Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cu-Catalyzed Suzuki-Miyaura Reactions of Primary and Secondary Benzyl Halides with Arylboronates

Table of Contents

I. General Information

a. Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). Copper(I) iodide was purchased from Sinopharm Chemical Reagent Co., Ltd as a off-white powder and refluxed in THF for further purification. The following chemicals were purchased and used as received: LiO*t*Bu(99.9%,Alfa-Aesar), 2,2,6,6-tetramethylheptane-3,5-dione (95%, Acros organics), 1-phenyl-1,3-butanedione(>98.0%, TCI), 1,3-Diphenyl-1,3-propanedione (98%, 9-Ding chemistry), tricyclohexylphosphine (98%,Sinocompound),triphenylphosphine(98%, Sinocompound),1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone(99%,Henwns),1-Methyl-2-azepanone(99%,Heowns),1-Methyl-2-pyrrolidinone and *N,N*-dimethylformamide were purchased from Aldrich (anhydrous in a Sure-Seal® bottle).

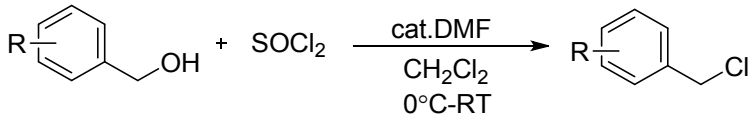
b. Analytical methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC system equipped with a flame-ionization detector. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

II. Preparation of Substrates

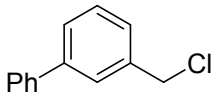
a. Synthesis and characterization of benzyl electrophiles

Benzyl chlorides corresponding to product **3a-3c, 3g, 3l and 3o-3p** were commercially available. Benzyl chlorides corresponding to product **3d-3f, 3h-3i, 3k, 3m-3n and 3q-3r** were prepared from the corresponding benzyl alcohol.



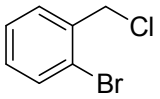
General procedure A[1-2]: To a stirring solution of the corresponding benzyl alcohol (10 mmol), N,N-dimethylformamide (20 μL) and CH_2Cl_2 (20 mL) were added thionyl chloride (12 mmol) dropwise at 0°C. After addition, the mixture was allowed to stir at room temperature for 1 h. The complete consumption of the benzyl alcohol was verified by TLC or GC. Then the mixture was poured into saturated $NaHCO_3$ (20 mL), and extract with dichloromethane (20 mL × 3). The combined organic layer was washed with water (20 mL), brine (20 mL), then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified on silica gel chromatography.

Characterization of the benzyl electrophiles



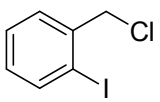
3-(chloromethyl)-1, 1'-biphenyl (CAS: 38580-82-4)

Following general procedure A. Purification by silica gel column chromatography gave the product as white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 3H), 7.58-7.54 (m, 1H), 7.49-7.43 (m, 3H), 7.41–7.35 (m, 2H), 4.67 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.96, 140.72, 138.09, 129.33, 128.96, 127.69, 127.57, 127.55, 127.37, 127.32, 46.41.



1-bromo-2-(chloromethyl)benzene (CAS: 578-51-8)

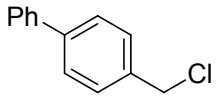
Following general procedure A. Purification by silica gel column chromatography gave the product as colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J*= 8.0, 1.0 Hz, 1H), 7.49 (dd, *J*= 7.6, 1.6 Hz, 1H), 7.33 (m, 1H), 7.20 (m, 1H), 4.71(s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.78 , 133.26, 131.02, 130.20, 127.99, 124.25, 46.30.



1-(chloromethyl)-2-iodobenzene (CAS: 59473-45-9)

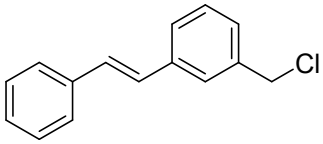
Following general procedure A. Purification by silica gel column chromatography gave the product as white solid**.**^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J*= 7.9, 0.9 Hz, 1H), 7.49 (dd, *J*= 7.7, 1.6 Hz, 1H), 7.41–7.33 (m, 1H), 7.07–6.97 (m, 1H), 4.68 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$)

δ 139.95, 139.92, 130.34, 130.2, 128.88, 99.68, 51.16.



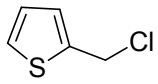
4-(chloromethyl)-1,1'-biphenyl (CAS: 1667-11-4)

Following general procedure A. Purification by silica gel column chromatography gave the product as white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4H), 7.50 -7.43 (m, 4H), 7.40 - 7.34 (m, 1H), 4.65 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.54, 140.63, 136.58, 129.21 , 128.97 , 127.68 , 127.64 , 127.27 , 46.20.



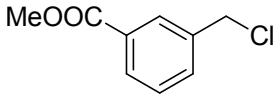
(E)-1-(chloromethyl)-3-styrylbenzene (CAS: 1429519-90-3)

Following general procedure A. Purification by silica gel column chromatography gave the product as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 3H), 7.48 (d, *J*= 7.7 Hz, 1H), 7.41–7.34 (m, 3H), 7.30 (d, *J*= 7.3 Hz, 2H), 7.13 (d, *J*= 4.7 Hz, 2H), 4.62 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.05 , 138.02 , 137.21 , 129.54 , 129.24 , 128.86 , 128.13 , 127.97 , 127.85 , 126.75, 126.71 , 126.68, 46.35.



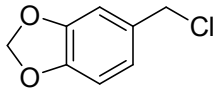
2-(chloromethyl)thiophene (CAS:765-50-4)

Following general procedure A. Purification by silica gel column chromatography gave the product as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J*= 5.0, 3.0 Hz, 1H), 7.30-7.28 (m, 1H), 7.14 (dd, *J*= 5.0, 1.3 Hz, 1H), 4.63 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.20, 127.71, 126.79, 124.13, 40.83.



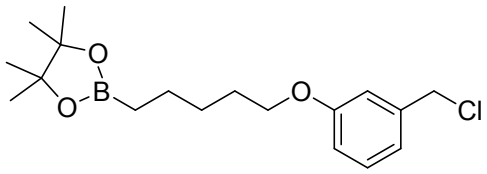
Methyl 3-(chloromethyl)benzoate (CAS: 34040-63-6)

Following general procedure A. Purification by silica gel column chromatography gave the product as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.98 (d, *J*= 7.8 Hz, 1H), 7.60 –7.55 (m, 1H), 7.43 (t, *J*= 7.7 Hz, 1H), 4.60 (s, 2H), 3.91 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.60, 137.93, 133.07, 130.74, 129.73, 129.60, 128.96, 52.31, 45.59.

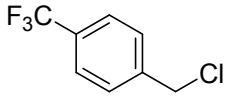


5-(chloromethyl)benzo[d][1,3]dioxole (CAS: 20850-43-5):

Following general procedure A. Purification by silica gel column chromatography gave the product as colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J*= 1.7 Hz, 1H), 6.86-6.83 (m, 1H), 6.77 (d, *J*= 7.9 Hz, 1H), 5.97 (s, 2H), 4.53 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.07 , 147.92 , 131.40 , 122.48 , 109.26 , 108.39 , 101.43 , 46.74 .



2-(5-(3-(chloromethyl)phenoxy)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (CAS: 1429519-91-4) Following general procedure A. Purification by silica gel column chromatography gave the product as colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J*= 7.9 Hz, 1H), 6.96–6.90 (m, 2H), 6.86–6.81 (m, 1H), 4.55 (s, 2H), 3.95 (t, *J*= 6.6 Hz, 2H), 1.84–1.70 (m, 2H), 1.52–1.42 (m, 4H), 1.25 (s, 12H), 0.81 (t, *J*= 7.2 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51 , 138.90 , 129.82 , 120.66 , 114.73 , 83.06 , 68.06 , 46.41 , 29.14, 28.82 , 24.95 , 23.90.

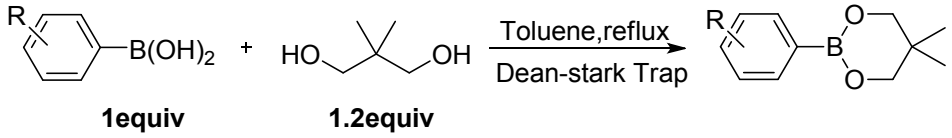


1-(chloromethyl)-4-(trifluoromethyl)benzene (CAS: 939-99-1)

Following general procedure A. Purification by silica gel column chromatography gave the product as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J*= 8.2 Hz, 2H), 7.52 (d, *J*= 8.1 Hz, 2H), 4.62 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.41, 130.68 (q, *J*= 32.6 Hz), 128.97, 125.85 (q, *J*= 3.8 Hz), 124.07 (q, *J*= 272.1 Hz), 45.12.

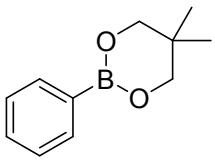
b. Synthesis and characterization of organoboronates

General procedure B organoboronates were prepared according to literature procedur es[3-7]: Organoboronates were prepared from organoboronic acids and 2,2-dimethyl-1,3-propanediol in toluene.



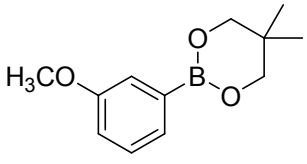
1equiv **1.2equiv**

.**Characterization of organoboronates:**



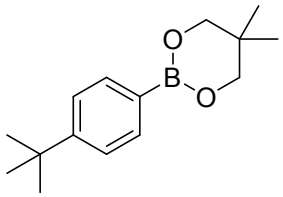
5, 5-dimethyl-2-phenyl-1,3,2-dioxaborinane(CAS: 5123-13-7)

Following general procedure B. Purification by silica gel column chromatography gave the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.71 (m, 2H), 7.45–7.39 (m, 1H), 7.38–7.32 (m, 2H), 3.76 (s, 4H), 1.01 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 133.94, 130.80, 127.70, 72.41, 32.00, 22.02.



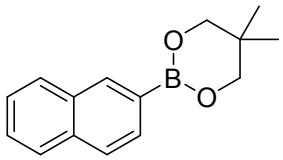
2-(3-methoxyphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS: 1003858-50-1)

Following general procedure B. Purification by silica gel column chromatography gave the product as a white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J*= 7.2 Hz, 1H), 7.33 (d, *J*= 2.6 Hz, 1H), 7.28–7.22 (m, 1H), 7.00–6.92 (m, 1H), 3.82 (s, 3H), 3.76 (s, 4H), 1.01 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.15, 128.89, 126.37, 118.00, 117.38, 72.44, 55.29, 32.01, 22.03.



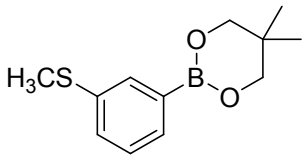
2-(4-(tert-butyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 905966-37-2)

Following general procedure B. Purification by silica gel column chromatography gave the product as a white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J*= 8.2 Hz, 2H), 7.38 (d, *J*= 8.3 Hz, 2H), 3.75 (s, 4H), 1.31 (s, 9H), 1.00 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.89, 133.87, 124.69, 72.41, 34.94, 32.03, 31.38, 22.04.



5, 5-dimethyl-2-(naphthalen-2-yl)-1, 3, 2-dioxaborinane (CAS: 627906-96-1)

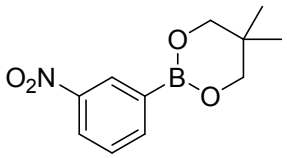
Following general procedure B. Purification by silica gel column chromatography gave the product as a white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.98-7.71 (m, 4H), 7.58 -7.33 (m, 2H), 3.83 (s, 4H), 1.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.17, 134.99, 133.02, 130.05, 128.80, 127.79, 126.92, 126.75, 125.72, 72.55, 32.09, 22.08.



5, 5-dimethyl-2-(3-(methylthio)phenyl)-1,3,2-dioxaborinane

Following general procedure B. Purification by silica gel column chromatography gave the product as a white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.43–7.26 (m, 2H), 3.76 (s, 4H), 2.50 (s, 3H), 1.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.65, 132.12, 130.71, 129.22, 128.21, 72.46, 32.03, 22.04, 16.09.

HRMS (EI) calcd for $C_{12}H_{17}BO_2S$ (M+): 236.1042; found: 236.1040.



5, 5-dimethyl-2-(3-nitrophenyl)-1, 3, 2-dioxaborinane (CAS: 585524-79-4)

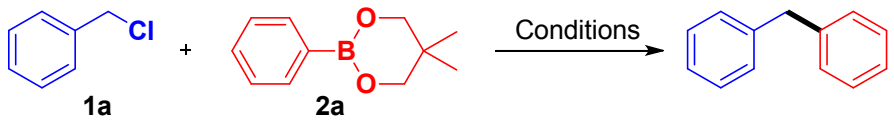
Following general procedure B. Purification by silica gel column chromatography gave the product as a white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 1.8 Hz, 1H), 8.31 – 8.20 (m, 1H), 8.09 (d, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 3.80 (s, 4H), 1.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.03, 139.97, 128.75, 128.66, 125.48, 72.59, 32.10, 21.99.

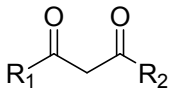
III. Experimental Procedures and Spectral Data

a. Experimental Procedures for cross coupling reaction

In air, CuI (0.1 mmol), Li*t*OBu (1.5 mmol), and 5, 5-dimethyl-2-phenyl-1,3,2- dioxaborinane (0.75 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (0.5 mL), ligand (0.1mmol), benzyl chloride (0.5 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 60 ^{O}C for 12h, then diluted with diethyl ether, filtered through silica gel with copious washings (ethyl acetate), benzophenone (91 mg, 0.5 mmol) was added as internal standard. The product was yielded by GC.

Table 1 Reaction optimization of the primary benzyl halides

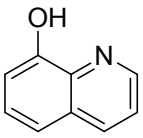




L1:TMEDA
L2:PCy_3
L3:PPh_3

L4:R_1=CH_3,R_2=Ph
L5:R_1=R_2=Ph
L6:R_1=R_2=*t*Bu

L7:

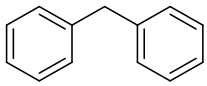


Entry	Catalyst	Solvent	Ligand	Yield [a]
1	CuI	DMF	-	35[b]
2	CuI	DMF	-	40
3	CuI	DMF	**L1**	33
4	CuI	DMF	**L2**	28
5	CuI	DMF	**L3**	25
6	CuI	DMF	**L4**	65
7	CuI	DMF	**L5**	70
8	CuI	DMF	**L6**	75
9	CuI	NMP	**L6**	66
10	CuI	DMPU	**L6**	68
11	CuI	THF	**L6**	20
12	CuI	NMCPL	**L6**	90(85[c])
13	CuCl	NMCPL	**L6**	50
14	CuI	NMCPL	**L7**	70
15[d]	$Pd(OAc)_2$	NMCPL	**L6**	18
16[d]	NiI_2	NMCPL	**L6**	trace
17	-	NMCPL	**L6**	0

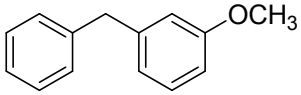
18[e]	CuI	NMCPL	**L6**	20
19[f]	CuI	NMCPL	**L6**	44
20[g]	CuI	NMCPL	**L6**	40
21[h]	CuI	NMCPL	**L6**	11

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), CuI (20 mol%), LiO*t*Bu (3 equiv), ligand (20 mol%) in 0.5mL solvent at 60°C for 12h under Ar atmosphere. The yield was determined by GC using benzophenone as internal standard (average of two GC runs). [b] CuI (10 mol%), LiO*t*Bu(2 equiv) in 0.5 mL solvent at 60 °C for 12h under Ar atmosphere. [c] Isolated yield. [d] Catalyst loading: 2 mol%. [e] 36 ul (2 mmol) of water was added. [f] Phenylboronic acid was used in the coupling. [g] CuI: 10 mol%. [h] CuI:5 mol%. DMF = N, N-dimethylformamide, NMP = 1-methyl-2-pyrrolidinone, DMPU = 1, 3-dimethyl-3, 4, 5, 6-te trahydro-2(1H)-pyrimidinone, THF = tetrahydrofuran. NMCPL = N-methylcaprolactam.

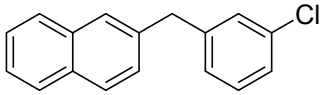
b. Substrate scope of the primary benzyl chlorides



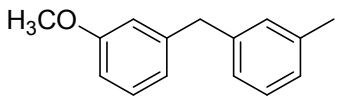
Diphenylmethane (CAS: 101-81-5): Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 4H), 7.20–7.14 (m, 6H), 3.96 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ141.23, 129.06, 128.58, 126.19, 42.06.
HRMS (EI) calcd for $C_{13}H_{12}$ (M+): 168.0939; found: 168.0936.



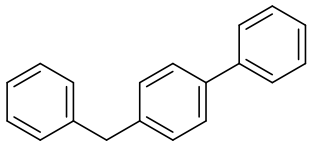
1-benzyl-3-methoxybenzene(3a). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.22–7.16 (m, 4H), 6.80–6.76 (m, 1H), 6.73 (d, *J* = 6.3 Hz, 2H), 3.94 (s, 2H), 3.75 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.86, 142.83, 141.04, 129.53, 129.04, 128.59, 126.23, 121.51, 114.93, 111.44, 55.25, 42.09.
HRMS (EI) calcd for $C_{14}H_{14}O$ (M+): 198.1045; found: 198.1043.



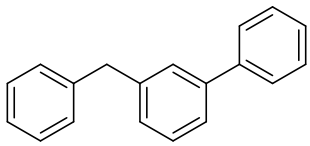
2-(3-chlorobenzyl)naphthalene(3b). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.73 (m, 3H), 7.61 (s, 1H), 7.51–7.39 (m, 2H), 7.28 (dd, *J*= 8.4, 1.2 Hz, 1H), 7.20 (d, *J*=6.7 Hz, 3H), 7.10 (d, *J*=6.6 Hz, 1H), 4.10 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.15, 137.79, 134.43, 133.70, 132.29, 129.85, 129.23, 128.42, 127.79, 127.70, 127.56, 127.36, 127.33, 126.53, 126.26, 125.69, 41.85.
HRMS (EI) calcd for $C_{17}H_{13}Cl$ (M+):252.0706; found: 252.0703.



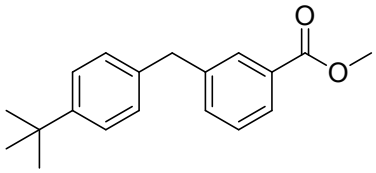
1-methoxy-3-(3-methylbenzyl)benzene(3c). Following general procedure, a colorless liquid
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.76 – 6.72 (m, 2H), 3.92 (s, 2H), 3.77 (s, 3H), 2.32 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.80, 142.97, 140.95, 138.16, 129.81, 129.51, 128.47, 126.99, 126.07, 121.50, 114.92, 111.34, 55.25, 42.04, 21.54.
HRMS (EI) calcd for $C_{15}H_{16}O$ (M+): 212.1201; found: 212.1203.



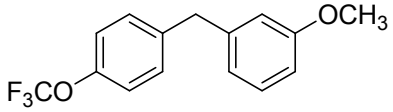
4-benzyl-1, 1'-biphenyl(3d). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.53–7.49 (m, 2H), 7.41 (t, *J*= 7.6 Hz, 2H), 7.30 (m, 3H), 7.25 – 7.19 (m, 5H), 4.02 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.14, 141.13, 140.39, 139.17, 129.46, 129.11, 128.86, 128.66, 127.36, 127.22, 127.15, 126.29, 41.72.
HRMS (EI) calcd for $C_{19}H_{16}$ (M+): 244.1252; found: 244.1251.



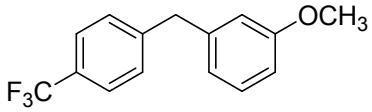
3-benzyl-1, 1'-biphenyl(3e). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J*= 7.4 Hz, 2H), 7.45–7.38 (m, 4H), 7.37–7.25 (m, 4H), 7.24–7.13 (m, 4H), 4.04 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.73 , 141.57 , 141.38 , 141.13 , 129.09 , 129.02 , 128.84 , 128.65 , 128.04 , 127.98 , 127.36 , 127.33 , 126.27 , 125.14 , 42.18.
HRMS (EI) calcd for $C_{19}H_{16}$ (M+): 244.1252; found: 244.1250.



Methyl 3-(4-(tert-butyl)benzyl)benzoate(3f). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.88 (d, *J*= 7.3 Hz, 1H), 7.42–7.34 (m, 2H), 7.31 (d, *J*= 8.2 Hz, 2H), 7.11 (d, *J*= 8.2 Hz, 2H), 4.00 (s, 2H), 3.90 (s, 3H), 1.30 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.35, 149.23, 141.77, 137.59, 133.74, 130.22, 128.65, 128.59, 127.51, 125.61, 52.22, 41.36, 34.52, 31.51.
HRMS (EI) calcd for $C_{19}H_{22}O_2$ (M+): 282.1620; found: 282.1624.



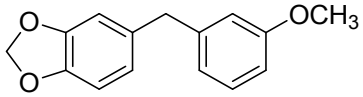
1-methoxy-3-(4-(trifluoromethoxy)benzyl)benzene(3g). Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.17 (m, 3H), 7.12 (d, *J*= 8.6 Hz, 2H), 6.80 – 6.74 (m, 2H), 6.71 (d, *J*= 1.5 Hz, 1H), 3.94 (s, 2H), 3.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.97 , 147.77 , 142.14, 139.83 , 130.25 , 129.72 , 121.45 , 121.15 , 120.66 (q, *J*= 256.6 Hz), 115.01 , 111.61 , 55.29 , 41.35.^{19}F NMR (376 MHz, $CDCl_3$) δ -57.90.
HRMS (EI) calcd for $C_{15}H_{13}F_3O_2$ (M+):282.0868; found: 282.0864.



1-methoxy-3-(4-(trifluoromethyl)benzyl)benzene(3h). Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J*= 8.1 Hz, 2H), 7.29 (d, *J*= 8.0 Hz, 2H), 7.21 (d, *J*= 7.9 Hz, 1H), 6.77 (d, *J*= 8.0 Hz, 2H), 6.71 (s, 1H), 4.00 (s, 2H), 3.77 (s, 3H).^{13}C NMR (101 MHz,

$CDCl_3$) δ 159.97 , 145.15 , 141.67 , 129.79, 129.31 , 128.63 (q, *J* = 32.5 Hz), 127.14 (q, J = 270 Hz), 125.54 (q, J = 3.8 Hz), 121.47, 115.04, 111.69, 55.30, 41.85.^{19}F NMR (376 MHz, CDCl3) δ -62.32.

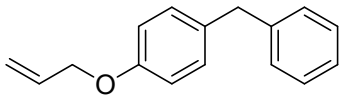
HRMS (EI) calcd for $C_{15}H_{13}F_3O$ (M+):266.0918; found: 266.0914.



5-(3-methoxybenzyl)benzo[d][1,3]dioxole (3i). Following general procedure, a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J*= 7.8 Hz, 1H), 6.79 (d, *J*= 0.5 Hz, 1H), 6.76–6.71 (m, 3H), 6.69–6.65 (m, 2H), 5.91 (s, 2H), 3.87 (s, 2H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 147.81, 146.00, 143.00, 134.91, 129.56, 121.86, 121.34, 114.78, 111.42, 109.53, 108.28, 100.96, 55.27, 41.75.

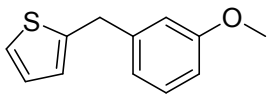
HRMS (EI) calcd for $C_{15}H_{14}O_3$ (M+): 242.0943; found: 242.0940.



1-(allyloxy)-4-benzylbenzene(3j). Following general procedure, a colorless liquid.

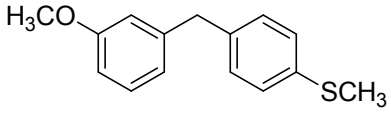
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J*= 7.4 Hz, 2H), 7.18 (t, *J*= 8.0 Hz, 3H), 7.09 (d, *J*= 8.6 Hz, 2H), 6.84 (d, *J*= 8.6 Hz, 2H), 6.11 – 5.98 (m, 1H), 5.39 (dd, *J*= 17.3, 1.5 Hz, 1H), 5.27 (dd, *J*= 10.5, 1.3 Hz, 1H), 4.52 – 4.47 (m, 2H), 3.91 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.10, 141.66, 133.55, 129.97, 128.95, 128.55, 126.11, 117.71, 114.83, 68.96, 41.16.

HRMS (EI) calcd for $C_{16}H_{16}O$ (M+): 224.1201; found: 224.1204.



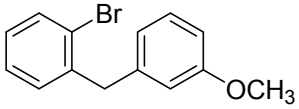
2-(3-methoxybenzyl)thiophene(3k). Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.16 (m, 2H), 6.95–6.89 (m, 2H), 6.84–6.72 (m, 3H), 3.95 (s, 2H), 3.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 142.31, 141.36, 129.55, 128.56, 125.74, 121.40, 121.29, 114.68, 111.51, 55.26, 36.66.

HRMS (EI) calcd for $C_{12}H_{12}OS$ (M+):204.0609; found: 204.0604.



(4-(3-methoxybenzyl)phenyl)(methyl)sulfane(3l). Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.78–6.67 (m, 3H), 3.89 (s, 2H), 3.75 (s, 3H), 2.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 142.68, 138.10, 135.87, 129.54, 127.21, 121.40, 114.84, 111.43, 55.24, 41.49, 16.31.

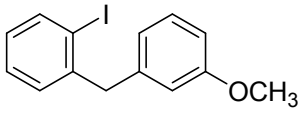
HRMS (EI) calcd for $C_{15}H_{16}OS$ (M+): 244.0922; found: 244.0918.



1-bromo-2-(3-methoxybenzyl)benzene(3m). Following general procedure, a light yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.25–7.19 (m, 2H), 7.17–7.13 (m, 1H), 7.12–7.05 (m, 1H), 6.82–6.71 (m, 3H), 4.10 (s, 2H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.84,

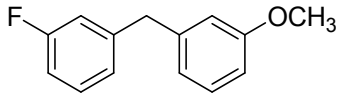
141.22, 140.33, 132.97, 131.21, 129.56, 128.06, 127.62, 125.01, 121.55, 115.01, 111.59, 55.27, 41.86.

HRMS (EI) calcd for $C_{14}H_{13}BrO$ (M+): 276.0150; found: 276.0146.



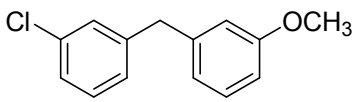
1-iodo-2-(3-methoxybenzyl)benzene(3n). Following general procedure, a light yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 1H), 7.30–7.18 (m, 2H), 7.11 (m, 1H), 6.90 (d, *J*= 1.4 Hz, 1H), 6.82–6.74 (m, 2H), 6.73 (s, 1H), 4.07 (s, 2H), 3.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.85, 143.58, 141.29, 139.67, 130.47, 129.57, 128.49, 128.18, 121.63, 115.07, 111.62, 101.42, 55.27, 46.61.

HRMS (EI) calcd for $C_{14}H_{13}IO$ (M+): 324.0011; found: 324.0008.



