Electronic Supplementary Information

Pd-Catalyzed Cross-Electrophile Coupling/C–H Alkylation Reaction Enabled by a Mediator Generated via C(sp^3)–H Activation

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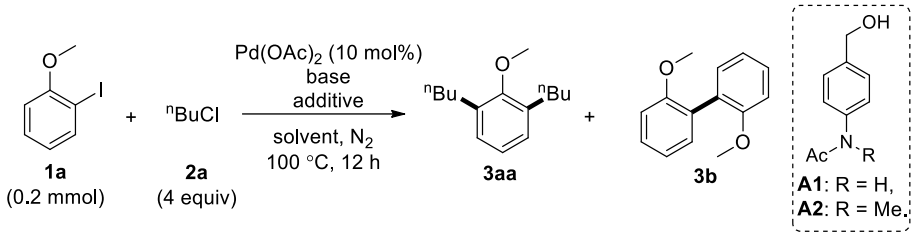
1. General Information

$Pd(OAc)_2$ was purchased from Strem Chemicals. All the solvents were purified by distillation prior to use. Unless otherwise noted, the other commercial chemicals were used without further purification.

^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

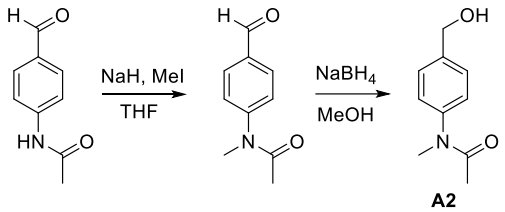
2. Optimization of Reaction Conditions



entry	base (equiv)	additive (equiv)	solvent	**3aa** (%)[a]	**3b** (%)[a]
1	K_2CO_3 (3)	—	DMF	7	0
2	$KHCO_3$ (3)	—	DMF	0	6
3	K_3PO_4 (3)	—	DMF	9	10
4	KOAc (3)	—	DMF	0	0
5	K_2CO_3 (3)	NBu_4Br (2)	DMF	38	0
6	K_2CO_3 (3)	NBu_4Br (2), MeOH (1)	DMF	48	0
7	K_2CO_3 (3)	NBu_4Br (2), *i*-PrOH (1)	DMF	47	0
8	K_2CO_3 (3)	NBu_4Br (2), BnOH (1)	DMF	55	0
9	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	DMF	64	0
10	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	DMAc	65	0
11	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	NMP	73	0
12	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	1,4-dioxane	61	0
13	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	THF	48	0
14	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	MeCN	14	16
15[c]	K_2CO_3 (5)	NBu_4Br (3), BnOH (1)	NMP	71	0
16[c]	K_2CO_3 (5)	NBu_4Br (3), **A1** (1)	NMP	66	0
17[c]	K_2CO_3 (5)	NBu_4Br (3), **A2** (1)	NMP	72 (68[b])	0
18[c]	K_2CO_3 (5)	NBu_4Br (3), MeOH (2)	NMP	62	0
19[c,d]	K_2CO_3 (5)	NBu_4Br (3), **A2** (1)	NMP	45	0
20[c,e]	K_2CO_3 (5)	NBu_4Br (3), **A2** (1)	NMP	14	0

[a] The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using $CHCl_2CHCl_2$ as the internal standard. [b] Isolated yield. [c] 85 °C. [d] *n*BuBr. [e] *n*BuI.

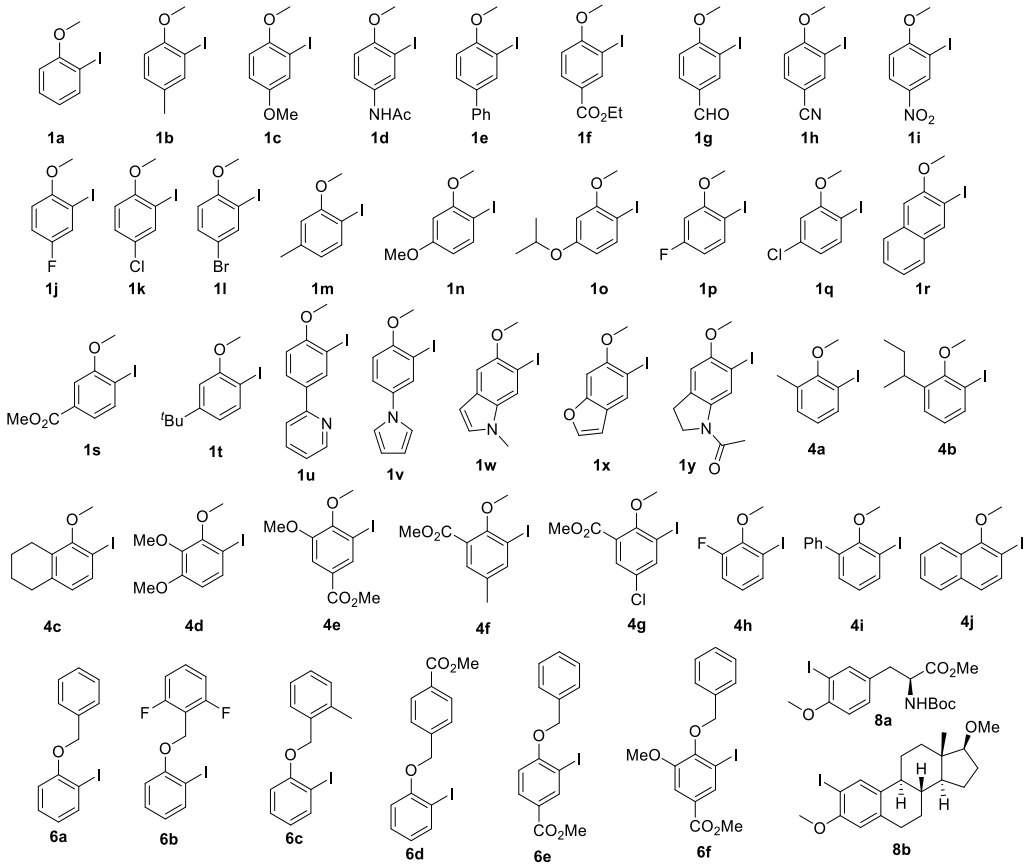
3. Experimental Procedure for the Synthesis of *N*-(4-(Hydroxymethyl)phenyl)-*N*-methylacetamide (A2)



Step 1: To the solution of *N*-(4-formylphenyl)acetamide (4.90 g, 30 mmol) in 50 mL of anhydrous THF, MeI (2.8 mL, 45 mmol) was added. Under nitrogen atmosphere, NaH (60% in mineral oil, 1.44 g, 36 mmol) was added in batches at 0 °C. Then the mixture was allowed to warm up to room temperature and stirred for 2 hours. After the reaction was quenched with MeOH, the mixture was diluted with ethyl acetate and washed with water. The aqueous phase was extracted with ethyl acetate twice. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* The crude product was used for the next step without further purification.

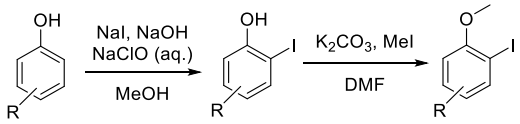
Step 2: To the solution of *N*-(4-formylphenyl)-*N*-methylacetamide in 20 mL of MeOH, $NaBH_4$ (0.56 g, 15 mmol) was added in batches. The reaction was stirred at room temperature for 3 hours before being quenched with saturated aqueous NH_4Cl solution. The mixture was diluted with ethyl acetate and washed with water. The aqueous phase was then extracted with ethyl acetate twice. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1:2) to afford *N*-(4-(Hydroxymethyl)phenyl)-*N*-methylacetamide (**A2**) as a white solid (3.52 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.71 (d, *J* = 5.2 Hz, 2H), 3.22 (s, 3H), 2.85 (br, 1H), 1.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 143.5, 140.8, 128.1, 127.0, 64.3, 37.1, 22.3. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{13}NNaO_2^+$: 202.0838 $(M + Na)^+$, found: 202.0840.

4. General Procedures for the Synthesis of the Substrates



1a, **1g**, **1i**, **1n**, and **4h** were commercially available. **1c**[1], **1d**[2], **1p**[3], **1s**[4], **4d**[5], **4g**[6], **8a**[7], and **8b**[8] were prepared by following reported procedures. **1b**, **1e**, **1j**, **1k**, **1l**, and **1t** were prepared by following method A. **4e** and **4f** were prepared by following method B. **1f** was prepared by following method C. **1h** was prepared by following method D. **1m** and **1q** were prepared by following method E. **1o** was prepared by following method F. **1r**, **4a**, **4b**, **4c**, **4i** and **4j** were prepared by following method G. **1u** was prepared by following method H. **1v** was prepared by following method I. **1y** was prepared by following method J. **1w** was prepared by following method K. **1x** was prepared by following method L. **6a – 6f** were prepared by method M.

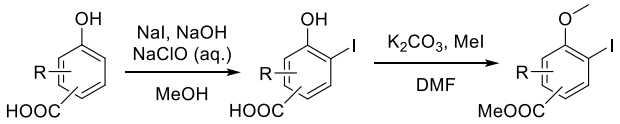
Method A[9]:



Step 1: In a round bottom flask, the phenol (1 equiv) was dissolved in methanol (0.25 M). Then NaI (1 equiv) and NaOH (1.2 equiv) were added to the solution. The reaction mixture was cooled down to 0 °C, and 7.5% aqueous solution of NaClO (1.2 equiv) was added dropwise slowly. After the reaction mixture was stirred at 0 °C for 2 hours, it was quenched with saturated aqueous $Na_2S_2O_3$ solution and acidified with diluted HCl (2 M) to pH < 5. The resulted mixture was then extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo.* The crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane to afford the corresponding 2-iodophenol.

Step 2： To the solution of 2-iodophenol (1 equiv) in DMF (0.25 M), K_2CO_3 (1.2 equiv) and MeI (1.2 equiv) was added. The reaction was stirred at room temperature for 3 hours. Then the mixture was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate to afford the corresponding 2-iodoanisole.

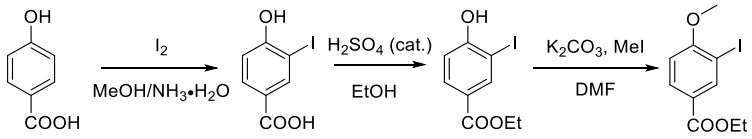
Method B:



Step 1: In a round bottom flask, the phenol (1 equiv) was dissolved in methanol (0.25 M). Then NaI (1 equiv) and NaOH (2.5 equiv) were added to the solution. The reaction mixture was cooled down to 0 °C, and 7.5% aqueous solution of NaClO (1.2 equiv) was added dropwise slowly. After the reaction mixture was stirred at 0 °C for 2 hours, it was quenched with saturated aqueous $Na_2S_2O_3$ solution and acidified with diluted HCl (2 M) to pH < 2. The resulted mixture was then extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo.* The crude product was used for the next step without further purification.

Step 2： To the solution of 2-iodophenol (1 equiv) in DMF (0.25 M), K_2CO_3 (2.5 equiv) and MeI (2.5 equiv) was added. The reaction was stirred at room temperature for 3 hours. Then the mixture was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate to afford the corresponding 2-iodoanisole.

Method C:



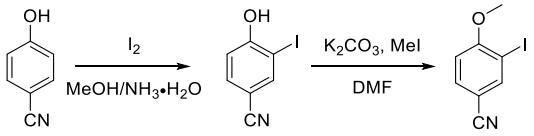
Step 1[9]***:*** In a round bottom flask, 4-hydroxybenzoic acid (2.76 g, 20 mmol) was dissolved in methanol (40 mL), and 20% ammonium hydroxide (40 mL) was added to the solution. A solution of iodine (6.35 g, 25 mmol) in methanol (50 mL) was added dropwise slowly. After the reaction mixture was stirred at room temperature for 3 hours, it was quenched with saturated aqueous $Na_2S_2O_3$ solution and acidified with diluted HCl (2 M) to pH < 2. The resulted mixture was extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was used for the next step without further purification.

Step 2： To the solution of 4-hydroxy-3-iodobenzoic acid (20 mmol) in 40 mL of EtOH, concentrated sulfuric acid (0.5 mL) was added. After the reaction mixture was stirred at 100 °C for 8 hours, it was diluted with water and extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with dichloromethane/methanol (100 : 1) to afford ethyl 4-hydroxy-3-iodobenzoate as a white solid. (3.76 g, 64%)

Step 3： To the solution of ethyl 4-hydroxy-3-iodobenzoate (3.76 g, 12.9 mmol) in DMF (15 mL), K_2CO_3 (2.14 g, 15.5 mmol) and MeI (0.96 mL, 15.5 mmol) were added. After the reaction mixture was stirred at room temperature for 3 hours, it was diluted with ethyl acetate, washed with water for 3 times,

dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20 : 1) to afford ethyl 3-iodo-4-methoxybenzoate as a white solid. (3.63 g, 92%)

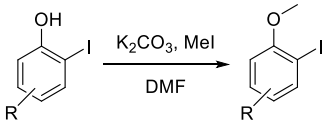
Method D:



Step 1[9]***:*** In a round bottom flask, 4-hydroxybenzonitrile (1.19 g, 10 mmol) was dissolved in methanol (20 mL), and 20% ammonium hydroxide (20 mL) was added to the solution. Then a solution of iodine (3.16 g, 12.5 mmol) in methanol (25 mL) was added dropwise slowly. After the reaction mixture was stirred at room temperature for 3 hours, it was quenched with saturated aqueous $Na_2S_2O_3$ solution and acidified with diluted HCl (2 M) to pH < 2. The resulted mixture was extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with dichloromethane/methanol (100:1) to afford 4-hydroxy-3-iodobenzonitrile as a white solid. (1.52 g, 62%)

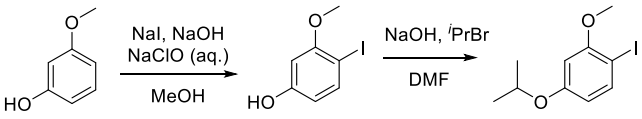
Step 2: To the solution of 4-hydroxy-3-iodobenzonitrile (1.52 g, 6.2 mmol) in DMF (10 mL), K_2CO_3 (1.02 g, 7.4 mmol) and MeI (0.46 mL, 7.4 mmol) was added. The reaction was stirred at room temperature for 3 hours. Then the mixture was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate to afford the corresponding 2-iodoanisole. (1.44 g, 90%)

Method E:



To the solution of 2-iodophenol (1 equiv) in DMF (0.25 M), K_2CO_3 (1.2 equiv) and MeI (1.2 equiv) were added. After the reaction mixture was stirred at room temperature for 3 hours, it was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate to afford the corresponding 2-iodoanisole.

Method F:

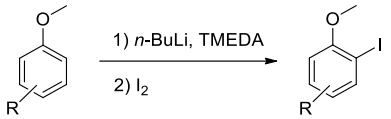


Step 1: In a round bottom flask, 3-methoxyphenol (2.48 g, 20 mmol) was dissolved in methanol (80 mL). Then NaI (3.0 g, 20 mmol) and NaOH (0.96 g, 24 mmol) were added to the solution. The reaction mixture was cooled down to 0 °C, and 7.5% aqueous solution of NaClO (24 g, 24 mmol) was added dropwise slowly. After the reaction mixture was stirred at 0 °C for 2 hours (*if the substrate was not consumed totally, a small amount of NaI and NaClO should be addtionally added*), it was quenched with saturated aqueous $Na_2S_2O_3$ solution and acidified with diluted HCl (2 M) to pH < 5. The resulted mixture

was then extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo.* The crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (1:1) to afford 4-iodo-3-methoxyphenol as a reddish oil (2.16 g, 43%).

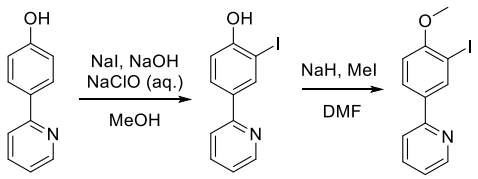
Step 2: To the solution of 4-iodo-3-methoxyphenol (0.46 g, 1.8 mmol) in DMF (1 mL), NaOH (0.11 g, 2.7 mmol) and 2-bromopropane (0.25 mL, 2.7 mmol) were added. The reaction mixture was stirred at 70 ^oC for 2 hours. After the mixture was cooled down to room temperature, it was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50 : 1) to afford 1-iodo-4-isopropoxy-2-methoxybenzene as a colorless oil. (0.43 g, 82%)

Method G[10]:



Under nitrogen atmosphere, TMEDA (*N*, *N*, *N*', *N*'-tetramethylethylenediamine, 1 equiv) was added to the solution of *n*-BuLi (1.6 M in hexane, 1 equiv) dropwise at 0 ^oC. A solution of an anisole (1 equiv) in hexane (2 M) was then added dropwise. The reaction mixture was allowed to warm up to room temperature and then stirred for 3 hours. After being cooled to 0 ^oC again, a solution of iodine (1 equiv) in anhydrous THF (1 M) was added dropwise slowly. The reaction mixture was stirred at room temperature for additional 5 hours and quenched with saturated aqueous solution of NH_4Cl. The resulted mixture was extracted with ethyl acetate, washed sequentially with saturated aqueous $Na_2S_2O_3$ solution and brine, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether to afford the corresponding 2-iodoanisole.

Method H:

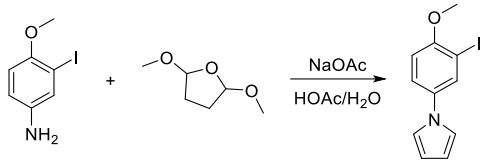


***Step 1*:** In a round bottom flask, 4-(pyridin-2-yl)phenol (1.71 g, 10 mmol) was dissolved in 40 mL of methanol. Then NaI (1.50 g, 10 mmol) and NaOH (0.48 g, 12 mmol) were added to the solution. The reaction mixture was cooled down to 0 ^oC, and 7.5% aqueous solution of NaClO (11.9 g, 12 mmol) was added dropwise slowly. After the reaction mixture was stirred at 0 ^oC for 5 hours, it was quenched with saturated aqueous $Na_2S_2O_3$ solution and acidified with diluted HCl (2 M) to pH = 7. The resulted mixture was then extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with dichloromethane/ methanol (100: 1) to afford 2-iodo-4-(pyridin-2-yl)phenol as a white solid. (1.22 g, 41%)

Step 2: To the solution of 2-iodo-4-(pyridin-2-yl)phenol (0.80 g, 2.7 mmol) in 10 mL of DMF, NaH (60% in mineral oil, 0.12 g, 3.0 mmol) was added in batches at room temperature. After 10 minutes, MeI (0.19 mL, 3.0 mmol) was added dropwise. The reaction mixture was stirred at room temperature for

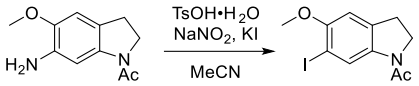
additional 3 hours. The mixture was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10 : 1) to afford 2-(3-iodo-4-methoxyphenyl)pyridine as a white solid (0.74 g, 88%).

Method I:



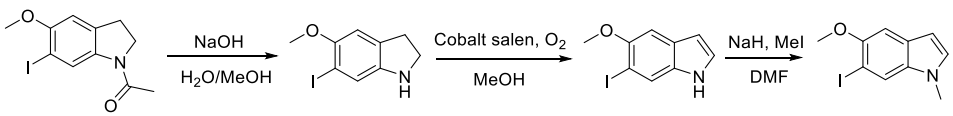
To the solution of sodium acetate (0.66 g, 8 mmol) in 20 mL of water, 3-iodo-4-methoxyaniline (2.0 g, 8 mmol) and acetic acid (4 mL) was added sequentially. The mixture was heated to 70 °C. Then 2,5-dimethoxytetrahydrofuran (1.0 mL, 8 mmol) was added dropwise. The reaction mixture was stirred at 70 °C for 2 hours. After cooling to room temperature, the mixture was extracted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20 : 1) to afford 1-(3-iodo-4-methoxyphenyl)-1H-pyrrole as a yellowish solid (1.56 g, 65%).

Method J:



1-(6-amino-5-methoxyindolin-1-yl)ethan-1-one[11] (1.0 g, 4.8 mmol) was added to a solution of *p*-toluenesulfonic acid monohydrate (2.74 g, 14.4 mmol) in acetonitrile (20 mL). The mixture was cooled down to 0 °C, and then a solution of sodium nitrite (0.66 g, 9.6 mmol) and potassium iodide (1.99 g, 12 mmol) in water (2 mL) was added dropwise. After stirring at 0 °C for 15 minutes, the reaction mixture was warmed up to room temperature and stirred for 2 hours. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ solution. Then the resulted mixture was diluted with water, basified by the addition of $NaHCO_3$, and extracted with ethyl acetate for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1 : 1) to afford 1-(6-iodo-5-methoxyindolin-1-yl)ethan-1-one as a white solid (0.84 g, 55%).

Method K:



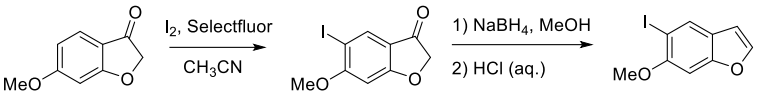
Step 1: 40% NaOH aqueous solution (20 mL) was added to the solution of 1-(6-iodo-5-methoxyindolin-1-yl)ethan-1-one (0.32 g, 1.0 mmol) in MeOH (20 mL). The reaction mixture was heated to 80 °C and stirred overnight. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was used for the next step without further purification.

***Step 2*:** 6-iodo-5-methoxyindoline (1 mmol) was dissolved in MeOH (30 mL), and *N,N'*-bis(salicylidene)ethylenediamine cobalt(II) (0.033 g, 0.1 mmol) was then added. The reaction mixture

was stirred at room temperature for 2 hours as air was bubbled through it. The mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8 : 1) to afford 6-iodo-5-methoxy-1H-indole as a white solid (0.16 g, 60%).

Step 3: To the solution of 6-iodo-5-methoxy-1*H*-indole (0.16 g, 0.6 mmol) in 1 mL of DMF, NaH (60% in mineral oil, 0.037 g, 0.9 mmol) was added at room temperature. After 10 minutes, MeI (56 uL, 0.9 mmol) was added dropwise. The reaction mixture was stirred at room temperature for additional 2 hours. The mixture was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20 : 1) to afford 6-iodo-5-methoxy-1-methyl-1H-indole as a white solid (0.15 g, 87%).

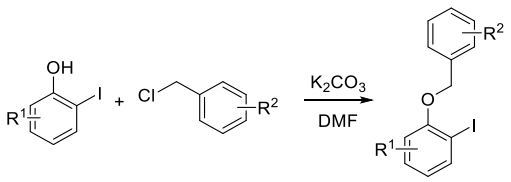
Method L:



***Step 1*:** To the solution of 6-methoxybenzofuran-3(2H)-one (0.6 g, 3.7 mmol) in 20 mL of MeCN, I_2 (0.56 g, 2.2 mmol) and Selecfluor (0.78 g, 2.2 mmol) were added. The mixture was stirred at room temperature for 5 hours before it was quenched with saturated aqueous $Na_2S_2O_3$ solution. After MeCN was evaporated *in vacuo*, the residue was dissolved in ethyl acetate and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1) to afford 5-iodo-6-methoxybenzofuran-3(2H)-one (0.76 g, 71%).

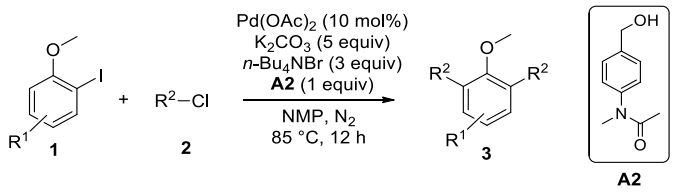
Step 2: To the solution of 5-iodo-6-methoxybenzofuran-3(2H)-one (0.76 g, 2.6 mmol) in 10 mL of MeOH, $NaBH_4$ (0.15 g, 3.9 mmol) was added in four equivalent portions (over 10 minutes) at room temperature. The reaction mixture was stirred for an additional hour before it was quenched with 1 mL of acetone. The resulting solution was then treated with 3 M aq. HCl (8 mL) and stirred at room temperature for 2 hours. The mixture was diluted with ethyl acetate, washed with water, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50 : 1) to afford 5-iodo-6-methoxybenzofuran as a white solid (0.63 g, 88%).

Method M:

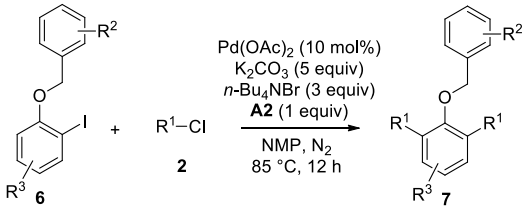


To the solution of 2-iodophenol (1 equiv) in DMF (0.25 M), K_2CO_3 (1.2 equiv) and the corresponding benzyl chloride (1.2 equiv) was added. The reaction mixture was stirred at room temperature overnight. Next, the mixture was diluted with ethyl acetate, washed with water for 3 times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate to afford the product.

5. General Procedures for the Dialkylation of 2-Iodoanisoles and 1-(Benzyloxy)-2-iodobenzenes

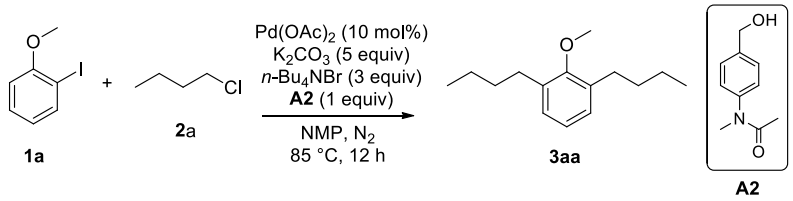


A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), K_2CO_3 (138 mg, 1.0 mmol), *n*-Bu_4NBr (193 mg, 0.6 mmol), *N*-(4-(hydroxymethyl)phenyl)-*N*-methylacetamide (**A2**, 35.8 mg, 0.2 mmol), the corresponding aryl iodide **1** (0.2 mmol), and NMP (1.5 mL). Then the alkyl chloride (0.8 mmol or 0.5 mmol) was added. The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen (5 times). The reaction mixture in the sealed Schlenk tube was stirred at 85 °C (preheated oil bath) at a stirring rate of 800 rpm for 12 hours. After being cooled down to room temperature, the reaction mixture was diluted with ethyl acetate (15 mL), washed with water (3 times), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate to give the corresponding products.



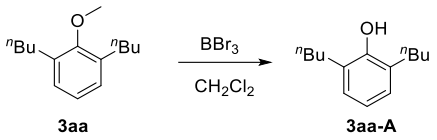
The reaction was carried out in 10 mL Schlenk-type tube and followed similar procedure described for the coupling of **1** with **2**.

Experimental procedure for **scale-up reaction** of **1a** with 1-chlorobutane:



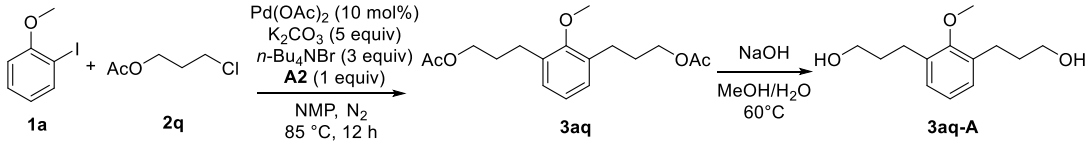
A 50 mL Schlenk flask equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (0.1123 g, 0.5 mmol), K_2CO_3 (3.46 g, 25 mmol, *when potassium carbonate was purchased as a granule, it was suggested to be ground into fine powder before it was used*), *n*-Bu_4NBr (4.84 g, 15 mmol), *N*-(4-(hydroxymethyl)phenyl)-*N*-methylacetamide (**A2**, 0.90 g, 5 mmol), **1a** (1.17 g, 5 mmol), and NMP (30 mL). After being capped with a rubber septum, the flask was evacuated and backfilled with nitrogen for 5 times until no obvious bubbles were generated in the liquid mixture during the evacuating. Then 1-chlorobutane (2.1 mL, 20 mmol) was added *via* a syringe. The reaction mixture was stirred at 85 °C (preheated oil bath) at a stirring rate of 800 rpm for 12 hours. After being cooled down to room temperature, the reaction mixture was diluted with ethyl acetate, washed with water (3 times), dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50 : 1) to give **3aa** as a colorless oil (0.74 g, 67%).

6. Experimental Procedures for the Transformation of Products



3aa **3aa-A**

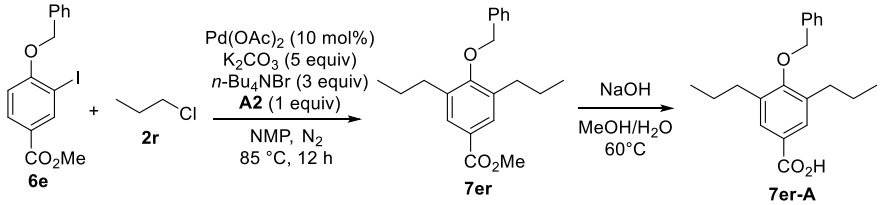
Under nitrogen atmosphere, BBr_3 (1 M in DCM, 0.5 mL, 0.5 mmol) was added dropwise to the solution of **3aa** (28 mg, 0.13 mmol) in 2 mL anhydrous CH_2Cl_2. After the reaction mixture was stirred at room temperature for 18 hours, it was quenched with CH_3OH (2 mL), diluted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (20 : 1) to give **3aa-A** as a white solid (23.3 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.4 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 4.65 (s, 1H), 2.60 (t, *J* = 7.7 Hz, 4H), 1.67 – 1.57 (m, 4H), 1.46 – 1.36 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 127.9, 127.6, 120.2, 31.9, 29.8, 22.7, 14.0.



1a **2q** **3aq** **3aq-A**

Step 1: **3aq** was synthesized by following the general procedure for the dialkylation of 2-iodoanisoles using **1a** (46.8 mg, 0.2 mmol, 1 equiv) and **2q** (68.2 mg, 0.5 mmol, 2.5 equiv). **3aq** was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (8 : 1), and obtained as a colorless oil (32.1 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.0 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 4.11 (t, *J* = 6.5 Hz, 4H), 3.74 (s, 3H), 2.71 (t, *J* = 7.8 Hz, 4H), 2.06 (s, 6H), 1.98 – 1.93 (m, 4H). ^{13}C NMR (151 MHz, CDCl3) δ 171.1, 156.6, 134.3, 128.1, 124.2, 64.1, 61.0, 29.4, 26.3, 21.0.

Step 2: **3aq** (32.1 mg, 0.1 mmol) was dissolved in 2 mL MeOH. Then, 0.3 mL aqueous solution of NaOH (2 M) was added. The reaction was stirred at 60 °C for 2 hours and then was acidified with diluted HCl (1 M), extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. **3aq-A** was obtanined as a colorless oil (20.6 mg, 92%) without further purification. ^{1}H NMR (600 MHz, $CDCl_3$): 7.06 – 7.03 (m, 3H), 3.76 (s, 3H), 3.58 (t, *J* = 6.4 Hz, 4H), 2.75 (t, *J* = 7.5 Hz, 4H), 1.90 – 1.82 (m, 4H). The data are identical to: Shi, J.-P.; Wu, D.-L.; Ding, Y.; Wu, D.-H.; Hu, H.-W.; Lu, G.-Y., *Tetrahedron* **2012,** *68*, 2770-2777.

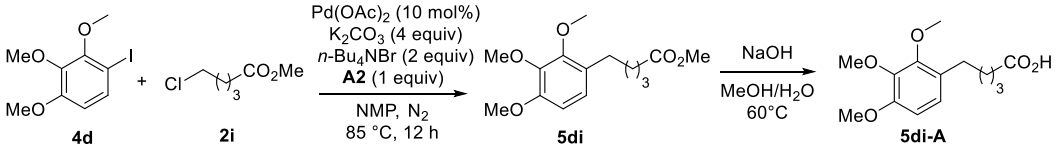


6e **2r** **7er** **7er-A**

Step 1: **7er** was synthesized by following the general procedure for the dialkylation of 1-(benzyloxy)-2-iodobenzenes using **6e** (73.6 mg, 0.2 mmol, 1 equiv) and **2r** (94.2 mg, 1.2 mmol, 6 equiv). **7er** was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (20 : 1), and obtained as a colorless oil (37.3 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 4.85 (s, 2H), 3.90 (s, 3H), 2.66 (t, *J* = 7.7 Hz, 4H), 1.72 – 1.65 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 167.1, 159.4, 137.3, 136.0, 129.4, 128.5,

128.0, 127.4, 125.8, 75.4, 51.9, 32.1, 23.7, 14.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{26}NaO_3^+$: 349.1774 $(M + Na)^+$, found: 349.1770.

Step 2: **7er** (37.3 mg, 0.11 mmol) was dissolved in 2 mL MeOH. Then, 0.3 mL aqueous solution of NaOH (2 M) was added. The reaction was stirred at 60 °C for 2 hours and then was acidified with diluted HCl (1 M), extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. **7er-A** was obtanined as a white solid (33.4 mg, 97%) without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 4.87 (s, 2H), 2.68 (t, *J* = 7.7 Hz, 4H), 1.74 – 1.66 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 6H). The data are identical to: Koura, M.; Matsuda, T.; Okuda, A.; Watanabe, Y.; Yamaguchi, Y.; Kurobuchi, S.; Matsumoto, Y.; Shibuya, K., *Bioorg. Med. Chem. Lett.* **2015,** *25*, 2668-2674.

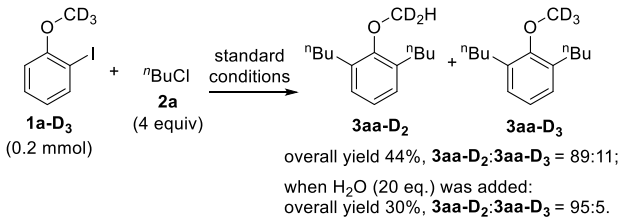


Step 1: **5di** was synthesized by following the general procedure for the dialkylation of 2-iodoanisoles using **4d** (58.8 mg, 0.2 mmol, 1 equiv), **2i** (60.2 mg, 0.4 mmol, 2 equiv), K_2CO_3 (111 mg, 0.8 mmol, 4 equiv), *n*-Bu_4NBr (129 mg, 0.4 mmol, 2 equiv). **5di** was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (20 : 1), and obtained as a colorless oil (48.0 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.65 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.62 – 1.54 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 151.9, 151.8, 142.2, 128.1, 123.7, 107.1, 60.8, 60.7, 56.0, 51.4, 33.9, 30.3, 29.2, 24.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{22}NaO_5^+$: 305.1359 $(M + Na)^+$, found: 305.1348.

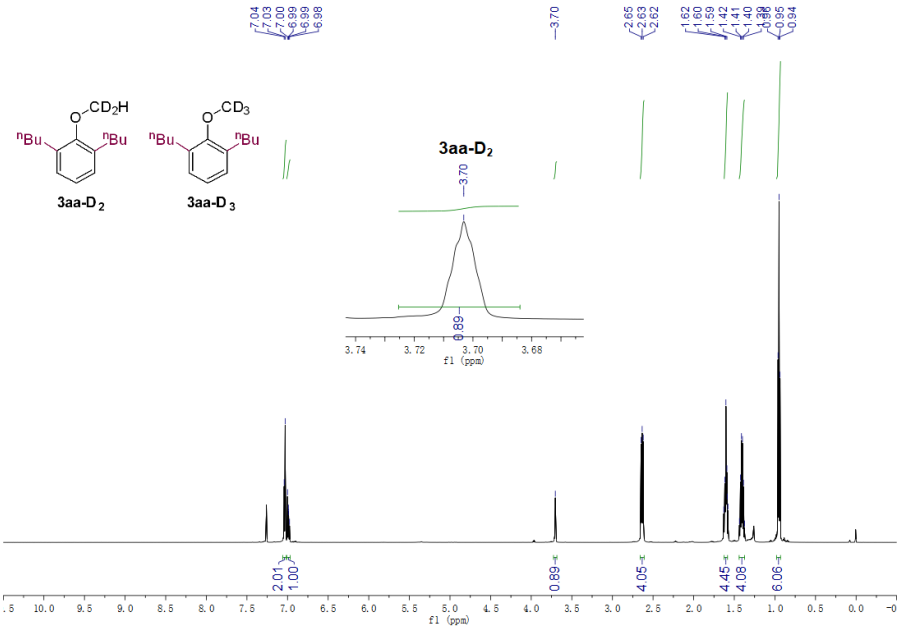
Step 2: **5di** (48.0 mg, 0.17 mmol) was dissolved in 3 mL MeOH. Then, 0.3 mL aqueous solution of NaOH (2 M) was added. The reaction was stirred at room temperature for 2 hours and then was acidified with diluted HCl (1 M), extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. **5di-A** was obtanined as a white solid (42.8 mg, 94%) without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.65 – 1.57 (m, 2H). The data are identical to: Tanpure, R. P.; George, C. S.; Strecker, T. E.; Devkota, L.; Tidmore, J. K.; Lin, C.-M.; Herdman, C. A.; MacDonough, M. T.; Sriram, M.; Chaplin, D. J.; Trawick, M. L.; Pinney, K. G., *Bioorg. Med. Chem.* **2013,** *21*, 8019-8032.

7. Experimental Procedure for Mechanistic Study

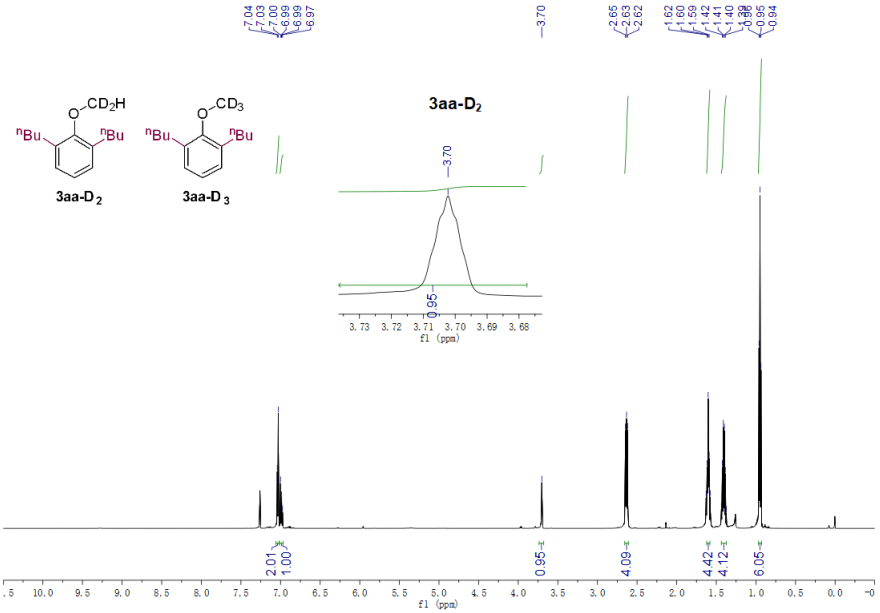
7.1 Deuterium-labeling experiments

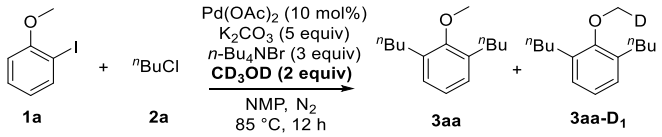


A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), K_2CO_3 (138 mg, 1.0 mmol), *n*-Bu_4NBr (193 mg, 0.6 mmol), **A2** (35.8 mg, 0.2 mmol), **1a-D₃** (47.4 mg, 0.2 mmol), and NMP (1.5 mL). Then 1-chlorobutane **2a** (84 uL, 0.8 mmol) were added. The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen (5 times). The reaction mixture in the sealed Schlenk tube was stirred at 85 ^oC (preheated oil bath) at a stirring rate of 800 rpm for 12 hours. After being cooled down to room temperature, the reaction mixture was diluted with ethyl acetate (15 mL), washed with water (3 times), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate to give **3aa-D₂** and **3aa-D₃** as a colorless oil (19.4 mg, 44%). The ratio of **3aa-D₂ and 3aa-D₃** was determined by ^1H NMR analysis after purification.

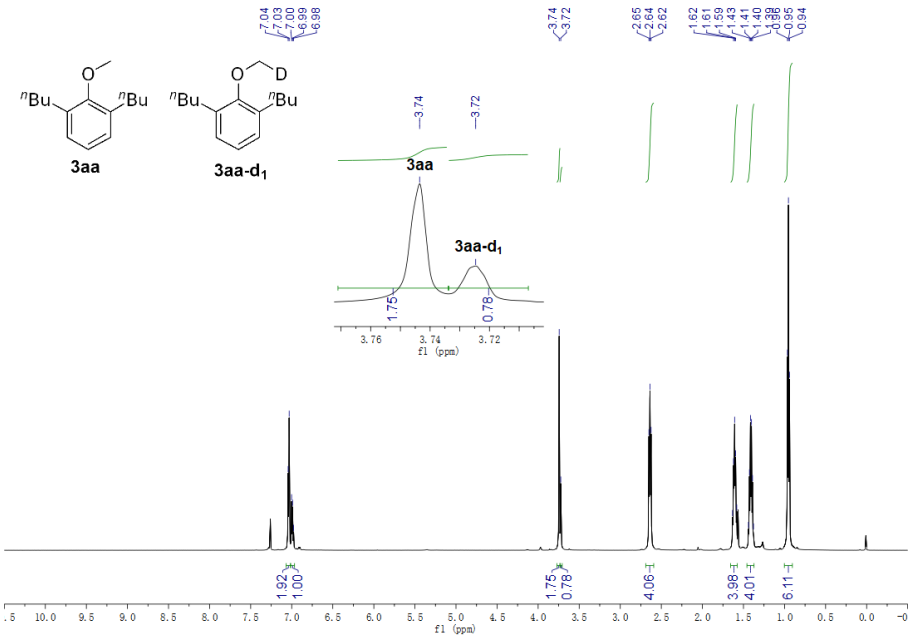


When an extra amount of H_2O (20 equiv.) was added:

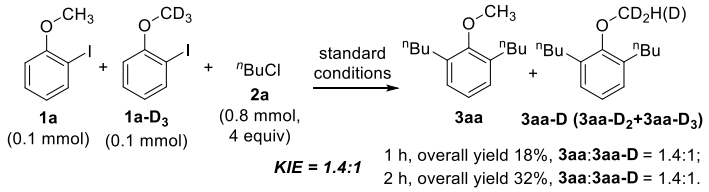




A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), K_2CO_3 (138 mg, 1.0 mmol), Bu_4NBr (193 mg, 0.6 mmol), **1a** (46.8 mg, 0.2 mmol), and NMP (1.5 mL). Then 1-chlorobutane **2a** (84 uL, 0.8 mmol) and CD_3OD (16 uL, 0.4 mmol) were added. The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen (5 times). The reaction mixture in the sealed Schlenk tube was stirred at 85 °C (preheated oil bath) at a stirring rate of 800 rpm for 12 hours. After being cooled down to room temperature, the reaction mixture was diluted with ethyl acetate (15 mL), washed with water (3 times), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate to give **3aa** and **3aa-D$_1$** as a colorless oil (22.9 mg, 52%). The ratio of **3aa** and **3aa-D$_1$** was determined by ^{1}H NMR analysis after purification.

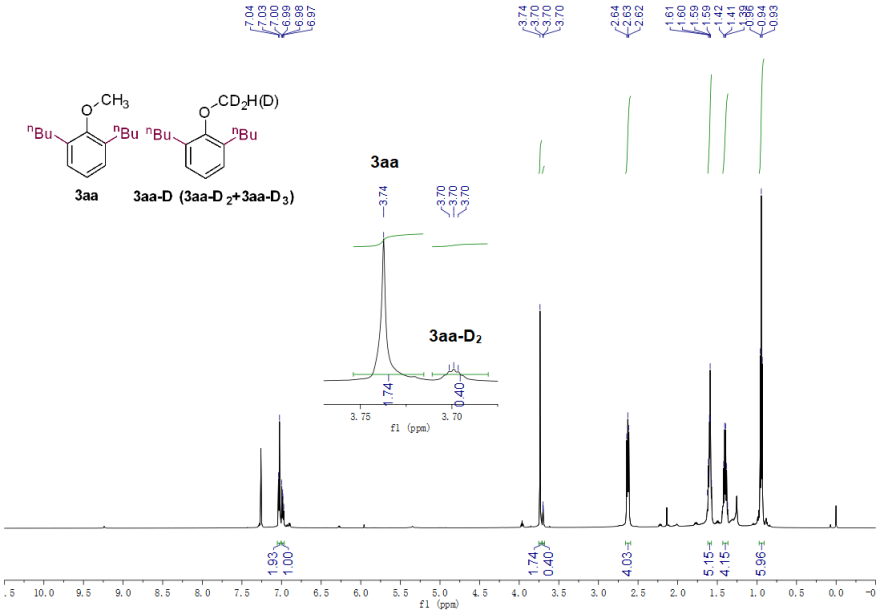


7.2 Intermolecular competition experiments

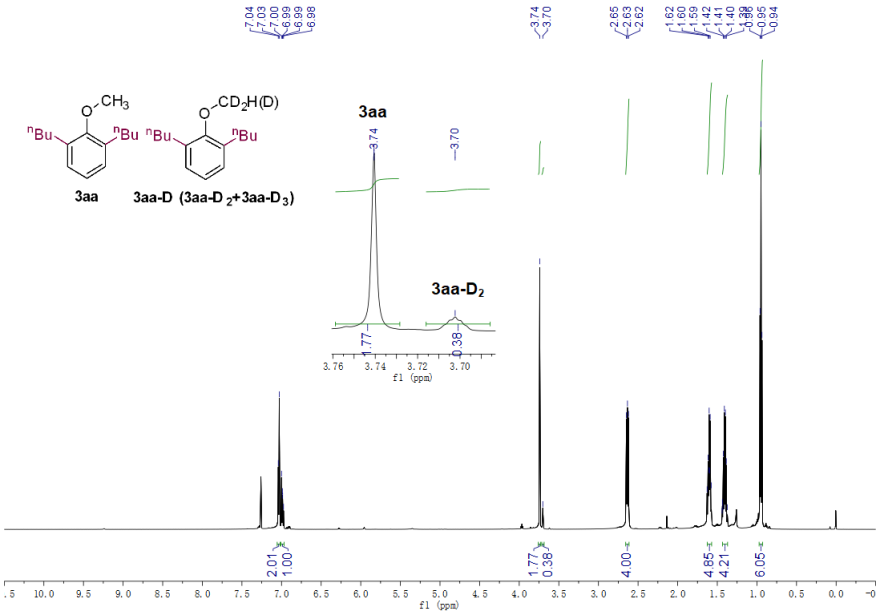


A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), K_2CO_3 (138 mg, 1.0 mmol), *n*-Bu_4NBr (193 mg, 0.6 mmol), **A2** (35.8 mg, 0.2 mmol), **1a** (23.4 mg, 0.1 mmol), **1a-D$_3$** (23.7 mg, 0.1 mmol), and NMP (1.5 mL). Then 1-chlorobutane **2a** (84 uL, 0.8 mmol) were added. The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen (5 times). The reaction mixture in the sealed Schlenk tube was stirred at 85 °C (preheated oil bath) at a stirring rate of 800 rpm for 1 or 2 hours. After being cooled down to room temperature, the reaction mixture was diluted with ethyl acetate (15 mL), washed with water (3 times), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate to give **3aa** and **3aa-D** as a colorless oil. The ratio of **3aa** and **3aa-D** was determined by ^1H NMR analysis after purification.

The reaction was run for 1 hour:



The reaction was run for 2 hours:



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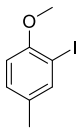
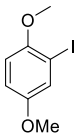
9. Characterization of the Substrates



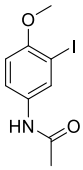
2-Iodo-1-methoxy-4-methylbenzene (1b): Colorless oil (1.53 g, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 139.7, 131.9, 129.9, 110.7, 85.7, 56.3, 19.9.

The data are identical to: Zhou, C.-Y.; Li, J.; Peddibhotla, S.; Romo, D. *Org. Lett.* **2010,** *12*, 2104-2107.

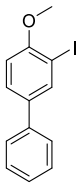


2-Iodo-1,4-dimethoxybenzene (1c): Colorless oil (1.73 g, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.86 (d, *J* = 8.9 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 152.6, 124.8, 114.7, 111.5, 86.0, 57.0, 55.9.

The data are identical to: Yamaguchi, Y.; Matsubara, Y.; Ochi, T.; Wakamiya, T.; Yoshida, Z.-i. *J. Am. Chem. Soc.* **2008**, *130*, 13867-13869.

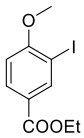


***N*-(3-Iodo-4-methoxyphenyl)acetamide (1d):** White solid (1.02 g, 87%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.32 (br, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 155.2, 132.0, 131.5, 121.8, 110.7, 85.5, 56.6, 24.3. HRMS (ESI-TOF) *m/z*: calcd for $C_9H_{10}INNaO_2^+$: 313.9648 (M + Na)$^+$, found: 313.9646.

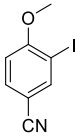


3-Iodo-4-methoxy-1,1'-biphenyl (1e): White solid (1.68 g, 54% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.56 – 7.50 (m, 3H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 139.3, 138.0, 135.8, 128.8, 128.1, 127.1, 126.7, 111.0, 86.4, 56.4.

The data are identical to: Wang, J.; Zhou, Y.; Xu, X.; Liu, P.; Dong, G. *J. Am. Chem. Soc.* **2020**, *142*, 3050-3059.

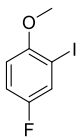


Ethyl 3-iodo-4-methoxybenzoate (1f) : White solid (3.63 g, 58% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.1 Hz, 1H), 8.01 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 161.5, 140.8, 131.6, 124.6, 109.9, 85.2, 61.0, 56.5, 14.3. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{11}INaO_3^+$: 328.9645 (M + Na)$^+$, found: 328.9651.



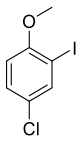
3-Iodo-4-methoxybenzonitrile (1h): White solid (1.44 g, 55% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 142.7, 134.1, 117.5, 110.7, 105.9, 86.0, 56.7.

The data are identical to: Leboeuf, D.; Ciesielski, J.; Frontier, A. J. *Synlett* **2014**, 25, 399-402.



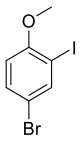
4-Fluoro-2-iodo-1-methoxybenzene (1j): Colorless oil (1.64 g, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 8.7 Hz, 1H), 6.74 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7 (d, *J* = 243.3 Hz), 154.7 (d, *J* = 2.3 Hz), 126.1 (d, *J* = 25.2 Hz), 115.5 (d, *J* = 22.6 Hz), 110.9 (d, *J* = 8.1 Hz), 85.2 (d, *J* = 8.6 Hz), 56.9.

The data are identical to: Perry, G. J. P.; Quibell, J. M.; Panigrahi, A.; Larrosa, I. *J. Am. Chem. Soc.* **2017,** *139*, 11527-11536.



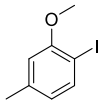
4-Chloro-2-iodo-1-methoxybenzene (1k): Colorless oil (1.83 g, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.27 (d, *J* = 8.9 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 138.5, 129.2, 126.3, 111.3, 86.0, 56.6.

The data are identical to: Perry, G. J. P.; Quibell, J. M.; Panigrahi, A.; Larrosa, I. *J. Am. Chem. Soc.* **2017,** *139*, 11527-11536.



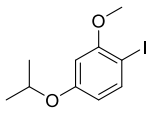
4-Bromo-2-iodo-1-methoxybenzene (1l): Colorless oil (1.65 g, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 141.1, 132.1, 113.3, 111.9, 86.6, 56.5.

The data are identical to: Perry, G. J. P.; Quibell, J. M.; Panigrahi, A.; Larrosa, I. *J. Am. Chem. Soc.* **2017,** *139*, 11527-11536.

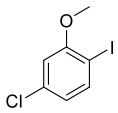


1-Iodo-2-methoxy-4-methylbenzene (1m): Colorless oil (1.16 g, 94% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.0 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.1 Hz, 1H), 3.86 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 139.8, 138.9, 123.4, 112.1, 81.8, 56.2, 21.4.

The data are identical to: Perry, G. J. P.; Quibell, J. M.; Panigrahi, A.; Larrosa, I. *J. Am. Chem. Soc.* **2017,** *139*, 11527-11536.

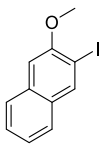


1-Iodo-4-isopropoxy-2-methoxybenzene (1o): Colorless oil (0.43 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.30 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.56 – 4.48 (m, 1H), 3.84 (s, 3H), 1.33 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 158.9, 139.0, 108.7, 101.0, 74.3, 70.2, 56.2, 21.9. MS (EI): (M^+): 292.01.



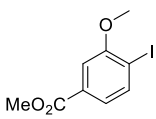
4-Chloro-1-iodo-2-methoxybenzene (1q): Colorless oil (1.20 g, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.73 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 139.7, 135.2, 122.5, 111.6, 83.2, 56.5.

The data are identical to: Perry, G. J. P.; Quibell, J. M.; Panigrahi, A.; Larrosa, I. *J. Am. Chem. Soc.* **2017,** *139*, 11527-11536.

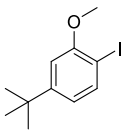


2-Iodo-3-methoxynaphthalene (1r): White solid (1.18 g, 42% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 139.1, 134.2, 130.3, 126.8, 126.6, 126.5, 124.2, 105.4, 88.1, 56.3.

The data are identical to: Kadiyala, R. R.; Tilly, D.; Nagaradja, E.; Roisnel, T.; Matulis, V. E.; Ivashkevich, O. A.; Halauko, Y. S.; Chevallier, F.; Gros, P. C.; Mongin, F. *Chem. -Eur. J.* **2013,** *19*, 7944-7960.

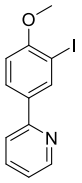


Methyl 4-iodo-3-methoxybenzoate (1s): White solid (1.03 g, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.43 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 158.2, 139.5, 131.6, 123.3, 111.1, 92.6, 56.5, 52.3. HRMS (ESI-TOF) *m/z*: calcd for $C_9H_9INaO_3^+$: 314.9489 $(M + Na)^+$, found: 314.9475.

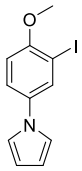


4-(*tert*-Butyl)-1-iodo-2-methoxybenzene (1t): White solid (1.85 g, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.1 Hz, 1H), 3.89 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 153.4, 138.7, 119.9, 108.7, 82.2, 56.2, 34.9, 31.2.

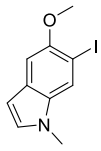
The data are identical to: Djordjevic, L.; Milano, D.; Demitri, N.; Bonifazi, D. *Org. Lett.* **2020,** *22*, 4283-4288.



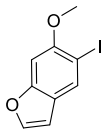
2-(3-Iodo-4-methoxyphenyl)pyridine (1u): White solid (0.74 g, 36% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.7 Hz, 1H), 8.45 (d, *J* = 2.1 Hz, 1H), 7.96 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.72 (td, *J* = 7.9, 1.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 6.9, 5.2 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 155.5, 149.6, 137.9, 136.7, 133.8, 128.0, 121.8, 119.8, 110.7, 86.3, 56.4. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{11}INO^+$: 311.9880 $(M + H)^+$, found: 311.9862.



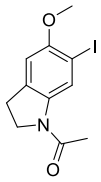
1-(3-Iodo-4-methoxyphenyl)-1H-pyrrole (1v): Yellowish solid (1.56 g, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.7 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.98 (t, *J* = 2.1 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.33 (t, *J* = 2.1 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 135.4, 132.0, 121.9, 119.6, 111.0, 110.3, 86.1, 56.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{11}H_{11}INO^+$: 299.9880 $(M + H)^+$, found 299.9877:.



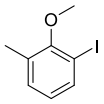
6-Iodo-5-methoxy-1-methyl-1H-indole (1w): White solid (0.15 g, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.07 (s, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 6.38 (dd, *J* = 3.0, 0.5 Hz, 1H), 3.90 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 133.4, 129.7, 129.1, 119.8, 101.8, 100.5, 79.9, 56.9, 33.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{11}INO^+$: 287.9880 $(M + H)^+$, found 287.9877.



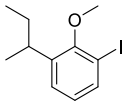
5-Iodo-6-methoxybenzofuran (1x): Whte solid **(**0.63 g, 62% yield**).** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.02 (s, 1H), 6.65 (d, *J* = 1.3 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 155.5, 144.6, 130.7, 122.8, 105.5, 94.8, 80.2, 56.6. MS (EI): (M^+): 273.95.



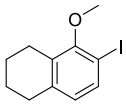
1-(6-Iodo-5-methoxyindolin-1-yl)ethan-1-one (1y): White solid (0.84 g, 55% yield). NMR spectra showed a 7 : 1 mixture of rotamers. Only signals for the major rotamer are recorded. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (s, 1H), 6.69 (s, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 3.17 (t, *J* = 8.4 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 154.6, 137.7, 132.8, 127.1, 107.5, 83.5, 56.7, 49.0, 28.2, 23.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{11}H_{13}INO_2^+$: 317.9985 $(M + H)^+$, found: 317.9982.



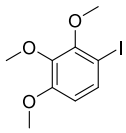
1-Iodo-2-methoxy-3-methylbenzene (4a): Colorless oil (1.34 g, 54%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 7.7 Hz, 1H), 3.78 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 137.1, 132.3, 131.5, 125.9, 91.9, 60.1, 17.0. MS (EI): (M^+): 247.99.



1-(*sec*-Butyl)-3-iodo-2-methoxybenzene (4b): Colorless oil (1.51 g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.18 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 3.79 (s, 3H), 3.10 (h, *J* = 7.1 Hz, 1H), 1.58 (p, *J* = 7.4 Hz, 2H), 1.20 (d, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 142.2, 136.8, 127.3, 126.3, 92.2, 61.5, 34.4, 30.7, 21.9, 12.3. MS (EI): (M^+): 290.03.

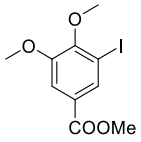


6-Iodo-5-methoxy-1,2,3,4-tetrahydronaphthalene (4c): Colorless oil (1.63 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 2.79 (d, *J* = 6.0 Hz, 2H), 2.73 (d, *J* = 6.0 Hz, 2H), 1.82 – 1.73 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 139.6, 135.7, 132.1, 126.9, 87.5, 59.9, 29.0, 24.3, 22.6, 22.5. MS (EI): (M^+): 288.02.

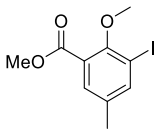


1-Iodo-2,3,4-trimethoxybenzene (4d): Colorless oil (2.50 g, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 153.4, 142.7, 132.6, 109.8, 81.3, 61.0, 60.9, 56.2.

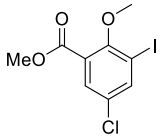
The data are identical to: Bochicchio, A.; Cefola, R.; Choppin, S.; Colobert, F.; Di Noia, M. A.; Funicello, M.; Hanquet, G.; Pisano, I.; Todisco, S.; Chiummiento, L. *Tetrahedron Lett.* **2016,** *57*, 4053-4055.



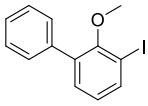
Methyl 3-iodo-4,5-dimethoxybenzoate (4e): White solid (2.13 g, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.8 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 3.90 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 152.1, 132.3, 127.4, 113.7, 91.7, 60.5, 56.1, 52.4. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{11}INaO_4^+$: 344.9594 ($M + Na)^+$, found:344.9599.



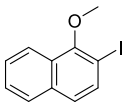
Methyl 3-iodo-2-methoxy-5-methylbenzoate (4f): Colorless oil (1.97 g, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 157.0, 143.7, 135.5, 132.2, 124.9, 93.7, 62.2, 52.4, 20.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{11}INaO_3^+$: 328.9645 ($M + Na)^+$, found:328.9641.



Methyl 5-chloro-3-iodo-2-methoxybenzoate (4g): White solid (2.04 g, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 2.6 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 158.1, 142.4, 131.6, 130.0, 126.0, 94.4, 62.5, 52.7. HRMS (ESI-TOF) *m/z*: calcd for $C_9H_8ClINaO_3^+$: 348.9099 ($M + Na)^+$, found: 348.9095.

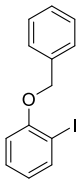


3-Iodo-2-methoxy-1,1'-biphenyl (4i): Colorless oil (1.78 g, 57% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 3.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 138.5, 138.0, 135.8, 131.5, 128.9, 128.4, 127.6, 126.1, 93.1, 60.3. MS (EI): (M^+): 309.99.

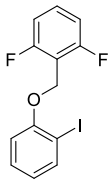


2-Iodo-1-methoxynaphthalene (4j): yellowish oil (1.71 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 1H), 7.87 – 7.81 (m, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.38 (d, *J* = 8.7 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 135.1, 134.7, 128.2, 128.0, 126.7, 126.6, 125.7, 122.2, 87.0, 61.5.

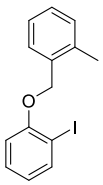
The data are identical to: Jumde, V. R.; Iuliano, A. *Eur. J. Org. Chem.* **2013**, *2013*, 4294-4302.



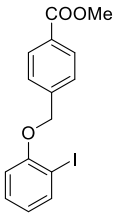
1-(Benzyloxy)-2-iodobenzene (6a): Colorless oil (1.42 g, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (td, *J* = 8.3, 1.6 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.74 (td, *J* = 7.6, 1.3 Hz, 1H), 5.17 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 139.5, 136.5, 129.4, 128.5, 127.8, 126.9, 122.8, 112.7, 86.8, 70.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{11}INaO^+$: 332.9747 (M + Na)$^+$, found: 332.9746.



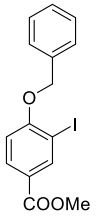
1,3-Difluoro-2-((2-iodophenoxy)methyl)benzene (6b): White solid (1.49 g, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.02 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.75 (td, *J* = 7.6, 1.2 Hz, 1H), 5.19 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 (dd, *J* = 251.5, 7.5 Hz), 157.2, 139.6, 130.8 (t, *J* = 10.4 Hz), 129.4, 123.3, 113.3, 112.2 (t, *J* = 18.9 Hz), 111.4 (dd, *J* = 20.9, 4.7 Hz), 59.4 (t, *J* = 3.6 Hz). HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_9F_2INaO^+$: 368.9558 (M + Na)$^+$, found: 368.9549.



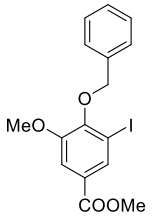
1-Iodo-2-((2-methylbenzyl)oxy)benzene (6c): White solid (1.34 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.16 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 5.09 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.3, 139.6, 136.2, 134.3, 130.3, 129.4, 128.2, 128.1, 126.0, 122.7, 112.5, 86.7, 69.4, 19.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{13}INaO^+$: 346.9903 (M + Na)$^+$, found: 346.9890.



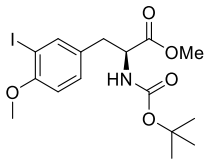
Methyl 4-((2-iodophenoxy)methyl)benzoate (6d): White solid (0.63 g, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 5.19 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 156.9, 141.6, 139.6, 129.9, 129.7, 129.4, 126.6, 123.1, 112.6, 86.7, 70.2, 52.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{13}INaO_3^+$: 390.9802 (M + Na)$^+$, found: 390.9783.



Methyl 4-(benzyloxy)-3-iodobenzoate (6e): White solid (1.10 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, *J* = 1.8 Hz, 1H), 7.98 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 5.21 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 160.7, 141.0, 135.7, 131.4, 128.6, 128.1, 126.9, 124.5, 111.4, 86.0, 70.9, 52.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{13}INaO_3^+$: 390.9802 (M + Na)$^+$, found: 390.9793.

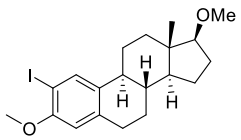


Methyl 4-(benzyloxy)-3-iodo-5-methoxybenzoate (6f): White solid (1.71 g, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.6 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 5.10 (s, 2H), 3.91 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 152.2, 151.5, 136.6, 132.5, 128.6, 128.3, 128.2, 127.5, 113.7, 92.3, 74.6, 56.1, 52.3. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{15}INaO_4^+$: 420.9907 $(M + Na)^+$, found: 420.9914.



Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(3-iodo-4-methoxyphenyl)propanoate (8a): Colorless foam (1.96 g, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.04 (d, *J* = 7.9 Hz, 1H), 4.51 – 4.45 (m, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.01 (dd, *J* = 13.9, 5.6 Hz, 1H), 2.91 (dd, *J* = 13.9, 6.1 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 157.1, 154.9, 140.1, 130.1, 110.7, 85.8, 79.8, 56.2, 54.4 52.1, 36.8, 28.2.

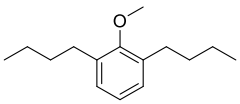
The data are identical to: Dufour, J.; Neuville, L.; Zhu, J. *Chem. Eur. J.* **2010,** *16*, 10523-10534.



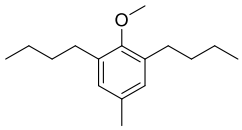
(8*R*,9*S*,13*S*,14*S*,17*S*)-2-Iodo-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (8b) : White solid (1.15 g, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (s, 1H), 6.53 (s, 1H), 3.83 (s, 3H), 3.38 (s, 3H), 3.31 (t, *J* = 8.3 Hz, 1H), 2.86 – 2.78 (m, 2H), 2.27 – 2.20 (m, 1H), 2.15 (td, *J* = 11.1, 4.1 Hz, 1H), 2.10 – 2.02 (m, 2H), 1.91 – 1.84 (m, 1H), 1.73 – 1.65 (m, 1H), 1.56 – 1.46 (m, 2H), 1.45 – 1.29 (m, 4H), 1.23 – 1.15 (m, 1H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 138.3, 136.4, 135.0, 111.4, 90.7, 82.5, 57.9, 56.3, 50.2, 43.6, 43.2, 38.3, 37.9, 29.7, 27.7, 27.0, 26.4, 23.0, 11.5.

The data are identical to: Zhao, B.; Fu, Y.; Shang, R. *Org. Lett.* **2019,** *21*, 9521-9526.

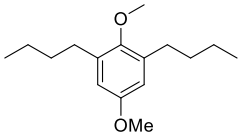
10. Characterization of the Products



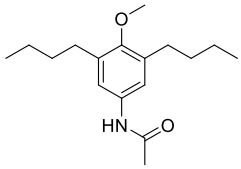
1,3-Dibutyl-2-methoxybenzene (3aa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (30.7 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 3.74 (s, 3H), 2.64 (t, *J* = 7.9 Hz, 4H), 1.63 – 1.57 (m, 4H), 1.44 – 1.37 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 135.7, 127.6, 123.9, 61.1, 33.0, 29.5, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{24}NaO^+$: 243.1719 $(M + Na)^+$, found: 243.1724.



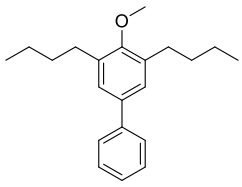
1,3-Dibutyl-2-methoxy-5-methylbenzene (3ba): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (32.9 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (s, 2H), 3.71 (s, 3H), 2.59 (t, *J* = 8.0 Hz, 4H), 2.27 (s, 3H), 1.62 – 1.57 (m, 4H), 1.45 – 1.36 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 135.4, 133.1, 128.2, 61.2, 33.1, 29.5, 22.9, 20.9, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{26}NaO^+$: 257.1876 $(M + Na)^+$, found: 257.1862.



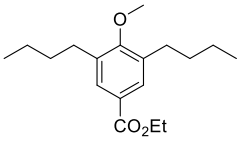
1,3-Dibutyl-2,5-dimethoxybenzene (3ca): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 40 : 1 as the eluent to give the title compound as a colorless oil (31.3 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (s, 2H), 3.77 (s, 3H), 3.69 (s, 3H), 2.61 (t, *J* = 8.0, 4H), 1.63 – 1.56 (m, 4H), 1.45 – 1.36 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 150.2, 136.6, 112.4, 61.3, 55.3, 33.0, 29.7, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{26}NaO_2^+$: 273.1825 $(M + Na)^+$, found: 273.1811.



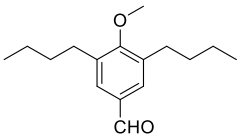
***N*-(3,5-Dibutyl-4-methoxyphenyl)acetamide (3da)**: Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 2 : 1 as the eluent to give the title compound as a colorless oil (36.8 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (bs, 1H), 7.15 (s, 2H), 3.68 (s, 3H), 2.58 (t, *J* = 7.9 Hz, 4H), 2.13 (s, 3H), 1.60 – 1.51 (m, 4H), 1.41 – 1.33 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 153.0, 136.2, 133.6, 119.4, 61.2, 32.9, 29.5, 24.4, 22.8, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{17}H_{27}NNaO_2^+$: 300.1934 $(M + Na)^+$, found: 300.1938.



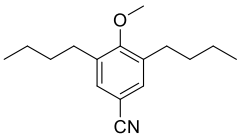
3,5-Dibutyl-4-methoxy-1,1'-biphenyl (3ea): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (41.9 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.25 (s, 2H), 3.77 (s, 3H), 2.69 (t, *J* = 7.9 Hz, 4H), 1.70 – 1.60 (m, 4H), 1.50 – 1.36 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 141.3, 136.8, 136.0, 128.6, 127.0, 126.8, 126.4, 61.3, 33.1, 29.7, 22.9, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{29}O^+$: 297.2213 $(M + H)^+$, found: 297.2208.



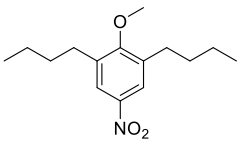
Ethyl 3,5-dibutyl-4-methoxybenzoate (3fa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (43.4 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.64 (t, *J* = 7.9 Hz, 4H), 1.64 – 1.58 (m, 4H), 1.44 – 1.35 (m, 7H), 0.95 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 160.5, 135.9, 129.2, 125.9, 61.2, 60.7, 32.8, 29.6, 22.8, 14.4, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{18}H_{28}NaO_3^+$: 315.1931 (M + Na)$^+$, found: 315.1930.



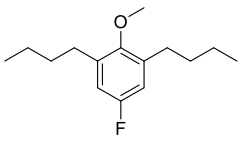
3,5-Dibutyl-4-methoxybenzaldehyde (3ga): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (27.1 mg, 55%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.58 (s, 2H), 3.78 (s, 3H), 2.68 (t, J = 7.8 Hz, 4H), 1.65 – 1.59 (m, 4H), 1.44 – 1.38 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.9, 162.0, 136.9, 132.4, 129.5, 61.2, 32.6, 29.5, 22.7, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{24}NaO_2^+$: 271.1669 (M + Na)$^+$, found: 271.1677.



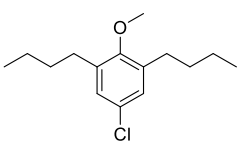
3,5-Dibutyl-4-methoxybenzonitrile (3ha): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (30.5 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (s, 2H), 3.75 (s, 3H), 2.62 (m, *J* = 7.9 Hz, 4H), 1.61 – 1.53 (m, 4H), 1.42 – 1.33 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 137.4, 131.6, 119.3, 107.5, 61.3, 32.4, 29.2, 22.6, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{23}NNaO^+$: 268.1672 (M + Na)$^+$, found: 268.1673.



1,3-Dibutyl-2-methoxy-5-nitrobenzene (3ia): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50 : 1 as the eluent to give the title compound as a colorless oil (24.4 mg, 46%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 2H), 3.78 (s, 3H), 2.68 (t, *J* = 7.9 Hz, 4H), 1.64 – 1.58 (m, 5H), 1.44 – 1.37 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 143.9, 137.3, 123.0, 61.3, 32.4, 29.5, 22.6, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{23}NNaO_3^+$: 288.1570 (M + Na)$^+$, found: 288.1566.

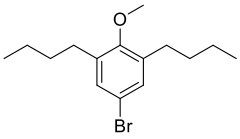


1,3-Dibutyl-5-fluoro-2-methoxybenzene (3ja): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (29.5 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 9.2 Hz, 2H), 3.69 (s, 3H), 2.60 (t, *J* = 7.9 Hz, 4H), 1.62 – 1.55 (m, 4H), 1.45 – 1.34 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.68 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9 (d, *J* = 240.9 Hz), 152.3 (d, *J* = 2.3 Hz), 137.4 (d, *J* = 7.8 Hz), 113.5 (d, *J* = 22.3 Hz), 61.3, 32.6, 29.5, 22.7, 14.0. MS (EI): (M$^+$): 238.20.

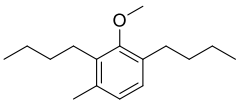


1,3-Dibutyl-5-chloro-2-methoxybenzene (3ka): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (26.5 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (s, 2H), 3.70 (s, 3H), 2.59 (t, *J* = 7.9 Hz, 4H), 1.61 –

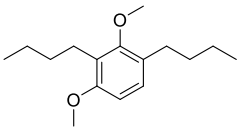
1.54 (m, 4H), 1.42 – 1.36 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 137.6, 128.8, 127.3, 61.3, 32.7, 29.4, 22.7, 14.0. MS (EI): (M^+): 254.16.



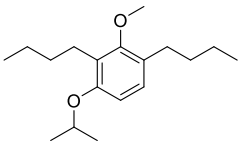
5-Bromo-1,3-dibutyl-2-methoxybenzene (3la): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (29.8 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (s, 2H), 3.70 (s, 3H), 2.58 (t, *J* = 8.0 Hz, 4H), 1.61 – 1.53 (m, 4H), 1.43 – 1.35 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 138.1, 130.3, 116.7, 61.2, 32.7, 29.4, 22.7, 13.9. MS (EI): (M^+): 298.12.



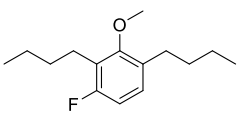
1,3-Dibutyl-2-methoxy-4-methylbenzene (3ma): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (30.1 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 3.73 (s, 3H), 2.63 – 2.57 (m, 4H), 2.28 (s, 3H), 1.61 – 1.58 (m, 2H), 1.49 – 1.38 (m, 6H), 0.94 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 135.2, 134.6, 133.1, 127.0, 125.9, 61.4, 33.0, 32.3, 29.4, 26.9, 23.3, 22.9, 19.2, 14.0, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{26}NaO^+$: 257.1876 $(M + Na)^+$, found: 257.1866.



1,3-Dibutyl-2,4-dimethoxybenzene (3na): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 40 : 1 as the eluent to give the title compound as a colorless oil (33.2 mg, 66%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.58 (t, J = 7.9 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.55 – 1.48 (m, 2H), 1.46 – 1.36 (m, 4H), 0.95 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 156.8, 127.9, 126.9, 124.7, 106.3, 61.4, 55.5, 33.2, 32.2, 29.2, 24.0, 23.2, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{27}O_2^+$: 251.2006 $(M + H)^+$, found: 251.1997.

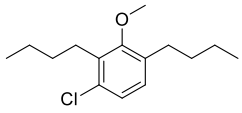


1,3-Dibutyl-4-isopropoxy-2-methoxybenzene (3oa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 40 : 1 as the eluent to give the title compound as a colorless oil (27.4 mg, 49%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 4.53 – 4.45 (m, 1H), 3.73 (s, 3H), 2.61 (t, *J* = 7.9 Hz, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.54 – 1.49 (m, 2H), 1.44 – 1.36 (m, 4H), 1.32 (d, *J* = 6.0 Hz, 6H), 0.97 – 0.91 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 155.0, 127.4, 126.8, 125.6, 108.6, 69.7, 61.4, 33.2, 32.1, 29.2, 24.0, 23.2, 22.8, 22.2, 14.0, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{18}H_{30}NaO_2^+$: 301.2138 $(M + Na)^+$, found: 301.2124.

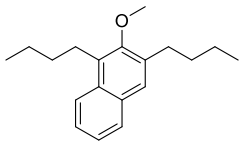


1,3-Dibutyl-4-fluoro-2-methoxybenzene (3pa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (33.5 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (t, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 8.8 Hz, 1H), 3.75 (s, 3H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 1.59 – 1.53 (m, 4H), 1.45 – 1.34 (m, 4H), 0.97 – 0.92 (m, 6H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.61 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1 (d, *J* = 242.9 Hz), 157.2 (d, *J* = 7.2 Hz), 131.2 (d, *J* = 3.4 Hz), 127.3 (d, *J* = 10.0 Hz), 123.5 (d, *J* = 16.5 Hz),

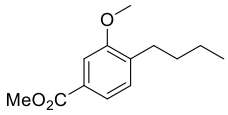
110.8 (d, *J* = 22.5 Hz), 61.6, 33.0, 32.4 (d, *J* = 1.2 Hz), 29.2, 23.5 (d, *J* = 2.4 Hz), 22.9, 22.7, 14.0, 13.9. MS (EI): (M^+): 238.19.



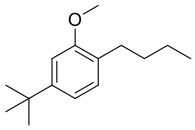
1,3-Dibutyl-4-chloro-2-methoxybenzene (3qa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (32.9 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 3.74 (s, 3H), 2.74 (t, *J* = 7.9 Hz, 2H), 2.59 (t, *J* = 7.9 Hz, 2H), 1.60 – 1.54 (m, 4H), 1.47 – 1.41 (m, 2H), 1.41 – 1.35 (m, 2H), 0.98 – 0.92 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.3, 134.5, 134.4, 132.1, 127.9, 125.1, 61.6, 32.8, 31.8, 29.3, 27.6, 23.1, 22.7, 14.0, 14.0. MS (EI): (M^+): 254.17.



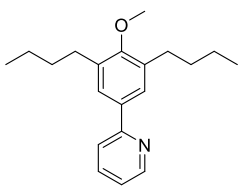
1,3-Dibutyl-2-methoxynaphthalene (3ra): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (24.1 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.82 (s, 3H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.68 – 1.64 (m, 2H), 1.56 – 1.49 (m, 2H), 1.48 – 1.41 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 135.7, 131.8, 131.3, 129.8, 127.9, 126.7, 125.0, 124.3, 123.8, 61.6, 33.2, 32.7, 30.3, 25.8, 23.4 22.8, 14.0, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{26}NaO^+$: 293.1876 $(M + Na)^+$, found: 293.1884.



Methyl 4-butyl-3-methoxybenzoate (3sa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (25.3 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.49 (s, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.64 (t, J = 7.7 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.39 – 1.32 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 157.3, 137.1, 129.5, 128.7, 121.9, 110.8, 55.4, 52.0, 31.6, 30.0, 22.6, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_3^+$: 245.1148 $(M + Na)^+$, found: 245.1146.

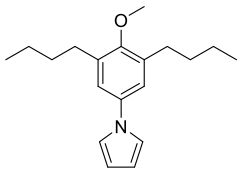


4-(*tert*-Butyl)-1-butyl-2-methoxybenzene (3ta): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (35.4 mg, 80%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 3.85 (s, 3H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.43 – 1.35 (m, 2H), 1.33 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 150.0, 129.1, 128.3, 117.1, 107.7, 55.3, 34.7, 32.1, 31.4, 29.4, 22.7, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{24}NaO^+$: 243.1719 $(M + Na)^+$, found: 243.1714.

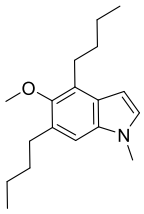


2-(3,5-Dibutyl-4-methoxyphenyl)pyridine (3ua): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (30.3 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.3 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.66 (s, 2H), 7.20 – 7.14 (m, 1H), 3.77 (s, 3H), 2.70 (t, *J* = 7.9 Hz, 4H), 1.70 – 1.62 (m, 4H),

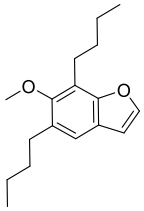
1.47 – 1.39 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 157.5, 149.5, 136.5, 136.1, 135.0, 126.3, 121.5, 120.3, 61.2, 33.1, 29.8, 22.9, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{27}NNaO^+$: 320.1985 $(M + Na)^+$, found: 320.1985.



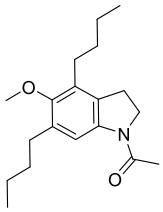
1-(3,5-Dibutyl-4-methoxyphenyl)-1H-pyrrole (3va): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 30 : 1 as the eluent to give the title compound as a colorless oil (35.1 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (s, 2H), 7.02 (t, *J* = 2.1 Hz, 2H), 6.32 (t, *J* = 2.1 Hz, 2H), 3.75 (s, 3H), 2.66 (t, *J* = 8.0 Hz, 4H), 1.66 – 1.59 (m, 4H), 1.46 – 1.38 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 137.0, 136.8, 120.0, 119.6, 109.8, 61.3, 32.9, 29.6, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{28}NO^+$: 286.2165 $(M + H)^+$, found: 286.2158.



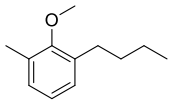
4,6-Dibutyl-5-methoxy-1-methyl-1H-indole (3wa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 40 : 1 as the eluent to give the title compound as a colorless oil (34.3 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 – 6.96 (m, 2H), 6.43 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 1.73 – 1.66 (m, 4H), 1.50 – 1.43 (m, 4H), 1.00 – 0.95 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 133.5, 130.7, 128.1, 126.9, 126.6, 107.3, 99.4, 61.9, 33.7, 33.0, 32.9, 30.6, 27.4, 23.3, 22.9, 14.1, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{18}H_{28}NO^+$: 274.2165 $(M + H)^+$, found: 274.2170.



5,7-dibutyl-6-methoxybenzofuran (3xa): Purified by preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless oil (31.3 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.23 (s, 1H), 6.66 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 2.90 (t, *J* = 7.9 Hz, 2H), 2.70 (t, *J* = 7.9 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.67 – 1.60 (m, 2H), 1.49 – 1.38 (m, 4H), 0.99 – 0.93 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 153.0, 144.6, 131.3, 123.0, 119.6, 118.2, 106.3, 61.9, 33.4, 32.1, 30.0, 24.5, 23.1, 22.8, 14.0, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{17}H_{25}O_2^+$: 261.1849 $(M + H)^+$, found: 261.1836.

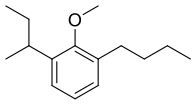


1-(4,6-Dibutyl-5-methoxyindolin-1-yl)ethan-1-one (3ya): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 2 : 1 as the eluent to give the title compound as a colorless oil (39.2 mg, 65%). NMR spectra showed a 6 : 1 mixture of rotamers. Only signals for the major rotamer are recorded. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 4.02 (t, *J* = 8.4 Hz, 2H), 3.70 (s, 3H), 3.08 (t, *J* = 8.4 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.19 (s, 3H), 1.62 – 1.56 (m, 2H), 1.54 – 1.46 (m, 2H), 1.42 – 1.37 (m, 4H), 0.96 – 0.90 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 152.7, 138.8, 134.9, 131.9, 128.6, 115.8, 61.6, 49.0, 33.3, 31.9, 30.0, 27.5, 26.7, 24.1, 23.0, 22.9, 13.9, 13.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{30}NO_2^+$: 304.2271 $(M + H)^+$, found: 304.2272.

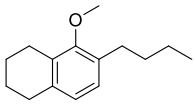


1-Butyl-2-methoxy-3-methylbenzene (5aa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (25.3 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 –

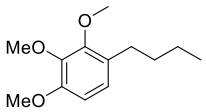
7.00 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 3.74 (s, 3H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.30 (s, 3H), 1.63 – 1.56 (m, 2H), 1.43 – 1.37 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 135.6, 130.9, 128.8, 127.7, 123.8, 60.3, 33.1, 29.5, 22.8, 16.2, 14.0. MS (EI): (M^+): 178.16.



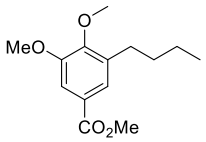
1-(*sec*-Butyl)-3-butyl-2-methoxybenzene (5ba): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (41.3 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 7.01 (m, 3H), 3.72 (s, 3H), 3.10 – 3.03 (m, 1H), 2.66 – 2.61 (m, 2H), 1.63 – 1.55 (m, 4H), 1.44 – 1.37 (m, 2H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 140.7, 135.6, 127.3, 124.4, 124.1, 61.6, 33.3, 33.0 30.9, 29.6, 22.9, 21.9, 14.0, 12.4. MS (EI): (M^+): 220.20.



