Comptes Rendus Chimie

Supporting Information

for

Synthesis of New Functionalized Triarylmethanes *Via* Suzuki Cross-Coupling and Heck-Type Vinylation Reactions

Kazem Mohammadiannejad,*[a] Rezieh Hosseini,[b] and Reza Ranjbar-Karimi,*[b]

[a]NMR Laboratory, Faculty of Science, Vali-e-Asr University of Rafsanjan, Rafsanjan 77176,, Islamic Republic of Iran, Fax: +98-34-3131-2148; Tel: +98-913-292-8115, E-mail: kmmohammadi@gmail.com or k.mohammadian@vru.ac.ir

[b]Department of Chemistry, Faculty of Science, Vali-e-Asr University of Rafsanjan, Rafsanjan 77176, Islamic Republic of Iran, Tel: +98-913-291-6602, E-mail: r.ranjbarkarimi@vru.ac.ir

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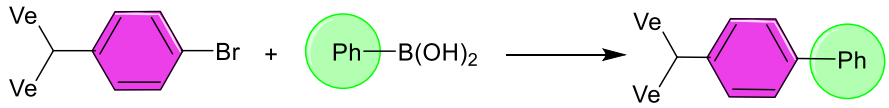
1. Optimization of reaction conditions for the Suzuki-Miyaura cross-coupling reaction of brominated-TRAMs 10a-h with arylboronic acids 11a-d catalyzed by $Pd(PPh_3)_4$

We commenced our search by choosing the reaction of TRAM **10a** with phenylboronic acid **11a** as a model to identify the best experimental reaction conditions (Table 1). Our initial assessments showed the efficiency of $Pd(PPh_3)_4$ for promoting this coupling reaction. Thus, several experiments were carried out to optimize the reaction parameters such as solvent, temperature, molar ratio of reactants, base, as well as catalyst loading, and the results are summarized in Table 1. The effect of various solvents including CH_3CN, MeOH, toluene, DMF, benzene, CH_2Cl_2, and 1,4-dioxane were ascertained on the reaction of **10a** (1 mmol) with **11a** (1.0 mmol) in the presence of $Pd(PPh_3)_4$ (5 mol%) and K_2CO_3 (2 mmol) under N_2 atmosphere. The highest yield of the desired product **6a** was obtained in THF under reflux conditions (entry 1). When the reaction was performed at a lower temperature, inferior yield of **6a** was obtained (entry 2). To improve the progress of the reaction, the molar ratio of **10a** to **11a** was changed to 1:1.2 and the product **6a** was isolated in 87% yield (entry 3). Using lower molar ratio of reactants resulted in lower yield (entry 4), while higher molar ratios of **10a**:**11a** did not improve the reaction yield (entries 5 and 6). The model reaction was also studied in the presence of various amounts of $Pd(PPh_3)_4$ to find the appropriate amount of catalyst loading. Maximum yield of **6a** was obtained with 5 mol% of the catalyst (entry 3). Increasing the amount of $Pd(PPh_3)_4$ to 7 mol% did not affect the yield of **6a** significantly (entry 7), while using lower amounts of catalyst led to lower yields (entries 8 and 9). Finally, the effect of various bases was examined on the model reaction (entries 3 and 10-12). The results revealed that both K_2CO_3 and Cs_2CO_3 were effective bases for the Suzuki-Miyaura coupling reaction of **10a** with **11a**. Hence, K_2CO_3, which is a cheaper base than Cs_2CO_3, was selected for the model reaction. In addition, further trials showed that the optimal loading for the K_2CO_3 was 2 mmol (1 mL of a 2M solution in water). Accordingly, TRAM **10a** (1 mmol), **11a** (1.2 mmol),

$Pd(PPh_3)_4$ (5 mol%), and K_2CO_3 (1mL, 2M) in refluxing THF (5 mL) under N_2 atmosphere were selected as the optimized reaction conditions.

Table 1

Optimization of reaction conditions for the Suzuki-Miyaura cross-coupling reaction of TRAM **10a** with phenylboronic acid **11a** catalyzed by $Pd(PPh_3)_4$.[a]



10a (1 mmol) 11a Ve ≈ 3,4-$(MeO)_2C_6H_3$ (6a)

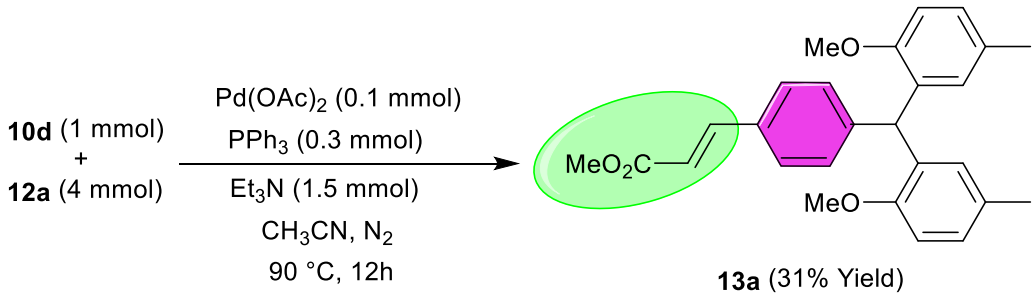
Entry	**11a** (mmol)	$Pd(PPh_3)_4$ (mol%)	Base	Solvent	T (°C)	Yield % [b]
1	1.0	5	K_2CO_3	THF	reflux	58[c]
2	1.0	5	K_2CO_3	THF	50	35
3	**1.2**	**5**	**K_2CO_3**	**THF**	**reflux**	**87**
4	1.1	5	K_2CO_3	THF	reflux	71
5	1.3	5	K_2CO_3	THF	reflux	87
6	1.4	5	K_2CO_3	THF	reflux	87
7	1.2	7	K_2CO_3	THF	reflux	87
8	1.2	3	K_2CO_3	THF	reflux	51
9	1.2	4	K_2CO_3	THF	reflux	72
10	1.2	5	Cs_2CO_3	THF	reflux	87
11	1.2	5	Et_3N	THF	reflux	60
12	1.2	5	NaOH	THF	reflux	51

[a] All the reactions were run for 12 h. [b] Isolated yield. [C] Carrying out the reaction under the same conditions in solvents including CH_3CN, MeOH, toluene, DMF, benzene, CH_2Cl_2, and 1,4-dioxane afforded **6a** in yields ranging from 21 to 36%.

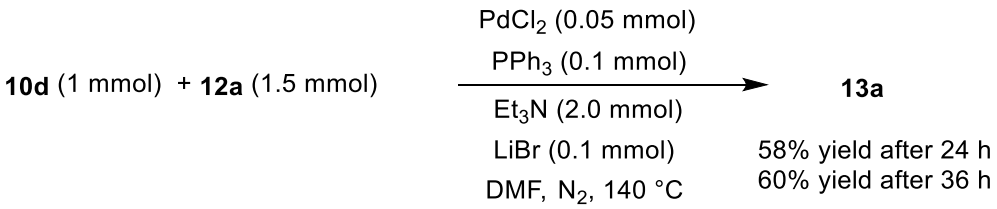
2. Optimization of reaction conditions for the Mizoroki-Heck cross-coupling reaction of brominated-triarylmethanes with olefins

Initially, TRAM **10d** and methyl acrylate **12a** were chosen as model substrates. According to the conditions reported by Qian and co-workers, the reaction between TRAM **10d** and **12a** resulted in only 31% yield of product **13a** (Scheme 1). To enhance the reaction yield, we set out to employ $PdCl_2(PPh_3)_2$ as precatalyst for the model reaction. Heating a DMF solution of reactants, $PdCl_2$ (5 mol%), PPh_3 (10 mol%), LiBr (10 mol%) and Et_3N (2 mmol) to 140 °C for 24 h provided coupling product **13a** in 58% yield. However, continuing the reaction for 12 additional hours did not considerably improve the yield (Scheme 2). Given these results, we followed the reaction at 140 °C for 36 h, after heating a reaction mixture for a short period of time at 140 °C. Surprisingly, the product **13a** was achieved in 62% yield when a 30 minute of time was considered for modification of catalyst (Scheme 3). We therefor postulated that the presumable decomposition of substrates due to the high temperature can be avoided through a one-pot two-step reaction. So, we designed a protocol which in the first step $PdCl_2(PPh_3)_2$ (5 mol%) was prepared *in situ* by vigorously stirring a 1:2:2 mixture of $PdCl_2$, PPh_3, and LiBr, at 140 °C in DMF (2 mL) under N_2 atmosphere for 30 min. In the second step, a mixture of **10d**, **12a**, and Et_3N in DMF (3 mL) was added and the resulting mixture was heated at 100 °C for 36h. To optimize the experimental conditions, the effect of various parameters including the molar ratio of reactants, catalyst loading, base, and solvent was studied on the model reaction according to the above-mentioned protocol (Table 2). First, the model reaction was carried out in various solvents such as MeOH, THF, 1,4-dioxane, toluene, and DMF. The maximum yield of product **13a** was obtained in DMF (Entry 1). Thus, DMF was chosen as the reaction medium. The progress of the model reaction was also explored with different molar ratios of substrates (Table 2, entries 1-4) and the best result was obtained with 1:2 molar ratio of TRAM **10d** to methyl acrylate **12a** (Entry 3). To find the optimal amount of catalyst, the reaction was

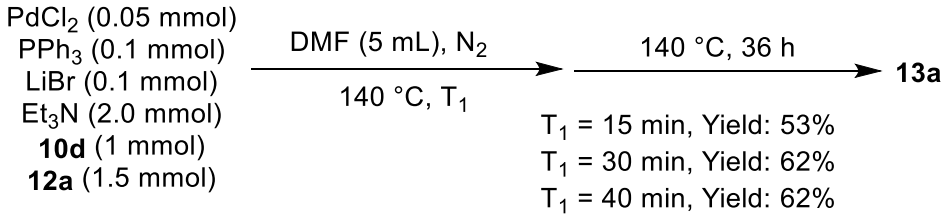
performed in the presence of different amounts of $PdCl_2$ along with the proportional amounts of PPh_3 and LiBr (Entries 3, 6, and 7). The maximum yield of **13a** was achieved with 5 mol% of $PdCl_2$ (Entry 3). However, the reaction did not work in the absence of $PdCl_2$ (Entry 5). The effect of base was also evaluated on the model reaction (Entries 3, 8 and 9), and Et_3N was realized more effective than other used organic and inorganic bases (Entry 3). Finally, the influence of temperature was explored on the second step of the model reaction (Entries 3, 10 and 11) and we found that 100 °C is the optimal temperature (Entry 3). Therefore, the optimal conditions for the one-pot two-step Heck coupling reaction of TRAM **10d** with **12a** was involved as following: initially a mixture of $PdCl_2$ (0.05 mmol), PPh_3 (0.1 mmol), and LiBr (0.1 mmol) in DMF (2 mL) was heated at 140 °C for 30 min. After addition a solution of DMF (3 mL), TRAM **10d** (1 mmol), **12a** (2.0 mmol), Et_3N (2 mmol) to the former, the resulting mixture was stirred at 100 °C for 36 h.



Scheme 1. Mizoroki-Heck coupling reaction of **10d** with **12a** in the presence of $Pd(OAc)_2/PPh_3$.



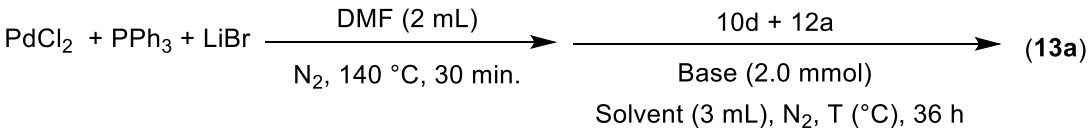
Scheme 2. Mizoroki-Heck coupling reaction of TRAM **10d** with **12a** using $PdCl_2/PPh_3$ catalytic system.



Scheme 6. The effect of pre-modification of [pd]-catalyst on the yield of Mizoroki-Heck coupling reaction of TRAM **10d** with **12a**.

Table 2

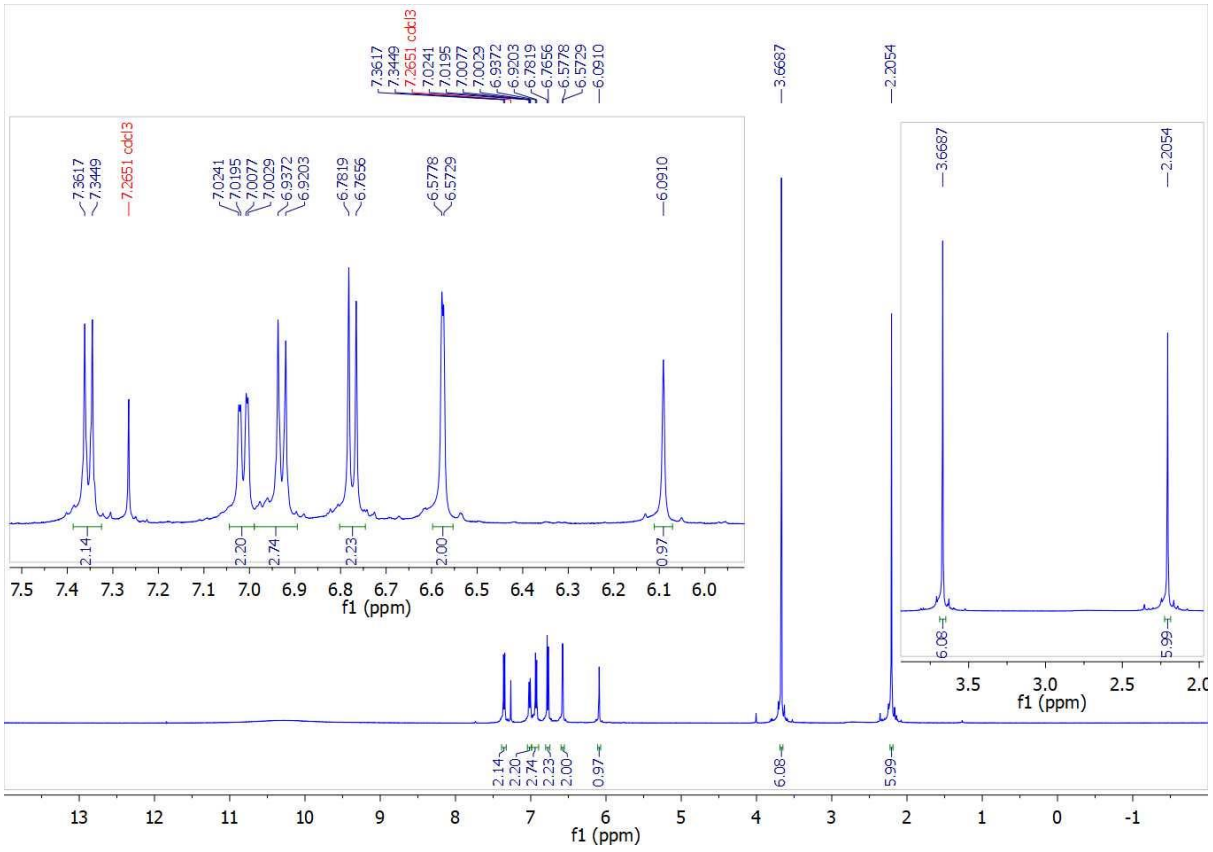
Optimization of the reaction conditions for the one-pot two-step Mizoroki-Heck coupling reaction of **10d** with **12a**.



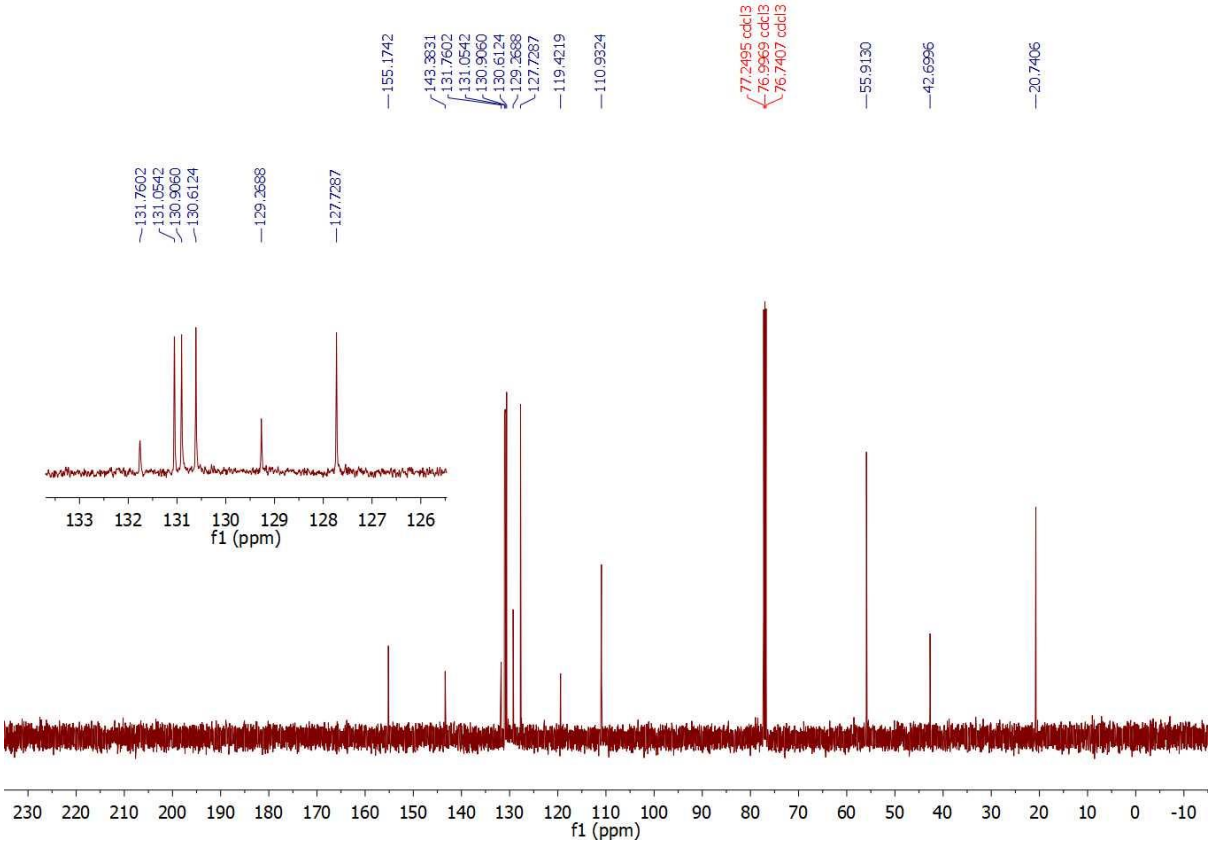
Entry	$PdCl_2$ (mmol)	PPh_3 (mmol)	LiBr (mmol)	10d (mmol)	12a (mmol)	Base	Solvent	T (°C)	Yield % [a]
1	0.05	0.1	0.1	1.0	1.5	Et_3N	DMF[b]	100	68
2	0.05	0.1	0.1	1.0	1.8	Et_3N	DMF	100	73
3	**0.05**	**0.1**	**0.1**	**1.0**	**2.0**	**Et_3N**	DMF	**100**	**89**
4	0.05	0.1	0.1	1.0	2.2	Et_3N	DMF	100	89
5	-	-	-	1.0	2.0	Et_3N	DMF	100	NR
6	0.04	0.08	0.08	1.0	2.0	Et_3N	DMF	100	63
7	0.06	0.12	0.12	1.0	2.0	Et_3N	DMF	100	89
8	0.05	0.1	0.1	1.0	2.0	K_2CO_3**(Cs_2CO_3)**	DMF	100	19**(20)**
9	0.05	0.1	0.1	1.0	2.0	DBU**(DABCO)**	DMF	100	25**(30)**
10	0.05	0.1	0.1	1.0	2.0	Et_3N	DMF	80	60
11	0.05	0.1	0.1	1.0	2.0	Et_3N	DMF	120	78

[a] Isolated yield. [b] Carrying out the reaction under the same conditions in solvents including MeOH, toluene, THF, and 1,4-dioxane afforded **13a** in yields ranging from 21 to 24%.

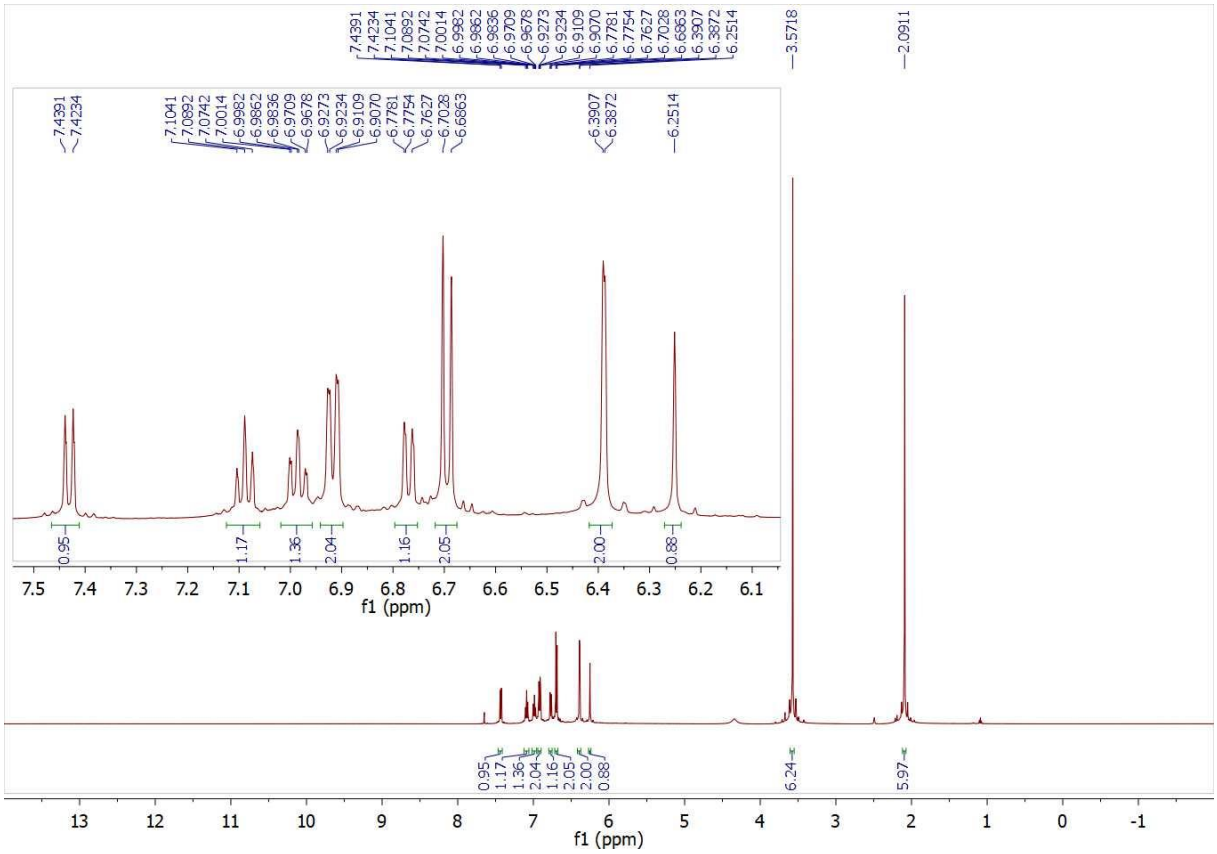
3. NMR spectra of halogenated triarylmethanes



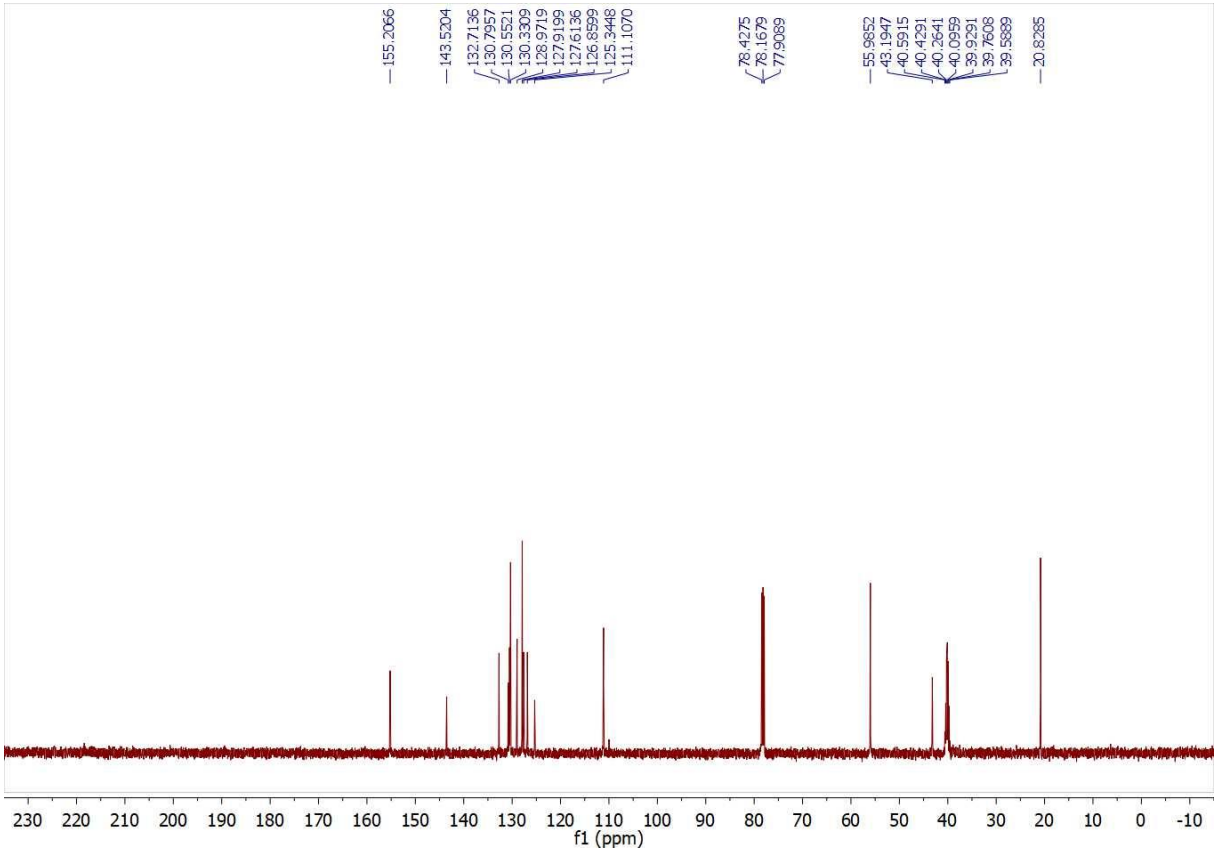
^{1}H NMR of 2,2'-((4-bromophenyl)methylene)bis(1-methoxy-4-methylbenzene) (10d)



^{13}C NMR of 2,2'-((4-bromophenyl)methylene)bis(1-methoxy-4-methylbenzene) (10d)



[1]H NMR of 2,2'-((2-bromophenyl)methylene)bis(1-methoxy-4-methylbenzene) (10f)