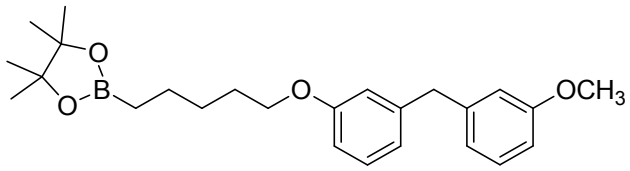
1-fluoro-3-(3-methoxybenzyl)benzene(3o). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J*= 12.9, 5.0 Hz, 2H), 6.96 (d, *J*= 7.6 Hz, 1H), 6.87 (d, *J*= 9.1 Hz, 2H), 6.76 (dd, *J*= 9.0, 4.2 Hz, 2H), 6.71 (s, 1H), 3.93 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.11 (d, *J*= 245.6 Hz), 159.94 , 143.62 (d, *J*= 7.2 Hz), 141.98 , 129.96 (d, *J*= 8.3 Hz), 129.68 , 124.66 (d, *J*= 2.8 Hz), 121.48, 115.90 (d, *J*= 21.2 Hz), 114.97 , 113.15 (d, *J*= 21.1 Hz), 111.66, 55.28 , 41.77 (d, *J*= 1.7 Hz)^{19}F NMR (376 MHz, $CDCl_3$) δ -113.51.

HRMS (EI) calcd for $C_{14}H_{13}FO$ (M+): 216.0950; found: 216.0952.



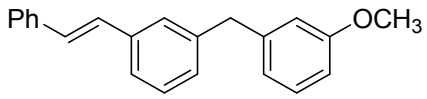
1-chloro-3-(3-methoxybenzyl)benzene(3p). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.15 (m, 4H), 7.06 (d, *J*= 7.0 Hz, 1H), 6.76 (d, *J*= 7.8 Hz, 2H), 6.71 (s, 1H), 3.91 (s, 2H), 3.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.94 , 143.09 , 141.89 , 134.38 , 129.82 , 129.71 , 129.13 , 127.22 , 126.48 , 121.48 , 114.99, 111.67 , 55.30 , 41.71 .

HRMS (EI) calcd for $C_{14}H_{13}ClO$ (M+): 232.0655; found: 232.0653.



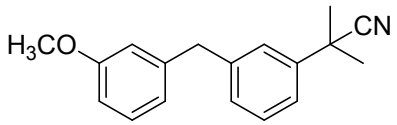
2-(5-(3-(3-methoxybenzyl)phenoxy)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(3q).
Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.12 (m, 2H), 6.81–6.76 (m, 2H), 6.75–6.67 (m, 4H), 3.94–3.87 (m, 4H), 3.76 (s, 3H), 1.80–1.71 (m, 2H), 1.52 – 1.40 (m, 4H), 1.24 (s, 12H), 0.80 (t, *J*= 7.2 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.79, 159.41, 142.70, 142.50, 129.50, 129.45, 121.49, 121.22, 115.48, 114.85, 111.98, 111.45, 83.04, 67.86, 55.25, 42.12, 29.22, 28.85, 24.94, 23.92, 14.33.

HRMS (EI) calcd for $C_{25}H_{35}BO_4$ (M+):410.2628; found: 410.2625.

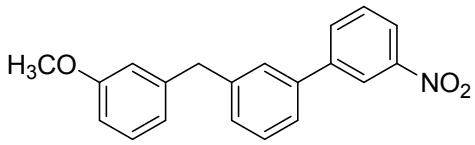


(E)-1-methoxy-3-(3-styrylbenzyl)benzene (**3r**)**.** Following general procedure, a colorless liquid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*= 7.8 Hz, 2H), 7.35 (m, 4H), 7.30–7.18 (m, 4H), 7.08 (s, 2H), 6.81 (d, *J*= 7.5 Hz, 1H), 6.77 (s, 2H), 3.98 (s, 2H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.90, 142.69, 141.41, 137.65, 137.50, 129.60, 128.95, 128.87, 128.80, 128.48, 127.72, 127.38, 126.63, 124.44, 121.53, 119.89, 114.98, 111.49, 55.30, 42.07.
HRMS (EI) calcd for $C_{22}H_{20}O$ (M+): 300.1514; found: 300.1512.

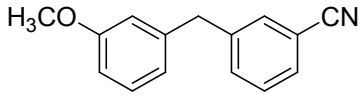
c. Functionalization of the reaction products[8-12]



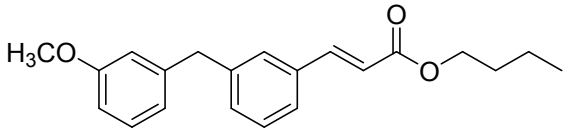
2-(3-(3-methoxybenzyl)phenyl)-2-methylpropanenitrile
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 3H), 7.22 (t, *J*= 7.9 Hz, 1H), 7.15–7.10 (m, 1H), 6.8 –6.71 (m, 3H), 3.98 (s, 2H), 3.78 (s, 3H), 1.71 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.88, 142.28, 141.85, 141.71, 129.65, 129.19, 128.53, 125.81, 124.73, 122.98, 121.42, 114.88, 111.57, 55.29, 42.07, 37.25, 29.31.
HRMS (EI) calcd for $C_{18}H_{19}NO$ (M+):265.1467; found: 265.1468.



3-(3-methoxybenzyl)-3'-nitro-1, 1'-biphenyl
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (t, *J*= 1.9 Hz, 1H), 8.21–8.15 (m, 1H), 7.91–7.83 (m, 1H), 7.58 (t, *J*= 8.0 Hz, 1H), 7.50–7.37 (m, 3H), 7.30–7.19 (m, 2H), 6.88–6.72 (m, 3H), 4.04 (s, 2H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.91, 148.81, 143.01, 142.35, 142.12, 139.03, 133.26, 129.78, 129.70, 129.45, 129.31, 127.88, 125.19, 122.13, 122.13, 121.46, 115.03, 111.50, 55.30, 42.07.
HRMS (EI) calcd for $C_{20}H_{17}NO_3$ (M+):319.1208; found: 319.1206.



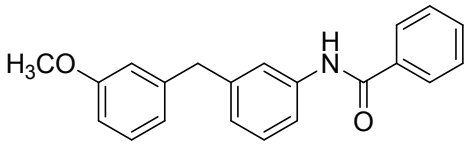
3-(3-methoxybenzyl)benzonitrile (CAS: 1013931-19-5)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.33 (m, 4H), 7.33–7.19 (m, 1H), 6.83–6.74 (m, 2H), 6.70 (d, *J*= 1.8 Hz, 1H), 3.98 (s, 2H), 3.79 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.00, 142.55, 141.06, 133.52, 132.45, 130.08, 129.90, 129.35, 121.40, 119.09, 115.03, 112.61, 111.82, 55.30, 41.50.



(E)-butyl 3-(3-(3-methoxybenzyl)phenyl)acrylate

^{1}H NMR (400 MHz, $CDCl_3$) δ7.64 (d, *J*= 16.0 Hz, 1H), 7.44-7.27 (m, 3H), 7.22 (m, 2H), 6.84-6.70 (m, 3H), 6.41 (d, *J*= 16.0 Hz, 1H), 4.20 (t, *J*= 6.7 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H), 1.75-1.63 (m, 2H), 1.51-1.38 (m, 2H), 0.97 (t, *J*= 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$)δ167.24, 159.88, 144.71, 142.20, 141.77, 134.77, 131.01, 129.67, 129.13, 128.75, 126.01, 121.44, 118.37, 114.95, 111.53, 64.53, 55.27, 41.86, 30.89, 19.33, 13.89.

HRMS (EI) calcd for $C_{21}H_{24}O_3$ (M+):324.1725; found: 324.1728.



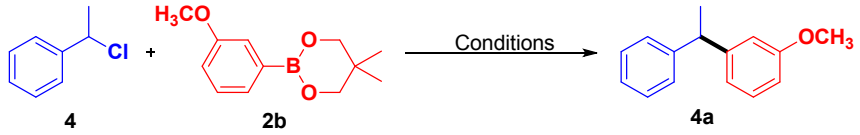
N-(3-(3-methoxybenzyl)phenyl)benzamide

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.77 (s, 1H), 7.55 (m, 2H), 7.48 (t, *J*= 7.3 Hz, 2H), 7.42 (s, 1H), 7.29 (t, *J*= 7.8 Hz, 1H), 7.24–7.17 (m, 1H), 7.00 (d, *J*= 7.7 Hz, 1H), 6.81 (d, *J*= 7.6 Hz, 1H), 6.77–6.72 (m, 2H), 3.97 (s, 2H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.79, 159.86, 142.47, 142.22, 138.18, 135.14, 131.97, 129.62, 129.35, 128.93, 127.12, 125.33, 121.55, 120.65, 118.18, 114.92, 111.59, 55.30, 42.04.

HRMS (EI) calcd for $C_{21}H_{19}NO_2$ (M+):317.1416; found: 317.1412.

d. Substrate scope of the secondary benzyl halides

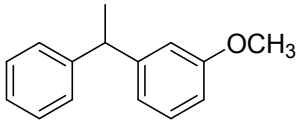
Table 4 Reaction optimization of the secondary benzyl halides



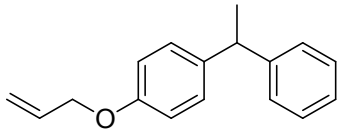
4 2b 4a

Entry	Base	Solvent	Ligand	Yield[a]
1	LiO^{t}Bu	NMCPL	**L6**	20
2	CH_3OLi	NMCPL	**L6**	12
3	KO^{t}Bu	NMCPL	**L6**	13
4	$CsCO_3$	NMCPL	**L6**	15
5	K_3PO4	NMCPL	**L6**	2
6	LiO^{t}Bu	NMCPL	**L4**	15
7	LiO^{t}Bu	NMCPL	**L5**	17
8	LiO^{t}Bu	NMCPL	**L7**	60
9[b]	LiO^{t}Bu	NMCPL	**L7**	83
10	LiO^{t}Bu	NMP	**L7**	30
11	LiO^{t}Bu	DMPU	**L7**	36
12	LiO^{t}Bu	DMF	**L7**	40

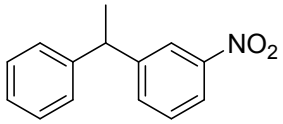
[a] Reaction conditions: **4** (0.5 mmol), **2b** (0.75 mmol), CuI (20 mol%), base (3 equiv), ligand (20 mol%) in 0.5 mL solvent at 60 ^{O}C for 12h under ar atmosphere. NMCPL = N-methylcaprolactam. The yield was determined by GC using benzophenone as internal standard (average of two GC runs). [b] (1-bromoethyl)benzene was used.



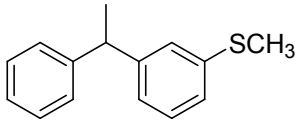
1-methoxy-3-(1-phenylethyl)benzene(4a). Following general procedure, a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.24–7.15 (m, 4H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.79 – 6.77 (m, 1H), 6.75 – 6.70 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.50, 147.97 , 146.09 , 129.22, 128.29, 127.50, 125.98, 120.05 , 113.70, 110.83, 55.05, 44.70 , 21.72
HRMS (EI) calcd for $C_{15}H_{16}O$ (M+):212.1201; found: 212.1200.



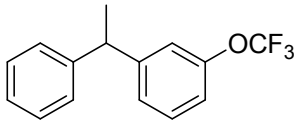
1-(allyloxy)-4-(1-phenylethyl)benzene(4b). Following general procedure, a yellow liquid
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.24–7.16 (m, 3H), 7.15–7.10 (m, 2H), 6.87–6.81 (m, 2H), 6.10–5.98 (m, 1H), 5.44–5.36 (m, 1H), 5.30–5.24 (m, 1H), 4.52– 4.48 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.99, 146.87, 138.83, 133.60, 128.62, 128.46, 127.66, 126.06, 117.68, 114.66, 68.95, 44.06, 22.18.
HRMS (EI) calcd for $C_{17}H_{18}O$ (M+):238.1358; found: 238.1356.



1-nitro-3-(1-phenylethyl)benzene(4c). Following general procedure, a colorless liquid
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.05 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26–7.18 (m, 3H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.69 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.59, 148.51, 144.84, 134.16, 129.39, 128.86, 127.65, 126.81, 122.51, 121.42, 44.66, 21.74.
HRMS (EI) calcd for $C_{14}H_{13}NO_2$ (M+):227.0946; found: 227.0944.

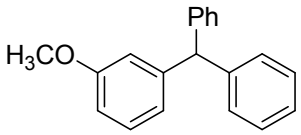


Methyl (3-(1-phenylethyl)phenyl)sulfane(4d). Following general procedure, a light yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.24–7.15 (m, 4H), 7.13 (s, 1H), 7.09–7.05 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.16, 146.04, 138.40, 128.97, 128.52, 127.71, 126.25, 126.12, 124.67, 124.23, 44.85, 21.90, 15.95.
HRMS (EI) calcd for $C_{15}H_{16}S$ (M+):228.0973; found: 228.0970



1-(1-phenylethyl)-3-(trifluoromethoxy)benzene(4e). Following general procedure, a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 3H), 7.24–7.18 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 7.06–7.02 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR

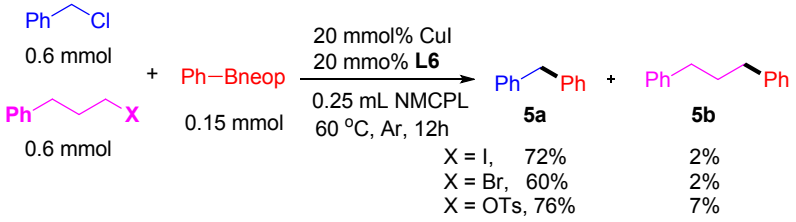
(101 MHz, $CDCl_3$) δ 149.50, 148.89, 145.53, 129.71, 128.67, 127.69, 126.51, 126.23, 120.62 (q, *J*=255Hz), 120.34, 116.78, 44.65, 21.85.^{19}F NMR (376 MHz, $CDCl_3$) δ -57.69.
HRMS (EI) calcd for $C_{15}H_{13}F_3O$ (M+):266.0918; found: 266.0912.



((3-methoxyphenyl)methylene)dibenzene(4f). Following general procedure, a colorless liquid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.20 (t, *J*= 8.0 Hz, 3H), 7.15–7.09 (m, 4H), 6.76 (m, 1H), 6.69 (m, 2H), 5.52 (s, 1H), 3.73 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 145.66, 143.87, 129.56, 129.35, 128.43, 126.46, 122.14, 115.73, 111.44, 56.94, 55.25.
HRMS (EI) calcd for $C_{20}H_{18}O$ (M+):274.1358; found: 274.1354.

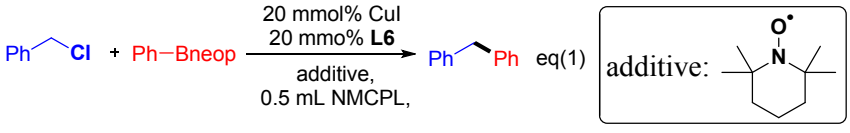
e. Selectivity in the competitive experiment

In air, CuI (5.7 mg, 0.03 mmol), Li*O*tBu (24 mg, 0.3 mmol) and 5, 5-dimethyl-2-phenyl-1, 3, 2-dioxaborinane (28.5 mg, 0.15 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (0.25 mL), **L6** (0.03 mmol) benzyl chloride (0.6 mmol), alkyl-X (X: Br, I, OTs, 0.6 mmol) were added in turn by syringe. The reaction mixture was stirred vigorously at 60 ^{O}C for 12h, and then diluted with diethyl ether, filtered through silica gel with copious washings (ethyl acetate); benzophenone (27.3 mg, 0.15mmol) was added as internal standards. The product was yielded by GC.

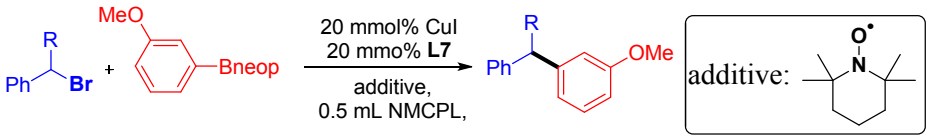


f. The effect of TMEPO additive

In air, CuI (0.1 mmol), Li*t*OBu (1.5 mmol), arylboronates (0.75 mmol) and 2,2,6,6-Tetramethylpiperidinooxy were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (0.5 mL), ligand (0.1 mmol), benzyl halides (0.5 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 60 ^{O}C for 12h, then diluted with diethyl ether, filtered through silica gel with copious washings (ethyl acetate), benzophenone (91mg, 0.5mmol) was added as internal standard. The GC yield of product is illustrated as following: [a]



	Additive(0equiv)	Additive(1.0equiv)
Yield	90%	45%



R	Additive(0equiv)	Additive(1.0equiv)
R = Ph	63%	trace
R = CH_3	83%	25%

[a] Reaction conditions: LiO*t*Bu (3 equiv) in 0.5 mL solvent at 60 °C for 12h under ar atmosphere. The yield was determined by GC using benzophenone as internal standard (average of two GC runs). Neop = ($OCH_2CMe_2CH_2O$). NMCPL = N-methylcaprolactam.

References

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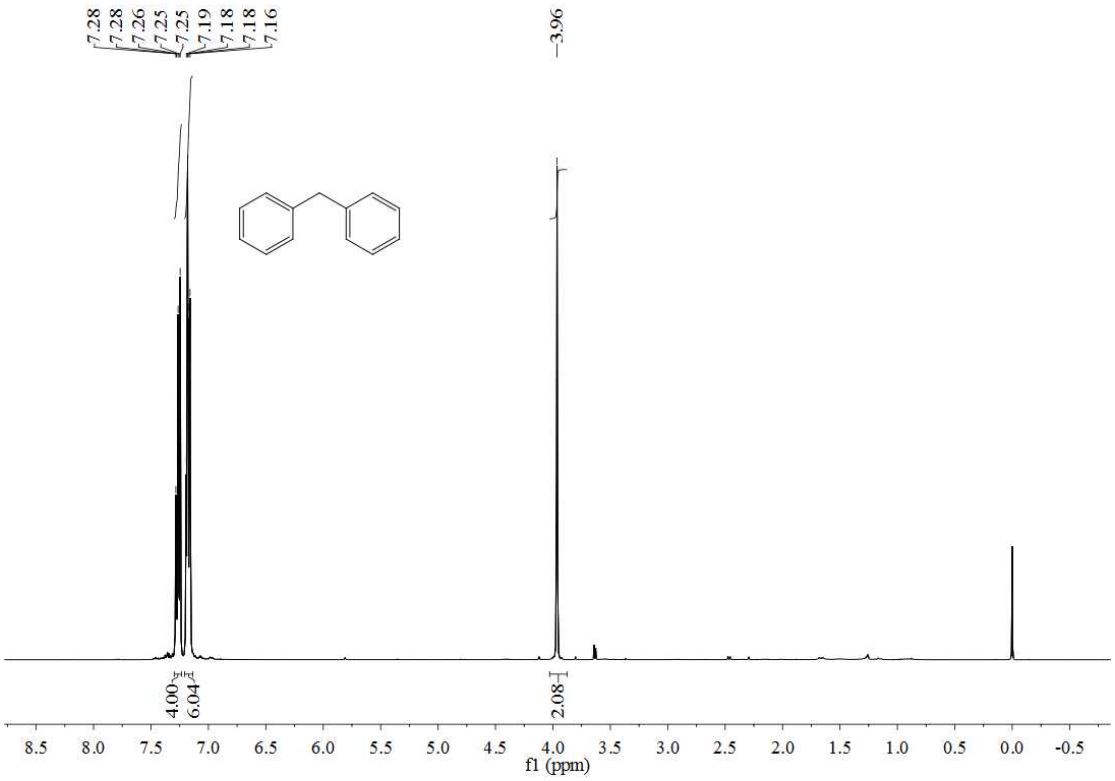
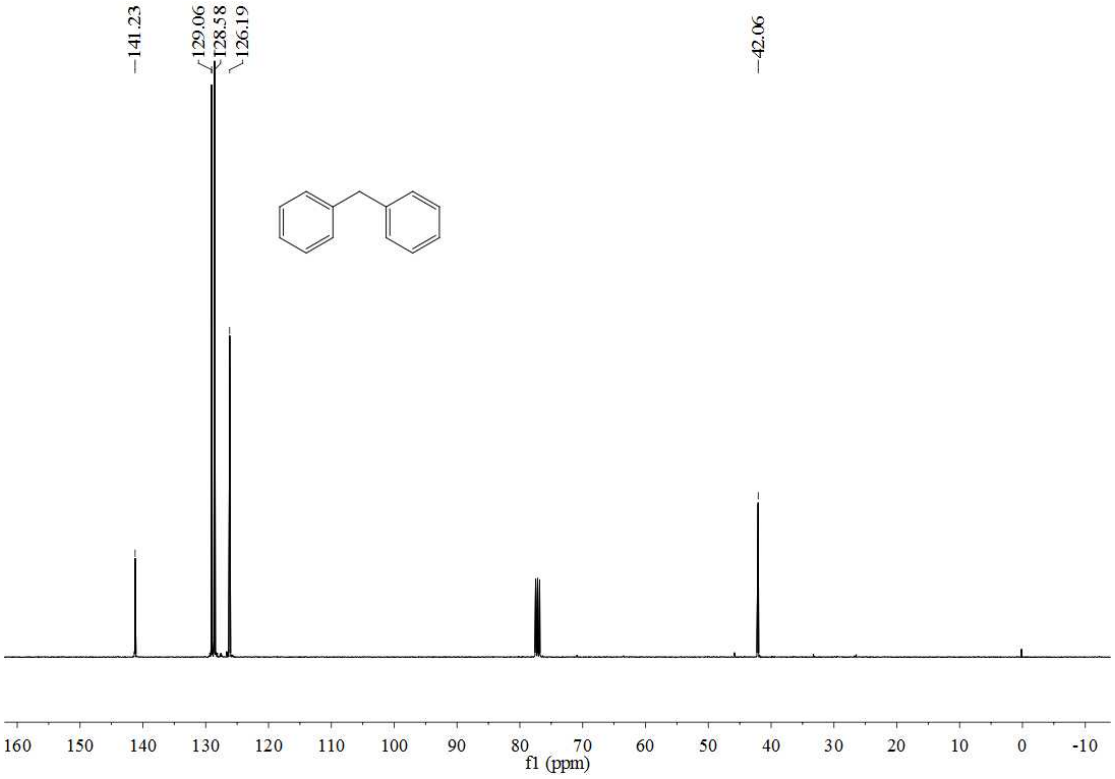
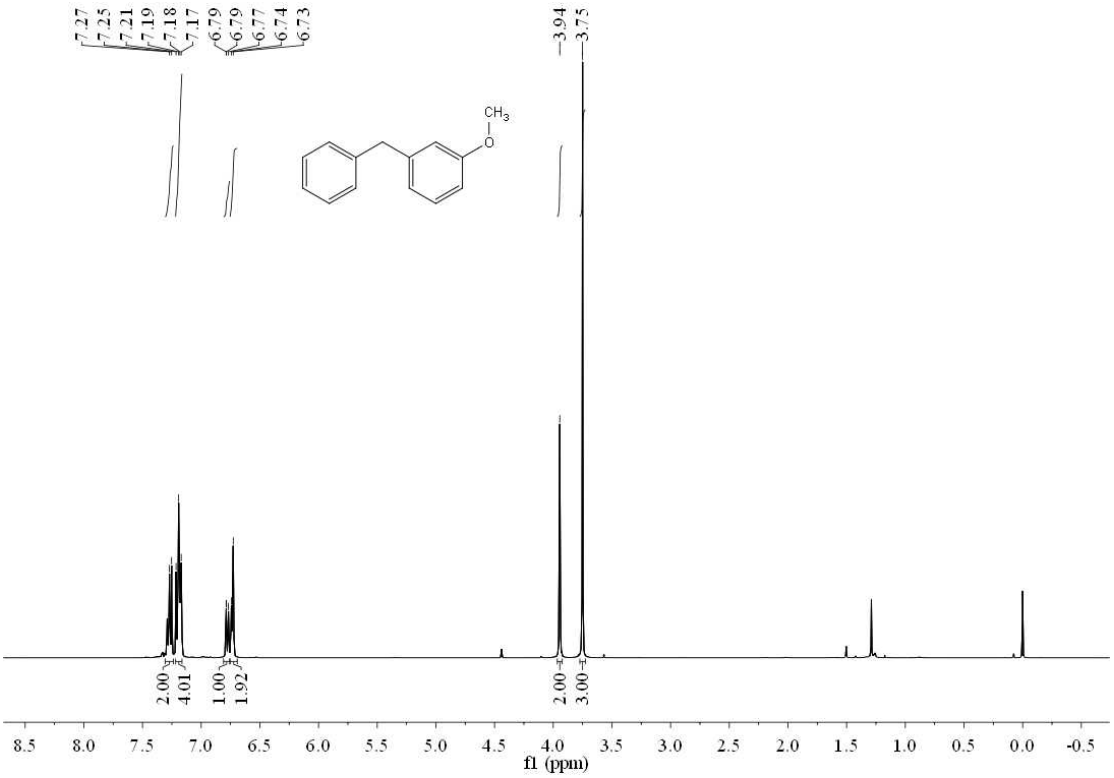
Ⅴ. NMR Spectras

