Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Base-Catalyzed Synthesis of Amides and Imines *via* C C and C=C Bond Cleavage

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1. General information:

Materials and Method:

All chemicals and reagents were purchased from Sigma Aldrich, S. D. fine chemical, Alfa Aesar and commercial suppliers. Solvents were purchased from commercial suppliers and used without purification. Reaction monitor by using Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm, column flow 2 $mLmin^{-1}$, 80 °C to 240 °C at 10 °C/min rise) was used for the mass analysis of the products. Products were purified by column chromatography on silca (100-200 mesh) and basic alumina. The ^{1}H NMR spectrum was recorded on Bruker-400 MHz and 500 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. The ^{13}C NMR spectrum was recorded on Bruker-100 MHz and 125 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. *J* (coupling constant) values were reported in Hz. Splitting patterns of proton are described as s (singlet), d (doublet), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC-MS spectra, and/or ^{1}H and ^{13}C NMR spectra with those of authentic data.

2. General procedure for the synthesis of amide from *N*-arylurea and 1,3-dicarbonyl:

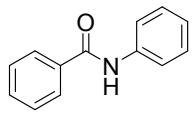
A 20 mL schlenk tube equipped with magnetic stirring bar was charged with *N*-arylurea (1 mmol), 1,3-dicarbonyl (1.5 mmol), KOH (0.4 mmol) and was placed in a preheated oil bath for 24 h at 135 °C. After cooling down reaction mixture to room temperature, it was extracted with ethyl acetate (3×5 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The crude product was directly purified by column chromatography (silica gel, 100-200 mesh, PE–EtOAc) to furnish the corresponding pure product. The identity of product was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.

3. General procedure for the synthesis of imine from *N*-arylurea and α,β-unsaturated ketone:

A mixture of *N*-arylurea (1 mmol), α,β-unsaturated ketone (1.5 mmol), KOH (0.4 mmol) was heated at 135 °C for 24 h in a sealed 20 mL schlenk tube. After cooling the reaction mixture to room temperature, it was extracted with ethyl acetate (3×5 mL), combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduce pressure to afford the crude product. The crude product was purified by column chromatography (basic alumina saturated with Et_3N, 100-200 mesh, PE) to provide the desired pure product. The identity of product was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.

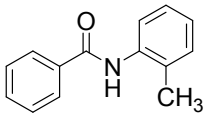
4. Spectral data of compounds:

***N*-phenylbenzamide (3a)[1]**



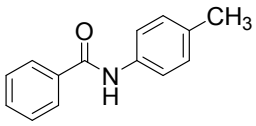
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.88 (d, 2H, J = 7.92 Hz), 7.72 (d, 2H, J = 7.68 Hz), 7.48-7.37 (m, 3H), 7.23 (t, 2H, J = 8 Hz), 6.99 (t, 1H, J = 7.16 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.65, 138.95, 135.01, 131.06, 128.21, 127.91, 127.47, 123.40, 120.29 ppm. GC-MS (EI): *m/z* 197 (30) $[M]^+$, 105 (100), 77 (55), 51 (13).

***N*-(*o*-tolyl)benzamide (3b)[1]**



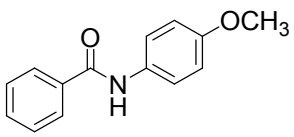
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.48-7.41 (m, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.11 (d, J = 7.4 Hz, 2H), 7.01 (t, J = 6.4 Hz, 1H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.94, 135.77, 134.90, 131.85, 130.60, 130.14, 128.81, 127.17, 126.84, 125.55, 123.59, 17.88 ppm. GC-MS (EI): *m/z* 211 (31) $[M]^+$, 105 (100), 77 (90), 51 (9).

***N*-(*p*-tolyl)benzamide (3c)[1]**



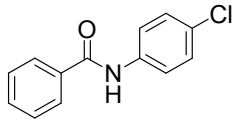
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.84 (d, J = 7.2 Hz, 2H), 7.53-7.49 (m, 3H), 7.43 (t, J = 7.76 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.74, 135.41, 135.10, 134.22, 131.70, 129.57, 128.72, 127.04, 120.38, 20.92 ppm. GC-MS (EI): *m/z* 211 (30) $[M]^+$, 105 (100), 77 (50), 51 (9).

***N*-(4-metoxyphenyl)benzamide (3d)[1]**



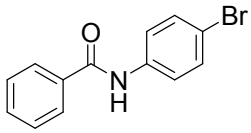
^{1}H NMR (400MHz, $CDCl_3$): δ 7.86 (d, J = 7.2 Hz, 2H), 7.55-7.52 (m, 3H), 7.52-7.51 (m, 2H), 6.89 (d, J = 6.8 Hz, 2H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.72, 156.64, 135.02, 131.73, 131.00, 128.76, 127.01, 122.16, 114.25, 55.52 ppm. GC-MS (EI): *m/z* 227 (56) $[M]^+$, 105 (100), 77 (62), 51 (11).

_N_-(4-chlorophenyl)benzamide (3e)[1]



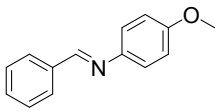
^{1} H NMR (400 MHz, $CDCl_3$): δ = 10.24 (s, 1H), 7.95 (d, J = 7.44 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.56-7.46 (m, 3H), 7.24 (d, J = 8.7 Hz, 2H) ppm. GC-MS (EI): *m/z* 233 (6) $[M + 2]^+$, 231 (18) $[M]^+$, 105 (100), 77 (46), 51 (10).

_N_-(4-bromophenyl)benzamide (3f)[1]



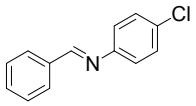
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.21 (s, 1H), 7.95 (d, J = 7.0 Hz, 2H), 7.77 (d, J = 6.9 Hz, 2H), 7.56-7.41 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.68, 138.30, 134.72, 131.21, 131.00, 127.93, 127.47, 121.90, 115.38 ppm. GC-MS (EI): *m/z* 277 (1) $[M + 2]^+$, 275 (1) $[M]^+$, 105 (100), 77 (4), 51 (1).

_N_-benzylidene-4-methoxyaniline (5d)[2]



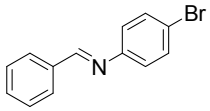
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.89-7.87 (m, 2H), 7.45 – 7.43 (m, 3H), 7.23 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.45, 158.31, 144.92, 136.47, 131.08, 128.77, 128.62,122.25, 114.41, 55.51 ppm. GC-MS (EI): *m/z* 211 (90) $[M]^+$, 196 (100), 167 (23), 141(13), 77 (14), 51 (4).

***N*-benzylidene-4-chloroaniline (5e)[2]**



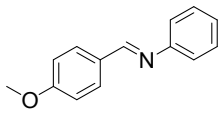
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.86−7.90 (m, 2H), 7.45−7.51 (m, 5H), 7.06 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 150.5, 135.9, 131.6, 131.4, 129.2, 128.9, 128.8, 122.2 ppm. GC-MS (EI): *m/z* 217 (31) $[M + 2]^+$, 215 (100) $[M]^+$, 138 (18), 111 (45), 89 (18), 75 (32), 63 (7), 51 (11).

***N*-benzylidene-4-bromoaniline (5f)[2]**



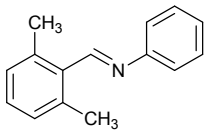
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1 H), 7.89-7.87 (m, 2 H), 7.50-7.47 (m, 5 H), 7.08-7.06 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.81, 151.02, 135.95, 132.22, 131.69, 128.93, 128.87, 122.64, 119.95 ppm. GC-MS (EI): *m/z* 261 (32) $[M + 2]^+$, 259 (32) $[M]^+$, 258 (30),179 (18), 155 (35), 91 (22), 77 (36), 76 (100), 51 (89).

***N*-(4-methoxybenzylidene)aniline (5h)[2]**



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.36 (t, J = 8.1 Hz, 2H), 7.21-7.19 (m, 3H), 6.96 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.28, 159.76, 152.39, 130.56, 129.29,129.15, 125.61, 120.93, 114.22, 55.45 ppm. GC-MS (EI): *m/z* 211 (25) $[M]^+$, 210 (100), 195 (8), 167 (14), 77 (52), 51 (15).