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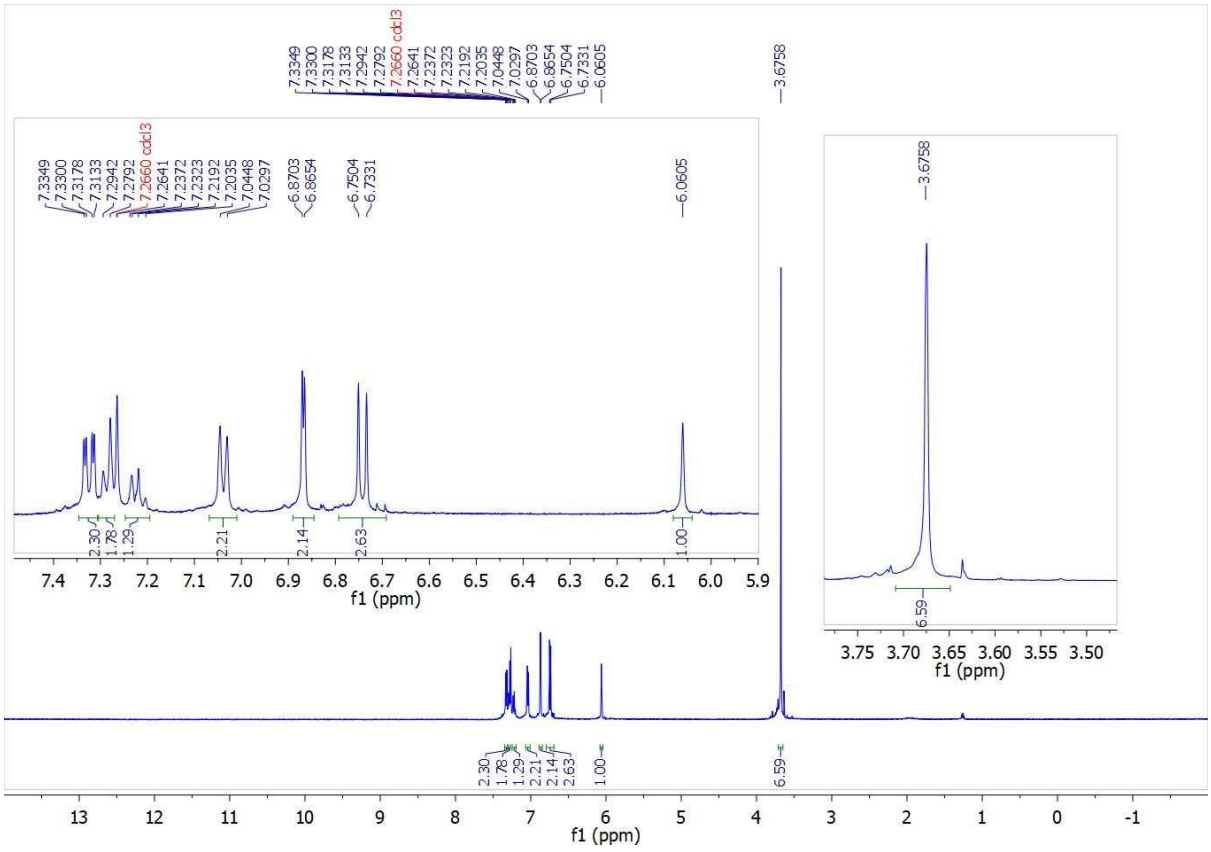
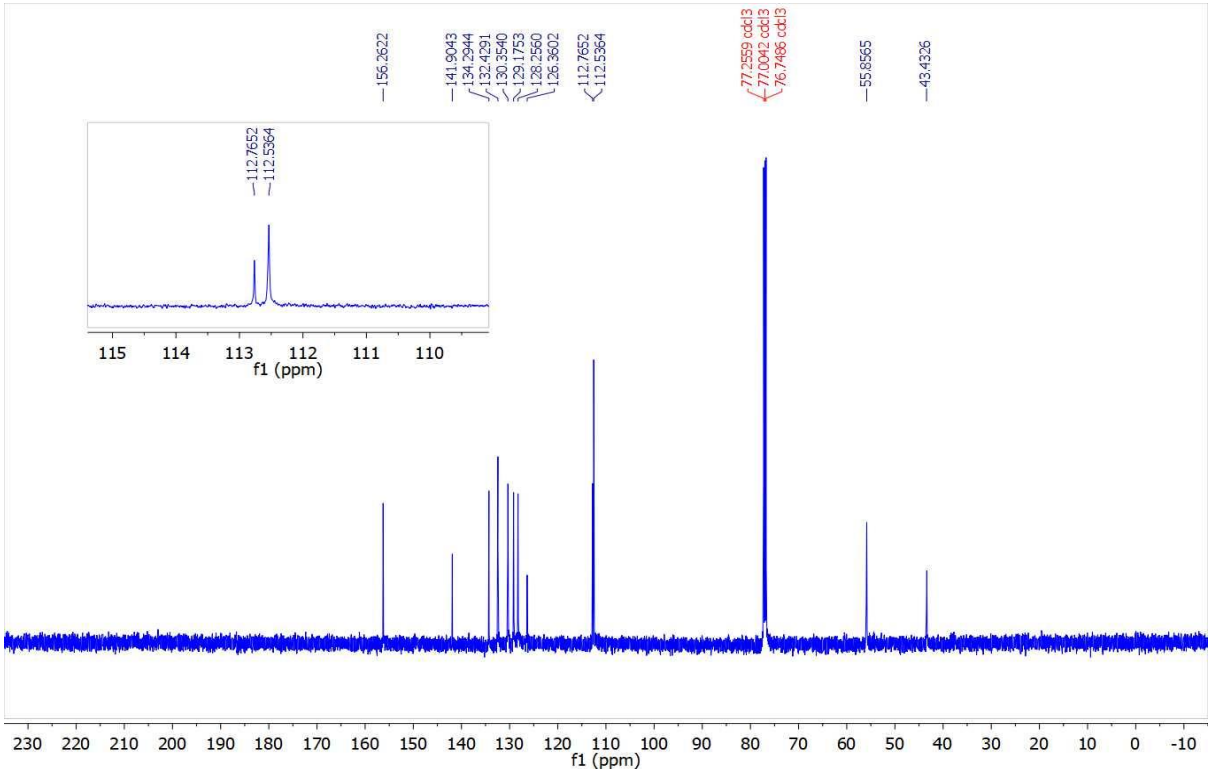
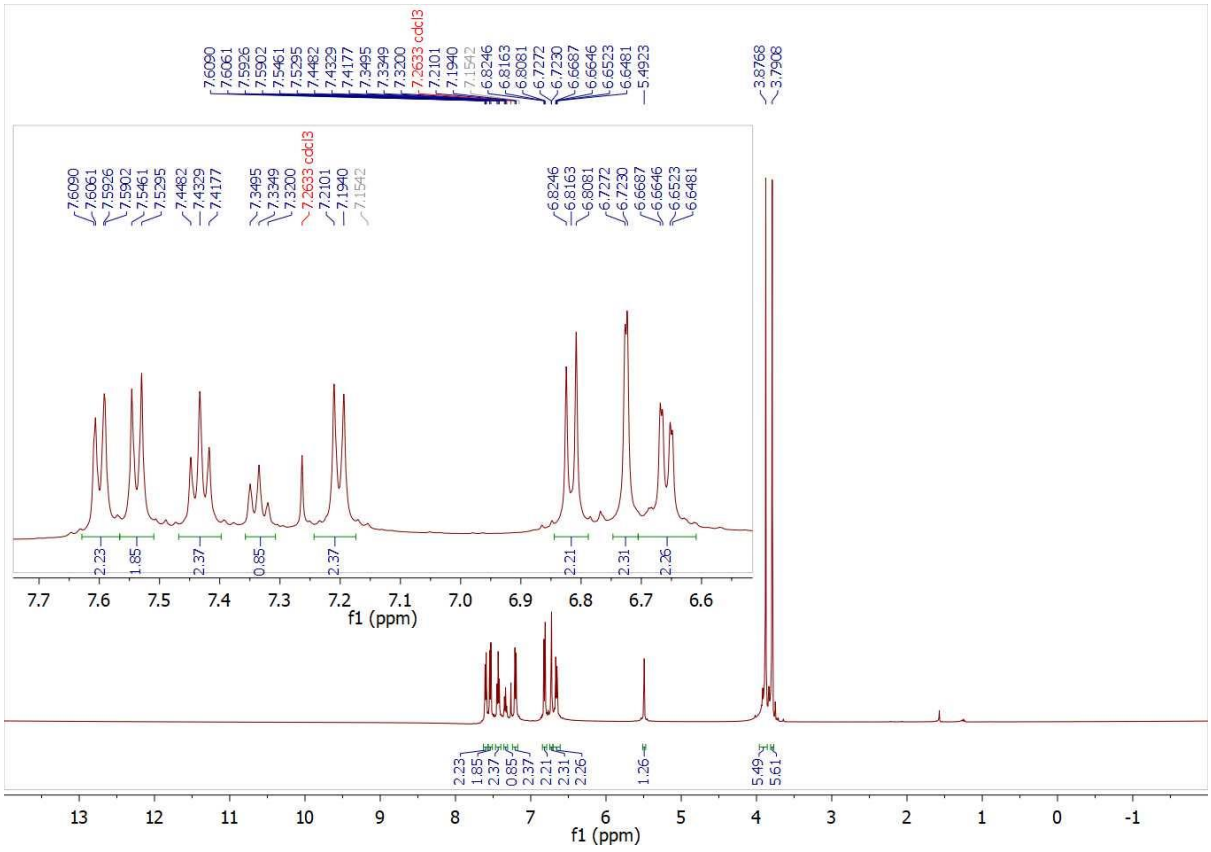


[1]H NMR of 2,2'-(phenylmethylene)bis(4-bromo-1-methoxybenzene) (10g)

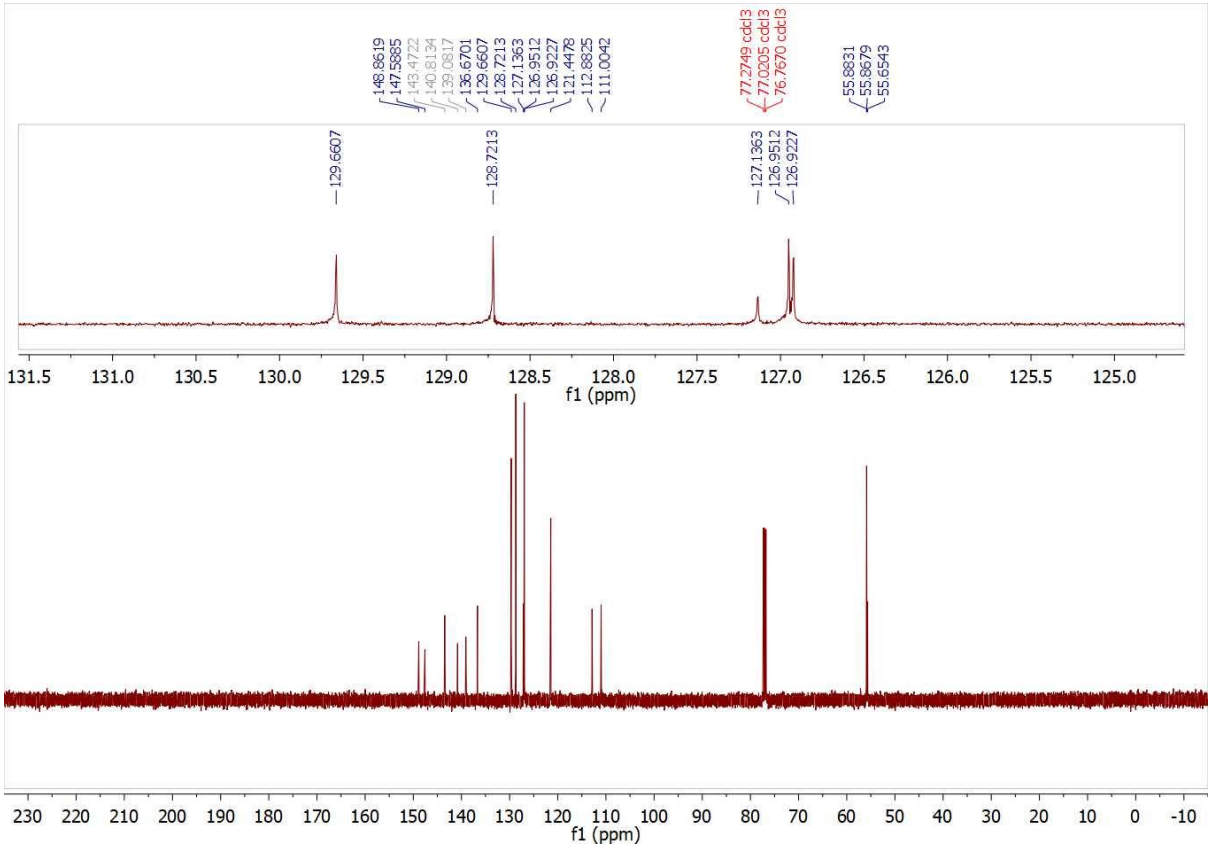


[13]C NMR of 2,2'-(phenylmethylene)bis(4-bromo-1-methoxybenzene) (10g)

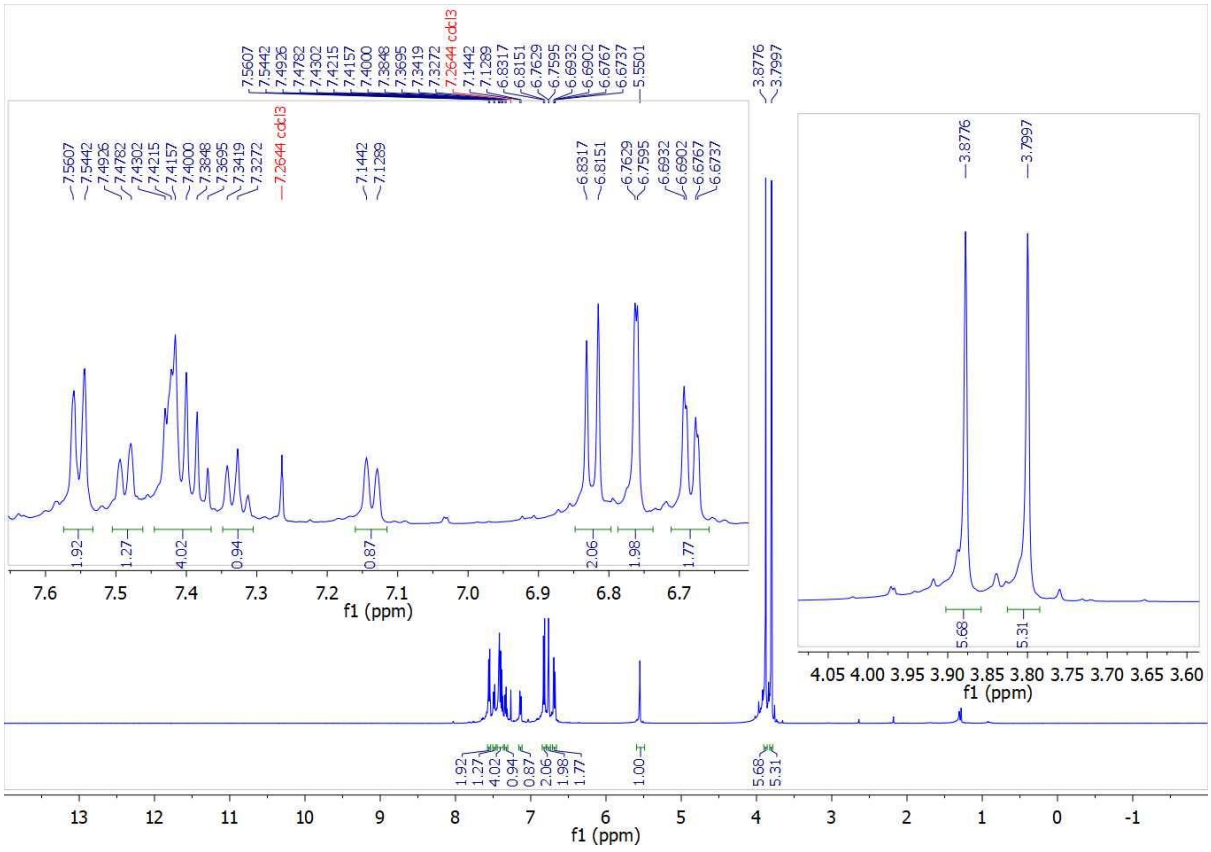
4. NMR spectra of Suzuki-Miyaura coupling triarylmethane-products (6a-l)



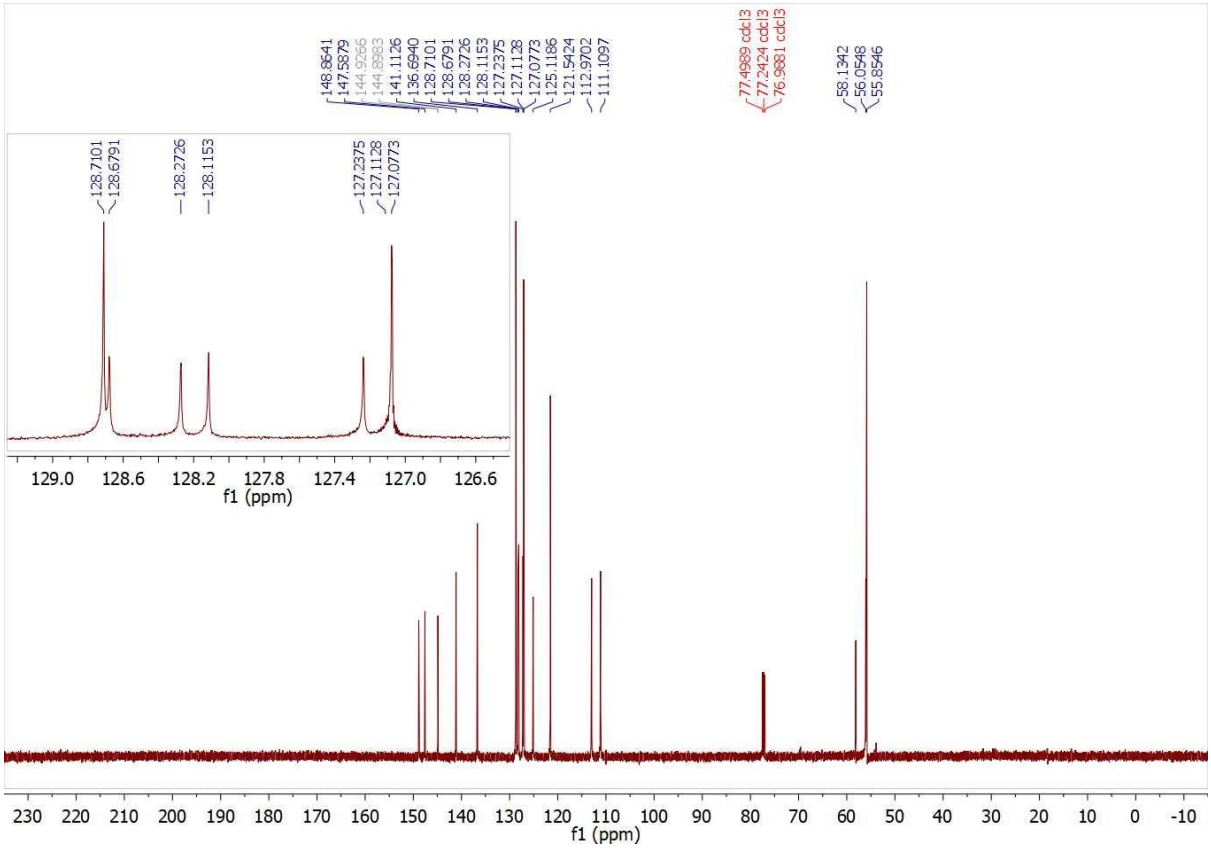
[1]H NMR of 4-(bis(3,4-dimethoxyphenyl)methyl)-1,1'-biphenyl (6a)



[13]C NMR of 4-(bis(3,4-dimethoxyphenyl)methyl)-1,1'-biphenyl (6a)



^{1}H NMR of 3-(bis(3,4-dimethoxyphenyl)methyl)-1,1'-biphenyl (6b)



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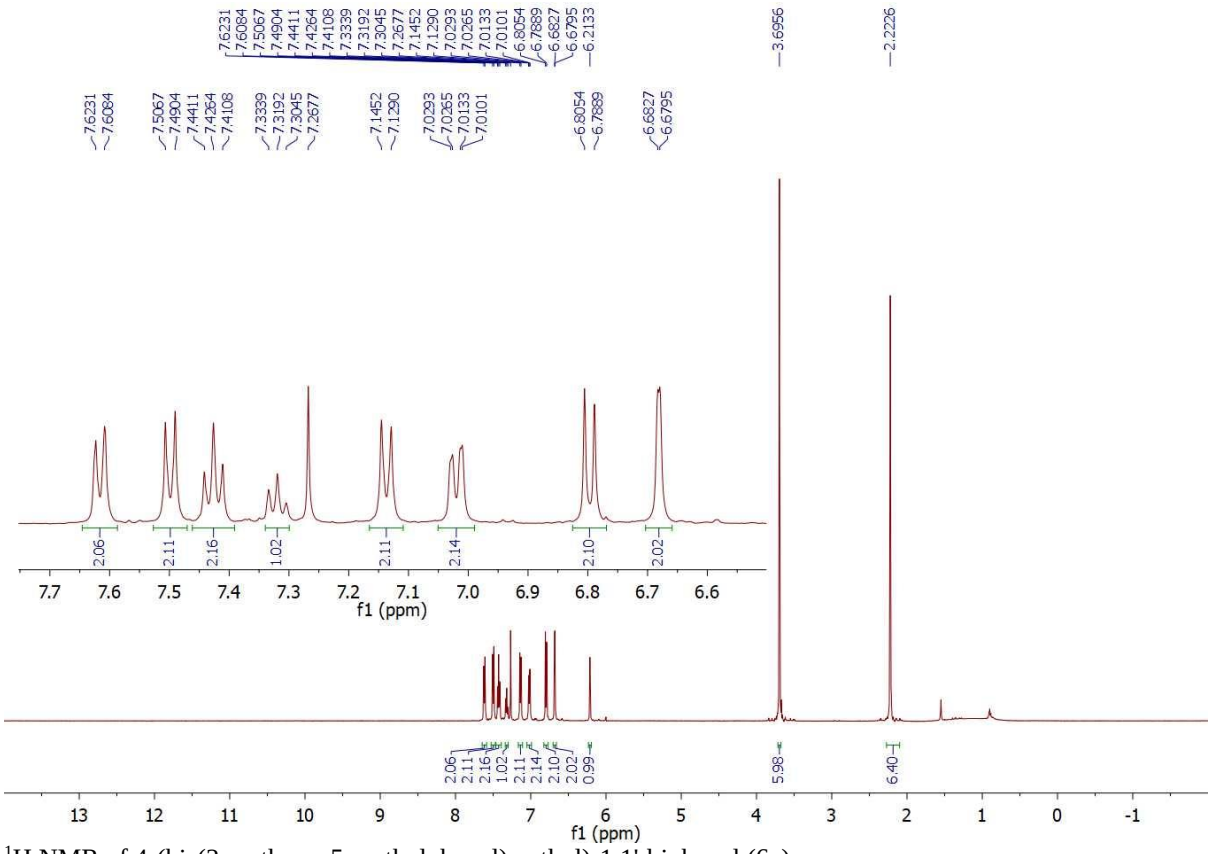
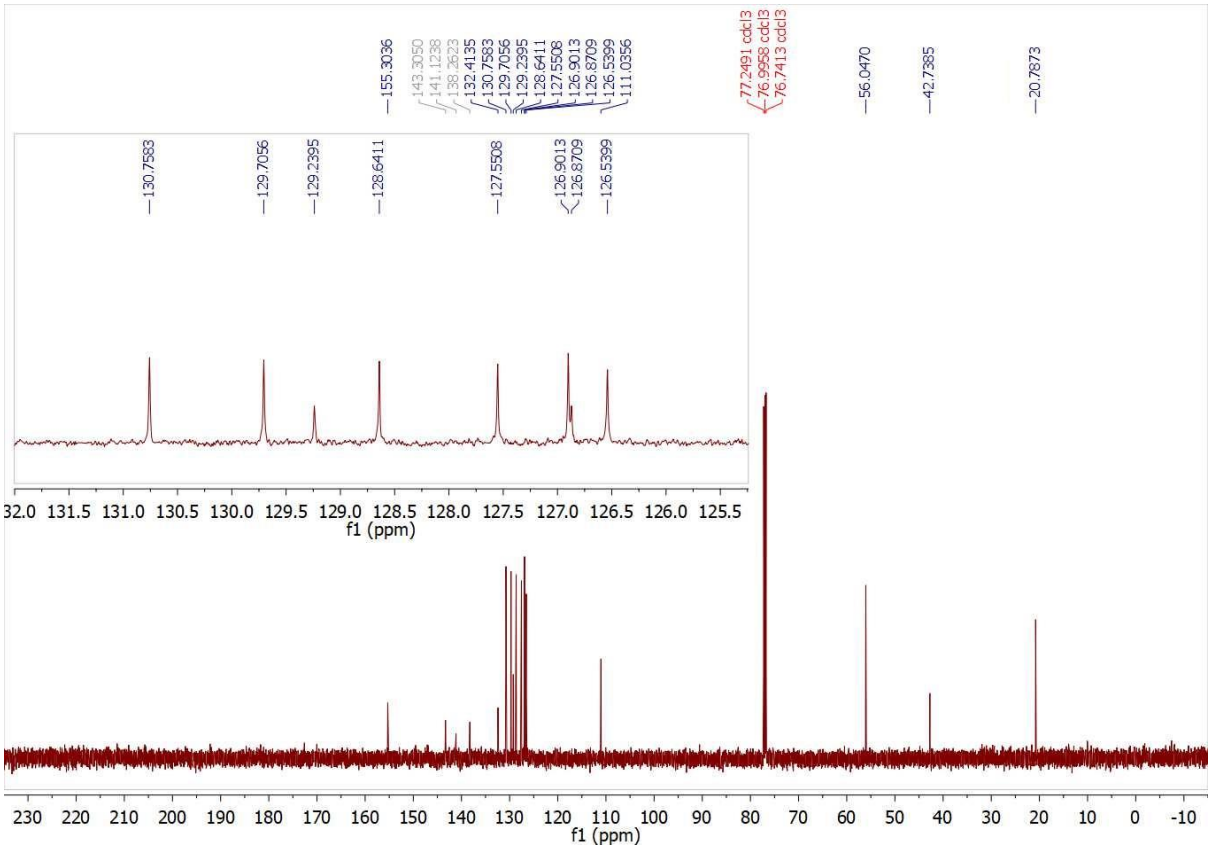


^{1}H NMR of 4-(bis(2-methoxy-5-methylphenyl)methyl)-1,1'-biphenyl (6c)



