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1,1'-双(二苯基膦基)二茂铁介导的芳烃碳氢键芳基化反应制备联芳基骨架

王庆兵，郭政伟，陈弓*，何刚*
南开大学化学学院元素有机国家重点实验室，天津 300071

DPPF-Mediated C－H Arylation of Arenes with Aryl Iodides for Synthesis of Biaryl Linkages

WANG Qingbing, GUO Zhengwei, CHEN Gong*, HE Gang *
State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071,
P. R. China.

*Corresponding authors. Email: gongchen@nankai.edu.cn (C.G.). Email: hegang@nankai.edu.cn; Tel: +86-18622363249 (H.G.).

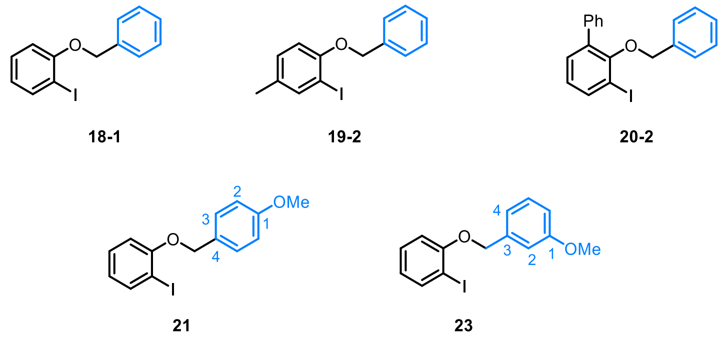
1 Reagents

All commercial materials were used as received unless otherwise noted. Benzene and toluene were dried by distillation overs sodium/benzophenone. Other superdried solvents were purchased from J&K Chemical and used without further purification. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using Silica gel (200–300 mesh) purchased from Qingdao Haiyang Chemical Co., China. 4-Iodoanisole (98%, Energe Chemical.), 18-crown-6 (98%, Heowns Biochemical Technology Co., Ltd.), dppf (98%, J&K Chemical) and t-BuOK (99%, J&K Chemical) were used in the dppf mediated radical arylation of arenes.

2 Instruments

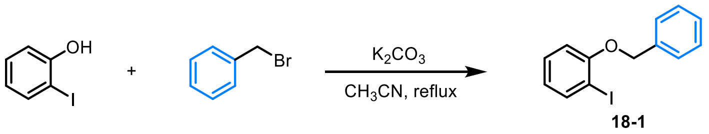
NMR spectra were recorded on Bruker AVANCE AV 400 instruments, using residual solvent peaks chloroform (δ = 7.26) or TMS (δ = 0.00) for ^{1}HNMR, chloroform (δ = 77.16) for ^{13}CNMR as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, brs = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Thermo Fisher Q Exactive Focus of instrument. All reactions were carried out in a 8 mL glass vial (Thermo Scientific National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with a PTEF cap on bench top. GC-MS was performed on an Agilent Technologies 7890B and 5977A System.

3 Synthesis of substrates



Scheme S1 List of substrates synthesized in this research

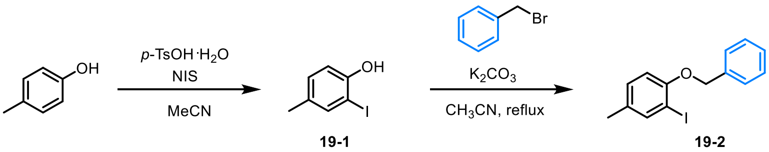
3.1 Synthesis of compound 18-1



Scheme S2 Synthesis of compound 18-1

To a solution of 2-iodophenol (1.1 g, 5 mmol, 1 equiv) in acetonitrile (20 mL), K_2CO_3 (1.73 g, 12.5 mmol, 2.5 equiv) and benzyl bromide (0.59 mL, 5 mmol, 1 equiv) were added. The resulting solution was heated to reflux overnight. After being cooled to room temperature, the mixture was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 30 mL), the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with PE : EtOAc (*v*/*v* 50 : 1) to give **18-1** in 95% yield. R_f = 0.4, PE : EtOAc (*v*/*v* 30 : 1). The characterization data was consistent with those reported in the literature [1]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.49–7.39 (m, 2H), 7.40–7.27 (m, 2H), 6.89 (d, J = 8.2 Hz, 1H), 6.76 (t, J = 7.6 Hz, 1H), 5.18 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2, 139.6, 136.59, 129.5, 128.6, 127.9, 127.1, 122.9, 112.8, 86.9, 70.9.

3.2 Synthesis of compound 19-2

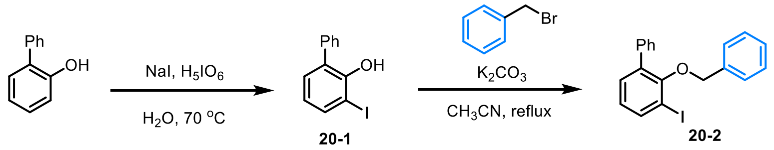


Scheme S3 Synthesis of compound 19-2

To a stirred solution of 4-methylphenol (1.05 mL, 10 mmol, 1 equiv) in 10 mL of MeCN were added *p*-TsOH·H_2O (1.90 g, 10 mmol, 1 equiv) and N-iodosuccinimide (NIS, 2.25 g, 10 mmol, 1 equiv) at room temperature. After being stirred for 24 h, the reaction was quenched with saturated $Na_2S_2O_3$, and extracted with EtOAc (3 × 30 mL). The combined organic layers was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (20% hexane/CH_2Cl_2) to afford **19-1** as a yellow oil in 86% yield.

The observed characterization data was consistent with that reported in the literature [2]. To a solution of **19-1** (1.17 g, 5 mmol, 1 equiv) in acetonitrile (20 mL), K_2CO_3 (1.73 g, 12.5 mmol, 2.5 equiv), and benzyl bromide (0.59 mL, 5 mmol, 1 equiv) were added. The resulting solution was heated to reflux overnight. After being cooled to room temperature, the mixture was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 30 mL) and the combined organic phase were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with PE : EtOAc (*v*/*v* 50 : 1) to afford **19-2** in 95% yield. $R_f = 0.4$, PE : EtOAc (*v*/*v* 30 : 1). The observed characterization data was consistent with that reported in the literature [3]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.5 Hz, 1H), 7.46 (d, J = 7.5 Hz, 2H), 7.39–7.31 (m, 2H), 7.32–7.24 (m, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 5.05 (s, 2H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 139.9, 136.8, 132.4, 129.9, 128.5, 127.8, 127.0, 112.7, 86.8, 71.0, 20.1.

3.3 Synthesis of compound 20-2

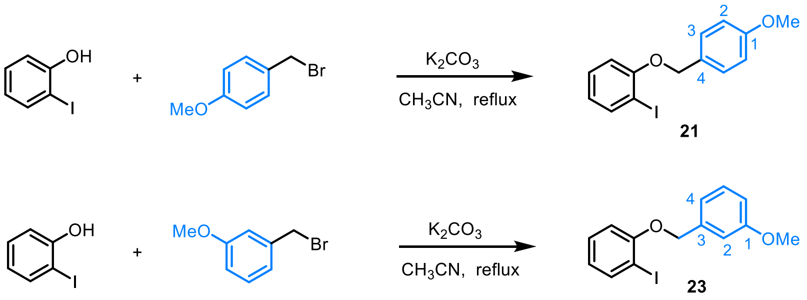


Scheme S4 Synthesis of compound 20-2

2-Phenylphenol (340 mg, 2 mmol, 1 equiv) and orthoperiodic acid (228 mg, 1 mmol, 50% (molar fraction)) were added to a solution of NaI (372 mg, 2 mmol, 1 equiv) in 4 mL water at room temperature. The reaction mixture were stired at 70 °C for 1 h. After being cooled to room temperature, the reaction mixture was treated with $Na_2S_2O_3$ (10% (molar fraction), 5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude product was purified by silica gel column chromatography (eluted with hexane/ Dichloromethane (*v*/*v* 100:1)) to afford **20-1** in 85% yield. The characterization data was consistent with that reported in the literature [4].

To the solution of **20-1** (592.2 mg, 2 mmol, 1 equiv) in acetonitrile (8 mL), K_2CO_3 (690 mg, 5 mmol, 2.5 equiv) and benzyl bromide (0.24 mL, 2 mmol, 1 equiv) were added. The resulting solution was heated to reflux overnight. After being cooled to room temperature, the mixture was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organic phase were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with PE : EtOAc (*v*/*v* 50 : 1) to give **20-2** in 80% yield. $R_f = 0.3$, PE : EtOAc (*v*/*v* 30 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.8, 1.7 Hz, 1H), 7.62–7.54 (m, 2H), 7.47–7.33 (m, 4H), 7.33–7.25 (m, 3H), 7.17 (dd, J = 6.6, 3.0 Hz, 2H), 6.95 (t, J = 7.7 Hz, 1H), 4.45 (s, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 155.6, 138.8, 138.0, 136.5, 136.3, 131.5, 129.35, 129.0, 128.5, 128.3, 128.3, 127.8, 126.4, 93.8, 74.8. **HRMS (ESI)** Calcd for $C_{19}H_{15}INaO^+$[M + Na$^+$]: 409.0060, found: 409.0056.

3.4 Synthesis of compound 21 and 23



Scheme S5 Synthesis of compounds 21 and 23

To a solution of 2-iodophenol (1.1 g, 5 mmol, 1 equiv) in acetonitrile (20 mL), K_2CO_3 (1.73 g, 12.5 mmol, 2.5 equiv), 4-Methoxybenzyl bromide (1.01 g, 5 mmol, 1 equiv) or 3-Methoxybenzyl bromide (1.01 g, 5 mmol, 1 equiv) were added at room temperature. The resulting solution was heated to reflux overnight. After being cooled to room temperature, the mixture was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 30 mL) and the combined organic phase were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with PE : EtOAc (*v*/*v* 50 : 1) to give compounds **21** and **23** in 90% and 91% yield respectively. $R_f = 0.4$, PE : EtOAc (*v*/*v* 30 : 1). The observed characterization data was consistent with that reported in the literature [5,6].

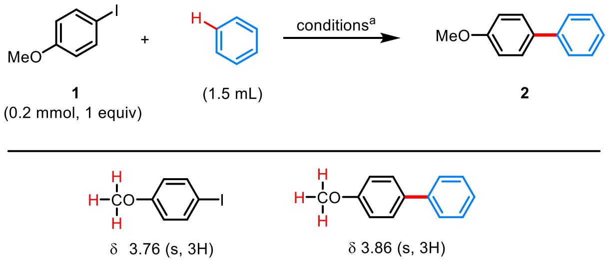
Compound 21: ^{1}**H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.30–7.23 (m, 1H), 6.92 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.2 Hz, 1H), 6.71 (t, J = 7.5 Hz, 1H), 5.08 (s, 2H), 3.81 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 159.5, 157.4, 139.7, 129.5, 128.8, 128.7, 122.9, 114.1, 113.1, 87.1, 70.9, 55.4.

Compound 23: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 7.8, 1.6 Hz, 1H), 7.33–7.20 (m, 2H), 7.11 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.83 (t, J = 6.4 Hz, 2H), 6.71 (d, J = 8.7 Hz, 1H), 5.11 (s, 2H), 3.81 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 159.9, 157.1, 139.6, 138.2, 129.6, 129.5, 122.8, 119.1, 113.6, 112.8, 112.3, 86.9, 70.6, 55.4.

4 Optimization of dppf mediated Intermolecular C—H arylation of benzene

All screening reactions were carried out at a 0.2 mmol scale in a 8 mL glass vial (Thermo Scientific, National B7999-2) sealed with a PTEF cap and stirred on bench top.

Aryl iodide (0.2 mmol, 1 equiv), dppf and other specified reagents were added into a 8 mL glass vial at room temperature, then benzene (1.5 mL) was added. The vial was sealed with a PTEF cap. The reaction mixture was vigorously stirred at specified temperature for 48 hours. After being cooled to room temperature, the reaction mixture was diluted with DCM (5 mL) and filtered. The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and yields are based on ^{1}HNMR analysis of the crude reaction solution using 1,1,2,2- tetrachloroethane (33.6 mg, 0.2 mmol, 1.0 equiv, a singlet peak around 5.96 was set as 1.00) as internal standard. Yield of **2** = integration of peak (δ 3.86, s) × 67%.



Scheme S6 Model reaction

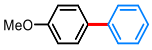
Table S1 Optimization of dppf mediated Intermolecular C—H arylation of benzene

Entry [a]	Condition	Yield (%) [b]
1	dppf (0.1), Cs_2CO_3 (2.0), 110 °C, 48 h	< 10
2	dppf (0.1), *t*-BuONa (2.0), 110 °C, 48 h	NR
3	dppf (0.1), *t*-BuOLi (2.0), 110 °C, 48 h	NR
4	dppf (0.1), *t*-BuONa (2.0), 130 °C, 48 h	NR
5	dppf (0.1), *t*-BuOK (2.0), 110 °C, 48 h	64
6	dppf (0.1), *t*-BuOK (2.0), 130 °C, 48 h	73
7	dppf (0.1), *t*-BuOK (2.0), TBAI (0.2), 130 °C, 48 h	28
8	dppf (0.1), *t*-BuOK (2.0), TBAB (0.2), 130 °C, 48 h	30
9	dppf (0.1), *t*-BuOK (2.0), 140 °C, 48 h	78 (73) [c]
10	dppf (0.1), *t*-BuOK (2.0), 145 °C, 48 h	77
11	dppf (0.1), *t*-BuOK (2.0), 140 °C, 30 h	66
12	dppf (0.1), *t*-BuOK (2.0), 140 °C, 48 h	60 [d]
13	dppf (0.1), *t*-BuOK (2.0), 140 °C, 48 h	65 [e]
14	dppf (0.1), *t*-BuOK (2.0), 18-crown-6 (0.4), 140 °C, 48 h	61
15	*t*-BuOK (2.0), 18-crown-6 (0.4), 140 °C, 48 h	51
16	*t*-BuOK (2.0),140 °C, 48 h	25

[a] All screening reactions were carried on a 0.2 mmol scale at a 0.13 mol·L^{-1} concentration; [b] Yields are based on ^{1}HNMR analysis of the crude reaction solution using 1,1,2,2-tetrachloroethane as internal standard; [c] Isolated yield; [d] The screening reaction was carried on a 0.2 mmol scale at a 0.1 mol·L^{-1} concentration; [e] The screening reaction was carried on a 0.2 mmol scale at a 0.2 mol·L^{-1} concentration; NR: no reaction, most of the starting material recovered. TBAB: tetrabutylammonium bromide. TBAI: tetrabutylammonium iodide.

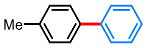
5 General experimental procedures for aryl iodides with benzene

Aryl iodide (0.2 mmol, 1 equiv), dppf (11.1 mg, 0.02 mmol, 10% (molar fraction)), *t*-BuOK (45 mg, 0.4 mmol, 2.0 equiv) and 1.5 mL anhydrous benzene were added to a 8 mL glass vial at room temperature in glove box. The vial was sealed with PTFE cap and moved out of the glove box. The mixture was stirred at room temperature for 10 min, then heated to 140 °C for 48 h. After being cooled to room temperature, the reaction mixture was diluted with DCM (5 mL). The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, the resulting residue was purified by silica gel flash chromatography on 200–300 mesh silica gel with hexane/ethyl acetate as eluent to give the desired product.



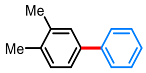
2 R_f = 0.6, Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **2** was isolated in 73% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (t, J = 8.3 Hz, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 140.9, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5.



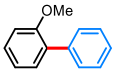
3 R_f = 0.7, Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **3** was isolated in 70% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60–7.55 (m, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.37–7.31 (m, 1H), 7.26 (t, J = 3.9 Hz, 3H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 138.5, 137.1, 129.6, 128.9, 128.8, 127.3, 127.1, 21.2.



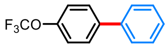
4 R_f = 0.7, Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **4** was isolated in 69% yield as colorless oil following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [8]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.38 (s, 1H), 7.35–7.30 (m, 2H), 7.21 (d, J = 7.7 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 139.0, 137.0, 135.8, 130.2, 128.8, 128.6, 127.1, 127.0, 124.6, 20.1, 19.6.



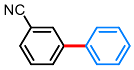
5 R_f = 0.7, Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **5** was isolated in 73% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.37-7.33 (m, 3H), 7.06 (t, J = 7.5 Hz, 1H), 7.03–6.98 (m, 1H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.6, 138.7, 131.0, 130.8, 129.7, 128.7, 128.1, 127.0, 121, 111.3, 55.7.



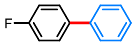
6 R_f = 0.7, Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **6** was isolated in 70% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61–7.49 (m, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.8, 140.1, 140.12, 140.0, 129.0, 128.6, 127.8, 127.3, 121.4.



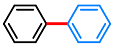
7 R_f = 0.6, Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **7** was isolated in 63% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [9]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 8.1 Hz, 3H), 7.48 (t, J = 7.4 Hz, 2H), 7.45–7.38 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 139.0, 131.6, 130.8, 129.7, 129.3, 128.5, 127.2, 119.0 113.1.



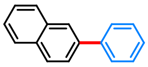
8 R_f = 0.5, Hexane : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **8** was isolated in 70% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62–7.51 (m, 4H), 7.46–7.42 (m, 2H), 7.37–7.32 (m, 1H), 7.17–7.08 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 161.4, 140.4, 137.5, 137.46, 129.0, 128.9, 128.85, 128.8, 127.4, 127.3, 127.2, 115.9, 115.6.



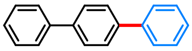
9 R_f = 0.8, Hexane : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **9** was isolated in 72% yield as white sold following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.5 Hz, 4H), 7.49 (t, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 7.3 Hz, 2H);**^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.4, 128.9, 127.8, 127.3.



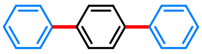
10 R_f = 0.7, Hexane : Ethyl Acetate = 100 : 1 (*v*/*v*)

Compound **10** was isolated in 73% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [10]. **^{1}H NMR** (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.96–7.84 (m, 3H), 7.78–7.71 (m, 3H), 7.54–7.45 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.2, 138.6, 133.8, 132.7, 129.0, 128.6, 128.3, 127.8, 127.6, 127.5, 126.4, 126.1, 125.9, 125.7.



11 R_f = 0.7, Hexane : Ethyl Acetate = 100 : 1 (*v*/*v*)

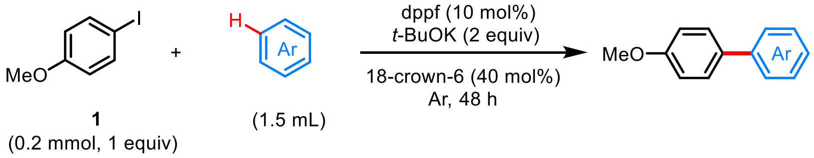
Compound **11** was isolated in 72% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that previously reported in the literature [11]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (s, 4H), 7.67–7.62 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.83, 140.25, 128.96, 127.64, 127.49, 127.19.



11 R_f = 0.7, Hexane : Ethyl Acetate = 100 : 1 (*v*/*v*)

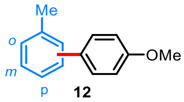
Compound **11** was isolated in 69% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [11]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (s, 4H), 7.67–7.62 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.83, 140.25, 128.96, 127.64, 127.49, 127.19.

6 General procedure for arylation of arenes with 4-iodoanisole



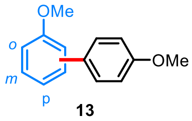
Scheme S7 Arylation of arenes with 4-iodoanisole

4-iodoanisole (0.2 mmol, 1 equiv), dppf (11.1 mg, 0.04 mmol, 10% (molar fraction)) and 18-crown-6 (21.1 mg, 0.08 mmol, 40% (molar fraction)), *t*-BuOK (0.4 mmol, 2.0 equiv) and 1.5 mL anhydrous arene were added to a 8 mL glass vial at room temperature in glove box. The vial was sealed with PTFE cap and moved out of glove box.The mixture was stirred at room temperature for 10 min, then heated to 140 °C for 48 h under Ar atmosphere. After being cooled to room temperature, the reaction mixture was diluted with DCM (5 mL). The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, the resulting residue was purified by silica gel flash chromatography on 200–300 mesh silica gel with hexane/ethyl acetate as eluent to give the desired product.



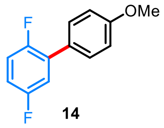
12 R_f = 0.35, Hexane : Ethyl Acetate = 50 : 1 (*v*/*v*)

Compound **12** (*o* : *m* : *p* = 6.1 : 2.5 : 1) was isolated in 52% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.48 (m, 0.78H), 7.45 (d, *J* = 8.2 Hz, 0.27H), 7.38–7.29 (m, 0.85H), 7.29–7.19 (m, 4.14H), 7.12 (d, *J* = 7.5 Hz, 0.32H), 7.00–6.92 (m, 1.92H), 3.85 (d, *J* = 2.1 Hz, 3H), 2.41 (s, 1H), 2.28 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 141.7, 135.6, 134.5, 130.4, 130.38, 130.0, 129.6, 128.8, 128.3, 128.1, 127.7, 127.5, 127.1, 126.7, 125.9, 124.0, 114.3, 113.6, 55.4, 21.7, 20.7.



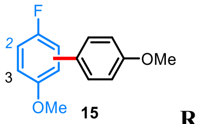
13 R_f = 0.4, Hexane : Ethyl Acetate = 50 : 1 (*v*/*v*)

Compound **13** (o : m : p = 24.7 : 9.3 : 1)was isolated in 65% yield as white solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.50 (d, J = 8.7 Hz, 0.54H), 7.48–7.41 (m, 1.6H), 7.32–7.25 (m, 1.36H), 7.16–7.04 (m, 0.6H), 6.98 (t, J = 6.9 Hz, 0.74H), 6.93 (d, J = 8.9 Hz, 2.75H), 6.83 (dd, J = 8.2, 2.5 Hz, 0.28H), 3.81 (s, 0.8H), 3.79 (d, J = 2.5 Hz, 3.05H), 3.76 (s, 1.98H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 160.0, 159.3, 158.8, 158.7, 156.5, 142.4, 133.6, 133.5, 131.0, 130.7, 130.7, 130.4, 129.8, 128.3, 127.8, 120.9, 119.3, 114.2, 113.6, 112.6, 112.1, 111.3, 55.6, 55.4, 55.3.



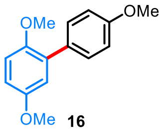
14 R_f = 0.35, Hexane : Ethyl Acetate = 50 : 1 (v/v)

Compound **14** was isolated in 72% yield as light yellow solid following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.51 (dd, J = 8.8, 1.7 Hz, 2H), 7.19–7.06 (m, 2H), 7.05–6.92 (m, 3H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 160.1, 159.7, 157.7, 157.0, 154.6, 130.2, 130.1, 130.1, 127.2, 117.3, 117.2, 117.1, 117.0, 116.8, 116.7, 116.5, 116.48, 114.8, 114.7, 114.5, 114.4, 114.1, 55.4.



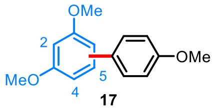
15 R_f = 0.3, Hexane : Ethyl Acetate = 50 : 1 (v/v)

Compound **15** was isolated in 55% (2 : 3 = 1 : 1.6) yield as light yellow oil following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.49 (dd, J = 11.8, 7.8 Hz, 1.87H), 7.11–7.01 (m, 0.99H), 7.03–6.90 (m, 2.93H), 6.89 (dd, J = 8.9, 4.6 Hz, 0.69H), 6.84–6.76 (m, 0.4H), 3.86 (s, 1.07H), 3.86 (s, 1.72H), 3.83 (s, 1.12H), 3.79 (s, 1.86H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 159.4, 159.1, 158.5, 156.1, 155.9, 155.5, 152.7, 131.8, 130.6, 130.2, 130.19, 129.9, 128.3, 127.8, 117.4, 117.1, 116.8, 116.5, 115.4, 115.37, 114.3, 114.0, 113.98, 113.8, 113.7, 113.4, 113.3, 112.4, 112.35, 56.3, 55.9, 55.4.



16 R_f = 0.4, Hexane : Ethyl Acetate = 60 : 1 (v/v)

Compound **16** was isolated in 60% yield as light yellow oil following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [12]. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.49 (d, J = 8.7 Hz, 2H), 7.00–6.87 (m, 4H), 6.83 (dd, J = 8.8, 3.1 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 158.9, 153.9, 150.9, 131.5, 130.9, 130.7, 116.7, 113.6, 112.7, 112.69, 56.4, 55.9, 55.4.

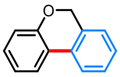


17 R_f = 0.4, Hexane : Ethyl Acetate = 60 : 1 (v/v)

Compound **17** (2 : 4 : 5 = 6 : 7.8 : 1) was isolated in 56% yield as light yellow oil following the general arylation procedure. The observed characterization data was consistent with that reported in the literature [13]. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.51 (d, J = 8.7 Hz, 0.18H), 7.42 (d, J = 8.7 Hz, 0.93H), 7.34–7.18 (m, 2.06H), 7.00–6.89 (m, 1.98H), 6.69 (d, J = 2.3 Hz, 0.15H), 6.65 (d, J = 8.4 Hz, 0.84H), 6.59–6.52 (m, 0.94H), 6.43 (s, 0.07H), 3.84 (d, J = 3.7 Hz, 4.82H), 3.79 (s, 1.65H), 3.74 (s, 2.55H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.1, 160.1, 158.44, 158.4, 157.9, 132.1, 131.1, 130.9, 130.6, 128.5, 128.3, 126.2, 123.4, 119.2, 114.2, 113.6, 113.4, 105.2, 104.6, 104.3, 99.1, 98.8, 56.0, 55.7, 55.5, 55.4, 55.3.