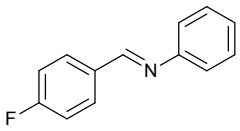
***N*-(2,6-dimethylbenzylidene)aniline (5i)**



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.46-7.43 (m, 2H), 7.28-7.24 (m, 4H), 7.23-7.13 (m, 2H), 2.59 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0, 152.8, 138.3, 133.4,

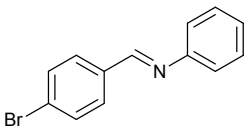
129.7,129.6, 129.1, 125.7, 120.7, 20.9 ppm. GC-MS (EI): *m/z* 209 (55) $[M]^+$, 208 (57), 192 (100), 178 (12), 165 (9),132 (70),117 (26),115 (12),104 (20), 91(20), 77 (87), 51 (40).

_N_-(4-Fluorobenzylidene)aniline (5k)[3]



^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.92-7.89 (m, 2H), 7.42-7.38 (m, 2H), 7.25-7.14 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.7 (d, *J* C-F = 250Hz), 158.7, 151.8, 132.6 (d, *J* C-F = 3 Hz), 130.8 (d, *J* C-F = 9 Hz), 129.1, 126.0, 120.8, 115.9 (d, *J* C-F = 22 Hz). GC-MS (EI, 70 eV): *m/z* (%) = 199 (80) $[M]^+$, 198 (100), 170 (3), 107 (9), 104 (17), 89 (9), 77 (89), 51 (36).

_N_-(4-bromobenzylidene)aniline (5n)[2]



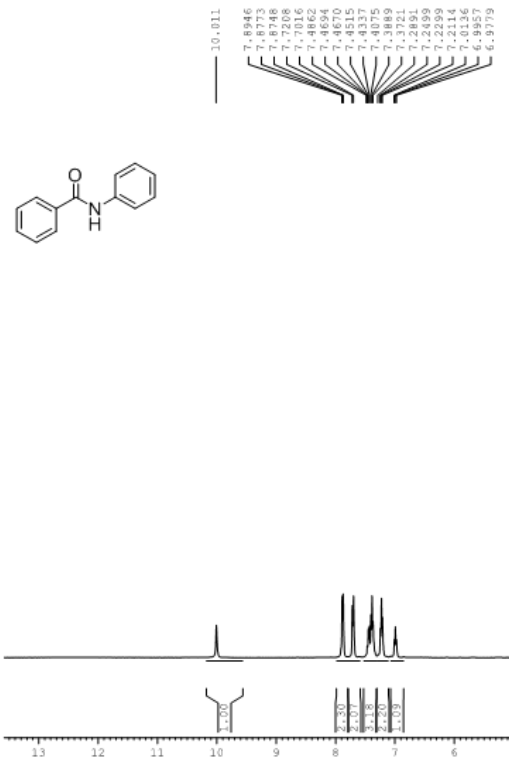
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.41 (s, 1 H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.42-7.39 (m, 2 H), 7.25-7.21 (m, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.9, 151.6, 135.1, 132.0, 130.1, 129.2, 126.2, 125.9, 120.8 ppm. GC-MS (EI): *m/z* (%) 261 (39), 260 (37), 259 (40), 258 (35), 179 (8), 152 (4), 126 (1),104 (18), 89 (17), 77 (100), 63 (6), 51 (28).

5. References:

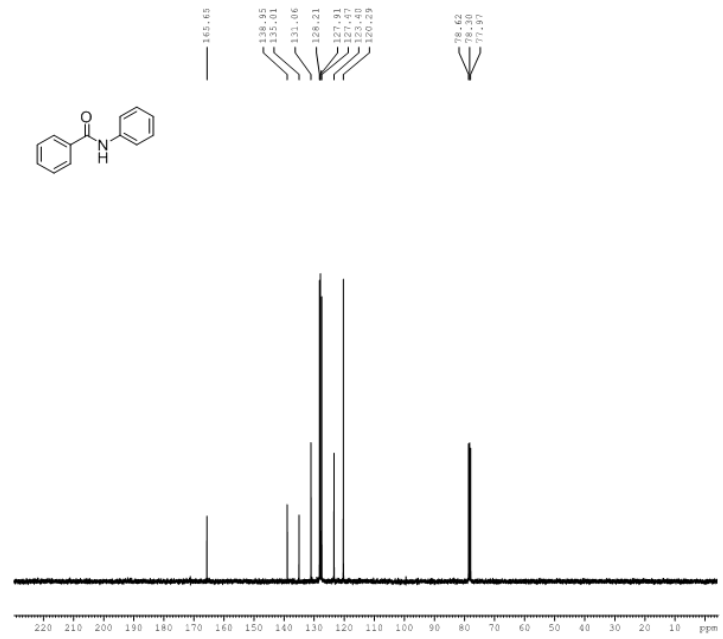
1. F. Xiao, Y. Liu, C. Tang and G.-J. Deng, *Org. Lett.*, 2012, **14**, 984.
2. Y.-S. Lan, B.-S. Liao, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Eur. J. Org. Chem.,* 2013, 5160.
3. E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.* 2013, **15**, 2704.

6. Copies of ^{1}H NMR and ^{13}C NMR Spectra:

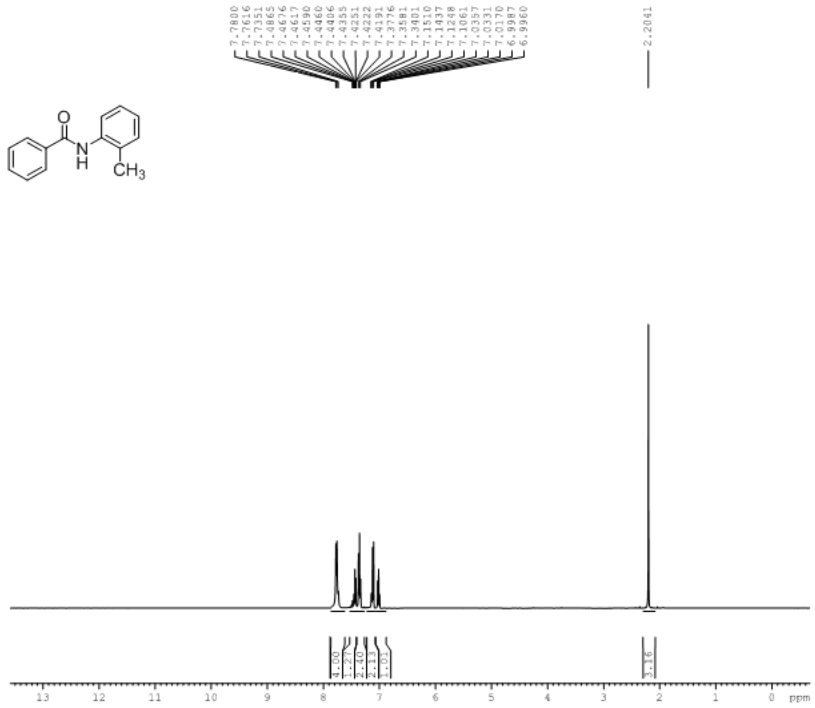
N-phenylbenzamide ^{1}H NMR (3a)



