# Supplementary Material

## Direct synthesis of benzofuro[3,2-*b*]benzofurans via a palladium-catalyzed dearomative cyclization

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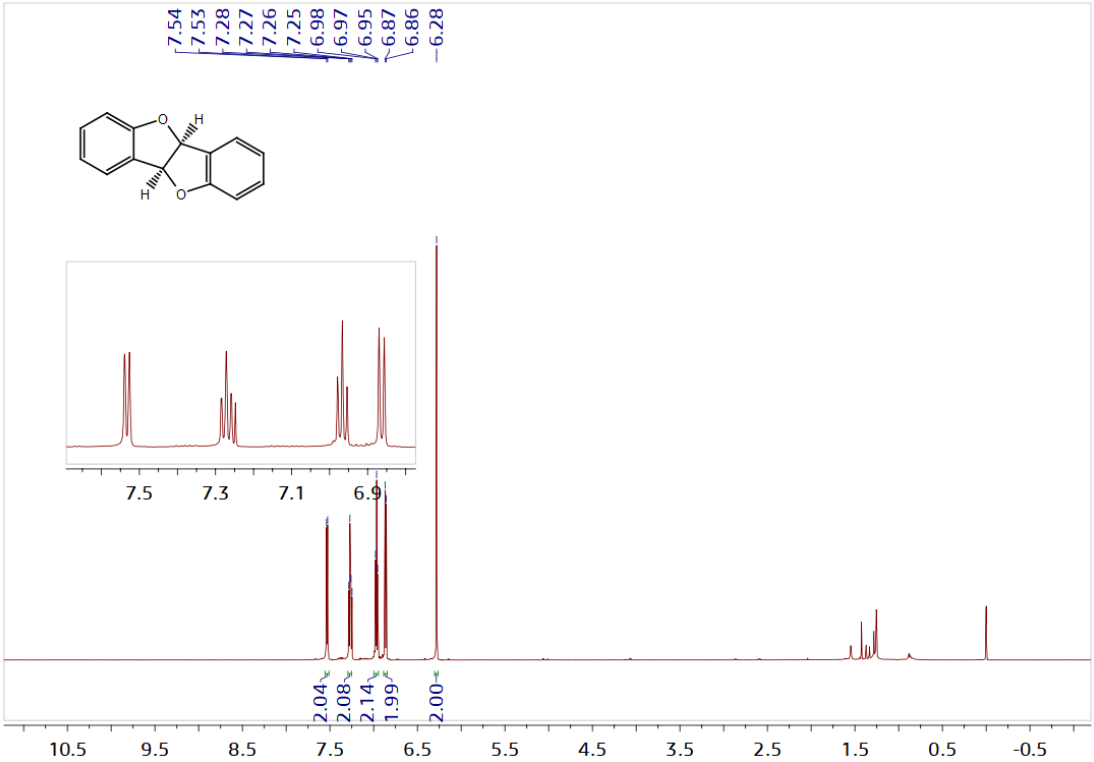
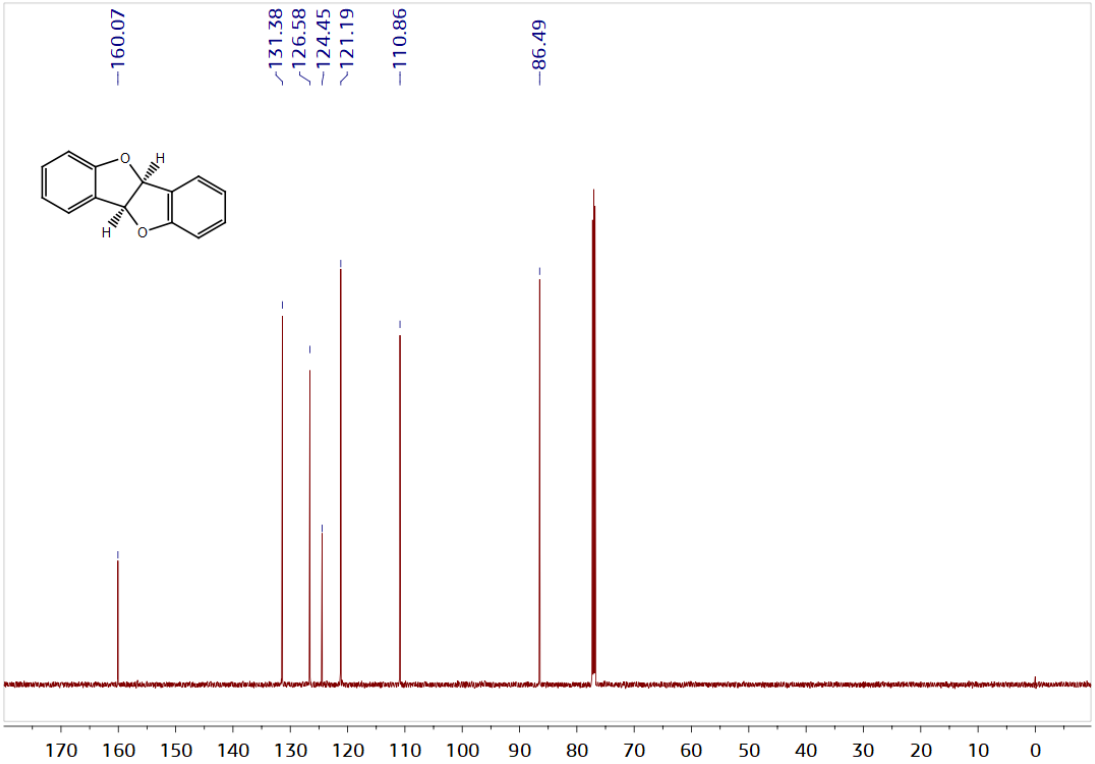
## 1. $^{1}$H NMR and $^{13}$C NMR Spectra

**4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3a)**. $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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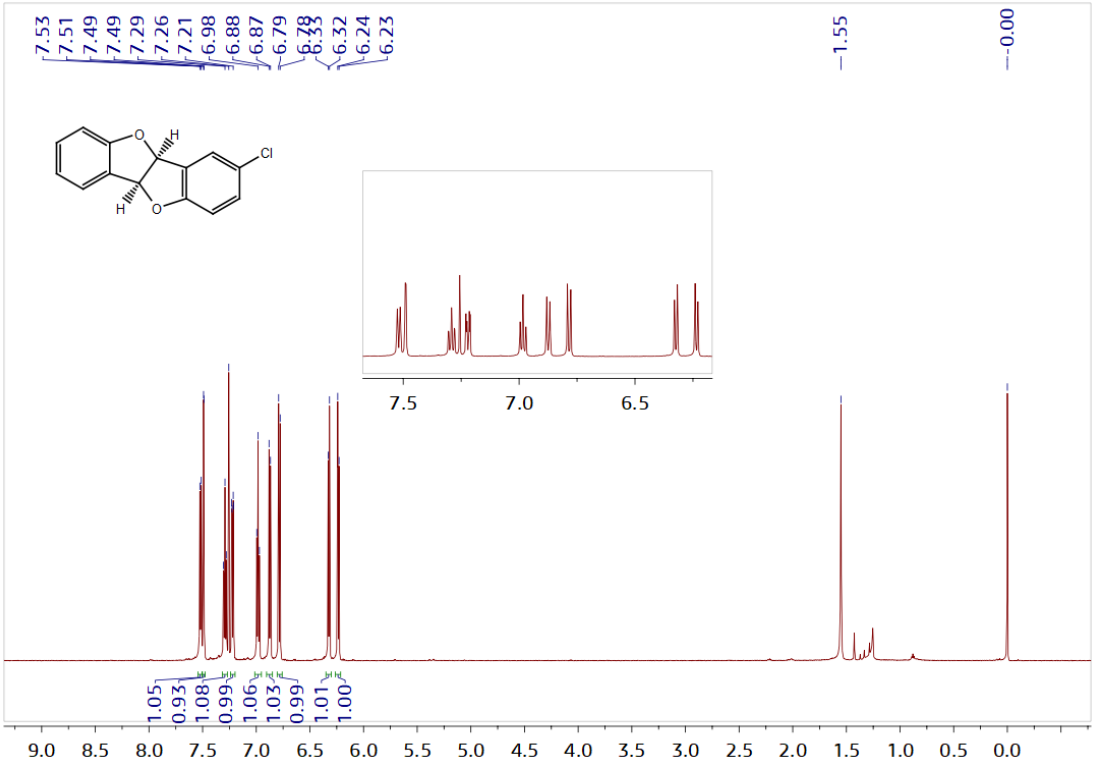
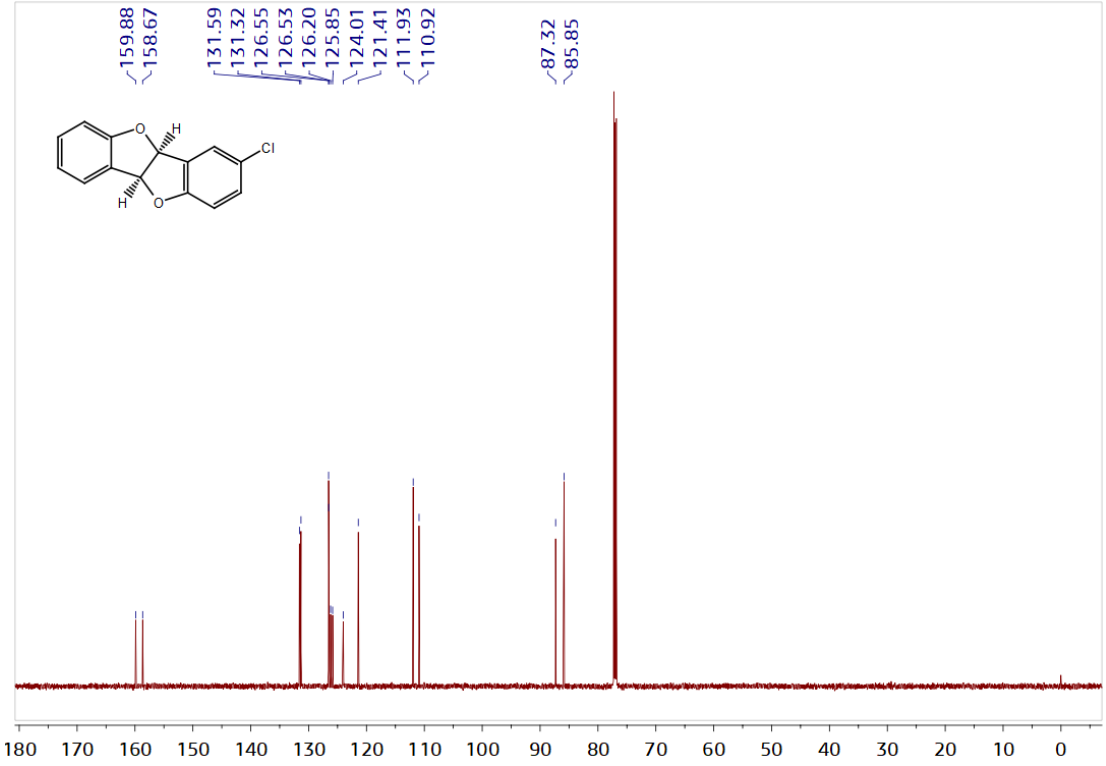
**3-Chloro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3b).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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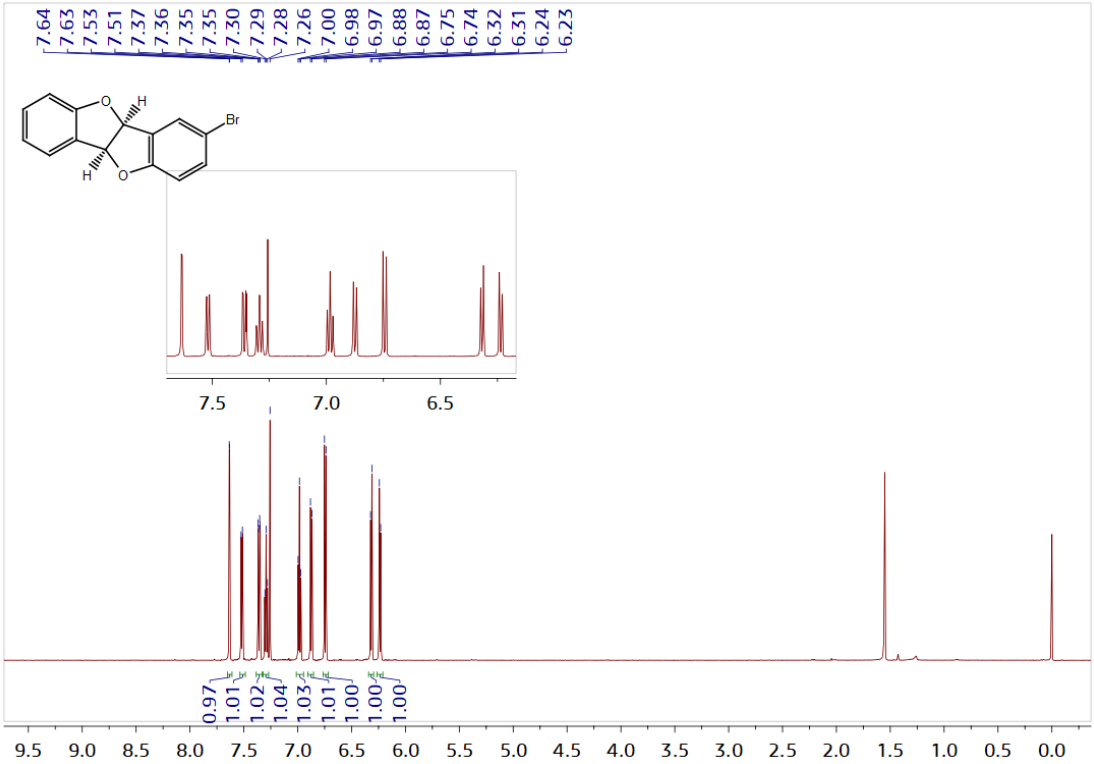
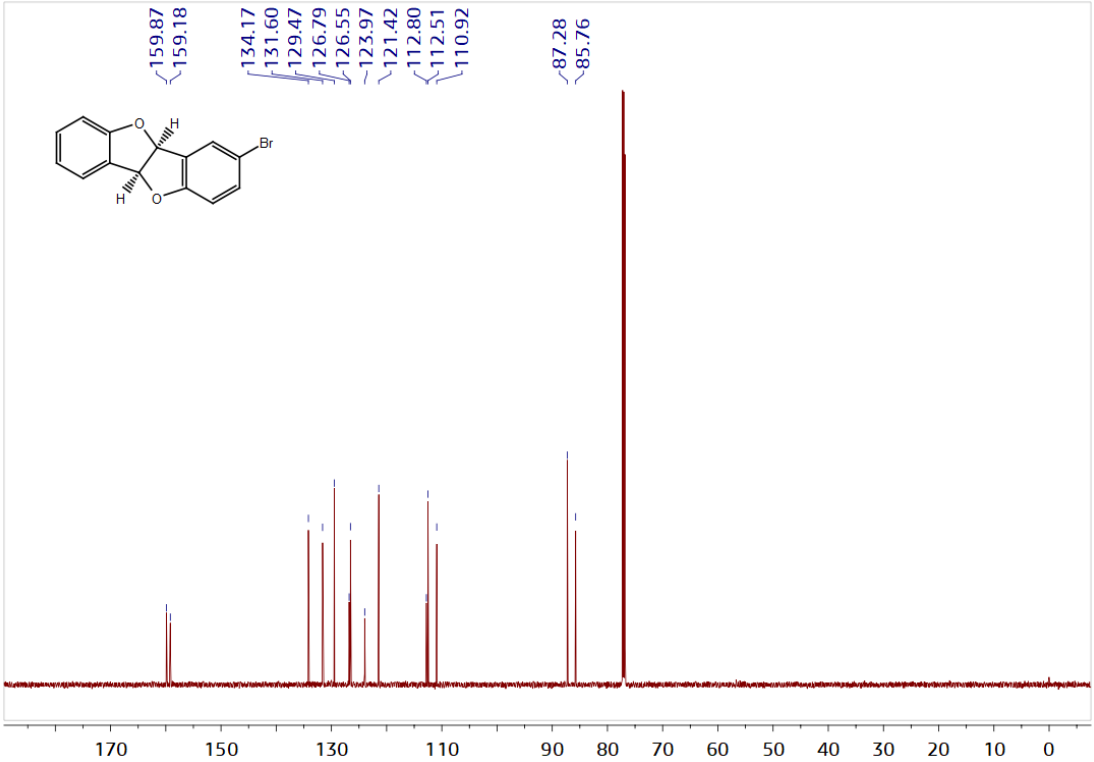
