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Graphical Abstract

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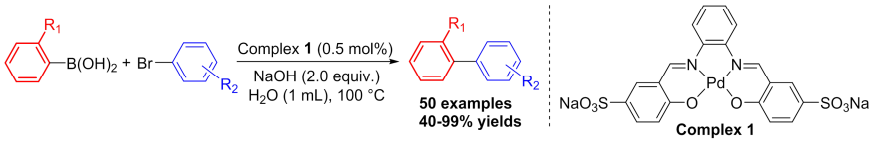
School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan，Shihezi University, Shihezi 832003, China



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School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan，Shihezi University, Shihezi 832003, China

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ABSTRACT

Water-soluble 2N2O-Salen ligands and their palladium complexes were synthesized and used as efficient catalysts for the Suzuki–Miyaura reactions in pure water. Notably, the reactions of substrates with sterically demanding ortho substituents (aryl bromides and/or arylboronic acids) proceed smoothly to generate corresponding products with moderate to high yields using 0.5 mol% (salph)Pd (salph = N,N′-bis(4-SO_3Na-salicylidene)-1,2-phenylenediamine) as the catalyst. Importantly, the catalytic system has the wide substrate scope and the high tolerance to various functional groups, including cyano, amino, nitro, methoxy, and acetyl. Moreover, the biaryl compounds were also obtained on a multi-gram scale by simple recrystallization with the system in the absence of any organic solvent, surfactant, or phase transfer agent and the catalyst was reused directly for the next cycle. Particularly, this protocol can be applied to synthesize aryl-substituted carbazolyl compounds.

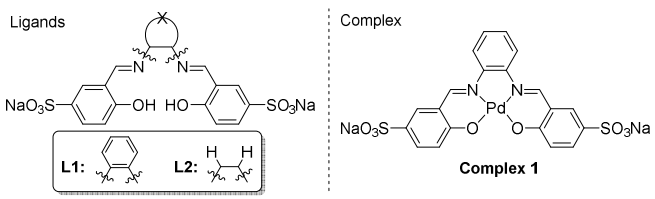
* Corresponding to: Tel.: +86 0993 2057213; fax: +86 0993 2057270; e-mail: liuping@shzu.edu.cn

1. Introduction

Biaryl units as important building blocks have been found in natural products, pharmaceutical intermediates, conducting polymers, pesticides, and liquid crystals.[1] Transition-metal-catalyzed coupling reactions play an important role in the formation of C_{aryl}-C_{aryl} bond. Especially, palladium-catalyzed Suzuki–Miyaura reaction has become one of the most powerful methods because organoboranes are air- and moisture-stable and shows the relatively low toxicity.[2]

To date, significant improvements were reported by the research groups of Buchwald,[3] Fu,[4] Nolan,[5] Beller,[6] and others.[7] In most bases, the Suzuki–Miyaura reaction proceeds in organic solvents and consumes expensive and toxic phosphine ligands. In recent years there has been an increasing interest in developing environmentally green processes, such as the usage of green solvents including aqueous solution, ionic liquid, and supercritical carbon dioxide.[8] Water has gained wide attention for it is cheap, readily available, non-corrosive, non-flammable and non-toxic. Water has unique properties in solvating molecules and can improve the rate and selectivity of reactions.[9] However, some problems, such as low solubility of the arylhalides and the poor stability of the metal catalysts in water, remain to be improved. To solve the above problems, water-soluble ligands, surfactants and/or phase-transfer reagents, co-solvents were often required.[10] Therefore, it is necessary to develop more efficient, air-stable, and cheaper ligands and complexes for facilitating this coupling reaction in pure water.

Salen as a popular 2N2O chelating ligand has been employed in coordination chemistry and homogeneous catalysis due to its advantages such as excellent catalytic performance, good stability, low cost, simple preparation process, and wide commercially available scope.[11] Phan and his co-workers first proposed that a polymer-supported Salen-Pd type complex catalyzed Suzuki-Miyaura reaction in DMF or water/toluene (30:1) for 24 h under N_2 atmosphere. Although the toluene amount used in the mixture solvent was much lower than that of water, water played a crucial role in the system because the reaction using pure water as a solvent was far from the complete conversion and afforded only 10% conversion.[12] Waghmode *et al*. reported that insoluble Salen-Pd complex could catalyze the Suzuki-Miyaura reaction in DMF/H_2O (1:1) at 100–110 °C.[13] However, we also noticed that insoluble Salen-Pd complex showed no catalytic activity toward Suzuki-Miyaura reactions in EtOH.[14] Recently, Lei *et al*. illustrated that Suzuki-Miyaura reaction was catalyzed heterogeneously by Pd(Salen)/polyoxometalate compound in EtOH/H_2O (1:1).[15] The above results showed that the presence of water could promote the occurrence of Suzuki-Miyaura reaction catalyzed by Salen-Pd type complex. To the best of our knowledge, there is no report on Salen-Pd catalyzed the Suzuki-Miyaura reaction in pure water without any organic solvent or phase-transfer reagents, especially the coupling reaction of the substrates with large steric hindrance. As a part of our research,[16] we herein report a simple and efficient water-soluble Salen-Pd complex catalyzing the Suzuki-Miyaura reaction in neat water.



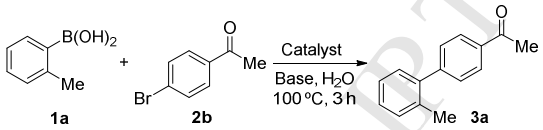
Scheme 1. Ligands and complex used in this study.

2. Results and Discussion

Salen are an important class of ligands and have been studied extensively. Much effort has been paid to investigating the syntheses, catalytic activities and electronic structures of salen-base metal complexes.[17] In general, the salen-Pd complex could be obtained by the reaction of salen ligand with $Pd(OAc)_2$ or $PdCl_2$, so we prepared the water-soluble salen-Pd complex **1** by the reaction of ligand **1** with $Pd(OAc)_2$ in 50% ethanol at 60 ºC for 2 h.

2.1. Optimization of the Suzuki–Miyaura reaction conditions

Table 1. Optimized Reaction Conditions[a]



Entry	Catalyst(mol%)	Base	Yield(%)[b]
1	**L1**+ Na_2PdCl_4 (1)	K_3PO_4	96
2	**L2**+ Na_2PdCl_4 (1)	K_3PO_4	91
3	**L1**+ Na_2PdCl_4 (1)	Na_2CO_3	84
4	**L1**+ Na_2PdCl_4 (1)	NEt_3	93
5	**L1**+ Na_2PdCl_4 (1)	NaOH	99
6	Na_2PdCl_4 (1)	NaOH	86
7	**L1**+ Na_2PdCl_4 (0.5)	NaOH	96
8	**L1**+ Na_2PdCl_4 (0.1)	NaOH	90
9	**L1**+ Na_2PdCl_4 (0.05)	NaOH	88
10	**Complex 1** (0.5%)	NaOH	99

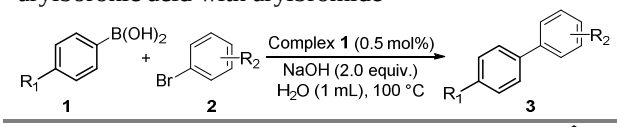
[a] Reaction conditions: 0.50 mmol p-bromoacetophenone, 0.75 mmol o-tolylboronic acid, 2 equiv. base, 1.0 mL H_2O, 100 °C, 3.0 h. [b] GC-MS yield.

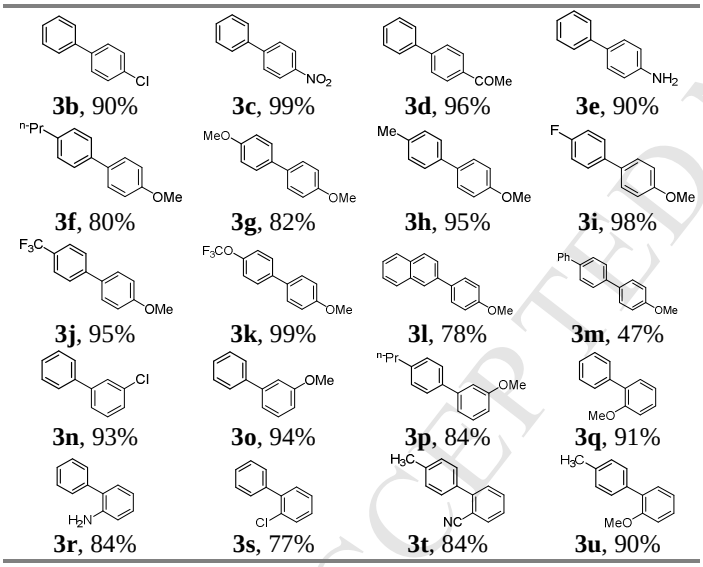
Initially, we chose *p*-bromoacetophenone (0.5 mmol) and *o*-tolylboronic acid (0.75 mmol) as model substrates for the coupling reaction catalyzed by Na_2PdCl_4 (1 mol%) in combination with ligands **L1** or **L2** (1 mol%) in the presence of K_3PO_4 at 100 °C in pure water and detected the yield with GC-MS. As shown in Table 1, when the catalyst was used with ligand **L1** or **L2**, an excellent yield of 96% or 91% was obtained respectively (Table 1, entries 1 and 2). The base usually plays an important role in Suzuki-Miyaura reaction, because the addition of bases exerts a remarkable acceleration effect on the transmetalation between R-Pd-X and organoboronic acid.[18] Among the screened bases, NaOH as the most effective base delivered the desired product with the yield of 99% (Table 1, entry 5), while other bases such as Na_2CO_3 and Et_3N afforded slightly lower yields (84% and 93%, entries 3 and 4 in Table 1). Meanwhile, for the reaction in the absence of ligand, the desired product with the yield of only 86% was obtained under other identical reaction conditions (Table 1, entry 6). The catalyst loading was then investigated, and the yield of the product declined from 96% to 86% when the catalyst loading decreased from 0.5 mol% to 0.05 mol% (Table 1, entries 7-9). However, to be our delight, the complex **1** (0.5 mol%) exhibited the preferable catalyst activity with the yield of 99%, which was higher than that of catalyst preparation *in situ* (Table 1, entry 8). Finally, the combination of complex **1** (0.5 mol%) and NaOH (2 equiv.) at 100 °C in H_2O (1 mL) was chosen as the optimized reaction conditions.

2.2. *Scope and limitations of substrates*

With the optimized reaction conditions in hand, we surveyed the substrate scope of this Suzuki-Miyaura reaction. First, the coupling reactions of para-substituted arylboronic acids with aryl bromides were explored in the presence of 0.5 mol% complex **1** in water. As shown in **Table 2**, the substrates bearing electron-withdrawing or electron-donating groups always afford the desired products **3b**-**3k** with good to excellent yields (80-99%). Meanwhile, naphthalen-2-ylboronic acid was also successfully coupled with 1-bromo-4-methoxybenzene to provide the product **3l** with the yield of 78%. However, the coupling of [1,1'-biphenyl]-4-ylboronic acid proceeded with the low yield to deliver 4-methoxy-1,1':4',1''-terphenyl product **3m**. Interestingly, the positions of substituents showed no significant influence on the efficiency. For example, 1-bromo-3-methoxybenzene and 1-bromo-3-chlorobenzene succeeded to give the coupling products **3n-3p** with the yield of 84-94%. In addition, the steric hindrance of the arylbromides were tolerated and furnished the corresponding products **3q-3u** with the yields of 77-91%. Especially, **3t** compound is an important intermediate for the synthesis of Valsartan, an angiotensin receptor blocker which is widely employed to treat high blood pressure and congestive heart failure.[19]

Table 2. The coupling reaction of para-substituted arylboronic acid with arylbromide[a]

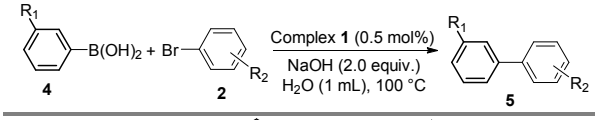


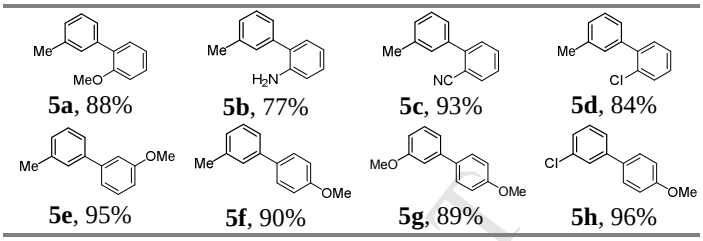


[a] Reaction conditions: 0.50 mmol arybromide, 0.75 mmol arylboronic acid, 0.5 mol% Complex **1**, 1.0 mmol NaOH, 1.0 mL H_2O, 100 °C, 3.0 h. The yields of isolated products are given.

Next, the coupling reactions of meta-substituted arylboronic acids with various aryl bromides in water were investigated (**Table 3**). A series of arylbromides bearing different functional groups, such as -OMe, -NH_2, -CN, and -Cl, are compatible with this catalytic system, and these groups can be easily further functionalized with traditional techniques. Moreover, neither the electronic property nor the steric hindrance of the substrates had an obvious influence on the coupling reaction. The desired products **5a-5h** were obtained with the yields of 77-95%.

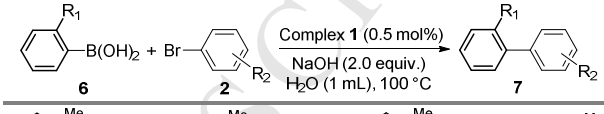
Table 3. The coupling reaction of meta-substituted arylboronic acid with arylbromide[a]

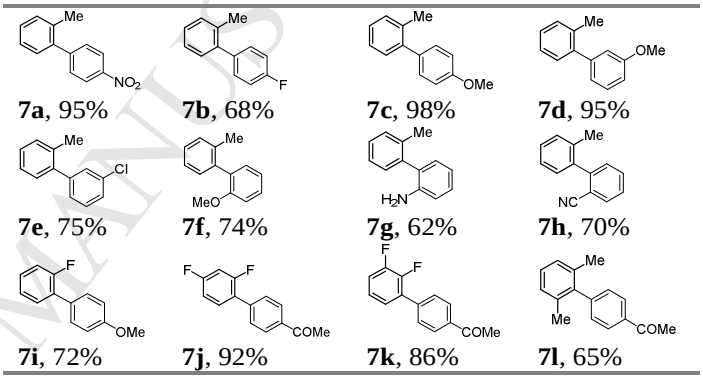




[a] Reaction conditions: 0.50 mmol arylbromide, 0.75 mmol arylboronic acid, 0.5 mol% complex **1**, 1.0 mmol NaOH, 1.0 mL H_2O, 100 °C, 3.0 h. The yields of isolated products are given.

Table 4. The coupling reaction of ortho-substituted arylboronic acid with aryl bromide[a]





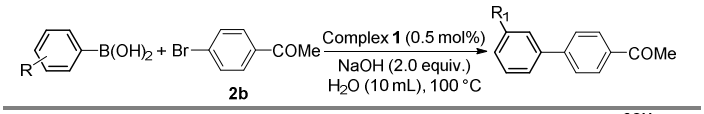
[a] Reaction conditions: 0.50 mmol arybromide, 0.75 mmol arylboronic acid, 0.5 mol% complex **1**, 1.0 mmol NaOH, 1.0 mL H_2O, 100 °C, 3.0 h. The yields of isolated products are given. [b] GC-MS yield.

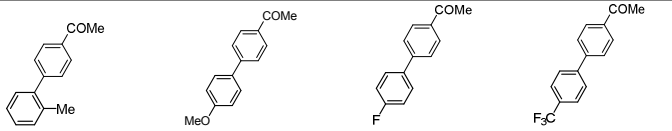
To further ascertain the applicable scope of the methodology, a variety of ortho-substituted substrates including arylboronic acids with aryl bromides were studied. As shown in **Table 4**, to the coupling reaction of 3- or 4-substituted arylbromides with ortho-tolylboronic acid, the arylbromides with electron-donating are obviously better than electron-withdrawing substituents for the coupling reactions smoothly and afforded the biaryl derivatives **7a-7e** with medium to excellent yields. Although 1-bromo-4-nitrobenzene exhibited the higher reactivity, 1-bromo-4-fluorobenzene as the substrate only gave the coupling product **7b** with the yield of 68%. To our delight, the reactions of 2-substituted arylbromides with o-tolylboronic acid were attempted under the standard reaction conditions and afforded the desired product **7f-7h** with the yields of 62-74%. Similarly, fluorinated arylboronic acids also showed good reactivity, such as (2-fluorophenyl)boronic acid, (2,4-difluorophenyl)boronic acid, and (2,3-difluorophenyl)boronic acid, all of which could be converted into the corresponding products **7i-7k** with the yields of 72-92%. Importantly, the increased steric hindrance on the aryl fragment was well tolerated, as demonstrated by the formation of product **7l** with the yield of 65%.

The resulting 4-acetyl-biphenyl derivatives are very important synthons that can be easily converted into other useful compounds.[20] A gram-scale synthesis was performed to verify the practical application with this catalysis system (**Table 5**). It is

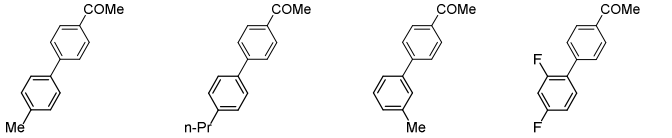
noteworthy that these 4-acetyl-biphenyl derivatives can be obtained on a multi-gram scale with excellent yields. Fortunately, the model reaction was performed with 50 mmol of 4-bromoacetophenone, and proceeded with the yield of 90%, leading to 9.40 g of the product **3a** by simple recrystallization in ethanol.

Table 5. A gram-scale synthesis of 4-acetyl-biphenyl derivatives[a]





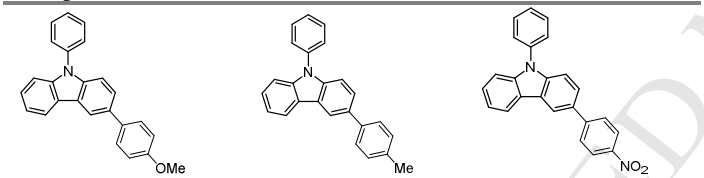
3a, 90% (9.40 g)[b] | **3v**, 93% (1.05 g) | **3w**, 99% (0.98 g) | **3i**, 99% (1.30 g)



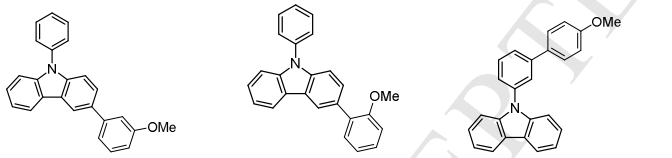
3x, 83% (0.87 g) | **3y**, 92% (1.10 g) | **5i**, 98% (1.00 g) | **7k**, 98% (1.13 g)

[a] Reaction conditions: 5.0 mmol p-bromoacetophenone, 7.5 mmol arylboronic acid, 0.5 mol% complex **1**, 10 mmol NaOH, 10 mL H_2O, 100 °C, 6.0 h. The yields of isolated products are given. [b] Carried out in a 50 mmol scale.

Table 6. The synthesis of aryl-substituted carbazolyl compounds[a]



8a, 77% | **8b**, 73% | **8c**, 71%



8d, 41% | **8e**, 40% | **8f**, 60%

[a] Reaction conditions: 5.0 mmol p-bromoacetophenone, 7.5 mmol arylboronic acid, 0.5 mol% complex **1**, 10 mmol NaOH, 10 mL H_2O, 100 °C, 6.0 h. The yields of isolated products are given. [b] Carried out in a 50 mmol scale.

The synthesis of aryl-substituted carbazolyl compounds has attracted the interest because of the importance of this structure in numerous photo devices, electroluminescent devices and photorefractive materials.[21] However, existing methods are always combined with organic solvents, harsh conditions, long reaction time, and low yields.[22] To the best of our knowledge, there is no report on the synthesis of aryl- substituted carbazolyl compounds through a palladium- catalyzed Suzuki-Miyaura reaction in pure water. Thus, this method was applied to prepare aryl-substituted carbazolyl compounds (Table **6**). The reactions of 1-bromo-4- methoxybenzene, 1-bromo-4-methylbenzene, and 1-bromo-4-nitrobenzene with (9-phenyl-9*H*-carbazol-3-yl)boronic acid in water proceeded smoothly to furnish the desired products **8a-8c**, which were isolated with the yields of 71-73%. However, the 1-bromo-3-methoxybenzene and 1-bromo-2-methoxybenzene gave the coupling products **8d** and **8e** with the yields of 41% and 40%, respectively. We hypothesized that the slightly lower level of coupling reaction in this case might be caused by the increased steric hindrance arising from ortho substitution and the electronic effects from meta-substitution on the aromatic group. In addition, (3-(9*H*-carbazol-9-yl)phenyl)boronic acid can react with 1-bromo-4-methoxybenzene to afford the functionalized carbazolyl product **8f** with the yield of 60%.

Table 7. Recycling experiments[a]

Cycle/n	0	1	2	3	4
Time/h	3	3	5	5	5
Yield/%	99	93	89	88	47

To evaluate the reusability of the complex **1** as the catalyst, recycling studies were carried out for the coupling reaction of 1-bromo-4-methoxybenzene with phenylboronic acid in water at 100 ºC. After the reaction was completed and cooled to room temperature, the product extracted with ethyl ether and the water phase containing the catalyst was loaded with the reactants and base for the next run. As shown in **Table 7**, the catalyst can be recycled for three times. However, a significant loss of catalytic activity was observed in the fourth run.

3. Conclusions

In summary, the water-soluble 2N2O-Salen palladium complex **1** as the efficient catalyst was applied to the Suzuki–Miyaura reaction of the substrates with sterically demanding ortho substituents, and gave the desired products with moderate to excellent yields in pure water without any organic solvent, surfactant, or phase-transfer agents. Importantly, the catalytic system has the wide substrate scope and good functional group tolerance. Particularly, the system was also suitable to synthesize biaryl compounds on a multi-gram scale, and the catalyst was reused directly for the next run. Moreover, this protocol can be applied in the synthesis of aryl-substituted carbazolyl compounds. The catalytic system for new reactions is advancing in our laboratory.

4. Experimental Section

4.1. Materials and instruments

Chemicals were obtained commercially and used as received. NMR spectra were recorded on a Bruker DPX–400 spectrometer using TMS as the internal standard. EI–Mass spectrum was measured on a LC/Q–TOF MS (Micromass, England) or GC-MS (Agilent 7890A/5975C) instrument. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Arylboronic acids and aryl bromides were of analytical grade quality, purchased from Adamas-beta Pharmaceuticals, Inc. Compounds described in the literature were characterized by 1H NMR spectra compared to reported data.

*4.2. Synthesis of ligands **1** and **2***

To a solution of ethane-1, 2-diamine or benzene-1, 2-diamine (2.5 mmol) in 85% EtOH (20 mL) was added sodium 3-formyl-4-hydroxybenzenesulfonate (5.0 mmol). The mixture was refluxed for 2 h, and standed a period time at room temperature. The yellow solid was filtrated and washed twice with EtOH to afford the desired ligand **1** or **2**.

Ligand **1**: yield 65%. ^{1}H NMR (400 MHz, d_6-DMSO): δ 13.21 (s, 2H, OH), 9.00 (s, 2H), 7.94 (s, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51 (m, 2H), 7.42, (m, 2H), 6.90 (d, *J* = 8.0 Hz, 2H) ppm. 13C

NMR (101 MHz, d_6-DMSO): δ 164.92, 161.07, 142.46, 140.12, 131.42, 130.38, 128.37, 120.39, 118.43, 116.38 ppm. Anal. Calcd for $C_{20}H_{14}N_2Na_2O_8S_2{\cdot}2H_2O$, %: C, 43.17; H, 3.26; N, 5.03; S, 11.52; Found, %: C, 43.06; H, 3.20; N, 5.09; S, 11.76. MS (ESI): m/z $[(M\text{-}Na)]^-$, calculated: 497.0; found, 497.0. IR (KBr, cm^{-1}): 3387 (-OH), 1616 (-C=N), 1111 (-SO_3Na).

Ligand **2**: yield 70%. ^{1}H NMR (400 MHz, d_6-DMSO): δ 13.59 (s, 2H, OH), 8.67 (s, 2H), 7.68 (d, J = 2.4 Hz, 2H), 7.52 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.90 (s, 4H) ppm. ^{13}C NMR (101 MHz, d_6-DMSO): δ 167.10, 161.20, 139.43, 130.37, 128.83, 117.37, 116.11, 59.22 ppm. Anal. Calcd for $C_{16}H_{14}N_2Na_2O_8S_2{\cdot}2H_2O$, %: C, 40.68; H, 2.99; N, 5.93; S, 13.57; Found, %: C, 40.96; H, 2.95; N, 6.05; S, 13.26. MS (ESI): m/z $[(M-Na)]^-$, calculated: 449.0; found, 449.1. IR (KBr, cm^{-1}): 3460 (-OH), 1635 (-C=N), 1188 (-SO_3Na).

*4.3. Synthesis of complex **1***

To a solution of ligand 1 (1.0 mmol) in 50% EtOH (20 mL) was added $Pd(OAc)_2$ (1.0 mmol). The mixture was stirred at 60 ºC for 2 h, and stand a period time at room temperature, the solid was filtrated and washed twice with EtOH to give the complex **1**.

