Supporting Information for

Selective synthesis of *N*-arylbenzene-1,2-diamines or 1-arylbenzimidazoles by irradiating 4-methoxy-4'-substituted-azobenzenes in different solvents

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Methods and Reagents

The photochemical reactor was from Rayonet with 16 monochromatic light tubes of 365 nm or 419 nm, equipping a merry-go-round type tube holder in the center. The average temperature inside the photochemical reactor during operation is about 35~40 ^{o}C. The quartz tubes of photolysis were 1.3 cm in diameter and 20 cm in length. NMR spectra were measured on a Bruker AM300 WB FT-NMR (300 MHz). Tetramethylsilane (TMS) was used as the standard for ^{1}H-NMR (0 ppm) and chloroform-d1 was for ^{13}C-NMR (77.0 ppm). Mass spectra were recorded on a Finnigan MAT TSCE-46C Mass spectrometer. Column chromatography used silica gel with 60-120 mesh. All solvent and commercial reagents used as received without further purification. The preparation of different concentration of HCl solutions was by a simple dilution of concentrated aqueous hydrochloride (12 M) with solvents.

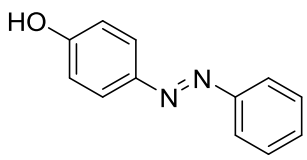
Synthesis of (E)-4-(phenyldiazenyl)phenol derivatives.

General procedure:

10 mmol of aniline was added to an aqueous solution (20 mL) containing 5 ml of 37 % $HCl_{(aq)}$ to prepare an Aniline solution, which was added dropwisely into another aqueous solution (5mL) containing 12.8 mmole $NaNO_2$ under ice water bath (0 ^{o}C) with strong stirring for about 6 minutes. After mixing, the resulting solution was stirred for 40 minutes at 0 ^{o}C to form a diazo salt solution. Then a separated aqueous phenol solution (20 mL) containing 10 mmol of phenol and 4 g of NaOH was prepared, and the diazo salt solution was added to the phenol solution slowly under ice water bath. The color of the solution would become dark during this process. After stirring at 0 ^{o}C for 1 hour, the resulting solution was acidified by adding 20 % $HCl_{(aq)}$ solution. Afterwards, the resulting solution was filtered by suction filtration to collect the dark solid which was washed by water, dissolved in acetone and reprecipitated by adding water slowly. Filtered the solution by suction filtration, and the brown powders were obtained as product with about 90 % yield.

Spectral data:

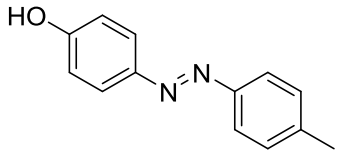
(*E*)-4-(phenyldiazenyl)phenol (**1a**):



Yield = 98 %. m.p.: 148–151 ^{o}C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.87 (m, 4H), 7.4 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.5, 152.7, 147.1, 130.4, 129.1, 125.0,

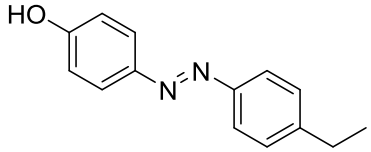
122.6, 115.9; EI-MS (70eV) *m/z* (relative intensity) 198 (M^+, 10), 144 (15), 122 (50), 93 (13), 78 (100); HRMS. calcd for $C_{12}H_{10}N_2O$: *m/z* 198.0793. Found: *m/z* 198.0792.

(*E*)-4-(p-tolyldiazenyl)phenol (**1b**):



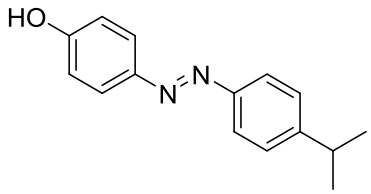
Yield = 96.8 %. m.p.: 135–138 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 150.7, 147.0, 140.9, 129.7, 124.8, 122.5, 115.8, 21.4; EI-MS (70eV) *m/z* (relative intensity) 212 (M^+, 100), 121 (25), 93 (67), 91 (45); HRMS. calcd for $C_{13}H_{12}N_2O$: *m/z* 212.0950.

(*E*)-4-((4-ethylphenyl)diazenyl)phenol (**1c**):



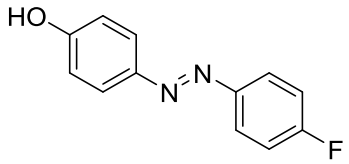
Yield = 97.3 %. m.p.: 71–73 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.83 (d, *J* = 8.65 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.68 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.2, 150.9, 147.2, 147.1, 128.5, 124.8, 122.8, 122.6, 115.8, 28.8, 15.4; EI-MS (70eV) *m/z* (relative intensity) 226 (M^+, 98), 178 (11), 121 (50), 105 (84), 93 (100); HRMS. calcd for $C_{14}H_{14}N_2O$: *m/z* 226.1106. Found: *m/z* 226.1092.

(*E*)-4-((4-isopropylphenyl)diazenyl)phenol (**1d**):



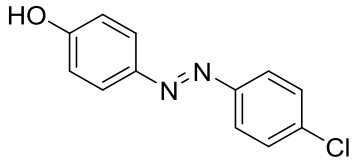
Yield = 94.8 %. m.p.: 71–72 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 2.70 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 151.8, 151.0, 147.0, 127.1, 124.8, 122.6, 115.8, 34.1, 23.8, 23.8; EI-MS (70eV) *m/z* (relative intensity) 240 (M^+, 46), 119 (72), 93 (100), 91 (48); HRMS. calcd for $C_{15}H_{16}N_2O$: *m/z* 240.1263. Found: *m/z* 240.1255.

(*E*)-4-((4-fluorophenyl)diazenyl)phenol (**1e**):



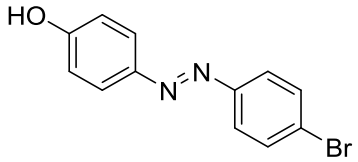
Yield = 95.9 %. m.p.: 145–147 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.88 - 7.82 (m, 4H), 7.18 - 7.13 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 164.0 (d, *J* = 249.53 Hz), 158.4, 149.2 (d, *J* = 22.5 Hz), 115.8; EI-MS (70eV) *m/z* (relative intensity) 217 (M+1, 14), 216 (M^+, 100), 121 (56), 111 (21), 93 (91), 65 (40); HRMS. calcd for $C_{12}H_9FN_2O$: *m/z* 216.0699. Found: *m/z* 216.0705.

(*E*)-4-((4-chlorophenyl)diazenyl)phenol (**1f**):



Yield = 98.4 %. m.p.: 150–152 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.5, 151.0, 147.0, 136.2, 129.3, 125.1, 123.8, 115.9; EI-MS (70eV) *m/z* (relative intensity) 234 (M+2, 23), 232 (M^+, 100), 121 (44), 111 (36), 93 (62), 65 (8); HRMS. calcd for $C_{12}H_9ClN_2O$: *m/z* 232.0403. Found: *m/z* 232.0406.

(*E*)-4-((4-bromophenyl)diazenyl)phenol (**1g**):



Yield = 99.4 %. m.p.: 154–155 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.73 (d, *J* = 8.76 Hz, 2H), 7.60 (d, *J* = 8.76 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.6, 151.4, 147.0, 134.0, 132.2, 125.1, 124.2, 115.9; EI-MS (70eV) *m/z* (relative intensity) 278 (M+2, 96), 276 (M^+, 100), 157 (27), 155 (28), 121 (53), 93 (30); HRMS. calcd for $C_{12}H_9BrN_2O$: *m/z* 275.9898. Found: *m/z* 275.9911.

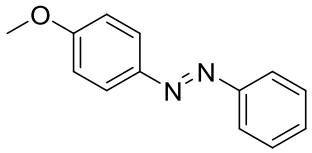
Synthesis of (E)-1-(4-methoxyphenyl)-2-phenyldiazene derivatives.

General procedure:

1 mmol of (*E*)-4-(phenyldiazenyl)phenol **(1a)** was dissolved in 15 mL of acetone, and then 1.6 mmol of K_2CO_3 was added into the reaction. After the solution stirring for a while (at least 1 minute), 1 mmol of dimethyl sulfate was added dropwisely. The reaction was stirred and refluxed for 12 hours and then cooled down to room temperature. Afterwards, poured the reaction solution into 50 mL of water, and the product was precipitated and filtered by suction filtration with about 90 % yield.

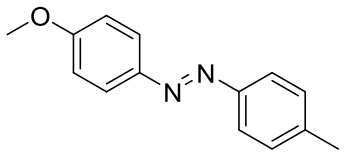
Spectral data:

(*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**2a**):



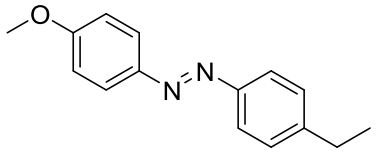
Yield = 93 %. m.p.: 49-50 ^{o}C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.49 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.0, 152.7, 147.0, 130.3, 129.0, 124.7, 122.5, 114.2, 55.5.

(*E*)-1-(4-methoxyphenyl)-2-(p-tolyl)diazene (**2b**):



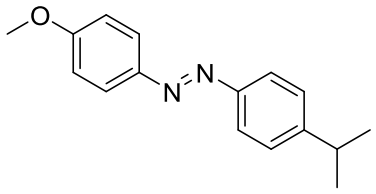
Yield = 90.8 %. m.p.: 100-102 ^{o}C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.8, 150.8, 147.0, 140.7, 129.6, 124.5, 122.5, 114.1, 55.5, 21.4; EI-MS (70eV) *m/z* (relative intensity) 226 (M^+, 92), 135 (47), 107 (100), 91 (77); HRMS. calcd for $C_{14}H_{14}N_2O$: *m/z* 226.1106. Found: *m/z* 226.1112.

(*E*)-1-(4-ethylphenyl)-2-(4-methoxyphenyl)diazene (**2c**):



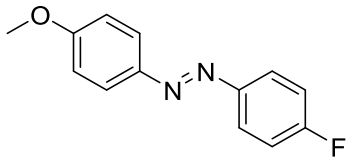
Yield = 89.3 %. m.p.: 73-74 ^{o}C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.8, 151.1, 147.1, 147.1, 128.5, 124.6, 122.6, 114.2, 55.5, 28.8, 15.4; EI-MS (70eV) *m/z* (relative intensity) 240 (M^+, 81), 144 (44), 135 (50), 116 (78), 107 (100), 105 (52), 77 (51); HRMS. calcd for $C_{15}H_{16}N_2O$: *m/z* 240.1263; Found: *m/z* 240.1263.

(*E*)-1-(4-isopropylphenyl)-2-(4-methoxyphenyl)diazene (**2d**):



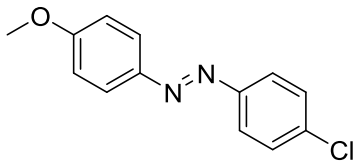
Yield = 91.6 %. m.p.: 92-94 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.89 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 2.97 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.8, 151.6, 151.1, 147.1, 127.0, 124.5, 122.6, 114.2, 55.5, 34.1, 23.9; EI-MS (70eV) *m/z* (relative intensity) 254 (M^+, 76), 206 (20), 158 (33), 135 (56), 119 (45), 115 (59), 107 (100), 91 (26), 77 (35); HRMS. calcd for $C_{16}H_{18}N_2O$: *m/z* 254.1419; Found: *m/z* 254.1374.

(*E*)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)diazene (**2e**):



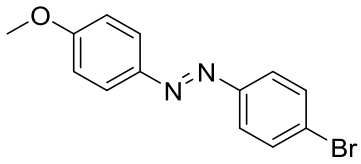
Yield = 89.4 %. m.p.: 82-84 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.87 (m, 4H), 7.16 (t, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.0, (d, *J* = 249.4 Hz) 162.1, 149.3 (d, *J* = 2.8 Hz), 146.8, 124.7, 124.4 (d, *J* = 8.7 Hz), 115.9 (d, *J* = 22.8 Hz), 114.2, 55.6; EI-MS (70eV) *m/z* (relative intensity) 230 (M^+, 76), 135 (48), 107 (100), 92 (29), 77 (50); HRMS. calcd for $C_{13}H_{11}FN_2O$: *m/z* 230.0855; Found: *m/z* 230.0857.

(*E*)-1-(4-chlorophenyl)-2-(4-methoxyphenyl)diazene (**2f**):



Yield = 90.7 %. m.p.: 113-115 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 151.1, 146.8, 136.1, 129.2, 124.9, 123.8, 114.3, 55.6; EI-MS (70eV) *m/z* (relative intensity) 248 (M^++2, 28), 246 (M^+, 83), 135 (48), 111 (35), 107 (100), 92 (30), 77 (33); HRMS. calcd for $C_{13}H_{11}ClN_2O$: *m/z* 246.0560; Found: *m/z* 246.0566.

(*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (**2g**):



Yield = 93.1 %. m.p.: 141-142 °C; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 151.5, 146.8, 132.2, 124.9, 124.5, 124.1, 114.3, 55.6; EI-MS (70eV) *m/z* (relative intensity) 292 (M^++2, 56), 290 (M^+, 58), 157 (23), 155 (24), 135 (65), 107 (100), 92 (29), 77 (34); HRMS. calcd for $C_{13}H_{11}BrN_2O$: *m/z* 290.0055; Found: *m/z* 290.0035.

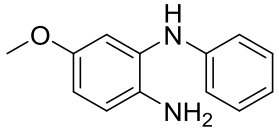
Synthesis of 4-methoxy-N^2-phenylbenzene-1,2-diamine derivatives by irradiation of (E)-1-(4-methoxyphenyl)-2-phenyldiazene derivatives in acidic DMF.

General procedure:

Prepared 8 quartz tubes of reaction solutions, and each tube contained 20 mg of (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**2a**), 11 mL of dimethylformamide (DMF), and 0.5 mL of 37 % $HCl_{(aq)}$. The tubes were sealed with septa, and the dissolving oxygen of the solution was removed by nitrogen gas bubbling for 15 minutes. And then the eight tubes were placed inside the photoreactor and irradiated with 365 nm UV light for 2.5 hours. After irradiation, the reaction solution (from eight tubes) was collected in an Erlenmeyer flask, diluted with a large amount of water, and neutralized with aqueous K_2CO_3 solution to neutral or weak basic. Extracted the solution with ethyl acetate for several times. Collected the organic layers whose dissolving water was removed with magnesium sulfate anhydrous. After evaporating organic solvents, the residue was weighed and measured ^{1}H-NMR spectra to estimate the reaction conversion and the yields of products. Afterwards, a further purification of 4-methoxy-N^2-phenylbenzene-1,2-diamine (**3a**) by a gravity column chromatography was performed for product characterization.

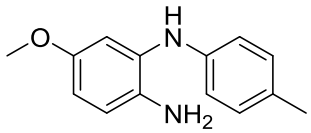
Spectral data:

4-Methoxy-N^2-phenylbenzene-1,2-diamine (**3a**):



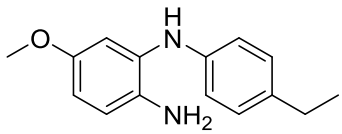
Yield = 97.1 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.24~7.19 (m, 2H), 6.87~6.81 (m, 3H), 6.75 (d, *J* = 2.8Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.55 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.69 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.5, 144.4, 133.7, 130.8, 129.3, 119.8, 117.6, 116.1, 109.8, 108.5, 55.7; EI-MS (70eV) *m/z* (relative intensity) 214 (M^+, 100), 199 (79), 182 (13), 171 (15), 154 (11), 118 (7), 104 (8), 91 (7), 77 (12); HRMS. calcd for $C_{13}H_{14}N_2O$: *m/z* 214.1106; Found: *m/z* 214.1108.

4-Methoxy-N^2-(*p*-tolyl)benzene-1,2-diamine (**3b**):



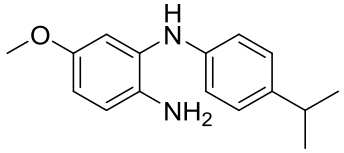
Yield = 95.2 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.03 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.73~6.70 (m, 2H), 6.48 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.69 (s, 3H), 2.26 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.7, 141.7, 132.8, 132.0, 129.8, 129.6, 117.6, 116.9, 108.8, 107.3, 55.7, 20.5; EI-MS (70eV) *m/z* (relative intensity) 228 (M^+, 100), 213 (38), 196 (11), 185 (6), 106 (4).

N^2-(4-Ethylphenyl)-4-methoxybenzene-1,2-diamine (**3c**):



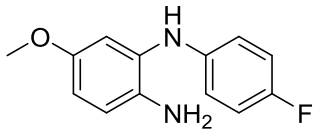
Yield = 97.8 %; ^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.72(d, *J* = 2.8 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.49 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.68 (s, 3H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.19 (t, *J* =7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.7, 141.9, 136.2, 132.9, 131.9, 128.7, 117.6, 116.8, 108.9, 107.5, 55.7, 28.1, 15.8; EI-MS (70eV) *m/z* (relative intensity) 242 (M^+, 100), 227 (70), 212 (14), 198 (8), 106 (13), 91(6), 77(4); HRMS. calcd for $C_{15}H_{18}N_2O$: *m/z* 242.1419; Found: *m/z* 242.1412.

***N*^{2}-(4-Isopropylphenyl)-4-methoxybenzene-1,2-diamine (3d)**:



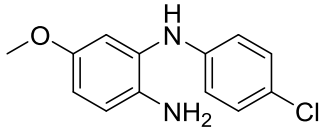
Yield = 97.6 %; ^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 2.8 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.49 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.69 (s, 3H), 2.83 (m, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.7, 142.0, 140.8, 132.9, 131.9, 127.2, 127.1, 117.6, 116.7, 115.2, 108.9, 107.6, 55.7, 33.3, 24.2, 24.2; EI-MS (70eV) *m/z* (relative intensity) 256 (M^+, 86), 241 (100), 226 (5), 178 (6), 149 (6), 113 (11), 91 (5); HRMS. calcd for $C_{16}H_{20}N_2O$: *m/z* 256.1576; Found: *m/z* 256.1562.

***N*^{2}-(4-Fluorophenyl)-4-methoxybenzene-1,2-diamine (3e)**:



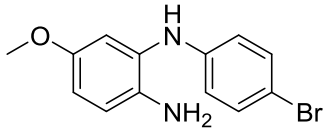
Yield = 98.0 %; ^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ 6.90 (m, 2H), 6.78 (m, 2H), 6.73 (d, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 6.49 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.2 (bs, 1H), 3.68 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.4 (d, *J* = 237 Hz), 153.7, 140.3, 132.7, 132.0, 118.2 (d, *J* = 7.7 Hz), 117.8, 115.8 (d, *J* = 22.4 Hz), 108.9, 107.3, 55.6; EI-MS (70eV) *m/z* (relative intensity) 232 (M^+, 100), 217 (32), 200 (14), 189 (12), 60 (16); HRMS. calcd for $C_{13}H_{13}N_2OF$: *m/z* 232.1012; Found: *m/z* 232.1017.

***N*^{2}-(4-Chlorophenyl)-4-methoxybenzene-1,2-diamine (3f)**:



Yield = 96.8 %; ^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ 6.86 (m, 2H), 6.74 (m, 4H), 6.53 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.6, 143.2, 130.9, 129.4, 129.2, 124.5, 117.1, 116.1, 110.3, 109.8, 55.7; EI-MS (70eV) *m/z* (relative intensity) 248 (M^+, 28), 214 (100), 199 (58), 182 (25); HRMS. calcd for $C_{13}H_{13}N_2OCl$: *m/z* 248.0716; Found: *m/z* 248.0722.

***N*^{2}-(4-Bromophenyl)-4-methoxybenzene-1,2-diamine (3g)**:



Yield = 96.3 %; ^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ 7.2 (d, *J* = 8.7 Hz, 1H), 6.69 (m, 4H), 6.55 (m, 2H), 5.3 (bs, 1H), 3.69 (S, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.1, 144.3, 134.6, 132.6, 130.5, 118.3, 117.3, 112.1, 111.1, 109.6, 56.3; EI-MS (70eV) *m/z* (relative intensity) 294 (M^++2, 100), 292 (M^+, 93), 279 (23), 214 (65), 198 (32), 178 (30); HRMS. calcd for $C_{13}H_{13}N_2OBr$: *m/z* 292.0211; Found: *m/z* 292.0217.

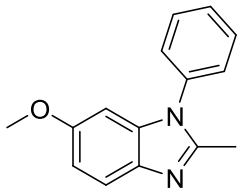
Synthesis of 6-methoxy-2-methyl-1-phenyl-1H-benzimidazole derivatives by irradiation of (E)-1-(4-methoxyphenyl)-2-phenyldiazene derivatives derivatives.