**3-Bromo-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3c).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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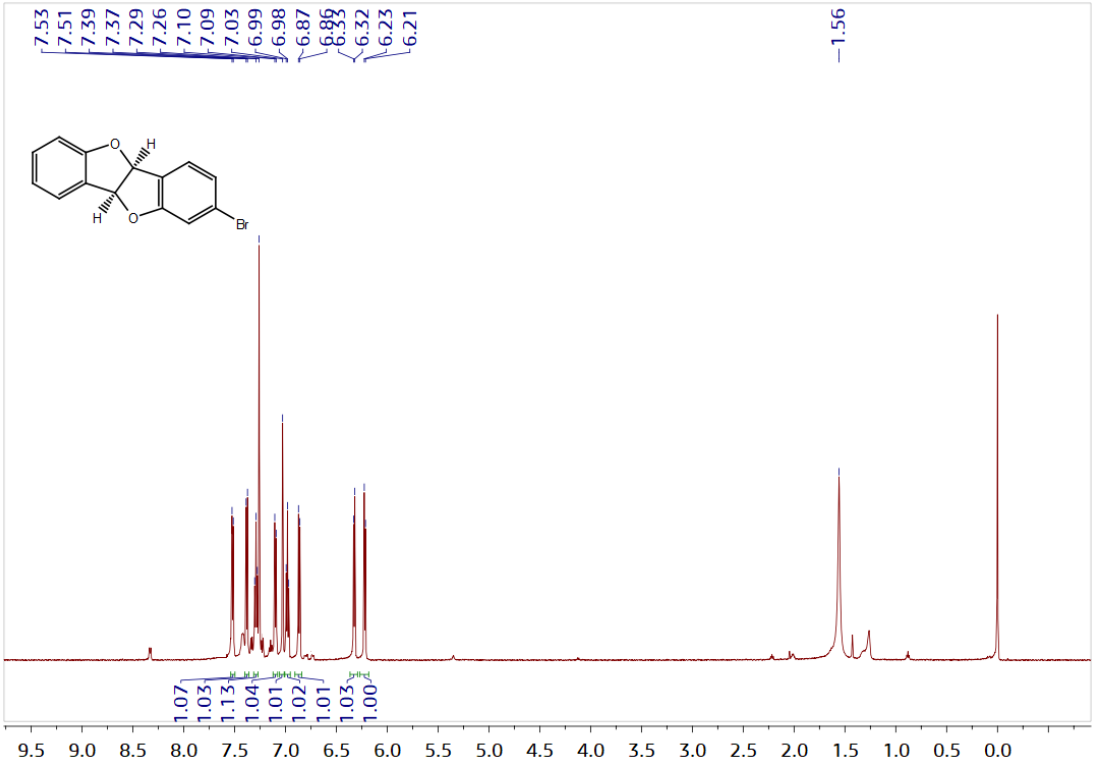
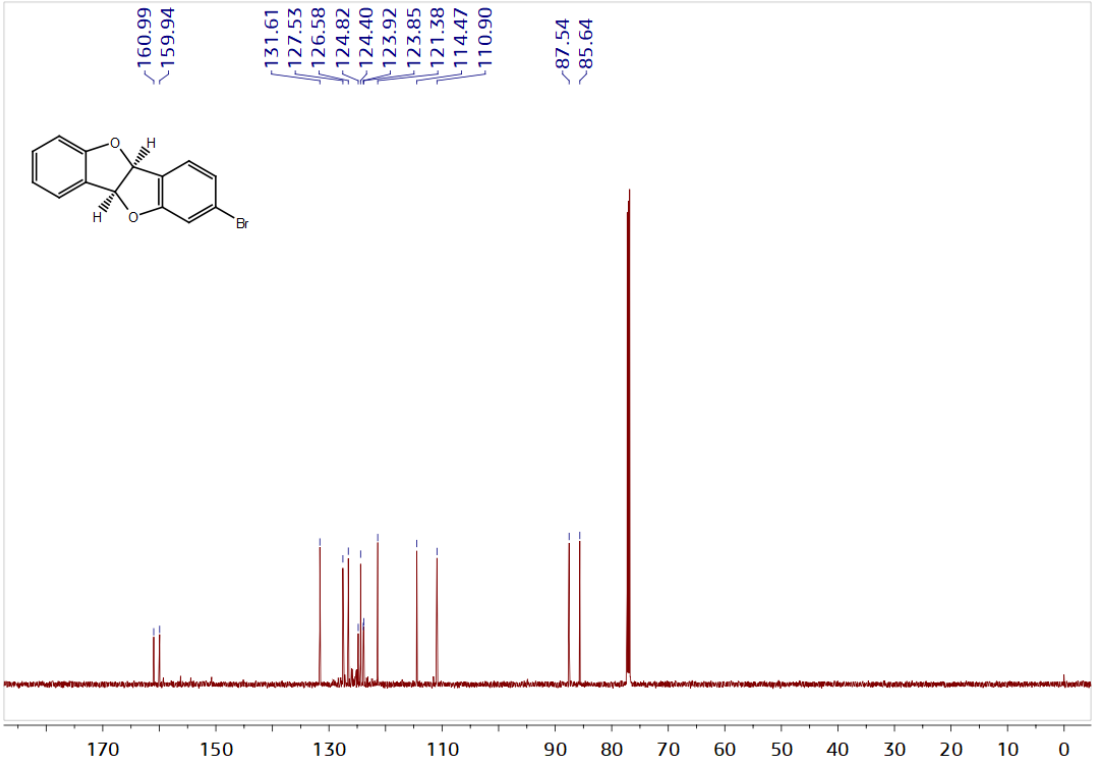
**2-Bromo-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3d).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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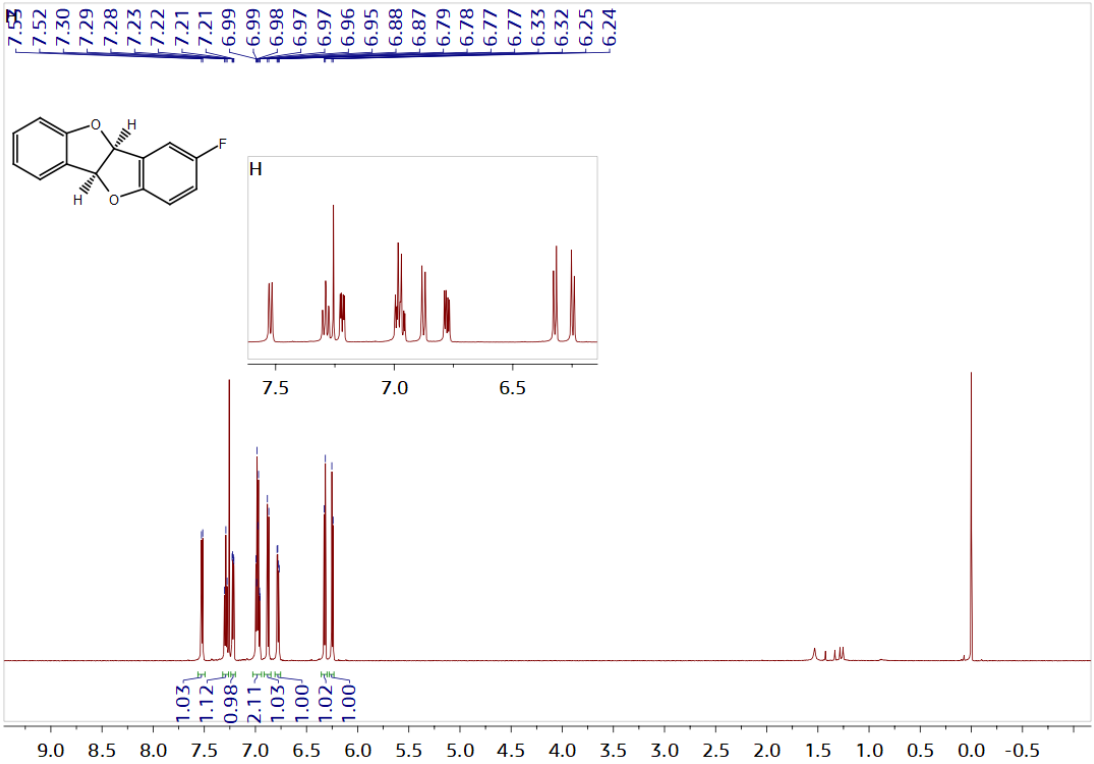
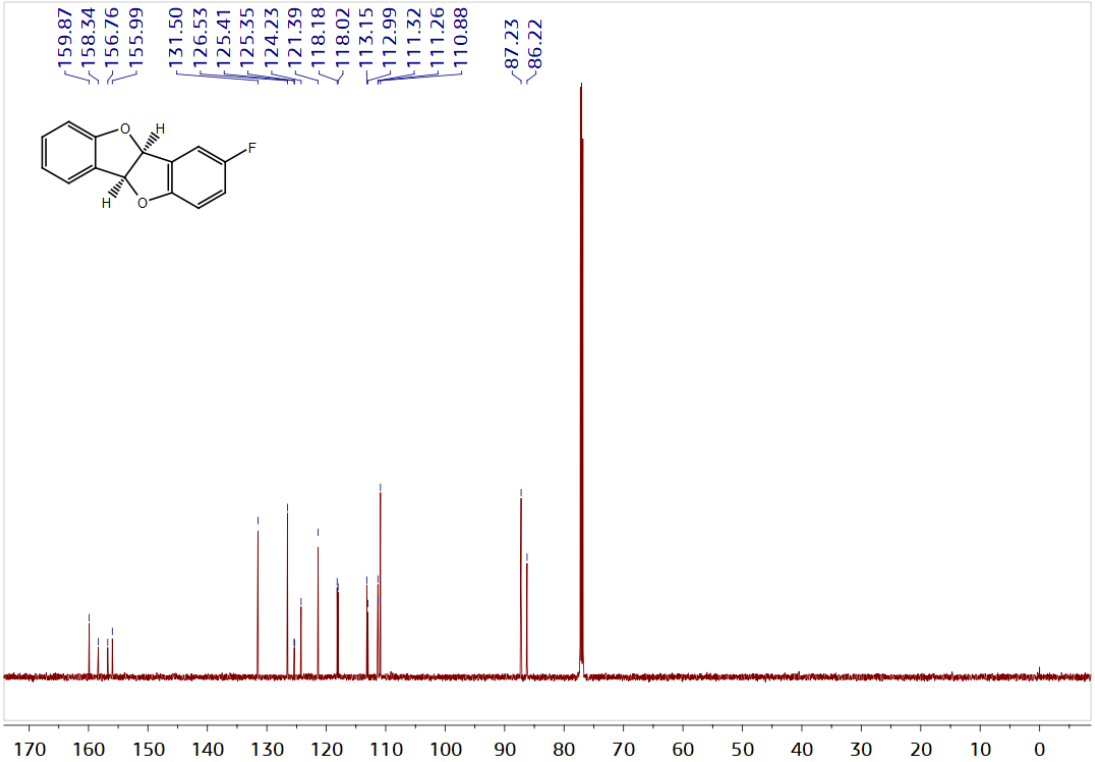
