

Supporting information

Direct Synthesis of 2-Methylbenzofurans from Calcium Carbide and Salicylaldehyde *p*-Tosylhydrazones

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1. Experimental Section

General Information: ^1H NMR and ^{13}C NMR spectra were recorded on a Mercury-600 MB or 400 MB instrument using CDCl_3 as solvent and Me_4Si as internal standard. Calcium carbide was purchased from Tianjin Chemical Company (purity: 74%), and ground into powder prior to use. Unless otherwise noted, the solvents and reagents were reagent grade and were used without any further purification. Column chromatographic separations were carried out on a flash chromatographic system using silica gel, and petroleum ether (60–90 °C) and ethyl acetate as eluent. For thin layer chromatography (TLC), silica gel plates precoated with GF-254 were used. Some salicylaldehydes were synthesized by formylation of the corresponding phenols according to the literature procedure.^[1] Various *p*-tosylhydrazones were synthesized by reactions of the corresponding salicylaldehydes or 2-hydroxyacetophenones with *p*-tosylhydrazine according to literature procedure.^[2]

The general procedure for the preparation of 2-methylbenzofurans from salicylaldehyde *p*-tosylhydrazones

Salicylaldehyde *p*-tosylhydrazones (1 mmol), calcium carbide (3 mmol, 0.26 g for 74 % purity), potassium *t*-butoxide (2 mmol), cuprous chloride (0.1 mmol) and water (4 mmol, 0.07 mL) in DMF (4 mL) were stirred at 90 °C for 5 h. The reaction was monitored by TLC. After the reaction was complete, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL),

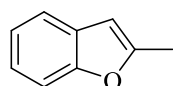
and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography by using petroleum ether and ethyl acetate as eluent to give the pure products.

The general procedure for the preparation of 2,3-dimethylbenzofurans from 2-hydroxyacetophenone *p*-tosyl hydrazones

2-Hydroxyacetophenone *p*-tosyl hydrazones (1 mmol), calcium carbide (3 mmol, 0.26 g for 74 % purity), potassium *t*-butoxide (2.5 mmol), cuprous chloride (0.1 mmol) and water (4 mmol, 0.07 mL) in DMF (4 mL) were stirred at 100 °C for 7 h. The reaction was monitored by TLC. After the reaction was complete, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography by using petroleum ether and ethyl acetate as eluent to give the pure products.

2. Analytical data of the products

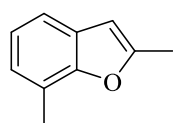
2-Methylbenzofuran (2a)^[3]



Colorless liquid, (90.7 mg, 69% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, *J* = 7.1 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.37 (d, *J* = 0.8 Hz, 1H), 2.46 (d, *J* = 0.8 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 155.37, 154.70, 129.16, 122.99, 122.36, 120.02, 110.58, 102.53, 14.04. Anal. Calcd. for C₉H₈O: C, 81.79; H, 6.10. Found: C, 81.85; H, 6.08.

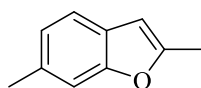
2,7-Dimethylbenzofuran (2b)^[4]



White solid, (81.2 mg, 56% yield), M.p. 44–47 °C. ¹H NMR (600 MHz, CDCl₃) δ

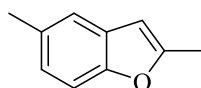
7.30 (d, $J = 7.7$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 7.3$ Hz, 1H), 6.35 (d, $J = 1.0$ Hz, 1H), 2.51 (s, 3H), 2.47 (d, $J = 0.8$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 155.03, 153.73, 128.61, 123.99, 122.37, 120.78, 117.48, 102.76, 15.03, 14.09. Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.90. Found: C, 82.09; H, 6.92.

2,6-Dimethylbenzofuran (2c)



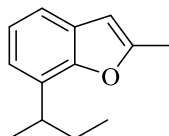
White solid, (73.8 mg, 51% yield), M.p. 51–54 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, $J = 7.8$ Hz, 1H), 7.20 (d, $J = 0.5$ Hz, 1H), 7.01 – 6.97 (m, 1H), 6.31 – 6.29 (m, 1H), 2.44 – 2.41 (m, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 155.12, 154.68, 133.07, 126.57, 123.66, 119.46, 110.90, 102.28, 21.56, 14.02. Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.90. Found: C, 82.21; H, 6.89.

2,5-Dimethylbenzofuran (2d)^[5]



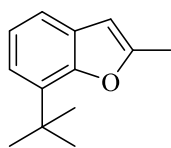
Colorless liquid, (97.2 mg, 67% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.29 (dd, $J = 8.3, 2.2$ Hz, 1H), 7.27 – 7.25 (m, 1H), 7.02 (d, $J = 8.3$ Hz, 1H), 6.32 – 6.28 (m, 1H), 2.44 (dd, $J = 9.5, 1.6$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 155.46, 153.13, 131.72, 129.29, 124.16, 119.98, 110.07, 102.31, 21.29, 14.07. Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.90. Found: C, 82.11; H, 6.91.

7-(*sec*-Butyl)-2-methylbenzofuran (2e)



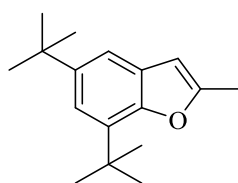
White solid, (125.8 mg, 67% yield), M.p. 153–154 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.31 (d, $J = 7.6$ Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.4$ Hz, 1H), 6.36 (d, $J = 1.0$ Hz, 1H), 3.19 (dd, $J = 14.2, 7.1$ Hz, 1H), 2.47 (s, 3H), 1.88 – 1.70 (m, 2H), 1.38 (d, $J = 7.0$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 154.80, 153.03, 130.64, 128.94, 122.49, 120.74, 117.39, 102.71, 35.89, 29.79, 20.50, 14.15, 12.32. Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 82.88; H, 8.60.

7-(*tert*-Butyl)-2-methylbenzofuran (2f)



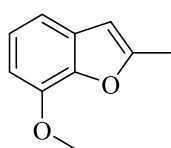
White solid, (99.1 mg, 53% yield), M.p. 77–78 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.33 – 7.30 (m, 1H), 7.11 – 7.08 (m, 2H), 6.34 (d, *J* = 1.0 Hz, 1H), 2.47 (d, *J* = 1.0 Hz, 3H), 1.49 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 154.33, 152.89, 134.18, 129.61, 122.23, 119.67, 118.02, 102.34, 34.26, 29.84, 14.17. Anal. Calcd. for C₁₃H₁₆O: C, 82.94; H, 8.57. Found: C, 82.99; H, 8.55.

5,7-Di-*tert*-butyl-2-methylbenzofuran (2g)



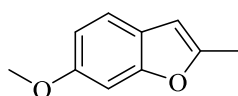
White solid, (174.6 mg, 72% yield), M.p. 74–76 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 1.9 Hz, 1H), 7.16 (d, *J* = 1.9 Hz, 1H), 6.30 (d, *J* = 1.0 Hz, 1H), 2.45 (d, *J* = 0.9 Hz, 3H), 1.49 (s, 9H), 1.36 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 154.41, 151.08, 145.00, 133.17, 129.20, 117.62, 114.15, 102.43, 34.76, 34.43, 31.91, 29.91, 14.19. Anal. Calcd. for C₁₇H₂₄O: C, 83.55; H, 9.90. Found: C, 83.62; H, 9.86.

7-Methoxy-2-methylbenzofuran (2h)^[4]



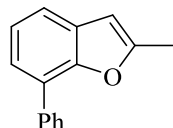
White solid, (107.8 mg, 67% yield), M.p. 52–54 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.12 – 7.05 (m, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 0.7 Hz, 1H), 4.00 (s, 3H), 2.47 (d, *J* = 0.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 155.51, 144.85, 143.77, 130.78, 123.05, 112.62, 105.32, 102.92, 55.91, 14.01. Anal. Calcd. for C₁₀H₁₀O₂: C, 74.06; H, 6.22. Found: C, 73.99; H, 6.25.

6-Methoxy-2-methylbenzofuran (2i)



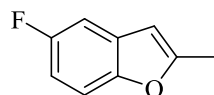
Yellow liquid, (114.8 mg, 71% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.5$ Hz, 1H), 6.96 (d, $J = 2.1$ Hz, 1H), 6.81 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.29 – 6.25 (m, 1H), 3.82 (s, 3H), 2.41 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.15, 155.63, 154.38, 122.49, 120.04, 110.97, 102.18, 95.84, 55.71, 14.00. Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.06; H, 6.22. Found: C, 74.11; H, 6.20.

2-Methyl-7-phenylbenzofuran (2j)



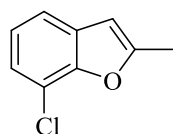
White solid, (80.8 mg, 39% yield), M.p. 326–328 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.85 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.51 – 7.46 (m, 2H), 7.44 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.40 – 7.33 (m, 2H), 7.26 – 7.23 (m, 2H), 6.43 – 6.42 (m, 1H), 2.48 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 155.63, 151.90, 136.76, 129.93, 128.61, 128.49, 127.45, 124.77, 122.90, 122.72, 119.26, 102.76, 14.19. Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}$: C, 86.51; H, 5.81. Found: C, 86.44; H, 5.83.

5-Fluoro-2-methylbenzofuran (2k)



White solid, (110.5 mg, 74% yield), M.p. 62–64 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.30 (dd, $J = 8.6, 4.1$ Hz, 1H), 7.11 (dd, $J = 8.7, 2.6$ Hz, 1H), 6.90 (td, $J = 9.1, 2.7$ Hz, 1H), 6.35 – 6.31 (m, 1H), 2.44 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.86, 158.29, 157.36, 150.91, 129.94 (d, $J = 10.8$ Hz), 111.01 (d, $J = 9.8$ Hz), 110.51, 110.33, 105.73, 105.56, 102.86 (d, $J = 3.8$ Hz), 14.13. Anal. Calcd. for $\text{C}_9\text{H}_7\text{FO}$: C, 71.99; H, 4.70. Found: C, 72.05; H, 4.69.

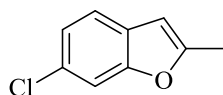
7-Chloro-2-methylbenzofuran (2l)



Colorless liquid, (130.6 mg, 79% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.35 (dd, $J = 7.7, 0.9$ Hz, 1H), 7.19 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.10 (t, $J = 7.8$ Hz, 1H), 6.40 (d, $J =$

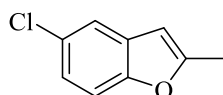
1.0 Hz, 1H), 2.49 (d, $J = 0.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 156.48, 150.42, 130.76, 123.312, 123.262, 118.60, 116.01, 103.29, 14.05. Anal. Calcd. for $\text{C}_9\text{H}_7\text{ClO}$: C, 64.88; H, 4.24. Found: C, 64.96; H, 4.22.

6-Chloro-2-methylbenzofuran (2m)



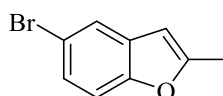
Colorless liquid, (128.7 mg, 78% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.38 (m, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.15 (dd, $J = 8.2, 1.8$ Hz, 1H), 6.34 – 6.32 (m, 1H), 2.43 (d, $J = 1.1$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 156.31, 154.75, 128.75, 127.79, 123.02, 120.45, 111.20, 102.41, 14.02. Anal. Calcd. for $\text{C}_9\text{H}_7\text{ClO}$: C, 64.88; H, 4.24. Found: C, 64.81; H, 4.27.

5-Chloro-2-methylbenzofuran (2n)



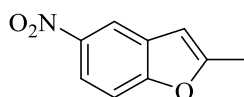
White solid, (87.2 mg, 53% yield), M.p. 57–59 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 2.1$ Hz, 1H), 7.30 (d, $J = 8.6$ Hz, 1H), 7.14 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.31 (d, $J = 0.7$ Hz, 1H), 2.44 (d, $J = 0.7$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 157.06, 153.09, 130.54, 127.91, 123.13, 119.66, 111.49, 102.31, 14.08. Anal. Calcd. for $\text{C}_9\text{H}_7\text{ClO}$: C, 64.88; H, 4.24. Found: C, 64.92; H, 4.23.

5-Bromo-2-methylbenzofuran (2o)^[3]



White solid, (146.5 mg, 70% yield), M.p. 97–98 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.58 (d, $J = 1.6$ Hz, 1H), 7.31 – 7.22 (m, 2H), 6.31 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 156.91, 153.46, 131.17, 125.84, 122.70, 115.43, 112.01, 102.16, 14.06. Anal. Calcd. for $\text{C}_9\text{H}_7\text{BrO}$: C, 51.22; H, 3.34. Found: C, 51.17; H, 3.36.

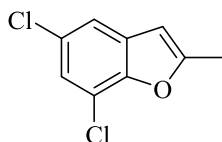
2-Methyl-5-nitrobenzofuran (2p)^[6]



White solid, (126.8 mg, 72% yield), M.p. 112–115 °C. ^1H NMR (600 MHz, CDCl_3) δ

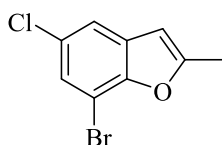
8.37 (d, $J = 2.3$ Hz, 1H), 8.12 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.44 (d, $J = 8.9$ Hz, 1H), 6.51 – 6.49 (m, 1H), 2.49 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.10, 157.59, 143.95, 129.54, 119.14, 116.49, 110.79, 103.44, 14.13. Anal. Calcd. for $\text{C}_9\text{H}_7\text{NO}_3$: C, 61.02; H, 3.98; N, 7.91. Found: C, 60.93; H, 3.99; N, 7.94.

5,7-Dichloro-2-methylbenzofuran (2q)



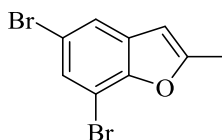
White solid, (169.1 mg, 85% yield), M.p. 73–74 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.31 (d, $J = 1.9$ Hz, 1H), 7.19 (d, $J = 1.9$ Hz, 1H), 6.34 (d, $J = 1.1$ Hz, 1H), 2.48 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 158.05, 149.08, 131.45, 128.17, 123.18, 118.40, 116.49, 103.06, 14.07. Anal. Calcd. for $\text{C}_9\text{H}_6\text{Cl}_2\text{O}$: C, 53.77; H, 3.01. Found: C, 53.82; H, 3.00.

7-Bromo-5-chloro-2-methylbenzofuran (2r)



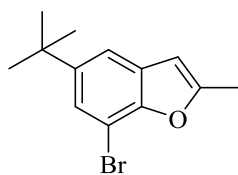
White solid, (162.6 mg, 67% yield), M.p. 78–79 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.36 (d, $J = 1.8$ Hz, 1H), 7.34 (d, $J = 1.8$ Hz, 1H), 6.37 (d, $J = 0.8$ Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (150MHz, CDCl_3) δ 158.02, 150.52, 131.07, 128.44, 125.80, 118.96, 103.56, 103.22, 14.12. Anal. Calcd. for $\text{C}_9\text{H}_6\text{BrClO}$: C, 44.03; H, 2.46. Found: C, 43.96; H, 2.47.

5,7-Dibromo-2-methylbenzofuran (2s)



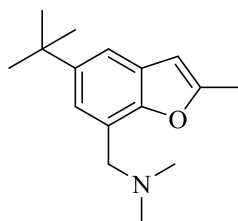
White solid, (204.7 mg, 71% yield), M.p. 83–84 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, $J = 1.8$ Hz, 1H), 7.48 (d, $J = 1.8$ Hz, 1H), 6.38 (d, $J = 1.0$ Hz, 1H), 2.49 (d, $J = 0.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 157.89, 150.90, 131.75, 128.31, 121.97, 115.56, 104.02, 103.06, 14.11. Anal. Calcd. for $\text{C}_9\text{H}_6\text{Br}_2\text{O}$: C, 37.28; H, 2.09. Found: C, 37.34; H, 2.07.

7-Bromo-5-(*tert*-butyl)-2-methylbenzofuran (2t)



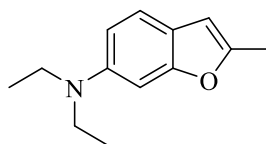
White solid, (161.8 mg, 61% yield), M.p. 73–74 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.39 (s, 2H), 6.38 (d, $J = 0.7$ Hz, 1H), 2.47 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 156.46, 149.99, 147.39, 130.06, 124.03, 115.73, 103.53, 102.66, 34.76, 31.75, 14.11. Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{BrO}$: C, 58.44; H, 5.66. Found: C, 58.51; H, 5.63.

1-(5-(*tert*-Butyl)-2-methylbenzofuran-7-yl)-*N,N*-dimethylmethanamine (2u)



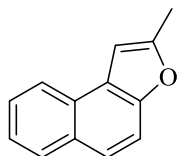
White solid, (177.9 mg, 73% yield), M.p. 61–63 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.37 (d, $J = 1.9$ Hz, 1H), 7.20 (d, $J = 1.7$ Hz, 1H), 6.31 (s, 1H), 3.72 (s, 2H), 2.44 (s, 3H), 2.31 (s, 6H), 1.36 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 155.36, 151.95, 145.34, 130.87, 128.72, 122.23, 115.23, 102.80, 58.06, 45.42, 34.59, 31.88, 14.19. Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.27; H, 9.49; N, 5.69.

N,N-Diethyl-2-methylbenzofuran-6-amine (2v)



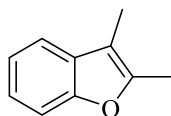
Yellow solid, (143.6 mg, 71% yield), M.p. 62–63 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.25 (d, $J = 6.1$ Hz, 1H), 6.75 (d, $J = 1.9$ Hz, 1H), 6.65 (dd, $J = 8.5, 2.2$ Hz, 1H), 6.20 (s, 1H), 3.35 (q, $J = 7.0$ Hz, 4H), 2.39 (d, $J = 1.0$ Hz, 3H), 1.16 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.72, 152.56, 145.68, 119.97, 118.86, 109.73, 101.94, 95.13, 45.17, 13.95, 12.48. Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.75; H, 8.48; N, 6.91.

2-Methylnaphtho[2,1-*b*]furan (2w)^[5]



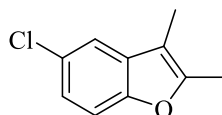
White solid, (68.7 mg, 38% yield), M.p. 56–57 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, $J = 8.2, 0.6$ Hz, 1H), 7.91 (d, $J = 8.2$ Hz, 1H), 7.64 (d, $J = 8.9$ Hz, 1H), 7.61 – 7.50 (m, 2H), 7.47 – 7.41 m, 1H), 6.88 – 6.83 (m, 1H), 2.55 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 154.63, 151.91, 130.23, 128.62, 127.38, 125.86, 124.17, 124.11, 123.73, 123.38, 112.02, 101.69, 14.18. Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{O}$: C, 85.69; H, 5.53. Found: C, 85.75; H, 5.51.

2,3-Dimethylbenzofuran (4a)



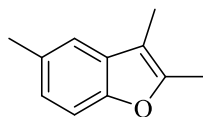
Colorless liquid, (68.5 mg, 47% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.44 – 7.40 (m, 1H), 7.38 (dd, $J = 5.7, 3.3$ Hz, 1H), 7.21 (dd, $J = 6.3, 2.8$ Hz, 2H), 2.39 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 153.79, 150.43, 130.45, 122.95, 121.92, 118.46, 110.36, 109.67, 11.75, 7.87. Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.90. Found: C, 82.22; H, 6.87.

5-Chloro-2,3-dimethylbenzofuran (4b)



White solid, (94.7 mg, 53% yield), M.p. 77–79 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.35 (d, $J = 2.0$ Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 (dd, $J = 8.6, 2.1$ Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 152.17, 152.16, 131.88, 127.56, 123.00, 118.26, 111.29, 109.58, 11.85, 7.80. Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{ClO}$: C, 66.49; H, 5.02. Found: C, 66.55; H, 5.00.

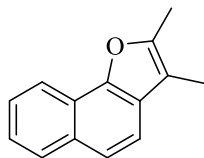
2,3,5-Trimethylbenzofuran (4c)



Colorless liquid, (90.1 mg, 56% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.24 (d, $J = 8.3$ Hz, 1H), 7.19 (s, 1H), 7.01 (dd, $J = 8.2, 1.0$ Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.13

(d, $J = 0.7$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 152.15, 150.53, 131.27, 130.51, 124.05, 118.46, 109.84, 109.40, 21.34, 11.80, 7.89. Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.58.

2,3-Dimethylnaphtho[1,2-*b*]furan (4d)



Colorless liquid, (65.7 mg, 34% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.56 – 7.51 (m, 2H), 7.42 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 1H), 2.49 (d, $J = 0.5$ Hz, 3H), 2.23 (d, $J = 0.6$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 149.79, 148.85, 130.84, 128.29, 125.94, 125.61, 124.25, 122.45, 121.05, 119.69, 117.82, 110.81, 11.94, 8.08. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68; H, 6.16. Found: C, 85.74; H, 6.14.

