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Moving of the tetramethylbutanediyl substituent over the catecholcarbaldehyde core

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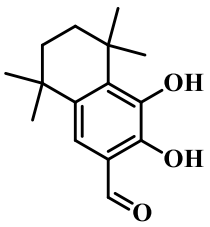
Chemical experimental details

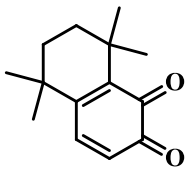
The solvents were purified following standard methods.[S1] ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance DPX-300 (300 MHz) instrument. The Fourier Transform infrared spectra of the compounds in the 4000–400 cm^{-1} range were recorded on a Specord M-80 in Nujol. Quantum-chemical calculations of compounds **1** and **2** with optimization of the geometry of isolated molecules were carried out by the DFT method implemented in the Gaussian 09[S2] software package, using the B3LYP[S3,S4] hybrid functional and the 6-31+G(d,p) basis set of H[S5,S6] and C, N, O[S7,S8] atoms. The melting point of organic compounds was measured using an M5000 automatic melting point meter.

3,4-Dihydroxy-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-2-carbaldehyde (2)



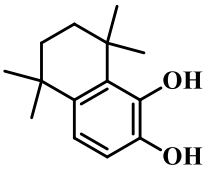
Compound **1** (0.1 g, 0.4 mmol) was stirred in methanesulfonic acid (2 ml) at room temperature for 24 h. The reaction mixture was poured onto ice and the resulting precipitate was filtered and dried. A dark yellow powder was isolated. Yield 0.09 g (90%). M. p. 100.2 °C. Calc. for $C_{15}H_{20}O_3$ (%): C, 72.55; H, 8.12. Found (%): C, 72.52; H, 8.09. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (s, 6H, CH_3), 1.45 (s, 6H, CH_3), 1.62-1.65 (m, 2H, CH_2), 1.68-1.71 (m, 2H, CH_2), 5.90 (s, 1H, OH), 7.11 (s, 1H, C_{ar}-H), 9.81 (s, 1H, C-H), 10.75 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 27.57, 32.09, 34.17, 34.86, 35.21, 37.25, 118.38, 121.83, 139.05, 139.60, 143.04, 145.09, 196.43. IR (Nujol, ν/cm^{-1}): 3400 (w), 1731 (s), 1651 (w), 1572 (m), 1343 (s), 1329 (s), 1306 (s), 1285 (s), 1252 (s), 1221 (s), 1200 (s), 1130 (m), 1086 (s), 1067 (m), 1053 (m), 1024 (s), 1003 (m), 939 (m), 889 (m), 872 (w), 796 (w), 779 (w), 735 (m), 613 (m), 590 (m).

5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-dione (5′)



Compound **5** (1 g, 4.9 mmol) was stirred with IBX (1.37 g, 4.9 mmol) in a chloroform-methanol (3:2) solvent mixture at room temperature for 2 h. The reaction mixture was washed three times (20 ml each) with soda solution and once with water, then the organic layer was dried over sodium sulfate. After removing the solvent under reduced pressure, a red oily substance was obtained. The target product was isolated by thin-layer chromatography using dichloromethane as an eluent. Red crystals were isolated. Yield 0.37 g (62%). M. p. 116.3 °C. Calc. for $C_{14}H_{18}O_2$ (%): C, 77.03; H, 8.31. Found (%): C, 77.52; H, 8.42. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.17 (s, 6H, CH_3), 1.25 (s, 6H, CH_3), 1.49-1.52 (m, 2H, CH_2), 1.57-1.60 (m, 2H, CH_2), 6.30 (d, 1H, J = 10.4 Hz, C_q-H), 7.11 (d, 1H, J = 10.4 Hz, C_q-H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 27.26, 28.00, 34.09, 34.48, 35.29, 36.39, 127.92, 142.12, 143.98, 153.50, 180.13, 180.56. IR (Nujol, ν/cm^{-1}): 1681 (s), 1656 (s), 1614 (s), 1551 (s), 1410 (s), 1391 (s), 1311 (s), 1290 (s), 1245 (s), 1199 (s), 1180 (s), 1085 (m), 1049 (s), 1010 (s), 930 (s), 895 (m), 877 (s), 844 (s), 797 (s), 774 (m), 626 (s), 580 (m), 547 (w), 498 (w).

5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-diol (3′)



Compound **5′** (0.37 g, 1.7 mmol) was stirred with hydrazine hydrate (0.43 g, 8.5 mmol) in methanol at room temperature for 3 h. Water (20 ml) was added to the reaction mixture and a precipitate formed, which was filtered and dried. A light-yellow powder was isolated. Yield 0.26 g (70%). M. p. 127.6 °C. Calc. for $C_{14}H_{20}O_2$ (%): C, 76.33; H, 9.15. Found (%): C, 76.25; H, 9.43. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.24 (s, 6H, CH_3), 1.43 (s, 6H, CH_3), 1.59-1.62 (m, 2H, CH_2), 1.66-1.68 (m, 2H, CH_2), 4.54 (s, 1H, OH), 6.67 (d, 1H, J = 8.4 Hz, C_{ar}-H), 6.75 (d, 1H, J = 8.4 Hz, C_{ar}-H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 28.15, 32.09, 34.16, 34.33, 35.27, 37.69, 112.73, 117.70, 139.59, 140.63, 143.39, 144.87. IR (Nujol, ν/cm^{-1}): 3499 (m), 3360 (m), 1617 (w), 1603 (w), 1586 (w), 1574 (w), 1304 (m), 1271 (m), 1229 (s), 1198 (s), 1117 (m), 1084 (s), 1057 (s), 1013 (m), 999 (m), 932 (m), 903 (m), 887 (s), 806 (w), 781 (m), 694 (s), 675 (s), 659 (s), 565 (s).

