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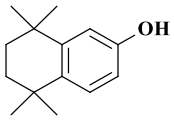
# New tri-*tert*-alkyl substituted *o*-quinones of tetraline family

**Anastasiya E. Tarakanova, Maxim A. Zherebtsov, Maxim V. Arsenyev, Evgeny V. Baranov, Sergey A. Chesnokov and Vladimir K. Cherkasov**

## Chemical experimental details

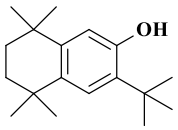
The solvents were purified following standard methods.[S1] $^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on Bruker Avance DPX-300 (300 MHz) instrument. The Fourier Transform infrared spectra of the compounds in the 4000–400 $cm^{-1}$ range were recorded on a Specord M-80 in Nujol. Electrochemical measurements were carried out using a "Elins P-45X" potentiostat. Conditions: the solvent is acetonitrile, the supporting salt is $Bu_4NClO_4$, the working electrode is glassy carbon electrode (d=2 mm), the reference electrode is silver chloride, the auxiliary electrode is a platinum wire, the sweep rate is 0.1 V/s, argon atmosphere. The concentration of *o*-benzoquinones were 5 mM.

**5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ol (2)**



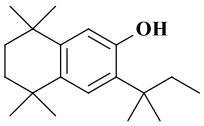

A solution of phenol (10.34 g, 110 mmol) and 2,4-dichloro-2,4-dimethylhexane (22.0 g, 120 mmol) in dichloromethane (50 ml) was cooled to 0 °C. Aluminium tribromide (5.9 g, 22 mmol) was added slowly to the solution. After stirring at 0 °C for 1 h, the mixture was heated to ambient temperature. Cold water (50 ml) was added, the organic layer was separated and washed with $H_2O$. The extract was dried ($Na_2SO_4$), filtered, and the solvent was evaporated. The target product was isolated by recrystallization from hexane to afford white crystalline solid (22.44 g, 96%). M.p. 144-145 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ: 1.24 (s, 6H, $CH_3$), 1.26 (s, 6H, $CH_3$), 1.66 (s, 4H, $CH_2$), 4.61 (s,1H, OH), 6.63 (dd, 1H, J = 2.71 Hz, 8.47 Hz, $C_{Ar}$-H), 6.76 (d, 1H, J = 2.68 Hz, $C_{Ar}$-H), 7.17 (d, 1H, J = 8.56 Hz, $C_{Ar}$-H).

**3-*tert*-Butyl-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-2-ol (3a)**



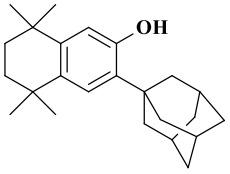

Compound **2** (2.0 g, 10 mmol) was dissolved in hexane (20 ml), and *tert*-butyl alcohol (14.6 g, 198.0 mmol) in a 20-fold molar excess was added. Concentrated sulfuric acid (1.1 g, 11.3 mmol) was added dropwise. The mixture was stirred at 60°C for 16 h and then extracted with diethyl ether, washed with water (3×200 ml), dried with $Na_2SO_4$, and the solvent was evaporated. The target product was isolated by column chromatography (eluent – hexane/diethyl ether, 60:1). After removing the solvent, a solid mass of white color was obtained. Yield 1.56 g (60%). M.p. 105-107°C. Calc. for $C_{18}H_{28}O$ (%): C, 83.02; H, 10.84. Found (%): C, 83.14; H, 11.04. $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.22-1.29 (m, 12H, $CH_3$), 1.40 (c, 9H, *t*-Bu), 1.65 (s, 4H, $CH_2$), 4.5 (s, H, OH), 6.55 (s, 1H, $C_{Ar}$-H), 7.16 (s, 1H, $C_{Ar}$-H). $^{13}$C NMR (300 MHz, $CDCl_3$) δ: 29.37, 29.78, 31.73, 32.01, 33.78, 34.35, 35.11, 35.41, 113.80, 125.05, 133.35, 136.53, 143.55, 151.70. IR (Nujol, ν/cm$^{-1}$): 3284(s), 2952(s), 1507(s), 1360(s), 1306(s), 1265(s), 1229(s), 1179(s), 1125(m), 1603(s), 1084(m), 1016(m), 989(m), 951(w), 932(w), 938(m), 849(m), 827(w), 779(m), 605(w), 551(w), 503(w).

**3-(2-Methylbut-2-yl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-2-ol (3b)**



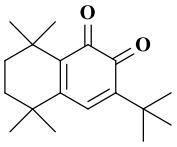

Compound **2** (3 g, 15 mmol) was dissolved in hexane (20 ml), and 2-methylbutan-2-ol (26 g, 300 mmol) in a 20-fold molar excess was added. Concentrated sulfuric acid (1.6 g, 17 mmol) was added dropwise, and the mixture was stirred at 60°C for 16 hours. Then it was extracted with hexane, the extract was washed with water (3×200 ml), dried with $Na_2SO_4$, and the solvent was evaporated. The target product was isolated by recrystallization from hexane. Colorless crystals. Yield 1.4 g (39%). M.p. 39-40°C. Calc. for $C_{19}H_{30}O$ (%): C, 83.25; H, 10.92. Found (%):C, 82.95; H, 11.26. $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.70 (t, 3H, J = 7.45 Hz, $CH_3$-$CH_2$), 1.24 (s, 12H, $CH_3$), 1.35 (s, 6H, $CH_3$ ), 1.64 (s, 4H, $CH_2$), 1.81 (q, 2H, J = 7.49 Hz, $CH_2$), 4.47(s, 1H, OH), 6.52 (s, 1H, $C_{Ar}$-H), 7.09 (s, 1H, $C_{Ar}$-H). $^{13}$C NMR (300 MHz, $CDCl_3$) δ: 9.42, 27.52, 31.74, 32.01, 33.55, 33.72, 33.71, 35.13, 35.40, 37.86, 113.67, 126.29, 131.71, 136.37, 143.40, 151.63. IR (Nujol, ν/cm$^{-1}$): 3280(s), 1733(m), 1611(m), 1567(m), 1513(s), 1397(s), 1306(s), 1240(m), 1105(s), 1084(m), 1045(m), 1024(m), 988(s), 957(m), 933(m), 912(m), 895(s), 866(s), 850(m), 781(s), 640(m), 509(w), 493(w).

