

Supplementary Information

Synthesis of Functionalized Diarylbenzofurans via Ru-Catalyzed C–H Activation and Cyclization under Air: Rapid Access to the Polycyclic Scaffold of Diptoindonesin G

Lufeng Ouyang, Zhigeng Lin, Shiqi Li, Baoyin Chen, Jidan Liu, Wen-Jing Shi,
and Liyao Zheng*

*School of Chemistry and Chemical Engineering, Guangzhou University
Guangzhou 510006, P.R. China*

*E-mail: zlychem@gzhu.edu.cn

Contents	Page
1. Experimental Section	
1.1 General Information	S2
1.2 Synthetic procedures	S3
1.3 Mechanistic Studies	S6
1.4 Characterization data	S7
2. X-Ray Structural Details	
ORTEP Drawing and Crystal Data of 3aa	S21
ORTEP Drawing and Crystal Data of 4ba	S22
ORTEP Drawing and Crystal Data of 3ap'	S23
ORTEP Drawing and Crystal Data of 4aq	S24
ORTEP Drawing and Crystal Data of 6ar	S25
3. Copies of NMR Spectra	
¹ H NMR, ¹³ C NMR (and ¹⁹ F NMR) Charts of 3 , 4 , 5 , 6 , diptoindonesin G, 7aa	S26

1. Experimental Section

1.1 General Information

Unless otherwise noted, all organic/inorganic compounds and solvents were analytically pure and used directly after purchased. NMR spectra were recorded on a Bruker AVANCE NEO spectrometer at 298 K. ^1H NMR (600 MHz) chemical shifts (δ) were referenced to internal standard TMS ($\delta = 0.00$ ppm). ^{13}C NMR (151 MHz) chemical shifts were referenced to internal solvent CDCl_3 ($\delta = 77.16$ ppm), CD_3OD ($\delta = 49.00$ ppm), $\text{DMSO}-d_6$ ($\delta = 39.52$ ppm) or acetone- d_6 ($\delta = 29.84$ ppm). HRMS data was obtained on a Thermo Q Exactive high-resolution mass spectrometer with electron spray ionization (ESI) source, using negative ion mode ($[\text{M} - \text{H}]^-$) for acidic products and positive ion mode ($[\text{M} + \text{H}]^+$) for other products. GC-MS was performed on a Shimadzu GCMS-QP2010 SE spectrometer. X-ray diffraction data was collected on a Bruker D8 VENTURE diffractometer equipped with $\text{MoK}\alpha$ radiation. The melting points were uncorrected.

All *m*-hydroxybenzoic acids used are commercial available. 3-Hydroxy-5-methoxybenzoic acid (**1c**) and 3-(benzyloxy)-5-hydroxybenzoic acid (**1d**) can be also synthesized via hydrolysis of their esters or from cheap 3,5-dihydroxybenzoic acid following a literature procedure.¹ Symmetric diarylalkynes are commercial available or can be synthesized from corresponding bromobenzenes or iodobenzenes by coupling with trimethylsilylacetylene or propiolic acid following reported methods.^{2,3} Asymmetric diarylalkynes **2p** and **2r** were synthesized via Sonogashira reaction from corresponding commercial available terminal alkynes and iodobenzenes according to literature.^{4,5}

References:

- [1] N. Koolaji, A. Abu-Mellal, V. H. Tran, R. K. Duke and C. C. Duke, *Eur. J. Med. Chem.*, 2013, **63**, 415–422.
- [2] (a) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199–3202; (b) L. Zheng, J. Ju, Y. Bin and R. Hua, *J. Org. Chem.*, 2012, **77**, 5794–5800
- [3] K. Park, G. Bae, J. Moon, J. Choe, K. H. Song and S. Lee, *J. Org. Chem.*, 2010, **75**, 6244–6251.
- [4] H. Wu, C. Shao, D. Wu, L. Jiang, H. Yin and F.-X. Chen, *J. Org. Chem.*, 2021, **86**, 5327–5335.
- [5] J. L. Jeffrey and R. Sarpong, *Tetrahedron Lett.*, 2009, **50**, 1969–1972.

1.2 Synthetic Procedures

Synthesis of 3aa (Typical Procedure A). To a 10 mL tube with a branch pipe, a magnetic stirrer, [Ru(*p*-cymene)Cl₂]₂ (4.9 mg, 0.008 mmol), 3-hydroxy-5-methylbenzoic acid **1a** (73.2 mg, 0.48 mmol), diphenylacetylene **2a** (71.3 mg, 0.40 mmol), Mg(OAc)₂·4H₂O (21.4 mg, 0.10 mmol) and GVL (0.50 mL) were added sequentially. The top of the tube was sealed and the branch pipe was open to air. The tube was put in a metallic heating mould at 100 °C and stirred for 20 h. The reaction mixture was then cooled down, diluted with EtOAc and filtered through a pad of celite. The obtained organic phase was washed with brine, dried over Na₂SO₄ and then concentrated. After purification by flash column chromatography on silica gel (200–300 mesh) with petroleum ether (PE)/EtOAc (gradient ratio from 10:1 to 2:1) as eluant, benzofuran **3aa** (95.7 mg, 73%) was obtained as a white solid.

Following *Typical Procedure A*, other benzofuran products **3** were synthesized from corresponding *m*-hydroxybenzoic acids **1** (0.48 mmol) and diaryl alkynes **2** (0.40 mmol).

Synthesis of 3ba and 4ba. In a similar procedure, when 3-hydroxybenzoic acid **1b** (66.3 mg, 0.48 mmol) and **2a** (71.3 mg, 0.40 mmol) were used, isocoumarin **4ba** (41.4 mg, 33%) and benzofuran **3ba** (60.2 mg, 48%) were isolated successively by column chromatography with PE/EtOAc (gradient ratio from 20:1 to 4:1) as eluant.

Synthesis of 3ha and 5haa. In a similar procedure, when 3,5-dihydroxybenzoic acid **1h** (74.0 mg, 0.48 mmol) and **2a** (71.3 mg, 0.40 mmol) were used, benzodifuran **5haa** (32.4 mg, 32% based on **2a**) and benzofuran **3ha** (70.8 mg, 54%) were isolated successively by column chromatography with PE/EtOAc (gradient mixture ratio from 50:1 to 1:1) as eluant. When **1h** (61.6 mg, 0.40 mmol) and **2a** (171.1 mg, 0.96 mmol) were reacted for 40 h, **5haa** (152.1 mg, 75% based on **1a**) were obtained.

Synthesis of 3ap and 3ap'. In a similar procedure, when **1a** (73.2 mg, 0.48 mmol) and **2p** (71.3 mg, 0.40 mmol) were used, two isomers were detected by both TLC and GC-MS. Pure **3ap'** (50.4 mg, 32%) and **3ap** (73.4 mg, 47%) were isolated successively by column chromatography with PE/EtOAc (gradient ratio from 15:1 to 2:1) as eluant. Using the pure products as standards, the ratio of **3ap** and **3ap'** in the crude reaction mixture was determined as ~1.2:1 by GC-MS. The difference of the ratio after isolation was due to more loss of **3ap'** during column chromatography purification as some unknown side products were very closed to it.

1 mmol scale synthesis of 3aa. In a similar procedure, [Ru(*p*-cymene)Cl₂]₂ (9.2 mg, 0.015 mmol), **1a** (182.6 mg, 1.2 mmol), **2a** (178.2 mg, 1.0 mmol), Mg(OAc)₂·4H₂O (53.6 mg, 0.25 mmol) and 0.8 mL GVL were added and reacted. After purification by column chromatography, **3aa** (220.7 mg, 67%) was obtained.

5 mmol scale synthesis of 3ca. In a similar procedure, [Ru(*p*-cymene)Cl₂]₂ (45.9 mg, 0.075 mmol), **1c** (1.009 g, 6.0 mmol), **2a** (0.891 g, 5.0 mmol), Mg(OAc)₂·4H₂O (0.268 g, 1.25 mmol) and 4.0 mL GVL were added and reacted in a 25 mL tube for 24 h. After purification by column chromatography,

3ca (1.261 g, 73%) was obtained.

Synthesis of 4aq. To a 25 mL tube with a branch pipe, a magnetic stirrer, [Ru(*p*-cymene)Cl₂]₂ (12.2 mg, 0.02 mmol), **1a** (60.9 mg, 0.40 mmol), guanidine carbonate (24.2 mg, 0.20 mmol), GVL (1.0 mL) and 3-hexyne **2q** (70 μL, 0.60 mmol) were added sequentially. The tube was sealed and stirred at 100 °C. After 8 h, the tube was cooled down and opened to refresh air. The tube was resealed and stirred at 100 °C for further 12 h. The reaction mixture was cooled down, diluted with EtOAc, washed with brine, dried over Na₂SO₄ and then concentrated. After purification by flash column chromatography on silica gel with PE/EtOAc (gradient ratio from 20:1 to 4:1) as eluant, isocoumarin **4aq** (69.7 mg, 75%) was obtained as a white solid.

Synthesis of 6aa (Typical Procedure B). To a 10 mL tube with a magnetic stirrer, **3aa** (65.7 mg, 0.20 mmol), anhydrous DCM (2.5 mL) and trifluoroacetic anhydride (70 μL, 0.50 mmol) were added sequentially. The tube was sealed and stirred at room temperature for 12 h. The reaction was quenched by MeOH (10 mL) and dried by a rotary evaporator to remove methyl trifluoroacetate and trifluoroacetic acid. After purification by flash column chromatography on silica gel with PE/EtOAc (gradient ratio from 150:1 to 50:1) as eluant, **6aa** (44.3 mg, 71%) was obtained as a yellow solid.

Following *Typical Procedure B*, **6ca** and **6ja** were synthesized from **3ca** and **3ja** respectively.

Synthesis of 6ha. To a 10 mL tube with a magnetic stirrer, **3ha** (71.6 mg, 0.20 mmol), K₂CO₃ (55.3 mg, 0.40 mmol), MeCN (1 mL) and MeI (35 μL, 0.56 mmol) were added sequentially. The tube was sealed and stirred at 60 °C for 4 h. The reaction mixture was cooled down, diluted with DCM and washed with brine. The organic phase was dried over Na₂SO₄, concentrated and then dried under vacuum. The obtained crude methylated product was transferred to a 25 mL tube using anhydrous DCM (5 mL). After the tube was sealed and cool down to -78 °C, BBr₃ (600 μL, 1.0 mol/L in DCM) was added under stirring. The reaction mixture was stirred under -78 °C for 2 h, and then at room temperature for 10 h. The reaction was quenched by ice water, and extracted with EtOAc. The organic phase was washed with brine, dried over Na₂SO₄ and dried by a rotary evaporator. The obtained solid was washed by PE/EtOAc (3:1, 2×4 mL) to remove trace of impurities, and dried under vacuum to afford product **6ha** (54.0 mg, 86%) as a yellow solid. **6ha** (57.3 mg, 92%) can be also synthesized from **3ca** (68.9 mg, 0.20 mmol) following the same procedure except that reduced amount of K₂CO₃ (41.5 mg, 0.30 mmol) and MeI (20 μL, 0.32 mmol) were used.

In a similar procedure, **6an** were synthesized from **3an** when K₂CO₃ (41.5 mg, 0.30 mmol) and MeI (20 μL, 0.32 mmol) were used for methylation. BBr₃ (1.0 mL, 1.0 mol/L in DCM) was added under -78 °C, after reacted under -78 °C for 2 h and then at rt for 6h, additional BBr₃ (600 μL, 1.0 mol/L in DCM) was replenished and the reaction was further stirred at rt for 12 h.

Synthesis of 6ar and 3ar'. Following *Typical Procedure A*, a mixture of two isomers **3ar** and **3ar'** were obtained from **1a** (73.2 mg, 0.48 mmol) and alkyne **2r** (107.3 mg, 0.40 mmol). The two isomers

can hardly be separated and the mixture was subjected for Friedel-Crafts acylation following *Typical Procedure B*. **6ar** (57.4 mg, 36% in two steps) and **3ar'** (34.8 mg, 21% in two steps) were isolated successively by column chromatography with PE/EtOAc (gradient ratio from 20:1 to 2:1) as eluant.

Synthesis of 3cr, 3cr' and 6cr. Following *Typical Procedure A*, a mixture of two isomers **3cr** and **3cr'** were obtained from **1c** (80.7 mg, 0.48 mmol) and alkyne **2r** (107.3 mg, 0.40 mmol). The mixture was subjected for Friedel-Crafts acylation following *Typical Procedure B*. **6cr** (73.5 mg, 44% in two steps) and **3cr'** (43.1 mg, 25% in two steps) were isolated successively by column chromatography with PE/EtOAc (gradient ratio from 15:1 to 2:1) as eluant.

In another trial, the obtained mixture of **3cr** and **3cr'** were recrystallized with MeOH to afford **3cr** (47.2 mg, 27%). The mother liquor was further separated by preparative thin-layer chromatography with PE/EtOAc (1:1) as developing solvent to afford **3cr** (17.5 mg, 10%, $R_f \approx 0.4$) and **3cr'** (32.8 mg, 19%, $R_f \approx 0.6$). The combined yield of **3cr** was 37% (64.7 mg).

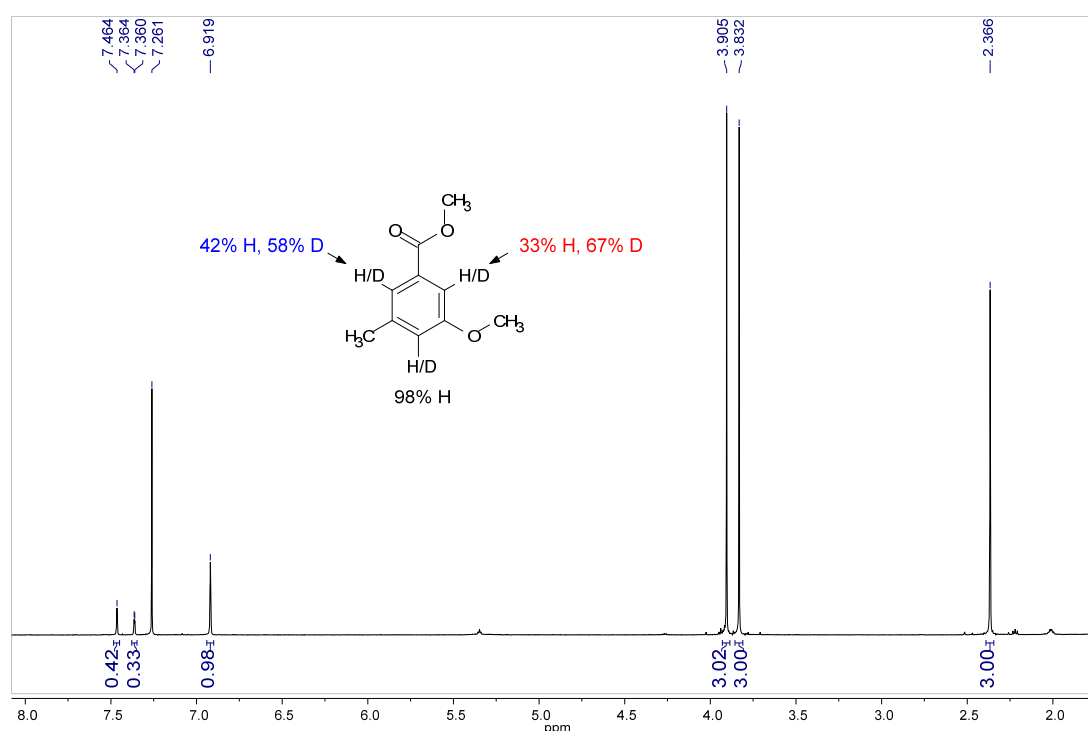
Synthesis of diptoindonesin G. Demethylation of **6cr** was conducted following a reported method⁶ with modification. In a 25 mL tube with a magnetic stirrer, **6cr** (62.5 mg, 0.15 mmol) and anhydrous DCM (3 mL) were added sequentially. After the tube was sealed and cool down to $-78\text{ }^\circ\text{C}$, BBr_3 (3.0 mL, 1.0 mol/L in DCM) was added dropwise under stirring. The cooling bath was removed to let the reaction mixture warm up to room temperature slowly. After stirring for further 16 h, dark insoluble material was formed, and the reaction was quenched by ice water. The precipitate was filtered, washed by water (2×10 mL) and DCM (2×5 mL) sequentially. The precipitate was then dissolved with acetone (1~2 mL), followed by adding PE (10 mL) to precipitate again to remove some impurities. The precipitate was filtered, washed by PE (2×5 mL) and dried under vacuum to afford diptoindonesin G (47.1 mg, 87%) as an orange-red solid. NMR data of the product was in accordance with those of natural diptoindonesin G.⁷

References:

- [6] K. Kim and I. Kim, *Org. Lett.*, 2010, **12**, 5314–5317.
[7] L. D. Juliawaty, Sahidin, E. H. Hakim, S. A. Achmad, Y. M. Syah, J. Latip and I. M. Said, *Nat. Prod. Commun.*, 2009, **4**, 947–950.

1.3 Mechanistic Studies

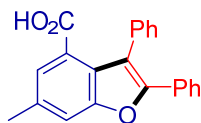
Deuteration experiments. To a 10 mL tube with a magnetic stirrer, $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (6.1 mg, 0.01 mmol), 3-hydroxy-5-methylbenzoic acid **1a** (60.9 mg, 0.40 mmol), $\text{Mg}(\text{OAc})_2$ (14.2 mg, 0.10 mmol), GVL (1 mL) and D_2O (50 μL , 2.8 mmol) were added sequentially. The tube was sealed and stirred at 100 °C for 6 h. The reaction mixture was cooled down, followed by adding K_2CO_3 (110.6 mg, 0.80 mmol), MeCN (2 mL) and MeI (75 μL , 1.2 mmol) sequentially. The tube was sealed and stirred at 60 °C for 4 h. The reaction mixture was then cooled down, diluted with EtOAc and filtered through a pad of celite. The organic phase was washed with brine, dried with Na_2SO_4 and then concentrated. After purification by flash column chromatography on silica gel with petroleum ether (PE)/EtOAc (100:1) as eluant, partially deuterated and fully methylated derivative of **1a** was obtained as a white solid. The deuterated ratio was determined by ^1H NMR.



Isolation of 7aa. To a 10 mL tube with a magnetic stirrer, $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (4.9 mg, 0.008 mmol), **1a** (73.2 mg, 0.48 mmol), **2a** (71.3 mg, 0.40 mmol), $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (21.4 mg, 0.10 mmol) and GVL (0.50 mL) were added sequentially. The tube was charged with N_2 by three evacuation-inflation cycles and stirred at 100 °C for 18 h. The reaction mixture was cooled down, followed by adding K_2CO_3 (110.6 mg, 0.80 mmol), MeCN (2 mL) and MeI (75 μL , 1.2 mmol) sequentially. The tube was sealed and stirred at 60 °C for 4 h. The reaction mixture was then cooled down, diluted with EtOAc and filtered through a pad of celite. The obtained organic phase was washed with brine, dried with Na_2SO_4 and then concentrated. After purification by flash column chromatography on silica gel with PE/EtOAc (gradient ratio from 80:1 to 20:1) as eluant, methylated alkenylation product **7aa** (65.5 mg, 46%) was obtained as a white solid.

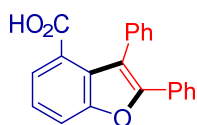
1.4 Characterization Data

6-Methyl-2,3-diphenylbenzofuran-4-carboxylic acid (**3aa**)



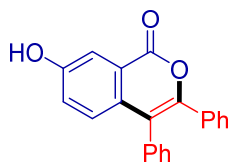
White solid (95.7 mg, 73%): mp 146–147 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.55–7.50 (m, 4H), 7.38–7.36 (m, 2H), 7.34–7.31 (m, 3H), 7.25–7.22 (m, 3H), 2.51 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 172.03, 154.96, 152.33, 134.45, 134.33, 130.55, 130.15, 128.52, 128.43, 128.39, 127.53, 127.15, 126.82, 126.51, 123.83, 118.07, 115.64, 21.53; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{O}_3$ $[\text{M} - \text{H}]^-$ 327.1027, found 327.1027.

2,3-Diphenylbenzofuran-4-carboxylic acid (**3ba**)



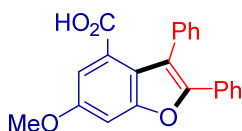
White solid (60.2 mg, 48%): mp 188–190 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76–7.72 (m, 2H), 7.55–7.53 (m, 2H), 7.40–7.32 (m, 6H), 7.28–7.25 (m, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.47, 154.57, 153.04, 134.33, 130.37, 130.18, 128.82, 128.80, 128.49, 128.46, 127.63, 127.34, 125.67, 124.36, 123.91, 118.17, 115.38. **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{14}\text{O}_3$ $[\text{M} - \text{H}]^-$ 313.0870, found 313.0872.

6-Hydroxy-3,4-diphenyl-1H-isochromen-1-one (**4ba**)



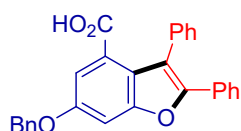
White solid (41.4 mg, 33%): mp 186–188 °C; $^1\text{H NMR}$ (600 MHz, CD_3OD) δ 7.66 (d, $J = 2.7$ Hz, 1H), 7.43–7.39 (m, 3H), 7.30–7.28 (m, 2H), 7.26–7.21 (m, 3H); 7.20–7.16 (m, 3H), 7.06 (d, $J = 8.8$ Hz, 1H); $^{13}\text{C NMR}$ (151 MHz, CD_3OD) δ 164.20, 159.29, 149.57, 135.90, 134.51, 132.44, 132.36, 130.13, 130.04, 129.71, 129.19, 128.90, 128.45, 125.10, 122.66, 118.65, 114.05. **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{14}\text{O}_3$ $[\text{M} - \text{H}]^-$ 313.0870, found 313.0878.

6-Methoxy-2,3-diphenylbenzofuran-4-carboxylic acid (**3ca**)



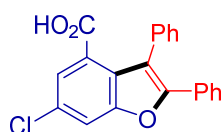
White solid (107.5 mg, 78%): mp 166–168 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.50–7.48 (m, 2H), 7.39–7.24 (m, 10H), 3.93 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.73, 157.28, 155.69, 152.01, 134.43, 130.59, 130.17, 128.46, 128.44, 128.36, 127.58, 126.89, 124.32, 122.57, 117.97, 113.83, 100.35, 56.20; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{O}_4$ $[\text{M} - \text{H}]^-$ 343.0976, found 343.0974.

6-(Benzyloxy)-2,3-diphenylbenzofuran-4-carboxylic acid (**3da**)



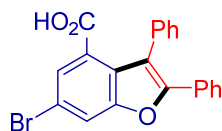
White solid (110.8 mg, 66%): mp 194–196 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.50–7.47 (m, 4H), 7.44–7.41 (m, 3H), 7.38–7.30 (m, 7H), 7.26–7.23 (m, 3H), 5.19 (s, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.86, 156.27, 155.57, 152.13, 136.55, 134.40, 130.55, 130.14, 128.86, 128.45, 128.42, 128.38, 128.35, 127.67, 127.59, 126.91, 124.33, 122.83, 117.99, 114.75, 101.47, 70.98; **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{20}\text{O}_4$ $[\text{M} - \text{H}]^-$ 419.1289, found 419.1292.

6-Chloro-2,3-diphenylbenzofuran-4-carboxylic acid (**3ea**)



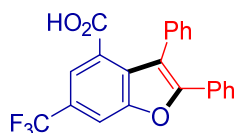
White solid (83.4 mg, 60%); $^1\text{H NMR}$ (600 MHz, CD_3OD) δ 7.48 (d, $J = 1.8$ Hz, 1H), 7.36–7.34 (m, 2H), 7.30–7.24 (m, 5H), 7.18–7.17 (m, 1H), 7.16–7.12 (m, 3H); $^{13}\text{C NMR}$ (151 MHz, CD_3OD) 174.00, 155.78, 153.22, 137.08, 134.18, 131.57, 131.44, 130.86, 129.55, 129.45, 129.34, 128.69, 127.99, 125.82, 123.05, 119.54, 111.87; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{13}\text{O}_3\text{Cl}$ $[\text{M} - \text{H}]^-$ 347.0480, found 347.0479.

6-Bromo-2,3-diphenylbenzofuran-4-carboxylic acid (**3fa**)



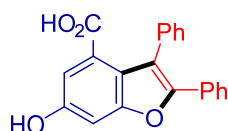
White solid (95.1 mg, 61%): mp 158–160 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.93 (d, $J = 1.4$ Hz, 1H), 7.87 (d, $J = 1.4$ Hz, 1H), 7.55–7.54 (m, 2H), 7.44–7.39 (m, 3H), 7.34–7.28 (m, 5H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.32, 154.86, 153.64, 133.70, 130.10, 129.86, 129.11, 128.56, 128.54, 128.08, 127.87, 127.30, 125.17, 118.46, 117.98, 116.74; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{13}\text{O}_3\text{Br}$ $[\text{M} - \text{H}]^-$ 390.9975, found 390.9980.

2,3-Diphenyl-6-(trifluoromethyl) benzofuran-4-carboxylic acid (**3ga**)



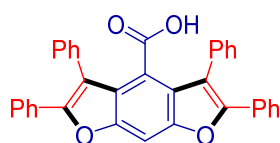
White solid (84.2 mg, 55%): mp 173–175 °C; $^1\text{H NMR}$ (600 MHz, CD_3OD) δ 7.93 (m, 1 H), 7.74 (m, 1H), 7.38–7.36 (m, 2H), 7.32–7.30 (m, 3H), 7.20–7.17 (m, 3H), 7.15–7.13 (m, 2H); $^{13}\text{C NMR}$ (151 MHz, CD_3OD) δ 169.05, 156.61, 155.05, 134.52, 131.85, 131.27, 130.72, 130.44, 129.61, 129.47, 128.95, 128.73, 128.42, 127.07 (q, $J = 33.2$ Hz), 125.53 (q, $J = 271.1$ Hz), 122.21 (q, $J = 3.8$ Hz), 119.27, 112.16 (q, $J = 3.9$ Hz); $^{19}\text{F NMR}$ (565 MHz, CD_3OD) δ -62.73; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{13}\text{O}_3\text{F}_3$ $[\text{M} - \text{H}]^-$ 381.0744, found 381.0743.

6-Hydroxy-2,3-diphenylbenzofuran-4-carboxylic acid (3ha)



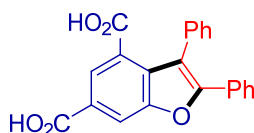
White solid (70.8 mg, 54%): mp 212–215 °C; $^1\text{H NMR}$ (600 MHz, CD_3OD) δ 7.41–7.35 (m, 6H), 7.34–7.31 (m, 1H), 7.22–7.18 (m, 3H), 6.92 (d, $J = 2.2$ Hz, 1H), 6.84 (d, $J = 2.2$ Hz, 1H); $^{13}\text{C NMR}$ (151 MHz, CD_3OD) δ 175.52, 156.84, 156.61, 150.87, 136.27, 135.11, 132.42, 131.46, 129.32, 129.17, 128.62, 128.33, 127.46, 119.81, 119.73, 111.85, 98.18; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{14}\text{O}_4$ $[\text{M} - \text{H}]^-$ 329.0819, found 329.0819.

2,3,5,6-Tetraphenylbenzo[1,2-b:5,4-b']difuran-4-carboxylic acid (5haa)



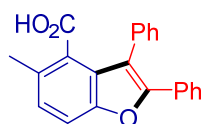
Pale yellow solid (32.4 mg, 32%, from 0.48 mmol **1h** and 0.40 mmol **2a**; 152.1 mg, 75%, from 0.40 mmol **1h** and 0.96 mmol **2a**): mp 262–264 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (s, 1H), 7.56–7.55 (m, 4H), 7.38–7.35 (m, 10H), 7.29–7.25 (m, 6H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.49, 152.29, 152.12, 132.78, 130.65, 130.41, 128.72, 128.55, 128.10, 126.75, 124.46, 117.12, 115.80, 95.85; **HRMS** (ESI) calcd for $\text{C}_{35}\text{H}_{22}\text{O}_4$ $[\text{M} - \text{H}]^-$ 505.1445, found 505.1452.

2,3-Diphenylbenzofuran-4,6-dicarboxylic acid (3ia)



White solid (57.5 mg, 40%): mp 288–290 °C; $^1\text{H NMR}$ (600 MHz, CD_3OD) δ 8.32 (d, $J = 1.3$ Hz, 1H), 8.26 (d, $J = 1.3$ Hz, 1H), 7.50–7.48 (m, 2H), 7.44–7.40 (m, 3H), 7.31–7.29 (m, 3H), 7.27–7.24 (m, 2H); $^{13}\text{C NMR}$ (151 MHz, CD_3OD) δ 169.81, 168.89, 156.68, 155.29, 134.78, 132.57, 131.27, 130.93, 130.35, 129.58, 129.45, 128.85, 128.43, 127.86, 127.71, 126.93, 119.54, 116.15; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{14}\text{O}_5$ $[\text{M} - \text{H}]^-$ 357.0768, found 357.0767.

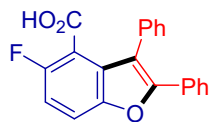
5-Methyl-2,3-diphenylbenzofuran-4-carboxylic acid (3ja)



White solid (106.7 mg, 81%): mp 205–206 °C; $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ 7.65 (d, $J = 8.4$ Hz, 1H), 7.47–7.41 (m, 5H), 7.34–7.31 (m, 5H), 7.27 (d, $J = 8.4$ Hz, 1H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, $\text{DMSO}-d_6$) δ 168.25, 151.61, 150.86, 131.80, 130.15, 129.70, 128.68, 128.56, 128.46, 128.00, 127.73,

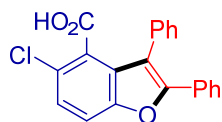
126.96, 126.36, 125.43, 117.27, 111.47, 18.54; **HRMS** (ESI) calcd for C₂₂H₁₆O₃ [M – H][–] 327.1027, found 327.1028.

5-Fluoro-2,3-diphenylbenzofuran-4-carboxylic acid (3ka)



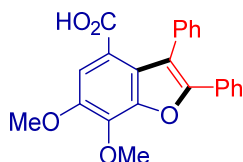
White solid (70.2 mg, 53%): mp 214–217 °C; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 13.17 (brs, 1 H), 7.82 (dd, *J* = 8.9, 3.7 Hz, 1H), 7.49–7.44 (m, 5H), 7.36–7.30 (m, 6H), **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 164.17, 154.91 (d, *J* = 239.8 Hz), 152.73, 149.41, 131.29, 130.00, 129.29, 129.18, 128.71, 128.70, 128.23, 126.55 (d, *J* = 7.2 Hz), 117.67 (d, *J* = 3.9 Hz), 115.28 (d, *J* = 22.1 Hz), 113.39 (d, *J* = 10.0 Hz), 112.76 (d, *J* = 26.6 Hz); **¹⁹F NMR** (565 MHz, DMSO-*d*₆) δ –123.93; **HRMS** (ESI) calcd for C₂₁H₁₃O₃F [M – H][–] 331.0776, found 331.0777.

5-Chloro-2,3-diphenylbenzofuran-4-carboxylic acid (3la)



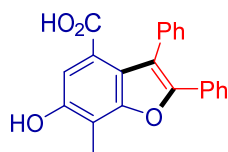
White solid (81.2 mg, 58%): mp 212–214 °C; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 13.20 (brs, 1 H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.50–7.43 (m, 6H), 7.36–7.34 (m, 5H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 165.48, 152.24, 151.66, 130.72, 130.27, 129.20, 129.14, 128.71, 128.43, 126.78, 126.53, 125.56, 123.81, 117.04, 113.16; **HRMS** (ESI) calcd for C₂₁H₁₃O₃Cl [M – H][–] 347.0480, found 347.0482.

6,7-Dimethoxy-2,3-diphenylbenzofuran-4-carboxylic acid (3ma)



White solid (85.7 mg, 57%): mp 156–160 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.50–7.47 (m, 2H), 7.4 (s, 1H), 7.40–7.37 (m, 2H), 7.35–7.33 (m, 1H), 7.33–7.31 (m, 2H), 7.25–7.26 (m, 3H), 4.38 (s, 3H), 4.0 (s, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 170.65, 152.73, 147.59, 146.05, 138.09, 134.39, 130.36, 130.16, 128.61, 128.47, 128.39, 127.53, 127.07, 126.10, 118.19, 116.40, 112.55, 61.25, 57.35; **HRMS** (ESI) calcd for C₂₃H₁₈O₅ [M – H][–] 373.1081, found 373.1082.

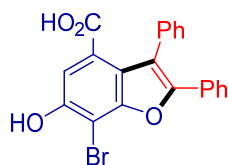
6-Hydroxy-7-methyl-2,3-diphenylbenzofuran-4-carboxylic acid (3na)



White solid (71.4 mg, 52%): mp 209–211 °C; **¹H NMR** (600 MHz, CD₃OD) δ 7.44–7.42 (m, 2H)

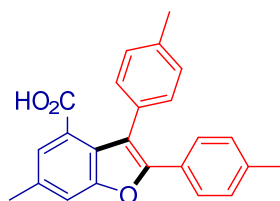
7.40–7.34 (m, 3H), 7.29–7.27 (m, 2H), 7.22–7.20 (m, 1H), 7.18 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 170.74, 155.76, 153.90, 152.12, 136.10, 132.09, 131.28, 129.34, 129.23, 129.01, 128.33, 127.63, 124.24, 121.49, 119.67, 114.25, 112.53, 8.86; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{O}_4$ $[\text{M} - \text{H}]^-$ 343.0976, found 343.0975.

7-Bromo-6-hydroxy-2,3-diphenylbenzofuran-4-carboxylic acid (30a)



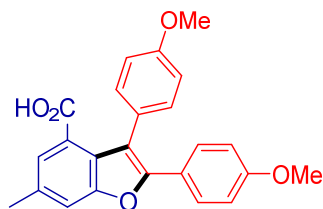
White solid (63.9 mg, 39%): mp 198–201 °C; ^1H NMR (600 MHz, CD_3OD) 7.45–7.46 (m, 2H), 7.43–7.39 (m, 3H), 7.32–7.30 (m, 2H), 7.25–7.22 (m, 4H); ^{13}C NMR (151 MHz, CD_3OD) δ 169.87, 154.25, 153.47, 152.83, 135.26, 131.43, 131.24, 129.51, 129.47, 129.36, 128.69, 127.70, 126.71, 122.11, 119.89, 114.60, 96.15; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{13}\text{O}_4\text{Br}$ $[\text{M} - \text{H}]^-$ 406.9924, found 406.9925.

6-Methyl-2,3-di-p-tolylbenzofuran-4-carboxylic acid (3ab)



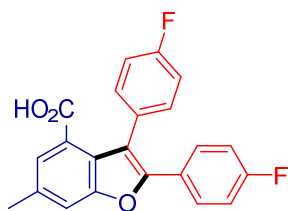
White solid (101.4 mg, 71%): mp 185–188 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.51 (s, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.20–7.16 (m, 4H), 7.07 (d, $J = 8.1$ Hz, 2H), 2.51 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.85, 154.88, 152.46, 138.51, 137.05, 133.96, 131.43, 129.96, 129.17, 129.11, 127.88, 127.02, 126.85, 126.46, 123.79, 117.34, 115.44, 21.52, 21.48, 21.44; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{O}_3$ $[\text{M} - \text{H}]^-$ 355.1340, found 355.1339.

2,3-Bis(4-methoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (3ac)



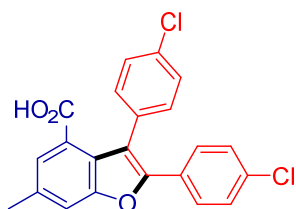
White solid (99.8 mg, 64%): mp 183–185 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.53 (s, 1H), 7.51–7.48 (m, 3H), 7.24–7.22 (m, 2H), 6.94–6.91 (m, 2H), 6.81–6.79 (m, 2H), 3.780 (s, 3H), 3.783 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.72, 159.78, 159.03, 154.77, 152.52, 133.72, 131.35, 128.53, 127.08, 126.85, 126.50, 123.53, 123.36, 116.11, 115.38, 114.01, 113.96, 55.38, 55.34, 21.50; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{O}_5$ $[\text{M} - \text{H}]^-$ 387.1238, found 387.1238.

2,3-Bis(4-fluorophenyl)-6-methylbenzofuran-4-carboxylic acid (3ad)



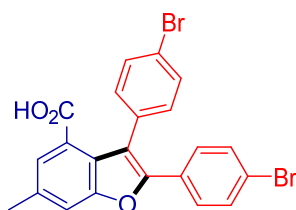
White solid (102.3 mg, 70%): mp 187–190 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.64 (s, 1H), 7.55 (s, 1H), 7.50–7.46 (m, 2H), 7.30–7.27 (m, 2H), 7.12–7.09 (m, 2H), 7.00–6.96 (m, 2H), 2.55 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.93, 162.82 (d, $J = 249.9$ Hz), 162.45 (d, $J = 246.3$ Hz), 154.89, 151.80, 134.65, 131.88 (d, $J = 7.9$ Hz), 130.44 (d, $J = 3.3$ Hz), 129.07 (d, $J = 8.2$ Hz), 127.31, 126.61 (d, $J = 3.3$ Hz), 126.47, 123.48, 116.73, 115.80 (d, $J = 21.8$ Hz), 115.58, 115.49 (d, $J = 21.4$ Hz), 21.51; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -111.76, -114.66; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{14}\text{O}_3\text{F}_2$ $[\text{M} - \text{H}]^-$ 363.0838, found 363.0839.

2,3-Bis(4-chlorophenyl)-6-methylbenzofuran-4-carboxylic acid (3ae)



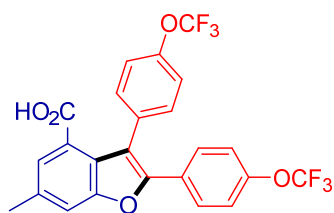
White solid (106.7 mg, 67%): mp 210–212 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.67 (s, 1H), 7.55 (s, 1H), 7.43–7.41 (m, 2H), 7.38–7.37 (m, 2H), 7.26–7.23 (m, 4H), 2.54 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.49, 154.98, 151.49, 134.99, 134.74, 133.63, 133.06, 131.56, 128.86, 128.75, 128.35, 127.53, 126.26, 123.49, 117.29, 115.96, 21.56; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{14}\text{O}_3\text{Cl}_2$ $[\text{M} - \text{H}]^-$ 395.0247, found 395.0248.

2,3-Bis(4-bromophenyl)-6-methylbenzofuran-4-carboxylic acid (3af)



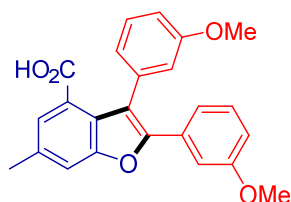
White solid (165.9 mg, 86%): mp 195–198 °C; $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$) δ 12.63 (s, 1H), 7.68 (s, 1H), 7.62–7.60 (m, 2H), 7.59–7.57 (m, 2H), 7.45 (m, 1H), 7.36–7.34 (m, 2H), 7.25–7.23 (m, 2H), 2.48 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, $\text{DMSO}-d_6$) δ 167.31, 154.18, 150.07, 134.98, 132.73, 131.95, 131.74, 131.38, 128.75, 128.50, 126.22, 125.77, 124.38, 122.28, 120.96, 117.22, 114.27, 20.91; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{14}\text{O}_3\text{Br}_2$ $[\text{M} - \text{H}]^-$ 482.9237, found 482.9246.

6-Methyl-2,3-bis(4-(trifluoromethyl)phenyl)benzofuran-4-carboxylic acid (**3ag**)



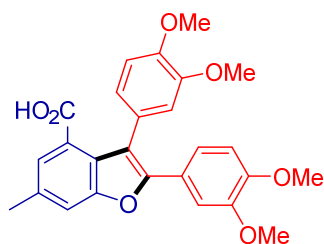
White solid (108.7 mg, 55%): mp 195–198 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.57 (s, 1H), 7.50 (s, 1H), 7.43–7.42 (m, 2H), 7.27–7.25 (m, 2H), 7.20–7.18 (m, 2H), 7.05–7.04 (m, 2H), 2.47 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.45, 155.04, 151.34, 149.31 (q, $J = 1.6$ Hz), 148.90 (q, $J = 1.7$ Hz), 135.14, 133.41, 131.73, 128.91, 128.58, 127.79, 126.34, 123.39, 120.92, 120.88, 120.71 (q, $J = 257.1$ Hz), 120.52 (q, $J = 257.8$ Hz), 117.33, 116.14, 21.46; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -57.67, -57.75; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{14}\text{O}_5\text{F}_6$ [$\text{M} - \text{H}$] $^-$ 495.0673, found 495.0672.

2,3-Bis(3-methoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (**3ah**)



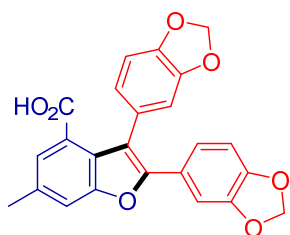
White solid (82.0 mg, 53%): mp 156–158 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (s, 1H), 7.54 (s, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.21–7.16 (m, 2H), 7.07 (s, 1H), 6.94 (d, $J = 7.4$ Hz, 1H), 6.88–6.86 (m, 2H), 6.81–6.79 (m, 2H), 3.72 (s, 3H), 3.60 (s, 3H), 2.53 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.81, 159.71, 159.38, 154.84, 152.04, 135.81, 134.46, 131.62, 129.50, 129.47, 126.76, 126.32, 123.89, 122.79, 119.54, 118.05, 115.58, 115.39, 115.28, 113.59, 111.69, 55.36, 55.09, 21.54; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{O}_5$ [$\text{M} - \text{H}$] $^-$ 387.1238, found 387.1237.

2,3-Bis(3,4-dimethoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (**3ai**)



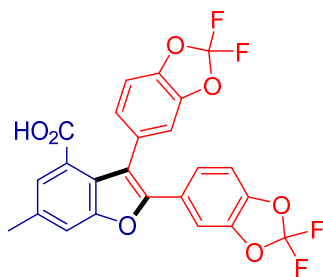
White solid (91.5 mg, 51%): mp 189–192 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.55 (s, 1H), 7.53 (s, 1H), 7.23 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.08 (d, $J = 2.0$ Hz, 1H), 6.92–9.88 (m, 3H), 6.79 (d, $J = 8.6$ Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.79 (s, 3H), 3.66 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.70, 154.67, 152.30, 149.34, 149.10, 148.57, 148.50, 133.94, 127.31, 126.77, 126.55, 123.55, 123.32, 122.76, 119.96, 116.33, 115.35, 113.65, 111.43, 110.99, 109.99, 56.07, 56.05, 55.94, 55.63, 21.51; **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{O}_7$ [$\text{M} - \text{H}$] $^-$ 447.1449, found 447.1449.

2,3-Bis(benzo[d][1,3]dioxol-5-yl)-6-methylbenzofuran-4-carboxylic acid (**3aj**)



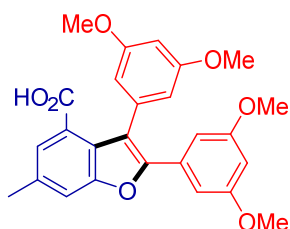
White solid (129.6 mg, 78%): mp 214–218 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.5 (s, 1H), 7.60 (m, 1H), 7.37 (s, 1H), 7.07 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.89 (d, *J* = 1.7 Hz, 1H), 6.83 (d, *J* = 1.6 Hz, 1H), 6.72 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.09 (s, 2H), 6.03 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 167.67, 153.72, 150.85, 147.66, 147.34, 147.20, 146.58, 134.06, 127.09, 126.25, 125.22, 125.09, 123.69, 123.33, 121.07, 116.26, 113.80, 110.42, 108.61, 108.41, 106.47, 101.43, 101.02, 20.87. HRMS (ESI) calcd for C₂₄H₁₆O₇ [M – H][–] 415.0823, found 415.0824.

2,3-Bis(2,2-difluorobenzo[d][1,3]dioxol-5-yl)-6-methylbenzofuran-4-carboxylic acid (**3ak**)



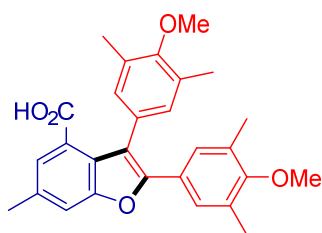
White solid (127.1 mg, 65%): mp 207–210 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.63 (s, 1 H), 7.68 (s, 1H), 7.48 (s, 1H), 7.45–7.40 (m, 4H), 7.25 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.10 (dd, *J* = 8.2, 1.5 Hz, 1H), 2.48 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 167.33, 153.99, 150.00, 142.94, 142.87, 142.83, 142.29, 135.02, 131.27 (t, *J* = 252.3 Hz), 131.11 (t, *J* = 253.8 Hz), 130.02, 126.21, 126.11, 126.07, 126.04, 124.76, 123.60, 116.88, 114.39, 112.00, 110.53, 109.99, 108.32, 20.88; ¹⁹F NMR (565 MHz, DMSO-*d*₆) δ –48.6, –49.15, –49.16, –49.17; HRMS (ESI) calcd for C₂₄H₁₂O₇F₄ [M – H][–] 487.0446, found 487.0446.

2,3-Bis(3,5-dimethoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (**3al**)



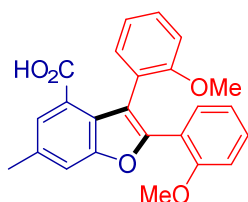
White solid (123.9 mg, 69%): mp 177–179 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.57–7.56 (m, 1H), 7.55–7.54 (m, 1H), 6.80 (d, *J* = 2.3 Hz, 2H), 6.54 (d, *J* = 2.3 Hz, 2H), 6.43 (t, *J* = 2.3 Hz, 1H), 6.38 (t, *J* = 2.3 Hz, 1H), 3.70 (s, 6H), 3.64 (s, 6H), 2.54 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 171.49, 160.90, 160.59, 154.72, 151.83, 136.38, 134.60, 131.93, 126.68, 126.09, 124.00, 118.22, 115.51, 108.20, 104.84, 101.83, 100.34, 55.51, 55.32, 21.56; HRMS (ESI) calcd for C₂₆H₂₄O₇ [M – H][–] 447.1449, found 447.1448.

2,3-Bis(4-methoxy-3,5-dimethylphenyl)-6-methylbenzofuran-4-carboxylic acid (3am)



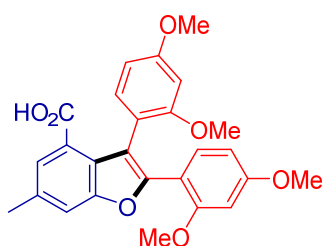
White solid (99.7 mg, 56%): mp 207–211 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.50 (s, 1H), 7.49 (s, 1H), 7.23 (s, 2H), 6.96 (s, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 2.51 (s, 3H), 2.26 (d, 6H), 2.18 (d, 6H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 172.25, 157.40, 156.49, 154.80, 152.21, 133.81, 130.87, 130.56, 130.44, 129.75, 127.75, 126.76, 126.39, 126.10, 123.67, 116.94, 115.42, 59.82, 59.78, 21.51, 16.34, 16.18. **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{O}_5$ $[\text{M} - \text{H}]^-$ 443.1864, found 443.1867.

2,3-Bis(2-methoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (3an)



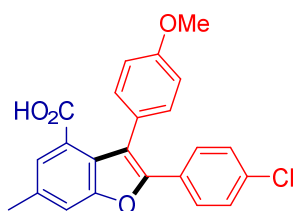
White solid (59.2 mg, 38%; 69.5 mg, 45%): mp 152–154 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (s, 1H), 7.51 (s, 1H), 7.39–7.37 (m, 1H), 7.32–7.29 (m, 1H), 7.14–7.11 (m, 1H), 6.95–6.92 (m, 2H), 6.81 (d, $J = 8.3$ Hz, 1H), 6.75 (d, $J = 8.2$ Hz, 1H), 6.70 (t, $J = 7.4$ Hz, 1H), 3.62 (s, 3H), 3.41 (s, 3H), 2.51 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 172.09, 157.60, 157.28, 155.62, 151.89, 133.41, 131.64, 130.60, 130.20, 128.16, 125.99, 125.92, 124.80, 124.18, 120.48, 120.09, 119.95, 116.38, 115.47, 111.42, 109.27, 55.17, 21.52; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{O}_5$ $[\text{M} - \text{H}]^-$ 387.1238, found 387.1238.

2,3-Bis(2,4-dimethoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (3ao)



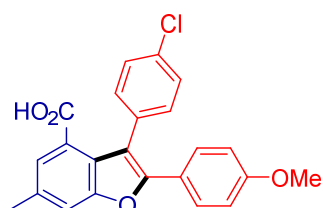
White solid (63.0 mg, 35%; 77.3 mg, 43%): mp 210–212 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (s, 1H), 7.51 (s, 1H), 7.28 (d, $J = 8.5$ Hz, 1H), 6.88 (d, $J = 8.3$ Hz, 1H), 6.47 (dd, $J = 8.5, 2.2$ Hz, 1H), 6.44 (d, $J = 2.2$ Hz, 1H), 6.40 (d, $J = 2.2$ Hz, 1H), 6.31 (dd, $J = 8.3, 2.3$ Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.63 (s, 3H), 3.47 (s, 3H), 2.51 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.98, 161.79, 160.14, 158.64, 155.49, 152.14, 133.07, 132.48, 130.48, 125.88, 125.20, 124.86, 116.79, 115.64, 115.41, 112.98, 104.79, 103.76, 98.94, 97.64, 55.49, 55.44, 55.38, 55.16, 21.46; **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{O}_7$ $[\text{M} - \text{H}]^-$ 447.1449, found 447.1447.

2-(4-Chlorophenyl)-3-(4-methoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (3ap)



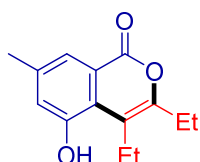
White solid (73.4 mg, 47%): mp 197–200 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (s, 1H), 7.53 (s, 1H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.25–7.21 (m, 4H), 6.93 (d, $J = 8.4$ Hz, 2H), 3.80 (s, 3H), 2.54 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.02, 159.26, 154.92, 151.25, 134.64, 134.40, 131.18, 129.15, 128.75, 128.24, 126.88, 126.67, 126.28, 123.90, 118.12, 115.59, 114.14, 55.36, 21.57; **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{O}_4\text{Cl}$ $[\text{M} - \text{H}]^-$ 391.0743 found 391.0747.

3-(4-Chlorophenyl)-2-(4-methoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (3ap')



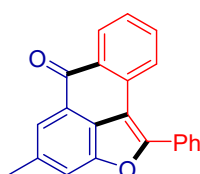
White solid (50.4 mg, 32%): mp 202–205 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.67–7.28 (m, 8H), 6.85–6.84 (m, 2H), 3.82 (s, 3H), 2.56 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.45, 160.01, 154.86, 152.84, 134.10, 133.60, 133.28, 131.78, 128.70, 128.62, 127.19, 126.65, 123.06, 122.93, 115.76, 115.35, 114.07, 55.42, 21.51; **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{O}_4\text{Cl}$ $[\text{M} - \text{H}]^-$ 391.0743 found 391.0747.

3,4-Diethyl-5-hydroxy-7-methyl-1H-isochromen-1-one (4aq)



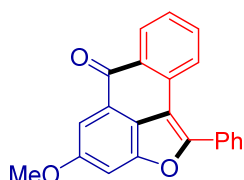
White solid (69.7 mg, 75%): mp 191–194 °C; $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$) δ 10.20 (s, 1H), 7.50–7.49 (m, 1H), 7.07 (m, 1H), 2.86 (q, $J = 7.2$ Hz, 2H), 2.55 (q, $J = 7.5$ Hz, 2H), 2.33 (s, 3H), 1.18 (t, $J = 7.5$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, $\text{DMSO}-d_6$) δ 161.80, 153.73, 151.72, 138.02, 122.68, 122.44, 122.05, 119.99, 112.93, 23.11, 20.88, 20.60, 15.87, 12.67; **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3$ $[\text{M} - \text{H}]^-$ 231.1027, found 231.1024.

