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Synthesis and structure of sterically hindered *o*-benzoquinone carboxylic acid

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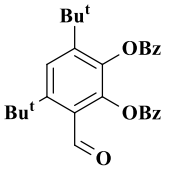
Chemical experimental details

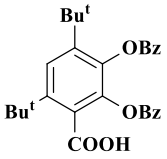
Solvents were purified following standard methods (J. Gordon, R. A. Ford, *The Chemist's Companion, A. Handbook of Practical Data, Techniques, and References.* A Wiley - Interscience, NewYork, 1972). ^{1}H NMR spectra were recorded on Bruker Avance DPX-200 (200 MHz) and Bruker Avance III (400 MHz). ^{13}C NMR spectra were recorded on Bruker Avance DPX-200 (50MHz). Chemical shifts are given on the δ scale (ppm). The solvent were DMSO-d_6 and $CDCl_3$. The infrared spectra of the compounds in the 4000–400 cm^{-1} range were recorded on a "Specord M-80" with a Fourier transform in Nujol.

2,3-Bis(benzoyloxy)-4,6-di-*tert*-butylbenzaldehyde (2)



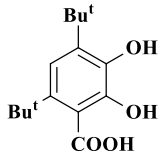
4,6-Di-*tert*-butyl-2,3-dihydroxybenzaldehyde **1** (11 g, 44 mmol) was dissolved in dichloromethane (200 ml), triethylamine (13.33 g, 132 mmol) was added, and the mixture was cooled to 0°C. With vigorous stirring, benzoyl chloride (12.36 g, 88 mmol) was added dropwise. The reaction mixture was stirred for 1 h, washed with water, dried, and the solvent was evaporated. Dibenzoate **2** was isolated as white powder. Yield 19.55 g (97%). M. p. 188-189°C. Calc. for $C_{29}H_{30}O_5$ (%): C, 75.96; H, 6.59. Found (%): C, 75.90; H, 6.55. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 1.34 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu), 7.33-7.48 (m, 4H(m), PhC(O)), 7.51 (s, 1H, C_{het}-H), 7.55-7.64 (m, 2H(p), PhC(O)), 7.75-7.95 (dd, 4H(o), PhC(O), J=7.92 Hz, J=7.85 Hz), 10.65 (s, 1H, C(O)H). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 30.21, 32.60, 35.77, 36.61, 123.20, 128.21, 128.30, 129.04, 129.22, 129.62, 129.74, 129.88, 130.06, 134.59, 134.89, 140.39, 145.73, 148.02, 163.88, 164.35, 193.57. IR (Nujol, ν/cm^{-1}): 3073 (s), 2725 (s), 2678 (s), 2564 (s),1990 (s), 1973 (s), 1921 (s), 1752 (w), 1694 (w), 1601 (w), 1454 (m), 1391 (m), 1366 (m), 1316 (s), 1247 (w), 1192 (s), 1175 (m), 1081 (m), 1062 (m), 935 (m), 888 (m), 849 (s), 797 (s), 775 (s), 667 (m), 617 (s), 548 (s).

2,3-Bis(benzoyloxy)-4,6-di-*tert*-butylbenzoic acid (3)



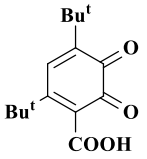
Compound **2 (**10 g, 22 mmol) was dissolved in dichloromethane (100 ml), and a solution of sulfamic acid (6.4 g, 66 mmol) in water (100 ml) was added. Sodium chlorite (9.96 g, 110 mmol) dissolved in water (100 ml) was added dropwise to the first solution. After stirring for one day, dichloromethane was removed, the solid was filtered off and washed with water. The product was recrystallized from chloroform and isolated as white powder. Yield 9.91 g (95%). M. p. 216-217°C. Calc. for $C_{29}H_{30}O_6$ (%): C, 73.40; H, 6.37. Found (%): C, 73.38; H, 6.35. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 1.33 (s, 9H, *t*-Bu), 1.41 (s, 9H, *t*-Bu), 7.38-7.44 (m, 4H(m), PhC(O)),7.46 (s, 1H, C_{het}-H), 7.54-7.61 (m, 2H(p), PhC(O)), 7.78-7.92 (dd, 4H(o), PhC(O), J =7.15 Hz, J =7.13 Hz). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 30.39, 31.55, 35.41, 36.56, 123.44, 128.20, 128.23, 128.35, 129.30, 129.56, 129.81, 129.96, 134.53, 134.80, 139.87, 140.43, 142.63, 144.16, 163.57, 164.30, 169.34. IR (Nujol, ν/cm^{-1}): 3476 (s), 2658 (s), 2575 (m), 1976 (s), 1960 (s), 1755 (w), 1703 (w), 1598 (m), 1584 (s), 1554 (s), 1424 (s), 1297 (m), 1239 (w), 1178 (m), 1162 (m), 1078 (w), 1059 (w), 1026 (w), 1001 (s), 954 (s), 932 (s), 885 (s), 844 (s), 772 (m), 758 (m), 667 (s), 557 (s).