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

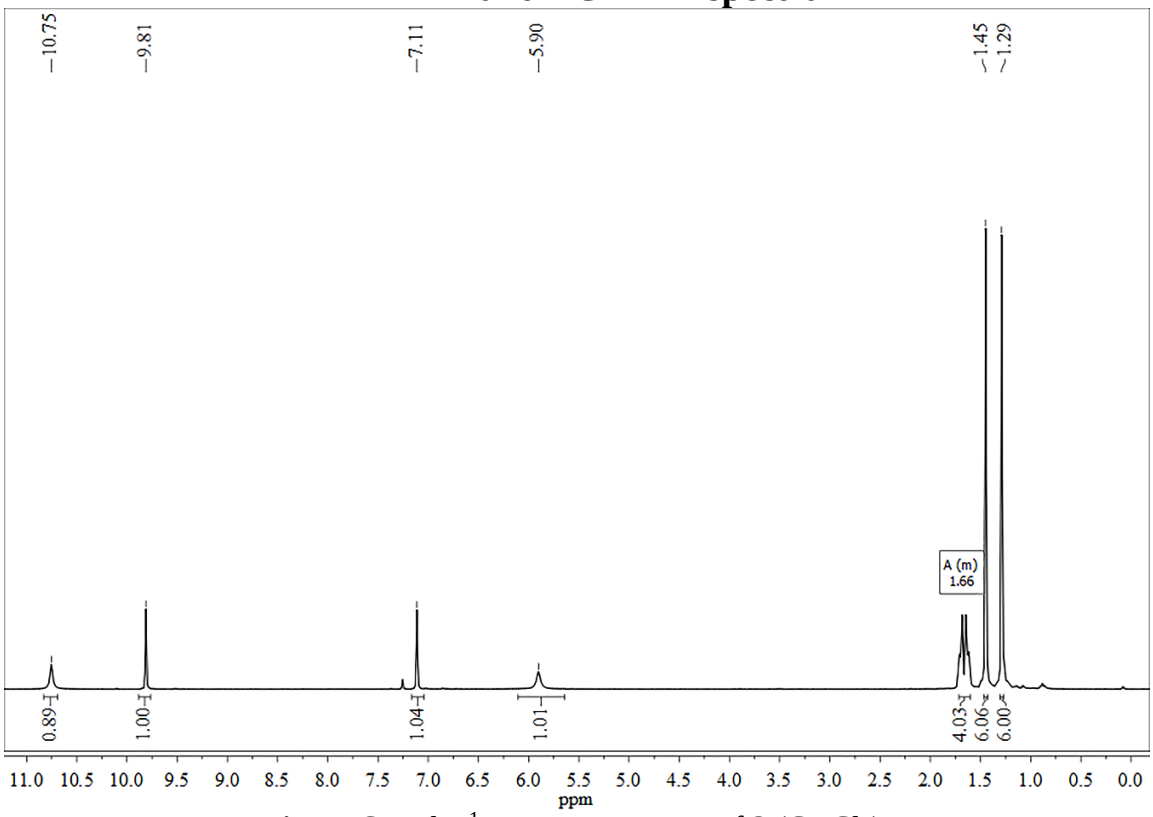

Figure S1. The ^{1}H NMR spectrum of **2** ($CDCl_3$).

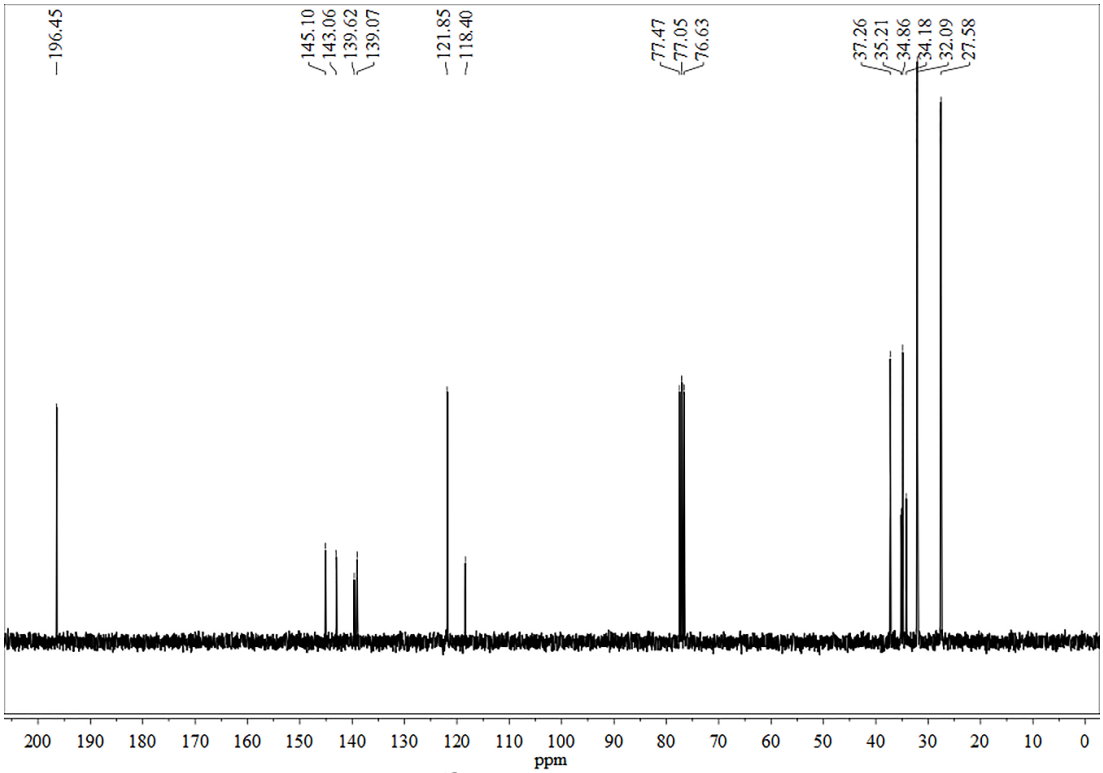

Figure S2. The ^{13}C NMR spectrum of **2** ($CDCl_3$).

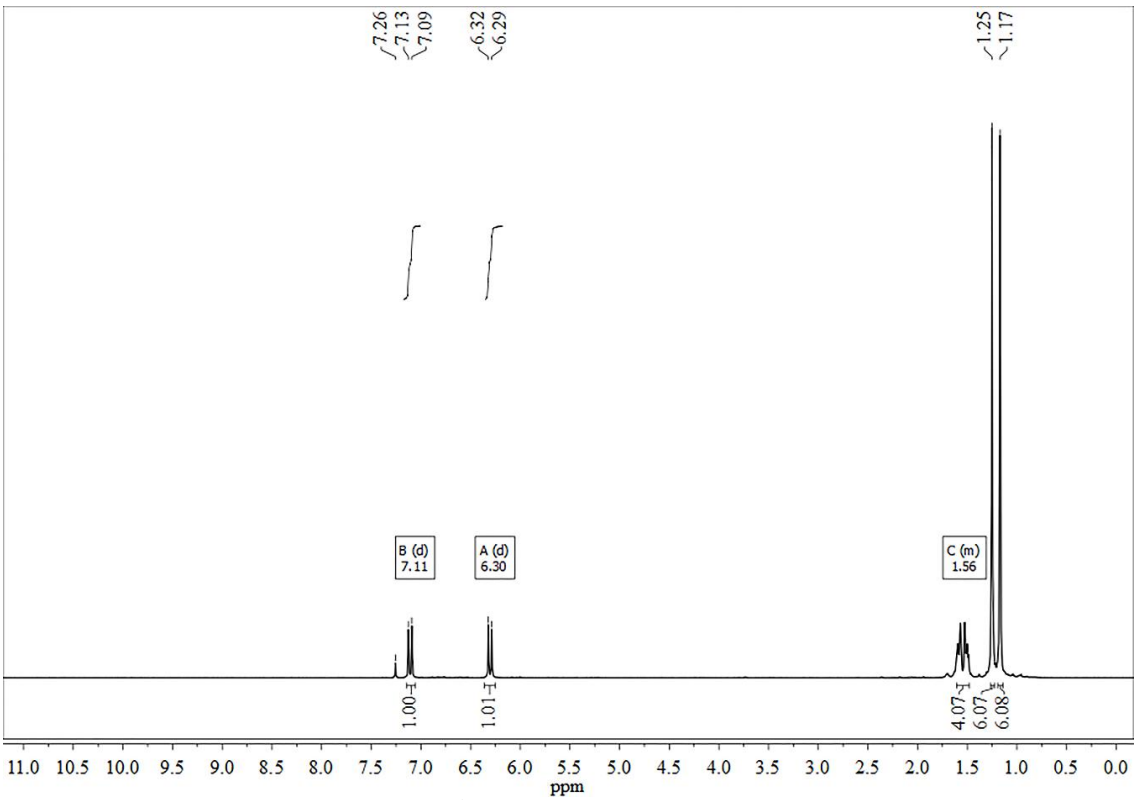

Figure S3. The ^{1}H NMR spectrum of **5′** ($CDCl_3$).

