Supplementary Material

Antioxidant properties of ethenyl indole: A DPPH assay and TDDFT studies

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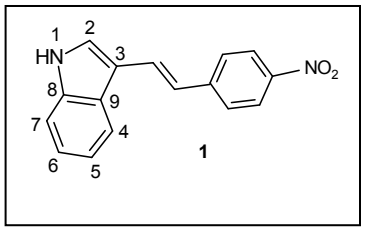
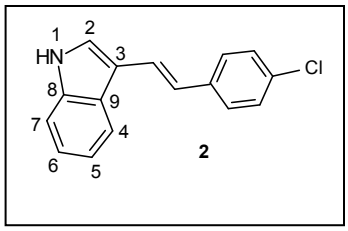
1 Experimental Section

1.1 Synthesis and characterization data of ethenyl indoles (1-6)

(*E*)-3-(4-Nitrostyryl)-1H-indole (1)[1]: 3-Formyl indole (1.45g, 0.01 mol) was taken in freshly distilled pyridine (10 mL), piperidine (0.6 mL) and *p*-nitrophenyl acetic acid (3.62 g, 0.02 mol) in a round bottom flask fitted with a reflux condenser. The reaction mixture was heated at 100 °C for eight hours. The progress of the reaction was monitored by thin layer chromatography. The reaction mixture was cooled to room temperature and poured in ice-cold water. The excess of pyridine from the crude product was removed by neutralizing the reaction mixture with 100 mL of diluted hydrochloric acid. A brick red colored product was obtained. The product was extracted in dichloromethane and purified by column chromatography using 2-5% ethyl acetate in petroleum ether as the eluting solvent. The yield of the product was 24%. M.p. 195-196 °C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 413 (27,900); IR (KBr): ν_{max} (cm^{-1}) 3370 (NHst), 3048 (C-Hst), 1626 (vinyl C=Cst), 1585, 1490, 1425 (Ar C=Cst), 1520 (Ar-NO_2, N=O Asym-st), 1330 (Ar-NO_2, N=O Sym-st); ^{1}H NMR ($CDCl_3$, 500 Hz): δ 7.17 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.27-7.31 (2H, m, -C_5-H, and -C_6-H), 7.44 (1H, d, J= 7.5 Hz, -C_4-H), 7.47 (1H, d, J = 2.7 Hz, -C_2-H), 7.50 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.61 (2H, d, J = 8.9 Hz, -Ar), 8.01 (1H, d, J= 6.9 Hz, -C_7-H), 8.21 (2H, d, J = 8.9 Hz, -ArNO_2), 8.35 (1H, s, br, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 145.8, 145.3, 136.9, 126.7, 125.8, 125.7, 125.2, 123.1, 122.8, 121.0, 120.2, 115.0, 111.7; MS (EI$^+$): m/z 264 (M^+); Analytical CHNS calculated for **1**: $C_{16}H_{12}N_2O_2$ (264.24) (%) C 72.71, H 4.57, N 10.59, Found C 72.65, H 4.55, N 10.58.

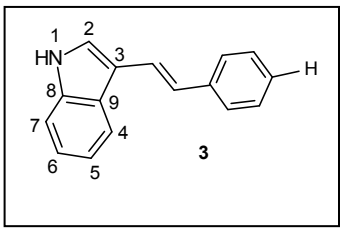


(*E*)-3-(4-Chlorostyryl)-1H-indole (2)[2]:



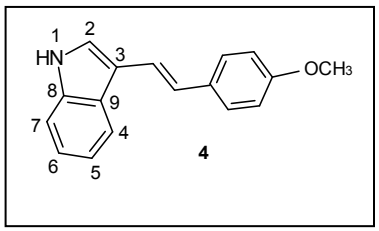
3-Formyl indole (1.45g, 0.01 mol) was taken in freshly distilled pyridine (10 mL), pipiridine (0.6 mL) and *p*-chlorophenyl acetic acid (3.40 g, 0.02 mol) in a round bottom flask fitted with a reflux condenser. The reaction mixture was heated at 100 ^{o}C for eight hours. The progress of the reaction was monitored by thin layer chromatography. The reaction mixture was cooled to room temperature and poured in ice-cold water. The excess of pyridine from the crude product was removed by neutralizing the reaction mixture with 100 mL of diluted hydrochloric acid. A pale white colored product was extracted in dichloromethane and purified by column chromatography using 2-5% ethyl acetate in petroleum ether as the eluting solvent. The yield of the product was 56 %. M.p. 191-192 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 335 (18,800); IR (KBr): ν_{max} (cm^{-1}) 3381 (NHst), 3048 (C-Hst), 1632 (vinyl C=Cst), 1524, 1488, 1455, 1403 (Ar, C=Cst); ^{1}H NMR ($CDCl_3$, 500 Hz): □δ 7.08 (1H, d, J = 16.5 Hz, -C=CH-Ar), 7.22-7.26 (2H, m, -C_5-H, -C_6-H), 7.29 (1H, d, J = 16.5 Hz, -CH=C-Ar), 7.31 (2H, d, J = 8.2 Hz, -Ar), 7.38 (1H, d, J = 2.0 Hz, -C_2-H), 7.41 (1H, d, J= 7.6 Hz, -C_4-H), 7.44 (2H, d, J = 8.2 Hz, -Ar-Cl), 7.98 (1H, d, J= 8.2 Hz, -C_7-H), 8.21 (1H, s, br, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 137.0, 136.8, 131.9, 131.2, 128.7, 126.8, 125.3, 124.2, 124.0, 122.8, 122.3, 120.5, 120.1, 115.3, 111.4; MS (EI^{+}): m/z 253 (M^{+}); Analytical CHNS calculated for **2**: $C_{16}H_{12}NCl$ (253.69) (%) C 75.73, H 4.76, N 5.52, Found C 75.70, H 4.74, N 5.51.

(*E*)-3-Styryl-1H-indole (3)[2]:



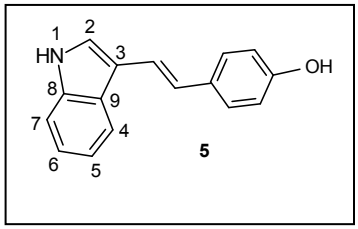
3-Formyl indole (1.45g, 0.01 mol) was taken in freshly distilled pyridine (10 mL), pipiridine (0.6 mL) and phenyl acetic acid (2.72 g, 0.02 mol) in a round bottom flask fitted with a reflux condenser. The reaction mixture was heated at 100 ^{o}C for eight hours. The progress of the reaction was monitored by thin layer chromatography. The reaction mixture was cooled to room temperature and poured in ice-cold water. The excess of pyridine from the crude product was removed by neutralizing the reaction mixture with 100 mL of diluted hydrochloric acid. A white colored product was extracted in dichloromethane and purified by column chromatography using 2-5% ethyl acetate in petroleum ether as the eluting solvent**.** The yield of the product was 45 %. M.p. 209-210 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 327 (10,800); IR (KBr): ν_{max} (cm^{-1}) 3381 (NHst), 3036 (C-Hst), 1630 (vinyl C=Cst), 1594, 1524, 1455, 1418 (Ar, C=Cst); ^{1}H NMR ($CDCl_3$, 500 Hz): □δ 7.08 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.15-7.22 (3H, m, -C_5-H, -C_6-H and -Ar-H), 7.29 (1H, d, J = 2.7 Hz, -C_2-H), 7.31 (2H, d, J = 7.5 Hz, -Ar), 7.33 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.34 (1H, d, J= 9.0 Hz, -C_4-H), 7.47 (2H, d, J = 7.5 Hz, -Ar), 7.95 (1H, d, J= 7.6 Hz, -C_7-H), 8.11 (1H, s, br, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 138.5, 136.8, 128.6, 126.6, 125.7, 125.5, 123.7, 122.7, 121.6, 120.4, 120.2, 115.6, 111.4; MS (EI^{+}): m/z 219 (M^{+}); Analytical CHNS calculated for **3**: $C_{16}H_{13}N$ (219.25) (%) C 87.63, H 5.97, N 6.38, Found C 87.53, H 5.96, N 6.37.

