Supporting information for

Combination of Aerobic/Moisture/Ambient Temperature Compatible Organolithium Chemistry with Sustainable Solvents: Selective and Efficient Synthesis of Guanidines and Amidines

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1.- General Methods and Materials

All reagents were obtained from commercial suppliers and used without further purification with the exception of the *Deep Eutectic Solvents* (*DESs*),[1] which were prepared by following the corresponding methods reported in the literature. *n*-Butyl lithium (1.6 M solution in hexanes) was purchased from Sigma Aldrich and its concentration was established by titration with *L*-menthol.[2]

Commercially available 2-MeTHF and CPME were directly employed without any previous purification technique (distillation/use of molecular sieves) and were directly opened and stored in the presence of air and moisture.

NMR spectra were recorded on Bruker 400 and 500 spectrometers at 298 K, using standard TOPSPIN 4.0 software. ^{1}H, ^{13}C and ^{19}F NMR spectra were referenced against the appropriate solvent signal. All ^{13}C spectra were proton decoupled. Characterisation details, including ^{1}H, and $^{13}C\{^{1}H\}$ NMR spectra, for compounds **3aa-la**, **3ab-ac**, **4a**, **6aa-la**, **6ab-ae** and **7a** are included in the following sections of this Supporting Information.

FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer, using an ATR accessory.

2.- Experimental procedure and characterisation details

2.1.- General procedure for the synthesis of guanidine compounds 3aa-la, at room temperature, in the presence of air and using 2-MeTHF as sustainable solvent by one-pot/one-step protocol.

Syntheses were performed under air and at room temperature. In a glass tube, the appropriate amine (**1a-l**, 0.5 mmol) and diisopropylcarbodiimide (**2a**, 0.5 mmol, 77.6 µl) were dissolved in the corresponding alternative solvent (1 mL) under air, followed by the addition over 10 seconds of 0.5 mmol of *n*-butyl lithium (1.6 M solution in hexanes) at room temperature, and the reaction mixture was stirred for 30 seconds. The reaction was then stopped by addition of 5 ml of distillated water and the mixture was extracted with 2-MeTHF (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was concentrated in vacuo. Yields of the reaction

crudes were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.5 mmol). Separation and purification of all compounds were carried out using TLC glass plate silica. All reactions were done in triplicate to ensure good reproducibility of obtained yields.

2.2.- General procedure for the synthesis of guanidine compounds 3aa-la and 3ab-ac, at room temperature, in the presence of air and using 2-MeTHF as sustainable solvent by one-pot/two-steps protocol.

Syntheses were performed under air and at room temperature. In a glass tube, the appropriate amine (**1a-l**, 0.5 mmol) was dissolved in the corresponding alternative solvent (1 mL) under air, followed by the addition of 0.5 mmol of *n*-butyl lithium (1.6 M solution in hexanes) at room temperature, and the reaction mixture was stirred for 10 seconds. Then, the corresponding carbodiimide (**2a-c**, 0.5 mmol) was added to the reaction mixture and leaved stirring for another 30 seconds. The reaction was then stopped by addition of 5 ml of distillated water and the mixture was extracted with 2-MeTHF (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was concentrated in vacuo. Yields of the reaction crudes were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.5 mmol). Separation and purification of all compounds were carried out using TLC glass plate silica. All reactions were done in triplicate to ensure good reproducibility of obtained yields.

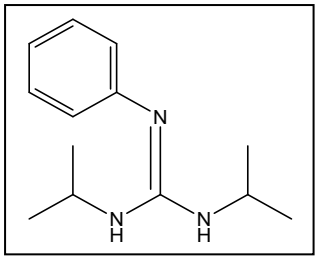
2.3.- General procedure of the screening for the synthesis of amidine compound 6aa, at room temperature by one-pot/one-step protocol.

Syntheses were performed under air and at room temperature. In a glass tube, aniline (**1a**, 0.5 mmol) and benzonitrile (**5a**, 0.5 mmol, 51.5 µl) were dissolved in the corresponding alternative solvent (1 mL) under air, followed by the addition over 10 seconds of 0.5 mmol of *n*-butyl lithium (1.6 M solution in hexanes) at room temperature, and the reaction mixture was stirred for 30 seconds. The reaction was then stopped by addition of 5 ml of distillated water and the mixture was extracted with 2-MeTHF (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was concentrated in vacuo. Yields of the reaction crudes were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.5 mmol). Separation and purification of every compound was carried out using TLC glass plate

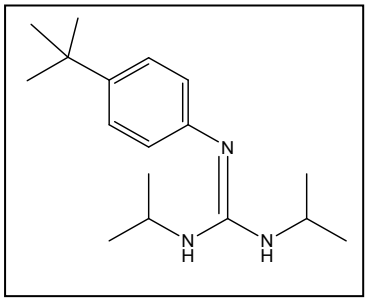
silica. All reactions were done in triplicate to ensure good reproducibility of obtained yields.

2.4.- General procedure for the synthesis of amidine compounds 6aa-la and 6ab-ae, at room temperature, in the presence of air and using CPME as sustainable solvent by one-pot/two-steps protocol.

Syntheses were performed under air and at room temperature. In a glass tube, the appropriate amine (**1a-l**, 0.5 mmol) was dissolved in the corresponding alternative solvent (1 mL) under air, followed by the addition of 0.5 mmol of *n*-butyl lithium (1.6 M solution in hexanes) at room temperature, and the reaction mixture was stirred for 10 seconds. Then the corresponding nitrile (**5a-e**, 0.5 mmol) was added to the reaction mixture and leaved stirring for another 90 seconds. The reaction was then stopped by addition of 5 ml of distillated water and the mixture was extracted with CPME (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was concentrated in vacuo. Yields of the reaction crudes were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.5 mmol). Separation and purification of every compound was carried out using TLC glass plate silica. All reactions were done in triplicate to ensure good reproducibility of obtained yields.

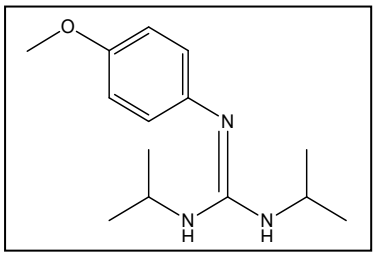


1,3-diisopropyl-2-phenylguanidine (3aa): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.17 (d, *J* = 6.4 Hz, 12H, CH_3), 3.74-3.81 (m, 2H, CH), 6.87-6.89 (m, 2Harom), 6.93-6.97 (m, 1Harom), 7.26-7.28 (m, 2Harom). ^{13}C{^{1}H} NMR ($CDCl_3$) δ (ppm) = 23.4 (4C), 43.6 (2C), 121.8, 123.6 (2C), 129.4 (2C), 150.7. FT-IR (cm^{-1}) = 3245, 3071, 2972, 2928, 2867, 1927, 1617, 1587, 1546, 1510, 1362, 1258, 1164, 1122, 1069.

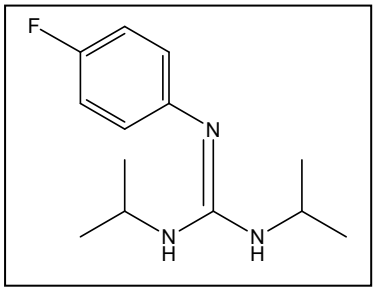


1,3-diisopropyl-2-(4-(tert-butyl)phenyl)guanidine (3ba): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.16 (d, *J* = 6.4 Hz, 12H, CH_3), 1.30 (s, 9H, CH_3), 3.76-3.78 (m, 2H, CH), 6.77-6.79 (d, *J* = 8.5 Hz, 2Harom), 7.24-7.26 (d, *J* = 8.5 Hz, 2Harom). ^{13}C{^{1}H} NMR ($CDCl_3$) δ (ppm) = 23.6 (4C), 31.7 (3C), 34.3, 43.5 (2C), 122.9 (2C), 126.2 (2C),

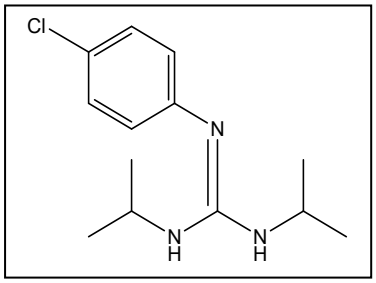
144.2, 147.1, 150.5. FT-IR (cm^{-1}) = 3224, 2963, 1627, 1600, 1510, 1463, 1332, 1261, 1189, 1113, 1074.



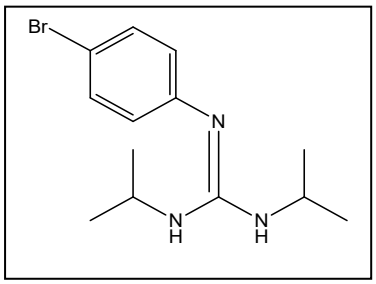
1,3-diisopropyl-2-(4-methoxyphenyl)guanidine (3ca): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.13 (d, *J* = 6.4 Hz, 12H, CH_3), 3.65 (bs, 2H, CH), 3.75 (s, 3H, CH_3), 6.75-6.81 (m, 4Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 23.5 (4C), 43.5 (2C), 55.6, 114.8 (2C), 124.4 (2C), 143.1, 150.9, 154.8. FT-IR (cm^{-1}) = 3243, 2967, 2833, 1643, 1611, 1502, 1462, 1362, 1263, 1165, 1036.



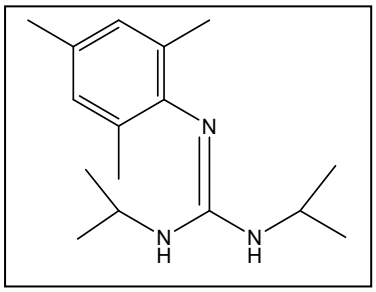
1,3-diisopropyl-2-(4-fluorophenyl)guanidine (3da): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.15 (d, *J* = 6.3 Hz, 12H, CH_3), 3.74-3.77 (m, 4H, NH, CH), 6.77-6.96 (m, 4Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 23.4 (4C), 43.5 (2C), 115.9 (2C), 124.6 (2C), 145.7, 150.9, 158.5 (2C). ^{19}F NMR ($CDCl_3$) δ (ppm) = 123.1. FT-IR (cm^{-1}) = 3293, 2973, 2869, 1716, 1635, 1541, 1498, 1365, 1258, 1214, 1093.



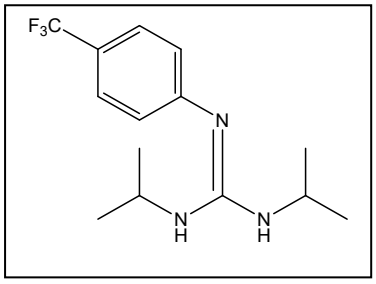
1,3-diisopropyl-2-(4-chlorophenyl)guanidine (3ea): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.16 (d, *J* = 6.4 Hz, 12H, CH_3), 3.74-3.79 (m, 2H, CH), 6.80 (d, *J* = 8.6 Hz, 2Harom) 7.20 (d, *J* = 8.6 Hz, 2Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 23.4 (4C), 43.6 (2C), 123.7, 124.9 (2C), 126.7, 129.4 (2C), 150.7. FT-IR (cm^{-1}) = 3026, 2969, 1878, 1738, 1632, 1583, 1483, 1364, 1263,1161, 1089.



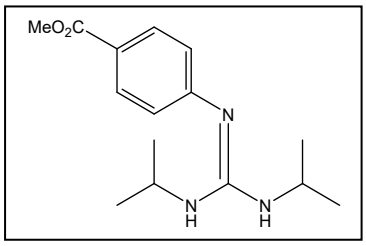
1,3-diisopropyl-2-(4-bromophenyl)guanidine (3fa): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.18 (d, *J* = 6.5 Hz, 12H, CH_3), 3.75-3.84 (m, 2H, CH), 6.84 (d, *J* = 8.5 Hz, 2Harom) 7.37 (d, *J* = 8.5 Hz, 2Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 23.3 (4C), 44.2 (2C), 125.1 (2C), 132.5 (4C), 151.5. FT-IR (cm^{-1}) = 3295, 2972, 2867, 1877, 1633, 1577, 1495, 1460, 1364, 1264, 1163, 1124, 1072.



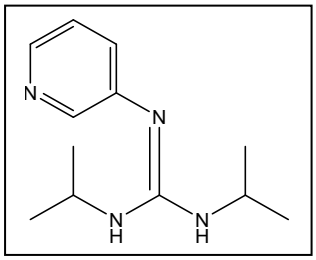
1,3-diisopropyl-2-mesitylguanidine (3ga): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.16 (bs, 12H, CH_3), 2.08 (s, 6H, CH_3), 2.23 (s, 3H, CH_3), 3.44 (bs, 2H, CH), 6.81 (s, 2Harom). ^{13}C{^{1}H} NMR ($CDCl_3$) δ (ppm) = 18.4 (4C), 20.9 (2C), 23.8, 43.5 (2C), 128.8 (3C), 131.0 148.4. FT-IR (cm^{-1}) = 3294, 2966, 2918, 1622, 1604, 1539, 1476, 1362, 1266, 1243, 1123.



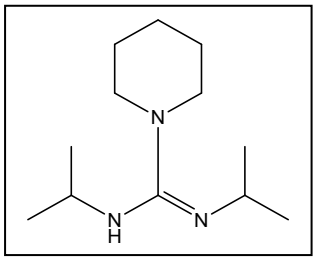
1,3-diisopropyl-2-(4-(trifluoromethyl) phenyl)guanidine (3ha): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.18 (d, *J* = 6.4 Hz, 12H, CH_3), 3.63(bs, 2H, NH), 3.74-3.81 (m, 2H, CH), 6.92 (d, *J* = 8.3 Hz, 2Harom) 7.48 (d, *J* = 8.3 Hz, 2Harom). ^{13}C{^{1}H} NMR ($CDCl_3$) δ (ppm) = 23.4 (4C), 43.4 (2C), 123.1, 123.5, 126.5 (2C), 150.2, 154.2. ^{19}F NMR ($CDCl_3$) δ (ppm) = -61.4. . FT-IR (cm^{-1}) = 3291, 2964, 1638, 1597, 1515, 1455, 1320, 1267, 1156, 1104, 1064, 1011.



methyl 4-((bis(isopropylamino)methylene)amino) benzoate (3ia): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.14 (d, *J* = 6.2 Hz, 12H, CH_3), 3.74 (bs, 4H, CH, NH), 3.85 (s, 3H, OCH_3), 6.87 (d, *J* = 8.6 Hz, 2Harom) 7.90 (d, *J* = 8.6 Hz, 2Harom). ^{13}C{^{1}H} NMR ($CDCl_3$) δ (ppm) = 23.3 (4C), 43.3 (2C), 51.7, 122.4, 123.1, 131.2, 150.2, 155.9, 167.5. FT-IR (cm^{-1}) = 3371, 2971, 1713, 1573, 1541, 1504, 1435, 1324, 1263, 1165, 1100, 1066, 1012.

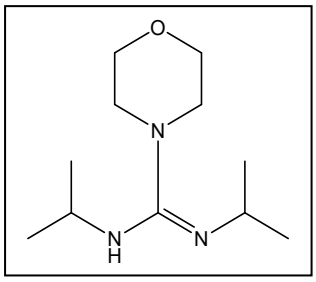


1,3-diisopropyl-2-(pyridin-3-yl)guanidine (3ja): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.16 (d, *J* = 6.4 Hz, 12H, CH_3), 3.75-3.80 (m, 2H, CH), 7.14-7.21 (m, 2Harom), 8.16-8.19 (m, 2Harom). ^{13}C{^{1}H} NMR ($CDCl_3$) δ (ppm) = 23.3 (4C), 43.6 (2C), 124.0, 130.7, 142.8, 145.6, 151.1. FT-IR (cm^{-1}) = 3283, 2969, 2929, 1608, 1543, 1476, 1383, 1262, 1169, 1126, 1069, 1040.

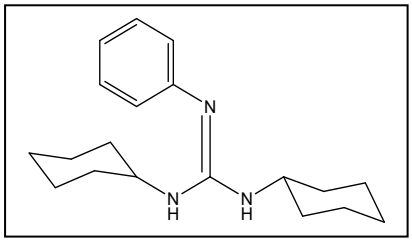


N,N'-diisopropylpiperidine-1-carboximidamide (3ka): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.08 (d, *J* = 6.3 Hz, 12H, CH_3), 1.51 (bs, 6H, CH_2), 3.02 (bs, 4H, CH_2), 3.36 (bs, 2H, CH). ^{13}C{^{1}H}

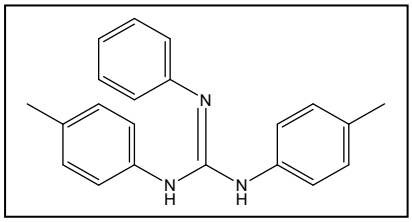
NMR ($CDCl_3$) δ (ppm) = 23.8 (2C), 25.2, 26.3 (4C), 46.7 (2C), 49.2 (2C), 156.3. FT-IR (cm^{-1}) = 2963, 2930, 2854, 1627, 1453, 1364, 1275, 1257, 1166, 1125, 1084.



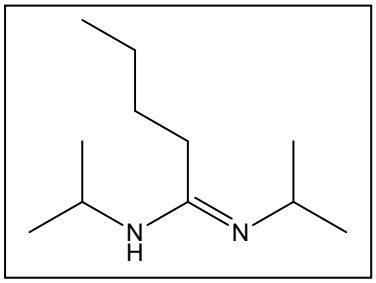
N,N'-diisopropylmorpholine-4-carboximidamide (3la): ^1H NMR ($CDCl_3$) δ (ppm) = 1.10 (bs, 12H, CH_3), 3.10 (bs, 4H, CH_2), 3.42 (bs, 2H, CH), 3.68-3.70 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 24.4 (4C), 46.9 (2C), 48.8 (2C), 67.2 (2C), 155.3. FT-IR (cm^{-1}) = 3369, 3178, 2964, 2852, 1624, 1454, 1363, 1299, 1260, 1166, 1116, 1007.



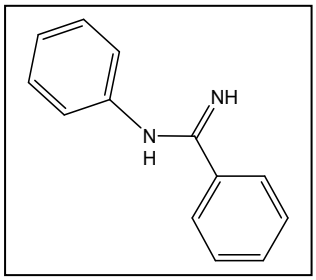
1,3-dicyclohexyl-2-phenylguanidine (3ab): ^1H NMR ($CDCl_3$) δ (ppm) = 1.08-2.01 (m, 20H, CH_2), 3.39-3.43 (m, 2H, CH), 3.79 (bs, 2H, NH), 6.85-7.26 (m, 5Harom). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 24.9 (4C), 25.8 (2C), 33.9 (4C), 50.4 (2C), 121.6, 123.7 (2C), 129.3 (2C), 150.3. FT-IR (cm^{-1}) = 3253, 3054, 2931, 2852, 1611, 1587, 1550, 1502, 1446, 1275, 1256, 1190, 1167, 1084.



1,3-di-p-tolylguanidine-2-phenyl (3ac): ^1H NMR ($CDCl_3$) δ (ppm) = 2.33 (s, 6H, CH_3), 7.03-7.32 (m, 13Harom). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 20.9 (2C), 115.2, 118.6, 121.7 (2C), 122.1 (2C), 123.1, 129.4 (2C), 130.0 (2C), 133.3, 145.9. FT-IR (cm^{-1}) = 3393, 3025, 2920, 1639, 1588, 1504, 1441, 1318, 1221, 1108, 1030.

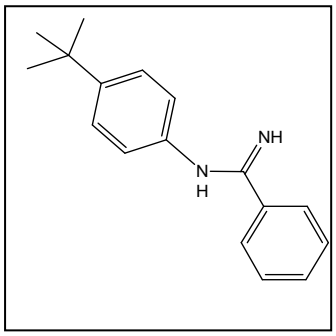


N,N'-diisopropylpentanimidamide (4a): ^1H NMR ($CDCl_3$) δ (ppm) = 0.91 (t, *J* = 7.3 Hz, 3H, CH_3), 1.09, (d, *J* = 6.3 Hz, 12, CH_3), 1.30-1.52 (m, 4H, CH_2), 2.10-2.14 (m, 2H, CH_2), 3.66 (bs, 2H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 14.0, 22.9, 24.1 (4C), 30.3, 44.9 (2C), 77.36, 156.9. . FT-IR (cm^{-1}) = 3307, 2961, 2870, 1609, 1493, 1467, 1378, 1360, 1266, 1180, 1125, 1025.

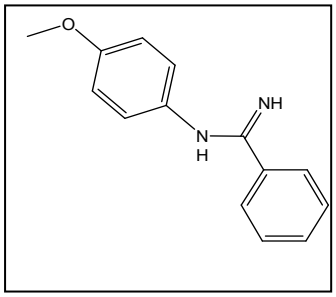


N-phenylbenzimidamide (6aa): ^1H NMR ($CDCl_3$) δ (ppm) = 4.94 (bs, 2H, NH), 6.98-7.82 (m, 10Harom). $^{13}C\{^1H\}$ NMR

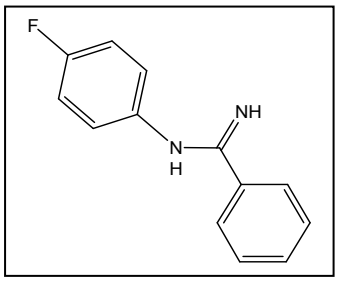
($CDCl_3$) δ (ppm) = 122.5, 124.1, 127.5, 128.9 (4C), 129.9 (4C), 131.4. FT-IR (cm^{-1}) = 3467,3346, 3052, 1955, 1614, 1589, 1568, 1481, 1447, 1377, 1238, 1169, 1076, 1023.



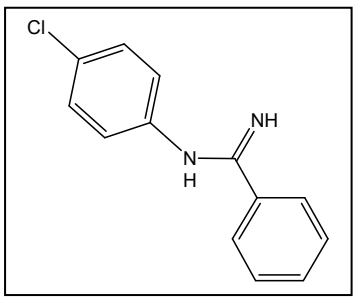
N-(4-(tert-butyl)phenyl)benzimidamide (6ba): ^1H NMR ($CDCl_3$) δ (ppm) = 1.33 (s, 9H, CH_3), 6.91-7.83 (m, 9Harom). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 31.8 (3C), 34.7, 122.0, 126.7 (4C), 127.5, 128.9 (4C), 129.9 (4C), 131.4. FT-IR (cm^{-1}) =3442, 3120, 2958, 2859, 1902, 1636, 1598, 1569, 1498, 1383, 1267, 1190, 1111, 1085.