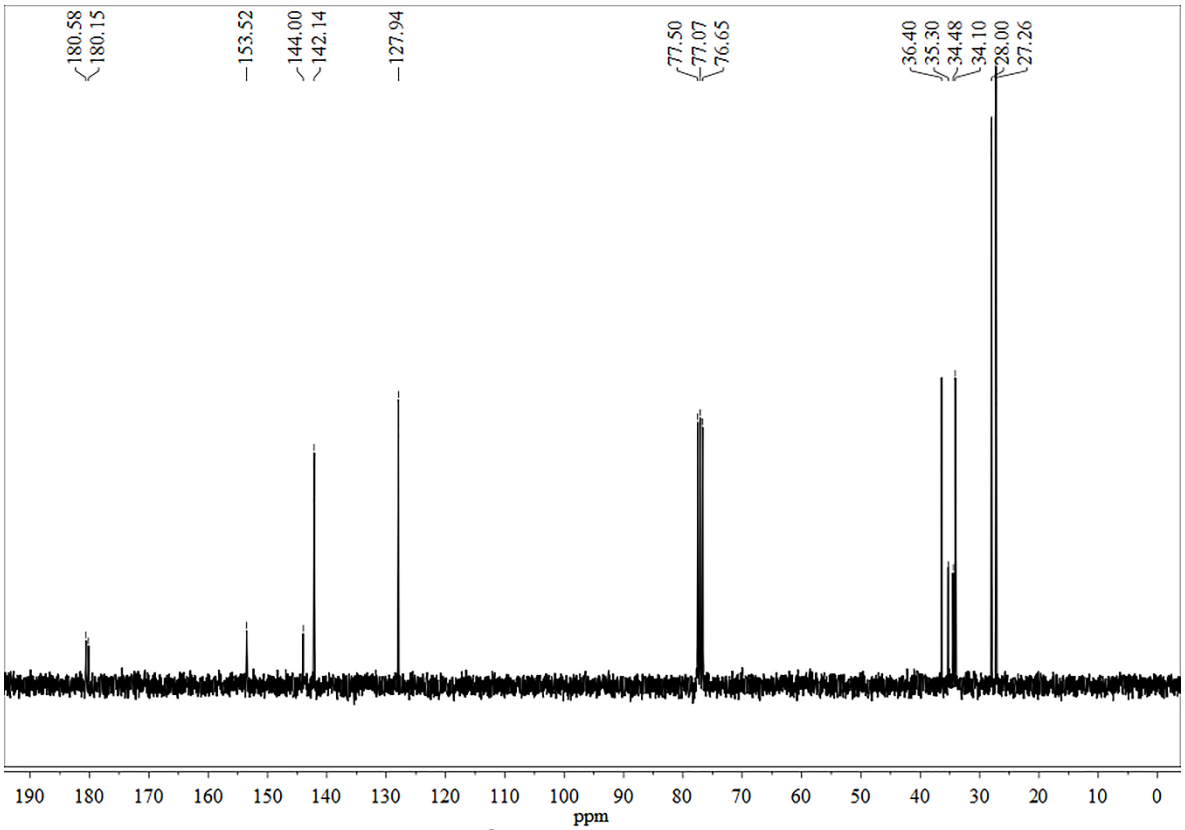

Figure S4. The ^{13}C NMR spectrum of **5′** ($CDCl_3$).

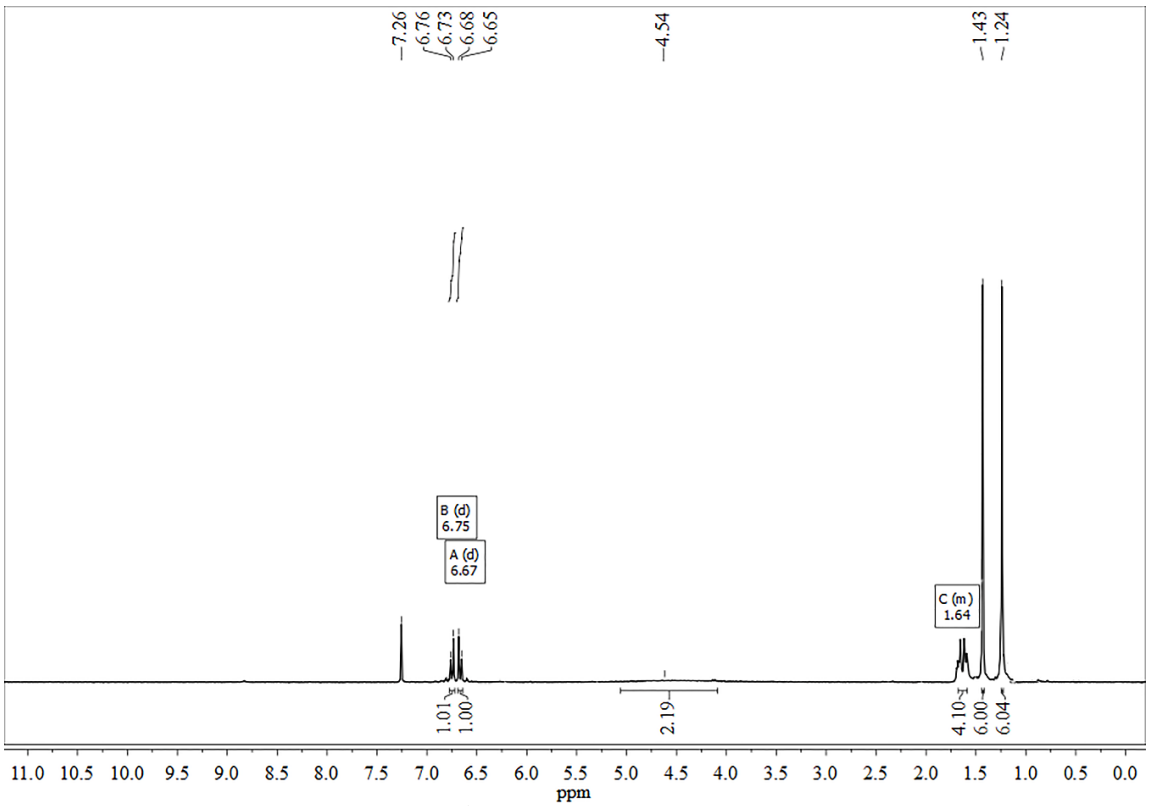

Figure S5. The ^{1}H NMR spectrum of **3′** ($CDCl_3$).