4,6-Di-*tert*-butyl-2,3-dihydroxybenzoic acid (4)



Compound **3 (**8 g, 17 mmol) was dissolved in methanol (30 ml), and hydrazine hydrate (8.25 g, 85 mmol) was added. The mixture was stirred for one hour at 30°C, dilute sulfuric acid (30 ml) was added, and methanol was evaporated. The solid was filtered off to afford acid **4** as a white solid. Yield 1.94 g (43%). M.p. 146-147°C. Calc. for $C_{15}H_{22}O_4$ (%): C, 67.64; H, 8.33. Found (%): C, 67.62; H, 8.30. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 1.28 (s, 9H, *t*-Bu), 1.32 (s, 9H, *t*-Bu), 6.77 (s, 1H, C_{het}-H), 8.00 (s, 1H, COOH). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 29.98, 31.96, 35.12, 35.71, 116.01, 124.24, 136.19, 136.63, 142.63, 143.08, 171.53. IR (Nujol, ν/cm^{-1}): 3340 (w), 2672 (s), 2562 (s), 1697 (w), 1664 (w), 1609 (s), 1562 (s), 1294 (m), 1222 (s), 1170 (s), 1026 (s), 974 (w), 872 (s), 750 (s).

2,4-Di-*tert*-butyl-5,6-dioxocyclohexa-1,3-diene-1-carboxylic acid (5)



Compound **4 (**2 g, 7.5 mmol) was dissolved in acetic acid (15 ml), and nitric acid (1.4 ml) was added. The mixture was extracted with a hexane-ether system, and the extract was washed with water, dried with Na_2SO_4, and the solvent was evaporated. The residue was recrystallized from hexane to afford red crystals. Yield 1.38 g (70%). M.p. 129-130°C. Calc. for $C_{15}H_{20}O_4$ (%): C, 68.16; H, 7.63. Found (%): C, 68.11; H, 7.60. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.28 (s, 9H, *t*-Bu), 1.37 (s, 9H, *t*-Bu), 7.02 (s, 1H, C_{het}-H), 8.67 (br s, 1H, COOH). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 28.38, 29.10, 35.72, 37.92, 128.91, 134.90, 150.30, 157.35, 169.85, 177.37, 178.12. IR (Nujol, ν/cm^{-1}): 3536 (m), 3396 (m), 3274 (s), 2656 (s), 2606 (s), 2570 (s), 1835 (m), 1683 (w), 1659 (w), 1632 (m), 1628 (s), 1576 (m), 1311 (m), 1272 (s), 1233 (s), 1173 (s), 946 (s), 883 (s), 783 (m), 747 (s), 617 (s), 584 (s).