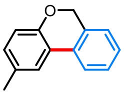
7 General procedure for intramolecular C−H arylation reaction

Aryl-iodide (0.2 mmol, 1 equiv), dppf (22.2 mg, 0.04 mmol, 20 mol %), t-BuOK (0.4 mmol, 2.0 equiv), 18-crown-6 (21.1 mg, 0.08 mmol, 40% (molar fraction)) and 1.5 mL anhydrous mesitylene were added to a 8 mL glass vial at room temperature in glove box. The vial was sealed with PTFE cap and moved out of glove box. The mixture was stirred at room temperature for 10 min, then heated to 120 °C for 30 h under Ar atmosphere. After being cooled to room temperature, the reaction mixture was diluted with DCM (5 mL). The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, the resulting residue was purified by silica gel flash chromatography on 200–300 mesh silica gel with Hexane/ethyl acetate as eluent to give the desired product.



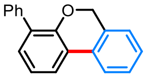
18 R_f = 0.6, Hexane : Ethyl Acetate = 40 : 1 (*v*/*v*)

Compound **18** was isolated in 50% yield as colorless oil following the general intramolecular arylation procedure. The observed characterization data was consistent with that reported in the literature [7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 14.1, 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28–7.20 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.10 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.9, 131.5, 130.2, 129.6, 129.57, 128.7, 128.6, 128.1, 127.8, 127.6, 124.8, 123.4, 123.1, 122.3, 122.1, 121.06, 117.5, 115.0, 68.6.



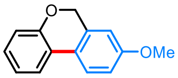
19 R_f = 0.6, Hexane : Ethyl Acetate = 40 : 1 (*v*/*v*)

Compound **19** was isolated in 68% yield as colorless oil following the general intramolecular arylation procedure. The observed characterization data was consistent with that reported in the literature [14]. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.73 (d, *J* = 7.7 Hz, 1H), 7.58 (s, 1H), 7.44–7.36 (m, 1H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 5.13 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 152.7, 131.7, 131.4 130.3, 130.2, 130.0, 128.6, 128.4, 127.6, 127.5, 124.72, 124.7, 123.7, 122.7, 122.0, 117.2, 114.8, 68.6, 21.0.



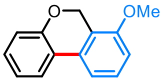
20 R_f = 0.5, Hexane : Ethyl Acetate = 40 : 1 (*v*/*v*)

Compound **20** was isolated in 66% yield as white solid following the general intramolecular arylation procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.76–7.70 (m, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.46–7.25 (m, 6H), 7.16–7.08 (m, 2H), 5.06 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 151.9, 138.1, 131.7, 131.1, 130.8, 130.5, 129.6, 128.6, 128.2, 127.8, 127.3, 124.7, 123.7, 122.9, 122.5, 122.1, 68.6. **HRMS (ESI)** Calcd for $C_{19}H_{15}O^+$[M + H$^+$]: 259.1117, found: 259.1113.



21 R_f = 0.5, Hexane : Ethyl Acetate = 40 : 1 (*v*/*v*)

Compound **21** was isolated in 45% yield as light yellow oil following the general intramolecular arylation procedure. The observed characterization data was consistent with that reported in the literature [14]. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.71–7.60 (m, 2H), 7.25–7.17 (m, 1H), 7.09–6.98 (m, 2H), 6.92 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 5.10 (s, 2H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 159.5, 154.0, 133.1, 128.5, 123.6, 123.1, 123.0, 122.7, 122.3, 117.3, 114.1, 110.1, 68.6, 55.5.

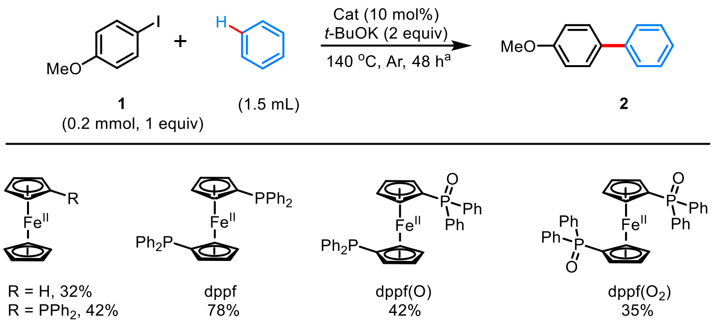


24 R_f = 0.5, Hexane : Ethyl Acetate = 40 : 1 (*v*/*v*)

Compound **24** was isolated in 47% yield as white solid following the general intramolecular arylation procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.67 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 4.3 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.06–6.91 (m, 2H), 6.79 (t, *J* = 4.4 Hz, 1H), 5.20 (s, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 155.0, 154.7, 131.2, 129.5, 128.8, 123.7, 122.8, 122.0, 120.0, 117.4, 114.4, 109.6, 63.1, 55.6.

8 Control experiments and KIE study

8.1 Comparation of different ferrocene based catalysts

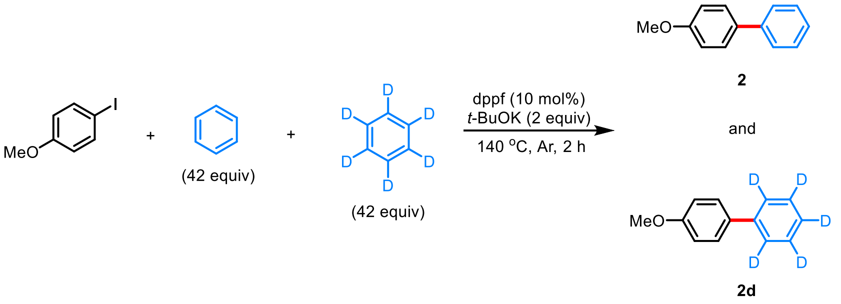


a) Yields are based on ^{1}HNMR analysis of the crude reaction solution using 1, 1, 2, 2- tetrachloroethane as internal srandard.

Scheme S8 Comparation of different ferrocene based catalysts

4-iodoanisole (0.2 mmol, 1 equiv), Catalyst (0.02 mmol, 10% (molar fraction)), *t*-BuOK (0.4 mmol, 2.0 equiv) and 1.5 mL superdried benzene were added to a 8 mL glass vial at room temperature in glove box. The vial was sealed with PTFE cap and moved out of the glove box. The mixture was stirred at room temperature for 10 min, then heated to 140 °C for 48 h. After being cooled to room temperature, the reaction mixture was diluted with DCM (5 mL). The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and yields are based on ^{1}HNMR analysis of the crude reaction solution using 1,1,2,2- tetrachloroethane (33.6 mg, 0.2 mmol, 1.0 equiv, a singlet peak around 5.96 was set as 1.00) as internal standard.

8.2 Kinetic isotopic effect of the reactions

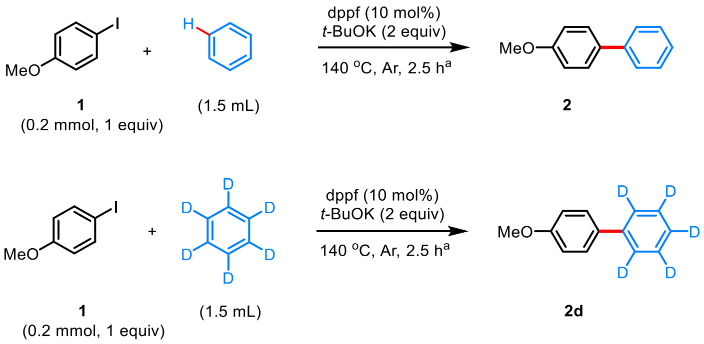


Scheme S9 Competition reaction

4-iodoanisole (46.8 mg, 0.2 mmol, 1 equiv), dppf (11.1 mg, 0.02 mmol, 10% (molar fraction)), *t*-BuOK (45mg, 0.4 mmol, 2.0 equiv), benzene (0.75 mL, 42 equiv) and benzene-d6 (0.75 mL, 42 equiv) were added to a 8 mL glass vial at room temperature in glove box. The vial was sealed with PTFE cap and moved out of the glove box.The mixture was stirred at room temperature for 10 min, then heated to 140 °C for 2 h under Ar atmosphere. After being cooled to room temperature, the reaction mixture diluted with DCM (5 mL). The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and the resulting residue was purified by silica gel flash chromatography on 200-300 mesh silica gel with Hexanes : Ethyl Acetate = 100 : 1 (*v*/*v*) as eluent to give the desired product. The KIE value was calculated from the relative amount of compound **2** and **2d**.

Table S2 KIE values of competition reaction

Entry	K_H/K_D
1	1.23
2	1.27
3	1.14
average	1.21



Scheme S10 Parallel reactions

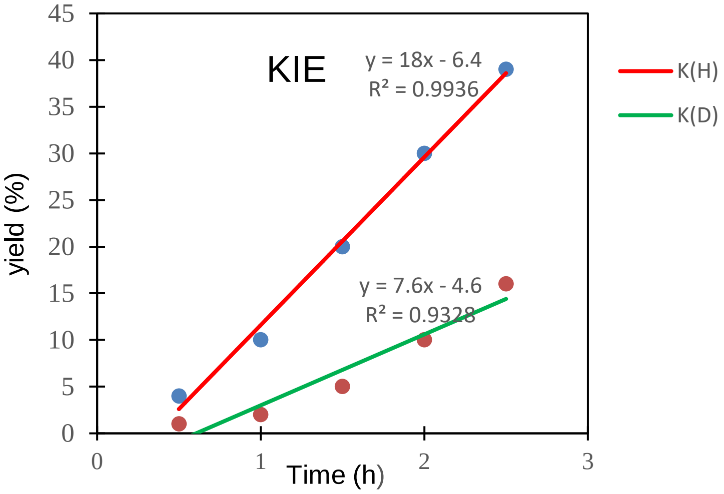
4-iodoanisole (0.2 mmol, 1 equiv), dppf (11.1 mg, 0.02 mmol, 10 mol %), *t*-BuOK (0.4 mmol, 2.0 equiv) and benzene (1.5 mL) or benzene-d$_6$ (1.5 mL) were added to a 8 mL glass vial at room temperature in glove box. The vial was sealed with PTFE cap and moved out of glove box. The mixture was stirred at room temperature for 10 min, then heated to 140 °C under Ar atmosphere. One of the reaction vials (three batch samples) was cooled to room temperature every 0.5 hours. The reaction mixture was then diluted with DCM (5 mL). The resulting mixture was allowed to stir for 10 min and then filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and yields (average yield of three batch samples) are based on ^{1}HNMR analysis of the crude reaction solution using 1, 1, 2, 2-tetrachloroethane (33.6 mg, 0.2 mmol, 1.0 equiv, a singlet peak around 5.96 was set as 1.00) was added as an internal standard.

Table S3 Yield (%) of arylation with benzene

Time (h)	Yield 1	Yield 2	Yield 3	Average
0.5	4.2	4.1	3.9	4
1.0	9.8	9.9	10.2	10
1.5	21	20.4	20	20
2.0	30.5	30	30	30
2.5	38.9	38.5	39	39

Table S4 Yield (%) of arylation with benzene-d$_6$

Time (h)	Yield 1	Yield 2	Yield 3	Average
0.5	0.8	0.9	1.1	1
1.0	1.9	1.9	2.1	2
1.5	4.9	4.9	5.1	5
2.0	10.8	11	9	10
2.5	15.8	15	16	16



KIE = 0.9936/0.9328 = 2.4

Fig. S1 KIE value of parallel reaction

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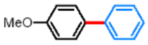
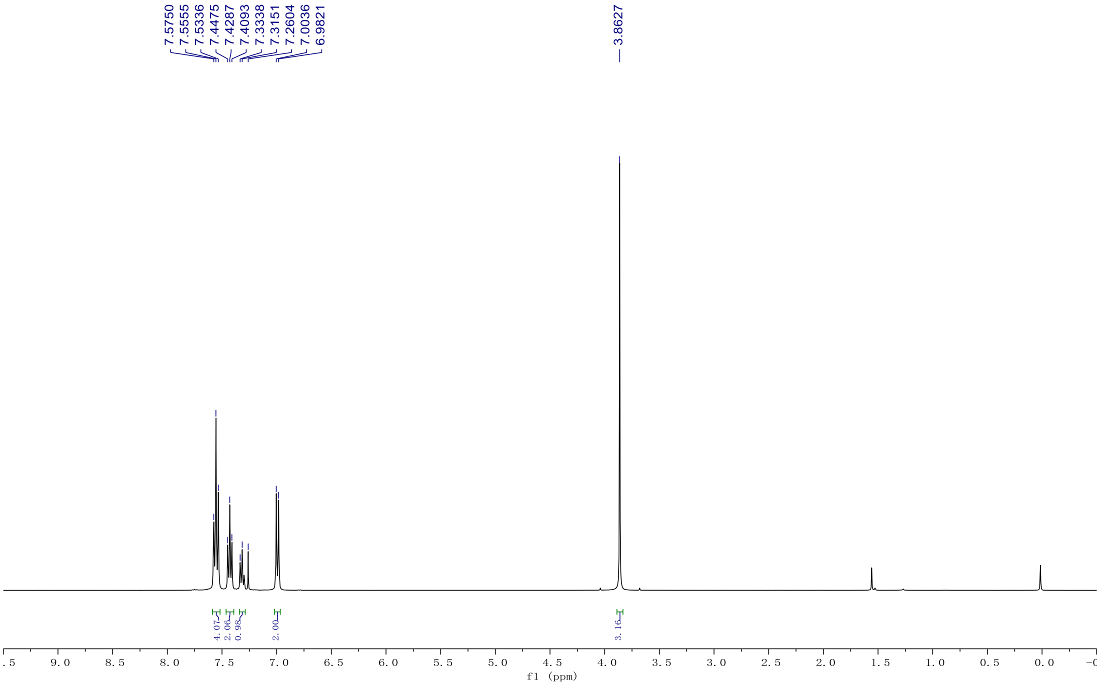
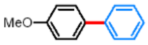
10 NMR spectra

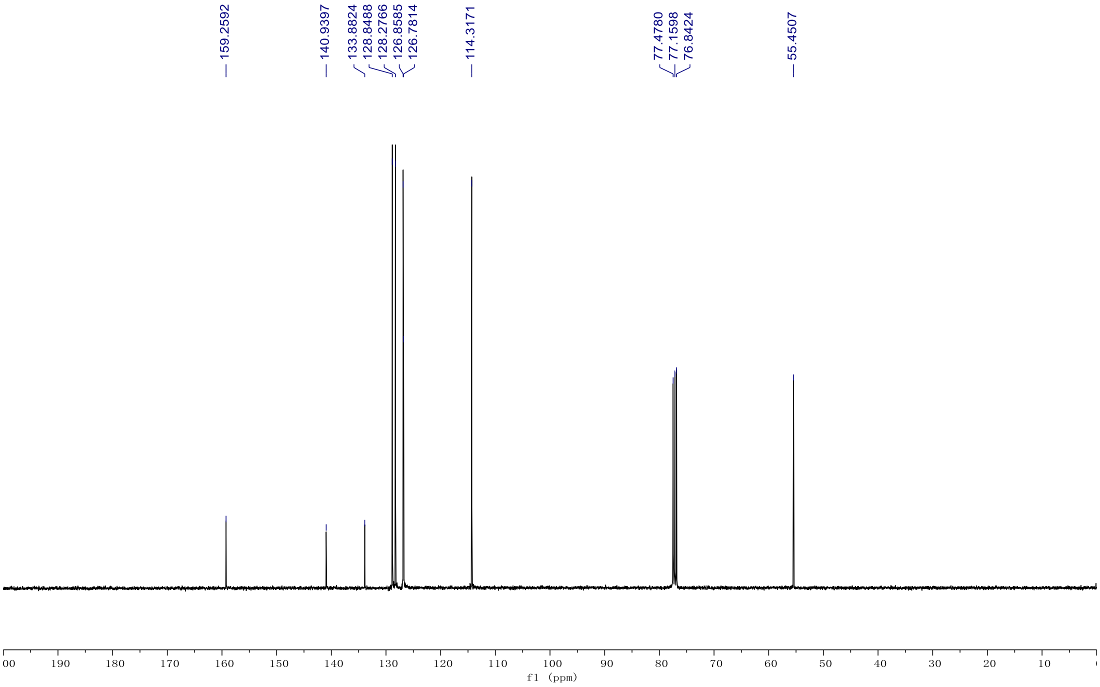


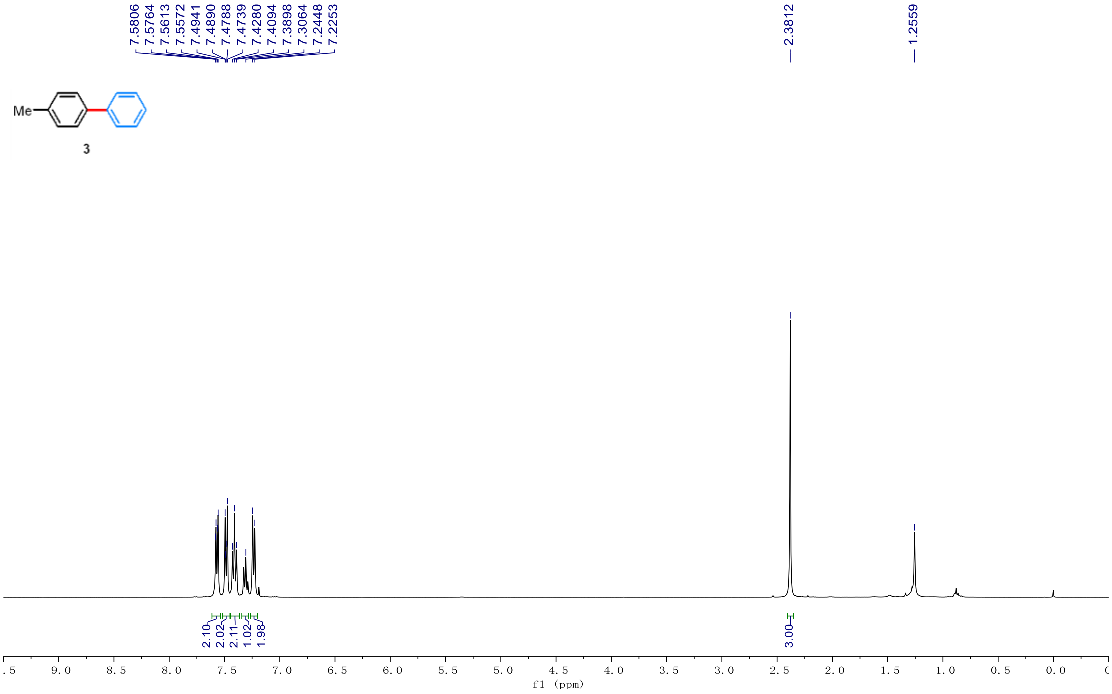
2



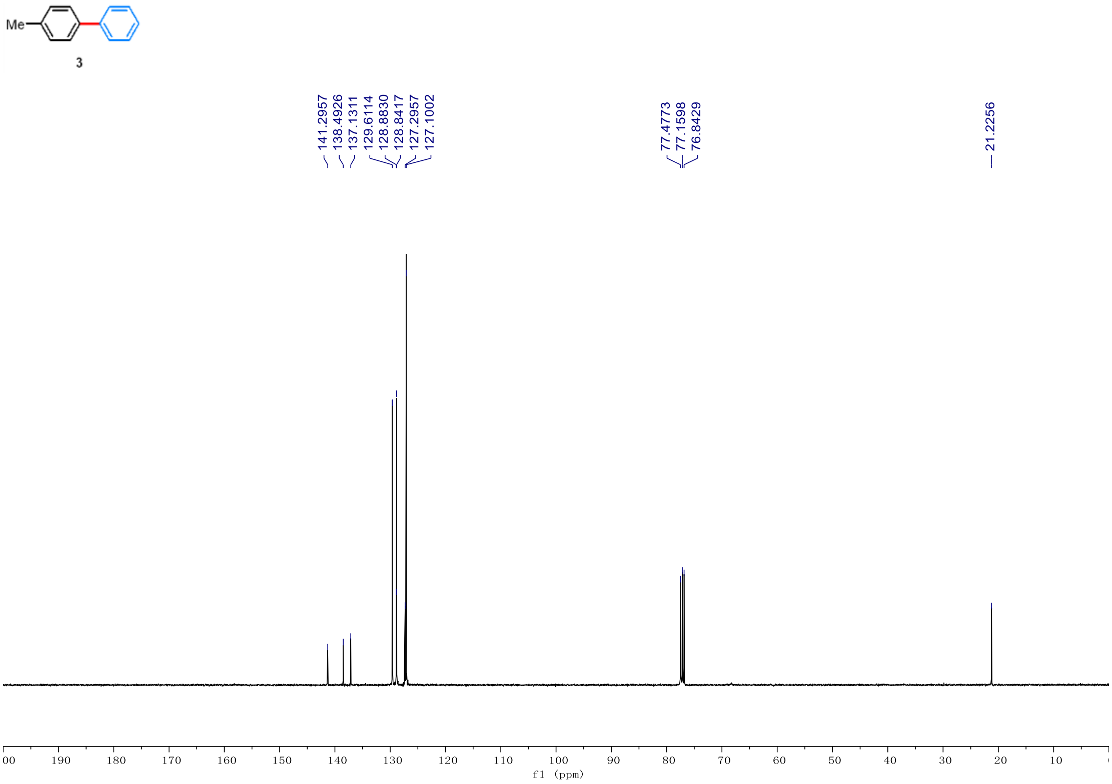


2

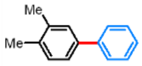



3

7.5806
7.5764
7.5613
7.5572
7.4941
7.4890
7.4788
7.4739
7.4280
7.4094
7.3898
7.3064
7.2448
7.2253
2.3812
1.2559
Me
2.10
2.02
2.11
1.02
1.98
3.00
.5
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
f1 (ppm)


3

141.2957
138.4926
137.1311
129.6114
128.8830
128.8417
127.2957
127.1002
77.4773
77.1598
76.8429
21.2256
Me
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