**3-(Adamantan-1-yl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-2-ol (3c)**



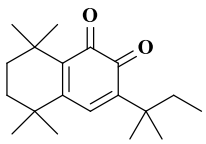

Compound **2** (2.04 g, 10 mmol) was dissolved in trifluoroacetic acid (10 ml), and adamantan-1-ol (2.28 g, 15 mmol) was added. The mixture was stirred at 60°C for 1 hour. The solid of light gray color that precipitated was filtered off, washed with cold trifluoroacetic acid (2 ml) and then with a large amount of water. Yield 2.64 g (78%). M.p. 205-207°C. Calc. for $C_{24}H_{34}O$ (%): 85.15; H, 10.12. Found (%): C, 85.11; H, 10.33. $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.25 (s, 6H, $CH_3$), 1.26 (s, 6H, $CH_3$), 1,65 (s, 4H, $CH_2$), 1.77-1.80 (m, 6H, $CH_2$ (Ad) ), 2.07-2.10 (m, 3H, CH (Ad)), 2.11 - 2.14 (m, 6H, $CH_2$), 3.89 (s, 1H, OH), 6.54 (s, 1 H, $C_{Ar}$-H), 7.12 (s, 1H, $C_{Ar}$-H). $^{13}$CNMR (300 MHz, $CDCl_3$) δ: 29.07, 31.71, 32.02, 33.75, 33.83, 35.08, 35.40, 36.50, 37.09, 40.77, 113.98, 124.96, 133.72, 136.64, 143.29, 151.89. IR (Nujol, ν/cm$^{-1}$): 3280 (s), 1613 (w), 1503 (m), 1399 (s), 1235 (s), 1154 (m), 1146 (m), 1101 (w), 1055 (w), 976 (w), 883 (w), 875 (w), 777 (w), 658 (w), 544 (w).

**3-(*tert*-Butyl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-dione (4a)**



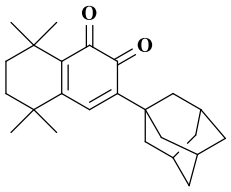

Phenol **3a** (2.47 g, 9.5 mmol) was dissolved in acetic acid (30 ml), and selenium dioxide (5.27 g, 47.5 mmol) was added. The mixture was stirred at 100°C for 20 hours. Excess selenium dioxide was filtered off, the filtrate was extracted with a mixture of hexane and ether, the extract was washed with water (3×200 ml), dried with $Na_2SO_4$, and the solvent was evaporated. The target product was isolated by column chromatography (eluent – hexane/diethyl ether, 30:1). The product was recrystallized from hexane and appeared as green crystals. Yield 1.3 g (50%). M.p.123-125°C. Calc. for $C_{18}H_{27}O_2$ (%): C, 78.79; H, 9.55. Found (%):C, 78.62; H, 9.96. $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.17 (s, 6H, $CH_3$), 1.23 (s, 9H, $CH_3$), 1.24 (s, 6H, $CH_3$), 1.48-1.60 (м, 4H, $CH_2$), 6.84 (с, 1H, $C_{Ar}$-H). $^{13}$C NMR (300 MHz, $CDCl_3$) δ: 27.28, 27.86, 29.08, 33.98, 34.29, 34.95, 35.53, 36.27, 135.07, 141.63, 148.13, 154.42, 180.47, 180.93. IR (Nujol, ν/cm$^{-1}$): 1681(s), 1654(s), 1557(m), 1397(s), 1360(s), 1306(s), 1265(s), 1229(s), 1179(s), 1125(m), 1603(s), 1084(m), 1016(m), 989(m), 951(w), 932(w), 938(m), 849(m), 827(w), 779(m), 605(w), 551(w), 503(w).

**3-(2-Methylbut-2-yl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-dione (4b)**



Compound **4b** was prepared similarly as **3b** from 3-(2-methylbut-2-yl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-2-ol **4a**. After removing the solvent, a fine crystalline substance of dark green color was obtained. Yield 0.54 g (43%). M.p. 90-92°C. Calc. for $C_{19}H_{29}O_2$ (%): C, 79.17; H, 9.73. Found (%): C, 78.45; H, 10.15. $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.67 (t, 3H, J = 7.45 Hz, $CH_3$ ), 1.18-1.19 (m, 12H, $CH_3$), 1.25 (s, 6H, $CH_3$), 1.52-1.59 (m, 4H, $CH_2$), 1.68-1.70 (q, 2H, J = 7.48 Hz, $CH_2$), 6.8 (c,1H, $C_{Ar}$-H). $^{13}$C NMR (300 MHz, $CDCl_3$) δ: 9.19, 26.78, 27.30, 27.91, 32.97, 34.01, 34.31, 35.51, 36.29, 38.60, 136.77, 141.58, 146.79, 154.41, 180.70, 181.20. IR (Nujol, ν/cm$^{-1}$): 1661 (s), 1559 (m), 1337 (m), 1318 (s), 1250 (s), 1208 (s), 1076 (m), 1043 (m), 1009 (s), 999 (m), 933 (m), 766 (m), 776 (m), 741 (m), 636 (w), 600 (m), 546 (w).

**3-(Adamantan-1-yl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-dione (4c)**



Phenol **3c** (1 g, 3 mmol) was dissolved in acetic acid (30 ml), and selenium dioxide (1.64 g, 15 mmol) was added. The mixture was stirred at 100°C for 7 hours. Excess selenium dioxide was filtered off, the filtrate was extracted with a mixture of hexane and ether, the extract was washed with water (3×200 ml), dried with $Na_2SO_4$, and the solvent was evaporated. The product was recrystallized from hexane and appeared as green crystals. Yield 0.5 g (50%). M.p. 155-156°C. Calc. for $C_{24}H_{33}O_2$ (%): C, 81.77; H, 9.15. Found (%): C, 81.75; H, 9.48. $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.18 (s, 6H, $CH_3$), 1.24 (s, 6H, $CH_3$), 1.51- 1.57 (m, 4 H, $CH_2$), 1.72-1.75 (m, 6H, $CH_2$ (Ad)), 1.86-1.89 (m, 6H, $CH_2$ (Ad)), 2.02-2.05 (m, 3H, CH (Ad)), 6.75 (s, 1H, $C_{Ar}$-H). $^{13}$C NMR (300 MHz, $CDCl_3$) δ: 27.33, 27.88, 28.48, 33.96, 34.34, 35.59, 36.30, 36.70, 37.36, 40.55, 135.40, 141.44, 148.37, 154.55, 180.38, 181.20. IR (Nujol, ν/cm$^{-1}$): 1671(s), 1656(s), 1559(m), 1312(m), 1248(m), 1196(m), 1161(m), 1103(m), 1084(m), 1045(w), 1007(m), 976(m), 926(m), 914(m), 872(m), 845(w), 812(w), 619(m), 588(m), 507(w).

**References**

[S1] J. Gordon, R. A. Ford, *The Chemist's Companion: A. Handbook of Practical Data, Techniques, and References*, Wiley-Interscience, New York, 1972.