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

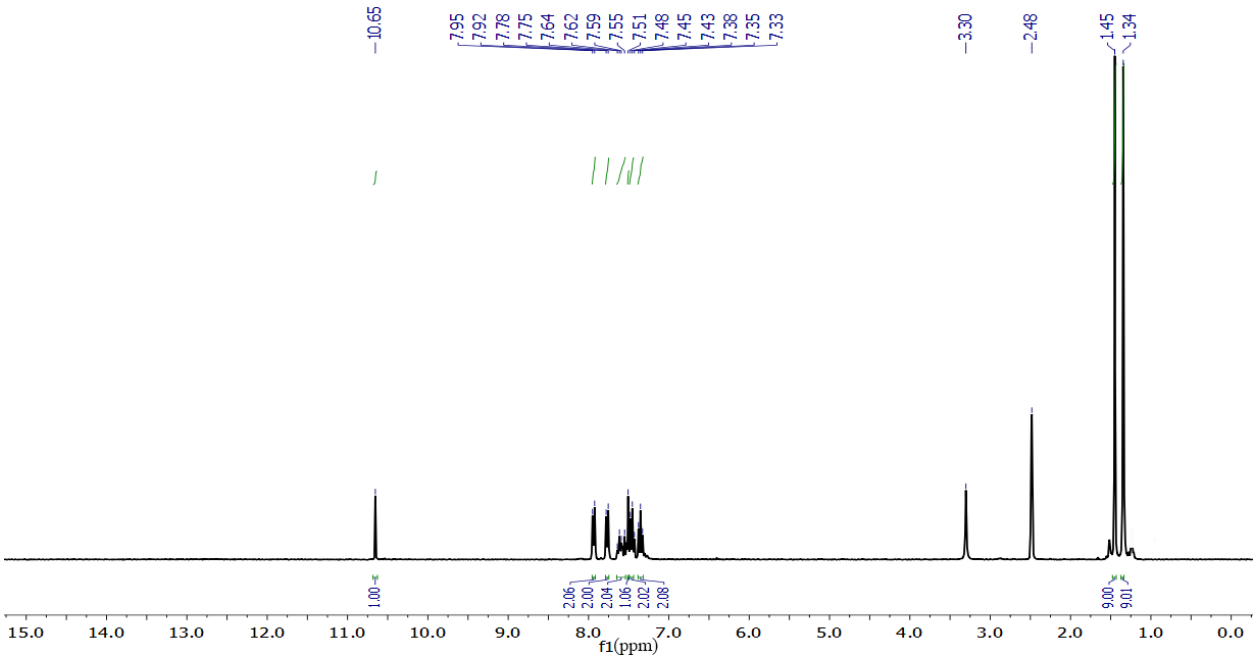


Figure S1. The ^{1}H NMR spectrum of **2** (DMSO-d_6).

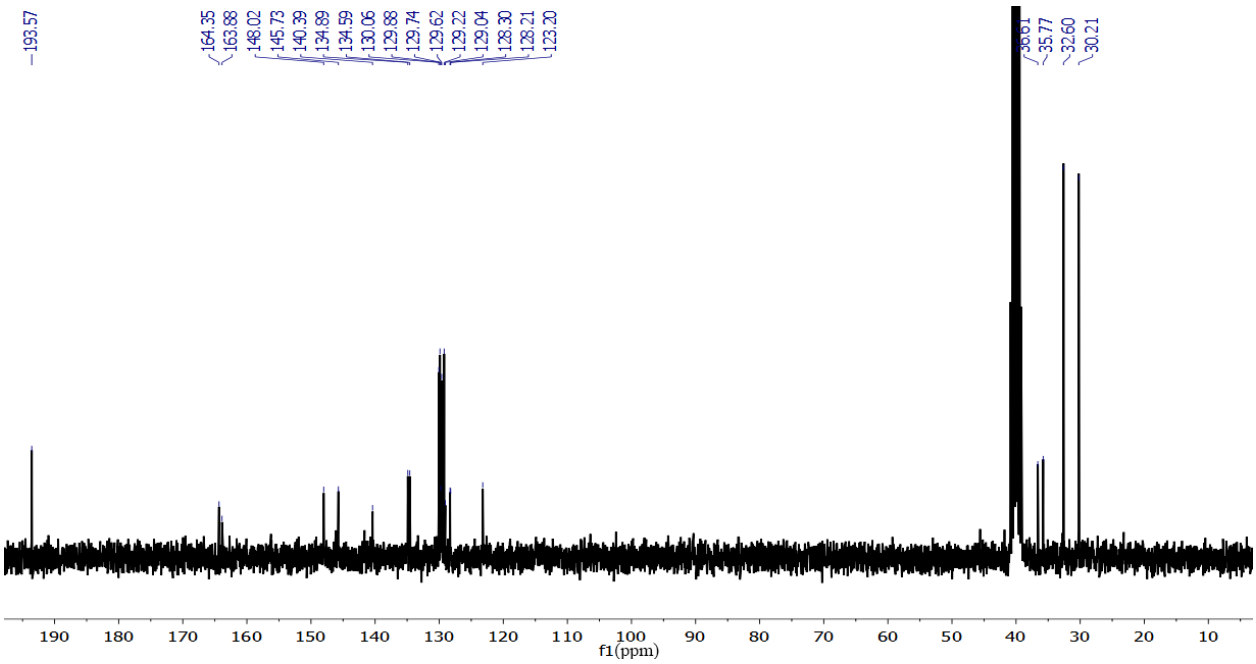


Figure S2. The ^{13}C NMR spectrum of **2** (DMSO-d_6).

