



Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2019

Environmentally Benign Approach for the Synthesis of Azo Dyes in the Presence of Mesoporous Sulfated Core-Shell Zirconia-Copper(I) Oxide Solid Acid Catalyst

Lakshminarayana Parashuram, Swamy Sreenivasa,* Sathyanarayana Rao Akshatha, Velu Udaya Kumar, and Sandeep Kumar

Author Contributions

P.L. Investigation:Lead; Writing - Original Draft:Lead

A.S. Investigation:Equal

U.V. Formal analysis:Equal; Project administration:Equal

S.K. Conceptualization:Equal; Formal analysis:Equal

Materials and Methods

Zirconyl oxy chloride octa hydrate, copper chloride dihydrate, ammonia were purchased from Merck chemicals. The chemicals were used without further purification unless mentioned. The X-ray diffraction patterns were recorded for all the samples with Panalytical x'pert X-ray diffractometer (PXRD), the FTIR spectra were recorded using Bruker-Alpha fourier transform infrared spectrometer. SEM micrographs were recorded with Zeiss field emission scanning electron microscope.

General procedure for the synthesis of sulfated core shell Cu(I)@ZrO₂-SO₄²⁻

ZrO₂:Cu(I) material was prepared by simple co-precipitation method described in detail elsewhere in our earlier report ^[1]. Further sulfation was achieved by treating ZrO₂:Cu(I) material with suitable volume of 2M sulfuric acid. In the typical procedure to a known amount of the ZrO₂:Cu(I) catalyst, 2M sulfuric acid was added drop wise resulting in a slurry after complete addition of acid, the slurry was subjected to drying in preheated hot air oven maintained at 120°C for a period of 2 hours. The catalyst was allowed to cool, then dried catalyst was ground into fine powder and further subjected to calcination in a preheated muffle furnace maintained at 500°C for 2 hours. The process leads to the stabilization of sulfate groups on the surface of metal oxide. Then, cooled catalyst was kept under vacuum desiccation till further use. ^[2]

General procedure for the synthesis of azo dyes

Azo synthesis reaction was performed in a clean mortar at room temperature. In the typical experiment, required amounts of aniline/substituted aniline (1.0 mmol), sodium nitrite (2.0 mmol) and 0.1 g of Cu(I)@ZrO₂-SO₄²⁻ catalyst were ground in mortar to get homogeneous mixture. The process lead to the formation of catalyst-diazonium complex, to this complex 1.0 mmol of coupling agents like 1-naphthol, 2-naphthol, phenol, 2-chlorophenol or

salicylaldehyde were added, further ground slowly till the formation of azo dye. After completion of the reaction, the crude azo dye was washed and dissolved in acetone. The products were recrystallized from ethanol and stored under vacuum desiccation till characterization. The recrystallized products were identified and analyzed by FTIR, ^1H NMR and ^{13}C NMR methods.

Spectral data of representative compounds:

3a. 4-[(*E*)-phenyldiazenyl]naphthalen-1-ol: FT-IR (KBr, cm^{-1}): 3440, 1596, 1259, 1128. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.438 (1H, d, $J = 8$); 7.681 (1H, d, $J = 7.60$); 7.646 (1H, d, $J = 7.60$); 7.225–7.627 (5H, m); 7.027 (1H, d, $J = 9.2$); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.838, 153.257, 145.234, 132.358, 129.637, 128.375, 127.682, 126.847, 126.337, 121.105, 117.746, 109.508.

3b. 4-[(*E*)-pyridin-2-yl diazenyl]naphthalen-1-ol: FT-IR (KBr, cm^{-1}): 3359, 1617, 1265, 1111. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.167 (1H, d, $J = 8$); 8.128 (1H, d, $J = 7.6$); 7.718 (1H, d, $J = 6.4$); 7.234–7.682 (5H, m); 7.219 (1H, d, $J = 9.6$); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 185.563, 164.975, 158.190, 147.108, 146.228, 141.814, 138.320, 134.491, 132.488, 130.869, 129.184, 126.786, 126.335, 122.317, 120.412, 113.878, 120.412, 113.878, 113.878, 109.118, 107.135.

3c. 4-[(*Z*)-benzyldiazenyl]naphthalen-1-ol: FT-IR (KBr, cm^{-1}): 3447, 1628, 1398, 1187, 1113. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.481 (1H, d, $J = 5.2$); 7.426 (1H, d, $J = 8.4$); 7.386 (1H, d, $J = 6.8$); 7.237–7.369 (5H, m); 7.230 (1H, d, $J = 6.4$), 6.809 (1H, d, $J = 7.2$), 5.082 (2H, s); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 129.668, 129.361, 129.032, 128.814, 128.580, 127.995, 127.741, 127.649, 127.284, 127.041, 126.384, 126.239, 125.863, 125.170, 124.918, 122.459, 121.638, 120.488, 118.673, 108.583, 67.338.

3d. 4-[(*Z*)-(4-bromophenyl)diazenyl]naphthalen-1-ol: FT-IR (KBr, cm^{-1}): 3450, 1630, 1600, 1265, 1110. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.186 (1H, ddd, $J = 9.6$); 7.818 (1H,

dd, $J = 7.6$); 7.465–7.539 (2H, m); 7.444 (1H, ddd, $J = 8.4$); 7.315 (2H, ddd, $J = 7.2$); 7.217–7.295 (1H, m); 6.545–6.818 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 151.423, 145.346, 134.788, 132.677, 132.564, 132.365, 132.037, 128.126, , 127.735, 127.674, 126.837, 126.500, 126.429, 125.829, 125.241, 124.388, 121.664, 121.547, 120.665, 119.484, 119.117, 116.780, 110.355, 108.605.

3e. 4-[(Z)-(4-nitrophenyl)diazenyl]naphthalen-1-ol: FT-IR (KBr, cm^{-1}): 3489, 1602, 1314, 1113. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.297 (1H, d, $J = 9.2$); 8.118–8.051(2H, m); 7.503–7.467 (2H, m); 7.440 (1H, d, $J = 8.2$); 7.297 (2H, d, $J = 8.2$); 6.630–6.592 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 152.446, 134.026, 127.666, 126.363, 125.844, 125.224, 124.397, 121.568, 120.630, 116.167, 113.401, 108.600

3f. 1-[(Z)-benzyldiazenyl]naphthalen-2-ol: FT-IR (KBr, cm_1): 3343, 1629, 1219, 1176. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.747 (2H, d, $J=8$); 7.722 (1H, d, $J=8.8$); 7.646 (2H, dd, $J=7.6$); 7.414–7.345 (1H, m); 7.314–7.274 (1H, m); 7.125 (2H, d, $J=8.8$); 4.701 (2H, s); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.678, 147.999, 144.891, 134.664, 131.074, 129.744, 129.016, 129.846, 128.613, 127.769, 127.739, 127.436, 127.102, 126.423, 126.349, 125.718, 123.460, 123.174, 122.273, 117.919, 110.804, 109.488, 65.434, 58.615

3g. 1-[(E)-(4-nitrophenyl)diazenyl]naphthalen-2-ol: FT-IR (KBr, cm^{-1}): 3483, 1632, 1478, 1285, 1115. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.328 (2H, d, $J = 9.2$); 8.078–8.055 (1H, m); 7.751 (2H, d, $J = 8.8$); 7.704–7.659 (1H, m); 7.543–7.396 (1H, m); 7.334–7.311 (1H, m); 6.711–6.687 (1H, $J=9.6$) 6.626–6.603 (1H, dd, $J = 9.2$) ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.496, 152.465, 147.953, 143.631, 134.632, 129.820, 129.221, 128.928, 128.673, 127.765, 127.643, 126.504, 126.370, 125.768, 124.879, 123.573, 122.571, 117.804, 116.649, 113.403, 109.487.

3h. 1-[(E)-(4-bromophenyl)diazenyl]naphthalen-2-ol: FT-IR (KBr, cm^{-1}): 3450, 1624, 1385, 1271, 1111. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.764 (1H, d, $J = 7.2$); 7.727 (1H, d,

$J = 8.8$); 7.672 (1H, d, $J = 8.4$ Hz); 7.602 (1H, d, $J = 8.8$ Hz); 7.554-7.468 (1H, m); 7.419-7.392 (1H, m); 7.332 (1H, d, $J = 8$ Hz); 7.258-7.082(1H, m); 7.308 (1H, d, $J = 11.2$ Hz); 6.566 (1H, $J=8.8$); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 171.792, 153.449, 143.940, 140.537, 134.614, 133.391, 132.699, 132.353, 132.034, 130.328, 129.830, 129.038, 128.929, 128.735, 128.194, 127.759, 126.505, 126.349, 126.007, 124.565, 123.581, 123.181, 121.785, 120.758, 120.004, 119.440, 117.792, 116.775, 110.329, 109.499

3i. 1-[(*E*)-(4-chlorophenyl)diazenyl]naphthalen-2-ol: FT-IR (KBr, cm^{-1}): 3454, 1634, 1598, 1505, 1275, 1105. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.753 (1H, d, $J = 8.8$); 7.722 (1H, d, $J = 9.2$); 7.680 (1H, d, $J = 8.4$ Hz); 7.565 (1H, d, $J = 10$); 7.437-7.403 (2H, m); 7.374 (1H, t, $J = 8$); 7.322-7.243 (1H, m); 7.162-7.145(1H, m) 7.113-7.085(1H, dd, $J_{1/4}=2.4$) ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.414, 153.415, 145.696, 141.091, 135.687, 135.213, 134.615, 133.409, 130.575, 130.512, 130.357, 130.023, 129.847, 129.200, 128.954, 128.777, 128.240, 127.767, 126.896, 126.522, 126.358, 126.244, 125.534, 124.940, 123.605, 121.943, 117.846, 117.770, 116.950, 109.504.

