

## Supporting Information

# Ring expansion of benzocyclobutenols toward benzo[*b*]furans

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### Contents

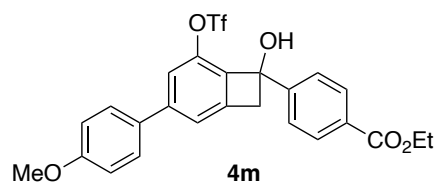
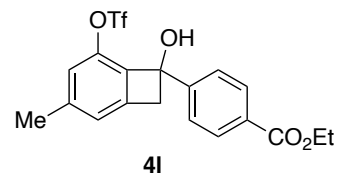
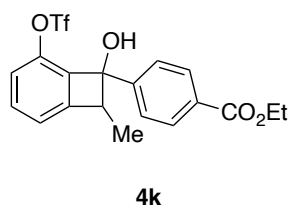
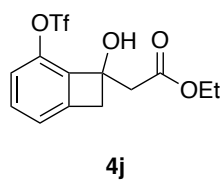
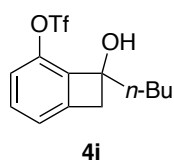
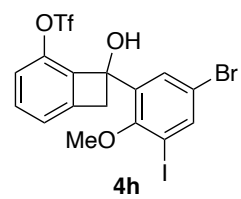
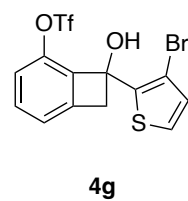
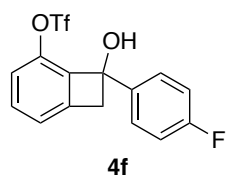
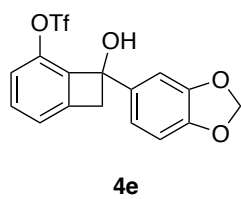
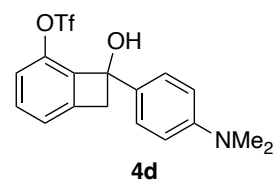
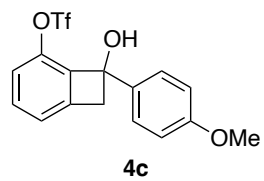
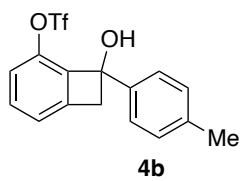
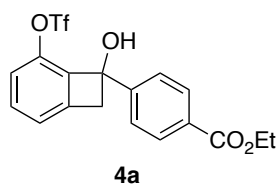
<b>General Information</b>	<b>S1</b>
<b>Structures of Benzocyclobutenols 4</b>	<b>S2</b>
<b>Optimization of the Conditions for the Synthesis of Benzo[<i>b</i>]furan 7a</b>	<b>S3</b>
<b>Experimental Procedures</b>	<b>S4</b>
<b>Characterization Data of New Compounds</b>	<b>S9</b>
<b>References for Supporting Information</b>	<b>S16</b>
<b><sup>1</sup>H and <sup>13</sup>C NMR Spectra of New Compounds</b>	<b>S17</b>

### General Information

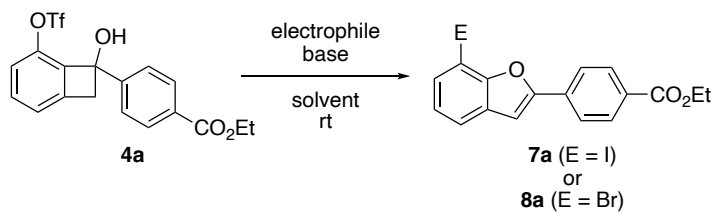
All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37562-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative TLC (PTLC) was performed on silica gel (Wako Pure Chemical Industries Ltd., Wakogel B-5F, Cat. No. 230-00043). Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. <sup>1</sup>H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 400 MHz. <sup>13</sup>C NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 101 MHz. <sup>19</sup>F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 °C. CDCl<sub>3</sub> was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from the solvent peak (δ 7.26 for <sup>1</sup>H NMR in CDCl<sub>3</sub>, δ 77.0 for <sup>13</sup>C NMR in CDCl<sub>3</sub>) as an internal reference with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. IR spectra were measured on a Shimadzu IRSpirit spectrometer with the absorption band given in cm<sup>-1</sup>. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-T100CS “AccuTOF CS” mass spectrometer under positive electrospray ionization (ESI<sup>+</sup>) conditions or negative electrospray ionization (ESI<sup>-</sup>) conditions, or JMS-700 (JEOL, Tokyo, Japan) mass spectrometer under electron impact ionization (EI) conditions.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 4-(7-Hydroxy-5-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4a**),<sup>S1</sup> 8-(4-fluorophenyl)-8-hydroxybicyclo[4.2.0]octa-1(6),2,4-trien-2-yl trifluoromethanesulfonate (**4f**),<sup>S1</sup> 8-(3-bromothiophen-2-yl)-8-hydroxybicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4g**),<sup>S1</sup> 8-hydroxy-8-(5-bromo-3-iodo-2-methoxyphenyl)bicyclo[4.2.0]octa-1,2,4-trien-2-yl trifluoromethanesulfonate (**4h**),<sup>S1</sup> ethyl 2-(7-hydroxy-5-(triflyloxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)acetate (**4j**),<sup>S2</sup> ethyl 4-((7*S*\*,8*R*\*)-7-hydroxy-8-methyl-5-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)benzoate (**4k**),<sup>S1</sup> ethyl 4-(7-hydroxy-3-methyl-5-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4l**),<sup>S1</sup> and 1,3-bis(triflyloxy)-2-iodo-5-(4-methoxyphenyl)benzene (**1b**)<sup>S3</sup> were prepared according to the reported methods.

## Structures of Benzocyclobutenols 4



## Optimization of the Conditions for the Synthesis of Benzo[*b*]furan 7a

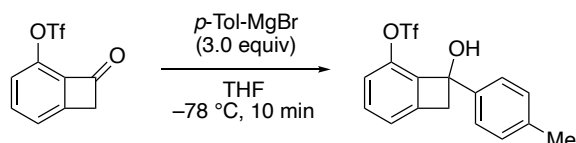


entry	electrophile	base	solvent	product	yield/% <sup>a</sup>
1	<i>N</i> -bromosuccinimide (NBS)	CsF	THF	<b>8a</b>	0
2	<i>N</i> -iodosuccinimide (NIS)	CsF	THF	<b>7a</b>	0
3	I <sub>2</sub>	CsF	THF	<b>7a</b>	0
4	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> I	CsF	THF	<b>7a</b>	51
5	I-C≡C-Ph	CsF	THF	<b>7a</b>	52
6	C <sub>6</sub> F <sub>5</sub> I	CsF	THF	<b>7a</b>	62 <sup>c</sup>
7	C <sub>6</sub> F <sub>5</sub> I	CsF	DMF	<b>7a</b>	c.m. <sup>b</sup>
8	C <sub>6</sub> F <sub>5</sub> I	CsF	toluene	<b>7a</b>	trace
9	C <sub>6</sub> F <sub>5</sub> I	CsF	1,4-dioxane	<b>7a</b>	62
10	C <sub>6</sub> F <sub>5</sub> I	CsF	MeCN	<b>7a</b>	64 <sup>c</sup>
11	C <sub>6</sub> F <sub>5</sub> I	AgF	MeCN	<b>7a</b>	44
12	C <sub>6</sub> F <sub>5</sub> I	LiOH	MeCN	<b>7a</b>	60
13	C <sub>6</sub> F <sub>5</sub> I	<i>t</i> -BuOK	MeCN	<b>7a</b>	c.m. <sup>b</sup>
14	C <sub>6</sub> F <sub>5</sub> I	K <sub>2</sub> CO <sub>3</sub>	MeCN	<b>7a</b>	66 [65] <sup>c</sup>

<sup>a</sup>NMR yields. <sup>b</sup>c.m. = complex mixture. <sup>c</sup>isolated yields.

## Experimental Procedures

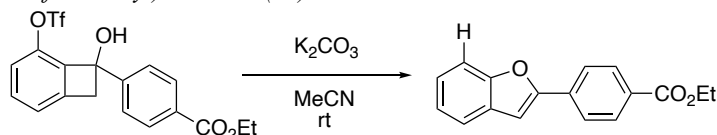
### Preparation of 8-hydroxy-8-(*p*-tolyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4b**)



To a solution of 2-(triflyloxy)bicyclo[4.2.0]octa-1,3,5-trien-8-one (**3**) (2.66 g, 10.0 mmol) dissolved in THF (100 mL) was slowly added *p*-tolylmagnesium bromide (1.0 M, THF solution, 30 mL, 30 mmol, 3.0 equiv) at -78 °C. After stirring for 10 min at the same temperature, to the resulting mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic extract was washed with brine (10 mL), and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 8-hydroxy-8-(*p*-tolyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4b**) (3.08 g, 8.60 mmol, 86%) as a colorless oil.

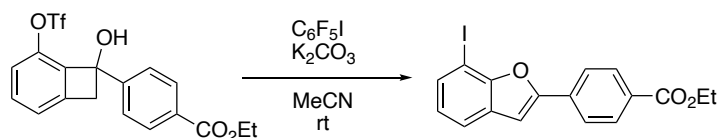
Similarly, benzocyclobutenols **4c–4e** and **4i** were prepared from **3** and the corresponding Grignard reagents.

### Synthesis of ethyl 4-(benzofuran-2-yl)benzoate (**6a**)



To a solution of ethyl 4-(7-hydroxy-5-((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4a**) (21.6 mg, 51.9  $\mu$ mol) dissolved in acetonitrile (0.50 mL) was added potassium carbonate (28.1 mg, 0.203 mmol, 3.9 equiv) at room temperature. After stirring for 12 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give ethyl 4-(benzofuran-2-yl)benzoate (**6a**) (5.6 mg, 21  $\mu$ mol, 40%) as a colorless solid.

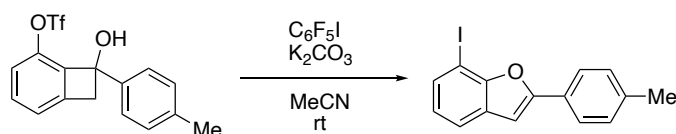
### A typical procedure for the synthesis of benzofurans **7**



To a mixture of ethyl 4-(7-hydroxy-5-((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4a**) (42.8 mg, 0.103 mmol) and iodopentafluorobenzene (147 mg, 0.501 mmol, 4.9 equiv) dissolved in acetonitrile (1.0 mL) was added potassium carbonate (55.7 mg, 0.403 mmol, 3.9 equiv) at room temperature. After stirring for 12 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give ethyl 4-(7-iodo-benzofuran-2-yl)benzoate (**7a**) (26.1 mg, 66.6  $\mu$ mol, 65%) as a colorless solid.

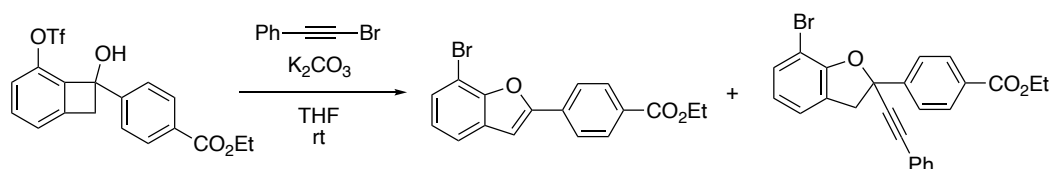
Similarly, benzofurans **7b–7m** were prepared from the corresponding benzocyclobutenols **4**.

### Gram-scale synthesis of 7-iodo-2-(*p*-tolyl)benzofuran (**7b**)



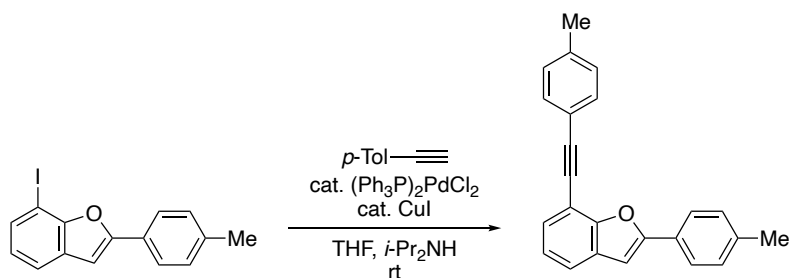
To a mixture of 8-hydroxy-8-(*p*-tolyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4b**) (1.79 g, 5.00 mmol) and iodopentafluorobenzene (7.35 g, 25.0 mmol, 5.0 equiv) dissolved in acetonitrile (50 mL) was added potassium carbonate (2.78 g, 20.1 mmol, 4.0 equiv) at room temperature. After stirring for 12 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 7-iodo-2-(*p*-tolyl)benzofuran (**7b**) (1.12 g, 3.32 mmol, 66%) as a colorless solid.

### A typical procedure for the synthesis of ethyl 4-(7-bromobenzofuran-2-yl)benzoate (**8a**)



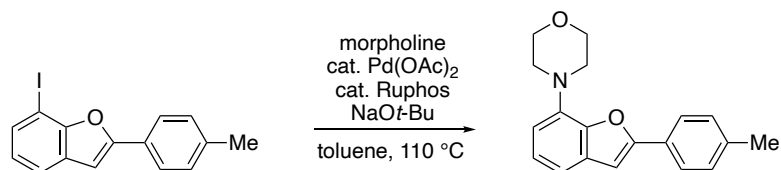
To a mixture of 4-(7-hydroxy-5-(((trifluoromethyl)sulfonyloxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4a**) (40.4 mg, 97.1  $\mu$ mol) and bromoethynylbenzene (89.5 mg, 0.497 mmol, 5.1 equiv) dissolved in THF (0.97 mL) was added potassium carbonate (53.2 mg, 0.384 mmol, 4.0 equiv) at room temperature. After stirring for 12 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give ethyl 4-(7-bromobenzofuran-2-yl)benzoate (**8a**) (8.5 mg, 25  $\mu$ mol, 25%) as a colorless solid and ethyl 4-(7-bromo-2-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)benzoate (**9a**) (9.1 mg, 20  $\mu$ mol, 21%) as a colorless oil.

### Synthesis of 2-(*p*-tolyl)-7-(*p*-tolylethynyl)benzofuran (**10**)



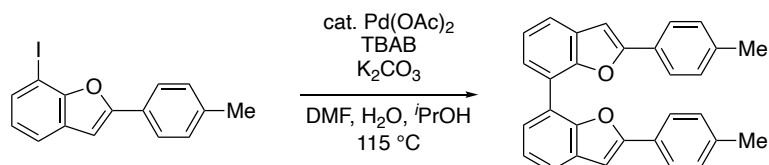
In a 5 mL screw-top V-vial<sup>®</sup> with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 7-iodo-2-(*p*-tolyl)benzofuran (**7b**) (17.5 mg, 49.4  $\mu$ mol) and *i*-Pr<sub>2</sub>NH (1.0 mL) in THF (0.50 mL) were added 1-ethynyl-4-methylbenzene (9.8 mg, 85  $\mu$ mol, 1.7 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.1 mg, 10  $\mu$ mol, 20 mol %), and copper(I) iodide (2.9 mg, 15  $\mu$ mol, 31 mol %) at room temperature. After stirring for 18 h at the same temperature, to the mixture was added water (2 + 8 mL). The mixture was extracted with EtOAc (20 mL  $\times$  3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 2-(*p*-tolyl)-7-(*p*-tolylethynyl)benzofuran (**10**) (15.6 mg, 48.4  $\mu$ mol, 97%) as a colorless solid.

### Synthesis of 4-(2-(*p*-tolyl)benzofuran-7-yl)morpholine (**11**)



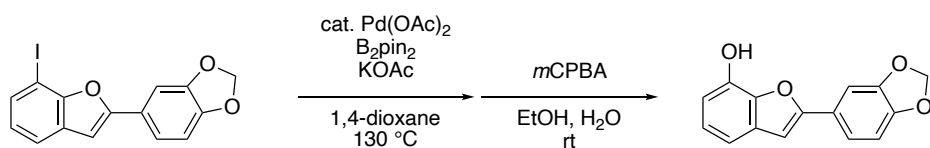
In a 5 mL screw-top V-vial<sup>®</sup> with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 7-iodo-2-(*p*-tolyl)benzofuran (**7b**) (33.2 mg, 99.4  $\mu$ mol), morpholine (12.0 mg, 0.138 mmol, 1.4 equiv), Pd(OAc)<sub>2</sub> (0.2 mg, 1  $\mu$ mol, 1 mol %), Ruphos (0.5 mg, 1  $\mu$ mol, 1 mol %), and NaOt-Bu (13.4 mg, 0.139 mmol, 1.4 equiv) was added toluene (1.0 mL) at room temperature. After stirring for 16 h at 110 °C (aluminium heating block), water (2.5 mL) was added to the resulting mixture. The mixture was extracted with EtOAc (5 mL  $\times$  3). The combined organic extract was washed with brine (5 mL). The extract was dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 5/1) to give 4-(2-(*p*-tolyl)benzofuran-7-yl)morpholine (**11**) (18.8 mg, 64.2  $\mu$ mol, 64%) as a green solid.

### Synthesis of 2,2'-di-*p*-tolyl-7,7'-bibenzofuran (**12**)



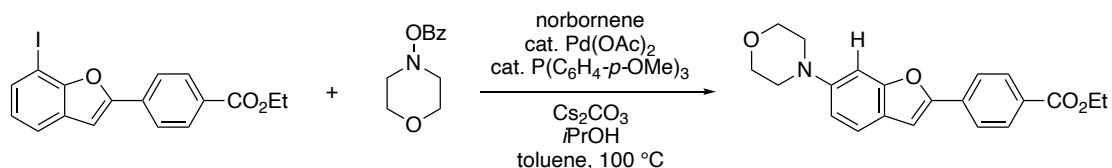
In a 5 mL screw-top V-vial<sup>®</sup> with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 7-iodo-2-(*p*-tolyl)benzofuran (**7b**) (16.8 mg, 47.5  $\mu$ mol), Pd(OAc)<sub>2</sub> (0.6 mg, 3  $\mu$ mol, 6 mol %), tetrabutylammonium bromide (8.9 mg, 28  $\mu$ mol, 58 mol %), and K<sub>2</sub>CO<sub>3</sub> (7.9 mg, 57  $\mu$ mol, 1.2 equiv) were added DMF (56  $\mu$ L), H<sub>2</sub>O (22  $\mu$ L), and *i*PrOH (78  $\mu$ L) at room temperature. After stirring for 16 h at 115 °C (aluminium heating block), water (2.5 mL) was added to the resulting mixture. The mixture was extracted with EtOAc (5 mL  $\times$  3). The combined organic extract was washed with brine (5 mL). The extract was dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 5/1) to give 2,2'-di-*p*-tolyl-7,7'-bibenzofuran (**12**) (5.8 mg, 14  $\mu$ mol, 58%) as a colorless solid.

### Synthesis of 2-(benzo[*d*][1,3]dioxol-5-yl)benzofuran-7-ol (**13**)



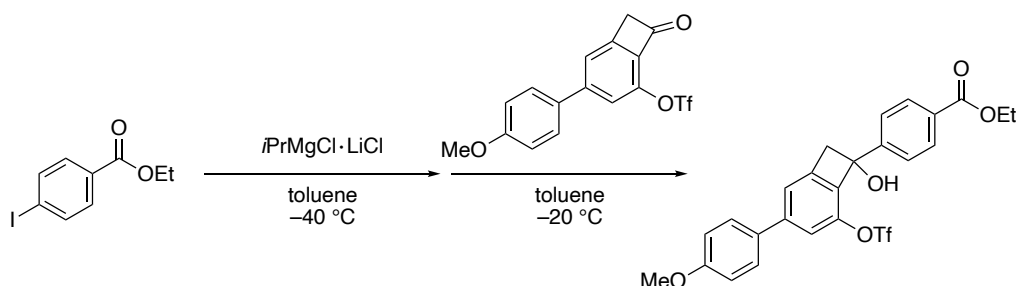
In a 5 mL screw-top V-vial<sup>®</sup> with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 5-(7-Iodobenzofuran-2-yl)benzo[*d*][1,3]dioxole (**7e**) (21.1 mg, 58.2  $\mu$ mol), PdCl<sub>2</sub>(dppf) (1.5 mg, 1.8  $\mu$ mol, 3.1 mol %), potassium acetate (17.5 mg, 0.179 mmol, 3.1 equiv), and B<sub>2</sub>pin<sub>2</sub> (18.6 mg, 73.2  $\mu$ mol, 1.3 equiv) was added 1,4-dioxane (0.18 mL) at room temperature. After stirring for 16 h at 130 °C (aluminium heating block), water (2.5 mL) was added to the resulting mixture. The mixture was extracted with EtOAc (5 mL  $\times$  3). The combined organic extract was washed with brine (5 mL). The extract was dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. To the resulting mixture in EtOH (0.12 mL) and H<sub>2</sub>O (60  $\mu$ L) was slowly added *m*CPBA (ca. 70%, 15.3 mg, ca. 62  $\mu$ mol, ca. 1.1 equiv) at 0 °C. After stirring for 10 min at the same temperature, the mixture was allowed to warm to room temperature. After stirring for 6 h at the same temperature, to the mixture was added an aqueous saturated solution of potassium carbonate (5 mL) and an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 2-(benzo[*d*][1,3]dioxol-5-yl)benzofuran-7-ol (**13**) (6.2 mg, 24  $\mu$ mol, 42%) as a colorless solid.

### Synthesis of ethyl 4-(6-morpholinobenzofuran-2-yl)benzoate (**15**)



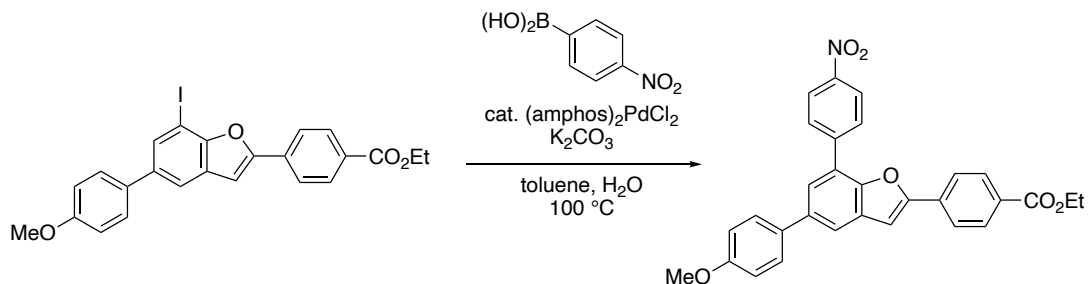
In a 5 mL screw-top V-vial<sup>®</sup> with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), a mixture of 4-(7-iodobenzofuran-2-yl)benzoate (**7a**) (19.3 mg, 49.2 μmol), 4-(benzyloxy)morpholine (**14**) (19.8 mg, 95.6 μmol, 1.9 equiv), Pd(OAc)<sub>2</sub> (1.4 mg, 6.2 μmol, 12 mol %), tris(4-methoxyphenyl)phosphine (2.4 mg, 6.8 μmol, 14 mol %), norbornene (4.7 mg, 50 μmol, 1.0 equiv), and Cs<sub>2</sub>CO<sub>3</sub> (40.1 mg, 0.123 mmol, 2.5 equiv) were added toluene (0.50 mL) and *i*PrOH (4 μL) at room temperature. After stirring for 16 h at 100 °C (aluminium heating block), water (2.5 mL) was added to the resulting mixture. The mixture was extracted with EtOAc (5 mL × 3). The combined organic extract was washed with brine (5 mL). The extract was dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 5/1) to give ethyl 4-(6-morpholinobenzofuran-2-yl)benzoate (**15**) (7.4 mg, 21 μmol, 42%) as a green solid.

### Synthesis of benzocyclobutenol **4m**



To a solution of ethyl 4-iodobenzoate (**16**) (0.149 mL, 0.896 mmol, 3.0 equiv) in toluene (3.0 mL) was added *i*PrMgCl·LiCl (0.692 mL, 0.900 mmol, 1.3 M in THF, 3.0 equiv) at -40 °C. The reaction mixture was stirred for 1 h at the same temperature. Then, the resulting solution was slowly added to a solution of 4-(4-methoxyphenyl)-2-(triflyloxy)bicyclo[4.2.0]octa-1,3,5-triene-8-one<sup>S4</sup> (111 mg, 0.299 mmol) in toluene (1.5 mL) at -20 °C. After stirring for 20 min at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 3/1) to give ethyl 4-(7-hydroxy-3-(4-methoxyphenyl)-5-((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4m**) (125 mg, 0.239 mmol, 80%) as a colorless oil.

### Synthesis of triarylbenzofuran **17**



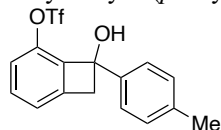
In a 5 mL screw-top V-vial<sup>®</sup> with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of ethyl 4-(7-iodo-5-(4-methoxyphenyl)benzofuran-2-yl)benzoate (**7m**) (4.6 mg, 9.2 μmol), (4-nitrophenyl)boronic acid (2.8 mg, 17 μmol, 1.8 equiv), (amphos)<sub>2</sub>PdCl<sub>2</sub> (1.0 mg, 1.4 μmol, 15 mol %), and K<sub>2</sub>CO<sub>3</sub> (4.4 mg, 32 μmol, 2.9 equiv) were added toluene (0.87 mL) and H<sub>2</sub>O (87 μL) at room temperature. After stirring for 16 h at 100 °C

(aluminium heating block), water (2.5 mL) was added to the resulting mixture. The mixture was extracted with EtOAc (5 mL  $\times$  3). The combined organic extract was washed with brine (5 mL). The extract was dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 5/1) to give ethyl 4-(5-(4-methoxyphenyl)-7-(4-(trifluoromethyl)phenyl)benzofuran-2-yl)benzoate (**17**) (3.6 mg, 7.3  $\mu$ mol, 79%) as a yellow solid.

## Characterization Data of New Compounds

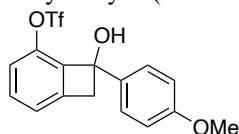
Ethyl 4-(benzofuran-2-yl)benzoate (**6a**)<sup>SS</sup> was identical in spectra data with those reported in the literature.

### 8-Hydroxy-8-(*p*-tolyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4b**)



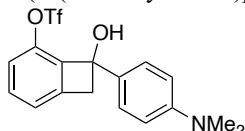
Yield: 86% (3.08 g, 8.60 mmol); Colorless oil; TLC  $R_f$  0.47 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.45 (dd, 1H,  $J = 8.4, 7.8$  Hz), 7.37–7.30 (AA'BB', 2H), 7.28 (d, 1H,  $J = 7.8$  Hz), 7.20–7.10 (m, 3H), 3.67 (d, 1H,  $J = 14.4$  Hz), 3.58 (d, 1H,  $J = 14.4$  Hz), 3.43–3.35 (br, 1H), 2.35 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  145.9, 141.2, 139.3, 139.2, 137.8, 131.8, 129.3, 125.2, 124.7, 119.6, 118.6 (q,  $J = 320$  Hz), 81.1, 49.5, 21.1;  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -72.7 (s); IR (NaCl,  $\text{cm}^{-1}$ ) 811, 993, 1042, 1140, 1215, 1422, 1462, 1514, 3679; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NaO}_4\text{S}^+$  381.0379; Found 381.0385.