Complex **1**: yield 65%. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.29 (s, 2H), 8.44-8.41 (m, 2H), 8.11 (s, 2H), 7.63-7.60 (m, 2H), 7.45-7.42 (m, 2H), 6.96 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (101 MHz, d_6-DMSO): δ 166.50, 155.69, 143.60, 136.39, 134.52, 133.72, 128.76, 120.36, 119.75, 117.87 ppm. Anal. Calcd for $C_{20}H_{12}N_2Na_2O_8PdS_2$, %: C, 38.44; H, 1.94; N, 4.48; S, 10.26; Found, %: C, 38.36; H, 1.96; N, 4.52; S, 10.18. MS (ESI): m/z $[M\text{-}2Na+3H]^+$ calculated: 580.9306, found, 580.9299.

4.4. General procedure for salen-Pd complex 1 catalyzed the Suzuki-Miyaura reaction

A solution of aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), NaOH (1.0 mmol), and complex 1 (0.5 mol%) in H_2O (1.0 mL) was stirred at 100 °C for 5 h. The reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined EtOAc extracts were dried over anhydrous Na_2SO_4, filtrated, and then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with PE or PE/EtOAc as the eluent to obtain the desired products.

8a: 3-(4-methoxyphenyl)-9-phenyl-9H-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.18 (m, 2H), 7.79 (m, 1H), 7.71–7.66 (m, 2H), 7.64–7.59 (m, 2H), 7.56–7.43 (m, 5H), 7.33 (m, 2H), 7.05–7.00 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.80, 141.44, 140.16, 137.84, 134.78, 133.32, 130.02, 128.43, 127.57, 127.17, 126.19, 125.35, 123.99 (s), 123.61, 120.47, 120.11, 118.46, 114.37, 110.05, 55.52. HRMS (ESI): calcd. for $C_{25}H_{19}NO$ $[M+H]^+$ 349.1467; found 349.1463.

8b: 9-phenyl-3-(p-tolyl)-9H-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.18 (d, J = 7.7 Hz, 1H), 7.65–7.58 (m, 7H), 7.47–7.40 (m, 4H), 7.29 (m, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 140.26, 139.16, 137.74, 136.27, 133.48, 129.93, 129.89, 129.54, 127.50, 127.22, 127.20, 127.18, 127.09, 126.10, 125.40, 123.89, 123.54, 120.39, 120.04, 118.60, 109.99, 109.92, 21.14. HRMS (ESI): calcd. for $C_{25}H_{19}N$ $[M+H]^+$ 333.1517; found 333.1514.

8c: 3-(4-nitrophenyl)-9-phenyl-9H-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, J = 1.6 Hz, 1H), 8.32 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 8.9 Hz, 2H), 7.63 (m, 5H), 7.53–7.41 (m, 4H), 7.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.58, 146.58, 141.67, 141.35, 137.40, 130.80, 130.17, 127.99, 127.72, 127.20, 126.75, 125.51, 124.29, 123.30, 120.59, 119.46, 110.58, 110.30. HRMS (ESI): calcd. for $C_{24}H_{16}N_2O_2$ $[M+H]^+$ 364.1212; found 364.1209.

8d: 3-(3-methoxyphenyl)-9-phenyl-9H-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 1.4 Hz, 1H), 8.18 (d, J = 7.7 Hz, 1H), 7.62 (m, 5H), 7.47–7.36 (m, 5H), 7.33–7.28 (m, 2H), 7.25 (s, 1H), 6.90 (dd, J = 8.1, 2.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.14, 143.70, 141.49, 140.60, 137.78, 133.46, 129.97, 127.67, 127.21, 126.28, 125.63, 123.97, 123.60, 120.50, 120.13, 119.00, 113.28, 112.04, 110.08, 55.50. HRMS (ESI): calcd. for $C_{25}H_{19}NO$ $[M+H]^+$ 349.1467; found 349.1463.

8e: 3-(2-methoxyphenyl)-9-phenyl-9H-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.58 (s, 5H), 7.41 (m, 5H), 7.29 (m, 2H), 7.09–7.00 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 140.26, 139.16, 137.74, 136.27, 133.48, 129.93, 129.89, 129.54, 127.50, 127.22, 127.20, 127.18, 127.09, 126.10, 125.40, 123.89, 123.54, 120.39, 120.04, 118.60, 109.99, 109.92, 21.14. HRMS (ESI): calcd. for $C_{25}H_{19}NO$ $[M+H]^+$ 349.1467; found 349.1465.

8f: 9-(4'-methoxy-[1,1'-biphenyl]-3-yl)-9H-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.66 (m, 7H), 7.54–7.44 (m, 4H), 7.37–7.31 (m, 1H), 7.06 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.69, 142.82, 141.02, 138.29, 132.72, 130.33, 128.33, 126.09, 125.77, 125.33, 123.51, 120.45, 120.06, 114.51, 109.98, 55.49. HRMS (ESI): calcd. for $C_{25}H_{19}NO$ $[M+H]^+$ 349.1467; found 349.1465.

4.5. Catalyst recycling for the Suzuki-Miyaura reaction

When the reaction was completed, the mixture was cooled to room temperature and extracted with ethyl ether (2 mL). NaOH (1 mmol), p-bromoacetophenone (0.5 mmol), ortho-tolylboronic acid (0.75 mmol) were added to the aqueous phase that was separated from the previous catalytic run, and reacted at 100 °C.

Acknowledgments

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Water-soluble salen-Pd complex as an efficient catalyst for Suzuki-Miyaura reaction of sterically hindered substrates in pure water

Yashuai Liu, Ningning Gu, Ping Liu*, Xiaowei Ma, Yan Liu*, Jianwei Xie and Bin Dai

School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, China, Tel.: +86 0993 2057213; fax: +86 0993 2057270; e-mail: liuping1979112@aliyun.com and liuyan1979810@aliyun.com

Supporting Information

1. Materials and instruments

Chemicals were obtained commercially and used as received. NMR spectra were recorded on a Bruker DPX–400 spectrometer using TMS as the internal standard. EI–Mass spectrum was measured on a LC/Q–TOF MS (Micromass, England) or GC-MS (Agilent 7890A/5975C) instrument. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Arylboronic acids and aryl bromides were of analytical grade quality, purchased from Adamas-beta Pharmaceuticals, Inc. Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

2. General procedure for salen-Pd catalyzed the Suzuki-Miyaura reaction

A solution of aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), NaOH (1.0 mmol), and complex **1** (0.5 mol %) in H_2O (1.0 mL) was stirred at 100 ºC for 5 h. The reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined EtOAc extracts were dried over anhydrous Na_2SO_4, filtrated, and then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with PE or PE/EtOAc as the eluent to obtain the desired products.

3. The NMR Spectra Data

3a: 1-(2'-methyl-[1,1'-biphenyl]-4-yl)ethanone[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.99 (m, 2H), 7.45 – 7.40 (m, 2H), 7.30 – 7.20 (m, 4H), 2.65 – 2.63 (m, 3H), 2.27 (s, 3H).

3b: 4-chloro-1,1'-biphenyl[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.48 (m, 4H), 7.47 – 7.32 (m, 5H).

3c: 4-nitro-1,1'-biphenyl[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.28 (m, 2H), 7.76 – 7.71 (m, 2H), 7.63 (m, 2H), 7.53 – 7.42 (m, 3H).

3d: 1-([1,1'-biphenyl]-4-yl)ethanone[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 8.03 (m, 1H), 8.03 – 8.01 (m, 1H), 7.70 – 7.69 (m, 1H), 7.68 – 7.67 (m, 1H), 7.64 (t, J = 1.7 Hz, 1H), 7.62 (q, J = 1.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 2.64 (s, 3H).

3e: [1,1'-biphenyl]-4-amine[4]

^{1}H NMR (400 MHz, DMSO): δ 7.52 (m, 2H), 7.38 – 7.33 (m, 4H), 7.23 – 7.18 (m, 1H), 6.66 – 6.62 (m, 2H), 5.21 (s, 2H).

3f: 4-methoxy-4'-propyl-1,1'-biphenyl[5]

^{1}H NMR (400 MHz, DMSO): δ 7.59 – 7.55 (m, 2H), 7.52 – 7.49 (m, 2H), 7.25 – 7.22 (m, 2H), 7.02 – 6.98 (m, 2H), 3.78 (s, 3H), 2.59 – 2.54 (m, 2H), 1.64 – 1.57 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

3g: 4,4'-dimethoxy-1,1'-biphenyl[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.48 (m, 2H), 7.47 – 7.45 (m, 2H), 6.98 – 6.96 (m, 2H), 6.95 – 6.93 (m, 2H), 3.84 (s, 6H).

3h: 4-methoxy-4'-methyl-1,1'-biphenyl[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.47 (m, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.99 – 6.93 (m, 2H), 3.84 (d, J = 0.5 Hz, 3H), 2.38 (s, 3H).

3i:4-fluoro-4'-methoxy-1,1'-biphenyl[3]

^{1}H NMR (400 MHz, DMSO): δ 7.73-7.65 (m, 8H), 7.50– 7.46 (m, 2H), 7.38 (d, J = 7.4 Hz, 1H), 7.06-7.03 (m, 2H), 3.81 (s, 3H).

3j: 4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.44 (m, 4H), 7.12 – 7.06 (m, 2H), 6.99 – 6.97 (m, 1H), 6.96 – 6.94 (m, 1H), 3.84 (s, 3H).

3k:4-methoxy-4'-(trifluoromethoxy)-1,1'-biphenyl

^{1}H NMR (400 MHz, DMSO): δ 7.86-7.83 (m, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.71-7.68 (m, 2H), 7.08-7.05 (m, 2H), 3.81 (s, 3H).

3l: 2-(4-methoxyphenyl)naphthalene[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 8.03 (s, 1H), 7.67 – 7.66 (m, 1H), 7.65 (d, J = 3.3 Hz, 2H), 7.63 (s, 1H), 7.32 (dd, J = 8.8, 0.9 Hz, 2H), 2.64 (s, 3H).

3m: 4-methoxy-1,1':4',1''-terphenyl[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.97 (m, 1H), 7.90 – 7.83 (m, 3H), 7.73 – 7.65 (m, 3H), 7.51 – 7.43 (m, 2H), 7.05 – 6.99 (m, 2H), 3.87 (s, 3H).

3n: 3-chloro-1,1'-biphenyl[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 1H), 7.55 – 7.52 (m, 2H), 7.43 (m, 3H), 7.37 – 7.29 (m, 3H).

3o: 3-methoxy-1,1'-biphenyl[6]

^{1}H NMR (400 MHz, DMSO): δ 7.68 – 7.64 (m, 2H), 7.48 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.22 (m, 1H), 7.19 – 7.17 (m, 1H), 6.94 (m, 1H), 3.82 (s, 3H).

3p: 3-methoxy-4'-propyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.47 (m, 2H), 7.34 – 7.29 (m, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 7.13 – 7.10 (m, 1H), 6.86 (m, 1H), 3.82 (s, 3H), 2.63 – 2.59 (m, 2H), 1.71 – 1.62 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

3q: 2-methoxy-1,1'-biphenyl[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.1 Hz, 2H), 7.36 (dt, J = 14.3, 7.5 Hz, 5H), 7.01 (dd, J = 24.4, 7.7 Hz, 2H), 3.79 (s, 3H).

3r: [1,1'-biphenyl]-2-amine[6]

^{1}H NMR (400 MHz, DMSO): δ 7.47 – 7.39 (m, 4H), 7.35 – 7.31 (m, 1H), 7.04 (m, 1H), 6.98 (dd, J = 7.5, 1.6 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.64 (td, J = 7.4, 1.2 Hz, 1H), 4.74 (s, 2H).

3s: 2-chloro-1,1'-biphenyl[10]

^{1}H NMR (400 MHz, DMSO): δ 7.58 – 7.53 (m, 1H), 7.48 – 7.37 (m, 8H).

3t: 4'-methyl-[1,1'-biphenyl]-2-carbonitrile[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (m, 1H), 7.65 (td, J = 7.7, 1.4 Hz, 1H), 7.53 (dd, J = 7.9, 1.2 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.44 (td, J = 7.6, 1.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 2.45 (s, 3H).

3u: 2-methoxy-4'-methyl-1,1'-biphenyl[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 ‑ 7.40 (m, 2H), 7.33 ‑ 7.28 (m, 2H), 7.22 (m, 2H), 7.04 ‑ 6.95 (m, 2H), 3.80 (s, 3H), 2.39 (s, 3H).

3v: 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 2.62 (s, 3H).

3w: 1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethanone[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.59 (dd, J = 8.9, 5.3 Hz, 2H), 7.16 (t, J = 8.7 Hz, 2H), 2.63 (s, 3H).

3x: 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethanone[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 6.5 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 2.66 (s, 3H), 2.44 (s, 3H).

3y: 1-(4'-propyl-[1,1'-biphenyl]-4-yl)ethanone[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.6 Hz, 2H), 8.02 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 2.67 – 2.61 (m, 5H), 1.68 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H).

5a: 2-methoxy-3'-methyl-1,1'-biphenyl[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 ‑ 7.27 (m, 5H), 7.15 ‑ 7.11 (m, 1H), 7.03 ‑ 6.95 (m, 2H), 3.80 (s, 3H), 2.40 ‑ 2.38 (m, 3H).

5b: 3'-methyl-[1,1'-biphenyl]-2-amine[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.22 (m, 3H), 7.18 – 7.09 (m, 3H), 6.85 – 6.78 (m, 1H), 6.75 (dd, J = 7.9, 0.5 Hz, 1H), 3.71 (s, 2H), 2.39 (s, 3H).

5c: 3'-methyl-[1,1'-biphenyl]-2-carbonitrile[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J = 7.8, 1.1 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.33 (m, 4H), 7.27 – 7.23 (m, 1H), 2.42 (s, 3H).

5d: 2-chloro-3'-methyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 1H), 7.35 – 7.15 (m, 7H), 2.40 (s, 3H).

5e: 3-methoxy-3'-methyl-1,1'-biphenyl[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.8 Hz, 2H), 7.31 (q, J = 7.6 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.12 – 7.10 (m, 1H), 6.87 (m, 1H), 3.83 (s, 3H), 2.40 (s, 3H).

5f: 4'-methoxy-3-methyl-1,1'-biphenyl[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.50 (m, 2H), 7.37 – 7.29 (m, 3H), 7.12 (d, J = 7.0 Hz, 1H), 6.98 – 6.95 (m, 2H), 3.84 (s, 3H), 2.41 (s, 3H).

5g: 3,4'-dimethoxy-1,1'-biphenyl[15]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.50 (m, 2H), 7.33 (m, 1H), 7.16 – 7.12 (m, 1H), 7.10 – 7.07 (m, 1H), 6.99 – 6.95 (m, 2H), 6.85 (m, 1H), 3.85 (t, J = 2.8 Hz, 6H).

5h: 3-chloro-4'-methoxy-1,1'-biphenyl[16]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.47 (m, 3H), 7.42 (m, 1H), 7.36 – 7.31 (m, 1H), 7.29 – 7.25 (m, 1H), 7.00 – 6.95 (m, 2H), 3.85 (s, 3H).

5i: 1-(3'-methyl-[1,1'-biphenyl]-4-yl)ethanone[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.1 Hz, 1H), 2.63 (s, 3H), 2.43 (s, 3H).

7a:2-methyl-4'-nitro-1,1'-biphenyl[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.29 (m, 1H), 8.28 – 8.26 (m, 1H), 7.51 – 7.50 (m, 1H), 7.49 – 7.48 (m, 1H), 7.34 – 7.26 (m, 3H), 7.23 – 7.20 (m, 1H), 2.27 (s, 3H).

7b: 4'-fluoro-2-methyl-1,1'-biphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 2H), 7.26 – 7.18 (m, 4H), 7.12 – 7.06 (m, 2H), 2.25 (s, 3H).

7c: 4'-methoxy-2-methyl-1,1'-biphenyl[3]

^{1}H NMR (400 MHz, DMSO): δ 7.28 – 7.21 (m, 5H), 7.16 (m, 1H), 7.01 – 6.97 (m, 2H).

7d: 3'-methoxy-2-methyl-1,1'-biphenyl[16]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 1H), 7.27 – 7.21 (m, 4H), 6.92 – 6.85 (m, 3H), 3.82 (s, 3H), 2.27 (s, 3H).

7e: 3'-chloro-2-methyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 7.23 – 7.19 (m, 1H), 7.19 – 7.16 (m, 2H), 2.24 (d, J = 3.0 Hz, 3H).

7f: 2-methoxy-2'-methyl-1,1'-biphenyl[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 1H), 7.33 – 7.27 (m, 3H), 7.23 (m, 2H), 7.07 (m, 1H), 7.02 (d, J = 8.3 Hz, 1H), 3.82 (s, 3H), 2.20 (s, 3H).

7g: 2'-methyl-[1,1'-biphenyl]-2-amine[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.13 (m, 5H), 7.00 (m, 1H), 6.84 – 6.73 (m, 2H), 3.47 (s, 2H), 2.17 (s, 3H).

7h: 2'-methyl-[1,1'-biphenyl]-2-carbonitrile[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.71 (m, 1H), 7.64 – 7.59 (m, 1H), 7.46 – 7.41 (m, 1H), 7.38 – 7.23 (m, 4H), 7.20 (d, J = 7.4 Hz, 1H), 2.19 (s, 3H).

7i: 2-fluoro-4'-methoxy-1,1'-biphenyl[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.51 (m, 2H), 7.45 (m, 1H), 7.35 – 7.29 (m, 1H), 7.25 – 7.14 (m, 2H), 7.06 – 7.00 (m, 2H), 3.91 – 3.88 (m, 3H).

7j: 1-(2',4'-difluoro-[1,1'-biphenyl]-4-yl)ethanone[21]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 8.01 (m, 2H), 7.61 (dd, J = 8.4, 1.6 Hz, 2H), 7.44 (td, J = 8.7, 6.4 Hz, 1H), 7.03 – 6.90 (m, 2H), 2.64 (s, 3H).

7k: 1-(2',3'-difluoro-[1,1'-biphenyl]-4-yl)ethanone[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.68 – 7.62 (m, 2H), 7.24 – 7.14 (m, 3H), 2.65 (d, J = 2.7 Hz, 3H).

7l: 1-(2',6'-dimethyl-[1,1'-biphenyl]-4-yl)ethanone[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 – 7.04 (m, 5H), 6.98 – 6.94 (m, 2H), 3.86 (s, 3H), 2.04 (s, 6H).

8a: 3-(4-methoxyphenyl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.18 (m, 2H), 7.79 (m, 1H), 7.71 – 7.66 (m, 2H), 7.64 – 7.59 (m, 2H), 7.56 – 7.43 (m, 5H), 7.33 (m, 2H), 7.05 – 7.00 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.80, 141.44, 140.16, 137.84, 134.78, 133.32, 130.02, 128.43, 127.57, 127.17, 126.19, 125.35, 123.99, 123.61, 120.47, 120.11, 118.46, 114.37, 110.05, 55.52.

8b: 9-phenyl-3-(p-tolyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.18 (d, J = 7.7 Hz, 1H), 7.65 – 7.58 (m, 7H), 7.47 – 7.40 (m, 4H), 7.29 (m, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 140.26, 139.16, 137.74, 136.27, 133.48, 129.93, 129.89, 129.54, 127.50, 127.22, 127.20, 127.18, 127.09, 126.10, 125.40, 123.89, 123.54, 120.39, 120.04, 118.60, 109.99, 109.92, 21.14.

8c: 3-(4-nitrophenyl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, J = 1.6 Hz, 1H), 8.32 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 8.9 Hz, 2H), 7.63 (m, 5H), 7.53 – 7.41 (m, 4H), 7.34 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.58, 146.58, 141.67, 141.35, 137.40, 130.80, 130.17, 127.99, 127.72, 127.20, 126.75, 125.51, 124.29, 123.30, 120.59, 119.46, 110.58, 110.30.

8d: 3-(3-methoxyphenyl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 1.4 Hz, 1H), 8.18 (d, J = 7.7 Hz, 1H), 7.62 (m, 5H), 7.47 – 7.36 (m, 5H), 7.33 – 7.28 (m, 2H), 7.25 (s, 1H), 6.90 (dd, J = 8.1, 2.5 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.14, 143.70, 141.49, 140.60, 137.78, 133.46, 129.97, 127.67, 127.21, 126.28, 125.63, 123.97, 123.60, 120.50, 120.13, 119.00, 113.28, 112.04, 110.08, 55.50.

8e: 3-(2-methoxyphenyl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.58 (s, 5H), 7.41 (m, 5H), 7.29 (m, 2H), 7.09 – 7.00 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 140.26, 139.16, 137.74, 136.27, 133.48, 129.93, 129.89, 129.54, 127.50, 127.22, 127.20, 127.18, 127.09, 126.10, 125.40, 123.89, 123.54, 120.39, 120.04, 118.60, 109.99, 109.92, 21.14.

8f: 9-(4'-methoxy-[1,1'-biphenyl]-3-yl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.66 (m, 7H), 7.54 – 7.44 (m, 4H), 7.37 – 7.31 (m, 1H), 7.06 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.69, 142.82, 141.02, 138.29, 132.72, 130.33, 128.33, 126.09, 125.77, 125.33, 123.51, 120.45, 120.06, 114.51, 109.98, 55.49.

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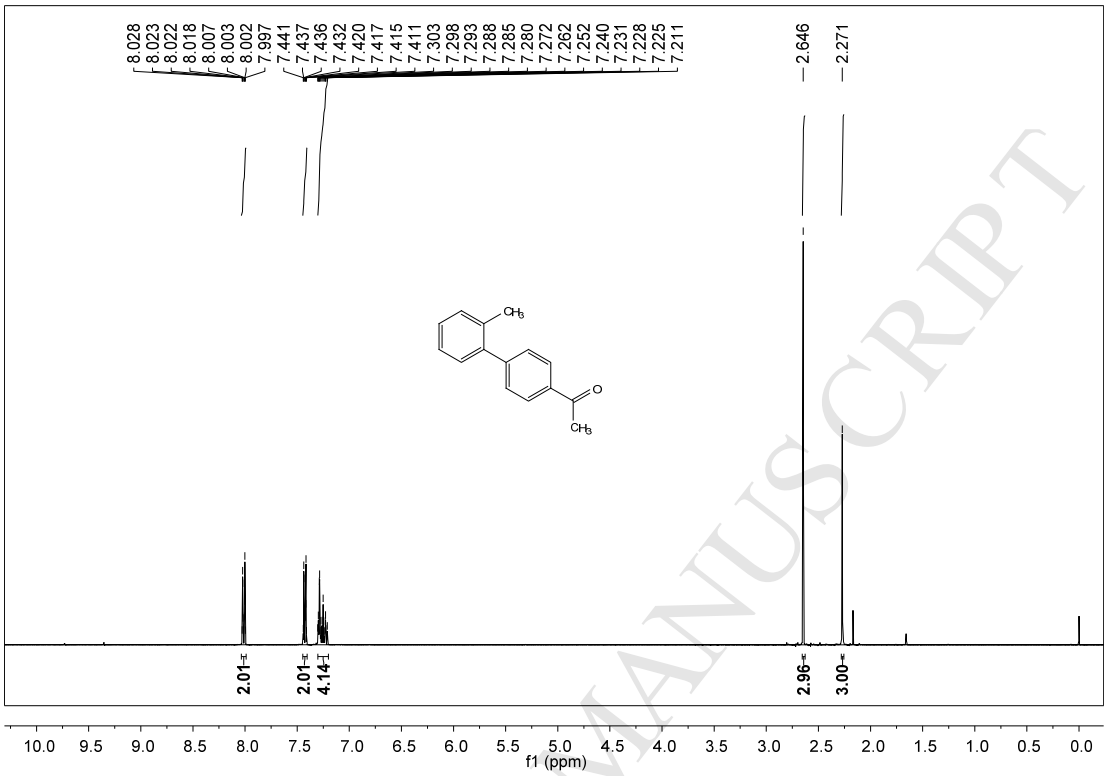
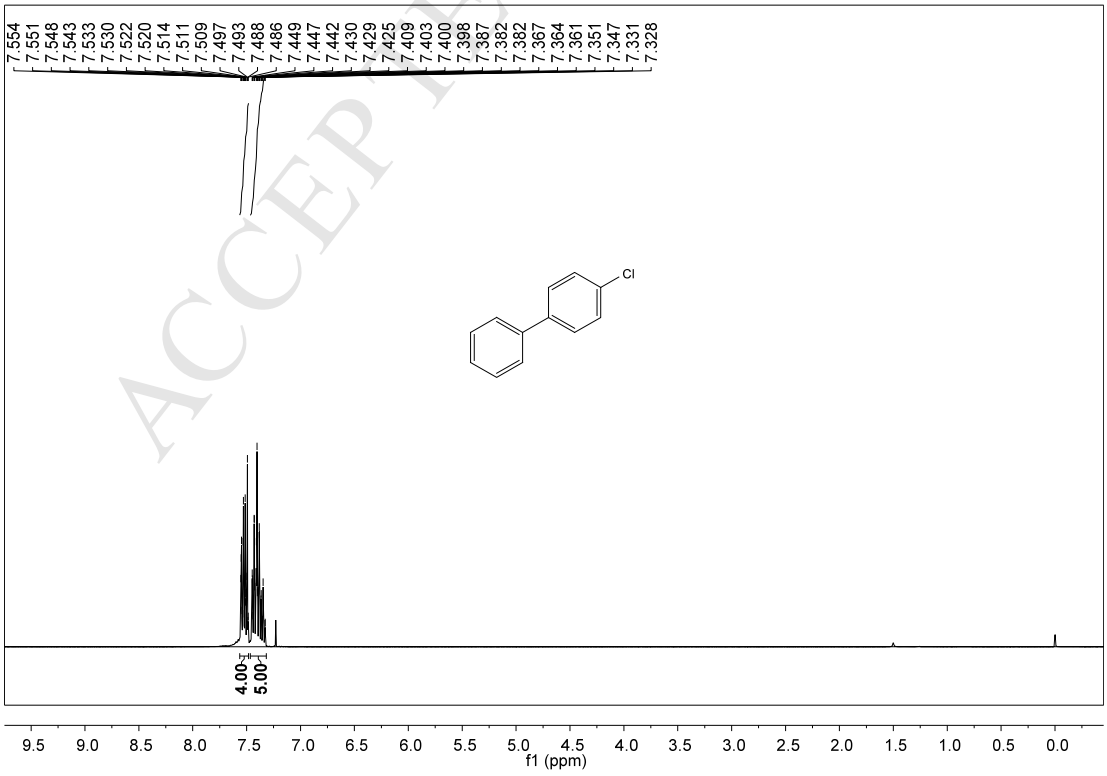
5. Copies of NMR