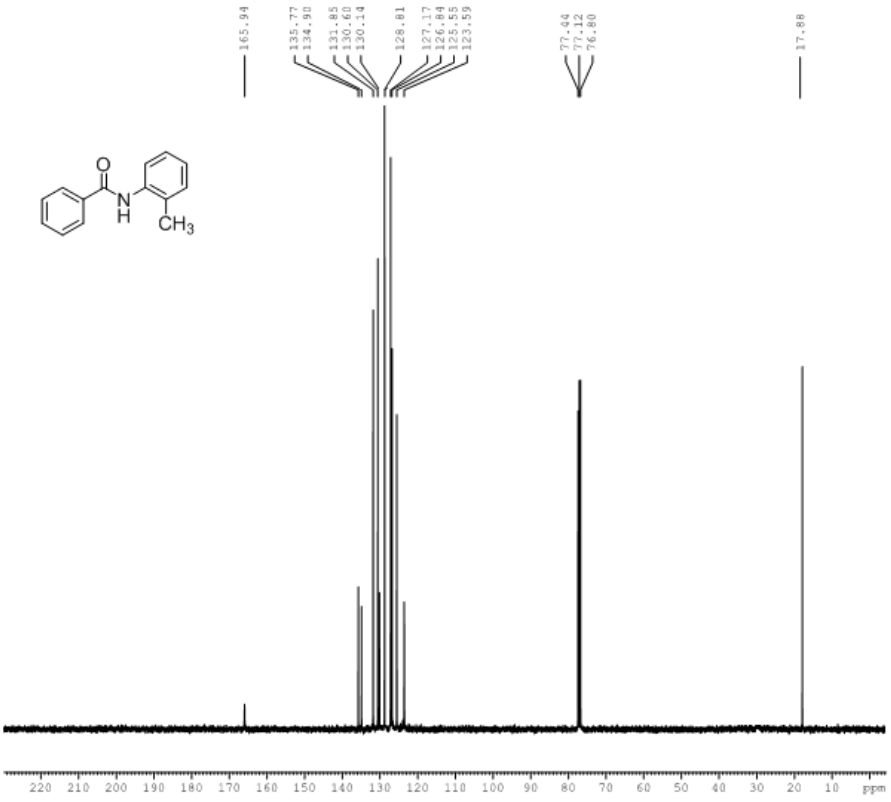
N-phenylbenzamide ^{13}C NMR (3a)



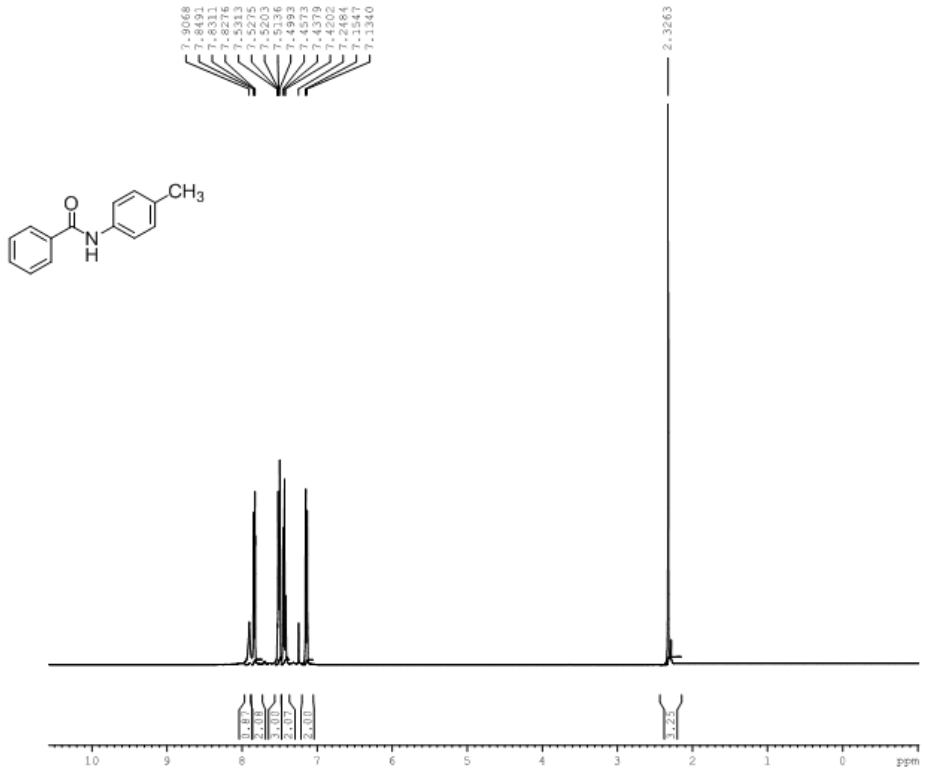
***N*-(*o*-tolyl)benzamide ^{1}H NMR (3b)**



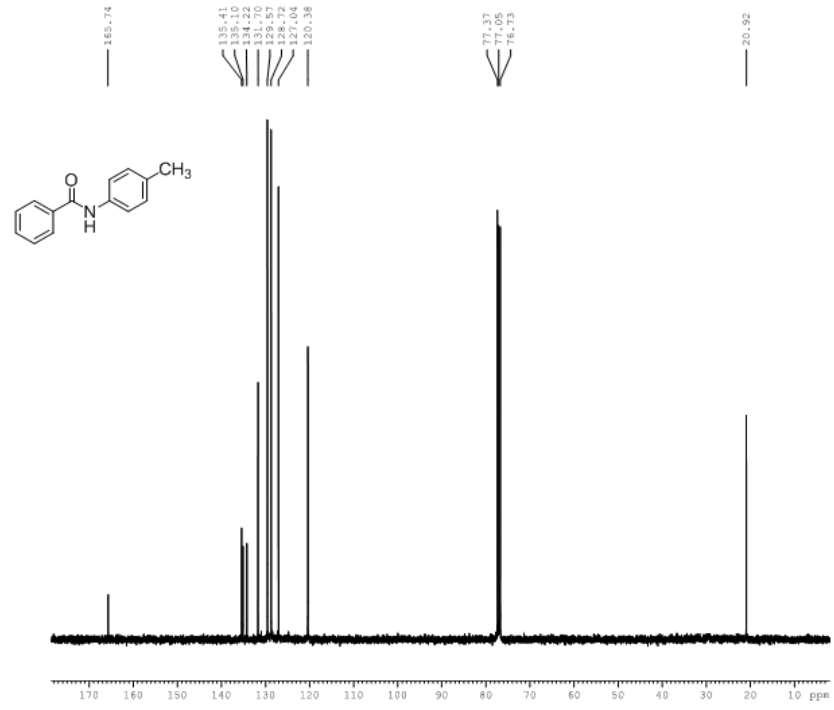
***N*-(*o*-tolyl)benzamide ^{13}C NMR (3b)**



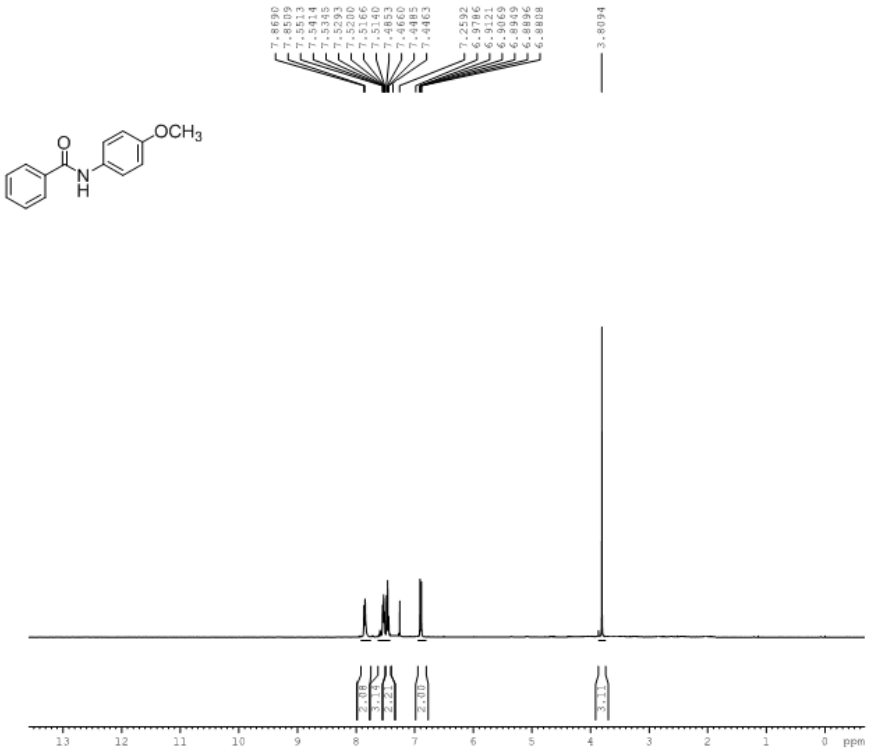
***N*-(*p*-tolyl)benzamide ^{1}H NMR (3c)**