# $^{1}$H NMR and $^{13}$C NMR spectra

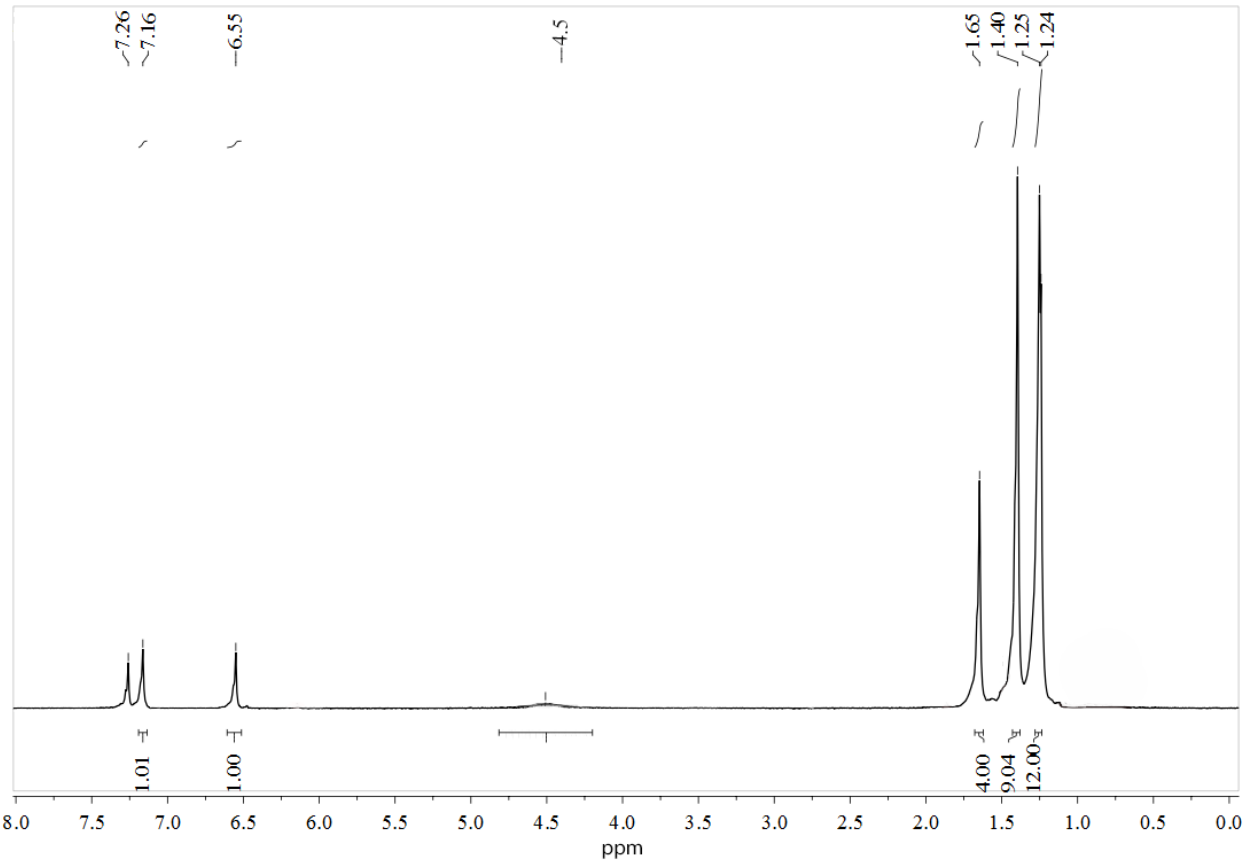



**Figure S1.** The $^{1}$H NMR spectrum of **3a** ($CDCl_3$).

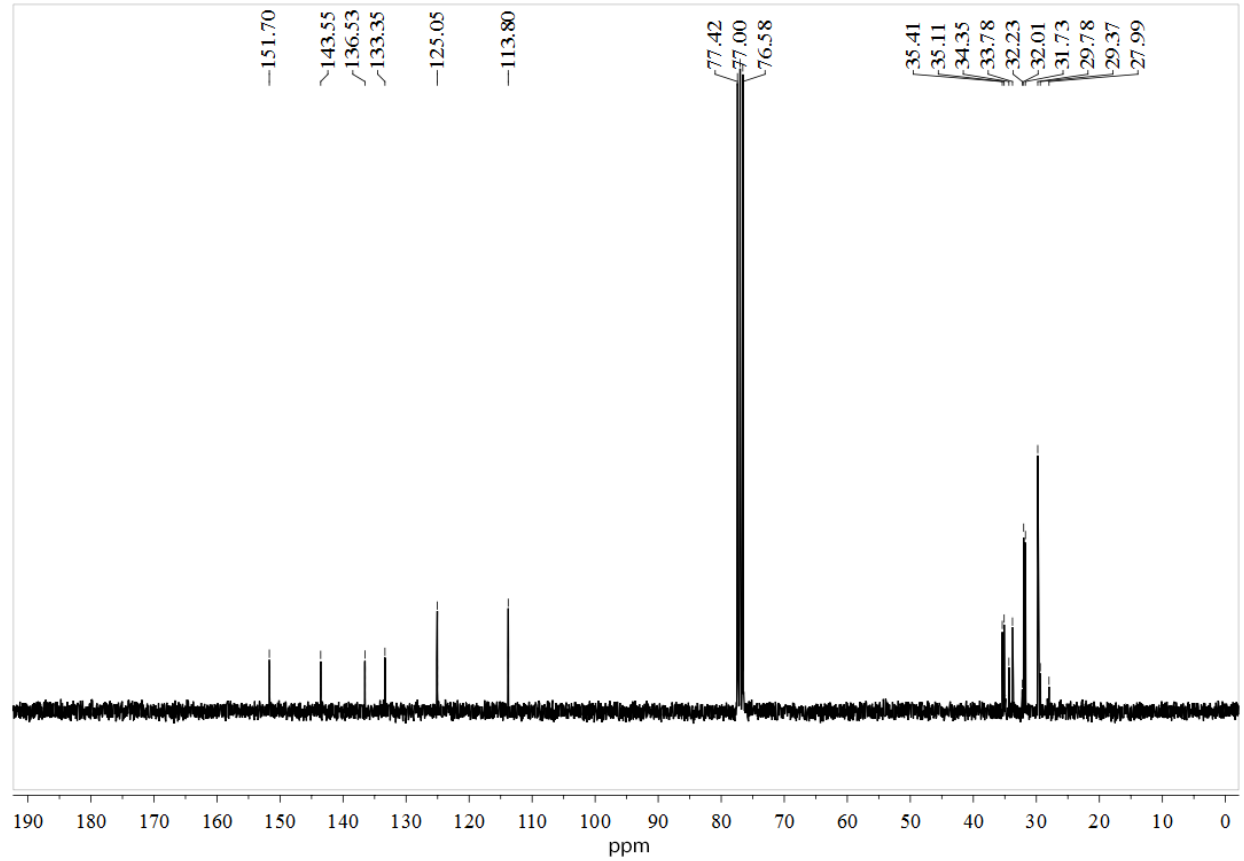