4-Methyl-1-phenyl-6H-anthra[1,9-bc]furan-6-one (6aa)



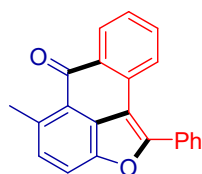
Yellow solid (44.3 mg, 71%): mp 201–203 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.51 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.11–8.10 (m, 1H), 7.93–7.91 (m, 3H), 7.60–7.54 (m, 3H), 7.53–7.46 (m, 3H), 2.59 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 183.05, 155.26, 153.30, 136.96, 133.30, 132.45, 131.66, 131.01, 130.50, 129.49, 129.18, 129.08, 127.89, 125.86, 124.18, 122.21, 116.04, 109.65, 22.39; HRMS (ESI) calcd for C₂₂H₁₄O₂ [M + H]⁺ 311.1067, found 311.1065.

4-Methoxy-1-phenyl-6H-anthra[1,9-bc]furan-6-one (6ca)



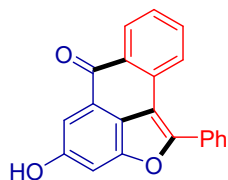
Yellow solid (47.7 mg, 73%): mp 168–170 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.55 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.96–7.95 (m, 2H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.62–7.59 (m, 2H), 7.58–7.54 (m, 2H), 7.53–7.50 (m, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 3.98 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 182.90, 160.08, 155.36, 153.80, 133.16, 132.52, 131.61, 130.99, 130.50, 129.54, 129.14, 129.12, 128.02, 126.16, 126.00, 124.28, 109.54, 105.85, 103.98, 56.64; HRMS (ESI) calcd for C₂₂H₁₄O₃ [M + H]⁺ 327.1015, found 327.1016.

5-Methyl-1-phenyl-6H-anthra[1,9-bc]furan-6-one (6ja)



Yellow solid (48.4 mg, 78%): mp 170–173 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.47–8.45 (m, 1 H), 8.05–8.03 (m, 1H), 7.89–7.87 (m, 2H), 7.58–7.50 (m, 4H), 7.47–7.42 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 2.88 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 183.92, 154.98, 151.14, 137.17, 133.81, 132.01, 131.52, 131.08, 130.98, 130.38, 129.19, 128.96, 128.96, 128.91, 127.70, 123.67, 123.40, 114.80, 109.89, 21.10; HRMS (ESI) calcd for C₂₂H₁₄O₂ [M + H]⁺ 311.1067, found 311.1066.

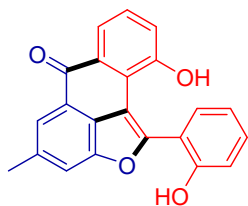
4-Hydroxy-1-phenyl-6H-anthra[1,9-bc]furan-6-one (6ha)



Yellow solid (54.0 mg, 86%): mp 258–260 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.29 (s, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.95–7.94 (m, 2H), 7.69–7.64 (m, 4H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.41 (s, 1H), ¹³C NMR (151 MHz, DMSO-*d*₆) δ 181.36, 157.87, 154.07, 153.32, 132.82, 132.15, 130.69, 130.56, 130.06, 129.16, 128.85, 128.58, 128.06, 125.14, 123.83, 123.44, 108.55, 107.74,

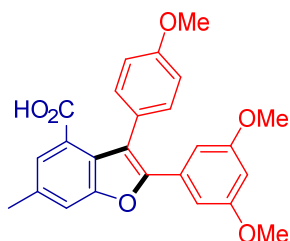
104.15; **HRMS** (ESI) calcd for C₂₁H₁₂O₃ [M + H]⁺ 313.0859, found 313.0857.

10-Hydroxy-1-(2-hydroxyphenyl)-4-methyl-6H-anthra[1,9-bc]furan-6-one (6an)



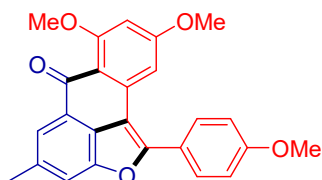
Yellow solid (62.3 mg, 91%): mp 281–283 °C; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 10.25 (s, 1H), 9.62 (s, 1H), 7.88–7.86 (m, 2H), 7.81 (s, 1H), 7.47 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.33 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.11 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.90 (ddd, *J* = 8.3, 7.5, 0.8 Hz, 1H), 2.61 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 182.01, 156.54, 155.73, 154.63, 152.45, 136.11, 133.88, 131.13, 130.51, 128.99, 128.00, 124.72, 121.11, 120.86, 119.73, 119.05, 118.76, 117.41, 115.90, 114.90, 108.74, 21.63. **HRMS** (ESI) calcd for C₂₂H₁₄O₄ [M – H][–] 341.0819, found 341.0819.

2-(3,5-Dimethoxyphenyl)-3-(4-methoxyphenyl)-6-methylbenzofuran-4-carboxylic acid (3ar')



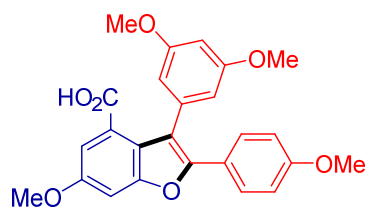
White solid (34.8 mg, 21%): mp 167–170 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.58–7.57 (m, 2H), 7.30–7.27 (m, 2H), 6.98–6.96 (m, 2H), 6.77 (d, *J* = 2.1 Hz, 2H), 6.40 (t, *J* = 2.1 Hz, 1H), 3.80 (s, 3H), 3.60 (s, 6H), 2.56 (s, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 171.33, 160.60, 159.18, 154.77, 152.05, 134.44, 132.21, 131.39, 126.81, 126.77, 123.87, 118.08, 115.59, 114.02, 104.83, 101.62, 55.43, 55.33, 21.55. **HRMS** (ESI) calcd for C₂₅H₂₂O₆ [M – H][–] 417.1344 found 417.1352.

7,9-Dimethoxy-1-(4-methoxyphenyl)-4-methyl-6H-anthra[1,9-bc]furan-6-one (6ar).



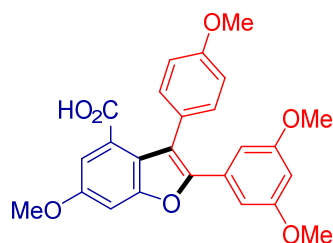
Yellow solid (57.4 mg, 36%): mp 201–204 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.88–7.86 (m, 3H), 7.42 (s, 1H), 7.28–7.27 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.51 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.75 (s, 3H), 2.60 (s, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 182.57, 164.54, 163.23, 161.32, 155.31, 152.72, 136.52, 136.32, 130.82, 128.40, 127.49, 123.36, 121.71, 116.91, 114.66, 114.40, 109.43, 100.52, 98.95, 56.42, 55.64, 55.53, 22.45; **HRMS** (ESI) calcd for C₂₅H₂₀O₅ [M + H]⁺ 401.1384, found 401.1381.

3-(3,5-Dimethoxyphenyl)-6-methoxy-2-(4-methoxyphenyl)benzofuran-4-carboxylic acid (**3cr**)⁶



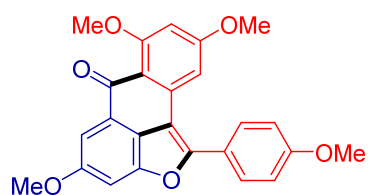
White solid (64.7 mg, 37%): mp 206–209 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.53–7.50 (m, 2H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.26 (m, 1H), 6.83–6.80 (m, 2H), 6.51 (d, *J* = 2.2 Hz, 2H), 6.45 (t, *J* = 2.2 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 3.71 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 170.13, 160.77, 159.64, 156.89, 155.30, 151.90, 136.28, 128.25, 124.01, 122.99, 122.31, 115.97, 113.85, 113.01, 108.04, 100.09, 56.06, 55.37, 55.27; HRMS (ESI) calcd for C₂₅H₂₂O₇ [M – H][–] 433.1293, found 433.1292.

2-(3,5-Dimethoxyphenyl)-6-methoxy-3-(4-methoxyphenyl) benzofuran-4-carboxylic acid (**3cr'**).



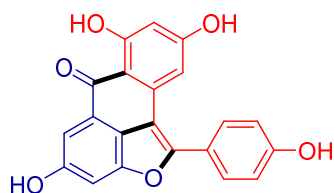
White solid (43.1 mg, 25%): mp 197–199 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.35 (d, *J* = 2.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.27–7.25 (m, 2H), 6.96–6.94 (m, 2H), 6.73 (d, *J* = 2.3 Hz, 2H), 6.37 (t, *J* = 2.3 Hz, 1H), 3.94 (s, 3H), 3.78 (s, 3H), 3.63 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 170.90, 160.61, 159.20, 157.35, 155.46, 151.68, 132.24, 131.36, 126.71, 124.44, 122.82, 118.02, 114.03, 113.72, 104.53, 101.44, 100.26, 56.17, 55.45, 55.32; HRMS (ESI) calcd for C₂₅H₂₂O₇ [M – H][–] 433.1293, found 433.1289.

4,7,9-Trimethoxy-1-(4-methoxyphenyl)-6H-anthra[1,9-bc]furan-6-one (**6cr**).⁶



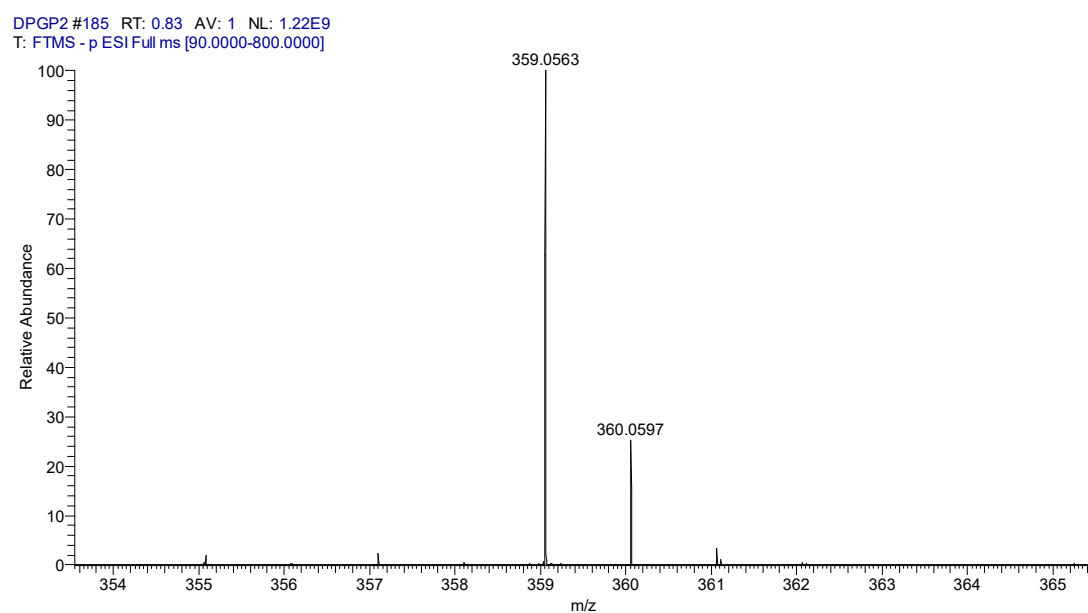
Yellow solid (73.5 mg, 44%): mp 207–208 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.09–7.06 (m, 2H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H), 3.75 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 182.21, 164.53, 163.27, 161.28, 159.91, 155.33, 153.13, 136.23, 130.72, 127.56, 124.90, 123.32, 116.74, 114.40, 109.22, 105.76, 102.36, 100.57, 98.99, 56.55, 56.35, 55.63, 55.50; HRMS (ESI) calcd for C₂₅H₂₀O₆ [M + H]⁺ 417.1333, found 417.1336.

4,7,9-trihydroxy-1-(4-hydroxyphenyl)-6H-anthra[1,9-bc]furan-6-one (diptoindonesin G).^{6,7}

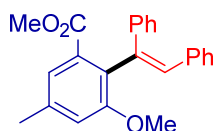


Orange-red solid (47.1 mg, 87%): mp = 293–295 °C; ¹H NMR (600 MHz, acetone-*d*₆) δ 14.24 (s, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.35 (d, *J* = 2.2 Hz, 1H); ¹³C NMR (151 MHz, acetone-*d*₆) δ 187.42, 168.17, 166.50, 160.95, 158.43, 157.38, 154.02, 135.55, 131.41, 126.23, 125.14, 122.09, 116.95, 111.55, 109.12, 108.14, 104.51, 104.32, 103.38; HRMS (ESI) calcd for C₂₁H₁₂O₆ [M – H][–] 359.0561, found 359.0563.

Note: Only one H in four OH groups was observed in ¹H NMR, which should be identified to the OH group near the carbonyl group (intramolecular hydrogen bond may be formed).⁷ The HRMS (ESI) signal using positive ion mode was very low, and only HRMS (EI) data was reported in literature.^{6,7} Fortunately, the HRMS (ESI) signal using negative ion mode was quite clear.



Methyl (*E*)-2-(1,2-diphenylvinyl)-3-methoxy-5-methylbenzoate (7aa).



White solid (65.5 mg, 46%); mp 140–144 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.40–7.38 (m, 3H), 7.34–7.32 (m, 2H), 7.28–7.27 (m, 1H), 7.18–7.12 (m, 4H), 7.06–7.05 (m, 2H), 6.95 (s, 1H), 3.60 (s, 3H), 3.59 (s, 3H), 2.48 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 159.19, 154.67, 150.08, 135.16, 135.11, 131.85, 130.97, 130.89, 130.38, 129.32, 128.46, 128.23, 128.00, 127.93, 127.67, 126.45, 125.79, 123.14, 120.12, 118.27, 114.00, 110.23, 55.42, 21.94. HRMS (ESI) calcd for C₂₄H₂₂O₃ [M + H]⁺ 359.1642, found 359.1633.

2. X-Ray Structural Details

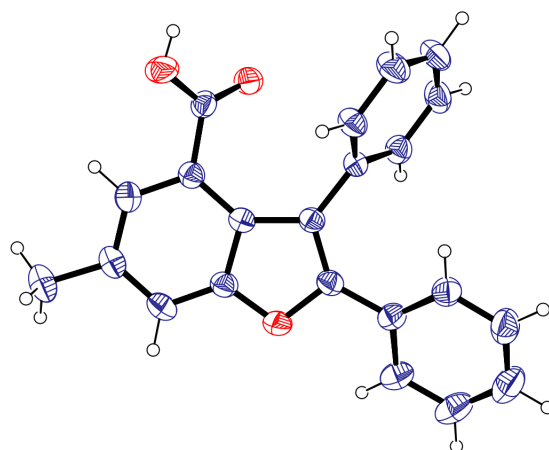


Figure S1. ORTEP drawing of **3aa** (CCDC 2086128) with 35% probability ellipsoids.

Table S2. Crystal Parameters and Refinement Metrics of **3aa**

Sample code	zly1_OY685
Empirical formula	C ₂₂ H ₁₆ O ₃
Formula weight	328.35
Temperature	298 K
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i>	9.1743(5) Å, 9.2287(5) Å, 11.7068(6) Å
<i>α</i> , <i>β</i> , <i>γ</i>	71.616(2)°, 68.548(2)°, 85.269(2)°
Volume	874.83(8) Å ³
<i>Z</i>	2
Density (calcd)	1.246 g·cm ⁻³
Absorption coefficient	0.082 mm ⁻¹
<i>F</i> (000)	344.0
Crystal size	0.15 × 0.08 × 0.05 mm ³
Radiation	MoKα (<i>λ</i> = 0.71073 Å)
2 <i>θ</i> range for data collection	4.976° to 55.086°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 12, -14 ≤ <i>l</i> ≤ 15
Reflections collected	10866
Independent reflections	3979 [<i>R</i> _{int} = 0.0438, <i>R</i> _{sigma} = 0.0568]
Data / restraints / parameters	3979 / 0 / 228
Goodness-of-fit on <i>F</i> ²	1.033
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0530, <i>wR</i> ₂ = 0.1171
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1038, <i>wR</i> ₂ = 0.1499
Largest diff. peak / hole	0.20 / -0.18 e·Å ⁻³

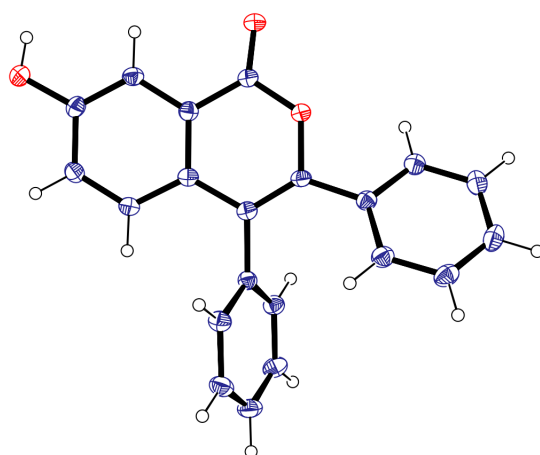


Figure S2. ORTEP drawing of **4ba** (CCDC 2086129) with 35% probability ellipsoids.

Table S3. Crystal Parameters and Refinement Metrics of 4ba

Sample code	zly2_OY820-P1
Empirical formula	C ₂₁ H ₁₄ O ₃
Formula weight	314.32
Temperature	170 K
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i>	6.1028(3) Å, 13.2506(5) Å, 18.8577(9) Å
<i>α</i> , <i>β</i> , <i>γ</i>	90°, 94.524(2)°, 90°
Volume	1520.19(12) Å ³
<i>Z</i>	4
Density (calcd)	1.373 g·cm ⁻³
Absorption coefficient	0.091 mm ⁻¹
<i>F</i> (000)	656.0
Crystal size	0.15 × 0.08 × 0.05 mm ³
Radiation	MoKα (<i>λ</i> = 0.71073 Å)
2 <i>θ</i> range for data collection	4.334° to 52.834°
Index ranges	-7 ≤ <i>h</i> ≤ 7, -15 ≤ <i>k</i> ≤ 16, -23 ≤ <i>l</i> ≤ 23
Reflections collected	17213
Independent reflections	3121 [<i>R</i> _{int} = 0.0762, <i>R</i> _{sigma} = 0.0560]
Data / restraints / parameters	3121 / 0 / 218
Goodness-of-fit on <i>F</i> ²	1.041
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0466, <i>wR</i> ₂ = 0.0961
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0866, <i>wR</i> ₂ = 0.1157
Largest diff. peak / hole	0.20 / -0.21 e·Å ⁻³

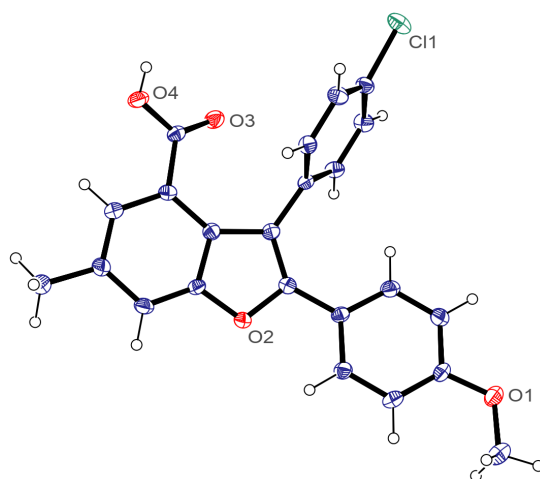


Figure S3. ORTEP drawing of **3ap'** (CCDC 2086130) with 35% probability ellipsoids.

Table S4. Crystal Parameters and Refinement Metrics of 3ap'

Sample code	zly3_OY819-P1
Empirical formula	C ₂₃ H ₁₇ ClO ₄
Formula weight	392.82
Temperature	170 K
Crystal system	monoclinic
Space group	<i>P</i> ₂ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i>	11.9608(17) Å, 5.8335(7) Å, 26.640(3) Å
<i>α</i> , <i>β</i> , <i>γ</i>	90°, 90.150(8)°, 90°
Volume	1858.7(4) Å ³
<i>Z</i>	4
Density (calcd)	1.404 g·cm ⁻³
Absorption coefficient	0.233 mm ⁻¹
<i>F</i> (000)	816.0
Crystal size	0.15 × 0.08 × 0.05 mm ³
Radiation	MoKα (<i>λ</i> = 0.71073 Å)
2 <i>θ</i> range for data collection	4.572° to 53.054°
Index ranges	-14 ≤ <i>h</i> ≤ 14, -7 ≤ <i>k</i> ≤ 7, -33 ≤ <i>l</i> ≤ 33
Reflections collected	16062
Independent reflections	3806 [<i>R</i> _{int} = 0.0945, <i>R</i> _{sigma} = 0.0892]
Data / restraints / parameters	3806 / 0 / 256
Goodness-of-fit on <i>F</i> ²	1.063
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0560, <i>wR</i> ₂ = 0.1029
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1190, <i>wR</i> ₂ = 0.1285
Largest diff. peak / hole	0.26 / -0.28 e·Å ⁻³

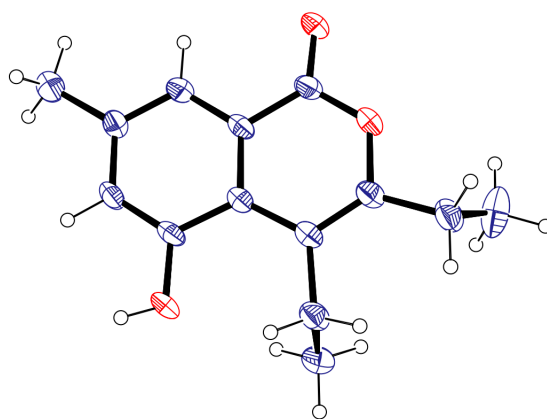


Figure S4. ORTEP drawing of **4aq** (CCDC 2086131) with 35% probability ellipsoids.

Table S5. Crystal Parameters and Refinement Metrics of 4aq

Sample code	zly4_OY811
Empirical formula	C ₁₄ H ₁₆ O ₃
Formula weight	232.27
Temperature	170 K
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i>	4.627(2) Å, 7.831(3) Å, 17.418(6) Å
α , β , γ	79.477(11)°, 87.815(12)°, 77.297(12)°
Volume	605.3(4) Å ³
<i>Z</i>	2
Density (calcd)	1.274 g·cm ⁻³
Absorption coefficient	0.089 mm ⁻¹
<i>F</i> (000)	248.0
Crystal size	0.12 × 0.08 × 0.05 mm ³
Radiation	MoK α (λ = 0.71073 Å)
2 θ range for data collection	5.42° to 50.214°
Index ranges	-5 ≤ <i>h</i> ≤ 5, -9 ≤ <i>k</i> ≤ 9, -20 ≤ <i>l</i> ≤ 20
Reflections collected	5990
Independent reflections	2141 [<i>R</i> _{int} = 0.0628, <i>R</i> _{sigma} = 0.0714]
Data / restraints / parameters	2141 / 0 / 158
Goodness-of-fit on <i>F</i> ²	1.034
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0717, <i>wR</i> ₂ = 0.1867
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1116, <i>wR</i> ₂ = 0.2182
Largest diff. peak / hole	0.23 / -0.27 e ⁻ ·Å ⁻³

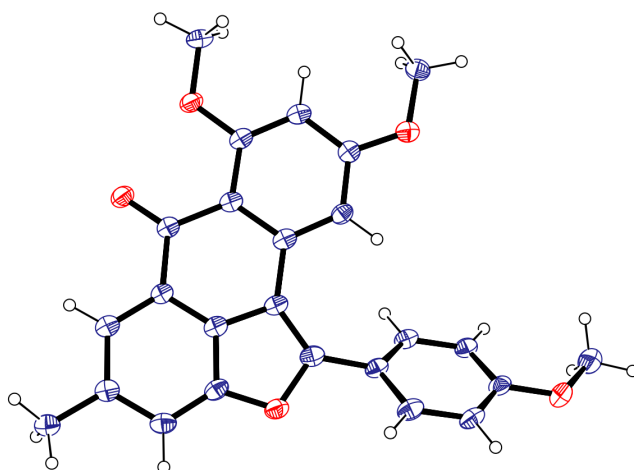


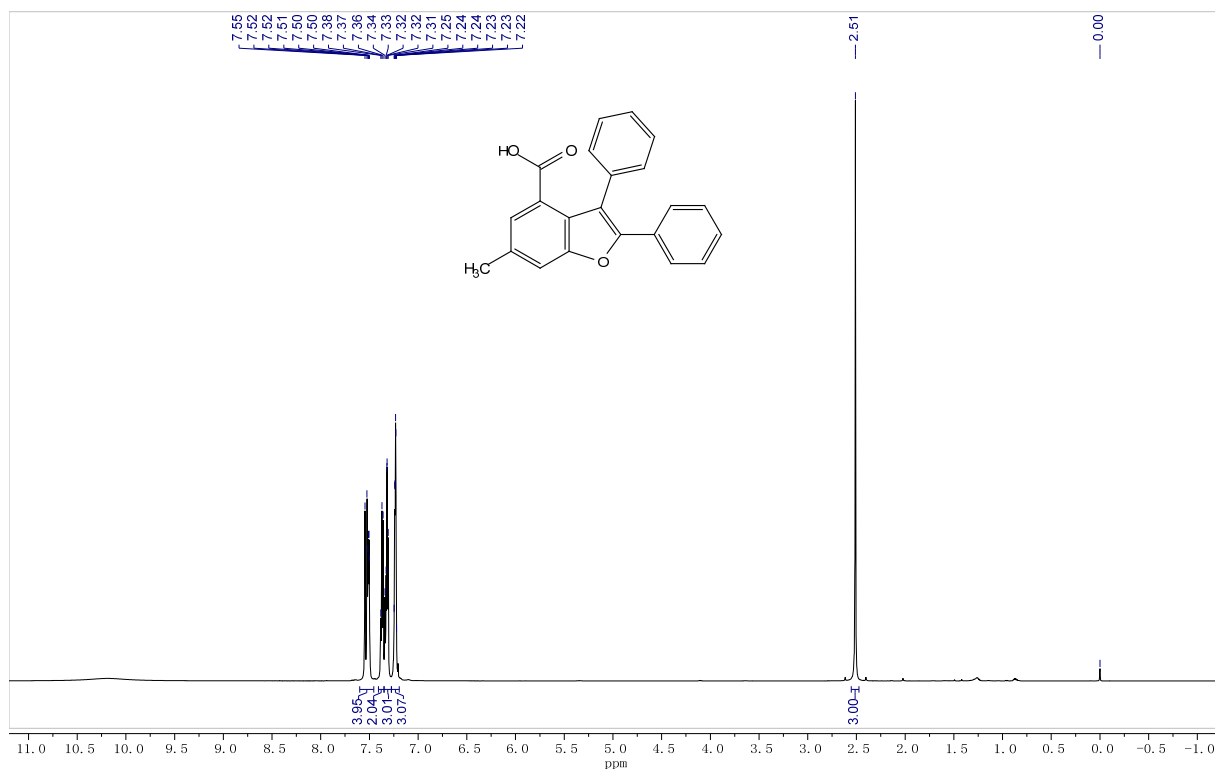
Figure S5. ORTEP drawing of **6ar** (CCDC 2086132) with 35% probability ellipsoids.

Table S6. Crystal Parameters and Refinement Metrics of 6ar

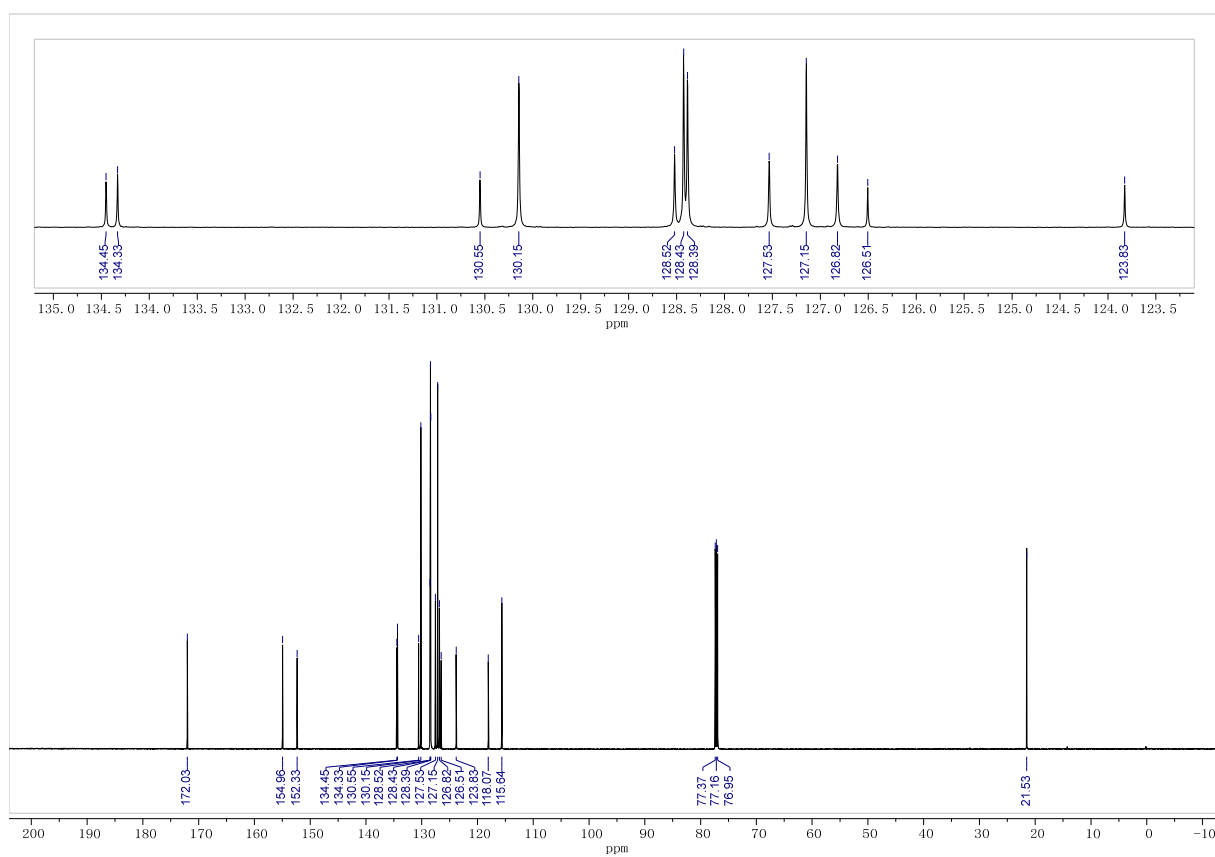
Sample code	zly5_OY742
Empirical formula	C ₂₅ H ₂₀ O ₅
Formula weight	400.41
Temperature	170 K
Crystal system	monoclinic
Space group	<i>P2₁/c</i>
<i>a</i> , <i>b</i> , <i>c</i>	10.1604(17) Å, 26.865(4) Å, 7.3080(11) Å
<i>α</i> , <i>β</i> , <i>γ</i>	90°, 108.982(5)°, 90°
Volume	1886.3(5) Å ³
<i>Z</i>	4
Density (calcd)	1.410 g·cm ⁻³
Absorption coefficient	0.098 mm ⁻¹
<i>F</i> (000)	840.0
Crystal size	0.15 × 0.08 × 0.03 mm ³
Radiation	MoKα (<i>λ</i> = 0.71073 Å)
2 <i>θ</i> range for data collection	4.24° to 52.746°
Index ranges	-12 ≤ <i>h</i> ≤ 12, -33 ≤ <i>k</i> ≤ 33, -9 ≤ <i>l</i> ≤ 8
Reflections collected	18045
Independent reflections	3807 [<i>R</i> _{int} = 0.0868, <i>R</i> _{sigma} = 0.0696]
Data / restraints / parameters	3807 / 0 / 275
Goodness-of-fit on <i>F</i> ²	1.072
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0651, <i>wR</i> ₂ = 0.1499
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1045, <i>wR</i> ₂ = 0.1729
Largest diff. peak / hole	0.21 / -0.26 e ⁻ ·Å ⁻³

3. Copies of NMR Spectra

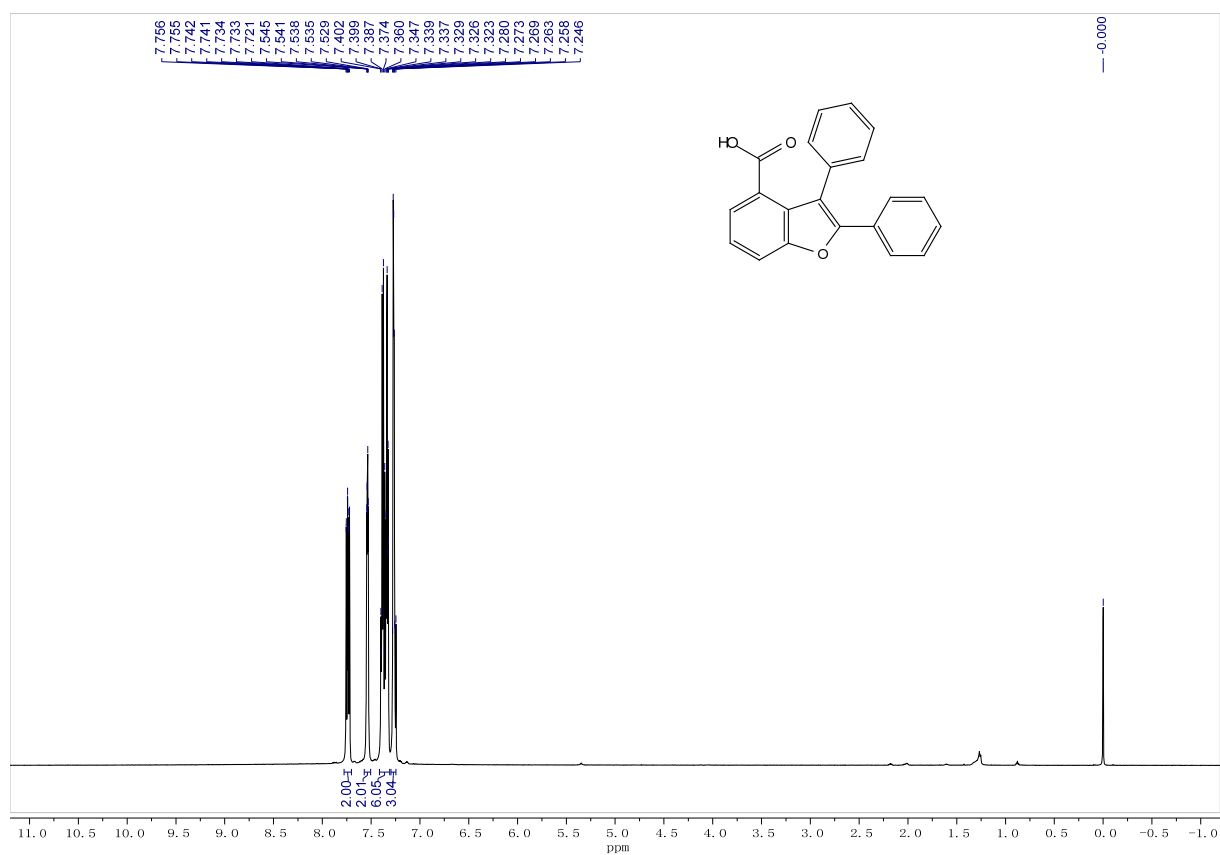
^1H NMR spectrum of **3aa** (600 MHz, CDCl_3)



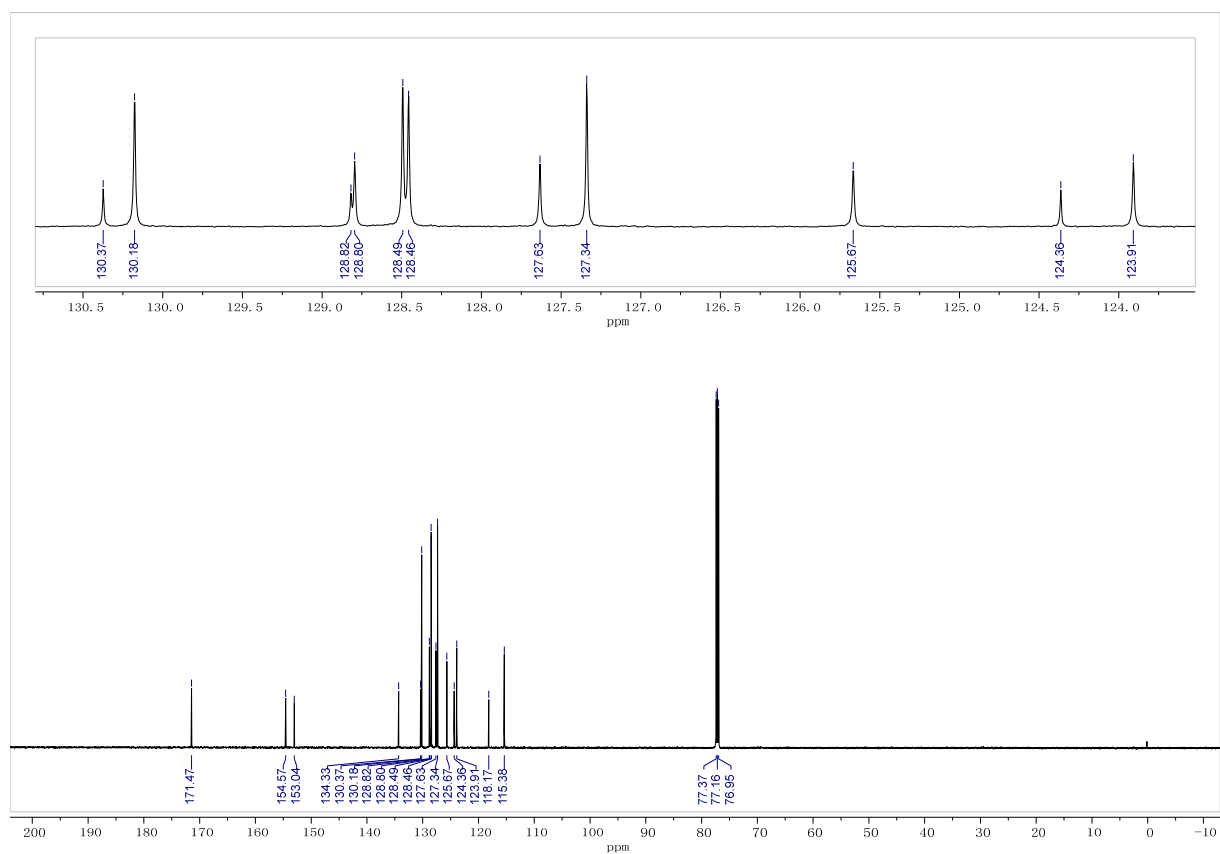
^{13}C NMR spectrum of **3aa** (151 MHz, CDCl_3)



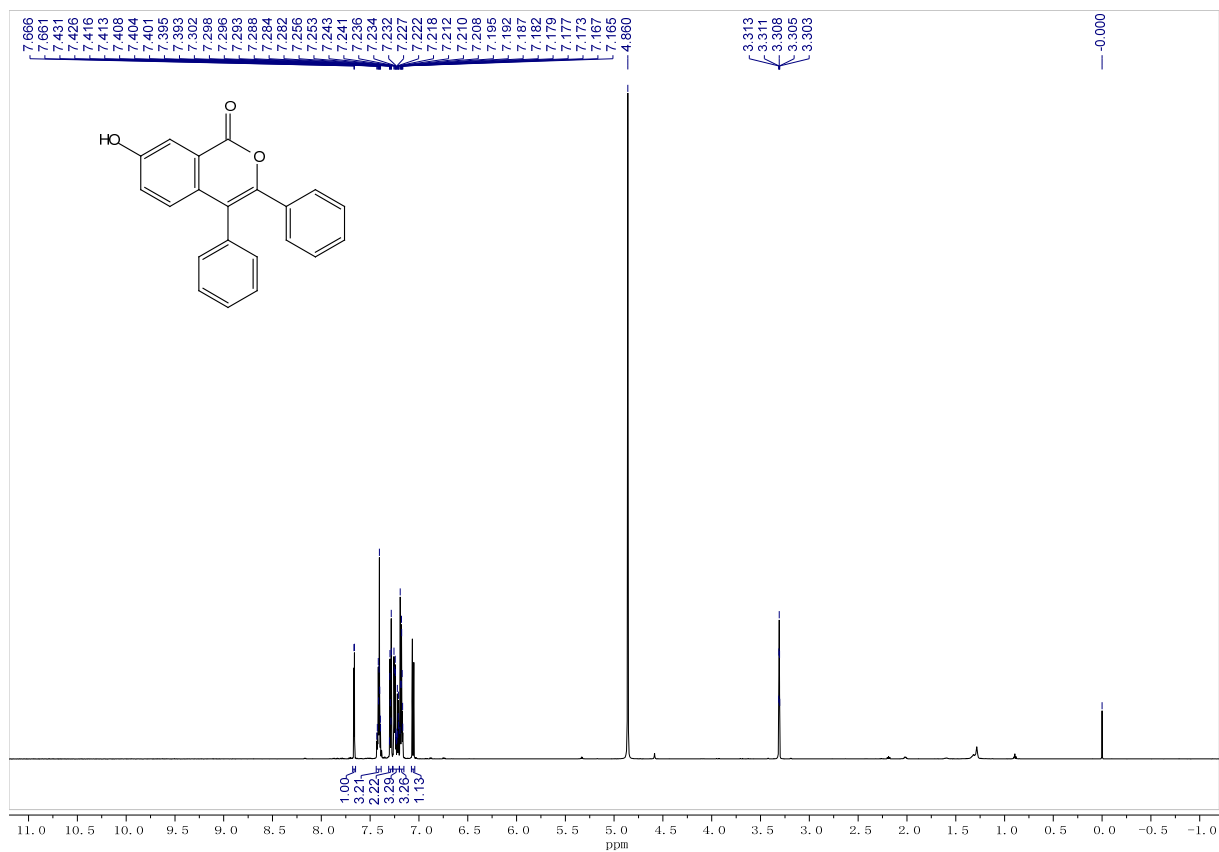
¹H NMR spectrum of **3ba** (600 MHz, CDCl₃)



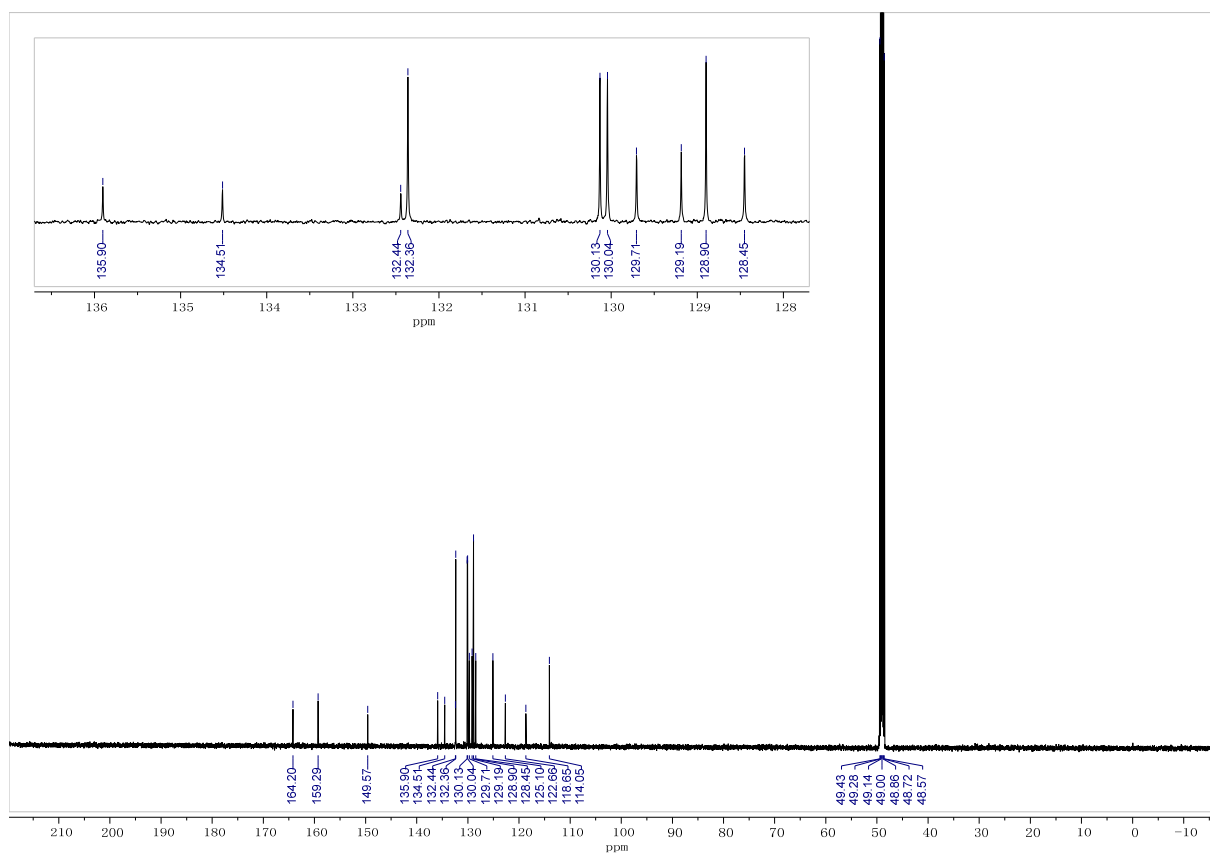
¹³C NMR spectrum of **3ba** (151 MHz, CDCl₃)



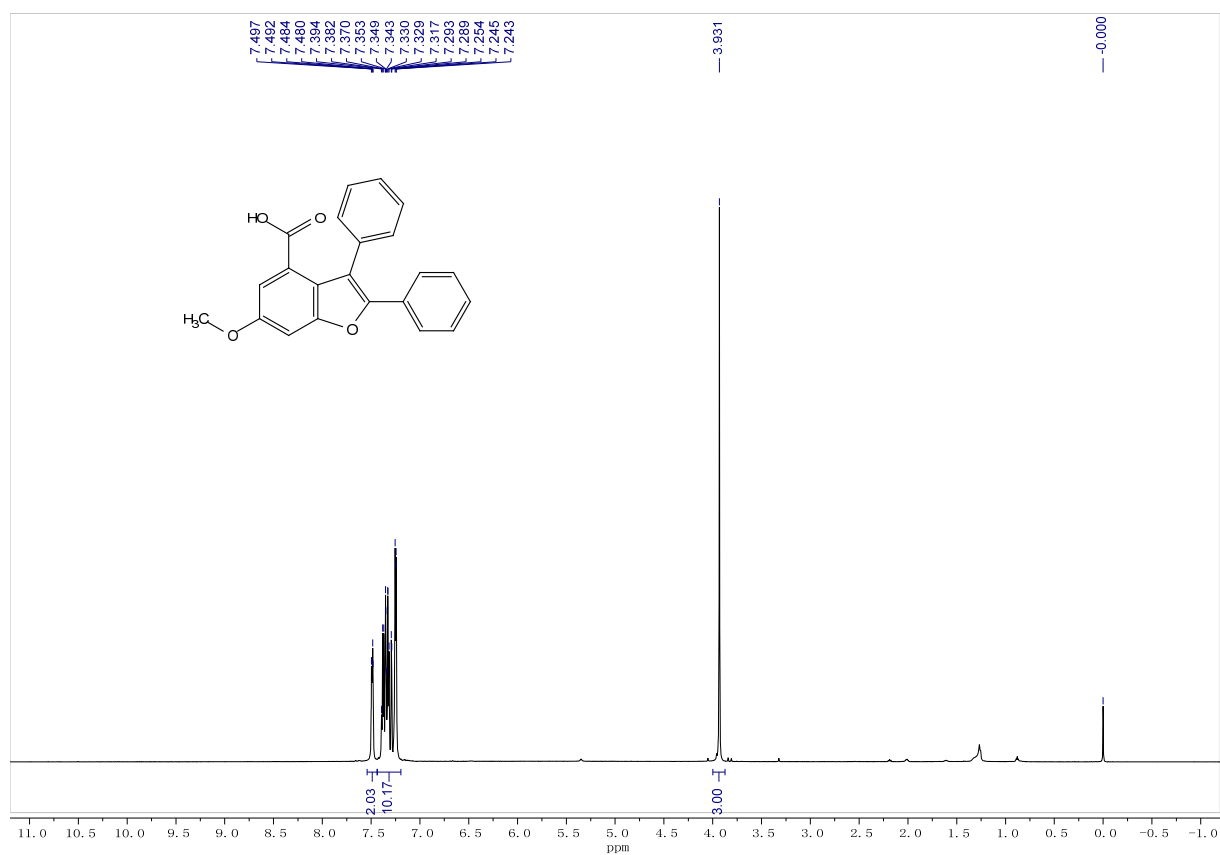
¹H NMR spectrum of **4ba** (600 MHz, CD₃OD)



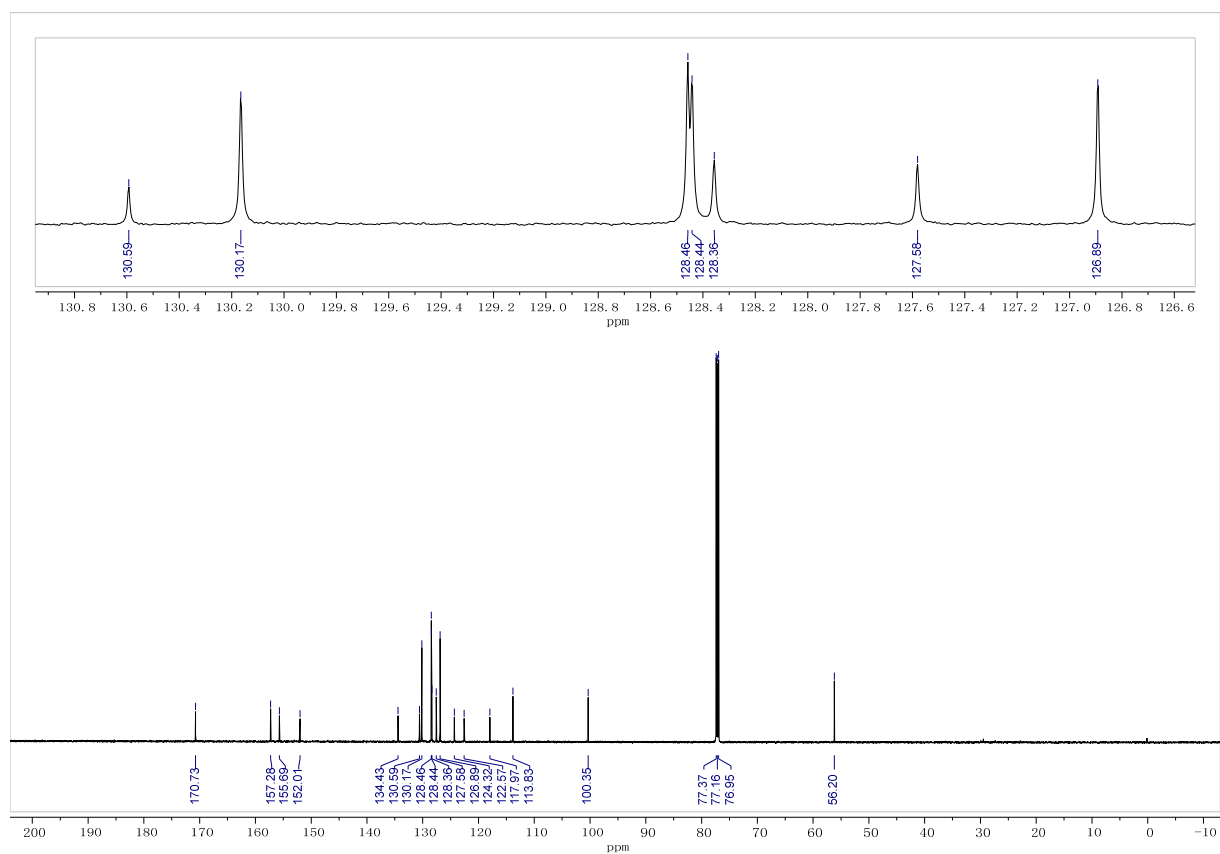
¹³C NMR spectrum of **4ba** (151 MHz, CD₃OD)