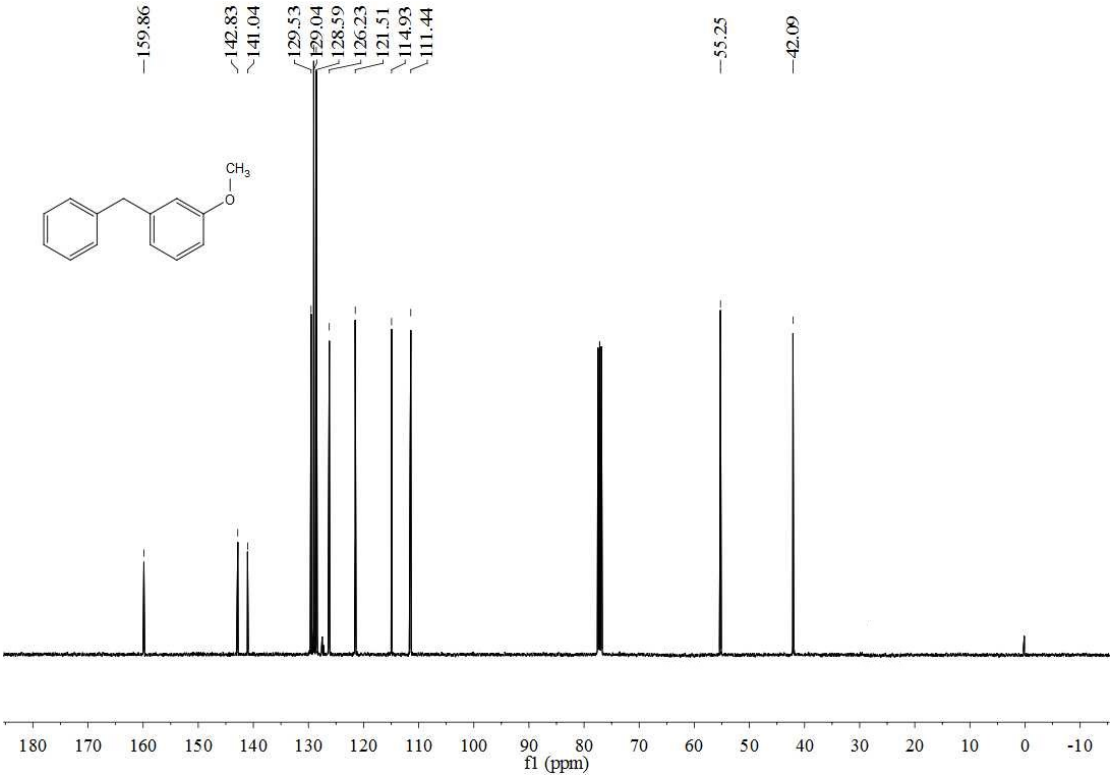
1. Diphenylmethane



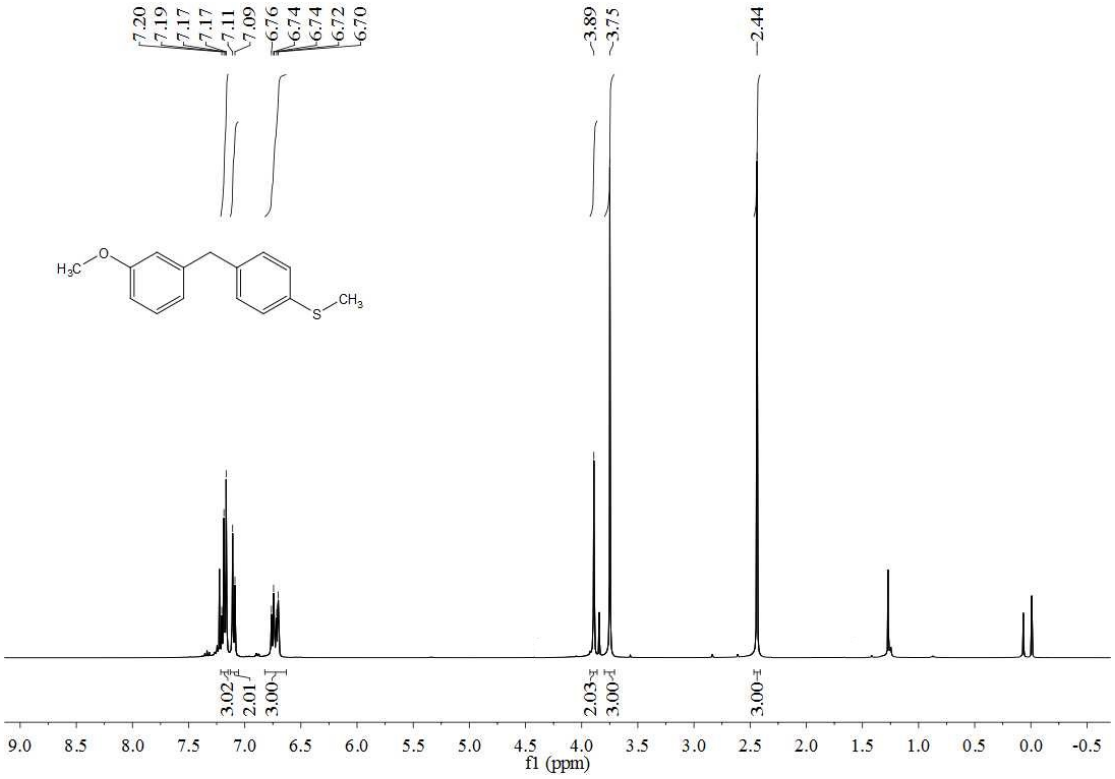


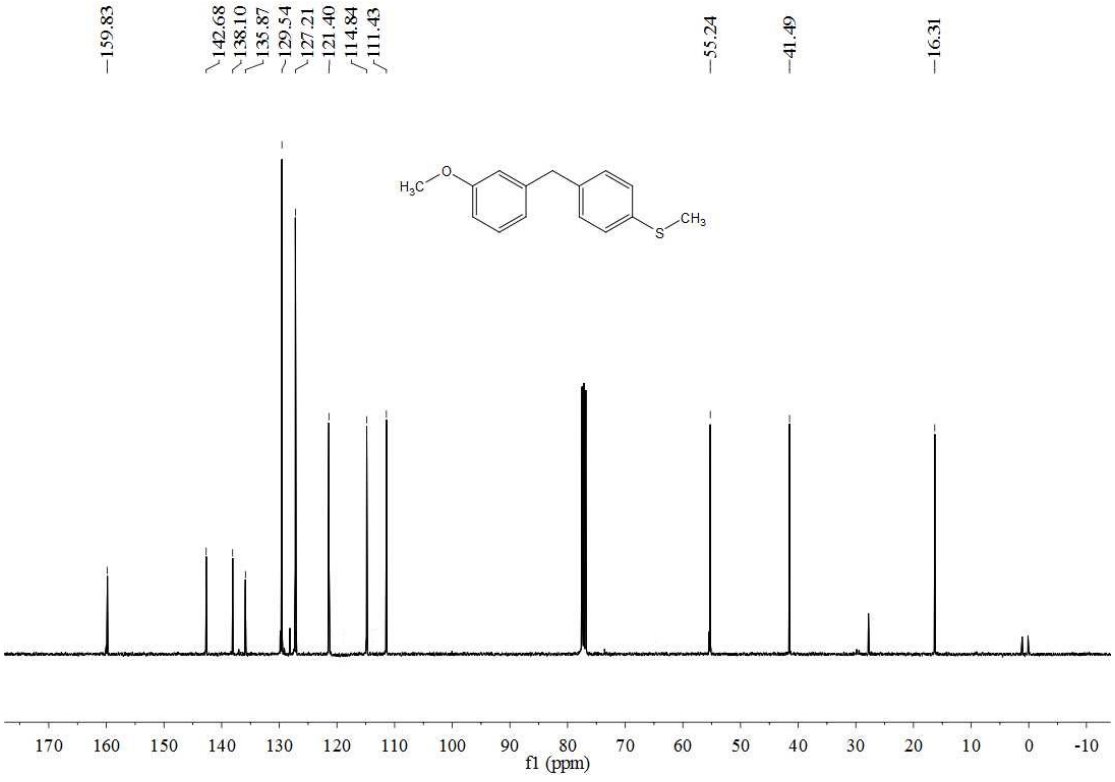
2.1-benzyl-3-methoxybenzene



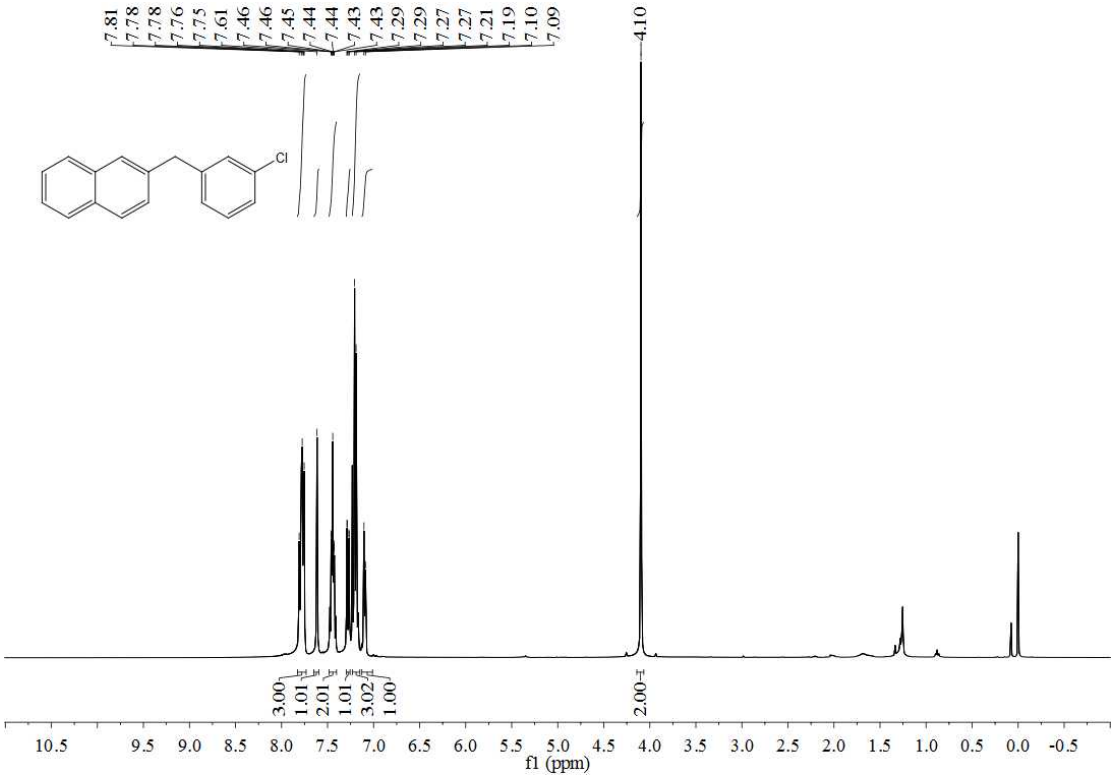


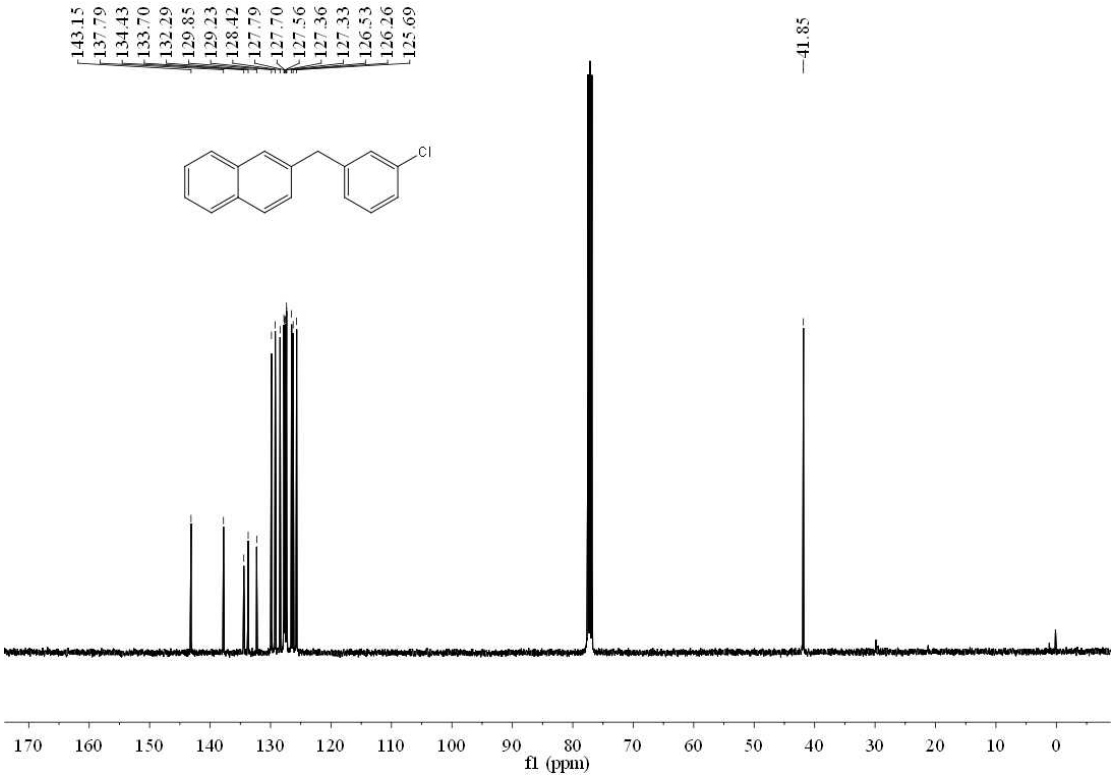
3. (4-(3-methoxybenzyl)phenyl)(methyl)sulfane