### 8-Hydroxy-8-(4-methoxyphenyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4c**)



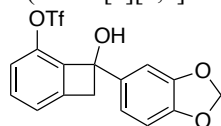
Yield: 58% (28.8 mg, 77.6  $\mu\text{mol}$ ); Colorless oil; TLC  $R_f$  0.55 (*n*-hexane/EtOAc = 3/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.44 (dd, 1H,  $J = 8.4, 7.9$  Hz), 7.41–7.34 (AA'BB', 2H), 7.28 (d, 1H,  $J = 7.9$  Hz), 7.13 (d, 1H,  $J = 8.4$  Hz), 6.92–6.86 (AA'BB', 2H), 3.81 (s, 3H), 3.67 (d, 1H,  $J = 14.3$  Hz), 3.57 (d, 1H,  $J = 14.3$  Hz), 3.38–3.33 (br, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  159.3, 145.9, 141.2, 139.3, 134.5, 131.8, 126.6, 123.3, 119.6, 118.6 (q,  $J = 322$  Hz), 113.9, 81.0, 55.3, 49.5;  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -72.7 (s); IR (NaCl,  $\text{cm}^{-1}$ ) 828, 993, 1140, 1250, 1422, 1514, 1610, 2840; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{14}\text{F}_3\text{O}_5\text{S}^+$  371.0187; Found 371.0186.

### 8-(4-(Dimethylamino)phenyl)-8-hydroxybicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4d**)



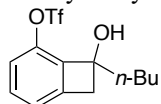
Yield: 37% (28.8 mg, 74.4  $\mu\text{mol}$ ); Colorless oil; TLC  $R_f$  0.47 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.42 (dd, 1H,  $J = 8.4, 7.3$  Hz), 7.37–7.31 (AA'BB', 2H), 7.28–7.23 (d, 1H,  $J = 7.3$  Hz), 7.13 (d, 1H,  $J = 8.4$  Hz), 6.75–6.68 (AA'BB', 2H), 3.66 (d, 1H,  $J = 14.3$  Hz), 3.59 (d, 1H,  $J = 14.3$  Hz), 3.30–3.22 (br, 1H), 2.95 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  150.3, 145.9, 141.3, 139.5, 131.5, 129.9, 126.4, 124.6, 119.5, 118.7 (q,  $J = 330$  Hz), 112.3, 81.3, 49.1, 40.5;  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -72.7 (s); IR (NaCl,  $\text{cm}^{-1}$ ) 844, 992, 1140, 1215, 1251, 1356, 1461, 1525, 1615, 3679; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NO}_4\text{S}^+$  388.0825; Found 388.0827.

### 8-(Benzo[*d*][1,3]dioxol-5-yl)-8-hydroxybicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4e**)



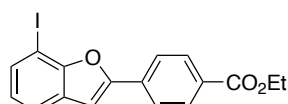
Yield: 49% (56.6 mg, 0.146 mmol); Colorless oil; TLC  $R_f$  0.54 (*n*-hexane/EtOAc = 3/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.45 (dd, 1H,  $J = 8.4, 7.3$  Hz), 7.28 (d, 1H,  $J = 7.3$  Hz), 7.13 (d, 1H,  $J = 8.4$  Hz), 6.95–6.87 (m, 2H), 6.77 (d, 1H,  $J = 8.0$  Hz), 5.96 (s, 2H), 3.64 (d, 1H,  $J = 14.4$  Hz), 3.53 (d, 1H,  $J = 14.4$  Hz), 3.44–3.39 (br, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  148.0, 147.4, 145.9, 141.1, 139.0, 136.4, 131.9, 124.8, 119.7, 118.6, 118.6 (q,  $J = 322$  Hz), 108.1, 106.1, 101.2, 81.0, 49.7;  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -72.7 (s); IR (NaCl,  $\text{cm}^{-1}$ ) 811, 936, 1108, 1162, 1591, 1607, 2782, 3079; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{NH}_4]^+$  Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}_6\text{S}^+$  406.0567; Found 406.0562.

8-Butyl-8-hydroxybicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4i**)



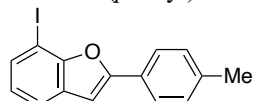
Yield: 30% (52.1 mg, 0.161 mmol); Colorless oil; TLC  $R_f$  0.63 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.36 (dd, 1H,  $J = 8.4, 7.8$  Hz), 7.20 (d, 1H,  $J = 7.8$  Hz), 7.04 (d, 1H,  $J = 8.4$  Hz), 3.35 (d, 1H,  $J = 14.4$  Hz), 3.23 (d, 1H,  $J = 14.4$  Hz), 2.96–2.88 (br, 1H), 2.00–1.88 (m, 2H), 1.56–1.31 (m, 4H), 0.92 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  145.3, 141.2, 140.5, 131.4, 124.6, 119.3, 118.6 (q,  $J = 322$  Hz), 80.6, 46.1, 39.0, 27.1, 22.9, 14.0;  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -72.9 (s); IR (NaCl,  $\text{cm}^{-1}$ ) 840, 992, 1102, 1142, 1251, 1422, 1590, 2935, 3652; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NaO}_4\text{S}^+$  347.0541; Found 347.0535.

Ethyl 4-(7-iodo-benzofuran-2-yl)benzoate (**7a**)



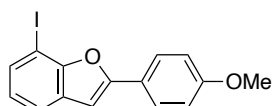
Yield: 65% (26.1 mg, 66.6  $\mu\text{mol}$ ); Colorless solid; Mp 134–136  $^\circ\text{C}$ ; TLC  $R_f$  0.45 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.18–8.10 (AA'BB', 2H), 7.98–7.92 (AA'BB', 2H), 7.68 (dd, 1H,  $J = 7.8, 1.0$  Hz), 7.56 (dd, 1H,  $J = 7.8, 1.0$  Hz), 7.24 (s, 1H), 7.02 (dd, 1H,  $J = 7.8, 7.8$  Hz), 4.41 (q, 2H,  $J = 7.1$  Hz), 1.43 (t, 3H,  $J = 7.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.2, 155.4, 155.0, 133.9, 133.8, 130.5, 130.1, 129.0, 125.0, 124.8, 121.3, 104.1, 74.9, 61.2, 14.4; IR (NaCl,  $\text{cm}^{-1}$ ) 810, 930, 1016, 1182, 1312, 1418, 1574, 1721, 2980; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{14}\text{IO}_3^+$  392.9982; Found 392.9983.

7-Iodo-2-(*p*-tolyl)benzofuran (**7b**)



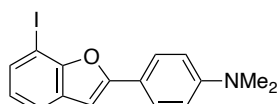
Yield: 66% (1.11 g, 3.32 mmol); Colorless solid; Mp 67–69  $^\circ\text{C}$ ; TLC  $R_f$  0.54 (*n*-hexane/EtOAc = 3/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.86–7.77 (AA'BB', 2H), 7.64 (dd, 1H,  $J = 7.7, 0.9$  Hz), 7.54 (dd, 1H,  $J = 7.7, 0.9$  Hz), 7.33–7.26 (AA'BB', 2H), 7.08 (s, 1H), 7.01 (dd, 1H,  $J = 7.7, 7.7$  Hz), 2.44 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  156.6, 155.1, 139.1, 132.9, 129.6, 129.4, 127.1, 125.1, 124.6, 120.8, 101.3, 74.8, 21.5; IR (NaCl,  $\text{cm}^{-1}$ ) 821, 1016, 1119, 1285, 1322, 1415, 1505, 1617, 2919; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{15}\text{H}_{11}\text{IO}^+$  333.9855; Found 333.9854.

7-Iodo-2-(4-methoxyphenyl)benzofuran (**7c**)



Yield: 67% (39.4 mg, 0.113 mmol); Colorless solid; Mp 99–101  $^\circ\text{C}$ ; TLC  $R_f$  0.51 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.87–7.80 (AA'BB', 2H), 7.60 (dd, 1H,  $J = 7.7, 1.0$  Hz), 7.50 (dd, 1H,  $J = 7.7, 1.0$  Hz), 7.03–6.94 (m, 4H), 3.87 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  160.3, 156.4, 154.9, 132.6, 129.6, 126.7, 124.6, 122.7, 120.6, 114.3, 100.4, 74.6, 55.4; IR (NaCl,  $\text{cm}^{-1}$ ) 807, 1007, 1112, 1235, 1306, 1412, 1614, 2958; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{15}\text{H}_{11}\text{IO}_2^+$  349.9803; Found 349.9804.

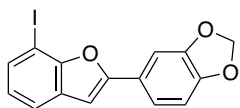
4-(7-Iodobenzofuran-2-yl)-*N,N*-dimethylaniline (**7d**)



Yield: 57% (15.4 mg, 42.4  $\mu\text{mol}$ ); Colorless solid; Mp 166–168  $^\circ\text{C}$ ; TLC  $R_f$  0.87 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.87–7.80 (AA'BB', 2H), 7.55 (dd, 1H,  $J = 7.7, 1.0$  Hz), 7.46 (dd, 1H,  $J = 7.7, 1.0$  Hz), 6.94 (dd, 1H,  $J = 7.7, 7.7$  Hz), 6.87 (s, 1H), 6.82–6.75 (AA'BB', 2H), 3.03 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  157.5, 154.7, 150.8, 131.9, 130.0, 126.4, 124.4, 120.1, 118.0, 112.1, 98.7, 74.5, 40.3; IR (NaCl,

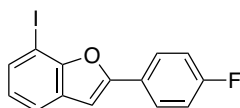
cm<sup>-1</sup>) 841, 1022, 1115, 1212, 1238, 1415, 1458, 2923; HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>INO<sup>+</sup> 364.0193; Found 364.0193.

5-(7-Iodobenzofuran-2-yl)benzo[*d*][1,3]dioxole (7e)



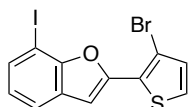
Yield: 71% (27.4 mg, 75.3 μmol); Colorless solid; Mp 107–109 °C; TLC *R<sub>f</sub>* 0.65 (*n*-hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.60 (d, 1H, *J* = 7.7 Hz), 7.49 (d, 1H, *J* = 7.7 Hz), 7.43 (dd, 1H, *J* = 8.1, 1.3 Hz), 7.34 (d, 1H, *J* = 1.3 Hz), 7.00–6.93 (m, 2H), 6.90 (d, 1H, *J* = 8.1 Hz), 6.03 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz): δ 156.1, 154.8, 148.4, 148.1, 132.8, 129.4, 124.7, 124.1, 120.7, 119.5, 108.8, 105.6, 101.5, 100.9, 74.7; IR (NaCl, cm<sup>-1</sup>) 831, 910, 1023, 1105, 1238, 1361, 1435, 1502, 1601, 2779; HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>9</sub>IO<sub>3</sub><sup>+</sup> 363.9596; Found 363.9596.

2-(4-Fluorophenyl)-7-iodobenzofuran (7f)



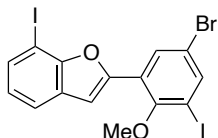
Yield: 72% (20.0 mg, 59.2 μmol); Colorless solid; Mp 67–69 °C; TLC *R<sub>f</sub>* 0.80 (*n*-hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.91–7.83 (AA'BB', 2H), 7.64 (dd, 1H, *J* = 7.7, 1.0 Hz), 7.53 (dd, 1H, *J* = 7.7, 1.0 Hz), 7.20–7.12 (AA'BB', 2H), 7.05 (s, 1H), 6.99 (dd, 1H, *J* = 7.7, 7.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz): δ 164.4, 161.9, 155.2 (d, *J* = 29.6 Hz), 133.2, 127.7 (d, *J* = 304 Hz), 127.0 (d, *J* = 8.5 Hz), 124.8, 120.0, 116.1, 115.9, 101.8 (d, *J* = 1.3 Hz), 74.7; <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 377 MHz): δ -111.6 (s); IR (NaCl, cm<sup>-1</sup>) 807, 976, 1032, 1130, 1233, 1315, 1408, 1504, 2926; HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>8</sub>FIO<sup>+</sup> 337.9606; Found 337.9604.

2-(3-Bromothiophen-2-yl)-7-iodobenzofuran (7g)



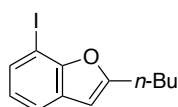
Yield: 69% (21.8 mg, 53.8 μmol); Colorless solid; Mp 146–148 °C; TLC *R<sub>f</sub>* 0.87 (*n*-hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.66 (d, 1H, *J* = 7.7 Hz), 7.60–7.53 (m, 2H), 7.37 (d, 1H, *J* = 5.3 Hz), 7.10 (d, 1H, *J* = 5.3 Hz), 7.01 (dd, 1H, *J* = 7.7, 7.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz): δ 154.3, 149.7, 133.8, 132.1, 128.9, 128.0, 126.4, 125.0, 121.3, 108.9, 104.5, 74.5; IR (NaCl, cm<sup>-1</sup>) 810, 999, 1165, 1292, 1351, 1427, 1568; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>7</sub>BrIOS<sup>+</sup> 403.8365; Found 403.8367.

2-(5-Bromo-3-iodo-2-methoxyphenyl)-7-iodobenzofuran (7h)



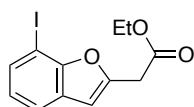
Yield: 75% (14.6 mg, 26.4 μmol); Colorless solid; Mp 152–154 °C; TLC *R<sub>f</sub>* 0.77 (*n*-hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.14 (d, 1H, *J* = 2.4 Hz), 7.92 (d, 1H, *J* = 2.4 Hz), 7.69 (dd, 1H, *J* = 7.7, 0.9 Hz), 7.58 (dd, 1H, *J* = 7.7, 0.9 Hz), 7.50 (s, 1H), 7.03 (dd, 1H, *J* = 7.7, 7.7 Hz), 3.83 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz): δ 155.8, 154.5, 150.0, 141.3, 134.2, 130.7, 129.2, 125.6, 125.0, 121.6, 118.4, 108.4, 93.8, 74.8, 60.3; IR (NaCl, cm<sup>-1</sup>) 856, 990, 1035, 1132, 1238, 1374, 1458, 1541; HRMS (ESI) *m/z*: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>BrI<sub>2</sub>NO<sub>2</sub><sup>+</sup> 571.8214; Found 571.8217.

2-Butyl-7-iodobenzofuran (7i)



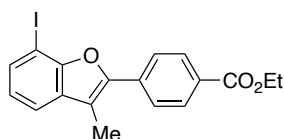
Yield: 51% (10.3 mg, 34.3  $\mu\text{mol}$ ); Colorless solid; Mp 67–69 °C; TLC  $R_f$  0.63 (*n*-hexane/EtOAc = 10/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.56 (dd, 1H,  $J = 7.7, 1.0$  Hz), 7.42 (dd, 1H,  $J = 7.7, 1.0$  Hz), 6.93 (dd, 1H,  $J = 7.7, 7.7$  Hz), 6.48 (s, 1H), 2.81 (dd, 2H,  $J = 7.5, 7.5$  Hz), 1.80–1.69 (m, 2H), 1.50–1.37 (m, 2H), 0.97 (t, 3H,  $J = 7.5$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  160.5, 154.9, 132.0, 129.1, 124.2, 120.2, 102.8, 74.5, 29.7, 28.1, 22.3, 13.8; IR (NaCl,  $\text{cm}^{-1}$ ) 821, 1016, 1119, 1285, 1322, 1415, 1505, 1617, 1906, 2919; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{12}\text{H}_{13}\text{IO}^+$  300.0012; Found 300.0011.

Ethyl 2-(7-iodobenzofuran-2-yl)acetate (7j)



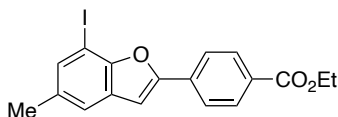
Yield: 21% (8.0 mg, 24  $\mu\text{mol}$ ); Colorless oil; TLC  $R_f$  0.57 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.61 (dd, 1H,  $J = 7.7, 1.0$  Hz), 7.48 (dd, 1H,  $J = 7.7, 1.0$  Hz), 6.97 (dd, 1H,  $J = 7.7, 7.7$  Hz), 6.76 (s, 1H), 4.23 (q, 2H,  $J = 7.1$  Hz), 3.87 (s, 2H), 1.30 (t, 3H,  $J = 7.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  168.6, 155.1, 151.5, 133.0, 128.6, 125.0, 120.8, 106.1, 74.6, 61.5, 34.6, 14.2; IR (NaCl,  $\text{cm}^{-1}$ ) 810, 930, 1016, 1182, 1312, 1418, 1574, 1721, 2980; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{12}\text{H}_{12}\text{IO}_3^+$  330.9826; Found 330.9824.

Ethyl 4-(7-iodo-3-methylbenzofuran-2-yl)benzoate (7k)



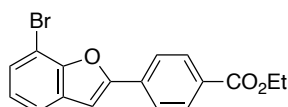
Yield: 41% (8.4 mg, 21  $\mu\text{mol}$ ); Colorless solid; Mp 116–118 °C; TLC  $R_f$  0.60 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.20–8.13 (AA'BB', 2H), 7.96–7.88 (AA'BB', 2H), 7.69 (dd, 1H,  $J = 7.7, 0.9$  Hz), 7.52 (dd, 1H,  $J = 7.7, 0.9$  Hz), 7.04 (dd, 1H,  $J = 7.7, 7.7$  Hz), 4.42 (q, 2H,  $J = 7.1$  Hz), 2.50 (s, 3H), 1.43 (t, 3H,  $J = 7.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.3, 154.3, 150.0, 134.9, 133.9, 131.0, 129.9, 129.7, 126.4, 124.3, 120.0, 114.3, 74.9, 61.2, 14.4, 10.0; IR (NaCl,  $\text{cm}^{-1}$ ) 855, 1010, 1109, 1272, 1366, 1419, 1608, 1714; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{IO}_3^+$  407.0139; Found 407.0138.

Ethyl 4-(7-iodo-5-methylbenzofuran-2-yl)benzoate (7l)



Yield: 62% (6.9 mg, 17  $\mu\text{mol}$ ); Colorless solid; Mp 117–119 °C; TLC  $R_f$  0.56 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.16–8.09 (AA'BB', 2H), 7.96–7.90 (AA'BB', 2H), 7.51 (s, 1H), 7.34 (s, 1H), 7.16 (s, 1H), 4.41 (q, 2H,  $J = 7.1$  Hz), 2.42 (s, 3H), 1.42 (t, 3H,  $J = 7.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.2, 155.1, 153.9, 135.0, 134.8, 133.9, 130.3, 130.1, 128.9, 124.7, 121.2, 103.9, 74.3, 61.2, 20.9, 14.4; IR (NaCl,  $\text{cm}^{-1}$ ) 841, 1022, 1106, 1115, 1610, 1714; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{IO}_3^+$  407.0139; Found 407.0138.

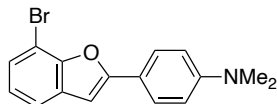
Ethyl 4-(7-bromobenzofuran-2-yl)benzoate (8a)



Yield: 25% (8.5 mg, 25  $\mu\text{mol}$ ); Colorless solid; Mp 96–98 °C; TLC  $R_f$  0.48 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.18–8.10 (AA'BB', 2H), 7.99–7.91 (AA'BB', 2H), 7.55 (dd, 1H,  $J = 7.8, 1.0$  Hz), 7.48 (dd, 1H,  $J = 7.8, 1.0$  Hz), 7.20 (s, 1H), 7.13 (dd, 1H,  $J = 7.8, 7.8$  Hz), 4.41 (q, 2H,  $J = 7.1$  Hz), 1.43 (t, 3H,  $J = 7.1$  Hz).

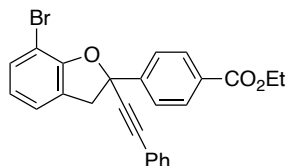
Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.1, 155.4, 152.3, 133.7, 130.5, 130.2, 130.1, 128.0, 124.8, 124.5, 120.4, 104.1, 103.9, 61.2, 14.4; IR ( $\text{NaCl}$ ,  $\text{cm}^{-1}$ ) 855, 1010, 1106, 1508, 1560, 1654; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{14}\text{BrO}_3^+$  345.0121; Found 345.0119.

4-(7-Bromobenzofuran-2-yl)-*N,N*-dimethylaniline (**8b**)



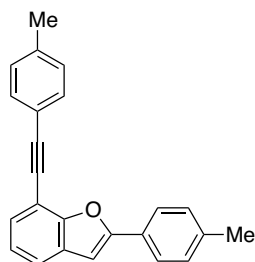
Yield: 34% (13.3 mg, 42.2  $\mu\text{mol}$ ); Colorless solid; Mp 111–113  $^\circ\text{C}$ ; TLC  $R_f$  0.56 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.80–7.74 (AA'BB', 2H), 7.44 (dd, 1H,  $J$  = 7.8, 1.0 Hz), 7.35 (dd, 1H,  $J$  = 7.8, 1.0 Hz), 7.06 (dd, 1H,  $J$  = 7.8, 7.8 Hz), 6.84 (s, 1H), 6.80–6.74 (AA'BB', 2H), 3.03 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  157.9, 151.6, 150.8, 131.2, 126.4, 126.0, 123.9, 119.2, 117.8, 112.0, 103.6, 98.5, 40.3; IR ( $\text{NaCl}$ ,  $\text{cm}^{-1}$ ) 847, 999, 1033, 1173, 1201, 1329, 1445, 1505, 1651; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{15}\text{BrNO}^+$  316.0332; Found 316.0329.

Ethyl 4-(7-bromo-2-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)benzoate (**9a**)



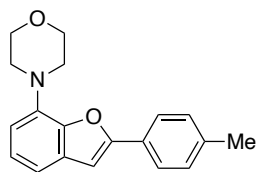
Yield: 21% (9.1 mg, 20  $\mu\text{mol}$ ); Colorless oil; TLC  $R_f$  0.39 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.10–8.04 (AA'BB', 2H), 7.78–7.71 (AA'BB', 2H), 7.50–7.43 (AA'BB'C, 2H), 7.40–7.27 (m, 4H), 7.10 (dd, 1H,  $J$  = 7.4, 1.1 Hz), 6.82 (dd, 1H,  $J$  = 7.4, 7.4 Hz), 4.38 (q, 2H,  $J$  = 7.1 Hz), 4.07 (d, 1H,  $J$  = 15.8 Hz), 3.69 (d, 1H,  $J$  = 15.8 Hz), 1.39 (t, 3H,  $J$  = 7.1 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.2, 155.8, 147.2, 132.0, 131.8, 130.5, 129.9, 129.0, 128.3, 126.6, 125.2, 123.8, 122.7, 121.8, 102.9, 88.7, 87.6, 84.7, 61.1, 48.4, 14.3; IR ( $\text{NaCl}$ ,  $\text{cm}^{-1}$ ) 859, 964, 1023, 1107, 1275, 1368, 1408, 1584, 1611, 2236; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{20}\text{BrO}_3^+$  447.0590; Found 447.0589.

2-(*p*-Tolyl)-7-(*p*-tolylethynyl)benzofuran (**10**)



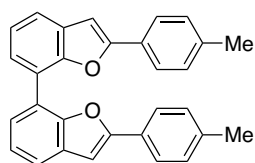
Yield: 97% (15.6 mg, 48.4  $\mu\text{mol}$ ); Colorless solid; Mp 118–120  $^\circ\text{C}$ ; TLC  $R_f$  0.73 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.85–7.79 (AA'BB', 2H), 7.59–7.51 (m, 3H), 7.43 (dd, 1H,  $J$  = 7.5, 1.2 Hz), 7.30–7.24 (AA'BB', 2H), 7.24–7.17 (m, 3H), 6.99 (s, 1H), 2.410 (s, 3H), 2.405 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  156.6, 154.5, 138.9, 138.6, 131.7, 129.51, 129.45, 129.2, 127.5, 127.4, 125.1, 122.9, 121.0, 120.3, 107.5, 100.7, 94.0, 83.4, 21.6, 21.5; IR ( $\text{NaCl}$ ,  $\text{cm}^{-1}$ ) 841, 1022, 1115, 1212, 1508, 1654; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}^+$  322.1358; Found 322.1360.

4-(2-(*p*-Tolyl)benzofuran-7-yl)morpholine (**11**)



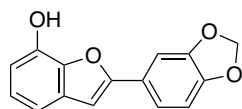
Yield: 64% (18.8 mg, 64.2  $\mu\text{mol}$ ); Colorless solid; Mp 109–111  $^{\circ}\text{C}$ ; TLC  $R_f$  0.50 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.76–7.68 (AA'BB', 2H), 7.30–7.23 (AA'BB', 2H), 7.21 (dd, 1H,  $J$  = 7.7, 1.1 Hz), 7.15 (dd, 1H,  $J$  = 7.7, 7.7 Hz), 6.95 (s, 1H), 6.75 (dd, 1H,  $J$  = 7.7, 1.1 Hz), 4.06–3.97 (AA'BB', 4H), 3.45–3.37 (AA'BB', 4H), 2.40 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  155.5, 146.3, 137.0, 130.6, 129.5, 127.7, 124.8, 123.8, 114.2, 110.9, 101.0, 67.1, 50.3, 21.4; IR (NaCl,  $\text{cm}^{-1}$ ) 893, 920, 1035, 1271, 1487, 1508, 1607; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$  294.1489; Found 294.1490.

2,2'-Di-*p*-tolyl-7,7'-bibenzofuran (**12**)



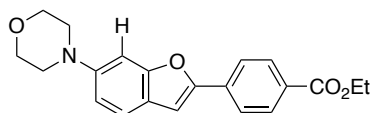
Yield: 58% (5.8 mg, 14  $\mu\text{mol}$ ); Colorless solid; Mp 194–196  $^{\circ}\text{C}$ ; TLC  $R_f$  0.63 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.89 (dd, 2H,  $J$  = 7.6, 1.2 Hz), 7.75–7.68 (AA'BB', 4H), 7.64 (dd, 2H,  $J$  = 7.6, 1.2 Hz), 7.89 (dd, 2H,  $J$  = 7.6, 7.6 Hz), 7.22–7.15 (AA'BB', 4H), 7.08 (s, 2H), 2.37 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  156.3, 152.1, 138.6, 130.2, 129.4, 127.6, 125.3, 125.0, 123.2, 120.7, 120.3, 100.7, 21.4; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{30}\text{H}_{22}\text{O}_2^+$  414.1620; Found 414.1622.