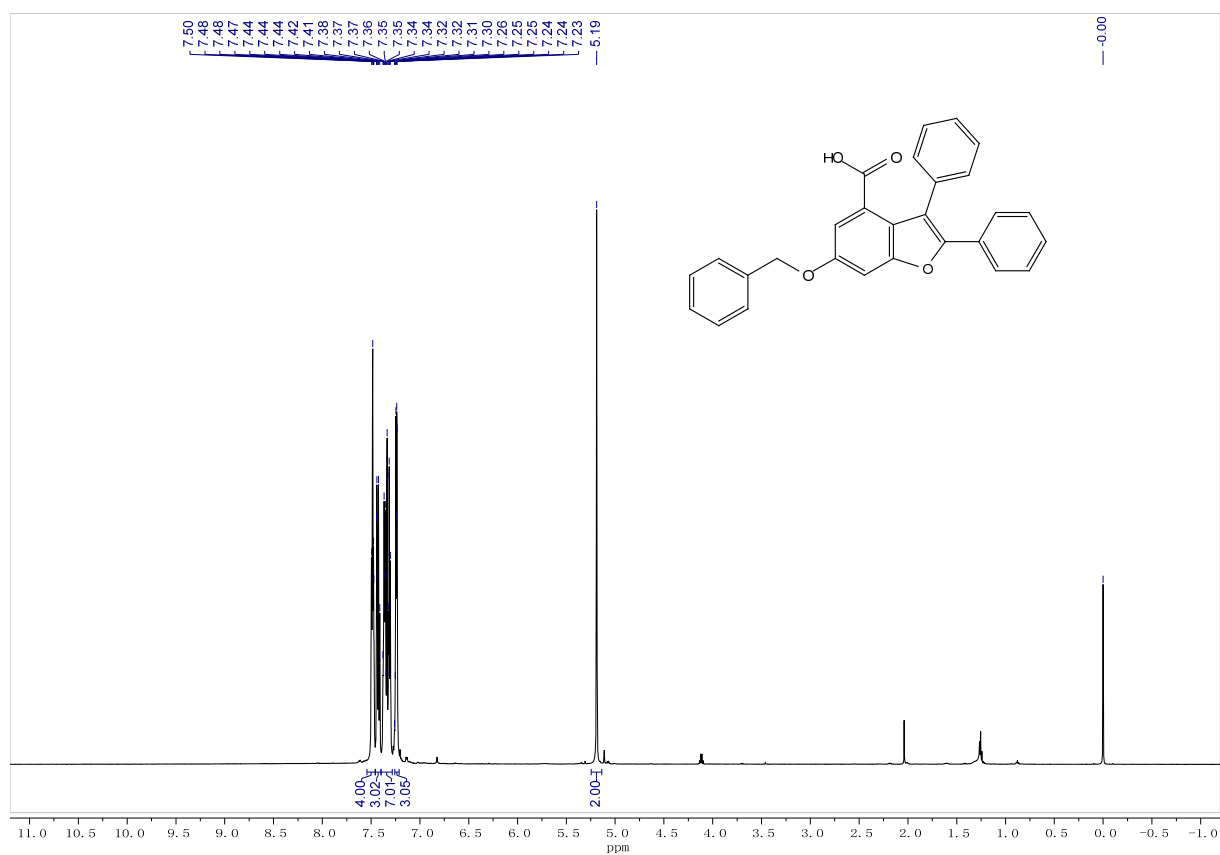
¹H NMR spectrum of **3ca** (600 MHz, CDCl₃)



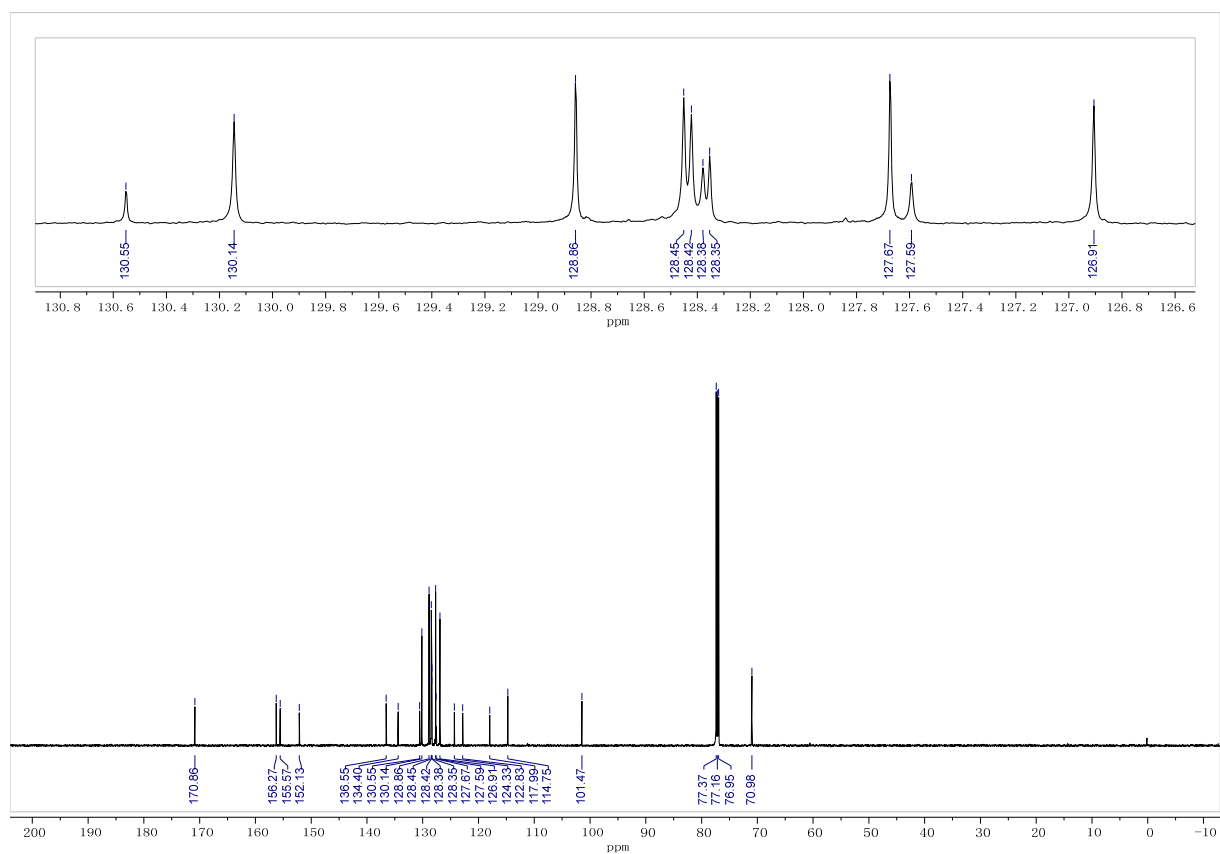
¹³C NMR spectrum of **3ca** (151 MHz, CDCl₃)



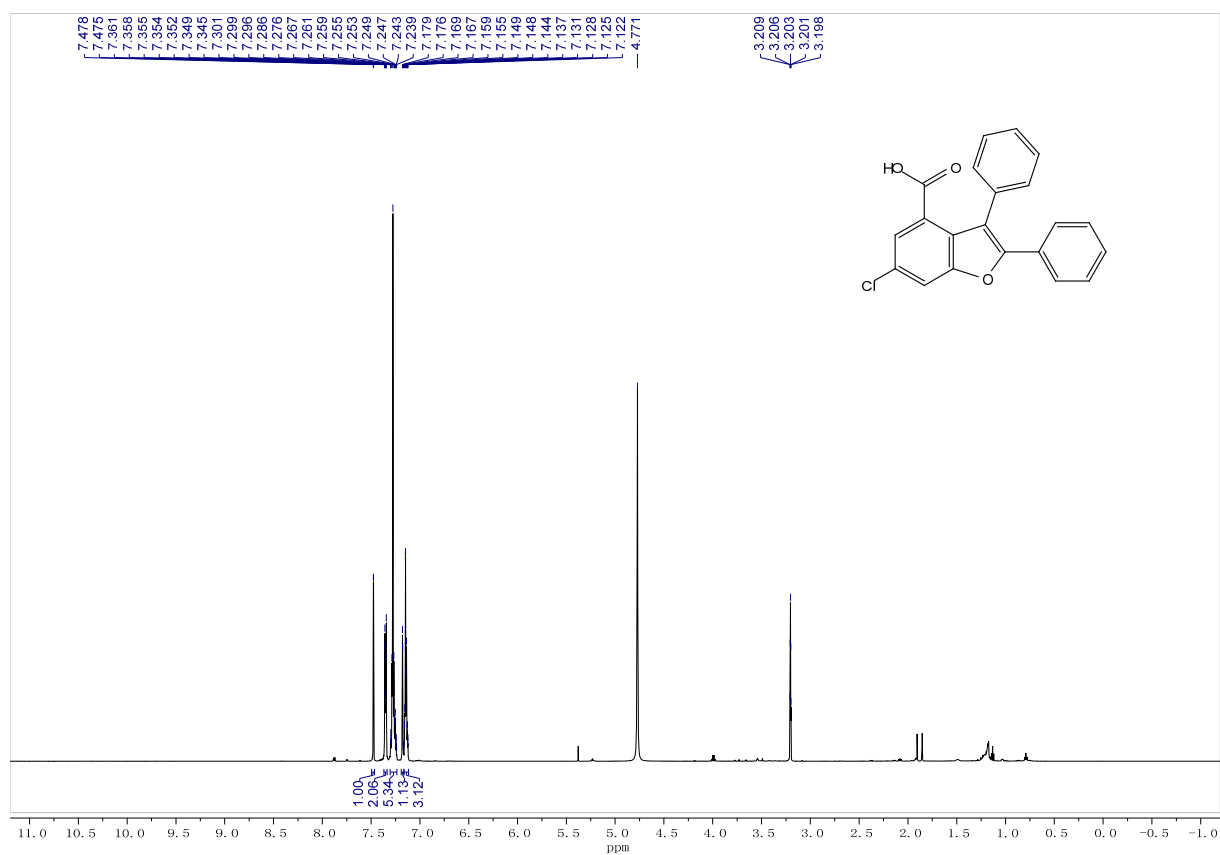
¹H NMR spectrum of **3da** (600 MHz, CDCl₃)



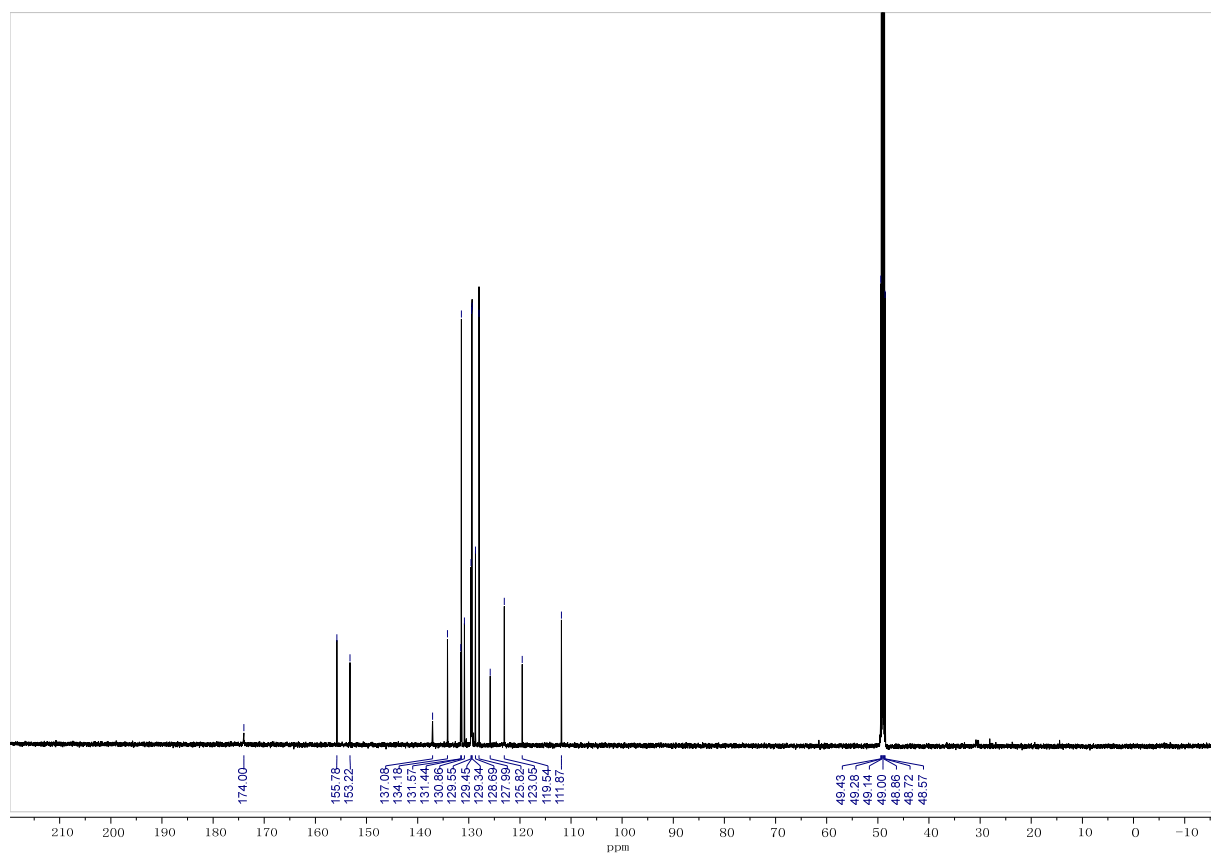
¹³C NMR spectrum of **3da** (151 MHz, CDCl₃)



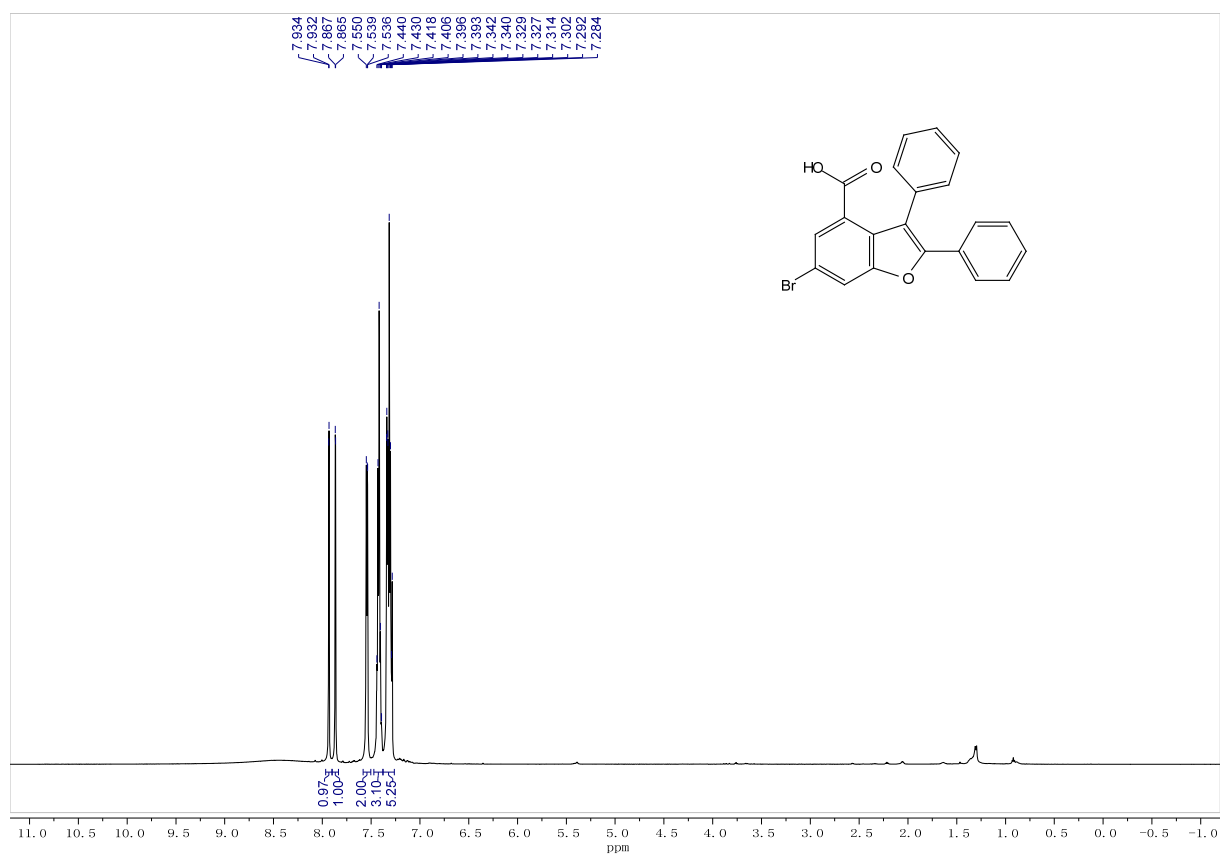
¹H NMR spectrum of **3ea** (600 MHz, CD₃OD)



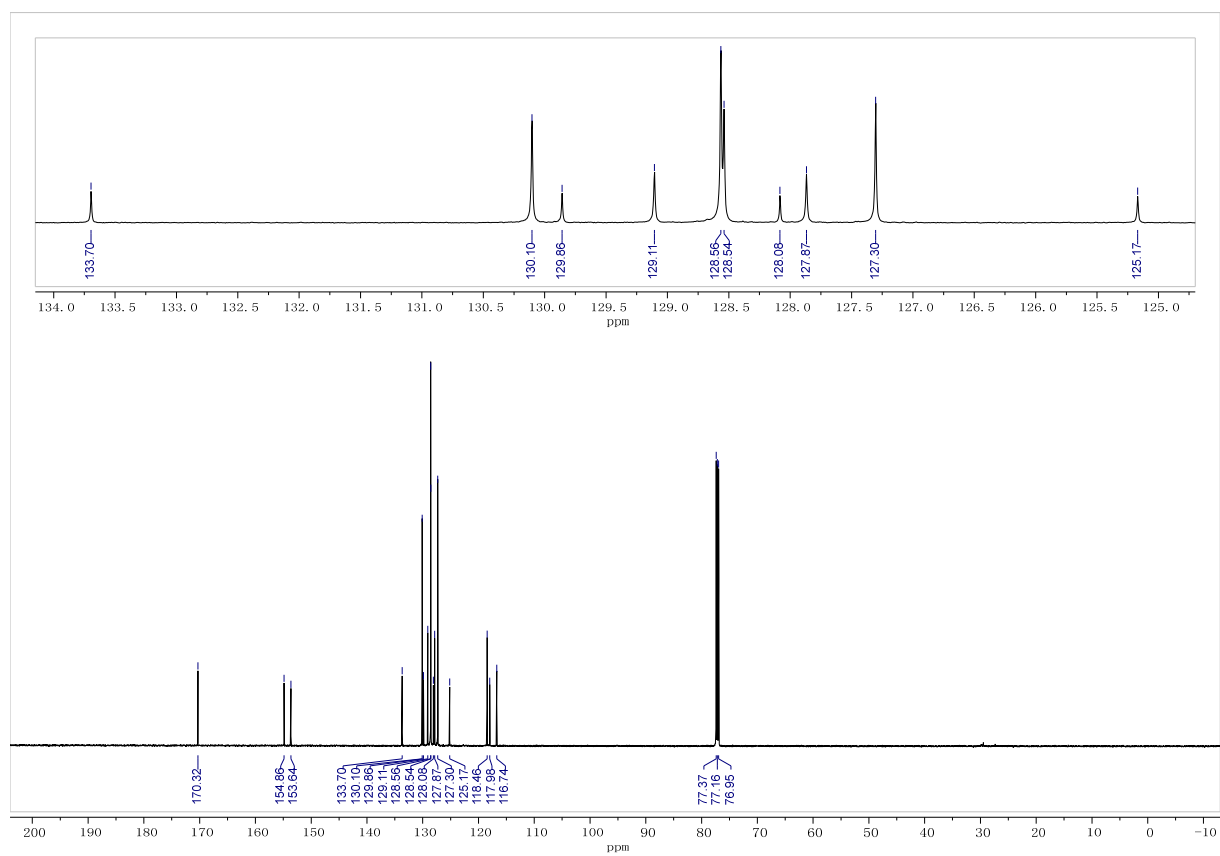
¹³C NMR spectrum of **3ea** (151 MHz, CD₃OD)



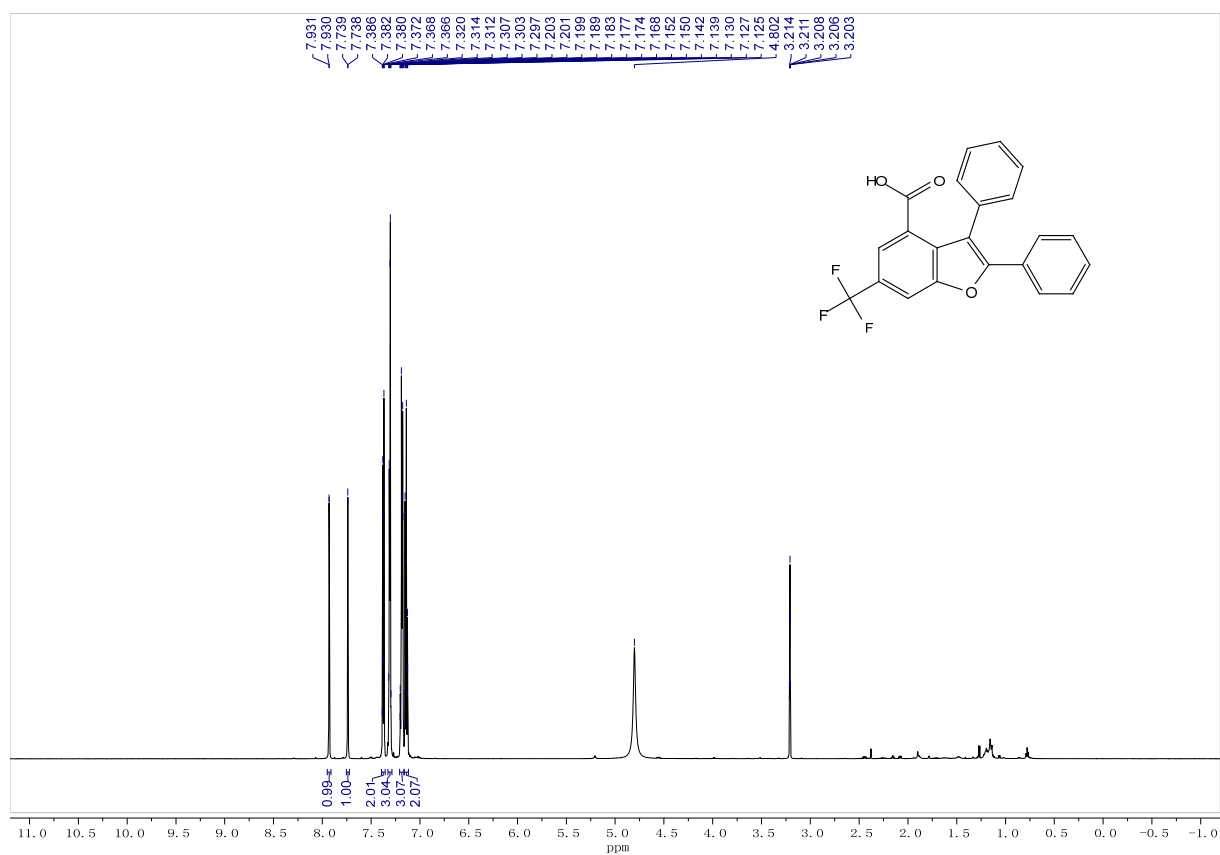
¹H NMR spectrum of **3fa** (600 MHz, CDCl₃)



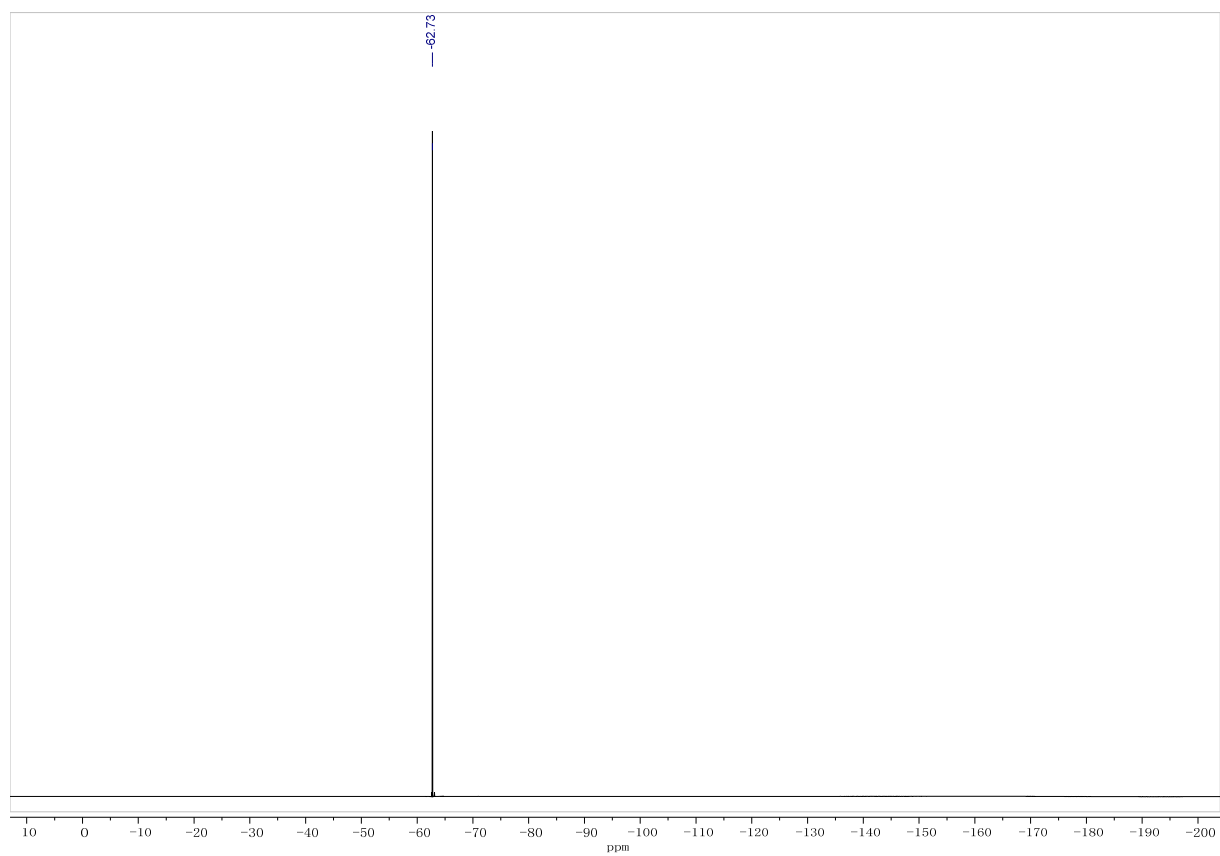
¹³C NMR spectrum of **3fa** (151 MHz, CDCl₃)



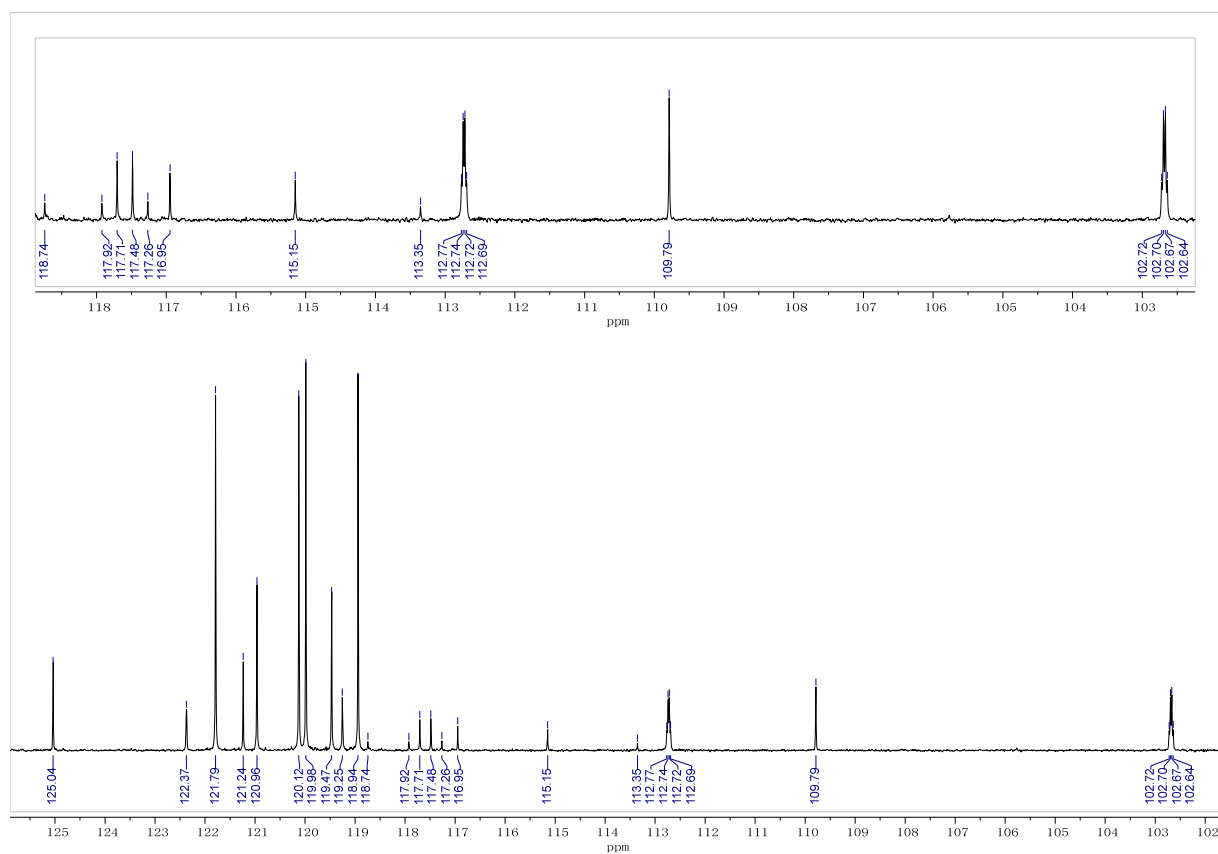
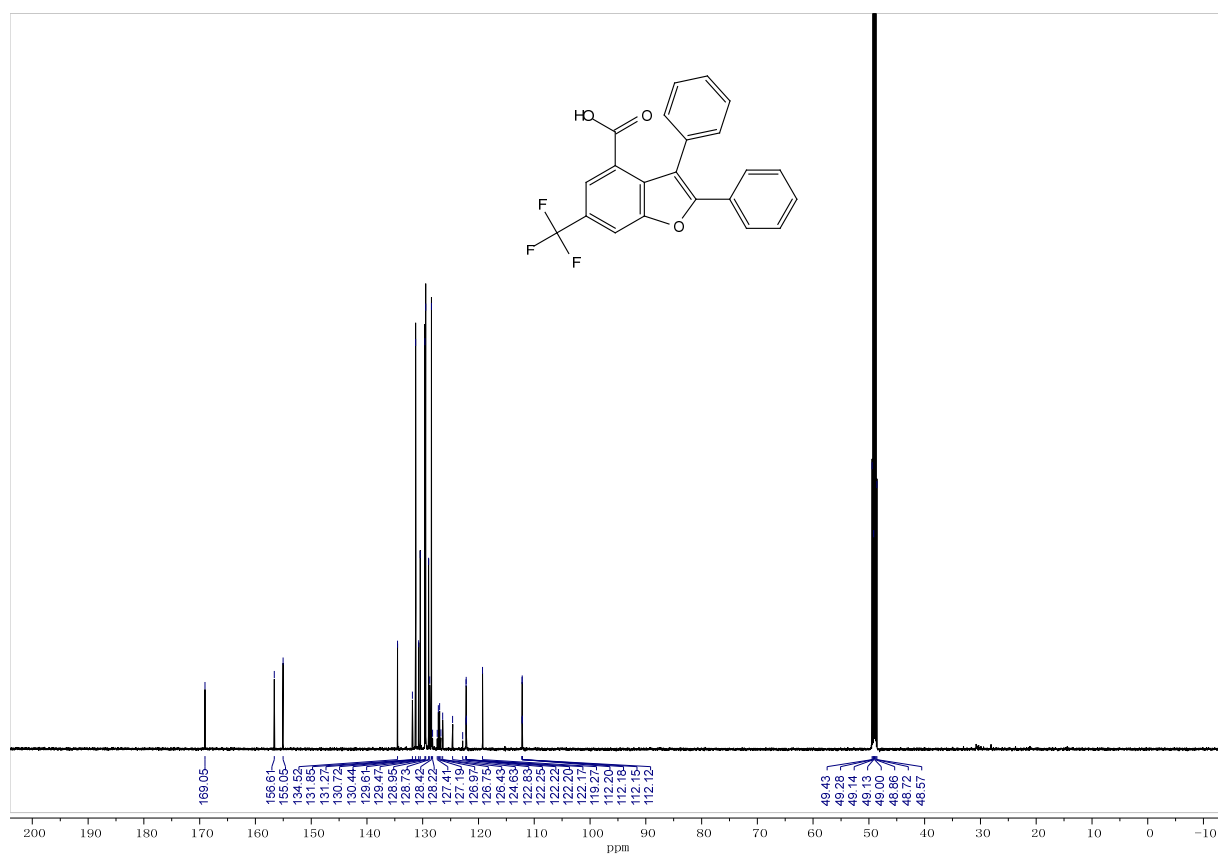
¹H NMR spectrum of **3ga** (600 MHz, CD₃OD)



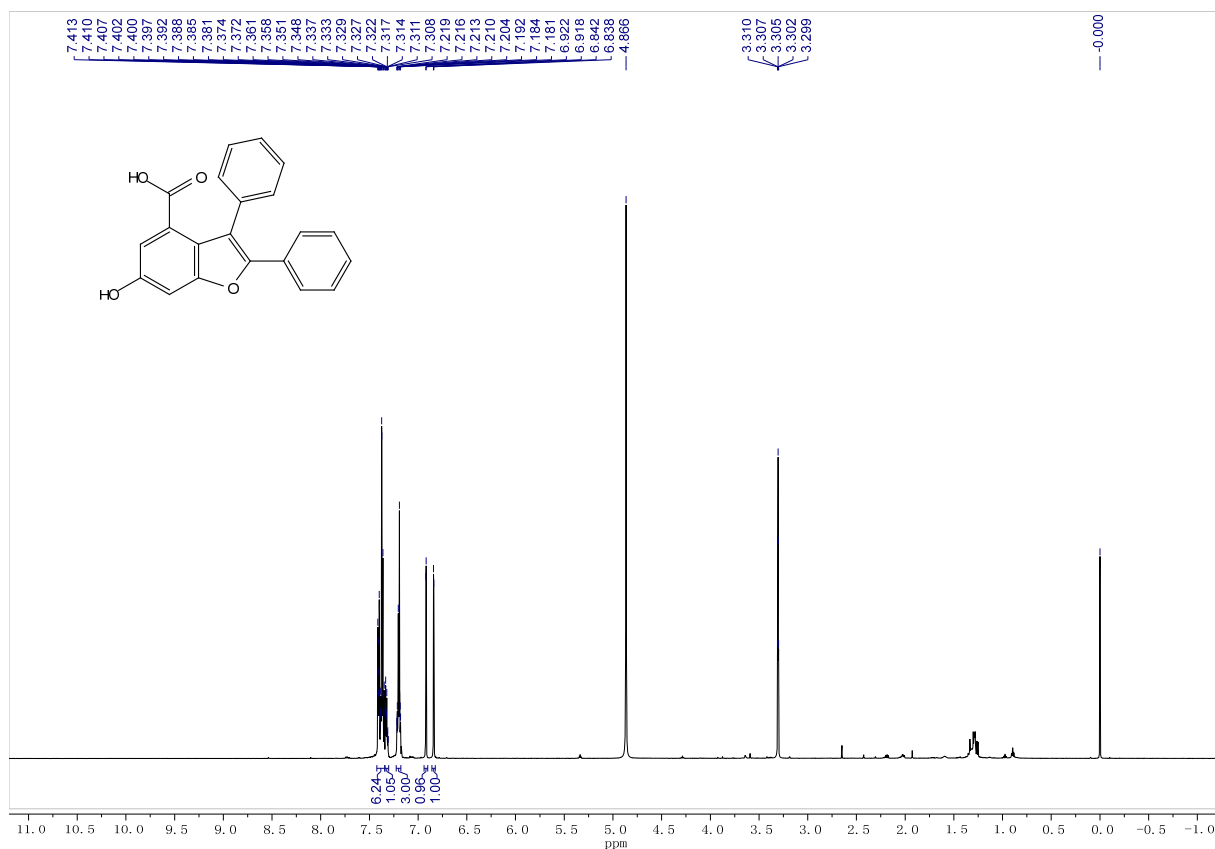
¹⁹F NMR spectrum of **3ga** (565 MHz, CD₃OD)



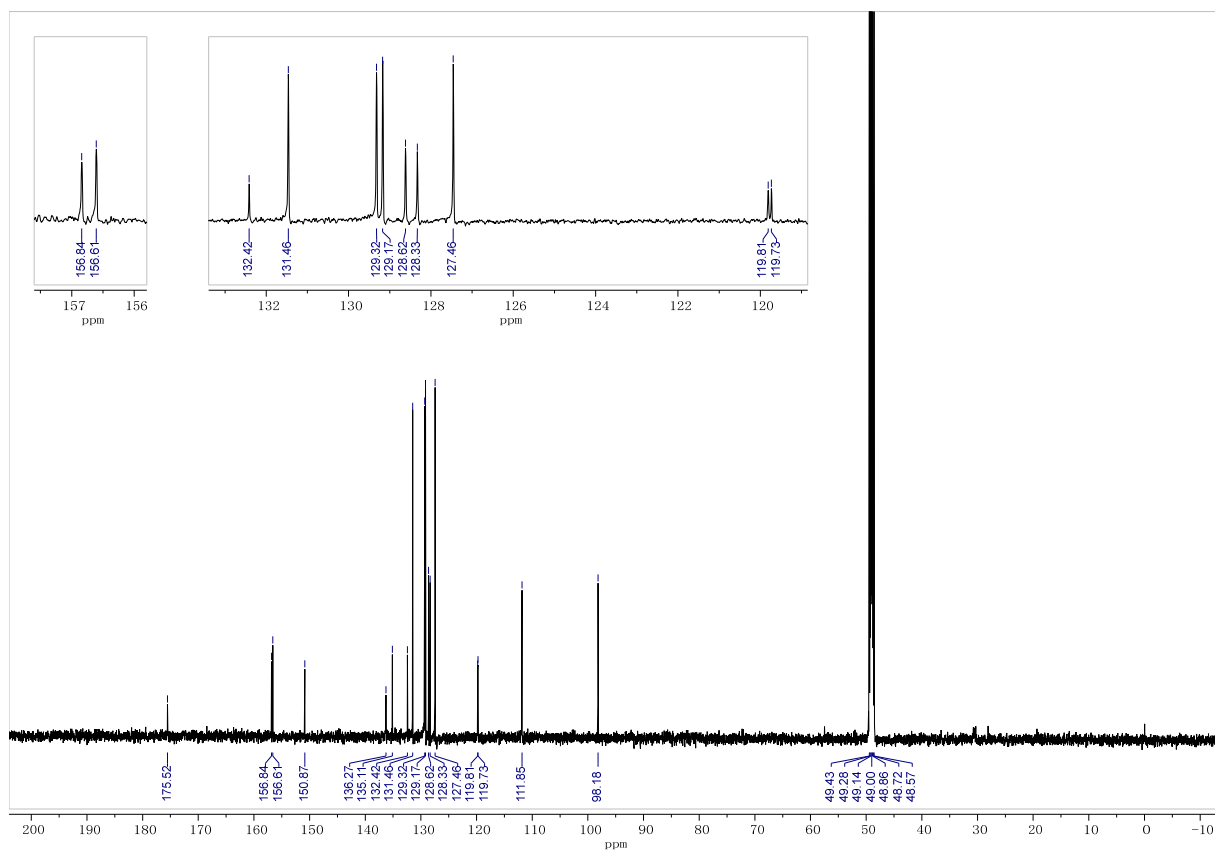
^{13}C NMR spectrum of **3ga** (151 MHz, CD_3OD)



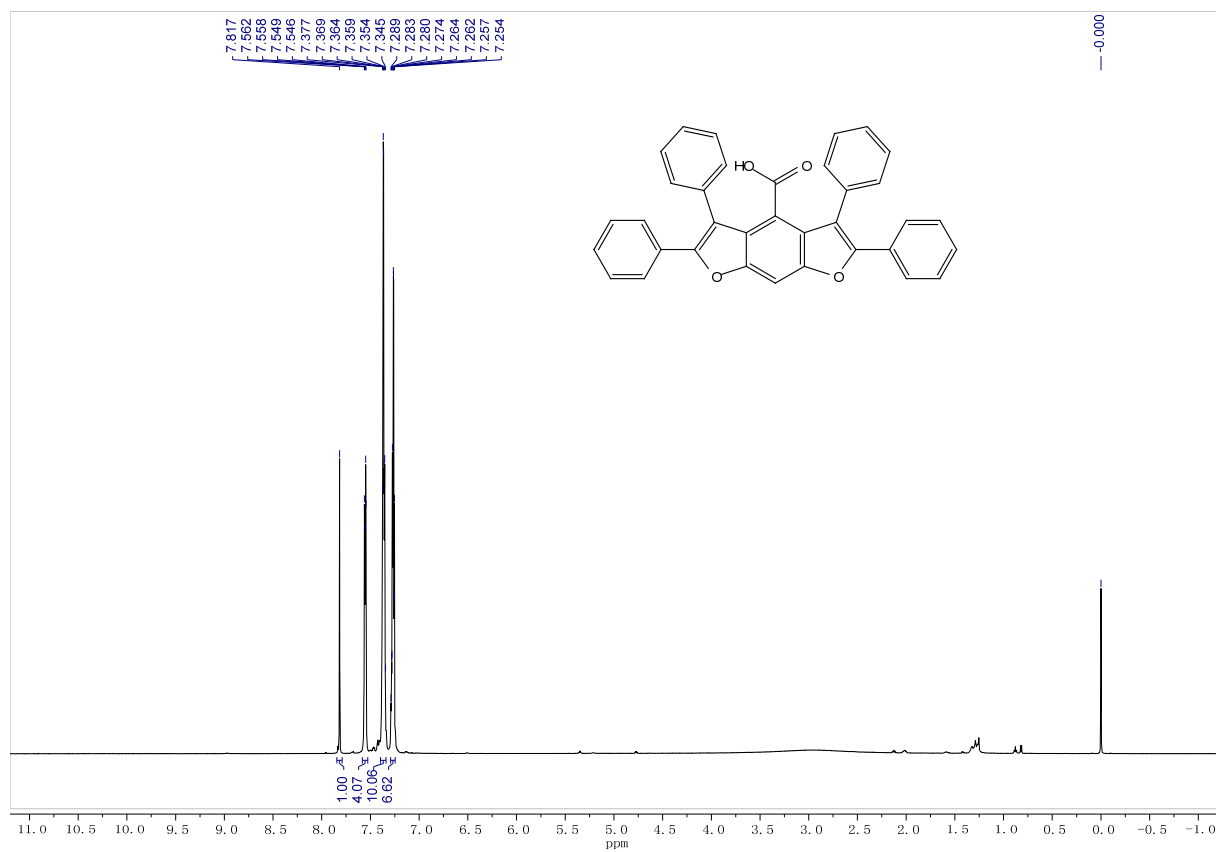
¹H NMR spectrum of **3ha** (600 MHz, CD₃OD)



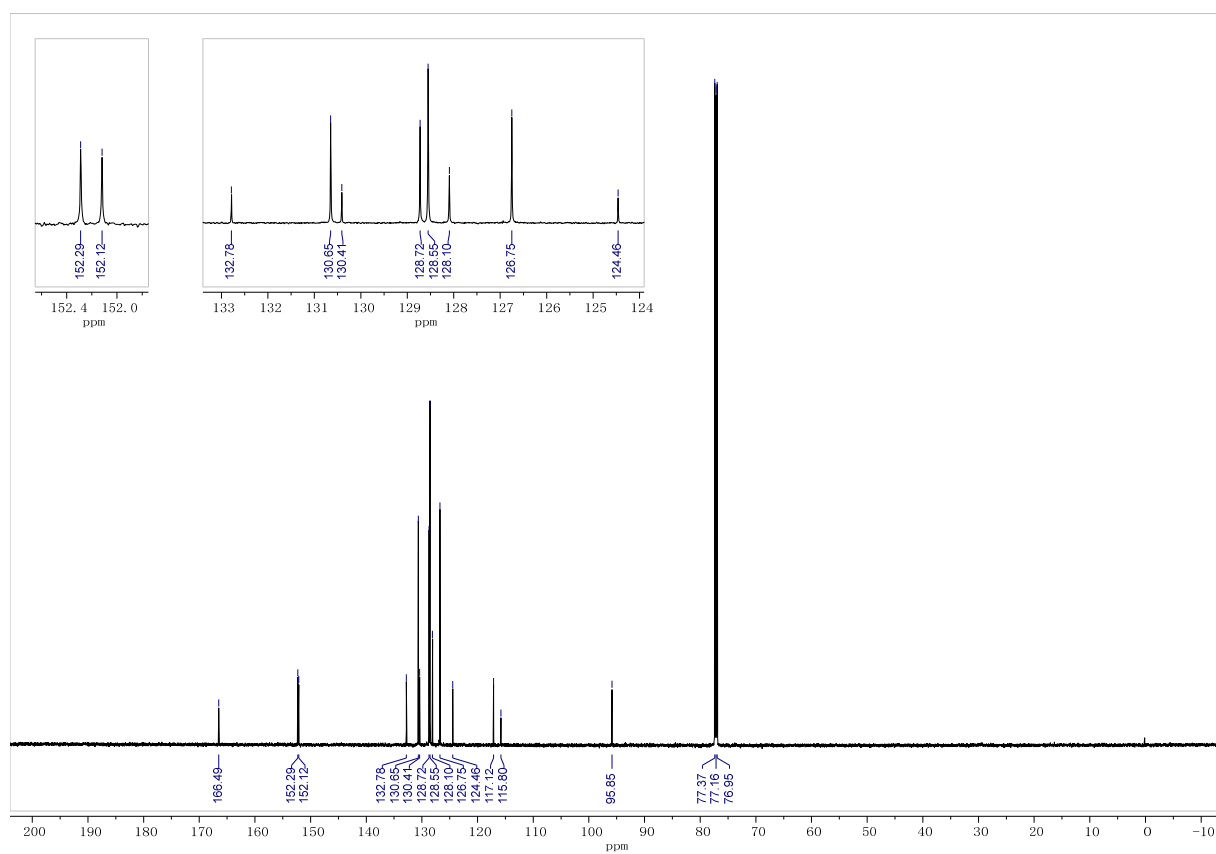
¹³C NMR spectrum of **3ha** (151 MHz, CD₃OD)



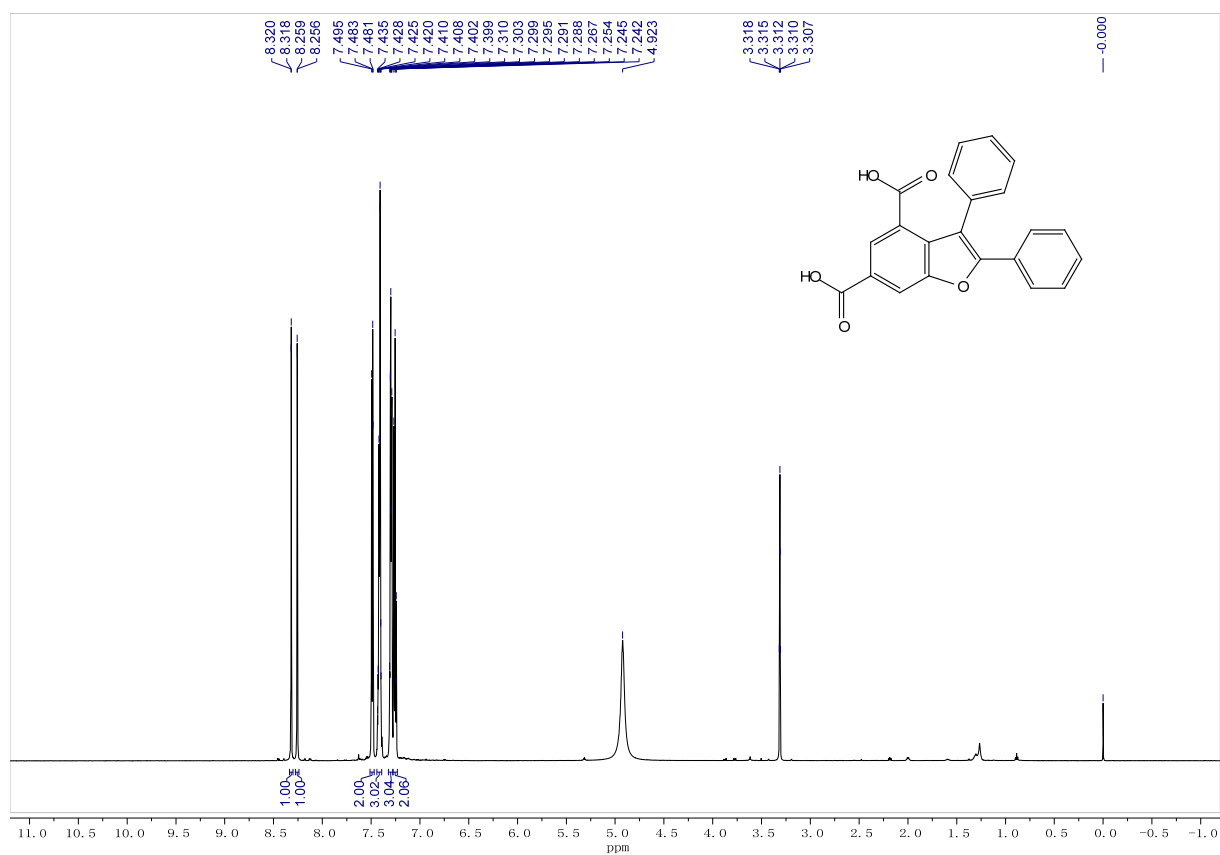
¹H NMR spectrum of **5haa** (600 MHz, CDCl₃)



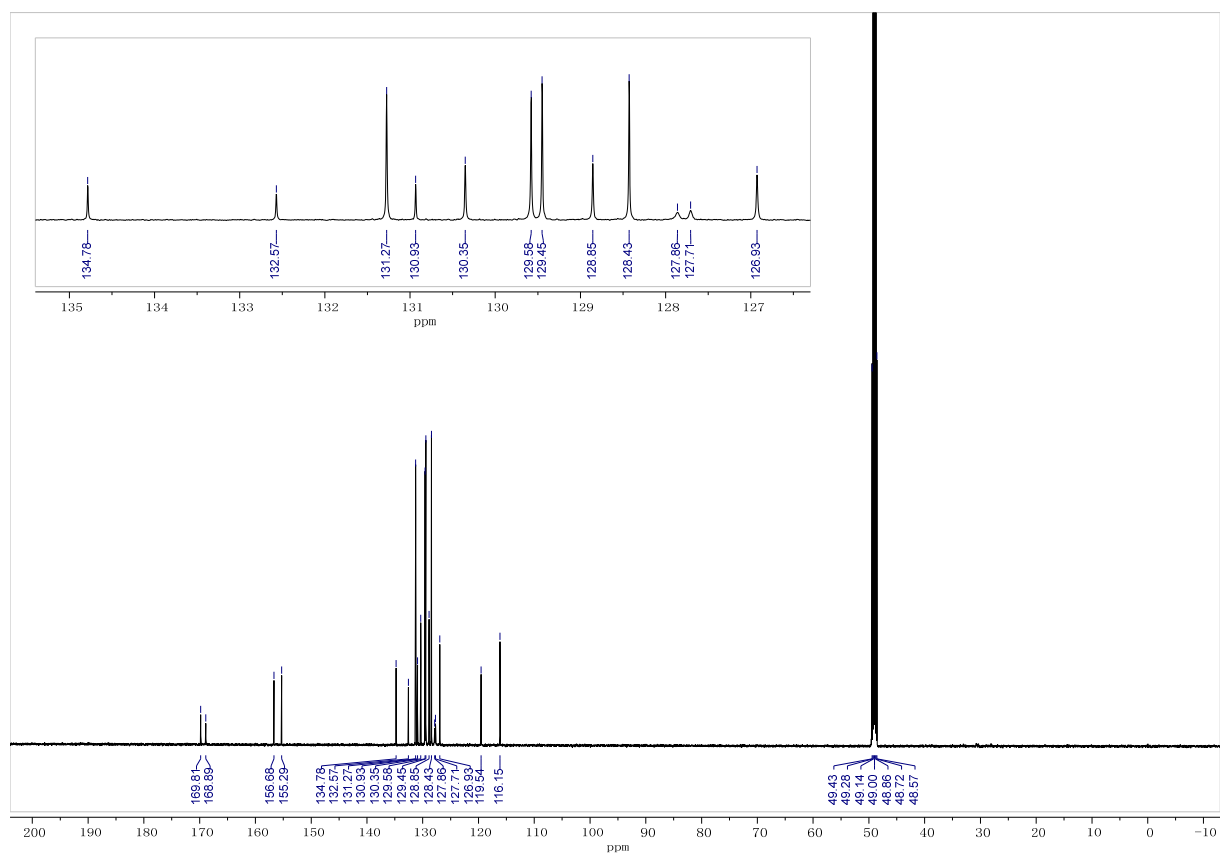
¹³C NMR spectrum of **5haa** (151 MHz, CDCl₃)