(*E*)-3-(4-Methoxystyryl)-1H-indole (**4**):



3-Formyl indole (1.45g, 0.01 mol) was taken in freshly distilled pyridine (10 mL), piperidine (0.6 mL) and *p*-methoxyphenyl acetic acid (3.32 g, 0.02 mol) in a round bottom flask fitted with a reflux condenser. The reaction mixture was heated at 100 ^{o}C for six hours. The progress of the reaction was monitored through thin layer chromatography. The reaction mixture was cooled to room temperature and poured in ice-cold water. The excess of pyridine from the crude product was removed by neutralizing the reaction mixture with 100 mL of diluted hydrochloric acid. A white colored product was extracted in dichloromethane and purified by column chromatography using 2-5% ethyl acetate in petroleum ether as the eluting solvent. The yield of the product was 34 %. M.p. 232-233 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 327 (17,800); IR (KBr): ν_{max} (cm^{-1}) 3377 (NHst), 3034 (C-Hst), 1634 (vinyl C=Cst), 1604,1574, 1505, 1456, 1428 (Ar, C=Cst), 1244 (Ar-O-Cst); ^{1}H-NMR ($CDCl_3$, 500 Hz): □δ 3.83 (3H, s, -OCH_3), 6.90 (2H, d, J = 8.9 Hz, -Ar-OCH_3), 7.09 (1H, d, J = 16.4 Hz, -CH=C-Ar), 7.19 (1H, d, J = 16.4 Hz, -C=CH-Ar), 7.21-7.25 (2H, m, -C_5-H, -C_6-H), 7.35 (1H, d, J=2.7 Hz, -C_2-H), 7.39 (1H, d, J = 7.6 Hz, -C_7-H), 7.46 (2H, d, J = 8.9 Hz, -Ar), 7.99 (1H, d, J = 7.6 Hz, -C_4-H), 8.16 (1H, br, s, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 158.5, 136.8, 131.3, 130.4, 126.8, 125.6, 125.2, 123.1, 122.6, 120.3, 120.1, 119.6, 115.8, 114.0, 111.3, 55.3; MS (EI^{+}): m/z 249 (M^{+}); Analytical CHNS calculated for **4**: $C_{17}H_{15}NO$ (249.27) (%) C 81.89, H 6.06, N 5.61, Found C 81.81, H 6.04, N 5.60.

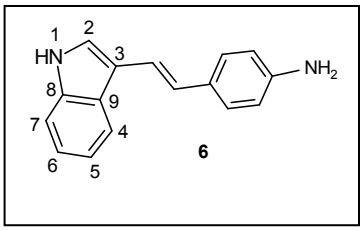
(*E*)-3-(4-Hydroxystyryl)-1H-indole (5):



5

3-Formyl indole (1.45g, 0.01 mol) was taken in freshly distilled pyridine (10 mL), piperidine (0.6 mL) and *p*-hydroxyphenyl acetic acid (3.04 g, 0.02 mol) in a round bottom flask fitted with a reflux condenser. The reaction mixture was heated at 100 ^{o}C for six hours. The progress of the reaction was monitored by thin layer chromatography. The reaction mixture was cooled to room temperature and poured in ice-cold water. The excess of pyridine from the crude product was removed by neutralizing the reaction mixture with 100 mL of diluted hydrochloric acid and extracted in dichloromethane and purified by column chromatography using 2-5% ethyl acetate in petroleum ether as the eluting solvent. The yield of the product was 33 %. M.p. 225-226 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 322 (24,400); IR (KBr): ν_{max} (cm^{-1}) 3379 (NHst), 3126 (OHst), 3030 (C-Hst), 1636 (vinyl C=Cst), 1587, 1540, 1505, 1456, 1420, 1358 (Ar, C=Cst); ^{1}H-NMR ($CDCl_3$, 500 Hz): δ 4.74 (3H, s, -OH), 6.83 (2H, d, J = 8.2 Hz, -Ar-OH), 7.08 (1H, d, J = 16.5 Hz, -CH=C-Ar), 7.18 (1H, d, J = 16.5 Hz, -C=CH-Ar), 7.21-7.23 (2H, m, -C_5-H, -C_6-H), 7.35 (1H, d, J=2.7 Hz, -C_2-H), 7.39 (1H, d, J = 6.2 Hz, -C_7-H), 7.41 (2H, d, J = 8.2 Hz, -Ar), 7.98 (1H, d, J = 8.2 Hz, -C_4-H), 8.16 (1H, br, s, -NH); MS (EI^{+}): m/z 235 (M^{+}); Analytical CHNS calculated for **5**: $C_{16}H_{13}NO$ (235.25) (%) C 81.67, H 5.57, N 5.95, Found C 81.61, H 5.55, N 5.93.

(*E*)-3-(4-Aminostyryl)-1H-indole (6)[1]:



Compound **6** was prepared by the reduction of ethanolic solution of nitro compound **1** (**1**: 0.2 g, 0.001 mol) in presence of aqueous ferrous sulfate (1.5 g, 0.01 mol) and ammonia solution (3 mL). The reaction mixture was heated at 100 ^{o}C for two hours and the excess organic layer was removed under reduced pressure to extract crude product. The product was purified by column chromatography using 2-10% ethyl acetate in petroleum ether (60-80 ^{o}C). The yield of the product was 47 %. M.p. 263-264 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 324 (12,200); IR (KBr): ν_{max} (cm^{-1}) 3394, 3341 (H-N-Hst), 3026 (C-Hst), 1610 (vinyl C=Cst), 1507, 1456, 1420, 1337 (Ar, C=Cst); ^{1}H-NMR ($CDCl_3$, 500 Hz): δ 3.70 (2H, br, s, -NH_2), 6.69 (2H, d, J = 8.2 Hz, -Ar-NH_2), 7.05 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.14 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.18-7.25 (2H, m, -C_5-H, -C_6-H), 7.33 (1H, d, J=2.7 Hz, -C_2-H), 7.34 (2H, d, J = 8.9 Hz, -Ar), 7.38 (1H, d, J = 7.5 Hz, -C_7-H), 7.97 (1H, d, J = 7.5 Hz, -C_4-H), 8.13 (1H, br, s, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 145.2, 136.7, 129.3, 126.9, 125.8, 125.6, 122.7, 122.5, 120.2, 120.1, 118.1, 115.9, 115.3, 111.3; MS (EI^{+}): m/z 234 (M^{+}); Analytical CHNS calculated for **6**: $C_{16}H_{14}N_2$ (234.26) (%) C 82.01, H 6.02, N 11.95, Found C 81.95, H 6.01, N 11.93.