General procedure:

Prepared 8 tubes of reaction solutions, and each tube contained 20 mg of (*E*)-1-(4-methoxy-phenyl)-2-phenyldiazene (**2a**), 11 mL of acetaldehyde diethyl acetal (Acetal), and 0.15 mL of 37 % $HCl_{(aq)}$. The tubes were sealed with septa, and the dissolving oxygen of the solution was removed by nitrogen gas bubbling for 15 minutes. And then the eight tubes were placed inside the photoreactor and irradiated with 419 nm UV light for 40 minutes. After irradiation, the reaction solution (from eight tubes) was collected in an Erlenmeyer flask, diluted with a large amount of water, and neutralized with aqueous K_2CO_3 solution to neutral or weak basic. Extracted the solution with ethyl acetate for several times. Collected the organic layers whose dissolving water was removed with magnesium sulfate anhydrous. After evaporating organic solvents, the residue was weighed and measured ^{1}H-NMR spectra to estimate the reaction conversion and the yields of products. Afterwards, a further purification of 6-methoxy-2-methyl-1-phenyl-1*H*-benzimidazole (**4a**) by a gravity column chromatography was performed for product characterization.

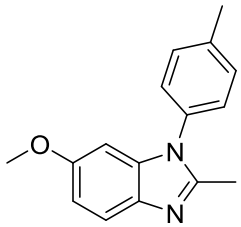
Spectral data:

6-Methoxy-2-methyl-1-phenyl-1*H*-benzimidazole (**4a**):



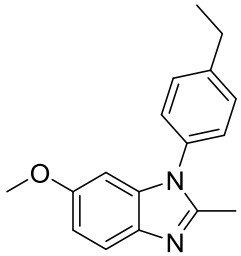
Yield = 95.7 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.6~7.52 (m, 3H), 7.36~7.34 (m, 2H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 3.75 (s, 3H), 2.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.0, 150.5, 136.6, 135.6, 135.2, 130.1, 129.1, 127.0, 119.0, 111.9, 94.1, 55.9, 14.1; EI-MS (70eV) *m/z* (relative intensity) 238 (M^+, 86), 223 (93.7), 195 (12), 154 (12), 77 (17); HRMS. calcd for $C_{15}H_{14}N_2O$: *m/z* 238.1106; Found: *m/z* 238.1125.

6-Methoxy-2-methyl-1-(*p*-tolyl)-1*H*-benzimidazole (**4b**):



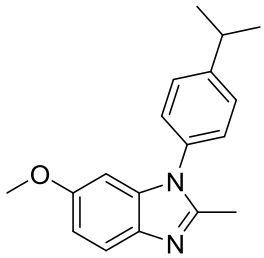
Yield = 85.9 %; ^{1}H-NMR (200 MHz, TMS, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H); EI-MS (70eV) *m/z* (relative intensity) 252 (M^+, 94), 237 (90), 209 (8), 196 (4), 168 (8), 107 (8), 91 (10); HRMS. calcd for $C_{16}H_{16}N_2O$: *m/z* 252.1263; Found: *m/z* 252.1267.

1-(4-Ethylphenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4c**):



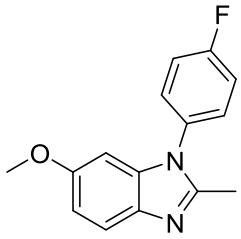
Yield = 85.5 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 3.74 (s, 3H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.6, 150.8, 145.1, 137.1, 136.9, 133.6, 129.3, 126.9, 119.3, 111.2, 94.1, 55.9, 28.6, 15.3, 14.3; EI-MS (70eV) *m/z* (relative intensity) 266 (M^+, 50), 251 (49), 195 (19), 176 (26), 144 (56), 116 (100), 108 (43), 82 (43), 77 (21); HRMS. calcd for $C_{17}H_{18}N_2O$: *m/z* 266.1419; Found: *m/z* 266.1421.

1-(4-Isopropylphenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4d**):



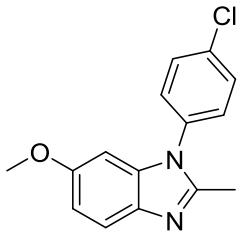
Yield = 73.1 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 3.74 (s, 3H), 3.03 (m, *J* = 6.9 Hz, 1H), 2.46 (s, 3H), 1.30 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.7, 150.7, 149.9, 136.8, 135.8, 133.3, 128.0, 126.8, 119.0, 111.5, 94.1, 55.9, 33.9, 23.9, 14.2; EI-MS (70eV) *m/z* (relative intensity) 280 (M^+, 29), 265 (25), 178 (100), 91 (19), 77 (12); HRMS. calcd for $C_{18}H_{20}N_2O$: *m/z* 280.1576; Found: *m/z* 280.1565.

1-(4-Fluorophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4e**):



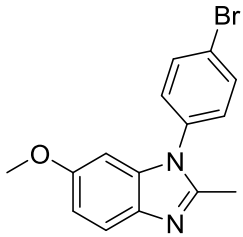
Yield = 91.1 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.33~7.26 (m, 4H), 6.88 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 3.74 (s, 3H), 2.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 280 Hz), 156.9, 150.6, 136.9, 136.2, 132.0, 128.9 (d, *J* = 8.7Hz), 119.3, 117.1 (d, *J* = 22.7 Hz), 111.6, 93.8, 55.9, 14.2; EI-MS (70eV) *m/z* (relative intensity) 258 (M^++2, 1.2), 256 (M^+, 76), 241 (94), 230 (15), 213 (16), 172 (19), 146 (10), 135 (13), 107 (24), 95 (26), 77 (13); HRMS. calcd for $C_{15}H_{13}N_2OF$: *m/z* 156.1012; Found: *m/z* 256.1019.

1-(4-Chlorophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4f**):



Yield = 90.7 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 3.74 (s, 3H), 2.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.8, 150.4, 136.8, 134.8, 134.6, 130.3, 130.0, 128.4, 127.0, 119.5, 111.5, 93.7, 55.9, 14.2; EI-MS (70eV) *m/z* (relative intensity) 274 (M^++2, 34), 272 (M^+, 100), 257 (84), 238 (48), 223 (44), 188 (9), 153 (13), 129 (6), 111 (9), 77 (8); HRMS. calcd for $C_{15}H_{13}N_2OCl$: *m/z* 272.0716; Found: *m/z* 272.0712.

1-(4-Bromophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4g**):



Yield = 90.3 %; ^{1}H-NMR (400 MHz, TMS, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.87 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 3.74 (s, 3H), 2.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.8, 150.3, 136.7, 135.1, 133.3, 128.7, 122.8, 119.5, 111.5, 93.7, 55.9, 14.3; EI-MS (70eV) *m/z* (relative intensity) 318 (M^++2, 99), 316 (M^+, 100), 303 (68), 273 (5), 238 (9), 222 (13), 194 (11), 153 (27), 118 (8), 76 (5); HRMS. calcd for $C_{15}H_{13}N_2OBr$: *m/z* 316.0211; Found: *m/z* 316.0208.

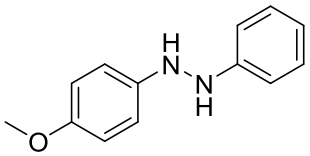
Synthesis of the hydrazobenzenes 5a and 5c.

General procedure:

1 mmol of azobenzenes and 3 mmol of tributyltin hydride were dissolved in 10 mL of benzene and the resulting solution was stirred and refluxed for ten hours. After cooling down to room temperature, the reaction was concentrated to form the precipitates which were collected by filtration. The precipitates were washed with a small amount of benzene and then with a large amount of hexane to afford a pale yellow solid as the hydrazobenzene products. (Beware of the quick oxidation of hydrazobenzenes back to azobenzenes in chloroform-*d* during the NMR measurement process. In our experiments, about 5 % of azobenzenes (**2a** and **2c**) could be observed on the ^{1}H-NMR spectra of hydrazobenzenes **5a** and **5c** which were measured about 2 hours later after the NMR tubes preparation. However, when the same NMR tube of **5a** was measured again after about 24 hours, an increasing amount of azobenzene **2a** (~18 %) could be observed on the ^{1}H-NMR spectrum.)

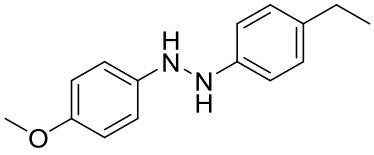
Spectral data:

4-Methoxyhydrazobenzene (**5a**):



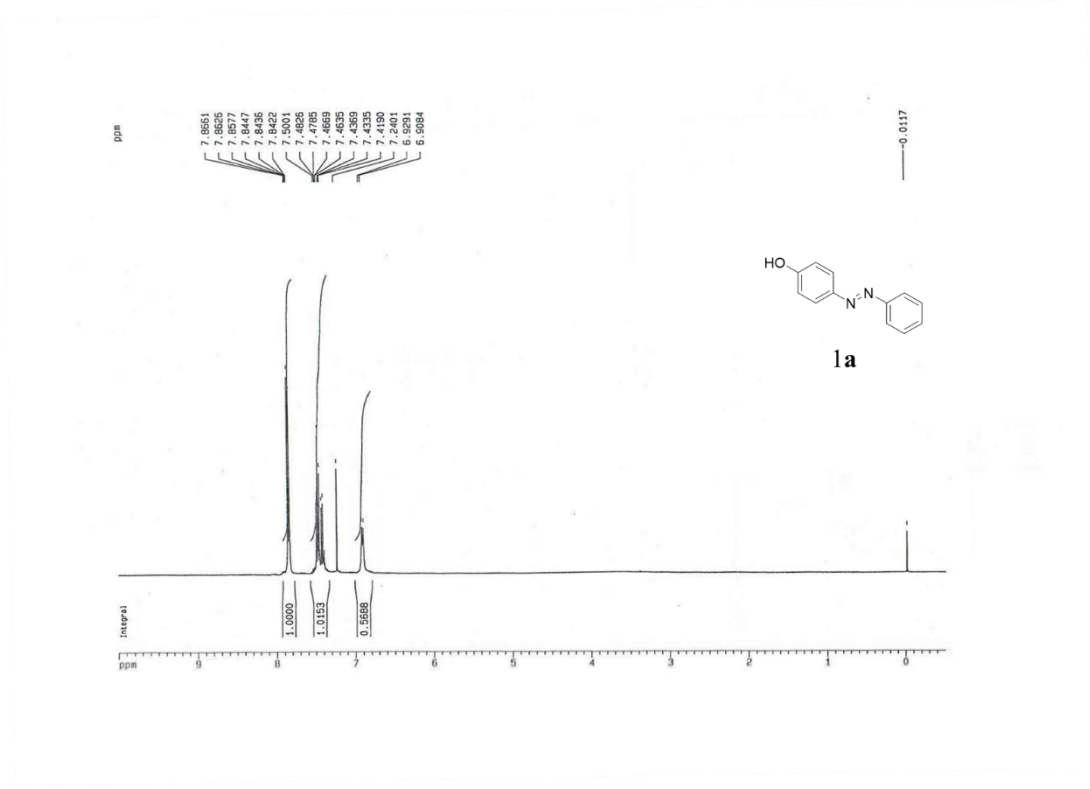
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 2H), 6.87-6.75 (m, 7H), 5.59 (bs, 1H), 5.45 (bs, 1H), 3.75 (s, 3H).

4-Ethyl-4'-methoxyhydrazobenzene (**5c**):

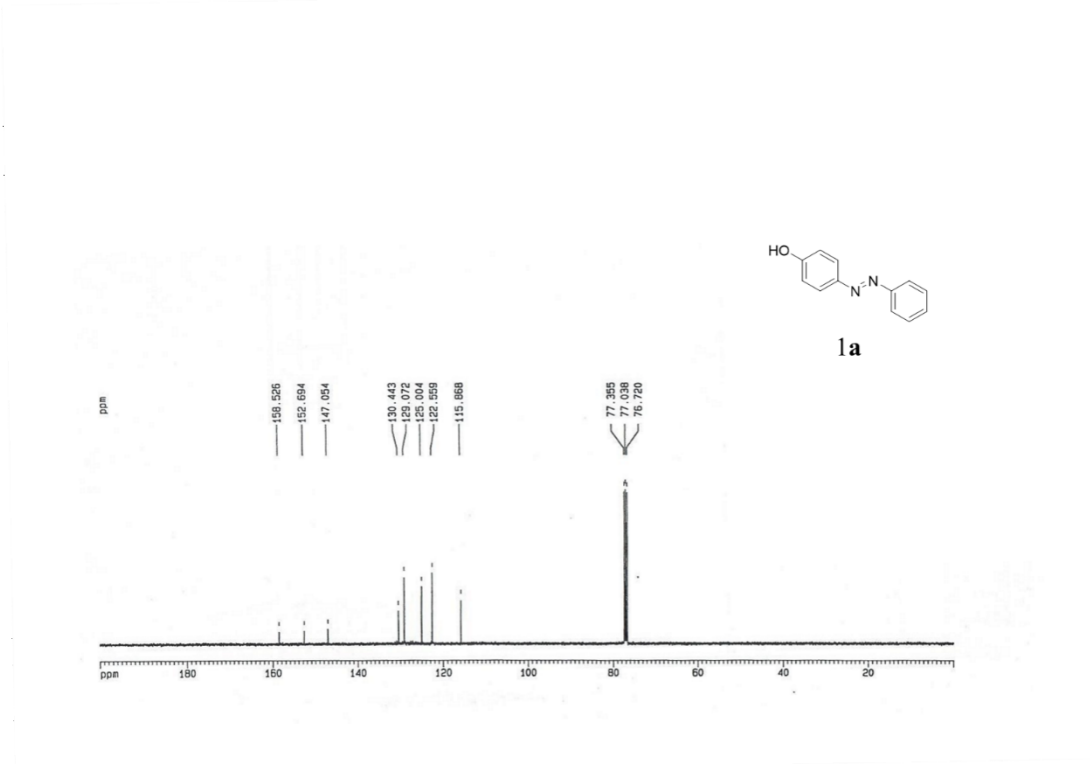


^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.5 Hz, 2H), 6.84-6.77 (m, 6H), 5.53 (bs, 1H), 5.43 (bs, 1H), 3.75 (s, 3H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 153.6, 147.0, 143.0, 135.7, 128.6, 114.8, 113.7, 112.5, 55.7, 28.0, 15.9.

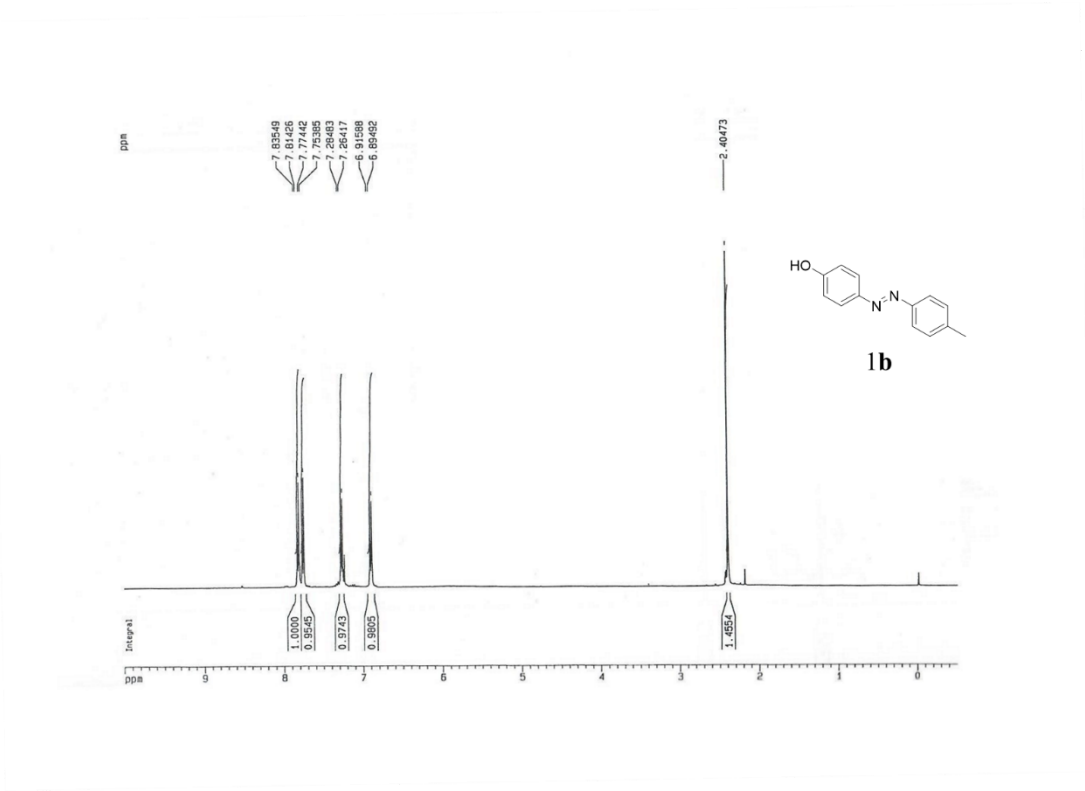
(*E*)-4-(phenyldiazenyl)phenol (**1a**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



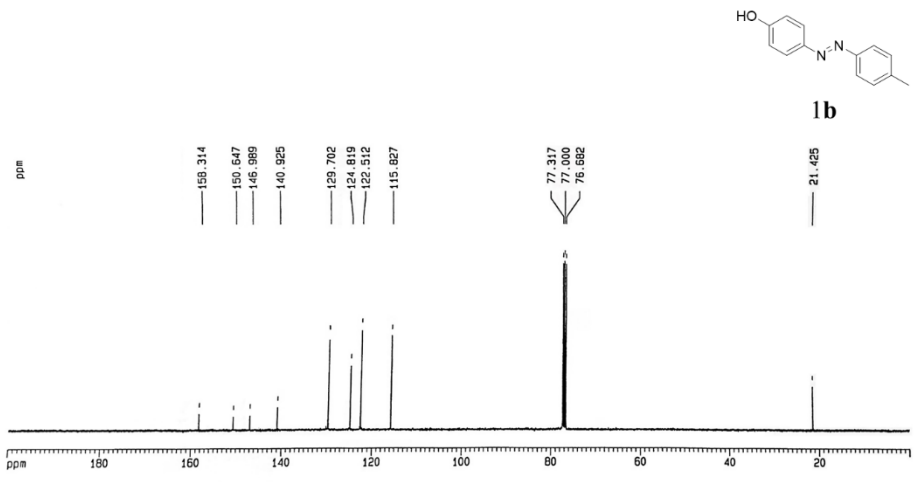
(*E*)-4-(phenyldiazenyl)phenol (**1a**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



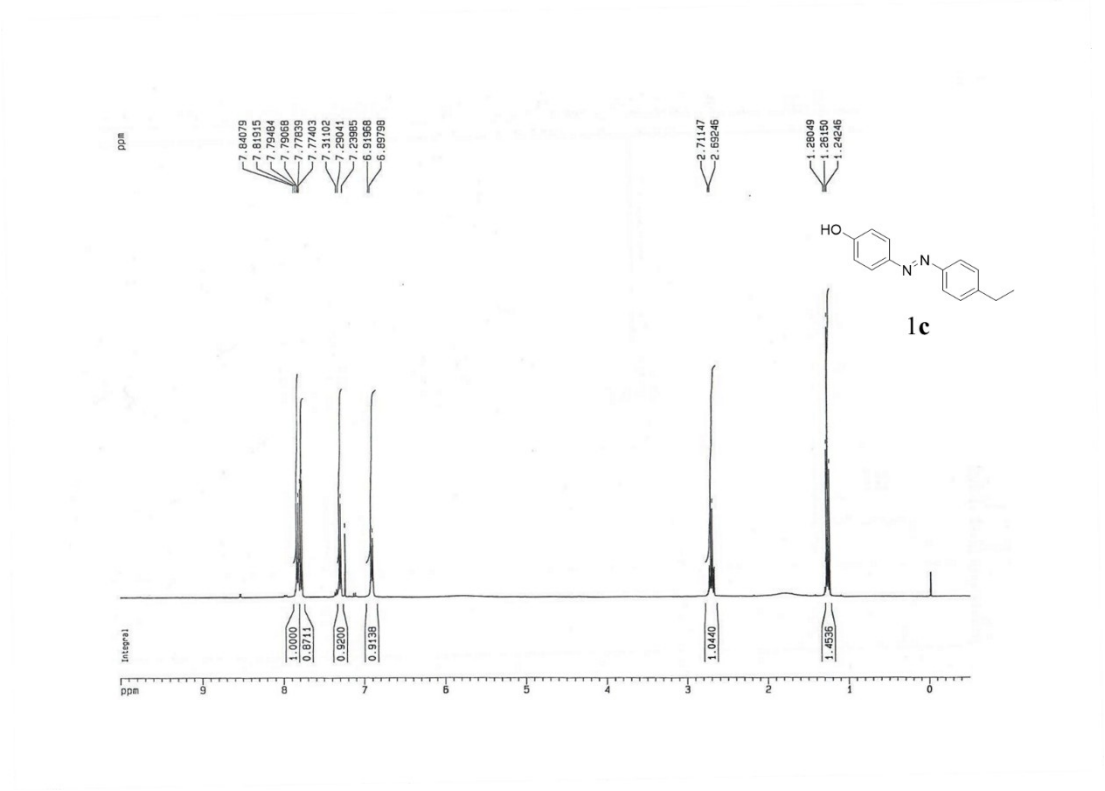
(*E*)-4-(p-tolyldiazenyl)phenol (**1b**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