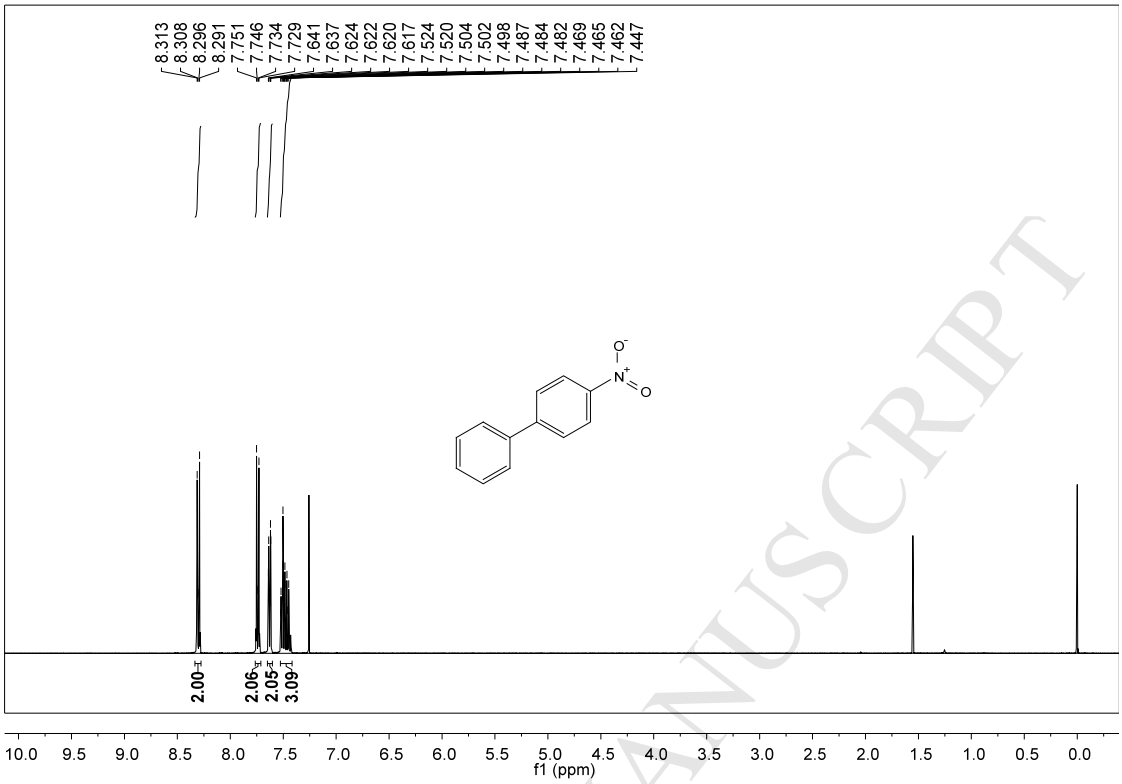
3a: 1-(2'-methyl-[1,1'-biphenyl]-4-yl)ethanone



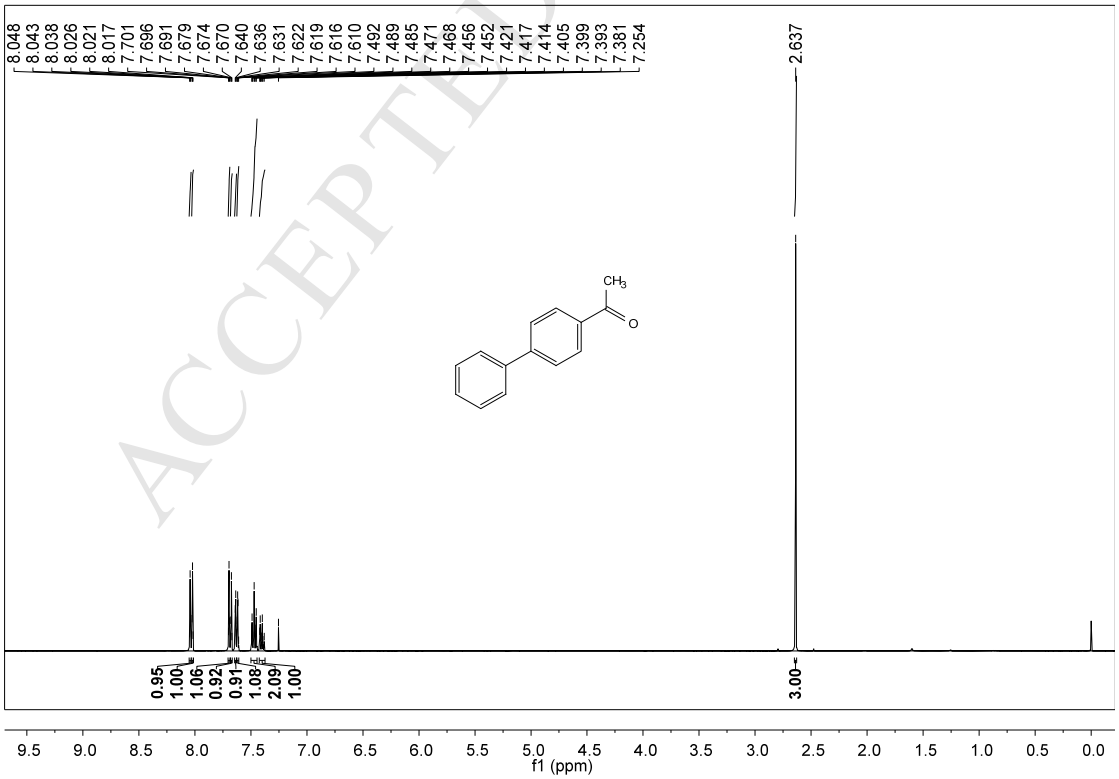
3b: 4-chloro-1,1'-biphenyl



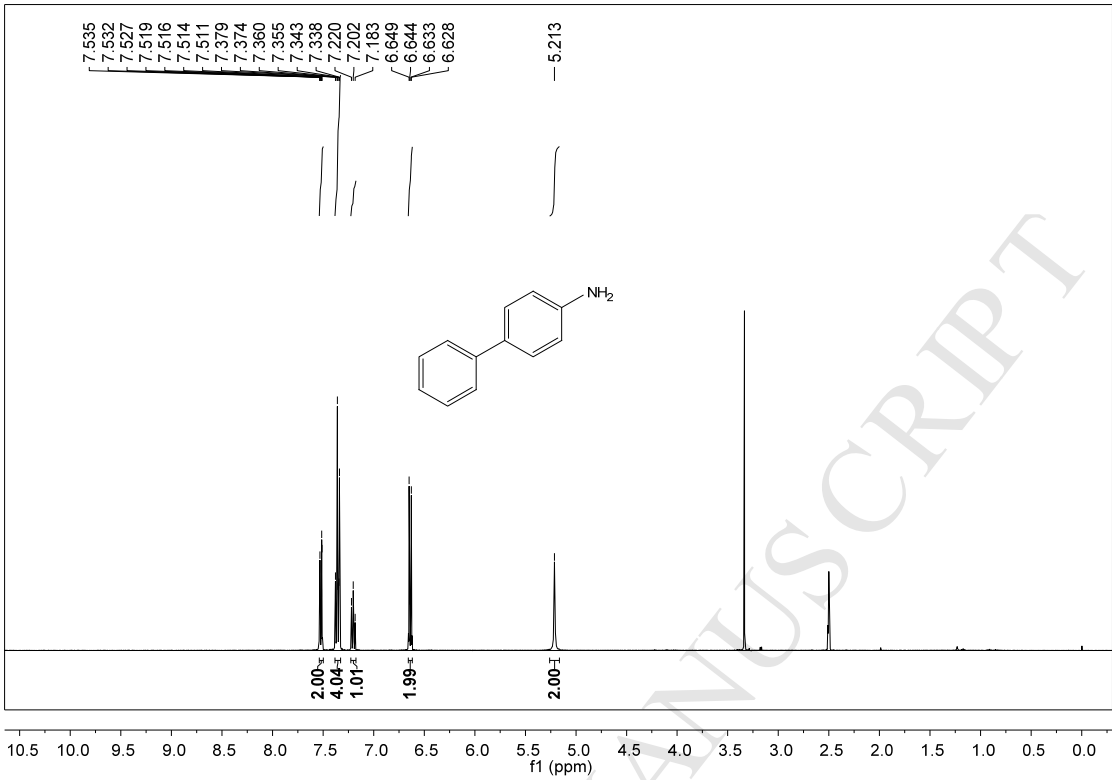
3c: 4-nitro-1,1'-biphenyl



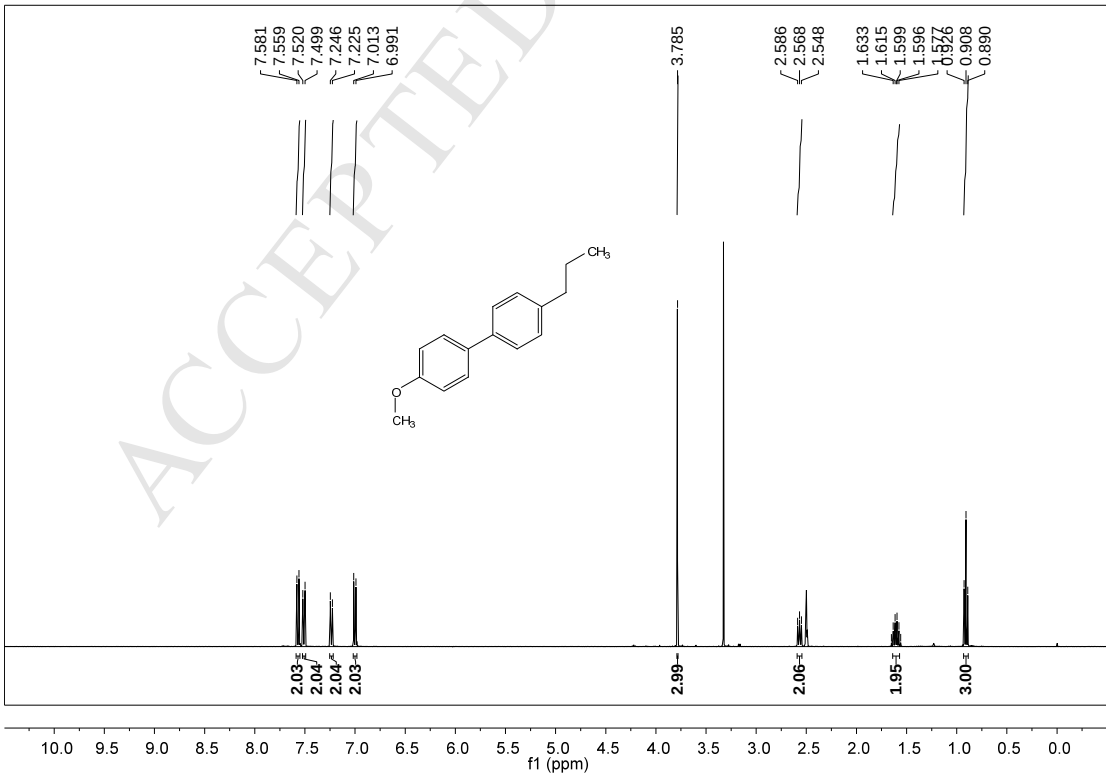
3d: 1-([1,1'-biphenyl]-4-yl)ethanone



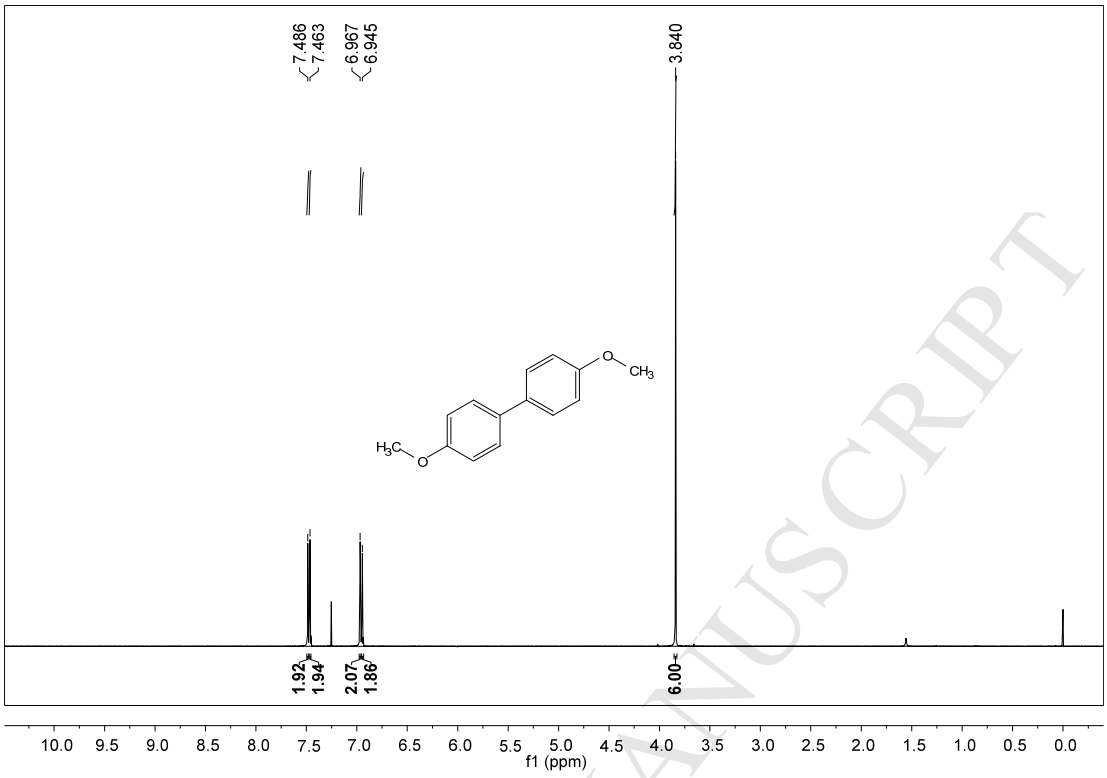
3e: [1,1'-biphenyl]-4-amine



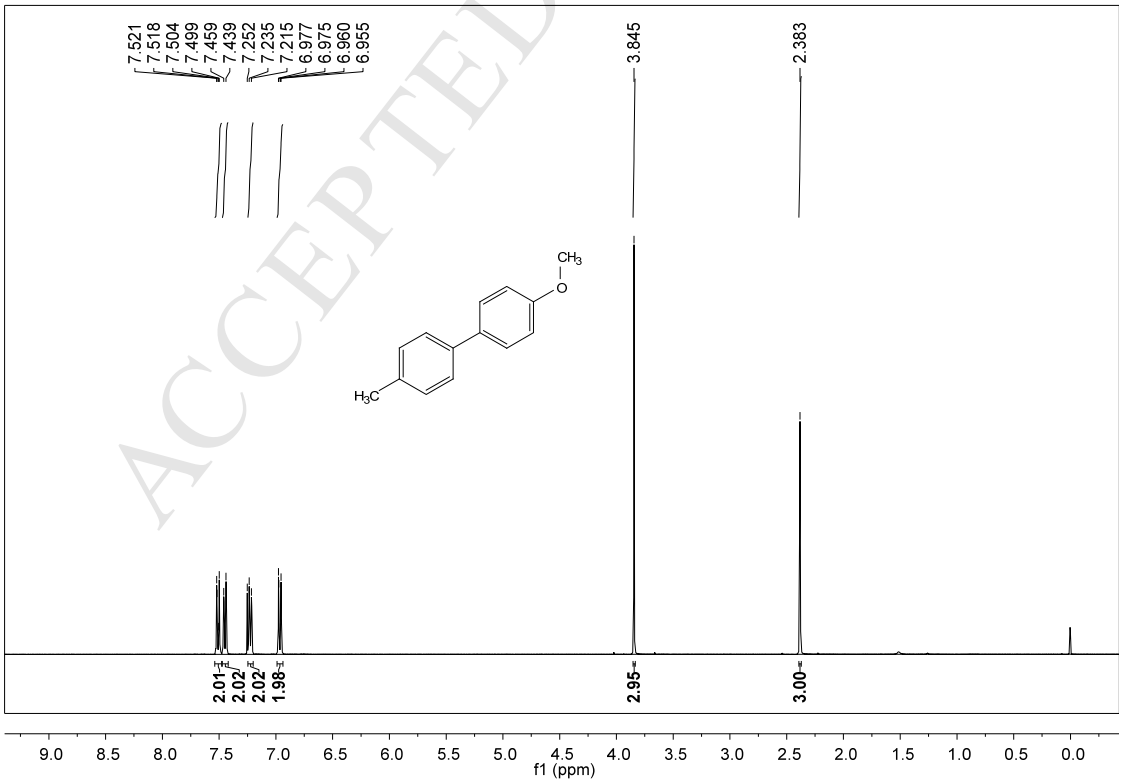
3f: 4-methoxy-4'-propyl-1,1'-biphenyl



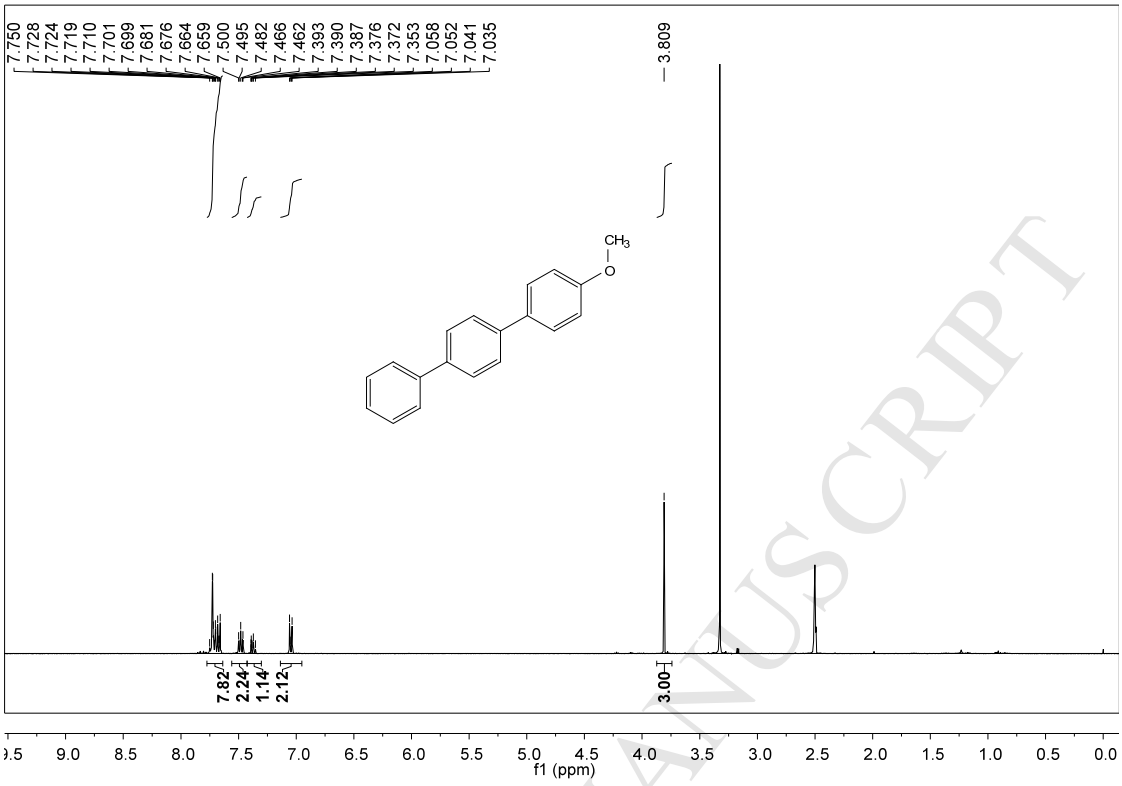
3g: 4,4'-dimethoxy-1,1'-biphenyl



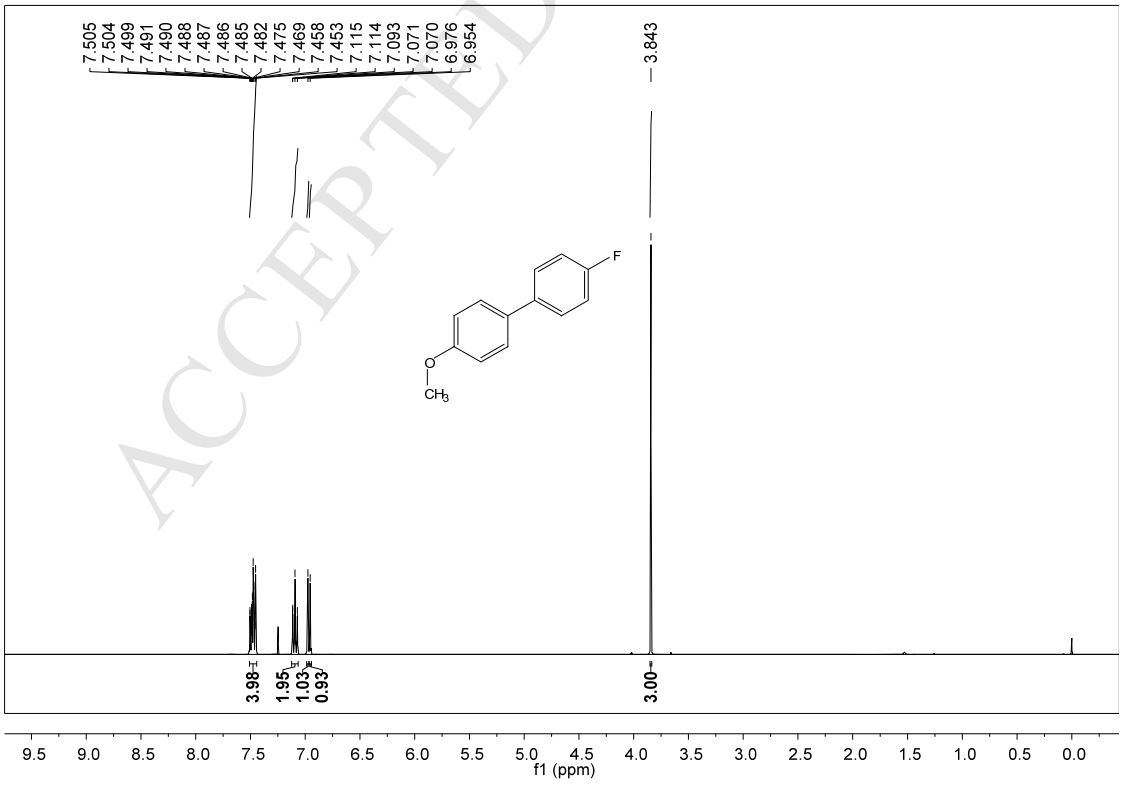
3h: 4-methoxy-4'-methyl-1,1'-biphenyl



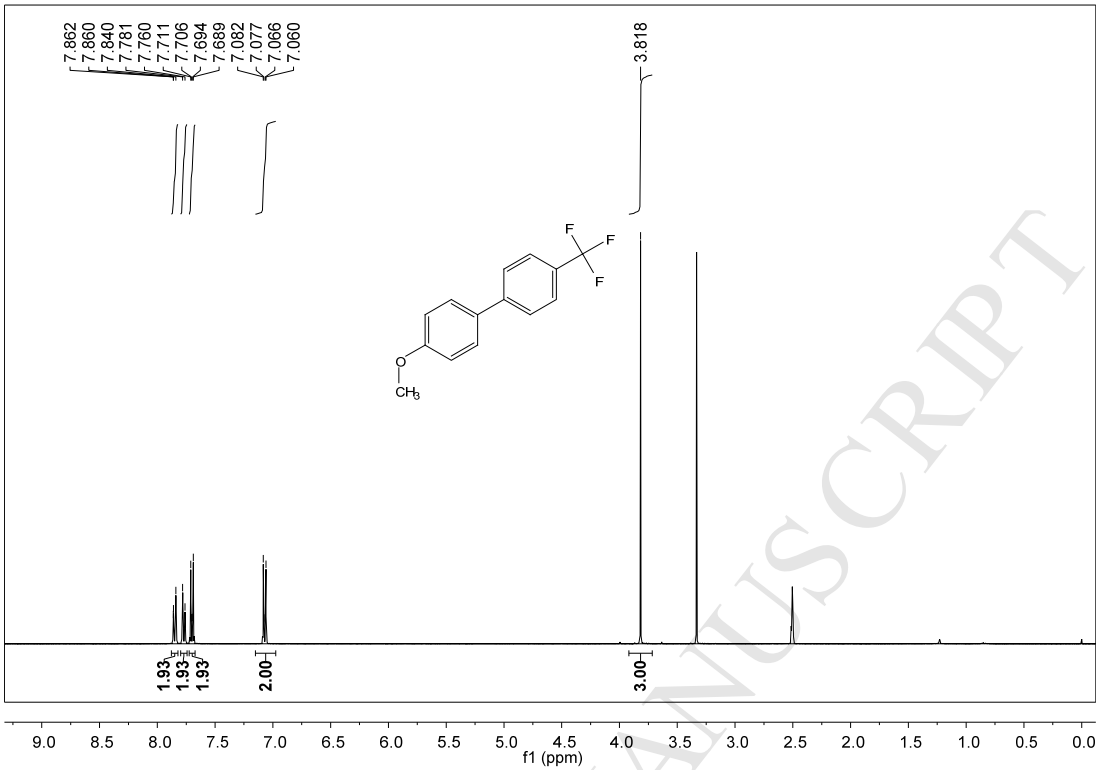
3i:4-fluoro-4'-methoxy-1,1'-biphenyl



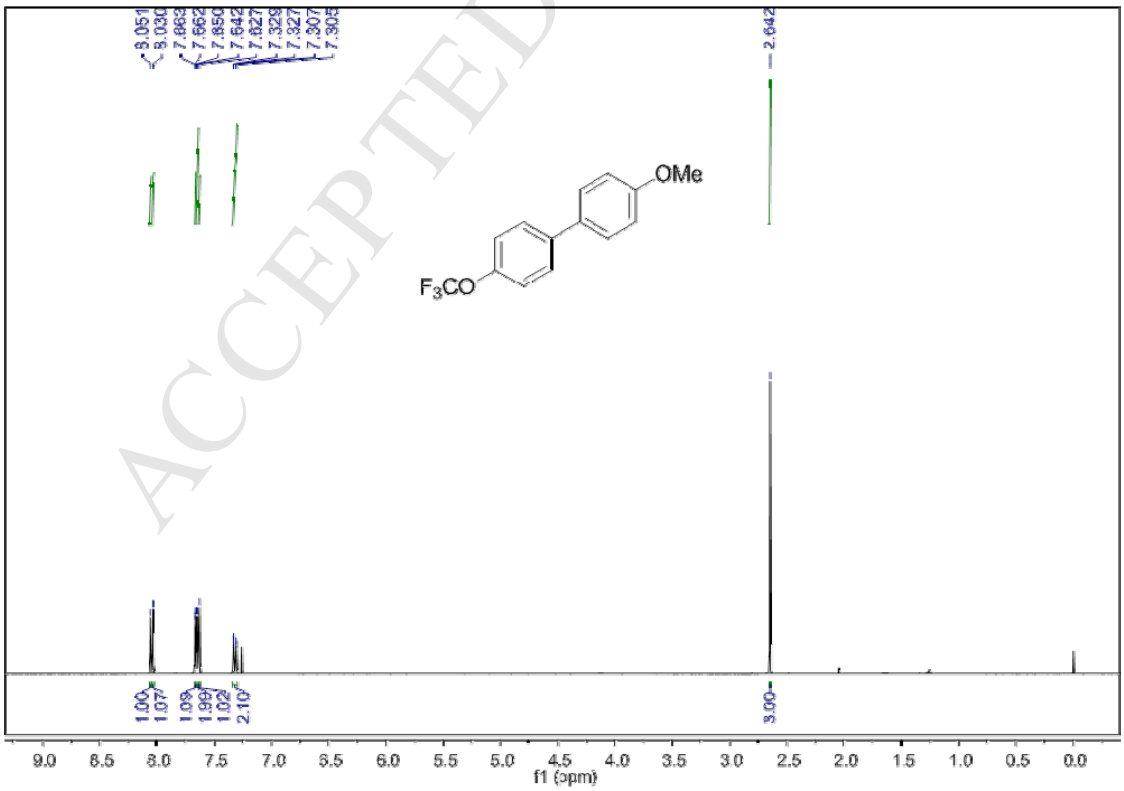
3j: 4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl



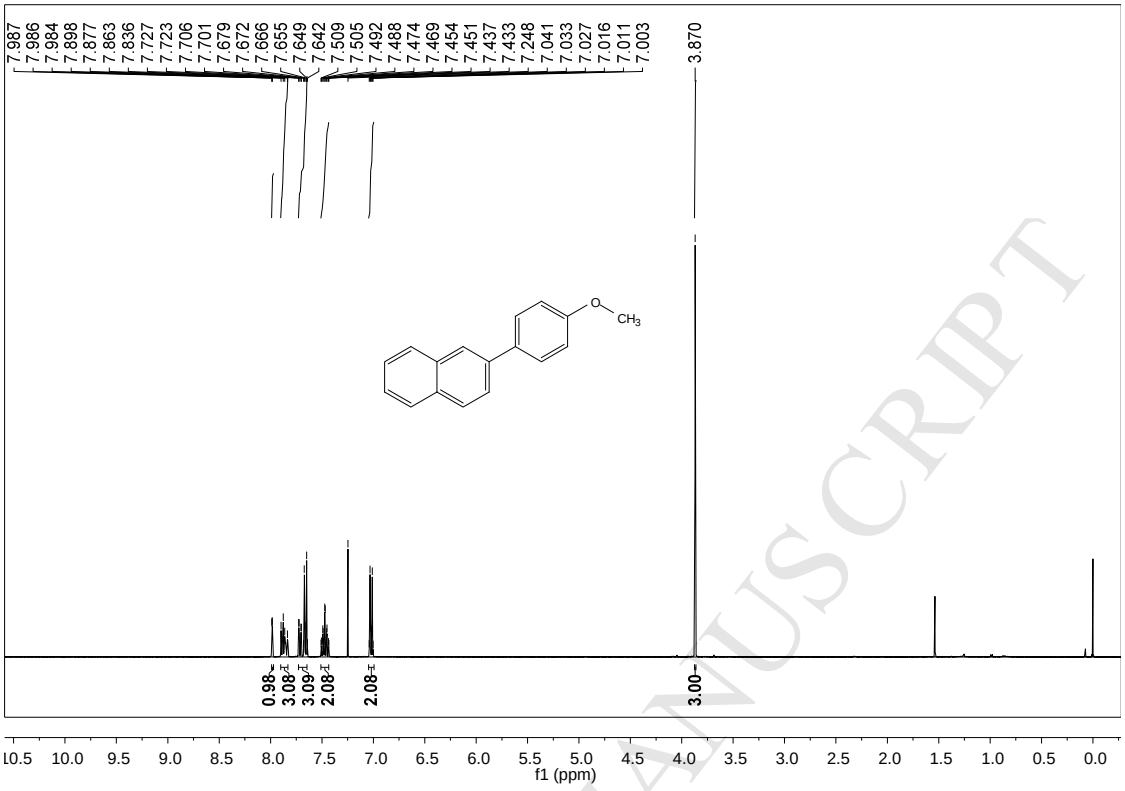
3k: 4-methoxy-4'-(trifluoromethoxy)-1,1'-biphenyl



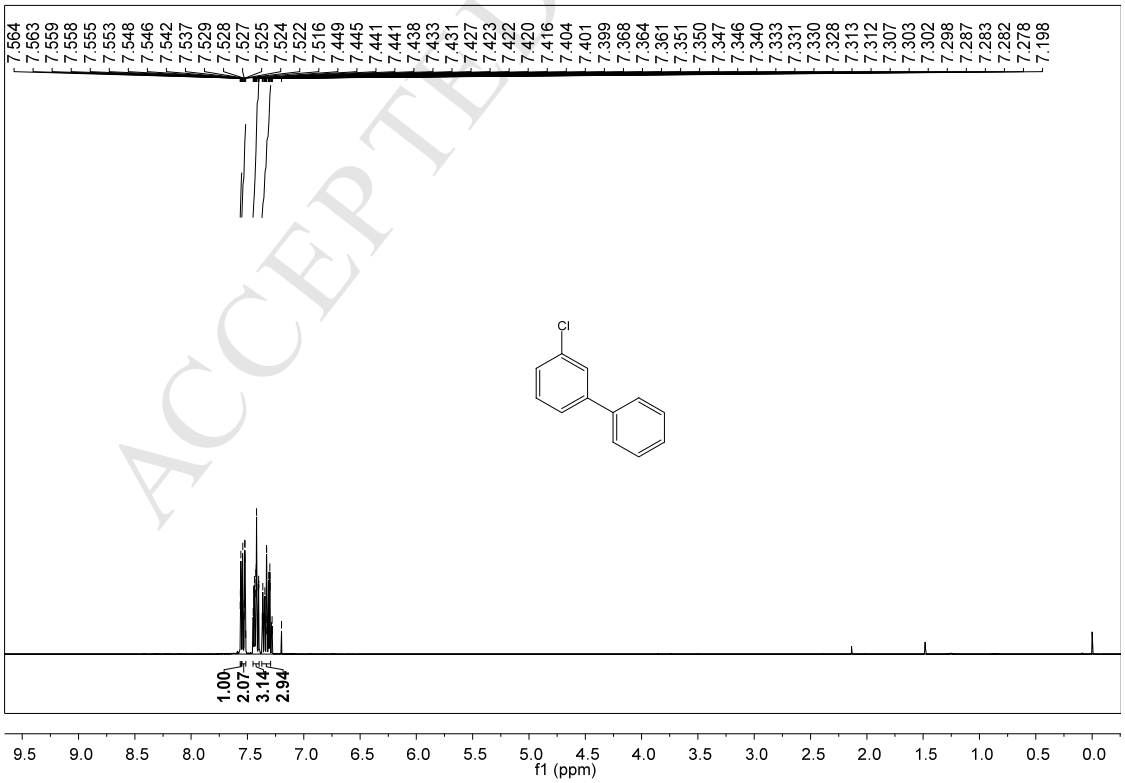
3l: 2-(4-methoxyphenyl)naphthalene[7]



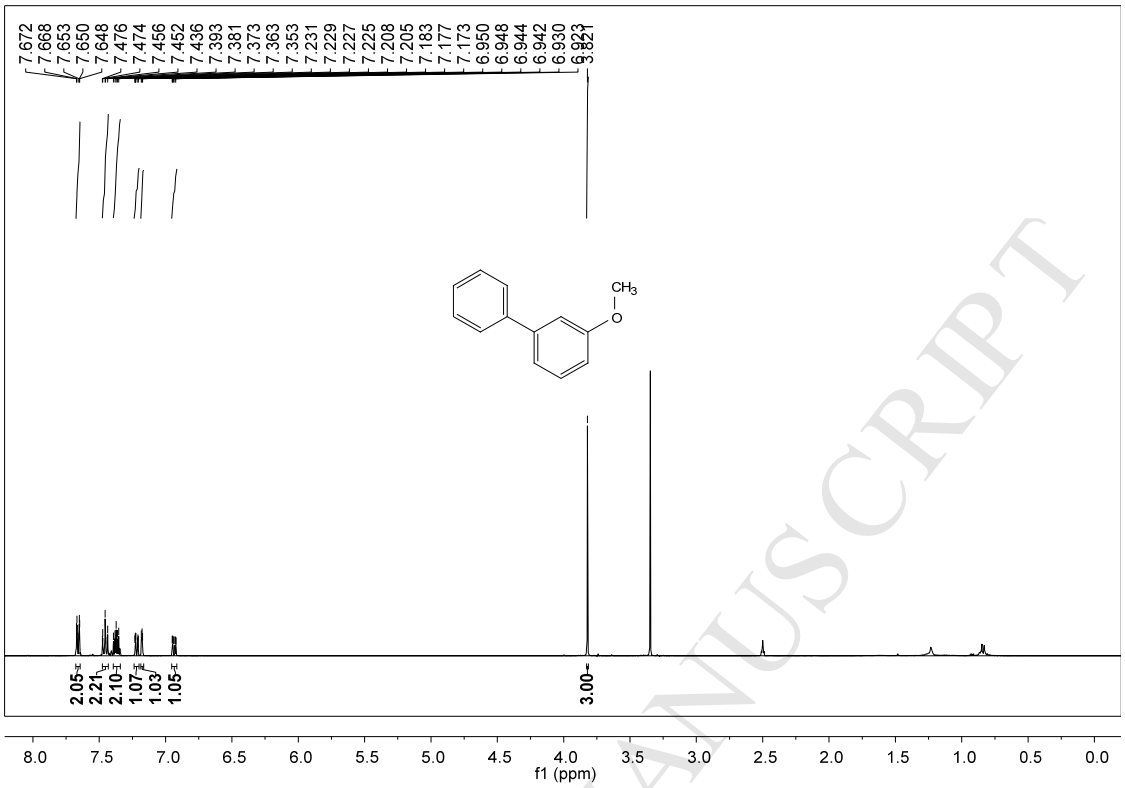
3m: 4-methoxy-1,1':4',1''-terphenyl



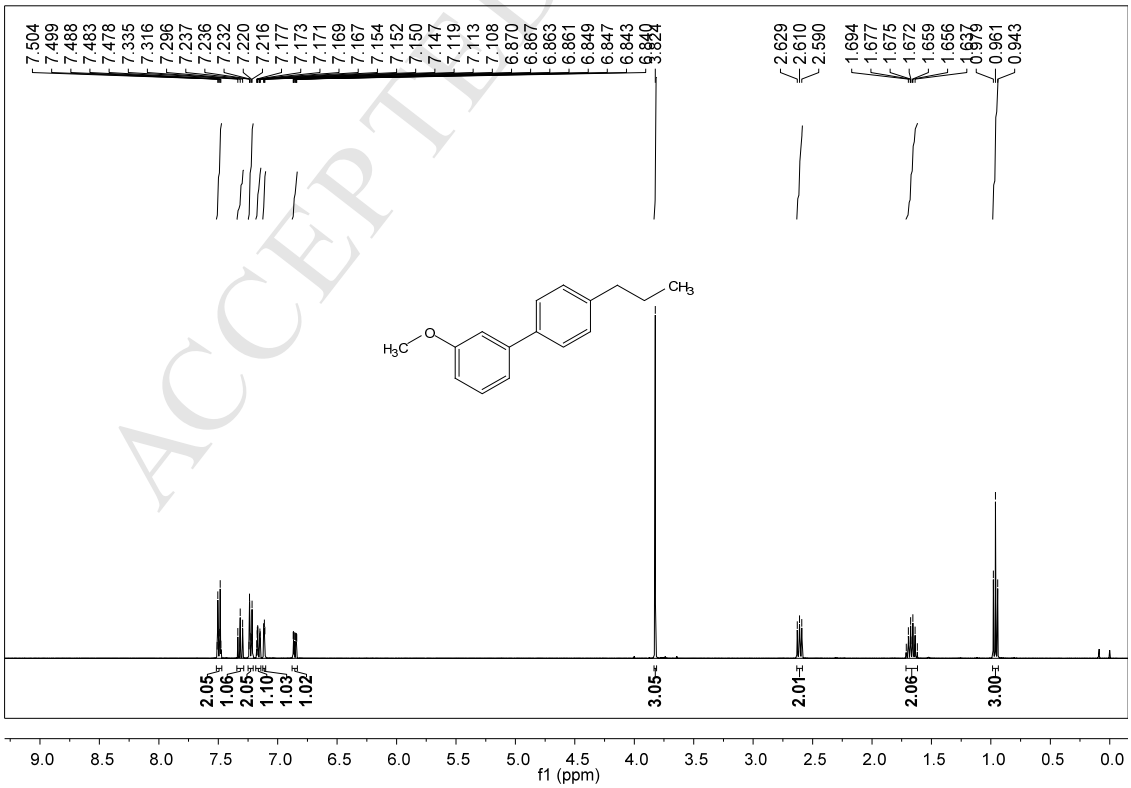
3n: 3-chloro-1,1'-biphenyl[9]