3k. 2-chloro-4-[(*E*)-(4-nitrophenyl)diazenyl]phenol: FT-IR (KBr, cm^{-1}): 3479, 1637, 1389, 1268, 1111. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.422-8.356 (1H, m); 8.207-8.183 (1H, m); 8.091-7.982 (2H, m); 7.924-7.897 (1H, m); 7.560-7.185 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 154.868, 133.393, 132.496, 131.852, 131.293, 128.978, 128.941, 128.420, 126.364, 125.734, 124.894, 124.776, 123.347, 116.598, 113.407

3l. 2-hydroxy-5-[(*E*)-(4-nitrophenyl)diazenyl]benzaldehyde: FT-IR (KBr, cm_1): 3484, 1605, 1514, 1337, 1112. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 11.023 (1H, s); 9.907 (1H, s); 8.103 (1H, d, $J = 8$); 7.578-7.470 (3H, m); 7.264 (1H); 7.047-6.988 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.64, 163.34, 154.23, 148.23, 146.78, 137.03, 133.75, 130.11, 122.36, 119.87, 117.64

3m. 4-[(E)-(3-chloro-4-hydroxyphenyl)diazenyl]benzoic acid: FT-IR (KBr, cm^{-1}): 3477, 1593, 1383, 1261, 1126. ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm): 8.554 (1H, d, $J = 8$); 7.759 (1H, d, $J = 8$); 7.729 (1H, d, $J = 7.60$); 7.687 (1H, $J=9.2$); 7.591 (1H, d, $J = 8$); 7.561-7.108 (2H,m) ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 172.36, 153.83, 144.60, 140.29, 134.68, 133.61, 130.08, 129.76, 129.63, 129.31, 128.93, 128.80, 128.67, 128.06, 127.76, 127.42, 126.43, 126.35, 125.78, 125.24, 124.92, 123.44, 121.74, 118.66, 118.54, 118.00, 115.19, 109.47