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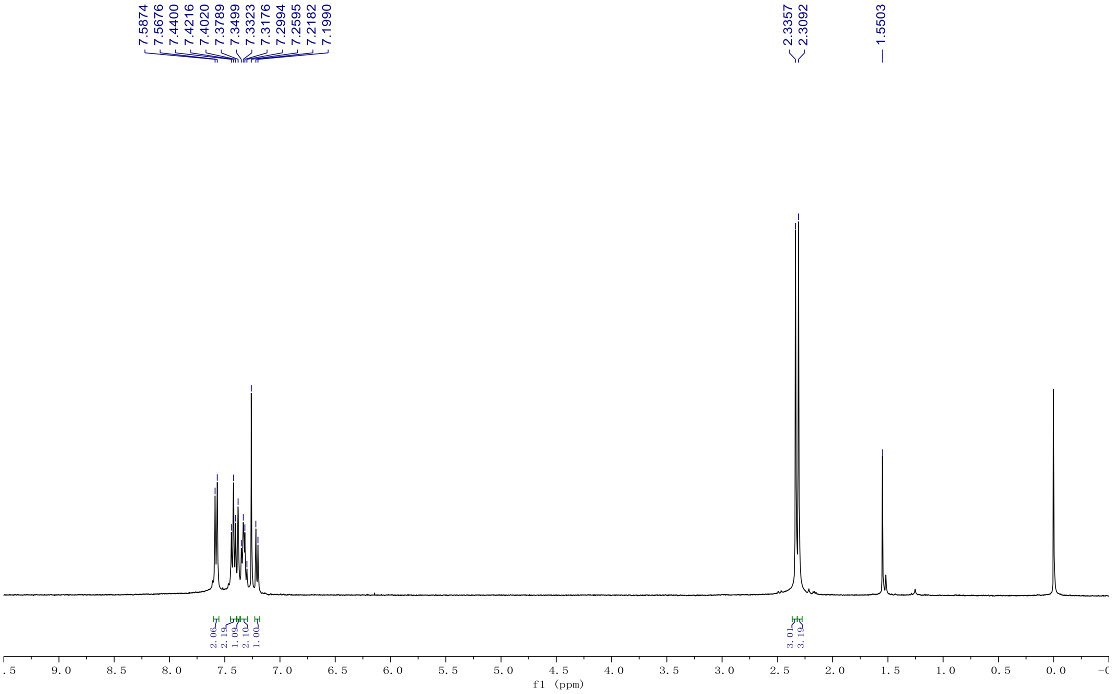
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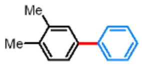
7.5676
7.4400
7.4216
7.4020
7.3789
7.3499
7.3323
7.3176
7.2994
7.2595
7.2182
7.1990
2.3357
2.3092
1.5503
2.06
2.19
1.09
2.10
1.00
3.01
3.19
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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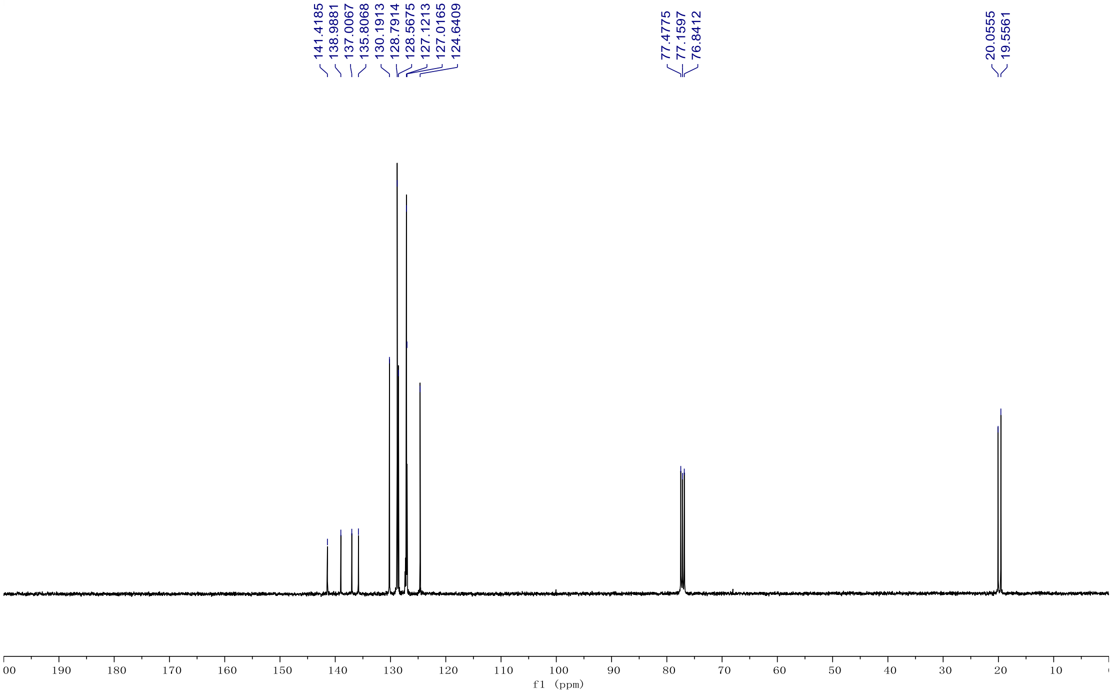
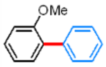
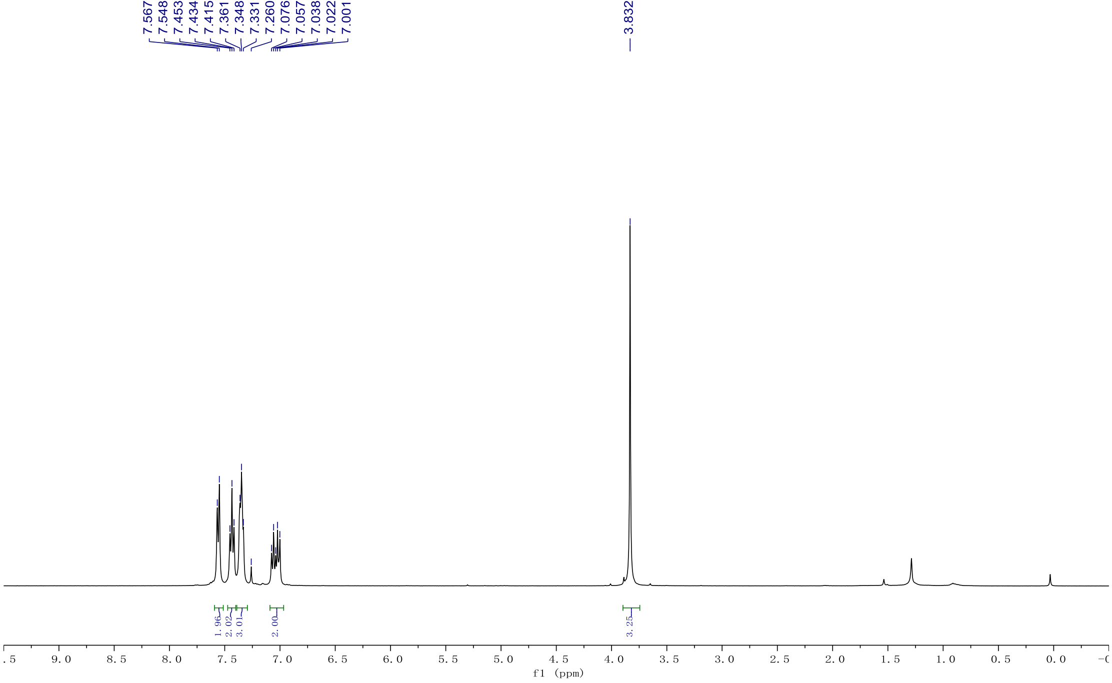
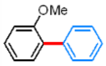

141.4185
138.9881
137.0067
135.8068
130.1913
128.7914
128.5675
127.1213
127.0165
124.6409
77.4775
77.1597
76.8412
20.0555
19.5561
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

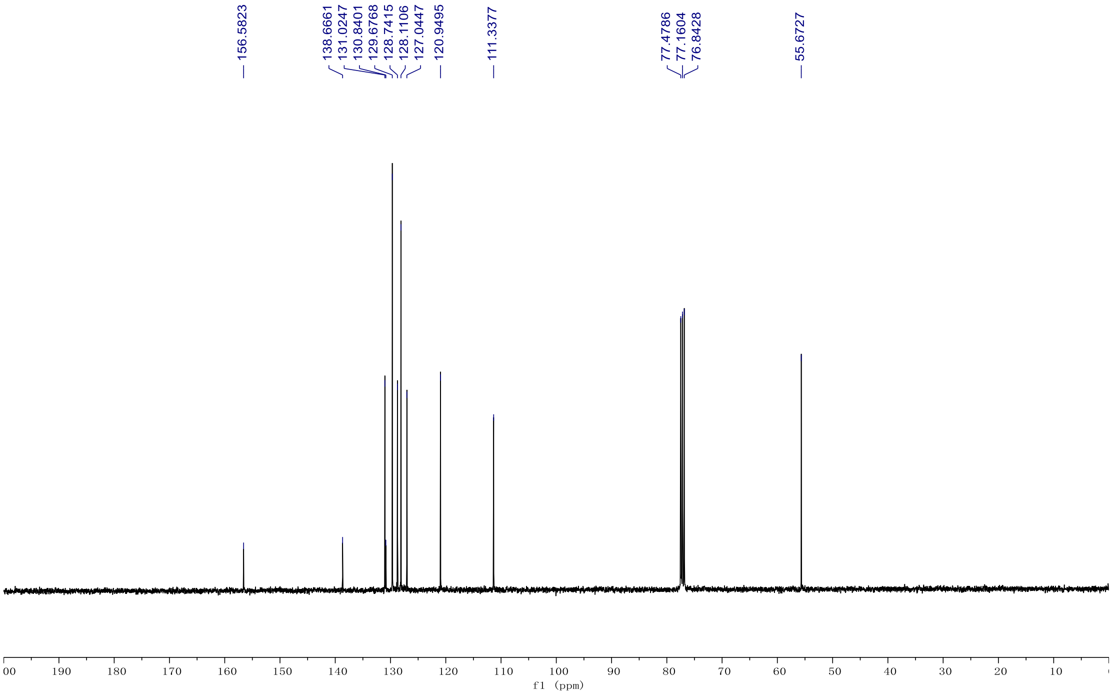

OMe

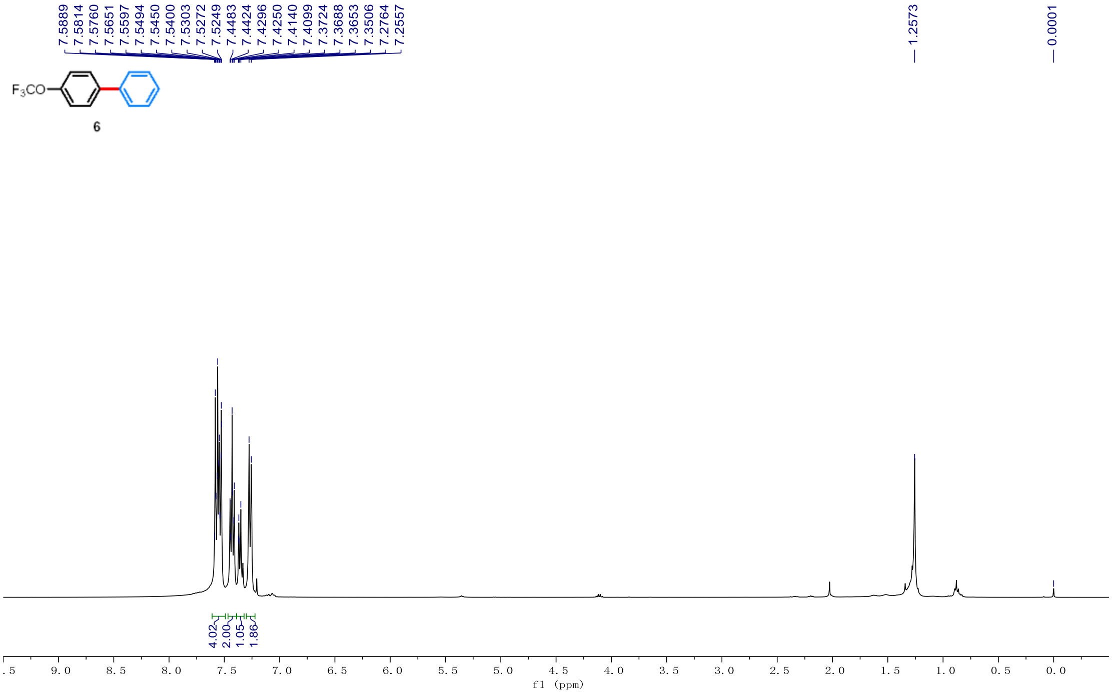
5


7.5673
7.5488
7.4531
7.4347
7.4158
7.3617
7.3481
7.3314
7.2600
7.0760
7.0576
7.0389
7.0225
7.0013
3.8321
1.96
2.02
3.01
2.00
3.25
.5
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
f1 (ppm)

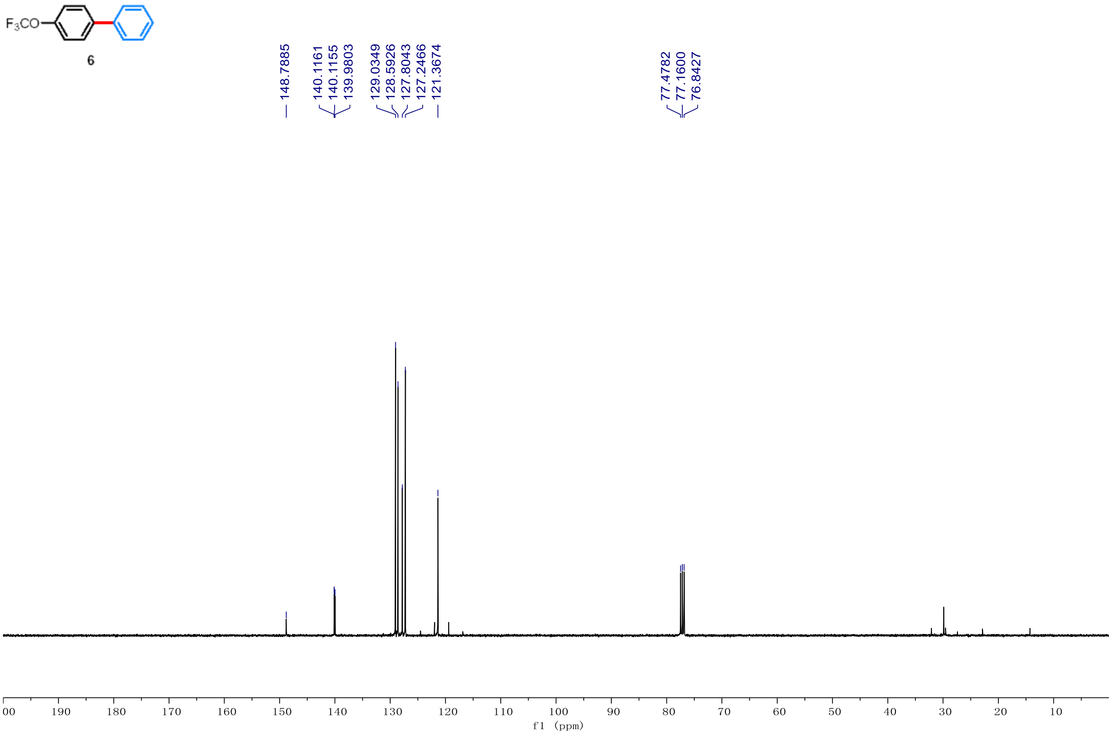

OMe

5

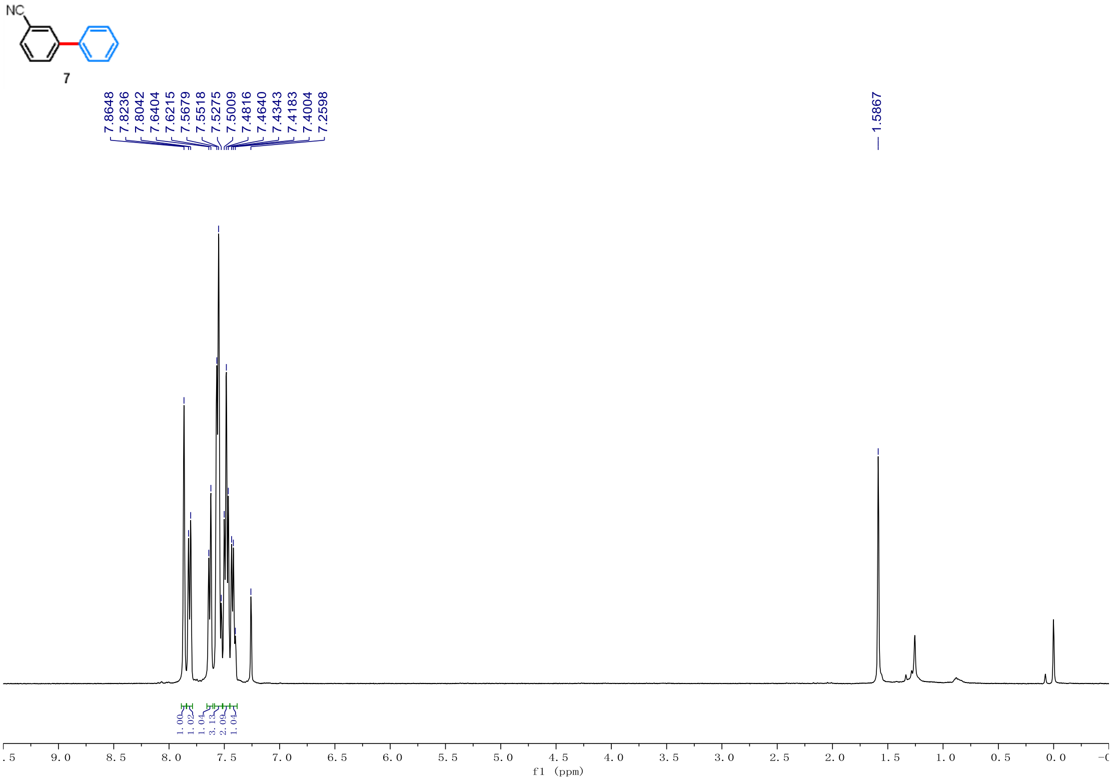

156.5823
138.6661
131.0247
130.8401
129.6768
128.7415
128.1106
127.0447
120.9495
111.3377
77.4786
77.1604
76.8428
55.6727
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

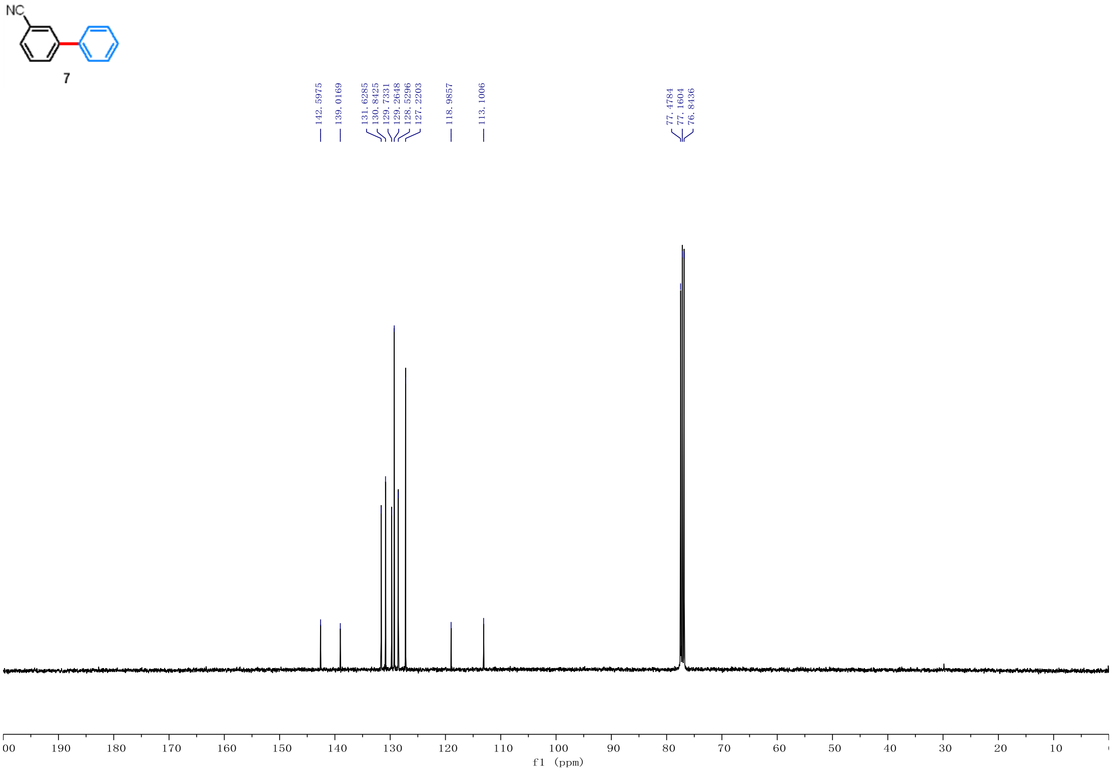

6

7.5889
7.5814
7.5760
7.5651
7.5597
7.5494
7.5450
7.5400
7.5303
7.5272
7.5249
7.4483
7.4424
7.4296
7.4250
7.4140
7.4099
7.3724
7.3688
7.3653
7.3506
7.2764
7.2557
1.2573
0.0001
F3CO
4.02
2.00
1.05
1.86
.5
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
f1 (ppm)


6

F3CO
148.7885
140.1161
140.1155
139.9803
129.0349
128.5926
127.8043
127.2466
121.3674
77.4782
77.1600
76.8427
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


NC
7
7.8648
7.8236
7.8042
7.6404
7.6215
7.5679
7.5518
7.5275
7.5009
7.4816
7.4640
7.4343
7.4183
7.4004
7.2598
1.5867
1.00
1.02
1.04
3.13
2.09
1.04
.5
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
f1 (ppm)


NC
7
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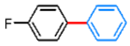
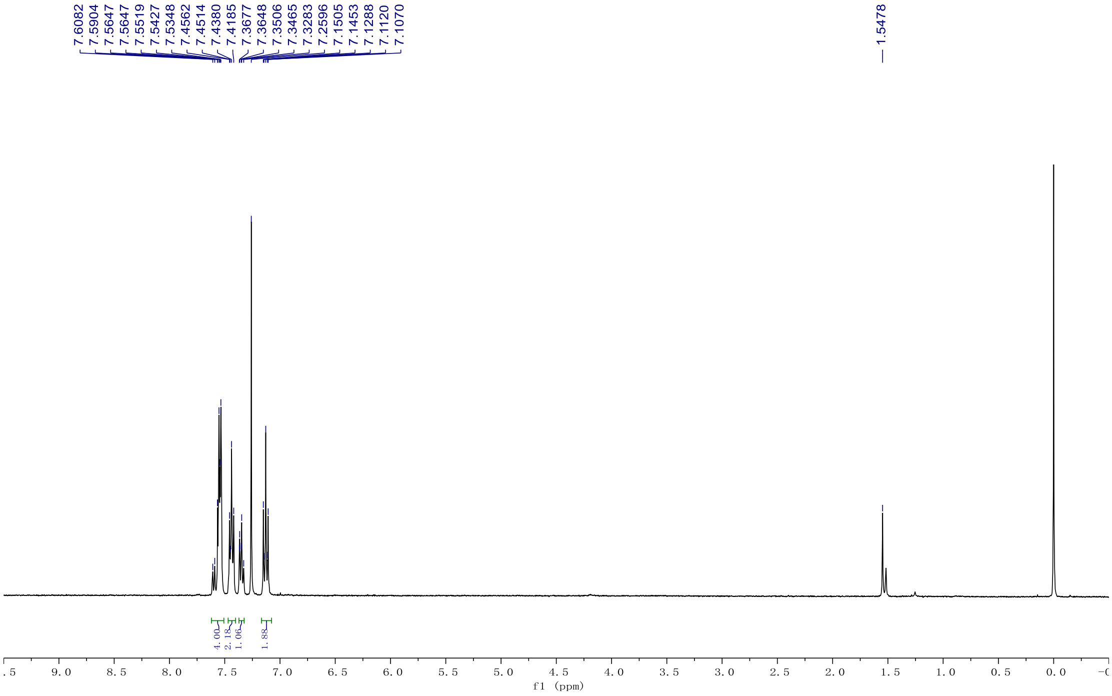
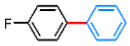
139.0169
131.6285
130.8425
129.7331
129.2648
128.5296
127.2203
118.9857
113.1006
77.4784
77.1604
76.8436
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

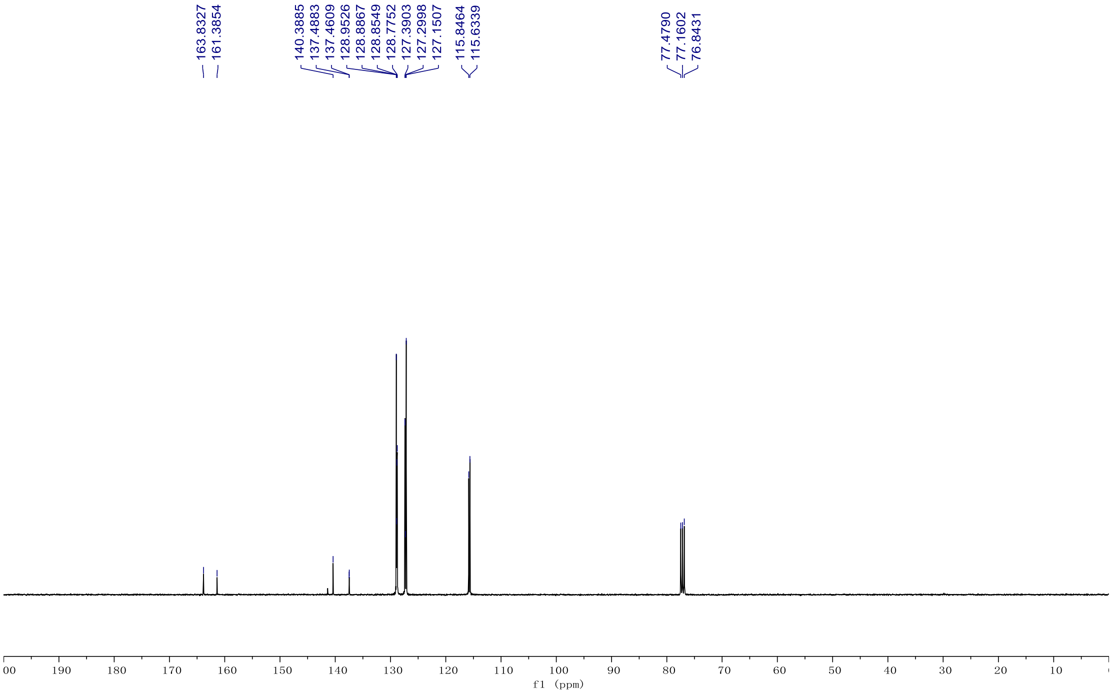

F

8


7.6082
7.5904
7.5647
7.5647
7.5519
7.5427
7.5348
7.4562
7.4514
7.4380
7.4185
7.3677
7.3648
7.3506
7.3465
7.3283
7.2596
7.1505
7.1453
7.1288
7.1120
7.1070
1.5478
4.00
2.18
1.06
1.88
.5
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
f1 (ppm)