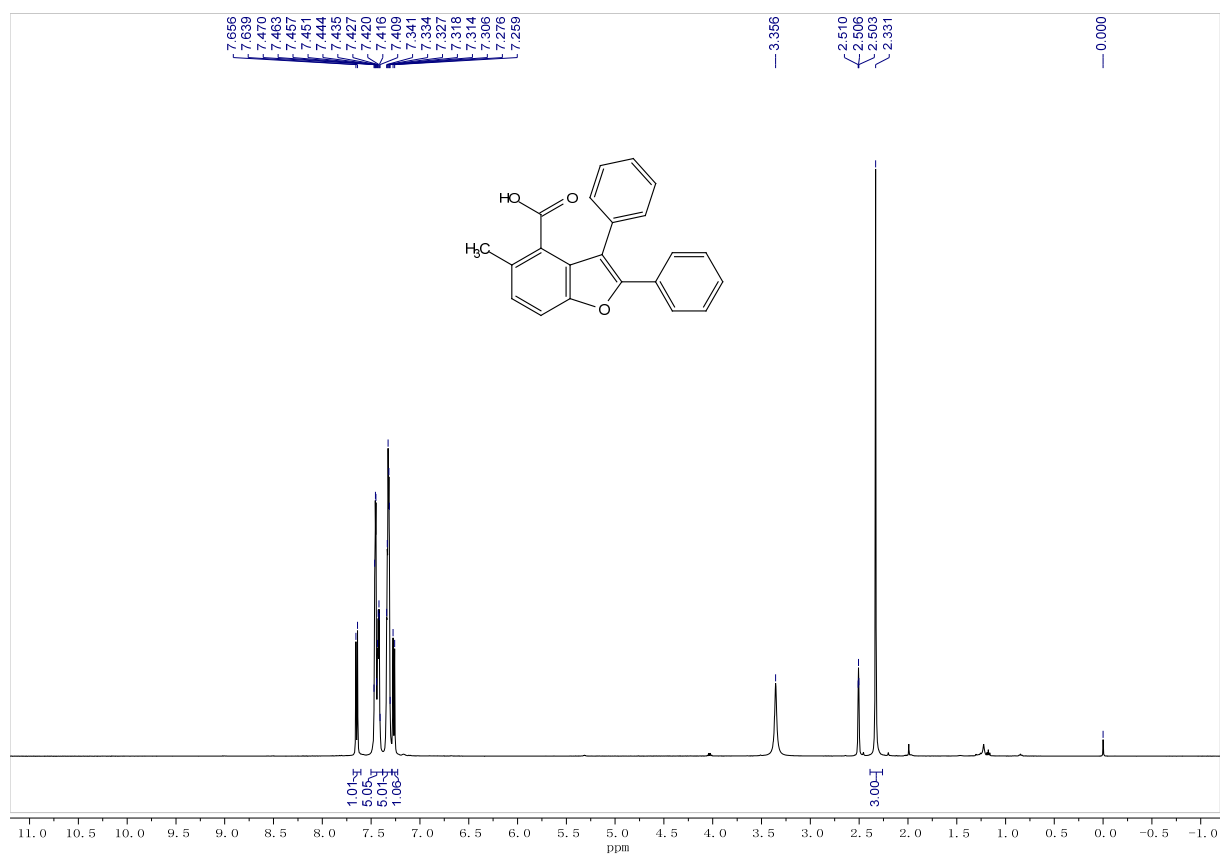
¹H NMR spectrum of **3ia** (600 MHz, CD₃OD)



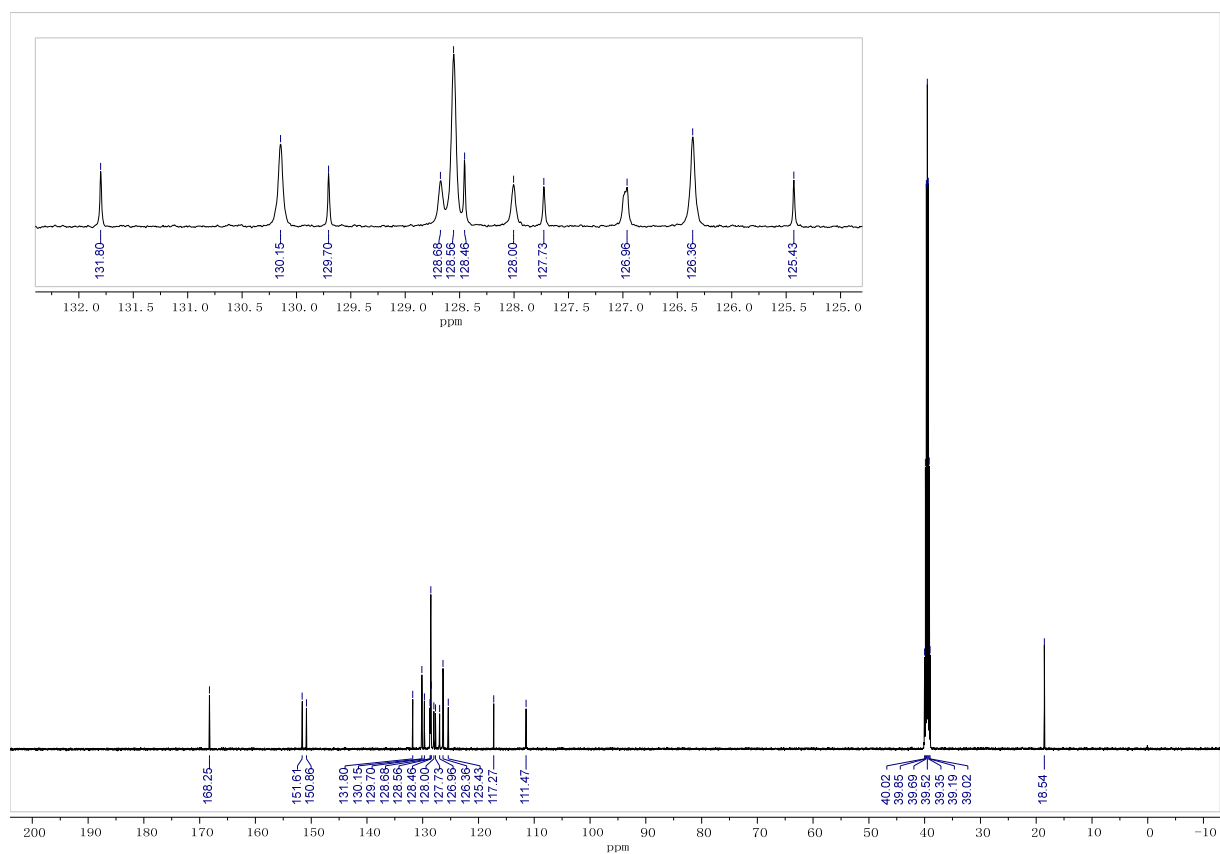
¹³C NMR spectrum of **3ia** (151 MHz, CD₃OD)



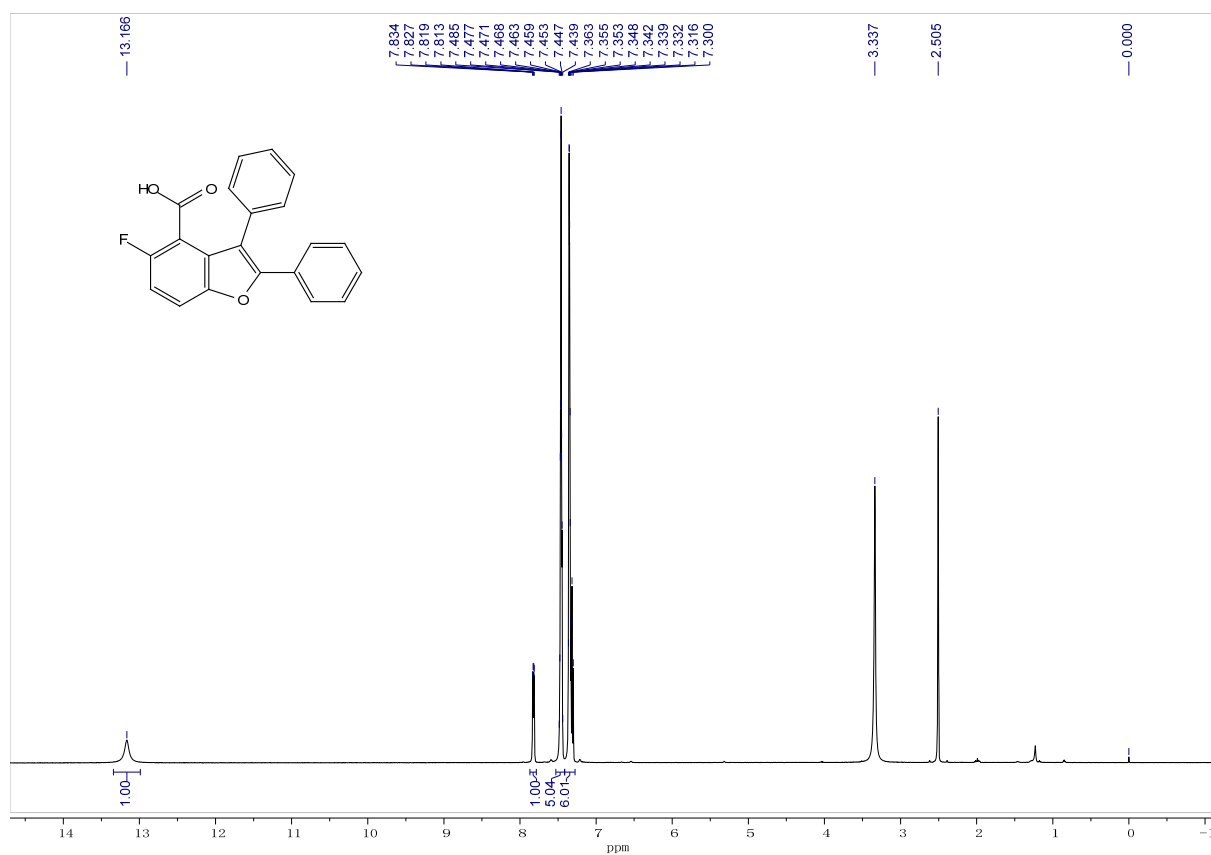
¹H NMR spectrum of **3ja** (500 MHz, DMSO-*d*₆)



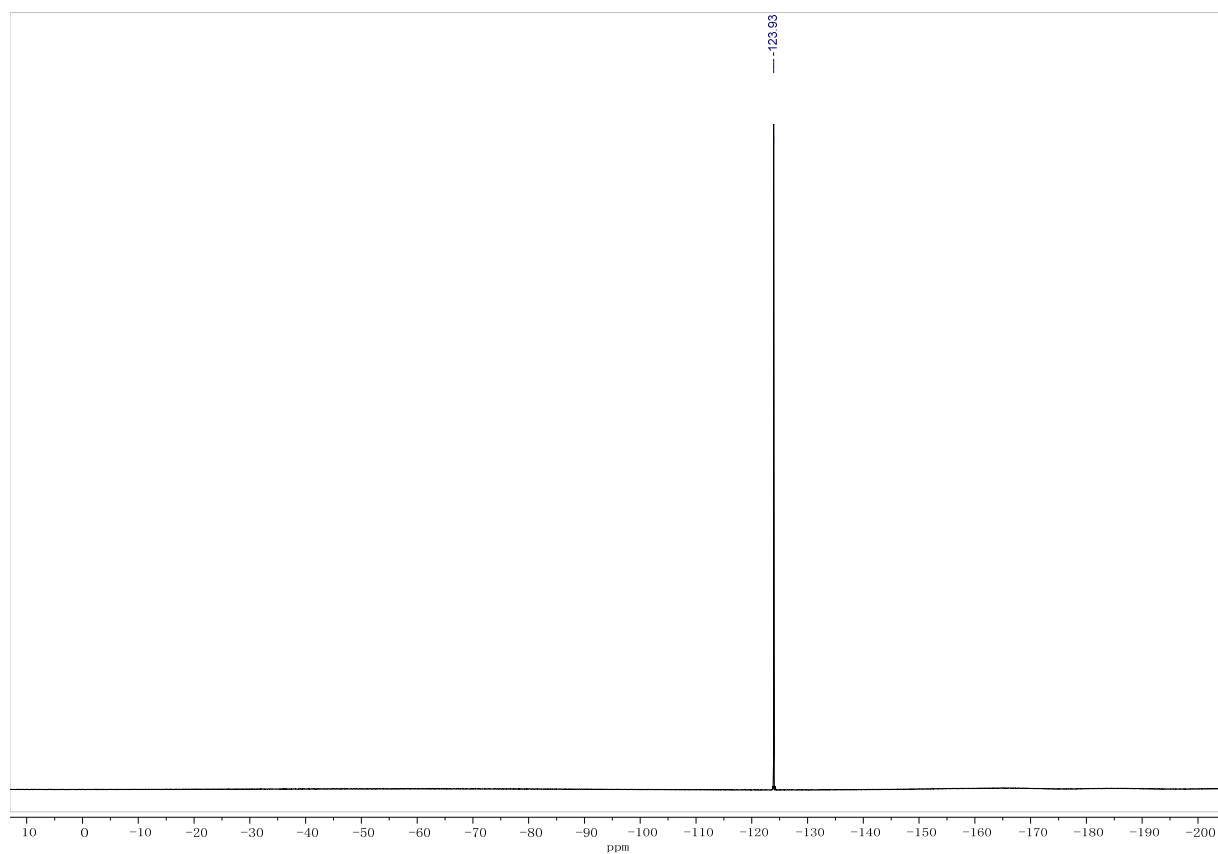
¹³C NMR spectrum of **3ja** (126 MHz, DMSO-*d*₆)



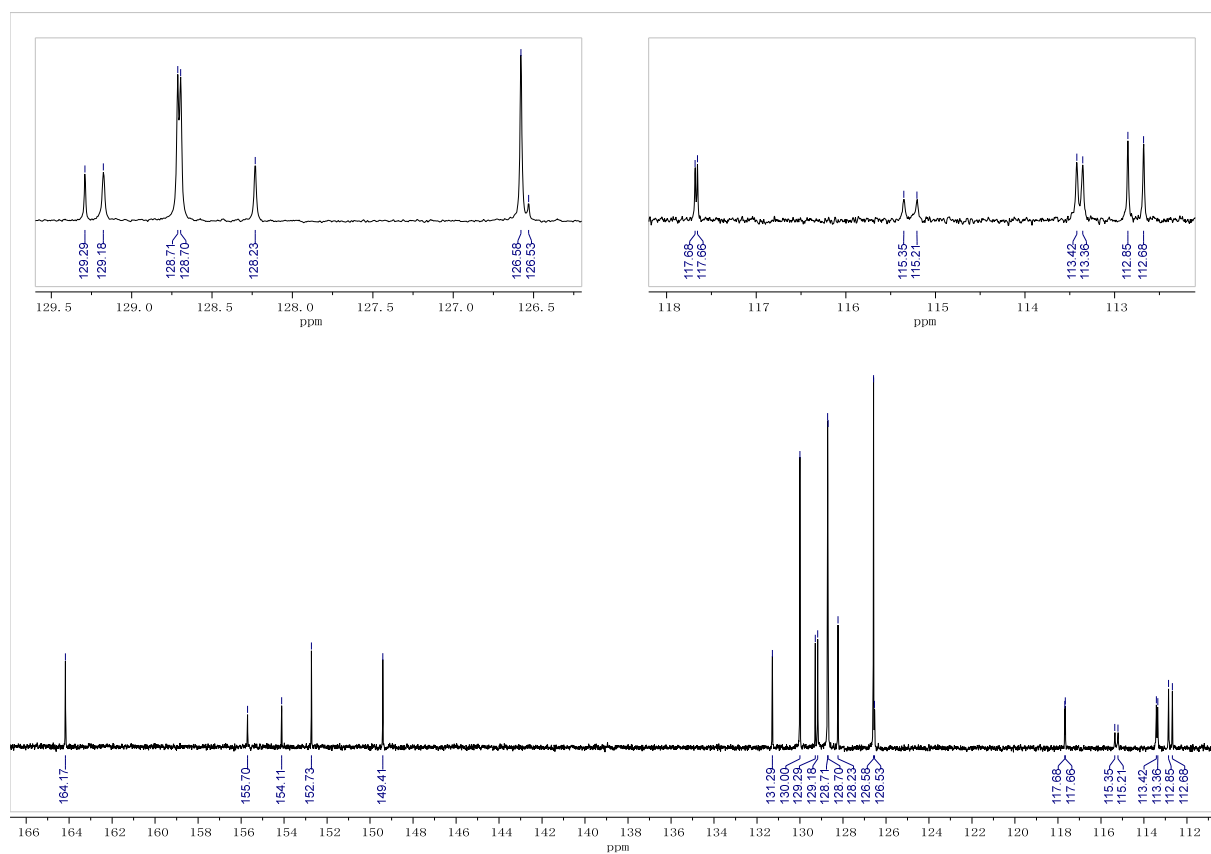
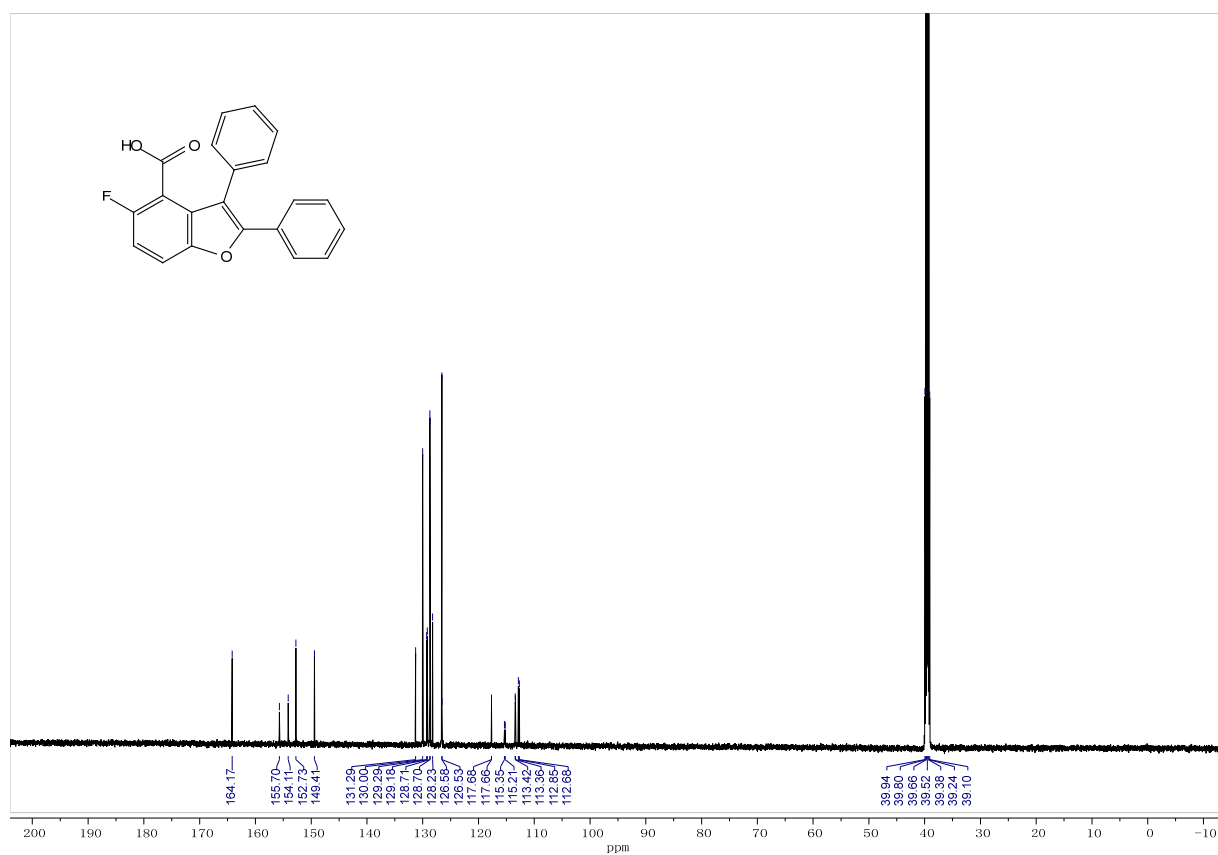
¹H NMR spectrum of **3ka** (600 MHz, DMSO-*d*₆)



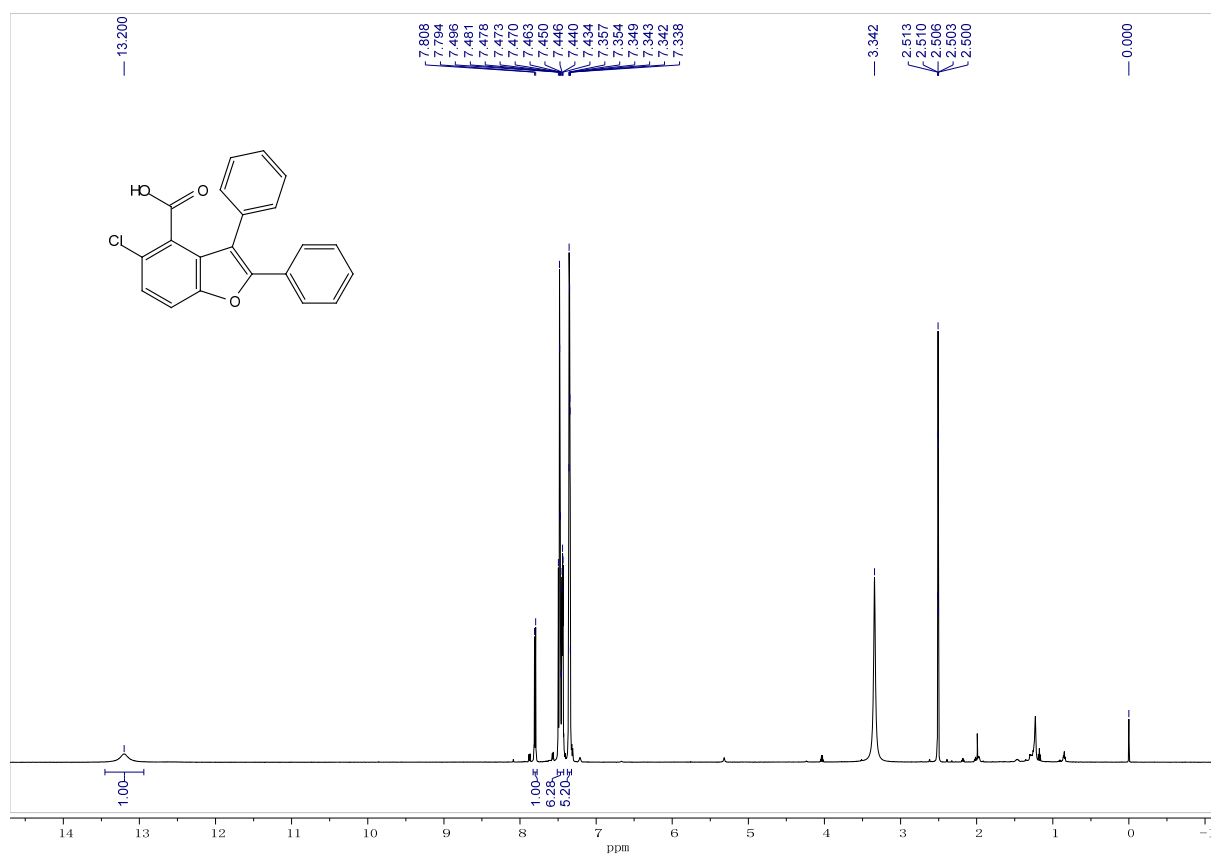
¹⁹F NMR spectrum of **3ka** (565 MHz, DMSO-*d*₆)



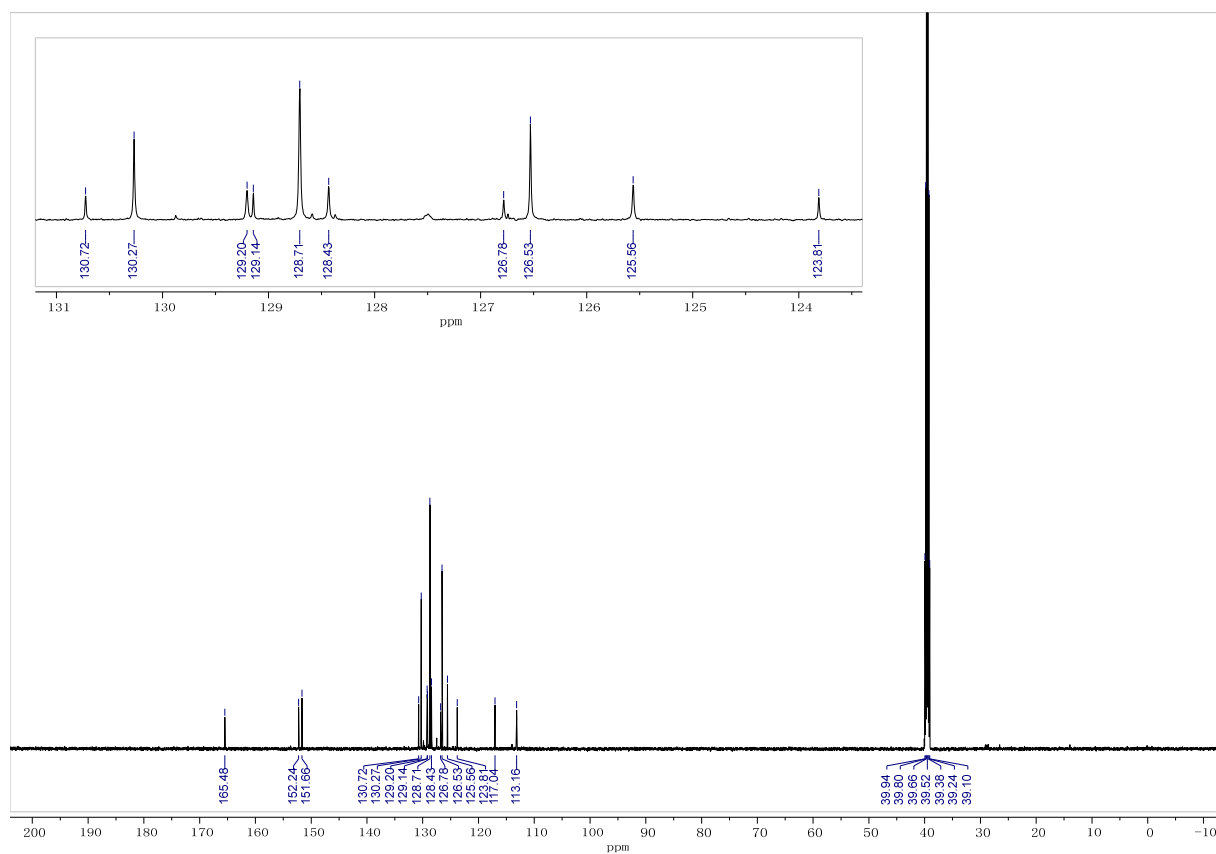
¹³C NMR spectrum of **3ka** (600 MHz, DMSO-*d*₆)



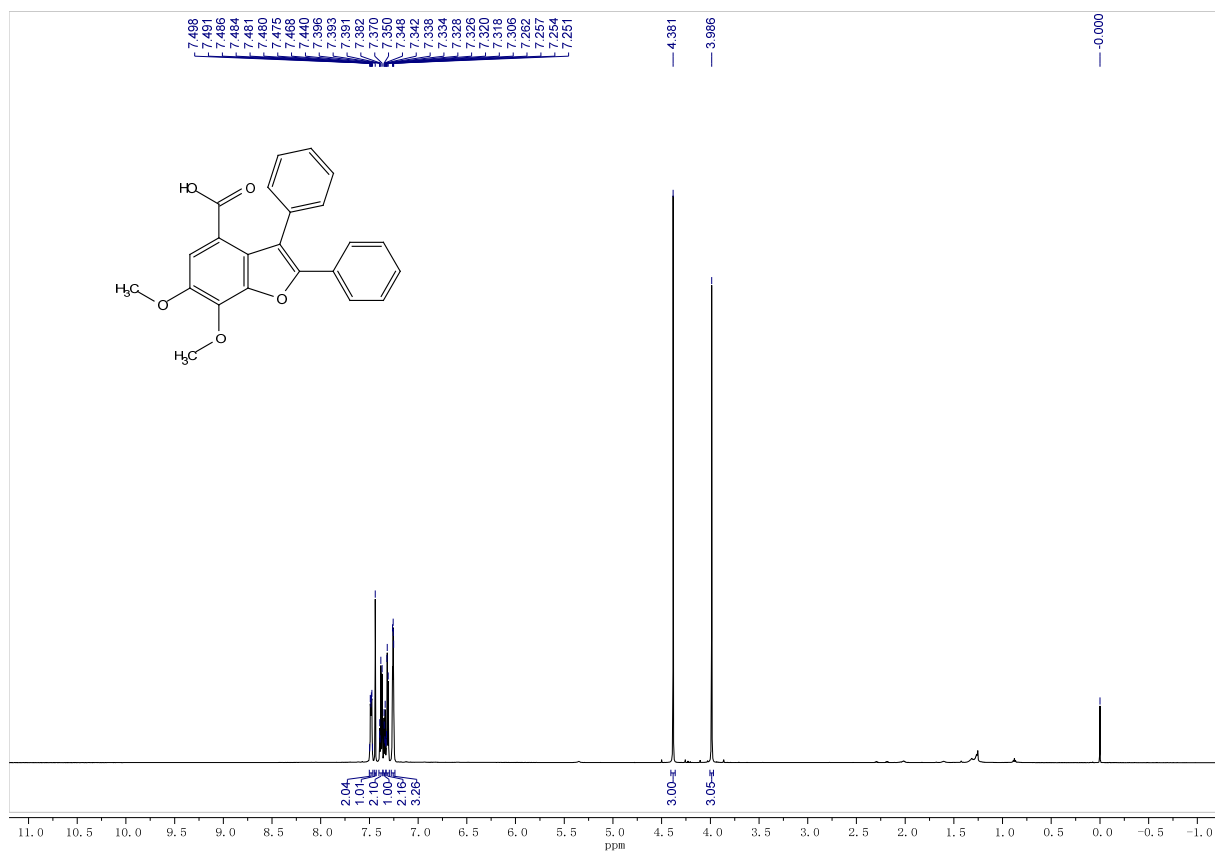
¹H NMR spectrum of **3la** (600 MHz, DMSO-*d*₆)



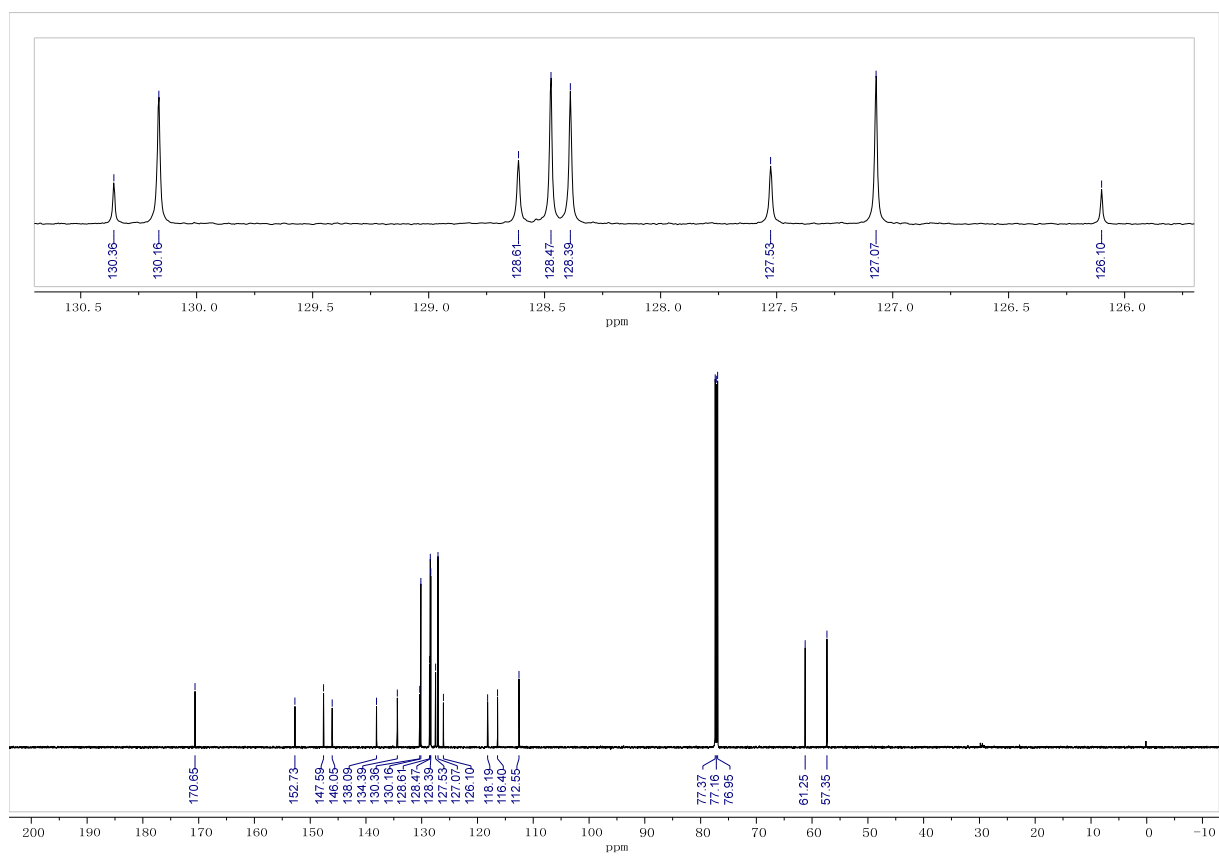
¹³C NMR spectrum of **3la** (151 MHz, DMSO-*d*₆)



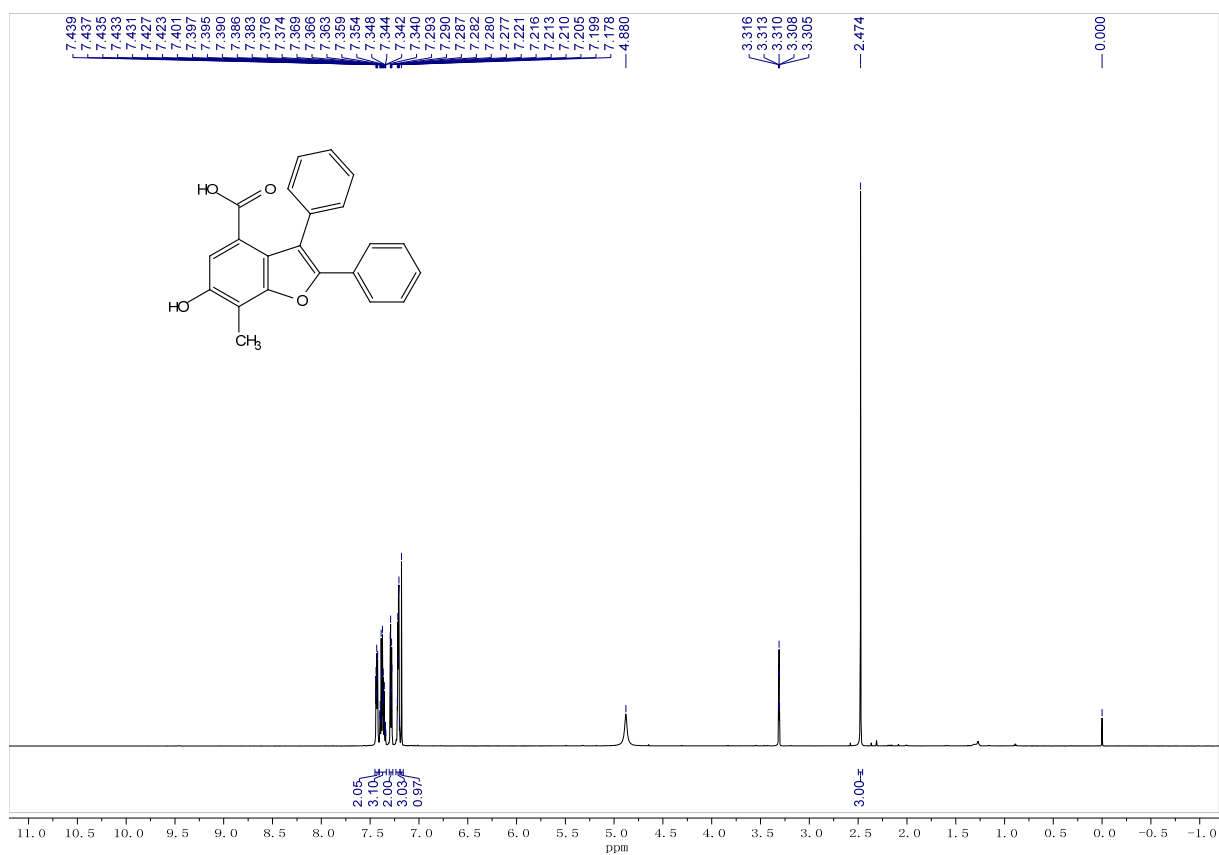
¹H NMR spectrum of **3ma** (600 MHz, CDCl₃)



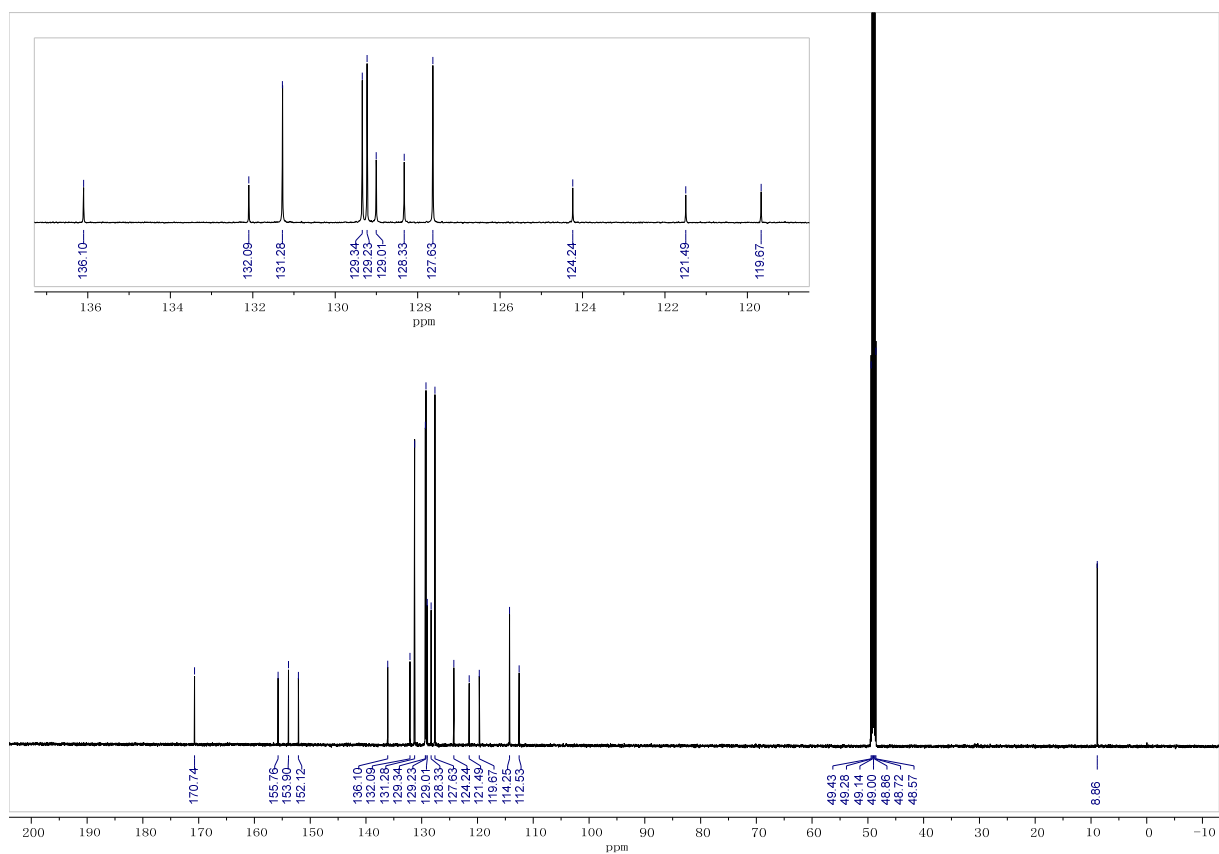
¹³C NMR spectrum of **3ma** (151 MHz, CDCl₃)



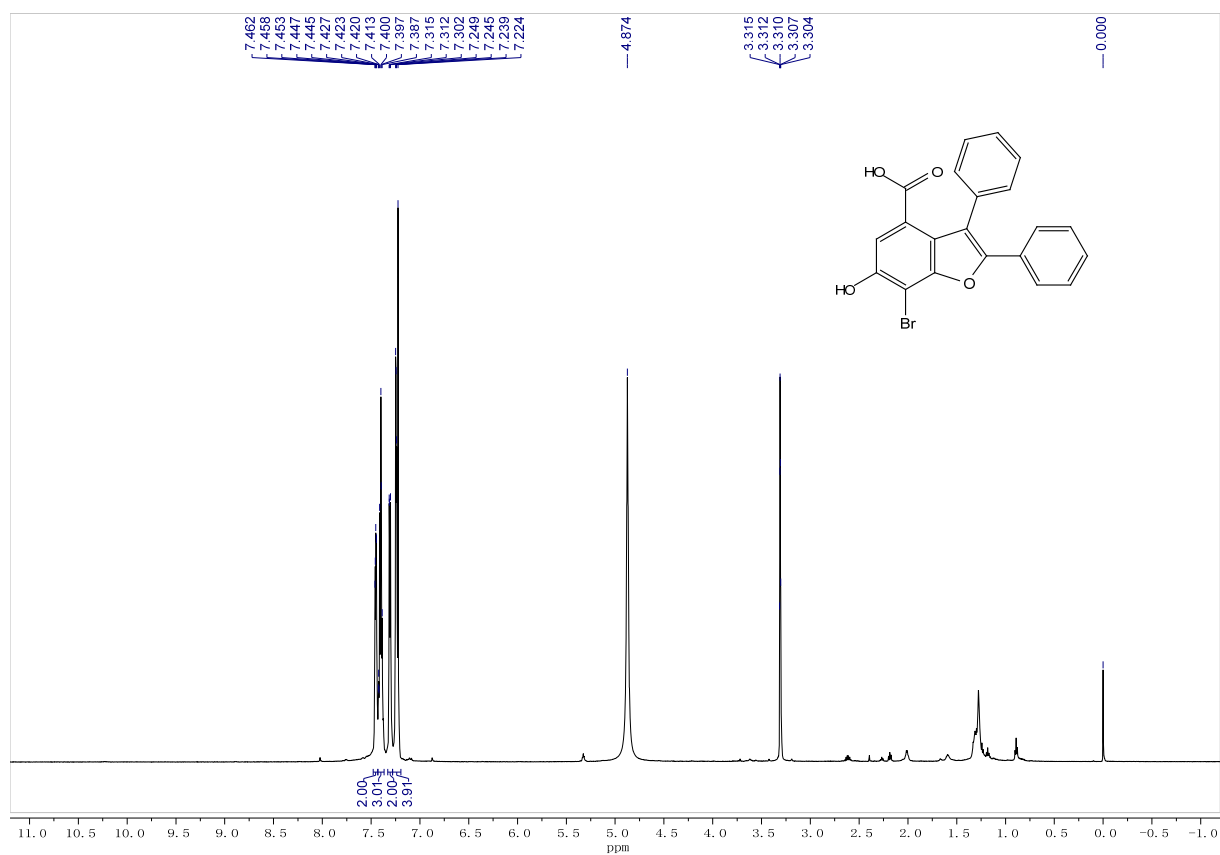
¹H NMR spectrum of **3na** (600 MHz, CD₃OD)



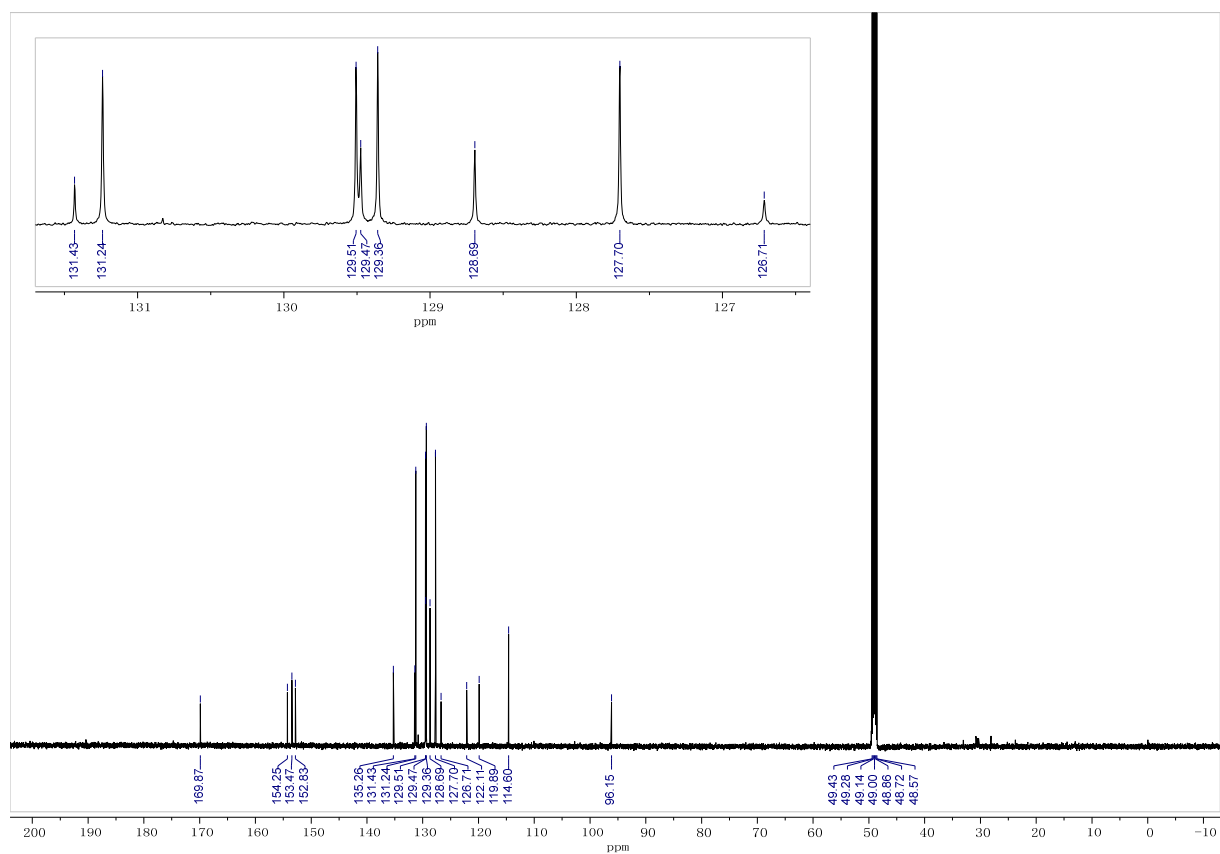
¹³C NMR spectrum of **3na** (151 MHz, CD₃OD)



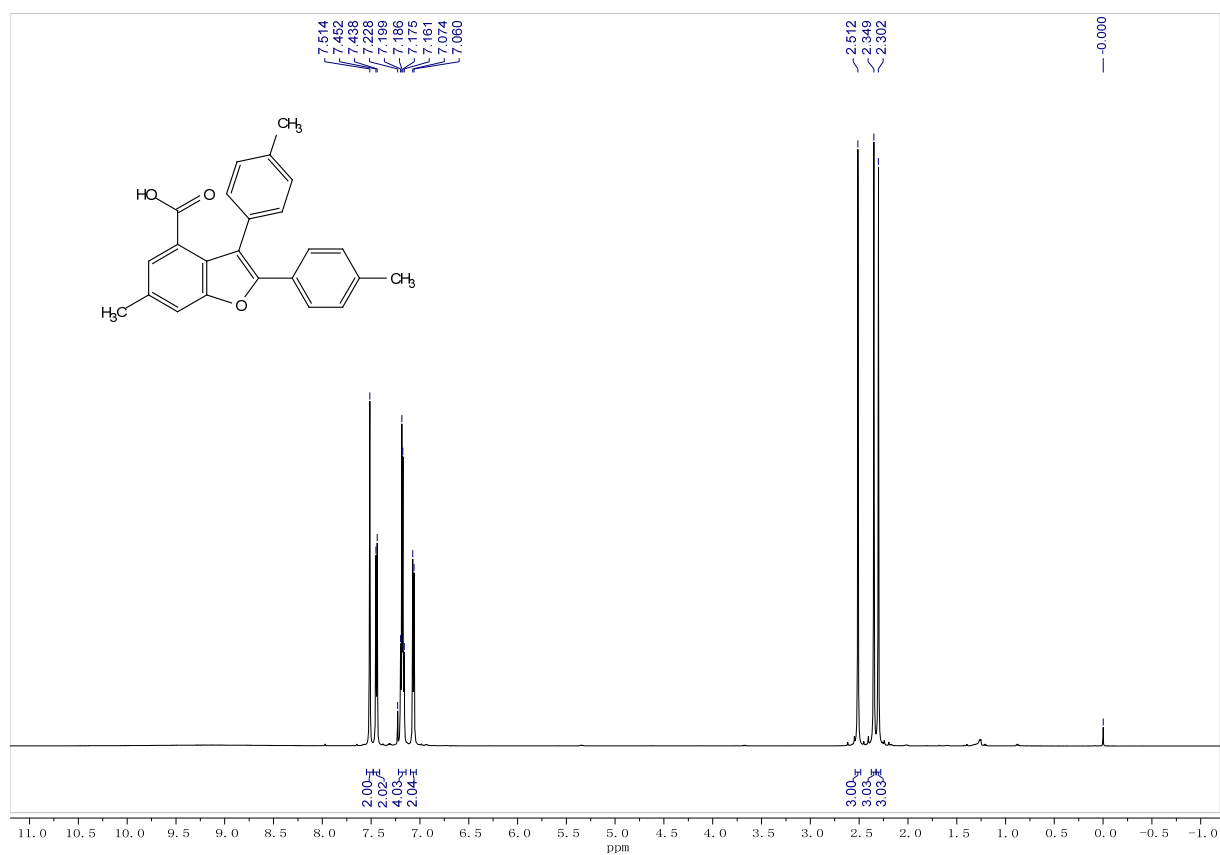
¹H NMR spectrum of **30a** (600 MHz, CD₃OD)