2-(Benzo[*d*][1,3]dioxol-5-yl)benzofuran-7-ol (**13**)



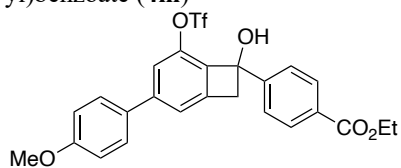
Yield: 42% (6.2 mg, 24  $\mu\text{mol}$ ); Colorless solid; Mp 137–139  $^{\circ}\text{C}$ ; TLC  $R_f$  0.26 (*n*-hexane/EtOAc = 3/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.39 (dd, 1H,  $J$  = 8.1, 1.7 Hz), 7.31 (d, 1H,  $J$  = 1.7 Hz), 7.15–7.06 (m, 2H), 6.91–6.85 (m, 2H), 6.81 (dd, 1H,  $J$  = 7.4, 1.5 Hz), 6.03 (s, 2H), 5.30 (br s, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  155.9, 148.18, 148.16, 142.8, 140.6, 130.9, 124.5, 123.9, 119.2, 113.1, 110.5, 108.8, 105.5, 101.4, 101.0; IR (NaCl,  $\text{cm}^{-1}$ ) 930, 1040, 1106, 1233, 1451, 1504, 1595; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{O}_4^+$  254.0581; Found 254.0579.

Ethyl 4-(6-morpholinobenzofuran-2-yl)benzoate (**15**)



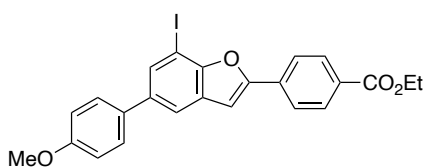
Yield: 42% (7.4 mg, 21  $\mu\text{mol}$ ); Green solid; Mp 157–159  $^{\circ}\text{C}$ ; TLC  $R_f$  0.51 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.14–8.05 (AA'BB', 2H), 7.90–7.85 (AA'BB', 2H), 7.47 (d, 1H,  $J$  = 8.6 Hz), 7.10–7.02 (m, 2H), 6.94 (dd, 1H,  $J$  = 8.6, 2.1 Hz), 4.40 (q, 2H,  $J$  = 7.2 Hz), 3.97–3.85 (AA'BB', 4H), 3.28–3.16 (AA'BB', 4H), 1.42 (t, 3H,  $J$  = 7.2 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.3, 156.6, 153.7, 150.3, 134.7, 130.1, 129.4, 124.0, 122.0, 121.4, 113.7, 103.4, 98.2, 66.9, 61.0, 50.1, 14.4; IR (NaCl,  $\text{cm}^{-1}$ ) 816, 964, 1122, 1271, 1448, 1607, 1713; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{22}\text{NO}_4^+$  352.1543; Found 352.1540.

Ethyl 4-(7-hydroxy-3-(4-methoxyphenyl)-5-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4m**)



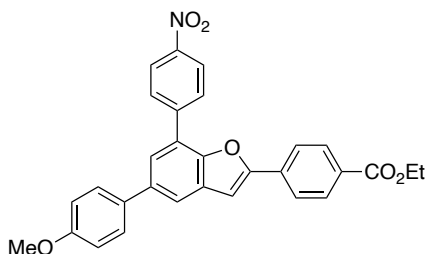
Yield: 80% (125 mg, 0.239 mmol); Colorless oil; TLC  $R_f$  0.52 (*n*-hexane/EtOAc = 3/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.09–8.01 (AA'BB', 2H), 7.57–7.43 (m, 5H), 7.28 (s, 1H), 7.04–6.95 (AA'BB', 2H), 4.37 (q, 2H,  $J$  = 7.1 Hz), 3.86 (s, 3H), 3.79–3.64 (m, 2H), 3.60 (d, 1H,  $J$  = 14.4 Hz), 1.39 (t, 3H,  $J$  = 7.1 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.4, 160.0, 147.2, 146.2, 145.9, 141.3, 136.4, 132.0, 130.1, 129.9, 128.5, 125.2, 123.0, 118.6 (q,  $J$  = 322 Hz), 118.4, 115.2, 80.3, 61.1, 55.4, 49.8, 14.3;  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 367 MHz):  $\delta$  -72.9 (s); IR (NaCl,  $\text{cm}^{-1}$ ) 934, 1063, 1123, 1245, 1368, 1574, 2840, 2938; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{22}\text{F}_3\text{O}_7\text{S}^+$  523.1033; Found 523.1033.

Ethyl 4-(7-iodo-5-(4-methoxyphenyl)benzofuran-2-yl)benzoate (**7m**)



Yield: 47% (20.0 mg, 40.2  $\mu\text{mol}$ ); Colorless solid; Mp 146–148  $^\circ\text{C}$ ; TLC  $R_f$  0.50 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.19–8.10 (AA'BB', 2H), 8.01–7.92 (AA'BB', 2H), 7.86 (d, 1H,  $J$  = 1.6 Hz), 7.68 (d, 1H,  $J$  = 1.6 Hz), 7.57–7.48 (AA'BB', 2H), 7.26 (s, 1H), 7.03–6.96 (AA'BB', 2H), 4.42 (q, 2H,  $J$  = 7.1 Hz), 3.87 (s, 3H), 1.30 (t, 3H,  $J$  = 7.1 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.2, 159.3, 155.6, 154.5, 138.6, 133.7, 133.2, 132.7, 130.5, 130.1, 129.2, 128.4, 124.8, 119.3, 114.3, 104.3, 75.0, 61.2, 55.4, 14.4; IR (NaCl,  $\text{cm}^{-1}$ ) 820, 910, 1110, 1231, 1365, 1517, 1614, 1713; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{IO}_4^+$  499.0401; Found 499.0401.

Ethyl 4-(5-(4-methoxyphenyl)-7-(4-nitrophenyl)benzofuran-2-yl)benzoate (**17**)



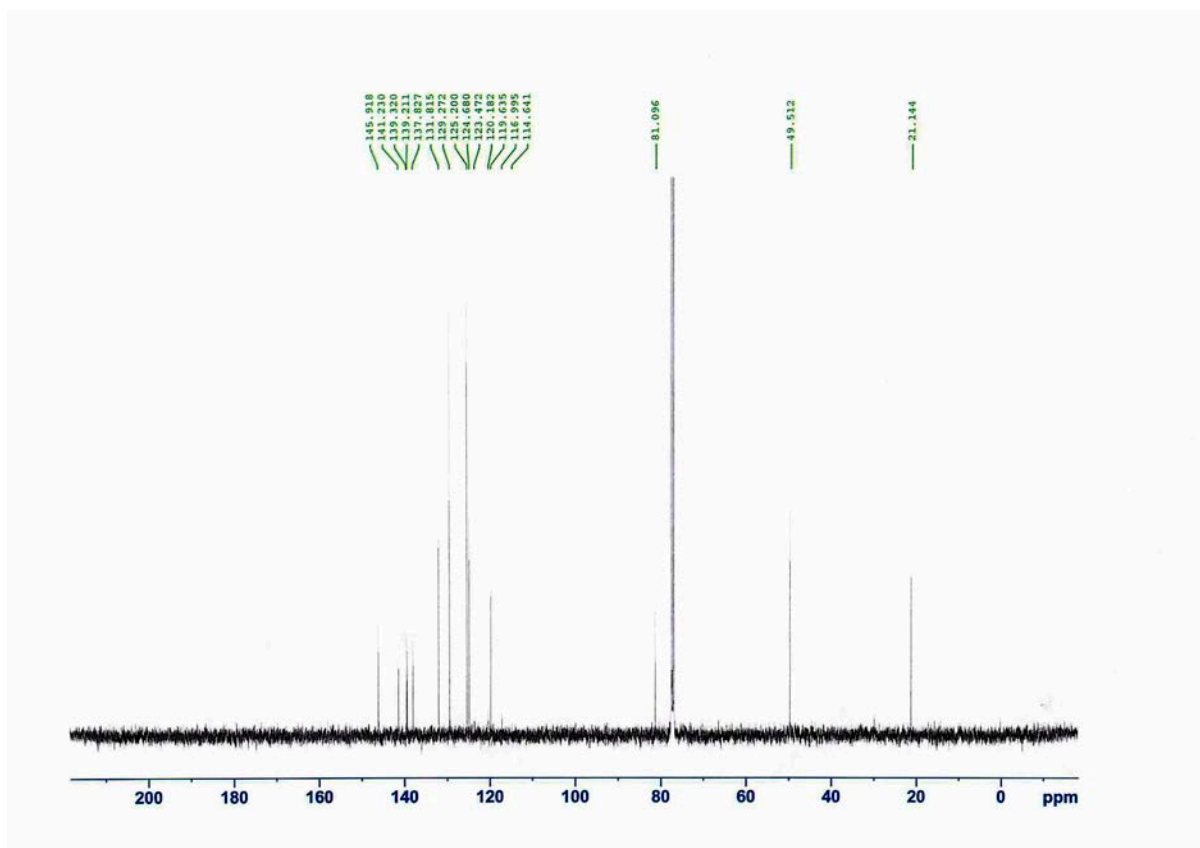
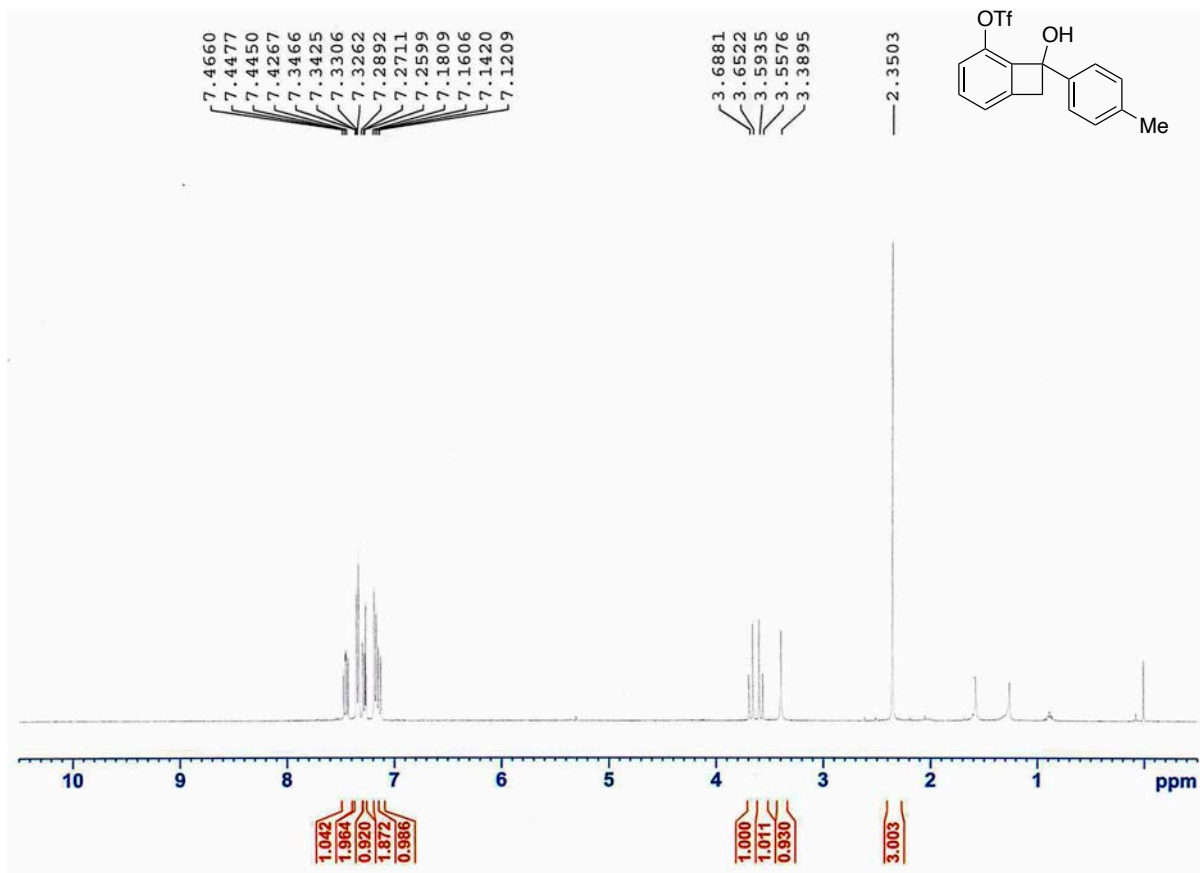
Yield: 79% (3.6 mg, 7.3  $\mu\text{mol}$ ); Yellow solid; Mp 163–165  $^\circ\text{C}$ ; TLC  $R_f$  0.50 (*n*-hexane/EtOAc = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.47–8.40 (AA'BB', 2H), 8.19–8.12 (m, 4H), 7.96–7.90 (AA'BB', 2H), 7.81 (d, 1H,  $J$  = 1.8 Hz), 7.68 (d, 1H,  $J$  = 1.8 Hz), 7.64–7.58 (AA'BB', 2H), 7.27 (s, 1H), 7.08–7.01 (AA'BB', 2H), 4.42 (q, 2H,  $J$  = 7.1 Hz), 3.89 (s, 3H), 1.43 (t, 3H,  $J$  = 7.1 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  166.1, 159.3, 155.9, 151.4, 147.3, 143.0, 137.6, 133.8, 133.4, 130.7, 130.6, 130.2, 129.3, 128.5, 124.7, 124.2, 124.1, 123.1, 120.1, 114.4, 103.7, 61.2, 55.4, 14.4; IR (NaCl,  $\text{cm}^{-1}$ ) 820, 910, 1110, 1231, 1365, 1517, 1614, 1713; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{30}\text{H}_{24}\text{NO}_6^+$  494.1599; Found 494.1599.

### References for Supporting Information

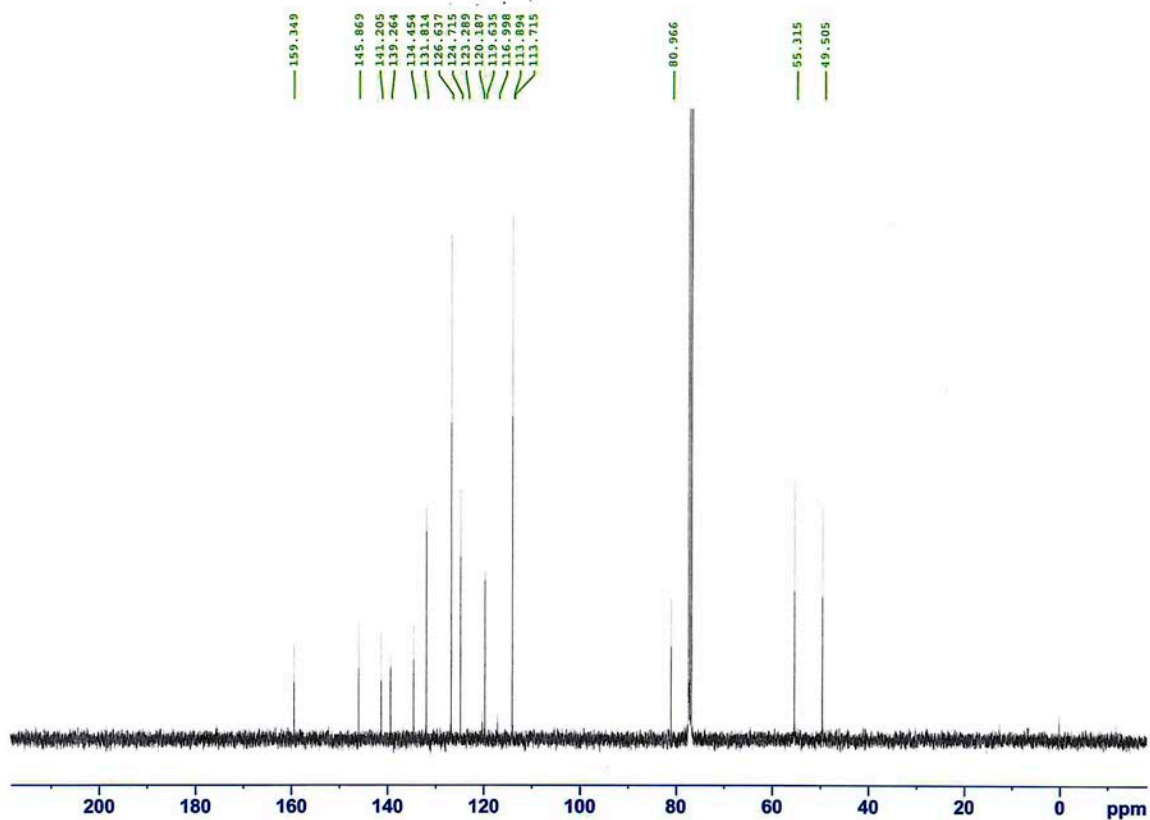
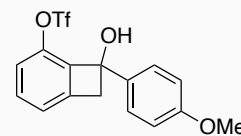
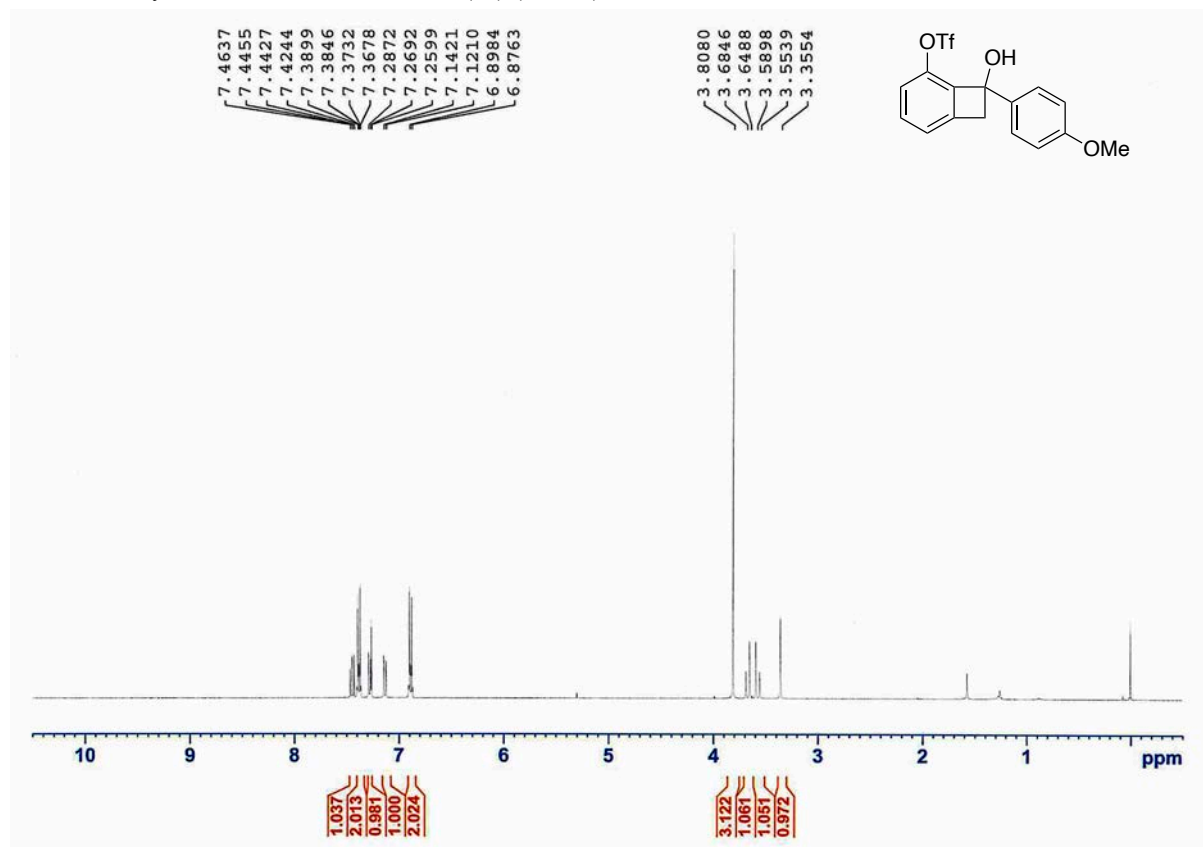
- S1 Y. Hoshi, S. Tabata, S. Yoshida, *Chem. Commun.* **2025**, 61, 3752.
- S2 K. Uchida, Y. Minami, S. Yoshida, T. Hosoya, *Org. Lett.* **2019**, 21, 9019.
- S3 K. Uchida, S. Yoshida, T. Hosoya, *Synthesis* **2016**, 48, 4099.
- S4 K. Uchida, S. Yoshida, T. Hosoya, *Org. Lett.* **2017**, 19, 1184.
- S5 T. Dao-Huy, M. Haider, F. Glatz, M. Schnürch, M. D. Mihovilovic, *Eur. J. Org. Chem.* **2014**, 8119.

### <sup>1</sup>H and <sup>13</sup>C NMR Spectra of New Compounds

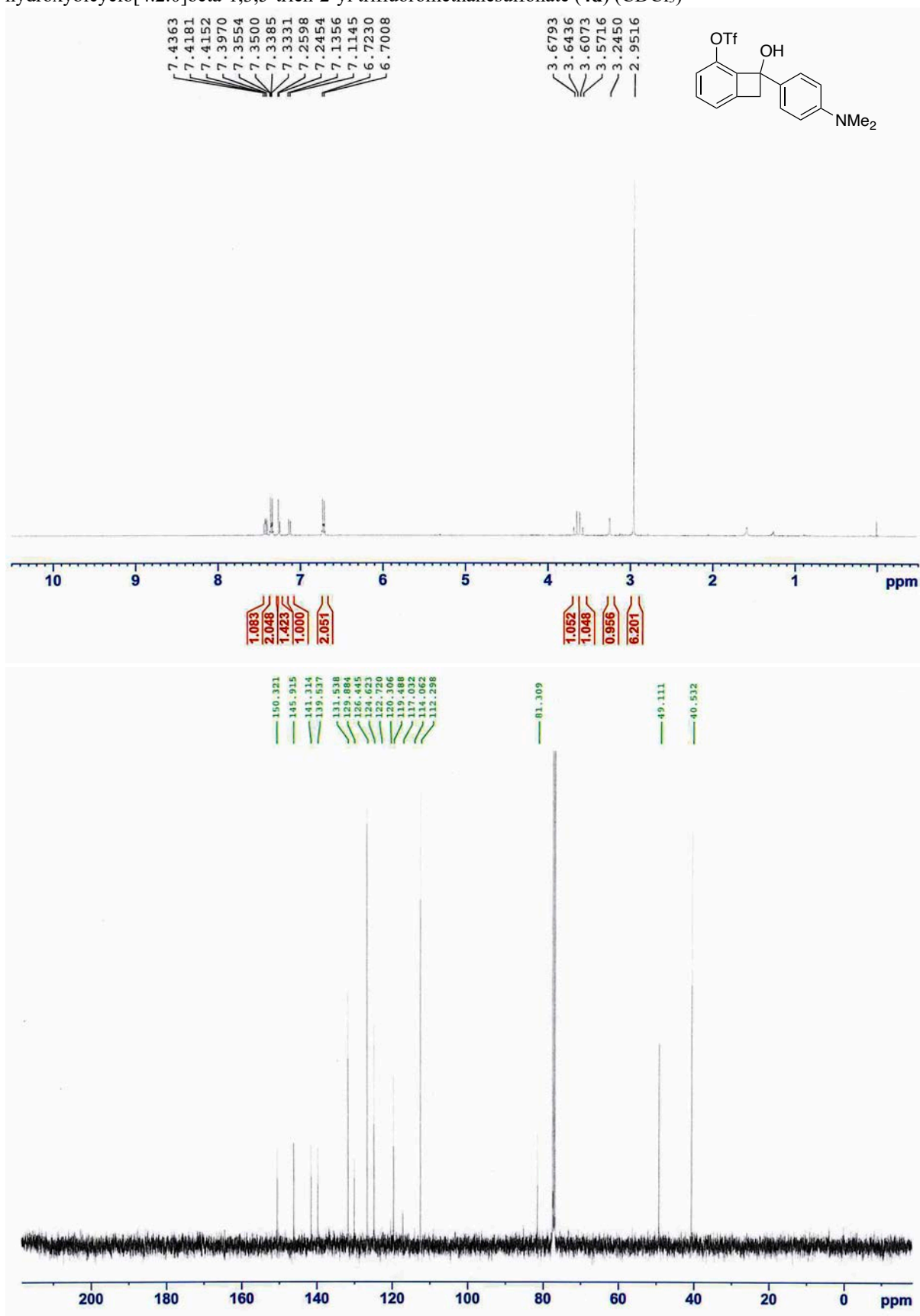
<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (101 MHz) spectra of 8-hydroxy-8-(*p*-tolyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4b**) (CDCl<sub>3</sub>)