F

8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137.4609
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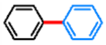
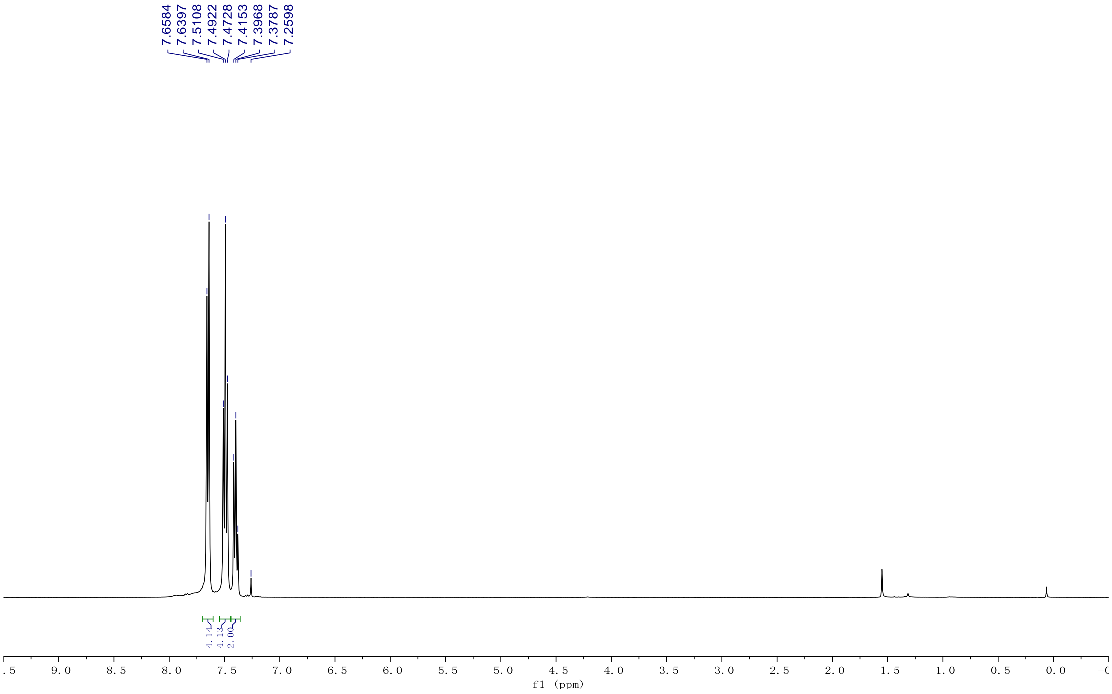
128.8867
128.8549
128.7752
127.3903
127.2998
127.1507
115.8464
115.6339
77.4790
77.1602
76.8431
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



9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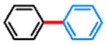
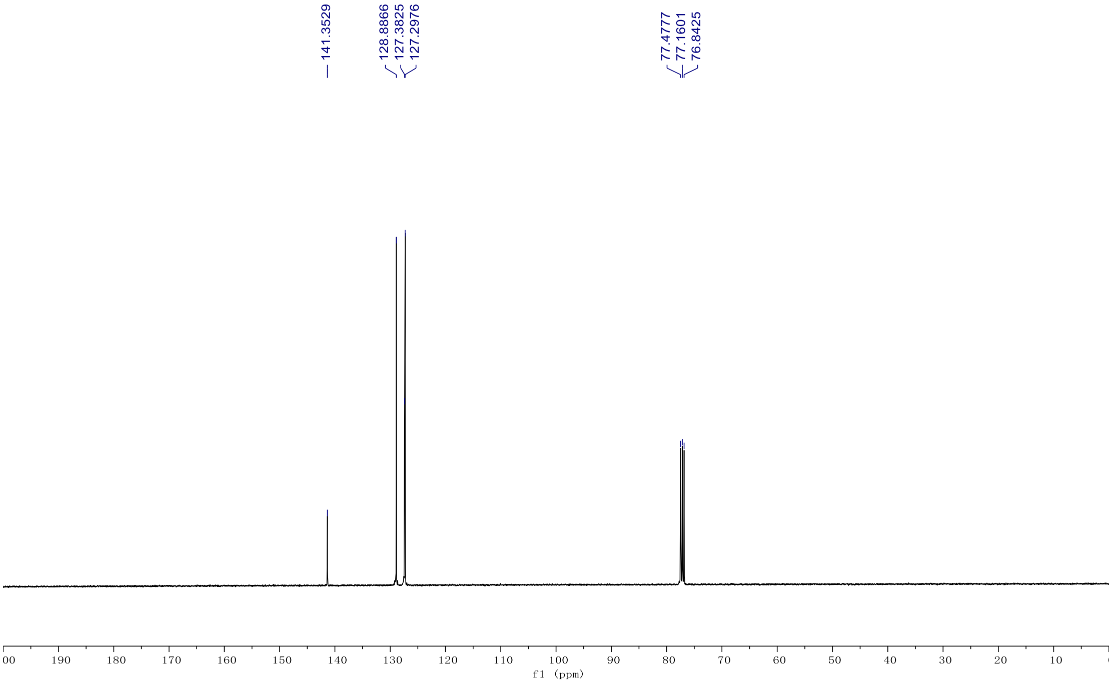
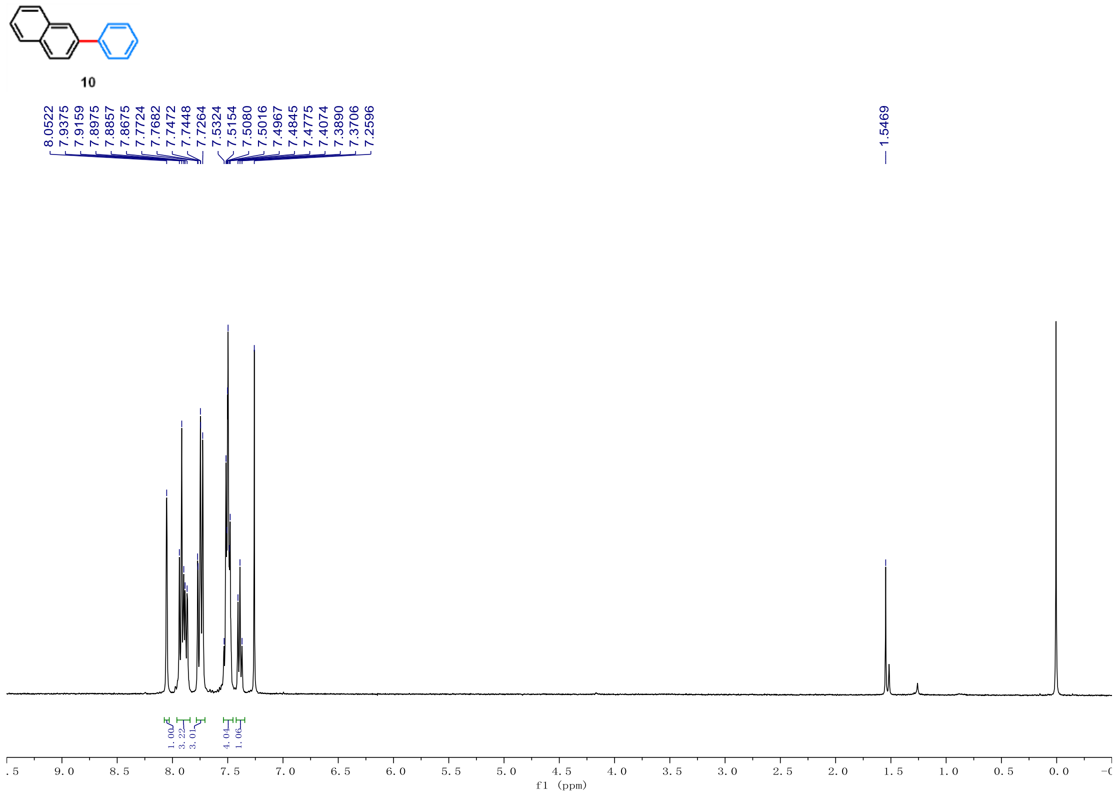
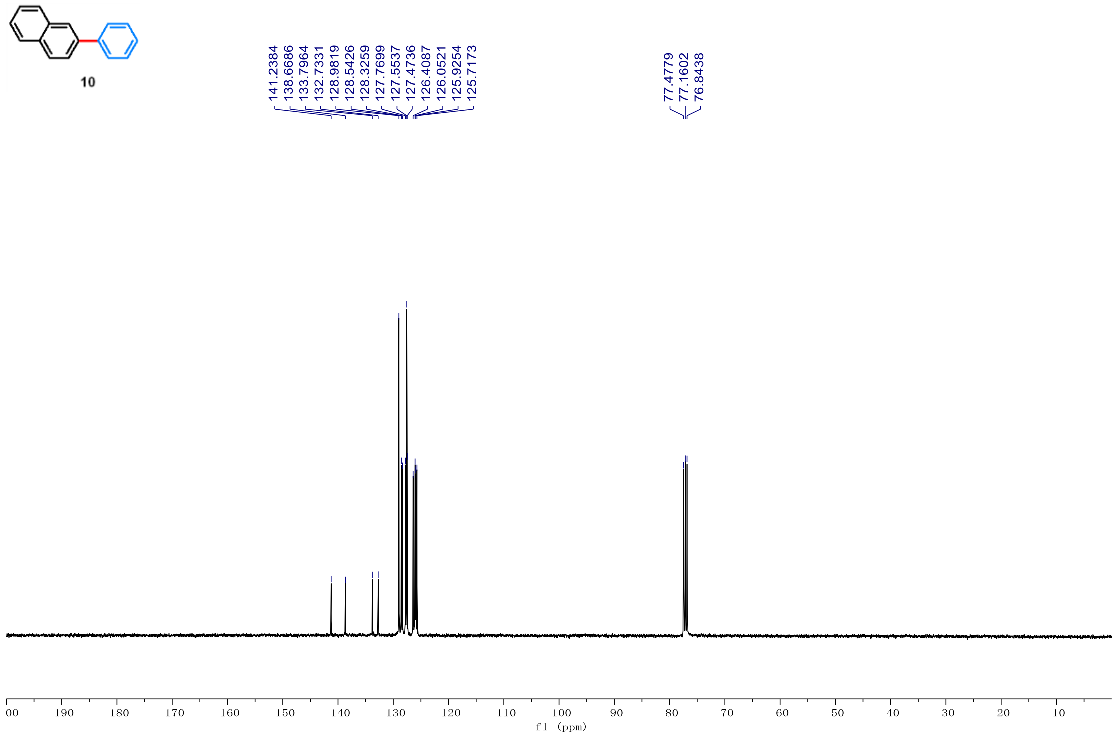
7.6397
7.5108
7.4922
7.4728
7.4153
7.3968
7.3787
7.2598
4.14
4.13
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

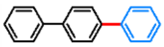


9

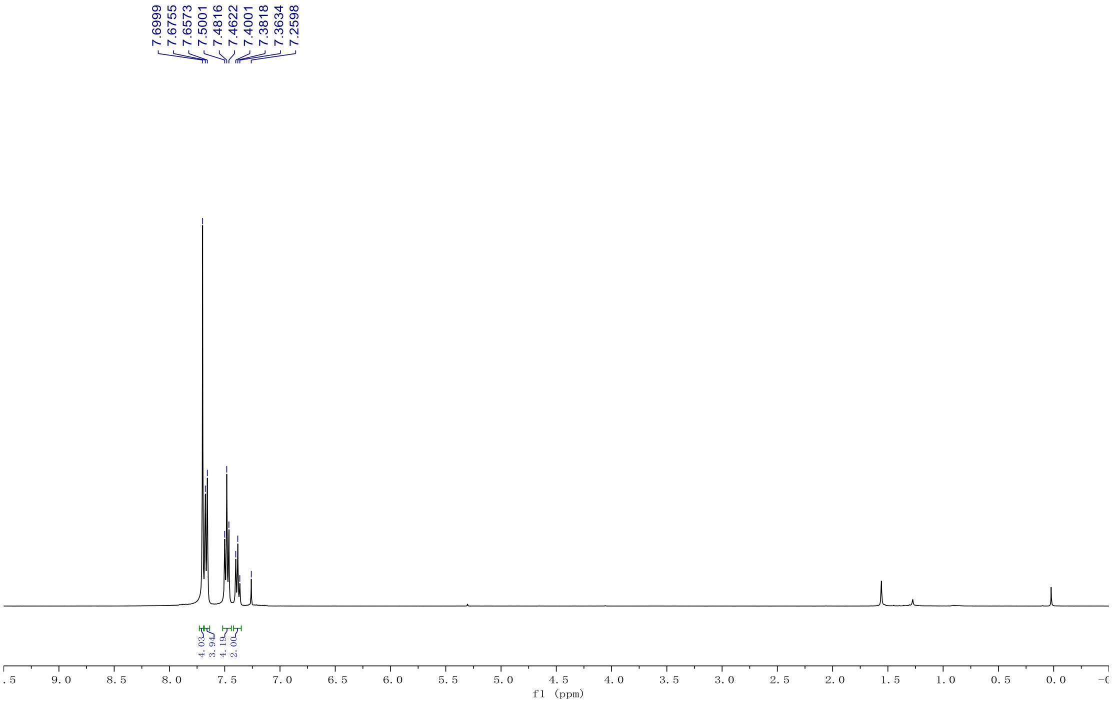

141.3529
128.8866
127.3825
127.2976
77.4777
77.1601
76.8425
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

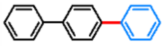

10
8.0522
7.9375
7.9159
7.8975
7.8857
7.8675
7.7724
7.7682
7.7472
7.7448
7.7264
7.5324
7.5154
7.5080
7.5016
7.4967
7.4845
7.4775
7.4074
7.3890
7.3706
7.2596
1.5469
1.00
3.22
3.01
4.04
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


10
141.2384
138.6686
133.7964
132.7331
128.9819
128.5426
128.3259
127.7699
127.5537
127.4736
126.4087
126.0521
125.9254
125.7173
77.4779
77.1602
76.8438
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

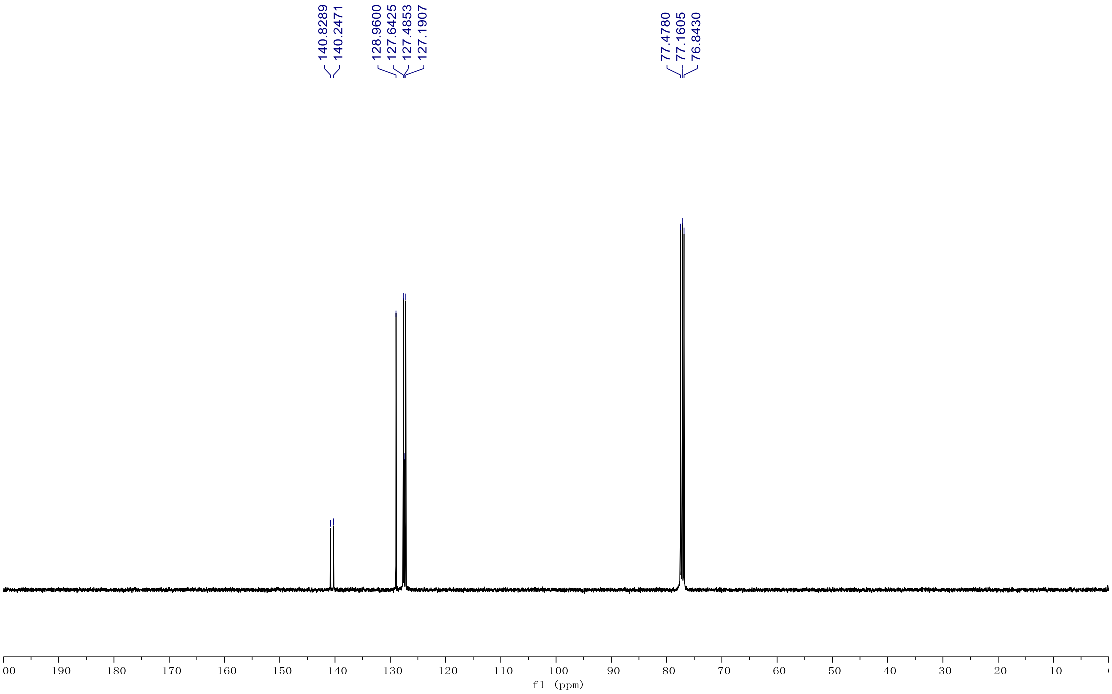


11


7.6999
7.6755
7.6573
7.5001
7.4816
7.4622
7.4001
7.3818
7.3634
7.2598
4.03
3.94
4.19
2.00
.5
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
f1 (ppm)



11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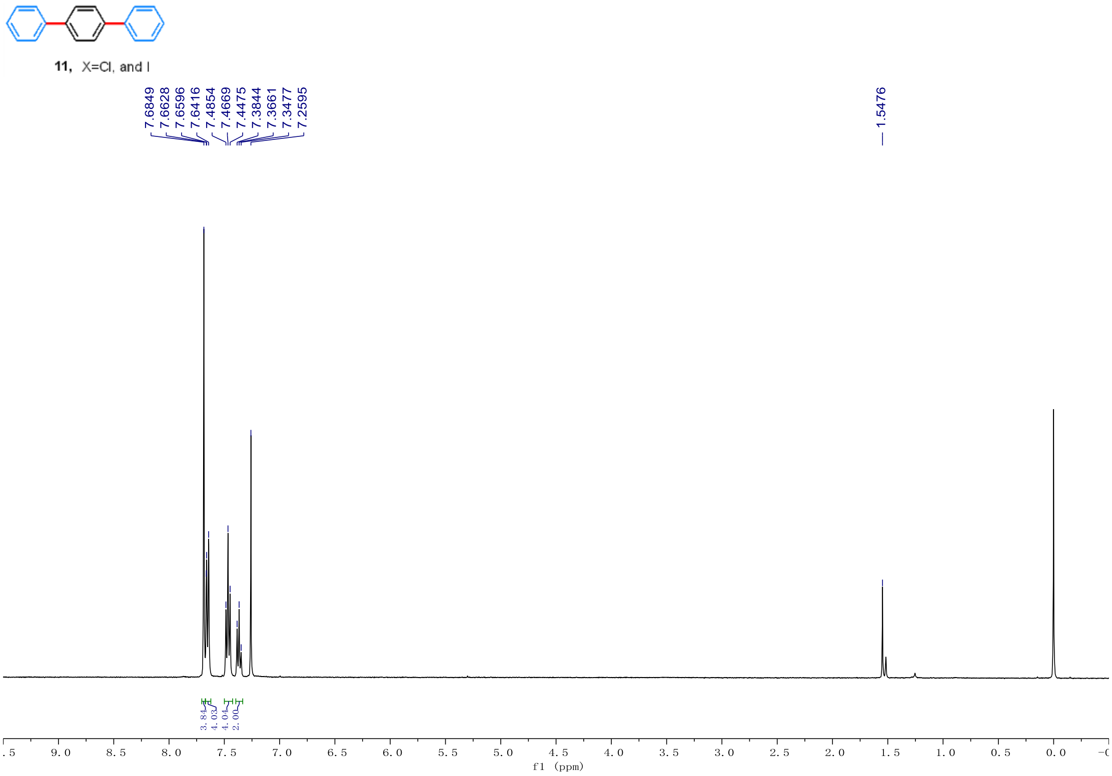
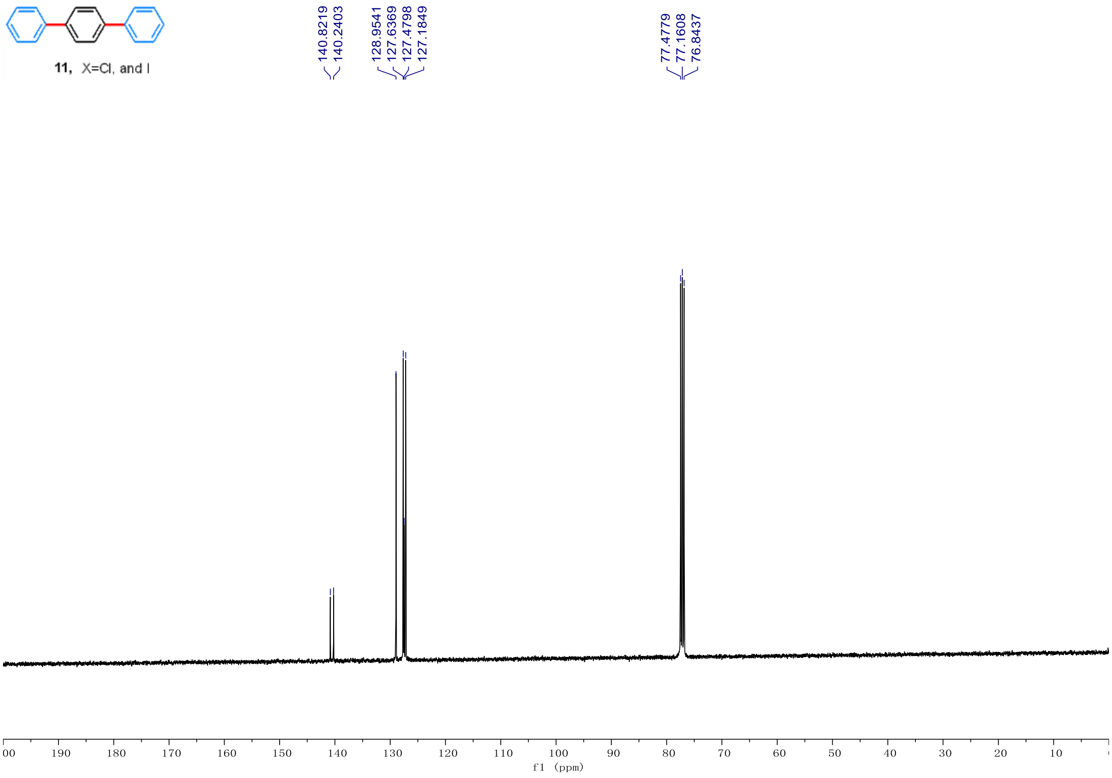
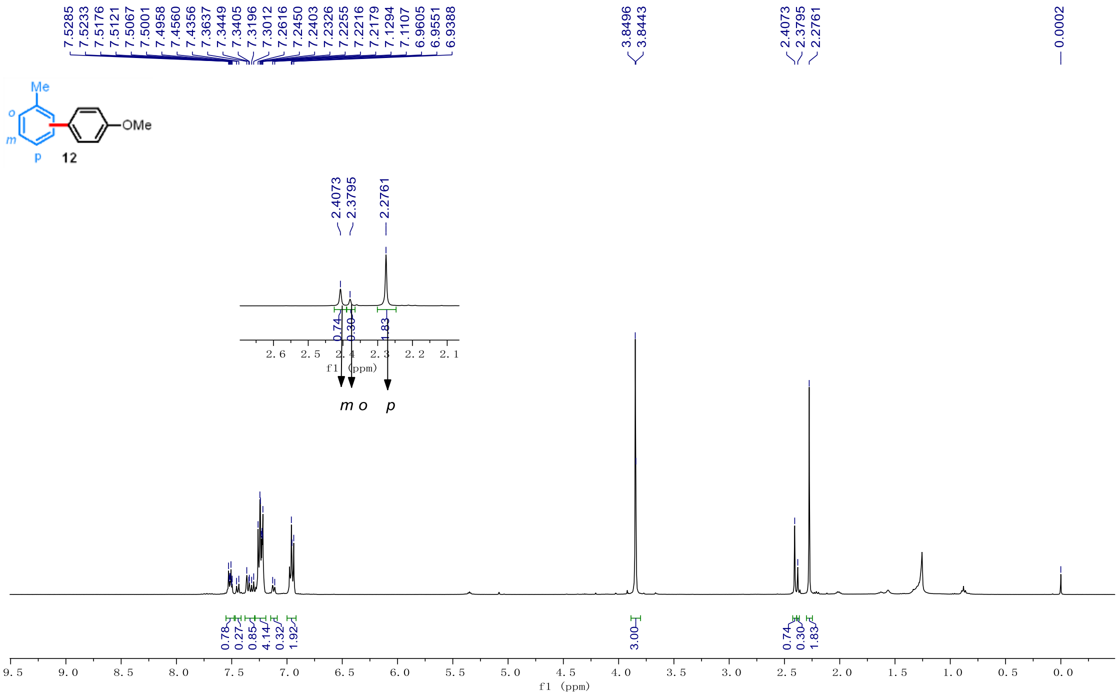
128.9600
127.6425
127.4853
127.1907
77.4780
77.1605
76.8430
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