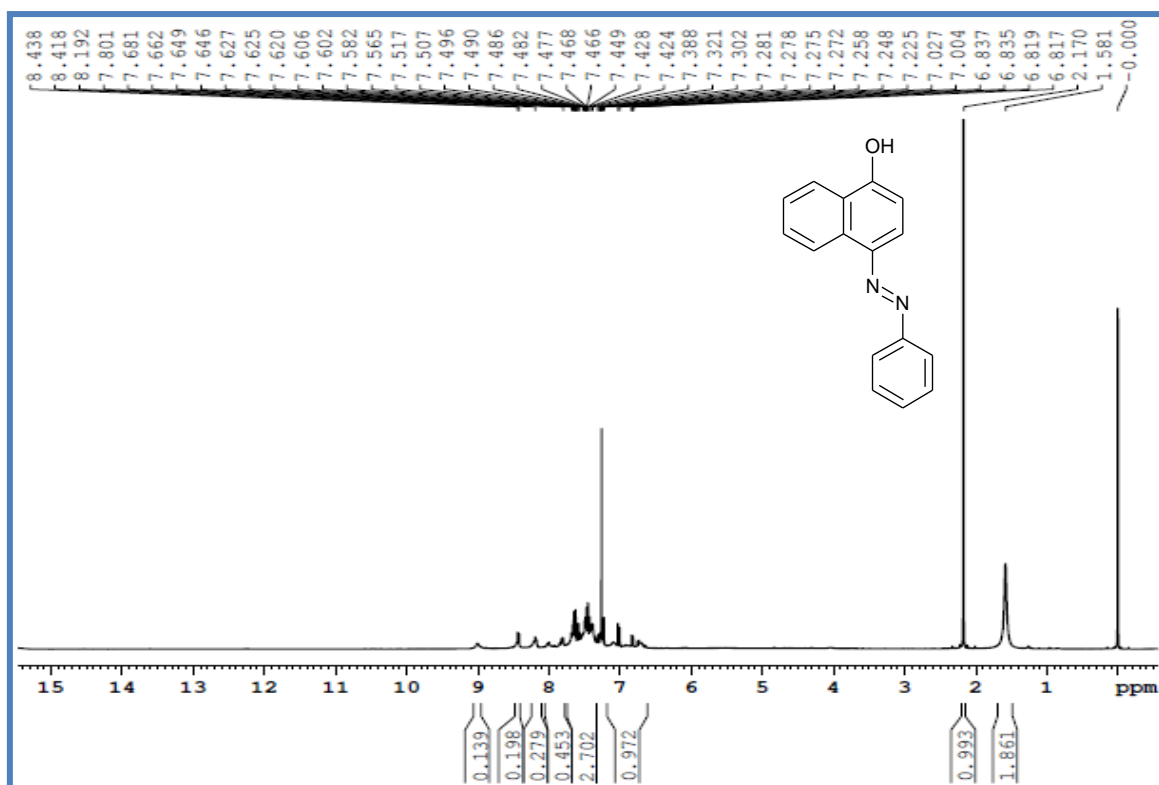


Figure S1 : ^1H NMR spectrum of the compound 3a

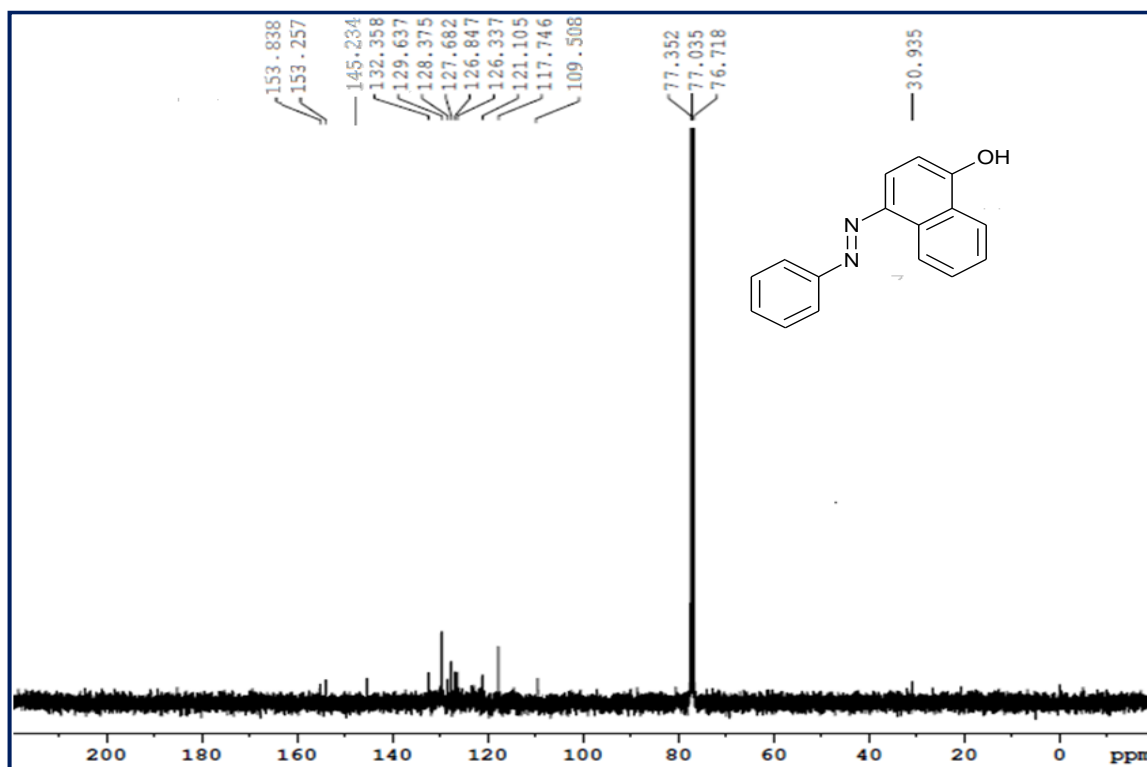


Figure S2: ^{13}C NMR spectrum of the compound 3a

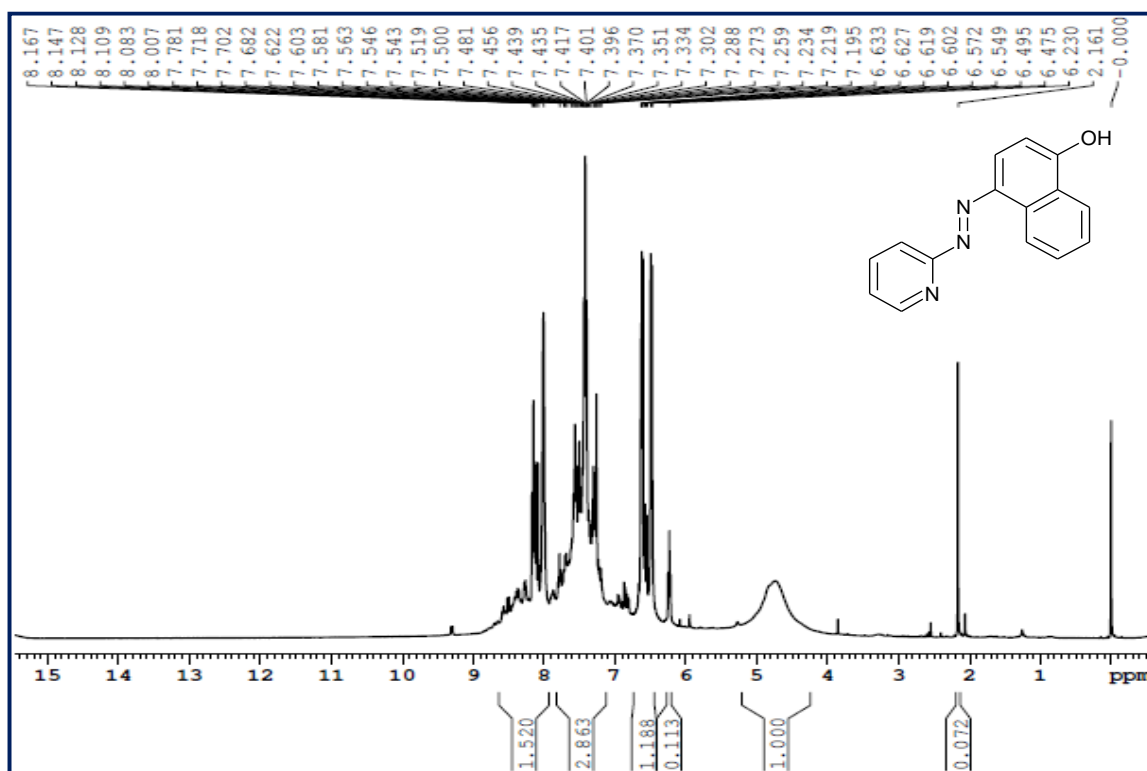


Figure S3: ¹H NMR spectrum of the compound 3b

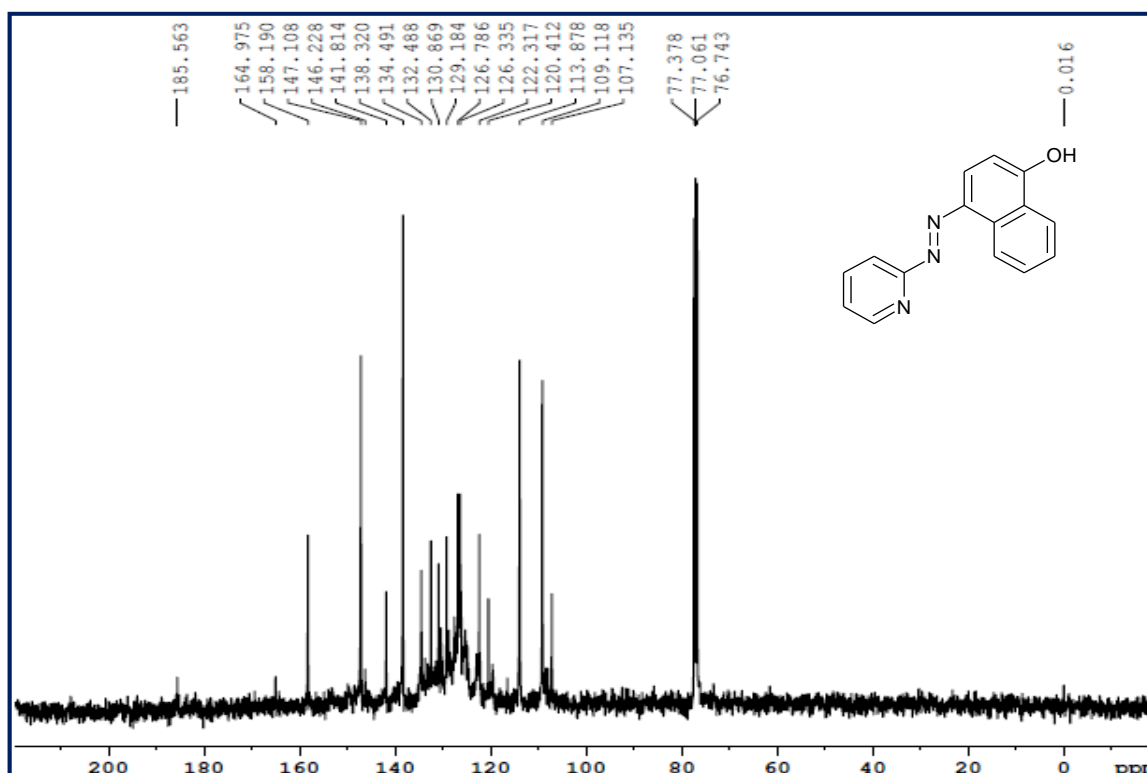


Figure S4: ¹³C NMR spectrum of the compound 3b

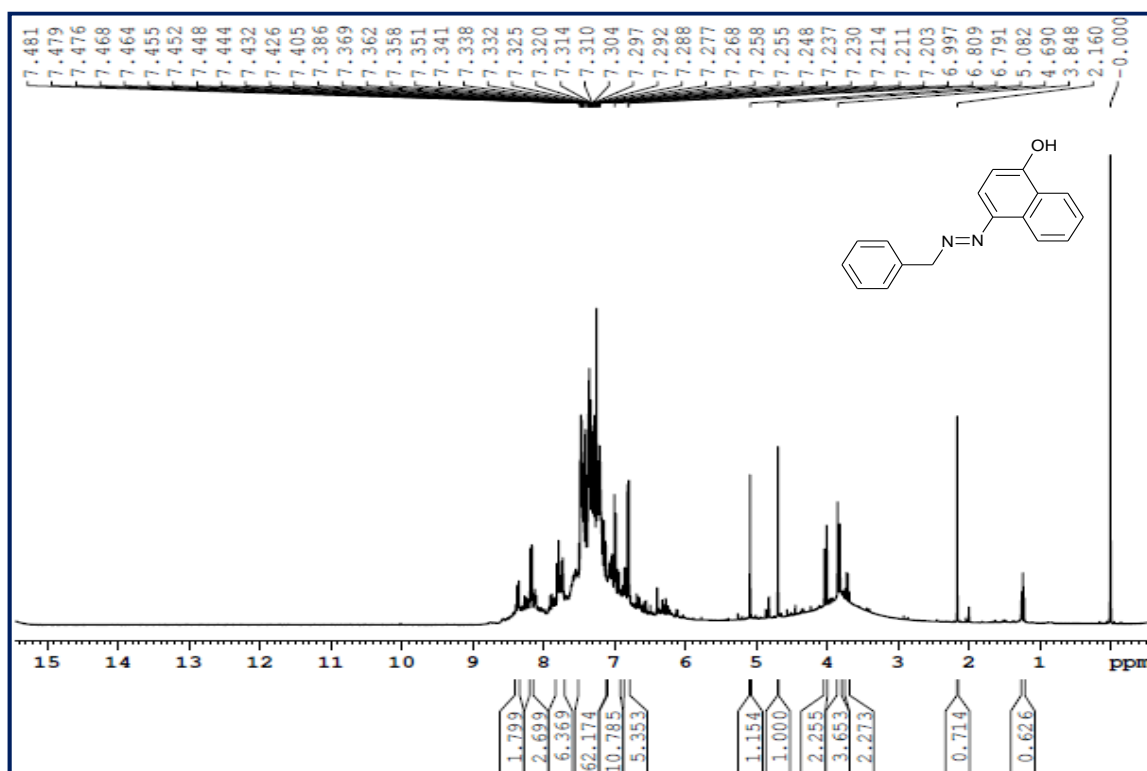


Figure S5: ^1H NMR spectrum of the compound 3c