3. The ^1H NMR and ^{13}C NMR spectra for products



Fig. 1 ^1H NMR of 2-methylbenzofuran (2a)

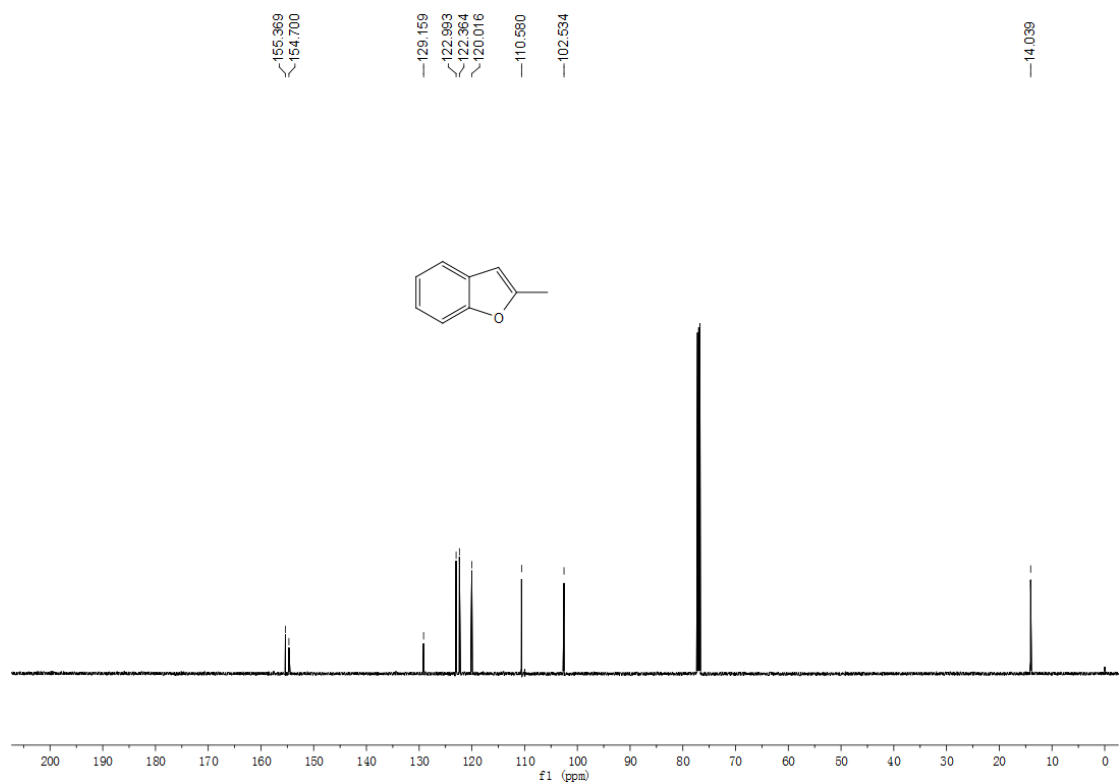


Fig. 2 ^{13}C NMR of 2-methylbenzofuran (2a)

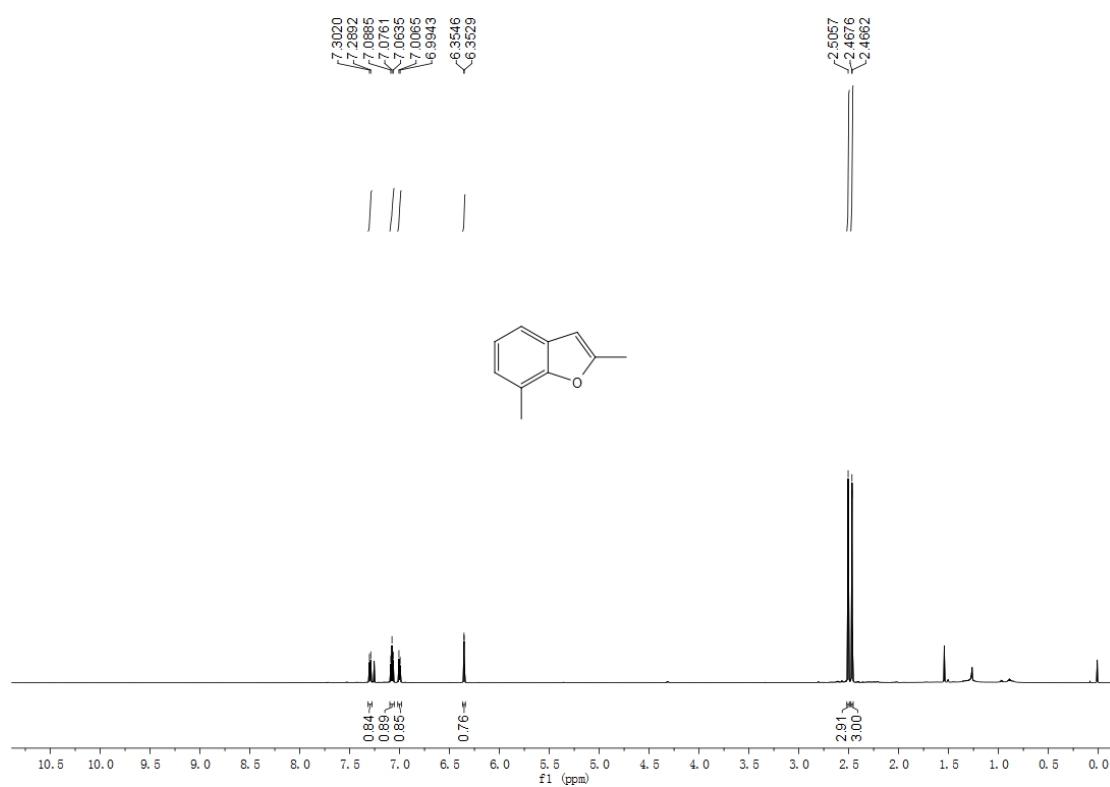


Fig. 3 ^1H NMR of 2,7-dimethylbenzofuran (2b)

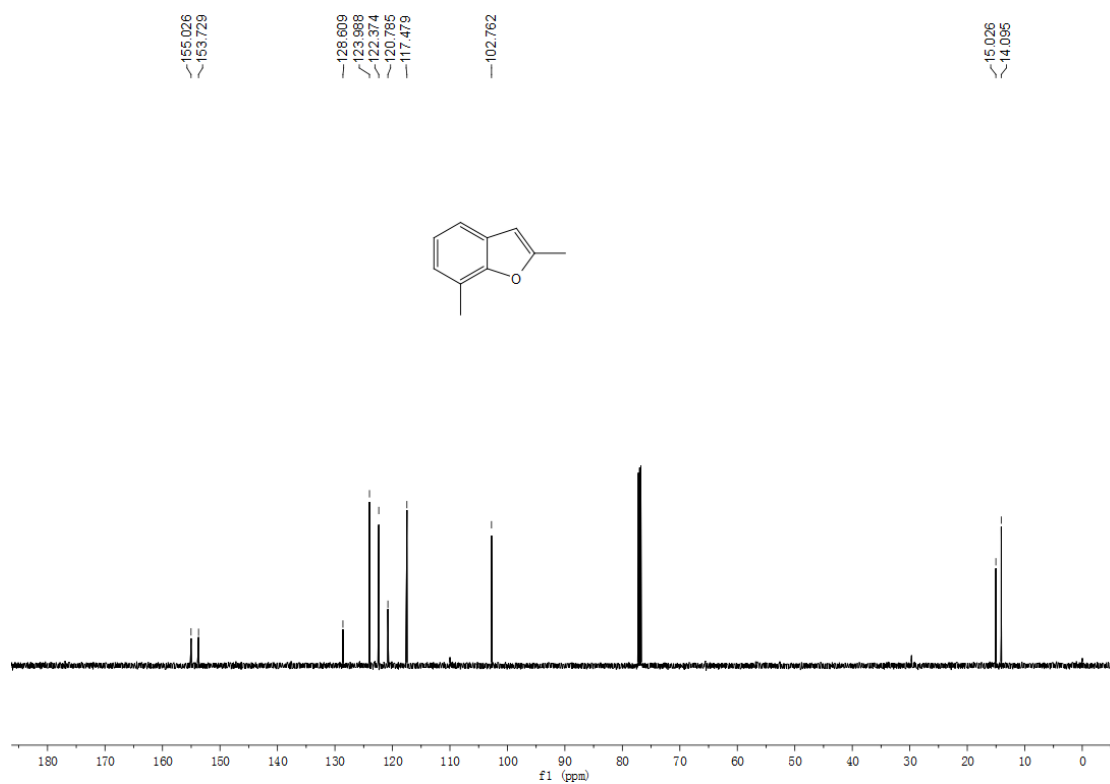


Fig. 4 ^{13}C NMR of 2,7-dimethylbenzofuran (2b)

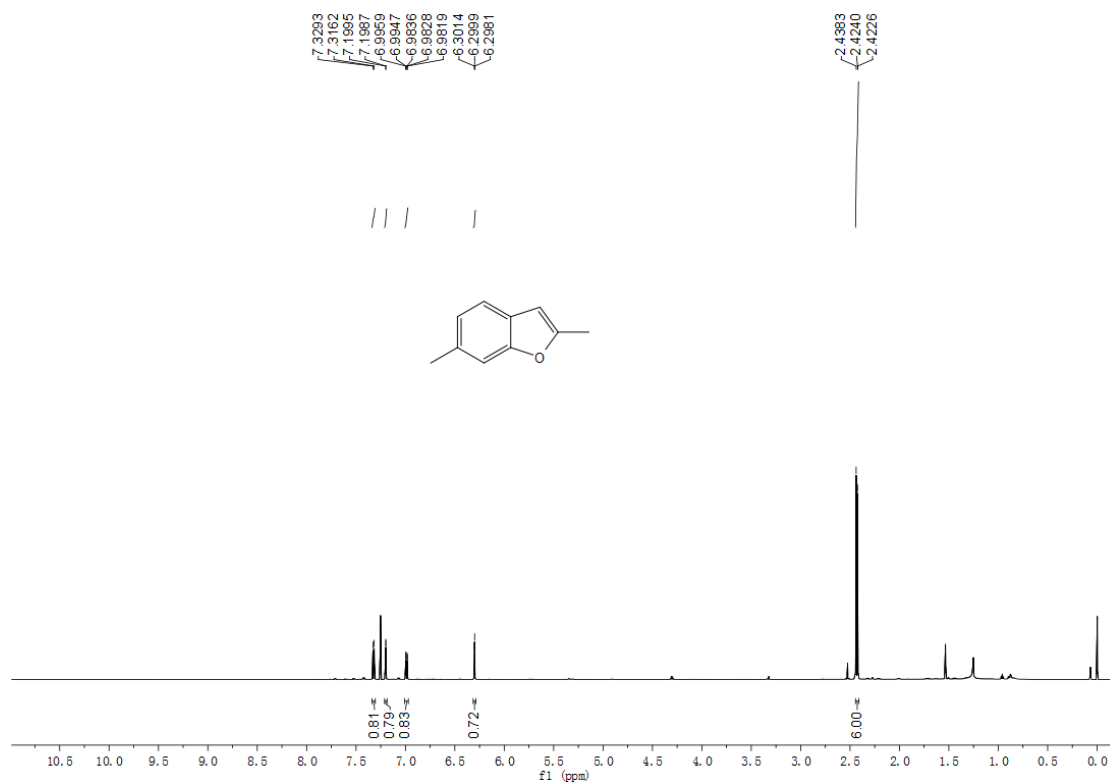


Fig. 5 ^1H NMR of 2,6-dimethylbenzofuran (2c)

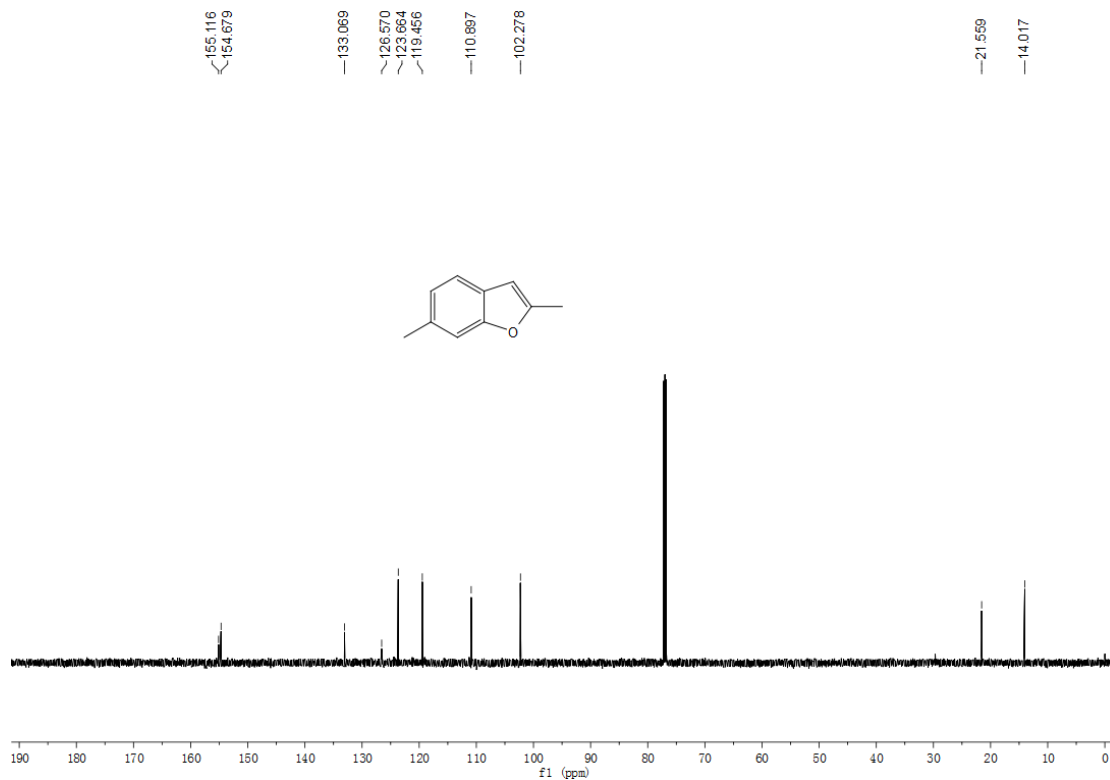


Fig. 6 ^{13}C NMR of 2,6-dimethylbenzofuran (2c)

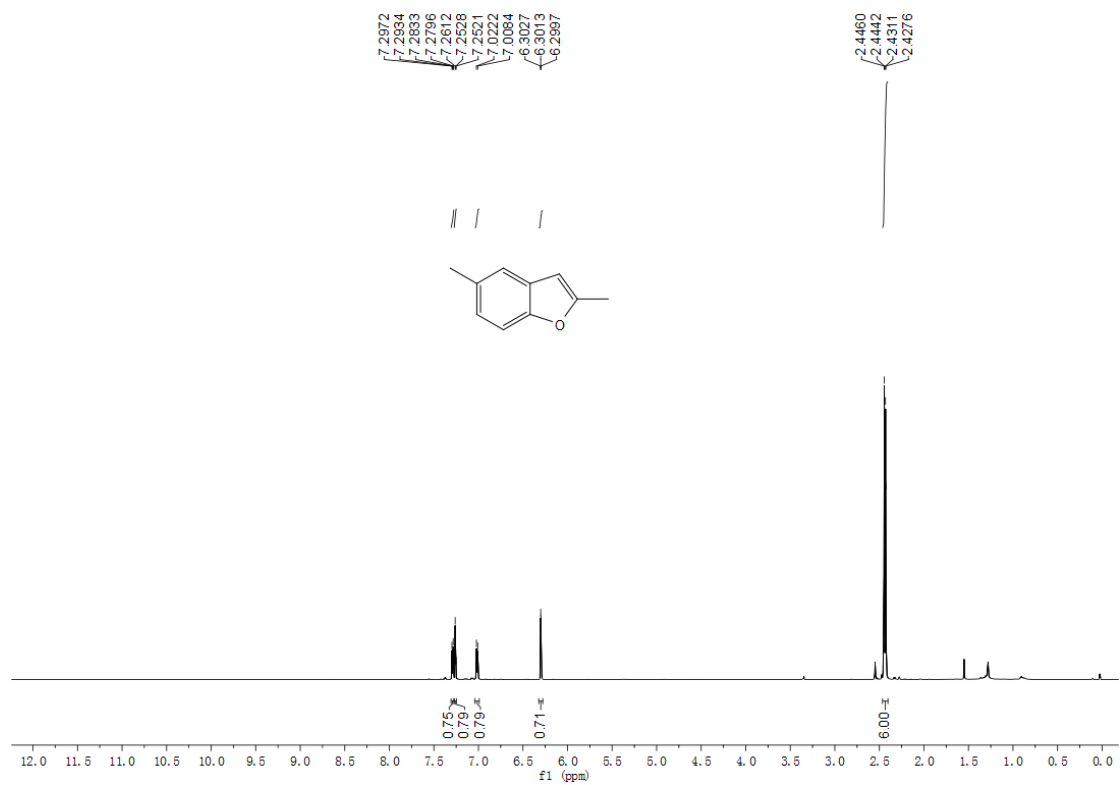


Fig. 7 ^1H NMR of 2,5-dimethylbenzofuran (2d)

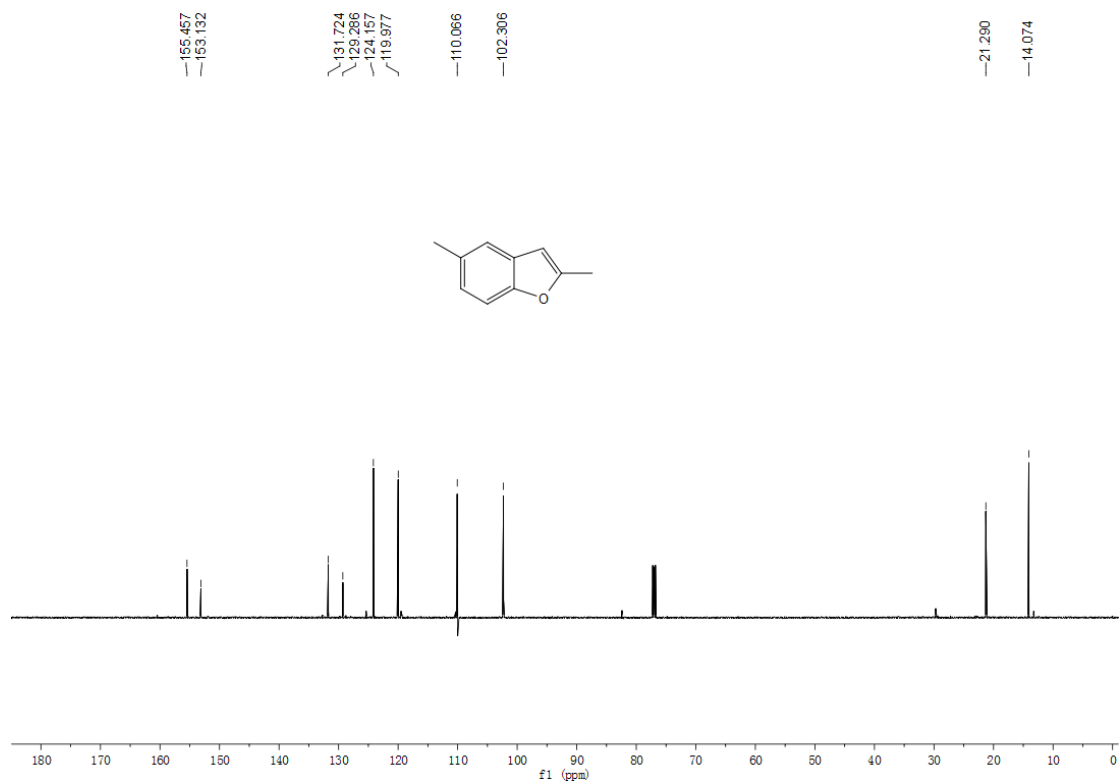


Fig. 8 ^{13}C NMR of 2,5-dimethylbenzofuran (2d)