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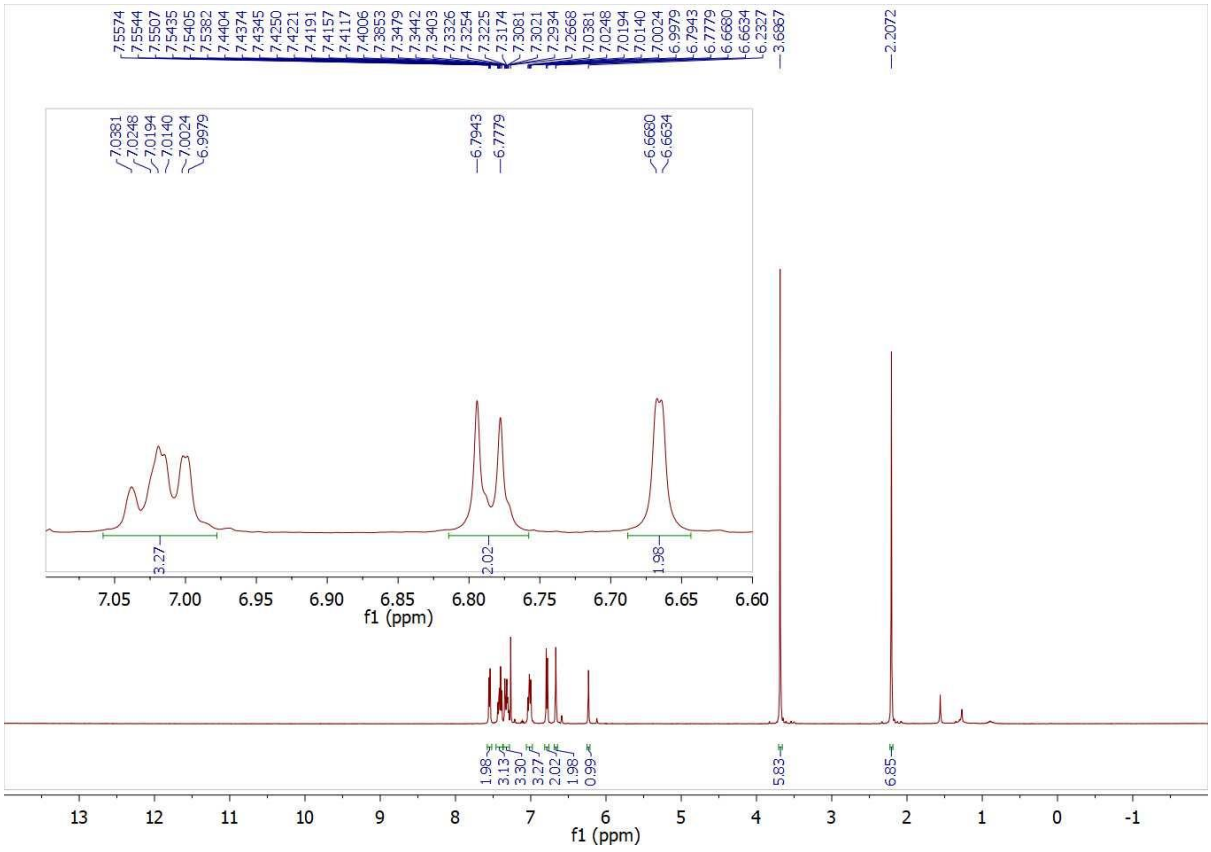
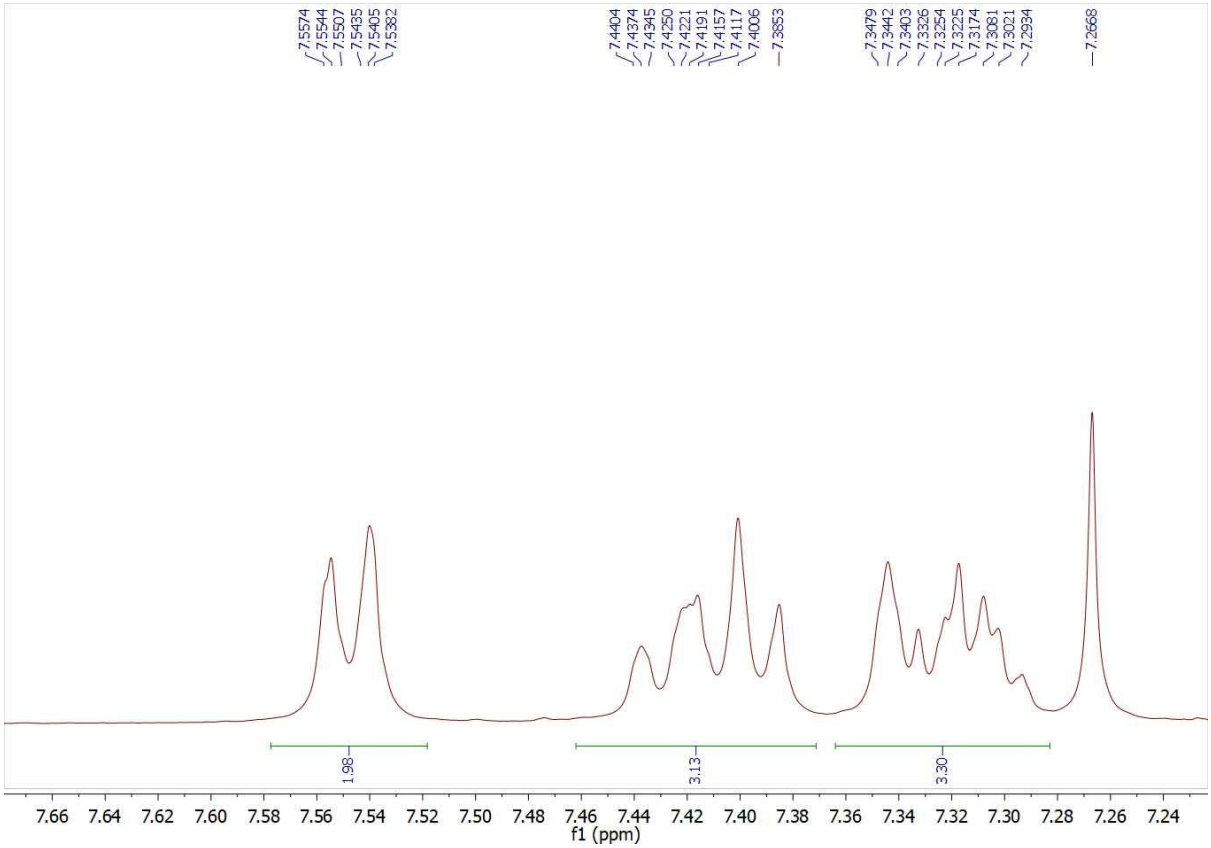


^{1}H NMR of 3-(bis(2-methoxy-5-methylphenyl)methyl)-1,1'-biphenyl (6d)



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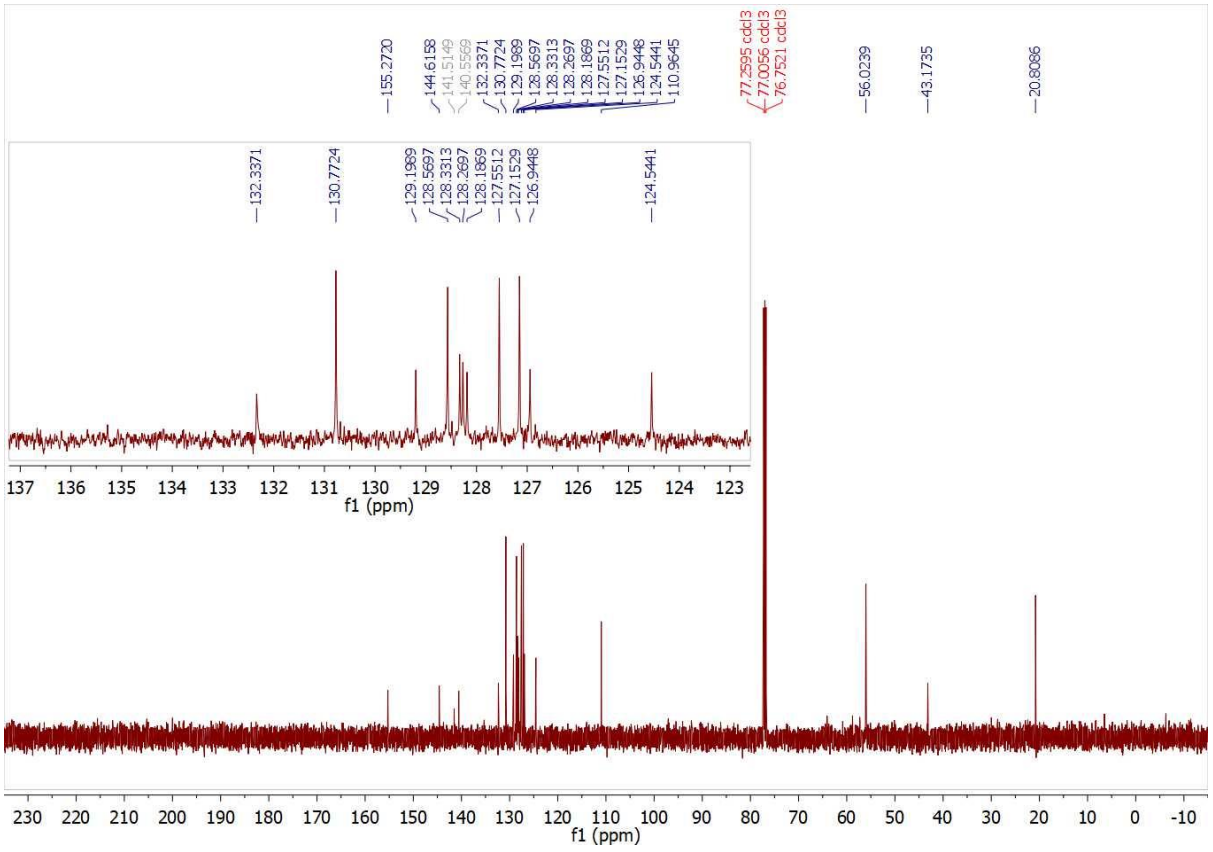

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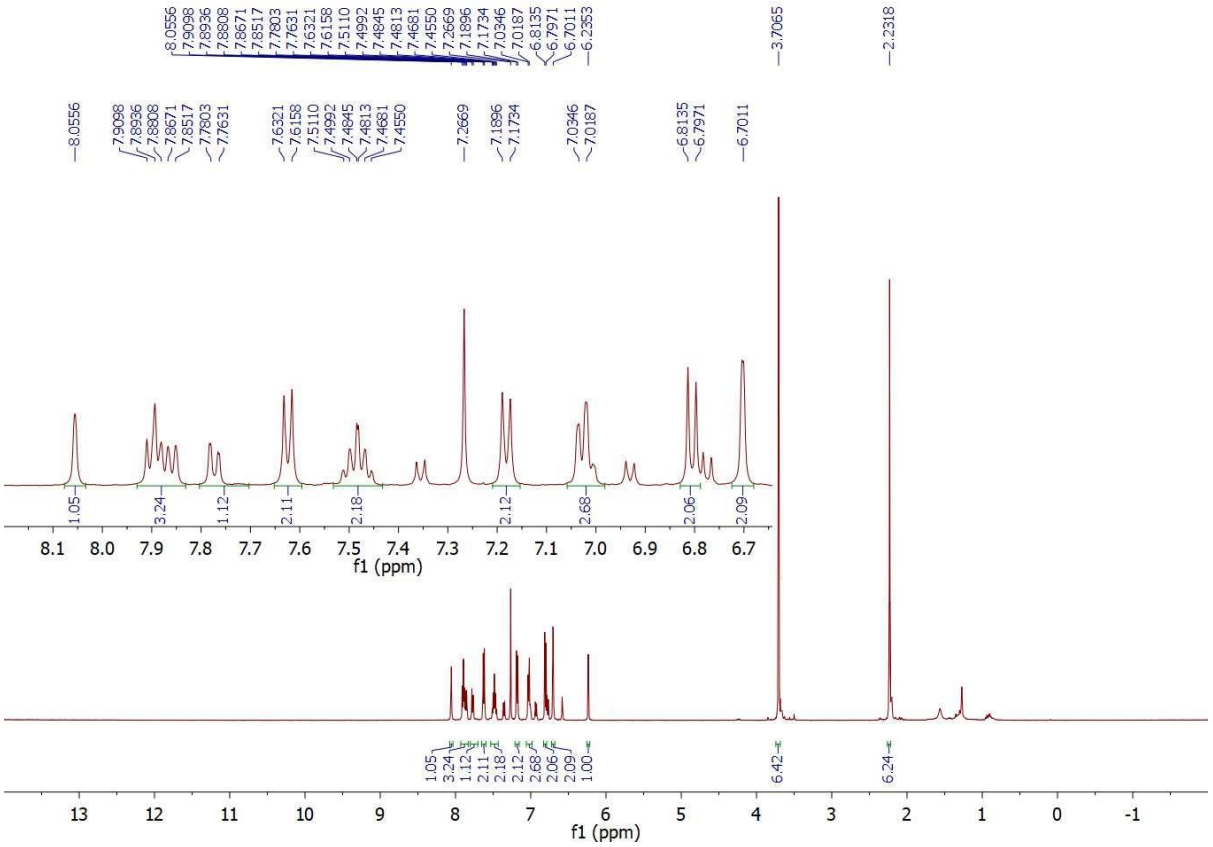
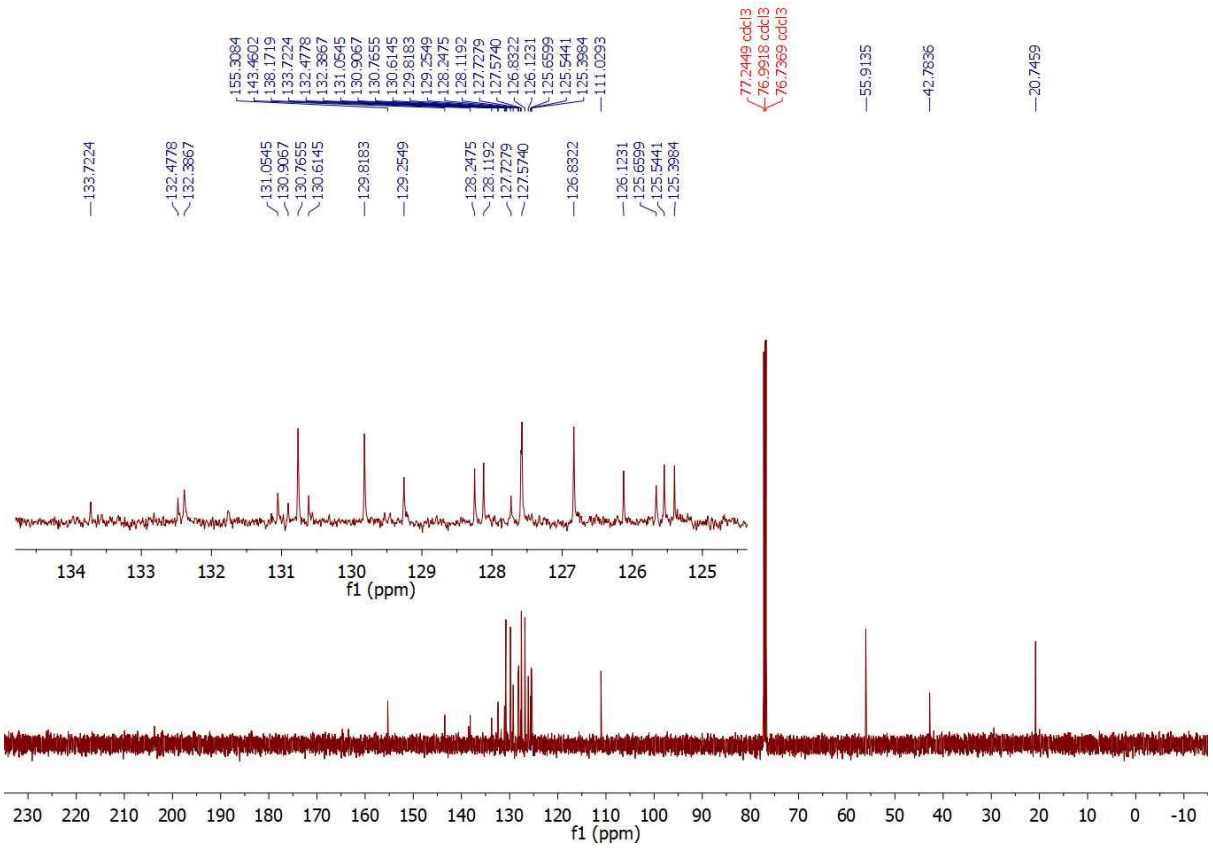
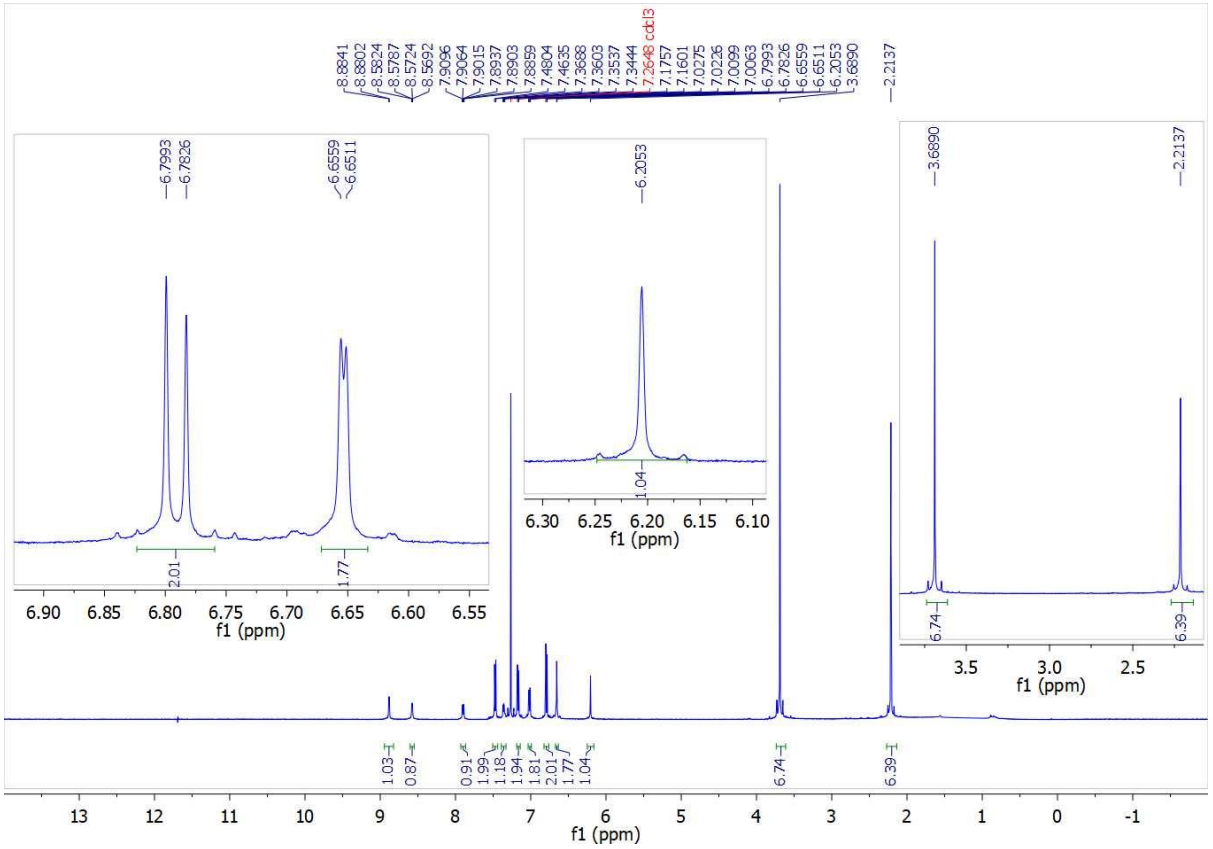


^{1}H NMR of 1-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)naphthalene (6e)



^{13}C NMR of 1-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)naphthalene (6e)



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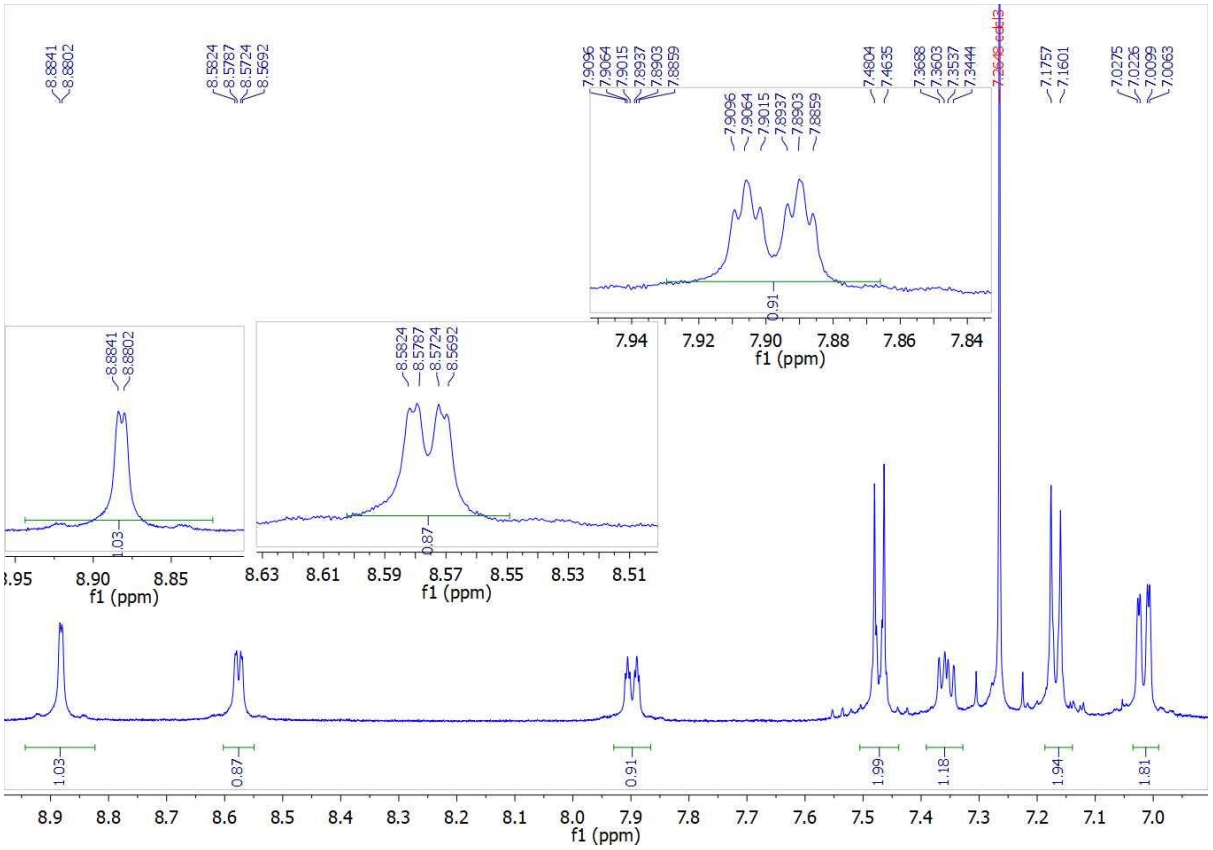

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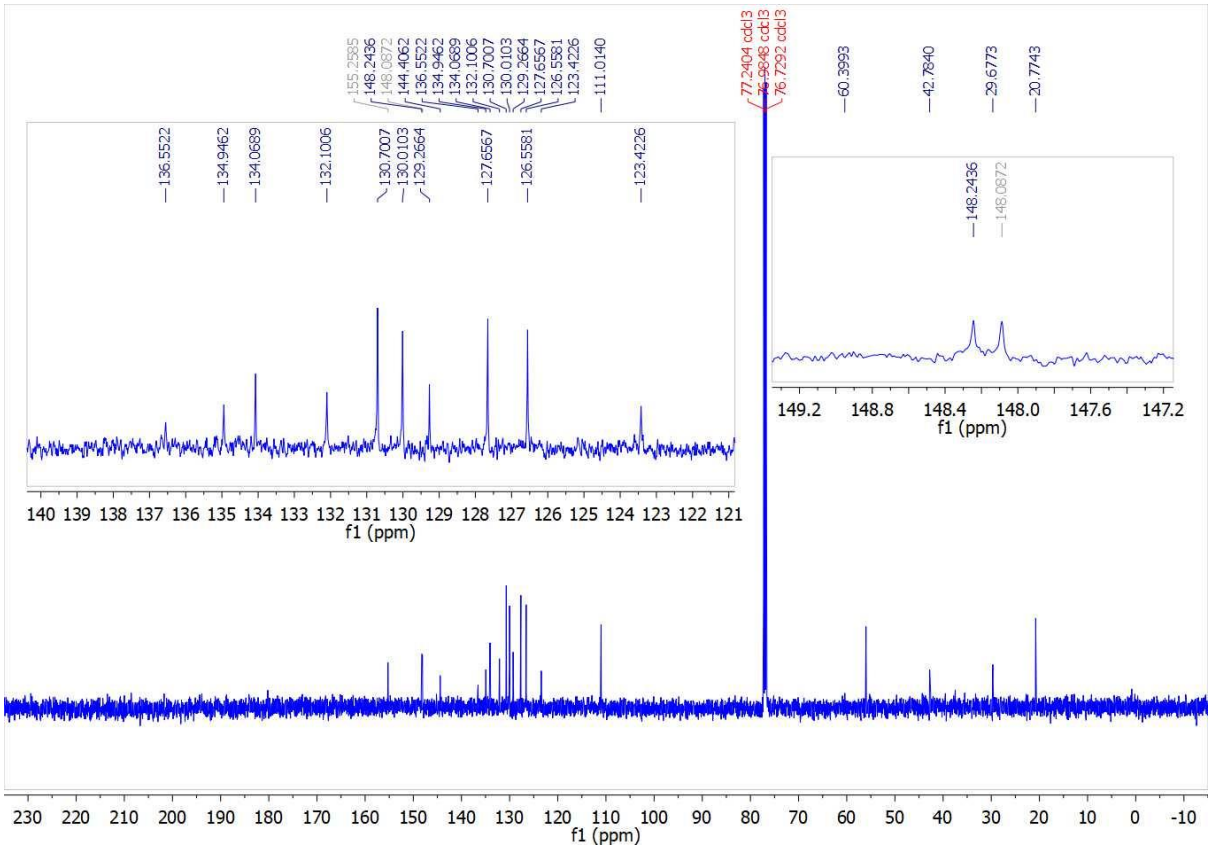
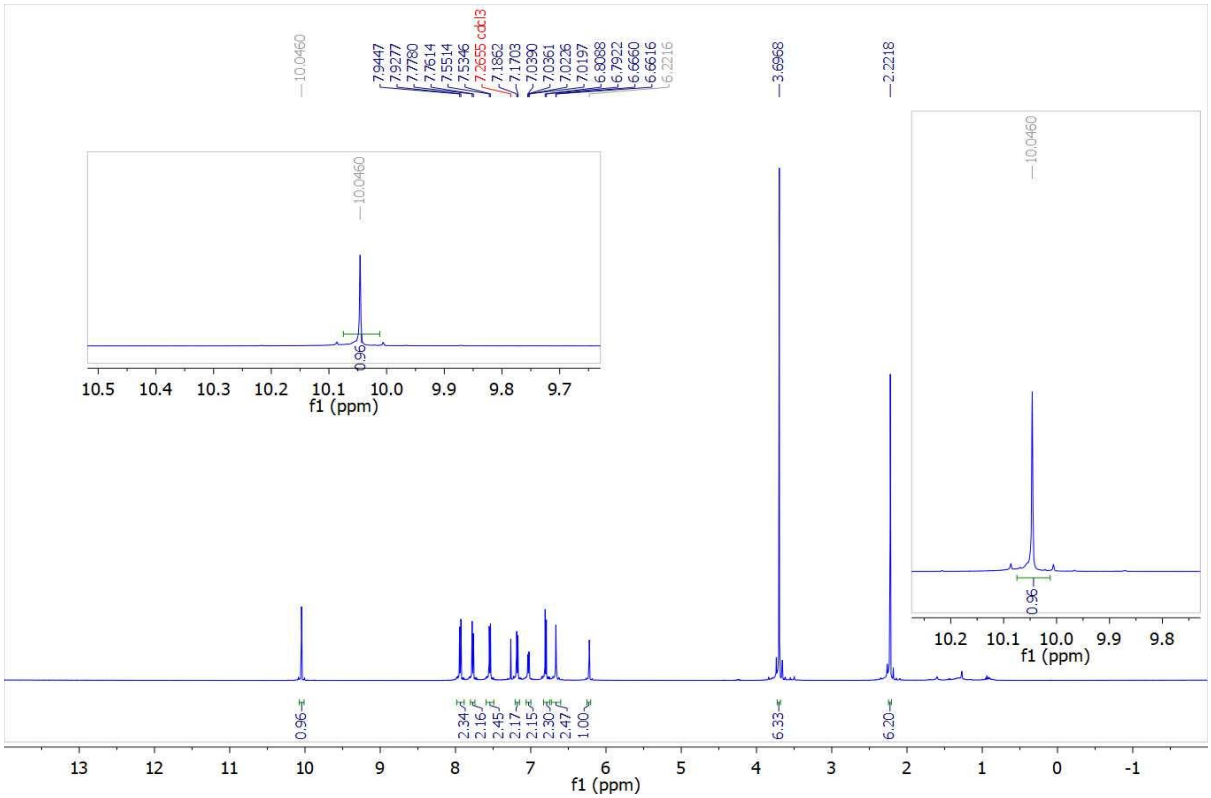
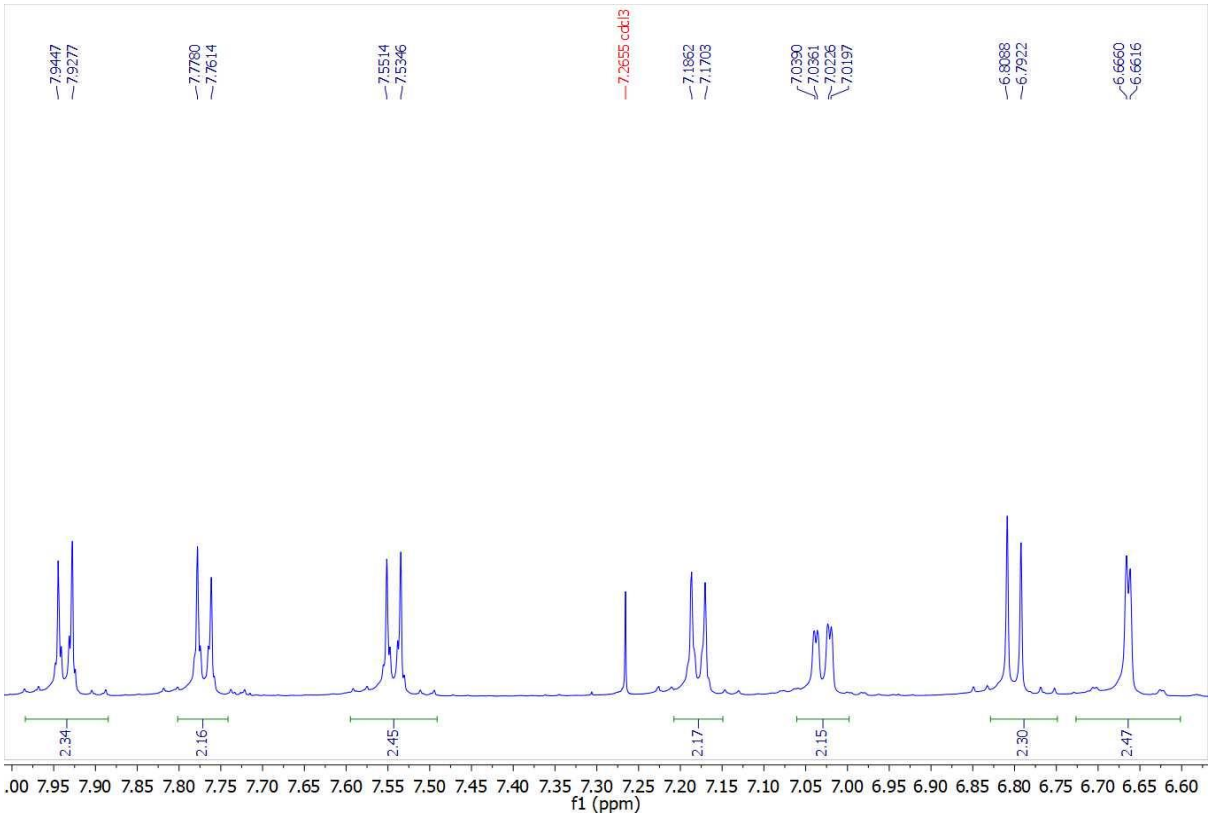