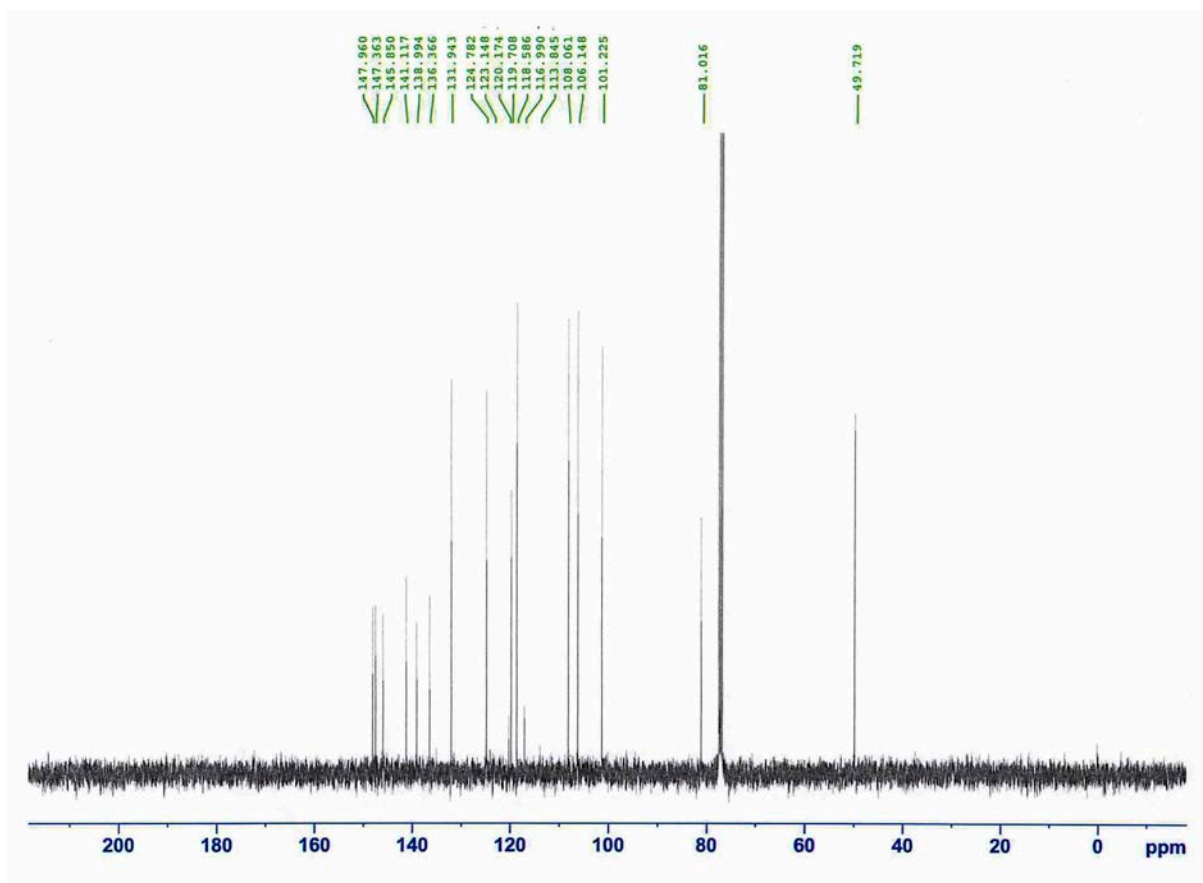
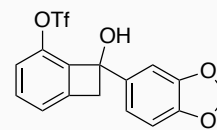
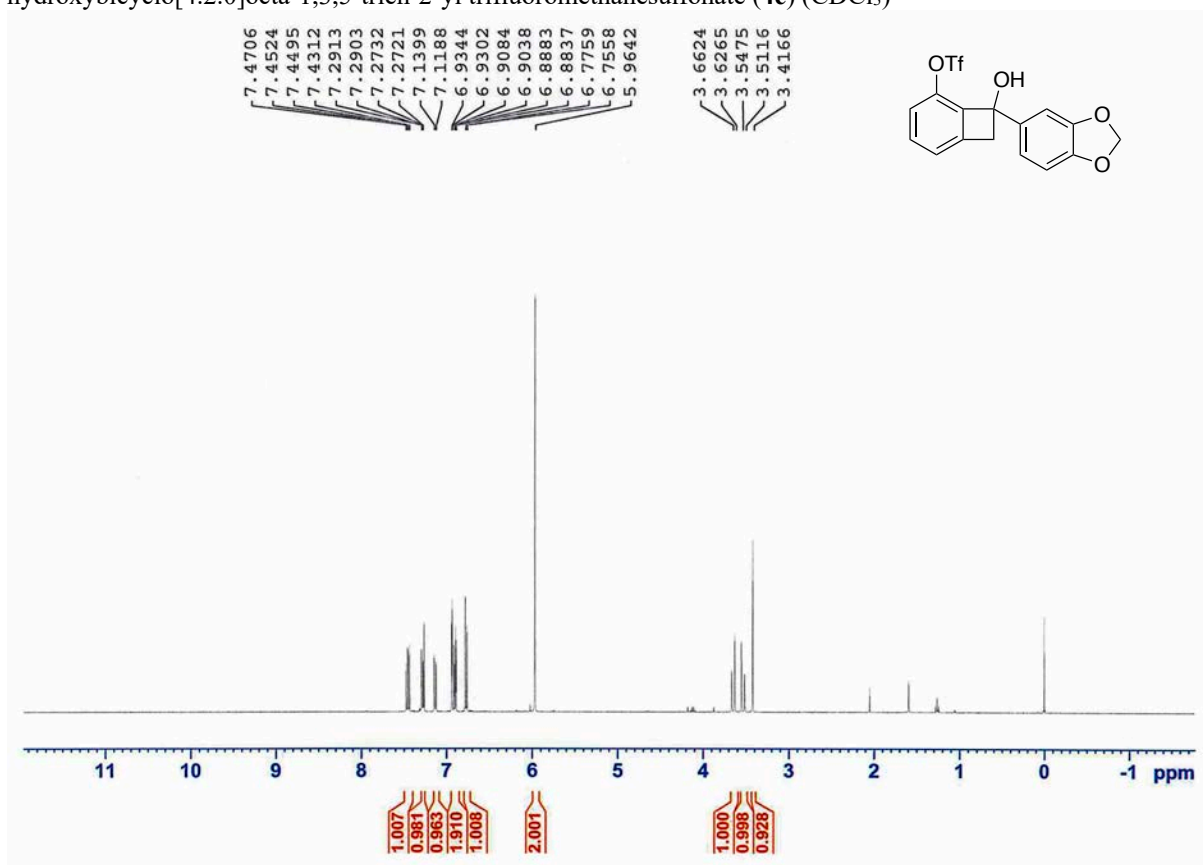
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of 8-hydroxy-8-(4-methoxyphenyl)bicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4c**) ( $\text{CDCl}_3$ )



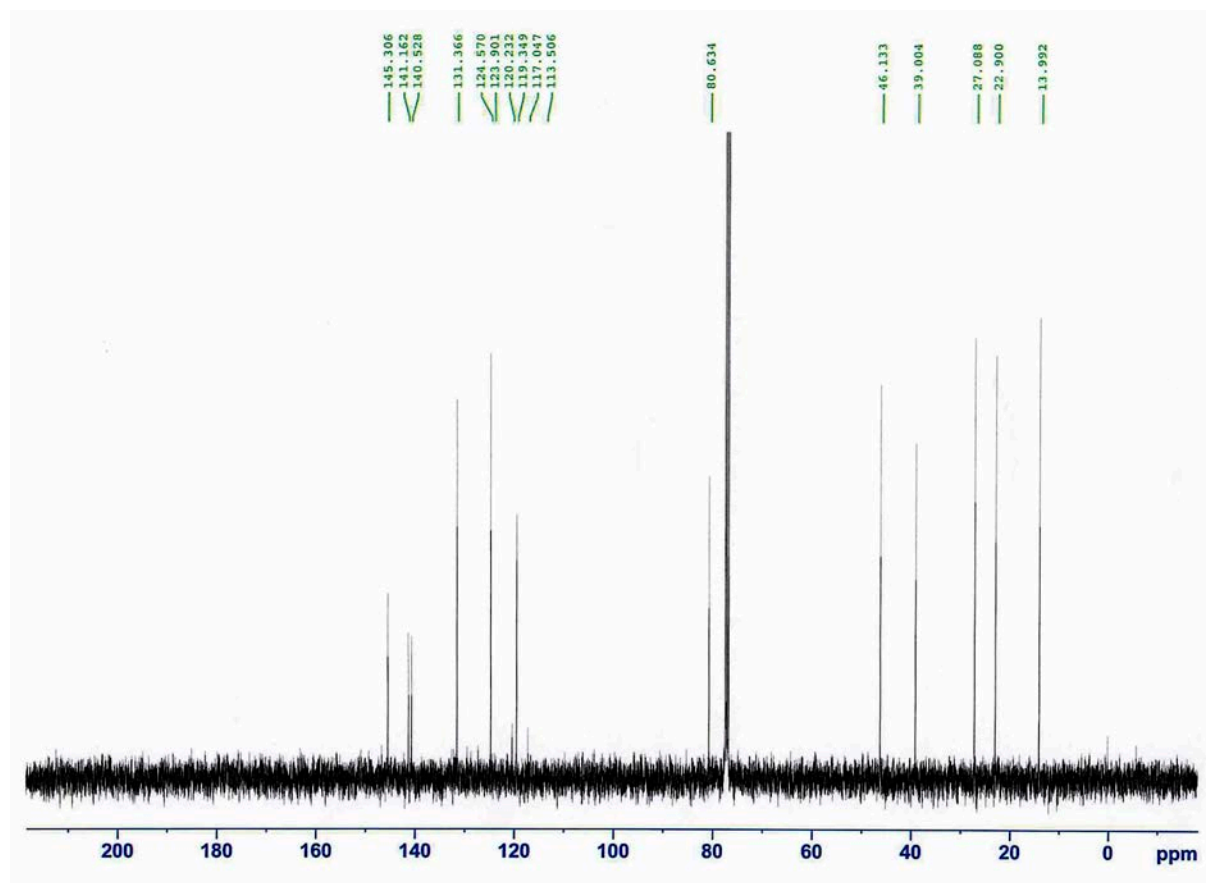
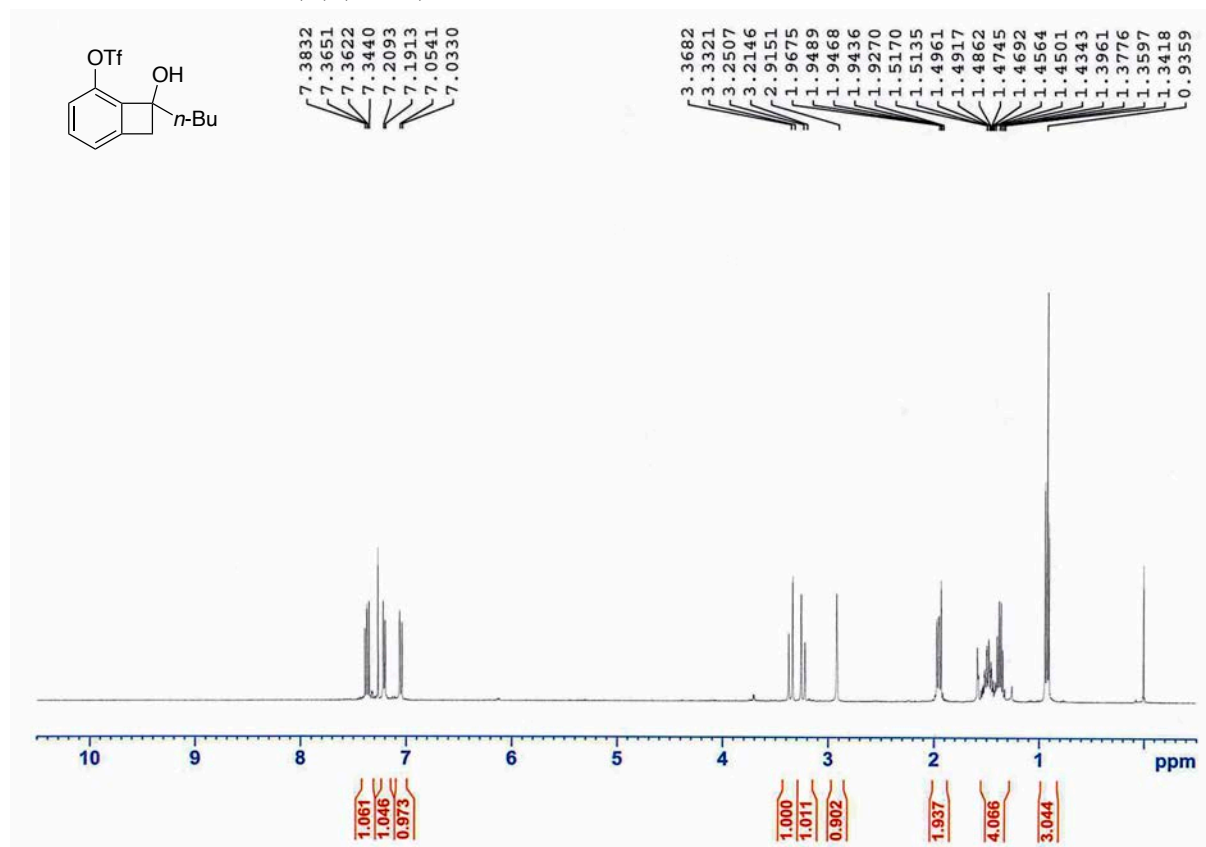
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of 8-(4-(dimethylamino)phenyl)-8-hydroxybicyclo[4.2.0]octa-1,3,5-trien-2-yl trifluoromethanesulfonate (**4d**) ( $\text{CDCl}_3$ )



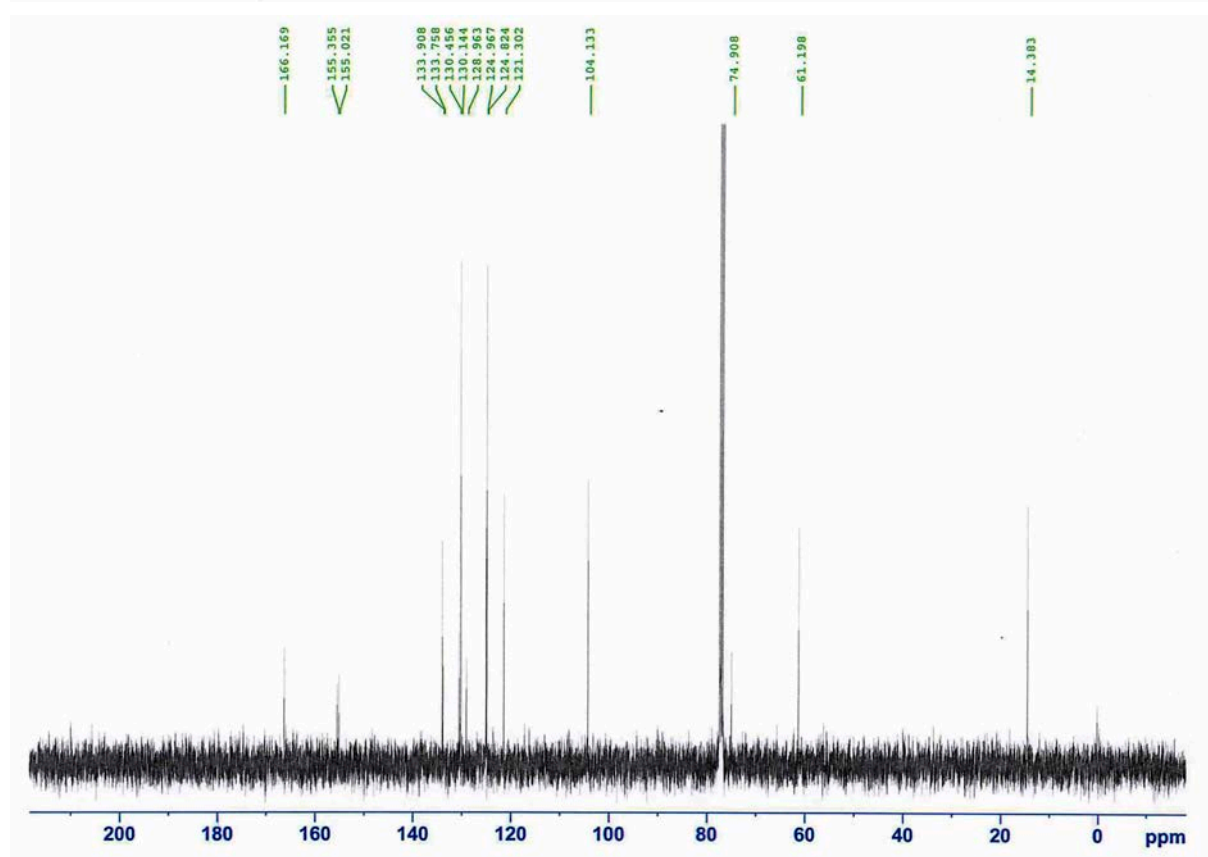
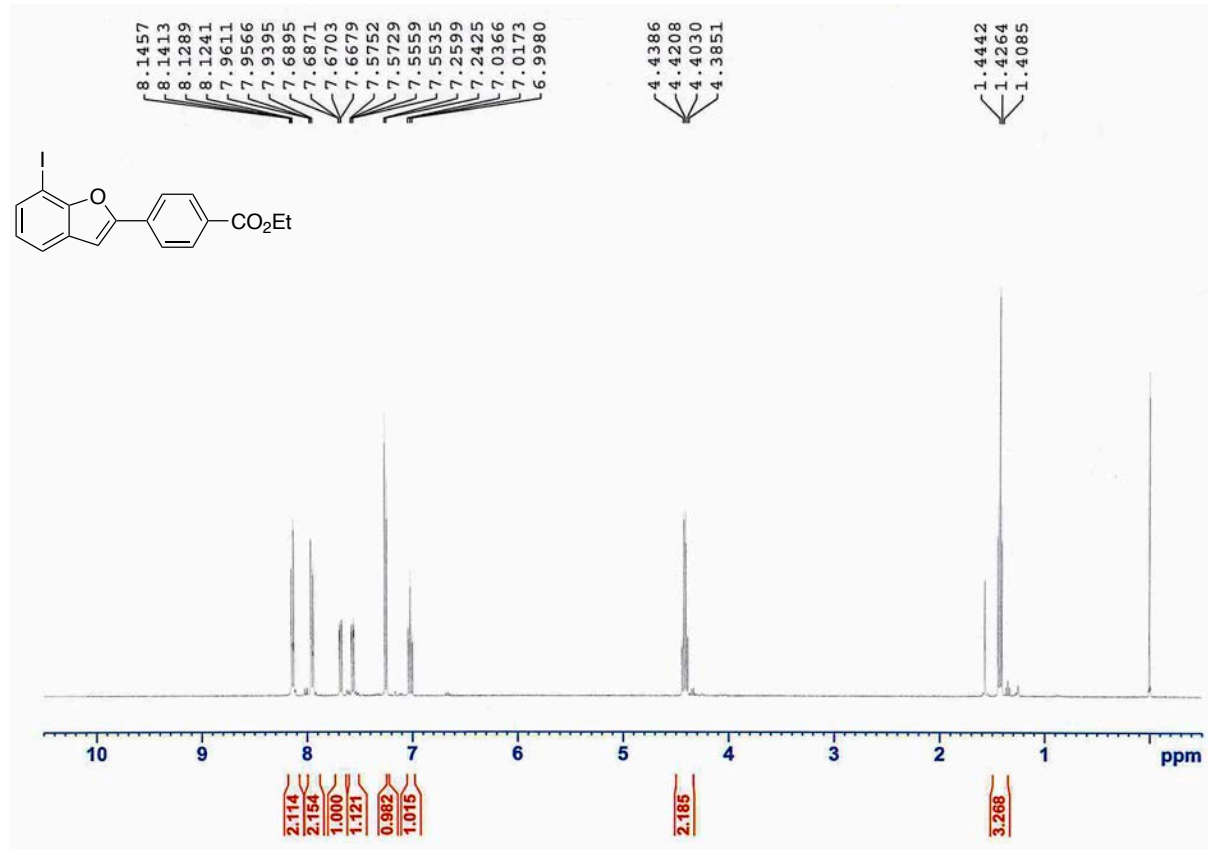
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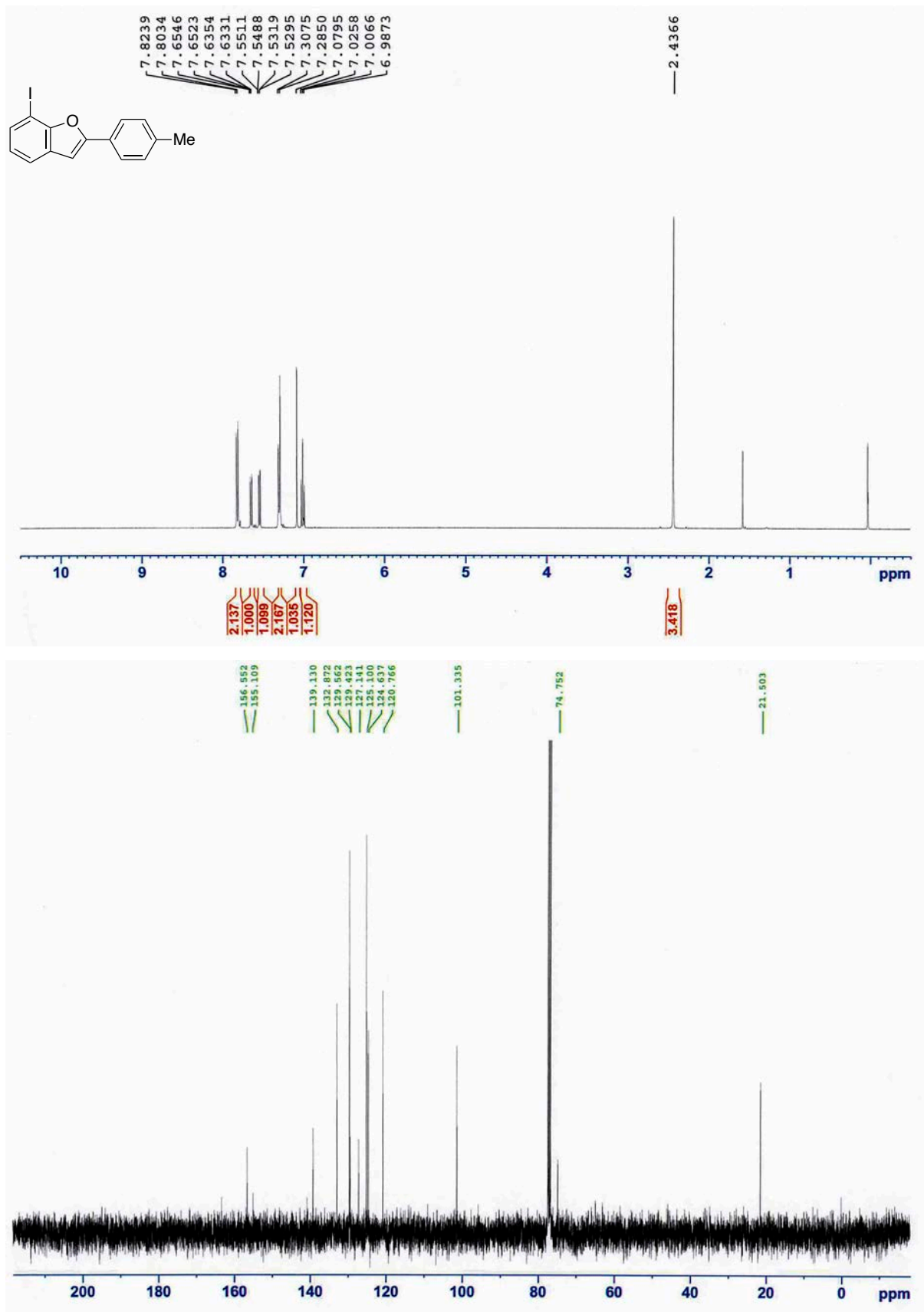
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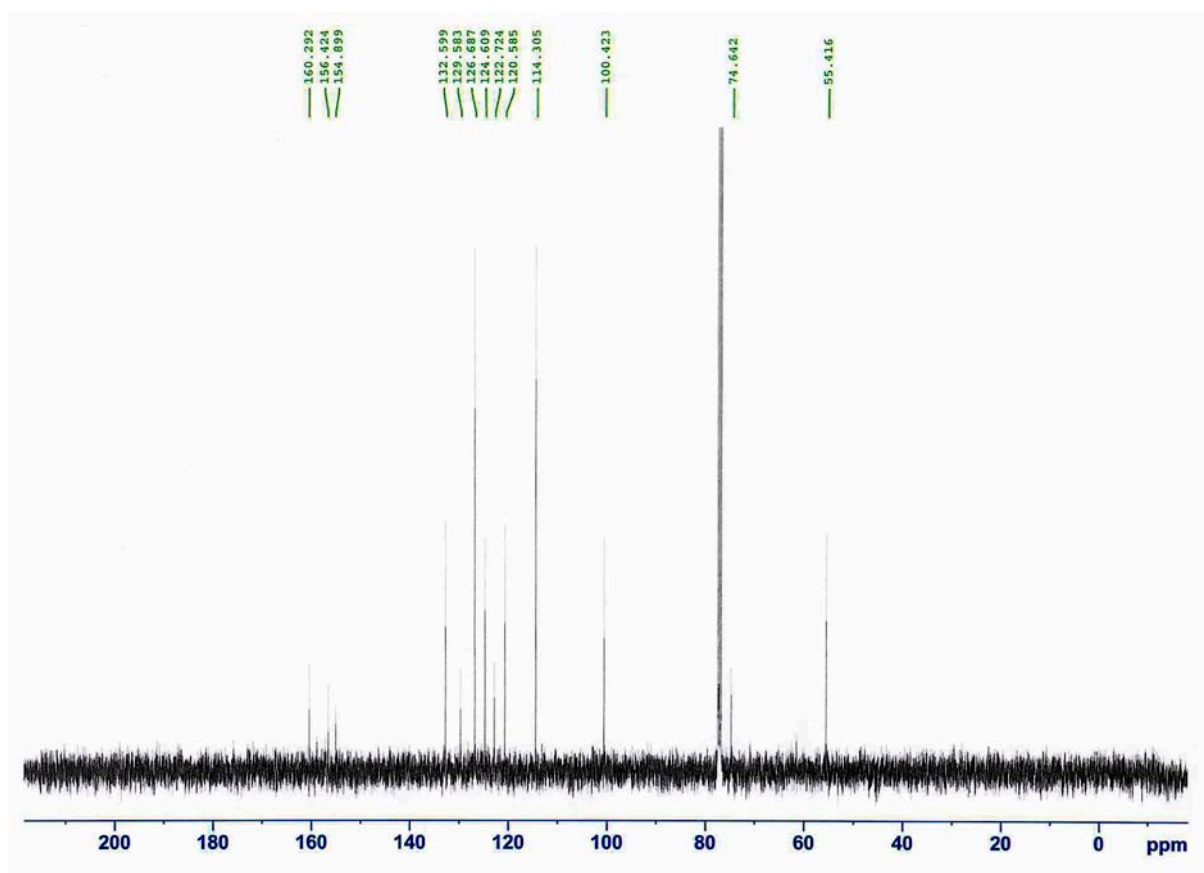
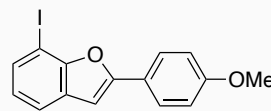
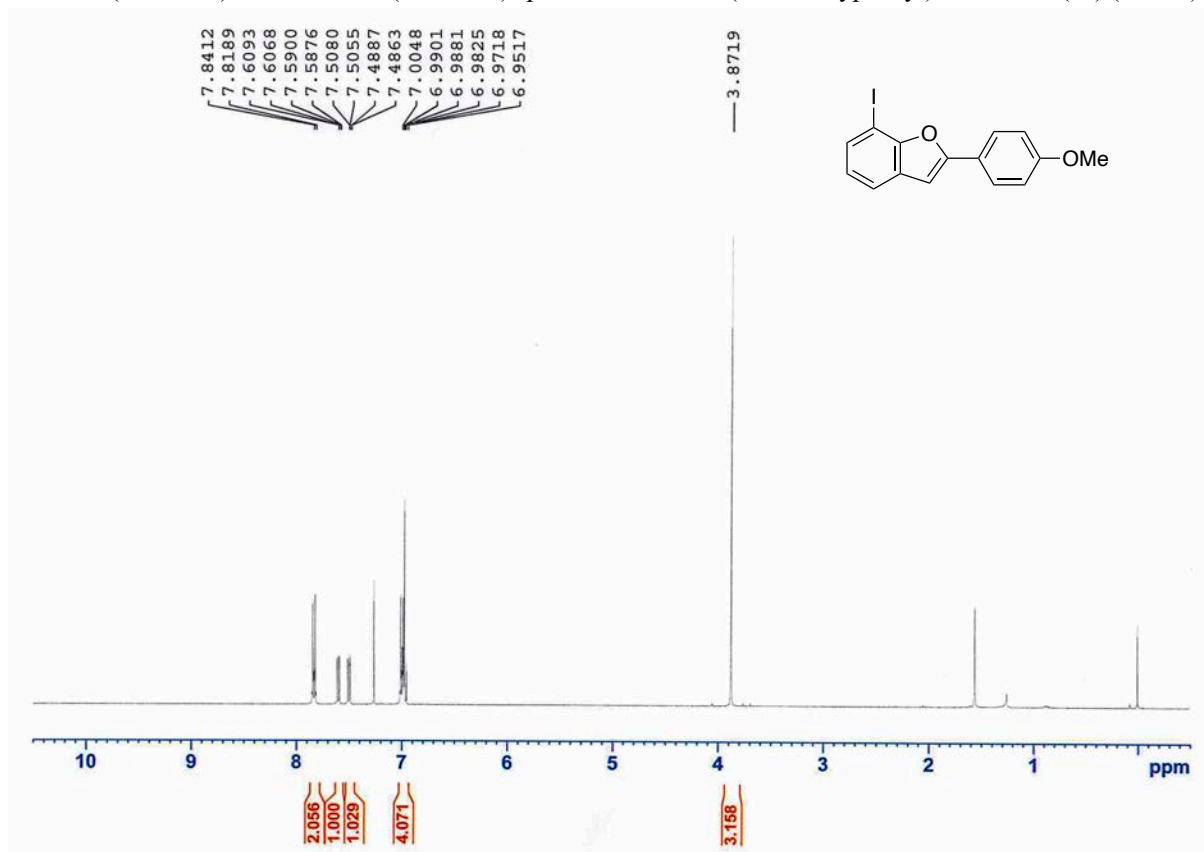
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of ethyl 4-(7-iodo-benzofuran-2-yl)benzoate (**7a**) ( $\text{CDCl}_3$ )