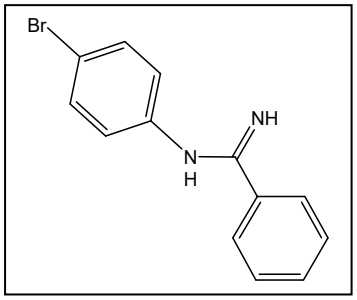
N-(4-methoxyphenyl)benzimidamide (6ca): ^1H NMR ($CDCl_3$) δ (ppm) = 3.80 (s, 3H, CH_3), 6.88-7.78 (m, 9Harom). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 55.8, 115.2 (4C), 124.4, 127.8, 129.1 (4C), 131.9. FT-IR (cm^{-1}) = 2949, 2835, 1631, 1569, 1502, 1444, 1373, 1235, 1177, 1104, 1029.



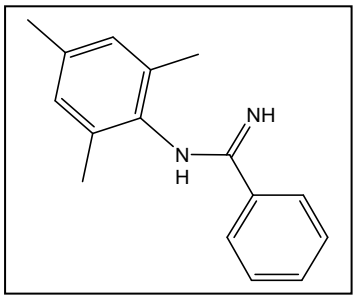
N-(4-fluorophenyl)benzimidamide (6da): ^1H NMR ($CDCl_3$) δ (ppm) = 5.06 (bs, 2H, NH), 6.91-7.81 (m, 9Harom). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 116.5 (2C), 123.4, 127.2 (2C), 128.9 (3C), 131.2 (2C), 158.6, 160.5. ^{19}F NMR ($CDCl_3$) δ (ppm) = 120.8. FT-IR (cm^{-1}) = 3470, 3342, 3057, 2857, 2356, 1903, 1612, 1568, 1496, 1445, 1409, 1377, 1211, 1092.



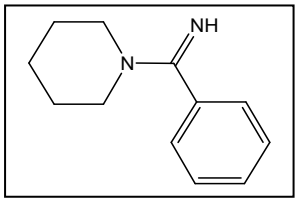
N-(4-chlorophenyl)benzimidamide (6ea): ^1H NMR ($CDCl_3$) δ (ppm) = 5.07 (bs, 2H, NH), 6.90-7.80 (m, 9Harom). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) = 123.6 (2C), 127.2, 128.9 (2C), 129.9 (3C), 131.3 (2C), 135.2, 147.7, 156.2. FT-IR (cm^{-1}) = 3470, 3343, 3081, 2679, 1915, 1611, 1566, 1484, 1445, 1377, 1238, 1169, 1095, 1009.



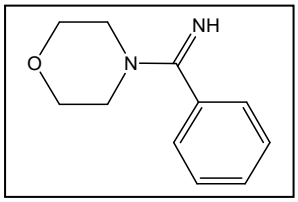
N-(4-bromophenyl)benzimidamide (6fa): ^{1}H NMR ($CDCl_3$) δ (ppm) = 5.02 (bs, 2H, NH), 6.86-7.80 (m, 9Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 116.7, 124.1 (2C), 127.3 (3C), 129.0 (2C), 131.4, 132.9 (2C). FT-IR (cm^{-1}) = 3471, 3348, 3077, 2367, 1917, 1610, 1566, 1481, 1375, 1238, 1172, 1100, 1073, 1004.



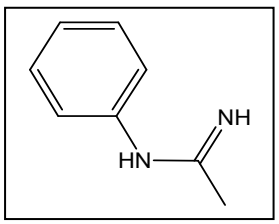
N-mesitylbenzimidamide (6ga): ^{1}H NMR ($CDCl_3$) δ (ppm) = 2.11 (s, 6H, CH_3), 2.28 (s, 3H, CH_3), 4.58 (bs, 2H, NH), 6.89-7.92 (m, 7Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 17.9 (2C), 20.9, 127.0 (2C), 128.8 (3C), 129.1 (2C), 130.9 (2C), 132.6, 135.5, 142.8, 154.2. FT-IR (cm^{-1}) = 3448, 3290, 3132, 2910, 2363, 1899, 1634, 1575, 1476, 1376, 1228, 1024, 1005.



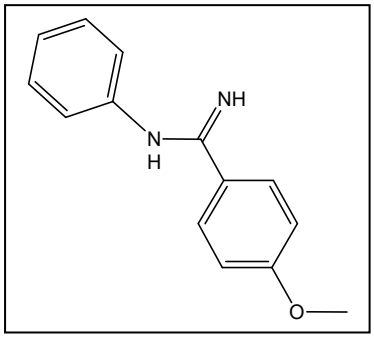
phenyl(piperidin-1-yl)methanimine (6ka): ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.52-1.61 (m, 6H, CH_2), 3.29-3.31 (m, 4H, CH_2), 5.83 (bs, 1H, NH), 7.29-7.34 (m, 5Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 24.8 (2C), 25.9, 47.3 (2C), 126.9 (2C), 128.6 (2C), 129.1, 138.7, 169.7. FT-IR (cm^{-1}) = 3311, 2933, 2852, 2228, 1678, 1584, 1566, 1443, 1374, 1305, 1181, 1106, 1027.



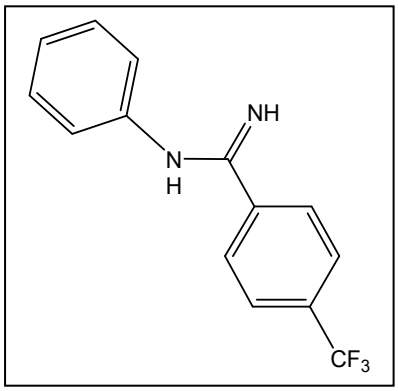
morpholino(phenyl)methanimine (6la): ^{1}H NMR ($CDCl_3$) δ (ppm) = 3.32-3.34 (m, 4H, CH_2), 3.66-3.68 (m, 4H, CH_2), 5.18 (bs, 1H, NH), 7.29-7.36 (m, 5Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 46.8 (2C), 66.7 (2C), 127.1 (2C), 128.8 (2C), 129.6, 137.4, 169.9. FT-IR (cm^{-1}) = 3300, 2964, 2952, 1675, 1569, 1445, 1367, 1263, 1192, 1112, 1009.



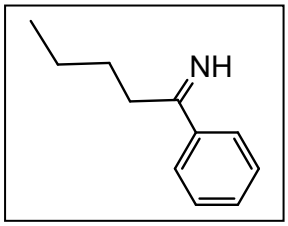
N-phenylacetimidamide (6ab): ^{1}H NMR ($CDCl_3$) δ (ppm) = 2.06 (s, 3H, CH_3), 5.01 (bs, 2H, NH), 6.88-7.32 (m, 5Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 21.3, 122.6 (2C), 123.7 (2C), 129.6, 147,9, 157.4. FT-IR (cm^{-1}) = 2949, 2835, 1631, 1569, 1502, 1444, 1373, 1235, 1177, 1104, 1029.



4-methoxy-N-phenylbenzimidamide (6ad): ^{1}H NMR ($CDCl_3$) δ (ppm) = 3.86 (s, 3H, CH_3), 5.07 (bs, 2H, NH), 6.92-7.80 (m, 9Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 55.7, 114.1 (2C), 122.4 (2C), 123.7, 128.9 (2C), 129.8 (2C), 162.0. FT-IR (cm^{-1}) = 3440, 3309, 3140, 2959, 2839, 1945, 1633, 1609, 1589, 1564, 1518, 1417, 1384, 1193, 1115, 1070, 1024.



N-phenyl-4-(trifluoromethyl)benzimidamide (6ae): ^{1}H NMR ($CDCl_3$) δ (ppm) = 5.26 (bs, 2H, NH), 6.97-7.95 (m, 9Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 122.0 (2C), 124.2 (2C), 125.8, 127.8 (2C), 129.9 (2C), 155.0. ^{19}F NMR ($CDCl_3$) δ (ppm) = -62.84. FT-IR (cm^{-1}) = 3445, 3292, 3118, 2321, 1948, 1634, 1568, 1484, 1409, 1387, 1321, 1233, 1168, 1125, 1064, 1015.



1-phenylpentan-1-imine (7a): ^{1}H NMR ($CDCl_3$) δ (ppm) = 0.95 (t, *J* = 7.3 Hz, 3H, CH_3), 1.37-1.46, (m, 2H, CH_2), 1.55-1.67 (m, 2H, CH_2), 2.67-2.83 (m, 2H, CH_2), 7.39-7.44 (m, 3Harom), 7.70-7.72 (m, 2Harom). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ (ppm) = 14.0, 22.5, 28.5, 37.6, 126.5, 128.6, 128.7, 130.4, 179.5. . FT-IR (cm^{-1}) = 3062, 2958, 2872, 1684, 1598, 1449, 1375, 1265, 1208, 1180, 1108, 1014.

3.- ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra data

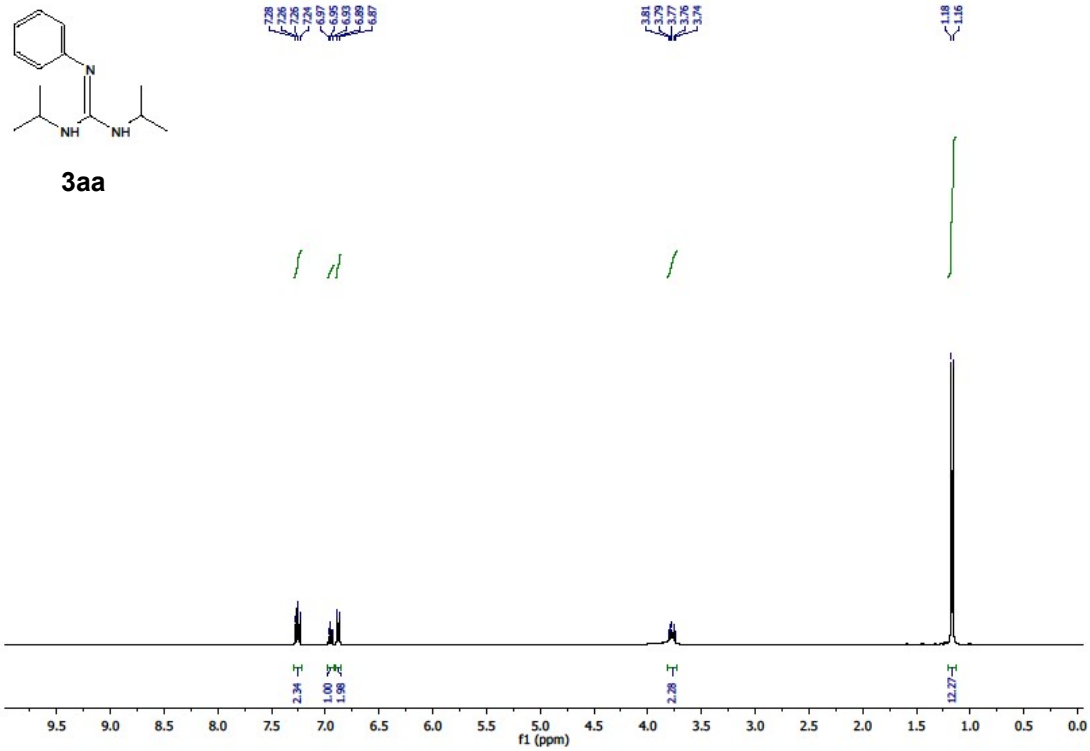


Figure S1. ^{1}H-NMR full chart for **3aa** in $CDCl_3$.

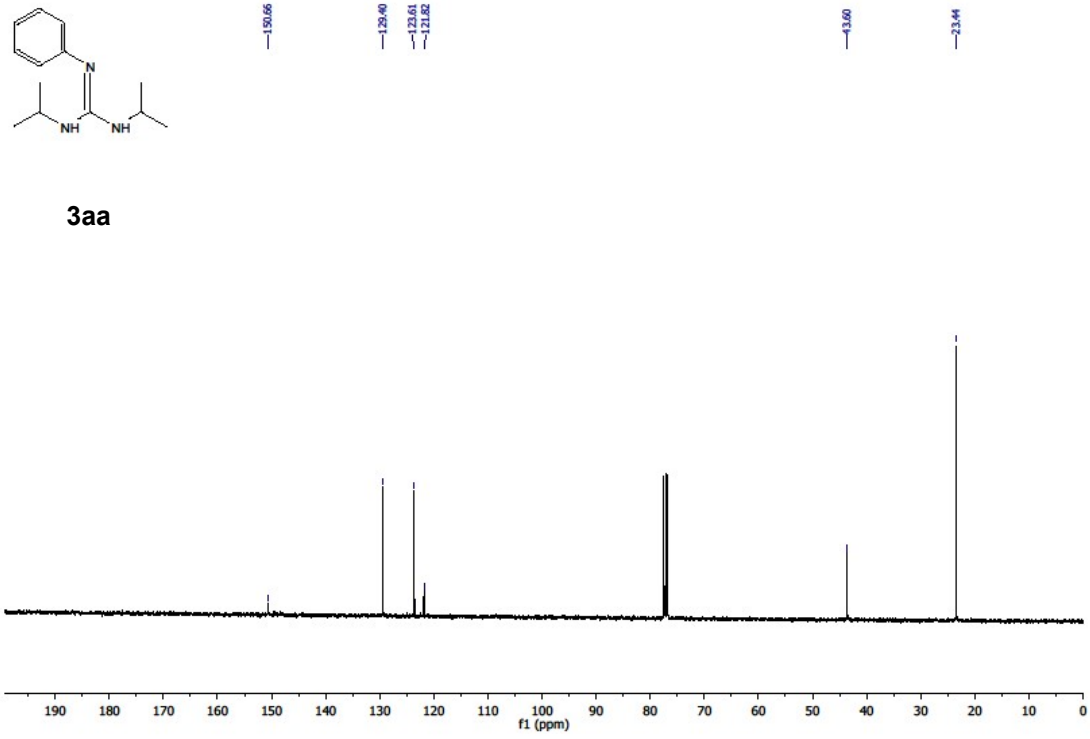


Figure S2. ^{13}C-NMR full chart for **3aa** in $CDCl_3$.

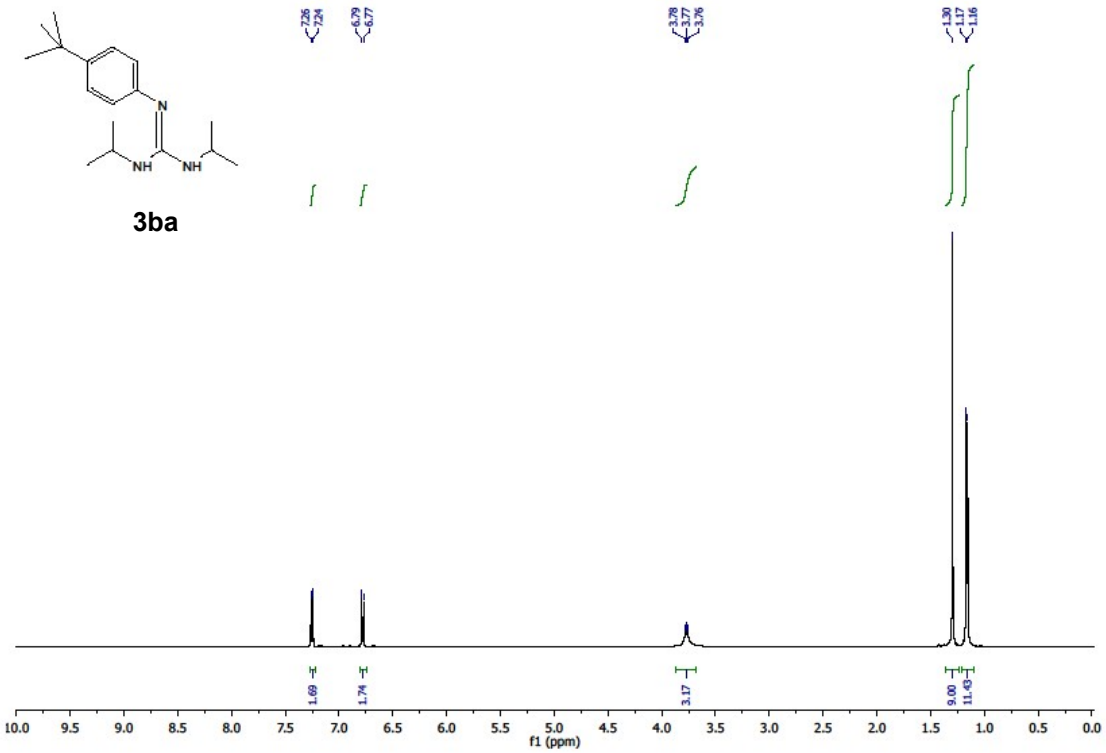


Figure S3. ^{1}H-NMR full chart for **3ba** in $CDCl_3$.

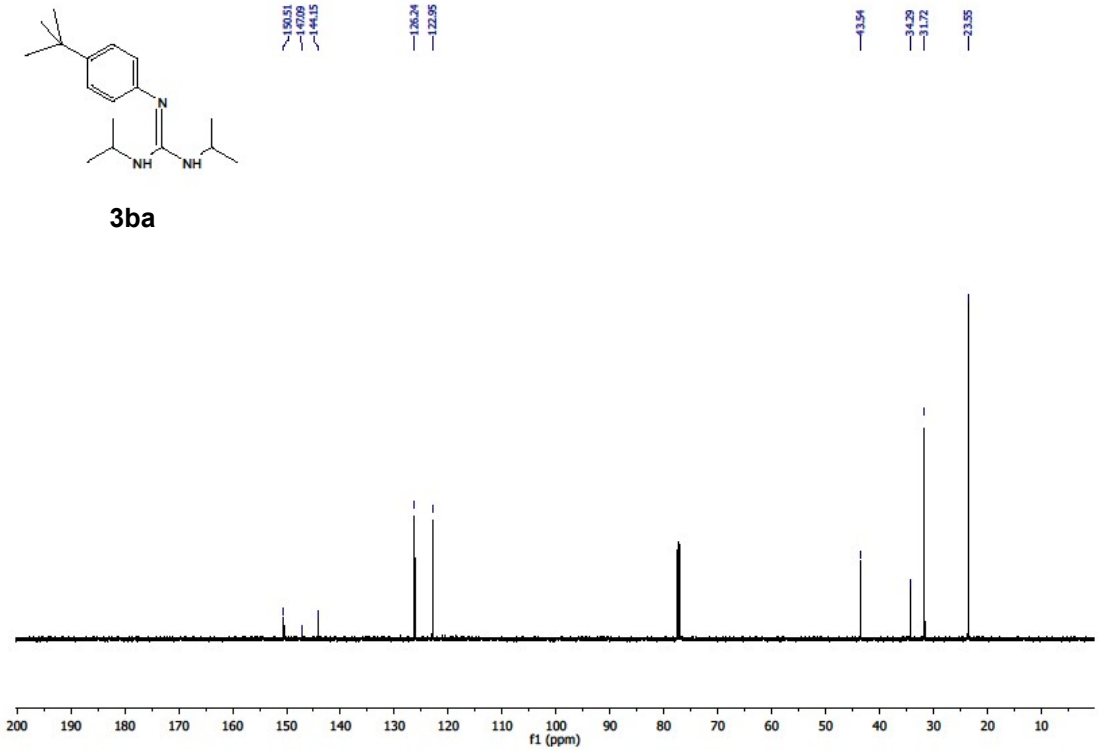


Figure S4. ^{13}C-NMR full chart for **3ba** in $CDCl_3$.

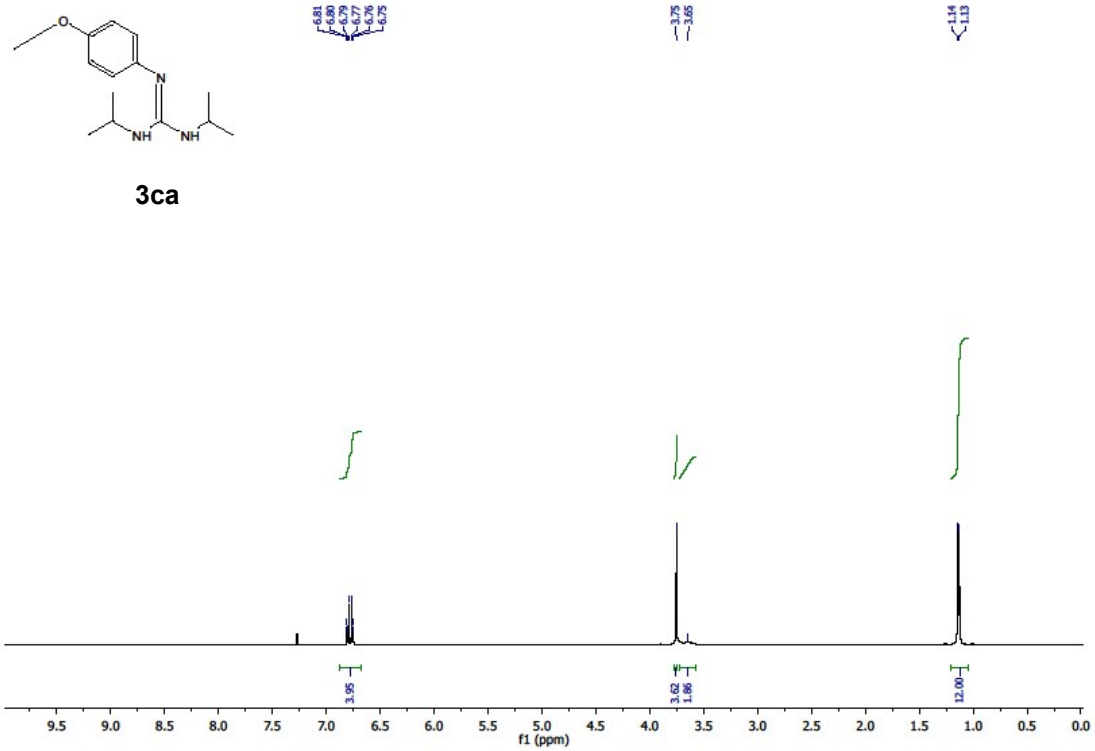


Figure S5. ^{1}H-NMR full chart for **3ca** in $CDCl_3$.