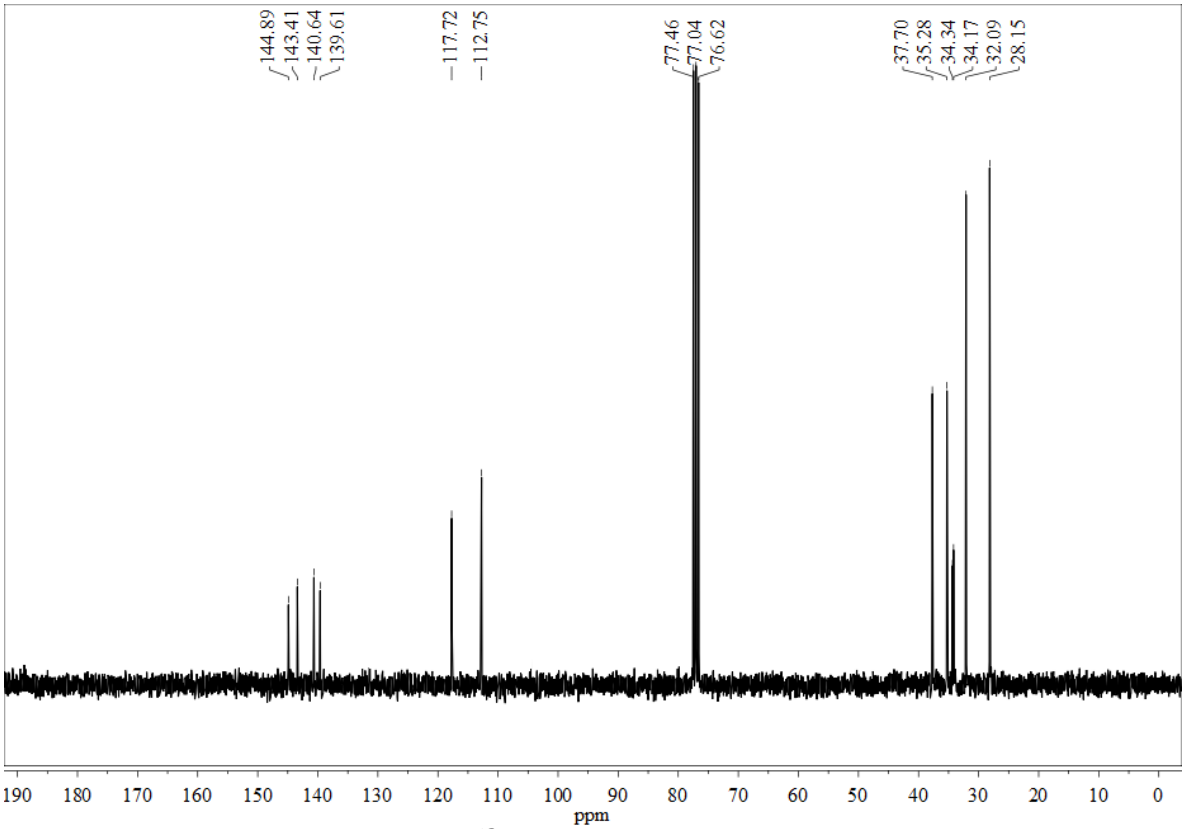

Figure S6. The ^{13}C NMR spectrum of **3′** ($CDCl_3$).

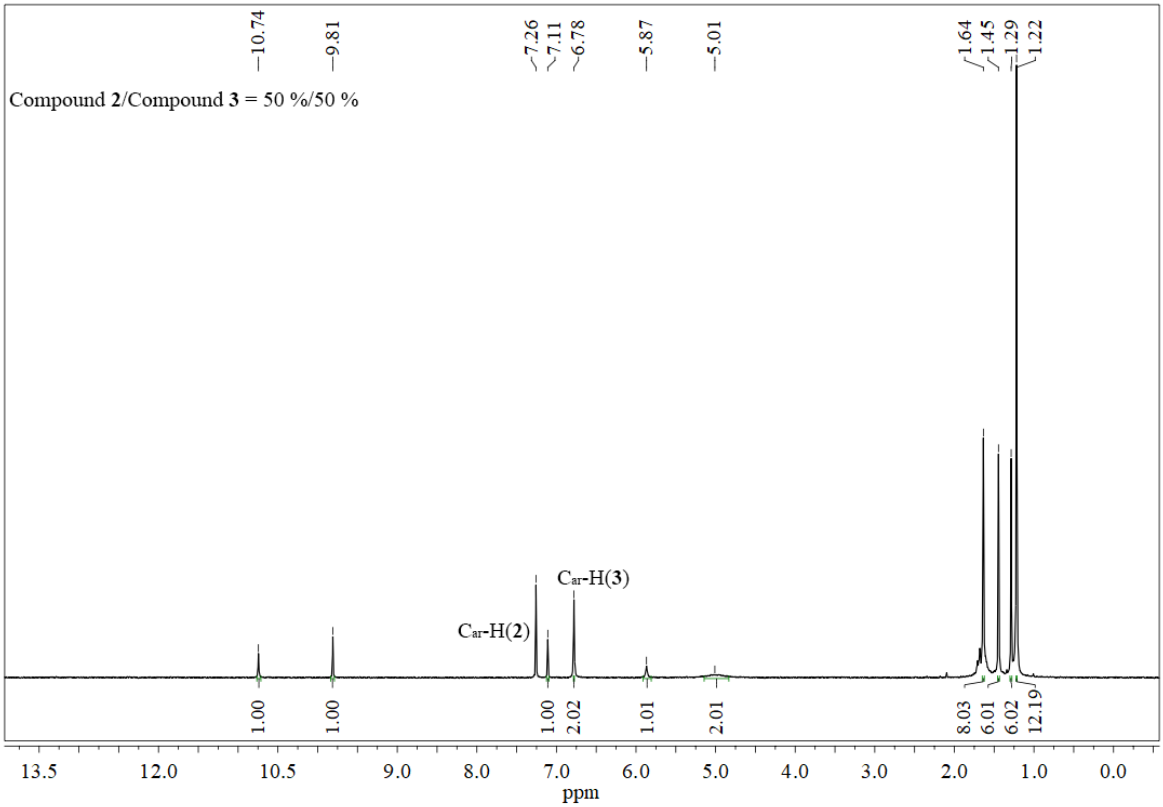

Figure S7. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** (HBr, 120 °C).

