Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-Catalyzed Bisarylation of 3-Alkylbenzofurans to 3-Arylalkyl-2-arylbenzofurans on Water: Tandem C(sp^3)-H and C(sp^2)-H Activations of 3-Alkylbenzofurans

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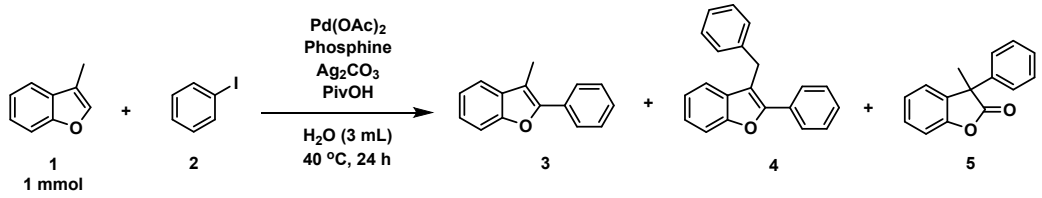
General Information

All reactions for preparation of novel compounds were conducted under nitrogen using standard Schlenk-type flasks. ^{1}H and ^{13}C NMR spectra were recorded with Agilent 400-MR DD2 (400 MHz and 100 MHz, respectively) spectrometer. ^{1}H NMR spectra were taken in $CDCl_3$ and were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.16 ppm). High-Resolution Mass Spectra were obtained using the electronic impact (EI) mode at the Korea Basic Science Institute (Daegu, South Korea) on a Jeol JMS 700 high resolution mass spectrometer using a magnetic sector-electric sector focusing mass analyzer. IR spectra were measured on a Thermo Scientific Nicolet 6700 spectrometer. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel plates (60F-254). The TLC plates were visualized by UV-light (254 nm). Workup procedures were done in air. Flash column chromatography was carried out on Merck 60 silica gel (230 – 400 mesh).

● Table s1. Optimization studies of Pd-catalyzed bisarylation.

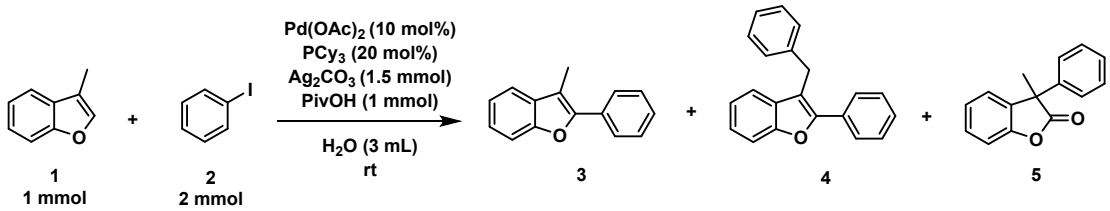


Entry	$Pd(OAc)_2$ (mol%)	**2** (mmol)	Phosphine (mol%)	Ag_2CO_3 (mmol)	PivOH (mmol)	Yield [%][a] **3:4:5**
1	5	2	-	1	4	41:23:28
2	10	2	-	1	4	30:27:33
3	10	2	-	1.5	4	16:34:16
4	10	2	-	1.5	2	12:42:16
5	10	2	-	1.5	1	9:47:12
6	10	3	-	1.5	1	30:40:14
7	10	4	-	1.5	1	12:42:14
8	10	2	PCy_3 20	1.5	1	3:60:10
9	10	2	PPh_3 20	1.5	1	N.R.
10	10	2	$PtBu_3$ 20	1.5	1	trace
11[b]	10	2	PCy_3 20	1.5	1	15:35:17
12[c]	10	2	PCy_3 20	1.5	1	trace:58:10
13[d]	10	2	PCy_3 20	1.5	1	trace:64:10
14[e]	10	2	PCy_3 20	1.5	1	trace:71:8
15[f]	10	2	PCy_3 20	1.5	1	trace:85:9

[a]Isolated yields. [b]Runs at 60 °C. [c]Runs at room temperature. [d]30 h. [e]40 h. [f]$Pd(OAc)_2$ and PCy_3 were pre-stirred for 30 min.

- **Changes in yield of 4 and 5 as a function of time**

With the optimized reaction conditions, yields of bisarylated product **4** and lactone **5** are plotted as a function of time. No monoarylated product **3** was observed in the reaction. The yield of bisarylated product rapidly increased within 5 h and then continuously increased to 90%. However, the yield of lactone reached at its highest point (7%) within 5 h and then increased no more.



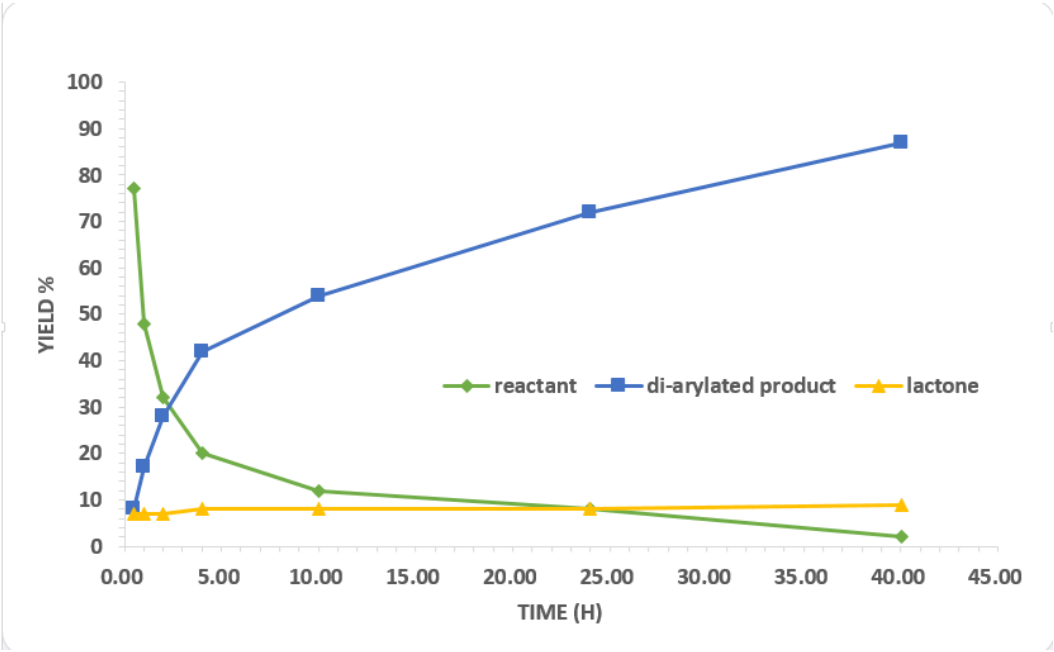
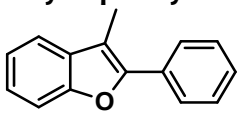


Figure S1. Changes in yield of **4** and **5** as a function of time

Starting materials

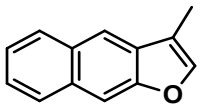
Compound **3, 15, 17, 20, 24, 26, 29** were prepared according to literature procedures.[1]
Compound **1** were commercially obtained.

3-Methyl-2-phenylbenzofuran (3)



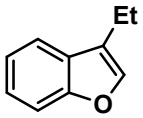
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.33 – 7.28 (m, 1H), 7.28 – 7.23 (m, 1H), 7.21 (ddd, *J* = 7.7, 4.3, 1.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.89, 150.77, 131.52, 131.27, 128.71, 127.95, 126.80, 124.42, 122.44, 119.38, 111.37, 111.03, 9.56. HRMS(EI+) m/z: Calcd for $C_{15}H_{12}O$: 208.0888, found: 208.0888.

3-Methylnaphtho[2,3-b]furan (15)



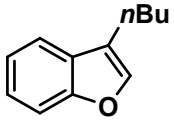
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 4.6 Hz, 2H), 7.93 – 7.89 (m, 1H), 7.84 (s, 1H), 7.49 (d, *J* = 1.3 Hz, 1H), 7.46 – 7.39 (m, 2H), 2.32 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.33, 143.68, 131.49, 130.48, 130.26, 128.19, 127.98, 124.92, 124.01, 117.35, 115.31, 106.91, 8.17, m.p : 54°C. HRMS(EI+) m/z: Calcd for $C_{13}H_{10}O$: 182.0732, found: 182.0732.

3-Ethylbenzofuran (17)



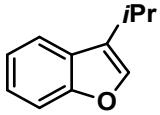
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.52 (m, 1H), 7.47 – 7.43 (m, 1H), 7.38 (d, *J* = 1.1 Hz, 1H), 7.27 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 1H), 7.22 (ddd, *J* = 7.3, 4.4, 1.2 Hz, 1H), 2.72 – 2.65 (m, 2H), 1.34 – 1.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.55, 140.67, 128.36, 124.17, 122.44, 122.25, 119.70, 111.52, 17.09, 13.62. HRMS(EI+) m/z: Calcd for $C_{10}H_{10}O$: 146.0732, found: 146.0729.

3-*n*Butylbenzofuran (20)



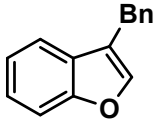
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.49 (m, 1H), 7.45 – 7.42 (m, 1H), 7.35 – 7.33 (m, 1H), 7.21 (dddd, *J* = 8.7, 5.0, 4.2, 2.3 Hz, 2H), 2.64 – 2.59 (m, 2H), 1.68 – 1.62 (m, 2H), 1.42 – 1.36 (m, 2H), 0.93 (dd, *J* = 7.4, 5.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.52, 141.06, 128.52, 124.09, 122.22, 120.74, 119.73, 111.48, 31.30, 23.34, 22.68, 13.99. HRMS(EI+) m/z: Calcd for $C_{12}H_{14}O$: 174.1045, found: 174.1044

3-*i*Proprylbenzofuran (24)



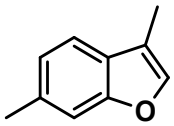
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 1H), 7.45 (ddd, *J* = 8.1, 1.1, 0.6 Hz, 1H), 7.36 (d, *J* = 0.9 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 3.12 – 3.04 (m, 1H), 1.35 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.73, 139.81, 127.74, 127.42, 124.09, 122.18, 120.23, 111.63, 24.79, 22.57. HRMS(EI+) m/z: Calcd for $C_{11}H_{12}O$: 160.0888, found: 160.0886.

3-Benzylbenzofuran (26)



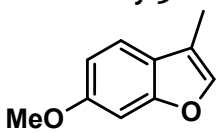
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.37 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.31 (d, *J* = 1.0 Hz, 1H), 7.28 – 7.21 (m, 5H), 7.20 – 7.16 (m, 1H), 7.14 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.67, 142.23, 139.29, 128.74, 128.61, 128.12, 126.47, 124.33, 122.46, 120.00, 119.80, 111.55, 30.07. HRMS(EI+) m/z: Calcd for $C_{15}H_{12}O$: 208.0888, found: 208.0887.

3,6-Dimethylbenzofuran (29)



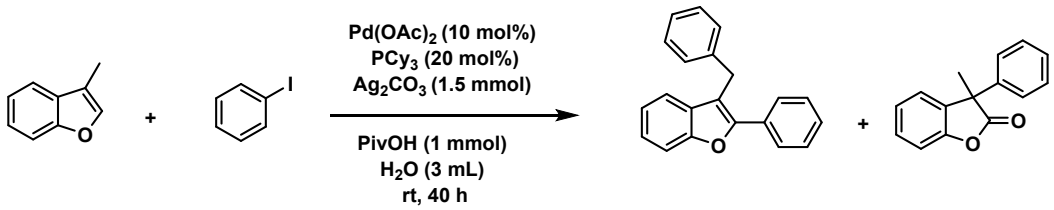
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 0.8 Hz, 1H), 7.36 (s, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 2.56 (s, 3H), 2.30 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.80, 140.86, 134.28, 126.66, 123.69, 118.94, 115.51, 111.63, 21.68, 7.96. HRMS(EI+) m/z: Calcd for $C_{10}H_{10}O$: 146.0732, found: 146.0728.

6-methoxy-3-methylbenzofuran (31)



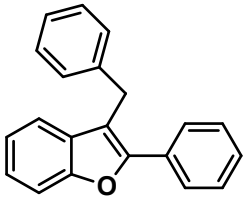
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 0.8 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.80 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.77 (s, 3H), 2.13 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.09, 156.33, 140.58, 122.60, 119.60, 115.61, 111.35, 96.08, 55.86, 8.08. HRMS(EI+) m/z: Calcd for $C_{10}H_{10}O_2$: 162.0681, found: 162.0683.

- **General procedure for palladium-catalyzed bisarylation of 3-alkylbenzofuran**



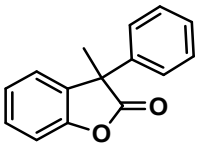
Reactions were performed in a schlenk tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube flask in order: 0.1 mmol of catalyst, 0.2 mmol of phosphine, 2 mmol of iodobenzene, 1.5 mmol of silver carbonate, 1 mmol of pivalic acid, 1 mmol of 3-methylbenzofuran, and 3 mL of deionized water (used without any treatment). The mixture was stirred at room temperature for 40 h. The mixture was extracted with ethyl acetate, filtered to remove catalyst residue, and finally evaporated under reduced pressures. The mixture was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate) and the product **4, 5** was obtained with 71%, 8% yield, respectively. When a mixture of $Pd(OAc)_2$ and PCy_3 which was stirred for 30 min was used as catalyst, the product **4, 5** was obtained with 85%, 9% yield, respectively. The compounds **4 ~ 14** were prepared by both the general procedure and the pre-stirred solution of $Pd(OAc)_2$ and PCy_3 as a catalyst. The compounds **16**, **18~19**, **21~23**, **25, 27~28**, and **30** were prepared by using the pre-stirred solution of $Pd(OAc)_2$ and PCy_3 as a catalyst.

3-Benzyl-2-phenylbenzofuran (4). The desired product was obtained as a colorless oil in 71% yield (0.202 g). When pre-stirred solution was used, the desired product was obtained in 85% yield (0.242 g).



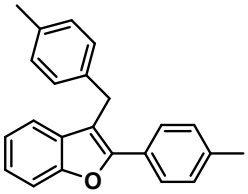
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.39 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.22 (m, 5H), 7.13 (t, *J* = 7.5 Hz, 2H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.24, 152.22, 139.39, 131.00, 130.62, 128.83, 128.75, 128.48, 128.29, 127.05, 126.44, 124.57, 122.69, 120.08, 113.88, 111.19, 30.22. HRMS(EI+) m/z: Calcd for $C_{21}H_{16}O$: 284.1201, found: 284.1198

3-Methyl-3-phenylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 8% yield (0.018 g). When pre-stirred solution was used, the desired product was obtained in 9% yield (0.02 g).



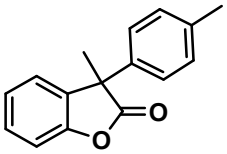
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.25 (m, 6H), 7.22 – 7.15 (m, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.76, 152.77, 139.53, 132.69, 129.09, 128.87, 127.92, 126.53, 124.63, 124.61, 111.05, 50.92, 24.86. HRMS(EI+) m/z: Calcd for $C_{15}H_{12}O_2$: 224.0837, found: 224.0835. IR (neat): 1801.47 cm^{-1} (C=O).

3-(4-Methylbenzyl)-2-(p-tolyl)benzofuran (5). The desired product was obtained as a colorless oil in 58% yield (0.181 g). When pre-stirred solution was used, the desired product was obtained in 72% yield (0.225 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 6.6 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.24 – 7.18 (m, 3H), 7.15 – 7.11 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 2H), 4.21 (s, 2H), 2.34 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.13, 152.34, 138.40, 136.39, 135.82, 129.52, 129.40, 128.15, 126.94, 124.28, 122.58, 119.95, 113.45, 111.07, 29.79, 21.45, 21.13. HRMS(EI+) m/z: Calcd for $C_{23}H_{20}O$: 312.1514, found: 312.1512.

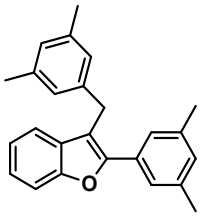
3-Methyl-3-(p-tolyl)benzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 8% yield (0.019 g). When pre-stirred solution was used, the desired product was obtained in 9% yield (0.021 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 1H), 7.23 – 7.10 (m, 7H), 2.30 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.97, 152.83, 137.76, 136.65, 132.93, 129.59, 129.03, 126.45, 124.60, 111.06, 50.66, 24.86, 21.06. HRMS(EI+) m/z: Calcd for $C_{16}H_{14}O_2$: 238.0994, found: 238.0994. IR (neat): 1805.09 cm^{-1} (C=O).

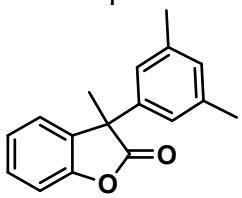
3-(3,5-Dimethylbenzyl)-2-(3,5-dimethylphenyl)benzofuran (6). The desired product was obtained as a colorless oil in 79% yield (0.269 g). When pre-stirred solution was used, the

desired product was obtained in 90% yield (0.306 g).



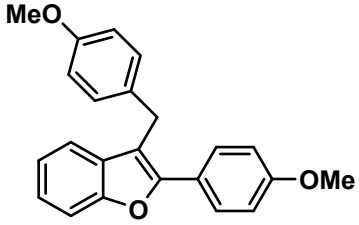
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.47 (m, 1H), 7.39 (d, *J* = 0.5 Hz, 2H), 7.36 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.16 – 7.11 (m, 1H), 6.97 (d, *J* = 0.6 Hz, 1H), 6.88 (s, 2H), 6.82 (s, 1H), 4.19 (s, 2H), 2.31 (d, *J* = 0.5 Hz, 6H), 2.22 (d, *J* = 0.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.12, 152.38, 139.67, 138.28, 138.12, 130.91, 130.89, 130.19, 128.04, 126.22, 124.91, 124.29, 122.57, 120.12, 114.09, 111.05, 30.24, 21.51, 21.44. HRMS(EI+) m/z: Calcd for $C_{25}H_{24}O$: 340.1827, found: 340.1827.

3-(3,5-Dimethylphenyl)-3-methylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 2% yield (0.005 g). When pre-stirred solution was used, the desired product was obtained in 8% yield (0.02 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 1H), 7.18 (ddd, *J* = 5.2, 3.3, 1.3 Hz, 3H), 6.91 (s, 3H), 2.26 (s, 6H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.04, 152.77, 139.46, 138.46, 133.15, 129.65, 128.95, 124.60, 124.57, 124.27, 111.02, 50.86, 24.72, 21.50. HRMS(EI+) m/z: Calcd for $C_{17}H_{16}O_2$: 252.1150, found: 252.1148. IR (neat): 1803.21 cm^{-1} (C=O).

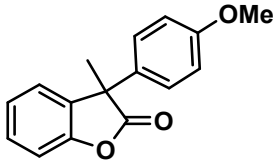
3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)benzofuran (7). The desired product was obtained as a colorless oil in 32% yield (0.11 g). When pre-stirred solution was used, the desired product was obtained in 28% yield (0.096 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.65 (m, 2H), 7.50 – 7.47 (m, 1H), 7.32 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.17 – 7.12 (m, 3H), 6.97 – 6.93 (m, 2H), 6.83 – 6.79 (m, 2H), 4.20 (s, 2H), 3.82 (d, *J* = 0.9 Hz, 3H), 3.75 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.83, 158.20, 154.06, 152.21, 131.55, 130.80, 129.20, 128.47, 124.11, 123.73, 122.58, 119.81,

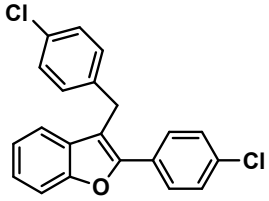
114.32, 114.13, 112.81, 111.02, 55.47, 55.38, 29.32. HRMS(EI+) m/z: Calcd for $C_{23}H_{20}O_3$: 344.1412, found: 344.1410.

3-(4-Methoxyphenyl)-3-methylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 16% yield (0.041 g). When pre-stirred solution was used, the desired product was obtained in 12% yield (0.031 g).



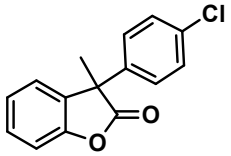
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.32 (m, 1H), 7.26 – 7.16 (m, 5H), 6.88 – 6.83 (m, 2H), 3.77 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.10, 159.27, 152.84, 132.93, 131.62, 129.07, 127.82, 124.63, 114.26, 111.12, 55.47, 55.43, 55.39, 55.37, 50.33, 25.05. HRMS(EI+) m/z: Calcd for $C_{16}H_{14}O_3$: 254.0943, found: 254.0940. IR (neat): 1802.87 cm^{-1} (C=O).

3-(4-Chlorobenzyl)-2-(4-chlorophenyl)benzofuran (8). The desired product was obtained as a colorless oil in 51% yield (0.181 g). When pre-stirred solution was used, The desired product was obtained in 42% yield (0.149 g).



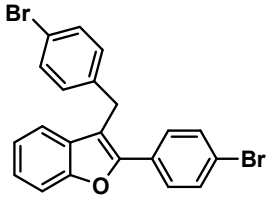
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.40 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.11 (ddd, *J* = 10.7, 5.4, 3.4 Hz, 2H), 7.05 – 7.01 (m, 2H), 7.00 – 6.96 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.12, 151.03, 137.44, 134.42, 132.29, 130.17, 129.47, 129.17, 129.05, 128.87, 128.02, 124.95, 122.92, 119.87, 113.79, 111.25, 29.46. HRMS(EI+) m/z: Calcd for $C_{21}H_{14}Cl_2O$: 352.0422, found: 352.0422.

3-(4-Chlorophenyl)-3-methylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 12% yield (0.031 g). When pre-stirred solution was used, the desired product was obtained in 19% yield (0.05 g).



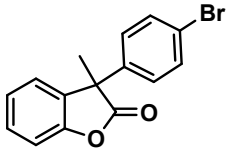
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.35 (m, 1H), 7.32 – 7.25 (m, 4H), 7.21 (dt, *J* = 10.8, 3.9 Hz, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.43, 152.82, 138.08, 134.13, 132.17, 129.43, 129.08, 128.12, 124.83, 124.61, 111.32, 50.56, 25.11. HRMS(EI+) m/z: Calcd for $C_{15}H_{11}ClO_2$: 258.0448, found: 258.0446. IR (neat): 1802.48 cm^{-1} (C=O).

3-(4-Bromobenzyl)-2-(4-bromophenyl)benzofuran (9). The desired product was obtained as a white solid in 38% yield (0.169 g). When pre-stirred solution was used, the desired product was obtained in 23% yield (0.101 g). m.p : 130 °C



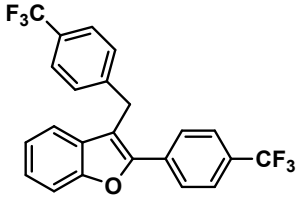
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.48 (m, 5H), 7.37 (dd, *J* = 9.7, 2.6 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.16 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.19, 151.17, 137.98, 132.08, 131.89, 130.20, 129.91, 129.67, 128.34, 125.04, 122.99, 122.78, 120.41, 119.92, 113.83, 111.33, 29.63. HRMS(EI+) m/z: Calcd for $C_{21}H_{14}Br_2O$: 441.9392, found: 441.9393.

3-(4-Bromophenyl)-3-methylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 7% yield (0.022 g). When pre-stirred solution was used, the desired product was obtained in 7% yield (0.022 g).



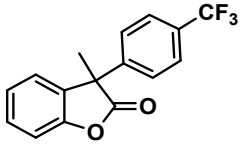
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (ddd, *J* = 4.0, 2.3, 1.2 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.22 – 7.19 (m, 5H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.35, 152.86, 138.65, 132.13, 132.07, 129.46, 128.46, 124.84, 124.62, 122.32, 111.35, 50.66, 25.08. HRMS(EI+) m/z: Calcd for $C_{15}H_{11}BrO_2$: 301.9942, found: 301.9943. IR (neat): 1802.86 cm^{-1} (C=O).

3-(4-(Trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)benzofuran (10). The desired product was obtained as a white solid in 40% yield (0.169 g). When pre-stirred solution was used, the desired product was obtained in 31% yield (0.131 g). m.p : 113 °C



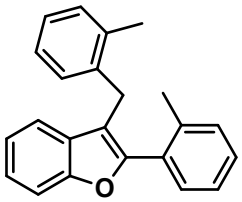
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.78 (m, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.37 – 7.31 (m, 4H), 7.20 (ddd, *J* = 7.8, 3.9, 0.9 Hz, 1H), 4.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.46, 150.82, 143.00, 142.99, 134.11, 130.50, 130.17, 130.05, 129.33, 129.01, 128.52, 127.01, 125.90 (dq, *J* = 7.7, 3.8 Hz, C*2), 123.26, 120.09, 114.77, 111.57, 30.07. HRMS(EI+) m/z: Calcd for $C_{23}H_{14}F_6O$: 420.0949, found: 420.0948

3-Methyl-3-(4-(trifluoromethyl)phenyl)benzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 6% yield (0.017 g). When pre-stirred solution was used, the desired product was obtained in 6% yield (0.018 g).



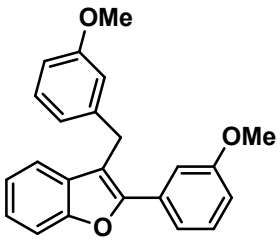
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.26 – 7.21 (m, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.10, 152.86, 143.48, 131.87, 130.50, 130.18, 129.64, 127.20, 125.93 (q, *J* = 3.8 Hz), 124.95, 124.65, 111.44, 51.00, 25.13. HRMS(EI+) m/z: Calcd for $C_{16}H_{11}F_3O_2$: 292.0711, found: 292.0709. IR (neat): 1804.51 cm^{-1} (C=O).

3-(2-Methylbenzyl)-2-(o-tolyl)benzofuran (11). The desired product was obtained as a colorless oil in 43% yield (0.135 g). When pre-stirred solution was used, the desired product was obtained in 44% yield (0.137 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.18 – 7.14 (m, 1H), 7.13 – 7.08 (m, 3H), 7.03 (dd, *J* = 9.3, 2.5 Hz, 2H), 3.96 (s, 2H), 2.36 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.58, 153.65, 138.47, 137.52, 136.36, 120.78, 130.48, 130.12, 129.36, 130.78, 130.48, 130.12, 129.36, 128.38, 126.35, 126.09, 125.73, 124.14, 122.92, 122.48, 120.59, 120.42, 119.68, 114.62, 111.22, 27.97, 20.52, 19.77. HRMS(EI+) m/z: Calcd for $C_{23}H_{20}O$: 312.1514, found: 312.1511.

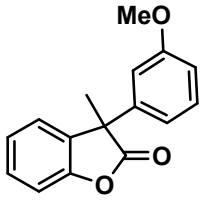
3-(3-Methoxybenzyl)-2-(3-methoxyphenyl)benzofuran (12). The desired product was obtained as a colorless oil in 30% yield (0.103 g). When pre-stirred solution was used, the desired product was obtained in 21% yield (0.074 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.32 (d, *J* = 6.6 Hz, 2H), 7.28 (dd, *J* = 5.3, 4.4 Hz, 2H), 7.19 – 7.14 (m, 2H), 6.90 (dt, *J* = 6.7, 2.4 Hz, 1H), 6.85 (dd,

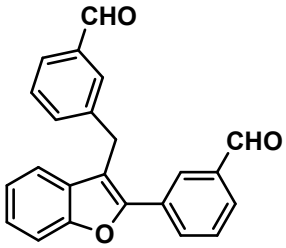
J = 7.6, 0.5 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.27 (s, 2H), 3.76 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.98, 159.90, 154.15, 152.16, 141.10, 132.18, 130.66, 129.87, 129.72, 124.63, 122.74, 120.68, 120.01, 119.48, 114.69, 114.25, 113.97, 112.10, 111.53, 111.19, 55.37, 55.22, 30.22. HRMS(EI+) m/z: Calcd for $C_{23}H_{20}O_3$: 344.1412, found: 344.1411.

3-(3-Methoxyphenyl)-3-methylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 15% yield (0.037 g). When pre-stirred solution was used, the desired product was obtained in 6% yield (0.016 g).



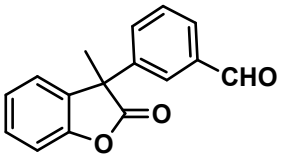
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 1H), 7.27 – 7.16 (m, 4H), 6.93 – 6.87 (m, 2H), 6.84 – 6.80 (m, 1H), 3.76 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.68, 159.94, 152.81, 141.11, 132.70, 129.92, 129.16, 124.66, 124.64, 118.95, 113.13, 112.82, 111.11, 55.36, 50.95, 24.87. HRMS(EI+) m/z: Calcd for $C_{16}H_{14}O_3$: 254.0943, found: 254.0941. IR (neat): 1801.76 cm^{-1} (C=O).

3-(3-(3-Formylbenzyl)benzofuran-2-yl)benzaldehyde (13). The desired product was obtained as a yellow oil in 56% yield (0.191 g). When pre-stirred solution was used, the desired product was obtained in 54% yield (0.185 g).



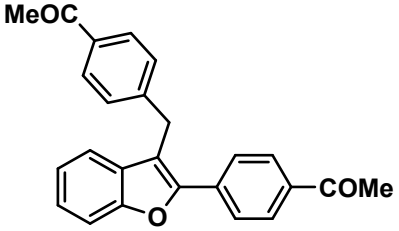
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 9.85 (s, 1H), 8.16 (s, 1H), 7.86 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.35 (s, 1H), 7.25 (dt, *J* = 11.3, 5.5 Hz, 2H), 7.11 (s, 1H), 4.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.26, 191.76, 154.19, 150.58, 140.04, 136.81, 136.80, 134.26, 132.16, 131.63, 129.96, 129.57, 129.48, 129.34, 129.19, 128.23, 127.87, 125.29, 123.07, 119.91, 114.39, 111.38, 29.85. HRMS(EI+) m/z: Calcd for $C_{23}H_{16}O_3$: 340.1099, found: 340.1100.

3-(3-Methyl-2-oxo-2,3-dihydrobenzofuran-3-yl)benzaldehyde. The desired product was obtained as a yellow liquid in 11% yield (0.027 g). When pre-stirred solution was used, the desired product was obtained in 11% yield (0.027 g).



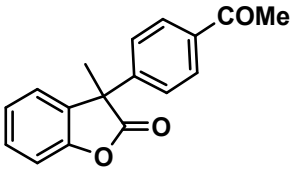
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.81 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.16 (t, *J* = 6.1 Hz, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.93, 178.27, 152.84, 140.85, 136.92, 132.80, 131.89, 129.77, 129.62, 129.52, 127.65, 125.00, 124.62, 111.43, 50.88, 25.18. HRMS(EI+) m/z: Calcd for $C_{16}H_{12}O_3$: 252.0786, found: 252.0788. IR (neat): 1801.99 cm^{-1} (C=O).

1-(4-(3-(4-Acetylbenzyl)benzofuran-2-yl)phenyl)ethan-1-one (14). The desired product was obtained as a yellow oil in 36% yield (0.132 g). When pre-stirred solution was used, the desired product was obtained in 34% yield (0.126 g).



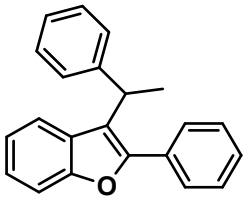
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.31 (s, 2H), 2.53 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.80, 197.48, 154.43, 151.01, 144.53, 136.48, 135.80, 135.03, 130.17, 129.01, 128.94, 128.43, 126.74, 125.59, 123.16, 120.07, 115.20, 111.50, 30.36, 26.76, 26.69. HRMS(EI+) m/z: Calcd for $C_{25}H_{20}O_3$: 368.1412, found: 368.1415.

3-(4-Acetylphenyl)-3-methylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 10% yield (0.027 g). When pre-stirred solution was used, the desired product was obtained in 14% yield (0.036 g).



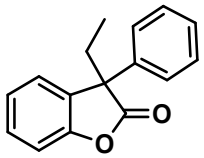
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.17 – 7.12 (m, 3H), 2.51 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.56, 178.14, 152.83, 144.59, 136.65, 132.07, 129.54, 128.94, 126.98, 124.91, 124.62, 111.38, 51.17, 26.78, 24.98. HRMS(EI+) m/z: Calcd for $C_{17}H_{14}O_3$: 266.0943, found: 266.0945. IR (neat): 1804.10 cm^{-1} (C=O).

2-Phenyl-3-(1-phenylethyl)benzofuran (18) The desired product was obtained as a colorless oil in 77% yield (0.23 g).



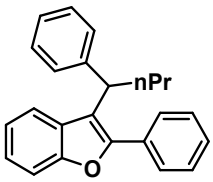
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 2H), 7.51 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.32 (m, 4H), 7.27 (ddd, *J* = 6.2, 5.6, 2.4 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.11 – 7.04 (m, 1H), 4.72 – 4.66 (m, 1H), 1.81 (dd, *J* = 7.3, 4.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.62, 151.43, 144.42, 131.17, 128.89, 128.77, 128.64, 128.55, 127.91, 127.38, 126.28, 124.19, 122.36, 121.74, 119.69, 111.39, 35.12, 20.46. HRMS(EI+) m/z: Calcd for $C_{22}H_{18}O$: 298.1358, found: 298.1356.