^{13}C NMR of 3-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)pyridine (6f)



[1]H NMR of 4'-(bis(2-methoxy-5-methylphenyl)methyl)-[1,1'-biphenyl]-4-carbaldehyde (6g)



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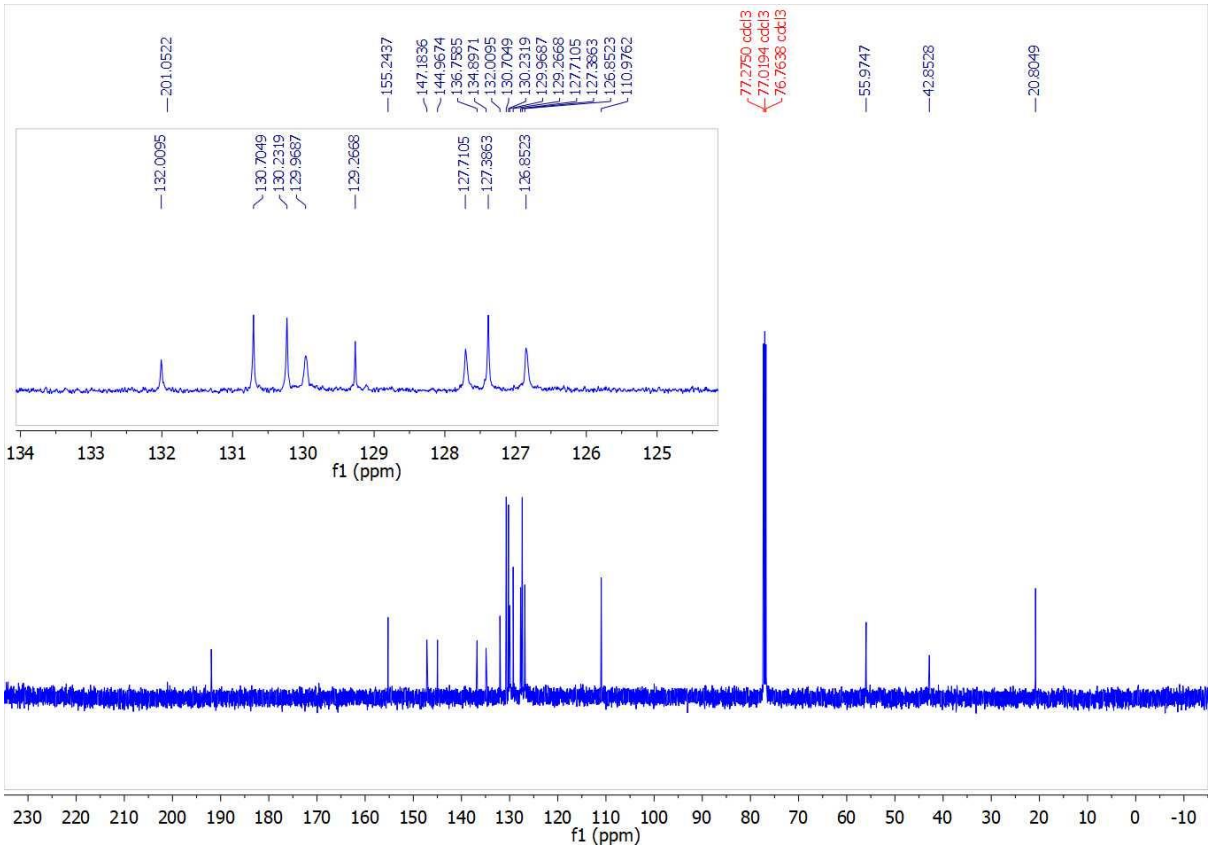
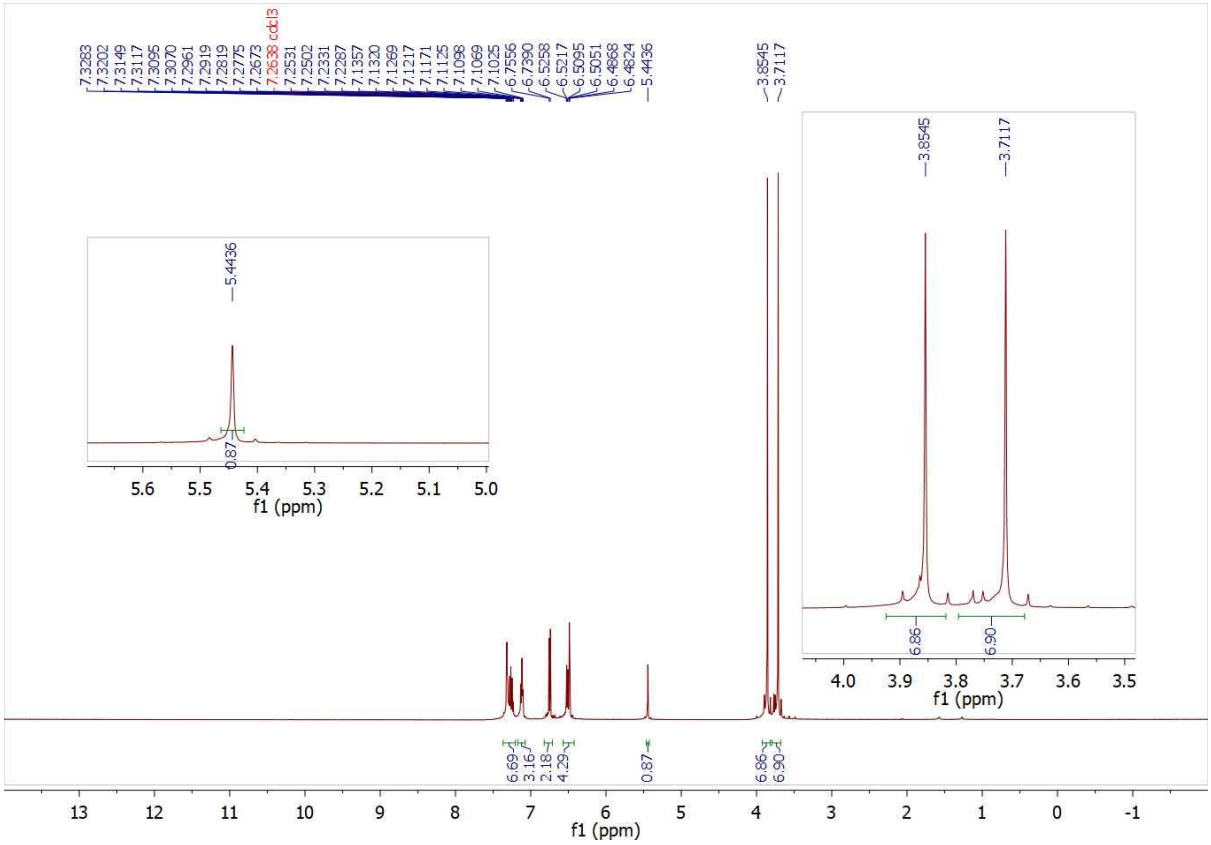


^{13}C NMR of 4'-(bis(2-methoxy-5-methylphenyl)methyl)-[1,1'-biphenyl]-4-carbaldehyde (6g)



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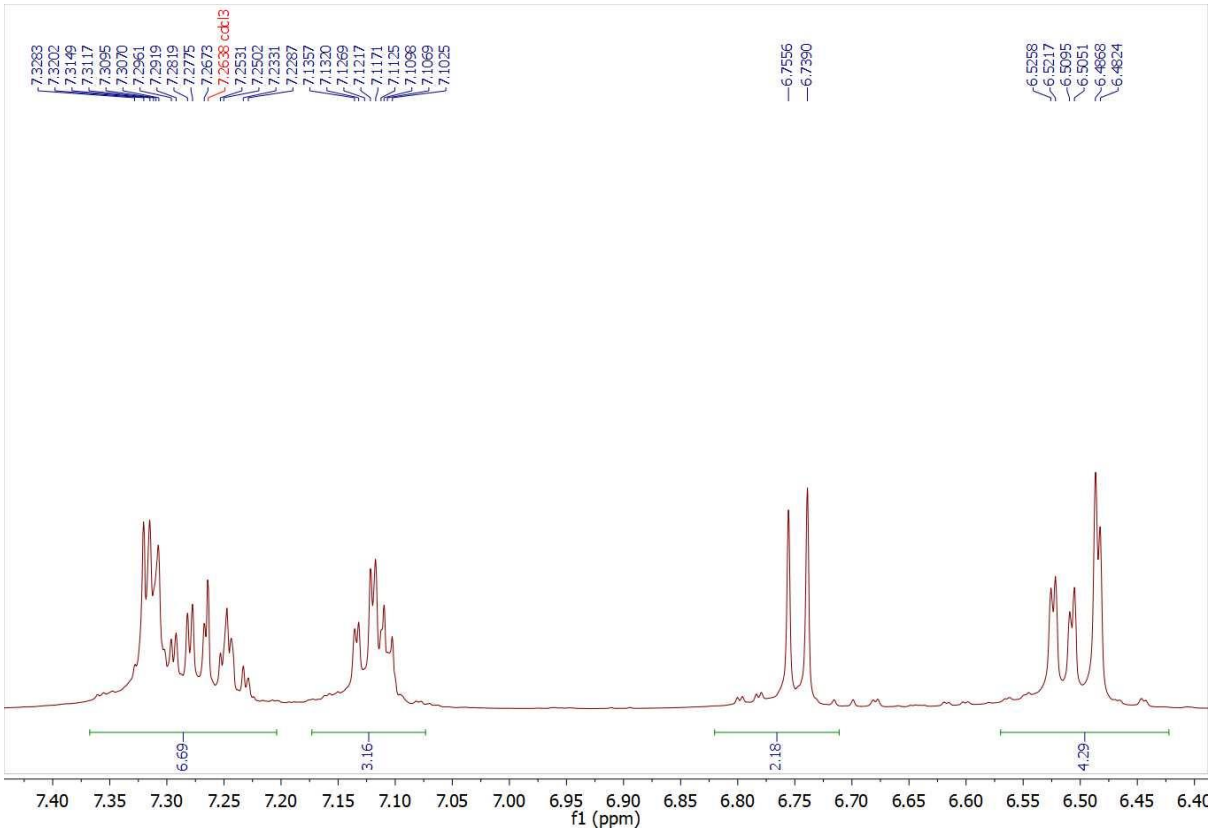

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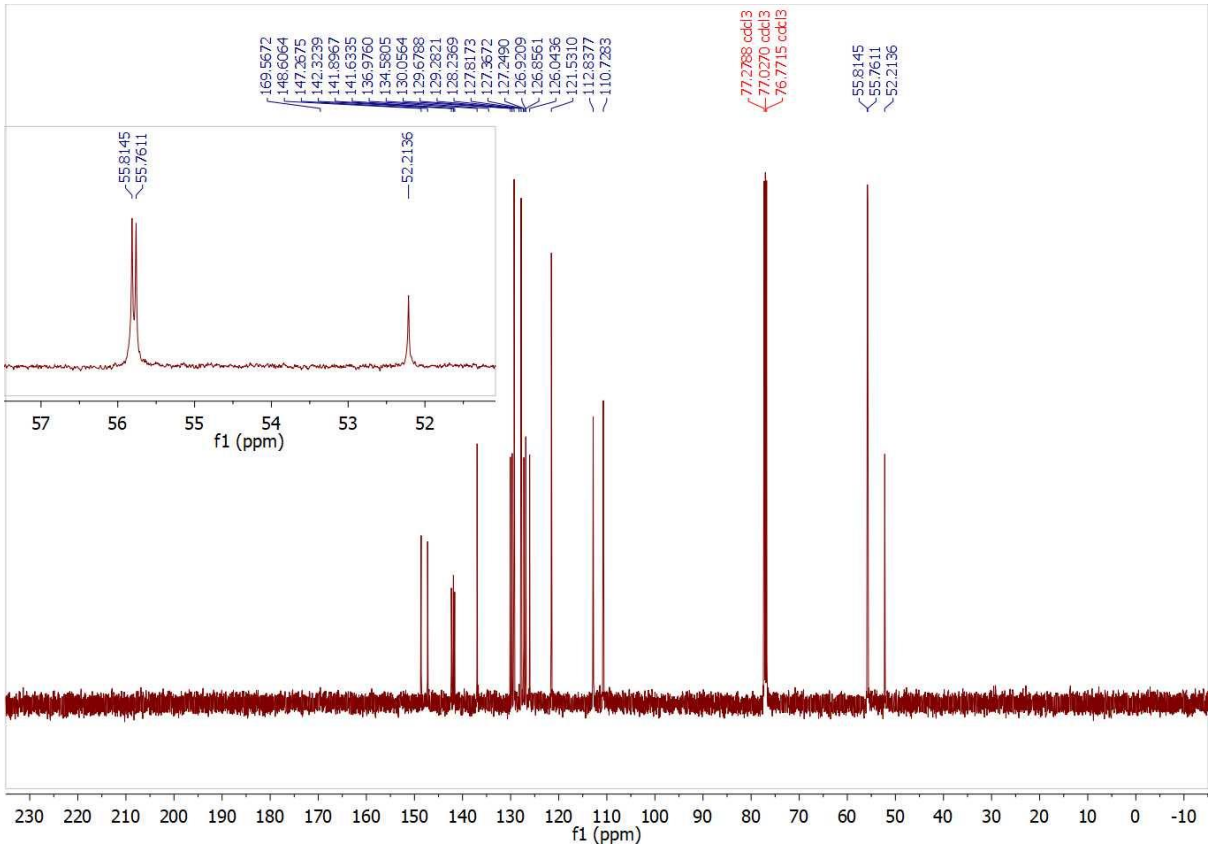
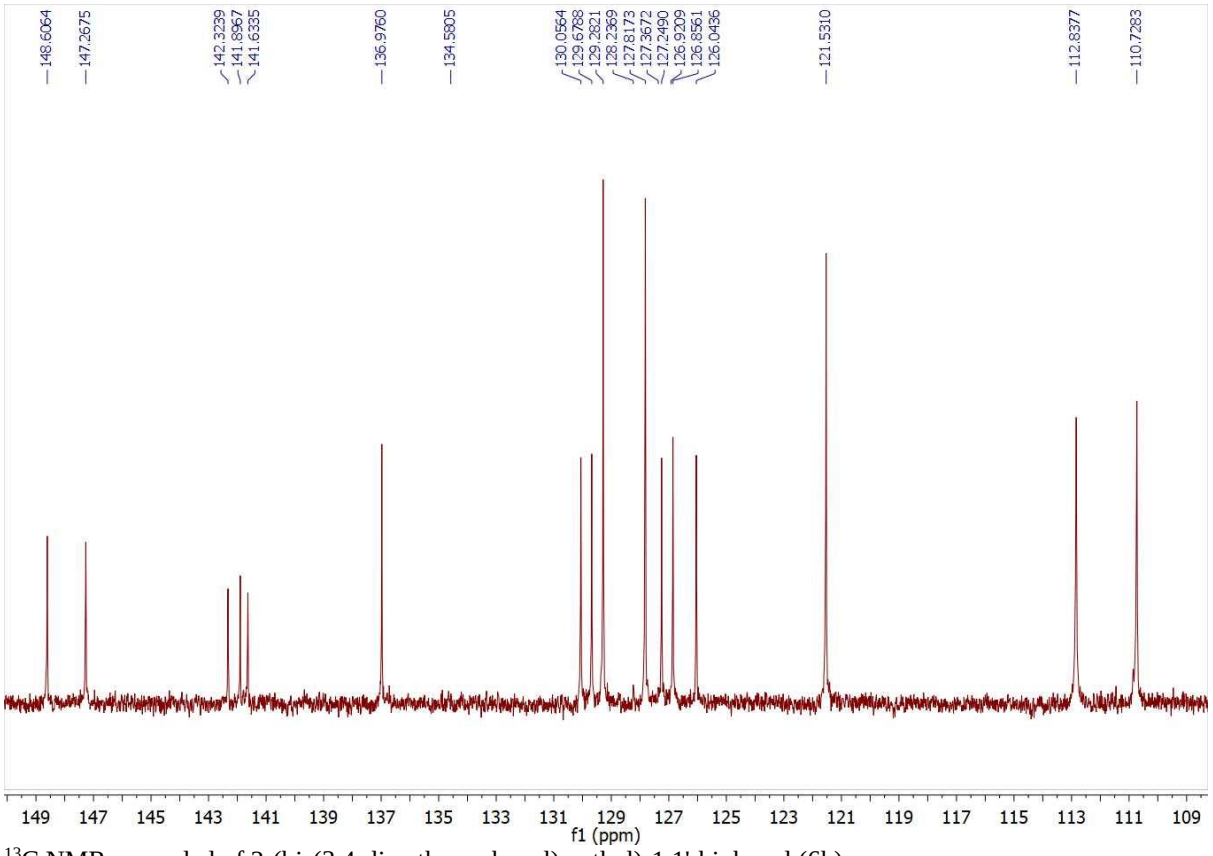
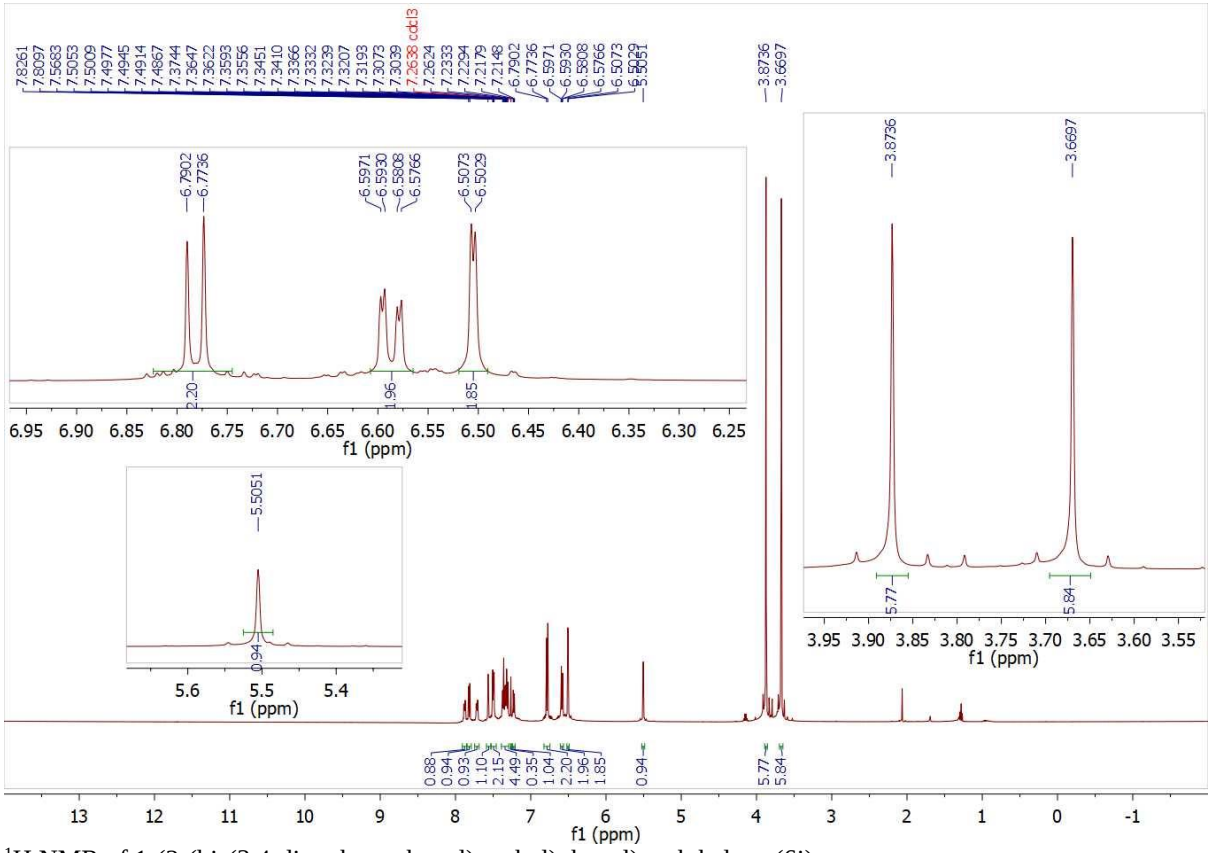


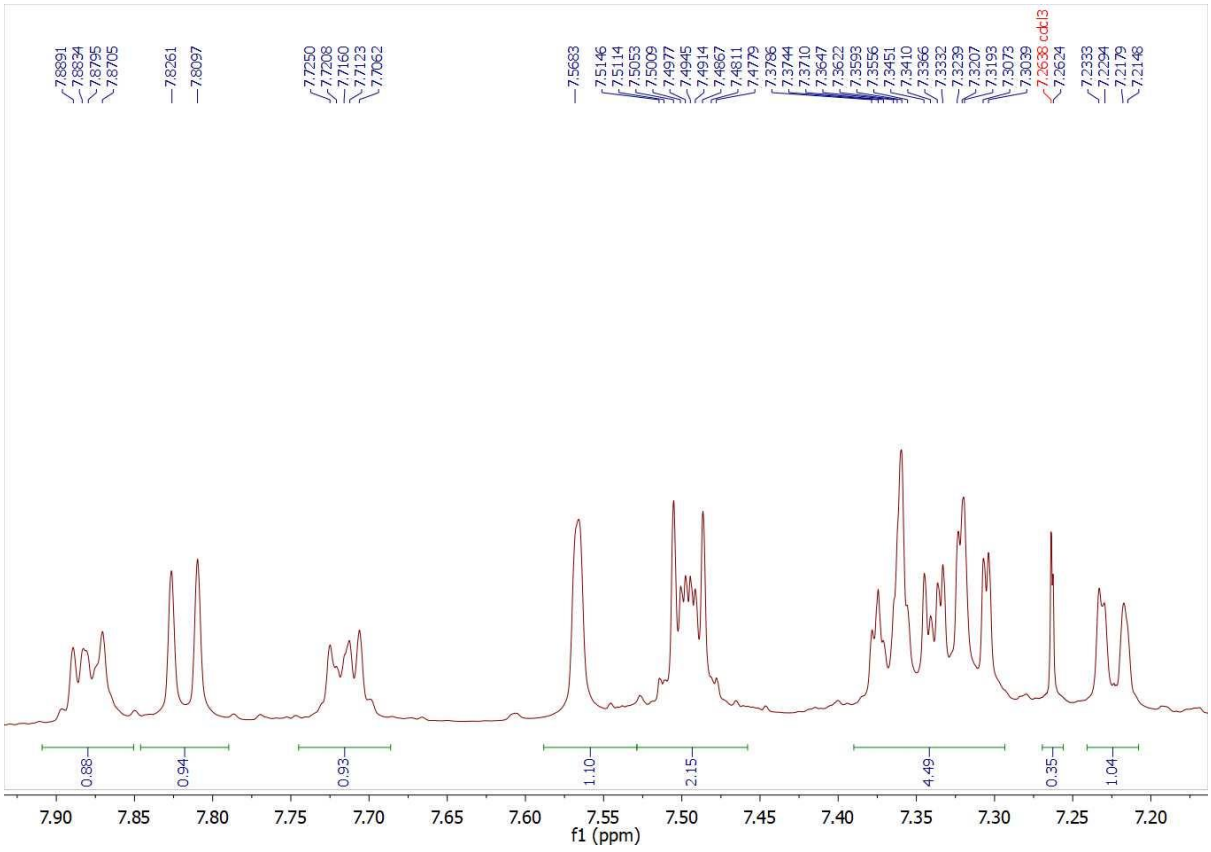
[13]C NMR of 2-(bis(3,4-dimethoxyphenyl)methyl)-1,1'-biphenyl (6h)



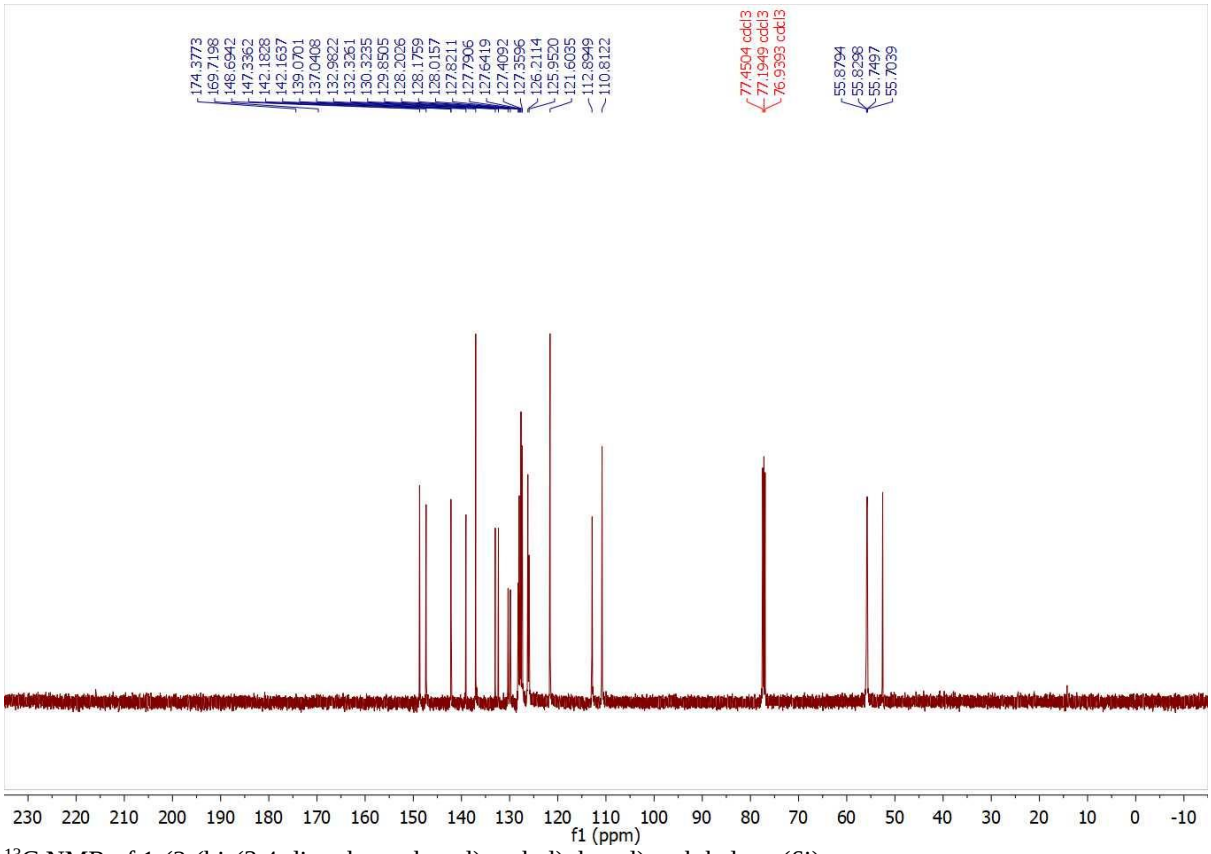
^{13}C NMR expanded of 2-(bis(3,4-dimethoxyphenyl)methyl)-1,1'-biphenyl (6h)