**Figure S2.** The $^{13}$C NMR spectrum of **3a** ($CDCl_3$).

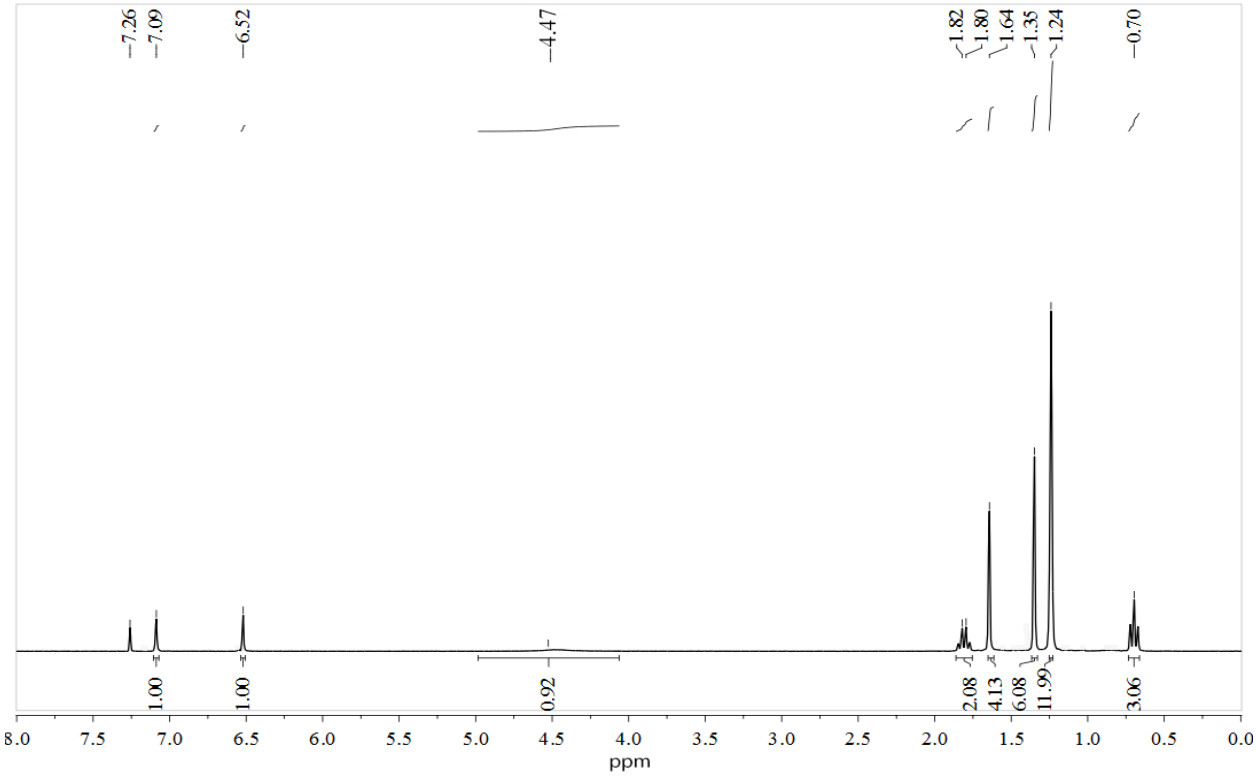



**Figure S3.** The $^{1}$H NMR spectrum of **3b** ($CDCl_3$).

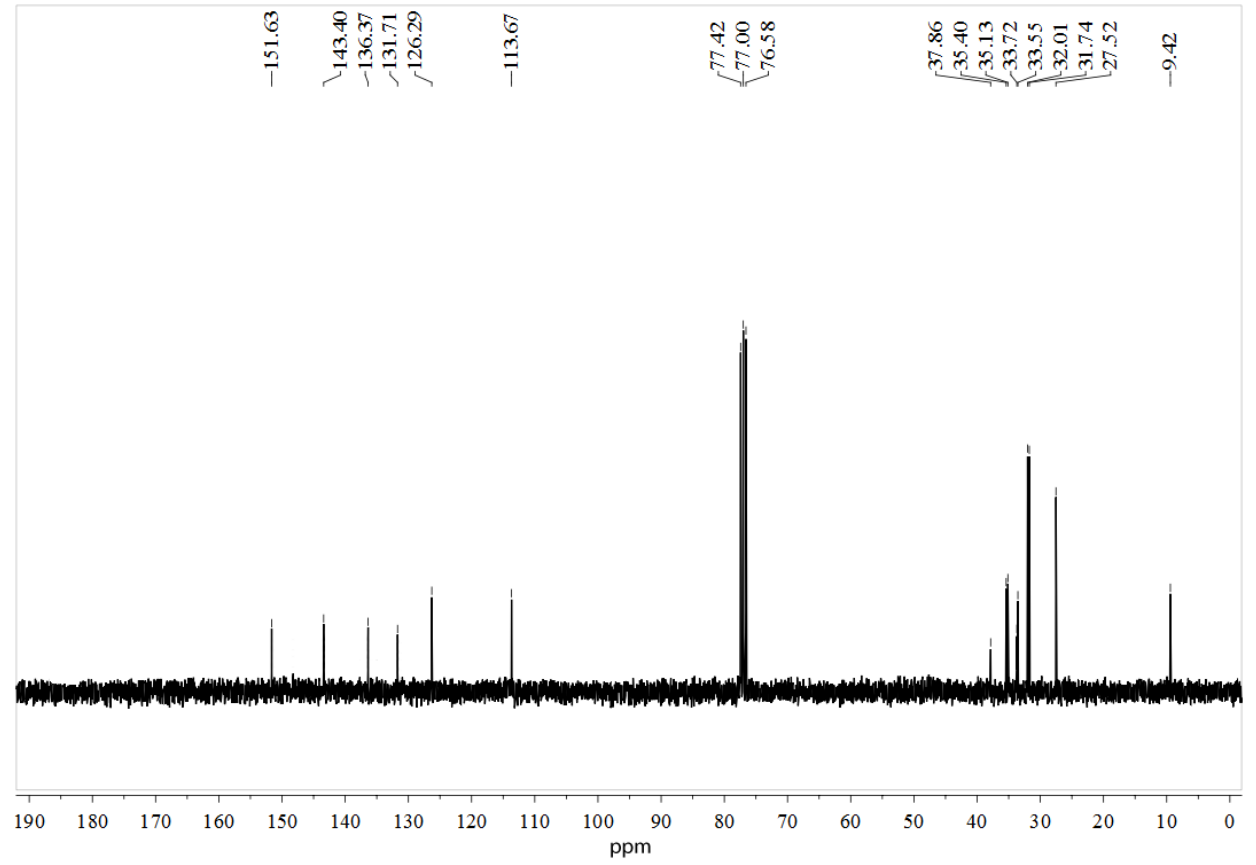



**Figure S4.