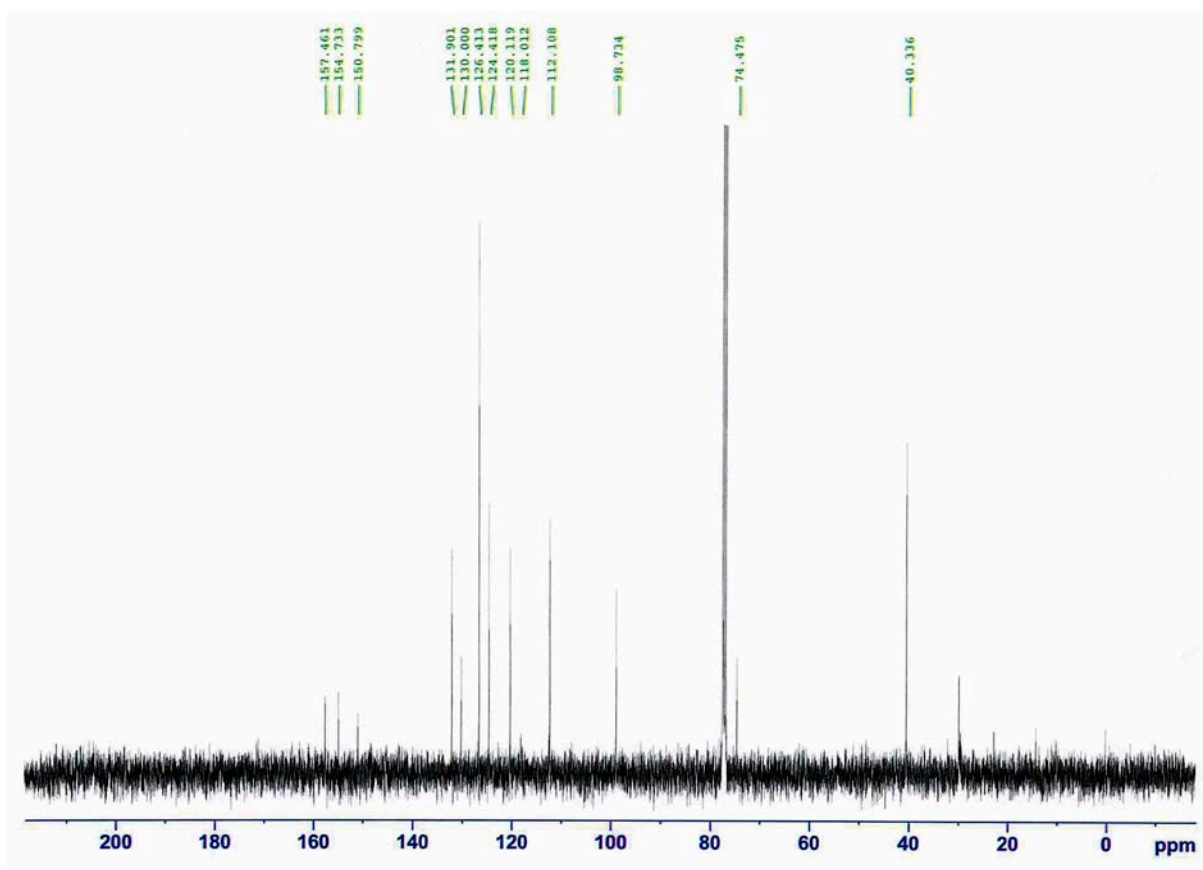
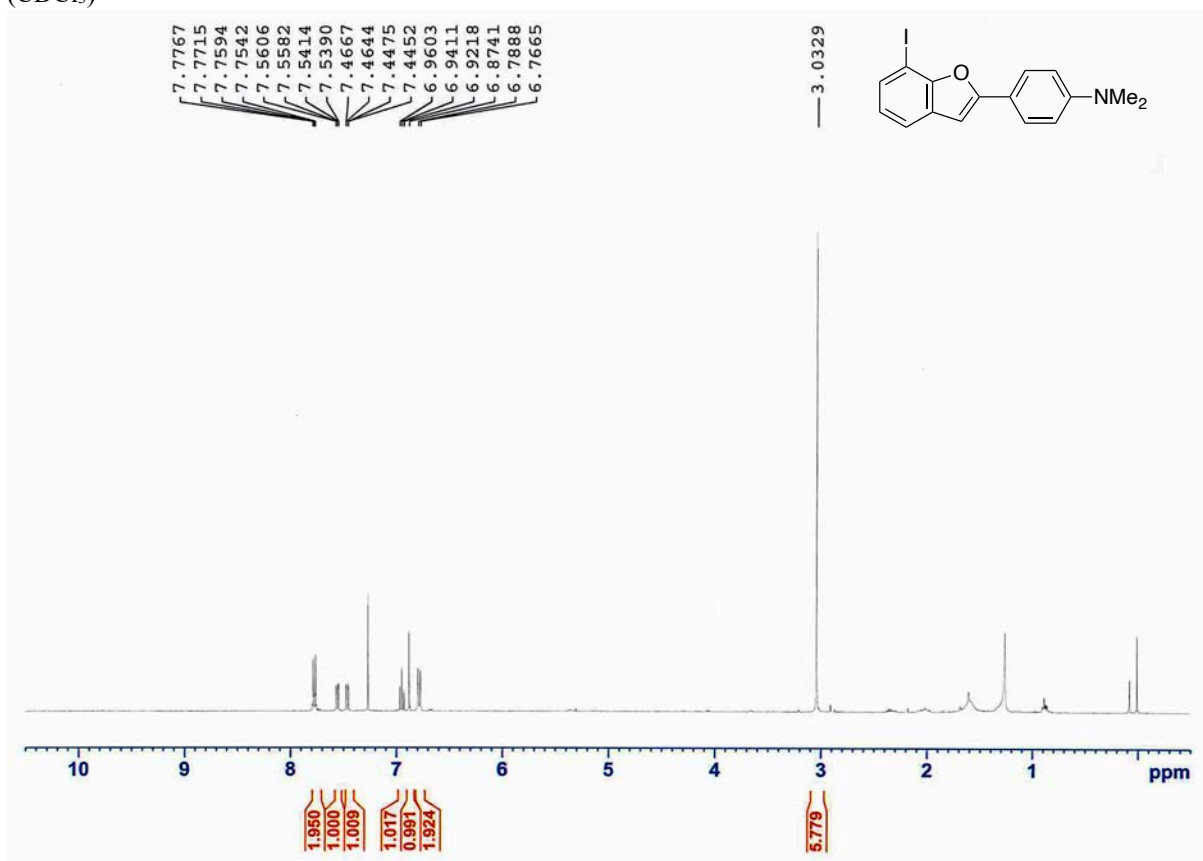
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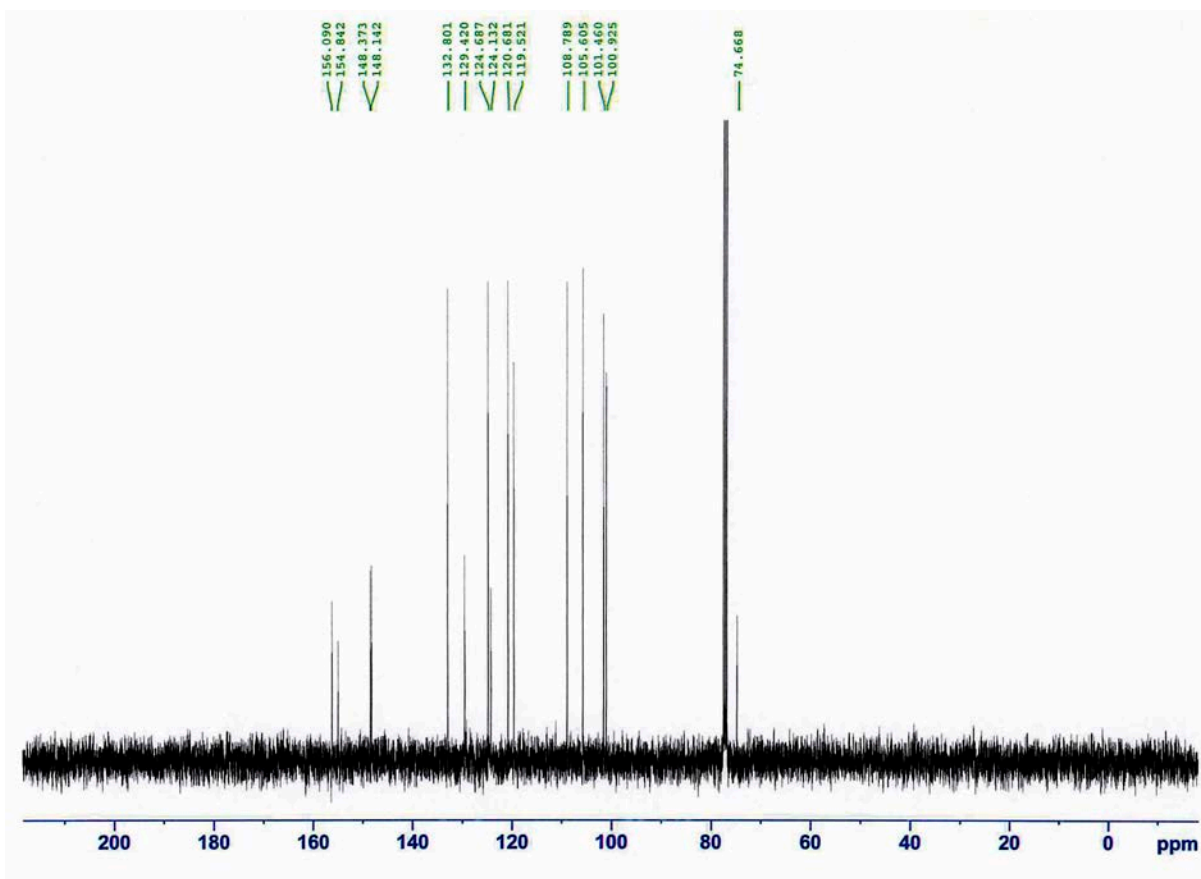
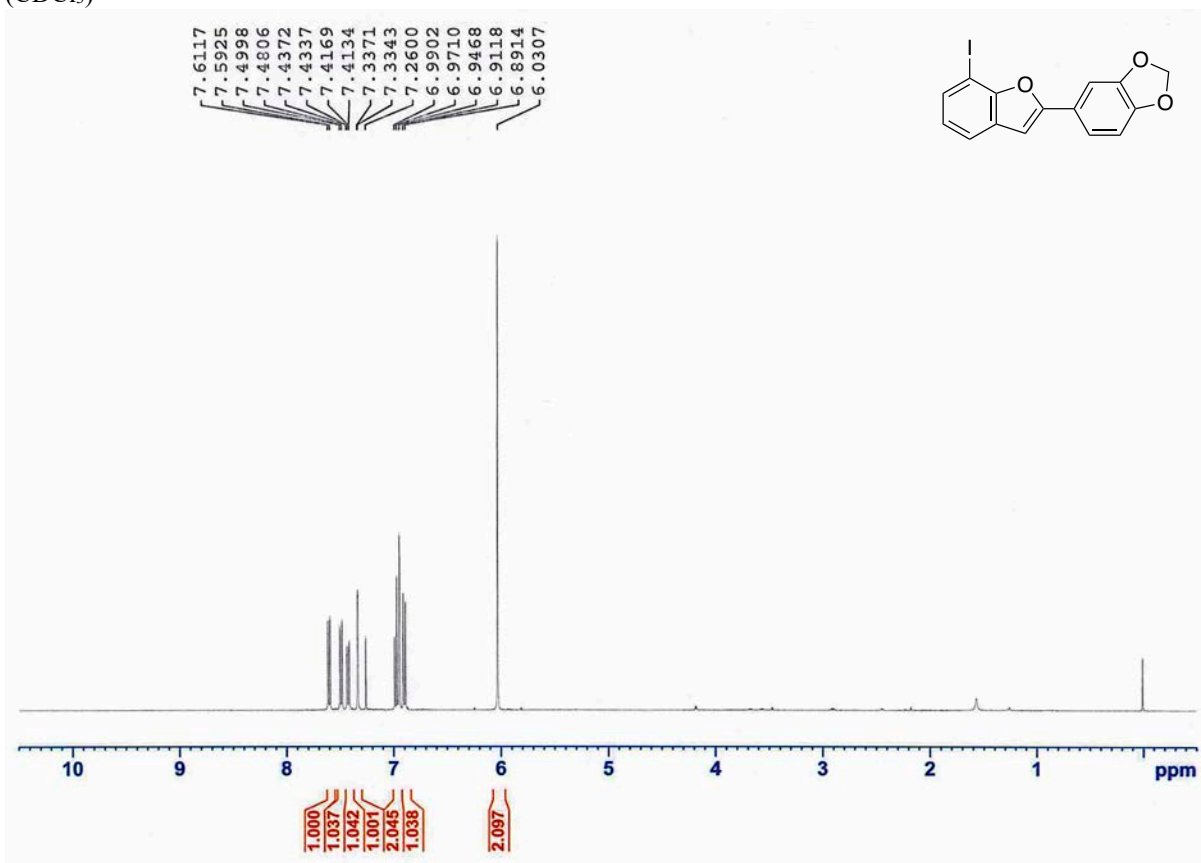
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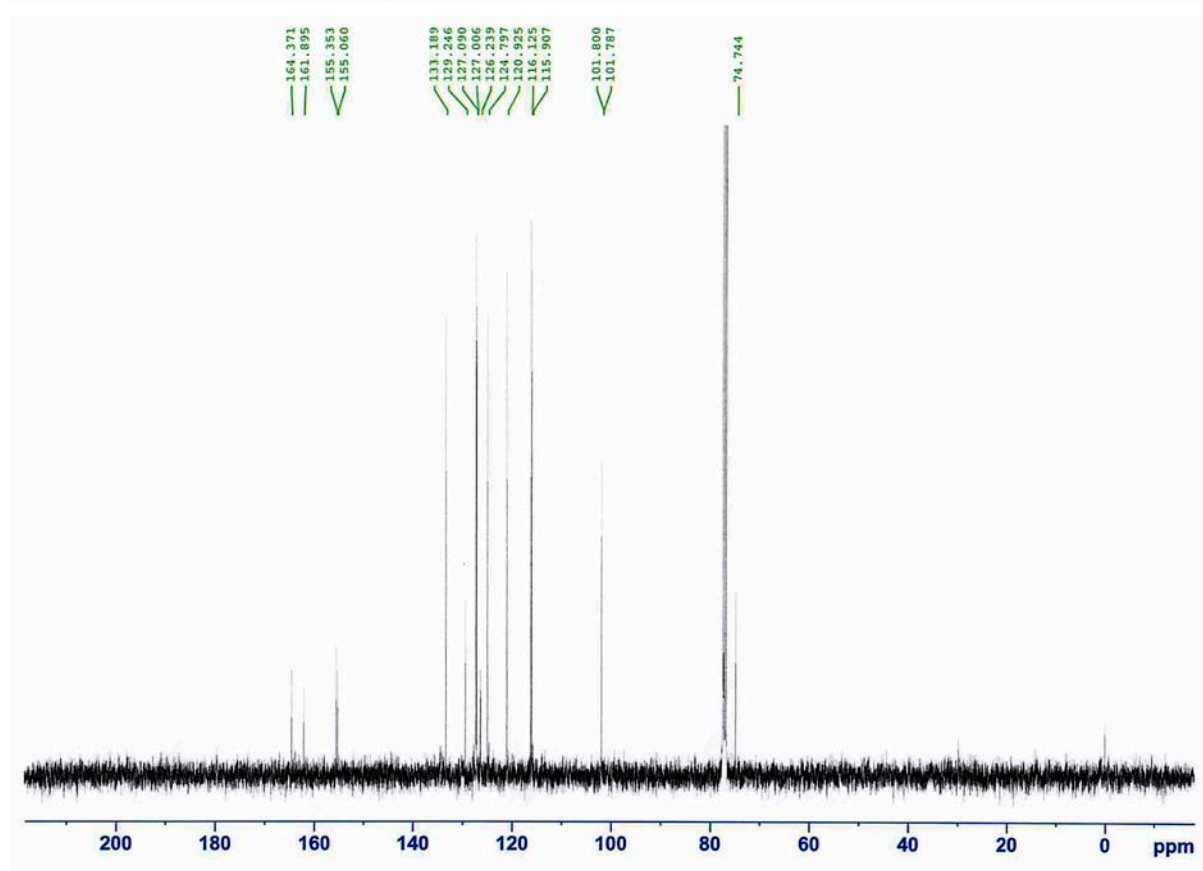
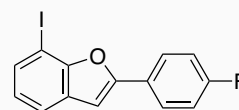
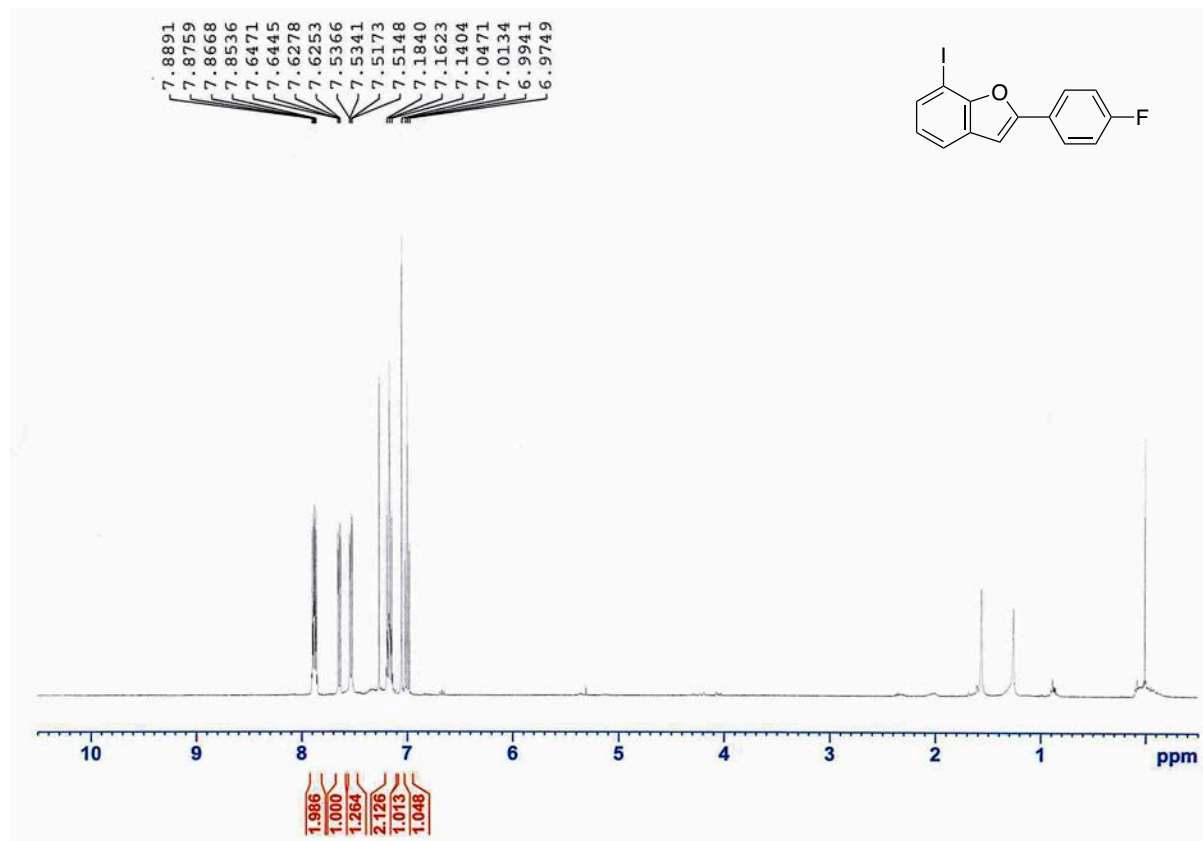
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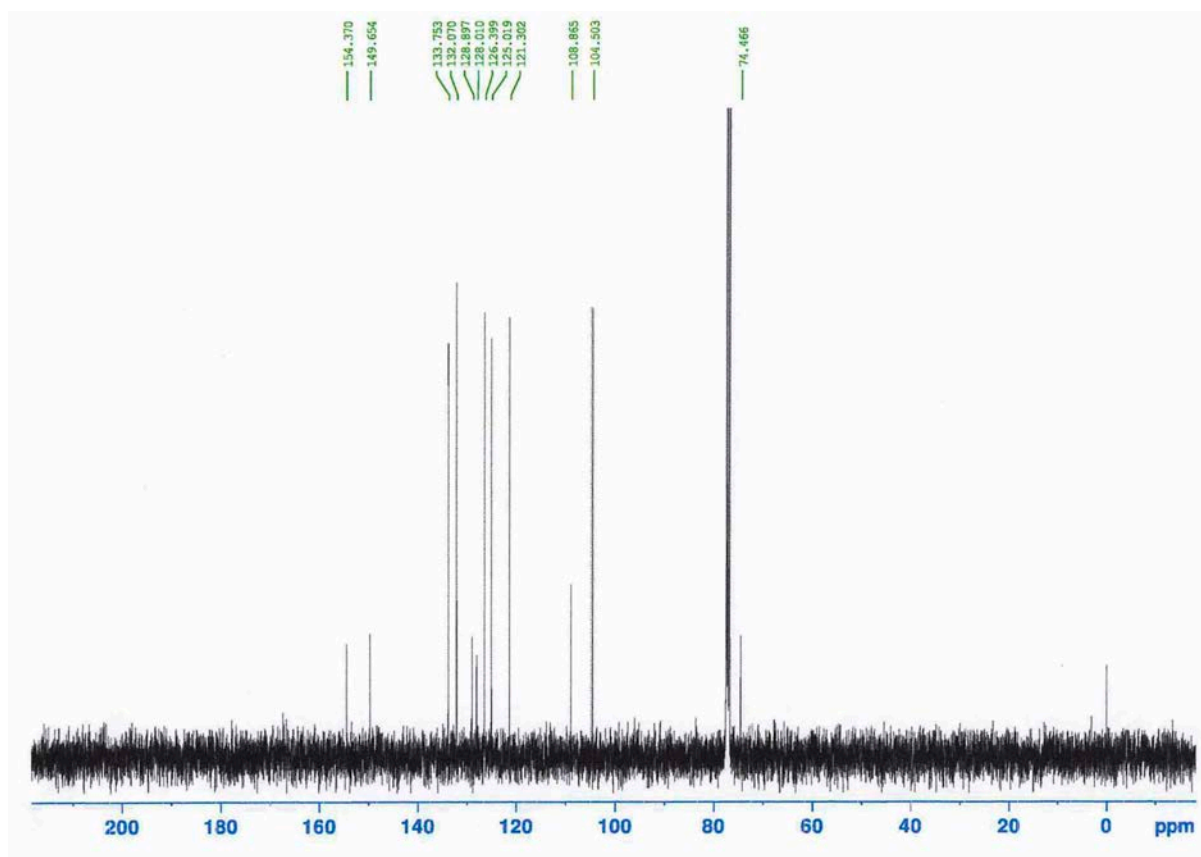
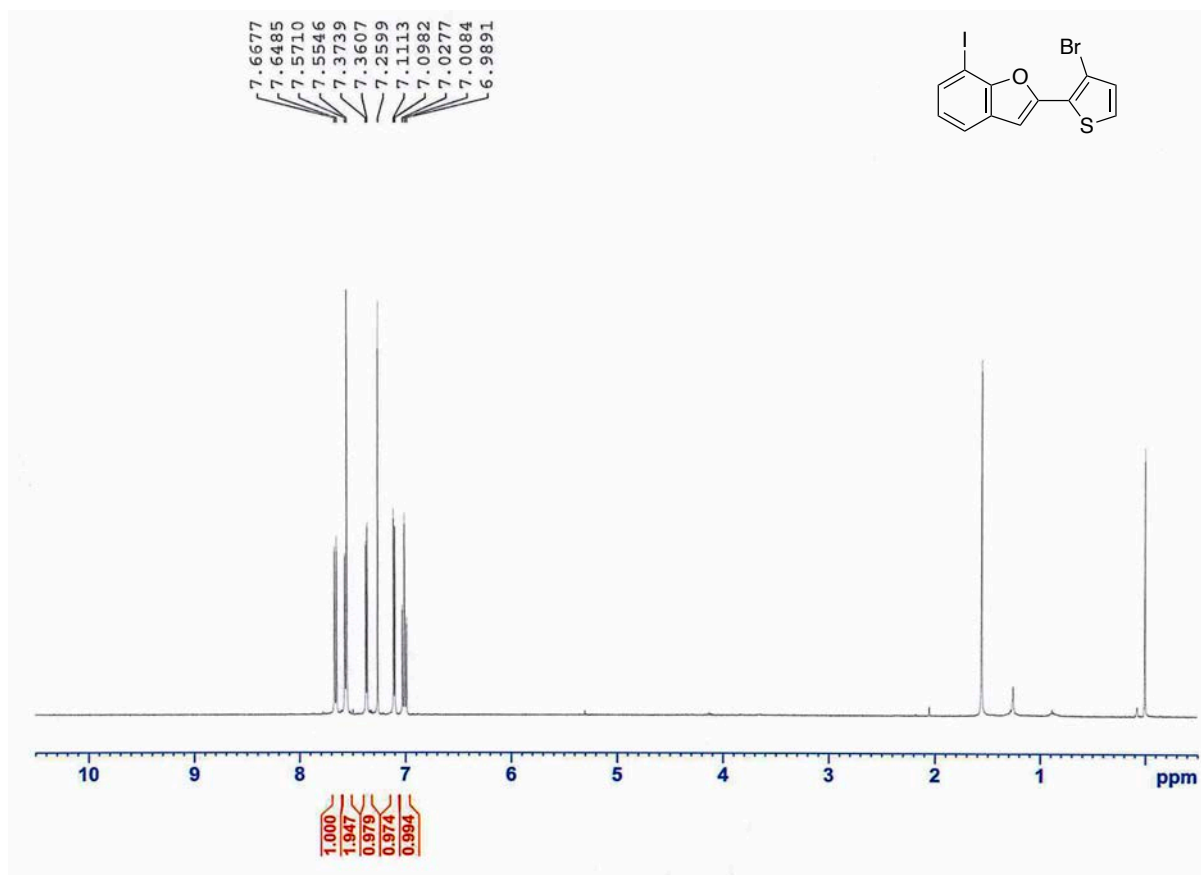
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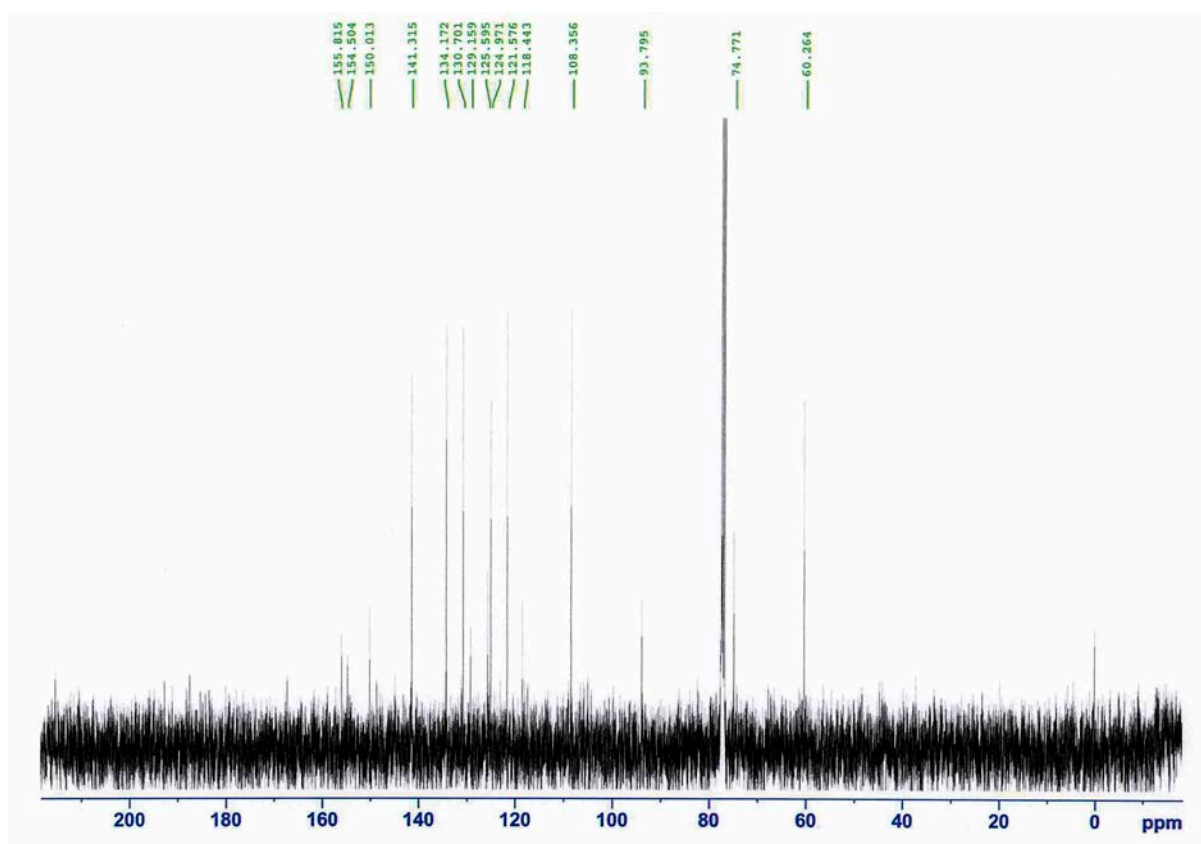
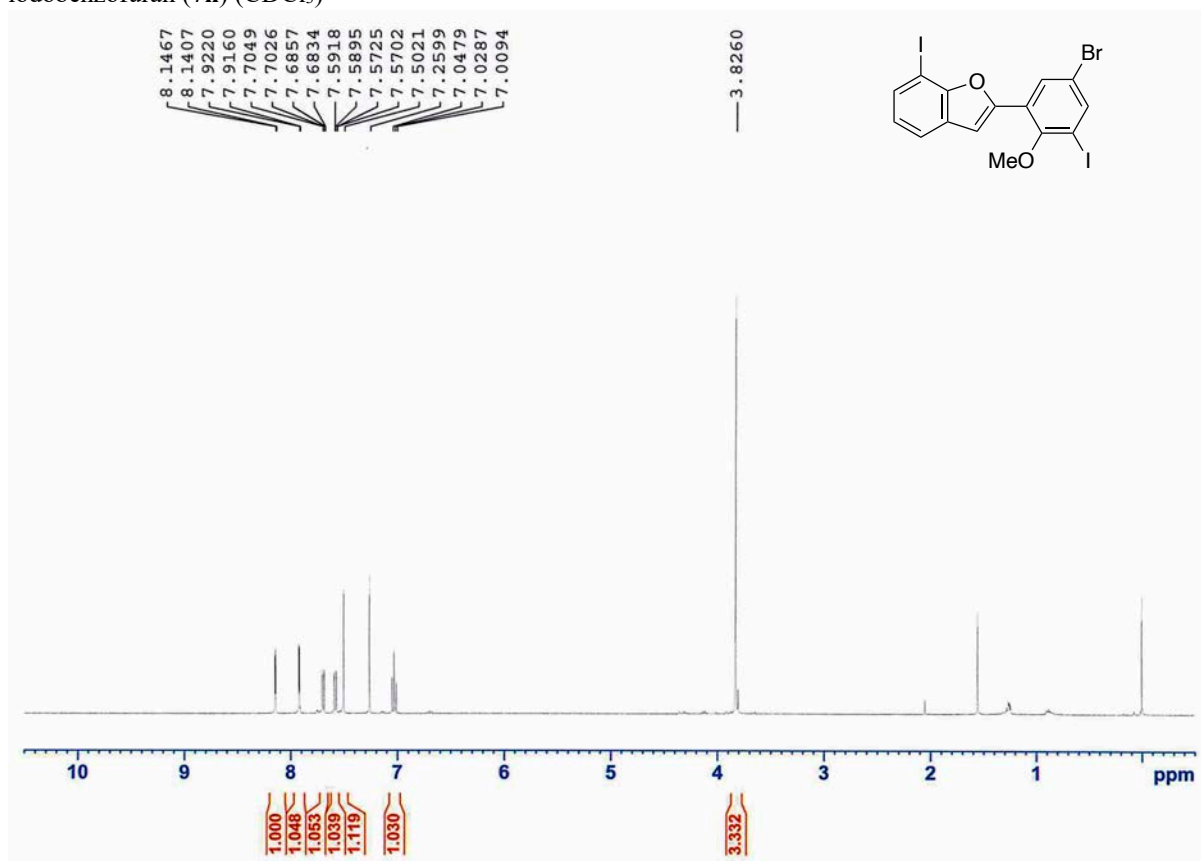