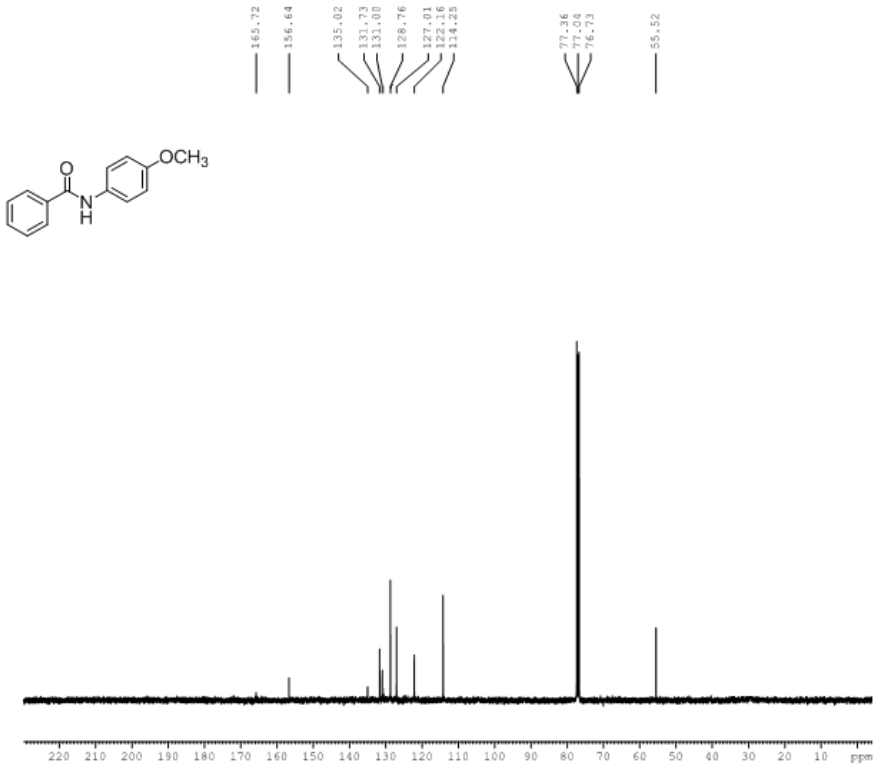
***N*-(*p*-tolyl)benzamide ^{13}C NMR (3c)**



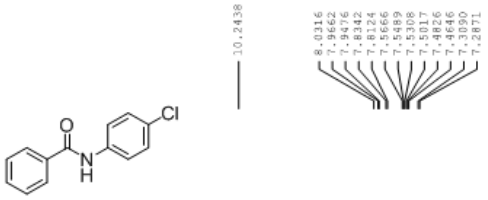
***N*-(4-metoxyphenyl)benzamide ^{1}H NMR (3d)**