References

1. (a) A. K. Singh, P.K. Hota, Photoreactivity of donor-acceptor ethenes. Indian J. Chem. 42B (2003) 2048-2053, (b) A. K. Singh, P.K. Hota, Fluorescence and photoisomerization studies of *p*-nitrophenyl substituted indolic ethenes, J. Phys. Org. Chem. 19 (2006) 43-52.
2. A. K. Singh, A Asefa, A fluorescence study of differently substituted 3-styrylindoles and their interaction with bovine serum albumin, Luminescence 24 (2009) 123-130.

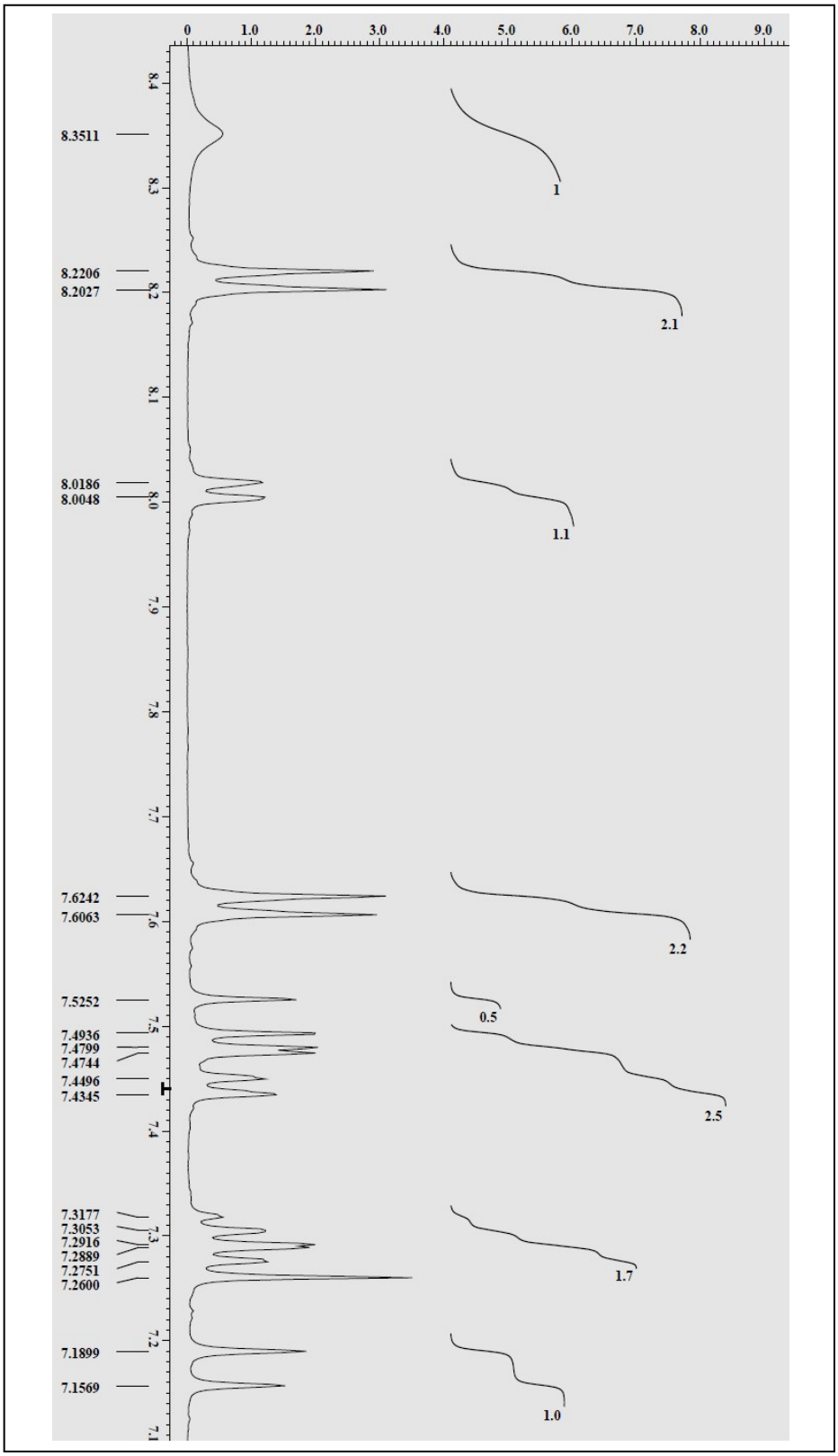


Figure S1a. 500 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$.