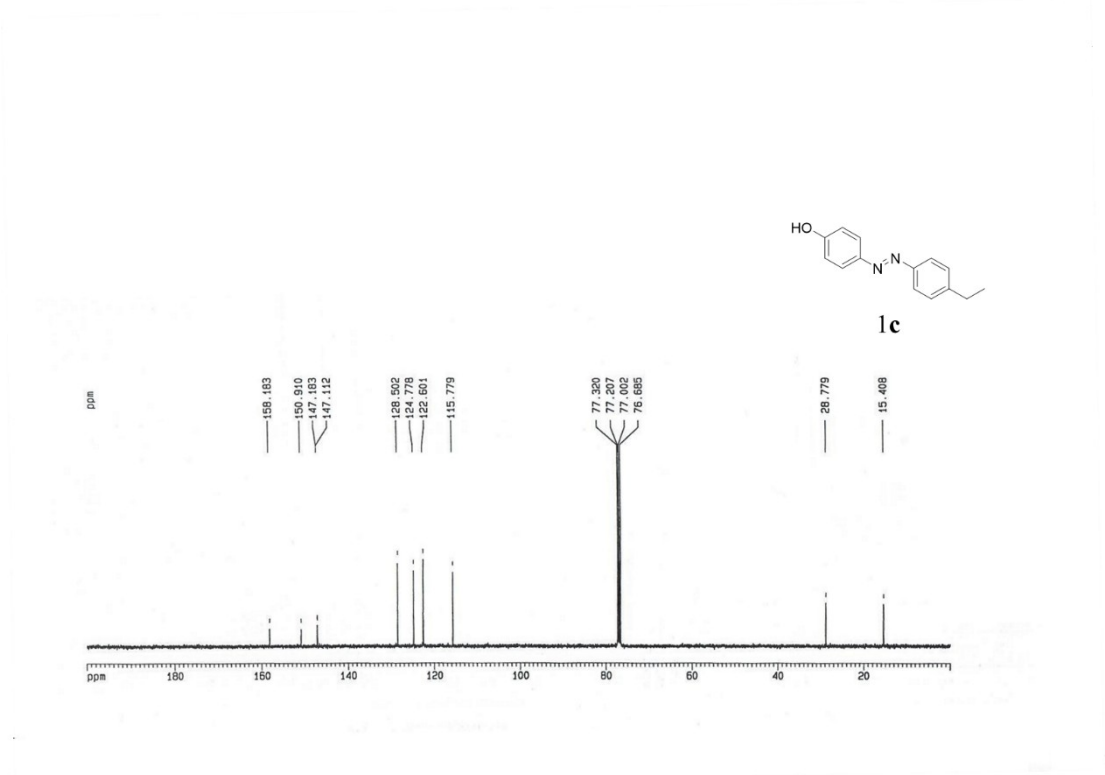
(*E*)-4-(p-tolyldiazenyl)phenol (**1b**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



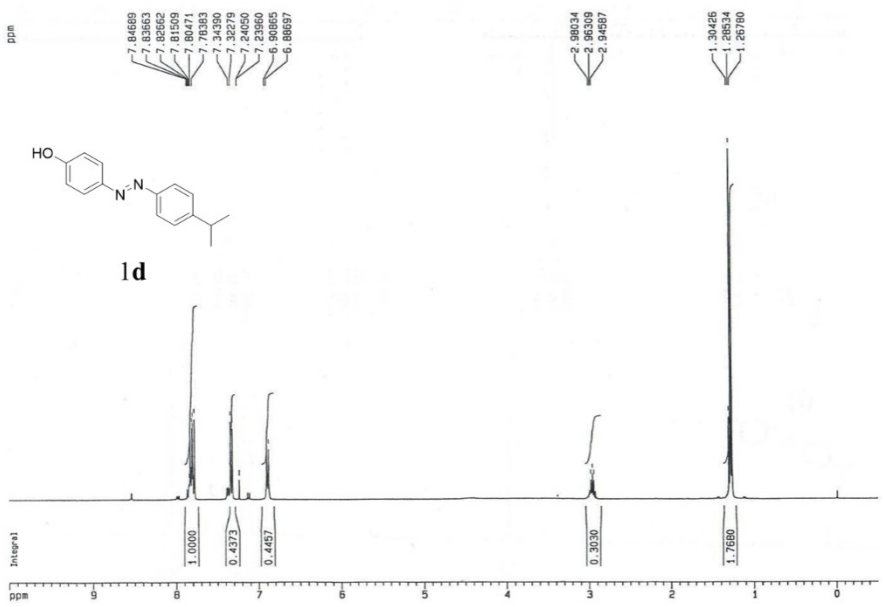
(*E*)-4-((4-ethylphenyl)diazenyl)phenol (**1c**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



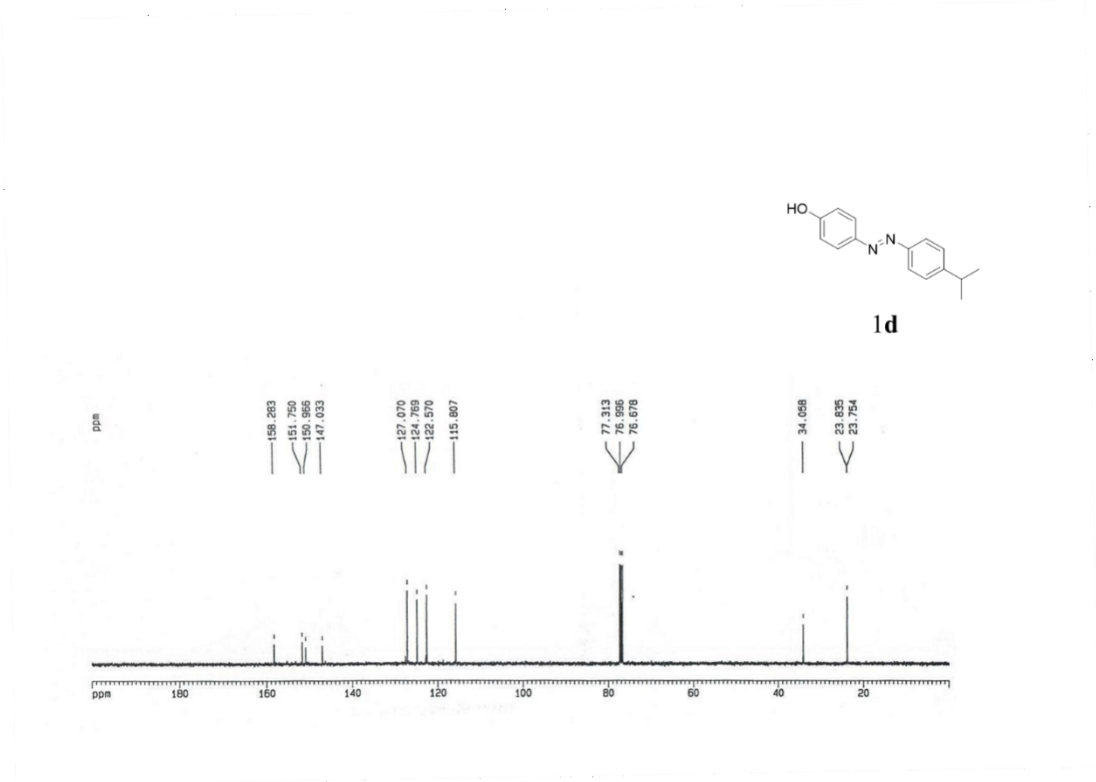
(*E*)-4-((4-ethylphenyl)diazenyl)phenol (**1c**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



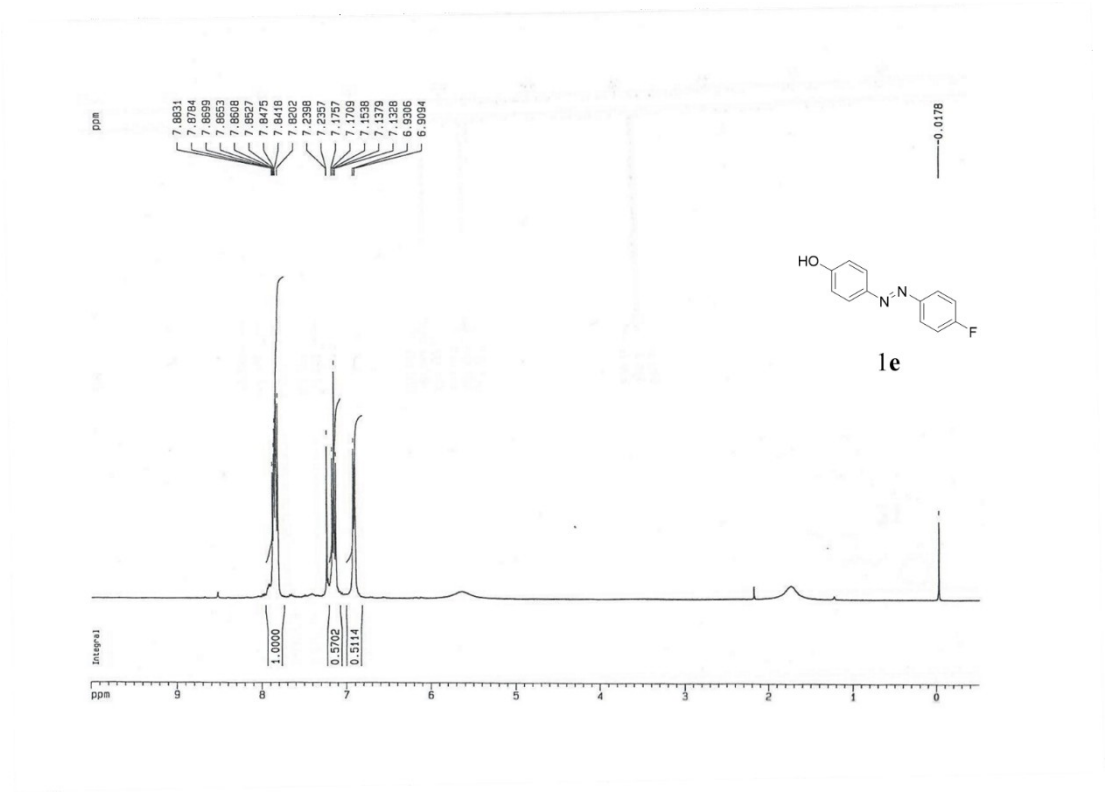
(*E*)-4-((4-isopropylphenyl)diazenyl)phenol (**1d**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



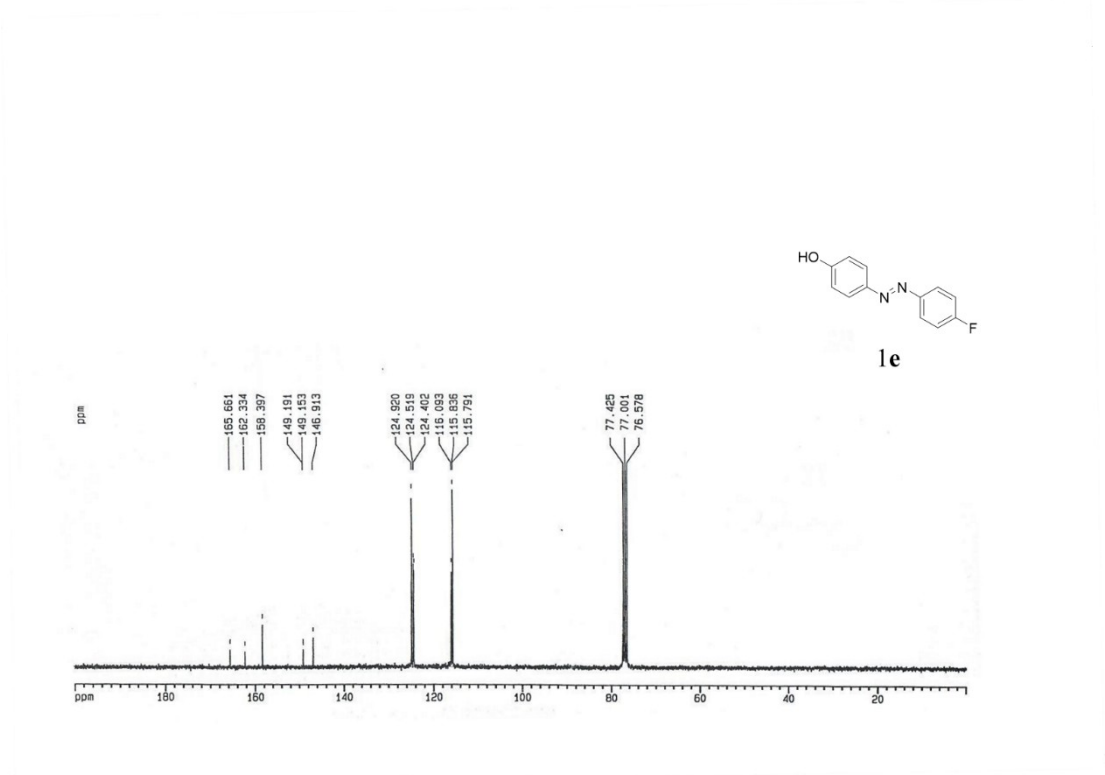
(*E*)-4-((4-isopropylphenyl)diazenyl)phenol (**1d**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



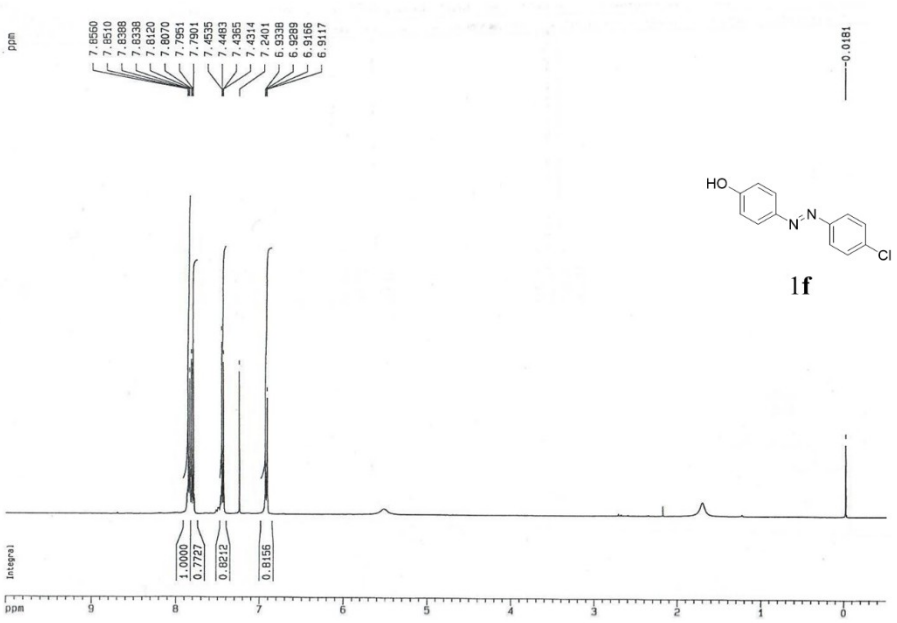
(*E*)-4-((4-fluorophenyl)diazenyl)phenol (**1e**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



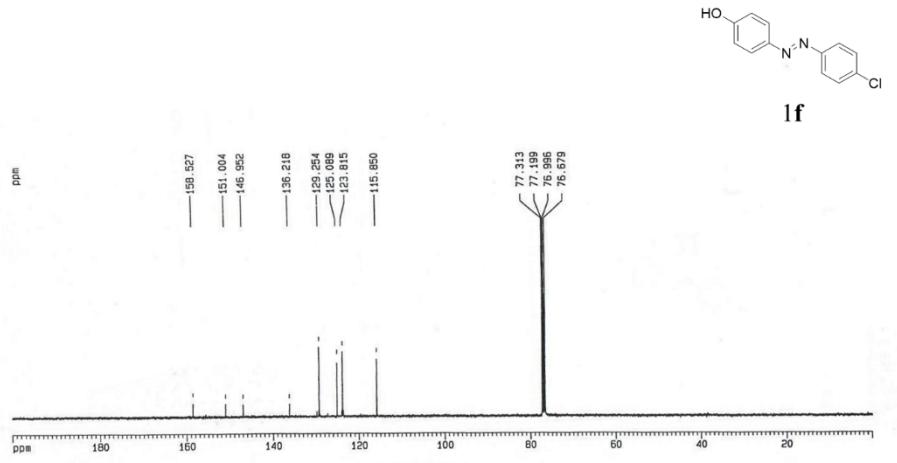
(*E*)-4-((4-fluorophenyl)diazenyl)phenol (**1e**): **^{13}C-NMR** (75 MHz, $CDCl_3$)



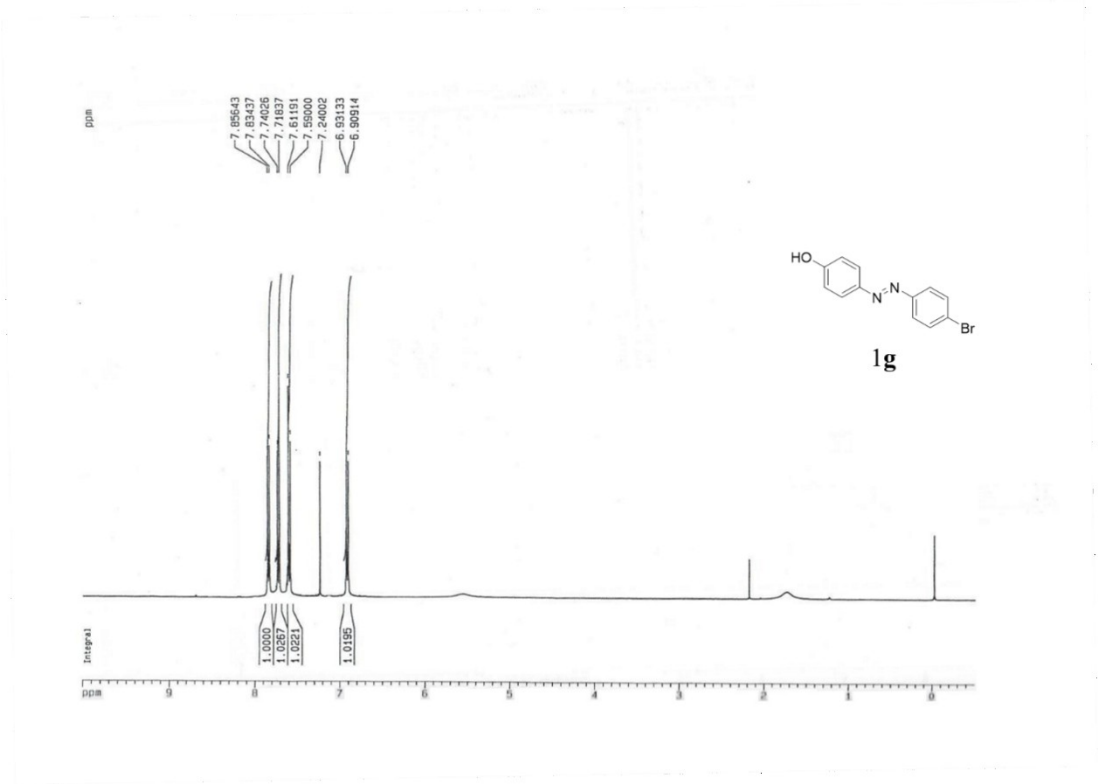
(*E*)-4-((4-chlorophenyl)diazenyl)phenol (1f): **^{1}H-NMR** (400 MHz, $CDCl_3$)



