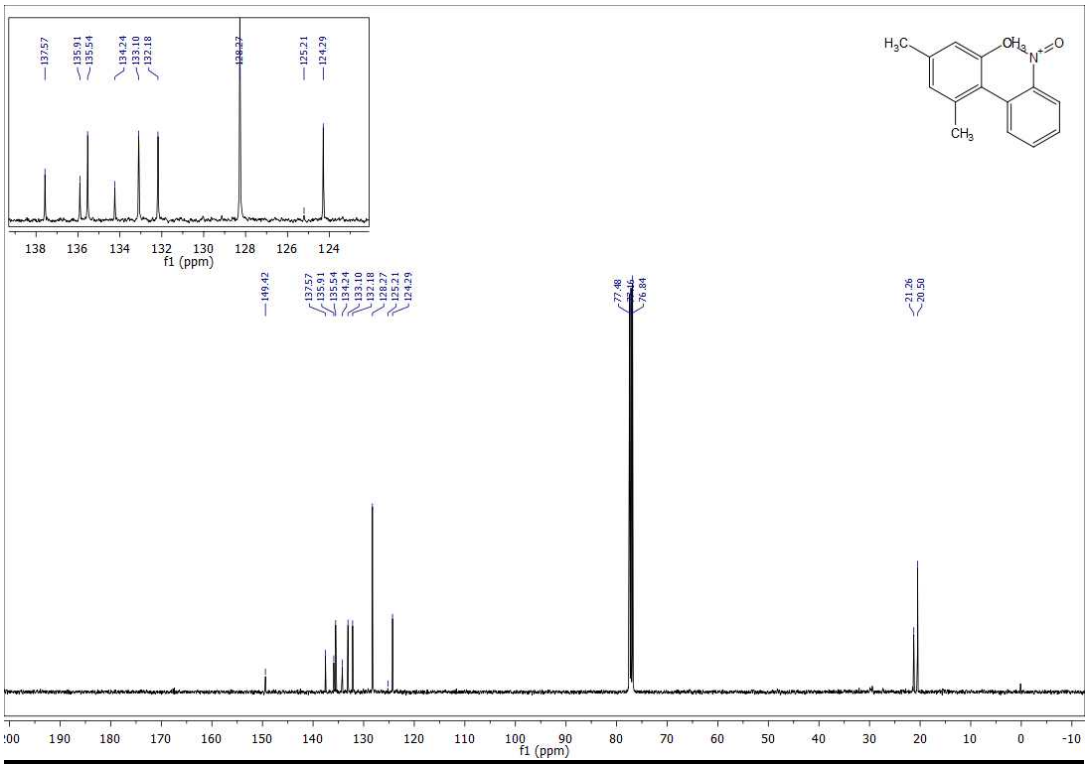

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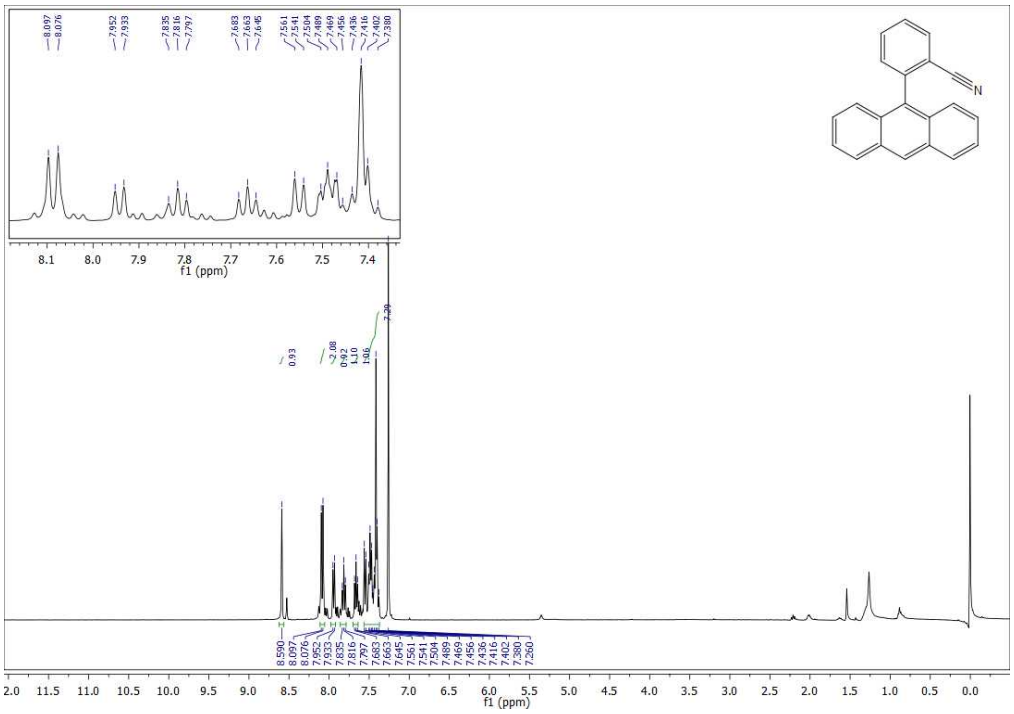

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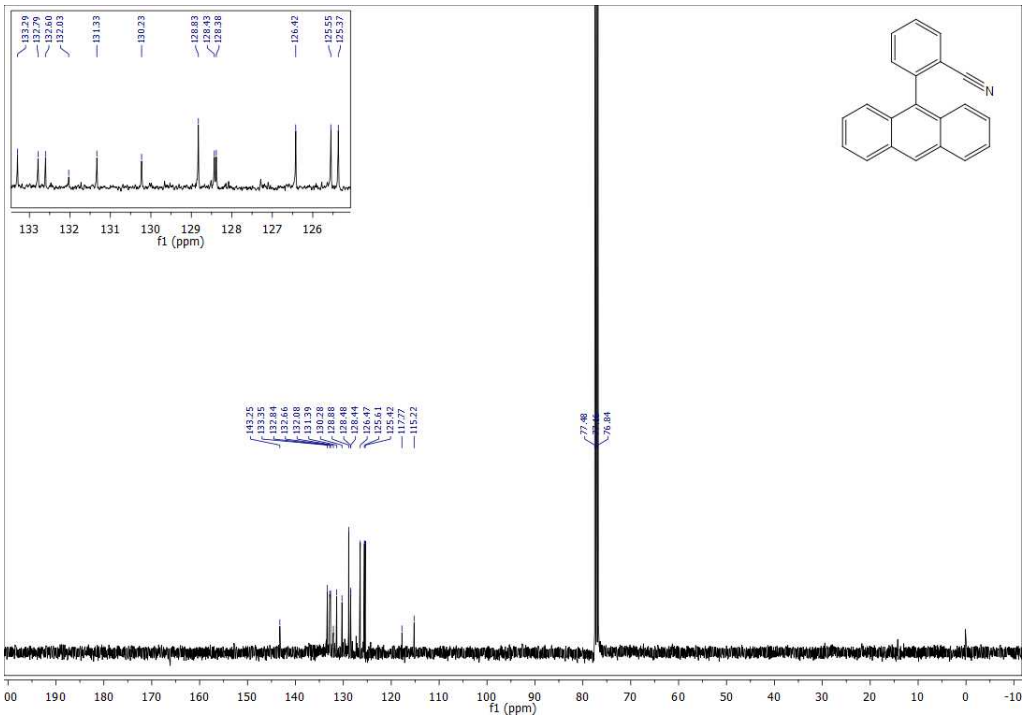

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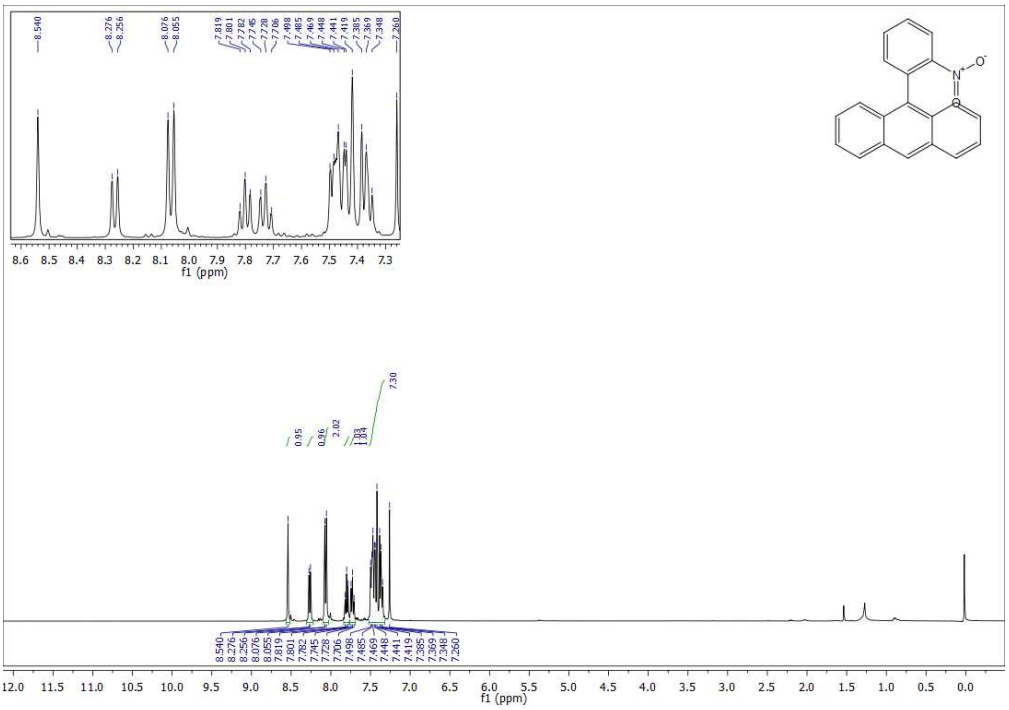