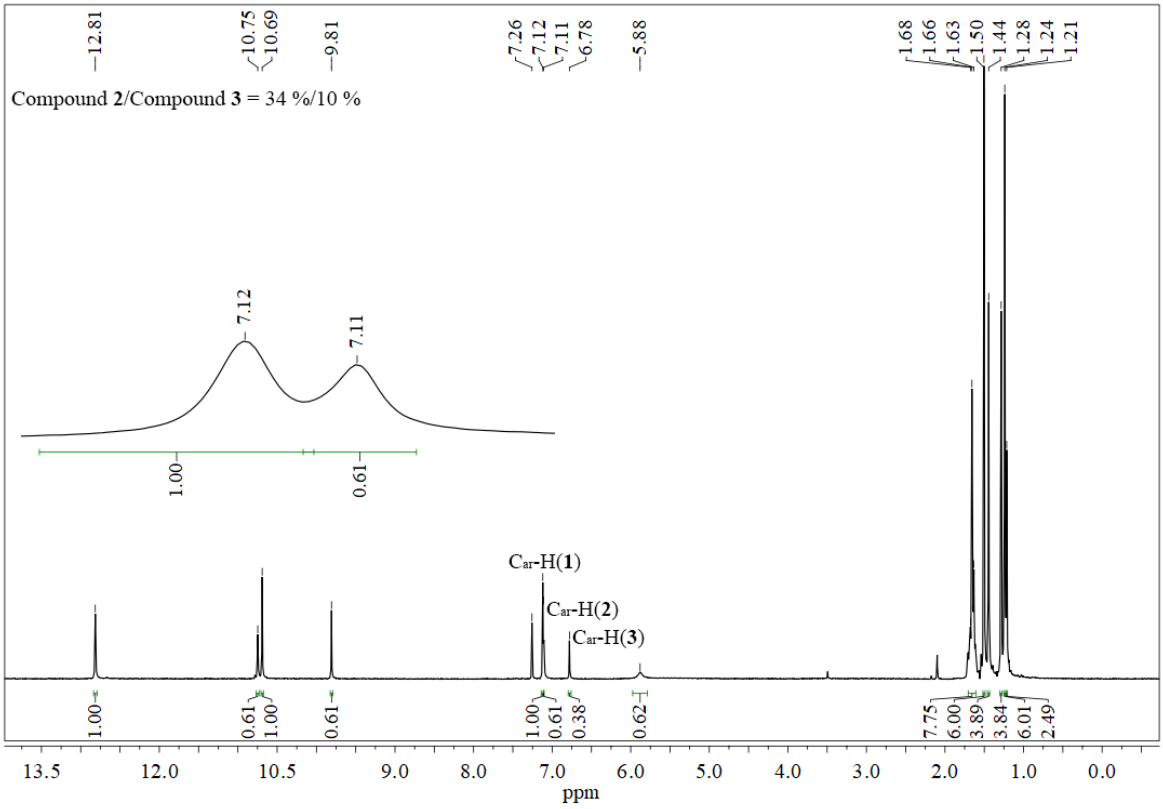

Figure S8. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** (HBr, 70 °C).

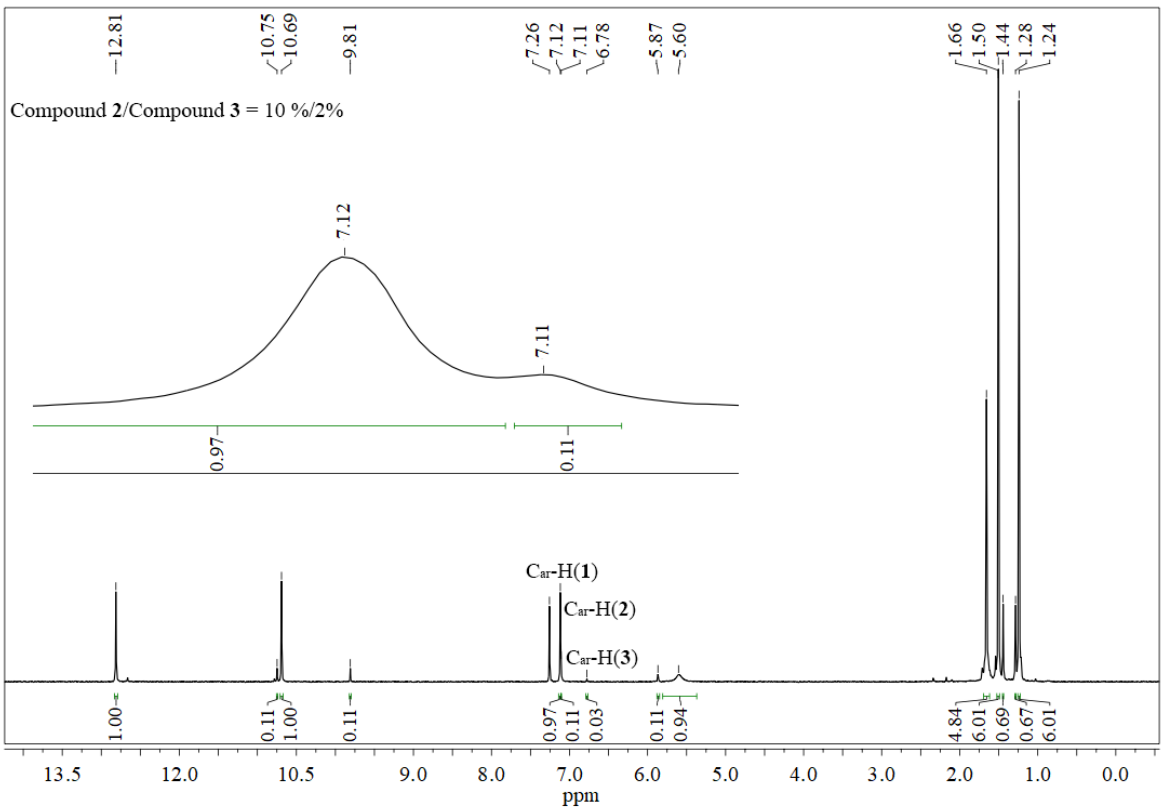

Figure S9. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** (TsOH, 70 °C).