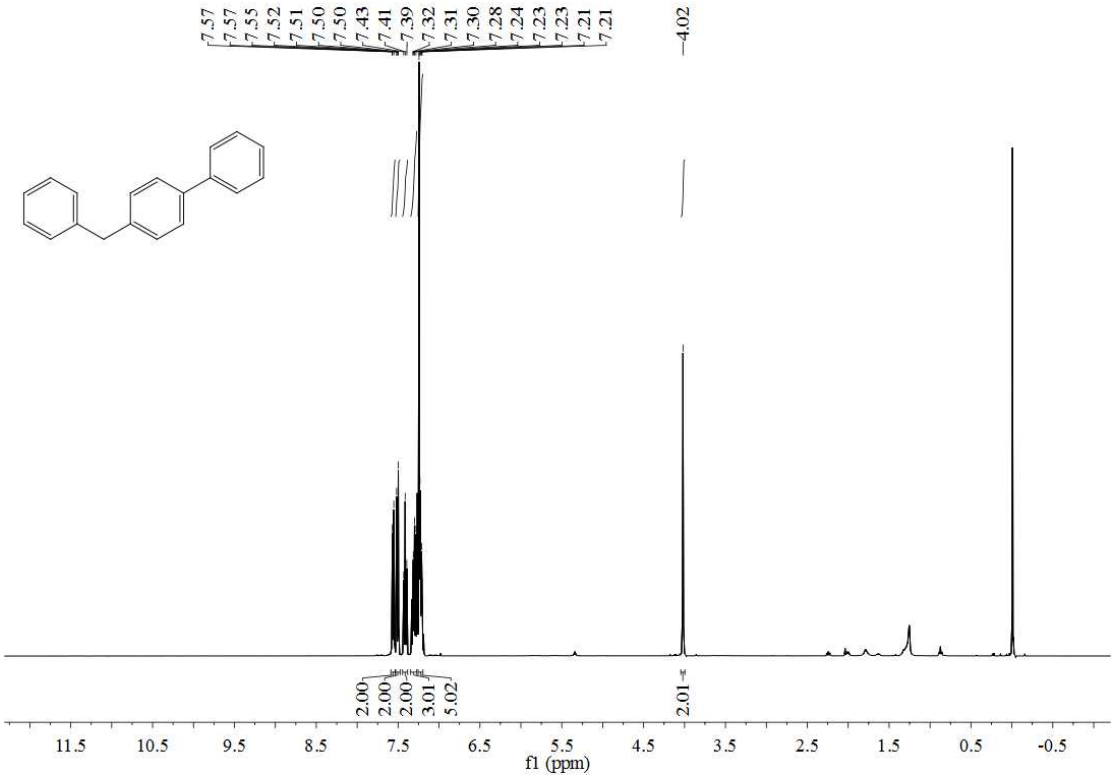


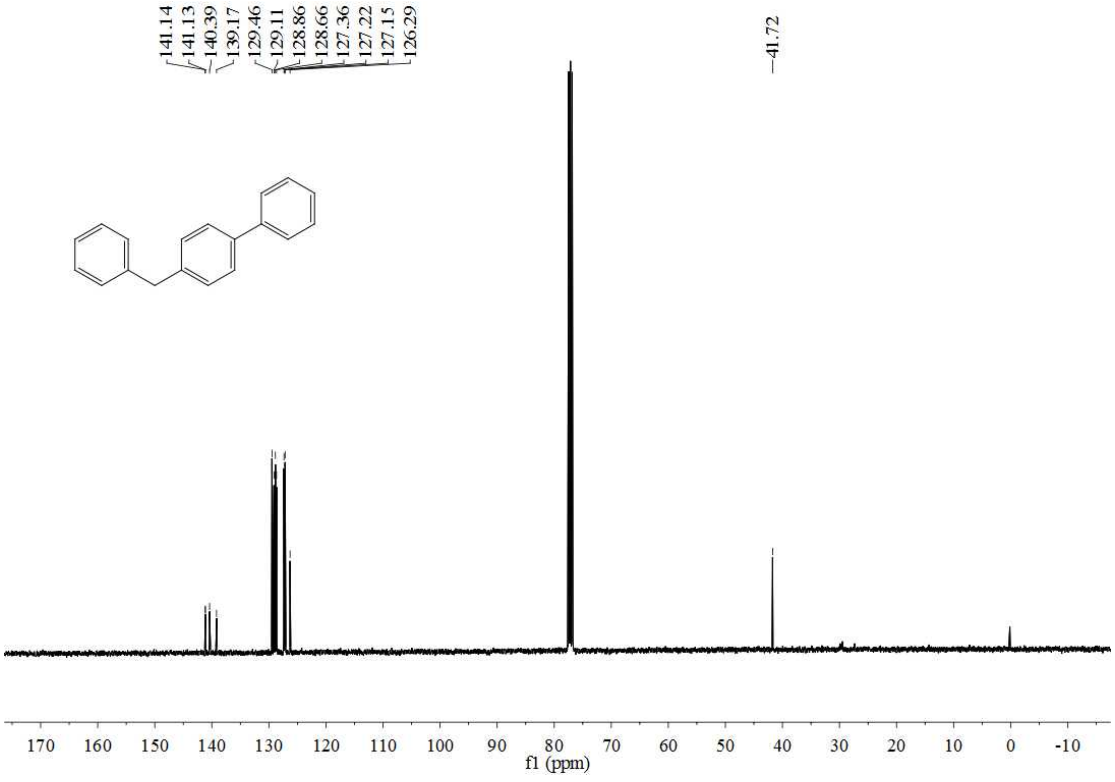
4. 2-(3-chlorobenzyl)naphthalene



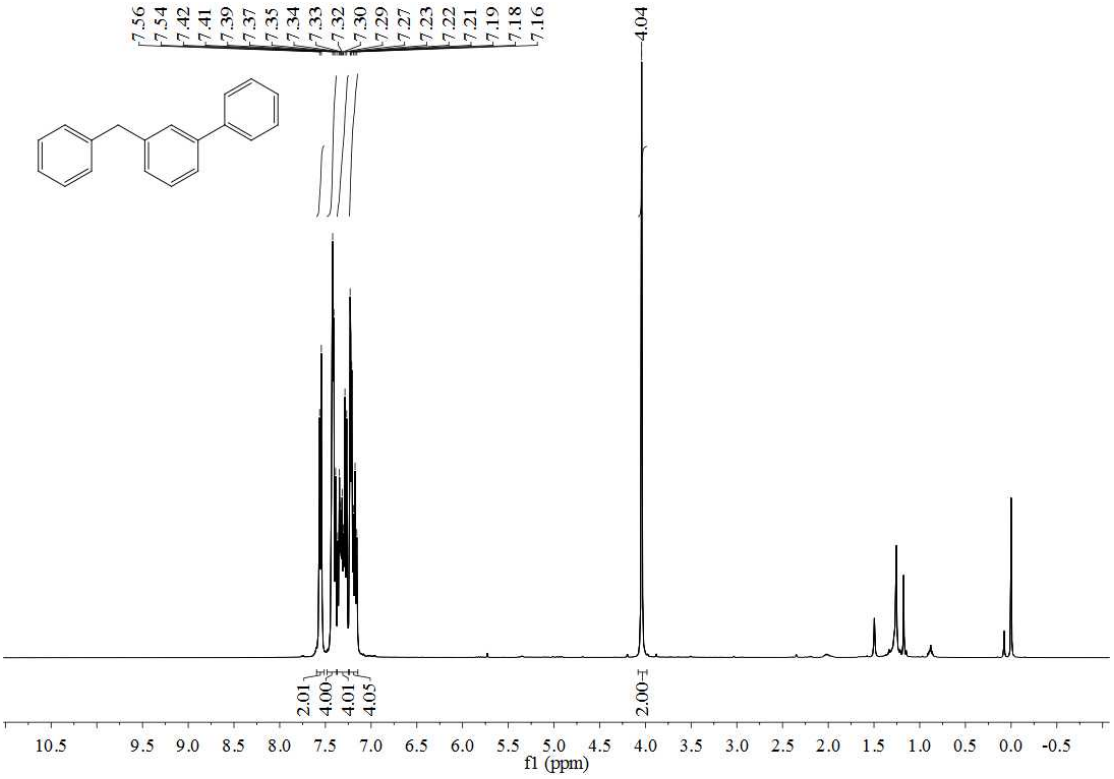


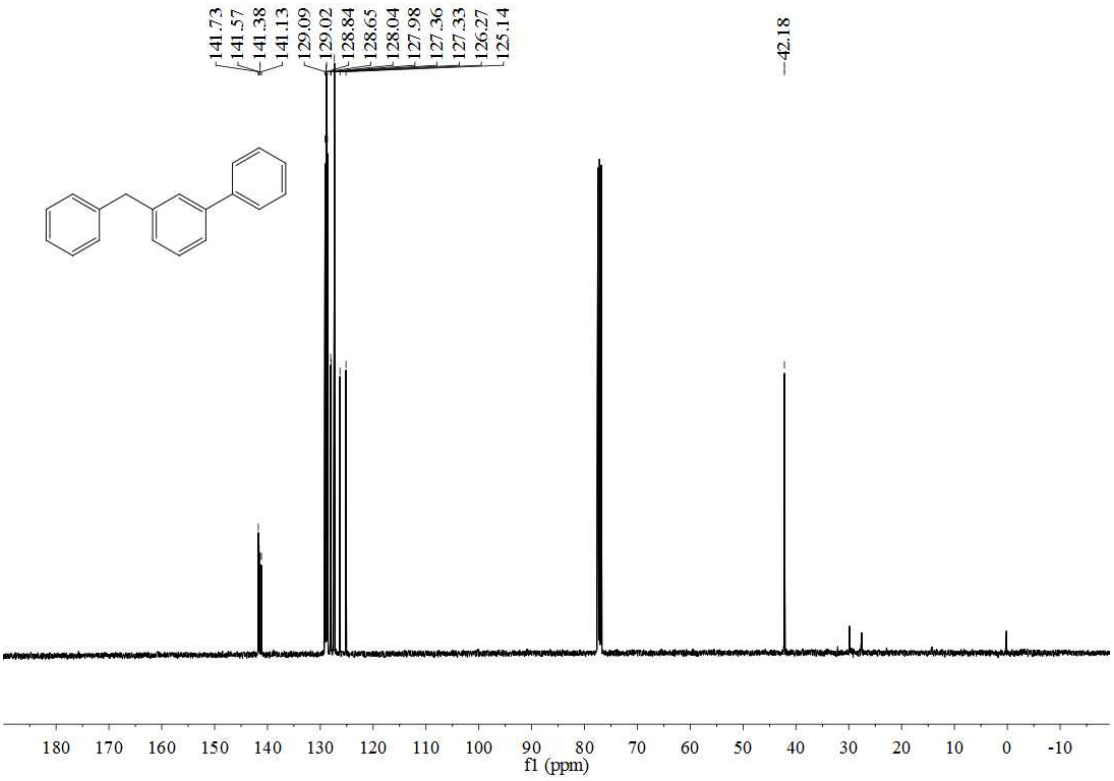
5. 4-benzyl-1,1'-biphenyl



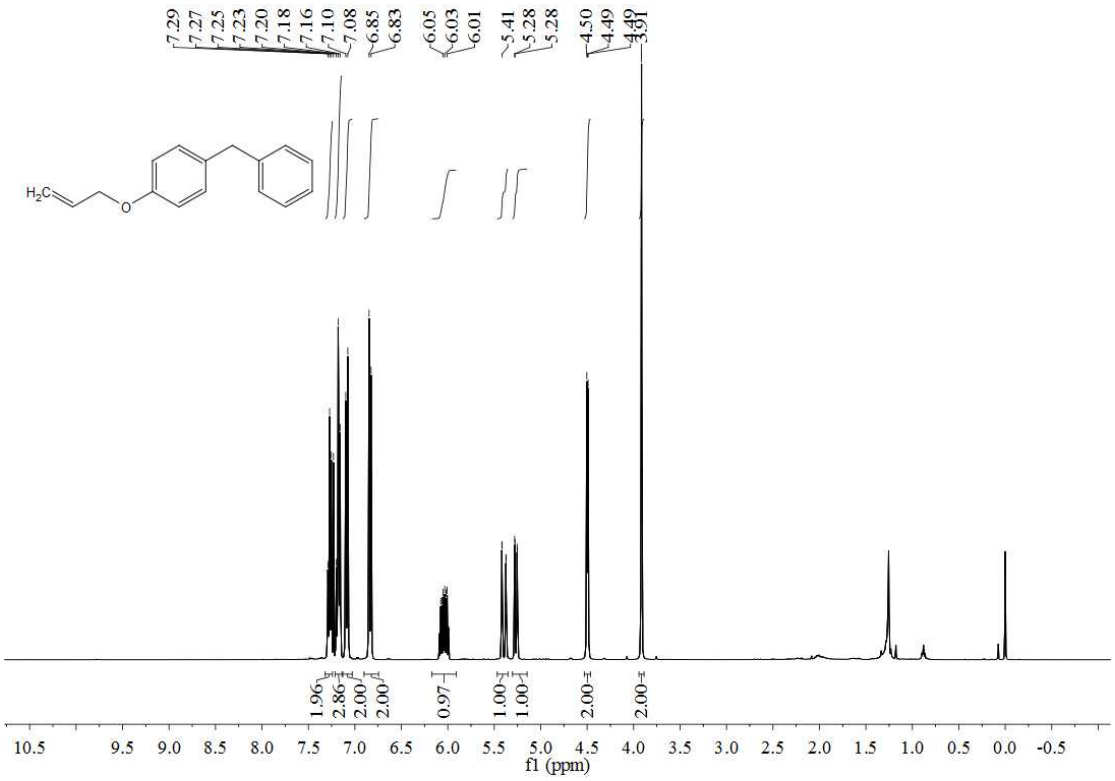


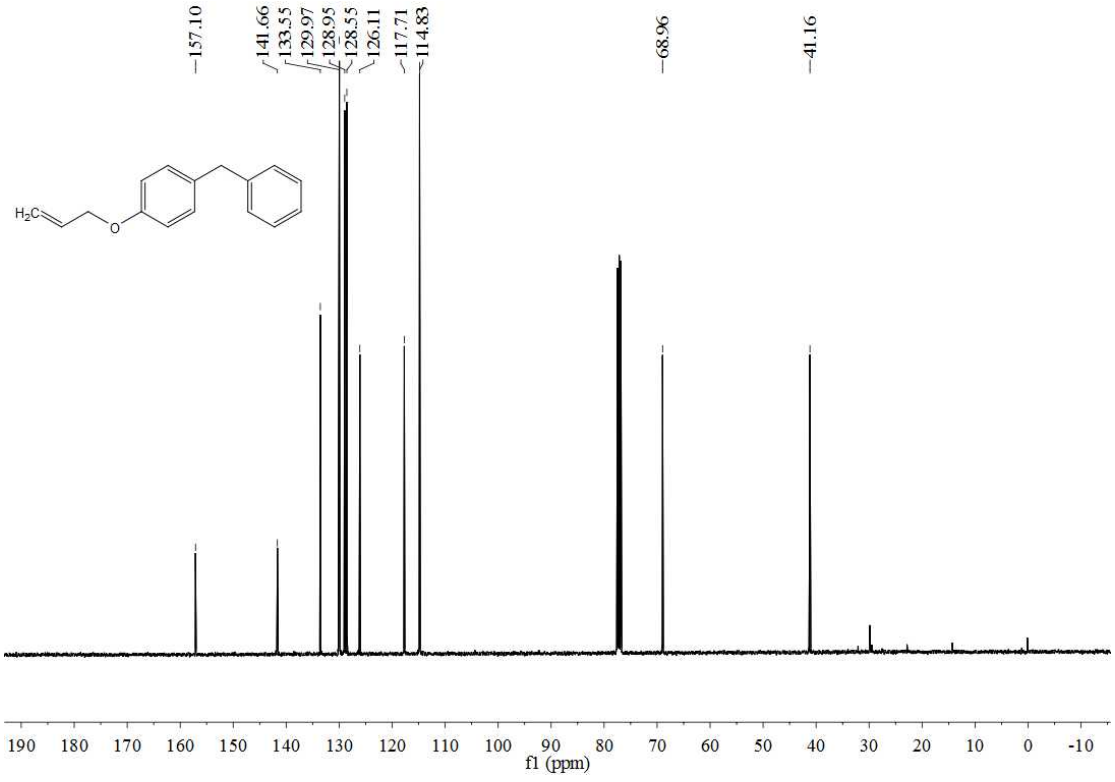
6. 3-benzyl-1, 1'-biphenyl



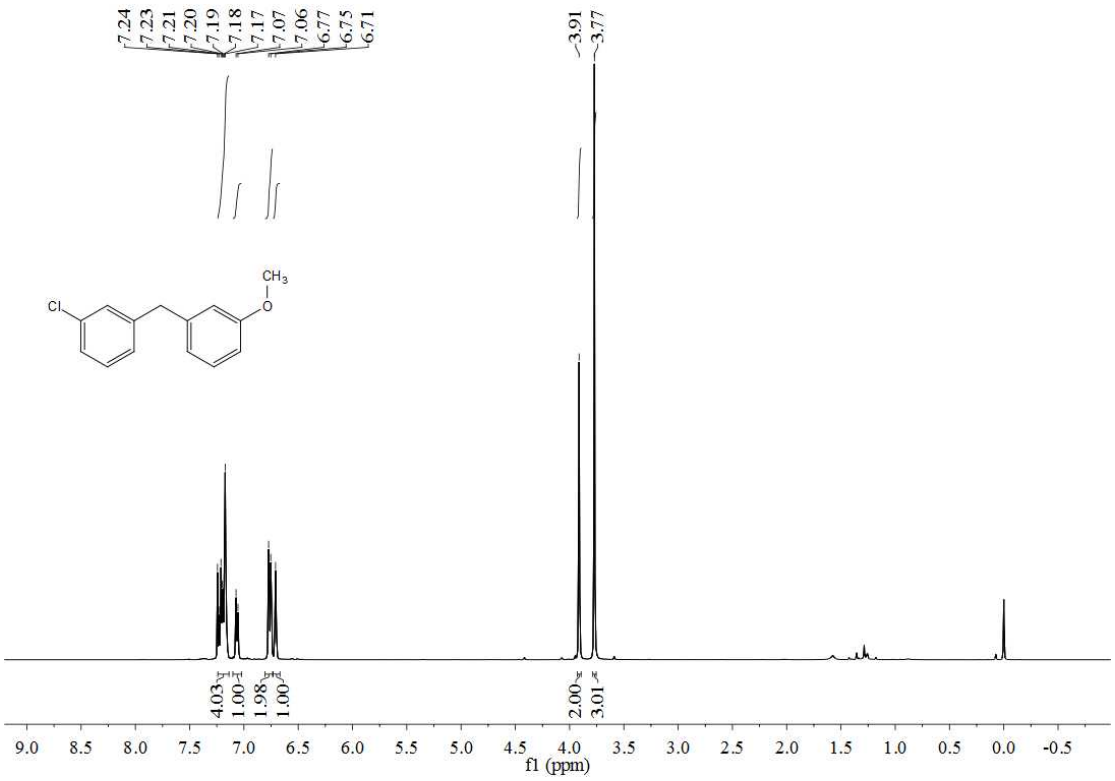


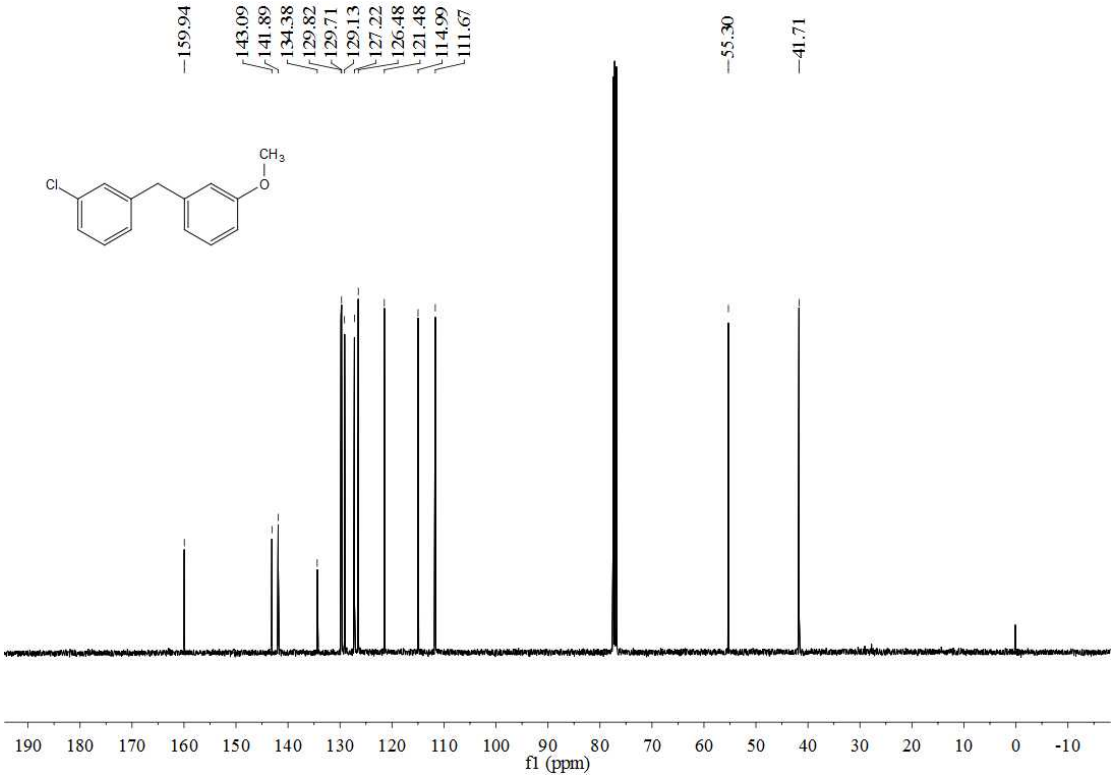
7. 1-(allyloxy)-4-benzylbenzene



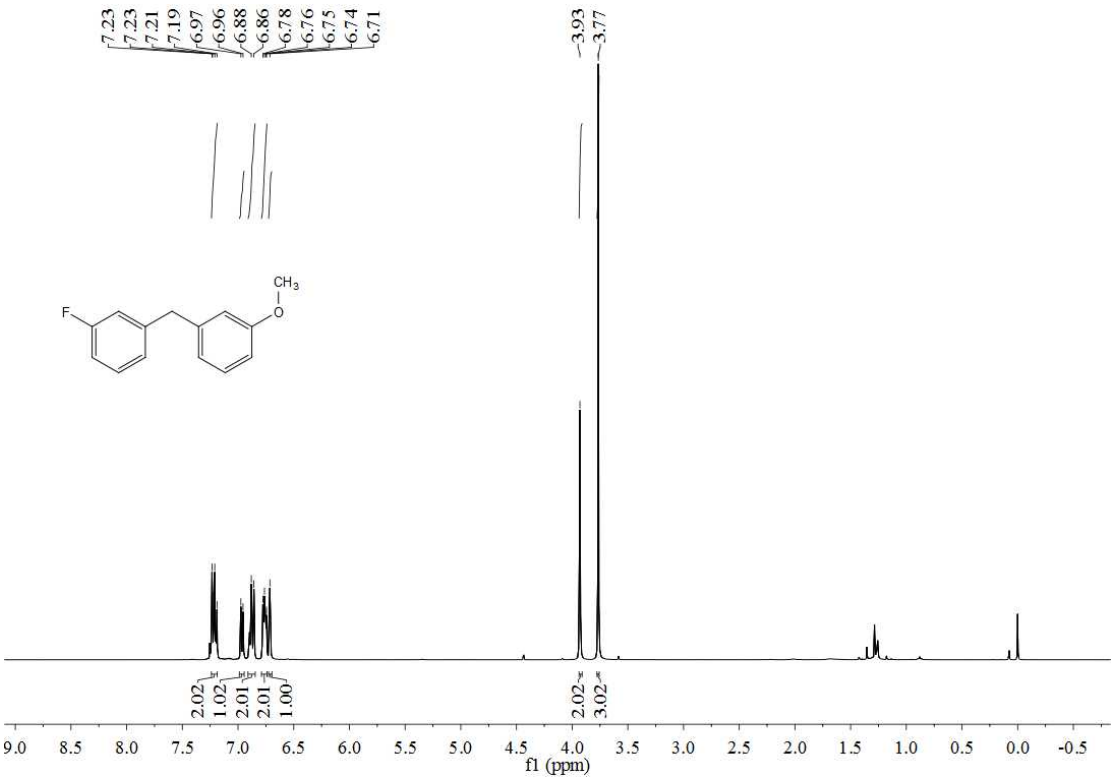


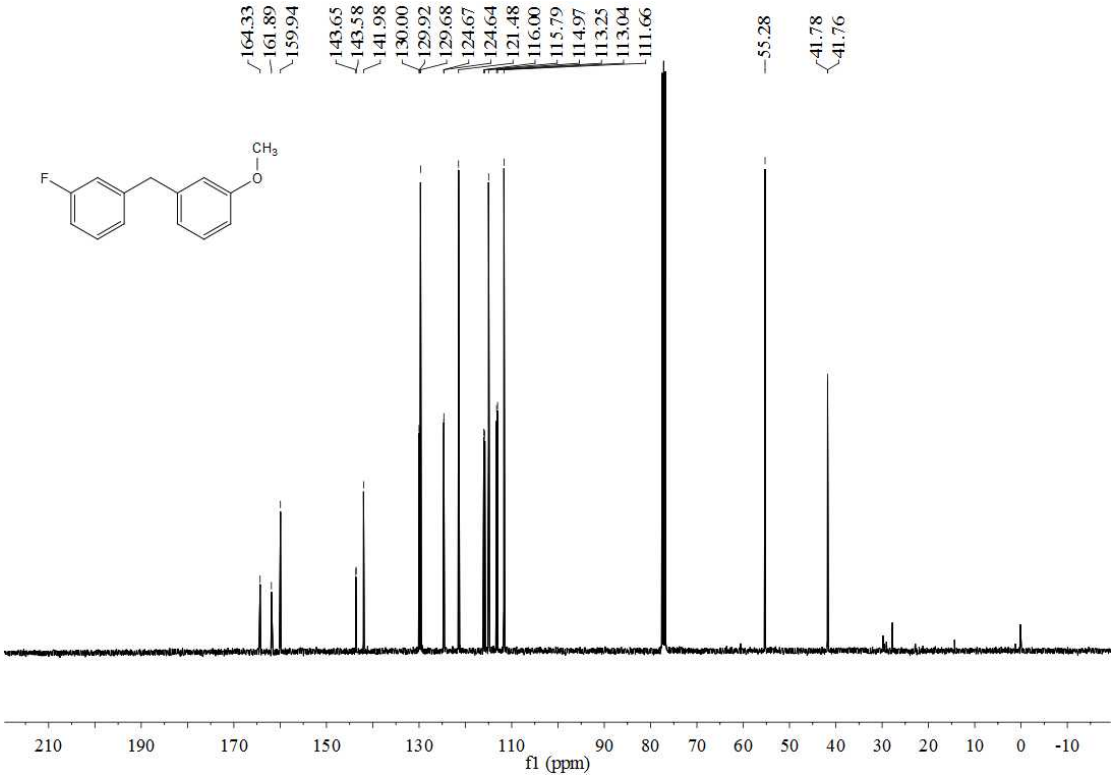
8. 1-chloro-3-(3-methoxybenzyl)benzene





9. 1-fluoro-3-(3-methoxybenzyl)benzene


7.23
7.23
7.21
7.19
6.97
6.96
6.88
6.86
6.78
6.76
6.75
6.74
6.71
3.93
3.77
F
CH3
O
2.02
1.02
2.01
2.01
1.00
2.02
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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159.94
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129.92
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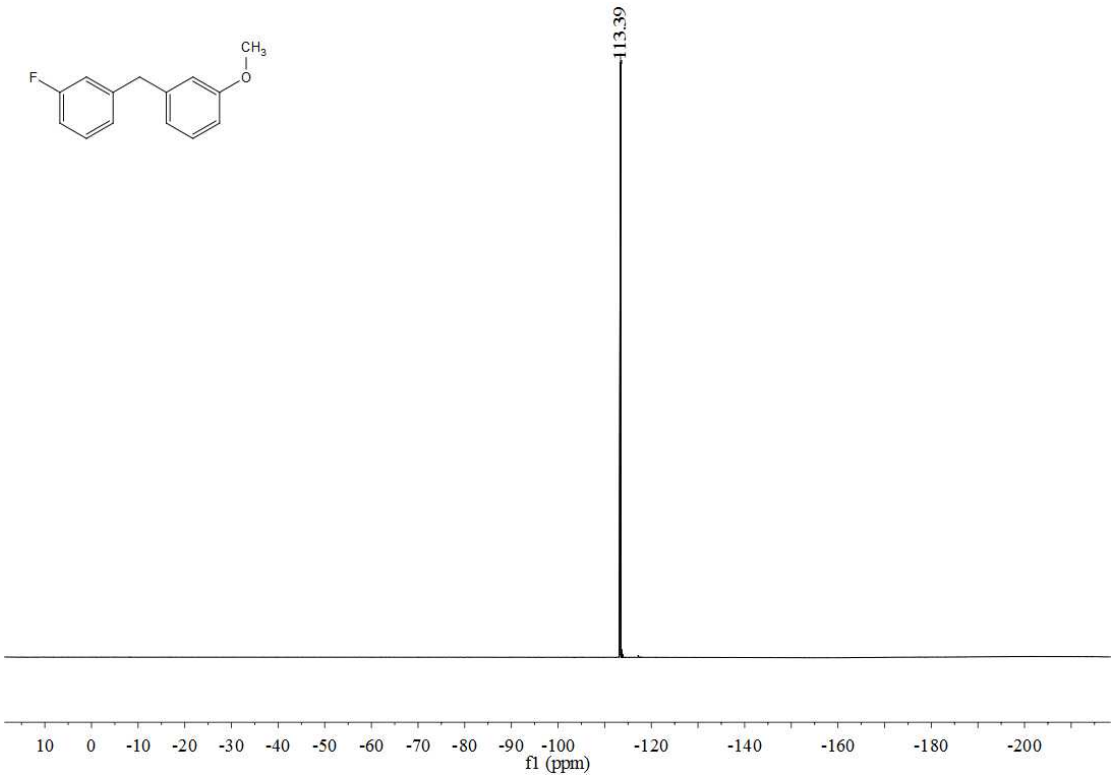
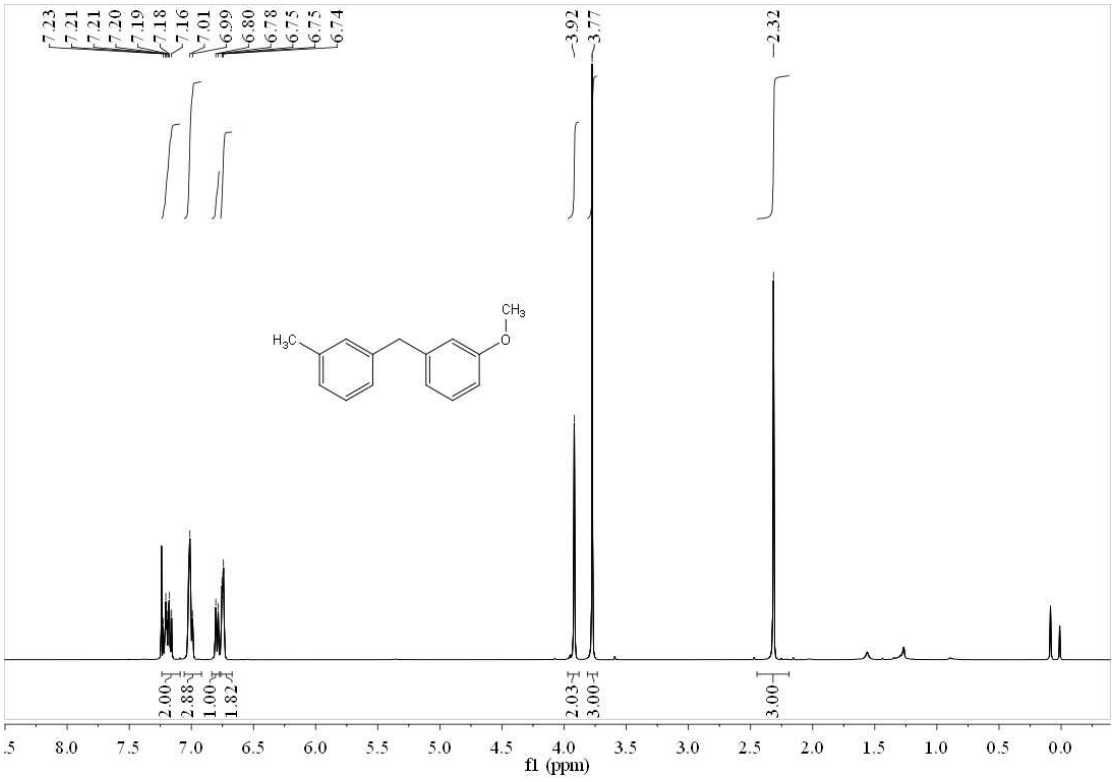
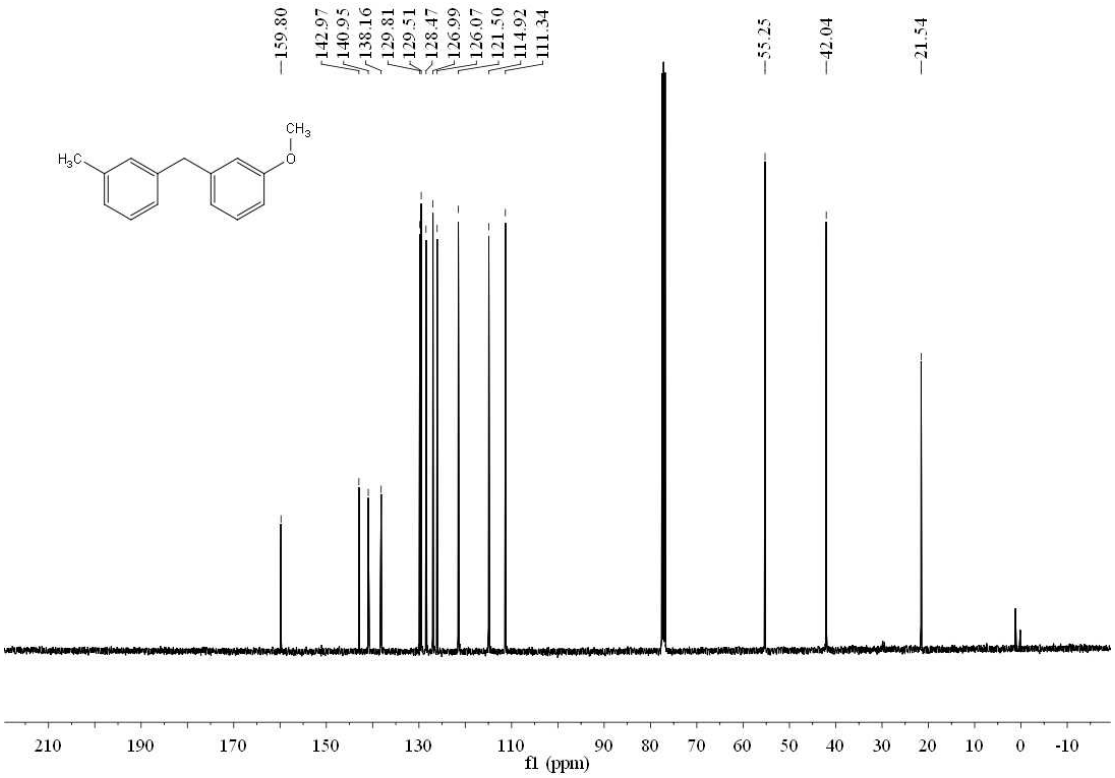
124.67
124.64
121.48
116.00
115.79
114.97
113.25
113.04
111.66
55.28
41.78
41.76
F
CH3
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