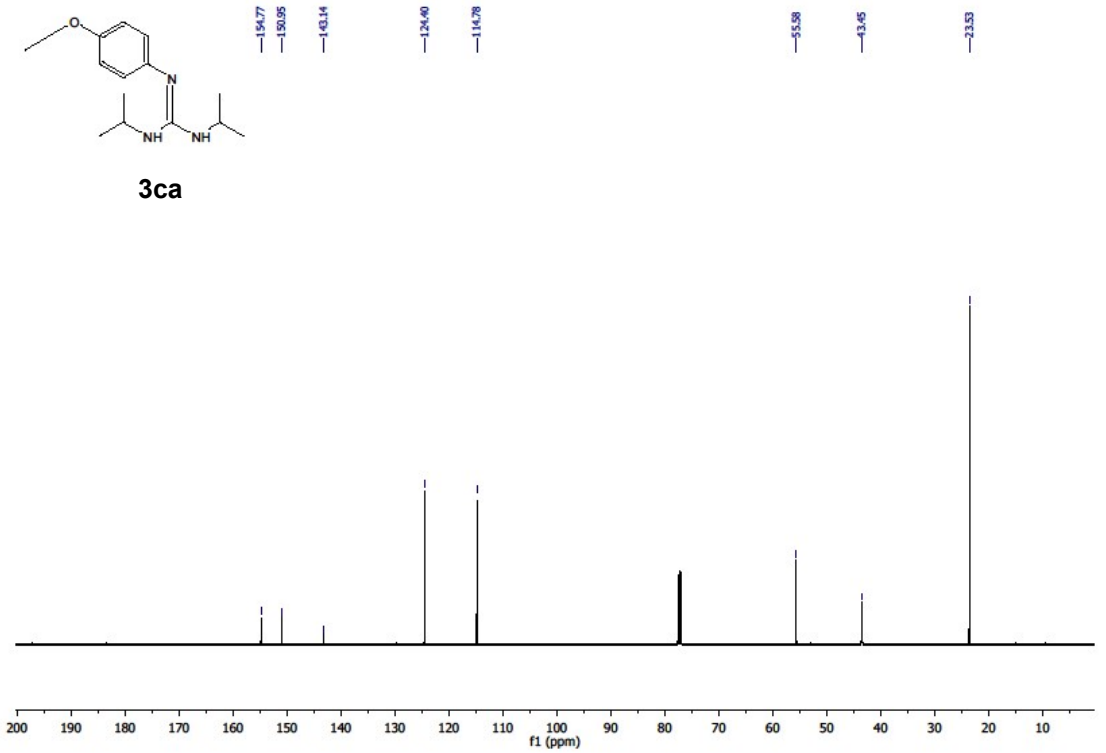


Figure S6. ^{13}C-NMR full chart for **3ca** in $CDCl_3$.

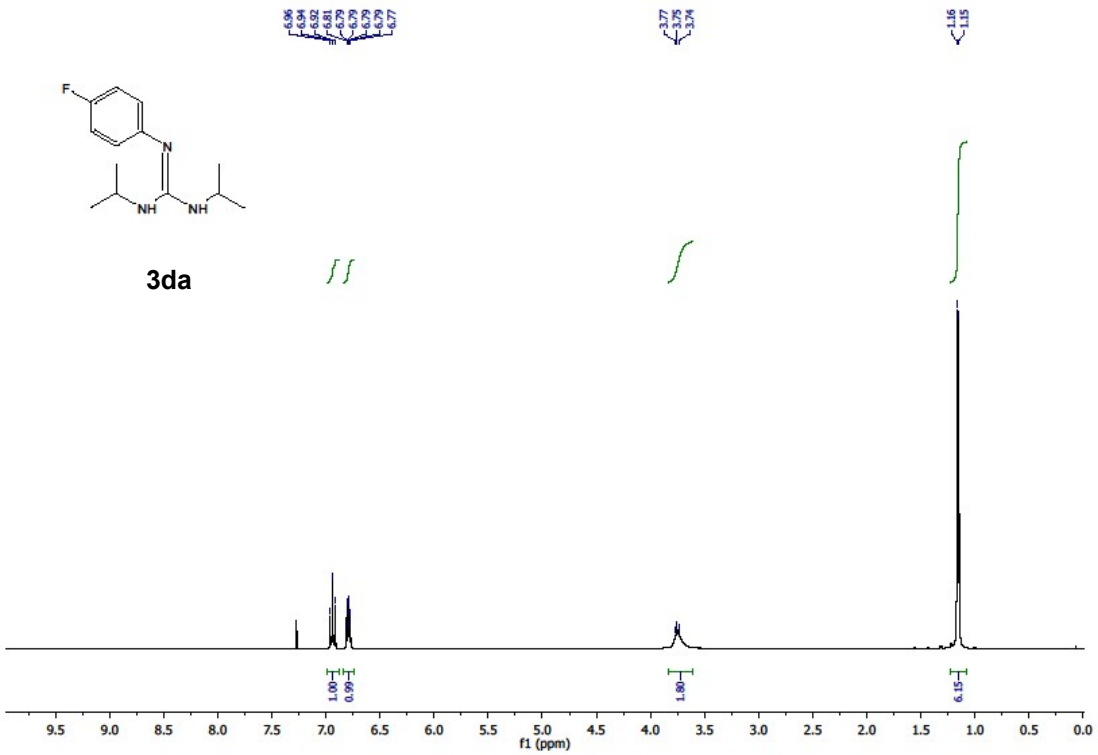


Figure S7. ^{1}H-NMR full chart for **3da** in $CDCl_3$.

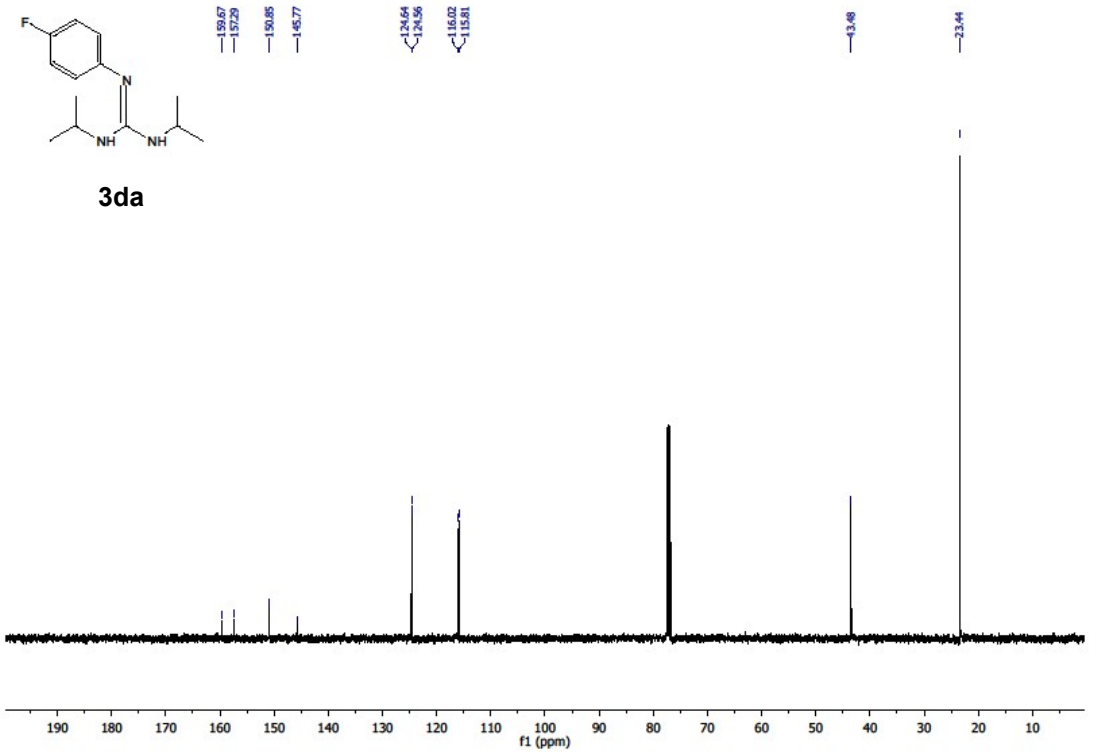


Figure S8. ^{13}C-NMR full chart for **3da** in $CDCl_3$.

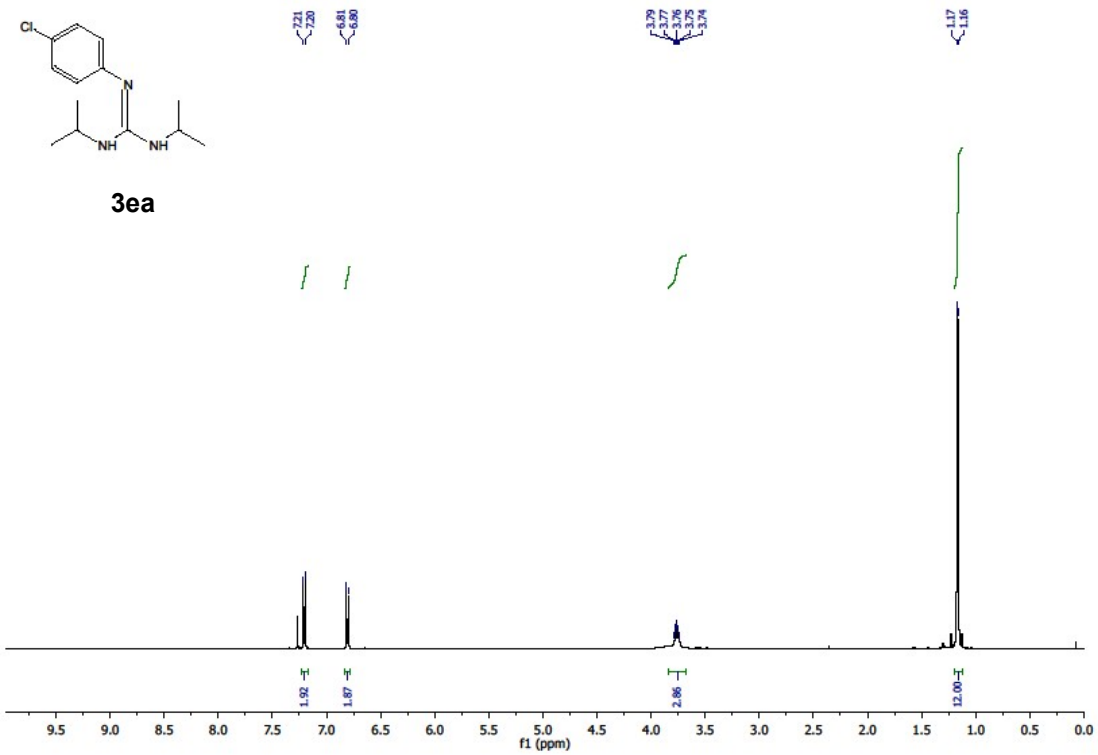


Figure S9. ^{1}H-NMR full chart for **3ea** in $CDCl_3$.

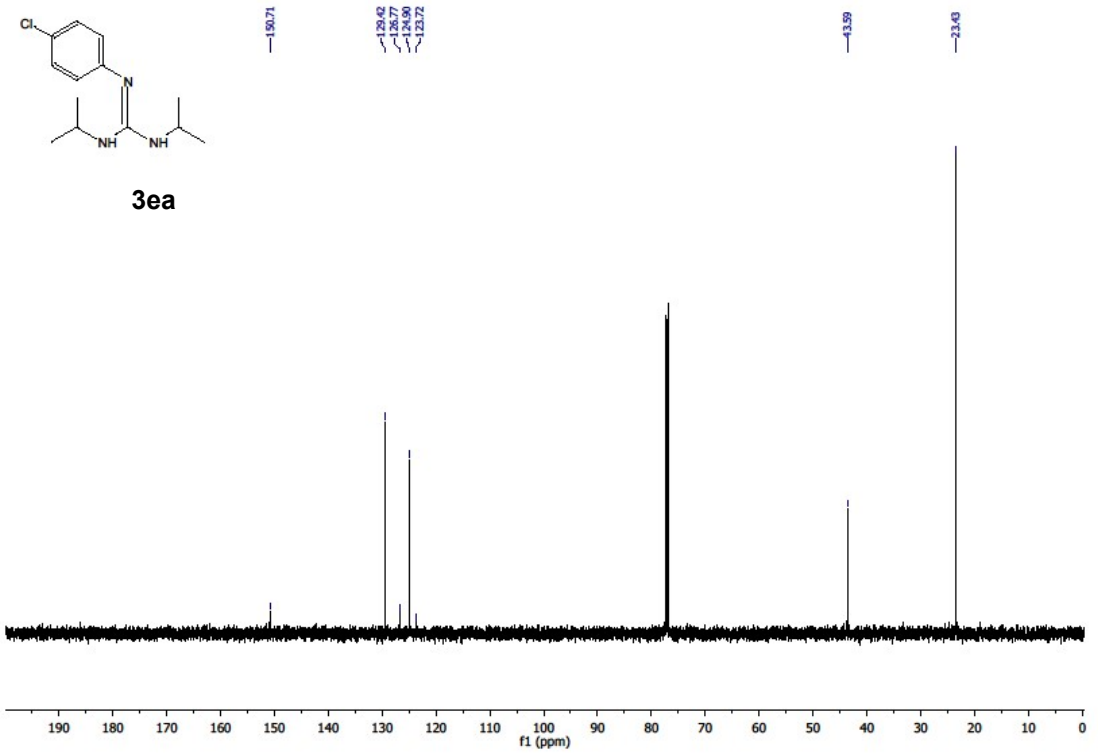


Figure S10. ^{13}C-NMR full chart for **3ea** in $CDCl_3$.

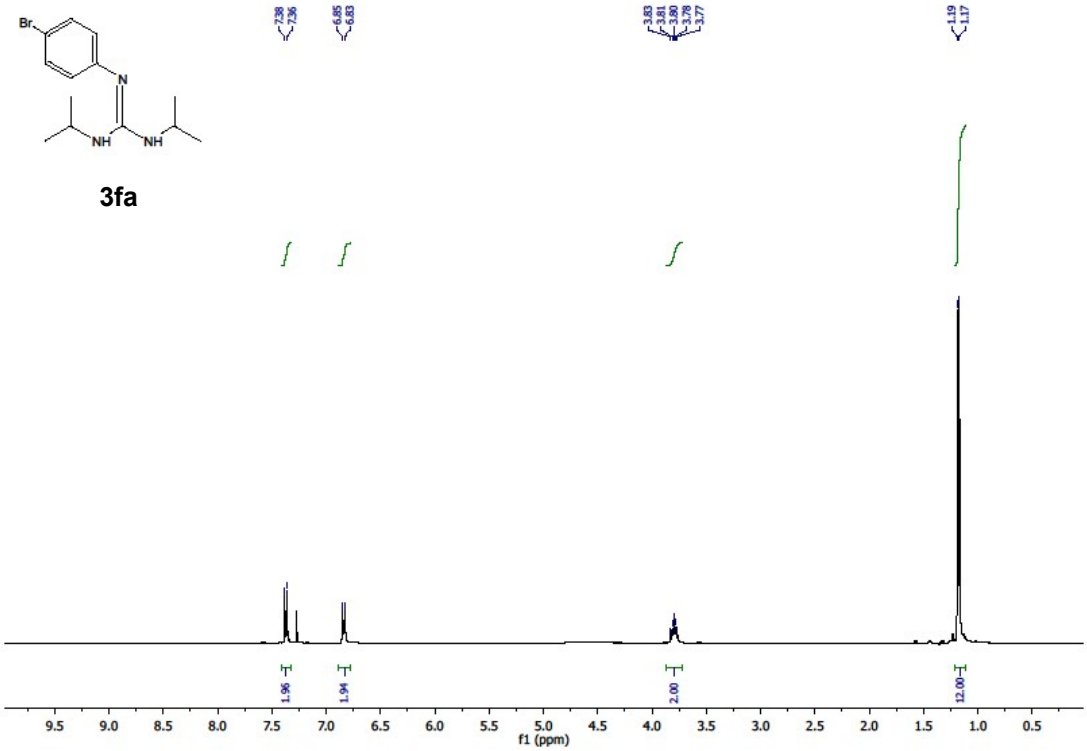


Figure S11. ^{1}H-NMR full chart for **3fa** in $CDCl_3$.

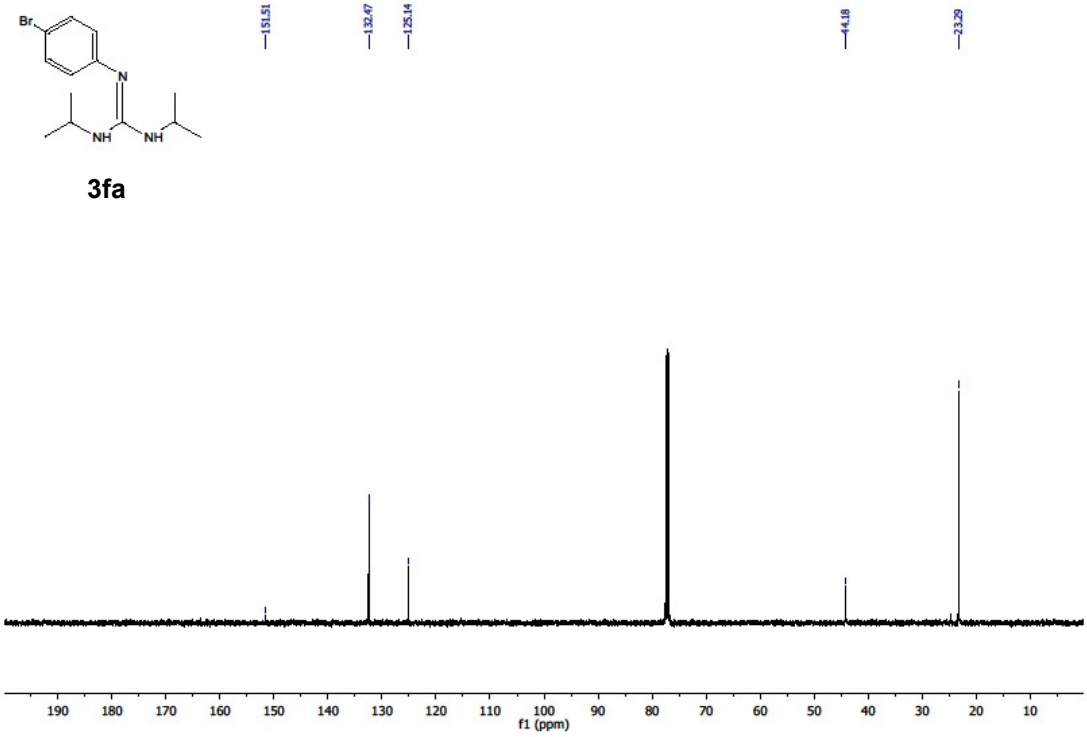


Figure S12. ^{13}C-NMR full chart for **3fa** in $CDCl_3$.

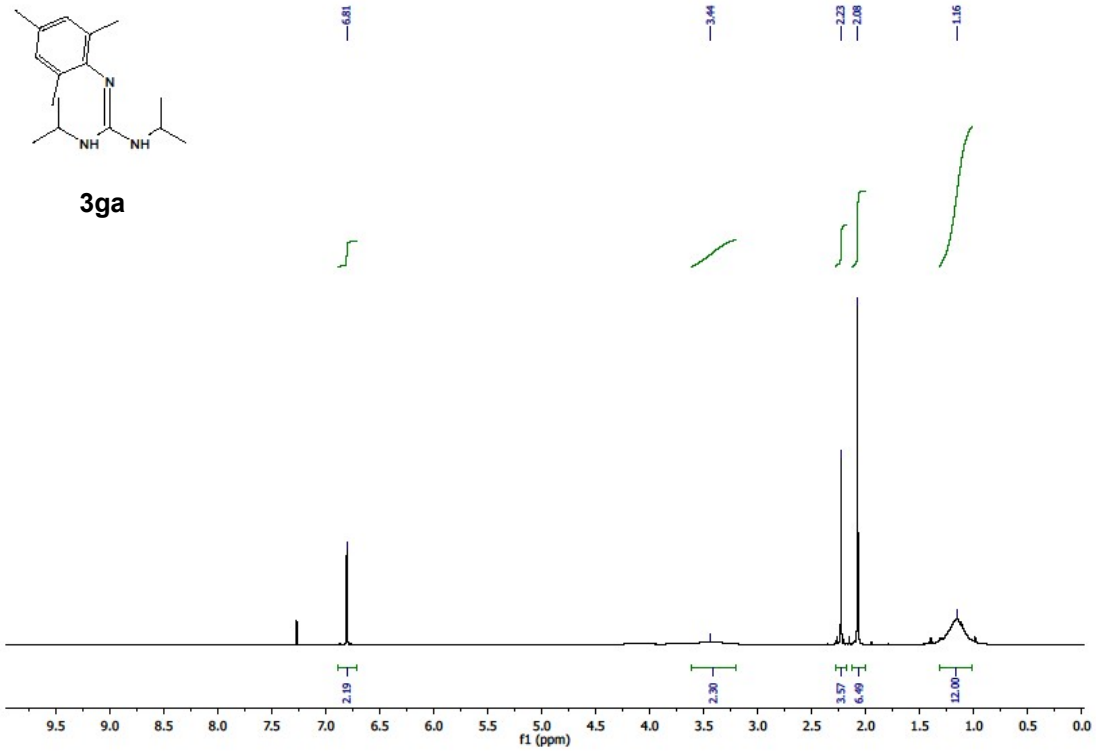


Figure S13. ^{1}H-NMR full chart for **3ga** in $CDCl_3$.

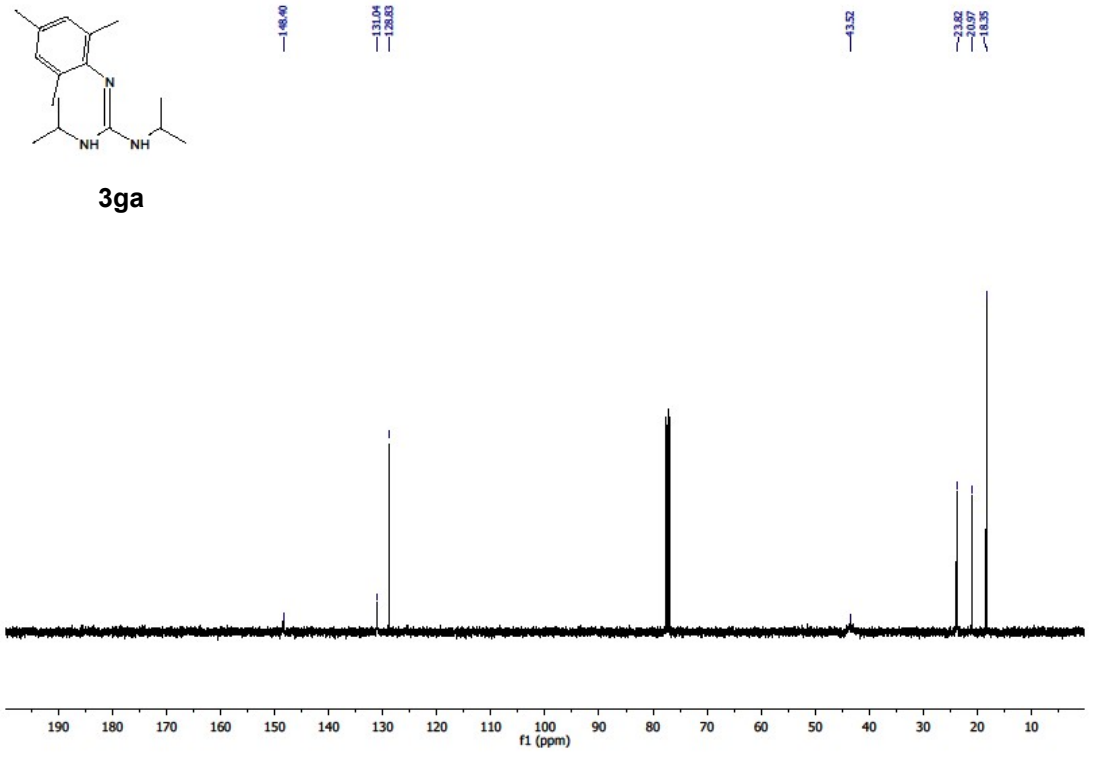


Figure S14. ^{13}C-NMR full chart for **3ga** in $CDCl_3$.