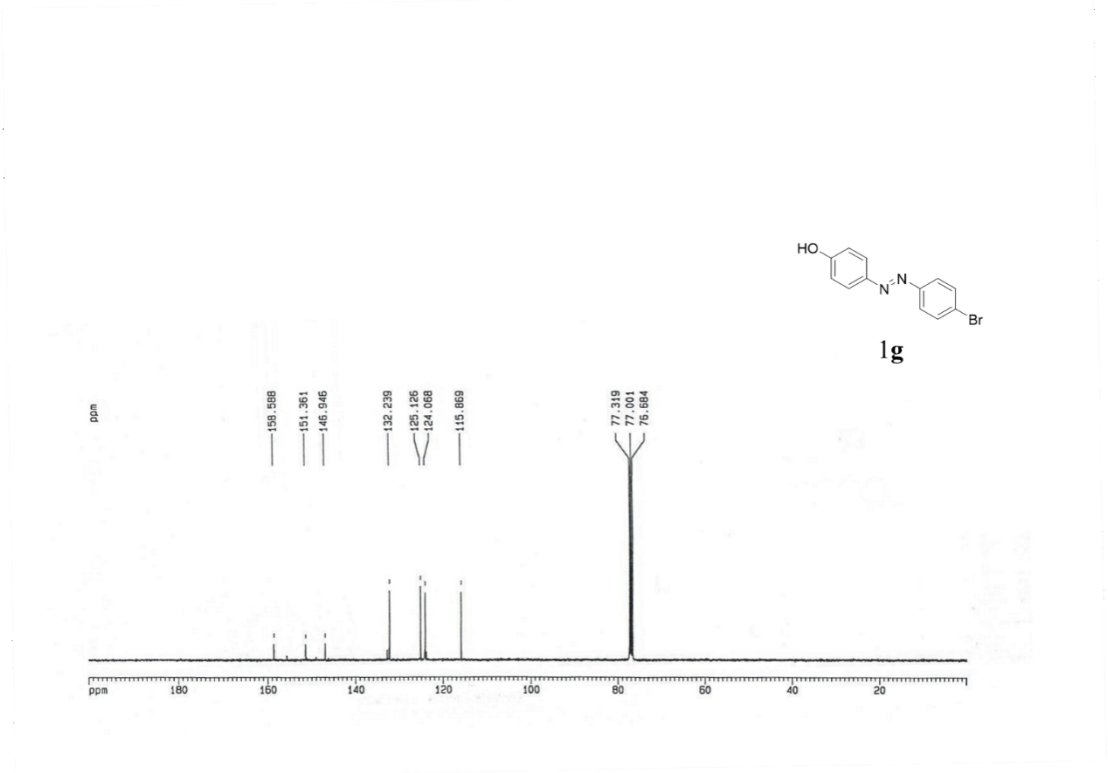
(*E*)-4-((4-chlorophenyl)diazenyl)phenol (1f): **^{13}C-NMR** (100 MHz, $CDCl_3$)



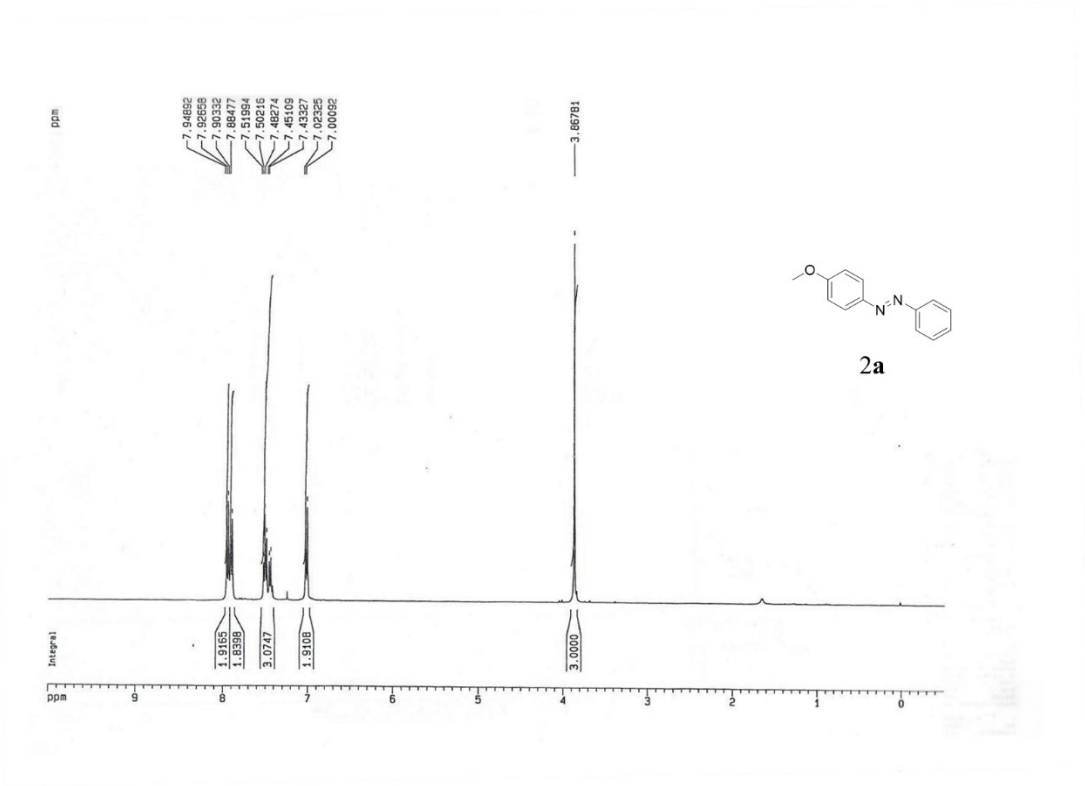
(*E*)-4-((4-bromophenyl)diazenyl)phenol (1g): **^{1}H-NMR** (400 MHz, $CDCl_3$)



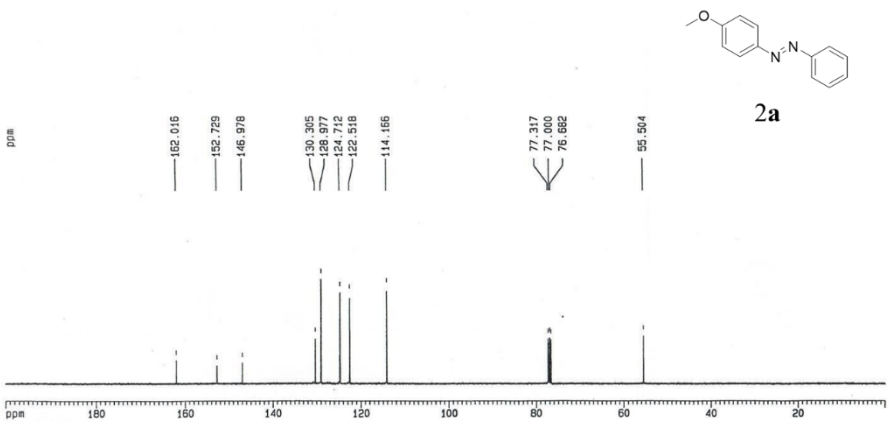
(*E*)-4-((4-bromophenyl)diazenyl)phenol (1g): **^{13}C-NMR** (100 MHz, $CDCl_3$)



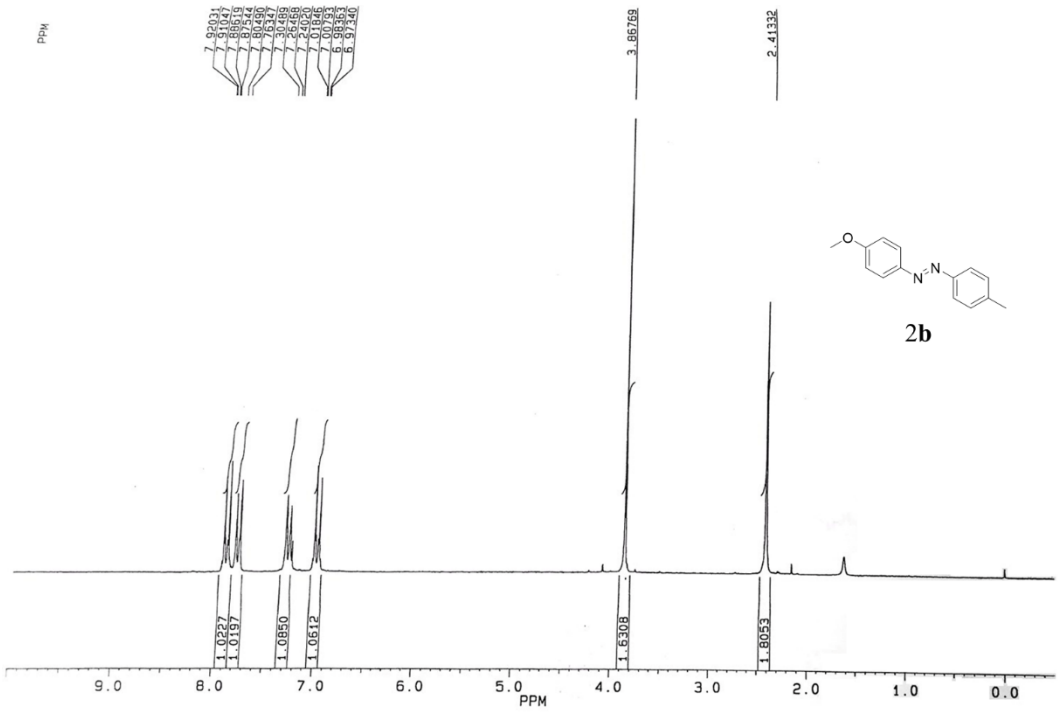
(*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**2a**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



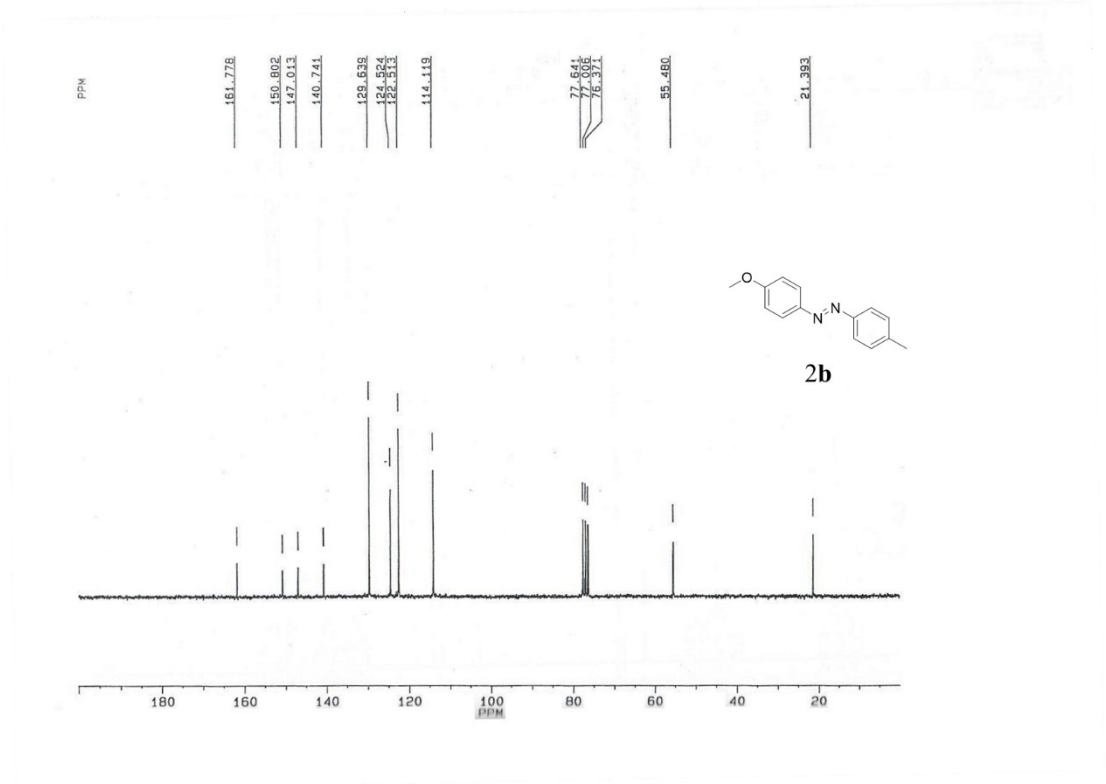
(*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**2a**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



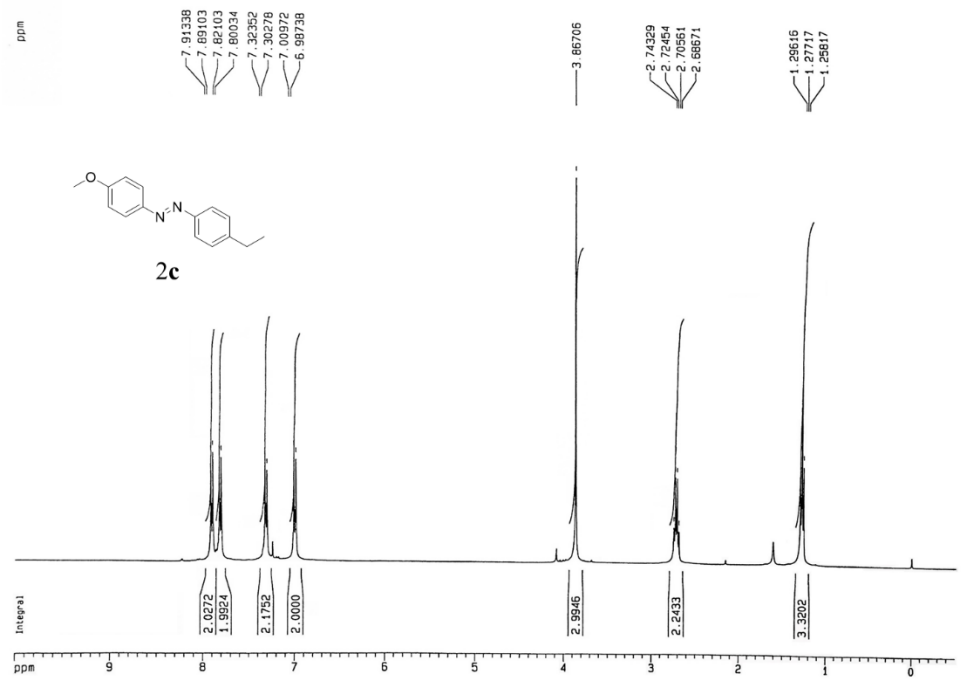
(*E*)-1-(4-methoxyphenyl)-2-(p-tolyl)diazene (**2b**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



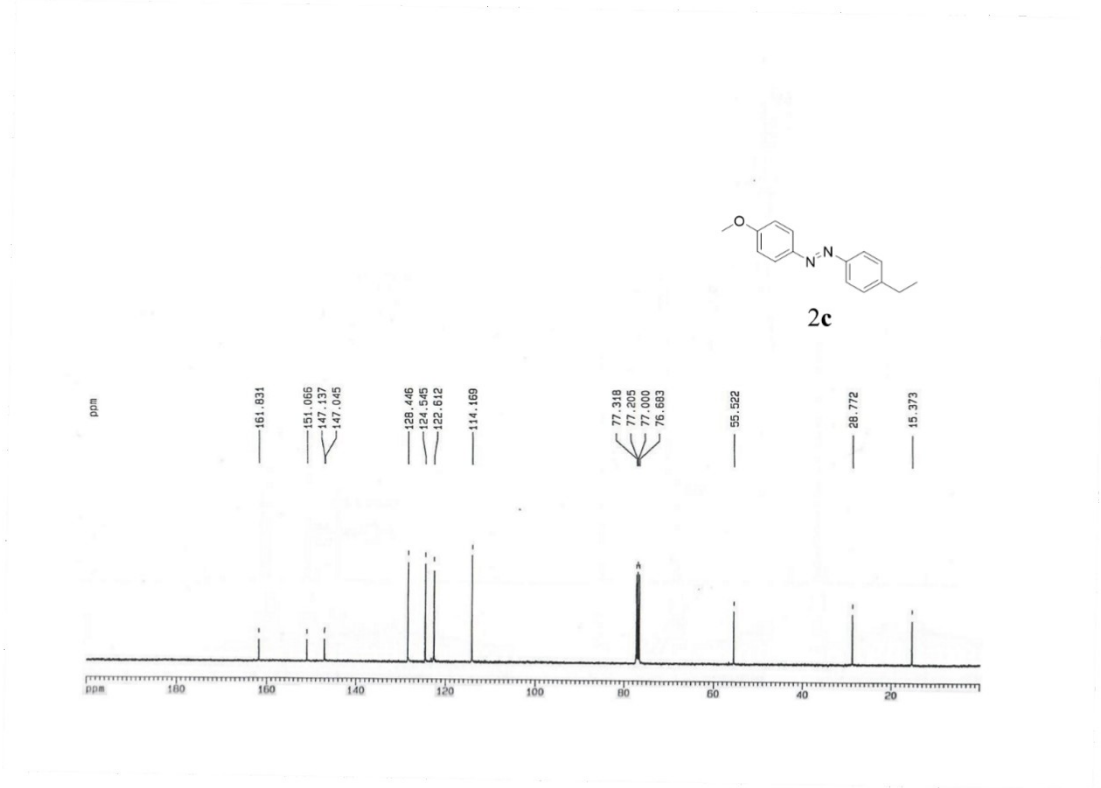
(*E*)-1-(4-methoxyphenyl)-2-(p-tolyl)diazene (**2b**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



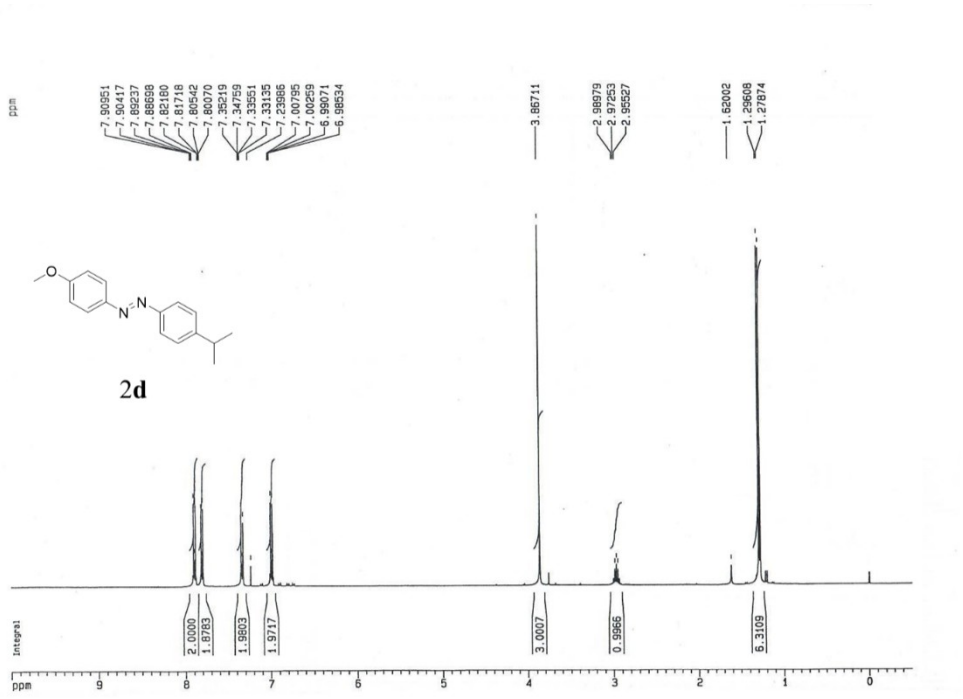
(*E*)-1-(4-ethylphenyl)-2-(4-methoxyphenyl)diazene (2c): **^{1}H-NMR** (400 MHz, $CDCl_3$)



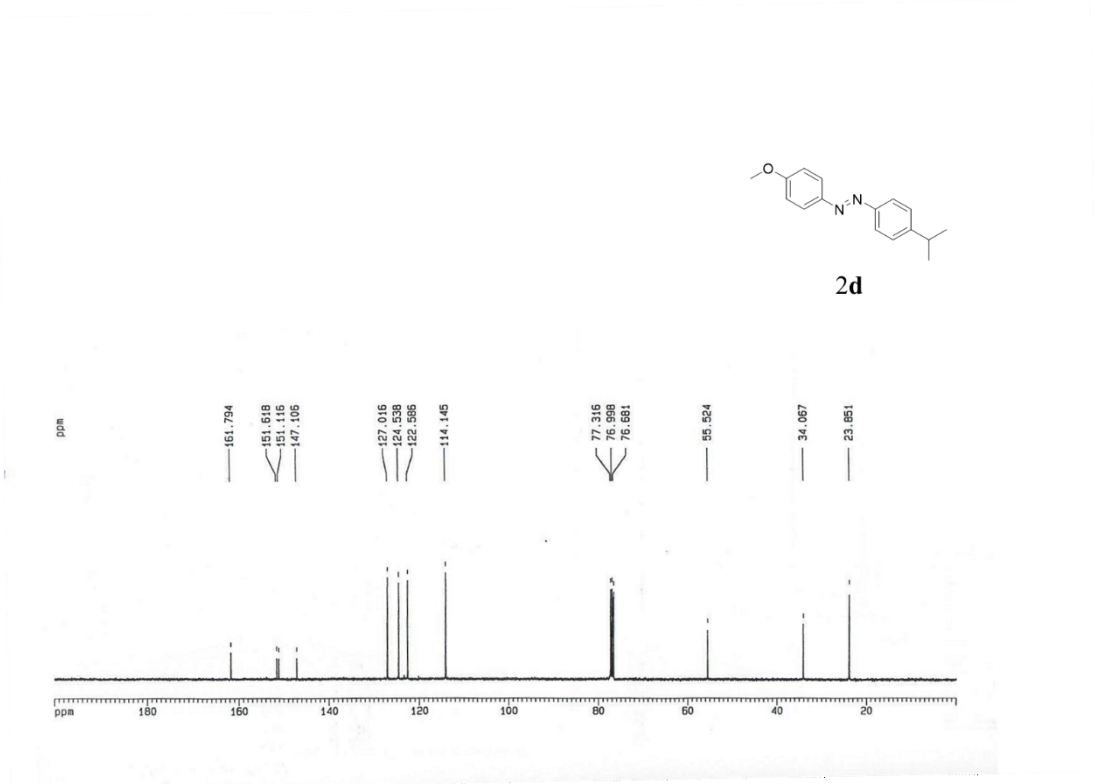
(*E*)-1-(4-ethylphenyl)-2-(4-methoxyphenyl)diazene (2c): **^{13}C-NMR** (100 MHz, $CDCl_3$)