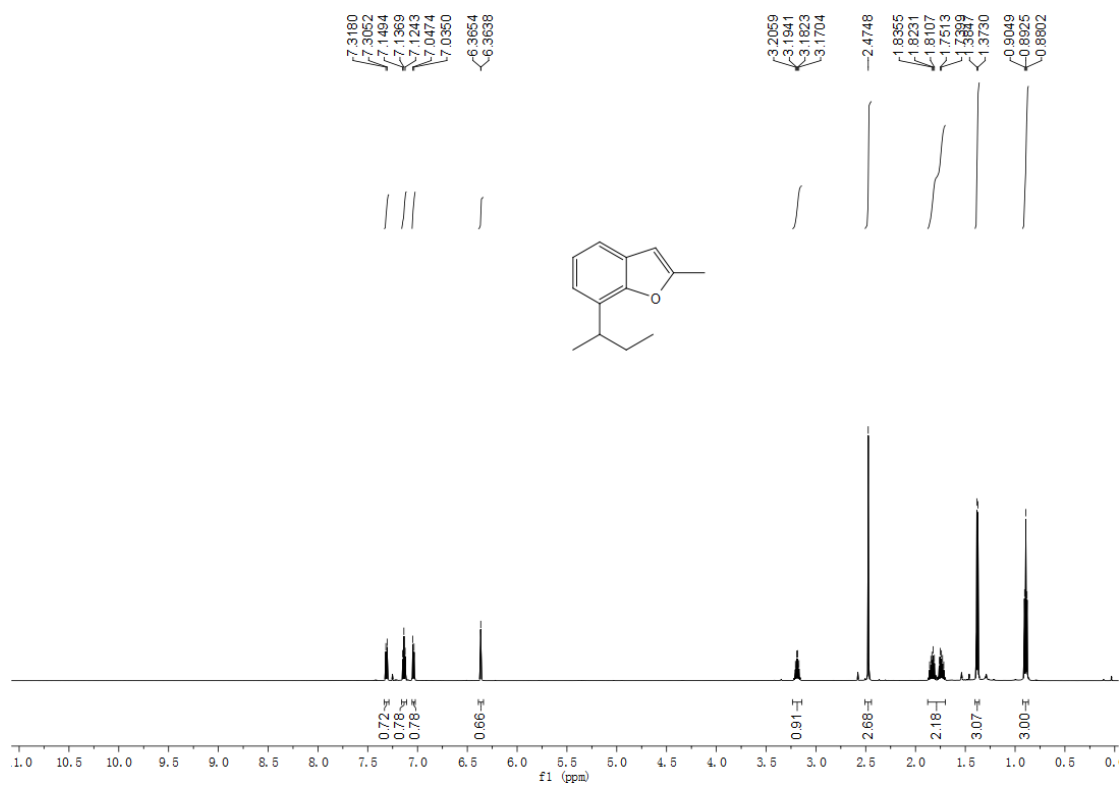


Fig. 9 ¹H NMR of 7-(*sec*-butyl)-2-methylbenzofuran (2e)

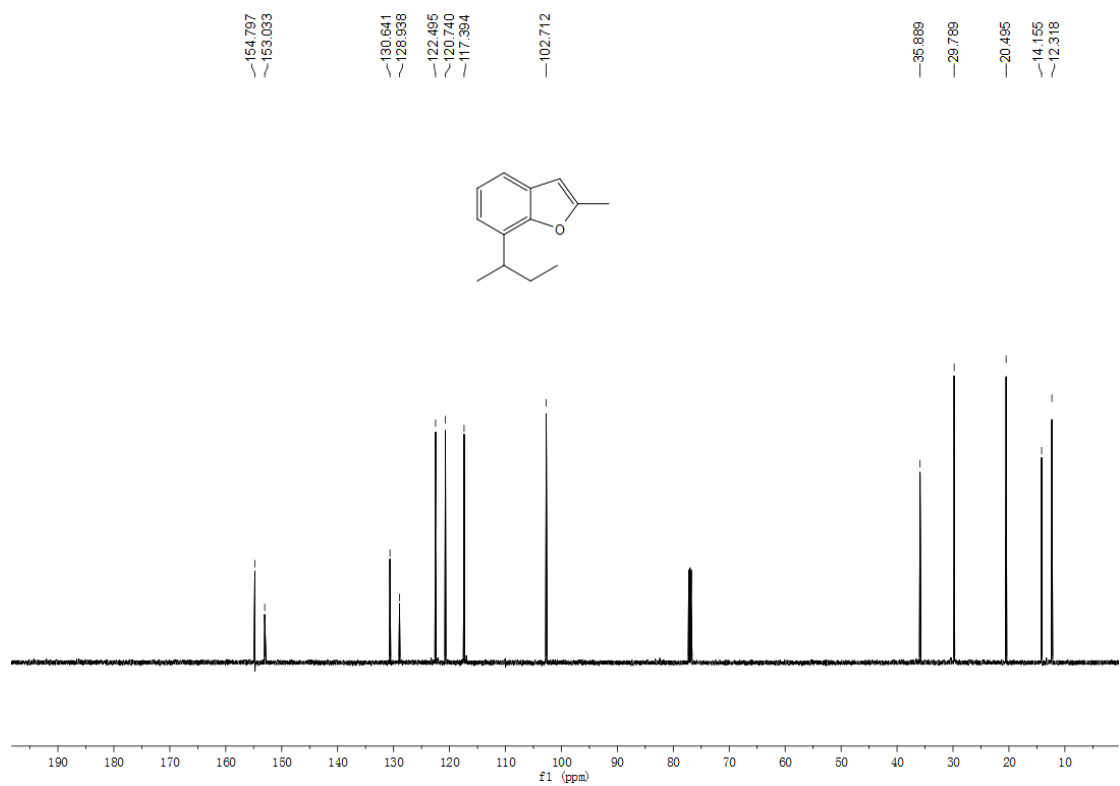


Fig. 10 ¹³C NMR of 7-(*sec*-butyl)-2-methylbenzofuran (2e)

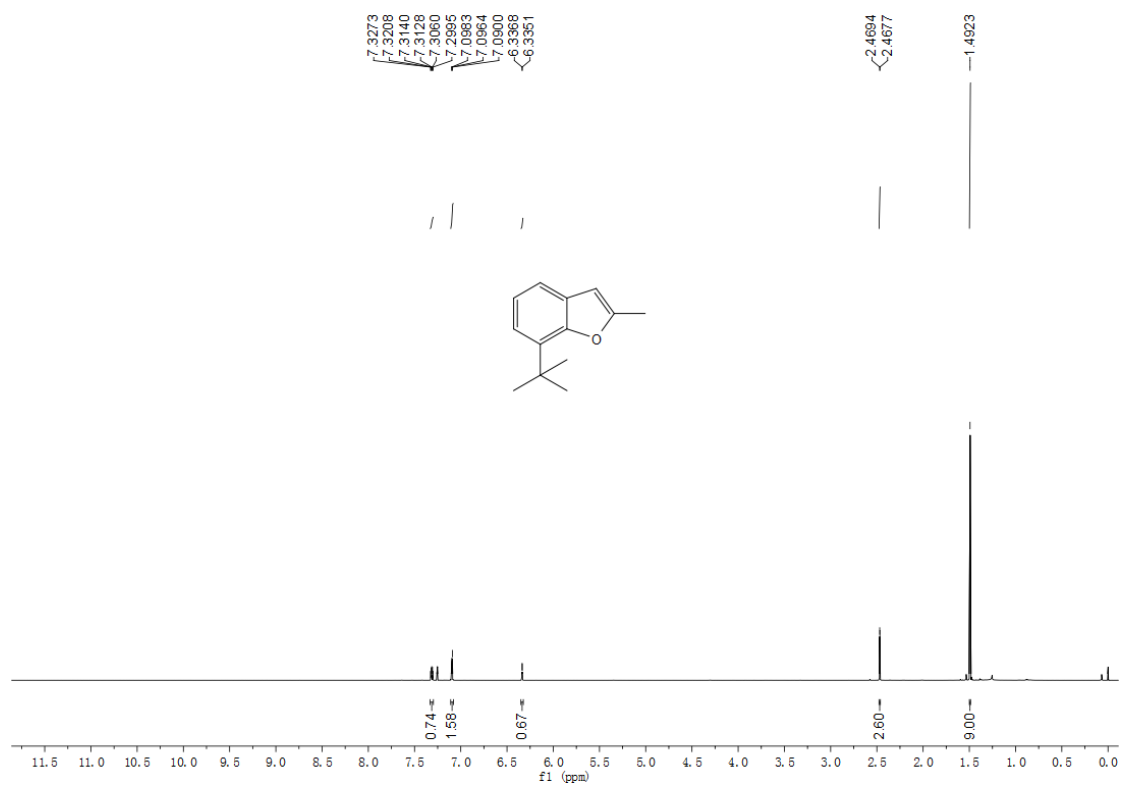


Fig. 11 ¹H NMR of 7-(*tert*-butyl)-2-methylbenzofuran (2f)

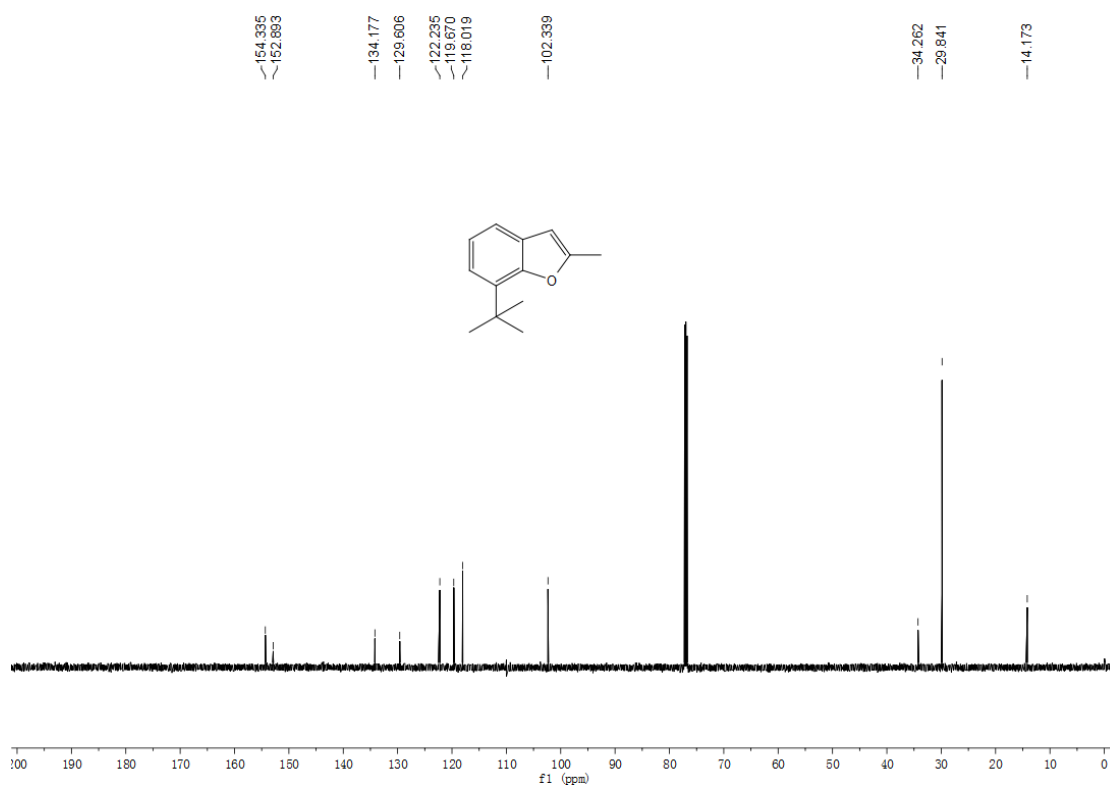


Fig. 12 ¹³C NMR of 7-(*tert*-butyl)-2-methylbenzofuran (2f)



Fig. 13 ¹H NMR of 5,7-di-*tert*-butyl-2-methylbenzofuran (2g)

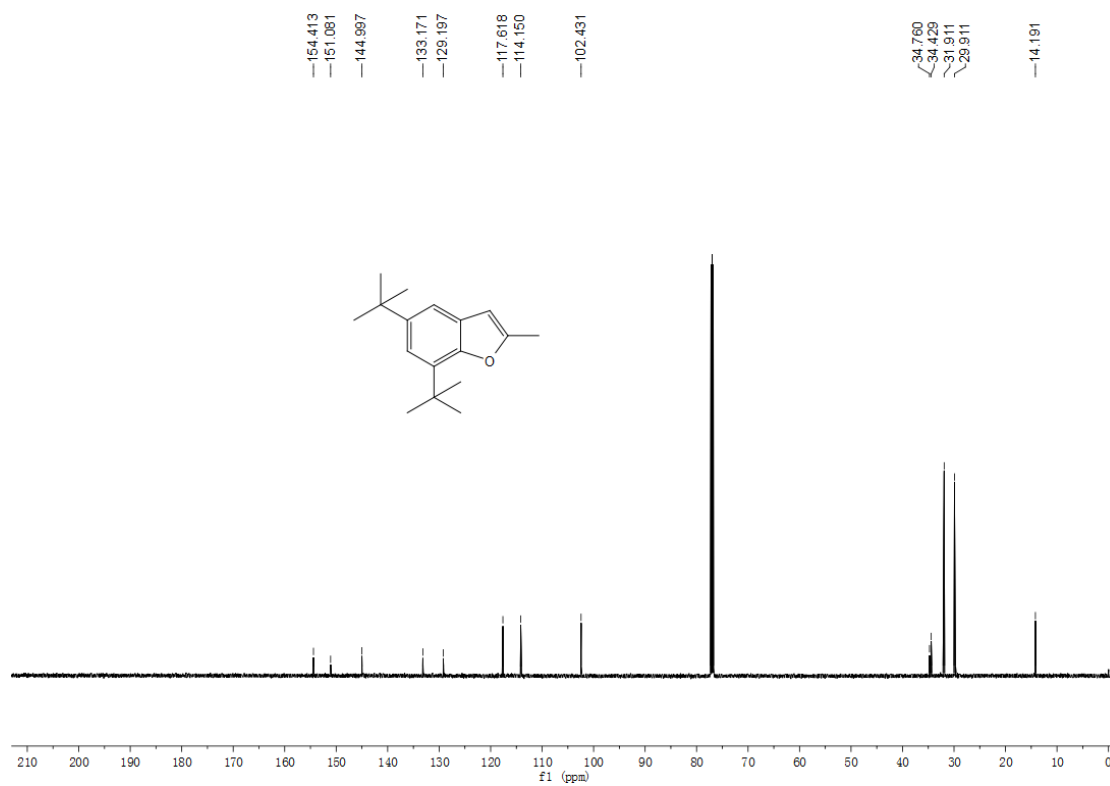


Fig. 14 ¹³C NMR of 5,7-di-*tert*-butyl-2-methylbenzofuran (2g)

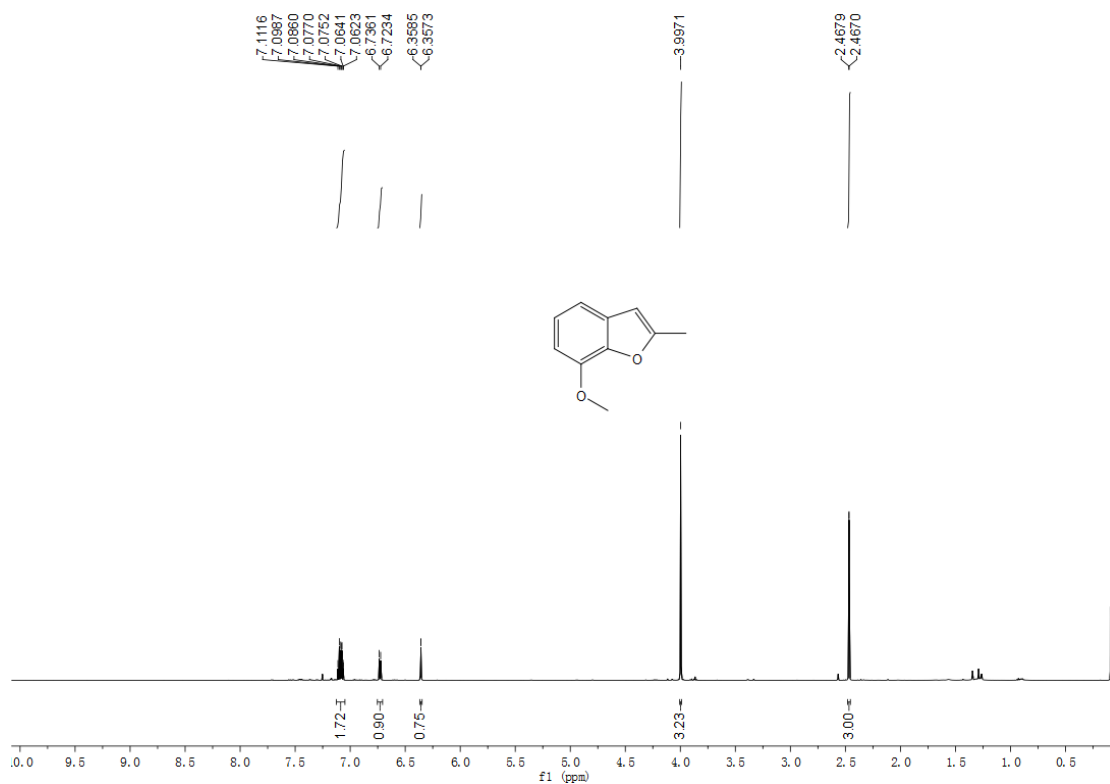


Fig. 15 ¹H NMR of 7-methoxy-2-methylbenzofuran (2h)

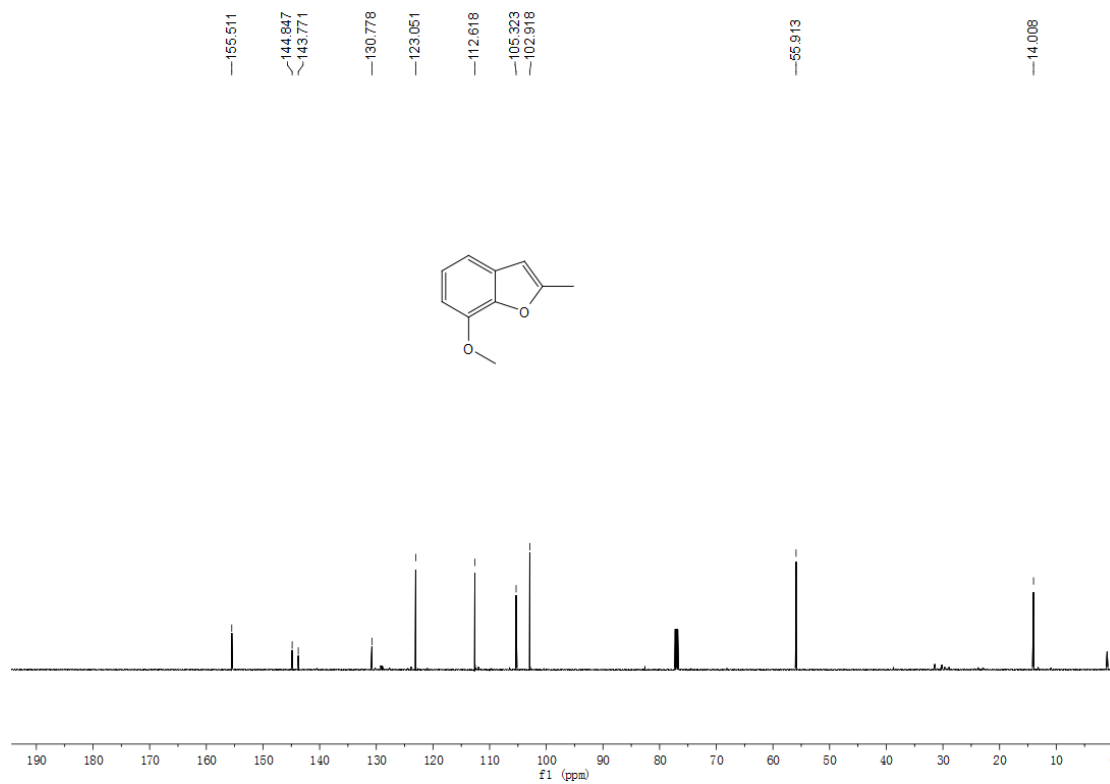


Fig. 16 ¹³C NMR of 7-methoxy-2-methylbenzofuran (2h)