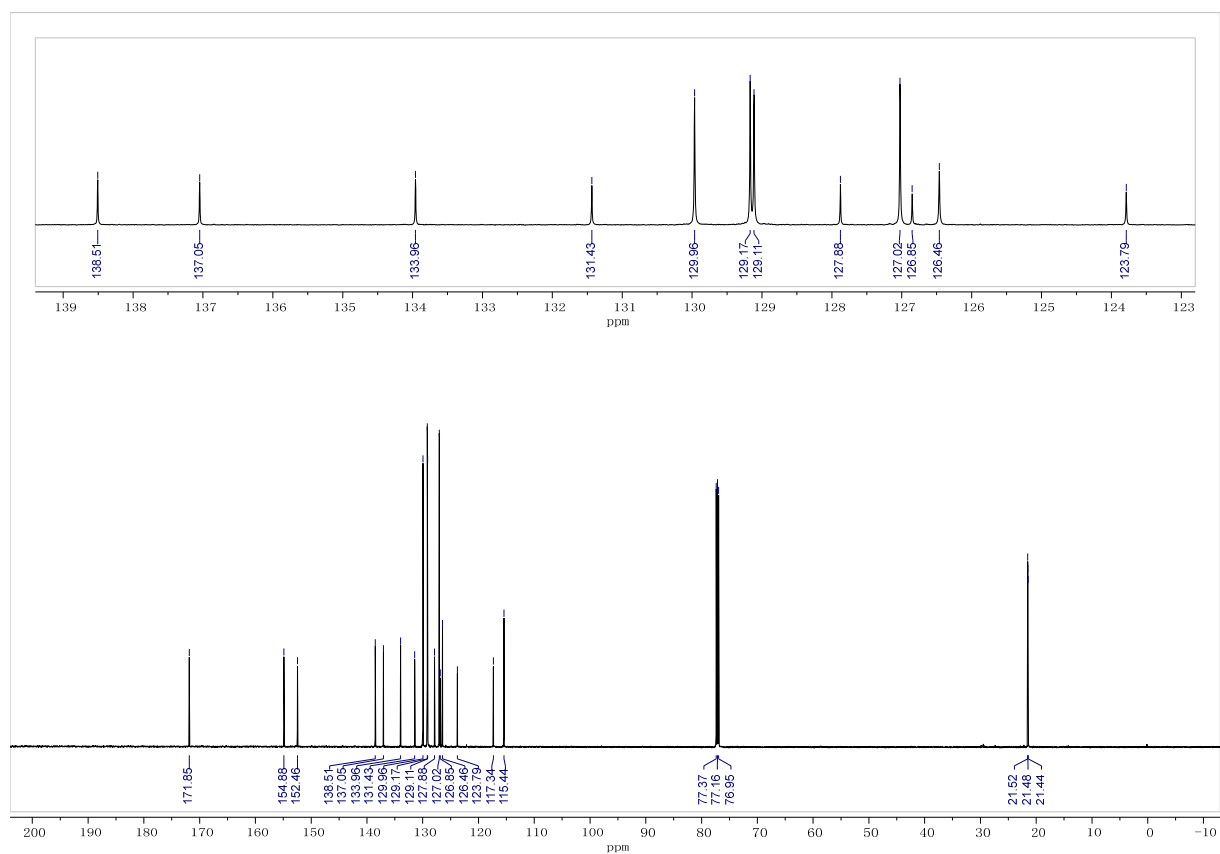
¹³C NMR spectrum of **30a** (151 MHz, CD₃OD)



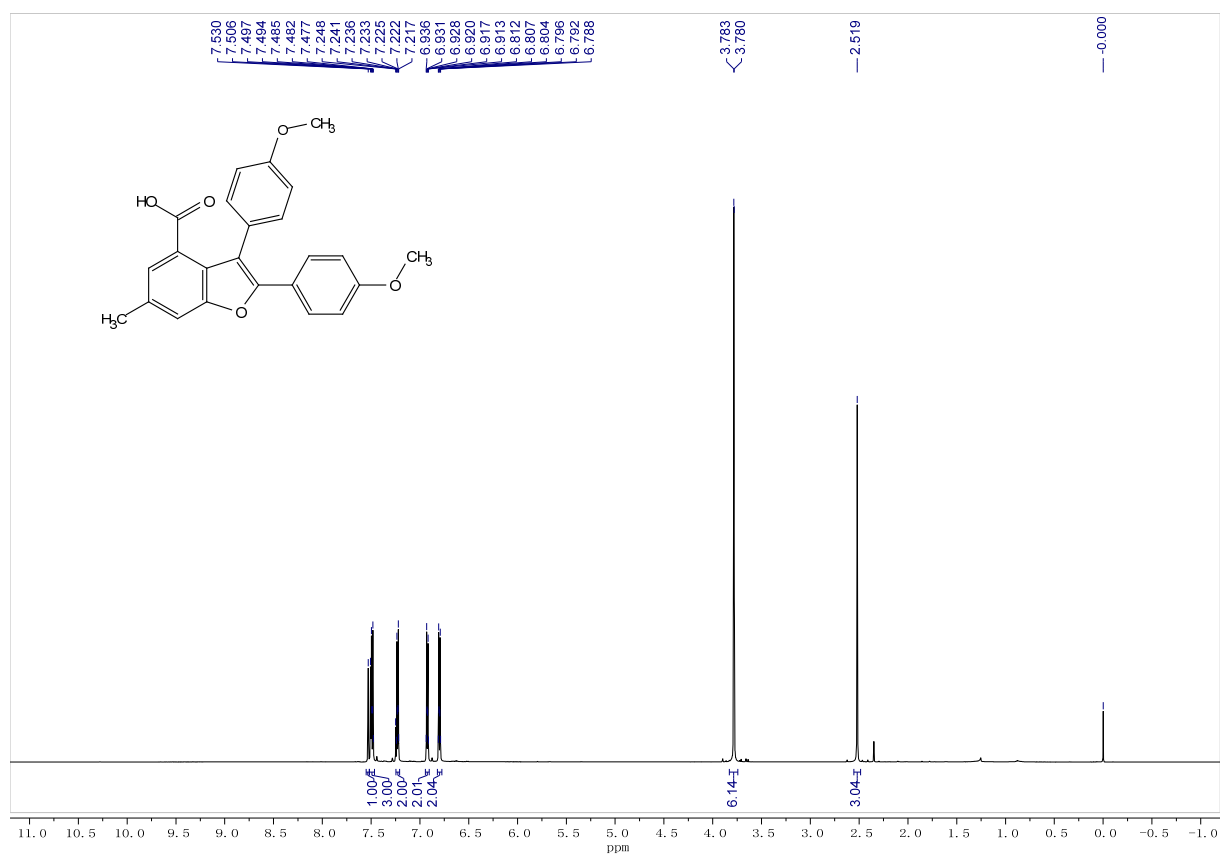
¹H NMR spectrum of **3ab** (600 MHz, CDCl₃)



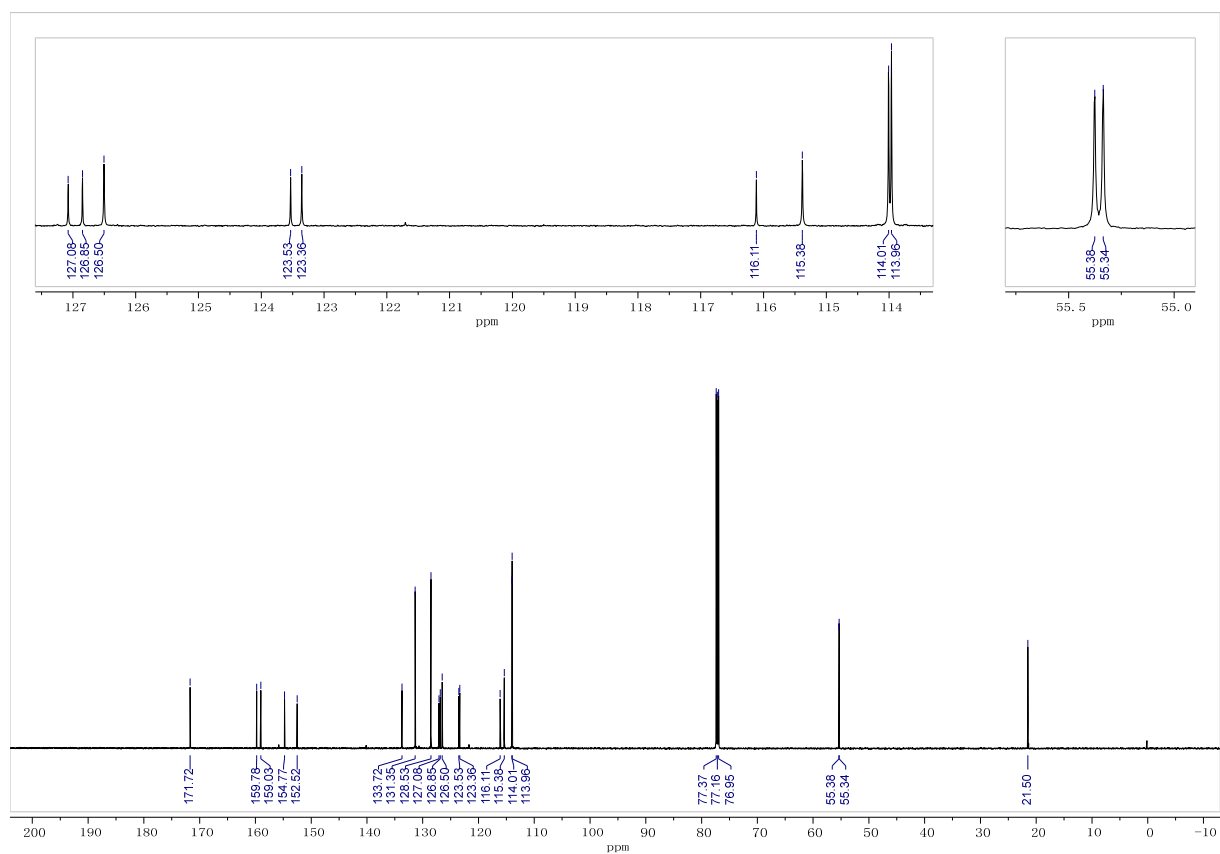
¹³C NMR spectrum of **3ab** (151 MHz, CDCl₃)



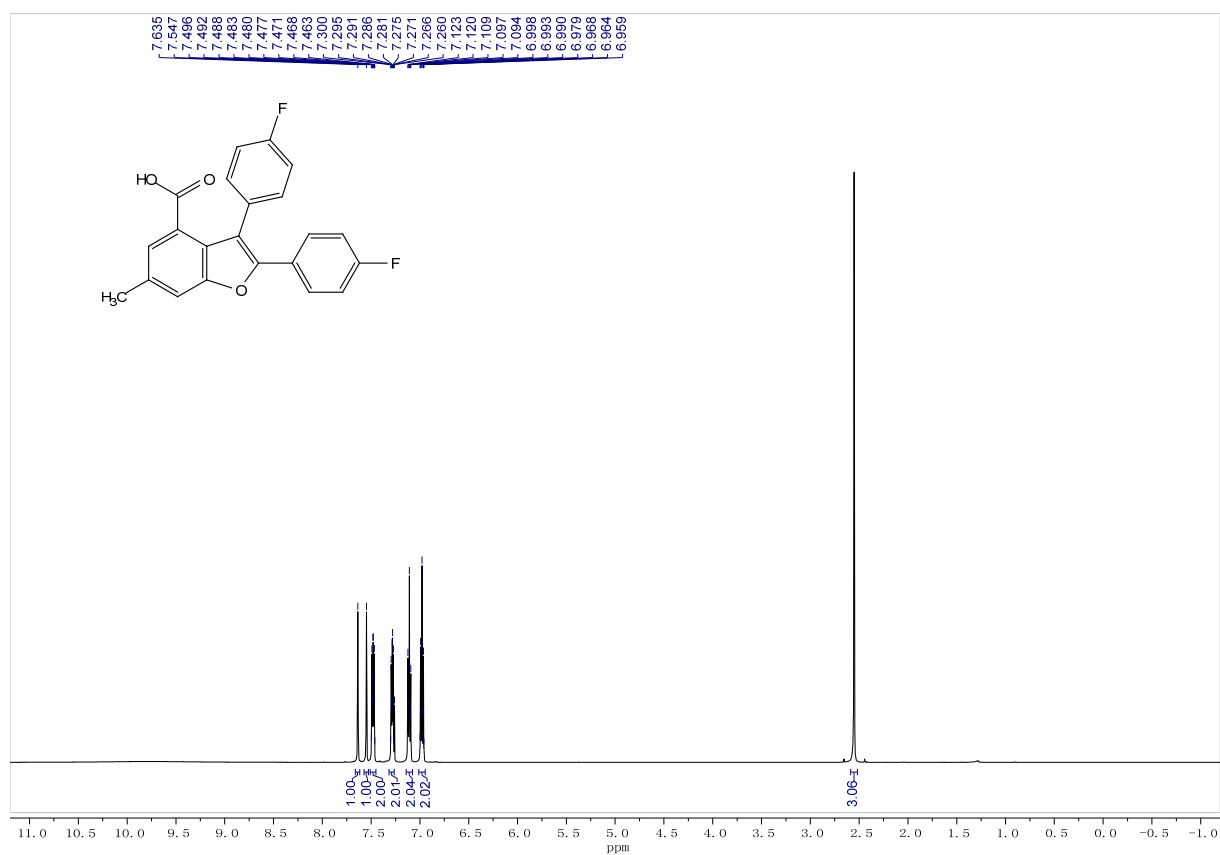
¹H NMR spectrum of **3ac** (600 MHz, CDCl₃)



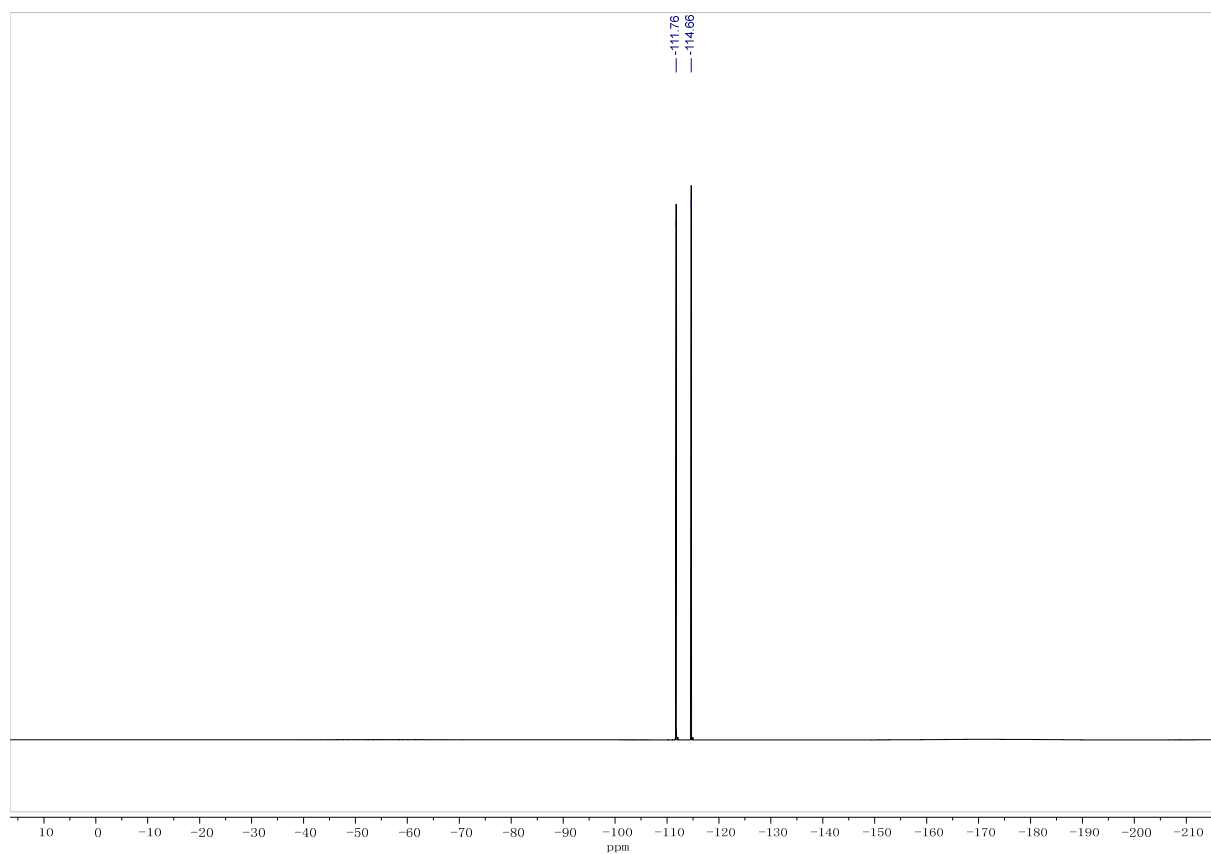
¹³C NMR spectrum of **3ac** (151 MHz, CDCl₃)



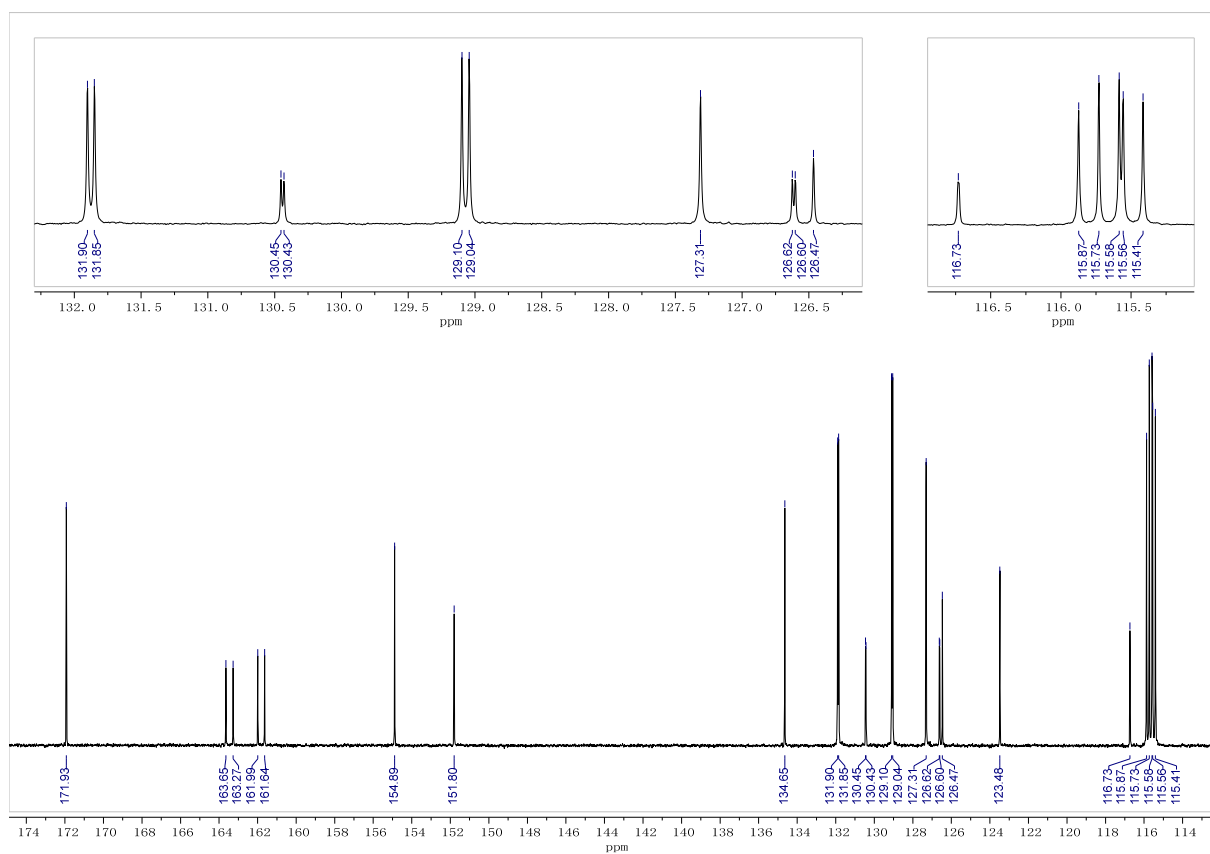
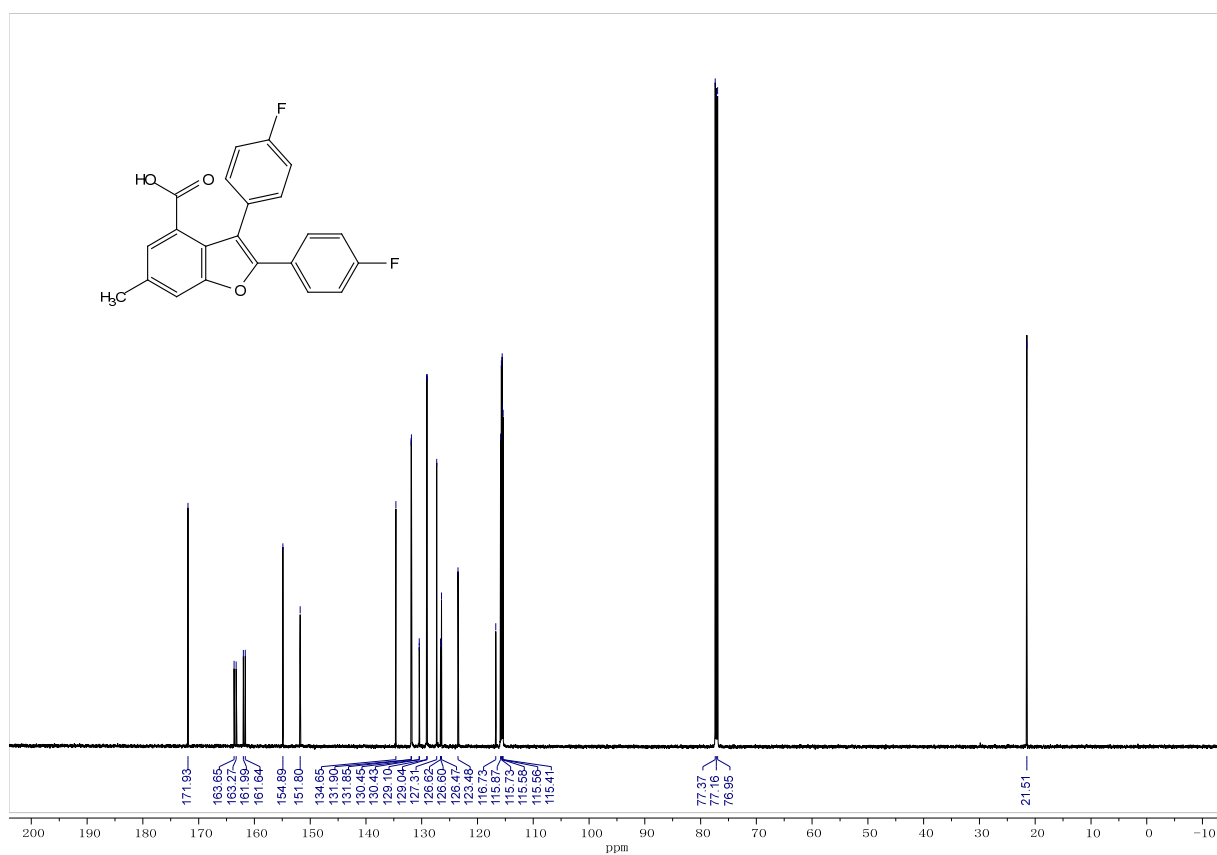
¹H NMR spectrum of **3ad** (600 MHz, CDCl₃)



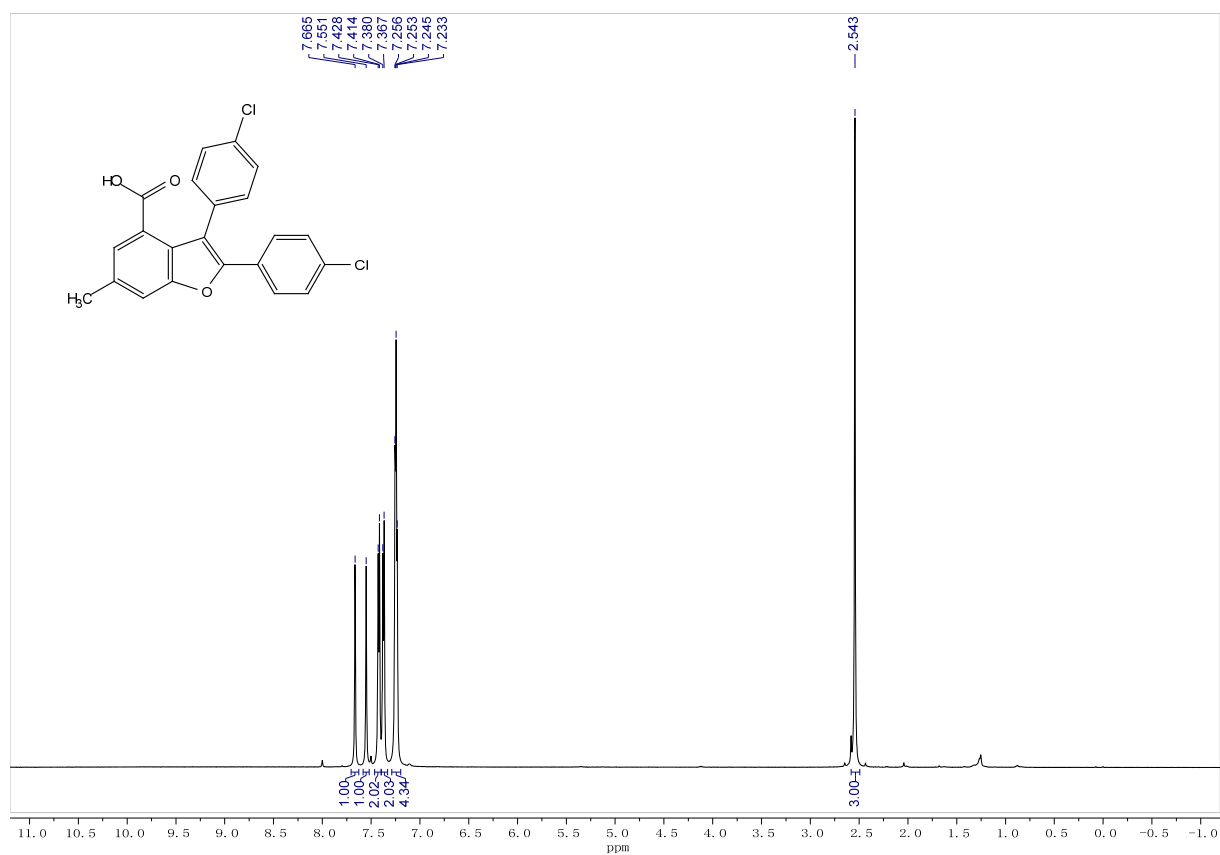
¹⁹F NMR spectrum of **3ad** (565 MHz, CDCl₃)



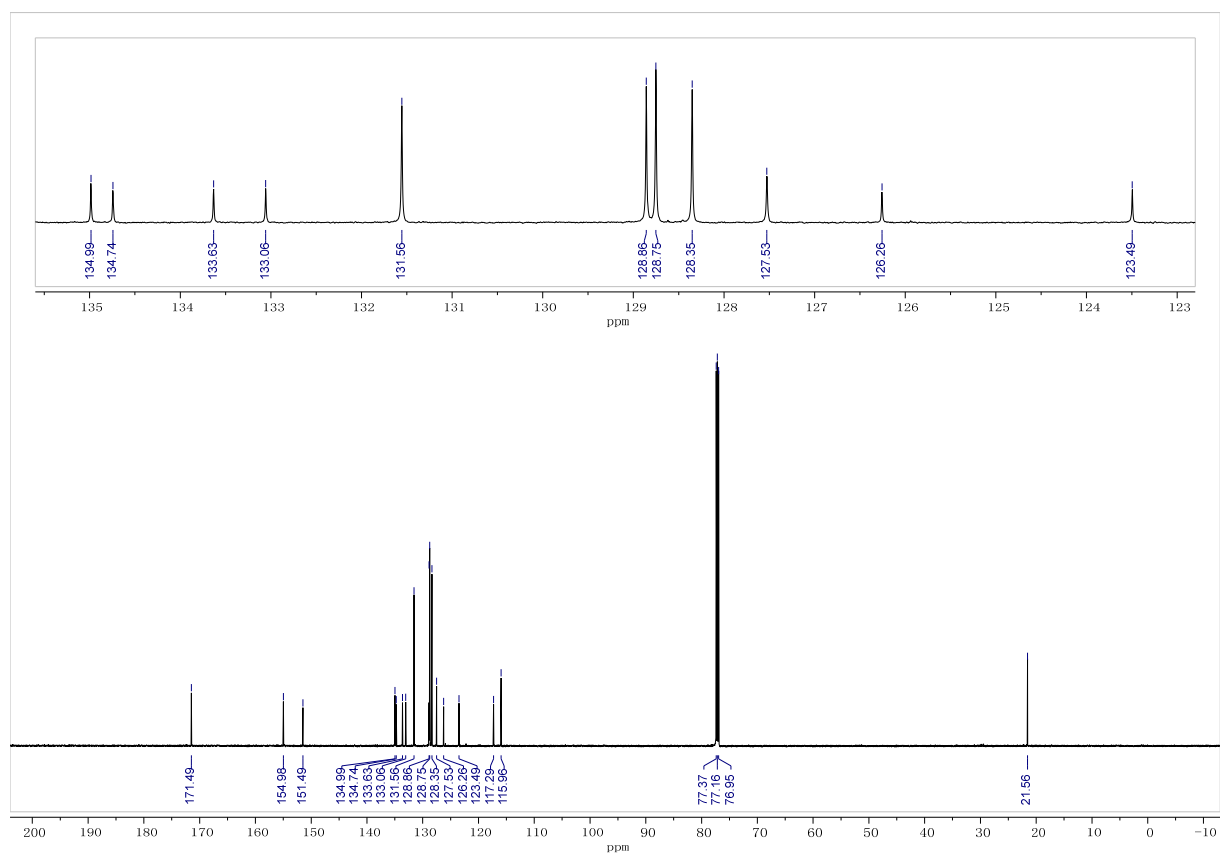
^{13}C NMR spectrum of **3ad** (151 MHz, CDCl_3)



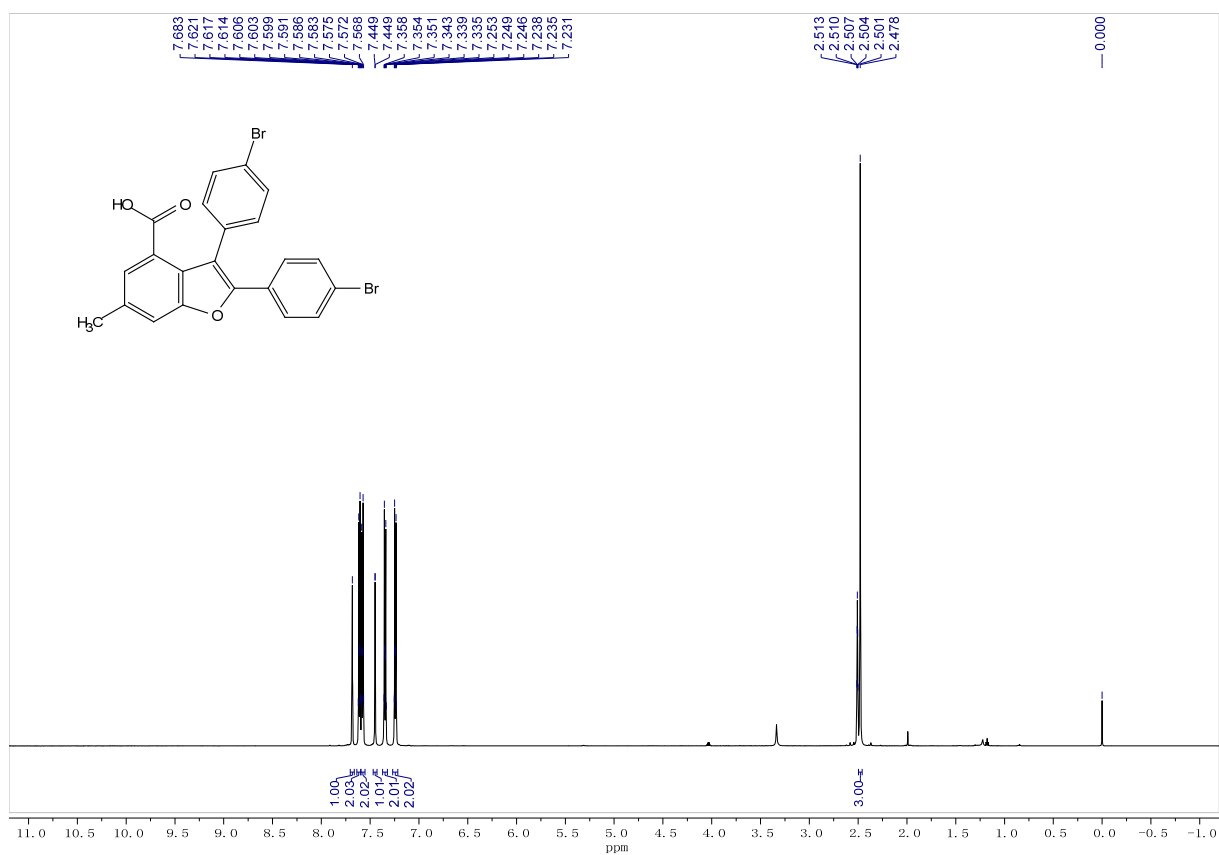
¹H NMR spectrum of **3ae** (600 MHz, CDCl₃)



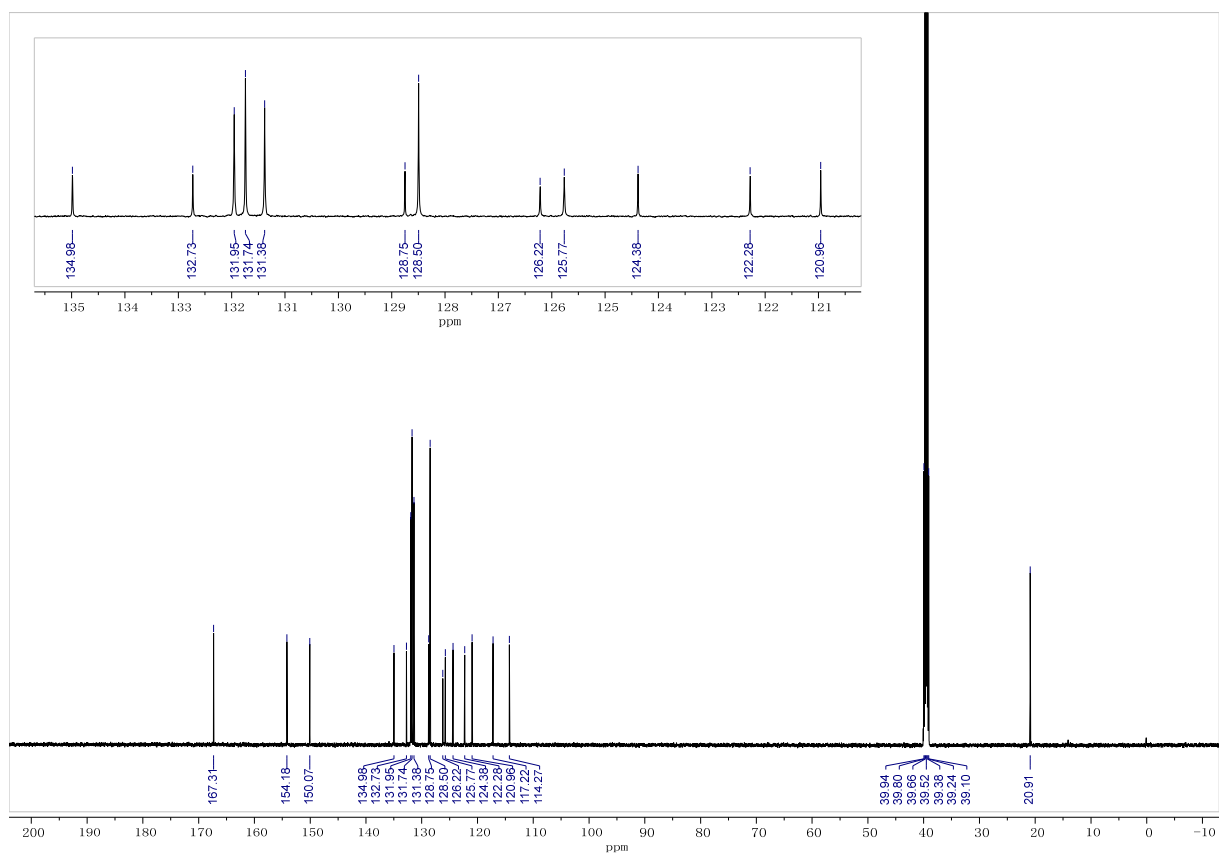
¹³C NMR spectrum of **3ae** (151 MHz, CDCl₃)



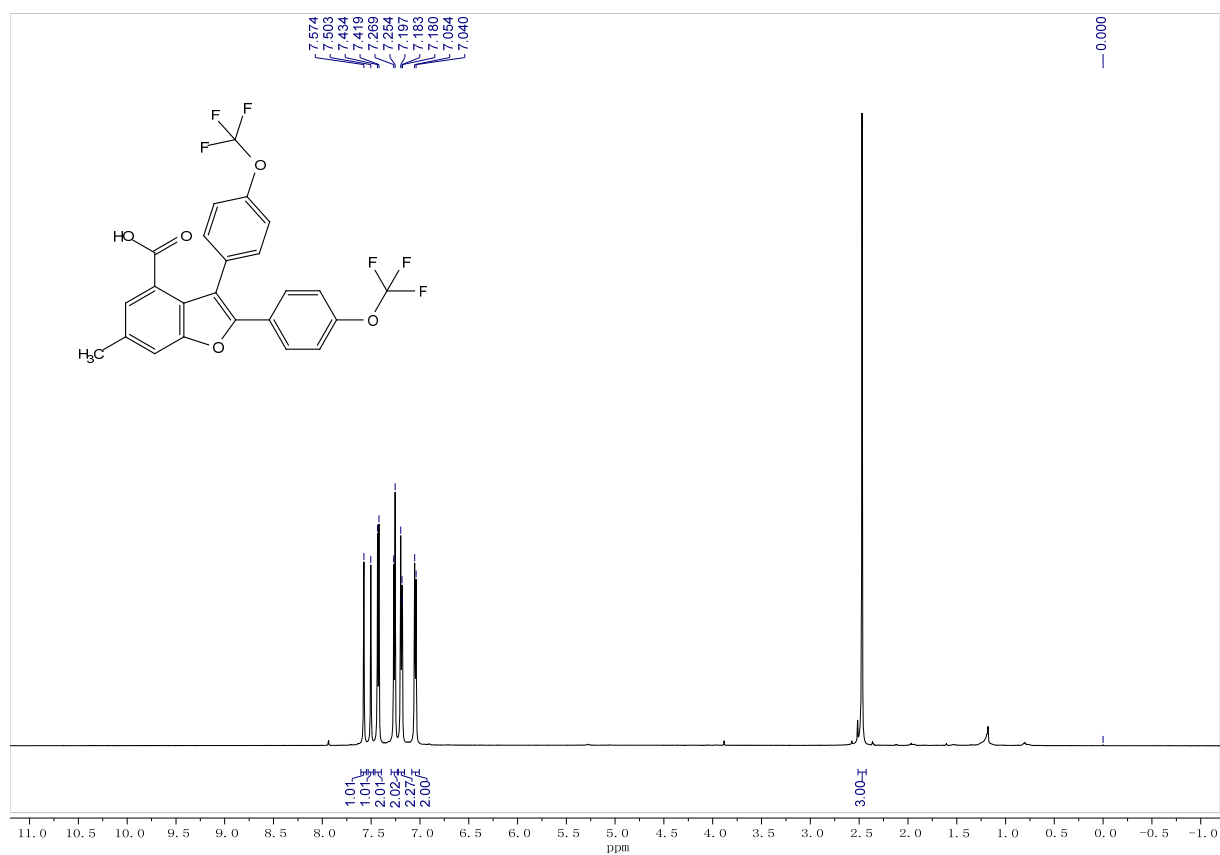
¹H NMR spectrum of **3af** (600 MHz, DMSO-*d*₆)



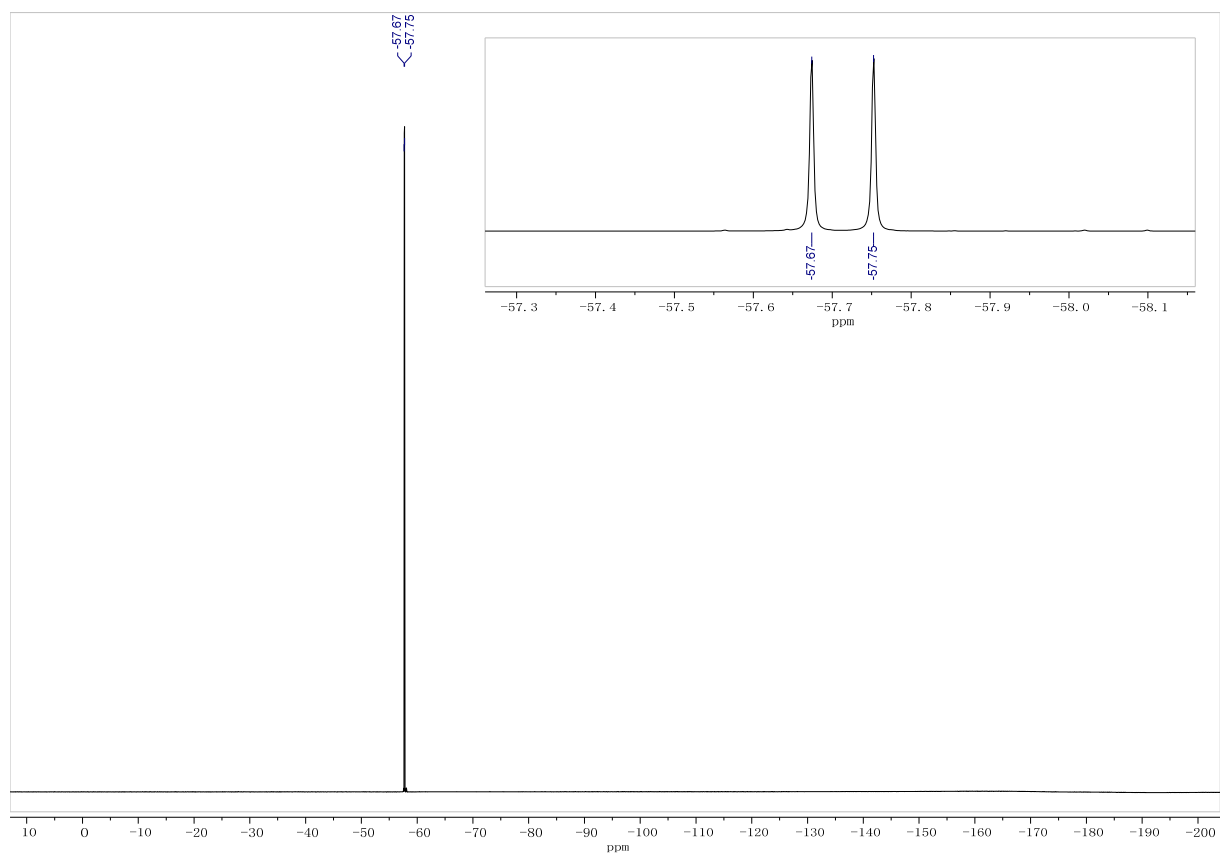
¹³C NMR spectrum of **3af** (151 MHz, DMSO-*d*₆)



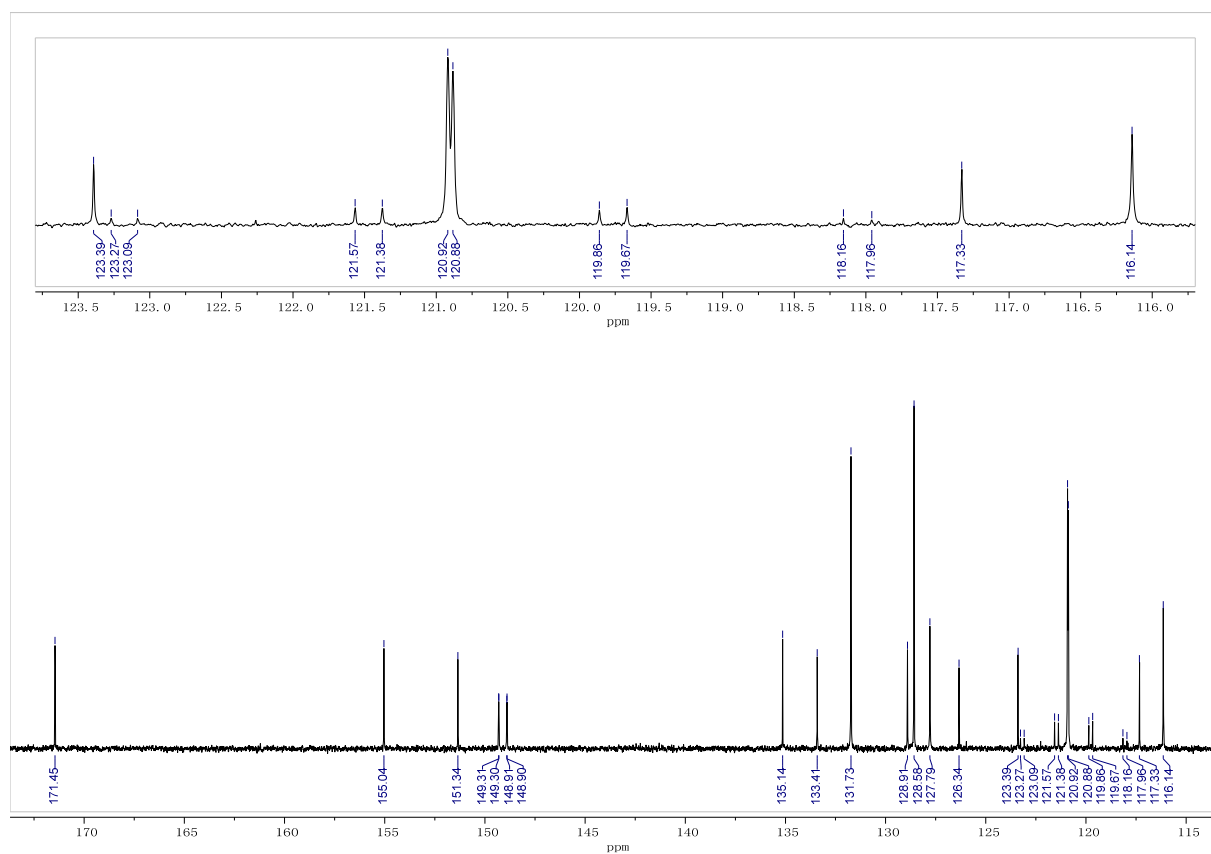
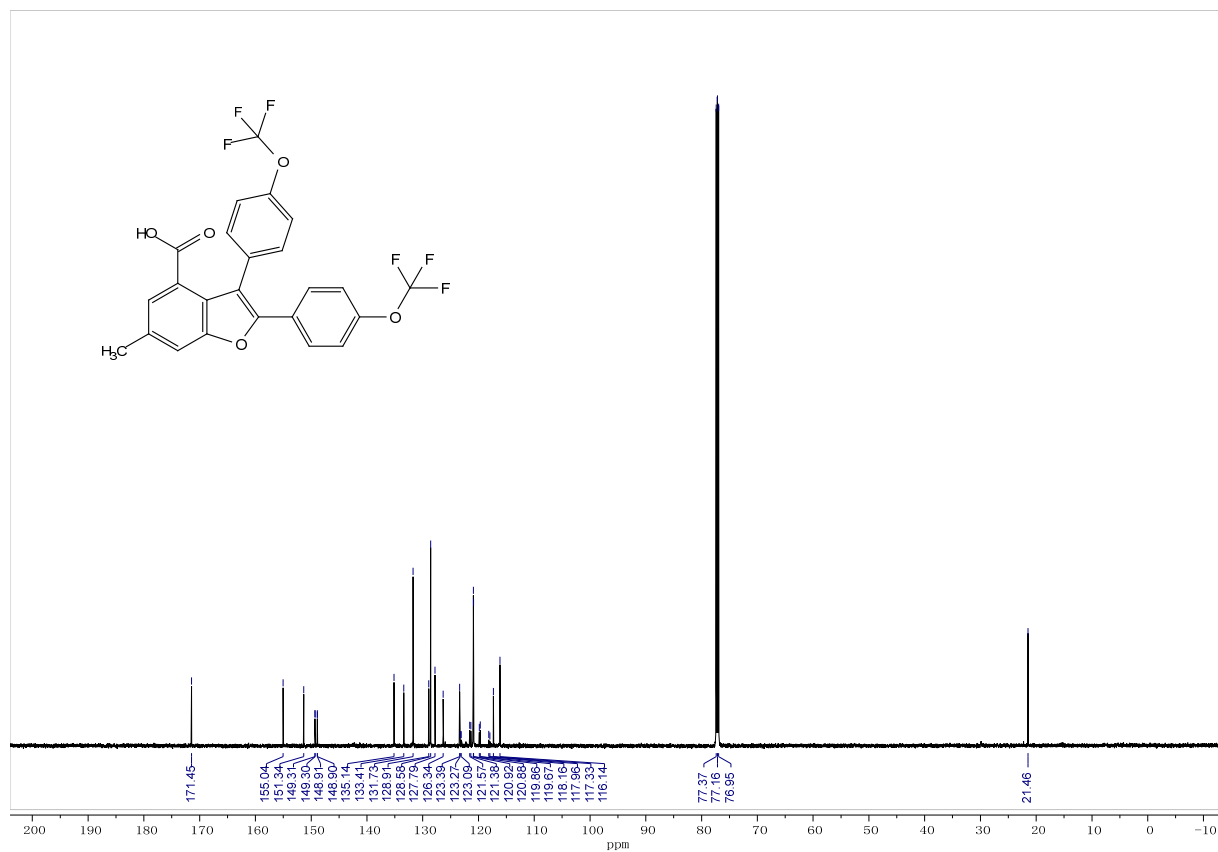
^1H NMR spectrum of **3ag** (600 MHz, CDCl_3)



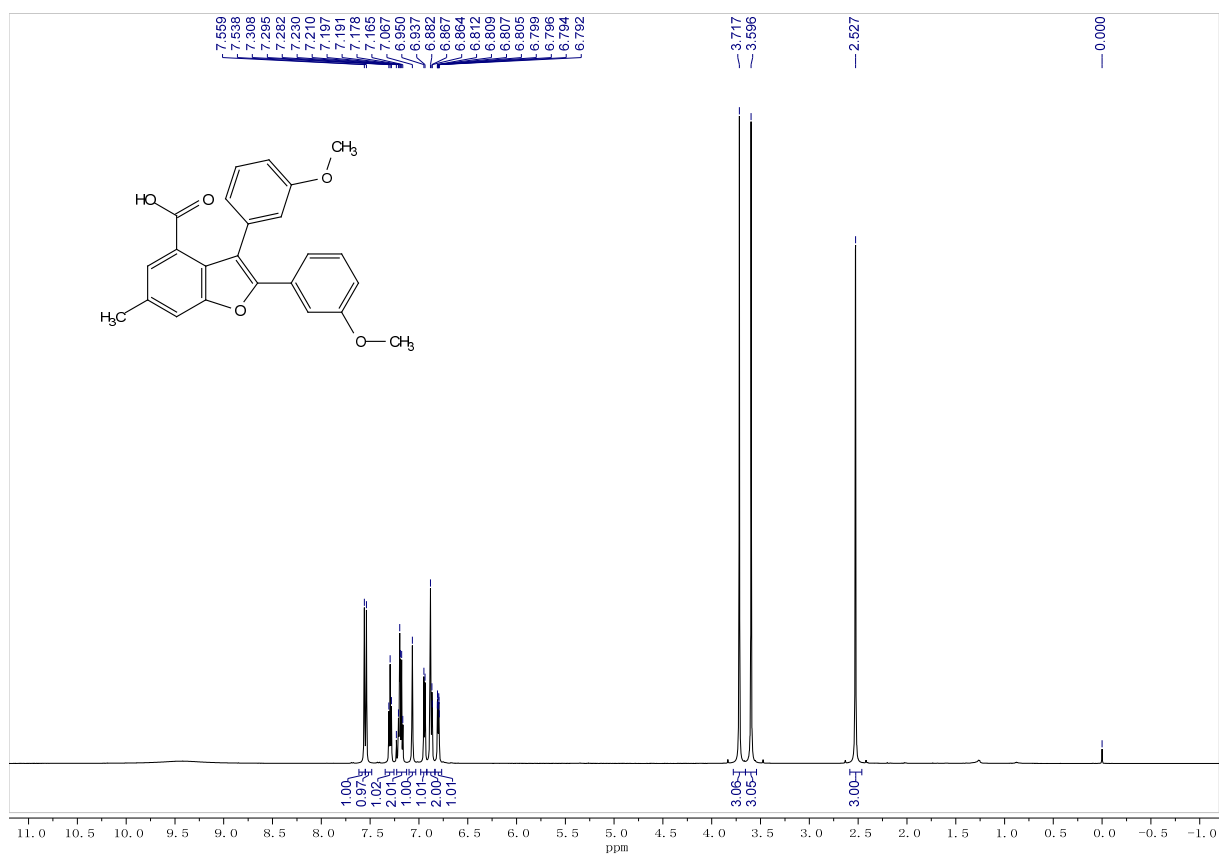
^{19}F NMR spectrum of **3ag** (565 MHz, CDCl_3)