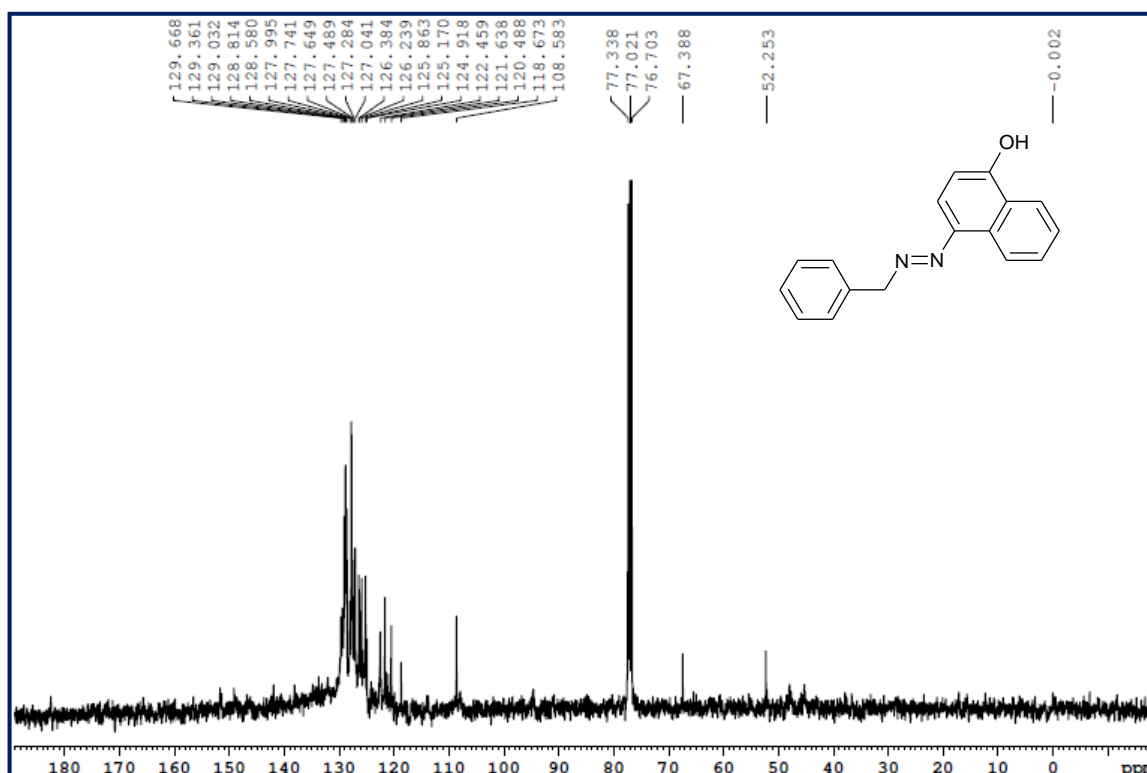


Figure S6: ^{13}C NMR spectrum of the compound 3c

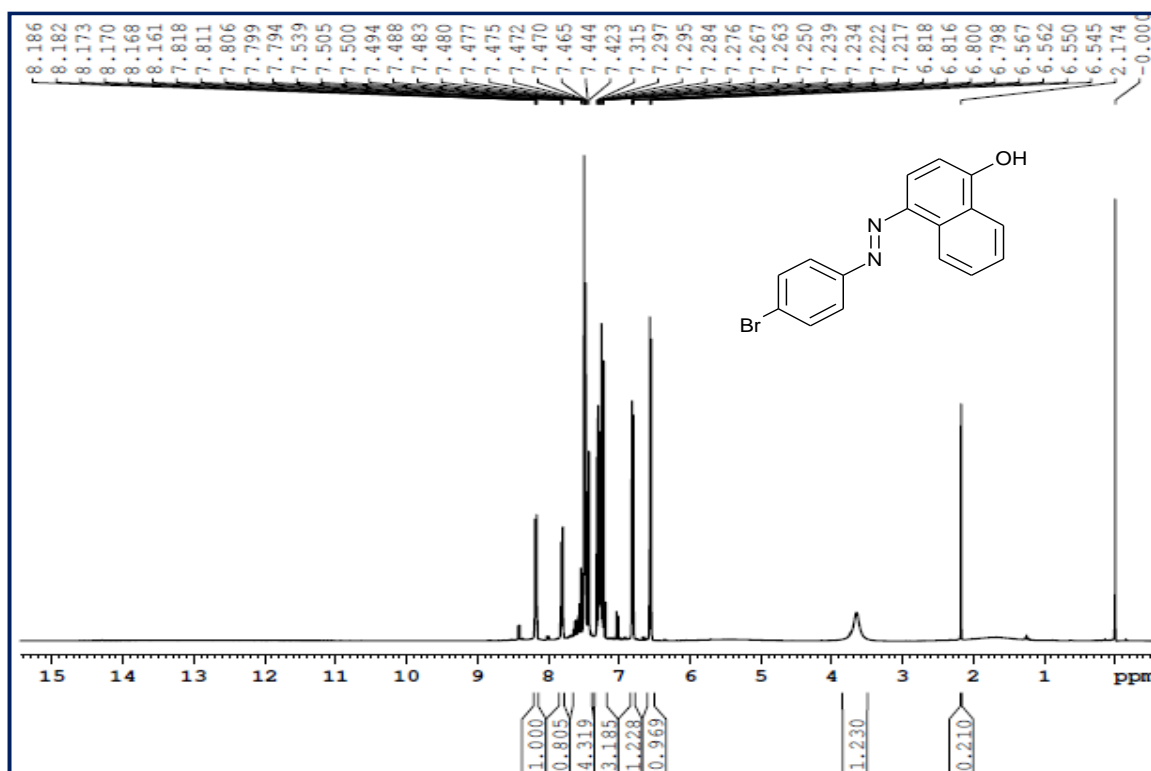


Figure S7: ¹H NMR spectrum of the compound 3d

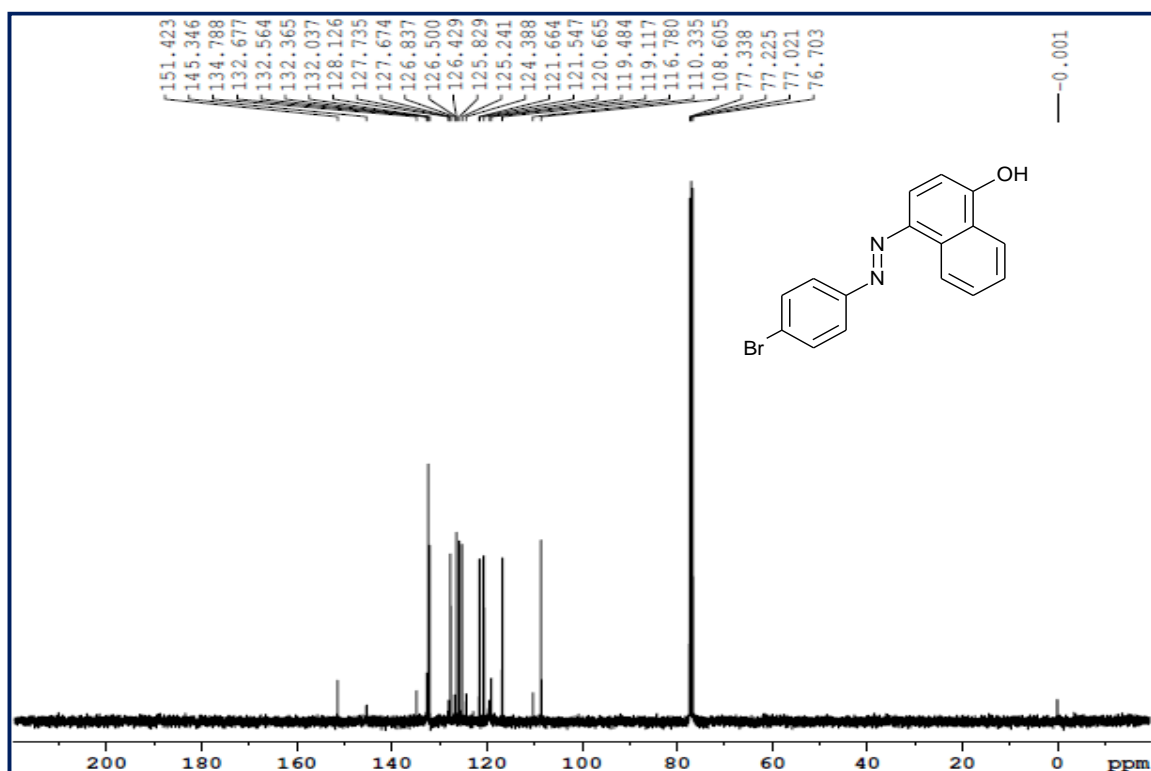


Figure S8: ¹³C NMR spectrum of the compound 3d

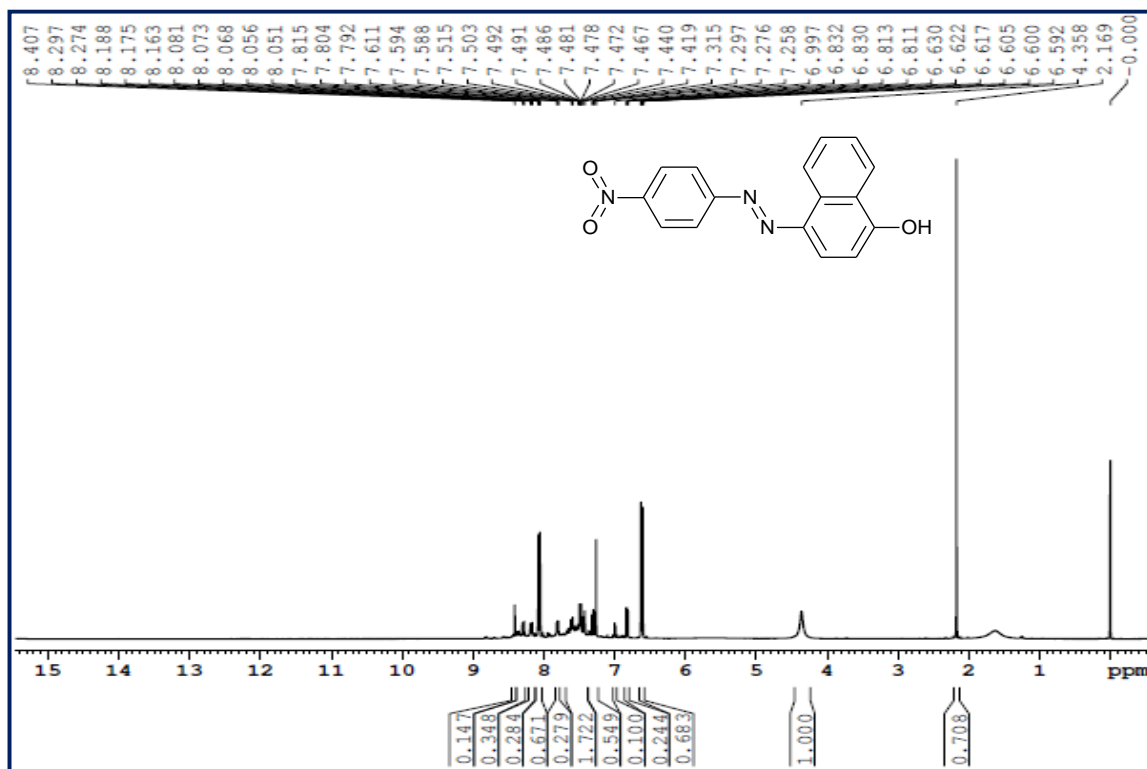


Figure S9: ^1H NMR spectrum of the compound 3e

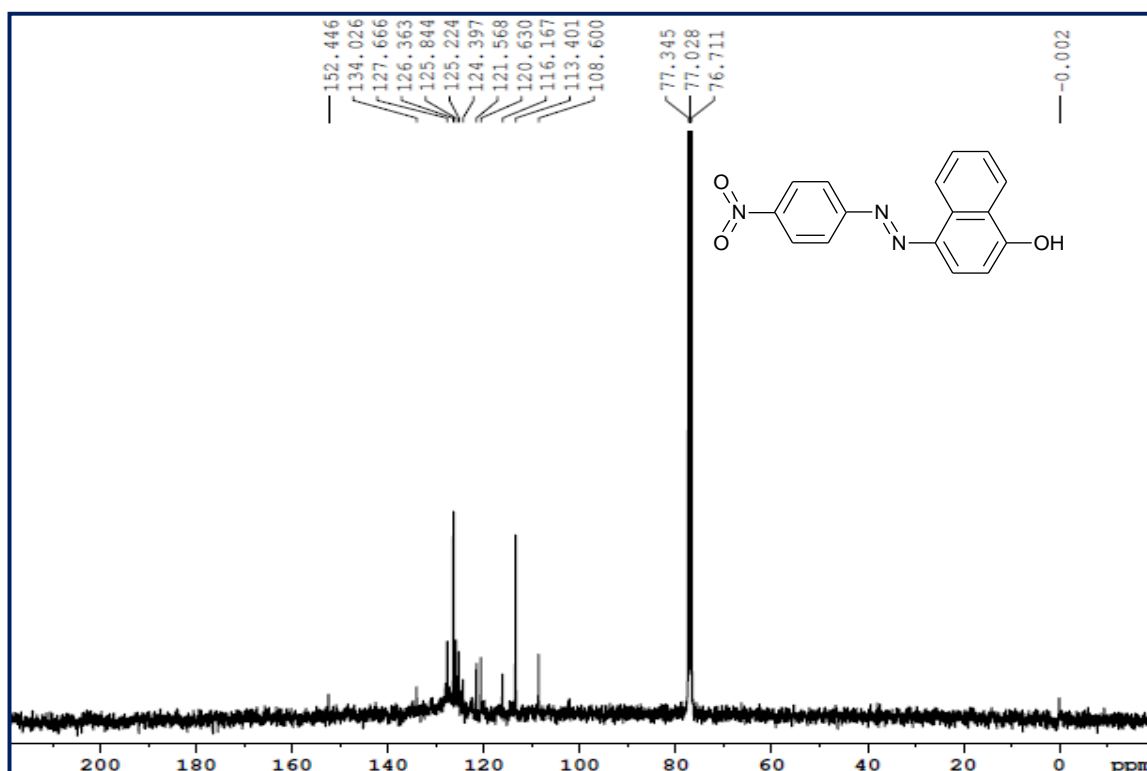


Figure S10: ^{13}C NMR spectrum of the compound 3e