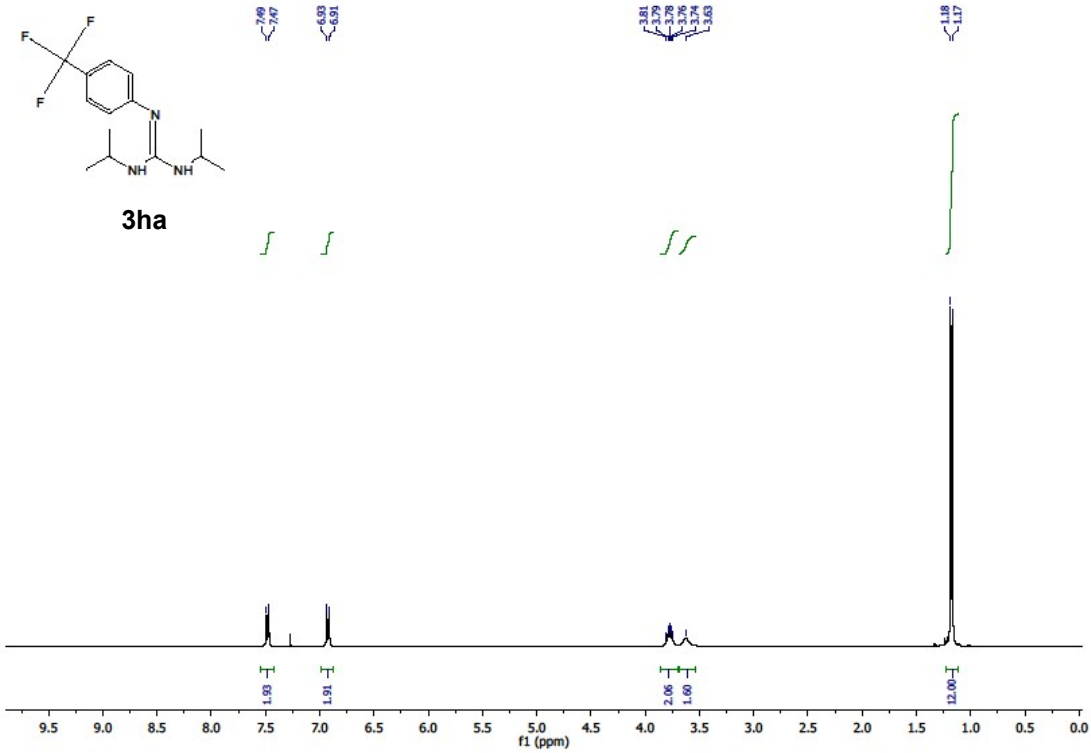


Figure S15. ^{1}H-NMR full chart for **3ha** in $CDCl_3$.

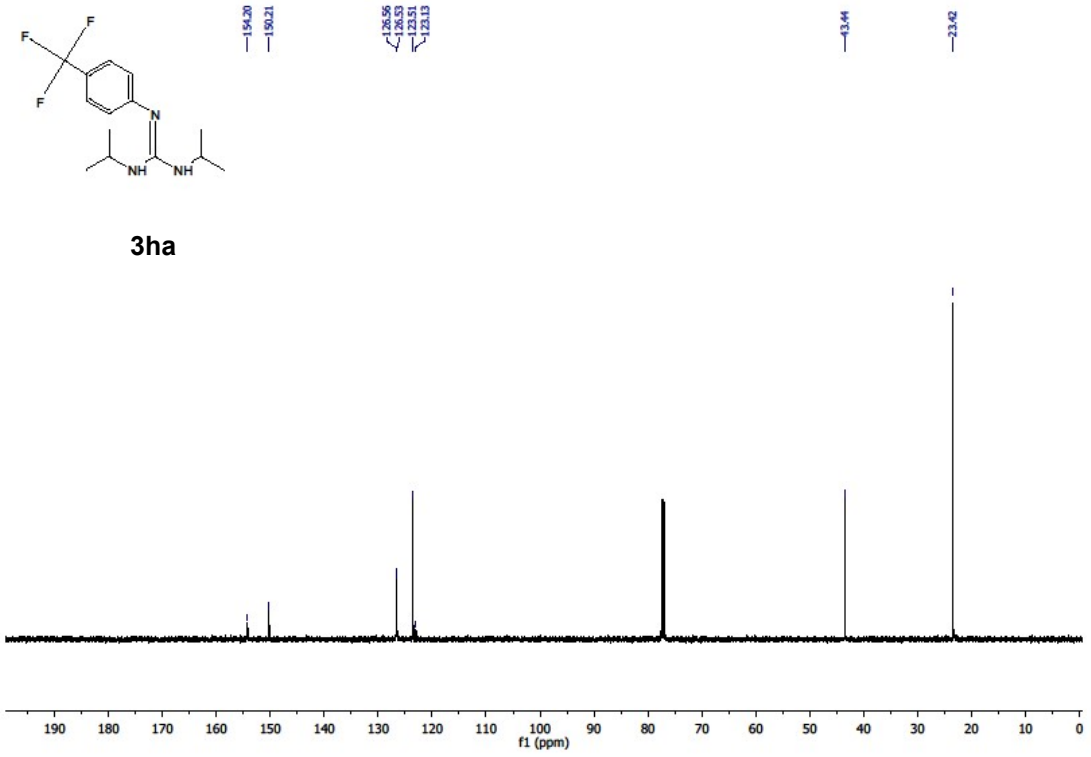


Figure S16. ^{13}C-NMR full chart for **3ha** in $CDCl_3$.

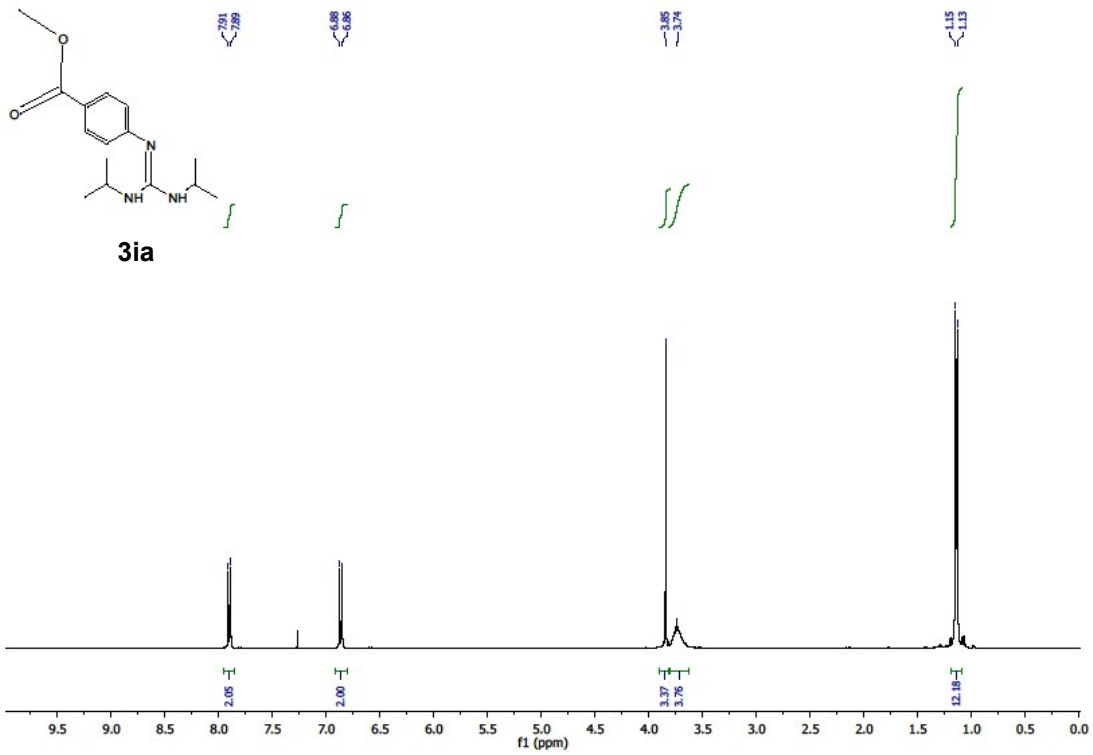


Figure S17. ^{1}H-NMR full chart for **3ia** in $CDCl_3$.

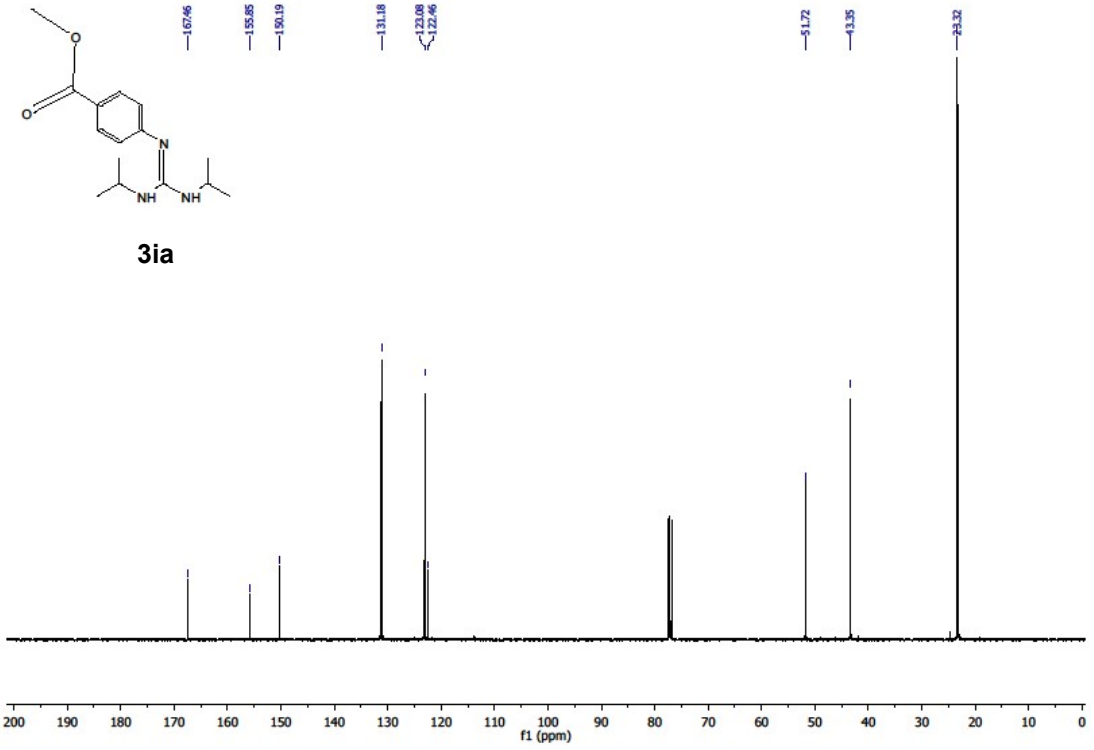


Figure S18. ^{13}C-NMR full chart for **3ia** in $CDCl_3$.

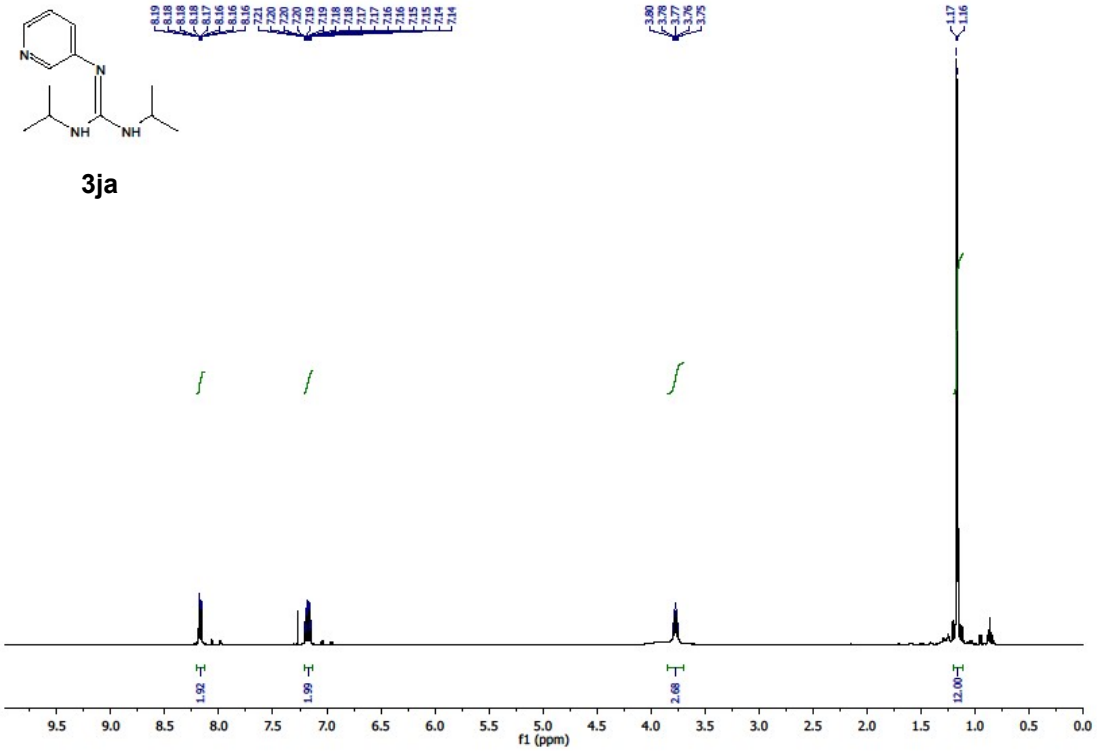


Figure S19. ^{1}H-NMR full chart for **3ja** in $CDCl_3$.

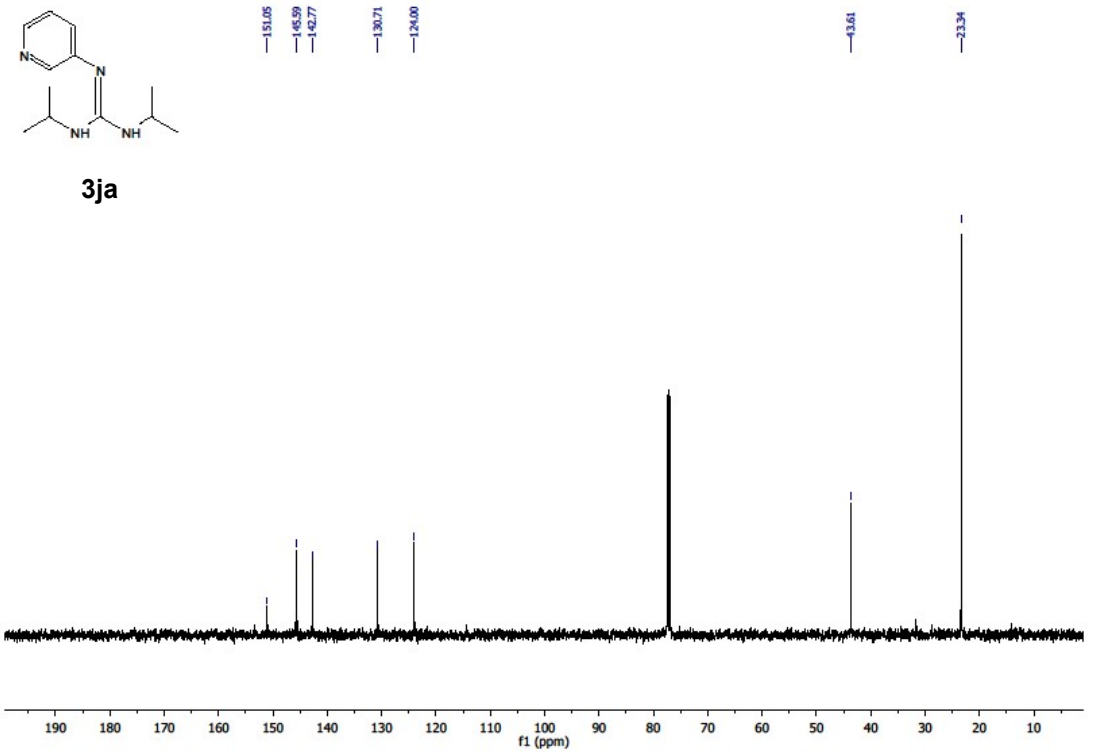


Figure S20. ^{13}C-NMR full chart for **3ja** in $CDCl_3$.

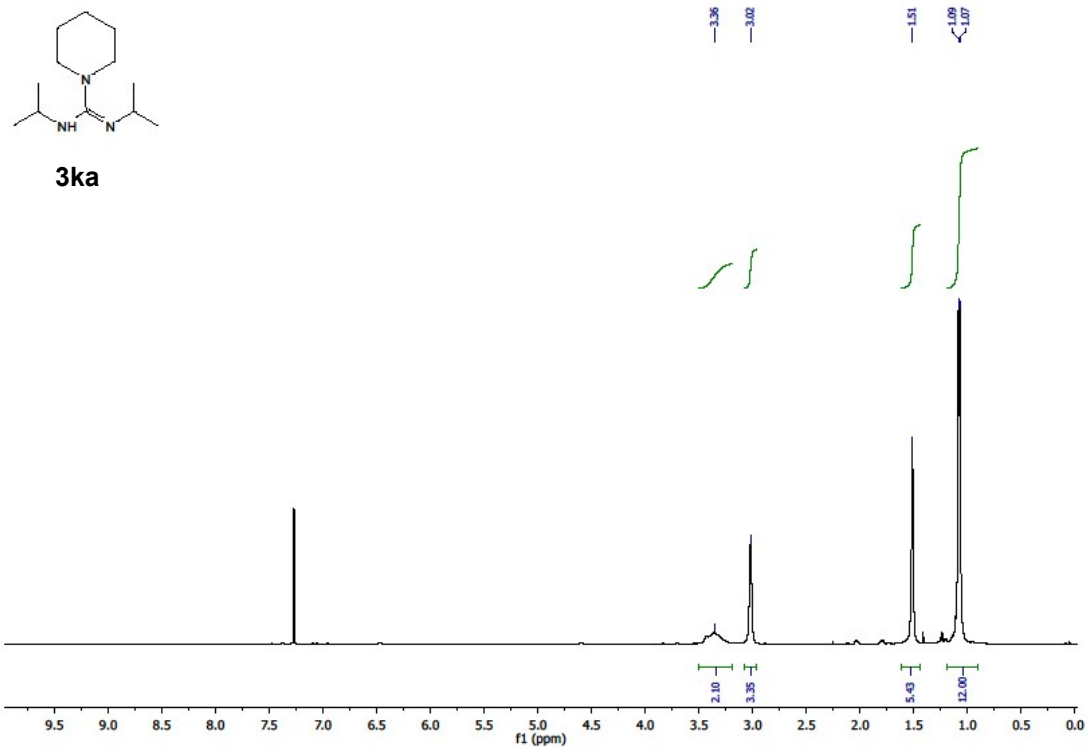


Figure S21. ^{1}H-NMR full chart for **3ka** in $CDCl_3$.