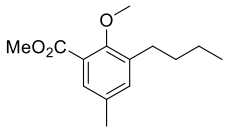
6-Butyl-5-methoxy-1,2,3,4-tetrahydronaphthalene (5ca): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (27.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.75 (s, 3H), 2.83 – 2.74 (m, 4H), 2.62 (t, *J* = 7.9 Hz, 2H), 1.86 – 1.75 (m, 4H), 1.64 – 1.57 (m, 2H), 1.49 – 1.38 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 136.3, 132.3, 130.5, 126.9, 124.8, 60.2, 33.2, 29.2, 23.6, 22.9, 22.9, 22.8, 14.0. MS (EI): (M^+): 218.19.



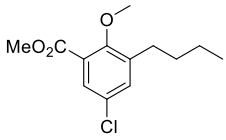
1-Butyl-2,3,4-trimethoxybenzene (5da): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (32.6 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.45 – 1.34 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 151.7, 142.2, 128.9, 123.7, 107.1, 60.9, 60.7, 56.0, 33.1, 29.3, 22.6, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{20}NaO_3^+$: 247.1305 $(M+Na)^+$, found: 247.1305.



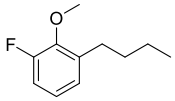
Methyl 3-butyl-4,5-dimethoxybenzoate (5ea): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (33.4 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.42 – 1.30 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 152.3, 151.2, 136.5, 125.2, 123.9, 111.0, 60.6, 55.8, 52.0, 32.7, 29.6, 22.6, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{20}NaO_4^+$: 275.1254 $(M+Na)^+$, found: 275.1259.



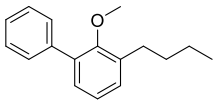
Methyl 3-butyl-2-methoxy-5-methylbenzoate (5fa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (38.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.15 (d, *J* = 1.9 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.29 (s, 3H), 1.63 – 1.52 (m, 2H), 1.43 – 1.31 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 155.9, 137.1, 134.9, 132.9, 129.4, 124.0, 62.3, 52.1, 32.9, 29.4, 22.7, 20.6, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{20}NaO_3^+$: 259.1305 $(M+Na)^+$, found: 259.1295.



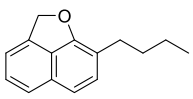
Methyl 3-butyl-5-chloro-2-methoxybenzoate (5ga): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (40.6 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 2.3 Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.42 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 156.9, 139.5, 133.8, 128.8, 128.6, 125.6, 62.5, 52.4, 32.5, 29.3, 22.6, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{17}ClNaO_3^+$: 279.0758 $(M+Na)^+$, found: 279.0756.



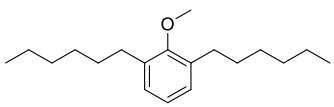
1-Butyl-3-fluoro-2-methoxybenzene (5ha): Purified by preparative thin-layer chromatograph using cyclohexane as the eluent to give the title compound as a colorless oil (26.1 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (t, *J* = 6.2 Hz, 3H), 3.91 (s, 3H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.60 – 1.54 (m, 2H), 1.42 – 1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -131.07 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7 (d, *J* = 246.1 Hz), 145.6 (d, *J* = 10.2 Hz), 137.6 (s), 125.0 (d, *J* = 2.9 Hz), 123.2 (d, *J* = 8.1 Hz), 114.2 (d, *J* = 19.3 Hz), 61.2 (d, *J* = 5.9 Hz), 32.8, 29.6, 22.6, 13.9. MS (EI): (M^+): 182.13.



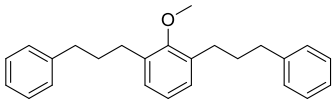
3-Butyl-2-methoxy-1,1'-biphenyl (5ia): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (38.4 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 3.34 (s, 3H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.47 – 1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 139.0, 136.3, 134.8, 129.3, 129.0, 128.8, 128.2, 126.9, 123.9, 60.5, 33.2, 29.8, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{17}H_{21}O^+$: 241.1587 $(M+H)^+$, found: 241.1582.



8-butyl-2*H*-naphtho[1,8-*bc*]furan (5ja): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (35.7 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.15 (m, 2H), 5.77 (s, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.43 – 1.37 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 138.6, 131.7, 130.3, 128.5, 127.5, 122.6, 116.0, 115.3, 115.0, 76.8, 32.4, 29.0, 22.5, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{17}O^+$: 213.1274 $(M+H)^+$, found: 213.1269.

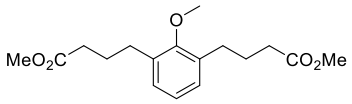


1,3-Dihexyl-2-methoxybenzene (3ab): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (41.8 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.2 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 3.73 (s, 3H), 2.62 (t, *J* = 8.0 Hz, 4H), 1.68 – 1.55 (m, 4H), 1.40 – 1.35 (m, 4H), 1.34 – 1.27 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 135.8, 127.6, 123.9, 61.1, 31.7, 30.8, 29.8, 29.5, 22.6, 14.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{32}NaO^+$: 299.2345 $(M+Na)^+$, found: 299.2331.

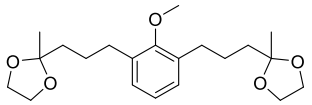


((2-Methoxy-1,3-phenylene)bis(propane-3,1-diyl))dibenzene (3ac): Purified by preparative thin-layer chromatograph using petroleum

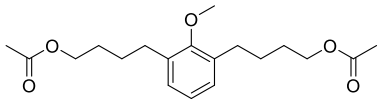
ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (50.4 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 4H), 7.20 (d, *J* = 7.6 Hz, 4H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.97 (t, J = 7.3 Hz, 1H), 3.61 (s, 3H), 2.70 – 2.64 (m, 8H), 1.98 – 1.92 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 142.3, 135.2, 128.4, 128.2, 127.8, 125.7, 124.0, 61.0, 35.8, 32.2, 29.5. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{28}NaO^+$: 367.2032 $(M+Na)^+$, found: 367.2023.



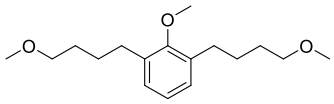
Dimethyl 4,4'-(2-methoxy-1,3-phenylene)dibutyrate (3ad): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 8 : 1 as the eluent to give the title compound as a colorless oil (39.5 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 6H), 2.66 (t, *J* = 7.7 Hz, 4H), 2.36 (t, *J* = 7.5 Hz, 4H), 1.98 – 1.91 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 156.6, 134.4, 128.1, 124.1, 61.1, 51.4, 33.7, 29.1, 25.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{17}H_{24}NaO_5^+$: 331.1516 $(M+Na)^+$, found: 331.1510.



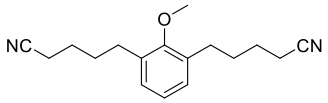
2,2'-((2-methoxy-1,3-phenylene)bis(propane-3,1-diyl))bis(2-methyl-1,3-dioxolane) (3ae): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (43.8 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 3.95 – 3.89 (m, 8H), 3.72 (s, 3H), 2.66 – 2.61 (m, 4H), 1.75 – 1.68 (m, 8H), 1.31 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 135.2, 127.7, 123.9, 110.0, 64.6, 61.2, 39.1, 29.7, 25.0, 23.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{32}NaO_5^+$: 387.2142 $(M+Na)^+$, found: 387.2137.



(2-methoxy-1,3-phenylene)bis(butane-4,1-diyl) diacetate (3af): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (48.9 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 4.08 (t, *J* = 6.2 Hz, 4H), 3.71 (s, 3H), 2.65 (t, *J* = 7.3 Hz, 4H), 2.03 (s, 6H), 1.70 – 1.66 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 156.4, 135.0, 127.8, 124.08, 64.3, 61.1, 29.3, 28.5, 26.9, 20.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{28}NaO_5^+$: 359.1829 $(M+Na)^+$, found: 359.1815.

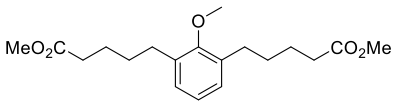


2-Methoxy-1,3-bis(4-methoxybutyl)benzene (3ag): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (39.7 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.4 Hz, 2H), 6.97 (t, J = 7,4 Hz, 1H), 3.73 (s, 3H), 3.40 (t, *J* = 5.9 Hz, 4H), 3.33 (s, 6H), 2.65 (t, *J* = 7.2 Hz, 4H), 1.71 – 1.61 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 135.3, 127.7, 123.9, 72.7, 61.1, 58.5, 29.6, 29.6, 27.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{17}H_{28}NaO_3^+$: 303.1931 $(M+Na)^+$, found: 303.1928.

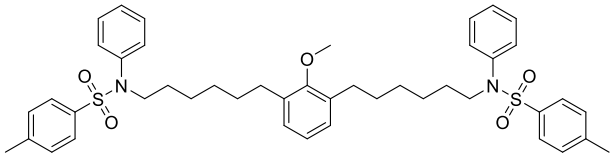


5,5'-(2-methoxy-1,3-phenylene)dipentanenitrile (3ah): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 8: 1 as the eluent to give the title compound as a colorless oil (39.0 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 6.99 (m, 3H),

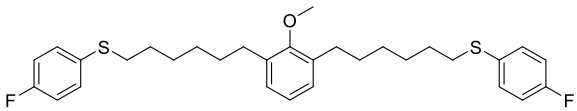
3.72 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 4H), 2.37 (t, *J* = 7.1 Hz, 4H), 1.82 – 1.75 (m, 4H), 1.72 – 1.66 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 134.3, 128.0, 124.3, 119.6, 61.2, 29.5, 28.8, 25.0, 16.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{17}H_{22}N_2NaO^+$: 293.1624 (M +Na)$^+$, found: 293.1602.



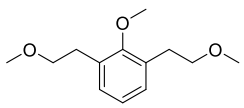
Dimethyl 5,5'-(2-methoxy-1,3-phenylene)dipentanoate (3ai): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 8: 1 as the eluent to give the title compound as a colorless oil (50.5 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 6H), 2.63 (t, *J* = 7.7 Hz, 4H), 2.35 (t, *J* = 7.3 Hz, 4H), 1.73 – 1.67 (m, 4H), 1.67 – 1.60 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 156.4, 135.0, 127.7, 124.0, 61.1, 51.4, 33.9, 30.1, 29.4, 24.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{28}NaO_5^+$: 359.1829 (M +Na)$^+$, found: 359.1811.



***N,N'*-((2-methoxy-1,3-phenylene)bis(hexane-6,1-diyl))bis(4-methyl-*N*-phenylbenzenesulfonamide) (3aj):** Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 7 : 1 as the eluent to give the title compound as a colorless oil (127.4 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 4H), 7.32 – 7.27 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.05 – 7.01 (m, 4H), 6.98 – 6.94 (m, 3H), 3.67 (s, 3H), 3.51 (t, *J* = 6.9 Hz, 4H), 2.56 (t, *J* = 7.7 Hz, 4H), 2.41 (s, 6H), 1.57 – 1.50 (m, 4H), 1.43 – 1.38 (m, 4H), 1.36 – 1.28 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 143.1, 139.1, 135.4, 135.3, 129.3, 128.8, 128.7, 127.7, 127.6, 127.5, 123.8, 61.1, 50.4, 30.5, 29.6, 29.1, 28.1, 26.2, 21.4. HRMS (ESI-TOF) *m/z*: calcd for $C_{45}H_{54}N_2NaO_5S_2^+$: 789.3366 (M +Na)$^+$, found: 789.3375.

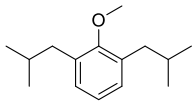


((2-Methoxy-1,3-phenylene)bis(hexane-6,1-diyl))bis((4-fluorophenyl)sulfane) (3ak): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 40 : 1 as the eluent to give the title compound as a colorless oil (56.0 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.04 – 6.96 (m, 7H), 3.71 (s, 3H), 2.86 (t, *J* = 7.4 Hz, 4H), 2.62 (t, *J* = 7.8 Hz, 4H), 1.67 – 1.57 (m, 8H), 1.49 – 1.43 (m, 4H), 1.41 – 1.35 (m, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.13 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5 (d, *J* = 245.7 Hz), 156.4, 135.5, 131.9 (d, *J* = 7.9 Hz), 131.6 (d, *J* = 3.2 Hz), 127.6, 123.9, 115.9 (d, *J* = 21.7 Hz), 61.1, 34.9, 30.6, 29.7, 29.1, 29.1, 28.5. HRMS (ESI-TOF) *m/z*: calcd for $C_{31}H_{39}F_2OS_2^+$: 529.2405 (M +H)$^+$, found: 529.2410.

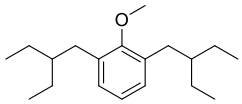


2-Methoxy-1,3-bis(2-methoxyethyl)benzene (3al): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (23.3 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.4 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.61 (t, *J* = 7.1 Hz, 4H), 3.37 (s, 6H), 2.93 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 131.8, 128.8, 124.1,

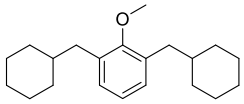
72.9, 61.3, 58.6, 30.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{20}NaO_3^+$: 247.1305 (M +Na)$^+$, found: 247.1298.



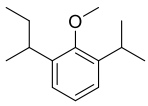
1,3-Diisobutyl-2-methoxybenzene (3am): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (22.9 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 – 6.95 (m, 3H), 3.71 (s, 3H), 2.50 (d, *J* = 7.2 Hz, 4H), 1.98 – 1.89 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 134.5, 128.5, 123.5, 60.9, 39.2, 29.4, 22.6. MS (EI): (M$^+$): 220.20.



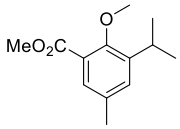
1,3-Bis(2-ethylbutyl)-2-methoxybenzene (3an): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (28.8 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.2 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 3.71 (s, 3H), 2.54 (d, *J* = 7.2 Hz, 4H), 1.62 – 1.55 (m, 2H), 1.32 – 1.26 (m, 8H), 0.87 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 134.8, 128.4, 123.4, 60.8, 41.6, 34.0, 25.3, 10.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{32}NaO^+$: 299.2345 (M +Na)$^+$, found: 299.2335.



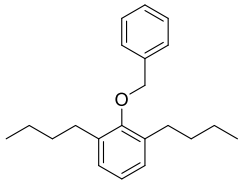
((2-Methoxy-1,3-phenylene)bis(methylene))dicyclohexane (3ao): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 60 : 1 as the eluent to give the title compound as a colorless oil (33.0 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 6.8 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 2.51 (d, *J* = 7.1 Hz, 4H), 1.73 – 1.66 (m, 8H), 1.65 – 1.57 (m, 4H), 1.24 – 1.13 (m, 6H), 1.02 – 0.93 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 134.1, 128.5, 123.3, 61.0, 38.9, 37.9, 33.4, 26.6, 26.4. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{32}NaO^+$: 323.2345 (M +Na)$^+$, found: 323.2325.



1-(*sec*-Butyl)-3-isopropyl-2-methoxybenzene (5bp): Purified by preparative thin-layer chromatograph using cyclohexane as the eluent to give the title compound as a colorless oil (19.6 mg, 48%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.02 (m, 3H), 3.73 (s, 3H), 3.41 – 3.30 (m, 1H), 3.13 – 3.03 (m, 1H), 1.63 – 1.56 (m, 2H), 1.26 – 1.19 (m, 9H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 141.6, 140.7, 124.4, 124.3, 123.9, 62.1, 33.4, 31.0, 26.5, 24.1, 24.0, 21.9, 12.4. MS (EI): (M$^+$): 206.19.

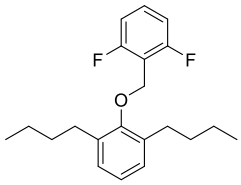


Methyl 3-isopropyl-2-methoxy-5-methylbenzoate (5fp): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (23.5 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.21 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.41 – 3.33 (m, 1H), 2.32 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 155.1, 142.9, 133.2, 131.5, 129.2, 124.0, 62.8, 52.1, 26.1, 23.7, 20.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_3^+$: 245.1148 (M +Na)$^+$, found: 245.1140.

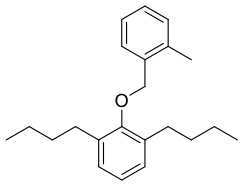


2-(Benzyloxy)-1,3-dibutylbenzene (7aa): Purified by preparative thin-layer chromatograph using cyclohexane as the eluent to give the title compound as a colorless oil (35.0 mg, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 2H),

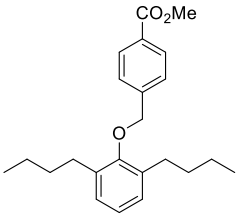
7.03 (t, *J* = 7.4 Hz, 1H), 4.83 (s, 2H), 2.67 (t, *J* = 8.0 Hz, 4H), 1.67 – 1.58 (m, 4H), 1.41 – 1.34 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 137.9, 136.0, 128.5, 127.8, 127.6, 127.5, 124.1, 75.4, 33.0, 29.8, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{28}NaO^+$: 319.2032 $(M+Na)^+$, found: 319.2026.



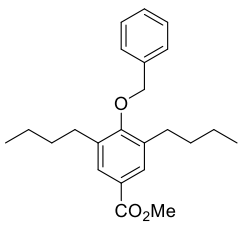
1,3-Dibutyl-2-((2,6-difluorobenzyl)oxy)benzene (7ba): Purified by preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless oil (37.7 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 1H), 7.07 (d, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.94 (m, 2H), 4.88 (s, 2H), 2.74 (t, *J* = 8.0 Hz, 4H), 1.65 – 1.57 (m, 4H), 1.45 – 1.37 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.57 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2 (dd, *J* = 250.9, 7.8 Hz), 154.5, 136.4, 130.6 (t, *J* = 10.4 Hz), 127.7 (s), 124.4, 113.3 (t, *J* = 19.7 Hz), 111.4 (dd, *J* = 21.2, 4.8 Hz), 62.4, 33.2, 29.4, 22.9, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{26}F_2NaO^+$: 355.1844 $(M+Na)^+$, found: 355.1845.



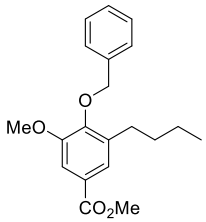
1,3-Dibutyl-2-((2-methylbenzyl)oxy)benzene (7ca): Purified by preparative thin-layer chromatograph using cyclohexane as the eluent to give the title compound as a colorless oil (23.0 mg, 37%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 1H), 7.28 – 7.23 (m, 2H), 7.22 – 7.18 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.83 (s, 2H), 2.64 (t, *J* = 7.9 Hz, 4H), 2.37 (s, 3H), 1.65 – 1.56 (m, 4H), 1.39 – 1.31 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 136.2, 136.1, 135.6, 130.1, 127.7, 127.7, 127.6, 126.0, 124.1, 73.5, 33.1, 29.8, 22.8, 18.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{22}H_{30}NaO^+$: 333.2189 $(M+Na)^+$, found: 333.2186.



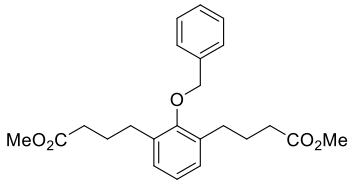
Methyl 4-((2,6-dibutylphenoxy)methyl)benzoate (7da): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (35.5 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 4.89 (s, 2H), 3.94 (s, 3H), 2.64 (t, *J* = 7.8 Hz, 4H), 1.65 – 1.58 (m, 4H), 1.40 – 1.32 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 155.0, 143.1, 135.9, 129.8, 129.5, 127.7, 126.8, 124.3, 74.5, 52.1, 33.0, 29.8, 22.8, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{23}H_{30}NaO_3^+$: 377.2087 $(M+Na)^+$, found: 377.2085.



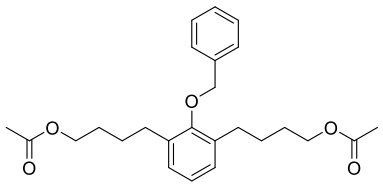
Methyl 4-(benzyloxy)-3,5-dibutylbenzoate (7ea): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a colorless oil (37.0 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 1H), 4.84 (s, 2H), 3.90 (s, 3H), 2.67 (t, *J* = 7.9 Hz, 4H), 1.66 – 1.59 (m, 4H), 1.41 – 1.32 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 159.3, 137.3, 136.3, 129.3, 128.5, 128.1, 127.5, 125.8, 75.5, 51.9, 32.8, 29.8, 22.7, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{23}H_{30}NaO_3^+$: 377.2087 $(M+Na)^+$, found: 377.2083.



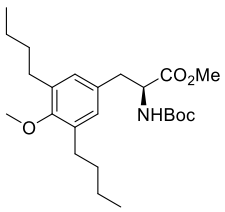
Methyl 4-(benzyloxy)-3-butyl-5-methoxybenzoate (7fa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (42.0 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.47 (s, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 5.06 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.55 – 1.48 (m, 2H), 1.36 – 1.27 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 152.4, 149.9, 137.6, 136.9, 128.3, 128.0, 127.9, 125.3, 123.9, 111.0, 74.6, 55.8, 52.0, 32.6, 29.8, 22.6, 13.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{24}NaO_4^+$: 351.1567 $(M+Na)^+$, found: 351.1561.



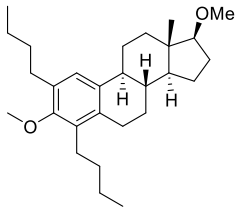
Dimethyl 4,4'-(2-(benzyloxy)-1,3-phenylene)dibutyrate (7ad): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (47.6 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.81 (s, 2H), 3.62 (s, 6H), 2.69 (t, *J* = 7.6 Hz, 4H), 2.32 (t, *J* = 7.4 Hz, 4H), 2.00 – 1.93 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 155.4, 137.6, 134.7, 128.5, 128.2, 127.9, 127.3, 124.4, 75.4, 51.4, 33.6, 29.3, 25.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{23}H_{28}NaO_5^+$: 407.1829 $(M+Na)^+$, found: 407.1813.



(2-(Benzyloxy)-1,3-phenylene)bis(butane-4,1-diyl) diacetate (7af): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colorless oil (43.7 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.1 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.82 (s, 2H), 4.06 (t, *J* = 6.1 Hz, 4H), 2.69 (t, *J* = 7.3 Hz, 4H), 2.02 (s, 6H), 1.73 – 1.62 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 155.3, 137.6, 135.3, 128.5, 127.9, 127.9, 127.3, 124.3, 75.4, 64.3, 29.6, 28.5, 27.0, 20.9. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{32}NaO_5^+$: 435.2142 $(M+Na)^+$, found: 435.2126.



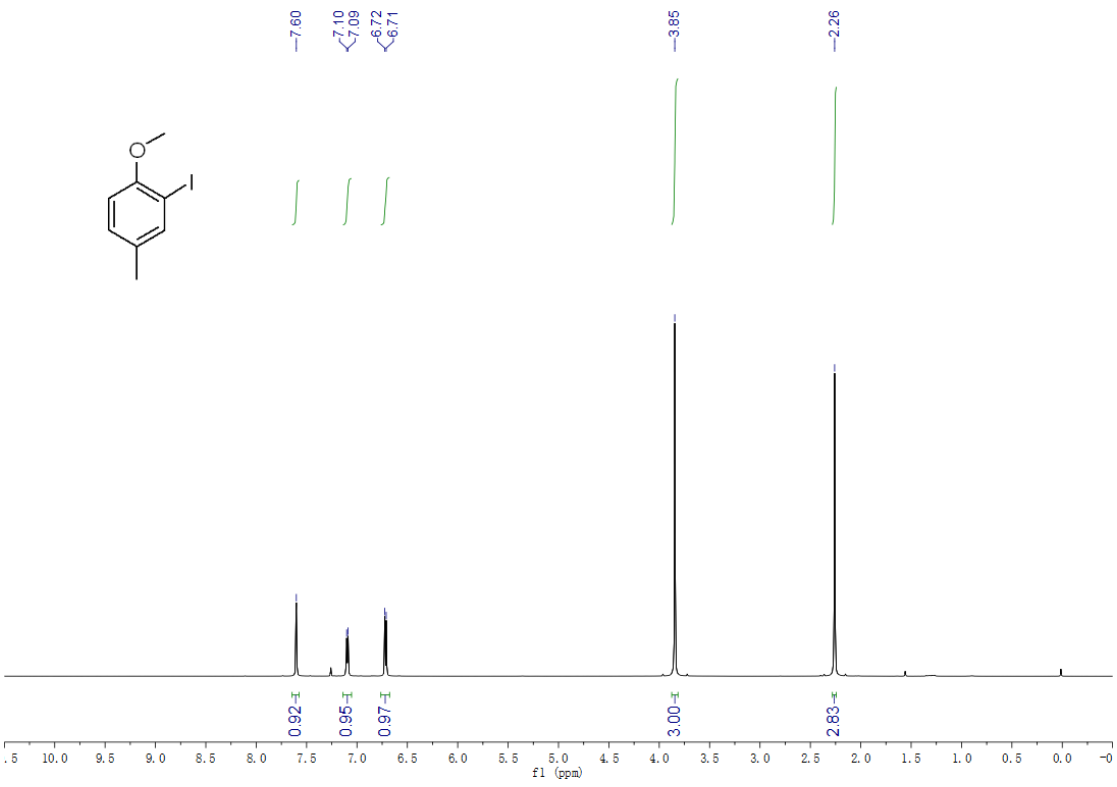
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(3,5-dibutyl-4-methoxyphenyl)propanoate (9aa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 4 : 1 as the eluent to give the title compound as a colorless oil (49.0 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.75 (s, 2H), 4.95 (d, *J* = 8.0 Hz, 1H), 4.57 – 4.50 (m, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.04 – 2.94 (m, 2H), 2.58 (t, *J* = 7.9 Hz, 4H), 1.60 – 1.52 (m, 4H), 1.41 (s, 9H), 1.40 – 1.34 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 155.4, 155.0, 135.6, 131.1, 128.5, 79.7, 61.1, 54.4, 52.1, 37.6, 33.0 29.4, 28.3, 22.8, 14.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{39}NNaO_5^+$: 444.2720 $(M+Na)^+$, found: 444.2720.

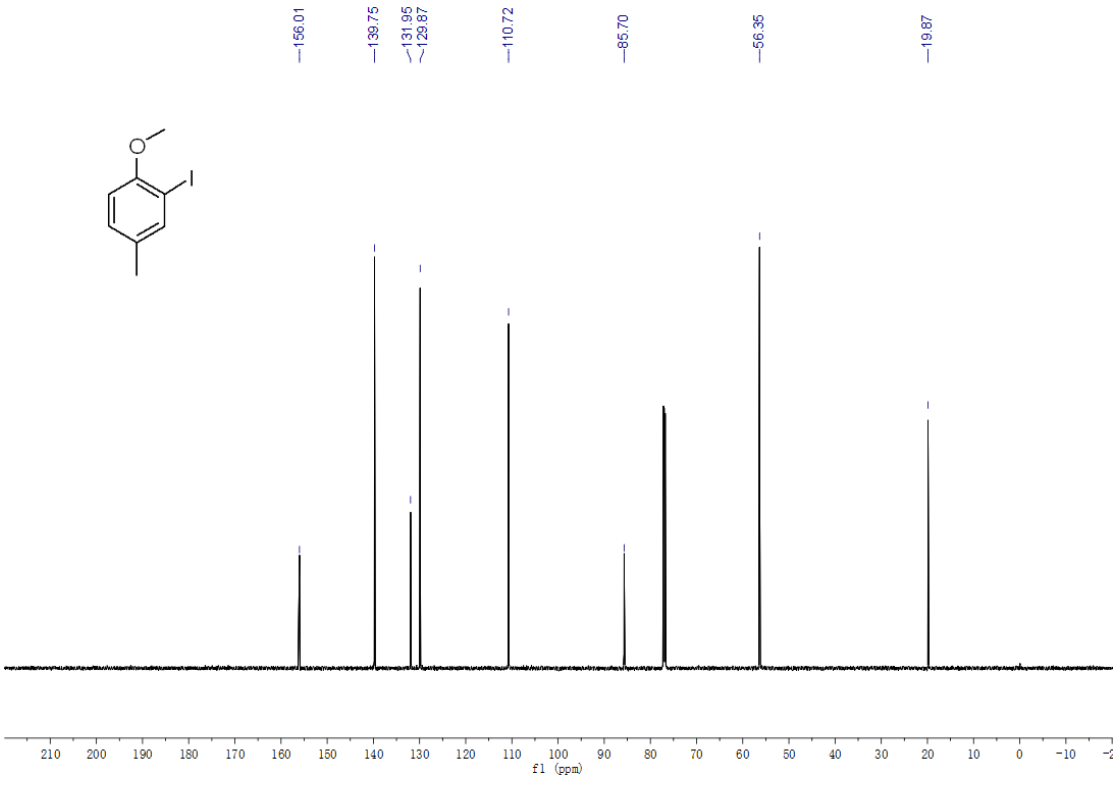


(8*R*,9*S*,13*S*,14*S*,17*S*)-2,4-Dibutyl-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (9ba): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50 : 1 as the eluent to give the title compound as a colorless oil (33.8 mg, 41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (s, 1H), 3.73 (s, 3H), 3.38 (s, 3H), 3.32 (t, *J* = 8.3 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.76 – 2.66 (m, 1H), 2.63 – 2.54 (m, 4H), 2.36 – 2.27 (m, 1H), 2.25 – 2.15 (m, 1H), 2.12 – 2.02 (m, 2H), 1.97 – 1.90 (m, 1H), 1.75 – 1.67 (m, 1H), 1.54 – 1.24 (m, 14H), 1.23 – 1.15 (m, 1H), 1.00 – 0.92 (m, 6H), 0.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 136.1, 133.9, 133.6, 132.4, 124.6, 90.8, 61.4, 57.9, 50.5, 44.5, 43.1, 38.1, 37.8, 33.3, 32.2, 29.8, 27.8, 27.5, 26.6, 26.5, 26.4, 23.5, 23.0, 14.0, 13.9, 11.5. HRMS (ESI-TOF) *m/z*: calcd for $C_{28}H_{44}NaO_2^+$: 435.3234 $(M+Na)^+$, found: 435.3245.

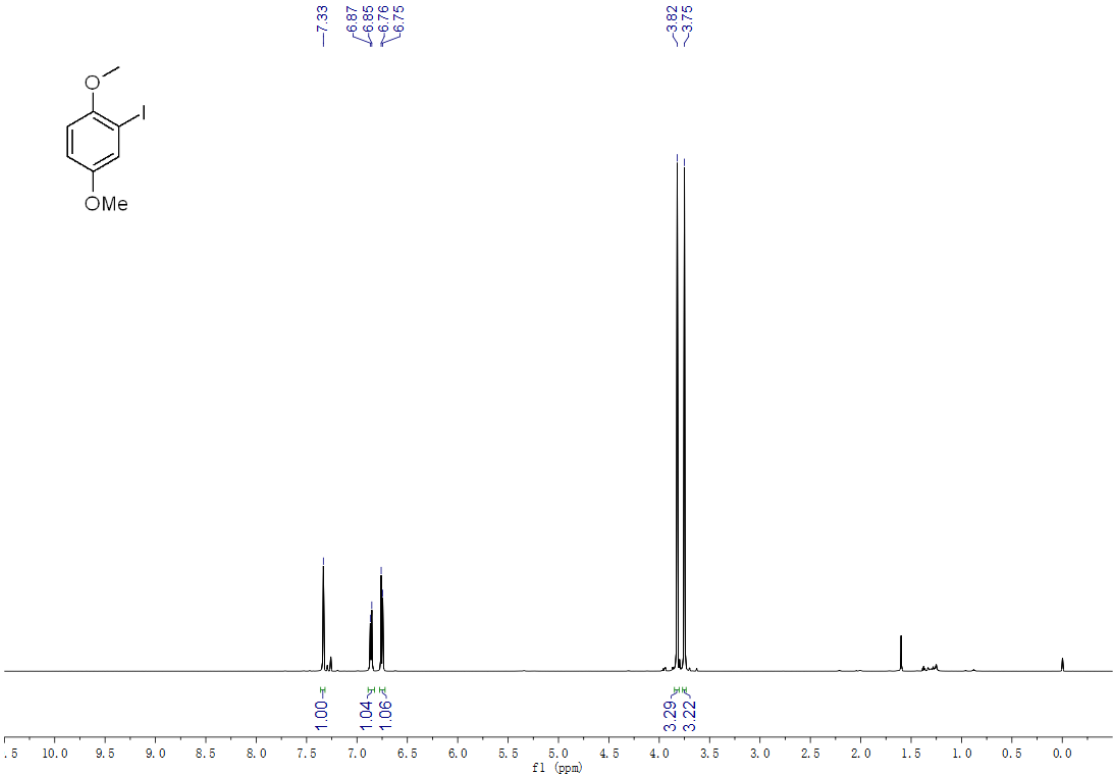
11. NMR Spectra

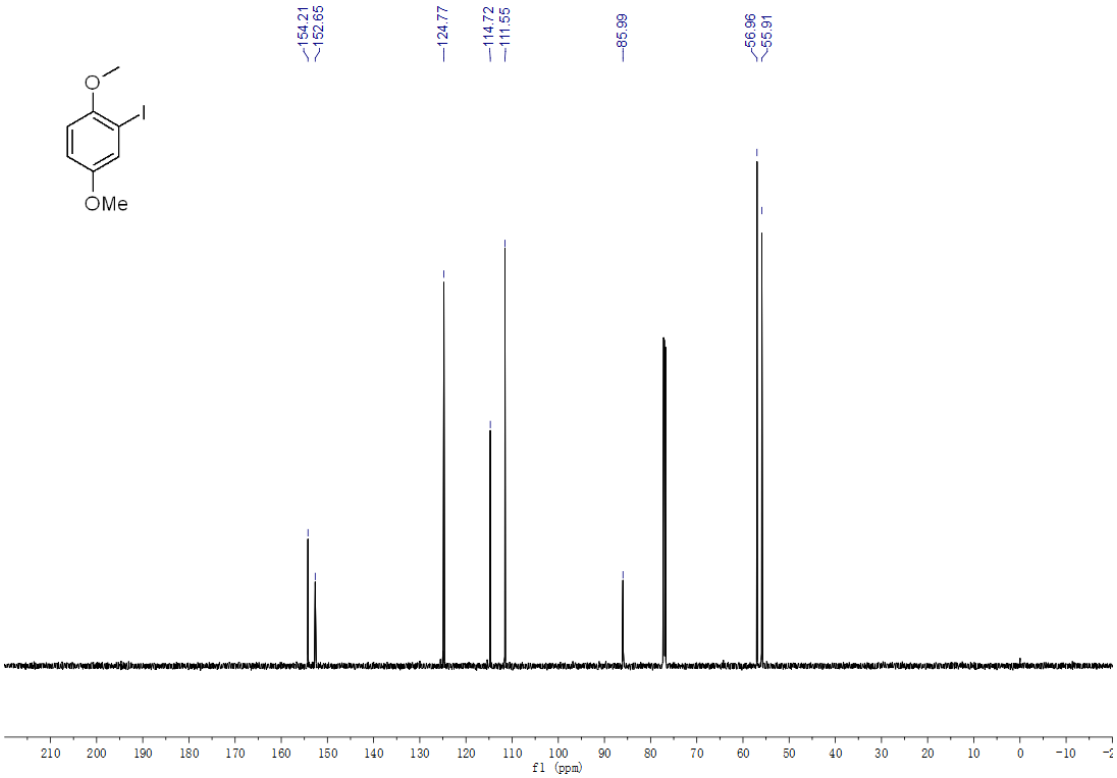
2-Iodo-1-methoxy-4-methylbenzene (1b):



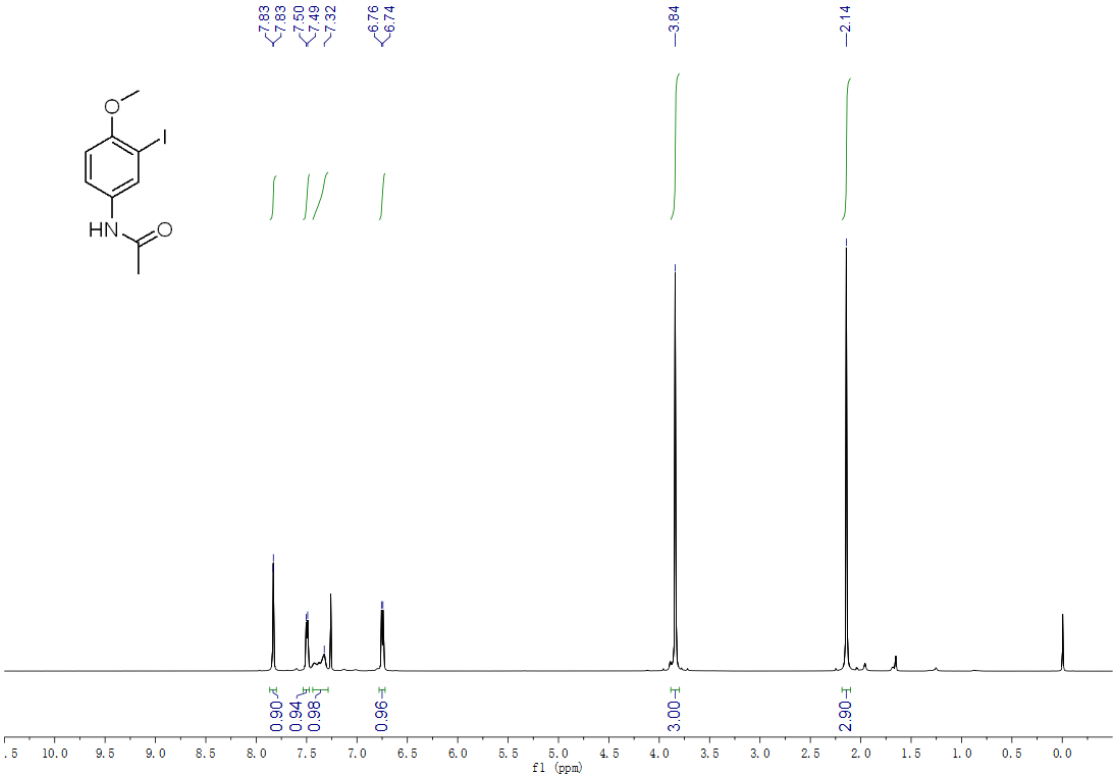


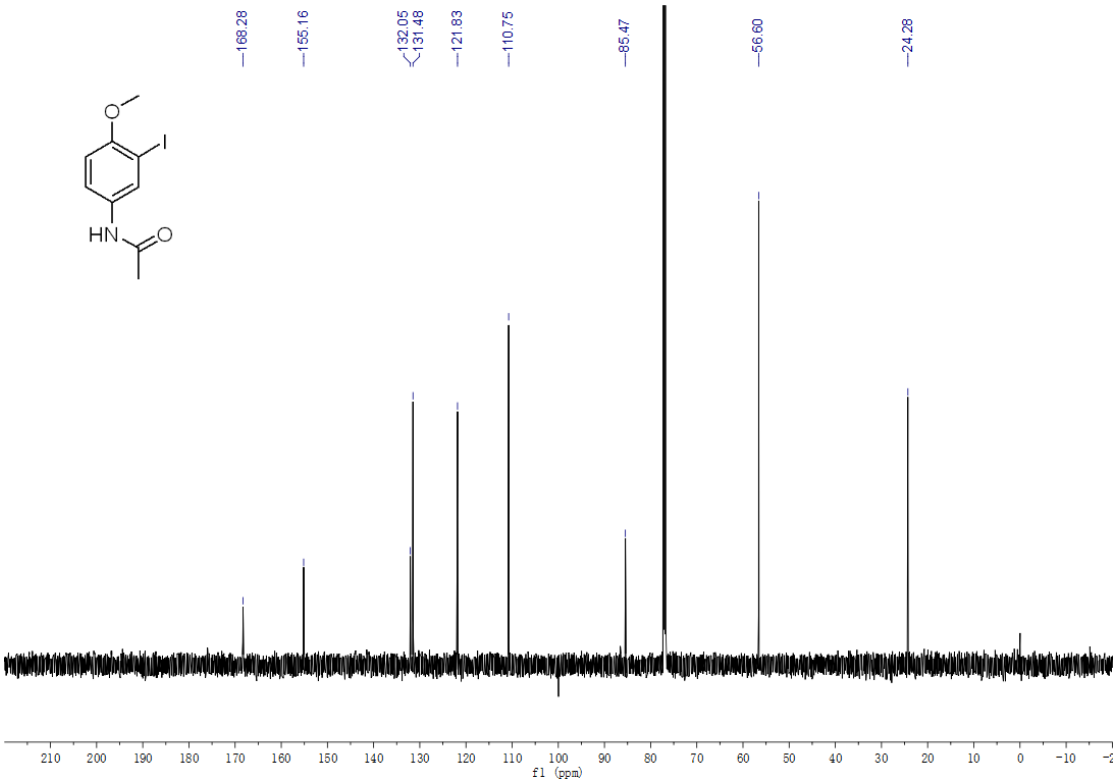
2-Iodo-1,4-dimethoxybenzene (1c):



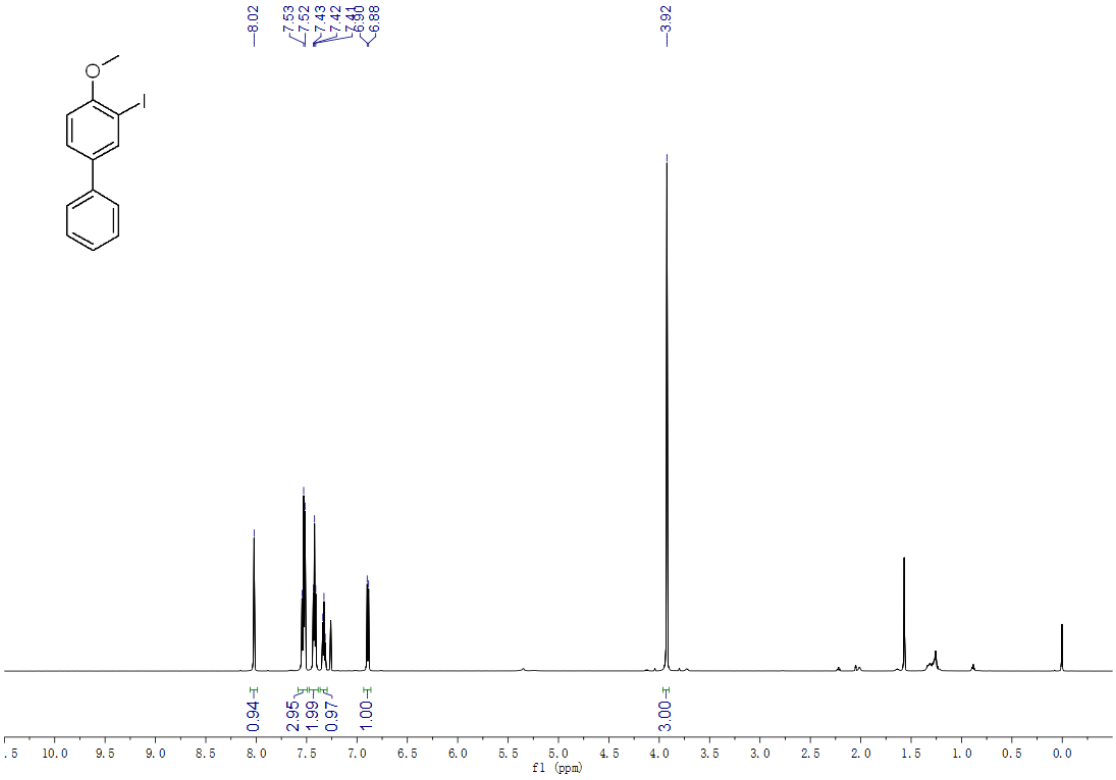


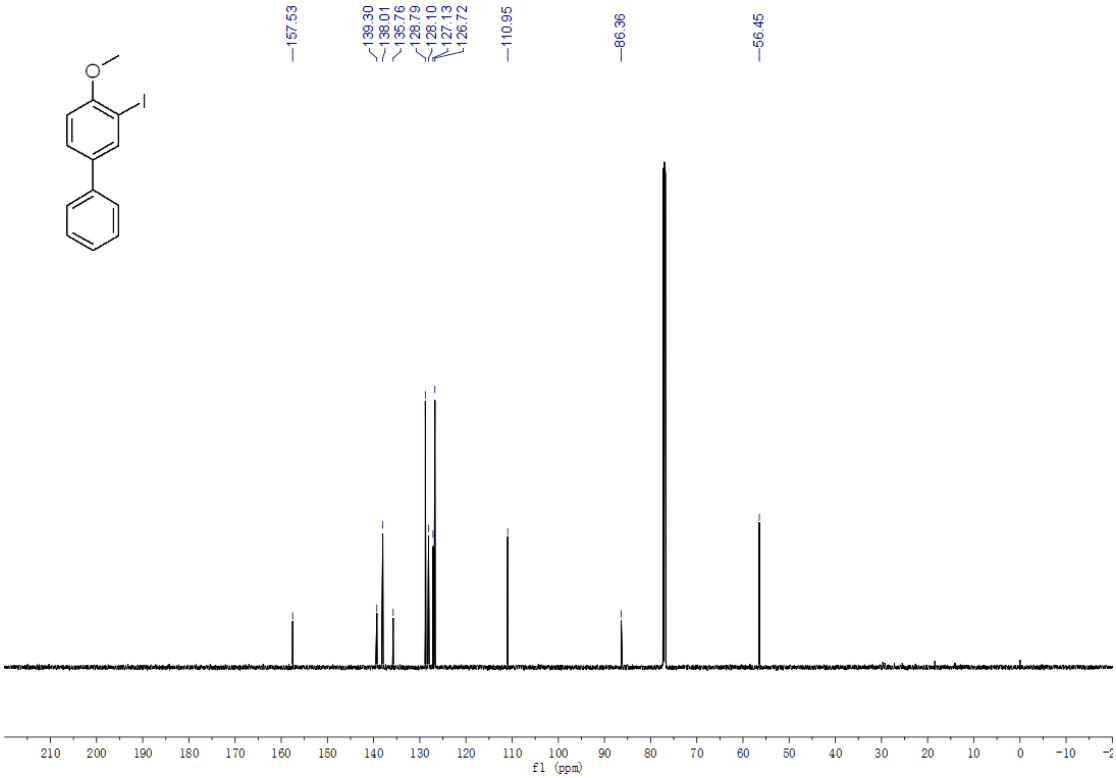
***N*-(3-Iodo-4-methoxyphenyl)acetamide (1d):**



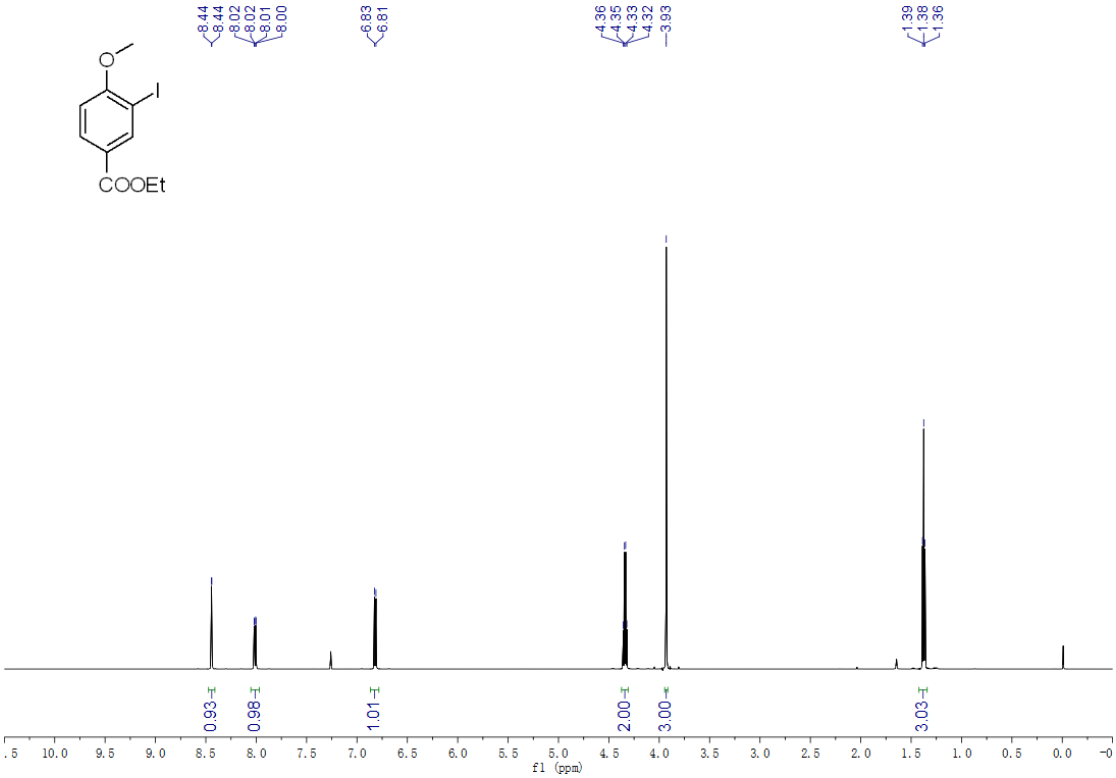


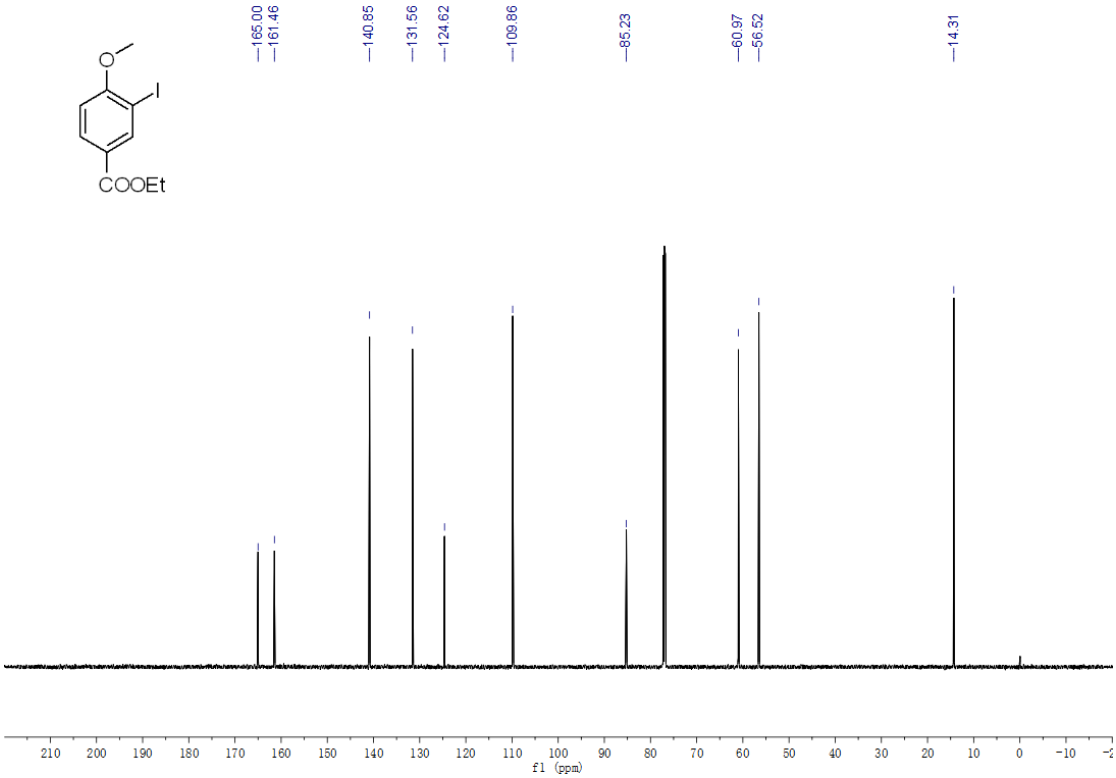
3-Iodo-4-methoxy-1,1'-biphenyl (1e):



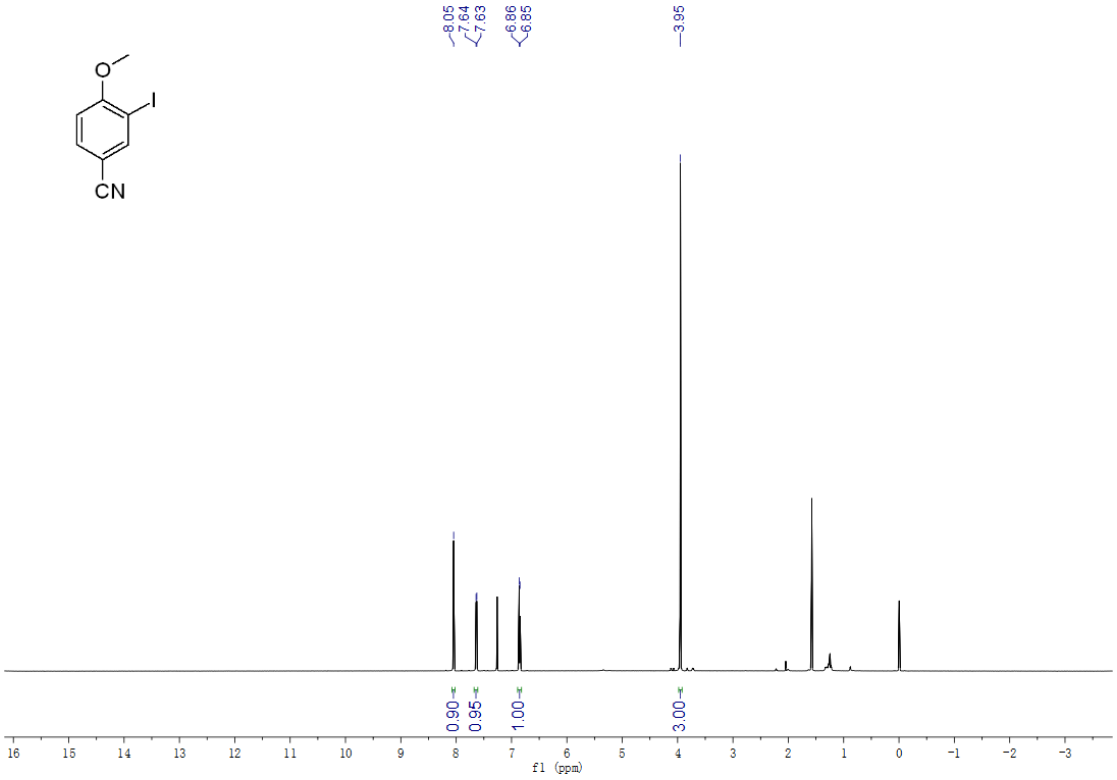


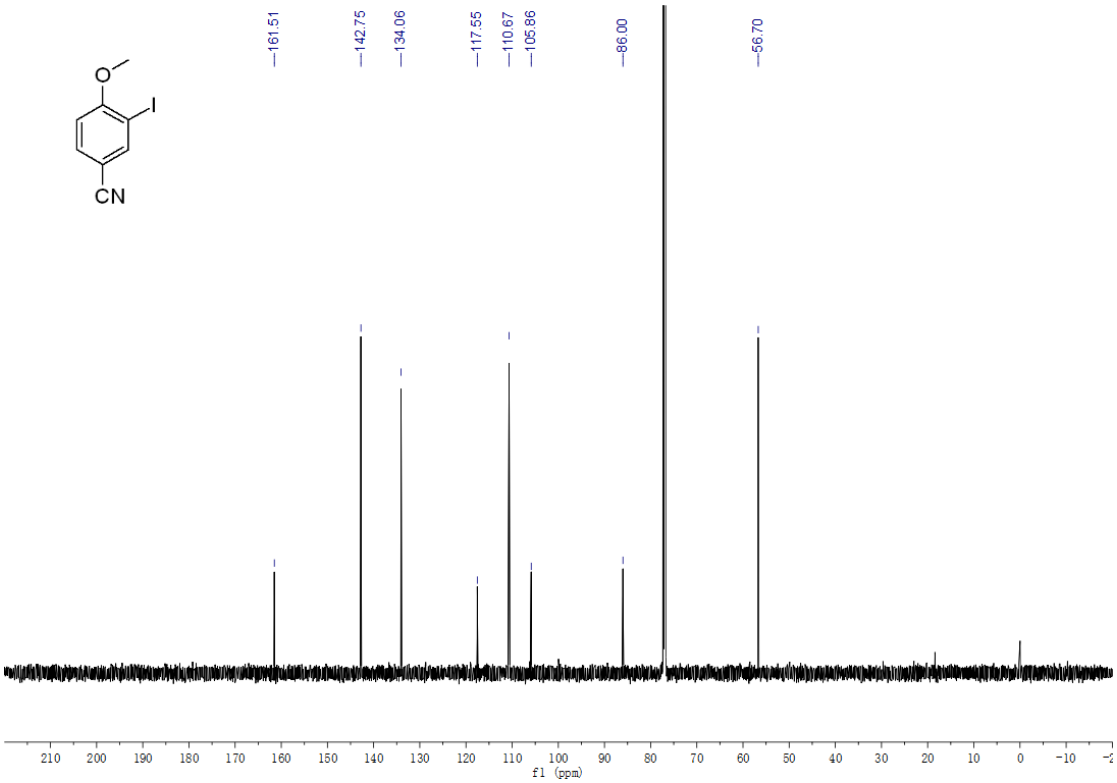
Ethyl 3-iodo-4-methoxybenzoate (1f):



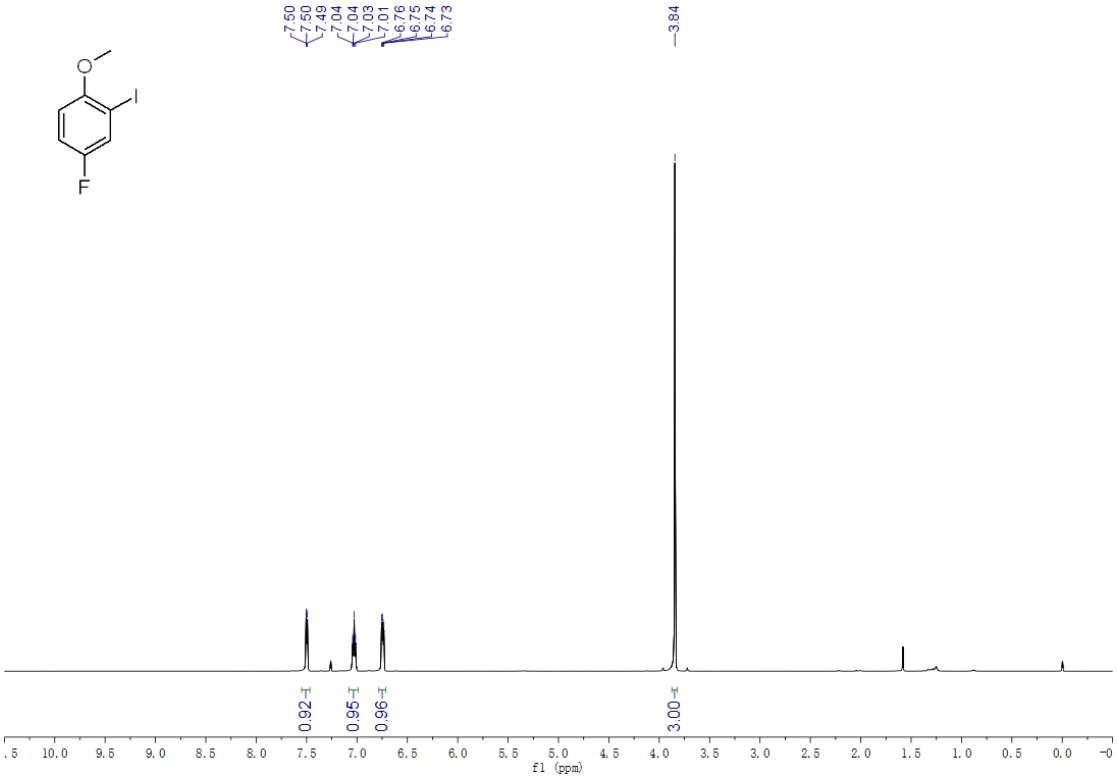


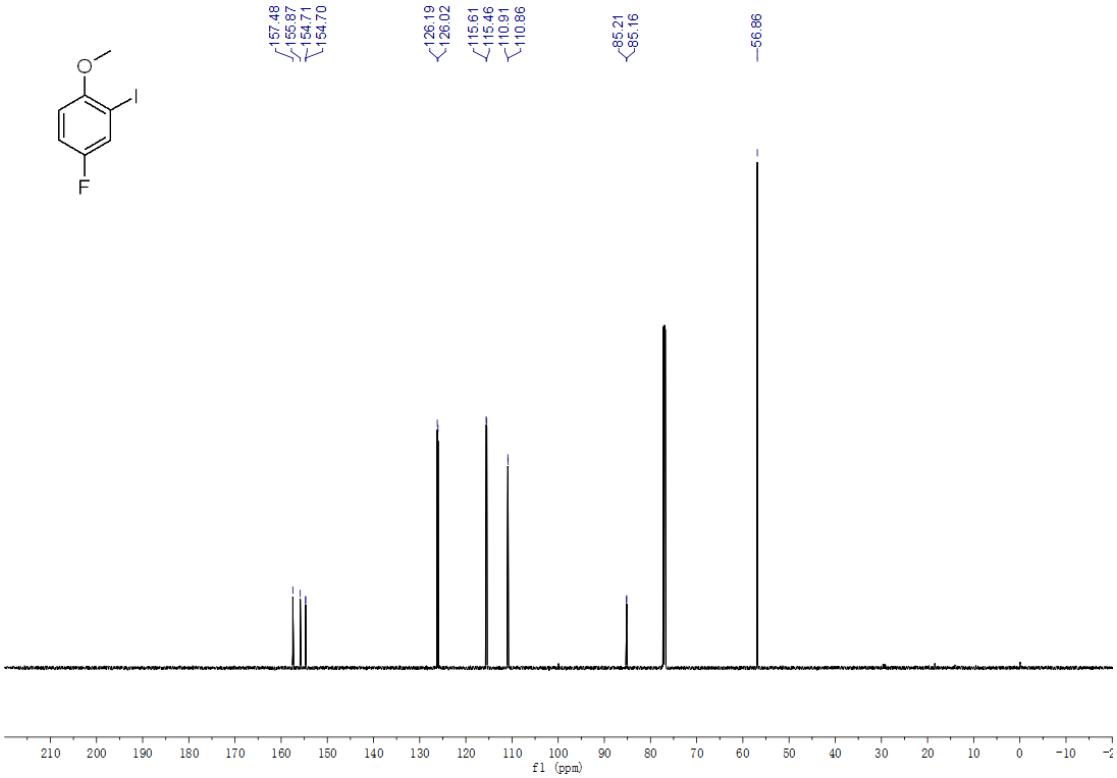
3-Iodo-4-methoxybenzonitrile (1h):



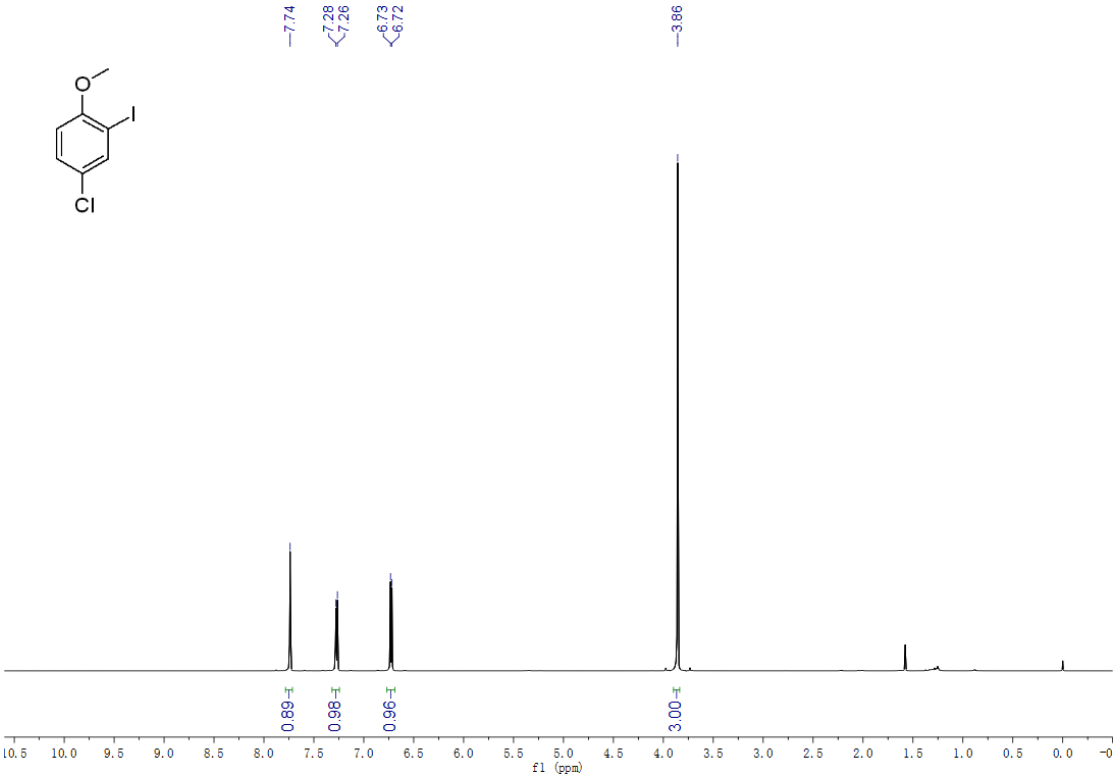


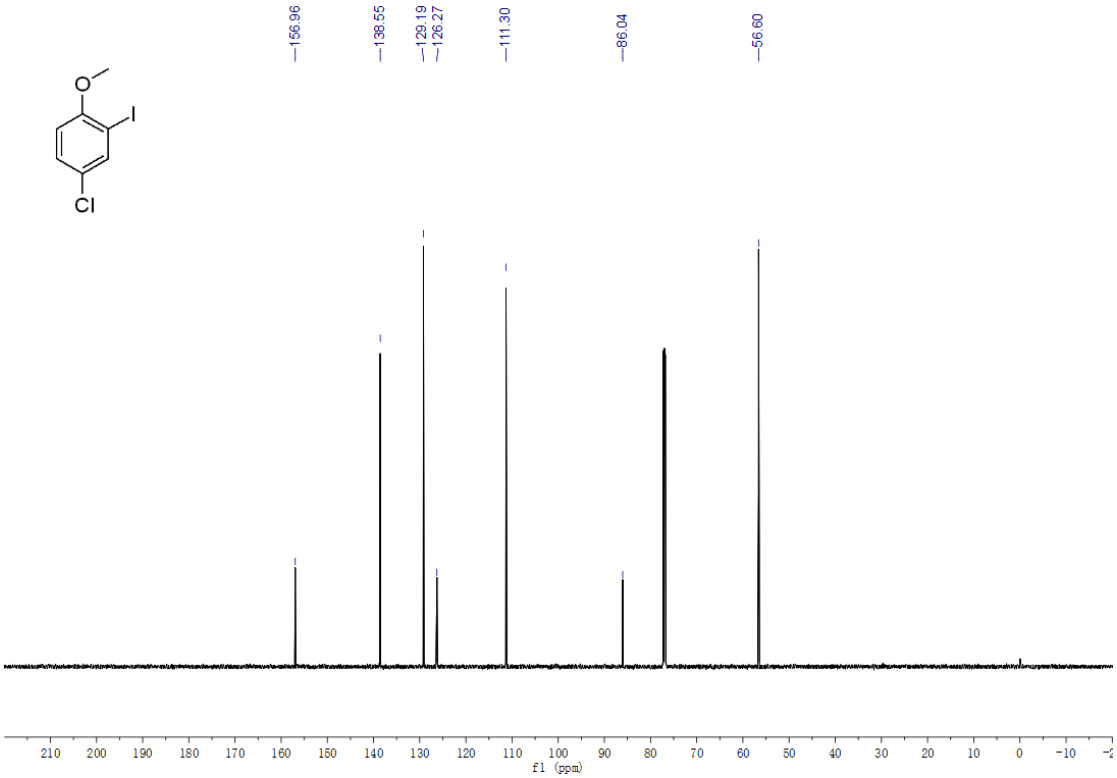
4-Fluoro-2-iodo-1-methoxybenzene (1j):



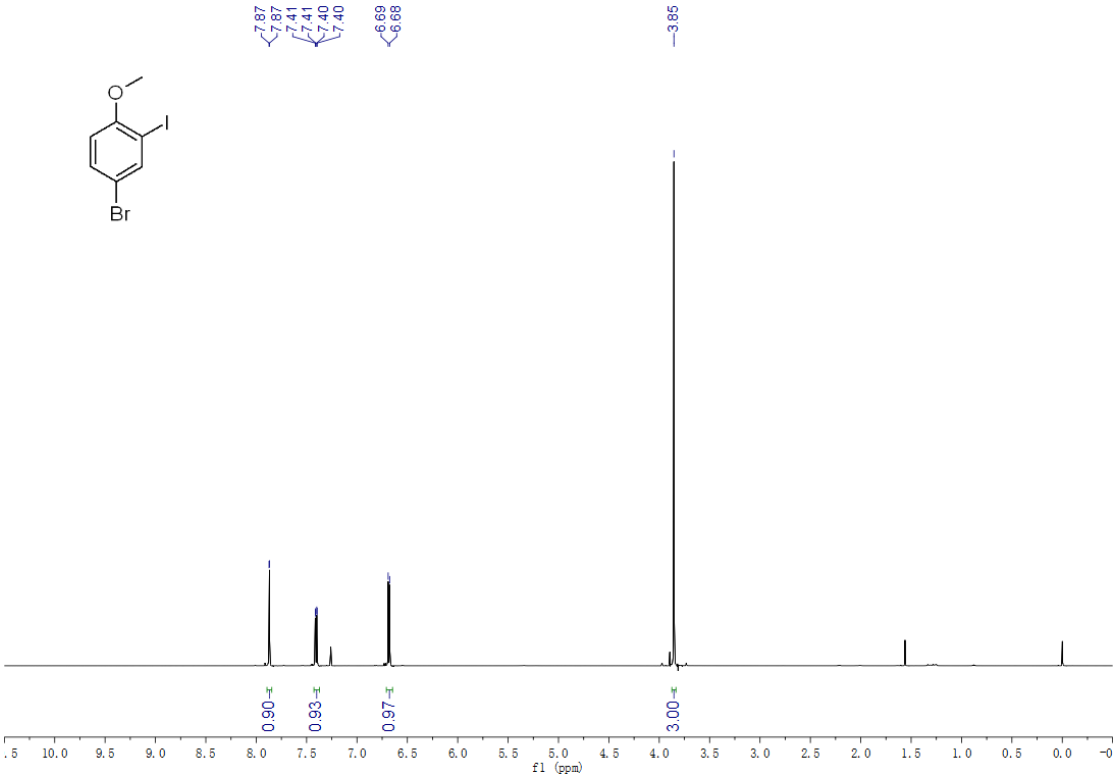


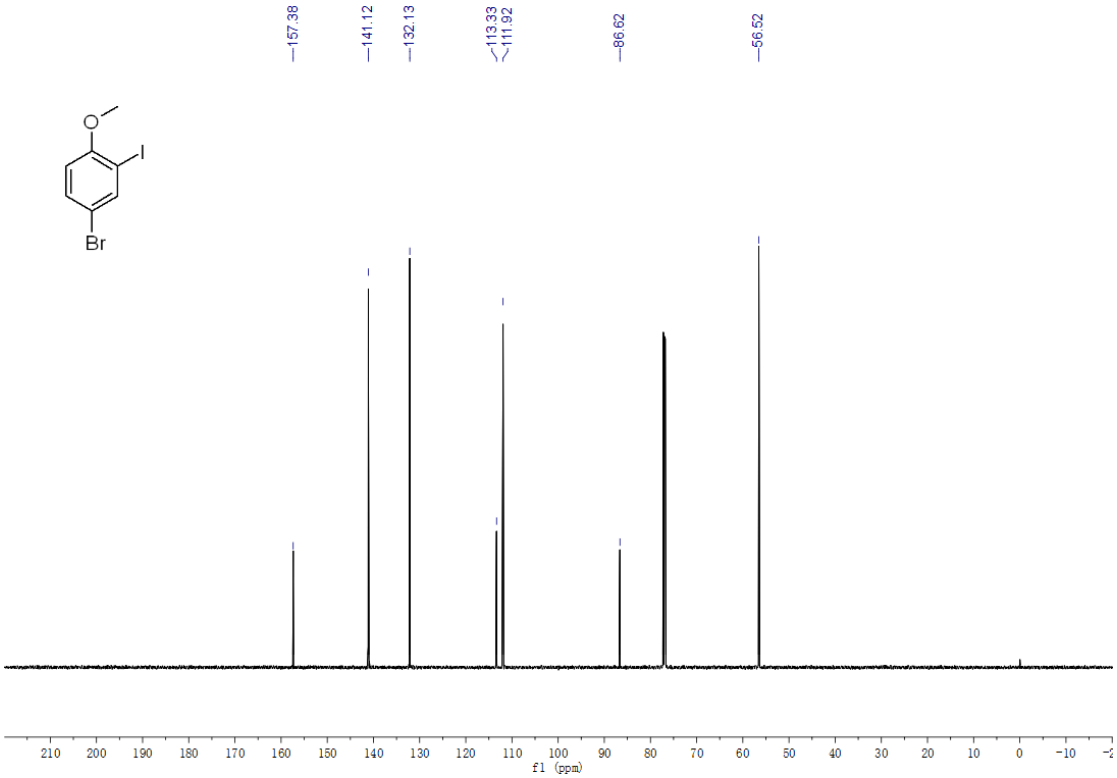
4-Chloro-2-iodo-1-methoxybenzene (1k):



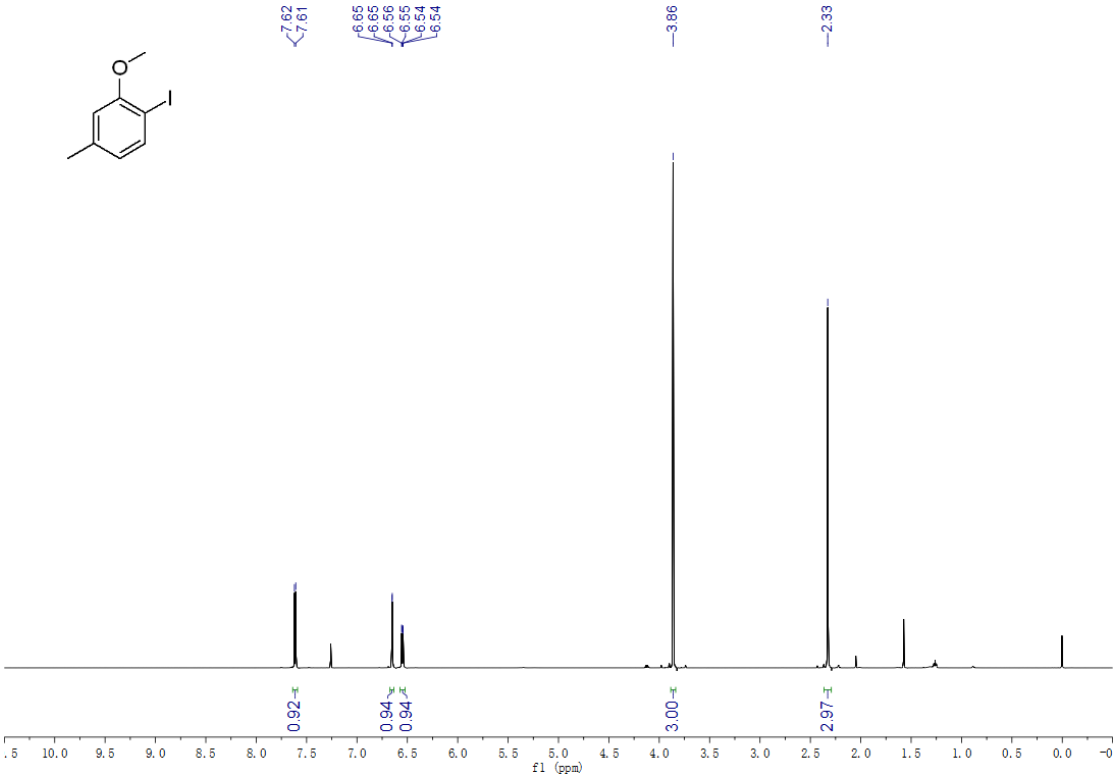


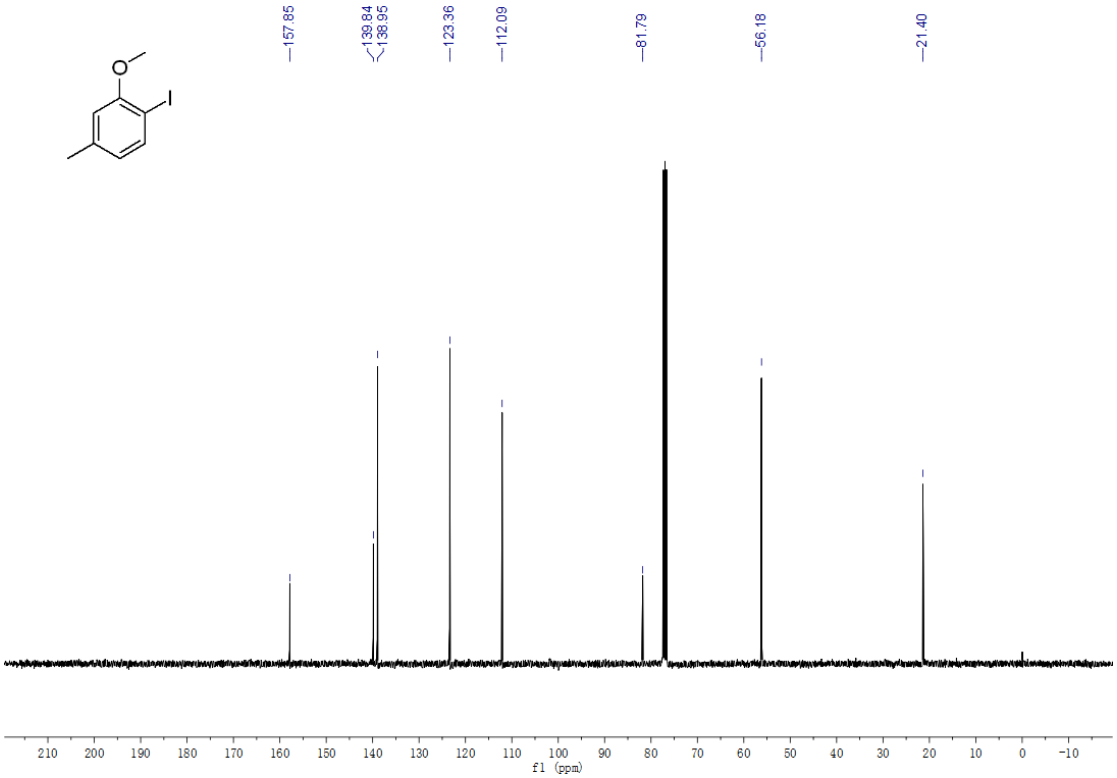
4-Bromo-2-iodo-1-methoxybenzene (1l):



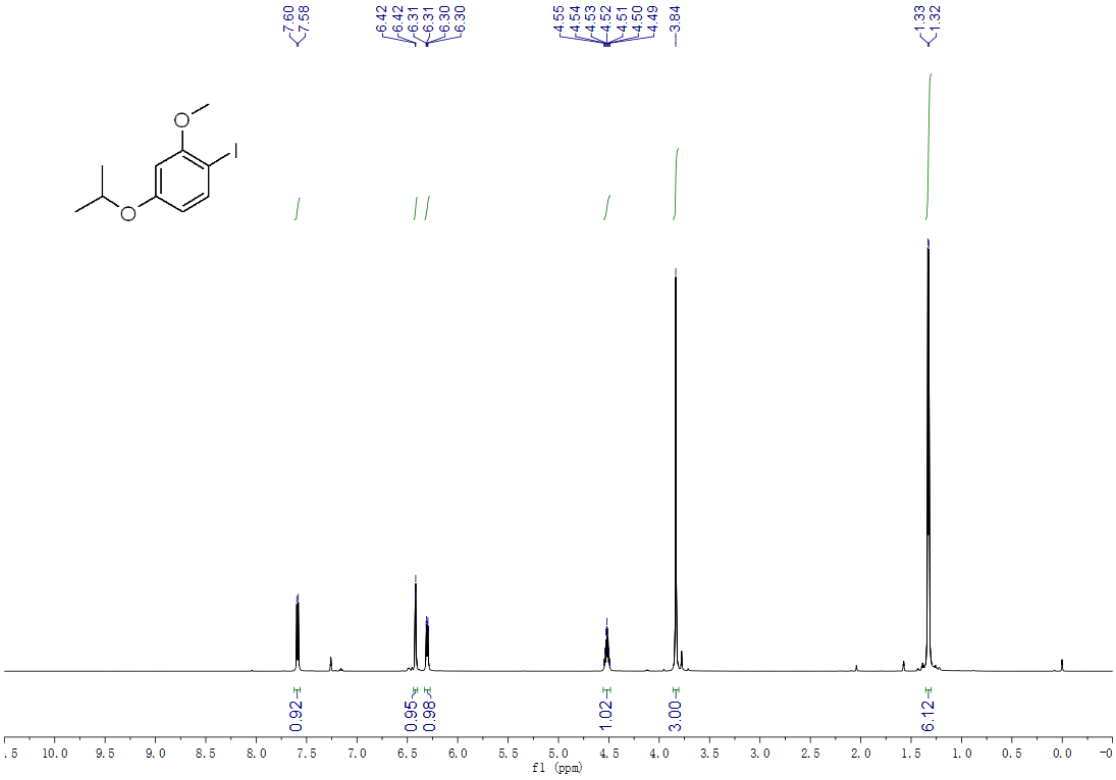


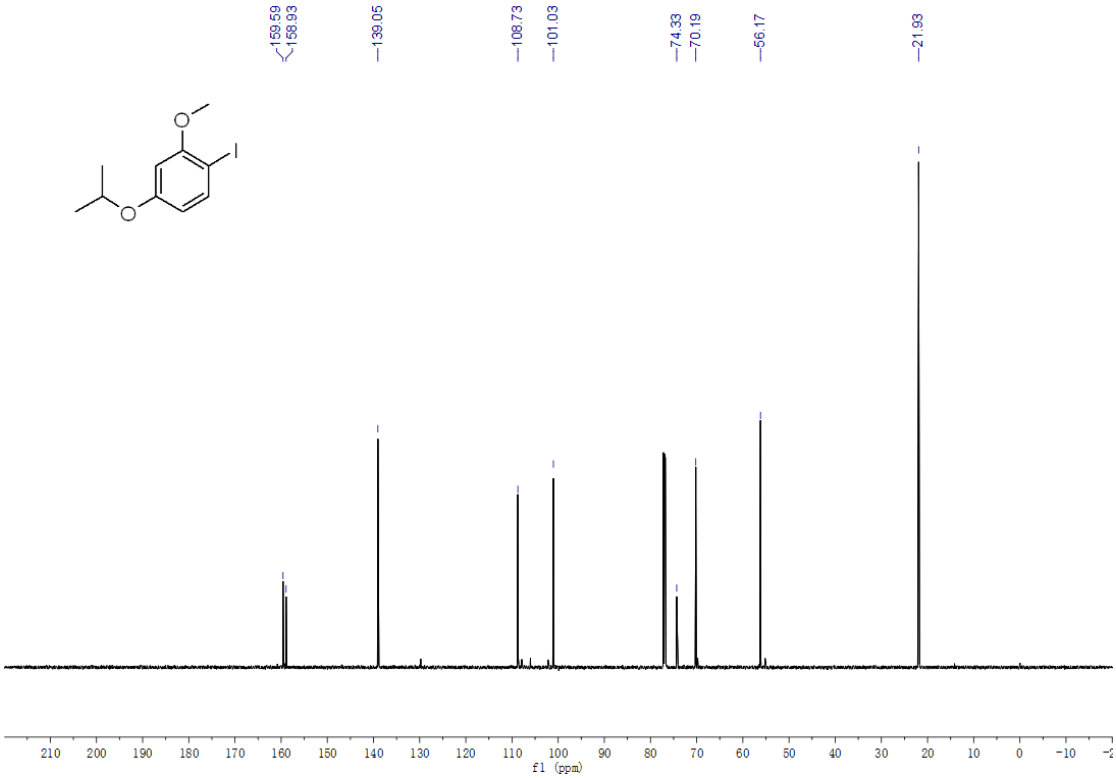
1-Iodo-2-methoxy-4-methylbenzene (1m):