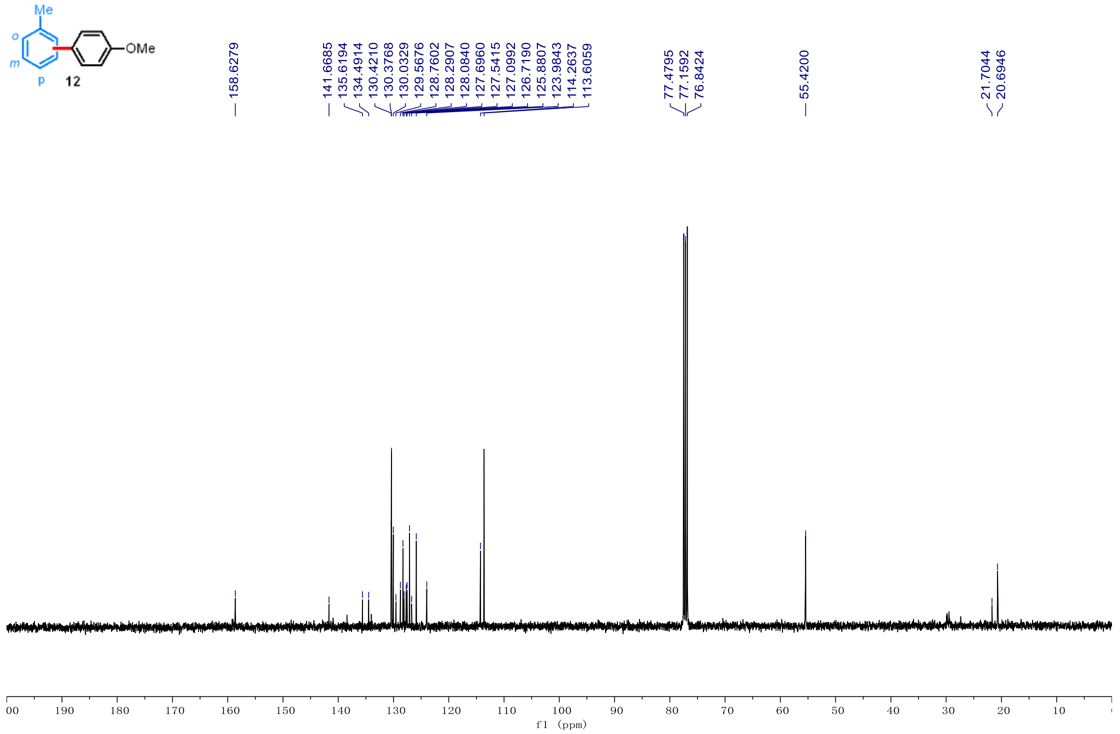


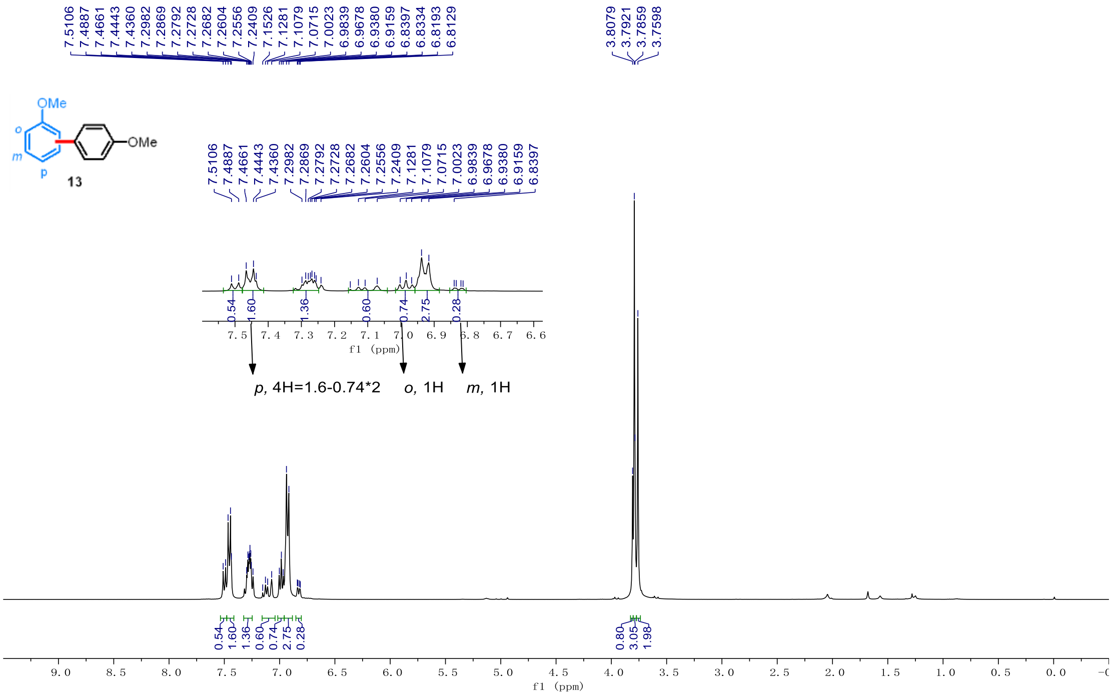
11, X=Cl, and I



11, X=Cl, and I


7.5285
7.5233
7.5176
7.5121
7.5067
7.5001
7.4958
7.4560
7.4356
7.3637
7.3449
7.3405
7.3196
7.3012
7.2616
7.2450
7.2403
7.2326
7.2255
7.2216
7.2179
7.1294
7.1107
6.9605
6.9551
6.9388
3.8496
3.8443
2.4073
2.3795
2.2761
0.0002
Me
o
m
p
OMe
12
2.4073
2.3795
2.2761
0.74
0.30
1.83
2.6 2.5 2.4 2.3 2.2 2.1
f1 (ppm)
m o p
0.78
0.27
0.85
4.14
0.32
1.92
3.00
0.74
0.30
1.83
9.5 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
f1 (ppm)


Me
o
m
p
OMe
12
158.6279
141.6685
135.6194
134.4914
130.4210
130.3768
130.0329
129.5676
128.7602
128.2907
128.0840
127.6960
127.5415
127.0992
126.7190
125.8807
123.9843
114.2637
113.6059
77.4795
77.1592
76.8424
55.4200
21.7044
20.6946
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.4661
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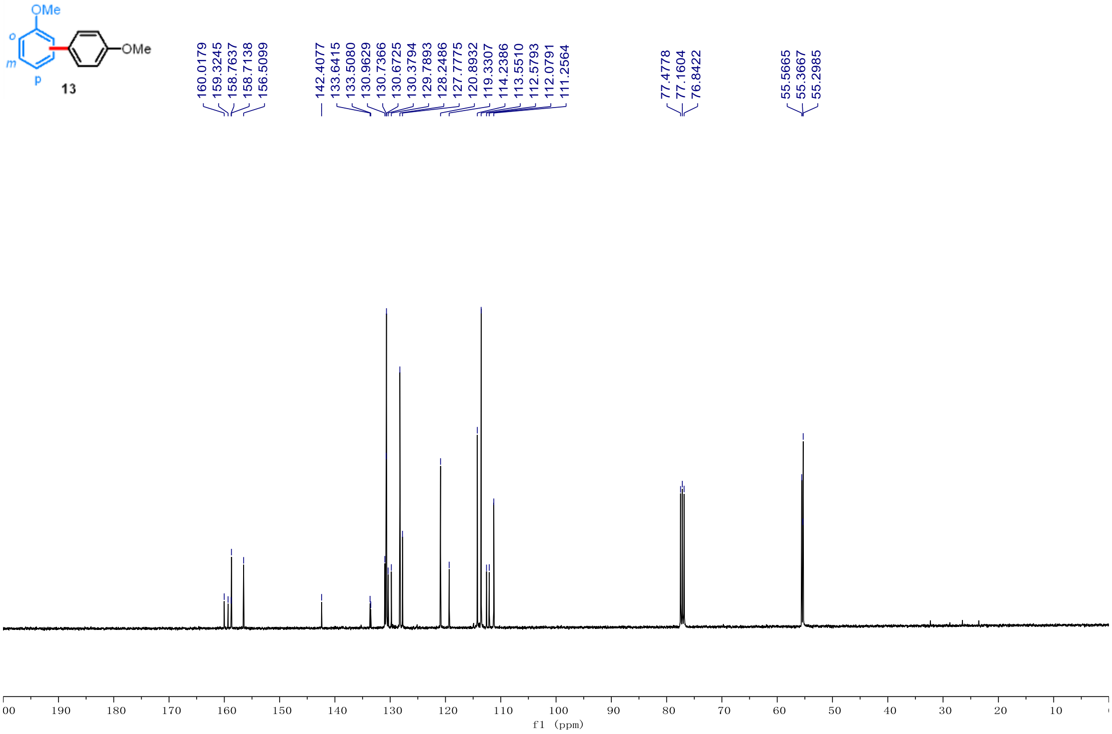
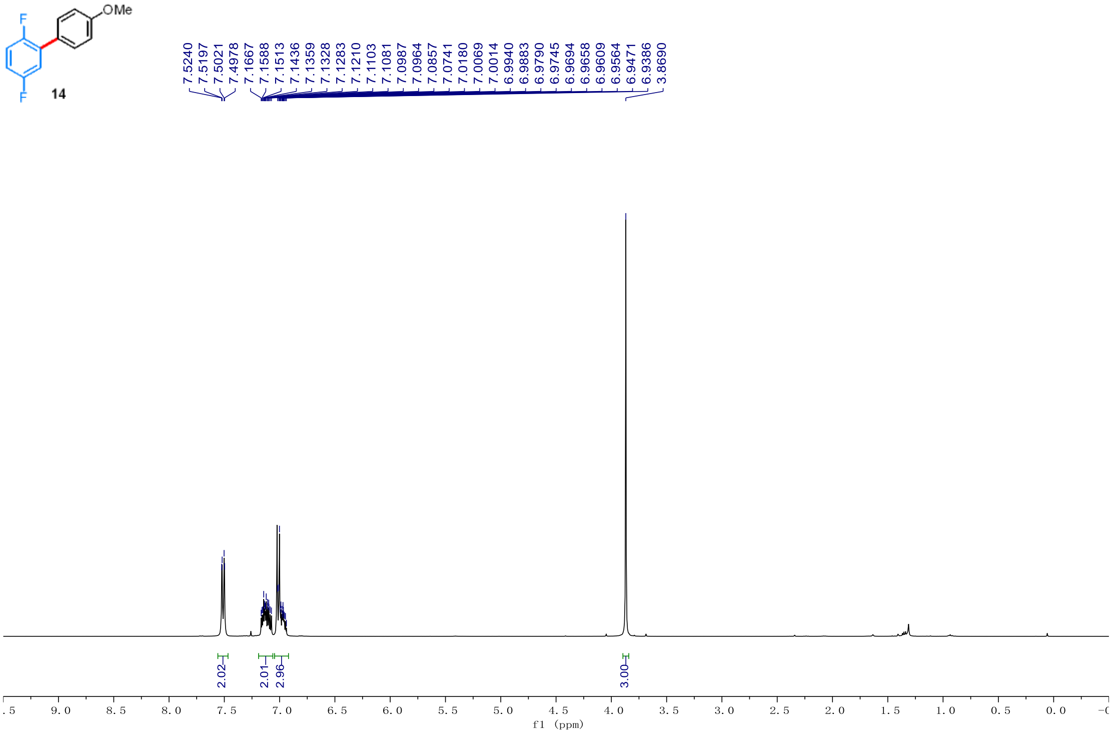
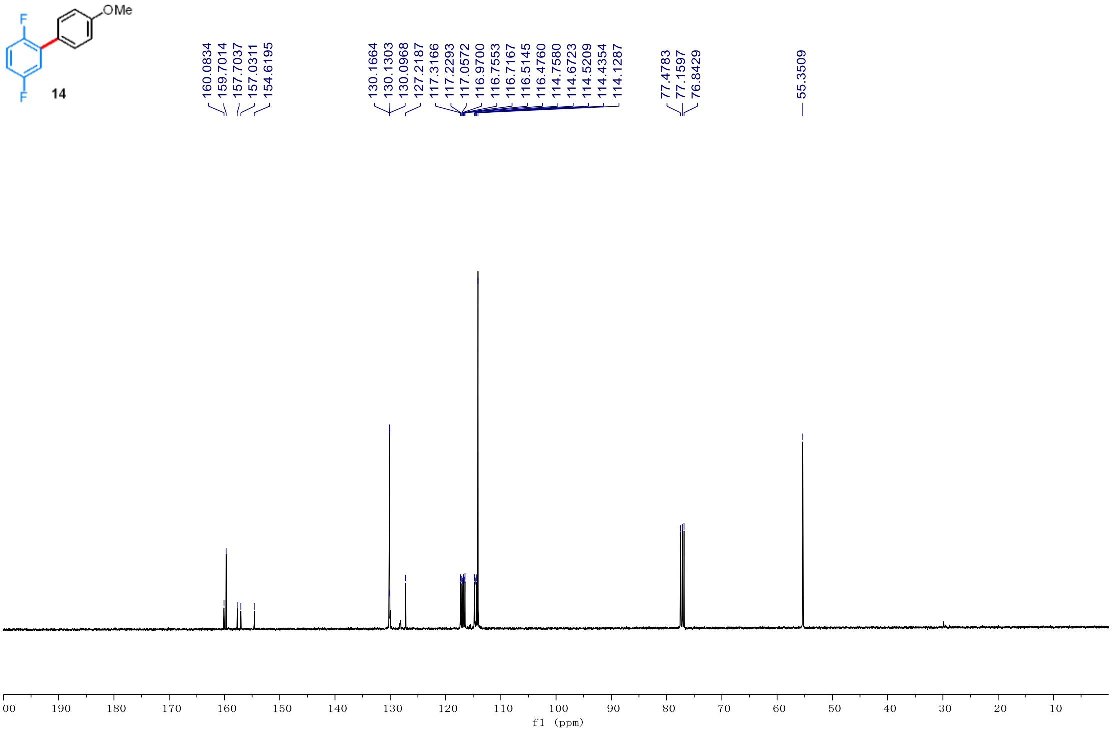
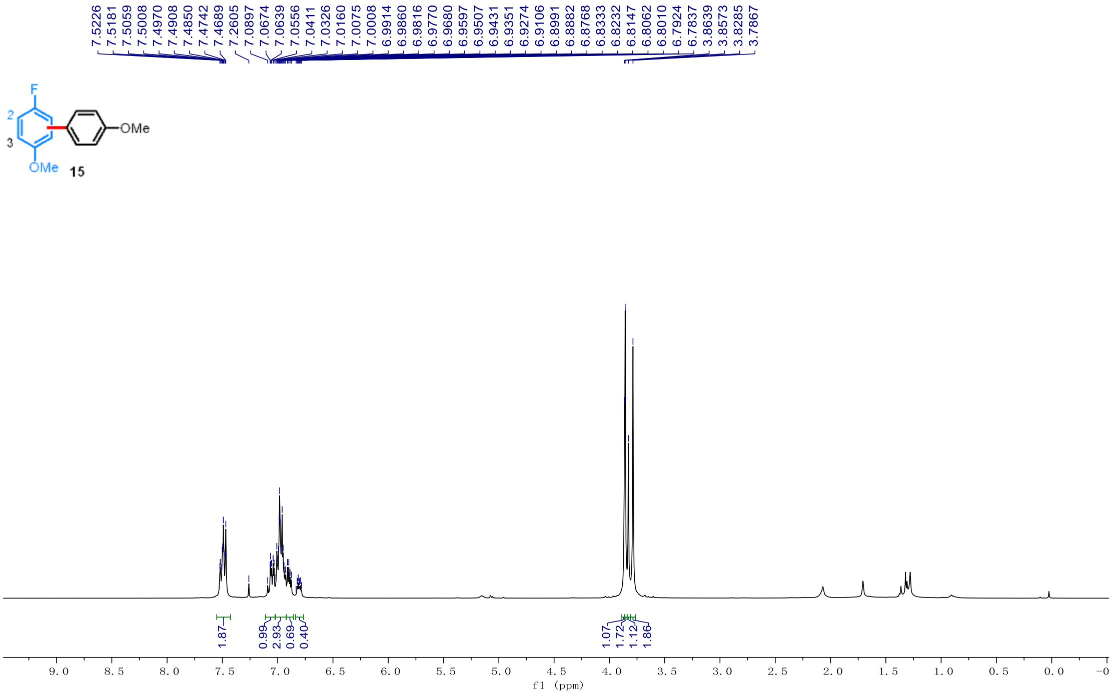
7.4360
7.2982
7.2869
7.2792
7.2728
7.2682
7.2604
7.2556
7.2409
7.1526
7.1281
7.1079
7.0715
7.0023
6.9839
6.9678
6.9380
6.9159
6.8397
6.8334
6.8193
6.8129
3.8079
3.7921
3.7859
3.7598
OMe
o
m
p
13
OMe
p, 4H=1.6-0.74*2
o, 1H
m, 1H
0.54
1.60
1.36
0.60
0.74
2.75
0.28
0.80
3.05
1.98
f1 (ppm)

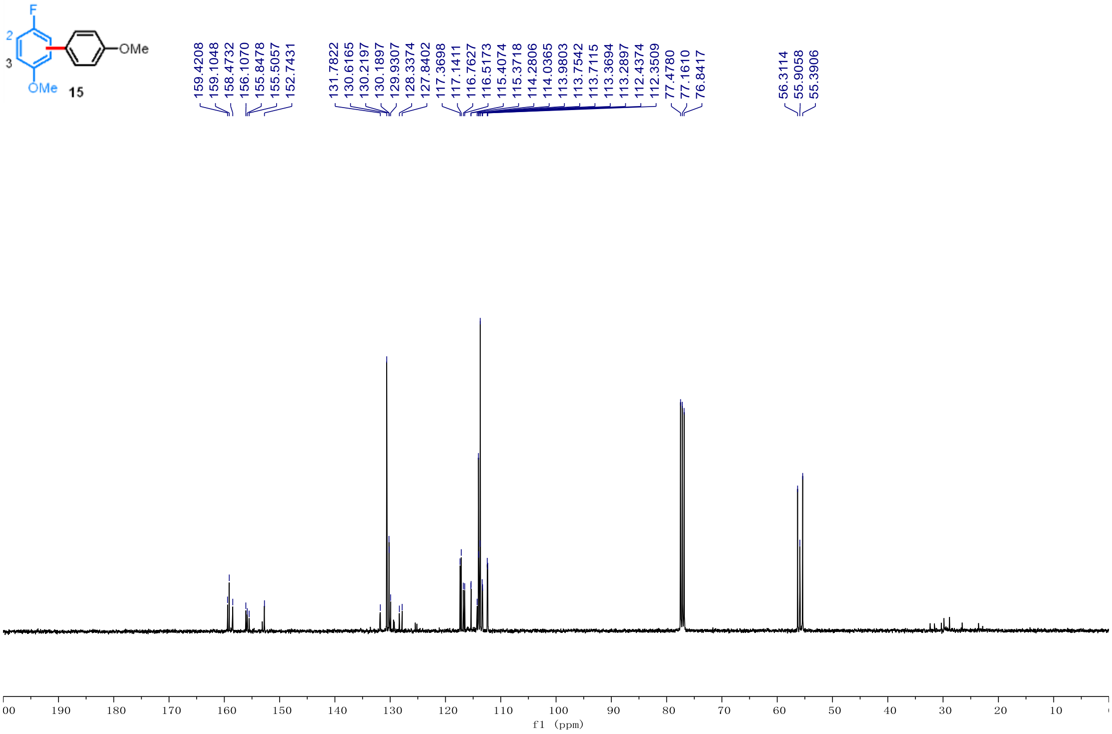

OMe
o
m
p
13
OMe
160.0179
159.3245
158.7637
158.7138
156.5099
142.4077
133.6415
133.5080
130.9629
130.7366
130.6725
130.3794
129.7893
128.2486
127.7775
120.8932
119.3307
114.2386
113.5510
112.5793
112.0791
111.2564
77.4778
77.1604
76.8422
55.5665
55.3667
55.2985
f1 (ppm)


OMe
F
F
14
7.5240
7.5197
7.5021
7.4978
7.1667
7.1588
7.1513
7.1436
7.1359
7.1328
7.1283
7.1210
7.1103
7.1081
7.0987
7.0964
7.0857
7.0741
7.0180
7.0069
7.0014
6.9940
6.9883
6.9790
6.9745
6.9694
6.9658
6.9609
6.9564
6.9471
6.9386
3.8690
2.02
2.01
2.96
3.00
.5
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
f1 (ppm)

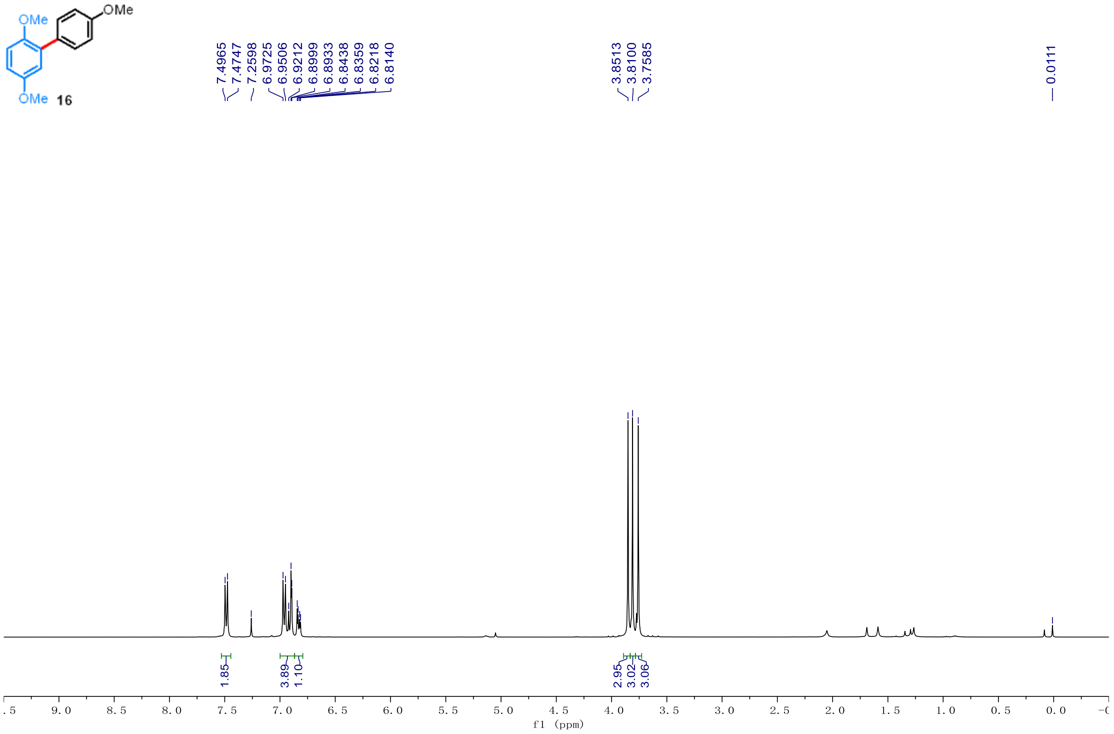

OMe
F
F
14
160.0834
159.7014
157.7037
157.0311
154.6195
130.1664
130.1303
130.0968
127.2187
117.3166
117.2293
117.0572
116.9700
116.7553
116.7167
116.5145
116.4760
114.7580
114.6723
114.5209
114.4354
114.1287
77.4783
77.1597
76.8429
55.3509
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.5226
7.5181
7.5059
7.5008
7.4970
7.4908
7.4850
7.4742
7.4689
7.2605
7.0897
7.0674
7.0639
7.0556
7.0411
7.0326
7.0160
7.0075
7.0008
6.9914
6.9860
6.9816
6.9770
6.9680
6.9597
6.9507
6.9431
6.9351
6.9274
6.9106
6.8991
6.8882
6.8768
6.8333
6.8232
6.8147
6.8062
6.8010
6.7924
6.7837
3.8639
3.8573
3.8285
3.7867
F
2
3
OMe
OMe
1.87
0.99
2.93
0.69
0.40
1.07
1.72
1.12
1.86
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
f1 (ppm)

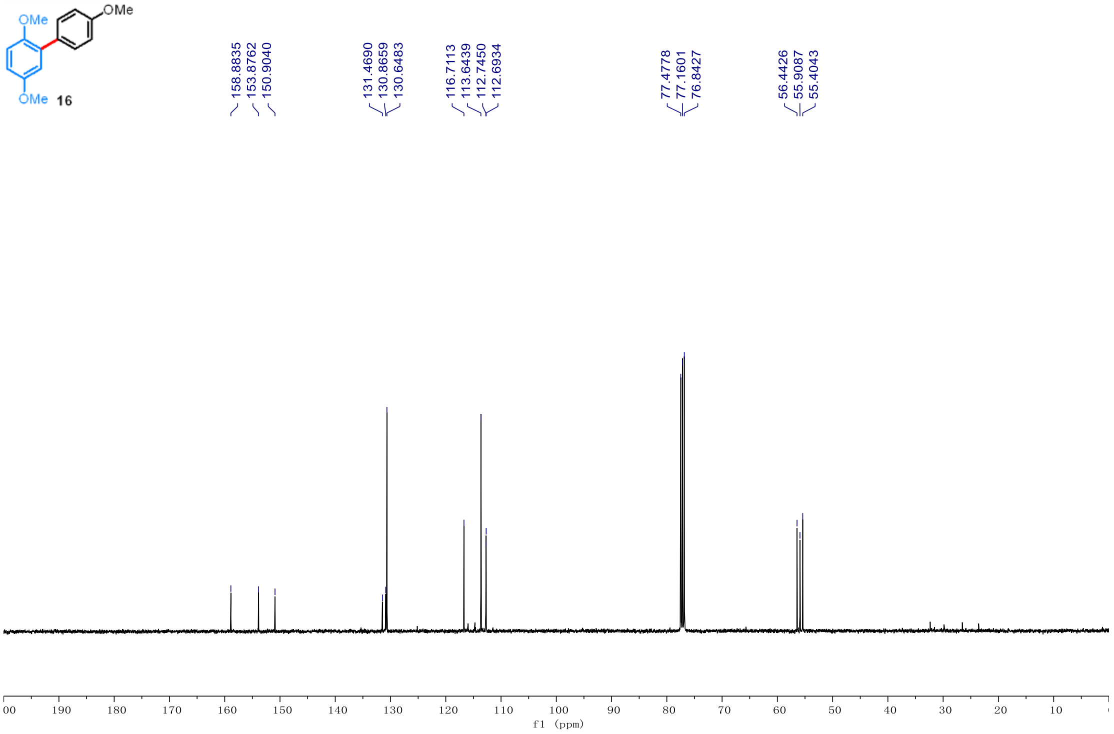
15


F
2
3
OMe
OMe
159.4208
159.1048
158.4732
156.1070
155.8478
155.5057
152.7431
131.7822
130.6165
130.2197
130.1897
129.9307
128.3374
127.8402
117.3698
117.1411
116.7627
116.5173
115.4074
115.3718
114.2806
114.0365
113.9803
113.7542
113.7115
113.3694
113.2897
112.4374
112.3509
77.4780
77.1610
76.8417
56.3114
55.9058
55.3906
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