** The $^{13}$C NMR spectrum of **3b** ($CDCl_3$).

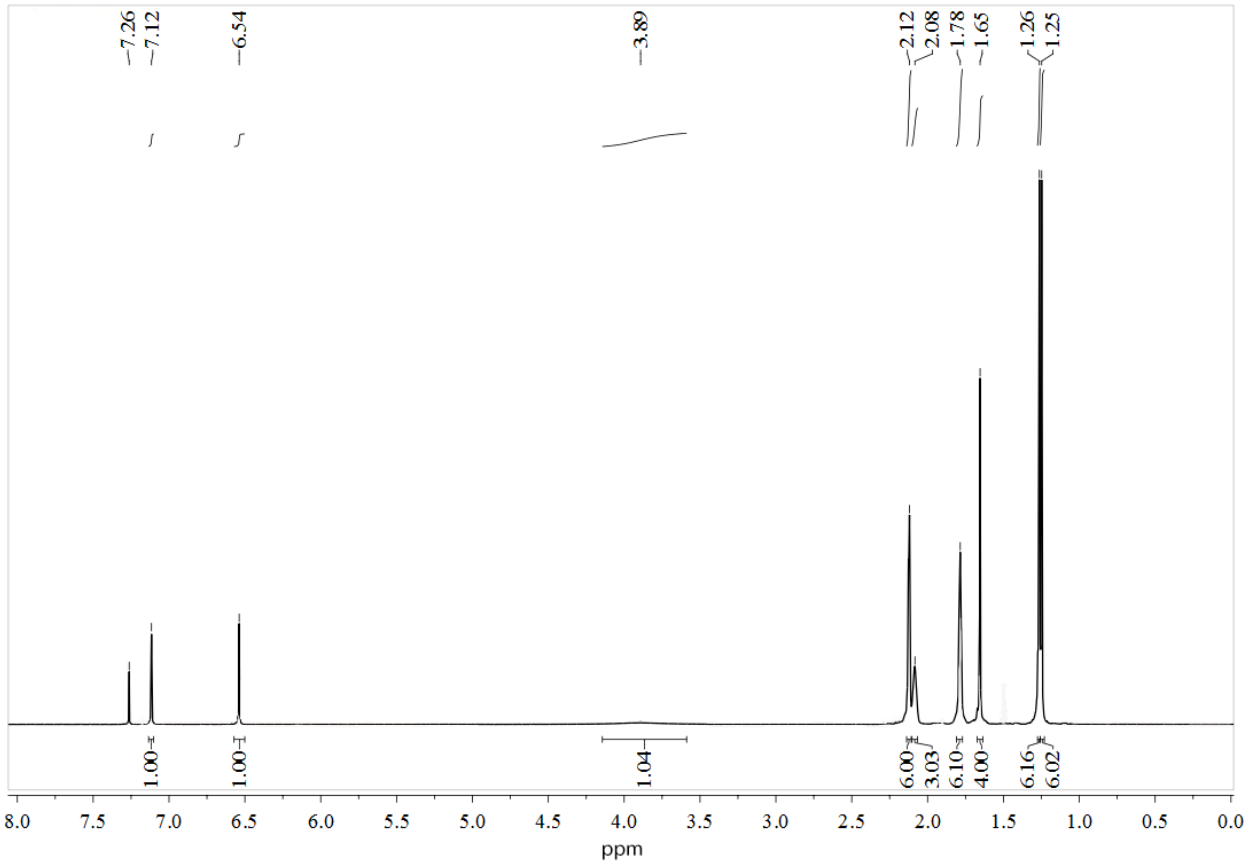



**Figure S5.** The $^{1}$H NMR spectrum of **3c** ($CDCl_3$).

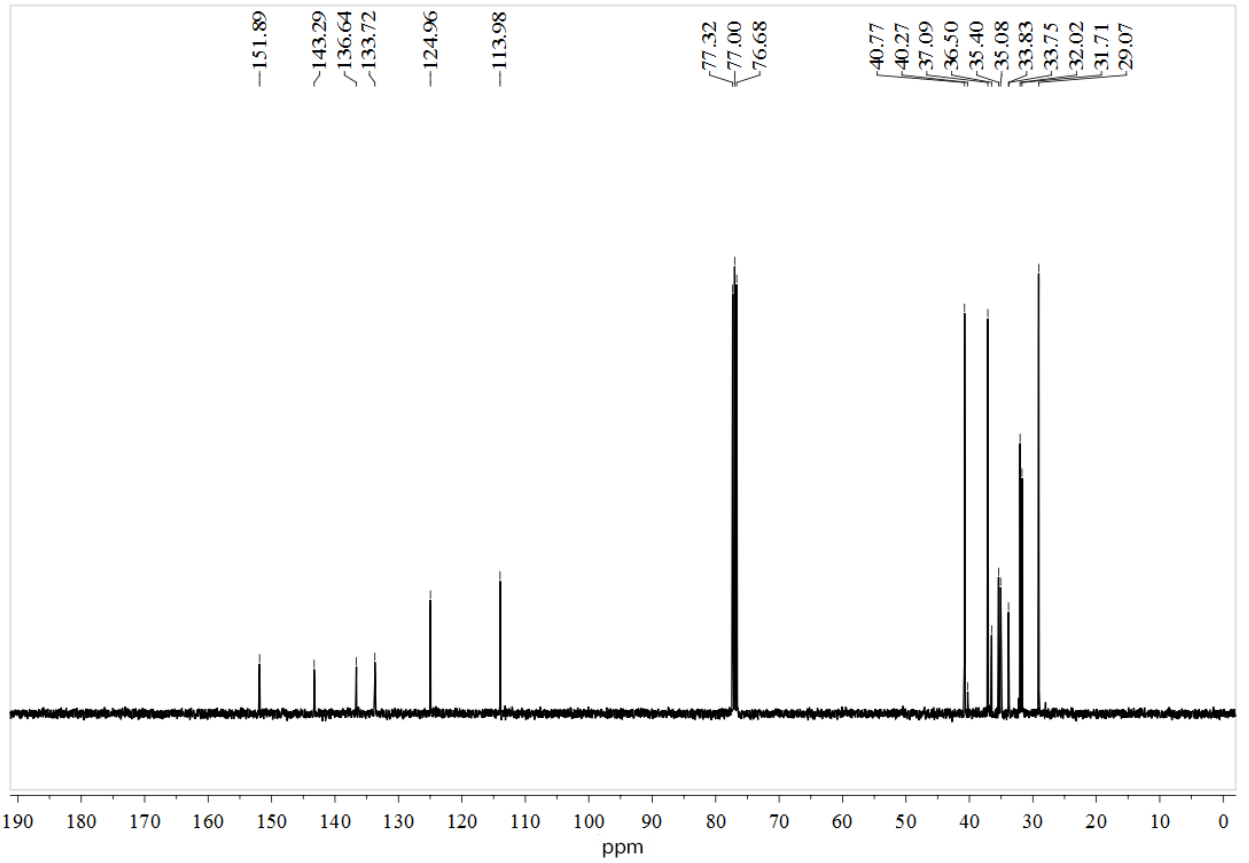



**Figure S6.** The $^{13}$C NMR spectrum of **3c** ($CDCl_3$).

