

Supplementary Material

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

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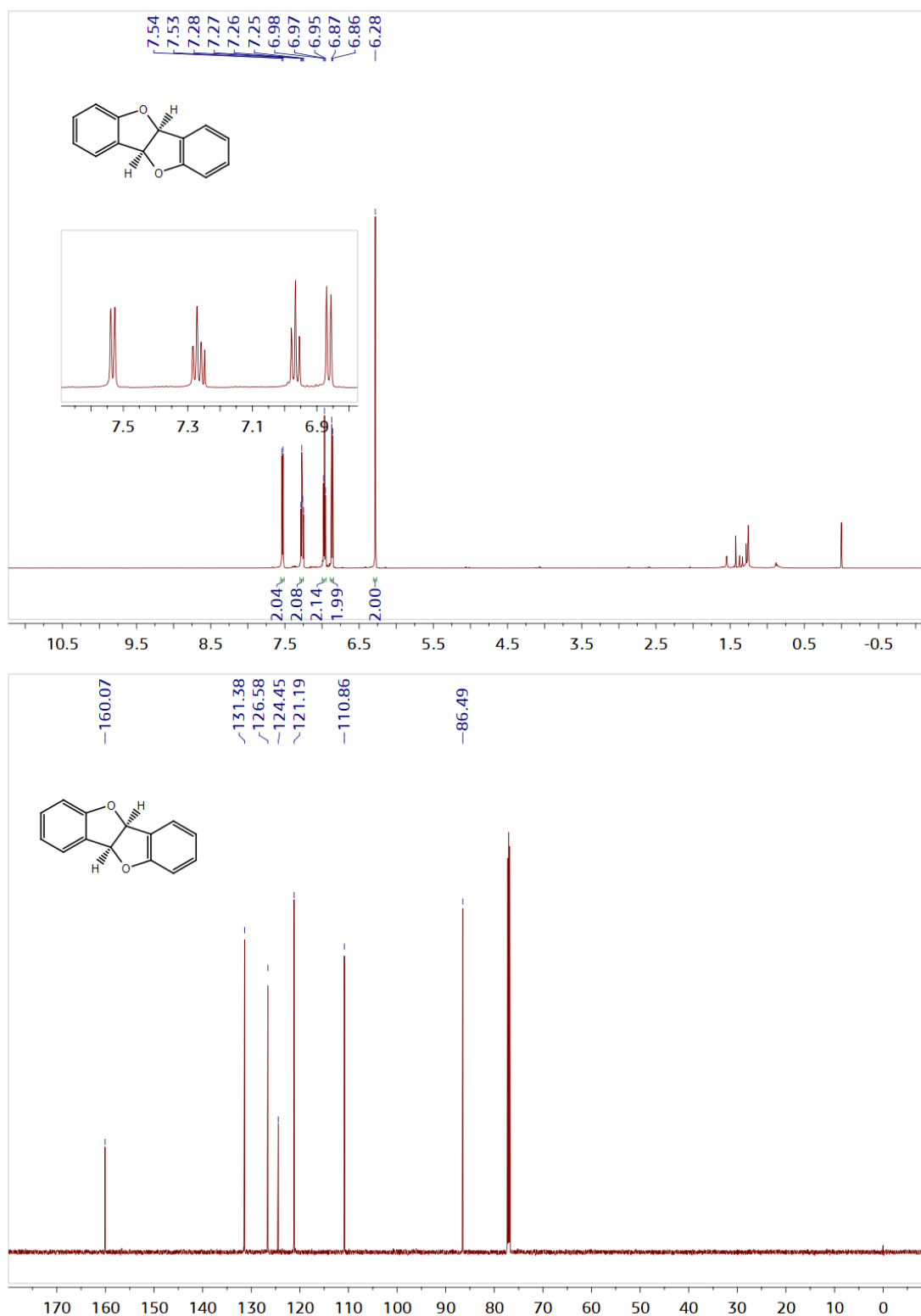
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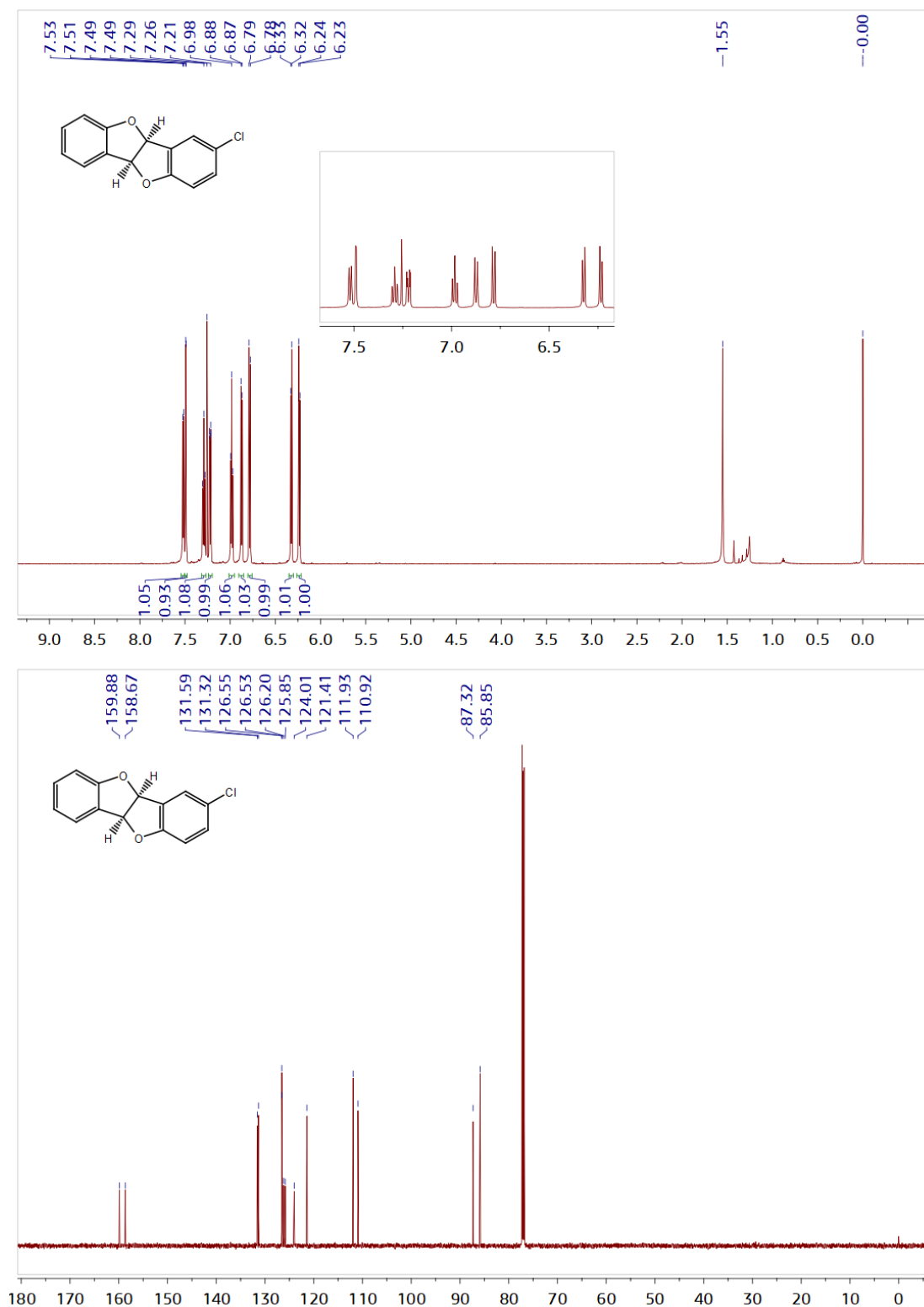
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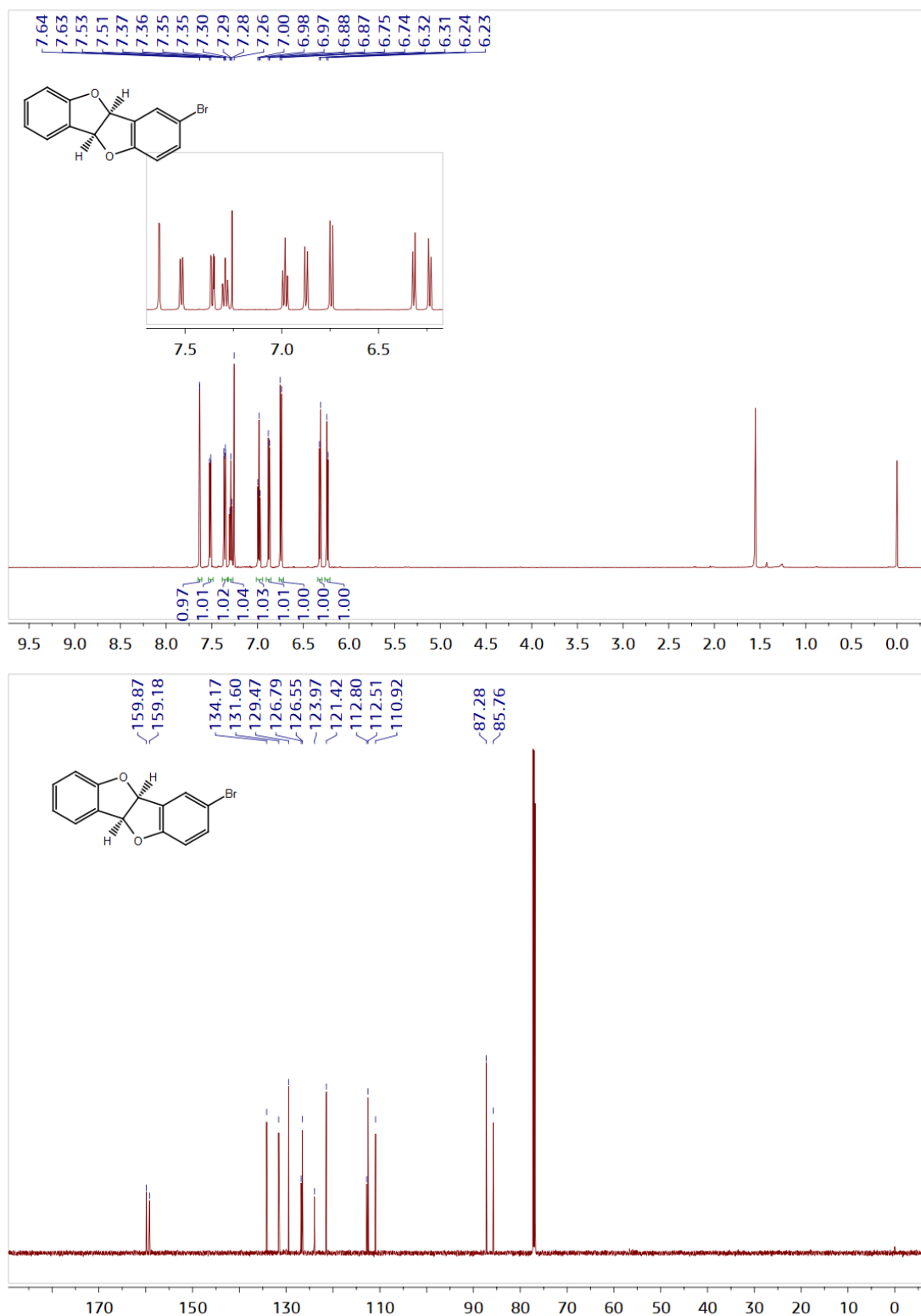
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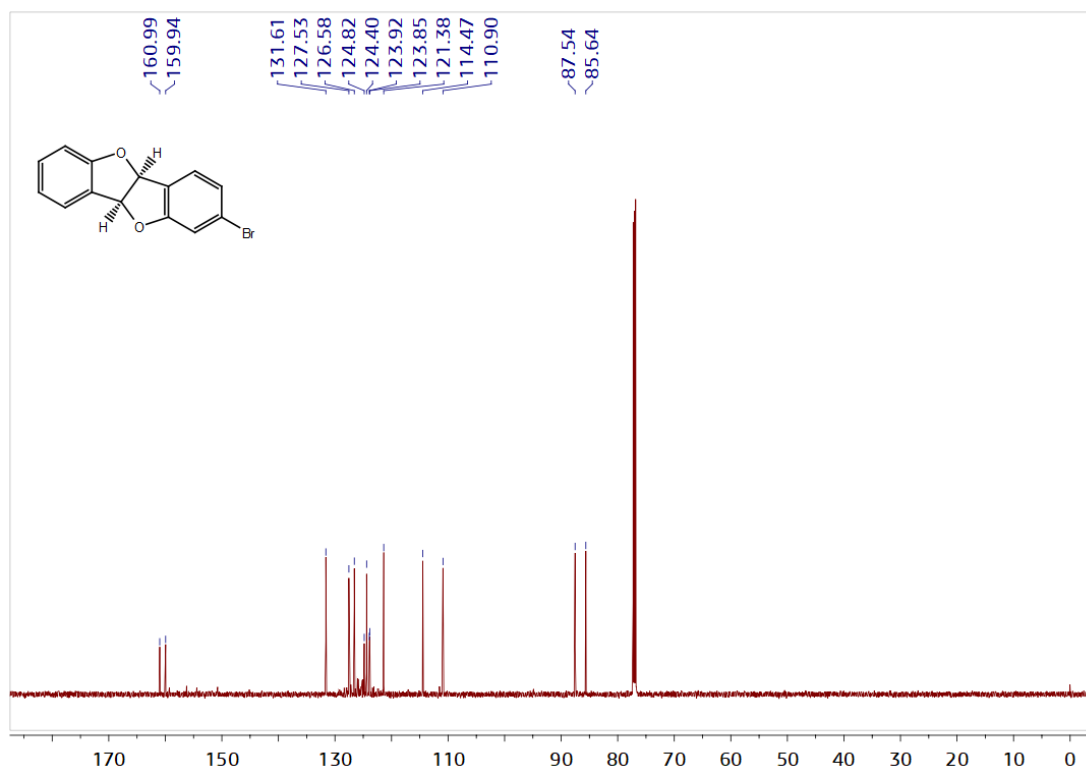
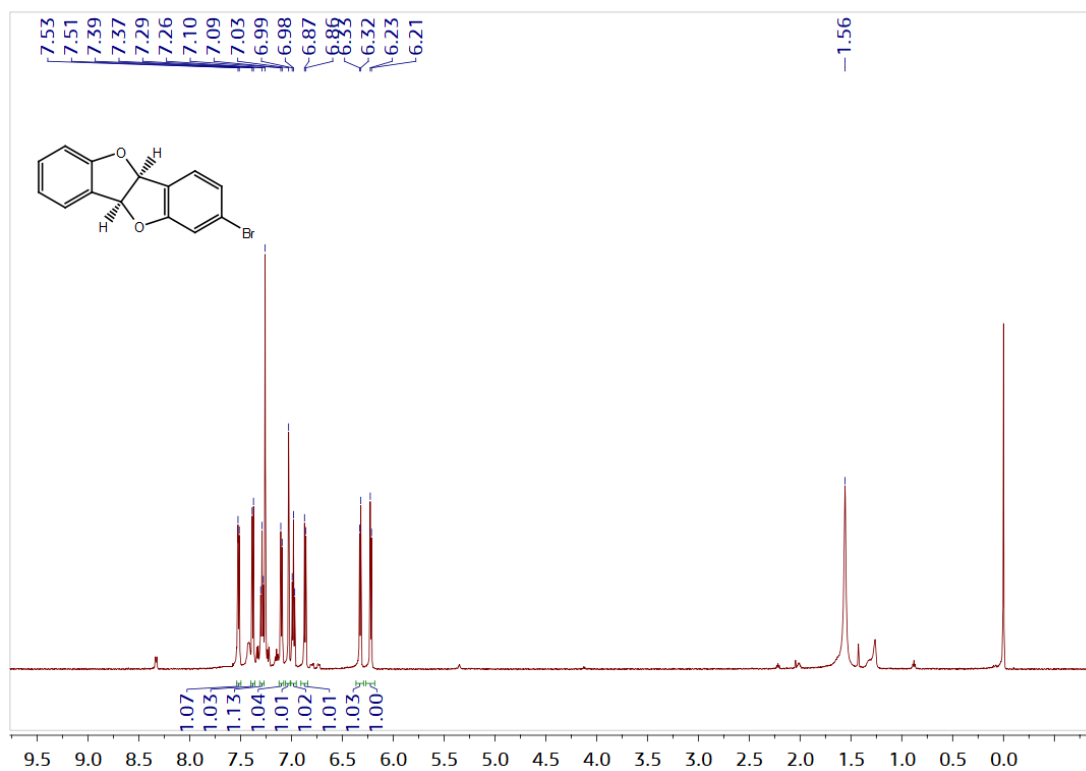
1. ^1H NMR and ^{13}C NMR Spectra