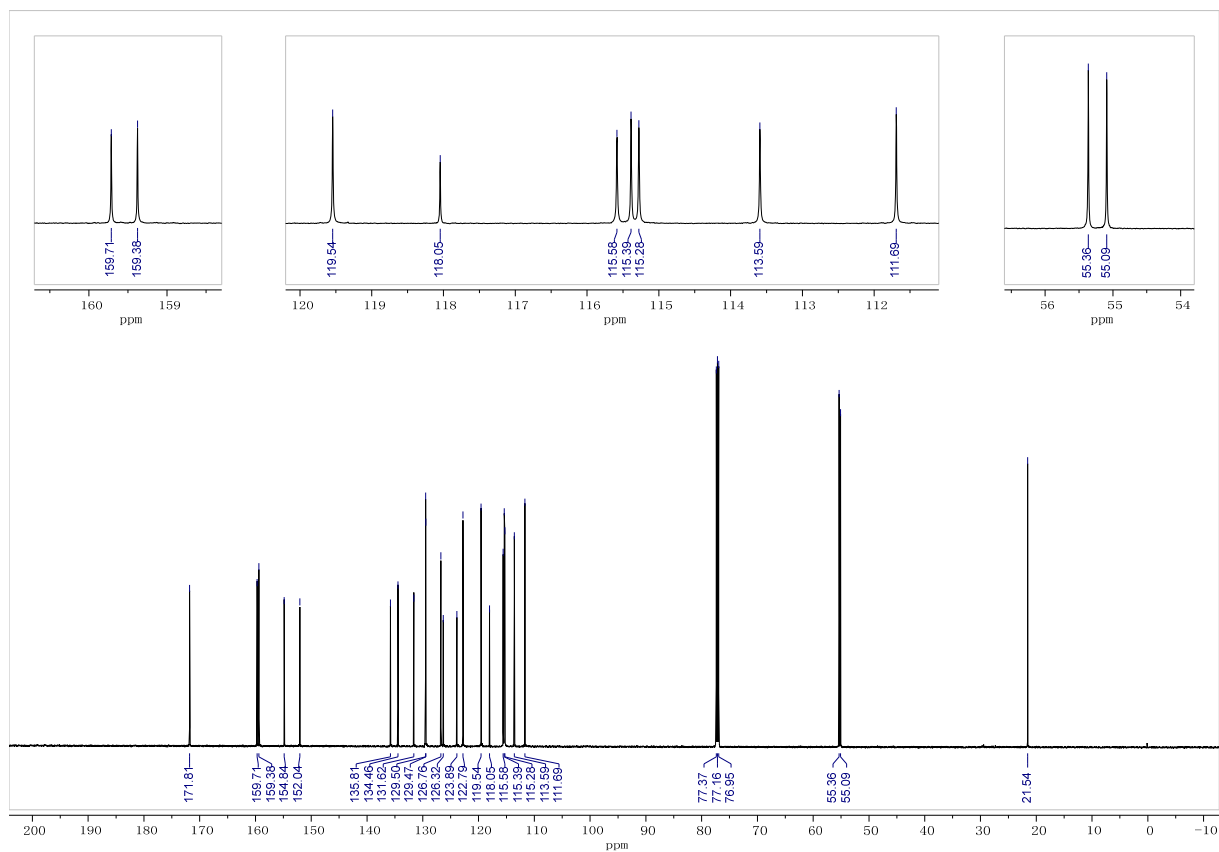
¹³C NMR spectrum of **3ag** (151 MHz, CDCl₃)



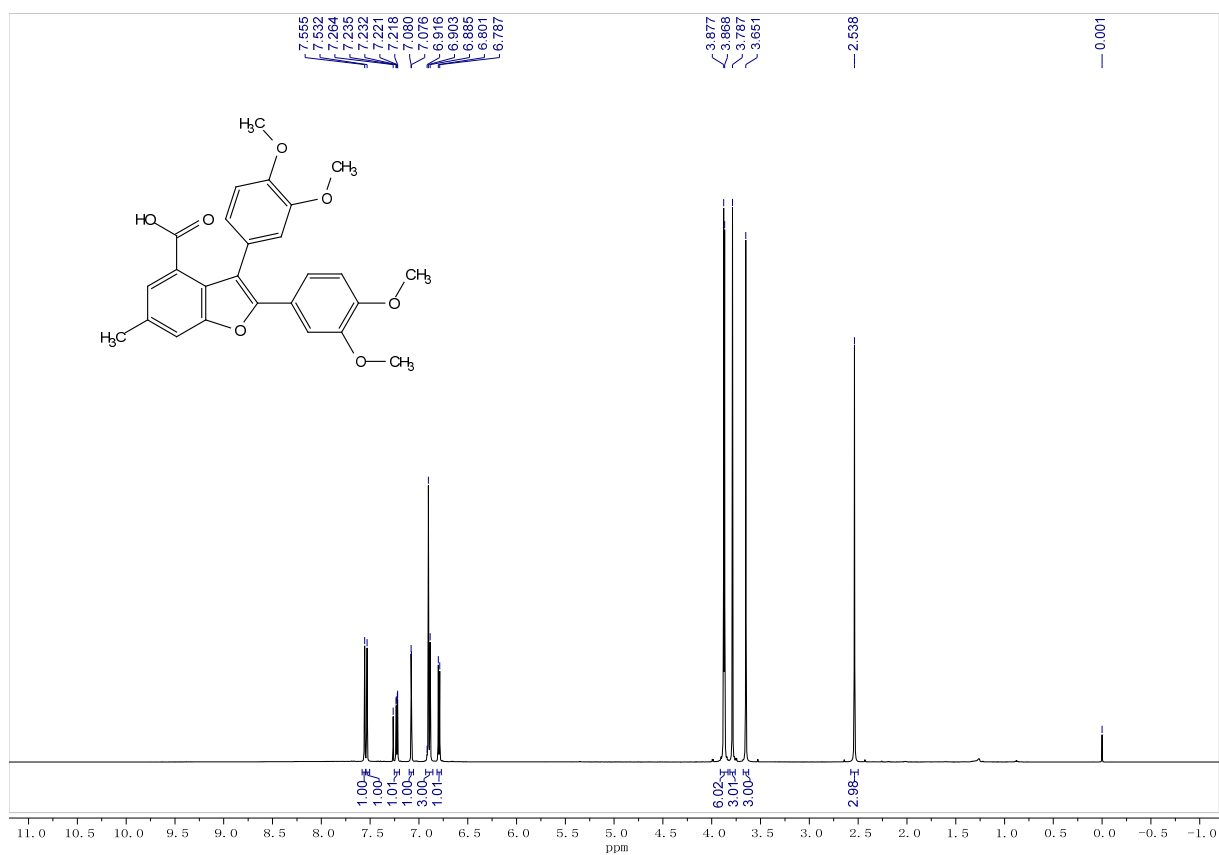
¹H NMR spectrum of **3ah** (600 MHz, CDCl₃)



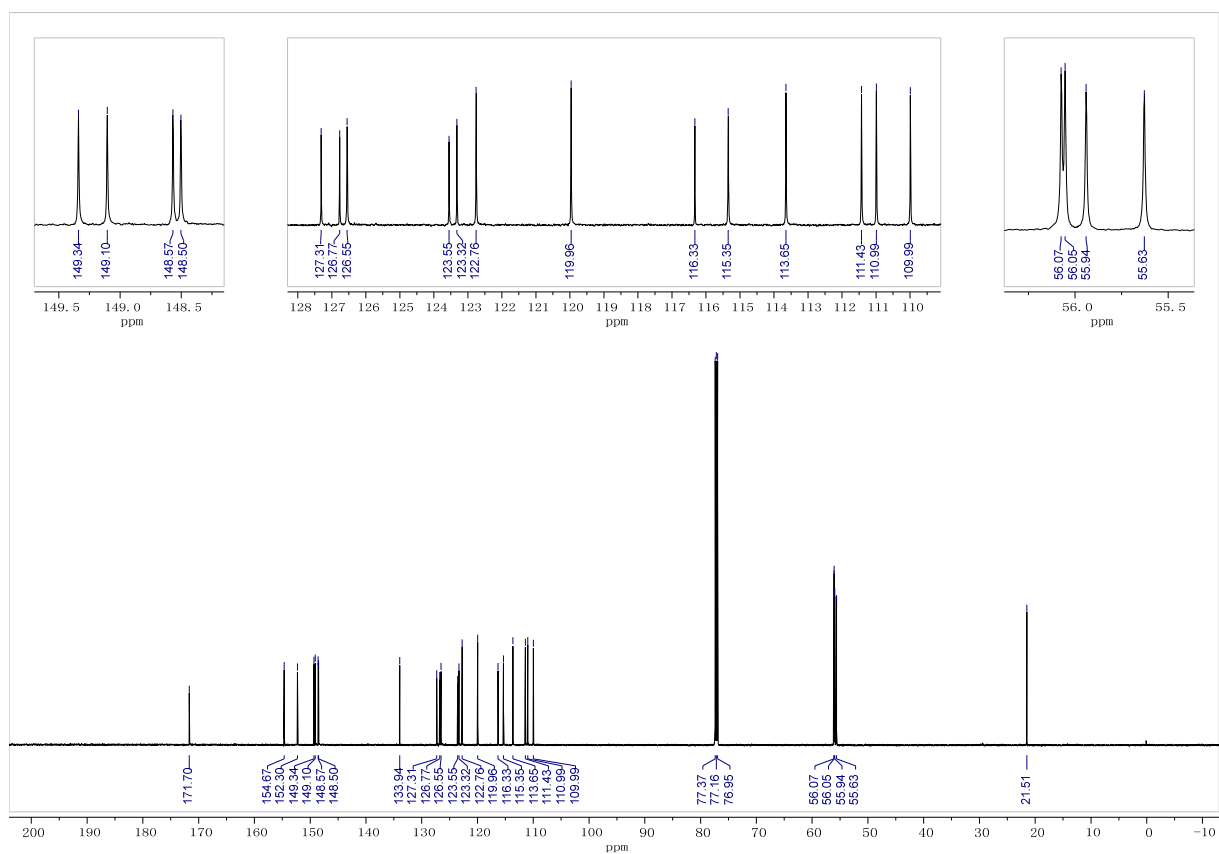
¹³C NMR spectrum of **3ah** (151 MHz, CDCl₃)



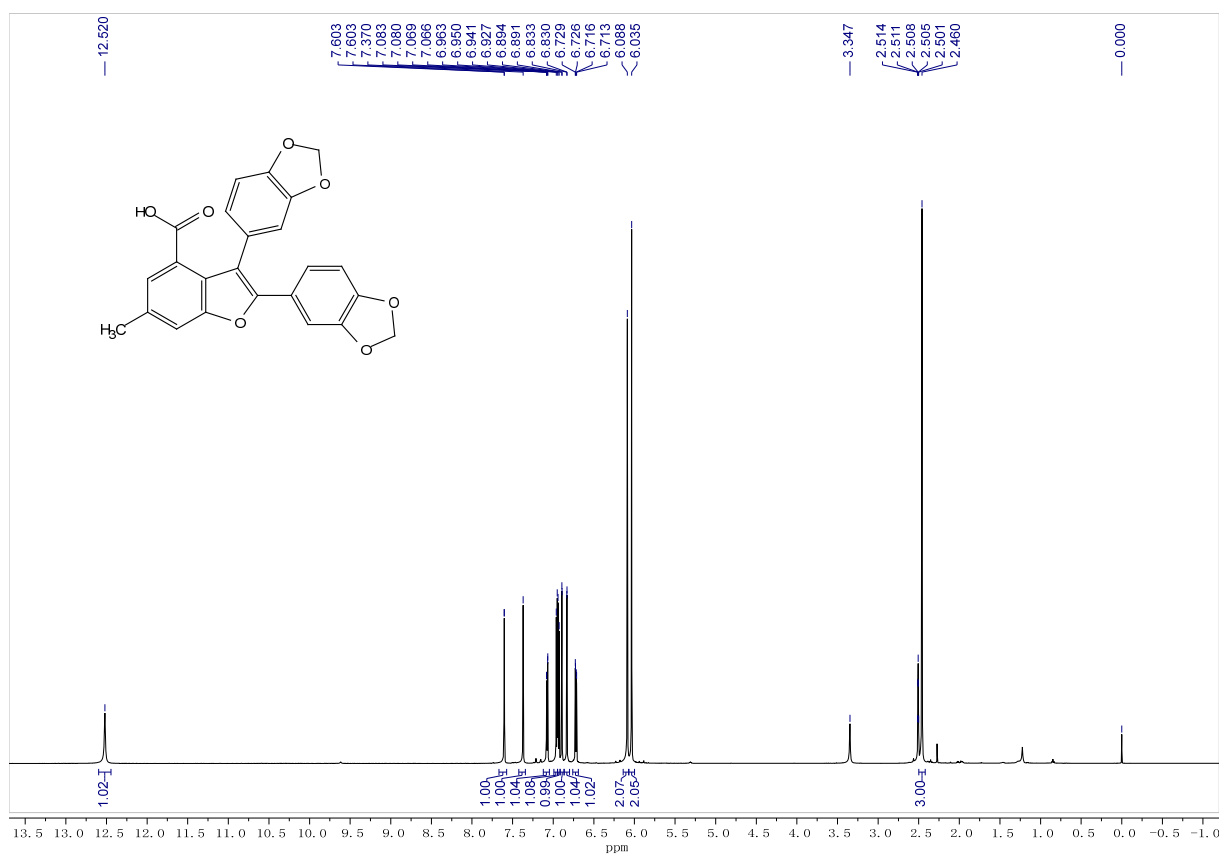
¹H NMR spectrum of **3ai** (600 MHz, CDCl₃)



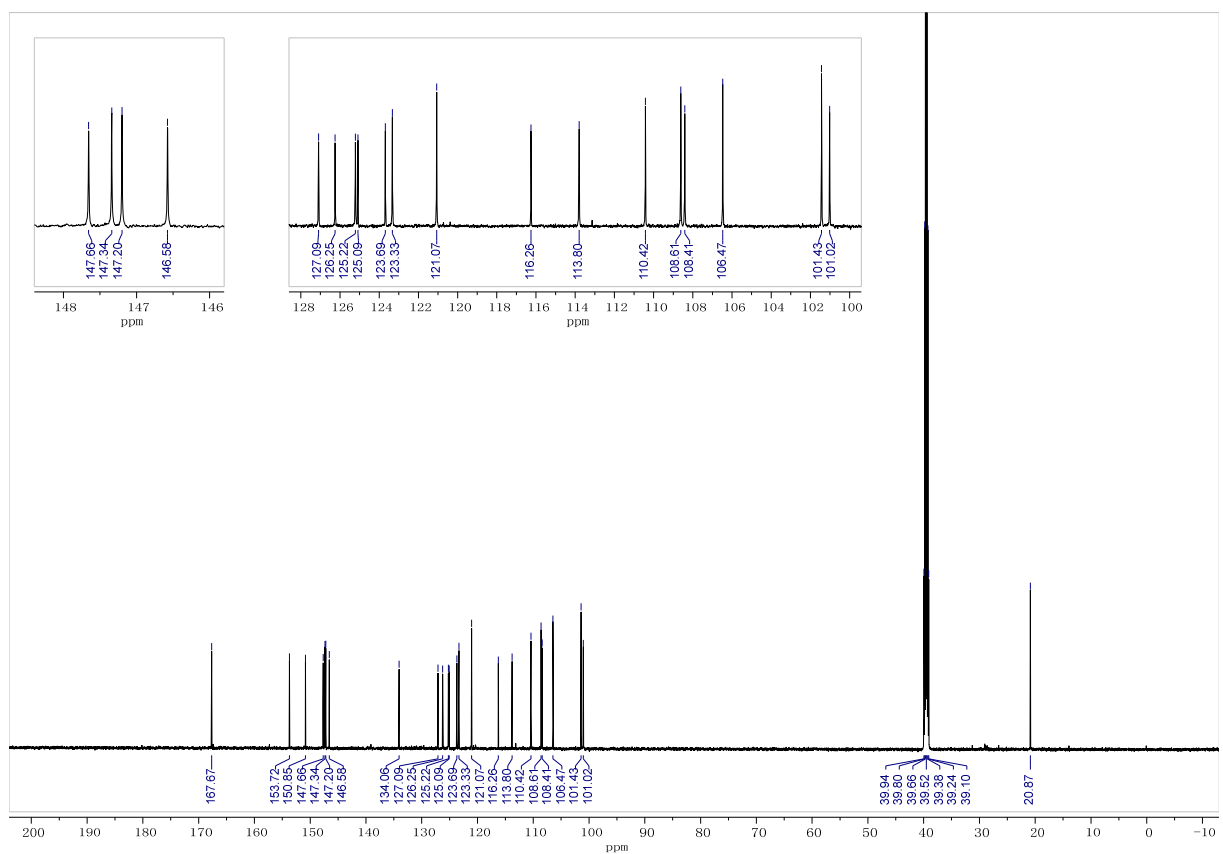
¹³C NMR spectrum of **3ai** (151 MHz, CDCl₃)



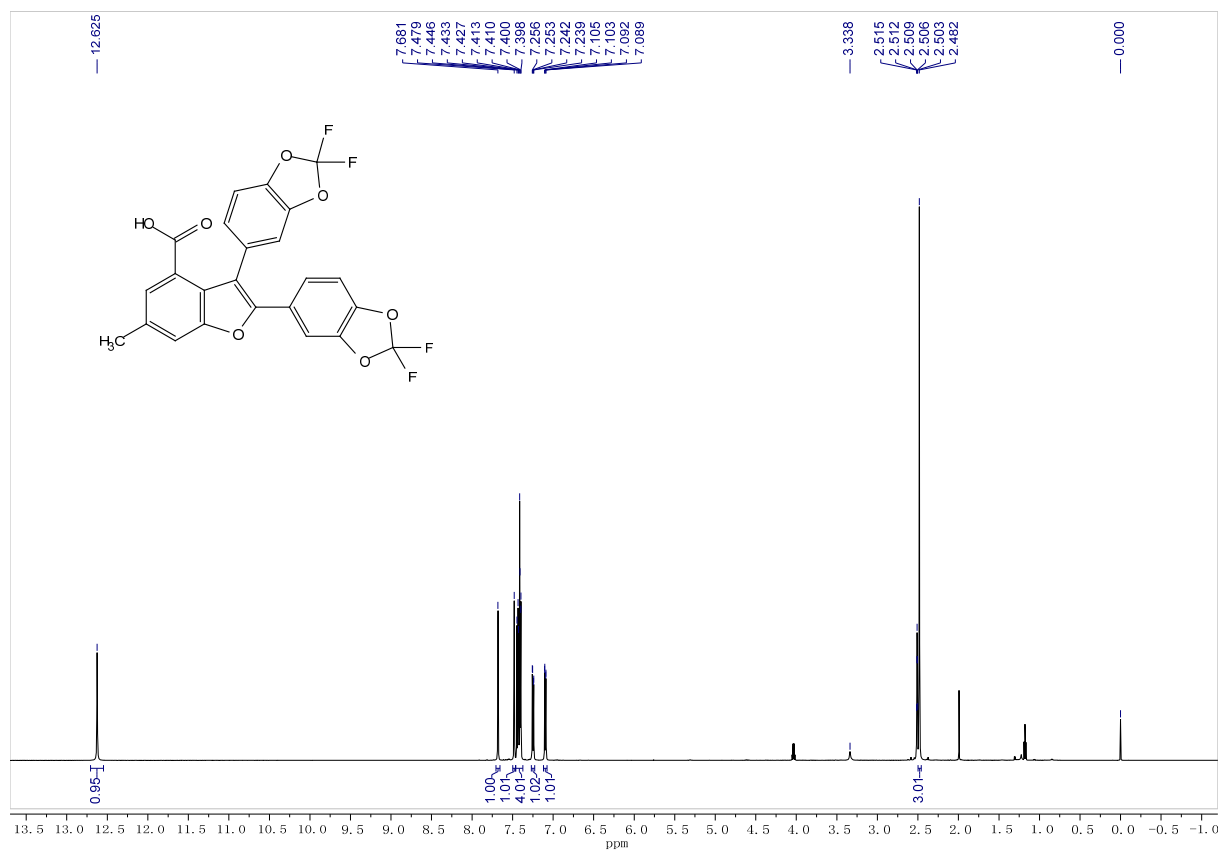
¹H NMR spectrum of **3aj** (600 MHz, DMSO-*d*₆)



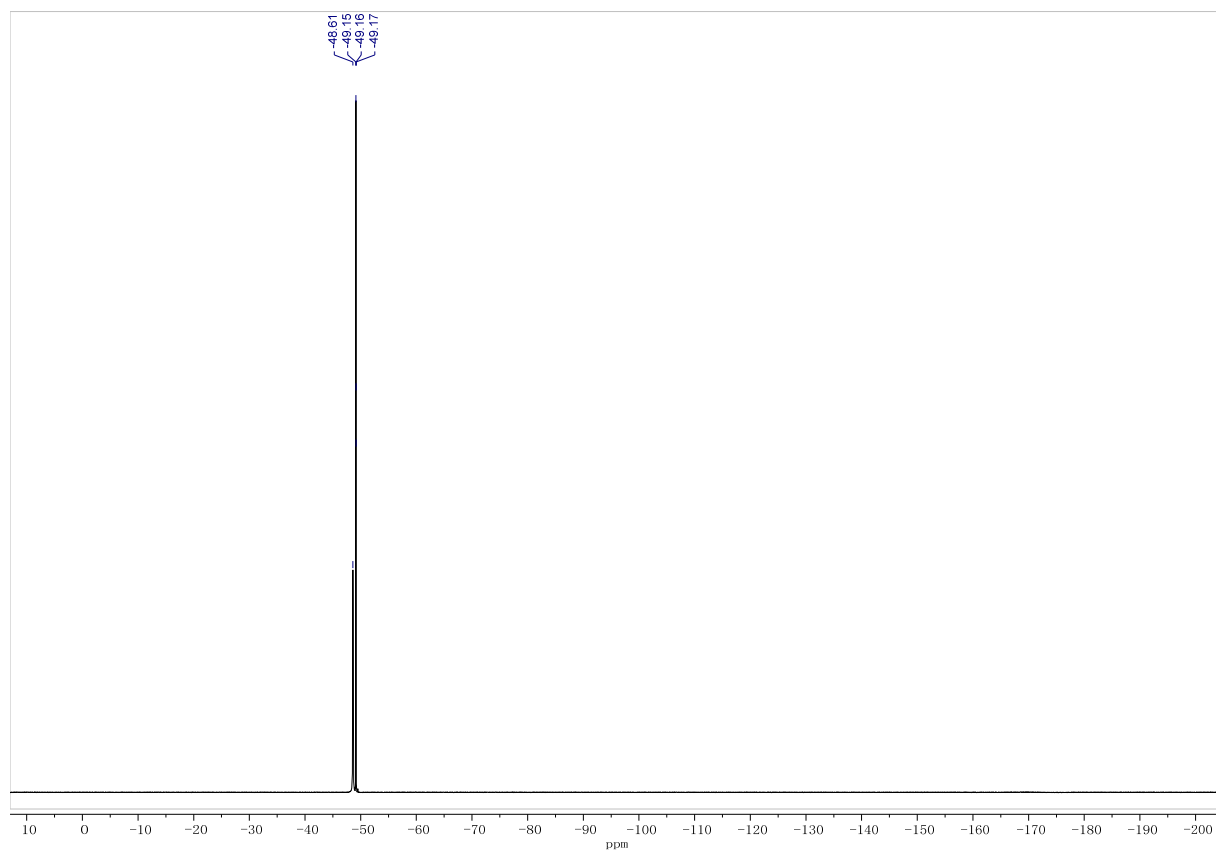
¹³C NMR spectrum of **3aj** (151 MHz, DMSO-*d*₆)



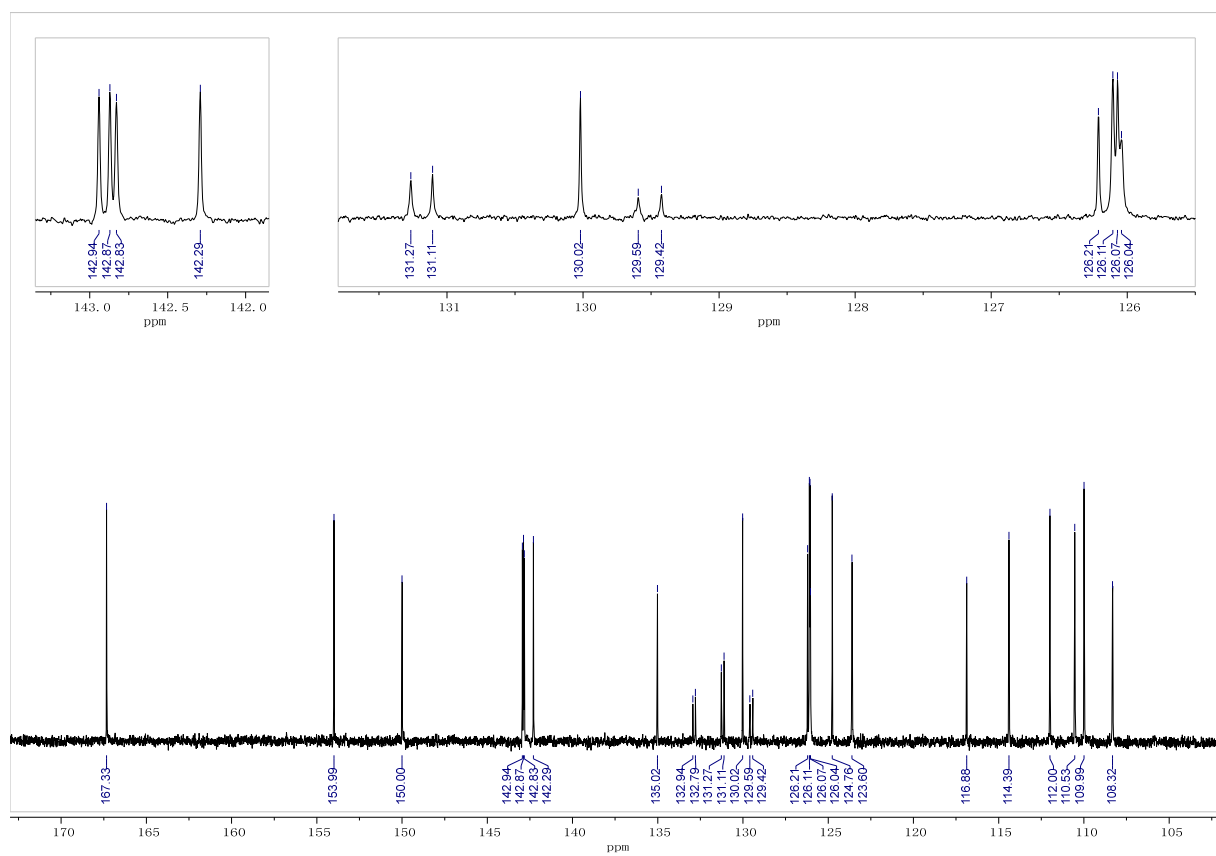
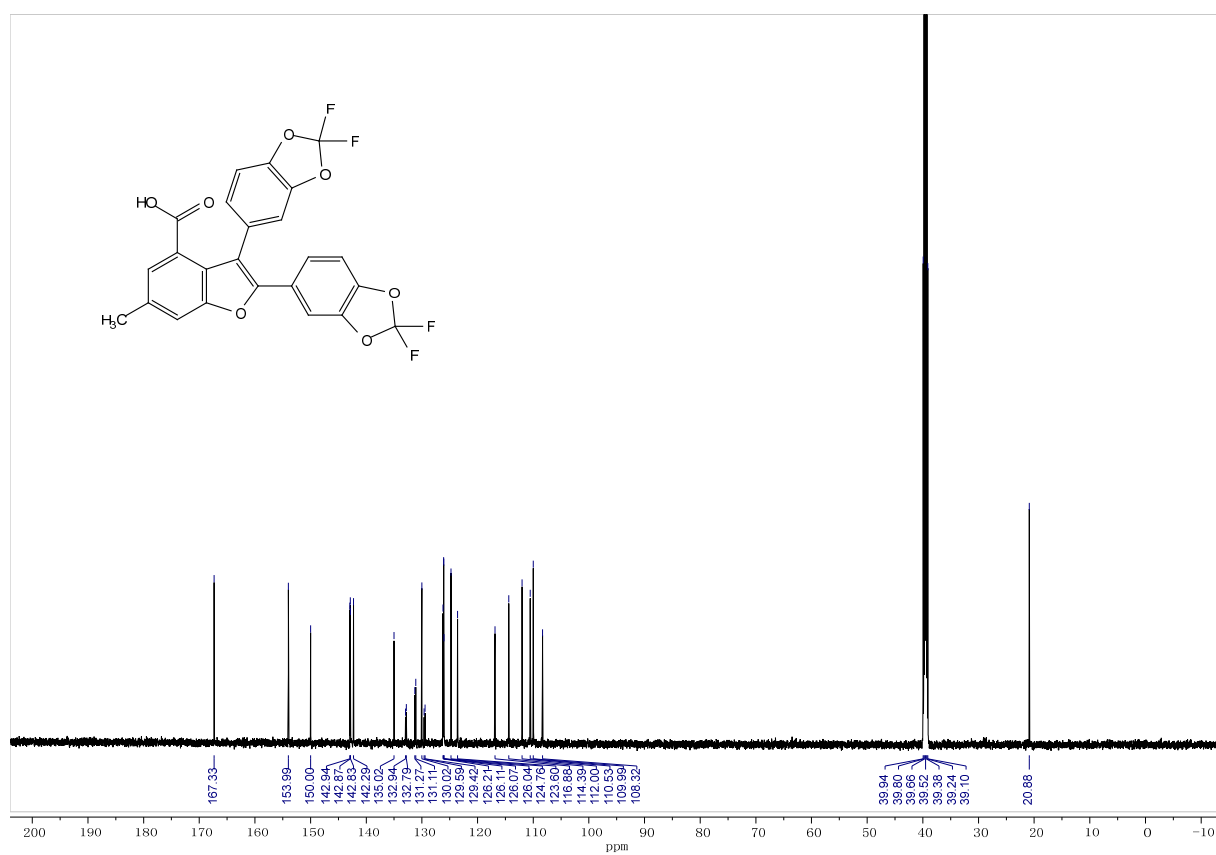
¹H NMR spectrum of **3ak** (600 MHz, DMSO-*d*₆)



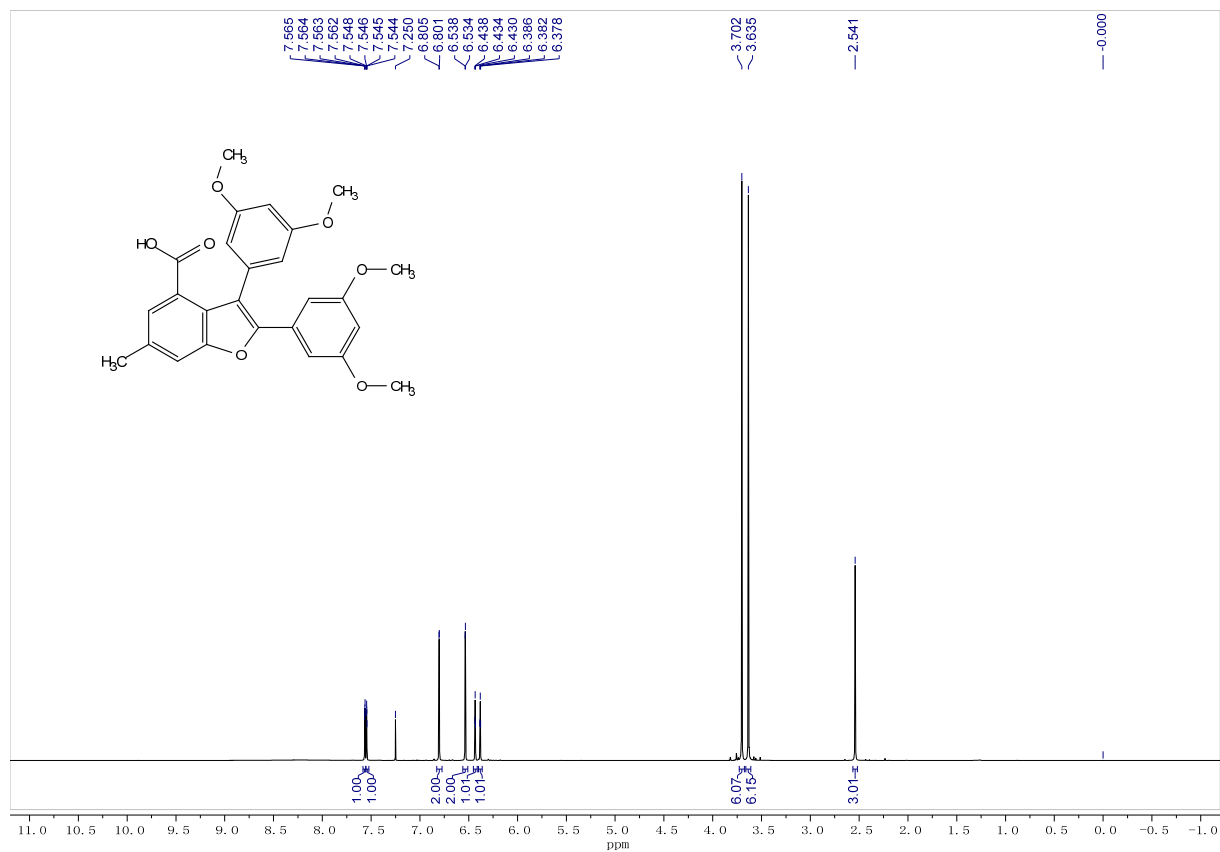
¹⁹F NMR spectrum of **3ak** (565 MHz, DMSO-*d*₆)



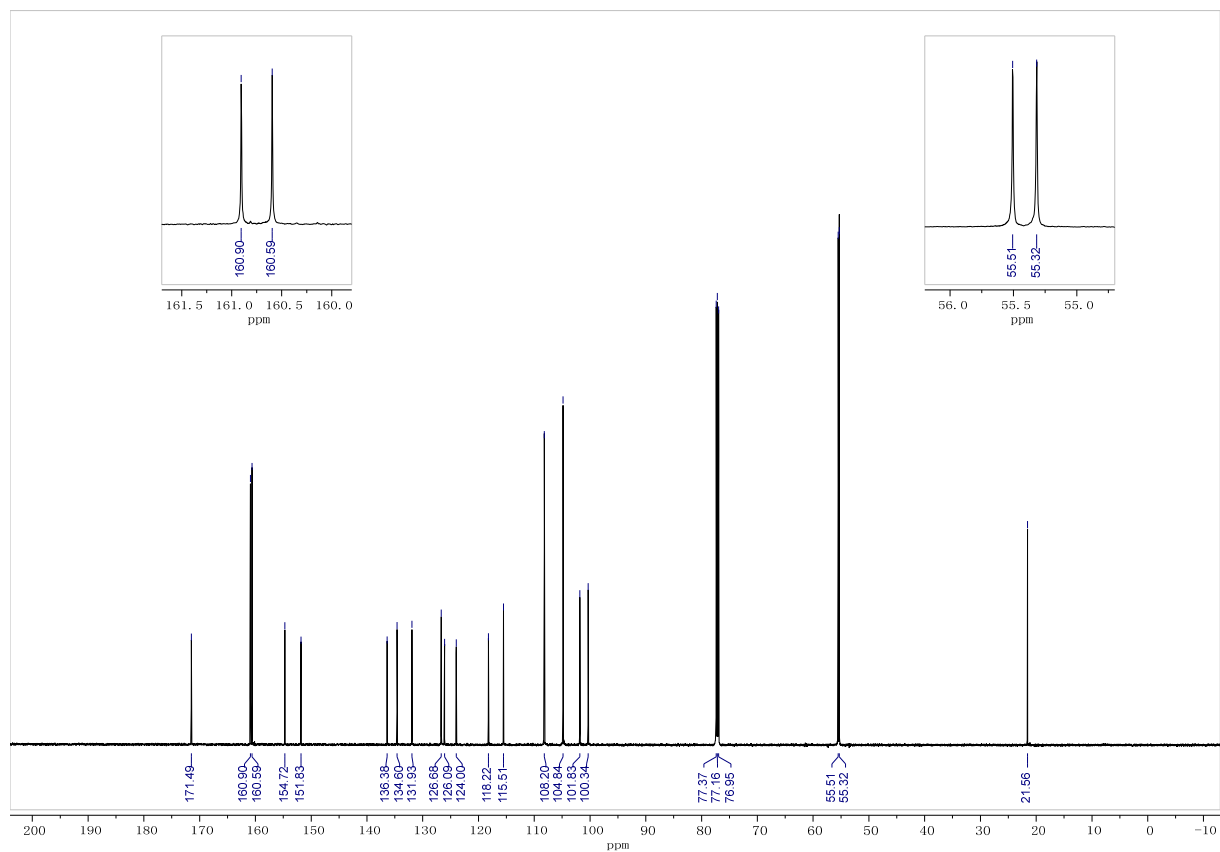
¹³C NMR spectrum of **3ak** (151 MHz, DMSO-*d*₆)



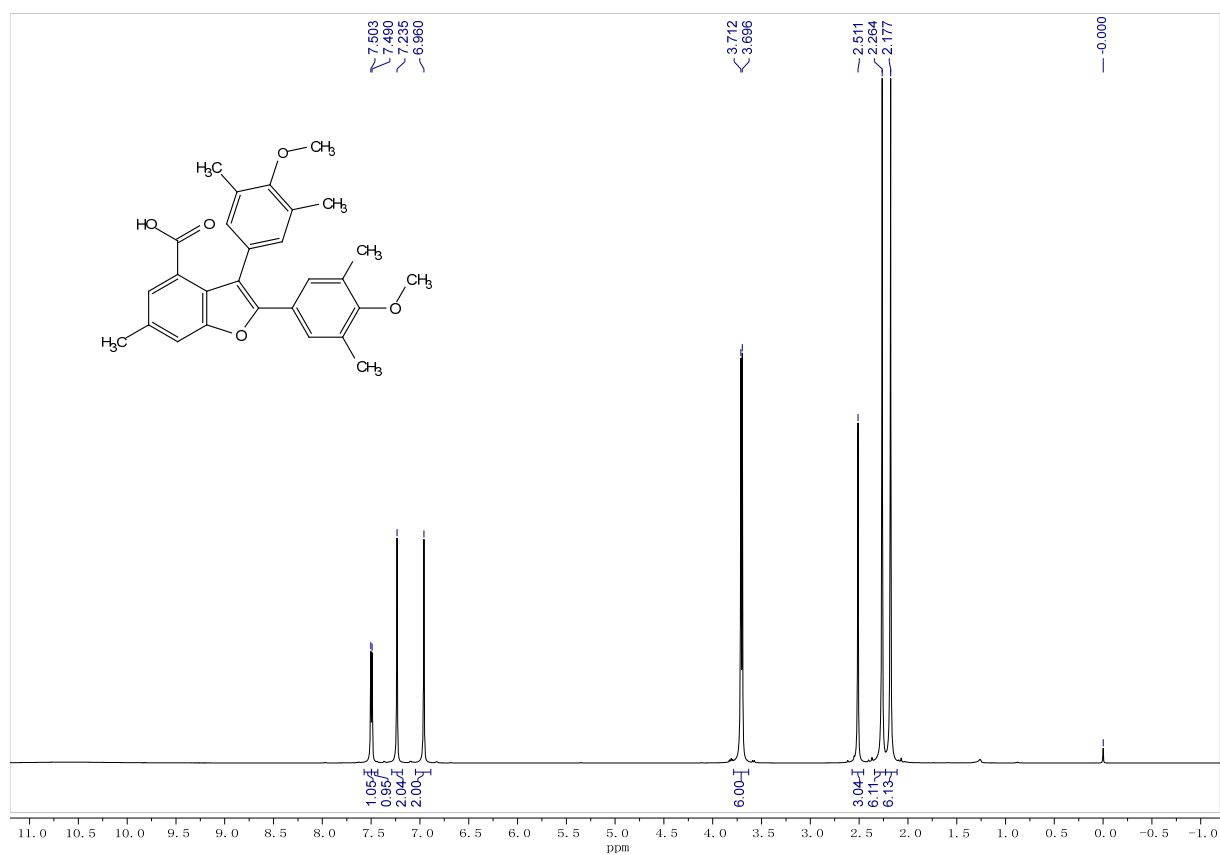
^1H NMR spectrum of **3al** (600 MHz, CDCl_3)



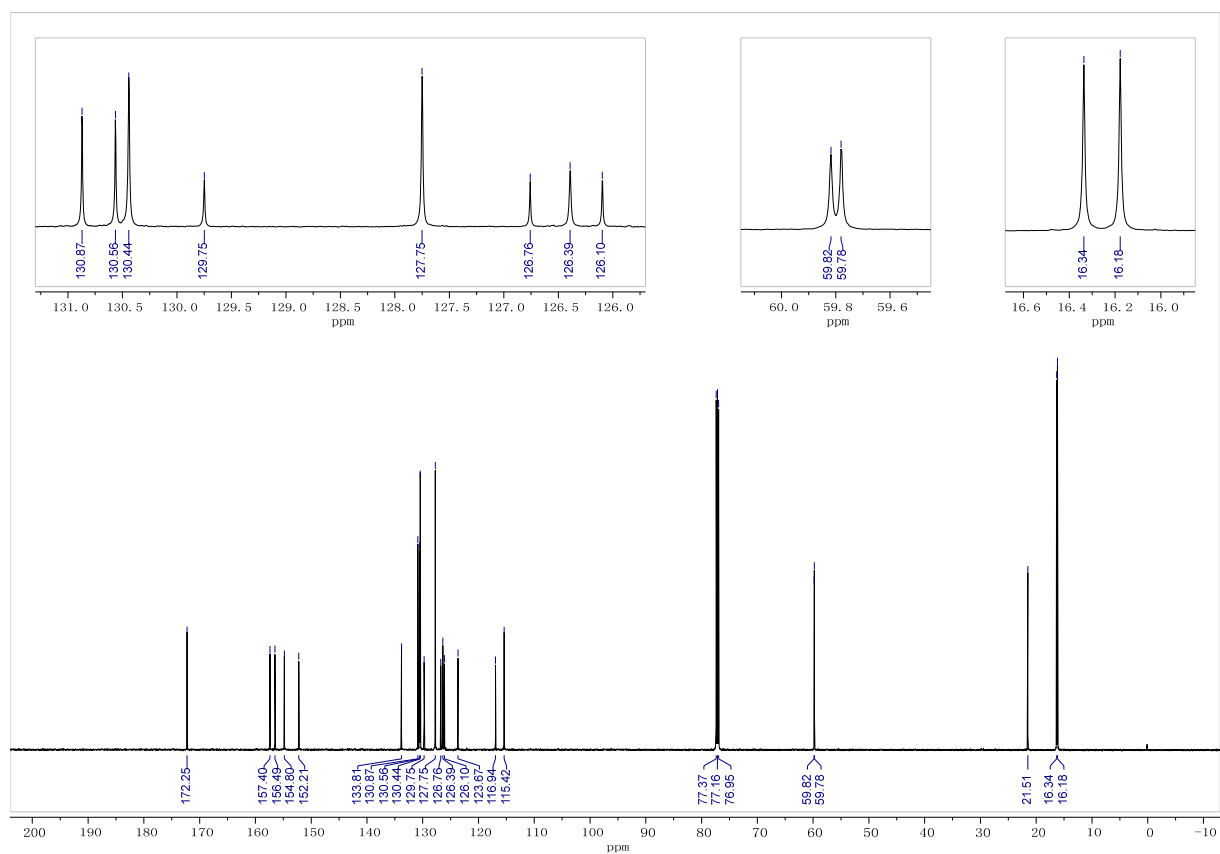
^{13}C NMR spectrum of **3al** (151 MHz, CDCl_3)



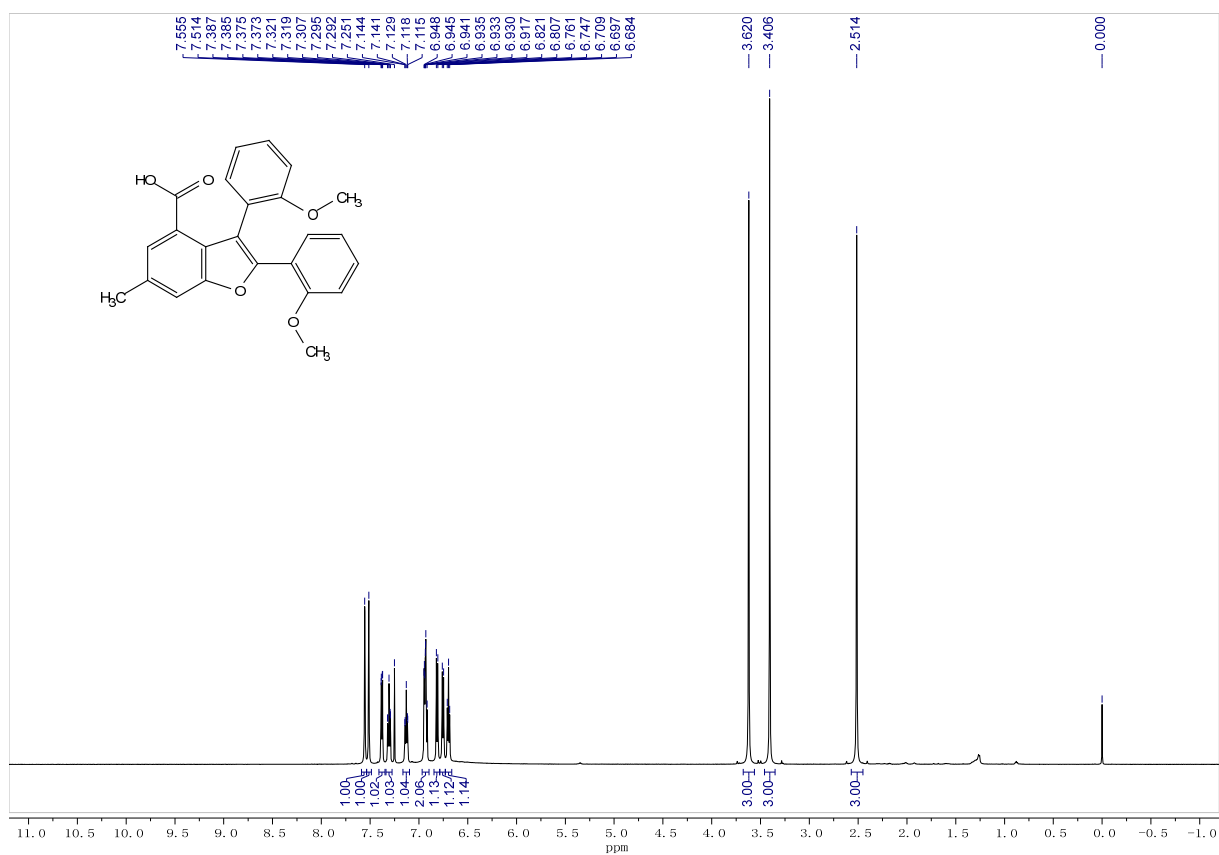
¹H NMR spectrum of **3am** (600 MHz, CDCl₃)



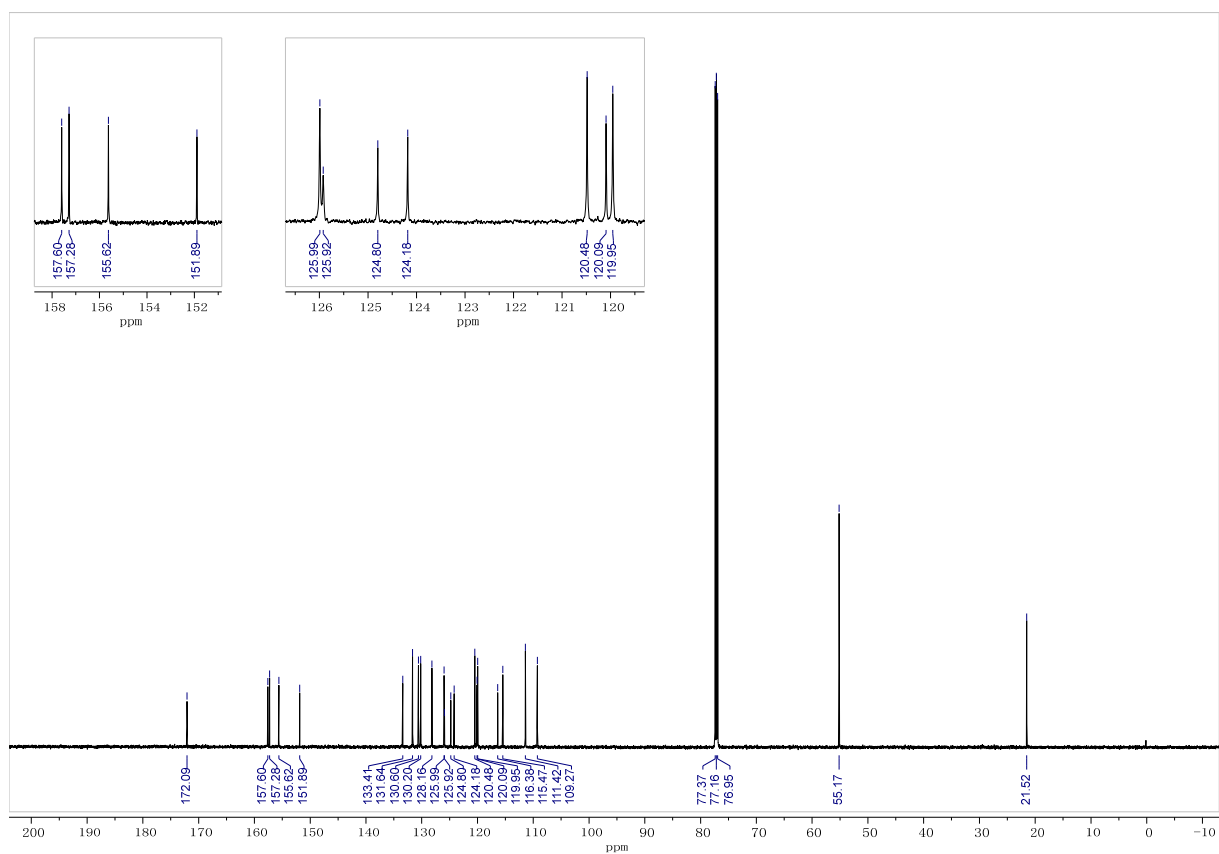
¹³C NMR spectrum of **3am** (151 MHz, CDCl₃)