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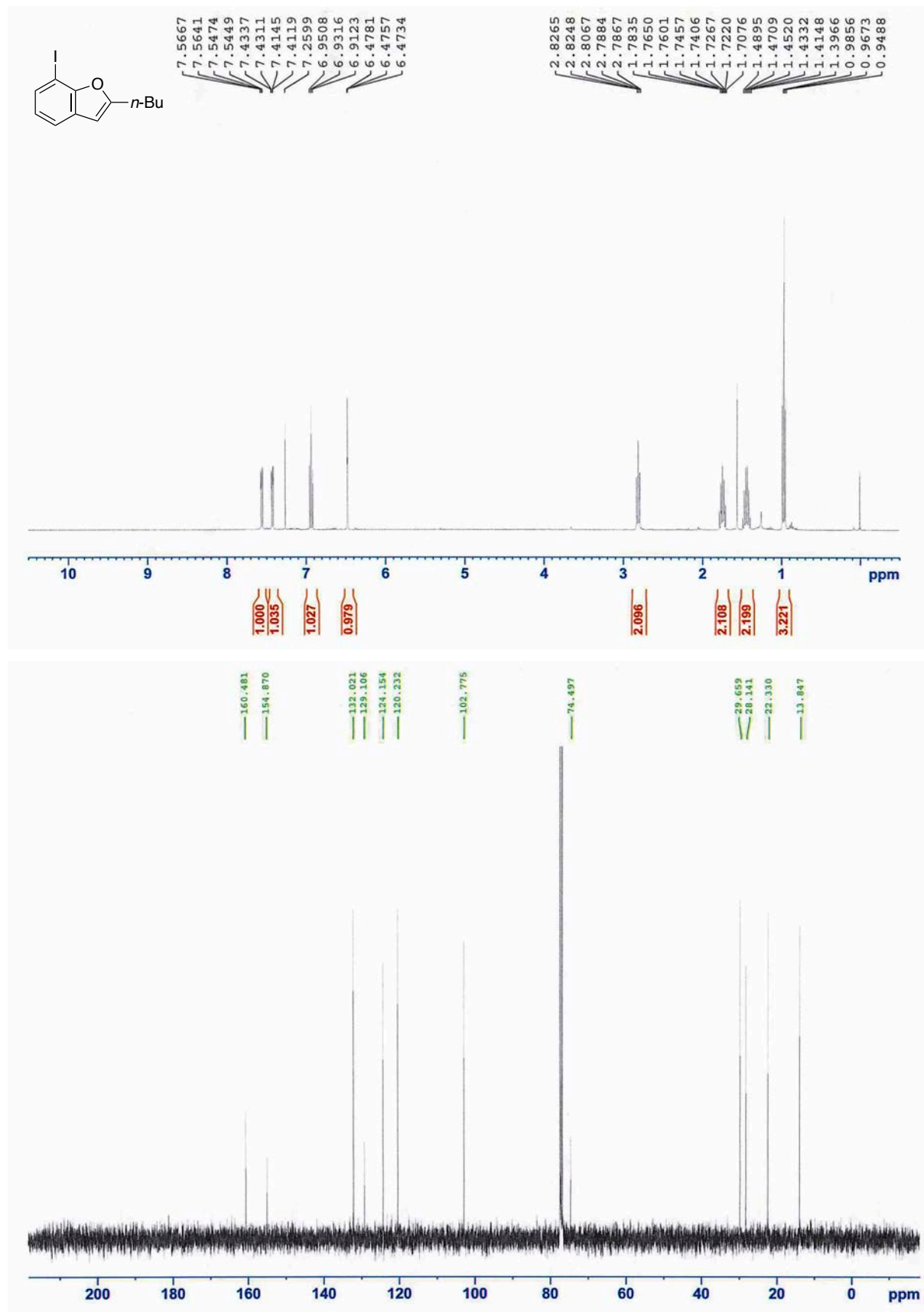
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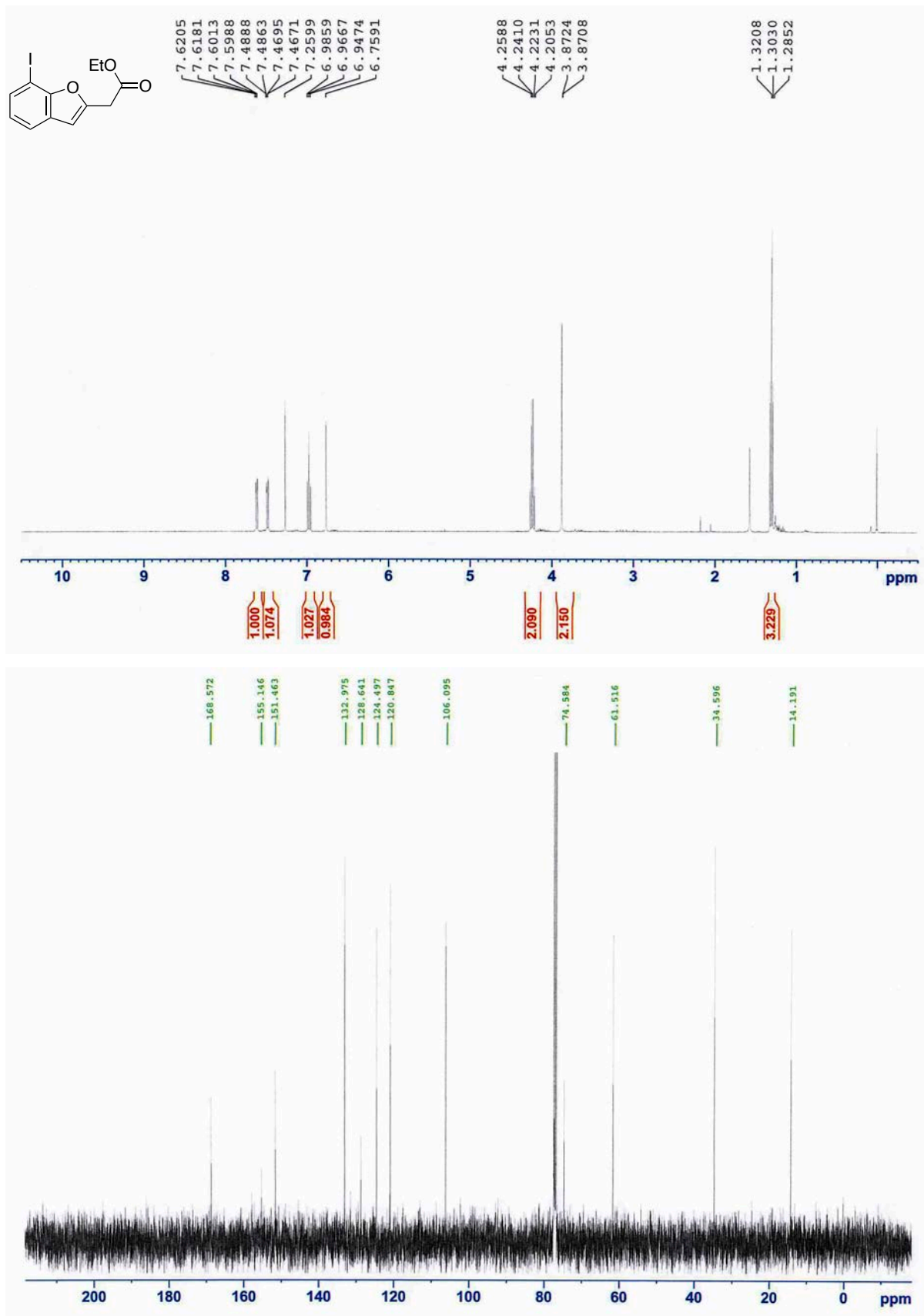
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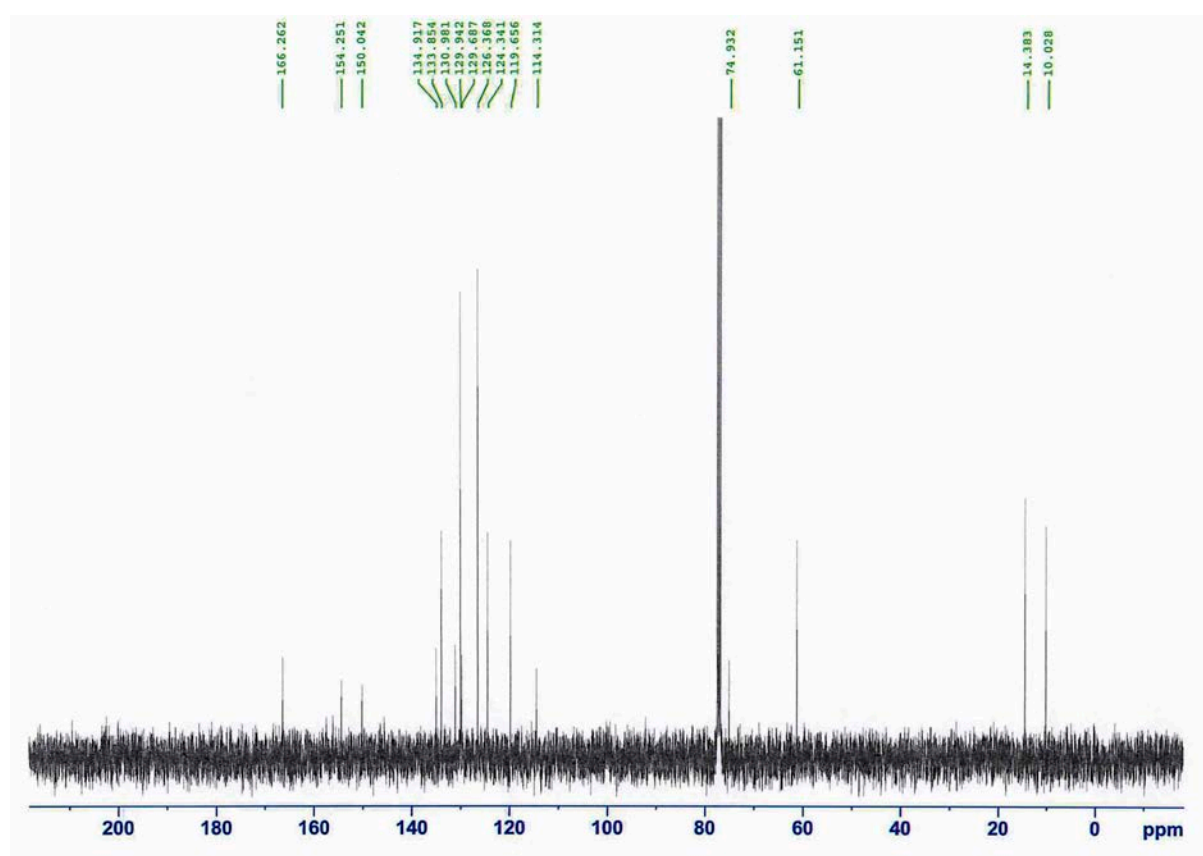
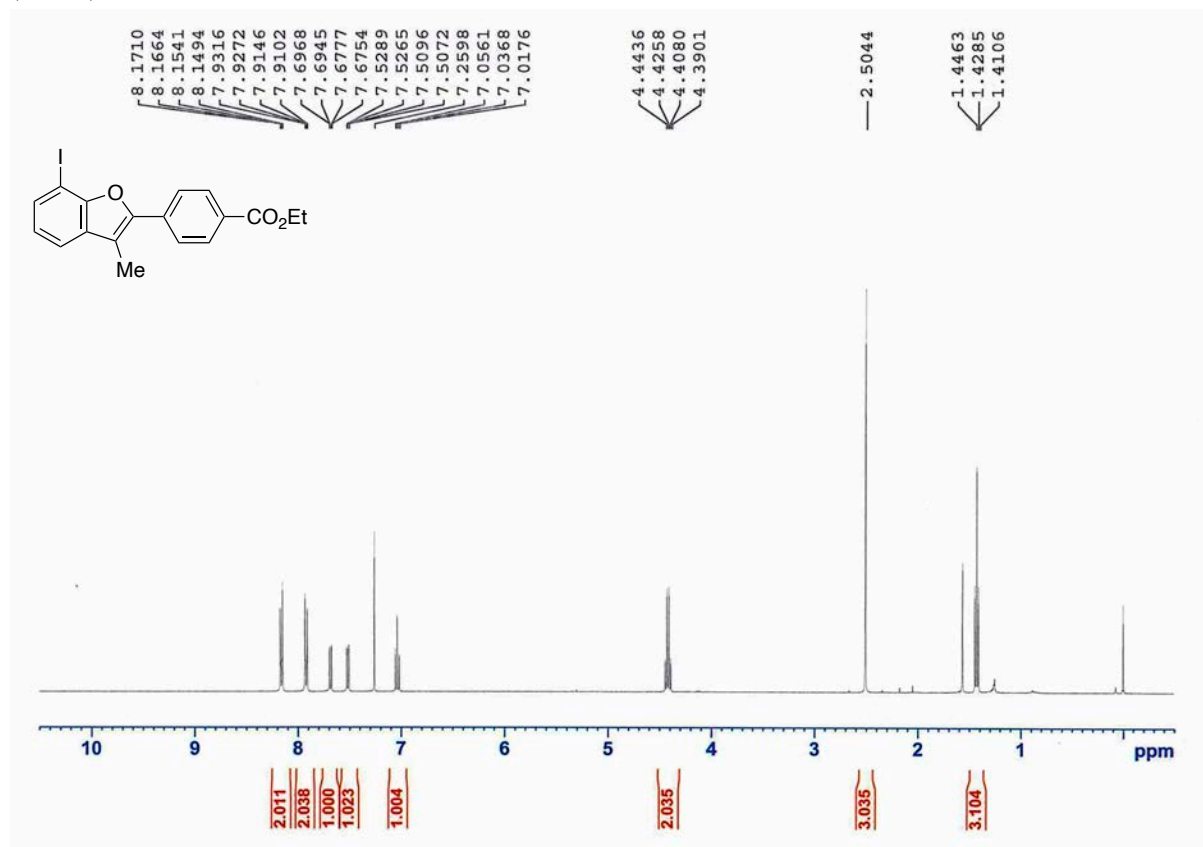
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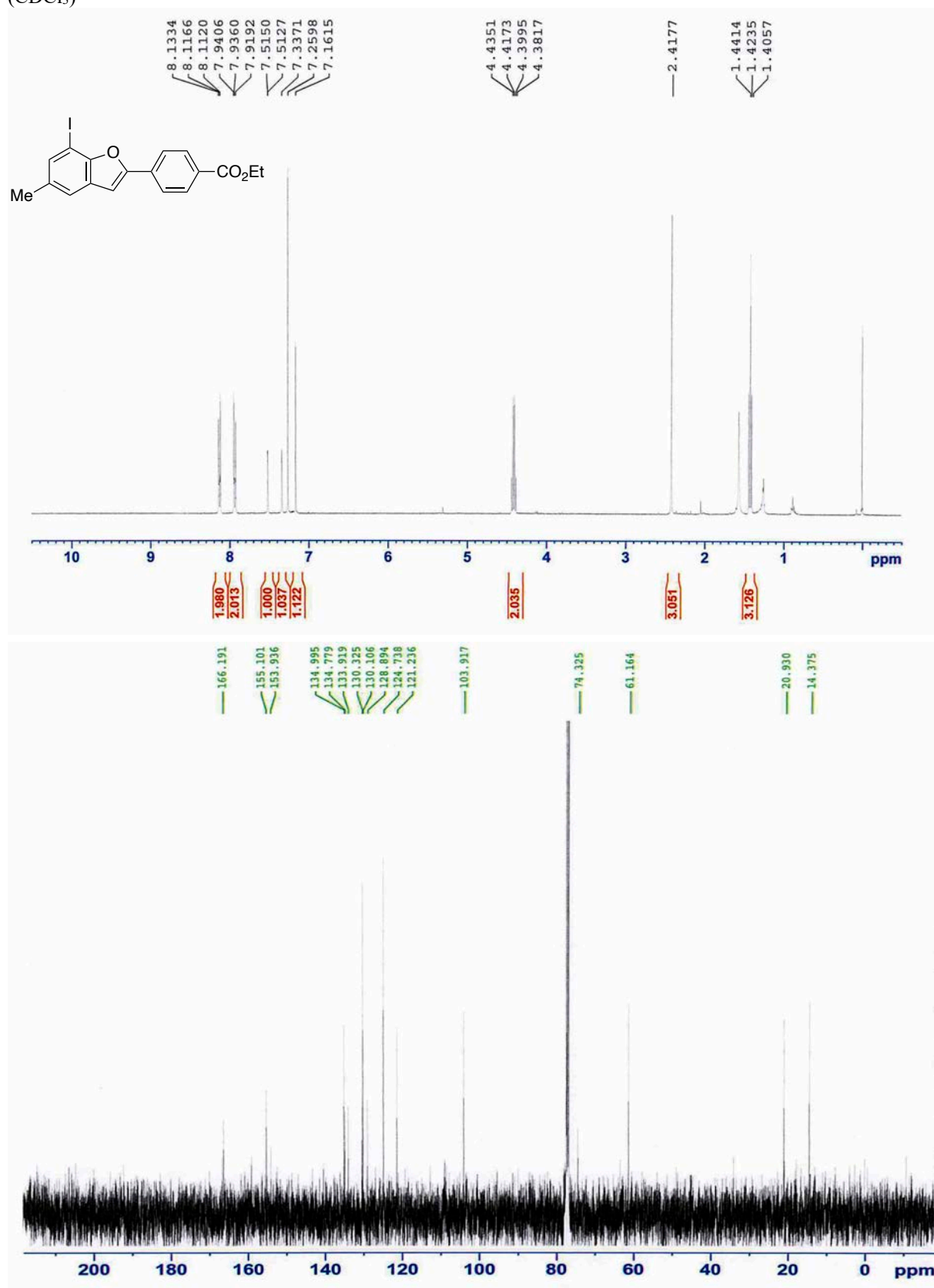
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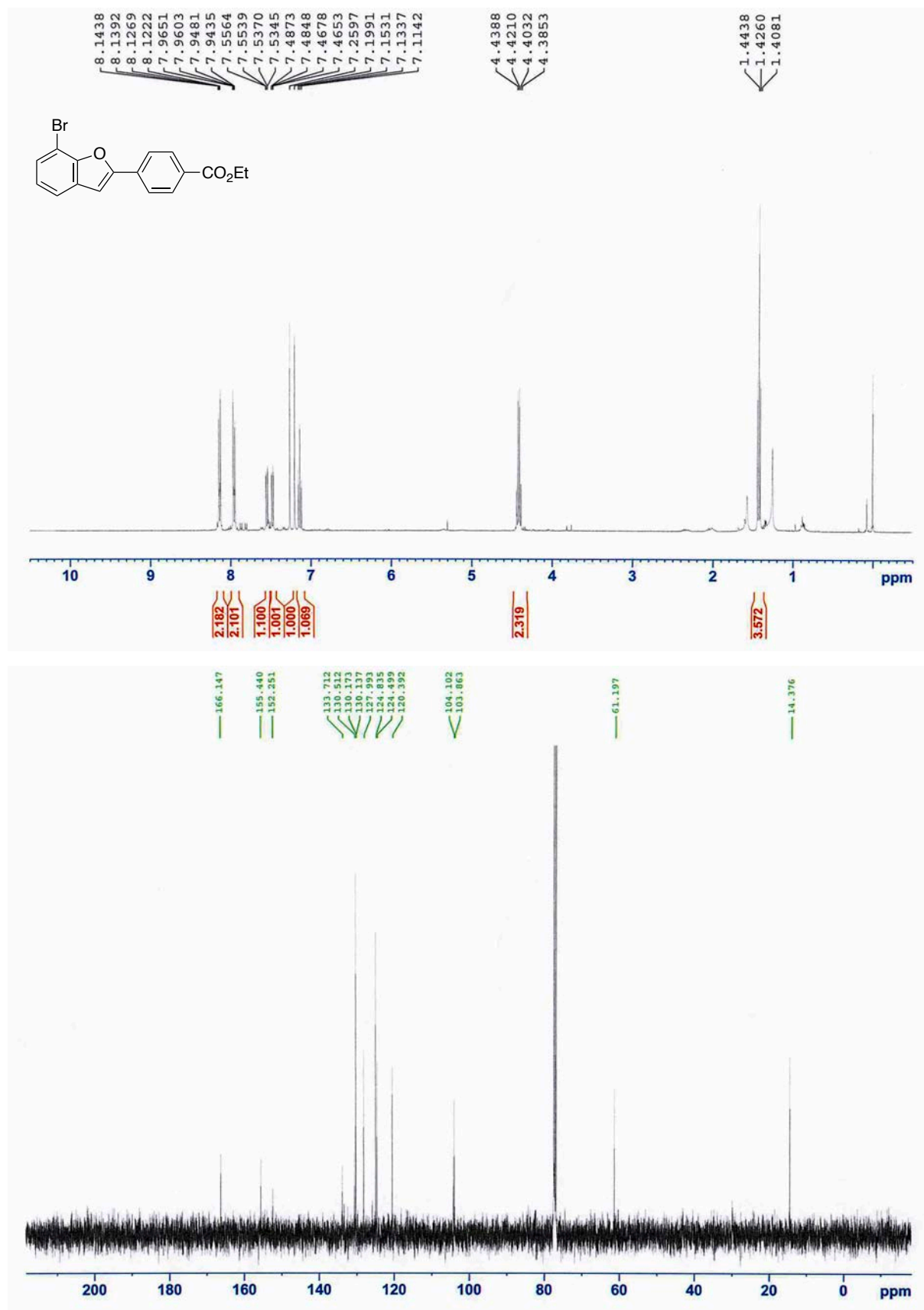
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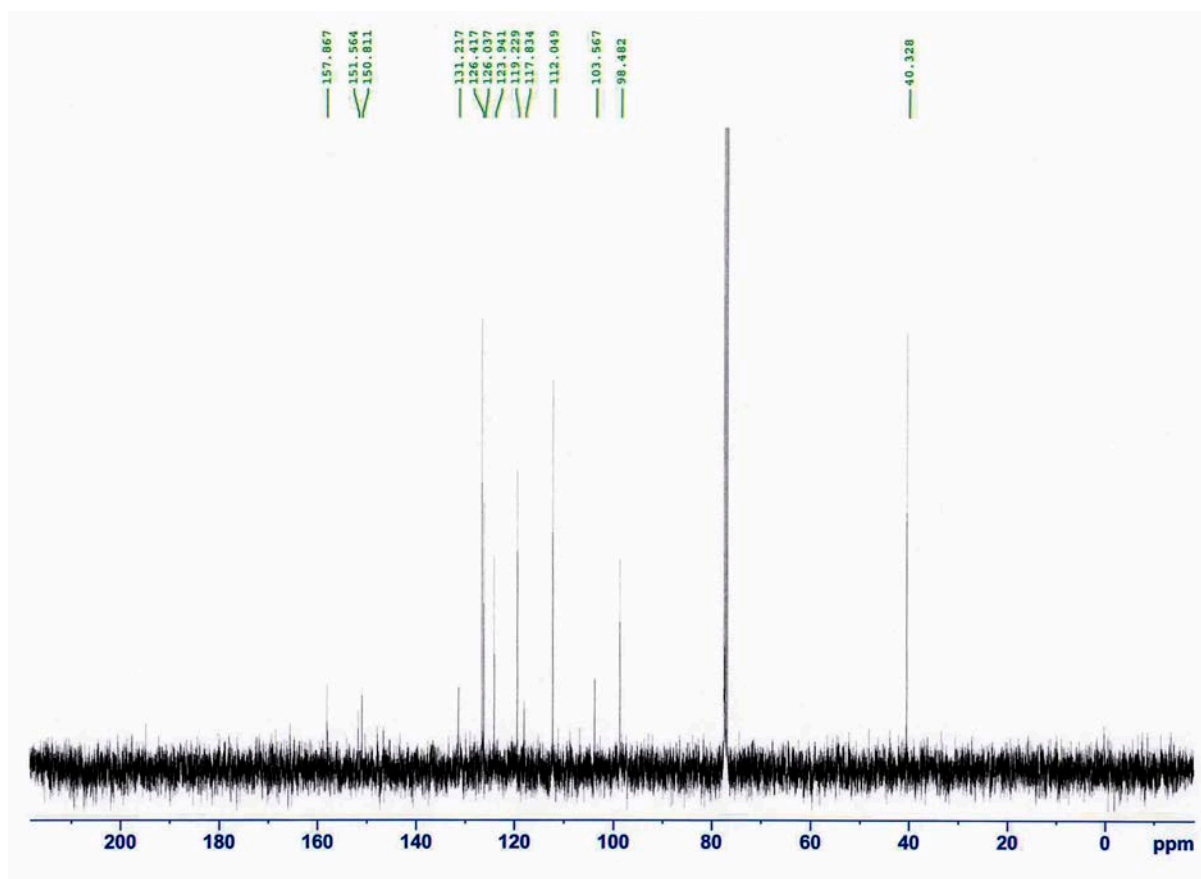
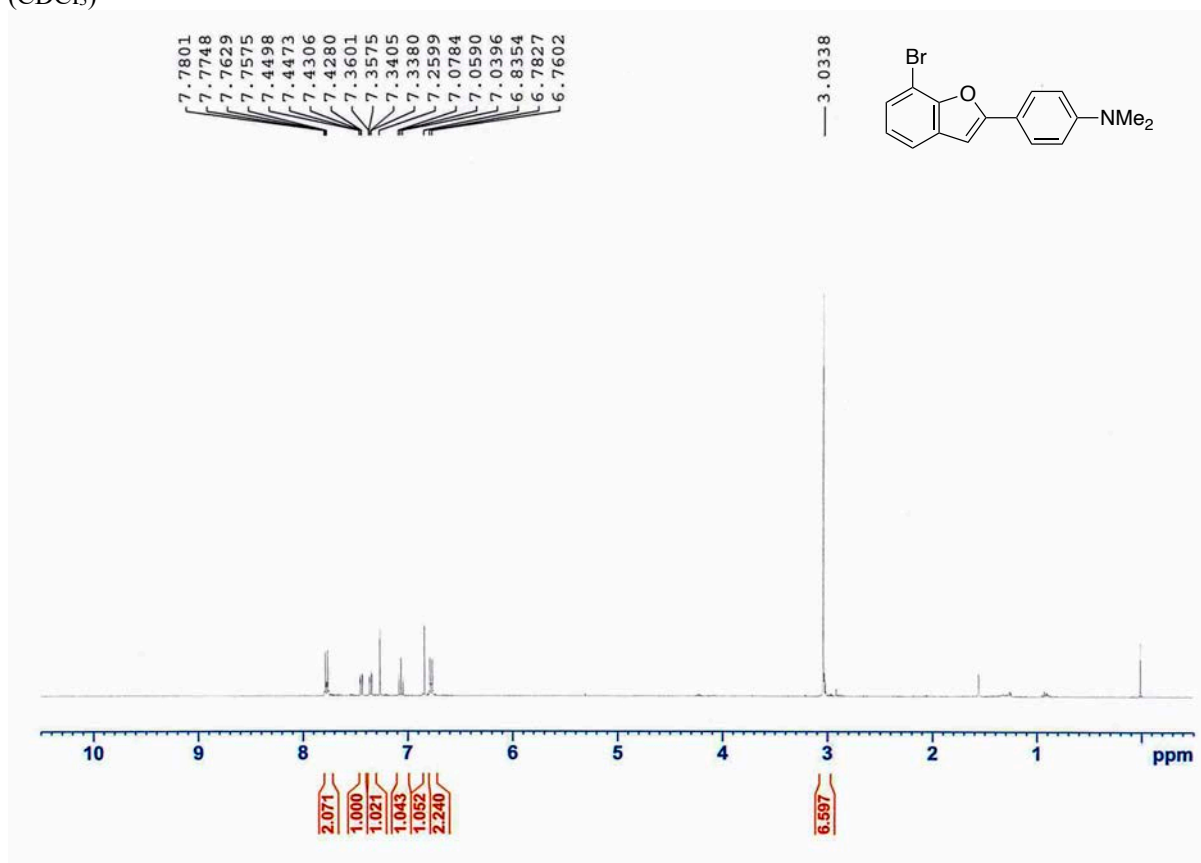