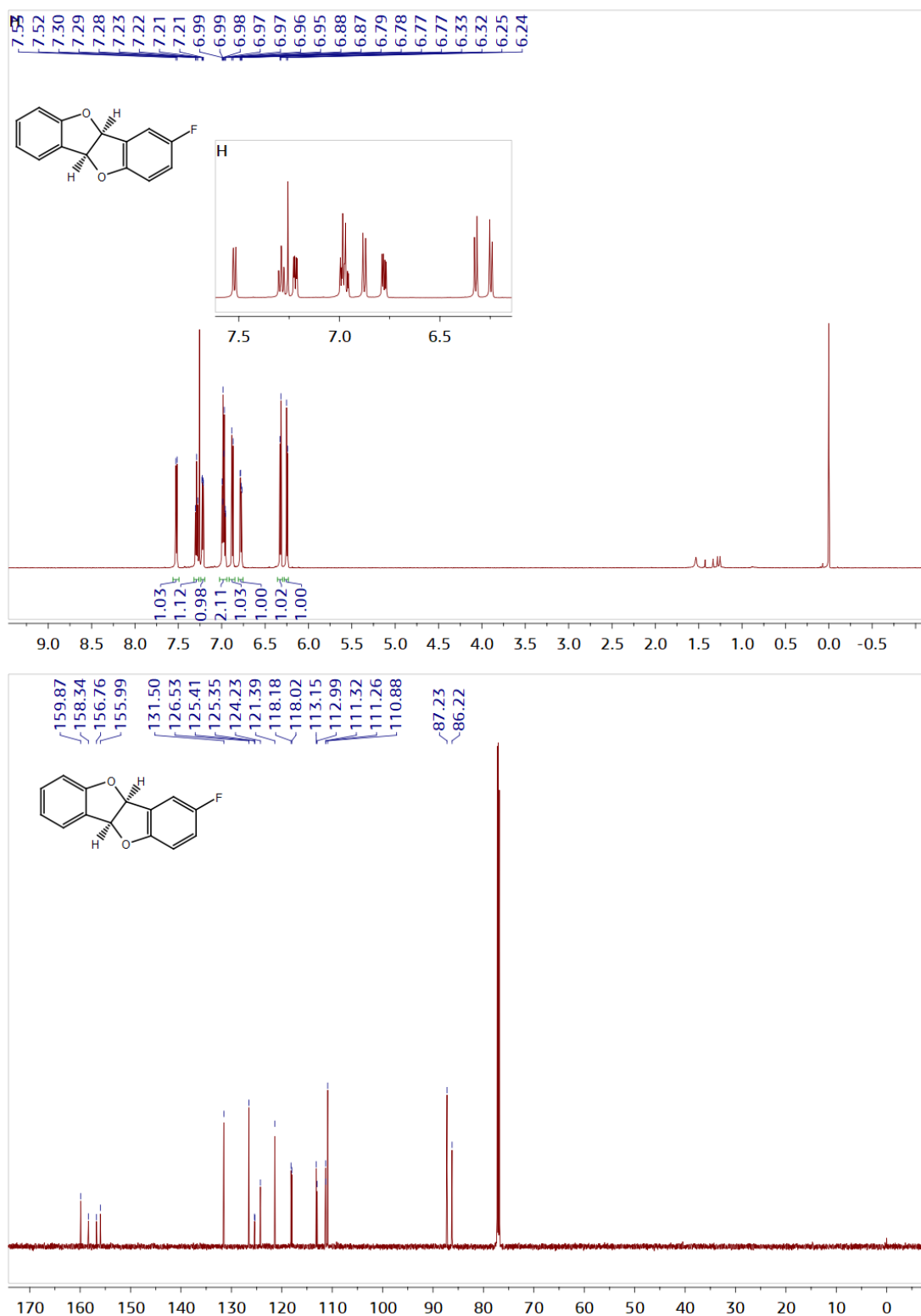
4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3a). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