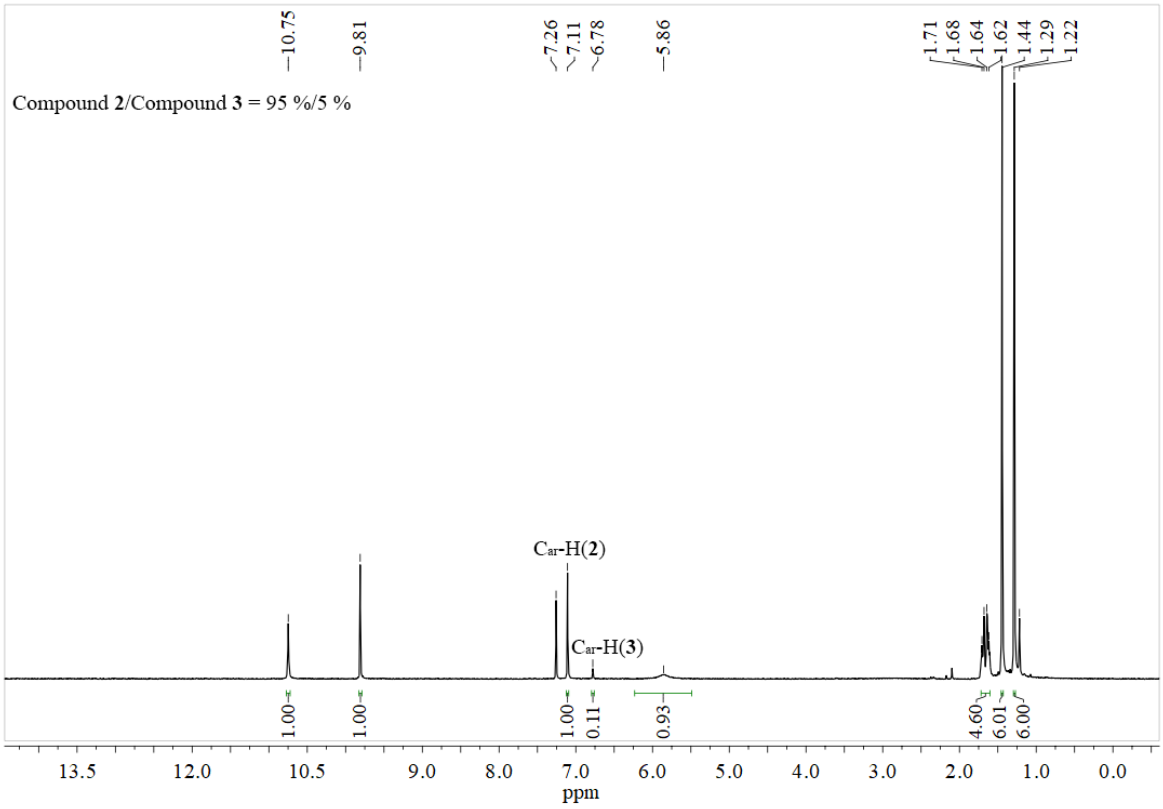

Figure S10. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** (H_2SO_4, 70 °C).

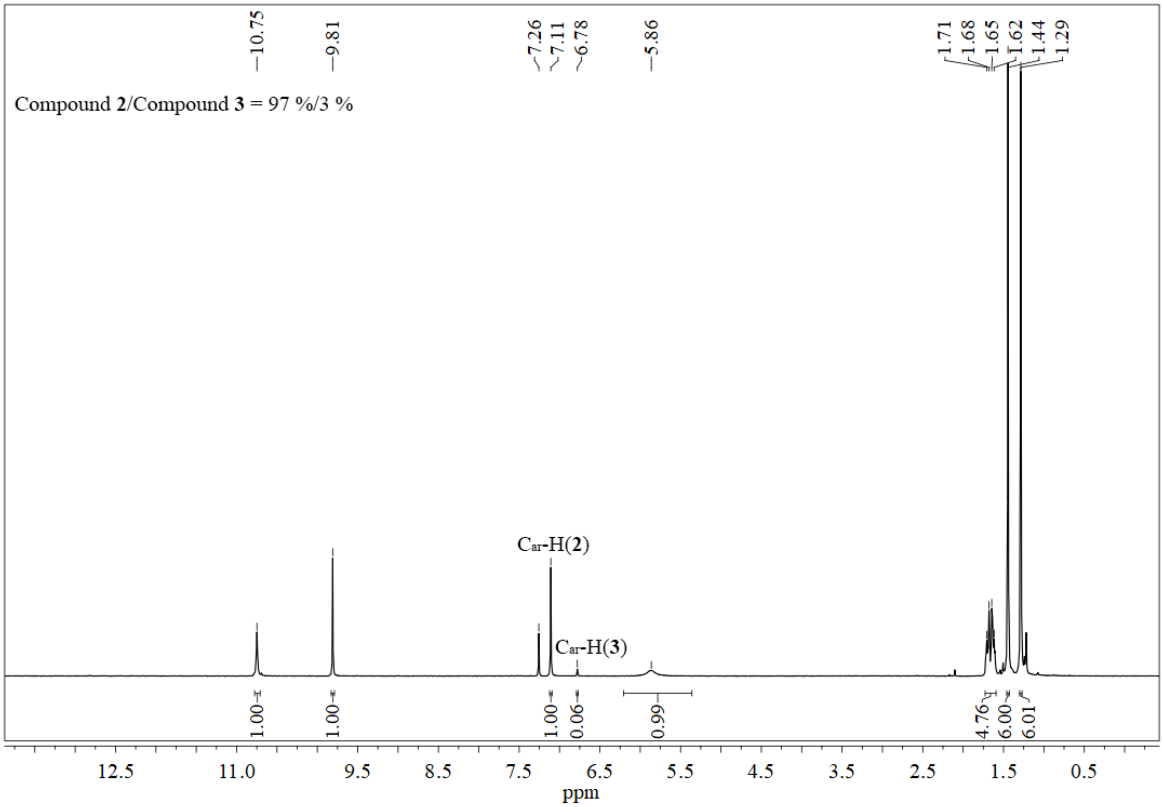

Figure S11. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** ($HClO_4$, 70 °C).

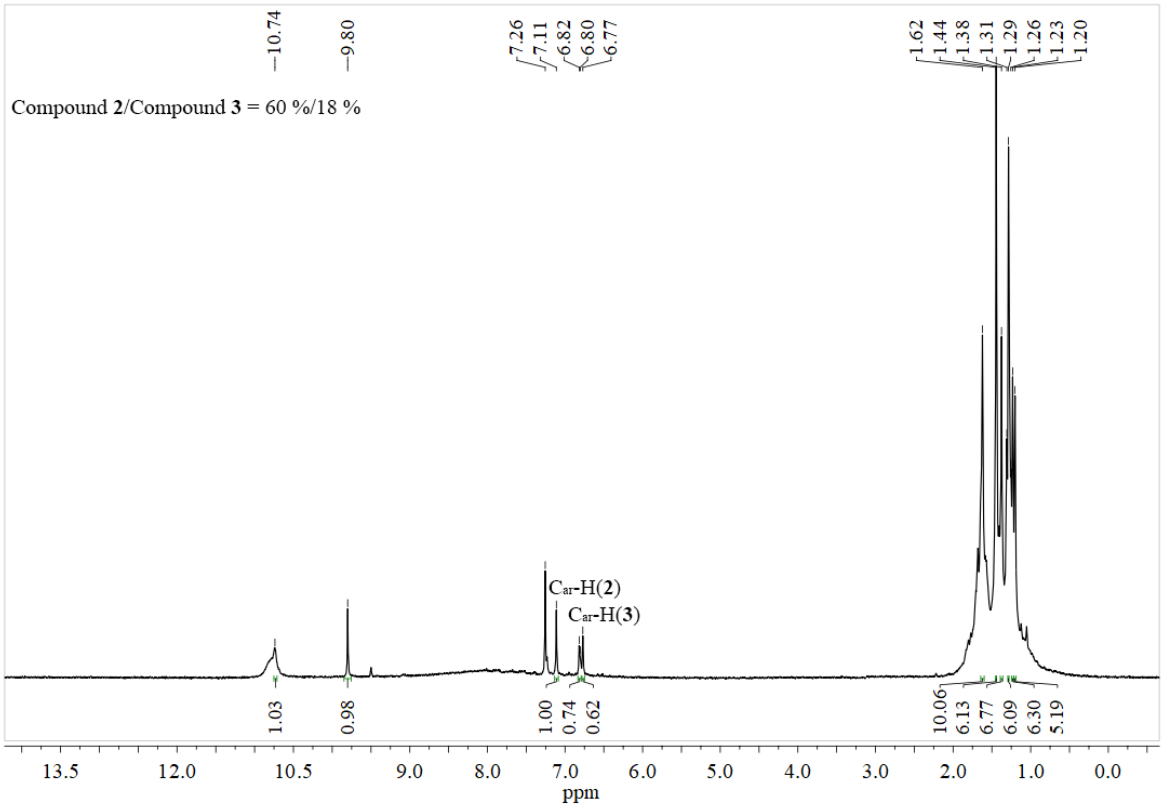

Figure S12. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** (MsOH, 40 °C).