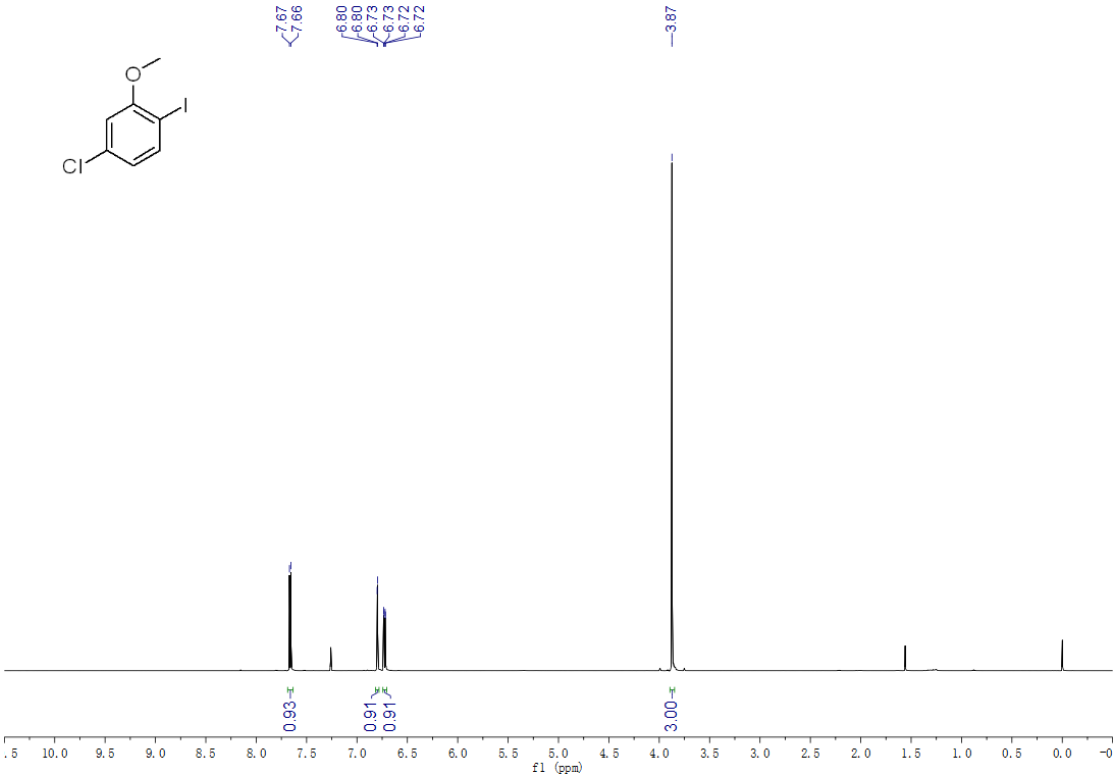


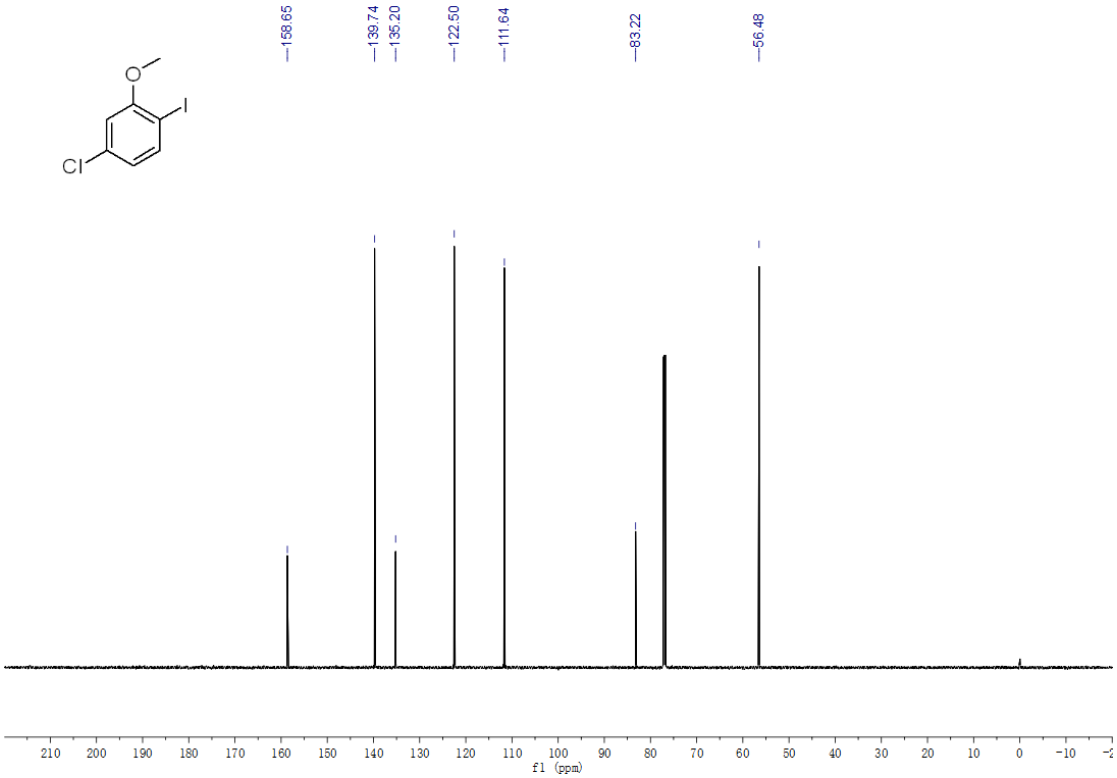
1-Iodo-4-isopropoxy-2-methoxybenzene (1o):



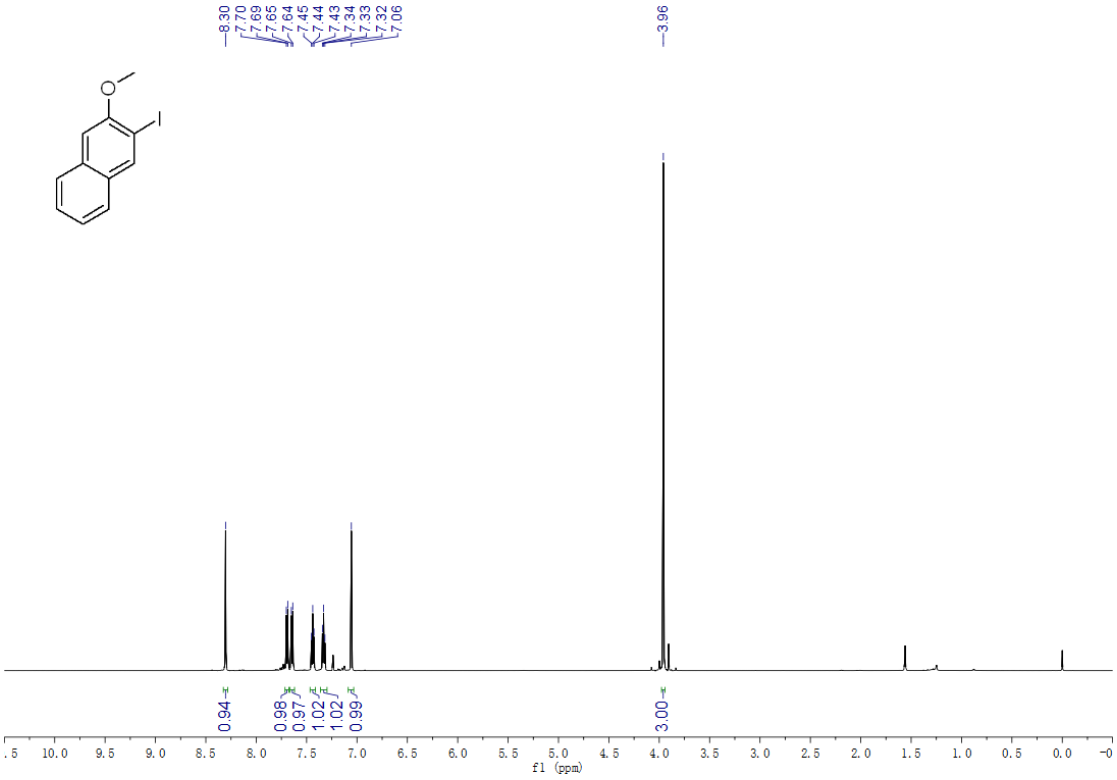


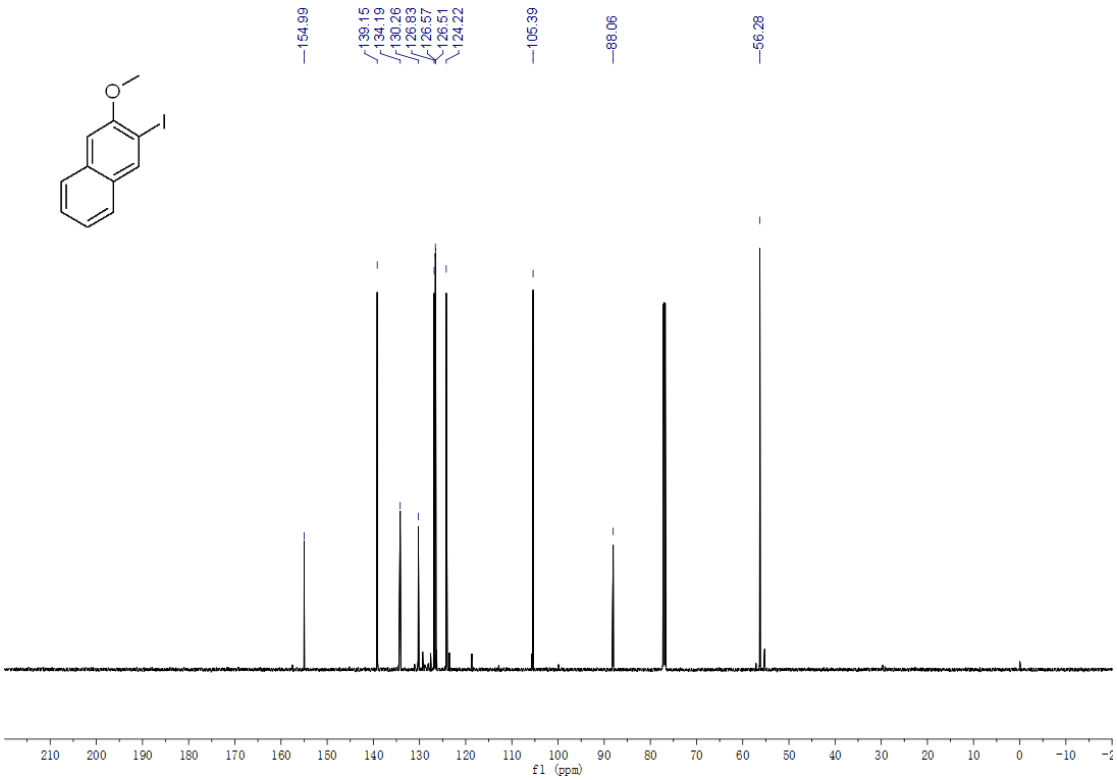
4-Chloro-1-iodo-2-methoxybenzene (1q):



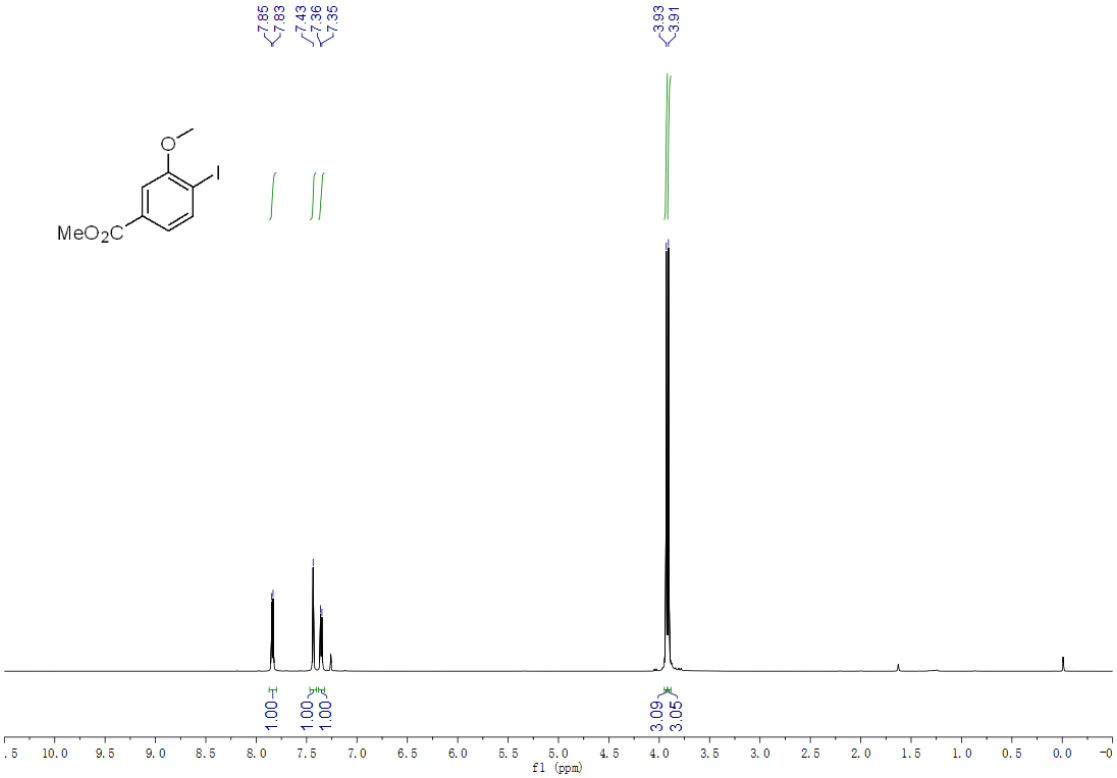


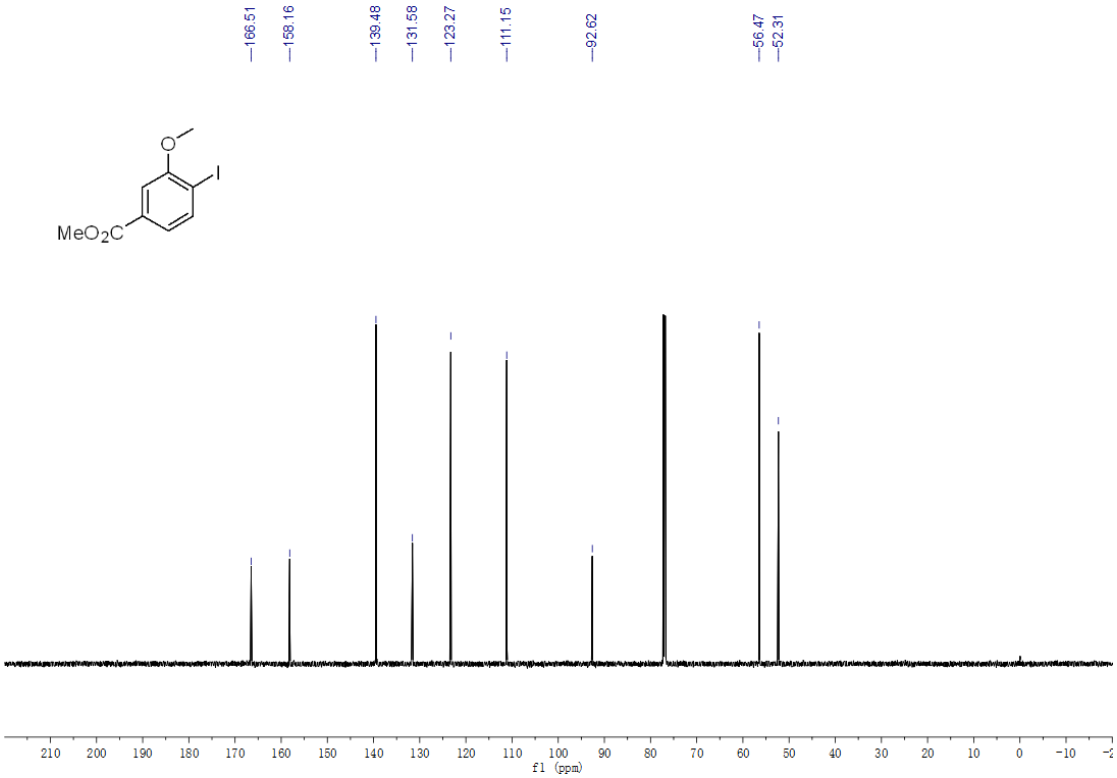
2-Iodo-3-methoxynaphthalene (1r):



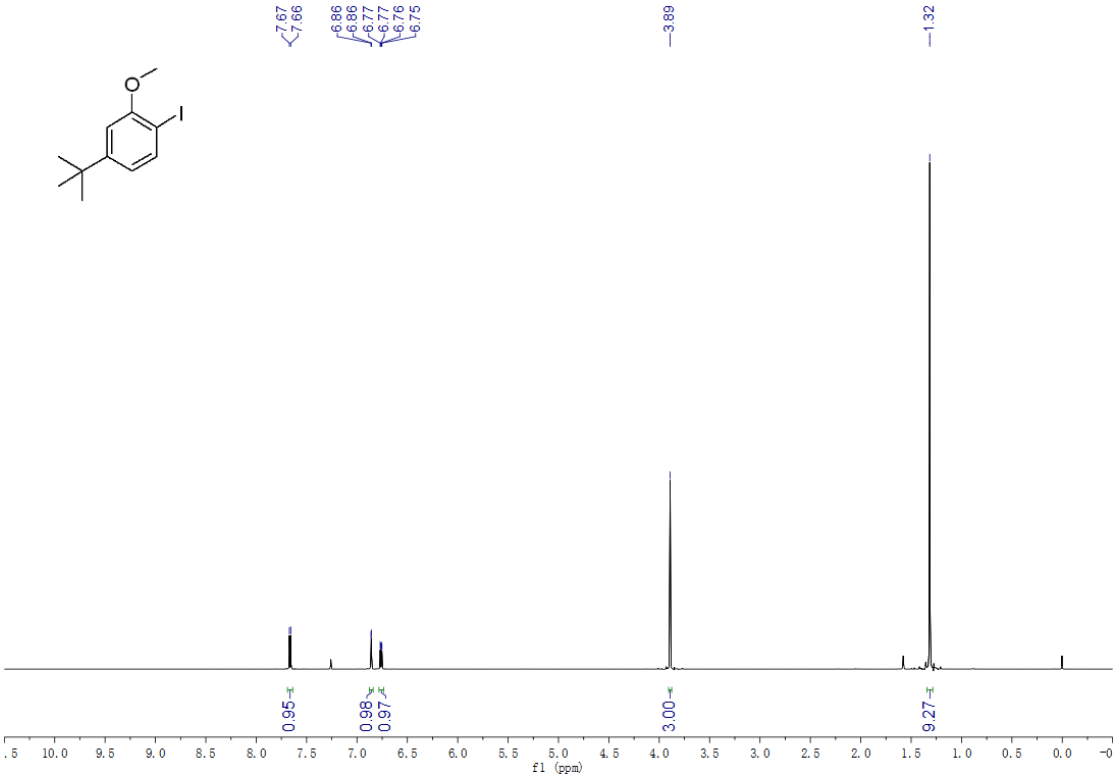


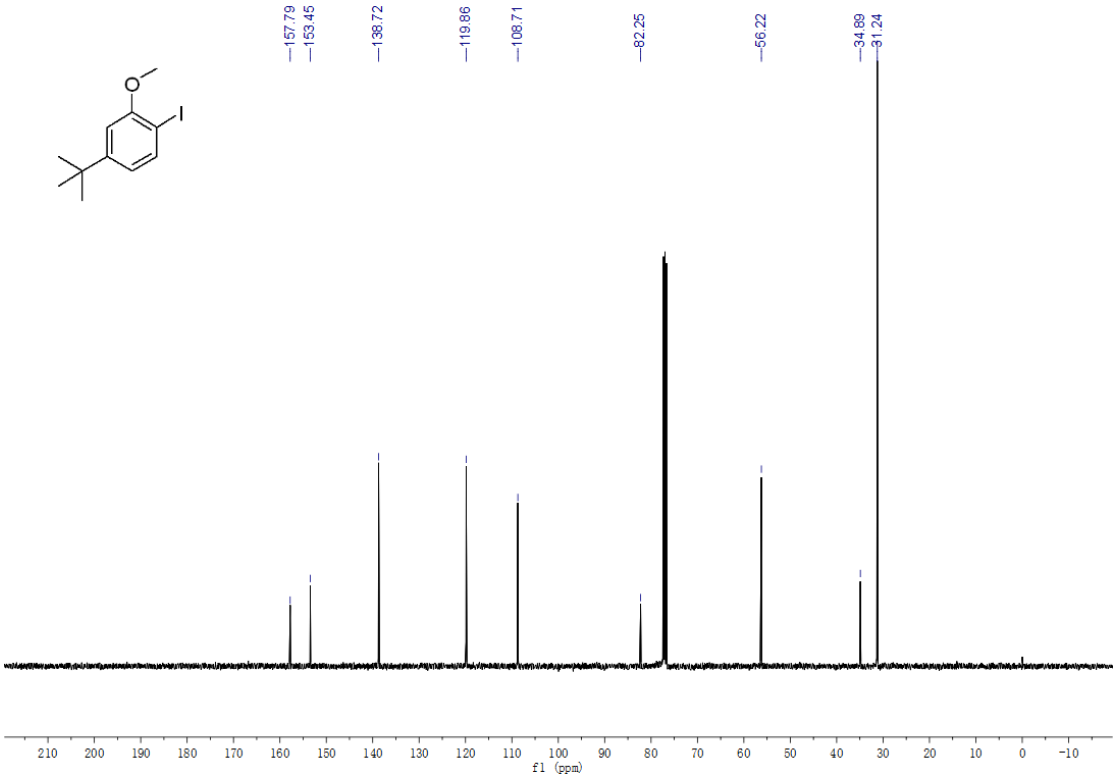
Methyl 4-iodo-3-methoxybenzoate (1s):



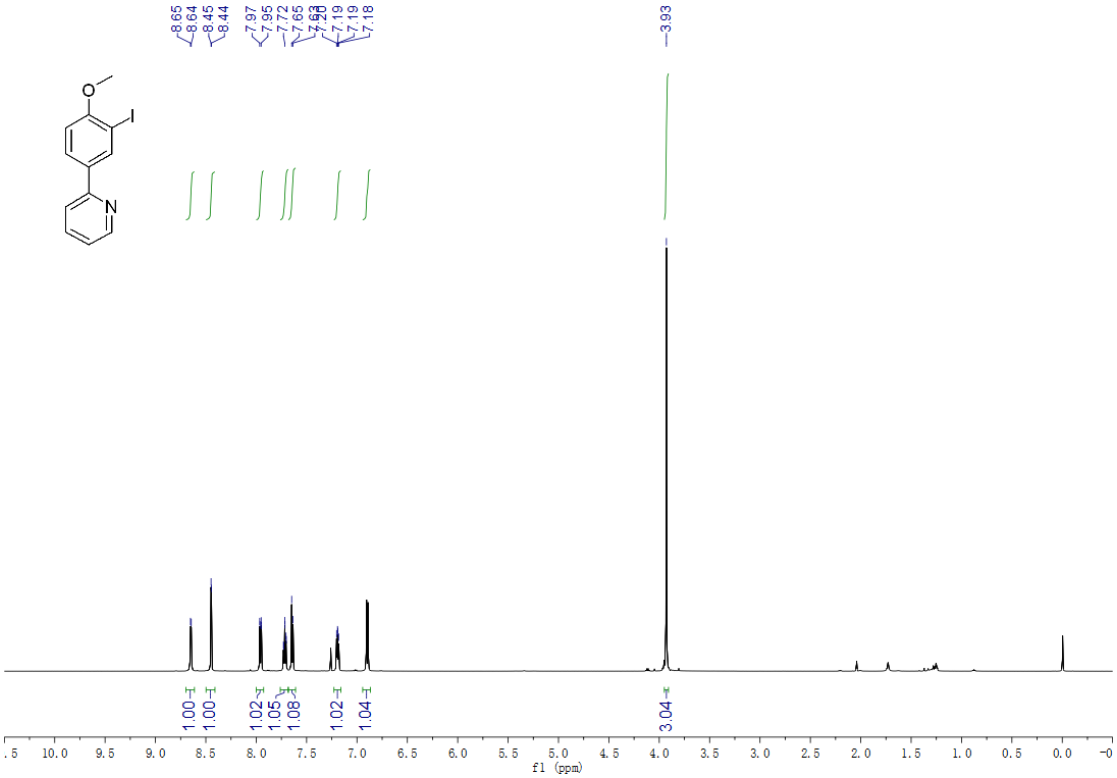


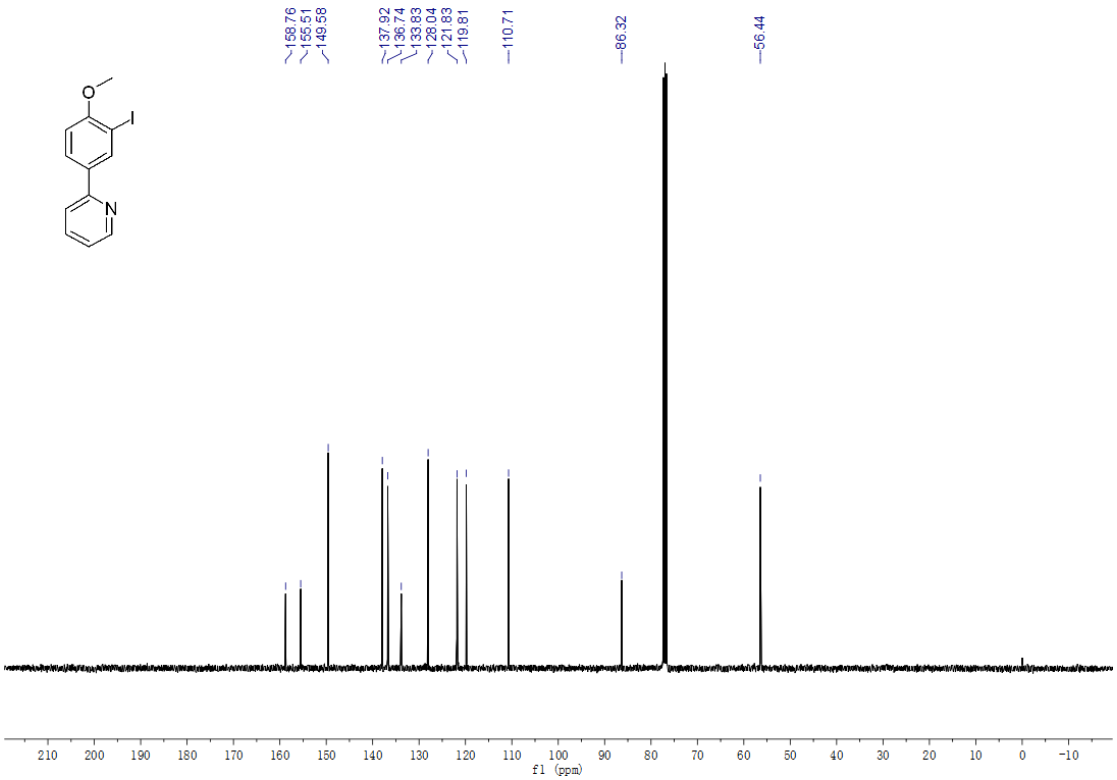
4-(*tert*-Butyl)-1-iodo-2-methoxybenzene (1t):



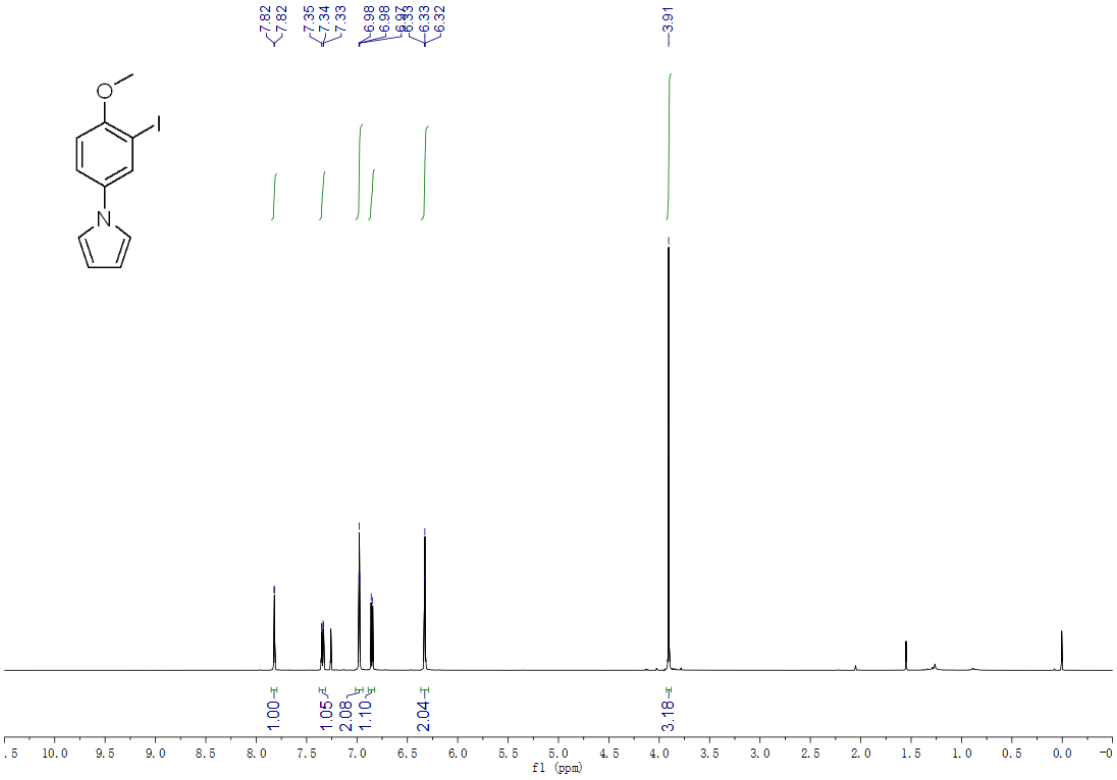


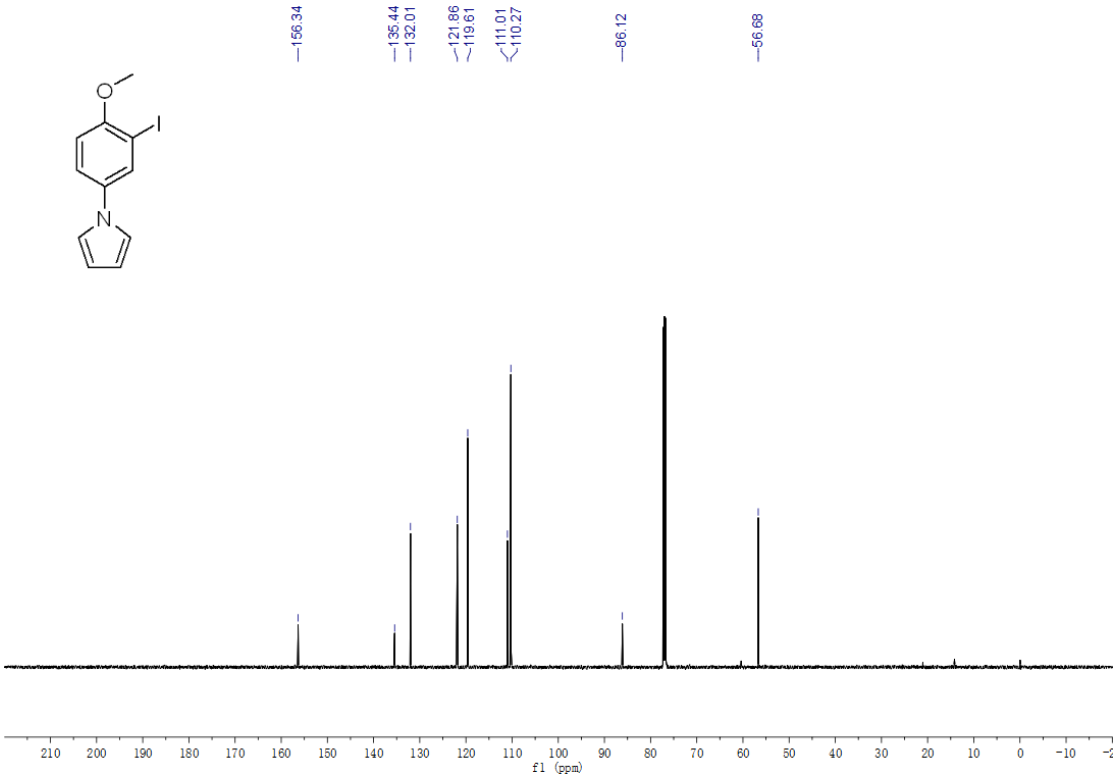
2-(3-Iodo-4-methoxyphenyl)pyridine (1u):



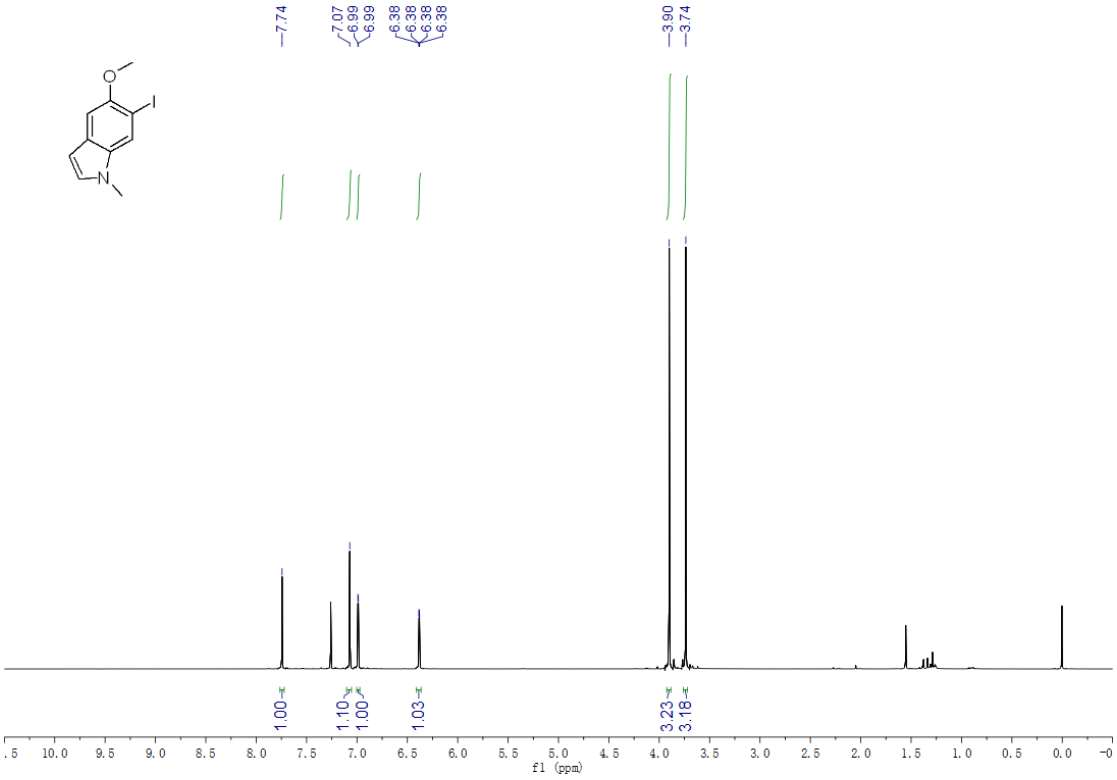


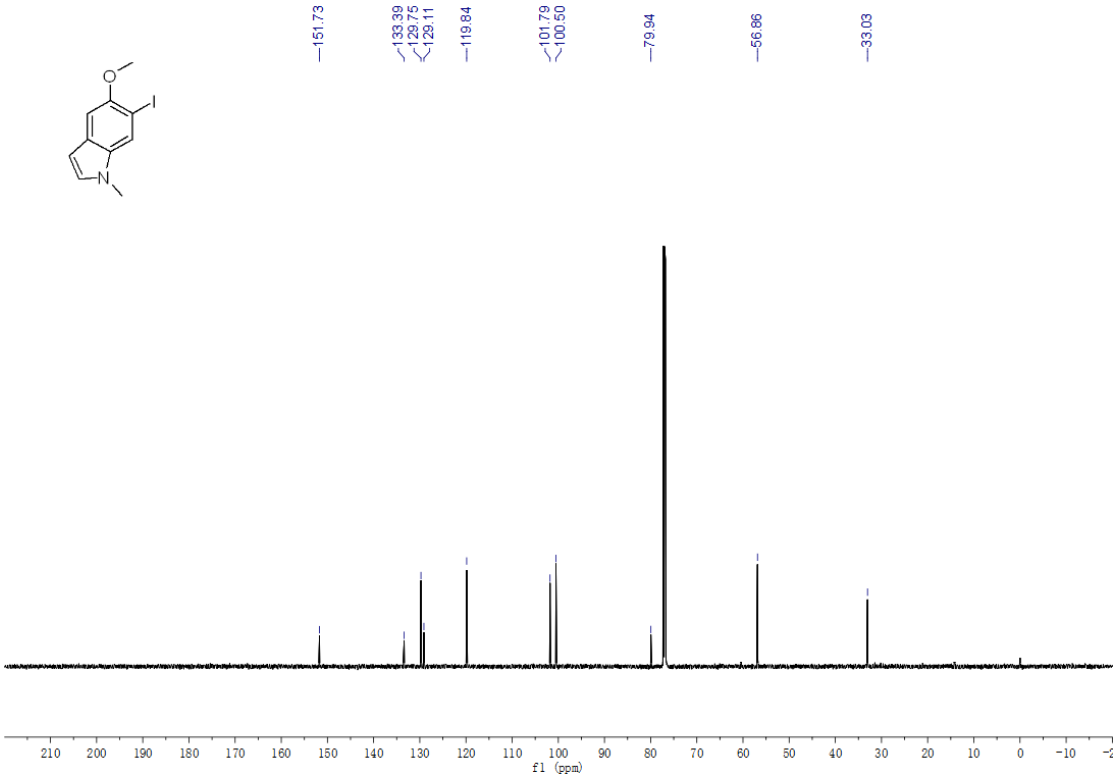
1-(3-Iodo-4-methoxyphenyl)-1H-pyrrole (1v):



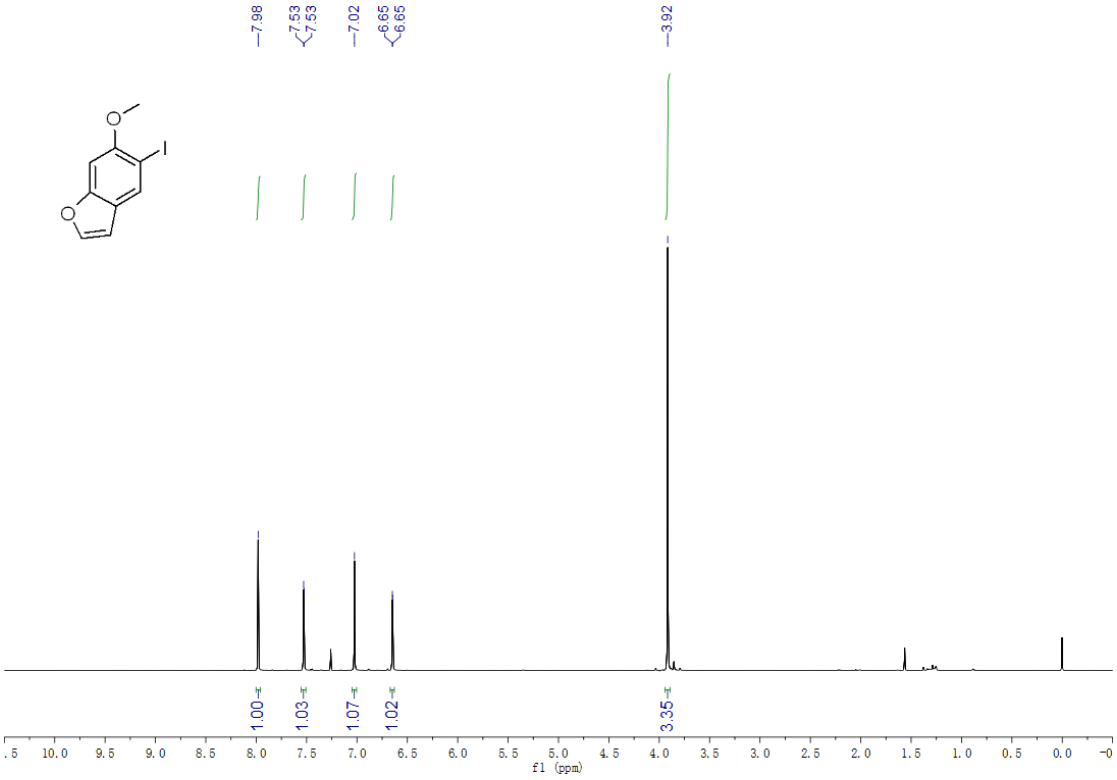


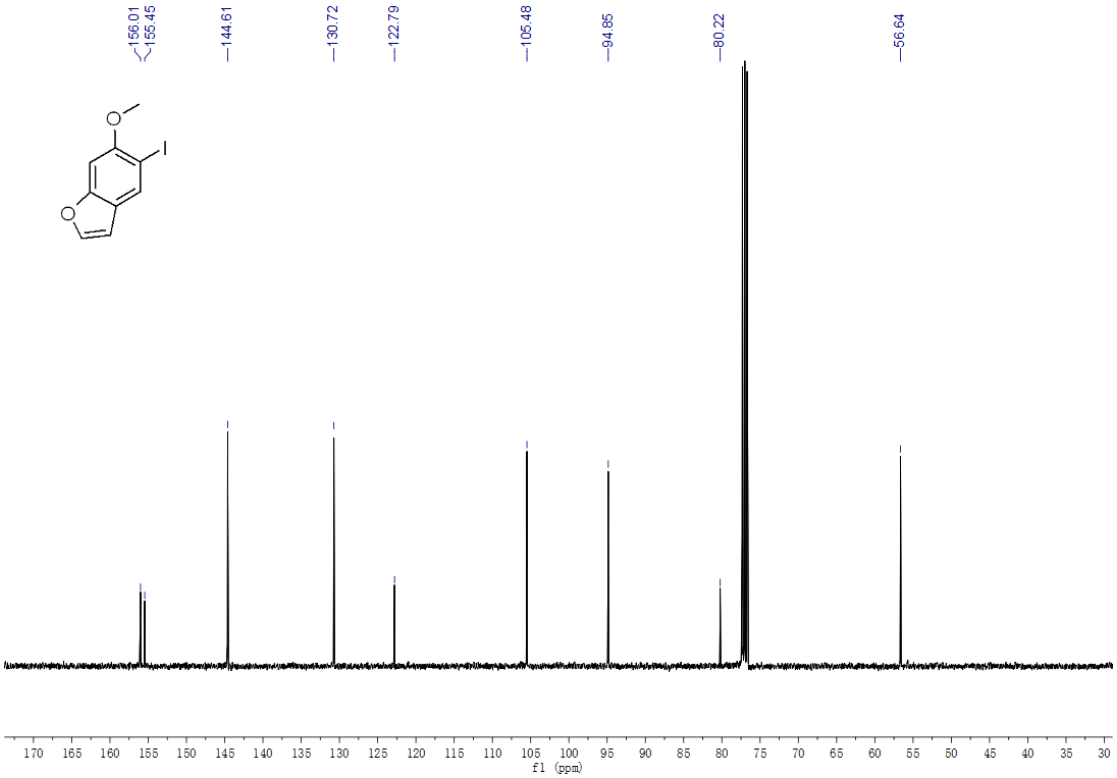
6-Iodo-5-methoxy-1-methyl-1H-indole (1w):



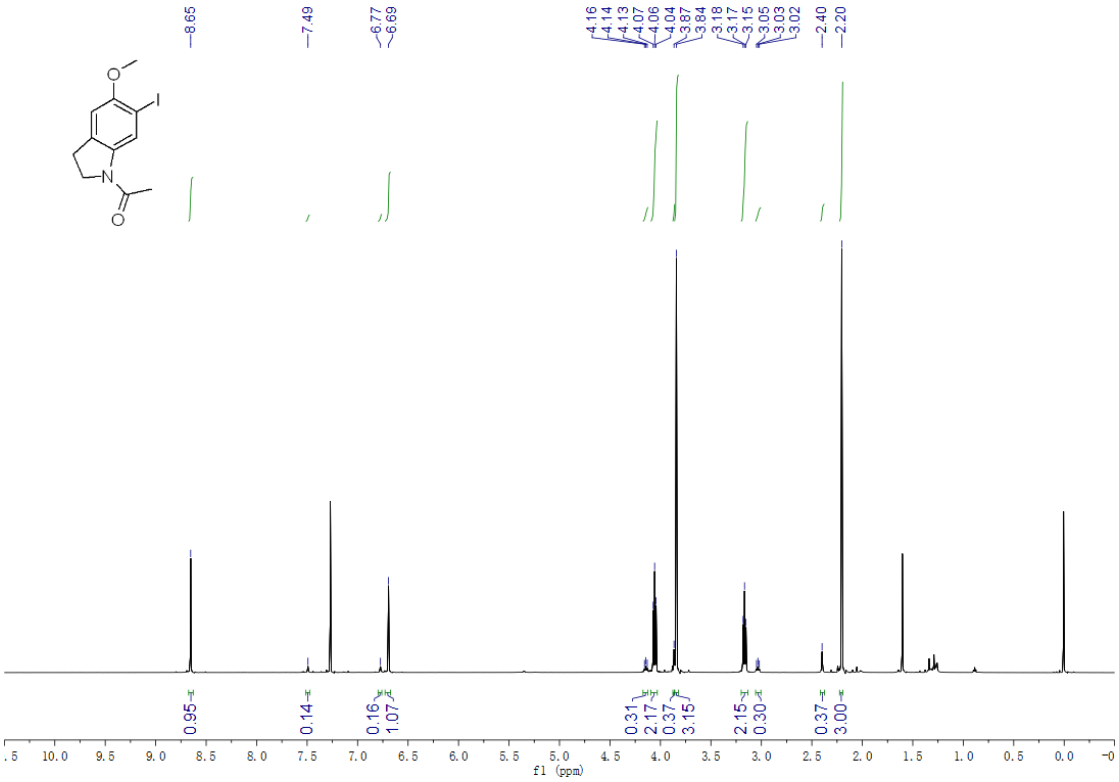


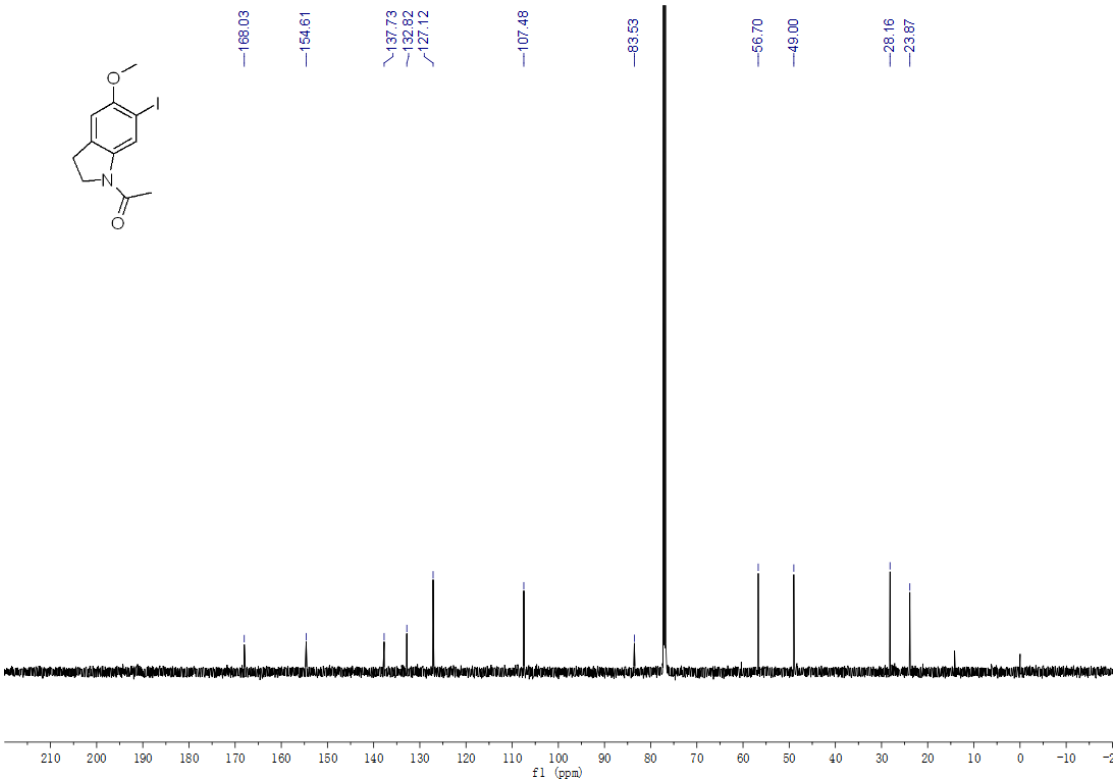
5-Iodo-6-methoxybenzofuran (1x):



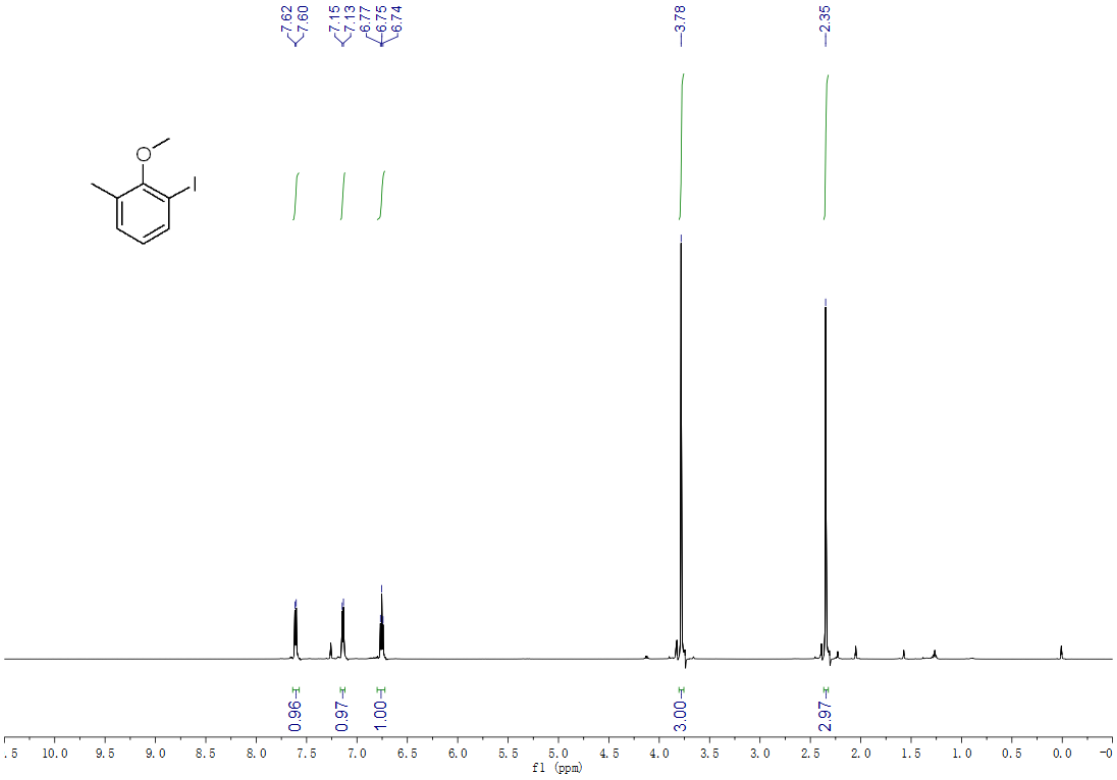


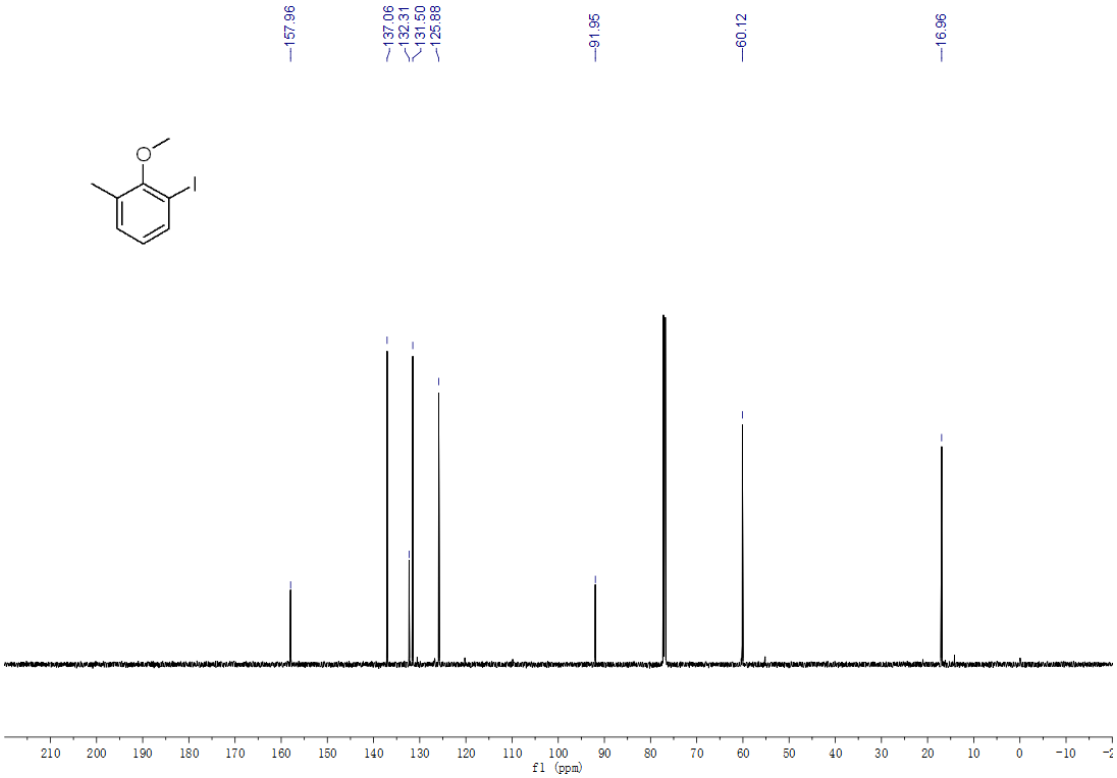
1-(6-Iodo-5-methoxyindolin-1-yl)ethan-1-one (1y):



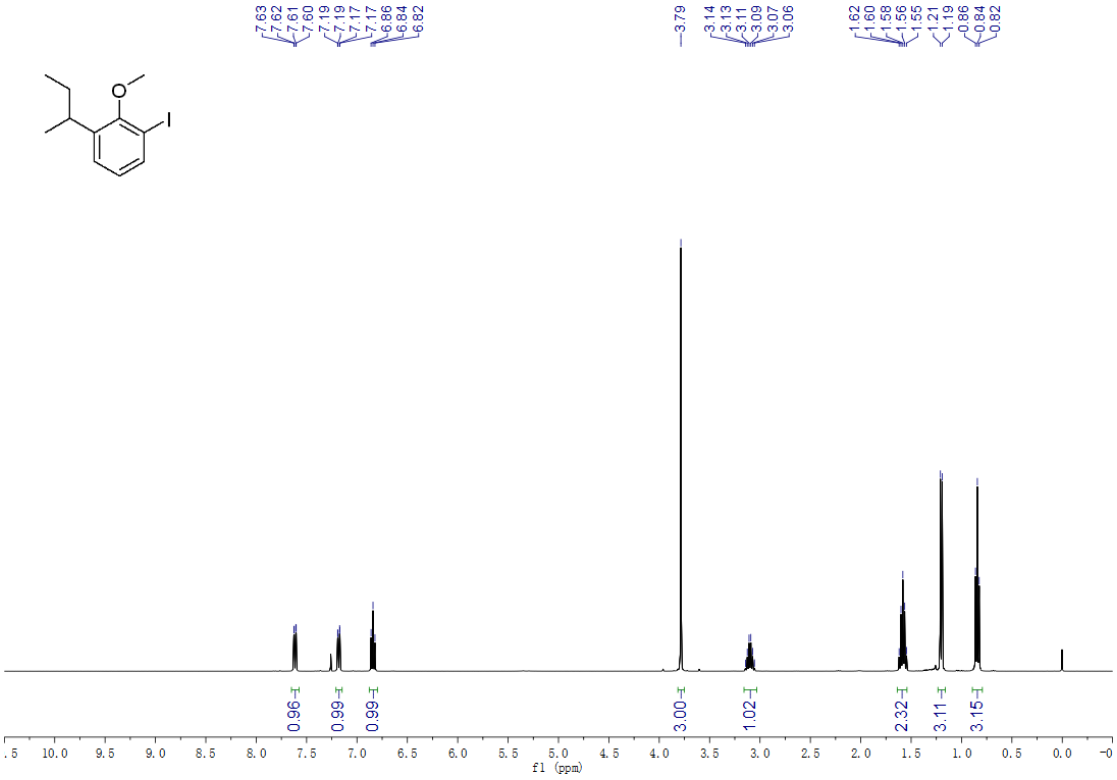


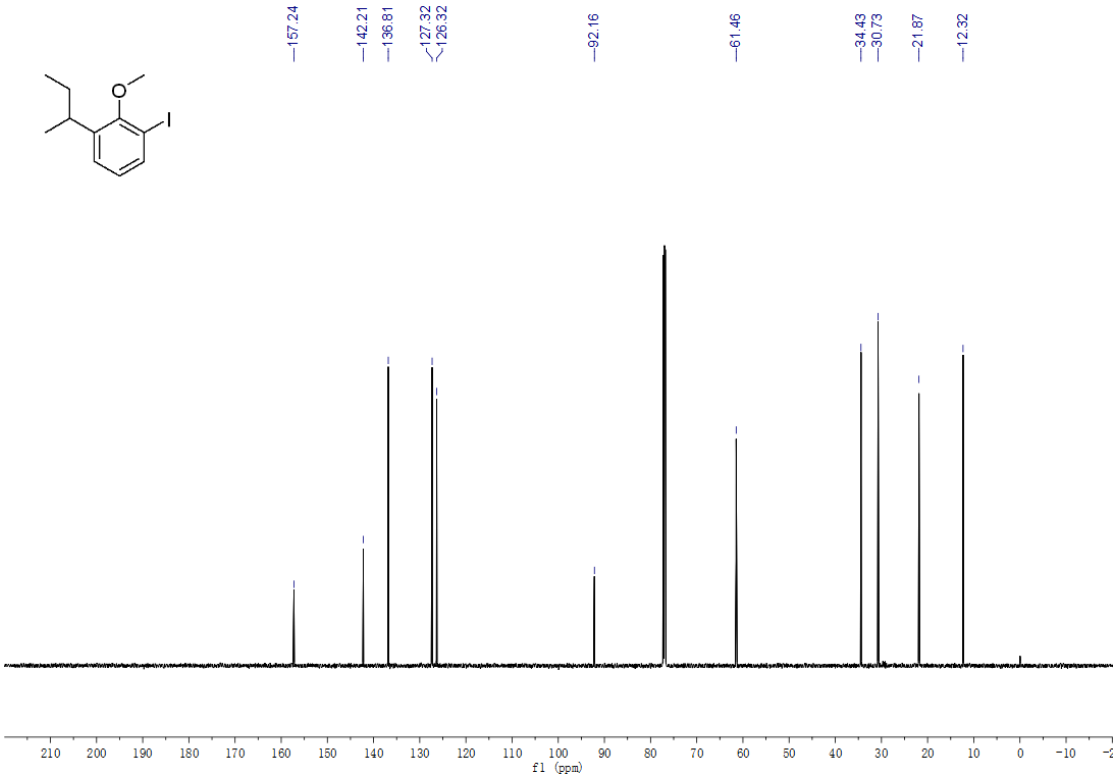
1-Iodo-2-methoxy-3-methylbenzene (4a):



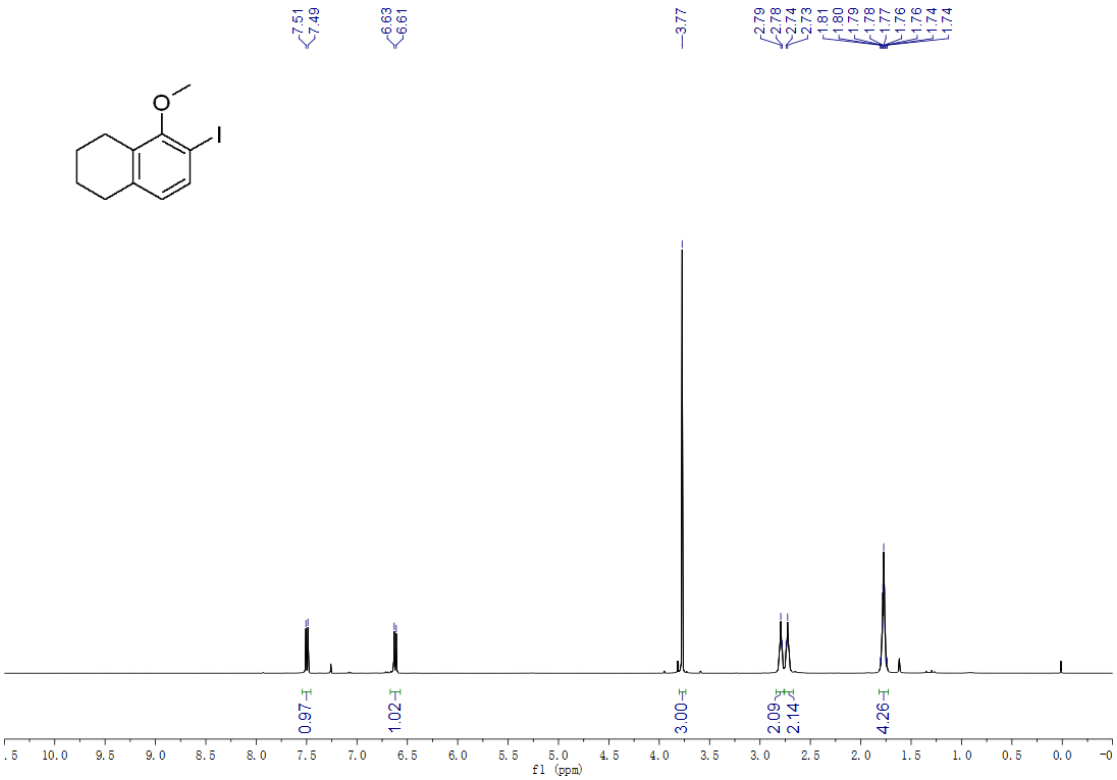


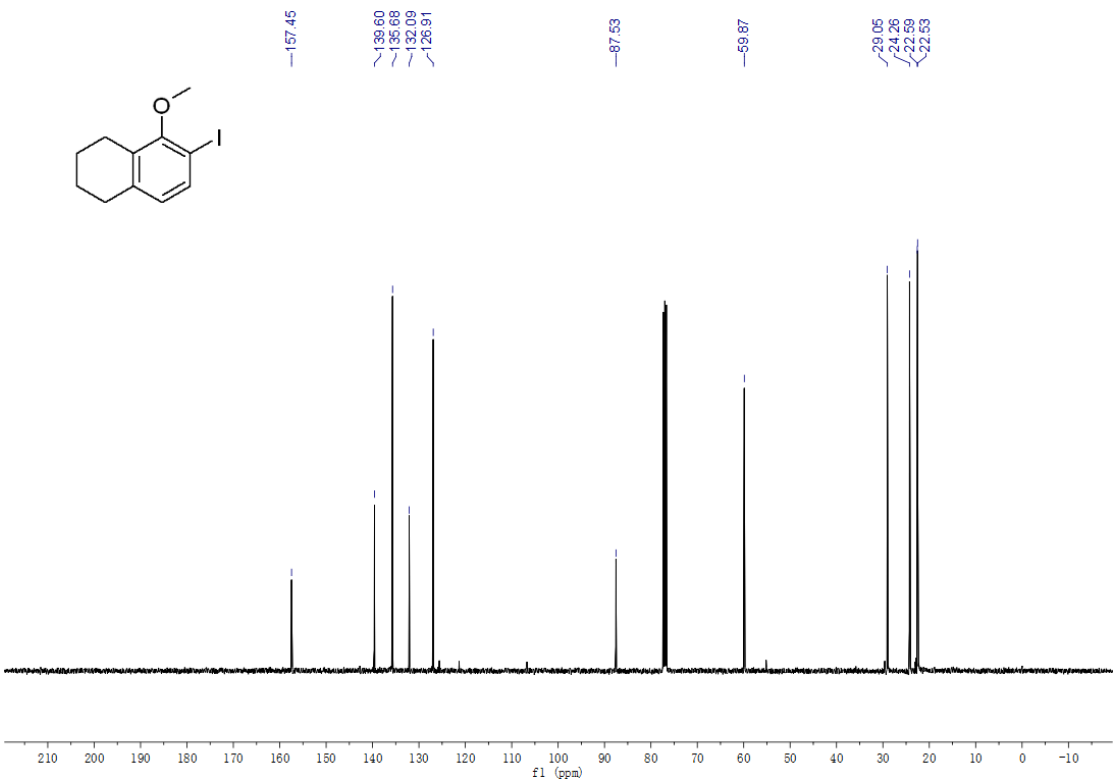
1-(*sec*-Butyl)-3-iodo-2-methoxybenzene (4b):



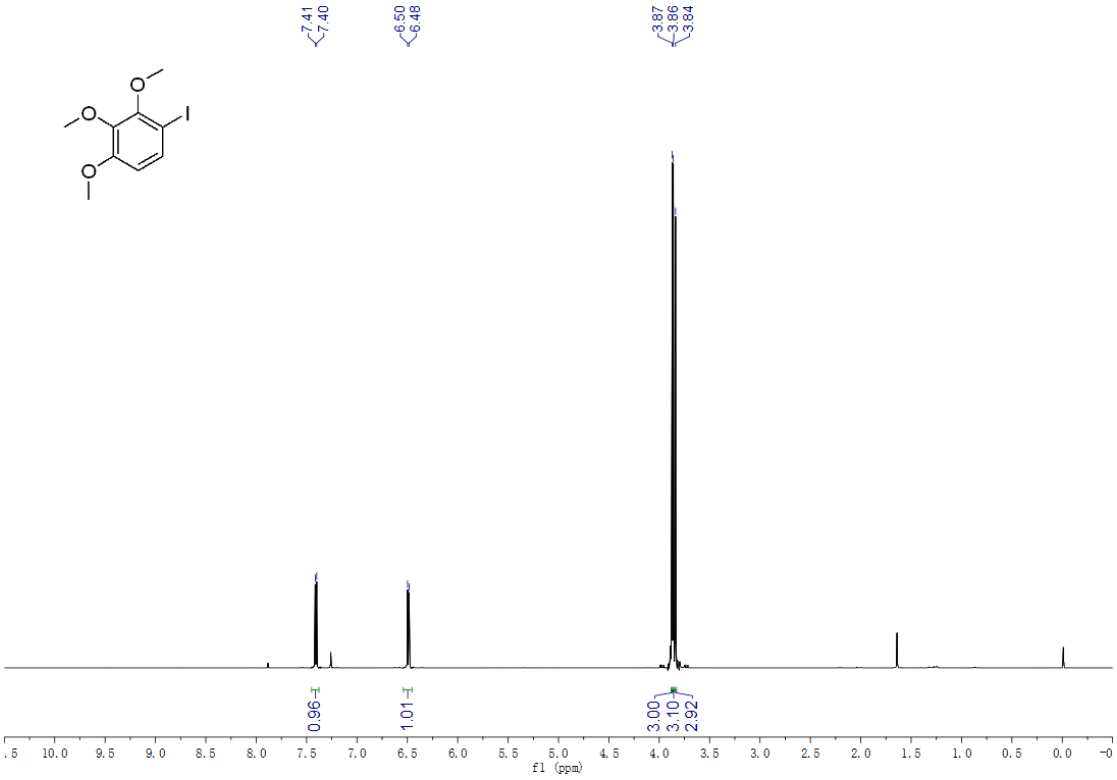


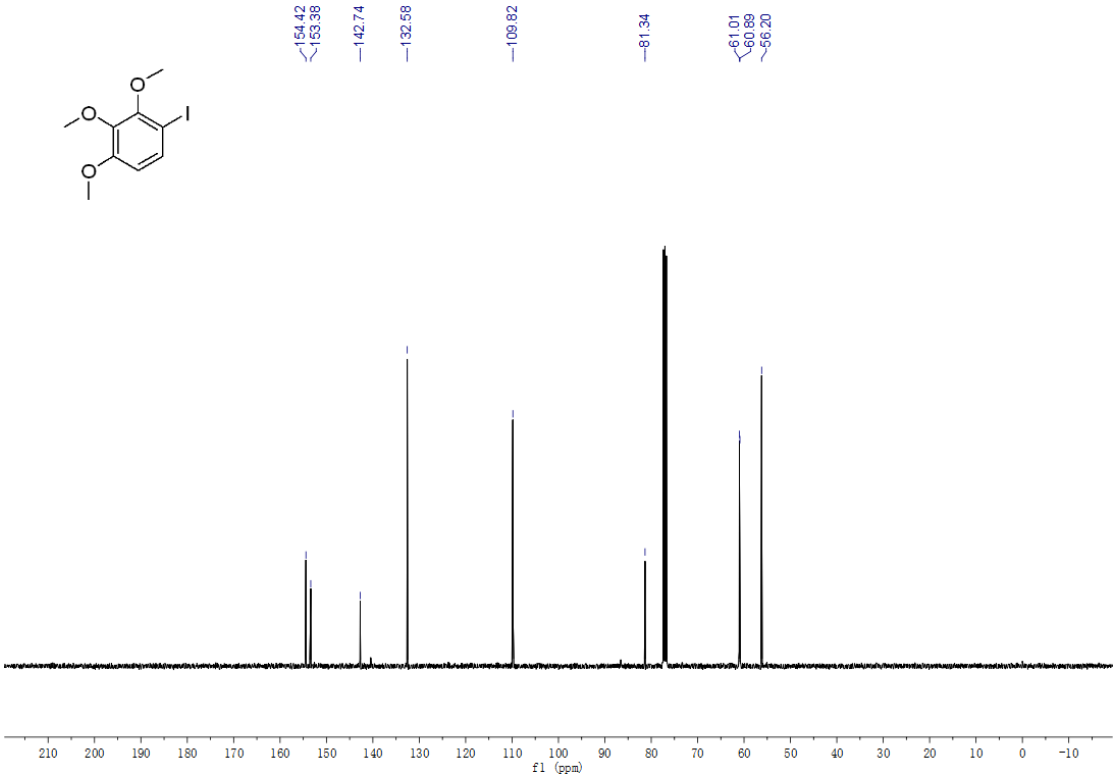
6-Iodo-5-methoxy-1,2,3,4-tetrahydronaphthalene (4c):



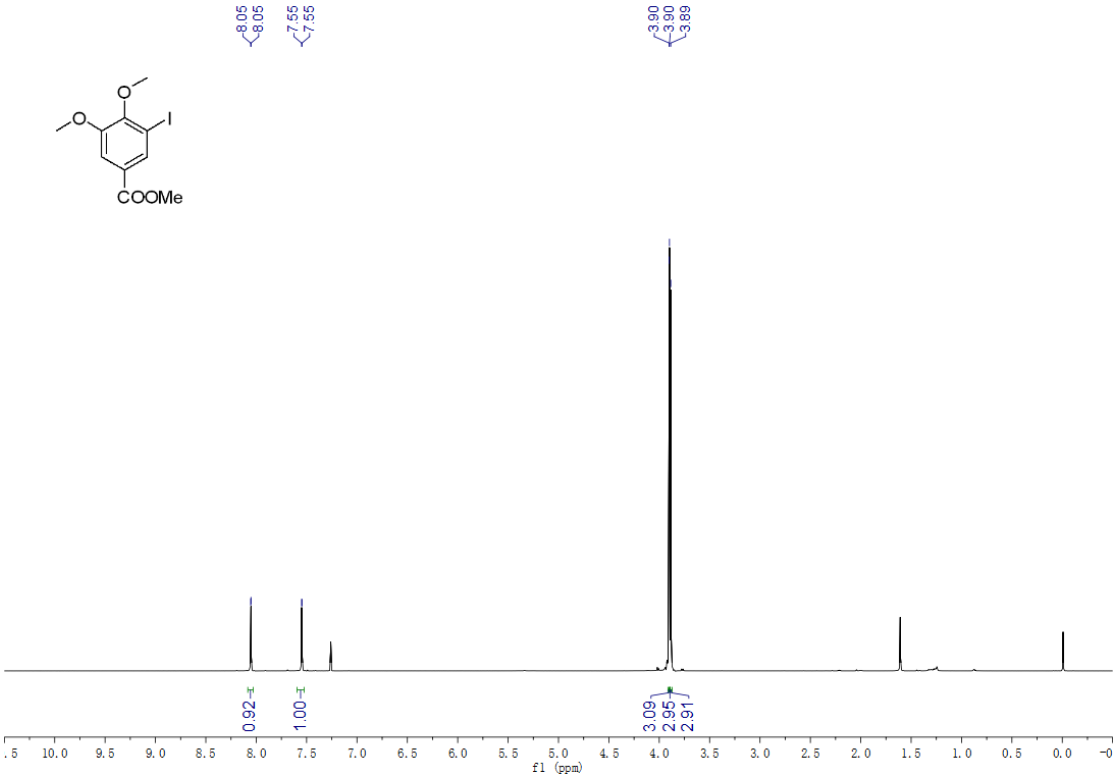


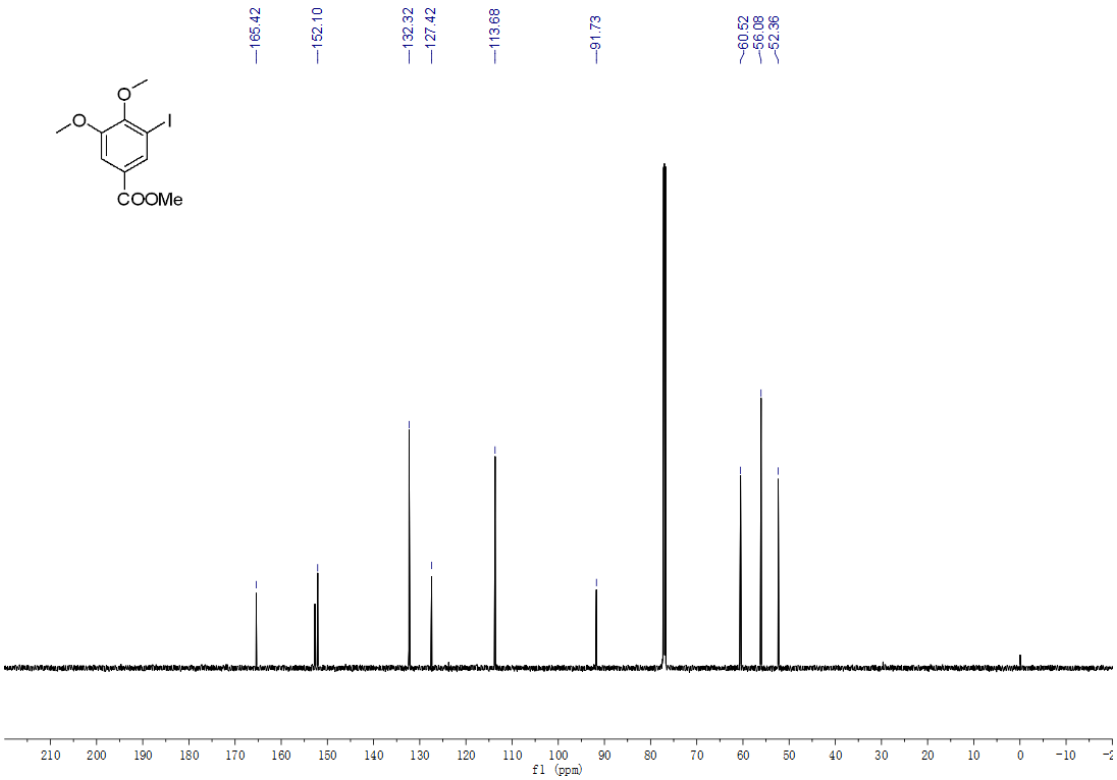
1-Iodo-2,3,4-trimethoxybenzene (4d):



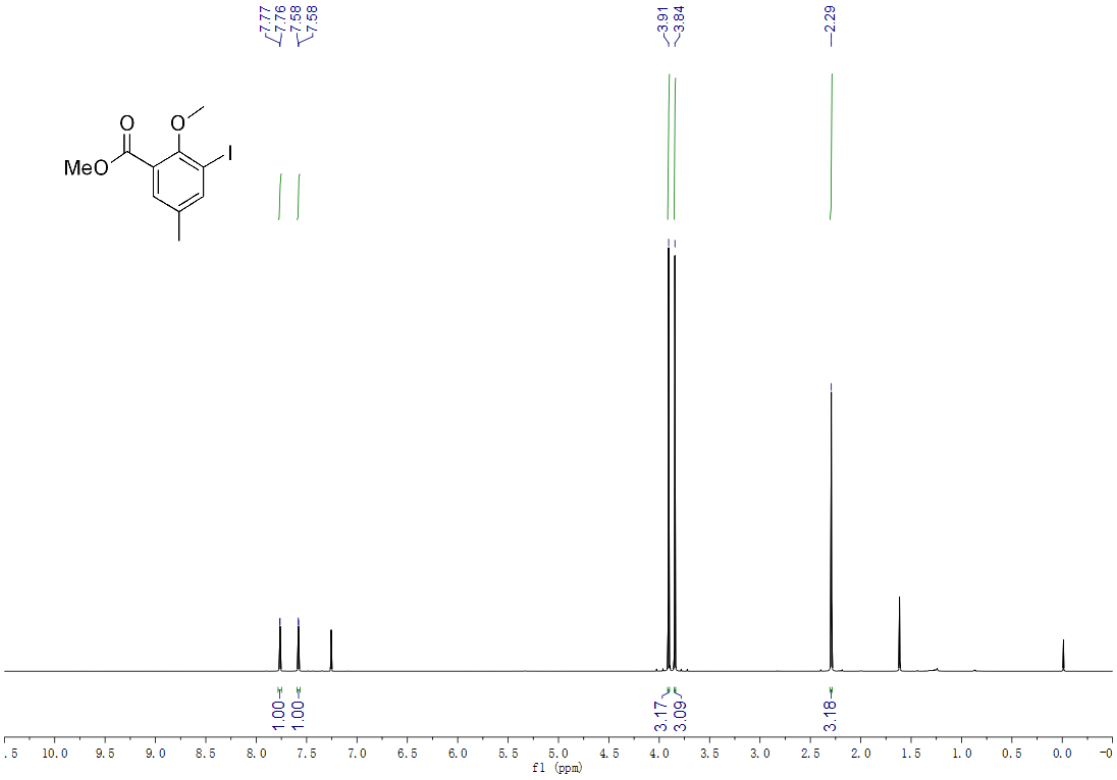


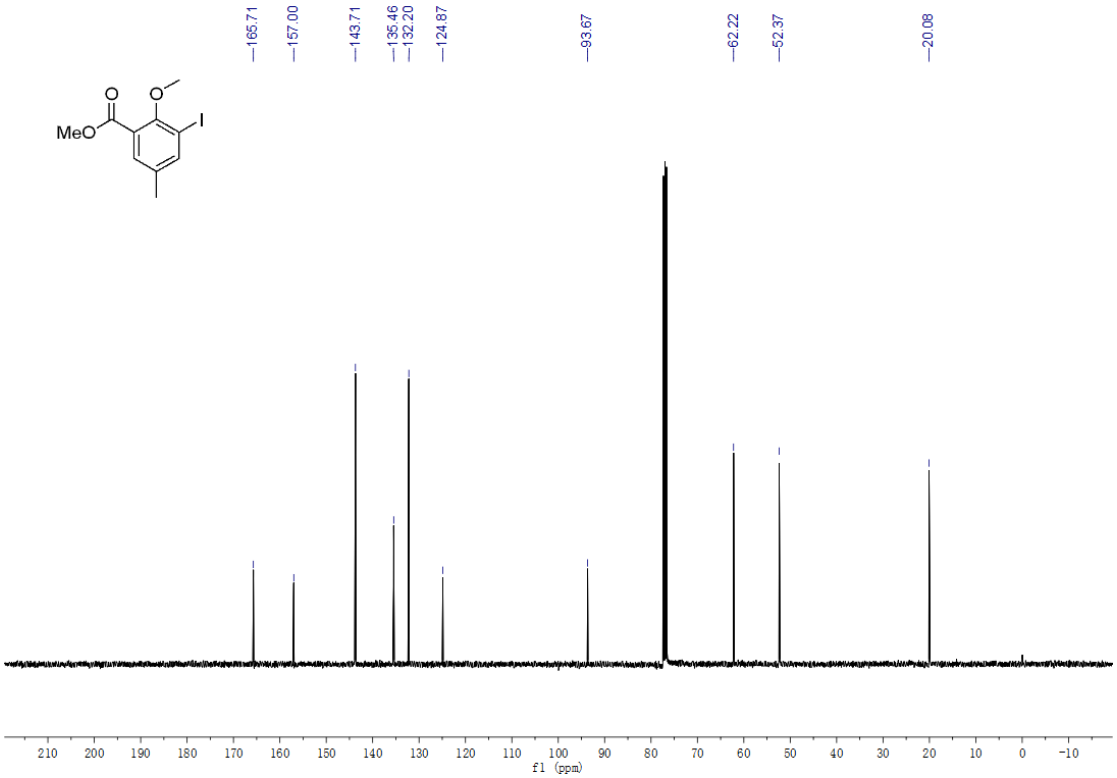
Methyl 3-iodo-4,5-dimethoxybenzoate (4e):