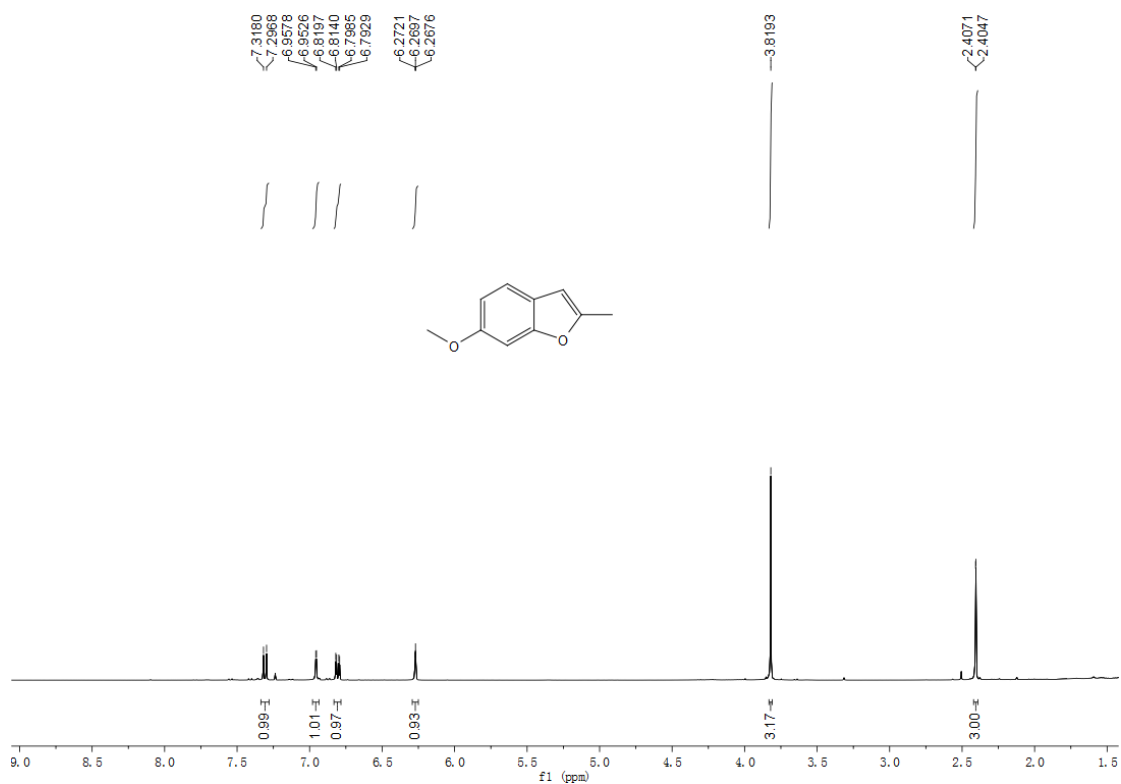


Fig. 17 ^1H NMR of 6-methoxy-2-methylbenzofuran (2i)

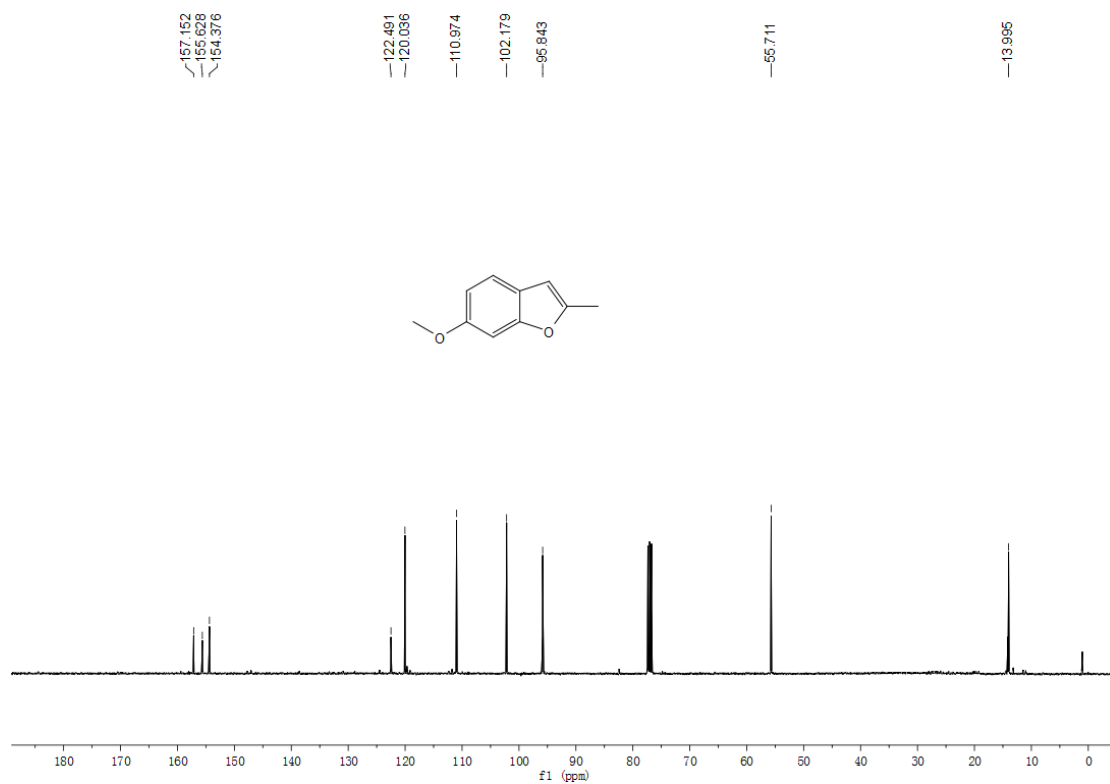


Fig. 18 ^{13}C NMR of 6-methoxy-2-methylbenzofuran (2i)

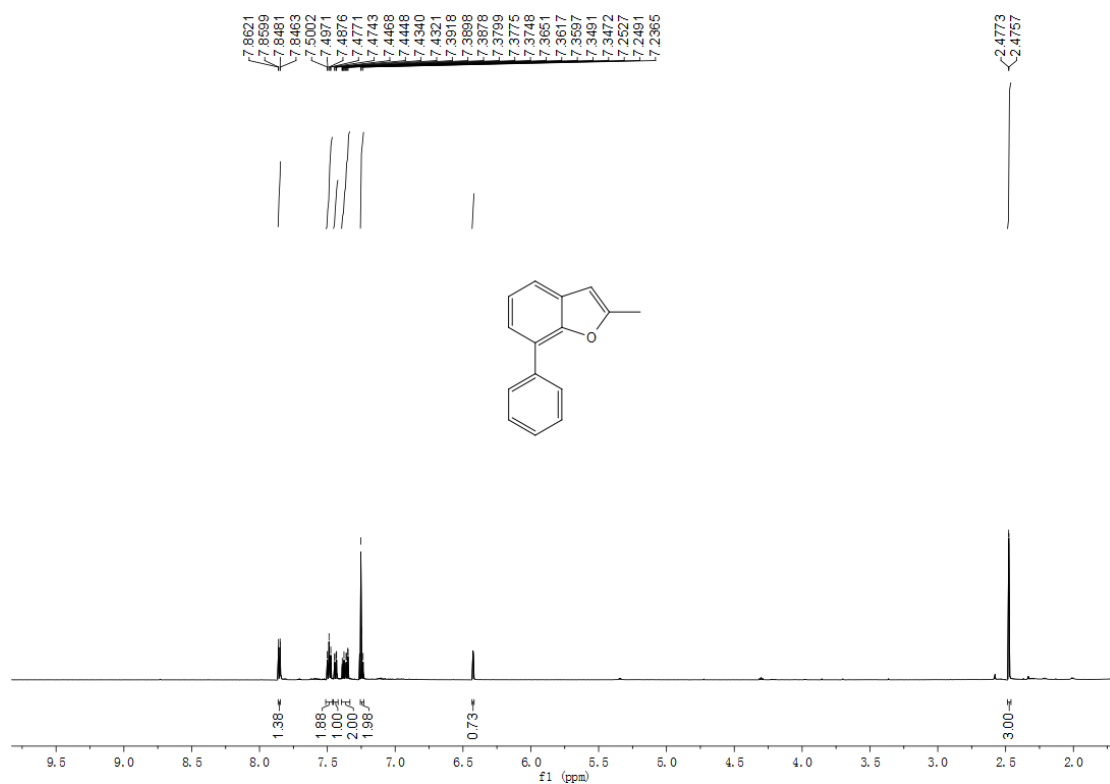


Fig. 19 ^1H NMR of 2-methyl-7-phenylbenzofuran (2j)

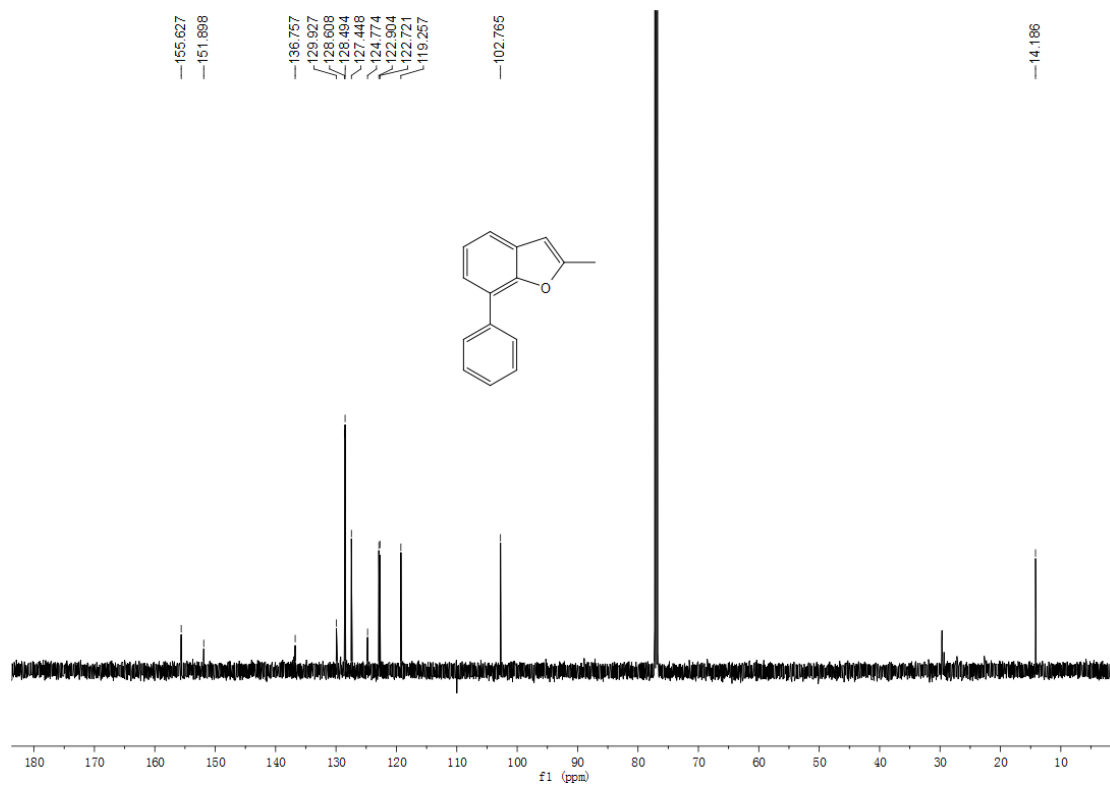


Fig. 20 ^{13}C NMR of 2-methyl-7-phenylbenzofuran (2j)

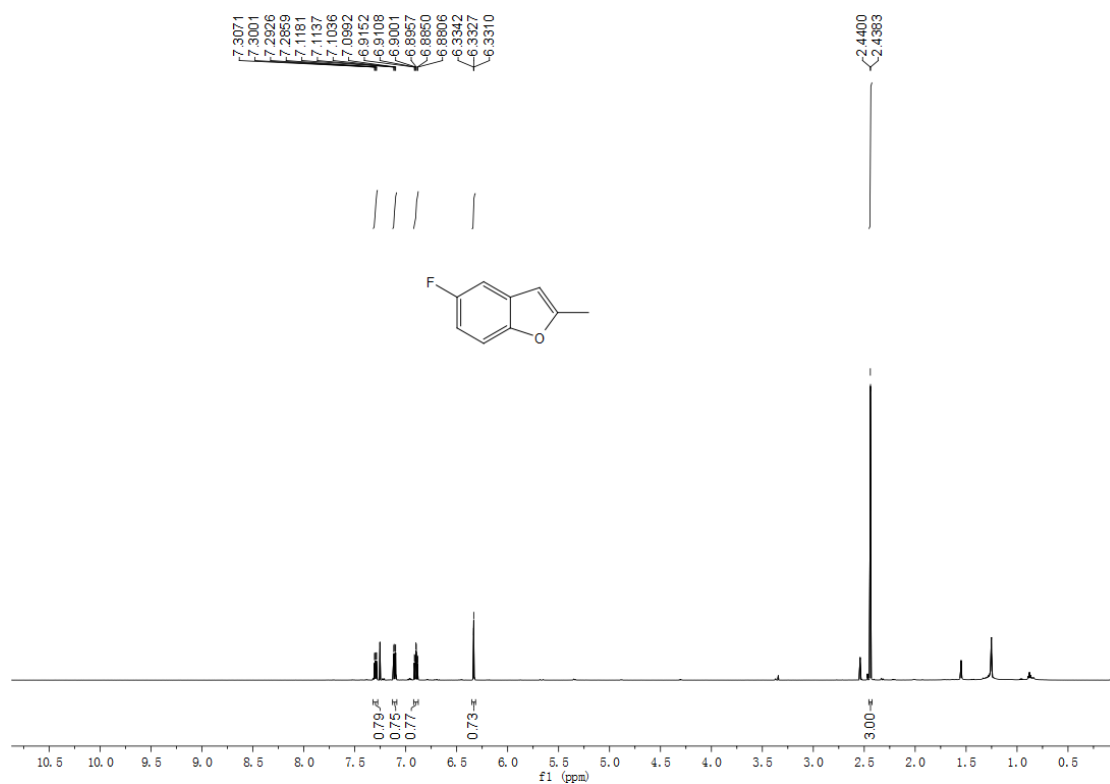


Fig. 21 ¹H NMR of 5-fluoro-2-methylbenzofuran (2k)

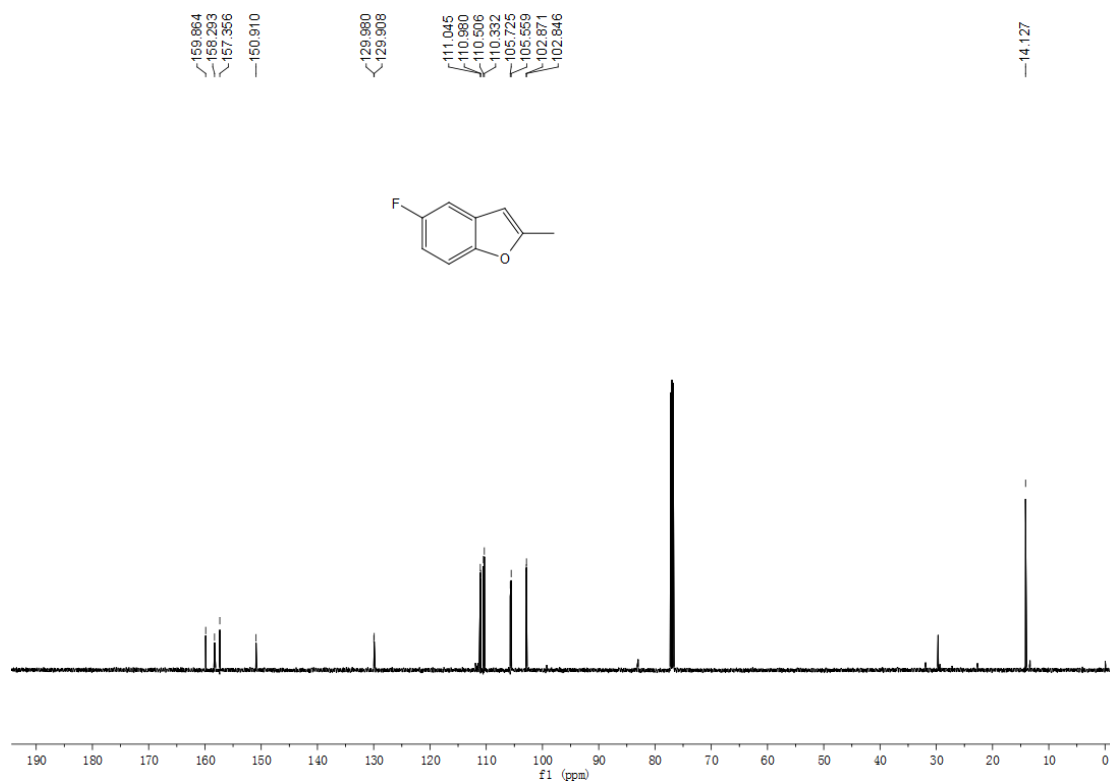


Fig. 22 ¹³C NMR of 5-fluoro-2-methylbenzofuran (2k)

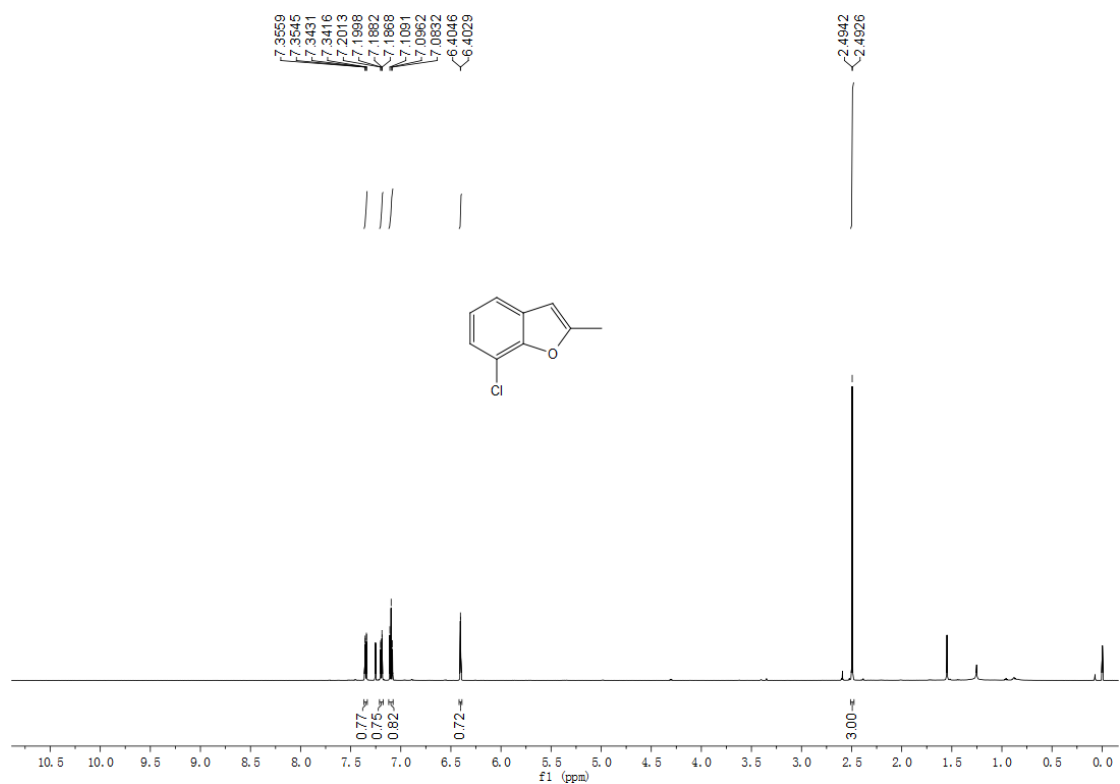


Fig. 23 ¹H NMR of 7-chloro-2-methylbenzofuran (2l)

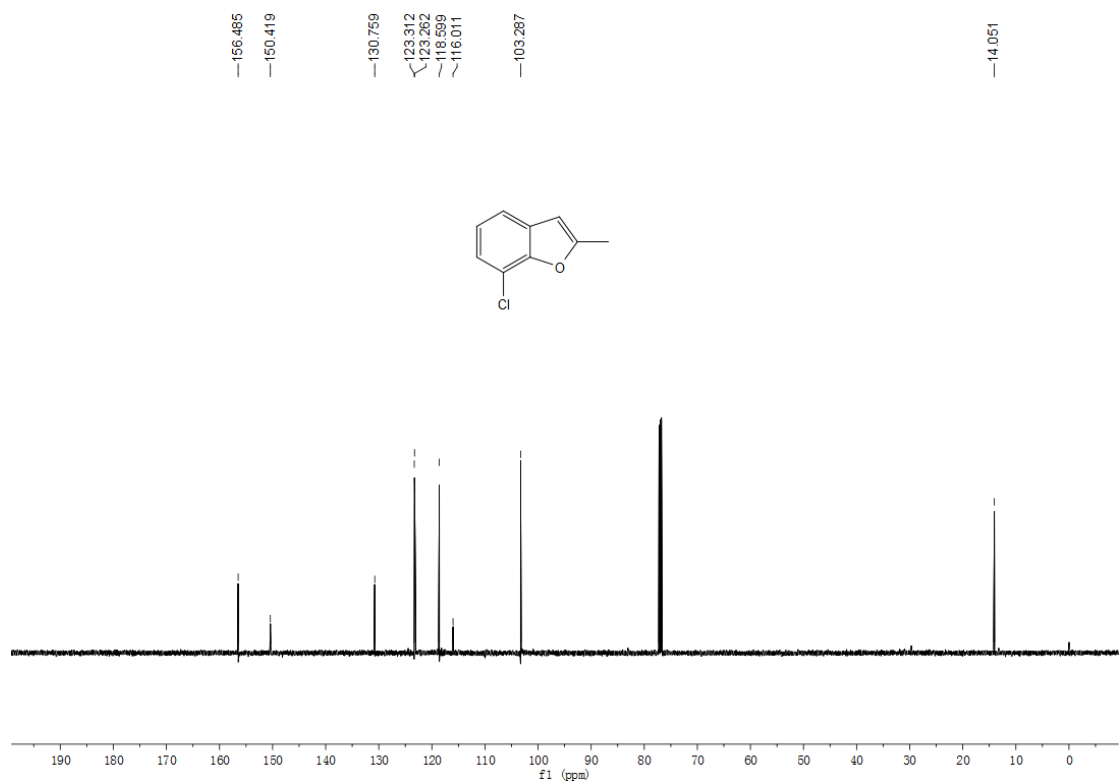


Fig. 24 ¹³C NMR of 7-chloro-2-methylbenzofuran (2l)