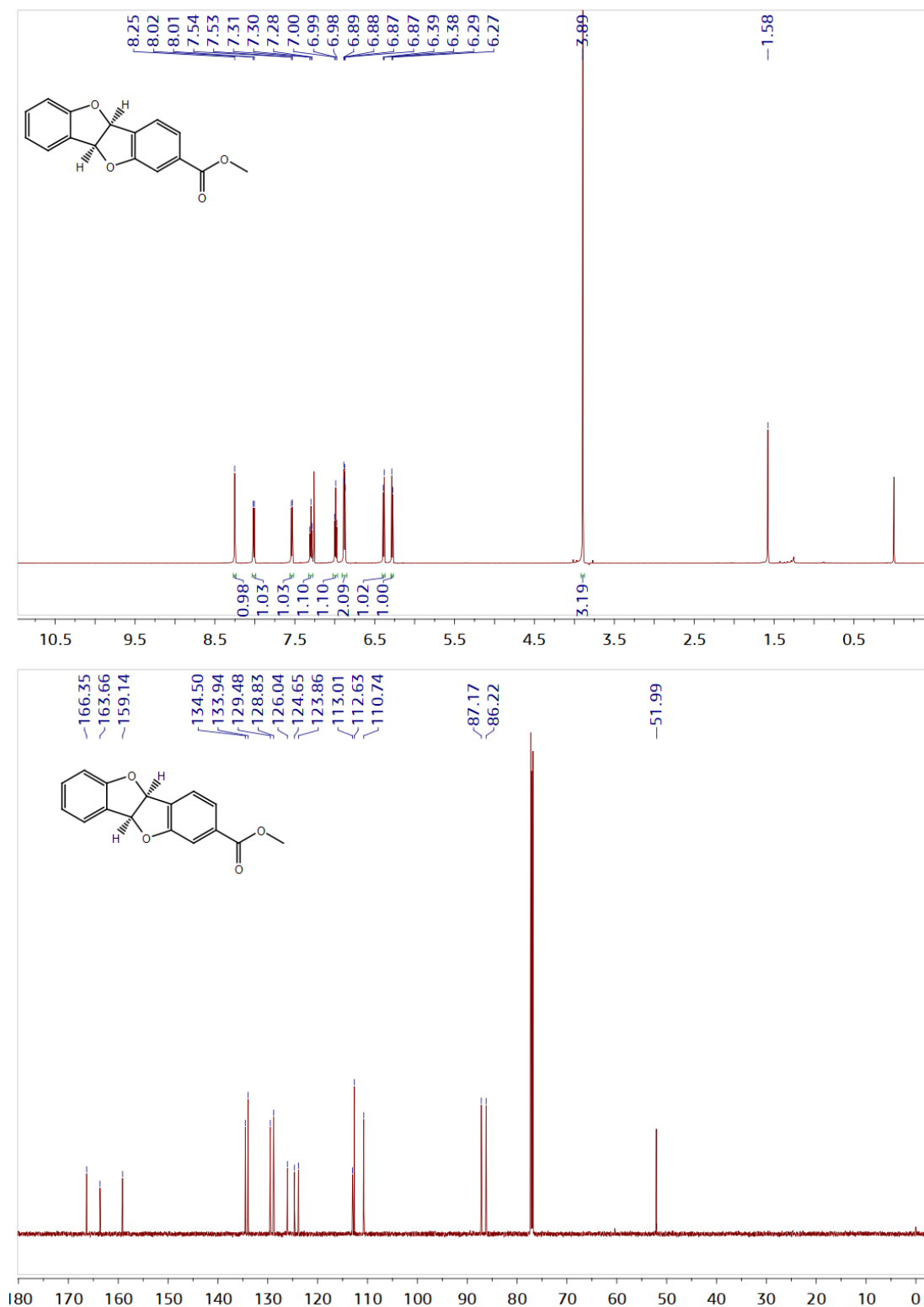


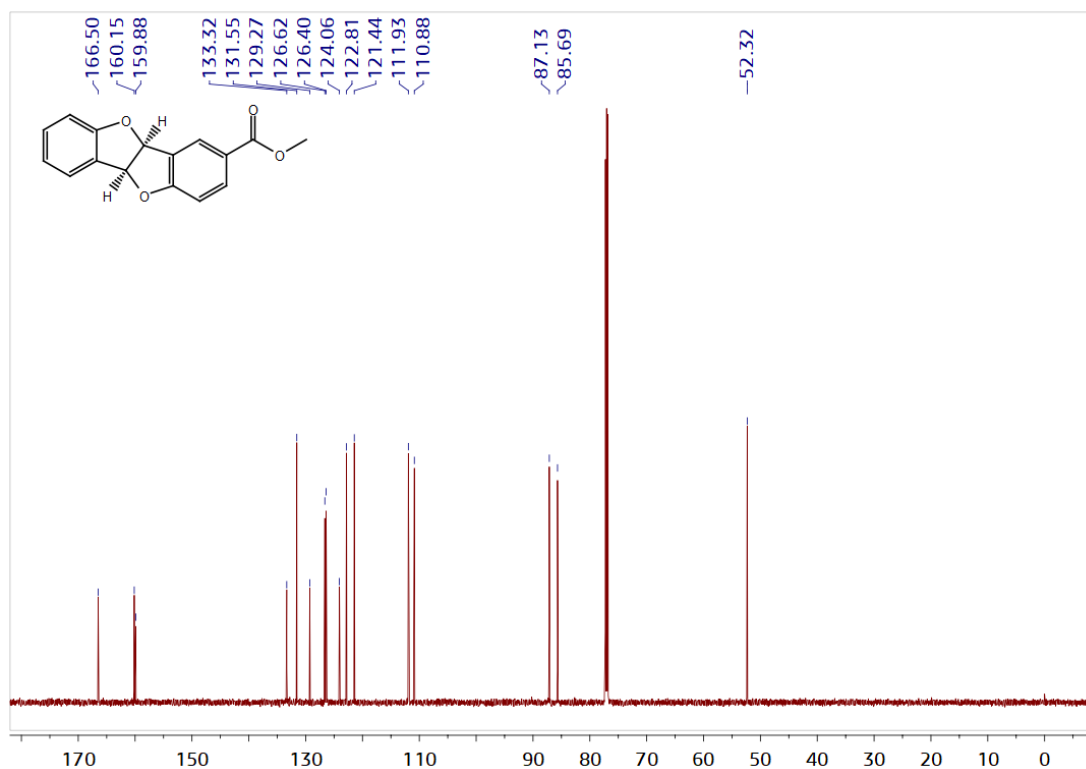
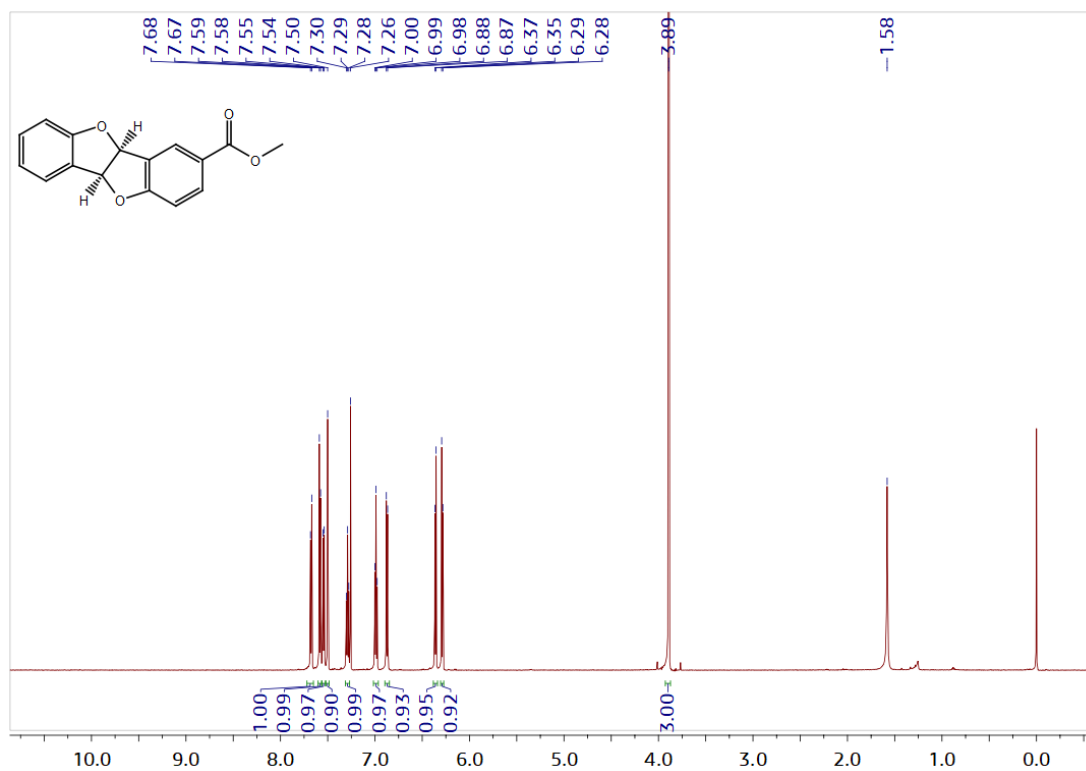
3-Chloro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3b). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