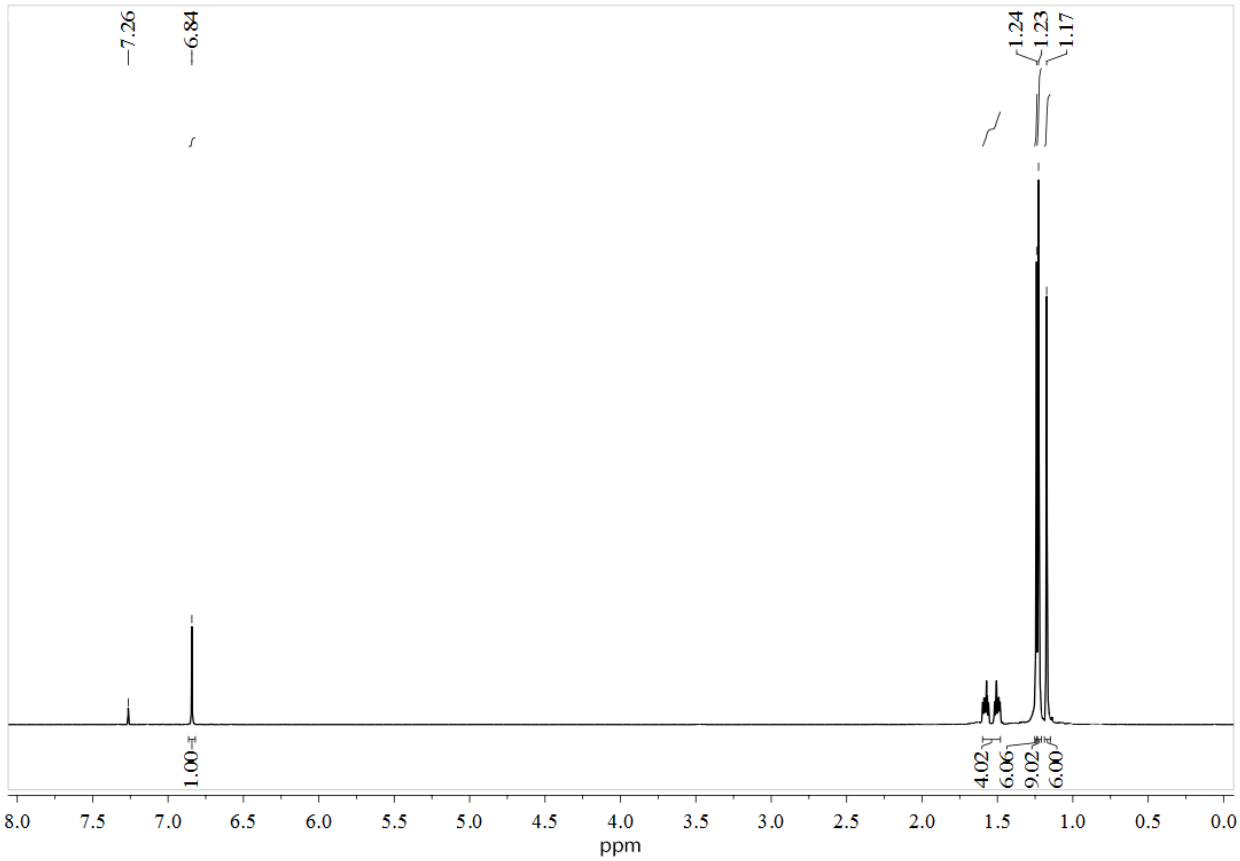



**Figure S9.** The $^{1}$H NMR spectrum of **4a** ($CDCl_3$).

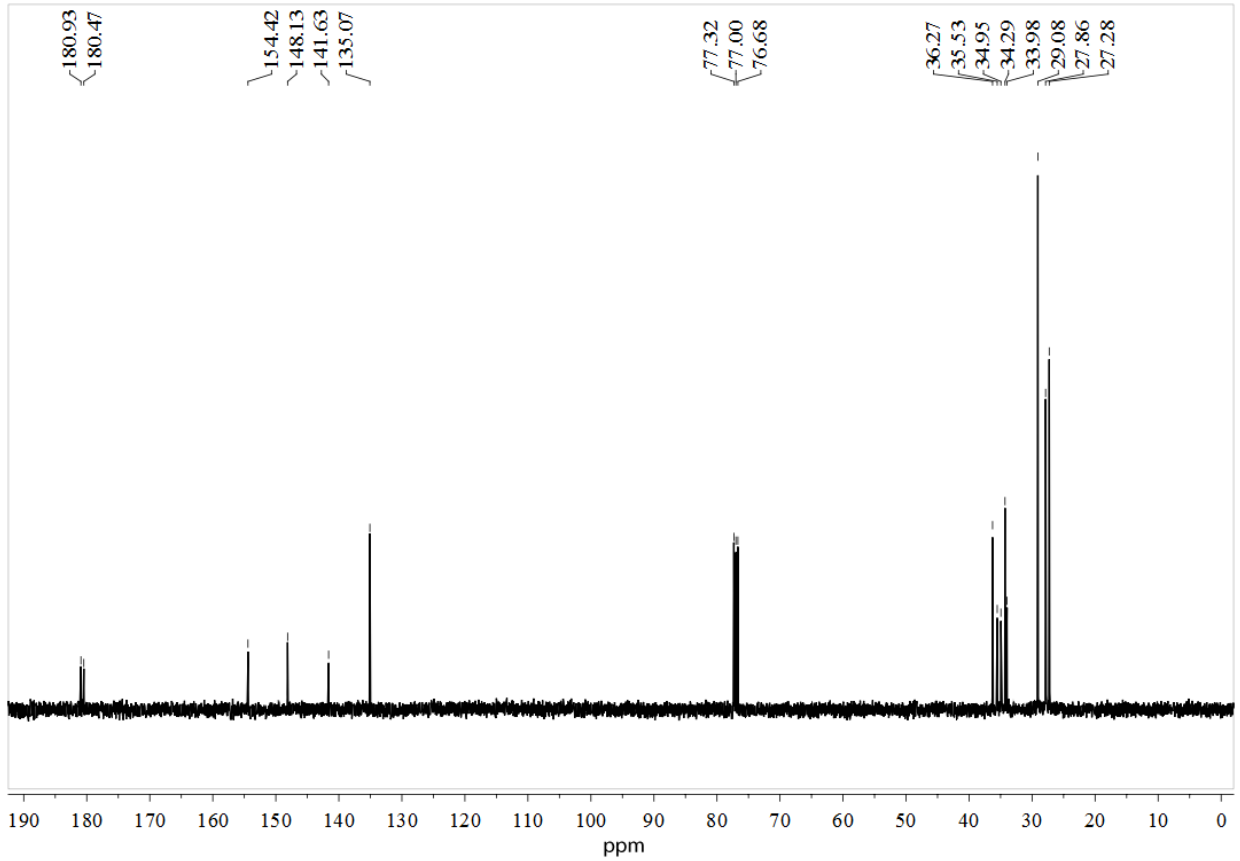



**Figure S10.** The $^{13}$C NMR spectrum of **4a** ($CDCl_3$).