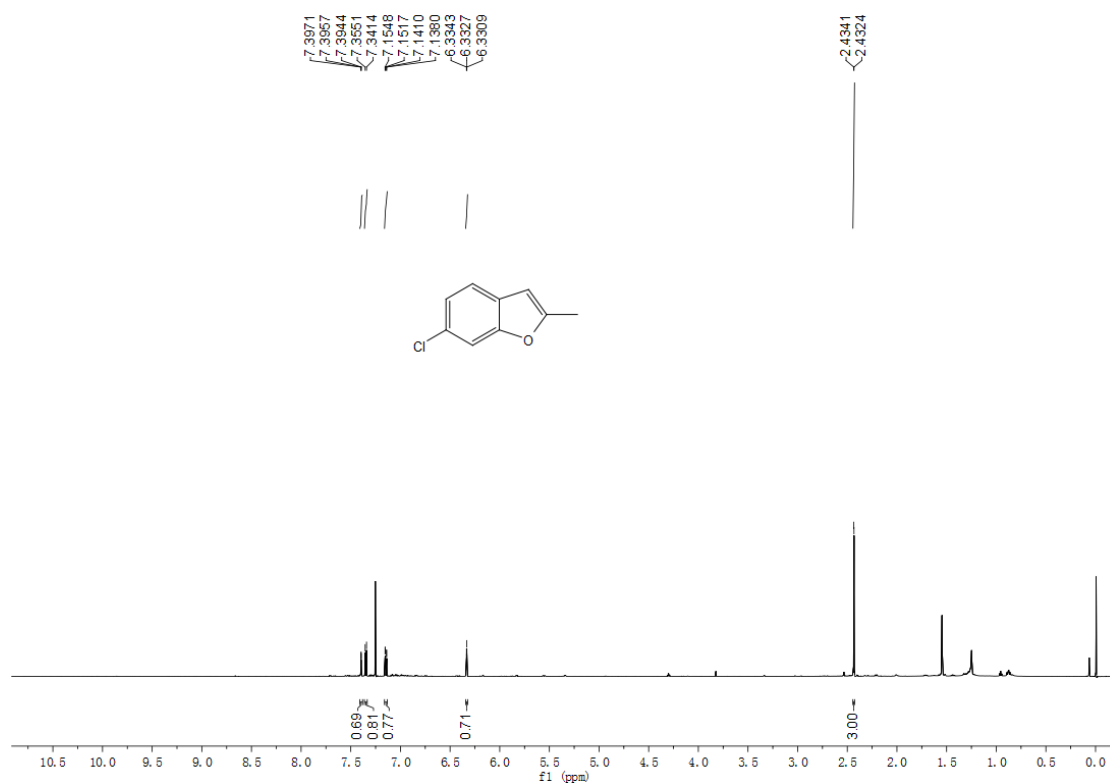


Fig. 25 ¹H NMR of 6-chloro-2-methylbenzofuran (2m)

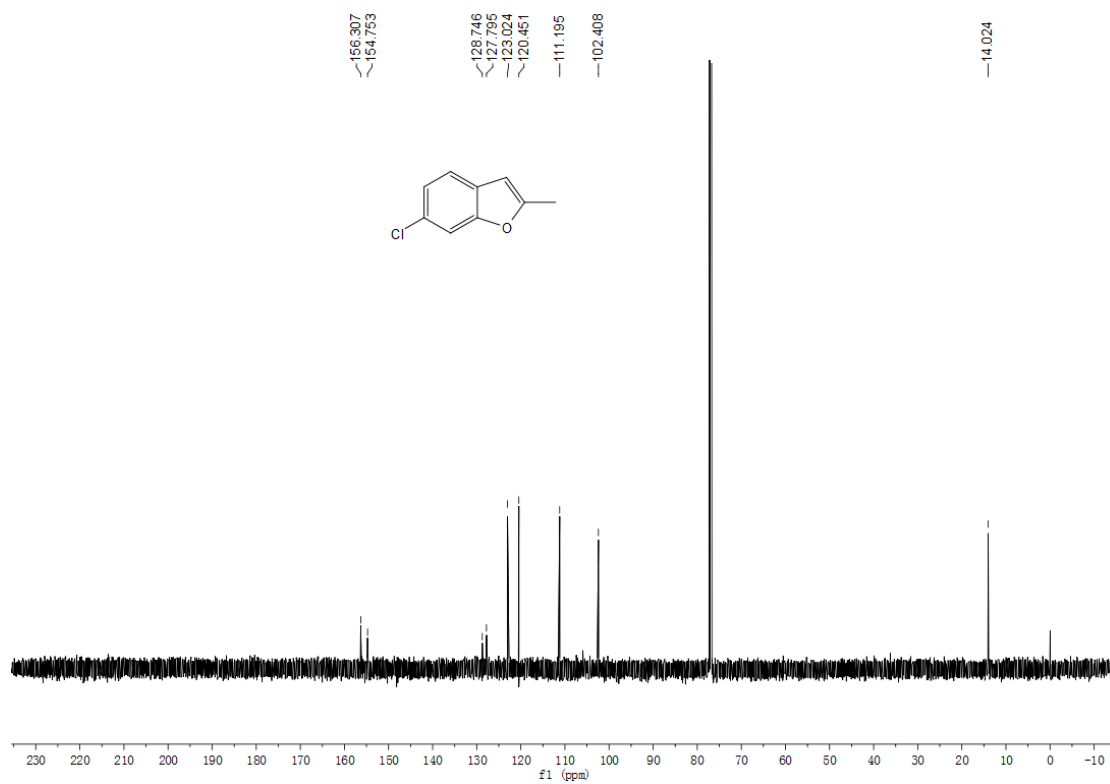


Fig. 26 ¹³C NMR of 6-chloro-2-methylbenzofuran (2m)

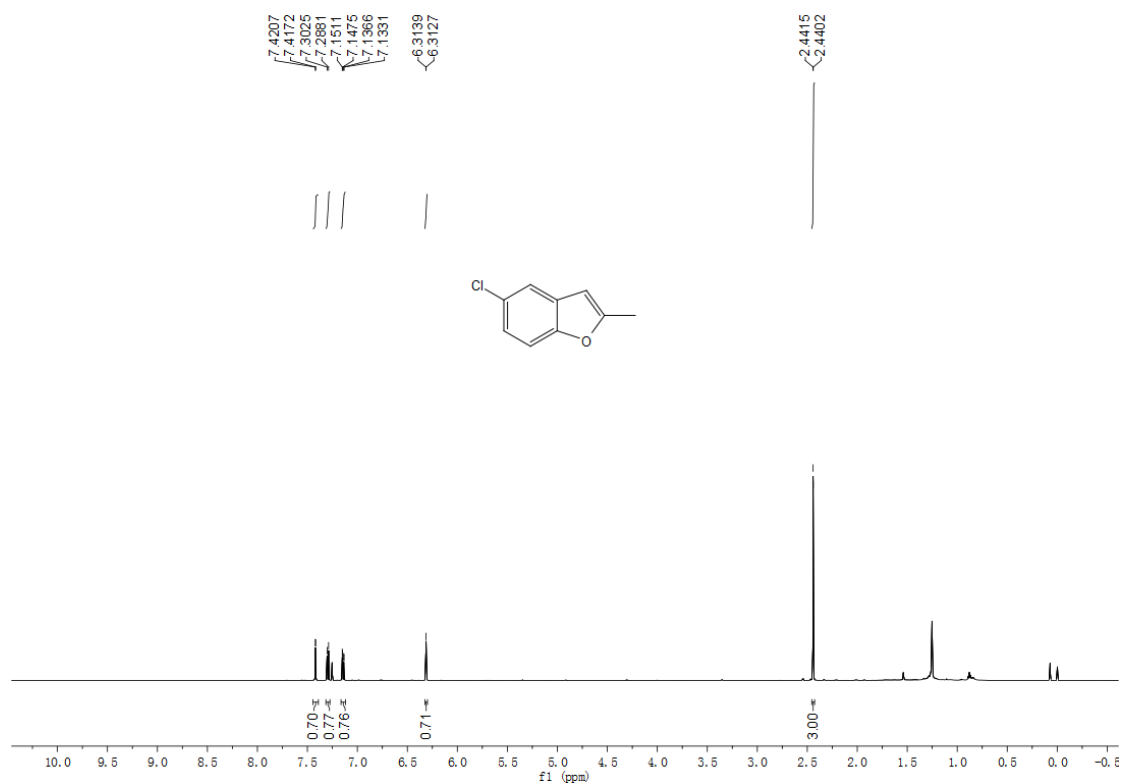


Fig. 27 ¹H NMR of 5-chloro-2-methylbenzofuran (2n)

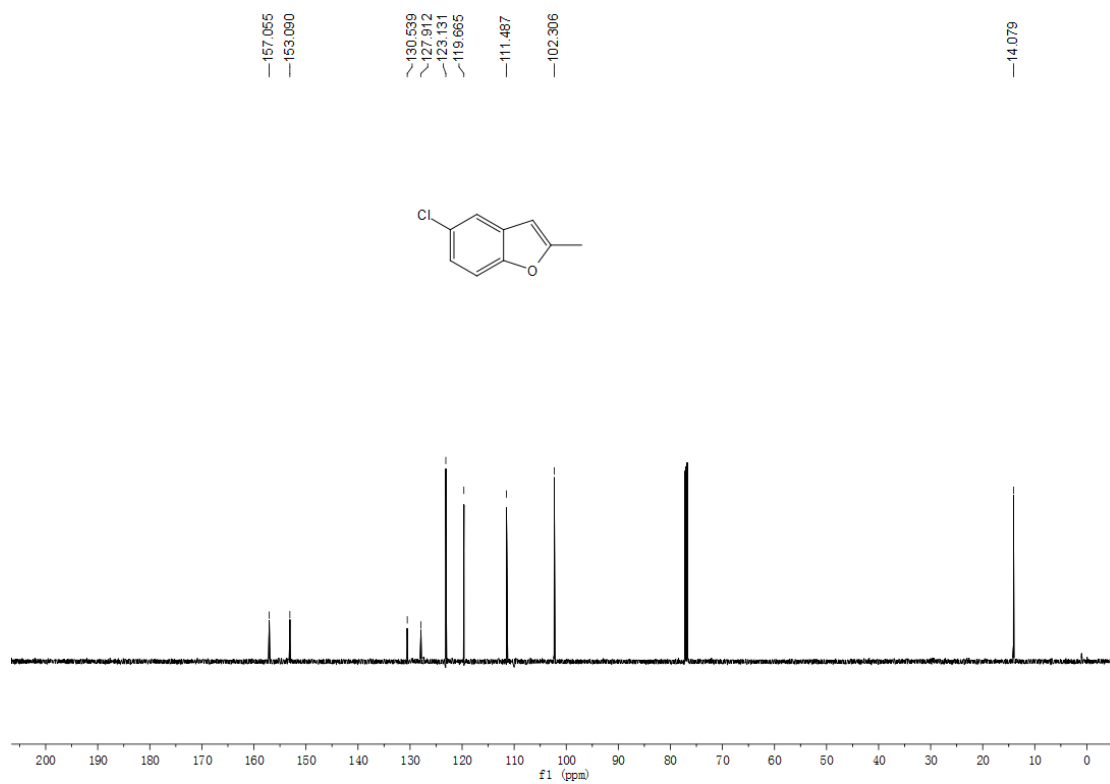


Fig. 28 ¹³C NMR of 5-chloro-2-methylbenzofuran (2n)



Fig. 29 ¹H NMR of 5-bromo-2-methylbenzofuran (2o)

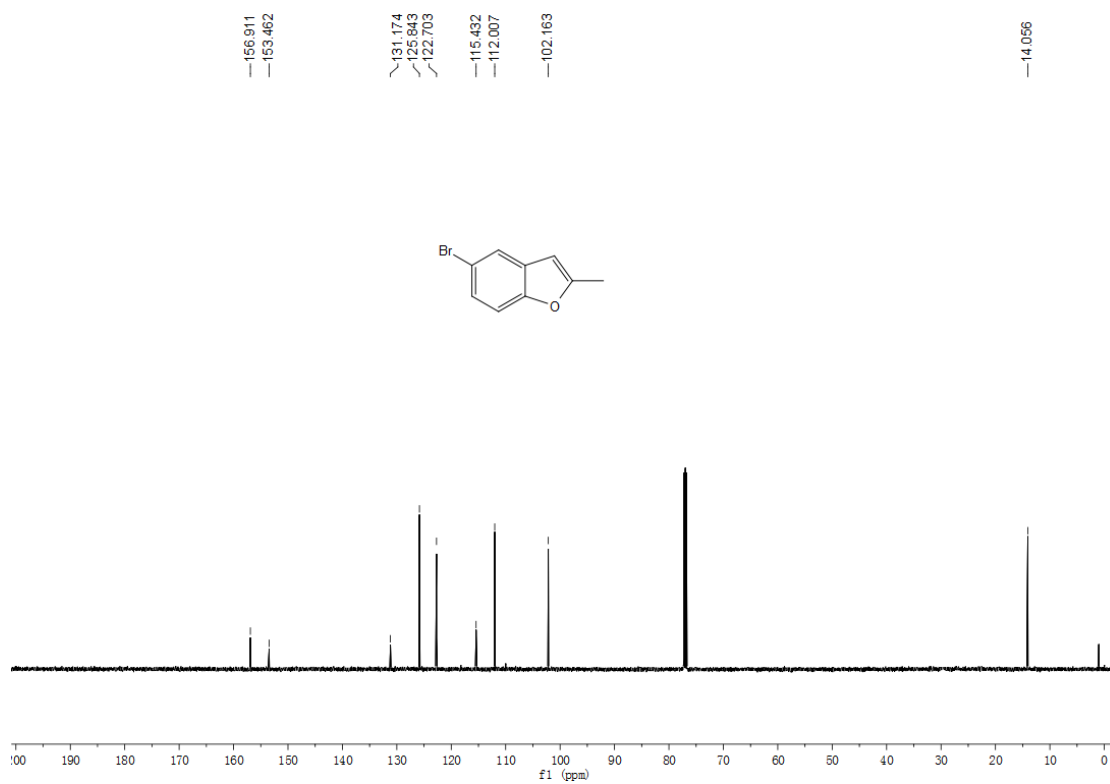


Fig. 30 ¹³C NMR of 5-bromo-2-methylbenzofuran (2o)

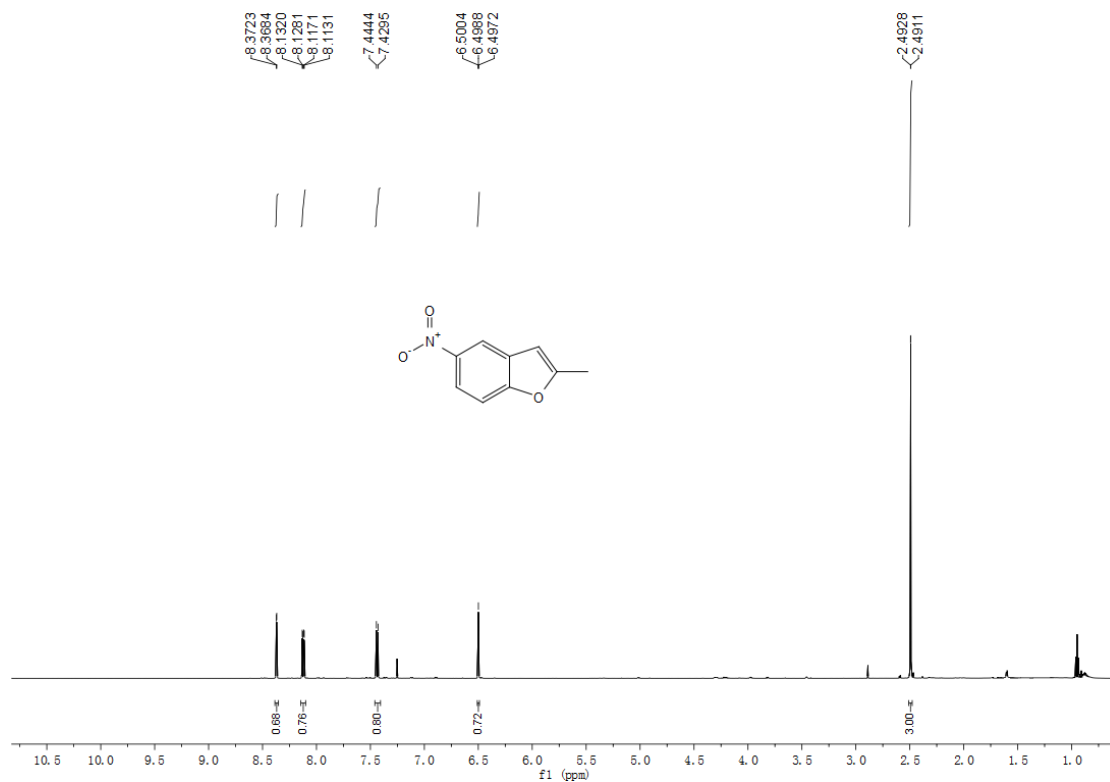


Fig. 31 ¹H NMR of 2-methyl-5-nitrobenzofuran (2p)

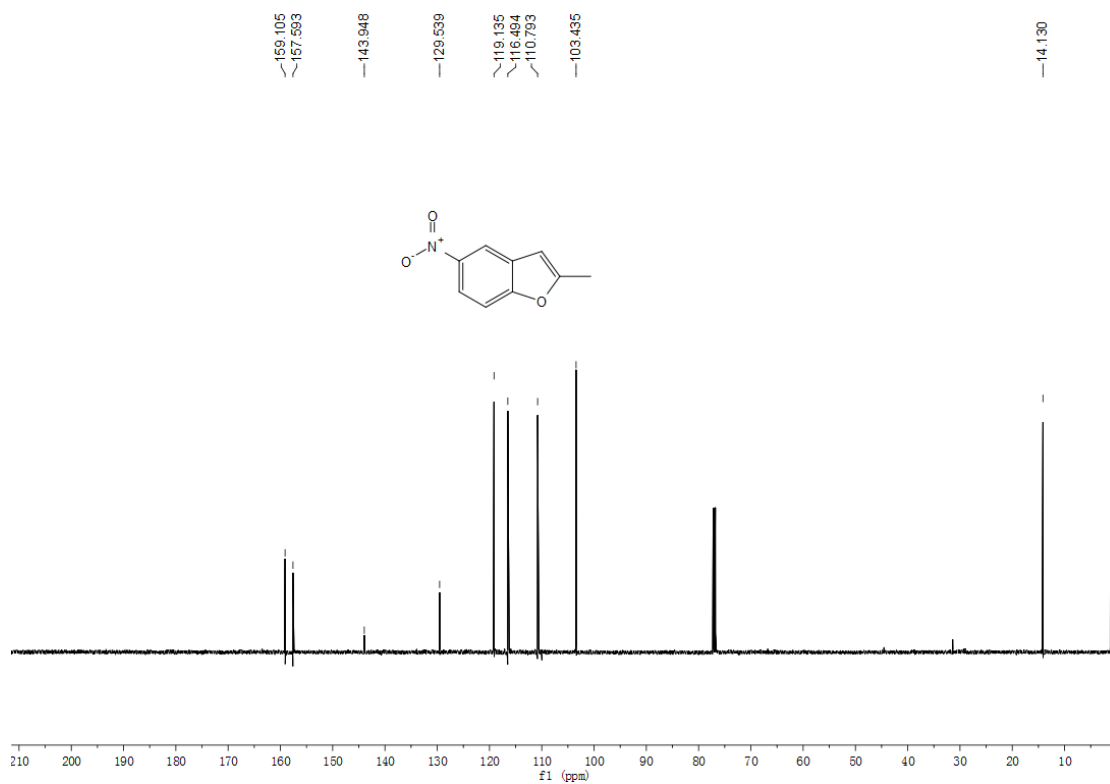


Fig. 32 ¹³C NMR of 2-methyl-5-nitrobenzofuran (2p)