3-Ethyl-3-phenylbenzofuran-2(3H)-one (19). The desired product was obtained as a yellow liquid in 12% yield (0.029 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.35 (d, *J* = 1.0 Hz, 3H), 7.30 – 7.22 (m, 4H), 7.19 (s, 1H), 2.54 – 2.45 (m, 1H), 2.32 – 2.22 (m, 1H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.28, 153.55, 138.92, 130.13, 129.16, 128.91, 127.97, 126.90, 125.25, 124.49, 111.10, 56.59, 32.14, 9.44. HRMS(EI+) m/z: Calcd for $C_{16}H_{14}O_2$: 238.0994, found: 238.0990. IR (neat): 1799.94 cm^{-1} (C=O).

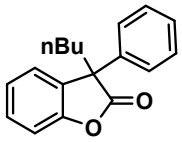
2-Phenyl-3-(1-phenylbutyl)benzofuran (21). The desired product was obtained as a colorless oil in 61% yield (0.198 g).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.29 – 7.22 (m, 3H), 7.19 – 7.12 (m, 2H), 4.47 (dd, *J* = 9.8, 6.1 Hz, 1H), 2.29 – 2.14 (m, 2H), 1.28 – 1.21 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.60, 152.50, 144.45, 131.19, 129.13, 128.69, 128.63, 128.60, 128.08, 127.76, 126.28, 124.19, 122.48, 121.77, 117.94, 111.46, 41.54, 37.13, 21.51, 14.11. HRMS(EI+) m/z: Calcd for $C_{24}H_{22}O$: 326.1671, found: 326.1669.

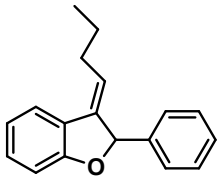
3-Butyl-3-phenylbenzofuran-2(3H)-one (22). The desired product was obtained as a yellow

liquid in 3% yield (0.008 g).



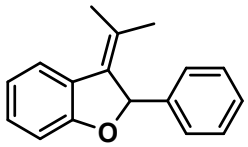
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.21 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.27 – 2.19 (m, 1H), 1.36 – 1.14 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.38, 153.42, 139.11, 130.47, 129.11, 128.90, 127.93, 126.82, 125.25, 124.46, 111.11, 55.92, 38.86, 27.10, 22.80, 13.88. HRMS(EI+) m/z: Calcd for $C_{18}H_{18}O_2$: 266.1307, found: 266.1308. IR (neat): 1801.36 cm^{-1} (C=O).

(E)-3-Butylidene-2-phenyl-2,3-dihydrobenzofuran (23). The desired product was obtained as a colorless oil in 12% yield (0.031 g).



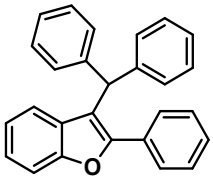
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.31 (m, 6H), 7.15 (dd, *J* = 11.2, 4.3 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.14 (dt, *J* = 2.9, 1.5 Hz, 1H), 5.97 (td, *J* = 7.7, 2.8 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.29 – 1.20 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.52, 139.81, 138.63, 129.58, 128.82, 128.77, 127.86, 126.76, 120.81, 120.44, 120.00, 110.40, 86.51, 31.43, 22.40, 13.83. HRMS(EI+) m/z: Calcd for $C_{18}H_{18}O$: 250.1358, found: 250.1356.

2-Phenyl-3-(propan-2-ylidene)-2,3-dihydrobenzofuran (25). The desired product was obtained as a colorless oil in 16% yield (0.037 g).



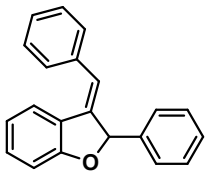
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 7.0, 2.7 Hz, 5H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.12 (s, 1H), 2.13 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.21, 140.14, 132.27, 128.82, 128.57, 127.77, 127.33, 127.20, 123.96, 120.55, 110.19, 87.08, 24.01, 21.64. HRMS(EI+) m/z: Calcd for $C_{17}H_{16}O$: 236.1201, found: 236.1199.

3-Benzhydryl-2-phenylbenzofuran (27). The desired product was obtained as a white solid in 4% yield (0.014 g). m.p : 127 °C



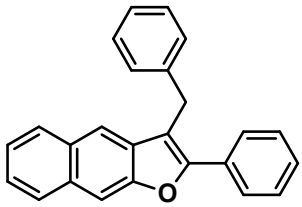
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.63 (m, 2H), 7.49 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.30 – 7.18 (m, 11H), 7.01 – 6.95 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 5.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.52, 152.39, 142.71, 130.82, 129.64, 129.31, 128.76, 128.59, 127.91, 126.73, 124.15, 122.54, 122.07, 117.90, 111.28, 47.34. HRMS(EI+) m/z: Calcd for $C_{27}H_{20}O$: 360.1514, found: 360.1513.

(E)-3-Benzylidene-2-phenyl-2,3-dihydrobenzofuran (28). The desired product was obtained as a colorless oil in 17% yield (0.048 g).



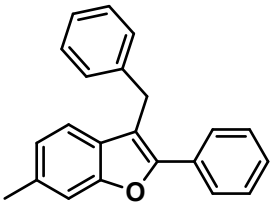
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.24 (m, 12H), 6.91 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.75 – 6.69 (m, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 6.15 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.68, 152.26, 141.04, 140.71, 136.93, 131.00, 128.92, 128.83, 128.54, 128.52, 127.64, 127.45, 123.97, 122.08, 120.61, 110.72, 88.56. HRMS(EI+) m/z: Calcd for $C_{21}H_{16}O$: 284.1201, found: 284.1203.

3-Benzyl-2-phenylnaphtho[2,3-b]furan (16). The desired product was obtained as a white solid in 34% yield (0.114 g). m.p : 153 °C



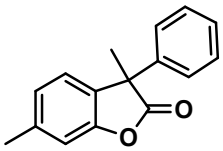
^{1}H NMR (400 MHz, $cdcl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.82 (dd, *J* = 15.3, 7.4 Hz, 4H), 7.48 – 7.37 (m, 5H), 7.33 – 7.26 (m, 4H), 7.23 (d, *J* = 3.3 Hz, 1H), 4.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.37, 153.18, 139.19, 131.92, 131.82, 130.75, 130.48, 128.98, 128.92, 128.85, 128.28, 128.18, 127.94, 127.32, 126.55, 124.98, 124.07, 117.85, 113.19, 106.61, 30.29. HRMS(EI+) m/z: Calcd for $C_{21}H_{16}O$: 334.1358, found: 334.1355.

3-Benzyl-6-methyl-2-phenylbenzofuran (30). The desired product was obtained as a colorless oil in 64% yield (0.192 g). When pre-stirred solution was used, the desired product was obtained in 72% yield (0.215 g).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 4.5 Hz, 4H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 1H), 4.12 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.65, 151.59, 139.47, 134.83, 128.78, 128.71, 128.26, 128.22, 126.86, 126.37, 124.08, 119.56, 30.23, 21.84. HRMS(EI+) m/z: Calcd for $C_{22}H_{18}O$: 298.1358, found: 298.1356.

3,6-Dimethyl-3-phenylbenzofuran-2(3H)-one. The desired product was obtained as a yellow liquid in 7% yield (0.017 g). When pre-stirred solution was used, the desired product was obtained in 4% yield (0.01 g).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 5H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 2H), 2.34 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.23, 152.95, 139.84, 139.65, 129.70, 128.91, 127.92, 126.62, 125.32, 124.31, 111.73, 50.90, 25.08, 21.86. HRMS(EI+) m/z: Calcd for $C_{16}H_{14}O_2$: 238.0994, found: 238.0991. IR (neat): 1801.62 cm^{-1} (C=O).

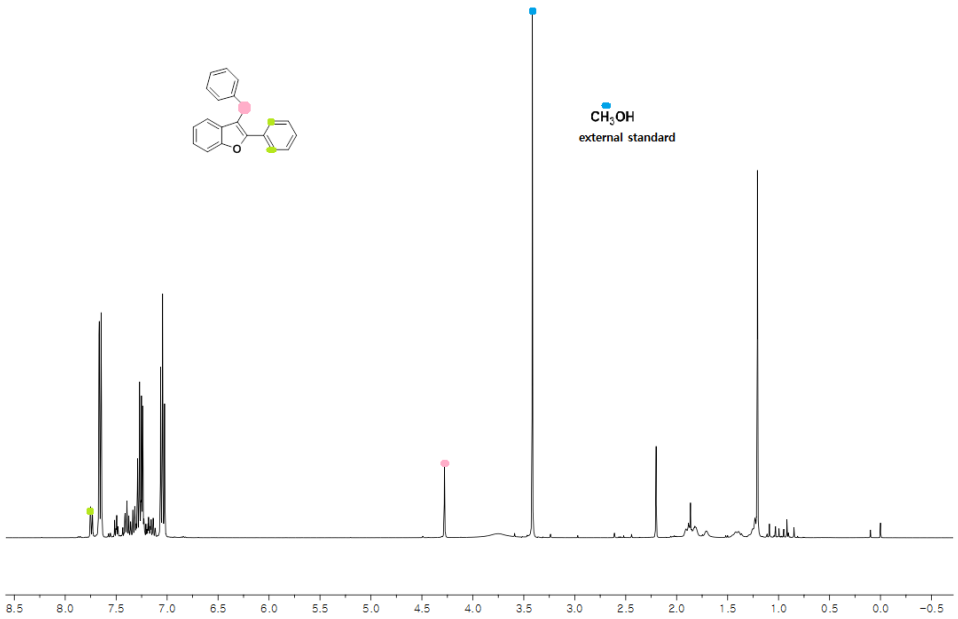
Kinetic isotope effect

The kinetic isotope effects in bis-arylation of 3-methylbenzofuran were derived from the following pseudo-first-order rate experiments. The results are shown in Figure S2. The yield corresponding to the point in the time axis was determined by a separate reaction. Experiments for both the deuterated (**1-D**, **1-CD_3**) and the non-deuterated substrates were conducted simultaneously. **1-D** and **1-CD_3** were prepared according to literature procedures.[2]

Experimental Procedure

In 5ml chem glass, Ag_2CO_3 (0.204 g, 0.3 mmol) was dried under high vacuum. In a separate dried flasks were made three solutions, two for the deuterated and one for the non-deuterated substrate. Each solution was prepared in the following manner: $Pd(OAc)_2$ (0.045 g, 0.2 mmol) and PCy_3 (0.112 g, 0.4 mmol), iodobenzene (4.08 g, 20 mmol), PivOH (0.204 g, 2 mmol) were added to a flame dried flask under argon. Next, 3-methylbenzofuran (0.264 g, 2 mmol) was added and the solution was stirred until it was homogeneous. An aliquot of catalyst solution (471 mg, 0.2 mmol scale of 3-methylbenzofuran), and H_2O (1 mL) were then added to the Ag_2CO_3. The resulting reaction was stirred at room temperature in the sealed. One set of reactions was taken off at the desired time points. The solutions were extracted with ethyl acetate and filtered to remove catalyst residue, and finally evaporated under reduced pressures. An aliquot of this solution was analyzed by NMR spectroscopy versus the external standard (Methanol, 0.02 mL, 0.5 mmol).

Representative crude NMR spectrum for KIE measurements



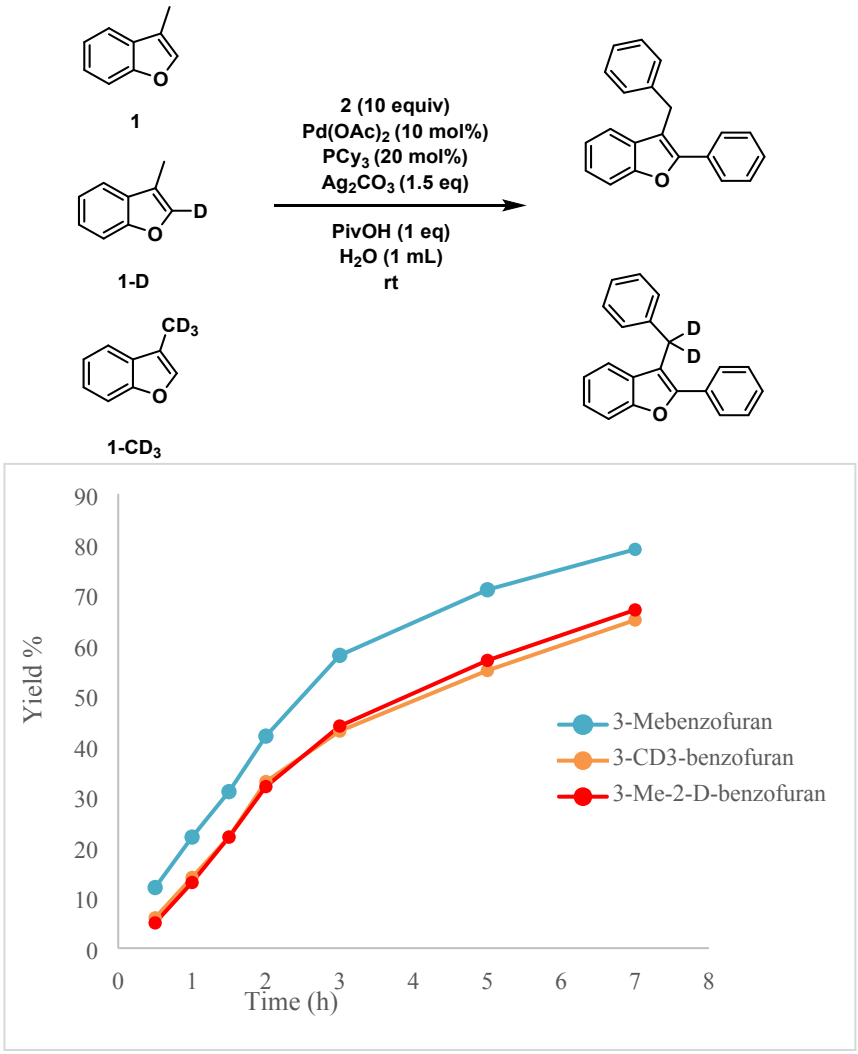


Figure S2. Pseudo-first-order rate constants and KIE for bis-arylation of **1**, **1-D** and **1-CD$_3$**.

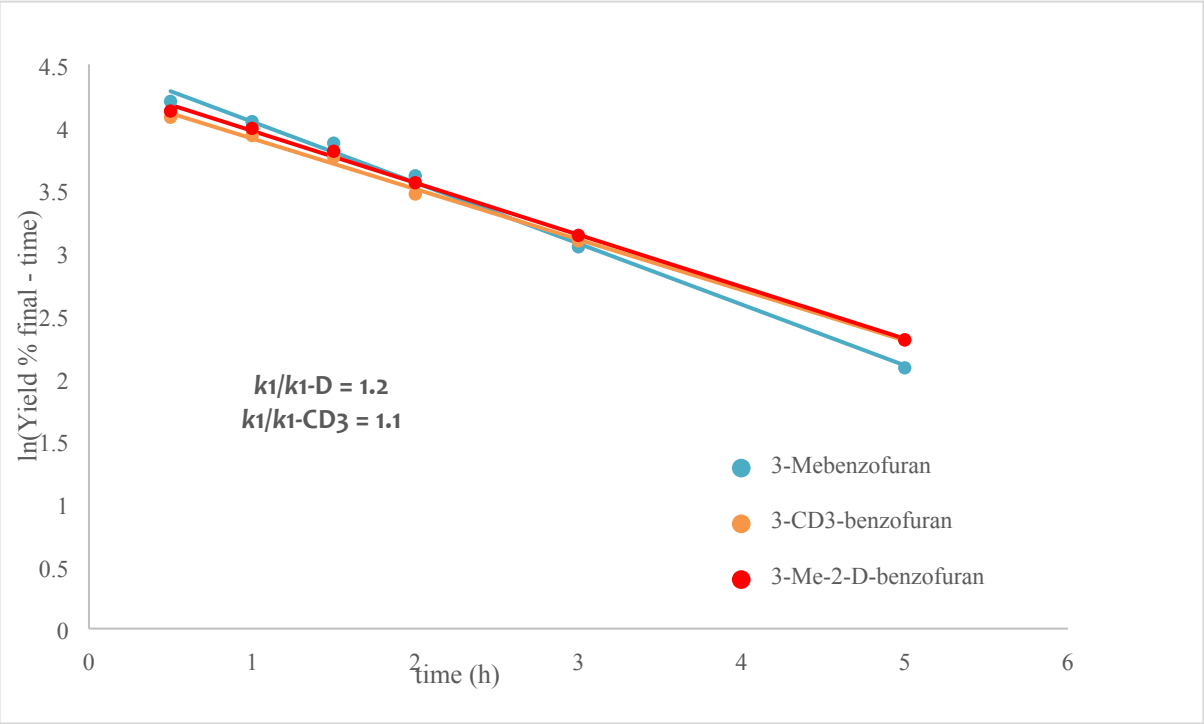
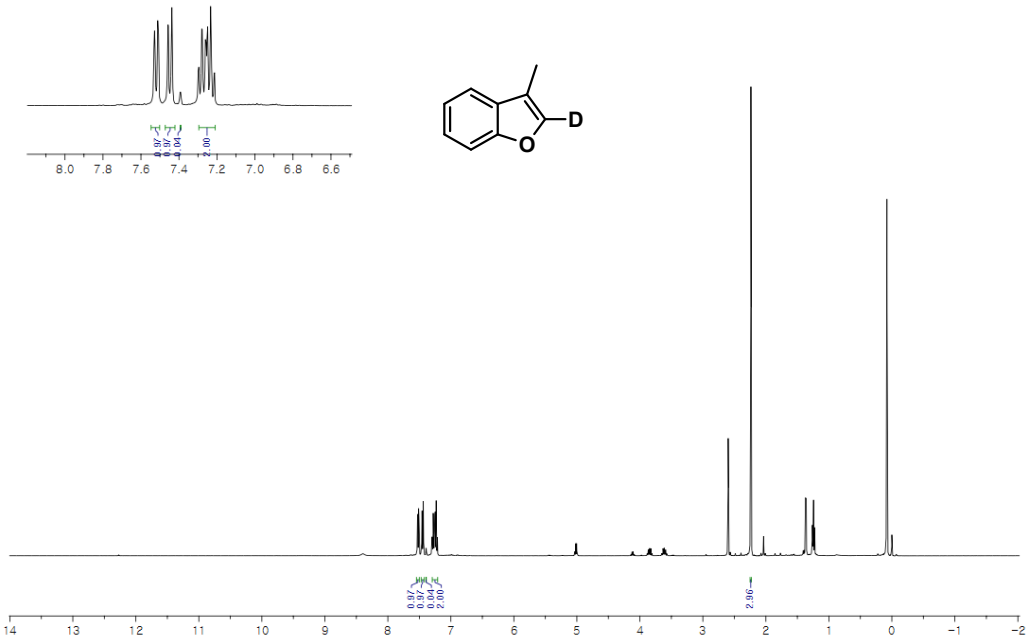
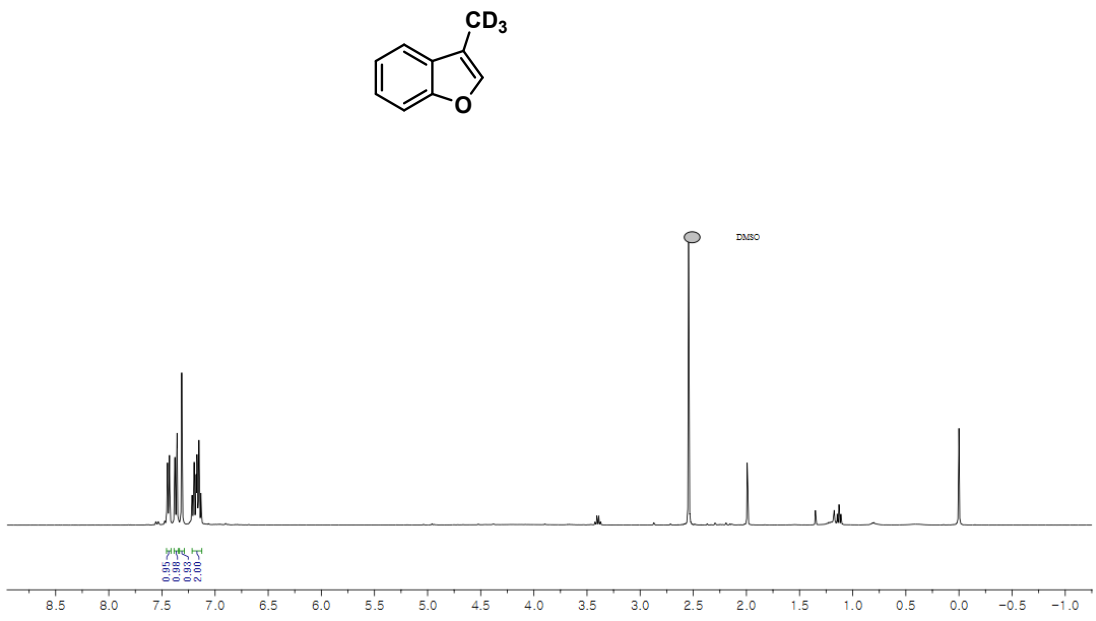


Figure S2 continued. Pseudo-first-order rate constants and KIE for bis-arylation of **1**, **1-D** and **1-CD$_3$**.

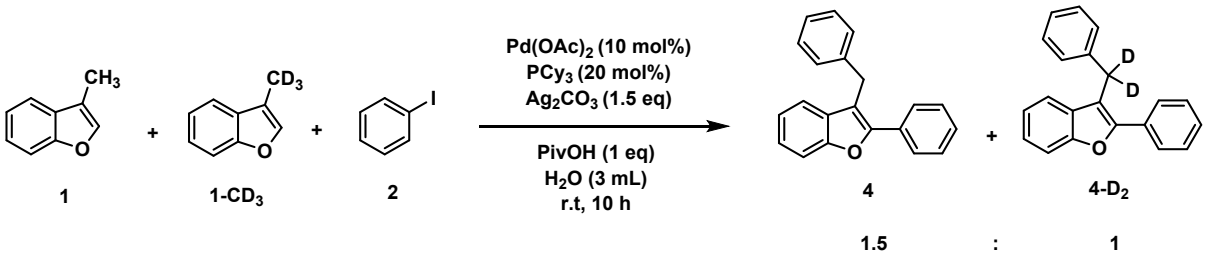
3-methylbenzofuran-2-d (1-D). Deutrium was 94% enriched in 2-position, as determined by ^{1}H NMR.



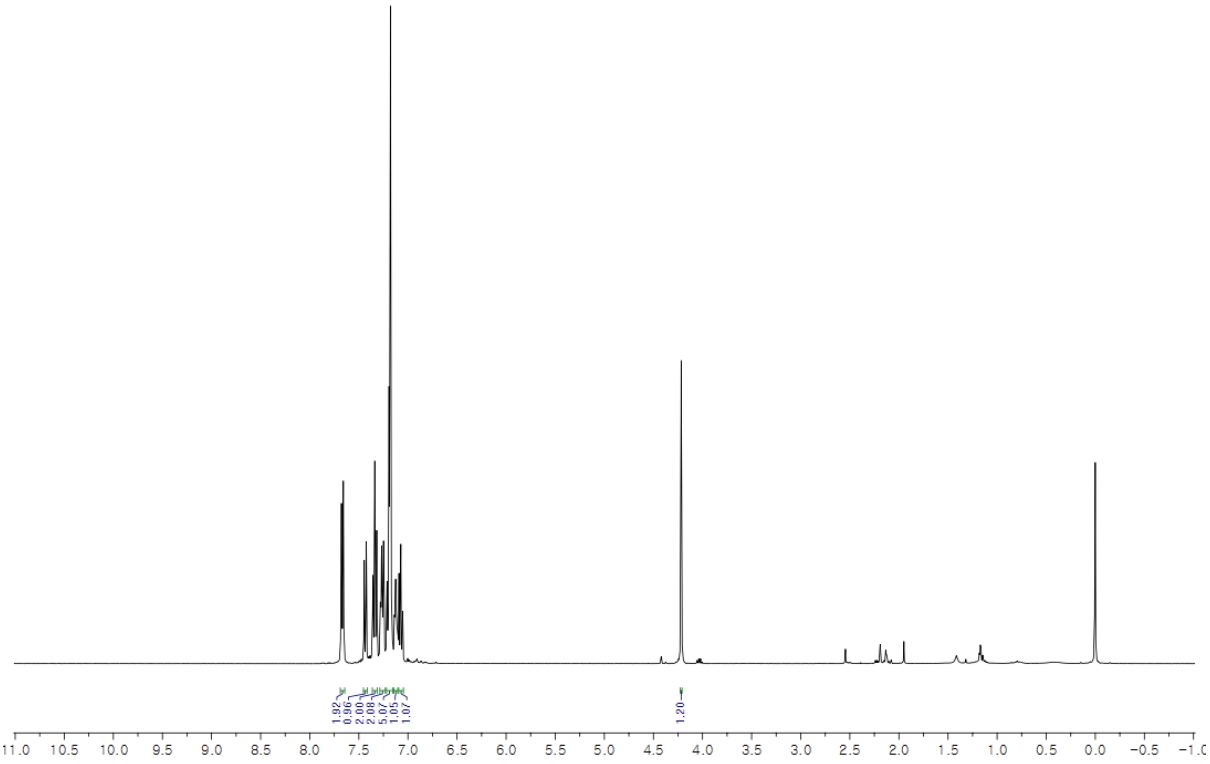
3-(methyl-d3)benzofuran (1-CD_3). Deutrium was 100% enriched in 3-methylposition, as determined by ^1H NMR.



Determination of KIE by the method of competing reacitons

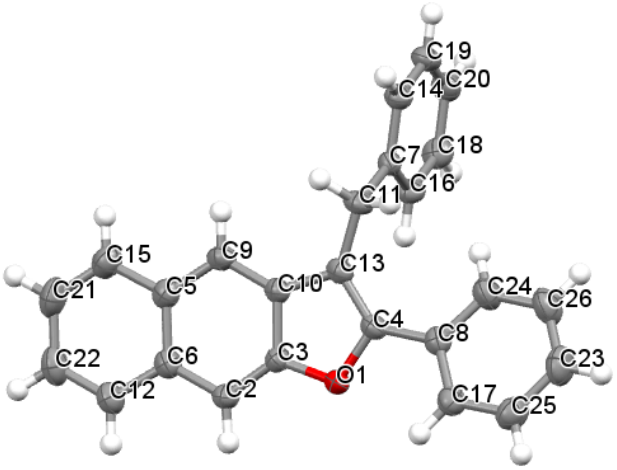


Reactions were performed in a schlenk tube equipped with a stirring bar charged with **1** (66 mg, 0.5 mmol), **1-CD$_3$** (68 mg, 0.5 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), PCy_3 (56 mg, 0.2 mmol), Ag_2CO_3 (413 mg, 1.5 mmol), PivOH (0.11 mL, 1 mmol), and H2O (3 mL). The mixture was stirred at room temperature for 10 h. The mixture was extracted with ethyl acetate, filtered to remove catalyst residue, and finally evaporated under reduced pressures. The mixture was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate) and the product **4** was obtained with 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 2.0H), 7.43 (d, *J* = 8.2 Hz, 1.0H), 7.34 (t, *J* = 7.6 Hz, 2.0H), 7.26 (dt, *J* = 14.3, 5.8 Hz, 2.0H), 7.22 – 7.16 (m, 5.0H), 7.14 – 7.10 (m, 1.0H), 7.07 (t, *J* = 7.5 Hz, 1.0H), 4.22 (s, 1.2H). The KIE value was calculated as $k1/k1\text{-}_{CD3}$ = 1.5



- **X-ray analysis**

Data sets were collected with a PHOTON 100 CMOS diffractometer. Programs used : solve structure XS (Sheldrick, 2008); refine structure XL (Sheldrick, 2008); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).



(Thermal ellipsoids are shown with 50% probability)

Table S2. Experimental details

Compound	**16**
CCDC number	1045349
Chemical formula	$C_{25}H_{18}O$
Molecular weight	334.39
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	223
a, *b*, *c* (Å)	8.2582 (2), 6.2091 (2), 17.8371 (5)
β (°)	103.1477 (14)
V (Å^3)	890.64 (4)

Z	2
Calculated density Mg/m^3	1.247
Radiation type	Mo $K\alpha$, λ = 0.71073 Å
μ (mm^{-1})	0.07
Crystal size (mm)	0.24 × 0.18 × 0.1
F(000)	352
Theta range for data collection	θ = 2.4–28.3°
Absorption correction	Multi-scan
T_{min}, T_{max}	0.982, 0.993
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31392, 4438, 3479
R_{int}	0.060
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.669
Limiting indices	h = −11 ~ 11, k = −8 ~ 8, l = −23~ 23
Radiation source: fine-focus sealed tube	
Refinement method	full matrix least-squares on F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.096, 1.08
No. of reflections	4438
No. of parameters	235
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.18

Table S3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.98315 (13)	−0.43300 (18)	−0.25200 (6)	0.0302 (3)
C2	−0.82171 (19)	−0.4148 (3)	−0.11916 (10)	0.0312 (4)
H2	−0.7728	−0.5510	−0.1207	0.037*

C3	−0.93398 (19)	−0.3361 (3)	−0.18060 (9)	0.0279 (4)
C4	−1.09181 (19)	−0.2887 (3)	−0.29875 (10)	0.0301 (4)
C5	−0.8591 (2)	−0.0775 (3)	−0.05212 (10)	0.0347 (4)
C6	−0.7812 (2)	−0.2843 (3)	−0.05272 (10)	0.0327 (4)
C7	−1.38173 (18)	0.1117 (2)	−0.27846 (9)	0.0274 (3)
C8	−1.15316 (19)	−0.3586 (3)	−0.37822 (10)	0.0320 (4)
C9	−0.97567 (19)	−0.0051 (3)	−0.11761 (10)	0.0333 (4)
H9	−1.0279	0.1292	−0.1172	0.040*
C10	−1.01252 (18)	−0.1333 (3)	−0.18246 (9)	0.0280 (3)
C11	−1.20523 (19)	0.0936 (3)	−0.28924 (11)	0.0334 (4)
H11A	−1.2088	0.1047	−0.3444	0.040*
H11B	−1.1418	0.2173	−0.2639	0.040*
C12	−0.6628 (2)	−0.3508 (3)	0.01433 (11)	0.0401 (4)
H12	−0.6105	−0.4854	0.0148	0.048*
C13	−1.11225 (18)	−0.1073 (3)	−0.25933 (10)	0.0295 (4)
C14	−1.4642 (2)	0.3073 (3)	−0.29340 (10)	0.0337 (4)
H14	−1.4096	0.4250	−0.3099	0.040*
C15	−0.8151 (2)	0.0506 (3)	0.01560 (11)	0.0455 (5)
H15	−0.8653	0.1859	0.0171	0.055*
C16	−1.4654 (2)	−0.0589 (3)	−0.25453 (10)	0.0341 (4)
H16	−1.4122	−0.1930	−0.2442	0.041*
C17	−1.0685 (2)	−0.5143 (3)	−0.41054 (11)	0.0384 (4)
H17	−0.9716	−0.5773	−0.3807	0.046*
C18	−1.6269 (2)	−0.0340 (3)	−0.24554 (11)	0.0401 (4)
H18	−1.6820	−0.1513	−0.2292	0.048*
C19	−1.6250 (2)	0.3320 (3)	−0.28443 (11)	0.0387 (4)
H19	−1.6787	0.4658	−0.2948	0.046*
C20	−1.7071 (2)	0.1612 (3)	−0.26037 (11)	0.0392 (4)
H20	−1.8165	0.1777	−0.2542	0.047*

C21	−0.7006 (3)	−0.0211 (4)	0.07856 (12)	0.0538 (6)
H21	−0.6728	0.0656	0.1228	0.065*
C22	−0.6241 (2)	−0.2226 (4)	0.07786 (11)	0.0495 (5)
H22	−0.5454	−0.2694	0.1216	0.059*
C23	−1.2680 (3)	−0.4853 (4)	−0.53134 (12)	0.0553 (6)
H23	−1.3057	−0.5264	−0.5831	0.066*
C24	−1.2981 (2)	−0.2718 (3)	−0.42382 (11)	0.0438 (5)
H24	−1.3590	−0.1698	−0.4027	0.053*
C25	−1.1262 (3)	−0.5767 (3)	−0.48642 (12)	0.0492 (5)
H25	−1.0683	−0.6824	−0.5076	0.059*
C26	−1.3531 (3)	−0.3336 (4)	−0.49958 (12)	0.0555 (6)
H26	−1.4500	−0.2713	−0.5298	0.067*