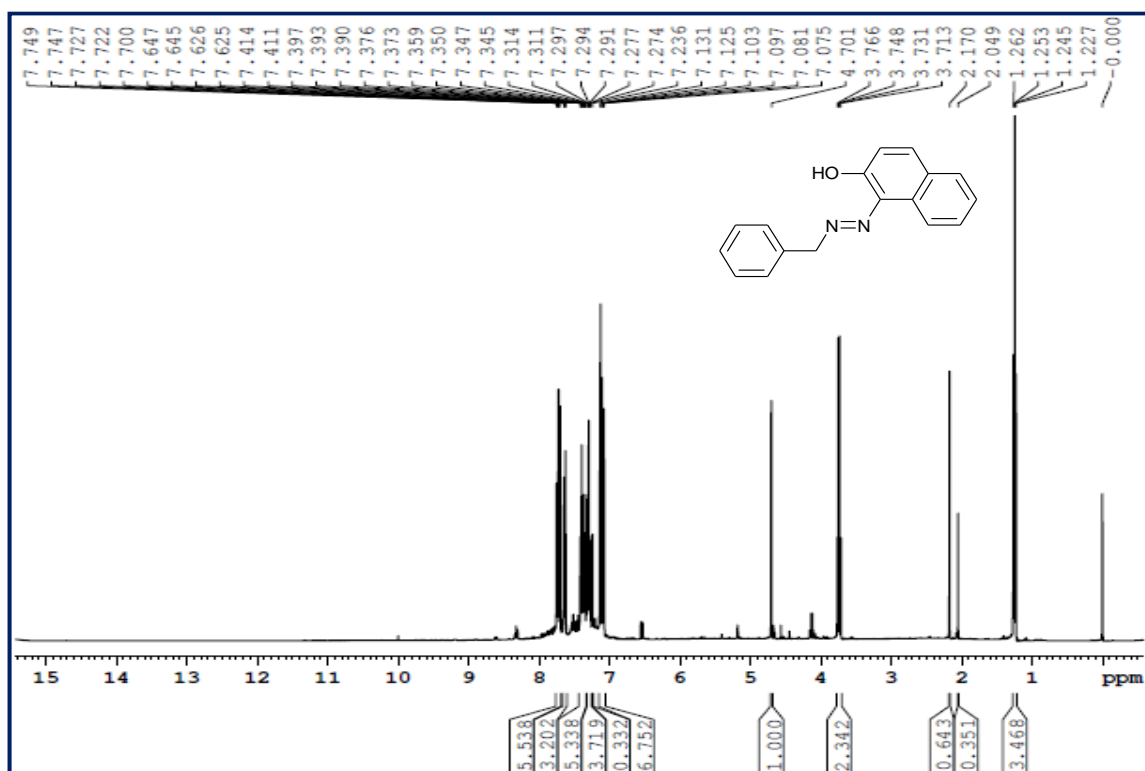


Figure S11: ¹H NMR spectrum of the compound 3f

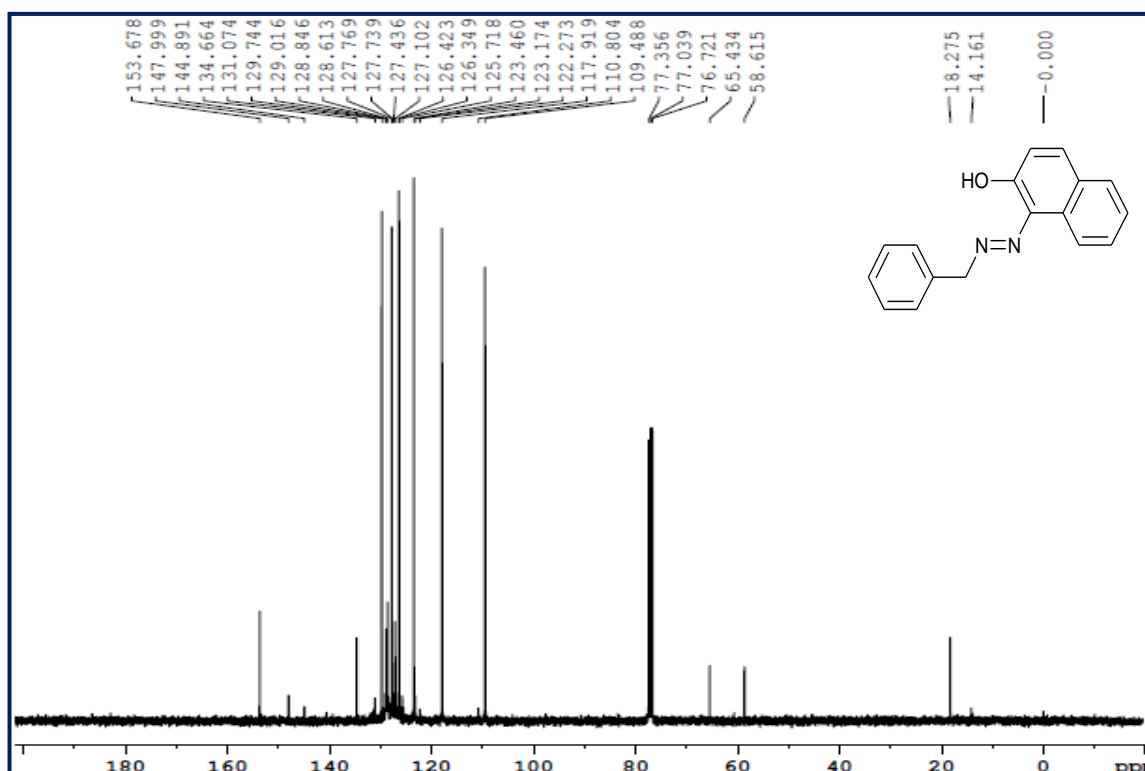


Figure S12: ¹³C NMR spectrum of the compound 3f

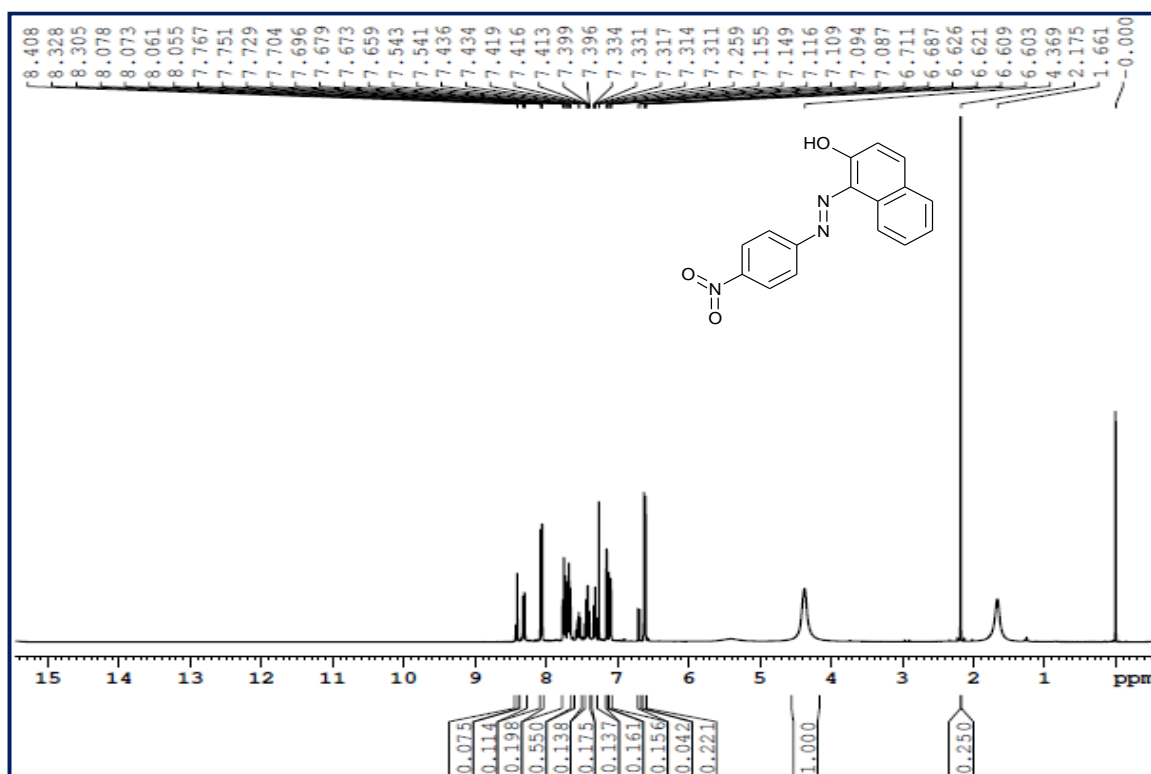


Figure S13: ^1H NMR spectrum of the compound 3g

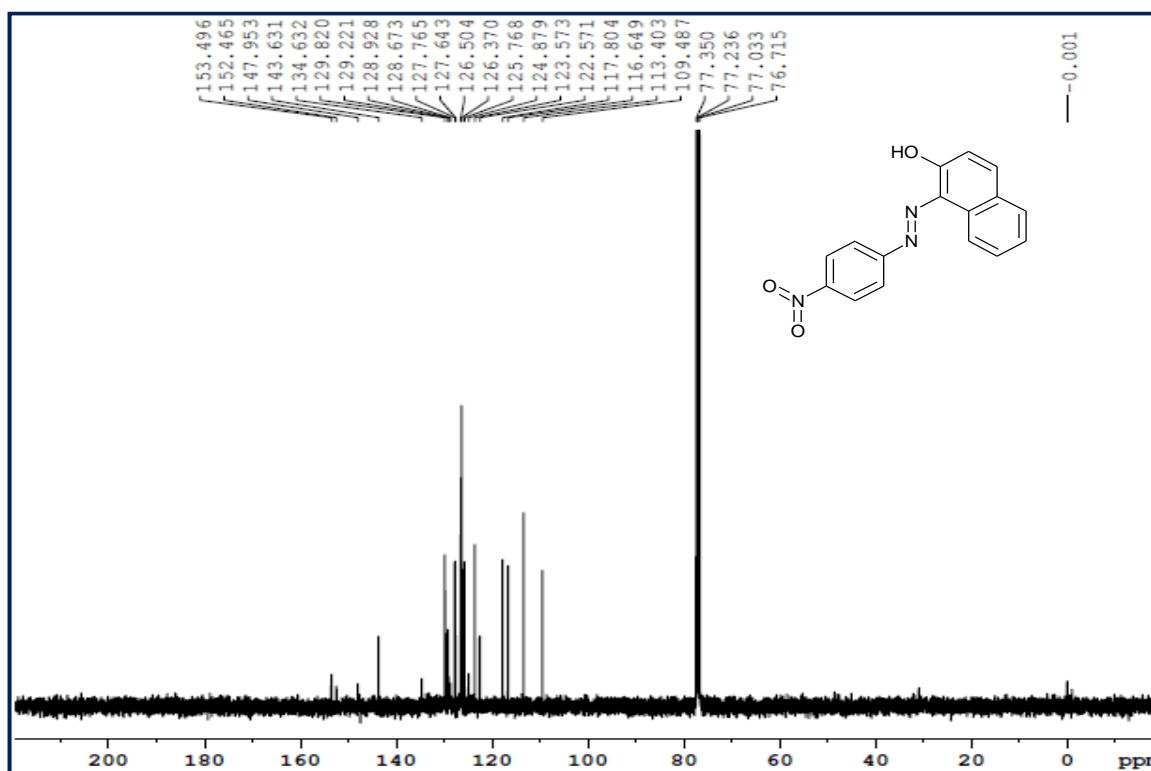


Figure S14: ^{13}C NMR spectrum of the compound 3g

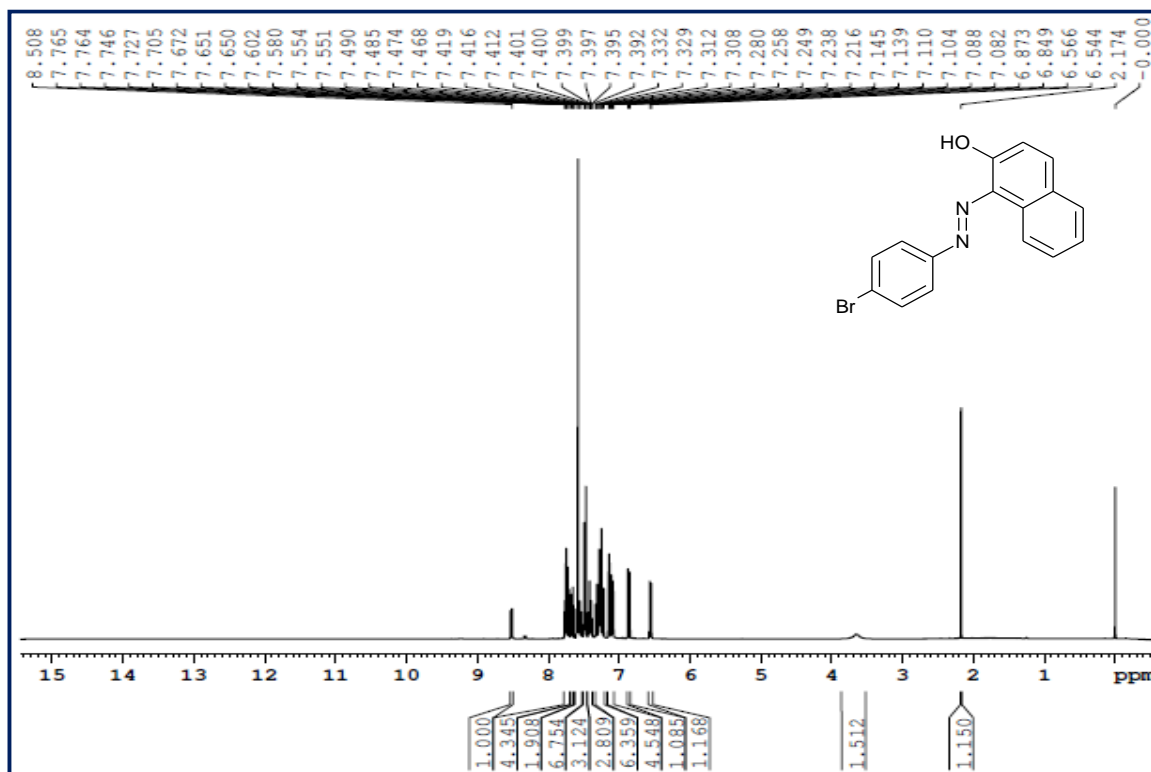