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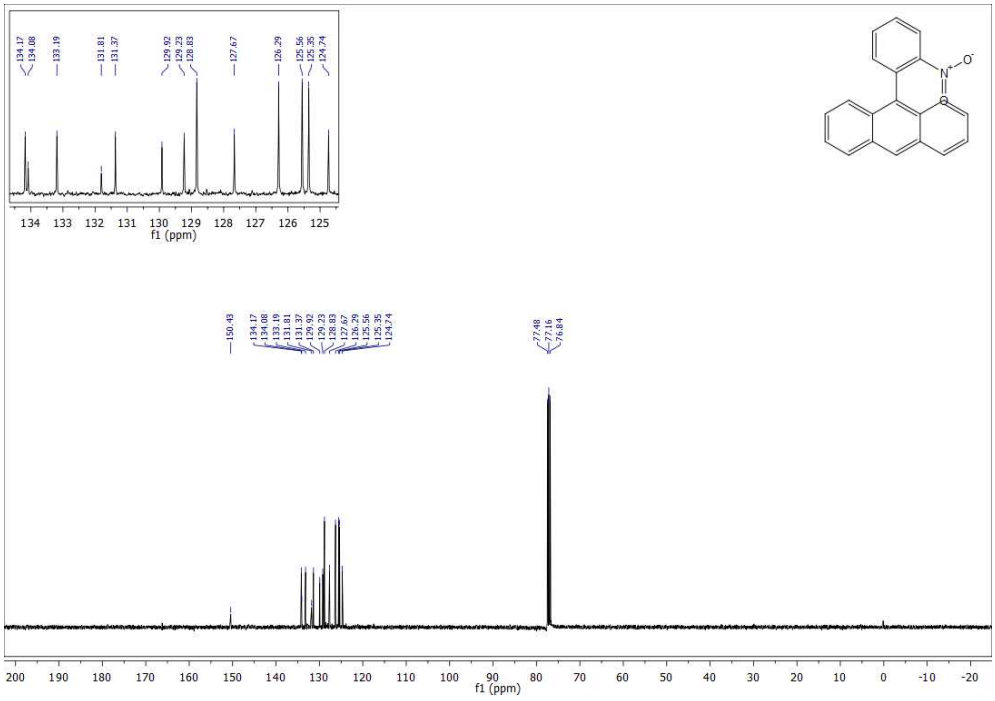

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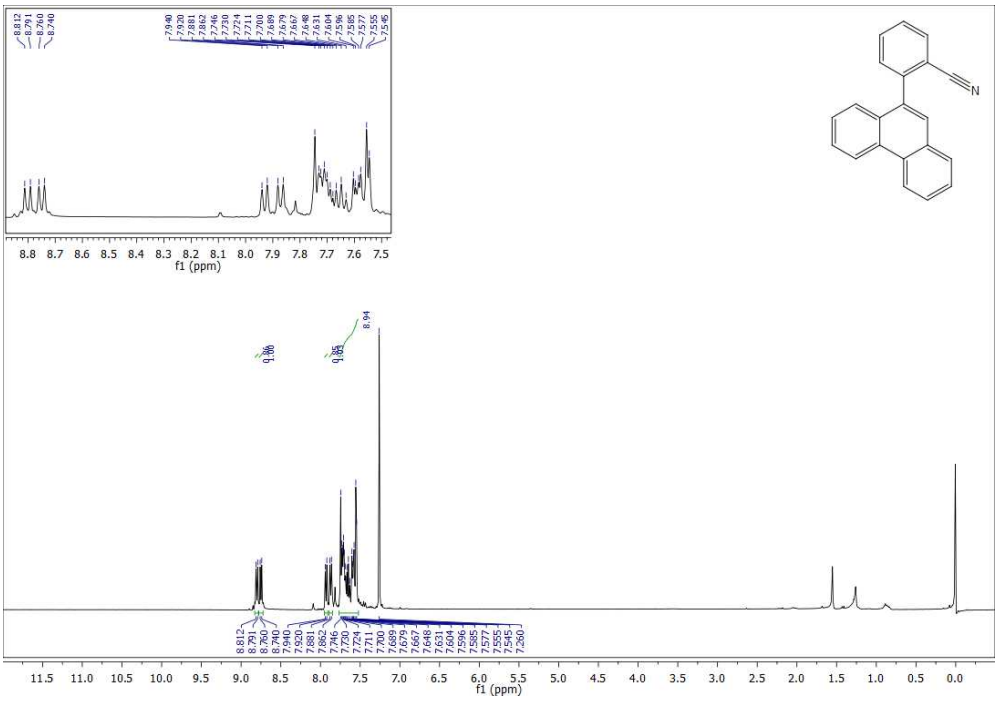
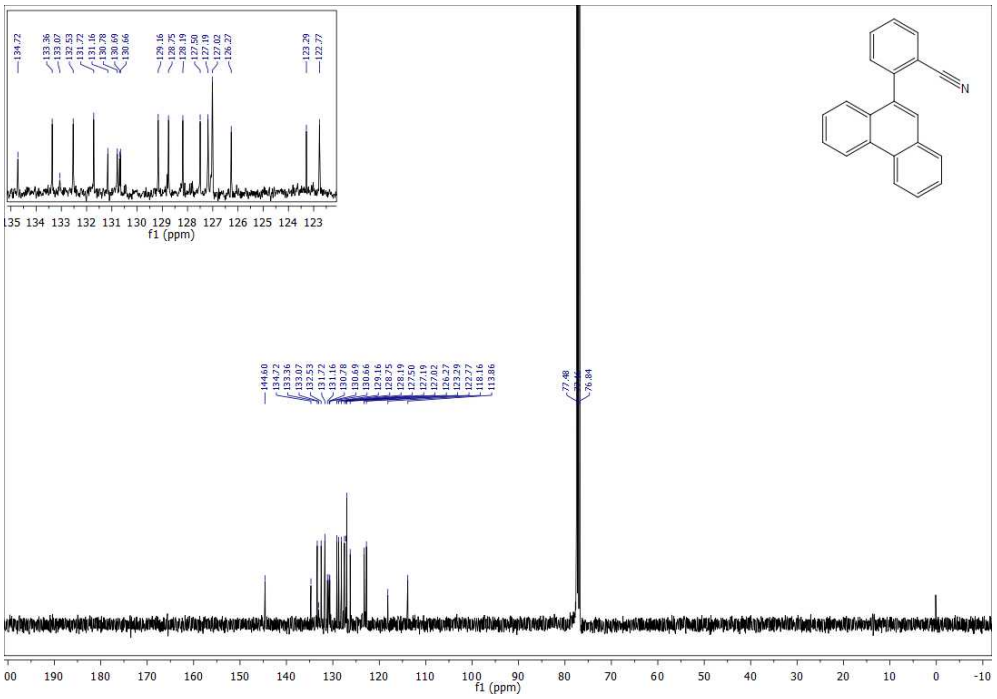


Figure S36: ^{13}C-NMR spectrum of **3fa** (100 MHz, $CDCl_3$)