Table S4. Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0302 (6)	0.0290 (6)	0.0297 (6)	0.0048 (5)	0.0031 (5)	0.0000 (5)
C2	0.0311 (8)	0.0282 (8)	0.0346 (9)	0.0024 (7)	0.0080 (7)	0.0014 (8)
C3	0.0276 (8)	0.0276 (8)	0.0294 (9)	−0.0022 (6)	0.0080 (7)	−0.0008 (7)
C4	0.0258 (7)	0.0295 (8)	0.0345 (9)	0.0010 (6)	0.0058 (7)	0.0051 (7)
C5	0.0307 (8)	0.0381 (10)	0.0375 (10)	−0.0050 (7)	0.0126 (7)	−0.0041 (8)
C6	0.0304 (8)	0.0351 (9)	0.0338 (10)	−0.0032 (7)	0.0099 (7)	0.0026 (7)
C7	0.0258 (7)	0.0274 (8)	0.0274 (8)	0.0005 (6)	0.0026 (6)	0.0007 (7)
C8	0.0315 (8)	0.0338 (9)	0.0312 (9)	−0.0036 (7)	0.0081 (7)	0.0033 (7)
C9	0.0288 (8)	0.0300 (8)	0.0429 (10)	0.0009 (7)	0.0122 (7)	−0.0013 (8)
C10	0.0220 (7)	0.0283 (8)	0.0342 (9)	−0.0015 (6)	0.0079 (7)	0.0012 (7)
C11	0.0283 (8)	0.0265 (8)	0.0463 (11)	0.0019 (7)	0.0104 (8)	0.0074 (7)
C12	0.0378 (9)	0.0461 (10)	0.0349 (10)	−0.0004 (8)	0.0051 (8)	0.0048 (9)
C13	0.0219 (7)	0.0302 (8)	0.0373 (9)	−0.0005 (6)	0.0084 (7)	0.0044 (7)

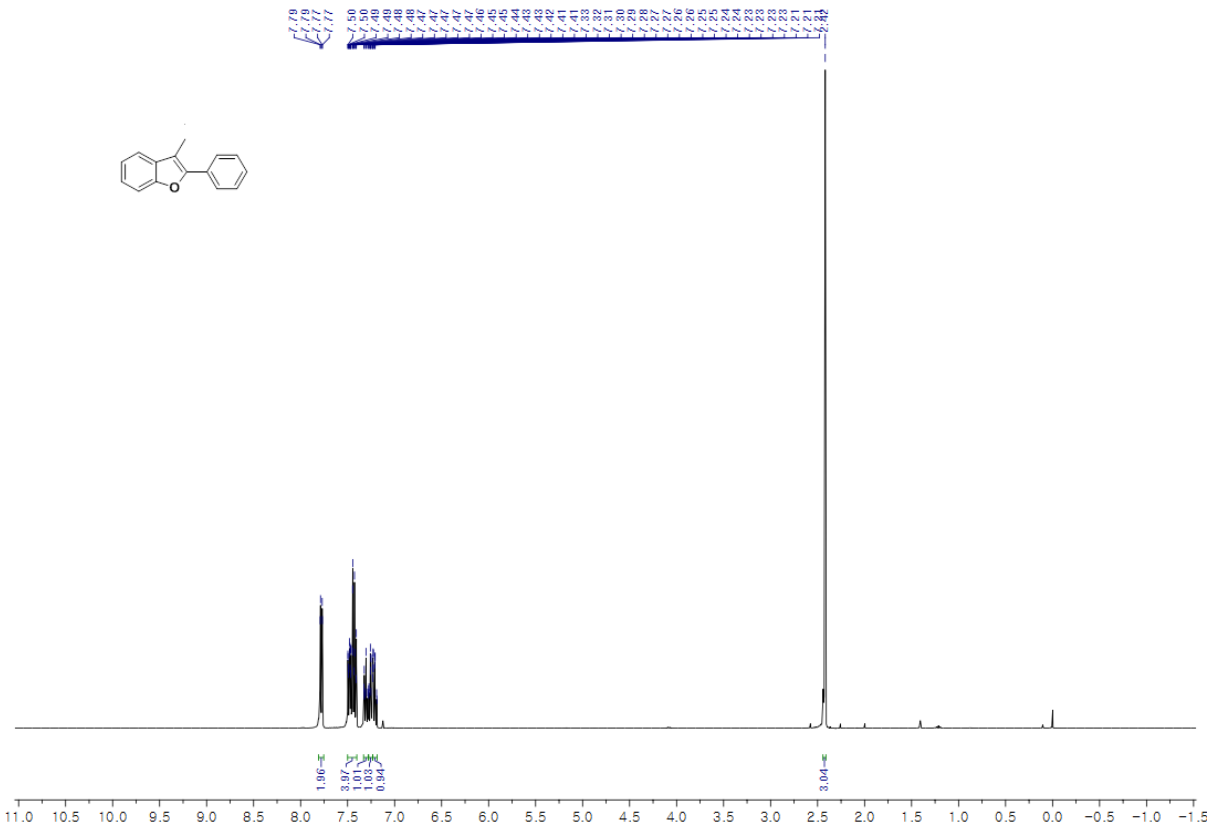
C14	0.0314 (9)	0.0289 (8)	0.0401 (10)	0.0011 (7)	0.0068 (7)	0.0034 (7)
C15	0.0446 (10)	0.0493 (11)	0.0445 (12)	−0.0034 (9)	0.0140 (9)	−0.0109 (10)
C16	0.0352 (9)	0.0266 (8)	0.0417 (10)	0.0012 (7)	0.0113 (8)	0.0047 (7)
C17	0.0420 (9)	0.0376 (9)	0.0348 (10)	0.0004 (8)	0.0071 (8)	0.0026 (8)
C18	0.0364 (9)	0.0392 (10)	0.0477 (11)	−0.0065 (8)	0.0158 (8)	0.0021 (9)
C19	0.0337 (9)	0.0344 (10)	0.0463 (11)	0.0094 (8)	0.0056 (8)	0.0018 (8)
C20	0.0278 (8)	0.0467 (11)	0.0439 (11)	0.0029 (8)	0.0098 (8)	−0.0040 (9)
C21	0.0572 (13)	0.0669 (15)	0.0359 (11)	−0.0116 (11)	0.0078 (10)	−0.0155 (11)
C22	0.0457 (11)	0.0678 (14)	0.0326 (11)	−0.0062 (10)	0.0038 (9)	0.0025 (10)
C23	0.0644 (14)	0.0655 (15)	0.0319 (11)	−0.0069 (12)	0.0024 (10)	−0.0018 (10)
C24	0.0392 (9)	0.0542 (12)	0.0359 (11)	0.0052 (9)	0.0042 (8)	0.0017 (9)
C25	0.0592 (12)	0.0486 (12)	0.0411 (11)	0.0002 (10)	0.0144 (10)	−0.0058 (10)
C26	0.0497 (11)	0.0732 (15)	0.0370 (12)	0.0088 (11)	−0.0040 (9)	0.0044 (11)

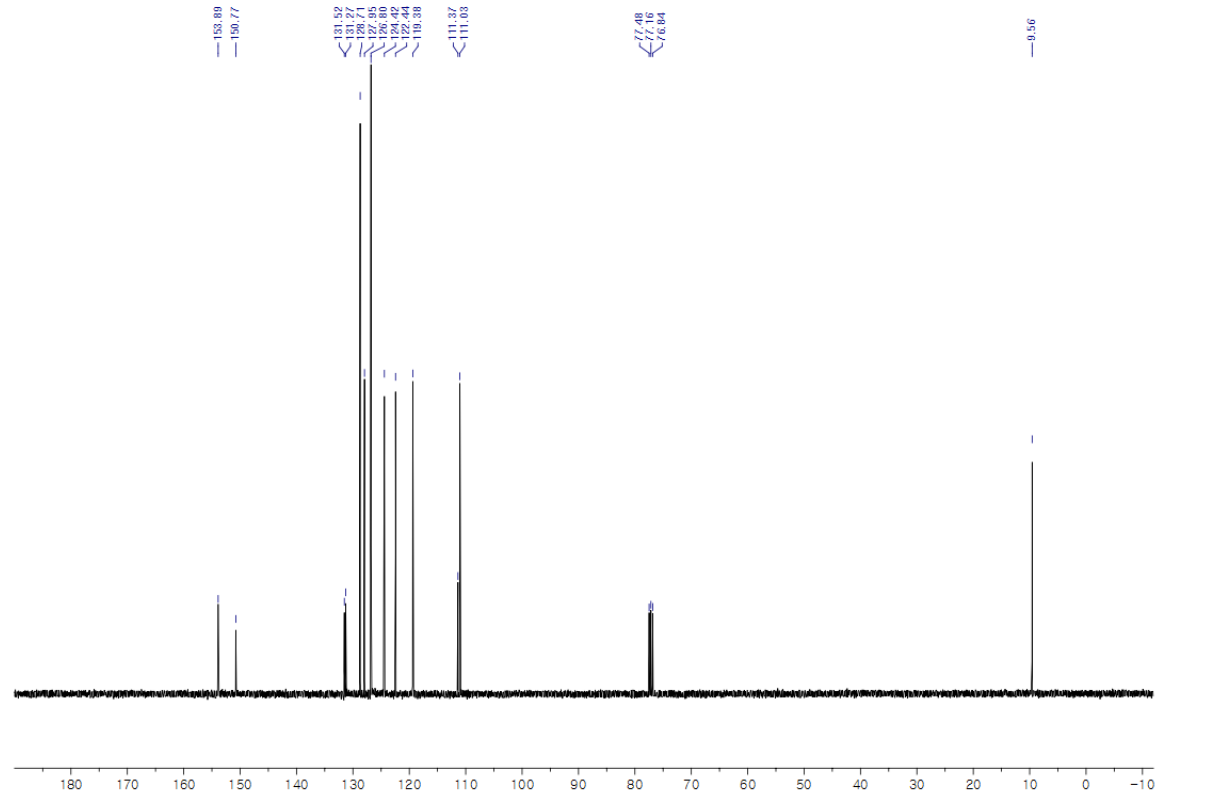
Table S5. Geometric parameters (Å, °)

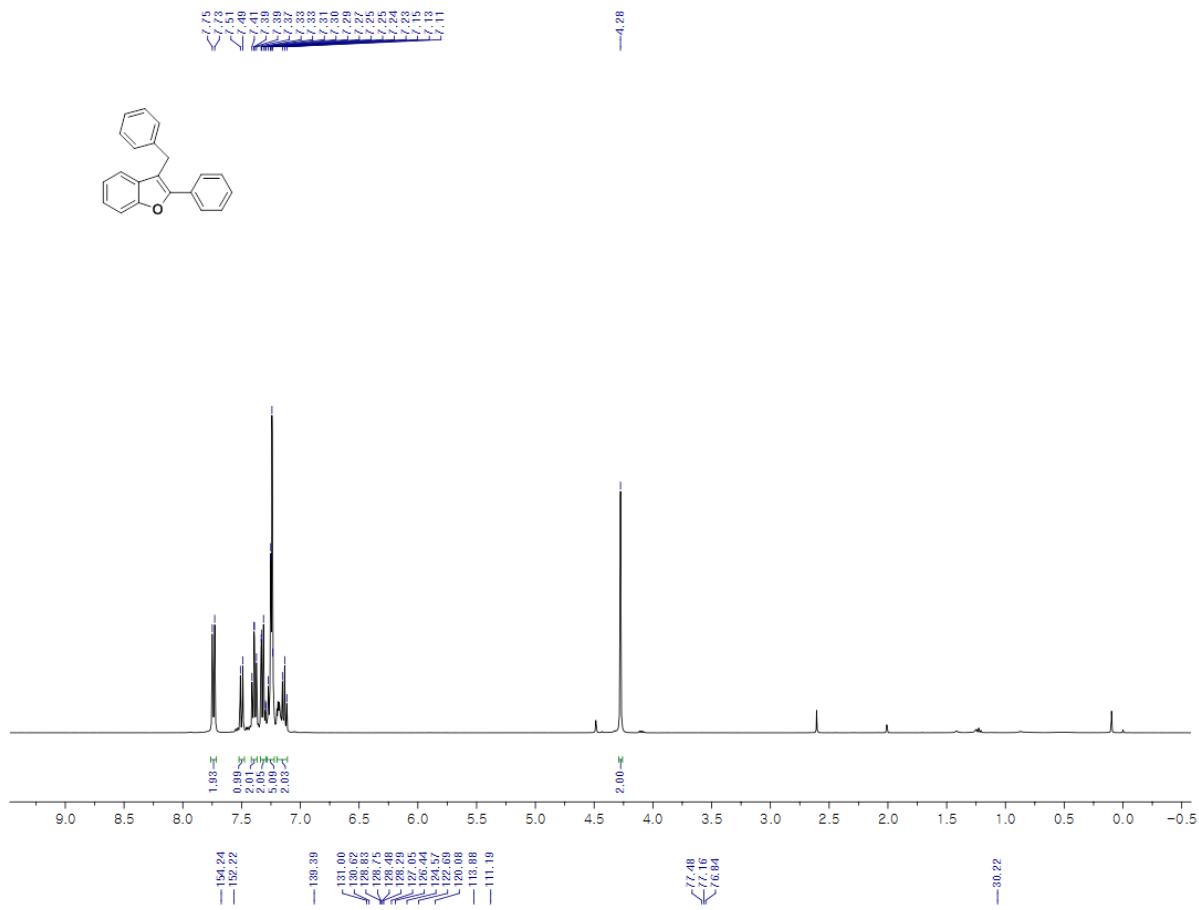
O1—C3	1.3833 (19)	C8—C24	1.393 (2)
O1—C4	1.4010 (18)	C9—C10	1.380 (2)
C2—C3	1.355 (2)	C10—C13	1.439 (2)
C2—C6	1.412 (2)	C11—C13	1.498 (2)
C3—C10	1.413 (2)	C12—C22	1.362 (3)
C4—C8	1.459 (2)	C14—C19	1.382 (2)
C4—C13	1.359 (2)	C15—C21	1.368 (3)
C5—C6	1.438 (2)	C16—C18	1.387 (2)
C5—C9	1.408 (2)	C17—C25	1.384 (3)
C5—C15	1.423 (2)	C18—C20	1.378 (3)
C6—C12	1.422 (2)	C19—C20	1.379 (3)
C7—C11	1.517 (2)	C21—C22	1.403 (3)
C7—C14	1.388 (2)	C23—C25	1.382 (3)
C7—C16	1.384 (2)	C23—C26	1.372 (3)
C8—C17	1.393 (2)	C24—C26	1.379 (3)

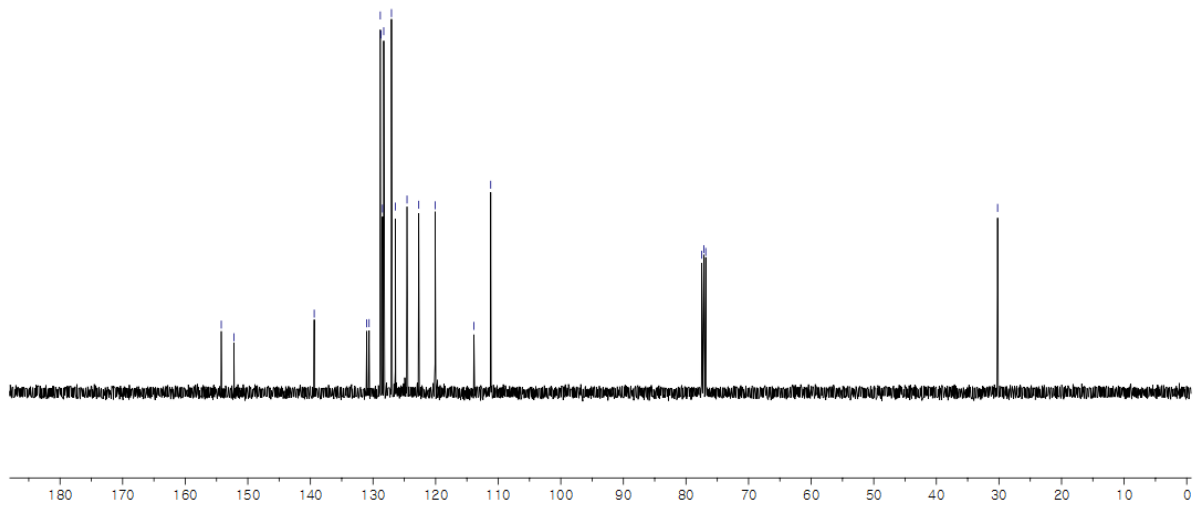
C3—O1—C4	106.51 (12)	C3—C10—C13	106.41 (14)
C3—C2—C6	117.37 (15)	C9—C10—C3	118.79 (15)
O1—C3—C10	109.19 (13)	C9—C10—C13	134.69 (15)
C2—C3—O1	126.24 (15)	C13—C11—C7	116.48 (13)
C2—C3—C10	124.48 (15)	C22—C12—C6	121.10 (19)
O1—C4—C8	114.97 (14)	C4—C13—C10	106.78 (14)
C13—C4—O1	111.11 (14)	C4—C13—C11	128.32 (16)
C13—C4—C8	133.87 (16)	C10—C13—C11	124.65 (15)
C9—C5—C6	120.12 (16)	C19—C14—C7	121.14 (16)
C9—C5—C15	121.36 (17)	C21—C15—C5	120.68 (19)
C15—C5—C6	118.52 (17)	C7—C16—C18	120.71 (15)
C2—C6—C5	119.86 (15)	C25—C17—C8	120.38 (18)
C2—C6—C12	121.72 (16)	C20—C18—C16	120.58 (16)
C12—C6—C5	118.41 (16)	C20—C19—C14	120.30 (16)
C14—C7—C11	118.93 (14)	C18—C20—C19	119.15 (15)
C16—C7—C11	122.94 (14)	C15—C21—C22	120.8 (2)
C16—C7—C14	118.12 (14)	C12—C22—C21	120.49 (19)
C17—C8—C4	120.84 (15)	C26—C23—C25	119.3 (2)
C17—C8—C24	118.19 (17)	C26—C24—C8	120.82 (19)
C24—C8—C4	120.97 (16)	C23—C25—C17	120.7 (2)
C10—C9—C5	119.36 (15)	C23—C26—C24	120.67 (19)

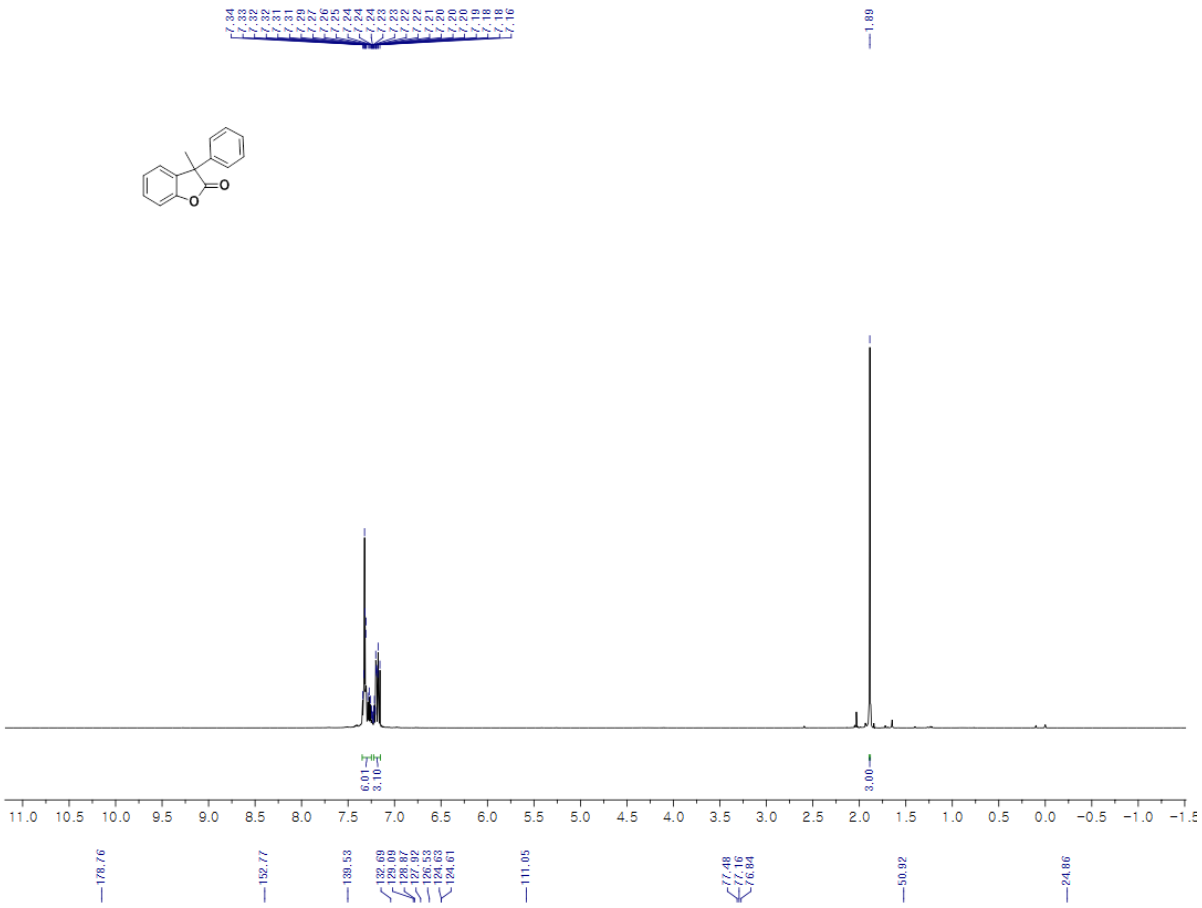
- **^{1}H and ^{13}C NMR Spectra of compounds**