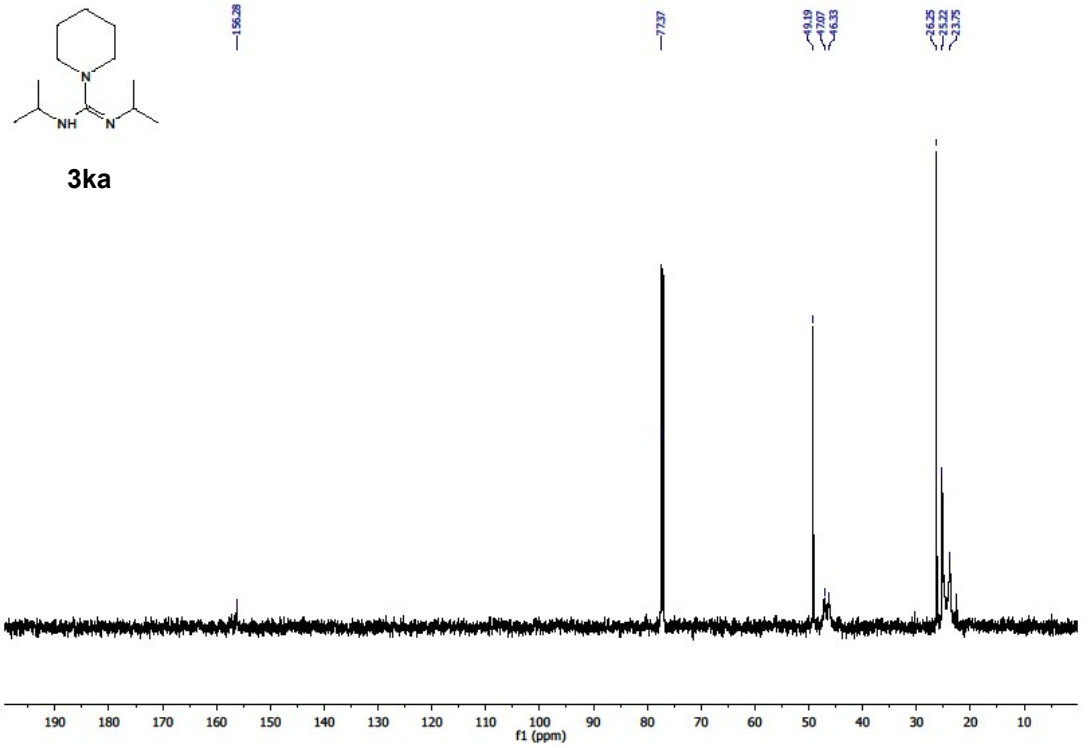
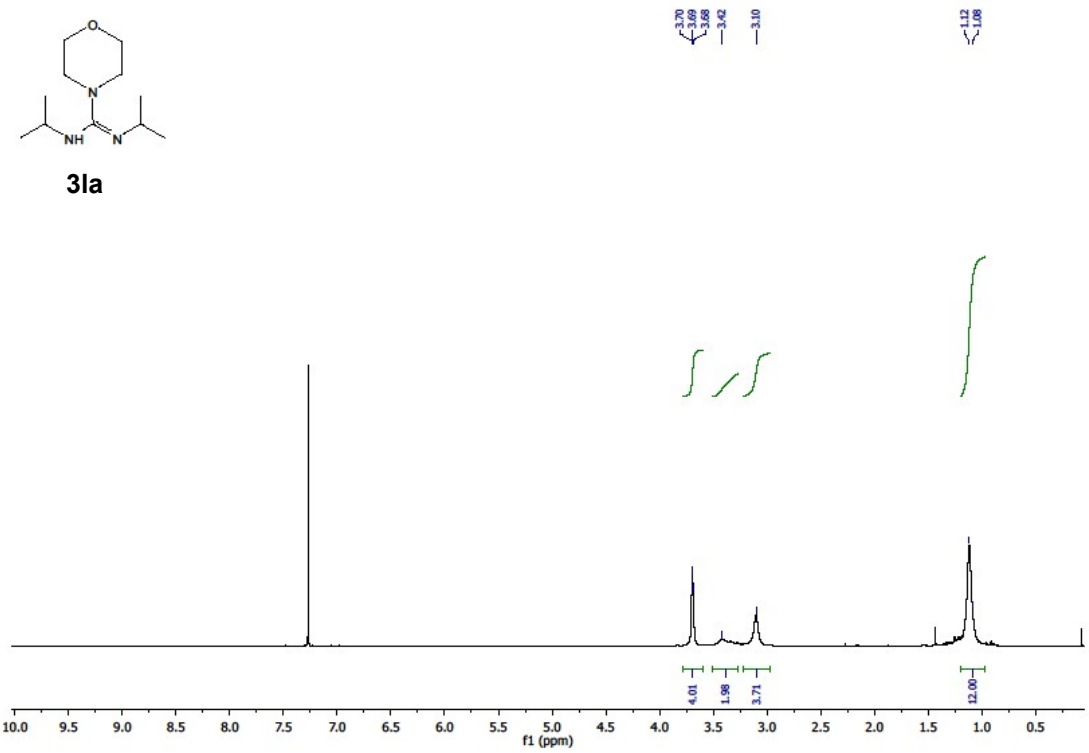
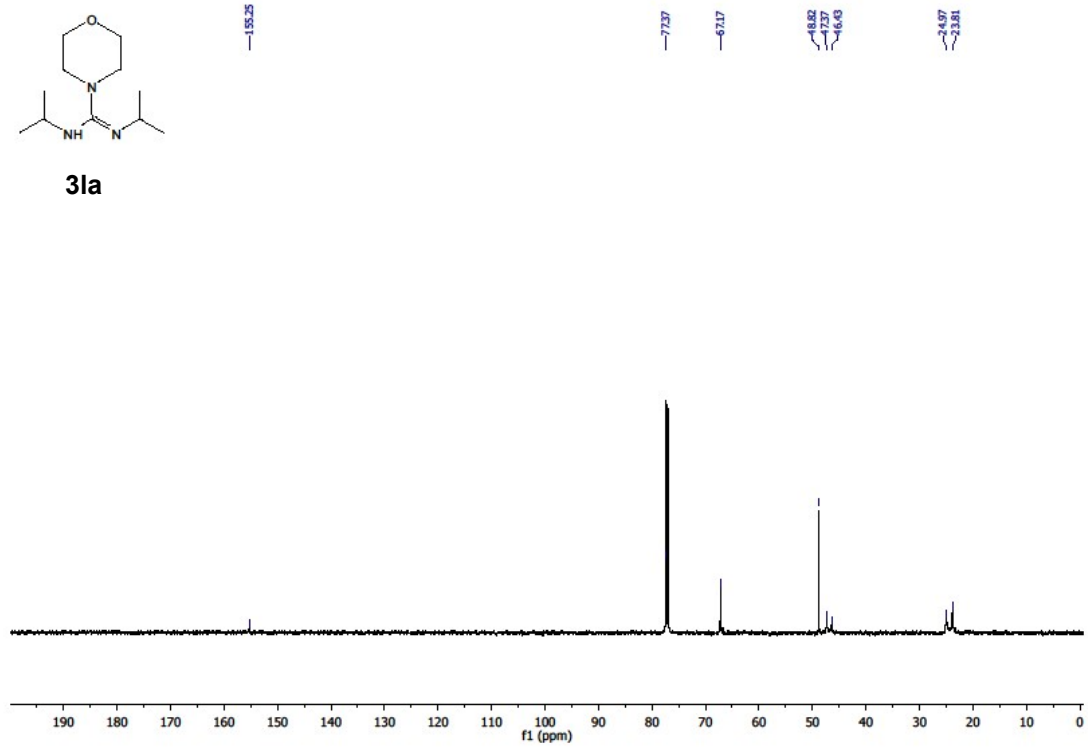


Figure S22. ^{13}C-NMR full chart for **3ka** in $CDCl_3$.



3la

Figure S23. ^{1}H-NMR full chart for **3la** in $CDCl_3$.



3la

Figure S24. ^{13}C-NMR full chart for **3la** in $CDCl_3$.

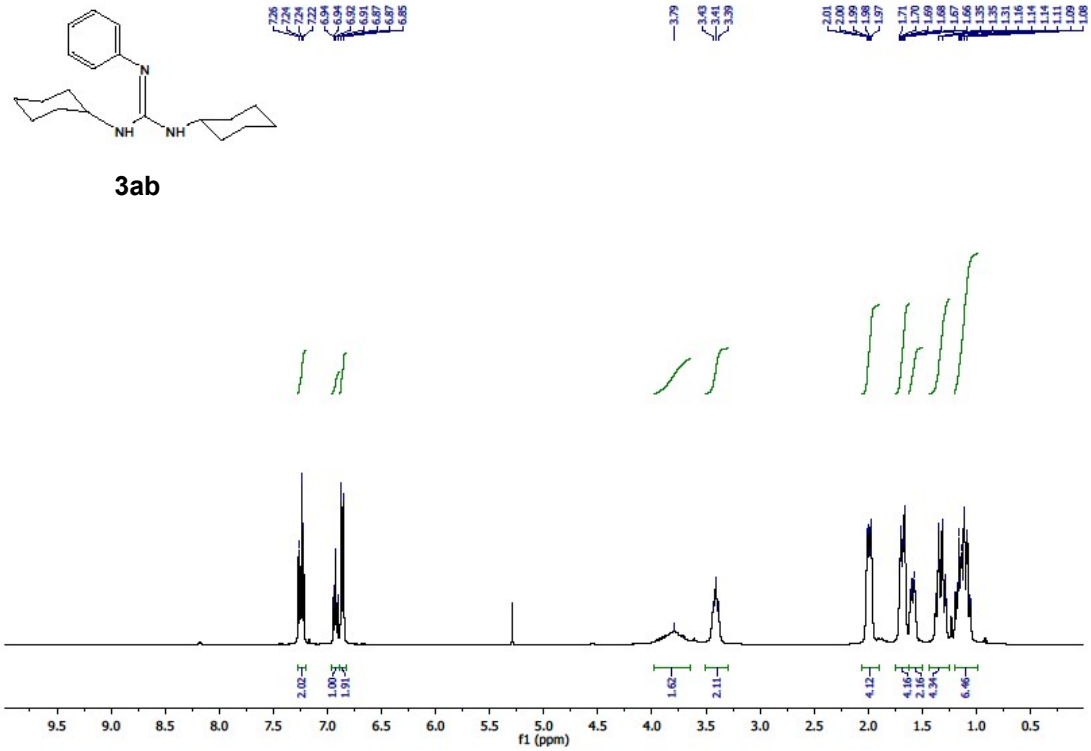


Figure S25. ^{1}H-NMR full chart for **3ab** in $CDCl_3$.

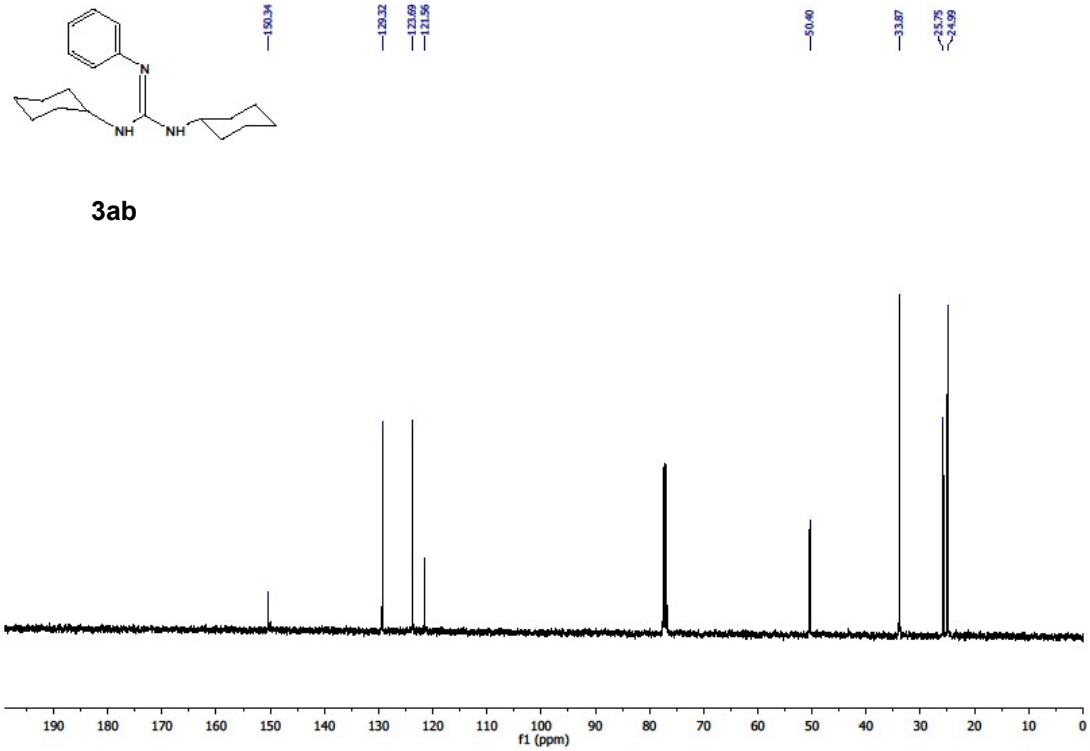


Figure S26. ^{13}C-NMR full chart for **3ab** in $CDCl_3$.

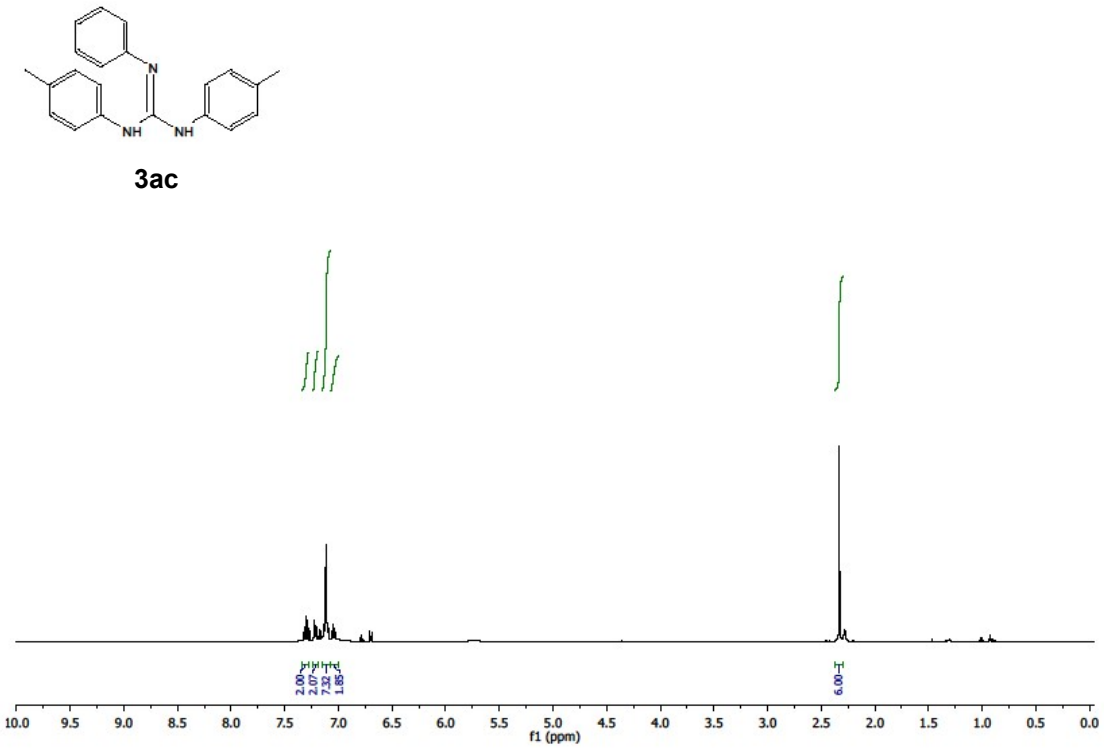


Figure S27. ^{1}H-NMR full chart for **3ac** in $CDCl_3$.

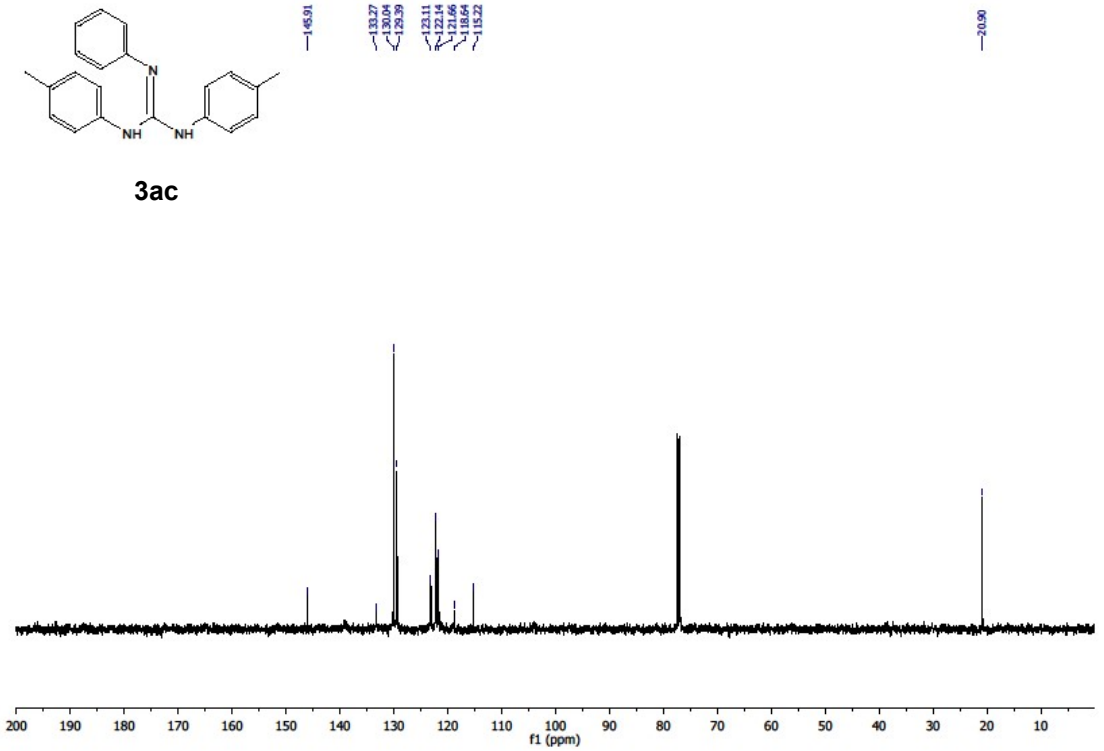


Figure S28. ^{13}C-NMR full chart for **3ac** in $CDCl_3$.

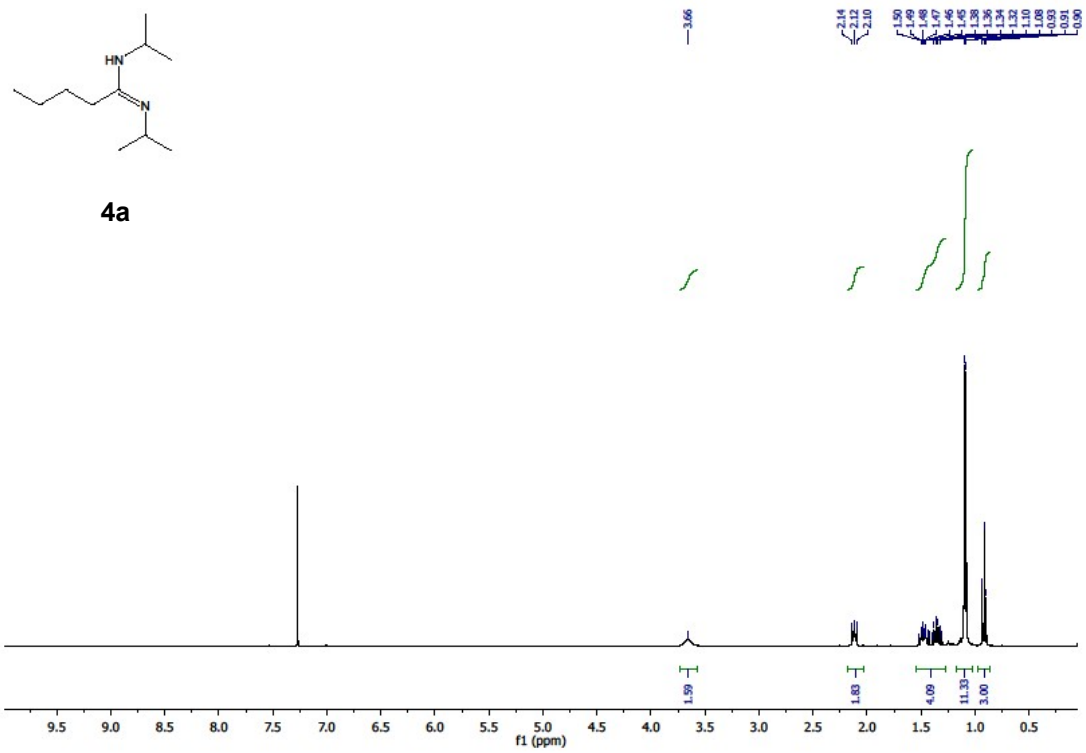


Figure S29. ^{1}H-NMR full chart for **4a** in $CDCl_3$.

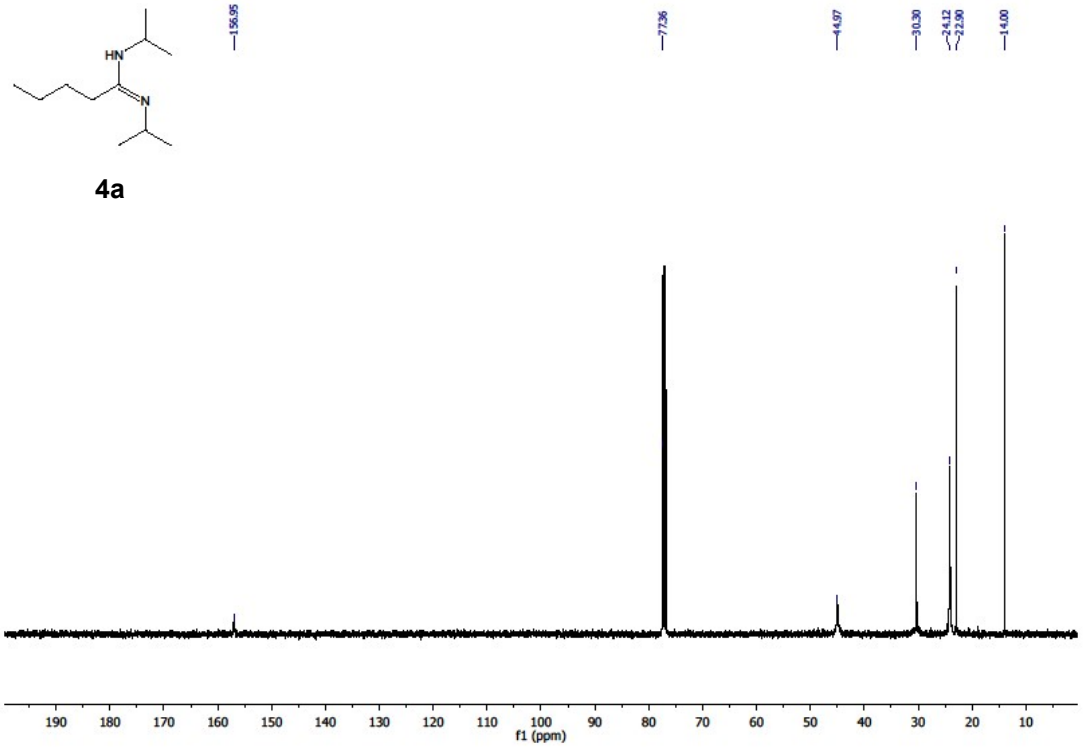


Figure S30. ^{13}C-NMR full chart for **4a** in $CDCl_3$.

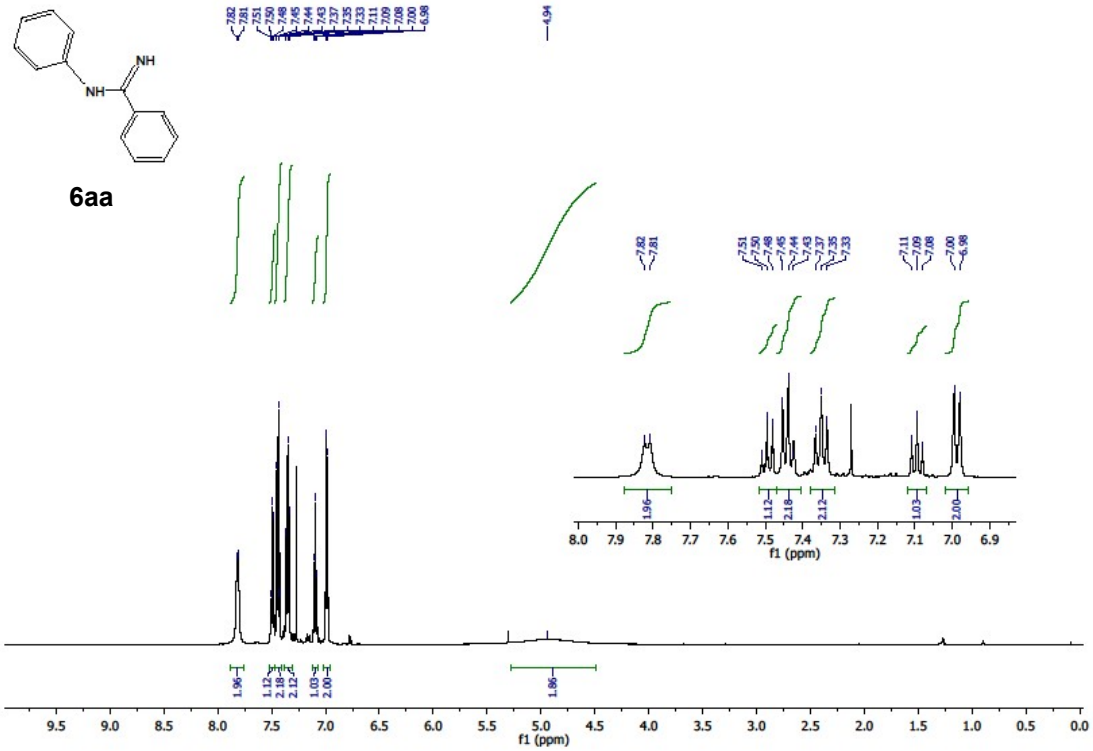


Figure S31. ^{1}H-NMR full chart for **6aa** in $CDCl_3$.