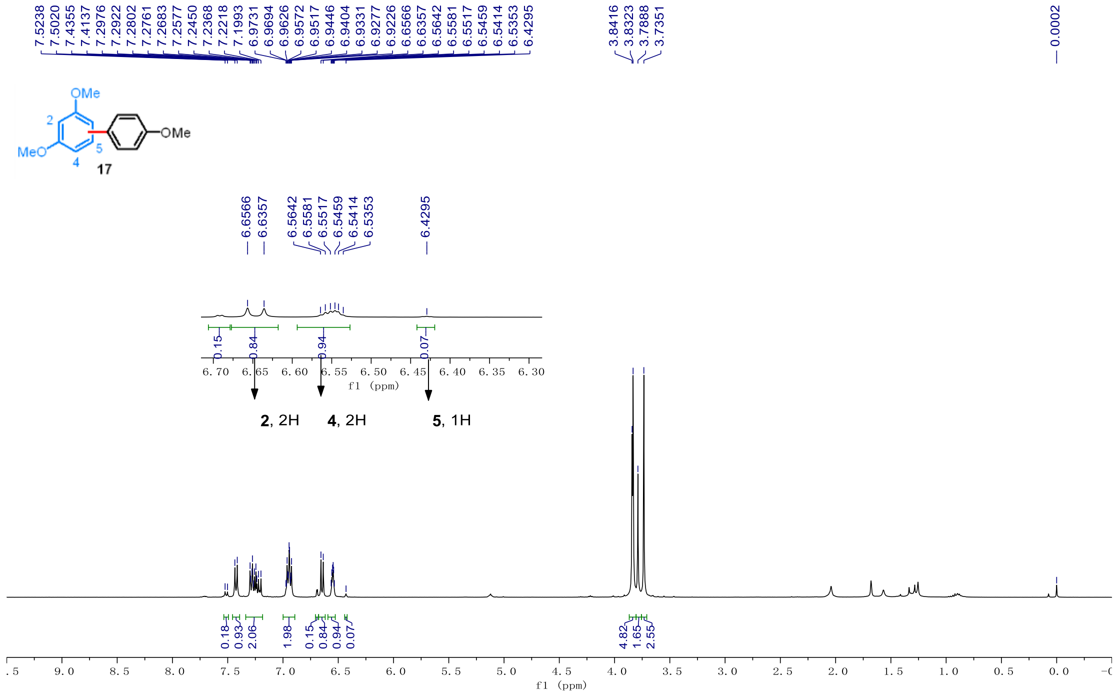
15

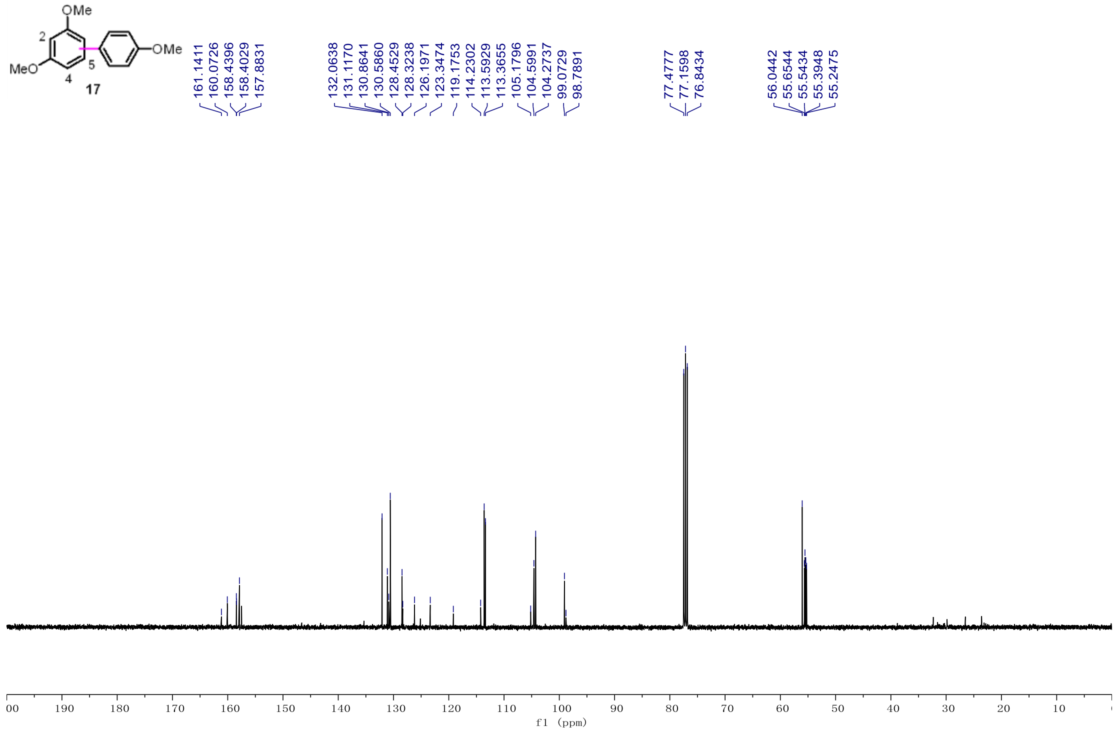


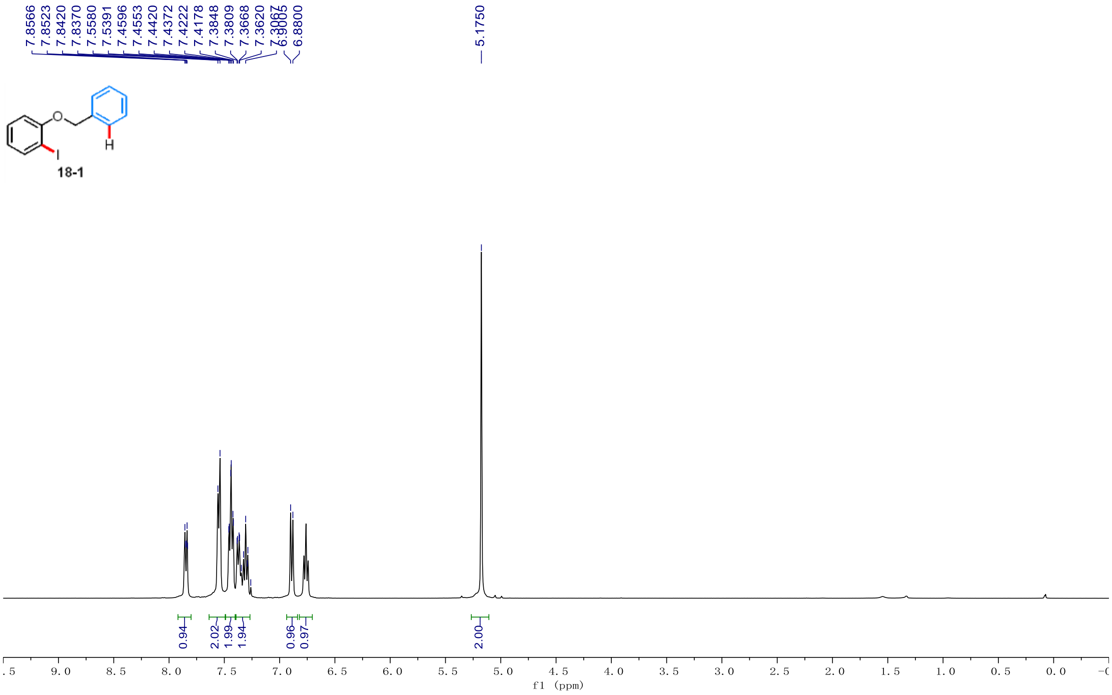
OMe
OMe
OMe
16
7.4965
7.4747
7.2598
6.9725
6.9506
6.9212
6.8999
6.8933
6.8438
6.8359
6.8218
6.8140
3.8513
3.8100
3.7585
0.0111
1.85
3.89
1.10
2.95
3.02
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

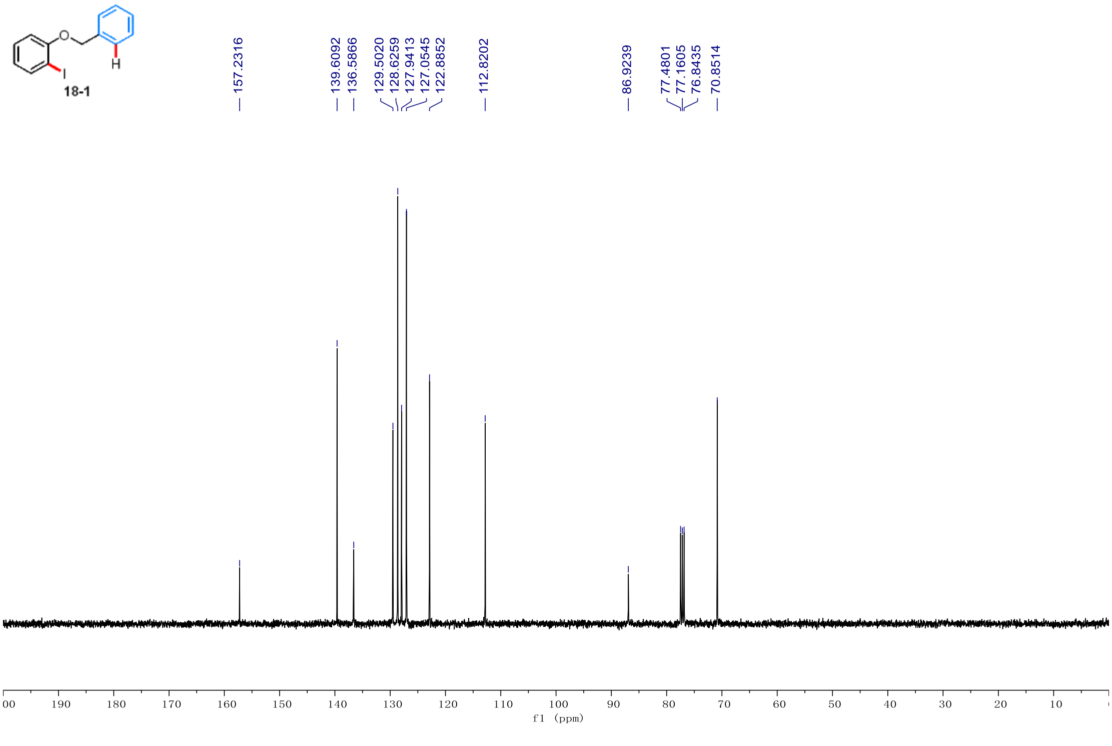


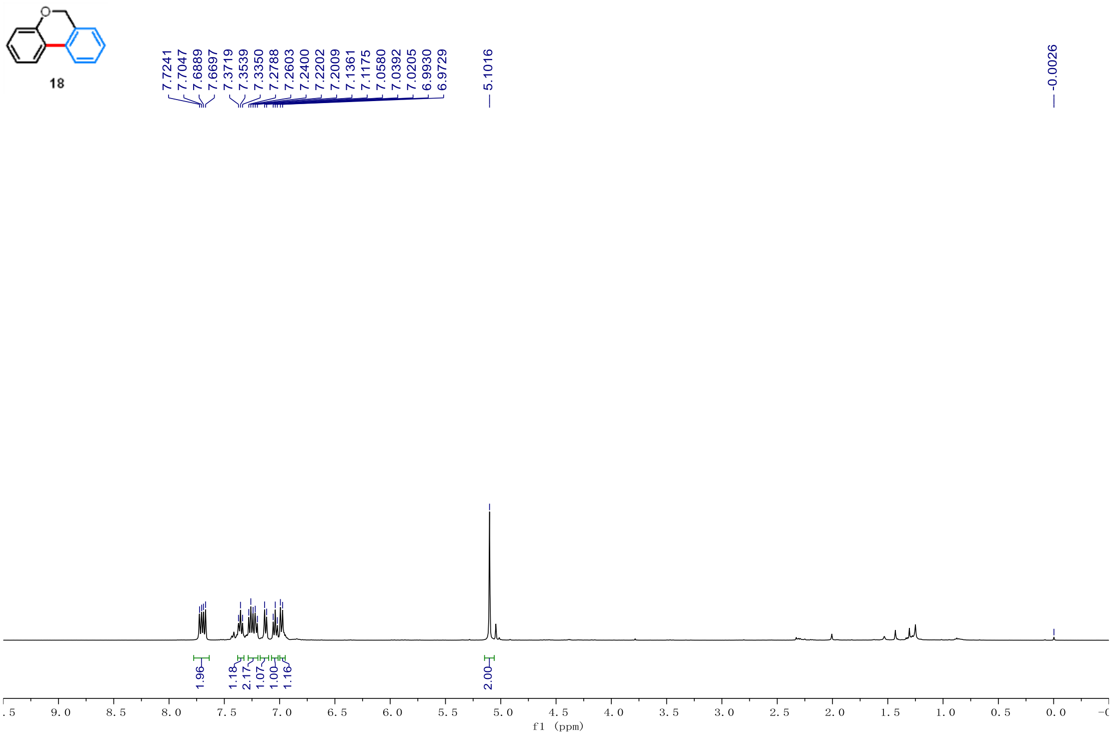
OMe
OMe
OMe
16
158.8835
153.8762
150.9040
131.4690
130.8659
130.6483
116.7113
113.6439
112.7450
112.6934
77.4778
77.1601
76.8427
56.4426
55.9087
55.4043
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

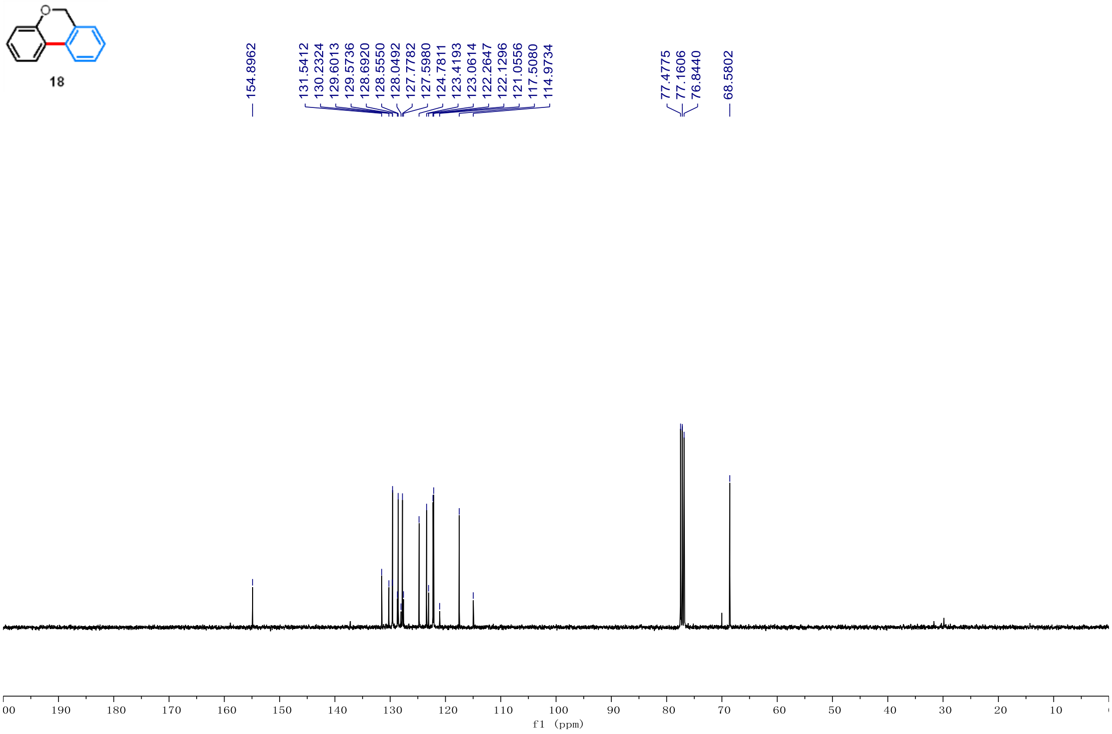

7.5238
7.5020
7.4355
7.4137
7.2976
7.2922
7.2802
7.2761
7.2683
7.2577
7.2450
7.2368
7.2218
7.1993
6.9731
6.9694
6.9626
6.9572
6.9517
6.9446
6.9404
6.9331
6.9277
6.9226
6.6566
6.6357
6.5642
6.5581
6.5517
6.5459
6.5414
6.5353
6.4295
3.8416
3.8323
3.7888
3.7351
0.0002
OMe
2
MeO
4
5
OMe
17
6.6566
6.6357
6.5642
6.5581
6.5517
6.5459
6.5414
6.5353
6.4295
0.15
0.84
0.94
0.07
6.70 6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30
f1 (ppm)
2, 2H
4, 2H
5, 1H
0.18
0.93
2.06
1.98
0.15
0.84
0.94
0.07
4.82
1.65
2.55
.5 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
f1 (ppm)

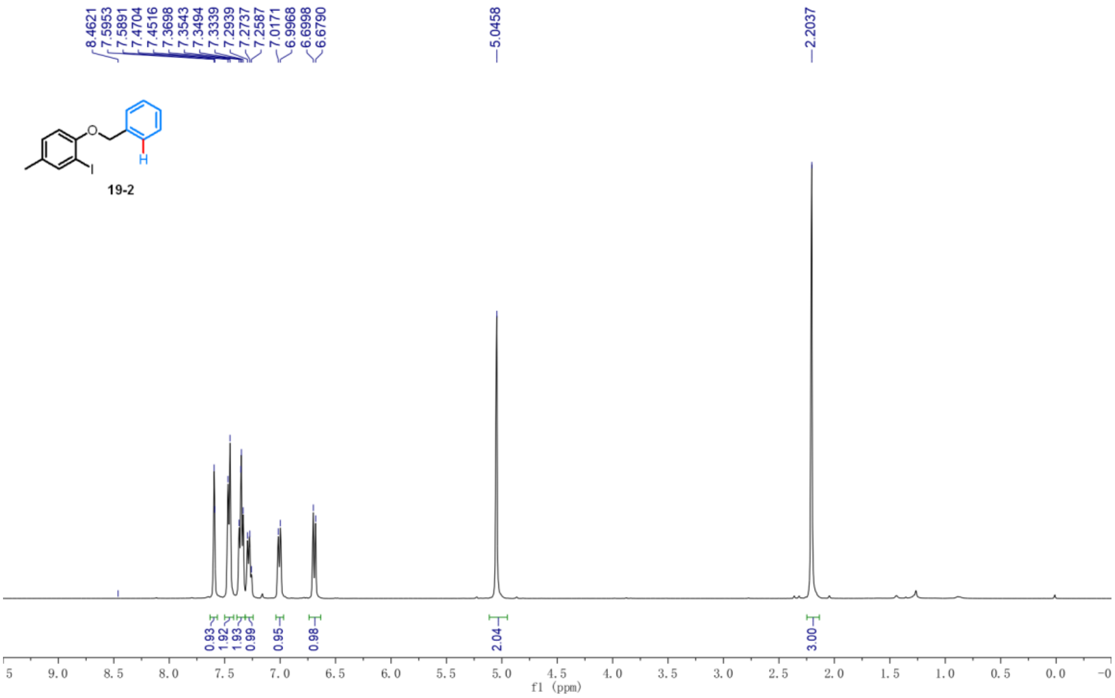

OMe
2
MeO
4
5
OMe
17
161.1411
160.0726
158.4396
158.4029
157.8831
132.0638
131.1170
130.8641
130.5860
128.4529
128.3238
126.1971
123.3474
119.1753
114.2302
113.5929
113.3655
105.1796
104.5991
104.2737
99.0729
98.7891
77.4777
77.1598
76.8434
56.0442
55.6544
55.5434
55.3948
55.2475
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

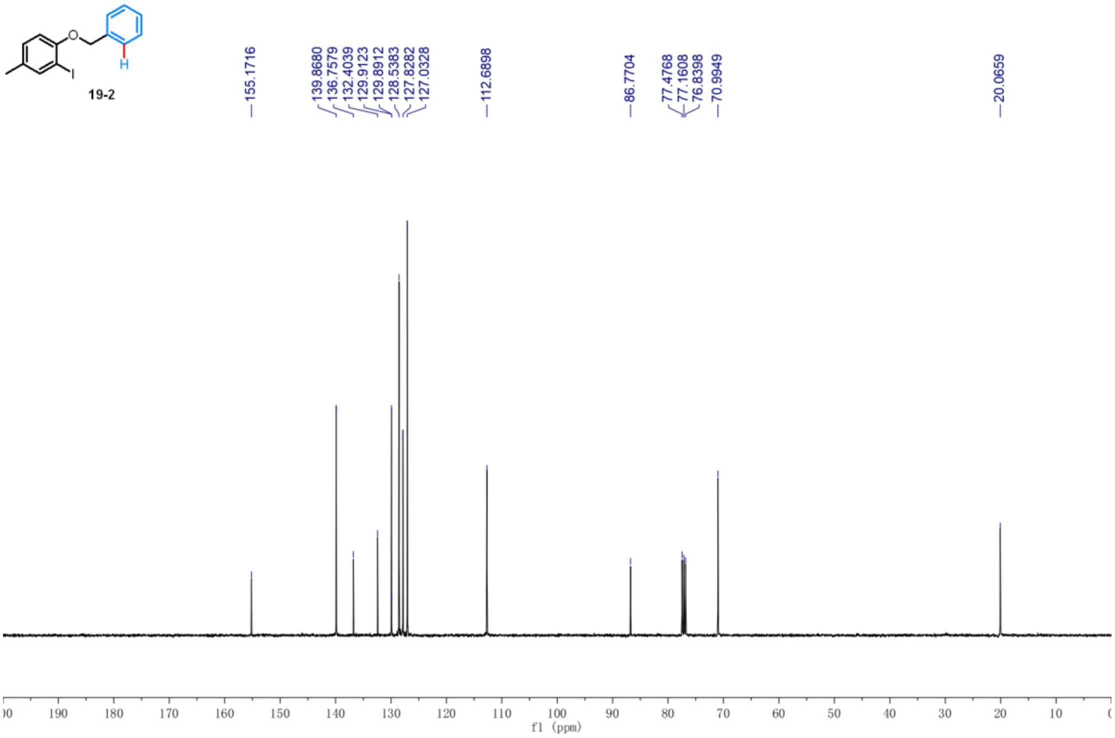

7.8566
7.8523
7.8420
7.8370
7.5580
7.5391
7.4596
7.4553
7.4420
7.4372
7.4222
7.4178
7.3848
7.3809
7.3668
7.3620
7.3067
6.9005
6.8800
5.1750
O
I
H
18-1
0.94
2.02
1.99
1.94
0.96
0.97
2.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

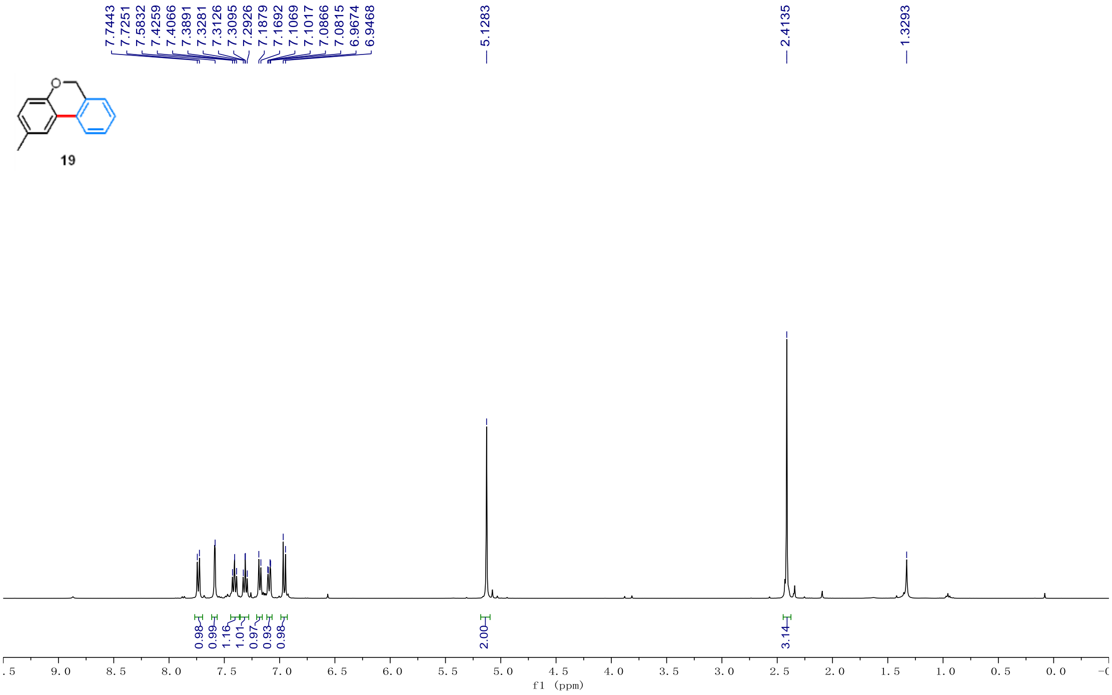

O
I
H
18-1
157.2316
139.6092
136.5866
129.5020
128.6259
127.9413
127.0545
122.8852
112.8202
86.9239
77.4801
77.1605
76.8435
70.8514
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