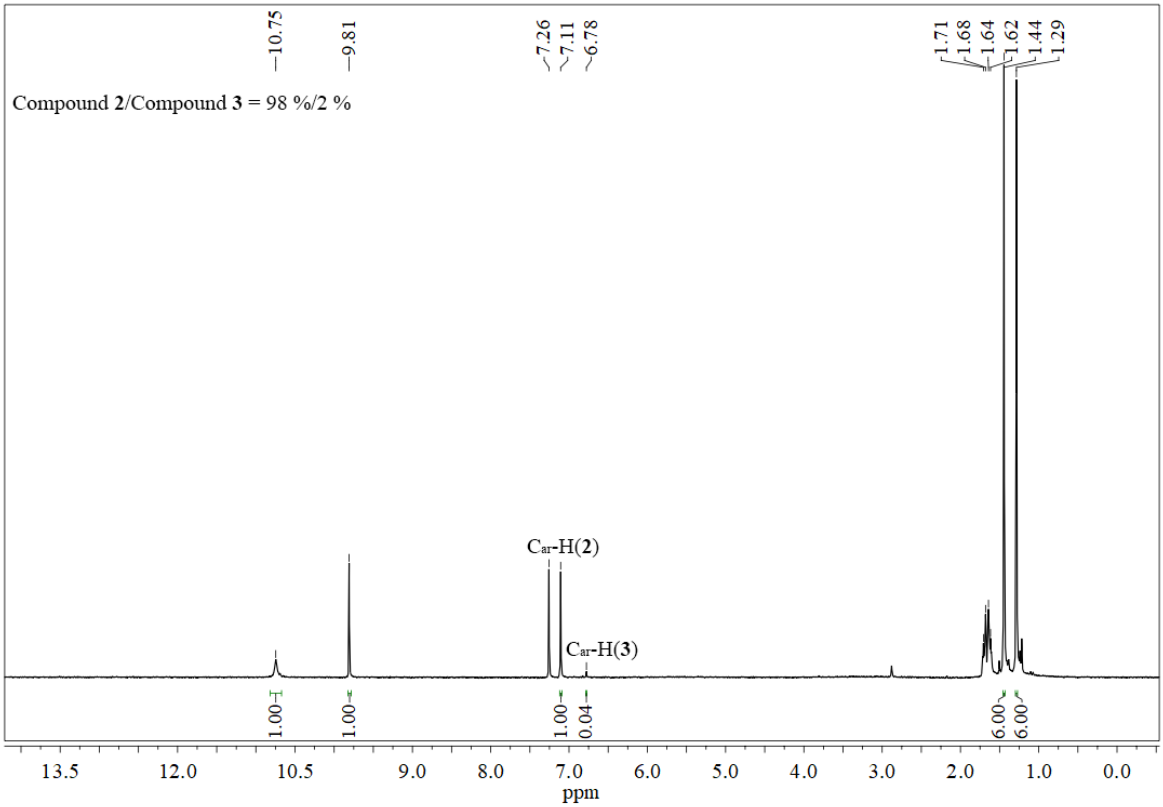

Figure S13. The ^{1}H NMR spectrum ($CDCl_3$) of a mixture of compounds **2** and **3** (MsOH, rt).

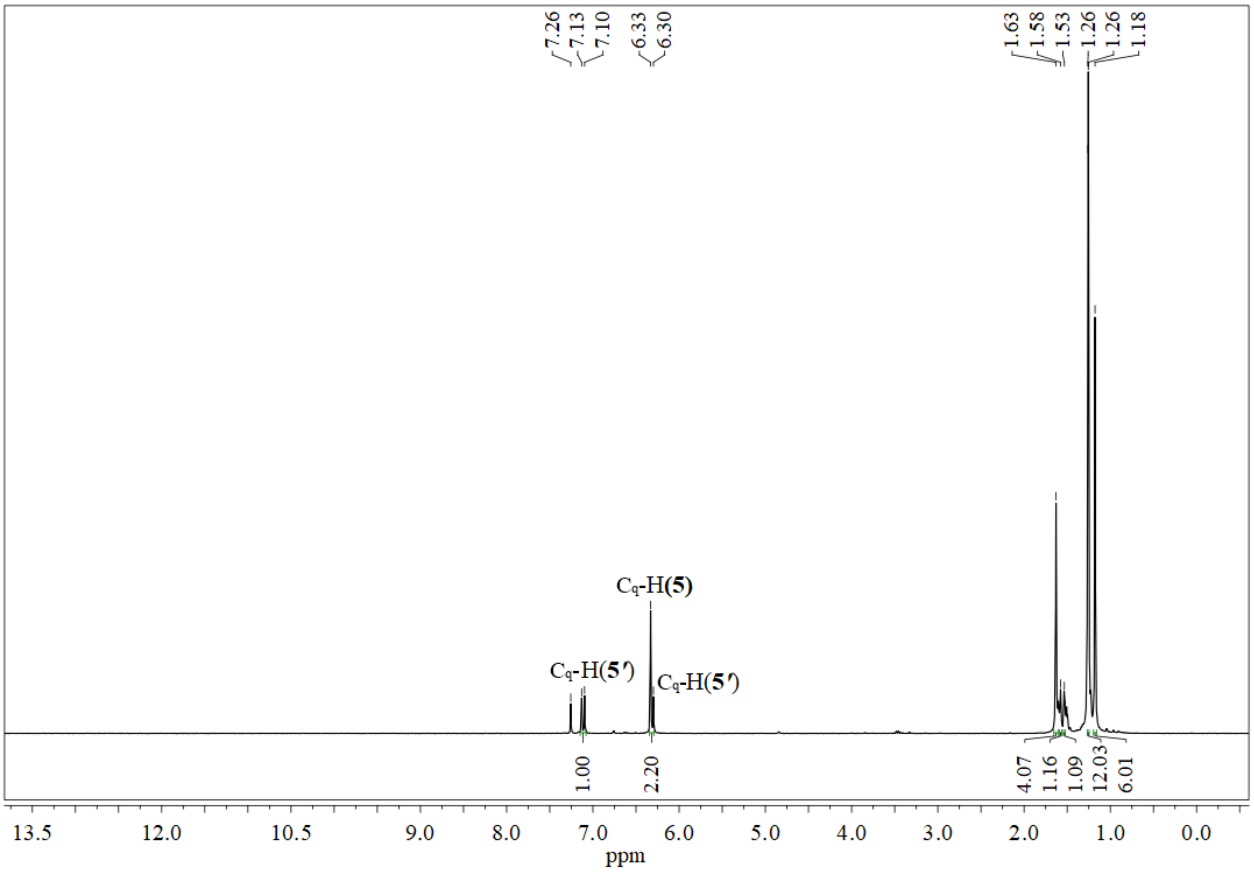

Figure S14. The ^{1}H NMR spectrum of a mixture of compounds **5′** and **5** ($CDCl_3$).