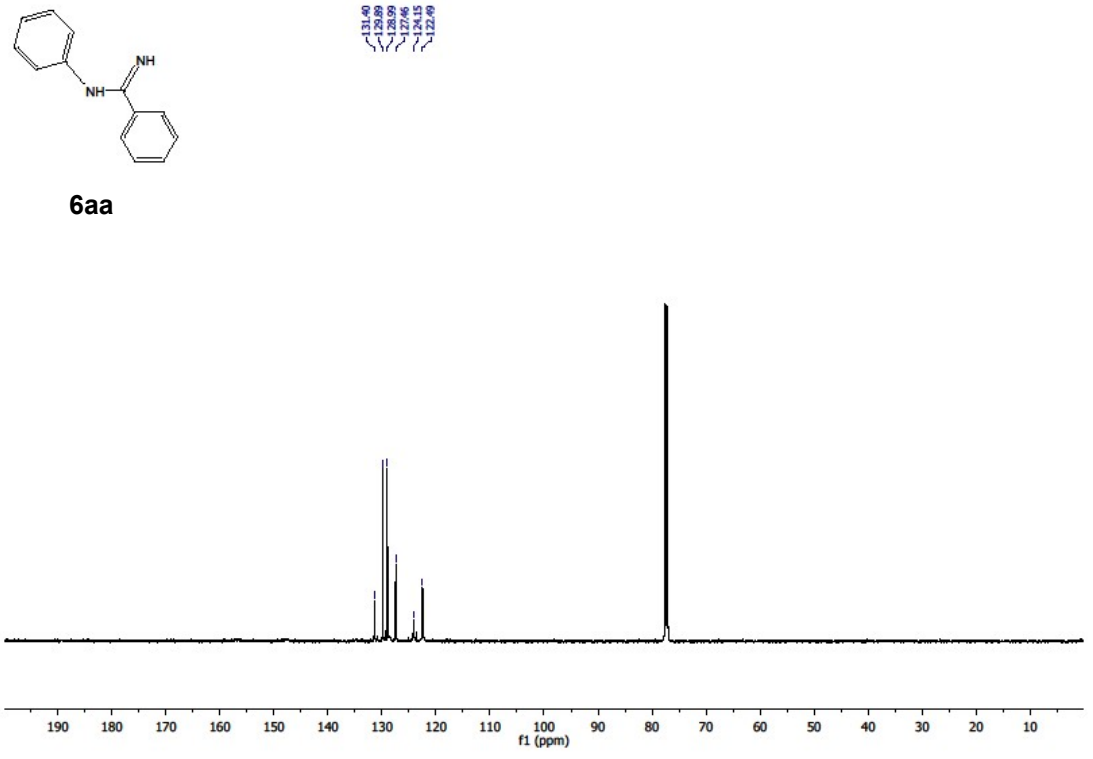


Figure S32. ^{13}C-NMR full chart for **6aa** in $CDCl_3$.

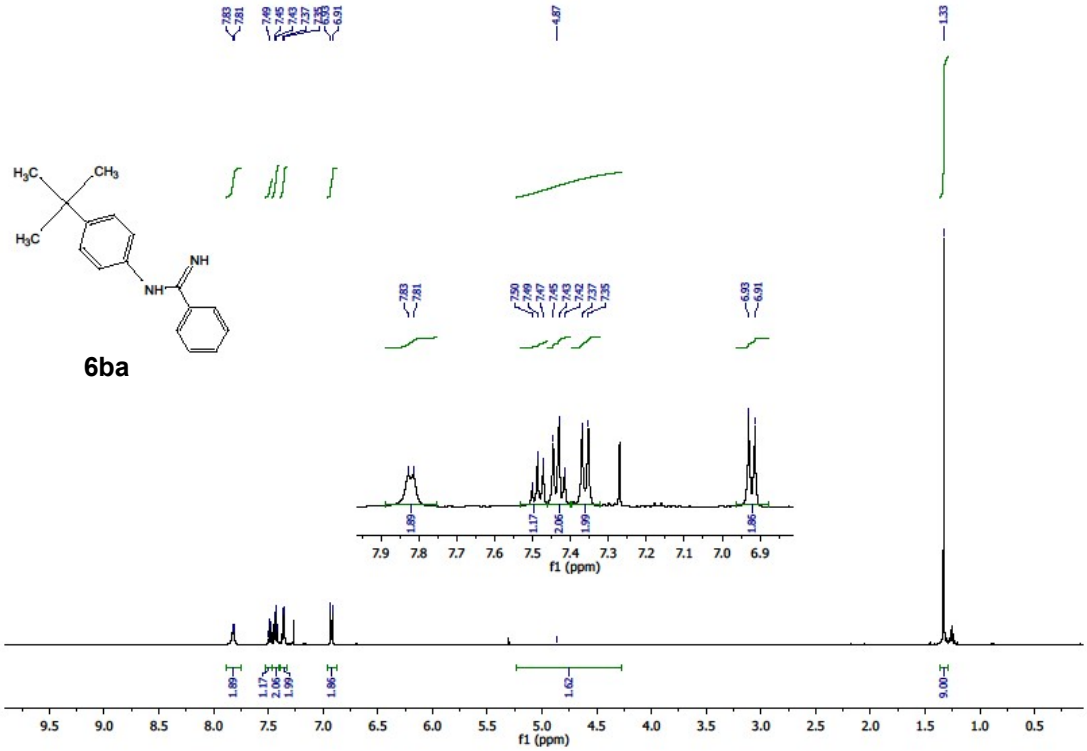


Figure S33. ^{1}H-NMR full chart for **6ba** in $CDCl_3$.

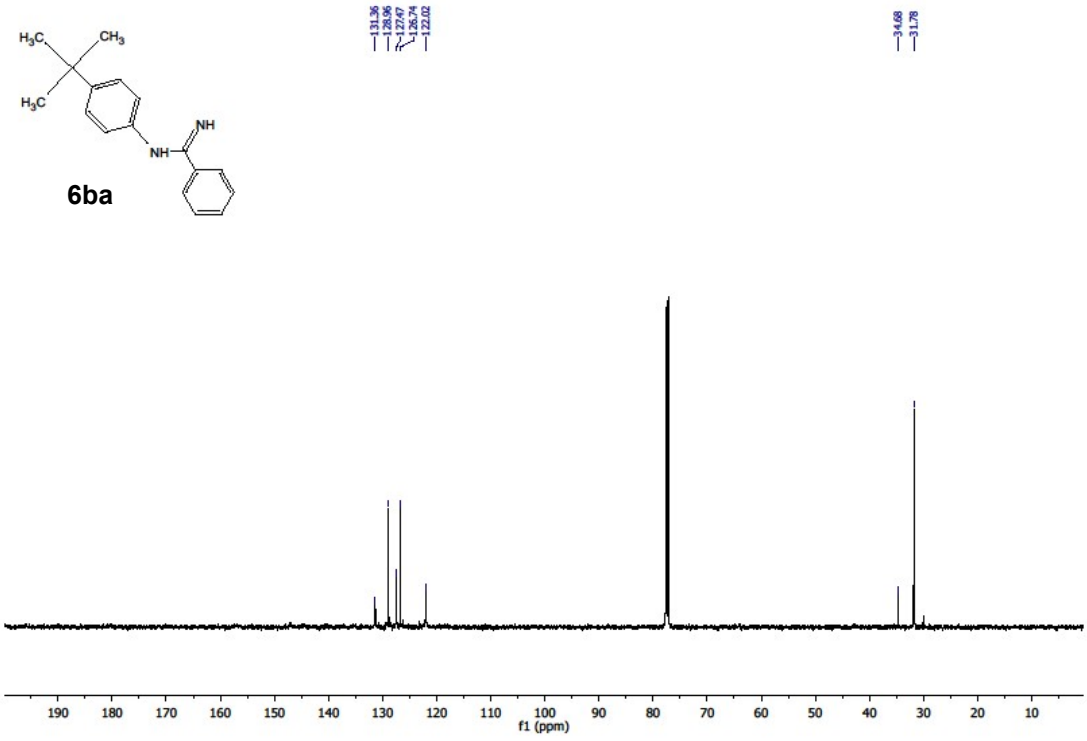


Figure S34. ^{13}C-NMR full chart for **6ba** in $CDCl_3$.

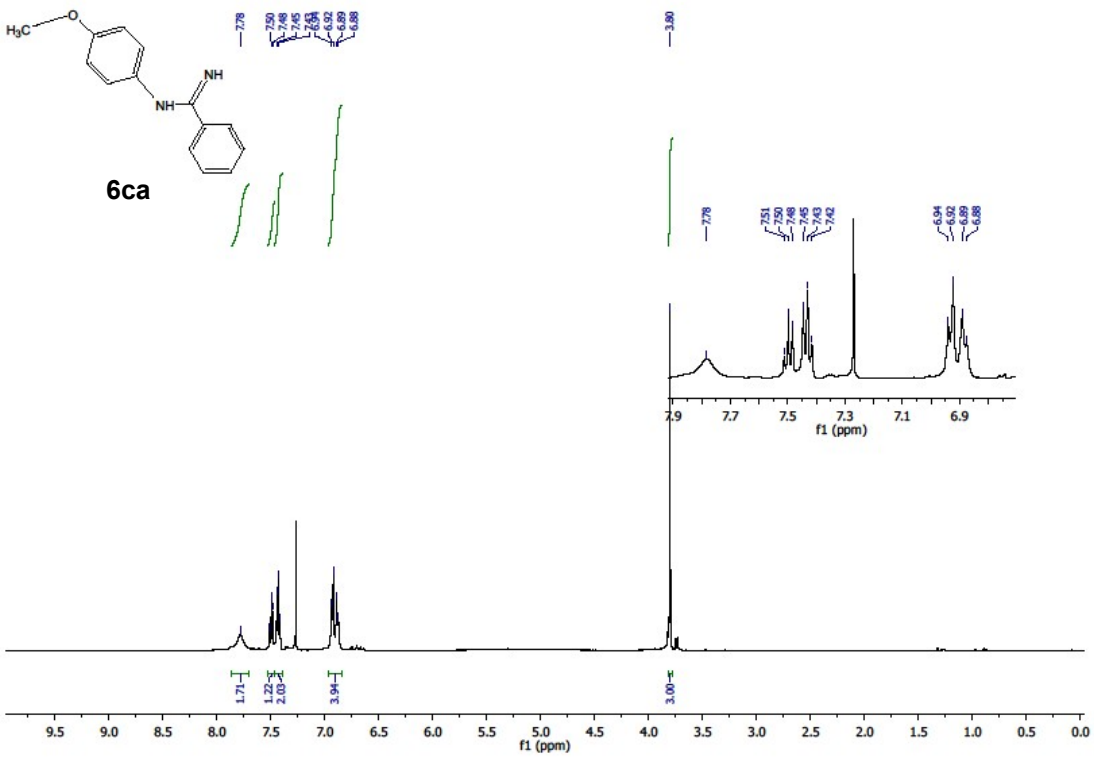


Figure S35. ^{1}H-NMR full chart for **6ca** in $CDCl_3$.

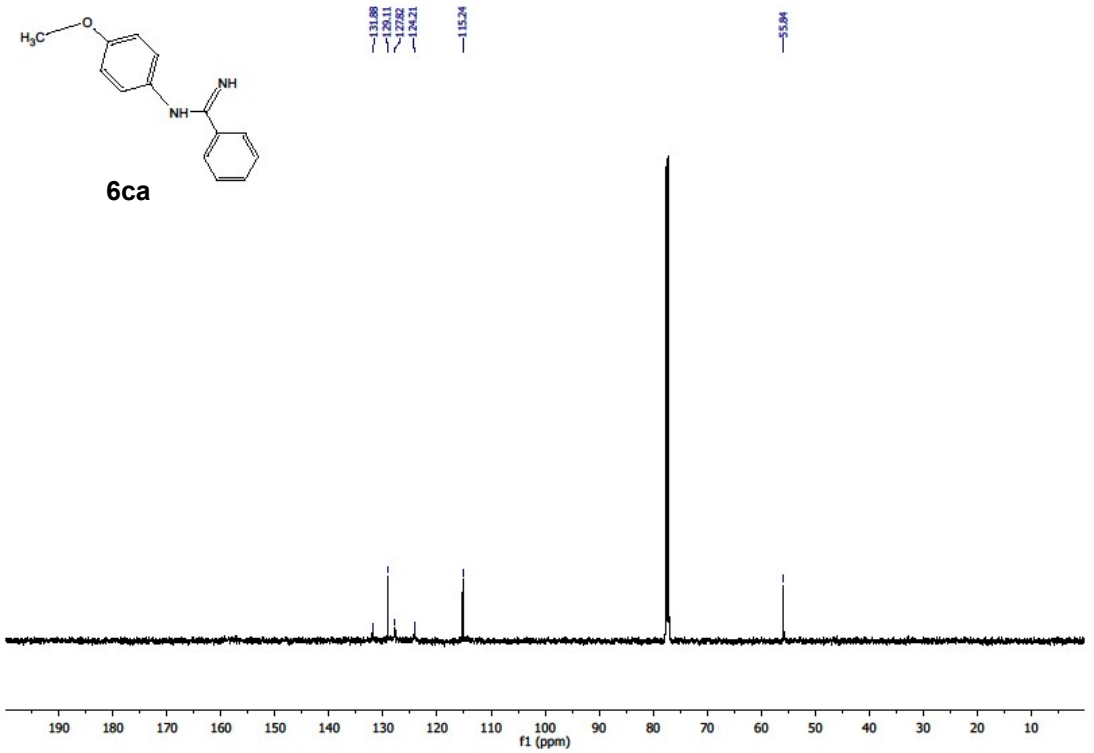


Figure S36. ^{13}C-NMR full chart for **6ca** in $CDCl_3$.

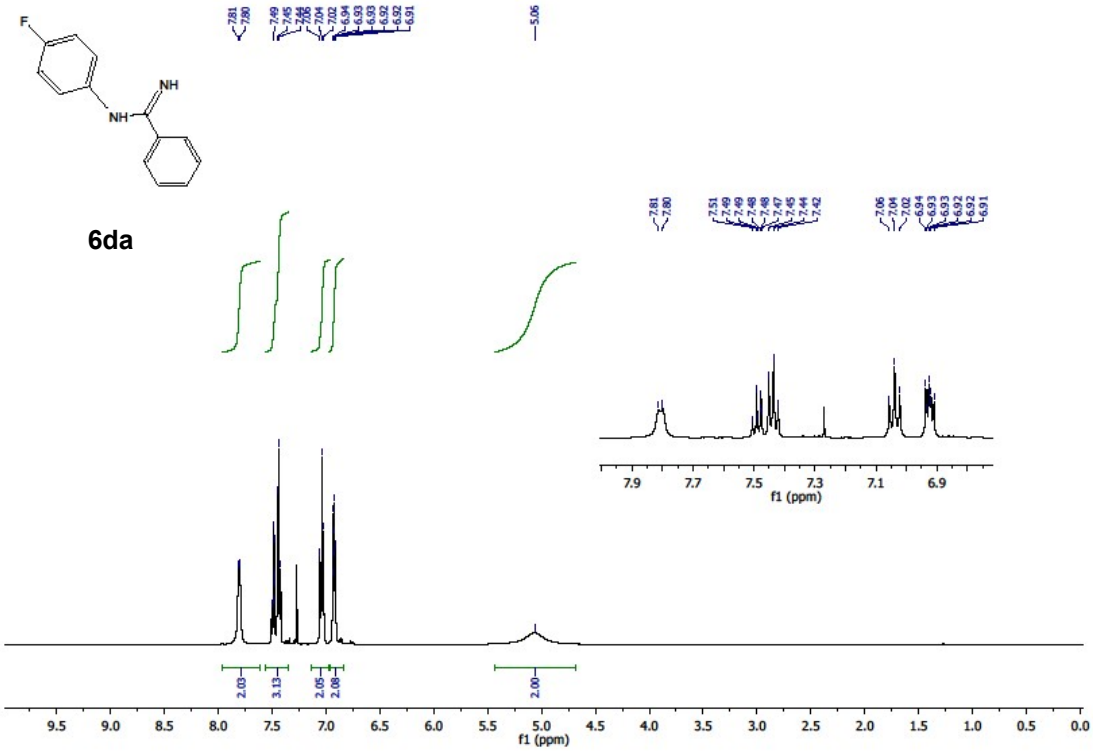


Figure S37. ^{1}H-NMR full chart for **6da** in $CDCl_3$.

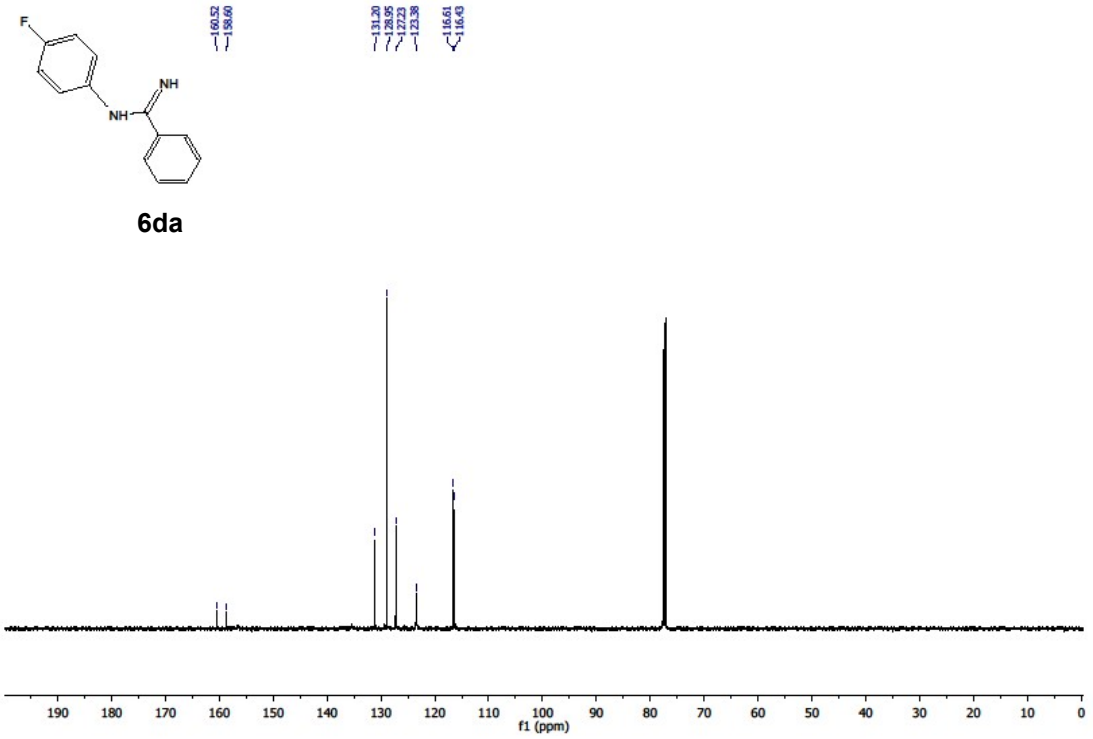


Figure S38. ^{13}C-NMR full chart for **6da** in $CDCl_3$.

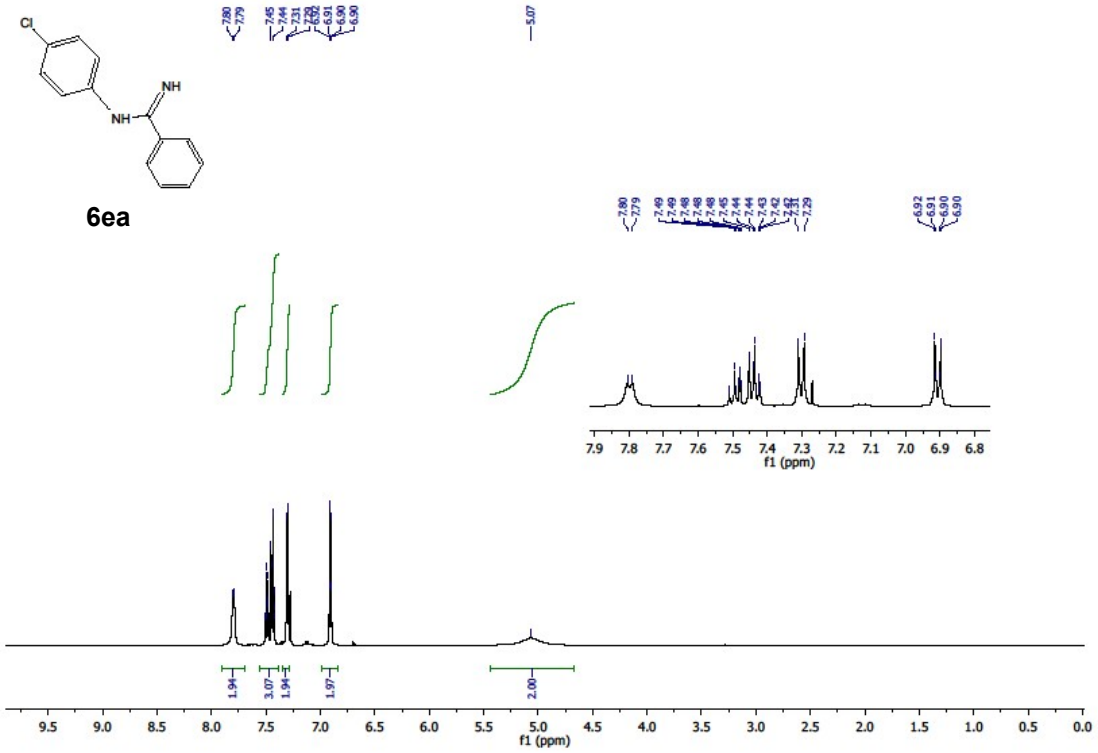


Figure S39. ^{1}H-NMR full chart for **6ea** in $CDCl_3$.