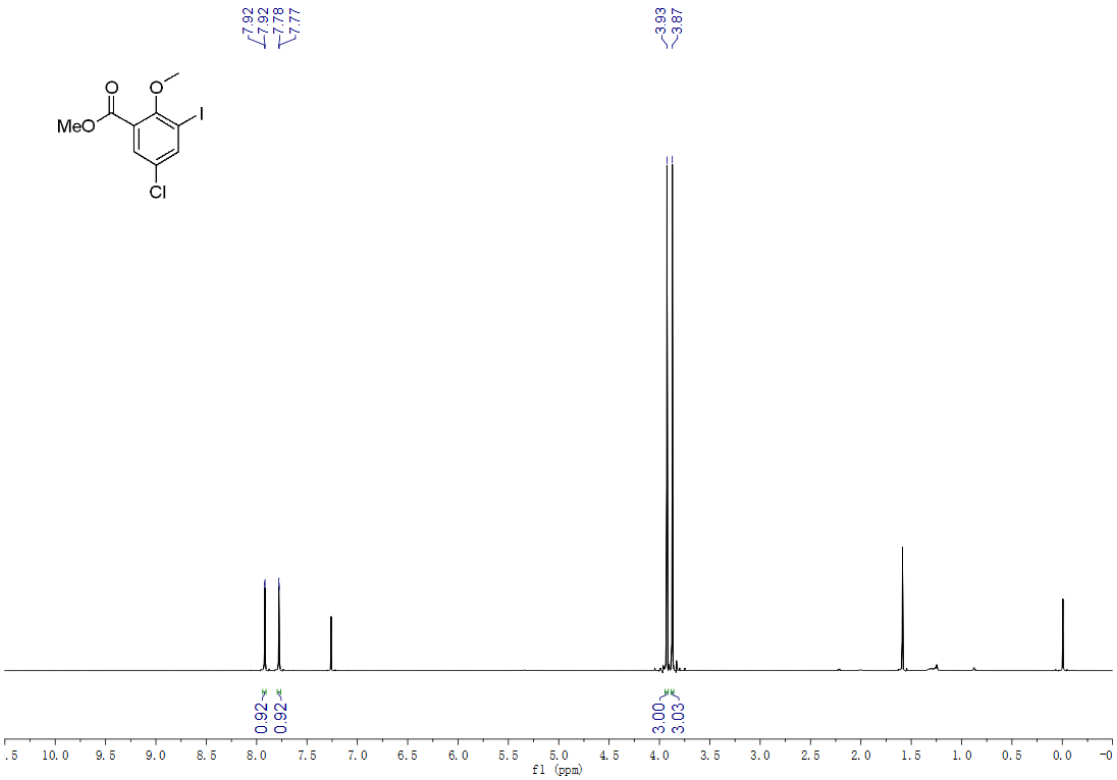


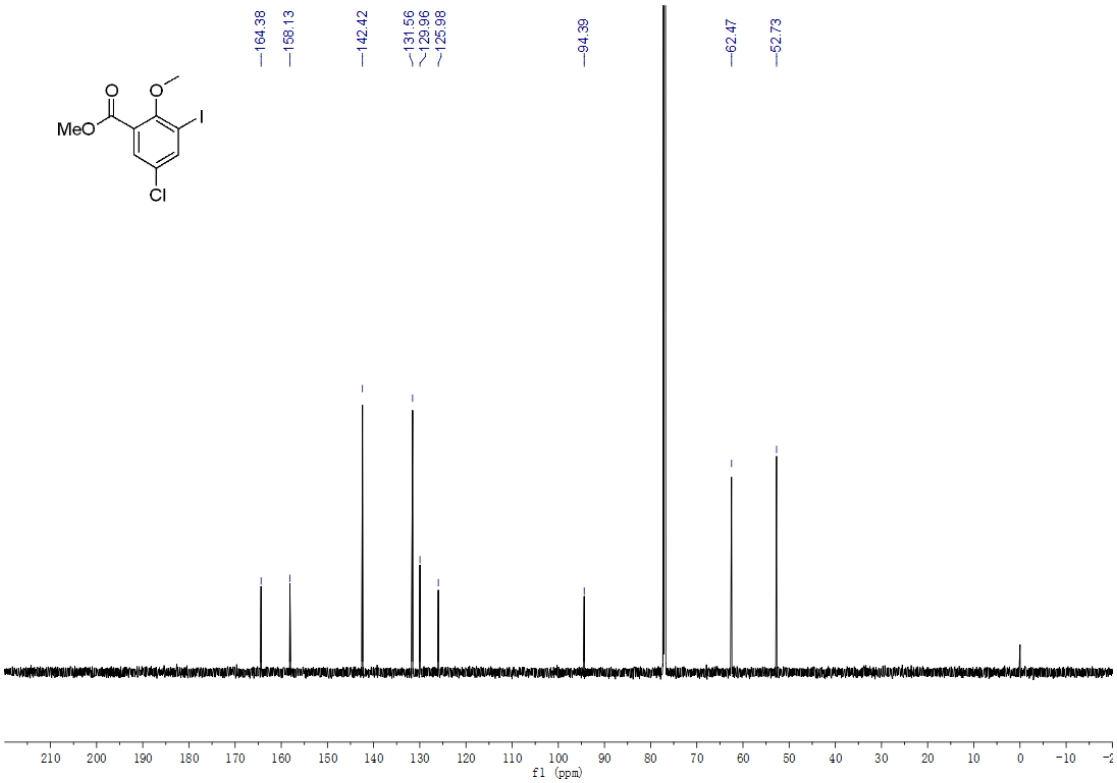
Methyl 3-iodo-2-methoxy-5-methylbenzoate (4f):



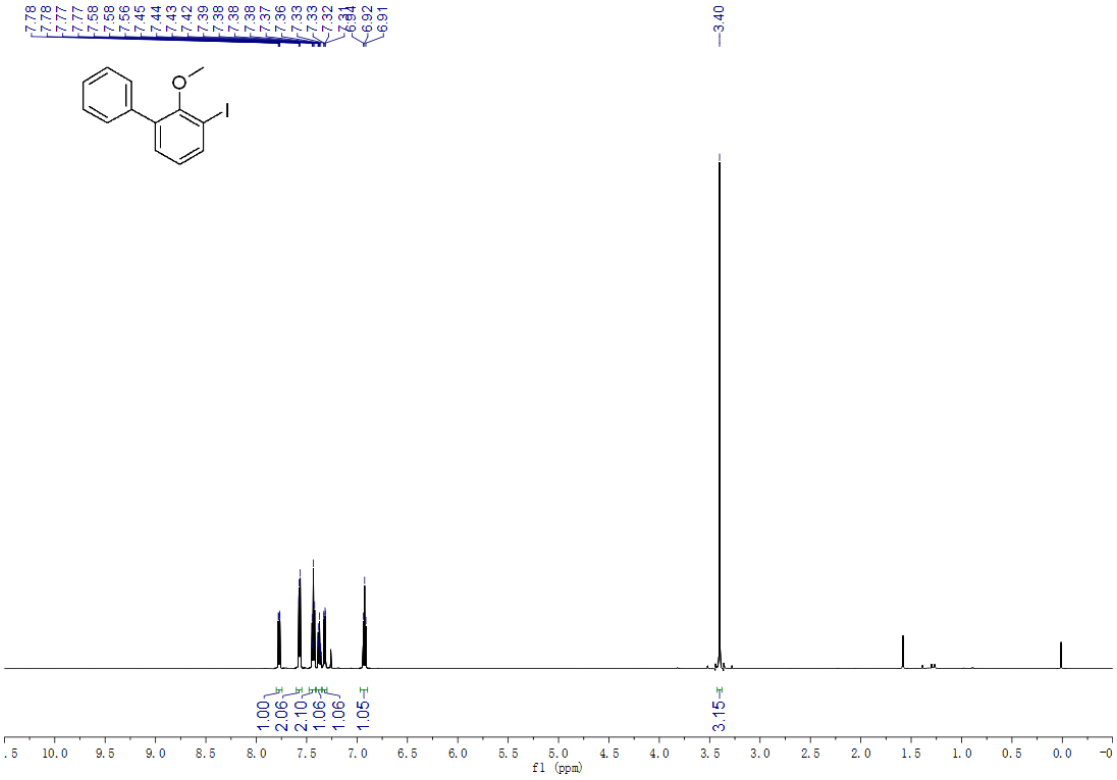


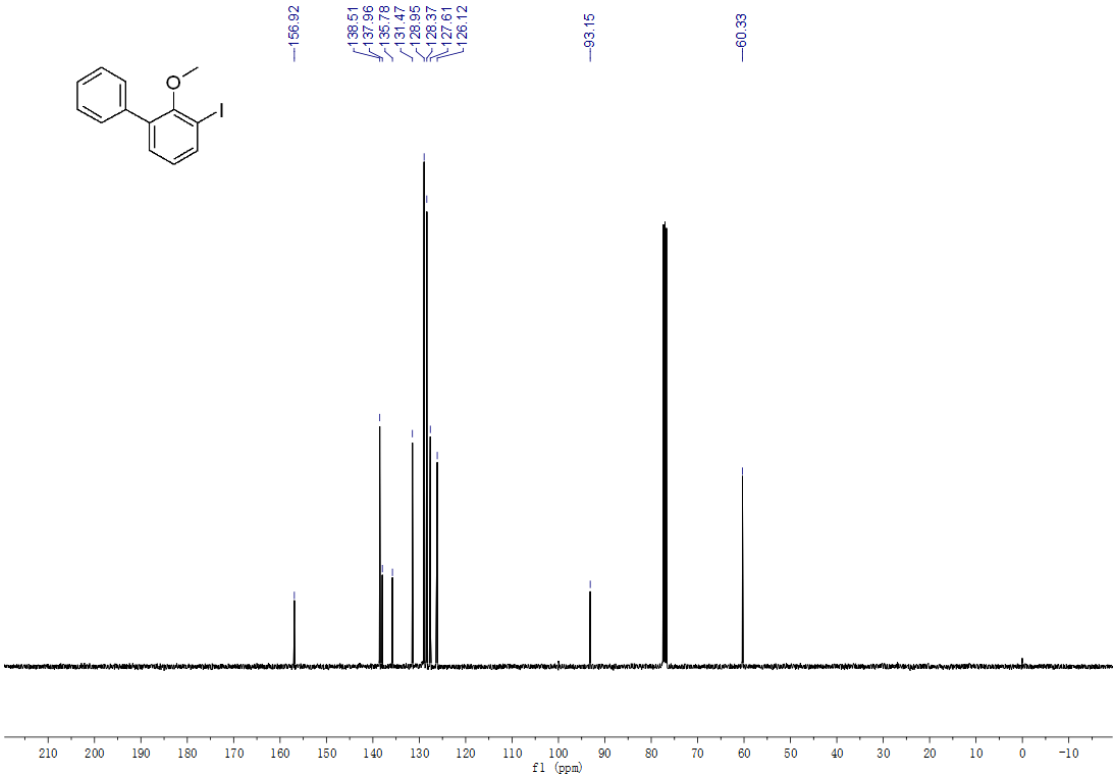
Methyl 5-chloro-3-iodo-2-methoxybenzoate (**4g**):



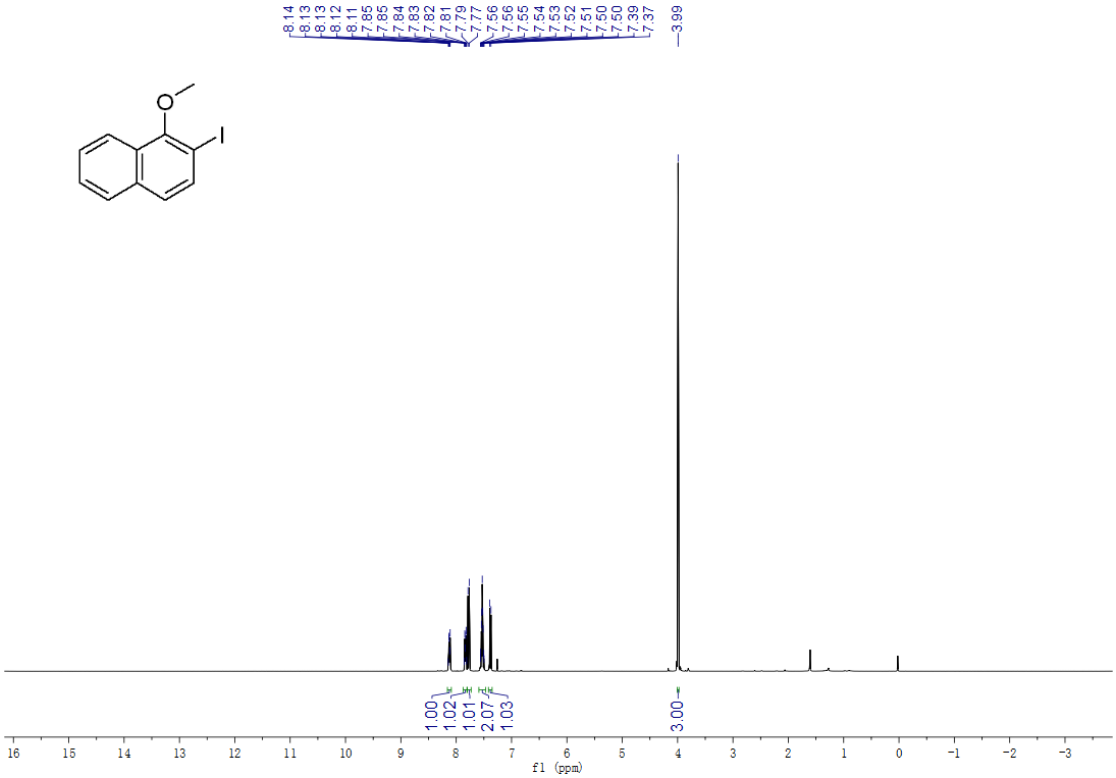


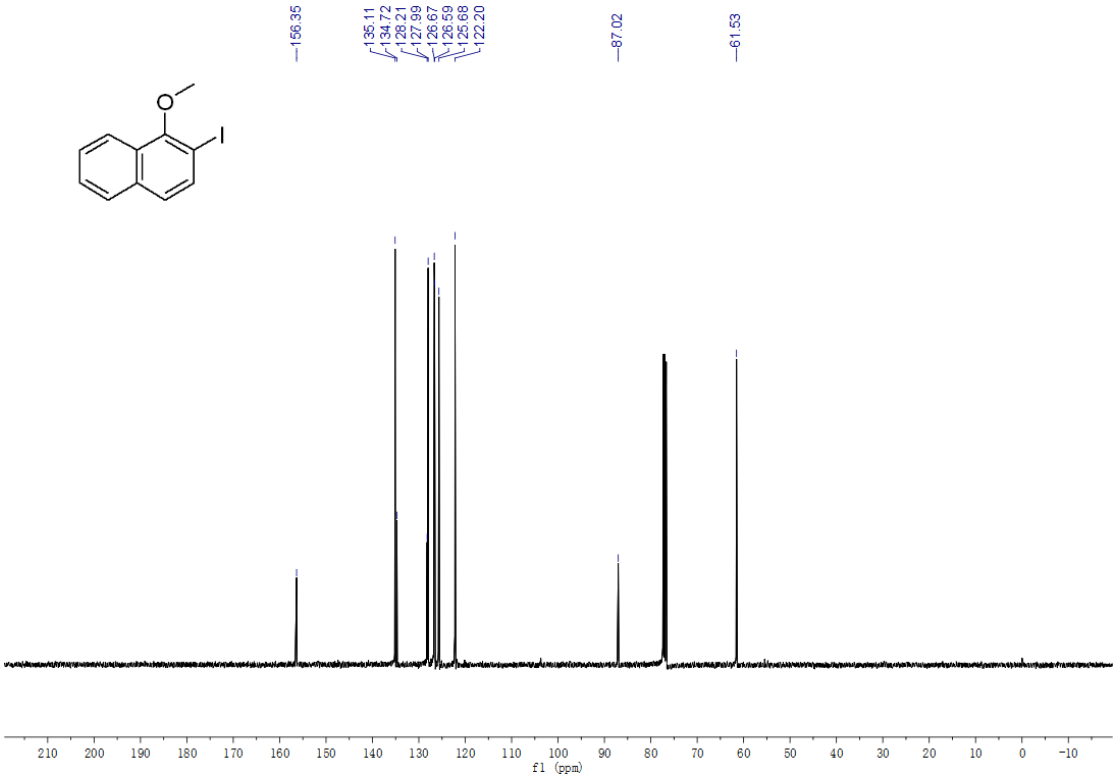
3-Iodo-2-methoxy-1,1'-biphenyl (4i):



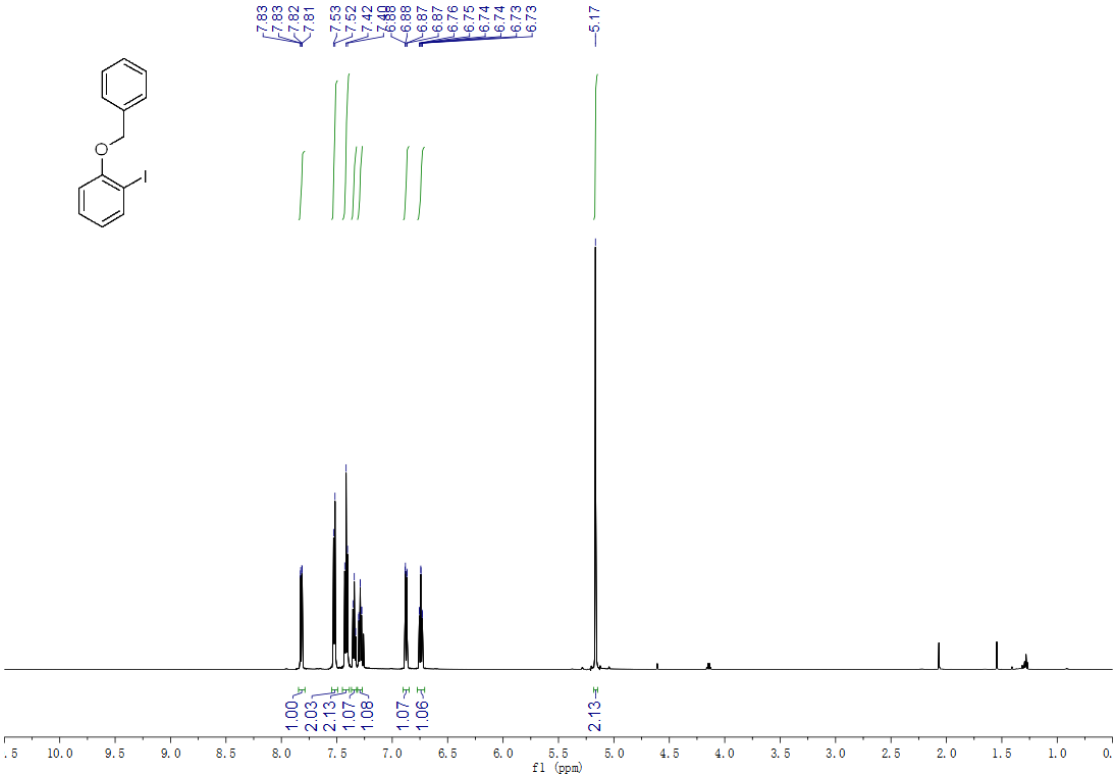


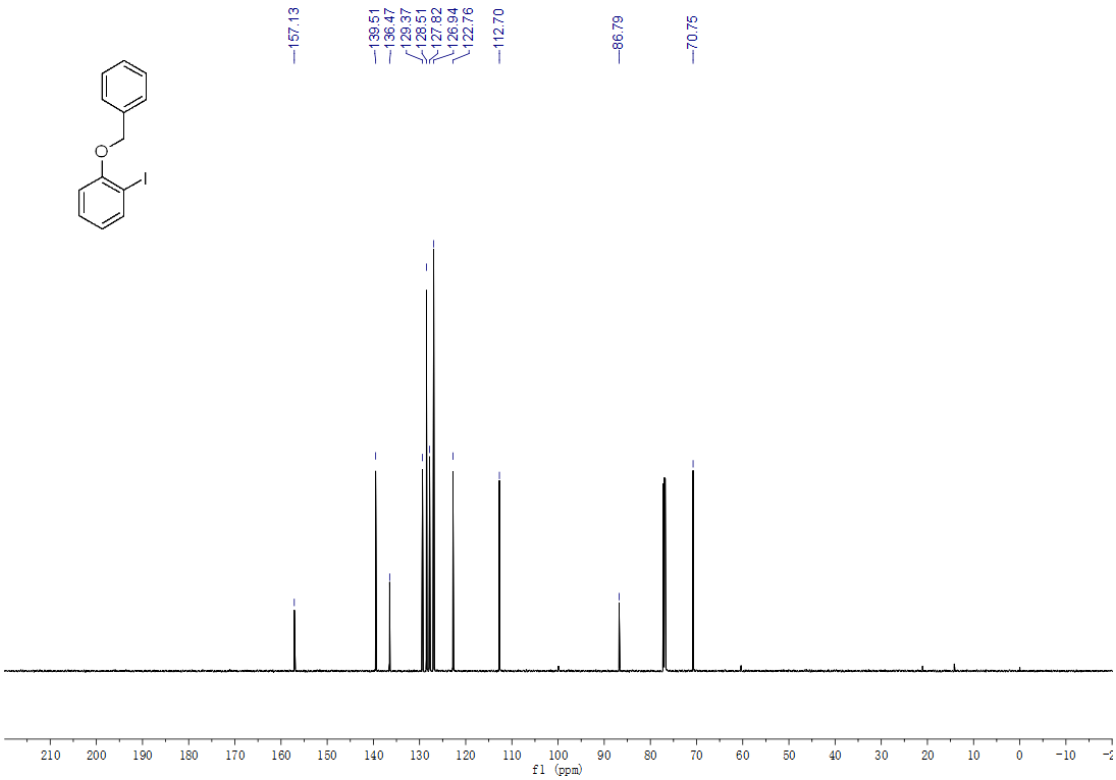
2-Iodo-1-methoxynaphthalene (4j):



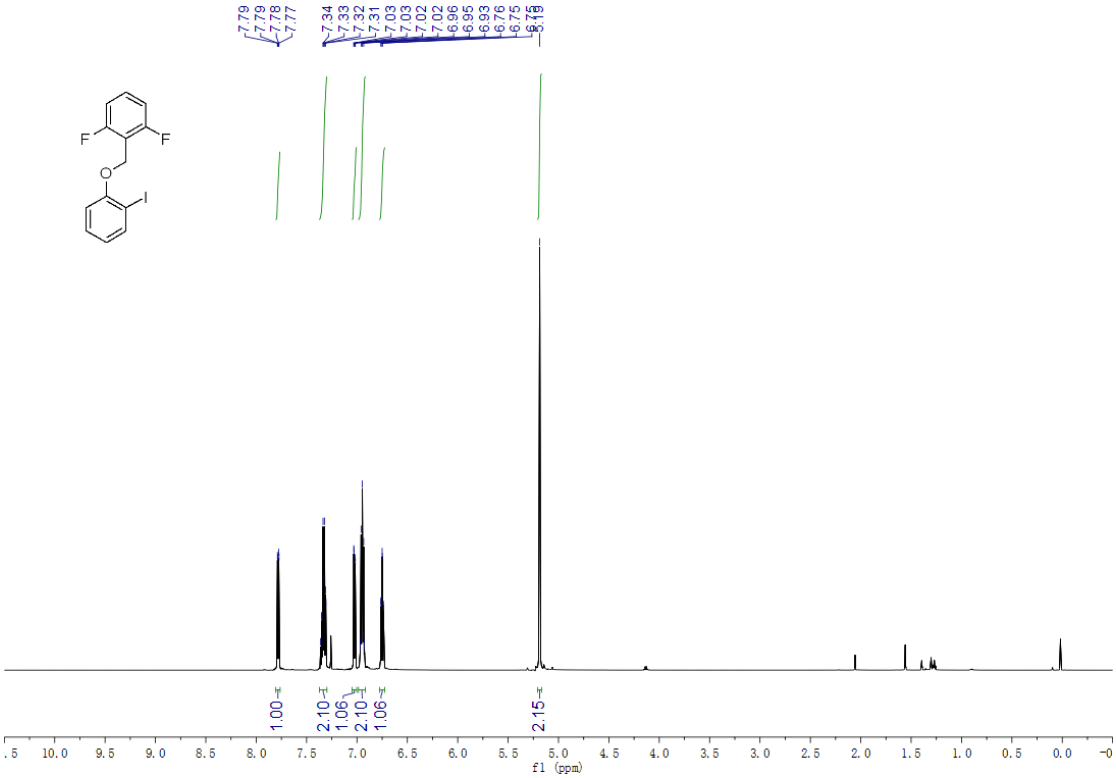


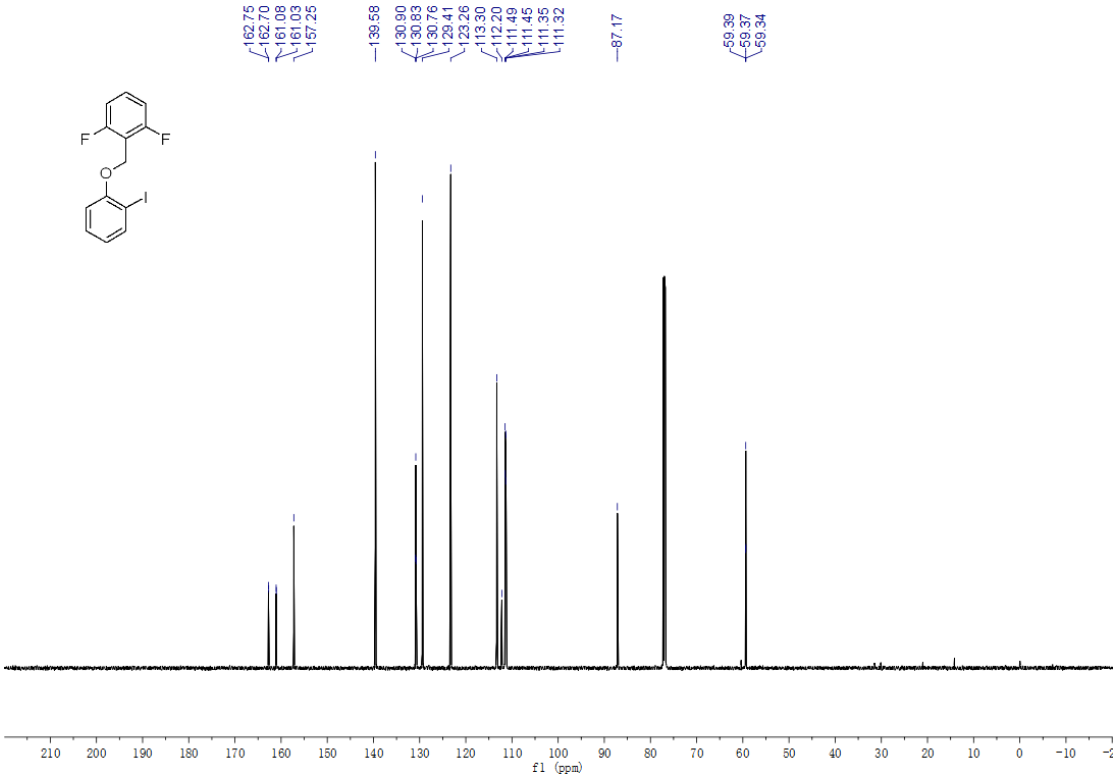
1-(Benzyloxy)-2-iodobenzene (6a):



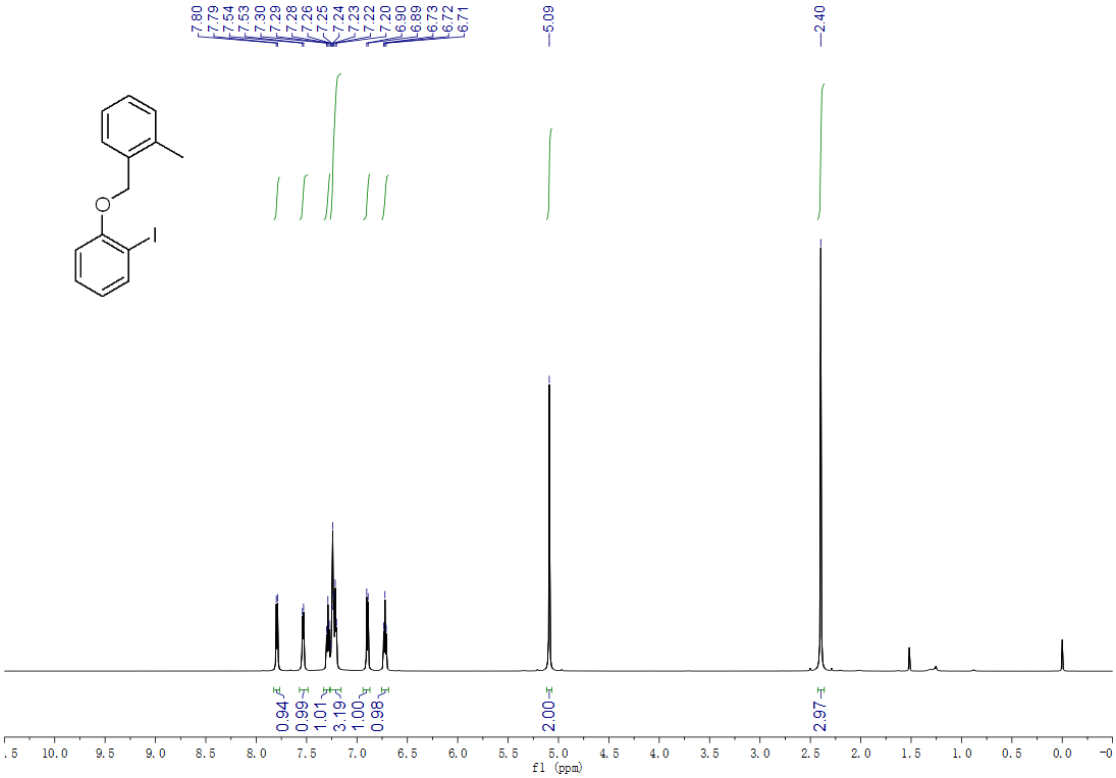


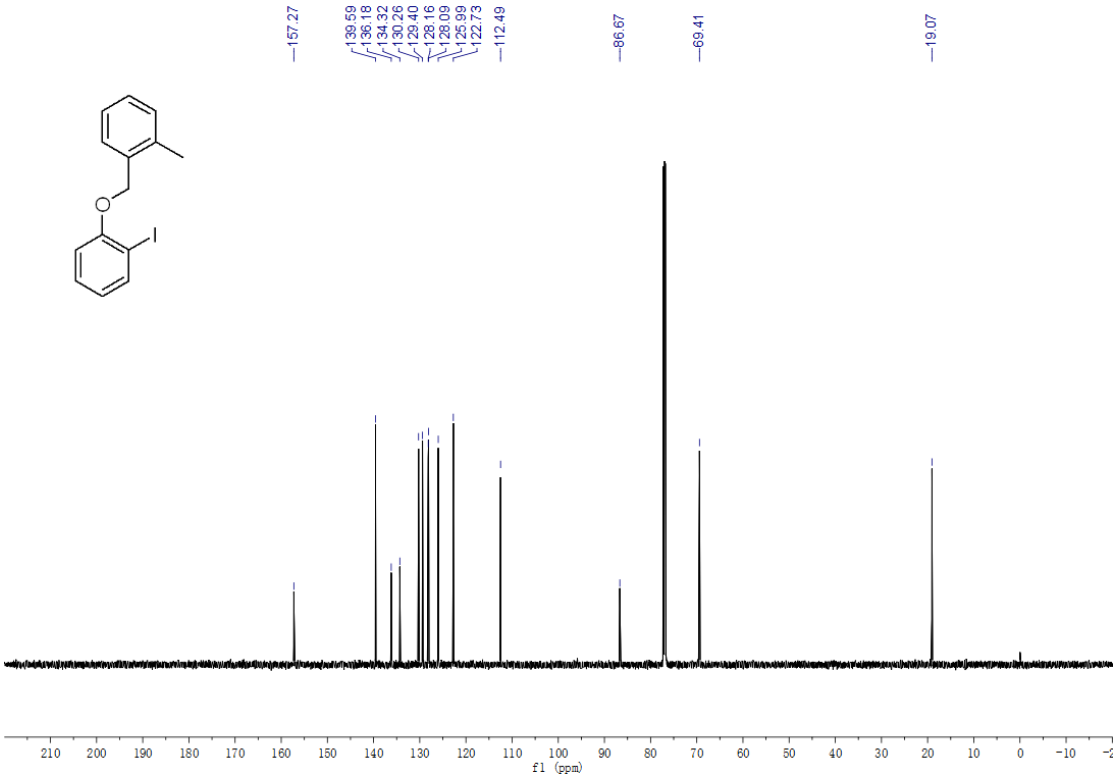
1,3-Difluoro-2-((2-iodophenoxy)methyl)benzene (6b):



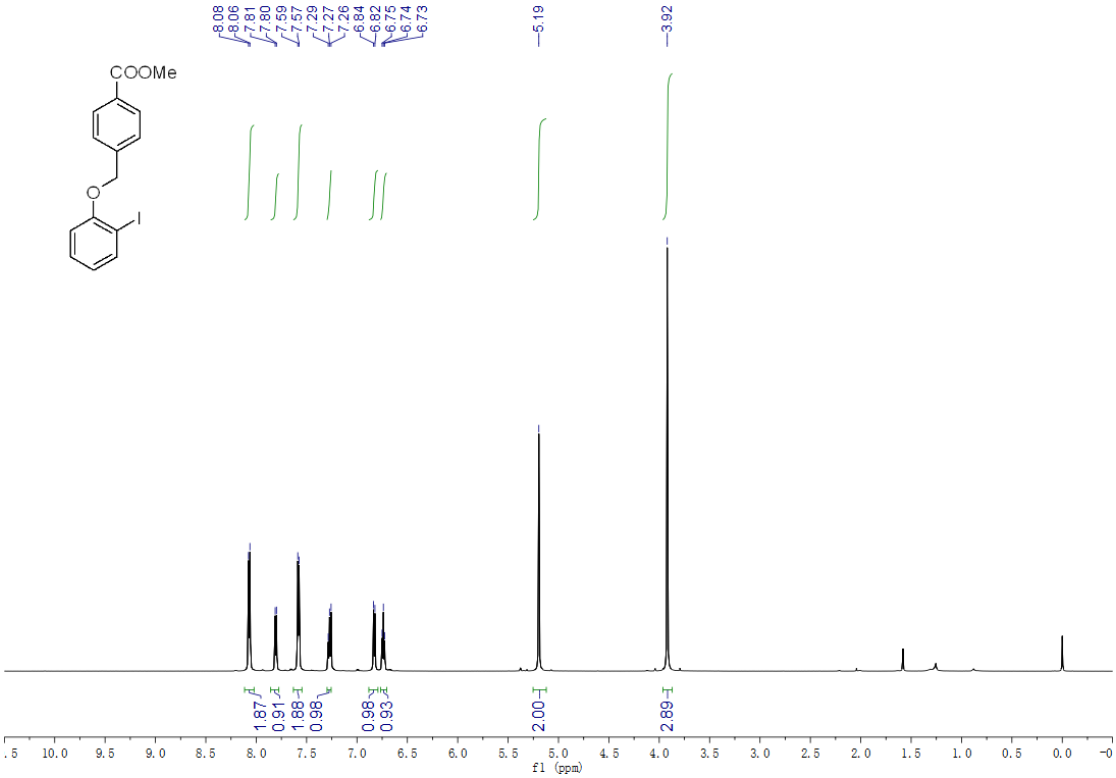


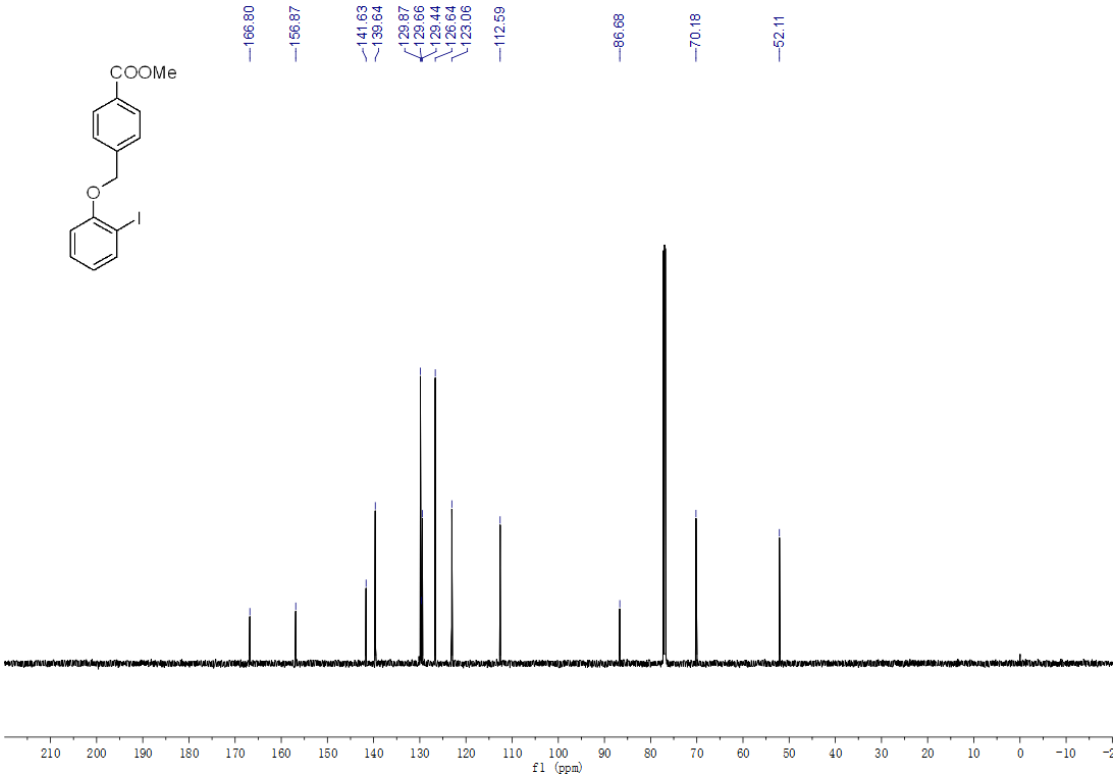
1-Iodo-2-((2-methylbenzyl)oxy)benzene (6c):



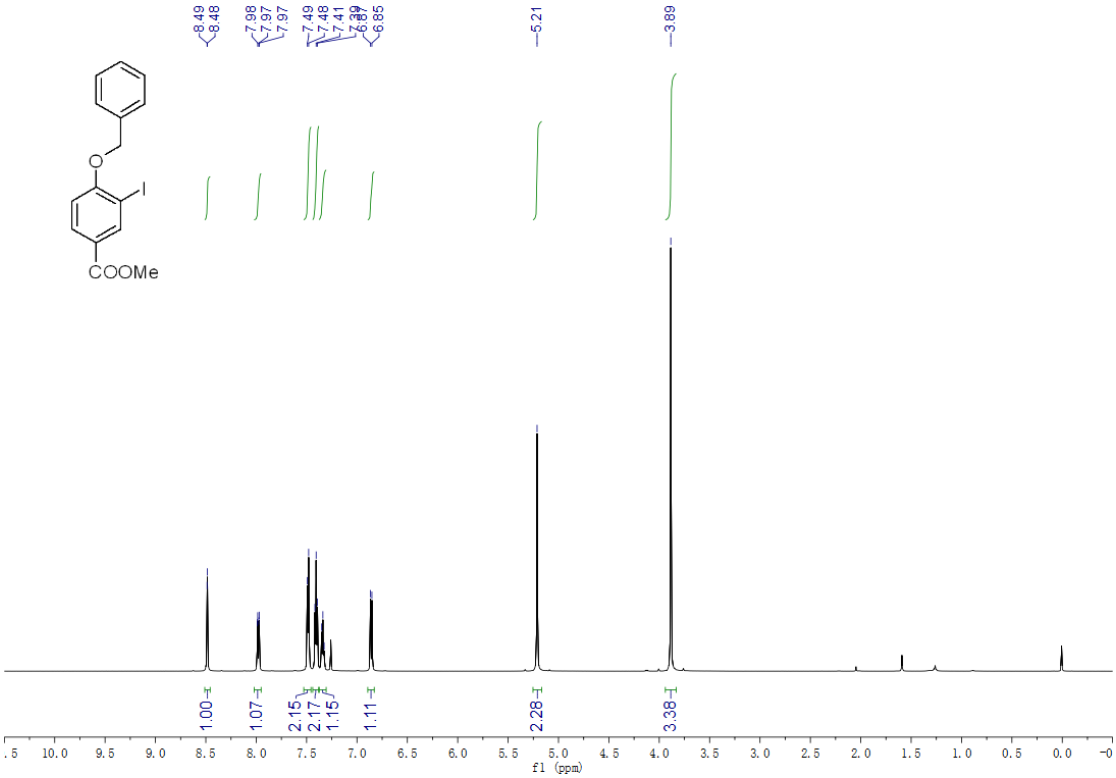


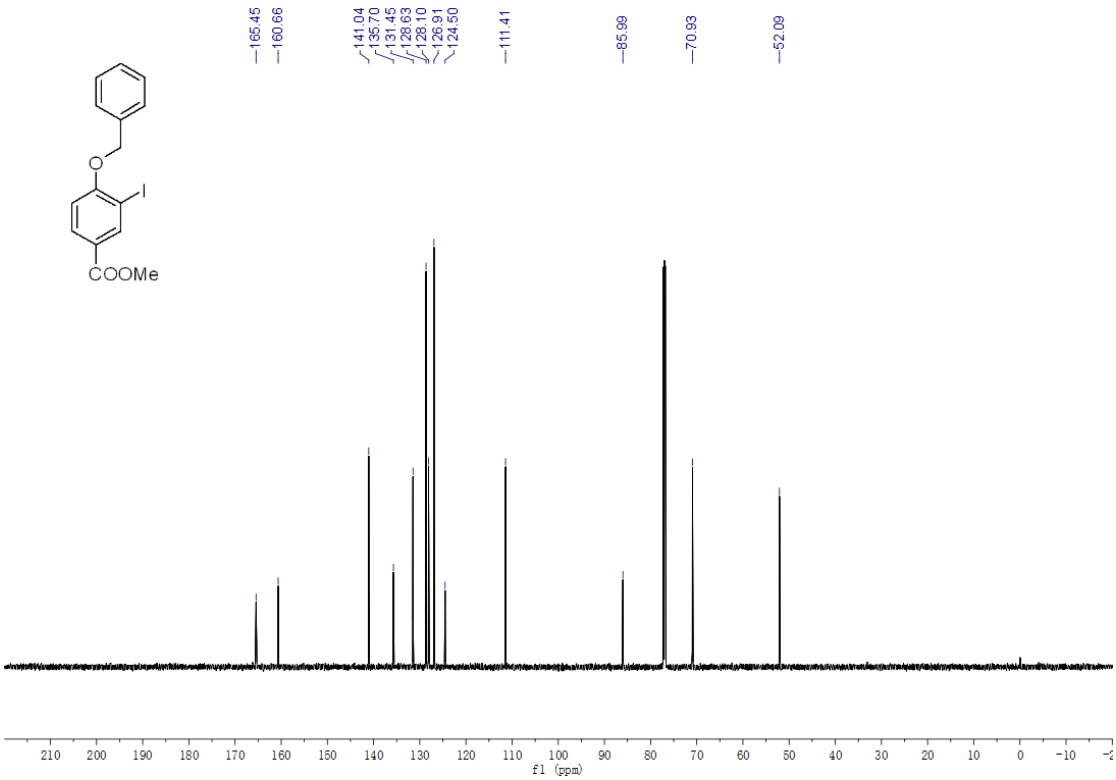
Methyl 4-((2-iodophenoxy)methyl)benzoate (6d):



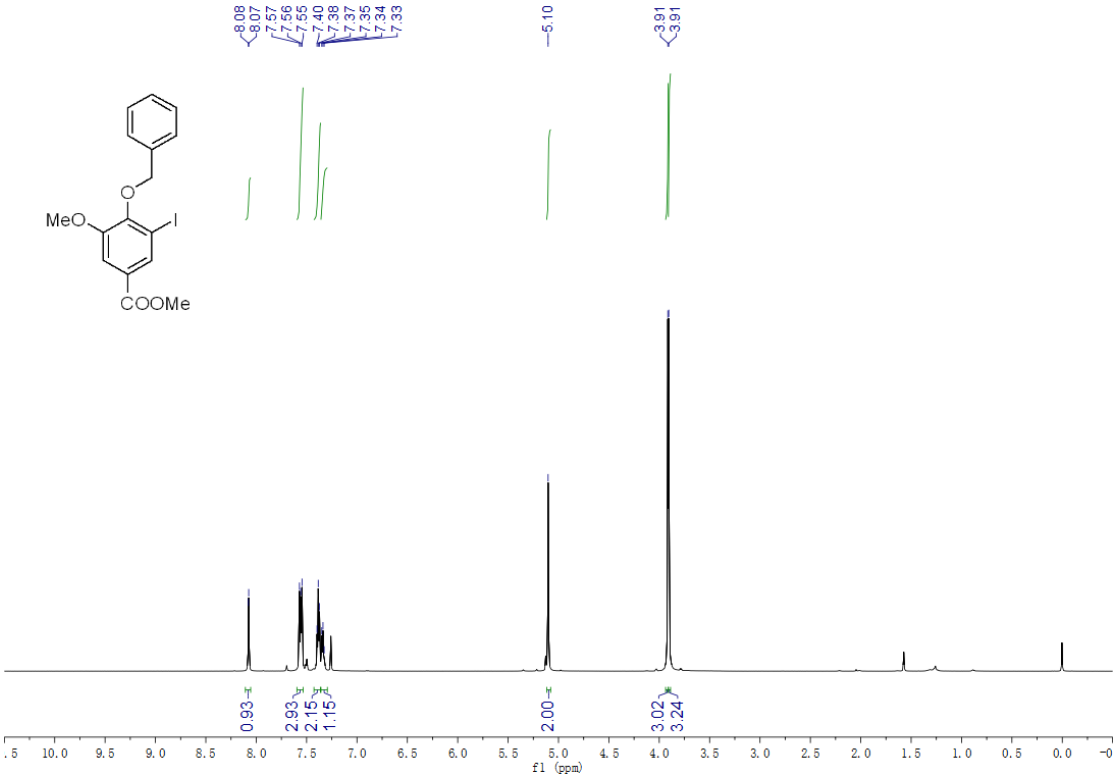


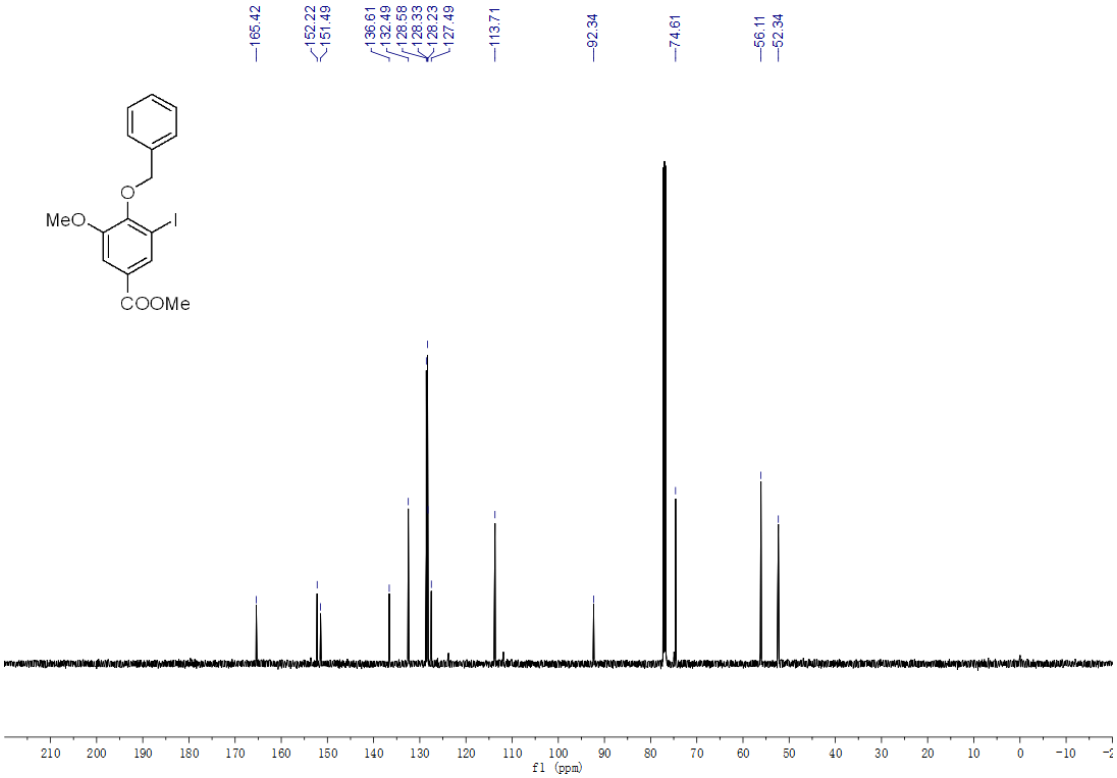
Methyl 4-(benzyloxy)-3-iodobenzoate (6e):



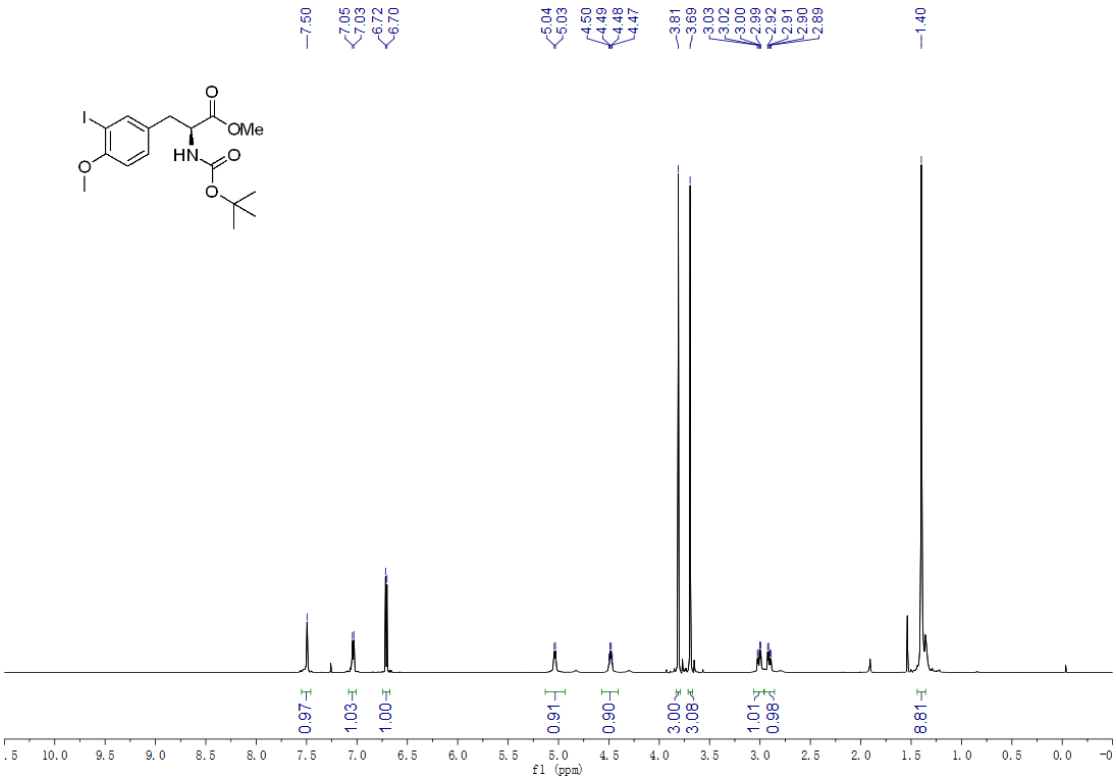


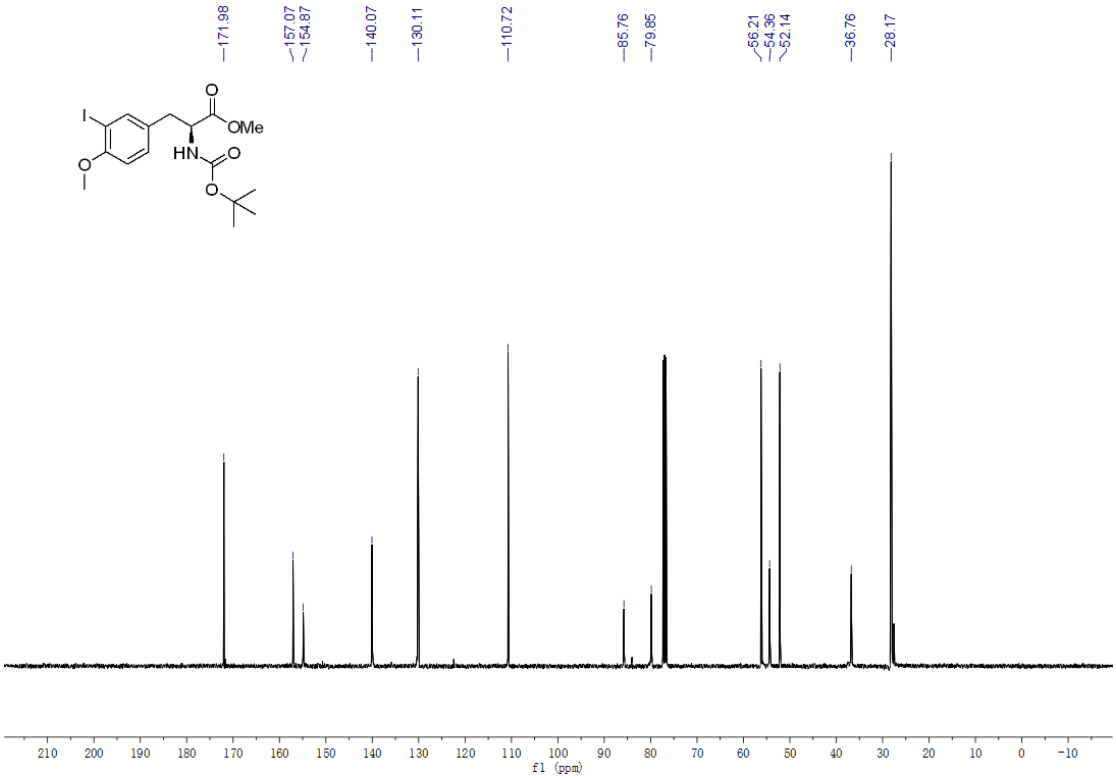
Methyl 4-(benzyloxy)-3-iodo-5-methoxybenzoate (6f):



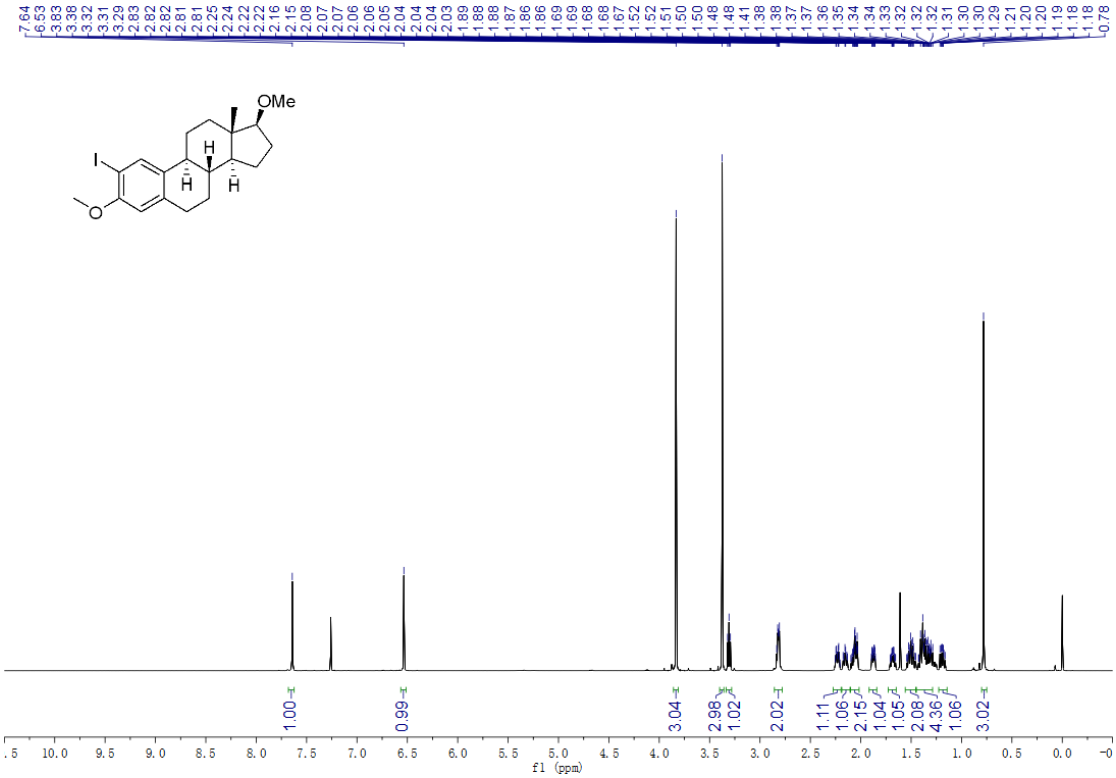


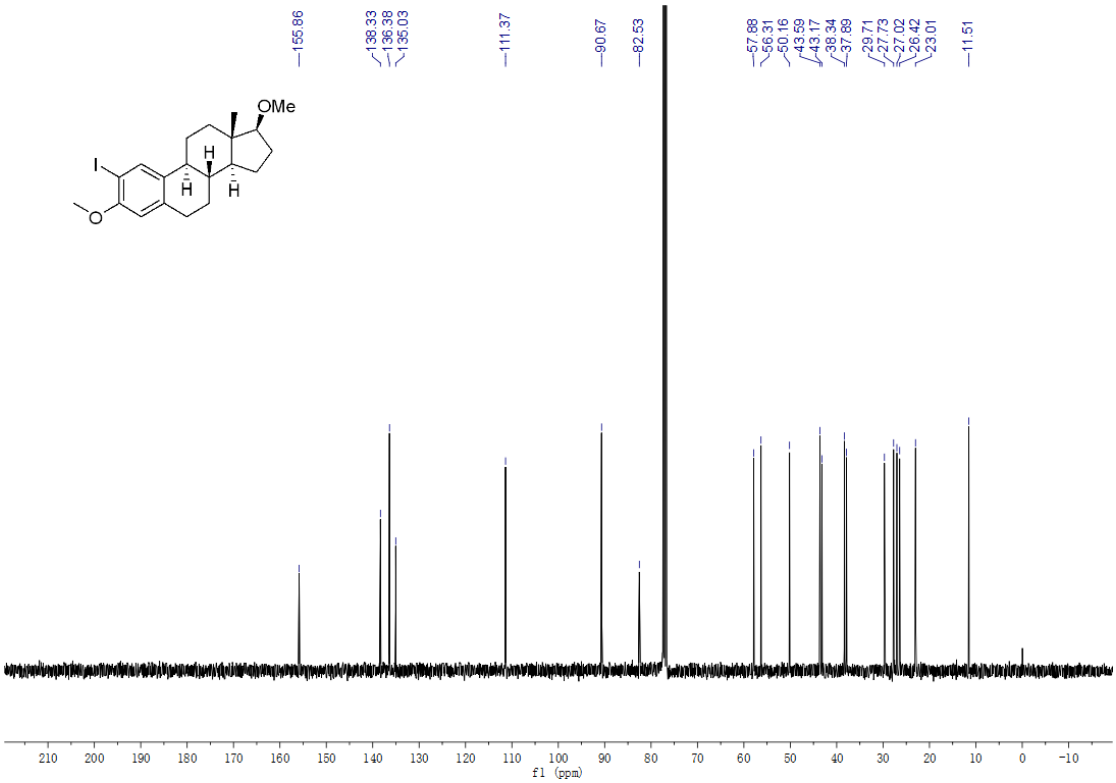
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(3-iodo-4-methoxyphenyl)propanoate (8a):



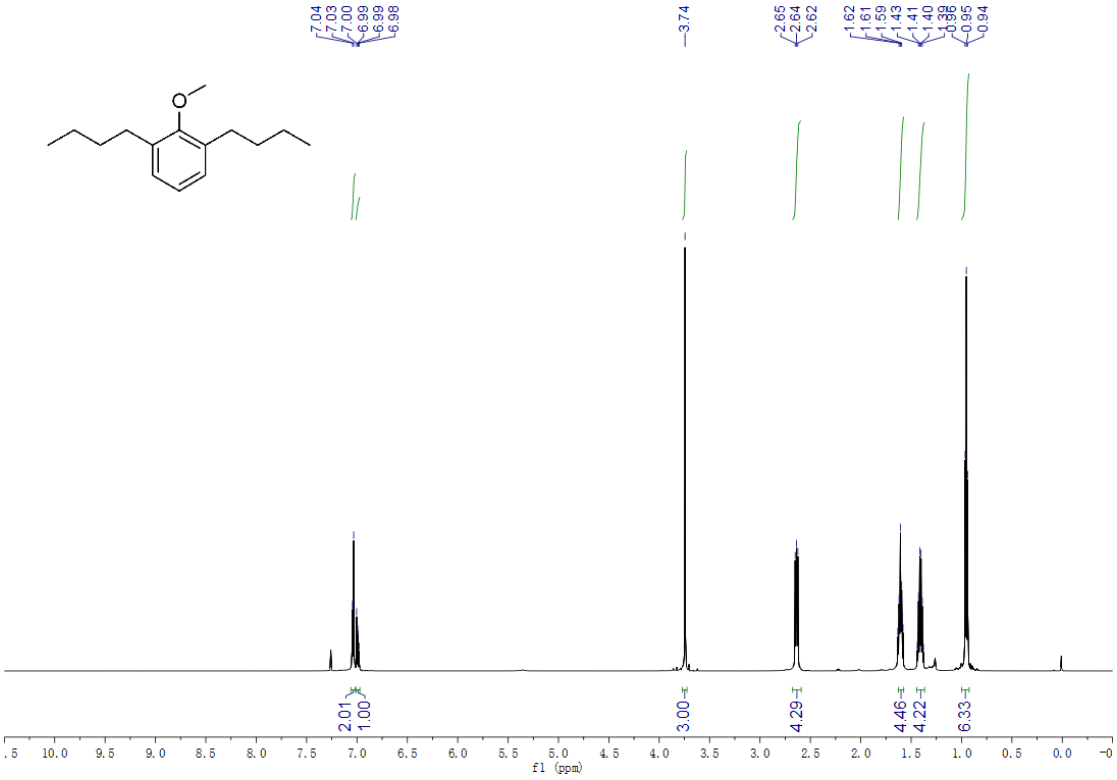


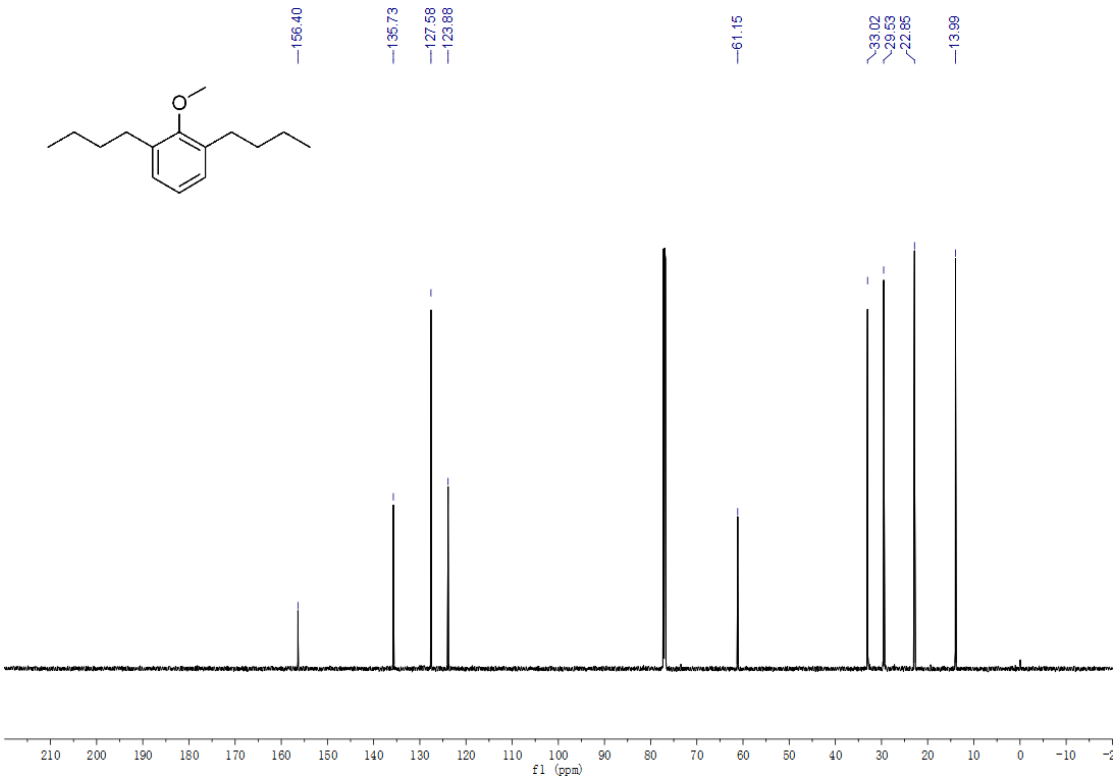
(8*R*,9*S*,13*S*,14*S*,17*S*)-2-Iodo-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (8b):



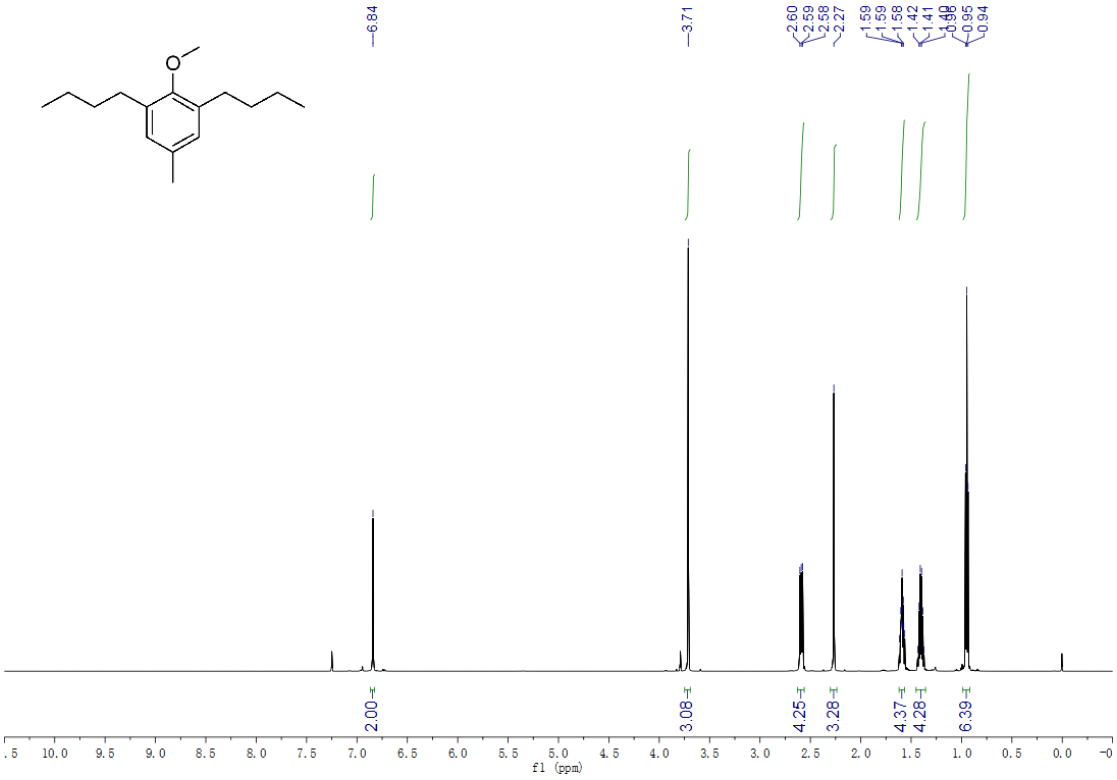


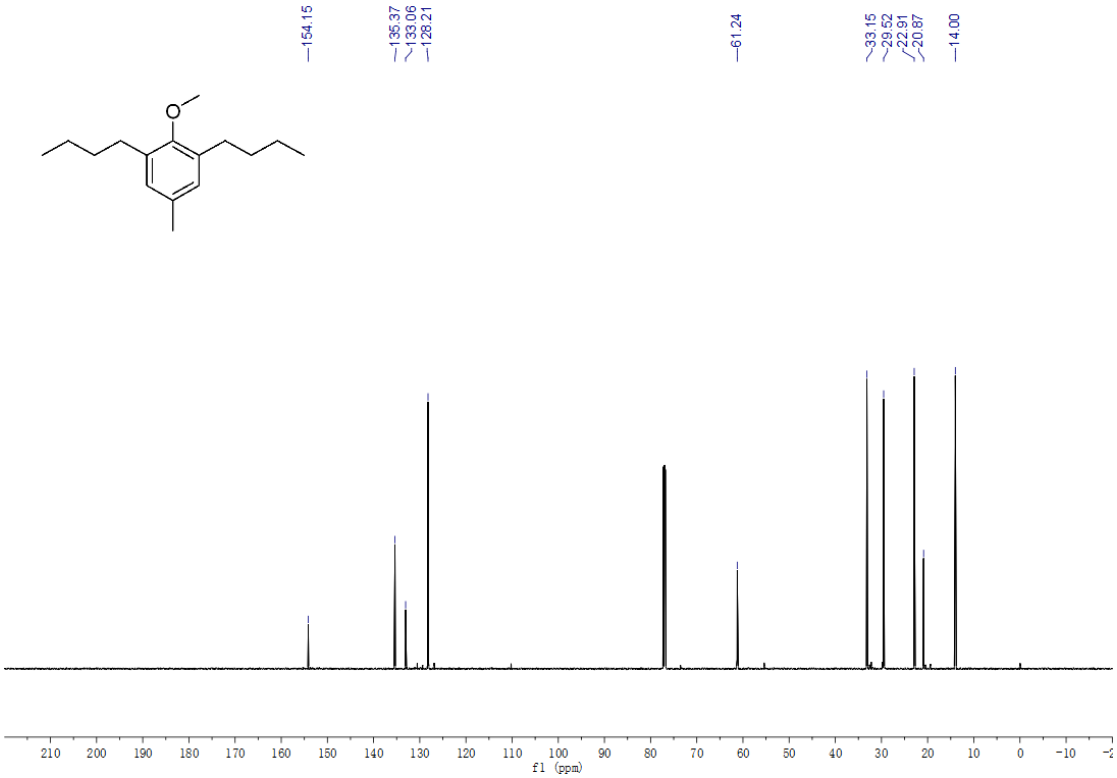
1,3-Dibutyl-2-methoxybenzene (3aa):



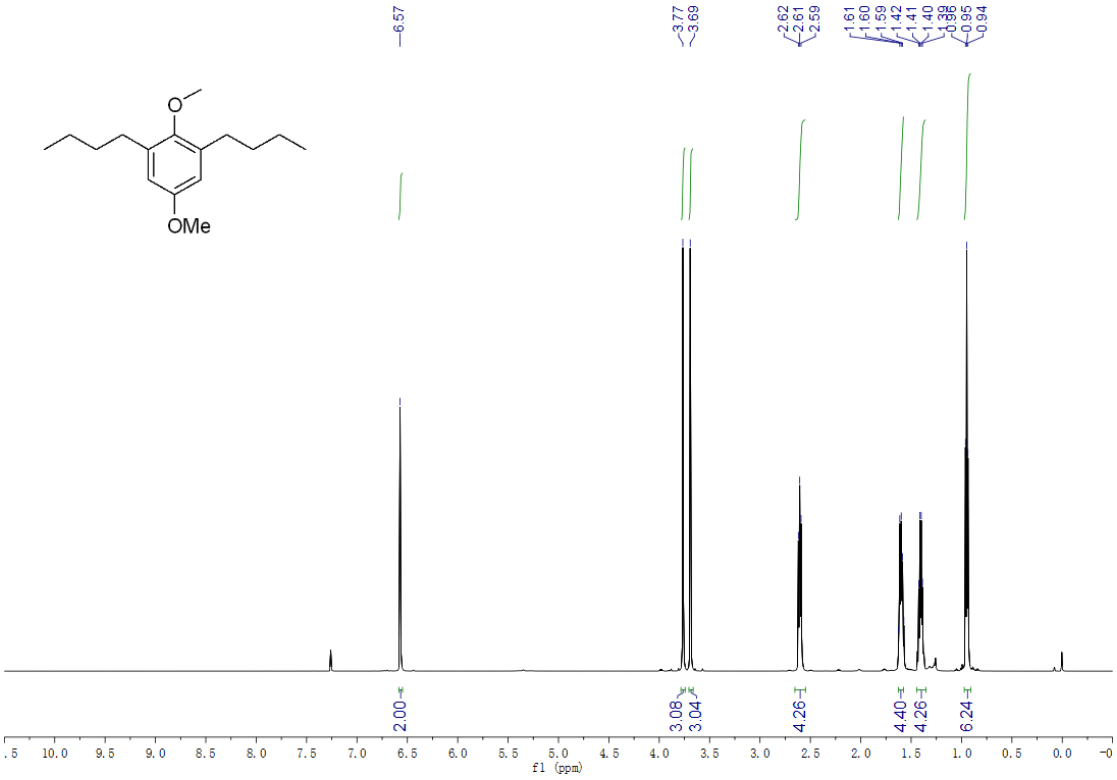


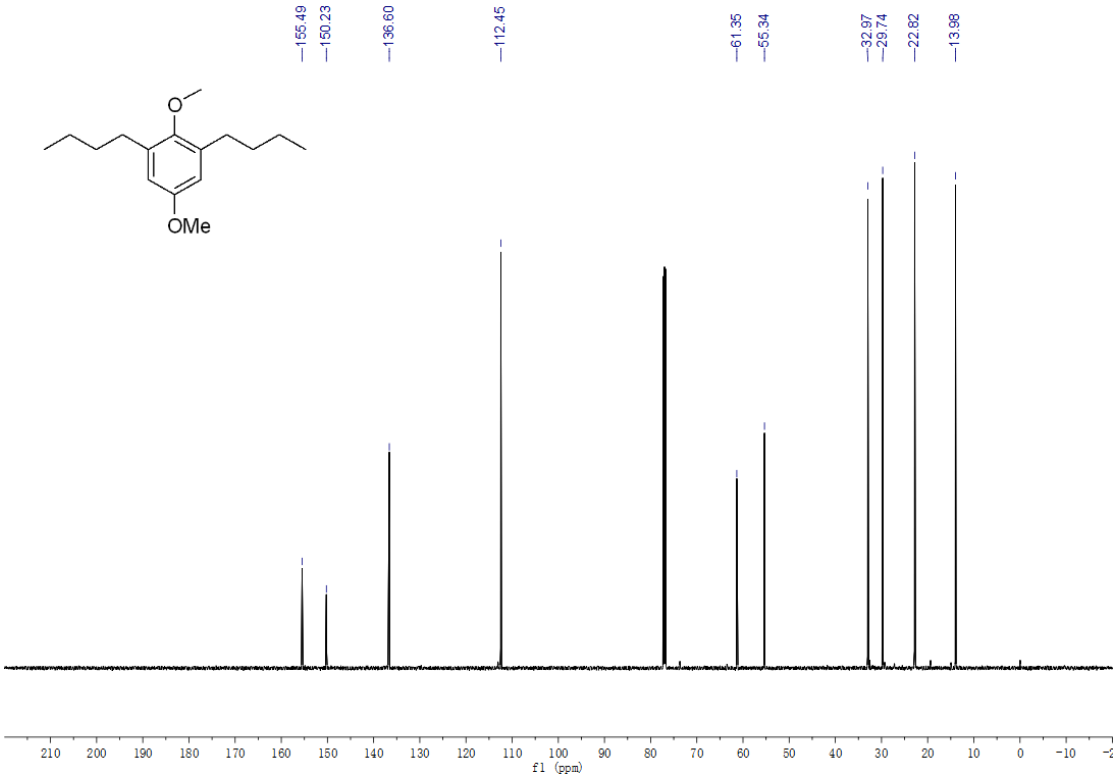
1,3-Dibutyl-2-methoxy-5-methylbenzene (3ba):



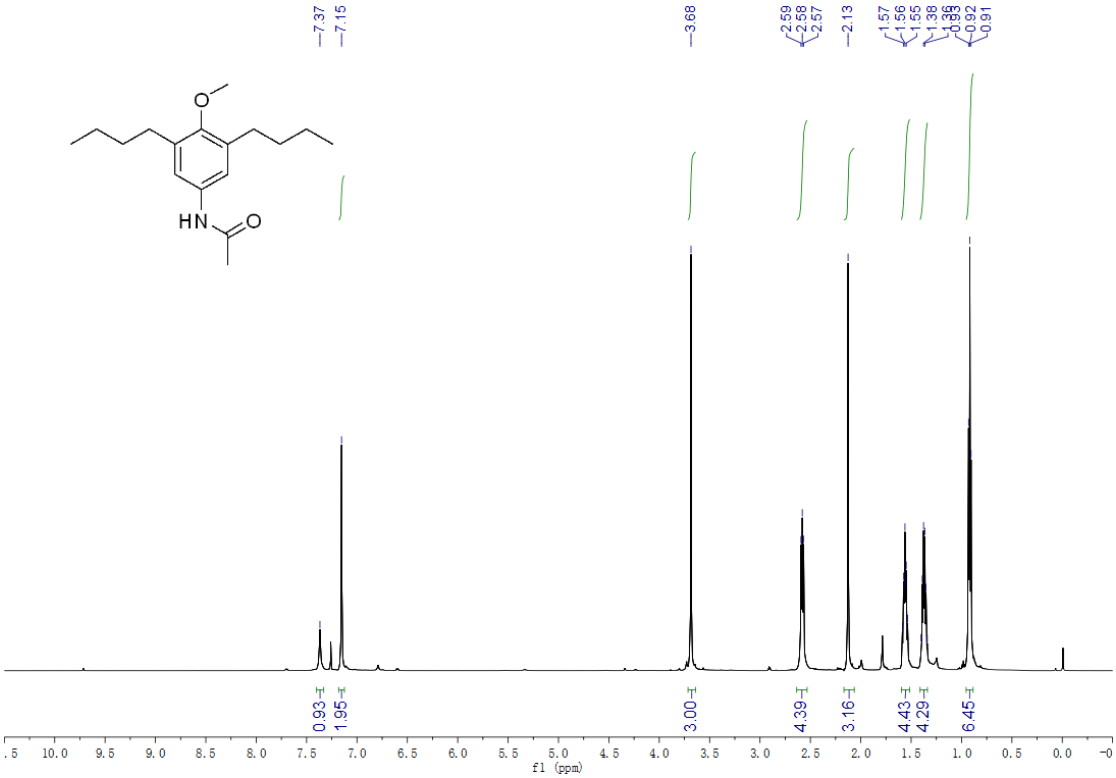


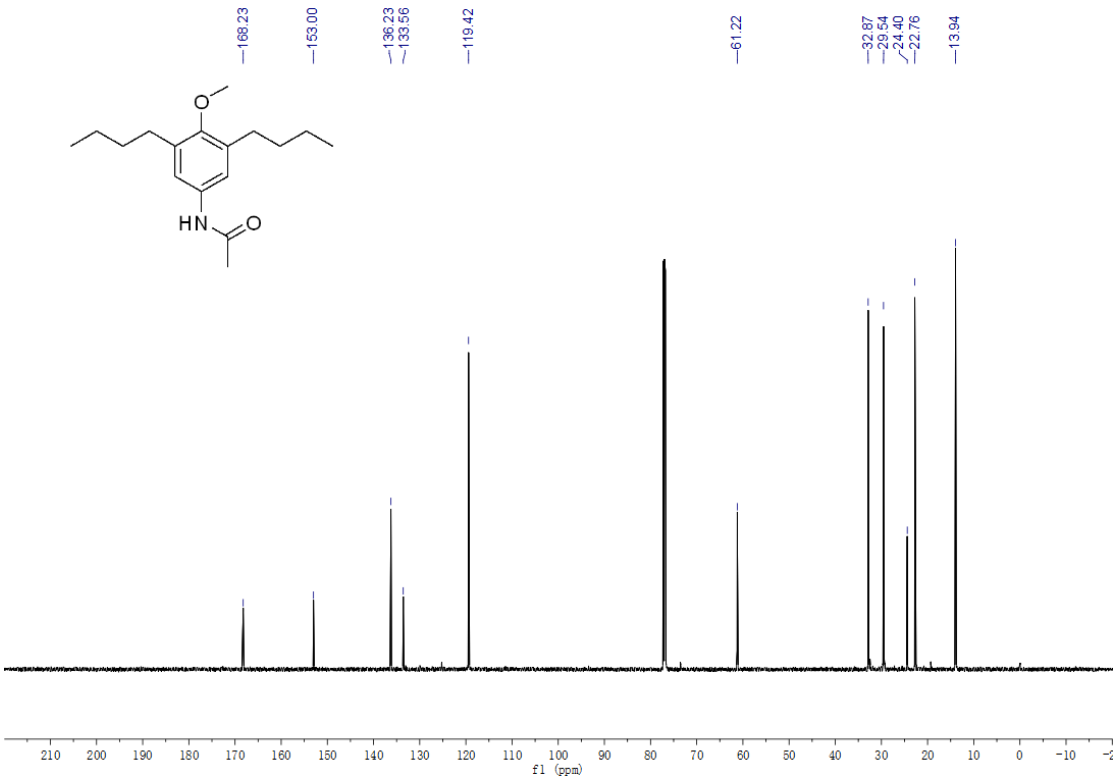
1,3-Dibutyl-2,5-dimethoxybenzene (3ca):



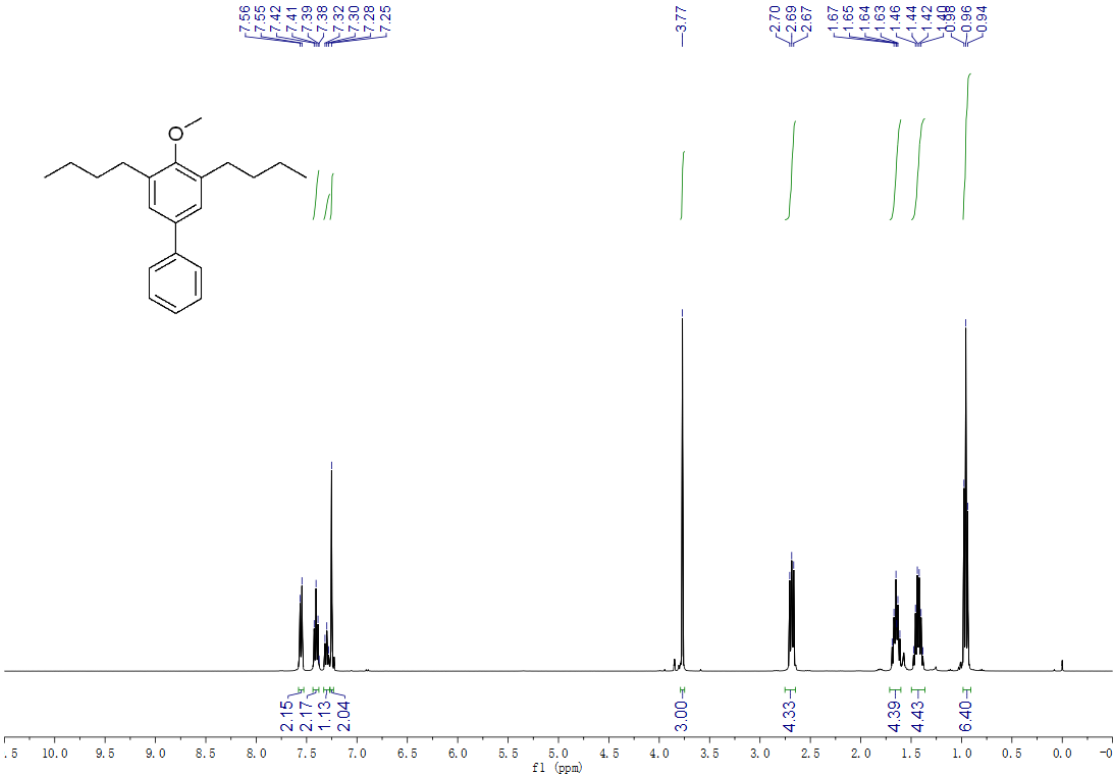


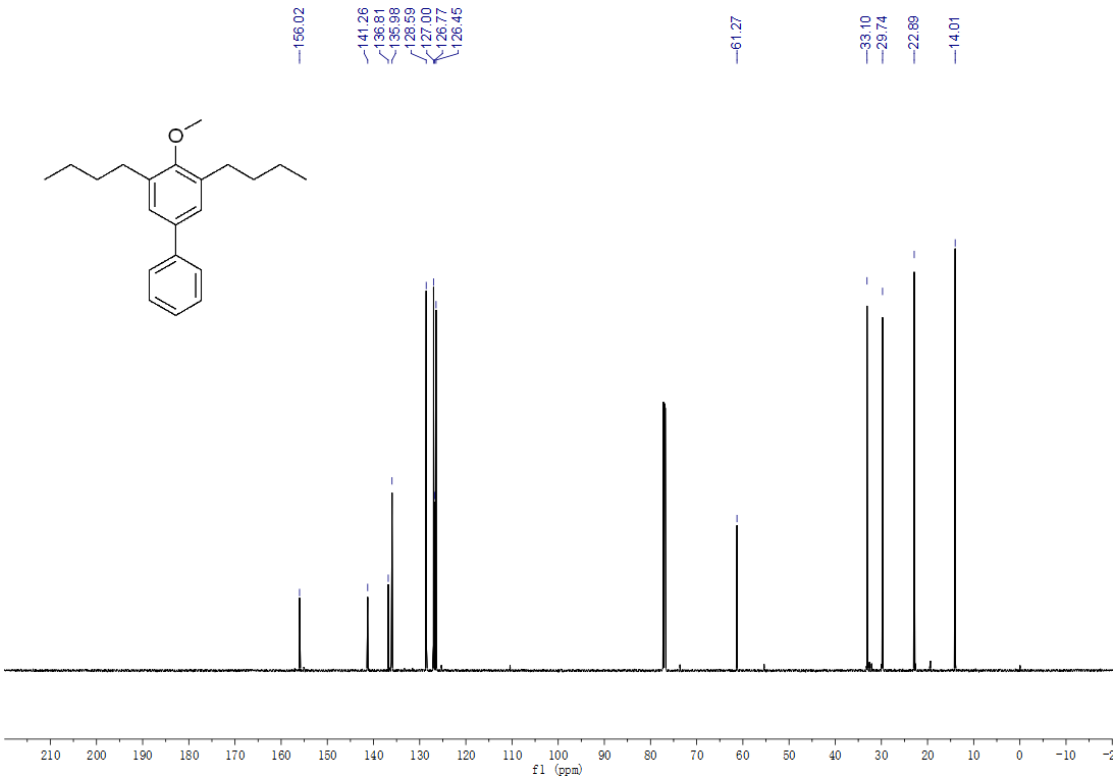
***N*-(3,5-Dibutyl-4-methoxyphenyl)acetamide (3da)**:



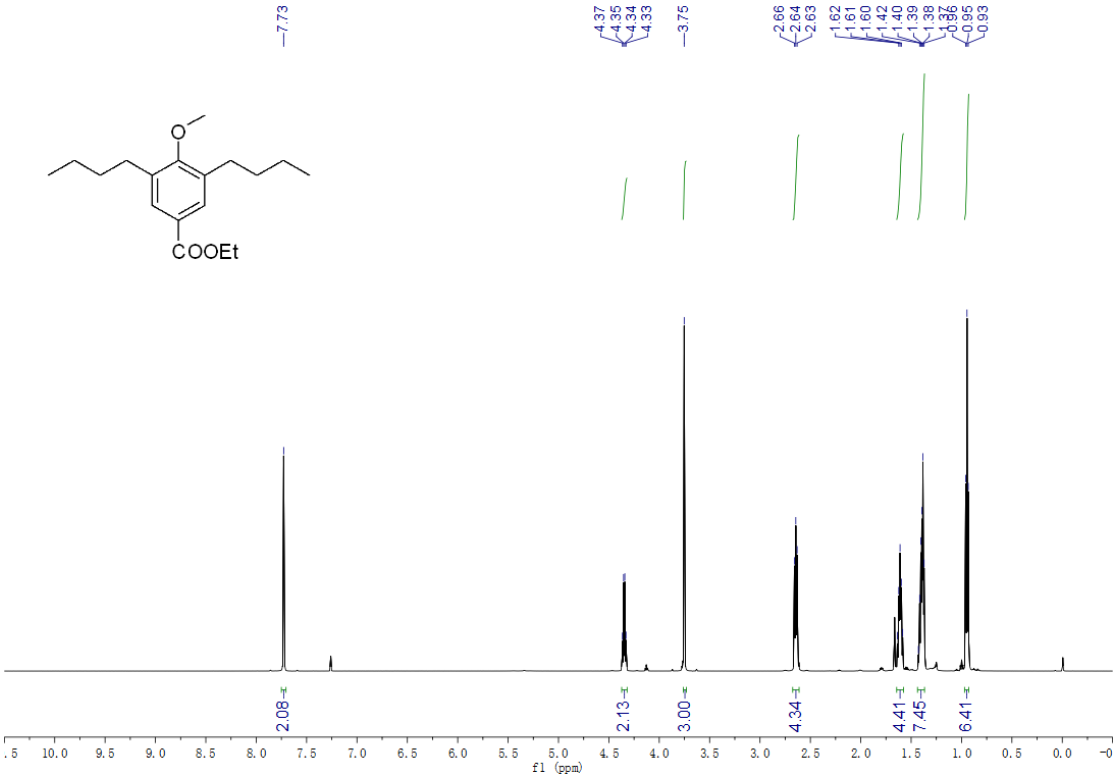


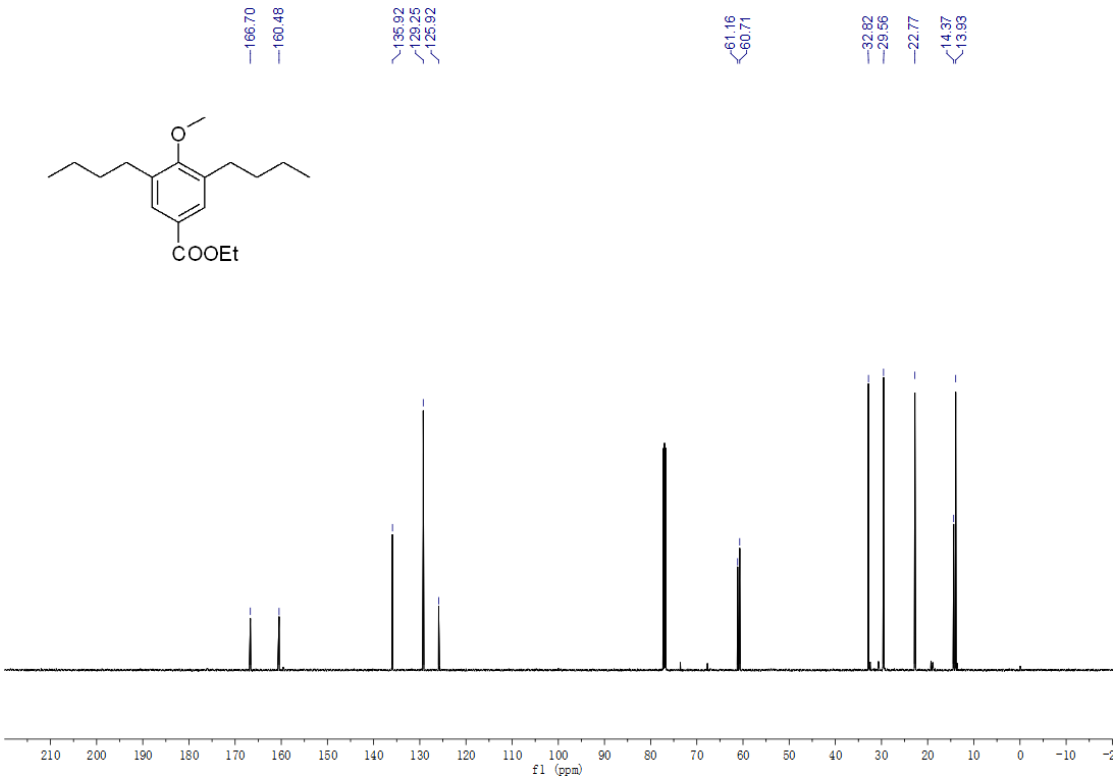
3,5-Dibutyl-4-methoxy-1,1'-biphenyl (3ea)



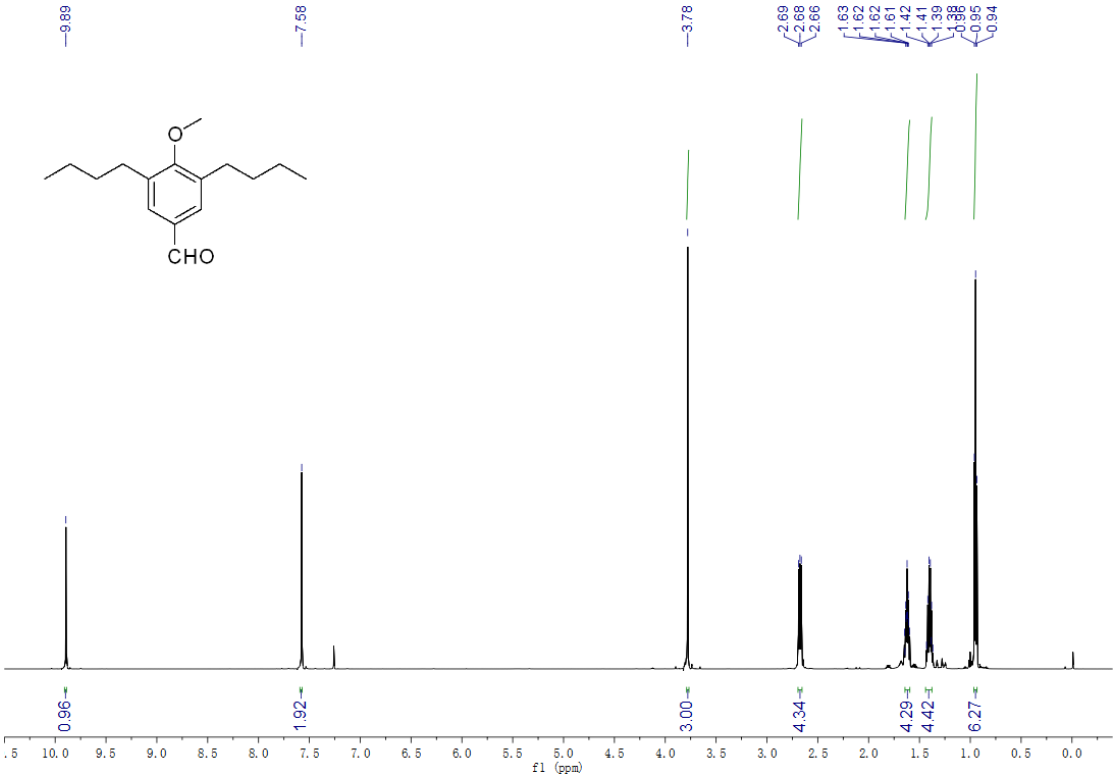


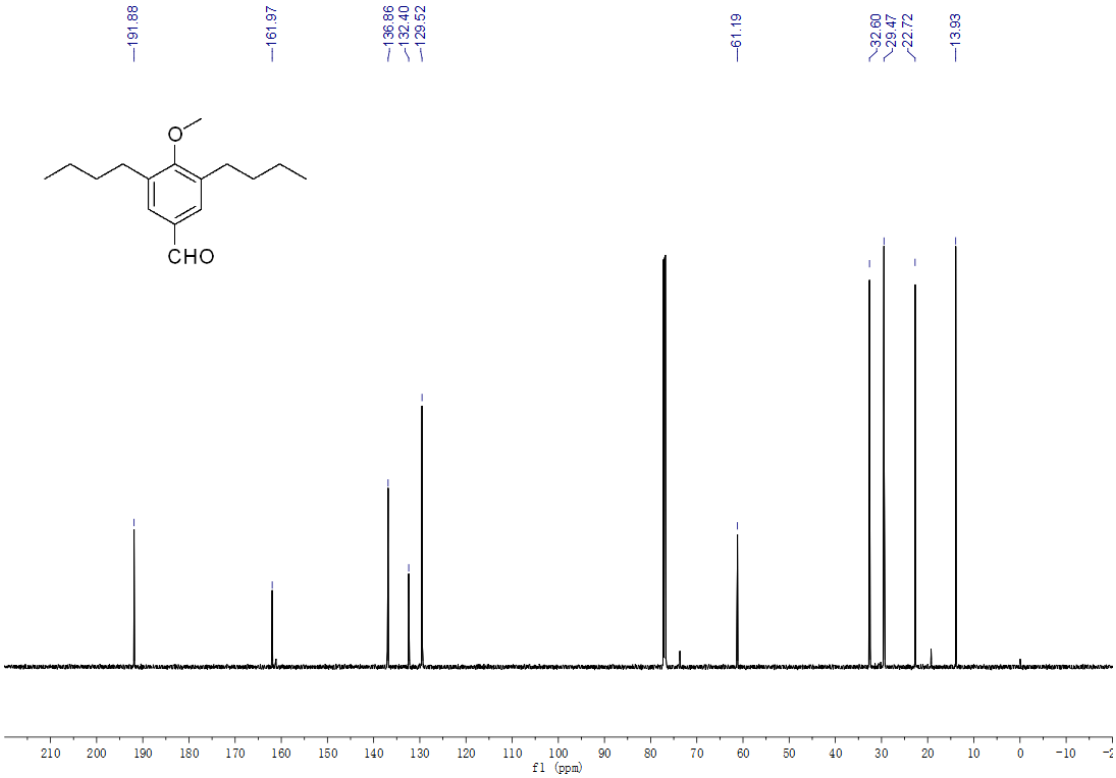
Ethyl 3,5-dibutyl-4-methoxybenzoate (3fa):



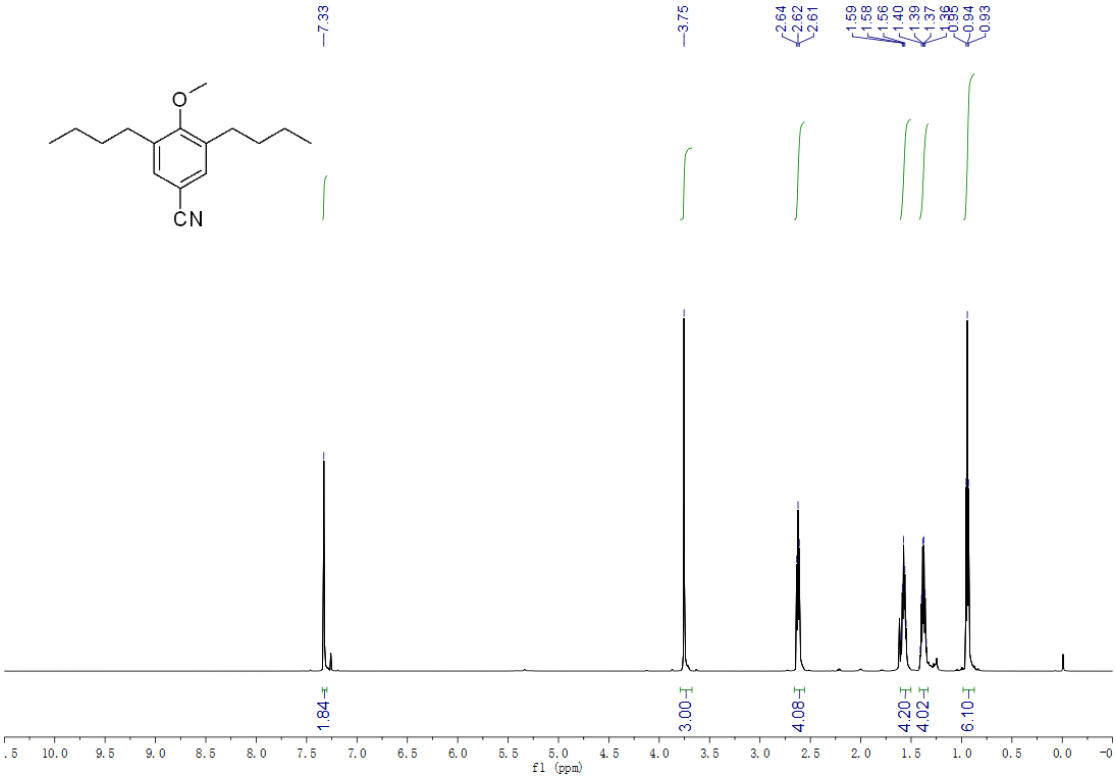


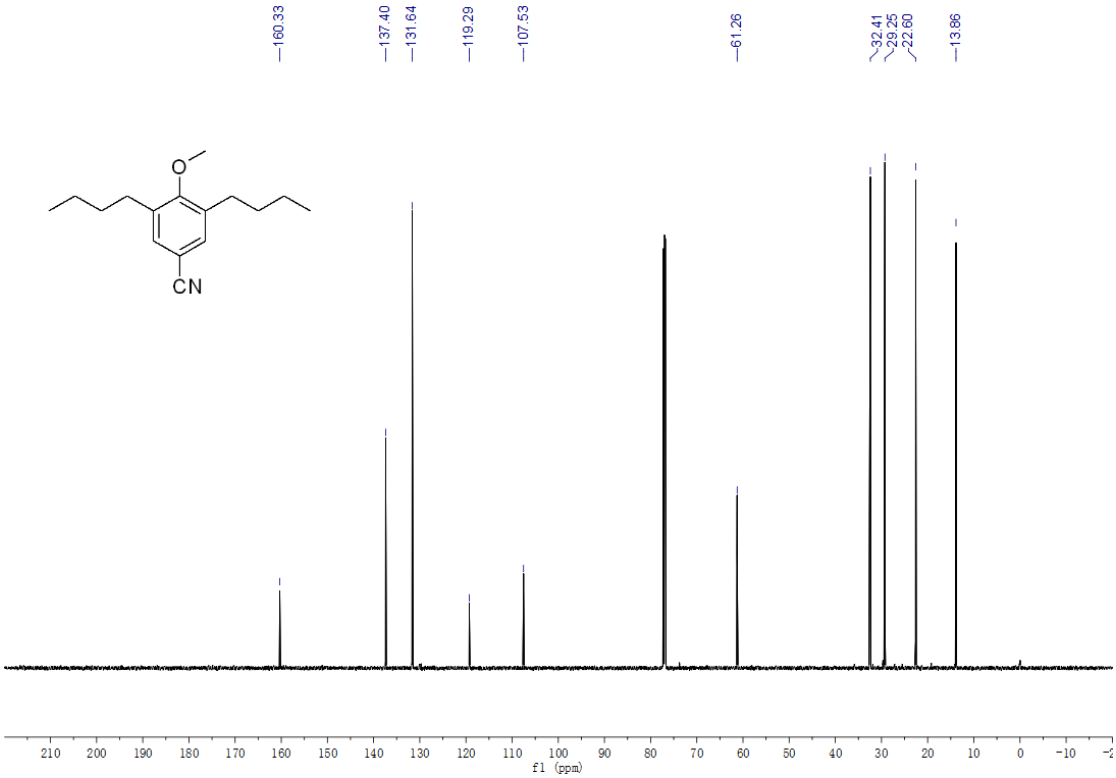
3,5-Dibutyl-4-methoxybenzaldehyde (3ga):



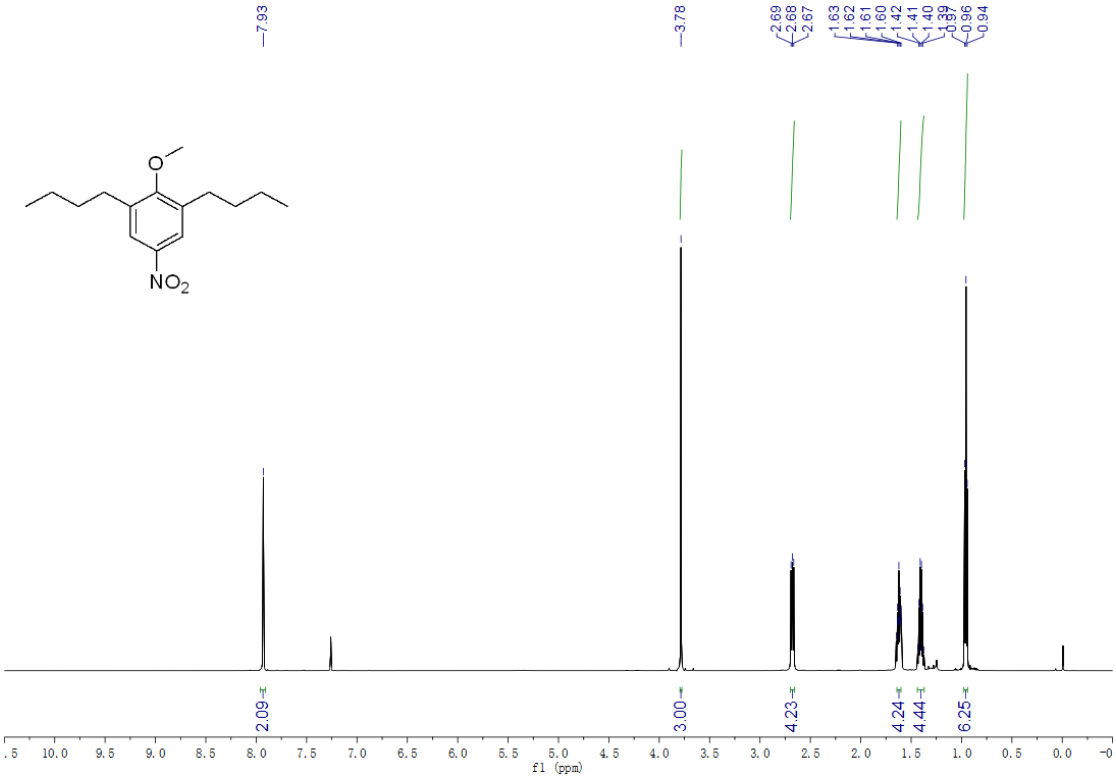


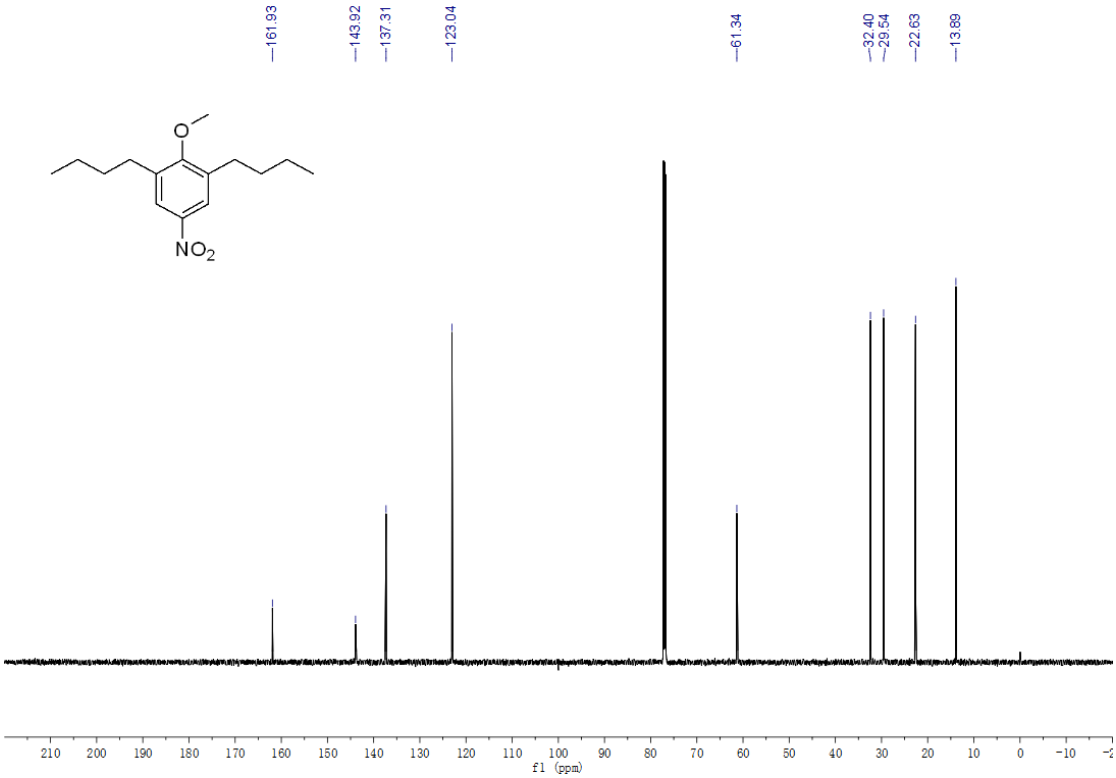
3,5-Dibutyl-4-methoxybenzonitrile (3ha):





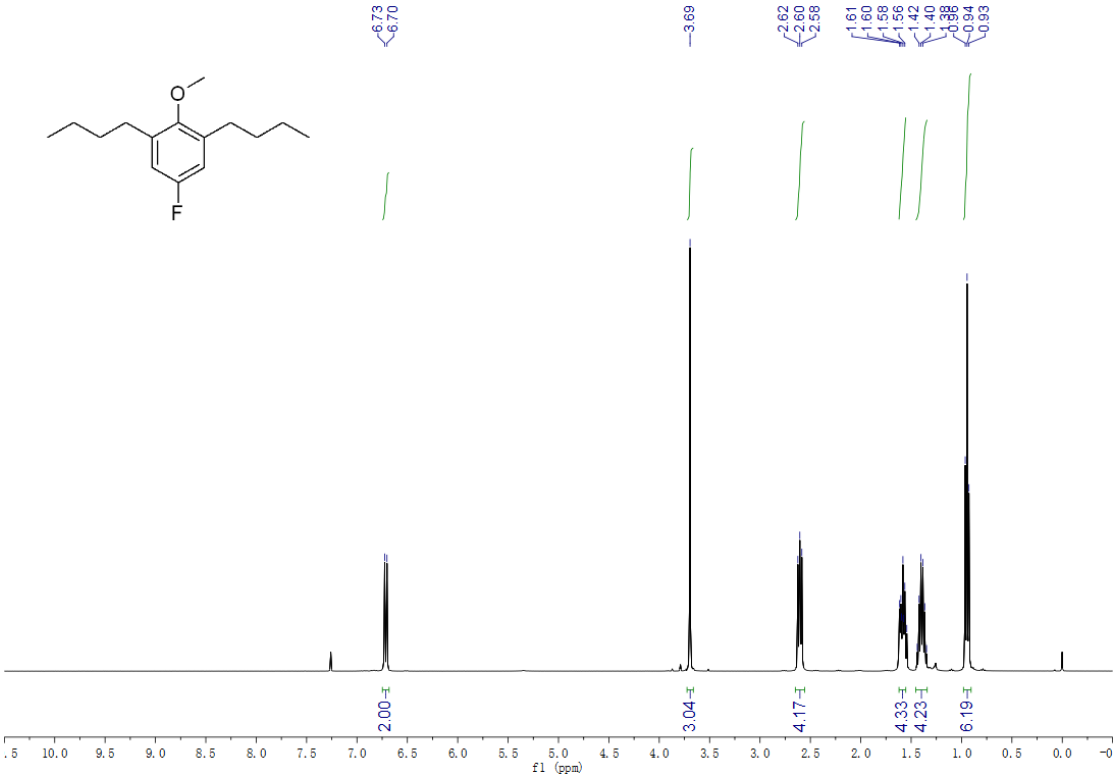
1,3-Dibutyl-2-methoxy-5-nitrobenzene (3ia):



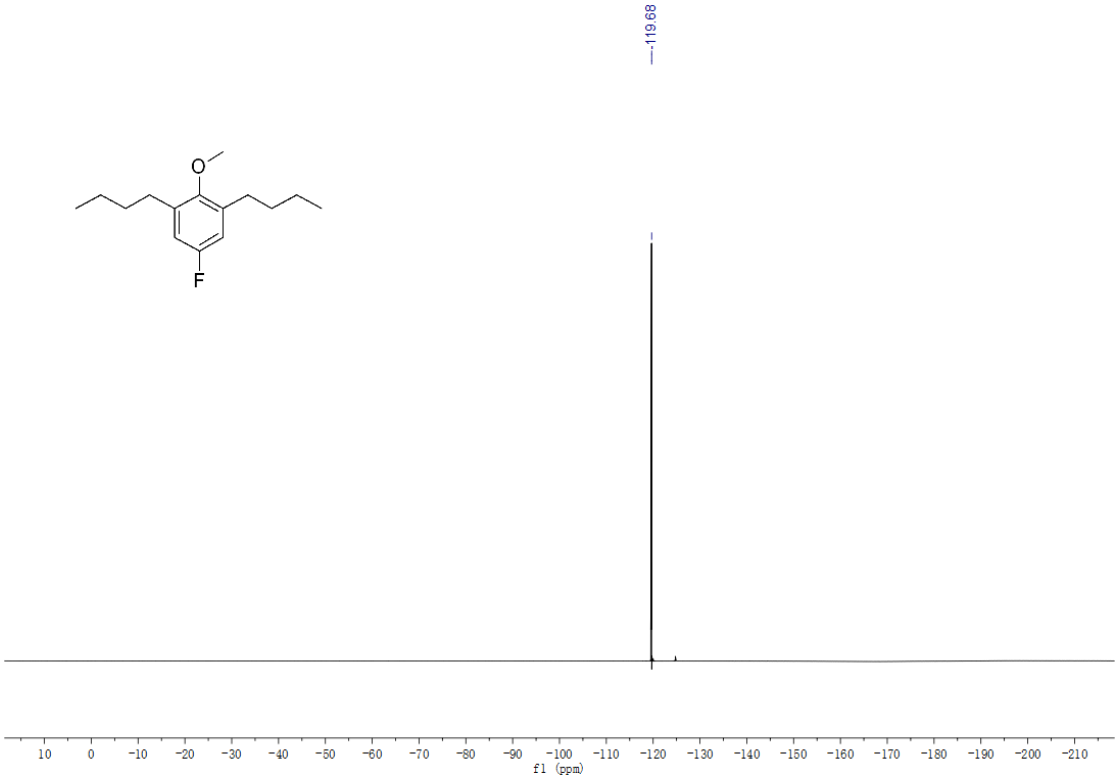


1,3-Dibutyl-5-fluoro-2-methoxybenzene (3ja):

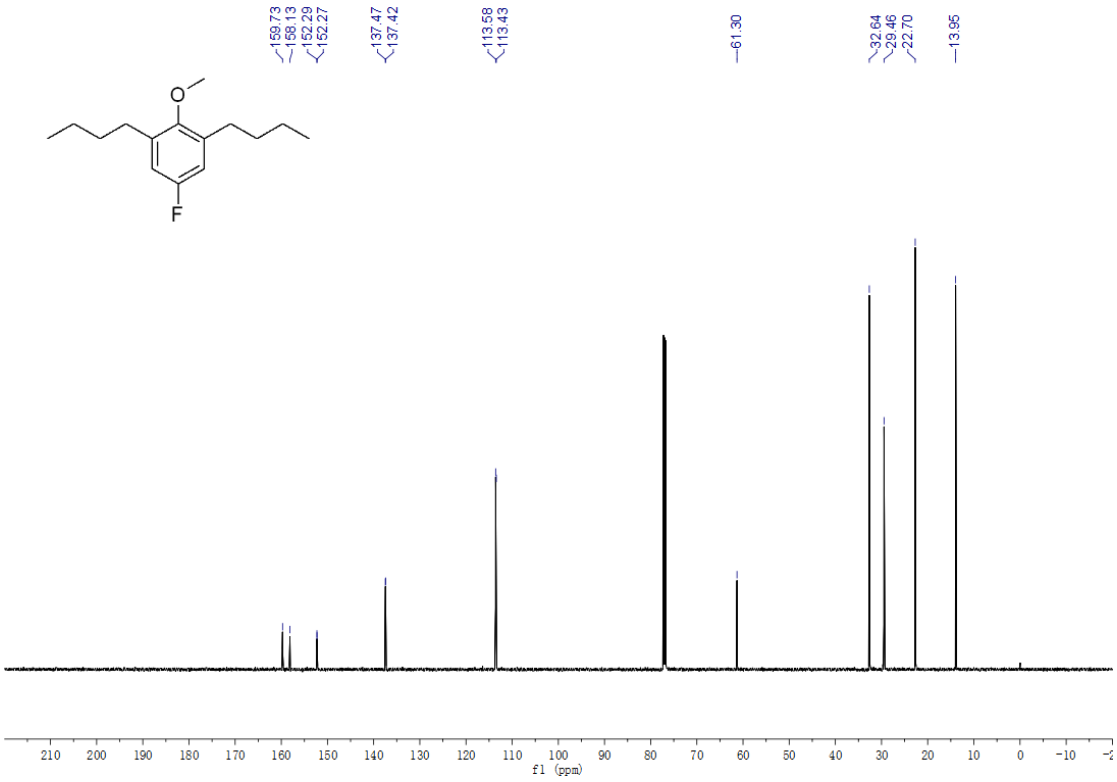
^{1}H NMR



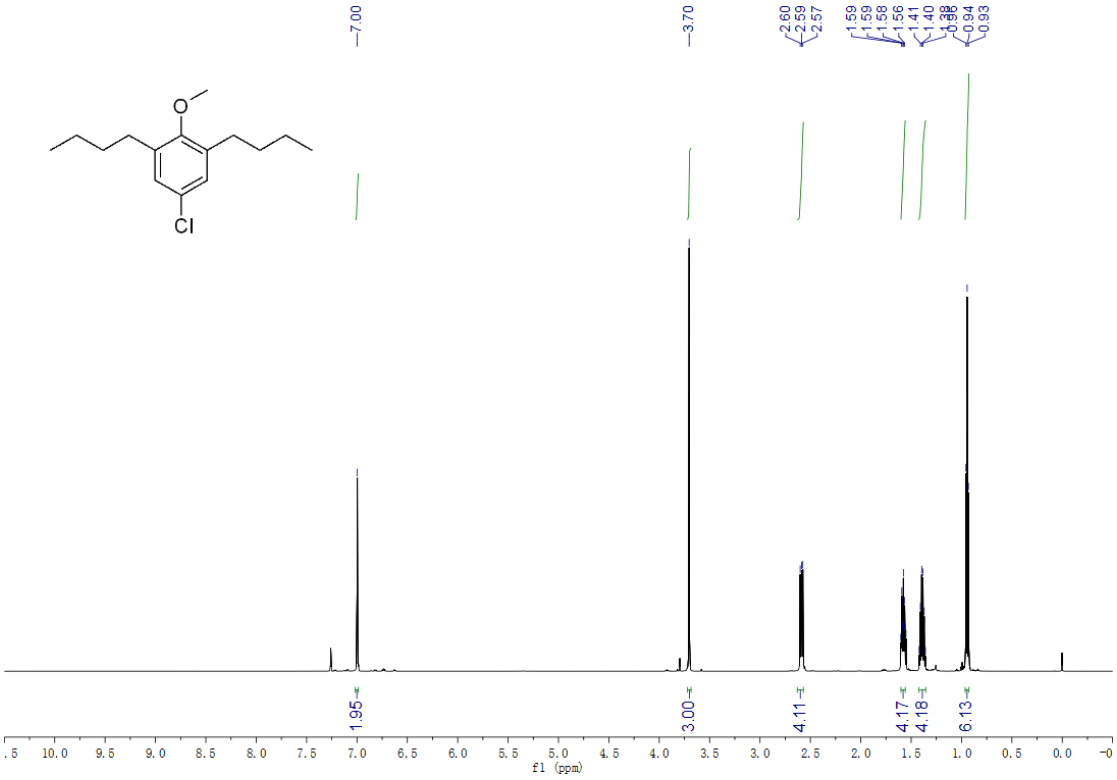
^{19}F NMR

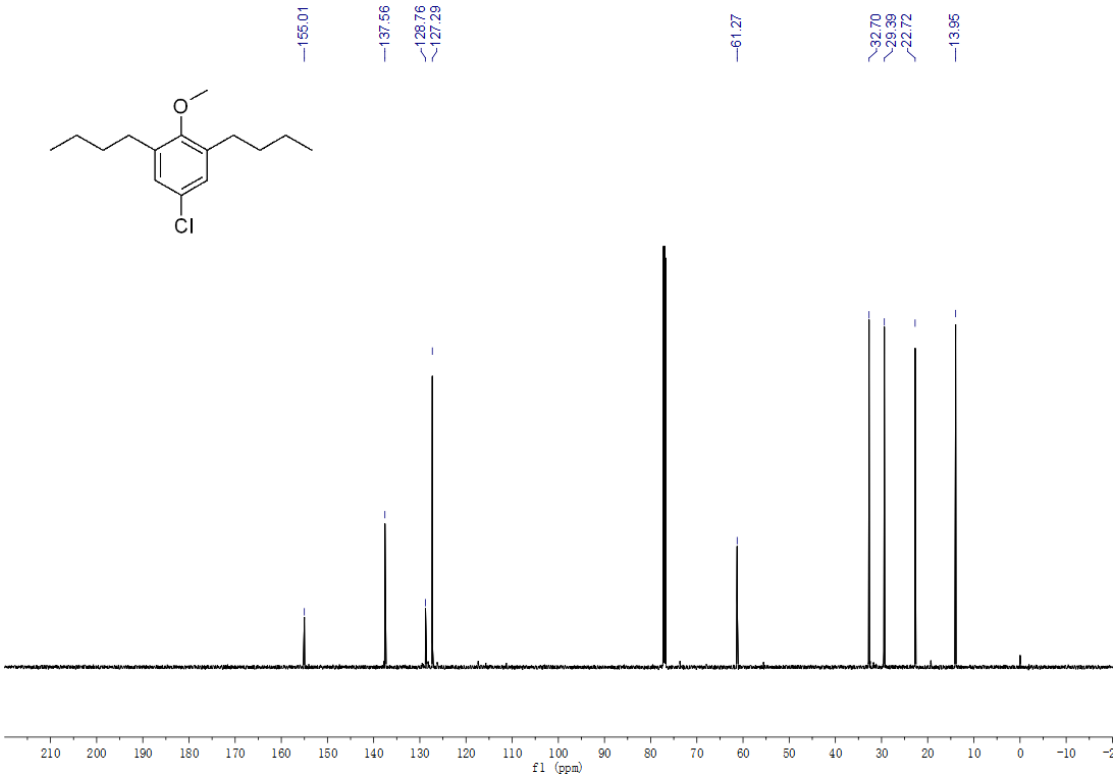


^{13}C NMR

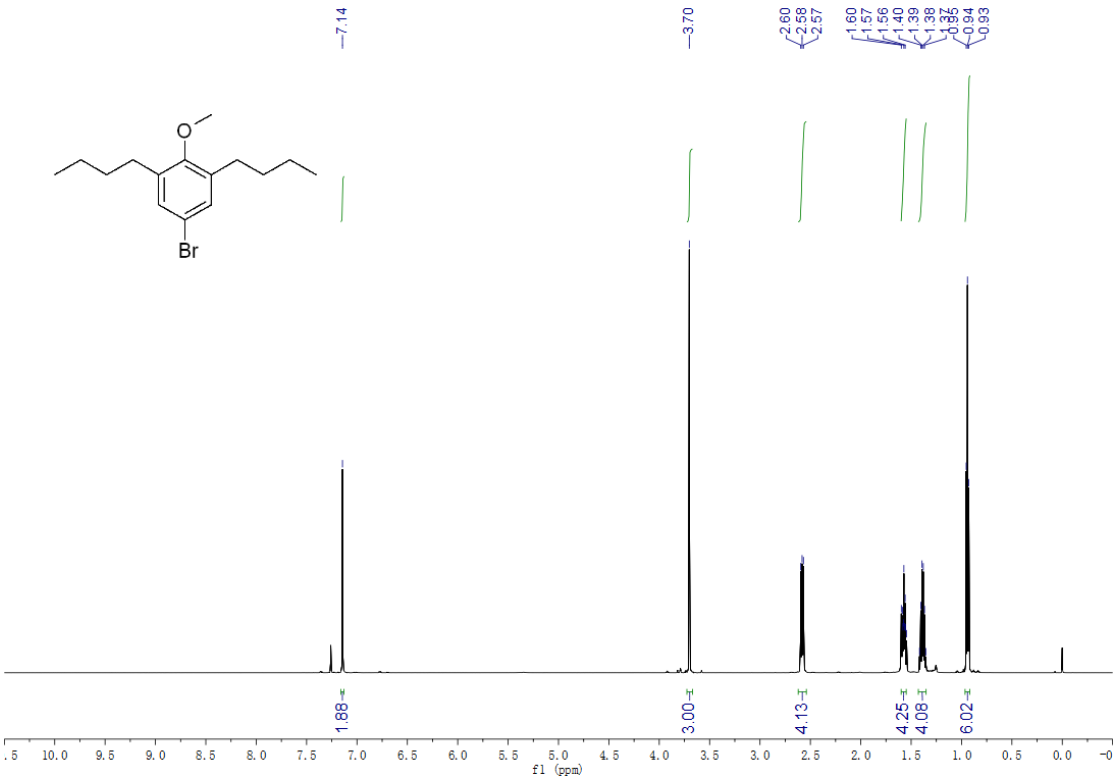

159.73
158.13
152.29
152.27
137.47
137.42
113.58
113.43
61.30
32.64
29.46
22.70
13.95
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

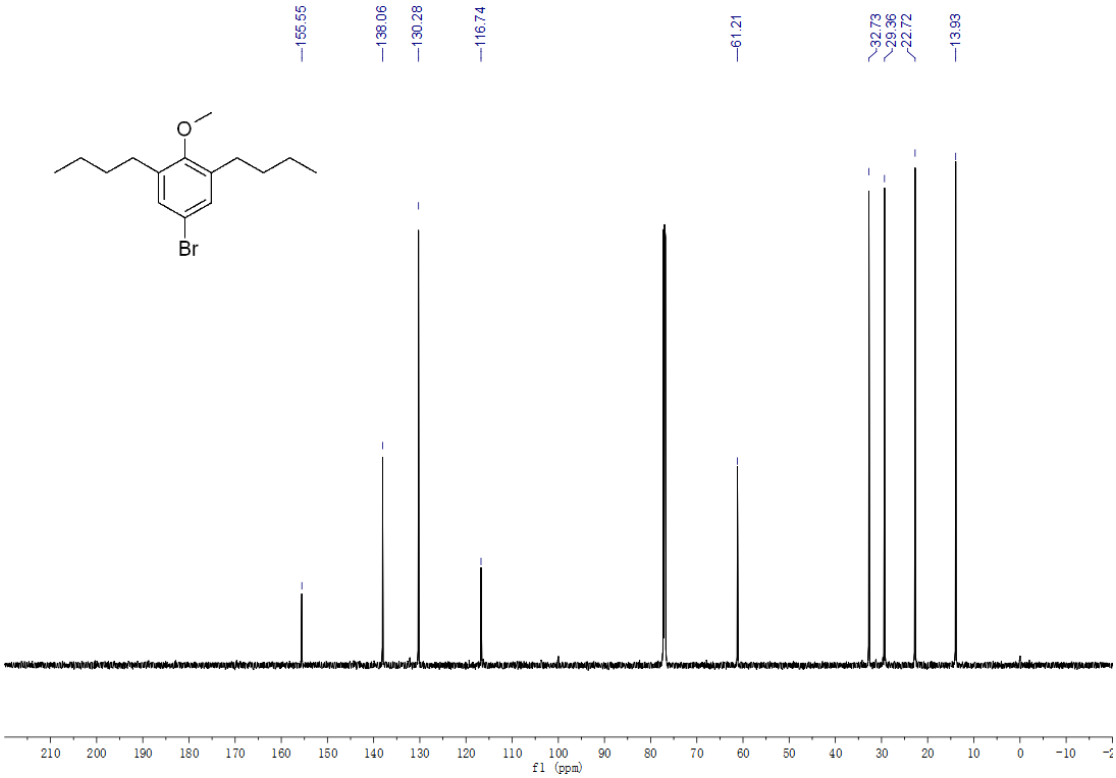
1,3-Dibutyl-5-chloro-2-methoxybenzene (3ka):



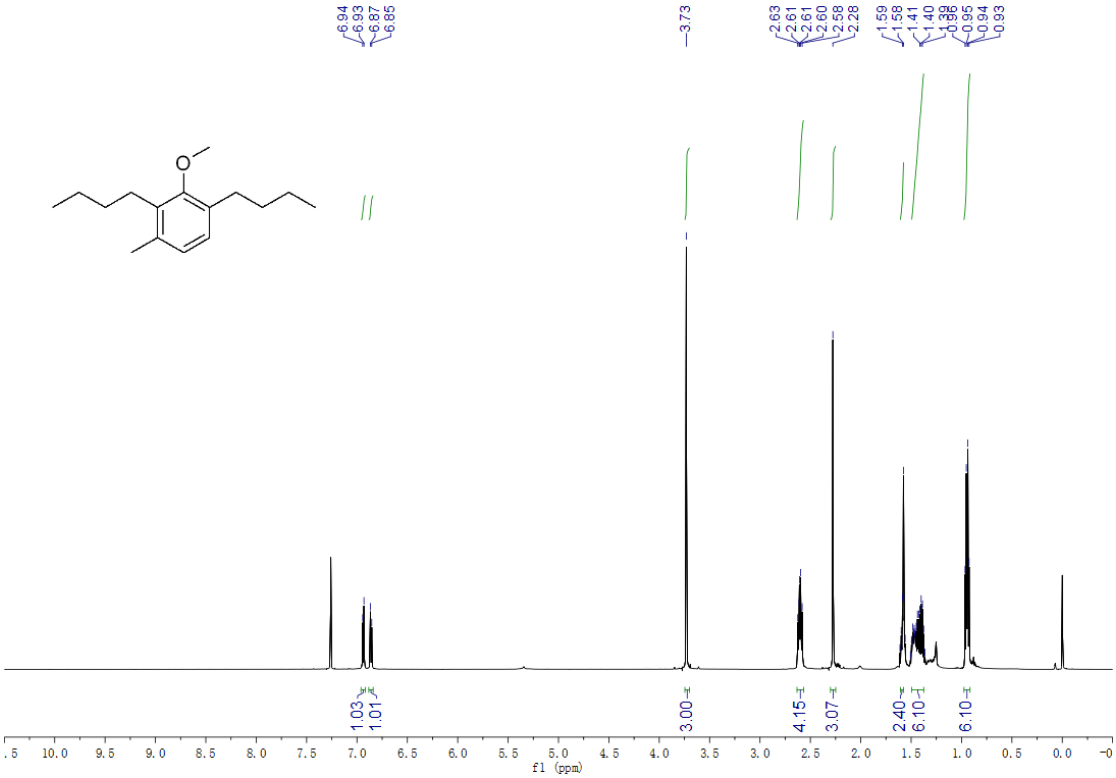


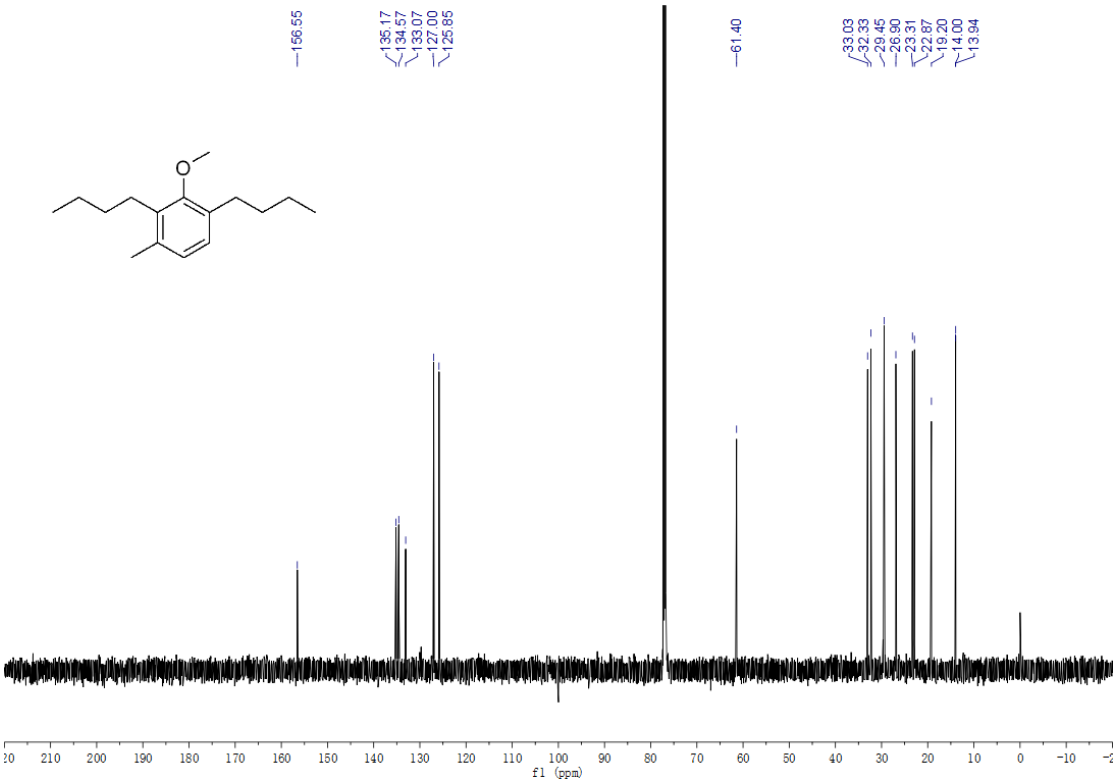
5-Bromo-1,3-dibutyl-2-methoxybenzene (3la):



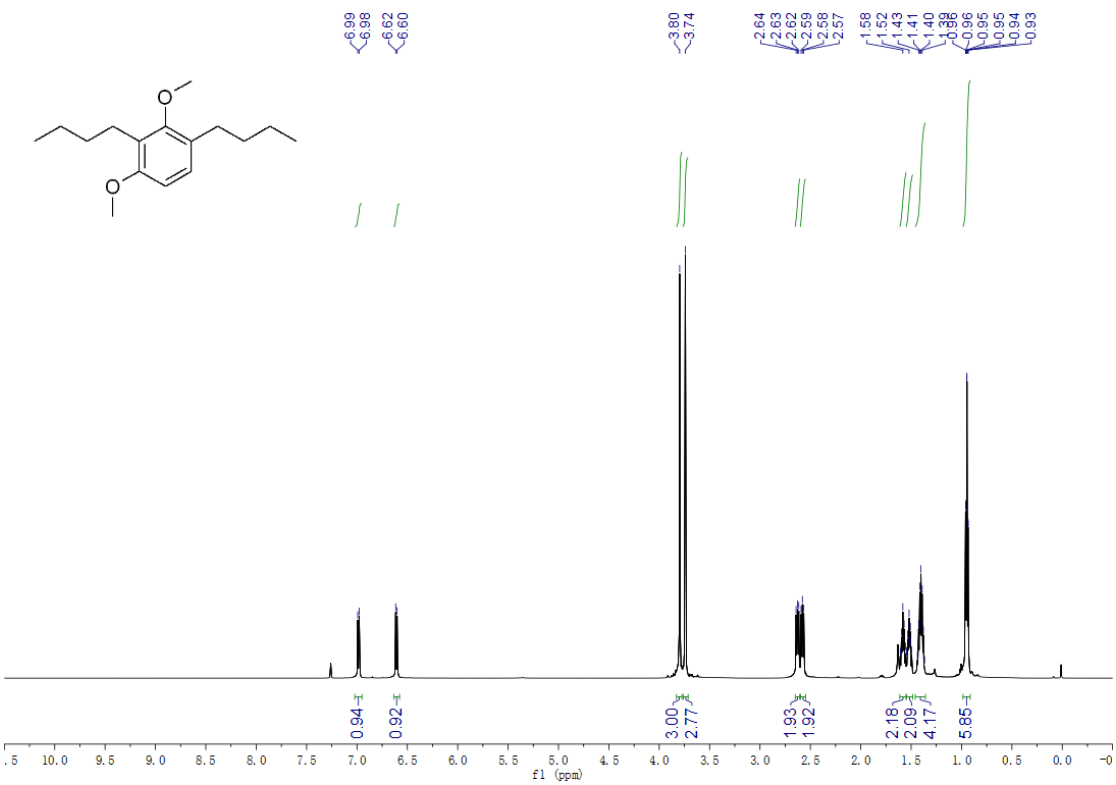


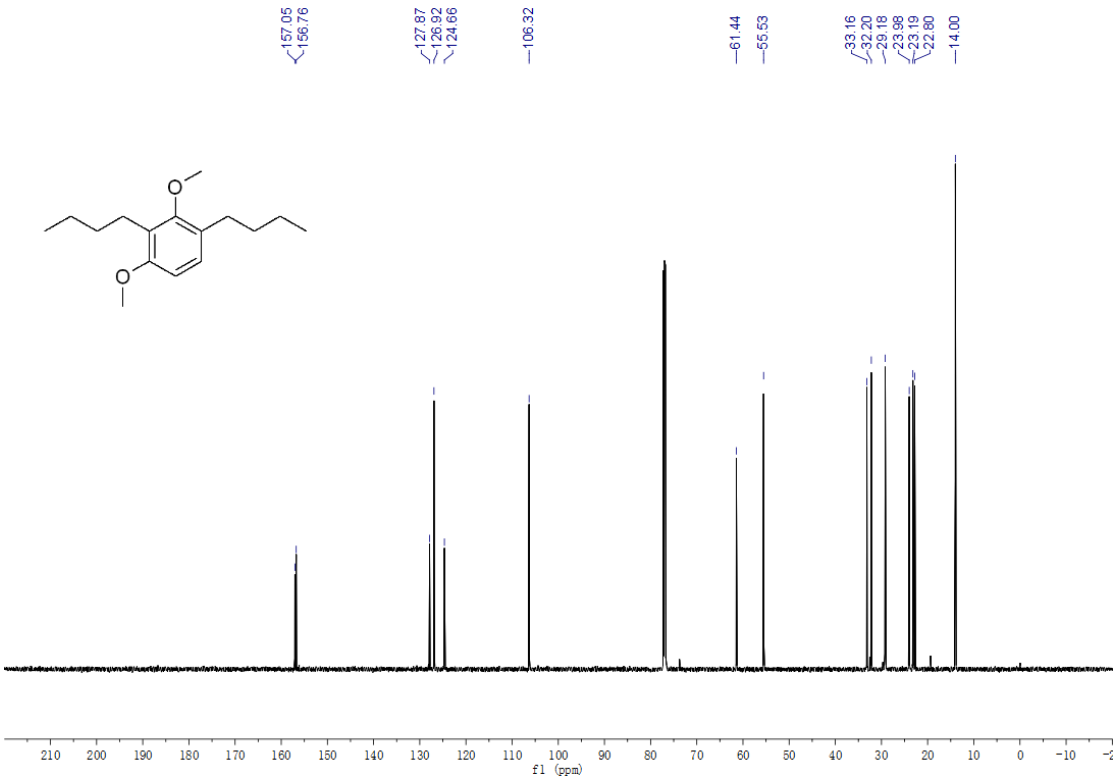
1,3-Dibutyl-2-methoxy-4-methylbenzene (3ma):



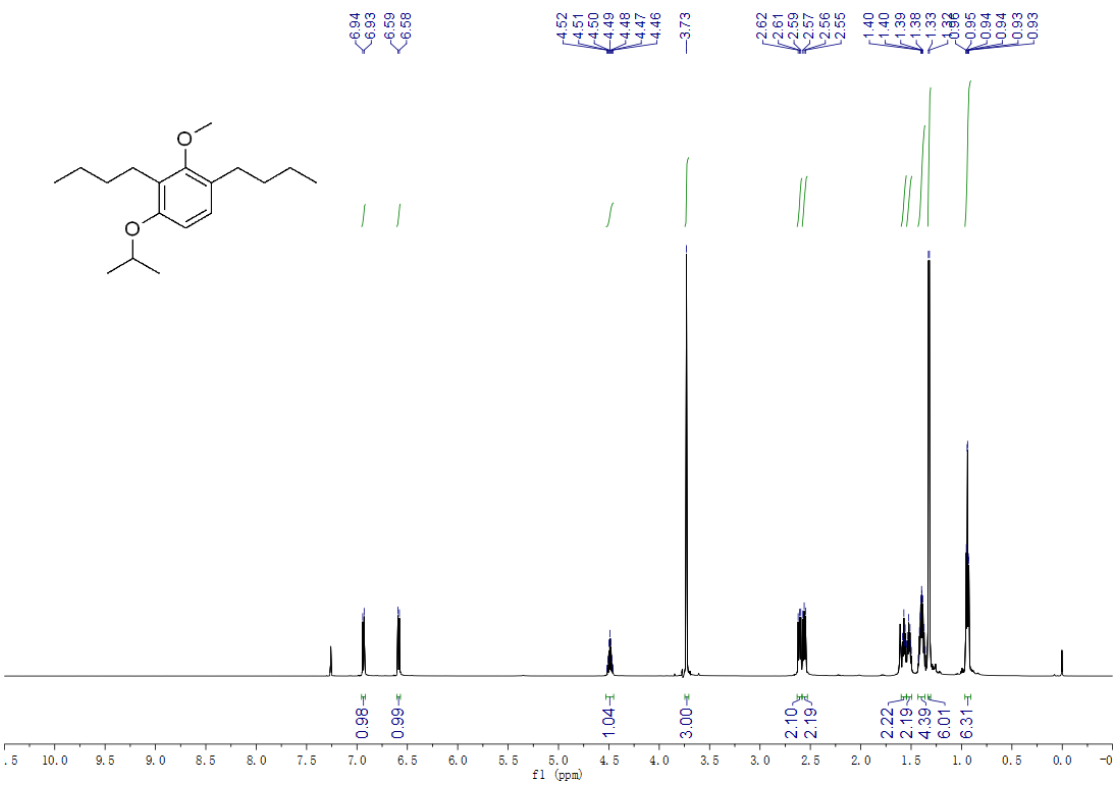


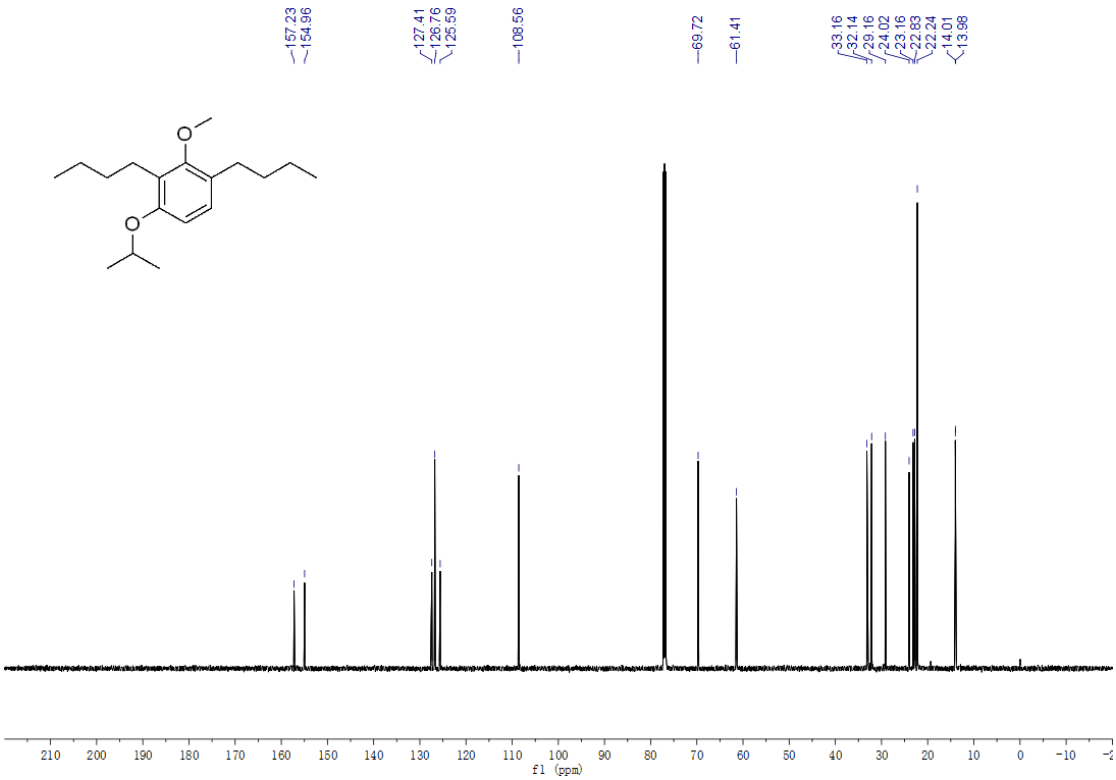
1,3-Dibutyl-2,4-dimethoxybenzene (3na):





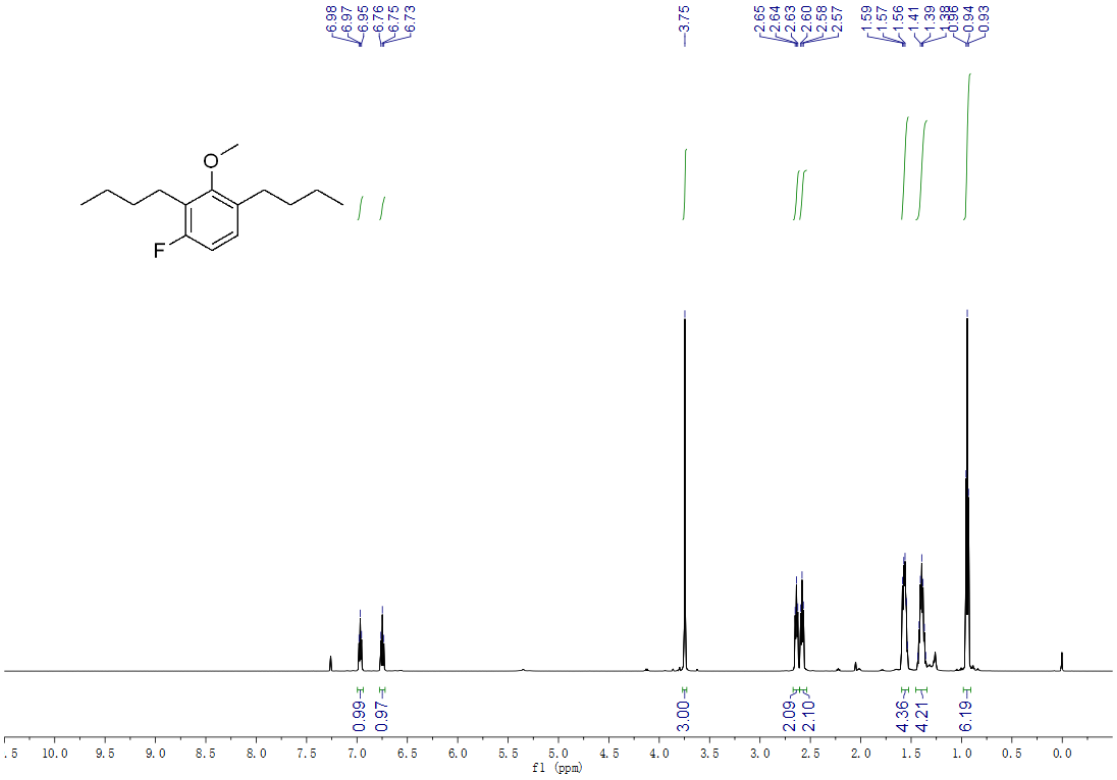
1,3-Dibutyl-4-isopropoxy-2-methoxybenzene (3oa):



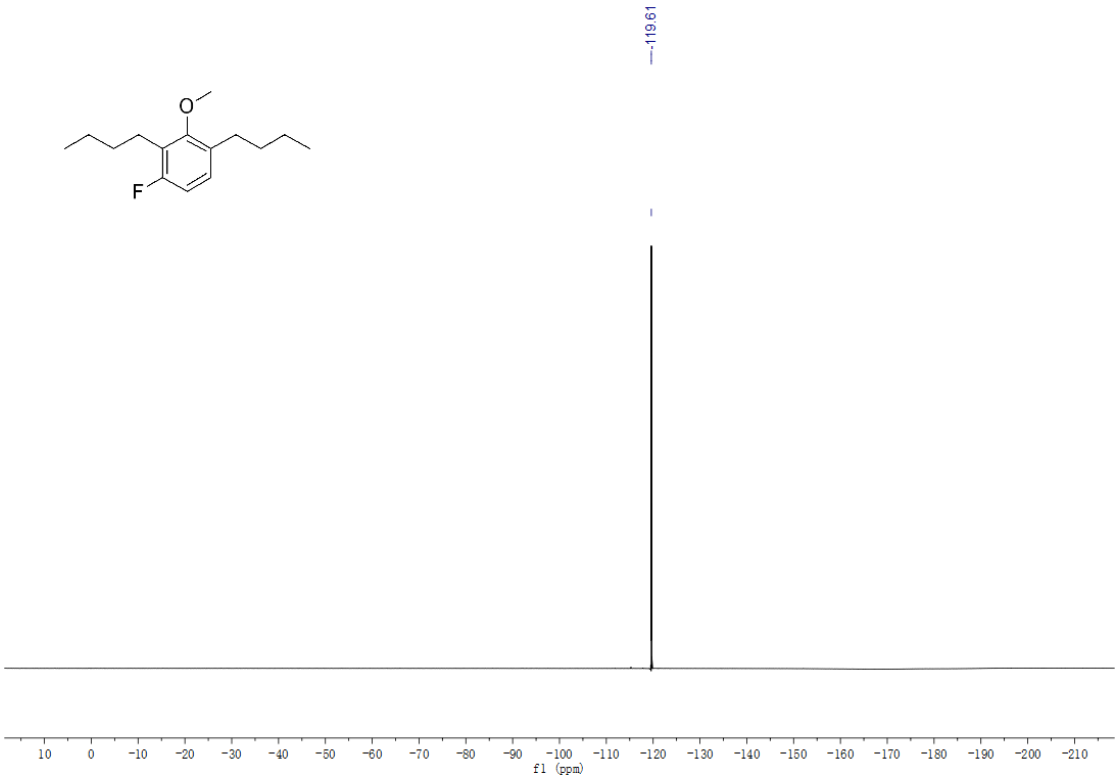


1,3-Dibutyl-4-fluoro-2-methoxybenzene (3pa):

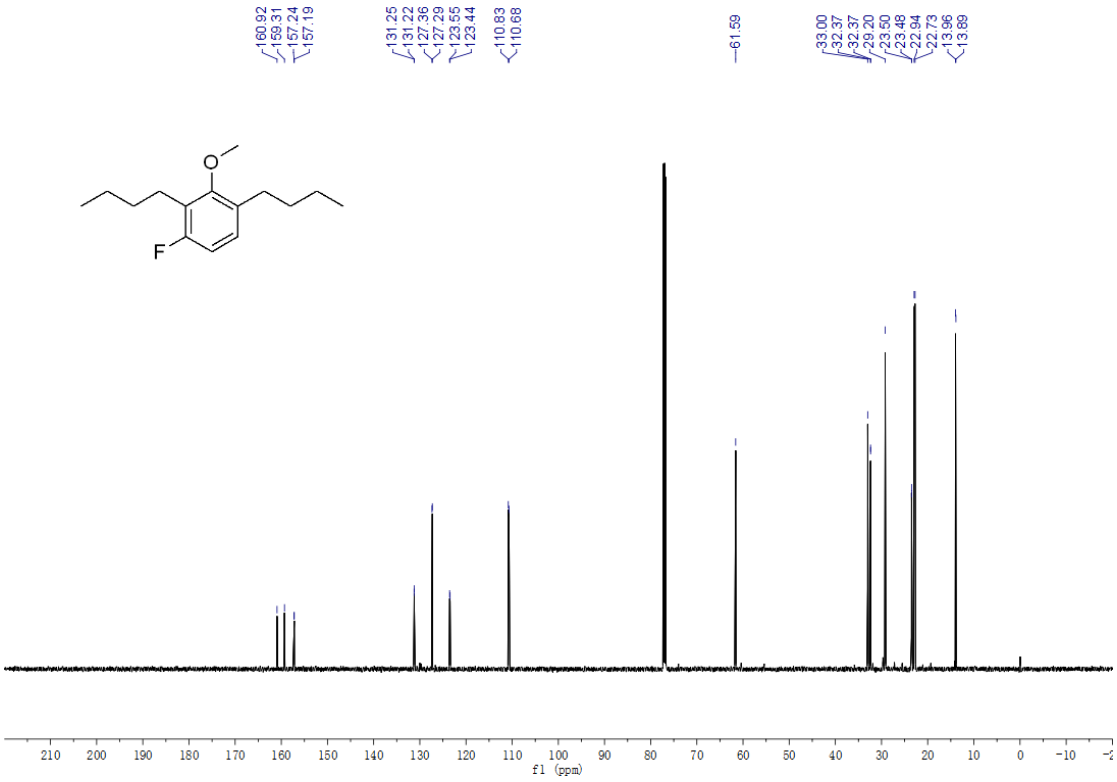
^{1}H NMR



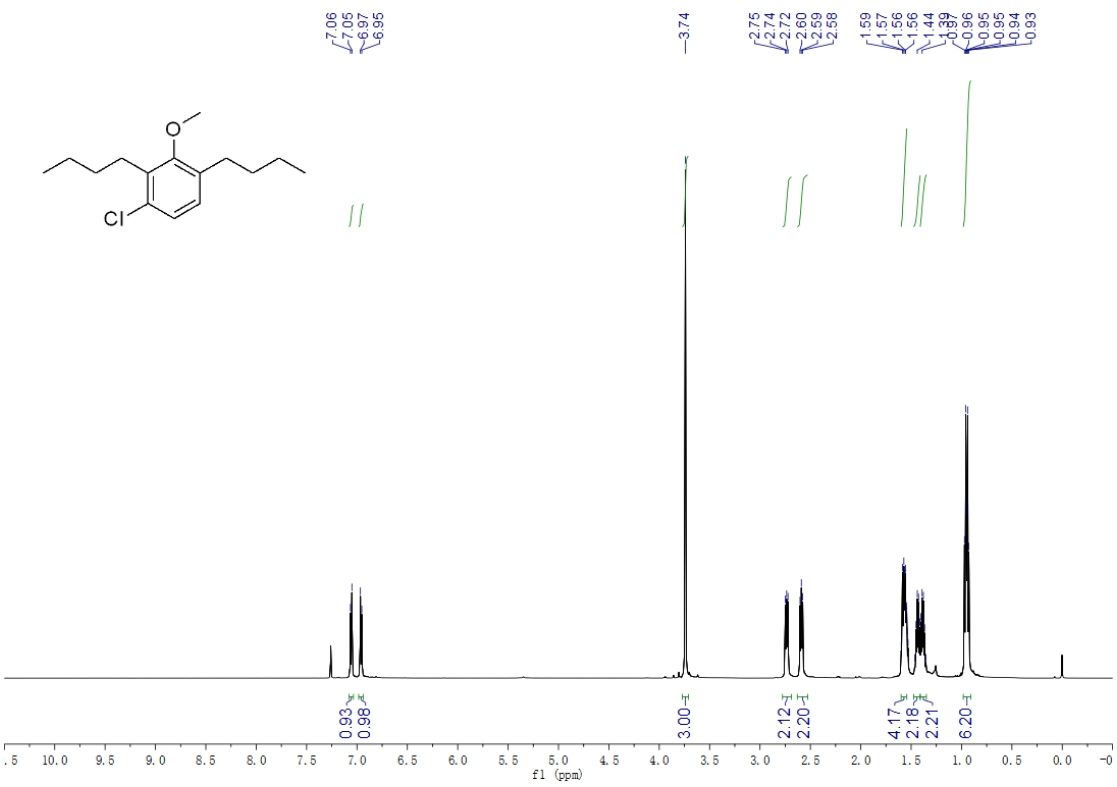
^{19}F NMR

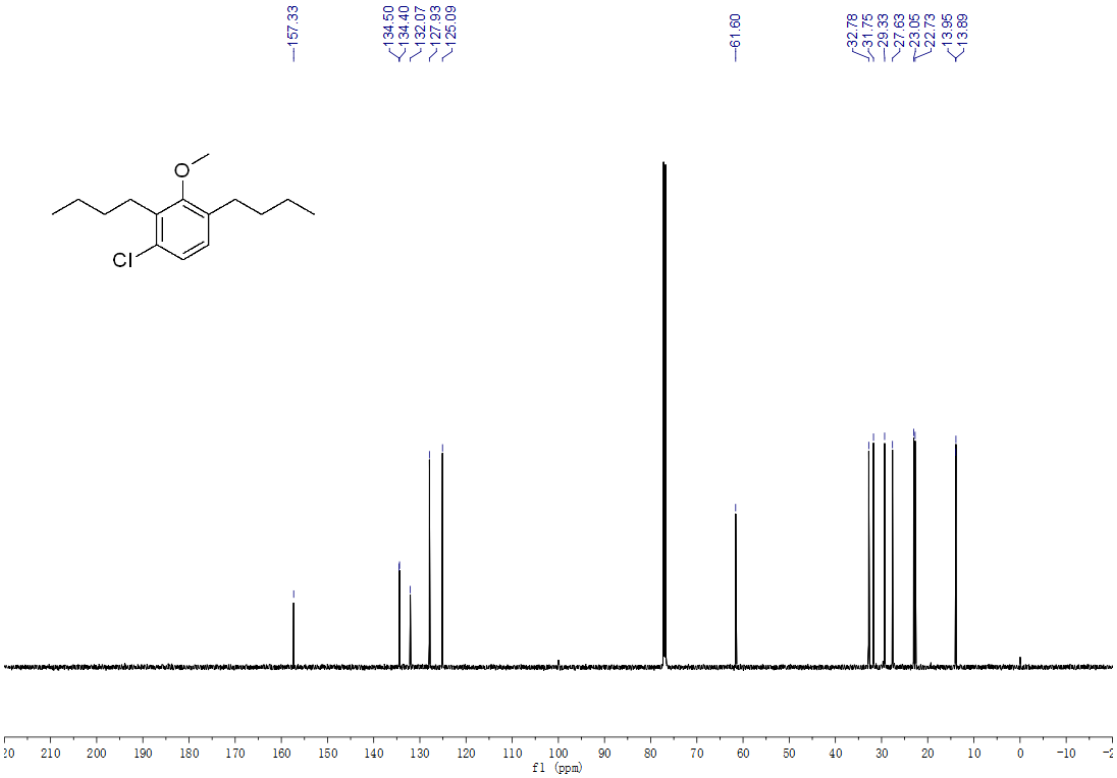


^{13}C NMR

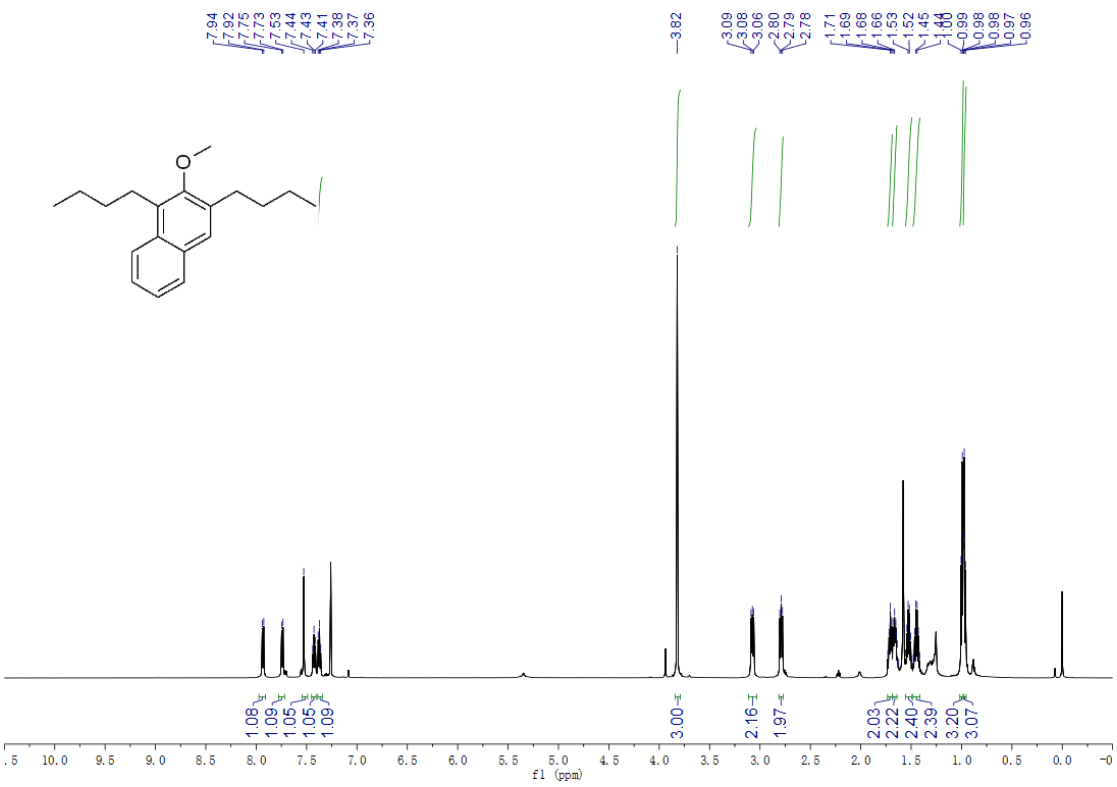

160.92
159.31
157.24
157.19
131.25
131.22
127.36
127.29
123.55
123.44
110.83
110.68
61.59
33.00
32.37
32.37
29.20
23.50
23.48
22.94
22.73
13.96
13.89
O
F
f1 (ppm)

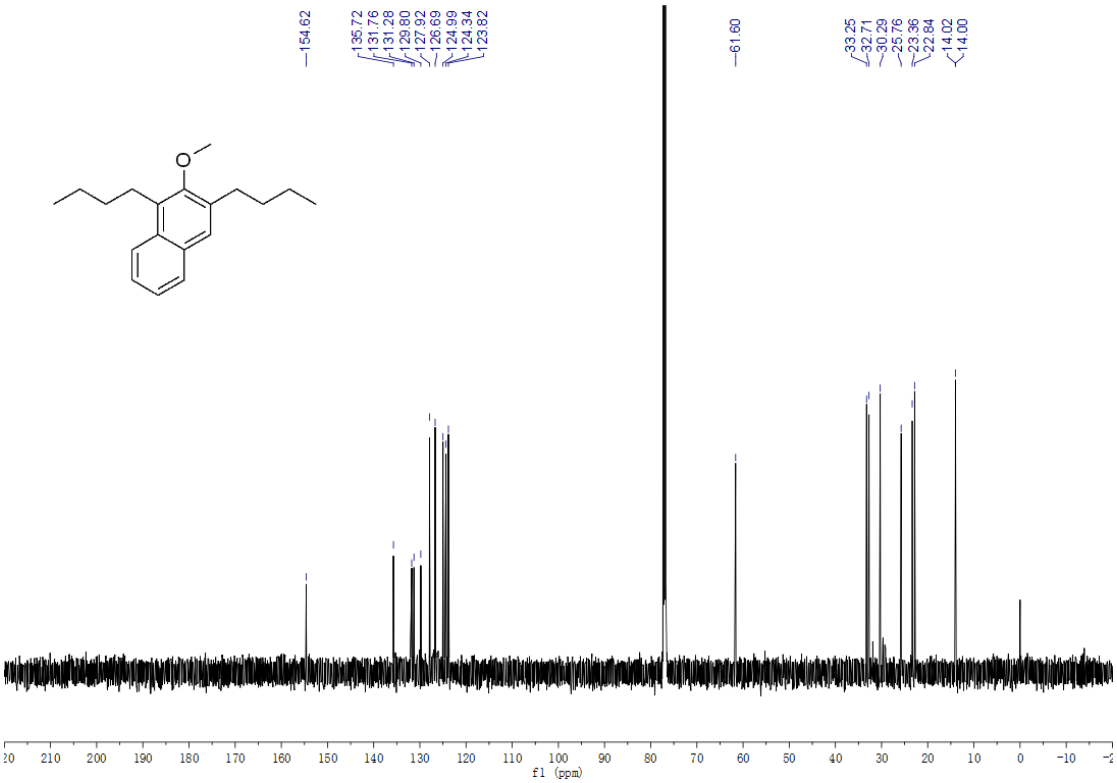
1,3-Dibutyl-4-chloro-2-methoxybenzene (3qa):



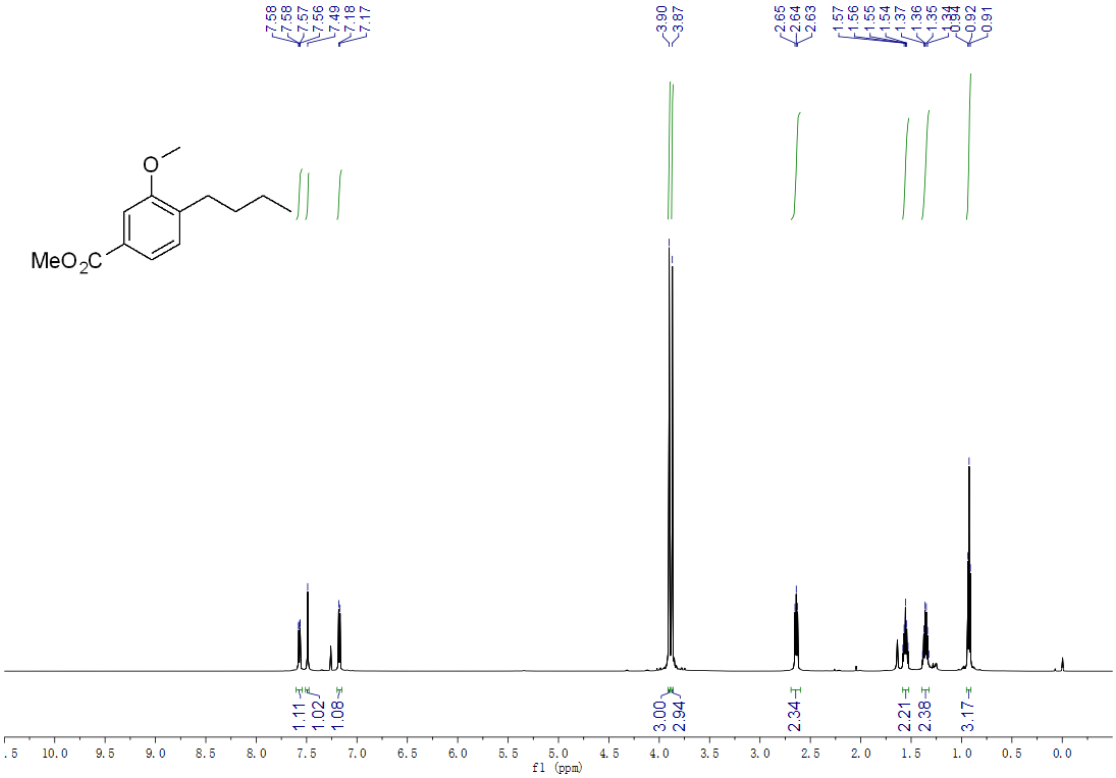


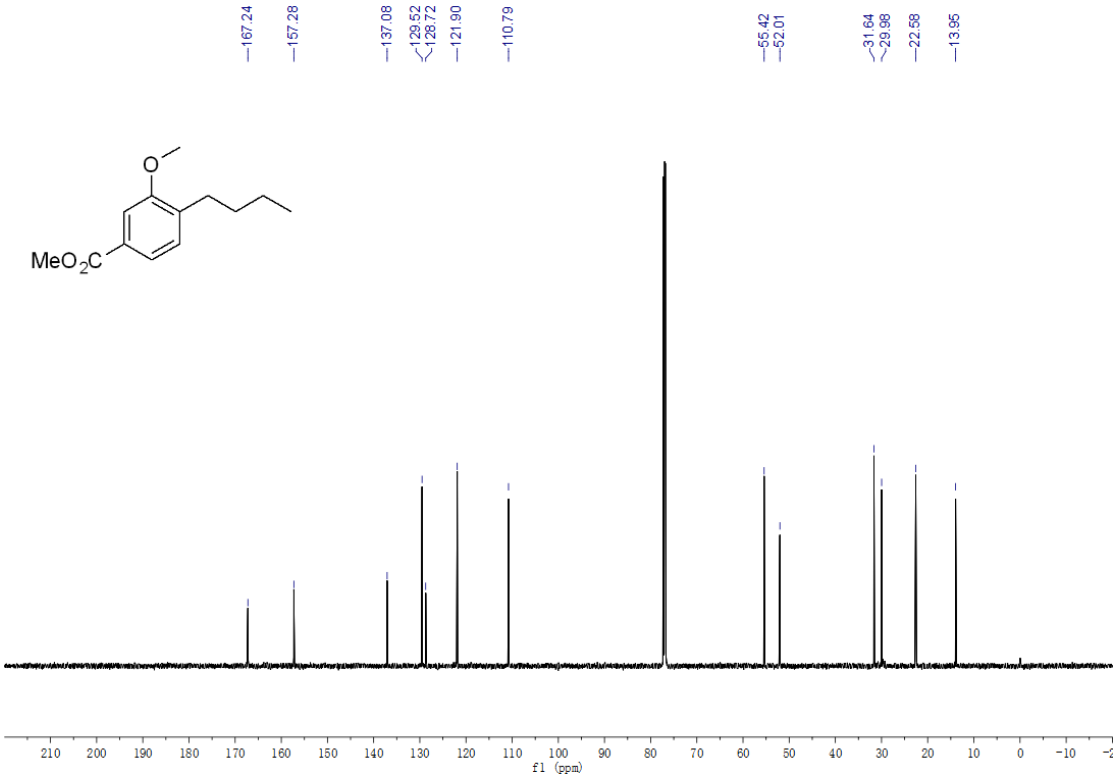
1,3-Dibutyl-2-methoxynaphthalene (3ra):