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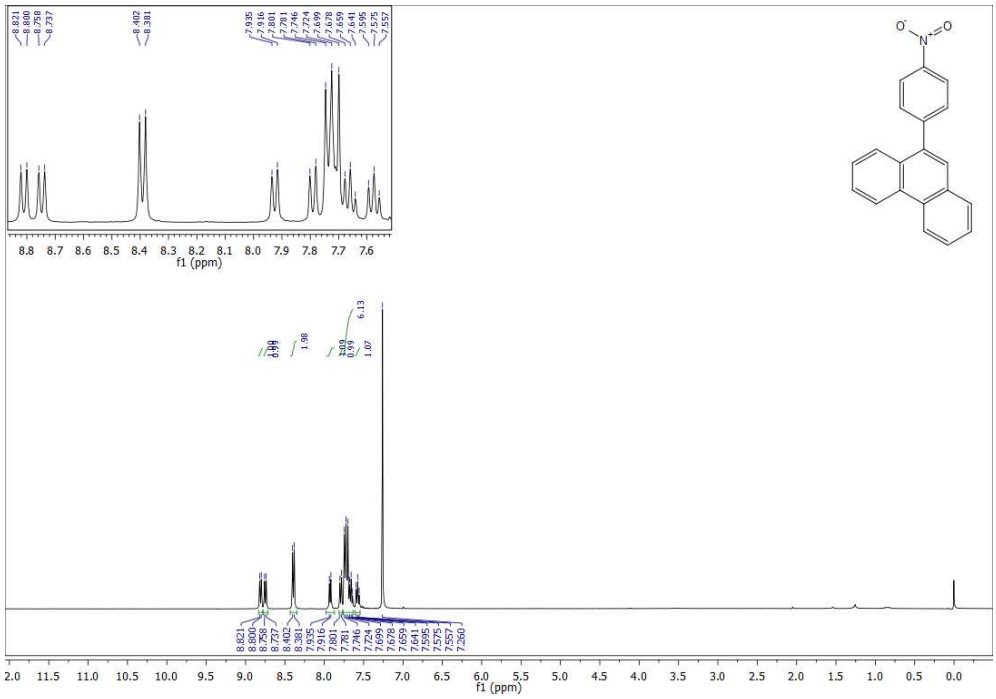

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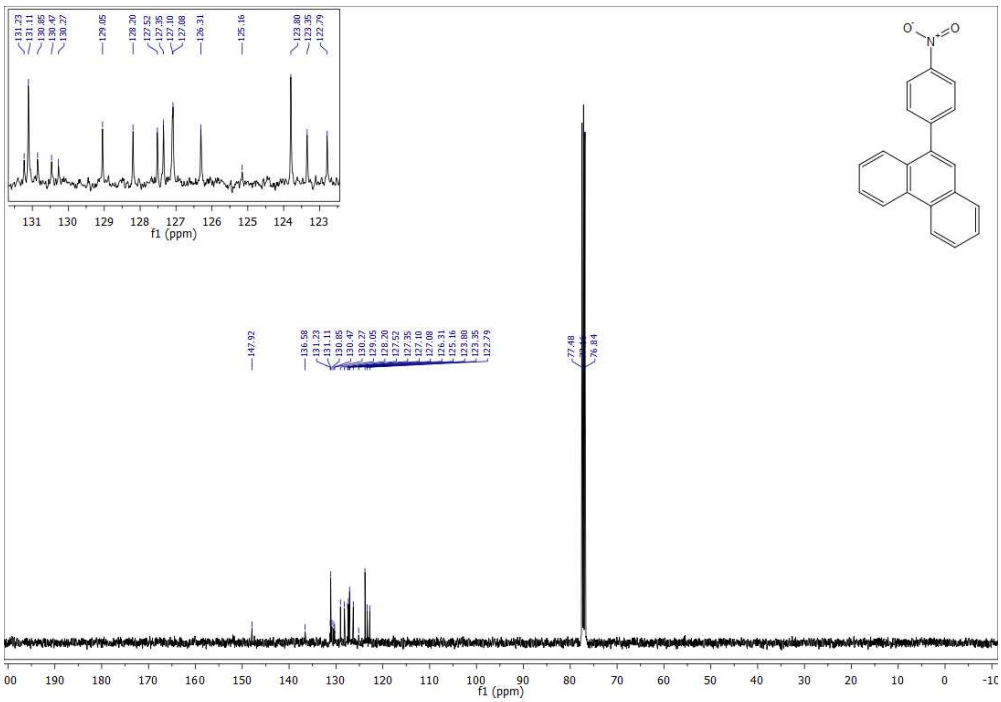


Figure S39: ^{1}H-NMR spectrum of **5af** (400 MHz, $CDCl_3$)

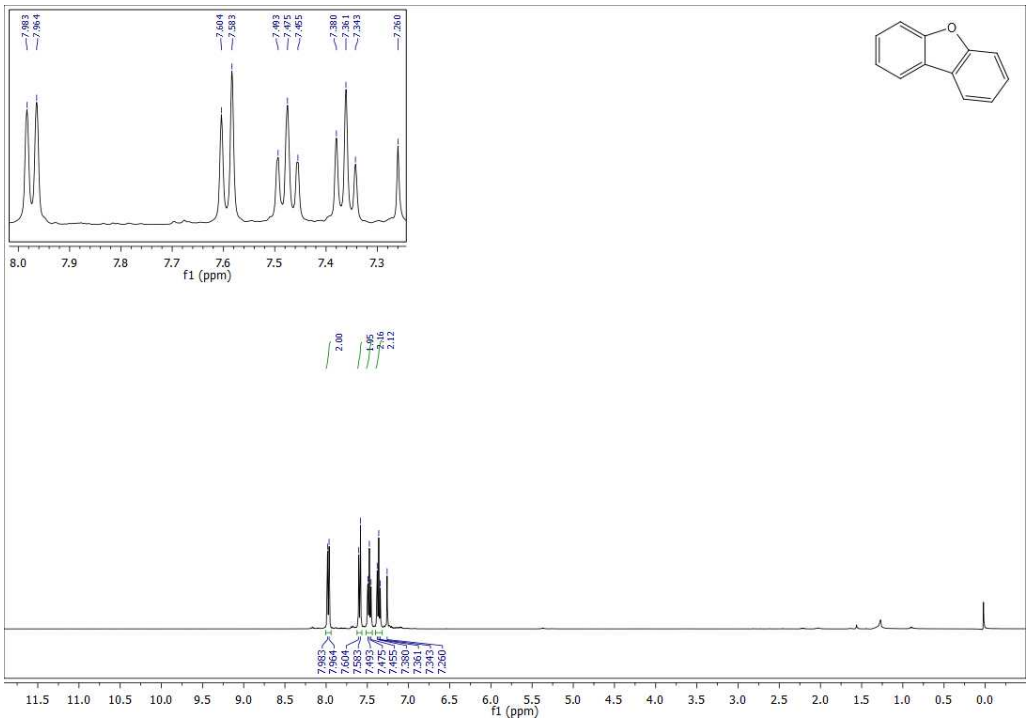
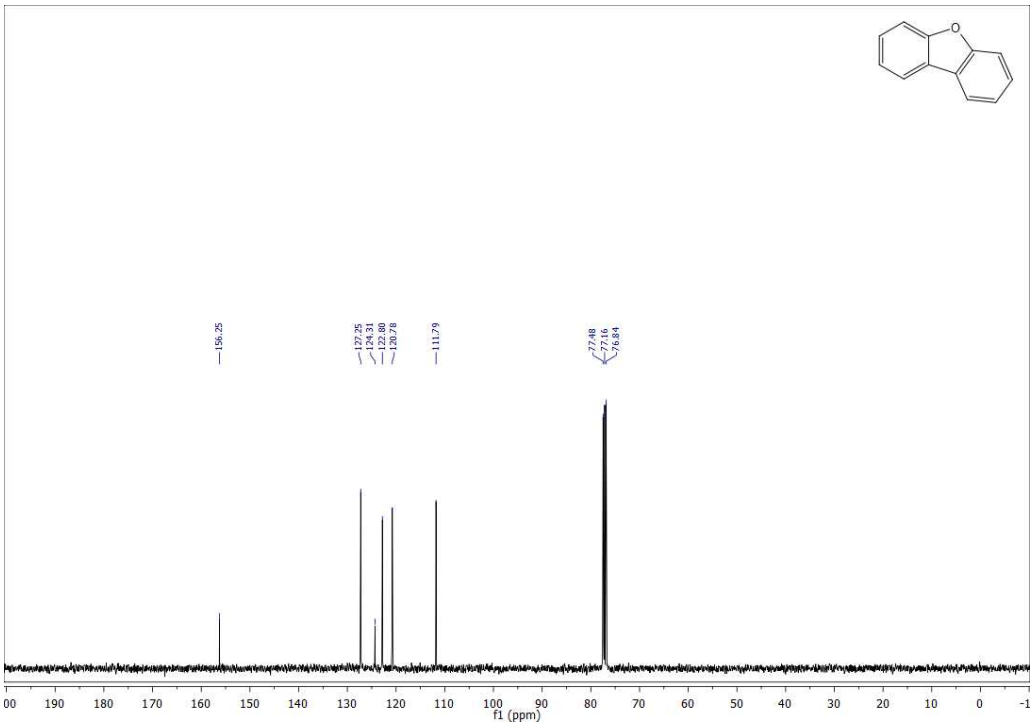


Figure S40: ^{13}C-NMR spectrum of **5af** (100 MHz, $CDCl_3$)