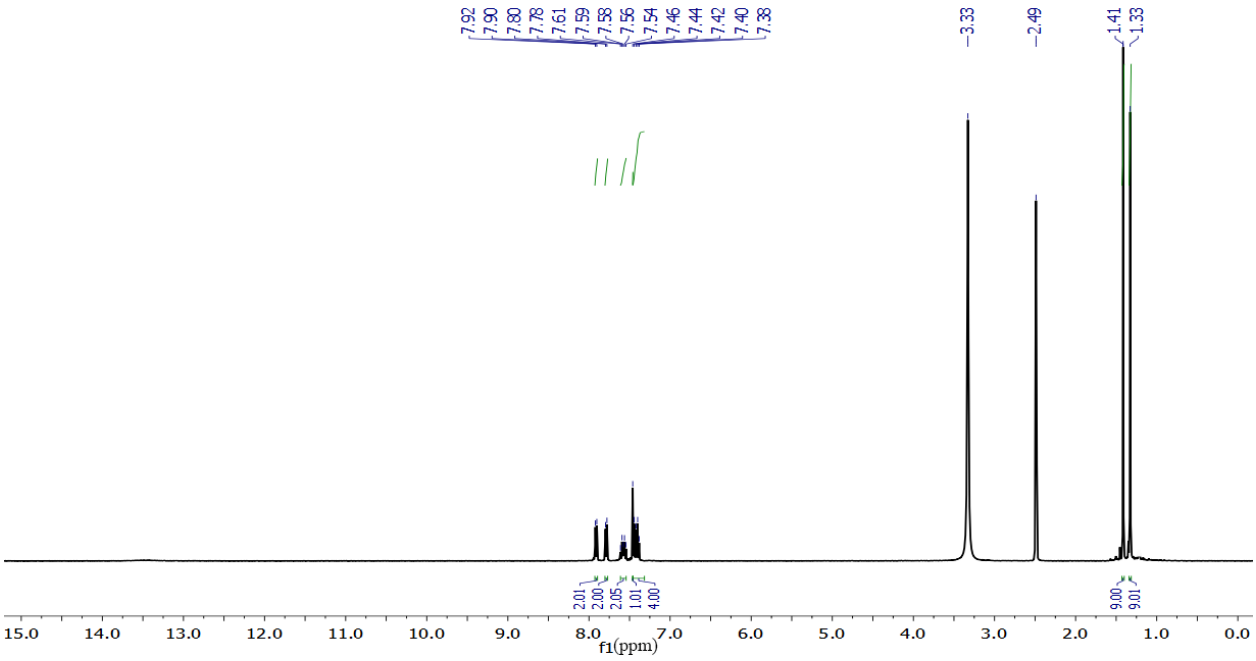


Figure S3. The ^{1}H NMR spectrum of **3** (DMSO-d_6).