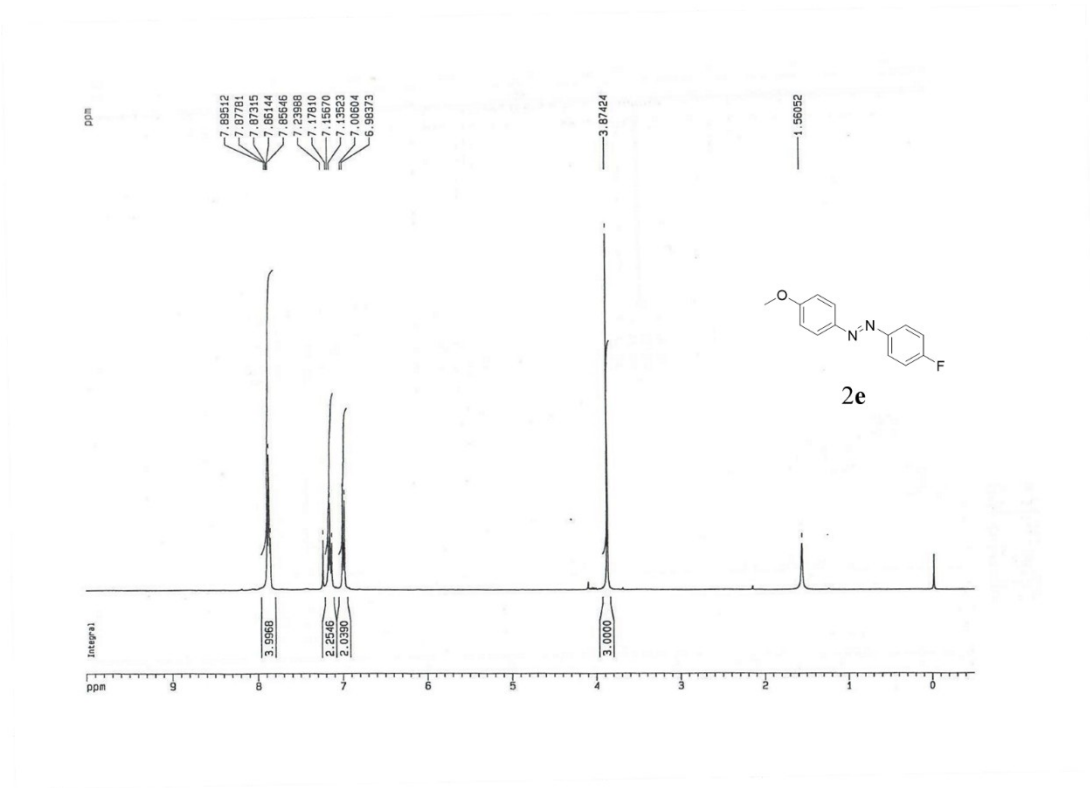
(*E*)-1-(4-isopropylphenyl)-2-(4-methoxyphenyl)diazene (**2d**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



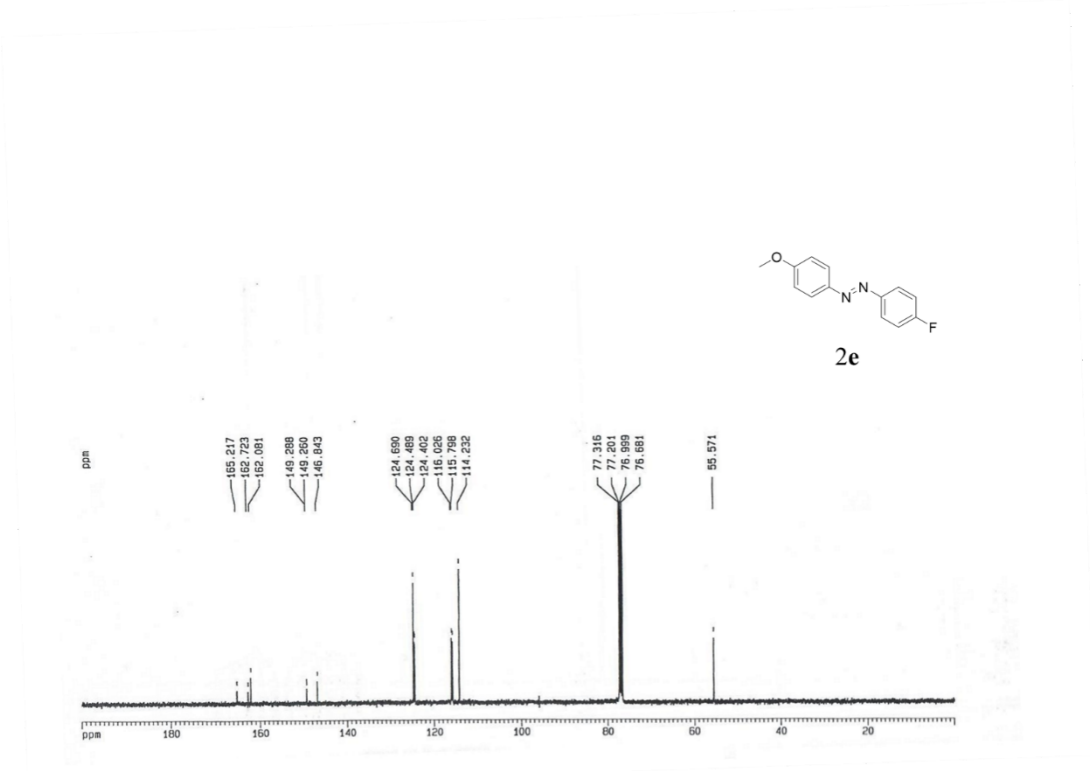
(*E*)-1-(4-isopropylphenyl)-2-(4-methoxyphenyl)diazene (**2d**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



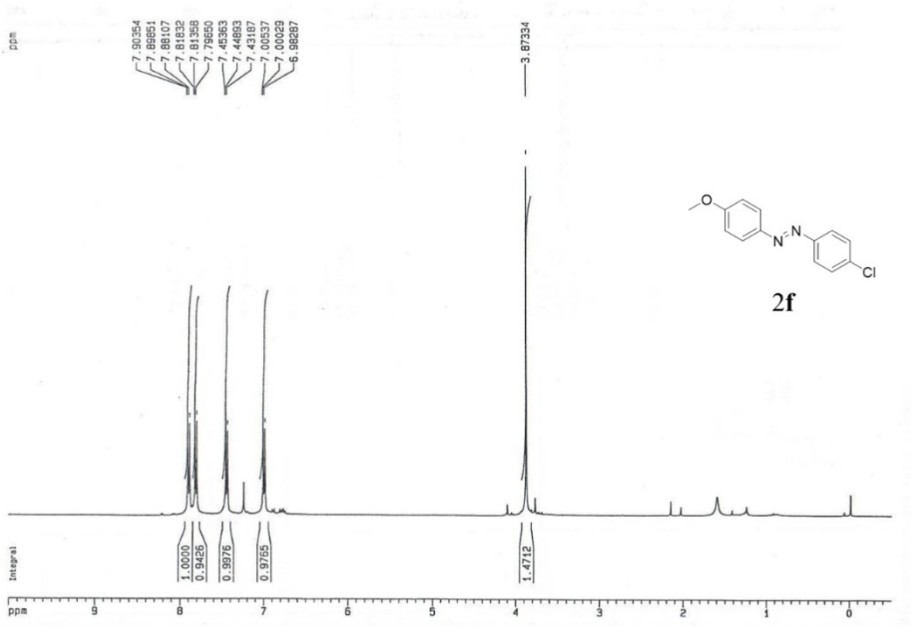
(*E*)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)diazene (**2e**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



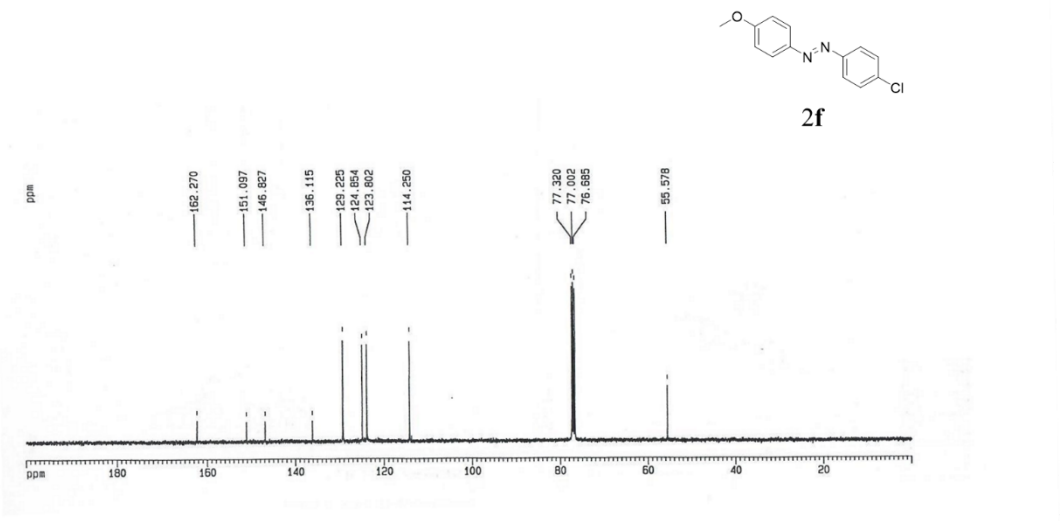
(*E*)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)diazene (**2e**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



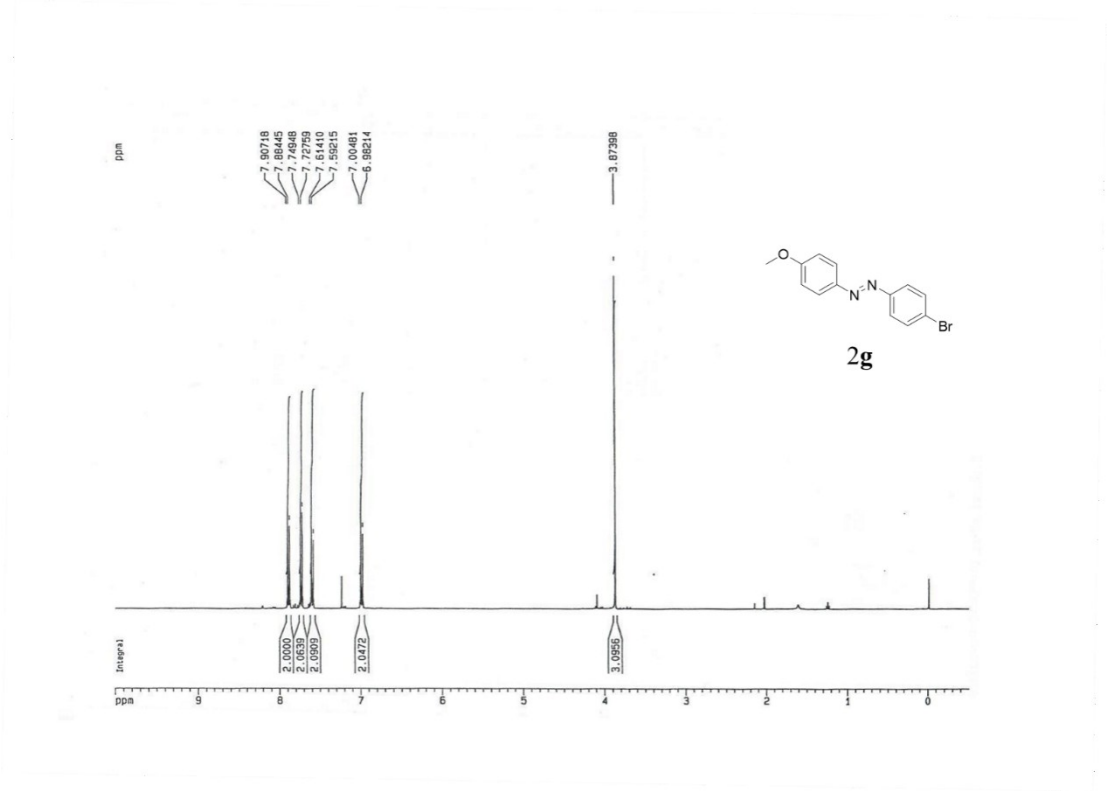
(*E*)-1-(4-chlorophenyl)-2-(4-methoxyphenyl)diazene (2f): **^{1}H-NMR** (400 MHz, $CDCl_3$)



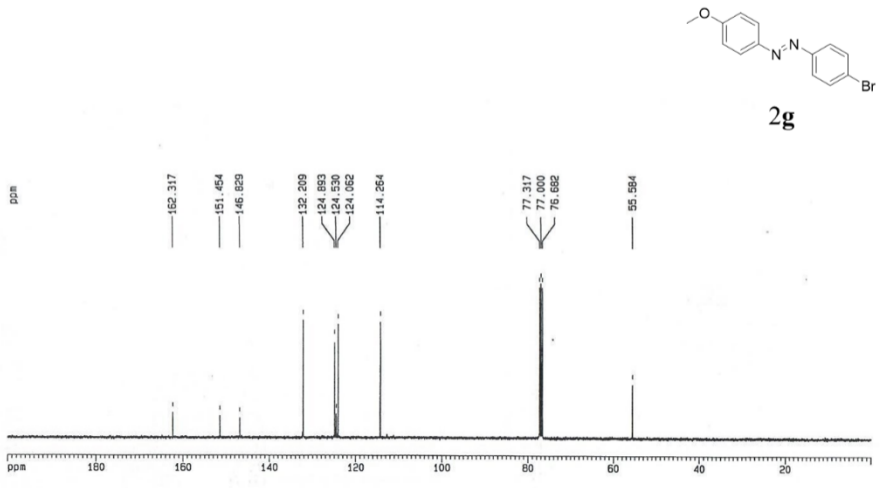
(*E*)-1-(4-chlorophenyl)-2-(4-methoxyphenyl)diazene (2f): **^{13}C-NMR** (100 MHz, $CDCl_3$)



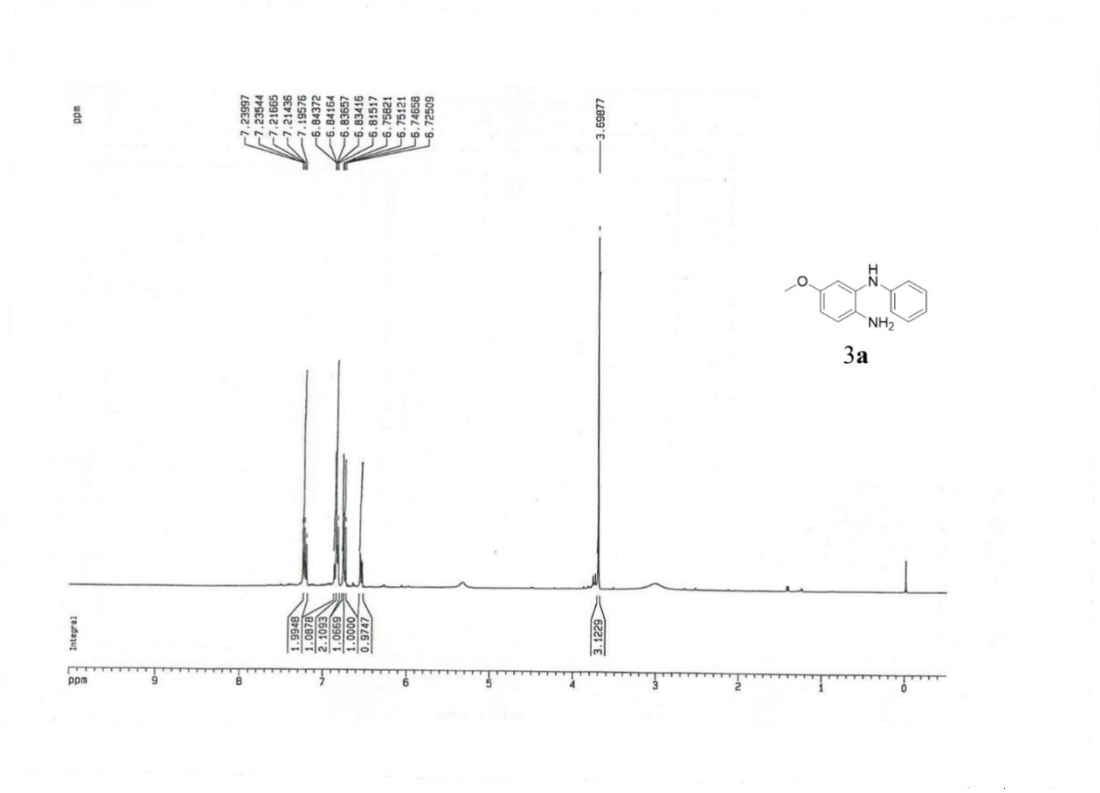
(*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (2g): **^{1}H-NMR** (400 MHz, $CDCl_3$)



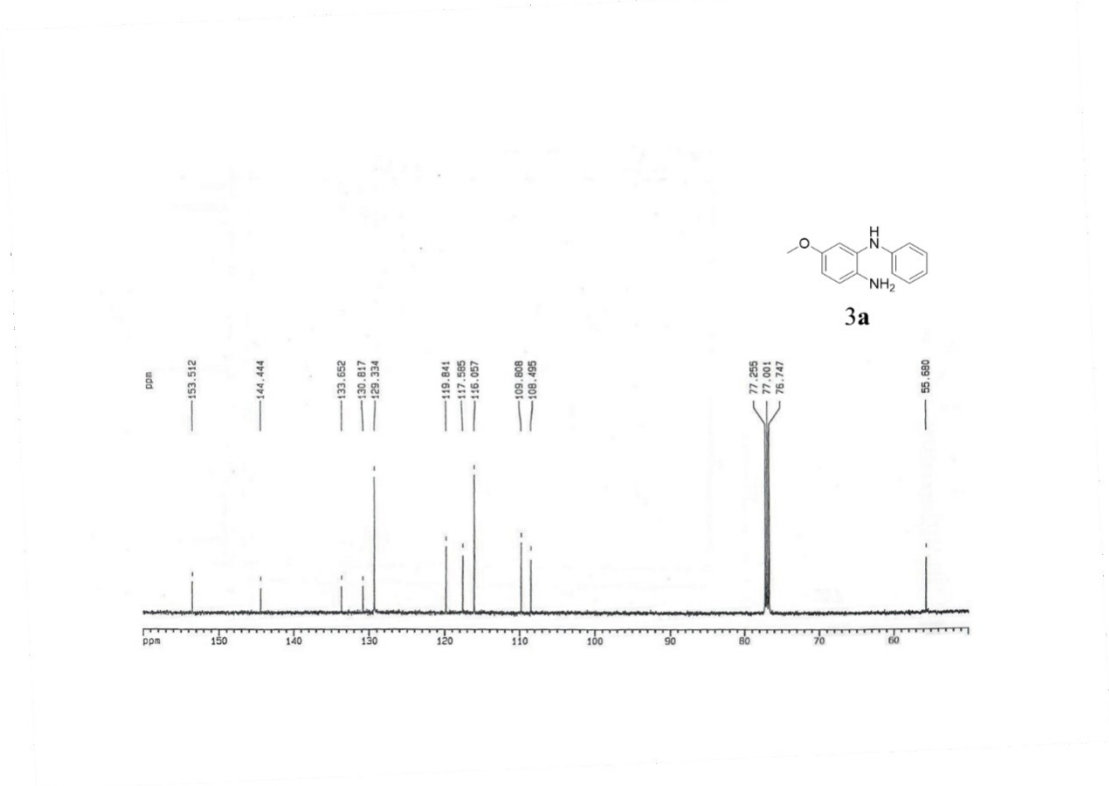
(*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (2g): **^{13}C-NMR** (100 MHz, $CDCl_3$)