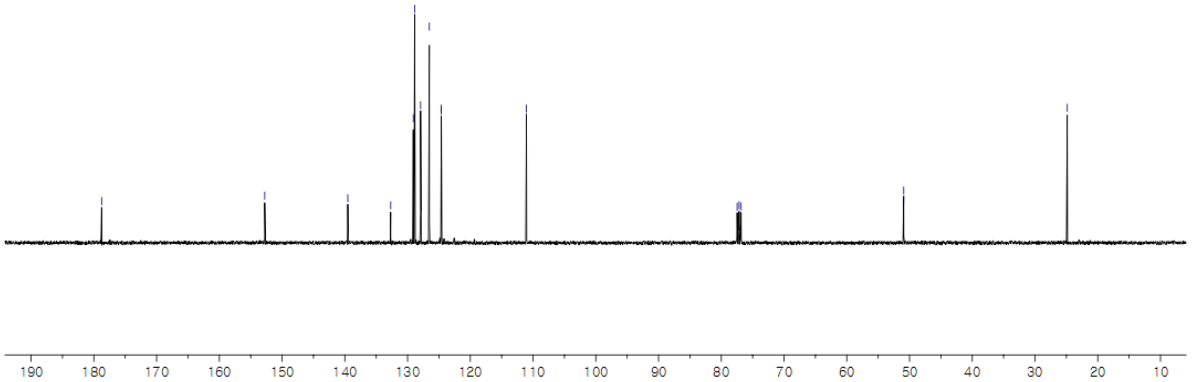


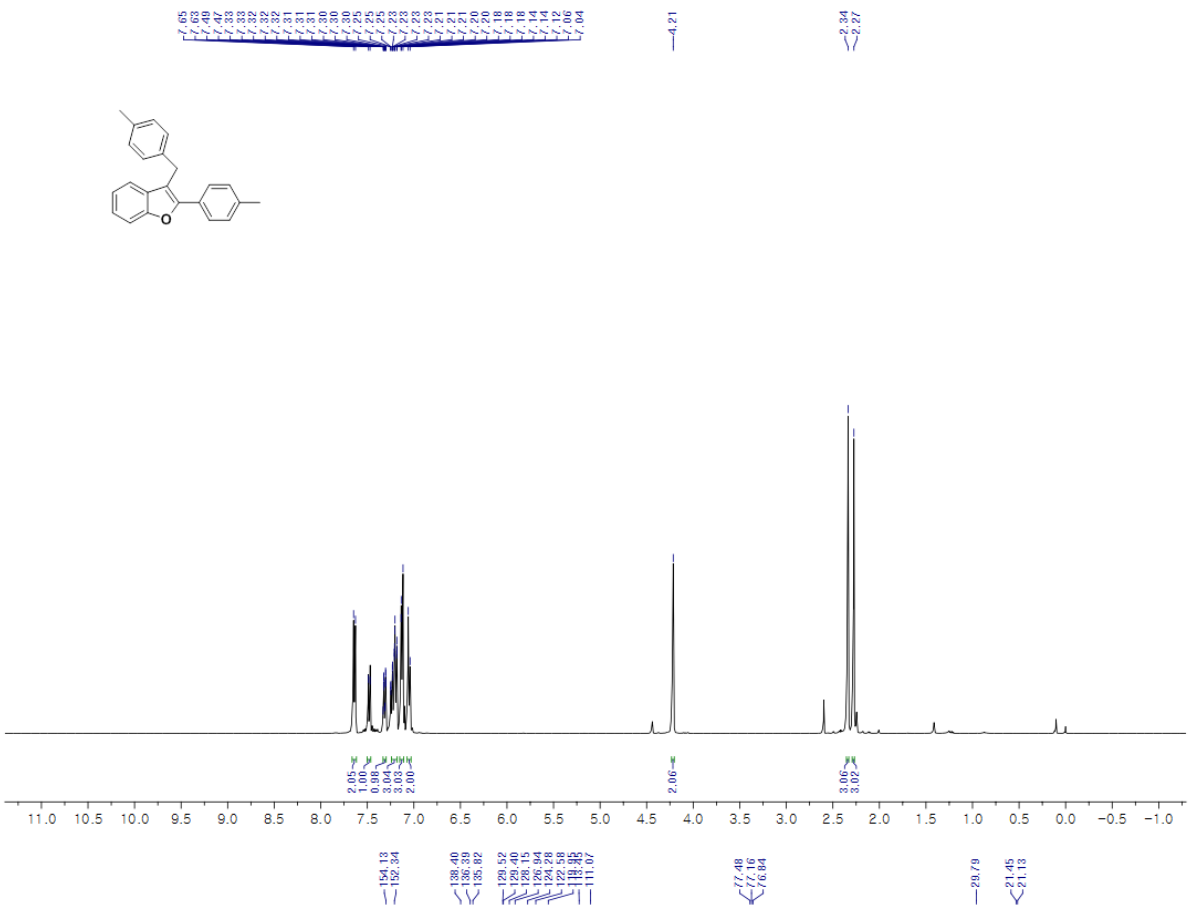


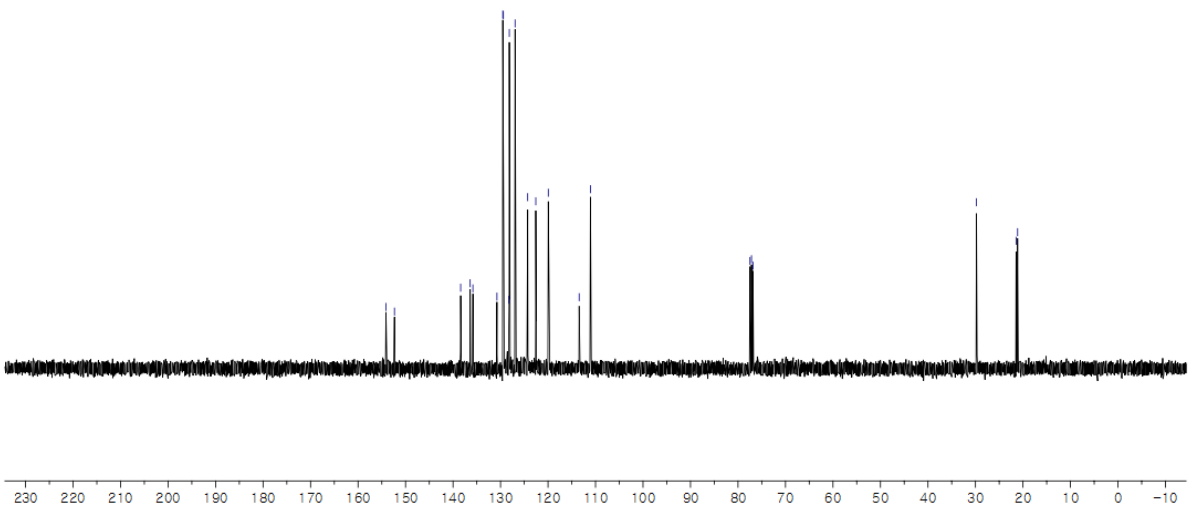


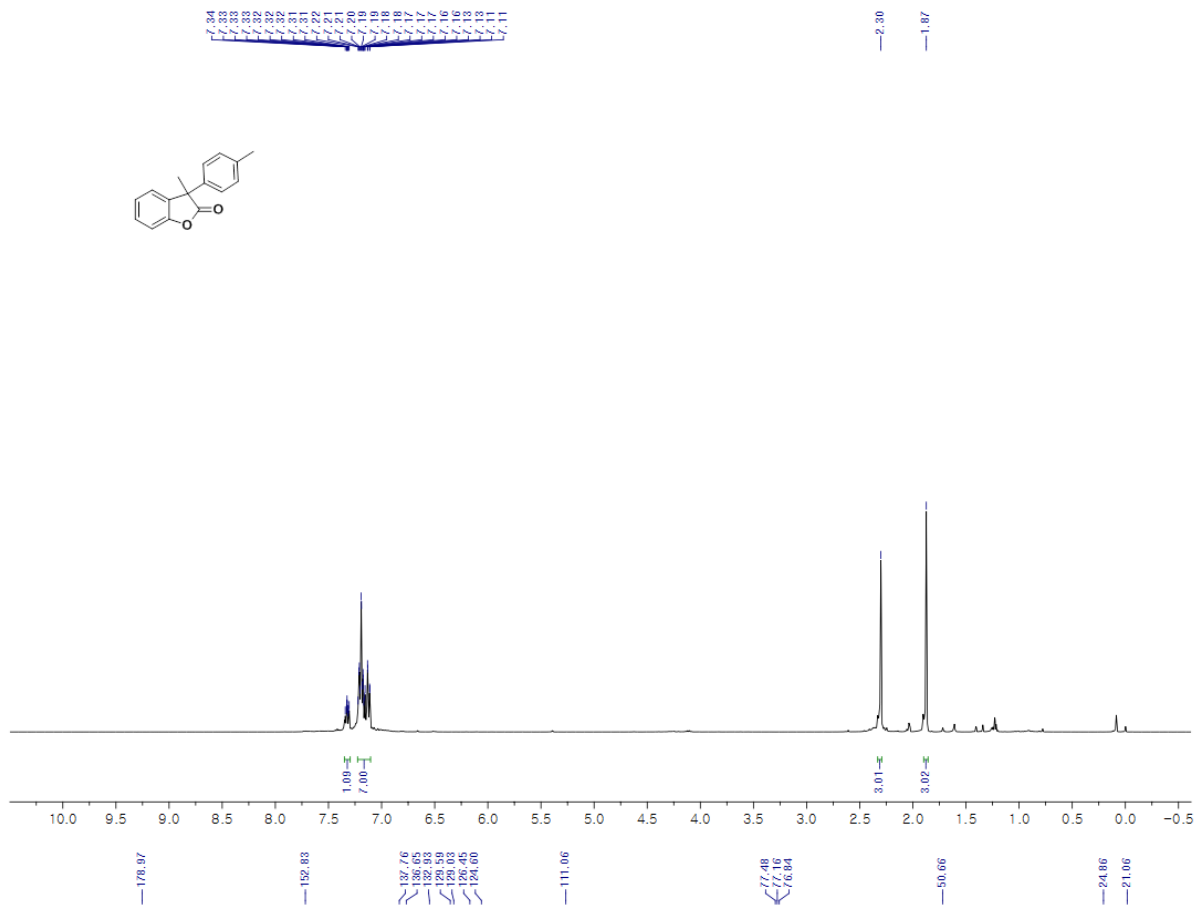


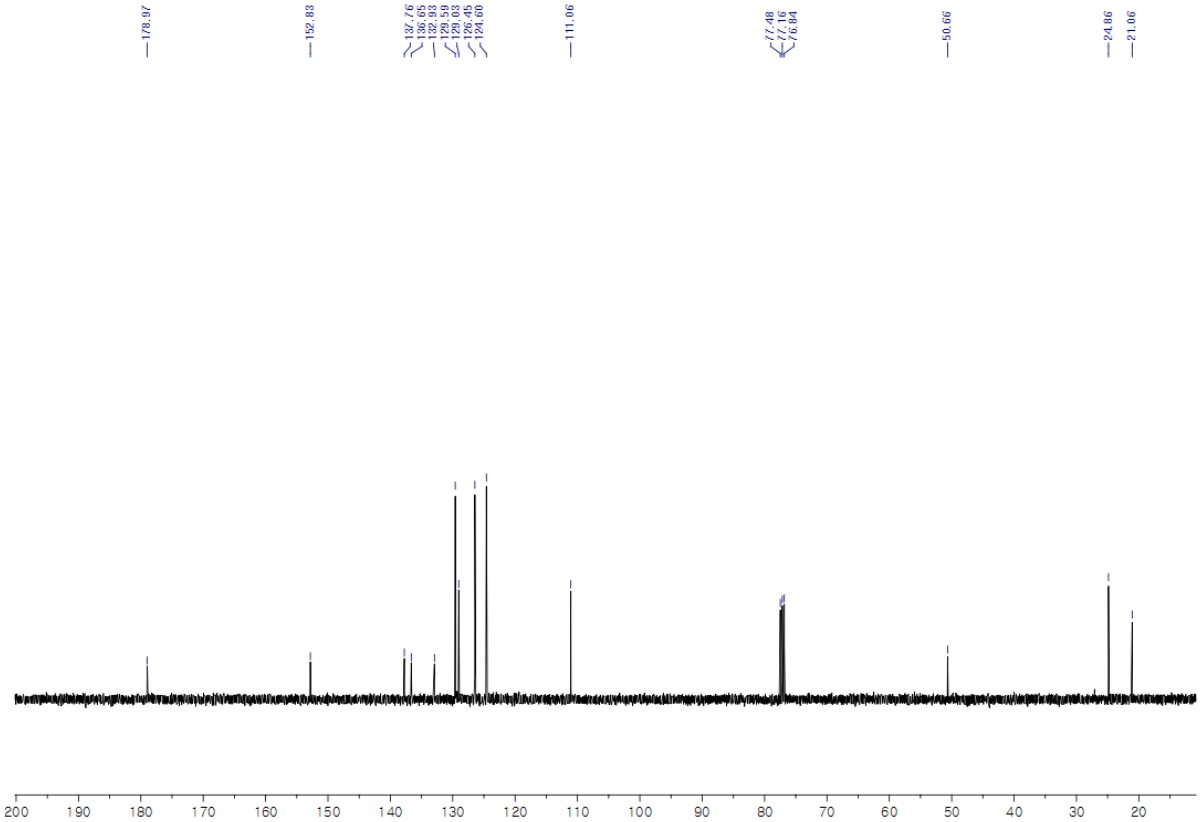


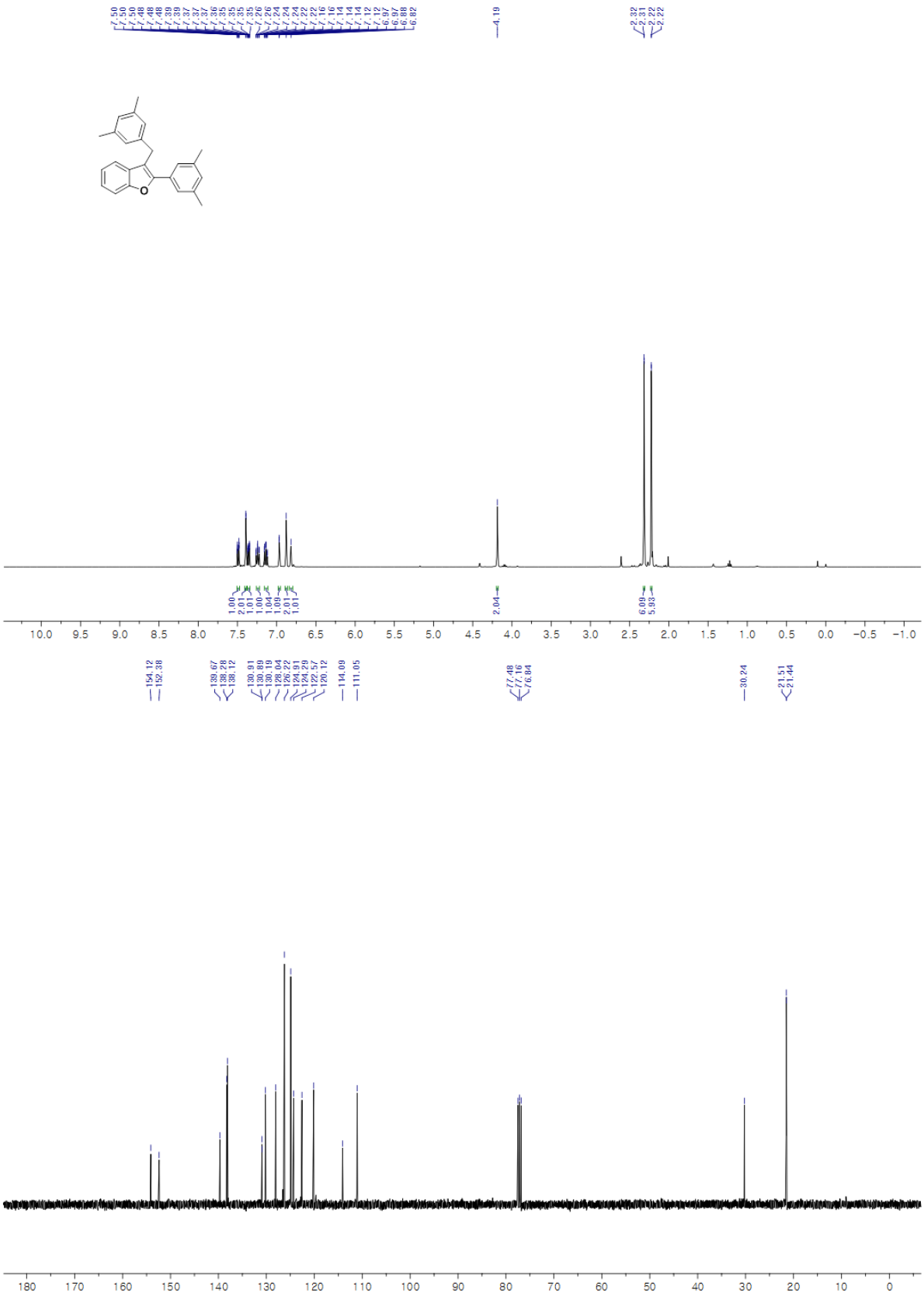


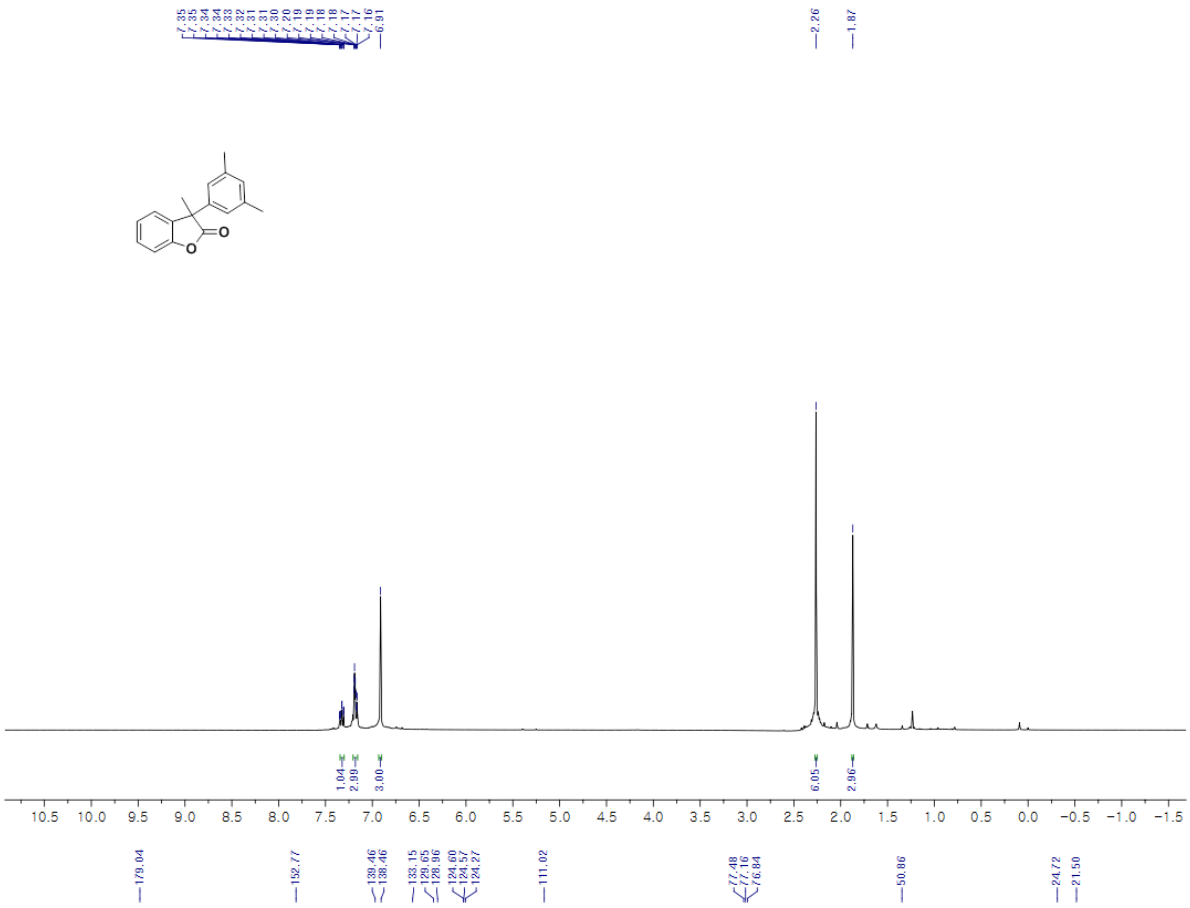








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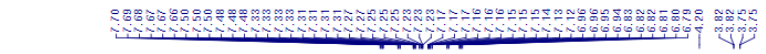

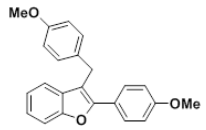
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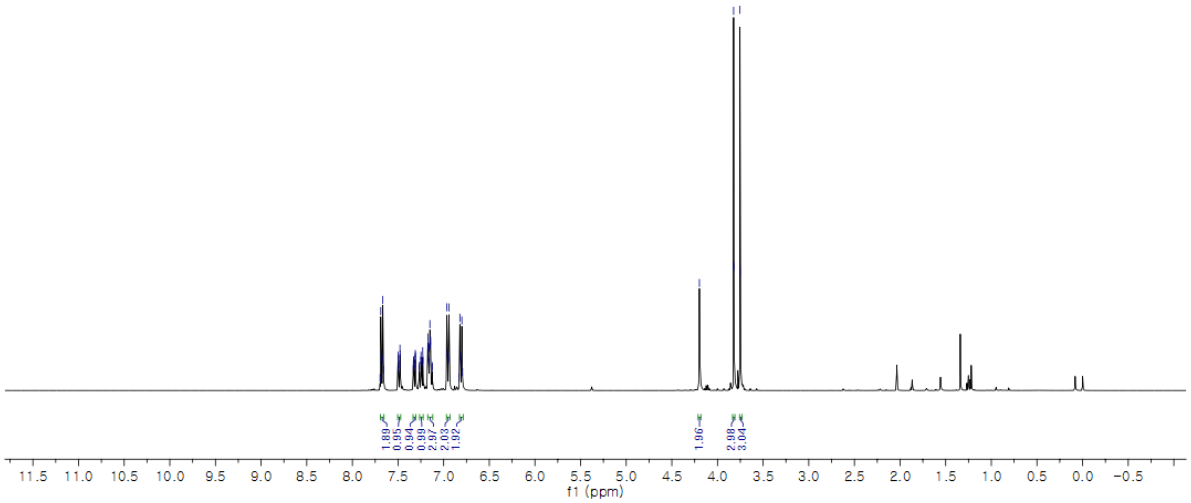
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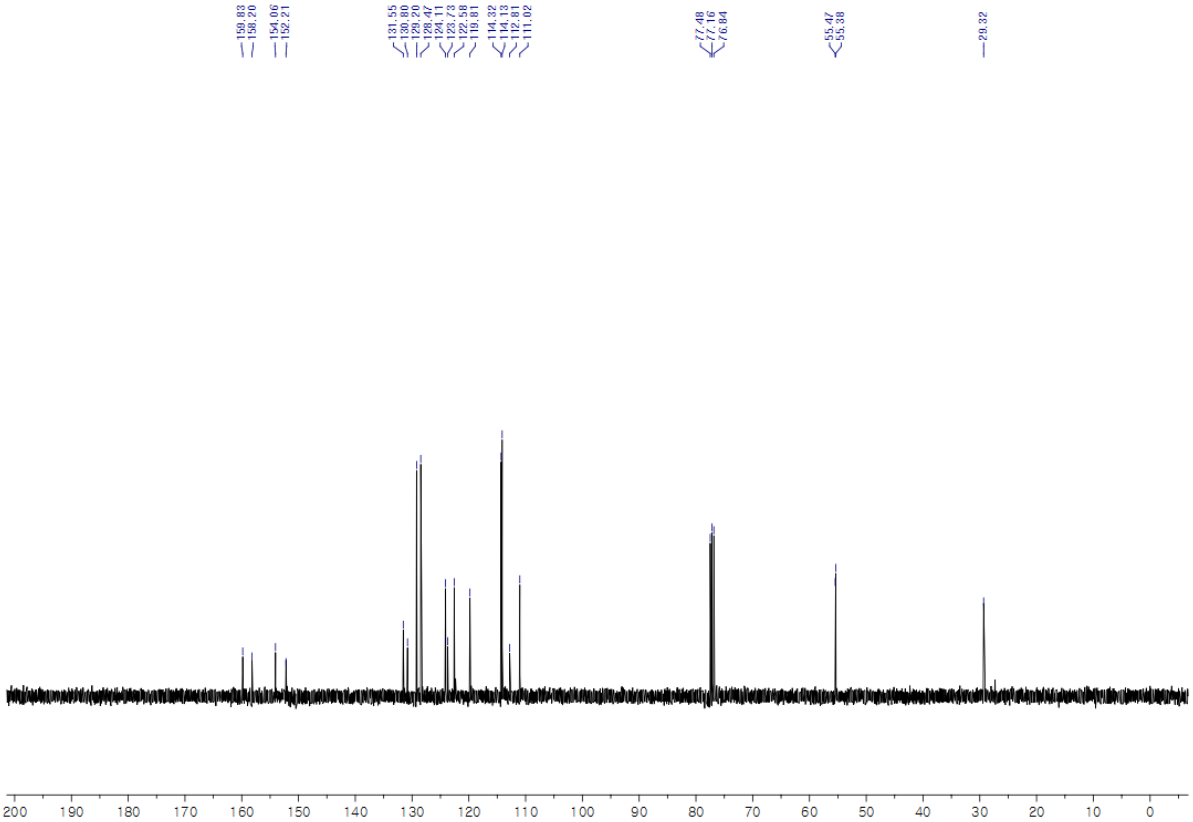
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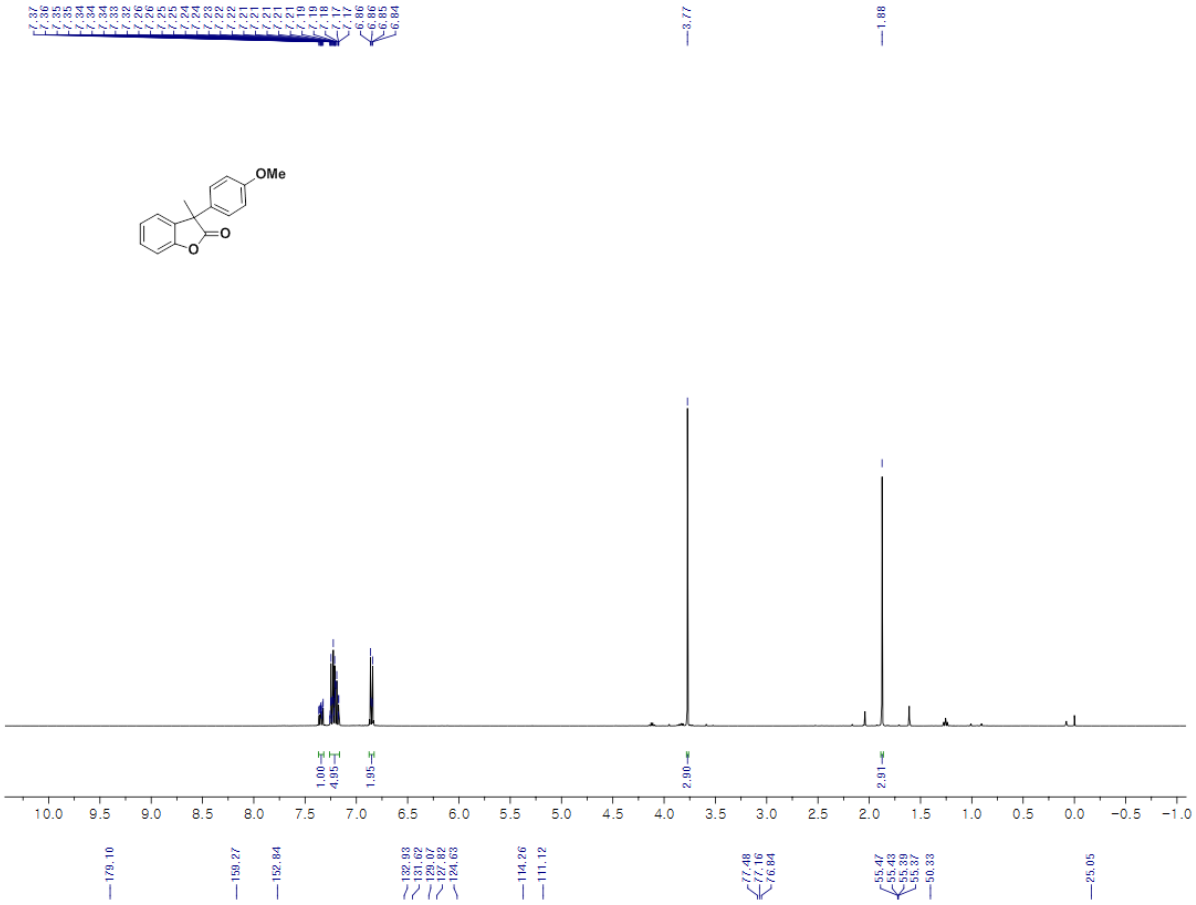
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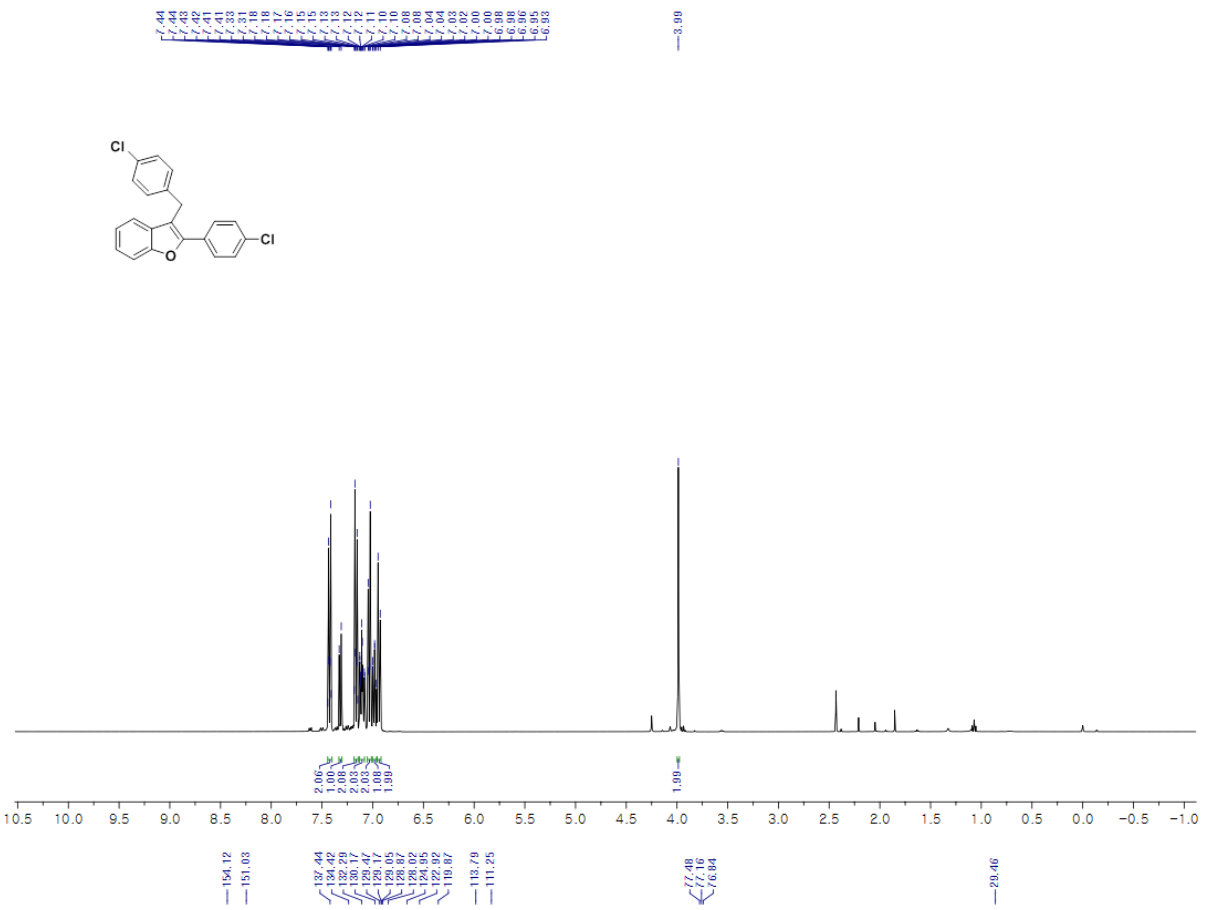
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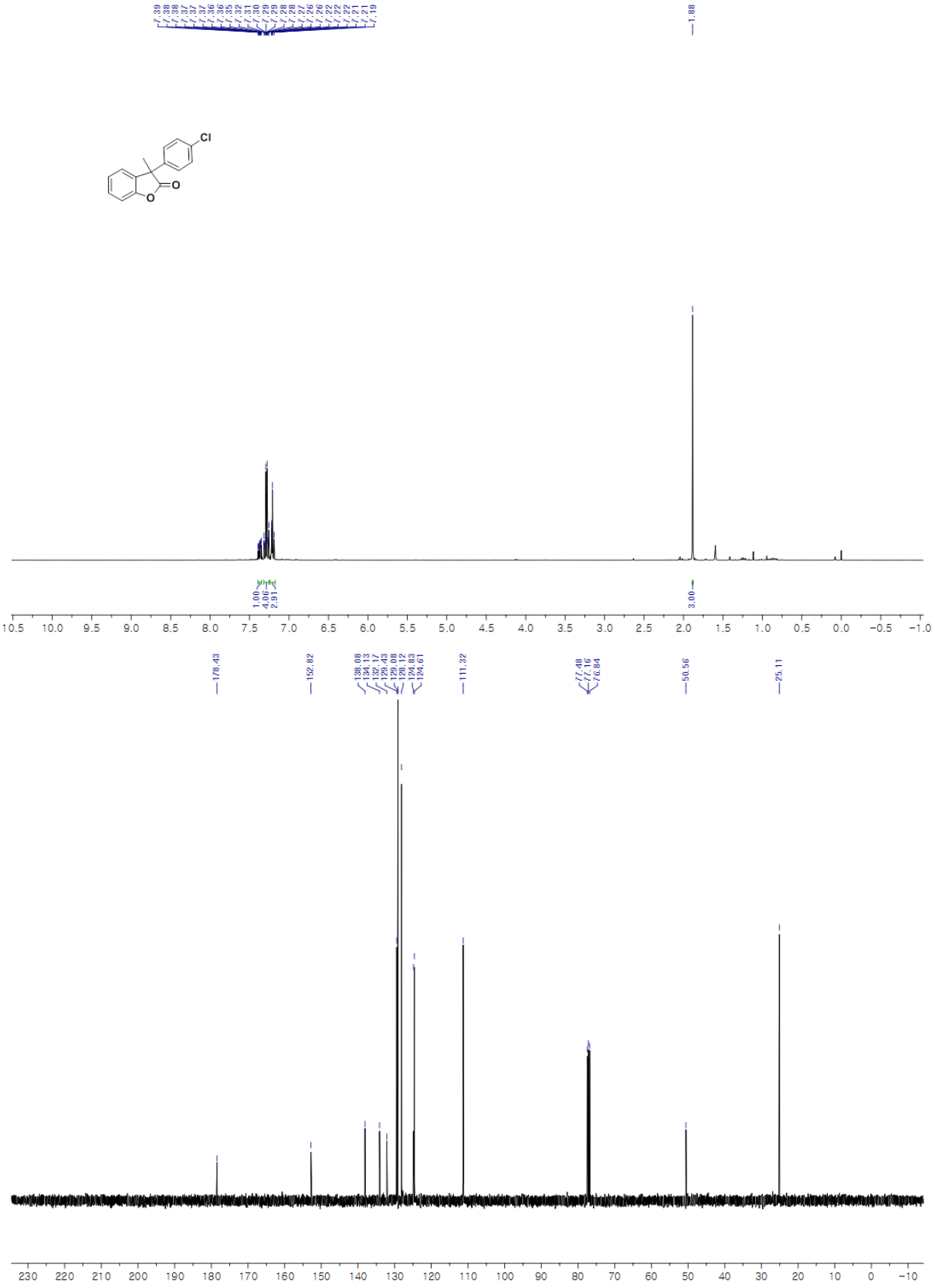
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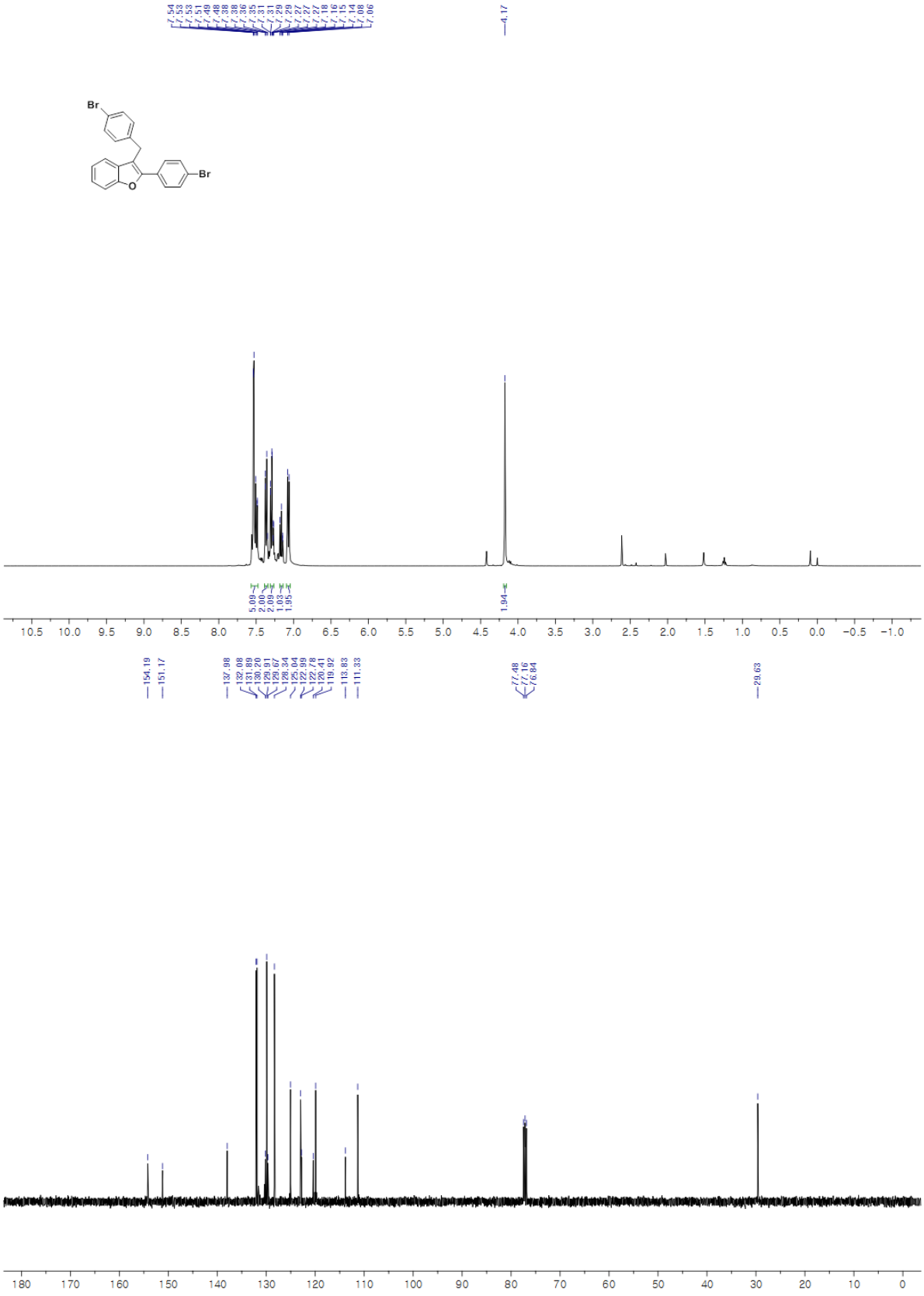
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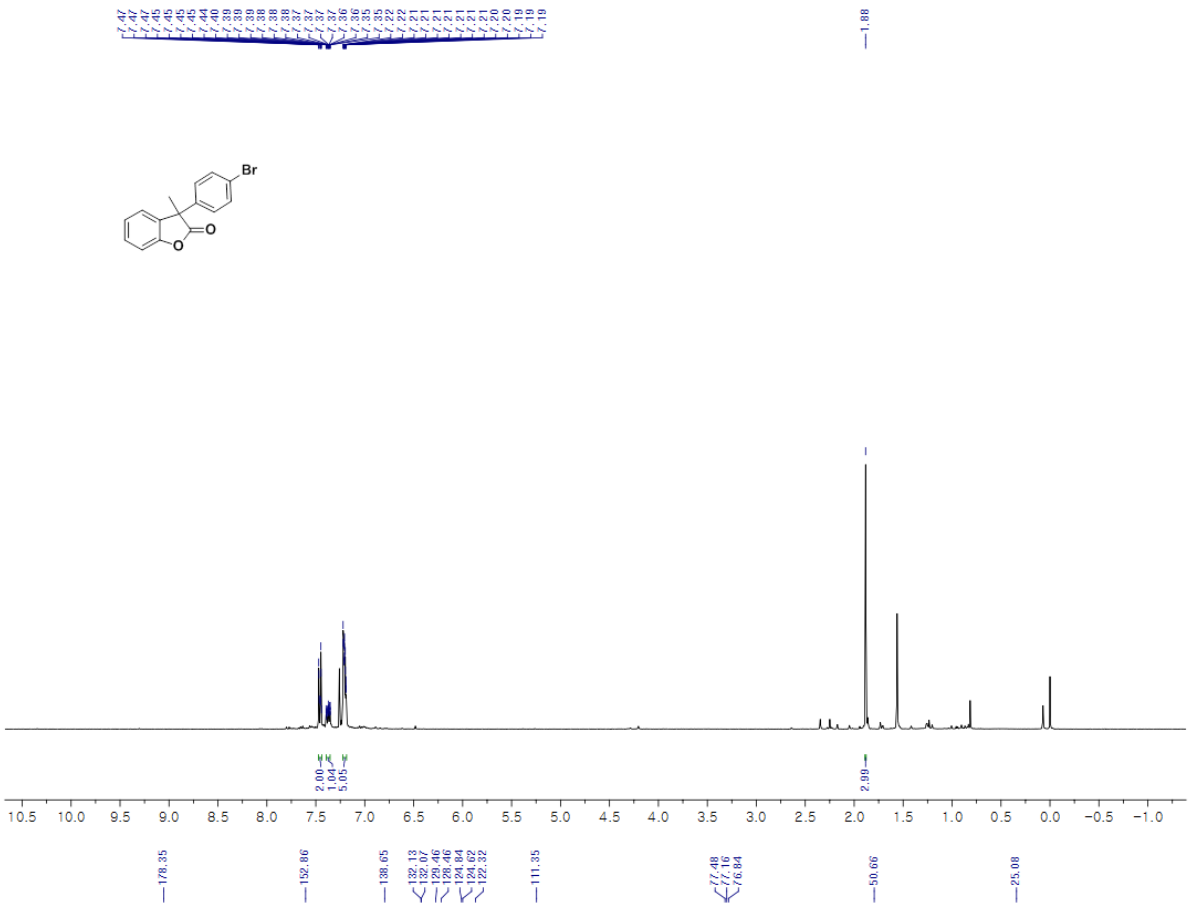
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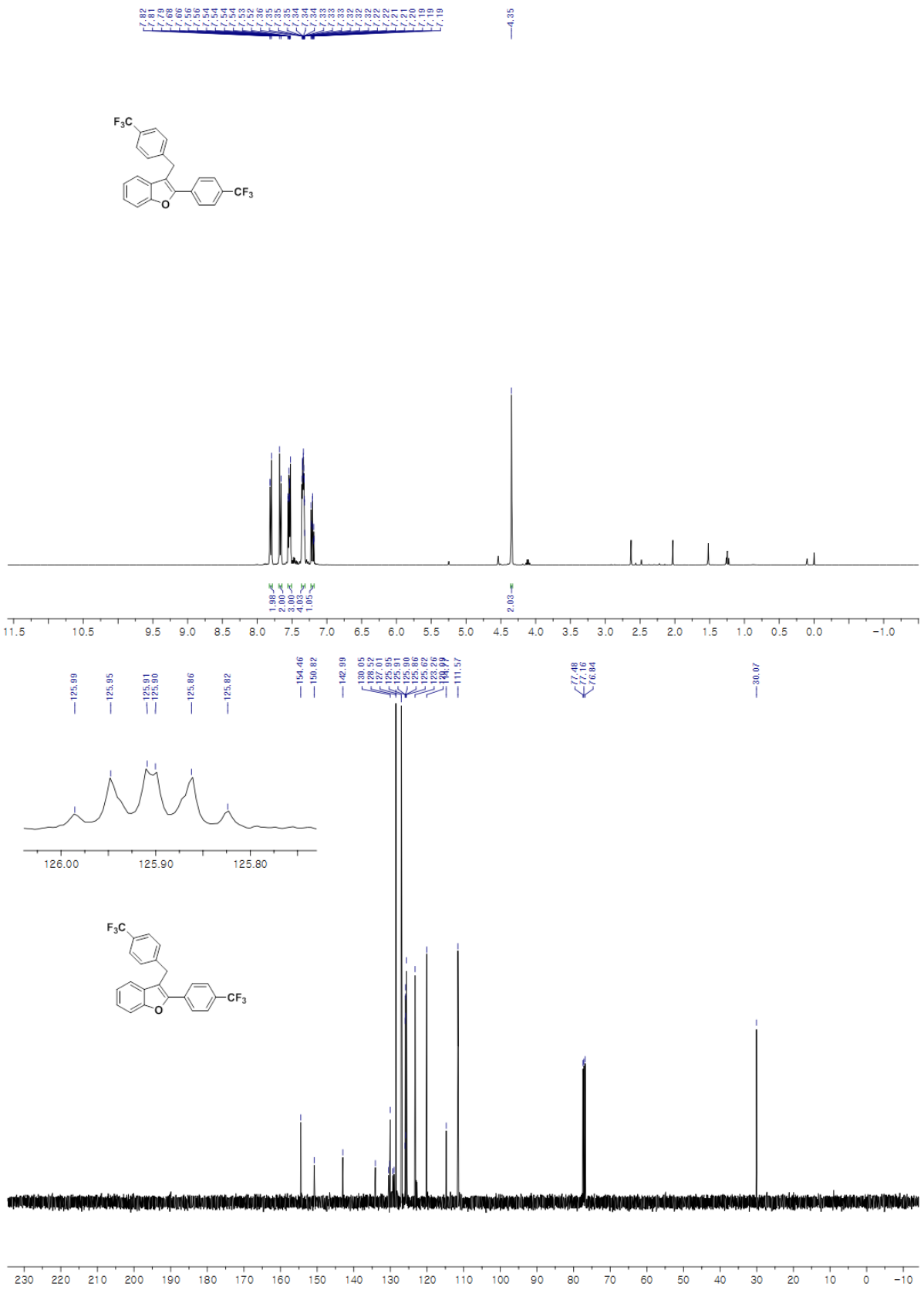
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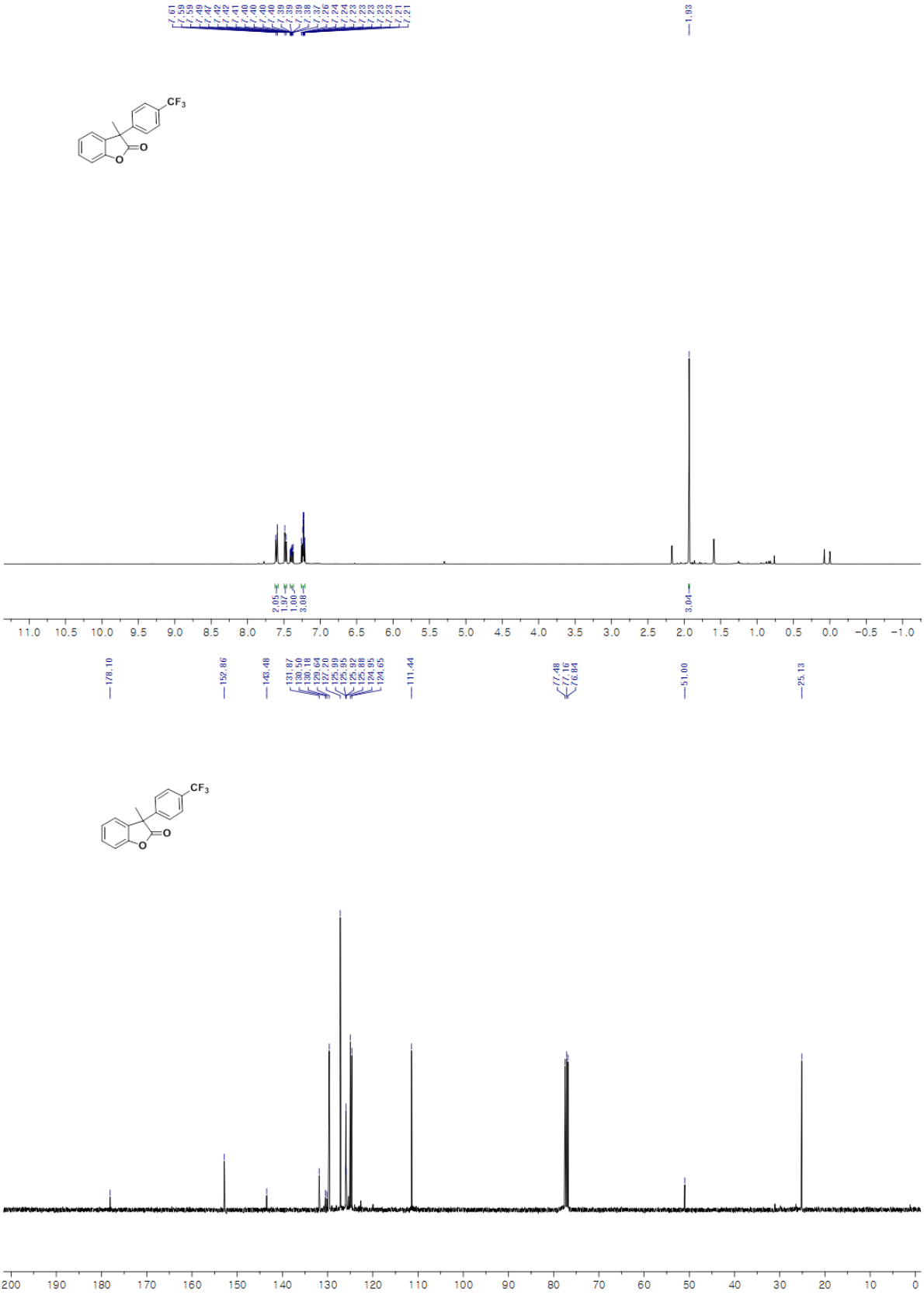