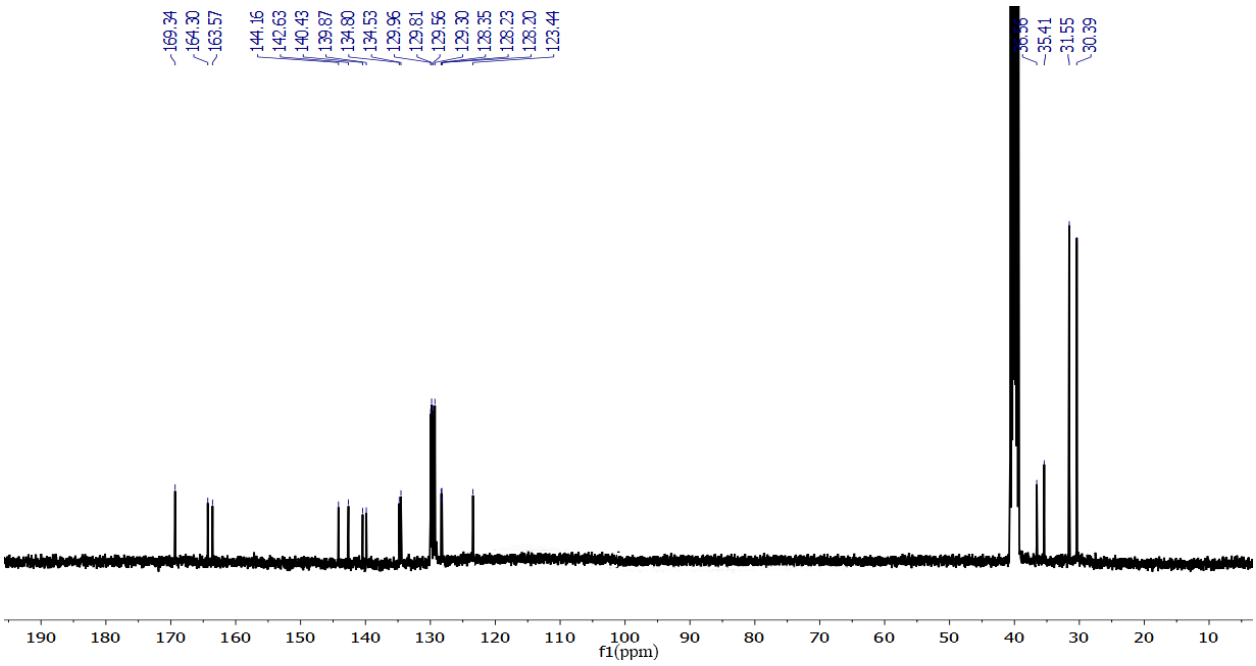


Figure S4. The ^{13}C NMR spectrum of **3** (DMSO-d_6).

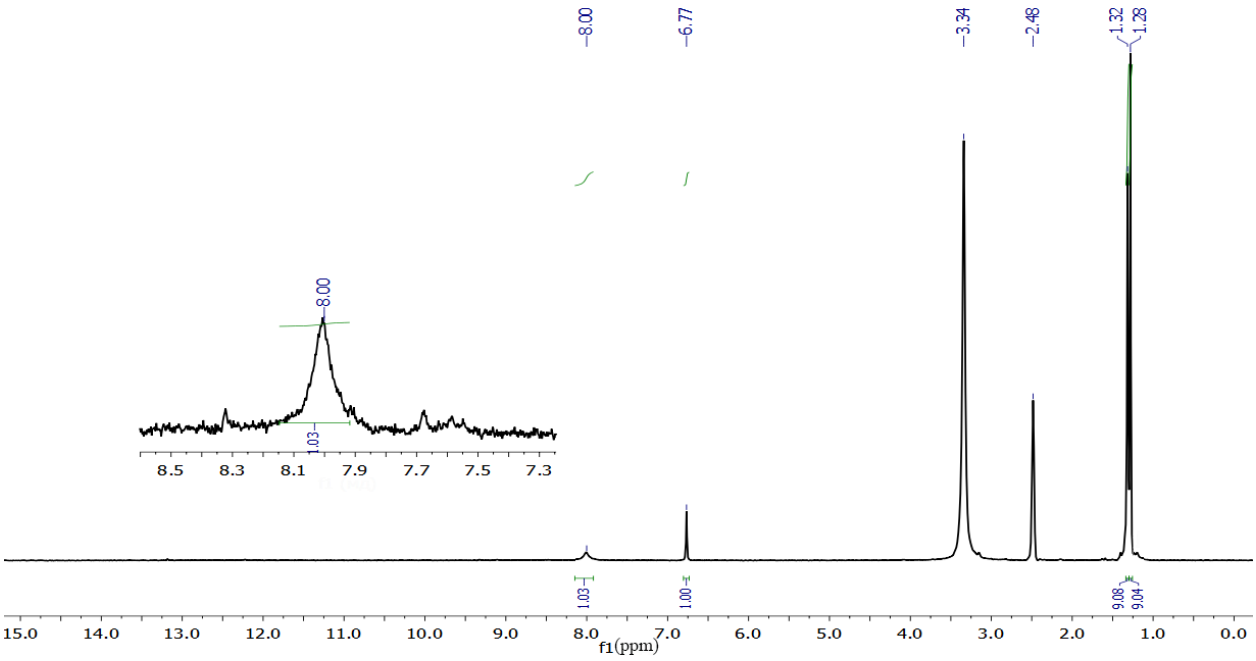


Figure S5. The ^{1}H NMR spectrum of **4** (DMSO-d_6).