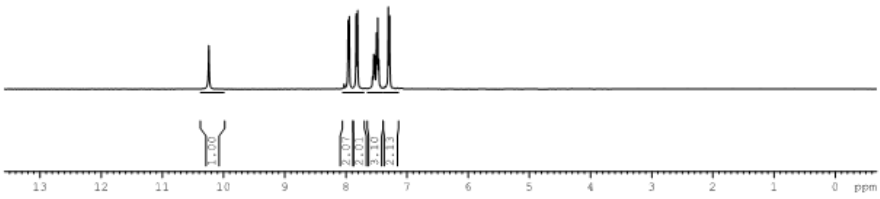


***N*-(4-metoxyphenyl)benzamide ^{13}C NMR (3d)**

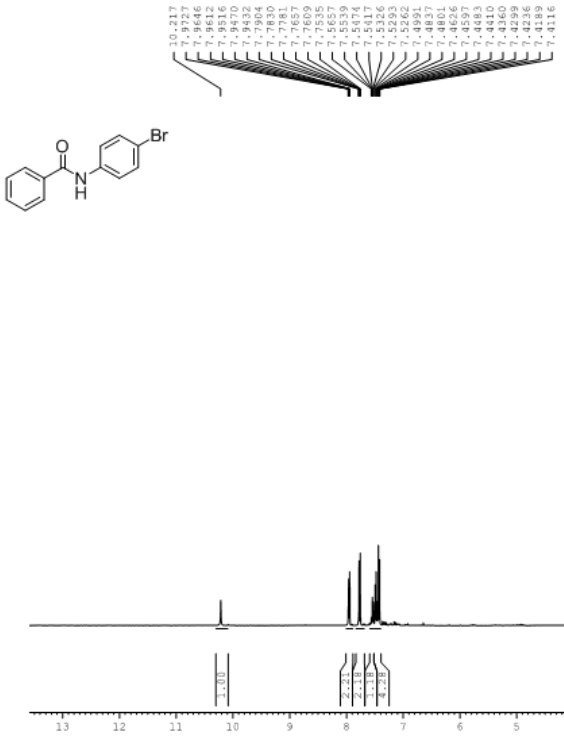


***N*-(4-chlorophenyl)benzamide ^{1}H NMR (3e)**

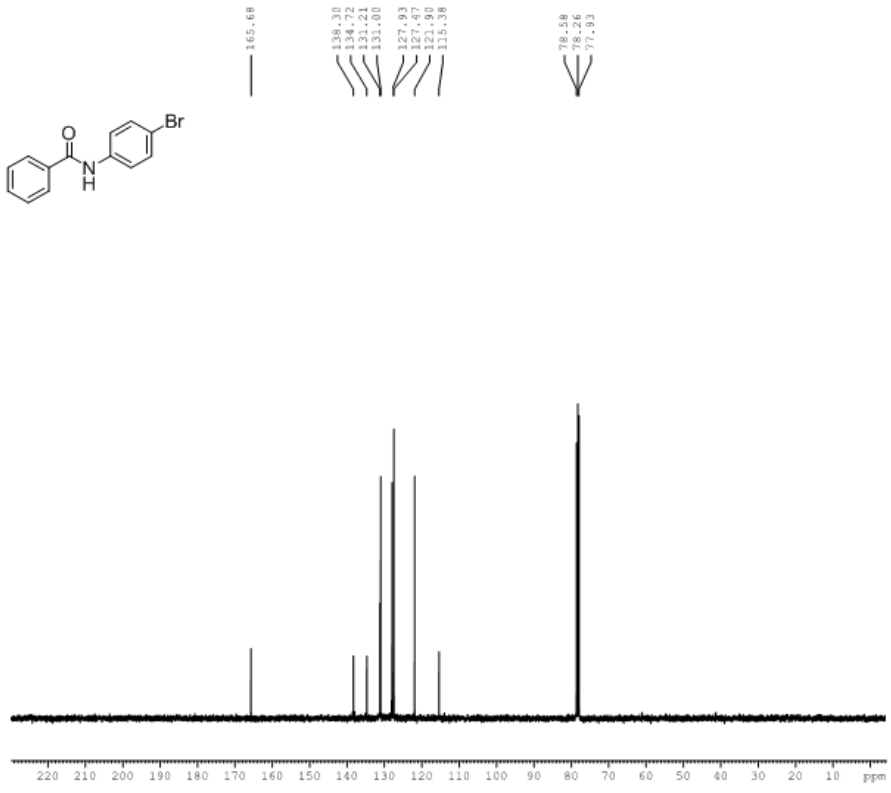




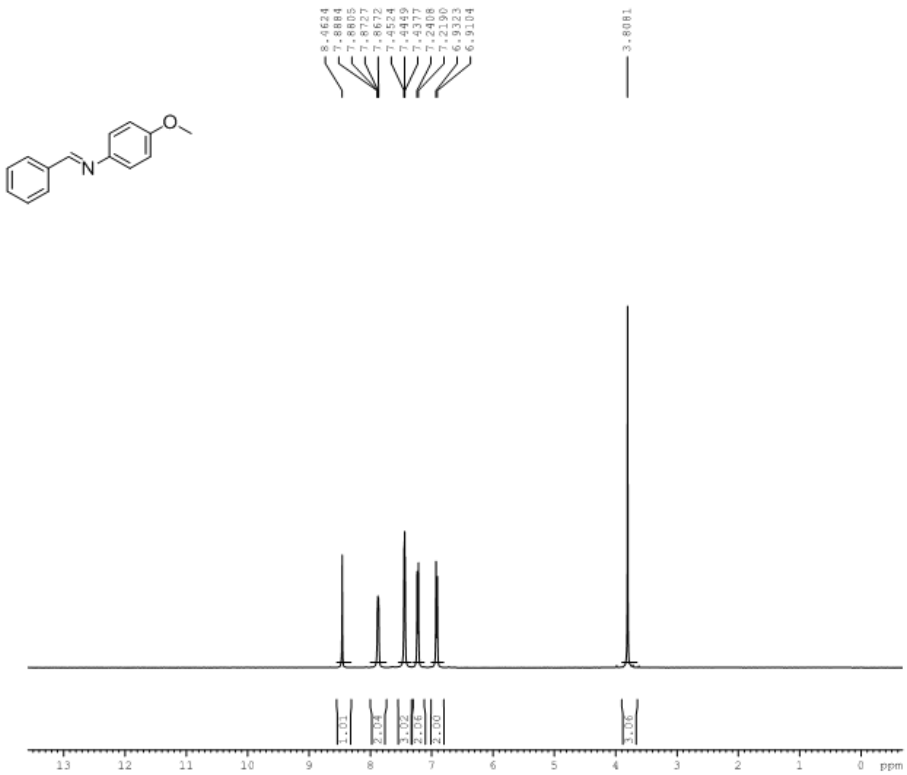
***N*-(4-bromophenyl)benzamide ^{1}H NMR (3f)**



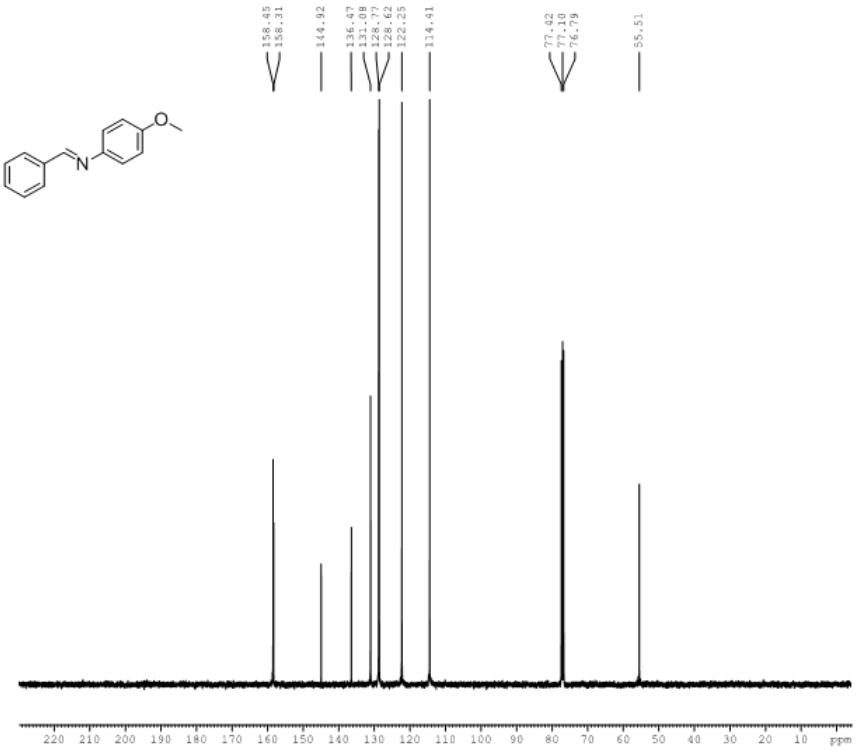
***N*-(4-bromophenyl)benzamide ^{13}C NMR (3f)**



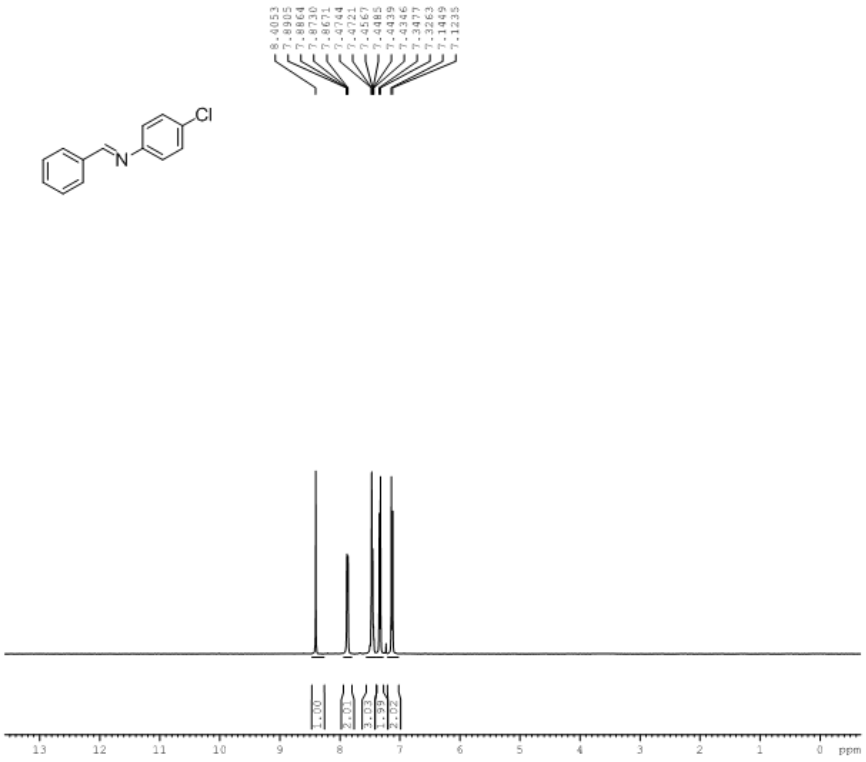
***N*-benzylidene-4-methoxyaniline ^{1}H NMR (5d)**



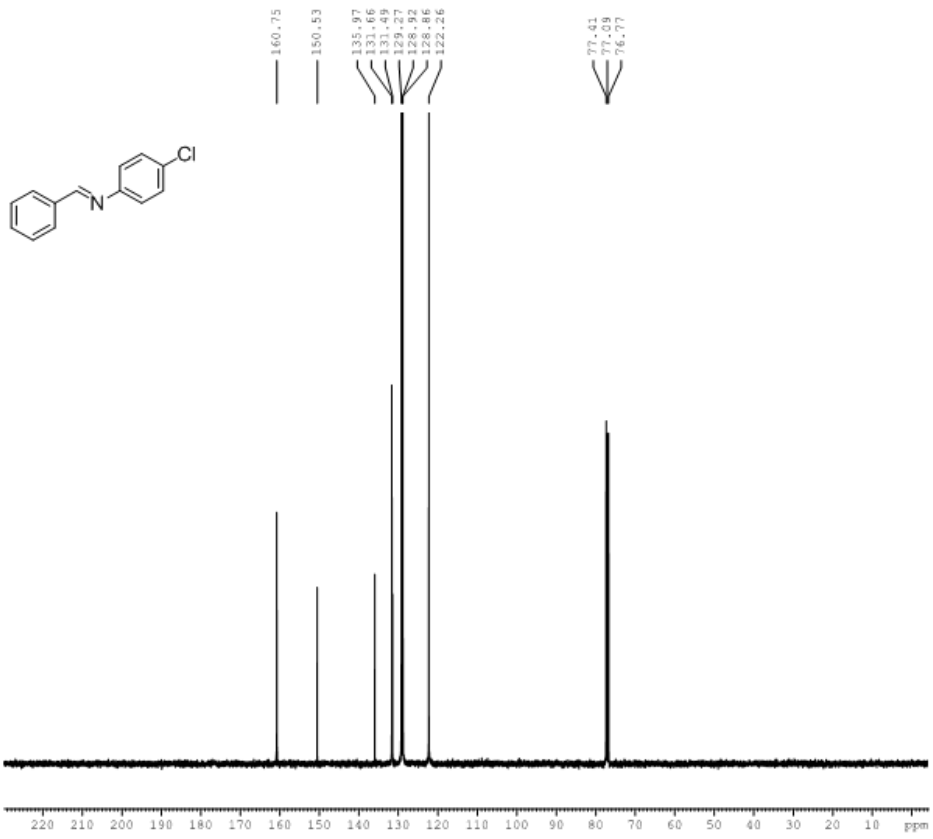
***N*-benzylidene-4-methoxyaniline ^{13}C NMR (5d)**