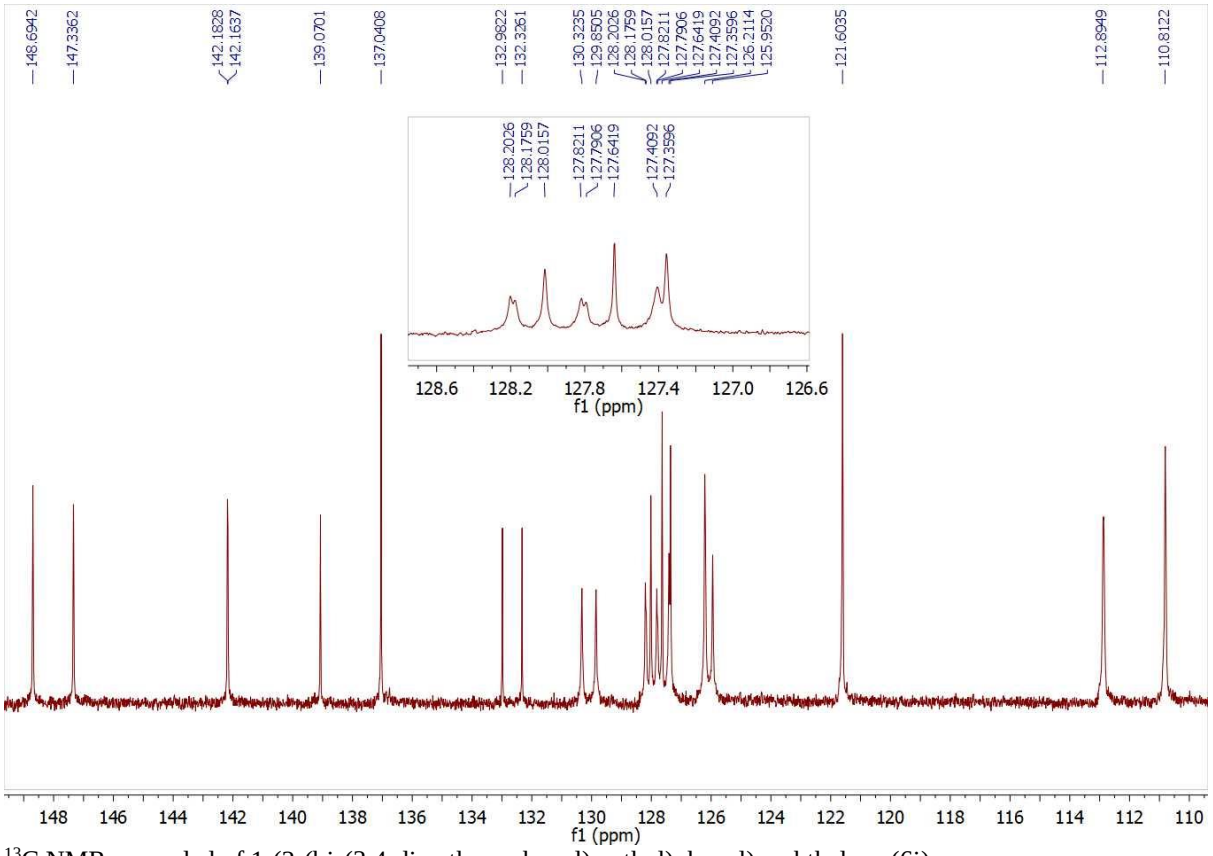
^{1}H NMR of 1-(2-(bis(3,4-dimethoxyphenyl)methyl)phenyl)naphthalene (6i)



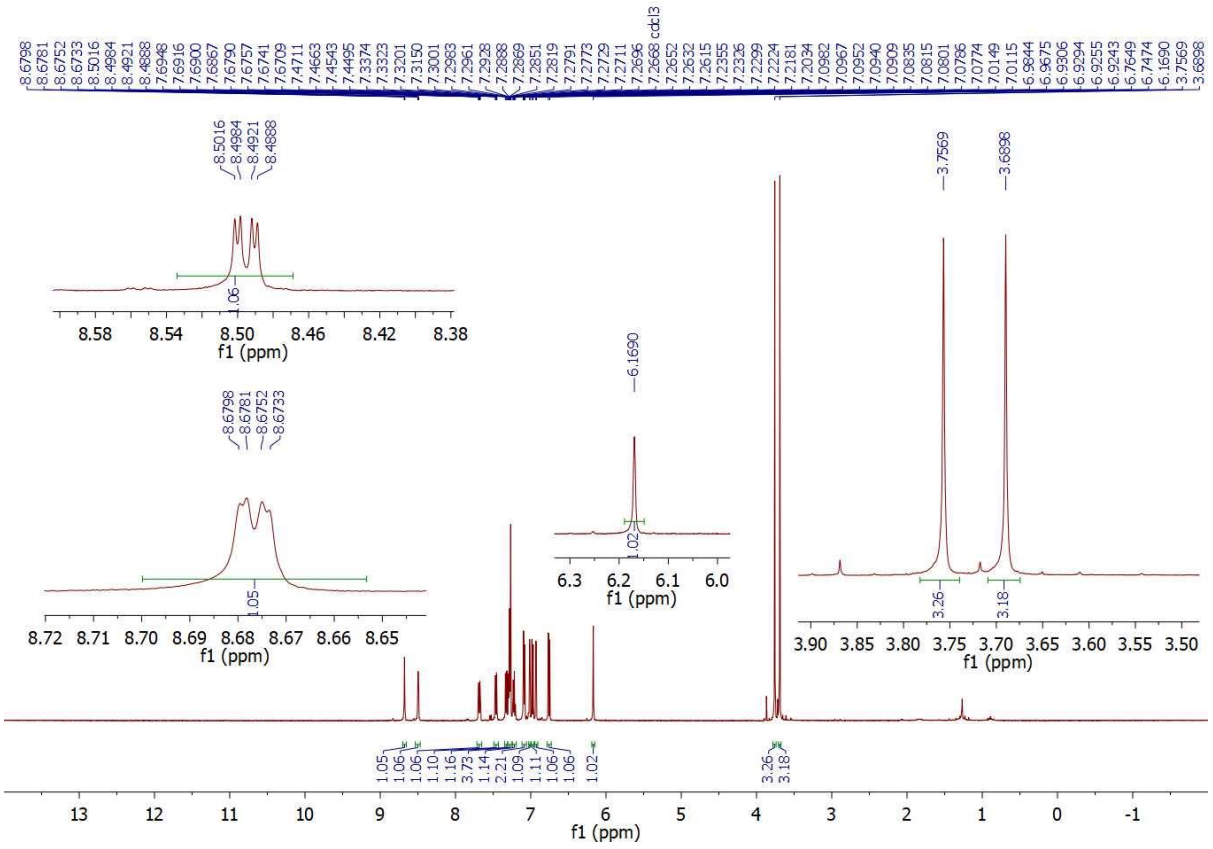
[1]H NMR expanded of 1-(2-(bis(3,4-dimethoxyphenyl)methyl)phenyl)naphthalene (6i)



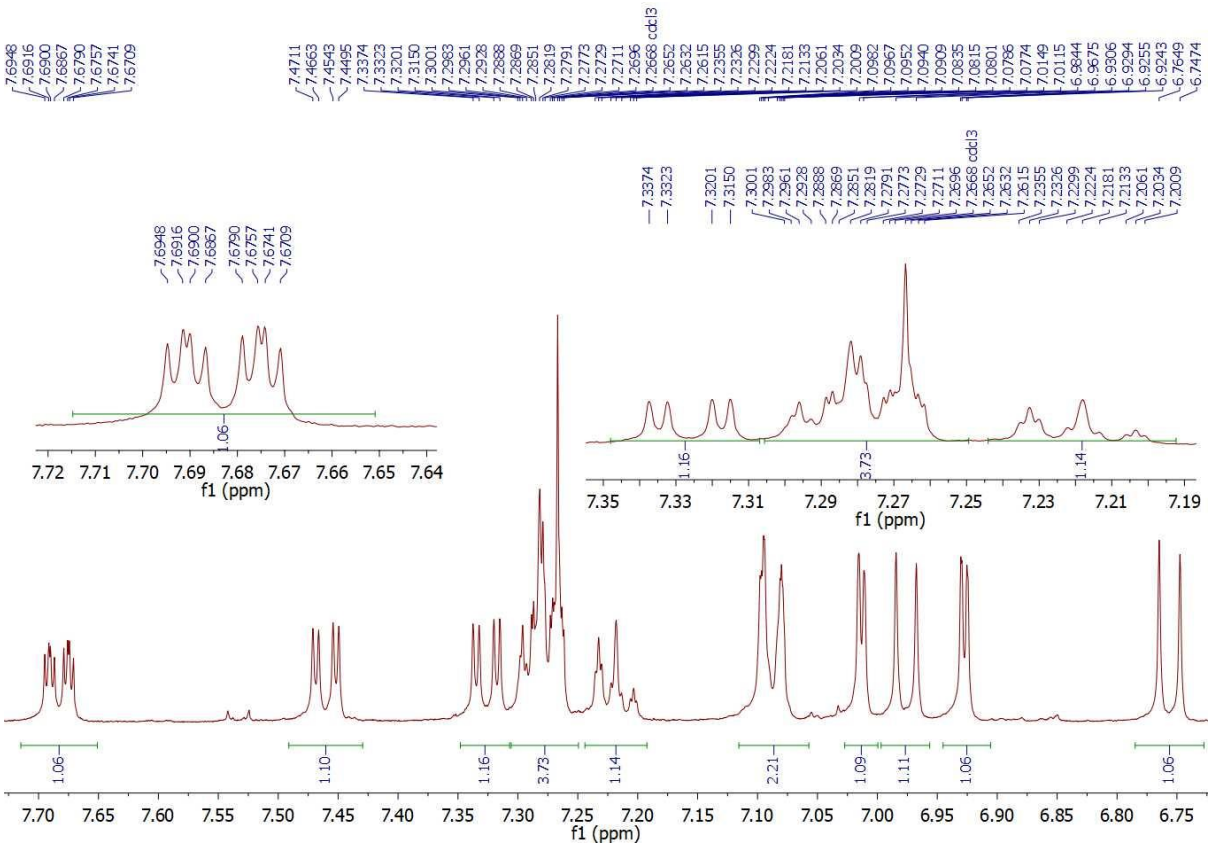
[13]C NMR of 1-(2-(bis(3,4-dimethoxyphenyl)methyl)phenyl)naphthalene (6i)



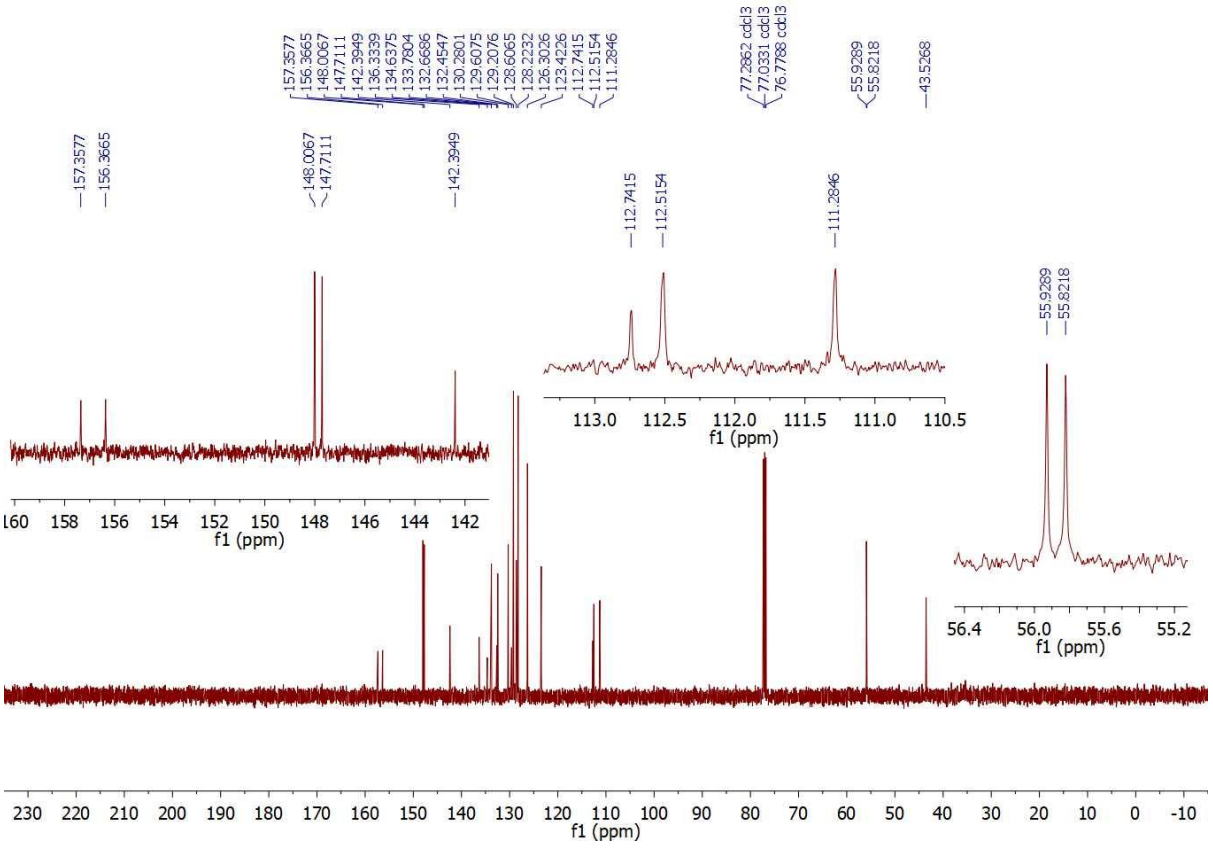
^{13}C NMR expanded of 1-(2-(bis(3,4-dimethoxyphenyl)methyl)phenyl)naphthalene (6i)



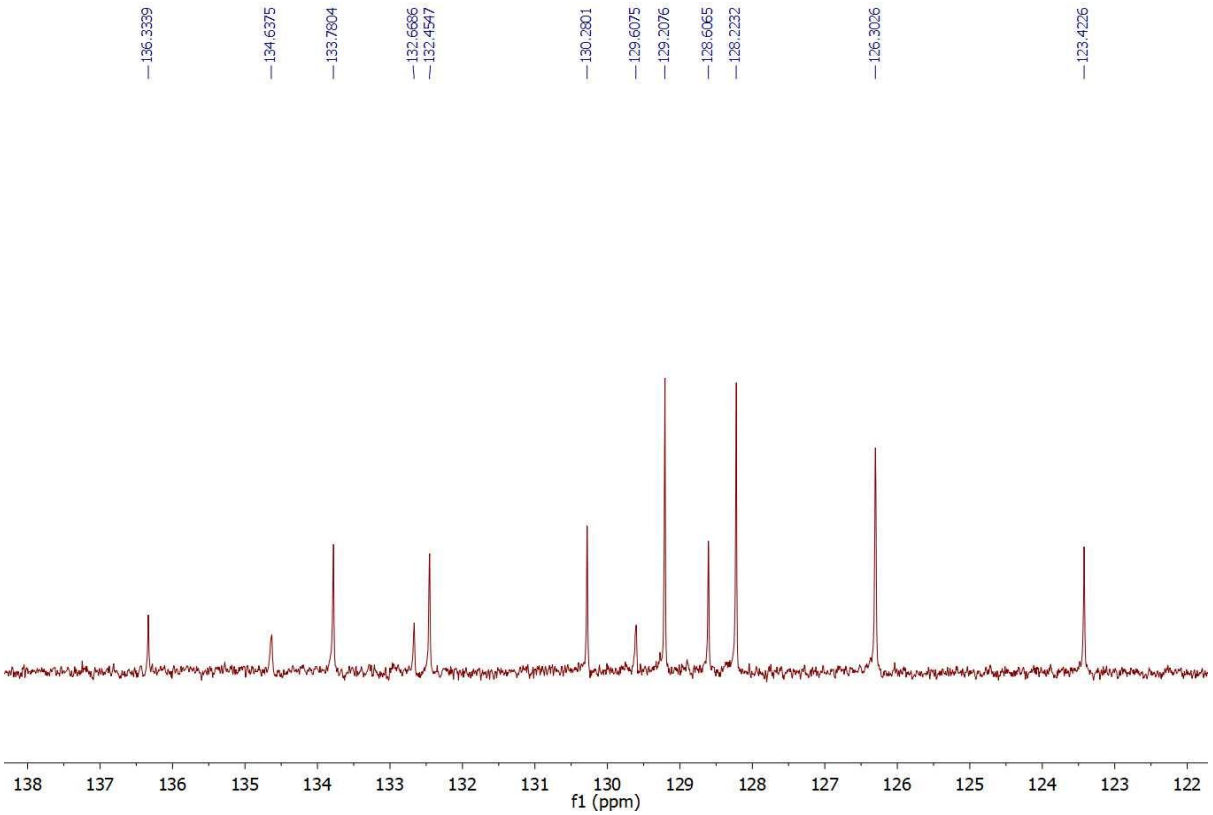
^{1}H NMR of 3-(3-((5-bromo-2-methoxyphenyl)(phenyl)methyl)-4-methoxyphenyl)pyridine (6j)



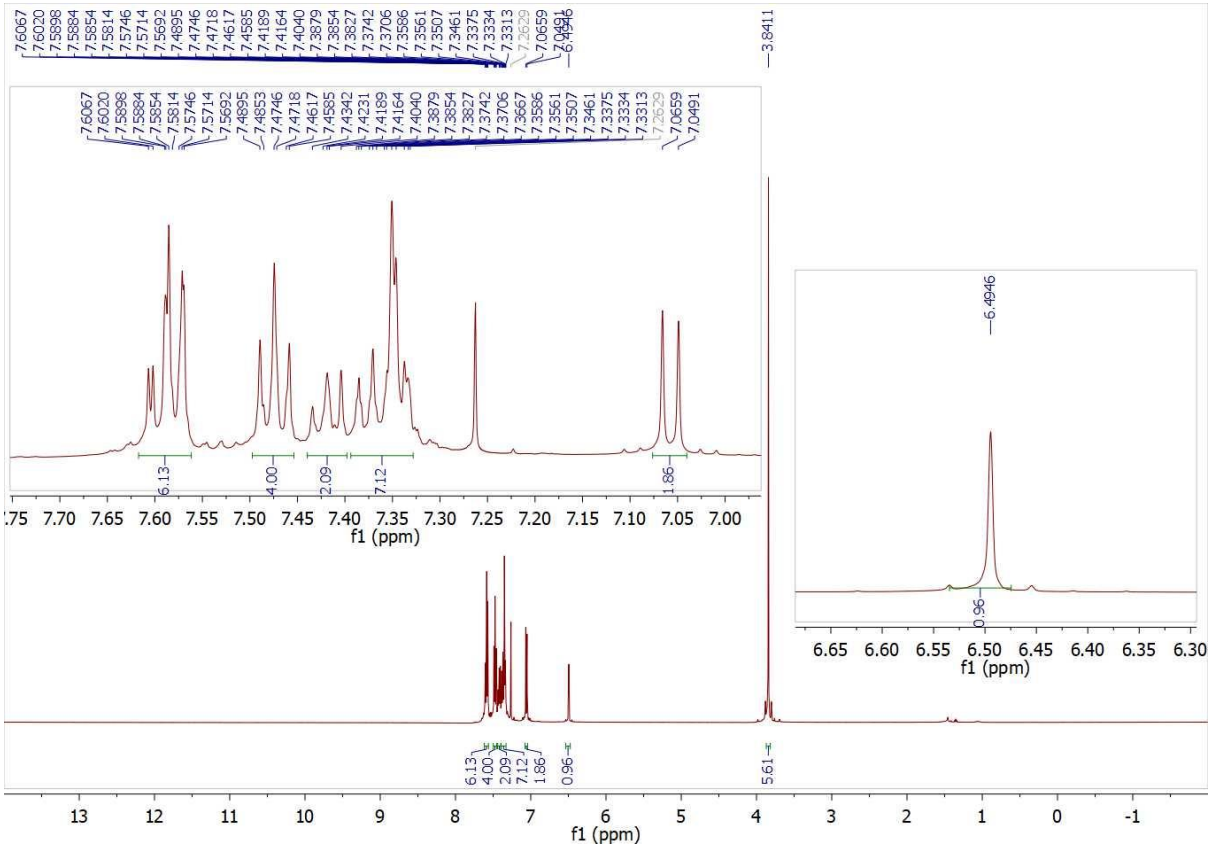
^{1}H NMR expanded of 3-(3-((5-bromo-2-methoxyphenyl)(phenyl)methyl)-4-methoxyphenyl)pyridine (6j)



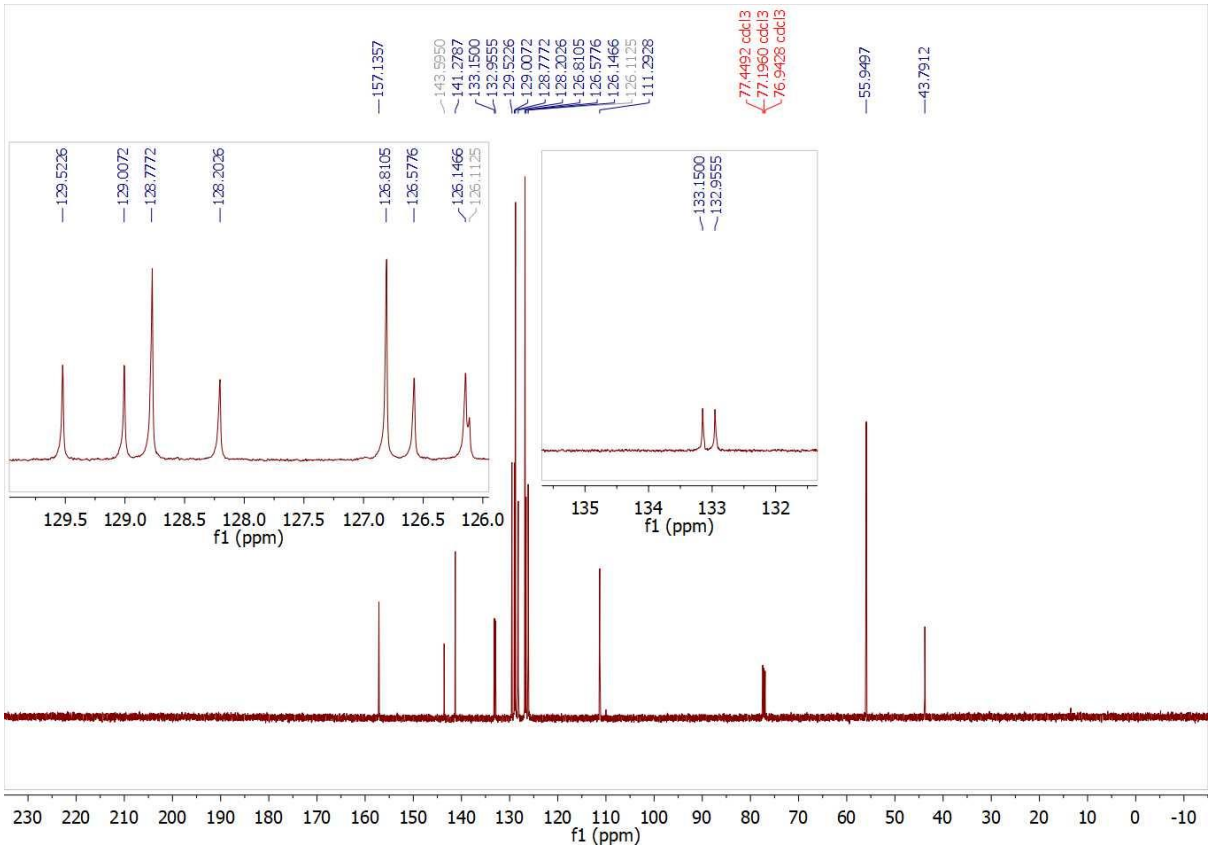
^{13}C NMR of 3-(3-((5-bromo-2-methoxyphenyl)(phenyl)methyl)-4-methoxyphenyl)pyridine (6j)



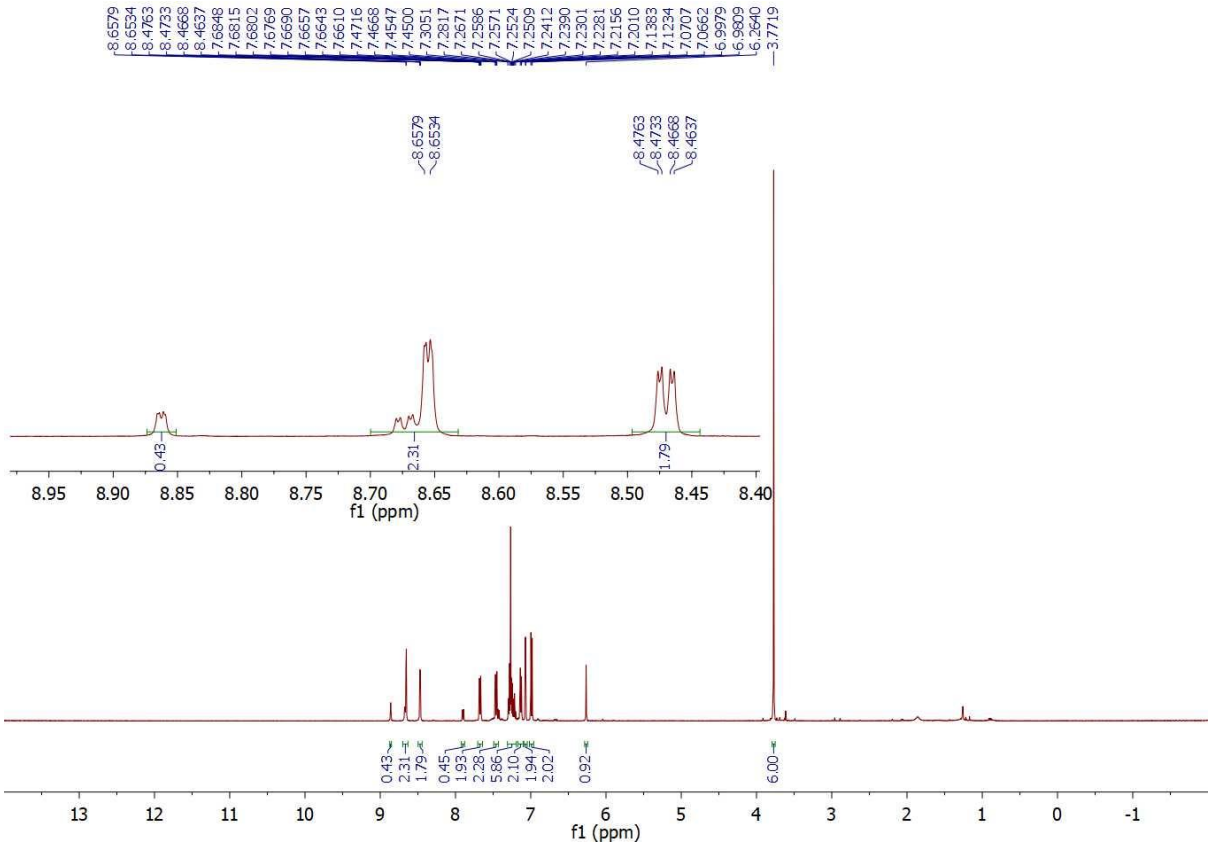
^{13}C NMR expanded of 3-(3-((5-bromo-2-methoxyphenyl)(phenyl)methyl)-4-methoxyphenyl)pyridine (6j)