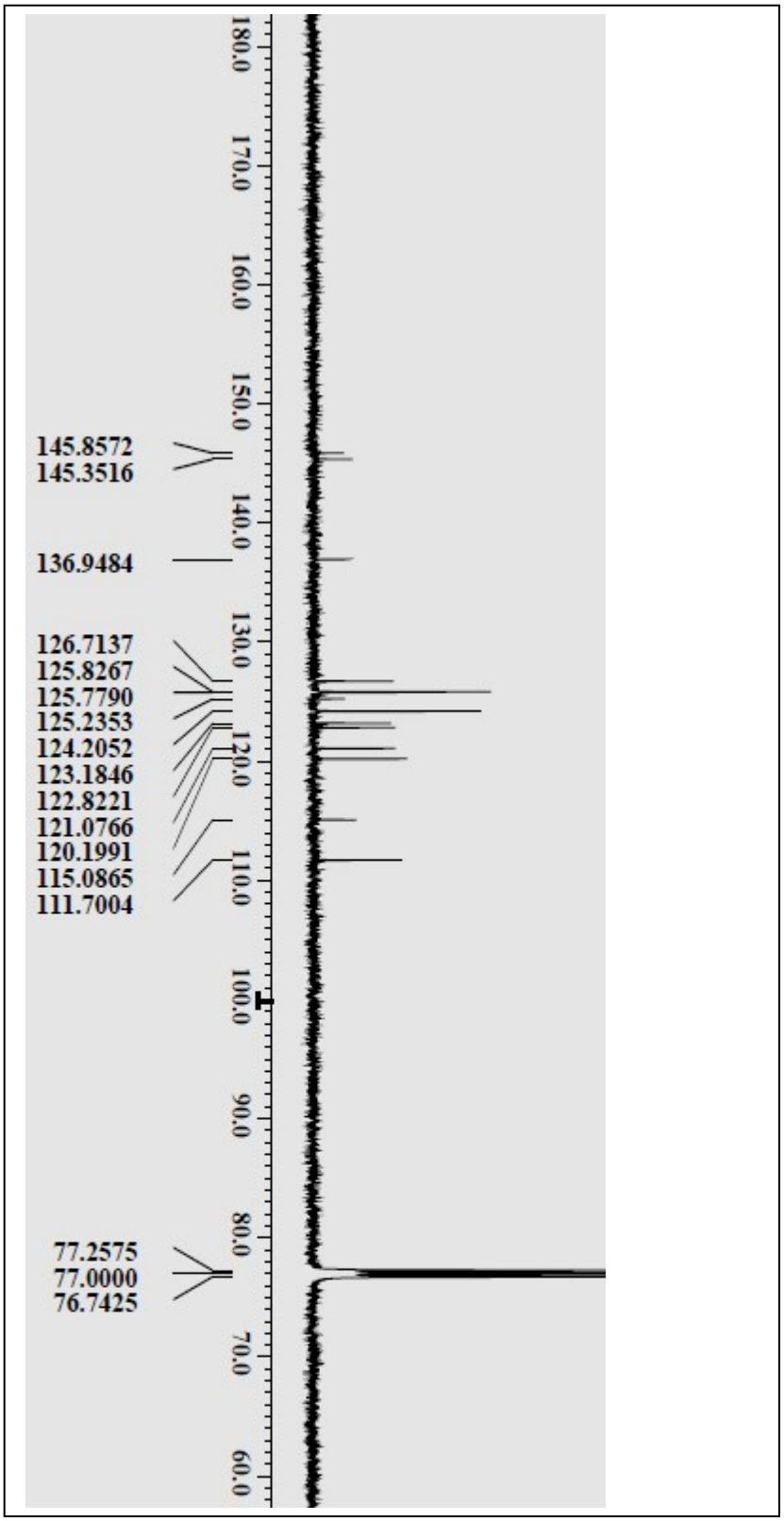


Figure S1b. 500 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$.

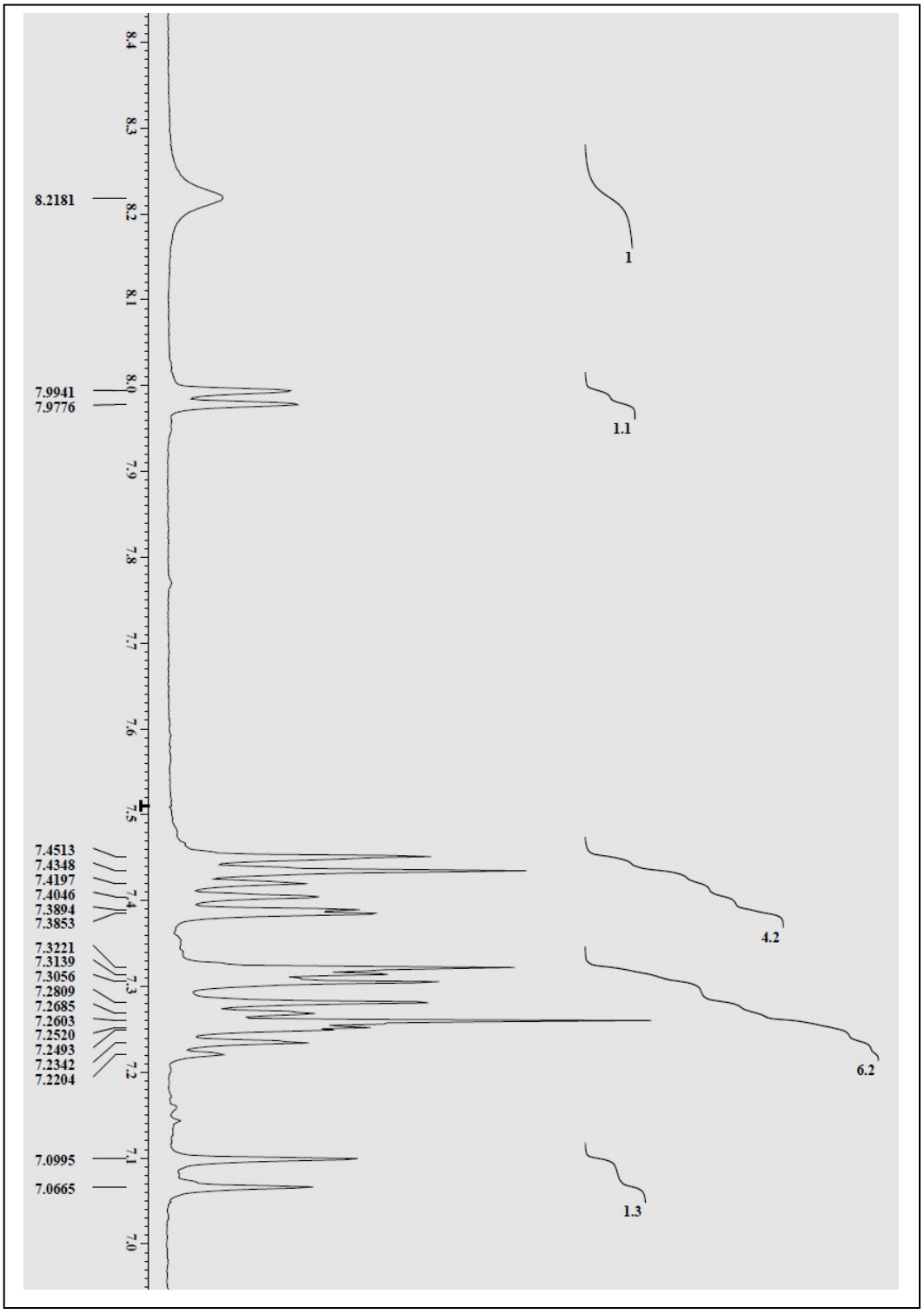


Figure S2a. 500 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$.