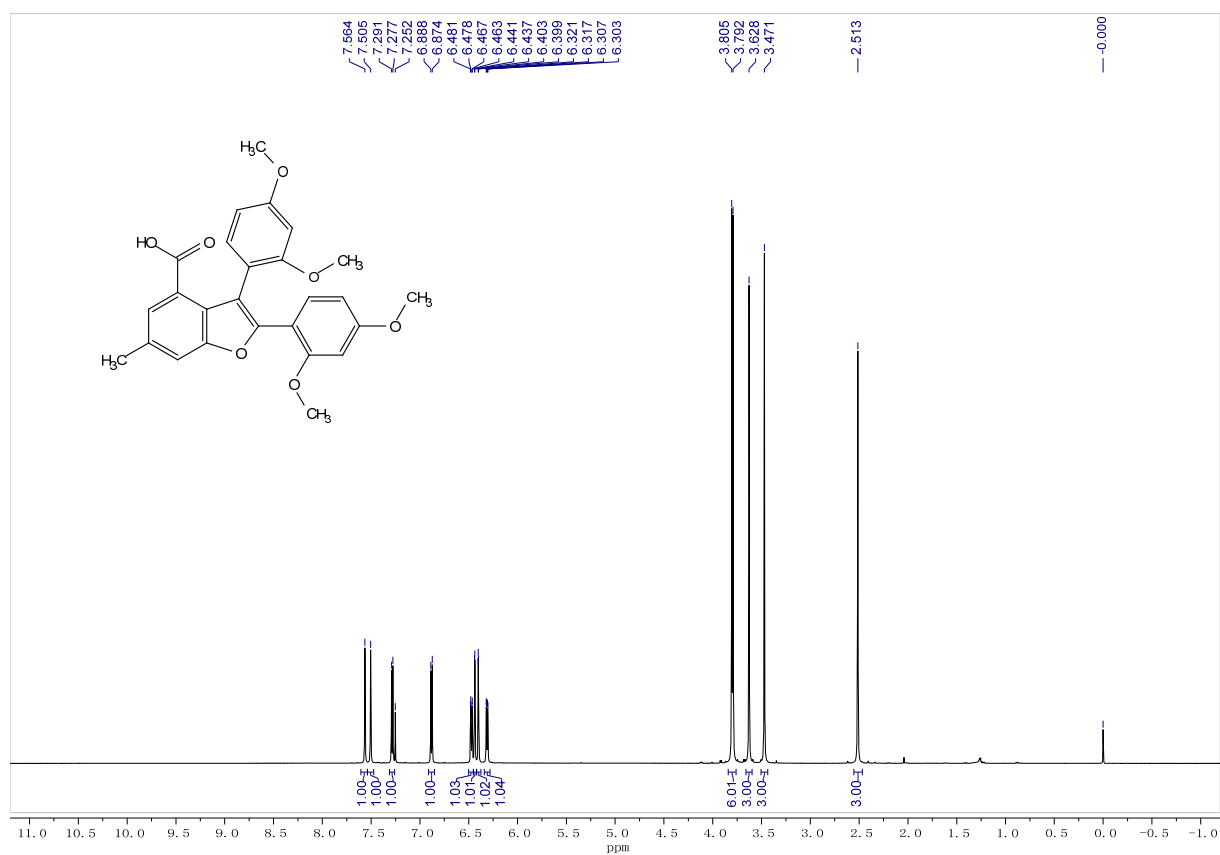
^1H NMR spectrum of **3an** (600 MHz, CDCl_3)



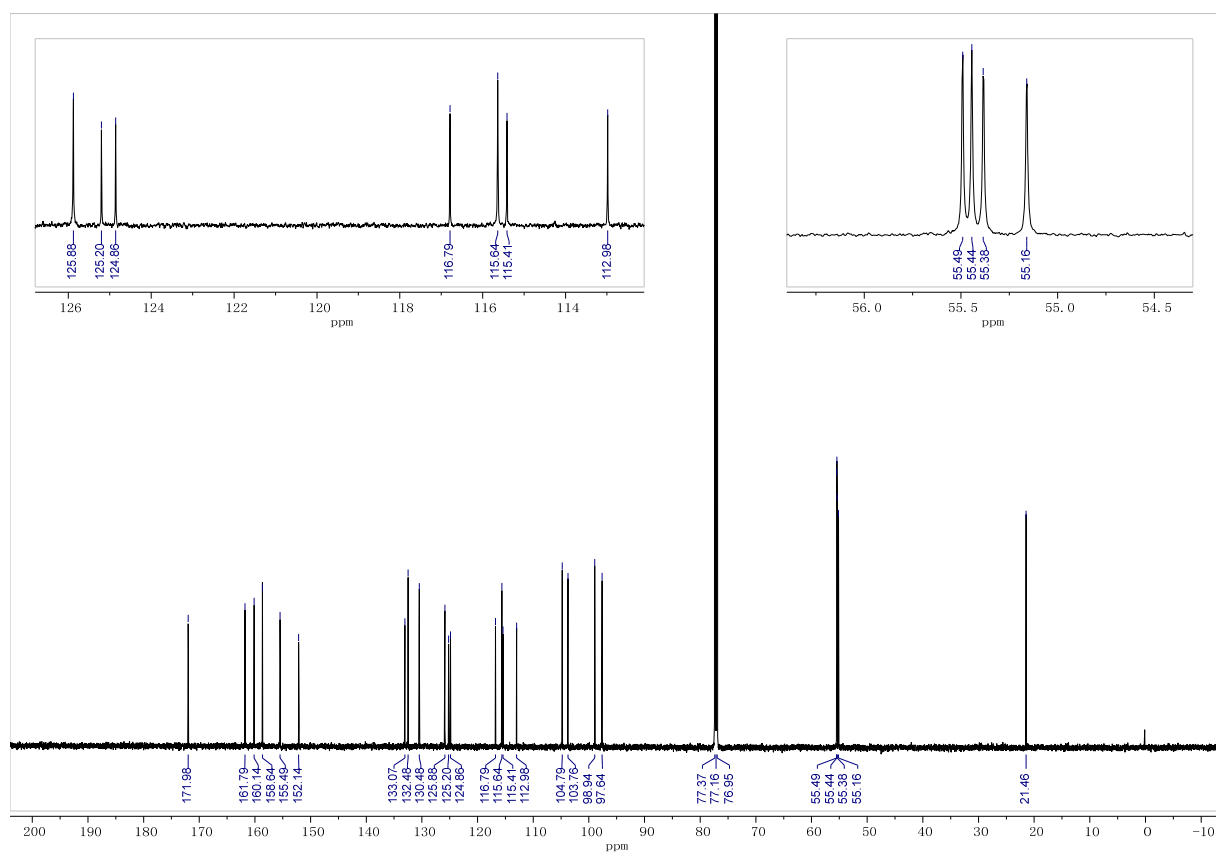
^{13}C NMR spectrum of **3an** (151 MHz, CDCl_3)



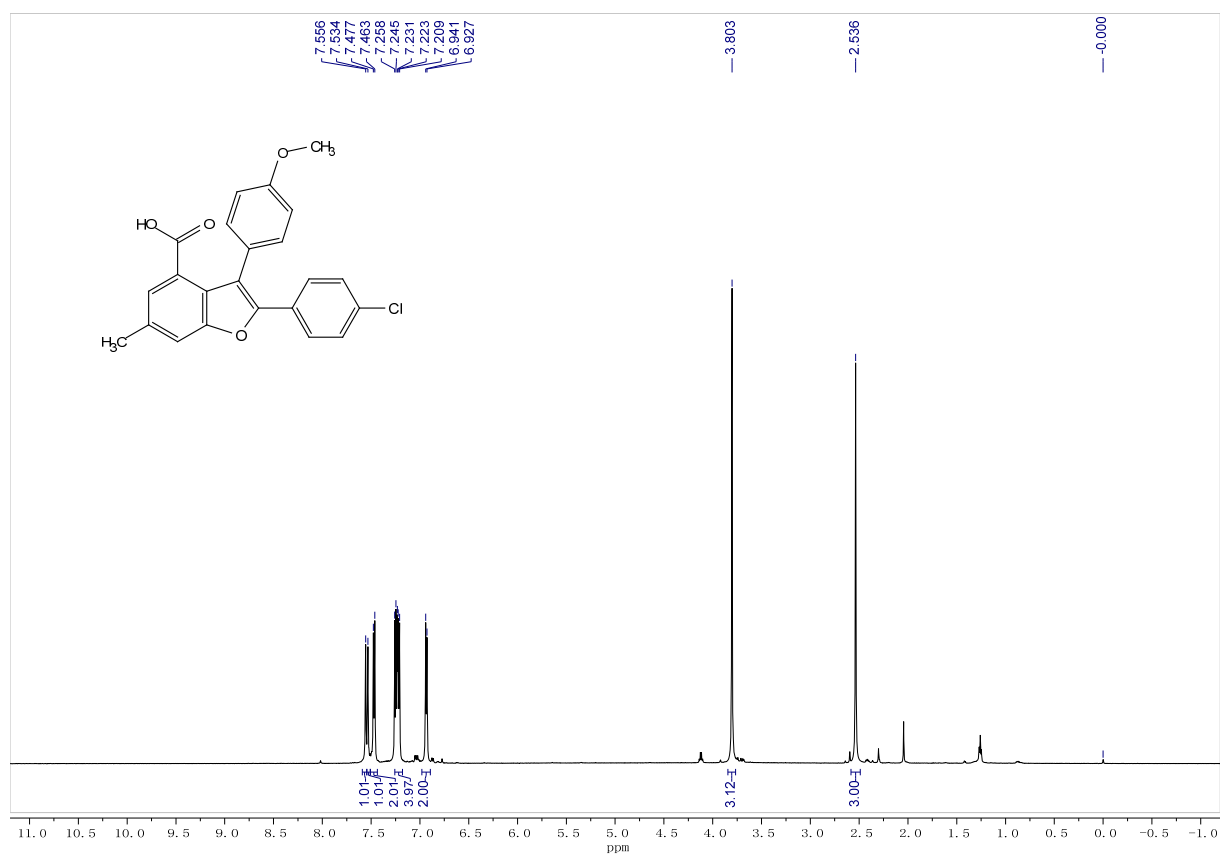
^1H NMR spectrum of **3ao** (600 MHz, CDCl_3)



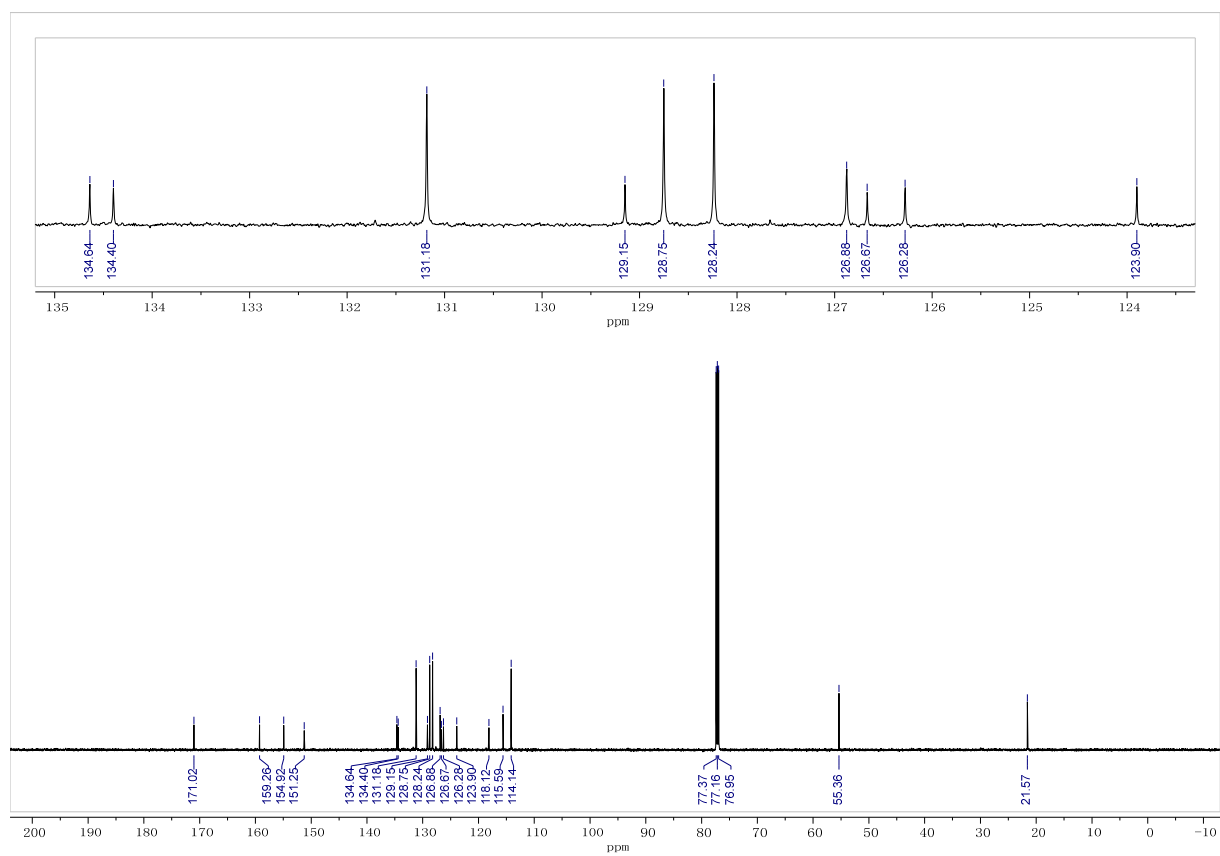
^{13}C NMR spectrum of **3ao** (151 MHz, CDCl_3)



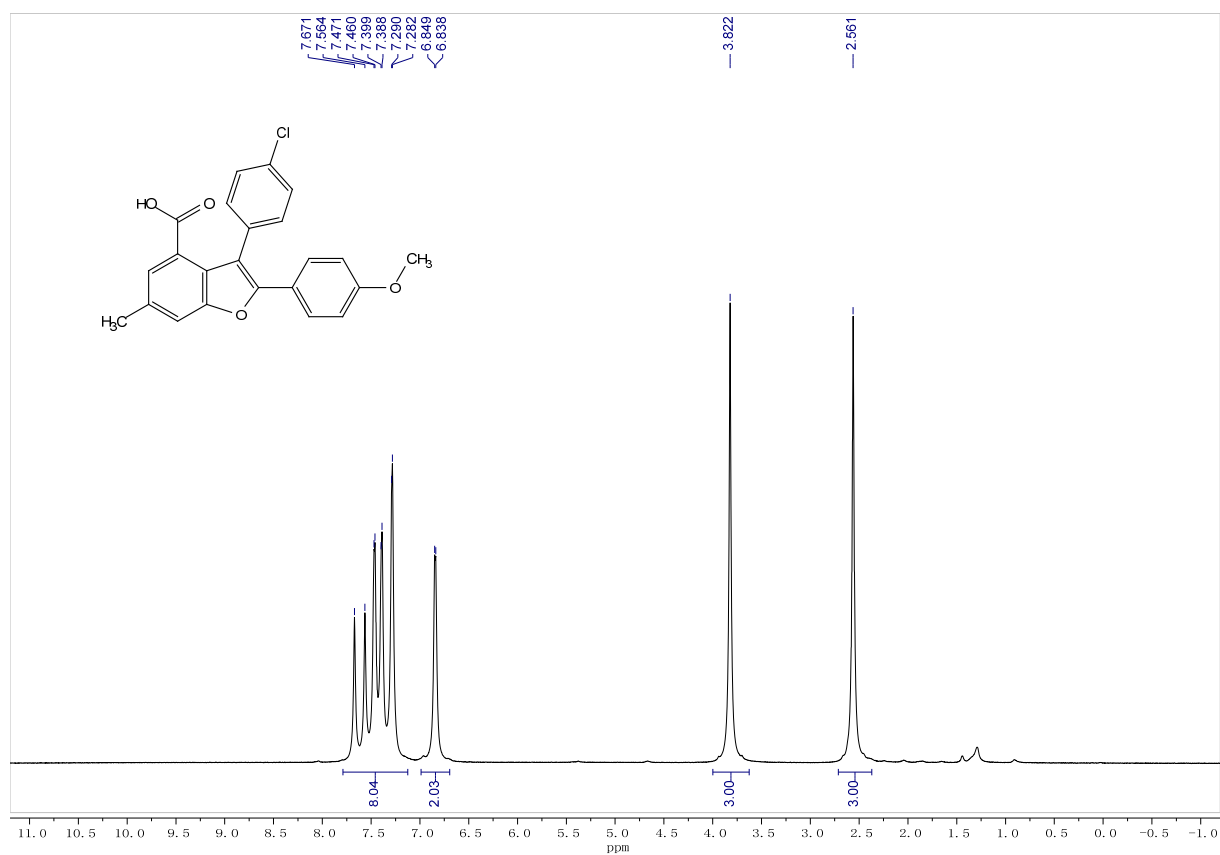
^1H NMR spectrum of **3ap** (600 MHz, CDCl_3)



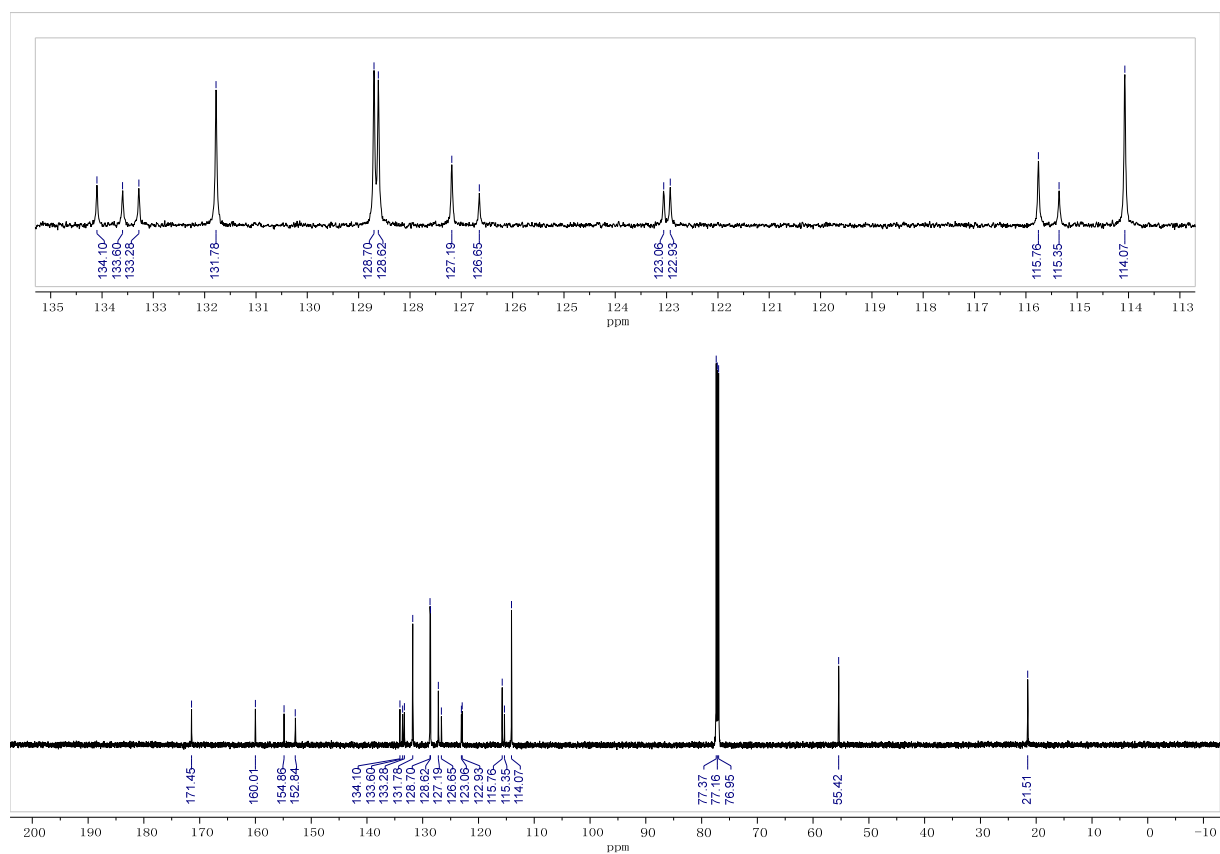
^{13}C NMR spectrum of **3ap** (151 MHz, CDCl_3)



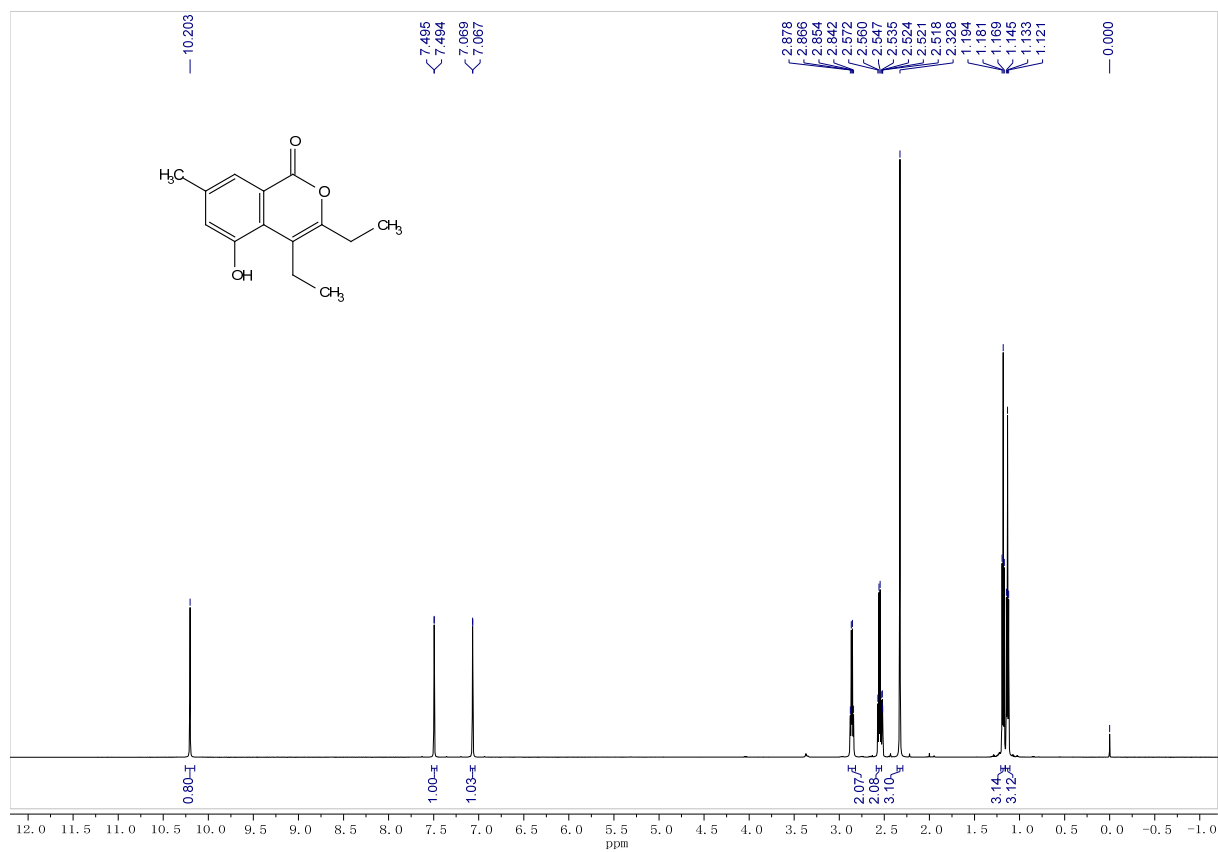
¹H NMR spectrum of **3ap'** (600 MHz, CDCl₃)



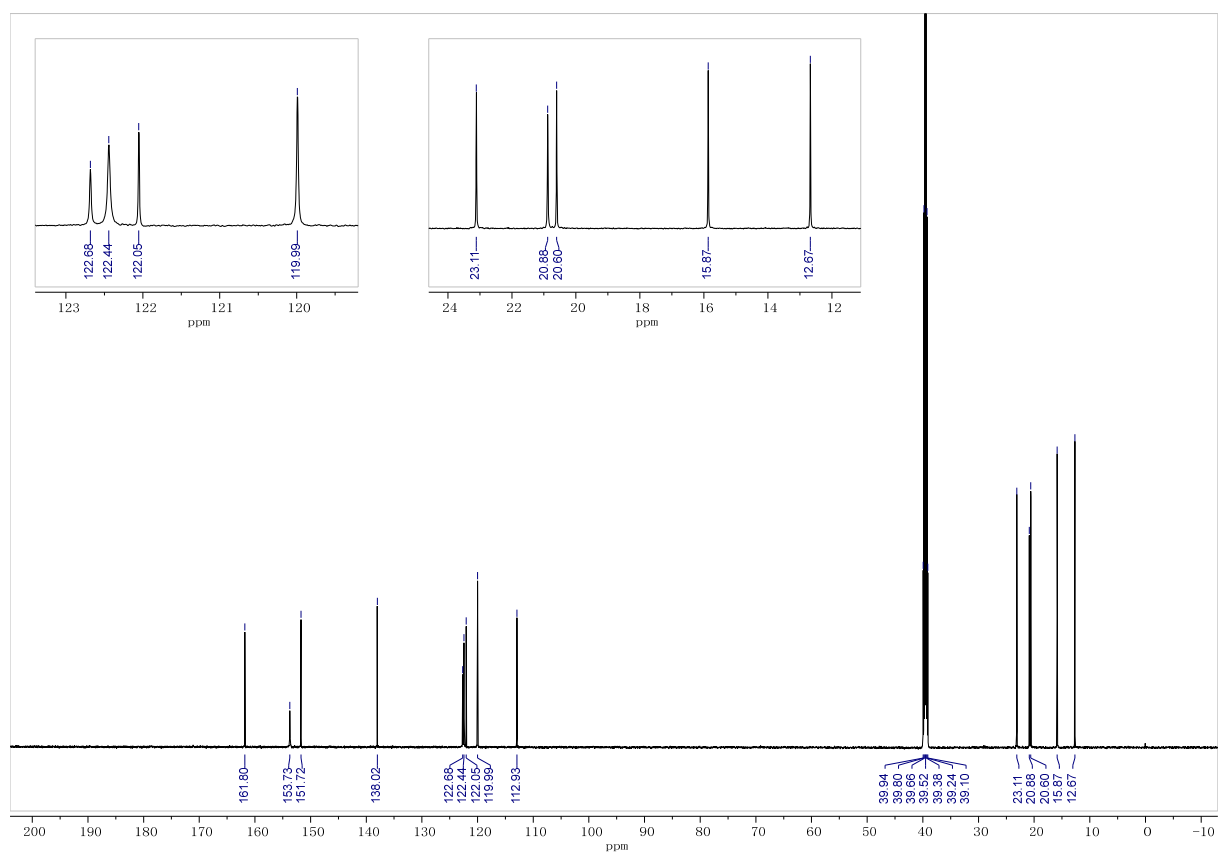
¹³C NMR spectrum of **3ap'** (151 MHz, CDCl₃)



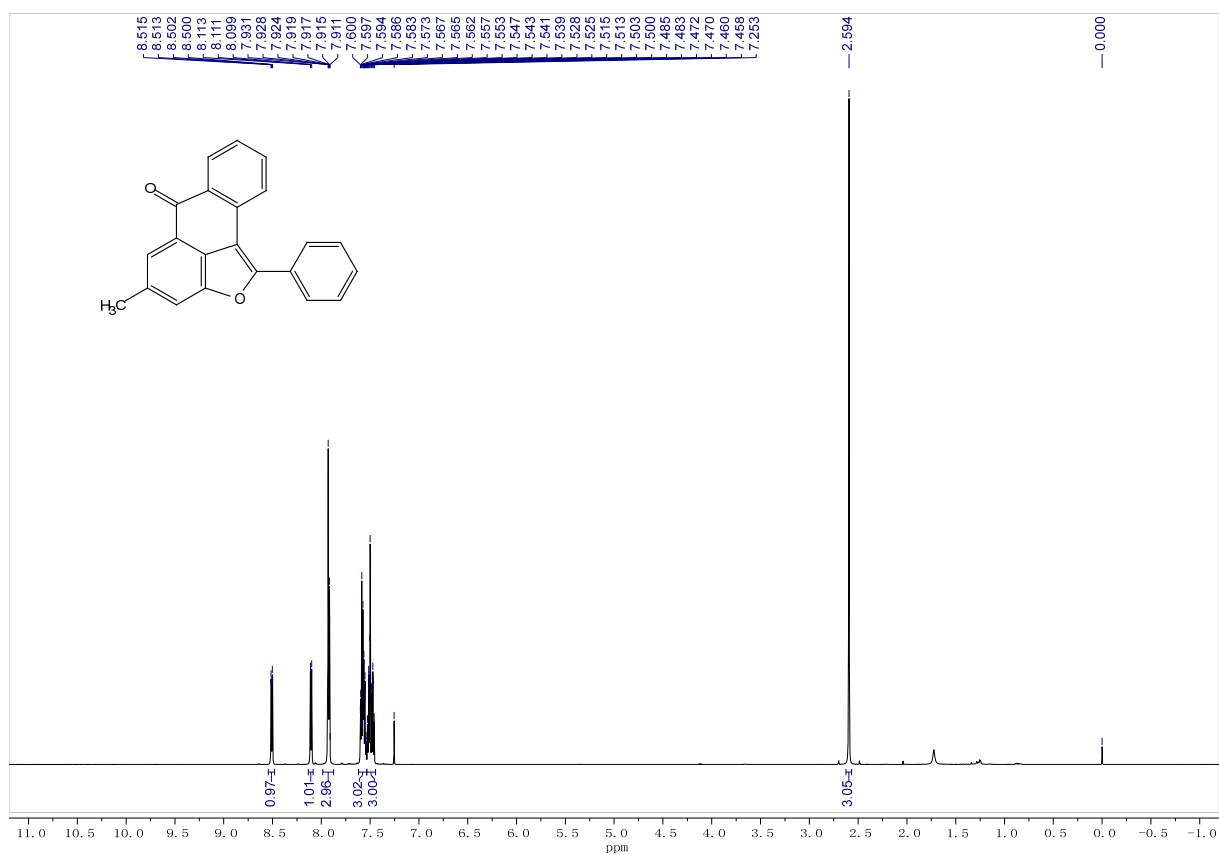
^1H NMR spectrum of **4aq** (600 MHz, $\text{DMSO-}d_6$)



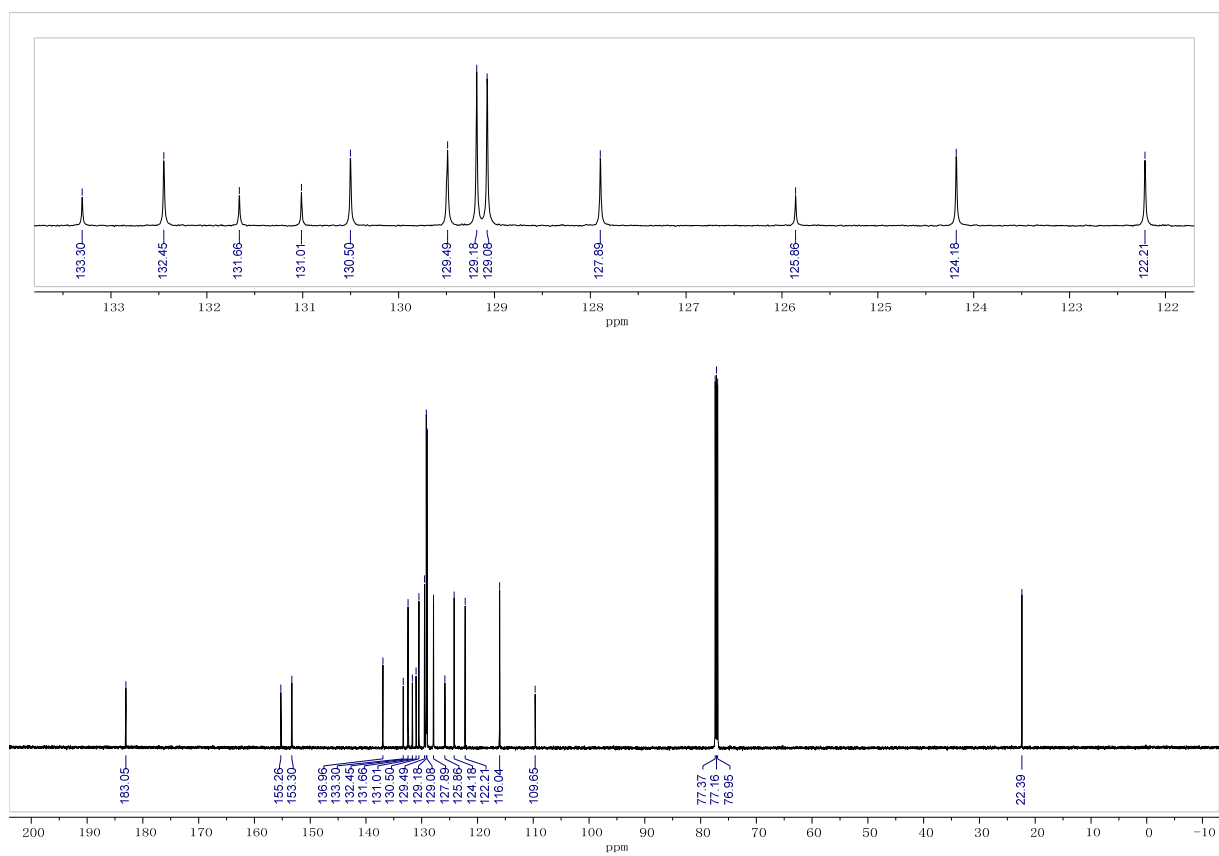
^{13}C NMR spectrum of **4aq** (151 MHz, $\text{DMSO-}d_6$)



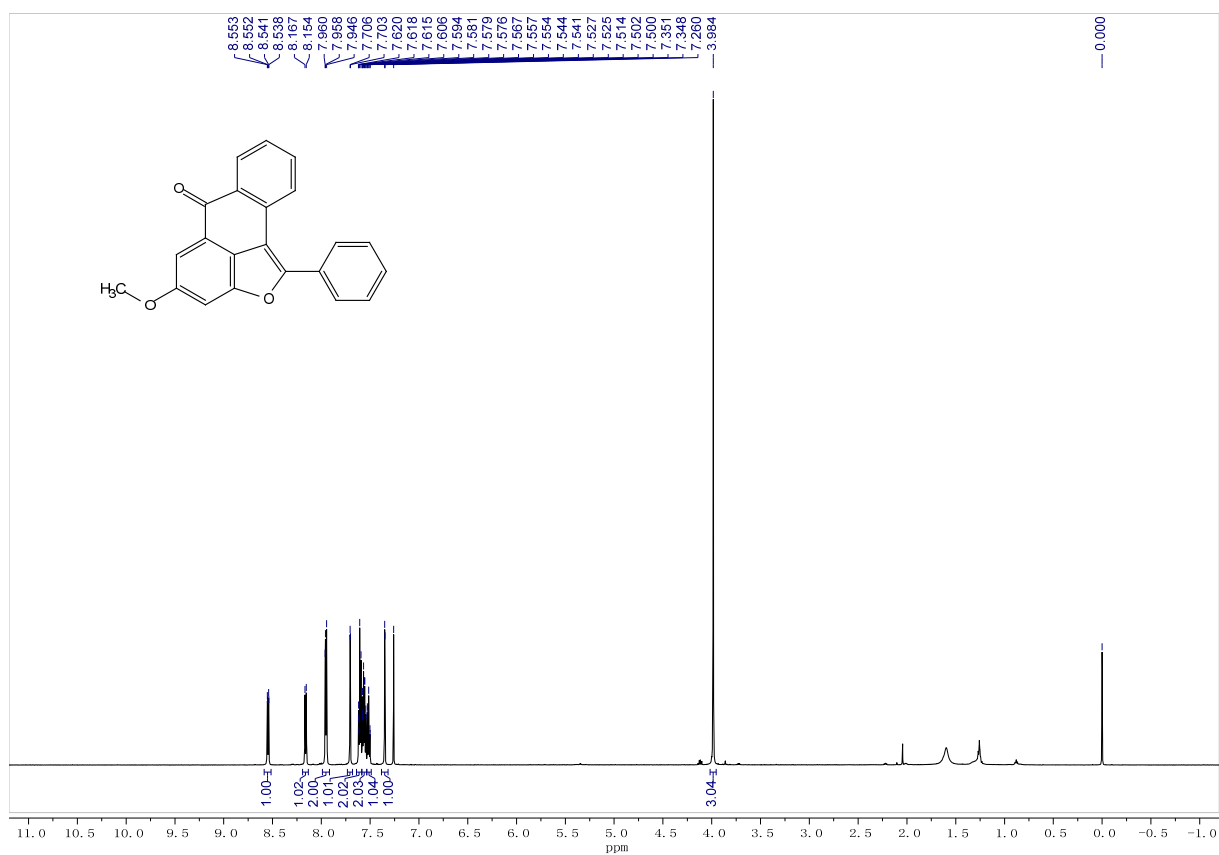
¹H NMR spectrum of **6aa** (600 MHz, CDCl₃)



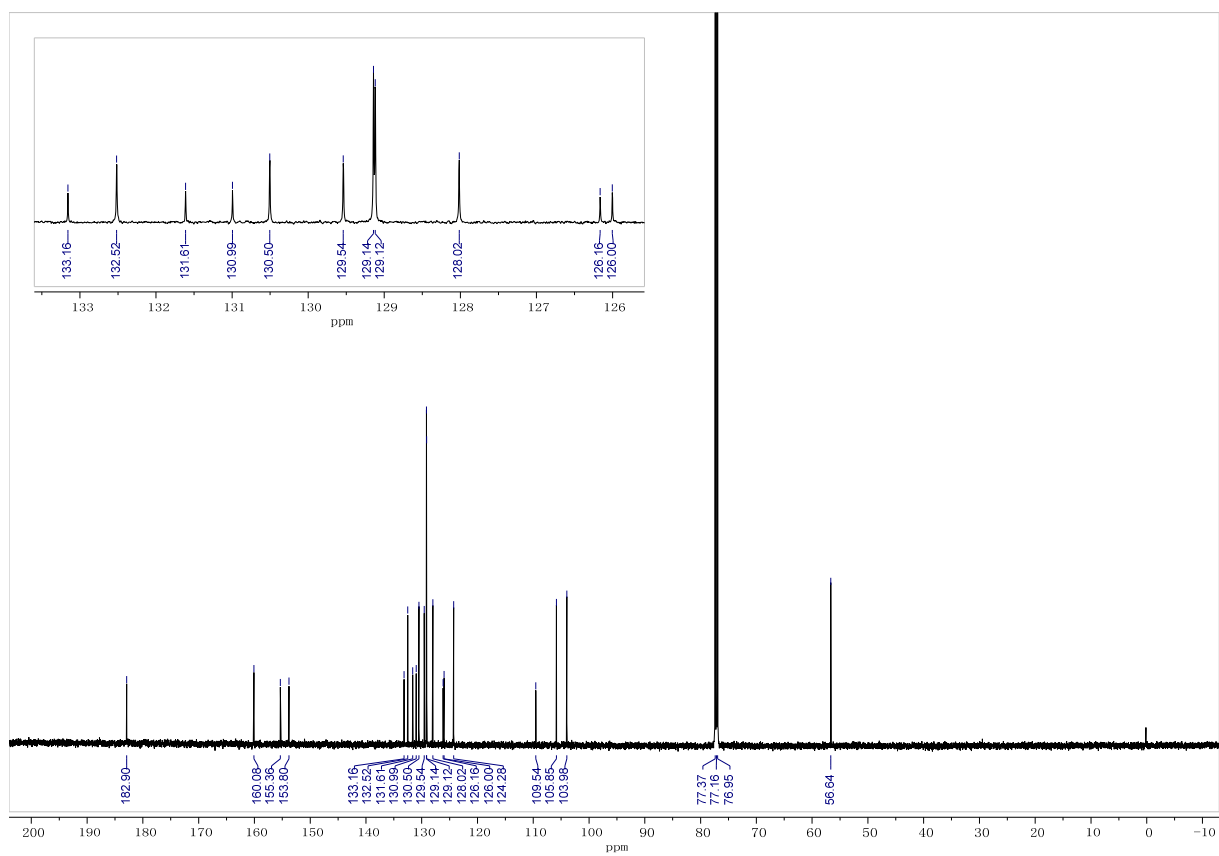
¹³C NMR spectrum of **6aa** (151 MHz, CDCl₃)



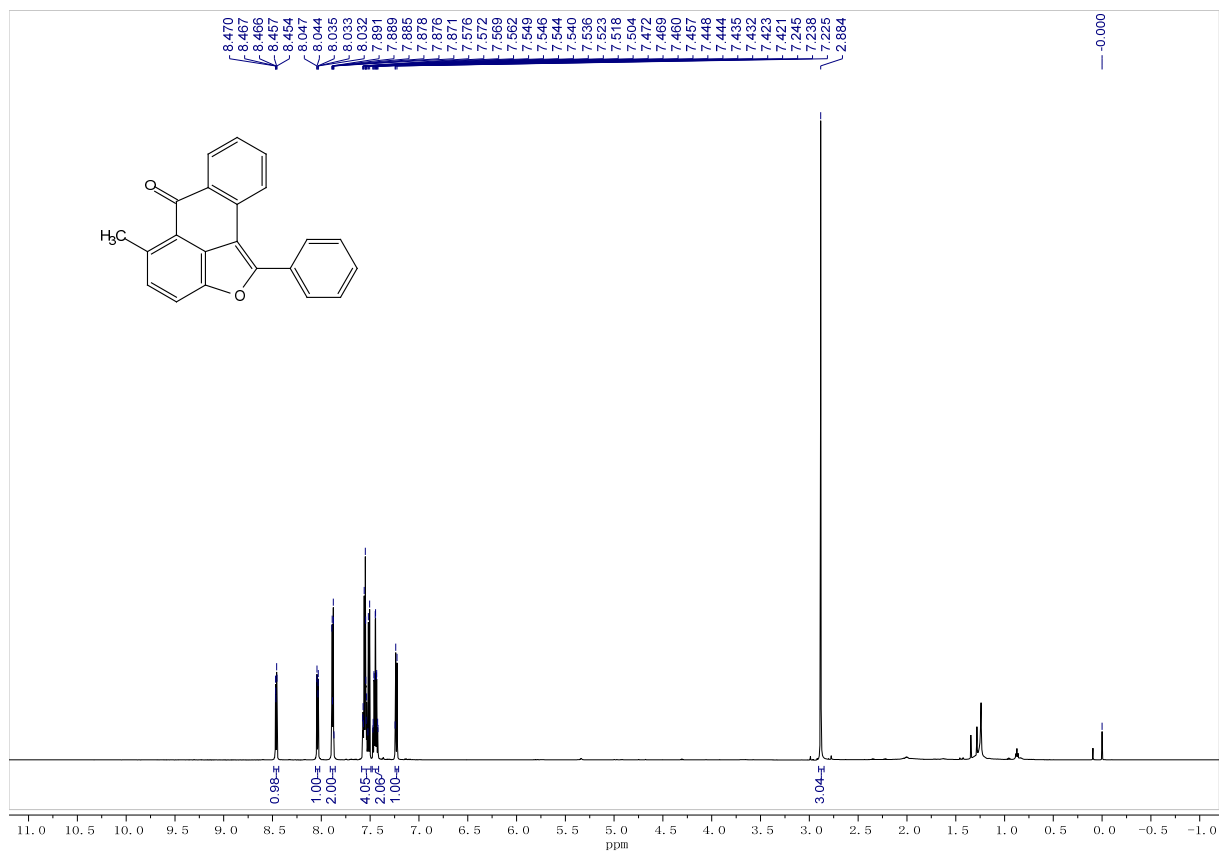
¹H NMR spectrum of **6ca** (600 MHz, CDCl₃)



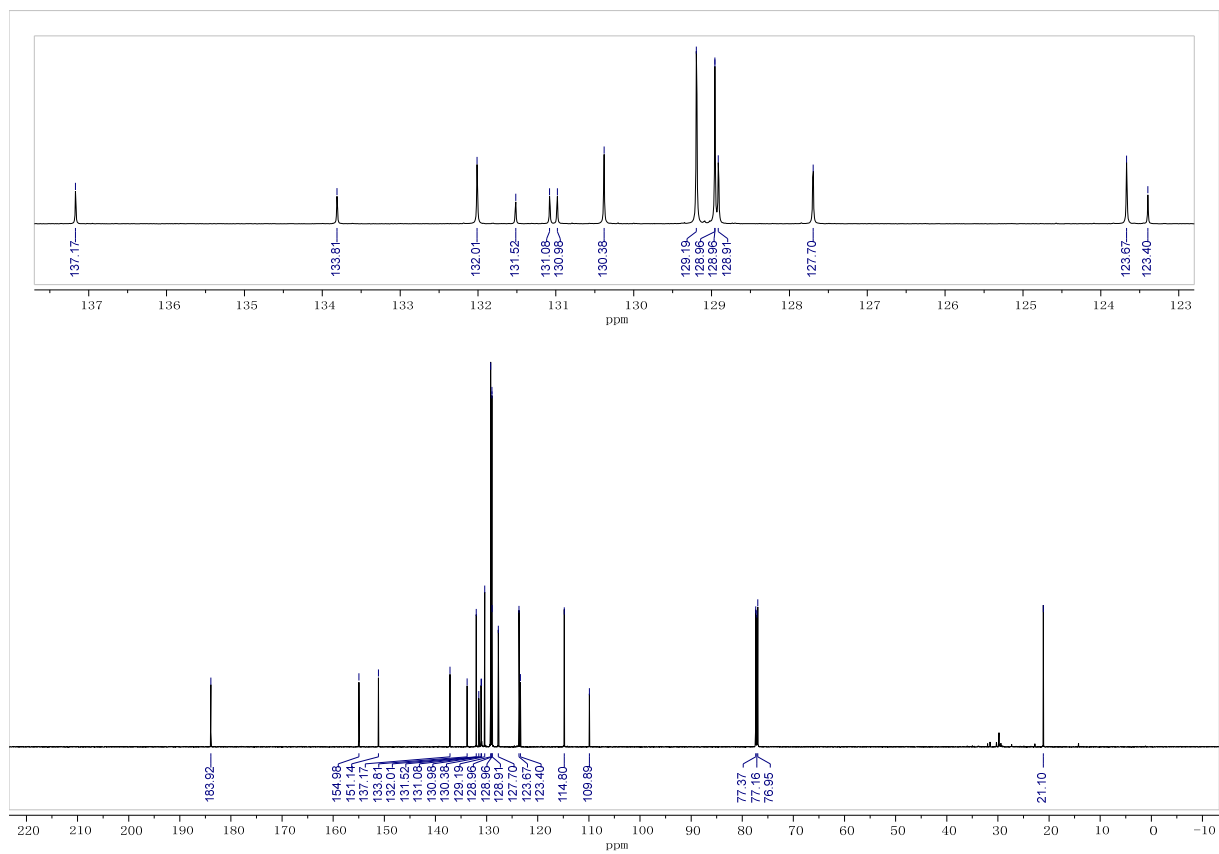
¹³C NMR spectrum of **6ca** (151 MHz, CDCl₃)



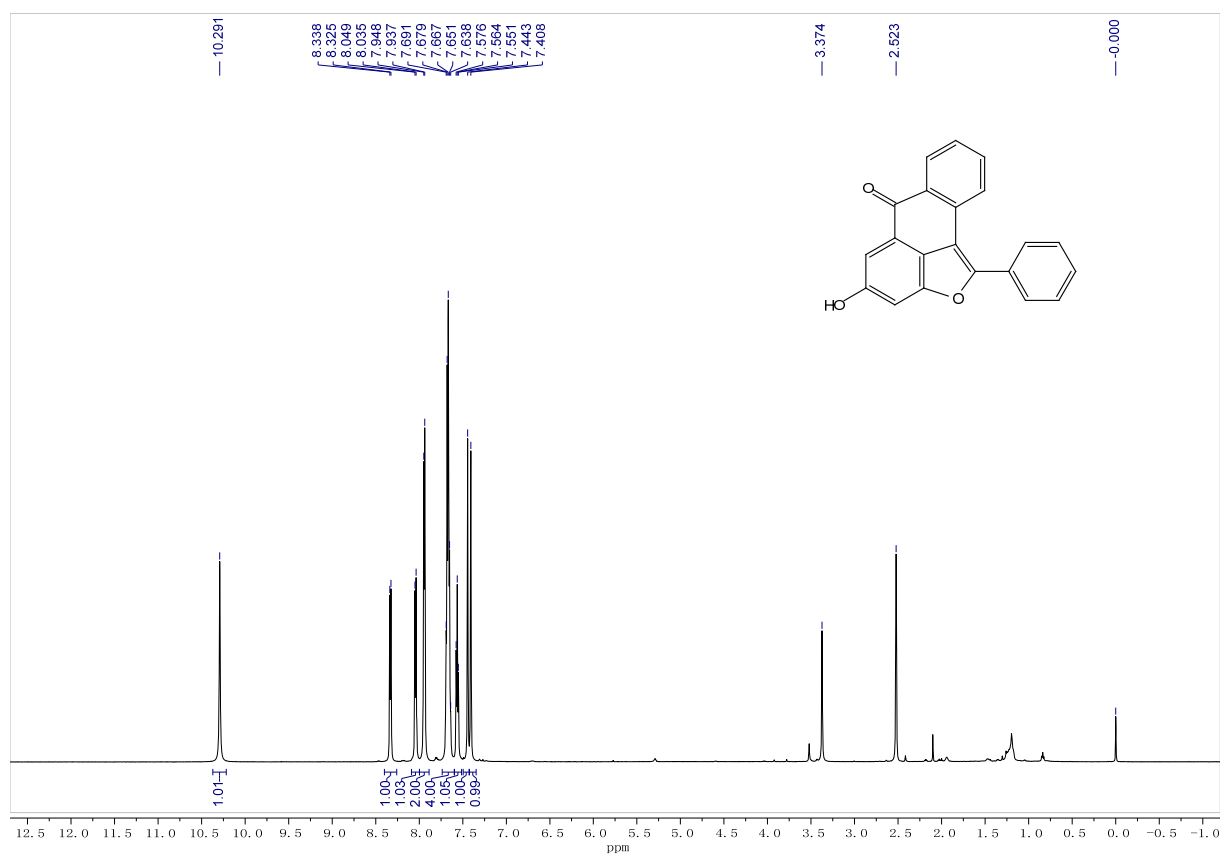
¹H NMR spectrum of **6ja** (600 MHz, CDCl₃)



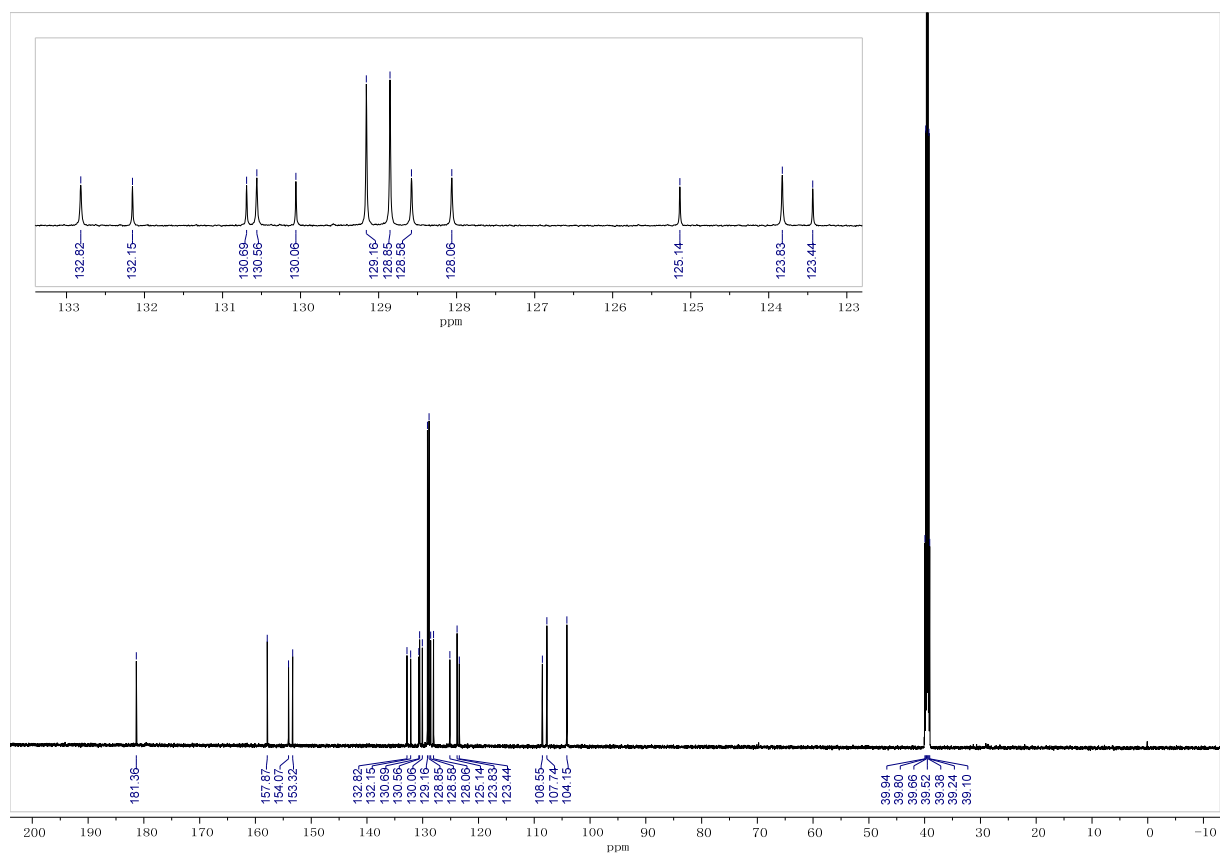
¹³C NMR spectrum of **6ja** (151 MHz, CDCl₃)