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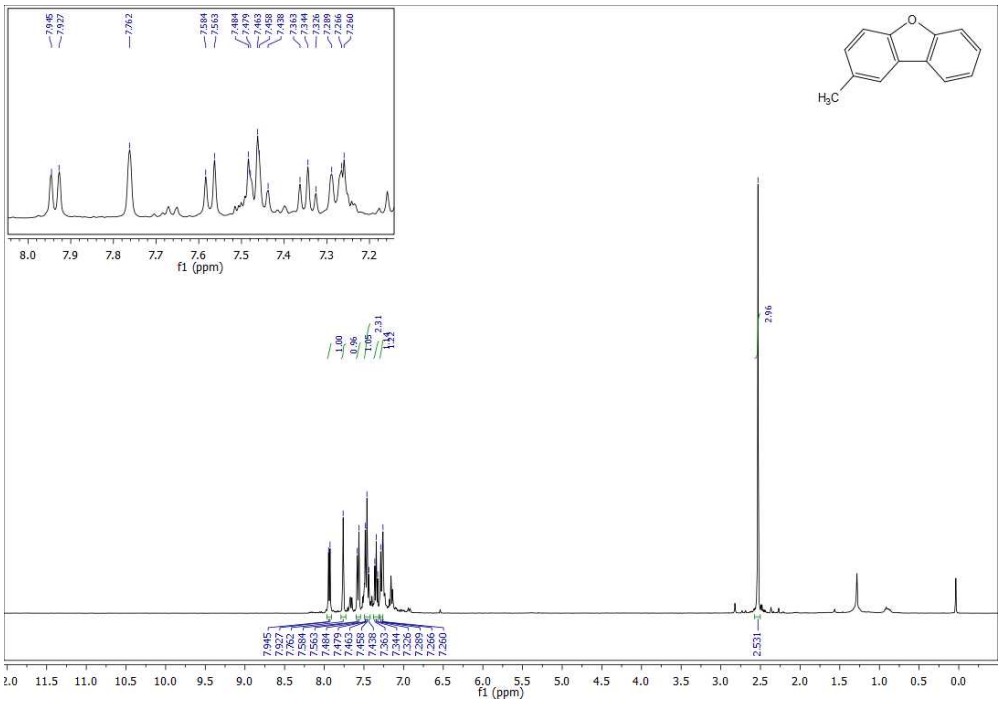


Figure S42: ^{13}C-NMR spectrum of **5bf** (100 MHz, $CDCl_3$)

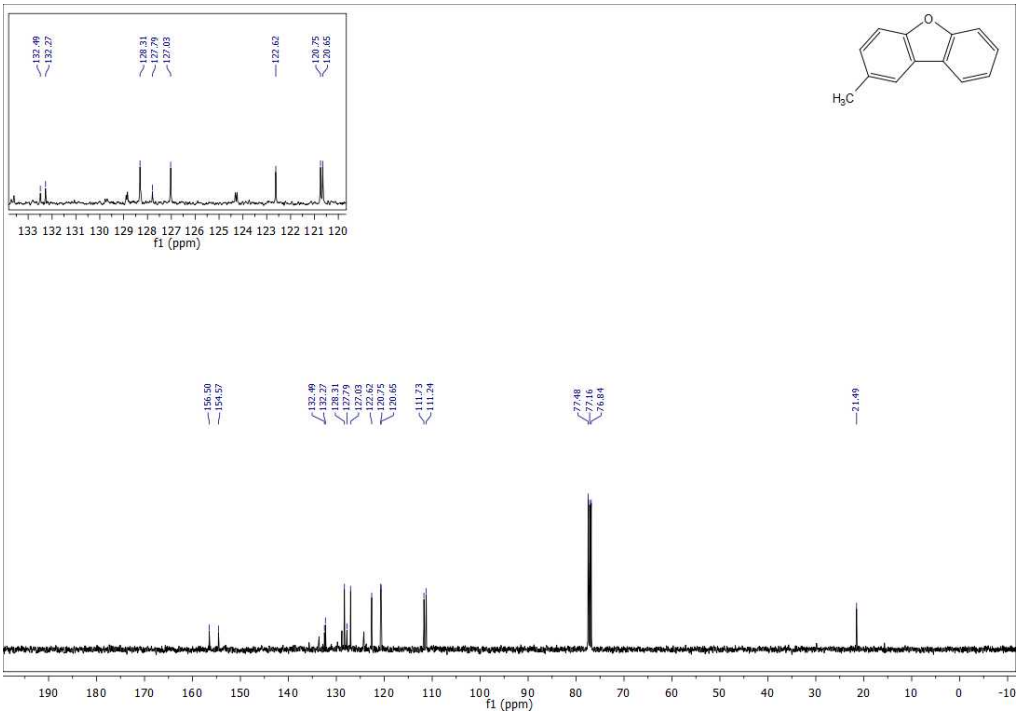


Figure S43: ^{1}H-NMR spectrum of **5cf** (400 MHz, $CDCl_3$)

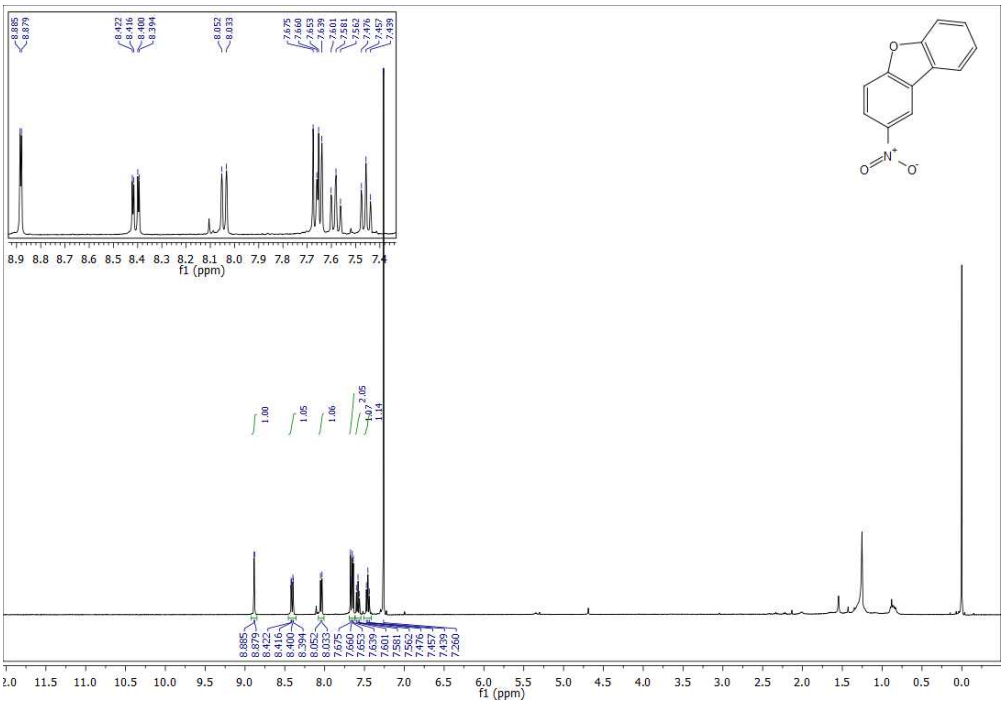


Figure S44: ^{13}C-NMR spectrum of **5cf** (100 MHz, $CDCl_3$)

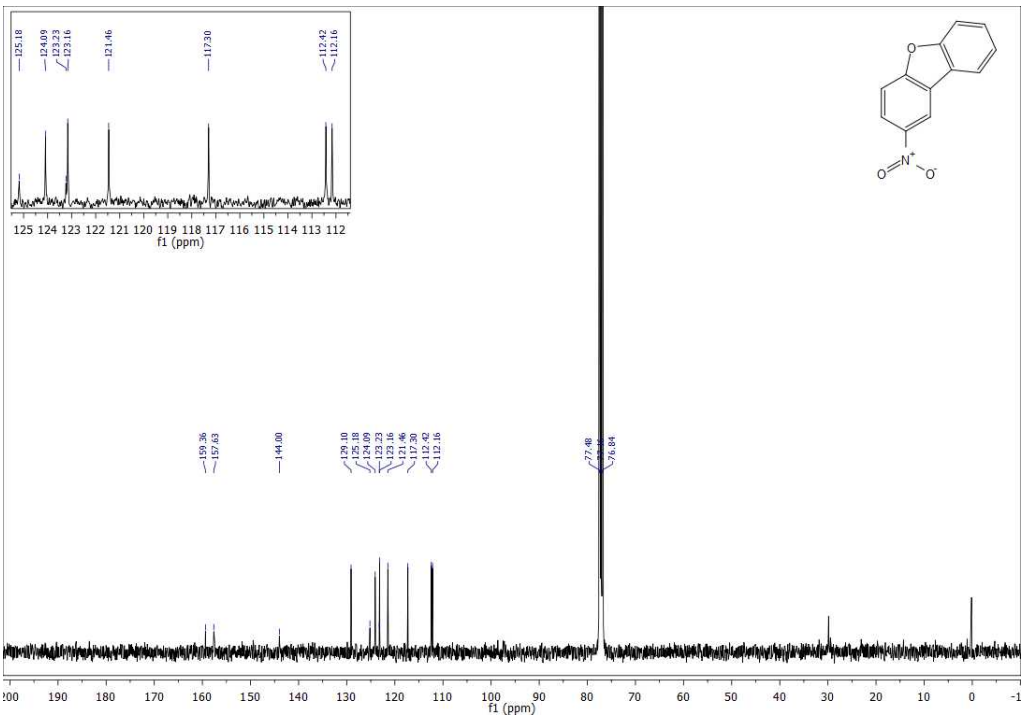


Figure S45: ^{1}H-NMR spectrum of **5df** (400 MHz, $CDCl_3$)