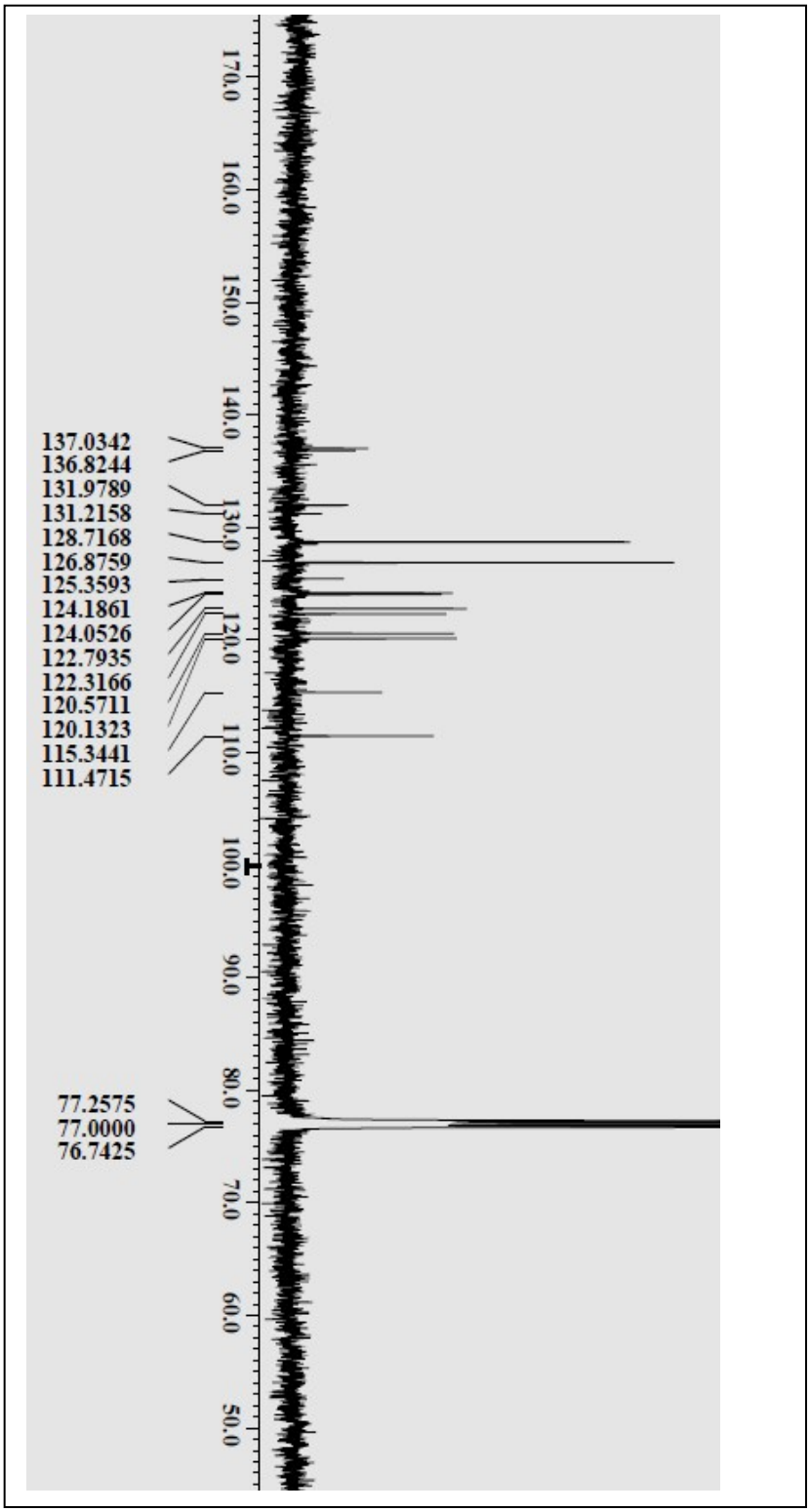


Figure S2b. 500 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$.

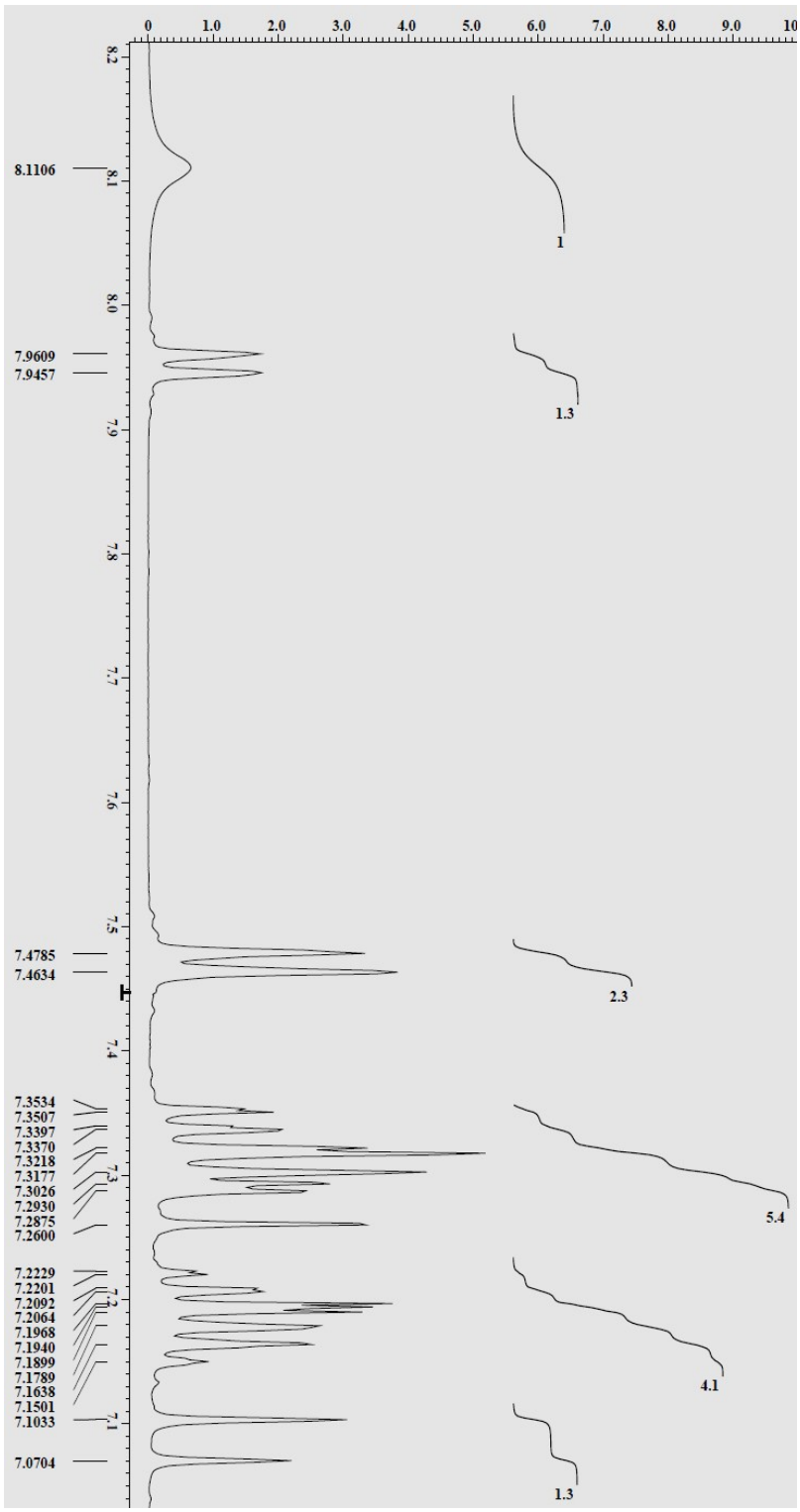


Figure S3a. 500 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$.