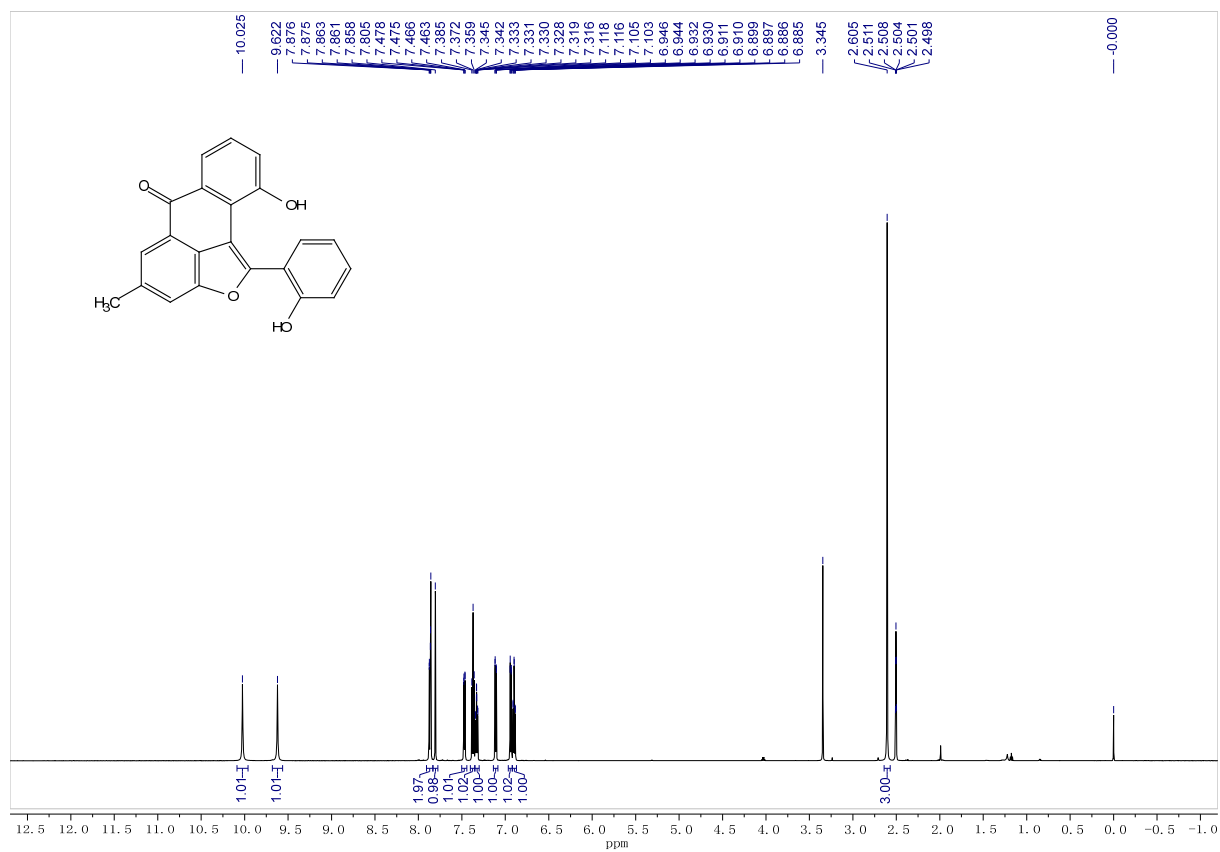
¹H NMR spectrum of **6ha** (600 MHz, DMSO-*d*₆)



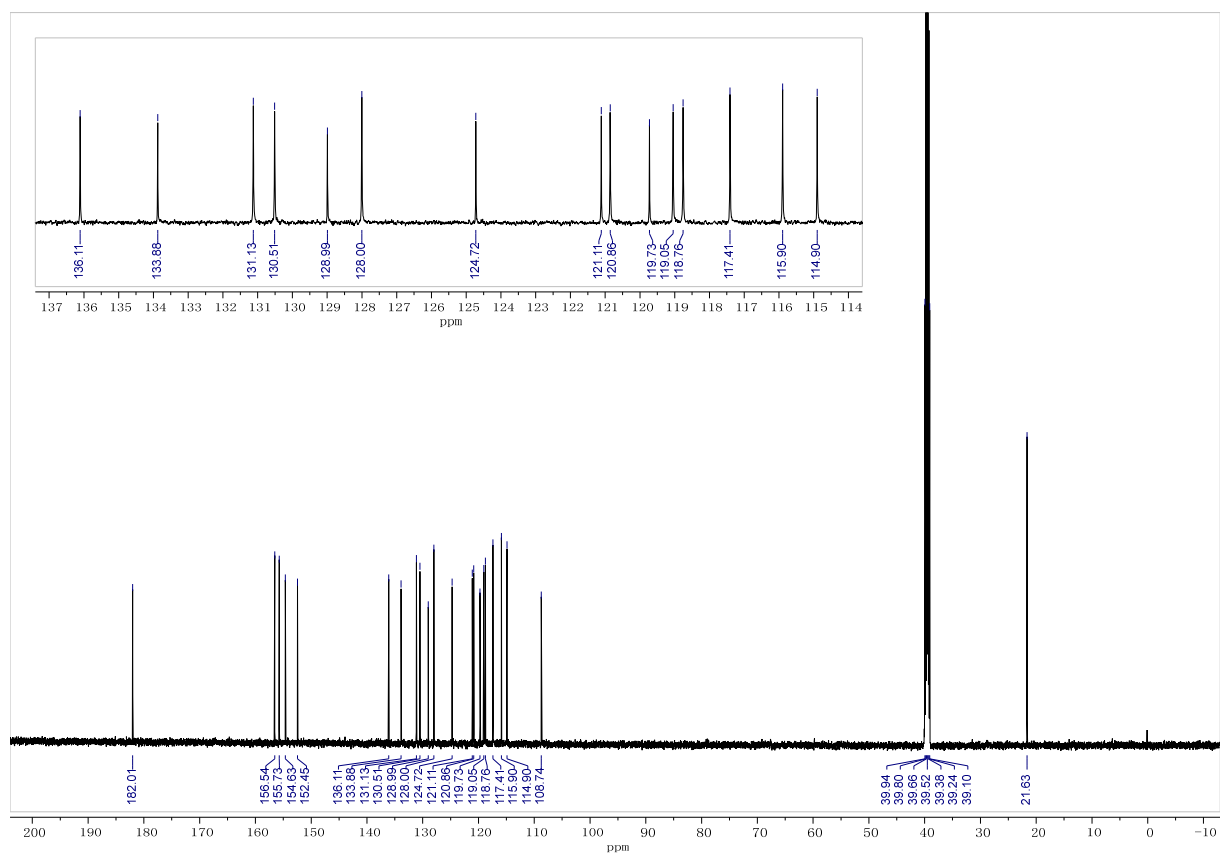
¹³C NMR spectrum of **6ha** (151 MHz, DMSO-*d*₆)



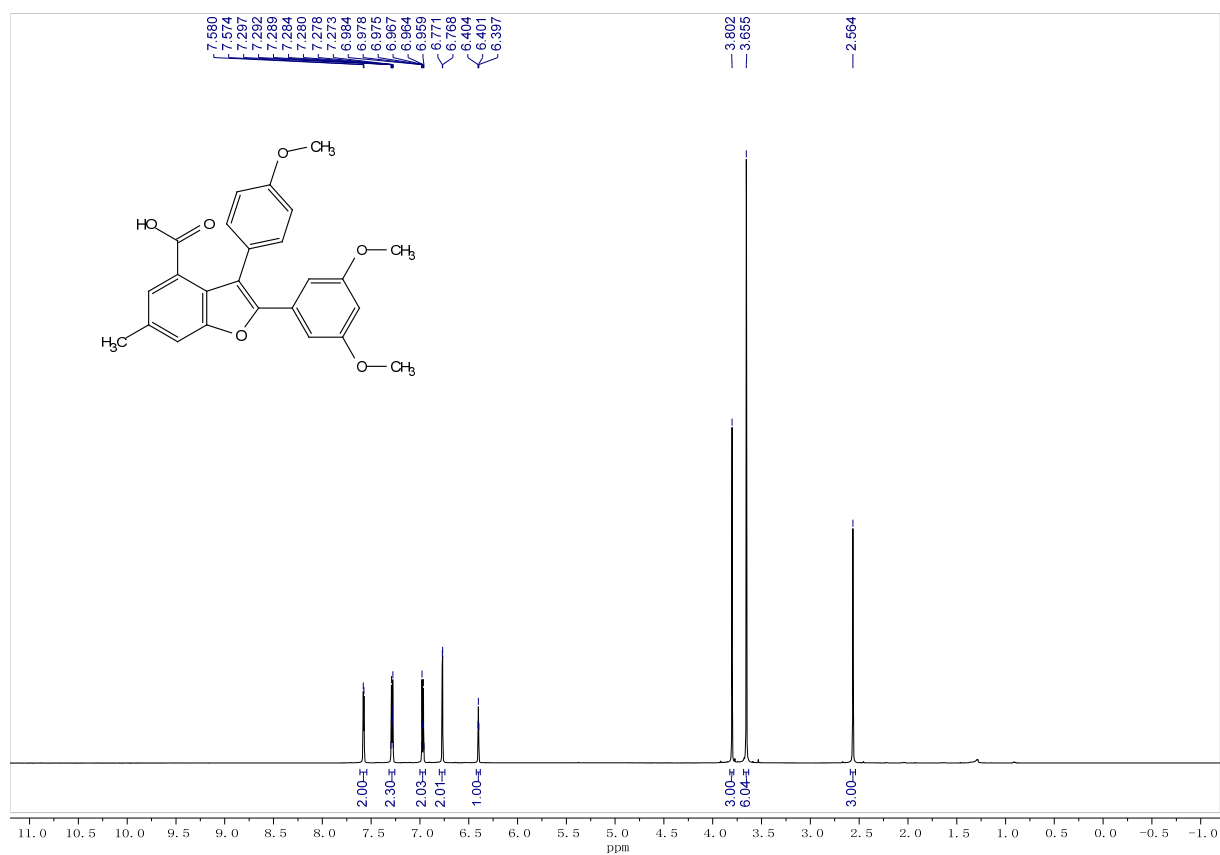
¹H NMR spectrum of **6an** (600 MHz, DMSO-*d*₆)



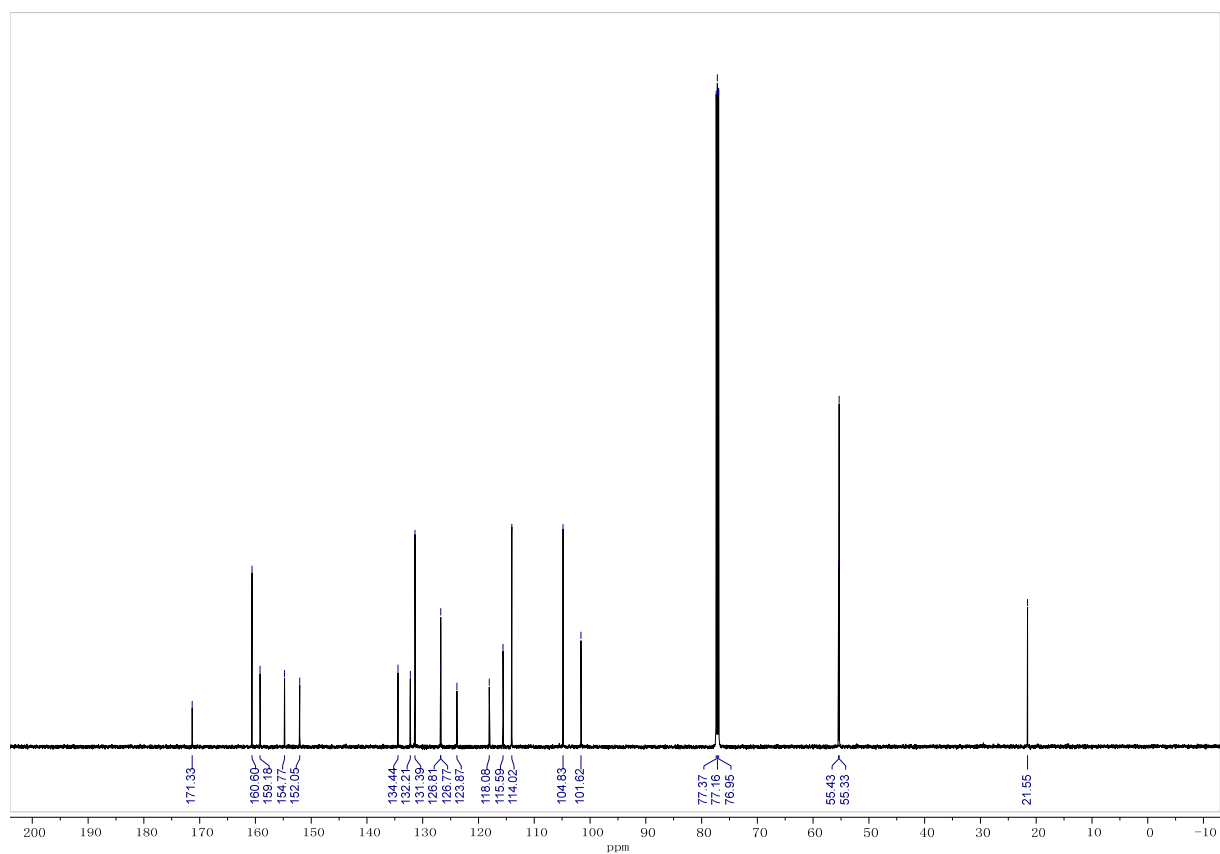
¹³C NMR spectrum of **6an** (151 MHz, DMSO-*d*₆)



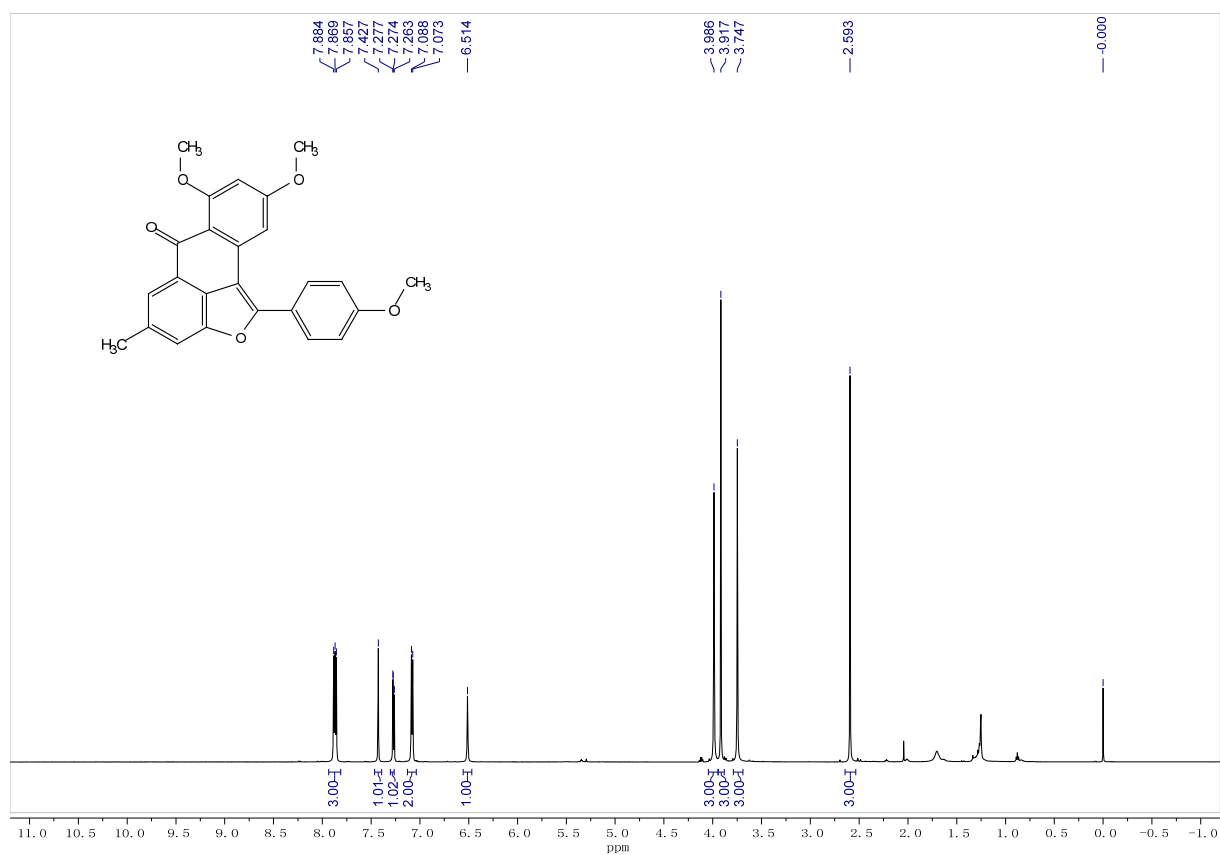
¹H NMR spectrum of **3ar'** (600 MHz, CDCl₃)



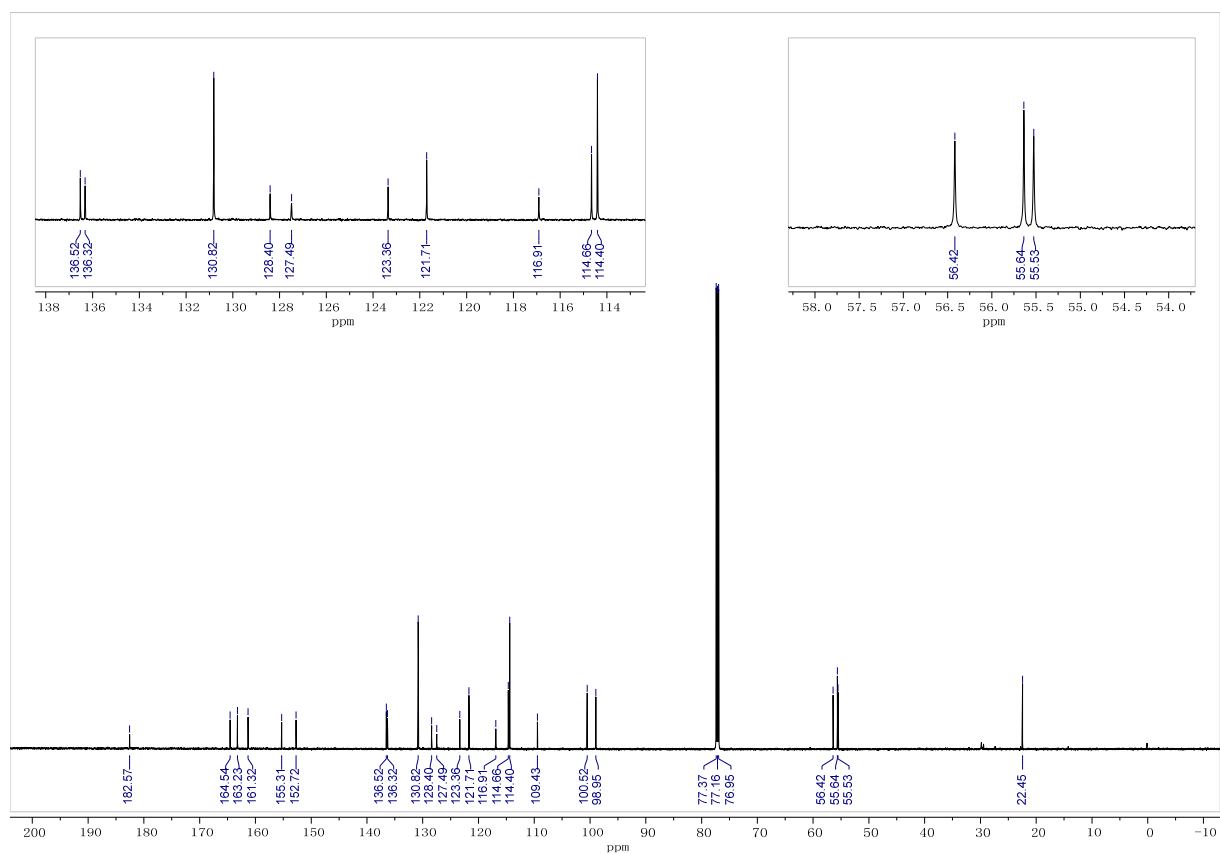
¹³C NMR spectrum of **3ar'** (151 MHz, CDCl₃)



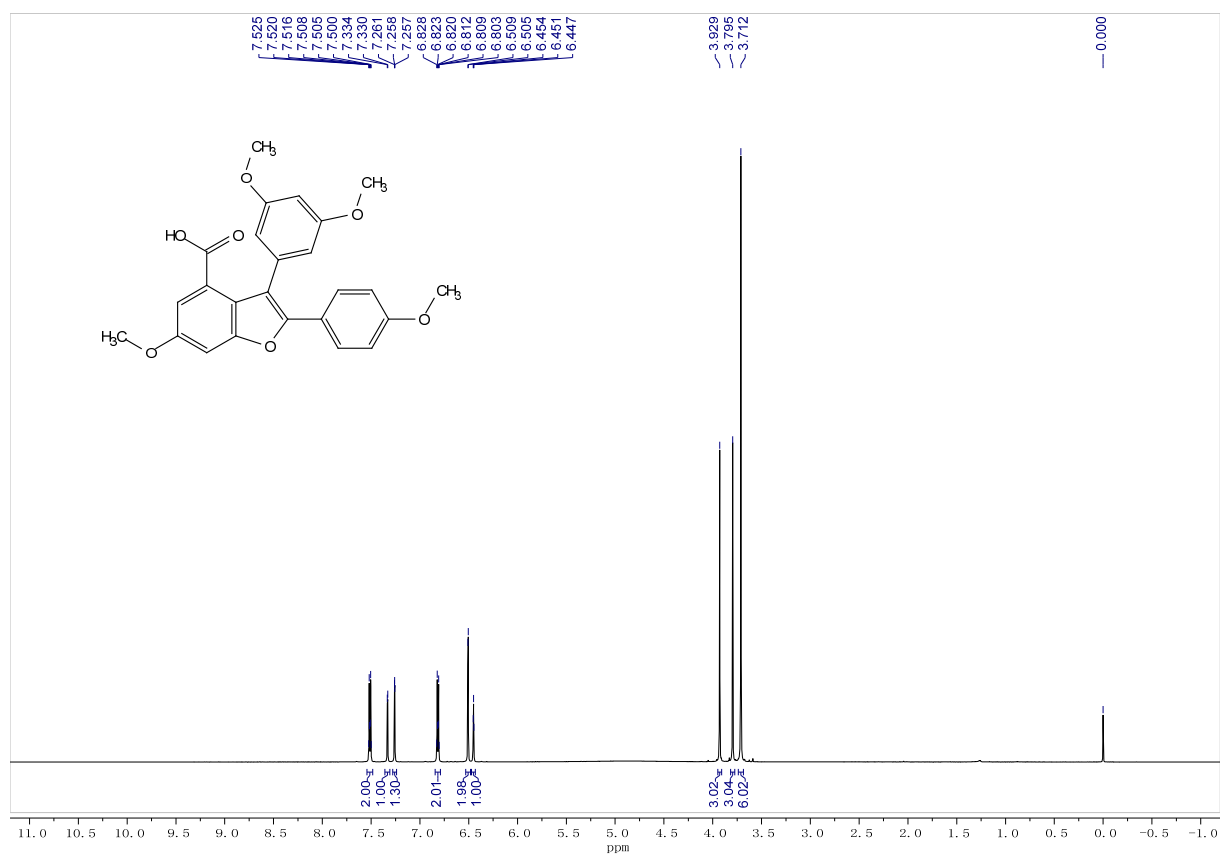
¹H NMR spectrum of **6ar** (600 MHz, CDCl₃)



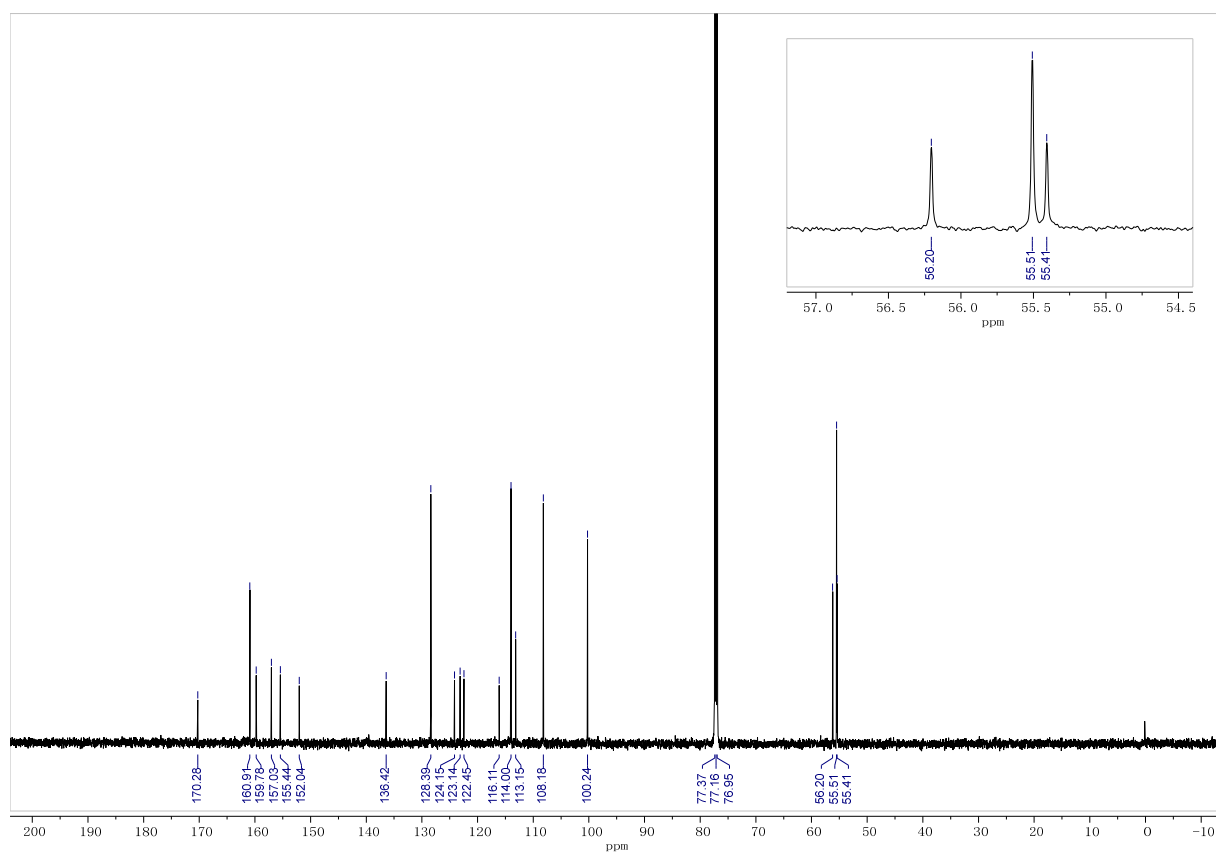
¹³C NMR spectrum of **6ar** (151 MHz, CDCl₃)



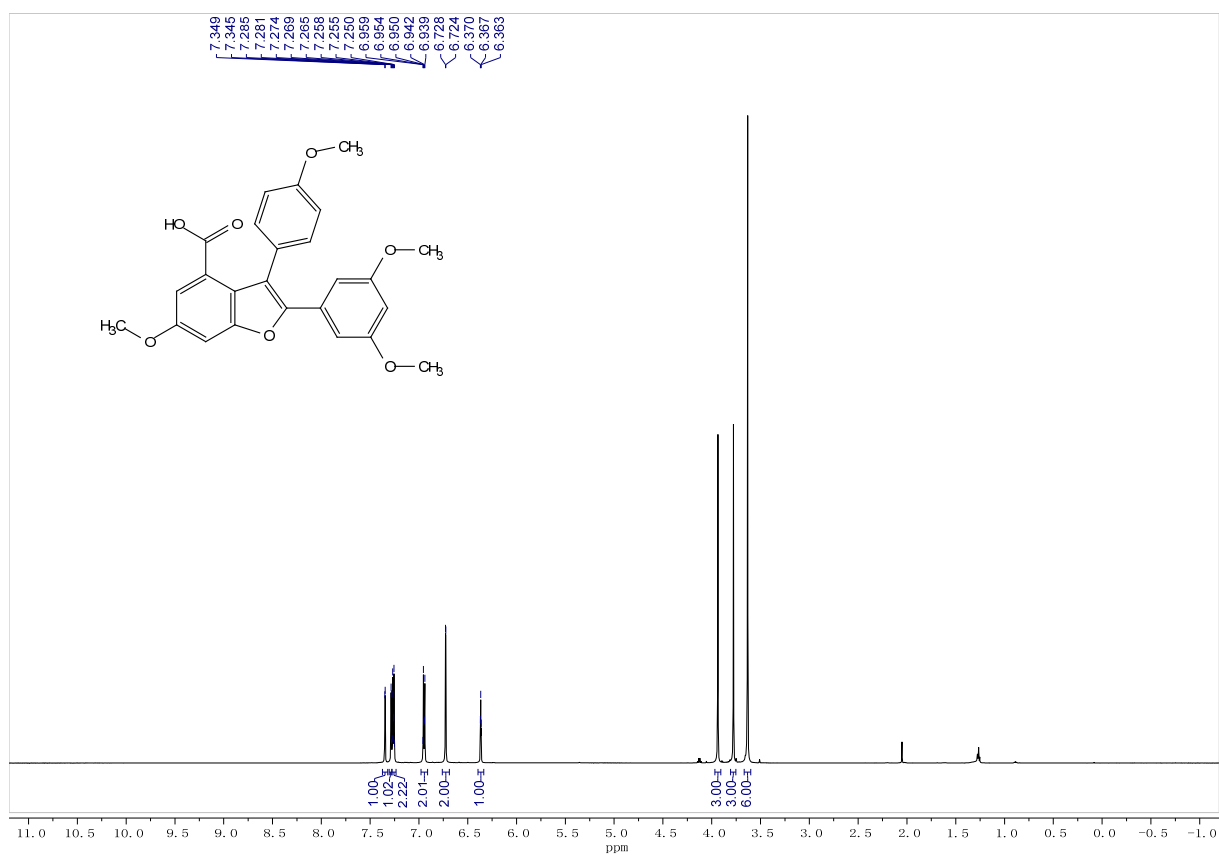
¹H NMR spectrum of **3cr** (600 MHz, CDCl₃)



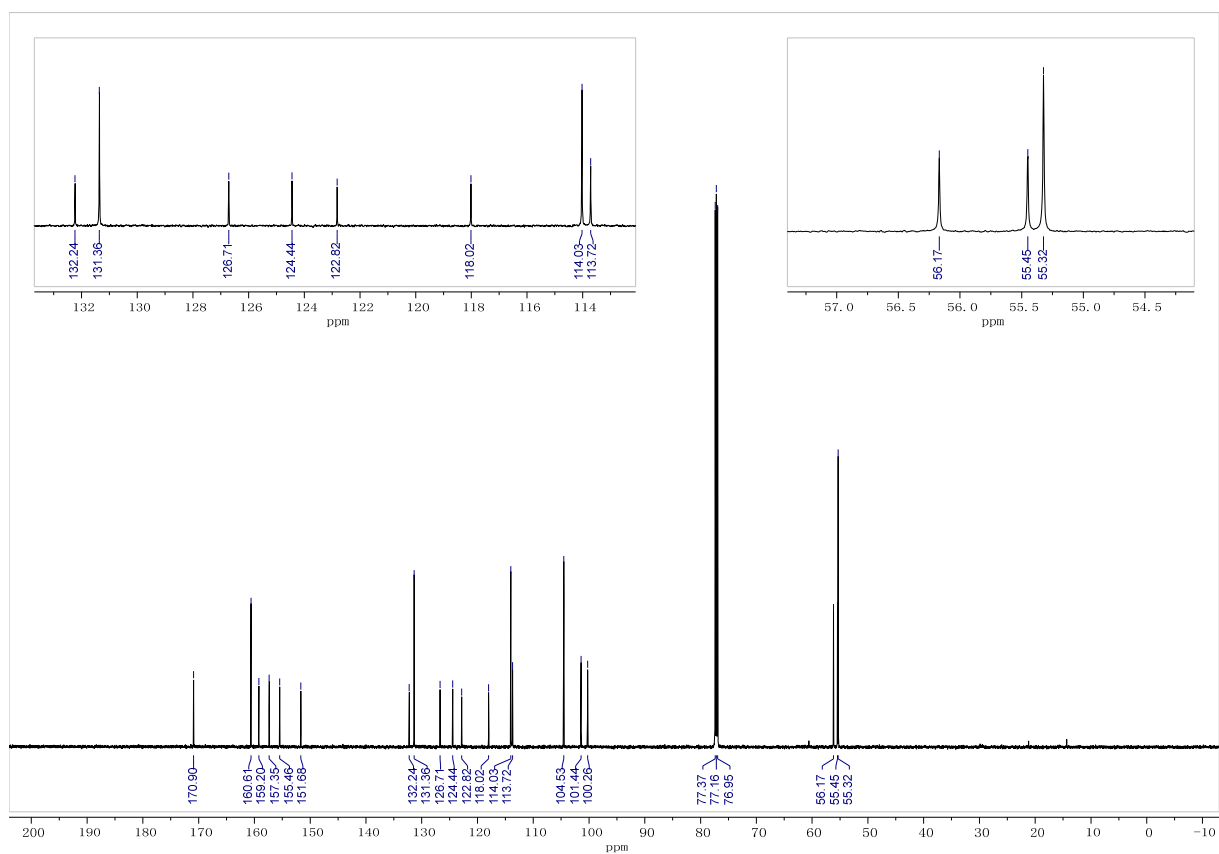
¹³C NMR spectrum of **3cr** (151 MHz, CDCl₃)



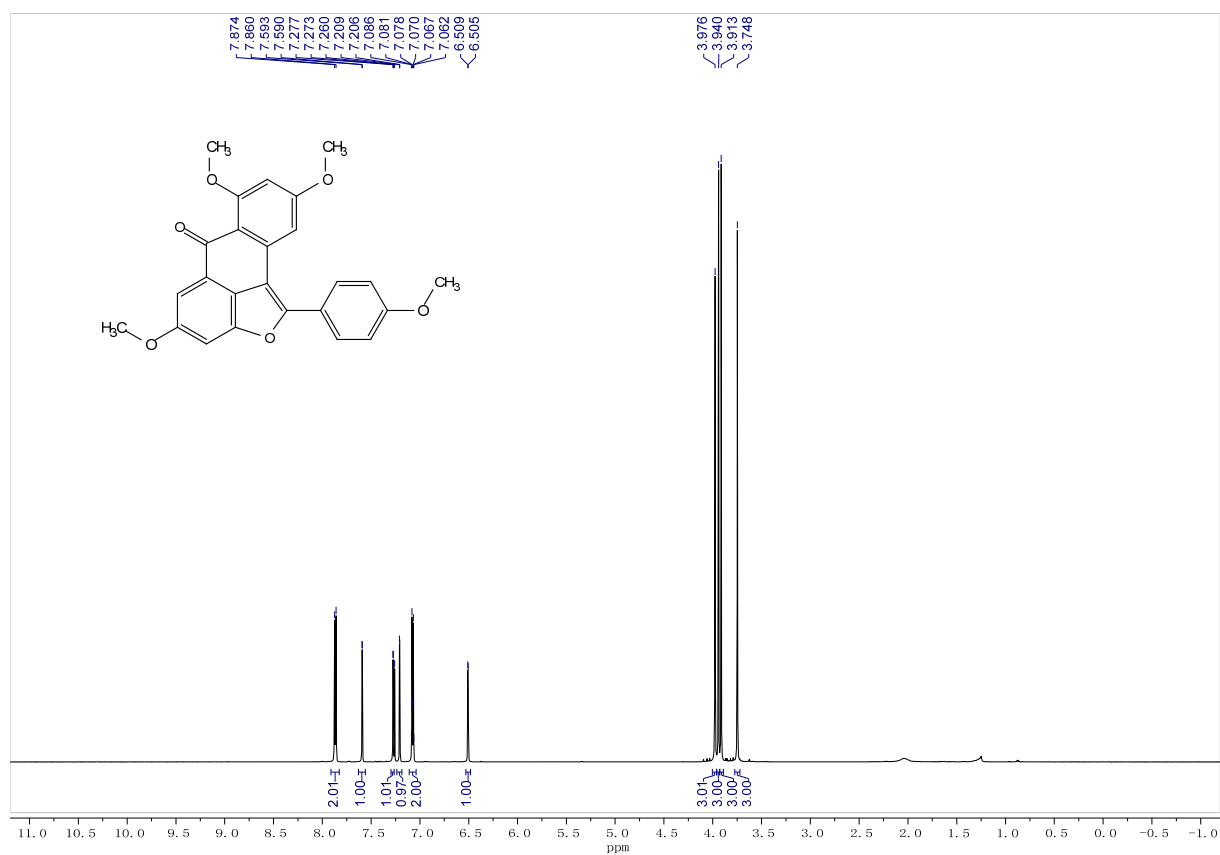
¹H NMR spectrum of **3cr'** (600 MHz, CDCl₃)



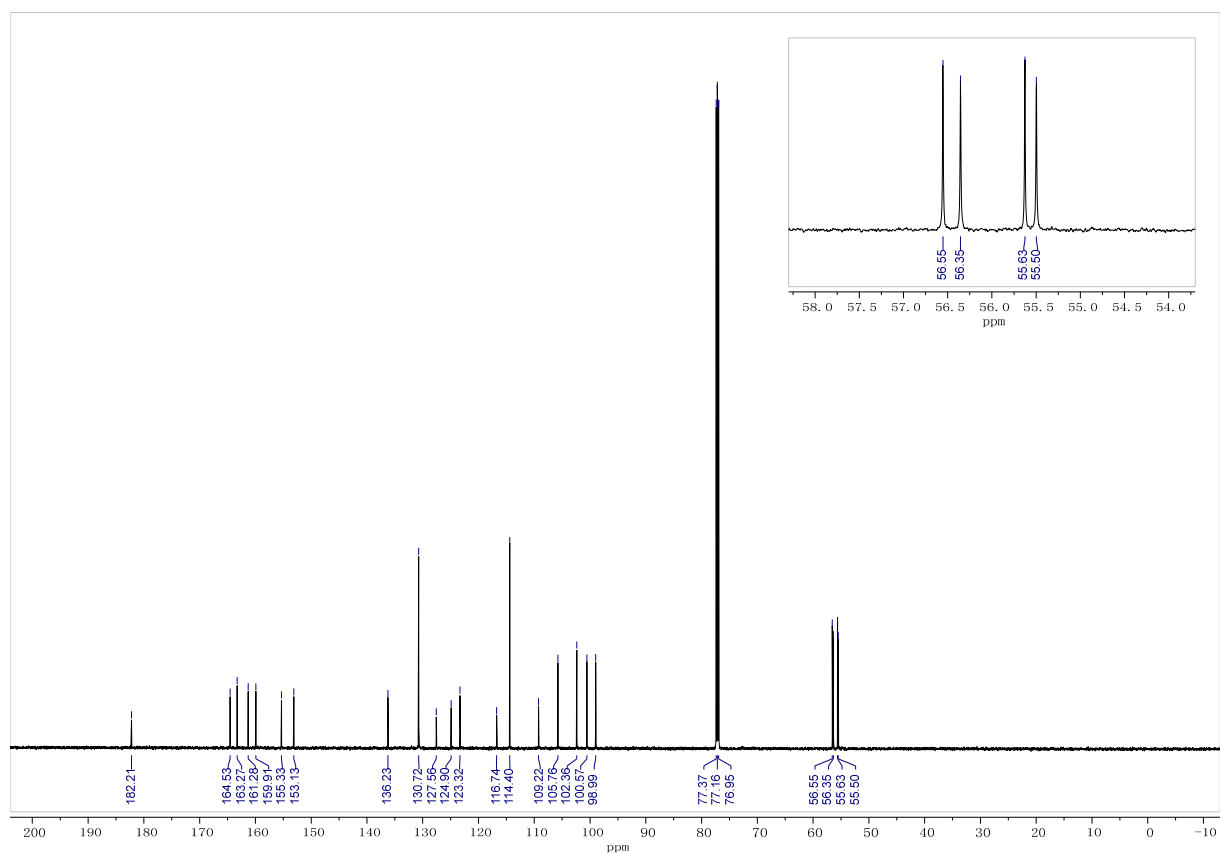
¹³C NMR spectrum of **3cr'** (151 MHz, CDCl₃)



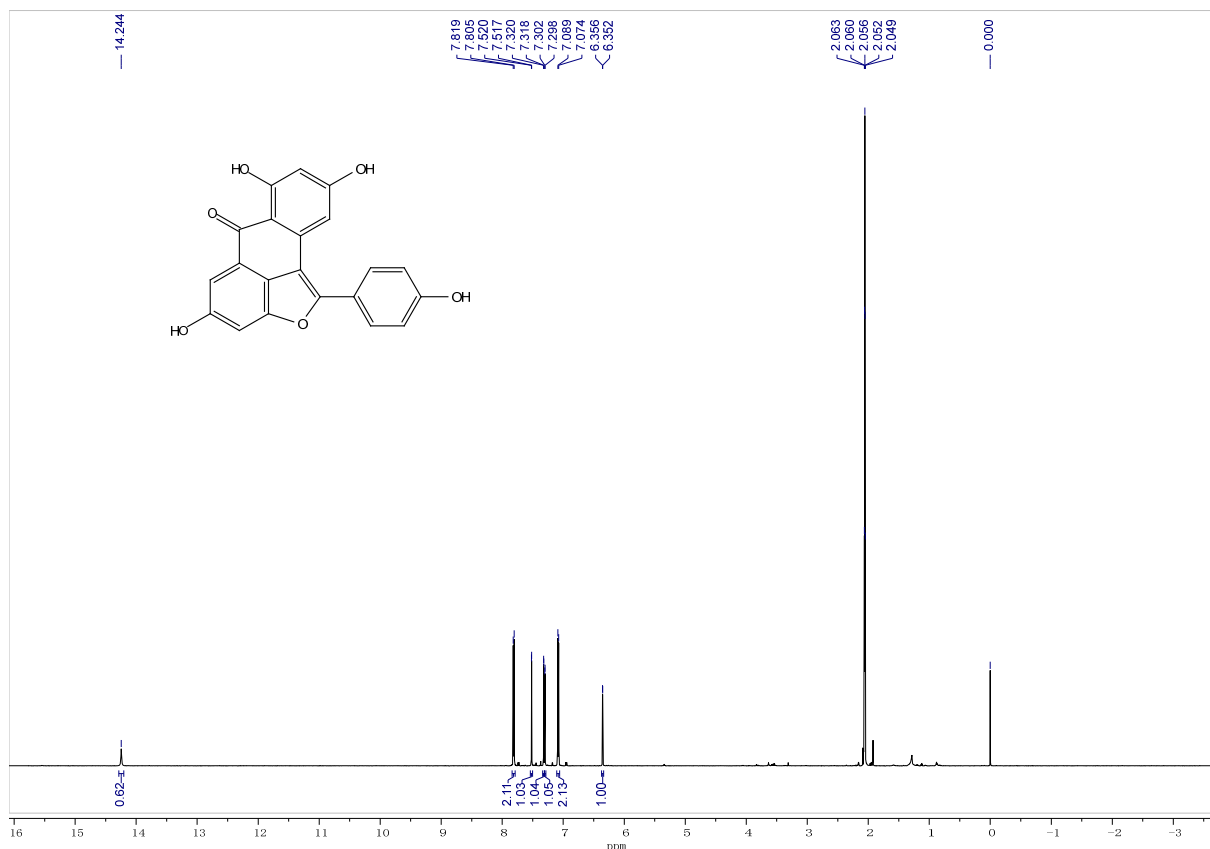
¹H NMR spectrum of **6cr** (600 MHz, CDCl₃)



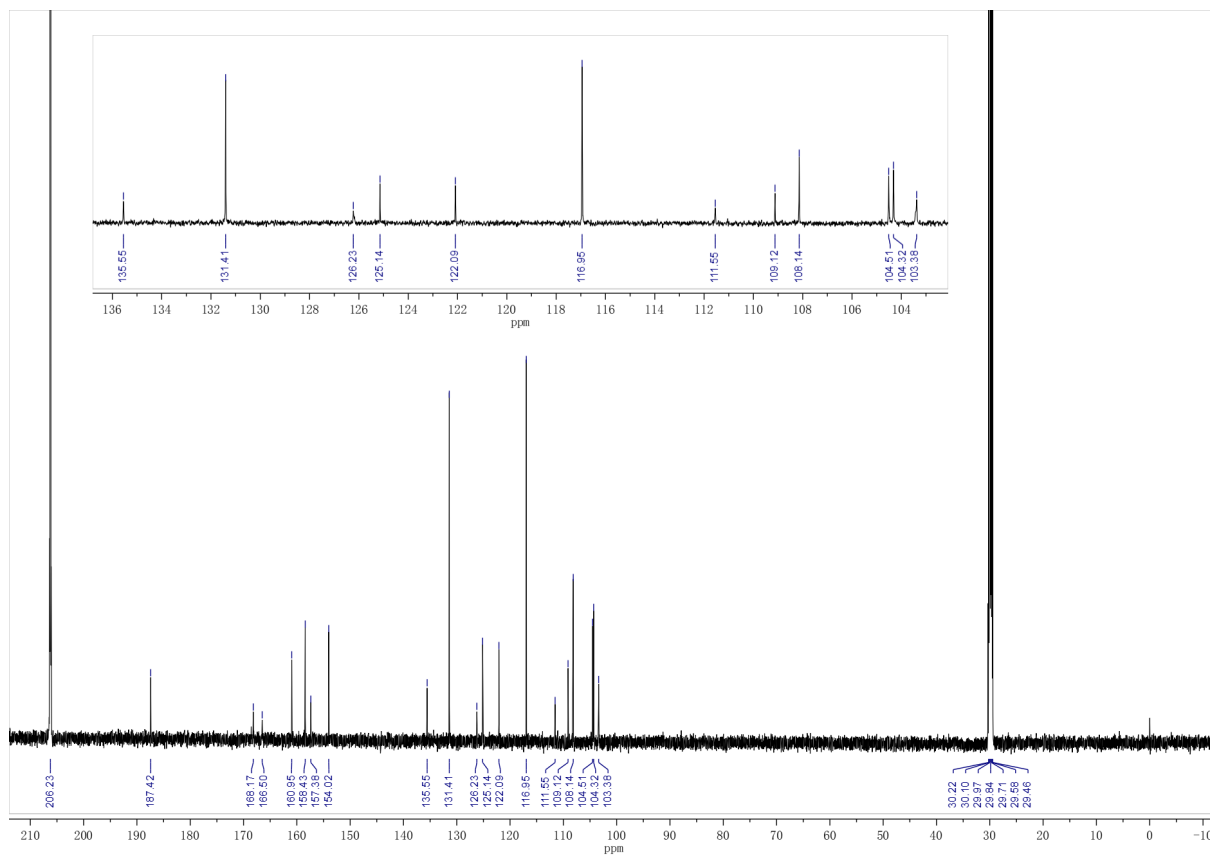
¹³C NMR spectrum of **6cr** (151 MHz, CDCl₃)



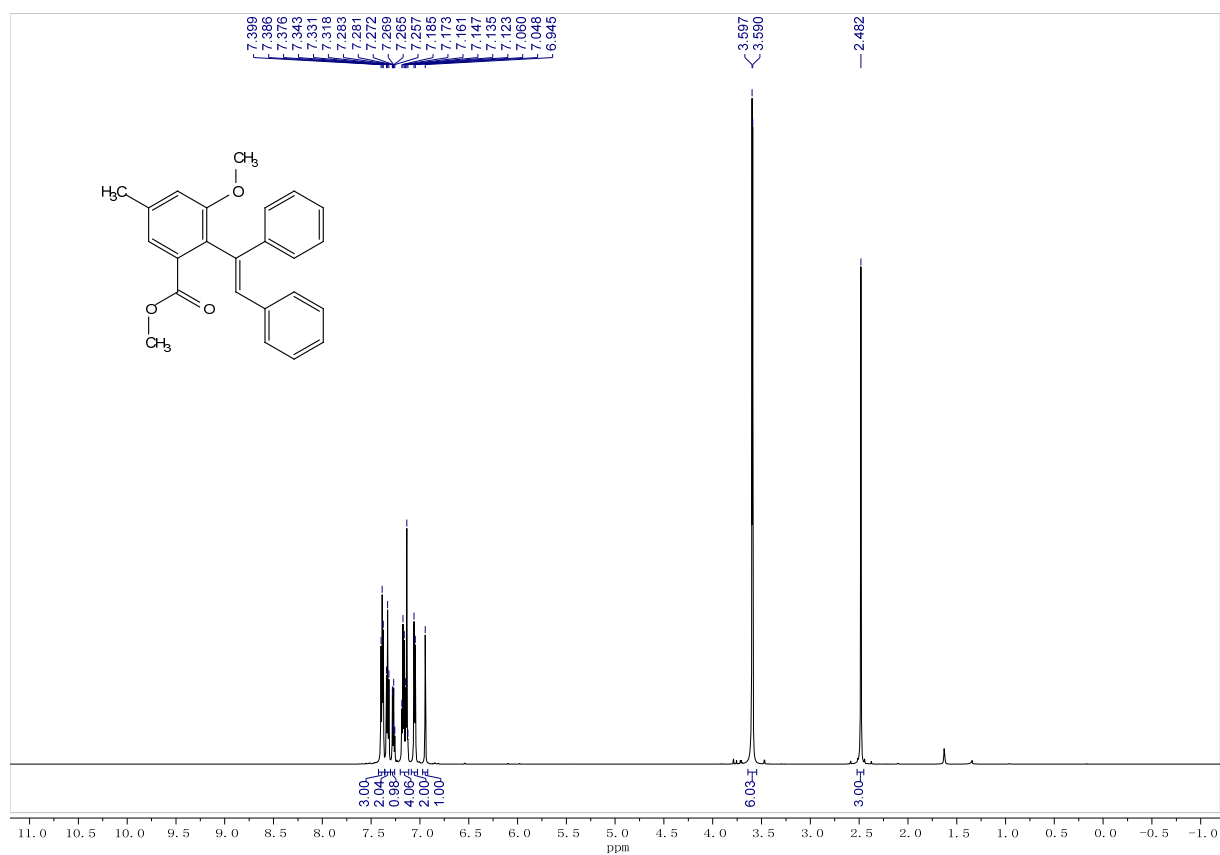
¹H NMR spectrum of **diptoindonesin G** (600 MHz, acetone-*d*₆)



¹³C NMR spectrum of **diptoindonesin G** (151 MHz, acetone-*d*₆)



¹H NMR spectrum of **7aa** (600 MHz, CDCl₃)



¹³C NMR spectrum of **7aa** (151 MHz, CDCl₃)