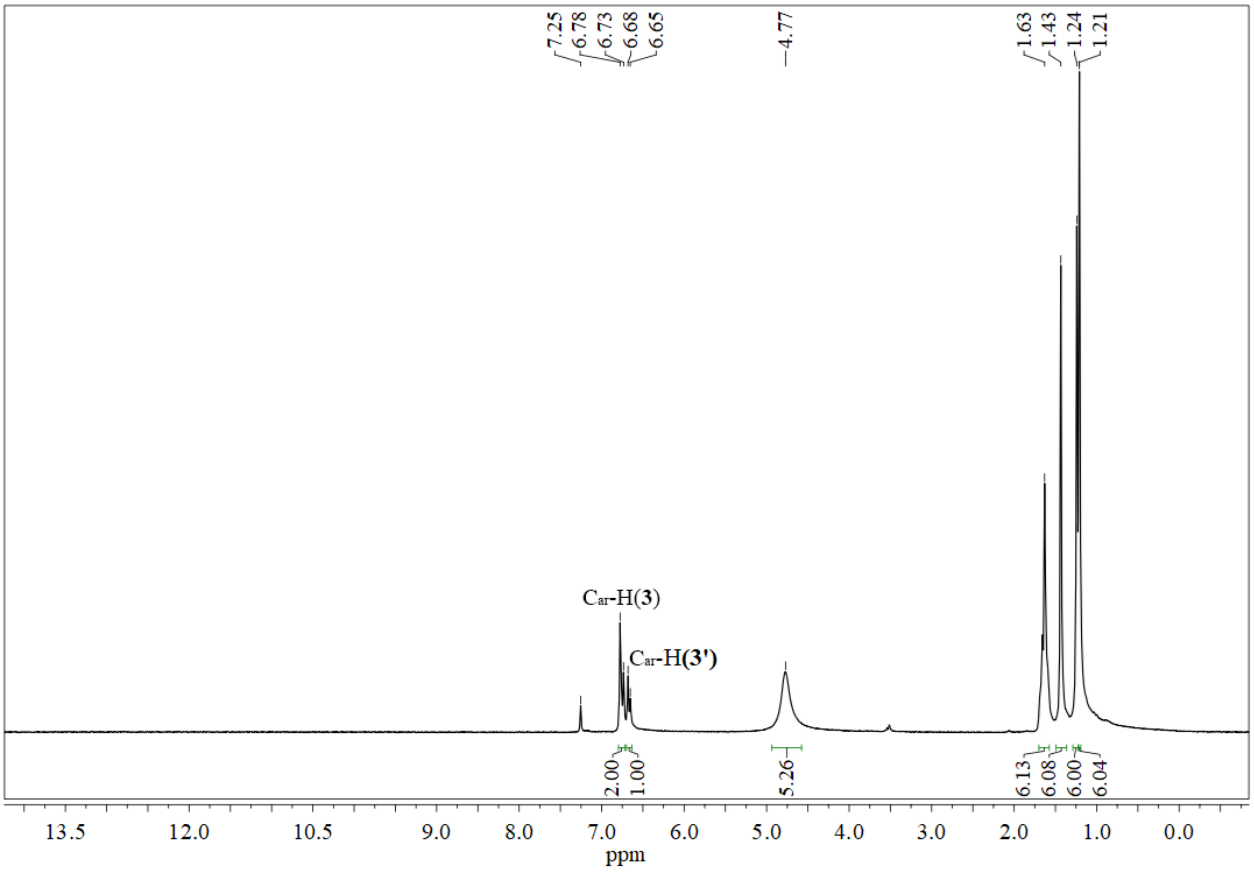

Figure S15. The ^{1}H NMR spectrum of a mixture of compounds **3** and **3′** ($CDCl_3$).

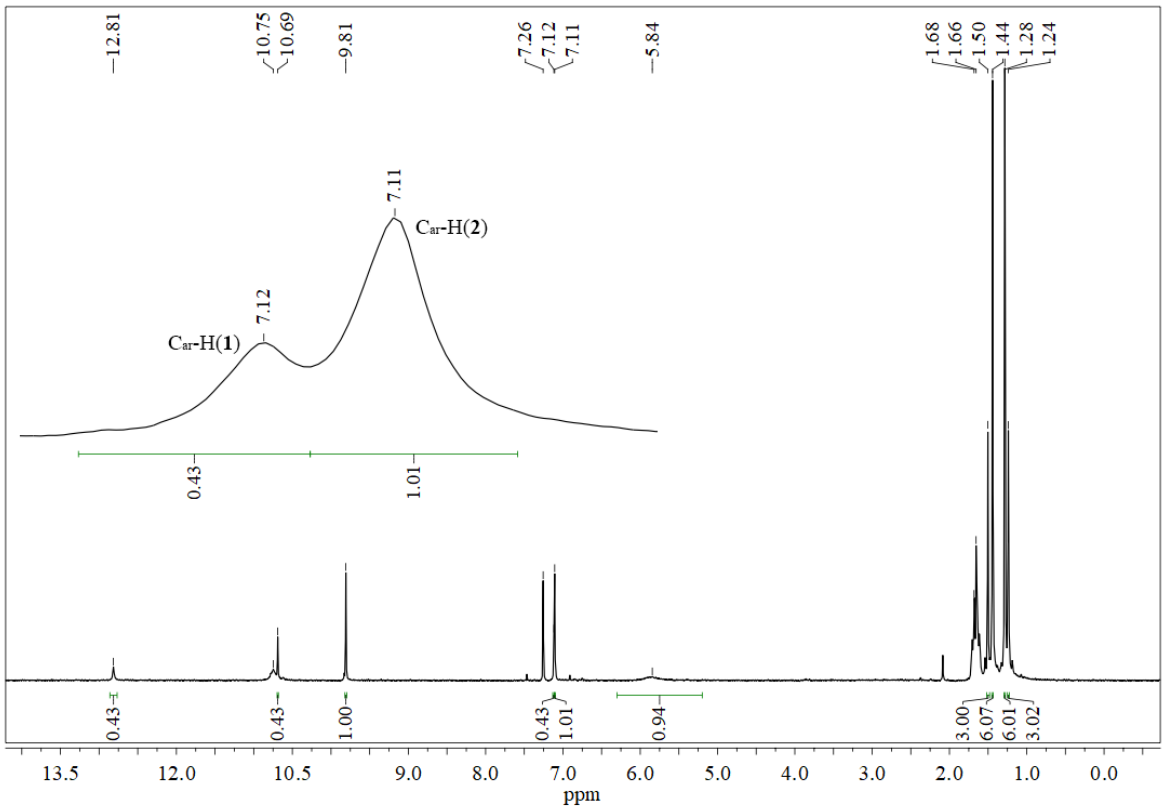

Figure S16. The ^{1}H NMR spectrum of a mixture of compounds **1** and **2** ($CDCl_3$).