18
7.7241
7.7047
7.6889
7.6697
7.3719
7.3539
7.3350
7.2788
7.2603
7.2400
7.2202
7.2009
7.1361
7.1175
7.0580
7.0392
7.0205
6.9930
6.9729
5.1016
-0.0026
1.96
1.18
2.17
1.07
1.00
1.16
2.00
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
f1 (ppm)


18
154.8962
131.5412
130.2324
129.6013
129.5736
128.6920
128.5550
128.0492
127.7782
127.5980
124.7811
123.4193
123.0614
122.2647
122.1296
121.0556
117.5080
114.9734
77.4775
77.1606
76.8440
68.5802
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.4621
7.5953
7.5891
7.4704
7.4516
7.3698
7.3543
7.3494
7.3339
7.2939
7.2737
7.2587
7.0171
6.9968
6.6998
6.6790
5.0458
2.2037
O
I
H
19-2
0.93
1.92
1.93
0.99
0.95
0.98
2.04
3.00
f1 (ppm)


O
I
H
19-2
155.1716
139.8680
136.7579
132.4039
129.9123
129.8912
128.5383
127.8282
127.0328
112.6898
86.7704
77.4768
77.1608
76.8398
70.9949
20.0659
f1 (ppm)


19
7.7443
7.7251
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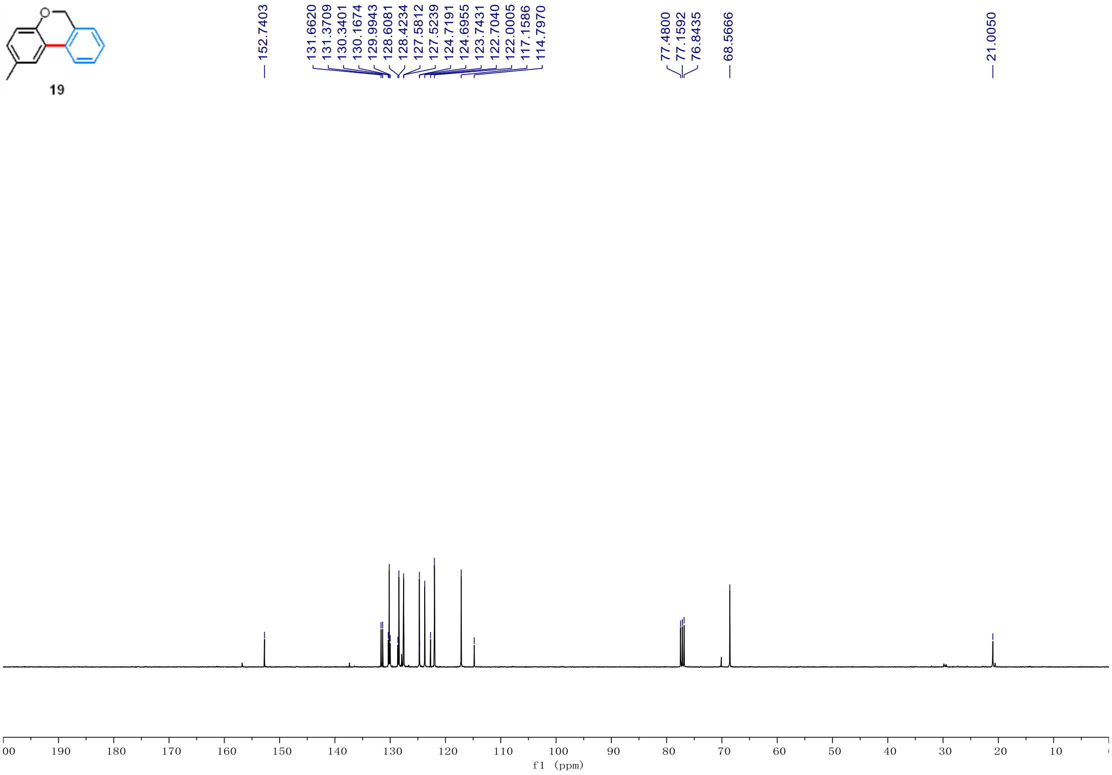
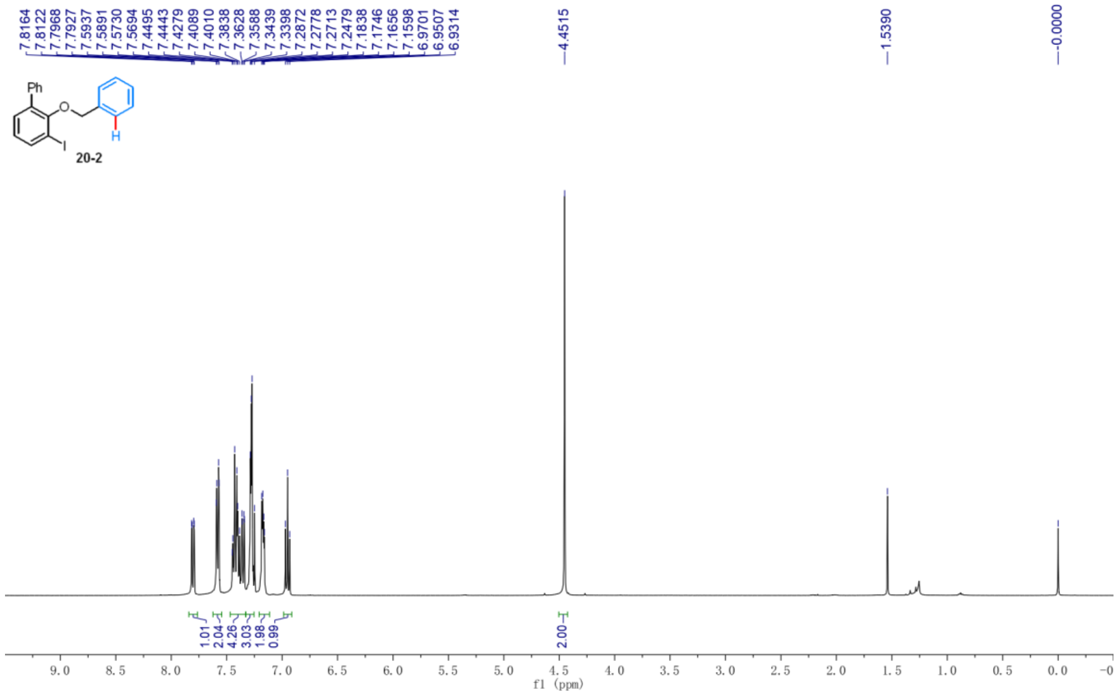
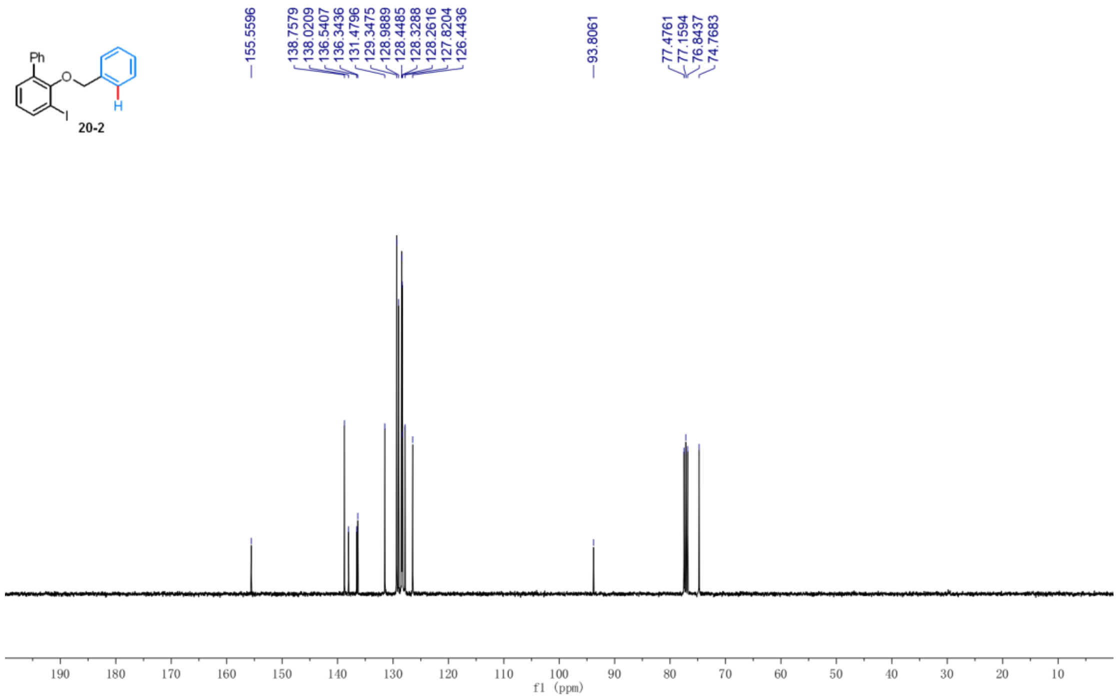
7.4259
7.4066
7.3891
7.3281
7.3126
7.3095
7.2926
7.1879
7.1692
7.1069
7.1017
7.0866
7.0815
6.9674
6.9468
5.1283
2.4135
1.3293
0.98
0.99
1.16
1.01
0.97
0.93
0.98
2.00
3.14
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


19
152.7403
131.6620
131.3709
130.3401
130.1674
129.9943
128.6081
128.4234
127.5812
127.5239
124.7191
124.6955
123.7431
122.7040
122.0005
117.1586
114.7970
77.4800
77.1592
76.8435
68.5666
21.0050
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.8164
7.8122
7.7968
7.7927
7.5937
7.5891
7.5730
7.5694
7.4495
7.4443
7.4279
7.4089
7.4010
7.3838
7.3628
7.3588
7.3439
7.3398
7.2872
7.2778
7.2713
7.2479
7.1838
7.1746
7.1656
7.1598
6.9701
6.9507
6.9314
4.4515
1.5390
-0.0000
Ph
O
H
I
20-2
1.01
2.04
4.26
3.03
1.98
0.99
2.00
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
f1 (ppm)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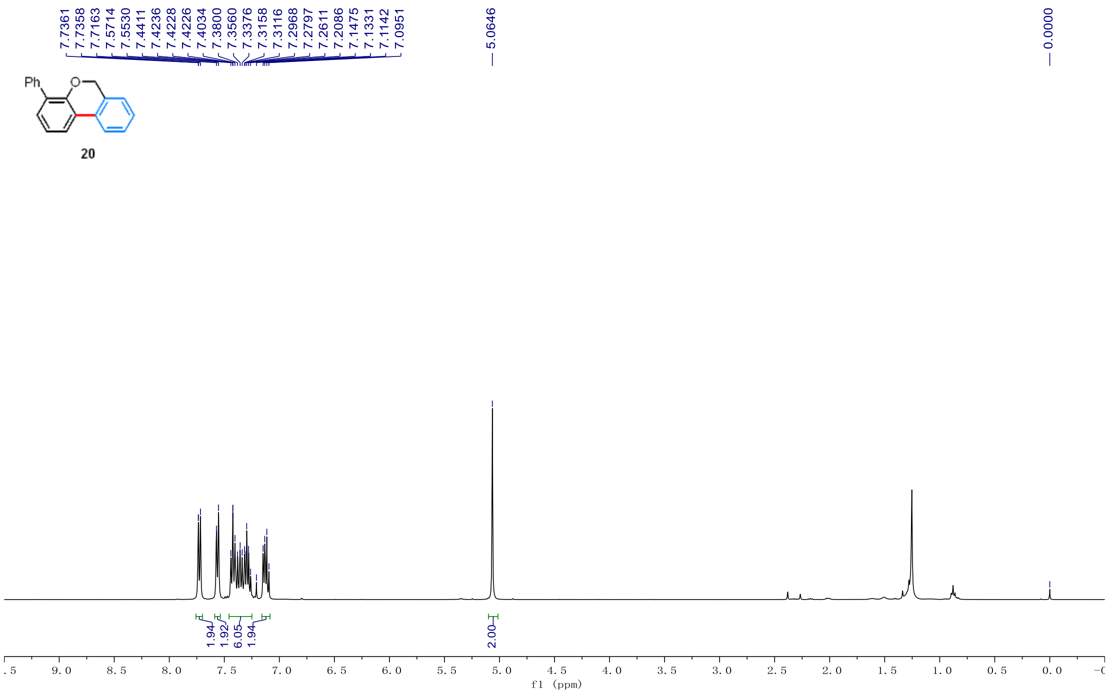
138.7579
138.0209
136.5407
136.3436
131.4796
129.3475
128.9889
128.4485
128.3288
128.2616
127.8204
126.4436
93.8061
77.4761
77.1594
76.8437
74.7683
Ph
O
H
I
20-2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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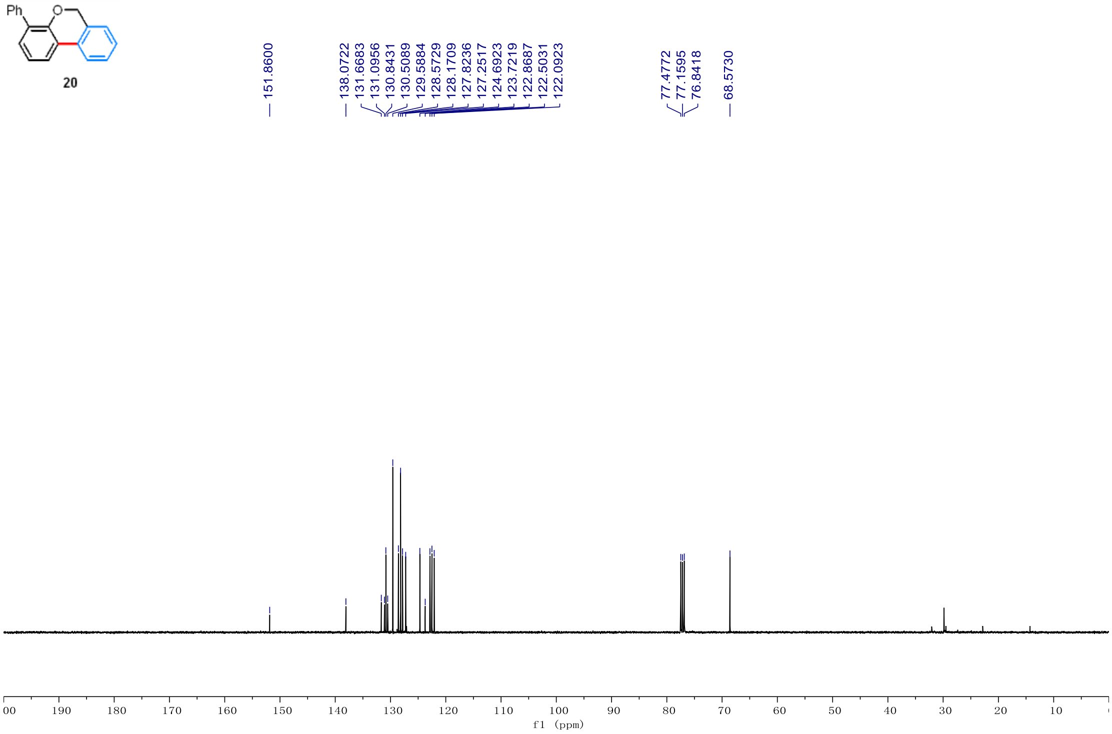
7.7358
7.7163
7.5714
7.5530
7.4411
7.4236
7.4228
7.4226
7.4034
7.3800
7.3560
7.3376
7.3158
7.3116
7.2968
7.2797
7.2611
7.2086
7.1475
7.1331
7.1142
7.0951
5.0646
0.0000
Ph
O
20
1.94
1.92
6.05
1.94
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
O
20
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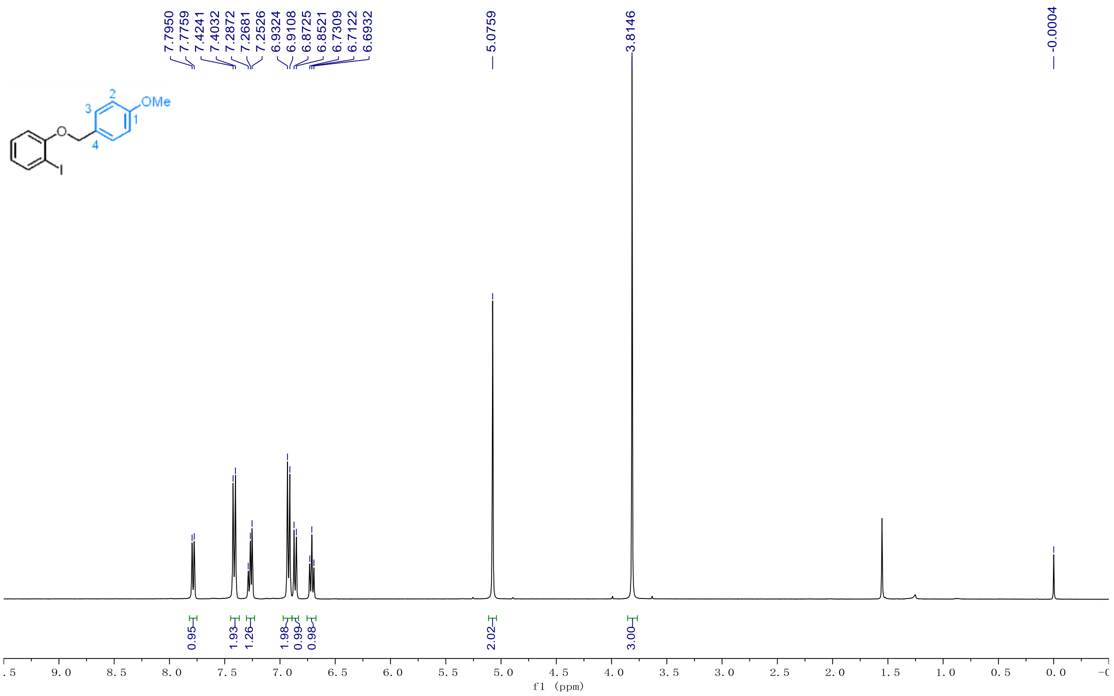
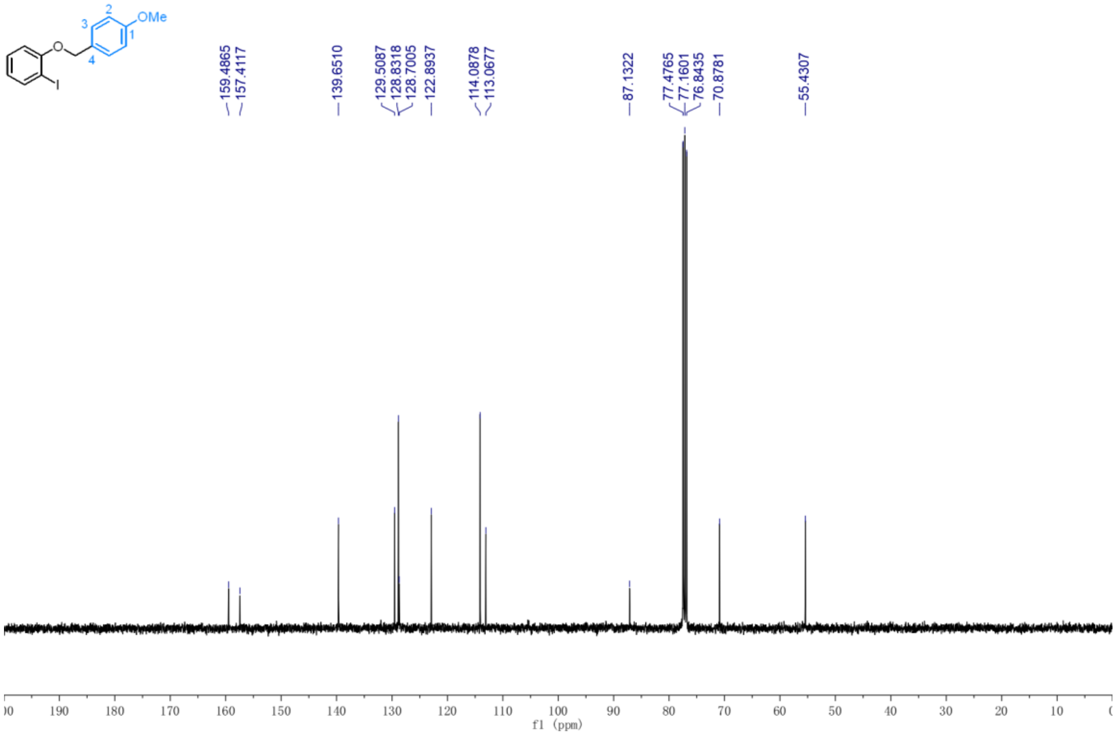
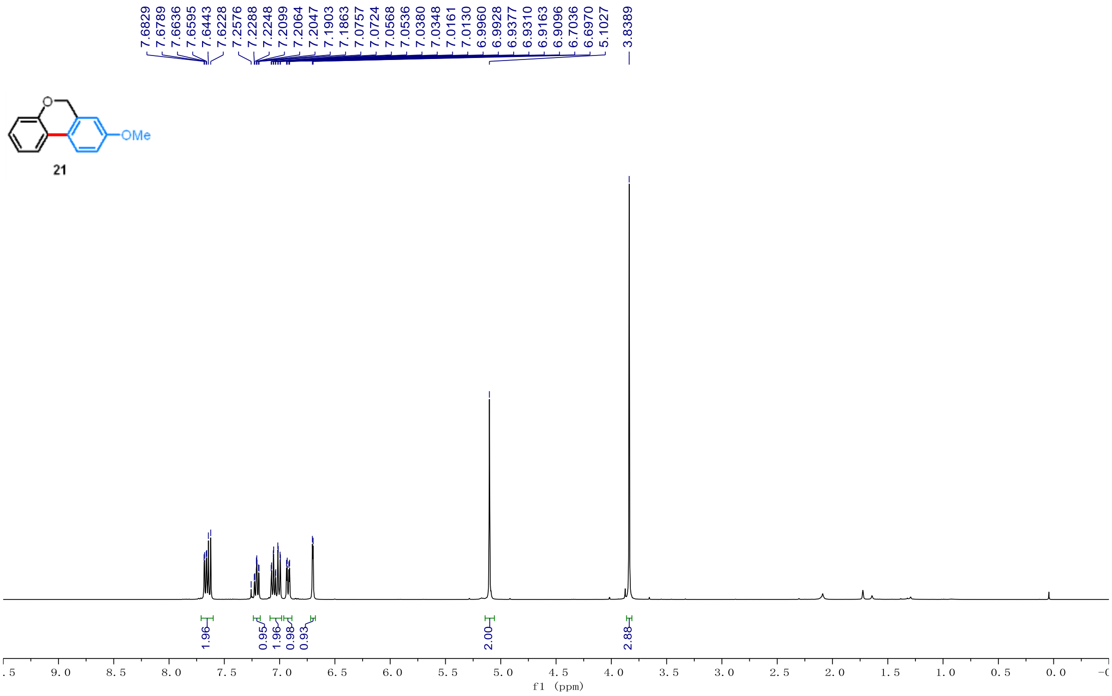
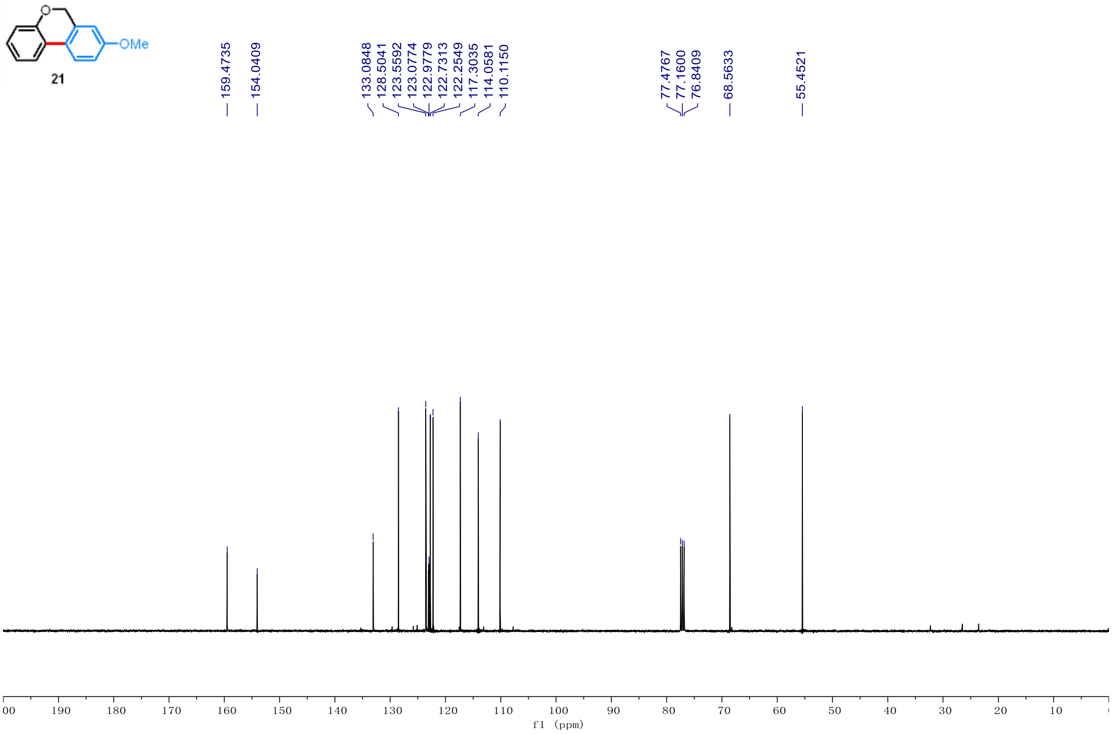
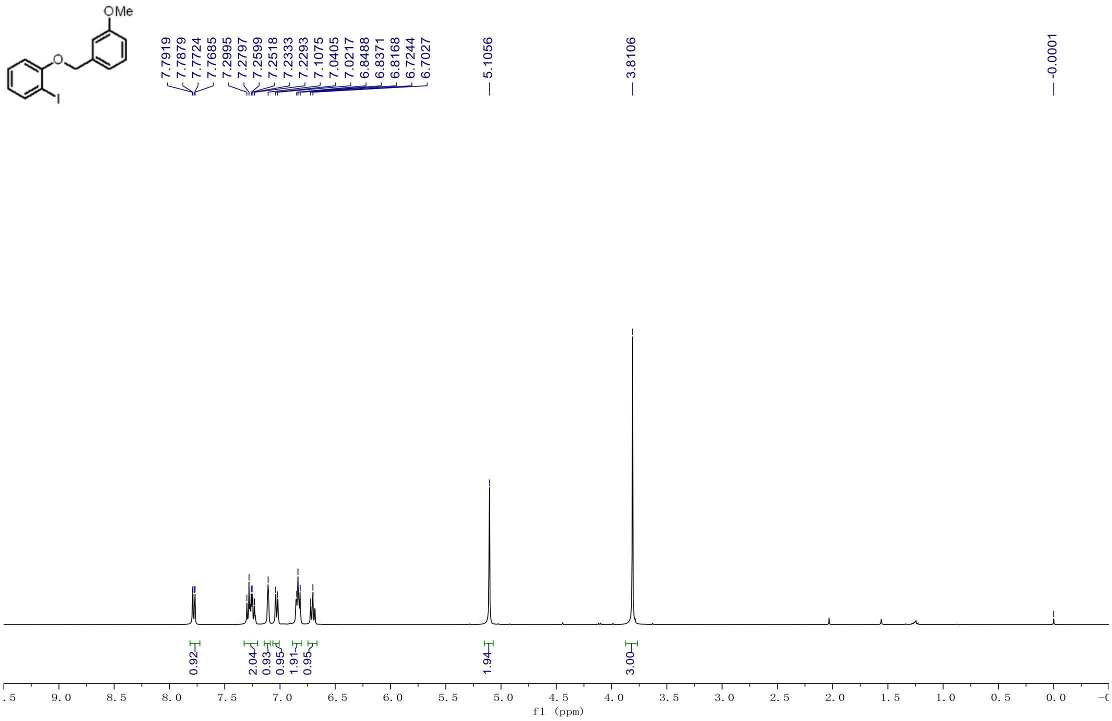
138.0722
131.6683
131.0956
130.8431
130.5089
129.5884
128.5729
128.1709
127.8236
127.2517
124.6923
123.7219
122.8687
122.5031
122.0923
77.4772
77.1595
76.8418
68.5730
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