**3-Fluoro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3e).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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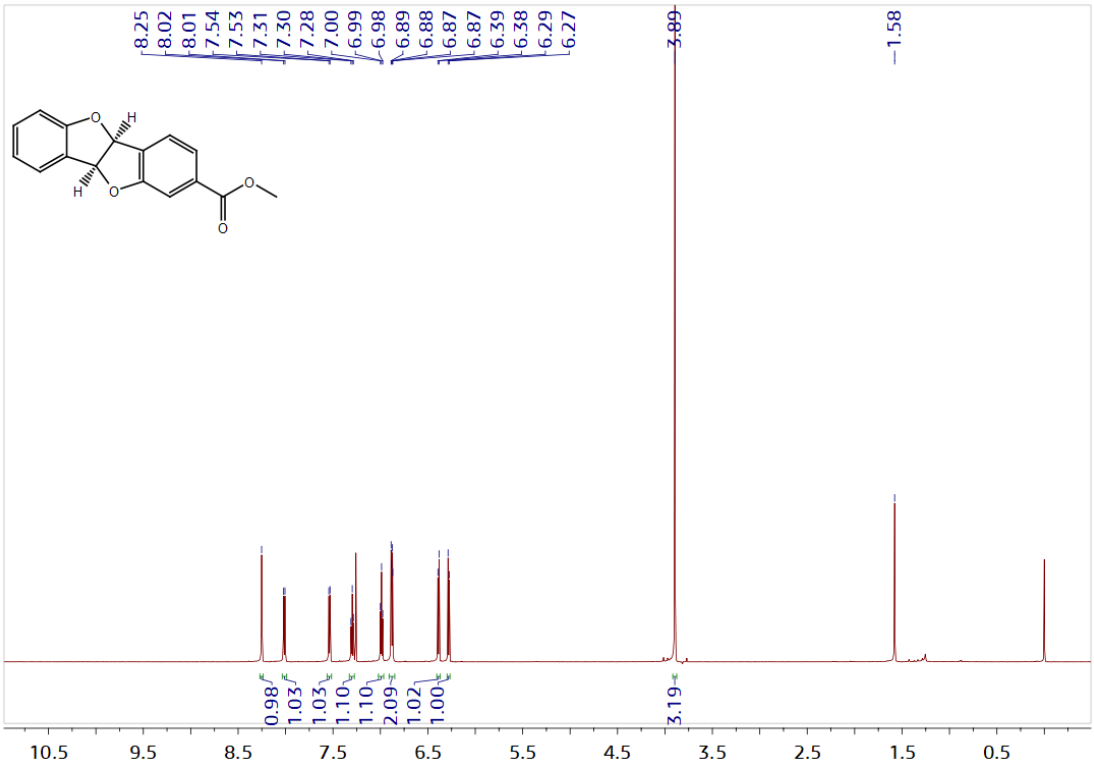
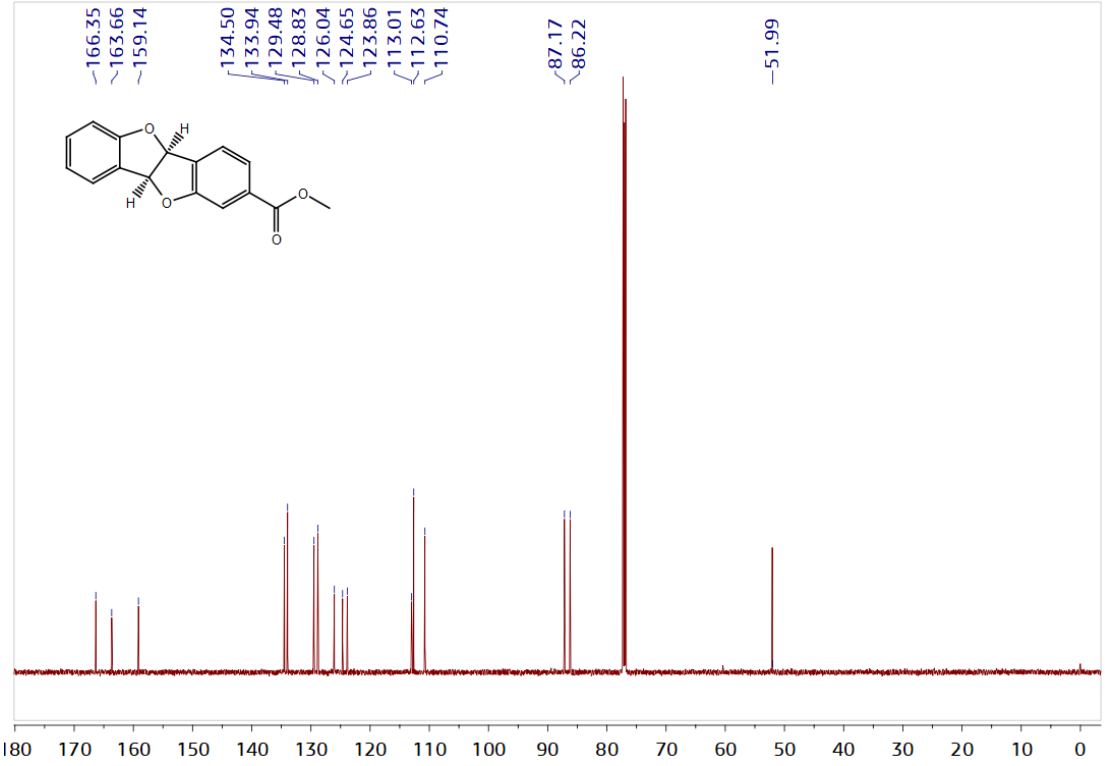
**Methyl 4b,9b-dihydrobenzofuro[3,2-b]benzofuran-2-carboxylate (3f).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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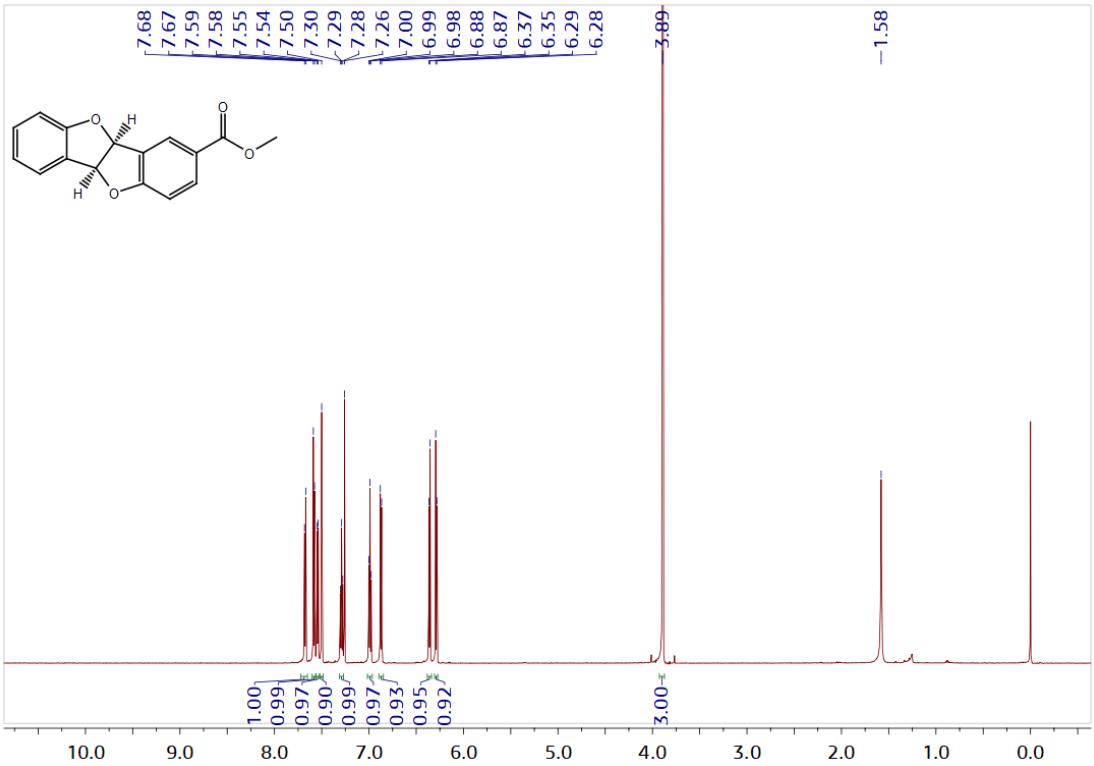
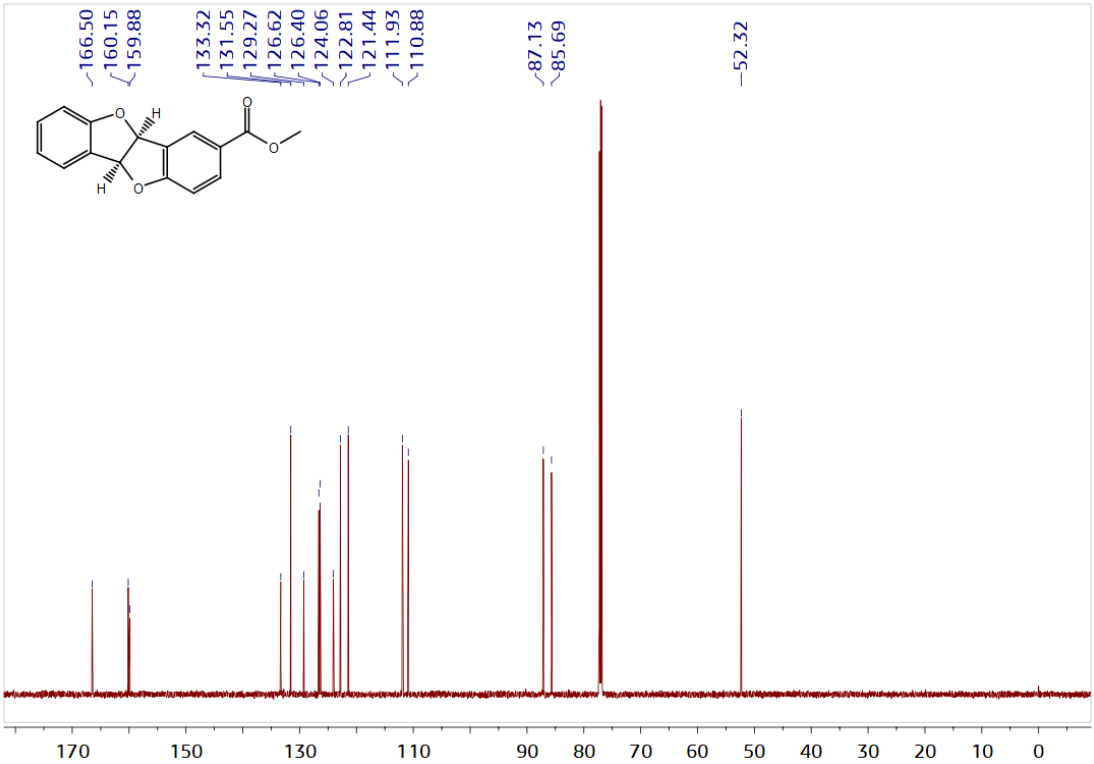
**Methyl 4b,9b-dihydrobenzofuro[3,2-b]benzofuran-3-carboxylate (3g).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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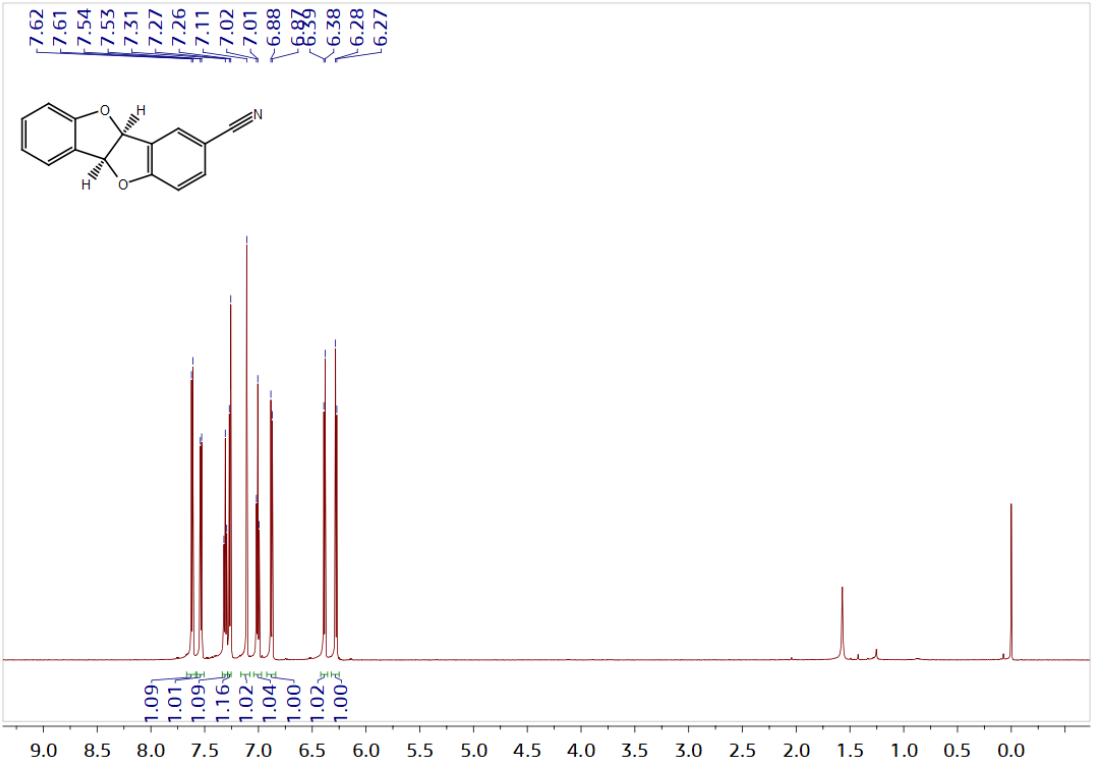
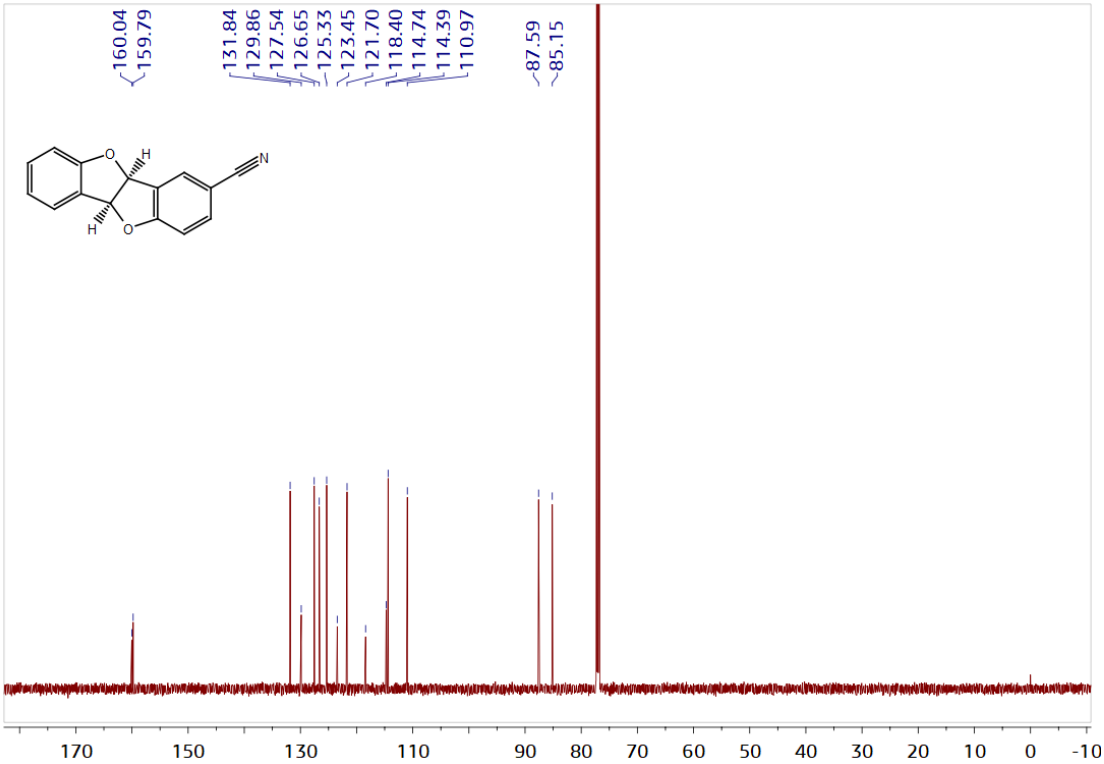