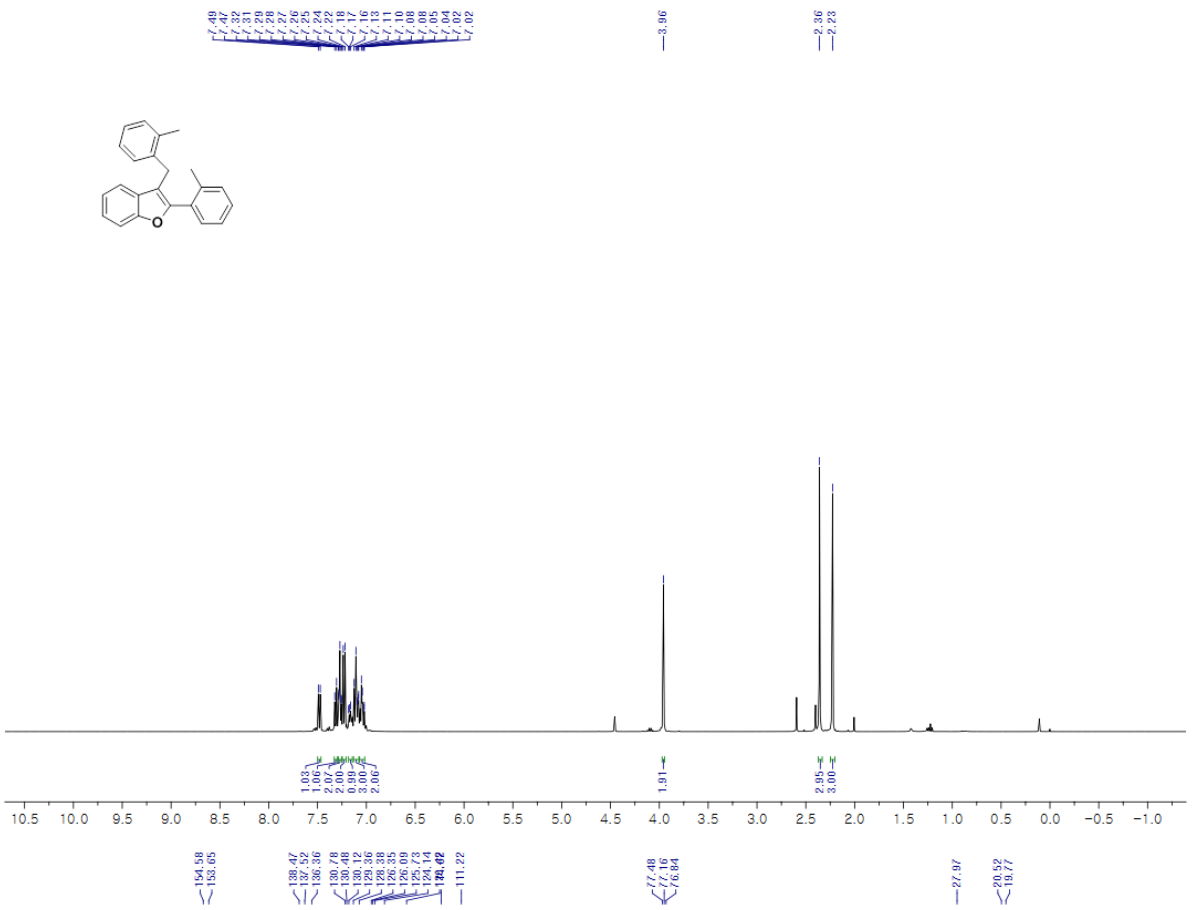

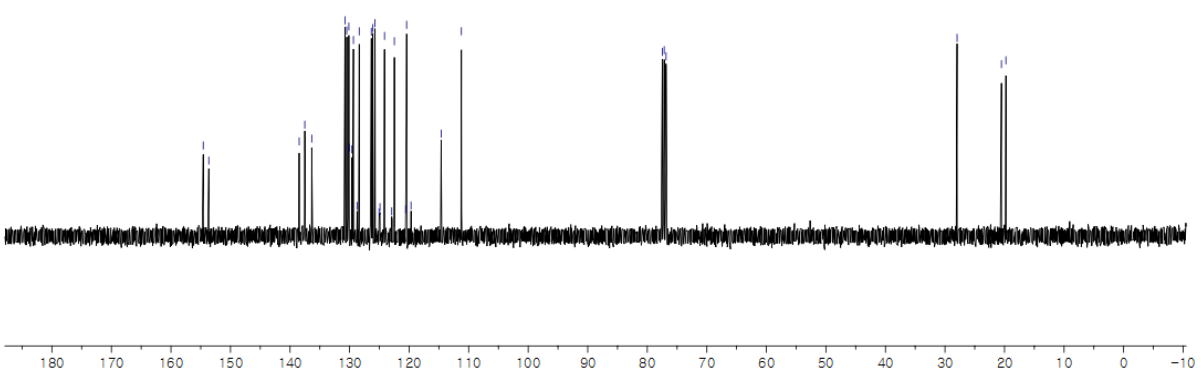

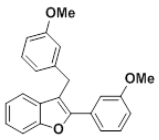
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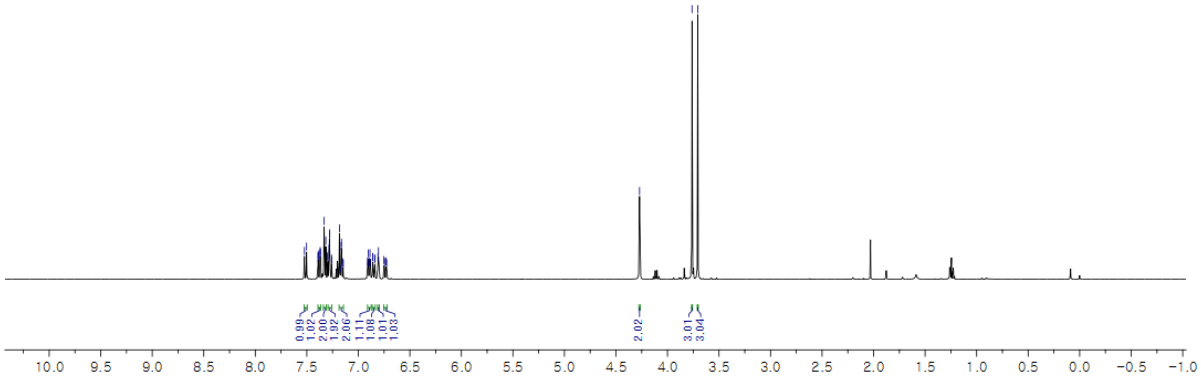

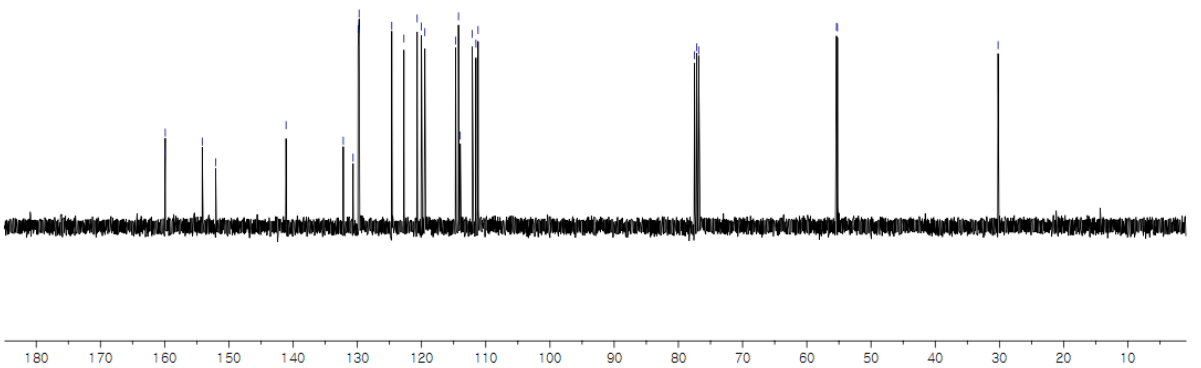

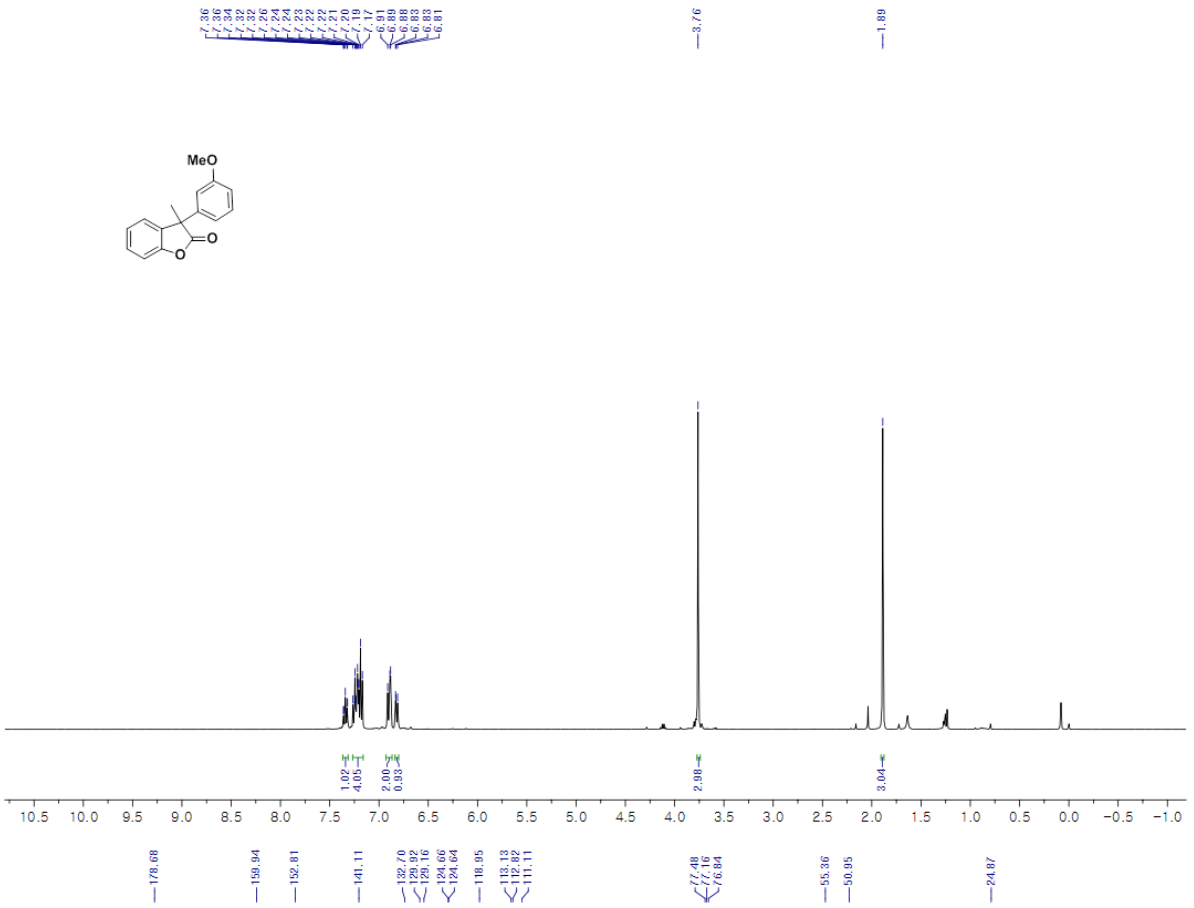
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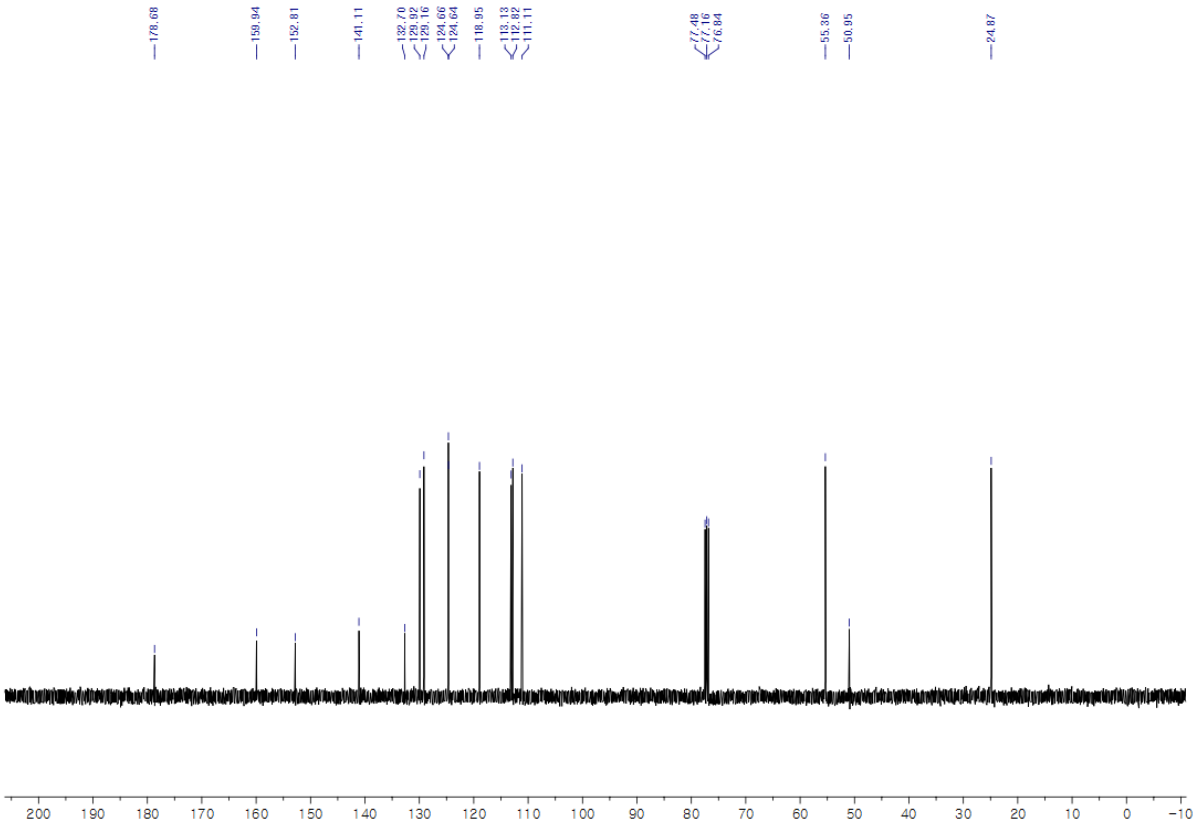
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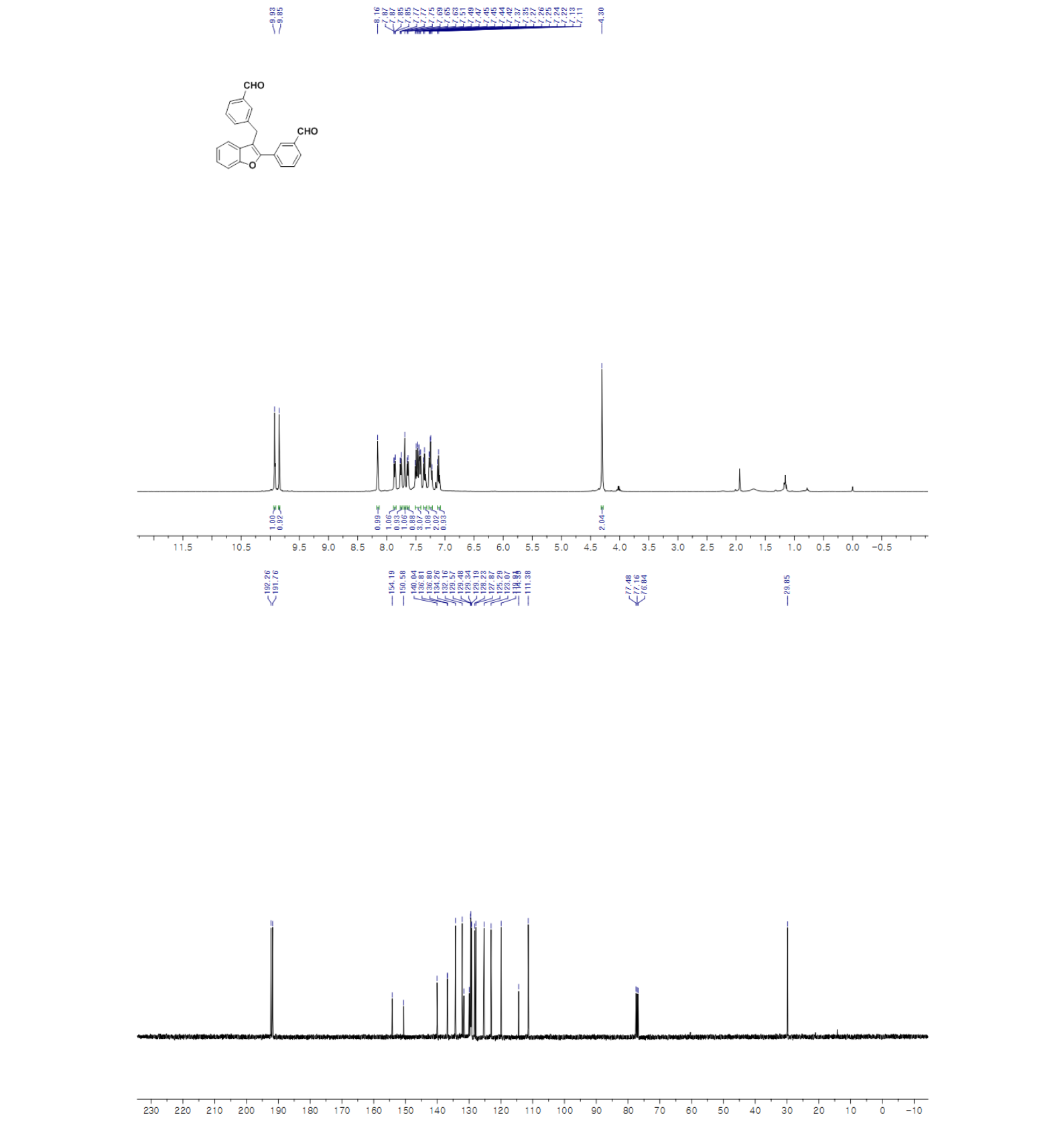
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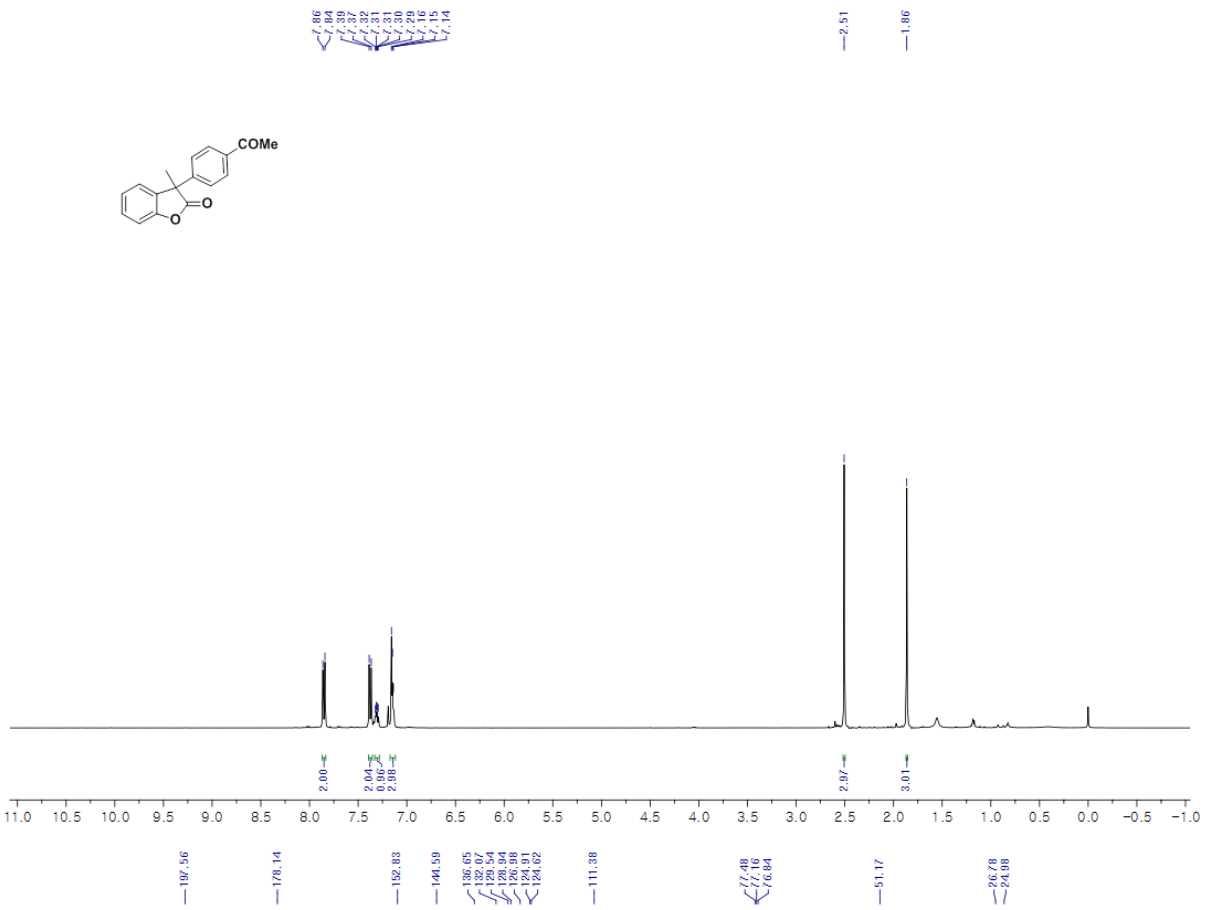
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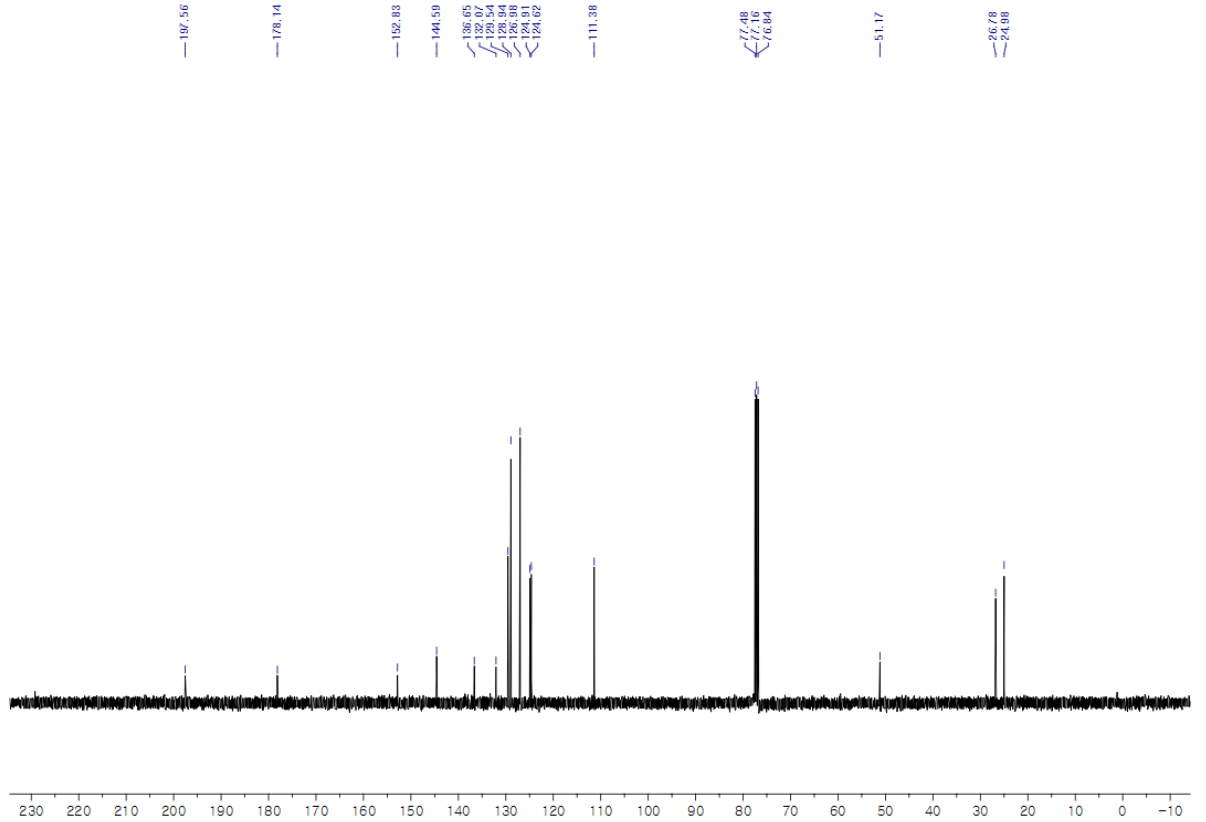
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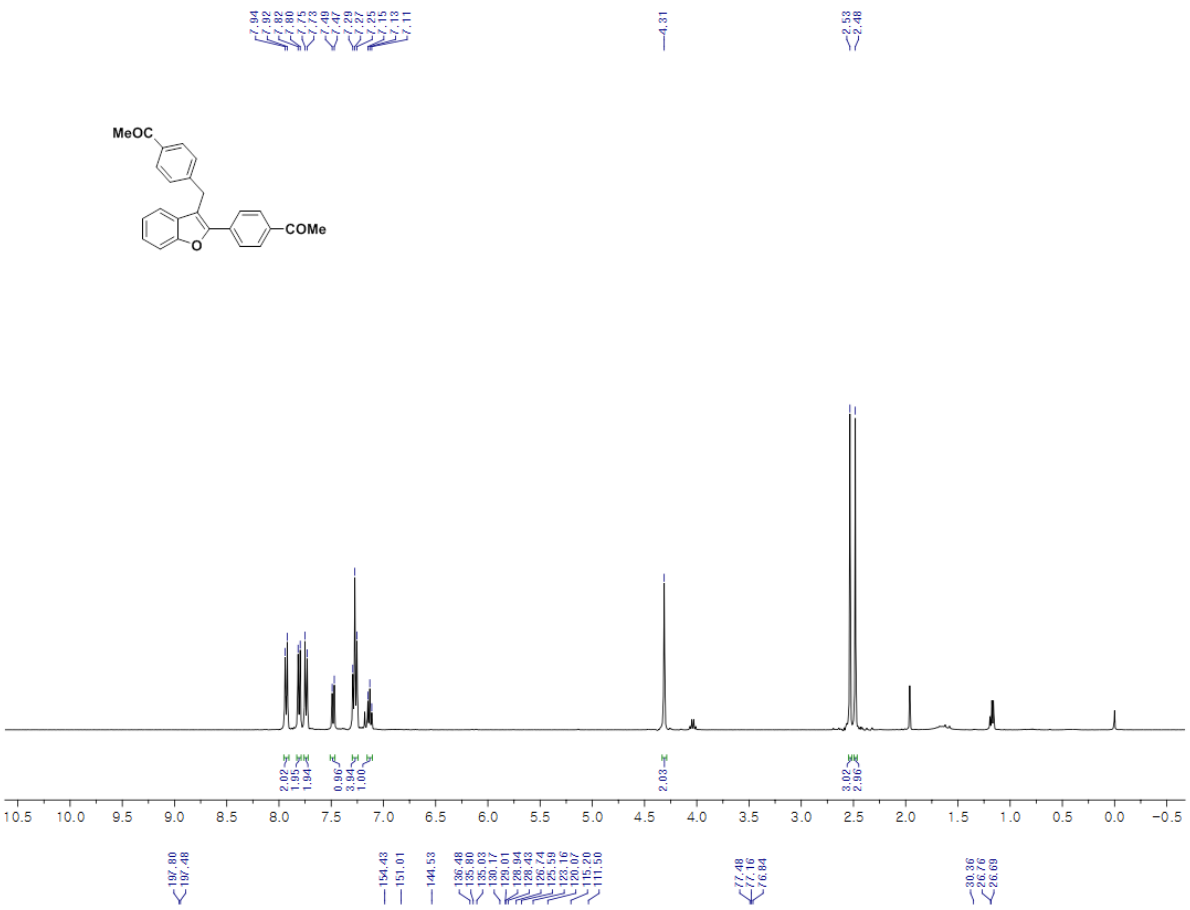
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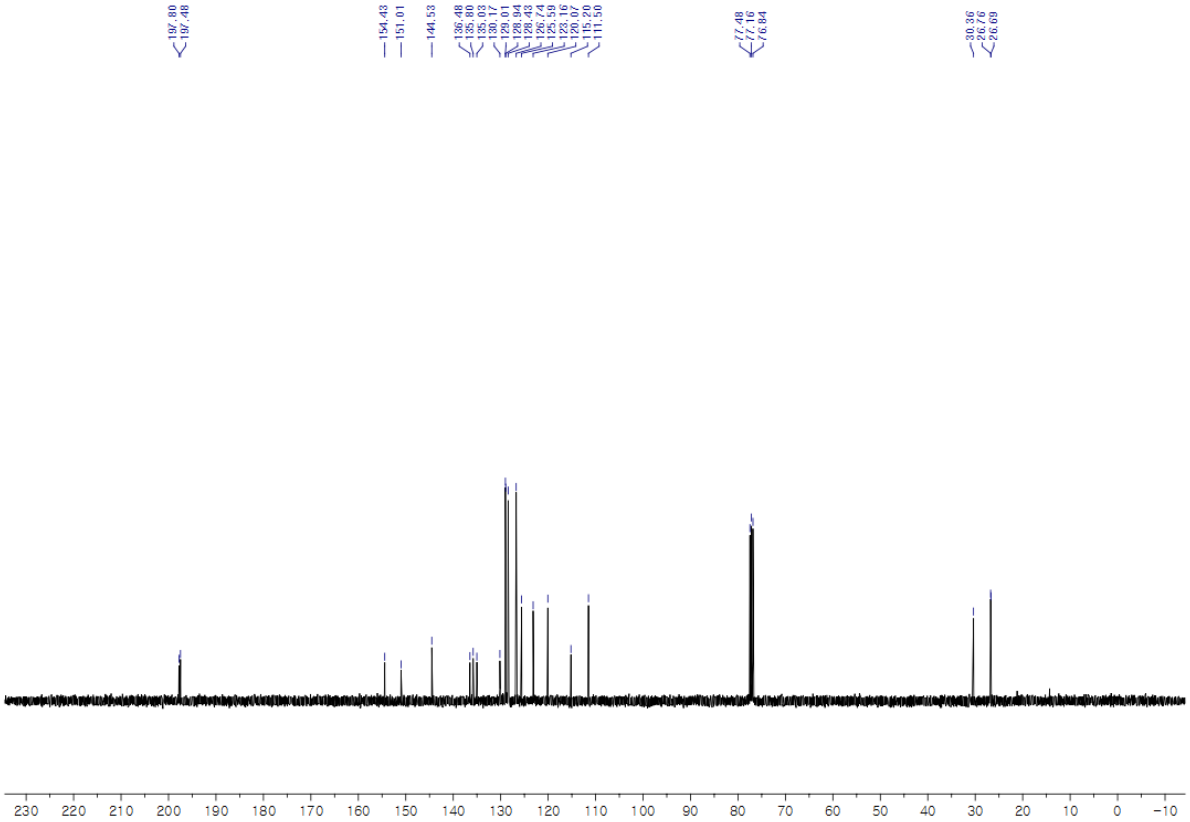
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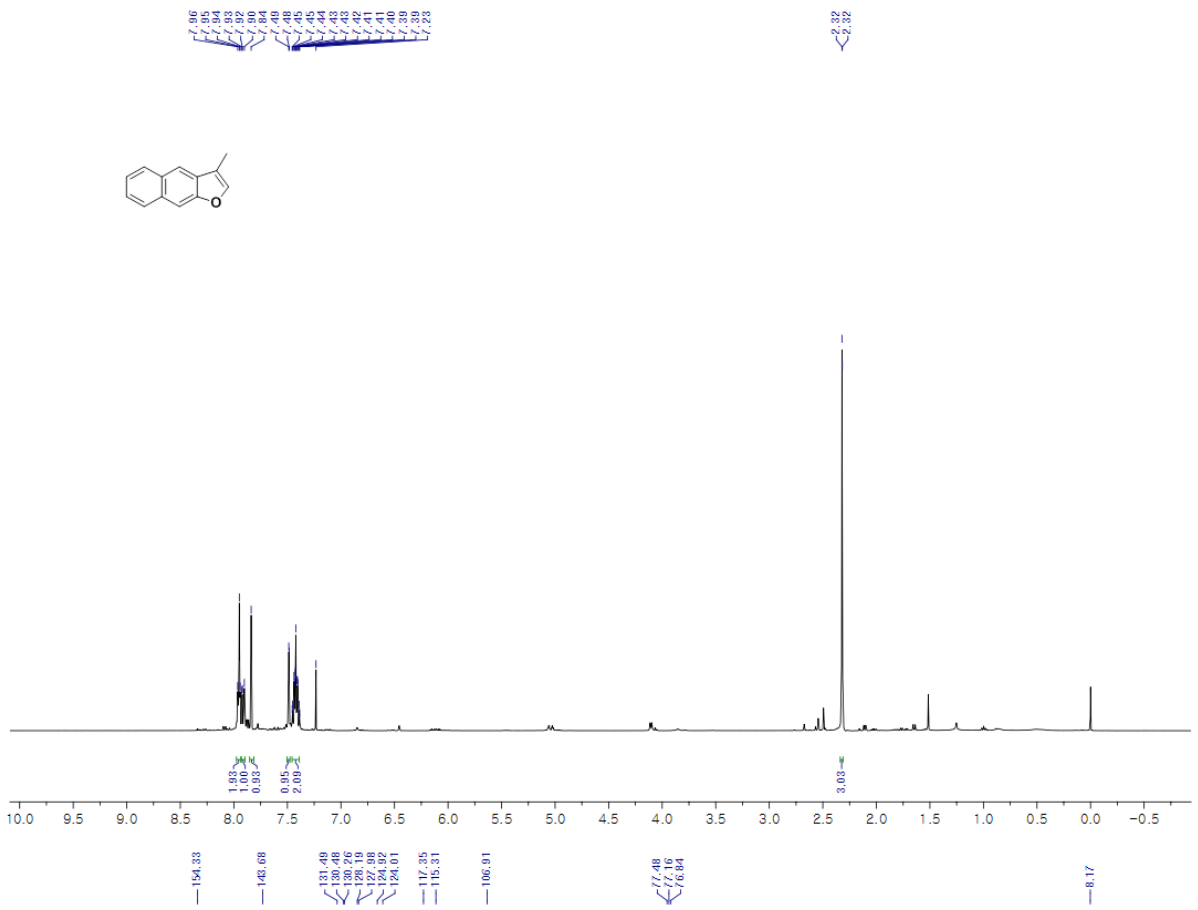
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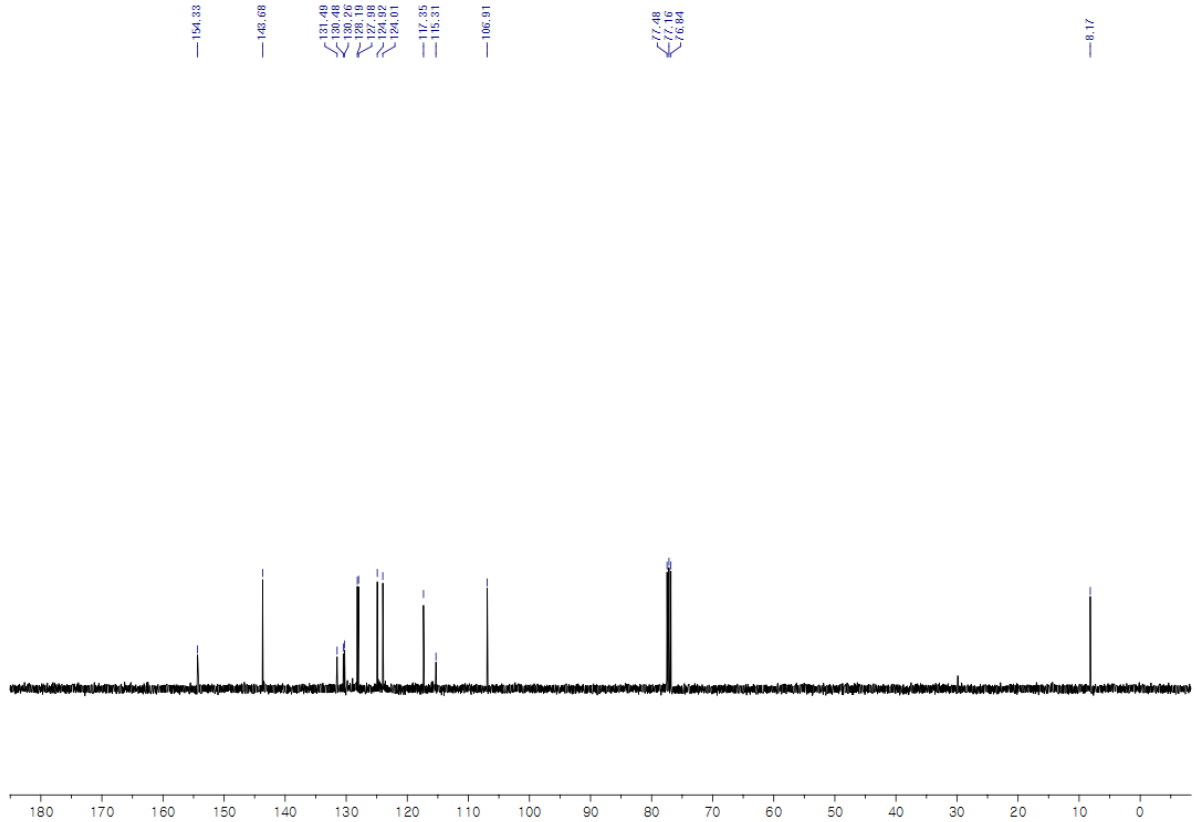
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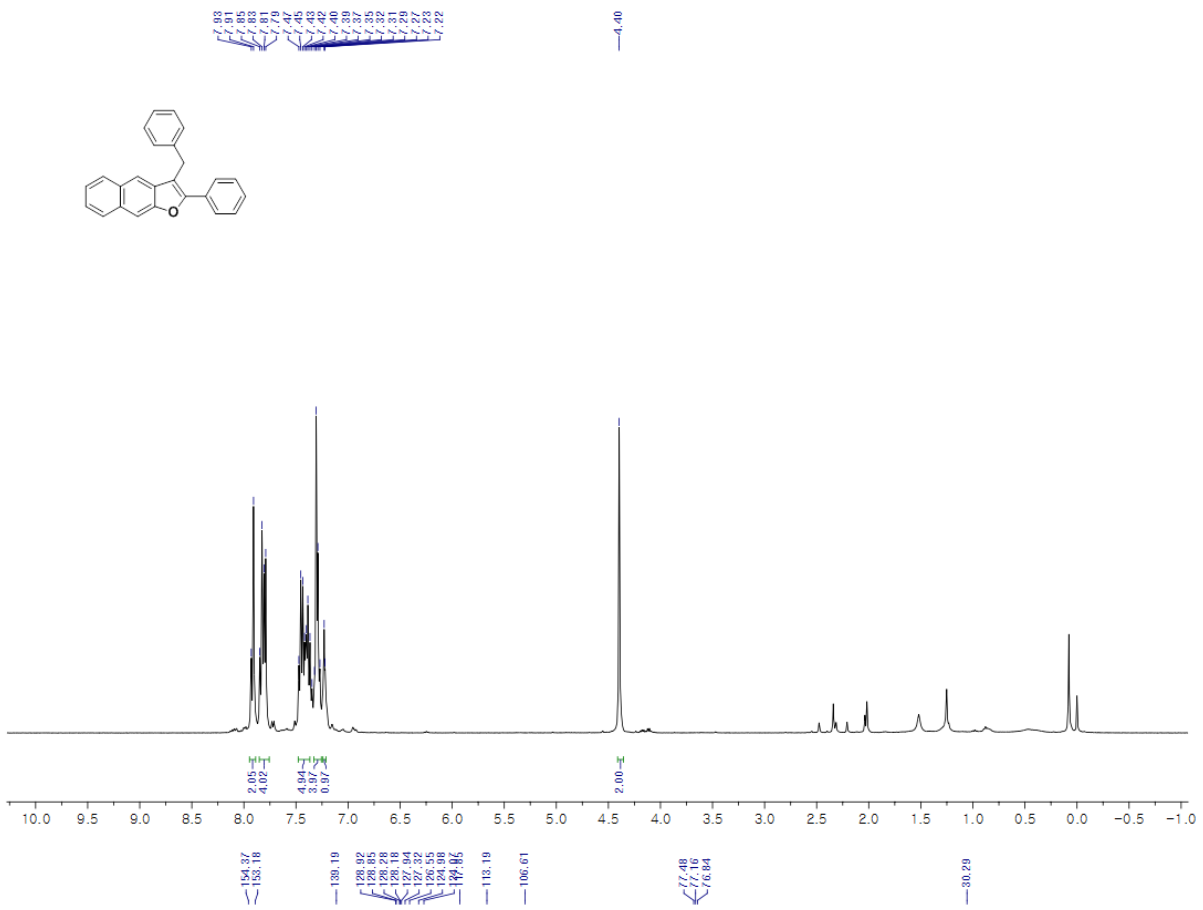