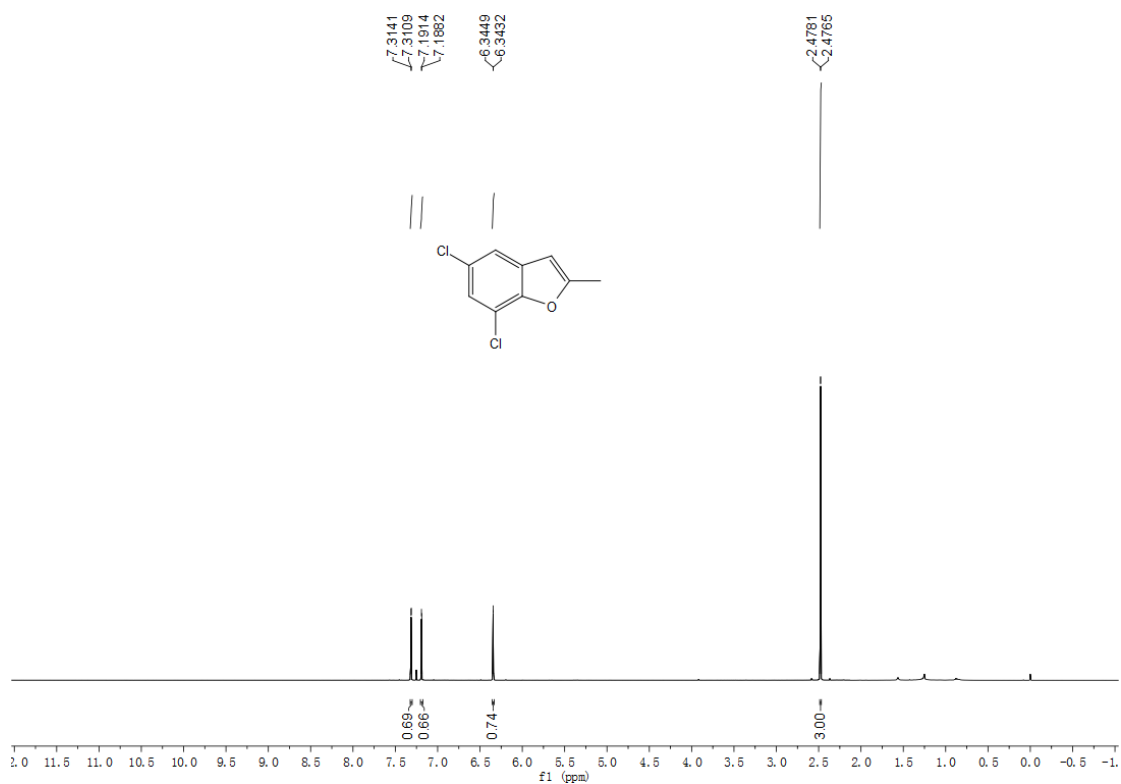


Fig. 33 ¹H NMR of 5,7-dichloro-2-methylbenzofuran (2q)

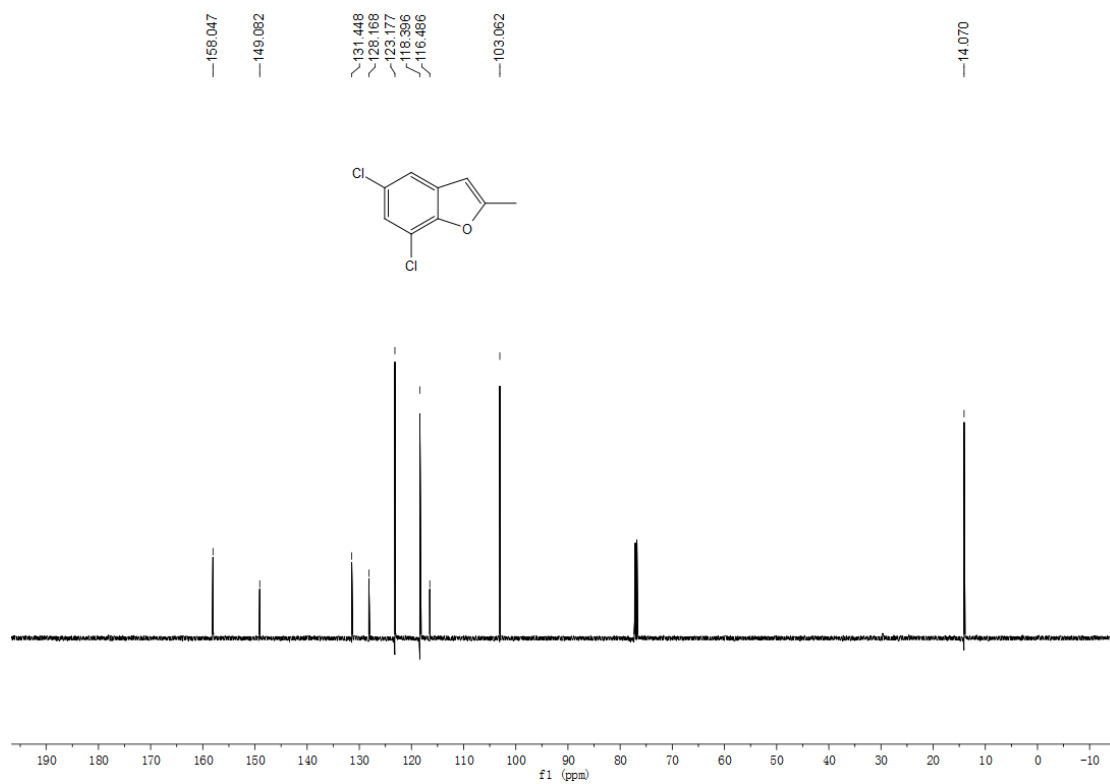


Fig. 34 ¹³C NMR of 5,7-dichloro-2-methylbenzofuran (2q)

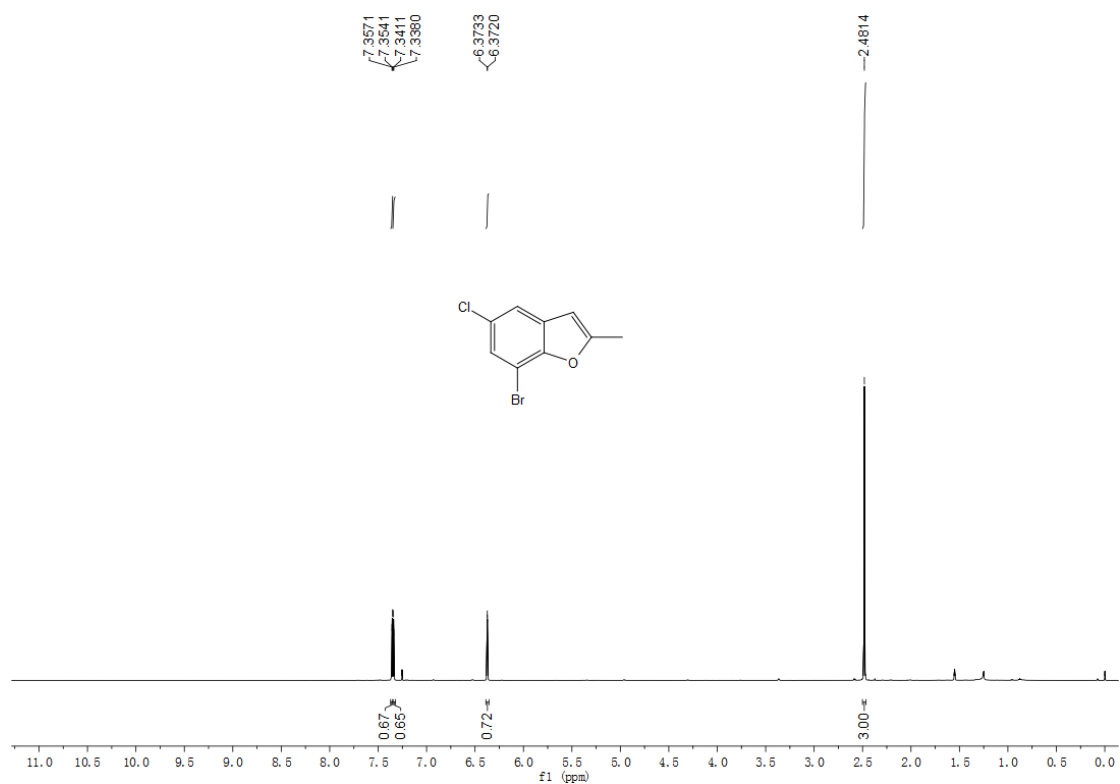


Fig. 35 ¹H NMR of 7-bromo-5-chloro-2-methylbenzofuran (2r)

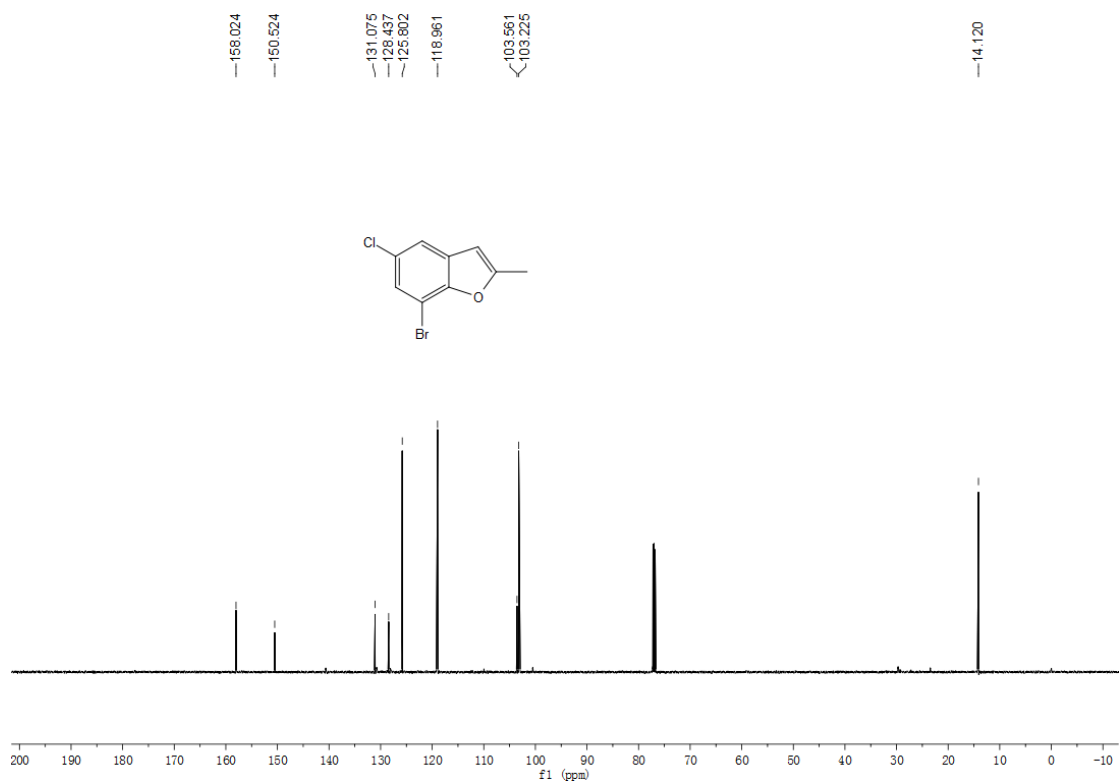


Fig. 36 ¹³C NMR of 7-bromo-5-chloro-2-methylbenzofuran (2r)

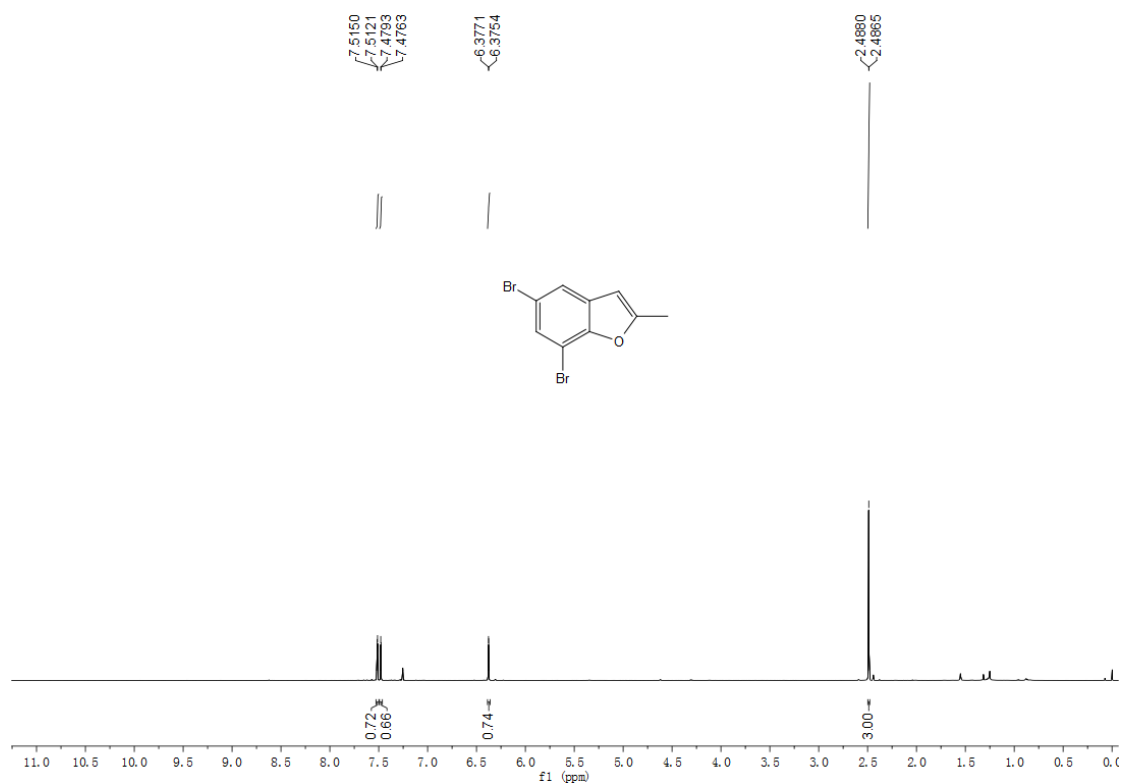


Fig. 37 ¹H NMR of 5,7-dibromo-2-methylbenzofuran (2s)

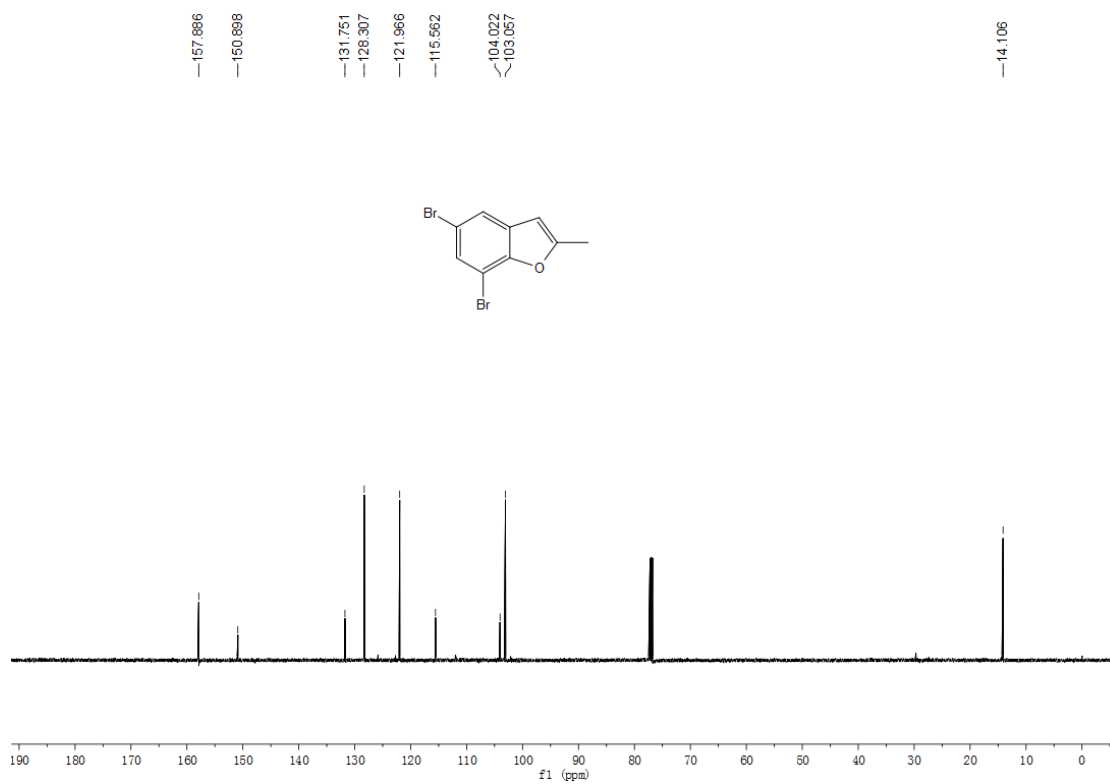


Fig. 38 ¹³C NMR of 5,7-dibromo-2-methylbenzofuran (2s)

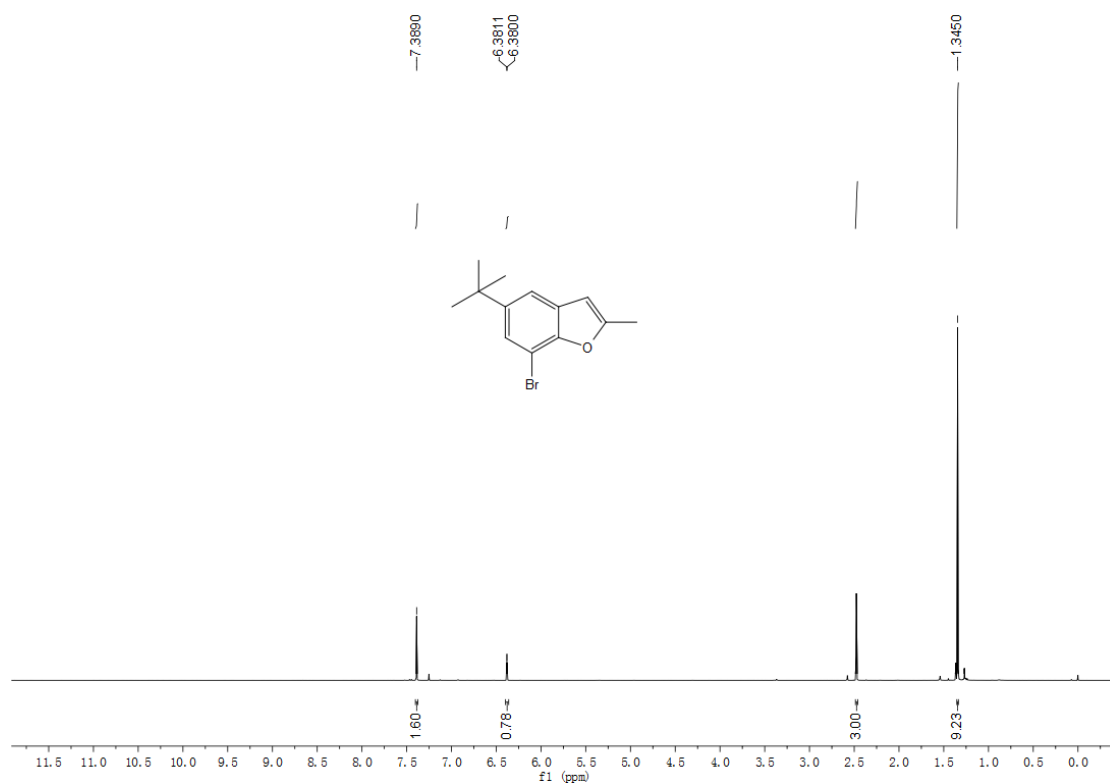


Fig. 39 ^1H NMR of 7-bromo-5-(*tert*-butyl)-2-methylbenzofuran (2t)