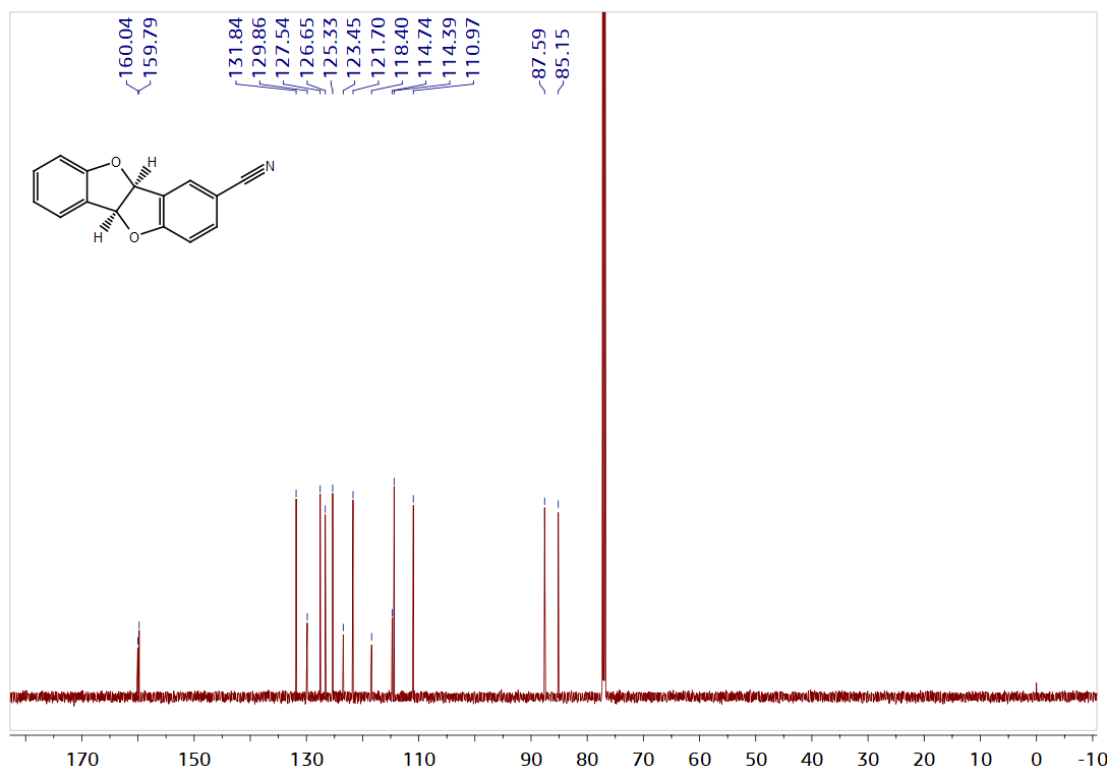
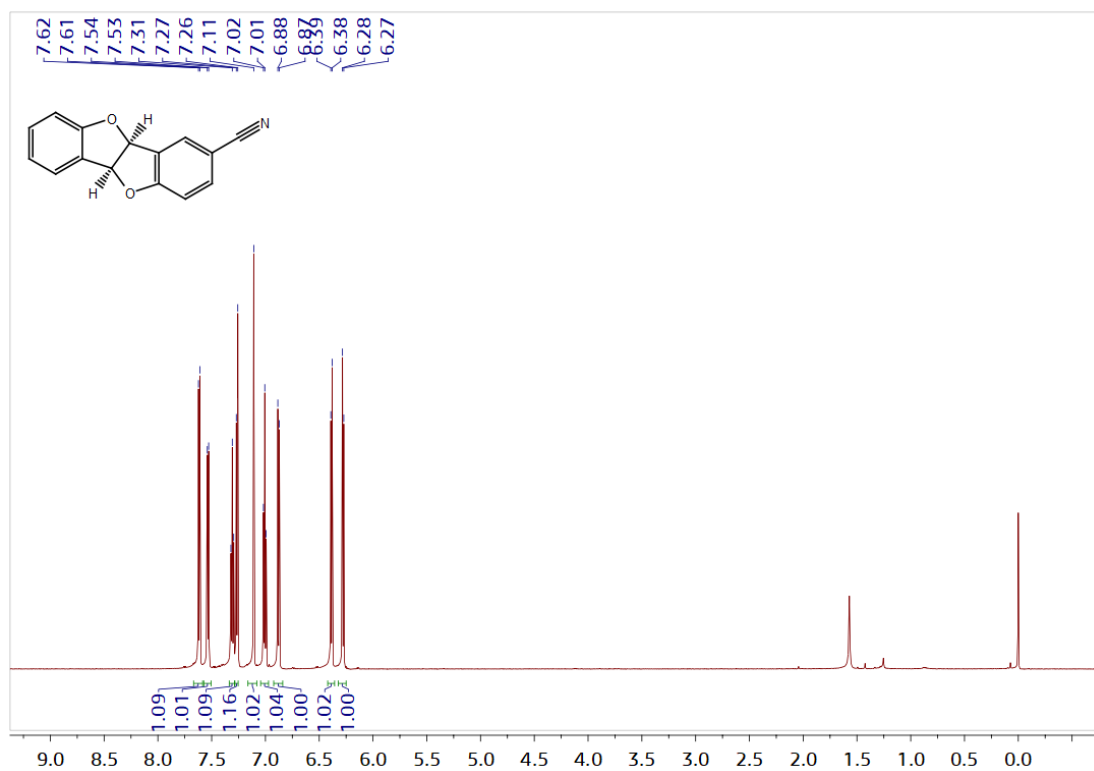
3-Bromo-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3c). ^1H NMR (600 MHz, CDCl_3);
 ^{13}C NMR (151 MHz, CDCl_3)

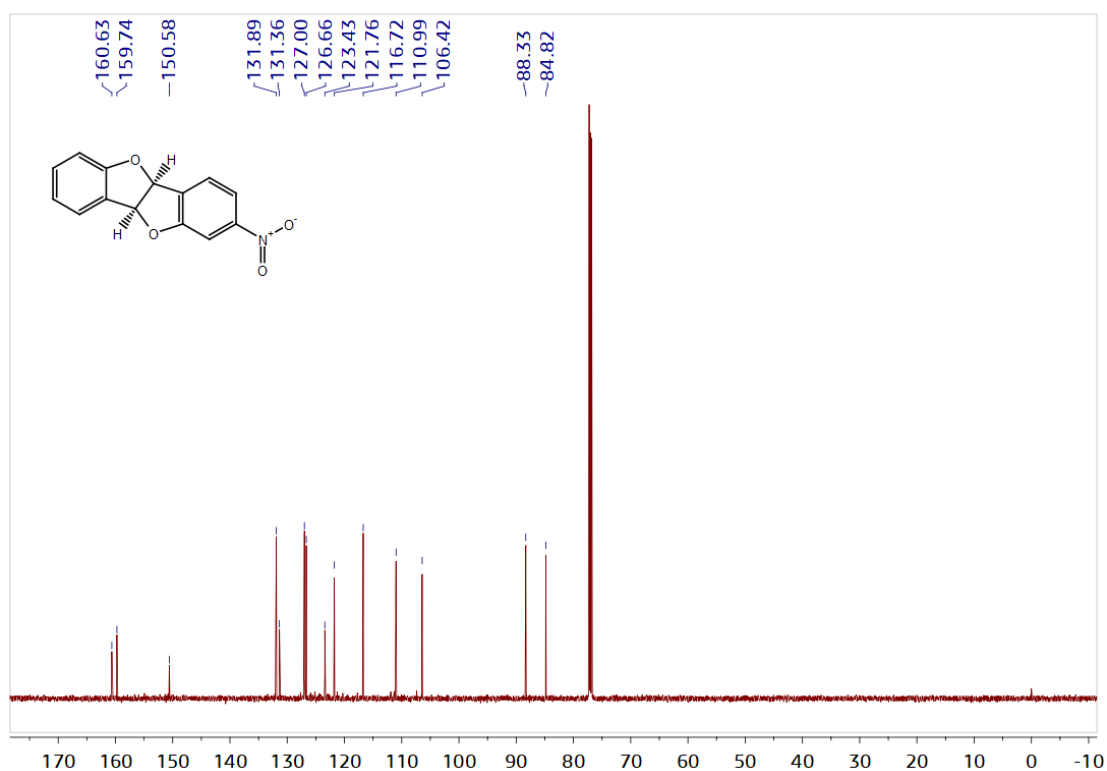
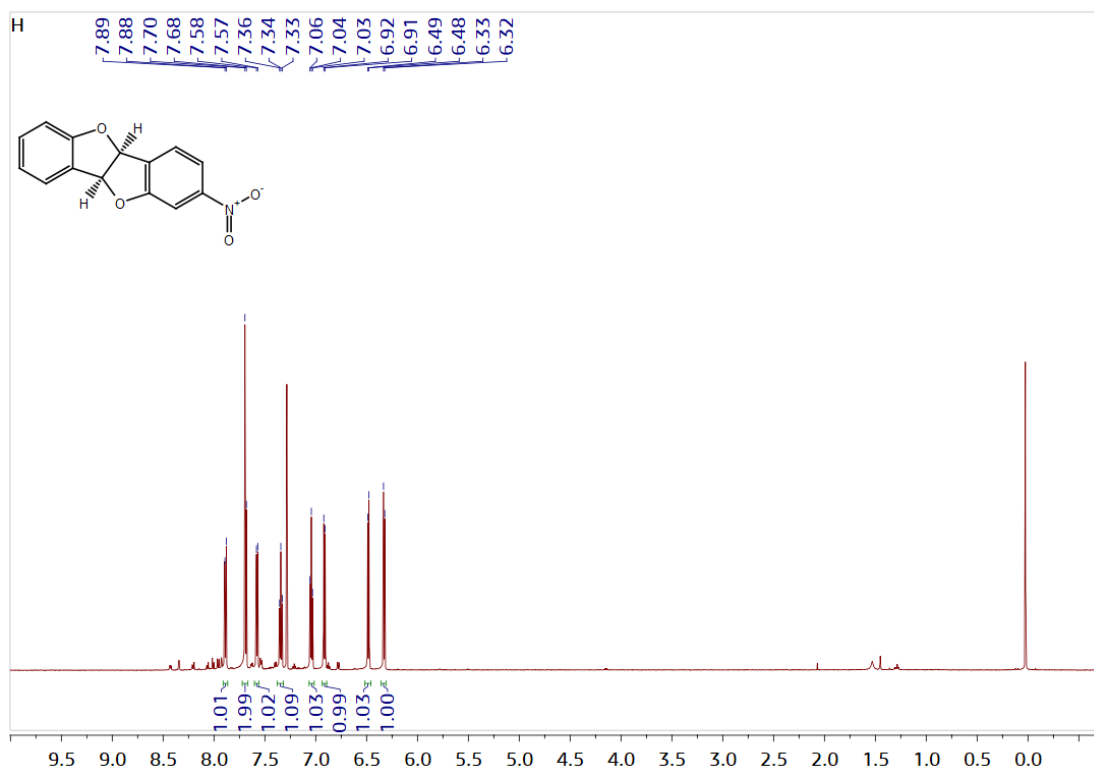
2-Bromo-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3d). ^1H NMR (600 MHz, CDCl_3);
 ^{13}C NMR (151 MHz, CDCl_3)