**4b,9b-Dihydrobenzofuro[3,2-b]benzofuran-3-carbonitrile (3h).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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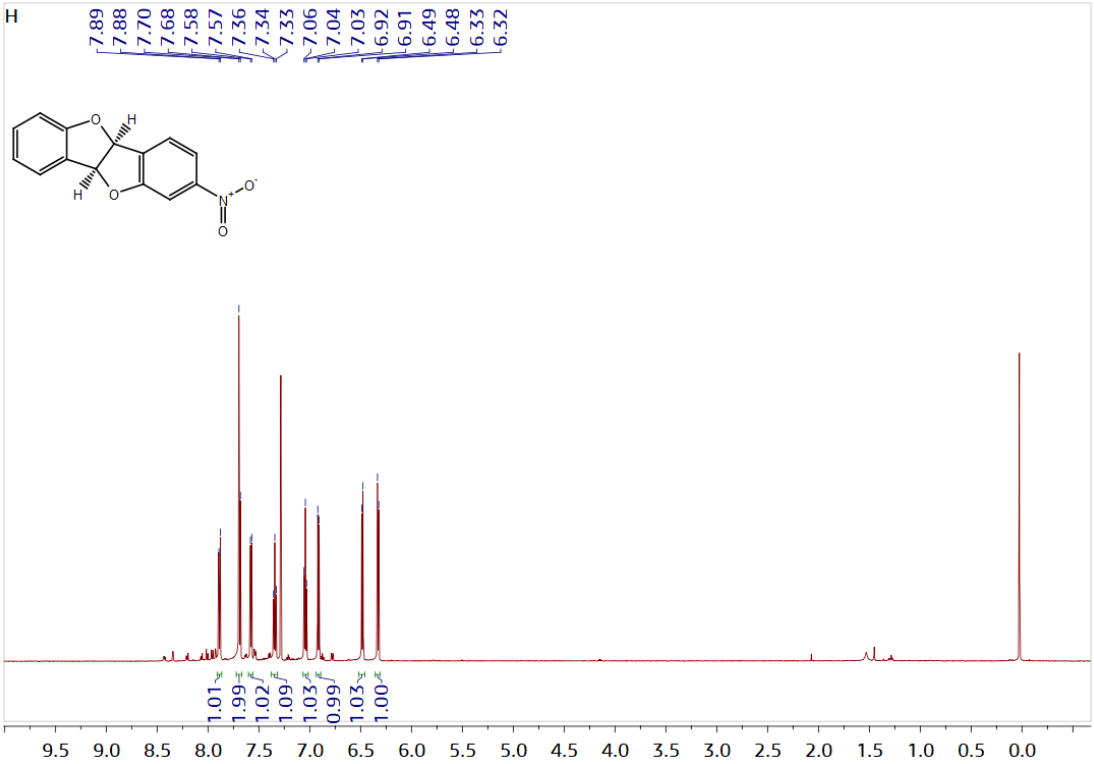
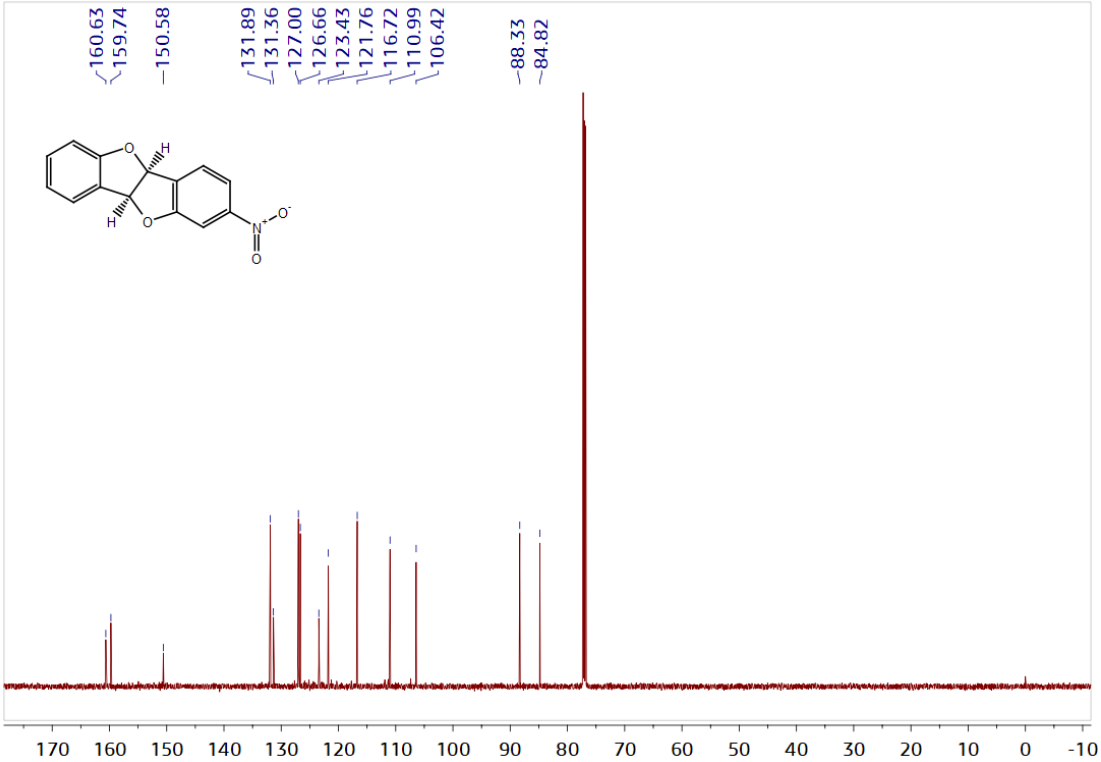
**2-Nitro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3i).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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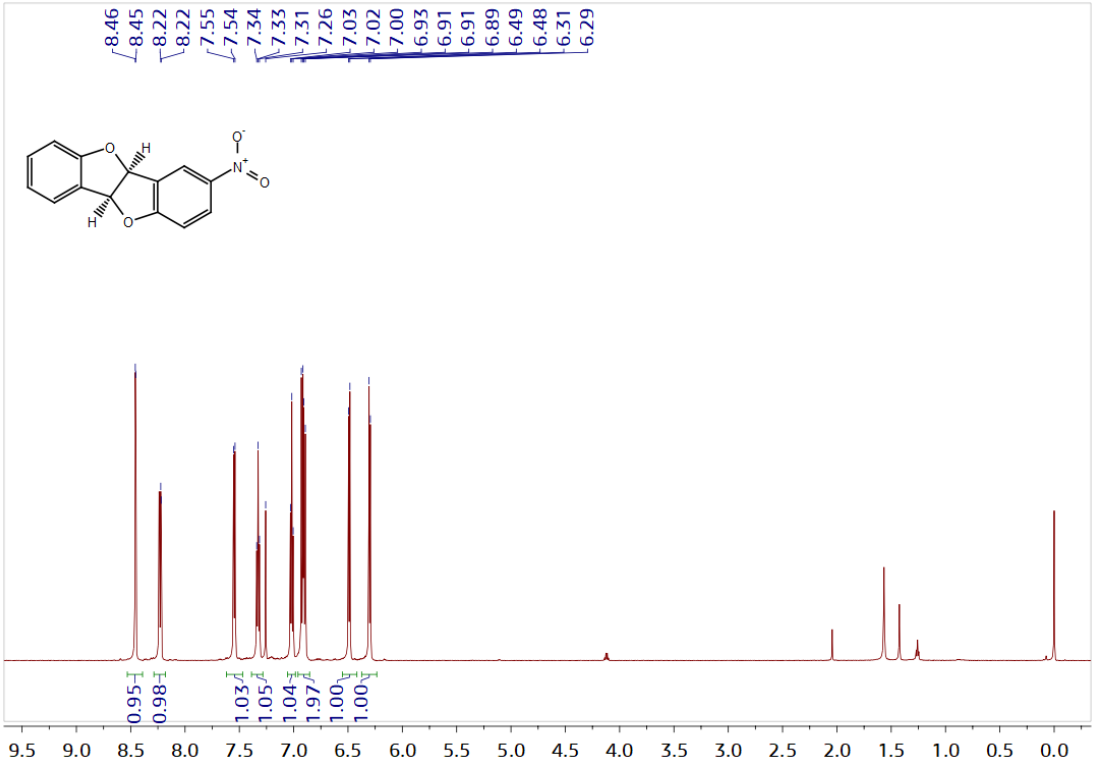
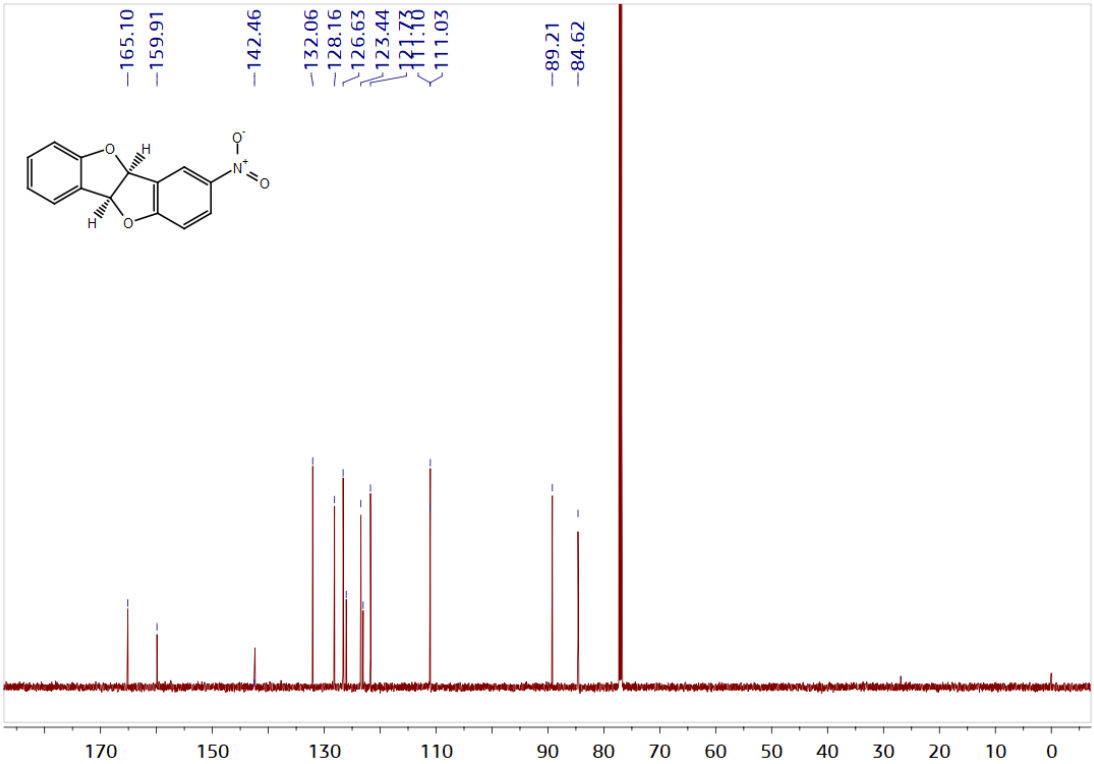
3-**Nitro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3j).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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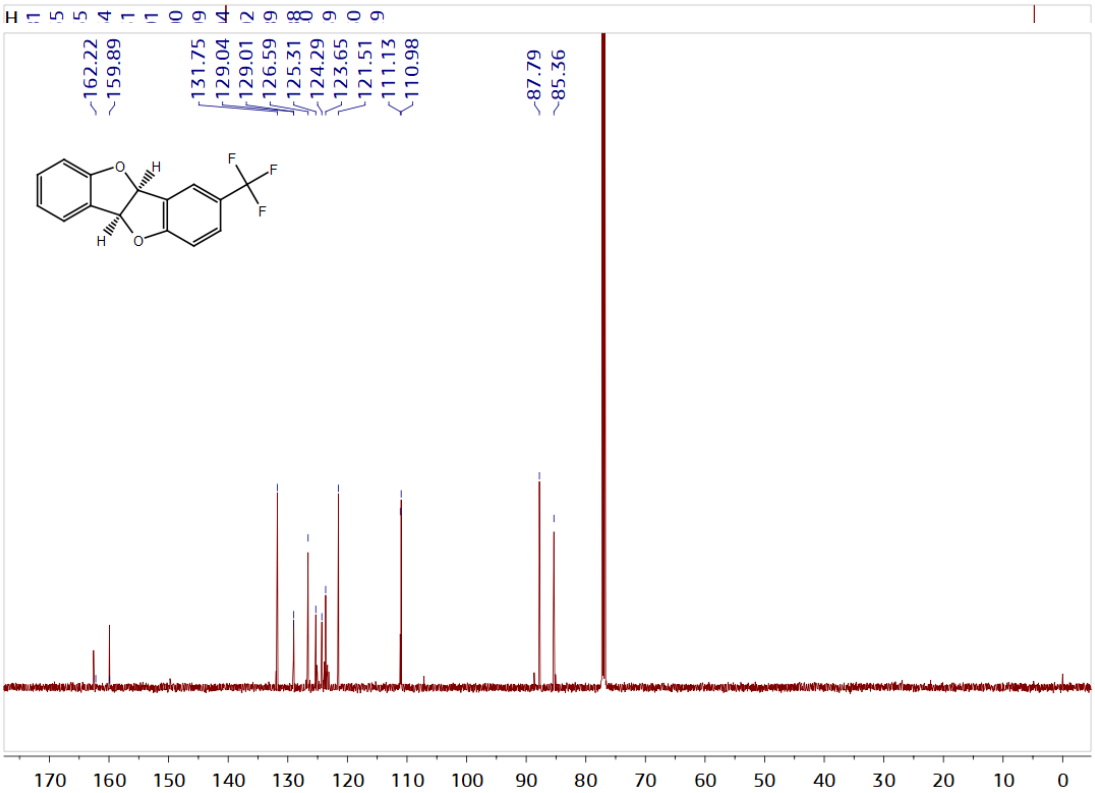
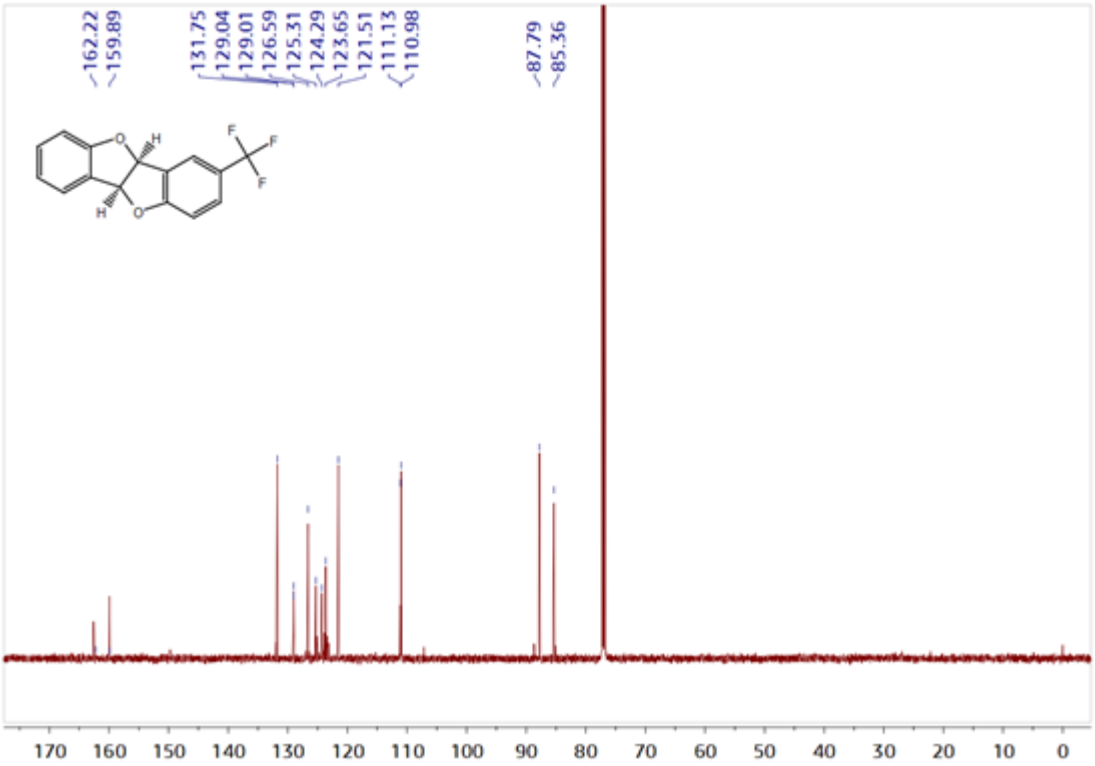