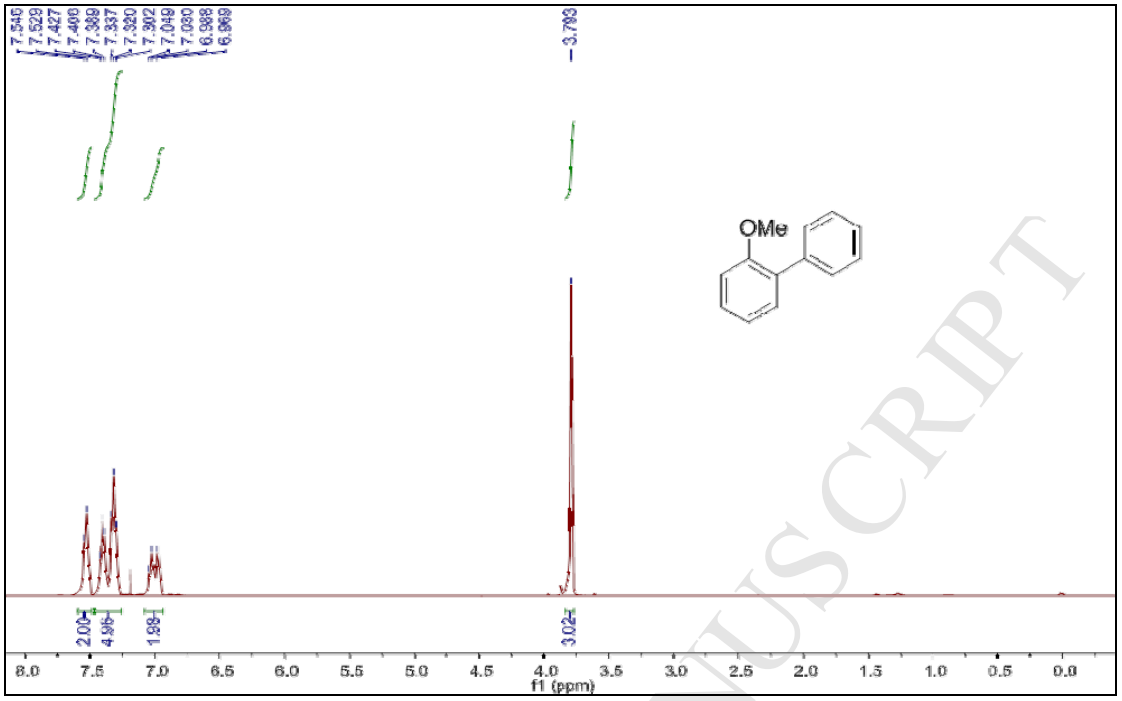
3o: 3-methoxy-1,1'-biphenyl



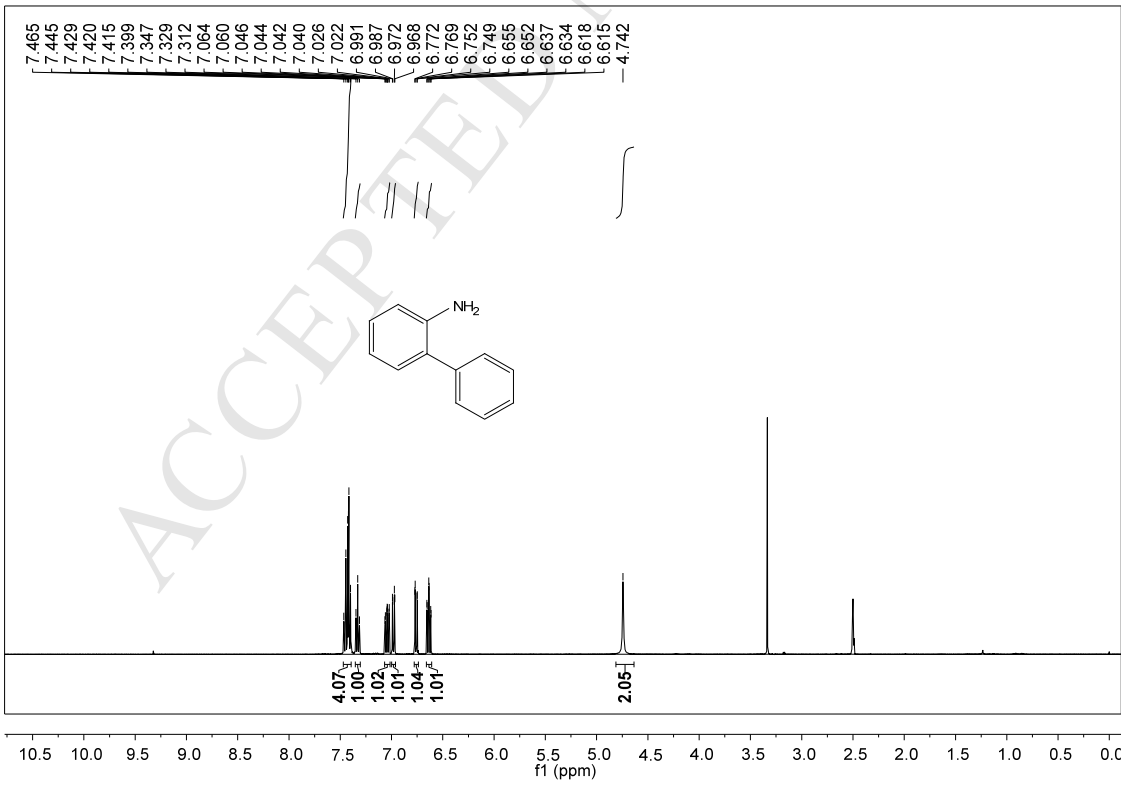
3p: 3-methoxy-4'-propyl-1,1'-biphenyl



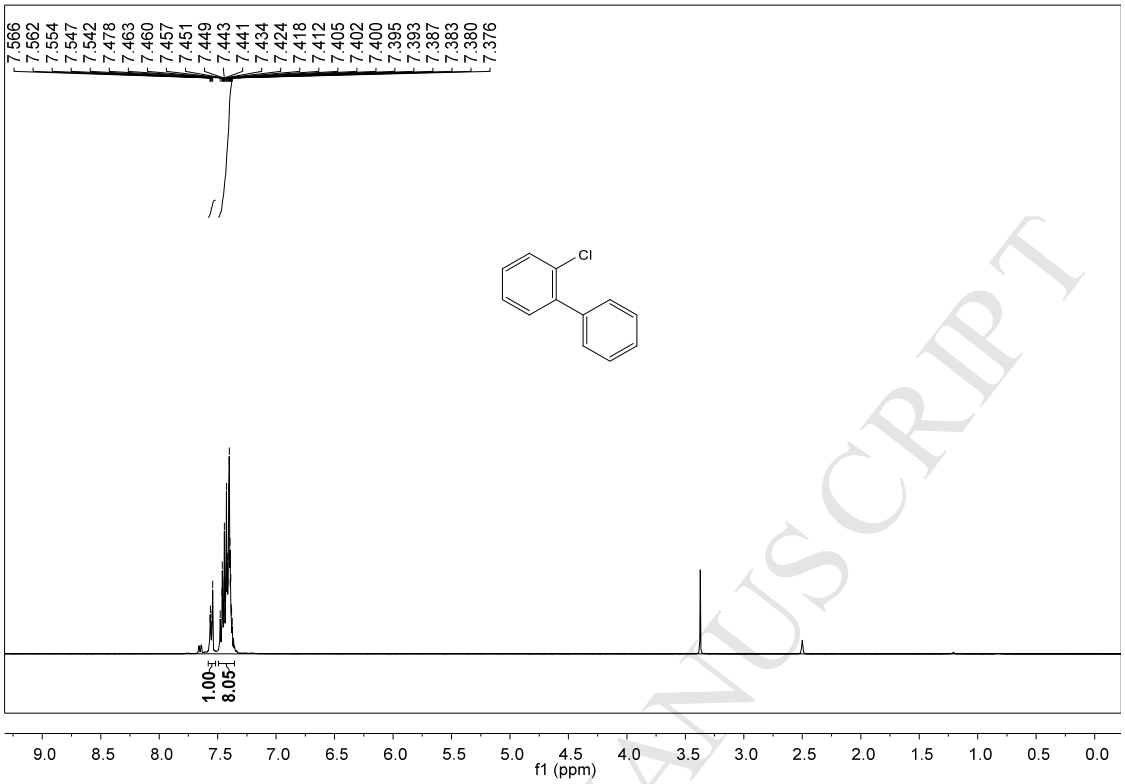
3q: 2-methoxy-1,1'-biphenyl



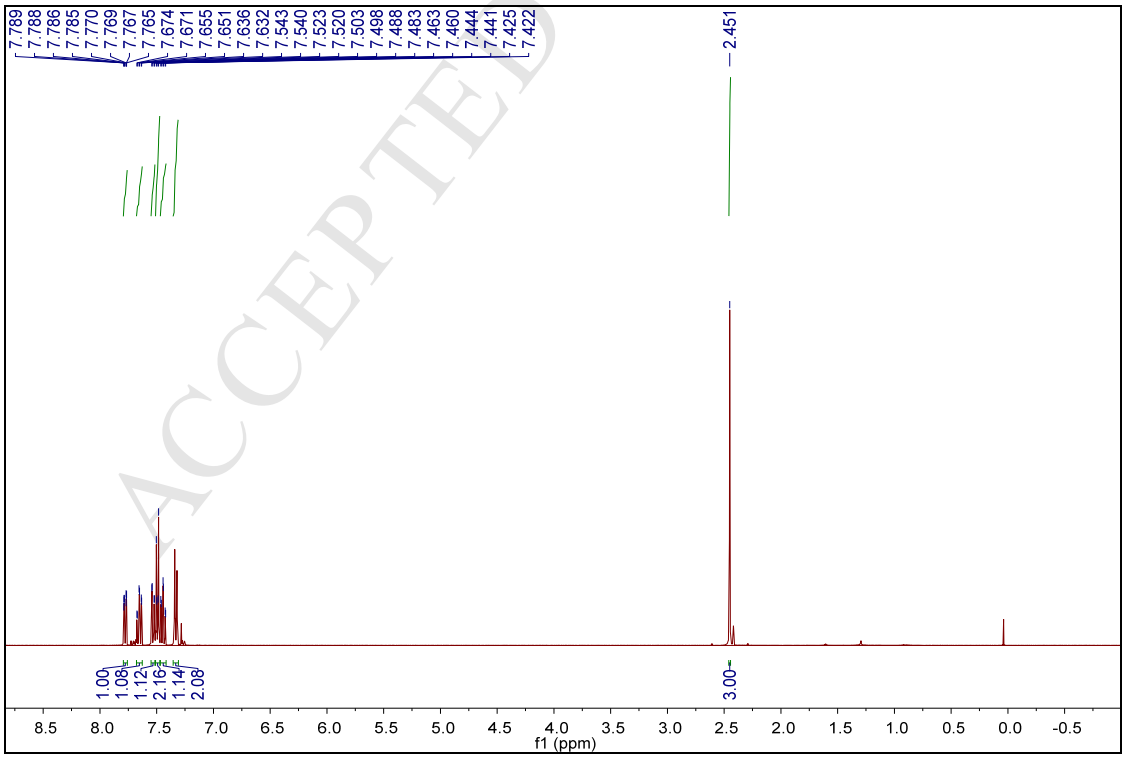
3r: [1,1'-biphenyl]-2-amine



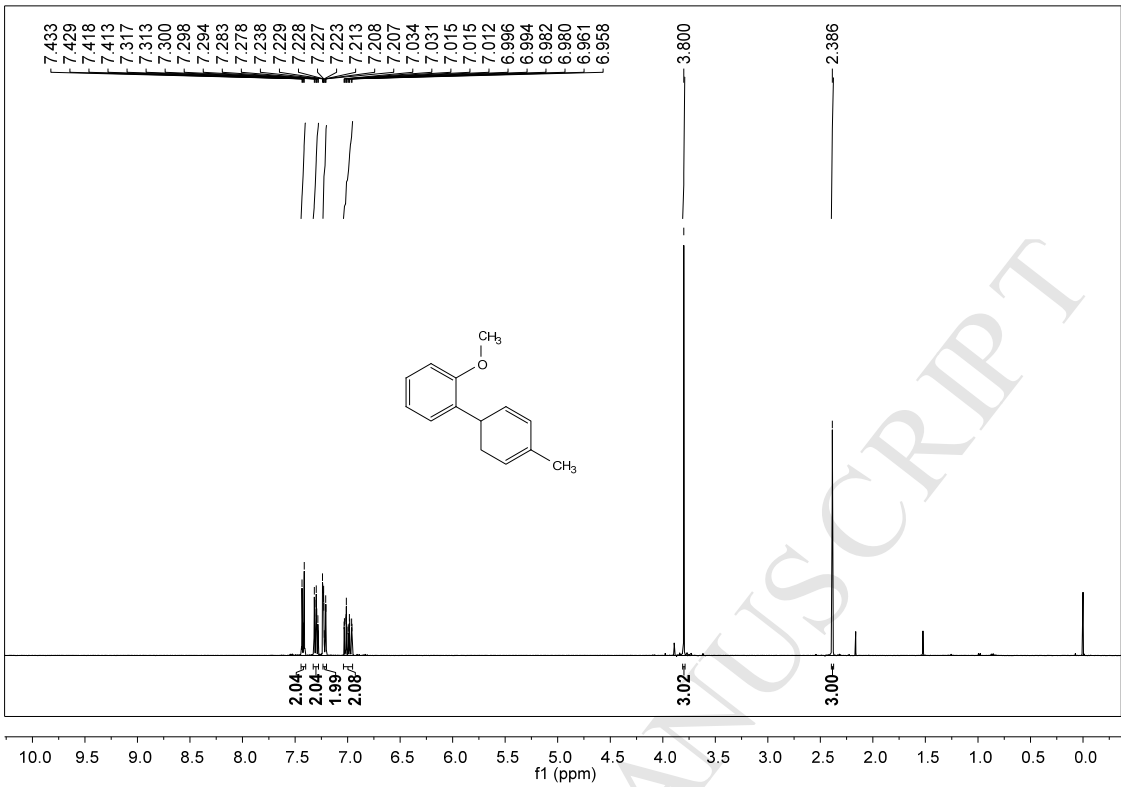
3s: 2-chloro-1,1'-biphenyl



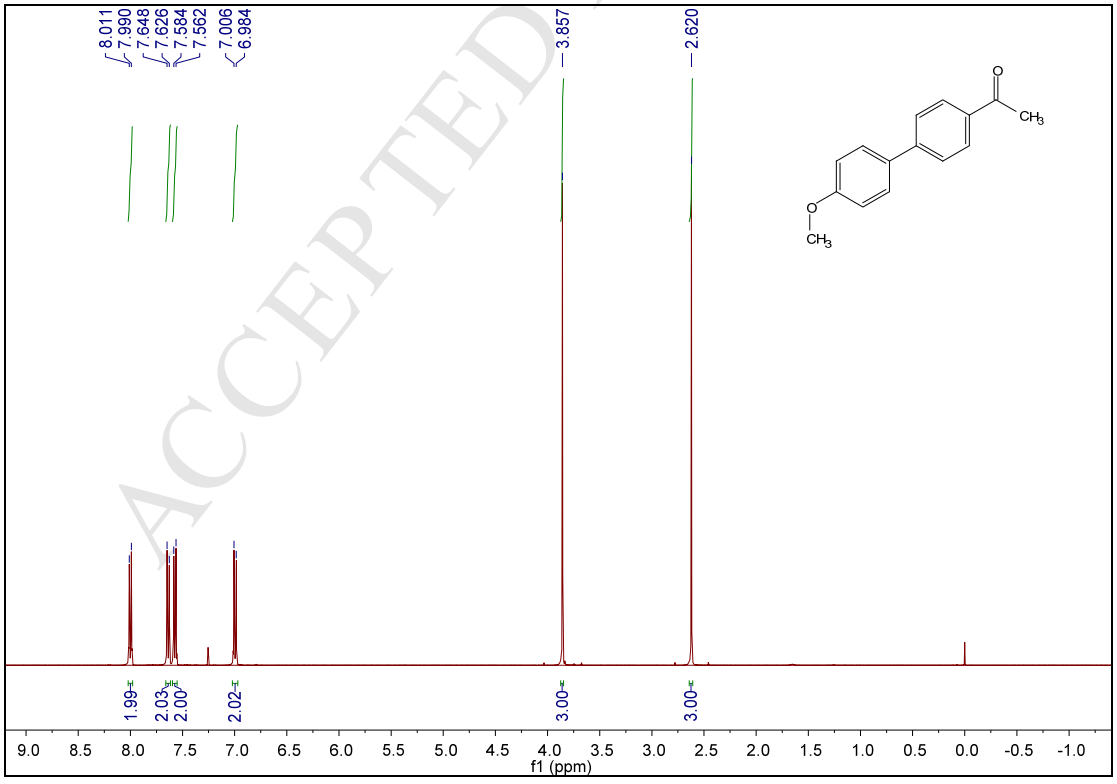
3t: 4'-methyl-[1,1'-biphenyl]-2-carbonitrile



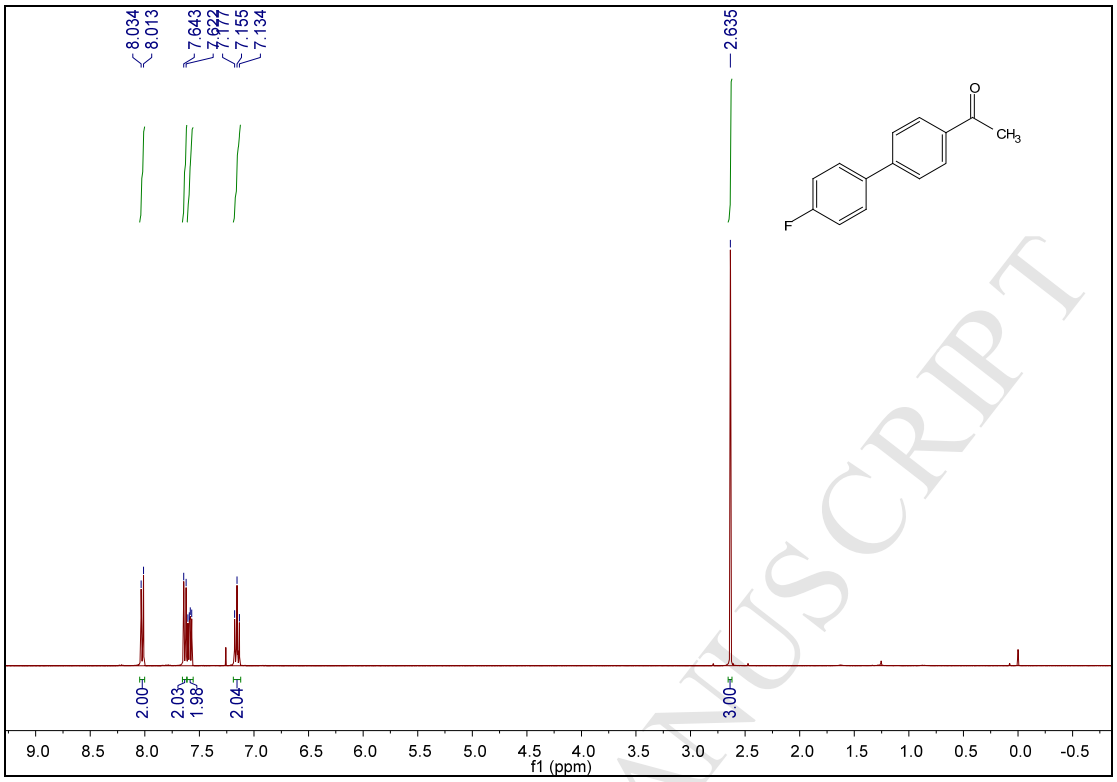
3u: 2-methoxy-4'-methyl-1,1'-biphenyl



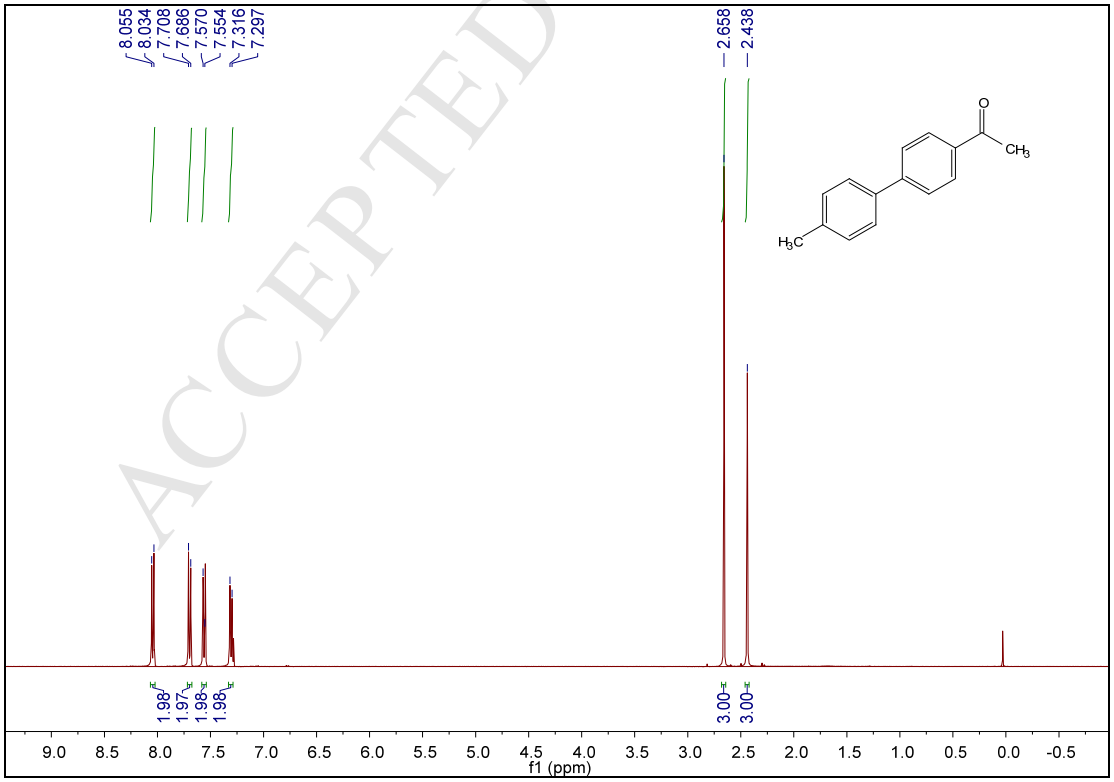
3v: 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone



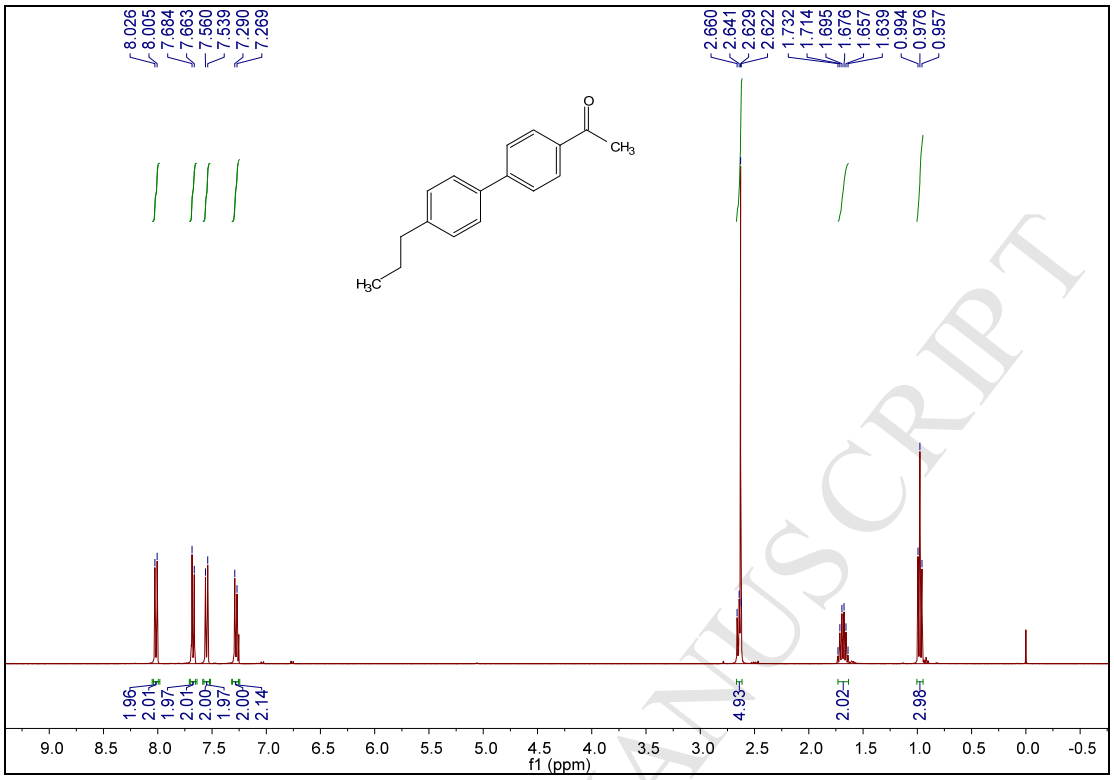
3w: 1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethanone



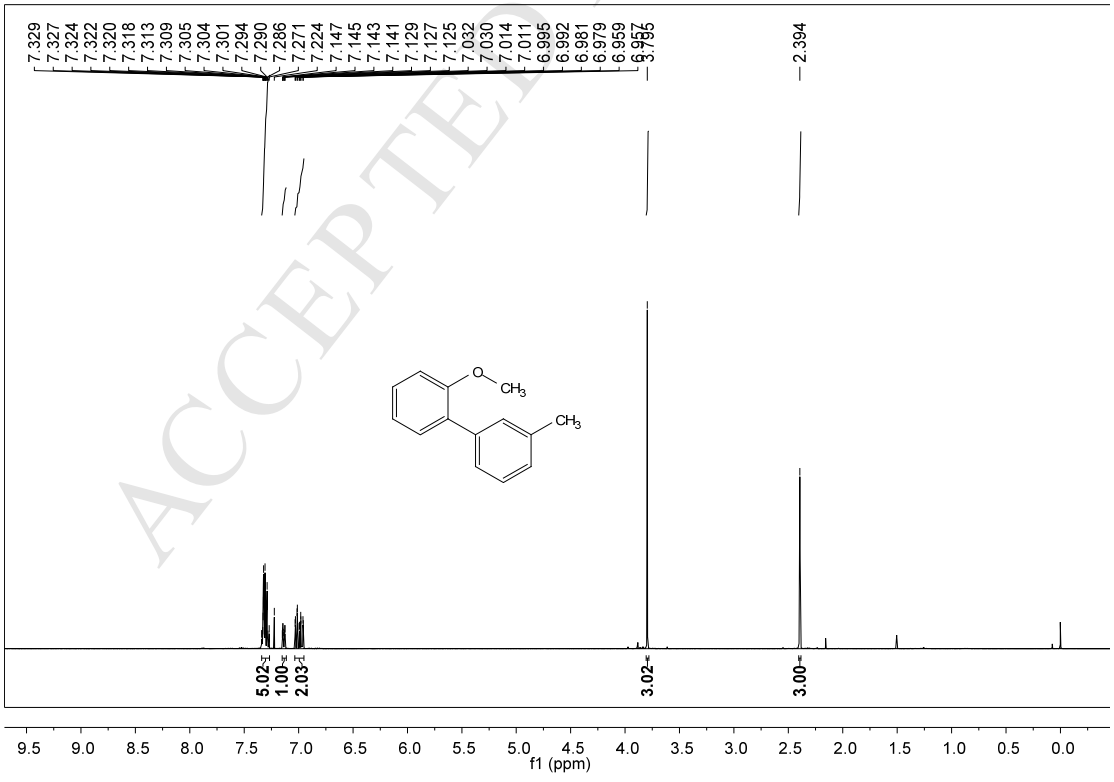
3x: 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethanone



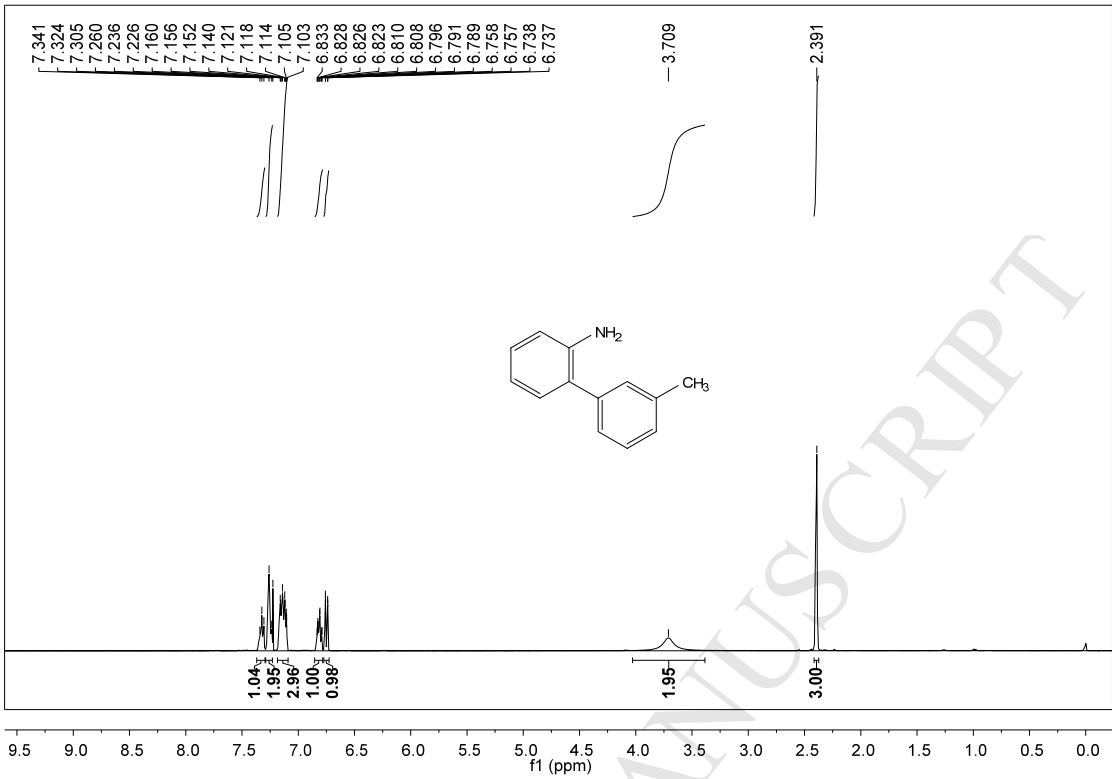
3y: 1-(4'-propyl-[1,1'-biphenyl]-4-yl)ethanone



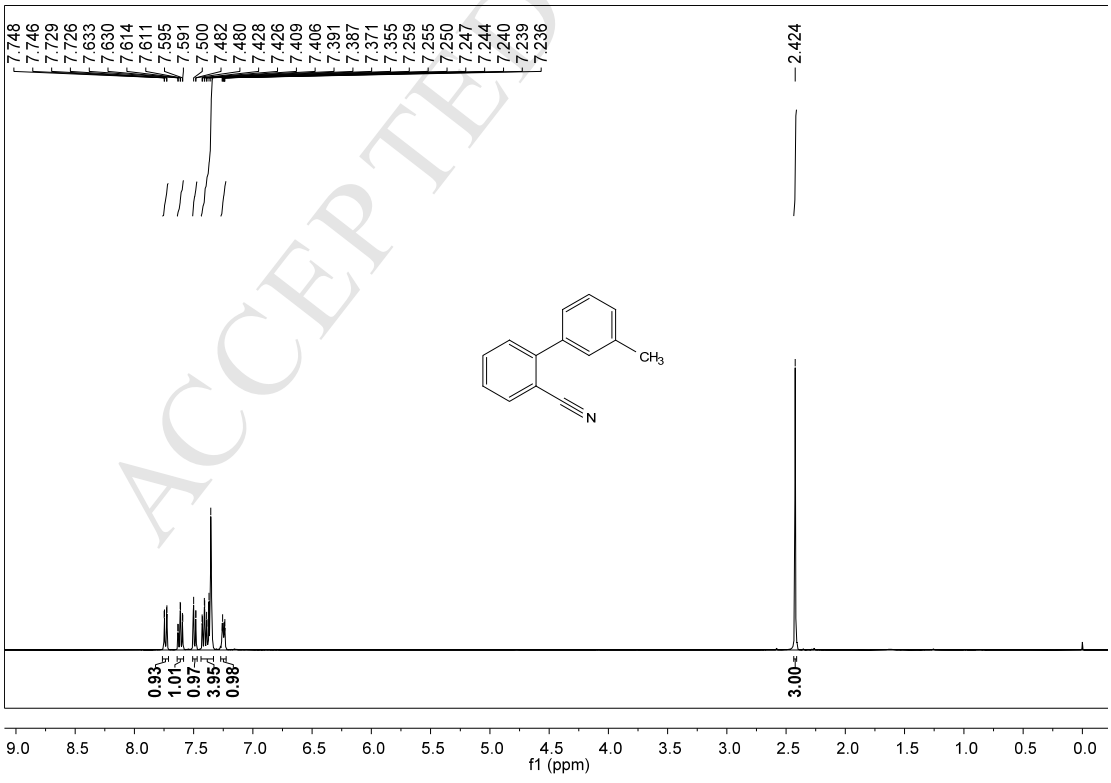
5a: 2-methoxy-3'-methyl-1,1'-biphenyl



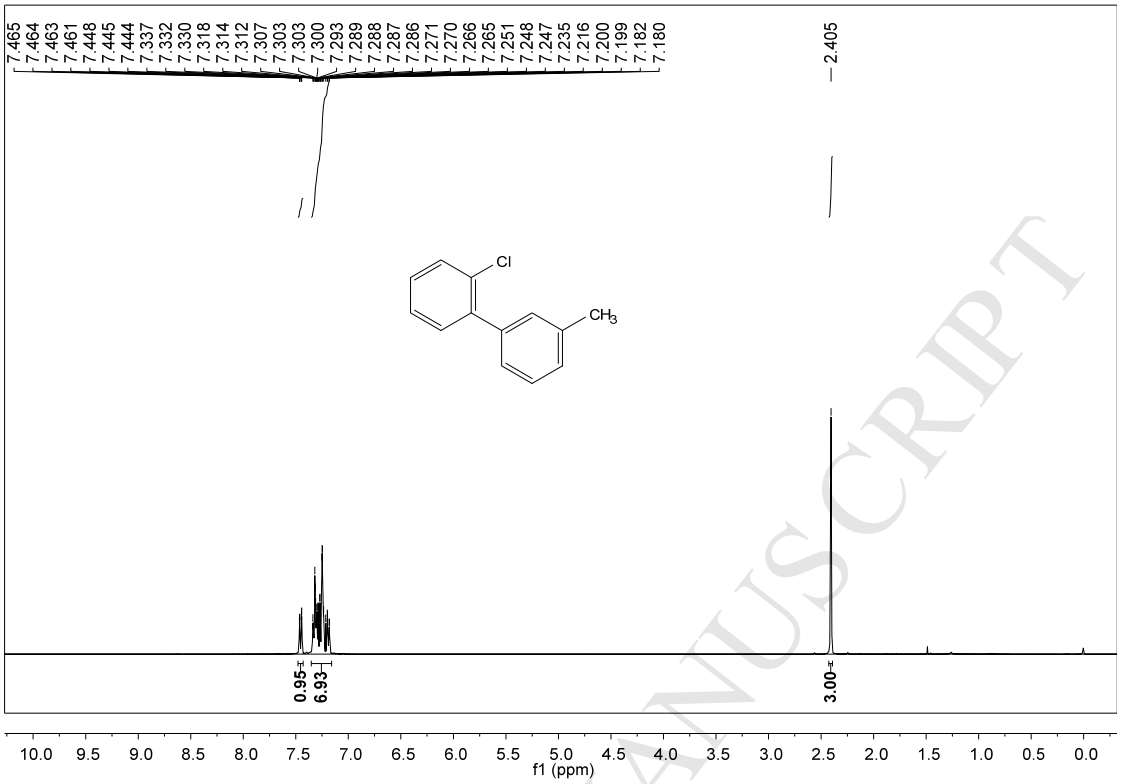
5b: 3'-methyl-[1,1'-biphenyl]-2-amine



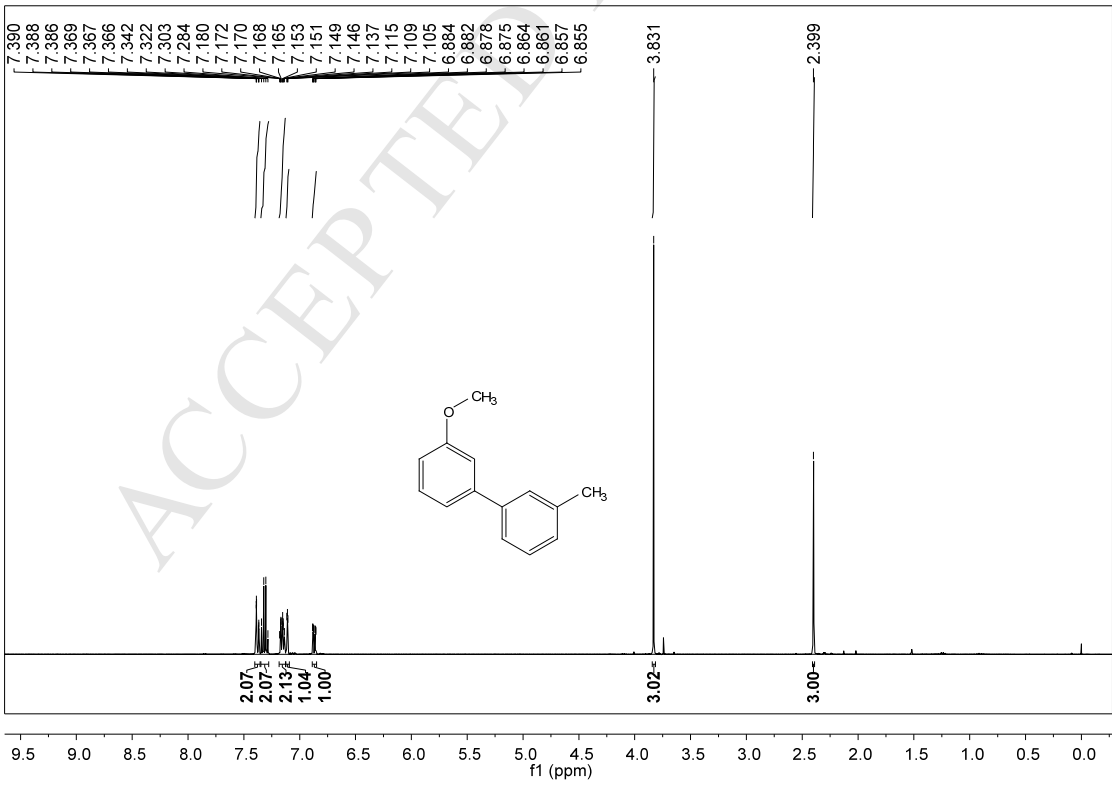
5c: 3'-methyl-[1,1'-biphenyl]-2-carbonitrile