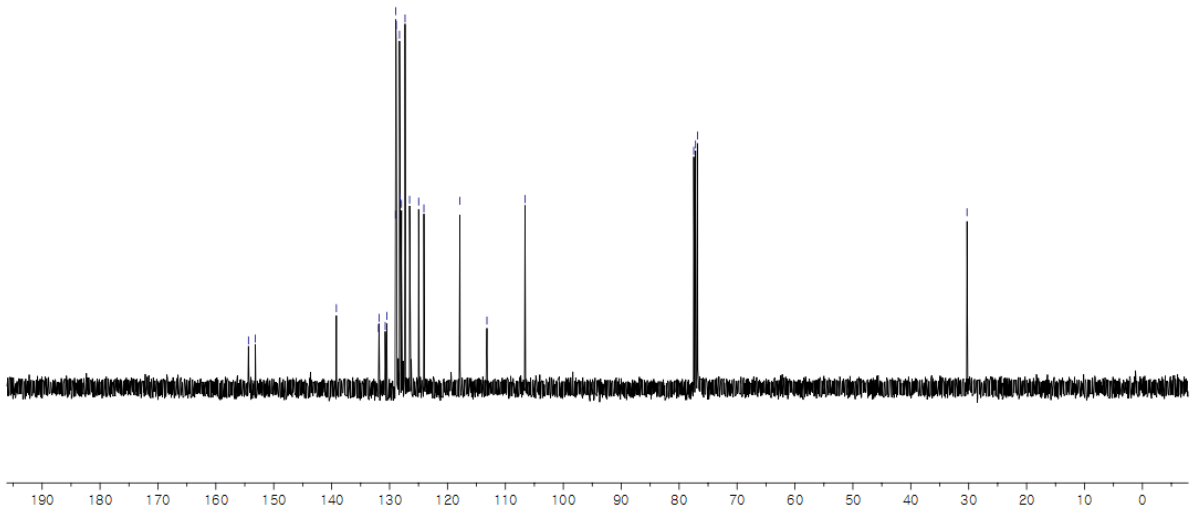

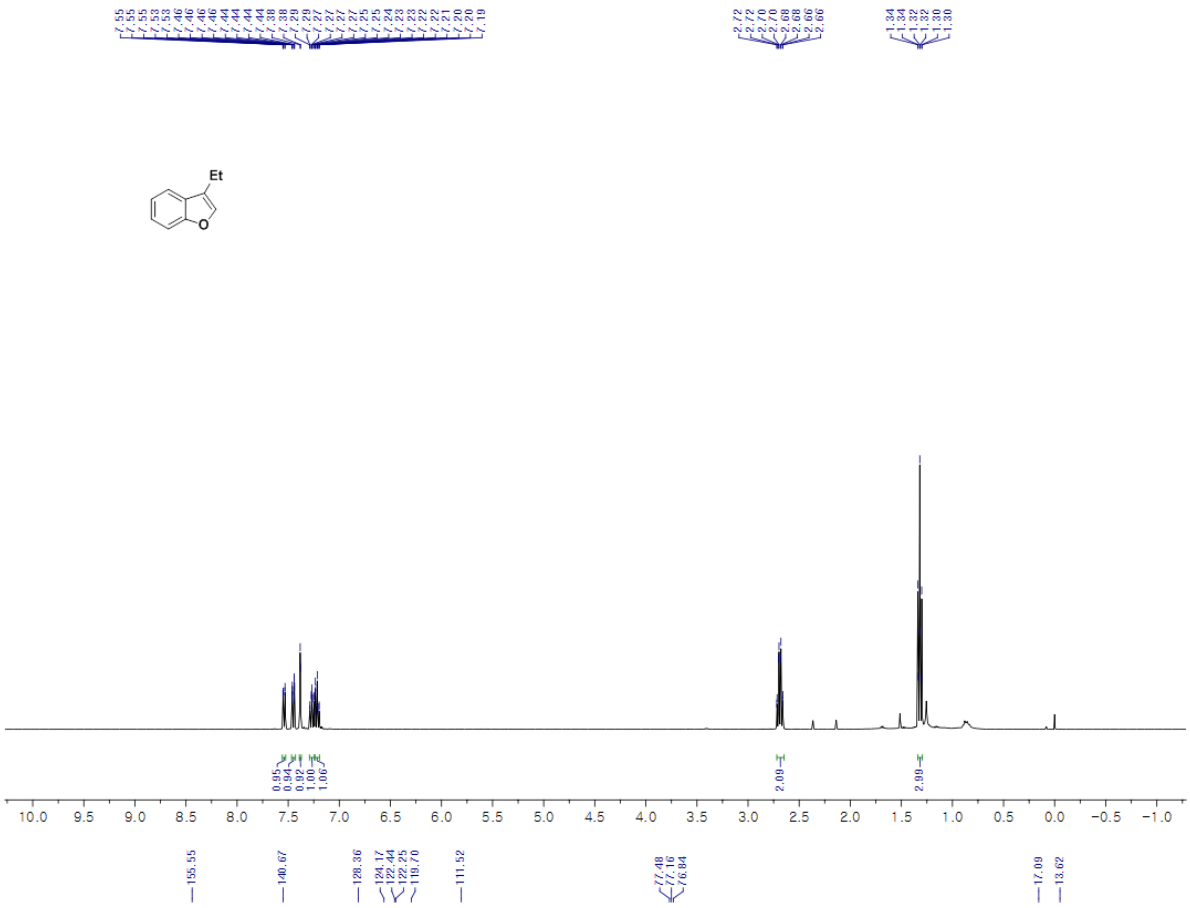
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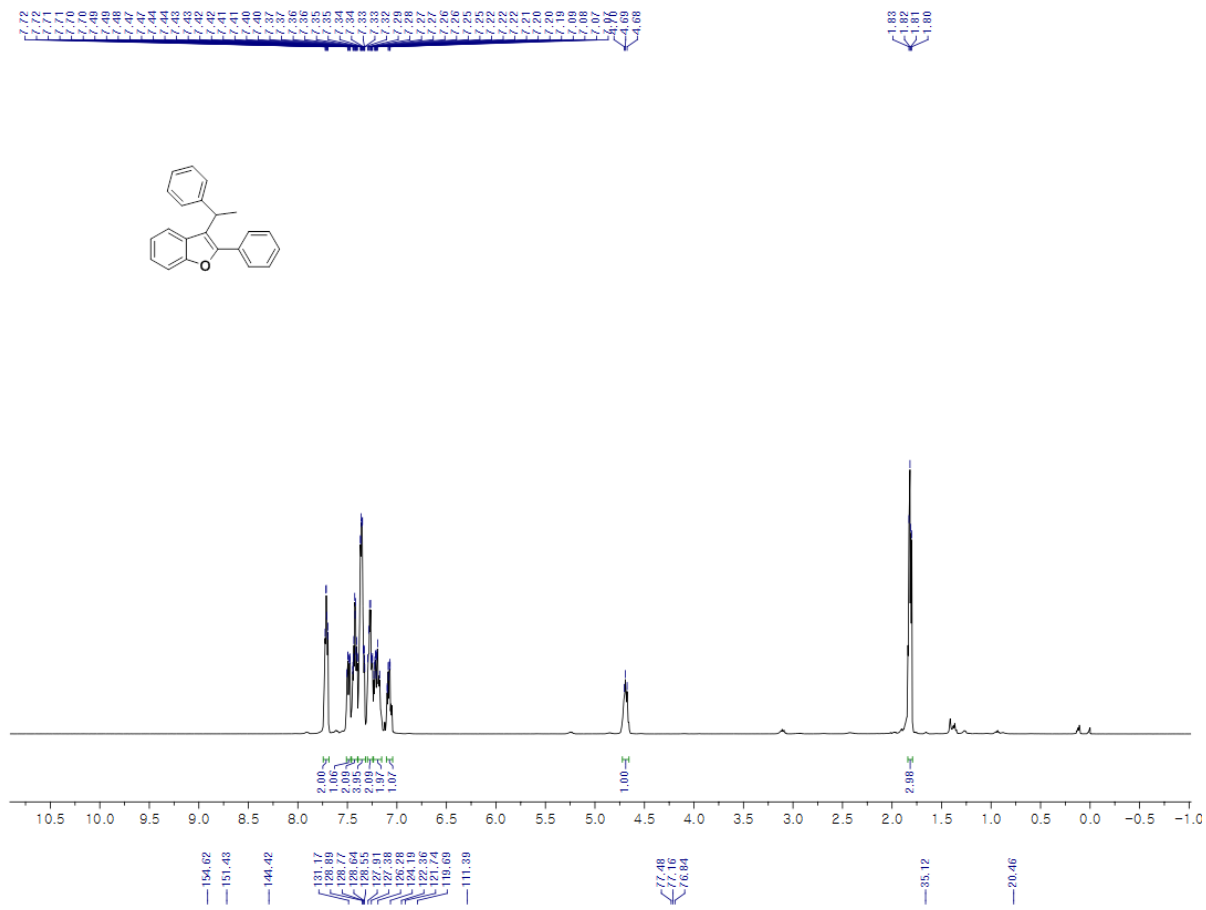

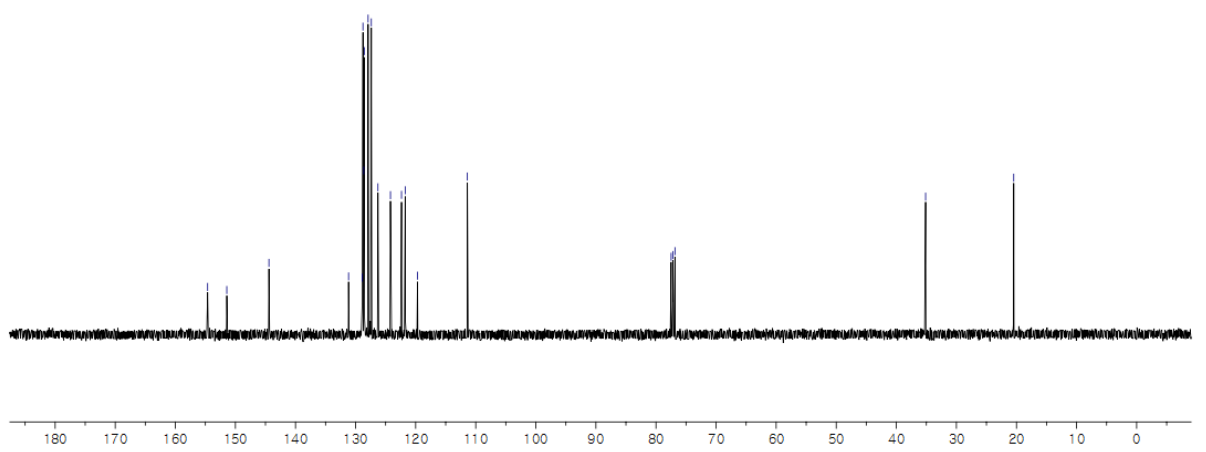

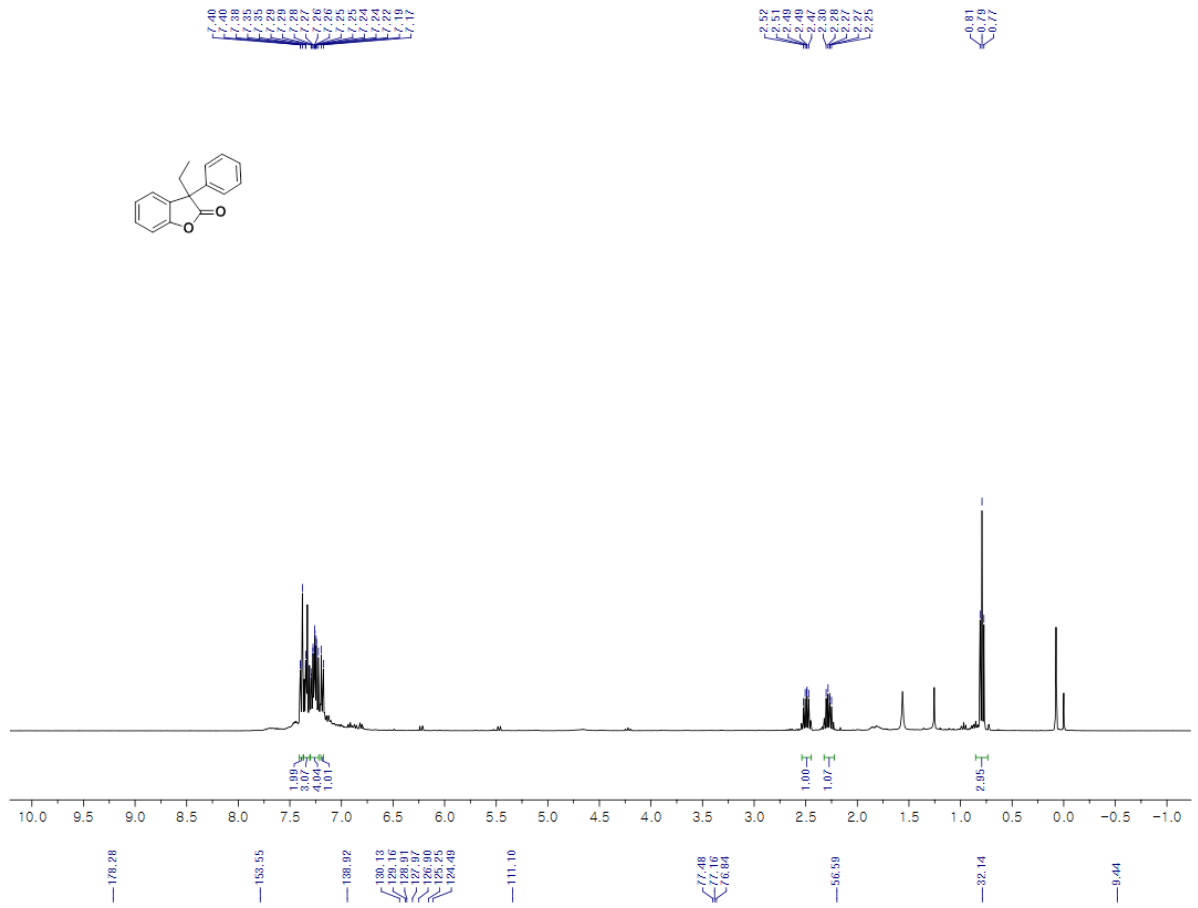

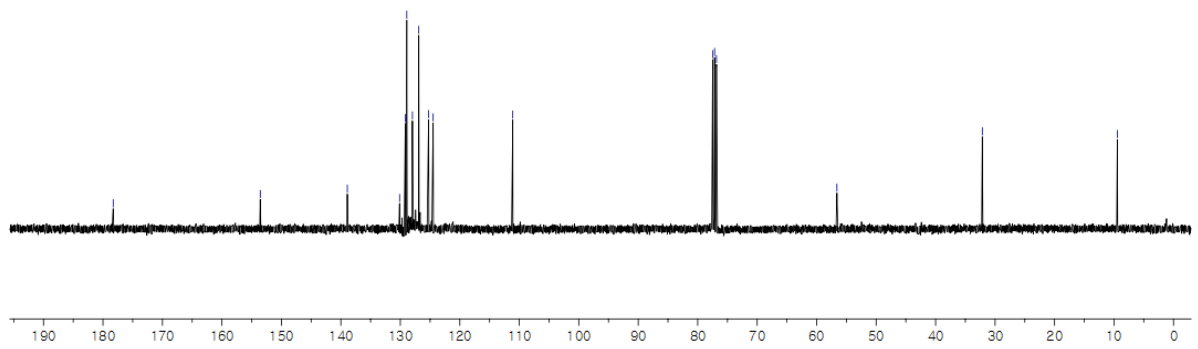

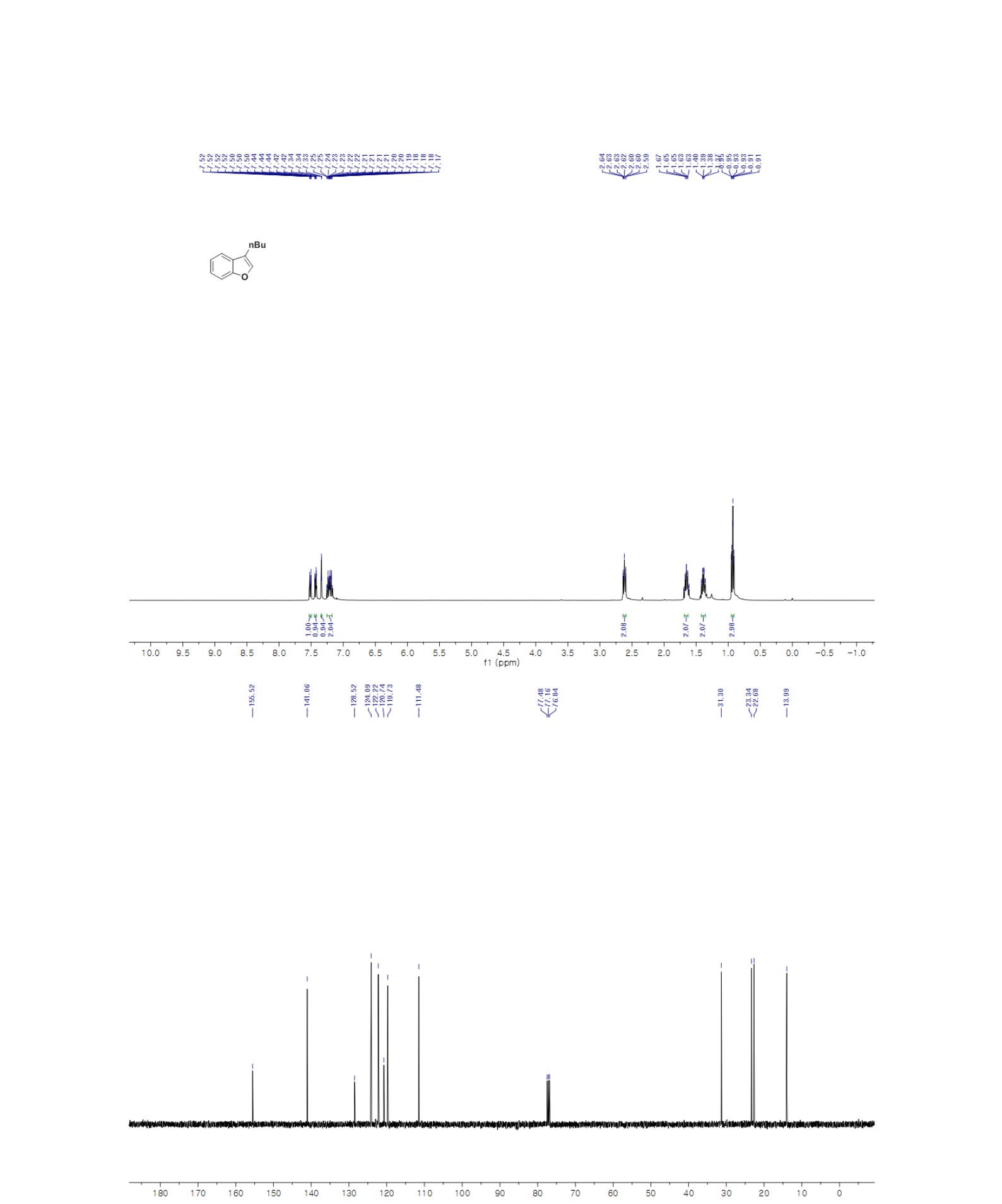
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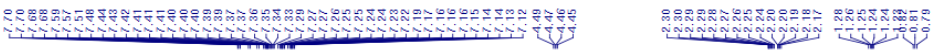