Figure S15: ^1H NMR spectrum of the compound 3h

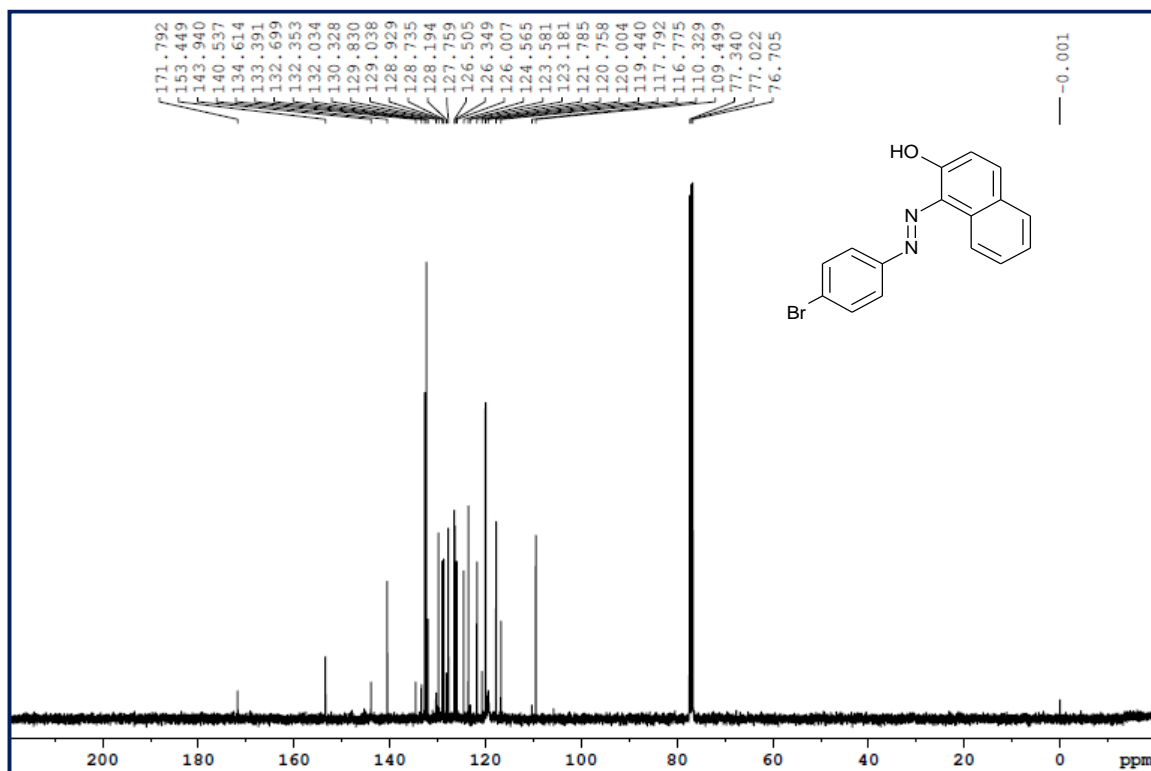


Figure S16: ^{13}C NMR spectrum of the compound 3h

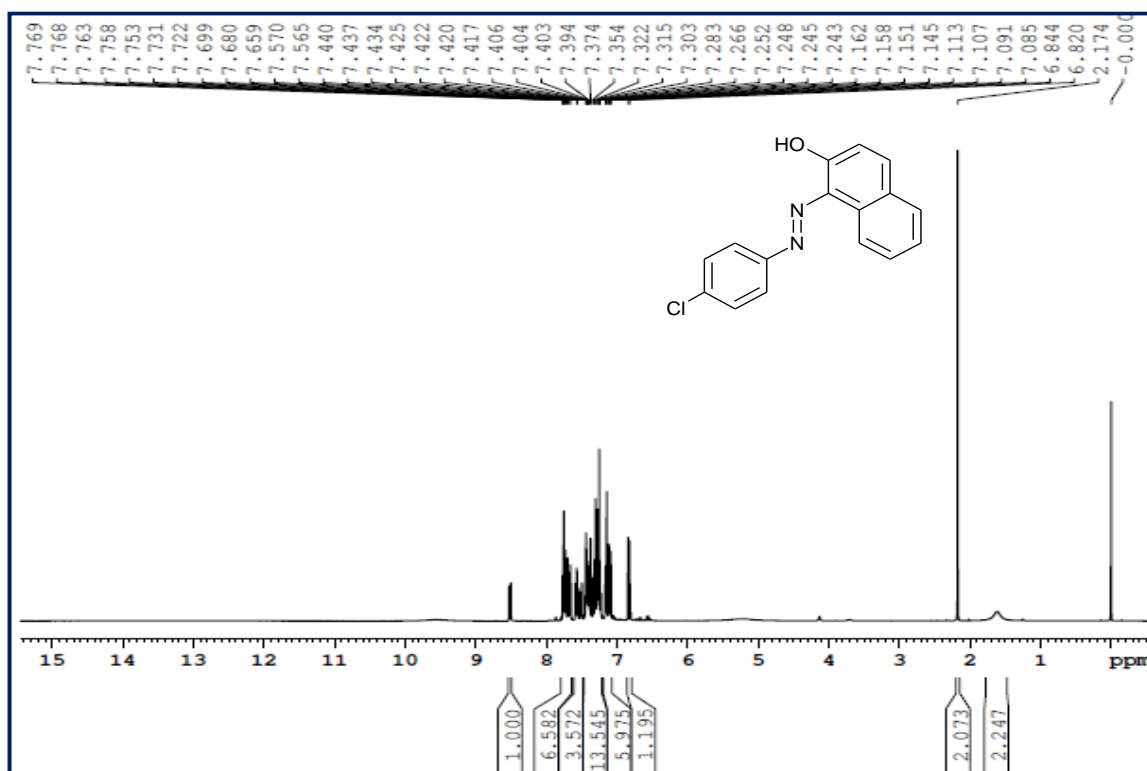


Figure S17: ^1H NMR spectrum of the compound 3i

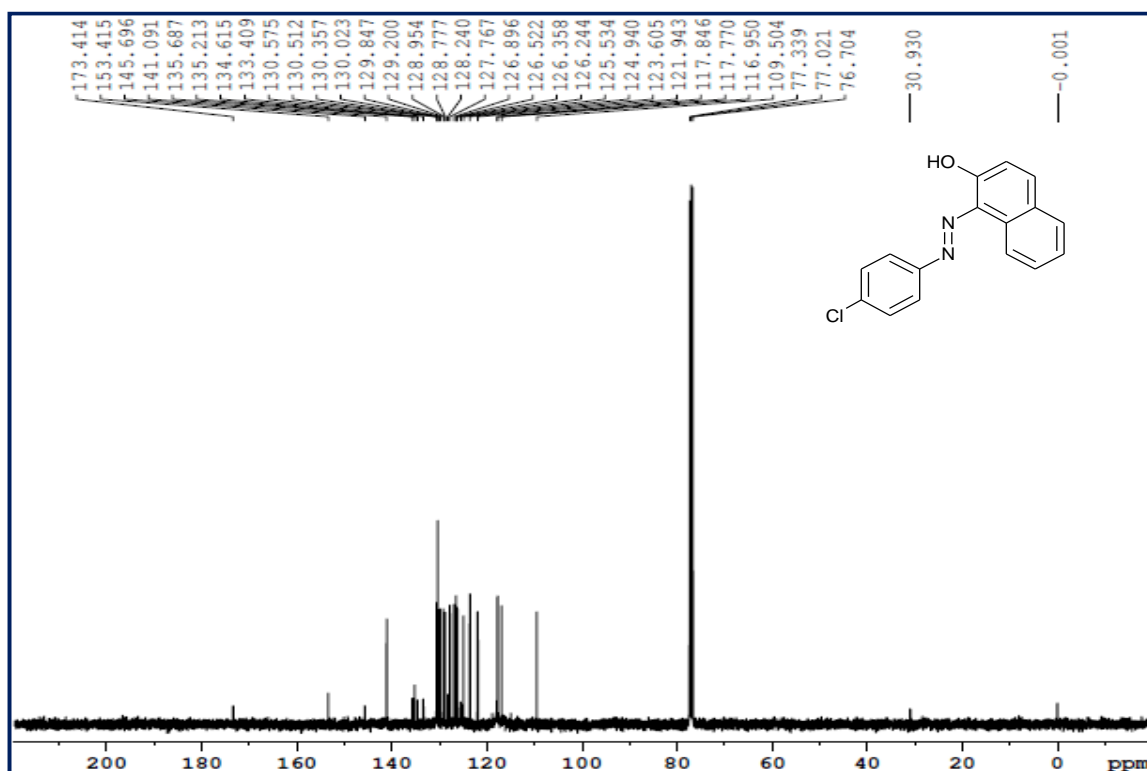


Figure S18: ^{13}C NMR spectrum of the compound 3i

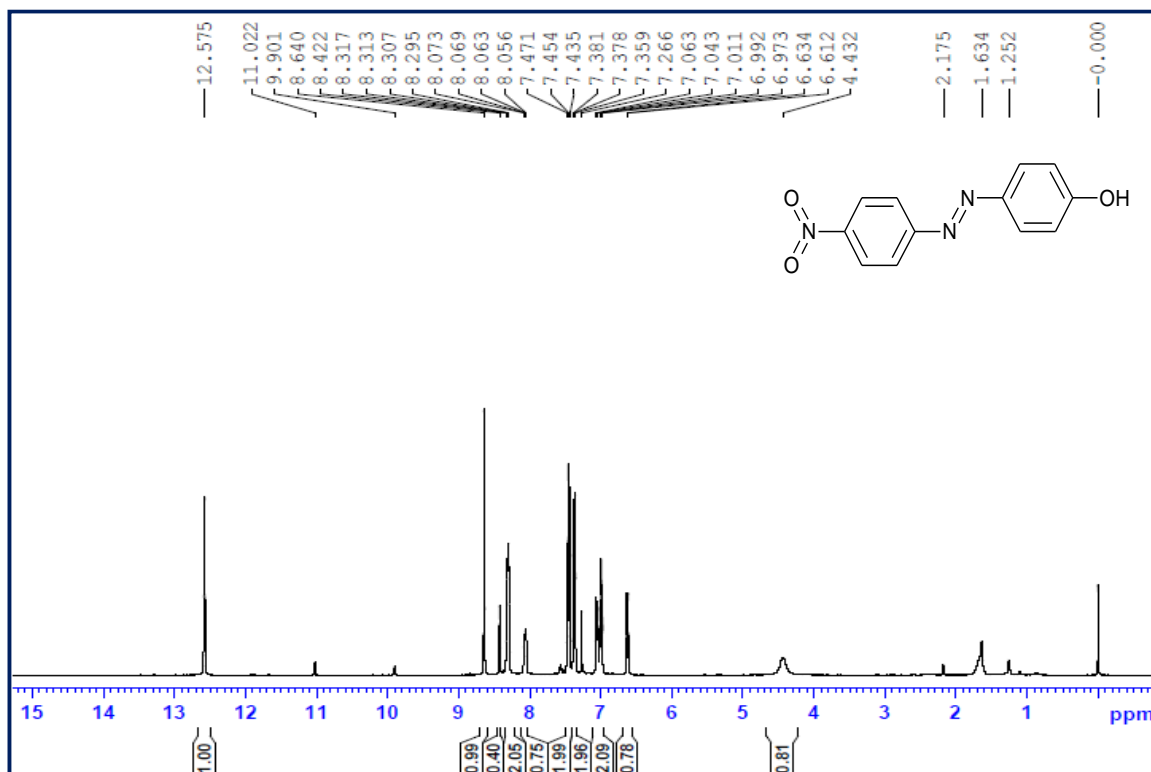


Figure S19: ¹H NMR spectrum of the compound 3j

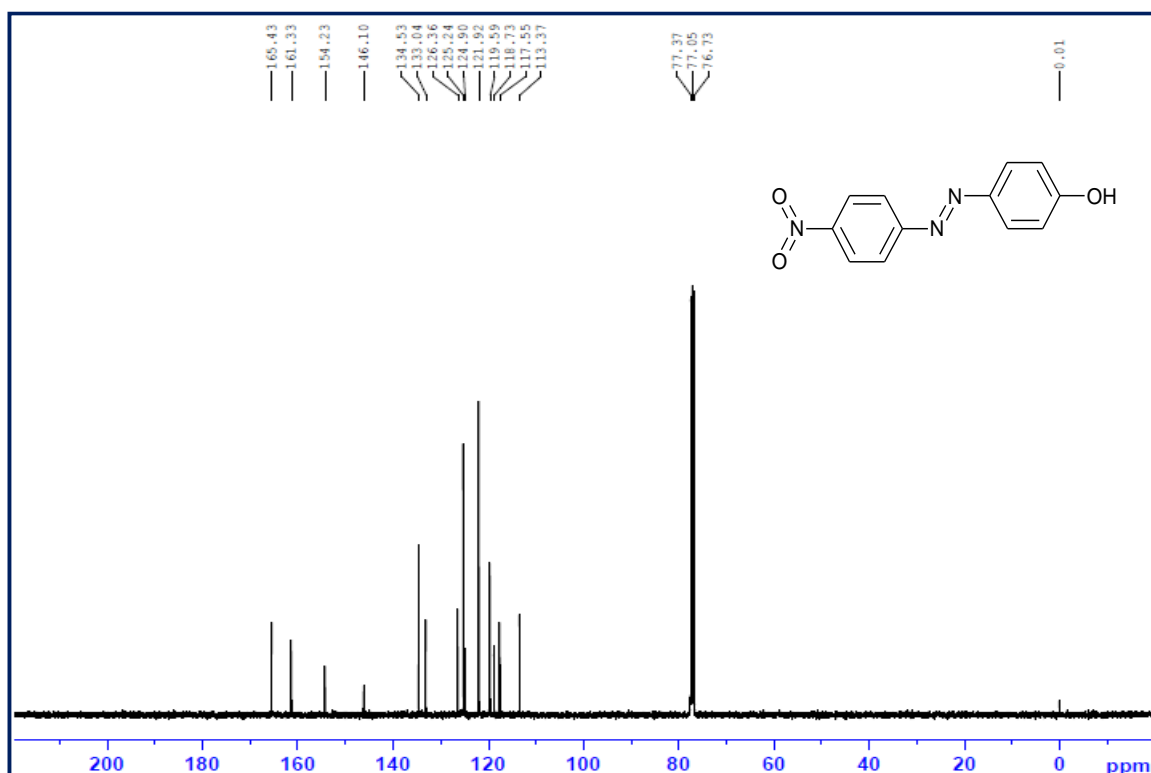