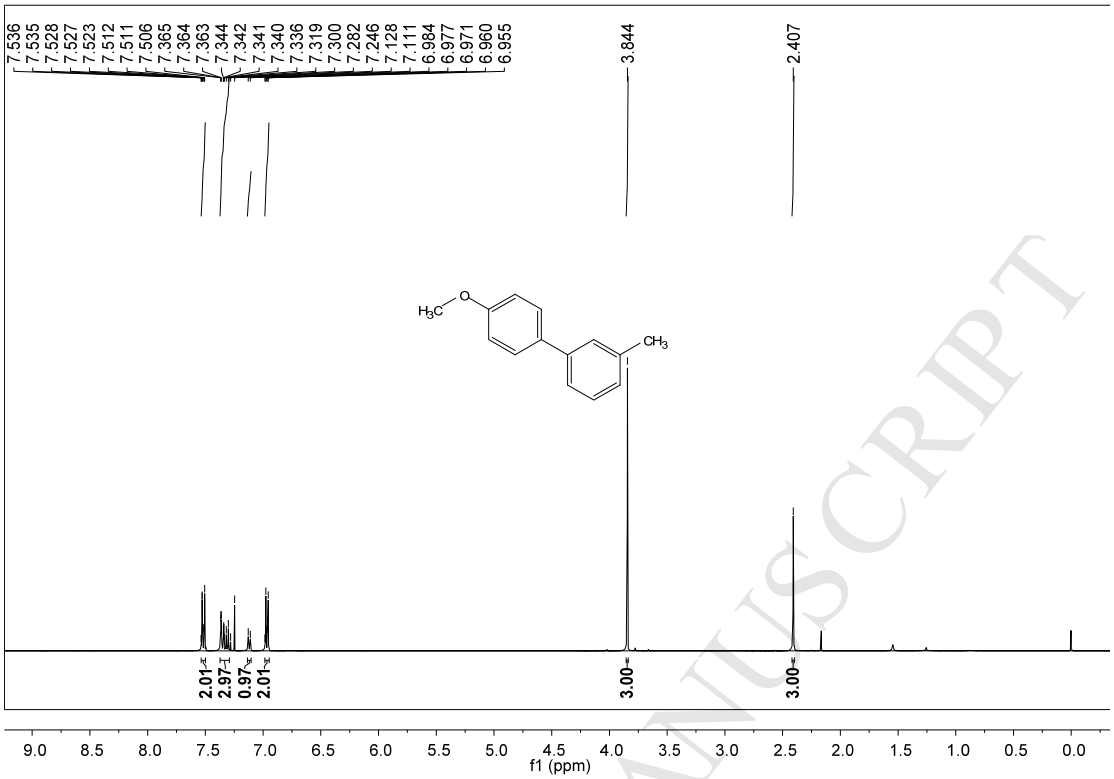
5d: 2-chloro-3'-methyl-1,1'-biphenyl



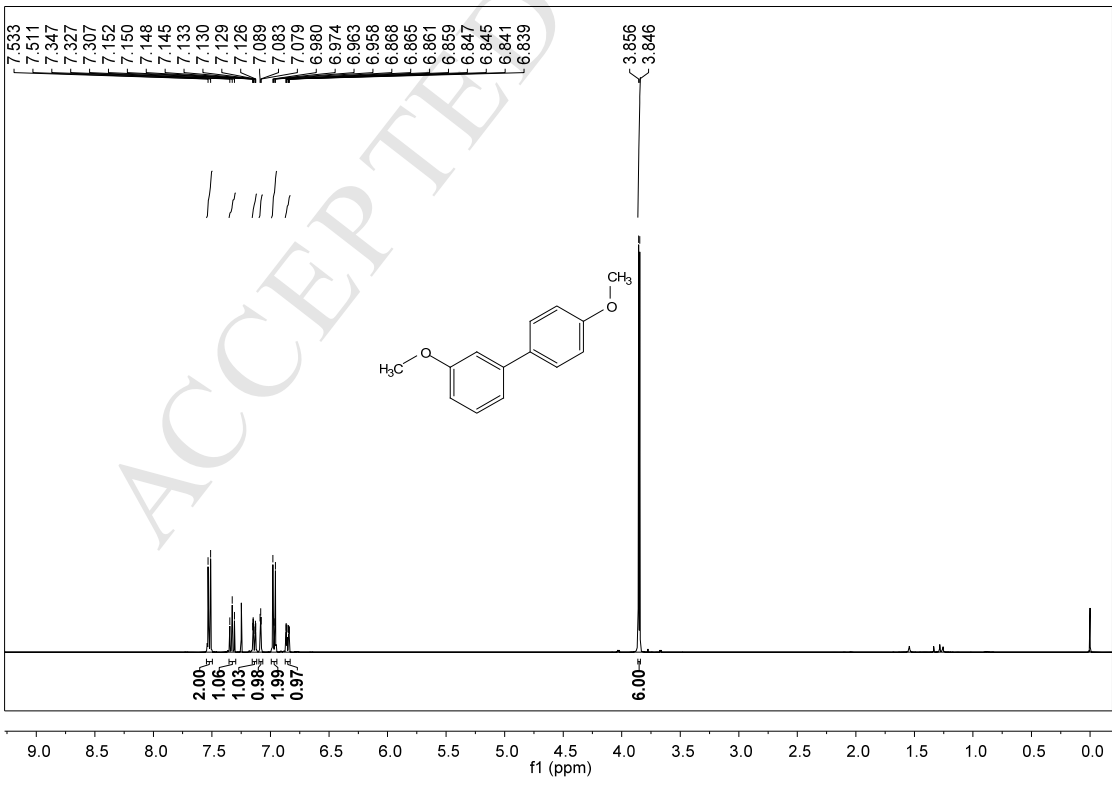
5e: 3-methoxy-3'-methyl-1,1'-biphenyl



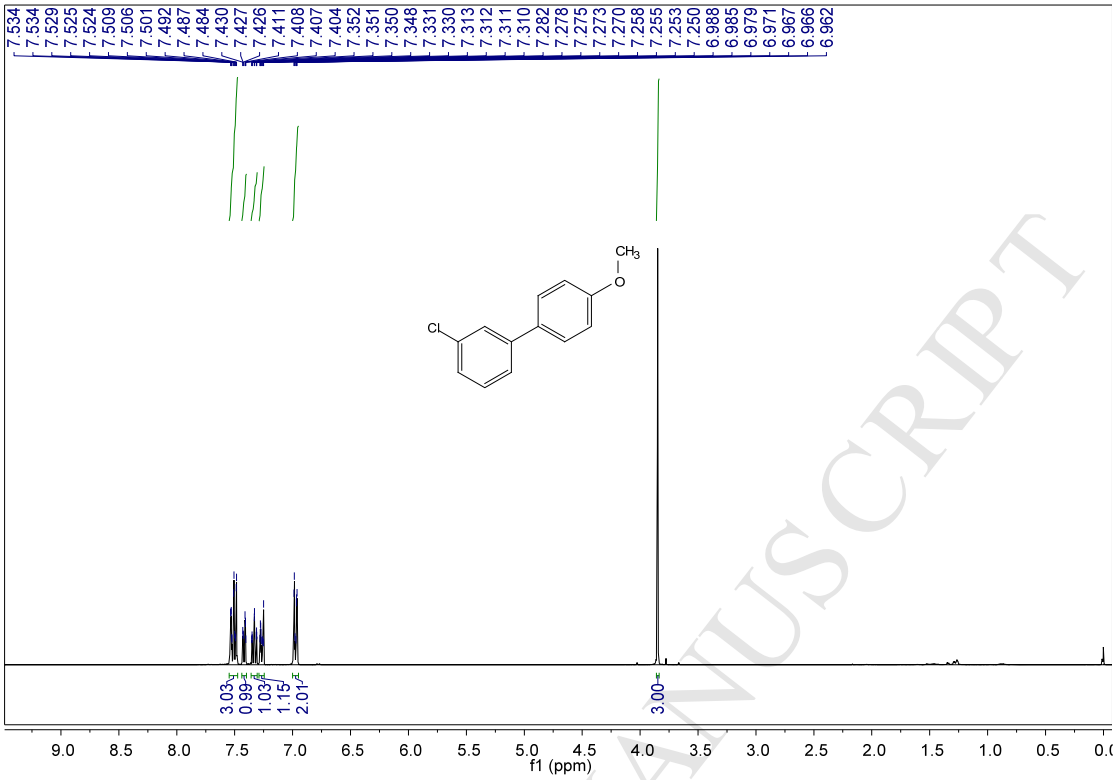
5f: 4'-methoxy-3-methyl-1,1'-biphenyl



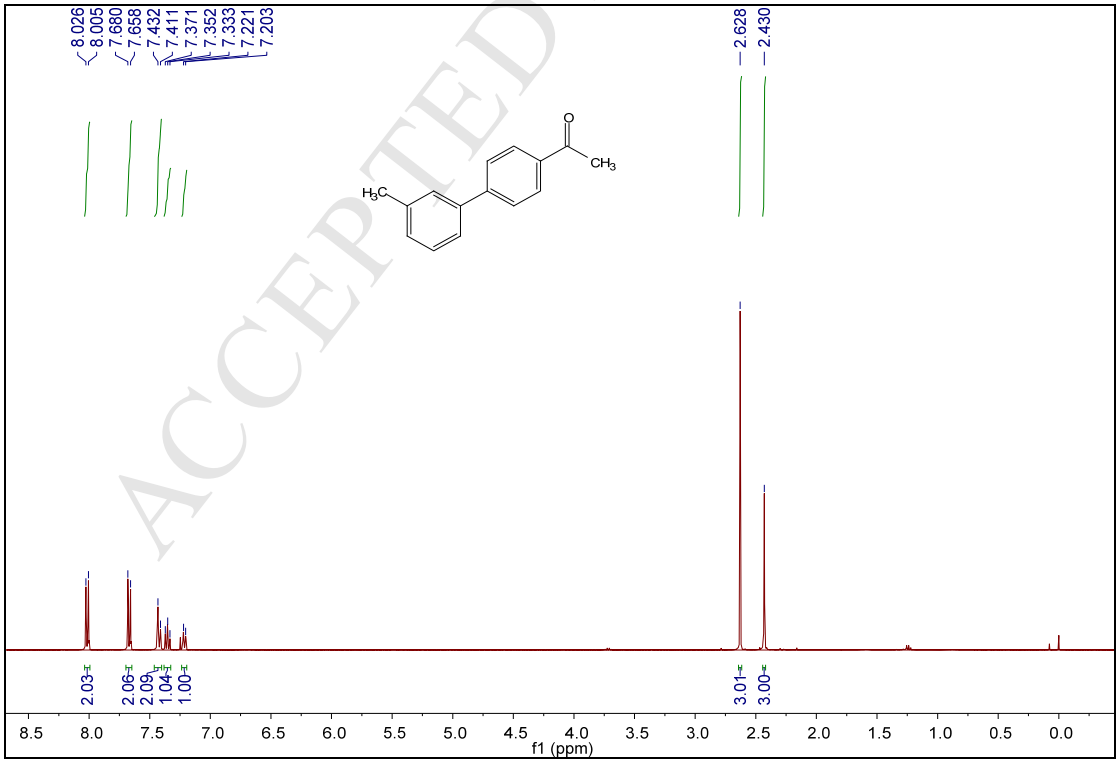
5g: 3,4'-dimethoxy-1,1'-biphenyl



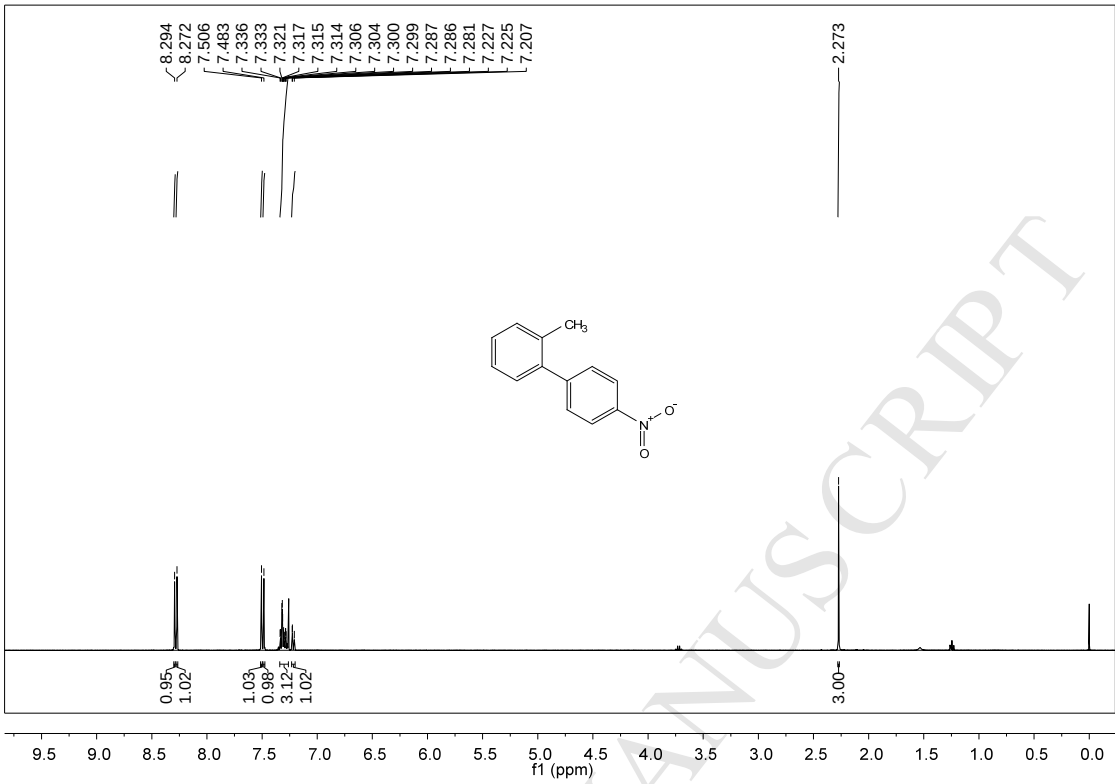
5h: 3-chloro-4'-methoxy-1,1'-biphenyl



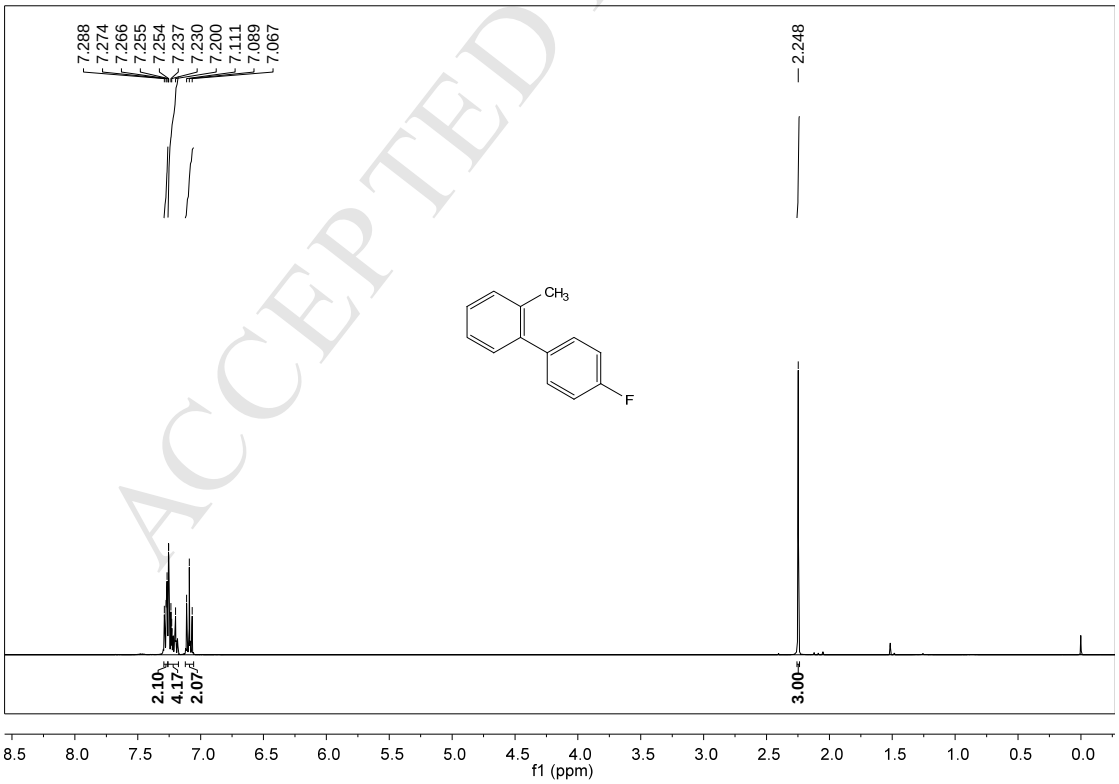
5i: 1-(3'-methyl-[1,1'-biphenyl]-4-yl)ethanone



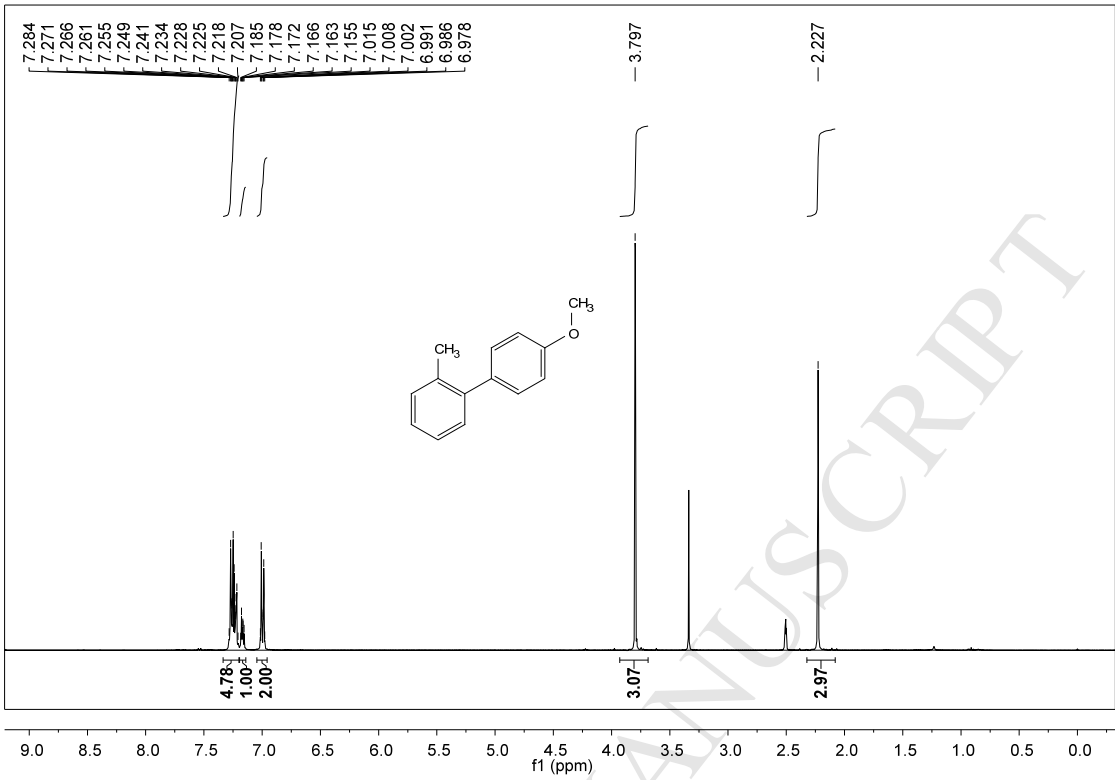
7b:2-methyl-4'-nitro-1,1'-biphenyl



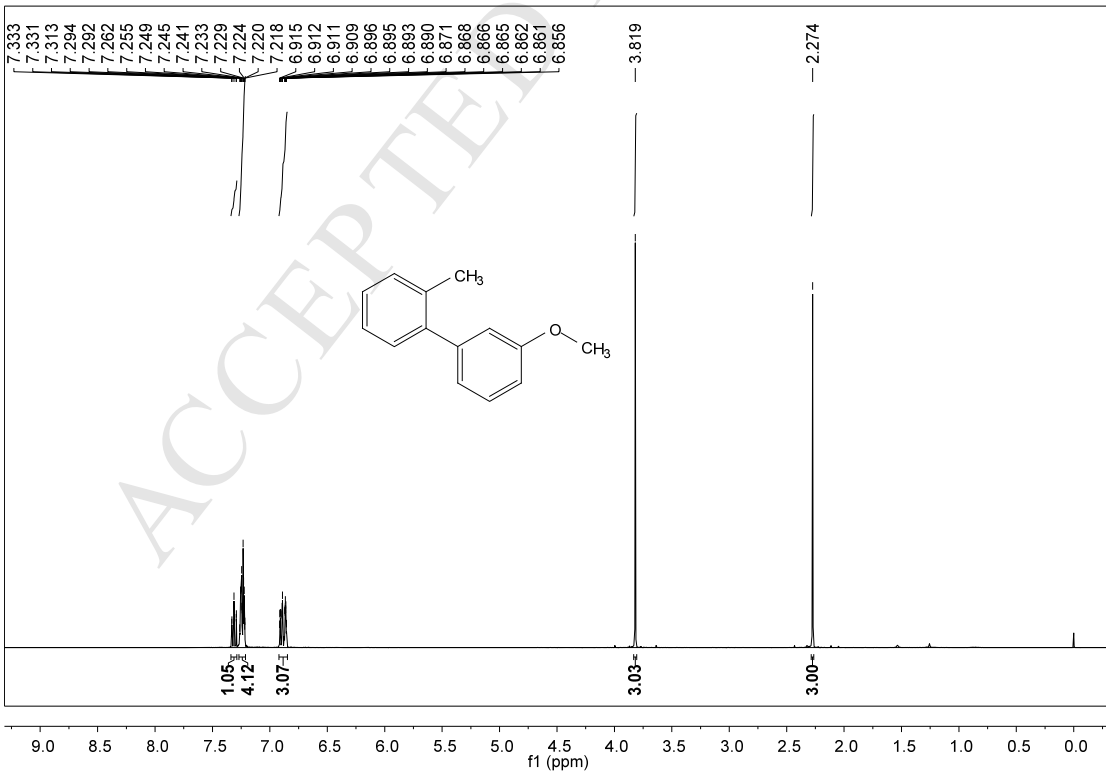
7c: 4'-fluoro-2-methyl-1,1'-biphenyl[1]