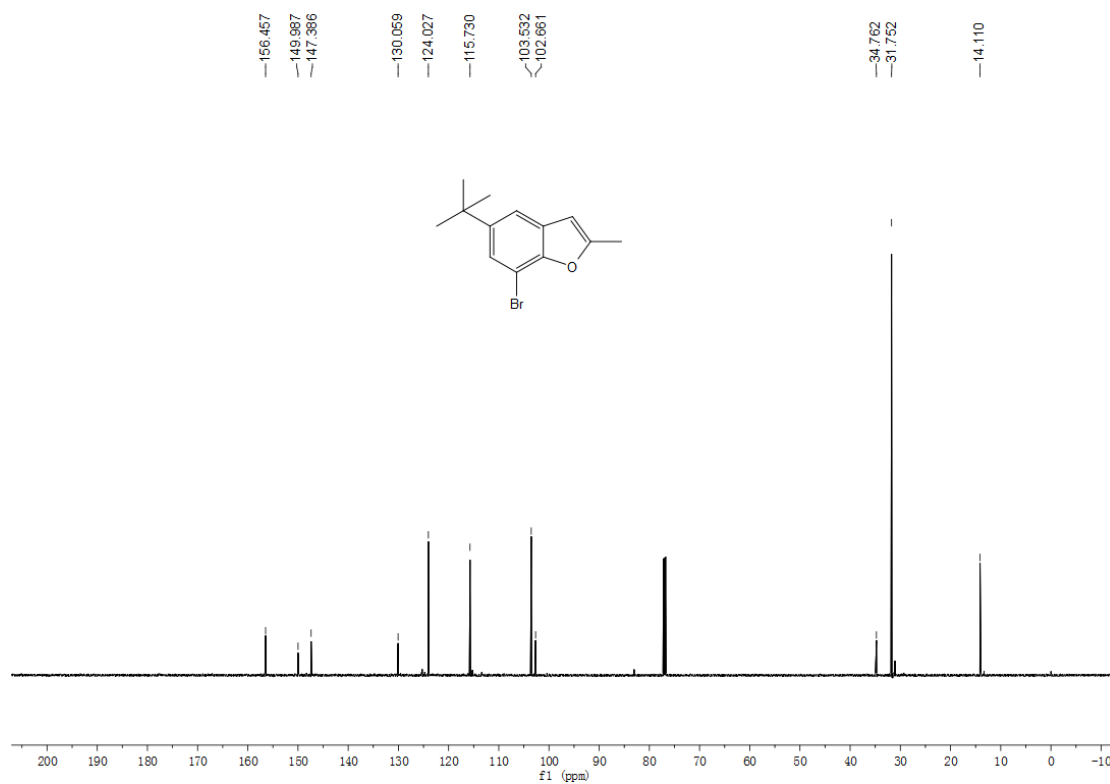


Fig. 40 ^{13}C NMR of 7-bromo-5-(*tert*-butyl)-2-methylbenzofuran (2t)

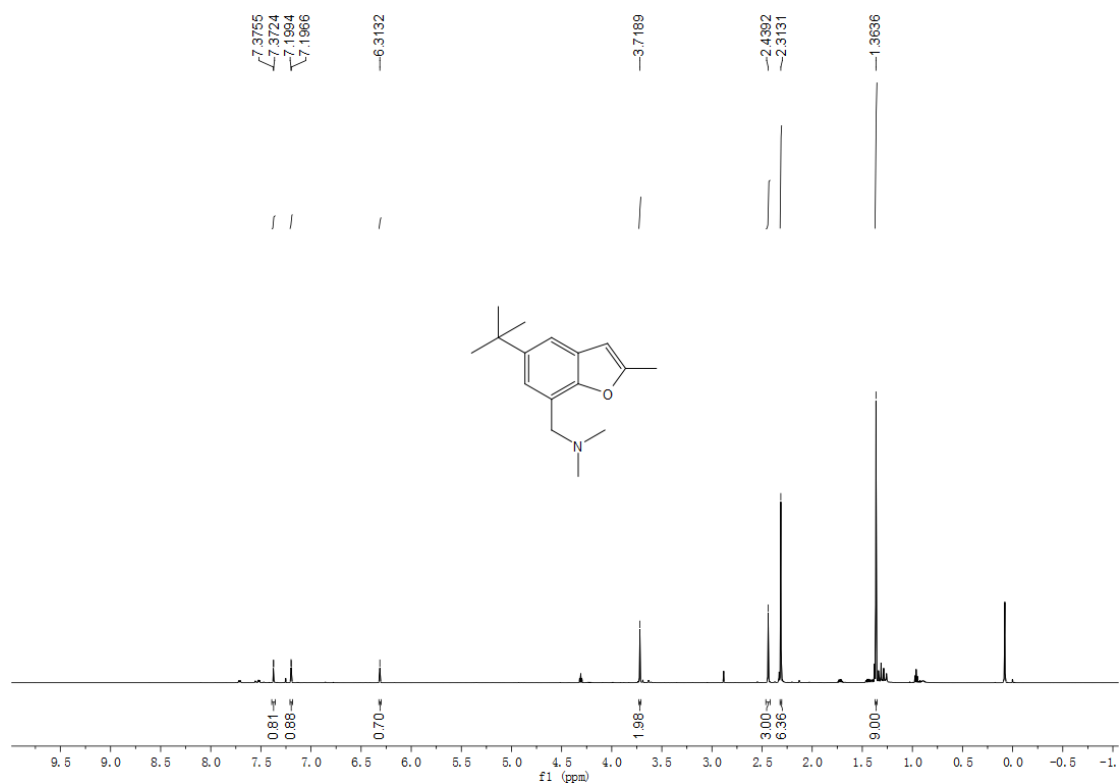


Fig. 41 ¹H NMR of 1-(5-(*tert*-butyl)-2-methylbenzofuran-7-yl)-*N,N*-dimethylmethanamine (2u)

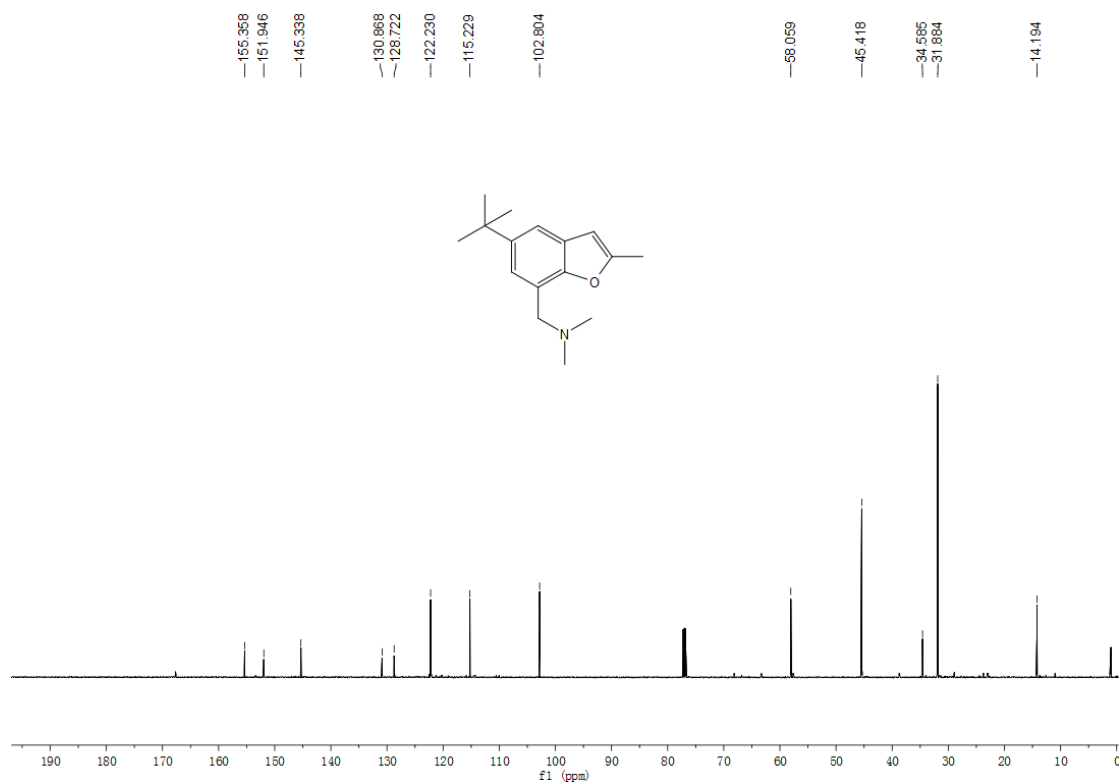


Fig. 42 ¹³C NMR of 1-(5-(*tert*-butyl)-2-methylbenzofuran-7-yl)-*N,N*-dimethylmethanamine

(2u)

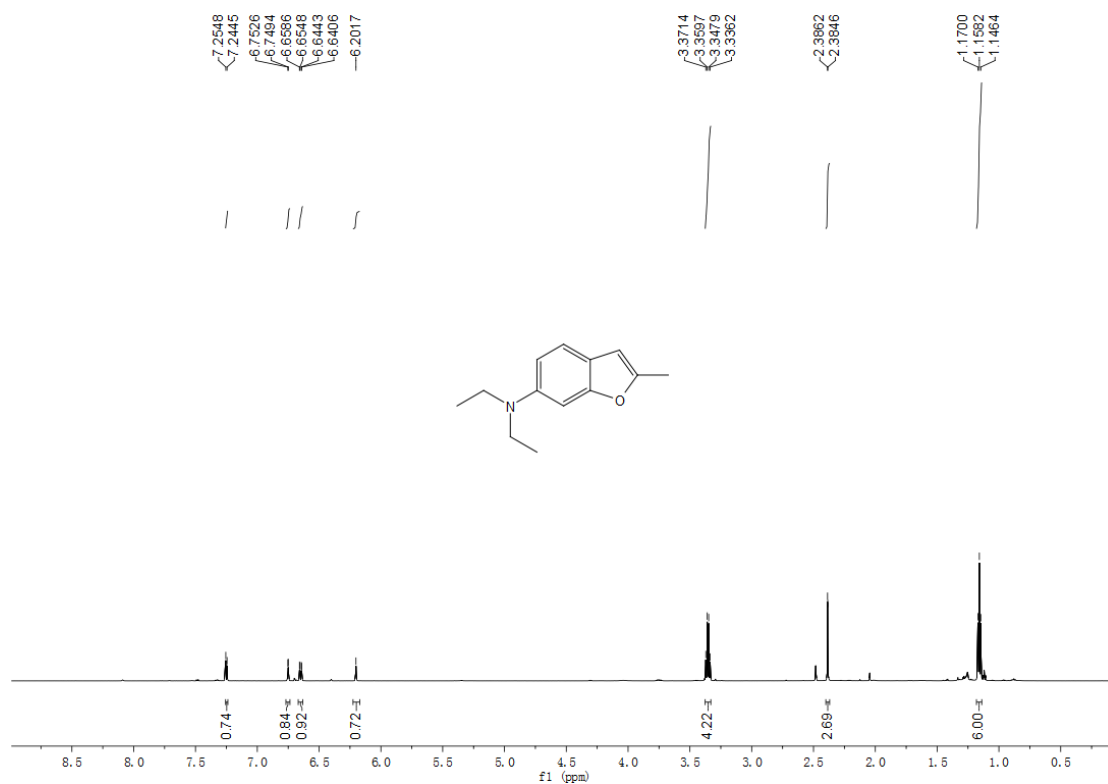


Fig. 43 ¹H NMR of *N,N*-diethyl-2-methylbenzofuran-6-amine (2v)

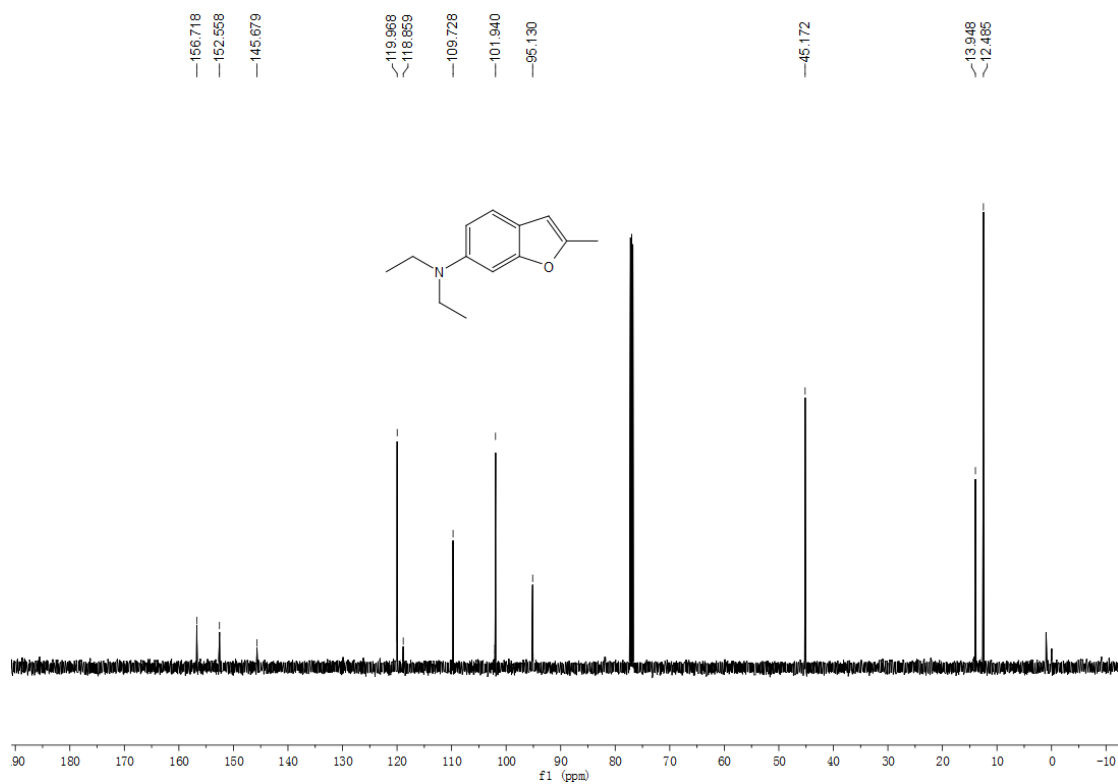


Fig. 44 ¹³C NMR of *N,N*-diethyl-2-methylbenzofuran-6-amine (2v)

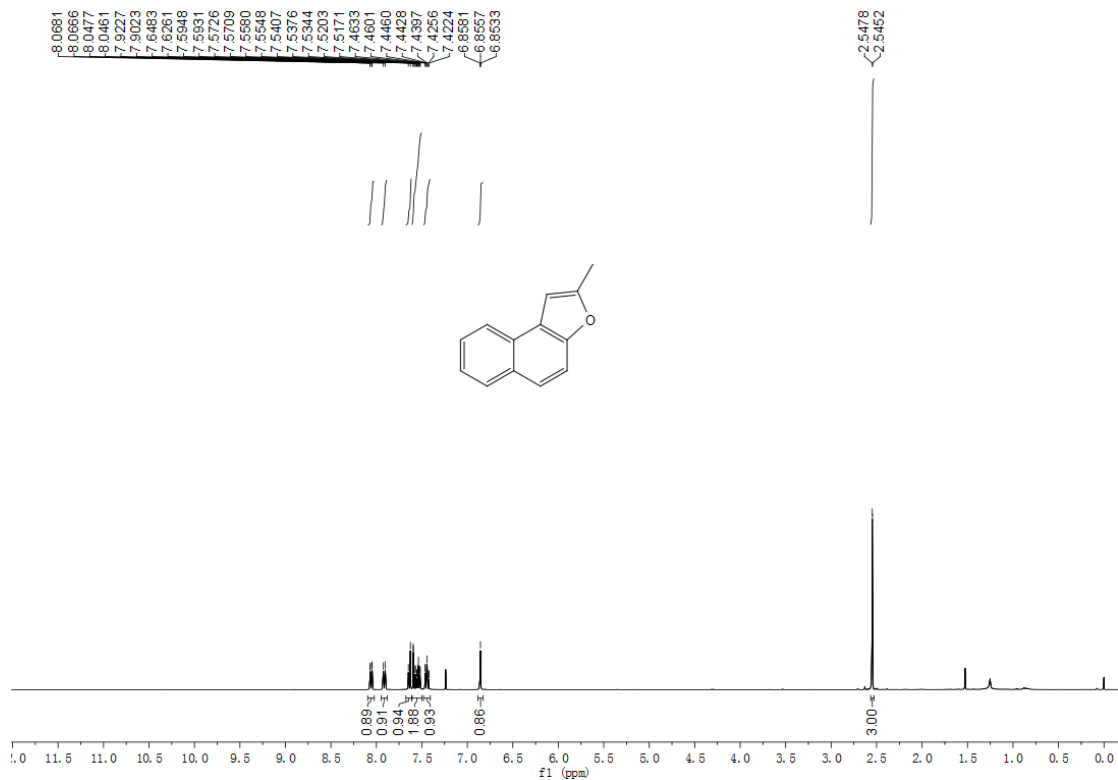


Fig. 45 ^1H NMR of 2-methylnaphtho[2,1-*b*]furan (2w)

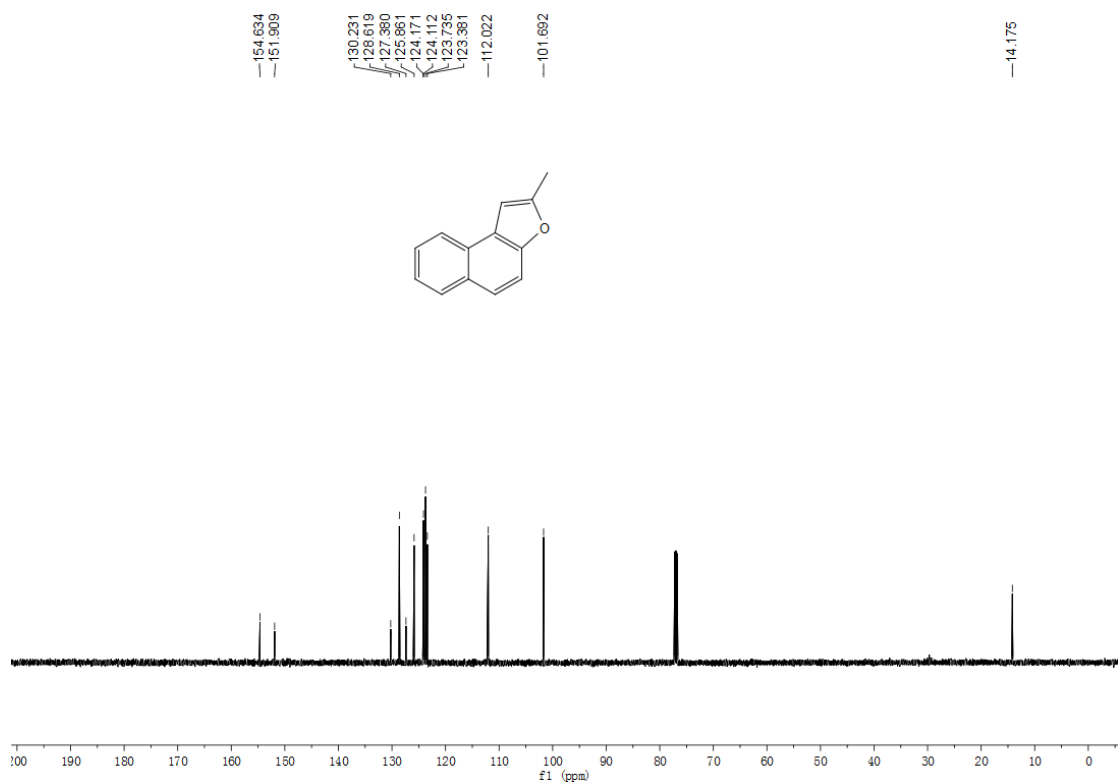


Fig. 46 ^{13}C NMR of 2-methylnaphtho[2,1-*b*]furan (2w)

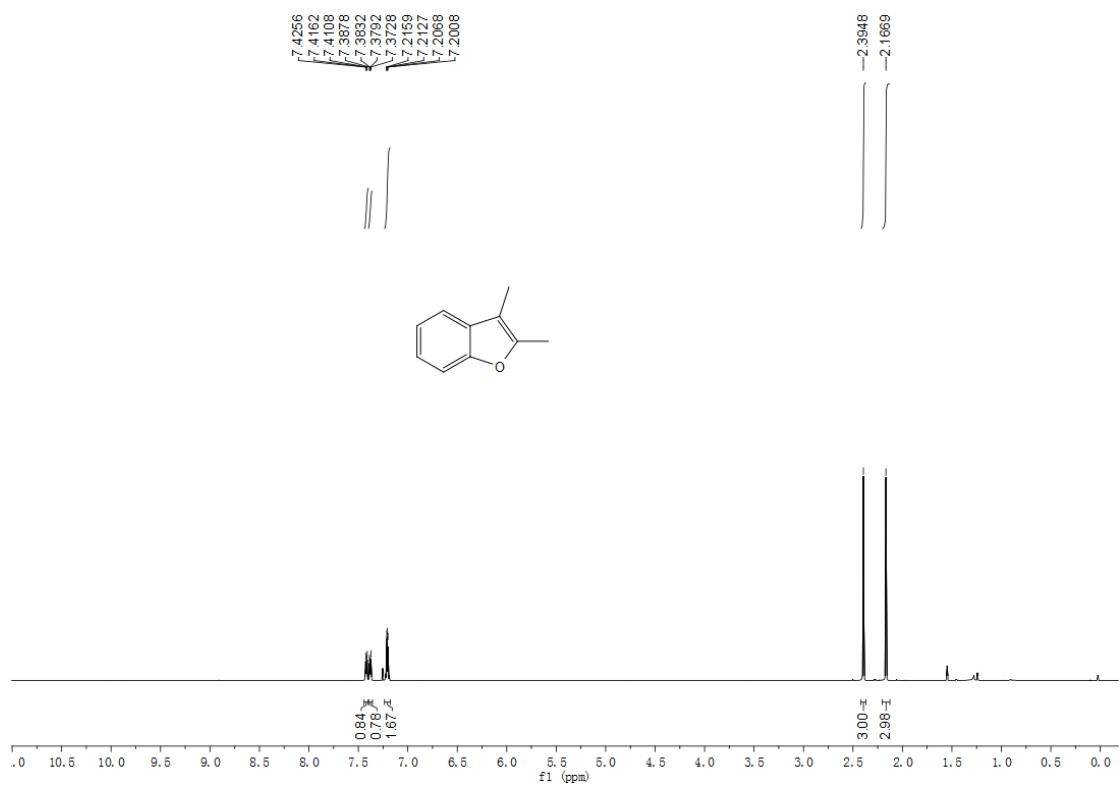


Fig. 47 ^1H NMR of 2,3-dimethylbenzofuran (4a)