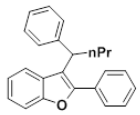
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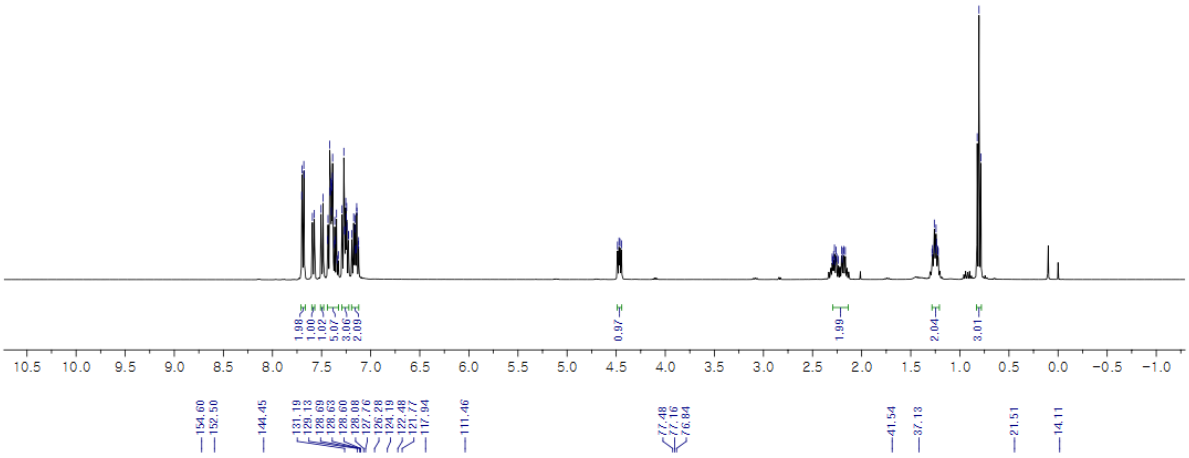
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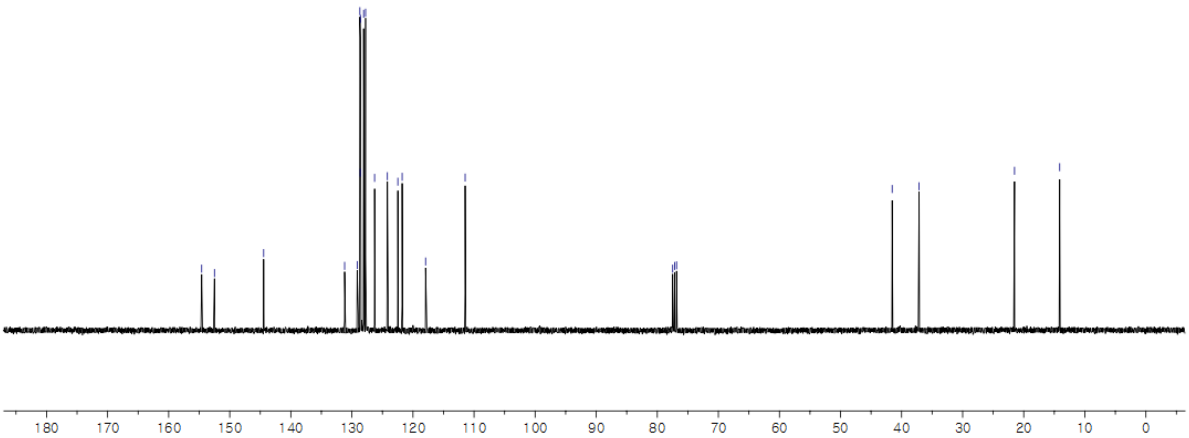
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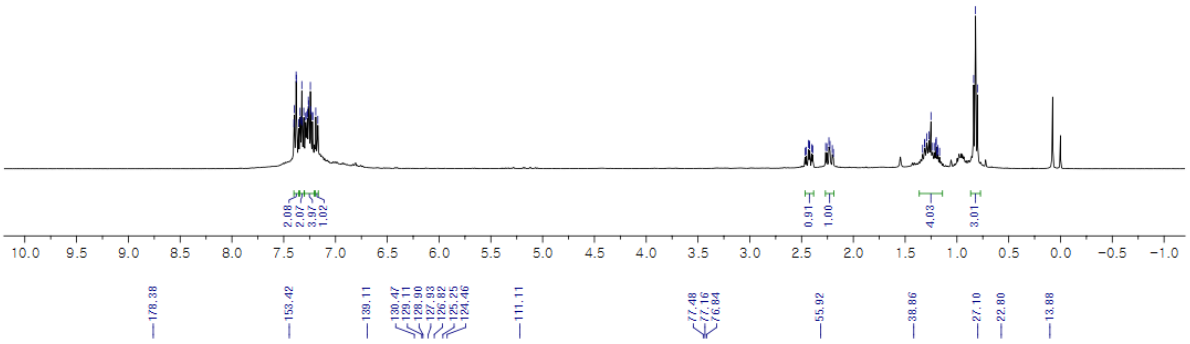
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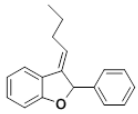

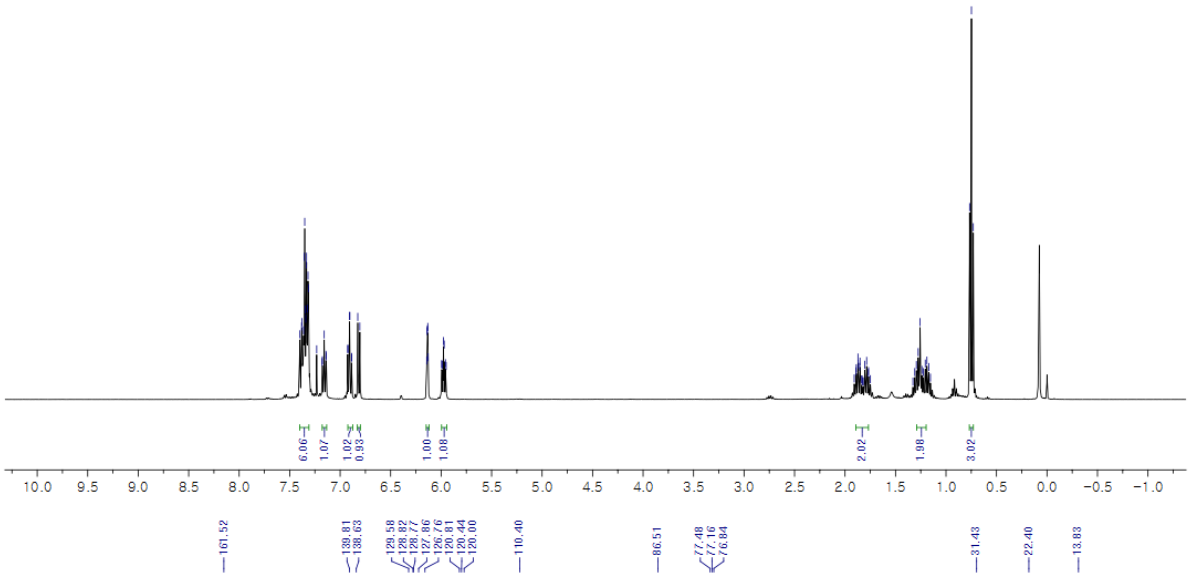

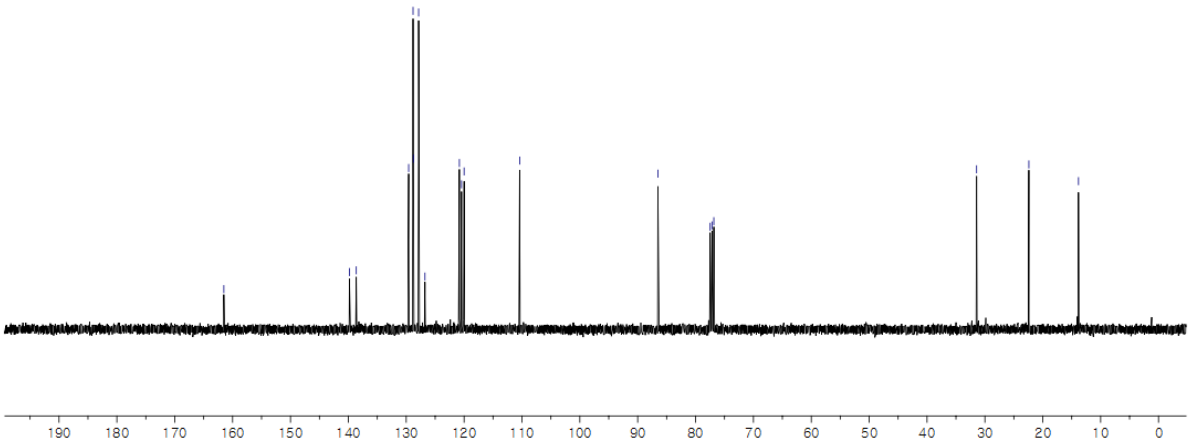

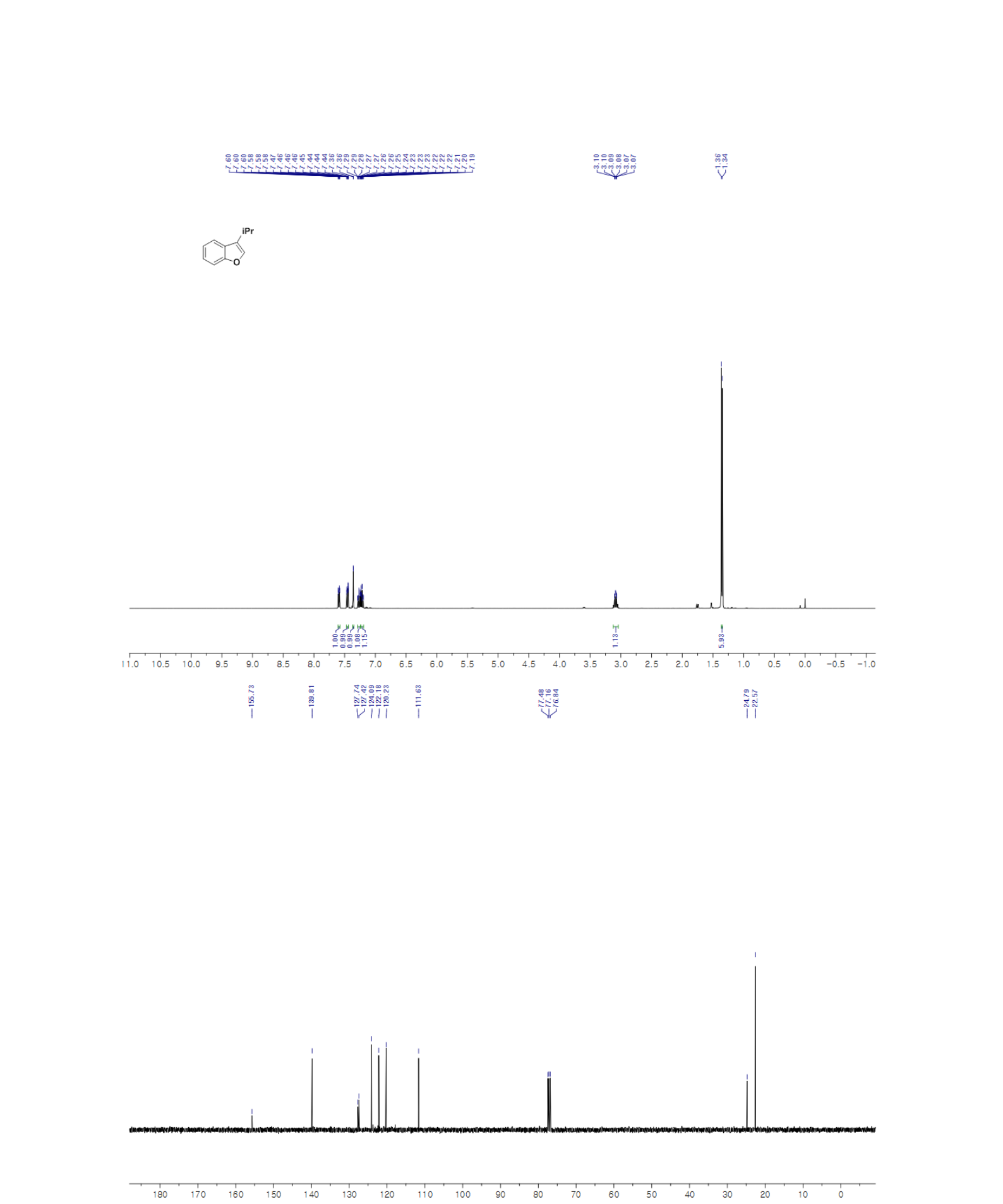
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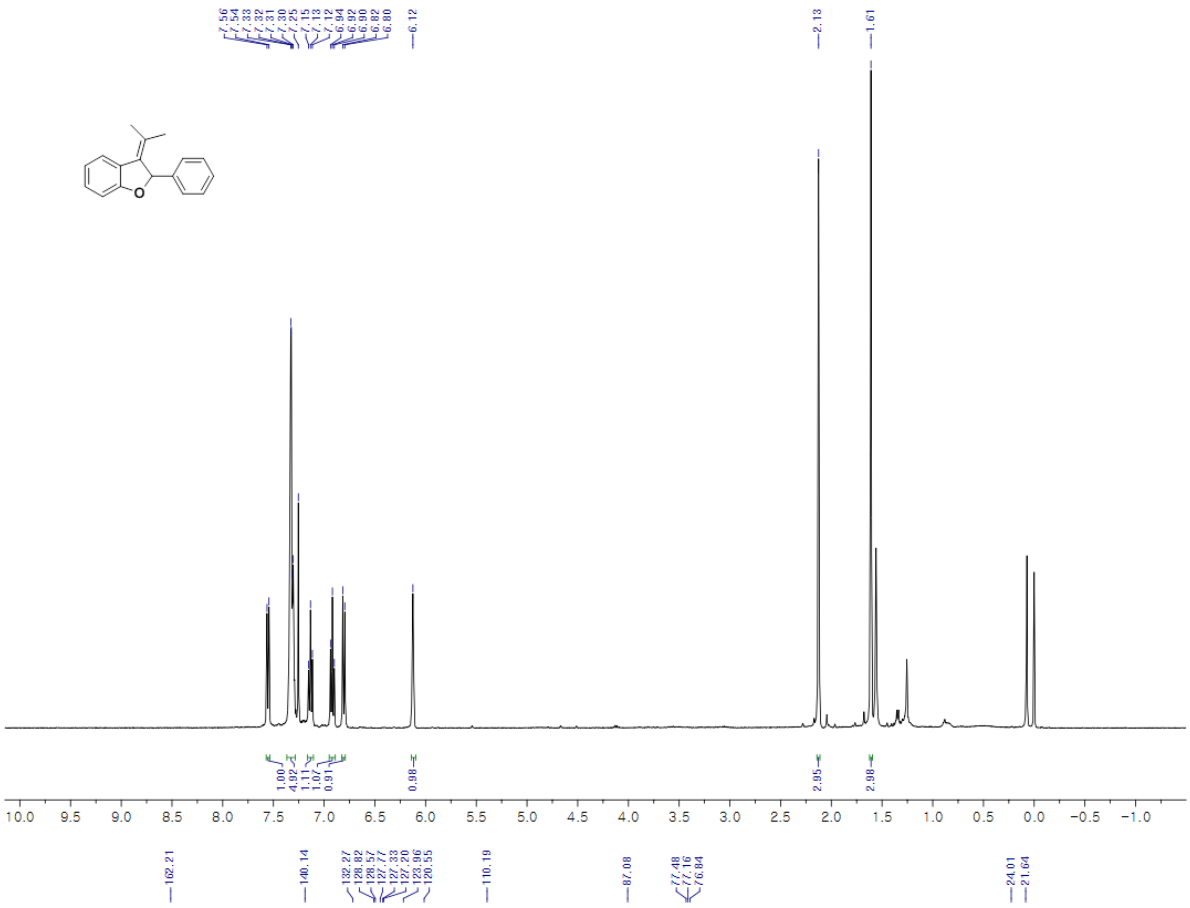
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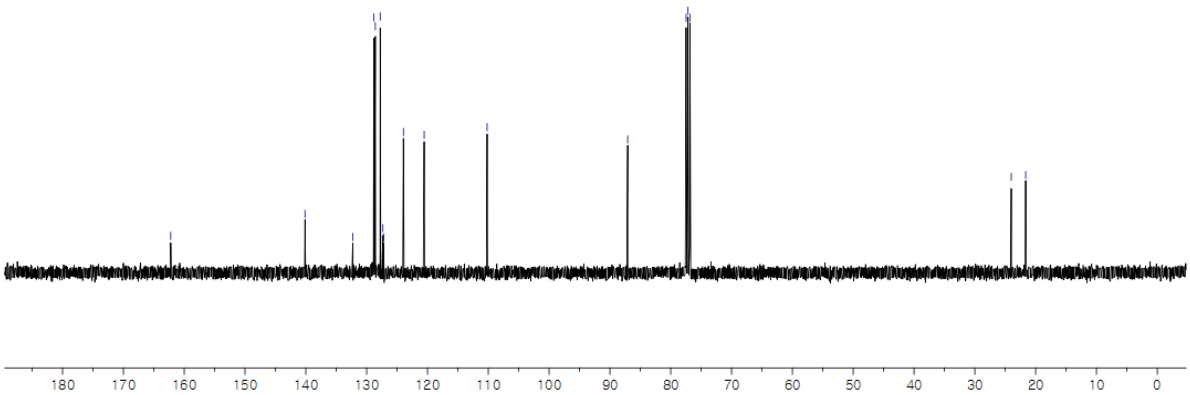
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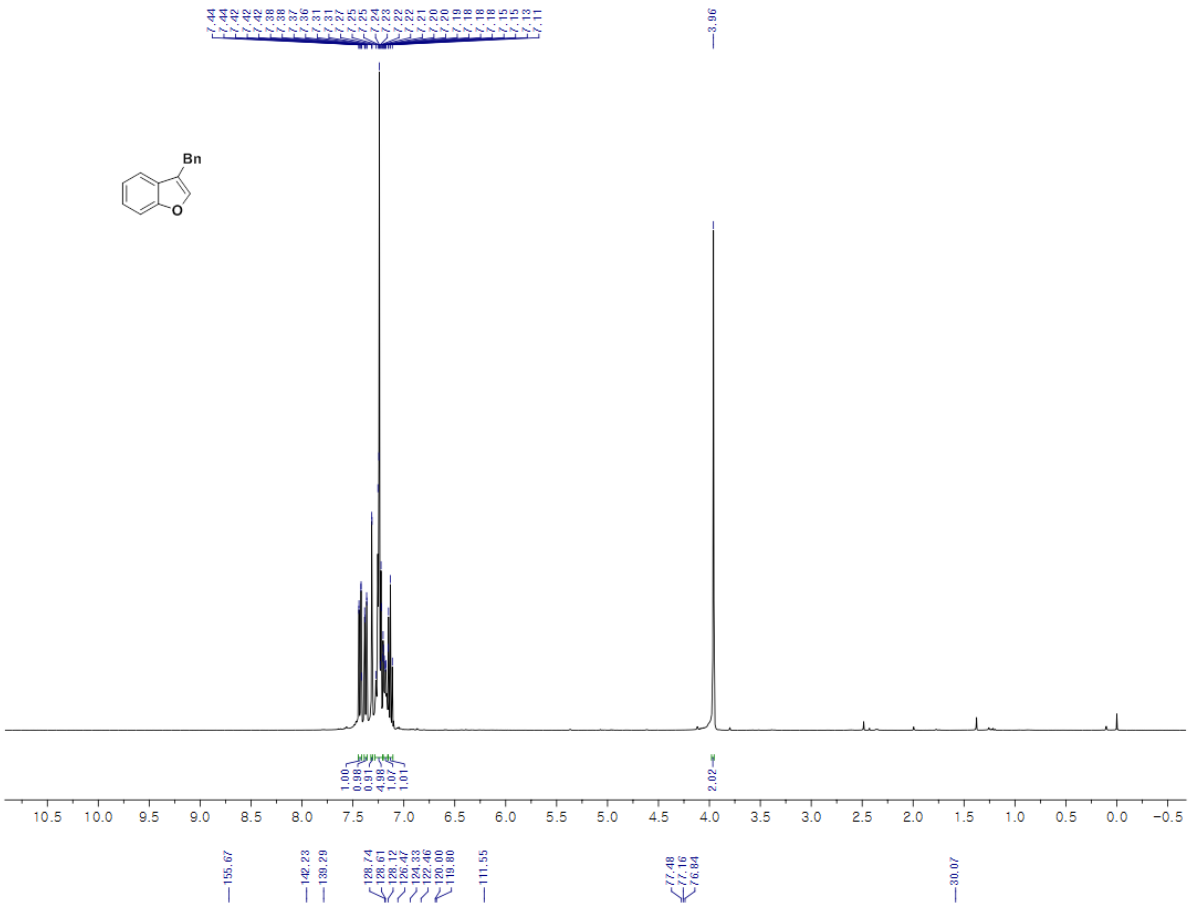
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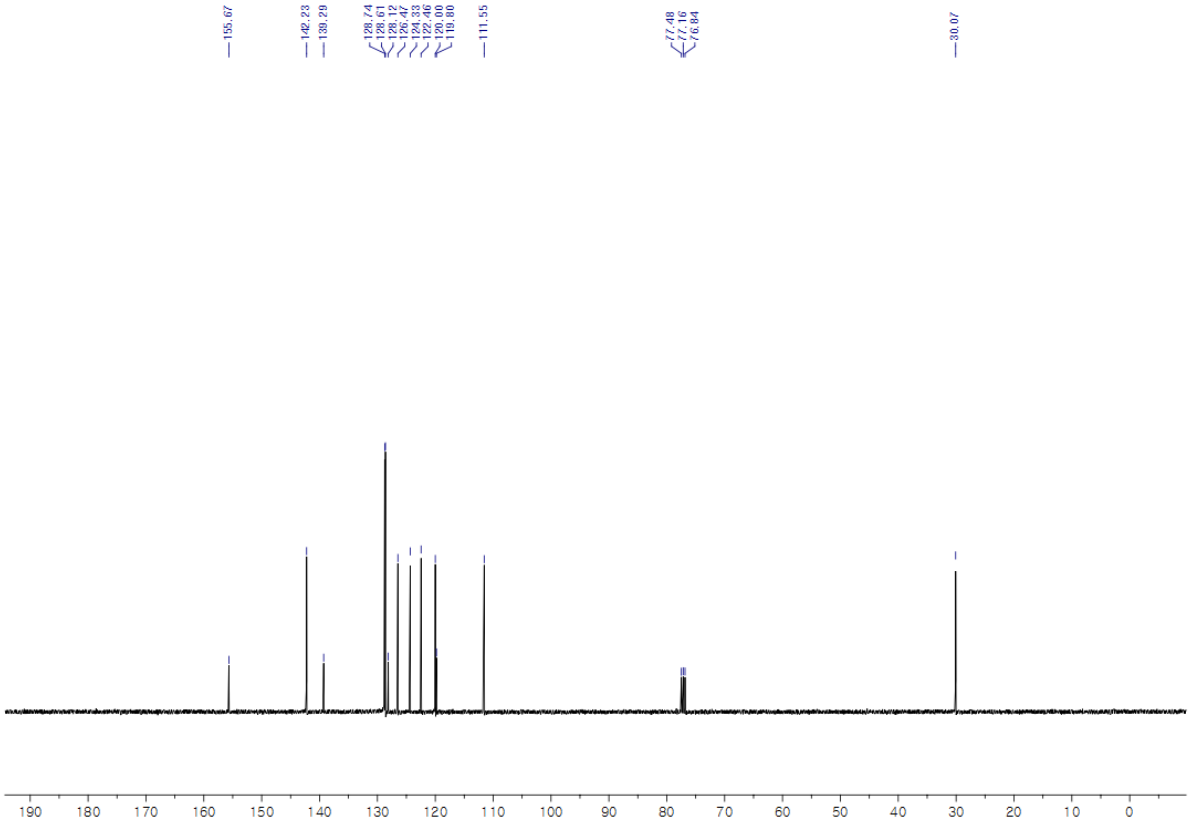
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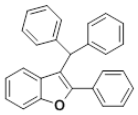

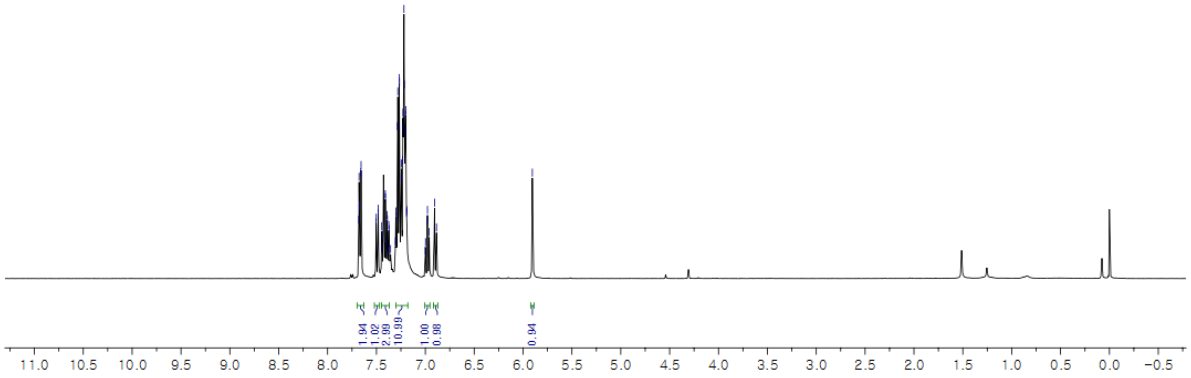

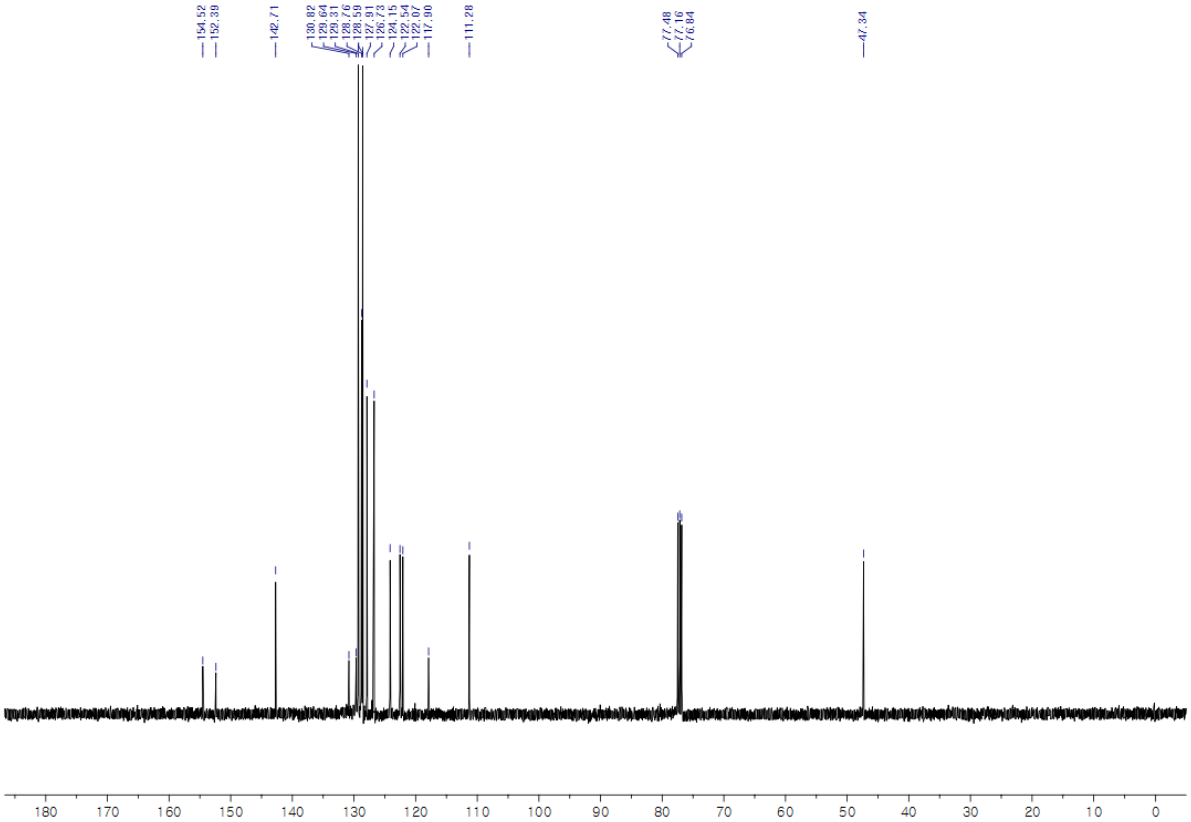


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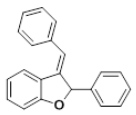
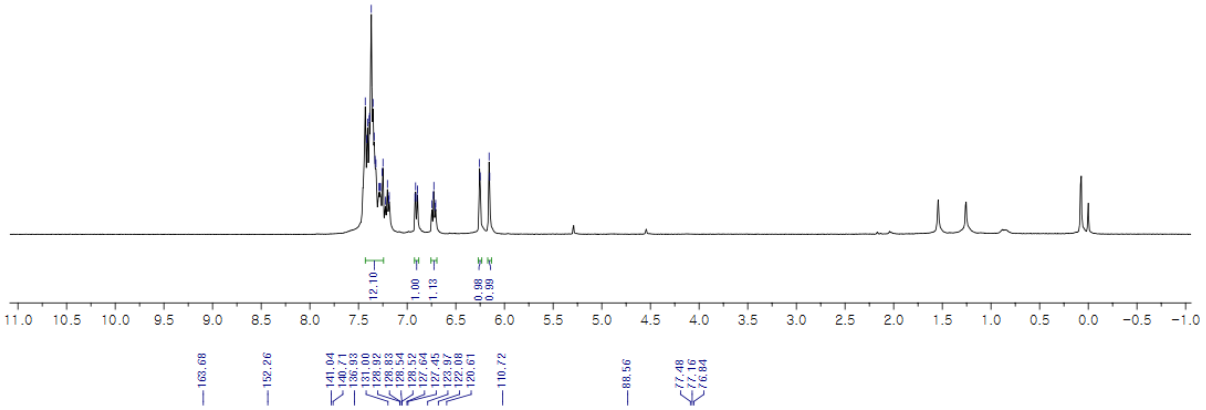
6.15