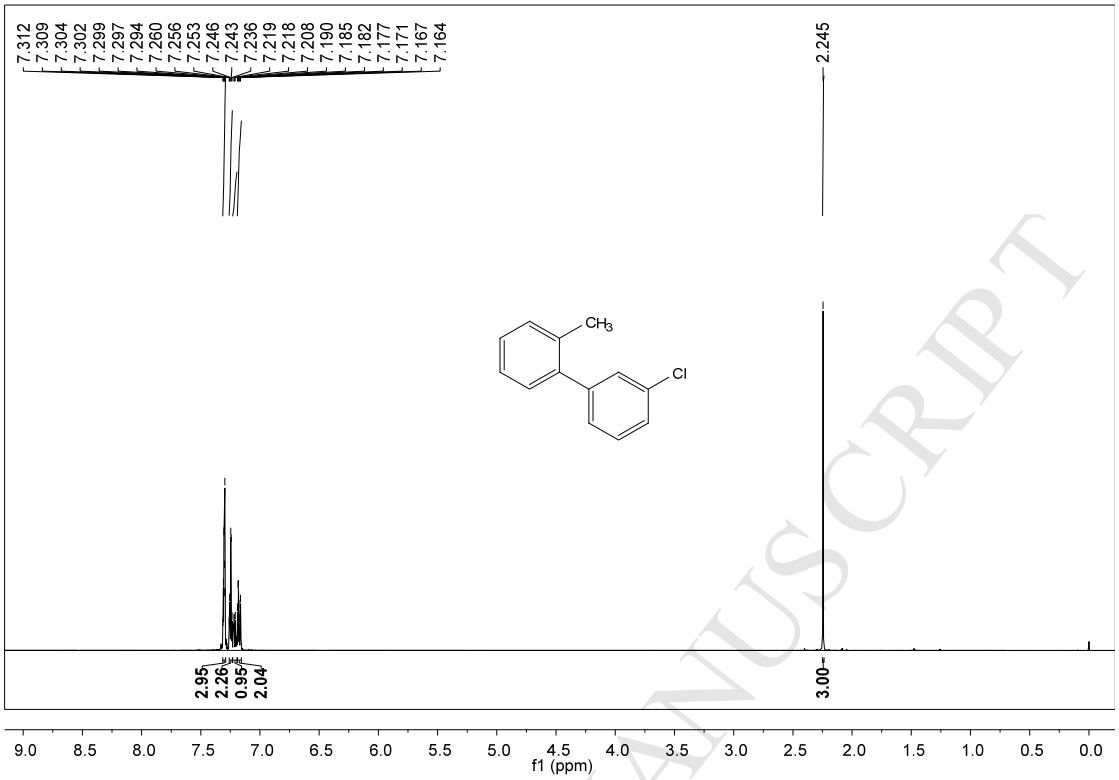
7d: 4'-methoxy-2-methyl-1,1'-biphenyl



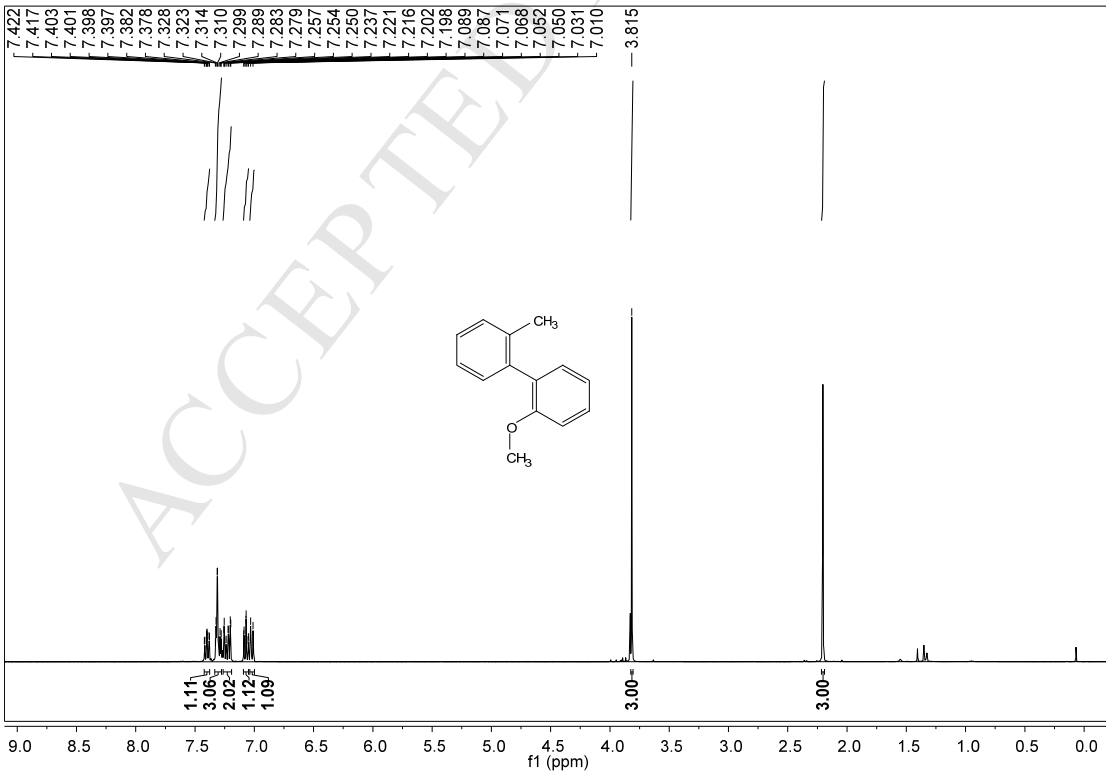
7e: 3'-methoxy-2-methyl-1,1'-biphenyl



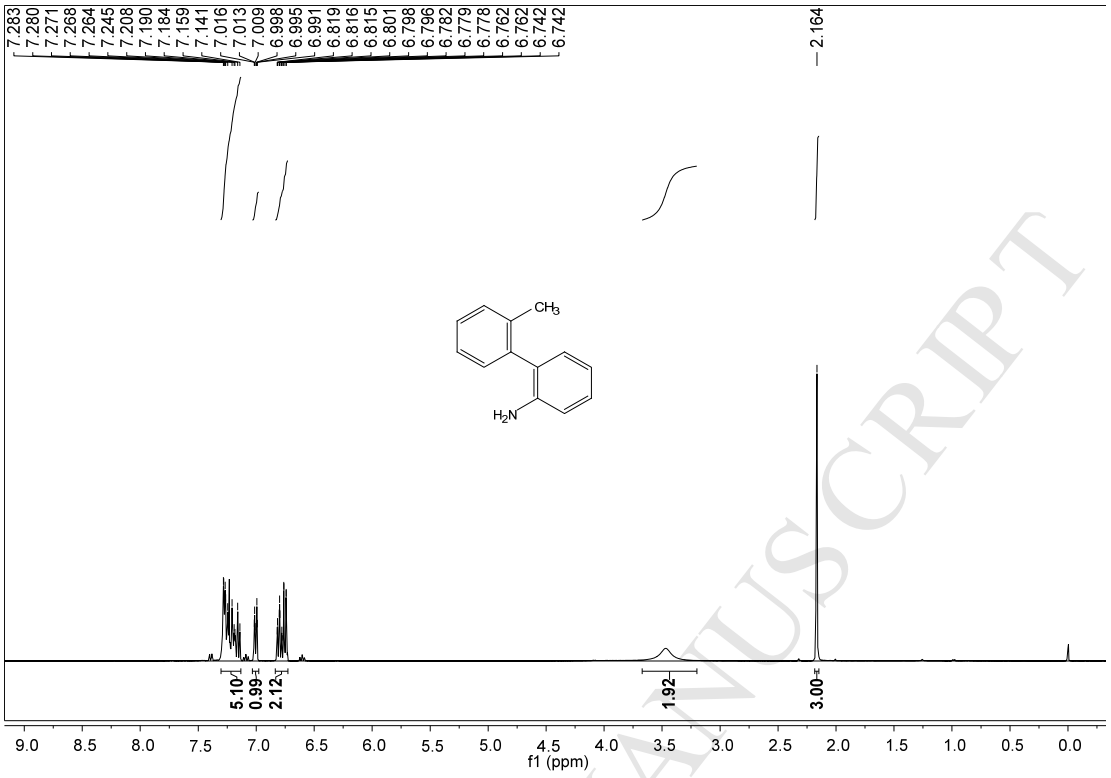
7f: 3'-chloro-2-methyl-1,1'-biphenyl



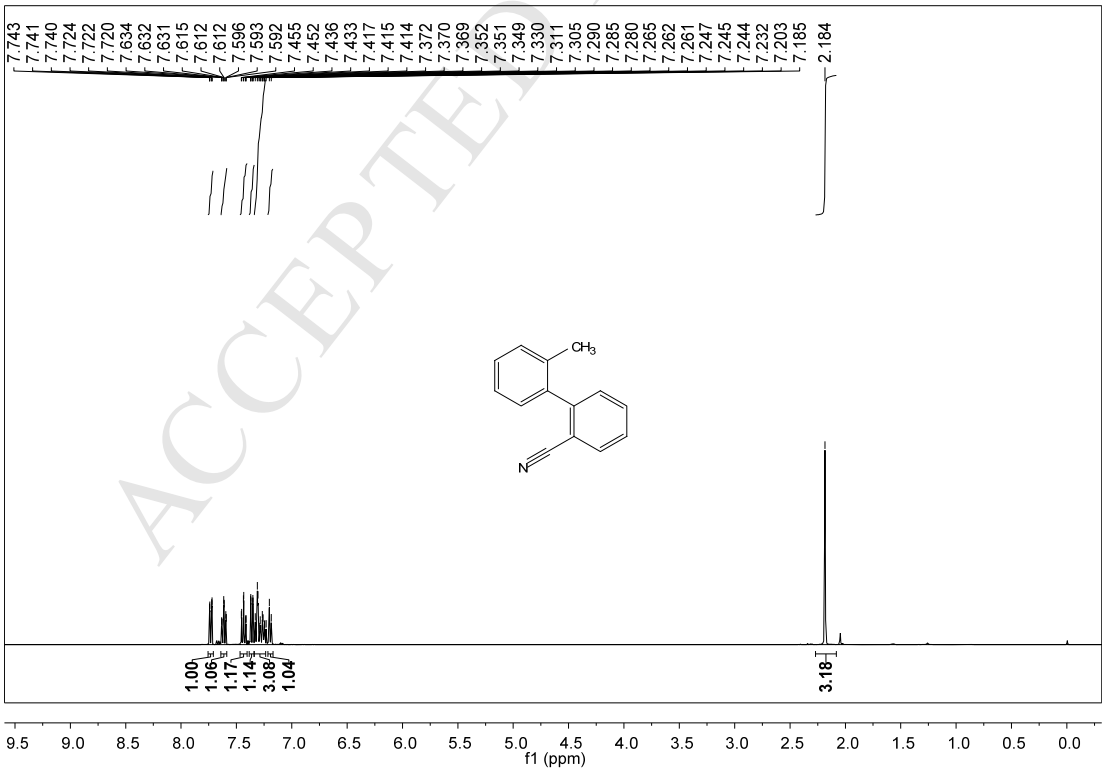
7g: 2-methoxy-2'-methyl-1,1'-biphenyl



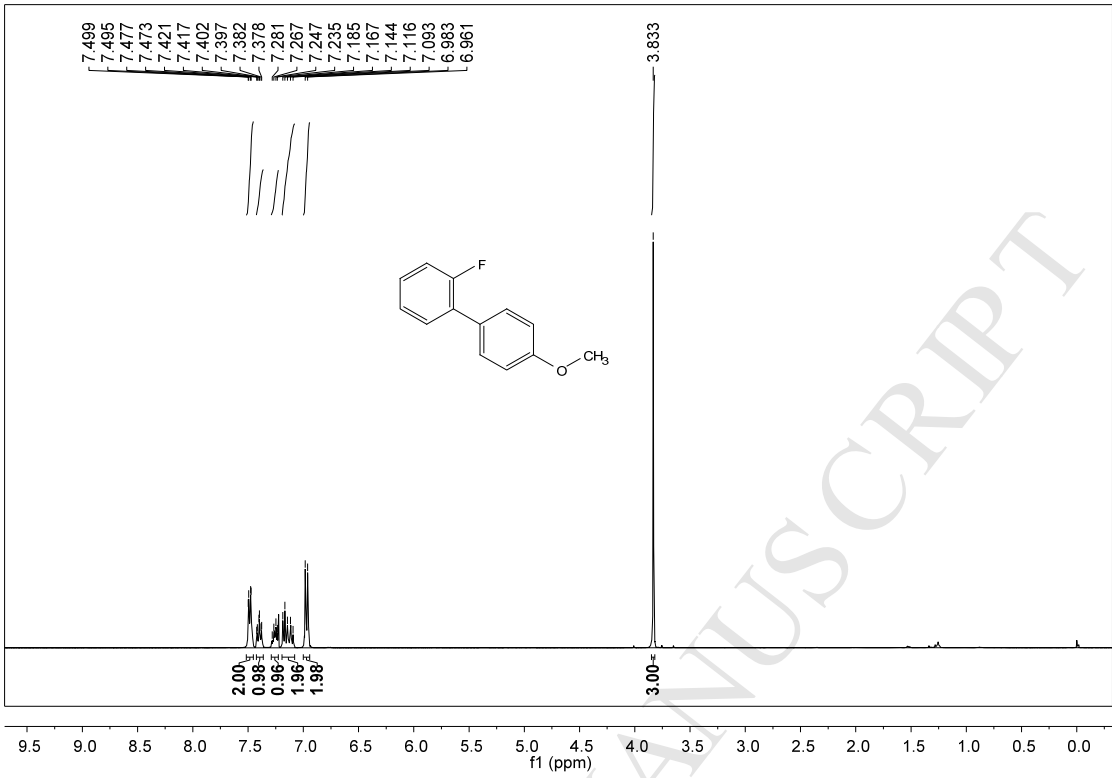
7h: 2'-methyl-[1,1'-biphenyl]-2-amine



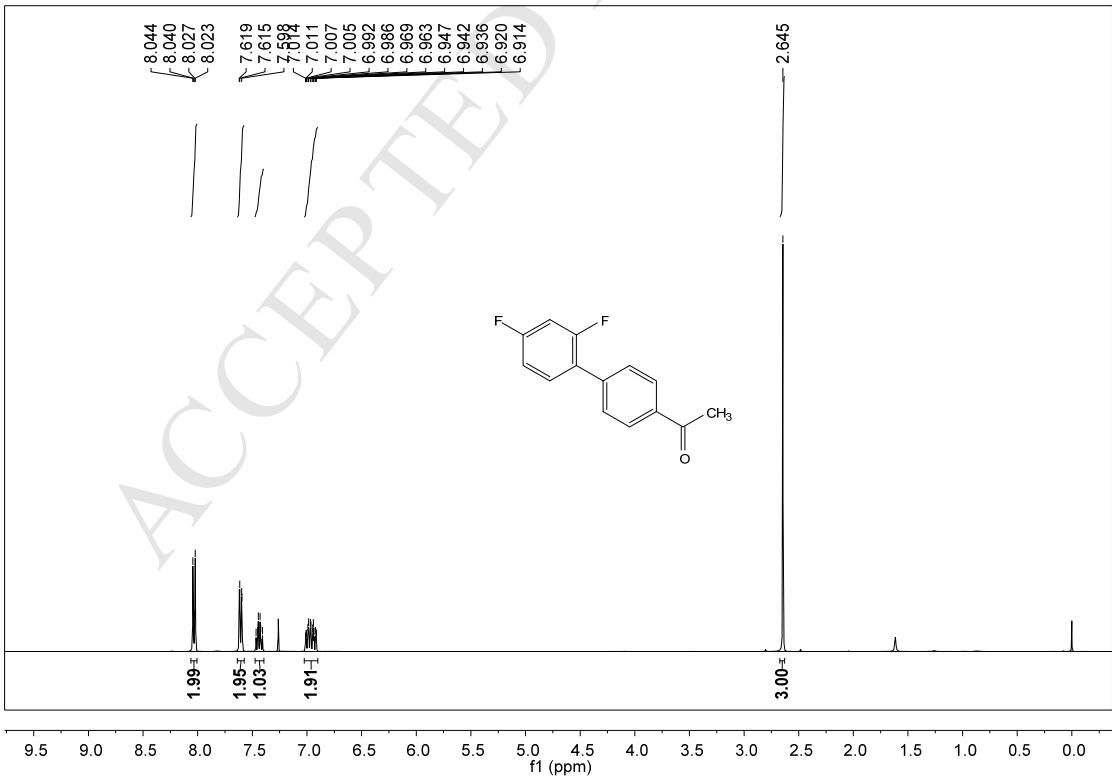
7i: 2'-methyl-[1,1'-biphenyl]-2-carbonitrile



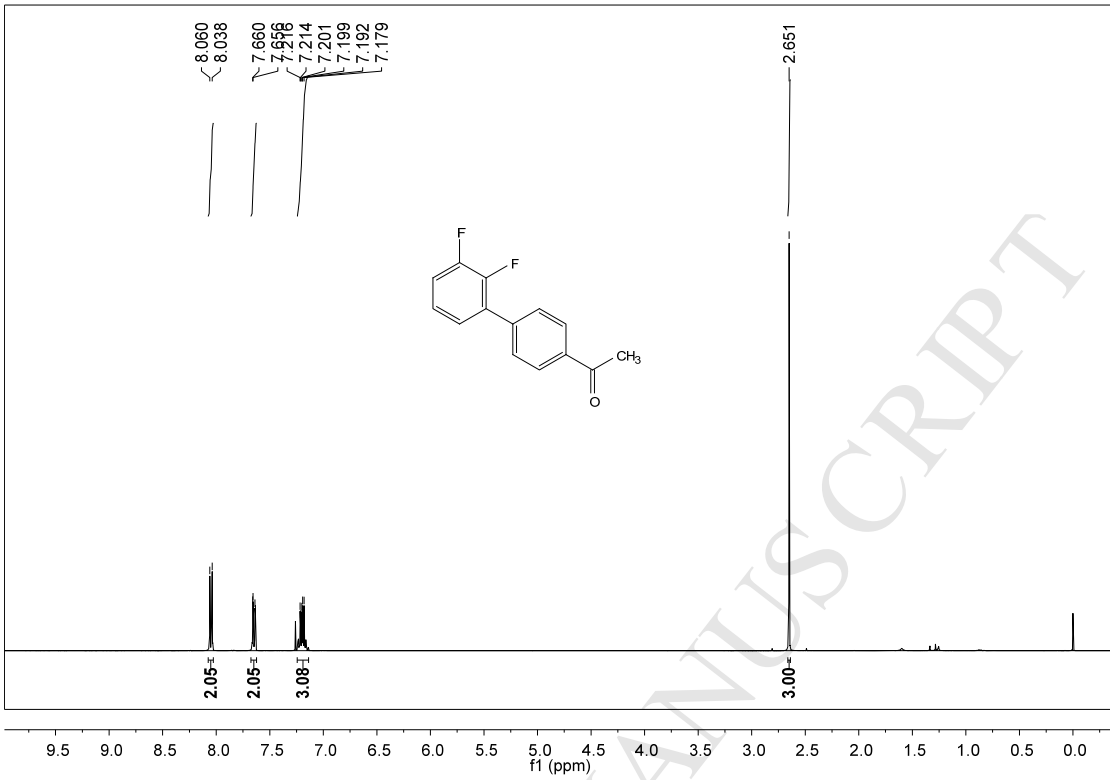
7j: 2-fluoro-4'-methoxy-1,1'-biphenyl



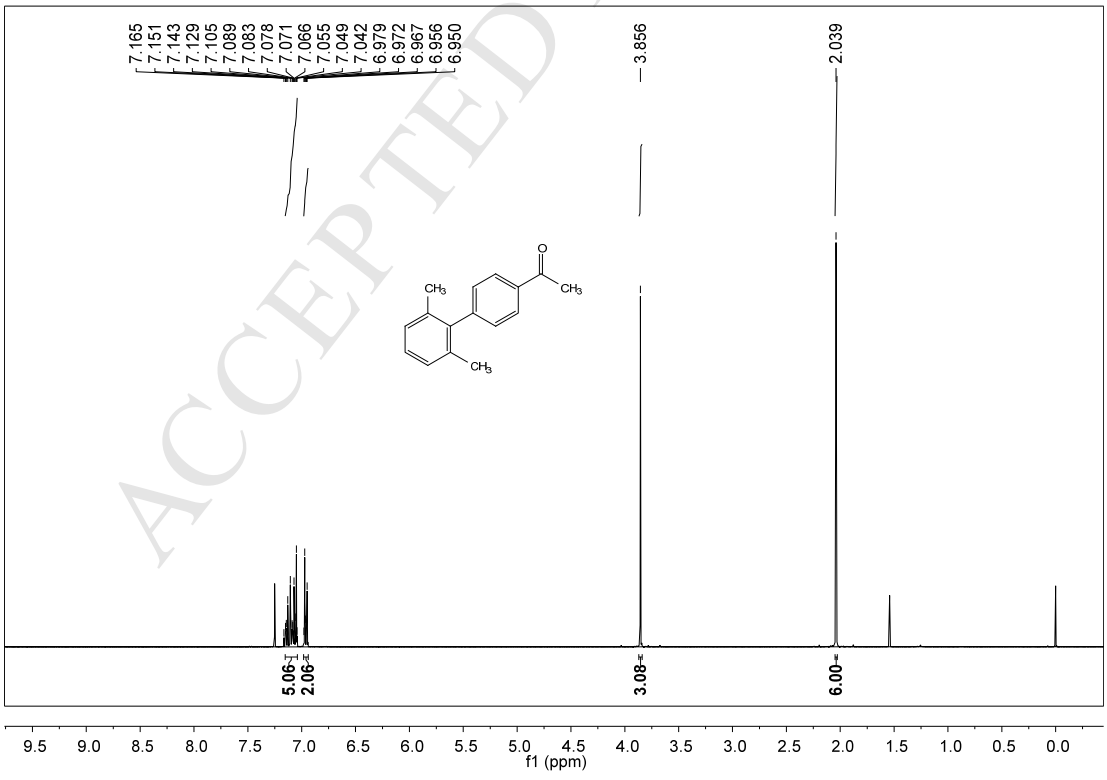
7k: 1-(2',4'-difluoro-[1,1'-biphenyl]-4-yl)ethanone



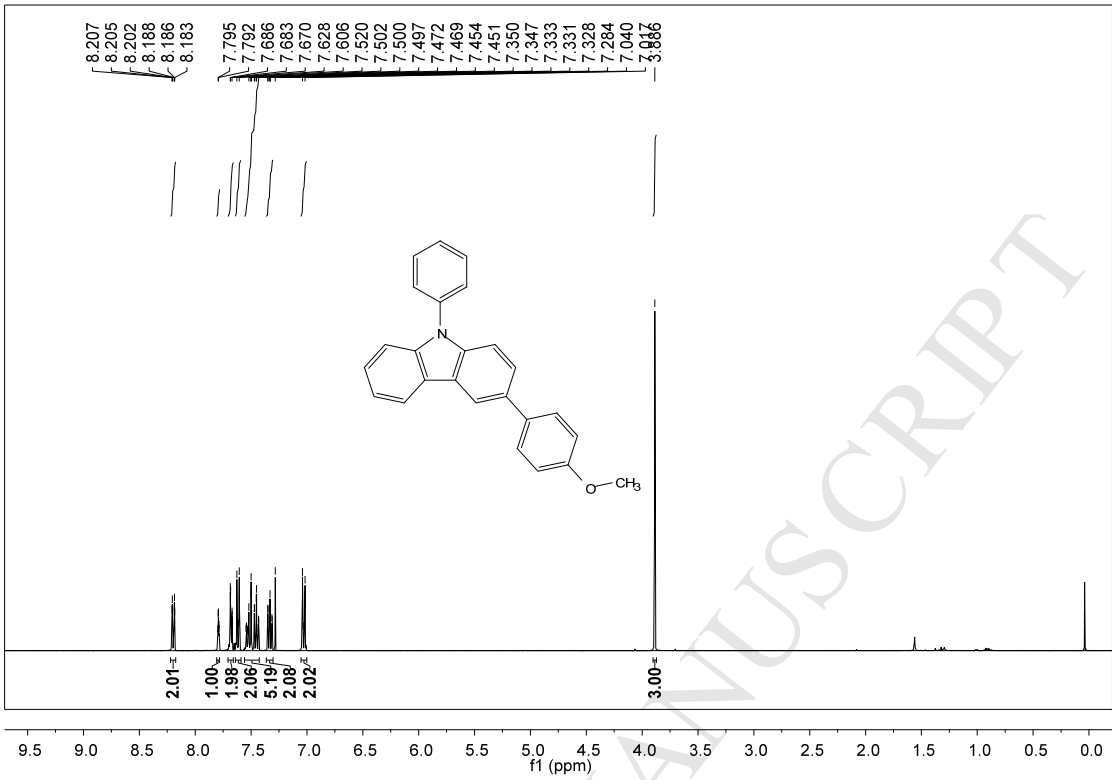
7l: 1-(2',3'-difluoro-[1,1'-biphenyl]-4-yl)ethanone