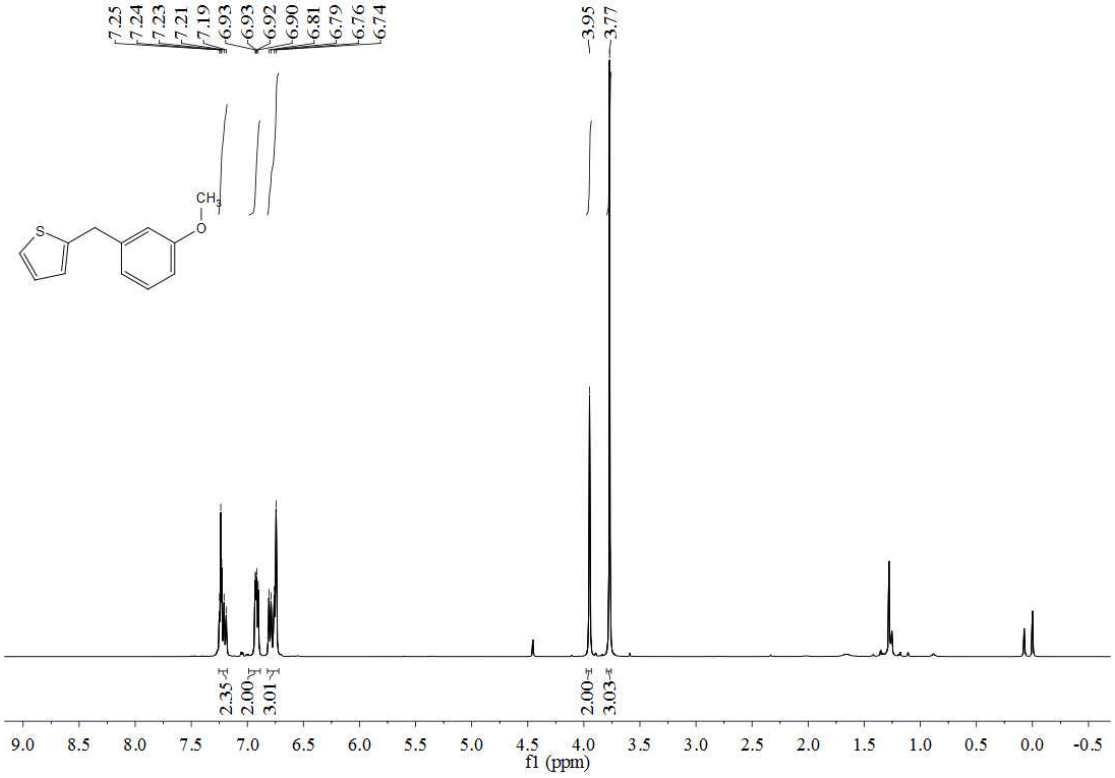


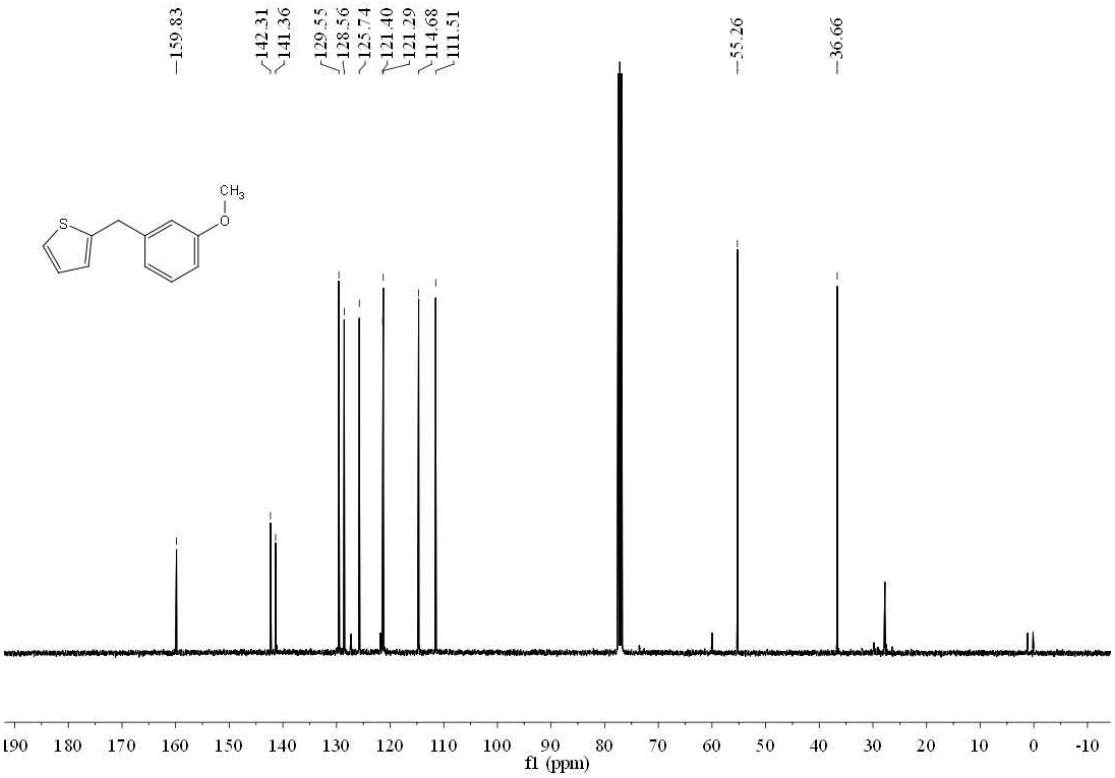
10.1-methoxy-3-(3-methylbenzyl)benzene



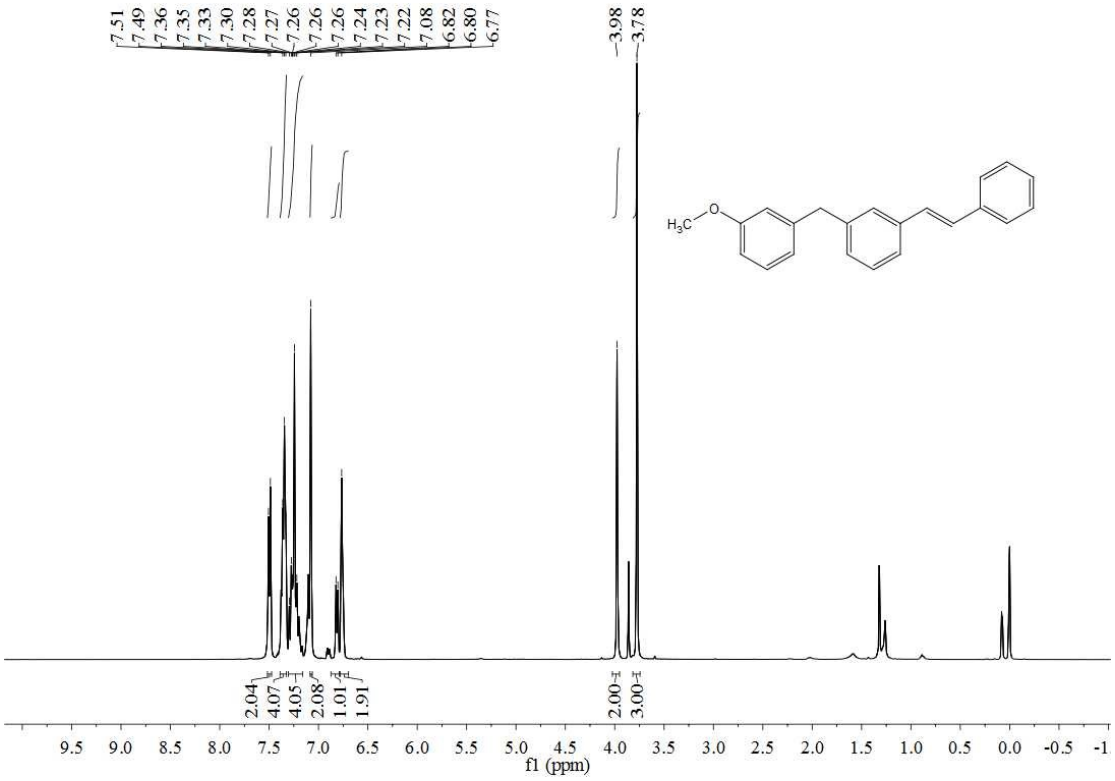


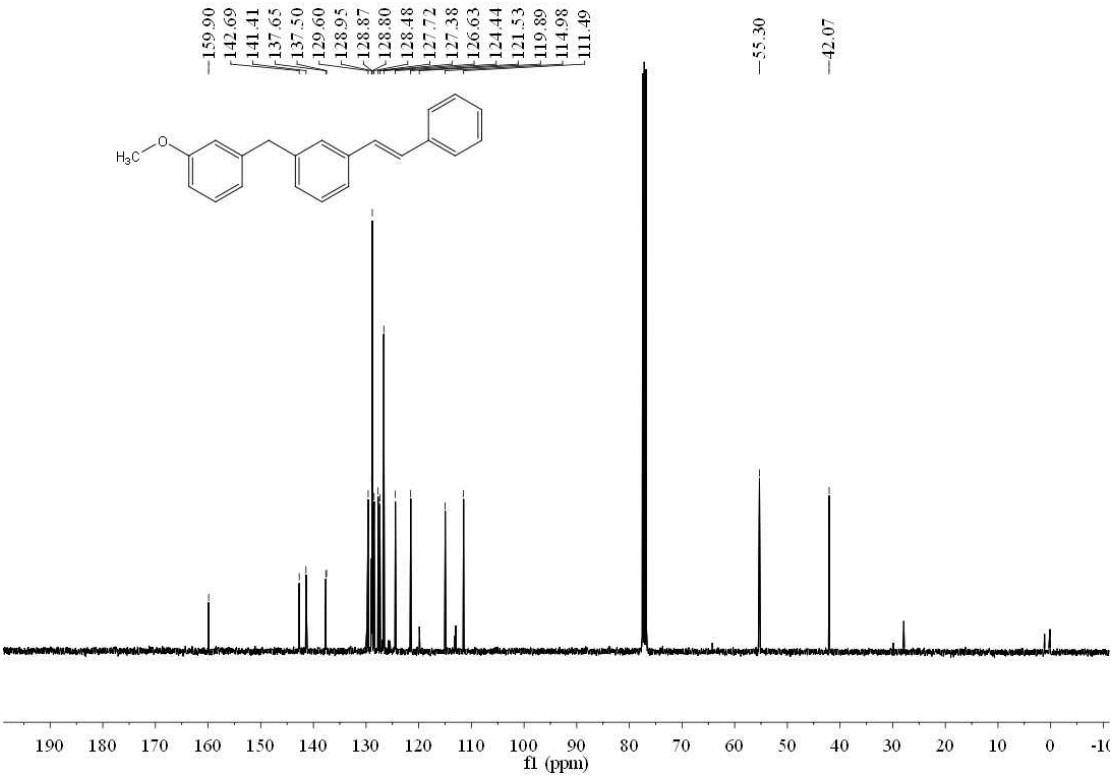
11. 2-(3-methoxybenzyl)thiophene



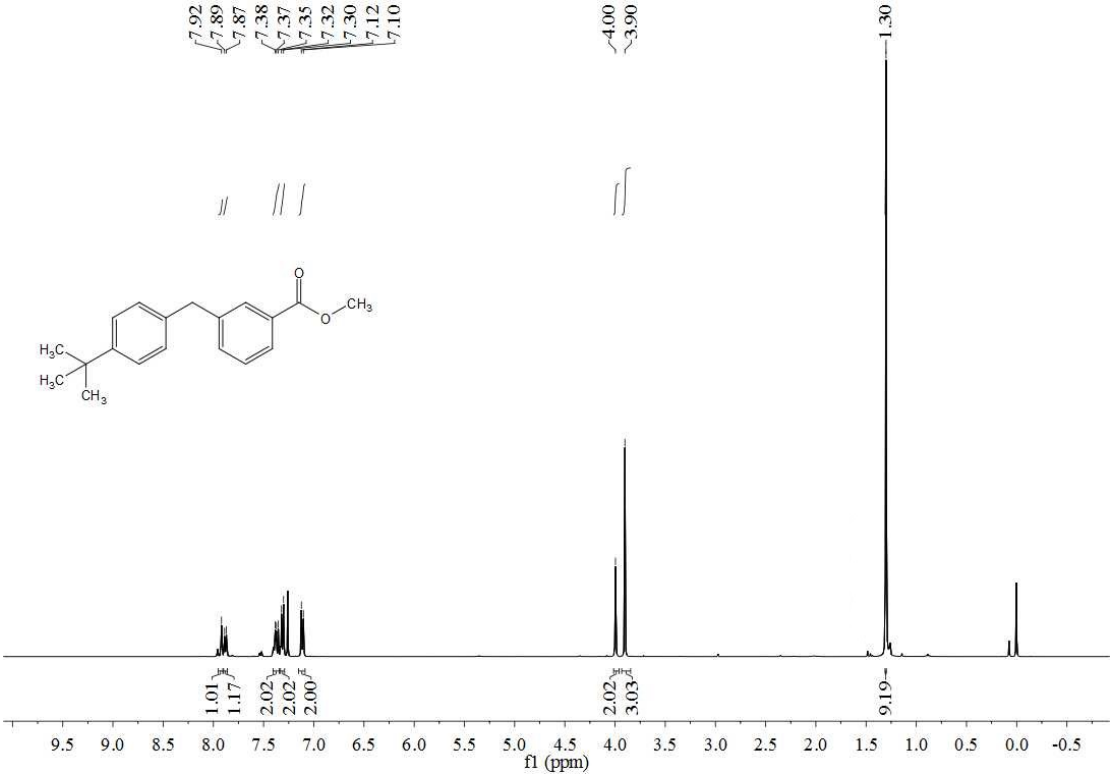


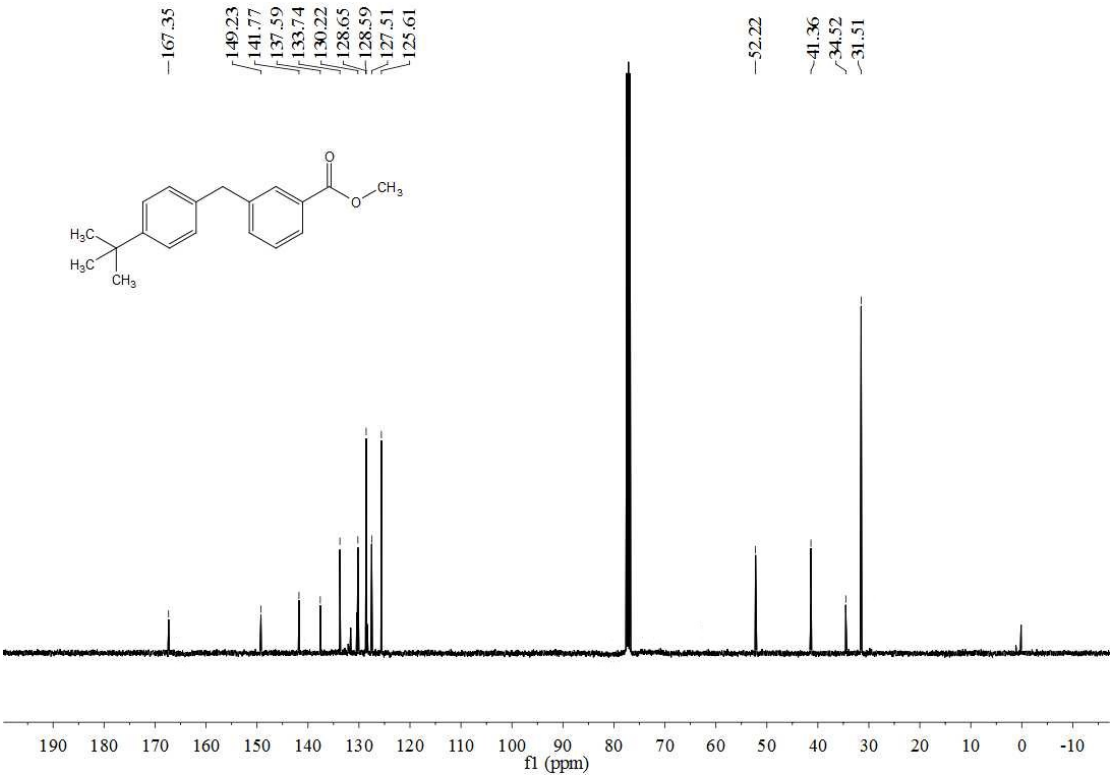
12. (E)-1-methoxy-3-(3-styrylbenzyl)benzene



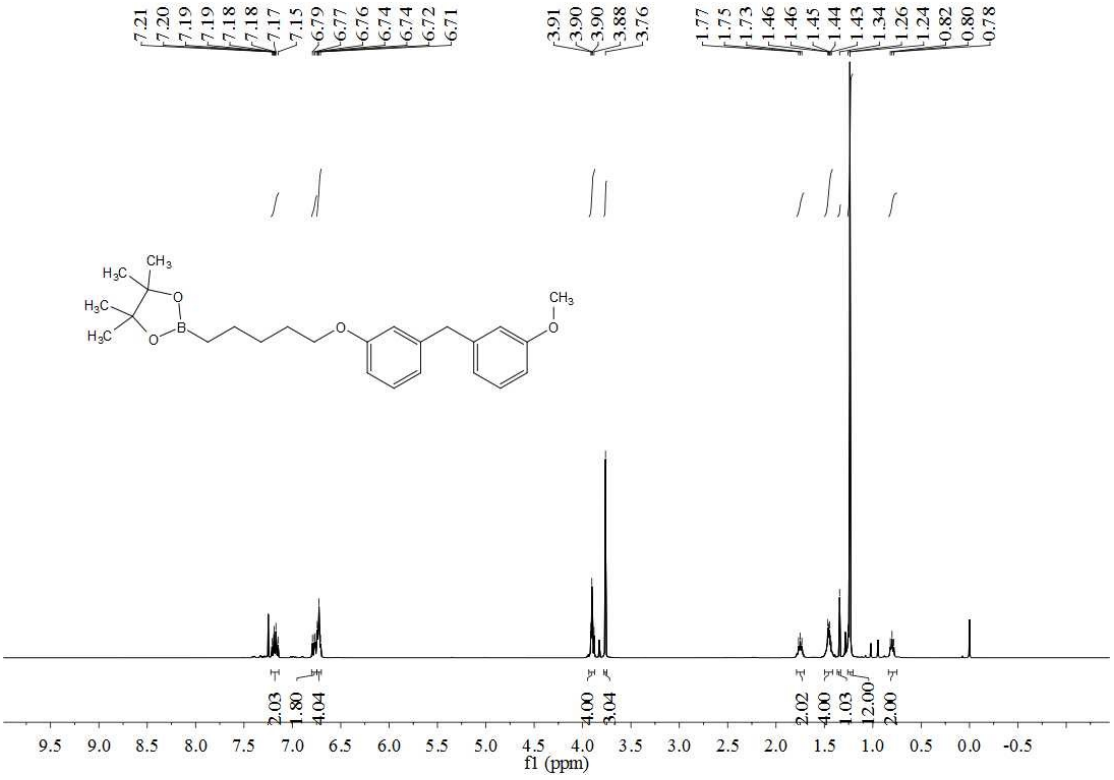


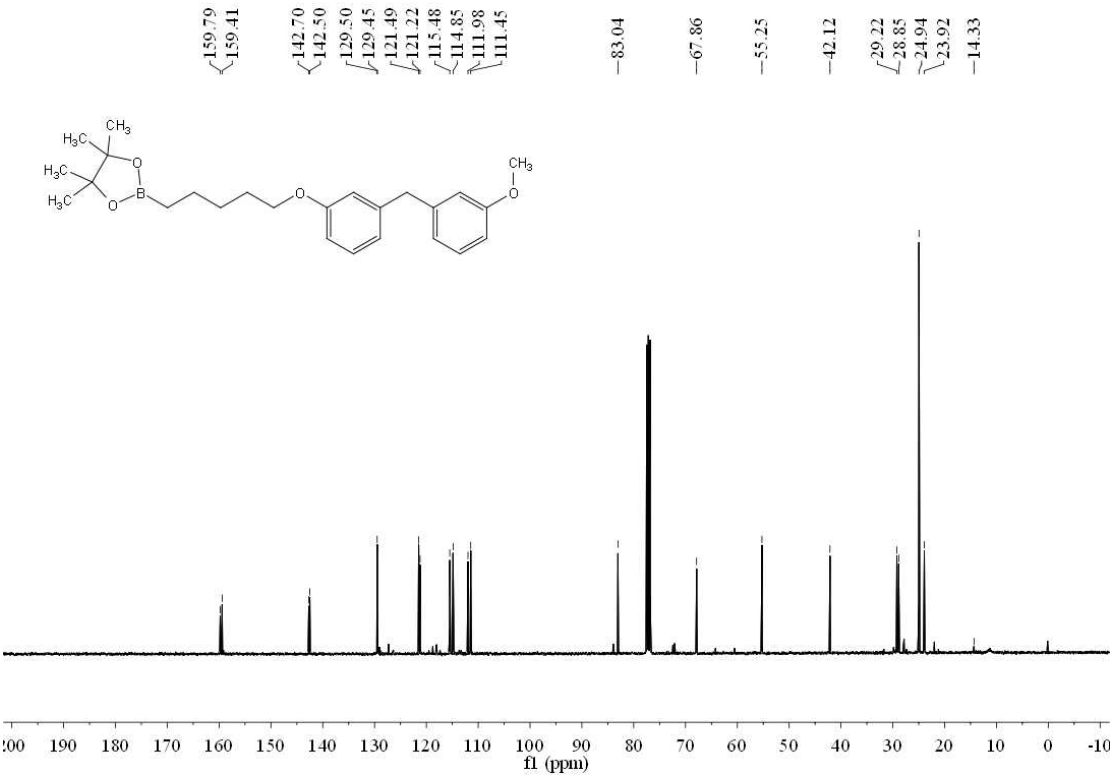
13. methyl 3-(4-(tert-butyl)benzyl)benzoate



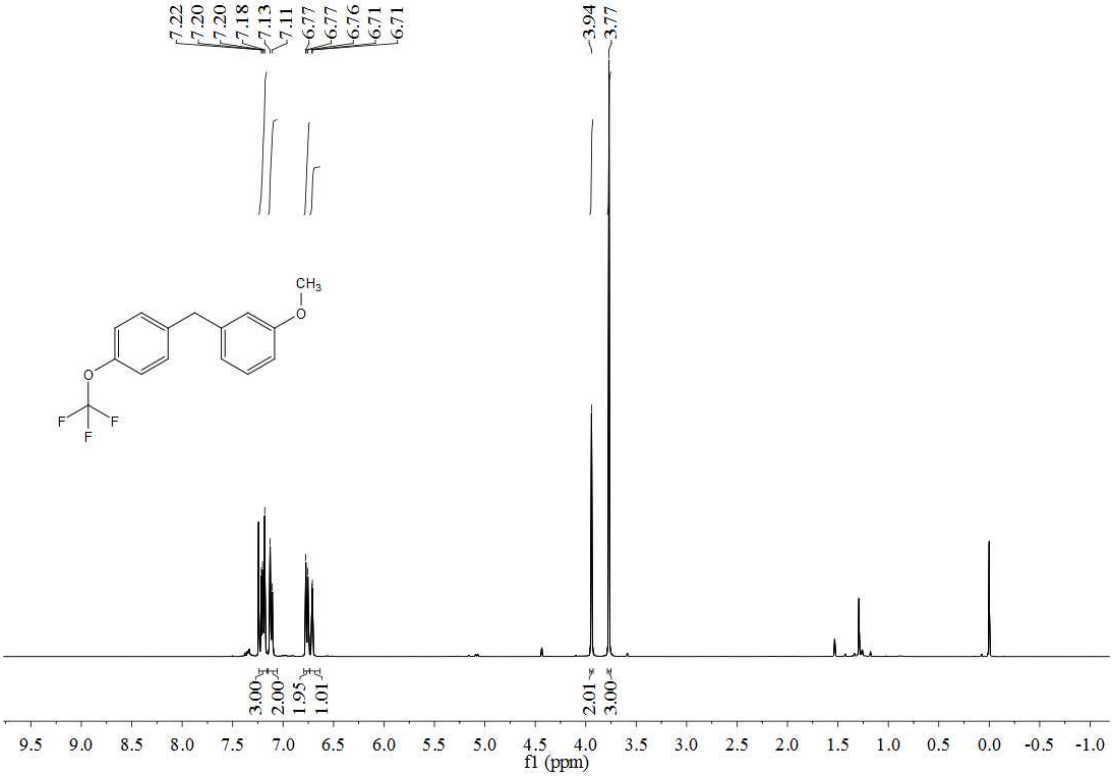


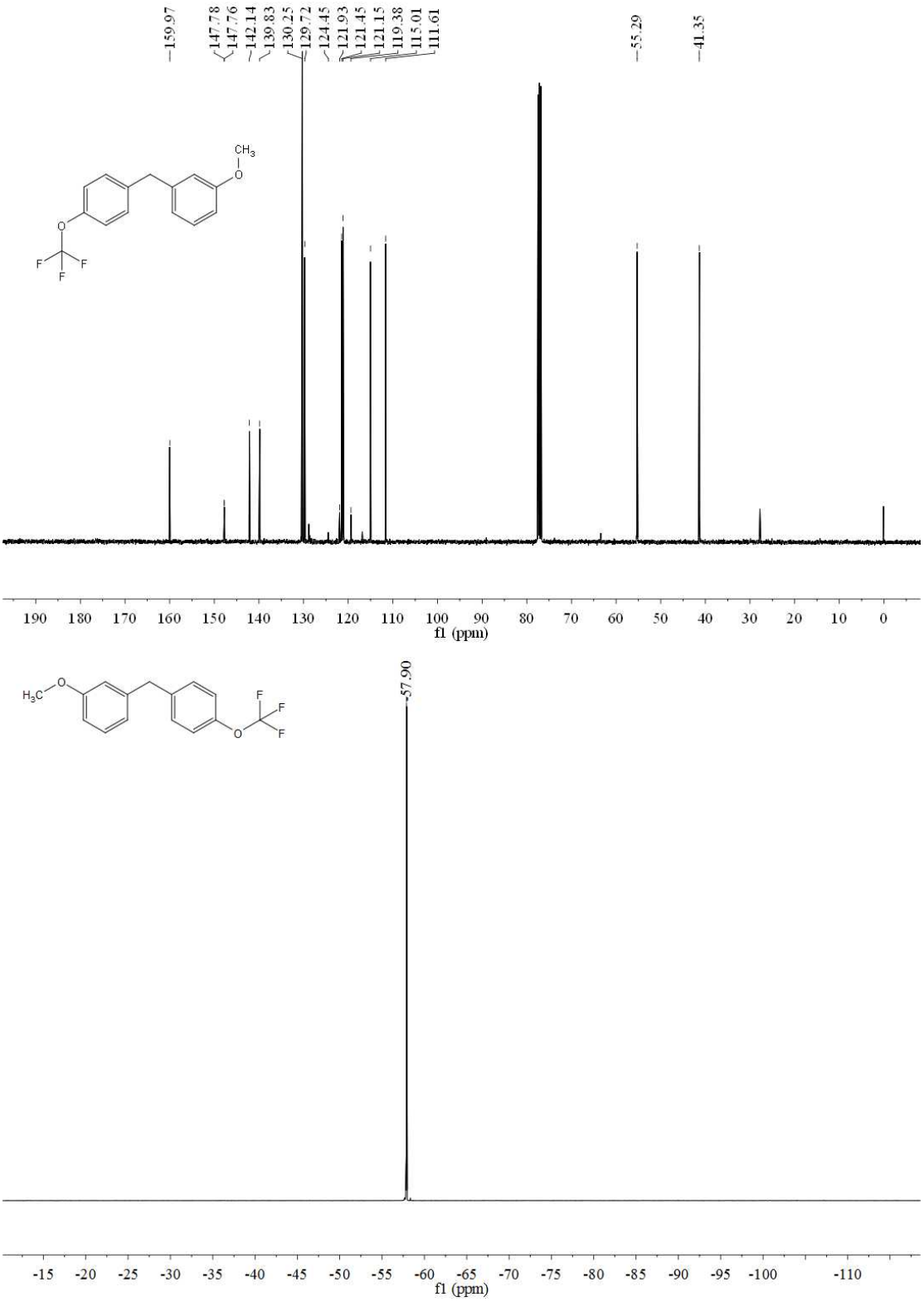
14. 2-(5-(3-(3-methoxybenzyl)phenoxy)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