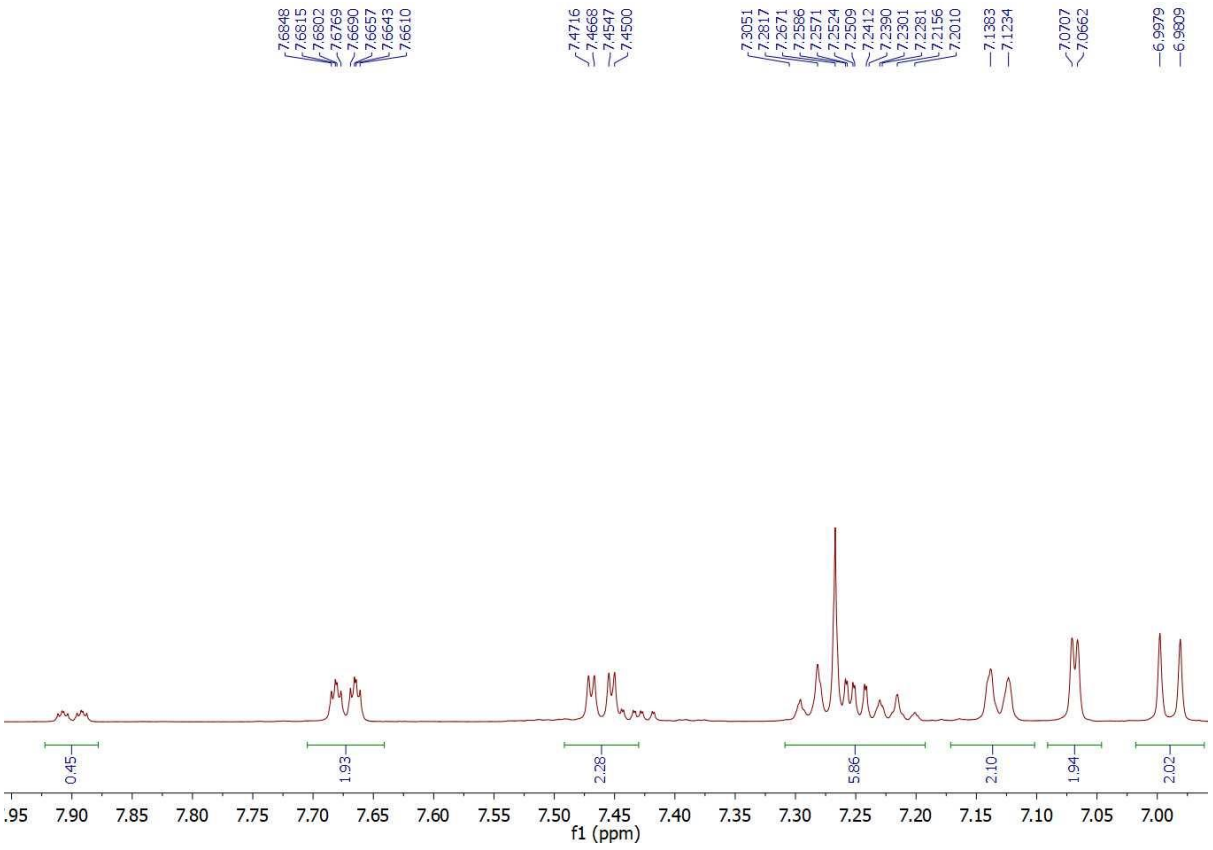
^{1}H NMR of 3,3"-(phenylmethylene)bis(4-methoxy-1,1'-biphenyl) (6k)



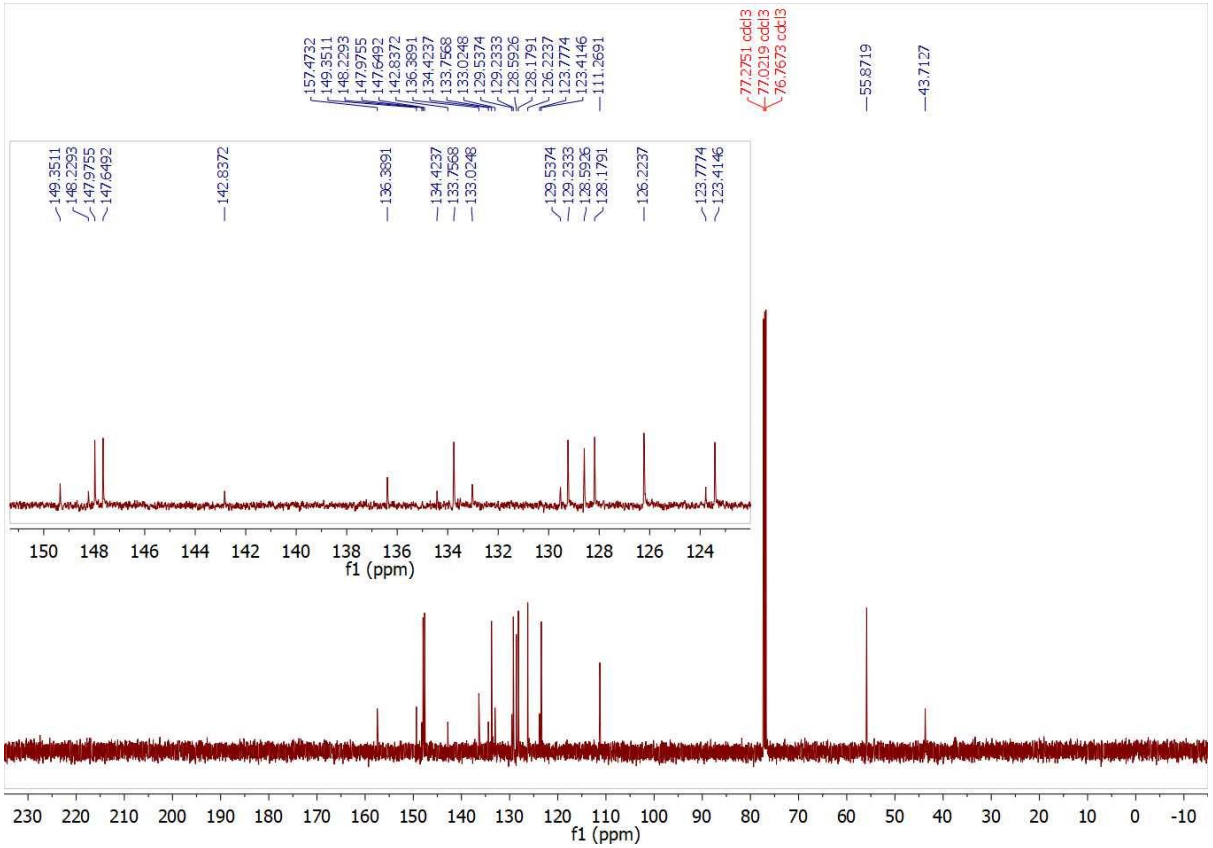
^{13}C NMR of 3,3"-(phenylmethylene)bis(4-methoxy-1,1'-biphenyl) (6k)



^{1}H NMR of 3,3'-((phenylmethylene)bis(4-methoxy-3,1-phenylene))dipyridine (6l)

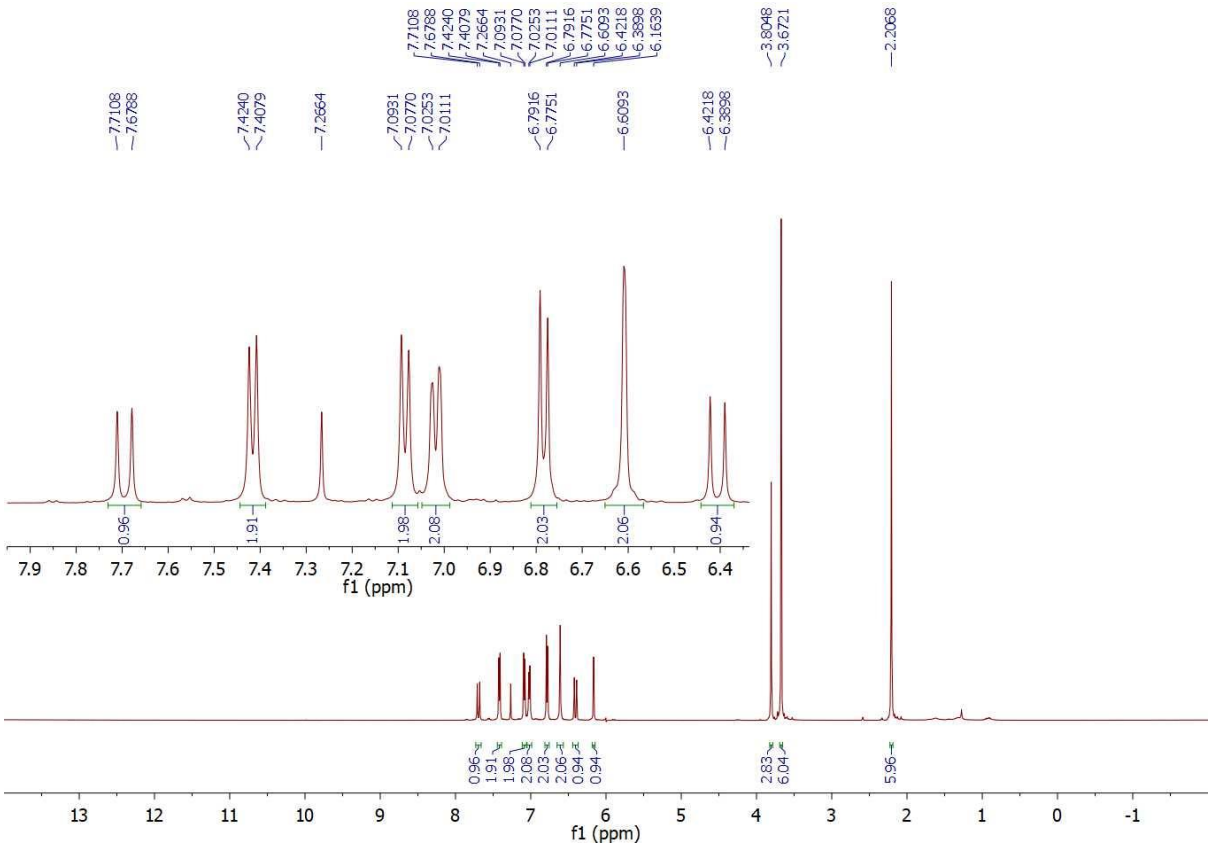


[1]H NMR expanded of 3,3'-((phenylmethylene)bis(4-methoxy-3,1-phenylene))dipyridine (6l)

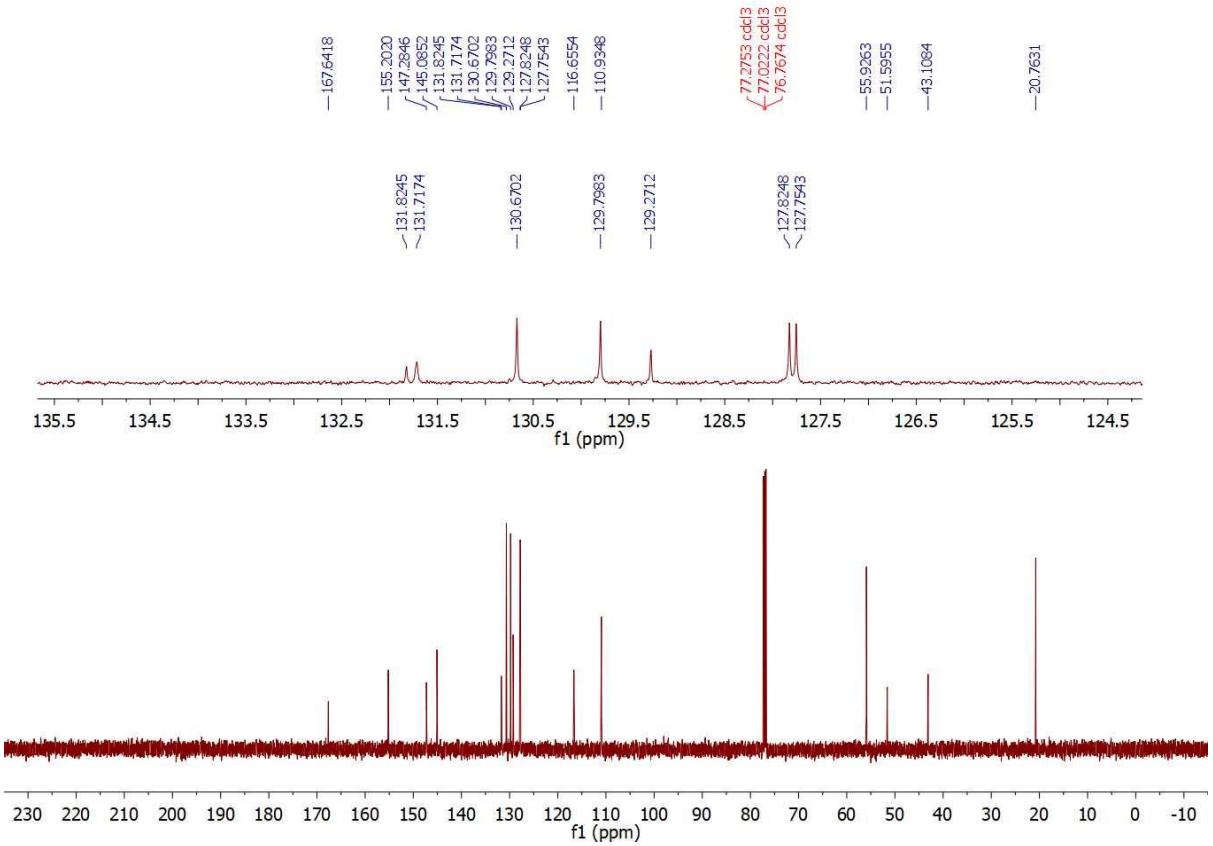


[13]C NMR of 3,3'-((phenylmethylene)bis(4-methoxy-3,1-phenylene))dipyridine (6l)

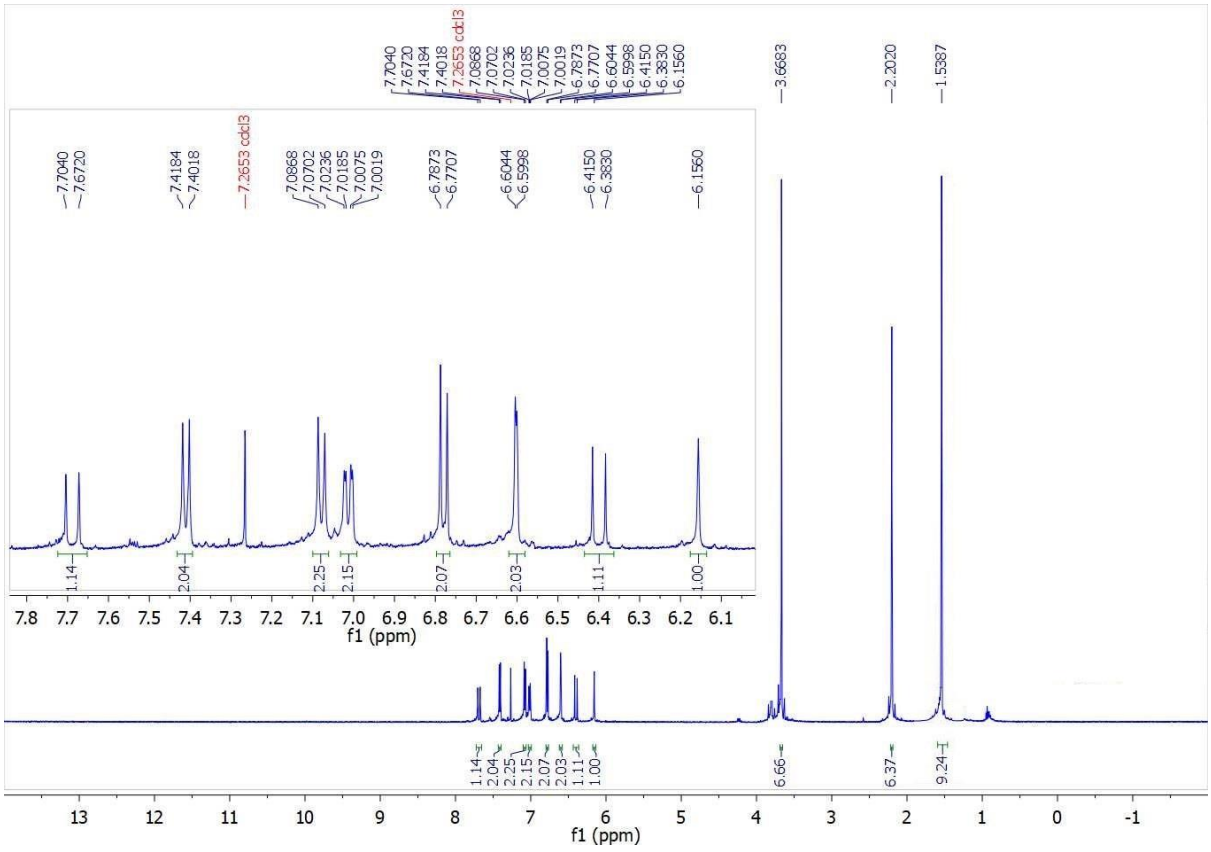
5. NMR spectra of Mizoroki-Heck coupling triarylmethane-products (13a-j)



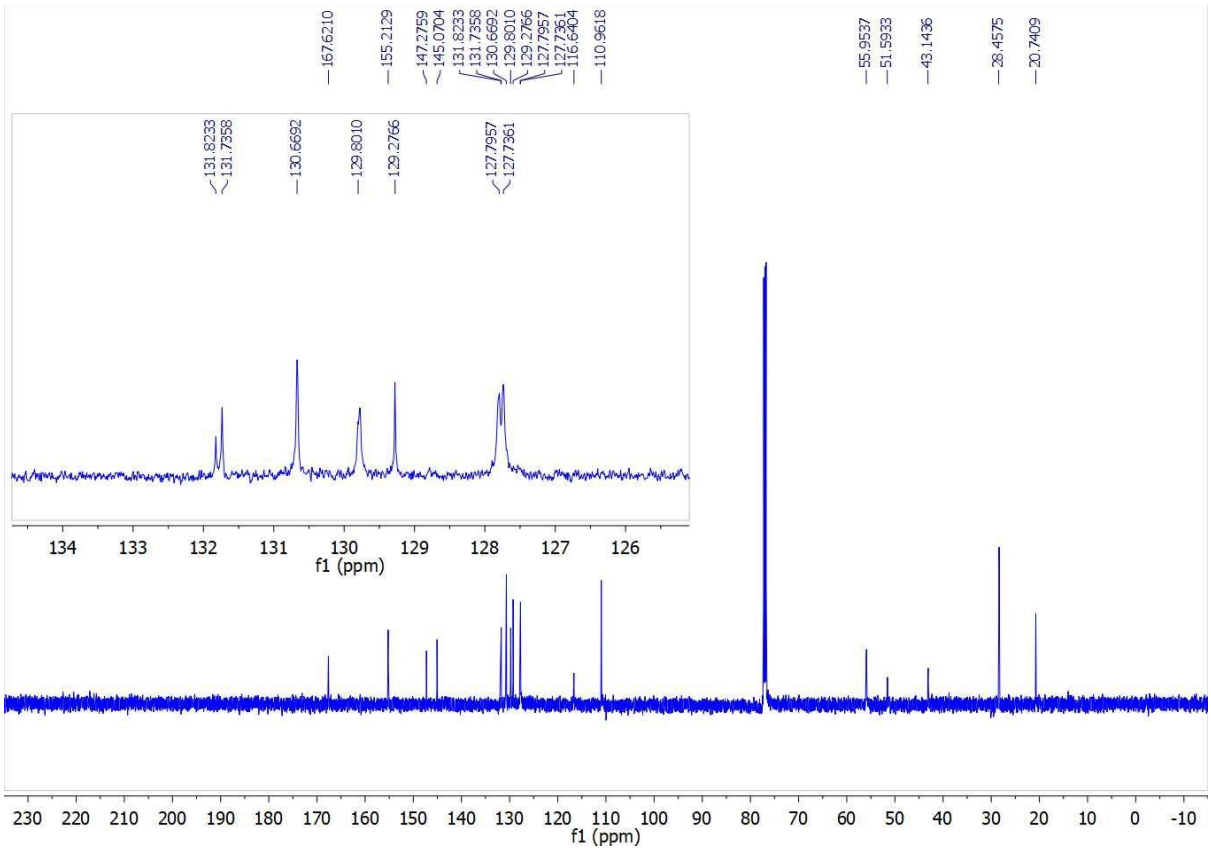
^{1}H NMR of Methyl (*E*)-3-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)acrylate (13a)



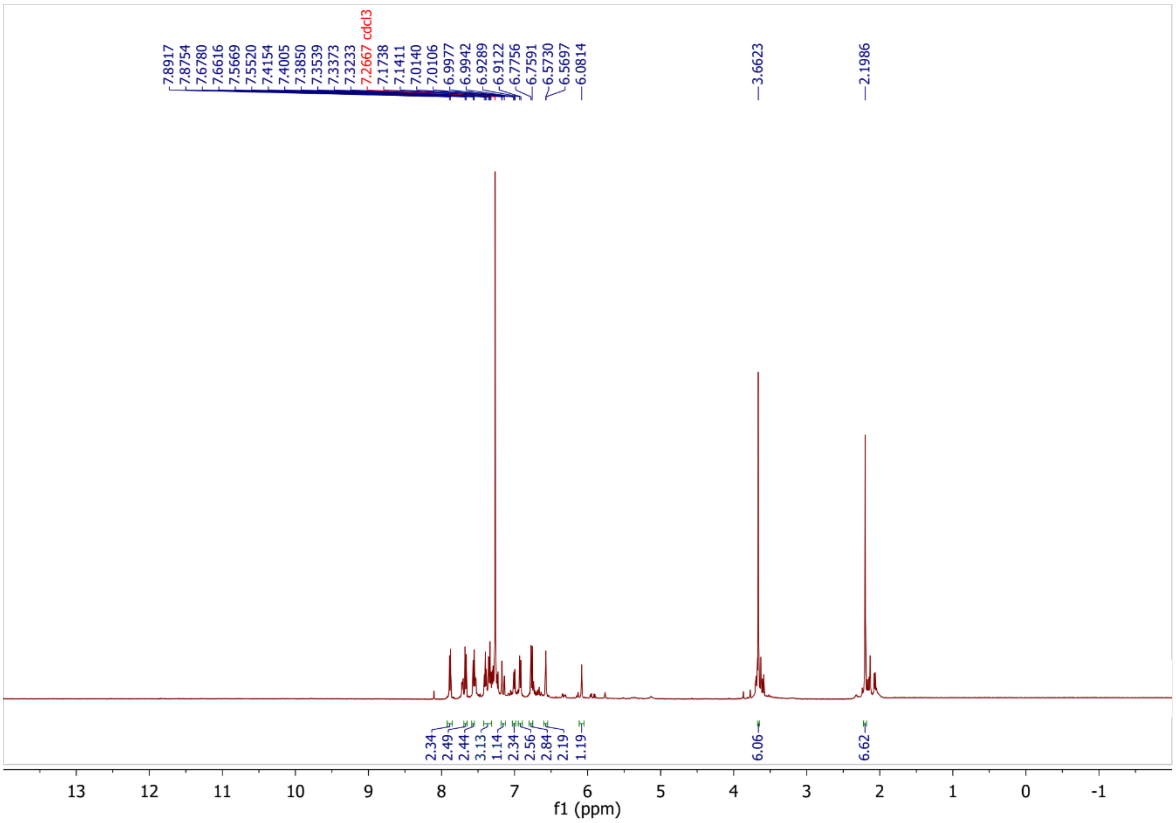
^{13}C NMR of Methyl (*E*)-3-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)acrylate (13a)



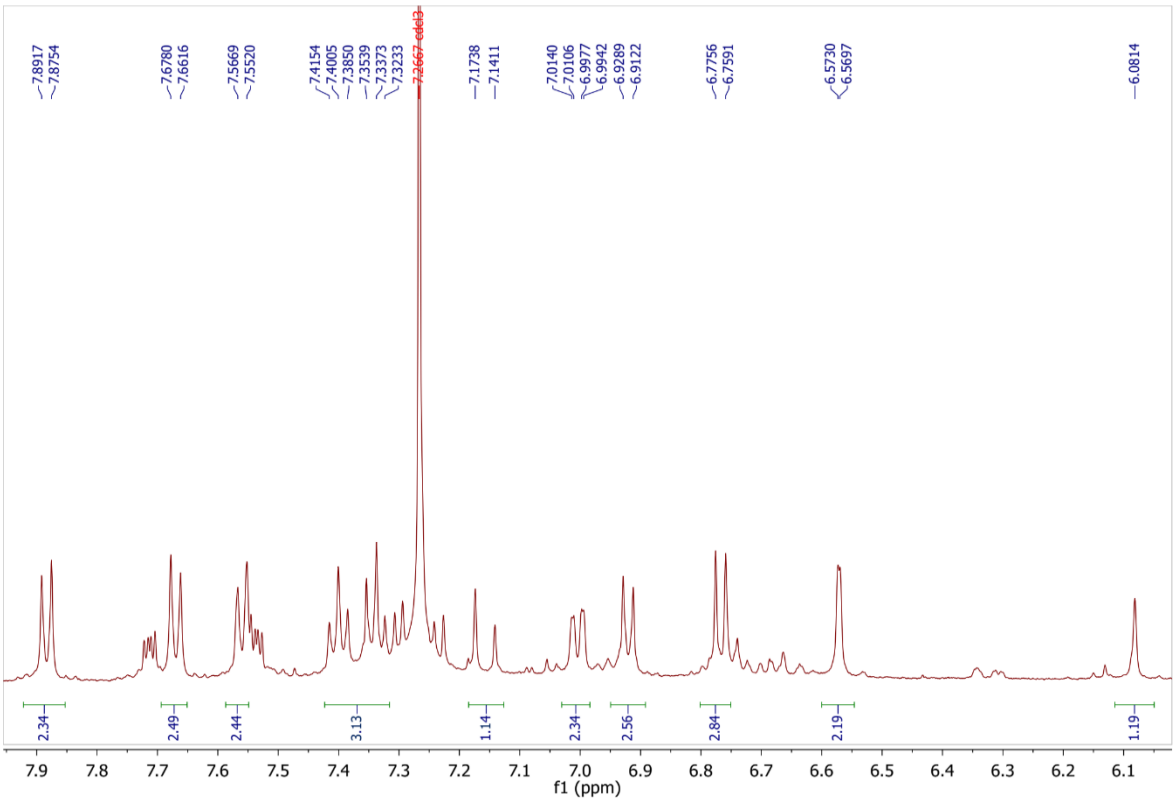
[1]H NMR of *tert*-butyl (*E*)-3-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)acrylate (13b)