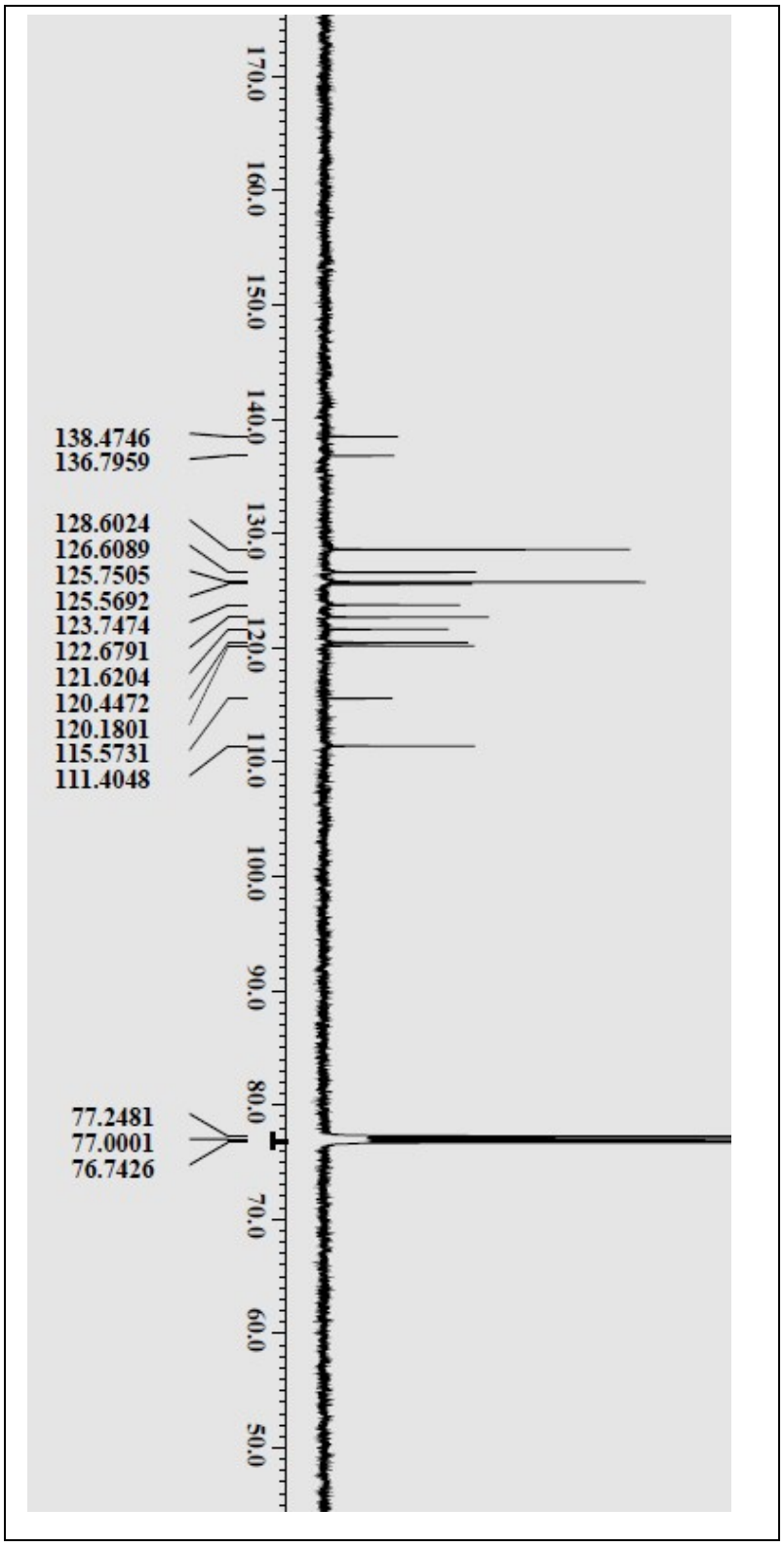


Figure S3b. 500 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$

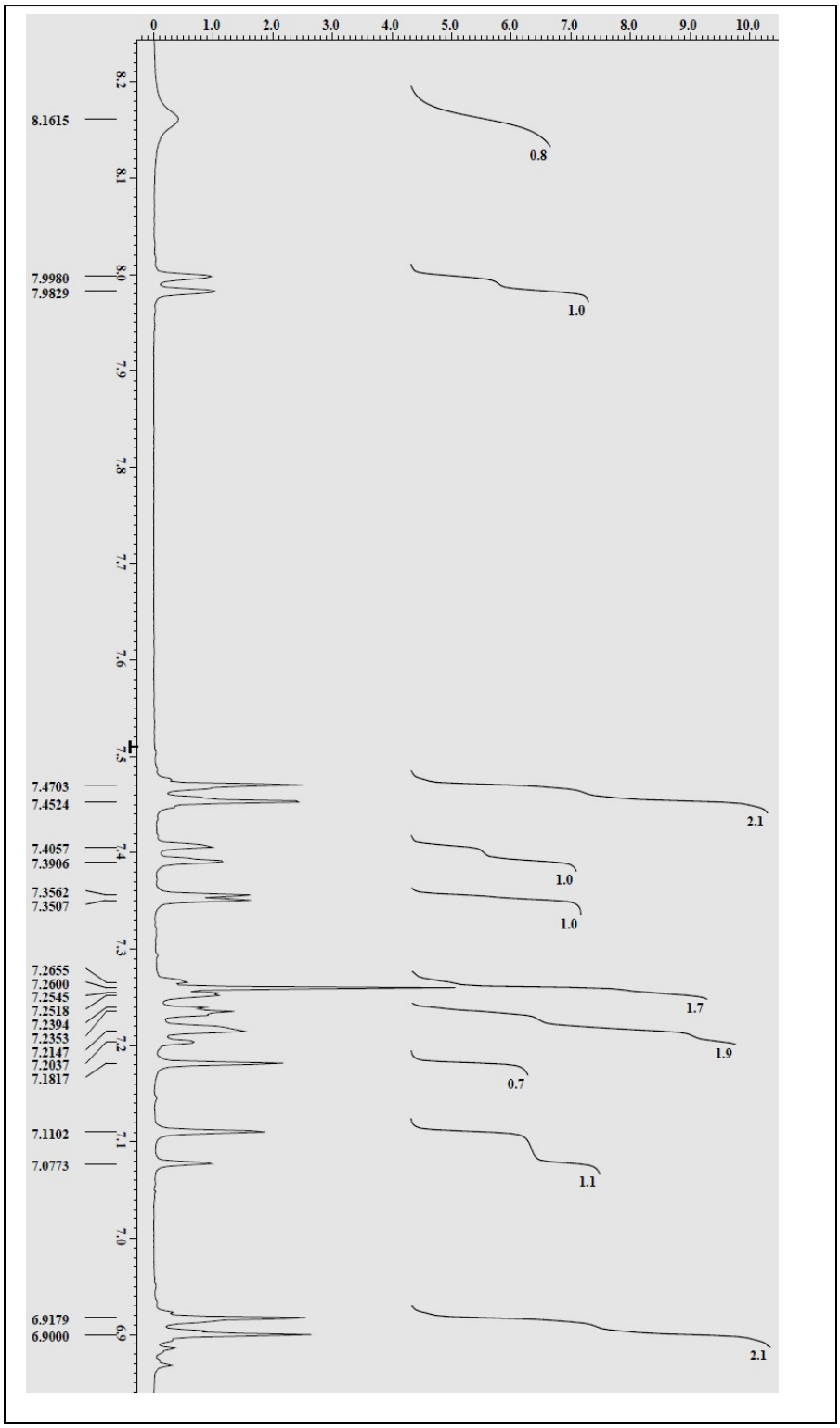


Figure S4a. 500 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$.