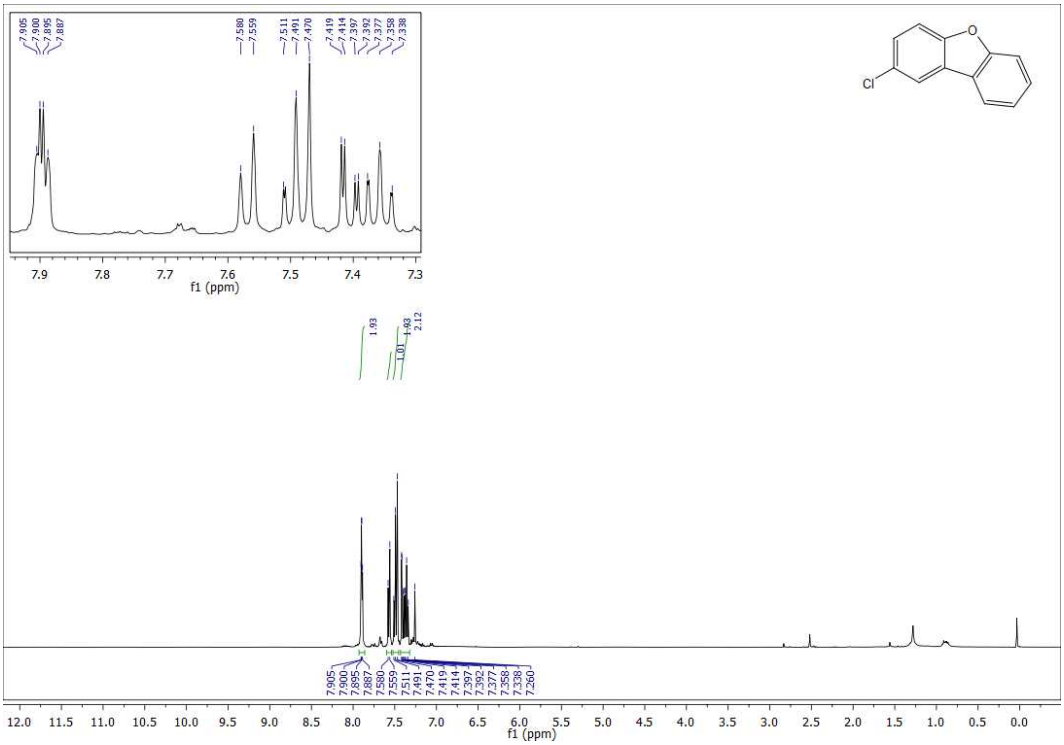


Figure S46: ^{13}C-NMR spectrum of **5df** (100 MHz, $CDCl_3$)

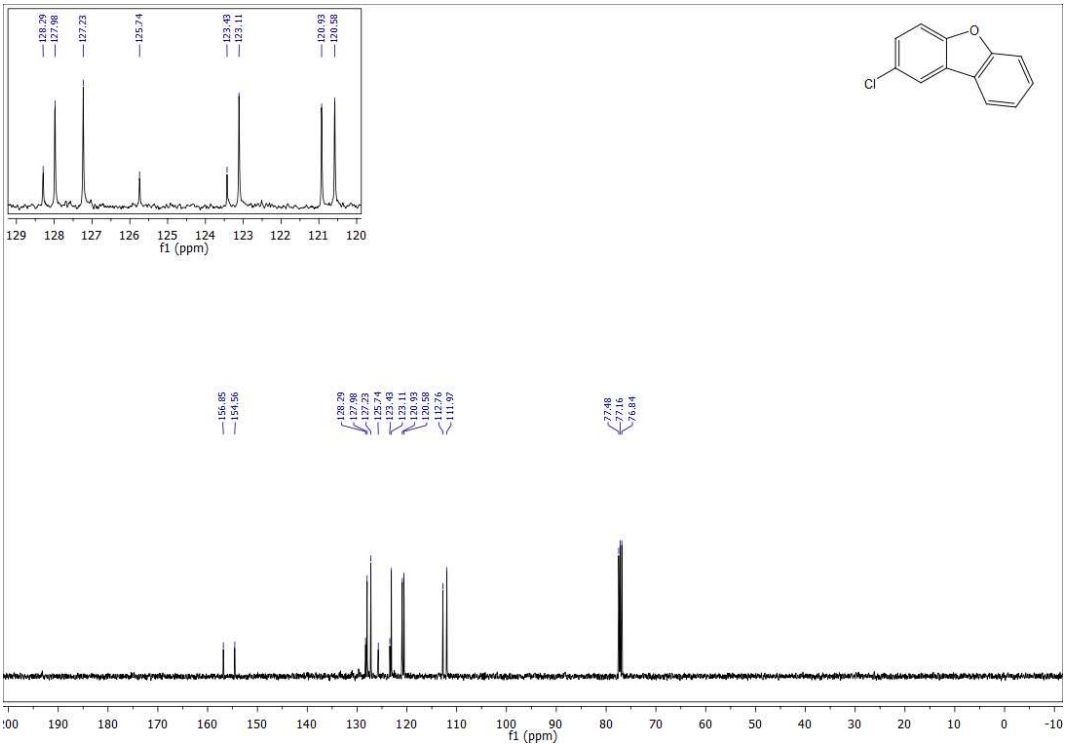


Figure S47: ^{1}H-NMR spectrum of **5ef** (400 MHz, $CDCl_3$)

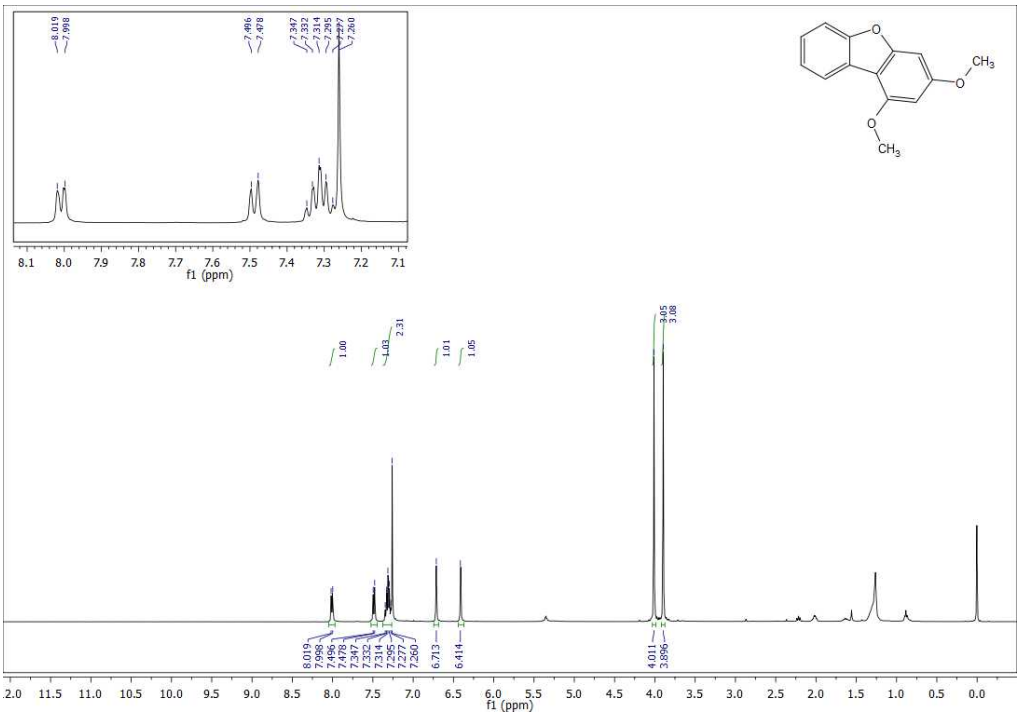


Figure S48: ^{13}C-NMR spectrum of **5ef** (100 MHz, $CDCl_3$)