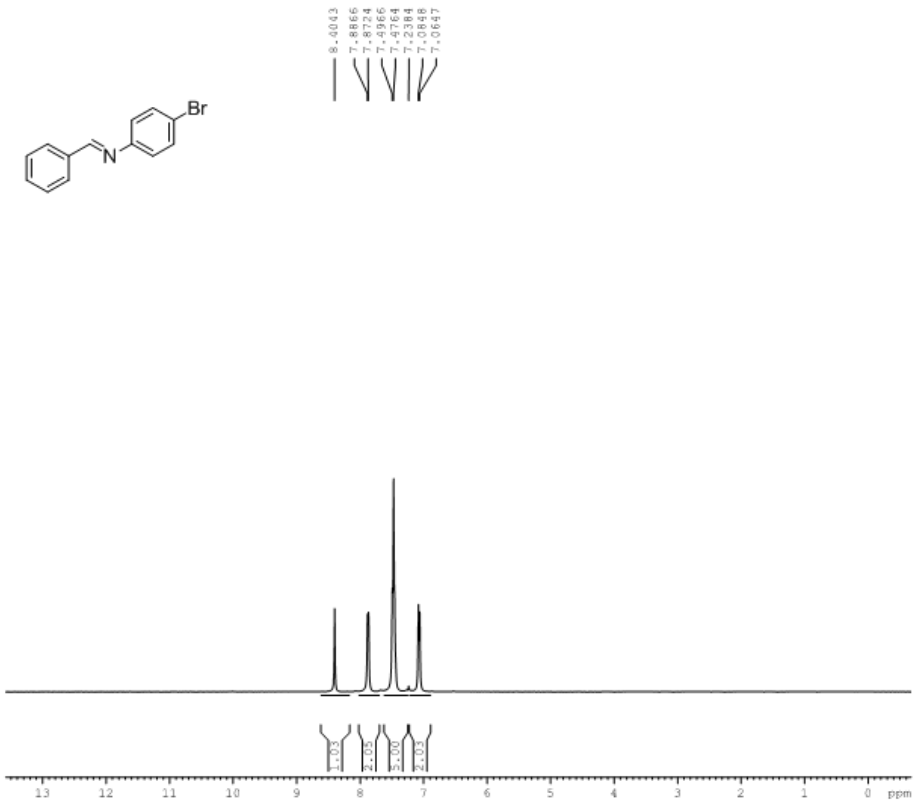
***N*-benzylidene-4-chloroaniline ^{1}H NMR (5e)**



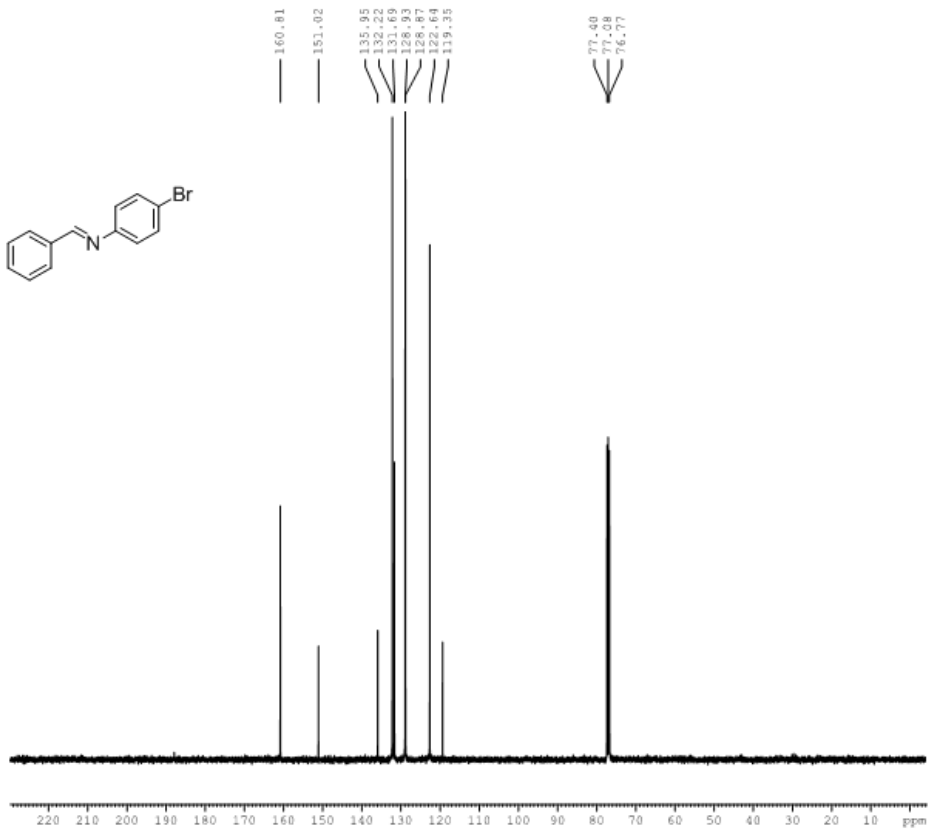
***N*-benzylidene-4-chloroaniline ^{13}C NMR (5e)**



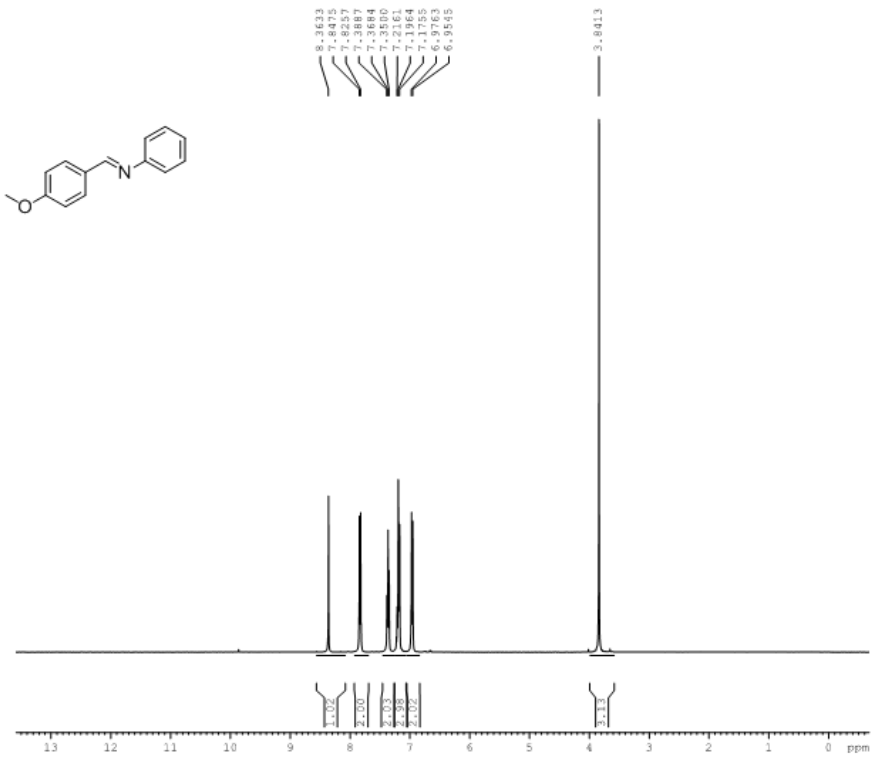
***N*-benzylidene-4-bromoaniline ^{1}H NMR (5f)**