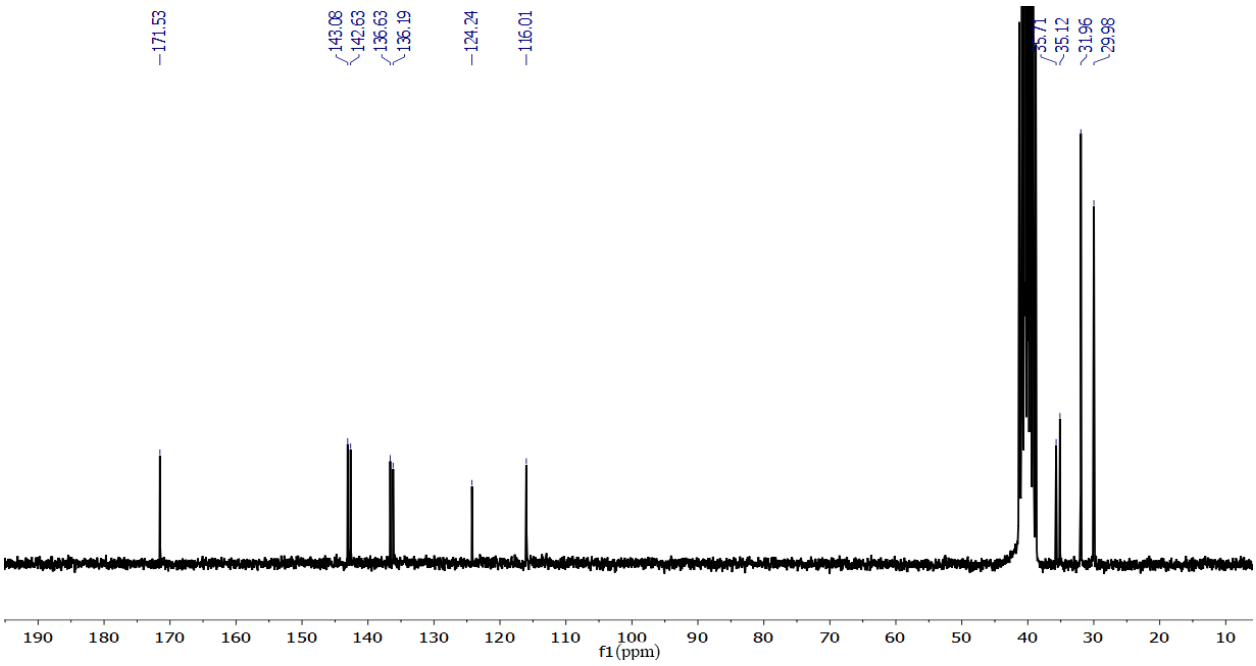


Figure S6. The ^{13}C NMR spectrum of **4** (DMSO-d_6).