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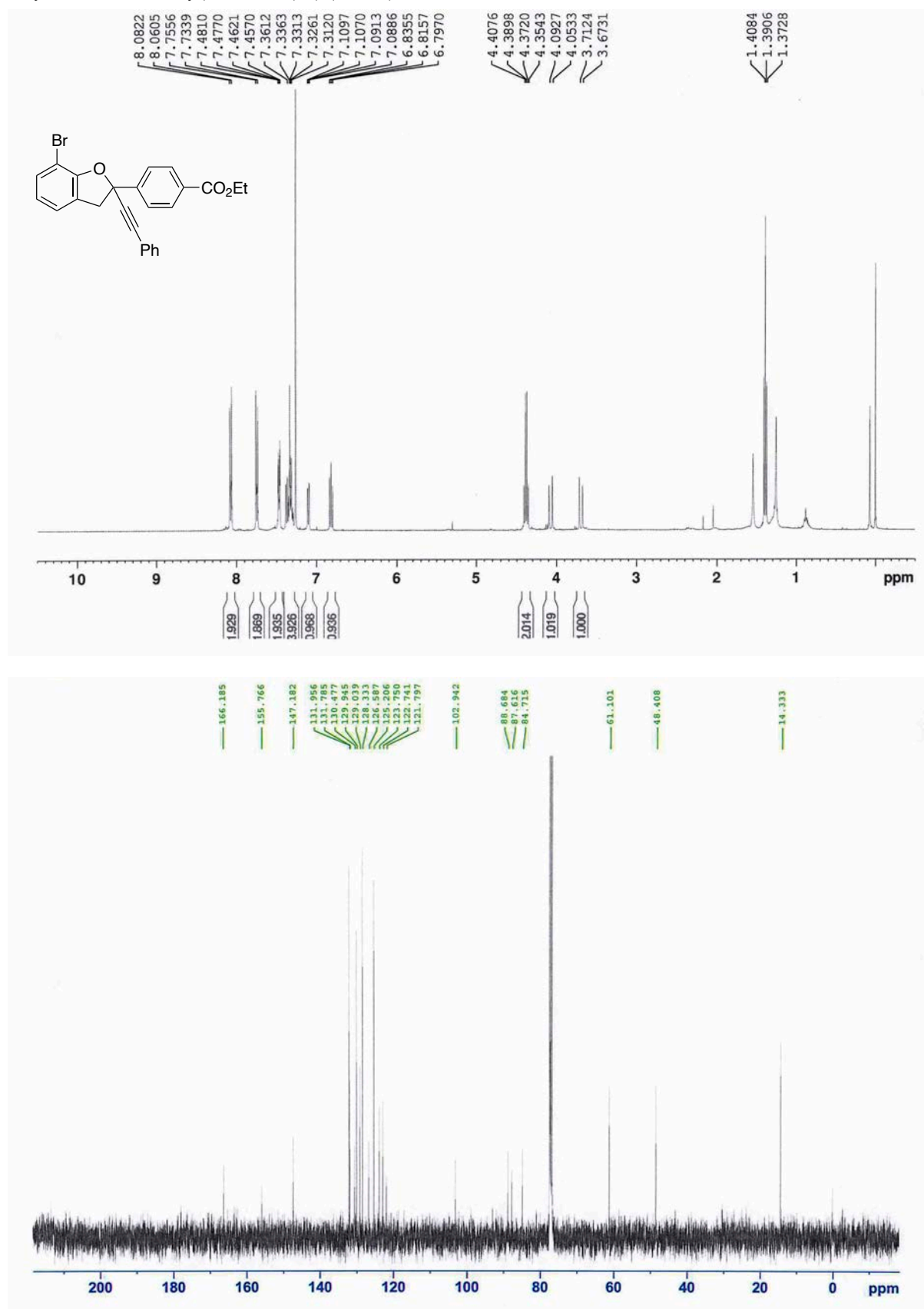
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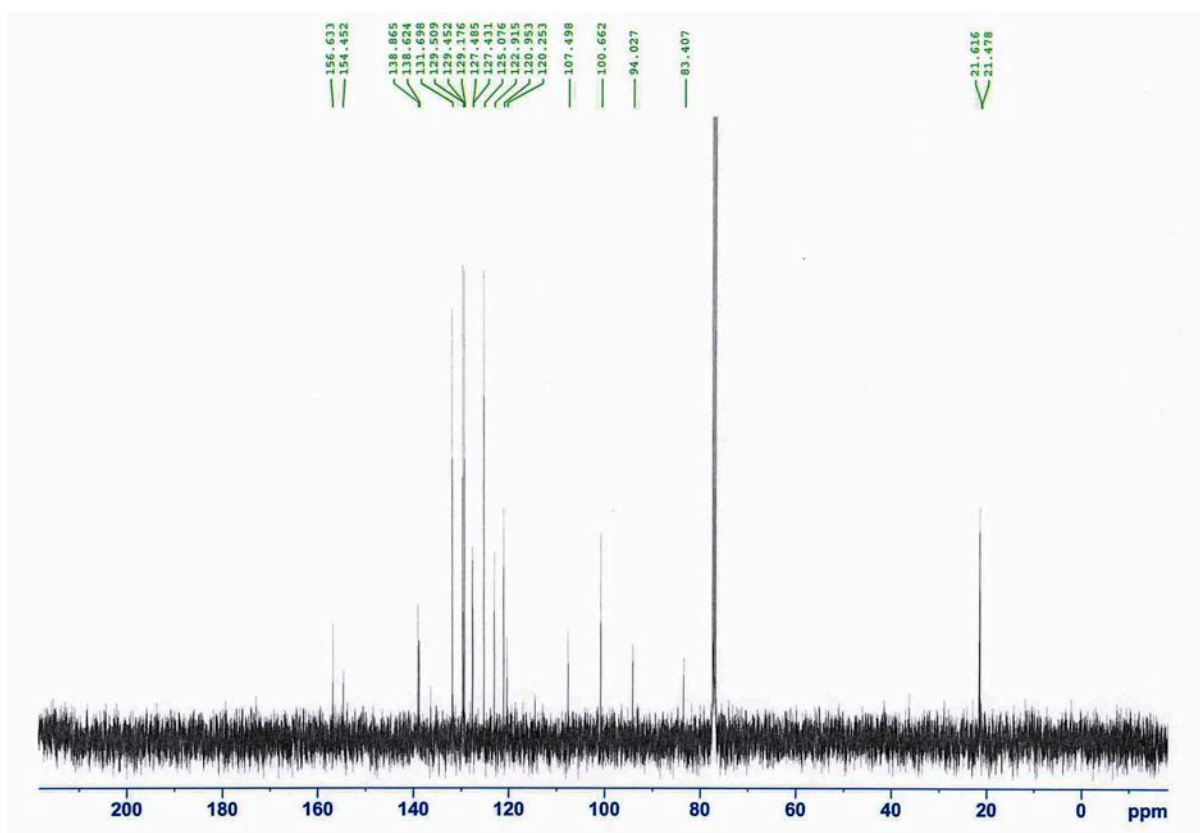
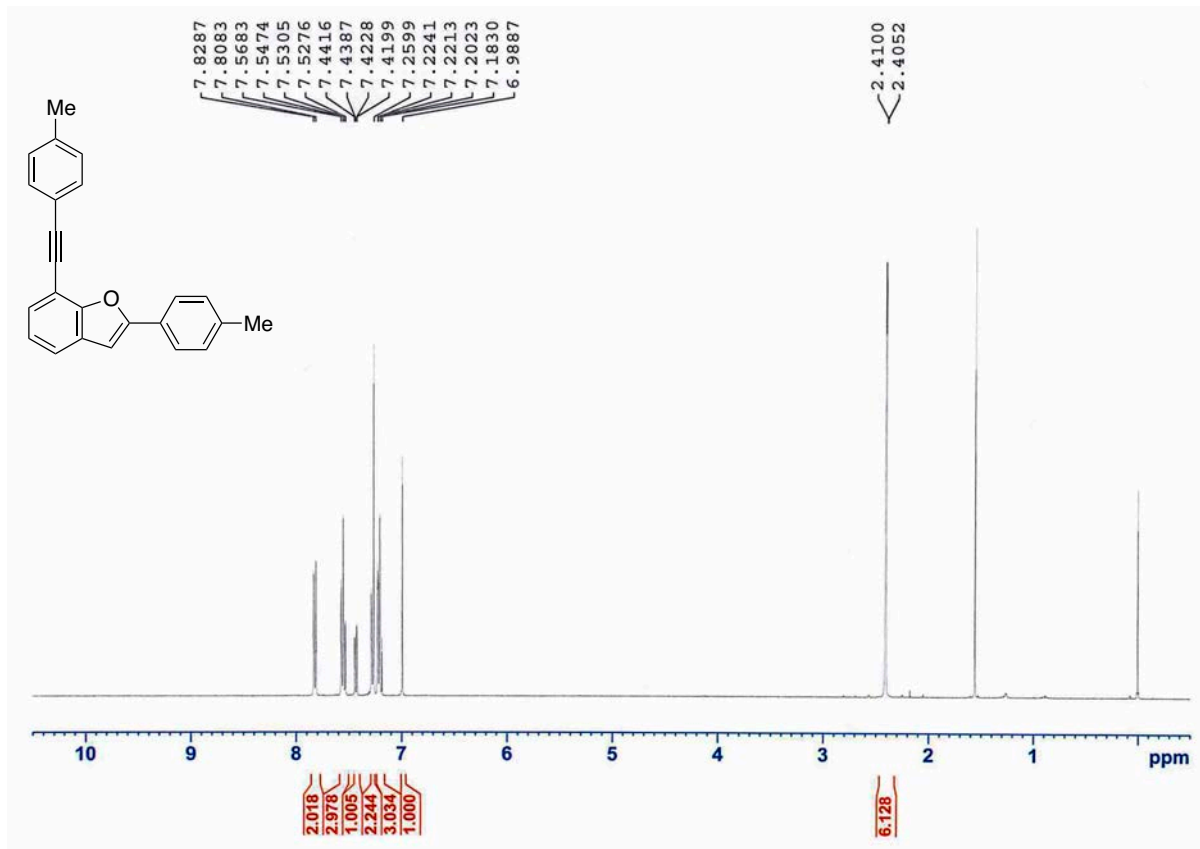
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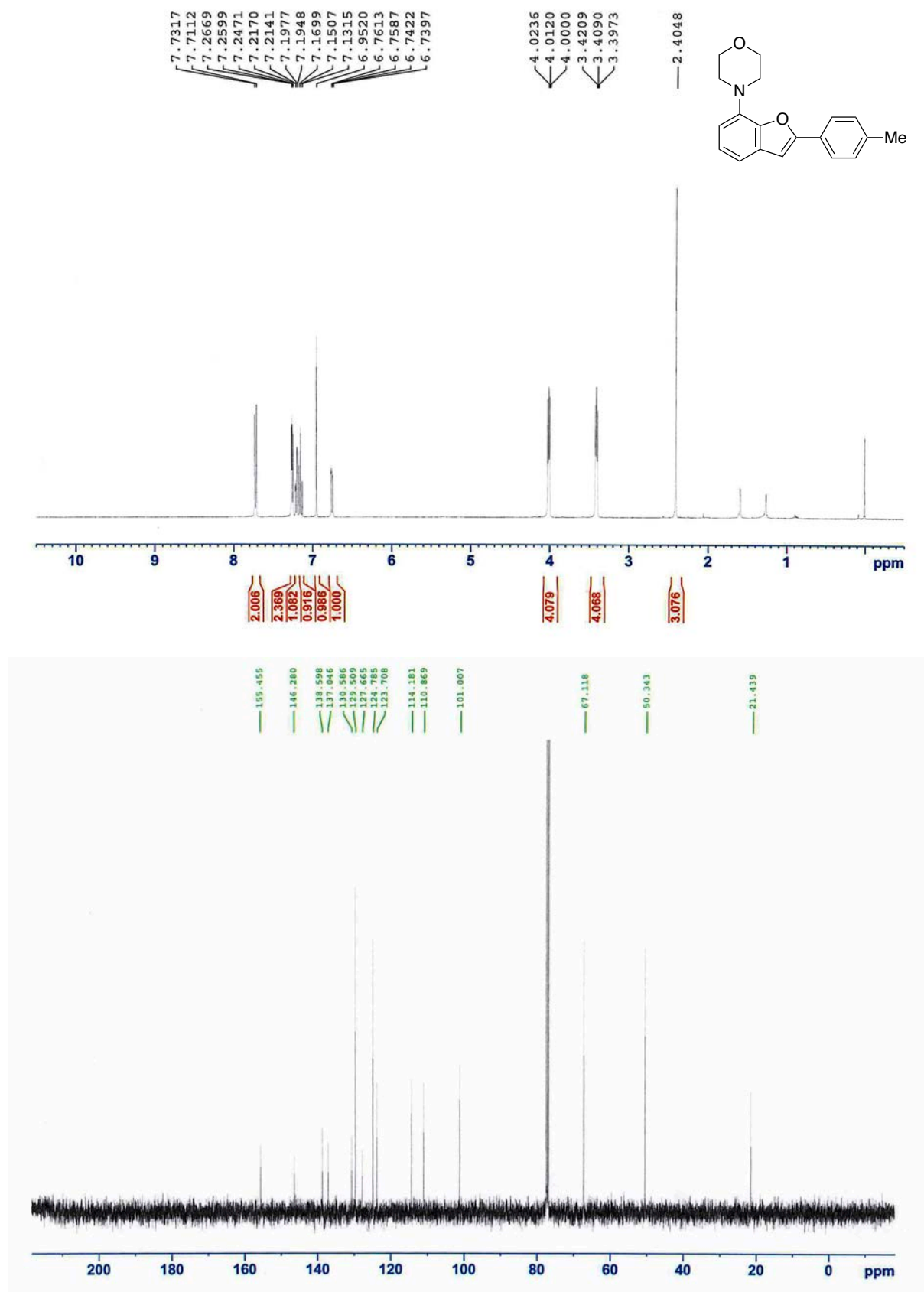
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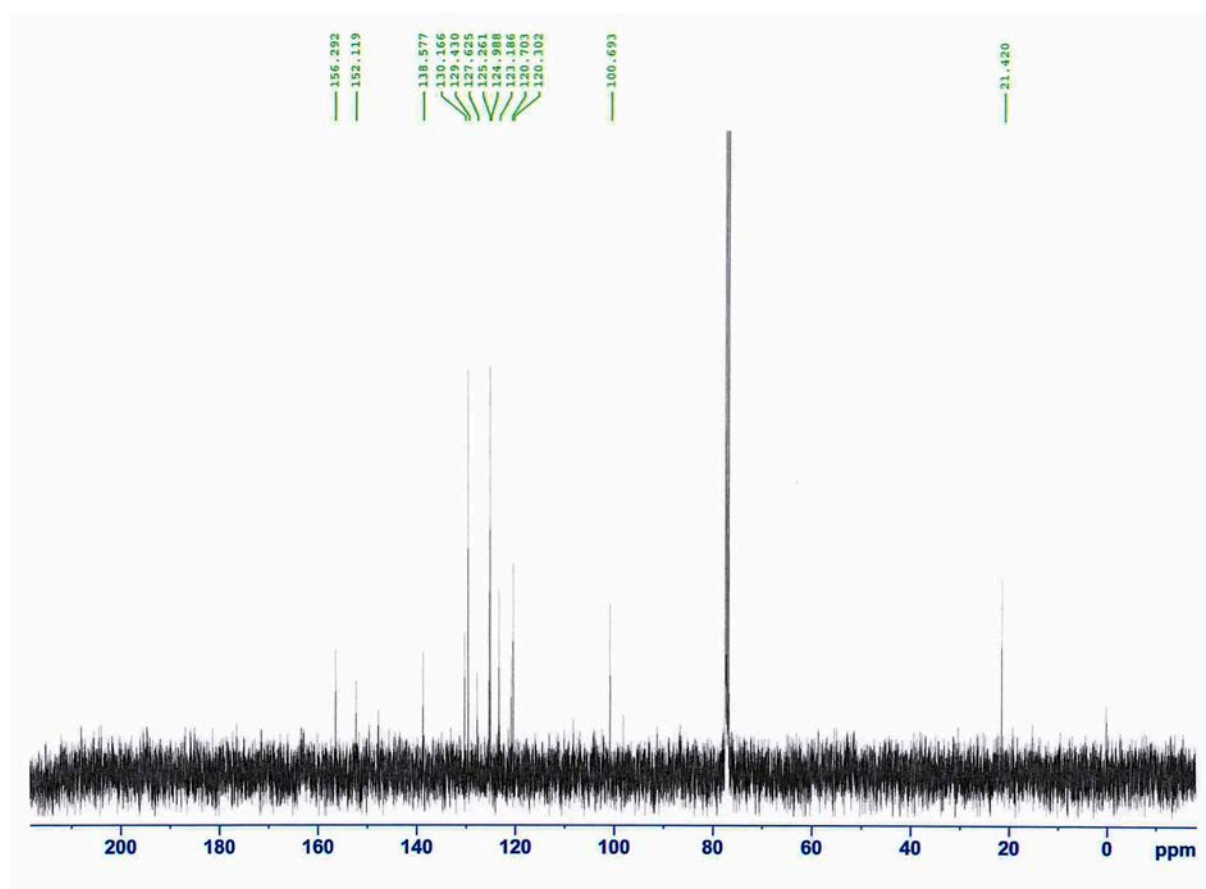
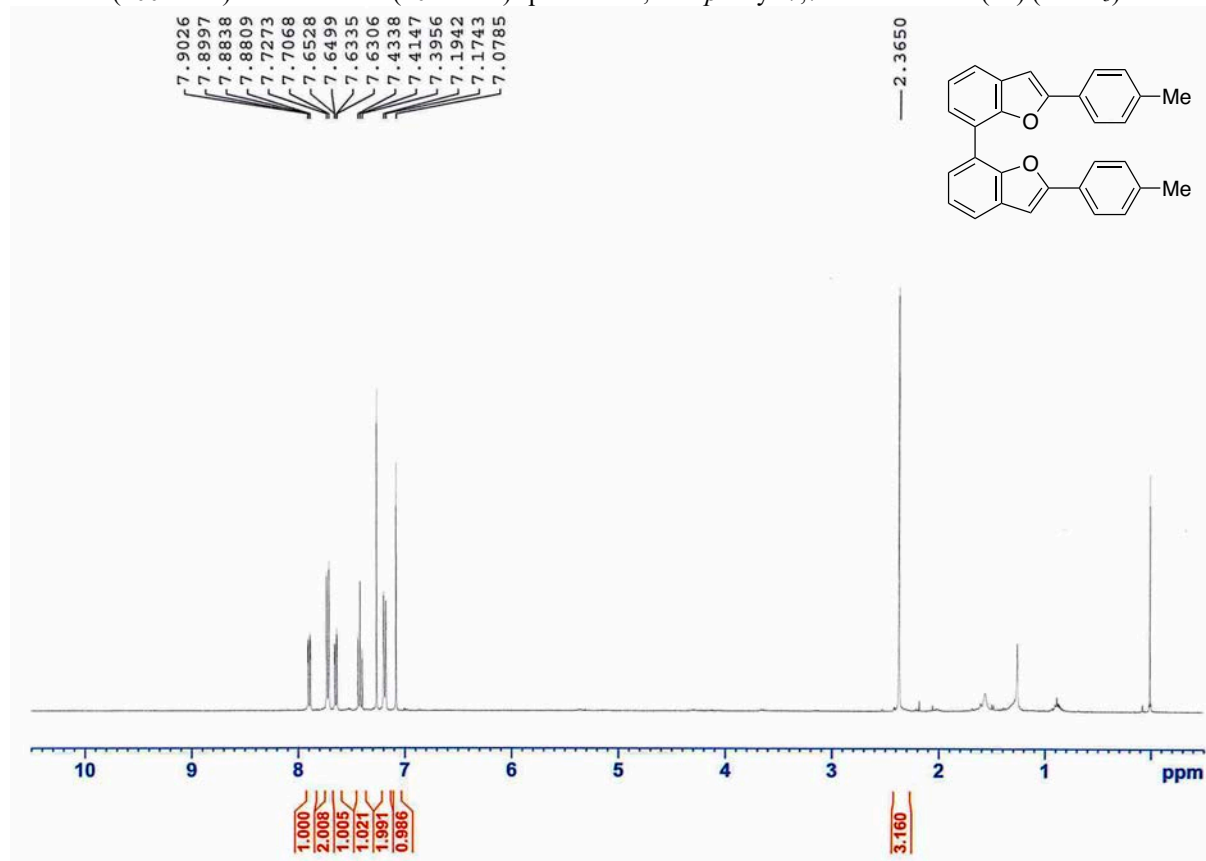
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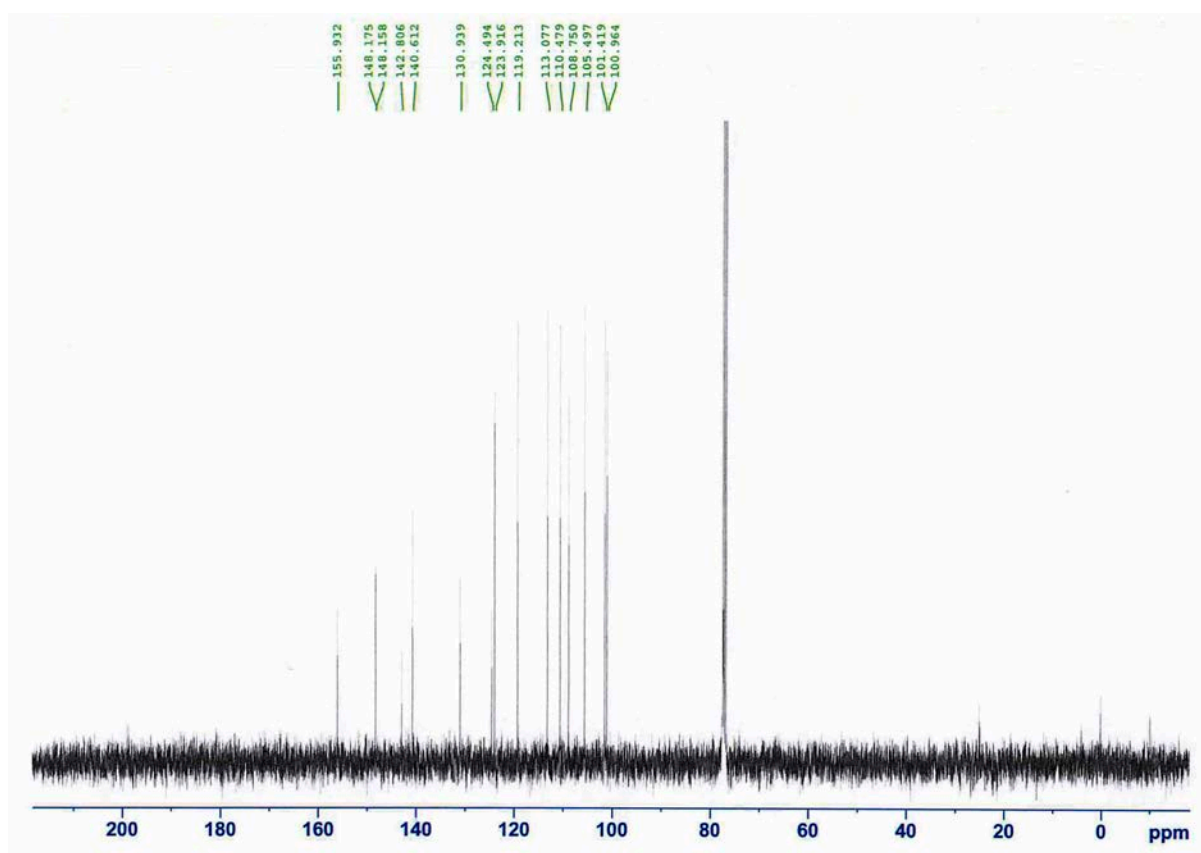
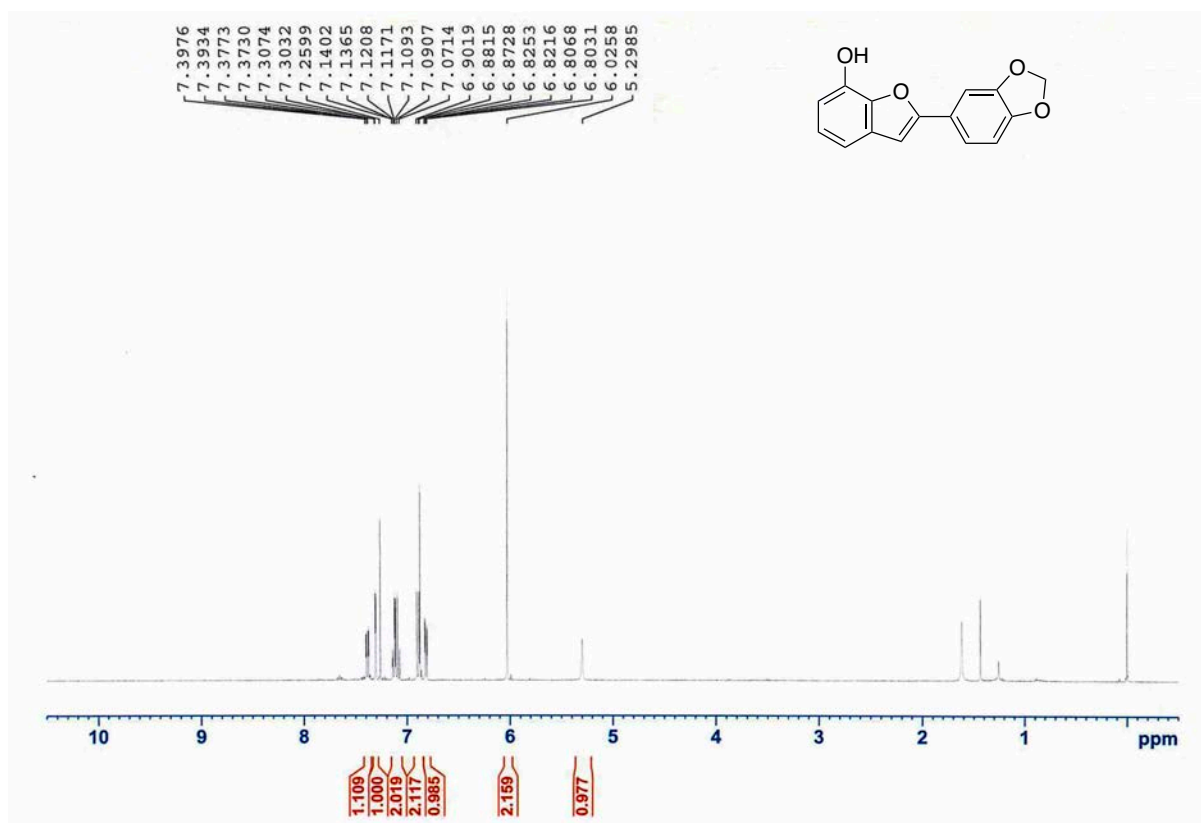
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of 4-(2-(*p*-tolyl)benzofuran-7-yl)morpholine (**11**) ( $\text{CDCl}_3$ )