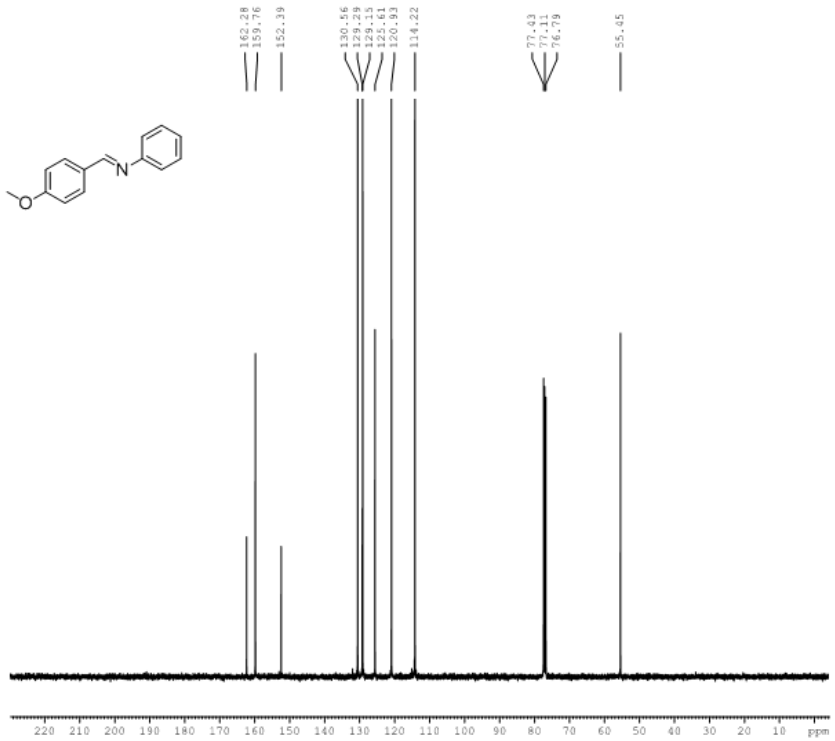
***N*-benzylidene-4-bromoaniline ^{13}C NMR (5f)**



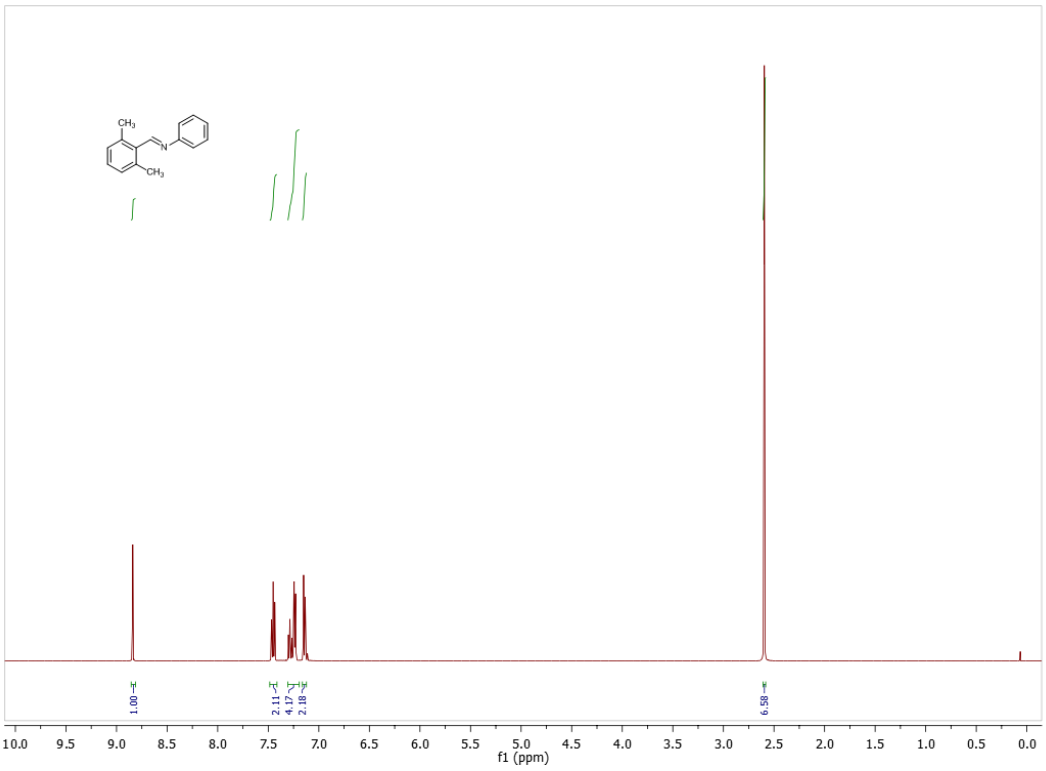
***N*-(4-methoxybenzyledine)aniline ^{1}H NMR (5h)**



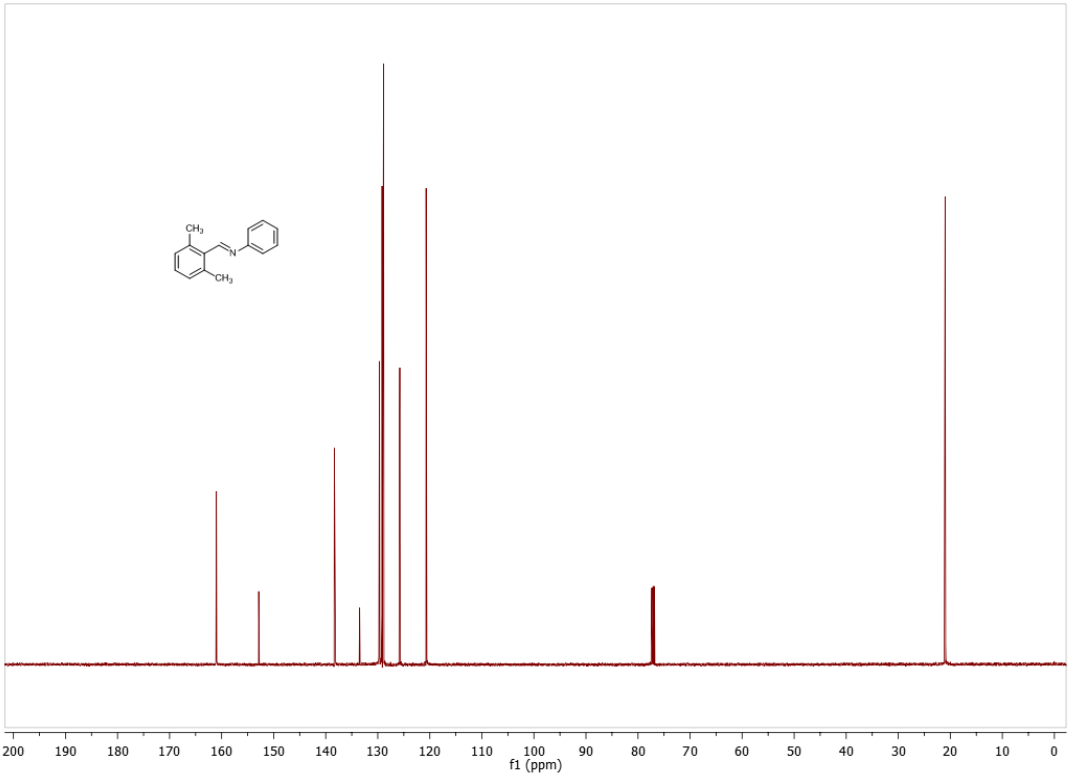
***N*-(4-methoxybenzylidene)aniline ^{13}C NMR (5h)**