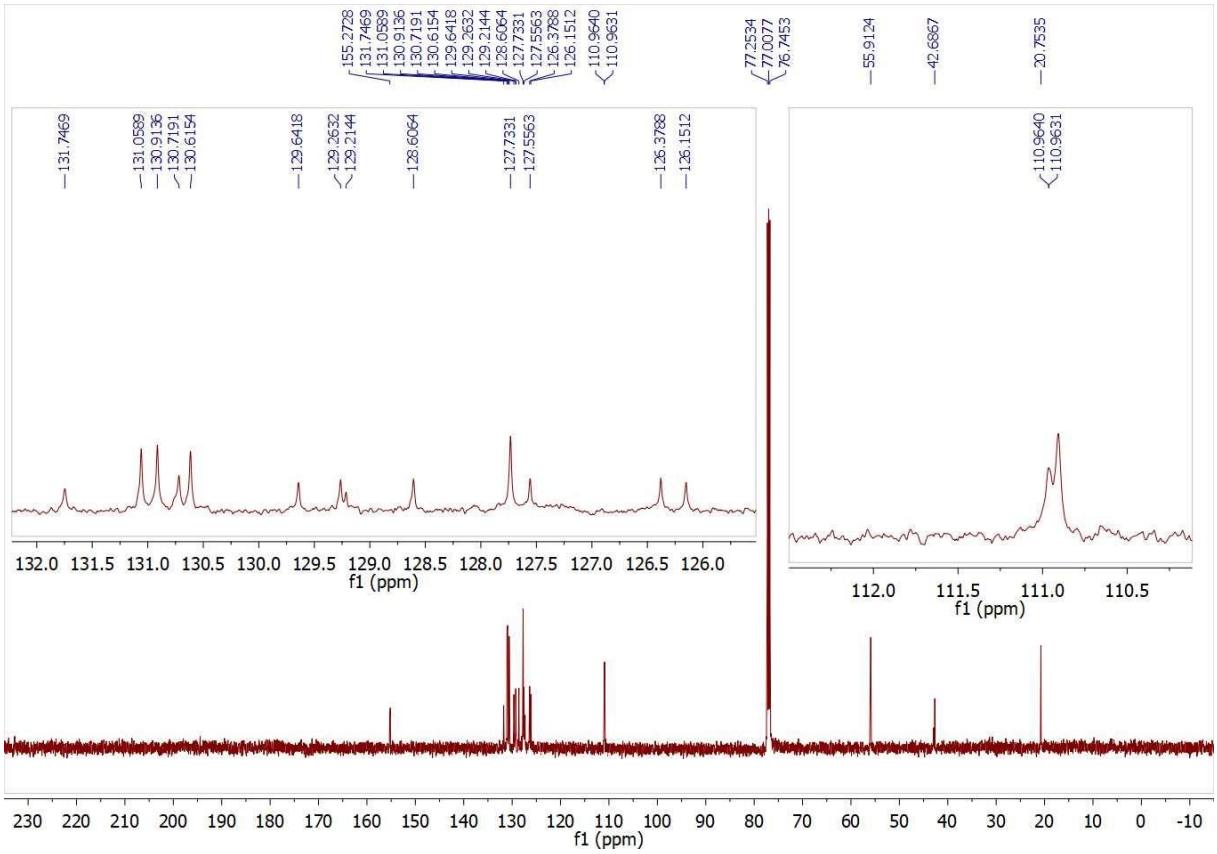
[13]C NMR of *tert*-butyl (*E*)-3-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenyl)acrylate (13b)



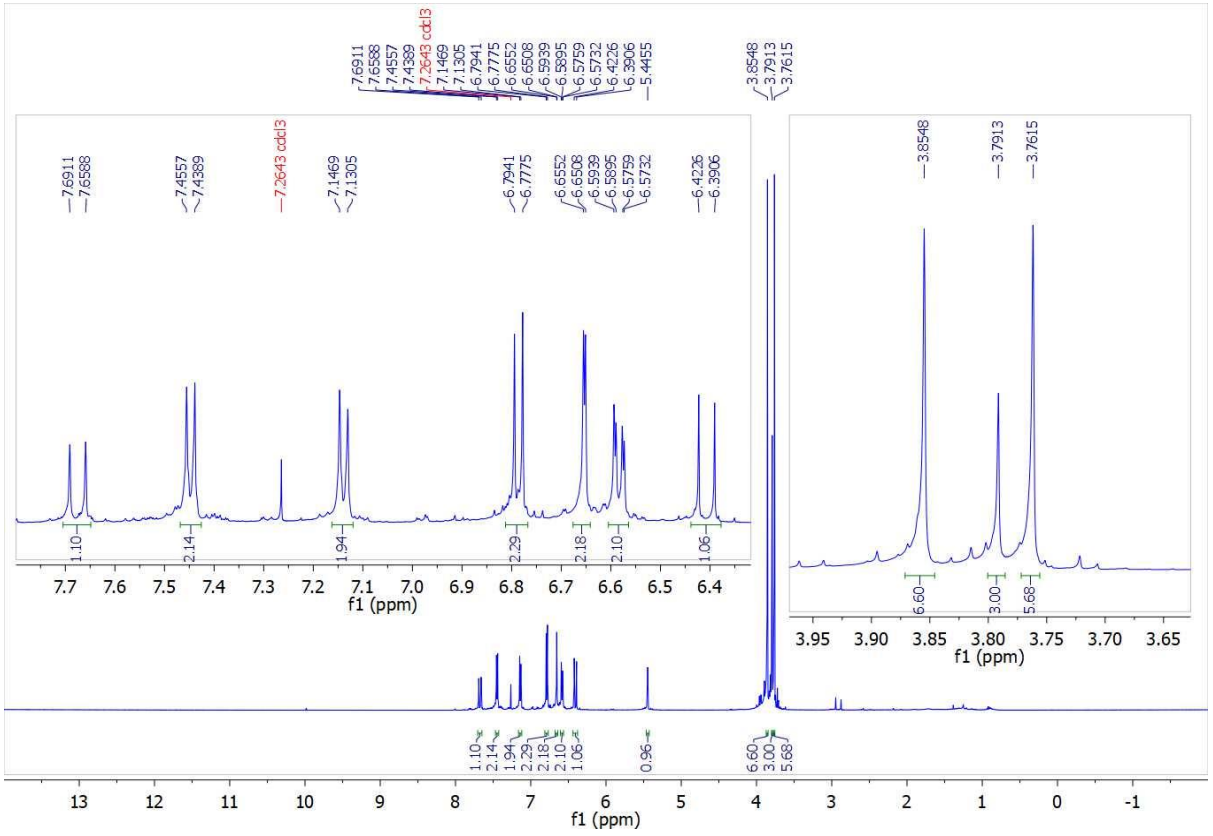
^{1}H NMR of (*E*)-2,2'-((4-styrylphenyl)methylene)bis(1-methoxy-4-methylbenzene) (13c)



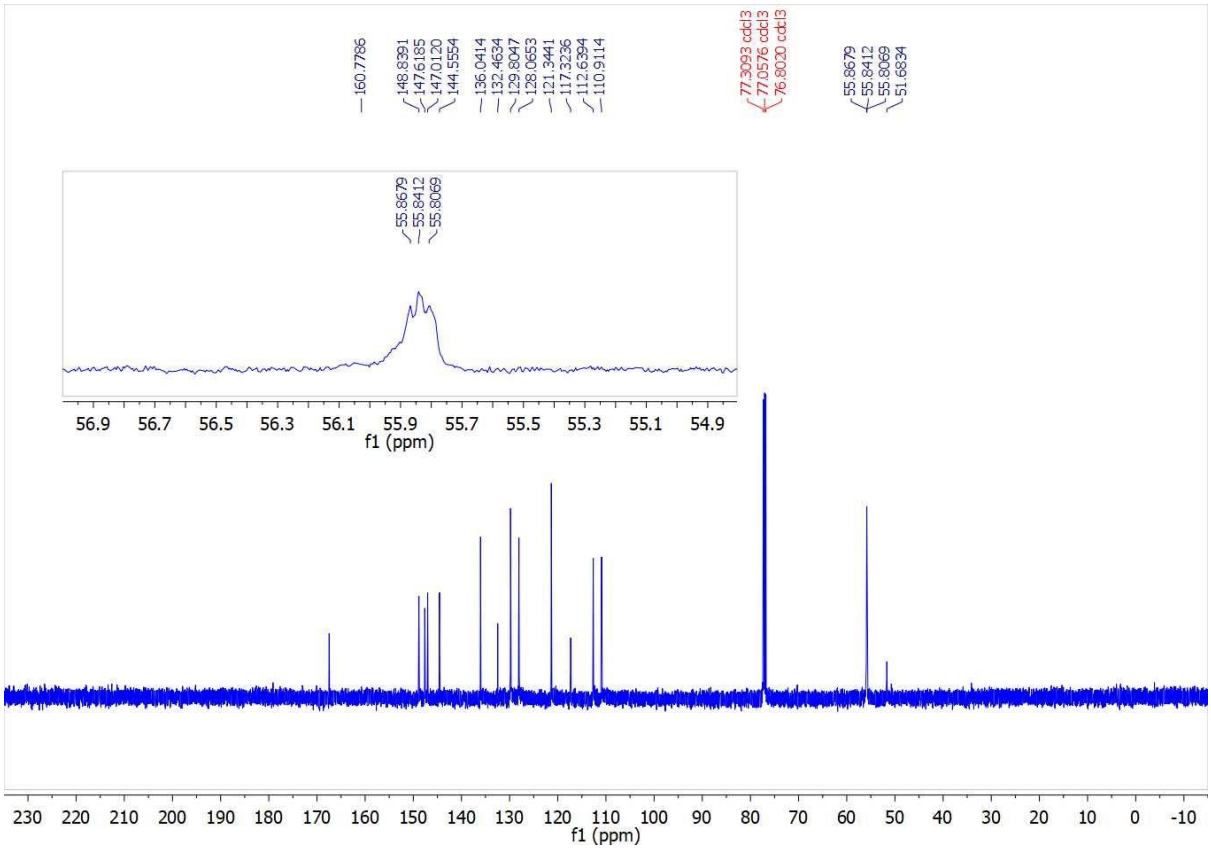
^{1}H NMR expanded of (*E*)-2,2'-((4-styrylphenyl)methylene)bis(1-methoxy-4-methylbenzene) (13c)



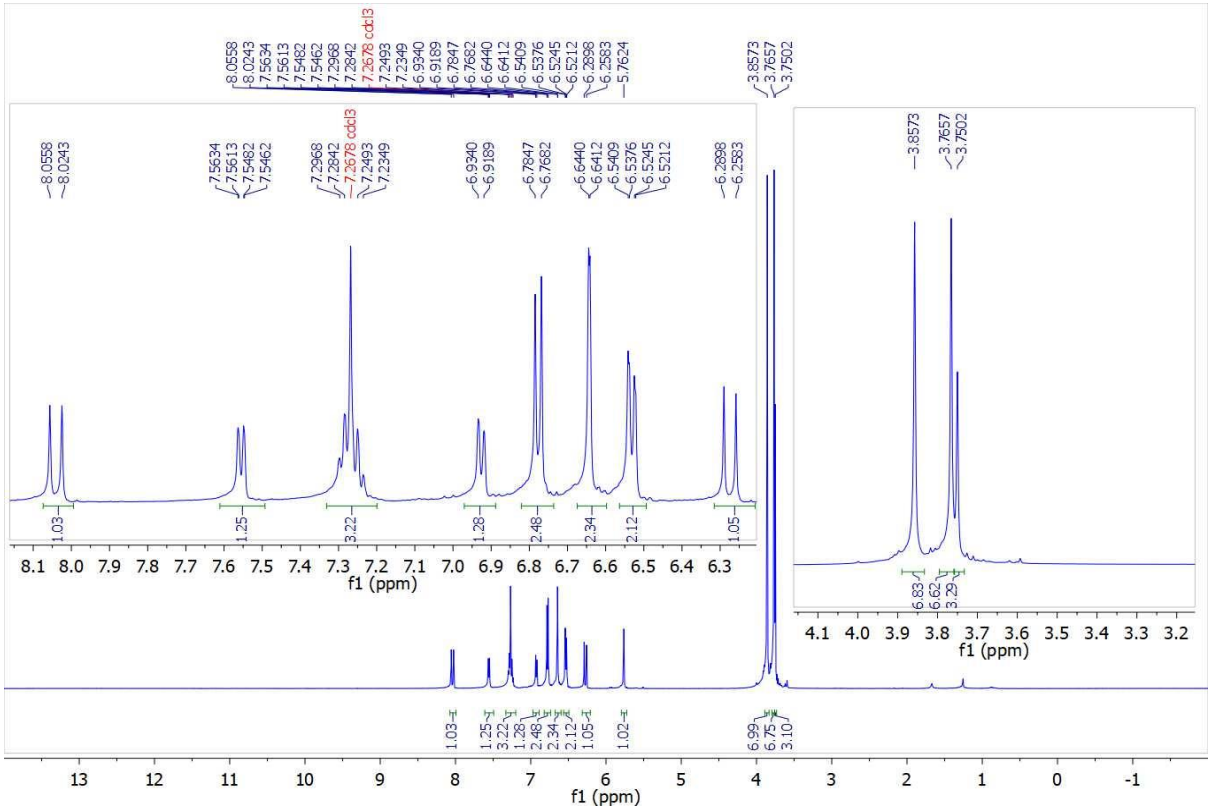
^{13}C NMR of (*E*)-2,2'-((4-styrylphenyl)methylene)bis(1-methoxy-4-methylbenzene) (13c)



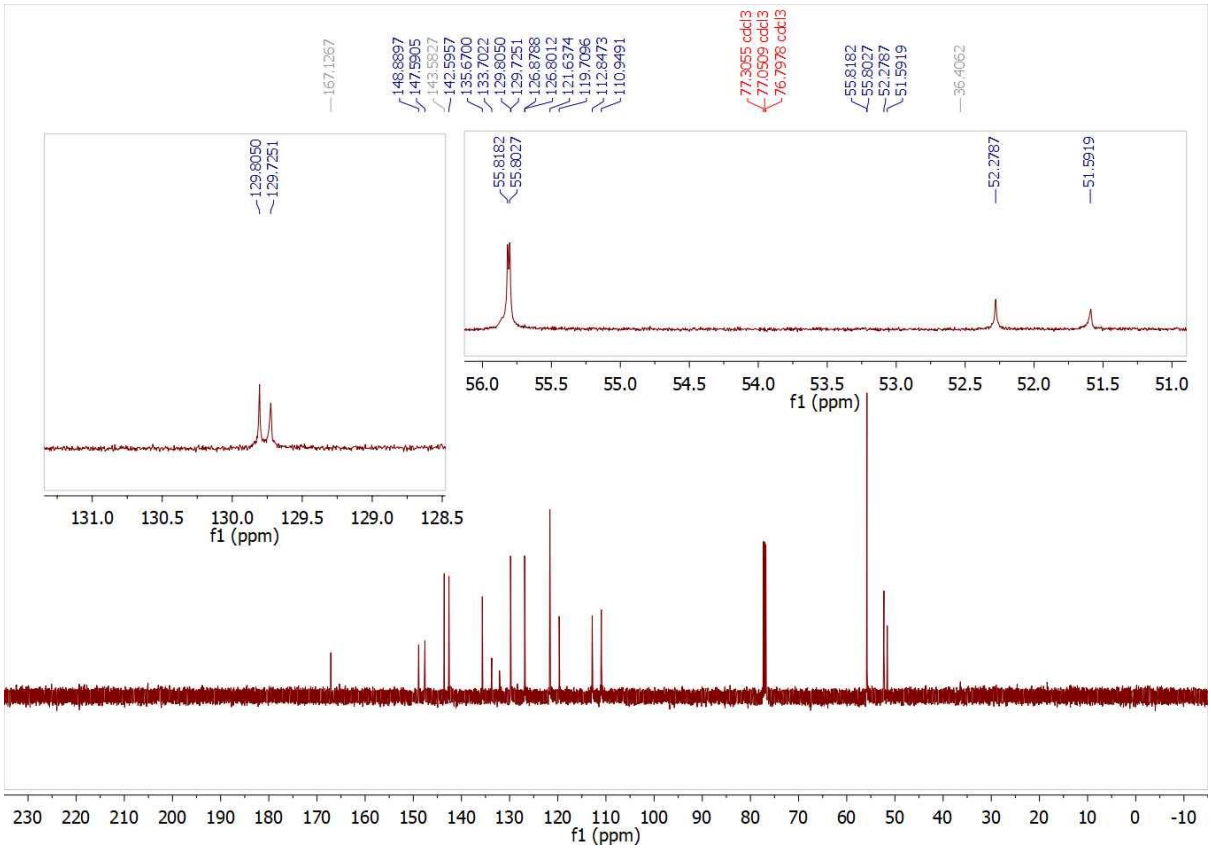
^{1}H NMR of methyl (*E*)-3-(4-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylate (13d)



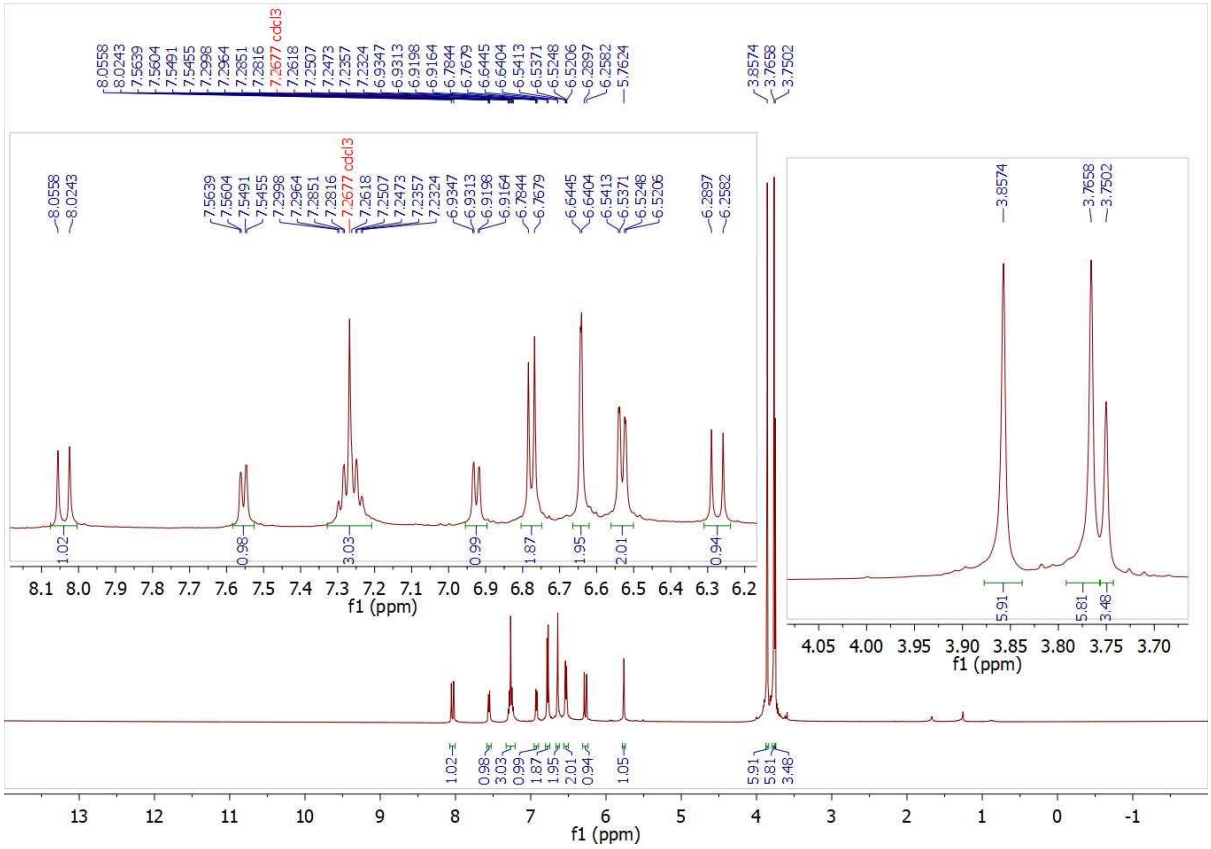
^{13}C NMR of methyl (*E*)-3-(4-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylate (13d)



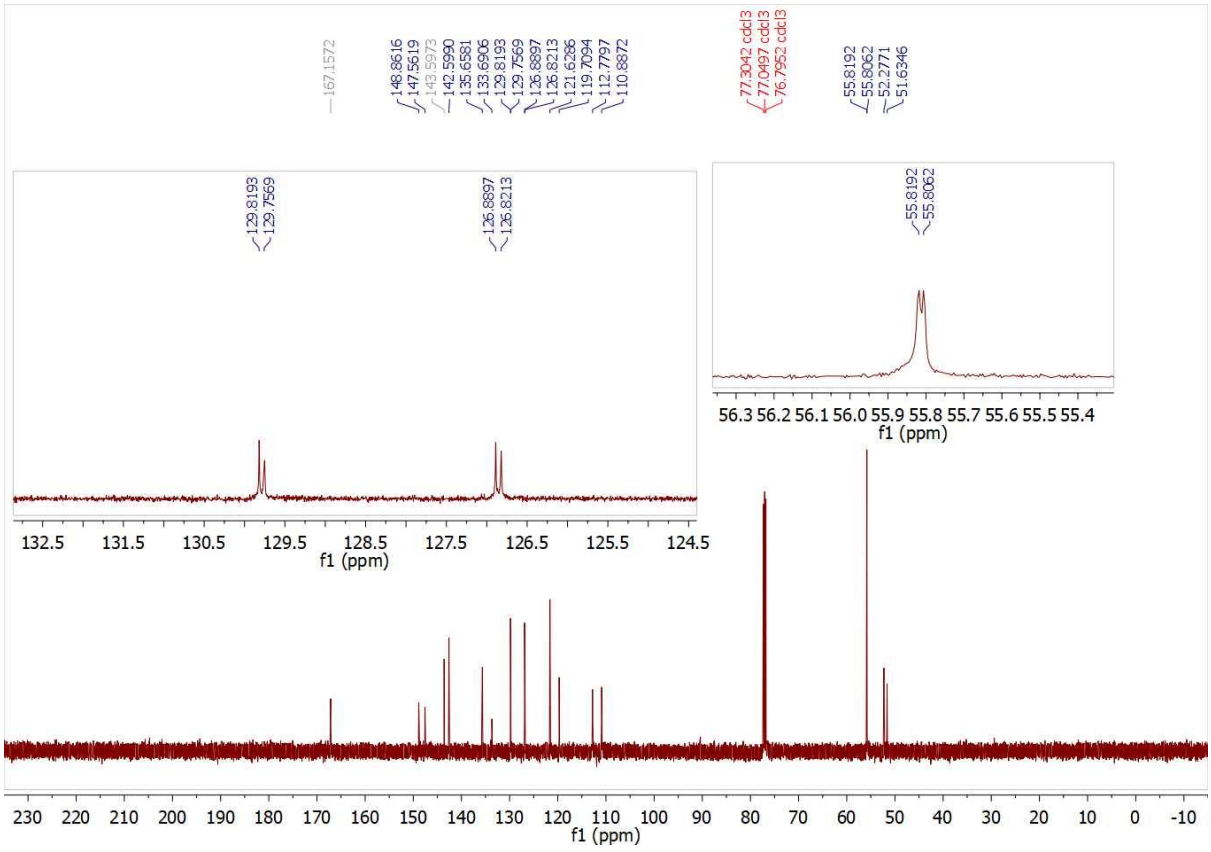
^{1}H NMR of Methyl (*E*)-3-(3-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylate (13e)



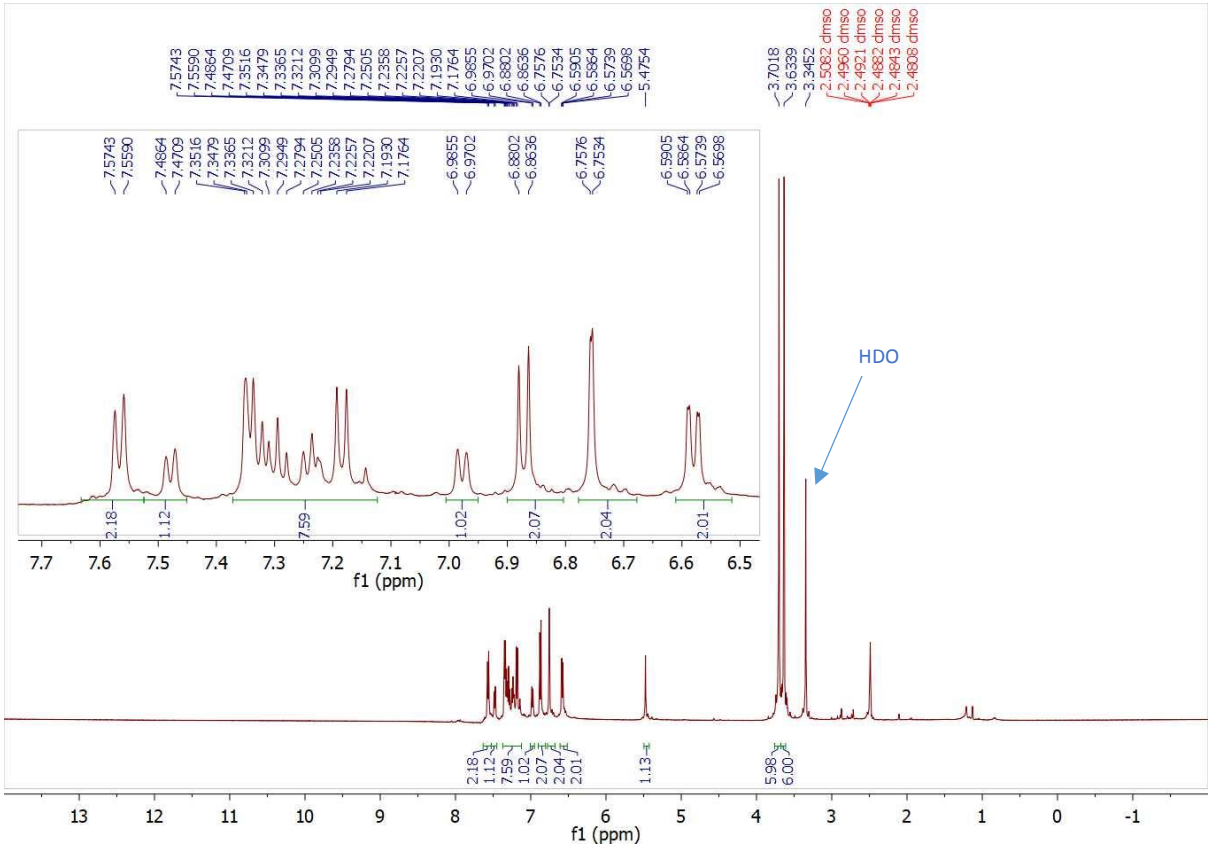
^{13}C NMR of Methyl (*E*)-3-(3-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylate (13e)



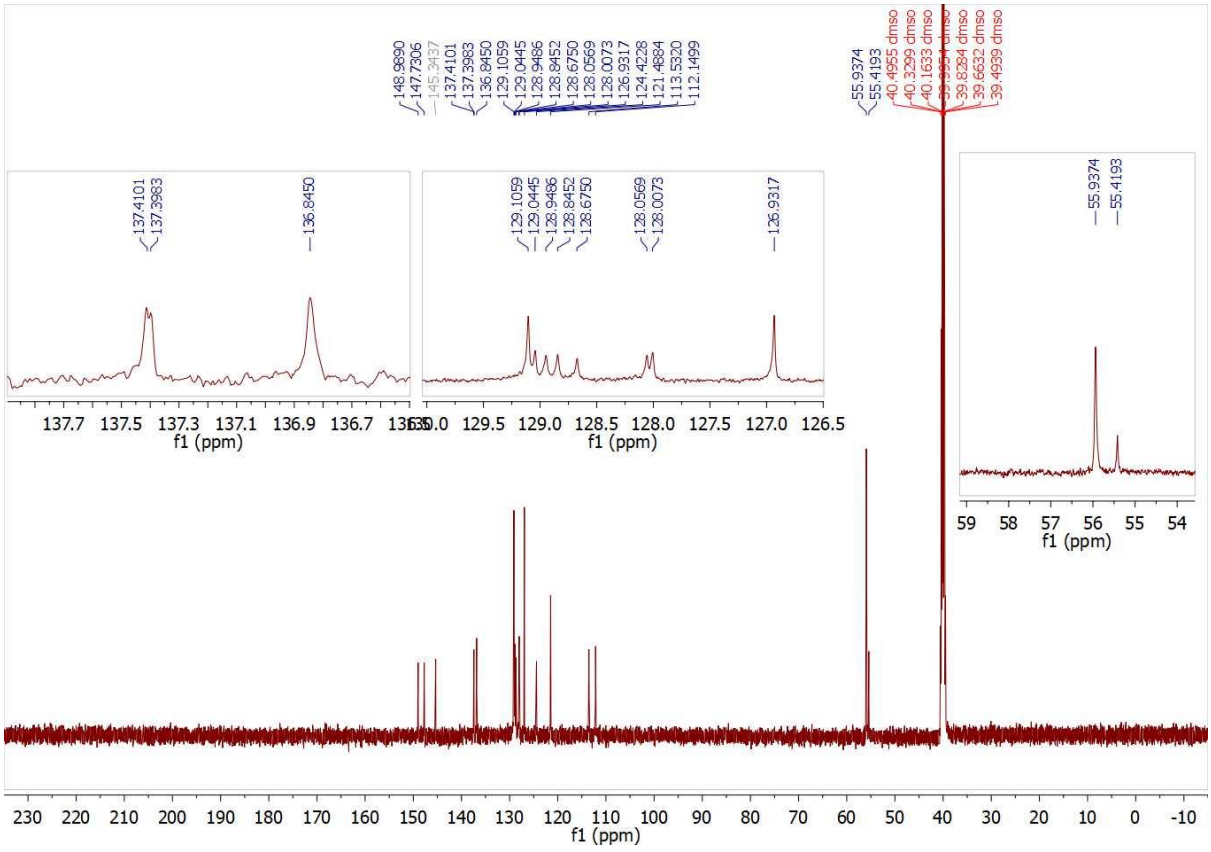
^{1}H NMR Methyl (*E*)-3-(2-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylate (13f)