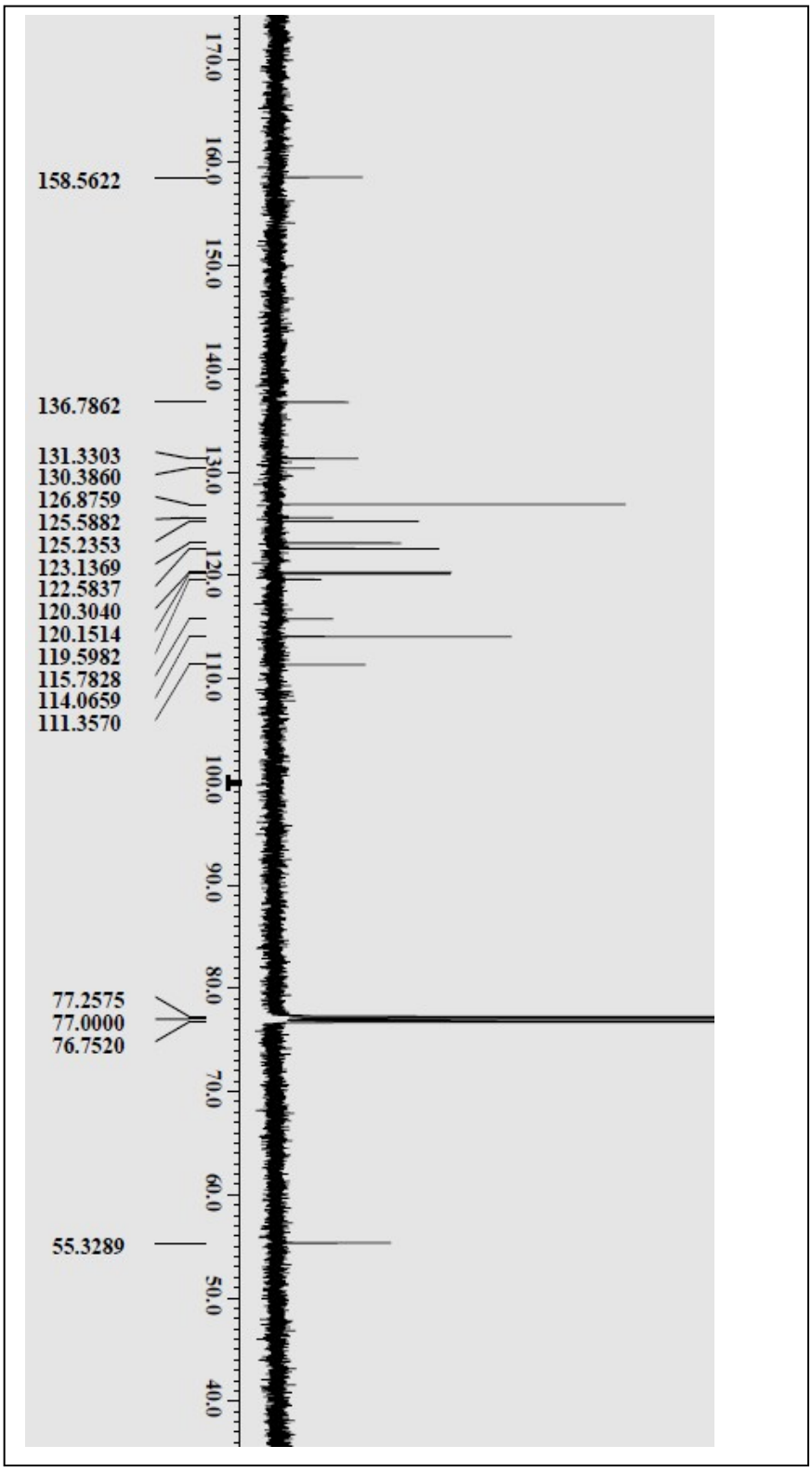


Figure S4b. 500 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$.

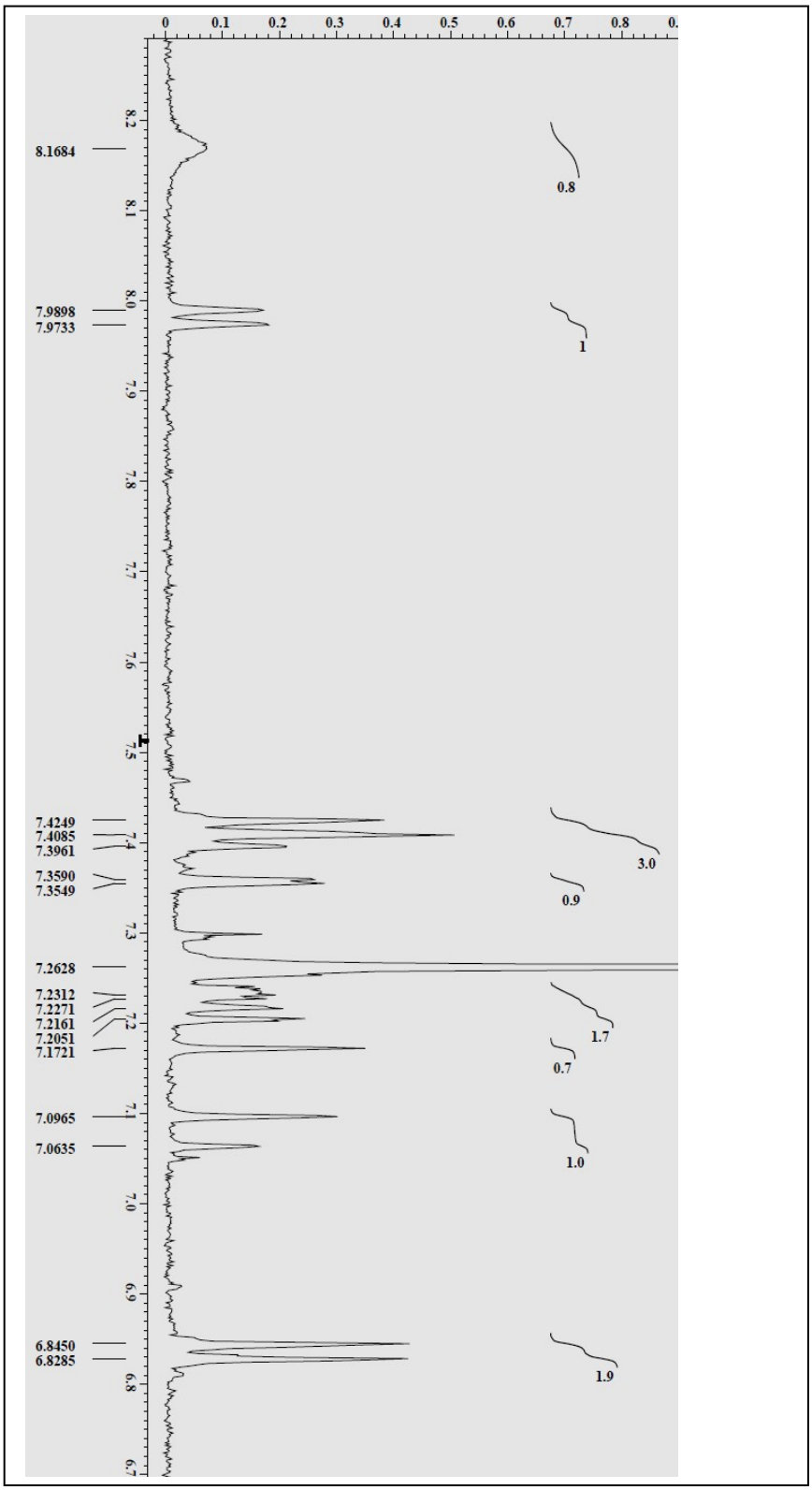


Figure S5a. 500 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$.