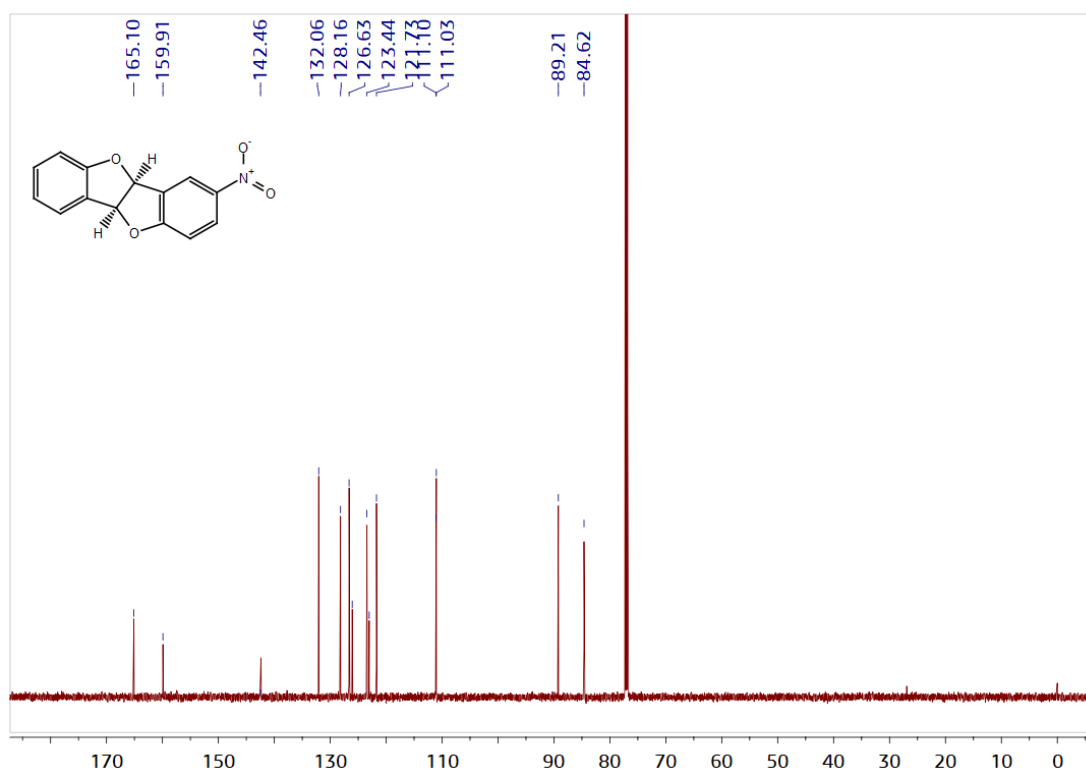
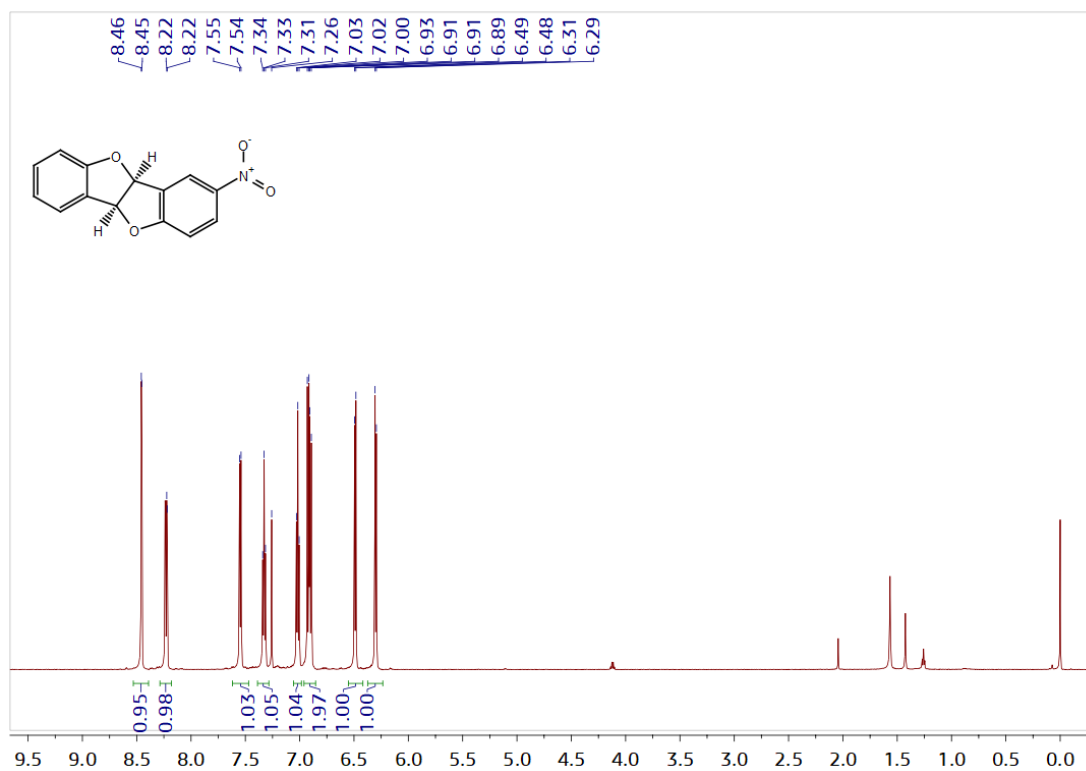
3-Fluoro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3e). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

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

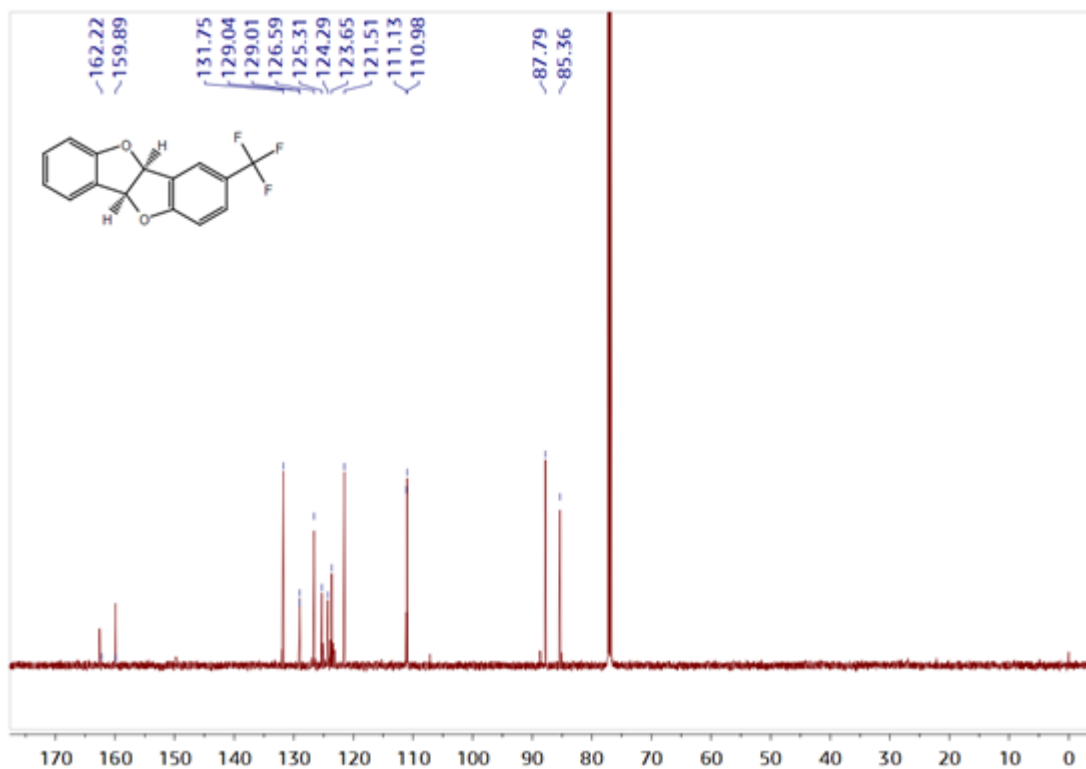
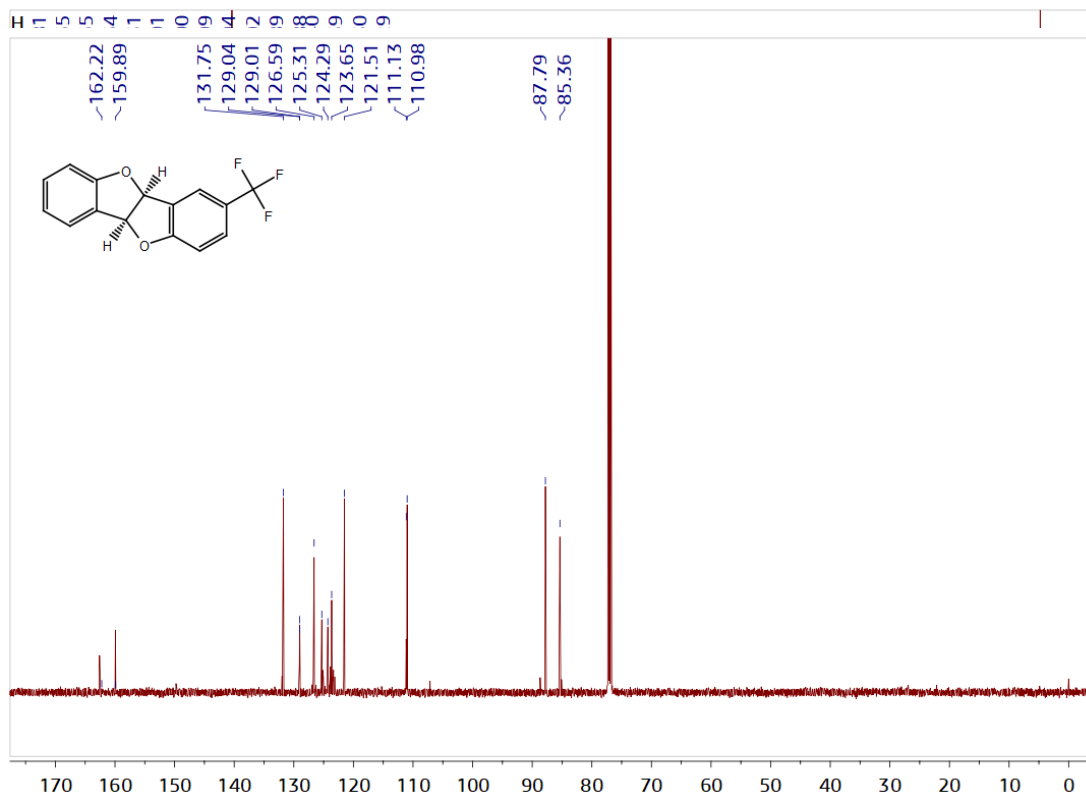
Methyl 4b,9b-dihydrobenzofuro[3,2-b]benzofuran-3-carboxylate (3g). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