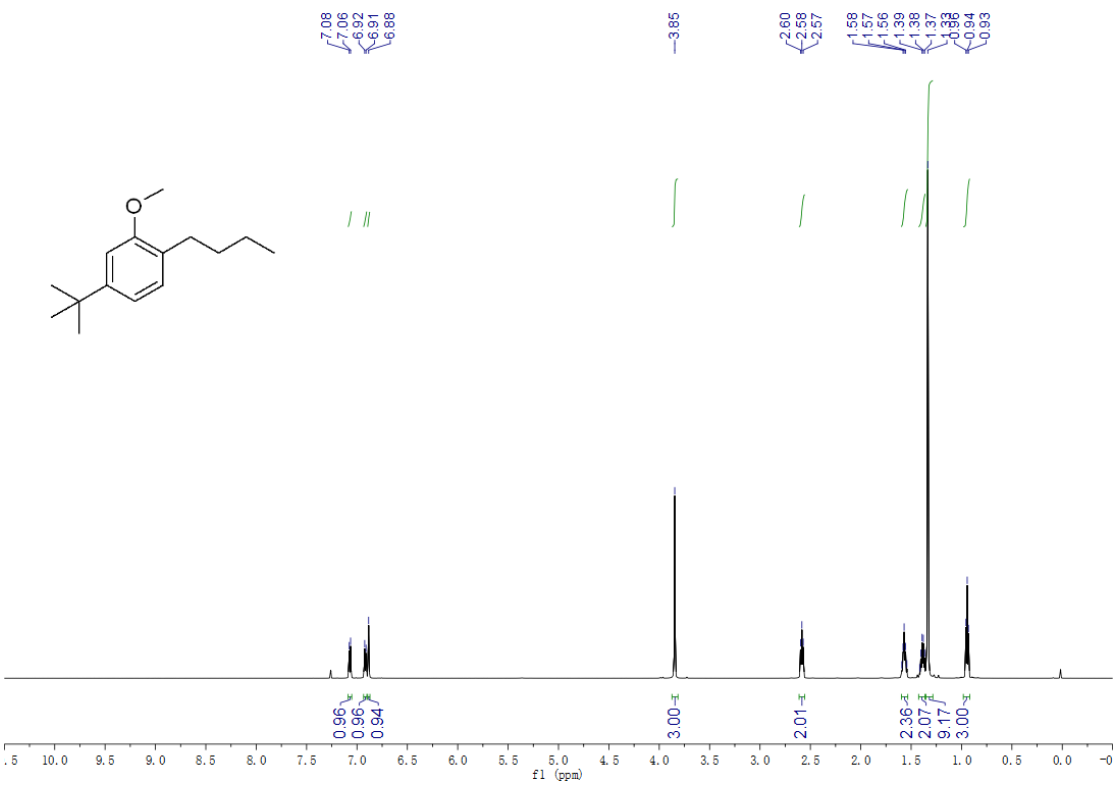


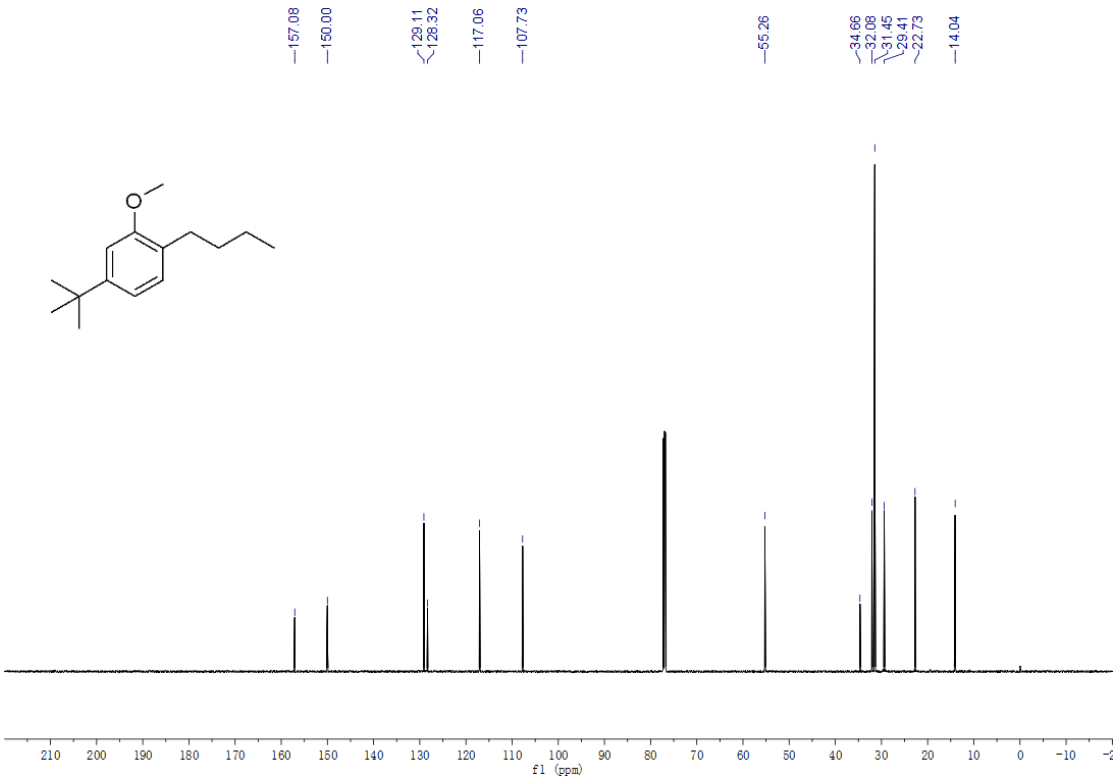
Methyl 4-butyl-3-methoxybenzoate (3sa):



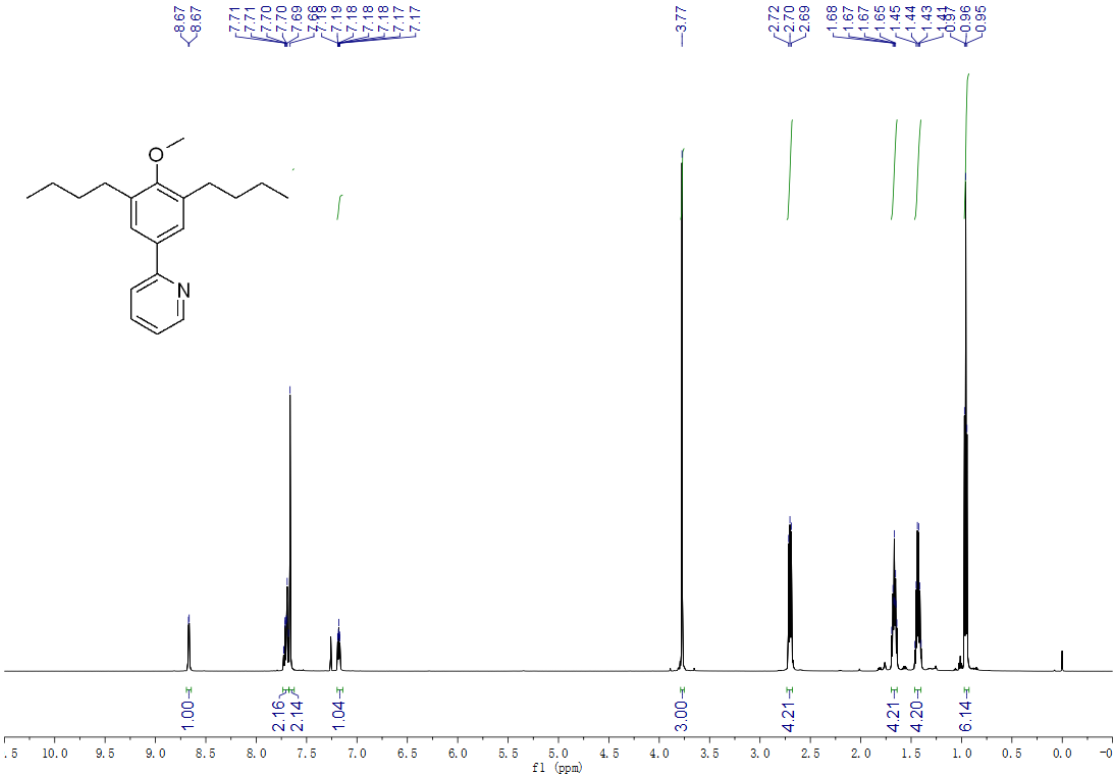


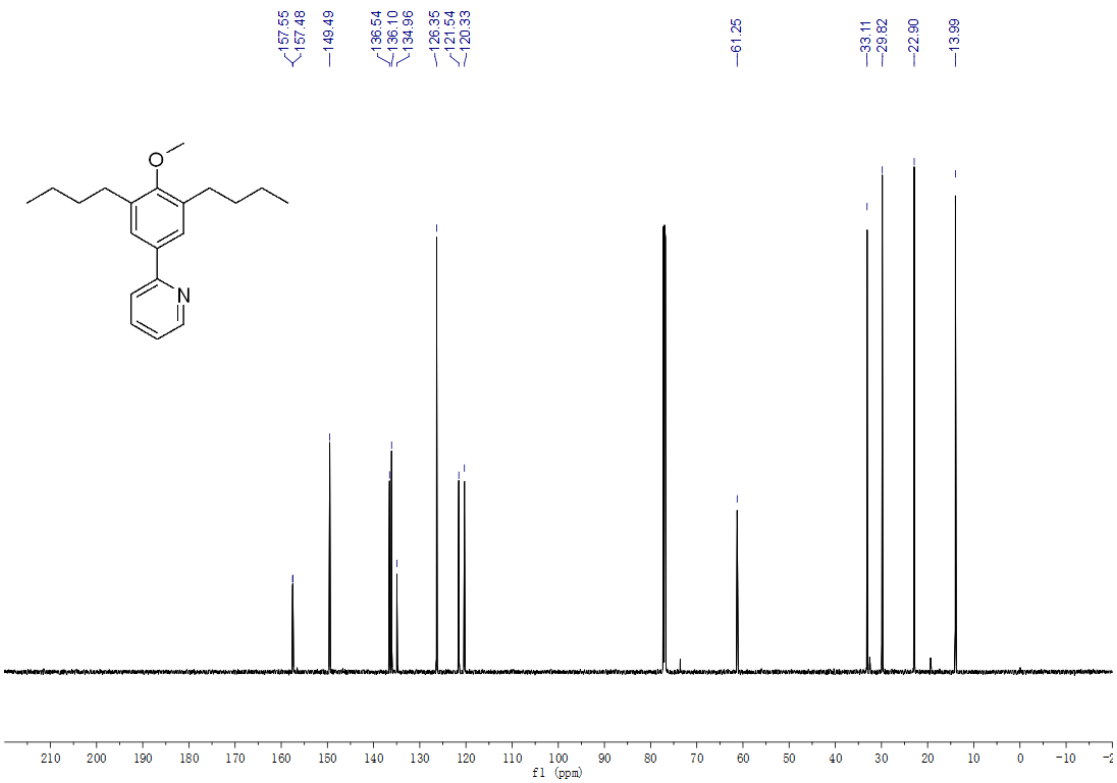
4-(*tert*-Butyl)-1-butyl-2-methoxybenzene (3ta):



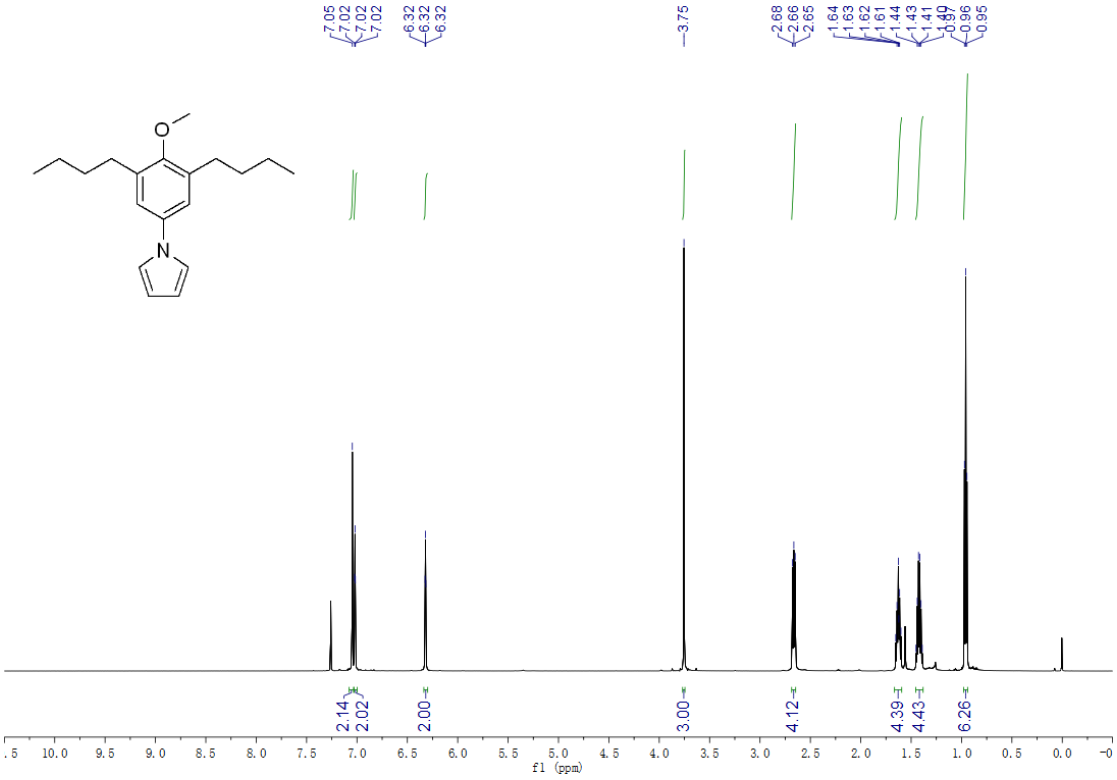


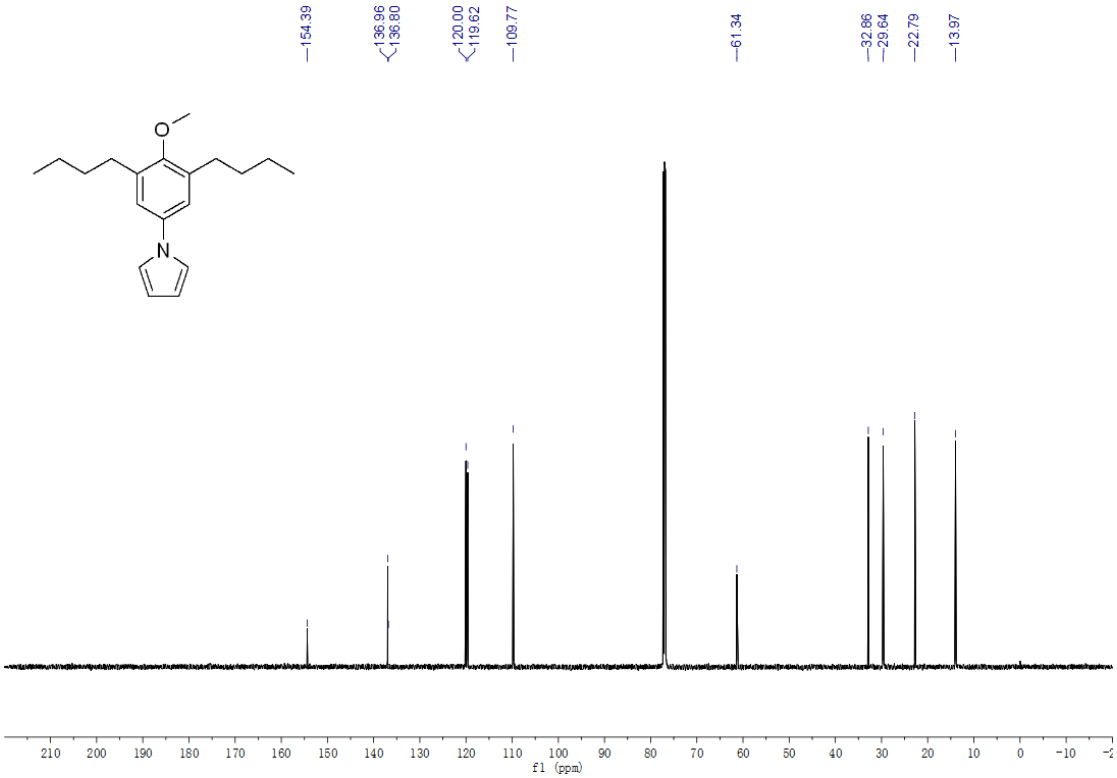
2-(3,5-Dibutyl-4-methoxyphenyl)pyridine (3ua):



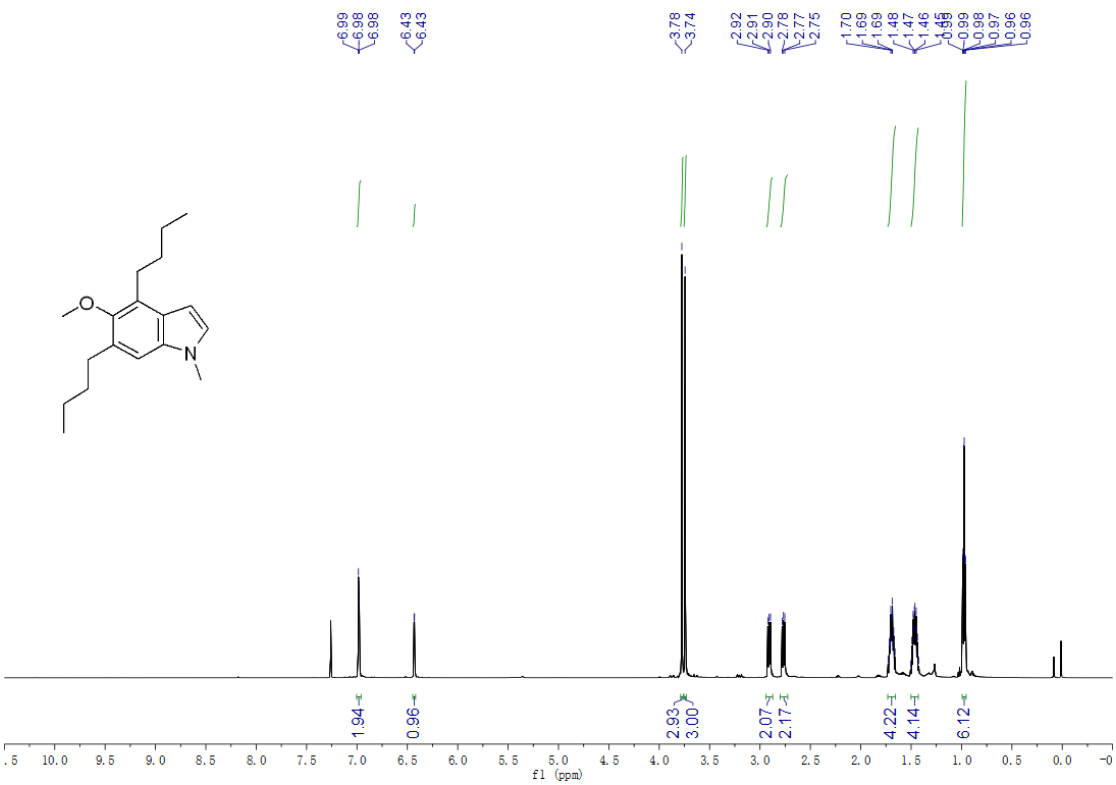


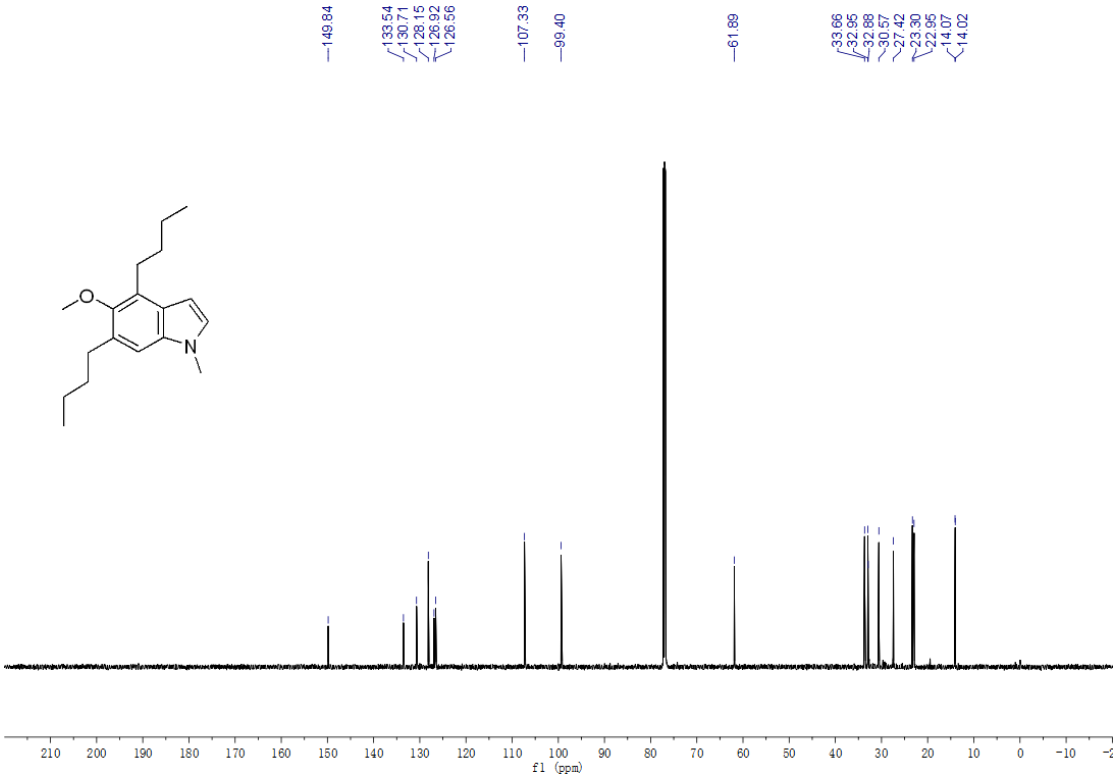
1-(3,5-Dibutyl-4-methoxyphenyl)-1H-pyrrole (3va):



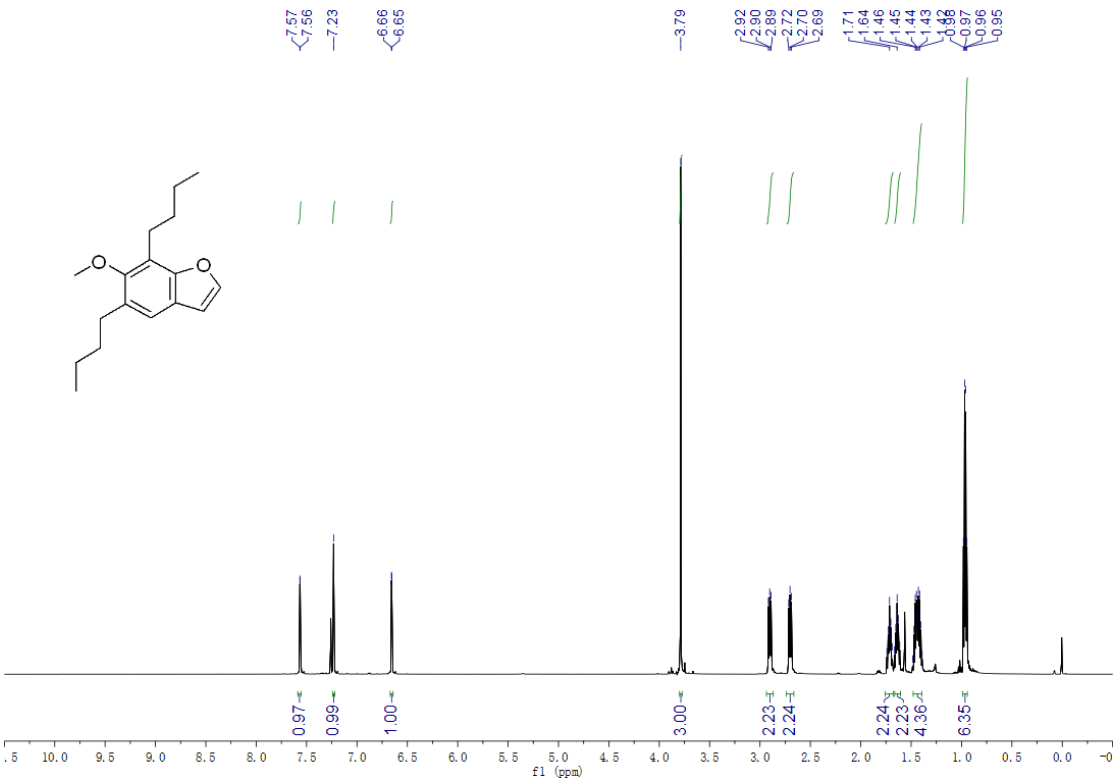


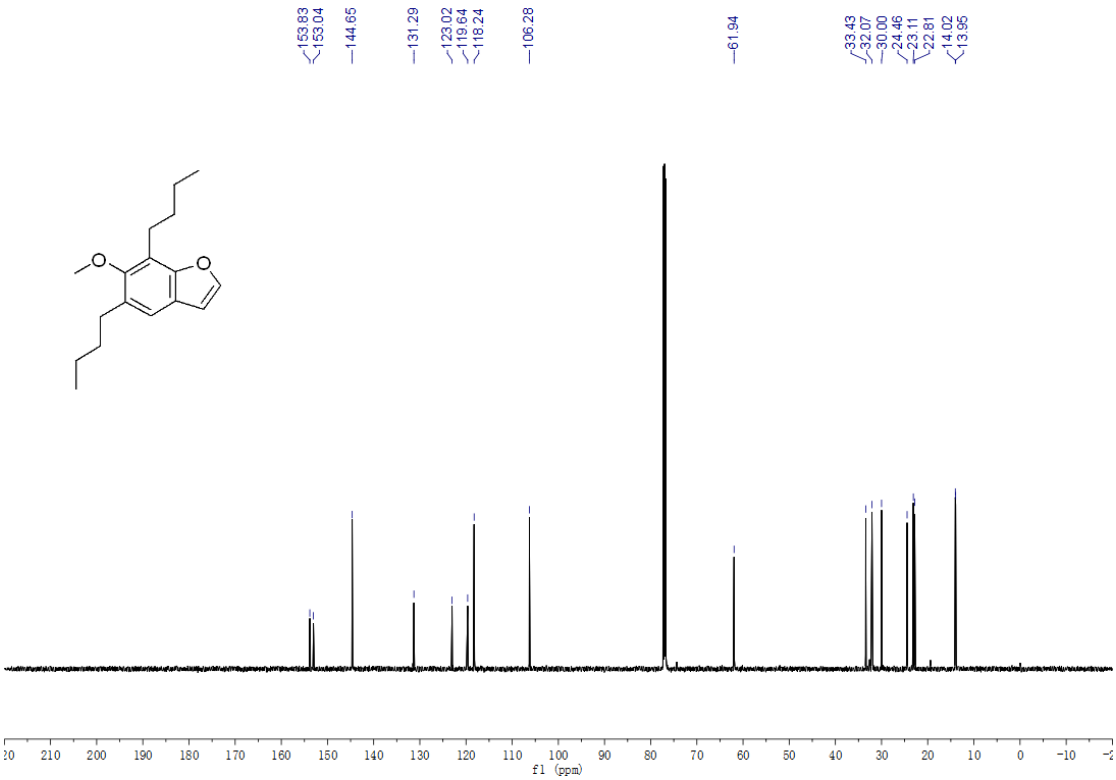
4,6-Dibutyl-5-methoxy-1-methyl-1H-indole (3wa):



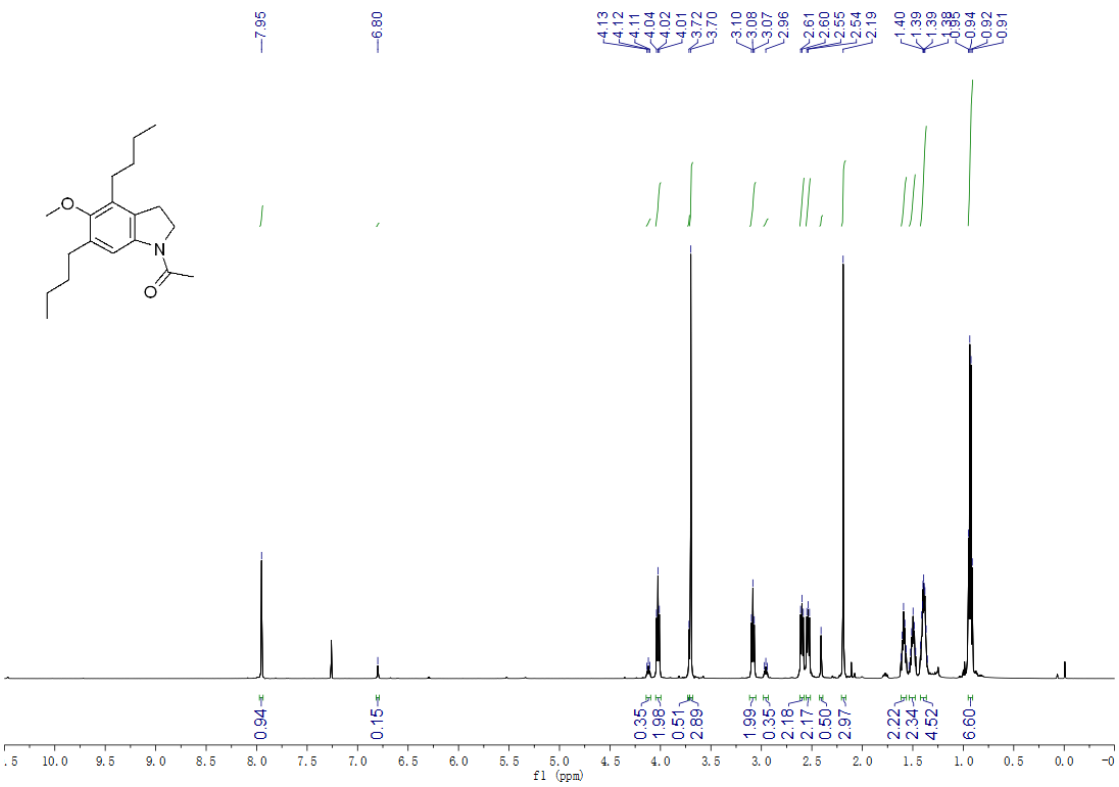


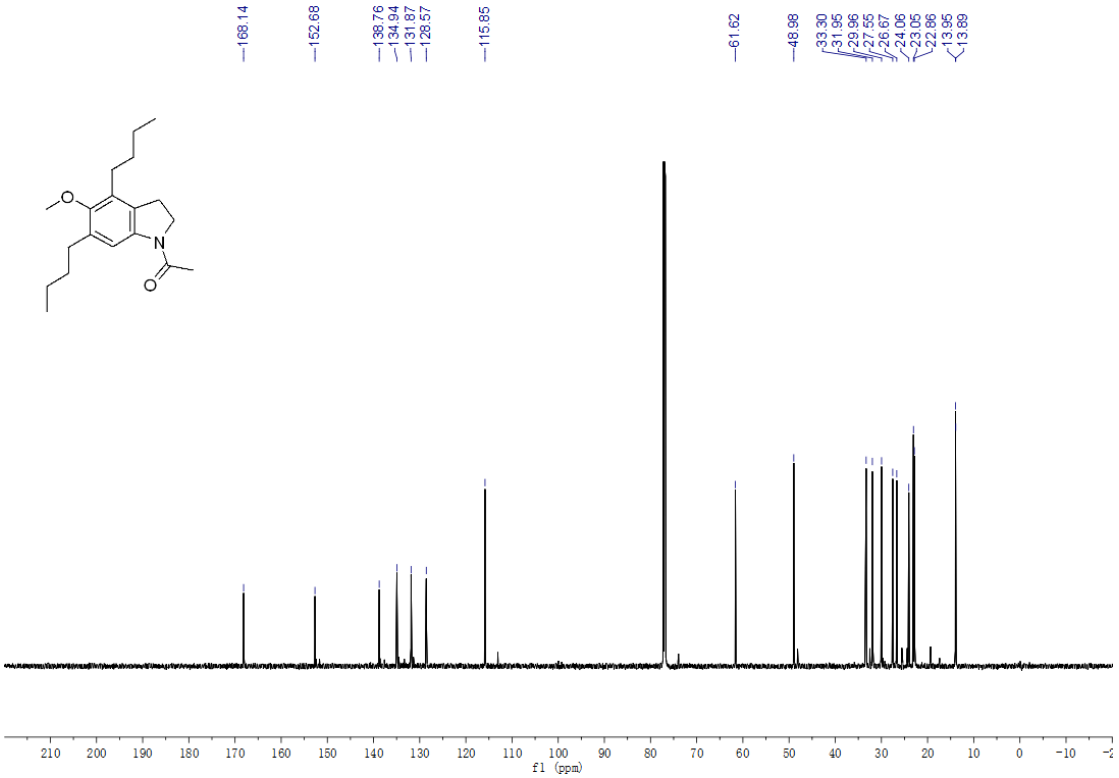
5,7-dibutyl-6-methoxybenzofuran (3xa):



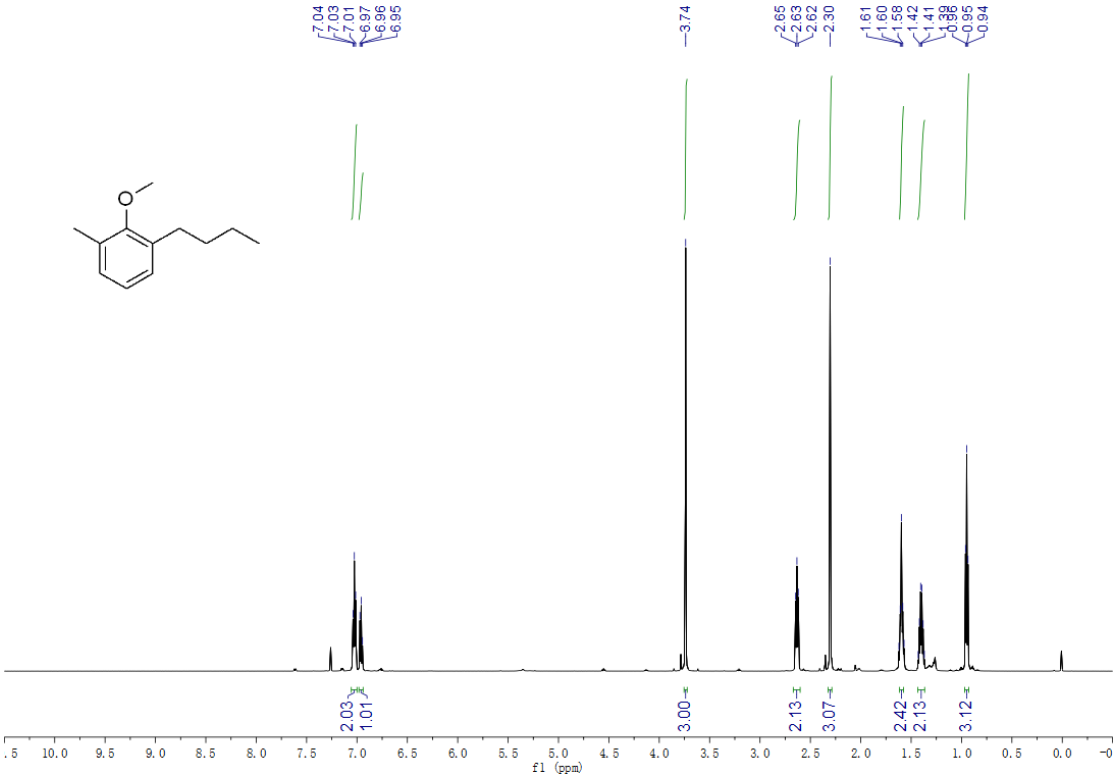


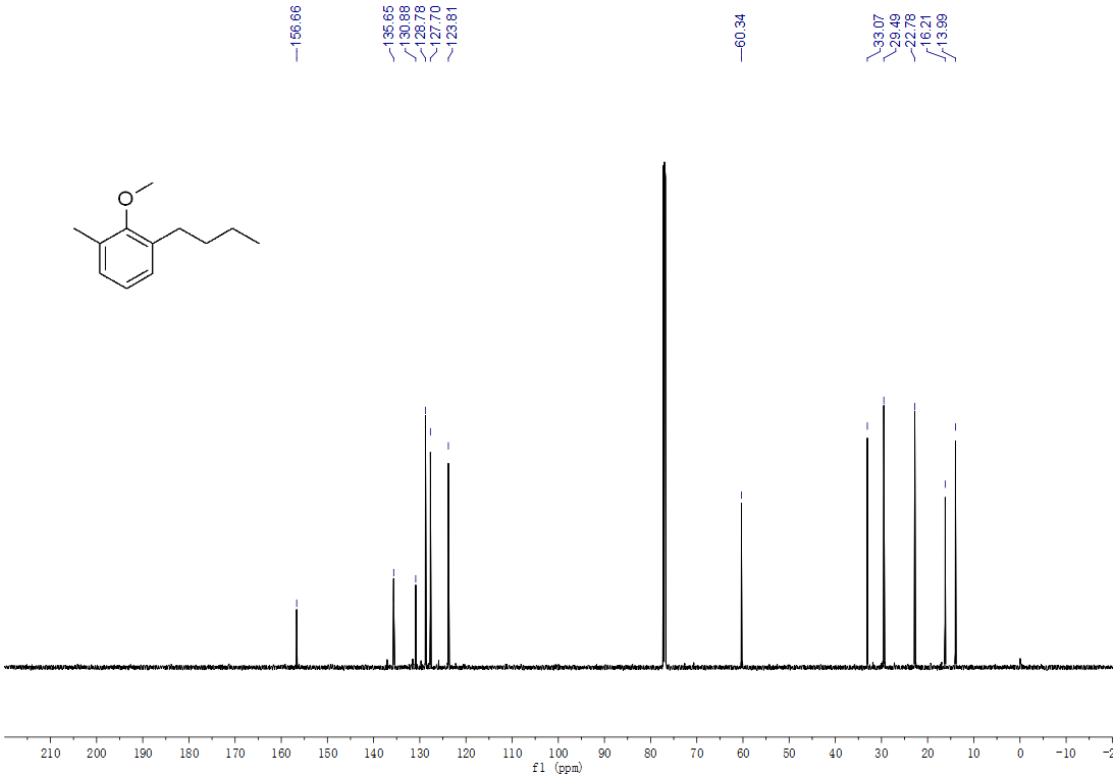
1-(4,6-Dibutyl-5-methoxyindolin-1-yl)ethan-1-one (3ya):



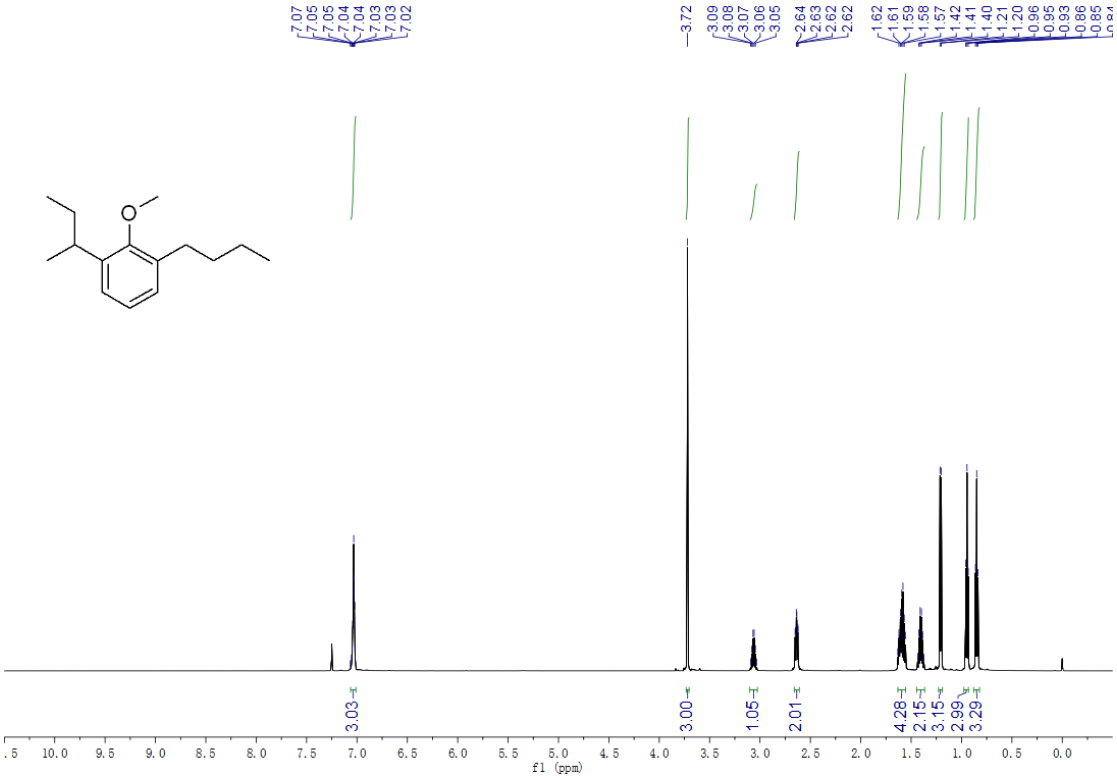


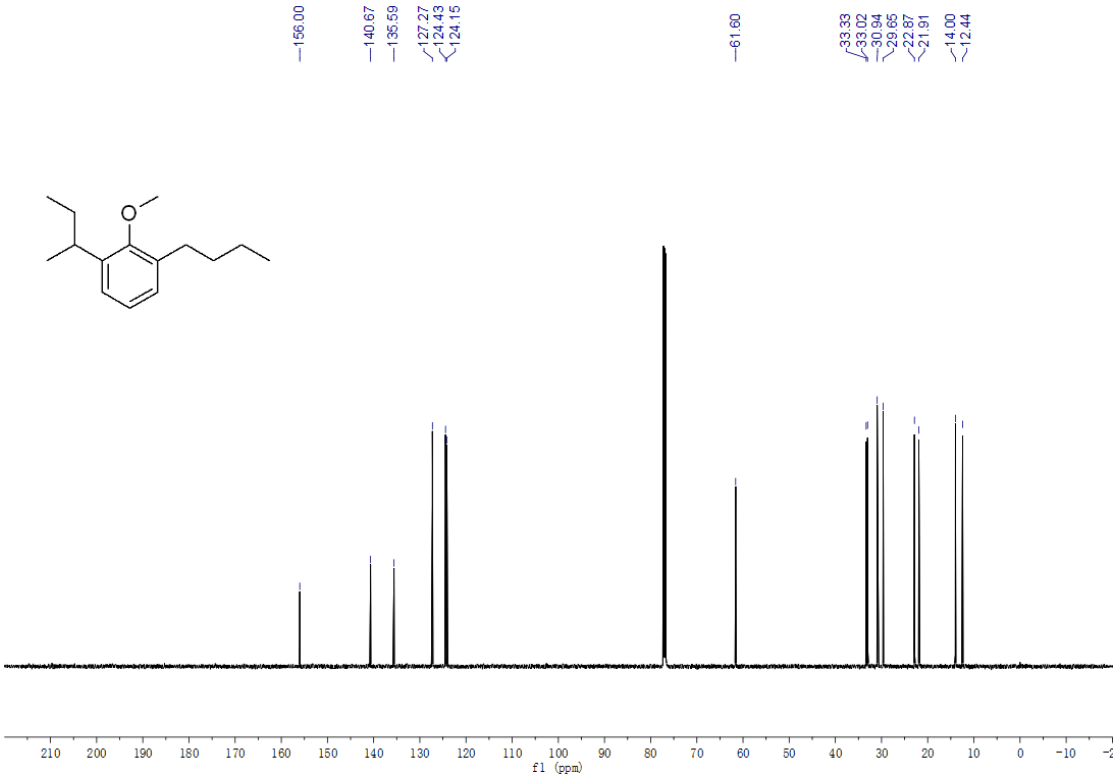
1-Butyl-2-methoxy-3-methylbenzene (5aa):



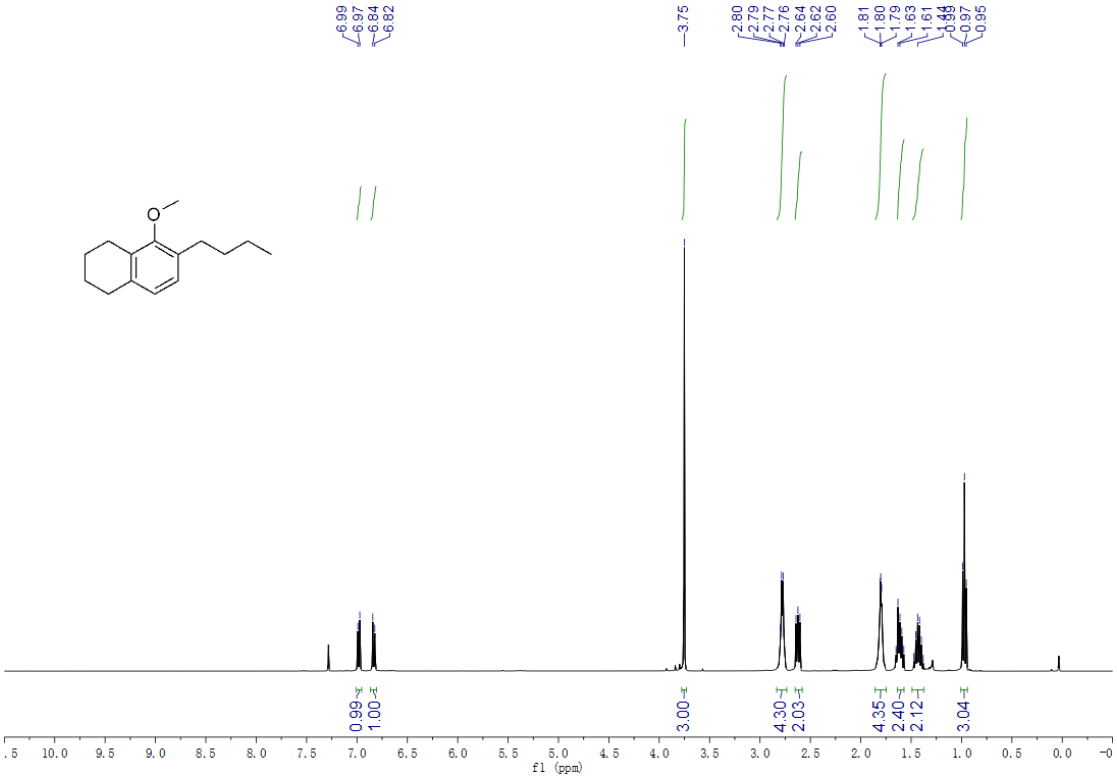


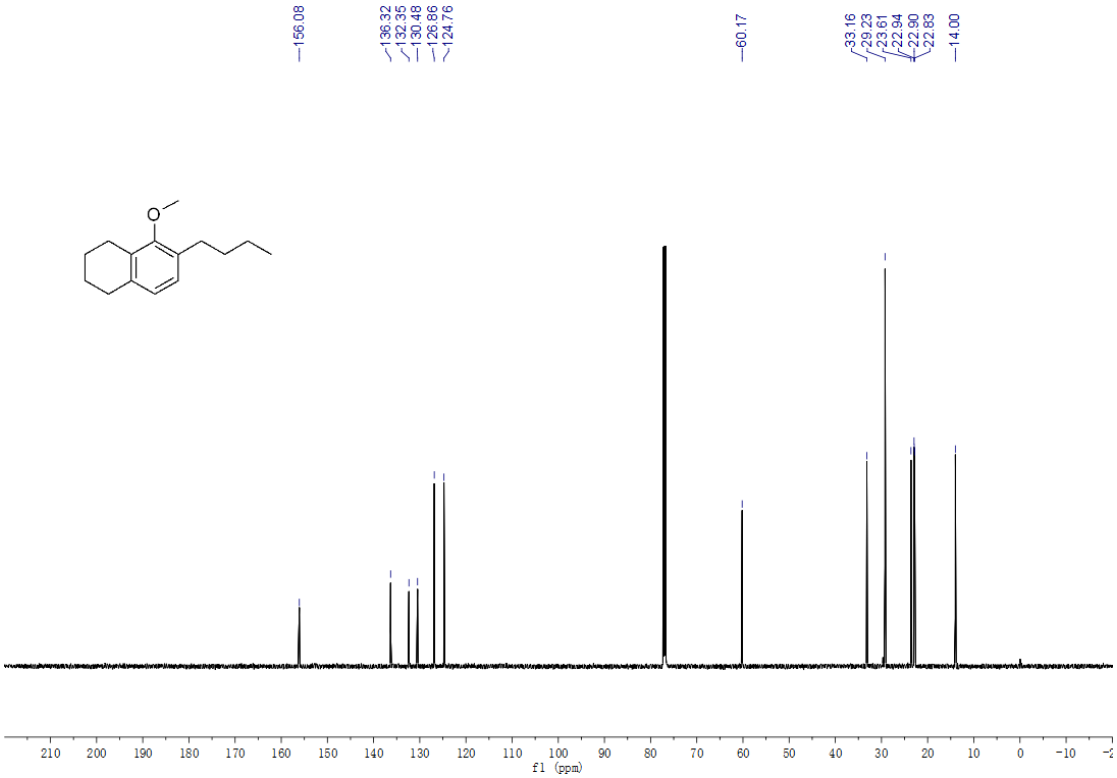
1-(*sec*-butyl)-3-butyl-2-methoxybenzene (5ba):



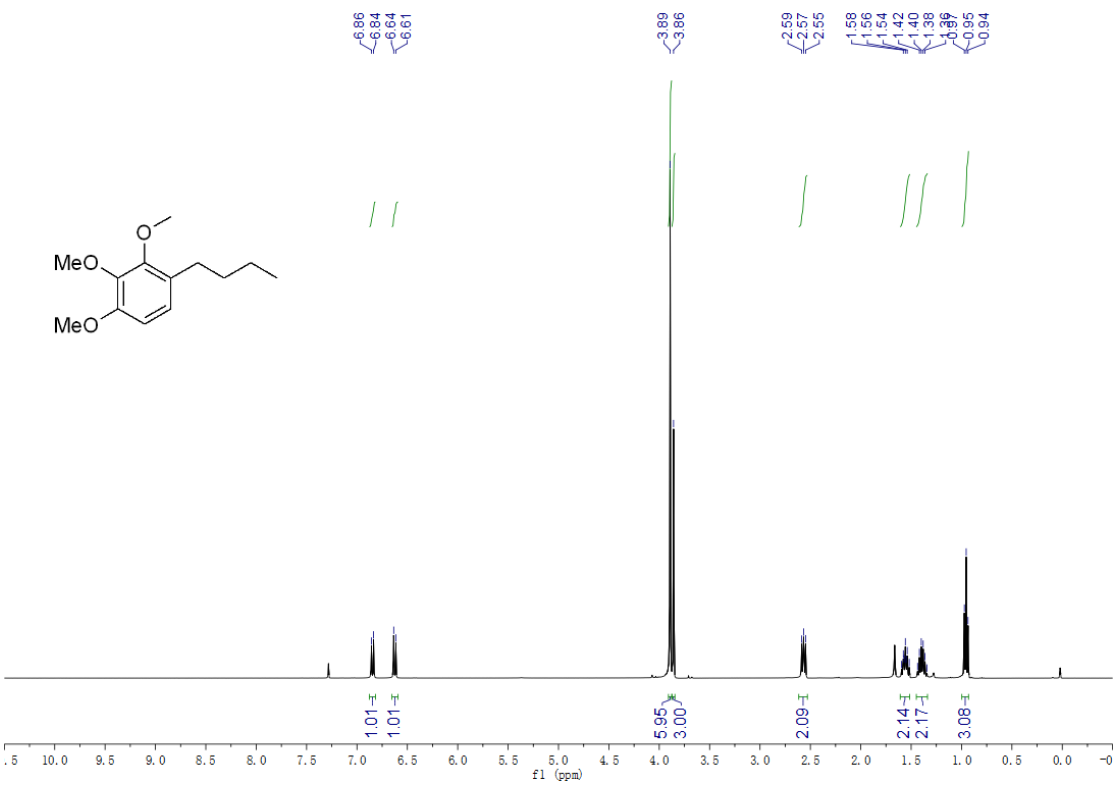


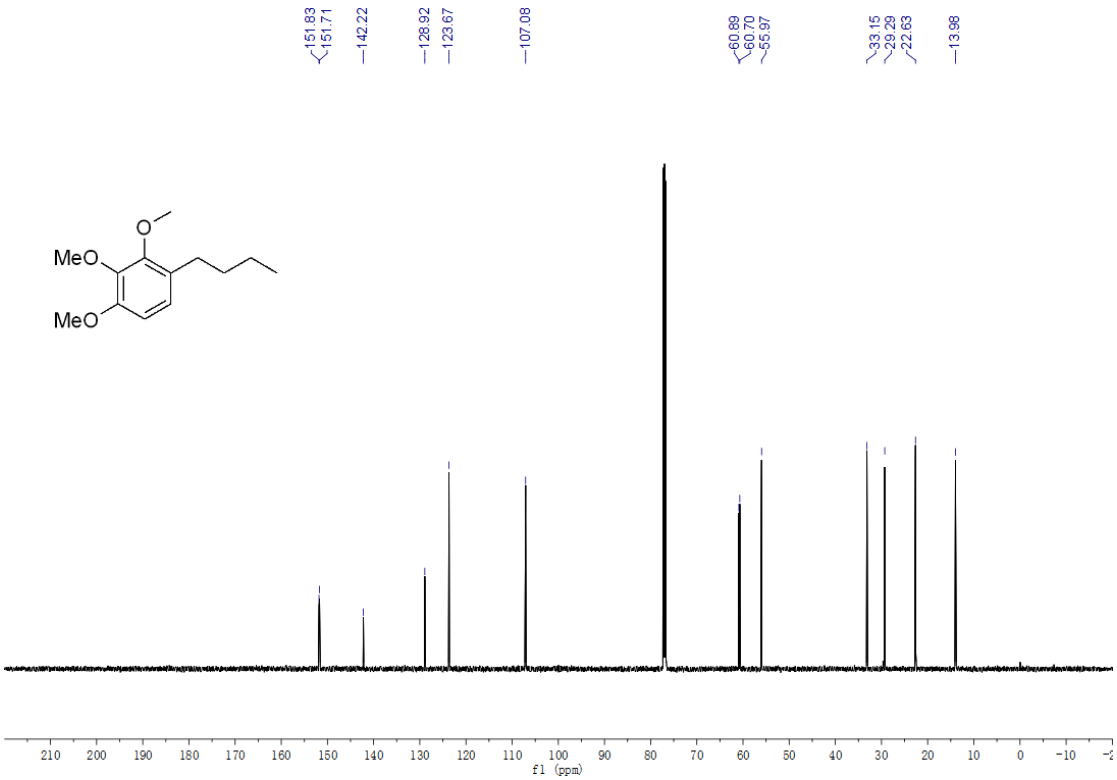
6-Butyl-5-methoxy-1,2,3,4-tetrahydronaphthalene (5ca):



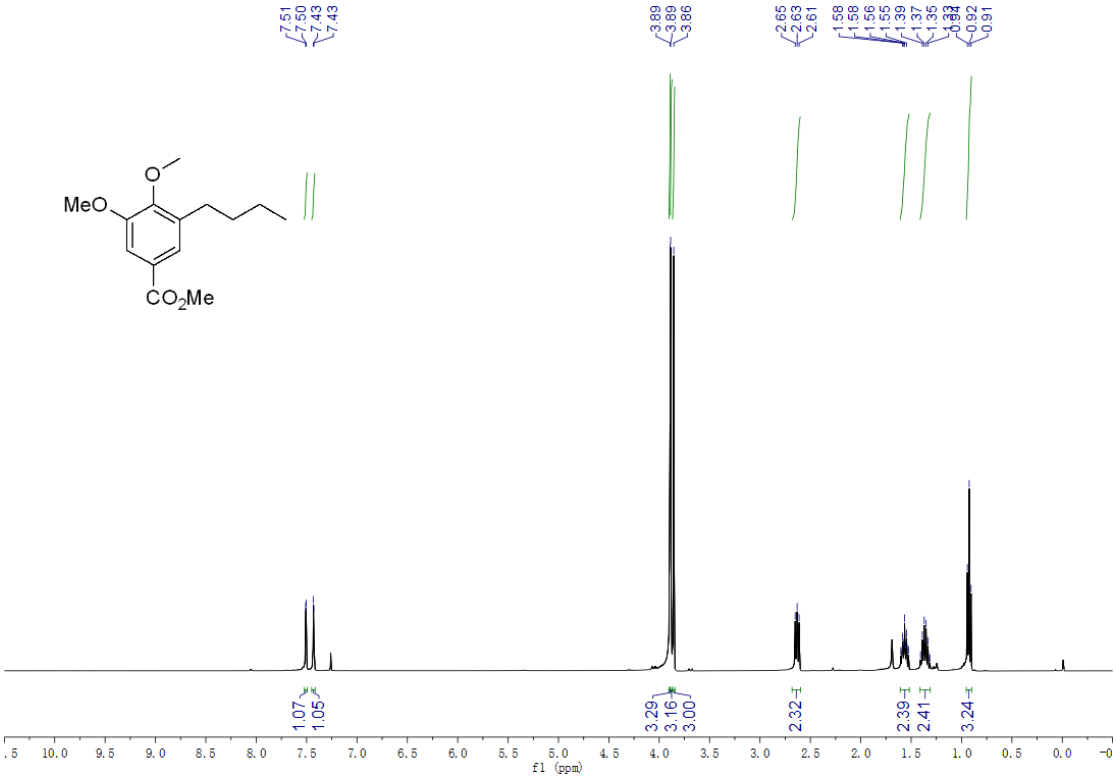


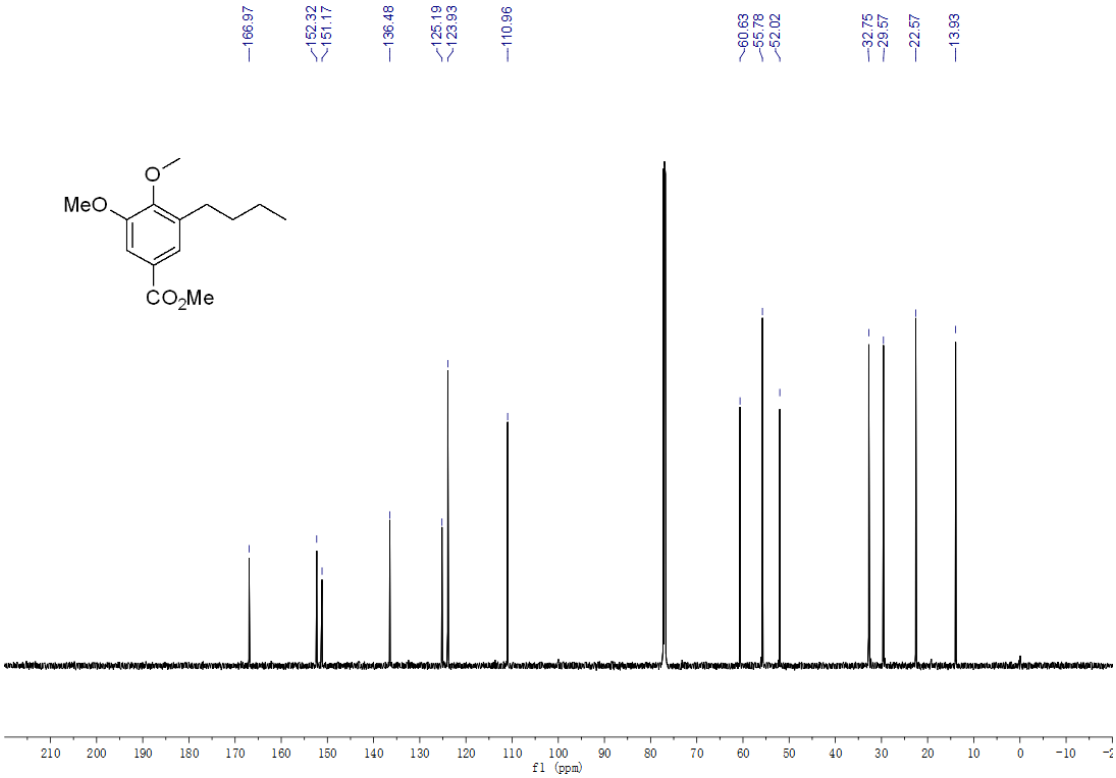
1-Butyl-2,3,4-trimethoxybenzene (5da):



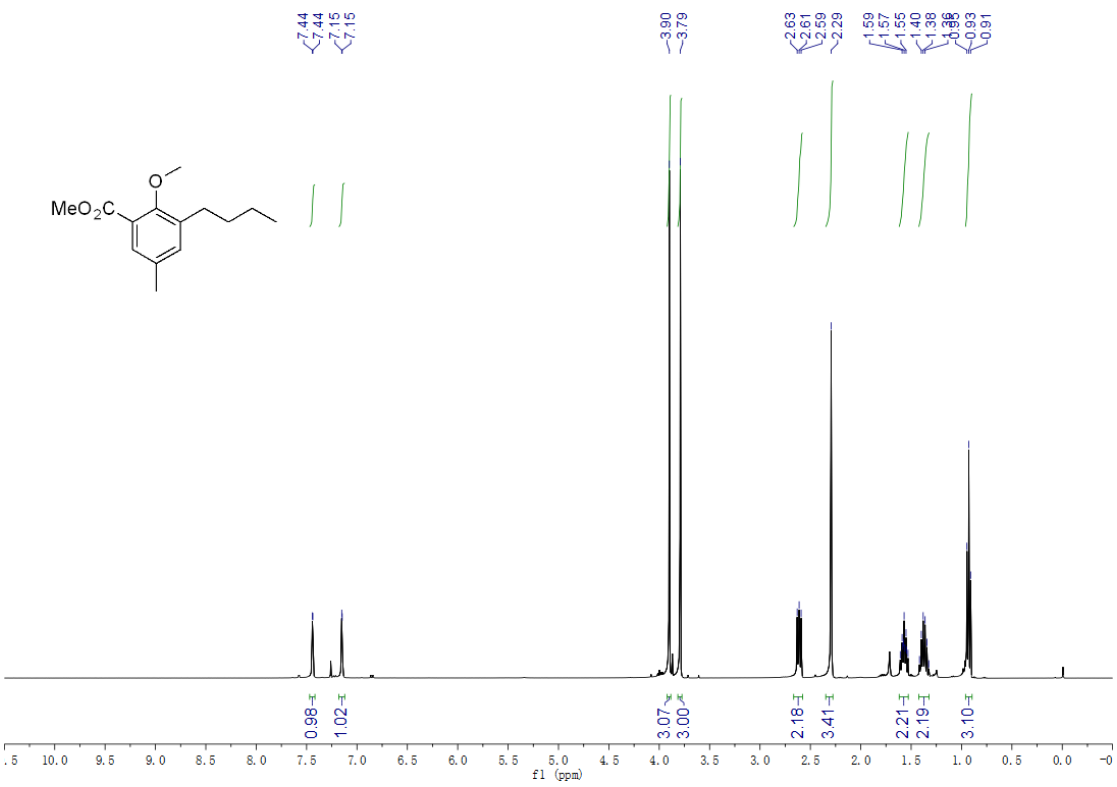


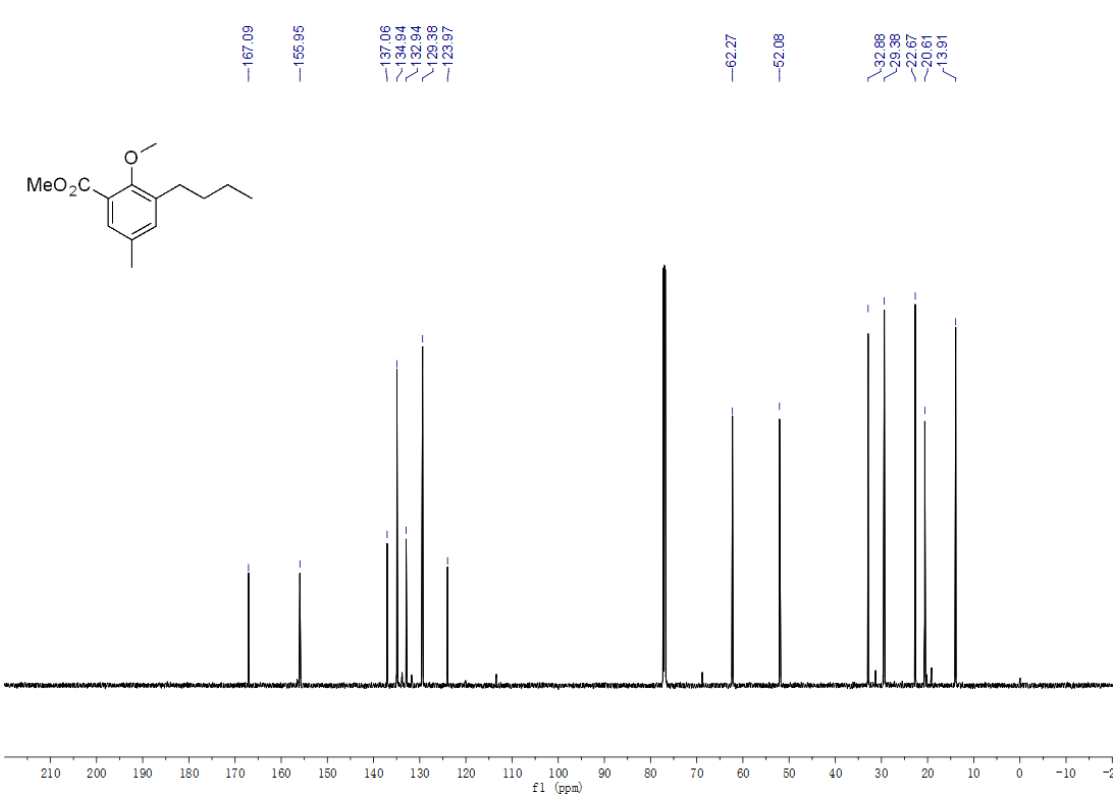
Methyl 3-butyl-4,5-dimethoxybenzoate (5ea):



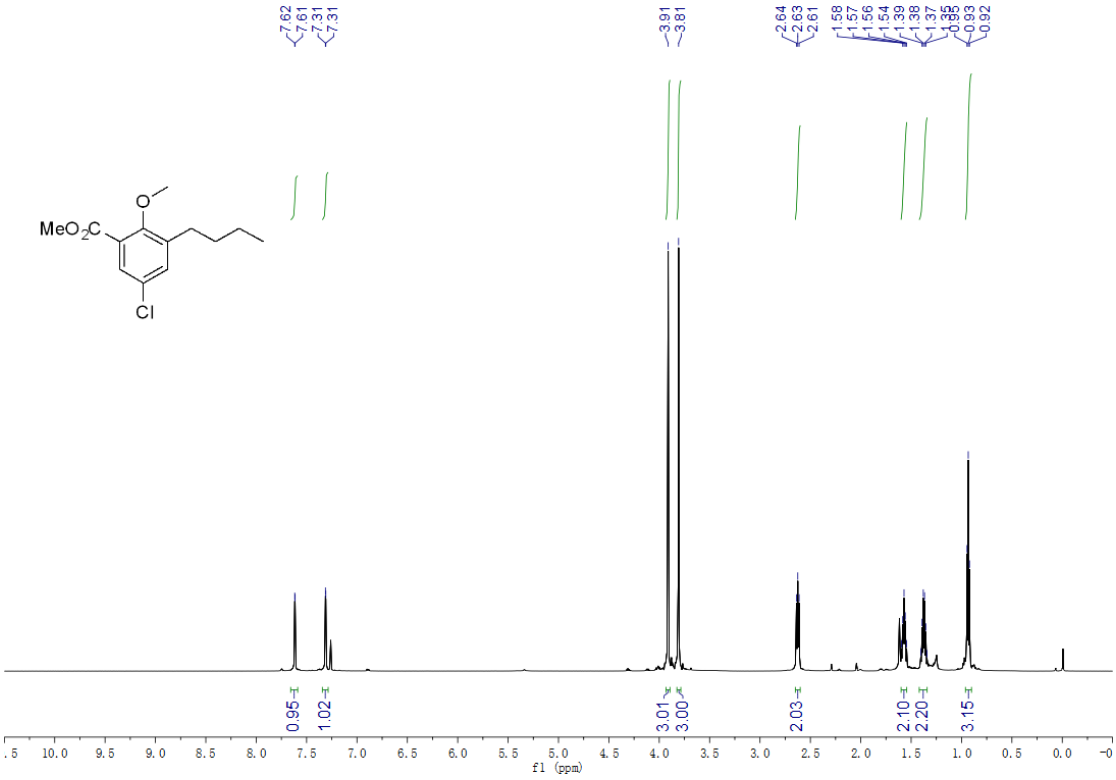


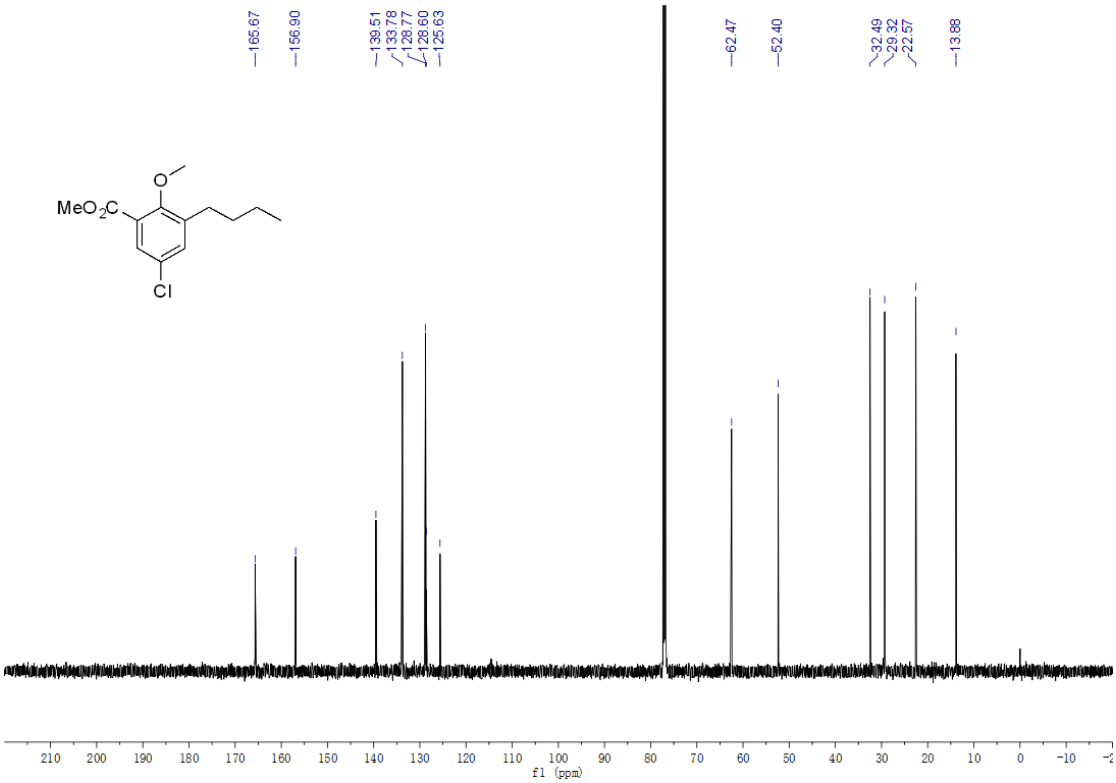
Methyl 3-butyl-2-methoxy-5-methylbenzoate (5fa):





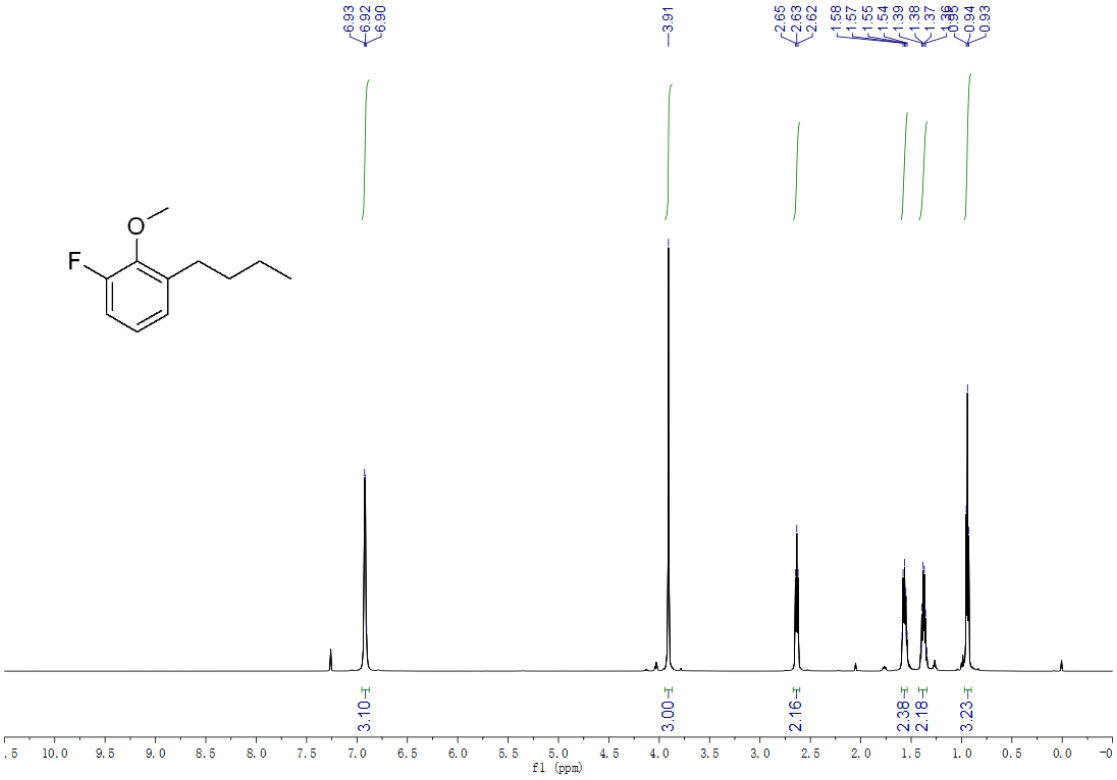
Methyl 3-butyl-5-chloro-2-methoxybenzoate (5ga):



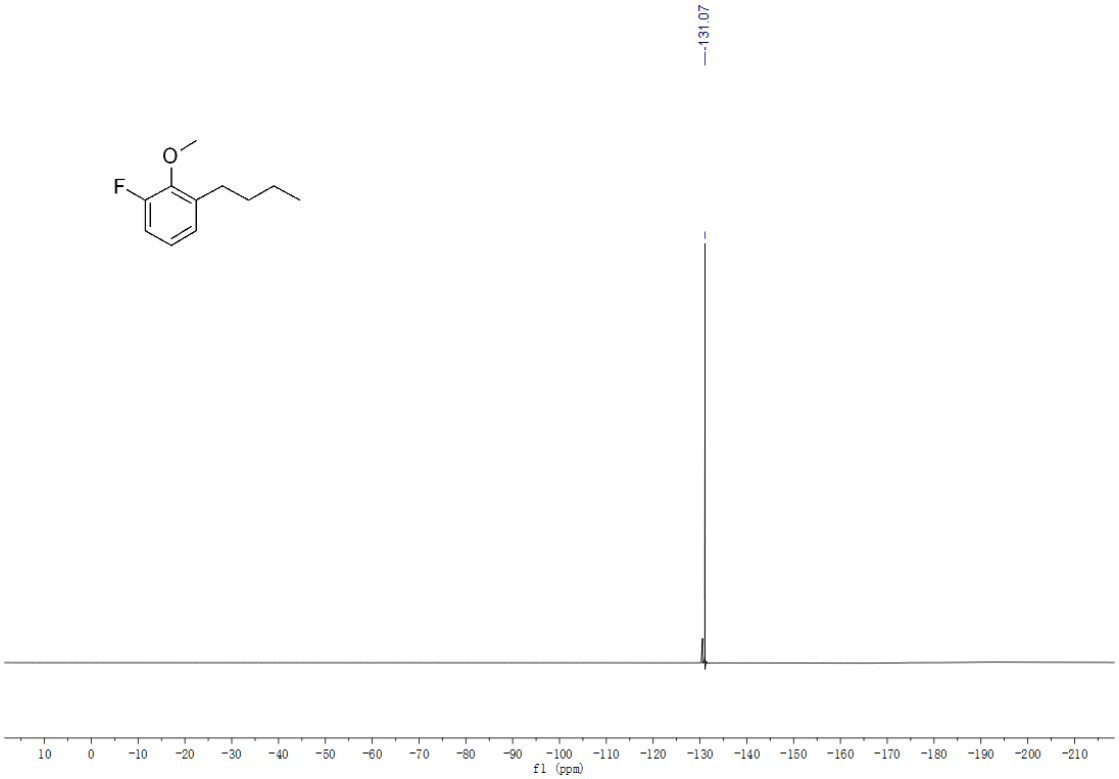


1-Butyl-3-fluoro-2-methoxybenzene (5ha):

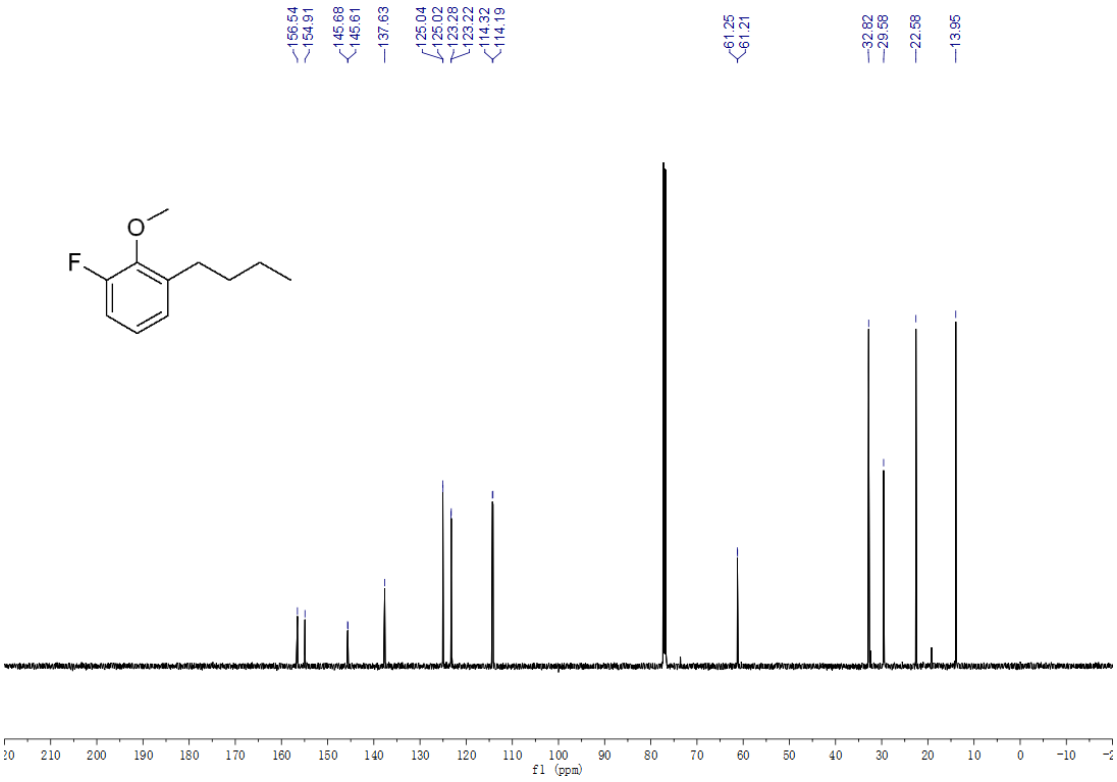
^{1}H NMR



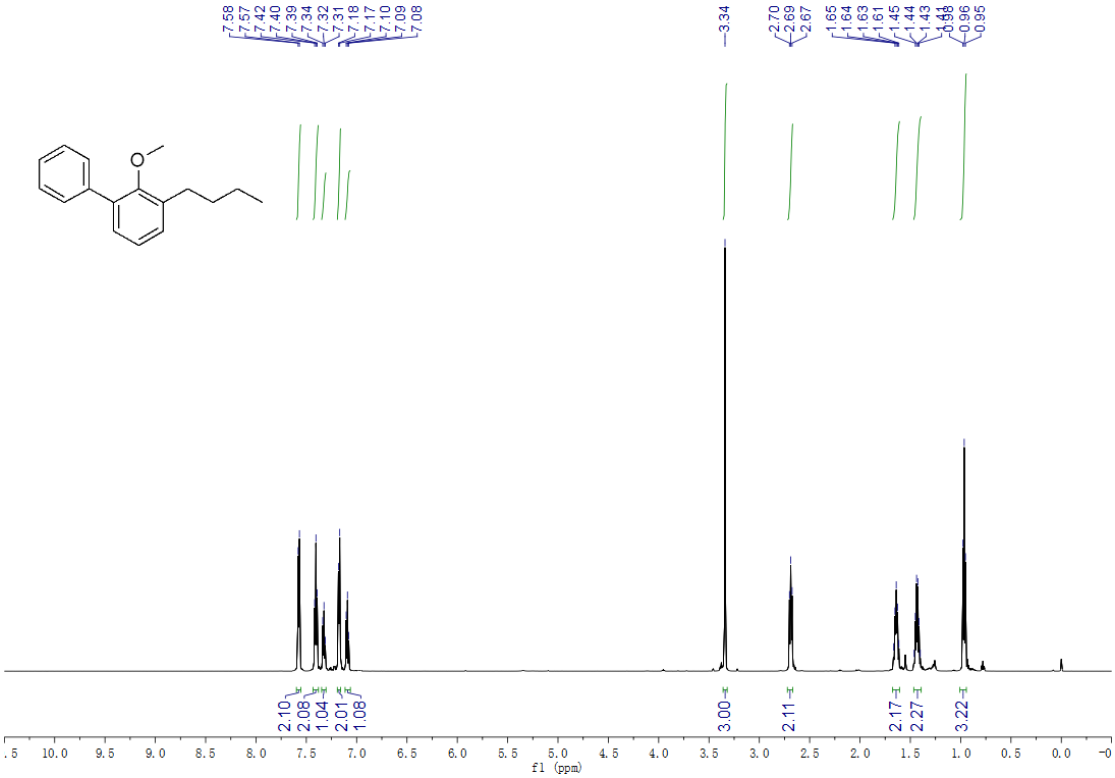
^{19}F NMR

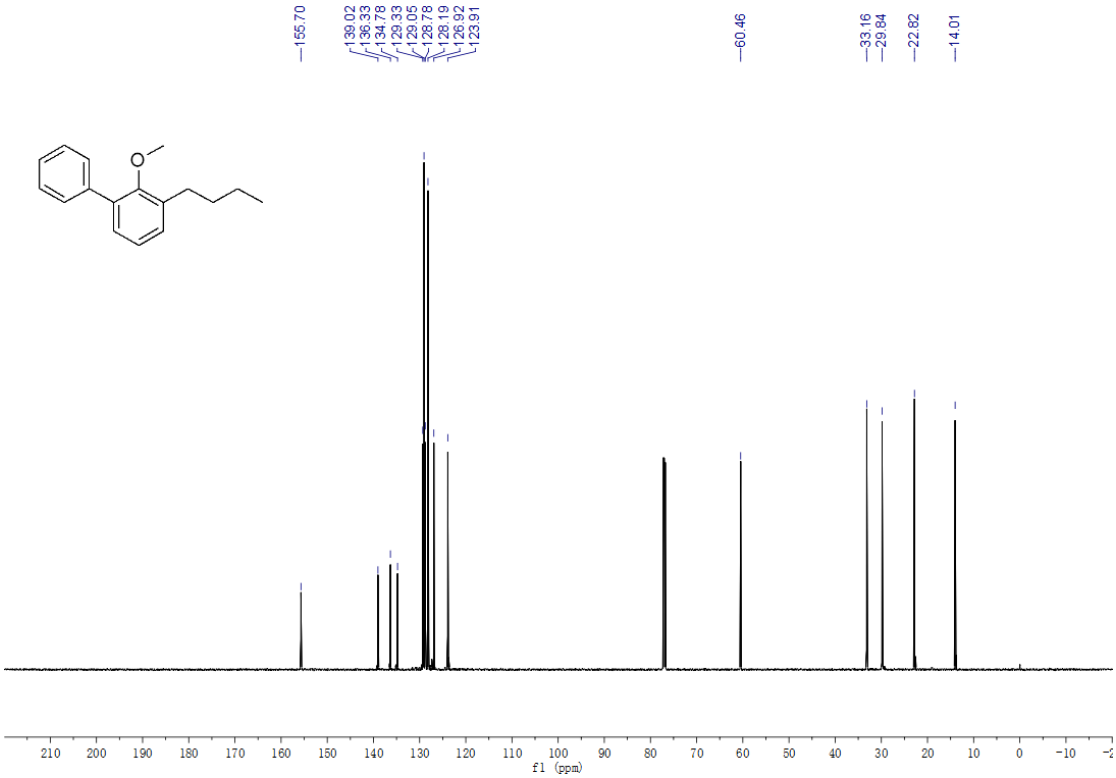


^{13}C NMR

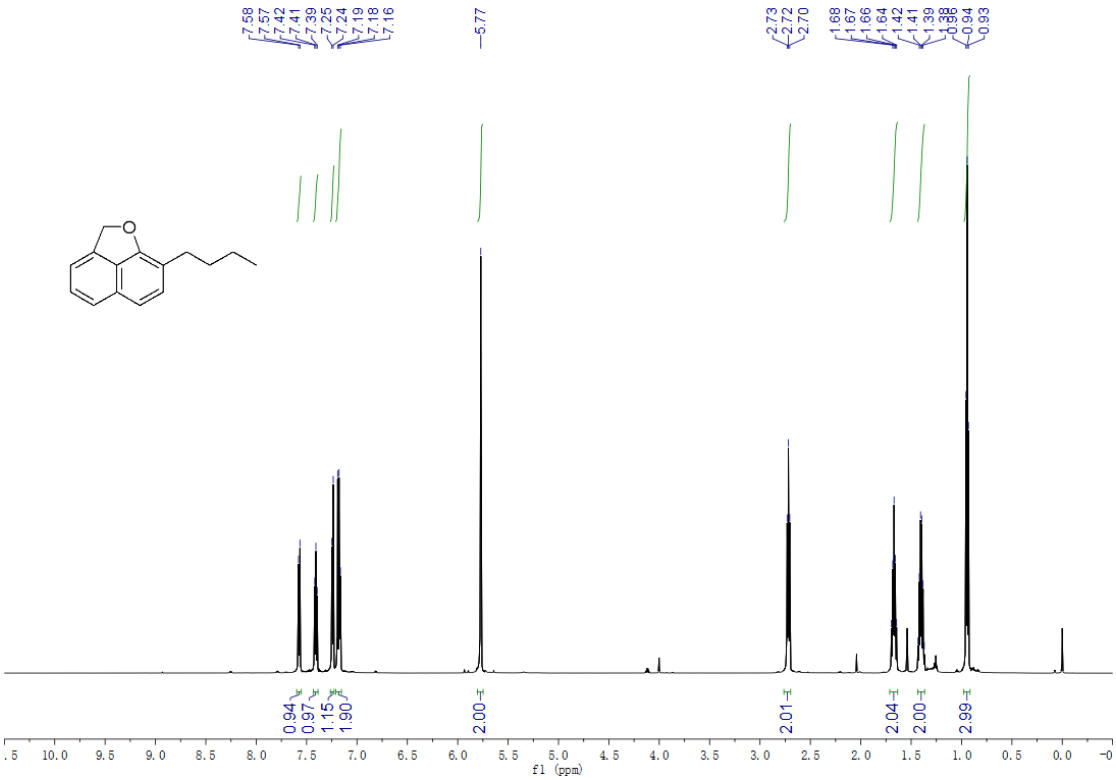

156.54
154.91
145.68
145.61
137.63
125.04
125.02
123.28
123.22
114.32
114.19
61.25
61.21
32.82
29.58
22.58
13.95
O
F
f1 (ppm)