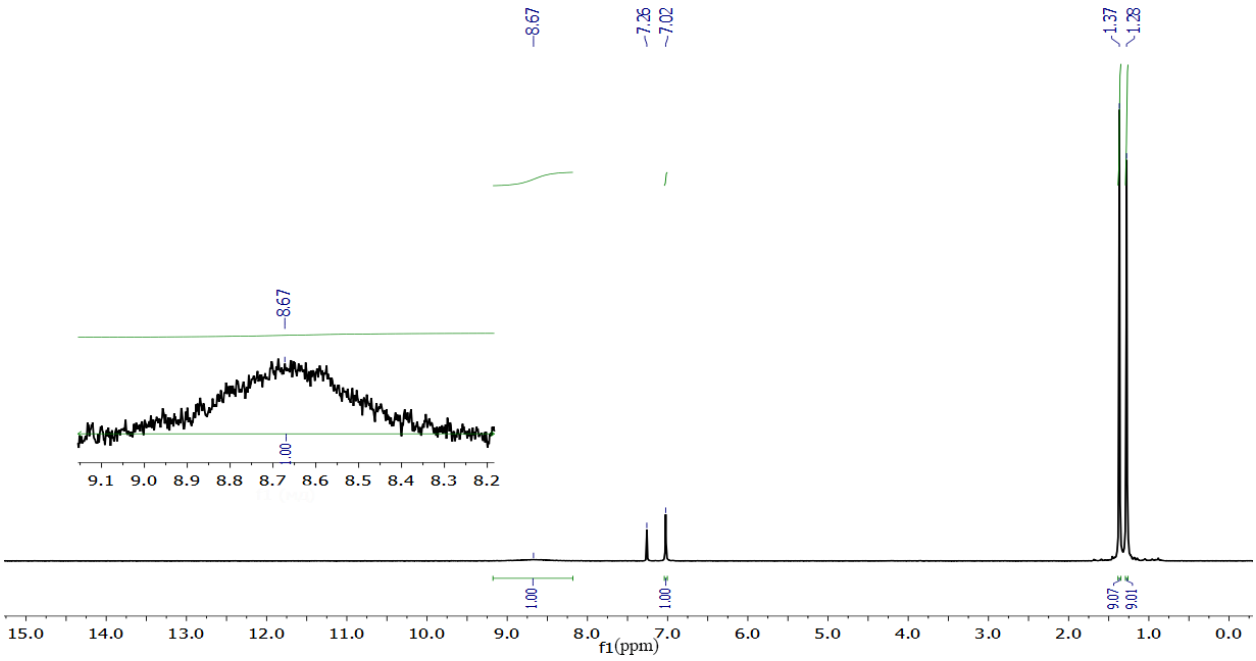


Figure S7. The ^{1}H NMR spectrum of **5** ($CDCl_3$).

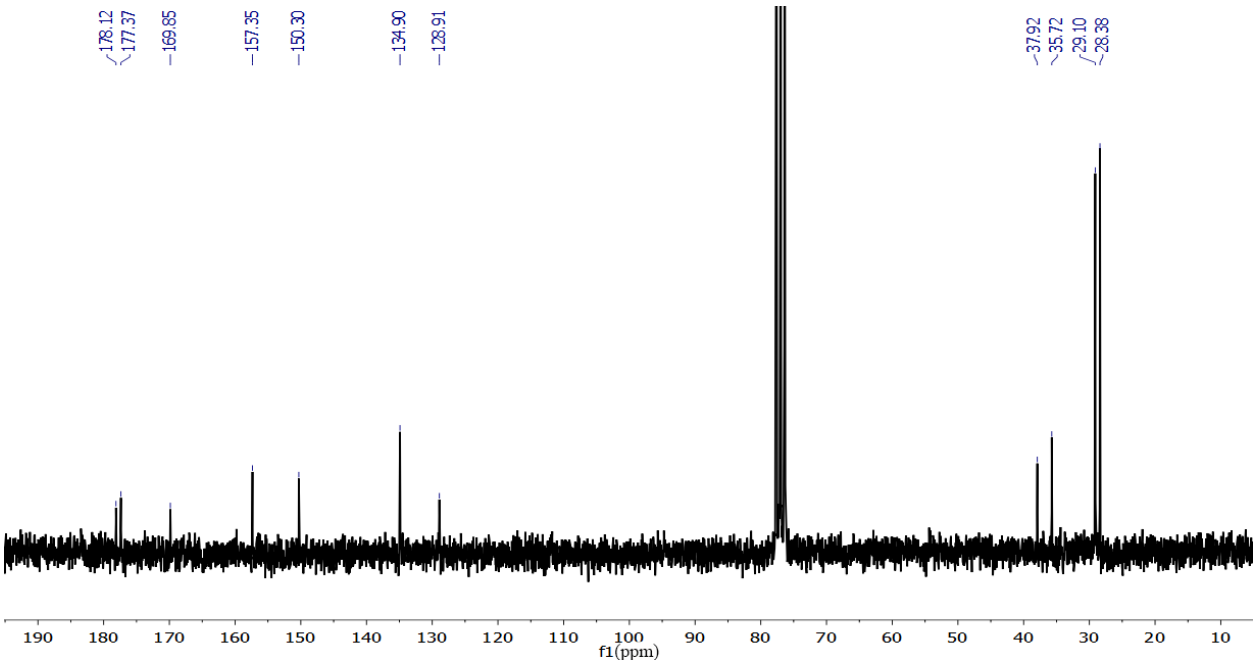


Figure S8. The ^{13}C NMR spectrum of **5** ($CDCl_3$).