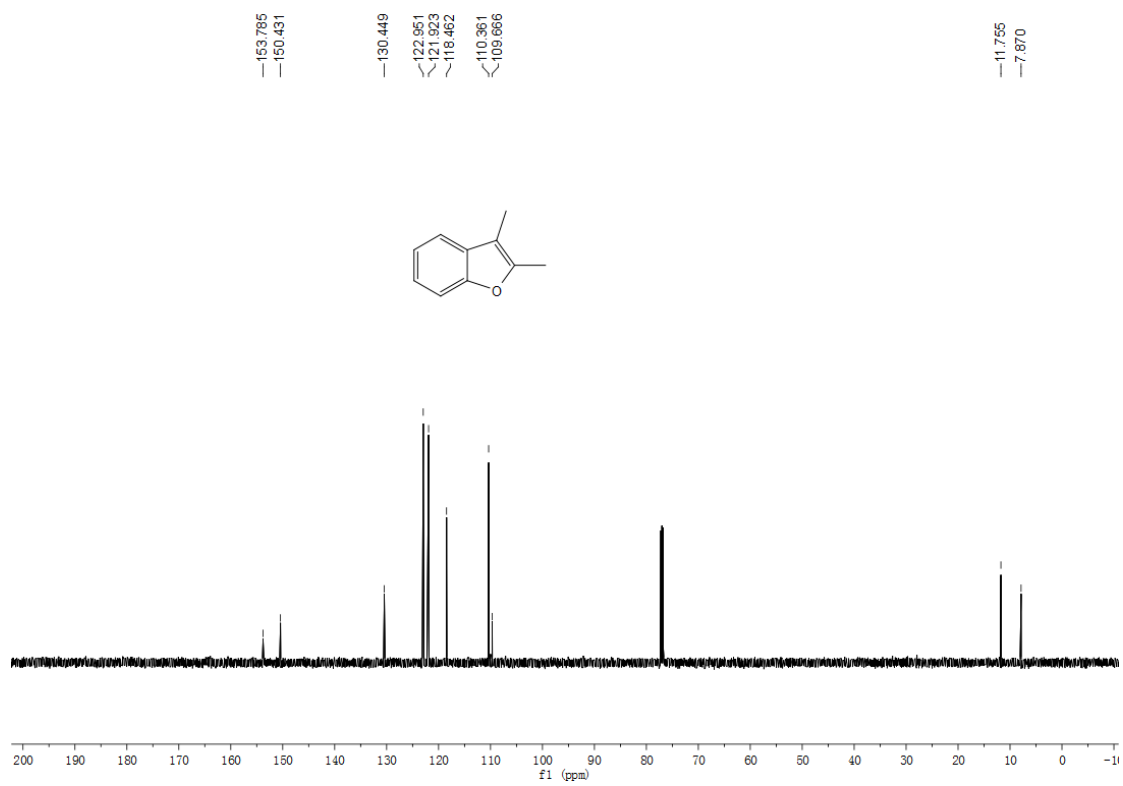


Fig. 48 ^{13}C NMR of 2,3-dimethylbenzofuran (4a)

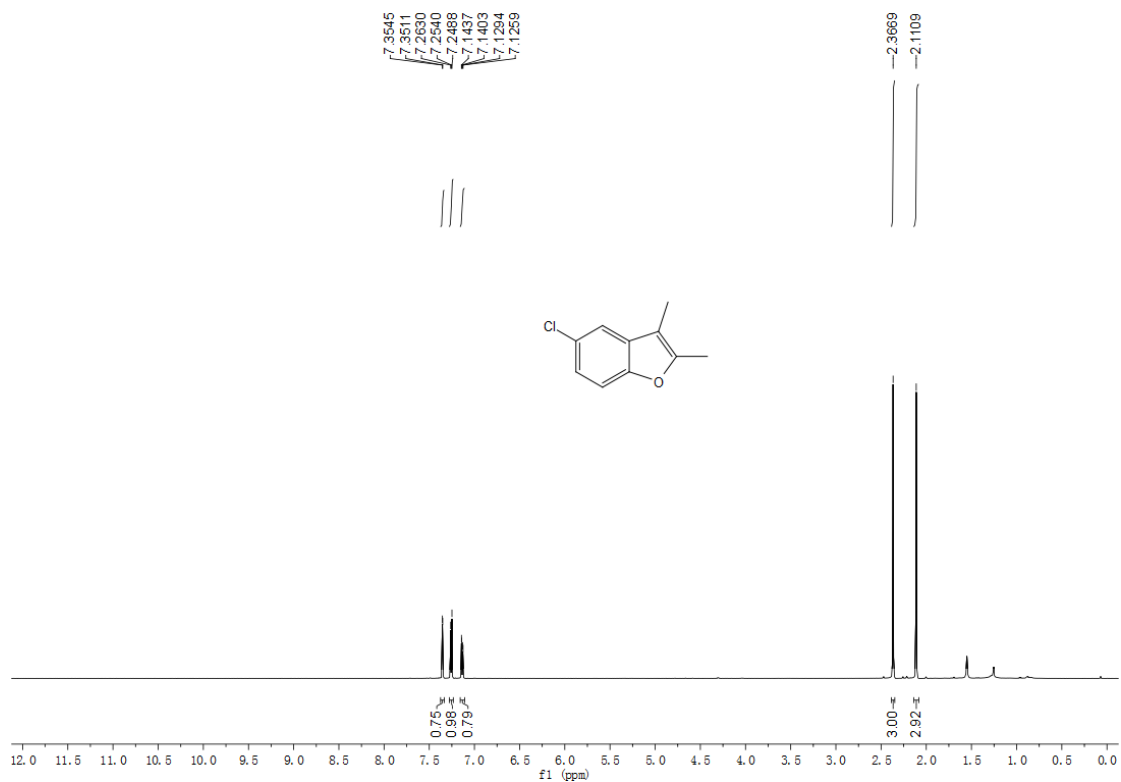


Fig. 47 ¹H NMR of 5-chloro-2,3-dimethylbenzofuran (4b)

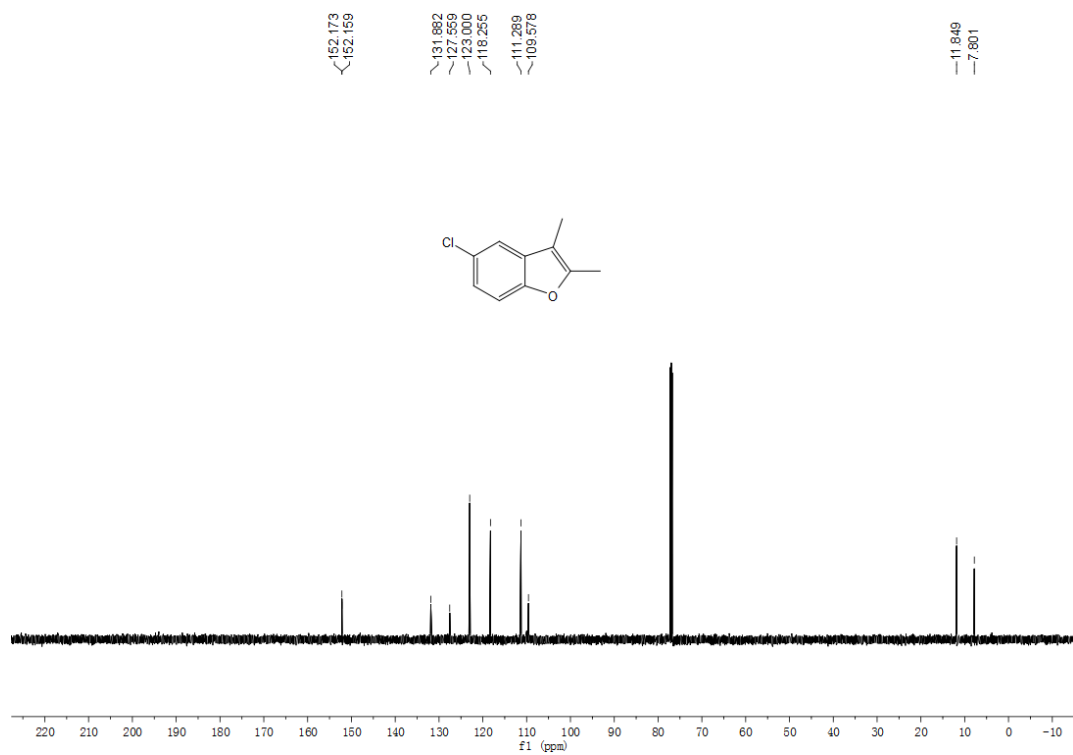


Fig. 48 ¹³C NMR of 5-chloro-2,3-dimethylbenzofuran (4b)

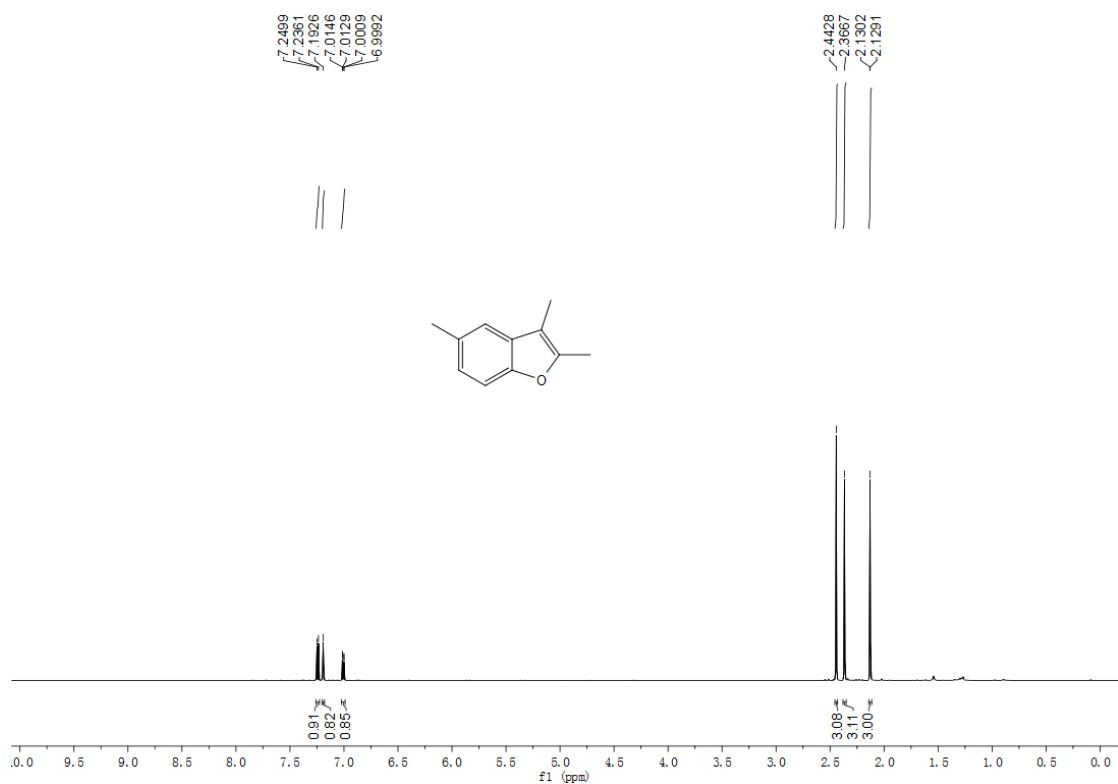


Fig. 49 ¹H NMR of 2,3,5-trimethylbenzofuran (4c)

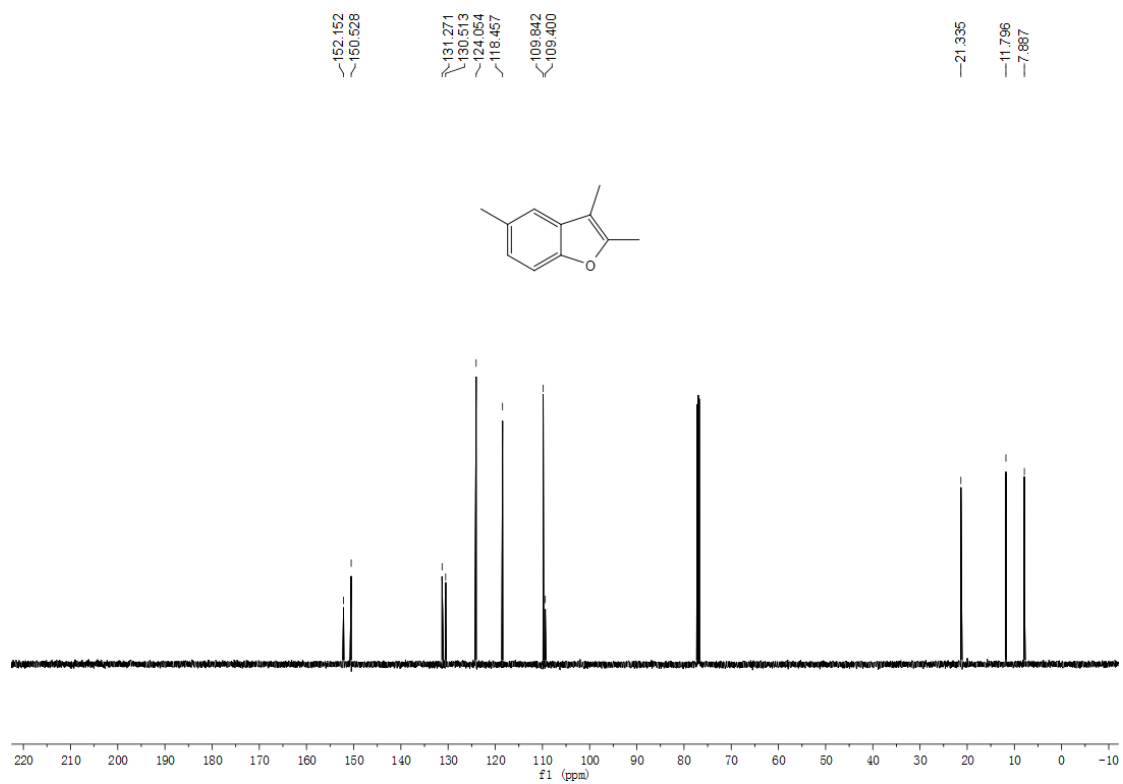


Fig. 50 ¹³C NMR of 2,3,5-trimethylbenzofuran (4c)

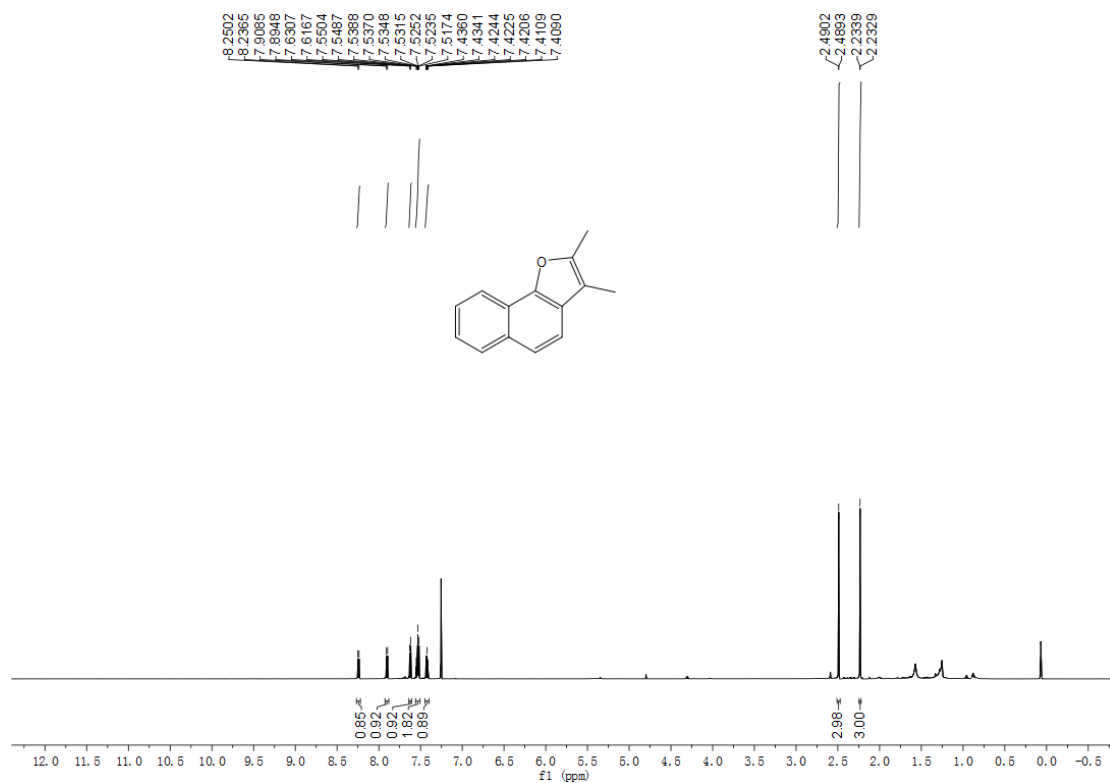


Fig. 53 ¹H NMR of 2,3-dimethylnaphtho[1,2-*b*]furan (4d)

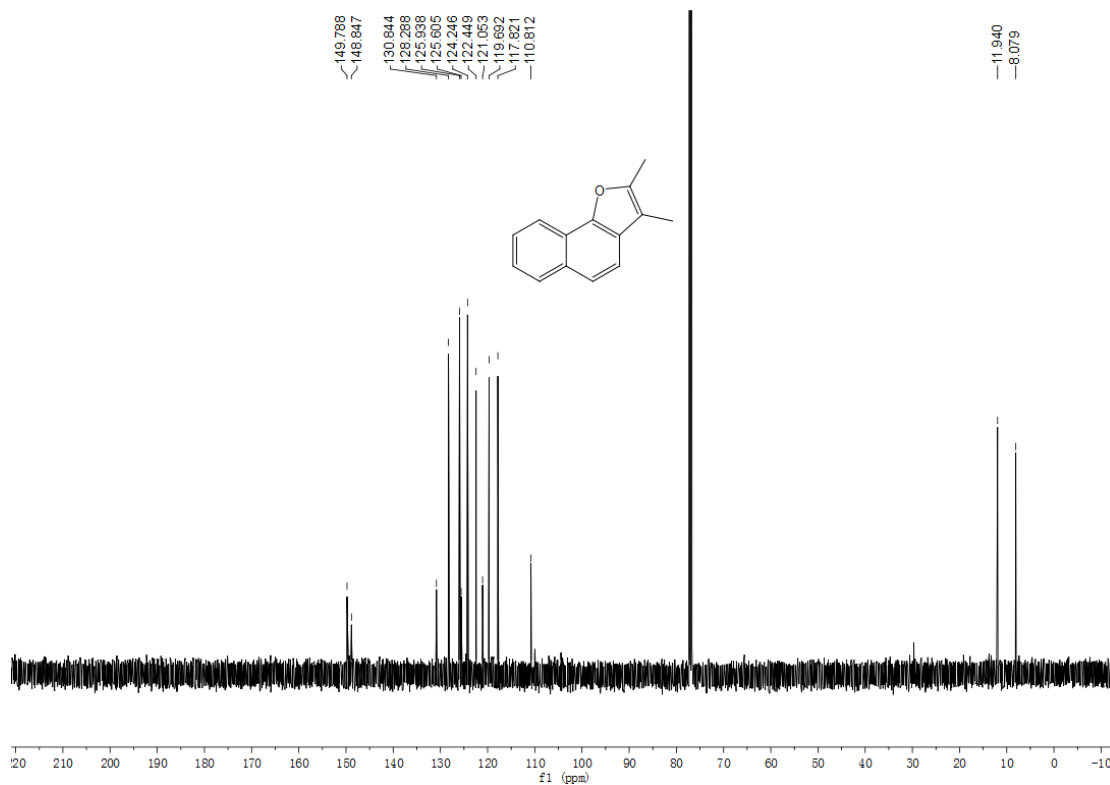


Fig. 54 ¹³C NMR of 2,3-dimethylnaphtho[1,2-*b*]furan (4d)

References

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