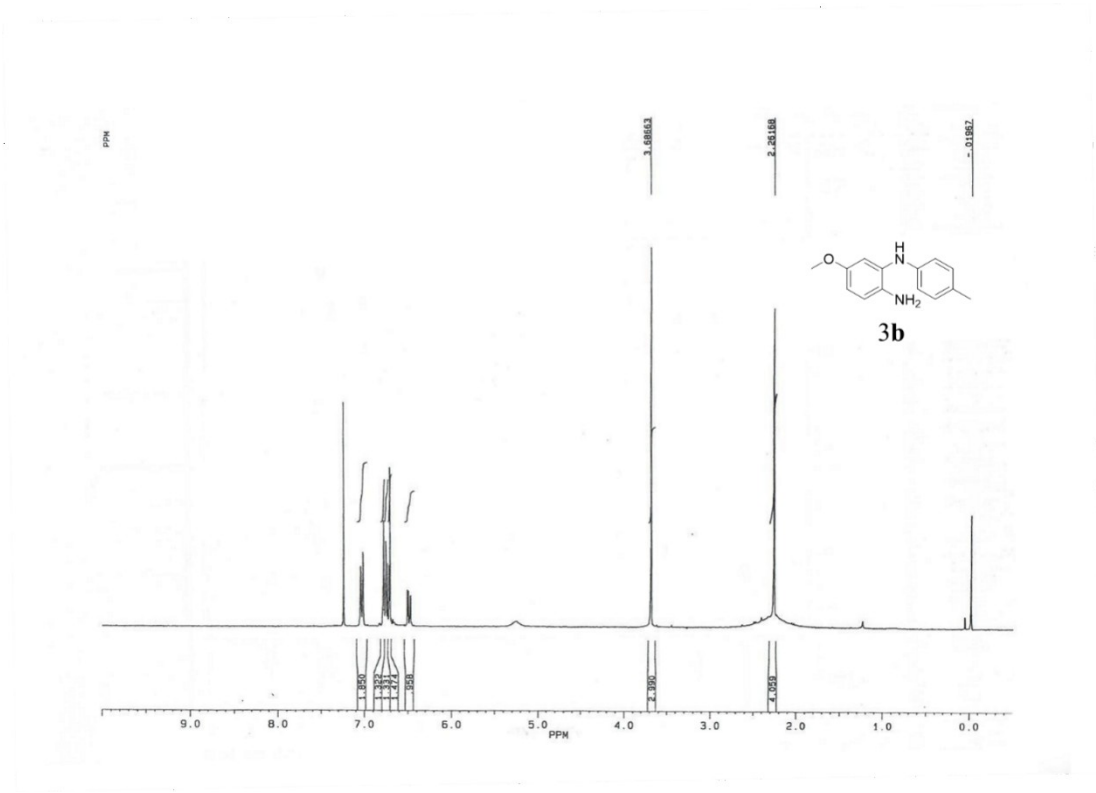
4-methoxy-N^2-phenylbenzene-1,2-diamine (**3a**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



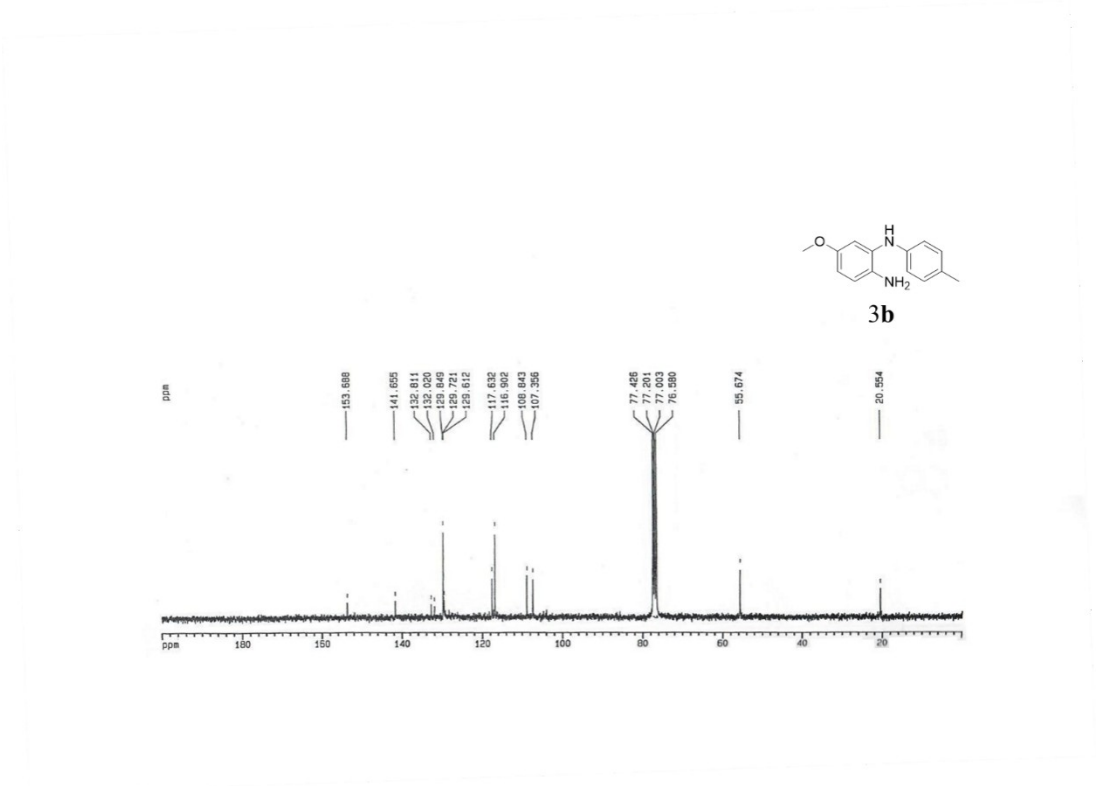
4-methoxy-N^2-phenylbenzene-1,2-diamine (**3a**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



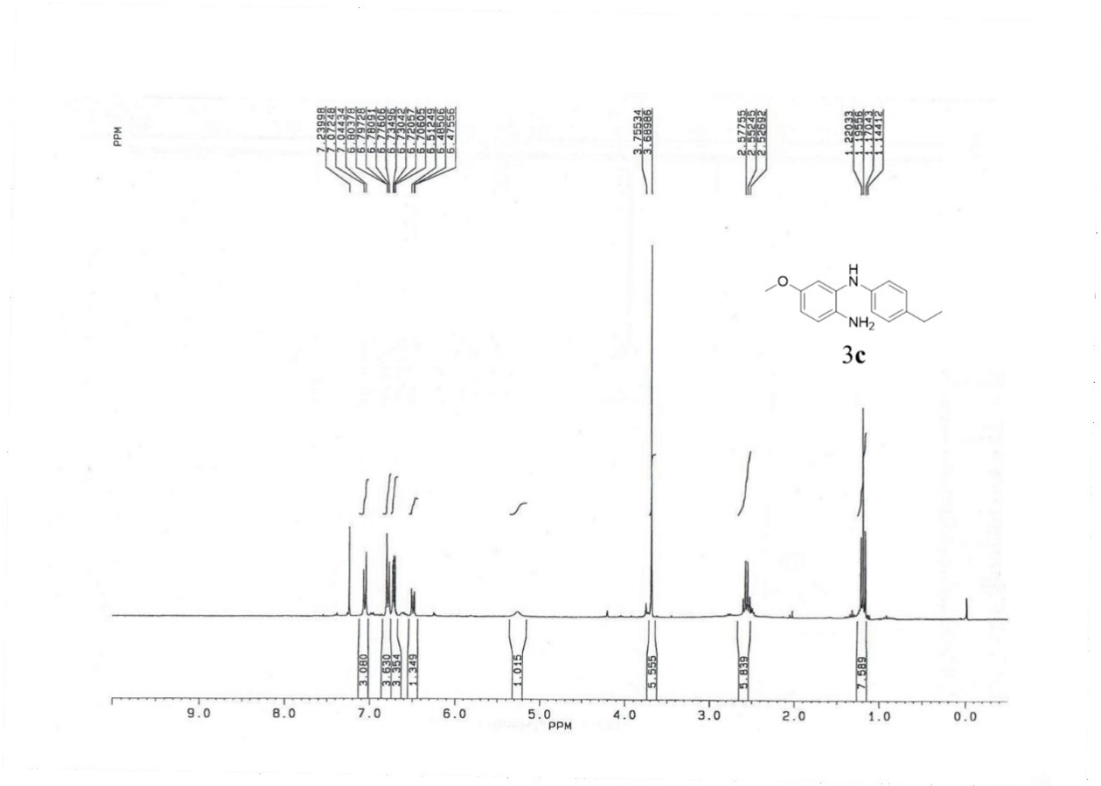
4-methoxy-N^2-(*p*-tolyl)benzene-1,2-diamine (**3b**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



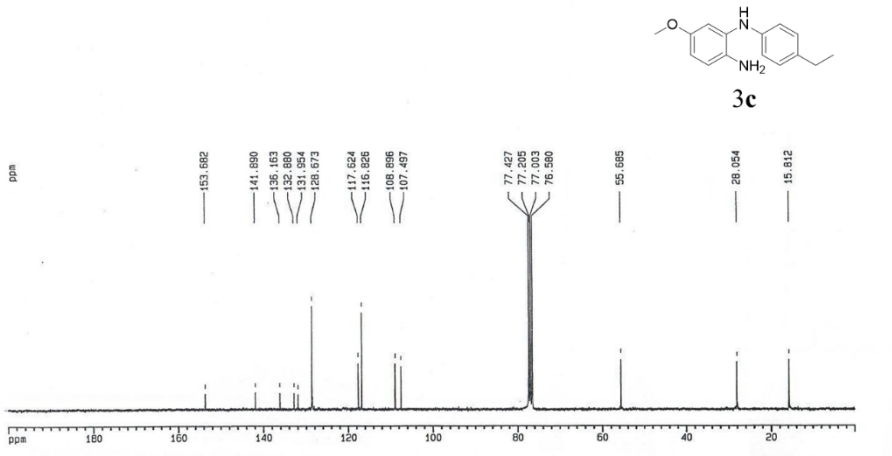
4-methoxy-N^2-(*p*-tolyl)benzene-1,2-diamine (**3b**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



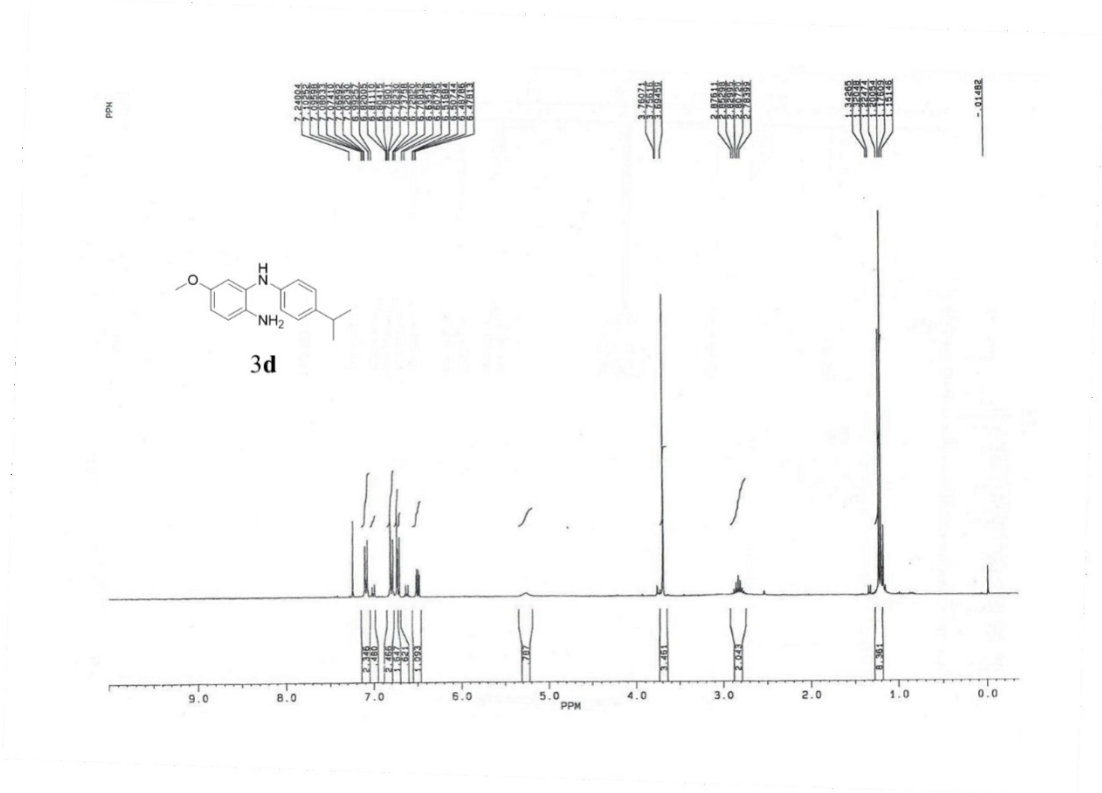
***N*^{2}-(4-ethylphenyl)-4-methoxybenzene-1,2-diamine (3c): ^{1}H-NMR** (300 MHz, $CDCl_3$)



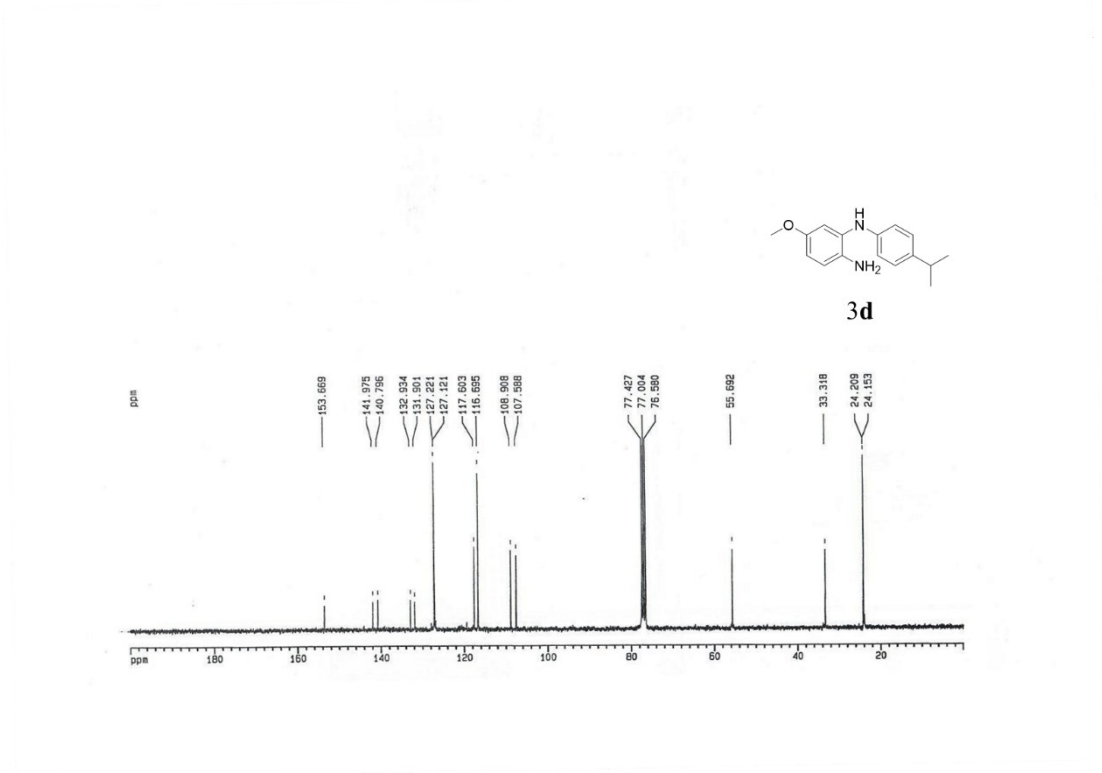
***N*^{2}-(4-ethylphenyl)-4-methoxybenzene-1,2-diamine (3c): ^{13}C-NMR** (75 MHz, $CDCl_3$)



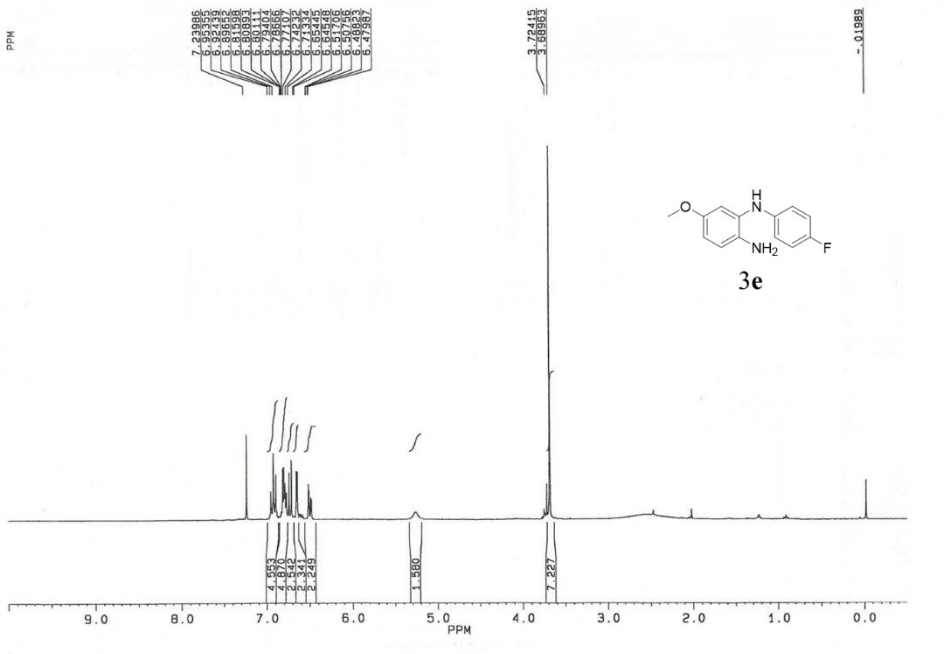
***N*^{2}-(4-isopropylphenyl)-4-methoxybenzene-1,2-diamine (3d)**: **^{1}H-NMR** (300 MHz, $CDCl_3$)



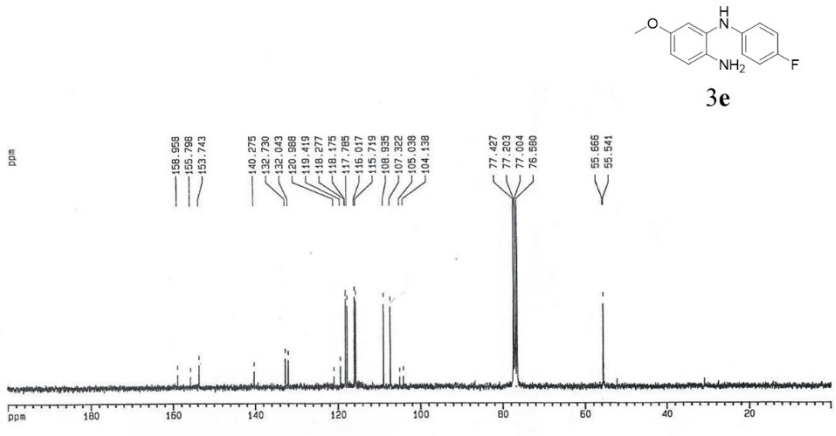
***N*^{2}-(4-isopropylphenyl)-4-methoxybenzene-1,2-diamine (3d)**: **^{13}C-NMR** (75 MHz, $CDCl_3$)



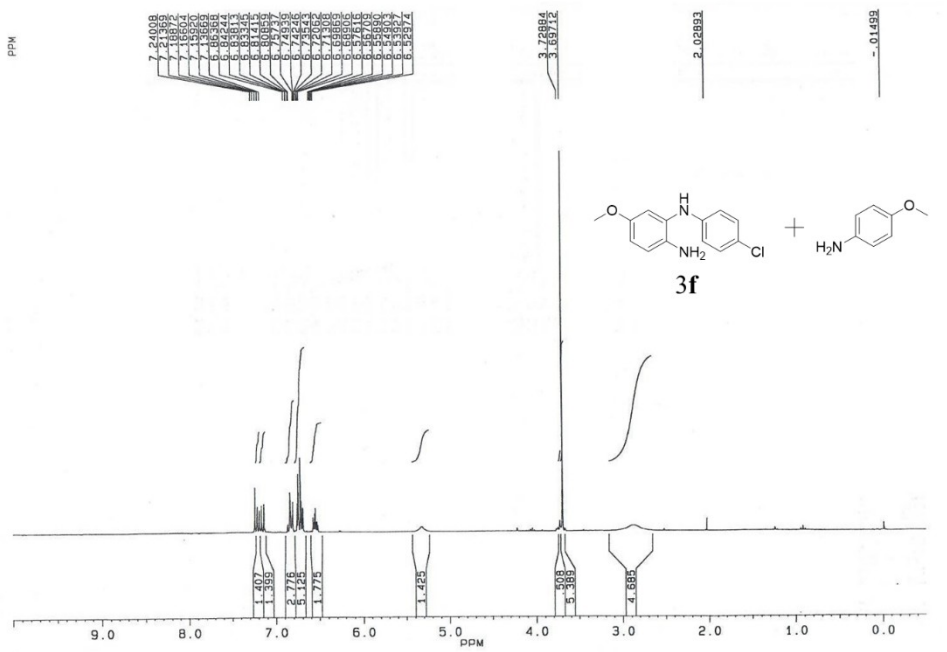
***N*^{2}-(4-fluorophenyl)-4-methoxybenzene-1,2-diamine (3e)**: **^{1}H-NMR** (300 MHz, $CDCl_3$)