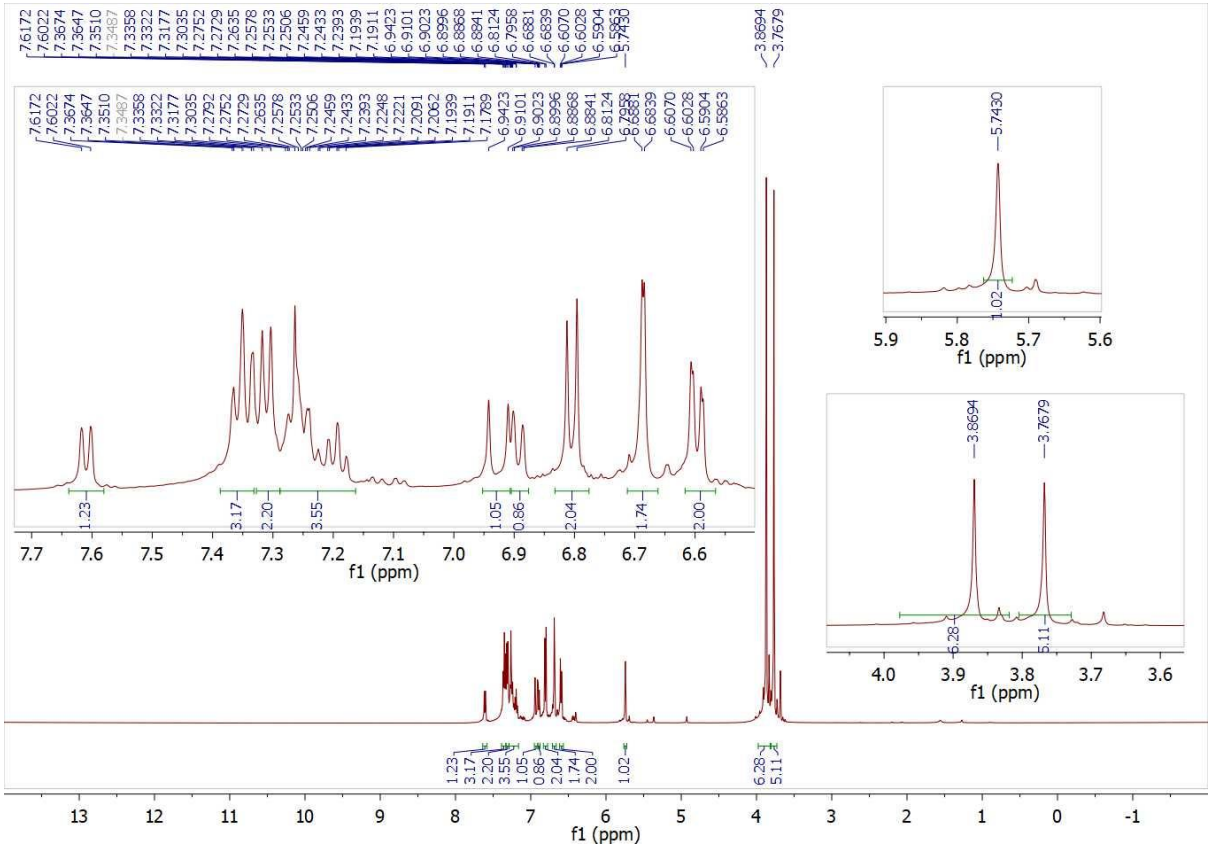
^{13}C NMR Methyl (*E*)-3-(2-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylate (13f)



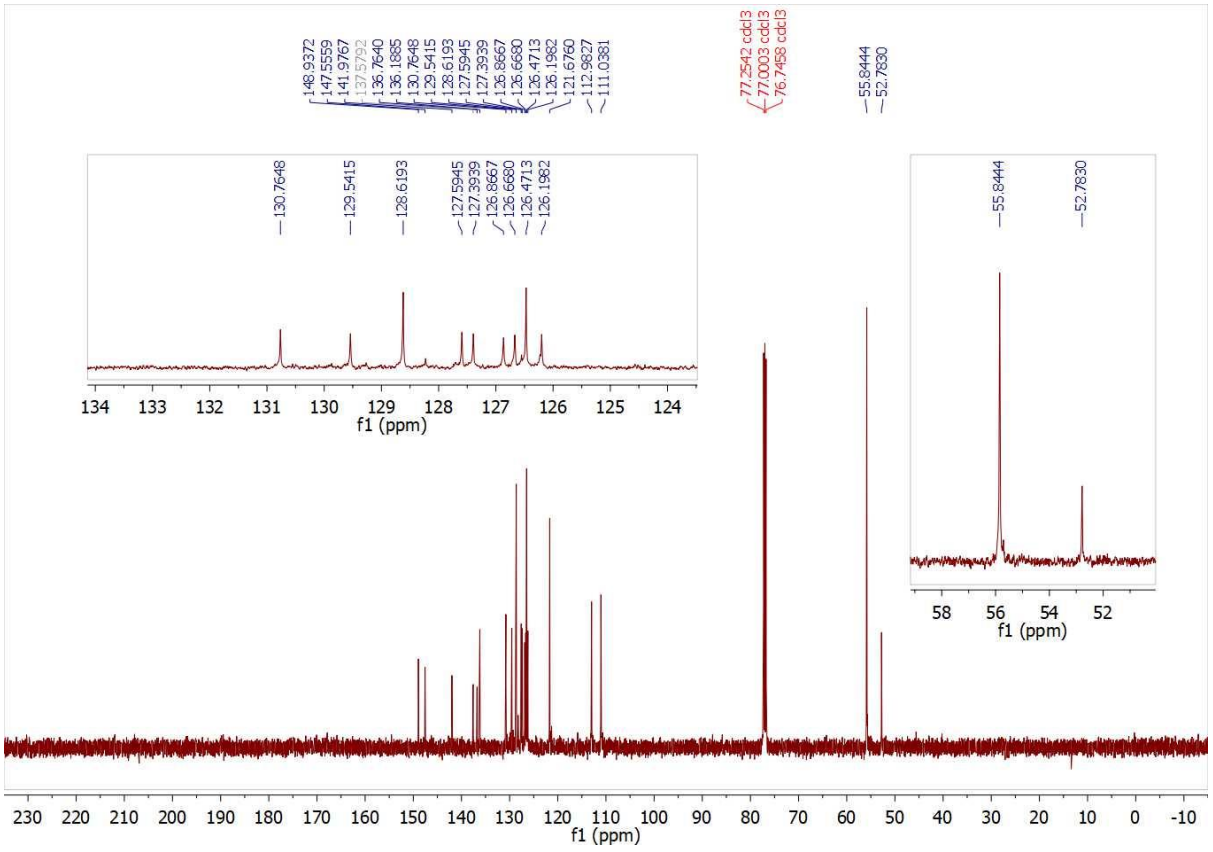
^{1}H NMR of (*E*)-4,4'-((3-styrylphenyl)methylene)bis(1,2-dimethoxybenzene) (13g)



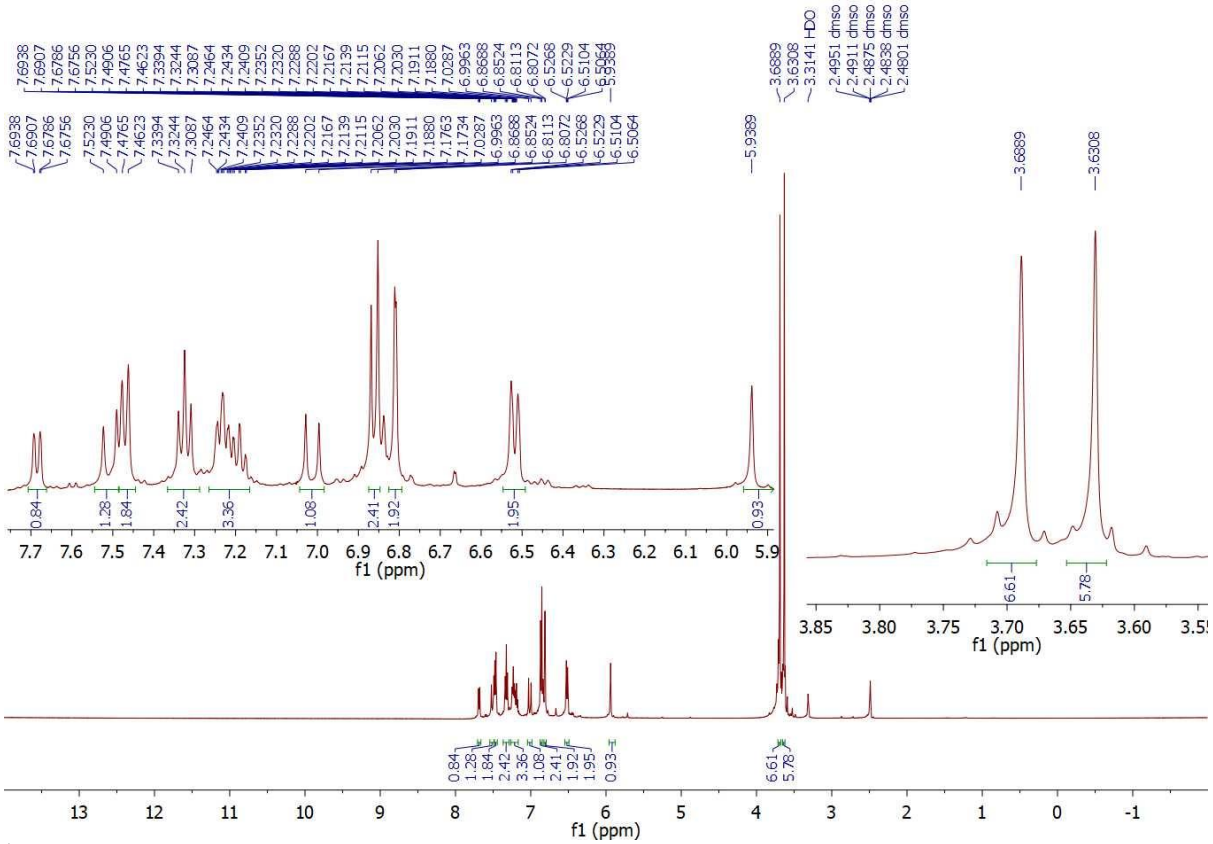
^{13}C NMR of (*E*)-4,4'-((3-styrylphenyl)methylene)bis(1,2-dimethoxybenzene) (13g)



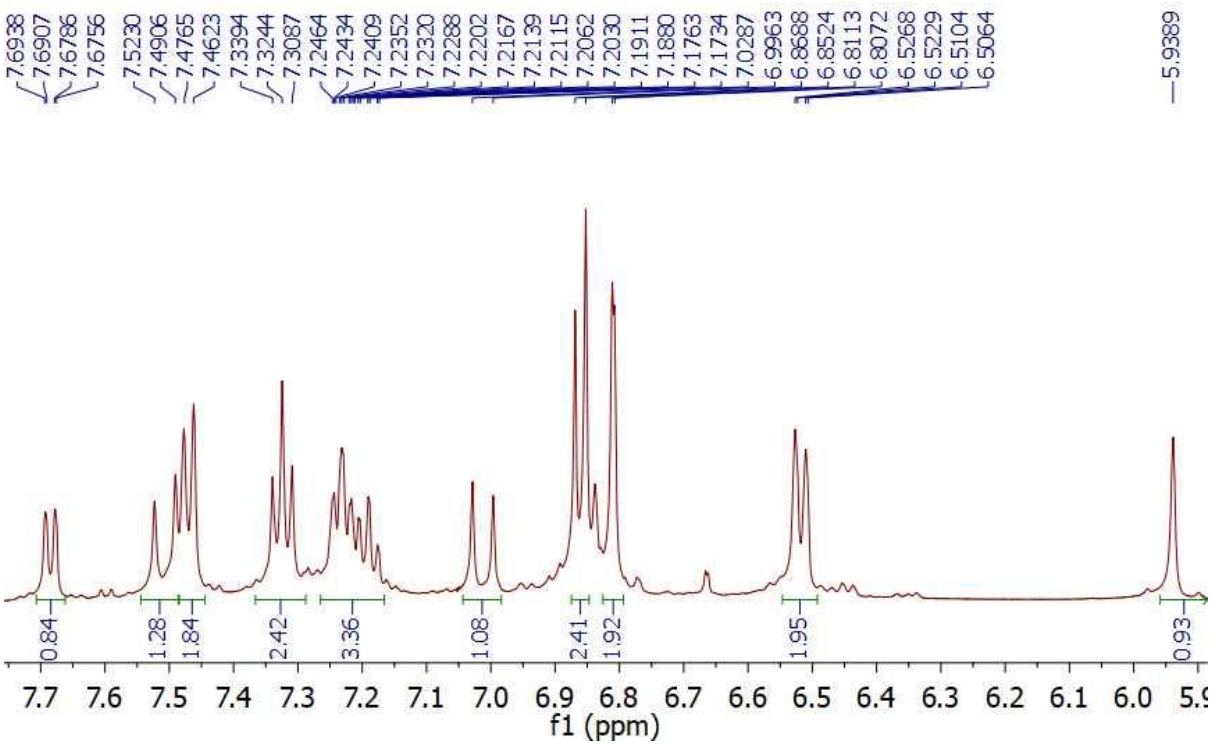
^{1}H NMR of (*E*)-4,4'-((2-styrylphenyl)methylene)bis(1,2-dimethoxybenzene) (13h)



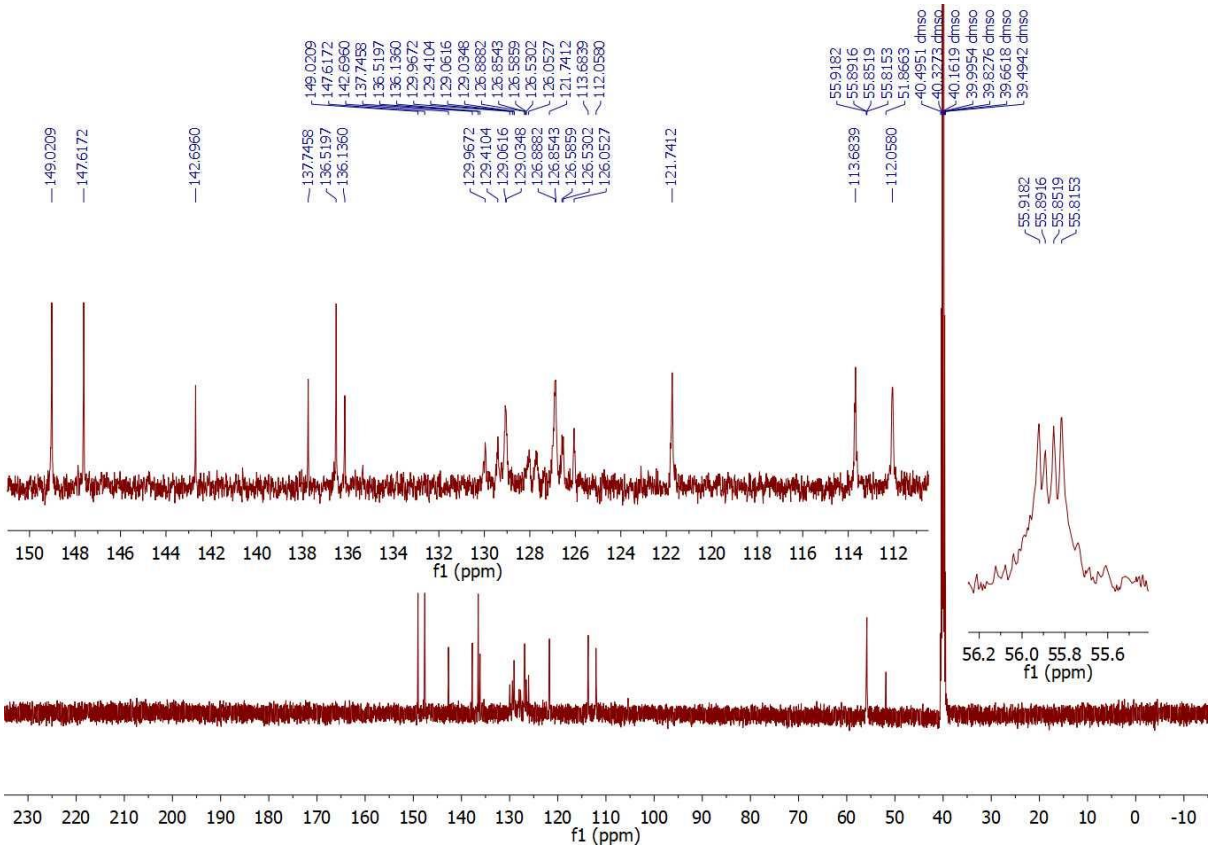
^{13}C NMR of (*E*)-4,4'-((2-styrylphenyl)methylene)bis(1,2-dimethoxybenzene) (13h)



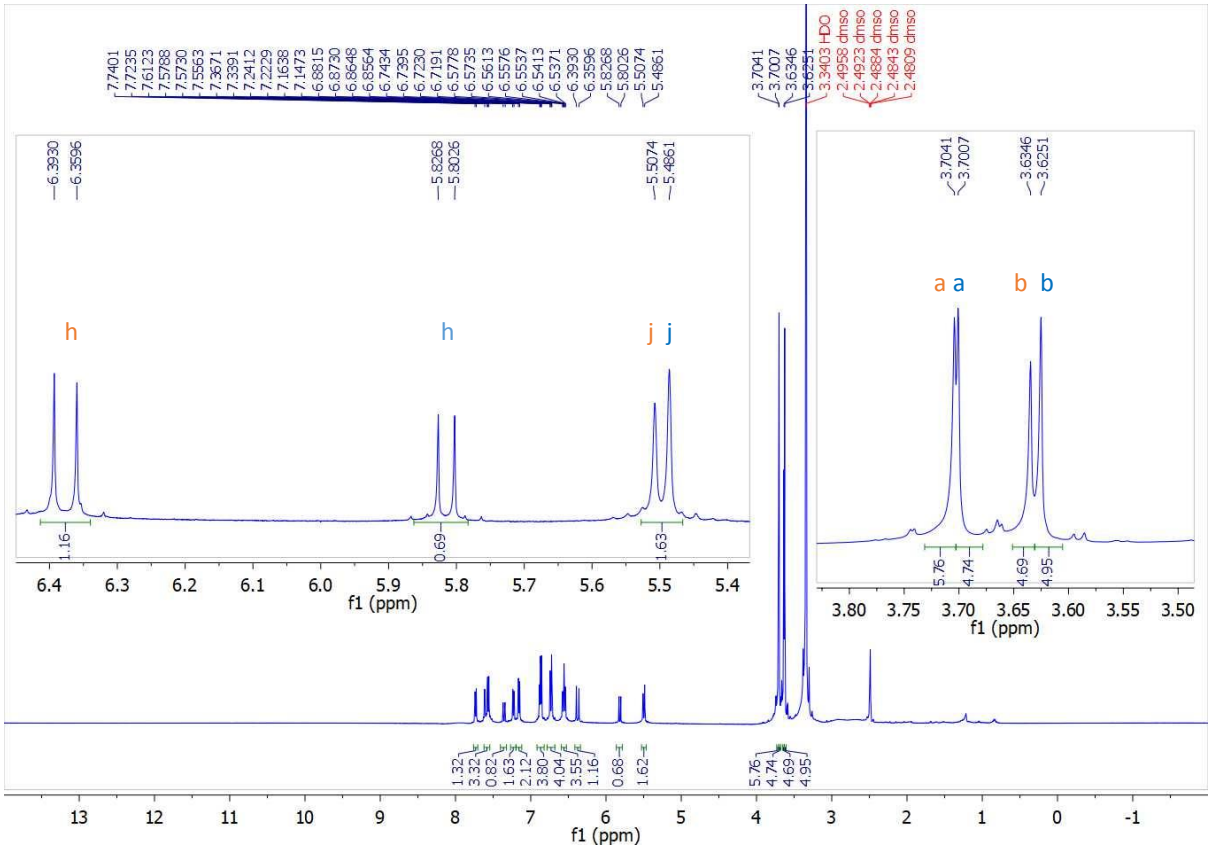
^{1}H NMR of (*E*)-4,4'-((2-(4-chlorostyryl)phenyl)methylene)bis(1,2-dimethoxybenzene) (13i)



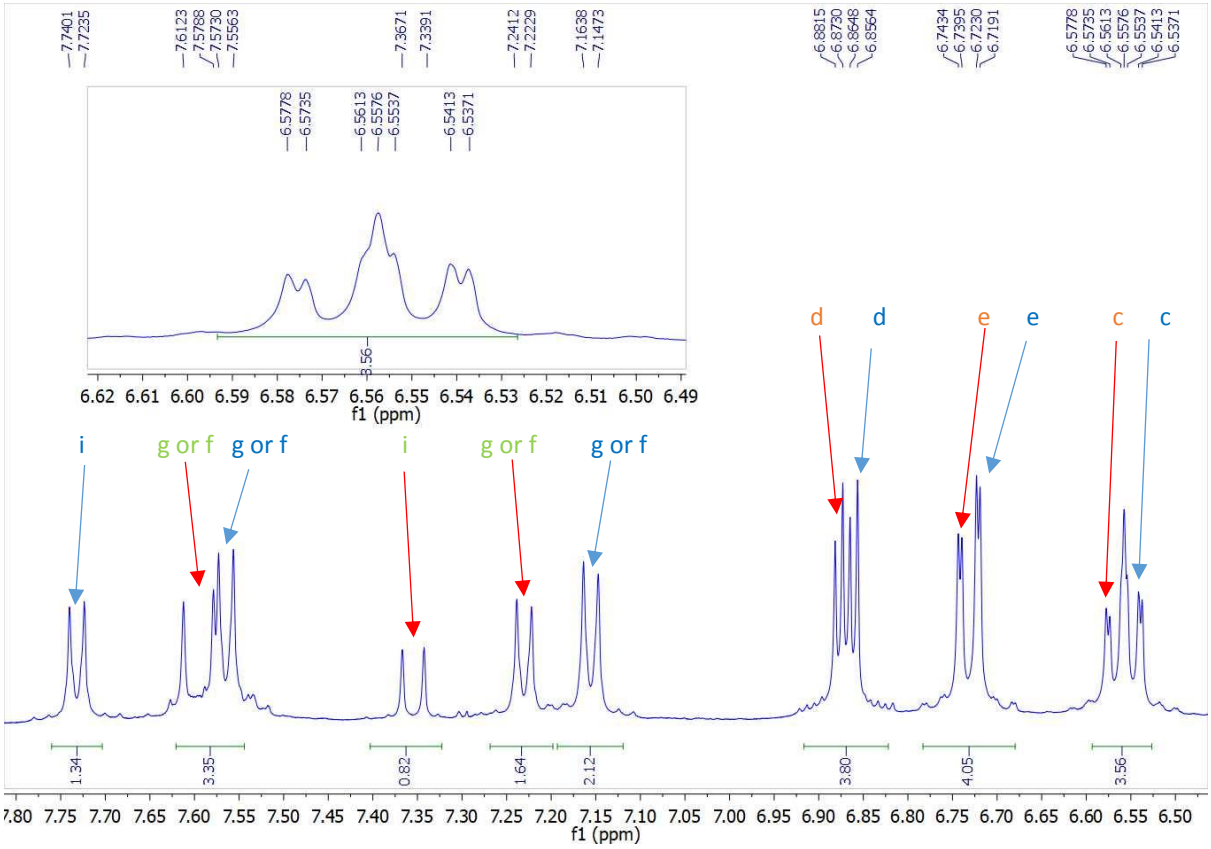
^{1}H NMR expanded of (*E*)-4,4'-((2-(4-chlorostyryl)phenyl)methylene)bis(1,2-dimethoxybenzene) (13i)



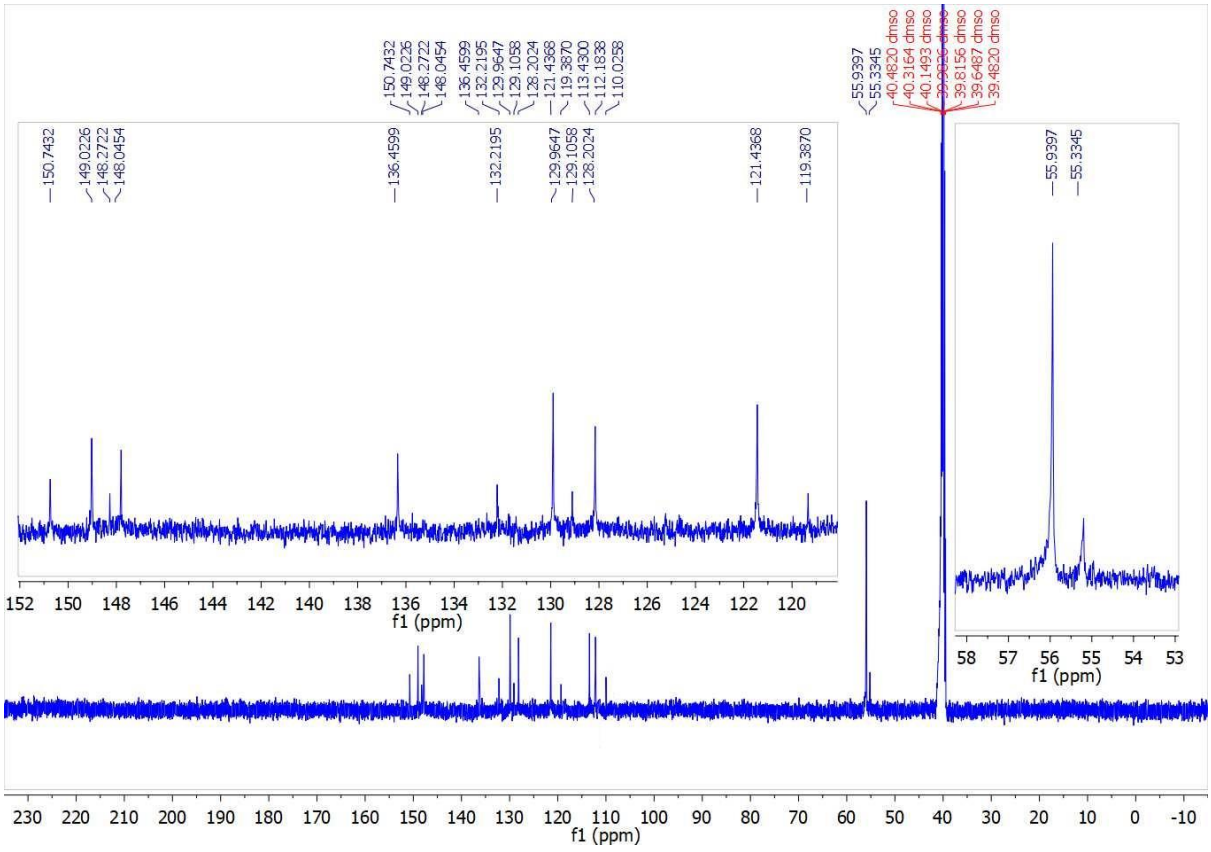
^{13}C NMR of (*E*)-4,4'-((2-(4-chlorostyryl)phenyl)methylene)bis(1,2-dimethoxybenzene) (13i)



[1]H NMR of 3-(4-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylonitrile (*Mixture of E and Z Isomers*) (13i)



[1]H NMR expanded of 3-(4-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylonitrile (*Mixture of E and Z Isomers*) (13i)



^{13}C NMR of 3-(4-(bis(3,4-dimethoxyphenyl)methyl)phenyl)acrylonitrile (13i)