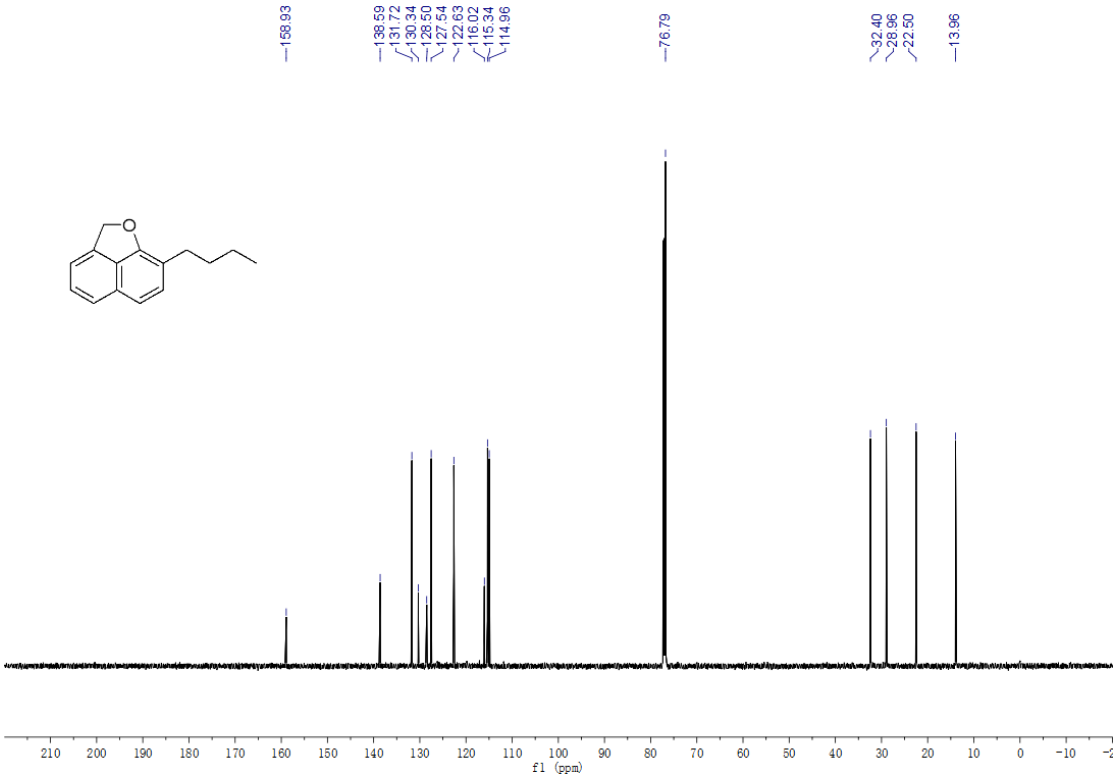
3-Butyl-2-methoxy-1,1'-biphenyl (5ia):



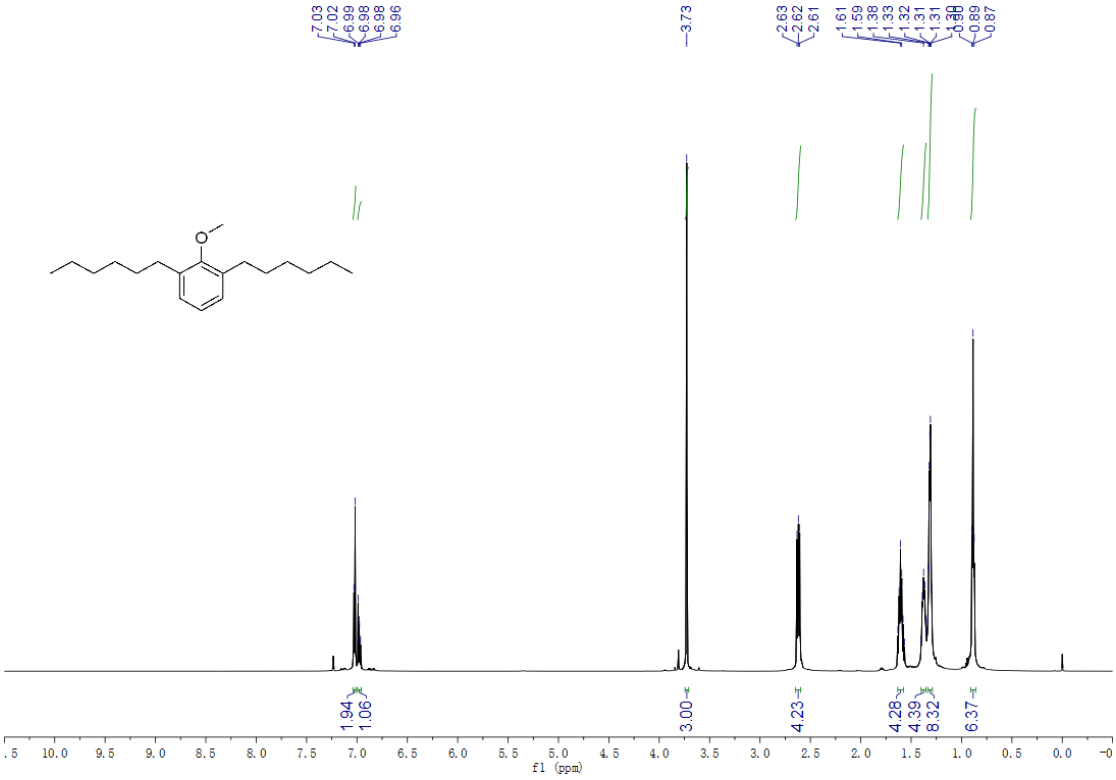


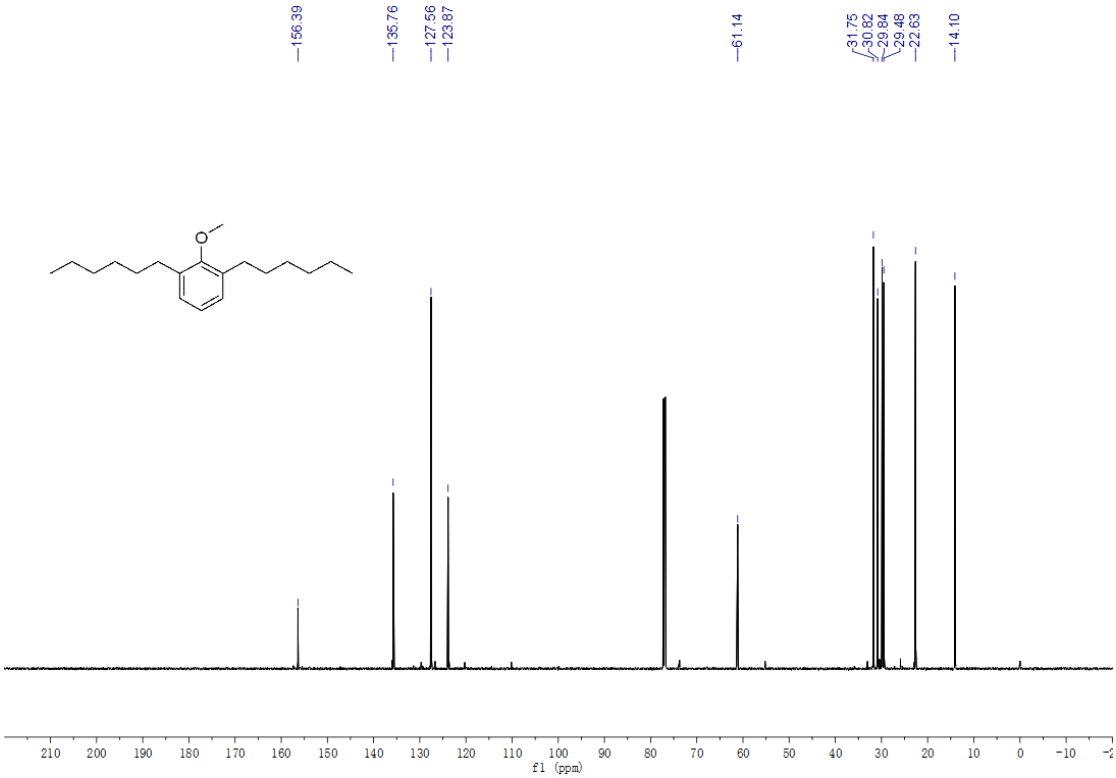
8-butyl-2*H*-naphtho[1,8-*bc*]furan (5ja):



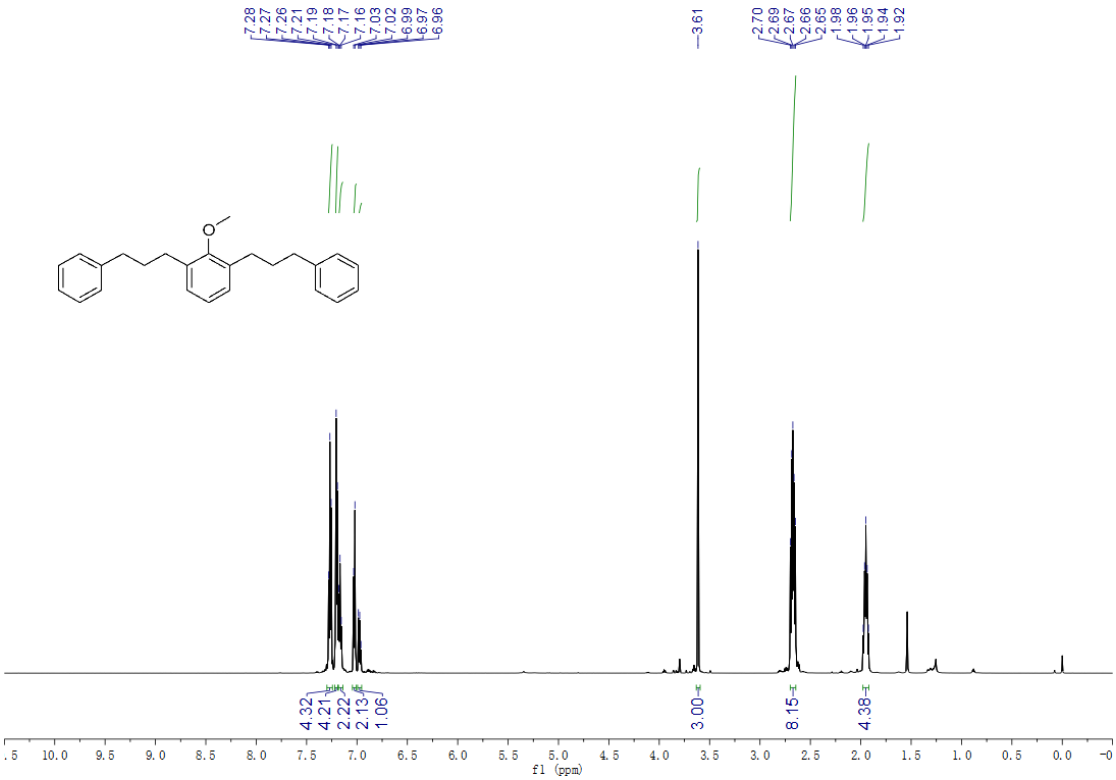


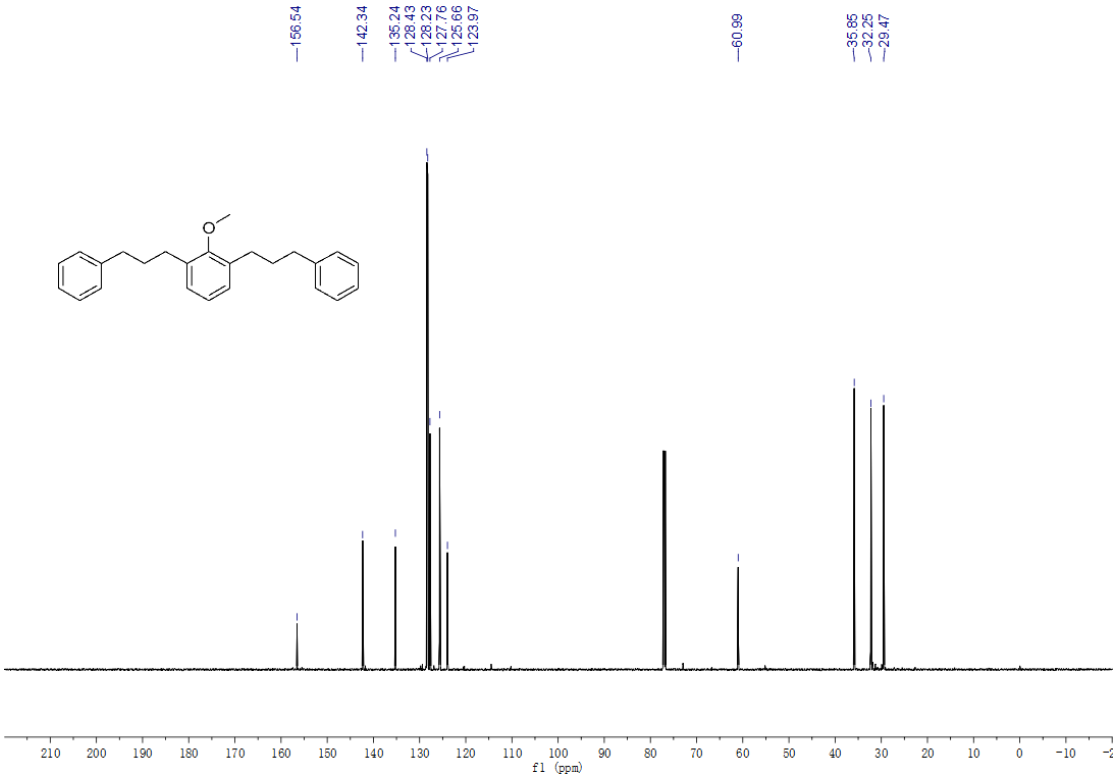
1,3-Dihexyl-2-methoxybenzene (3ab):



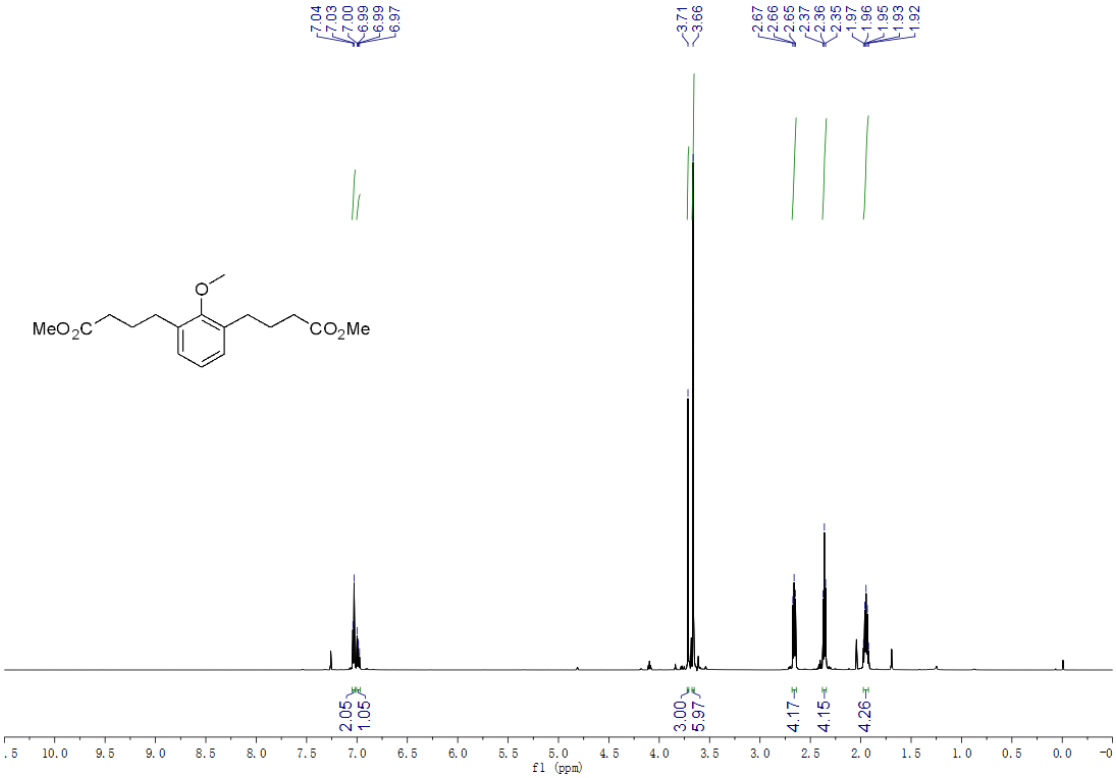


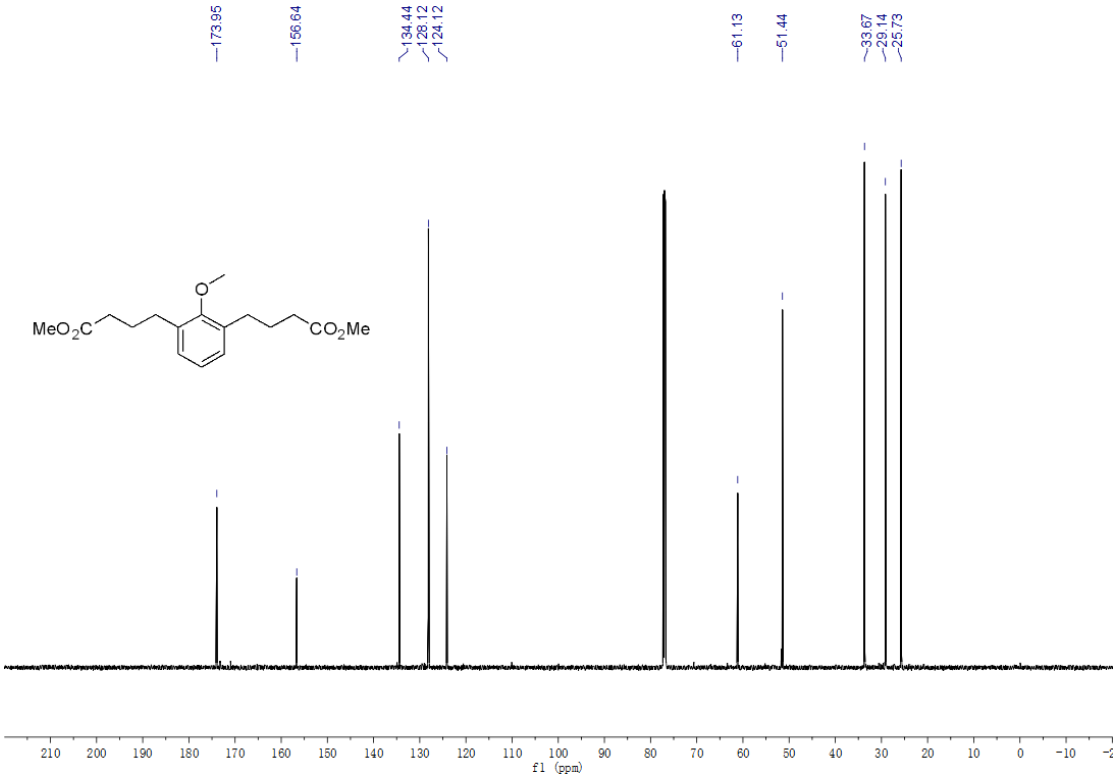
((2-Methoxy-1,3-phenylene)bis(propane-3,1-diyl))dibenzene (3ac):



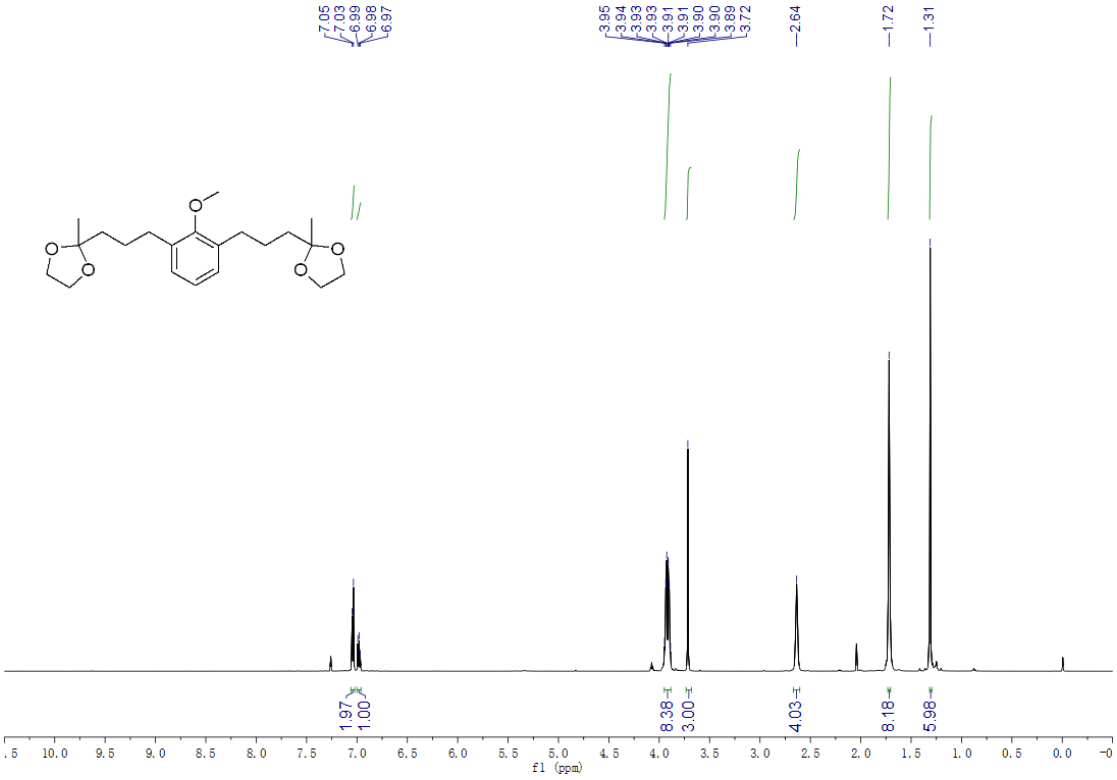


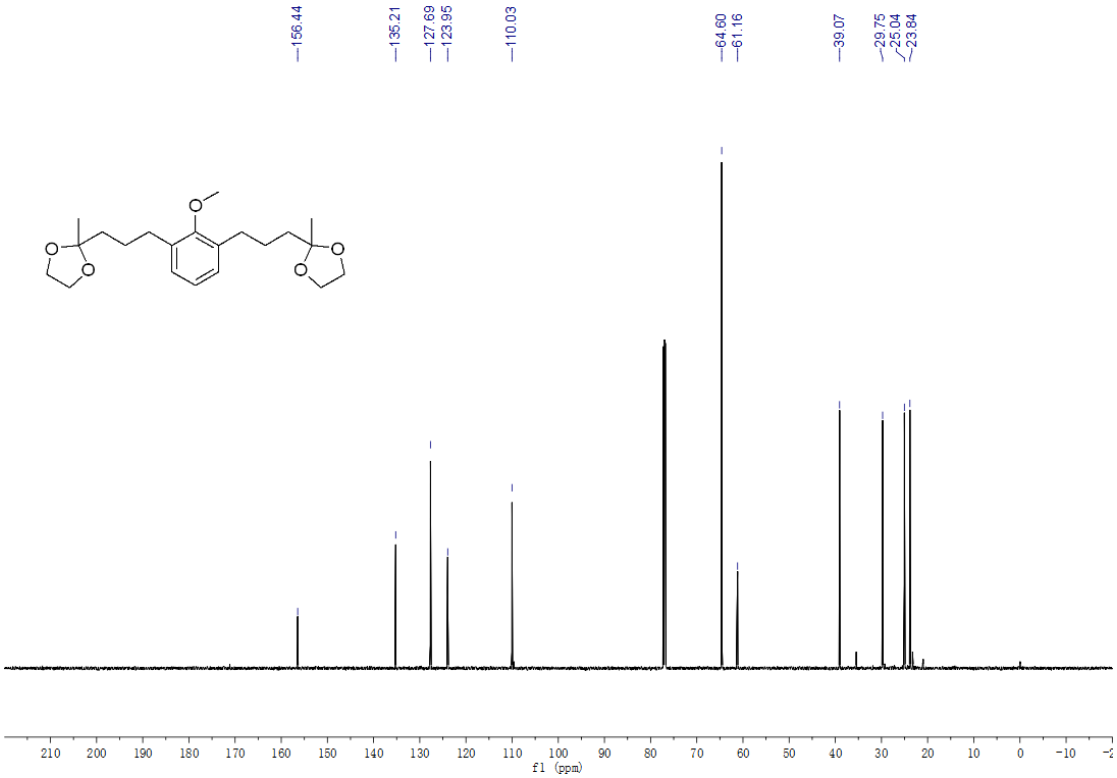
Dimethyl 4,4'-(2-methoxy-1,3-phenylene)dibutyrate (3ad):



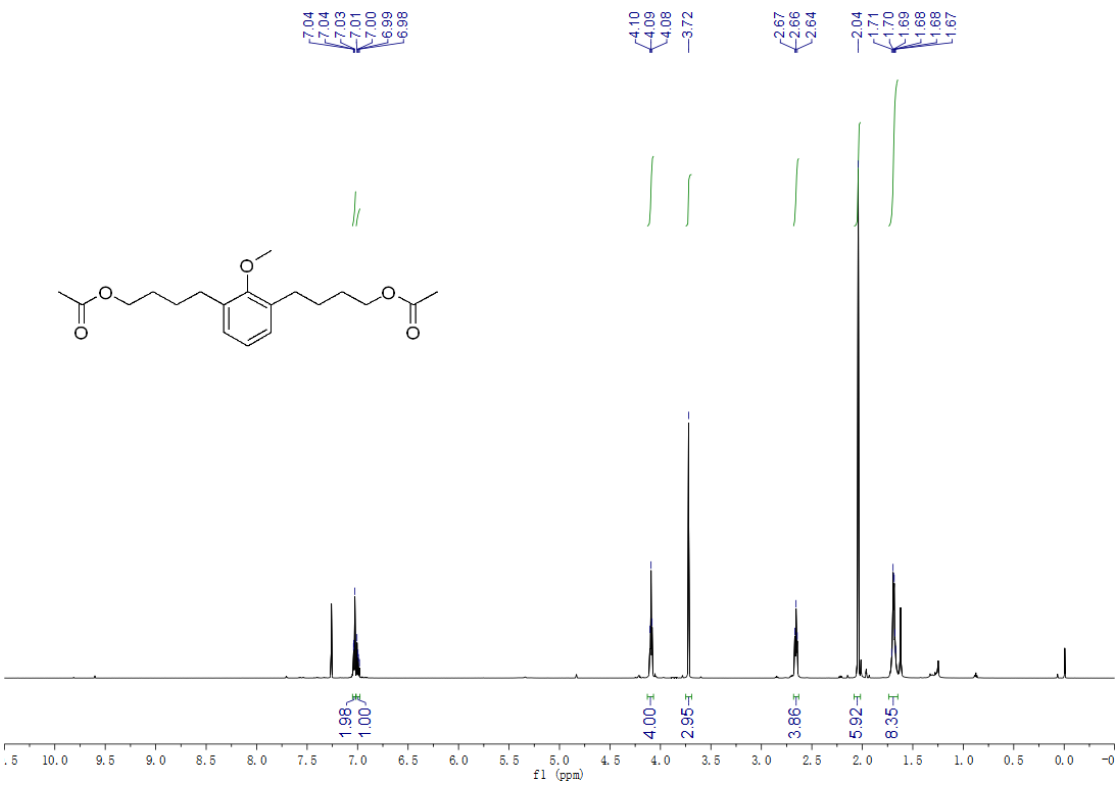


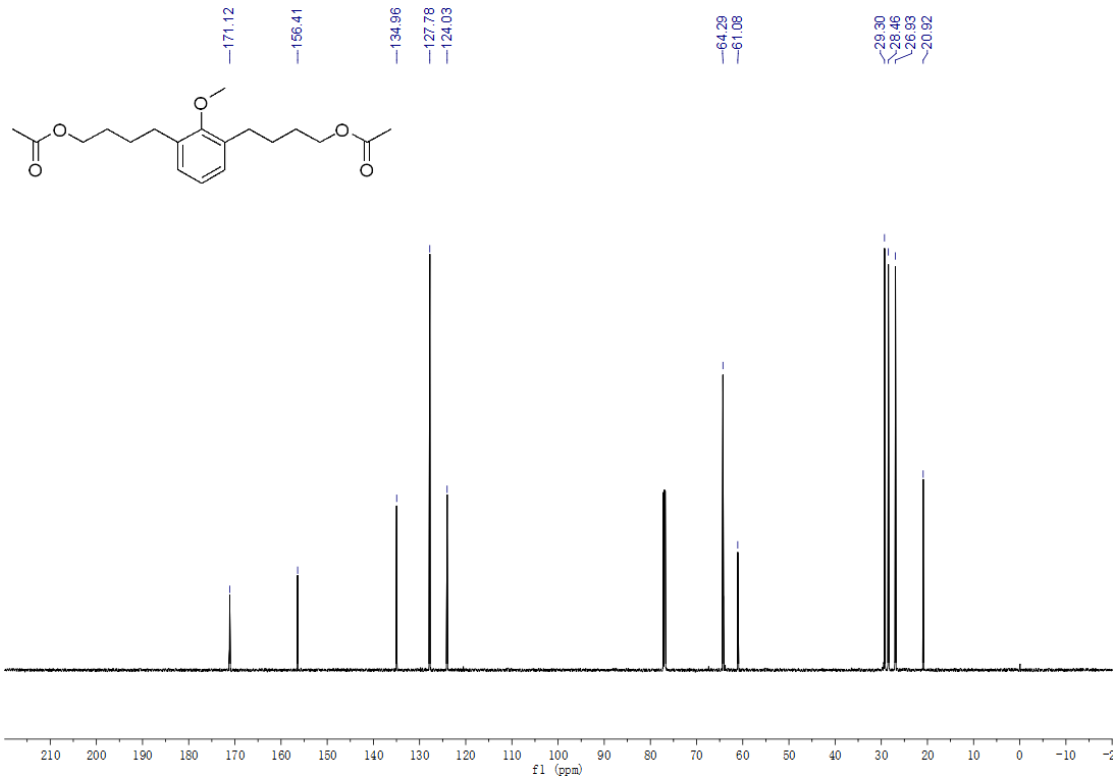
2,2'-((2-methoxy-1,3-phenylene)bis(propane-3,1-diyl))bis(2-methyl-1,3-dioxolane) (3ae):



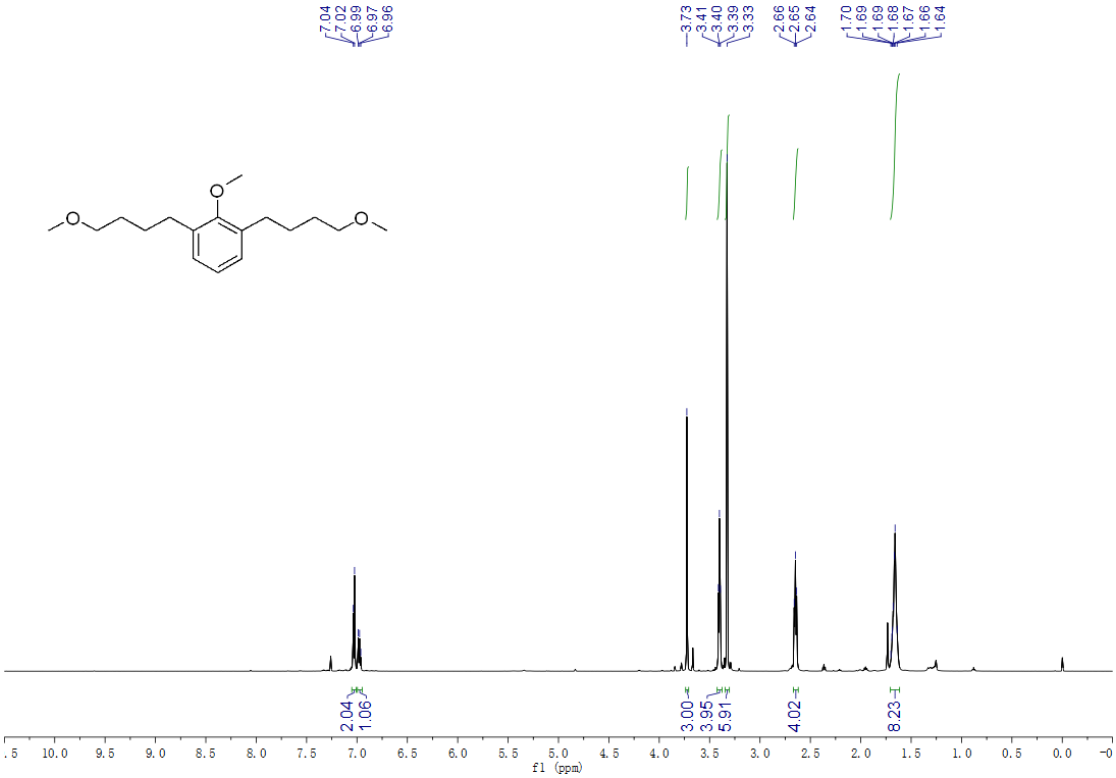


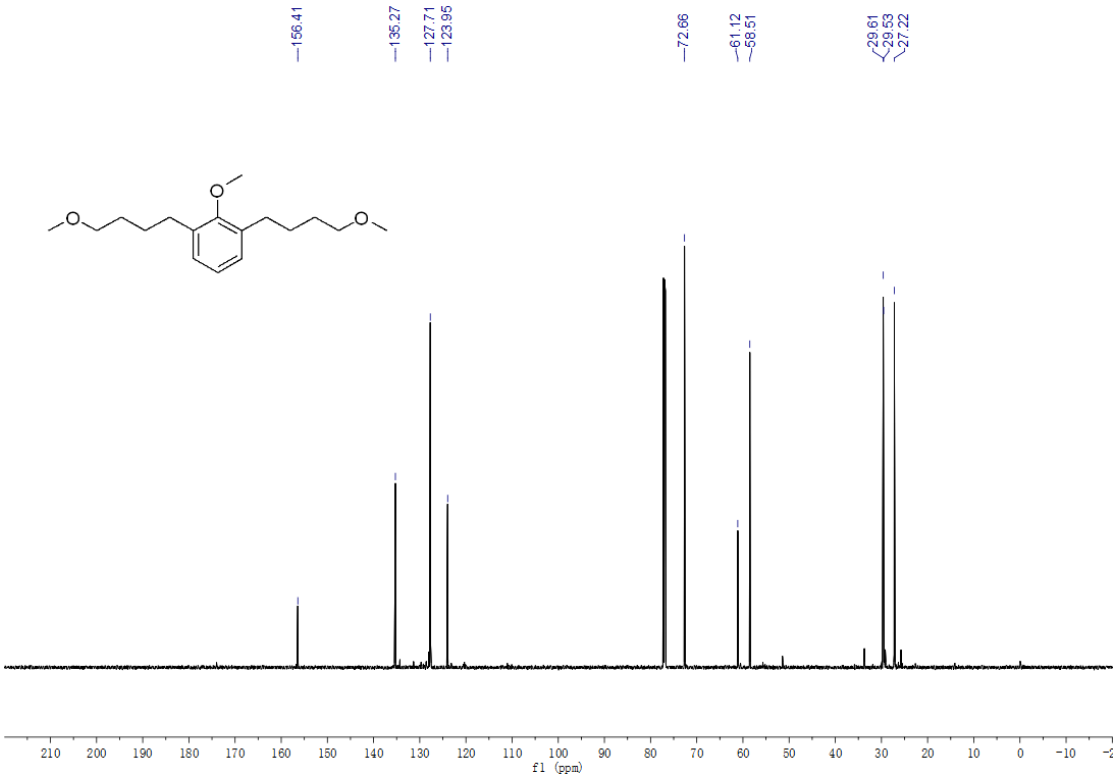
(2-methoxy-1,3-phenylene)bis(butane-4,1-diyl) diacetate (3af):



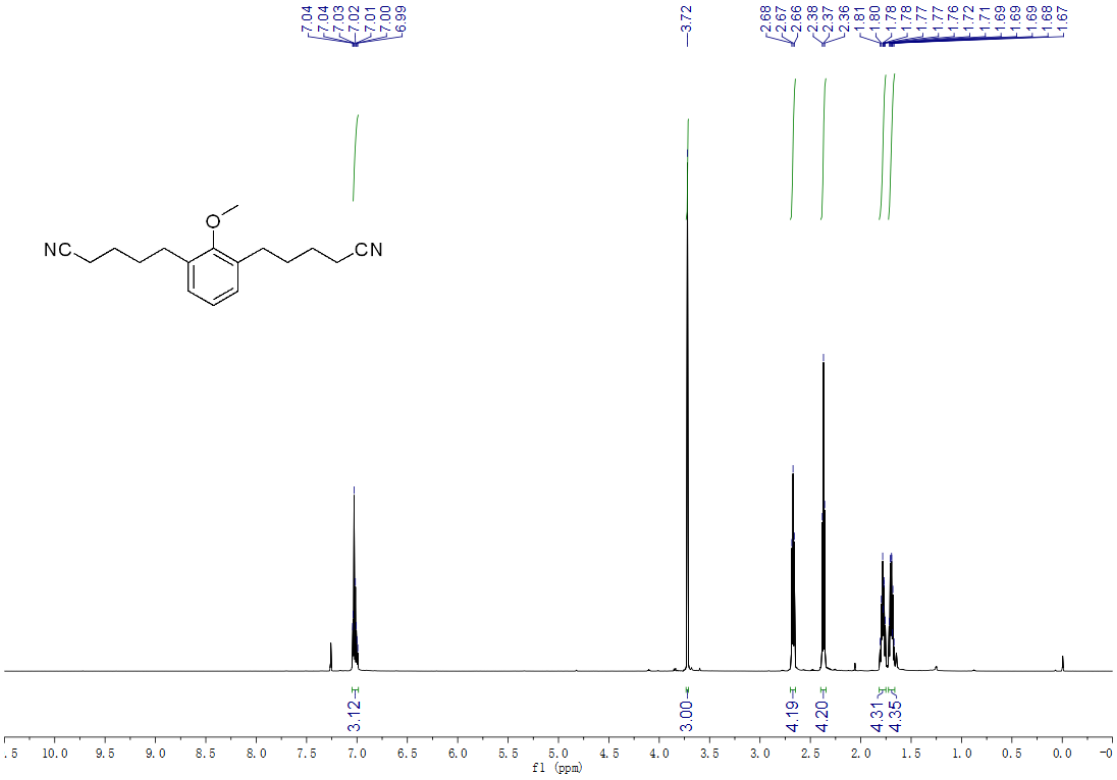


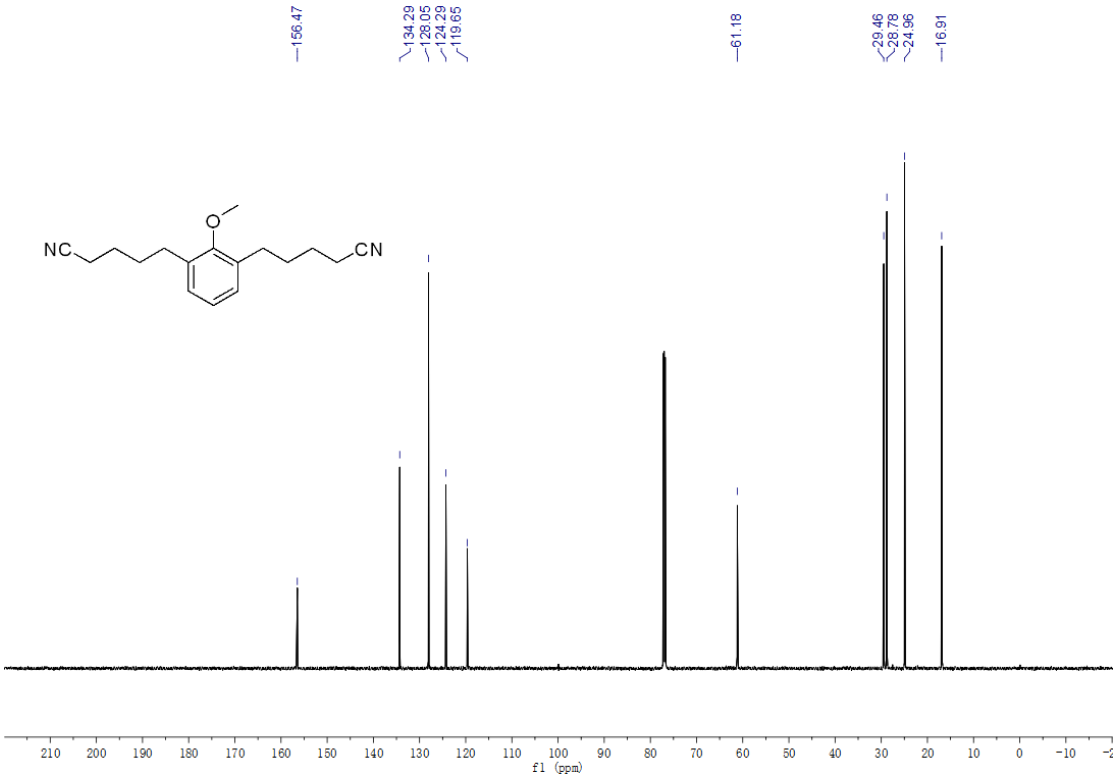
2-Methoxy-1,3-bis(4-methoxybutyl)benzene (3ag):



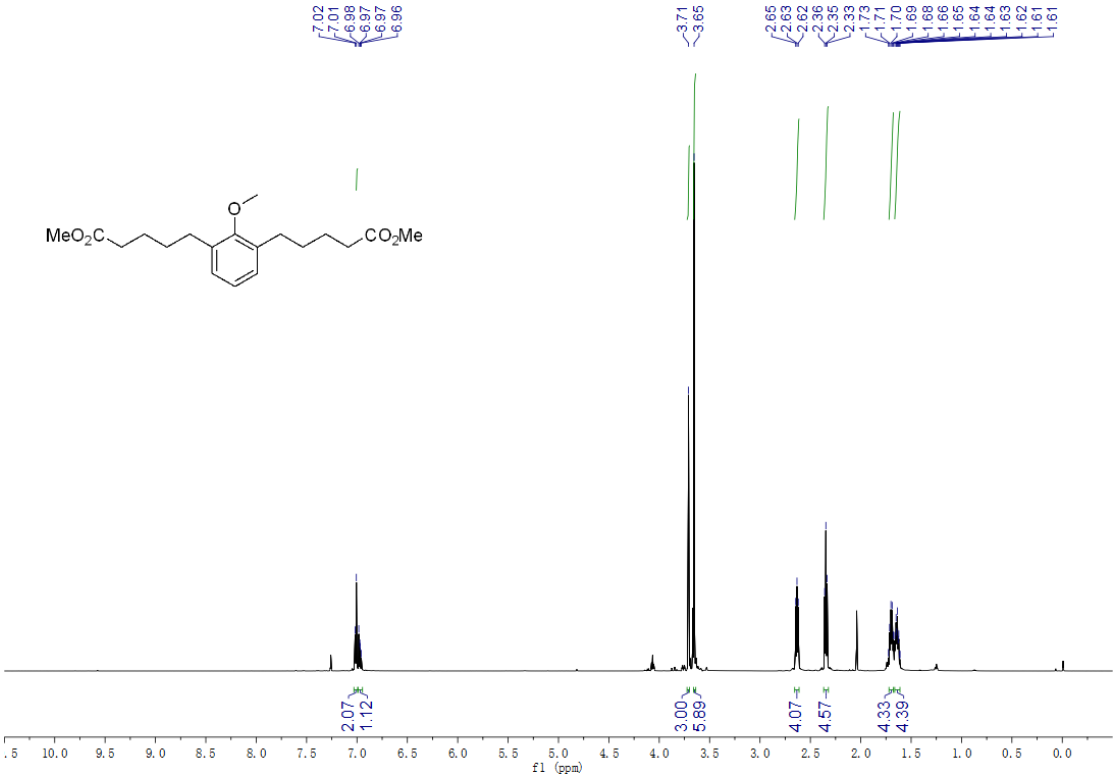


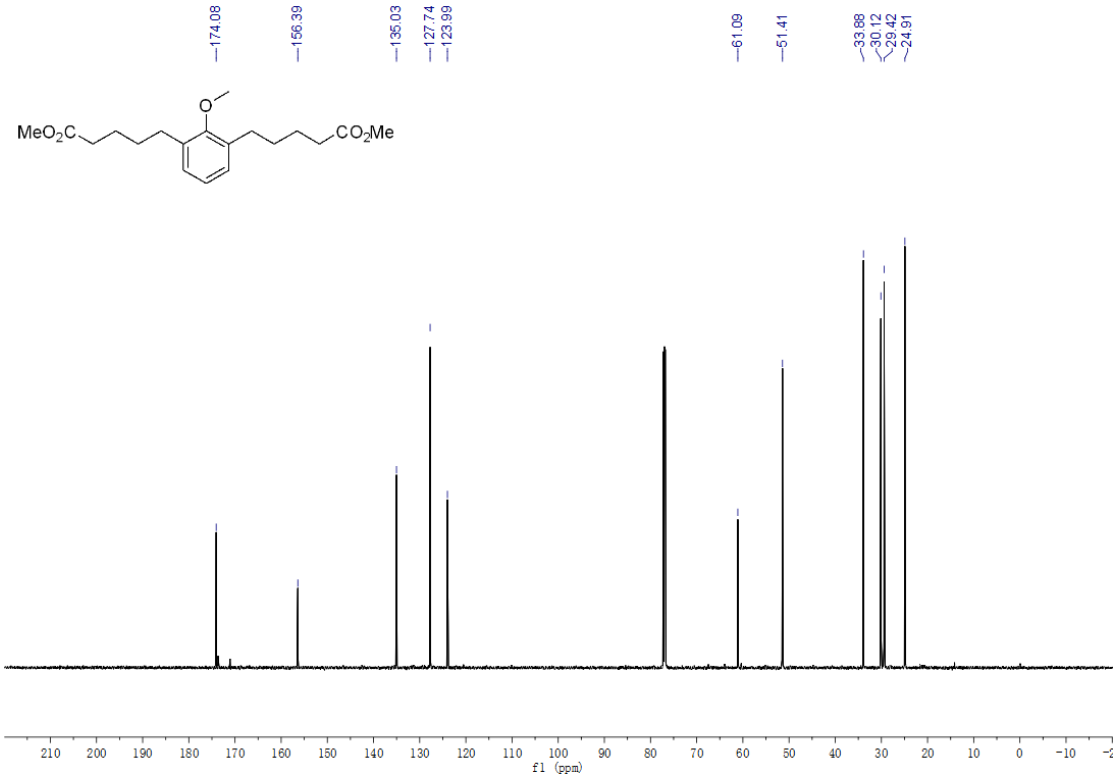
5,5'-(2-methoxy-1,3-phenylene)dipentanenitrile (3ah):



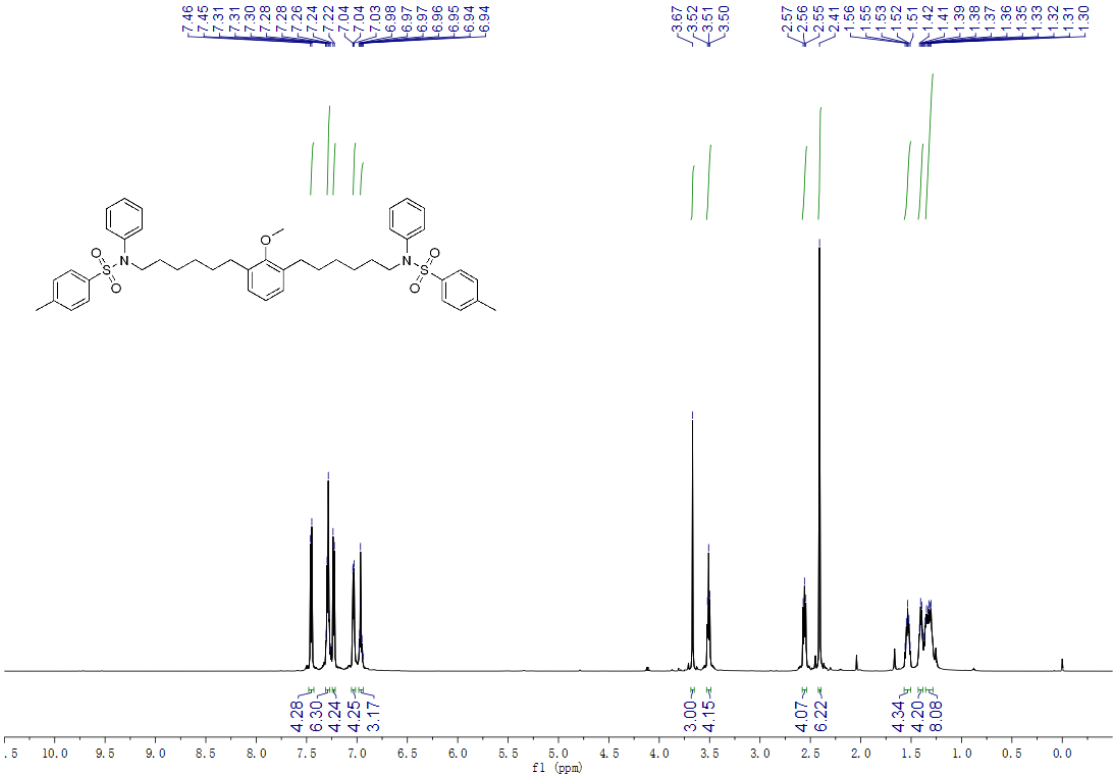


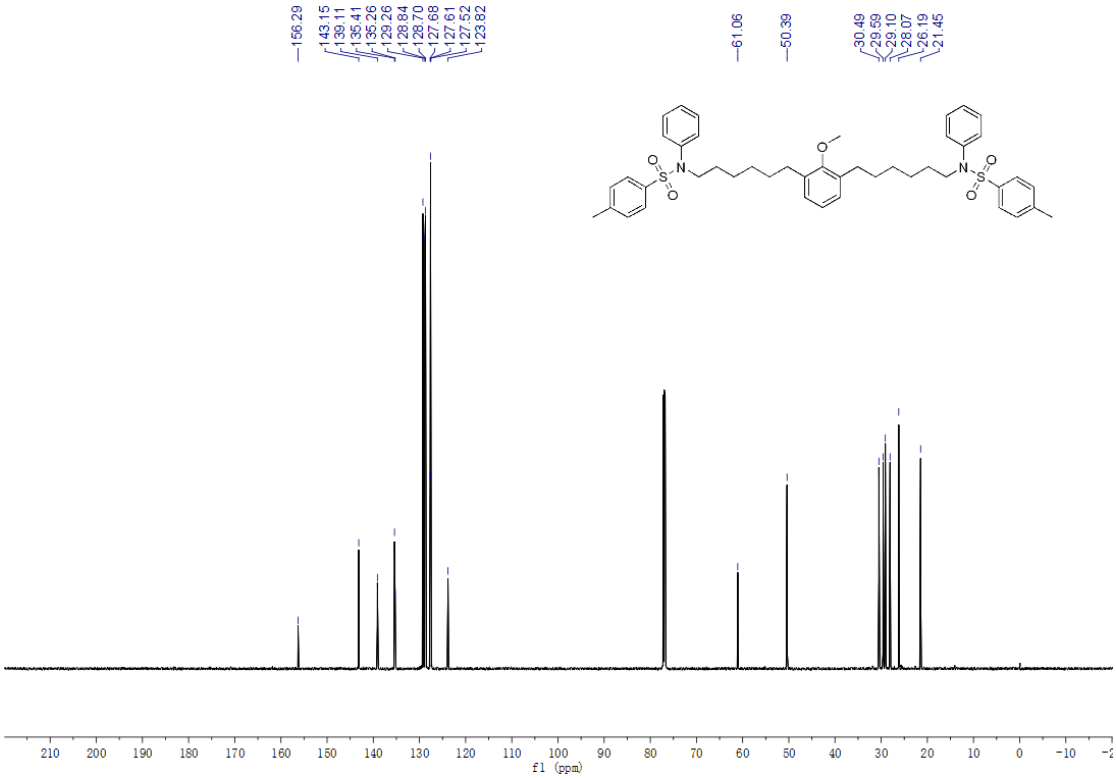
Dimethyl 5,5'-(2-methoxy-1,3-phenylene)dipentanoate (3ai):





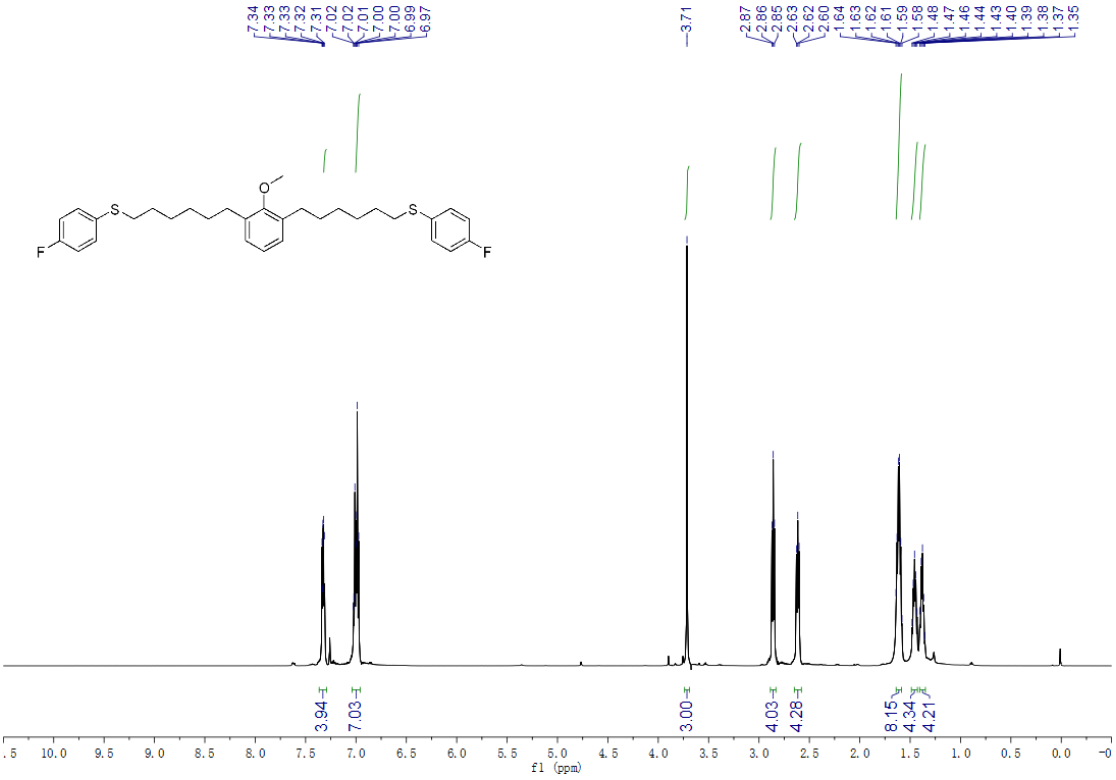
***N,N'*-((2-methoxy-1,3-phenylene)bis(hexane-6,1-diyl))bis(4-methyl-*N*-phenylbenzenesulfonamide) (3aj):**



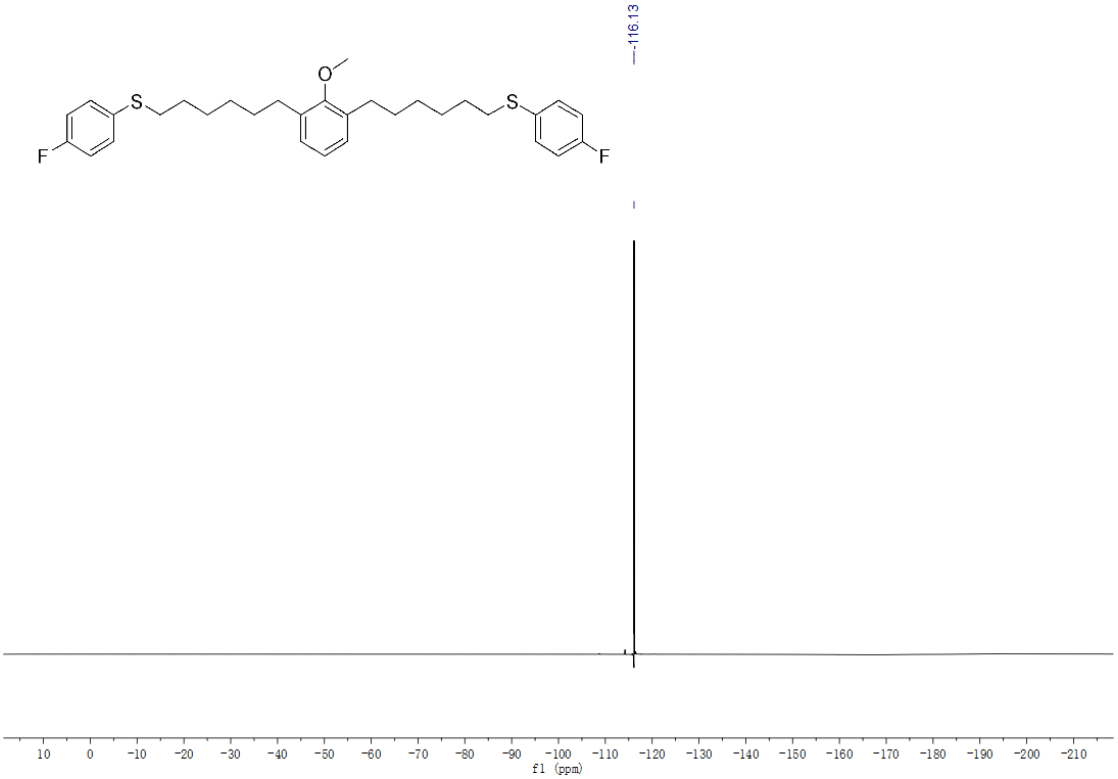


((2-Methoxy-1,3-phenylene)bis(hexane-6,1-diyl))bis((4-fluorophenyl)sulfane) (3ak):

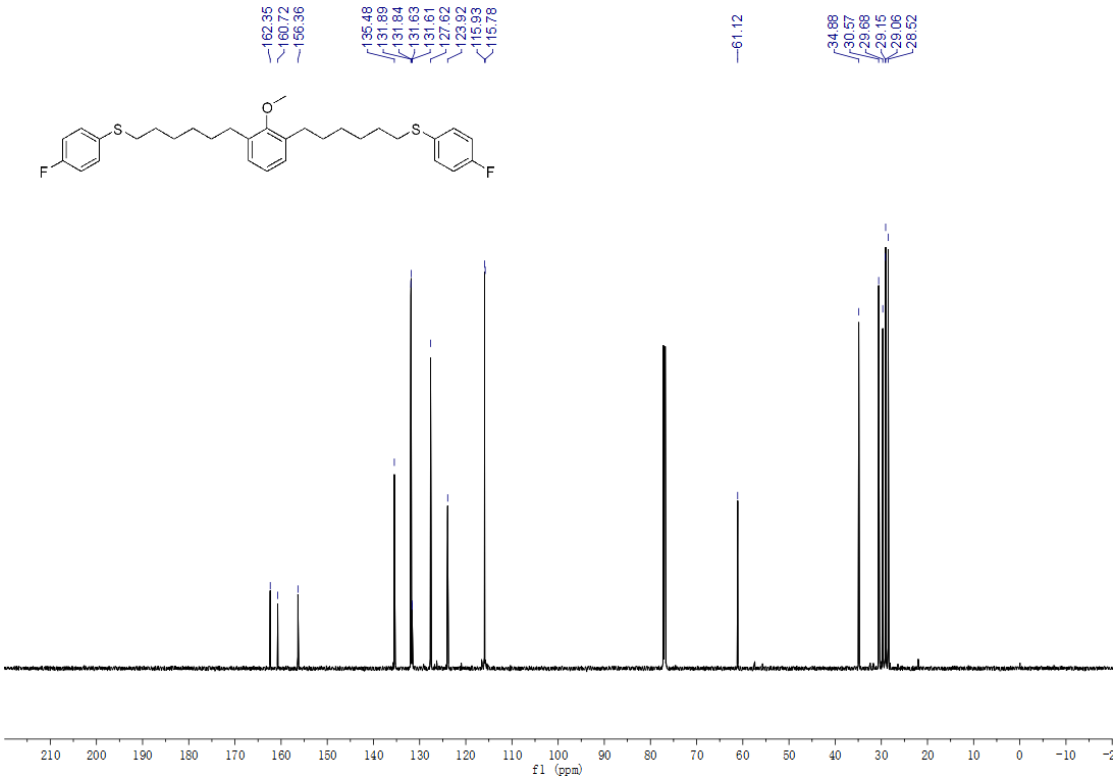
^{1}H NMR



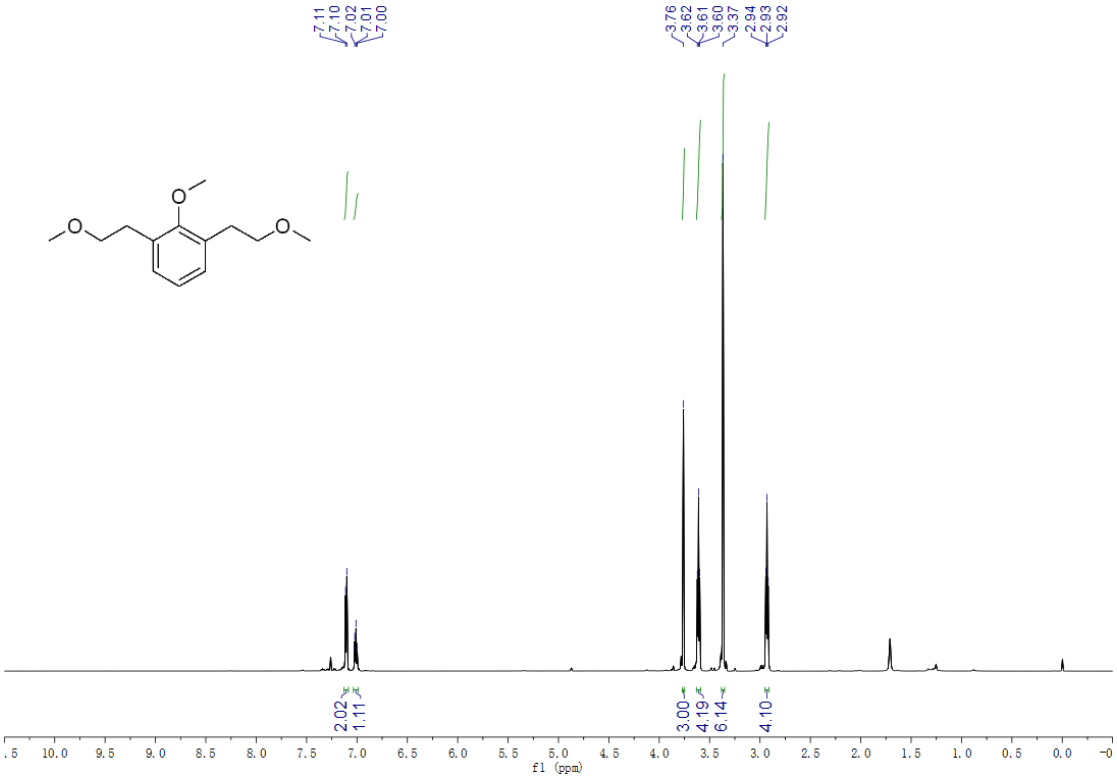
^{19}F NMR

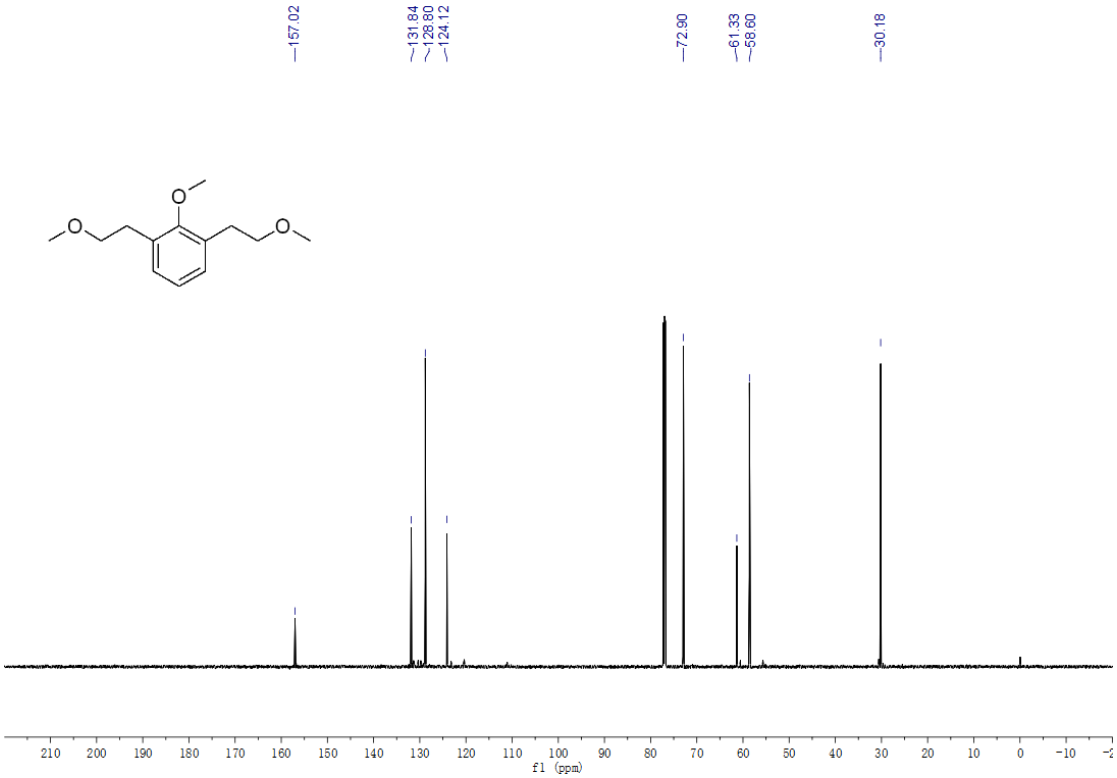


^{13}C NMR

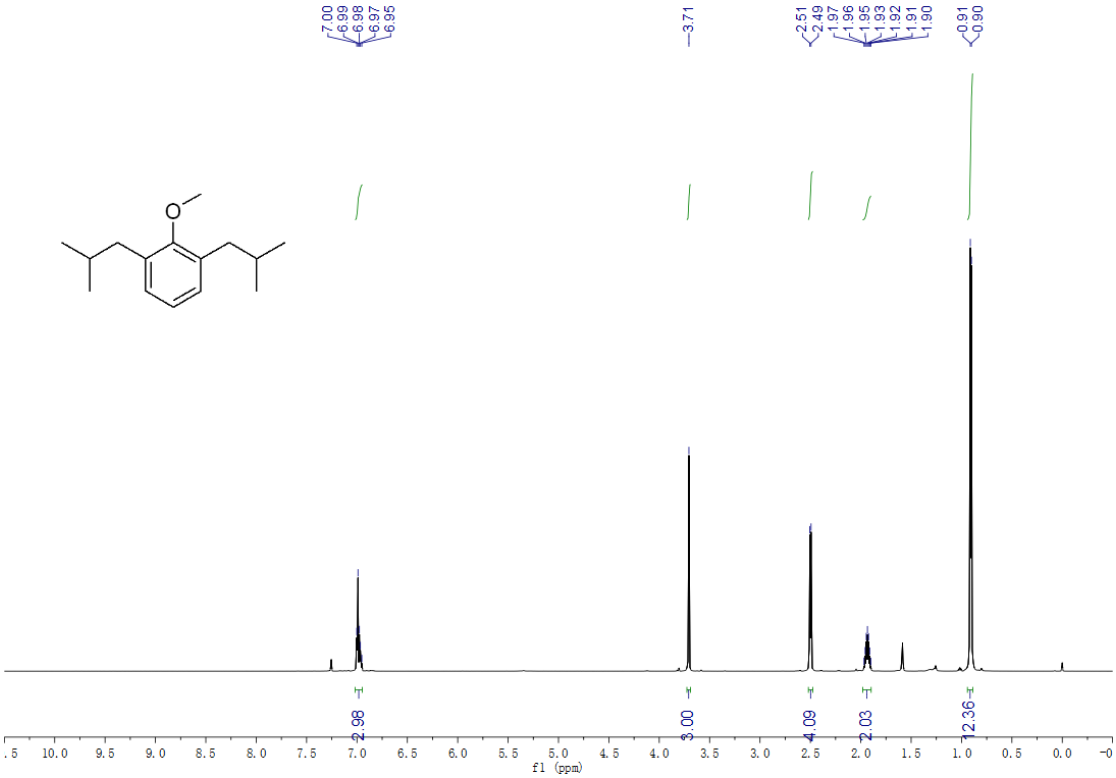

162.35
160.72
156.36
135.48
131.89
131.84
131.63
131.61
127.62
123.92
115.93
115.78
61.12
34.88
30.57
29.68
29.15
29.06
28.52
O
S
S
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

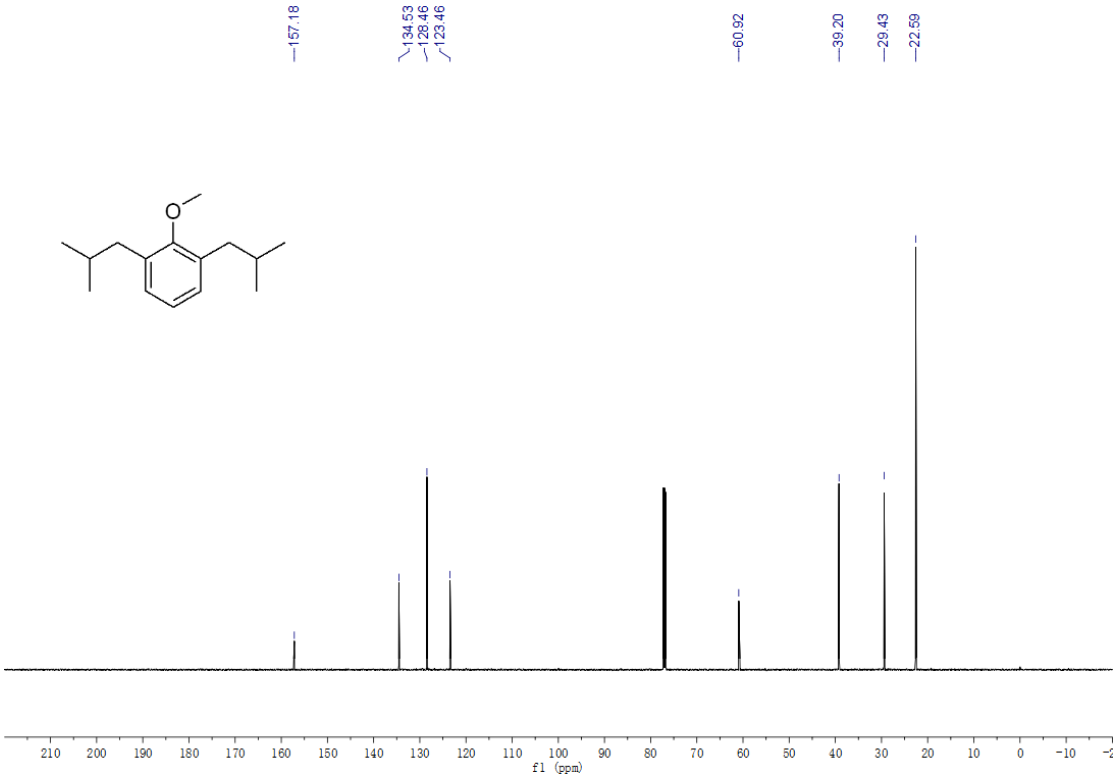
2-Methoxy-1,3-bis(2-methoxyethyl)benzene (3al):



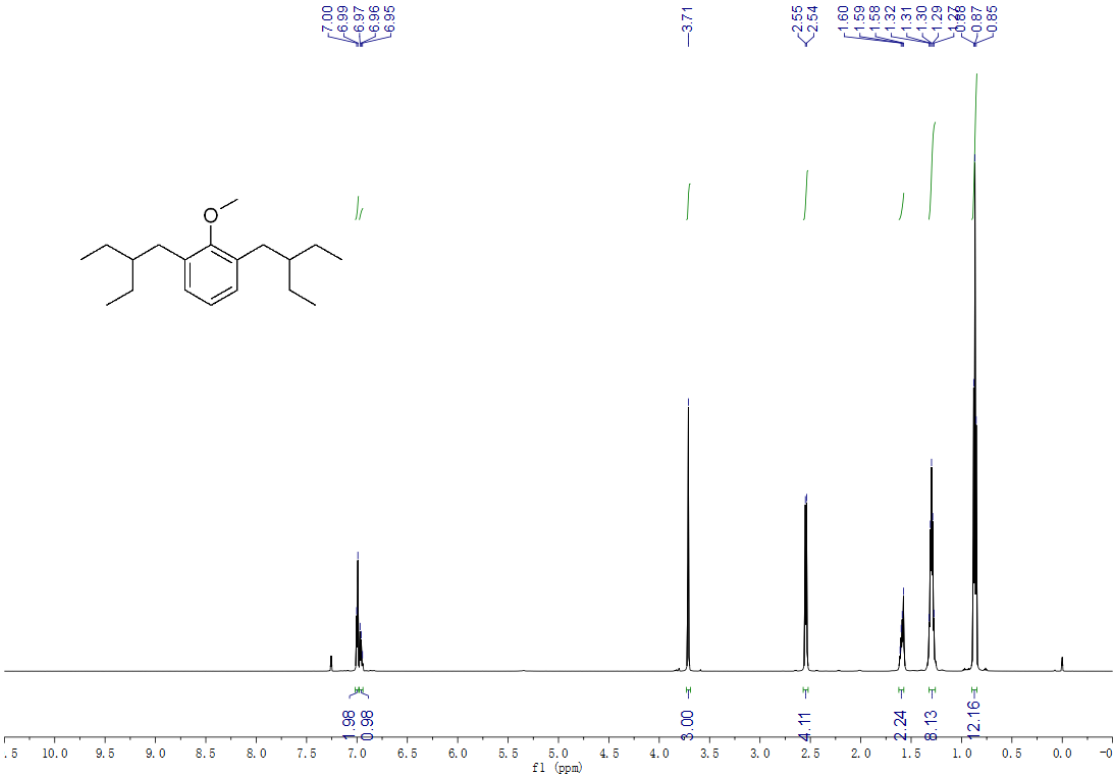


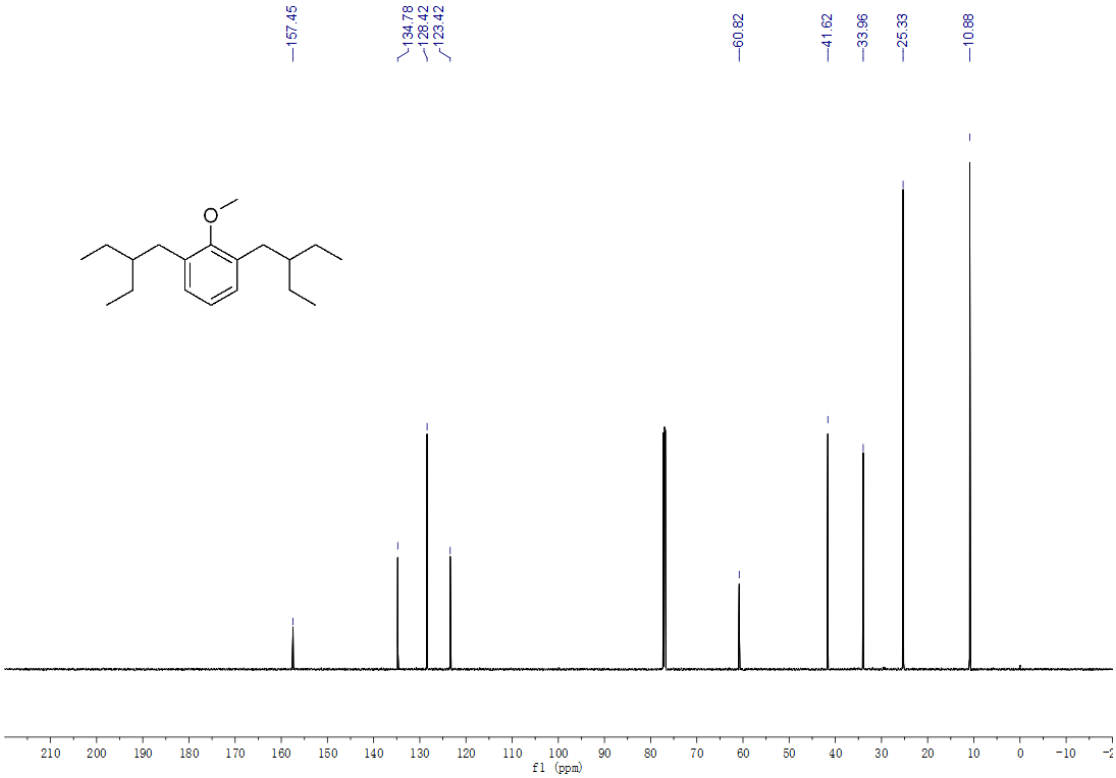
1,3-Diisobutyl-2-methoxybenzene (3am):



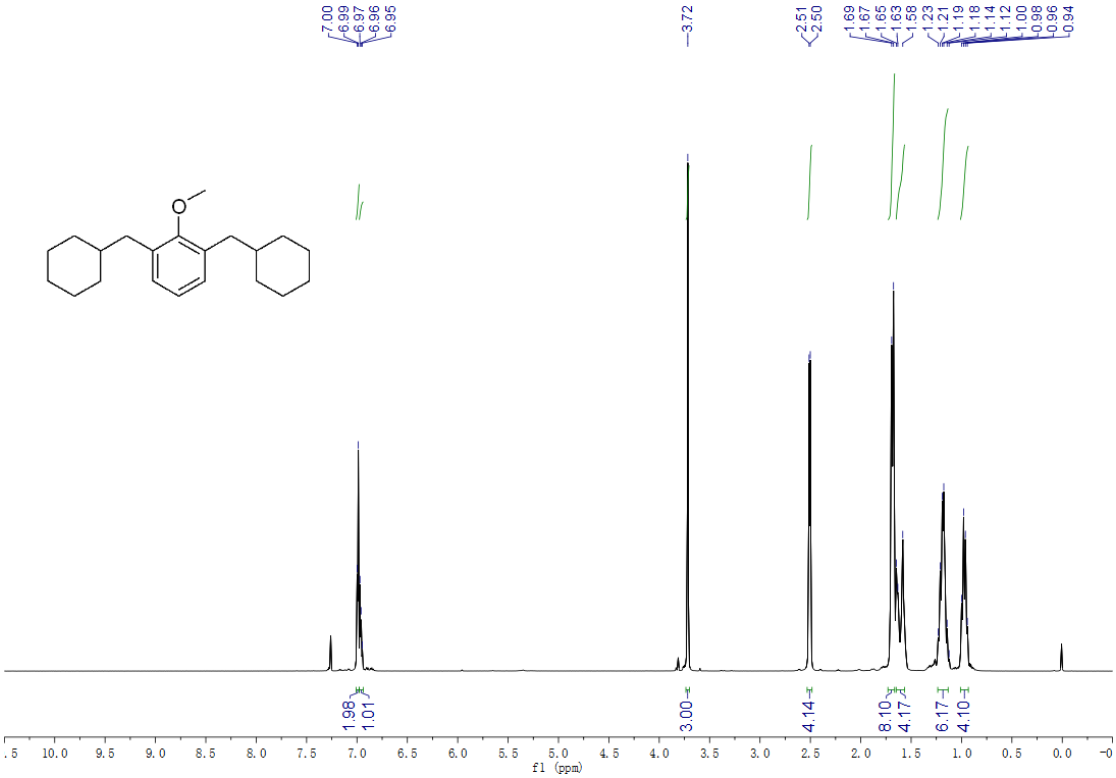


1,3-Bis(2-ethylbutyl)-2-methoxybenzene (3an):