**3-(Trifluoromethyl)-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3k).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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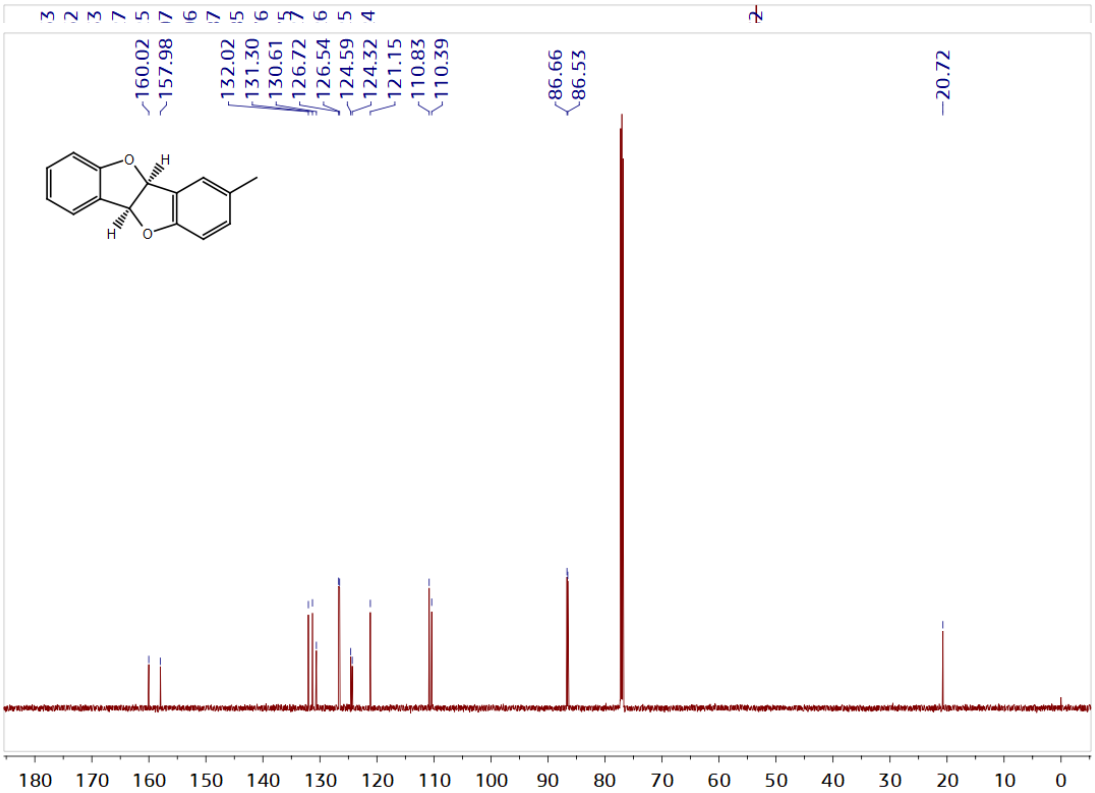
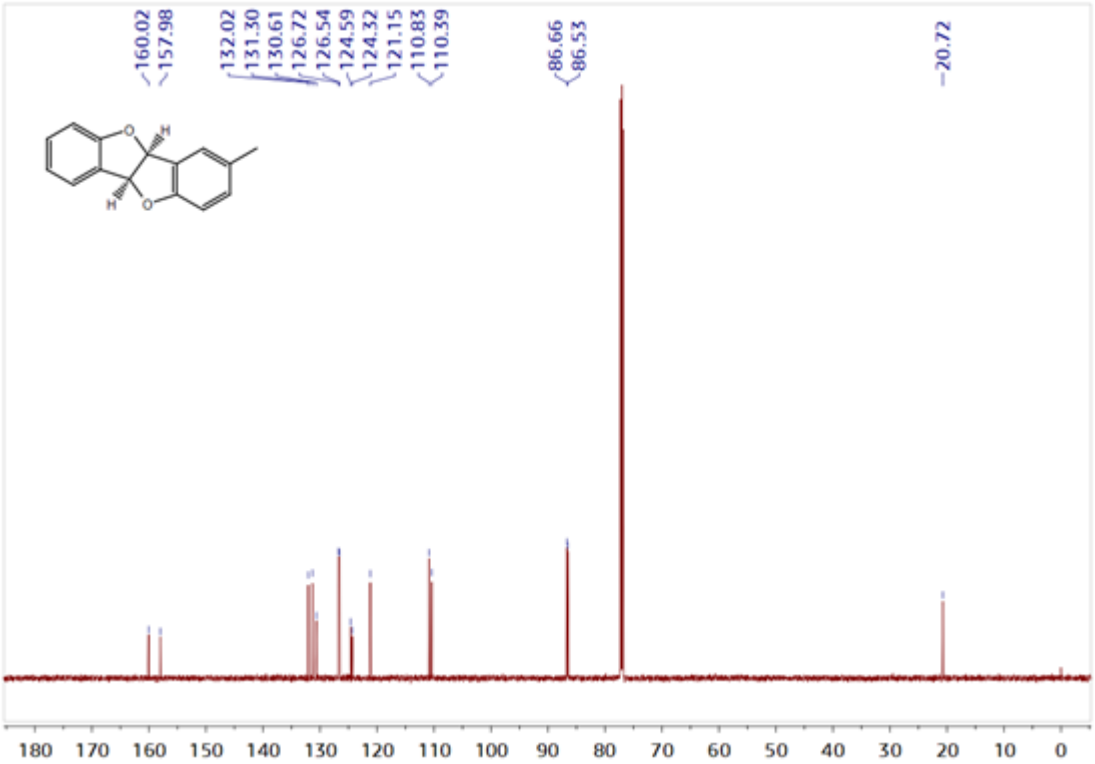
**3-Methyl-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3l).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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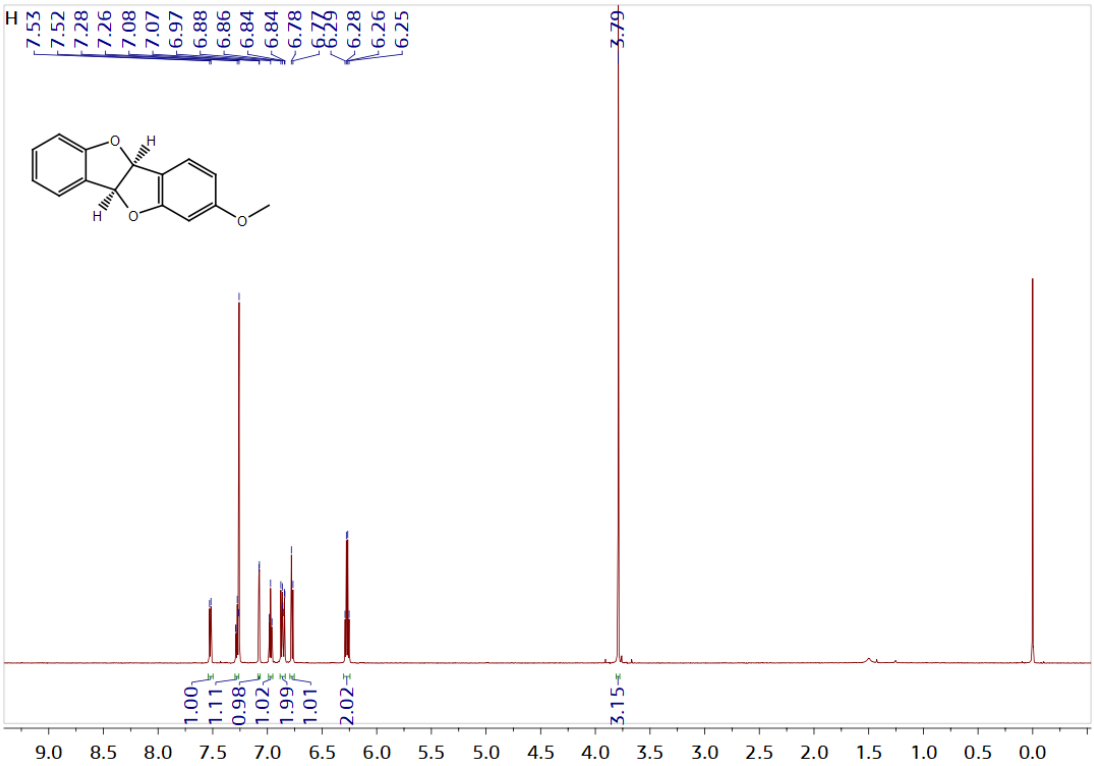
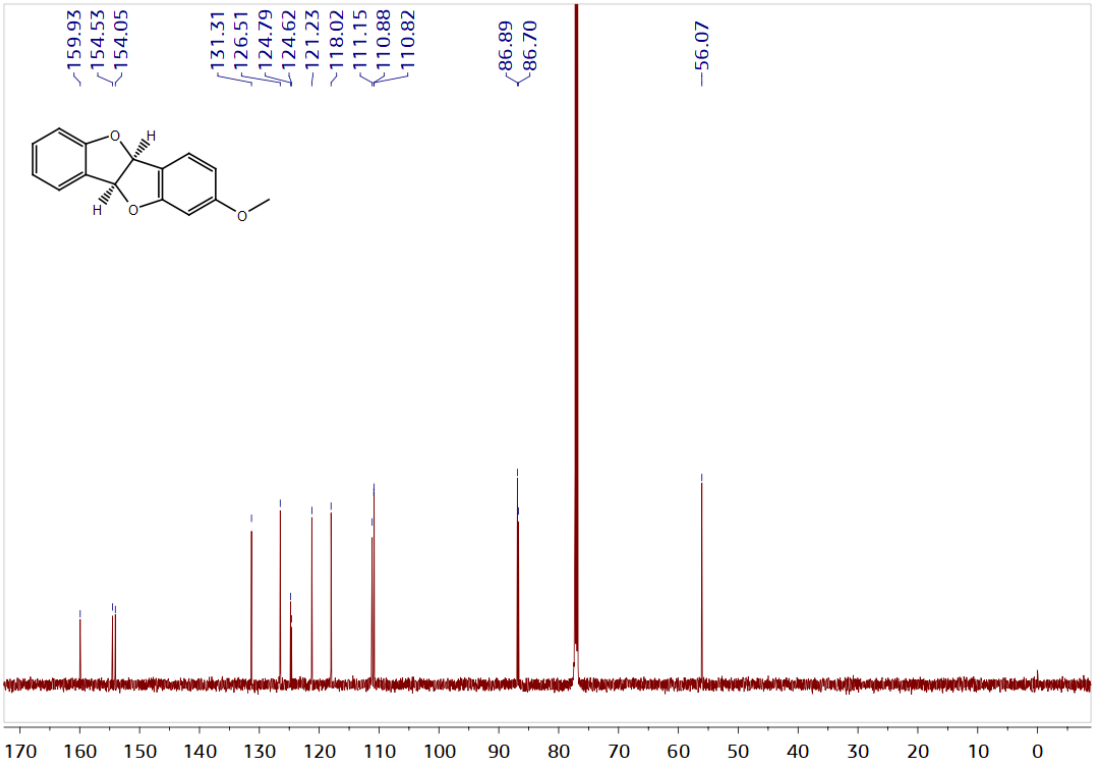
**3-Methoxy-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3m).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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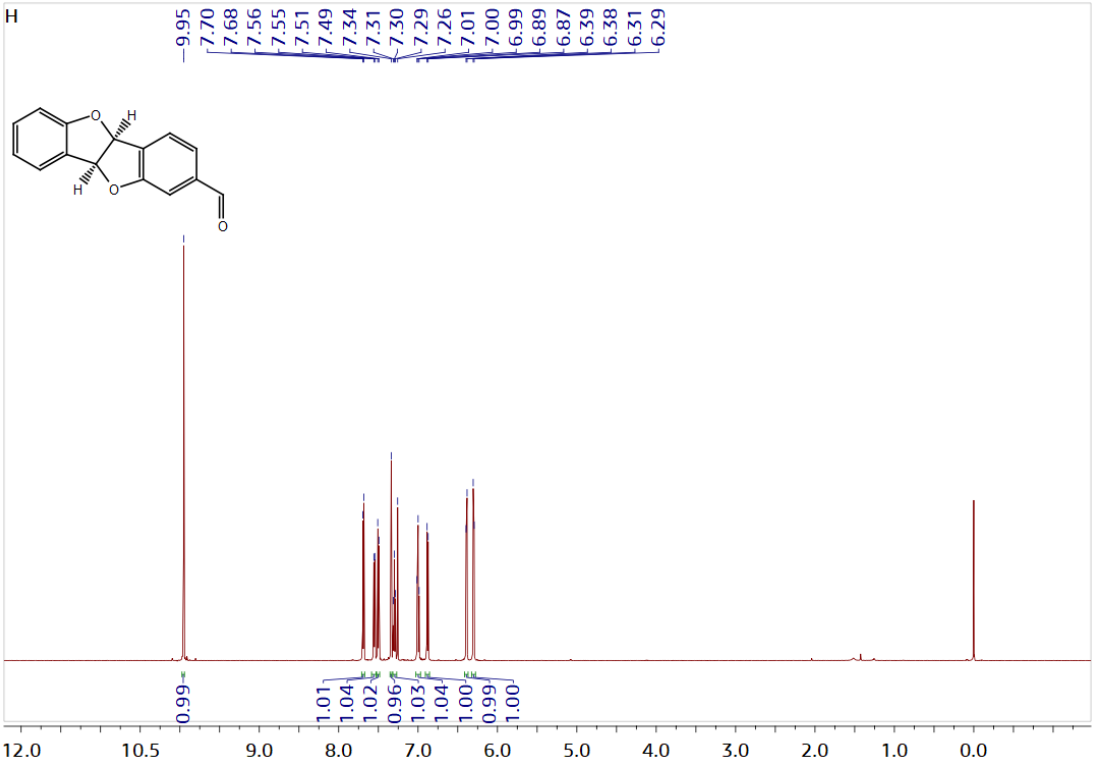
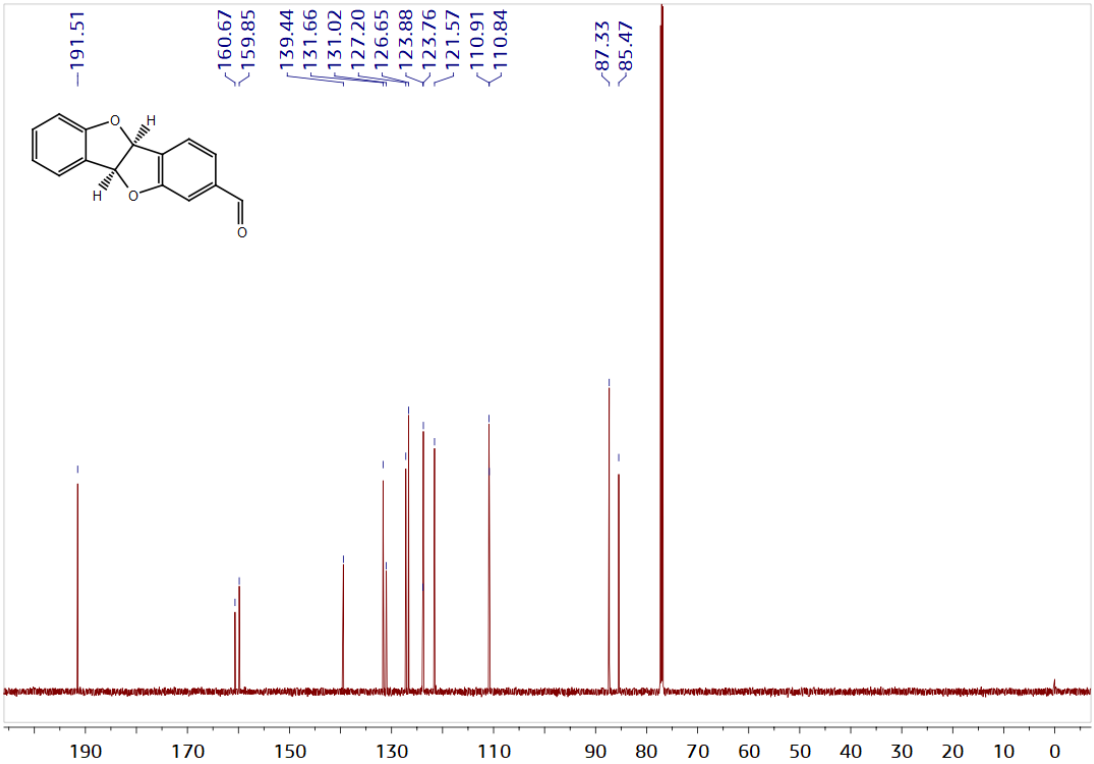