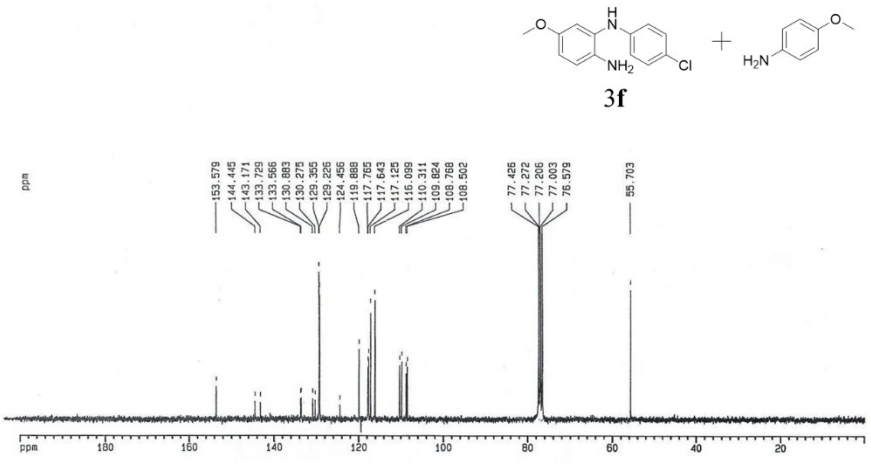
***N*^{2}-(4-fluorophenyl)-4-methoxybenzene-1,2-diamine (3e)**: **^{13}C-NMR** (75 MHz, $CDCl_3$)



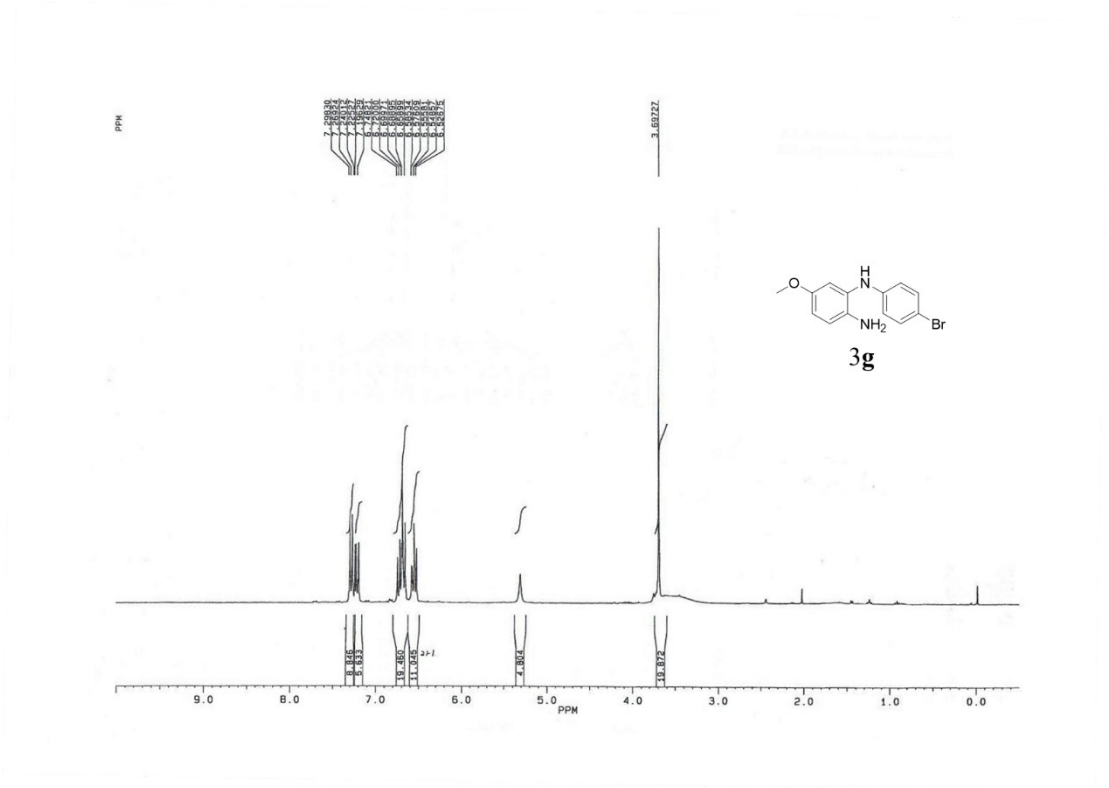
***N*^{2}-(4-chlorophenyl)-4-methoxybenzene-1,2-diamine (3f)**: **^{1}H-NMR** (300 MHz, $CDCl_3$)



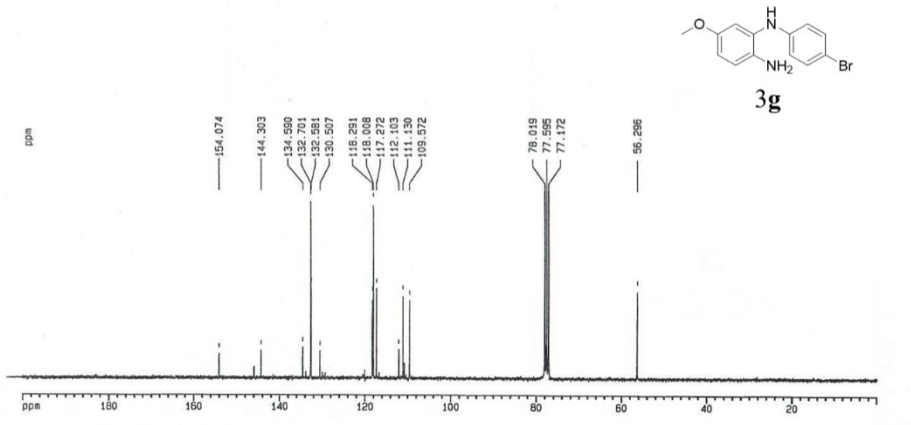
***N*^{2}-(4-chlorophenyl)-4-methoxybenzene-1,2-diamine (3f)**: **^{13}C-NMR** (75 MHz, $CDCl_3$)



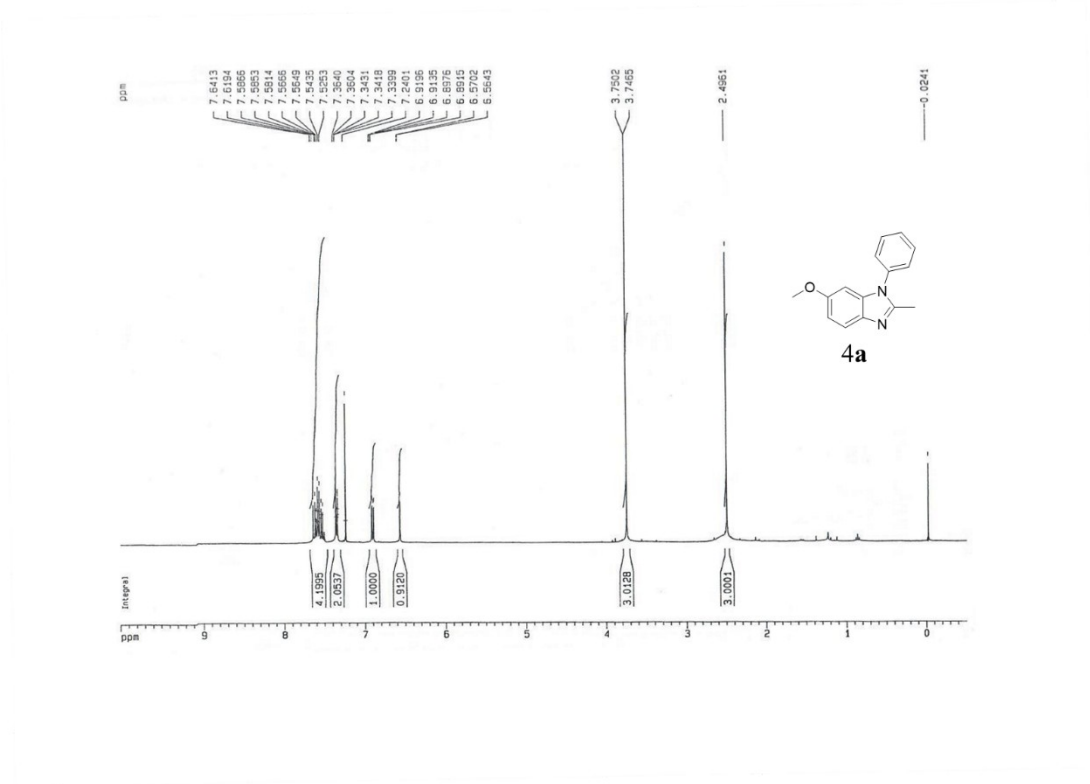
N^2-(4-bromophenyl)-4-methoxybenzene-1,2-diamine (**3g**): **^{1}H-NMR** (300 MHz, $CDCl_3$)



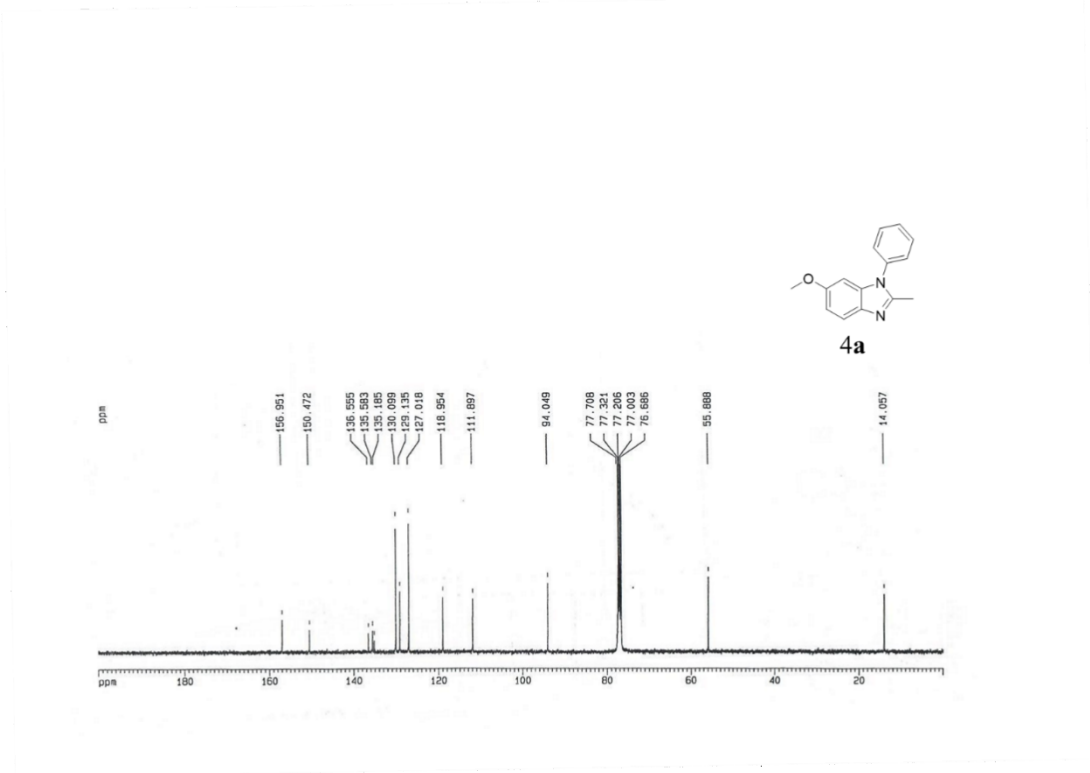
N^2-(4-bromophenyl)-4-methoxybenzene-1,2-diamine (**3g**): **^{13}C-NMR** (75 MHz, $CDCl_3$)



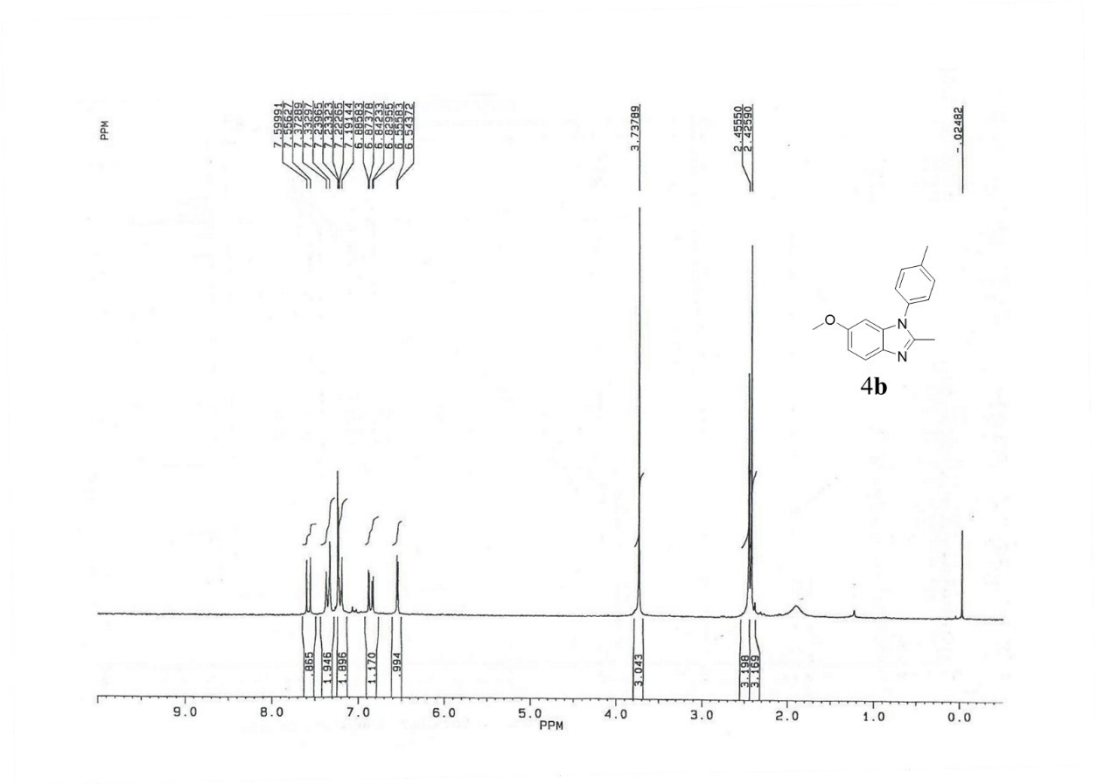
6-methoxy-2-methyl-1-phenyl-1*H*-benzimidazole (**4a**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



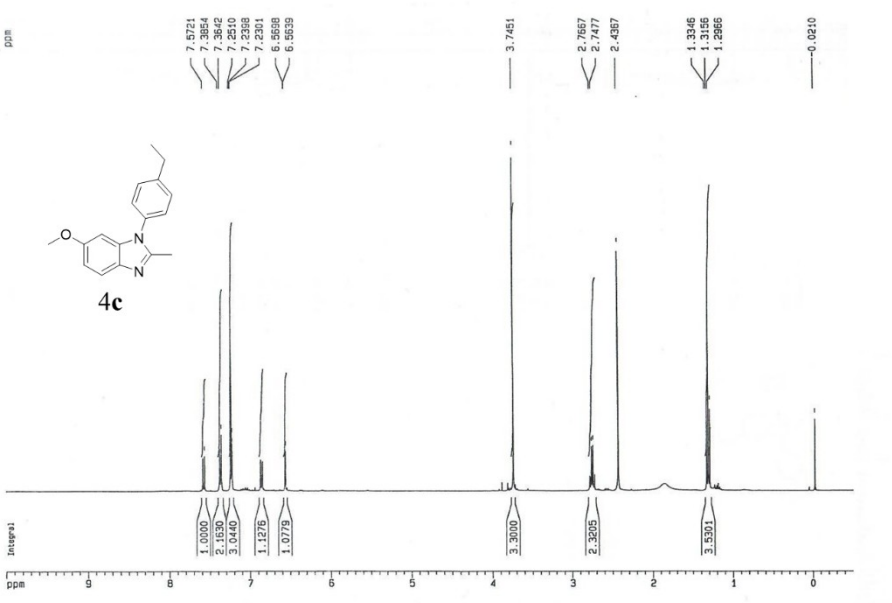
6-methoxy-2-methyl-1-phenyl-1*H*-benzimidazole (**4a**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



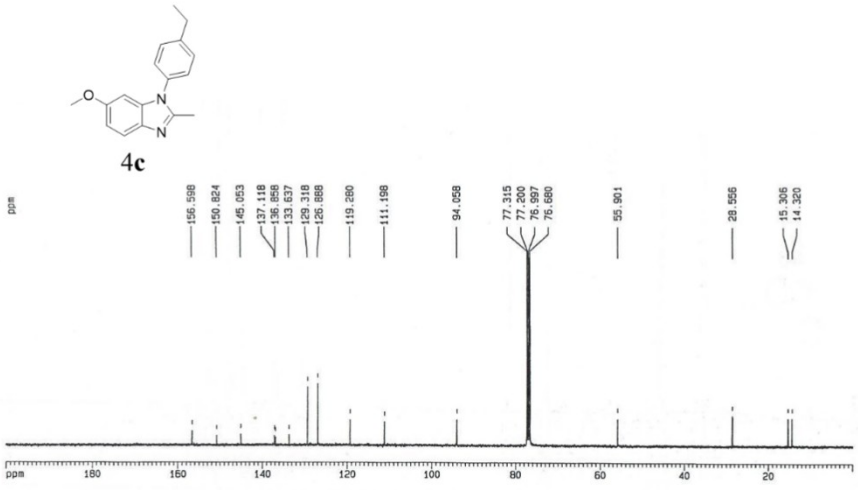
6-methoxy-2-methyl-1-(*p*-tolyl)-1*H*-benzimidazole (**4b**): **^{1}H-NMR** (200 MHz, $CDCl_3$)



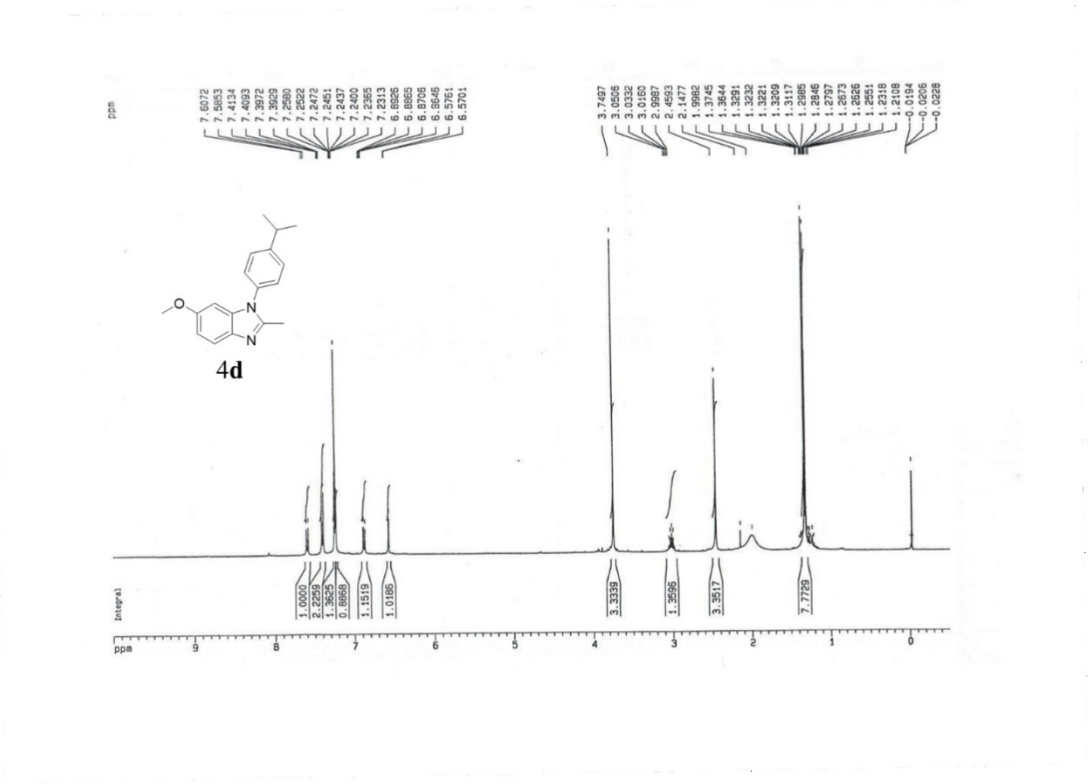
1-(4-ethylphenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4c**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