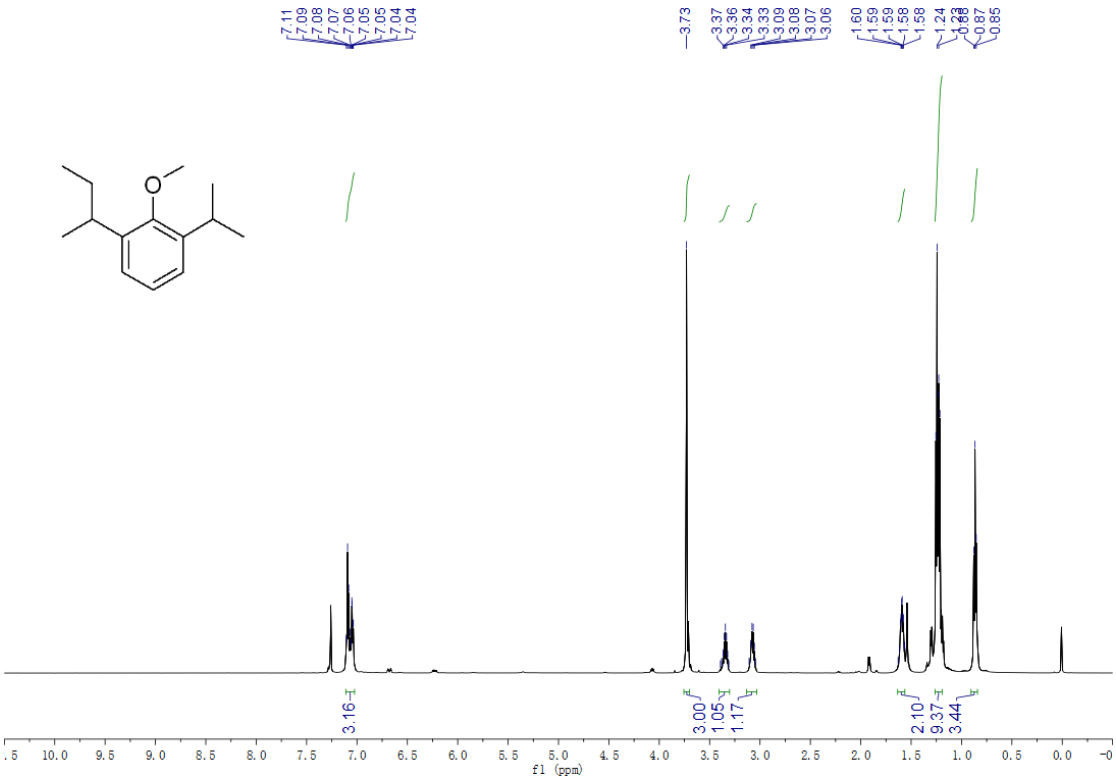


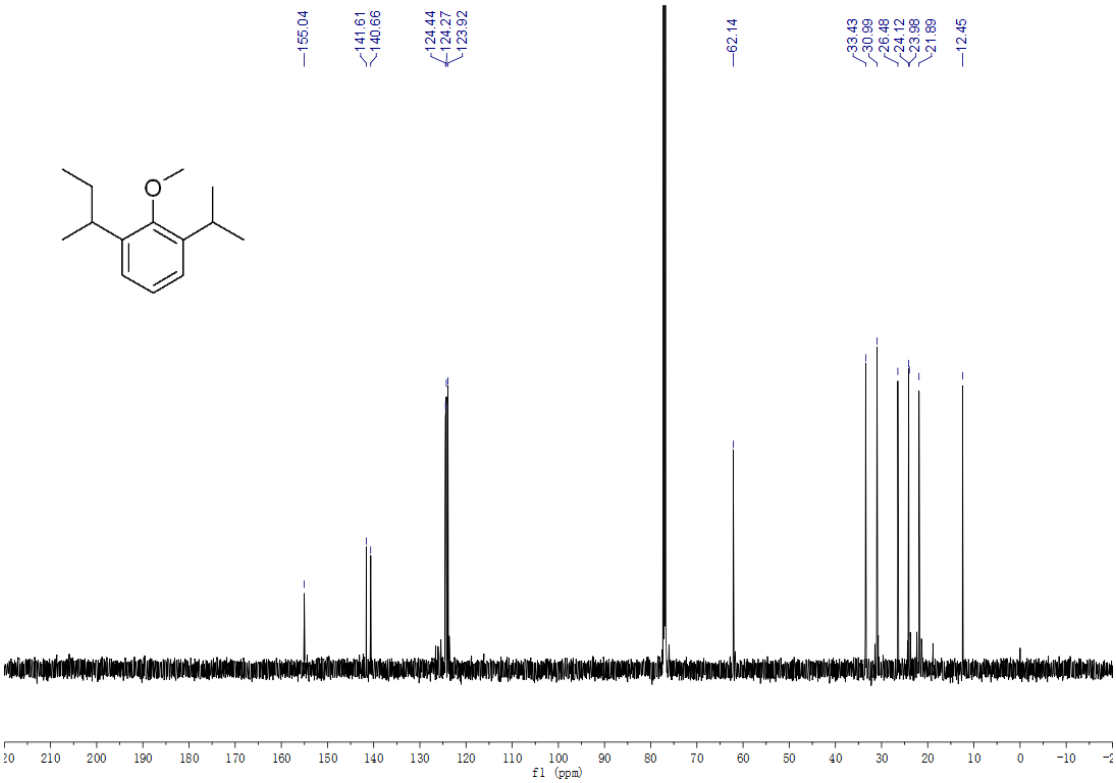


((2-Methoxy-1,3-phenylene)bis(methylene))dicyclohexane (3ao):

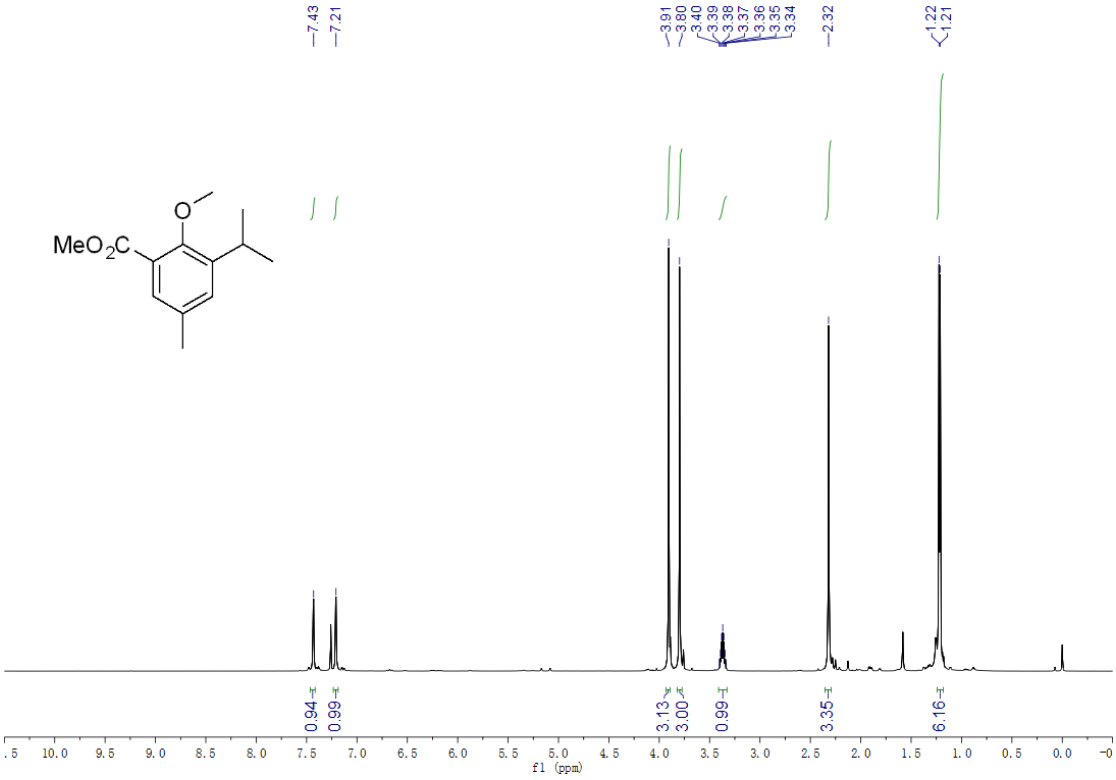


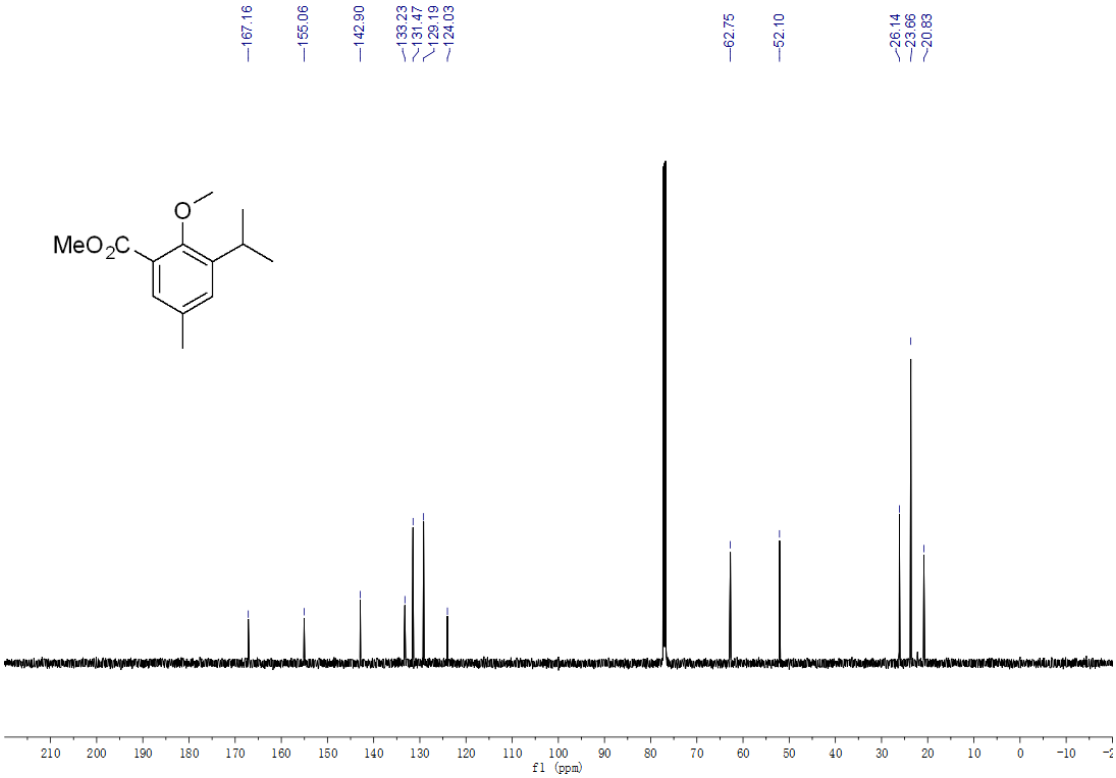
1-(*sec*-Butyl)-3-isopropyl-2-methoxybenzene (5bp):



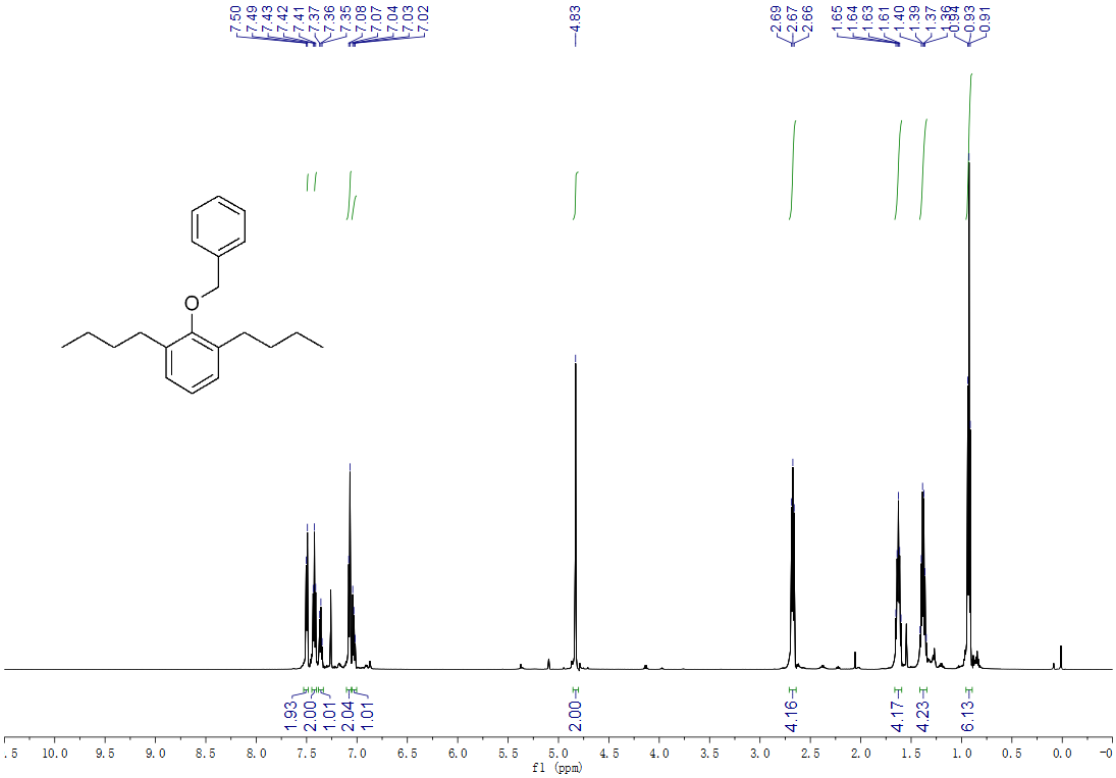


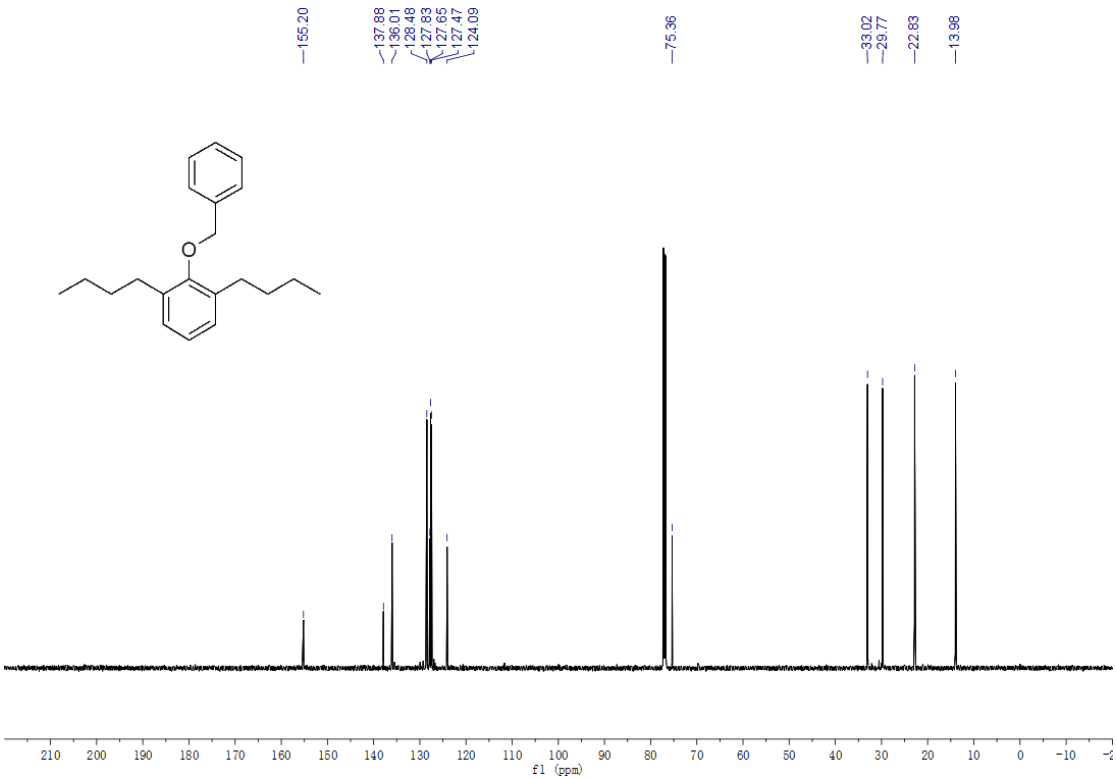
Methyl 3-isopropyl-2-methoxy-5-methylbenzoate (5fp):





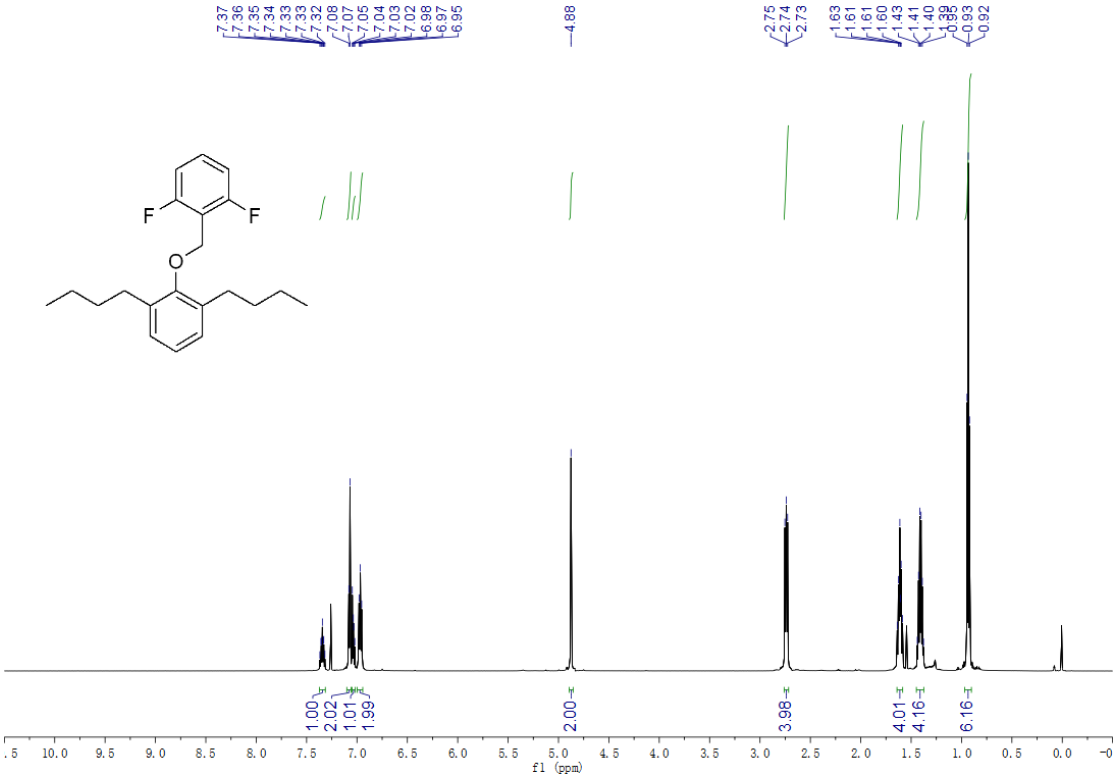
2-(Benzyloxy)-1,3-dibutylbenzene (7aa):





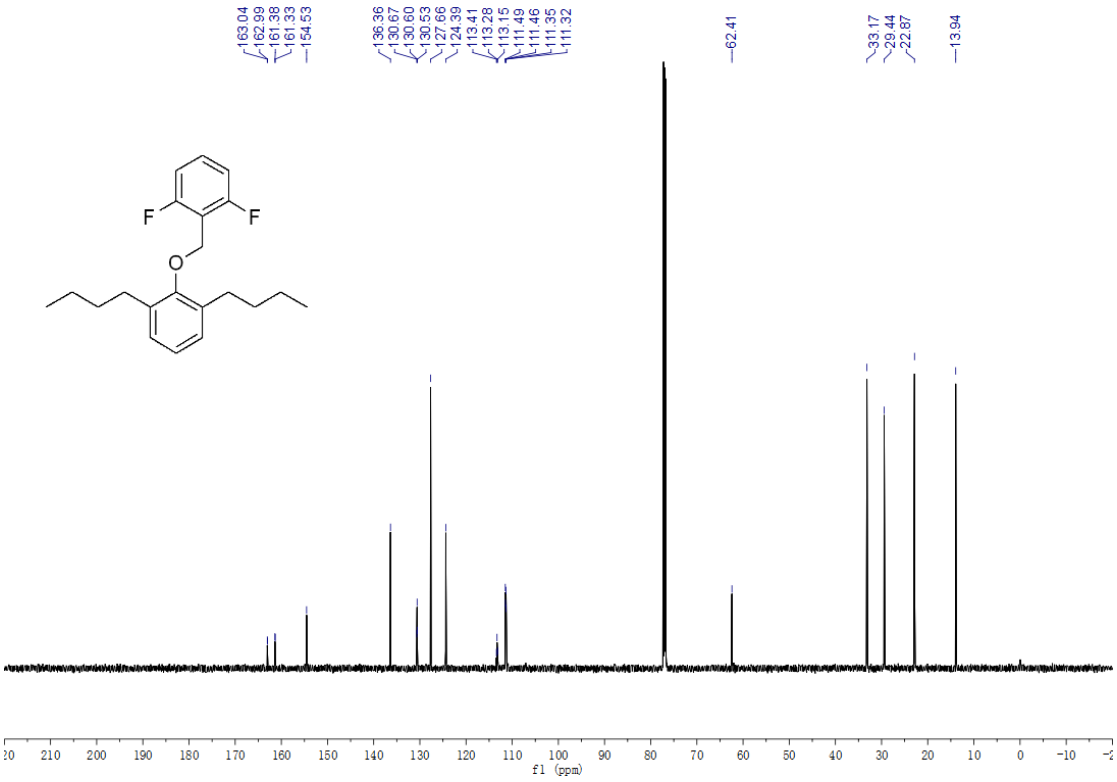
1,3-Dibutyl-2-((2,6-difluorobenzyl)oxy)benzene (7ba):

^{1}H NMR

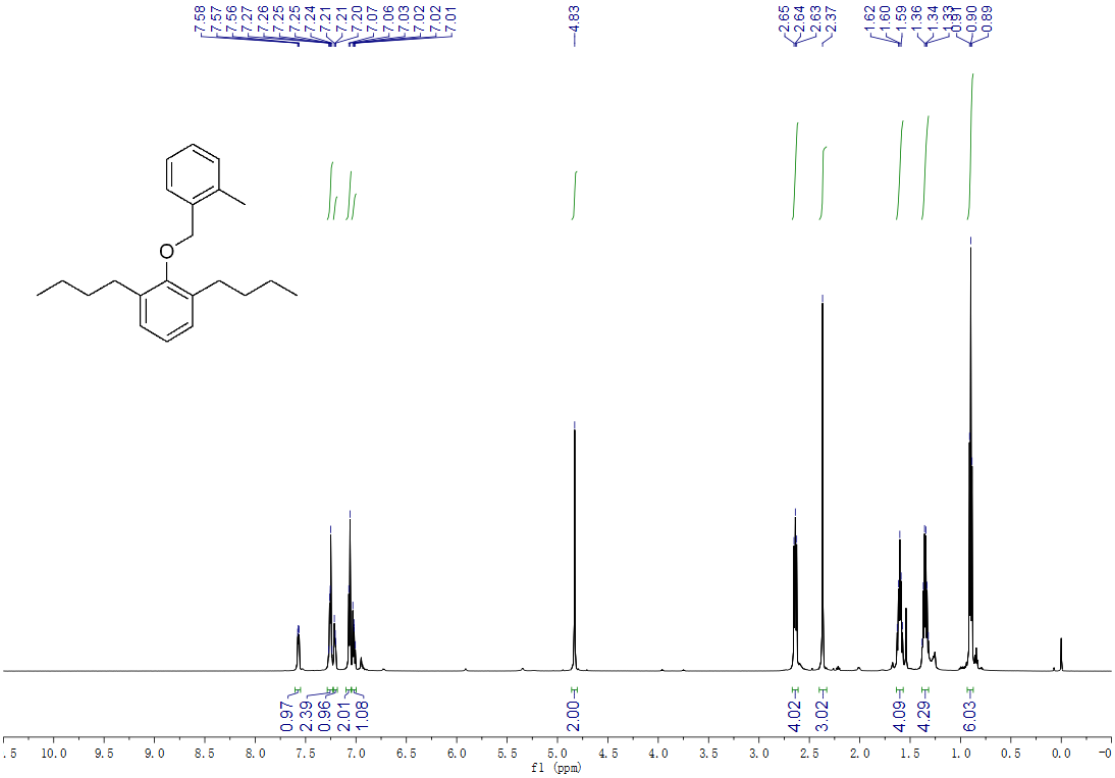


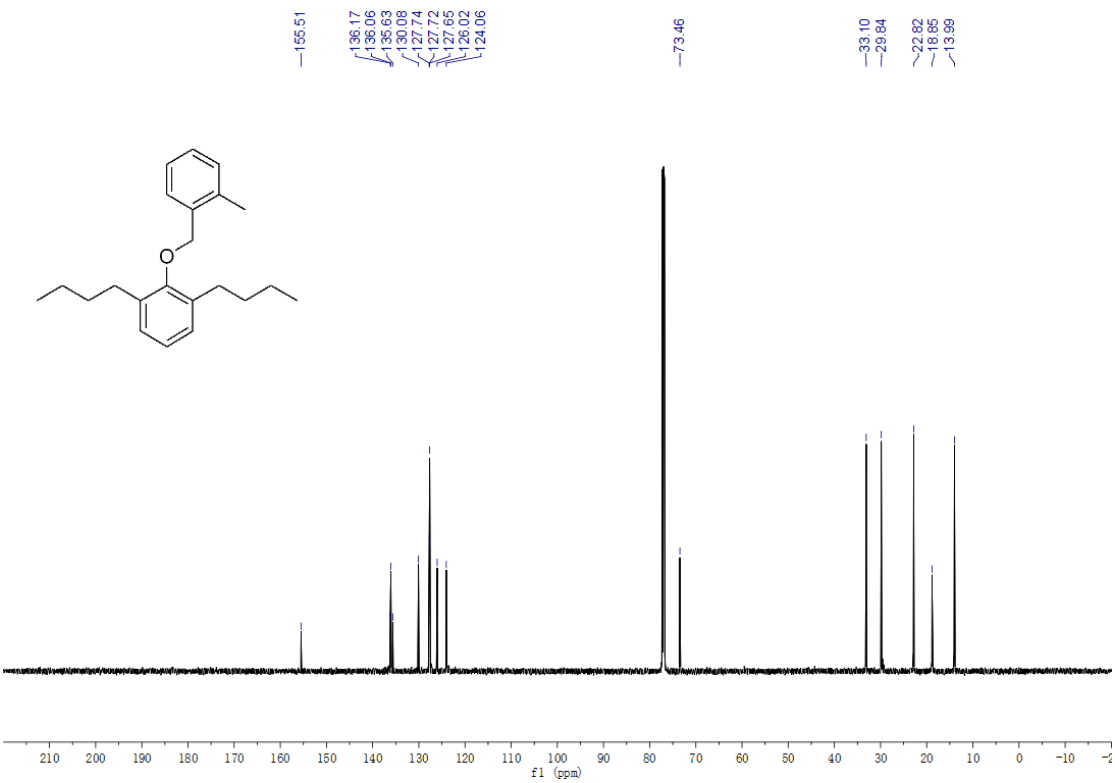
^{19}F NMR

^{13}C NMR

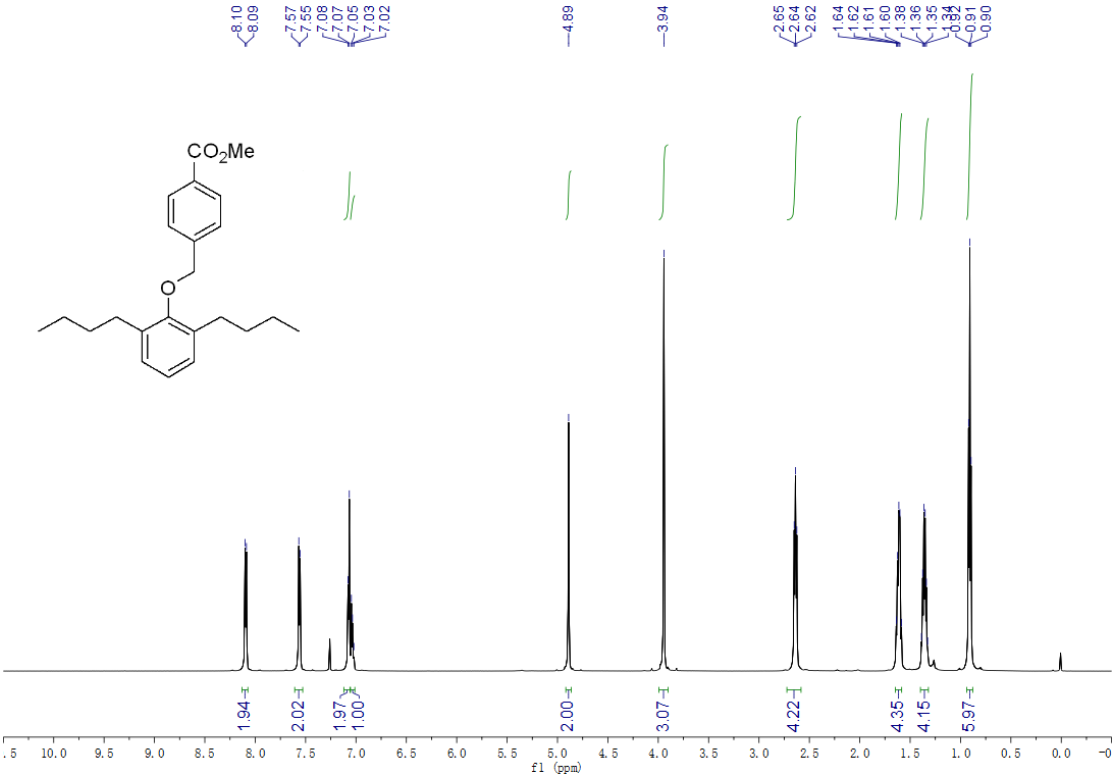

163.04
162.99
161.38
161.33
154.53
136.36
130.67
130.60
130.53
127.66
124.39
113.41
113.28
113.15
111.49
111.46
111.35
111.32
62.41
33.17
29.44
22.87
13.94
F
F
O
f1 (ppm)

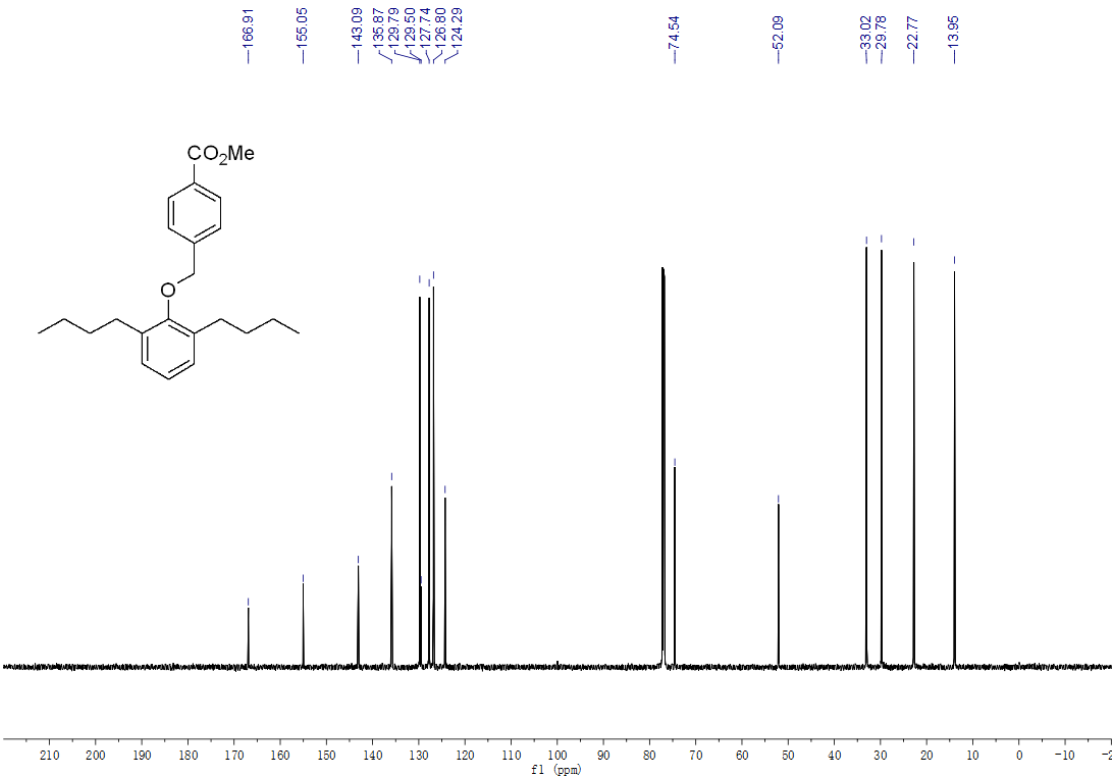
1,3-Dibutyl-2-((2-methylbenzyl)oxy)benzene (7ca):



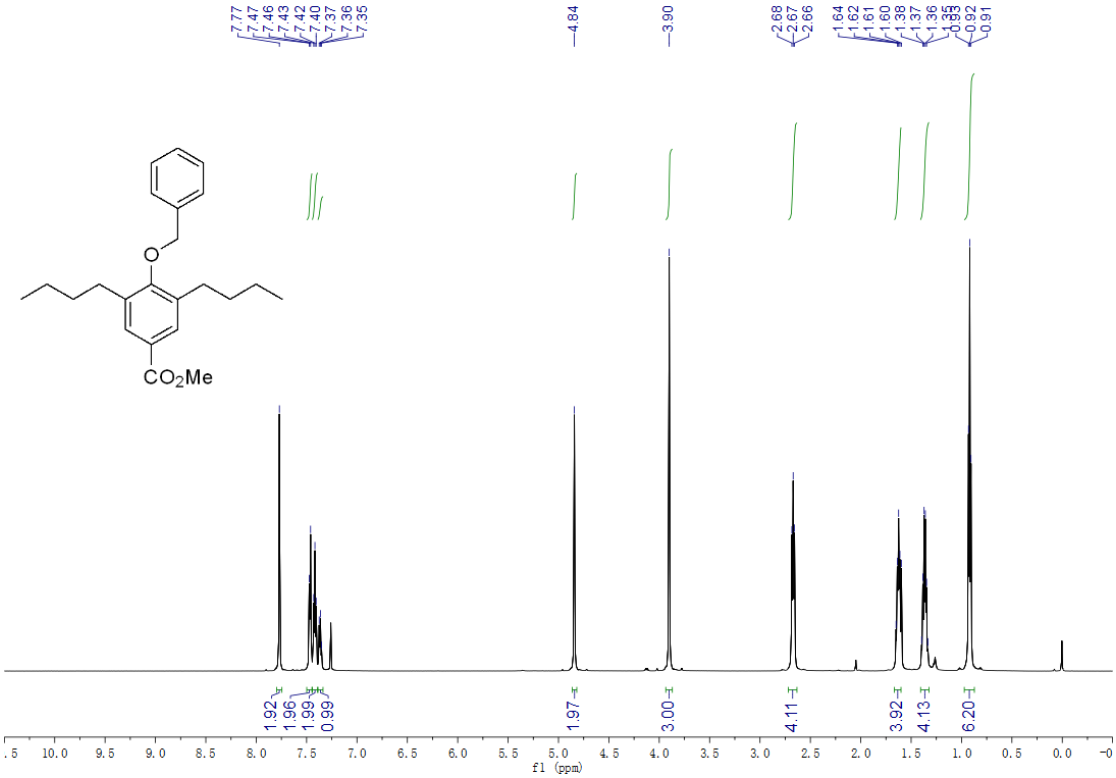


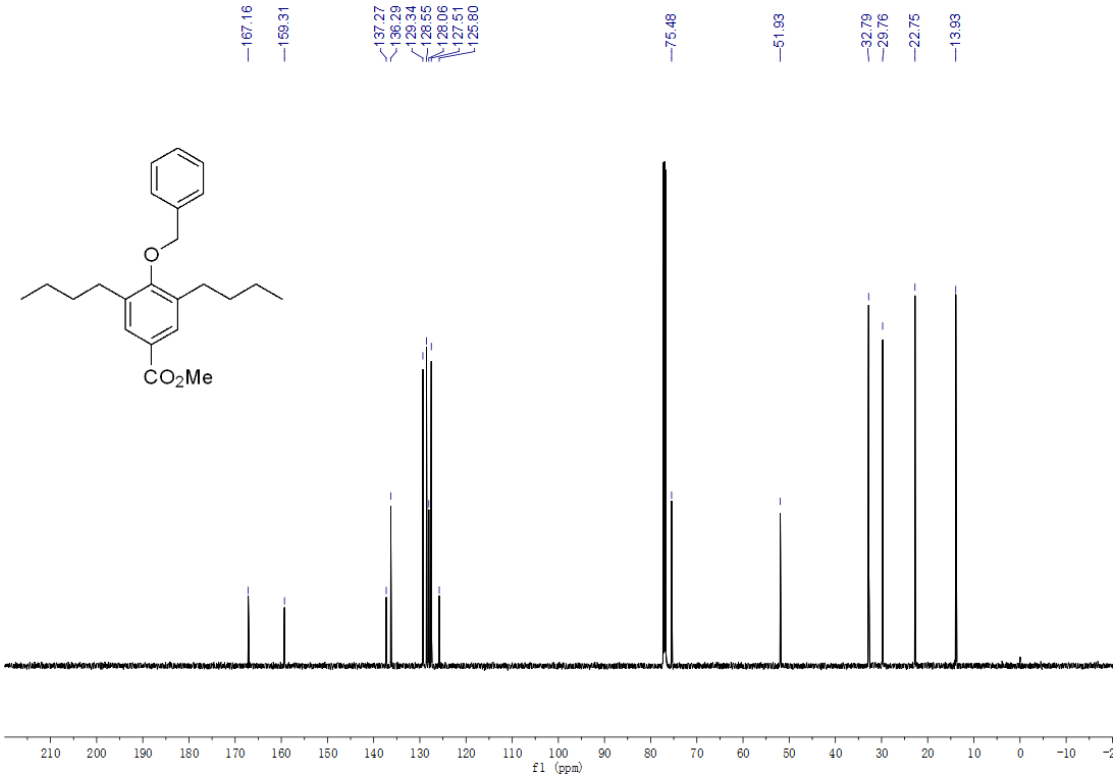
Methyl 4-((2,6-dibutylphenoxy)methyl)benzoate (7da):



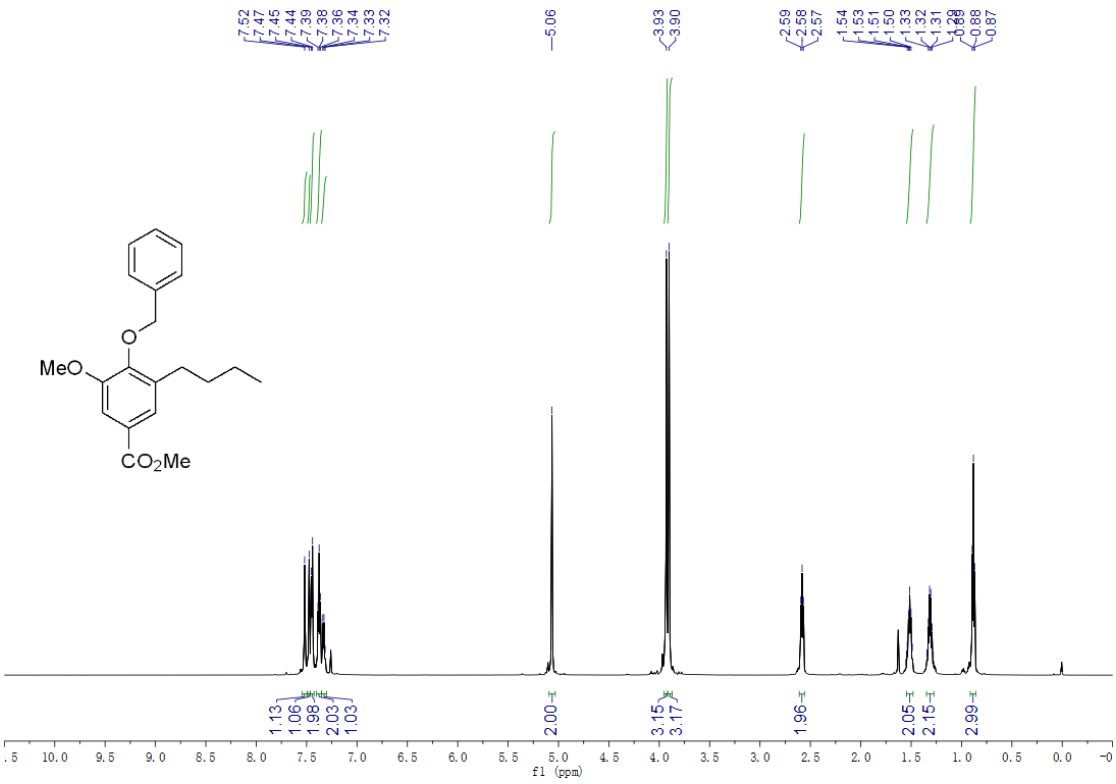


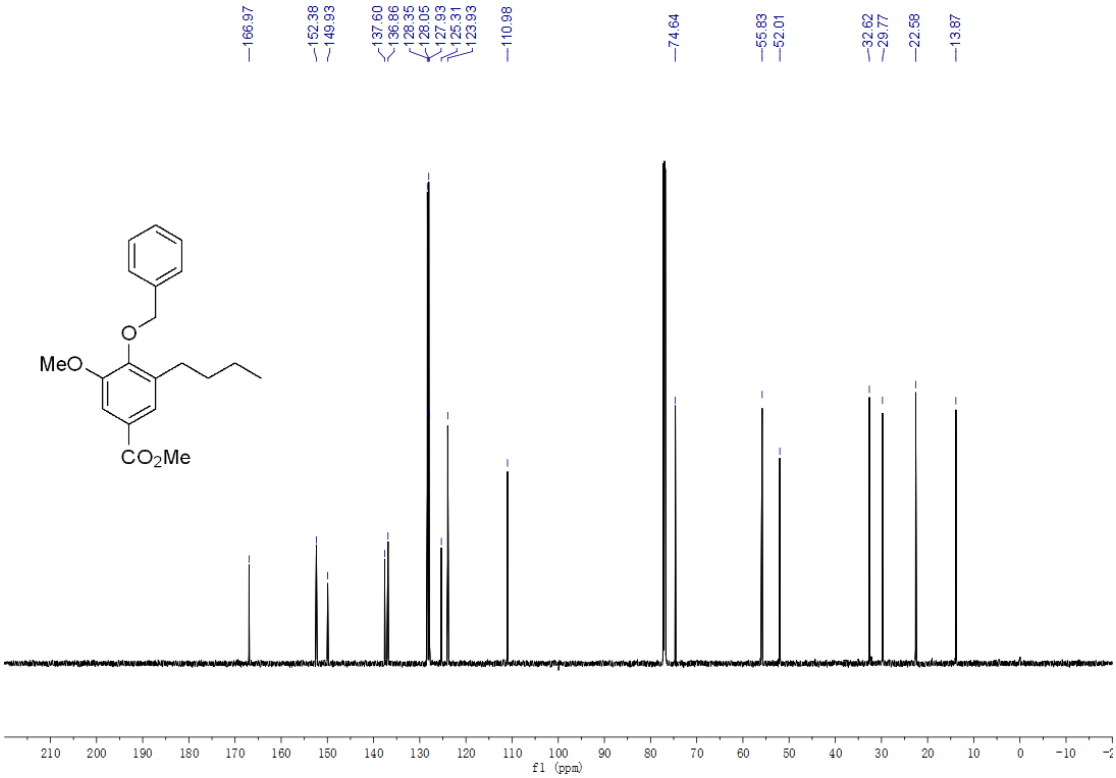
Methyl 4-(benzyloxy)-3,5-dibutylbenzoate (7ea):



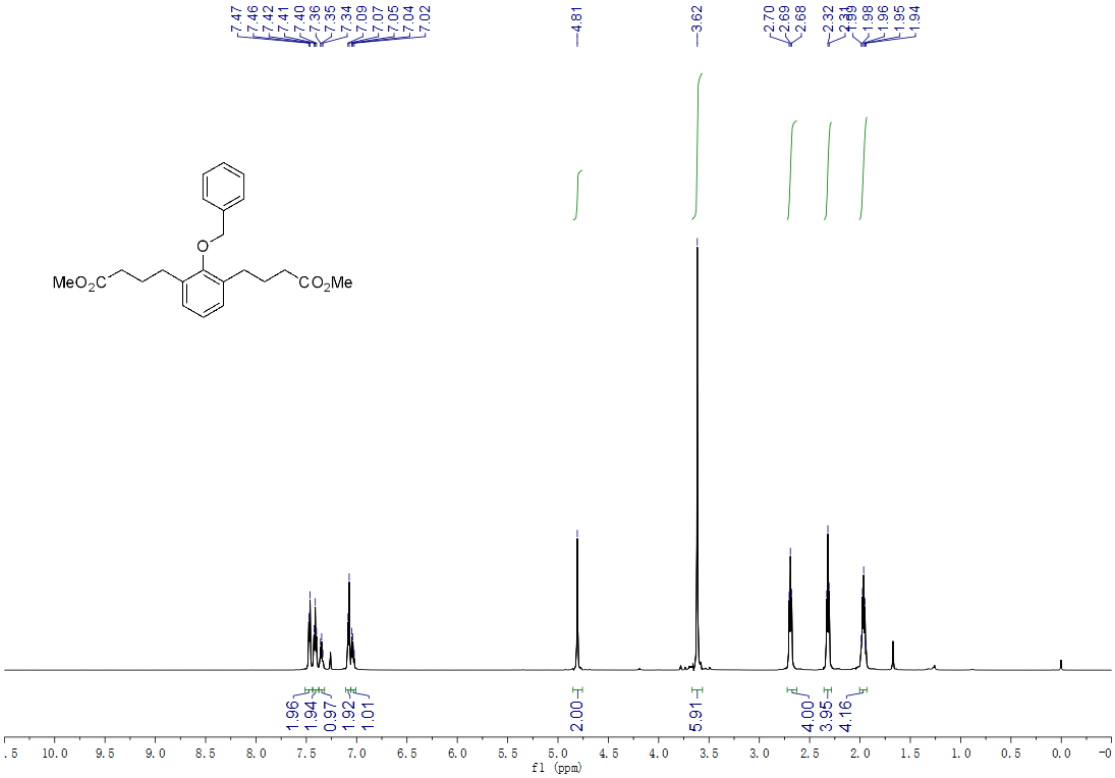


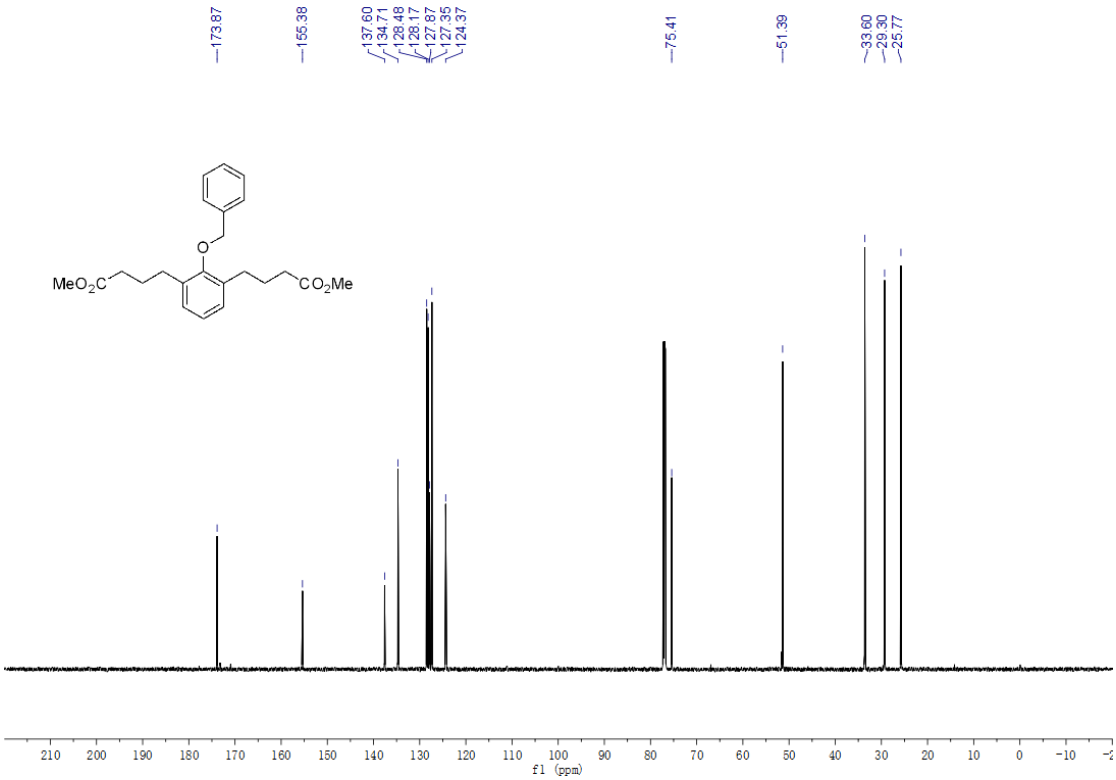
Methyl 4-(benzyloxy)-3-butyl-5-methoxybenzoate (7fa):



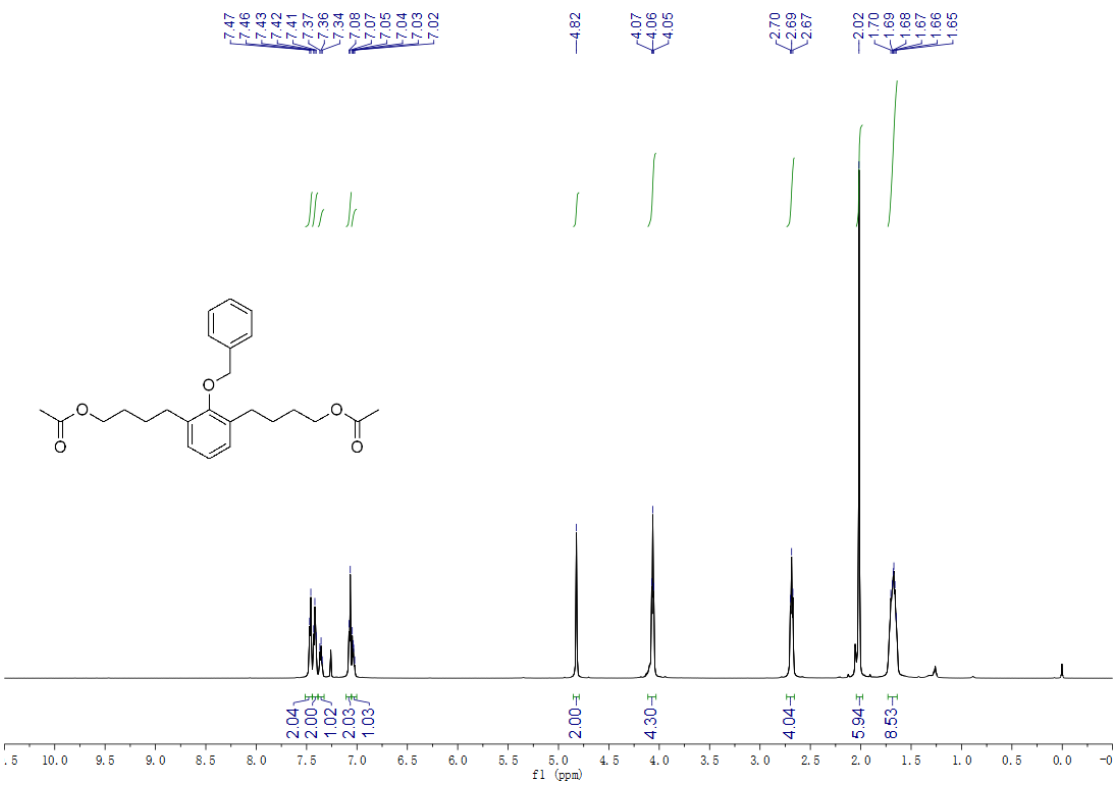


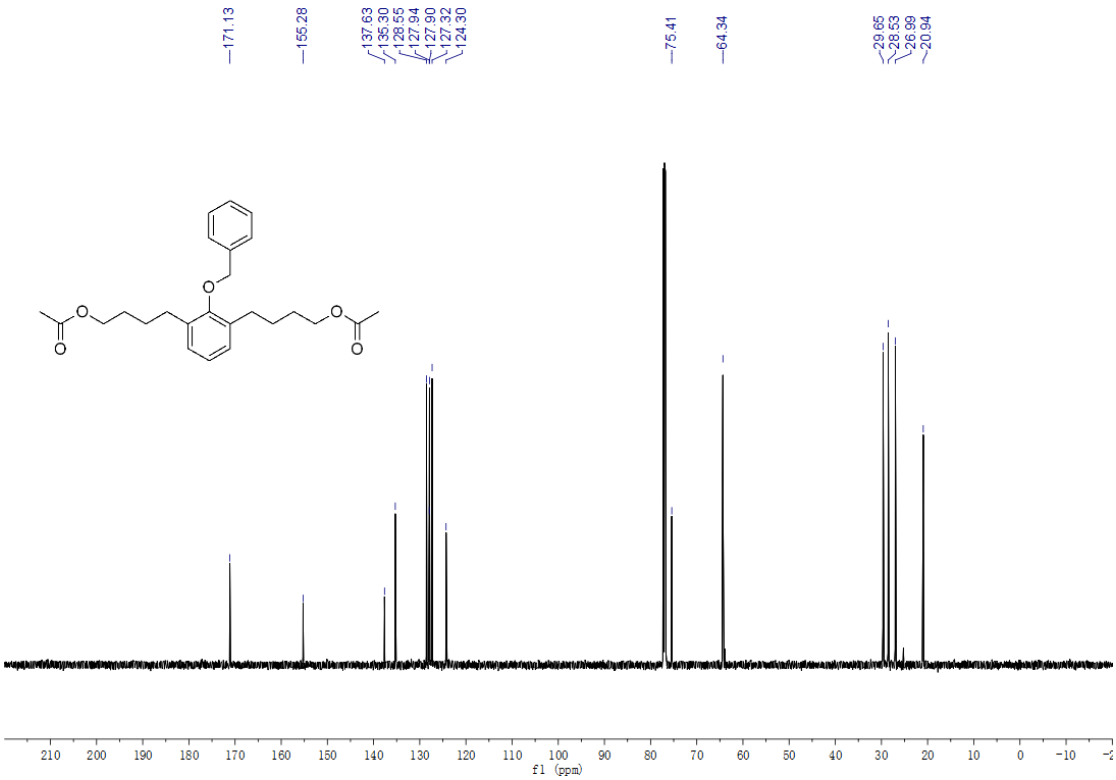
Dimethyl 4,4'-(2-(benzyloxy)-1,3-phenylene)dibutyrate (7ad):



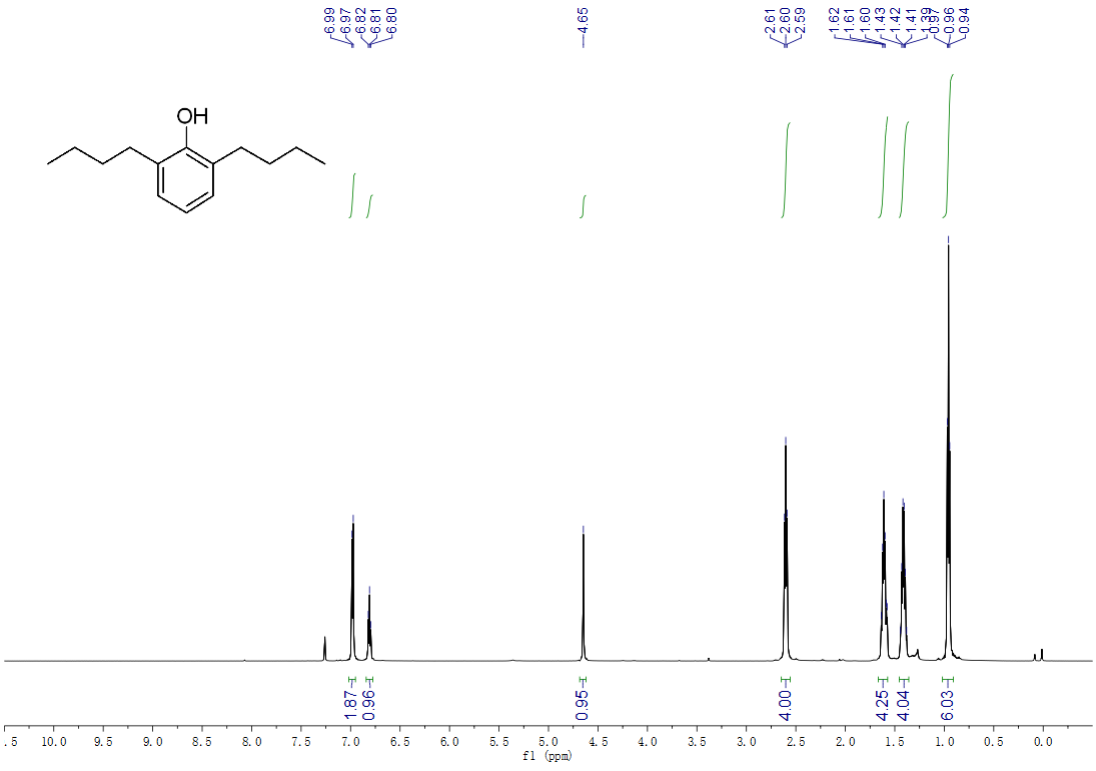


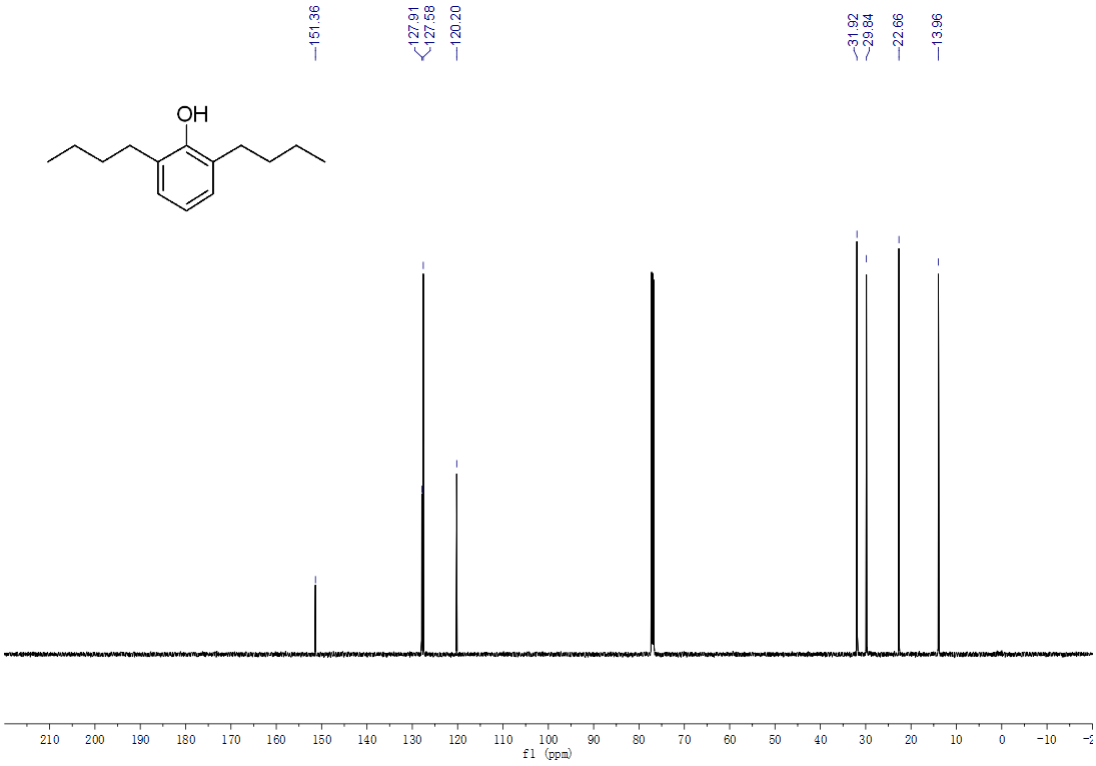
(2-(Benzyloxy)-1,3-phenylene)bis(butane-4,1-diyl) diacetate (7af):



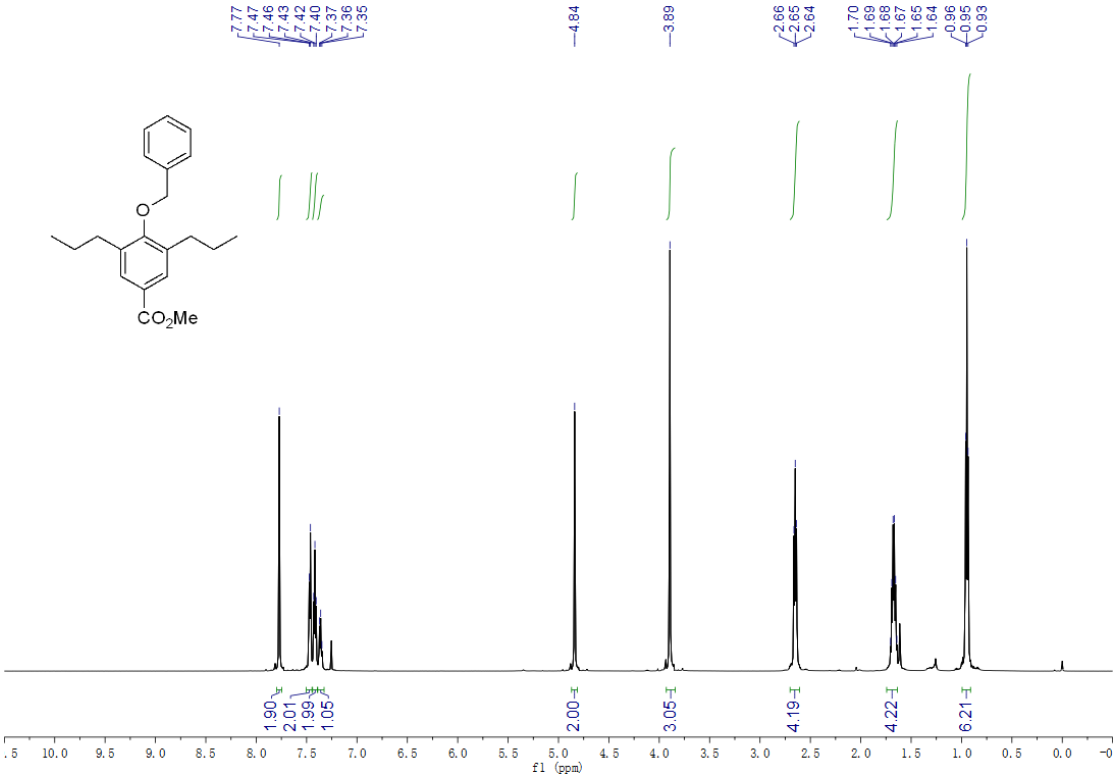


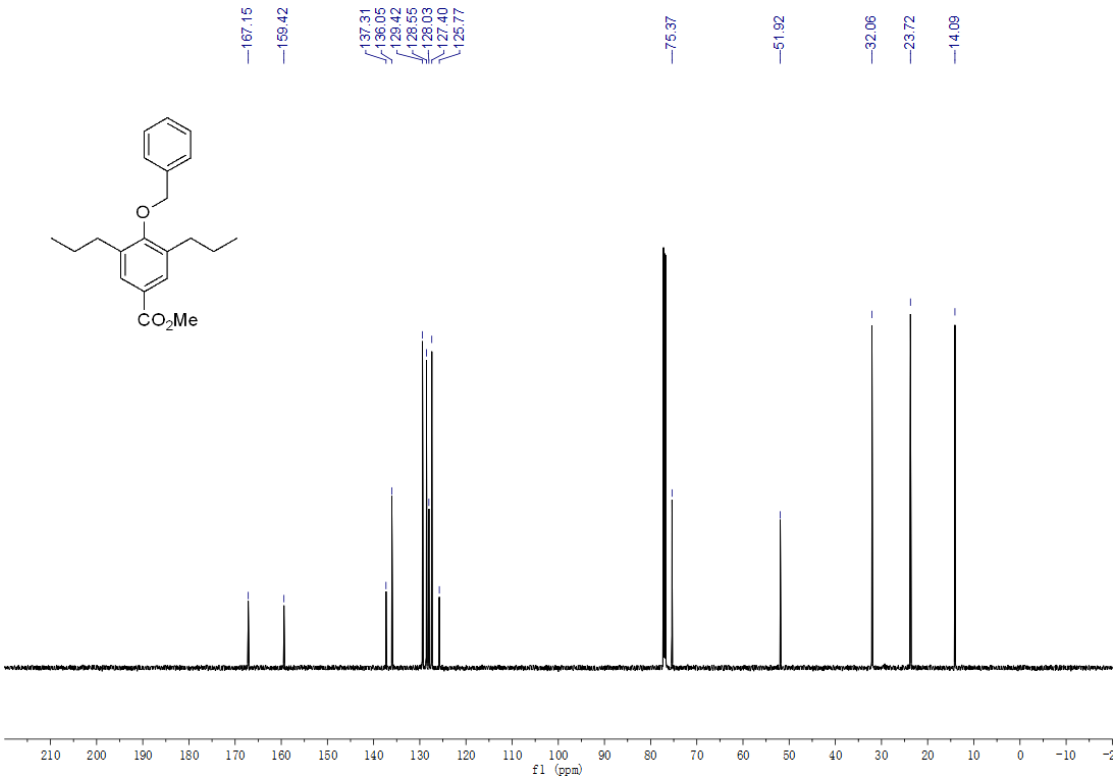
2,6-Dibutylphenol (3aa-D):



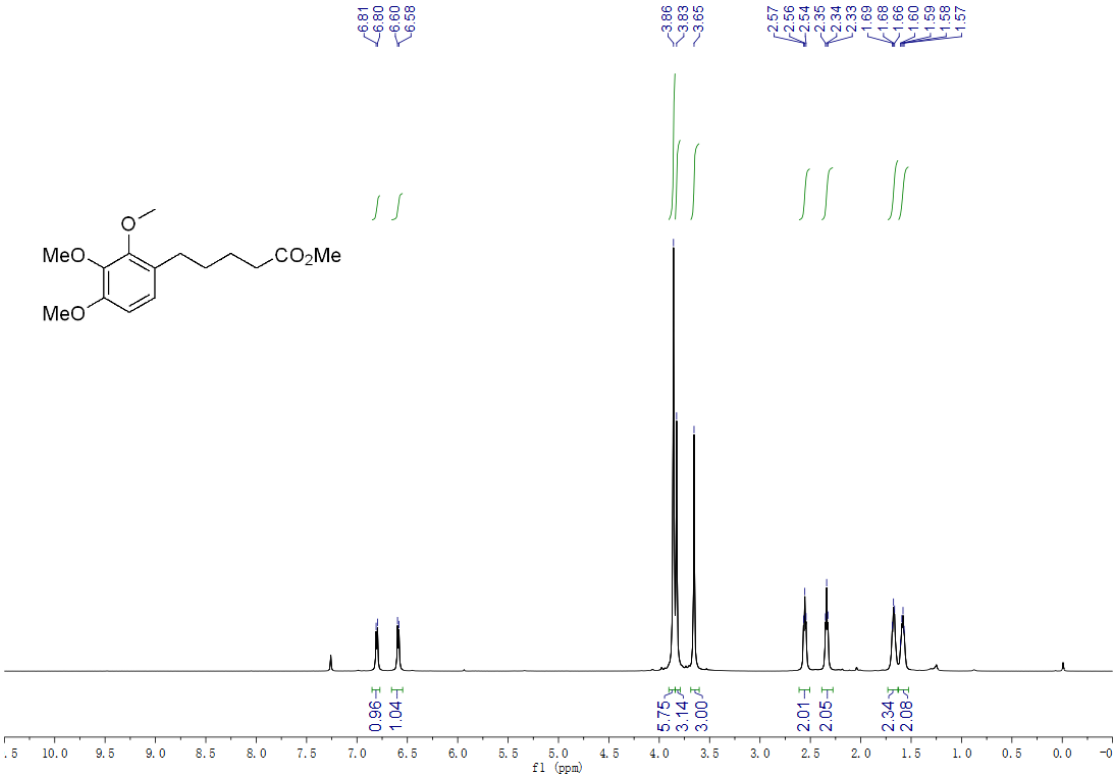


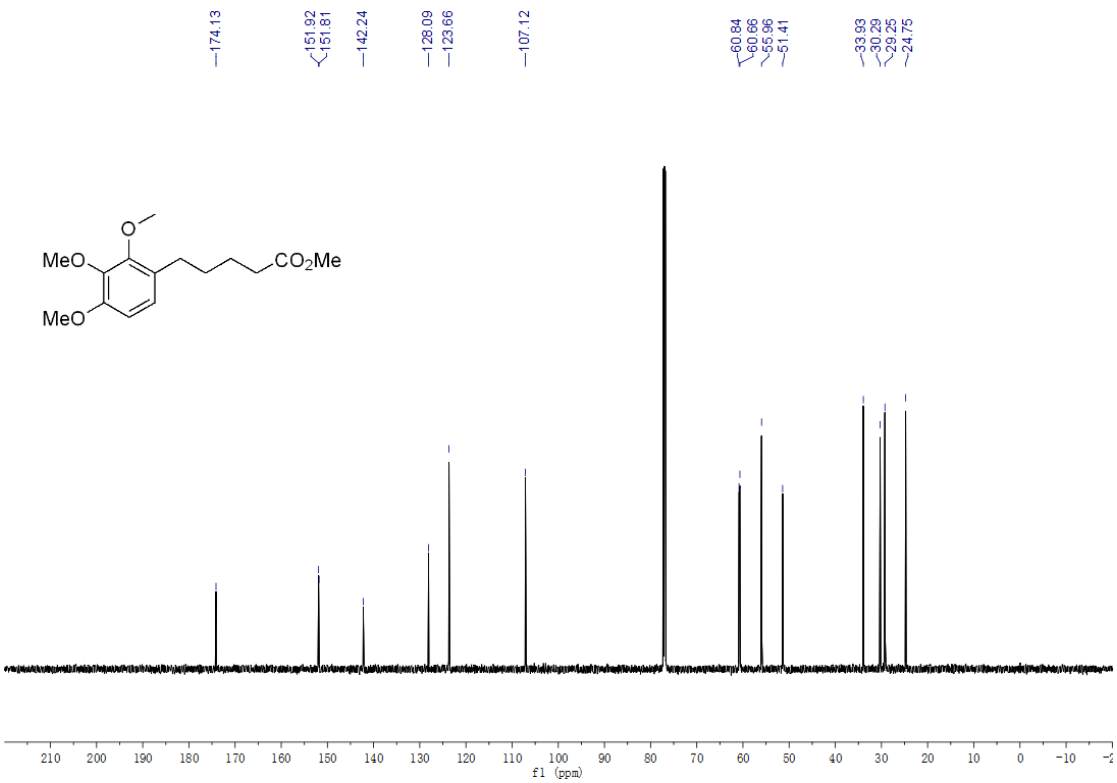
Methyl 4-(benzyloxy)-3,5-dipropylbenzoate (7er):



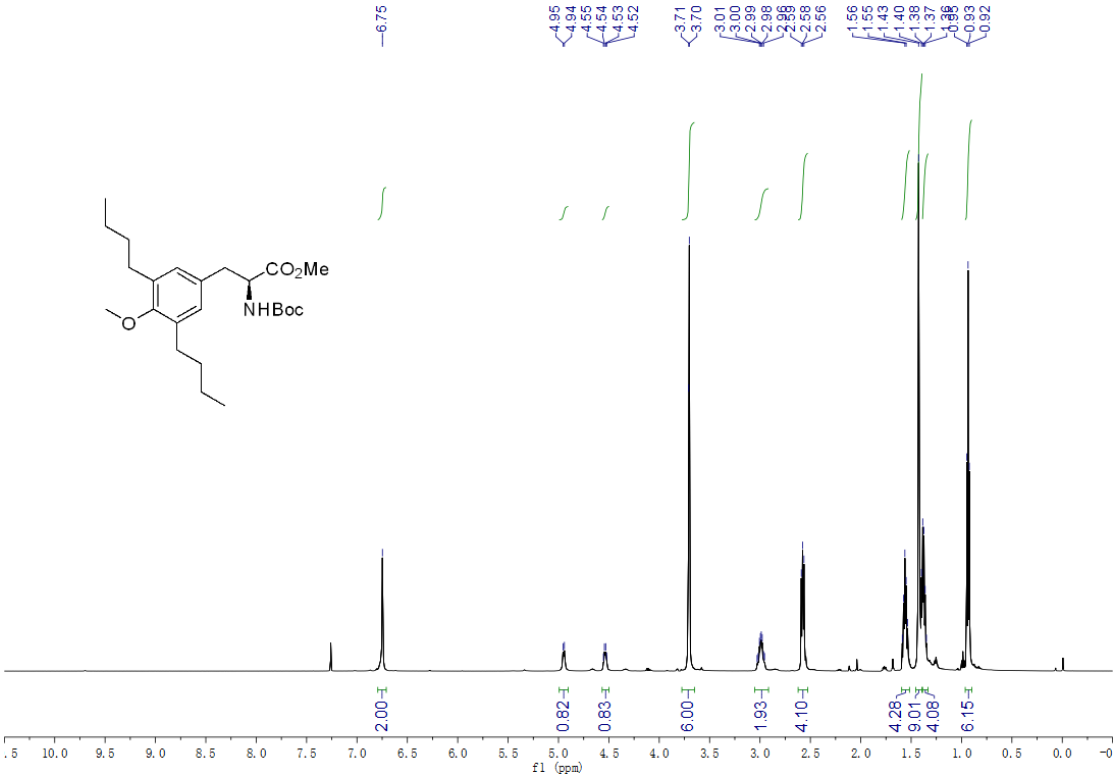


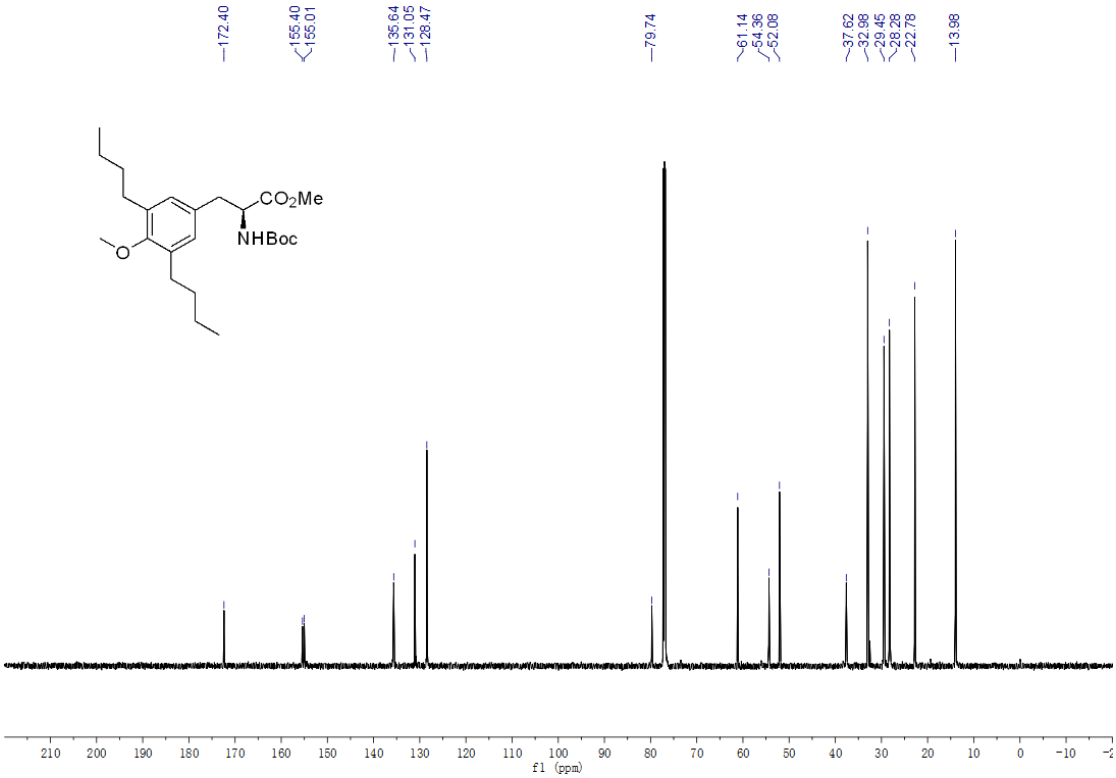
Methyl 5-(2,3,4-trimethoxyphenyl)pentanoate (5di):



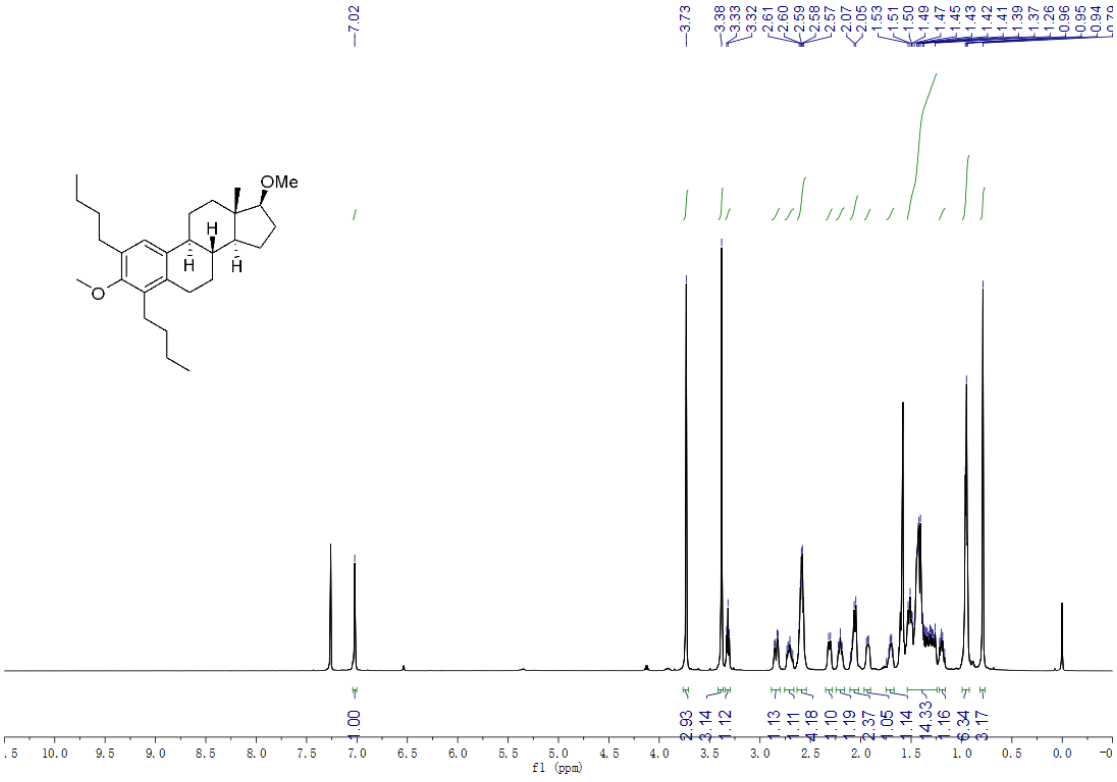


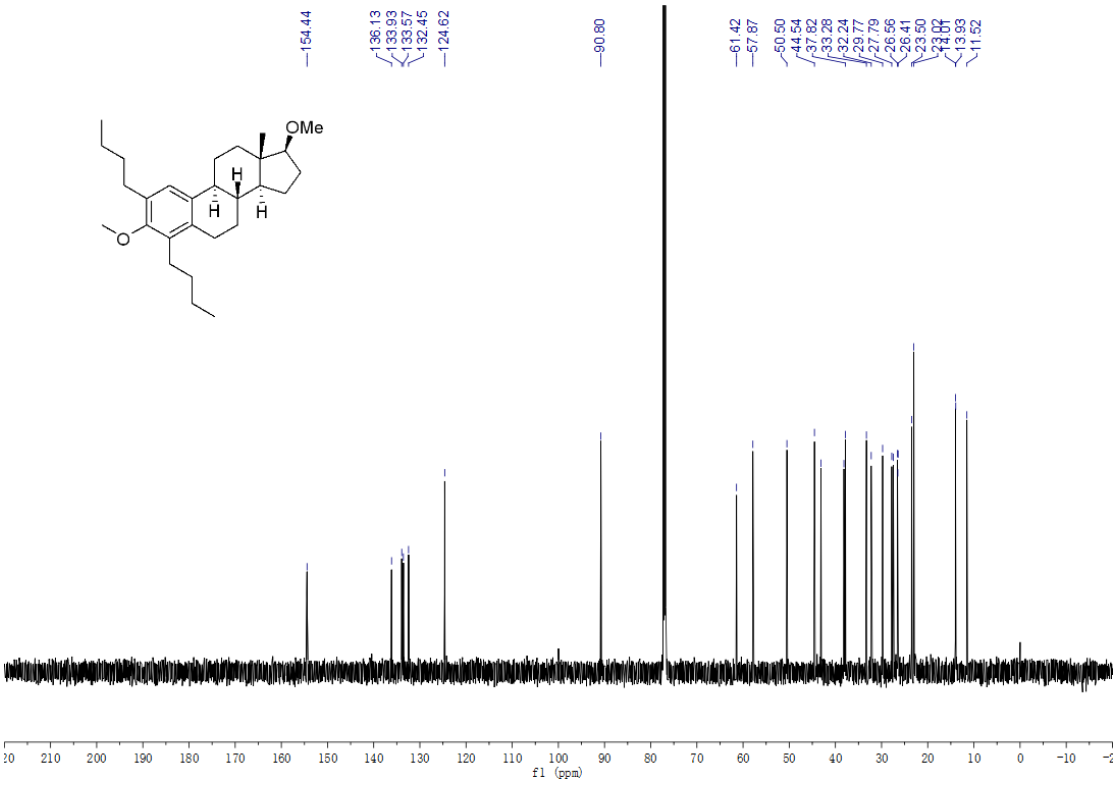
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(3,5-dibutyl-4-methoxyphenyl)propanoate (9aa):





(8*R*,9*S*,13*S*,14*S*,17*S*)-2,4-Dibutyl-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (9ba):





***N*-(4-(hydroxymethyl)phenyl)-*N*-methylacetamide (A2):**