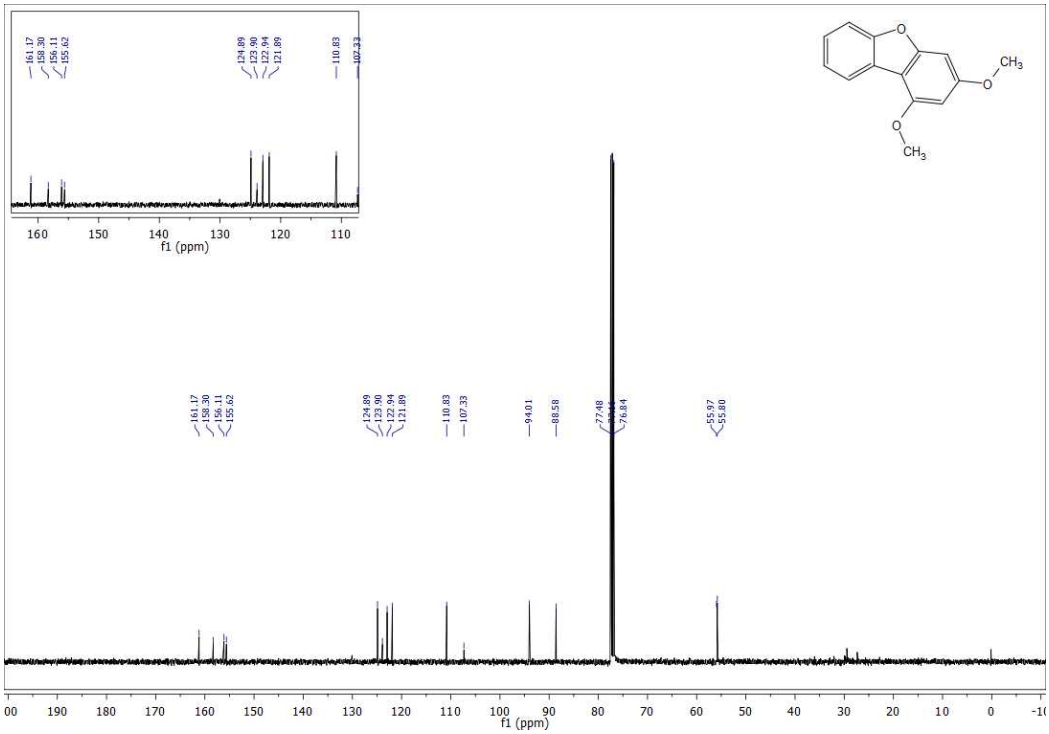


Figure S49: ^{1}H-NMR spectrum of **5ff** (400 MHz, $CDCl_3$)

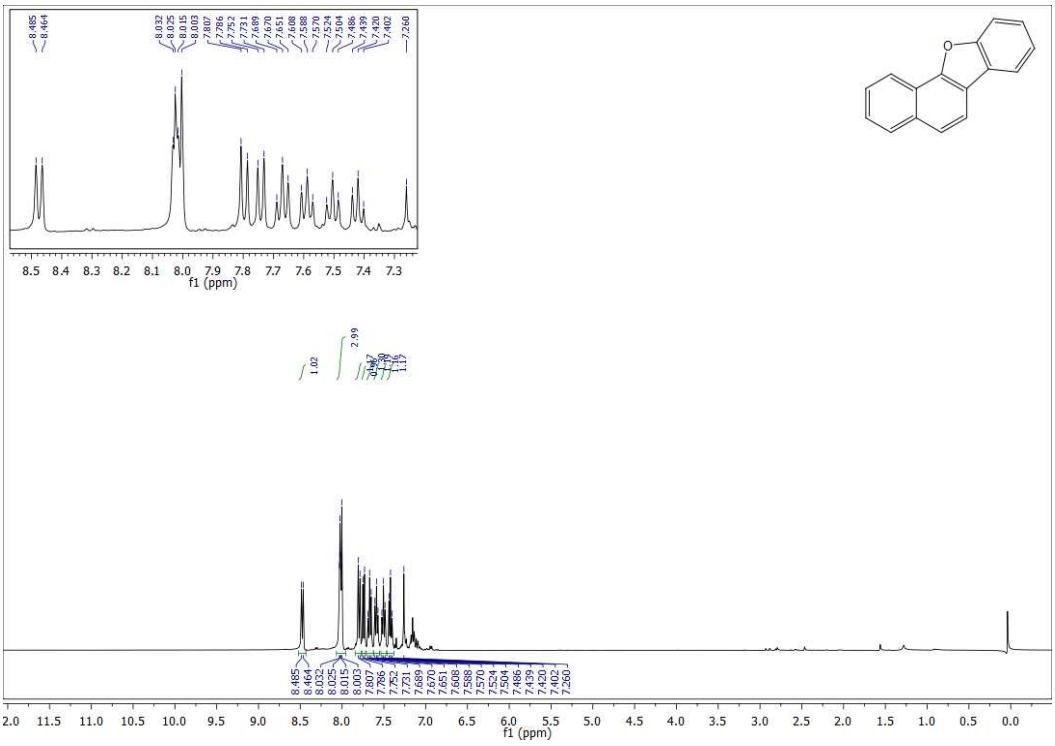


Figure S50: ^{13}C-NMR spectrum of **5ff** (100 MHz, $CDCl_3$)

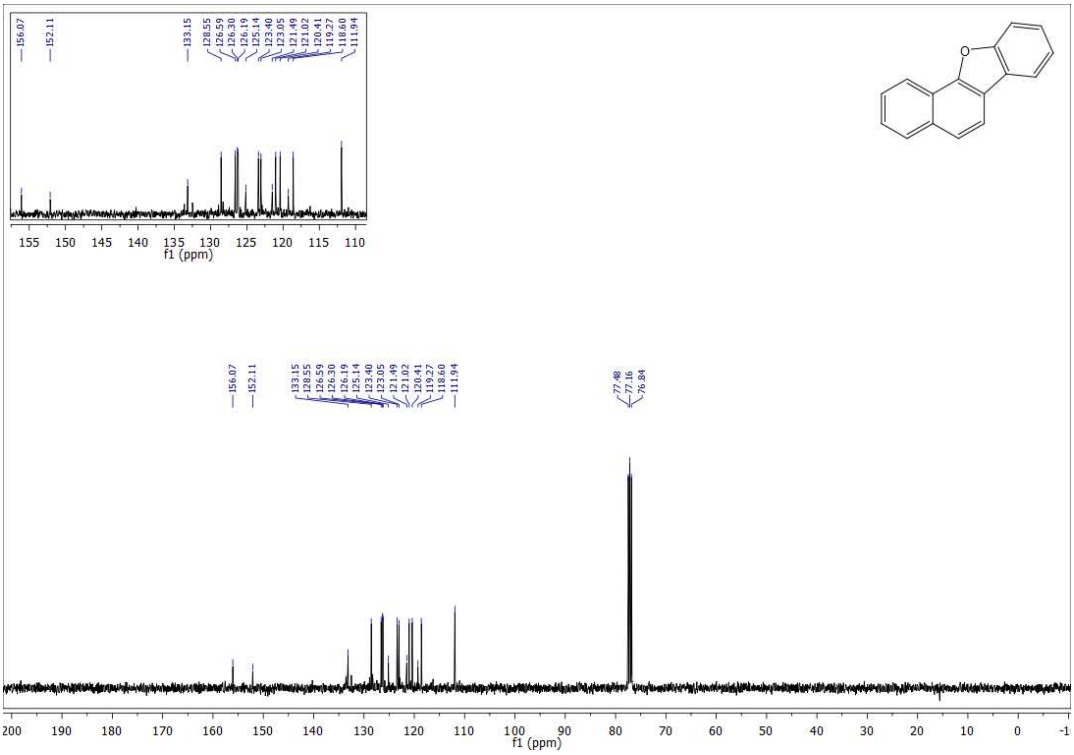


Figure S51: ^{1}H-NMR spectrum of **5gf** (400 MHz, $CDCl_3$)