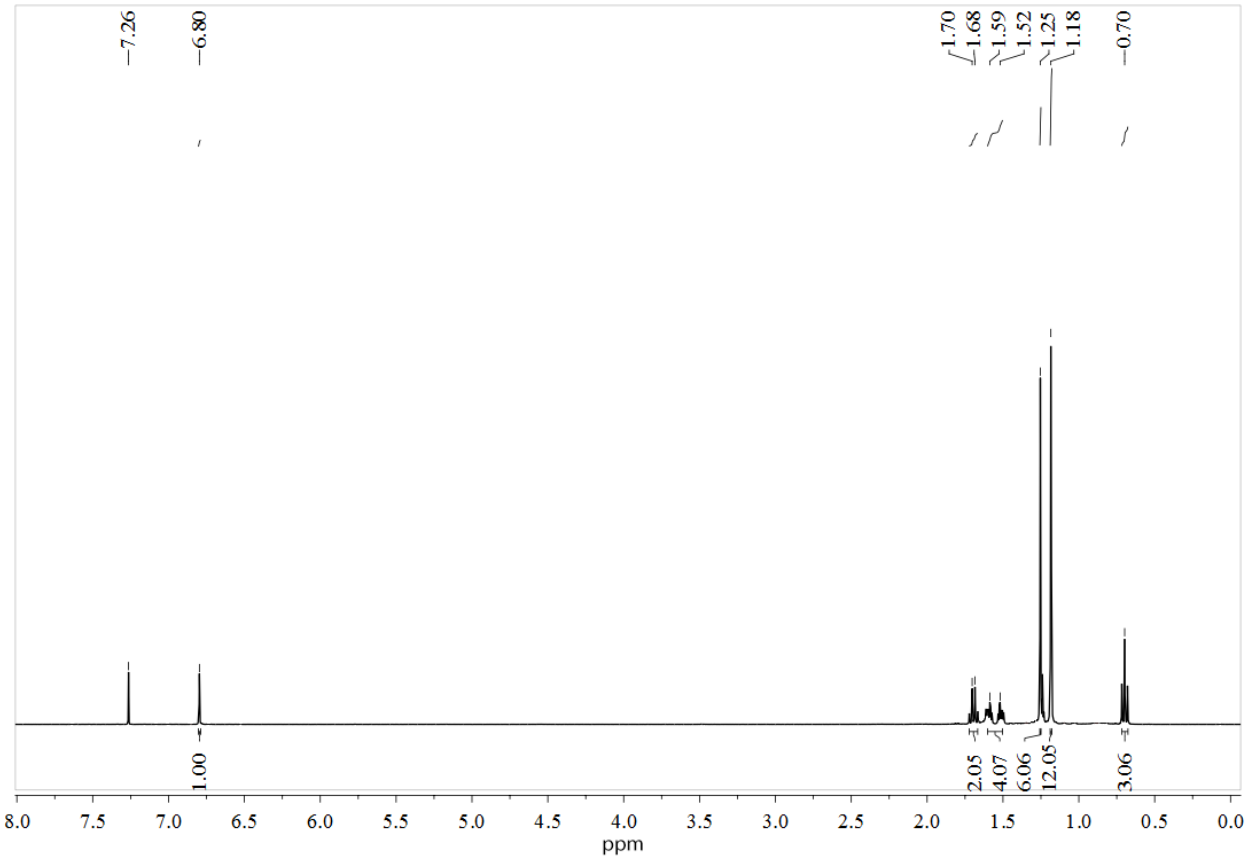



**Figure S7.** The $^{1}$H NMR spectrum of **4b** ($CDCl_3$).

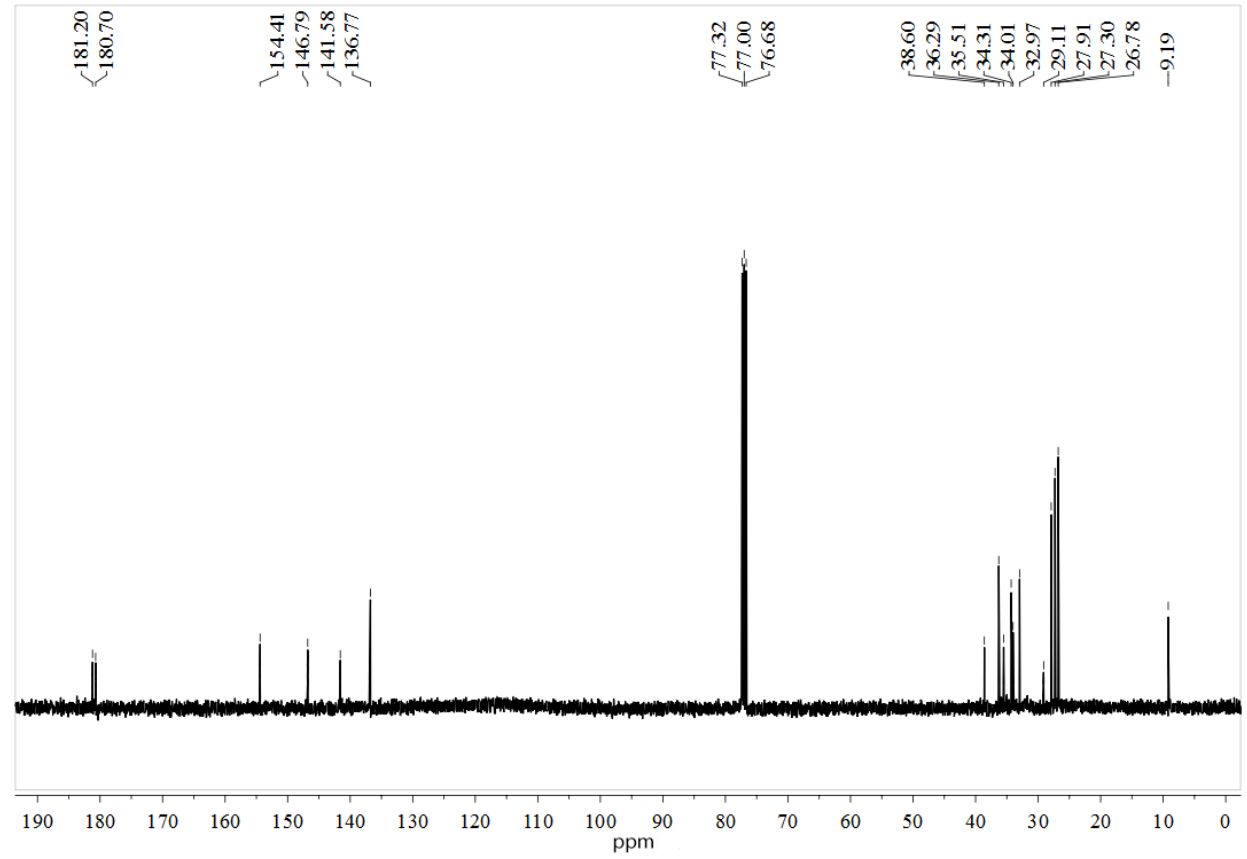



**Figure S8.** The $^{13}$C NMR spectrum of **4b** ($CDCl_3$).