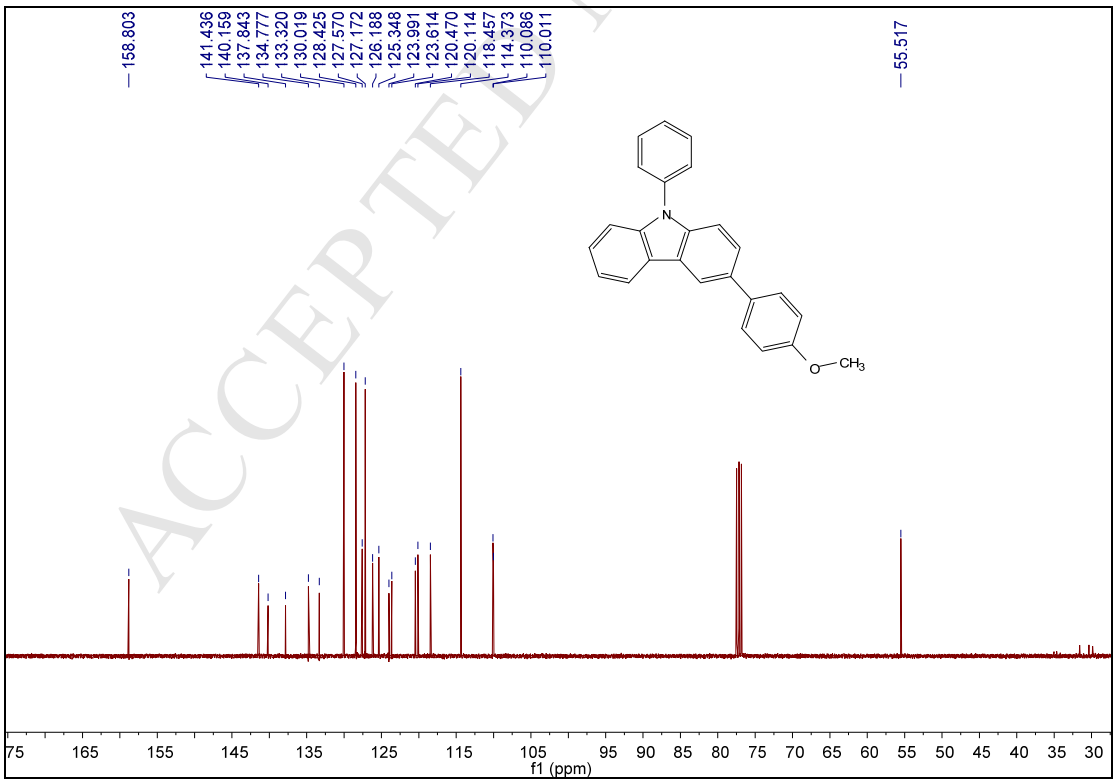


7m: 1-(2',6'-dimethyl-[1,1'-biphenyl]-4-yl)ethanone

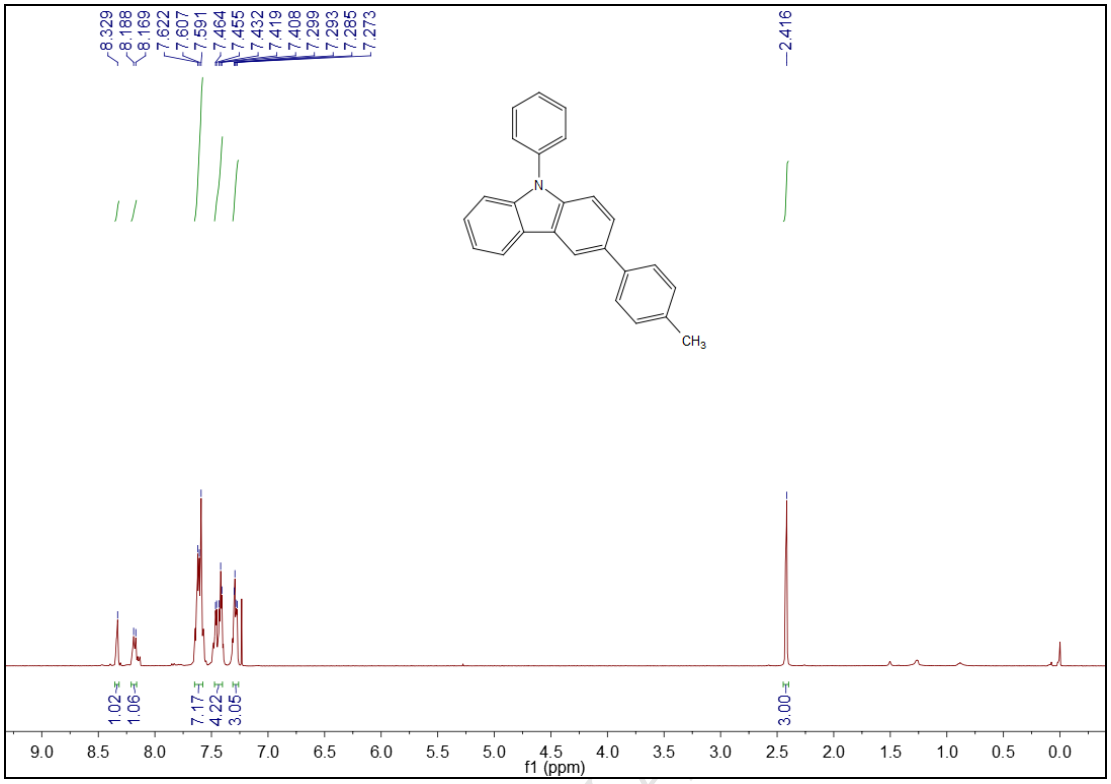


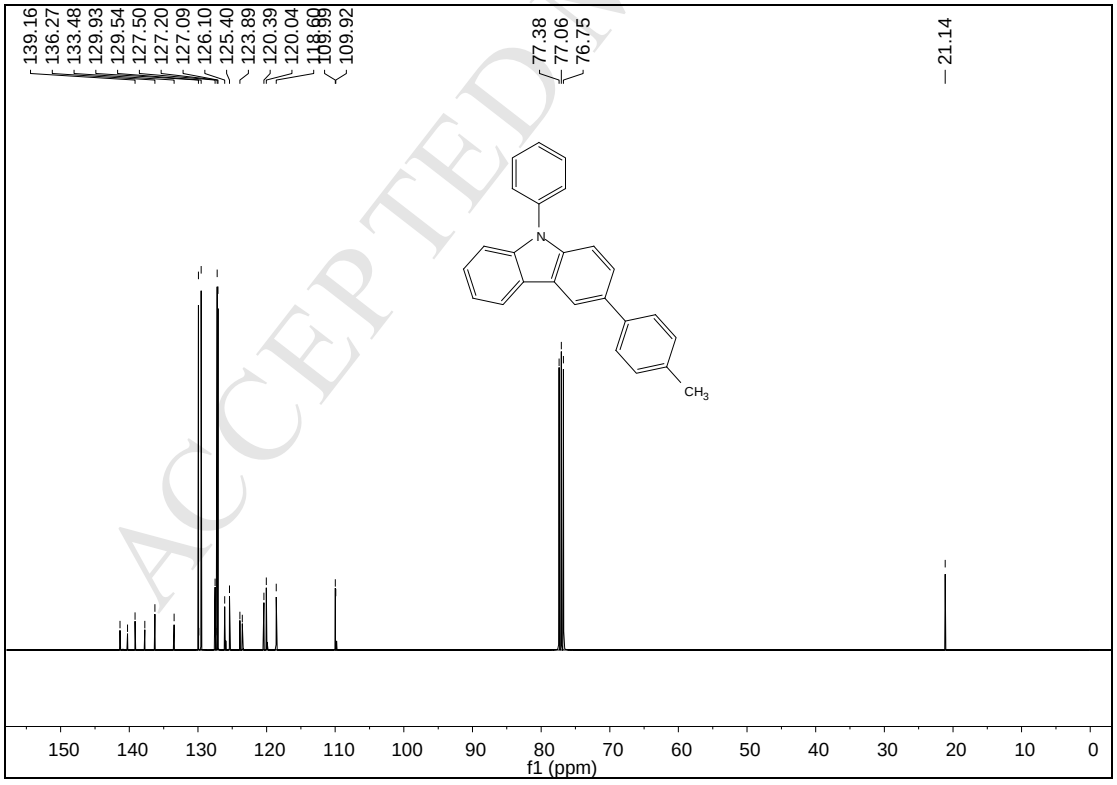
8a: 3-(4-methoxyphenyl)-9-phenyl-9H-carbazole



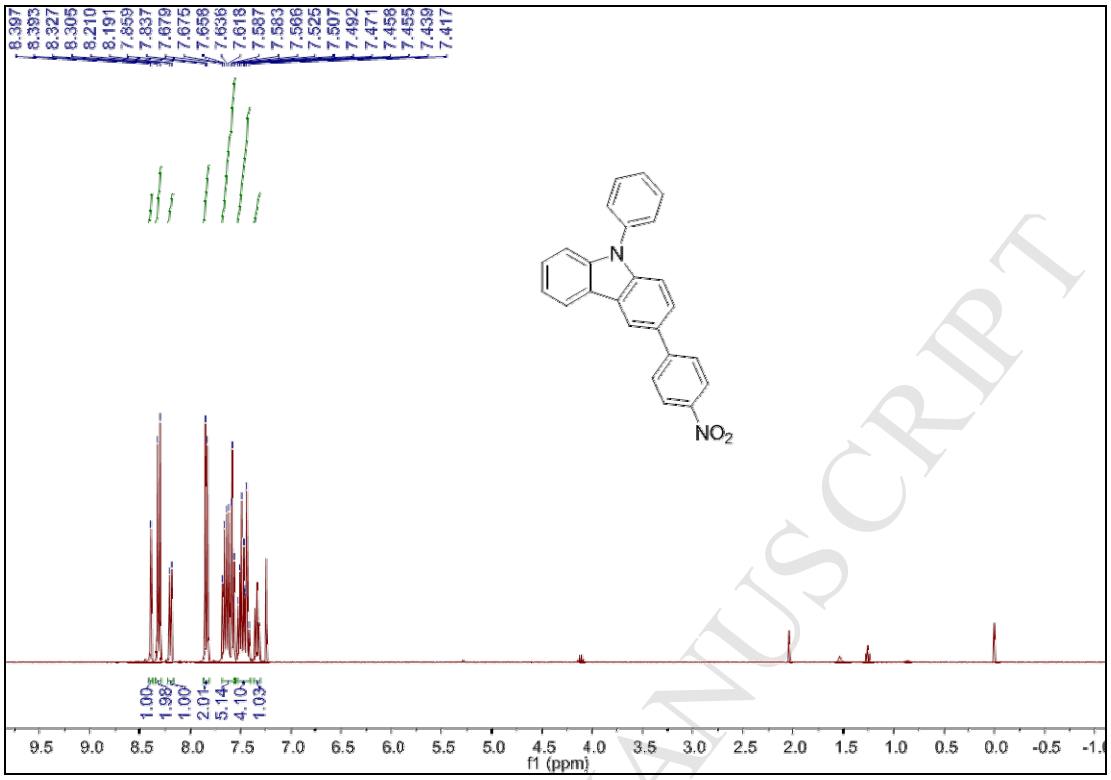


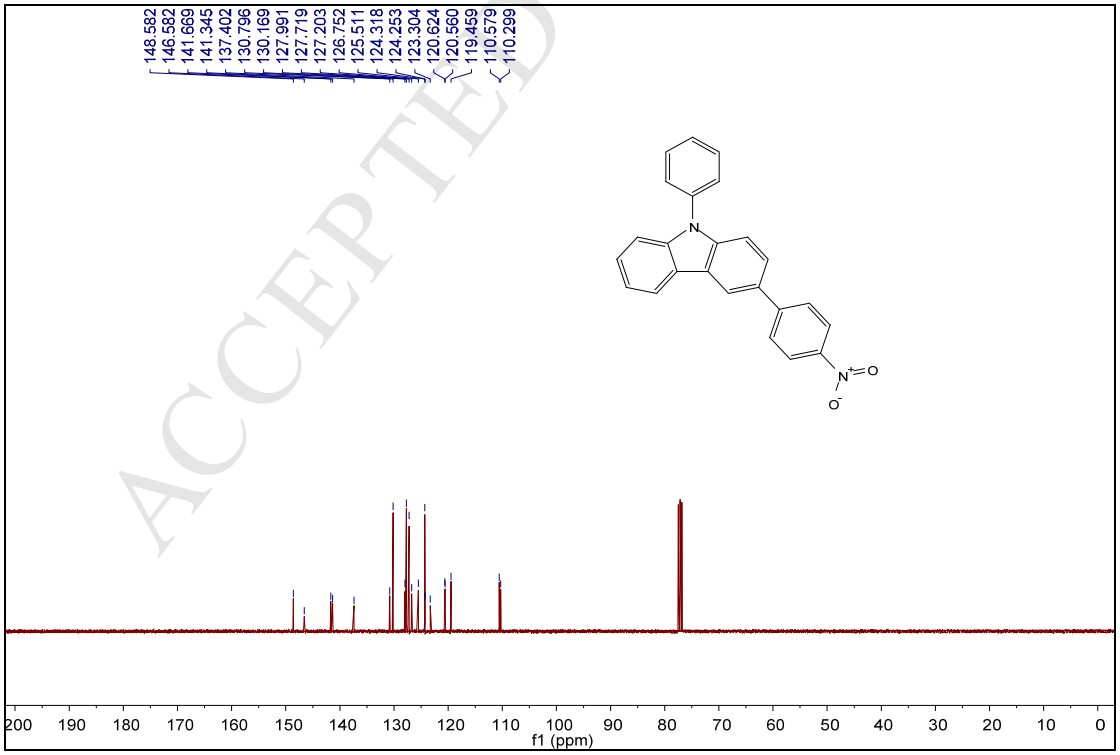
8b: 9-phenyl-3-(p-tolyl)-9H-carbazole



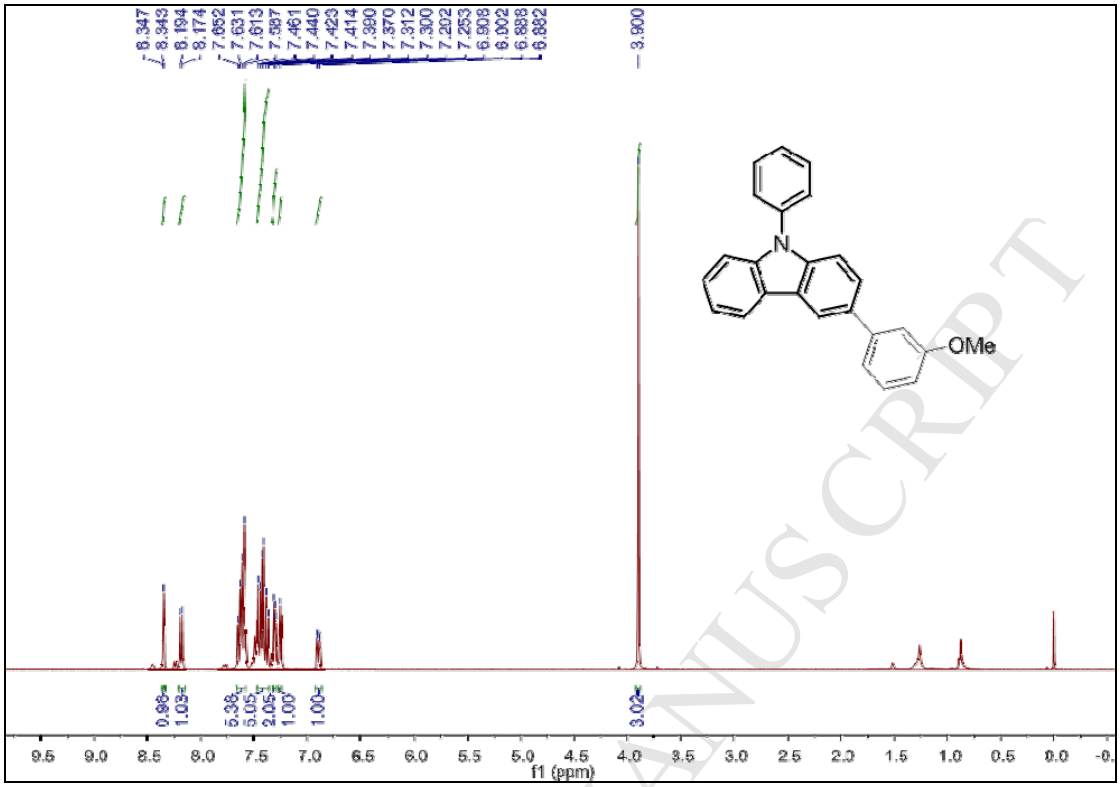


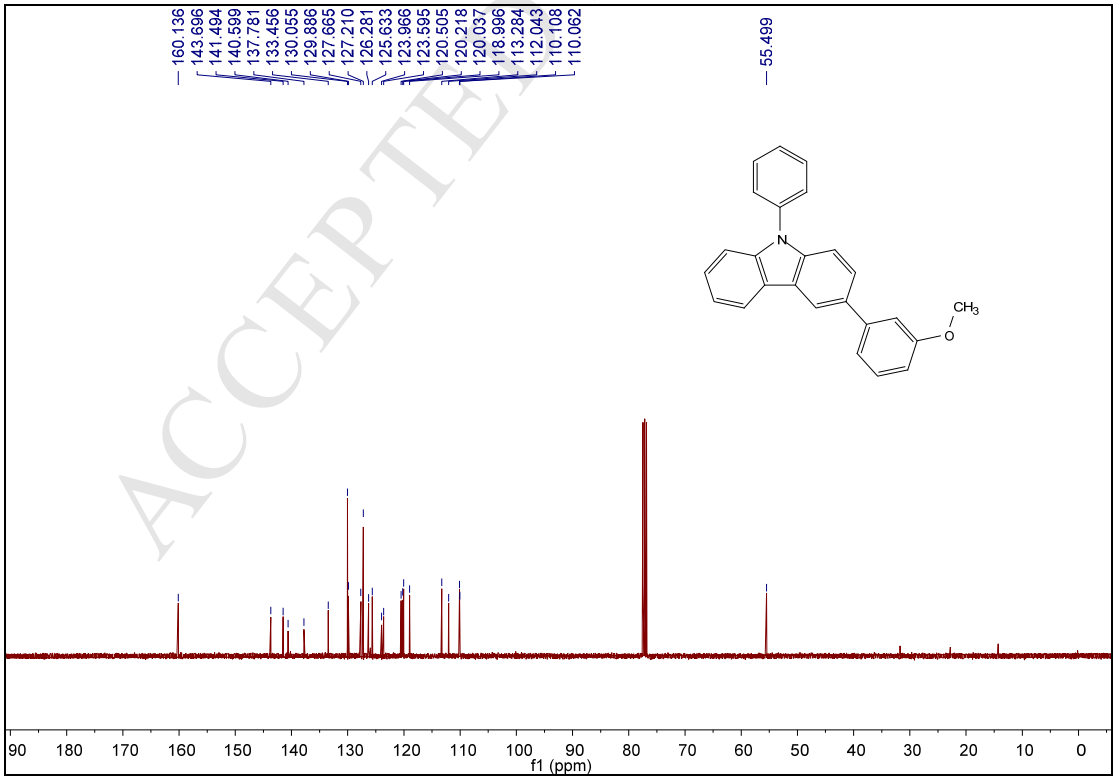
8c: 3-(4-nitrophenyl)-9-phenyl-9H-carbazole



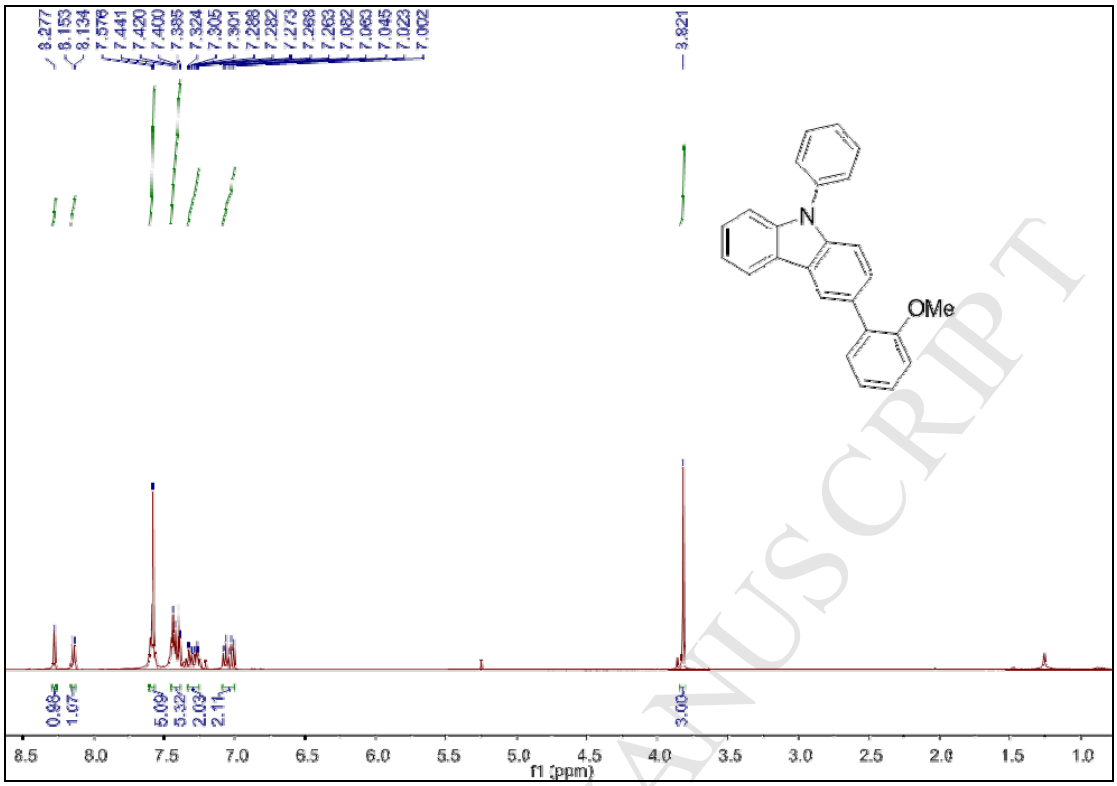


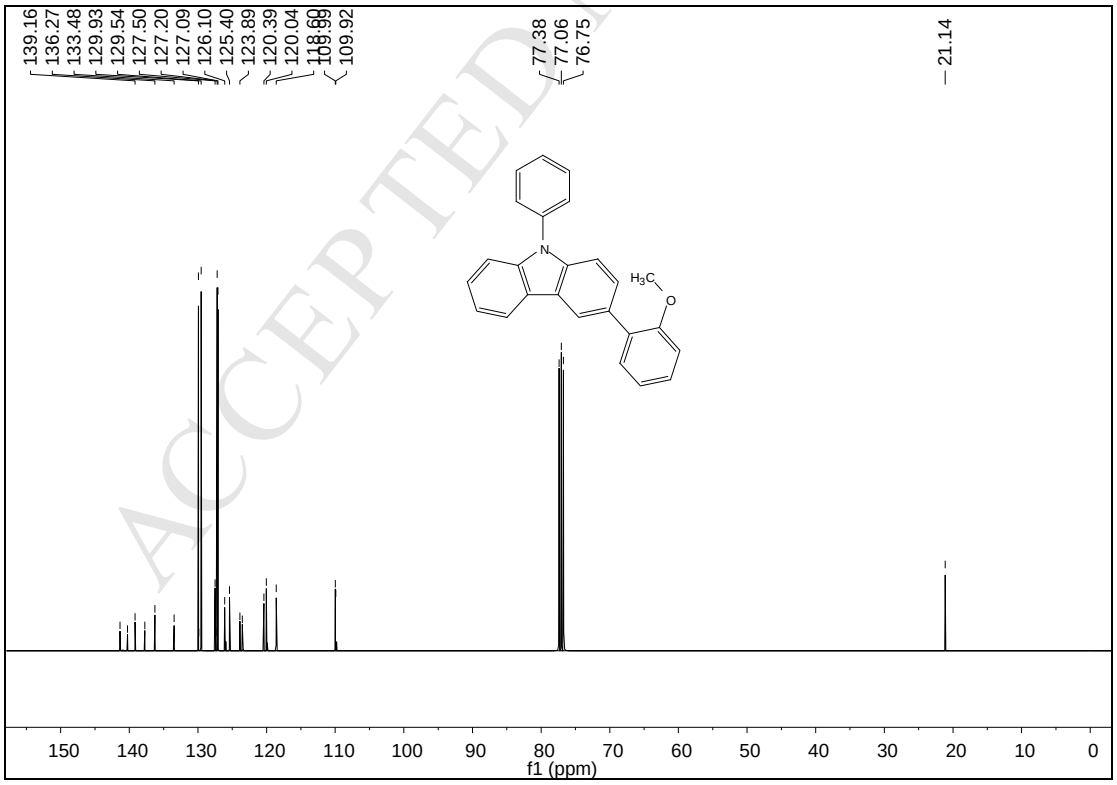
8d: 3-(3-methoxyphenyl)-9-phenyl-9H-carbazole





8e: 3-(2-methoxyphenyl)-9-phenyl-9H-carbazole





8f: 9-(4'-methoxy-[1,1'-biphenyl]-3-yl)-9H-carbazole