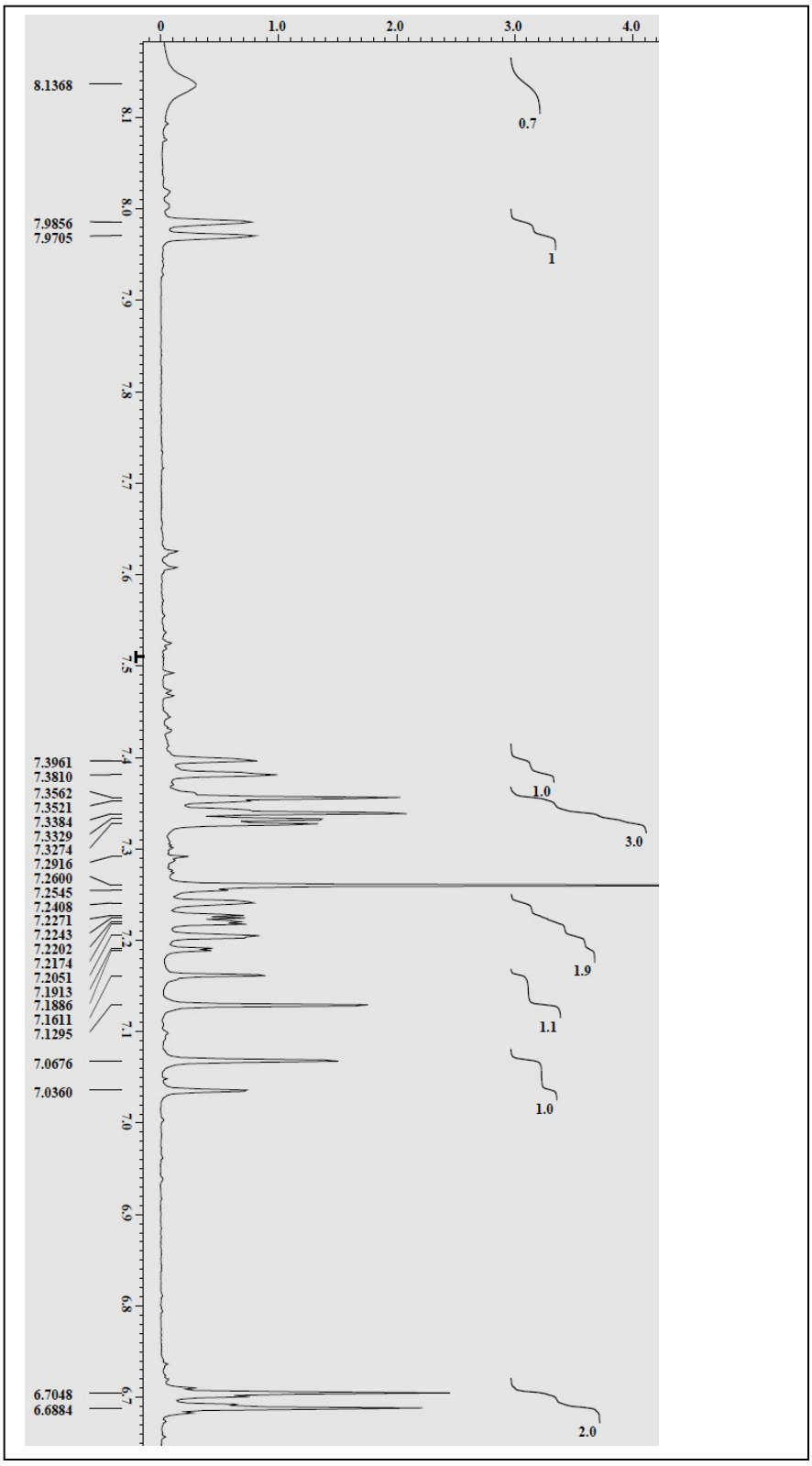


Figure S6a. 500 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$.

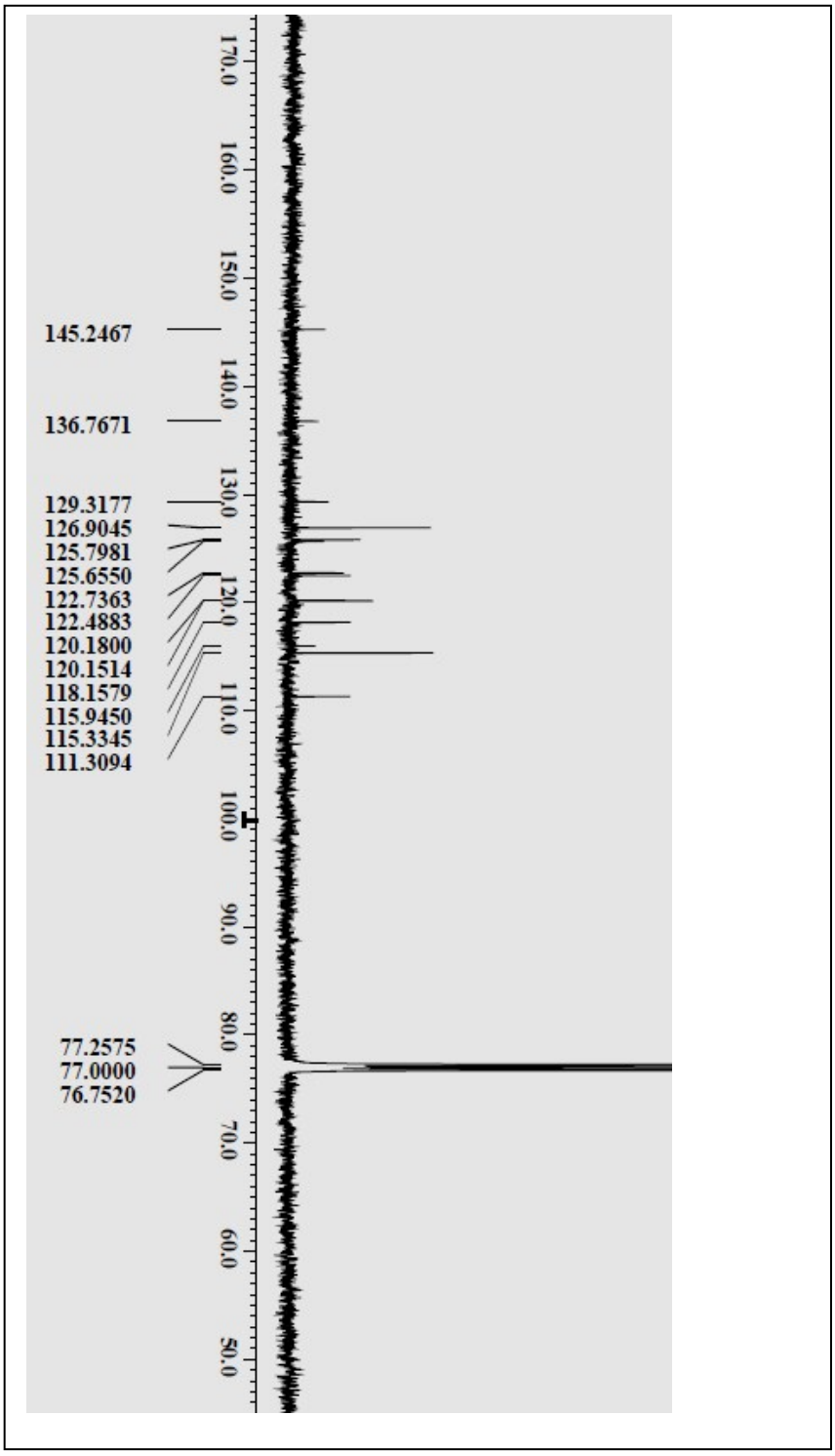


Figure S6b. 500 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$.