Figure S20: ¹³C NMR spectrum of the compound 3j

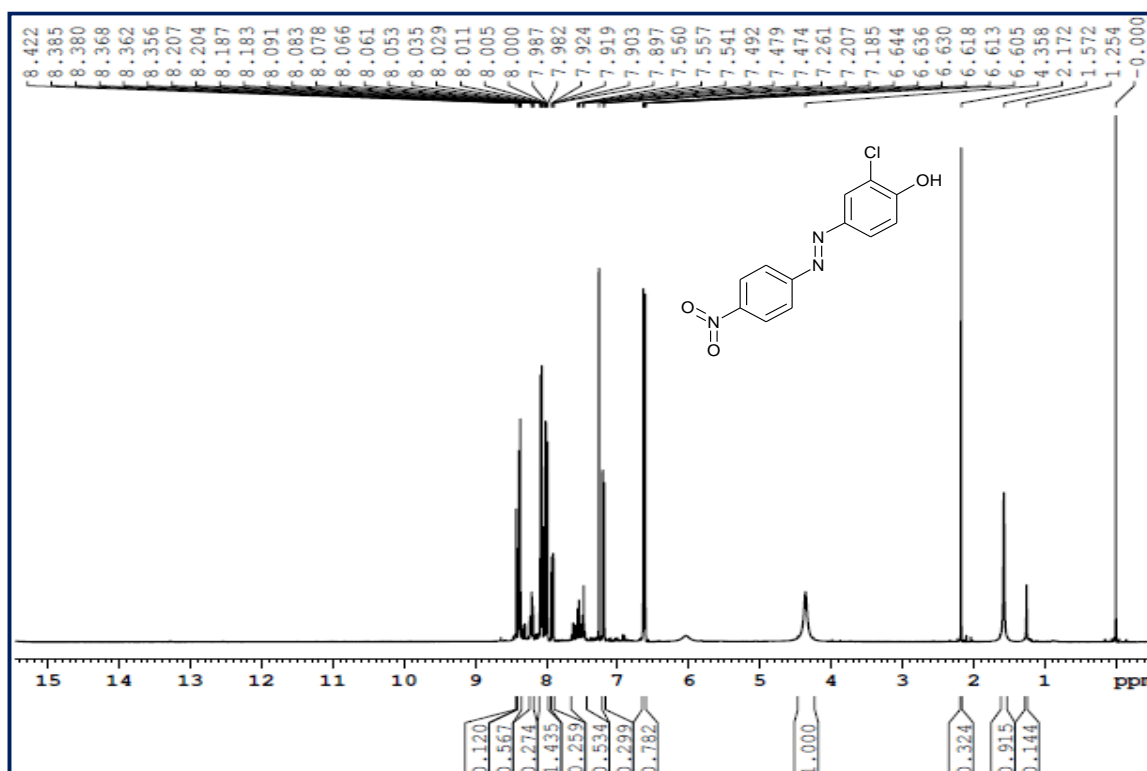


Figure S21: ^1H NMR spectrum of the compound 3k

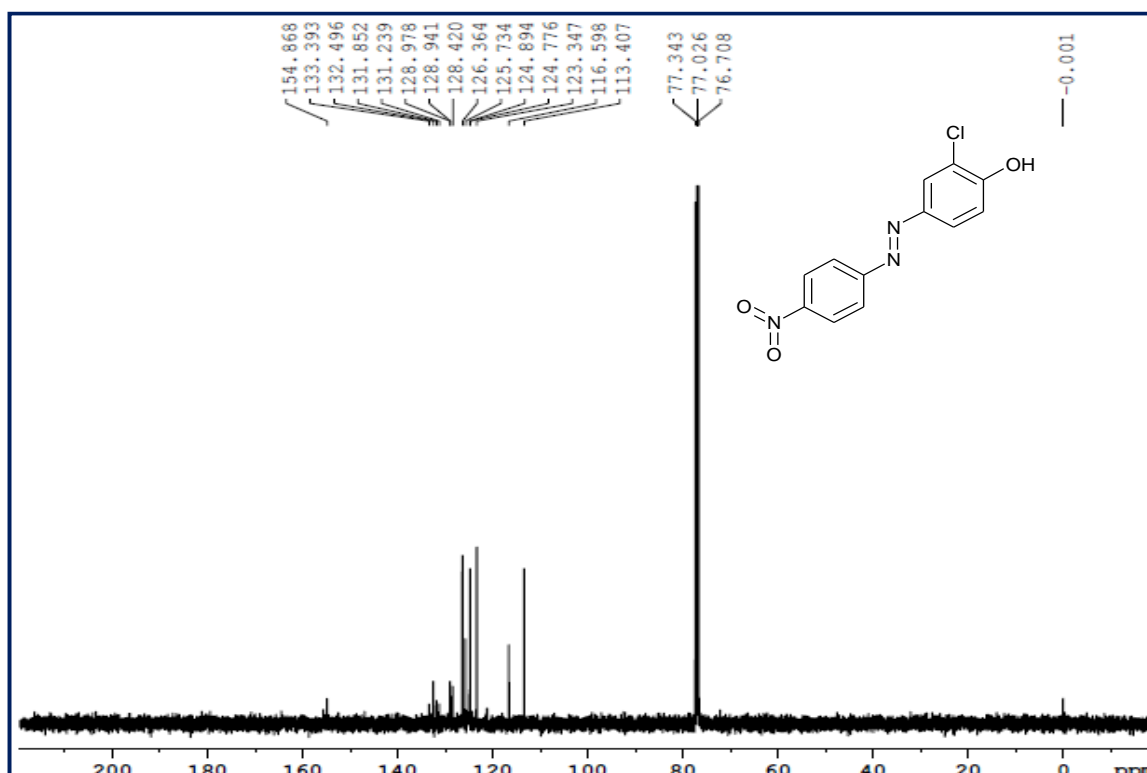


Figure S22: ^{13}C NMR spectrum of the compound 3k

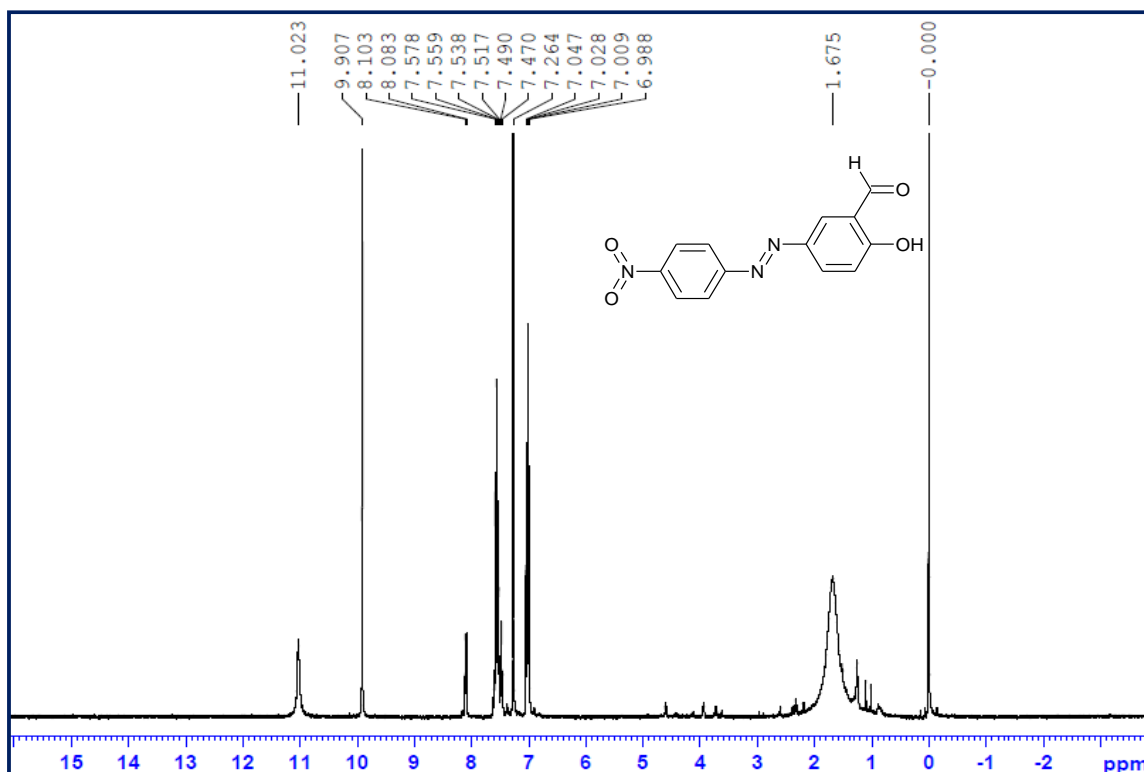


Figure S23: ^1H NMR spectrum of the compound 3l

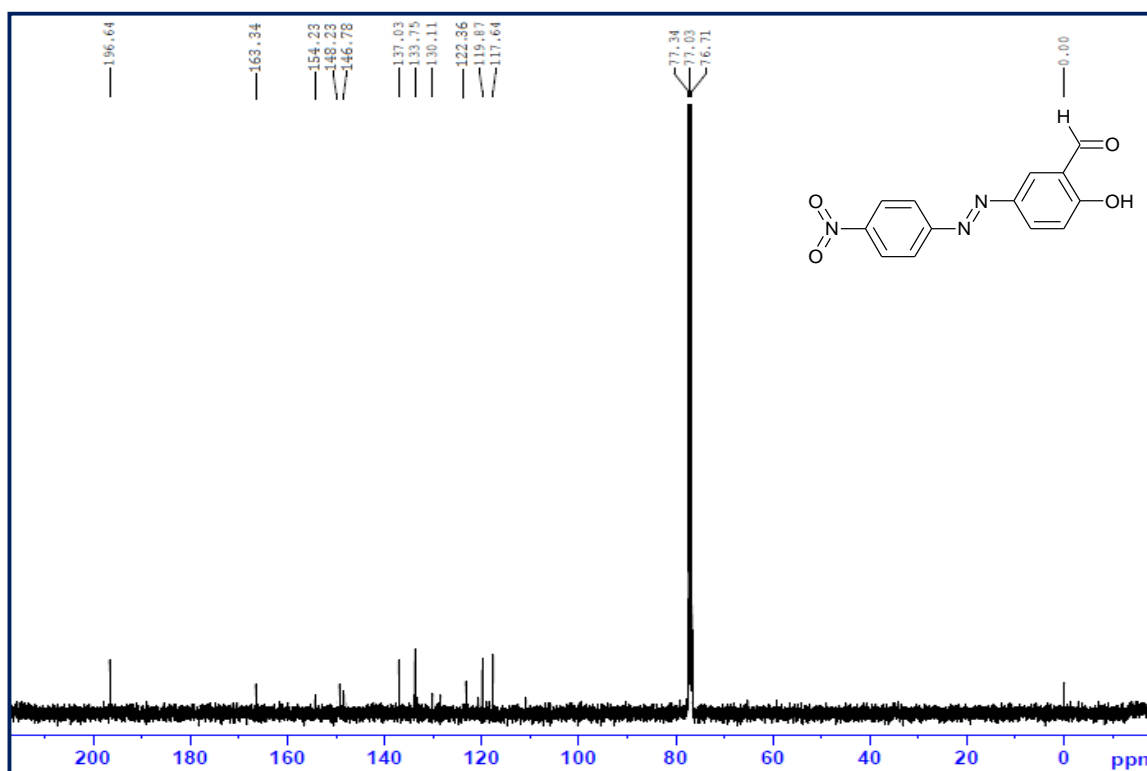


Figure S24: ^{13}C NMR spectrum of the compound 3l

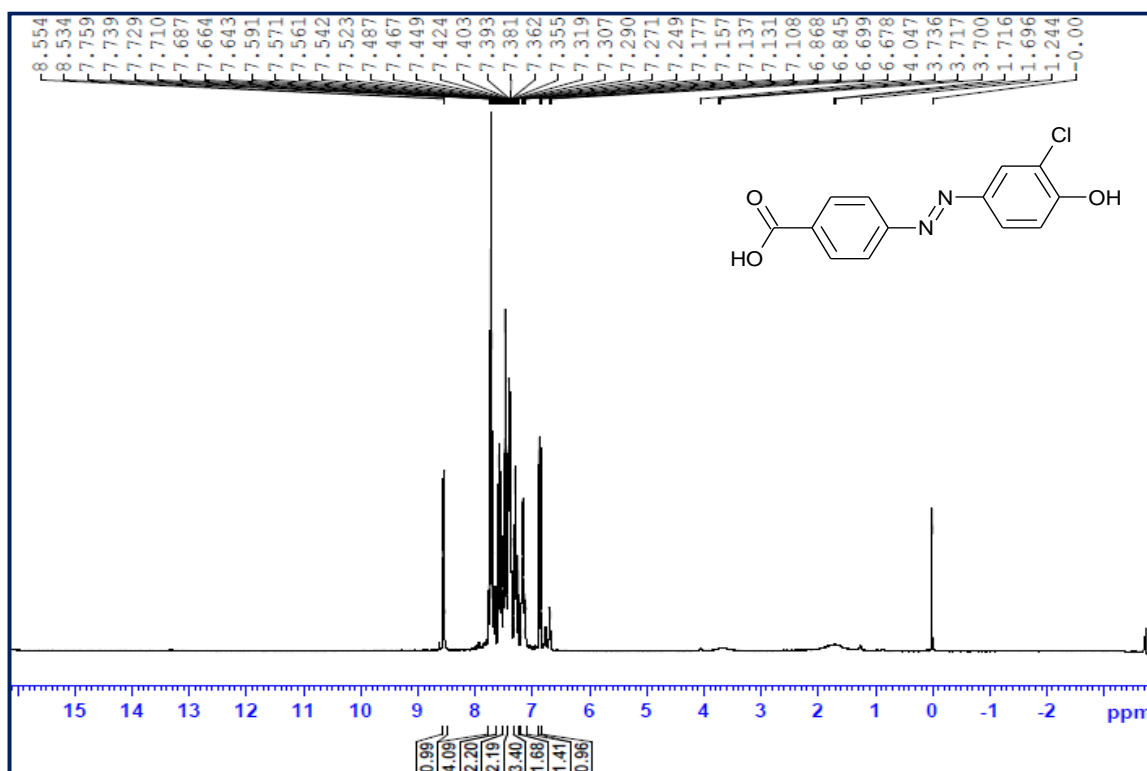