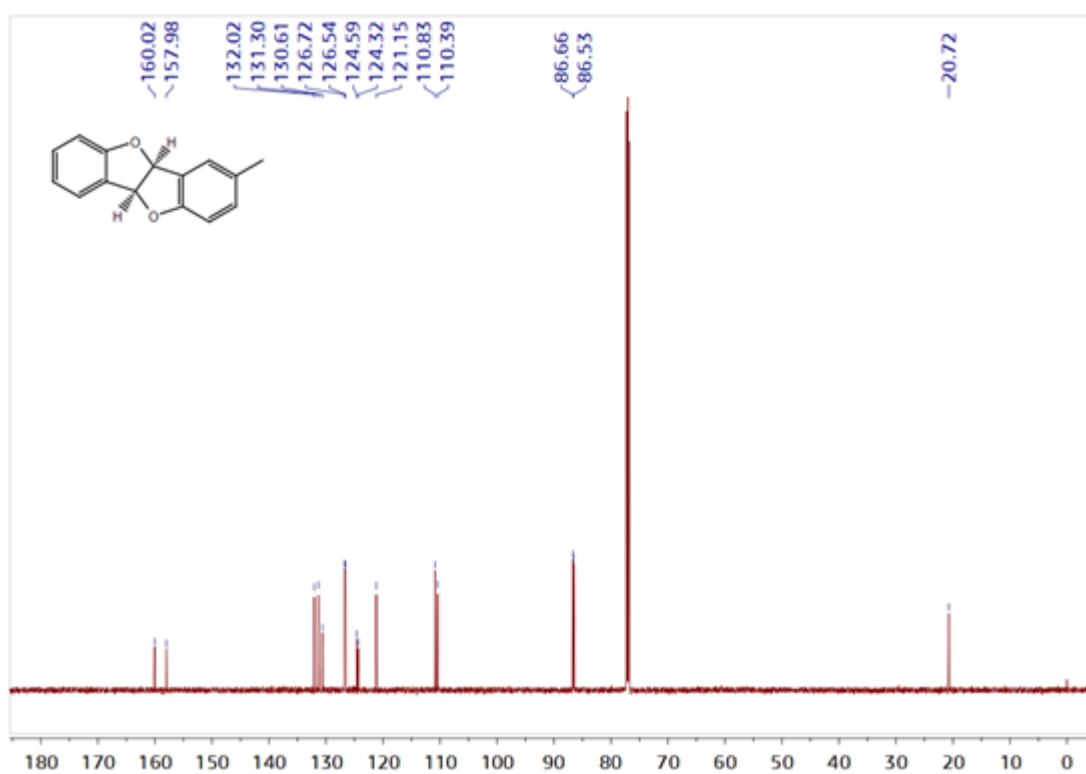
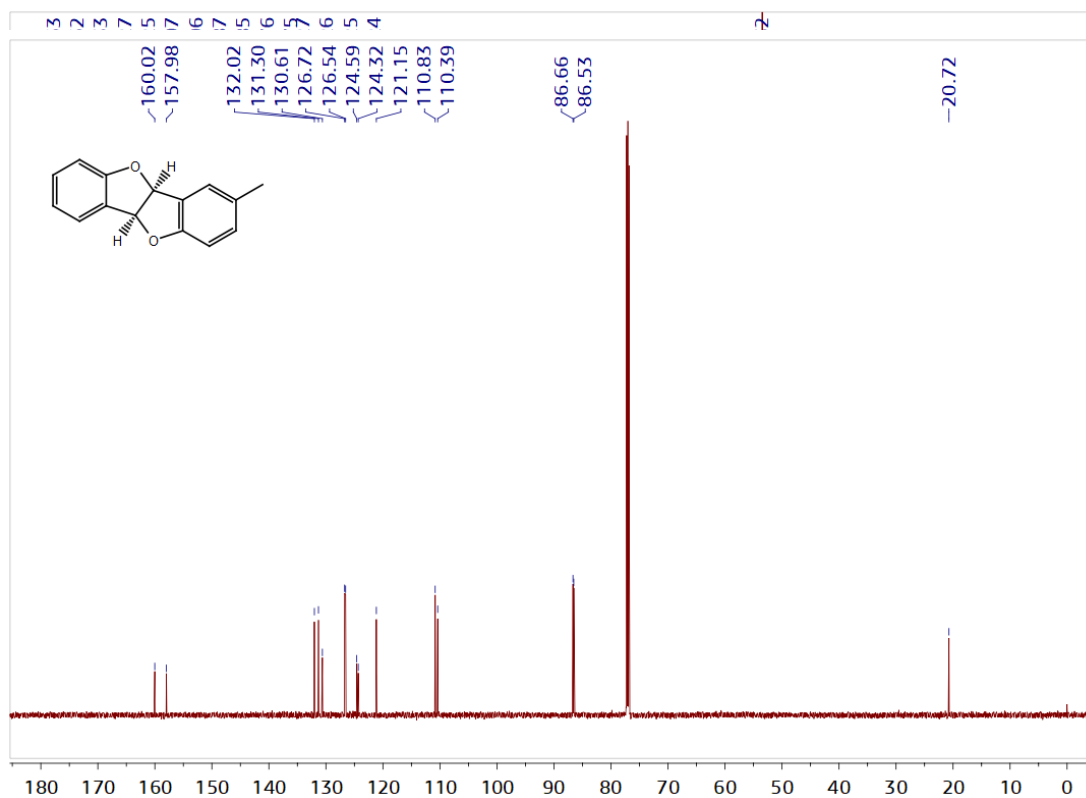
4b,9b-Dihydrobenzofuro[3,2-b]benzofuran-3-carbonitrile (3h). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

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

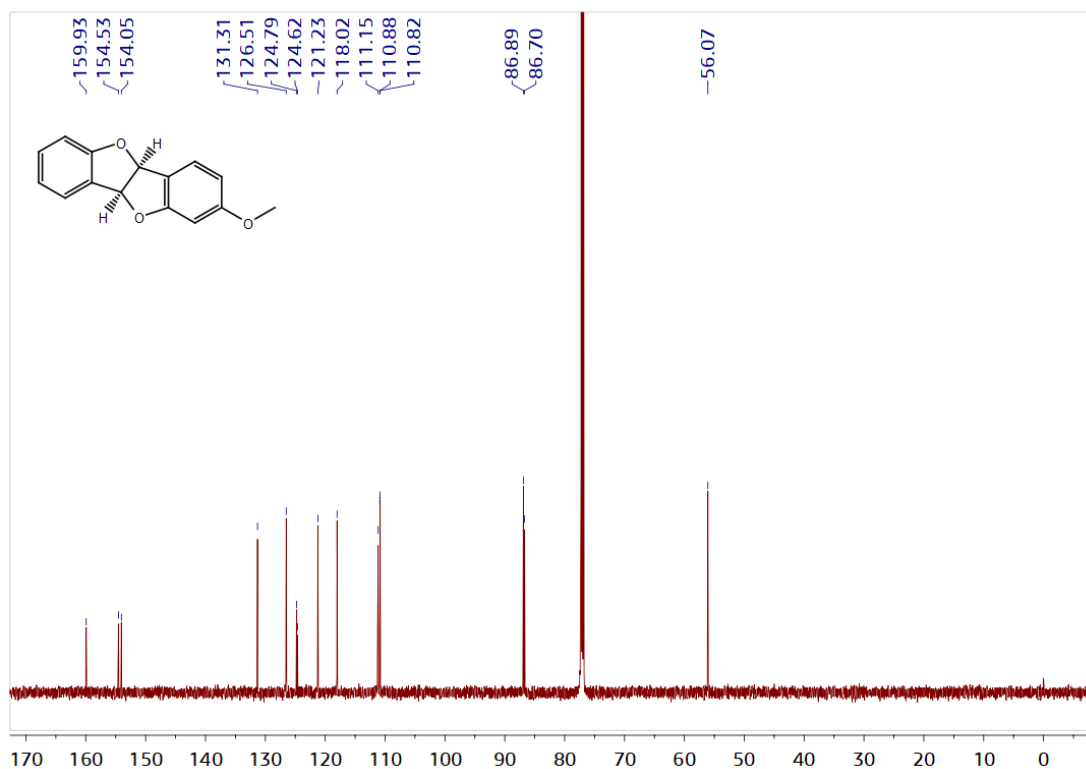
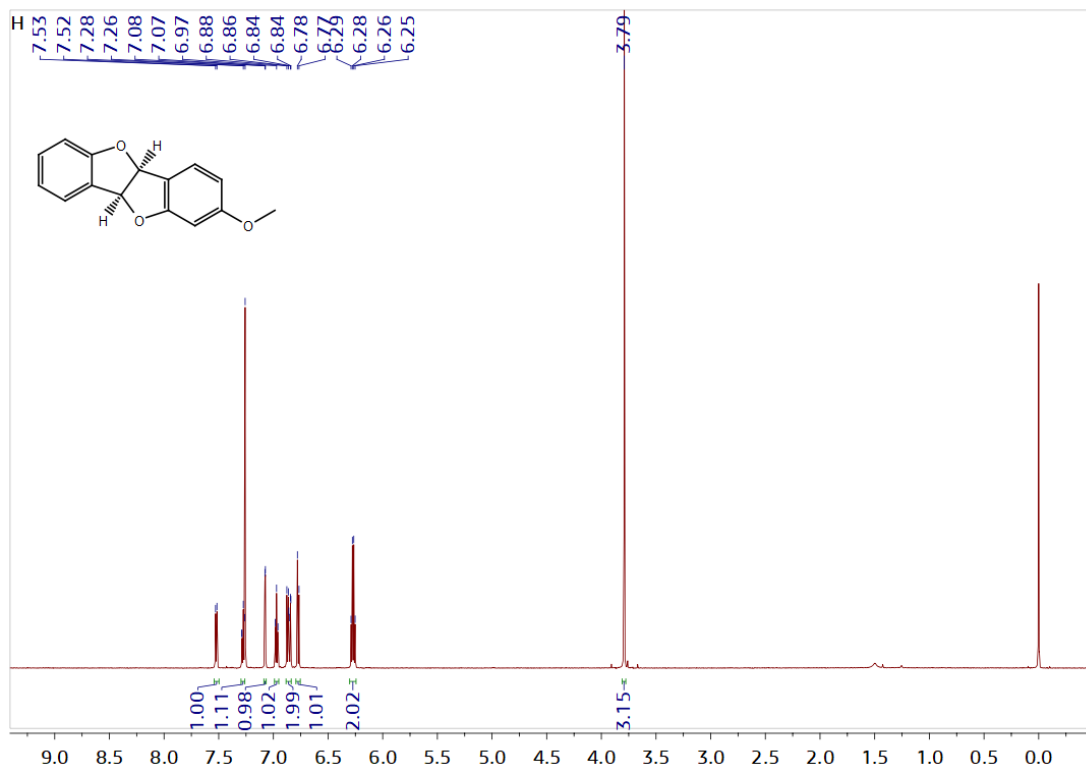
3-Nitro-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3j). ^1H NMR (600 MHz, CDCl_3);
 ^{13}C NMR (151 MHz, CDCl_3)