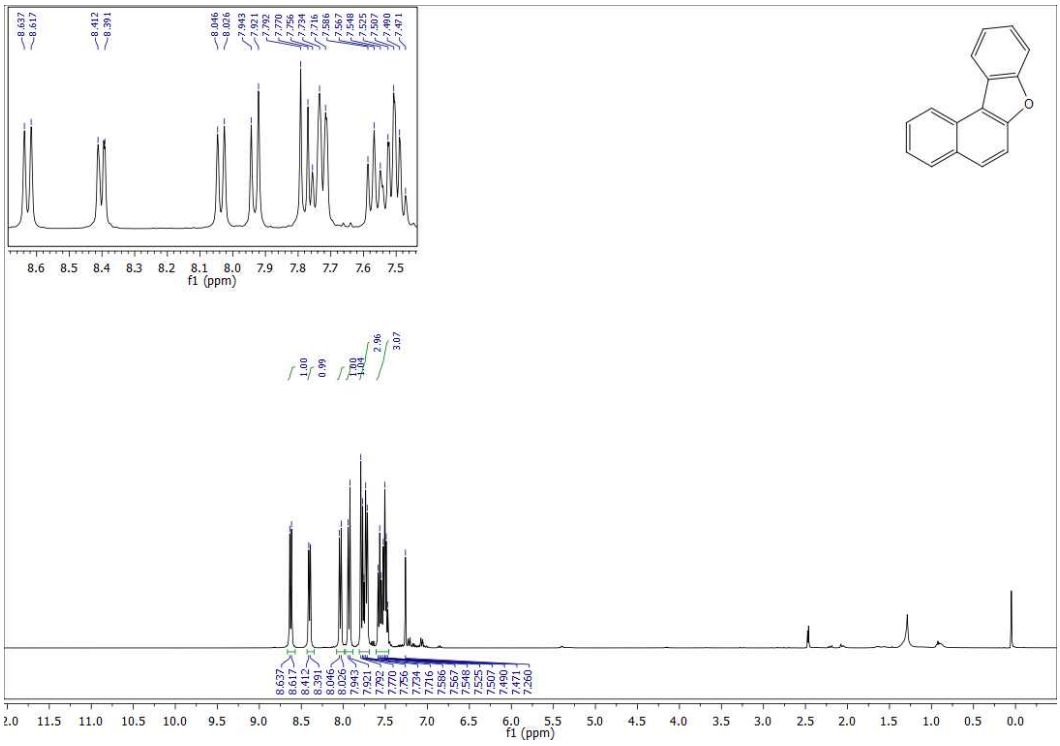
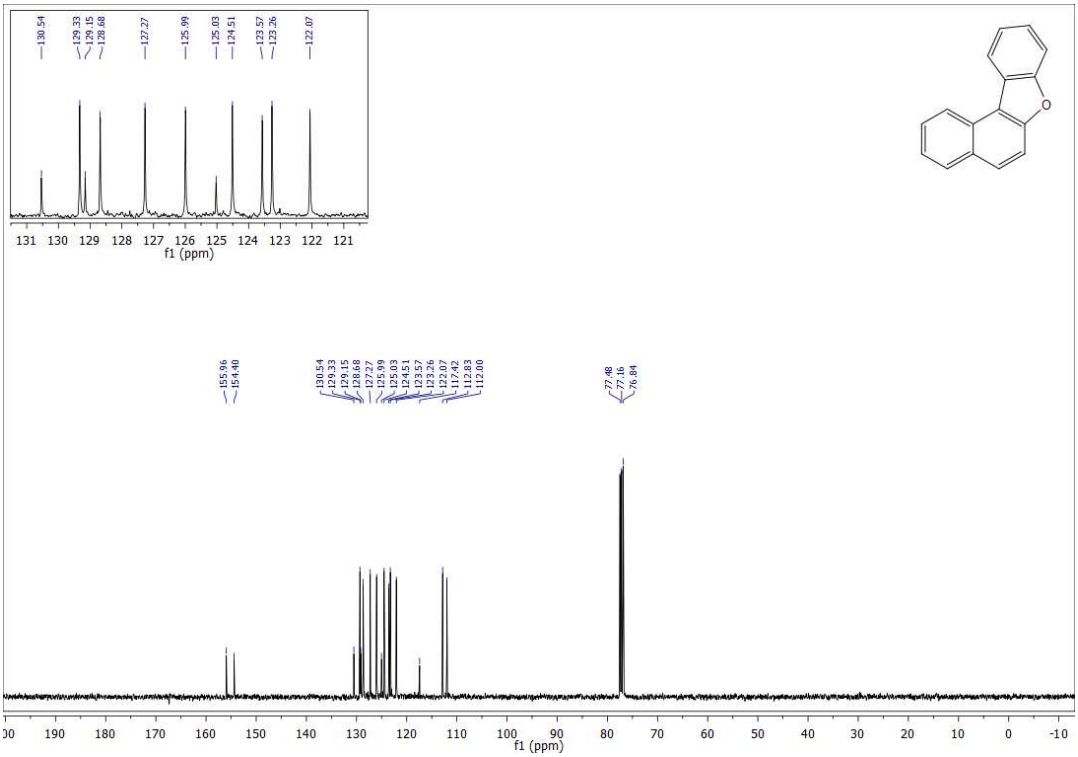


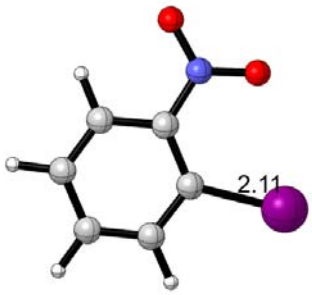
Figure S52: ^{13}C-NMR spectrum of **5gf** (100 MHz, $CDCl_3$)



2. Computational energies and cartesian coordinates of molecules

The computational studies of the interaction between cesium carbonate, and 2-iodonitrobenzene were calculated on Gaussian 09[1] by using M06/def2-TZVP, and thermal correction at 373.15 K[2-4]. The structures are visualized by using CYLview[5].

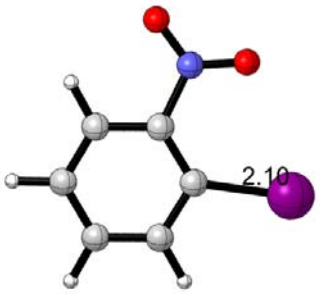
(1) $PhNO_2I$-d-relaxed



Name: PhNO2I-d-relaxed
Charge: -1
Multiplicity: 2
E(UM06) = -733.912188958 Ha
Zero Point Energies: -733.822529 Ha
Thermal Energies: -733.809806 Ha
Thermal Enthalpies: -733.808624 Ha
Thermal Free Energies: -733.871123 Ha

C	-2.670232	-0.141881	-0.000126
C	-2.919910	-1.490760	0.000061
C	-1.867776	-2.403795	0.000344
C	-0.567981	-1.918500	0.000351
C	-0.286278	-0.561213	0.000152
C	-1.352600	0.376767	-0.000027
N	-1.207163	1.756571	-0.000056
I	1.774449	-0.117006	-0.000129
O	-0.050136	2.276999	0.000333
O	-2.248699	2.485388	-0.000078
H	-3.477785	0.577051	-0.000341
H	-3.946852	-1.840868	-0.000016
H	-2.049543	-3.471842	0.000523
H	0.257892	-2.621839	0.000492

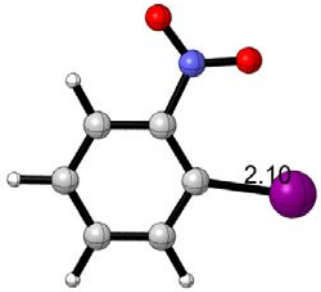
(2) $PhNO_2I$-s-ground



Name: PhNO2I-s-ground
Charge: 0
Multiplicity: 1
E(UM06) = -733.802581488 Ha
Zero Point Energies: -733.710378 Ha
Thermal Energies: -733.699118 Ha
Thermal Enthalpies: -733.697936 Ha
Thermal Free Energies: -733.755949 Ha
Imaginary Frequencies: -32.0997 cm-1

C	-2.664414	-0.129761	-0.000053
C	-2.928616	-1.480248	0.000062
C	-1.873515	-2.377051	0.000212
C	-0.570849	-1.918256	0.000220
C	-0.277836	-0.558062	0.000067
C	-1.354029	0.332334	-0.000033
N	-1.195714	1.795534	-0.000095
I	1.771036	-0.119720	-0.000031
O	-0.077057	2.261889	0.000332
O	-2.203091	2.472678	-0.000472
H	-3.470004	0.591137	-0.000125
H	-3.953232	-1.830058	0.000047
H	-2.060339	-3.444491	0.000324
H	0.245424	-2.630451	0.000332

(3) $PhNO_2I$-vert-d

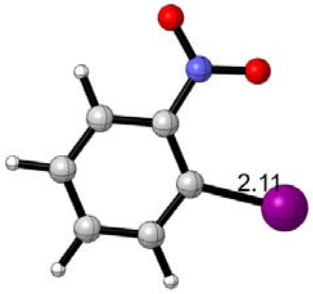


Name: PhNO2I-vert-d
Charge: -1
Multiplicity: 2
E(UM06) = -733.900538311 Ha
Zero Point Energies: -733.811127 Ha
Thermal Energies: -733.798758 Ha
Thermal Enthalpies: -733.797576 Ha
Thermal Free Energies: -733.862192 Ha
Imaginary Frequencies: -198.2927 cm-1

[the same as (2) PhNO2I-s-ground]

C	-2.664414	-0.129761	-0.000053
C	-2.928616	-1.480248	0.000062
C	-1.873515	-2.377051	0.000212
C	-0.570849	-1.918256	0.000220
C	-0.277836	-0.558062	0.000067
C	-1.354029	0.332334	-0.000033
N	-1.195714	1.795534	-0.000095
I	1.771036	-0.119720	-0.000031
O	-0.077057	2.261889	0.000332
O	-2.203091	2.472678	-0.000472
H	-3.470004	0.591137	-0.000125
H	-3.953232	-1.830058	0.000047
H	-2.060339	-3.444491	0.000324
H	0.245424	-2.630451	0.000332