**4b,9b-Dihydrobenzofuro[3,2-b]benzofuran-2-carbaldehyde (3n).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)





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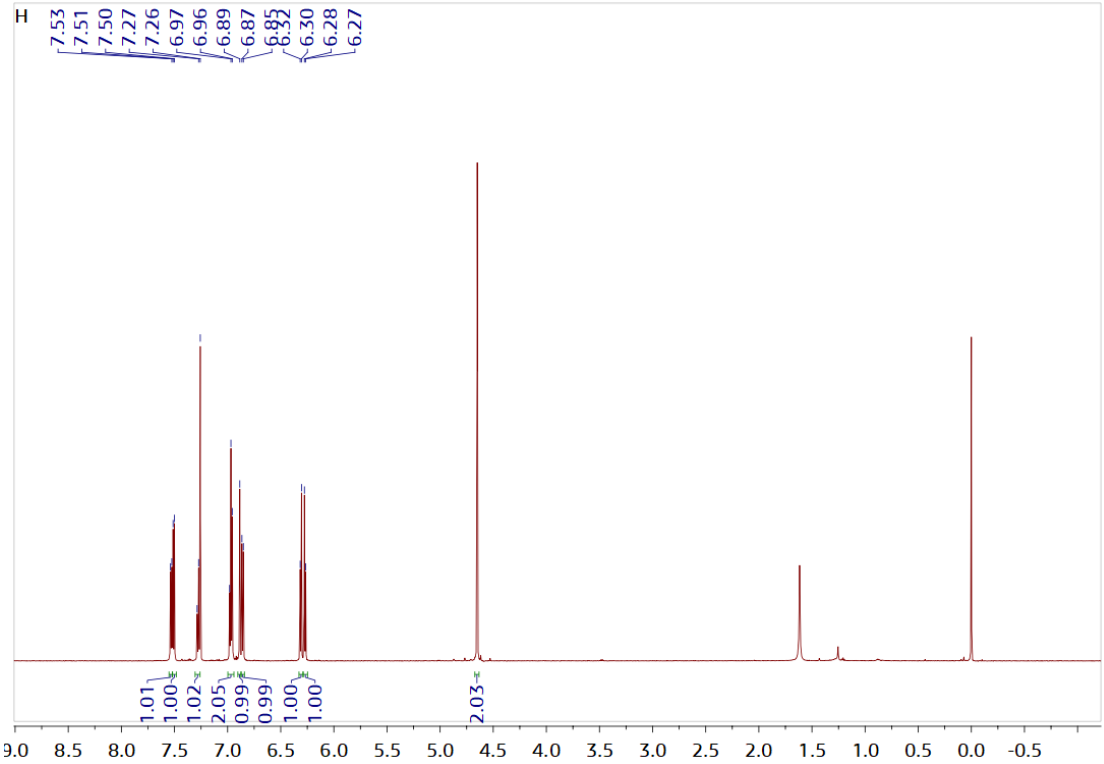
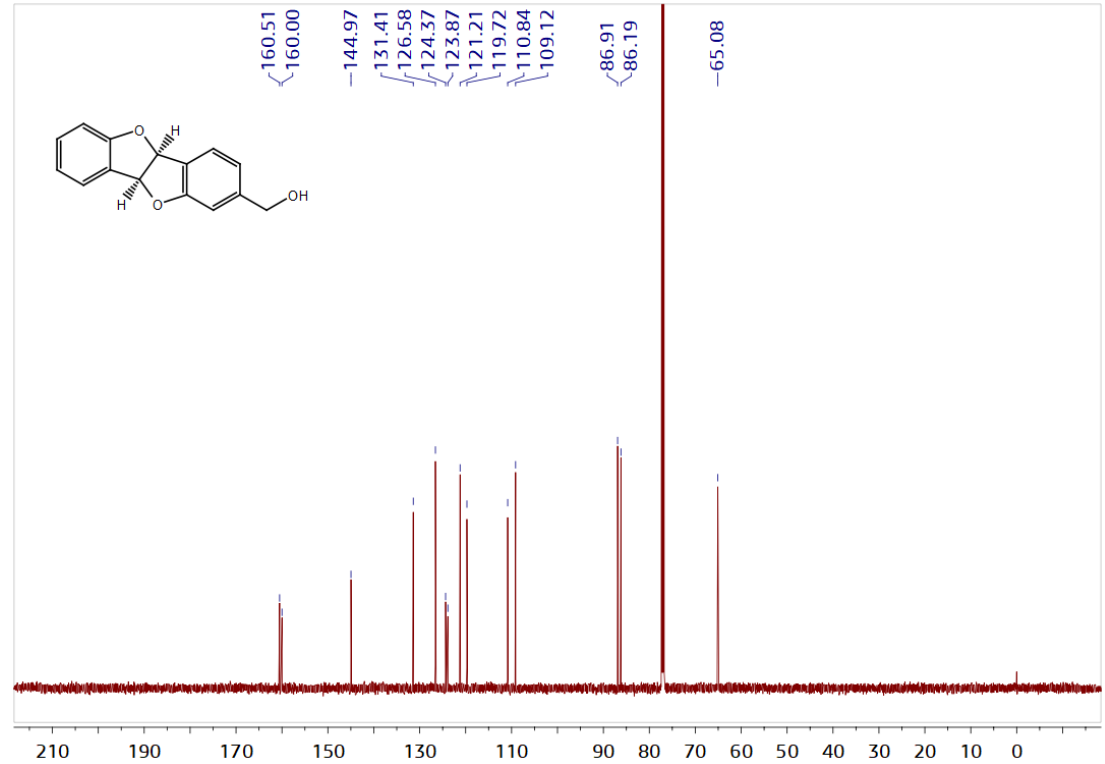
**(4b,9b-Dihydrobenzofuro[3,2-b]benzofuran-2-yl)methanol (3o).** $^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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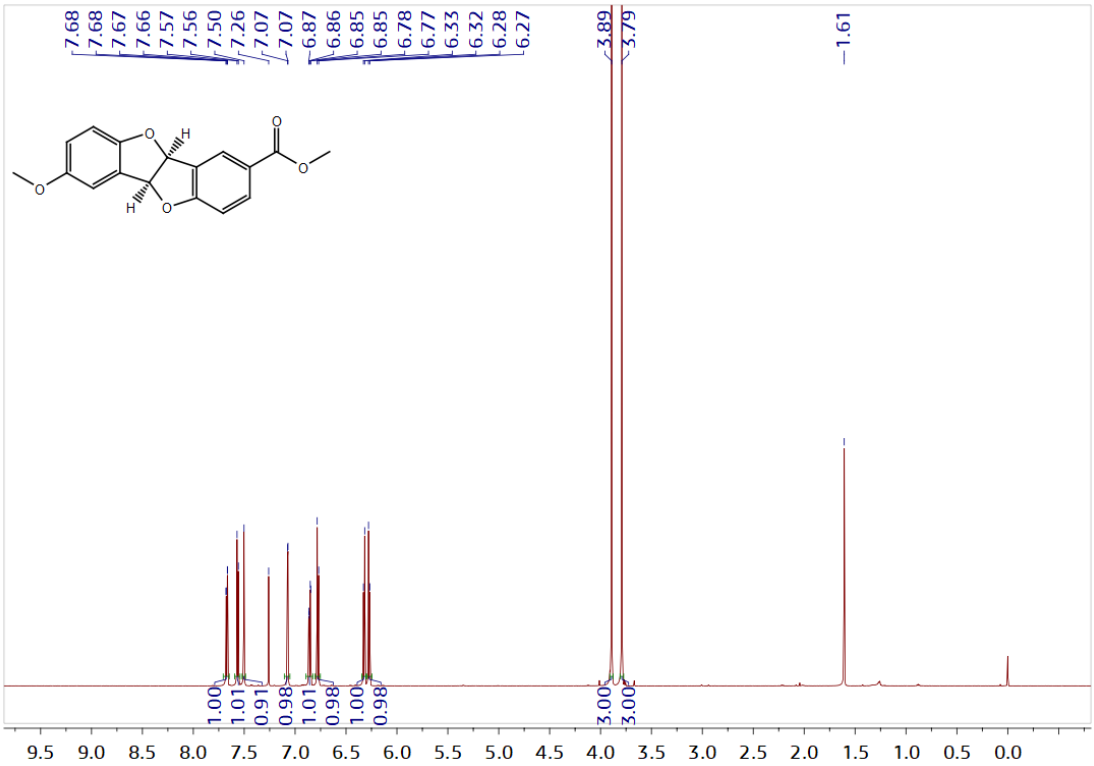
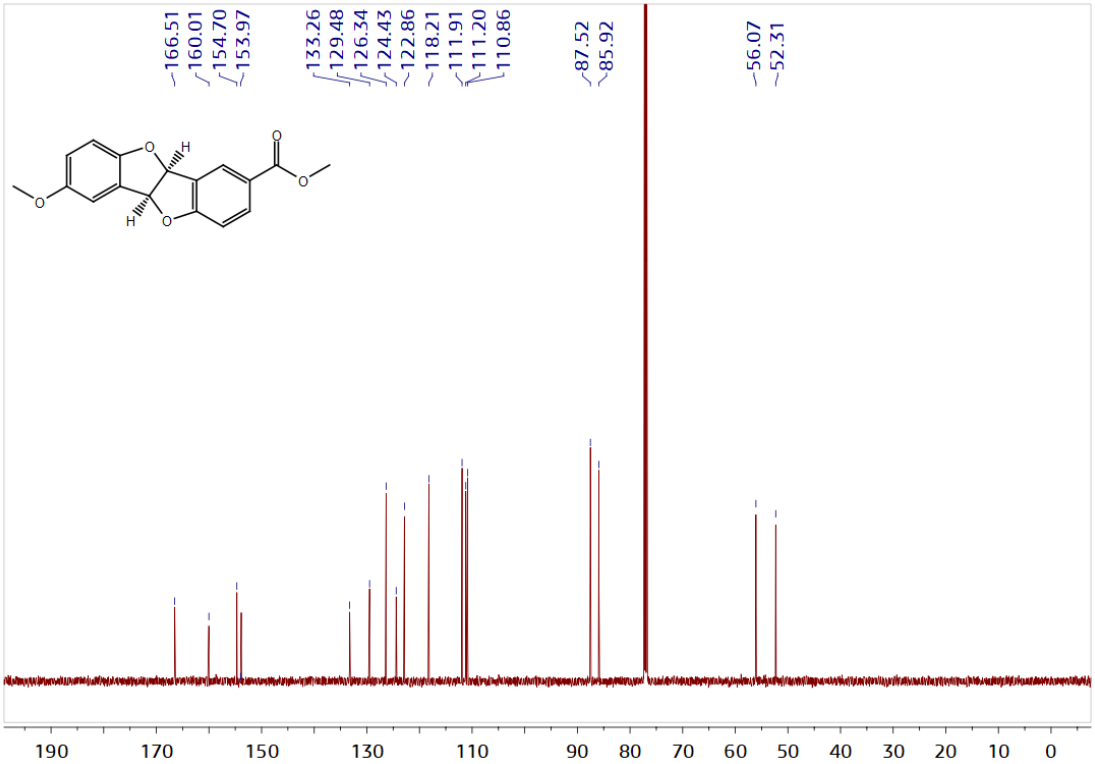
**Methyl 8-methoxy-4b,9b-dihydrobenzofuro[3,2-b]benzofuran-3-carboxylate (3p).**
$^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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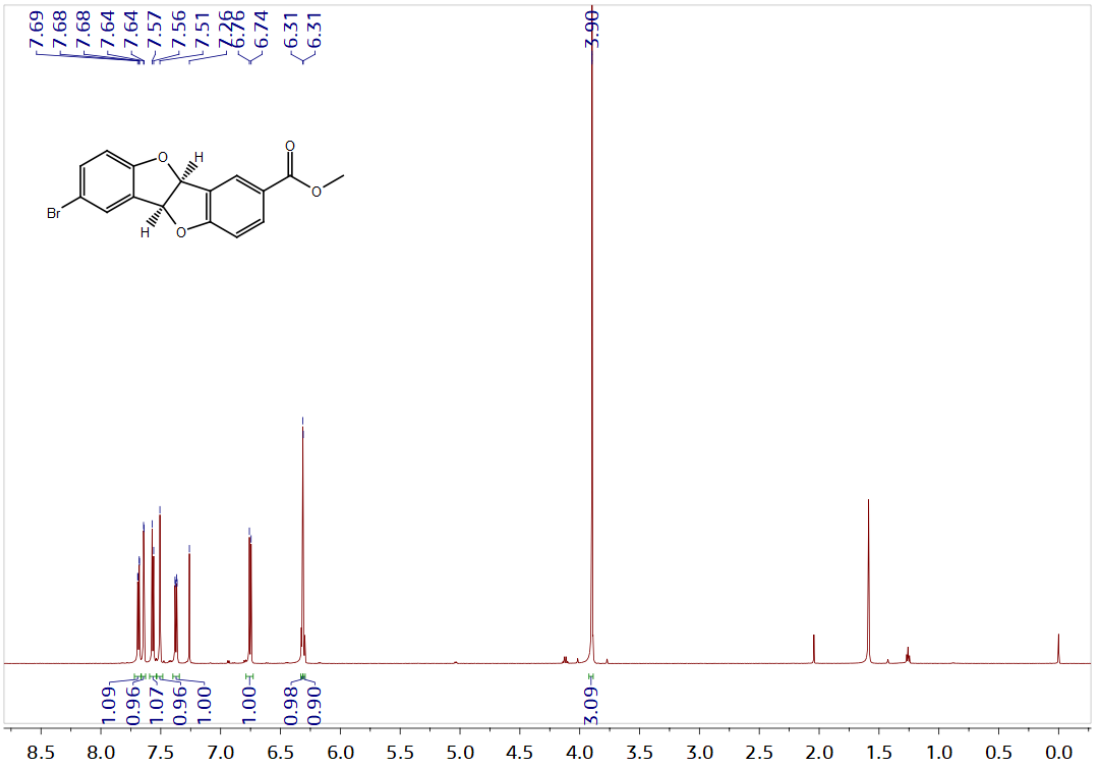