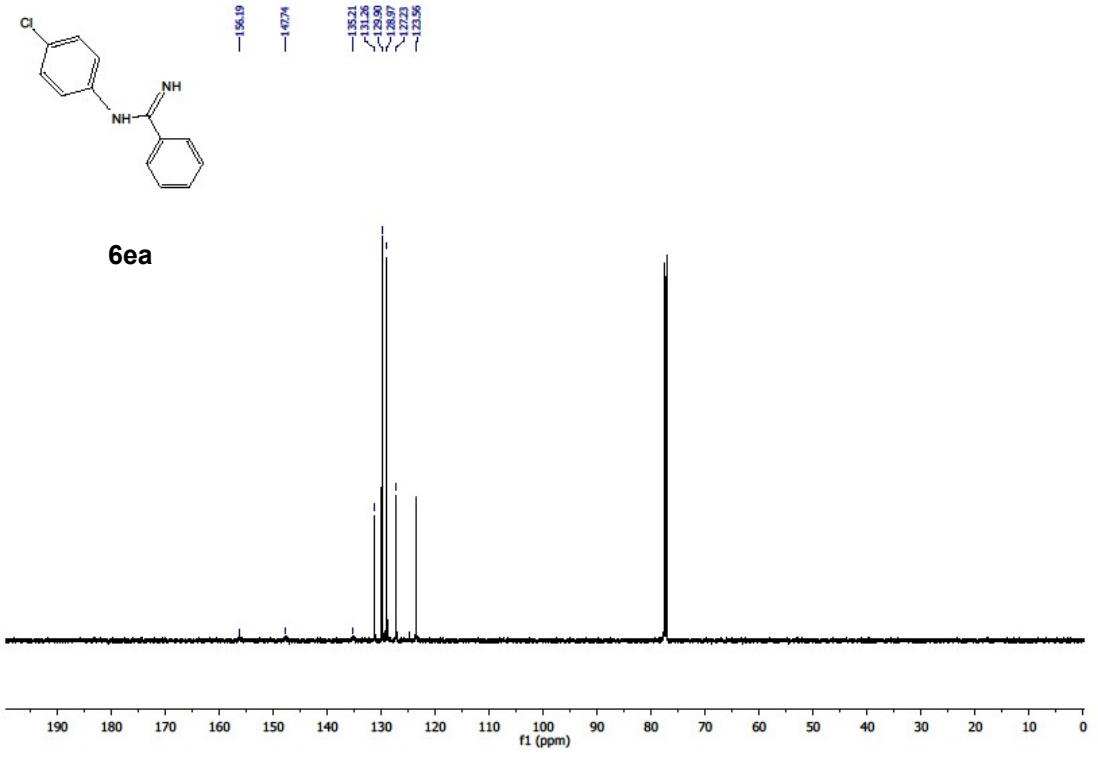


Figure S40. ^{13}C-NMR full chart for **6ea** in $CDCl_3$.

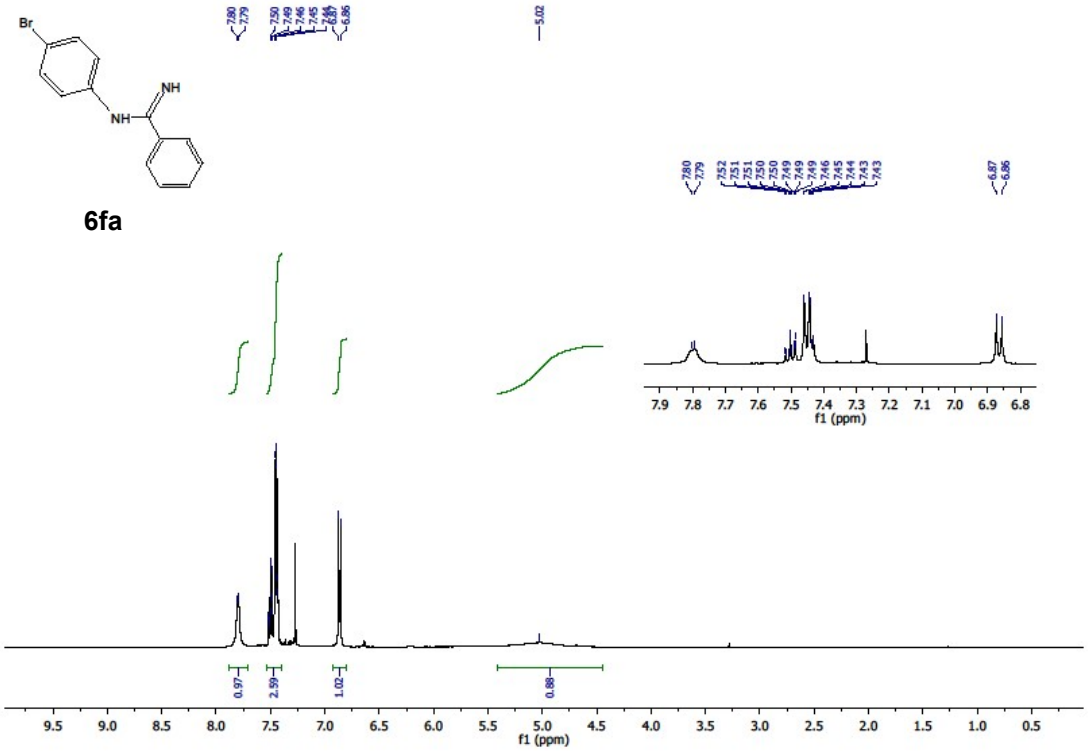


Figure S41. ^{1}H-NMR full chart for **6fa** in $CDCl_3$.

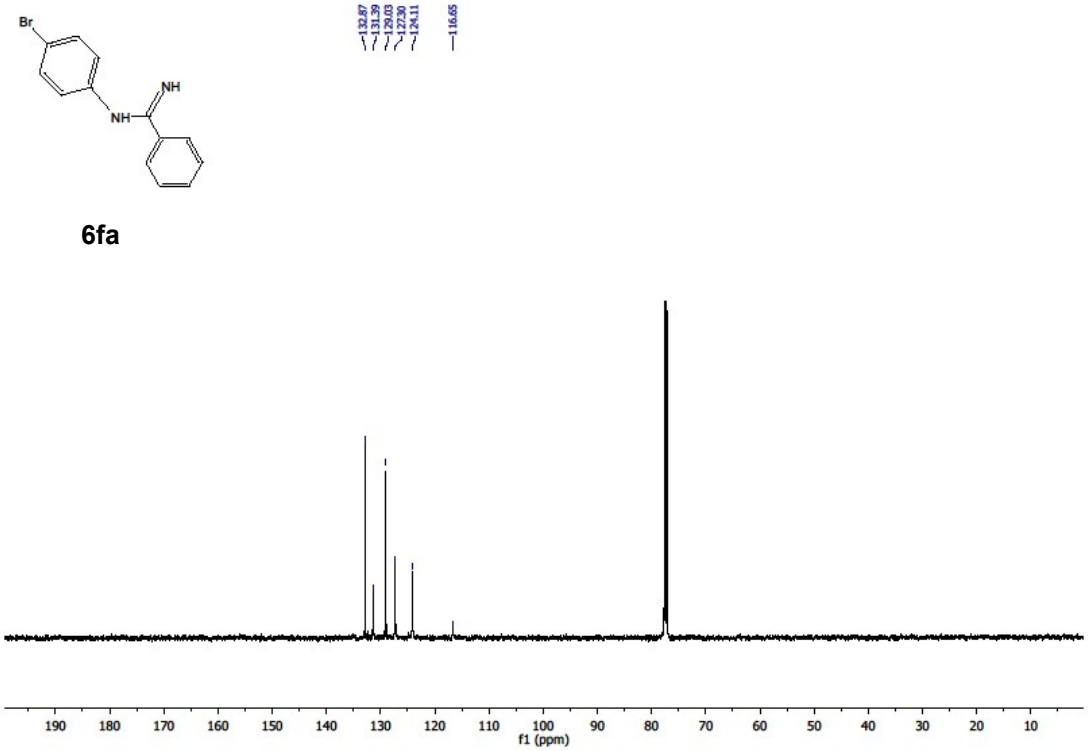


Figure S42. ^{13}C-NMR full chart for **6fa** in $CDCl_3$.

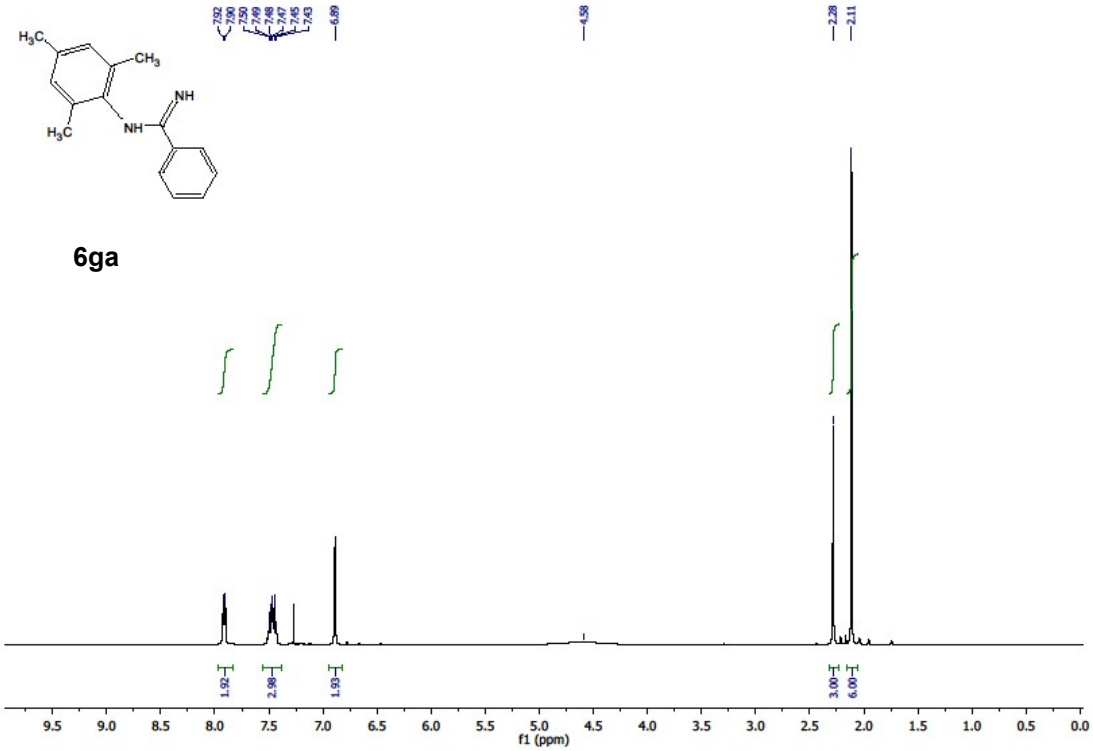


Figure S43. ^{1}H-NMR full chart for **6ga** in $CDCl_3$.

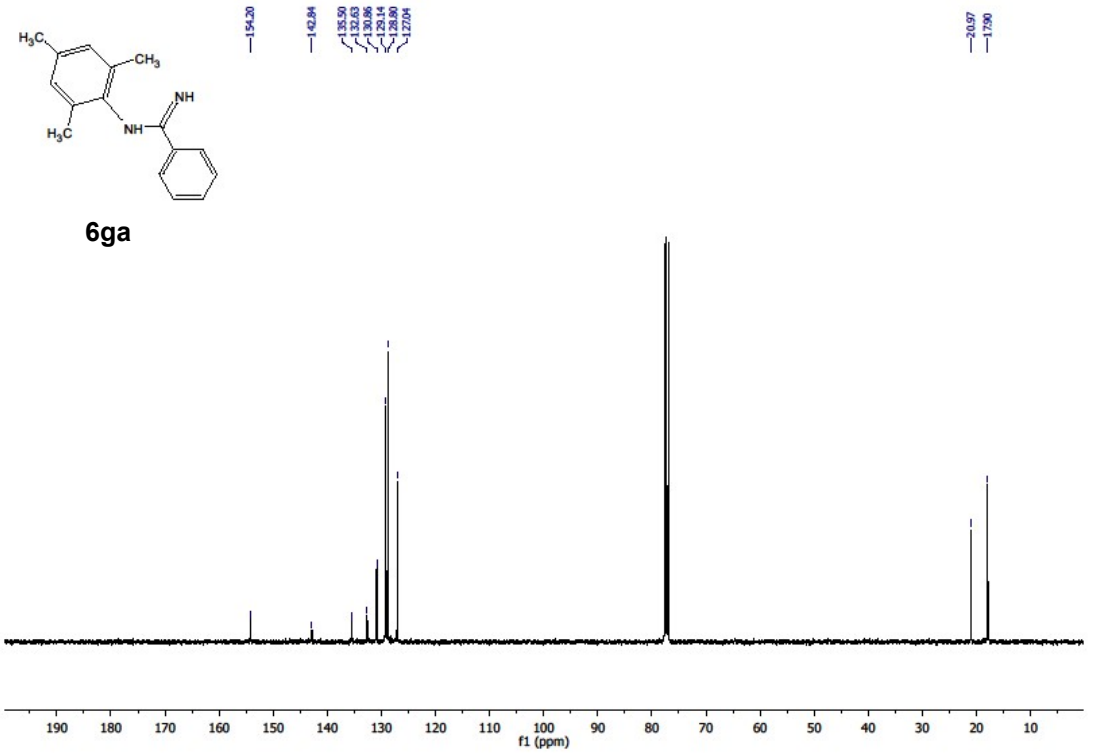


Figure S44. ^{13}C-NMR full chart for **6ga** in $CDCl_3$.

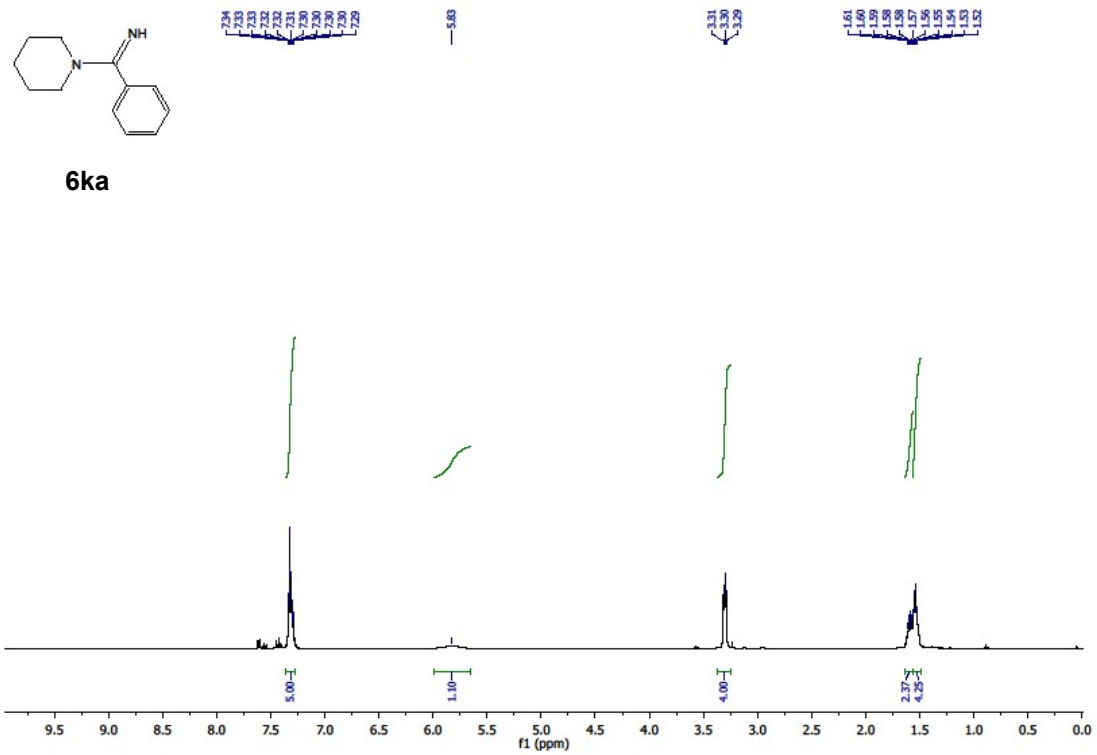


Figure S45. ^{1}H-NMR full chart for **6ka** in $CDCl_3$.

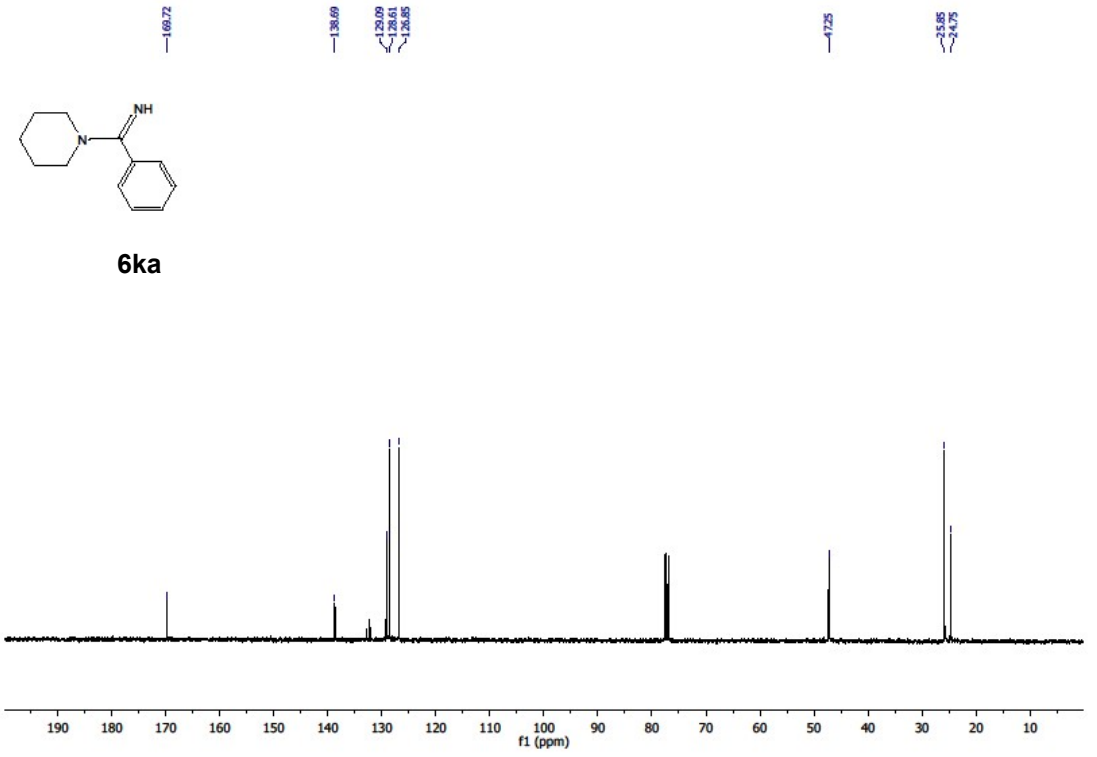


Figure S46. ^{13}C-NMR full chart for **6ka** in $CDCl_3$.

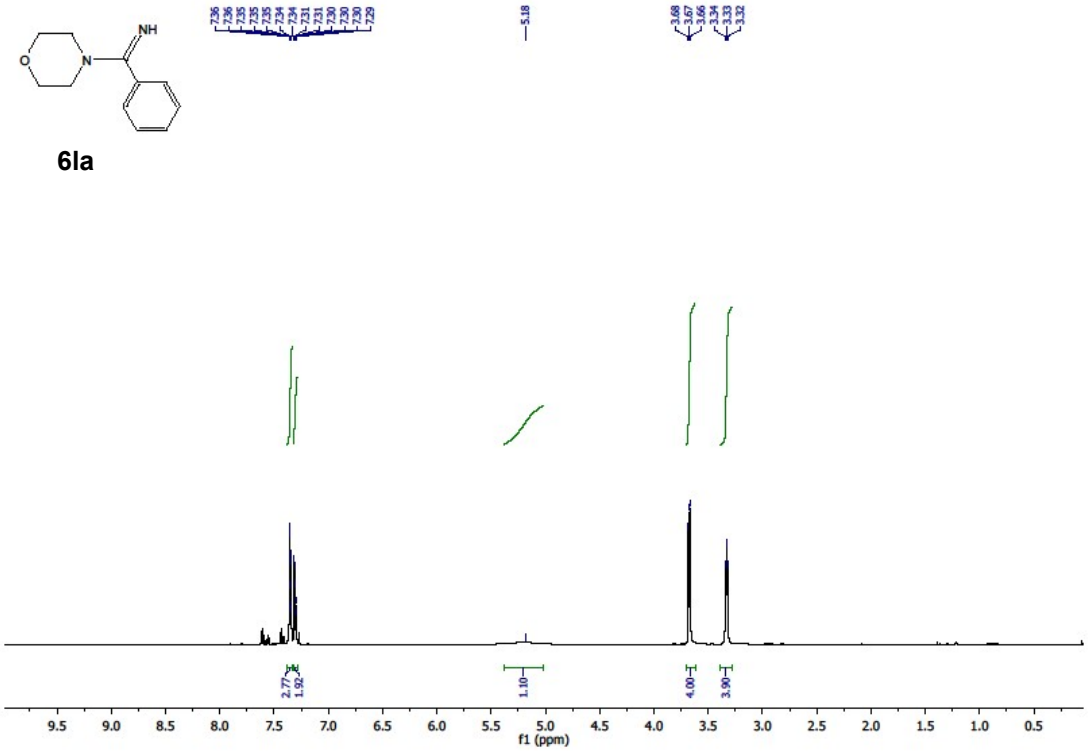


Figure S47. ^{1}H-NMR full chart for **6la** in $CDCl_3$.

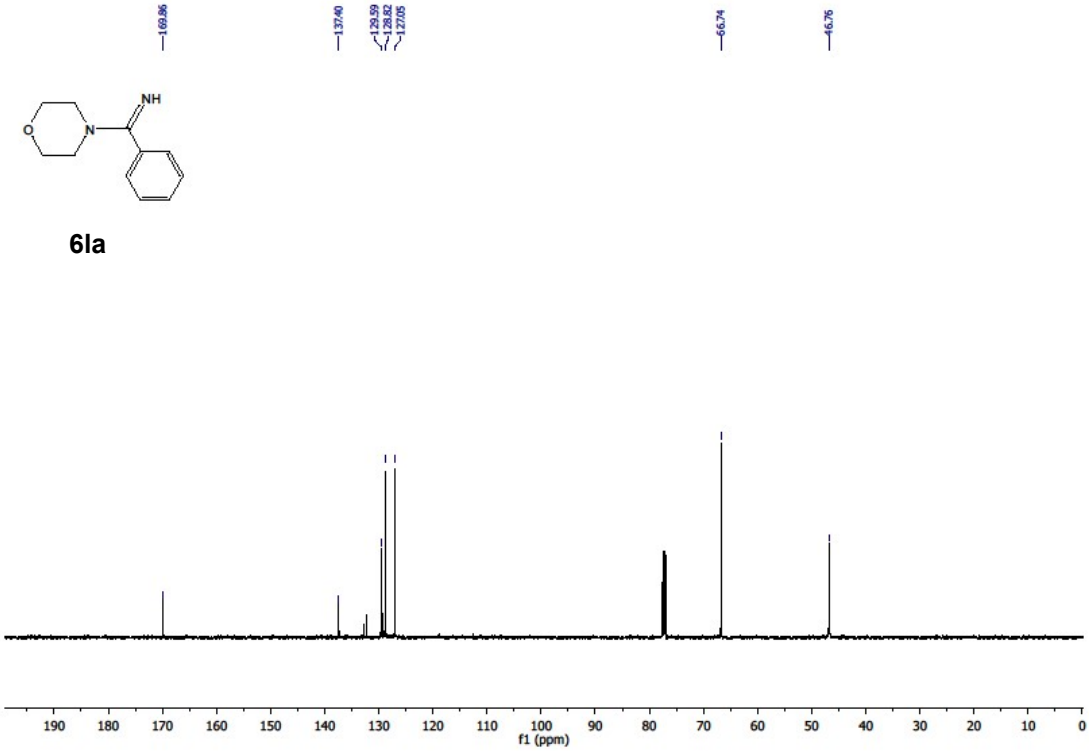


Figure S48. ^{13}C-NMR full chart for **6la** in $CDCl_3$.