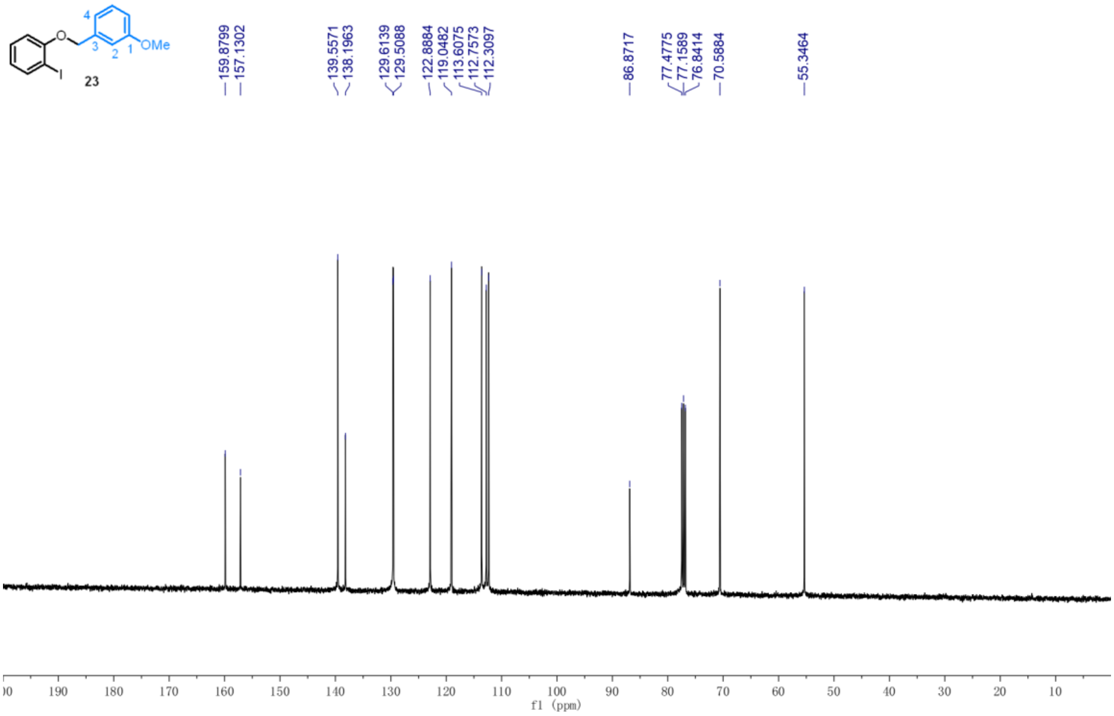

OMe
O
I
1
2
3
4
7.7950
7.7759
7.4241
7.4032
7.2872
7.2681
7.2526
6.9324
6.9108
6.8725
6.8521
6.7309
6.7122
6.6932
5.0759
3.8146
-0.0004
0.95
1.93
1.26
1.98
0.99
0.98
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

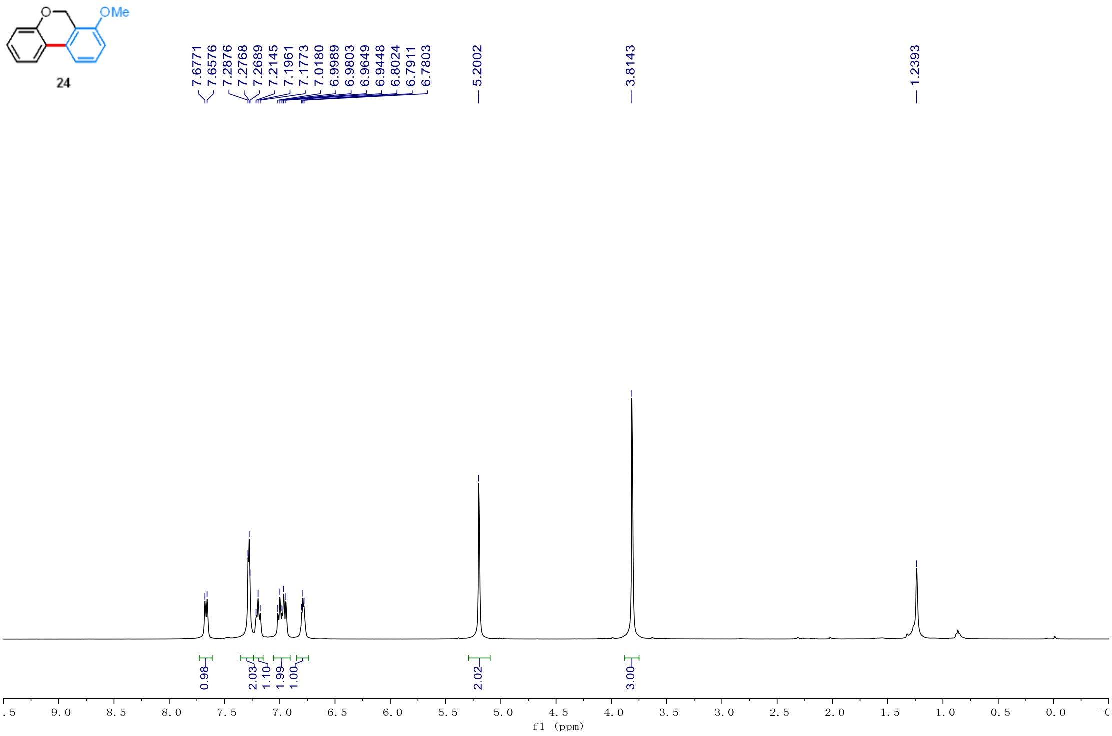

OMe
O
I
1
2
3
4
159.4865
157.4117
139.6510
129.5087
128.8318
128.7005
122.8937
114.0878
113.0677
87.1322
77.4765
77.1601
76.8435
70.8781
55.4307
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

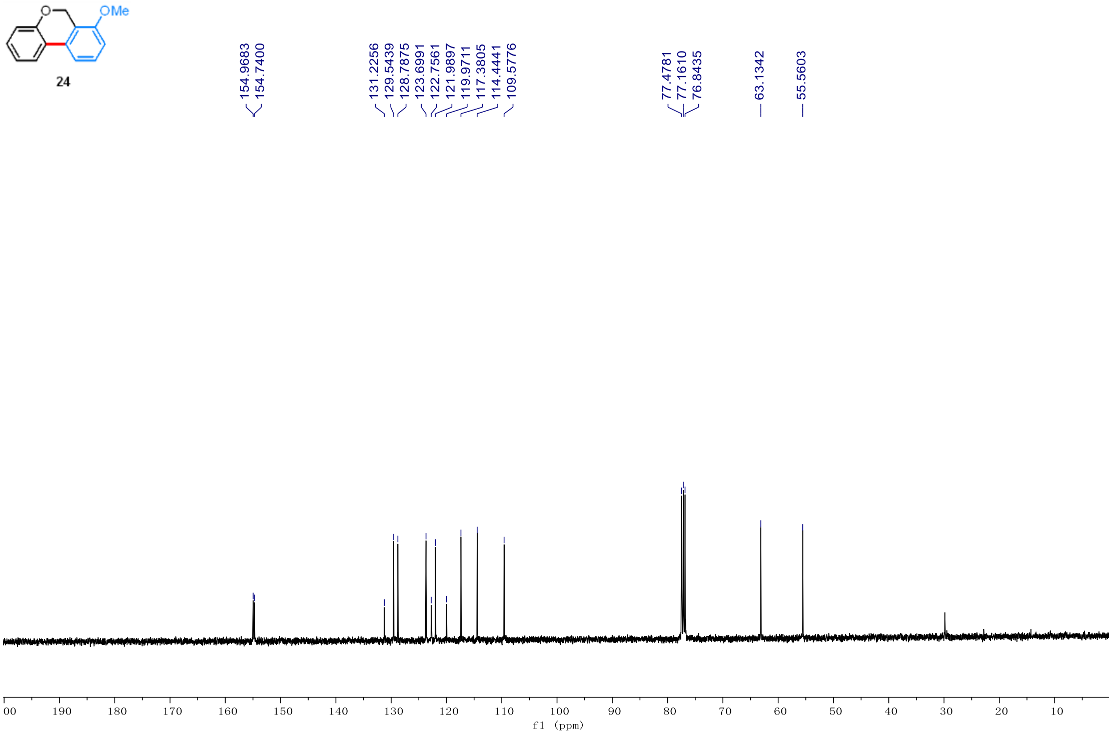

7.6829
7.6789
7.6636
7.6595
7.6443
7.6228
7.2576
7.2288
7.2248
7.2099
7.2064
7.2047
7.1903
7.1863
7.0757
7.0724
7.0568
7.0536
7.0380
7.0348
7.0161
7.0130
6.9960
6.9928
6.9377
6.9310
6.9163
6.9096
6.7036
6.6970
5.1027
3.8389
OMe
21
1.96
0.95
1.96
0.98
0.93
2.00
2.88
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

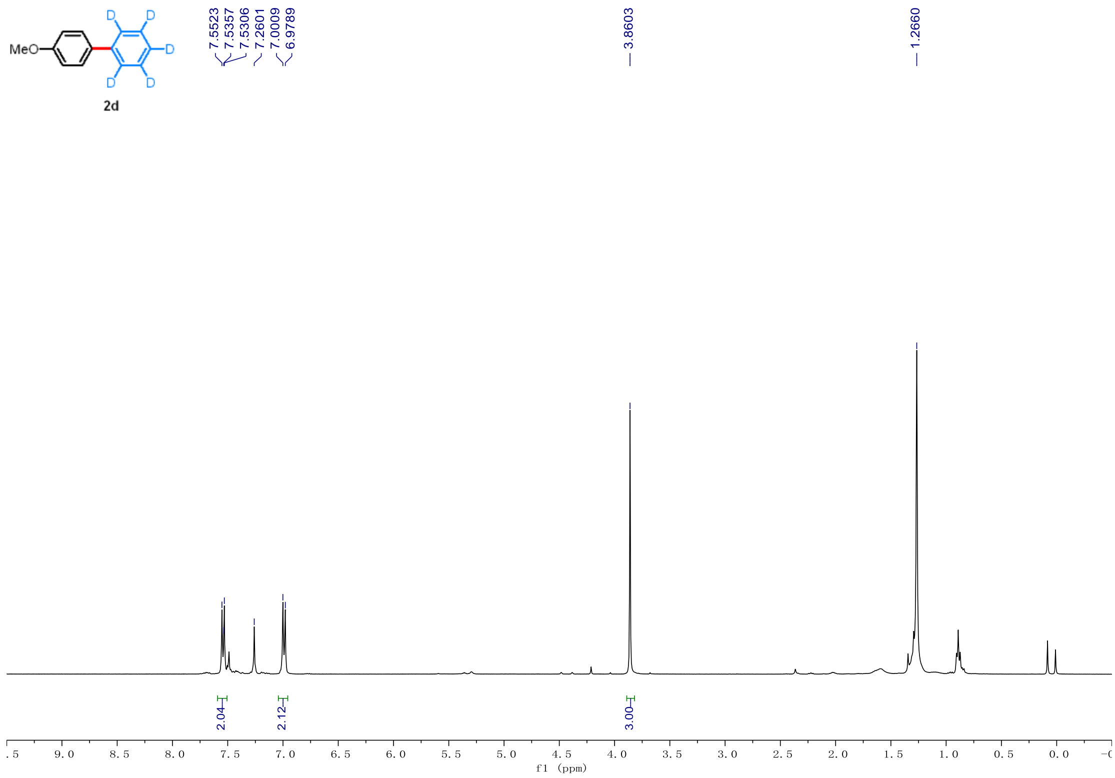

OMe
21
159.4735
154.0409
133.0848
128.5041
123.5592
123.0774
122.9779
122.7313
122.2549
117.3035
114.0581
110.1150
77.4767
77.1600
76.8409
68.5633
55.4521
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

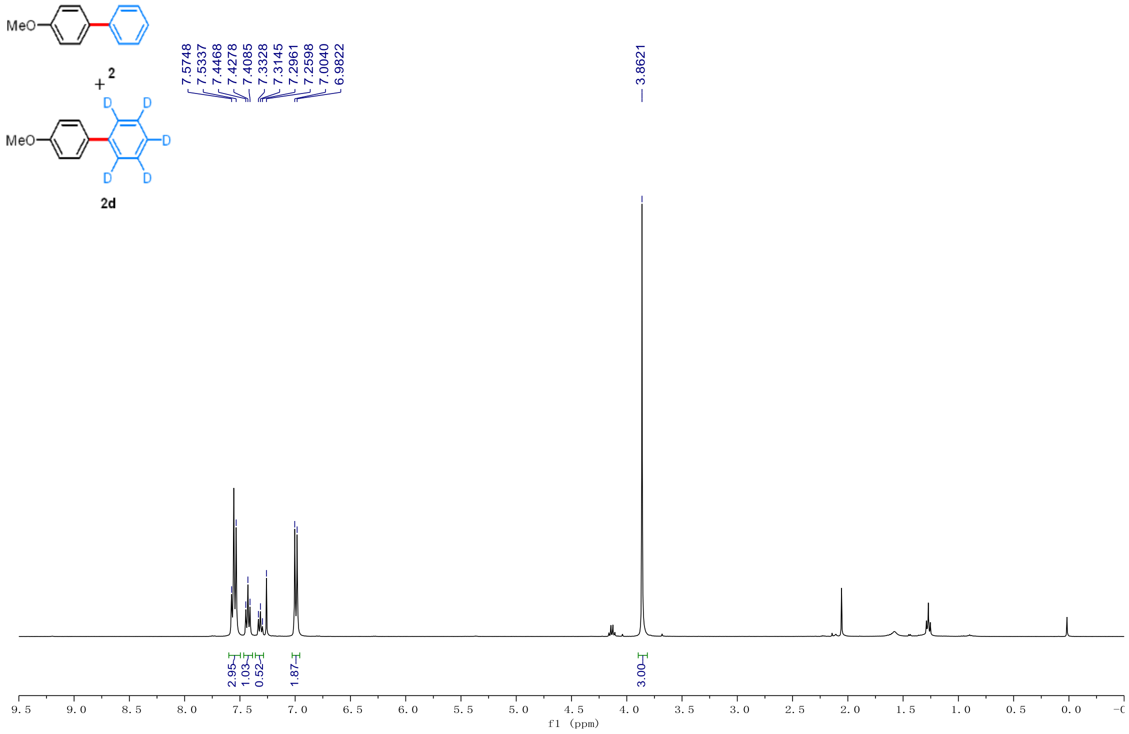

OMe
O
I
7.7919
7.7879
7.7724
7.7685
7.2995
7.2797
7.2599
7.2518
7.2333
7.2293
7.1075
7.0405
7.0217
6.8488
6.8371
6.8168
6.7244
6.7027
5.1056
3.8106
-0.0001
0.92
2.04
0.93
0.95
1.91
0.95
1.94
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

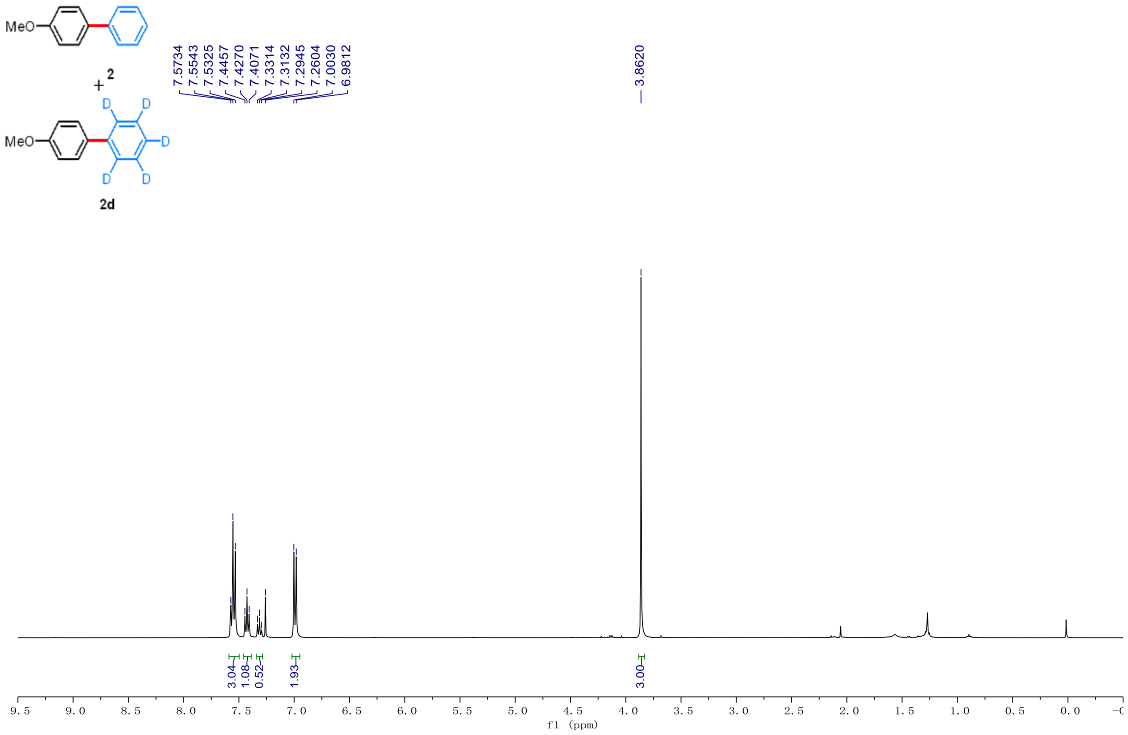

O
I
4
3
2
1
OMe
23
159.8799
157.1302
139.5571
138.1963
129.6139
129.5088
122.8884
119.0482
113.6075
112.7573
112.3097
86.8717
77.4775
77.1589
76.8414
70.5884
55.3464
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

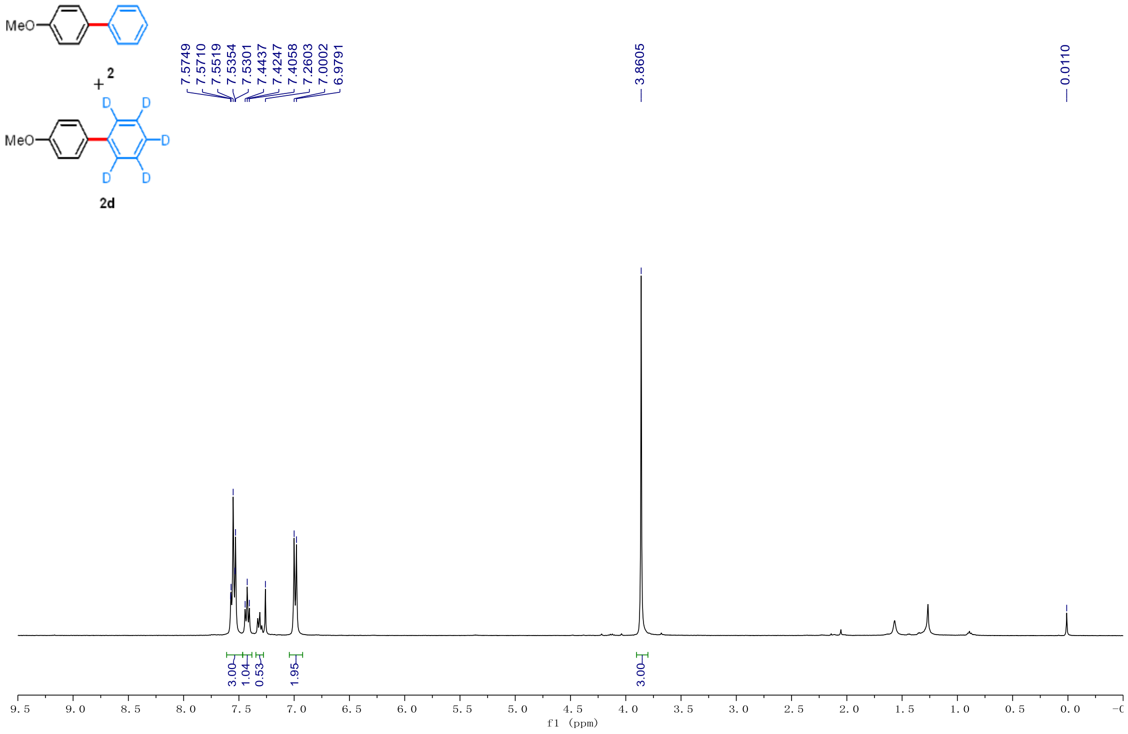

OMe
24
7.6771
7.6576
7.2876
7.2768
7.2689
7.2145
7.1961
7.1773
7.0180
6.9989
6.9803
6.9649
6.9448
6.8024
6.7911
6.7803
5.2002
3.8143
1.2393
0.98
2.03
1.10
1.99
1.00
2.02
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


OMe
24
154.9683
154.7400
131.2256
129.5439
128.7875
123.6991
122.7561
121.9897
119.9711
117.3805
114.4441
109.5776
77.4781
77.1610
76.8435
63.1342
55.5603
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO
D
D
D
D
D
2d
7.5523
7.5357
7.5306
7.2601
7.0009
6.9789
3.8603
1.2660
2.04
2.12
3.00
9.5 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
f1 (ppm)


MeO
+
2
MeO
D
D
D
D
D
2d
7.5748
7.5337
7.4468
7.4278
7.4085
7.3328
7.3145
7.2961
7.2598
7.0040
6.9822
3.8621
2.95
1.03
0.52
1.87
3.00
9.5 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
f1 (ppm)


MeO
+ 2
MeO
D D D D D
2d
7.5734
7.5543
7.5325
7.4457
7.4270
7.4071
7.3314
7.3132
7.2945
7.2604
7.0030
6.9812
3.8620
3.04
1.08
0.52
1.93
3.00
9.5 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
f1 (ppm)


MeO
+ 2
MeO
D D D D D
2d
7.5749
7.5710
7.5519
7.5354
7.5301
7.4437
7.4247
7.4058
7.2603
7.0002
6.9791
3.8605
0.0110
3.00
1.04
0.53
1.95
3.00
9.5 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
f1 (ppm)