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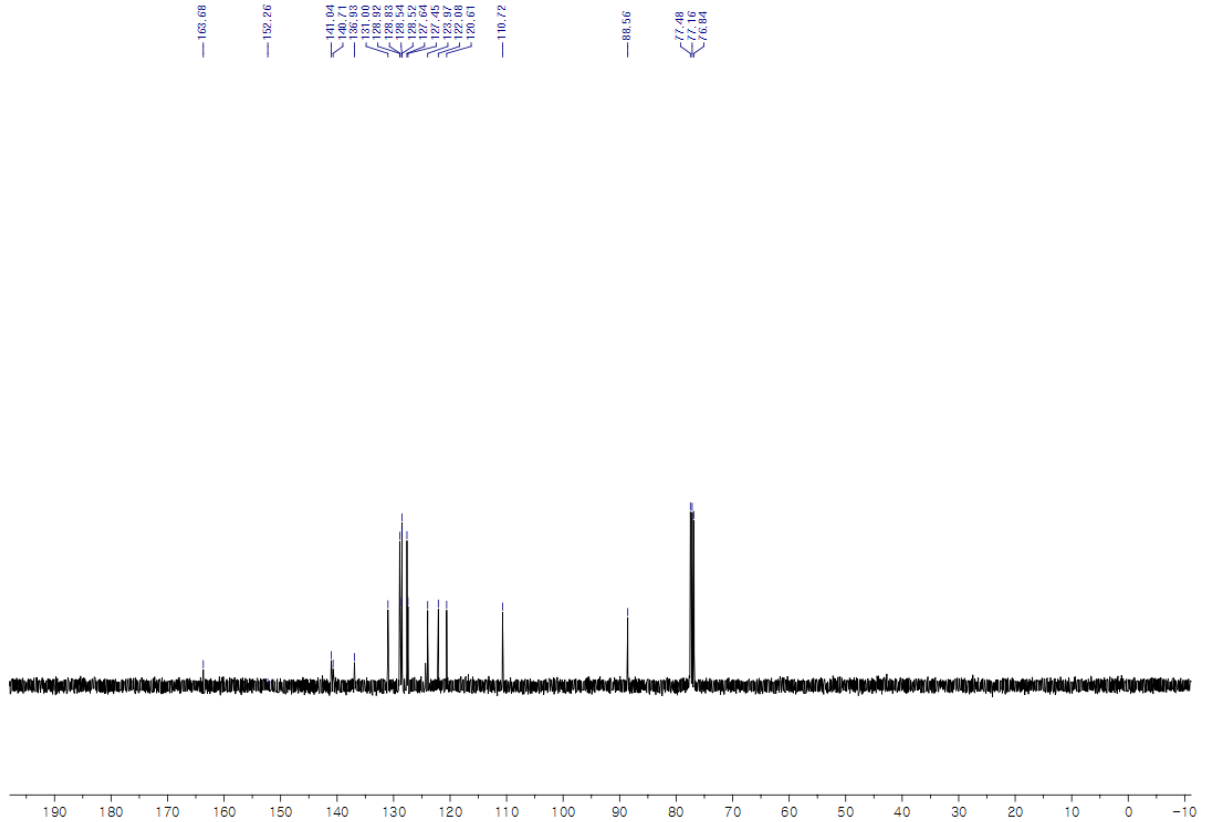
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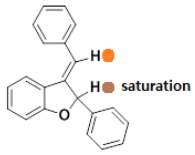
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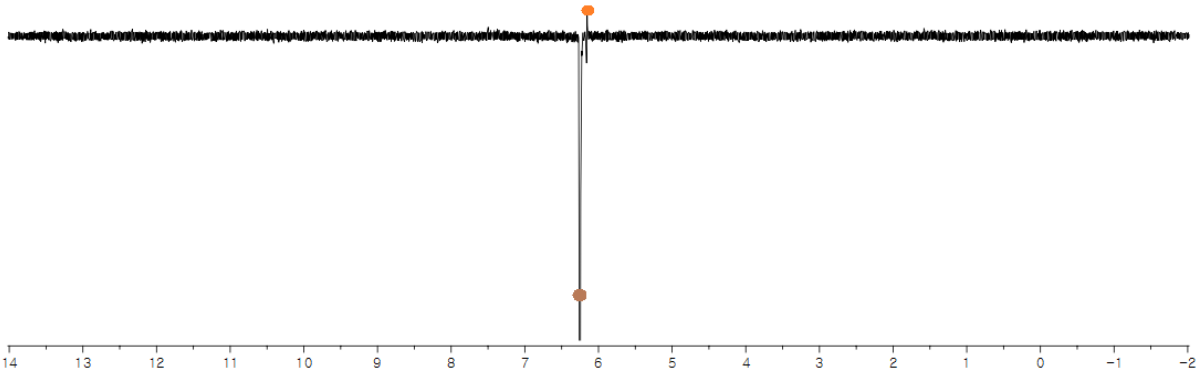
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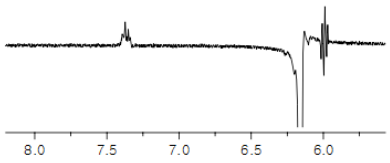
−1
−2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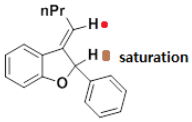
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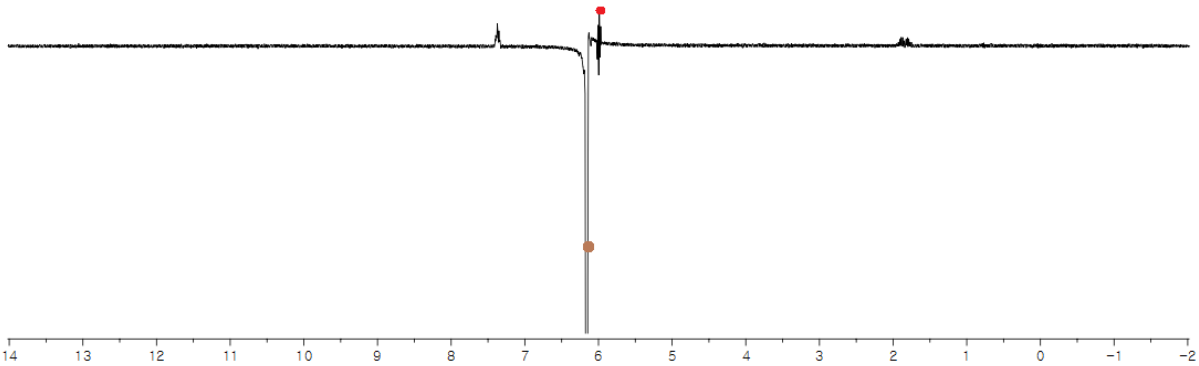
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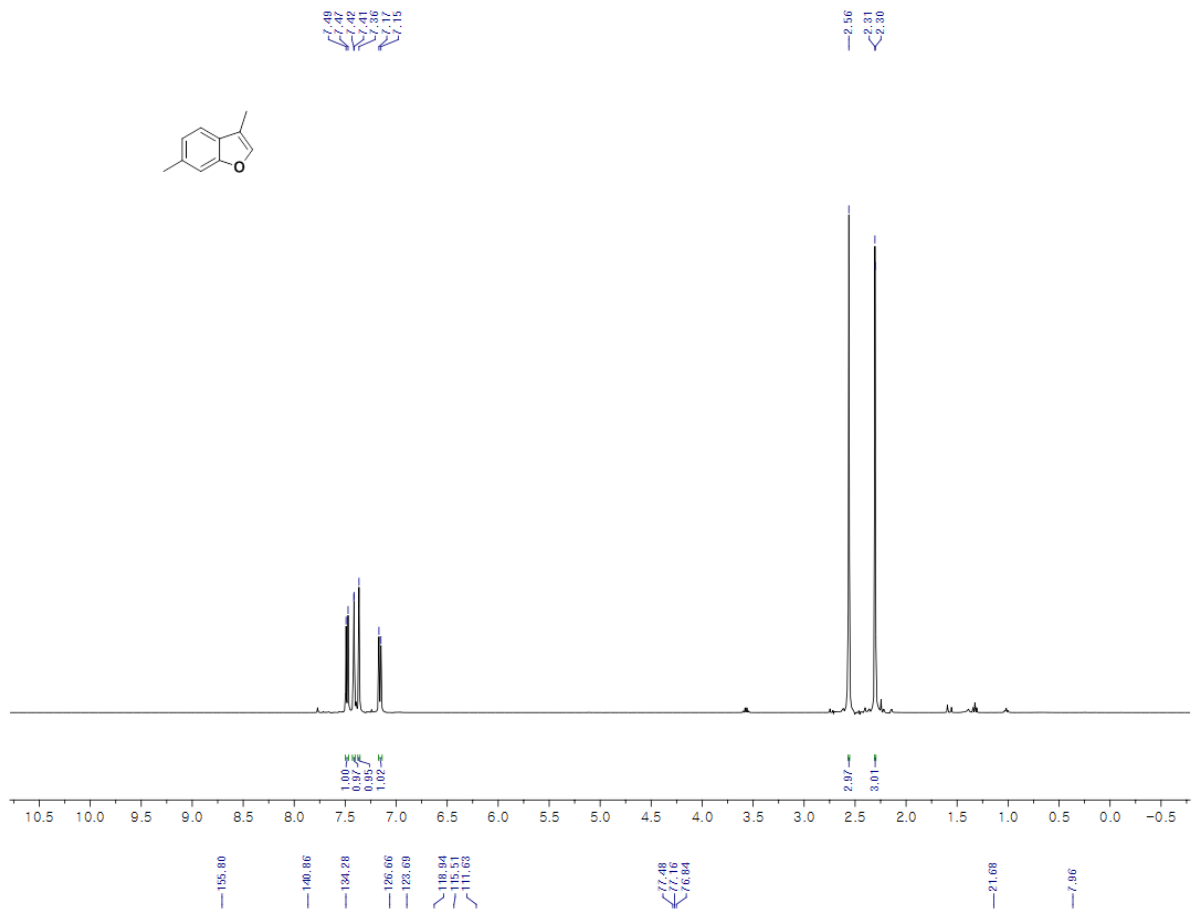
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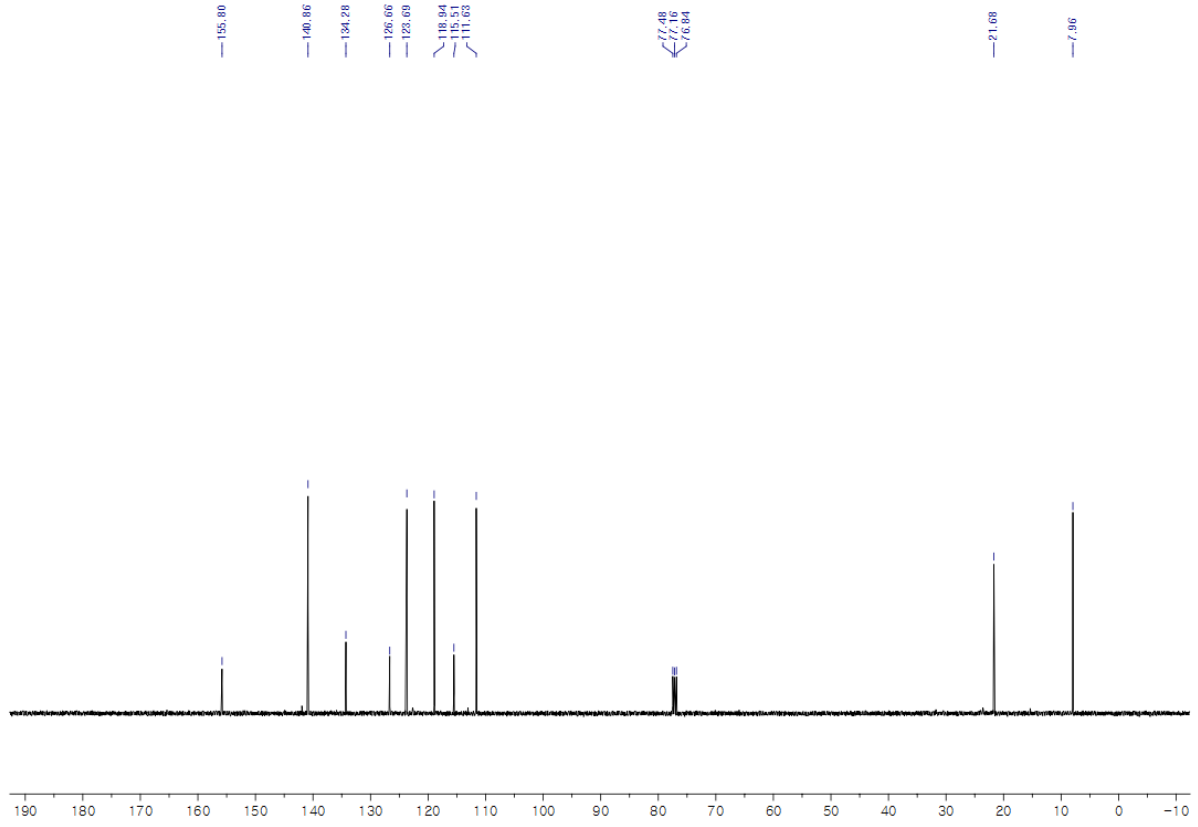
0.95
1.02
2.97
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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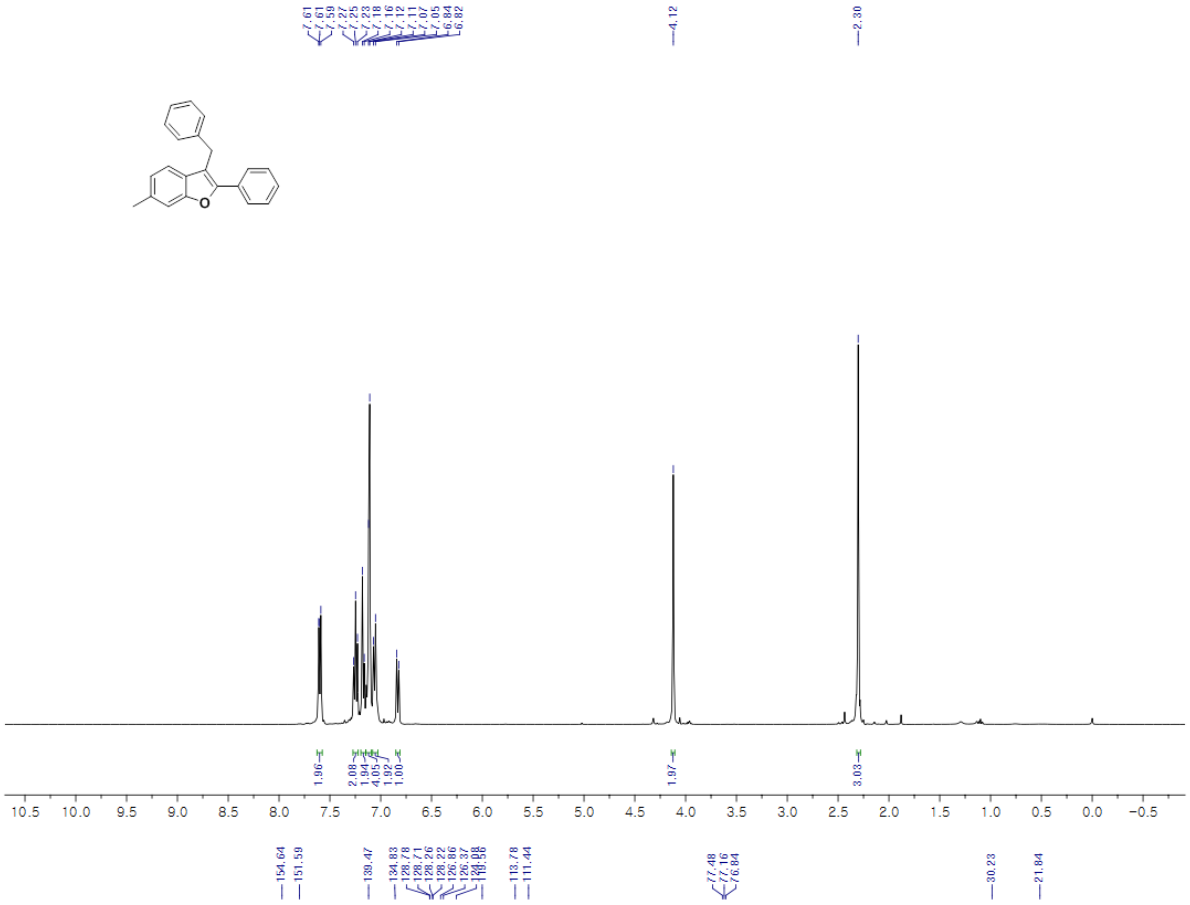
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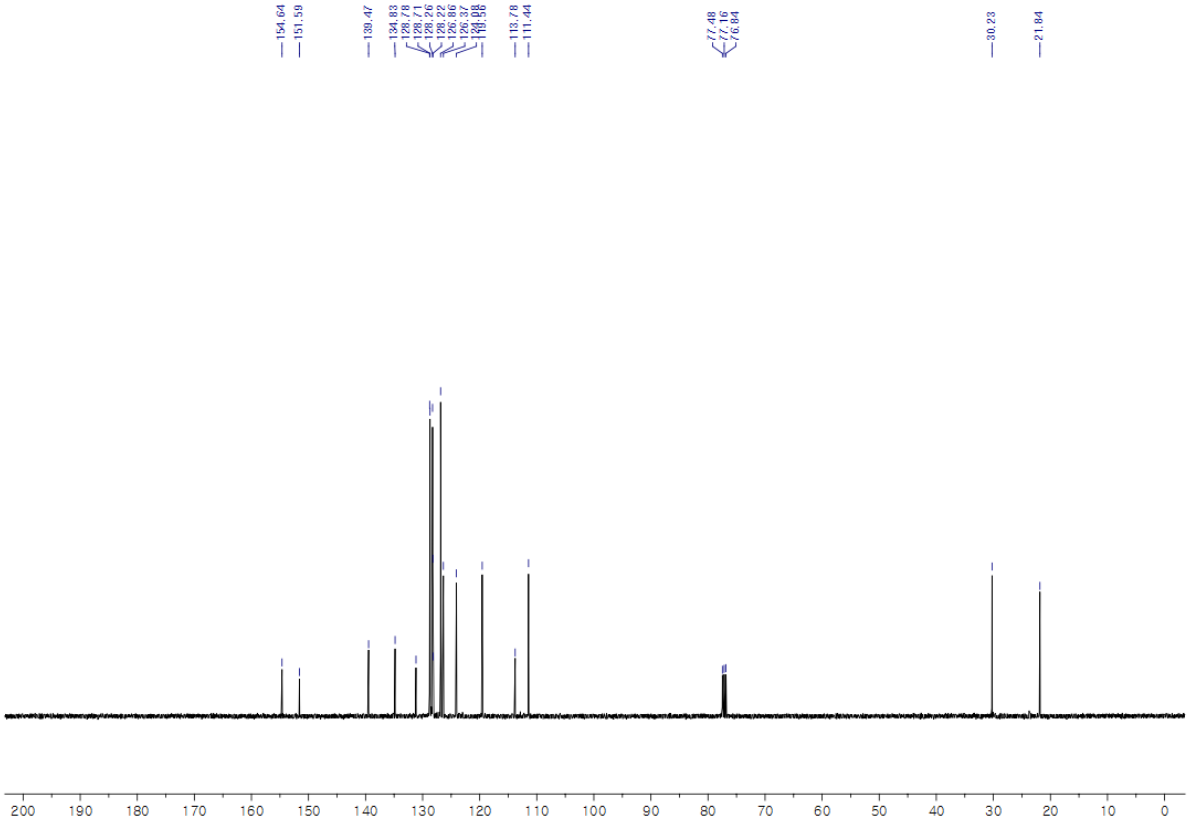
6.84
6.82
4.12
2.30
1.96
2.08
1.94
4.05
1.92
1.00
1.97
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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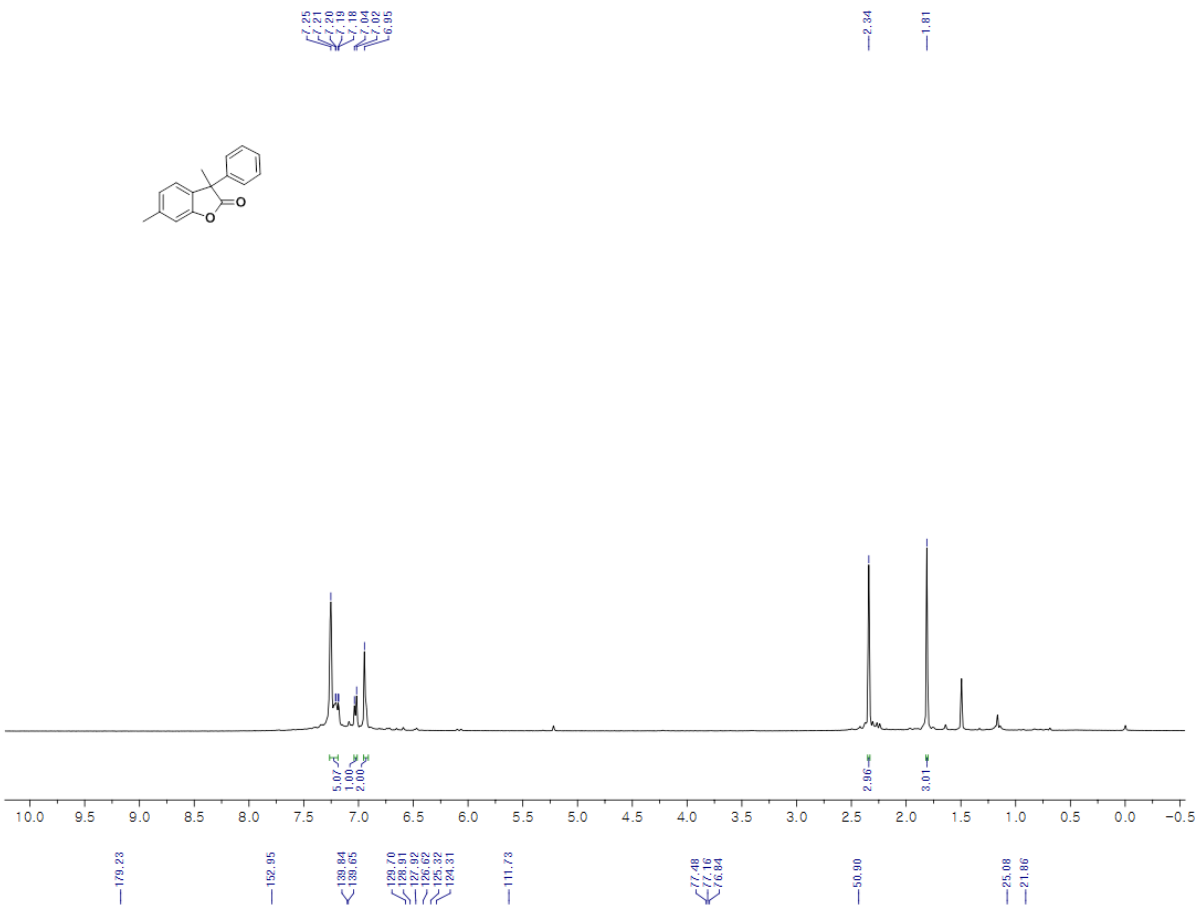
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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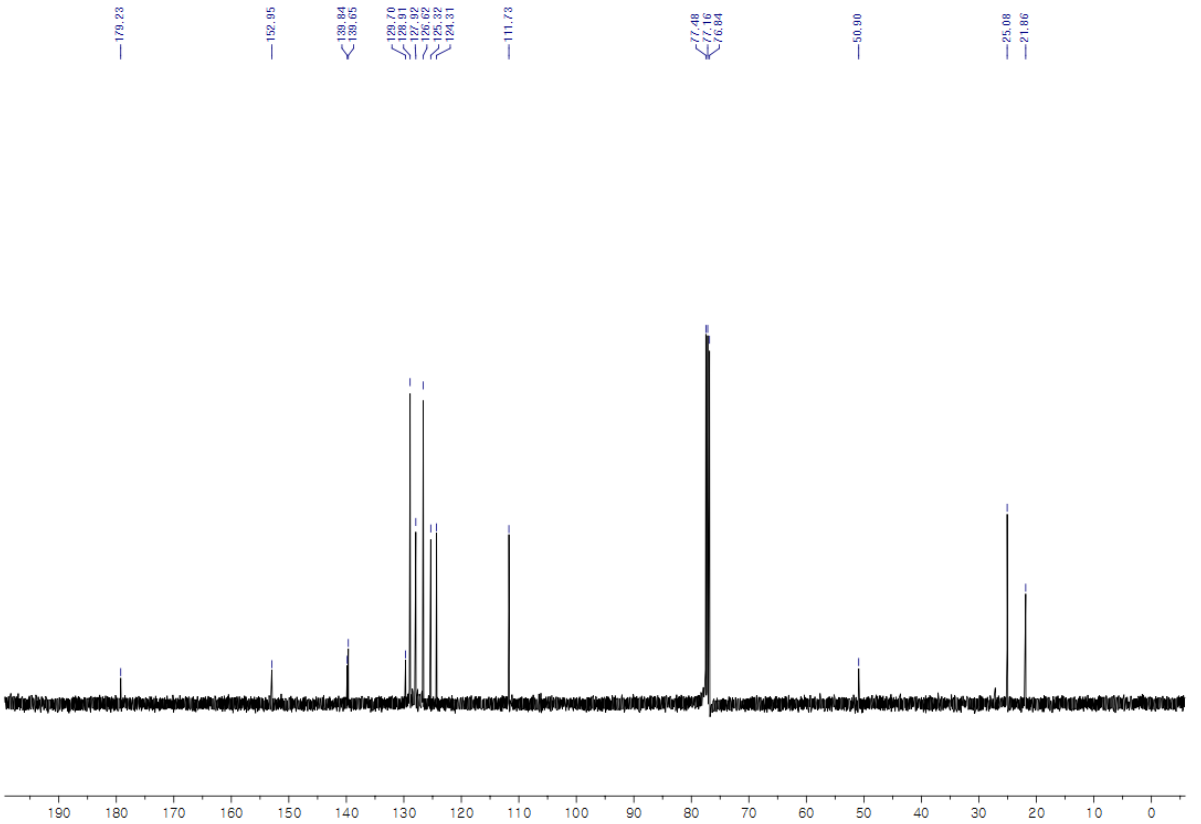
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21.86
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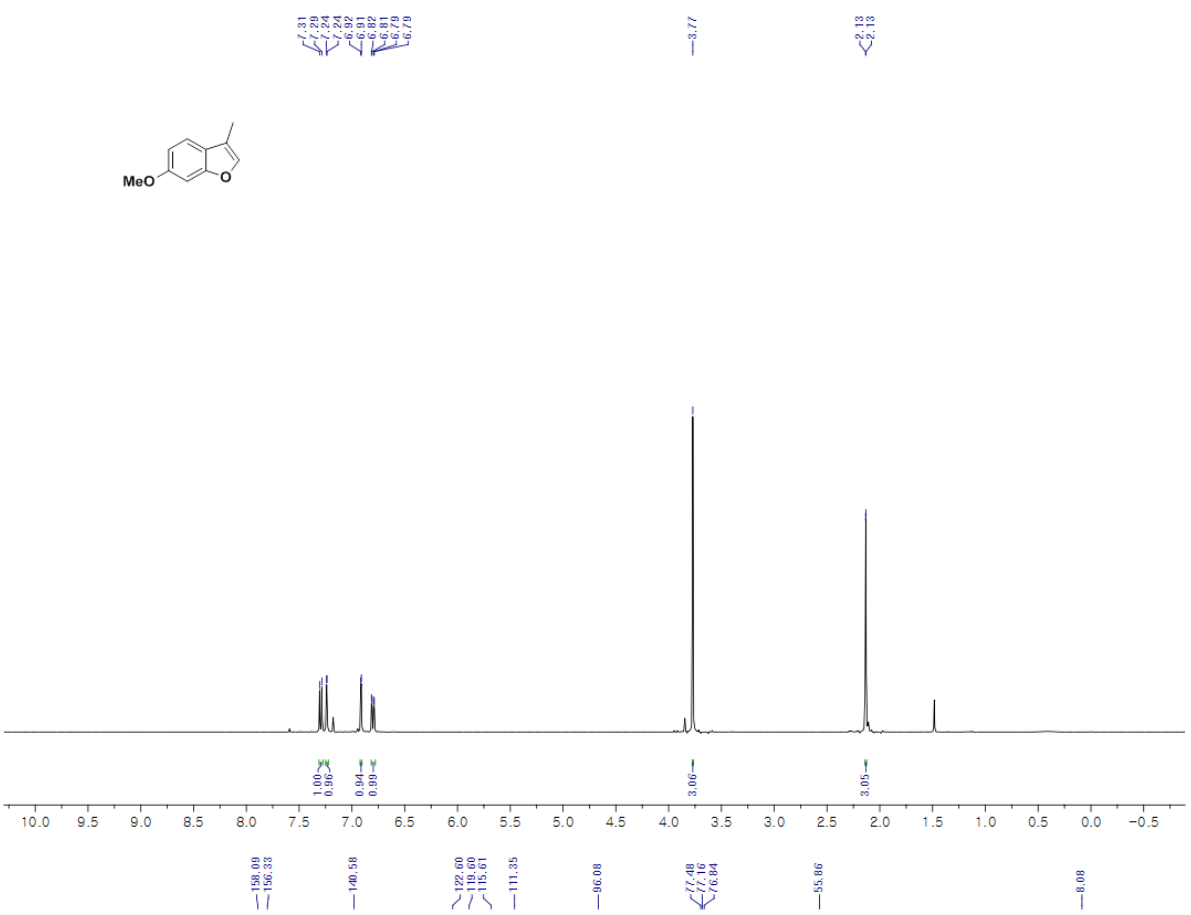
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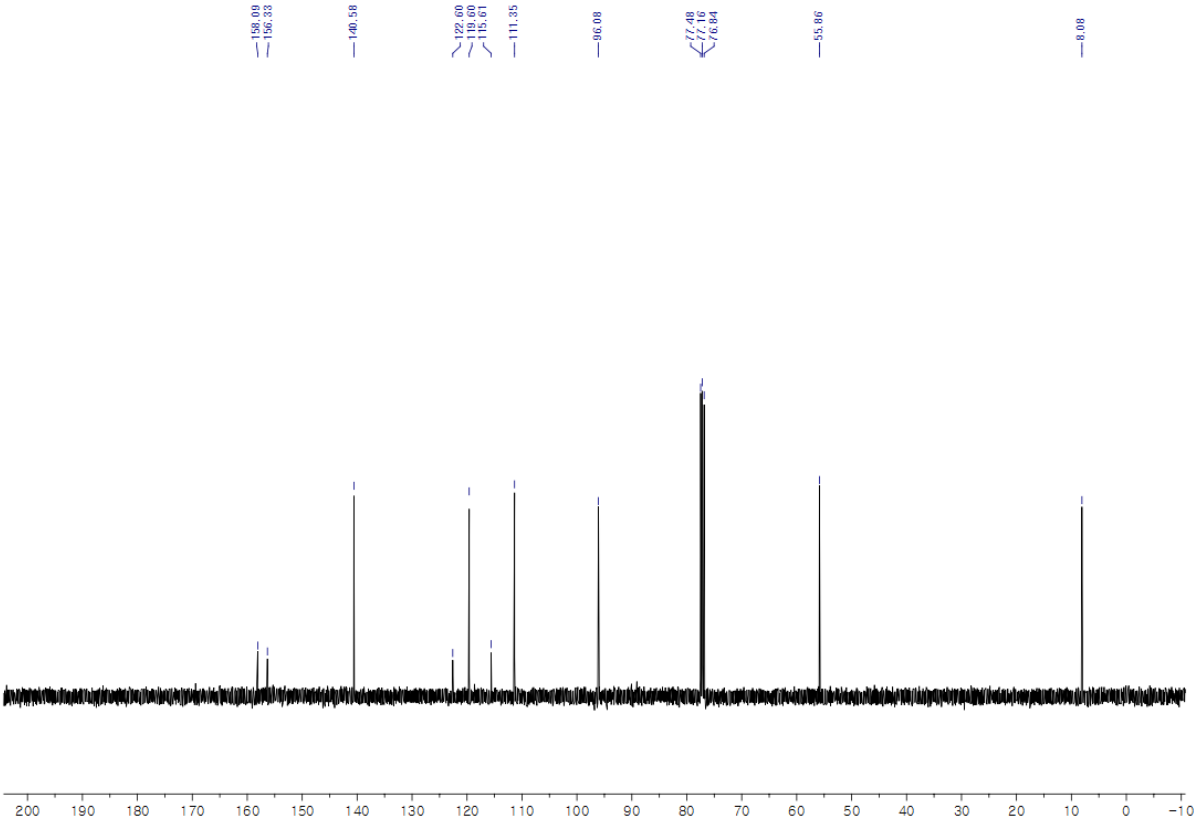
2.13
MeO
O
1.00
0.96
0.94
0.99
3.06
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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96.08
77.48
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200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

Reference

1. (a) R. C. Larock, T*etrahedron Lett.* **1988**, *29*, 4687-4690. (b) N. C. O. Tomkinson, *Synlett*, **2009**, *18*, 3003-3006. (c) A. Chihaya, *Chem. Commun.* **2012**, *48*, 5892-5894. (d) P. Lu, C. Sanchez, J. Cornella, I. Larrosa, *Org. Lett*, **2009** , 11, 5710 – 5713.
2. R. Grainger, A. Nikmal, J. Cornella, I. Larrosa, *Org. Biomol. Chem.* **2012**, *10*, 3172-3174.