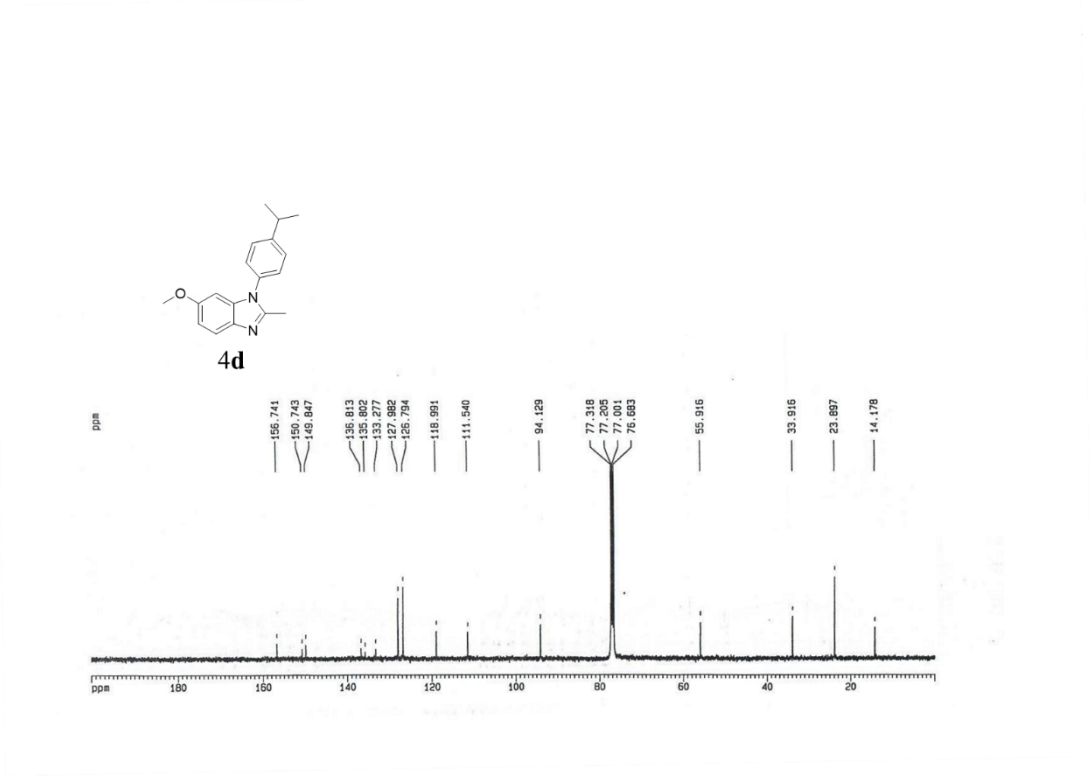
1-(4-ethylphenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4c**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



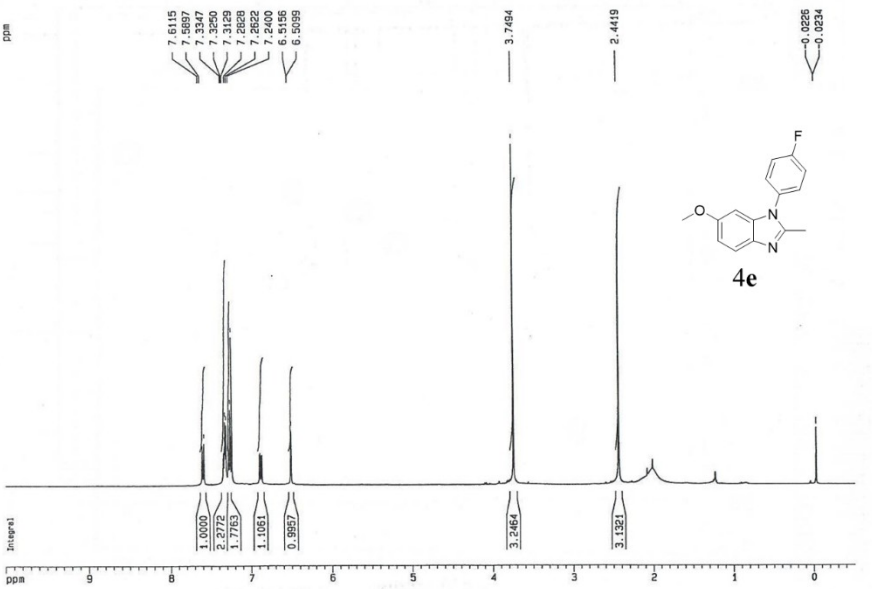
1-(4-isopropylphenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4d**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



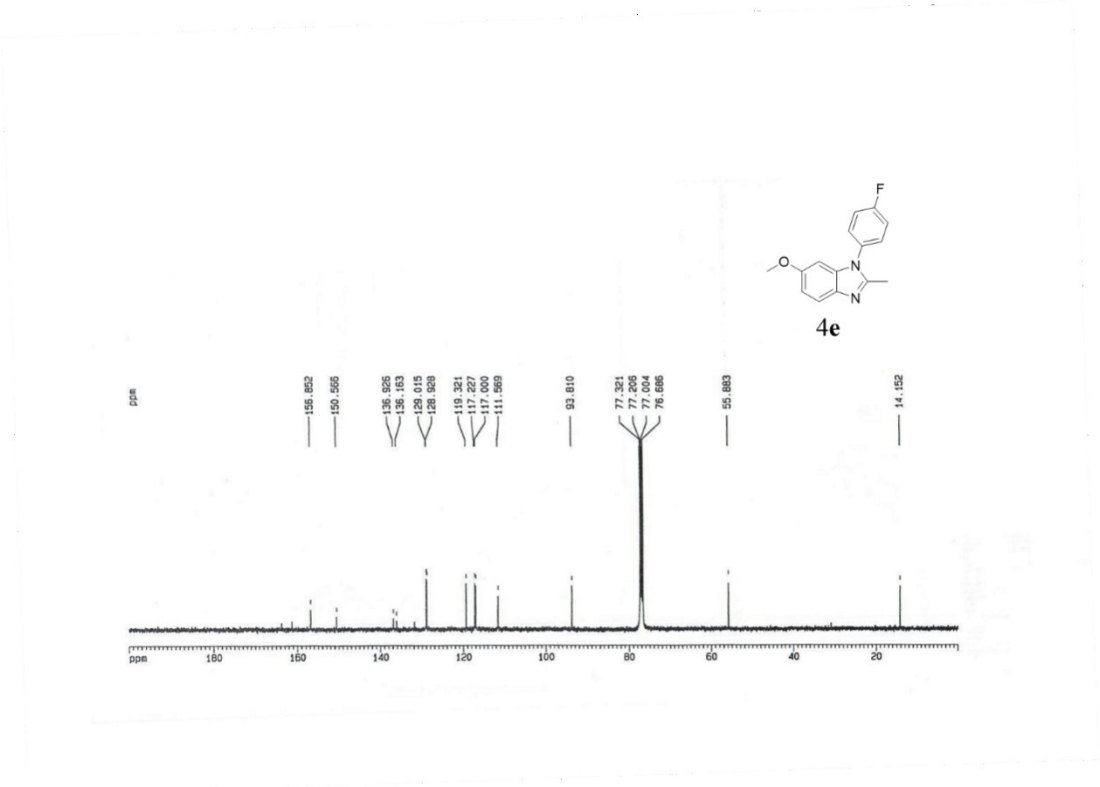
1-(4-isopropylphenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4d**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



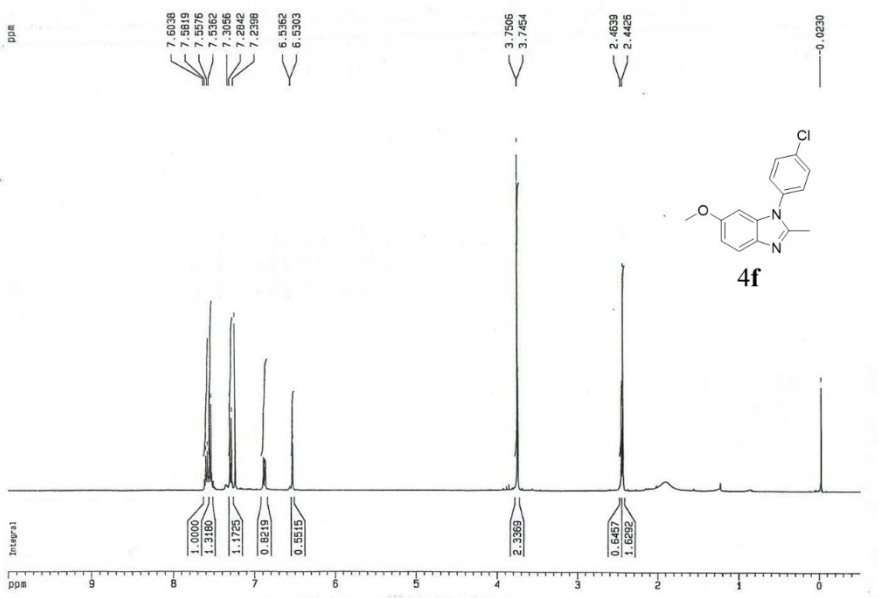
1-(4-fluorophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4e**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



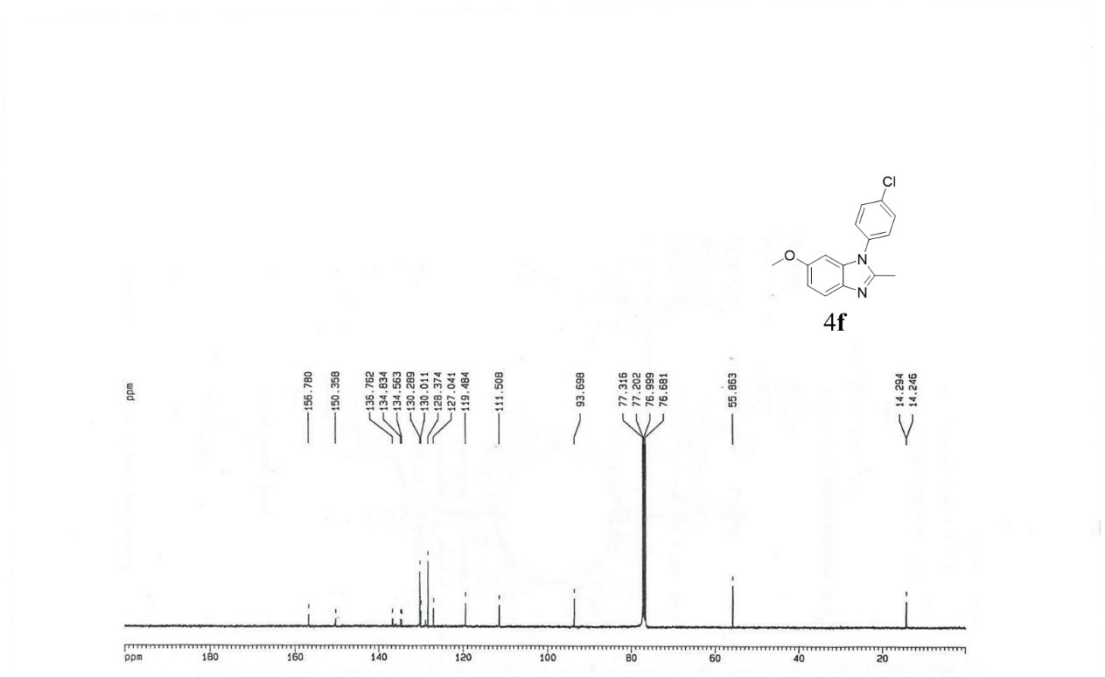
1-(4-fluorophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4e**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



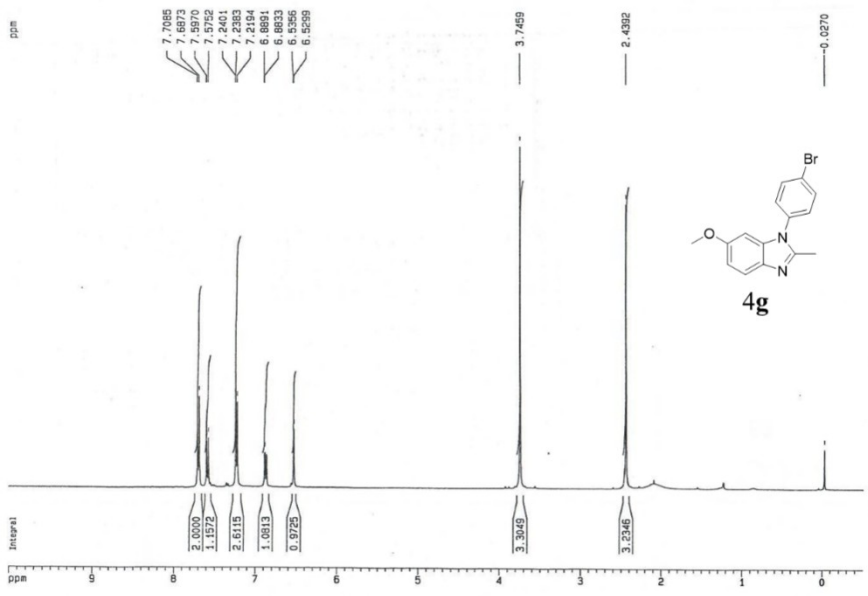
1-(4-chlorophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4f**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



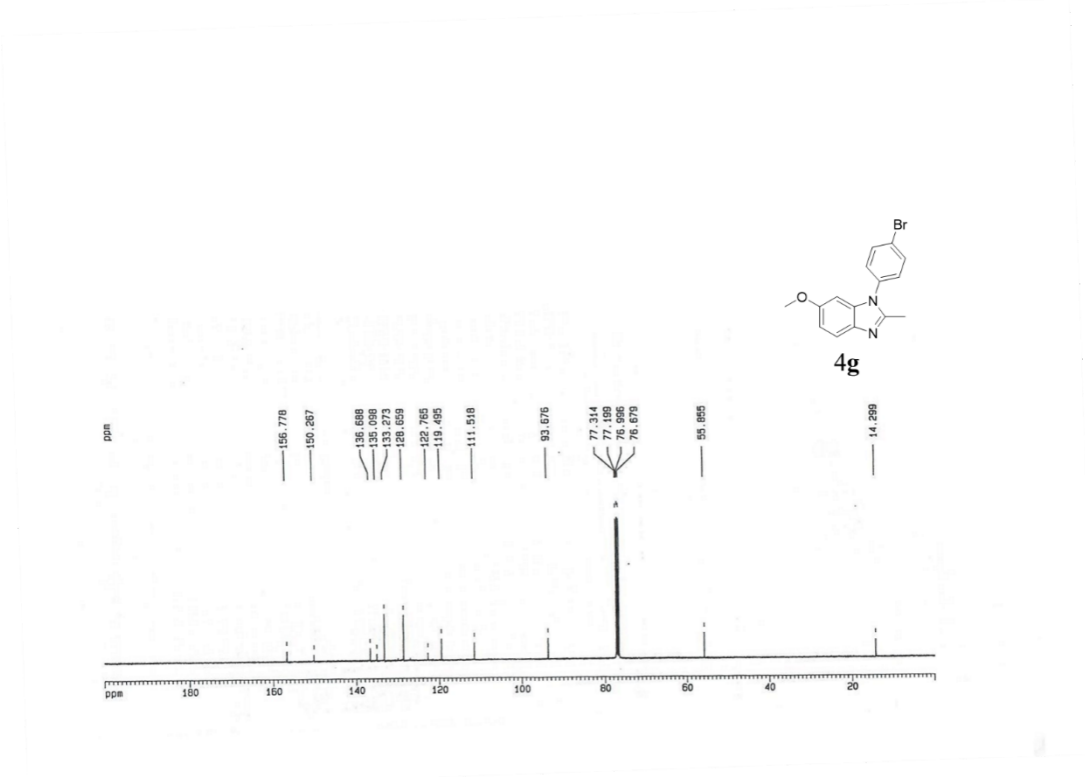
1-(4-chlorophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4f**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



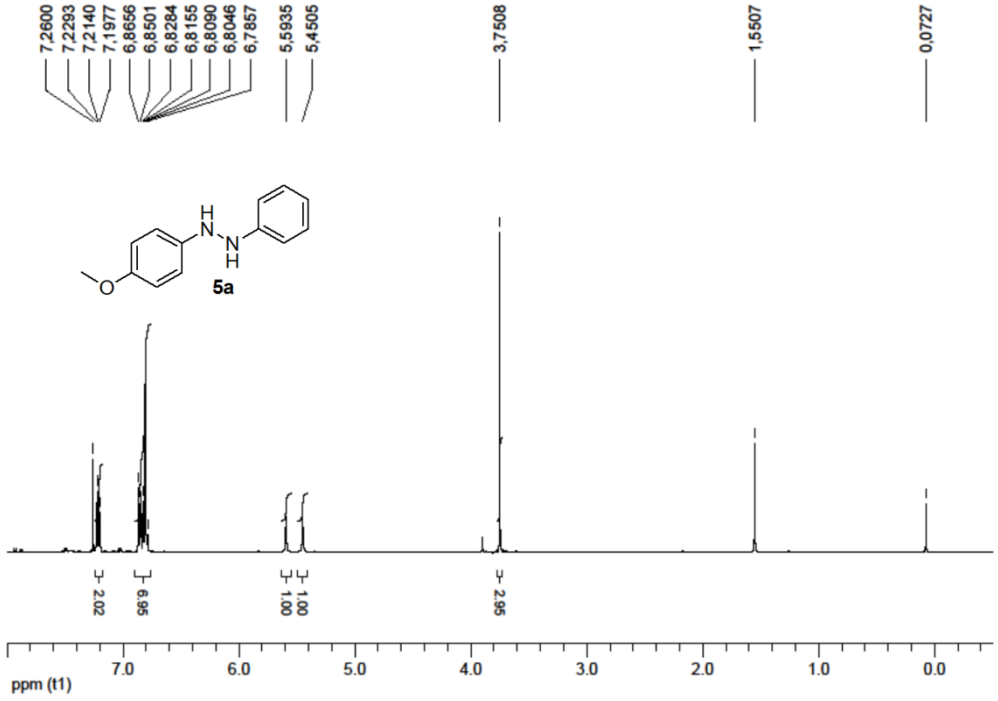
1-(4-bromophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4g**): **^{1}H-NMR** (400 MHz, $CDCl_3$)



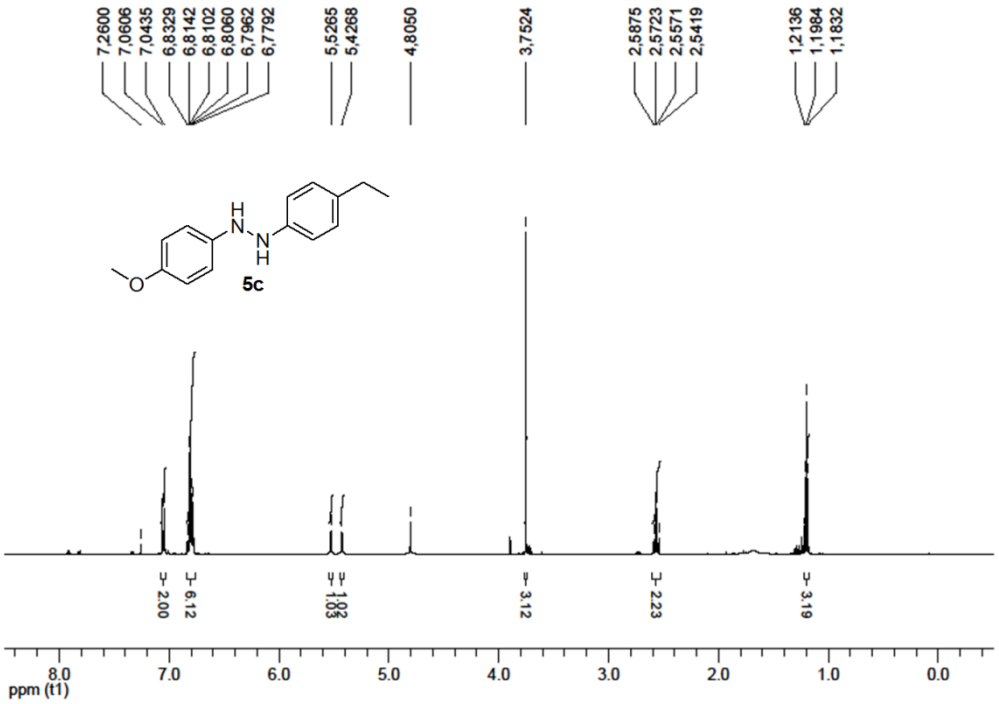
1-(4-bromophenyl)-6-methoxy-2-methyl-1*H*-benzimidazole (**4g**): **^{13}C-NMR** (100 MHz, $CDCl_3$)



4-Methoxyhydrazobene (**5a**): **^{1}H-NMR** (500 MHz, $CDCl_3$)



4-Ethyl-4'-methoxyhydrazobene (5c): **^{1}H-NMR** (500 MHz, $CDCl_3$)



4-Ethyl-4'-methoxyhydrazobene (5c): **^{13}C-NMR** (125 MHz, $CDCl_3$)