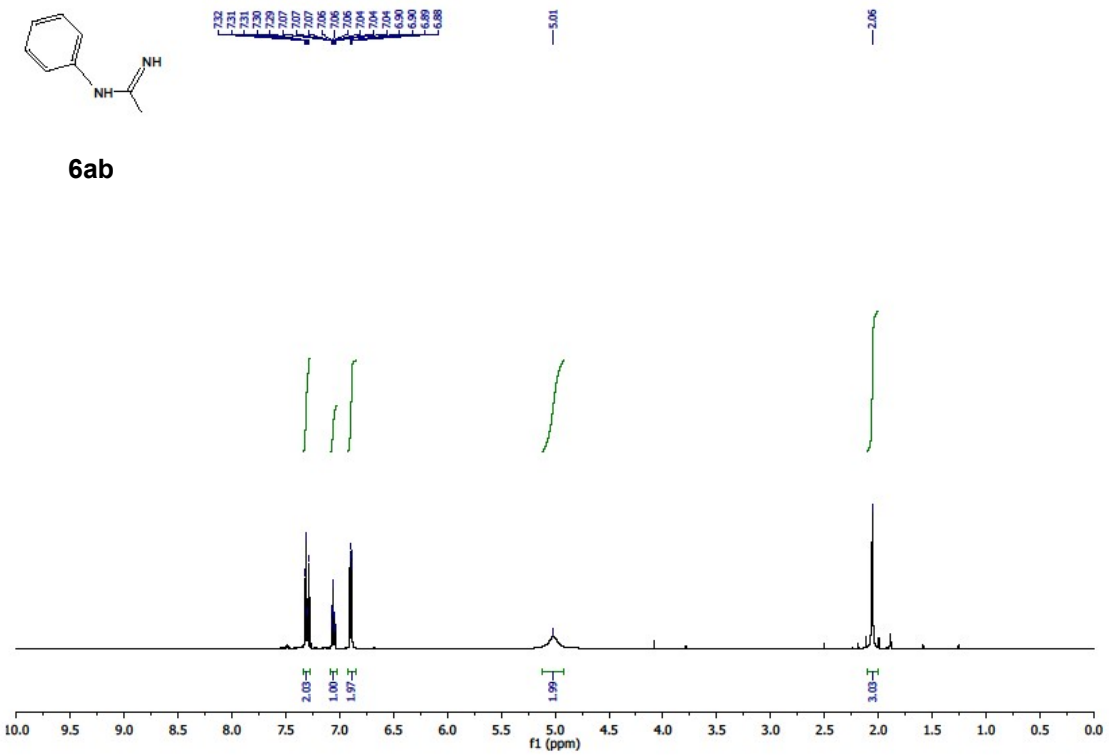


Figure S49. ^{1}H-NMR full chart for **6ab** in $CDCl_3$.

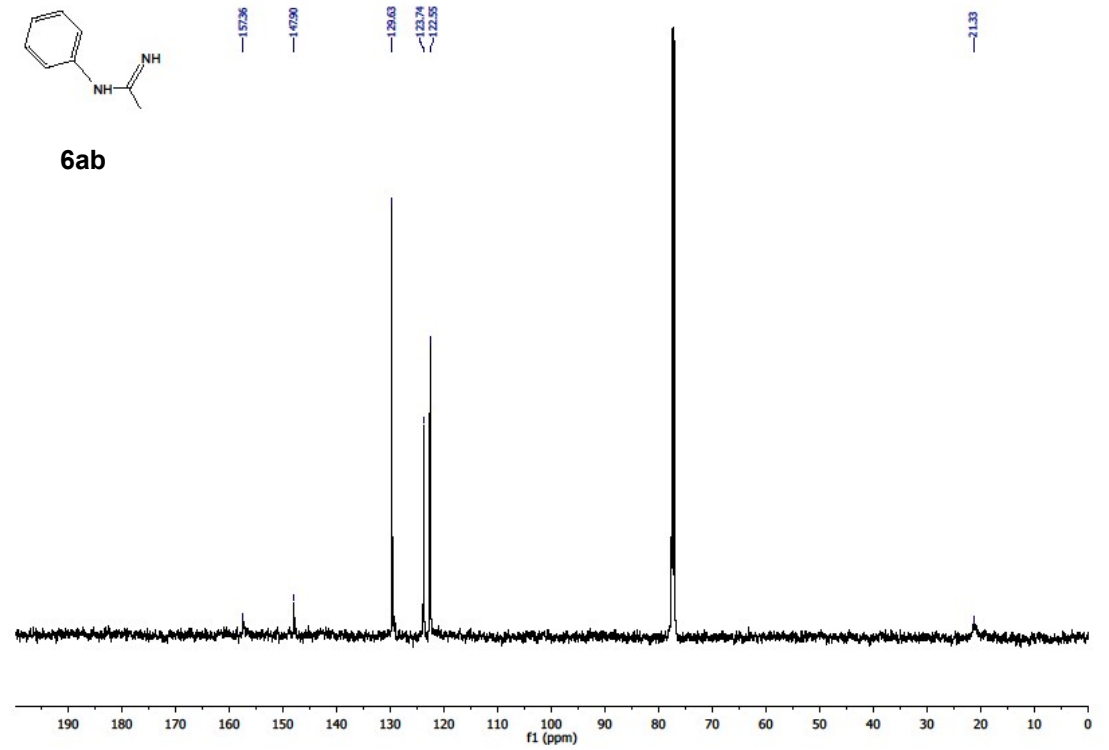


Figure S50. ^{13}C-NMR full chart for **6ab** in $CDCl_3$.

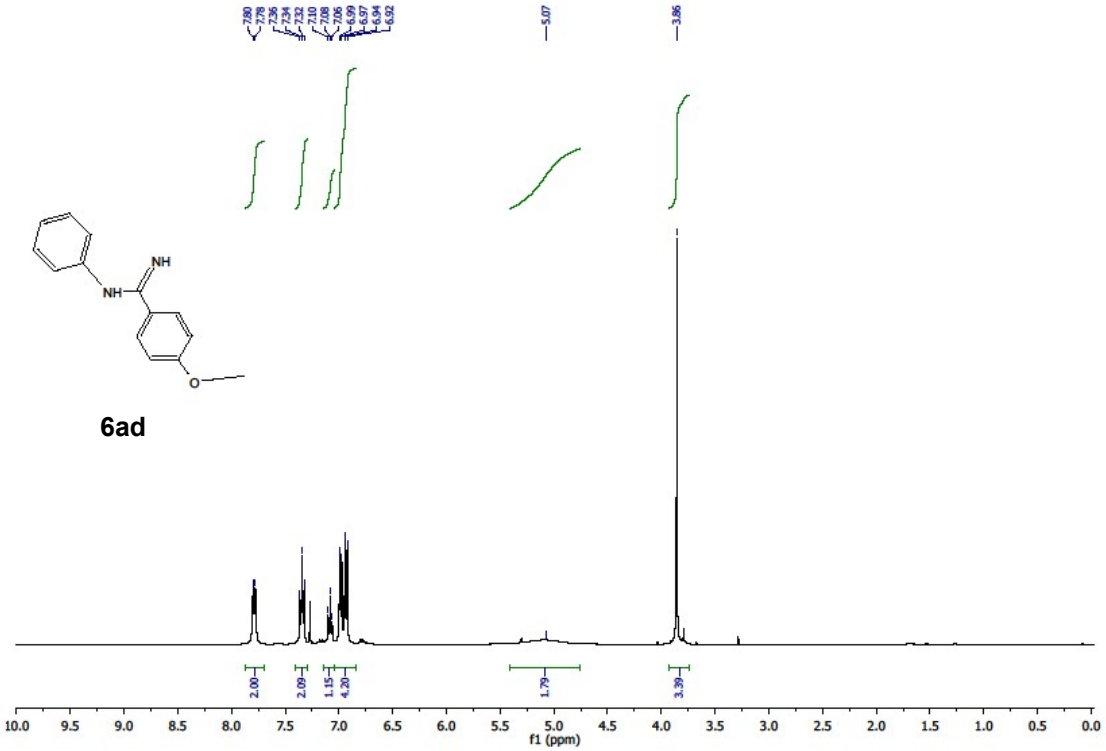


Figure S51. ^{1}H-NMR full chart for **6ad** in $CDCl_3$.

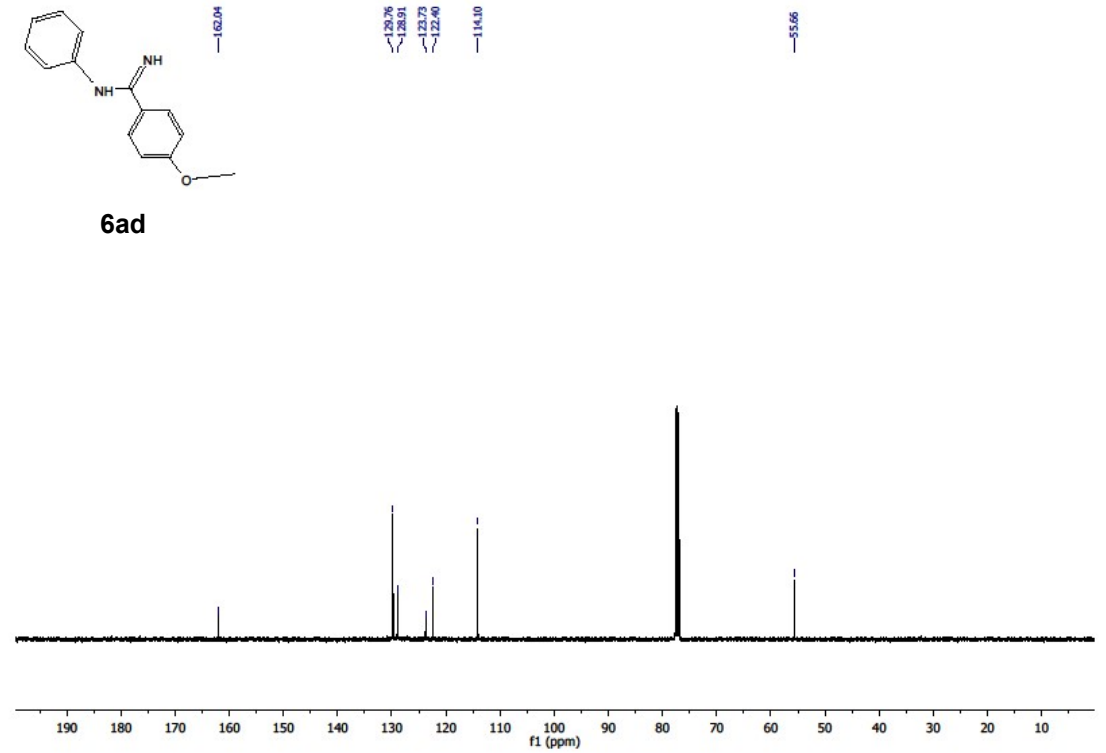


Figure S52. ^{13}C-NMR full chart for **6ad** in $CDCl_3$.

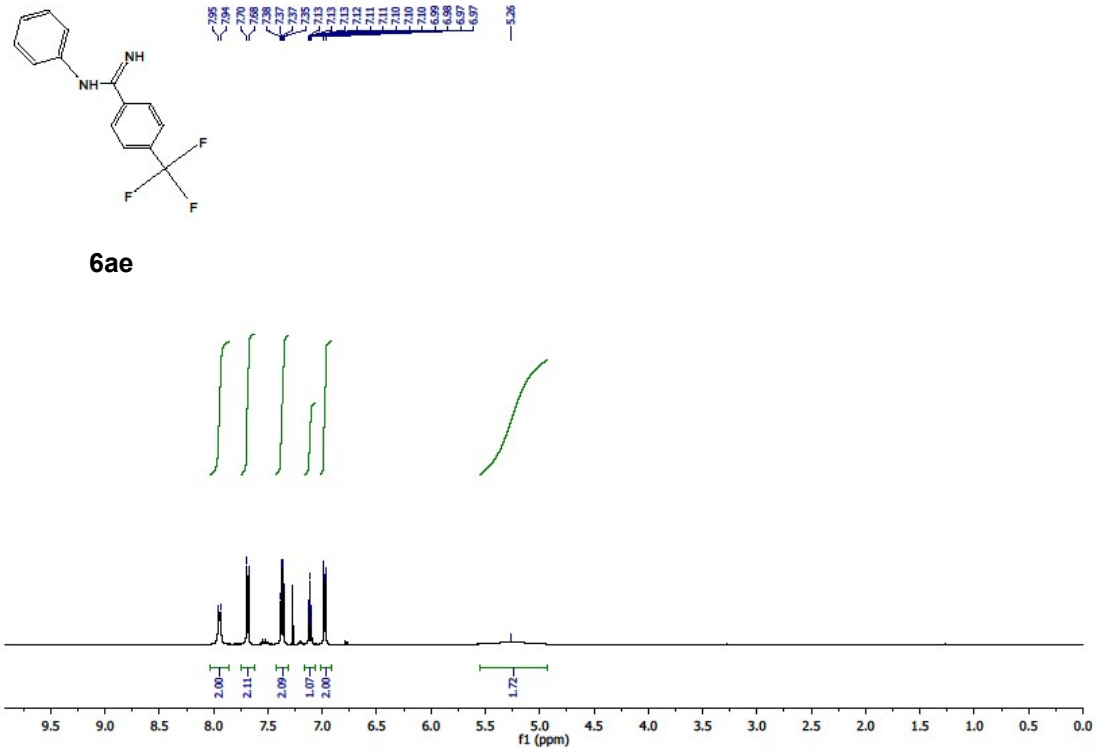


Figure S53. ^{1}H-NMR full chart for **6ae** in $CDCl_3$.

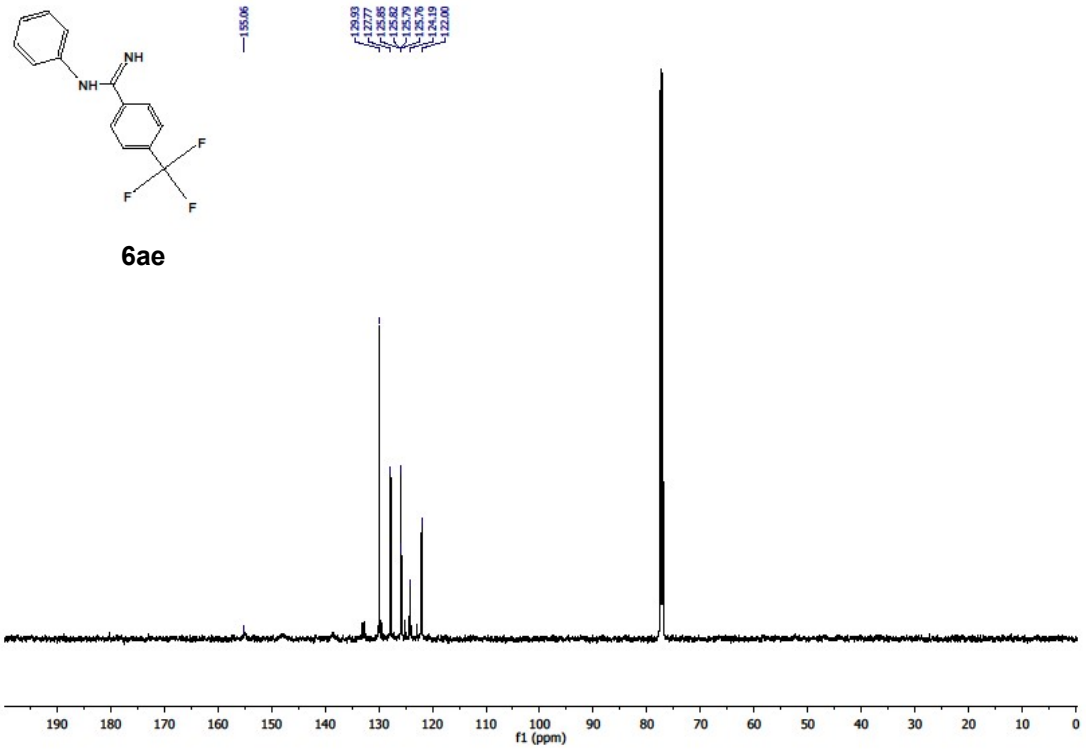


Figure S54. ^{13}C-NMR full chart for **6ae** in $CDCl_3$.

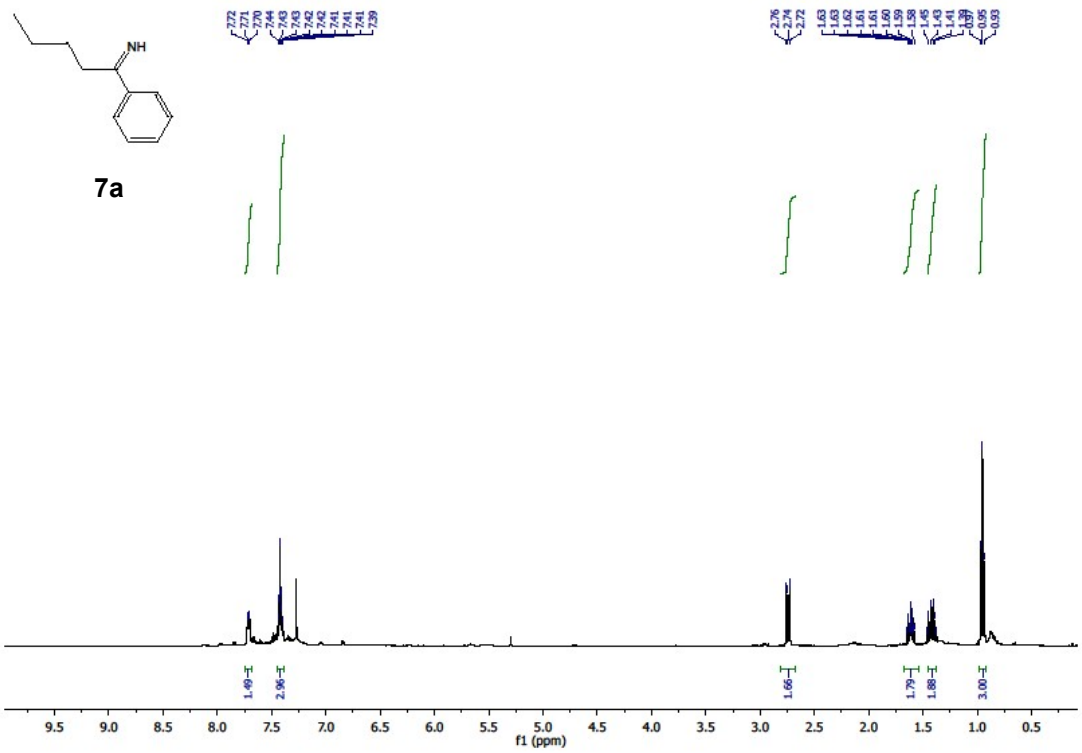


Figure S55. ^{1}H-NMR full chart for **7a** in $CDCl_3$.

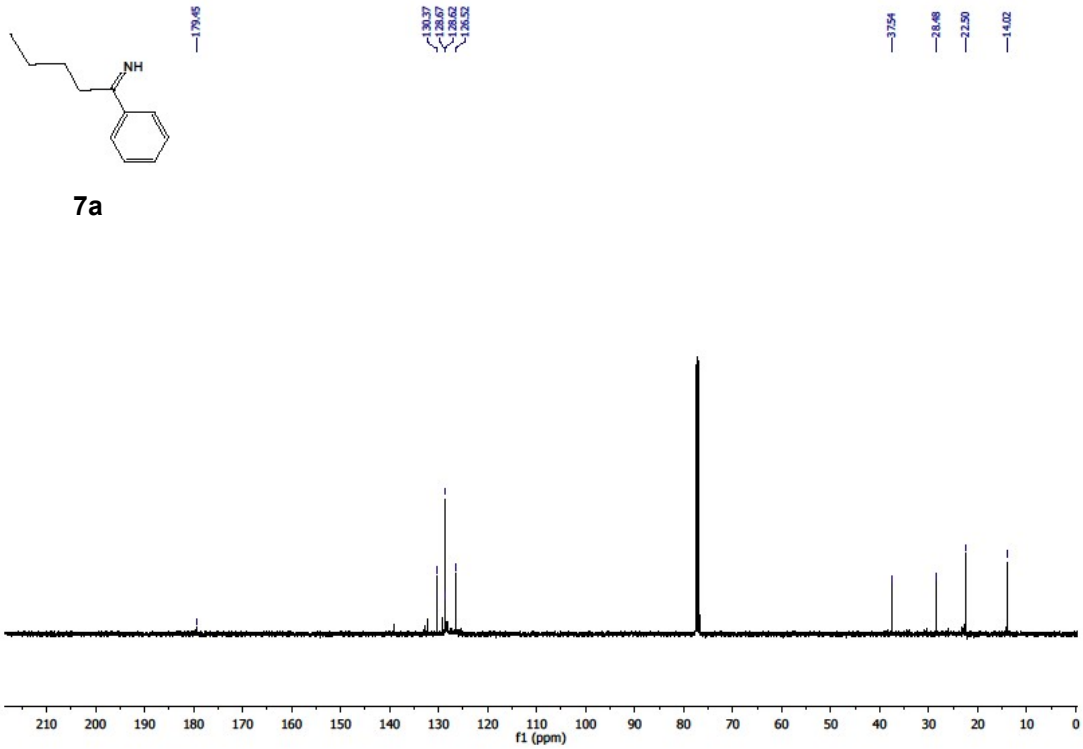


Figure S57. ^{13}C-NMR full chart for **7a** in $CDCl_3$.

4.- References

[1] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.,* **2003**, 70.

[2] (a) S. C. Watson, J. F. Eastham, *J. Organomet. Chem.,* **1967**, *9*, 165; (b) H.-S. Lin, L. A. Paquette, *Synth. Commun.,* **2007**, *24*, 2503.