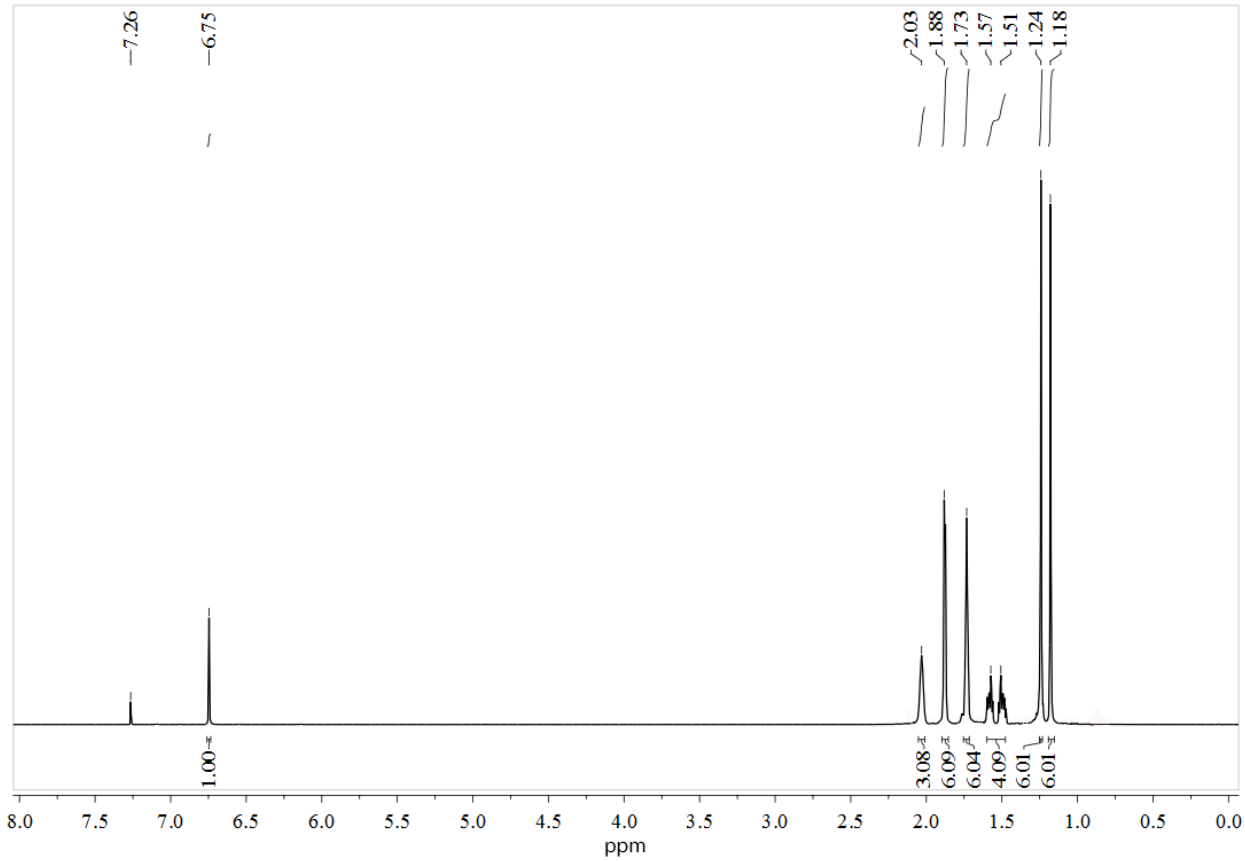



**Figure S11.** The $^{1}$H NMR spectrum of **4c** ($CDCl_3$).

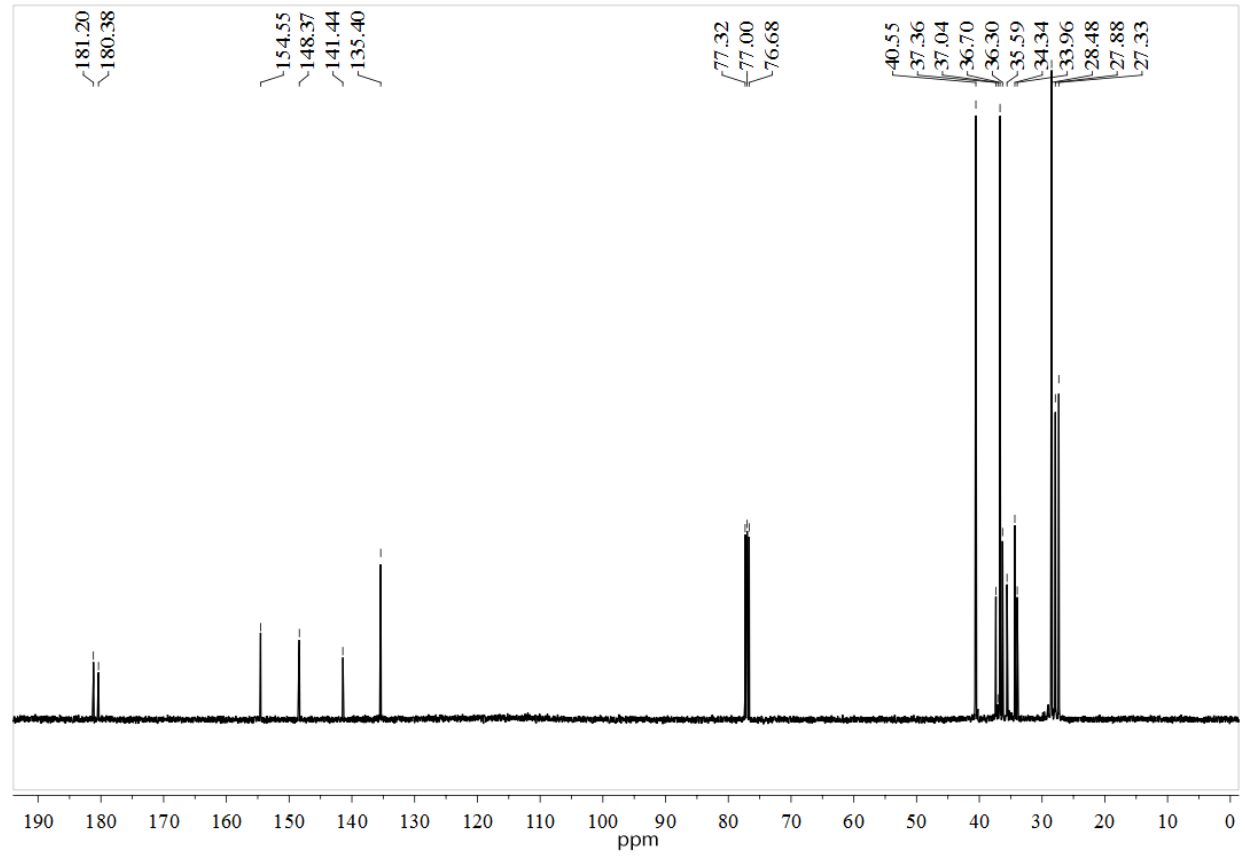



**Figure S12.** The $^{13}$C NMR spectrum of **4c** ($CDCl_3$).