(4) $PhNO_2I$-s-vib-excited

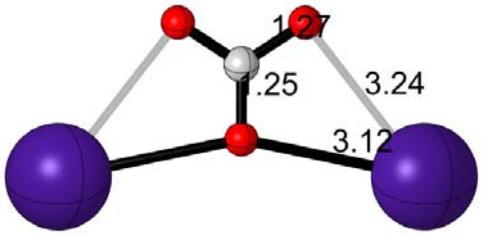


Name: PhNO2I-s-vib-excited
Charge: 0
Multiplicity: 1
E(UM06) = -733.791997231 Ha
Zero Point Energies: -733.700429 Ha
Thermal Energies: -733.688479 Ha
Thermal Enthalpies: -733.687297 Ha
Thermal Free Energies: -733.746467 Ha

[the same as (1) PhNO2I-d-relaxed]

C	-2.670232	-0.141881	-0.000126
C	-2.919910	-1.490760	0.000061
C	-1.867776	-2.403795	0.000344
C	-0.567981	-1.918500	0.000351
C	-0.286278	-0.561213	0.000152
C	-1.352600	0.376767	-0.000027
N	-1.207163	1.756571	-0.000056
I	1.774449	-0.117006	-0.000129
O	-0.050136	2.276999	0.000333
O	-2.248699	2.485388	-0.000078
H	-3.477785	0.577051	-0.000341
H	-3.946852	-1.840868	-0.000016
H	-2.049543	-3.471842	0.000523
H	0.257892	-2.621839	0.000492

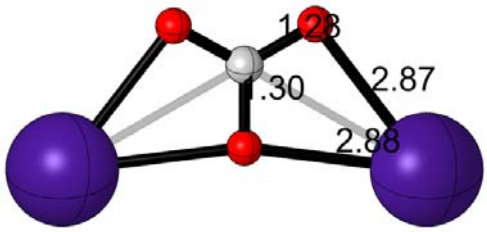
(5) Cs_2CO_3-d-relaxed



Name: Cs2CO3-d-relaxed
Charge: 1
Multiplicity: 2
E(UM06) = -304.054911050 Ha
Zero Point Energies: -304.042094 Ha
Thermal Energies: -304.030696 Ha
Thermal Enthalpies: -304.029515 Ha
Thermal Free Energies: -304.100798 Ha

O	1.065561	2.152613	-0.017246
C	0.001111	1.459191	-0.003254
O	-1.062512	2.154092	0.022286
O	-0.000463	0.212606	-0.013494
Cs	3.057421	-0.408448	0.001793
Cs	-3.057918	-0.408091	-0.000208

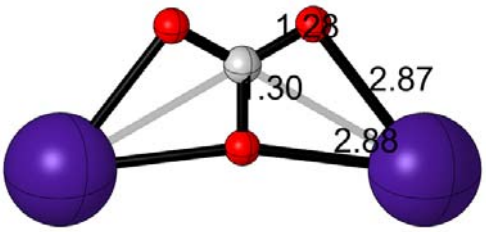
(6) Cs_2CO_3- s-ground



Name: Cs2CO3- s-ground
Charge: 0
Multiplicity: 1
E(UM06) = -304.213866509 Ha
Zero Point Energies: -304.198312 Ha
Thermal Energies: -304.188201 Ha
Thermal Enthalpies: -304.187020 Ha
Thermal Free Energies: -304.249202 Ha

O	-1.110398	1.923284	0.114821
C	0.000431	1.298168	-0.002882
O	1.111857	1.923981	-0.111412
O	-0.000226	-0.005659	-0.011901
Cs	-2.861268	-0.350083	-0.005615
Cs	2.861042	-0.350314	0.007164

(7) Cs_2CO_3-vert-d

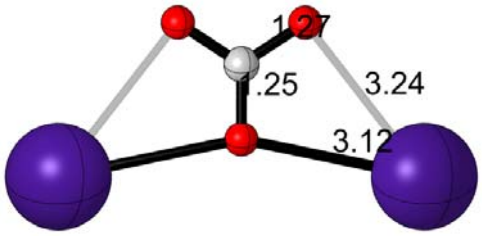


Name: Cs2CO3-vert-d
Charge: 1
Multiplicity: 2
E(UM06) = -304.042692650 Ha
Zero Point Energies: -304.031598 Ha
Thermal Energies: -304.022459 Ha
Thermal Enthalpies: -304.021277 Ha
Thermal Free Energies: -304.080212 Ha
Imaginary Frequencies: -393.6309 cm-1

[the same as (6) Cs2CO3- s-ground]

O	-1.110398	1.923284	0.114821
C	0.000431	1.298168	-0.002882
O	1.111857	1.923981	-0.111412
O	-0.000226	-0.005659	-0.011901
Cs	-2.861268	-0.350083	-0.005615
Cs	2.861042	-0.350314	0.007164

(8) Cs_2CO_3- s-vib-excited

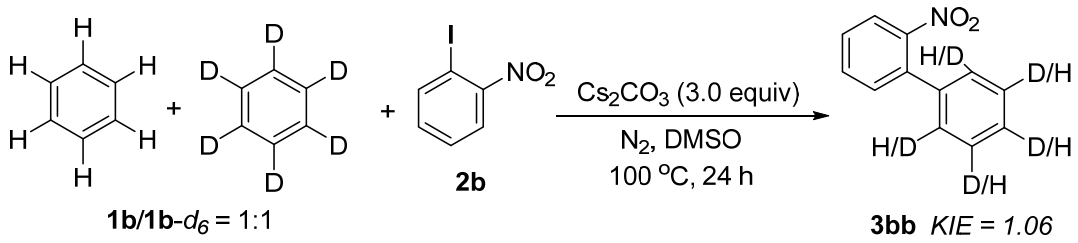


Name: Cs2CO3- s-vib-excited
Charge: 0
Multiplicity: 1
E(UM06) = -304.197948122 Ha
Zero Point Energies: -304.182649 Ha
Thermal Energies: -304.175211 Ha
Thermal Enthalpies: -304.174030 Ha
Thermal Free Energies: -304.230375 Ha
Imaginary Frequencies: -197.6198 cm-1

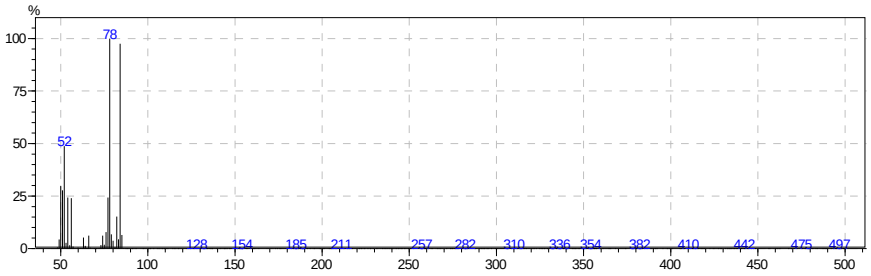
[the same as (5) Cs2CO3-d-relaxed]

O	1.065561	2.152613	-0.017246
C	0.001111	1.459191	-0.003254
O	-1.062512	2.154092	0.022286
O	-0.000463	0.212606	-0.013494
Cs	3.057421	-0.408448	0.001793
Cs	-3.057918	-0.408091	-0.000208

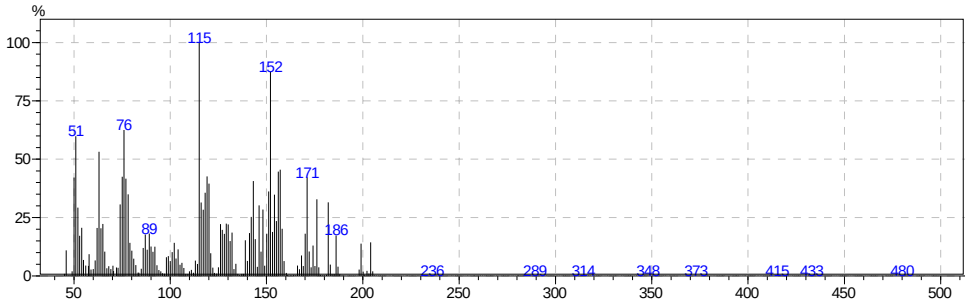
3. Kinetic isotopic effect (KIE) experiment



The GCMS of **1b**/**1b**-d_6



GCMS of 2-phenylnitrobenzene **3bb** obtained from the above reaction



KIE value = 1.06

	PhH				KIE
H	78.05	422805	100		
D	84.1	412595	97.59	1.024695	
	2-phenylnitrobenzene				
H	199.05	8443	13.79		
D	204.1	8796	14.36	0.960306	1.06705

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