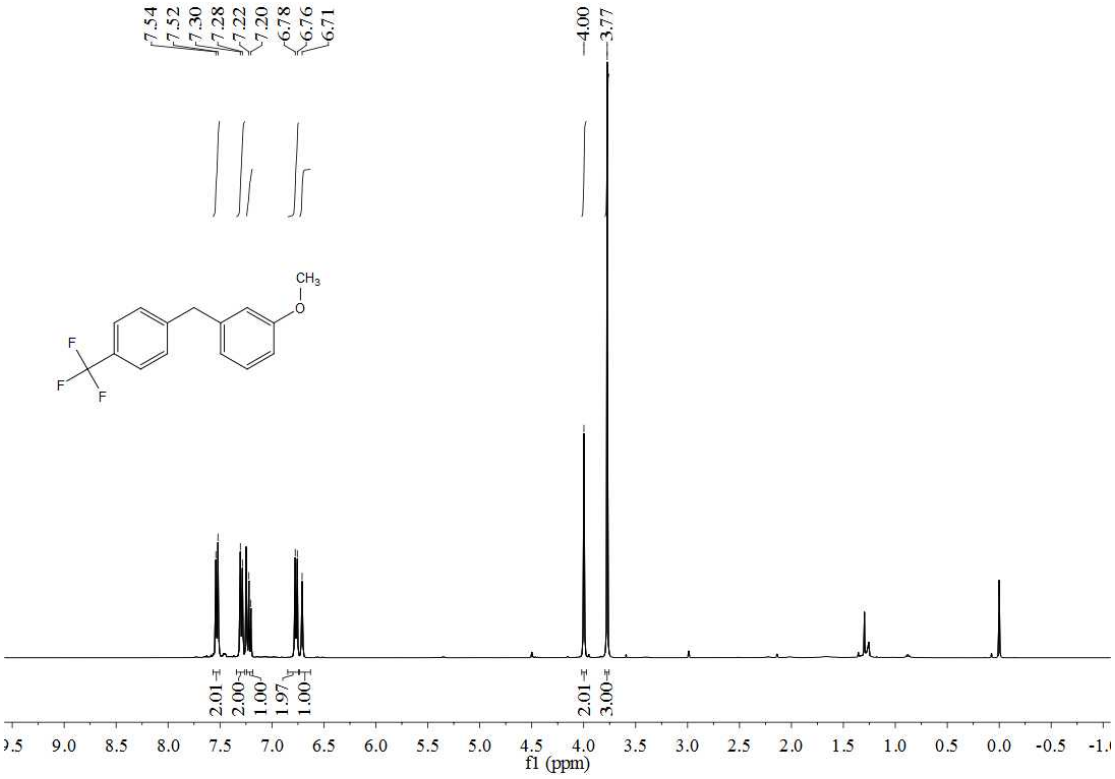


15. 1-methoxy-3-(4-(trifluoromethoxy)benzyl)benzene





16. 1-methoxy-3-(4-(trifluoromethyl)benzyl)benzene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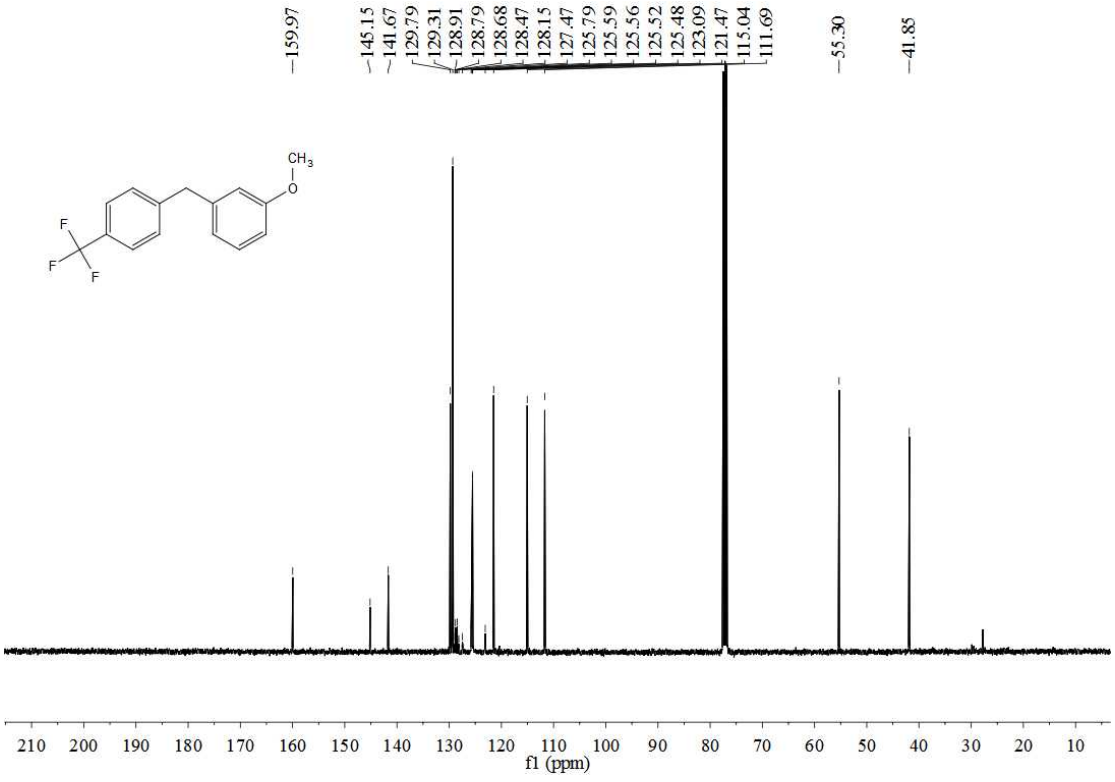
7.52
7.30
7.28
7.22
7.20
6.78
6.76
6.71
4.00
3.77
CH3
O
F
F
F
2.01
2.00
1.00
1.97
1.00
2.01
3.00
f1 (ppm)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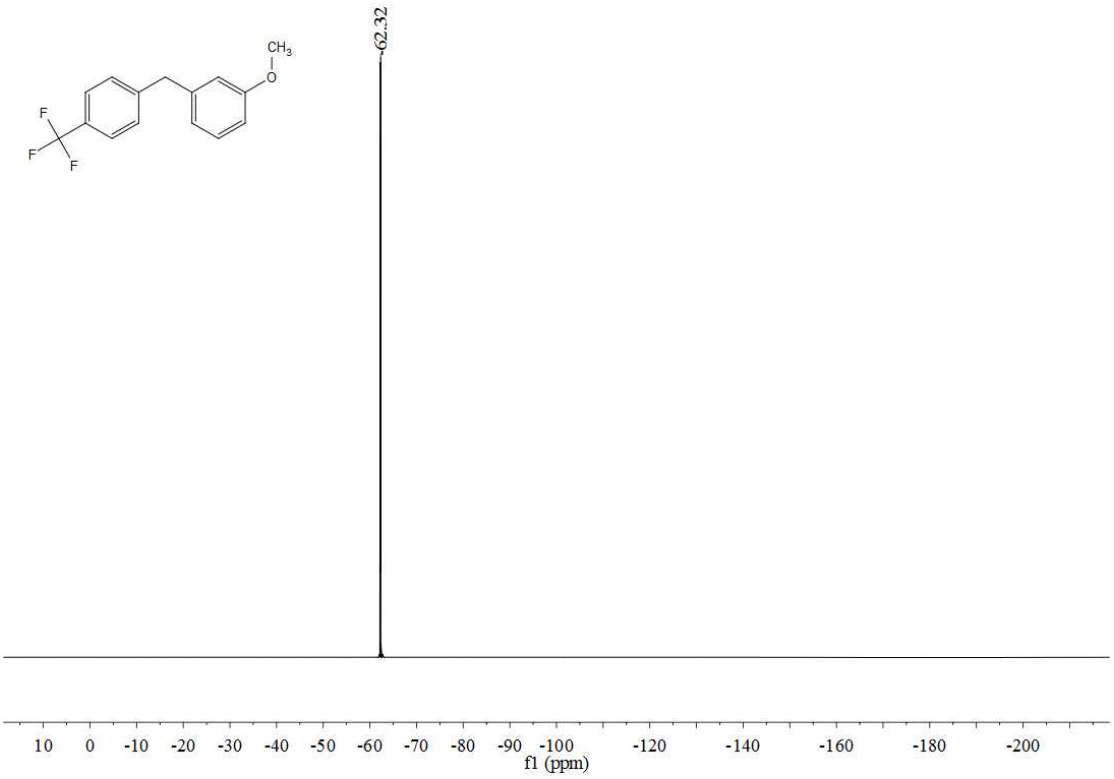
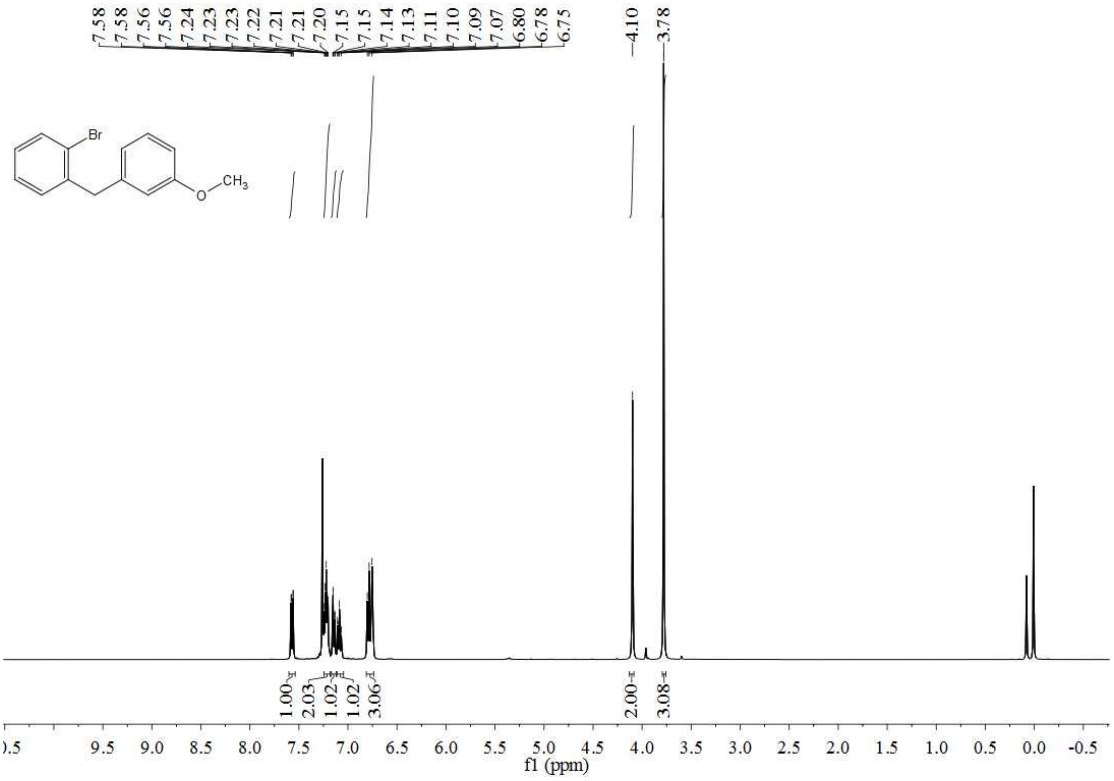
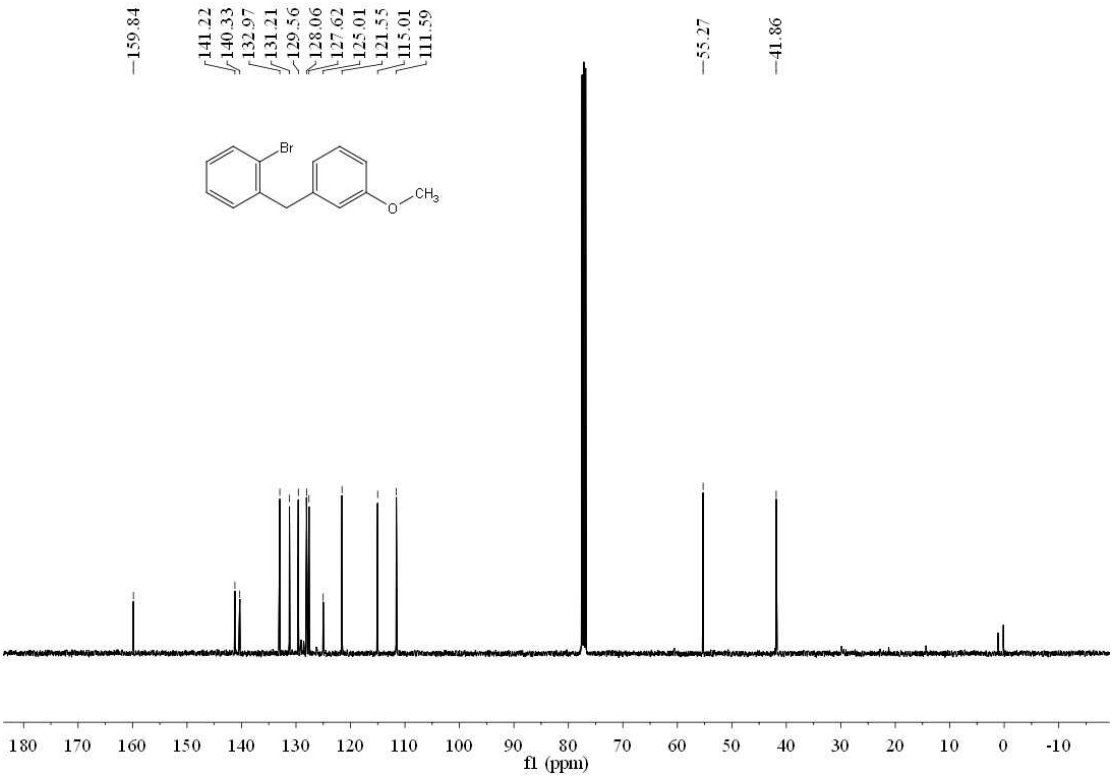
145.15
141.67
129.79
129.31
128.91
128.79
128.68
128.47
128.15
127.47
125.79
125.59
125.56
125.52
125.48
123.09
121.47
115.04
111.69
55.30
41.85
CH3
O
F
F
F
f1 (ppm)

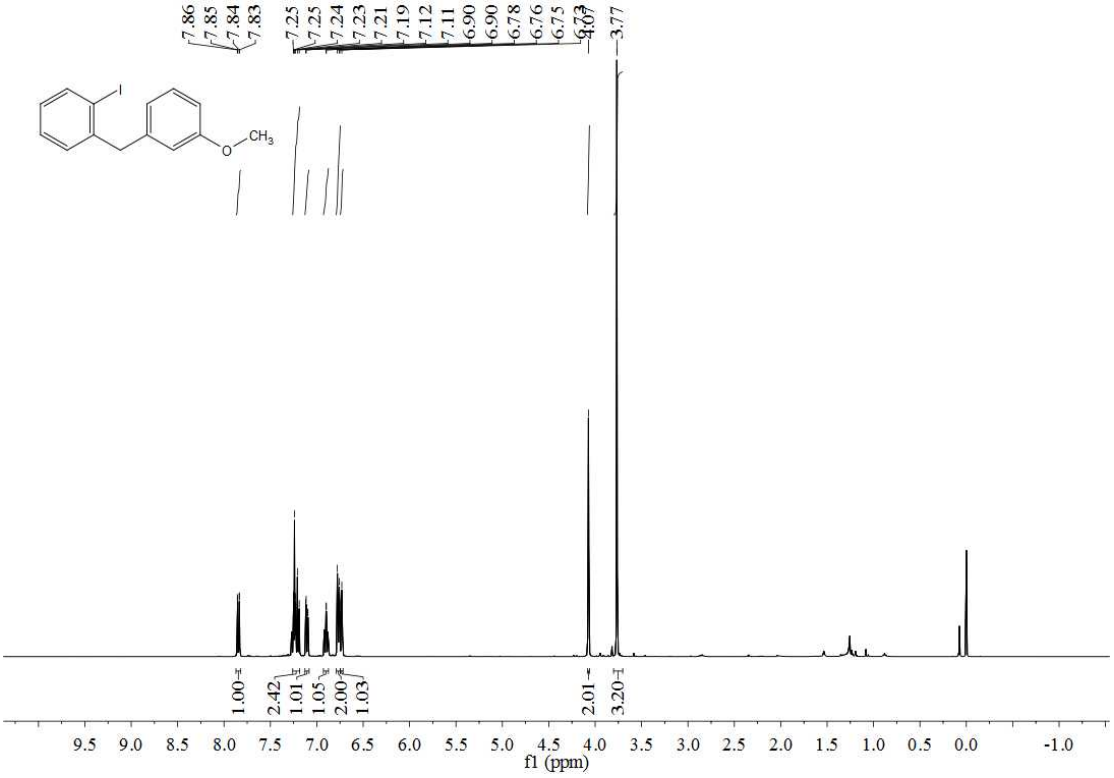


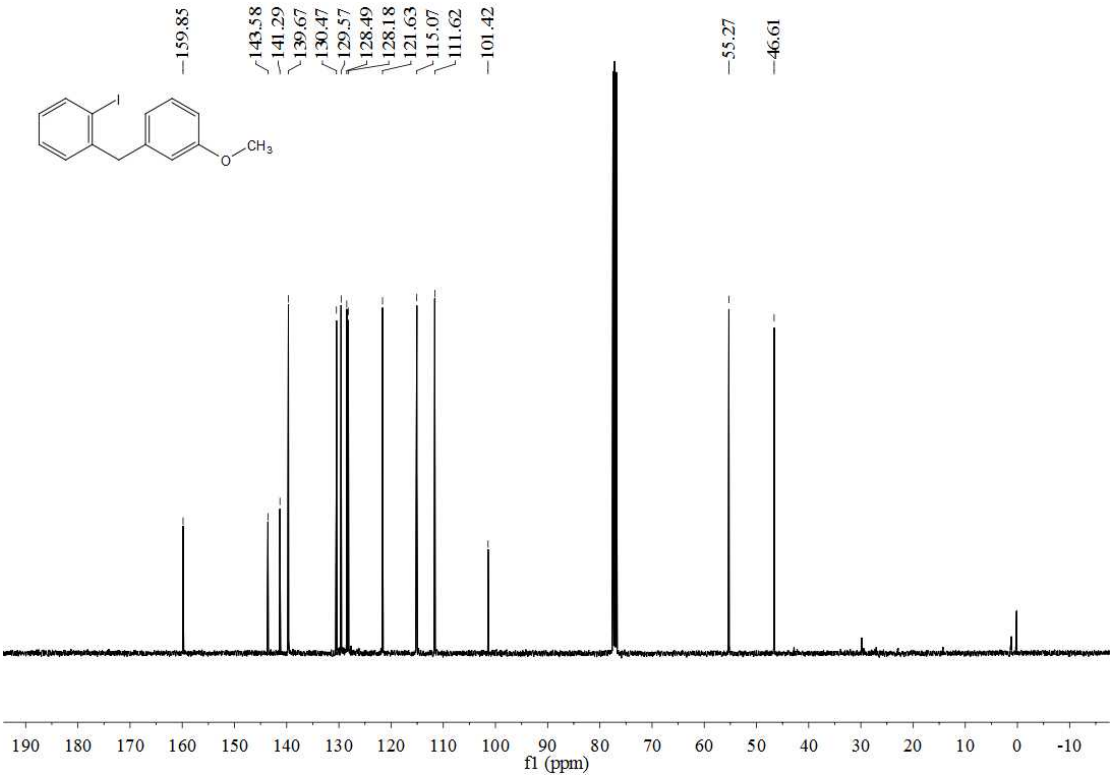
17. 1-bromo-2-(3-methoxybenzyl)benzene



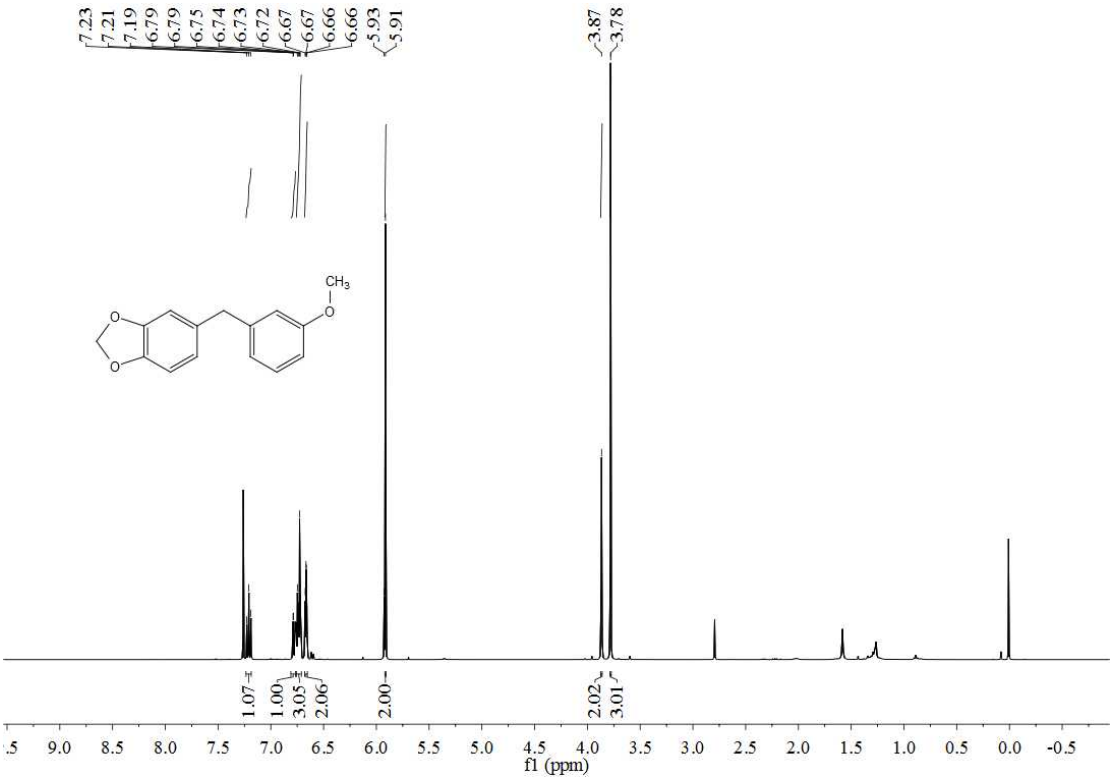


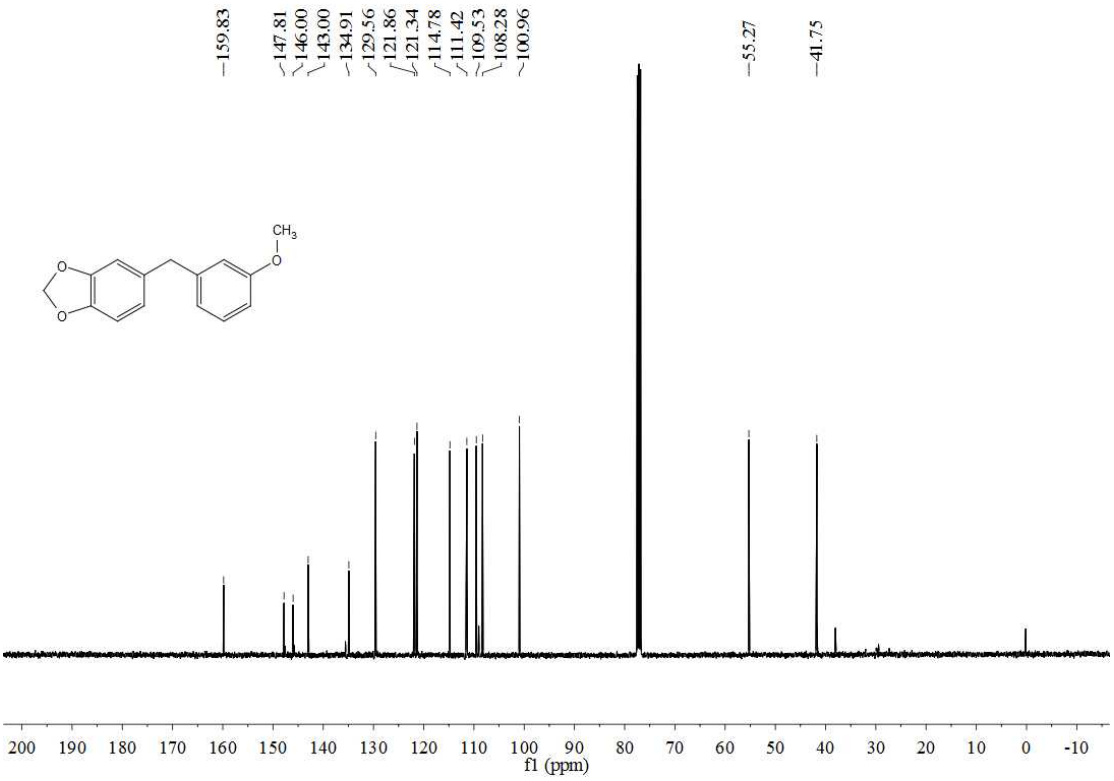
18. 1-iodo-2-(3-methoxybenzyl)benzene



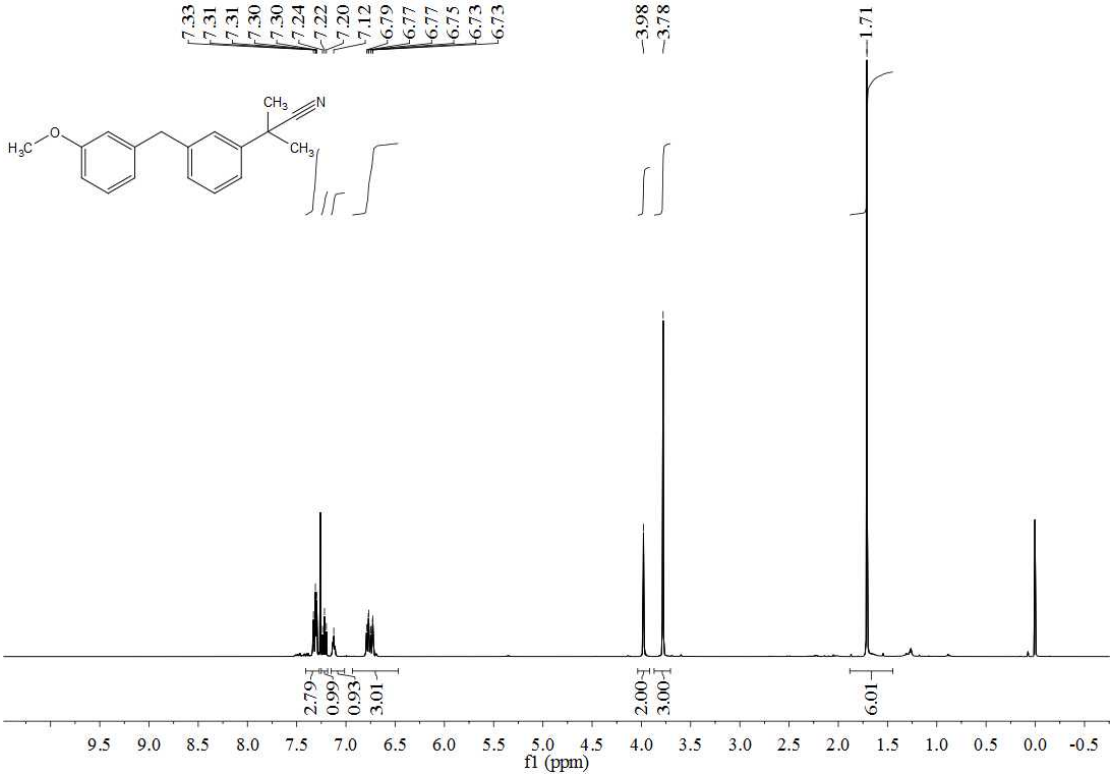


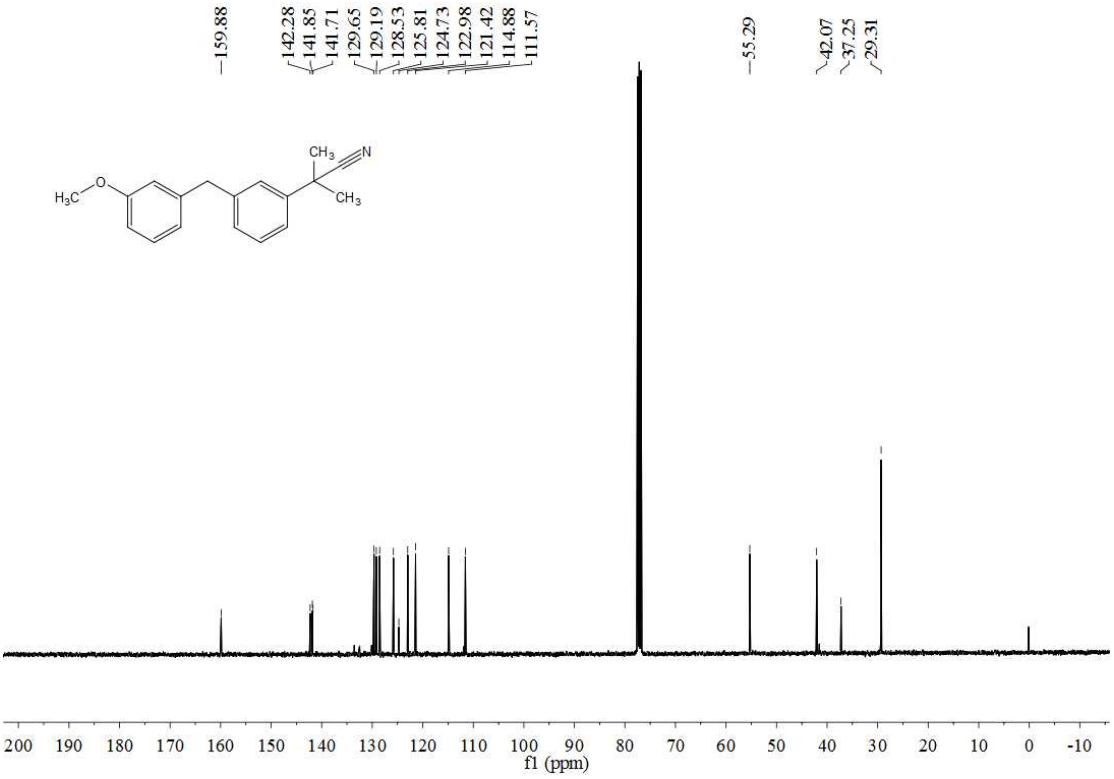
19. 5-(3-methoxybenzyl)benzo[d][1,3]dioxole



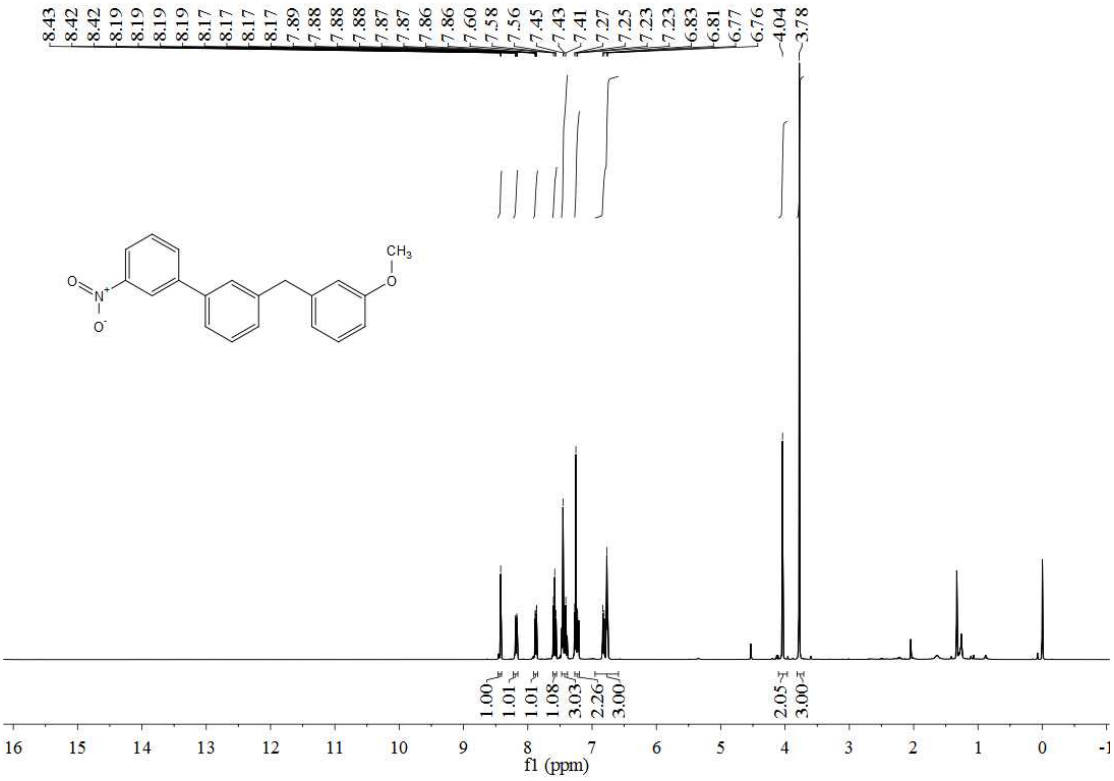


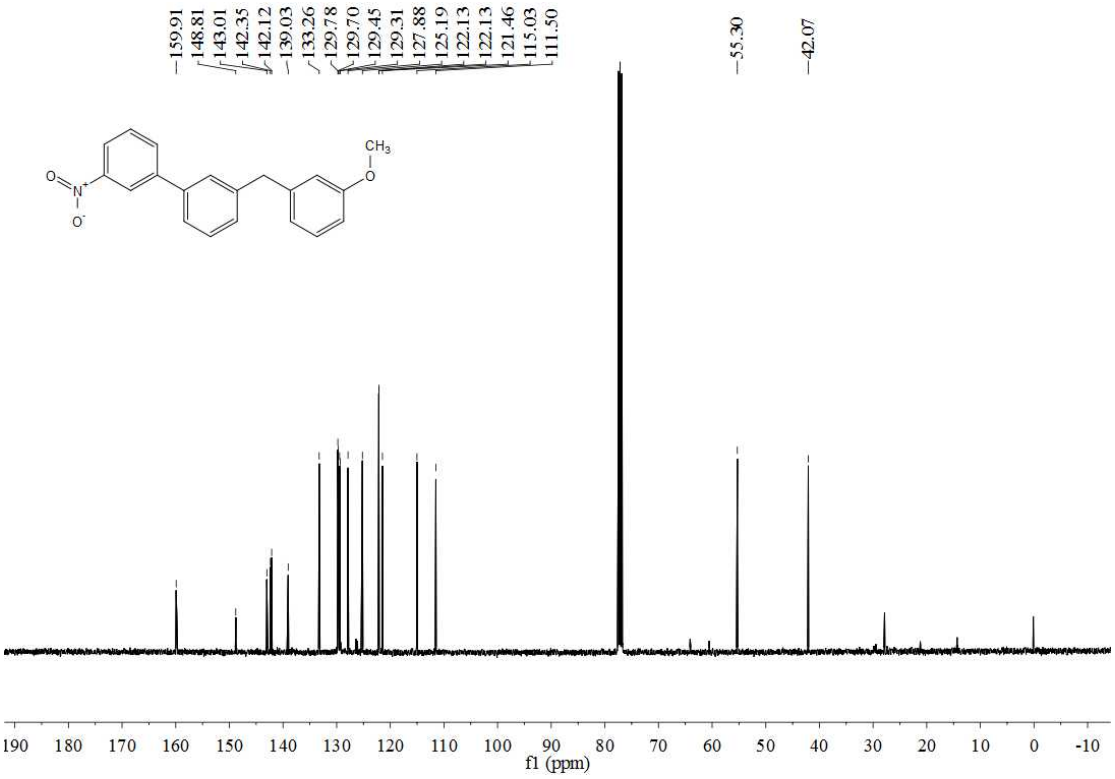
20. 2-(3-(3-methoxybenzyl)phenyl)-2-methylpropanenitrile