Figure S25: ¹H NMR spectrum of the compound 3m

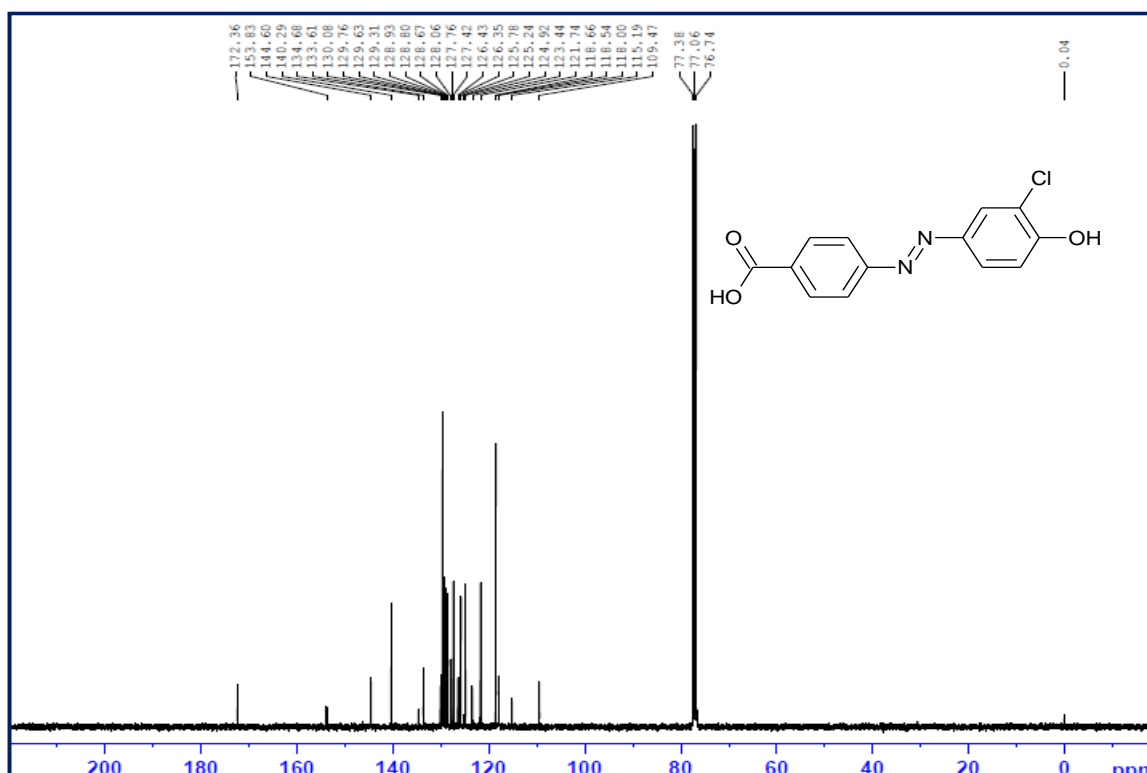


Figure S26: ¹³C NMR spectrum of the compound 3m

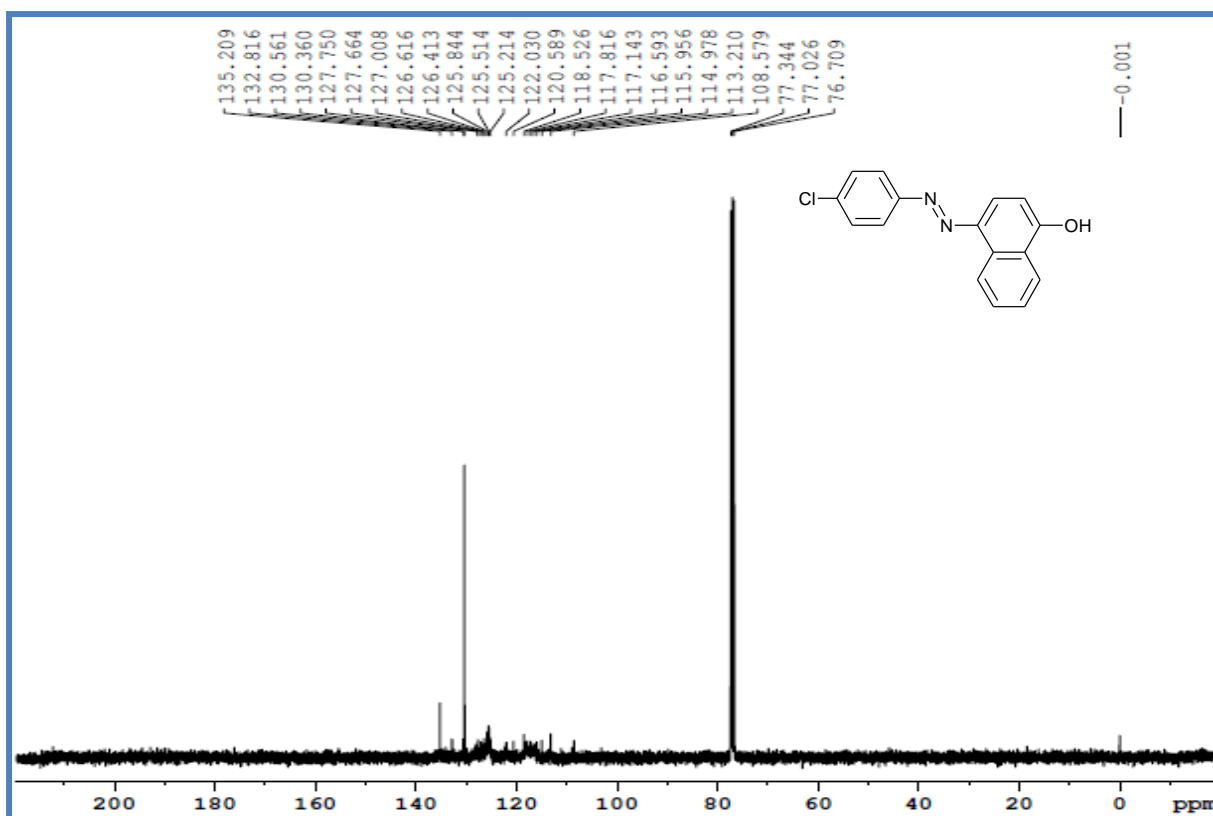


Figure S27: ^{13}C NMR spectrum of the compound 3n

- [1] L. Parashuram, S. Sreenivasa, S. Akshatha, V. U. Kumar, S. Kumar, *Asian J. Org. Chem.* **2017**, *6*, 1755–1759.
- [2] D. Fărcașiu, J. Q. Li, *Appl. Catal. A, Gen.* **1995**, *128*, 97–105.