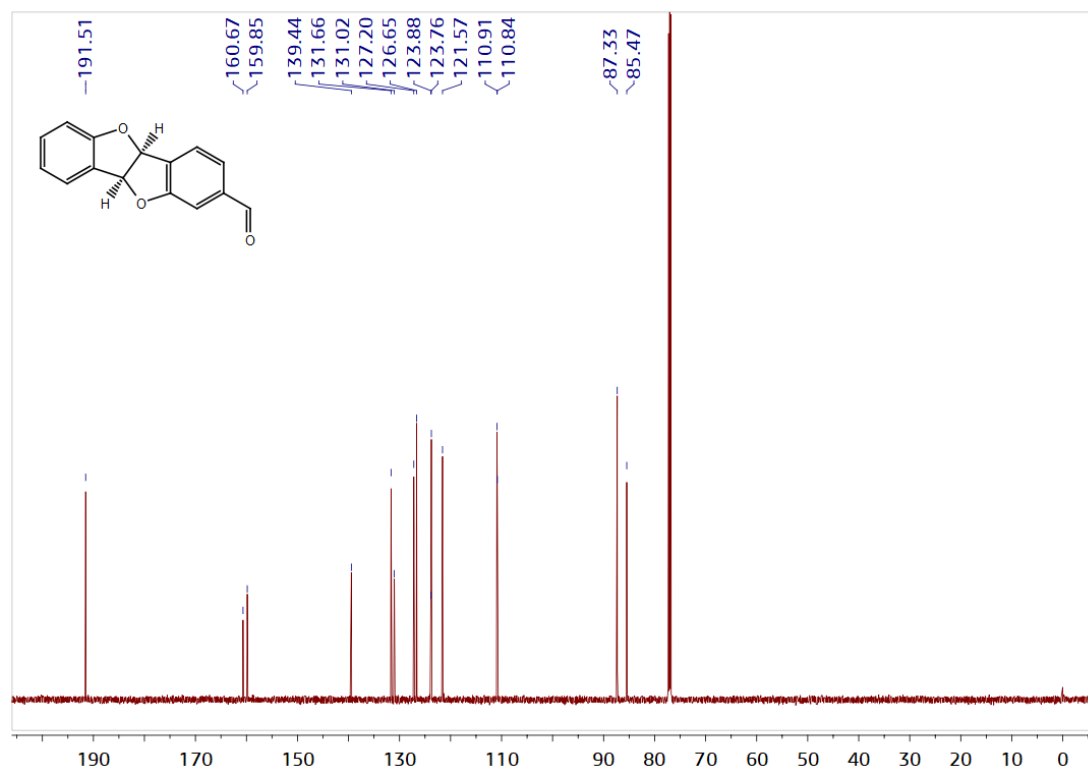
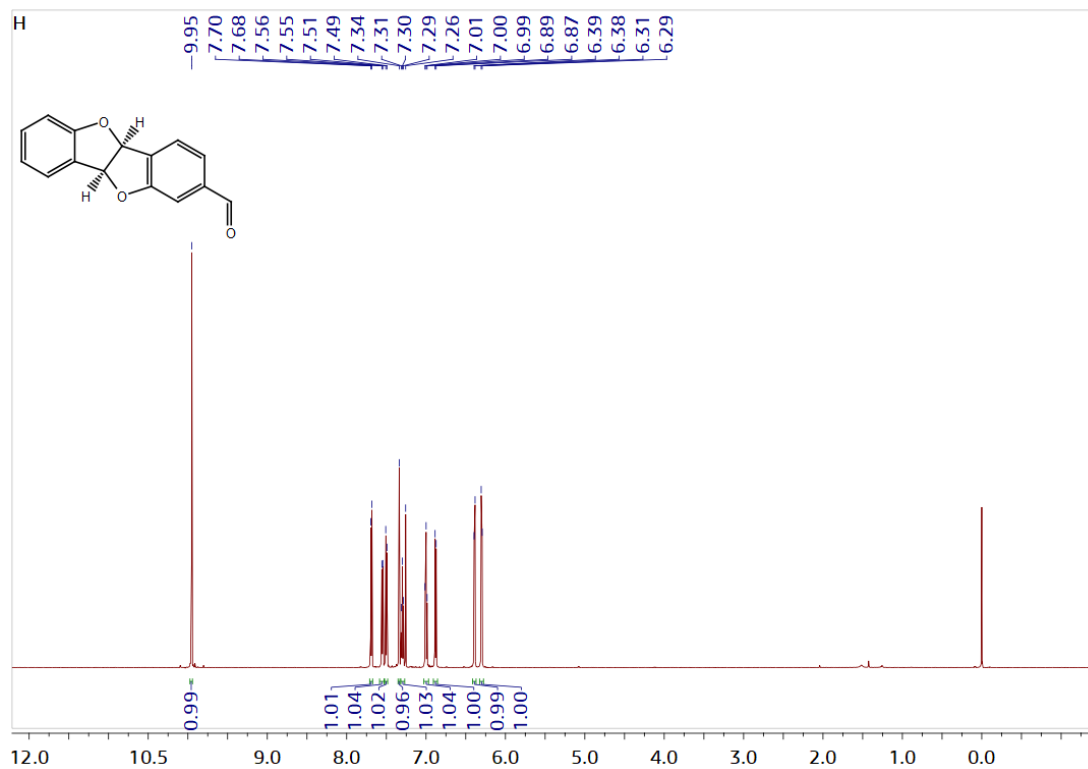
3-(Trifluoromethyl)-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3k). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)



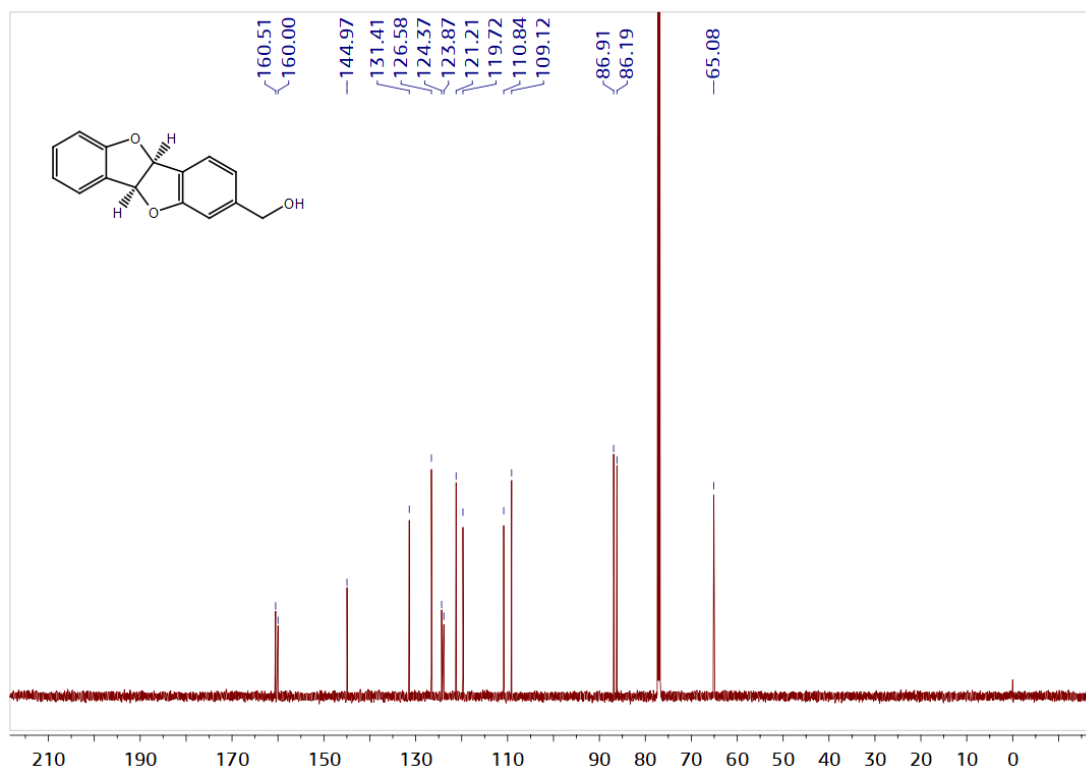
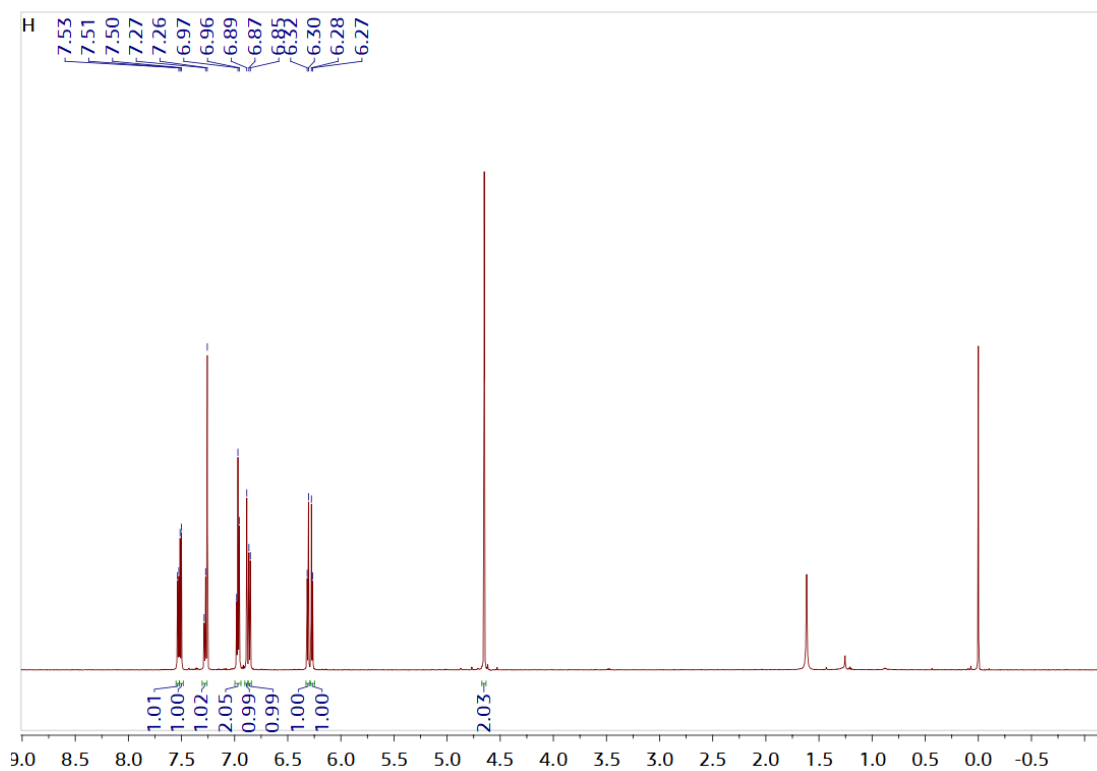
3-Methyl-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3I). ^1H NMR (600 MHz, CDCl_3);
 ^{13}C NMR (151 MHz, CDCl_3)