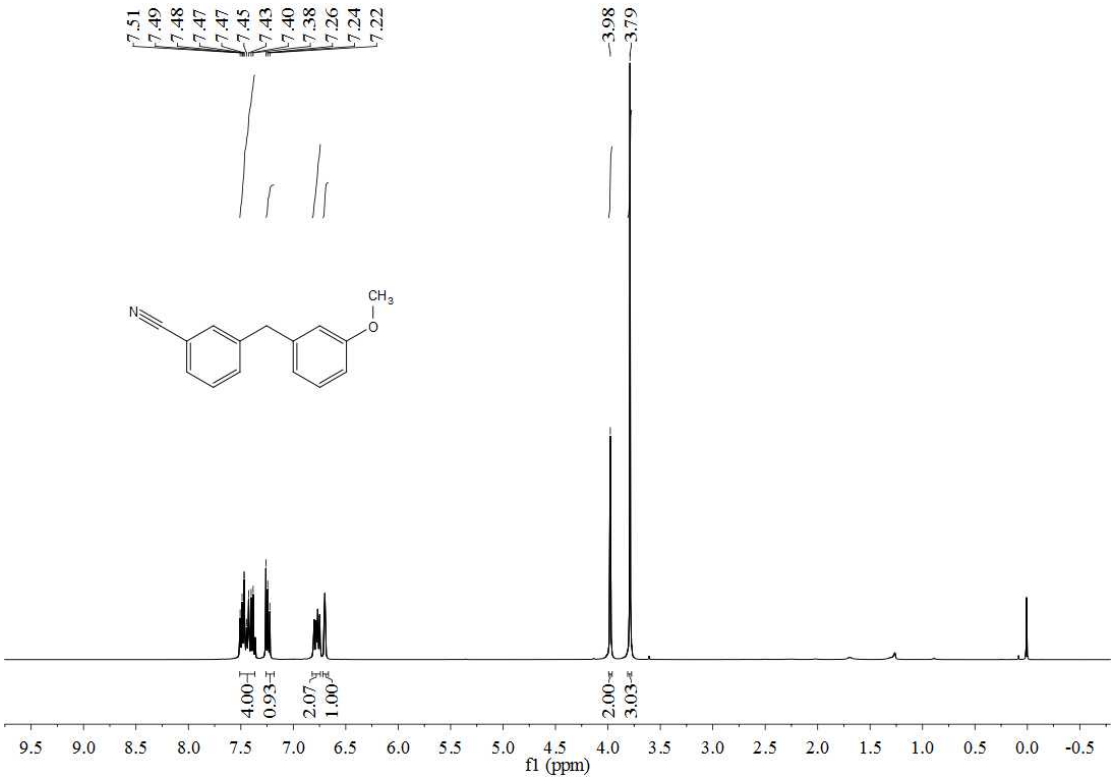


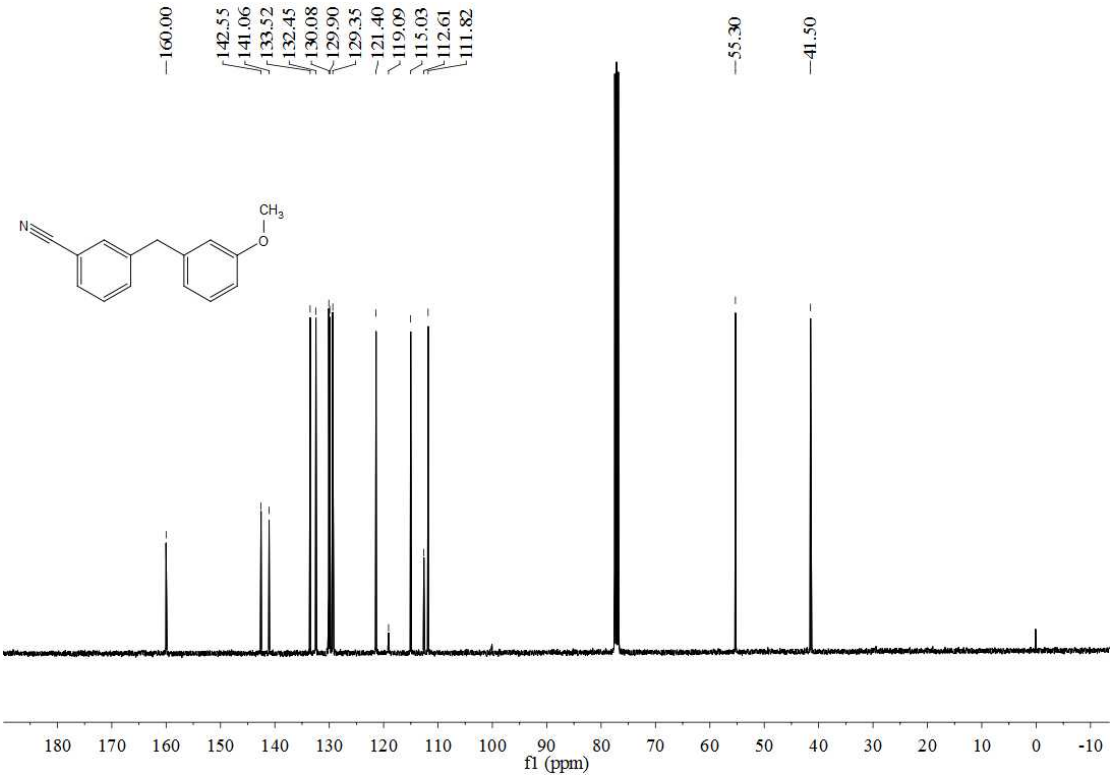
21. 3-(3-methoxybenzyl)-3'-nitro-1,1'-biphenyl



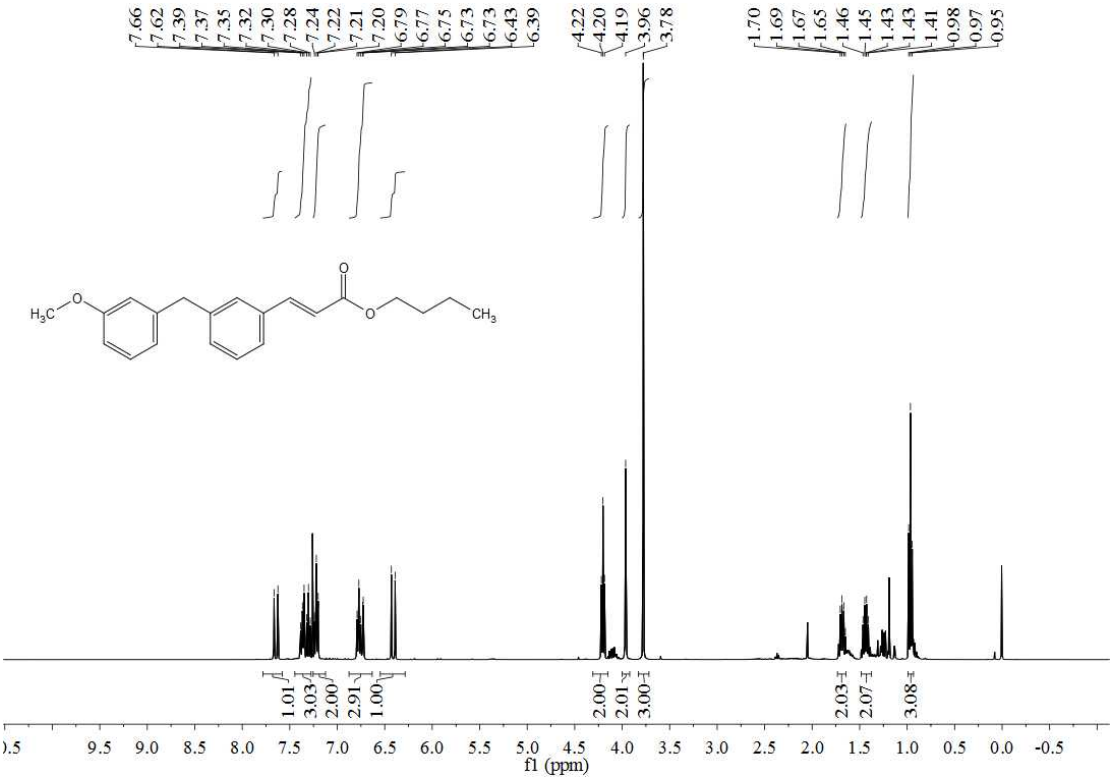


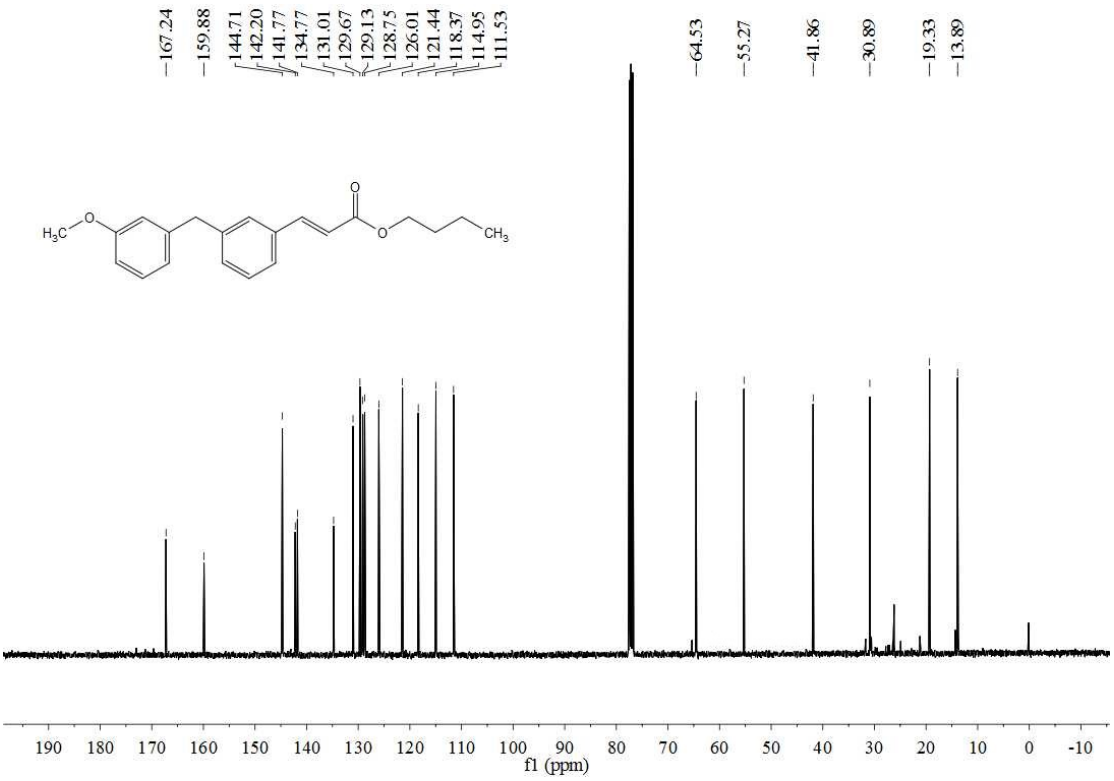
22. 3-(3-methoxybenzyl)benzonitrile



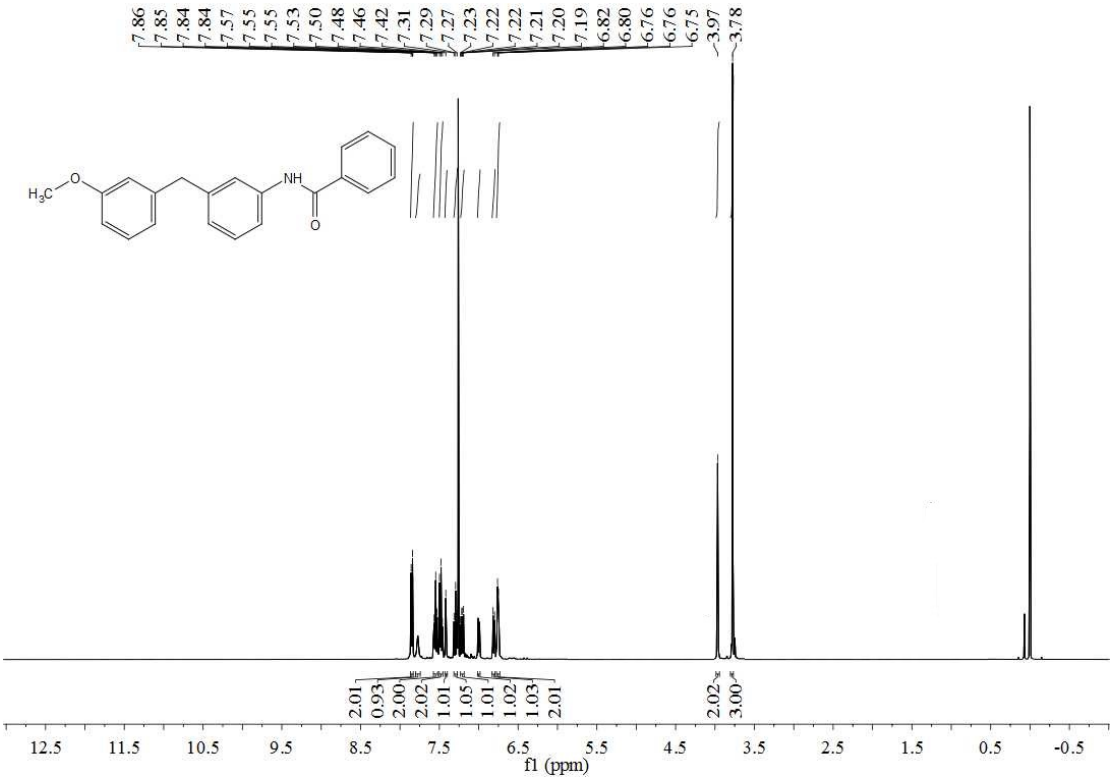


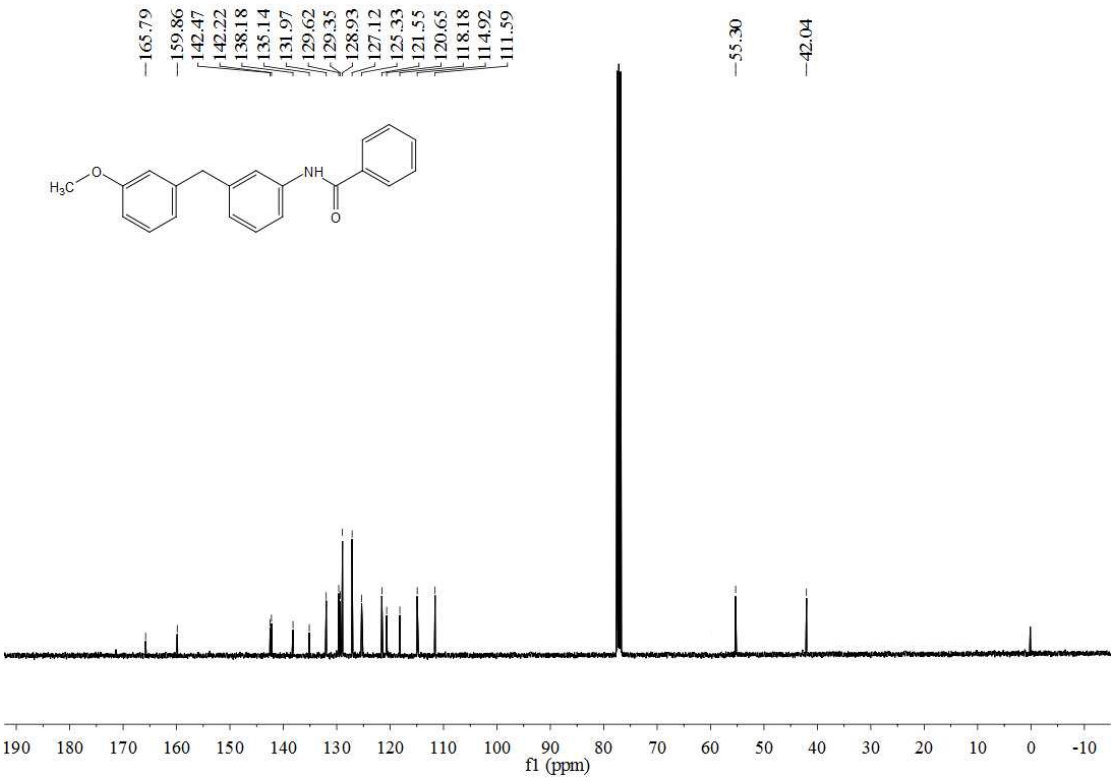
23. (E)-butyl 3-(3-(3-methoxybenzyl)phenyl)acrylate



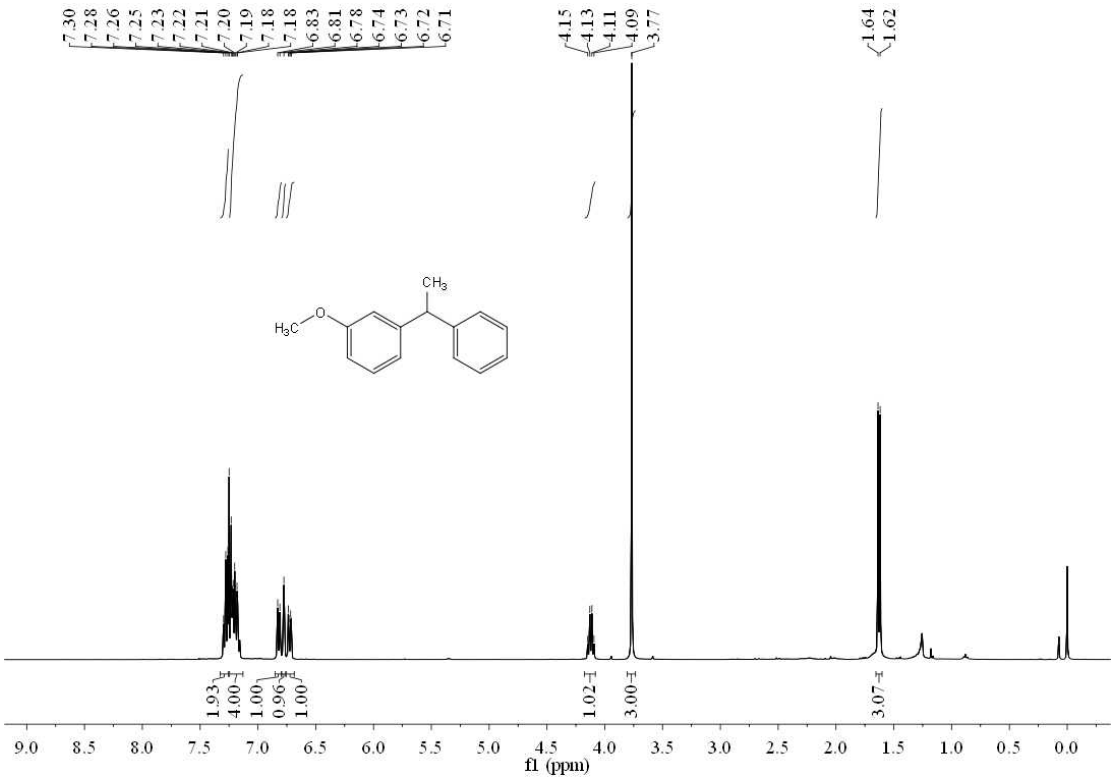


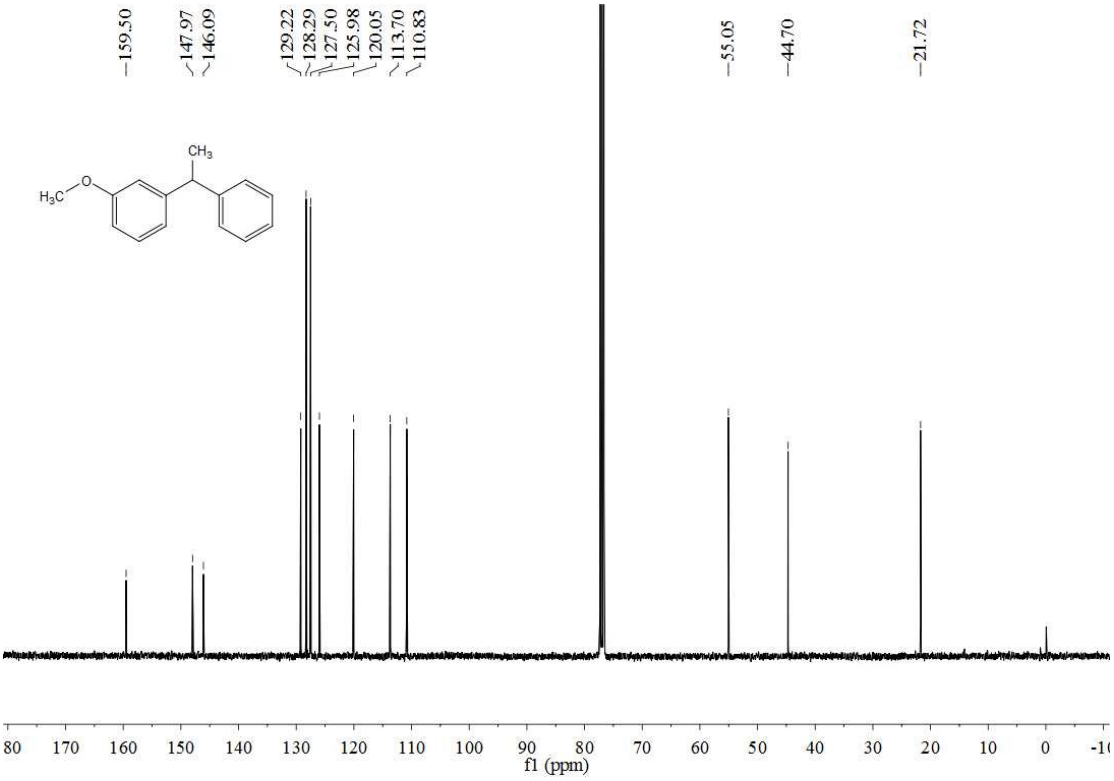
24. N-(3-(3-methoxybenzyl)phenyl)benzamide