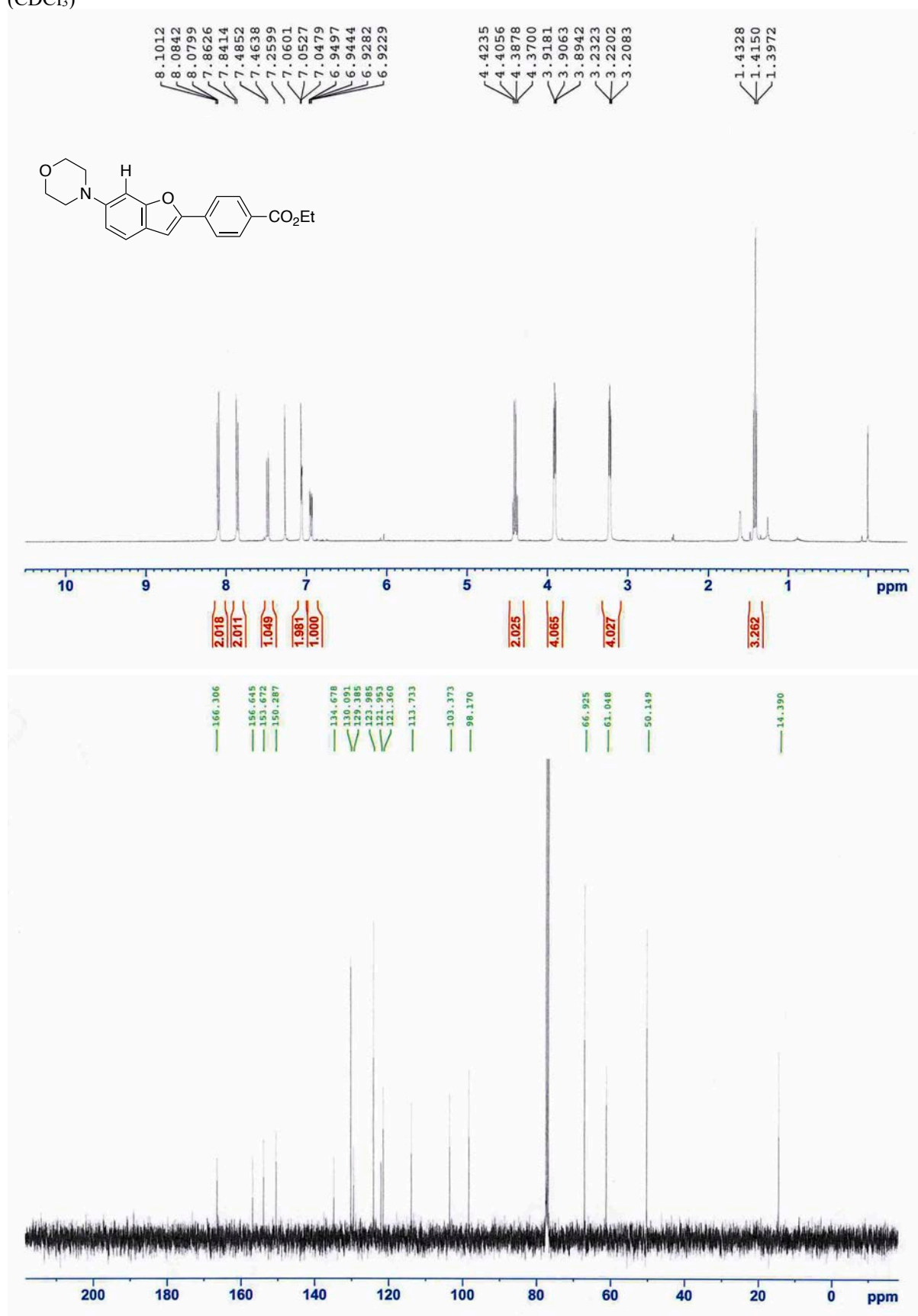
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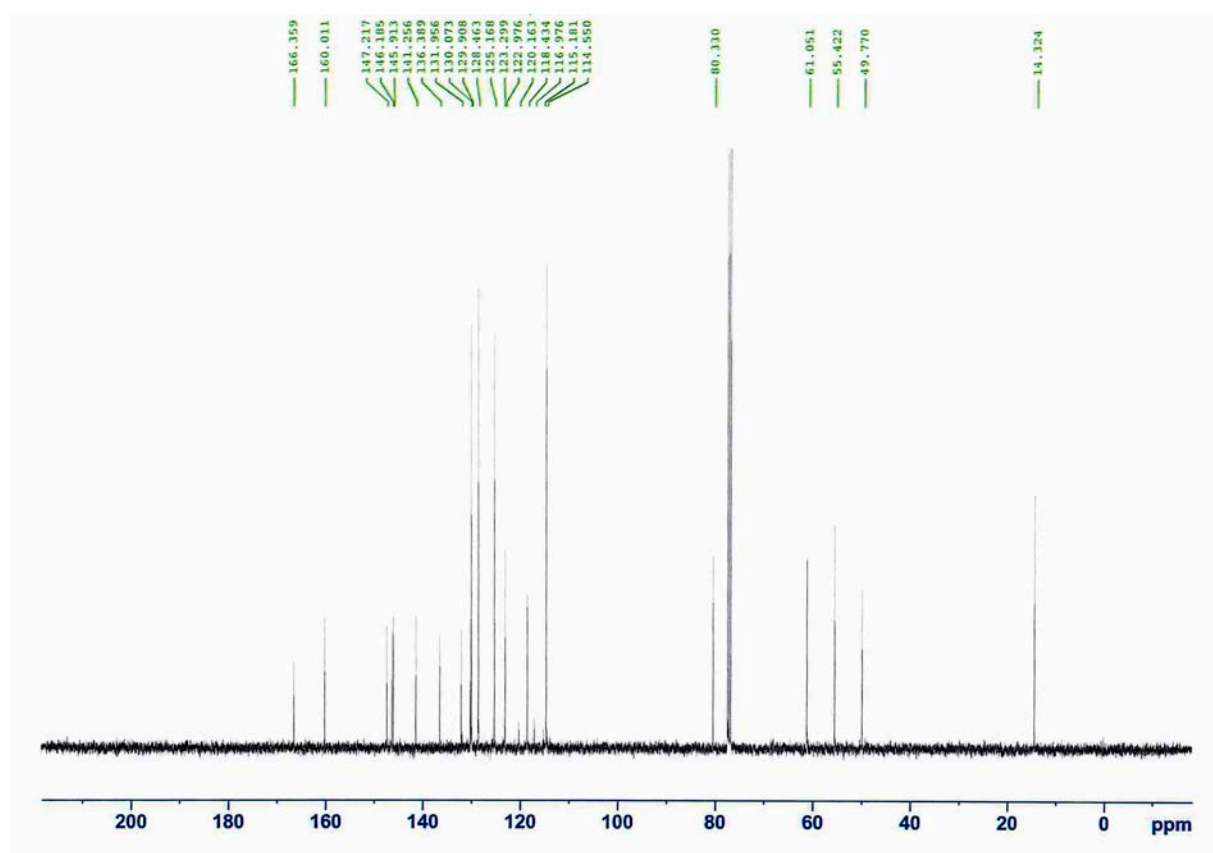
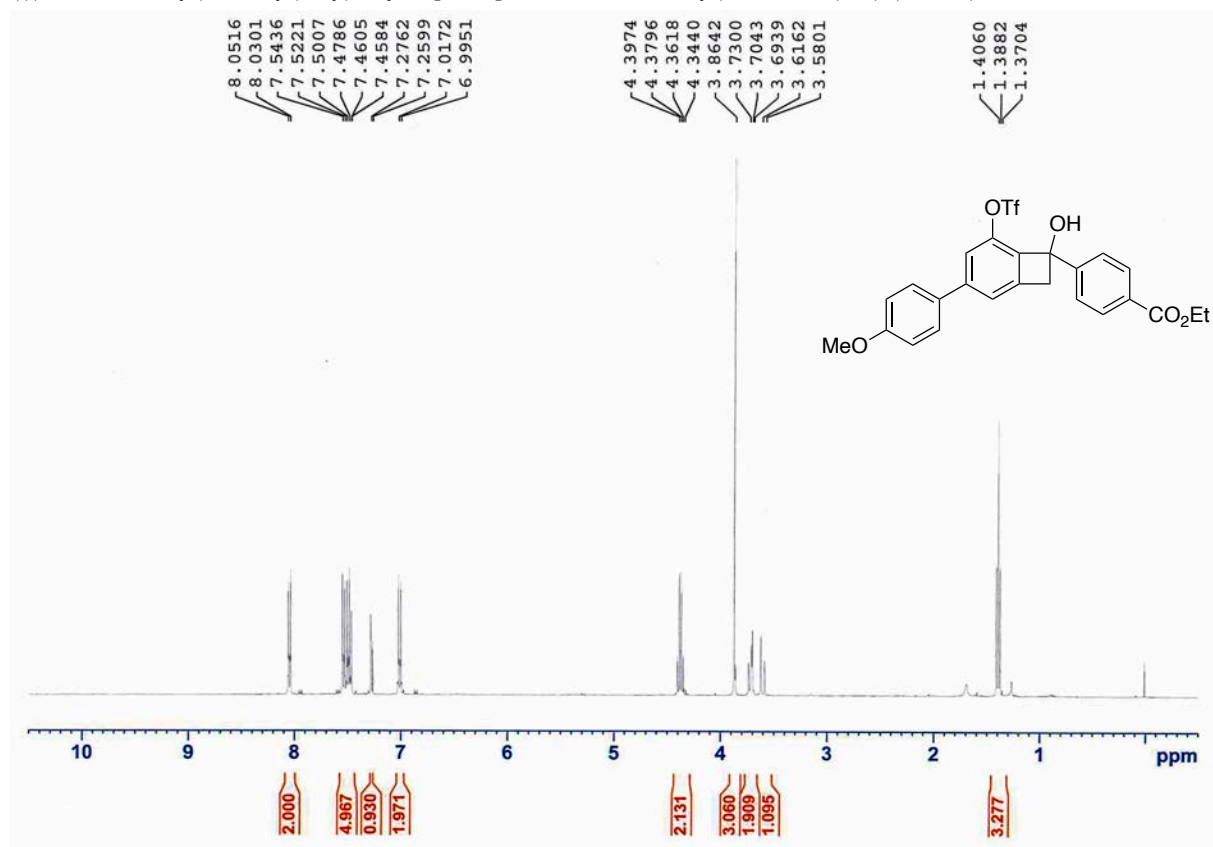
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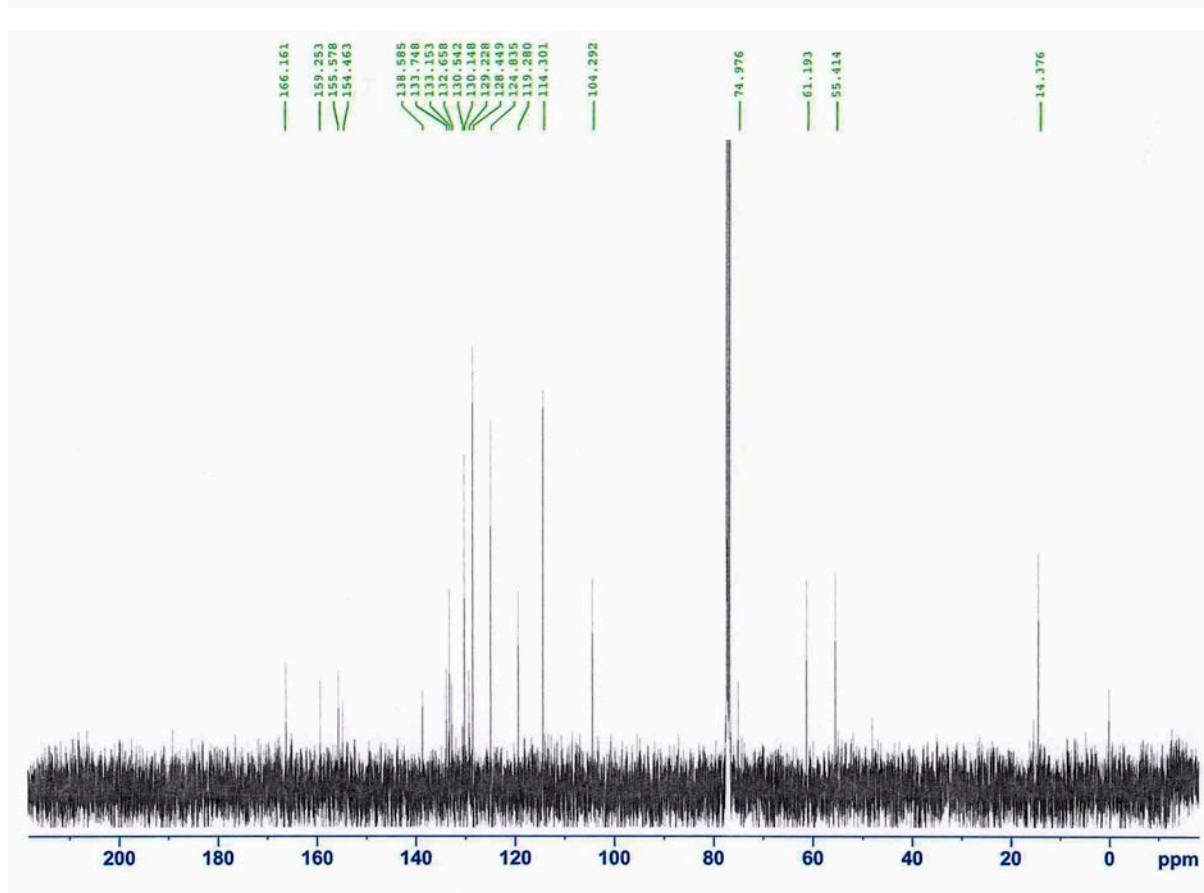
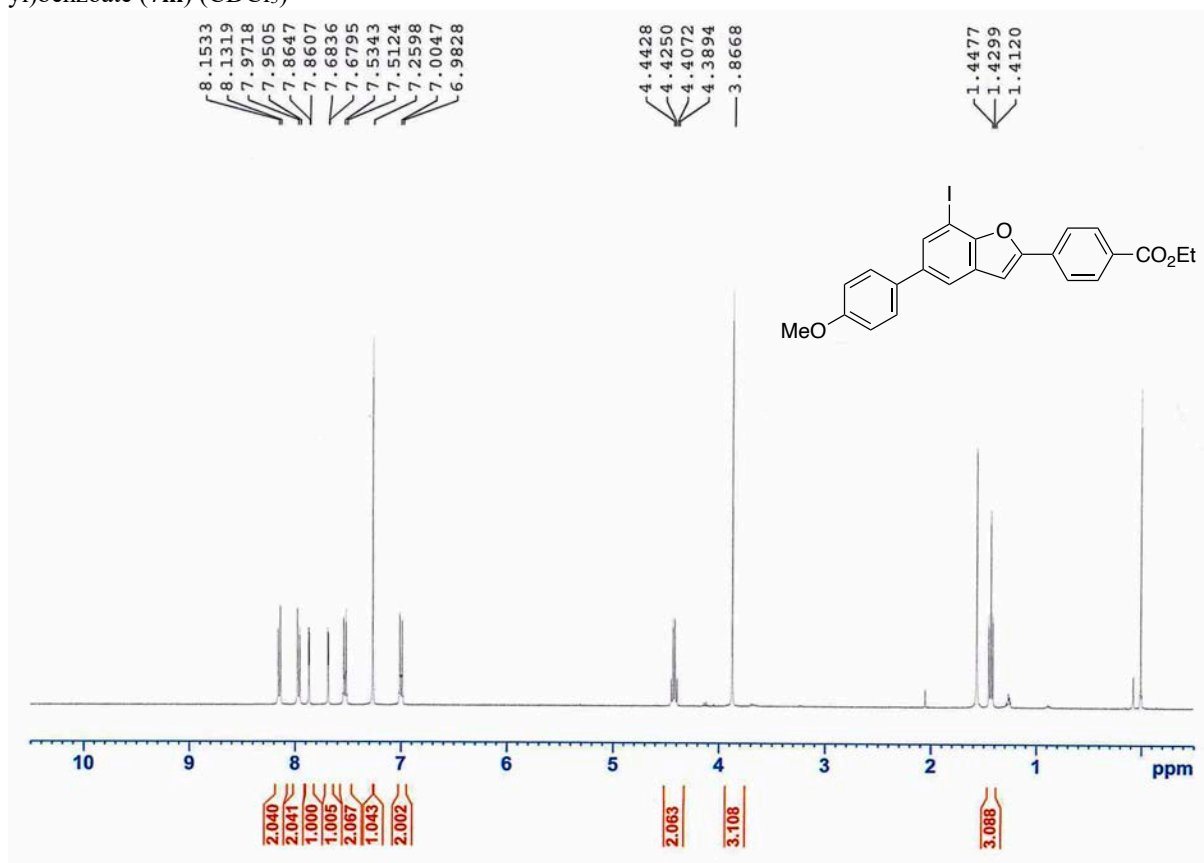
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of ethyl 4-(6-morpholinobenzofuran-2-yl)benzoate (**15**) ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of ethyl 4-(7-hydroxy-3-(4-methoxyphenyl)-5-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.2.0]octa-1,3,5-trien-7-yl)benzoate (**4m**) ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of ethyl 4-(7-iodo-5-(4-methoxyphenyl)benzofuran-2-yl)benzoate (**7m**) ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra of ethyl 4-(5-(4-methoxyphenyl)-7-(4-nitrophenyl)benzofuran-2-yl)benzoate (**17**) ( $\text{CDCl}_3$ )