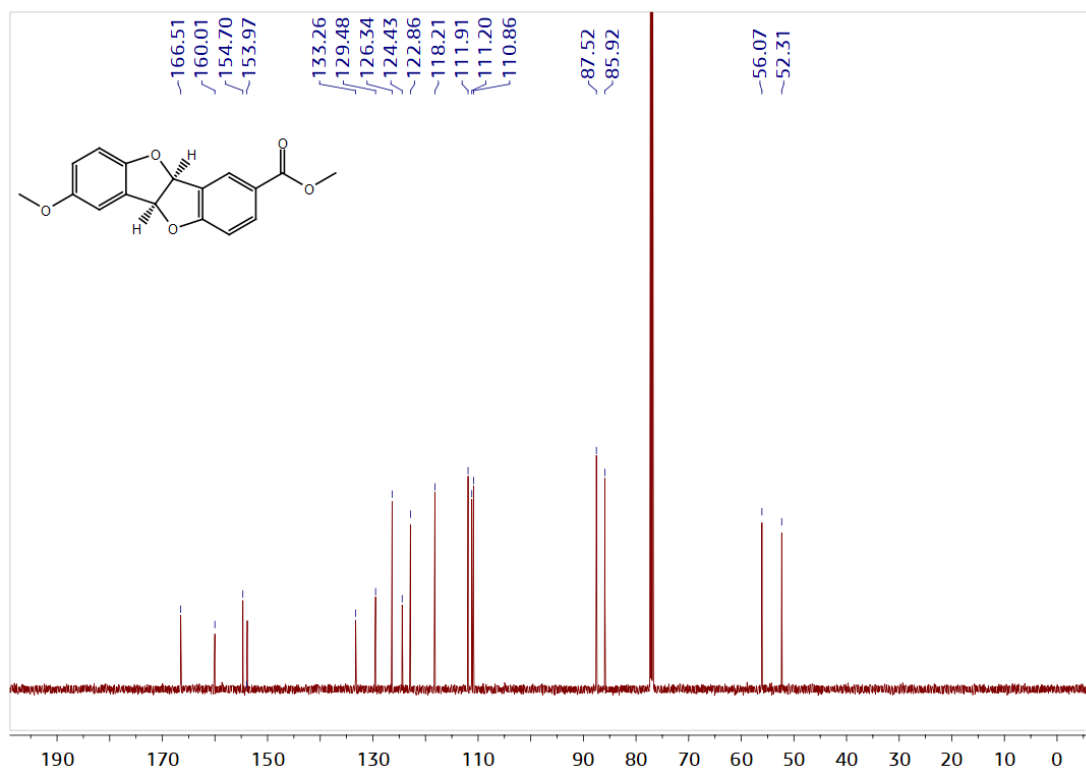
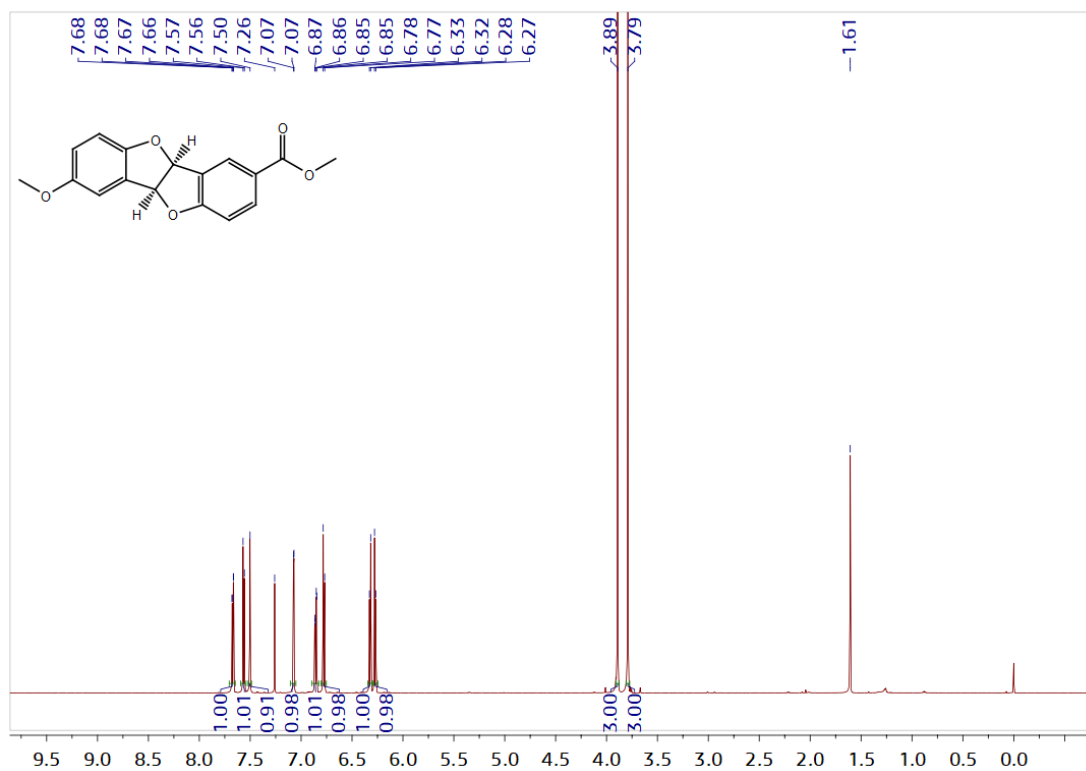
3-Methoxy-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (3m). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

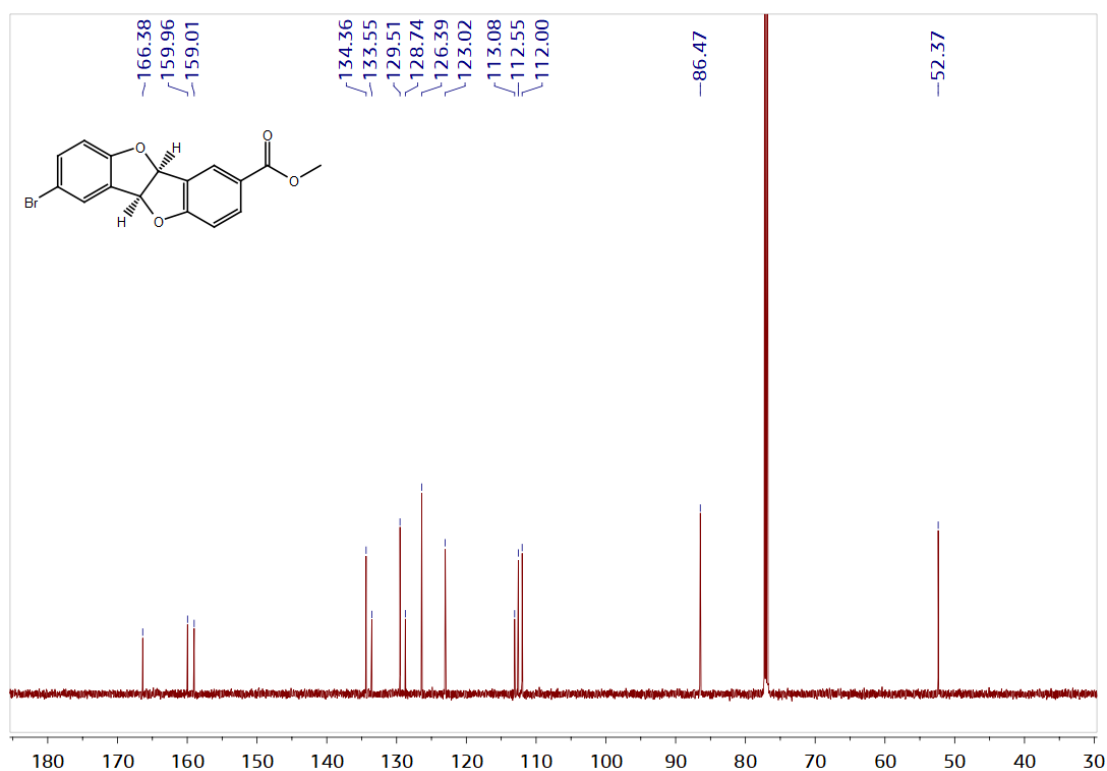
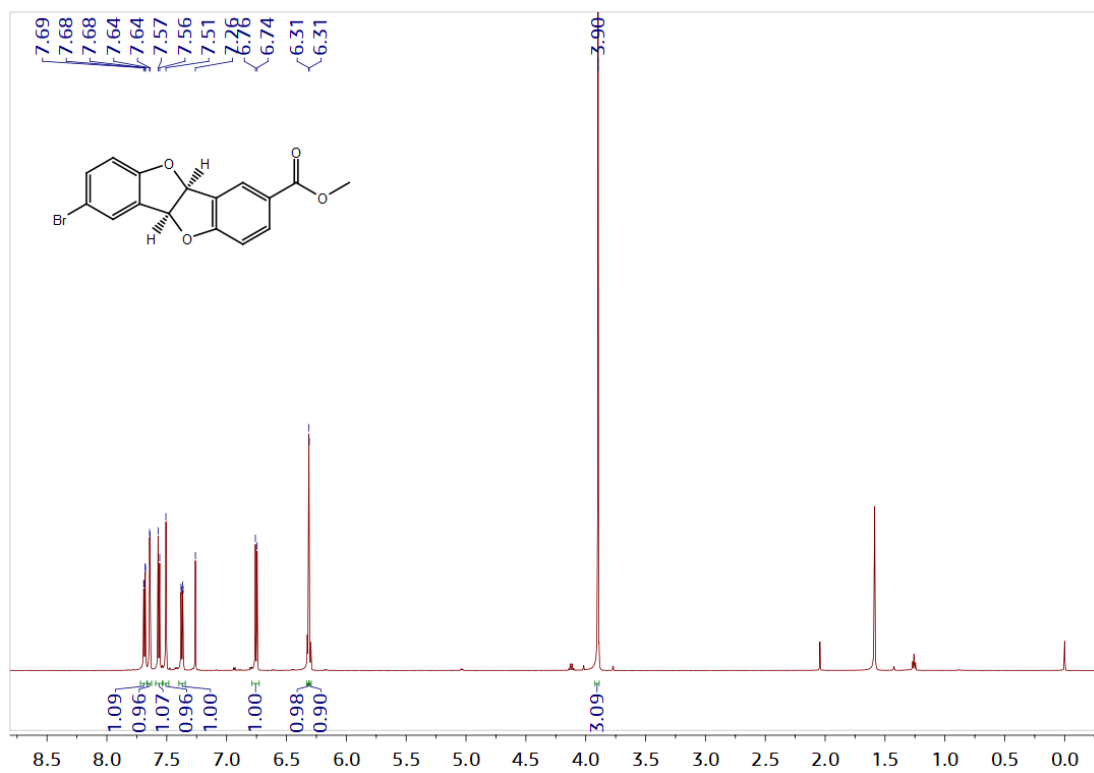


4b,9b-Dihydrobenzofuro[3,2-b]benzofuran-2-carbaldehyde (3n). ^1H NMR (600 MHz, CDCl_3); ^{13}C NMR (151 MHz, CDCl_3)

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



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

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

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
ρ _{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 ≤ h ≤ 7, -28 ≤ k ≤ 29, -9 ≤ l ≤ 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