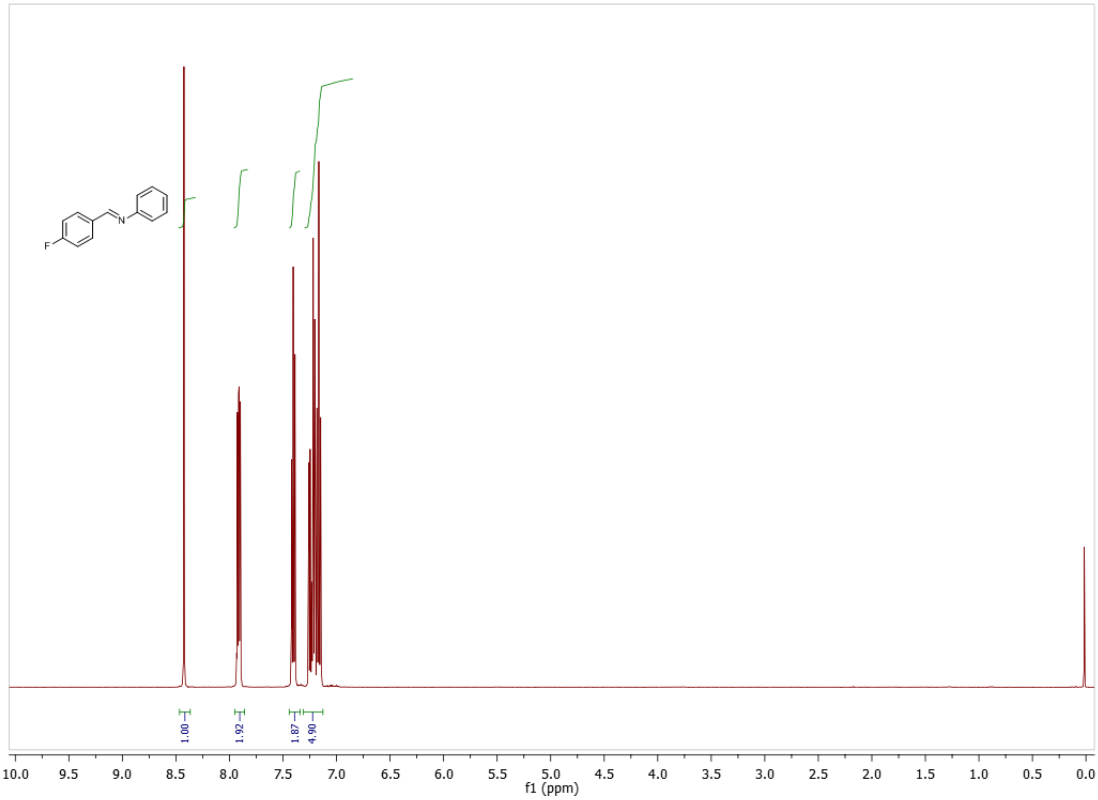
***N*-(2,6-dimethylbenzylidene)aniline ^{1}H NMR (5i)**



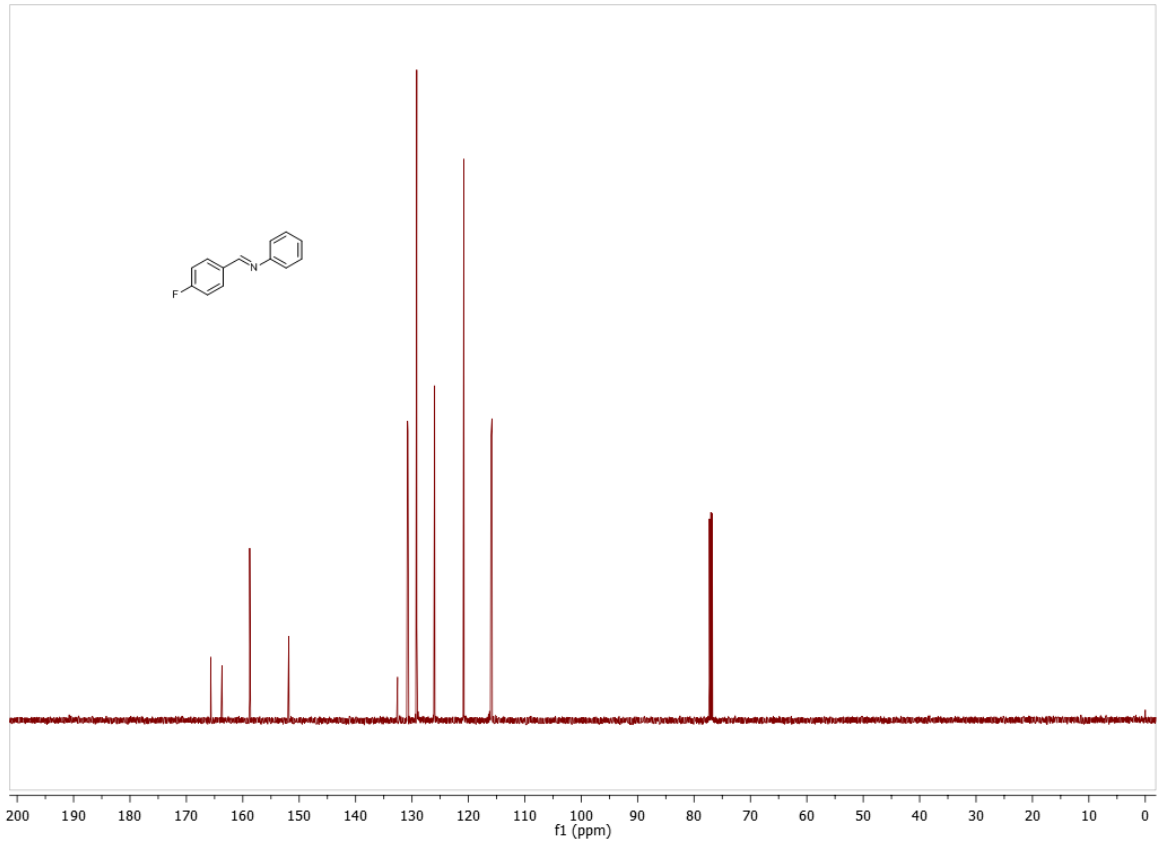
***N*-(2,6-dimethylbenzylidene)aniline ^{13}C NMR (5i)**



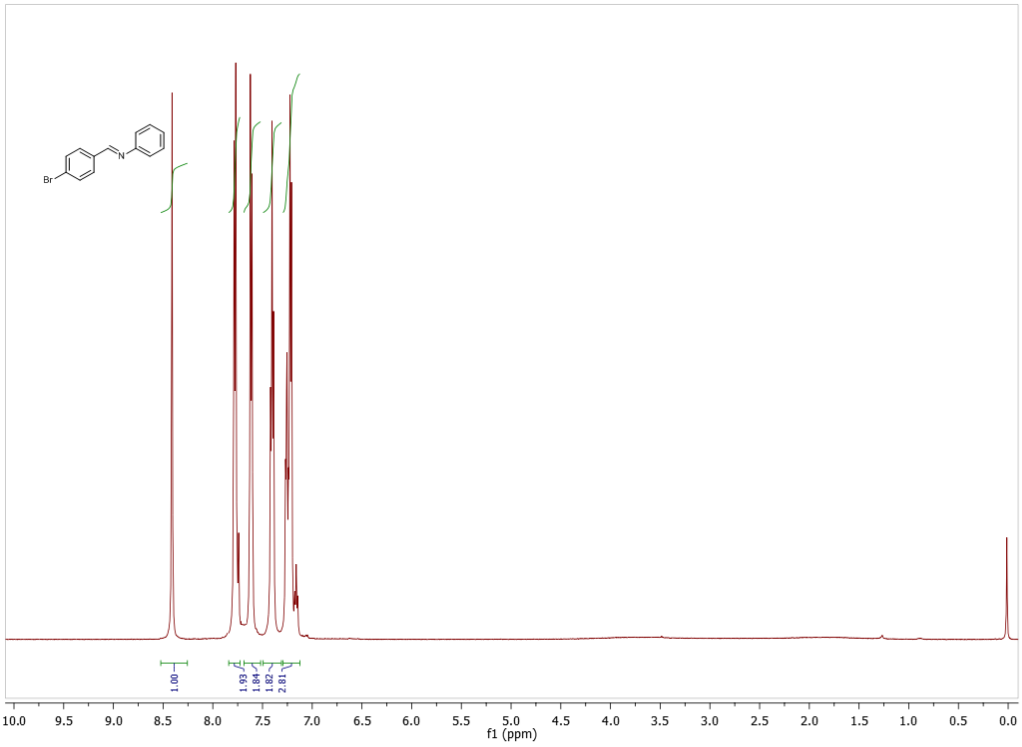
N-(4-Fluorobenzylidene)aniline ^{1}H NMR (5k)



N-(4-Fluorobenzylidene)aniline ^{13}C NMR (5k)



N-(4-bromobenzylidene)aniline ^{1}H NMR (5n)



N-(4-bromobenzylidene)aniline ^{13}C NMR (5n)