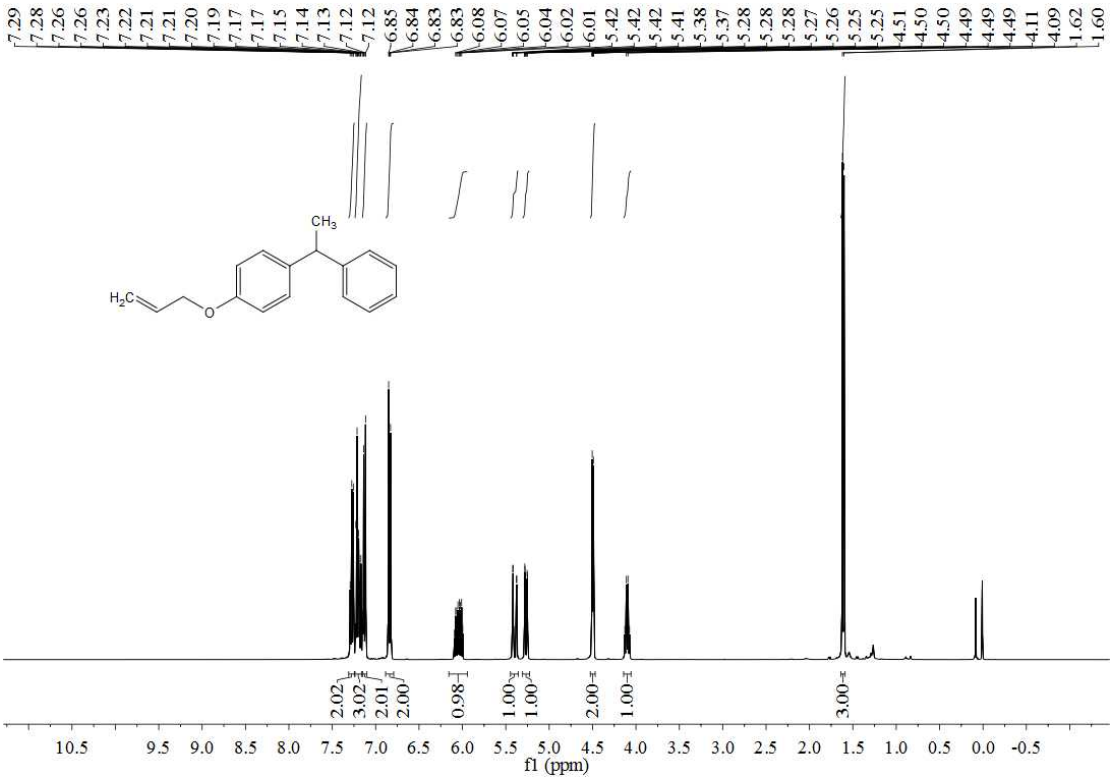


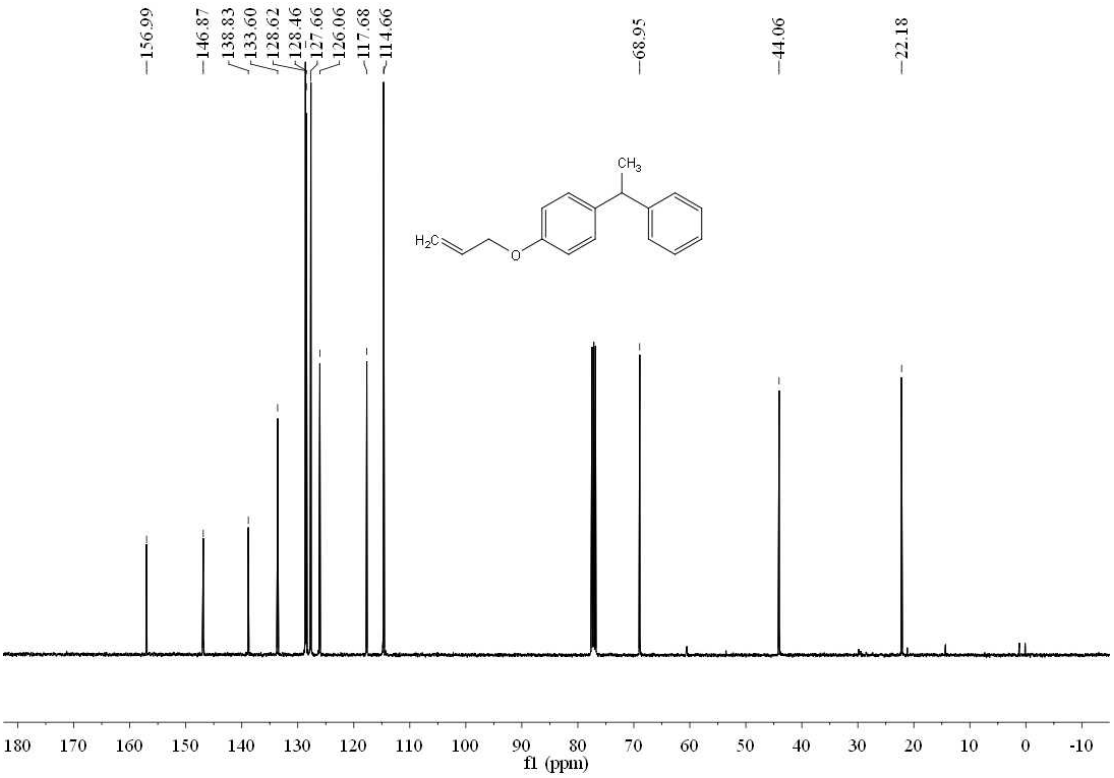
25. 1-methoxy-3-(1-phenylethyl)benzene



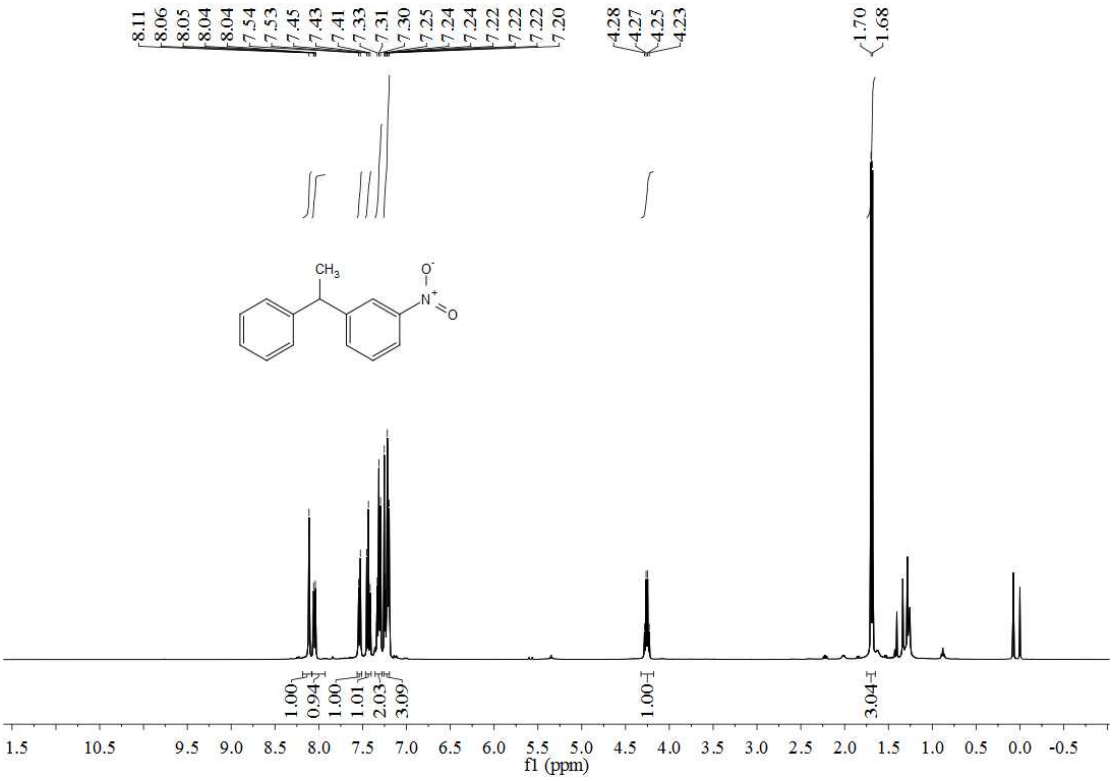


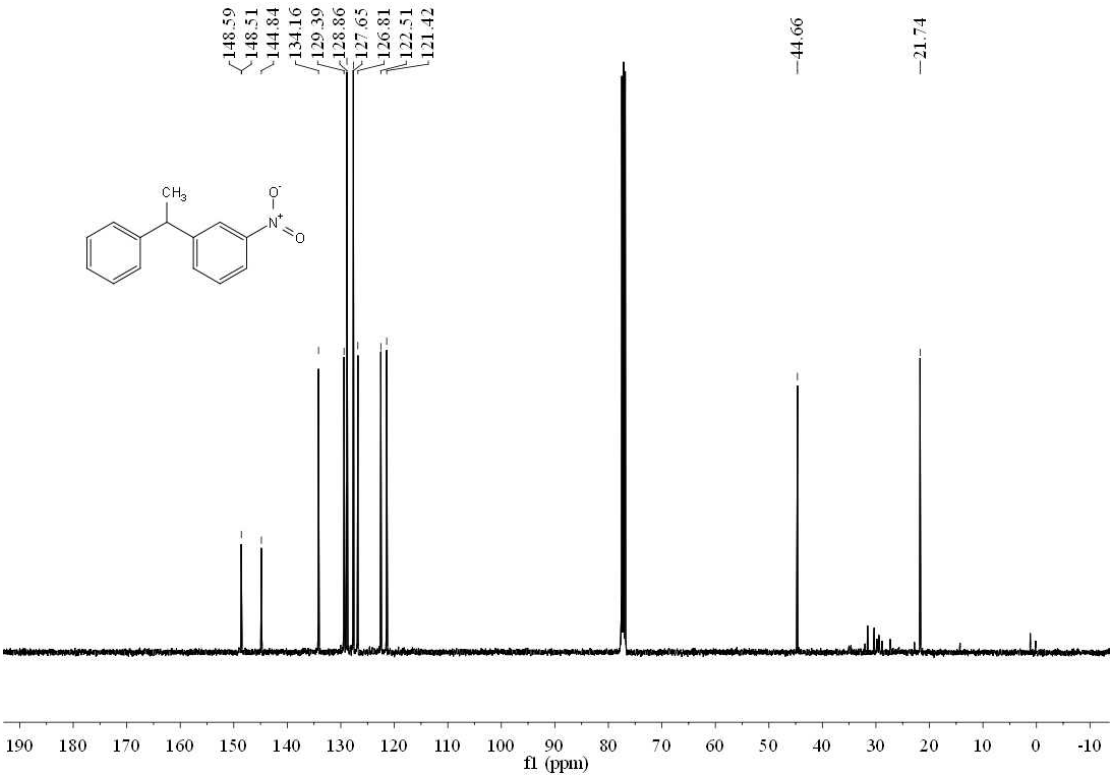
26. 1-(allyloxy)-4-(1-phenylethyl)benzene



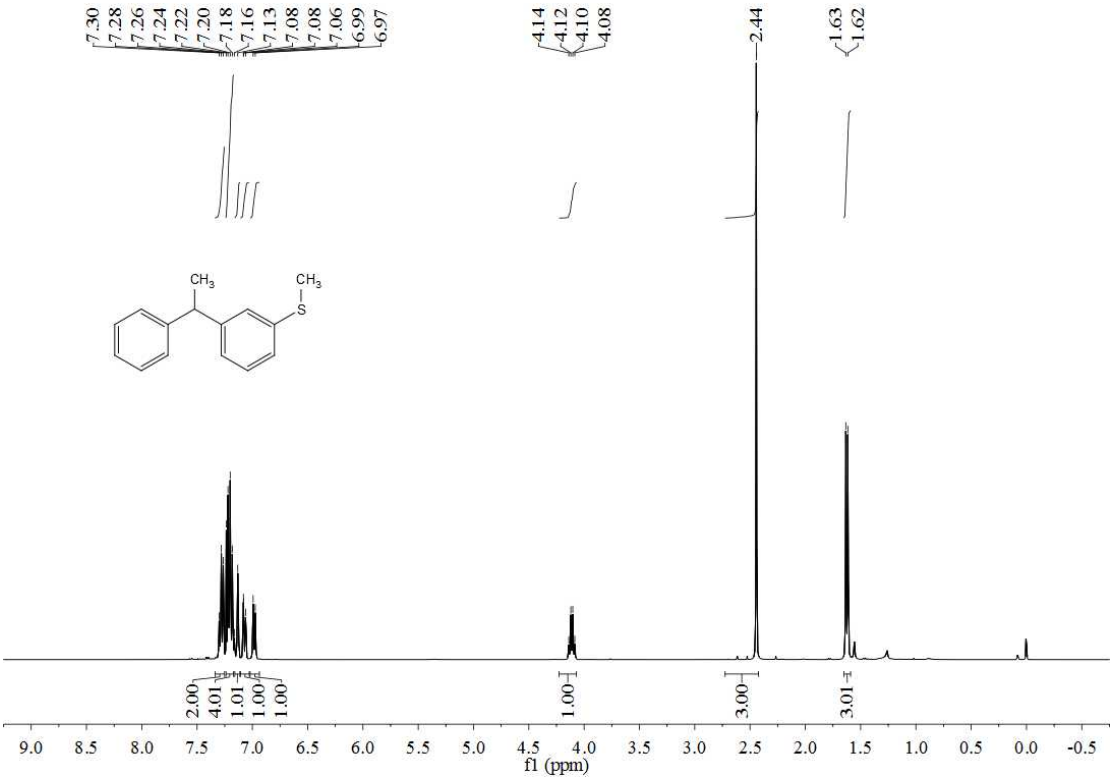


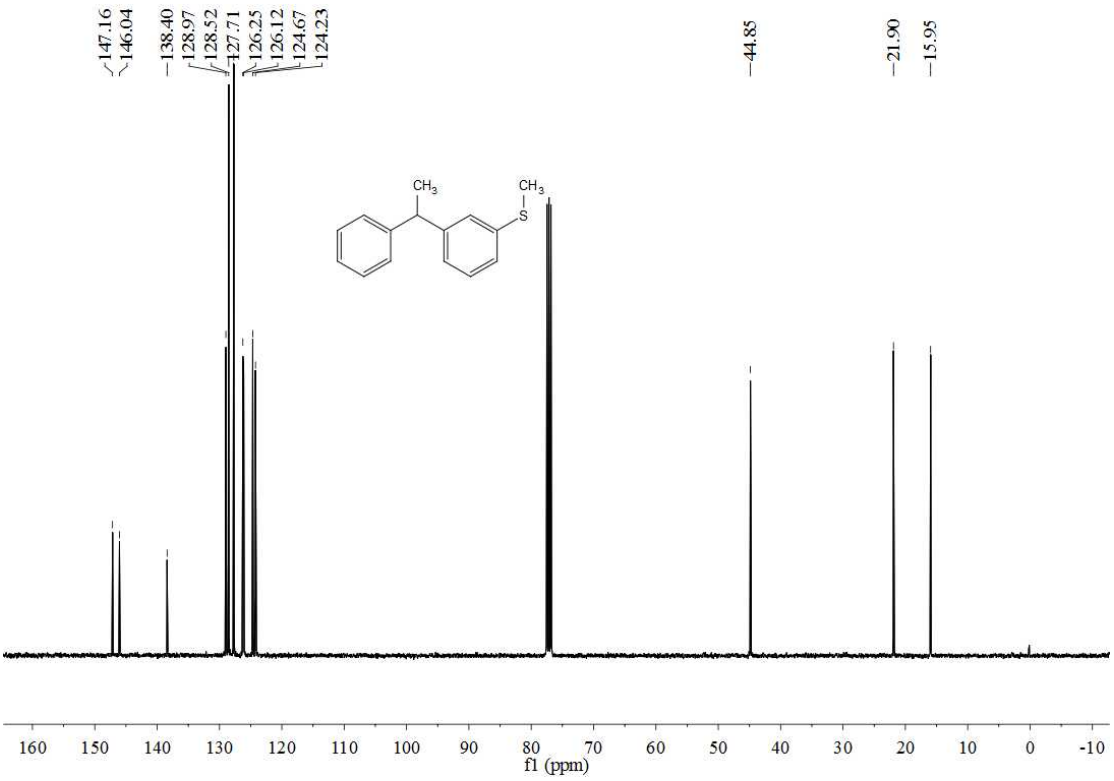
27. 1-nitro-3-(1-phenylethyl)benzene



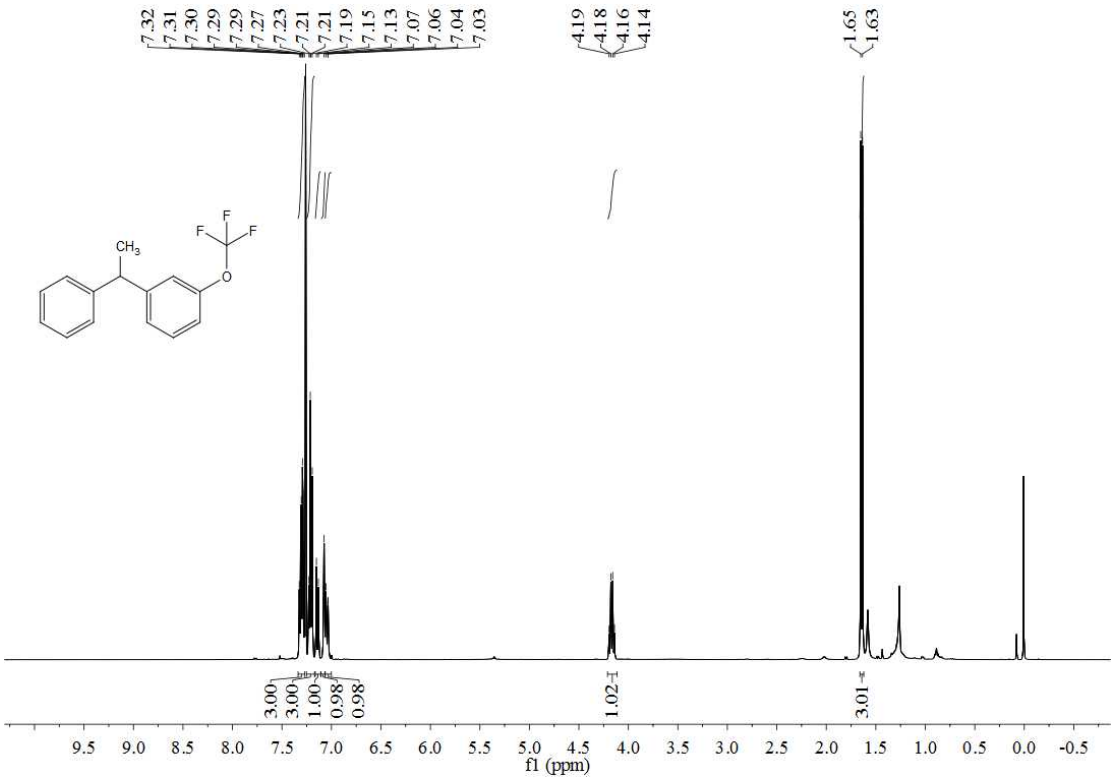


28. methyl(3-(1-phenylethyl)phenyl)sulfane





29. 1-(1-phenylethyl)-3-(trifluoromethoxy)benzene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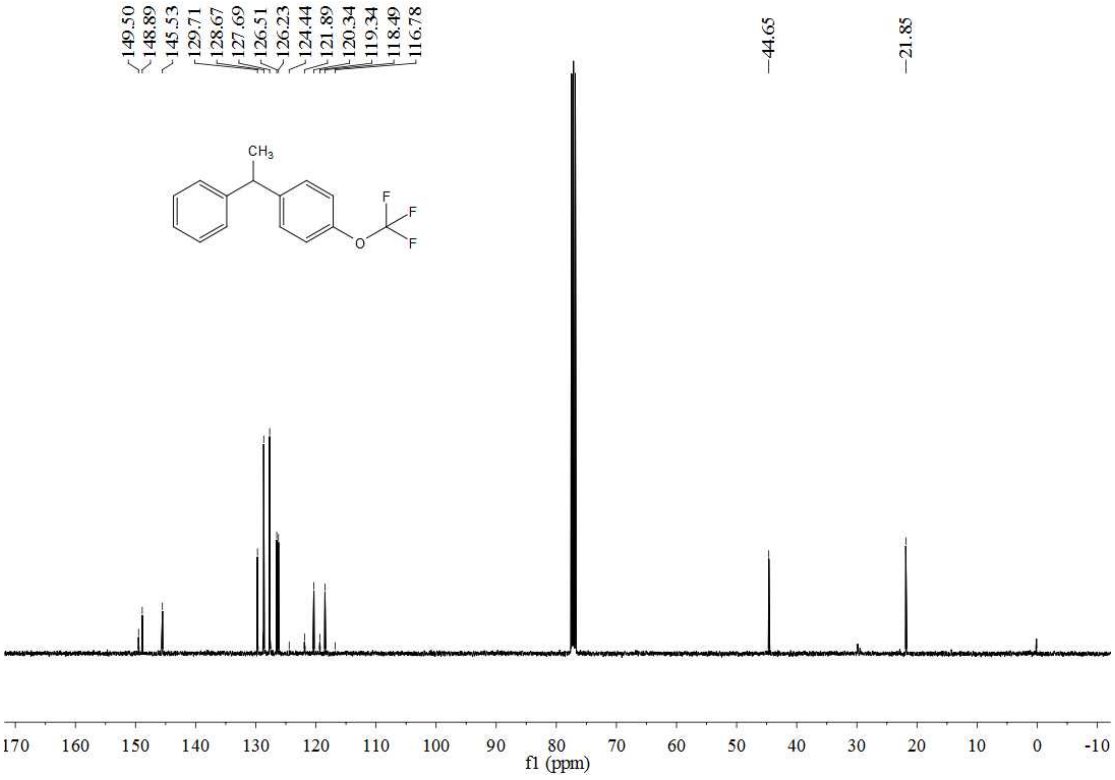
7.31
7.30
7.29
7.29
7.27
7.23
7.21
7.21
7.19
7.15
7.13
7.07
7.06
7.04
7.03
4.19
4.18
4.16
4.14
1.65
1.63
CH3
F
F
F
O
3.00
3.00
1.00
0.98
0.98
1.02
3.01
f1 (ppm)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127.69
126.51
126.23
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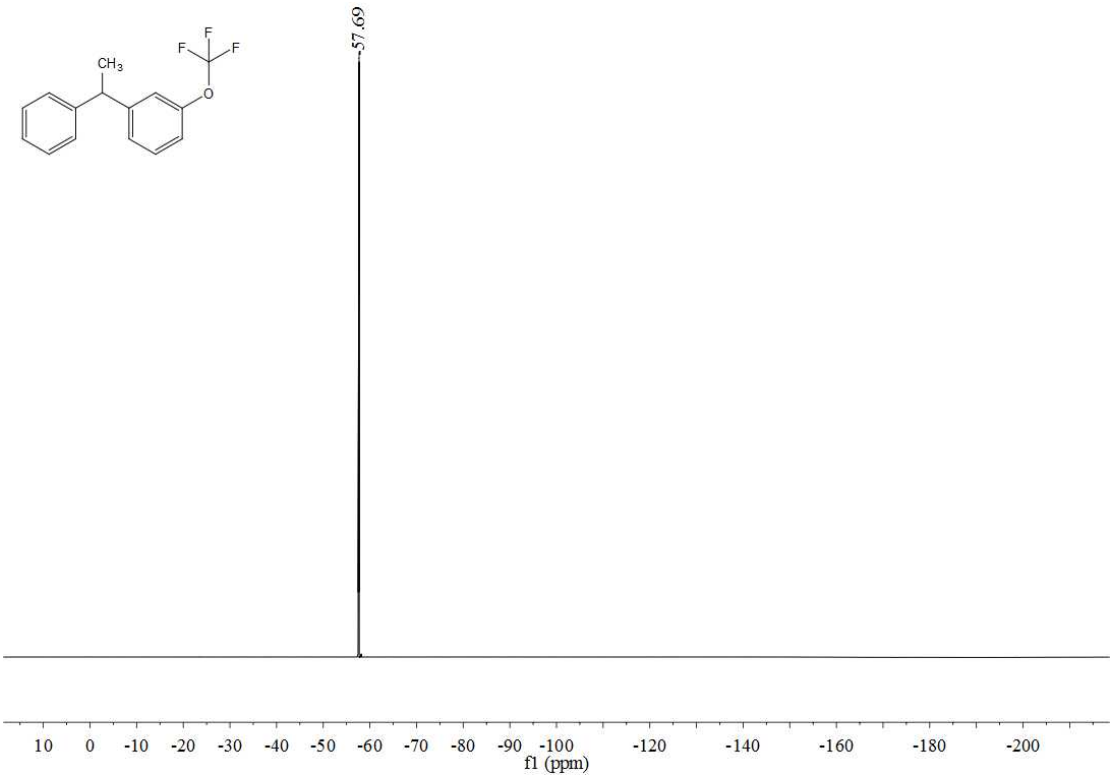
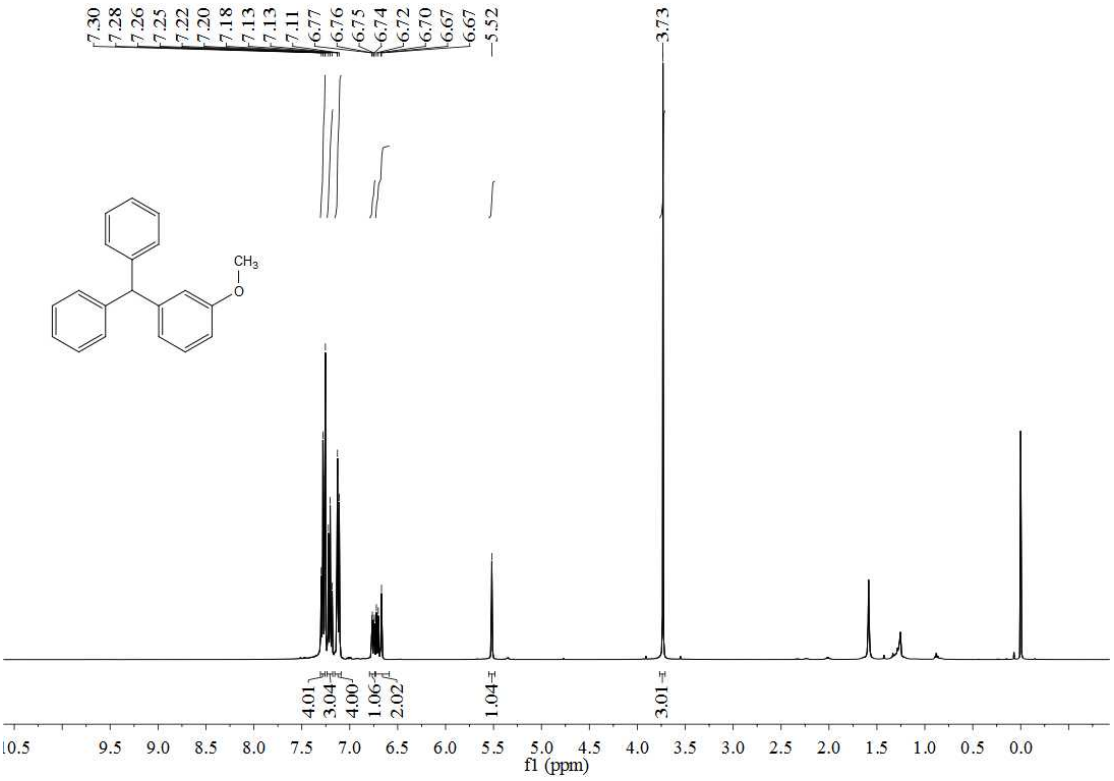
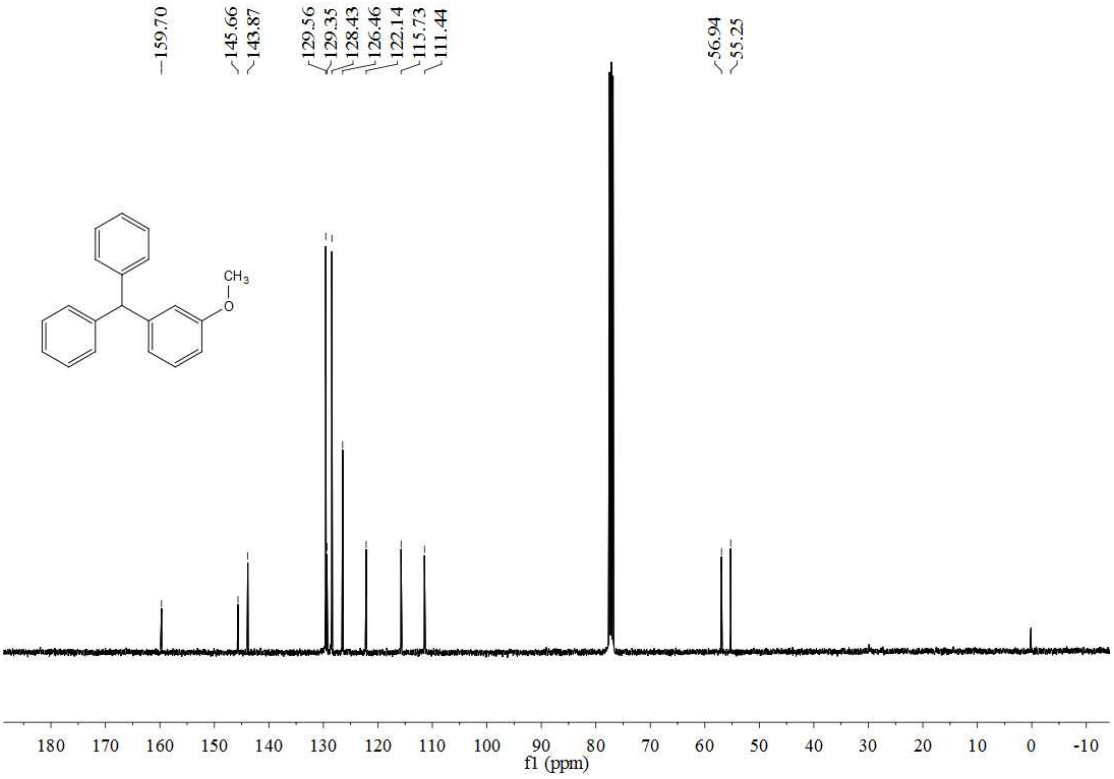
119.34
118.49
116.78
44.65
21.85
CH3
F
F
F
O
f1 (ppm)



30. ((3-methoxyphenyl)methylene)dibenzene




159.70
145.66
143.87
129.56
129.35
128.43
126.46
122.14
115.73
111.44
56.94
55.25
CH3
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)