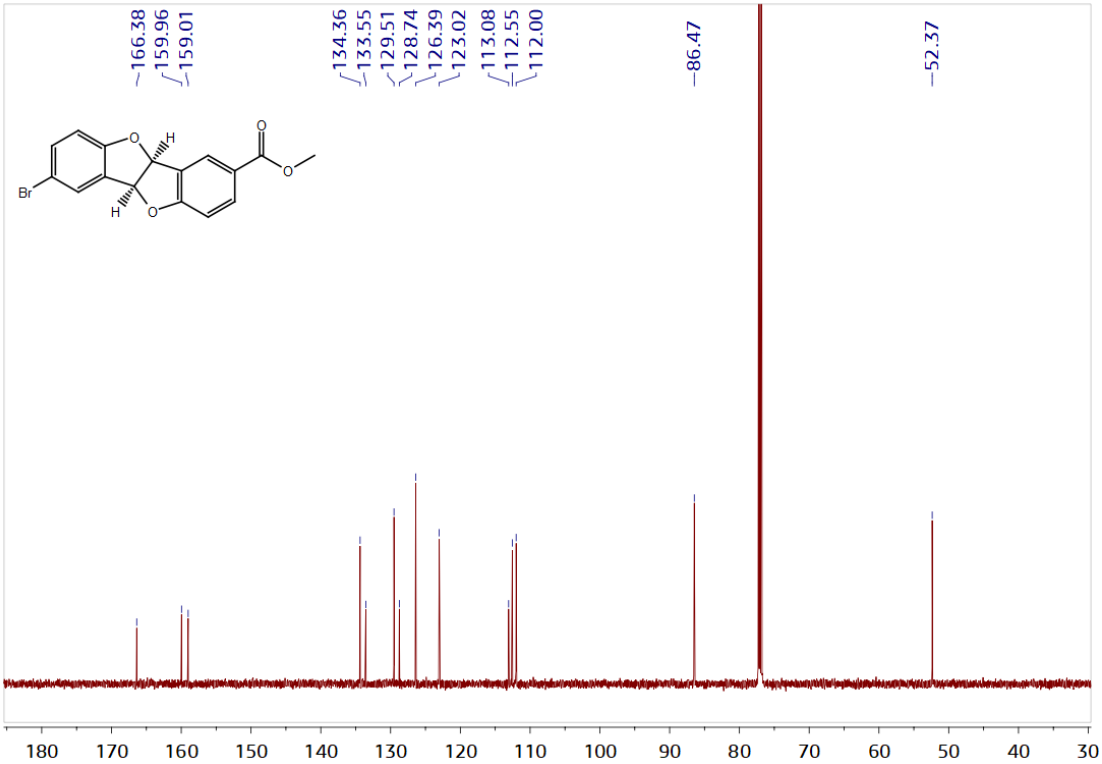
**Methyl 8-bromo-4b,9b-dihydrobenzofuro[3,2-b]benzofuran-3-carboxylate (3q).**
$^{1}$H NMR (600 MHz, $CDCl_3$); $^{13}$C NMR (151 MHz, $CDCl_3$)

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## 2. X-ray crystallographic data for 3e

Table S1. Crystal data and structure refinement for **3f**

| | |
|---|---|
| Empirical formula | $C_{16}H_{12}O_4$ |
| Formula weight | 268.26 |
| Temperature/K | 296(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 6.1865(18) |
| b/Å | 24.756(8) |
| c/Å | 8.275(3) |
| α/° | 90 |
| β/° | 101.442(9) |
| γ/° | 90 |
| Volume/Å$^3$ | 1242.2(7) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.434 |
| m/mm$^{-1}$ | 0.104 |
| F(000) | 560.0 |
| Crystal size/mm$^3$ | 0.3 × 0.25 × 0.2 |
| 2Θ range for data collection | 5.286 to 50.118° |
| Index ranges | $-7 \leq h \leq 7$, $-28 \leq k \leq 29$, $-9 \leq l \leq 9$ |
| Reflections collected | 19209 |
| Independent reflections | 2188[R(int) = 0.0635] |
| Data/restraints/parameters | 2188/0/183 |
| Goodness-of-fit on $F^2$ | 1.041 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0504, $wR_2$ = 0.0919 |
| Final R indexes [all data] | $R_1$ = 0.0860, $wR_2$ = 0.1081 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.17/-0.17 |

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